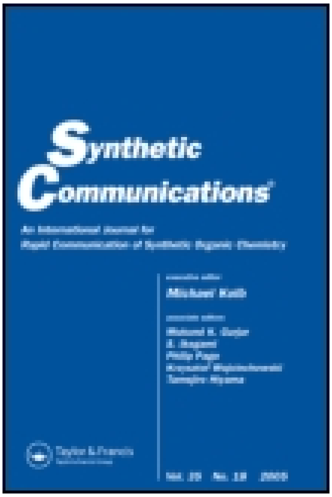


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthesis and Structure Elucidation of New Spiro Compounds with Polyfluoroalkyl and Phosphonate Ester Groups

Zhijian Shi [a b] , Yang Zhao [a] , Weiguo Cao [a b] , Shunli Zhang [a] & Mei Liu [a]

[a] Department of Chemistry , Shanghai University , Shanghai, China

[b] Key Laboratary of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences , Shanghai, China
Published online: 19 Mar 2009.

Synthetic Communications®, 39: 1494–1503, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802537143

Taylor & Francis
Taylor & Francis Group

Synthesis and Structure Elucidation of New Spiro Compounds with Polyfluoroalkyl and Phosphonate Ester Groups

Zhijian Shi,[1,2] Yang Zhao,[1] Weiguo Cao,[1,2] Shunli Zhang,[1] and Mei Liu[1]

[1]Department of Chemistry, Shanghai University, Shanghai, China
[2]Key Laboratary of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

Abstract: A series of spiro compounds with polyfluoroalkyl and phosphonate ester groups has been synthesized via several steps. The structures of these compounds were confirmed by ^{1}H NMR, ^{13}C NMR, infrared (IR), and mass spectrometry (MS) as well. The possible reaction mechanism for the formation of these products was also proposed.

Keywords: Phosphonate ester group, polyfluoroalkylated spiro compound, structure elucidation

INTRODUCTION

Fluorine-containing organic compounds have played an important role in synthetic organic chemistry and pharmaceutical chemistry because of their biological activities. The ability of the fluorine atom to enhance biological and therapeutical activities of certain organic compounds has led to widespread interest in selective introduction of fluorine atoms and fluoroalkyl groups into organic molecules.[1–3] The development of synthetic methodologies in organofluorine chemistry has always been of paramount importance. The cyclic compounds containing perflour-

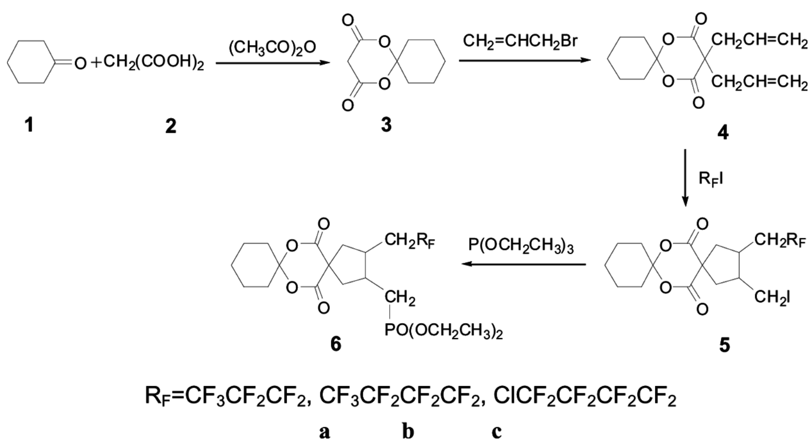
Received September 10, 2008.
Address correspondence to Zhijian Shi and Weiguo Cao, Shanghai University, Shanghai 200444, China. E-mail: shzhjian@shu.edu.cn; wgcao@staff.shu.edu.cn

oalkyl have drawn much more attention because of their unique physiological and potential biological properties, which can be imparted by a fluoroalkyl group. However, the preparation of perfluoroalkylated organic compounds suffered from long synthetic procedures and the difficulty of introducing the fluoroalkyl group.[4–14] In this article, we report a simple synthesis of a series of spiro compounds, **5a–c** and **6a–c**, with per(poly)fuoroalkyl and phosphonate ester groups. The possible mechanisms for the formation of these products were also proposed.

RESULTS AND DISCUSSION

In the presence of KOH and PEG-400 in acetone at 57–60°C, 1,5-dioxa-spiro[5.5]undecane-2,4-dione (**3**)[15] reacted with 3-bromopropene to give 3,3-diallyl-1,5-dioxa-spiro[5.5]undecane-2,4-dione (**4**). Compound **4** reacted with perfluoroalkyl iodides (**a–c**) in a water–acetonitrile biphasic solvent system, using $Na_2S_2O_4$ and Na_2CO_3 as initiators, to offer cyclic compounds **5a–c** with high yields. The reaction of compounds **5a–c** with triethyl phosphite proceeded at 200°C gave rise to the products **6a–c** (Scheme 1, Table 1).

The structures of compounds **4**, **5a–c**, and **6a–c** were confirmed by means of infrared (IR), mass spectrometry (MS) (Table 2), ^1H NMR, and ^{13}C NMR (Table 3).



Scheme 1. Synthesis of polyfluorinated spiro compounds.

Table 1. Preparation of compounds **4**, **5a–c**, and **6a–c**

Compound	Solvent	Reaction condition	State	Mp	Yield (%)
4	$(CH_3)_2CO$	60°C 5 h	Yellow oil	—	65
5a	H_2O/CH_3CN	0°C 3 h	White needle crystal	136.4–137.1	92
5b	H_2O/CH_3CN	0°C 3 h	White needle crystal	125.5–126.8	91
5c	H_2O/CH_3CN	0°C 3 h	White needle crystal	149.9–150.3	90
6a	$P(OCH_2CH_3)_3$	200°C 2 h	Yellow oil	—	76
6b	$P(OCH_2CH_3)_3$	200°C 2 h	Yellow oil	—	75
6c	$P(OCH_2CH_3)_3$	200°C 2 h	Yellow oil	—	70

The reaction mechanism is shown in Scheme 2. The $R_F^{\cdot}$ radical derived from perfluoroalkyl iodides in the presence of sodium dithionite and sodium carbonate attacked the carbon–carbon double bond of compound **4**, followed by cyclization, to form spiro compound **5**. Then, the spiro compound **6** with polyfluoroalkyl and phosphonate ester groups was obtained via the reaction of compound **5** with triethyl phosphite.

EXPERIMENTAL

Melting and boiling points are uncorrected. IR spectra were recorded on an Avatar 370 Fourier transform (FT) spectrophotometer; solid samples were examined as KBr discs, and oil samples were examined as liquid films. NMR spectra were determined with DRX 500-MHz spectrometer, using solutions in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard for ^1H and ^{13}C nuclei respectively. MS spectra were run on a 5979 MSD spectrometer.

General Procedure for the Preparation of 4

Potassium hydroxide (KOH) (5 mmol) and PEG-400 (0.2 mmol) were added to a suspension of 1,5-dioxa-spiro[5.5]undecane-2,4-dione (5 mmol) in acetone (25 ml), and the mixture was stirred at 50°C for 5 min. 3-Bromopropene (10 mmol) was added and refluxed for 5 h. The insoluble material was filtered off, and the solvent was evaporated under reduced pressure. Then, 3,3-diallyl-1,5-dioxa-spiro[5.5]undecane-2,4-dione (**4**) was collected by distillation (10 mmHg, 120–125°C fraction).

Table 2. MS and IR data of compounds **4**, **5a–c** and **6a–c**

Compound	MS (m/z, %)	IR (cm^{-1})
4	264 [M+, 5.0], 166 [$(M\text{-}C_6H_{10}O)^+$, 56.0], 148 [$(M\text{-}C_6H_{10}O\text{-}H_2O)^+$, 23.0], 138 [$(M\text{-}C_6H_{10}O\text{-}CO)^+$, 52.0], 122 [$(M\text{-}C_6H_{10}O\text{-}CO_2)^+$, 50.0], 107 [$(M\text{-}C_6H_{10}O\text{-}OH\text{-}CH_2CH{=}CH_2)^+$, 21.0], 98 [$C_6H_{10}O^+$, 100.0], 79 [$(M\text{-}C_6H_{10}O\text{-}CO\text{-}OH\text{-}CH_2CH{=}CH_2)^+$, 68.0]	3064.8 ($\nu_{=CH}$), 3002.5 ($\nu_{=CH}$), 2948.9 ($\nu_{C\text{-}H}$), 1769.9 ($\nu_{C=O}$), 1747.9 ($\nu_{C=O}$), 1639.0 ($\nu_{C=C}$)
5a	335 [$(M\text{-}I\text{-}C_6H_{10}O)^+$, 24.1], 291 [$(M\text{-}C_6H_{10}O\text{-}CO_2)^+$, 28.3], 263 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO_2\text{-}CO)^+$, 35.1], 127 [$(I)^+$, 5.9], 99 [$(C_6H_{10}O+1)^+$,70.9], 98 [$(C_6H_{10}O)^+$, 100.0], 94 [$(M\text{-}I\text{-}R_F\text{-}C_6H_{10}O\text{-}CO_2\text{-}CO)^+$, 66.6], 55 [$(M\text{-}I\text{-}R_F\text{-}C_6H_{10}O\text{-}\ 2CH_2CH{=}CH_2\text{-}CO)^+$, 66.6], 53 [$(M\text{-}I\text{-}R_F\text{-}C_6H_{10}O\text{-}\ CH_2CH{=}CH_2\text{-}CO\text{-}CO_2)^+$, 23.6], 41 [$(CH_2{=}CHCH_2)^+$, 75.9]	2947.5 ($\nu_{C\text{-}H}$), 2871.0 ($\nu_{C\text{-}H}$), 1770.2 ($\nu_{C=O}$), 1733.7 ($\nu_{C=O}$), 1305.7 ($\nu_{C\text{-}F}$), 532.9 ($\nu_{C\text{-}I}$)
5b	385 [$(M\text{-}I\text{-}C_6H_{10}O)^+$, 24.9], 313 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO\text{-}CO_2)^+$, 23.4], 293 [$(M\text{-}R_F\text{-}C_6H_{10}O)^+$, 3.6], 99 [$(C_6H_{10}OH)^+$, 100.0], 55 [$(M\text{-}I\text{-}R_F\text{-}C_6H_{10}O\text{-}2CH_2CH{=}CH_2\text{-}CO)^+$, 90.9], 41 [$(CH_2{=}CHCH_2)^+$, 47.1]	2953.0 ($\nu_{C\text{-}H}$), 2866.8 ($\nu_{C\text{-}H}$), 1763.6 ($\nu_{C=O}$), 1733.7 ($\nu_{C=O}$), 1307.0 ($\nu_{C\text{-}F}$), 530.9 ($\nu_{C\text{-}I}$)
5c	403 [$(M\text{-}I\text{-}C_6H_{10}O)^+$, 8.6], 401 [$(M\text{-}I\text{-}C_6H_{10}O)^+$, 25.3], 359 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO_2)^+$, 8.6], 357 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO_2)^+$, 27.8], 331 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO_2\text{-}CO)^+$, 8.6], 329 [$(M\text{-}I\text{-}C_6H_{10}O\text{-}CO_2\text{-}$	2953.6 ($\nu_{C\text{-}H}$), 2870.9 ($\nu_{C\text{-}H}$), 1762.9 ($\nu_{C=O}$), 1733.3 ($\nu_{C=O}$), 1306.3 ($\nu_{C\text{-}F}$), 795.0 ($\nu_{C\text{-}Cl}$),

(*Continued*)

Table 2. Continued

Compound	MS (m/z, %)	IR (cm^{-1})
	$CO)^+$, 29.3], 99 [$(C_6H_{10}O)^+$, 100.0], 55 [(M-I-R_F-C_6H_{10}O-2CH_2CH=CH_2-CO$)^+$, 64.7]	502.0 ($\nu_{C\text{-}I}$)
6a	428 [(M-C_6H_{10}O-$CO_2)^+$, 10.0], 400 [(M-C_6H_{10}O-CO_2-CO$)^+$, 18.0], 335 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2)^+$, 23.0], 263 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 35.0], 231 [(M-R_F-C_6H_{10}O-CO_2-CO$)^+$, 25.0], 219 [R_F^+, 6.2], 191 [(M-R_F-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 29.0], 169 [R_F^+, 6.2], 138 [(HPO$(CH_2CH_3)_2)^+$, 36.0], 99 [$C_6H_{11}O^+$, 100.0]	2997.7 ($\nu_{C\text{-}H}$), 2953.0 ($\nu_{C\text{-}H}$), 1778.3 ($\nu_{C=O}$), 1752.0 ($\nu_{C=O}$), 1311.6 ($\nu_{C\text{-}F}$), 1260.6 ($\nu_{P=O}$), 1041.9 ($\nu_{P\text{-}O\text{-}C}$), 712.8 ($\nu_{P\text{-}C}$)
6b	478 [(M-C_6H_{10}O-$CO_2)^+$, 6.0], 450 [(M-C_6H_{10}O-CO_2-CO$)^+$, 11.0], 385 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2)^+$, 25.0], 313 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 37.0], 231 [(M-R_F-C_6H_{10}O-CO_2-CO$)^+$, 27.0], 219 [R_F^+, 4.8], 191 [(M-R_F-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 20.0], 138 [(HPO$(CH_2CH_3)_2)^+$, 40.0], 99 [$C_6H_{11}O^+$, 100.0]	2999.7 ($\nu_{C\text{-}H}$), 2960.0 ($\nu_{C\text{-}H}$), 1776.3 ($\nu_{C=O}$), 1760.0 ($\nu_{C=O}$), 1318.6 ($\nu_{C\text{-}F}$), 1240.6 ($\nu_{P=O}$), 1042.9 ($\nu_{P\text{-}O\text{-}C}$), 712.9 ($\nu_{P\text{-}C}$)
6c	496 [(M-C_6H_{10}O-$CO_2)^+$, 2.8], 494 [(M-C_6H_{10}O-$CO_2)^+$, 9.0], 403 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2)^+$, 6.0], 401 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2)^+$, 18.0], 331 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 12.0], 329 [(M-C_6H_{10}O-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 37.0], 231 [(M-R_F-C_6H_{10}O-CO_2-CO$)^+$, 27.0], 235 [R_F^+, 3.8], 191 [(M-R_F-PO$(CH_2CH_3)_2$-CO_2-CO$)^+$, 20.0], 138 [(HPO$(CH_2CH_3)_2)^+$, 40.0], 99 [$C_6H_{11}O^+$,100.0]	2998.8 ($\nu_{C\text{-}H}$), 2952.2 ($\nu_{C\text{-}H}$), 1779.3 ($\nu_{C=O}$), 753.0 ($\nu_{C=O}$), 1311.6 ($\nu_{C\text{-}F}$), 1260.6 ($\nu_{P=O}$), 1041.9 ($\nu_{P\text{-}O\text{-}C}$), 769.2 ($\nu_{C\text{-}Cl}$), 710.8 ($\nu_{P\text{-}C}$)

Table 3. NMR data of compounds **4**, **5a–c** and **6a–c**

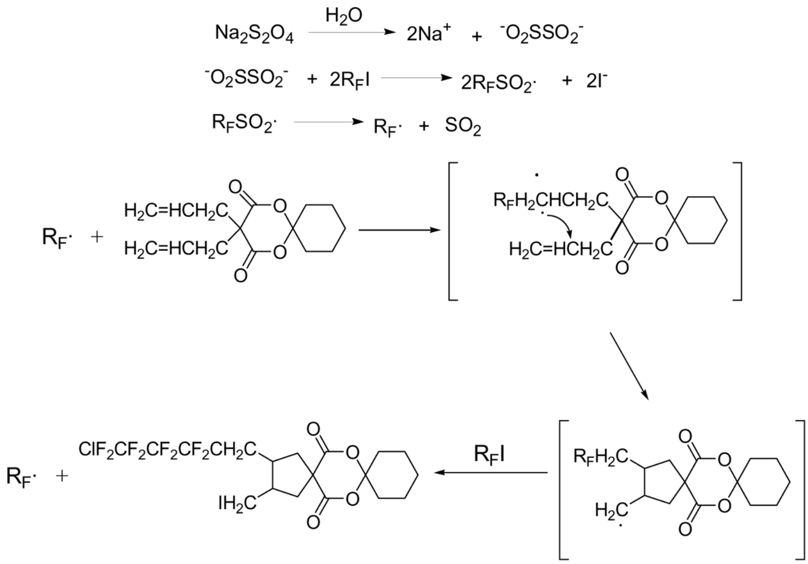
Compound	^{1}H NMR ($\delta \times 10^{-6}$) J (Hz)	^{13}C NMR ($\delta \times 10^{-6}$) J (Hz)
4	5.12 (d-d-d, 2H, CH_2 = /, $^2J = 1.52$, $^3J_{cis} = 10.28$, $^4J = 1.44$), 5.03 (d-d-t, 2H, $^2J = 1.52$, $^3J_{trans} = 17.20$, $^4J = 1.44$), 5.71 (d-d-t, 2H, CH=$^3J = 7.42$, $^3J_{trans} = 17.20$, $^3J_{cis} = 10.28$), 2.75 (d, 4H, *CH_2-CH =, $^3J = 7.42$), 1.93 (m, 4H, CH_2), 1.74 (m, 4H, CH_2), 1.50 (m, 2H, CH_2)	—
5a	2.25 (m, 2H, R_F-CH_2), 2.94 (m, 2H, 2 × CH), 2.55 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 3.30 (m, 2H, CH_2I), 1.93 (m, 4H, 2 × CH_2), 1.74 (m, 4H, 2 × CH_2), 1.50 (m, 2H, CH_2)	29.24 (t, R_F-CH_2, $^2J_{F\text{-}C} = 21.68$), 46.81 (s, *CH-CH_2 R_F), 44.70 (s, CH_2), 52.02 (s, C), 43.44(s, CH_2), 36.69 (s, CH), 4.68 (s, CH_2I), 171.43 (s, O=CO), 171.38 (s, O=CO), 105.90 (s, O-C-O), 37.74 (s, CH_2), 21.94 (s, CH_2), 23.79 (s, CH_2), 22.00 (s, CH_2), 37.57 (s, CH_2), 117.64 (t-t, CF_3CF_2*CF_2, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 252.68$), 108.58 (t-h, CF_3*CF_2, $^2J_{F\text{-}C} = 37.58$, $^1J_{F\text{-}C} = 262.95$), 117.71 (q-t, CF_3, $^2J_{F\text{-}C} = 33.00$, $^1J_{F\text{-}C} = 285.75$)
5b	2.25 (m, 2H, R_F-CH_2), 2.94 (m, 2H, 2 × CH), 2.54 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 3.31 (m, 2H, CH_2I), 1.94 (m, 4H, 2 × CH_2), 1.75 (m, 4H, 2 × CH_2), 1.51 (m, 2H, CH_2)	29.16 (t, R_F-CH_2, $^2J_{F\text{-}C} = 21.68$), 46.84 (s, *CH - CH_2R_F), 44.73 (s, CH_2), 52.05 (s, C), 43.50 (s, CH_2), 36.72 (s, CH), 4.62 (s, CH_2I), 171.43 (s, O=CO), 171.38 (s, O=CO), 105.88 (s, O-C-O), 37.77 (s, CH_2), 22.10 (s, CH_2), 23.80 (s, CH_2), 21.97 (s, CH_2), 37.62 (s, CH_2), 118.61 (t-t, $CF_3CF_2CF_2$*CF_2, $^2J_{F\text{-}C} = 31.90$, $^1J_{F\text{-}C} = 253.80$), 110.32 (t-p, CF_3CF_2*CF_2CF_2, $^2J_{F\text{-}C} = 31.90$, $^1J_{F\text{-}C} = 265.40$), 109.31 (t-h, CF_3*CF_2, $^2J_{F\text{-}C} = 31.90$,

(*Continued*)

Table 3. Continued

Compound	^{1}H NMR ($\delta \times 10^{-6}$) J (Hz)	^{13}C NMR ($\delta \times 10^{-6}$) J (Hz)
		$^1J_{F\text{-}C} = 234.45$), 117.30 (q-t, CF_3, $^2J_{F\text{-}C} = 33.00$, $^1J_{F\text{-}C} = 286.80$)
5c	2.26 (m, 2H, R_F-CH_2), 2.94 (m, 2H, 2 × CH, $^3J = 6.32$), 2.54 (m, 2H, CH2, $^2J = 13.59$, $^3J = 6.32$), 2.40 (m, 2H, CH_2), 3.31 (m, 2H, CH_2I, $^2J = 8.98$, $^3J = 6.31$), 1.94 (m, 4H, 2 × CH_2), 1.75 (m, 4H, 2 × CH_2), 1.51 (m, 2H, CH)	29.21 (t, R_F-CH_2, $^2J_{F\text{-}C} = 21.68$), 46.80 (s, *CH -CH_2 R_F), 44.69 (s, CH_2), 52.00 (s, C), 43.46 (s, CH_2), 36.75 (s, CH), 4.80 (s, CH_2I), 171.38 (s, O=CO), 171.34 (s, O=CO), 105.82 (s, O-C-O), 37.72 (s, CH_2), 21.94 (s, CH_2), 23.77 (s, CH_2), 21.98 (s, CH_2), 37.55 (s, CH_2), 118.27 (t-t, $ClCF_2CF_2CF_2{}^*CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 255.00$), 111.24 (t-p, $ClCF_2CF_2{}^*CF_2CF_2$, $^2J_{F\text{-}C} = 34.20$, $^1J_{F\text{-}C} = 265.20$), 109.46 (t-p, $ClCF_2{}^*CF_2CF_2CF_2$, $^2J_{F\text{-}C} = 33.00$, $^1J_{F\text{-}C} = 233.33$), 121.85 (t-t, $Cl^*CF_2CF_2CF_2CF_2$, $^2J_{F\text{-}C} = 35.25$, $^1J_{F\text{-}C} = 300.53$)
6a	2.10 (m, 2H, R_F-CH_2), 2.35 (m, 1H, CH), 2.21 (m, 2H, CH_2), 2.16 (m, 2H, CH_2), 2.35 (m, 1H, CH), 2.46 (m, 2H, P-CH_2, $^2J_{P\text{-}H} = 8.80$, $^3J = 6.20$), 1.90 (m, 4H, 2 × CH_2), 1.72 (m, 4H, 2 × CH_2), 1.50 (m, 2H, CH_2), 4.18 (m, 2H, OCH_2, $^3J = 5.28$, $^3J_{P\text{-}H} = 10.56$), 1.35 (m, 3H, CH_3, $^3J = 5.28$, $^4J_{P\text{-}H} = 1.46$), 4.20 (m, 2H, OCH_2, $^3J = 5.22$, $^3J_{P\text{-}H} = 10.99$), 1.37 (m, 3H, CH_3, $^3J = 5.28$, $^4J_{P\text{-}H} = 1.46$)	28.95 (t, R_F-CH_2, $^2J_{F\text{-}C} = 20.25$), 38.25 (d, CH, $^3J_{P\text{-}C} = 3.38$), 43.20 (s, CH_2), 51.53 (s, C), 43.98 (d, CH_2, $^3J_{P\text{-}C} = 4.50$), 36.80 (d, CH, $^2J_{P\text{-}C} = 13.65$), 24.36 (d, P-CH_2, $^1J_{P\text{-}C} = 141.15$), 171.20 (s, O=CO), 171.17 (s, O=CO), 105.14 (s, O-C-O), 28.62 (s, CH_2), 28.74 (s, CH_2), 61.60 (d, OCH_2, $^2J_{P\text{-}O\text{-}C} = 6.83$), 16.25 (s, CH_3), 16.10 (s, CH_3), 115.8 (t-t, $CF_3CF_2{}^*CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 252.67$), 108.5 (t-h, $CF_3{}^*CF_2$, $^2J_{F\text{-}C} = 37.50$, $^1J_{F\text{-}C} = 258.97$), 118.8 (q-t, CF_3, $^2J_{F\text{-}C} = 33.00$, $^1J_{F\text{-}C} = 285.67$)
6b	2.11 (m, 2H, R_F-CH_2), 2.34 (m, 1H, CH), 2.21 (m, 2H,	29.19 (t, R_F-CH_2, $^2J_{F\text{-}C} = 21.675$), 38.15 (d, CH, $^3J_{P\text{-}}$

	CH_2), 2.16 (m, 2H, CH_2), 2.34 (m, 1H, CH), 2.44 (m, 2H, P-CH_2, $^2J_{P\text{-}H} = 8.98$, $^3J = 6.31$), 1.91 (m, 4H, $2 \times CH_2$), 1.72 (m, 4H, $2 \times CH_2$), 1.49 (m, 2H, CH_2), 4.11 (m, 2H, OCH_2, $^3J = 5.22$, $^3J_{P\text{-}H} = 10.99$), 1.33 (m, 3H, CH_3, $^3J = 5.22$, $^4J_{P\text{-}H} = 1.09$), 4.16 (m, 2H, OCH_2, $^3J = 5.22$, $^3J_{P\text{-}H} = 10.99$), 1.33 (m, 3H, CH_3, $^3J = 5.22$, $^4J_{P\text{-}H} = 1.09$)	$_{C} = 3.375$), 39.94 (s, CH_2), 52.03 (s, C), 39.77 (d, CH_2, $^3J_{P\text{-}C} = 4.5$), 36.86 (d, CH, $^2J_{P\text{-}C} = 13.65$), 24.42 (d, P-CH_2, $^1J_{P\text{-}C} = 141.15$), 174.22 (s, O=CO), 174.00 (s, O=CO), 105.67 (s, O-C-O), 37.63 (s, CH_2), 22.33 (s, CH_2), 24.09 (s, CH_2), 21.80 (s, CH_2), 37.84 (s, CH_2), 61.50 (s, OCH_2), 15.76 (s, CH_3), 61.72 (s, OCH_2), 16.10 (s, CH_3), 118.3 (t-t, $CF_3CF_2CF_2{}^*CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 255.00$), 110.4 (t-p, $CF_3CF_2{}^*CF_2CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 264.10$), 108.8 (t-h, $CF_3{}^*CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 234.45$), 117.6 (q-t, CF_3, $^2J_{F\text{-}C} = 33.00$, $^1J_{F\text{-}C} = 285.67$)
6c	2.12 (m, 2H, R_F-CH_2), 2.56 (m, 1H, CH, $^3J = 6.34$), 2.19 (m, 2H, CH_2, $^2J = 13.59$, $^3J = 6.32$), 2.15 (m, 2H, CH_2), 2.36 (m, 1H, CH), 2.44 (m, 2H, P-CH_2, $^2J_{P\text{-}H} = 8.98$, $^3J = 6.31$), 1.90 (m, 4H, $2 \times CH_2$), 1.72 (m, 4H, $2 \times CH_2$), 1.51 (m, 2H, CH_2), 4.19 (m, 2H, OCH_2, $^3J = 5.24$, $^3J_{P\text{-}H} = 10.89$), 1.35 (m, 3H, CH_3, $^3J = 5.24$, $^4J_{P\text{-}H} = 1.29$), 4.19 (m, 2H, OCH_2, $^3J = 5.24$, $^3J_{P\text{-}H} = 10.89$), 1.35 (m, 3H, CH_3, $^3J = 5.24$, $^4J_{P\text{-}H} = 1.29$)	29.41 (t, R_F-CH_2, $^2J_{F\text{-}C} = 21.67$), 38.28 (d, CH, $^3J_{P\text{-}C} = 3.38$), 43.23 (s, CH_2), 51.67 (s, C), 44.15 (d, CH_2, $^3J_{P\text{-}C} = 4.58$), 36.91 (d, CH, $^2J_{P\text{-}C} = 14.77$), 24.37 (d, P-CH_2, $^1J_{P\text{-}C} = 141.15$), 171.29 (s, O=CO), 171.29 (s,O=CO), 105.05 (s,O-C-O), 28.74 (s, CH_2), 21.66 (s, CH_2), 24.09 (s, CH_2), 21.80 (s, CH_2), 28.90 (s, CH_2), 61.72 (d, OCH_2, $^2J_{P\text{-}O\text{-}C} = 6.83$), 15.76 (s, CH_3), 61.72 (d, OCH_2, $^2J_{P\text{-}O\text{-}C} = 6.83$), 15.76 (s, CH_3), 109.52 (t-t, $ClCF_2CF_2CF_2{}^*CF_2$, $^2J_{F\text{-}C} = 33.08$, $^1J_{F\text{-}C} = 268.65$), 114.88 (t-p, $ClCF_2CF_2{}^*CF_2CF_2$, $^2J_{F\text{-}C} = 31.87$, $^1J_{F\text{-}C} = 261.75$), 118.28 (t-p, $ClCF_2{}^*CF_2CF_2CF_2$, $^2J_{F\text{-}C} = 30.75$, $^1J_{F\text{-}C} = 255.00$), 121.88 (t-t, $Cl^*CF_2CF_2CF_2CF_2$, $^2J_{F\text{-}C} = 36.45$, $^1J_{F\text{-}C} = 295.68$)



Scheme 2. Mechanism for the formation of spiro compounds.

Typical Procedure for the Preparation of 5a–c

Compound **4** (2 mmol) reacted with perfluoroalkyl iodides (**a–c**) (2 mmol) in a water–acetonitrile biphasic solvent system (v/v = 8:1) at 0°C for 3 h using sodium dithionite ($Na_2S_2O_4$) and sodium carbonate (Na_2CO_3) as initiators. After that, water (4 mL) was added to dissolve the inorganic salts, and ethyl acetate (10 mL×3) was added to extract organic compounds. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed by evaporation under reduced pressure, and the residue was recrystallized from ethyl acetate–petroleum (v/v = 5:1) to obtain pure product **5a–c**.

Typical Procedure for the Preparation of 6a–c

Compounds **5a–c** (2 mmol) reacted with triethyl phosphite (2 ml) at 200°C and was kept boiling slightly for 2 h. Excess triethyl phosphite was removed by evaporation under reduced pressure to give **6a–c**.

ACKNOWLEDGMENTS

The authors are grateful to the National Natural Science Foundation of China (20872088), Leading Academic Discipline Project of Shanghai

Municipal Education Commission (Nos. J50102, 08ZZ44) for their financial support. We also thank the Instrumental Analysis and Research Center of Shanghai University for running all the NMR samples.

REFERENCES

1. Kanai, M.; Percy, J. M. Short, stereoselective syntheses of α-fluoroalkenoate derivatives, α-fluoroenones and α-fluoroenals from HFC-134a. *Tetrahedron Lett.* **2000**, *41*, 2453–2455.
2. Schlosser, M.; Brugger, N.; Schmidt, W.; Amrhein, N. β,β-Difluoro analogs of α-oxo-β-phenylpropionic acid and phenylalanine. *Tetrahedron* **2004**, *60*, 7731–7742.
3. Yang, X.; Zhang, L.; Liu, J. A straightforward preparation of fluorine-containing 1,2-dihydropyrimidines and pyrimidines with 2,2-dihydropoly-fluoroalkylaldehydes. *Tetrahedron* **2007**, *63*, 5643–5648.
4. Cao, W.; Shi, Z.; Fan, C.; Ding, W. Convenient synthesis of methyl 4-carboethoxy-3-perfluoroalkyl-5-methoxyhexa-2,4-dienoates. *J. Fluorine. Chem.* **2002**, *116*, 117–120.
5. Cao, W.; Shi, Z.; Fan, C.; Sun, R. A facile synthesis of ethyl 2,4-dimethoxy-6-perfluoroalkylbenzoates via acyclic precursors. *Chin. J. Chem.* **2004**, *22*, 1174–1176.
6. Shi, Z.; Ni, H.; Cao, W.; Liu, W.; Liang, C. Synthesis and structure elucidation of new spiro compounds with per(poly)fluoroalkyl group. *Chin. J. Chem.* **2006**, *24*, 980–982.
7. Wu, F.; Huang, W. Synthesis of polyfluoroalkyl substituted cyclopropane derivatives. *J. Xiamen University (Natural Science Ed.)* **1999**, *38*, 366–366.
8. Huang, W.; Wu, Y. The reaction of silyl enol ether of conjugated ketones with perfluoroalkyl iodide. *Chin. J. Org. Chem.* **1993**, *13*, 633–637.
9. Huang, W.; Ma, W.; Chen, J.; Zhan, B. Synthesis and properties of α-perfluoroalkyl pyrrole. *Chin. J. Org. Chem.* **1990**, *10*, 244–247.
10. Guo, X.; Chen, Q. The first example of addition reactions of sterically hindered terminal olefins, α-substituted styrenes, with perfluoroalkyl iodides initiated by sodium dithionite. *J. Fluorine. Chem.* **1999**, *93*, 81–86.
11. He, P.; Zhu, Z. Study on the reactions of fluoroalkanesulfonyl azides with cycloalkenyl ether and aryl ynamines. *Tetrahedron* **2006**, *62*, 549–555.
12. Wang, H.; Zhao, M.; Li, H.; Lu, L. Solvent-controlled asymmetric Strecker reaction: stereoselective synthesis of alpha-trifluoromethylated alpha-amino acids. *Organic Lett.* **2006**, *8*, 1379–1381.
13. Cao, P.; Xiao, C.; Chen, Y. Fluoroalkylation of aromatics: An intramolecular radical cyclization of 4-chloro-1,1,2,2,3,3,4,4-octafluorobutylbenzenes. *J. Fluorine. Chem.* **2006**, *127*, 1079–1086.
14. Taguchi, T.; Okada, M. Fluorinated cyclopropanes. *J. Fluorine. Chem.* **2000**, *105*, 279–283.
15. Jiang, H.; Zhang, J.; Du, W.; Zhu, S. A convenient synthesis of novel Meldrum's acid C60 fullerene derivatives. *Chin. J. Chem.* **2007**, *25*, 86–89.