Reductive Radical Reaction of *gem*-Difluorinated Organoselenium Compounds with an Indium(III) Chloride–Sodium Borohydride System

Ying-Ying Qin,[a] Yan-Yan Yang,[b] Xiao-Long Qiu,[b] Feng-Ling Qing*[a,b]

[a] College of Chemistry and Chemical Engineering, Donghua University, 1882 West Yanan Lu, Shanghai 200051, P. R. of China

[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. of China
Fax +86(21)64166128; E-mail: flq@mail.sioc.ac.cn

Received 9 November 2005; revised 6 December 2005

Abstract: As for *gem*-difluorinated phenylseleno compounds, indium hydride, in situ generated by transmetallation between $InCl_3$ and $NaBH_4$, was found to be a convenient radical reagent as an alternative to tributyltin hydride. Besides its excellent performance in intramolecular cyclization and radical deselenylation, the $NaBH_4$/$InCl_3$ system also succeeded in intermolecular radical addition between organoselenium compounds and styrene.

Key words: radical deselenylation, radical addition, organoselenium compounds, bromodifluoromethyl phenyl selenide

As the most useful and most common radical reagent, tributyltin hydride (Bu_3SnH) was extensively used in radical intramolecular cyclization,[1] radical dehalogenation[2] and intermolecular radical addition.[3] However, the toxicity of tributyltin compounds renders themselves defective, which limits their large-scale utilization in industry extremely. Exhilaratingly, the convenient and nontoxic system $NaBH_4$/$InCl_3$, in which indium hydride (Cl_2InH) was generated in situ, was recently reported by Baba and coworkers to be effective as an alternative to tributyltin hydride.[4] It is noteworthy that this system works well for radical dehalogenation, radical intramolecular cyclization and intermolecular radical addition of alkyl halides under very mild conditions without using any initiators. On the other hand, our group recently developed a novel fluorinating reagent, $PhSeCF_2TMS$, which could be conveniently applied to synthesize α,α-difluoro-β-hydroxy selenides.[5] As vinylic pseudohalide groups,[6] the phenylselenium compounds were reported to undergo reductive radical cyclization,[7]radical deselenylation[8] and intermolecular radical addition[9] in a similar manner to the Bu_3SnH-mediated reaction of alkyl halides, which reflected the great potential of $PhSeCF_2TMS$ as a fluorinated building block. Based on our ongoing project on the utilization of $PhSeCF_2TMS$ and as an extension to the utilization scope of the $NaBH_4$/$InCl_3$ system, we wish to report herein the $NaBH_4$/$InCl_3$-mediated radical intramolecular cyclization, radical deselenylation and radical intermolecular addition of *gem*-difluoromethyl-containing phenylseleno compounds.

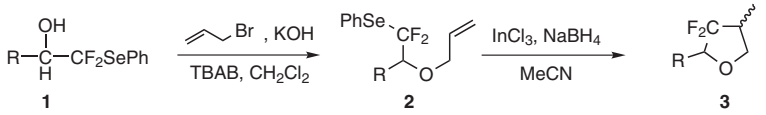
SYNTHESIS 2006, No. 9, pp 1475–1479
Advanced online publication: 04.04.2006
DOI: 10.1055/s-2006-926420; Art ID: F19505SS

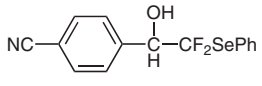
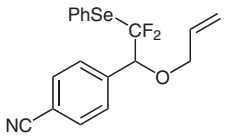
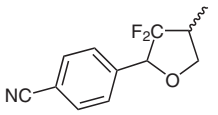
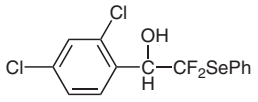
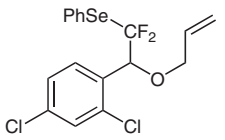
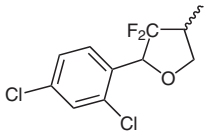
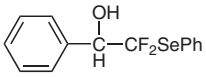
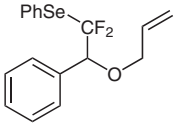
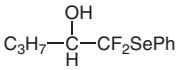
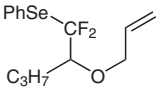
According to our reported approach,[5] we firstly synthesized a series of α,α-difluoro-β-hydroxy selenides **1**, which were supposed to be converted into cyclization precursors **2** by allylation with allyl bromide. Considering that the strong basicity of NaH would result in the dehydrofluorination of α,α-difluoro-β-hydroxy selenides, the inorganic base KOH[10] was used for the allylation of alcohol **1** providing the desired organoseleno compounds **2** in 85–92% yield (Table 1). With cyclization precursors **2** in hand, we carried out the reductive radical cyclization using the Baba group protocol.[4] Surprisingly, we found that although an $InCl_3$ catalyst loading of 10 mol% was reported to be effective for the cyclization of alkyl bromide and aryl iodide,[4] one equivalent of $InCl_3$ is needed to complete the cyclization of organoseleno compounds **2**. The resultant tetrahydrofuran derivatives **3** were obtained as mixtures of *trans* and *cis* isomers in moderate yields (Table 1, entries 1, 2). It should be mentioned that although reactions of organoseleno compounds **2c**,**d** with the $InCl_3$/$NaBH_4$ system were found to proceed well (^{19}F NMR spectroscopy), there are no corresponding products isolated because of the high volatility and low boiling point of the products (Table 1, entries 3, 4).

Engman's group reported that a series of Bu_3SnH-mediated reductive radical cyclizations of *O*-allylated β-hydroxyalkyl phenyl selenides furnished the corresponding 4-methyltetrahydrofuran in moderate to high yield and in low *cis*/*trans* selectivity (*cis*/*trans* = 2:3 to 1:10).[7a] Although lowering the reaction temperature can enhance the *cis*/*trans* selectivity to a certain extent, the yield decreased at the same time.[7a] Slightly surprisingly, $InCl_3$/$NaBH_4$-mediated reductive radical cyclization of *O*-allylated β-hydroxy-α,α-difluoroalkyl phenyl selenides **2** gave 4-methyltetrahydrofurans **3** with very high *cis*/*trans* selectivity, rendering the predominant *trans* isomer with a ratio of 16:1 to 20:1 over the *cis* isomer. In our opinion, higher diastereoselectivity may result from the utilization of the $NaBH_4$/$InCl_3$ system and/or the steric hindrance of the fluoride atoms, although the exact reason is not clear yet and remains to be investigated.

The assignment of *trans*/*cis* isomers of tetrahydrofuran derivatives **3** was based on NOESY experiments. As a representative example, the NOESY experiment observed for the *trans* isomer of compound **3a** is shown in Figure 1. No NOESY correlation between H^1 and H^4 of the furan ring was observed.

Table 1 Reductive Radical Cyclization Products and Organoselenium Intermediates



α,α-Difluoro-β-hydroxy selenides **1**	*O*-Allylation intermediates **2** (% yield)[a]	Reductive radical cyclization products **3** (% yield,[b] *trans*/*cis* ratio[c])
 **1a**	 **2a** (92%)	 **3a** (56%; 20/1)
 **1b**	 **2b** (86%)	 **3b** (65%; 16/1)
 **1c**	 **2c** (90%)	[d]
 **1d**	 **2d** (85%)	[d]

[a] Isolated yields.
[b] Isolated yields of *trans* isomers.
[c] Determined by ^{19}F NMR spectroscopy.
[d] Product could not be isolated due to high volatility and low boiling point.

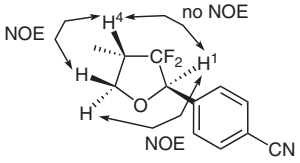
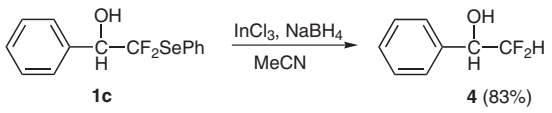


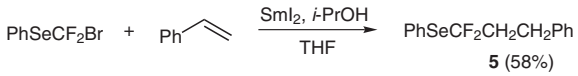
Figure 1 NOE correlation from NOESY spectra of *trans*-**3a**

Although the reduction of the phenylseleno group to a hydrogen atom could be readily achieved by traditional treatment with Bu_3SnH/AIBN,[5,8] there is, to the best of our knowledge, no correlative report on the reduction of the PhSe group to a hydrogen atom with the $NaBH_4/InCl_3$ system. In view of the distinct advantage of the $NaBH_4/InCl_3$ system over the Bu_3SnH/AIBN system,[4] we also investigated the $NaBH_4/InCl_3$-mediated radical deselenylation of α,α-difluoro-β-hydroxy phenyl selenide. We were pleased to discover that, upon treatment of compound **1c** with $NaBH_4/InCl_3$, the desired difluoromethyl alcohol **4** was formed in 83% yield (Scheme 1), which was a bit lower than the yield obtained by using the Bu_3SnH/AIBN system. Although Baba's group reported that the alkyl halide underwent radical dehalogenation with a catalytic amount of $InCl_3$ (0.1 equiv),[4] we found that even one equivalent of $InCl_3$ was not enough for completion of the deselenylation reaction of compound **1c**. Using an amount of about ten equivalents of $NaBH_4/InCl_3$ led to completion of the reaction within six hours.



Scheme 1

It has been discovered that phenylseleno esters were effective precursors of acyl radicals for the intermolecular alkene addition,[9] which is a potentially useful method for carbon–carbon bond formation. Thus, α,α-difluoro phenyl selenide was also envisioned as the precusor of the *gem*-difluoromethyl radical for intermolecular alkene addition. Considering that alkyl bromides could also undergo a radical reaction in the $NaBH_4/InCl_3$ system[4] and the fact that the bromine atom bound to the fluorocarbon moiety is more reactive than the one bound to the hydrocarbon moiety,[11] $PhSeCF_2CH_2CH_2Ph$ (**5**), prepared via SmI_2-mediated reaction of bromodifluoromethyl phenyl selenide with

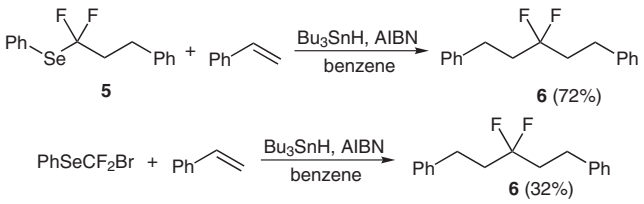


Scheme 2

styrene (Scheme 2), was used as the substrate for studying this kind of reaction.

With compound **5** in hand, we studied the $NaBH_4/InCl_3$-mediated intermolecular radical addition of compound **5** to styrene (Table 2). Besides by-product 1,1-difluoro-3-phenylpropane (**7**), the addition product **6** was afforded in 46% yield upon treatment of phenyl selenide **5** with styrene using the $NaBH_4$ (1.5 equiv)/$InCl_3$(1.5 equiv) system. As it can be seen from Table 2, the amount of $InCl_3$ had a great influence on the reaction products. An excess of $InCl_3$ and $NaBH_4$ greatly reduced the yield of addition product **6** and increased yield of by-product **7**.

Bu_3SnH/AIBN-mediated intermolecular radical addition of $PhSeCF_2CH_2CH_2Ph$ with styrene was also carried out in order to compare this system with the $InCl_3/NaBH_4$ one. The desired addition product **6** was provided in 72% yield (Scheme 3), which indicated that the $NaBH_4/InCl_3$ system was less effective in the intermolecular radical addition of phenylselenium compounds than the Bu_3SnH/AIBN system. In addition, we were pleasantly surprised to find that addition product **6** could be also afforded in 32% yield by Bu_3SnH/AIBN-mediated reaction of $PhSeCF_2Br$ with styrene in one step, which further demonstrated the great potential of $PhSeCF_2Br$ as *gem*-difluoromethylene diradical precursor. Although bromodifluorophenylsulfanylmethane ($PhSCF_2Br$) was also reported recently as synthetic equivalent of the *gem*-difluoromethylene diradical synthon,[12] three-step procedures, involved in the radical addition of the bromide atom (SmI_2, Bu_3SnH/AIBN or $Et_3B/Bu_3SnH/O_2$), the oxidation of the phenylthio group (*m*-CPBA) and the final radical addition of sulfone (SmI_2), were needed to profit from its function as biradical synthon. Therefore, $PhSeCF_2Br$ presented a distinct advantage over $PhSCF_2Br$ when acting as *gem*-difluoromethylene diradical synthon.



Scheme 3

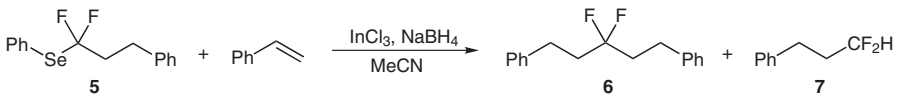
In summary, we investigated the $NaBH_4/InCl_3$-mediated radical intramolecular cyclization of *O*-allylated β-hydroxy-α,α-difluoroalkyl phenyl selenides **2** and found that the reaction proceeded well to afford 3,3-difluoro-4-methyl-tetrahydrofuran derivatives in high *cis*/*trans* selectivity. In addition, $NaBH_4/InCl_3$-mediated radical deselenylation and radical intermolecular addition of *gem*-difluoromethyl-containing phenylseleno compounds were also addressed. These studies demonstrate that the $NaBH_4/InCl_3$ system could not entirely substitute the Bu_3SnH/AIBN system in radical reactions despite its non-toxicity. Both systems can be efficiently utilized in different radical reactions, respectively, and they could supplement each other in some of them.

THF and benzene were distilled from Na metal. CH_2Cl_2 was distilled from CaH_2. All melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 spectrometer ($FCCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) in Hz. IR spectra were recorded on a Shimadzu IR-440 spectrometer and MS spectra on a Finnigan-MAT-8430 instrument using EI at 70 eV. Petroleum ether (PE) used for flash chromatography had a boiling range of 30–60 °C.

1,1-Difluoro-2-(allyloxy)-2-(4′-cyanophenyl)ethyl Phenyl Selenide (2a)

To a solution of the alcohol **1a** (163 mg, 0.48 mmol), allyl bromide (0.21 mL, 2.4 mmol) and tetrabutylammonium bromide (50 mg, 0.16 mmol) in CH_2Cl_2 (0.69 mL) was added aq KOH (5 M, 0.96 mL). The resultant mixture was vigorously stirred at r.t. After about 4 h, the biphasic system was treated with CH_2Cl_2 (10 mL) and sat. aq NH_4Cl (20 mL). The two layers were separated and the aqueous

Table 2 Indium-Catalyzed Intermolecular Radical Addition of Phenylseleno Group



Entry	$InCl_3$ (equiv)	$NaBH_4$ (equiv)	Ratio of **6**/**7**[a]
1	10	12	1/24
2	5	6	1/10
3	2.5	3	1/2.7
4	1.5	1.5	1/0.9
5	1	1	1/0.5

[a] Determined by ^{19}F NMR.

phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried (Na_2SO_4). After filtration and removal of the solvent in vacuo, the resultant residue was purified by flash chromatography (PE) to give pure compound **2a** (167 mg, 92%) as a colorless oil.

IR (neat): 2871, 2231, 1579, 1478, 1440, 1098 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.96 (dd, *J* = 12.6, 6.3 Hz, 1 H), 4.14 (dd, *J* = 12.9, 5.4 Hz, 1 H), 4.76 (dd, *J* = 12.9, 7.2 Hz, 1 H), 5.25–5.32 (m, 2 H), 5.90 (ddd, *J* = 23.4, 11.4, 6.6 Hz, 1 H), 7.26–7.42 (m, 3 H), 7.53–7.56 (m, 2 H), 7.62–7.68 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.5, 82.7 (dd, *J* = 27.2, 24.0 Hz), 113.1, 118.4, 118.8, 123.8, 125.0 (t, *J* = 298 Hz), 129.1, 129.2, 129.4, 132.0, 133.0, 137.2, 139.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –75.7 (dd, *J* = 212, 5.1 Hz, 1 F), –80.7 (dd, *J* = 210, 10.2 Hz, 1 F).

MS (EI, 70 eV): *m*/*z* (%) = 378 (M^+, 2), 322 (3), 172 (41), 157 (10), 130 (17), 77 (12), 41 (100).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{15}F_2NOSe$: 379.0286; found: 379.0301.

3,3-Difluoro-4-methyl-2-(4′-cyanophenyl)-tetrahydrofuran (3a)

A round-bottomed flask charged with $InCl_3$ (62 mg, 0.28 mmol) was heated at 150 °C in vacuo for 1 h. After N_2 was filled in, $NaBH_4$ (11 mg, 0.28 mmol) and MeCN (0.6 mL) were added and the resultant mixture was stirred at –78 °C for 5 min. After the heterogeneous solution was warmed up to r.t., **2a** (76 mg, 0.2 mmol) was added and the resulting mixture was stirred for 6 h. Then, deionized water was added and the reaction mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4). After filtration and removal of the solvent in vacuo, the residue was purified by flash chromatography with PE to give pure compound **3a** (25 mg, 56%) as a pale-yellow oil.

IR (neat): 3065, 2984, 2231, 1613, 1507, 1459, 1195, 1068 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.9 Hz, 3 H), 2.60 (tt, *J* = 25.5, 8.1 Hz, 1 H), 3.69 (t, *J* = 9.0 Hz, 1 H), 4.41 (t, *J* = 8.3 Hz, 1 H), 4.89 (t, *J* = 12.3 Hz, 1 H), 7.50–7.70 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.0 (dd, *J* = 7.4, 5.1 Hz), 40.2 (dd, *J* = 24.8, 21.2 Hz), 72.7 (dd, *J* = 5.4, 2.6 Hz), 82.3 (dd, *J* = 32.9, 25.4 Hz), 112.4, 118.6, 127.4, 127.8 (t, *J* = 255 Hz), 132.1, 140.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –105.6 (ddd, *J* = 230, 18.0, 11.8 Hz, 1 F), –113.5 (dt, *J* = 228, 10.7 Hz, 1 F).

MS (EI): *m*/*z* (%) = 223 (M^+, 30), 132 (34), 102 (11), 92 (29), 77 (100).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{11}F_2NO$: 223.0809; found: 223.0811.

2,2-Difluoro-1-phenylethanol (4)[13]

A round-bottomed flask charged with $InCl_3$ (220 mg, 1.0 mmol) was heated at 150 °C in vacuo for 1 h. After N_2 was filled in, $NaBH_4$ (45 mg, 1.2 mmol) and MeCN (3 mL) were added and the mixture was stirred at –78 °C for 5 min. After the heterogeneous solution was warmed up to r.t., **1c** (31 mg, 0.1 mmol) was added and the resulting mixture was stirred for 6 h. Then, deionized water was added and the reaction mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried (Na_2SO_4). After filtration and removal of the solvent in vacuo, the resultant residue was purified by flash chromatography (PE–EtOAc, 9:1) to give compound **4** (13 mg, 83%) as a pale-yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (br s, 1 H), 4.80–4.86 (m, 1 H), 5.77 (td, *J* = 56.0, 4.8 Hz, 1 H), 7.35–7.44 (m, 5 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –127.4 (ddd, *J* = 286, 56, 9.6 Hz, 1 F), –128.0 (ddd, *J* = 286, 56, 9.6 Hz, 1 F).

1,1-Difluoro-3-phenylpropyl Phenyl Selenide (5)

Under a N_2 atmosphere, samarium powder (40 mesh, 190 mg) was added to a solution of CH_2I_2 (60 μL, 0.75 mmol) in THF (10 mL). The mixture was stirred for 1 h at r.t. Then, a solution of bromodifluoromethyl phenyl selenide (143 mg, 0.5 mmol), styrene (0.12 mL, 1 mmol) and *i*-PrOH (77 μL, 1 mmol) in THF (2.5 mL) was added at 0 °C. The resultant mixture was stirred for 15 min at 0 °C and then allowed to warm up to r.t. within an additional 2 h. The reaction was quenched with sat. aq $NaHCO_3$ solution (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4). After filtration and removal of the solvent in vacuo, the resultant residue was purified by flash chromatography with PE to give compound **5** (90 mg, 58%) as a yellow oil.

IR (neat): 3064, 3030, 2930, 1580, 1478, 1440, 1164, 1033 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.33–2.49 (m, 2 H), 2.87–2.92 (m, 2 H), 7.14–7.44 (m, 8 H), 7.72–7.75 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (t, *J* = 4.0 Hz), 42.0 (t, *J* = 21.4 Hz), 126.4, 128.3, 128.5 (t, *J* = 301 Hz), 128.6, 129.3, 129.4, 130.2, 137.0, 139.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –70.2 (t, *J* = 14.1 Hz).

MS (EI): *m*/*z* (%) = 312 (M^+, 19), 158 (18), 91 (100), 77 (11).

Anal. Calcd for $C_{15}H_{14}F_2Se$: C, 57.89; H, 4.53. Found: C, 58.26; H, 4.72.

3,3-Difluoro-1,5-diphenylpentane (6)[14]

Method A: $InCl_3$ (33 mg, 0.15 mmol) was heated at 150 °C in vacuo for 1 h. Then, N_2 was filled into the vacuo system and a solution of $NaBH_4$ (6 mg, 0.15 mmol) in MeCN (0.3 mL) was added. The mixture was stirred at –78 °C for 5 min. After the heterogeneous mixture was warmed up to r.t., **5** (31 mg, 0.1 mmol) and styrene (0.12 mL, 1.0 mmol) were added and the resulting mixture was stirred for 6 h. The reaction was quenched with deionized water. The reaction mixture was extracted with Et_2O (3 × 20 mL) and the combined organic phases were dried (Na_2SO_4). After filtration and removal of the solvent in vacuo, the resultant residue was purified by flash chromatography with PE to give compound **6** (12 mg, 46%) as a pale-yellow oil.

Method B: Under N_2, to a solution of compound **5** (15 mg, 0.05 mmol) in anhyd benzene (0.8 mL) was added AIBN (3 mg, 0.015 mmol). Then, the mixture was heated to 90 °C and tributyltin hydride (17 μl, 0.06 mmol) was added dropwise. The reaction mixture was heated to reflux until TLC showed the complete consumption of the starting materi al. After cooling the solution to r.t., the solvent was removed in vacuo. The residue was purified by flash chromatography with PE to give compound **6** (9 mg, 72%) as a pale-yellow oil.

Method C: Under N_2, to a solution of bromodifluoromethyl phenyl selenide (29 mg, 0.1 mmol) in anhyd benzene (1.5 mL) was added AIBN (10 mg, 0.06 mmol). Then, the mixture was heated to 90 °C and tributyltin hydride (69 μl, 0.25 mmol) was added dropwise. The reaction mixture was heated to reflux until TLC showed the complete consumption of the starting material. After cooling the solution to r.t., the solvent was removed in vacuo. The residue was purified by flash chromatography with PE to give compound **6** (7 mg, 32%) as a pale-yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.09–2.26 (m, 4 H), 2.82 (t, *J* = 8.4 Hz, 4 H), 7.18–7.33 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.6 (t, *J* = 5.25 Hz), 38.5 (t, *J* = 25.1 Hz), 124.2 (t, *J* = 247 Hz), 126.3, 128.3, 128.6, 140.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –99.8 (q, *J* = 15.8 Hz).

Acknowledgment

We thank the National Natural Science Foundation of China, Ministry of Education of China and Shanghai Municipal Scientific Committee for funding this work.

References

(1) (a) Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1991**, *113*, 5791. (b) Baguley, P. A.; Binmore, G.; Milne, A.; Walton, J. C. *Chem. Commun.* **1996**, *18*, 2199. (c) Crimmins, M. T.; O'Mahony, R. *J. Org. Chem.* **1989**, *54*, 1157. (d) Marco-Contelles, J.; Gallego, P.; Rodriguez-Fernandez, M.; Khiar, N.; Destabel, C. *J. Org. Chem.* **1997**, *62*, 7397.

(2) (a) Roush, W. R.; Lin, X.-F. *J. Am. Chem. Soc.* **1995**, *117*, 2236. (b) Bonini, C.; Federici, C.; Rossi, L.; Righi, G. *J. Org. Chem.* **1995**, *60*, 4803. (c) Curran, D. P.; Jasperse, C. P.; Totleben, M. J. *J. Org. Chem.* **1991**, *56*, 7169. (d) Nakamura, E.; Machii, D.; Inubushi, T. *J. Am. Chem. Soc.* **1989**, *111*, 6849. (e) Neeson, S. J.; Stevenson, P. J. *Tetrahedron* **1989**, *45*, 6239.

(3) (a) Harrowven, D. C.; Dainty, R. F. *Tetrahedron* **1997**, *53*, 15771. (b) Chai, C. L. L.; King, A. R. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1173. (c) Giese, B.; Damm, W.; Dickhaut, J.; Wetterich, F.; Sun, S.; Curran, D. P. *Tetrahedron Lett.* **1991**, *32*, 6097. (d) Balczewski, P.; Mikolajczyk, M. *Synthesis* **1995**, 392.

(4) Inoue, K.; Sawada, A.; Shibata, I.; Baba, A. *J. Am. Chem. Soc.* **2002**, *124*, 906.

(5) Qin, Y.-Y.; Qiu, X.-L.; Yang, Y.-Y.; Meng, W.-D.; Qing, F.-L. *J. Org. Chem.* **2005**, *70*, 9040.

(6) (a) Huang, X.; Ma, Y. *Synthesis* **1997**, 417. (b) Comasseto, J. V.; Lo, W. L.; Petragnani, N. *Tetrahedron* **1997**, *53*, 7445. (c) Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 3411. (d) Procter, D. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 335.

(7) (a) Engman, L.; Gupta, V. *J. Org. Chem.* **1997**, *62*, 157. (b) Rawal, V. H.; Singh, S. P.; Dufour, C.; Michoud, C. *J. Org. Chem.* **1993**, *58*, 7718.

(8) (a) Miyashita, M.; Suzuki, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1989**, *111*, 3728. (b) Kang, Y. H.; Kim, K. *Tetrahedron* **1999**, *55*, 4271. (c) Ternon, M.; Outurquin, F.; Paulmier, C. *Tetrahedron* **2001**, *57*, 10259. (d) Billimoria, A. D.; Cava, M. P. *J. Org. Chem.* **1994**, *59*, 6777. (e) Kamimura, A.; Omata, Y.; Mitsudera, H.; Kakehi, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4499.

(9) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1989**, *54*, 1777.

(10) Arnone, A.; Bernardi, R.; Bravo, P.; Cardillo, R.; Ghiringhelli, D.; Cavicchio, G. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1887.

(11) Hu, C.-M.; Qiu, Y.-L. *J. Chem. Soc., Perkin Trans. 1* **1993**, 331.

(12) Reutrakul, V.; Thongpaisanwong, T.; Tuchinda, P.; Kuhakarn, C.; Pohmakotr, M. *J. Org. Chem.* **2004**, *69*, 6913.

(13) (a) Prober, M. *J. Am. Chem. Soc.* **1953**, *75*, 968. (b) Capriel, P.; Binsch, G. *Tetrahedron* **1979**, *35*, 2661.

(14) Reutrakul, V.; Thongpaisanwong, T.; Tuchinda, P.; Kuhakarrn, C.; Pohmakotr, M. *J. Org. Chem.* **2004**, *69*, 6913.