# Reaction of perfluorocyclopentene with various carbon nucleophiles—heteroaromatic lithium reagents, enolate and phosphonium ylide

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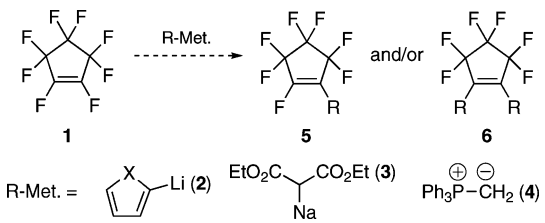
The addition of heteroaromatic lithium reagents **2** to a THF solution of perfluorocyclopentene (**1**) provided preferentially the corresponding monosubstituted products **5**, while the addition of **1** to **2** effectively gave the 1,2-disubstituted products **6** in good to excellent yields. The reaction of **1** with sodiomalonate **3** or phosphonium ylide **4** also proceeded smoothly to form the 1,3-disubstituted product **8** or **10** in high yield, respectively.

## 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.*[3,4]

The nucleophilic substitution reaction of perfluorocyclopentene (**1**) would provide a promising entry to the synthesis of such molecules. However, very little attention has been paid to the nucleophilic substitution reactions of **1** with carbon nucleophiles thus far,[5] though many studies have been made on the reaction of **1** with hetero nucleophiles, such as phenoxide,[6] arene- or alkanethiolates,[7] primary or secondary amines[8] and so on.[9,10] Herein, we wish to disclose the results of the reaction with heteroaromatic lithium reagents **2**, enolates **3** and phosphonium ylide **4** (Scheme 1).




**Scheme 1** Intended research outline.

## 2 Results and discussion

### 2.1 Reaction of 1 with heteroaromatic lithium reagents

**2.1.1 Screening of reaction conditions.** Initially, we examined the reaction of perfluorocyclopentene (**1**) with 2-furyllithium (**2a**) as a heteroaromatic lithium reagent. The results are summarized in Table 1. Thus, to a solution of 1.1 equiv. of 2-furyllithium (**2a**), prepared from furan and *n*-butyllithium in $Et_2O$, was added dropwise a THF solution of 1.1 equiv. of **1** at –78 °C. After stirring of the reaction mixture for 2 h, the corresponding monosubstituted perfluorocyclopentene **5a** was obtained in 34% yield, together with the 1,2-disubstituted product **6a** in 37% yield (entry 1). The use of 2.2 equiv. of **2a** resulted in the exclusive formation of **6a** in 74% yield (entry 2). In contrast, the addition of 1.0 equiv. of the lithium reagent **2a** to a THF solution of 1.1 equiv. of **1** (the reverse addition) gave the corresponding monosubstituted product **5a** in 79% yield as a sole product (entry 3). The reaction with 2.0 equiv. of **1** did not cause any change in the yield (entry 4).

**2.1.2 Reaction with a variety of heteroaromatic lithium reagents 2.** Subsequently, we carried out the reaction of perfluorocyclopentene (**1**) with various heteroaromatic lithium reagents, such as 3-furyl- (**2b**), 2-thienyl- (**2c**), 3-thienyllithium (**2d**), 2-lithio-*N*-methylpyrrole (**2e**), 2-lithiobenzo[*b*]furan (**2f**), 2-lithiobenzo[*b*]thiophene (**2g**) and 2-lithio-*N*-methylindole (**2h**) under the optimized reaction conditions (method A: entry 3 in Table 1, method B: entry 2 in Table 1). The results are summarized in Table 2.

On treating **1** with 3-furyllithium (**2b**) by method A, the mono 3-furylated perfluorocyclopentene **5b** was obtained in 57% yield (entry 3). Similarly, 3-thienyllithium (**2d**), 2-lithio-*N*-methylpyrrole (**2e**) and 2-lithio-*N*-methylindole (**2h**) were found to be good nucleophiles, the corresponding monosubstituted products **5d**, **5e** and **5h** being afforded in 44, 68 and 70% yields, respectively (entries 7, 9 and 15). As shown in entries 5, 11 and 13, the reaction with 2-thienyllithium (**2c**), 2-lithiobenzo[*b*]furan (**2f**), and 2-lithiobenzo[*b*]thiophene (**2g**) was somewhat sluggish, the mono- and 1,2-disubstituted perfluorocyclopentenes **5** and **6** being obtained as an inseparable mixture. On the other hand, the reactions by method B proceeded smoothly to give the corresponding disubstituted products **6** in good to excellent yields in all cases (entries 2, 4, 6, 8, 10, 12, 14, and 16).

### 2.2 Reaction of 1 with stabilized carbanions

**2.2.1 Reaction with an enolate derived from acetophenone.** We also attempted the reaction of perfluorocyclopentene (**1**) with an enolate species derived from acetophenone. Thus, the treatment

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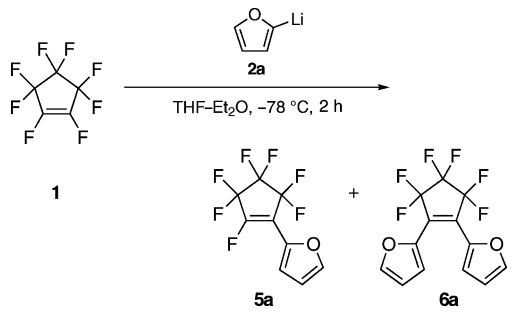
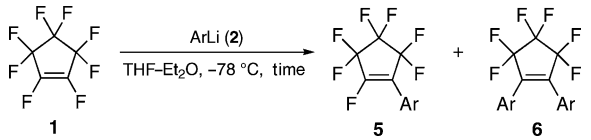
**Table 1** Reaction of **1** with 2-furyllithium (**2a**) in various reaction conditions

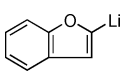
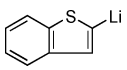
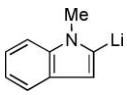



| Entry | Equivalents of **1** | Equivalents of **2a** | Yield[a] of **5a** (%) | Yield[a] of **6a** (%) |
|---|---|---|---|---|
| 1[b] | 1.0 | 1.1 | 34 | 37 |
| 2[b] | 1.0 | 2.2 | 0 | 74 |
| 3[c] | 1.1 | 1.0 | 79 | 0 |
| 4[c] | 2.0 | 1.0 | 78 | 0 |

[a] Determined by $^{19}$F NMR. [b] A solution of **1** in THF was added dropwise to a solution of 2-furyllithium (**2a**) at –78 °C. [c] To a solution of **1** in THF was slowly added a solution of 2-furyllithium (**2a**) at −78 °C (the reverse addition).

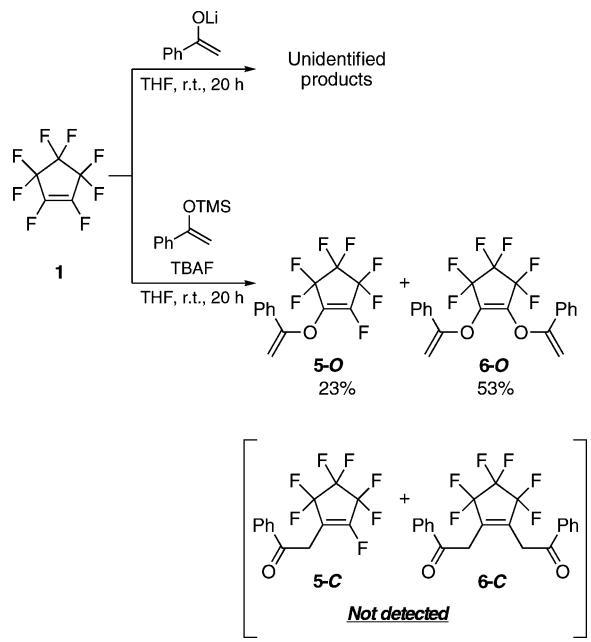
**Table 2** Reaction of **1** with various heteroaromatic lithium reagents **2**




| Entry | ArLi (**2**) | | Method[a] | Yield[b] of **5** (%) | Yield[c] of **6** (%) |
|---|---|---|---|---|---|
| 1 |  | **2a** | A | 79 | 0 |
| 2 | | | B | 0 | 74 (48) |
| 3[d] |  | **2b** | A | 57 | 0 |
| 4 | | | B | 0 | Quant (81) |
| 5 |  | **2c** | A | 36 | 23 |
| 6 | | | B | 0 | 68 |
| 7 |  | **2d** | A | 44 | 0 |
| 8 | | | B | 0 | 65 |
| 9 |  | **2e** | A | 68 | 0 |
| 10 | | | B | 0 | 60 (55) |
| 11 |  | **2f** | A | 29 | 32 |
| 12 | | | B | 0 | Quant (97) |
| 13 |  | **2g** | A | 65 | 25 |
| 14 | | | B | 0 | 87 (54) |
| 15 |  | **2h** | A | 70 | 0 |
| 16 | | | B | 0 | 77 (60) |

[a] Method A. To a solution of **1** (1.1 mmol) in THF was slowly added a solution of ArLi **2** (1.0 mmol) in $Et_2O$. Method B. To a solution of ArLi **2** (2.2 mmol) in $Et_2O$ was added slowly a solution of **1** (1.0 mmol) in THF. [b] Determined by $^{19}$F NMR based on **2**. [c] Determined by $^{19}$F NMR based on the substrate **1**. Values in parentheses are of isolated yield. [d] Easily vaporable unknown product was obtained in 32% yield.

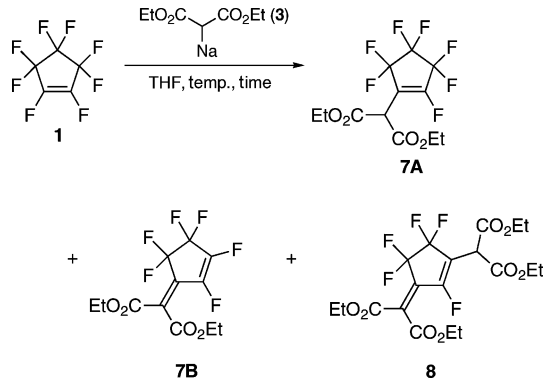
of **1** with lithium enolate, generated from acetophenone and LDA, at room temperature for 20 h did not give a satisfactory result, several unidentified products being formed. Additionally, we carried out the reaction of **1** with the silyl enol ether of acetophenone, 1-phenyl-1-(trimethylsilyloxy)ethene, in the presence of a catalytic amount of tetrabutylammonium fluoride (TBAF) at room temperature for 20 h. Interestingly, *O*-substituted products **5-*O*** and **6-*O*** were obtained in 23 and 53% yields, respectively, and neither **5-*C*** nor **6-*C*** were detected at all (Scheme 2).




**Scheme 2** Reaction of **1** with the enolate derived from acetophenone.

**2.2.2 Reaction with diethyl sodiomalonate.** We next examined the reaction of **1** with diethyl sodiomalonate (**3**). The results are collected in Table 3. Thus, on treating **1** with 1.1 equiv. of diethyl sodiomalonate (**3**) in THF at −78 °C for 2 h, the corresponding

**Table 3** Reaction of **1** with diethyl sodiomalonate (**3**)

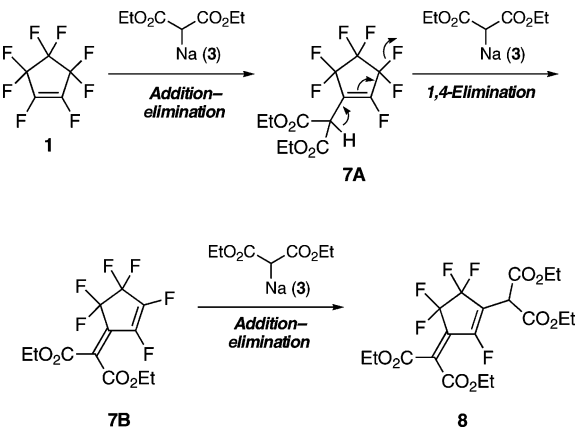



| Entry | Equivalents of **3** | Temperature/°C | Time/h | Yield[a] of **7A** (%) | Yield[a] of **7B** (%) | Yield[a] of **8** (%) |
|---|---|---|---|---|---|---|
| 1[b] | 1.1 | −78 | 2 | 18 | 5 | 0 |
| 2 | 2.2 | −78 | 2 | 46 | 7 | 0 |
| 3 | 2.2 | −78 | 6 | 38 | 15 | 0 |
| 4 | 2.2 | R.t. | 20 | 0 | 32 | 41 |
| 5 | 4.4 | R.t. | 20 | 0 | 0 | 81 |
| 6 | 6.6 | R.t. | 20 | 0 | 0 | 91 |

[a] Determined by $^{19}$F NMR. [b] The starting substrate **1** remained in the reaction mixture.

monosubstituted product **7A** was obtained in 18% yield, along with 5% of α,β,γ,δ-dienoate derivative **7B** (entry 1). The use of 2.2 equiv. of **3** increased the yield of **7A** (46% yield, entry 2), however, prolonged reaction time resulted in the decrease of **7A** and in the increase of **7B** (entry 3). The reaction at room temperature for 20 h gave the 1,3-disubstituted product **8** in 41% yield, together with 32% of **7B** (entry 4). When 4.4 equiv. of **3** was used, the reaction proceeded efficiently to provide **8** as a sole product (entry 5). Furthermore, when 6.6 equiv. of **3** were employed, the 1,3-disubstituted product **8** was given in 91% yield (entry 6).

On the basis of the above results, we propose the mechanism for the reaction of **1** with diethyl sodiomalonate (**3**), as shown in Scheme 3.




**Scheme 3** A proposed reaction mechanism.

First, the nucleophilic addition of diethyl sodiomalonate (**3**) to perfluorocyclopentene (**1**) and the subsequent elimination of a fluoride ion give rise to the monosubstituted product **7A**. The α-proton in **7A** may be abstracted by an excess of **3**, followed by elimination of a fluoride ion, leading to α,β,γ,δ-dienoate **7B**. The 1,6-conjugate addition of **3** to **7B**, followed by elimination of a fluoride ion, gives the 1,3-disubstituted product **8**.

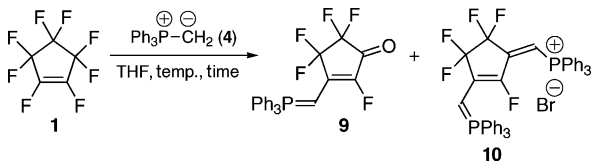
**2.2.3 Reaction with phosphonium ylide.** We also investigated the reaction of perfluorocyclopentene (**1**) with a phosphonium ylide as a carbon nucleophile as shown in Table 4. Thus, the treatment of **1** with 1.1 equiv. of triphenylphosphonium methylide (**4**) in THF at −78 °C for 2 h produced the corresponding cyclopentenone derivative **9** in 22% yield, which was formed after hydrolysis, together with a large amount of unreacted **1** (entry 1). When the reaction was carried out with 2.2 equiv. of **4** at –78 °C or at room temperature, the monosubstituted product **9** was obtained in 40 or 43% yields, respectively (entries 2 and 3). The prolonged reaction time (6 h) facilitated the formation of the 1,3-disubstituted phosphonium salt **10**, which was given in 54% yield (entry 4). After several attempts, the best yield (96%) was obtained when the reaction was performed by using 6.6 equiv. of **4** at room temperature for 2 h (entry 7).

A possible reaction mechanism of this reaction is outlined in Scheme 4. Thus, the nucleophilic addition–elimination reaction of **1** with ylide **4** produces a monosubstituted intermediate **11A**, which may be subject to 1,4-elimination of HF to form an intermediate **11B**. Hydrolysis of **11B** leads to the cyclopetenone derivative **9**, while further nucleophilic addition–elimination reaction of **11B** with an excess of ylide **4** may take place to afford the 1,3-disubstituted phosphonium salt **10**. The structures of the obtained cyclopentenone derivative **9** and phosphonium salt **10** were determined by single-crystal X-ray analysis.†

† CCDC reference numbers 635724–635725. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701702b

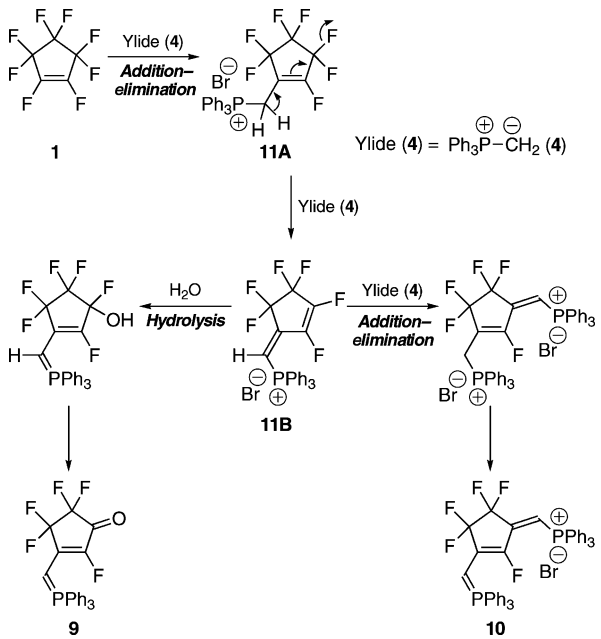
 

**Table 4** Reaction of **1** with phosphonium ylide **4**




| Entry | Equivalents of **4** | Temperature/°C | Time/h | Yield[a] of **9** (%) | Yield[a] of **10** (%) |
|---|---|---|---|---|---|
| 1[b] | 1.1 | −78 | 2 | 22 | 0 |
| 2[b] | 2.2 | −78 | 2 | 40 | 0 |
| 3[b] | 2.2 | R.t. | 2 | 43 (38) | 0 |
| 4[b] | 2.2 | R.t. | 6 | 6 | 54 |
| 5 | 4.4 | R.t. | 2 | 7 | 81 |
| 6 | 4.4 | R.t. | 6 | 7 | 86 |
| 7 | 6.6 | R.t. | 2 | 0 | 96 (80) |
| 8 | 6.6 | R.t. | 6 | 0 | 93 |

[a] Determined by $^{19}$F NMR. Values in parentheses are of isolated yield. [b] The substrate **1** remained in the reaction mixture.




**Scheme 4** A possible mechanism for the reaction of **1** with ylide **4**.

## 3 Conclusion

We have investigated the reactions of perfluorocyclopentene (**1**) with various carbon nucleophiles, such as heteroaromatic lithium reagents **2**, sodiomalonate **3** and phosphonium ylide **4**, and found that the addition of heteroaromatic lithium reagents **2** to a THF solution of **1** preferentially gave the corresponding monosubstituted perfluorocyclopentenes **5**, and the reverse addition led to the corresponding 1,2-disubstituted compounds **6** in good to excellent yields. The reaction of **1** with an excess amount of sodiomalonate **3** or phosphonium ylide **4** was found to proceed smoothly to provide exclusively the corresponding 1,3-disubstituted product **8** or **10** in high yields.

## 4 Experimental

### 4.1 Measurements and materials

Melting points were recorded on a Shimadzu MM-2 type instrument at atmospheric pressure. $^1$H and $^{13}$C NMR spectra were measured with a Bruker DRX-500 (500.13 MHz for $^1$H and 125.75 MHz for $^{13}$C) spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane as an internal reference. A JEOL JNM-AL400 (376.05 MHz) and a Bruker DPX-300 (282.38 MHz) spectrometer was used to measure $^{19}$F NMR spectra in $CDCl_3$ using trichlorofluoromethane as an internal standard. Infrared spectra (IR) were determined in a liquid film or KBr disk method with a Shimadzu FT-IR 8200PC spectrophotometer and AVATAR-370DTGS (Thermo ELECTRON) spectrometer. High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5 instrument.

Anhydrous tetrahydrofuran (THF) and diethyl ether were purchased from Wako chemicals. *n*-Butyllithium (a 1.6 M hexane solution) was commercially available from Wako chemicals. Heteroaromatic lithium reagents (2-furyllithium,[11] 3-furyllithium,[12] 2-thienyllithium,[3] 3-thienyllithium,[3] 2-lithio-*N*-methylpyrrole,[13] 2-lithiobenzo[*b*]furan,[11] 2-lithiobenzo[*b*]thiophene,[3] 2-lithio-*N*-methylindole[13]) were prepared according to the previous reports. 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 60 $F_{254}$ plates and column chromatography was carried out with Wako gel C-200.

### 4.2 Typical procedure for the preparation of monosubstituted perfluorocyclopentenes 5

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 1.1 mmol of perfluorocyclopentene (**1**, 0.233 g) in THF (2 mL). To this solution was slowly added 1.8 mL (1.0 mmol) of 2-furyllithium

(0.55 M, **2a**) in $Et_2O$ *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 pentane yielded the monosubstituted product, 1-(2-furyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**5a**). The monosubstituted products **5a**–**e** were obtained as pentane solutions due to their low boiling point and volatility.

**4.2.1 1-(2-Furyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5a).** $^1$H NMR ($CDCl_3$) $\delta$ 6.61 (1H, dd, $J$ = 3.5, 1.7 Hz), 6.99 (1H, d, $J$ = 3.5 Hz), 7.68 (1H, brs); $^{19}$F NMR ($CDCl_3$) $\delta$ −132.2 to −132.0 (1F, m), −129.98 (2F, s), −117.36 (1F, s), −117.32 (1F, s), −109.97 (1F, s), −109.94 (1F, s); IR (neat) $\nu$ 3156 (w), 2965 (w), 2876 (w), 1698 (w), 1412 (s), 1321 (*vs*), 1283 (*vs*), 1144 (*vs*), 1046 (s), 971 (*vs*) cm$^{-1}$; HRMS (EI) found: $m/z$ 260.0082. Calcd for $C_9H_3F_7O$: 260.0072.

**4.2.2 1-(3-Furyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5b).** $^1$H NMR ($CDCl_3$) $\delta$ 6.77 (1H, brs), 7.56 (1H, dd, $J$ = 1.6, 1.6 Hz), 7.95 (1H, brs); $^{19}$F NMR ($CDCl_3$) $\delta$ −132.8 to −132.3 (1F, m), −130.12 (2F, s), −117.79 (1F, s), −117.75 (1F, s), −110.30 (1F, s), −110.27 (1F, s); IR (neat) $\nu$ 2955 (s), 2848 (s), 1704 (m), 1589 (w), 1404 (m), 1327 (m), 1206 (m), 1149 (m), 1046 (m), 972 (m) cm$^{-1}$; HRMS (EI) found: $m/z$ 260.0070. Calcd for $C_9H_3F_7O$: 260.0072.

**4.2.3 1-(2-Thienyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5c).** $^1$H NMR ($CDCl_3$) $\delta$ 7.20 (1H, td, $J$ = 5.0, 1.1 Hz), 7.65 (1H, d, $J$ = 2.8 Hz), 7.68 (1H, d, $J$ = 5.0 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −131.5 to −131.4 (1F, m), −129.80 (2F, s), −117.29 (1F, s), −117.25 (1F, s), −109.58 (1F, s), −109.55 (1F, s); IR (neat) $\nu$ 3115 (w), 2959 (w), 2930 (w), 1817 (w), 1688 (m), 1428 (m), 1383 (*vs*), 1280 (s), 1202 (s), 1136 (*vs*), 968 (*vs*), 784 (s) cm$^{-1}$; HRMS (EI) found: $m/z$ 275.9854. Calcd for $C_9H_3F_7S$: 275.9844.

**4.2.4 1-(3-Thienyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5d).** The product **5d** could not be isolated as a pure product. $^1$H NMR ($CDCl_3$) $\delta$ 7.16 (1H, d, $J$ = 5.3 Hz), 7.59 (1H, d, $J$ = 5.3 Hz), 7.9–8.0 (1H, m);$^{19}$F NMR ($CDCl_3$) $\delta$ −132.3 to −132.2 (1F, m), −130.12 (2F, s), −117.85 (1F, s), −117.81 (1F, s), −109.57 (1F, s), −109.55 (1F, s); HRMS (EI) found: $m/z$ 275.9841. Calcd for $C_9H_3F_7S$: 275.9844.

**4.2.5 1-(2-*N*-Methylpyrrolyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5e).** $^1$H NMR ($CDCl_3$) $\delta$ 3.71 (1H, d, $J$ = 3.7 Hz), 6.28 (1H, dd, $J$ = 3.7, 2.6 Hz), 6.71 (1H, brs), 6.87 (1H, brs); $^{19}$F NMR ($CDCl_3$) $\delta$ −132.3 to −132.2 (1F, m), −130.60 (2F, s), −117.70 (1F, s), −117.65 (1F, s), −108.90 (1F, s), −108.88 (1F, s); IR (neat) $\nu$ 3035 (m), 2927 (m), 2852 (m), 1772 (*vs*), 1685 (s), 1531 (s), 1429 (s), 1321 (*vs*), 1280 (*vs*), 1140 (*vs*), 1041 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 273.0389. Calcd for $C_{10}H_6F_7N$: 273.0388.

**4.2.6 1-(2-Benzo[*b*]furyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5f).** Mp 35–37 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.31 (1H, s), 7.33 (1H, td, $J$ = 7.8, 0.6 Hz), 7.46 (1H, t, $J$ = 7.8 Hz), 7.58 (1H, d, $J$ = 8.4 Hz), 7.67 (1H, d, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.11 (tquint.d, $J$ = 218.8, 23.9, 4.8 Hz), 110.95 (tq, $J$ = 258.7, 22.9 Hz), 111.87, 112.53 (d, $J$ = 6.4 Hz), 114.16 (tt, $J$ = 27.2, 4.4 Hz), 114.79 (ttd, $J$ = 260.2, 24.9, 9.2 Hz), 122.35, 124.11, 126.94, 127.57, 140.95 (d, $J$ = 4.4 Hz), 147.7–151.0 (dm, $J$ = 304.4 Hz), 155.86 (d, $J$ = 1.9 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −129.95 (2F, s), −127.8 to −127.9 (1F, m), −117.63 (1F, s), −117.59 (1F, s), −109.57 (1F, s), −109.54 (1F, s); IR (KBr) $\nu$ 2959 (m), 2927 (m), 2844 (m), 1980 (w), 1634 (m), 1383 (w), 1074 (*vs*), 783 (w), 667 (m), 468 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 310.0211. Calcd for $C_{13}H_5F_7O$: 310.0229.

**4.2.7 1 - (2 - Benzo[*b*]thienyl) - 2,3,3,4,4,5,5 - heptafluorocyclopentene (5g).** Mp 47–48 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.46 (1H, quint., $J$ = 7.0 Hz), 7.80 (1H, s), 7.80–7.90 (2H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.16 (tquint.d, $J$ = 275.0, 24.7, 5.4 Hz), 110.90 (tq, $J$ = 257.4, 22.3 Hz), 115.37 (ttd, $J$ = 260.9, 24.8, 10.1 Hz), 117.8–118.5 (m), 122.09, 122.77 (d, $J$ = 14.0 Hz), 125.09, 125.29, 126.93, 128.42 (d, $J$ = 4.3 Hz), 138.31, 141.41 (d, $J$ = 5.5 Hz), 148.0–150.8 (dm, $J$ = 300.7 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −129.70 (2F, s), −129.6 to −129.5 (1F, m), −117.52 (1F, s), −117.48 (1F, s), −109.03 (1F, s), −109.00 (1F, s); IR (KBr) $\nu$ 3062 (w), 2922 (w), 1688 (m), 1384 (*vs*), 1272 (s), 1248 (m), 1136 (*vs*), 1021 (*vs*), 968 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 325.9995. Calcd for $C_{13}H_5F_7S$: 326.0000. Anal. calcd for $C_{13}H_5F_7S$: C, 47.86: H, 1.54. Found: C, 48.13; H, 1.63.

**4.2.8 1-(2-Indolyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (5h).** Mp 37–39 °C; $^1$H NMR ($CDCl_3$) $\delta$ 3.76 (3H, d, $J$ = 3.4 Hz), 7.00 (1H, s), 7.20 (1H, ddd, $J$ = 8.0, 6.4, 1.6 Hz), 7.3–7.4 (2H, m), 7.69 (1H, d, $J$ = 8.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 31.72 (d, $J$ = 7.3 Hz), 107.80, 110.06, 110.11 (tquint.d, $J$ = 275.5, 24.0, 3.6 Hz), 110.89 (tq, $J$ = 259.0, 23.9 Hz), 115.06 (ttd, $J$ = 260.1, 24.9, 10.4 Hz), 116.0–116.5 (m), 120.97, 121.96, 122.01, 124.71, 127.22, 139. 50, 148.8–152.0 (dm, $J$ = 294.0 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −130.39 (2F, s), −127.6 to −127.7 (1F, m), −118.24 (1F, s), −118.20 (1F, s), −108.90 (1F, s), −108.87 (1F, s); IR (KBr) $\nu$ 2099 (m), 1643 (s), 1461 (w), 1340 (m), 1277 (w), 1140 (m), 1038 (m), 974 (m), 910 (w) cm$^{-1}$; HRMS (FAB) found: $m/z$ 323.0545. Calcd for $C_{14}H_8F_7N$: 323.0545.

### 4.3 Typical procedure for the preparation of 1,2-disubstituted perfluorocyclopentenes 6

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 2-furyllithium (**2a**) in $Et_2O$. To this solution was slowly added 0.212 g (1.0 mmol) of perfluorocyclopentene **1** in THF (2 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). 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–ethyl acetate (12 : 1) gave 1,2-di(2-furyl)-3,3,4,4,5,5-hexafluorocyclopentene (**6a**).

**4.3.1 1,2-Di(2-furyl)-3,3,4,4,5,5-hexafluorocyclopentene (6a).** $^1$H NMR ($CDCl_3$) $\delta$ 6.57 (2H, dd, $J$ = 3.5, 1.6 Hz), 7.16 (2H, d, $J$ = 3.3 Hz), 7.61 (2H, brs); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.57 (tquint., $J$ = 245.6, 24.5 Hz), 112.41, 116.25 (tt, $J$ = 257.7, 24.0 Hz), 117.24, 122.5–123.0 (m), 143.46, 145.52; $^{19}$F NMR ($CDCl_3$) $\delta$ −131.8 to −131.9 (2F, m), −109.4 to −109.5 (4F, m); IR (neat) $\nu$ 3152 (w), 2959 (w), 2873 (w), 1619 (m), 1576 (s), 1486 (*vs*), 1342 (*vs*), 1223 (*vs*), 1195 (*vs*), 1071 (*vs*), 997 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 308.0280. Calcd for $C_{13}H_6F_6O_2$: 308.0272.

**4.3.2 1,2-Di(3-furyl)-3,3,4,4,5,5-hexafluorocyclopentene (6b).** $^1$H NMR ($CDCl_3$) $\delta$ 6.53 (2H, d, $J$ = 1.3 Hz), 7.50 (2H, t, $J$ = 1.7 Hz), 7.81 (2H, brs); $^{13}$C NMR ($CDCl_3$) $\delta$ 109.60, 110.74 (tquint., $J$ = 270.5, 24.8 Hz), 113.18, 116.41 (tt, $J$ = 258.7, 26.7 Hz), 130.0–130.5 (m), 143.93, 144.03; $^{19}$F NMR ($CDCl_3$) $\delta$ −131.9 to −131.5 (2F, m), −110.96 (4F, brs); IR (neat) $\nu$ 3157 (w), 2918 (w), 1657 (m), 1581 (s), 1515 (*vs*), 1342 (*vs*), 1281 (*vs*), 1168 (*vs*), 1128 (*vs*), 1098 (*vs*), 963 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 308.0279. Calcd for $C_{13}H_6F_6O_2$: 308.0272.

**4.3.3 1,2-Di(2-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (6c).** $^1$H NMR ($CDCl_3$) $\delta$ 7.15 (2H, dd, $J$ = 5.0, 3.8 Hz), 7.47 (2H, d, $J$ = 3.5 Hz), 7.55 (2H, dd, $J$ = 5.1, 0.7 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.77 (tquint., $J$ = 271.4, 24.8 Hz), 115.76 (tt, $J$ = 257.3, 23.9 Hz), 127.54, 127.76, 130.84, 131.77, 132.1–132.7 (m); $^{19}$F NMR ($CDCl_3$) $\delta$ −131.15 (2F, tt, $J$ = 4.9, 4.9 Hz), −110.56 (4F, t, $J$ = 4.9 Hz); IR (neat) $\nu$ 3097 (s), 2962 (s), 2856 (m), 1629 (s), 1527 (s), 1437 (s), 1336 (s), 1262 (*vs*), 1124 (*vs*), 977 (s), 796 (s) cm$^{-1}$; HRMS (FAB) found: $m/z$ 339.9822. Calcd for $C_{13}H_6F_6S_2$: 339.9815.

**4.3.4 1,2-Di(3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (6d).** $^1$H NMR ($CDCl_3$) $\delta$ 7.04 (2H, d, $J$ = 5.0 Hz), 7.36 (2H, dd, $J$ = 5.0, 3.0 Hz), 7.63 (2H, brs); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.91 (tquint., $J$ = 271.0, 24.8 Hz), 116.43 (tt, $J$ = 253.9, 26.4 Hz), 126.62, 127.35, 128.46, 130.60, 132.9–133.6 (m); $^{19}$F NMR ($CDCl_3$) $\delta$ −131.56 (2F, tt, $J$ = 4.9, 4.9 Hz), −110.68 (4F, t, $J$ = 4.9 Hz); IR (neat) $\nu$ 3117 (m), 2927 (m), 1640 (m), 1529 (s), 1432 (s), 1367 (s), 1275 (*vs*), 1123 (*vs*), 1076 (*vs*), 999 (*vs*), 782 (s) cm$^{-1}$; HRMS (FAB) found: $m/z$ 339.9825. Calcd for $C_{13}H_6F_6S_2$: 339.9815.

**4.3.5 1,2-Bis(2-*N*-methylpyrrolyl)-3,3,4,4,5,5-hexafluorocyclopentene (6e).** Mp 104–107 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.95 (6H, s), 6.29 (2H, dd, $J$ = 3.8, 2.8 Hz), 6.61 (2H, d, $J$ = 2.8 Hz), 6.73 (2H, d, $J$ = 1.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 34.33, 110.90 (tquint., $J$ = 270.0, 23.8 Hz), 116.16 (tt, $J$ = 255.3, 23.8 Hz), 121.22, 127.32, 132.1–132.7 (m); $^{19}$F NMR ($CDCl_3$) $\delta$ −132.30 (2F, tt, $J$ = 4.9, 4.9 Hz), −110.10 (4F, t, $J$ = 4.9 Hz); IR (KBr) $\nu$ 2959 (w), 2929 (w), 2885 (w), 1634 (m), 1535 (w), 1435 (w), 1257 (m), 1116 (*vs*), 1058 (*vs*), 811 (w), 701 (w) cm$^{-1}$; HRMS (FAB) found: $m/z$ 334.0909. Calcd for $C_{15}H_{12}F_6N_2$: 334.0905.

**4.3.6 1,2-Bis(2-benzo[*b*]furyl)–3,3,4,4,5,5-hexafluorocyclopentene (6f).** Mp 107–109 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.34 (2H, t, $J$ = 7.7 Hz), 7.45 (2H, t, $J$ = 7.9 Hz), 7.5–7.6 (4H, m), 7.72 (2H, d, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.64 (tquint., $J$ = 245.6, 24.4 Hz), 111.54, 113.93, 116.15 (tt, $J$ = 258.3, 24.0 Hz), 122.29, 123.89, 125.1–125.8 (m), 127.41, 127.52, 144.47, 155.58; $^{19}$F NMR ($CDCl_3$) $\delta$ −132.0 to −131.6 (2F, m), −109.39 (4F, brs); IR (KBr) $\nu$ 3050 (w), 2914 (w), 1609 (m), 1560 (s), 1393 (s), 1277 (*vs*), 1215 (*vs*), 1126 (*vs*), 1000 (*vs*), 947 (*vs*), 741 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 408.0590. Calcd for $C_{21}H_{10}F_6O_2$: 408.0585. Anal. calcd for $C_{21}H_{10}F_6O_2$: C, 61.78: H, 2.47. Found: C, 62.09; H, 2.42.

**4.3.7 1,2-Bis(2-benzo[*b*]thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (6g).** Mp 136–138 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.4–7.5 (4H, m), 7.7–7.8 (4H, m), 7.8–7.9 (2H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 110.81 (tquint., $J$ = 270.9, 24.4 Hz), 115.81 (tt, $J$ = 258.0, 23.9 Hz), 122.21, 124.87, 125.01, 126.55, 127.49, 129.65, 133.3–134.0 (m), 138.61, 141.51; $^{19}$F NMR ($CDCl_3$) $\delta$ −131.02 (2F, brs), −110.18 (4F, brs); IR (KBr) $\nu$ 3066 (w), 2926 (w), 1627 (m), 1526 (m), 1331 (m), 1277 (s), 1122 (*vs*), 1042 (*vs*), 974 (*vs*), 757 (s) cm$^{-1}$; HRMS (FAB) found: $m/z$ 440.0139. Calcd for $C_{21}H_{10}F_6S_2$: 440.0128. Anal. calcd for $C_{21}H_{10}F_6S_2$: C, 57.27: H, 2.29. Found: C, 57.15; H, 2.32.

**4.3.8 1,2-Di(2-indolyl)-3,3,4,4,5,5-hexafluorocyclopentene (6h).** Mp 208–210 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.99 (6H, s), 7.08 (4H, brs), 7.27 (4H, dd, $J$ = 13.9, 7.1 Hz), 7.27 (2H, ddd, $J$ = 15.3, 8.2, 1.0 Hz), 7.68 (2H, d, $J$ = 8.0 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 31.02, 107.89, 110.21, 110.86 (tquint., $J$ = 270.9, 25.3 Hz), 116.01 (tt, $J$ = 256.8, 23.0 Hz), 120.96, 121.88, 124.53, 127.40, 127.60, 130.6–131.4 (m), 139.29; $^{19}$F NMR ($CDCl_3$) $\delta$ −132.23 (2F, brs), −109.83 (4F, brs); IR (KBr) $\nu$ 2959 (w), 2848 (w), 1653 (m), 1529 (w), 1463 (m), 1338 (m), 1264 (s), 1112 (*vs*), 988 (s), 855 (m), 750 (m) cm$^{-1}$; HRMS (FAB) found: $m/z$ 434.1225. Calcd for $C_{23}H_{16}F_6N_2$: 434.1218.

### 4.4 Typical procedure for the preparation of 1,2-bis(1-phenylvinyloxy)-3,3,4,4,5,5-hexafluorocyclopentene (6-*O*)

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 2.2 equiv. of 1-phenyl-1-(trimethylsilyloxy)ethylene, prepared from acetophenone in THF. To this solution was added 0.212 g (1.0 mmol) of **1** in THF (2 mL) *via* a syringe at room temperature. To the solution was slowly added 0.5 mL (0.5 mmol) of 1.0 M tetrabutylammonium fluoride (TBAF) in THF *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), followed by extraction with diethyl 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 an eluent yielded 1,2-bis(1-phenylvinyloxy)-3,3,4,4,5,5-hexafluorocyclopentene (**6-*O***).

**4.4.1 1,2-Bis(1-phenylvinyloxy)-3,3,4,4,5,5-hexafluorocyclopentene (6-*O*).** $^1$H NMR ($CDCl_3$) $\delta$ 4.72 (1H, d, $J$ = 3.8 Hz), 5.05 (1H, d, $J$ = 3.8 Hz), 7.3–7.5 (5H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 93.64, 109.68 (tquint., $J$ = 273.1, 24.4 Hz), 113.05 (tt, $J$ = 257.7, 24.1 Hz), 125.23, 128.34, 129.42, 132.65, 134.2–134.9 (m), 155.14; $^{19}$F NMR ($CDCl_3$) $\delta$ −130.94 (2F, s), −114.77 (4F, s); IR (neat) $\nu$ 3060 (w), 1689 (*vs*), 1577 (m), 1494 (s), 1369 (*vs*), 1290 (*vs*), 1198 (*vs*), 1074 (*vs*), 982 (*vs*), 837 (m) cm$^{-1}$; HRMS (FAB) found: $m/z$ 412.0898. Calcd for $C_{21}H_{14}F_6O_2$: 412.0898.

**4.4.2 1-(1-Phenylvinyloxy)-2,3,3,4,4,5,5-heptafluorocyclopentene (5-*O*).** $^1$H NMR ($CDCl_3$) $\delta$ 5.06 (1H, dd, $J$ = 3.4, 1.1 Hz), 5.38 (1H, d, $J$ = 3.4 Hz), 7.4–7.5 (3H, m), 7.5–7.6 (2H, m); $^{19}$F NMR ($CDCl_3$) $\delta$ −150.4 to −150.1 (1F, m), −130.10 (2F, s), −116.14 (1F, s), −116.10 (1F, s), −116.07 (1F, s), −116.02 (1F, s); IR (neat) $\nu$ 3092 (w), 3064 (w), 2958 (w), 2929 (w), 1728 (*vs*), 1645 (s), 1496 (m), 1377 (*vs*), 1290 (*vs*), 1151 (*vs*), 1090 (s) cm$^{-1}$; HRMS (FAB) found: $m/z$ 312.0384. Calcd for $C_{13}H_7F_7O$: 312.0385.

### 4.5 Typical procedure for the preparation of diethyl 3-[bis(ethoxycarbonyl)]-methylene-2,4,4,5,5-pentafluorocyclopent-1-enylmalonate (8)

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 suspended solution of

4.4 equiv. of sodium hydride in THF. To this suspended solution was dropwise added 0.743 g (4.6 mmol) of diethyl malonate *via* 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 **1** in THF (1 mL) *via* 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). 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–ethyl acetate (3 : 1) gave diethyl 3-[bis(ethoxycarbonyl)]methylene-2,4,4,5,5-pentafluorocyclopent-1-enylmalonate (**8**). The products **7A** and **7B** could not be isolated as a pure product. $^{19}$F NMR of the mixture was as follows. **7A** : $\delta$ ($CDCl_3$) −130.59 (2F, brs), −126.81 (1F, brs), −119.662 (1F, brs), −119.62 (1F, brs), −110.45 (1F, brs), −110.41 (1F, brs); **7B** : $\delta$ ($CDCl_3$) −150.5 to −150.1 (1F, m), −130.47 (1F, brs), −123.5 −123.2 (2F, m), −114.33 (1F, brs), −114.30 (1F, brs).

#### 4.5.1 Diethyl-3-[bis(ethoxycarbonyl)]methylene-2,4,4,5,5-pentafluorocyclopent-1-enylmalonate (8)

Mp 35–37 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.30 (6H, t, $J$ = 7.1 Hz), 1.34 (6H, t, $J$ = 7.1 Hz), 4.28 (4H, q, $J$ = 7.1 Hz), 4.36 (4H, q, $J$ = 7.1 Hz), 4.42 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.58, 13.68, 46.91, 53.34, 62.84, 62.91, 112.94 (ttd, $J$ = 261.4, 24.4, 5.4 Hz), 116.22 (ttd, $J$ = 315.2, 25.9, 9.1 Hz), 127.64, 127.68, 130.80 (t, $J$ = 24.9 Hz), 130.93 (t, $J$ = 24.9 Hz), 159.0–161.8 (dm), 160.20, 162.02, 163.96; $^{19}$F NMR ($CDCl_3$) $\delta$ −114.56 (1F, brs), −114.51 (1F, brs), −111.07 (1F, brs), −110.94 (1F, brs), −109.0 to −108.4 (1F, m); IR (KBr) $\nu$ 2991 (m), 1740 (*vs*), 1678 (m), 1468 (m), 1371 (s), 1254 (*vs*), 1157 (s), 1099 (*vs*), 901 (s) cm$^{-1}$; HRMS (FAB) found: $m/z$ 473.1237. Calcd for $C_{19}H_{22}F_5O_8$: 473.1235.

### 4.6 Typical procedure for the preparation of 2,4,4,5,5-pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)methyl]-2-cyclopenten-1-one (9)

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 methyltriphenylphosphonium bromide in THF. To this solution was slowly added a solution of *n*-butyllithium in hexane (2.2 mmol) *via* syringe at –78 °C. The whole was stirred for 30 min at 0 °C and then cooled to –78 °C. To the solution was slowly added 0.212 g (1.0 mmol) of **1** in methylene chloride (4 mL) *via* 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 methylene chloride (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–ethyl acetate (1 : 2) as eluents yielded 2,4,4,5,5-pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)methyl]-2-cyclopenten-1-one (**9**).

**4.6.1 2,4,4,5,5-Pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)-methyl]-2-cyclopenten-1-one (9).** Mp 205–207 °C; $^1$H NMR ($CDCl_3$) $\delta$ 4.16 (1H, d, $J$ = 14.2 Hz), 7.5–7.6 (12H, m), 7.65–7.72 (3H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 55.36 (d, $J$ = 111.6 Hz), 110.29 (ttd, $J$ = 258.9, 23.3, 5.9 Hz), 114.25 (ttd, $J$ = 254.0, 28.3, 6.3 Hz), 123.67 (d, $J$ = 92.3 Hz), 129.53 (d, $J$ = 12.8 Hz), 132.64 (d, $J$ = 10.4 Hz), 133.56 (d, $J$ = 2.6 Hz), 140.9–143.5 (m), 146.2–146.9 (m), 163.93 (td, $J$ = 25.2, 11.4 Hz); $^{19}$F NMR ($CDCl_3$) $\delta$ −152.8 to −152.0 (1F, m), −124.91 (1F, brs), −124.80 (1F, brs), −116.06 (1F, brs), −115.96 (1F, brs); $^{31}$P NMR ($H_3PO_4$) $\delta$ 16.25–17.30 (1P, m); IR (KBr) $\nu$ 3055 (w), 2368 (w), 1685 (s), 1560 (*vs*), 1438 (s), 1303 (m), 1240 (m), 1101 (*vs*), 1016 (*vs*), 964 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 447.0938. Calcd for $C_{24}H_{17}F_5OP$: 447.0937.

### 4.7 Typical procedure for the preparation of {2,4,4,5,5-pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)methyl]-2-cyclopentenylidenemethyl}triphenylphosphonium bromide (10)

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 methyltriphenylphosphonium bromide in THF. To this solution was dropwise added a solution of *n*-butyllithium in hexane (6.6 mmol) *via* syringe at –78 °C. The whole was stirred for 30 min at 0 °C and then cooled to –78 °C. To the solution was slowly added 0.212 g (1.0 mmol) of **1** in methylene chloride (6 mL) *via* 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 methylene chloride (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 ethyl acetate–ethanol (5 : 1) gave {2,4,4,5,5-pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)methyl]-2-cyclopentenylidene-methyl}triphenylphosphonium bromide (**10**).

**4.7.1 {2,4,4,5,5-Pentafluoro-3-[(triphenyl-λ$^5$-phosphonylidene)-methyl]-2-cyclopentenylidenemethyl}triphenylphosphonium bromide (10).** Mp: >300 °C; $^1$H NMR ($CDCl_3$) $\delta$ 4.24 (2H, d, $J$ = 12.6 Hz), 7.27–7.35 (10H, m), 7.50–7.58 (13H, m), 7.6–7.8 (7H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ 57.99 (d, $J$ = 111.9 Hz), 114.53 (tt, $J$ = 242.3, 32.4 Hz), 121.76 (d, $J$ = 92.4 Hz), 129.08 (d, $J$ = 12.9 Hz), 131.52 (d, $J$ = 10.7 Hz), 133.34, 138.5–139.5 (m), 140.0–142.5 (m); $^{19}$F NMR ($CDCl_3$) $\delta$ −137.00 to −136.20 (1F, m), −113.92 (2F, brs), −113.81 (2F, brs); IR (KBr) $\nu$ 3049 (w), 2365 (w), 1524 (*vs*), 1437 (s), 1232 (m), 1107 (s), 1028 (*vs*), 964 (s), 767 (*vs*) cm$^{-1}$; HRMS (FAB) found: $m/z$ 705.1896. Calcd for $C_{43}H_{32}F_5P_2$: 705.1899.

### 4.8. X-Ray structural analysis of 9

A purple block crystal of $C_{24}H_{16}F_5OP$ having approximate dimensions of 0.30 × 0.27 × 0.25 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with filtered Cu Kα radiation and a rotating anode generator.

Compound **9**. $C_{24}H_{16}F_5OP$, $M$ = 446.36, orthorhombic, $a$ = 17.266(7), $b$ = 17.317(7), $c$ = 13.791(4) Å, $\alpha$ = 90.0000, $\beta$ = 90.0000, $\gamma$ = 90.0000°, $U$ = 4123(3) Å$^3$, $T$ = 198.1 K, space group *Pbca* (no. 61), $Z$ = 8, $\mu$(Mo Kα) = 1.54178 mm$^{-1}$, 15820 reflections measured, 3661 unique ($R_{int}$ = 0.077) which were used in all calculations. The final $R1$ and $wR2$ were 0.047 and 0.114 ($I > 2\sigma(I)$).†

All calculations were performed by using the CrystalStructure[14] crystallographic software package (Rigaku and Rigaku/MSC

(2000–2003)) except for refinement, which was performed using SHELXL-97.[15] The structure was solved by direct methods (SIR2002[16]) and expanded using Fourier techniques (DIRDIF99[17]). The goodness of fit indicator was 1.061.

### 4.9. X-Ray structural analysis of 10

A yellow block crystal of $C_{43}H_{32}P_2F_5Br$ having approximate dimensions of $0.25 \times 0.20 \times 0.30$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with filtered Cu Kα radiation and a rotating anode generator.

Compound **10**. $C_{43}H_{32}BrF_5P_2$, $M = 785.57$, monoclinic, $a = 16.463(9)$, $b = 18.19(1)$, $c = 13.50(1)$ Å, $\alpha = 90.0000$, $\beta = 111.93(4)$, $\gamma = 90.0000°$, $U = 3750(4)$ Å$^3$, $T = 198.1$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu$(Mo Kα) = 1.54178 mm$^{-1}$, 18854 reflections measured, 6653 unique ($R_{int} = 0.150$) which were used in all calculations. The final $R1$ and $wR2$ were 0.129 and 0.314 ($I > 2\sigma(I)$).†

All calculations were performed by using the CrystalStructure crystallographic software package (Rigaku and Rigaku/MSC (2000–2003)) except for refinement, which was performed using SHELXL-97.[15] The structure was solved by direct methods (SIR2002[16]) and expanded using Fourier techniques (DIRDIF99[17]). The goodness of fit indicator was 1.229.

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## References

1 (*a*) J.-P. Bégué and D. Bonnet-Delpon, *J. Fluorine Chem.*, 2006, **127**, 992–1012; (*b*) C. Isanbor and D. O'Hagan, *J. Fluorine Chem.*, 2006, **127**, 303–319; (*c*) K. Matsuda and M. Irie, *Chem. Lett.*, 2006, **35**, 1204–1209; (*d*) M. Morimoto and M. Irie, *Chem. Commun.*, 2005, 3895–3905; (*e*) R. Miethchen, *J. Fluorine Chem.*, 2004, **125**, 895–901; (*f*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716; (*g*) T. Hiyama, *Organofluorine Compounds, Chemistry and Applications*, Springer, New York, 2000; (*h*) I. Ojima, J. R. McCarthy, J. T. Welch, *Biomedical Frontiers of Fluorine Chemistry*, American Chemical Society, Washington, DC, 1996; (*i*) B. E. Smart, *Chem. Rev.*, 1996, **96**, 1555–1823; (*j*) J. T. Welch and S. Eswarakrishnan, *Fluorine in Bioorganic Chemistry*, Wiley, New York, 1991.

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 Ltd, Tokyo, 1998; (*c*) X. Qiu, W. Meng and F.-L. Qing, *Tetrahedron*, 2004, **60**, 6711–6745; (*d*) K. Mikami, Y. Itoh and M. Yamanaka, *Chem. Rev.*, 2004, **104**, 1–16; (*e*) J. Ichikawa, Y. Wada, M. Fujiwara and K. Sakoda, *Synthesis*, 2002, 1917–1936.

3 M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305–8309.

4 (*a*) M. Takeshita and M. Irie, *Tetrahedron Lett.*, 1999, **40**, 1345–1348; (*b*) J. P. Malval, I. Gosse, J. P. Morand and R. Lapouyade, *J. Am. Chem. Soc.*, 2002, **124**, 904–905; (*c*) T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y. Nagata, A. Itaya and M. Irie, *J. Am. Chem. Soc.*, 2002, **124**, 2015–2024; (*d*) A. Peters, C. Vitols, R. McDonald and N. R. Branda, *Org. Lett.*, 2003, **5**, 1183–1185; (*e*) S. Yamamoto, K. Matsuda and M. Irie, *Org. Lett.*, 2003, **5**, 1769–1772; (*f*) K. Yagi and M. Irie, *Chem. Lett.*, 2003, **32**, 848–849; (*g*) K. Morimitsu, S. Kobatake, S. Nakamura and M. Irie, *Chem. Lett.*, 2003, **32**, 858–859.

5 (*a*) S. Yamada, T. Konno, T. Ishihara and H. Yamanaka, *J. Fluorine Chem.*, 2005, **126**, 125–133; (*b*) J. D. Park, R. Sullivan and R. J. McMurtry, *Tetrahedron Lett.*, 1967, **8**, 173–176; (*c*) J. D. Park, C. D. Bertino and B. T. Nakata, *J. Org. Chem.*, 1969, **34**, 1490–1492.

6 (*a*) P. E. Lindner and D. M. Lemal, *J. Org. Chem.*, 1996, **61**, 5109–5115; (*b*) A. E. Bayliff, M. R. Bryce and R. D. Chambers, *J. Chem. Soc., Perkin Trans. 1*, 1987, 763–767; (*c*) R. F. Stockel, M. T. Beachem and F. H. Megson, *J. Org. Chem.*, 1965, **30**, 1629–1632; (*d*) R. F. Stockel, M. T. Beachem and F. H. Megson, *Can. J. Chem.*, 1964, **42**, 2880–2883.

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

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

9 (*a*) D. Su, C. Guo, D. Willett, B. Scott, R. L. Kirchmeier and J. M. Shreeve, *J. Am. Chem. Soc.*, 1990, **112**, 3152–3155; (*b*) R. F. Stockel, *Can. J. Chem.*, 1968, **46**, 2625–2628; (*c*) A. W. Frank, *J. Org. Chem.*, 1966, **31**, 917–921; (*d*) A. Matsui, H. Muramatsu and K. Inukai, *Nippon Kagaku Kaishi*, 1972, 602–608; (*e*) A. A. Kadyrov, D. V. Silaev, K. N. Makarov, L. L. Gervits and G. V. Roschenthaler, *J. Fluorine Chem.*, 2004, **125**, 1407–1410.

10 For the reaction of the related compound, perfluorocyclobutene, with hetero nucleophiles, see: (*a*) C. M. Timperley, *J. Fluorine Chem.*, 2004, **125**, 685–693; (*b*) ref. 7a; (*c*) R. D. Chambers, S. R. Korn and G. Sandford, *J. Fluorine Chem.*, 1994, **69**, 103–108; (*d*) ref. 6b.

11 E. M. Jung and J. Gervay, *J. Am. Chem. Soc.*, 1991, **113**, 224–232.

12 S. E. Drewes, P. A. Grieco and J. C. Huffman, *J. Org. Chem.*, 1985, **50**, 1309–1311.

13 A. Minato, K. Tamao, T. Hayashi, K. Suzuki and M. Kumada, *Tetrahedron Lett.*, 1981, **52**, 5319–5322.

14 *CrystalStructure 3.7.0: CrystalStructure Analysis Package*, Rigaku and Rigaku/MSC, 9009 New Trails Dr., The Woodlands, TX 77381, USA, 2000–2003.

15 G. M. Sheldrick, *SHELXL97*, 1997.

16 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori and R. Spagna, *SIR2002*, 2003.

17 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *DIRDIF99 Program system*, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.