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Preparation of *gem*-Difluorinated β -Phenylthio Substituted Allylic Bromides and Their Reactions

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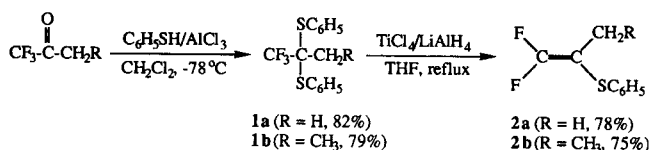
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The introduction of difluoromethylene (CF₂) unit into organic molecules has recently been received much attention because of enhancement of biological properties of pharmaceuticals and agrochemicals.^{1,2} A variety of biologically interesting compounds that contain the difluoromethylene group, such as the antitumor nucleoside Gemcitabine³ and α,α -difluoroalkylphosphonate-based mimics,⁴ have been discovered in recent work. Although there have been various methods for the introduction of difluoromethylene functionality, the synthetic methods which the difluoromethylene phosphonate group is directly attached to an vinyl carbon atom have been quite limited.⁵⁻⁸ *gem*-Difluoroallylation is one of valuable methods for the construction of difluoromethylene frameworks because of a wide range of functional group transformations of alkene group. The most potential reagent for *gem*-difluoroallylation is *gem*-difluoroallylic bromide. The synthetic method for the 3-bromo-3,3-difluoropropene as a *gem*-difluoroallylic bromide has been well known.⁹ However, we are interested in the preparation of *gem*-difluorinated β -phenylthio substituted allylic bro-

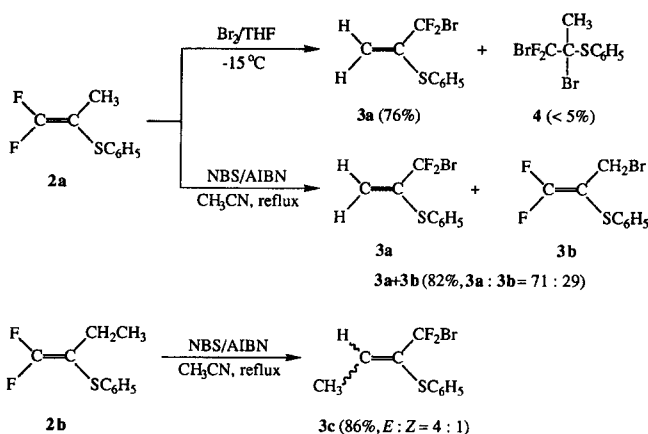
mides because the presence of phenylthio group at the vinyl carbon could provide more versatility for the functional group transformation than in the case of the presence of alkene group only. Unfortunately, there has been no methodology for the preparation of *gem*-difluorinated β -phenylthio substituted allylic bromides. In this paper, we wish to describe a new synthetic method for the preparation of *gem*-difluorinated β -phenylthio substituted allylic bromides and their reactions.

Perfluorinated dithioketals which we have developed¹⁰ are promising reagents to approach *gem*-difluorinated β -phenylthio substituted allylic bromides. Thus, the starting materials, 1,1,1-trifluoro-2,2-bis(phenylthio)propane (**1a**) and 1,1,1-trifluoro-2,2-bis(phenylthio)butane (**1b**), were prepared in 82% and 79% isolated yields, respectively, from the reaction of 1,1,1-trifluoro-2-propanone and 1,1,1-trifluoro-2-butanone with thiophenol in the presence of AlCl₃ at -78 °C for 20 hours. The treatment of **1a** and **1b** with a mixture of 2 equiv. of TiCl₄ and 3 equiv. of LiAlH₄ in THF at reflux temperature for 3 hours resulted in the formation of 1,1-difluoro-2-

phenylthio-1-propene (**2a**) and 1,1-difluoro-2-phenylthio-1-butene (**2b**) in 78% and 75% isolated yields, respectively.¹¹

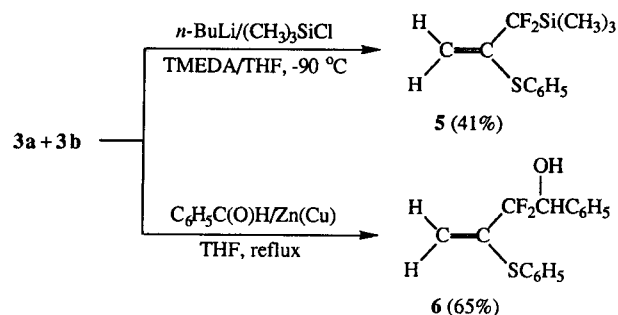


Since compound **2a** was reacted with *n*-BuLi to afford addition-elimination product instead of allylic anion,¹² we tried allylic bromination with two different approaches by using Br₂ or NBS. The reaction of **2a** with 2 equiv. of Br₂ in THF at -15 °C afforded regioselectively 3-bromo-3,3-difluoro-2-phenylthio-1-propene (**3a**) in 76% isolated yield. Addition product, 1,2-dibromo-1,2-difluoro-2-phenylthio-1-propene (**4**), was also obtained in less than 5% isolated yield. The use of chlorinated solvents, such as CCl₄, CH₂Cl₂, CHCl₃, and ClCH₂CH₂Cl decreased the yield of **3a**. The allylic bromination of alkene system, especially (*E*)-2,2,3,4,5,5-hexamethylhex-3-ene, with Br₂ has been reported in the previous literature.¹³ Alternatively, when **2a** was reacted with NBS in CH₃CN at reflux temperature for 3 hours, 3-bromo-3,3-difluoro-2-phenylthio-1-propene (**3a**) and 1,1-difluoro-3-bromo-2-phenylthio (**3b**) were obtained as a mixture of regioisomers (3a:3b=71:29) in 82% isolated yield. The use of other solvents, such as CCl₄, CH₂Cl₂ and benzene, needed prolonged reaction time and decreased the yield of **3a** and **3b**. Similarly, the treatment of **2b** with NBS under the same reaction condition resulted in the formation of 1-bromo-1,1-difluoro-2-phenylthio-2-butene (**3c**) (*E*:*Z*=4:1) in 86% isolated yield.



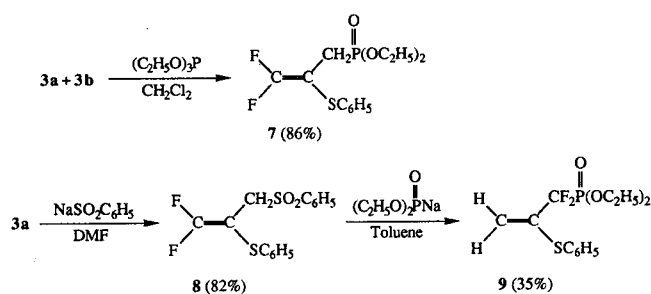
The oxidation reaction of a mixture of **3a** and **3b** with MCPBA provided a messy reaction mixture which is very difficult to identify products. It seems likely that product is not stable enough and decomposes quite easily. We tried to isolate difluorinated β-phenylsulfonyl allylic derivatives, but the products were always decomposed right after removal of solvent. When a mixture of **3a** and **3b** was treated with *n*-BuLi in the presence of trimethylsilyl chloride and TMEDA at -90 °C, only α,α-difluoroallylsilane **5** was obtained in 41% yield. The reaction of a mixture of **3a** and **3b** with Zn(Cu) in the presence of benzaldehyde in THF at reflux temperature for 3 hours afforded homoallylic alcohol **6** in 65% yield. Spectroscopic analysis of the products **5** and **6** indicated that only CF₂ terminus of a mixture of **3a** and **3b**

attacked the silicon and carbon of the carbonyl group. The ¹⁹F NMR spectrum of the CF₂-terminus-attacked product **5** exhibited a characteristic singlet at -109.4 ppm. The appearances of one singlet for **5** is due to the attachment of difluoromethylene moiety to silicon atom. Similarly, the ¹⁹F NMR spectrum of the CF₂-terminus-attacked product **6** exhibited a characteristic two sets of doublet at -107.8 (*J*_{H,F}=10.4 Hz) and -108.1 ppm (*J*_{H,F}=11.4 Hz). Also, the appearances of these two sets of doublet for **6** is due to the attachment of difluoromethylene moiety to a chiral center. The regioselectivity in these two reaction can be rationalized by Tonachini's theoretical explanation,¹⁴ in which metal ion (Li⁺, Zn²⁺) would be expected to be coordinated at the more negative CH₂ terminus and thus blocked the CH₂ terminus. This would serve to give more negative charge on the site of CF₂ terminus which can attack electrophiles. Generally, it has been well known that CF₂ carbanion is less stable than CH₂ carbanion because of the destabilizing repulsion between the lone-pair electrons on the



fluorine substituents and the electrons on the carbanion.¹⁵

However, the treatment of a mixture of **3a** and **3b** with triethylphosphite in CH₂Cl₂ at room temperature resulted in the formation of 1,1-difluoro-2-phenylthioallylic phosphonate **7** in 86% yield. In contrast to the results obtained from the above two reactions, this reaction showed that only the CH₂ terminus of a mixture of **3a** and **3b** attacked phosphorus. The ¹H NMR spectrum of **7** exhibited one set of doublet of triplet at 2.7 ppm (*J*=20.0, 2.2 Hz). Also, ¹⁹F NMR spectrum exhibited two characteristic peaks at -78.0 and -78.7 ppm which are due to two vinyl fluorines. The opposite regioselectivity may be due to more negative charge on CH₂ terminus of allylic anion which is formed by attacking of phosphorus on bromo atom of allylic bromide (halophilic reaction). In this case, there is no metal ion which can block the CH₂ terminus and thus more negative charge resides on CH₂ terminus. In order to prepare CF₂-terminus-attacked product, 3,3-difluoro-2-phenylthioallylic phosphonate (**9**), an allylic substituent which can not undergoes halophilic reaction was introduced in the allylic system. Therefore, the reaction of **3a** with sodium benzenesulfinate in DMF afforded only CH₂ terminus-attacked allylic sulfone **8** in 82% yield. The further reaction of **8** with sodium diethylphosphite in toluene at room temperature for 24 hours provided CF₂-terminus-attacked product **9** in 35% yield. The CF₂-terminus-attacked product **9** is potential synthetic intermediate to apply to the design of agent which has activity against retroviruses, including human immunodeficiency virus.¹⁶ A detailed study for the formation of α, α-(difluoroallyl)-phosphonates is now in progress.



Experimental

General. ^1H NMR spectra were recorded on a 100 MHz Bruker AC-100F NMR Spectrometer with tetramethylsilane (TMS) as an internal standard. ^{19}F NMR spectra were recorded on a 100 MHz Bruker AC-100F NMR spectrometer. CFCl_3 was used as an internal standard and chemical shifts are reported in parts per million. Infrared spectra were determined on a Mattson Genesis series FT High Resolution Spectrophotometer. Mass spectra were obtained Hewlett-Packard 5890 GC/5970B MSD (EI, 70 eV).

Commercially available reagents were purchased from Aldrich, PCR and Tokyo Kasei. All solvents were dried by general purification methods.

Preparation of 2,2-Bis(phenylthio)-1,1,1-trifluoropropane (1a). A mixture of 1,1,1-trifluoroacetone (2.24 g, 0.02 mol), thiophenol (4.40 g, 0.04 mol) and 200 mL of dry CH_2Cl_2 was cooled to -78°C by using dry-ice/isopropanol slush and then AlCl_3 was added in several portions *via* a solid addition tube. After stirring at -78°C for 20 hours, the reaction mixture was quenched with water at -78°C . The mixture was poured into 150 mL of water, extracted with CH_2Cl_2 (300 mL \times 2). After washing with saturated NaCl water solution, CH_2Cl_2 layer was dried with anhydrous Na_2CO_3 . Column chromatography (hexane) provided 5.15 g (82% yield) of **1a**: oil; ^1H NMR (CDCl_3) δ 7.69-7.27 (m, 10H), 1.38 (s, 3H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -71.60 (s, 3F); MS, *m/z* (relative intensity) 314 (M^+ , 5), 205(100), 165(37), 109(25), 77(12), 51(7); IR (neat) 3060, 2994, 1574, 1476, 1449, 1384, 1253, 1181, 756, 690 cm^{-1} .

Preparation of 2,2-Bis(phenylthio)-1,1,1-trifluorobutane (1b). After the reaction of a solution of 1,1,1-trifluoro-2-butanone (2.52 g, 0.02 mol), thiophenol (4.40 g, 0.04 mol) and 200 mL of dry CH_2Cl_2 with AlCl_3 (2.67 g, 0.02 mol) according to the procedure for the preparation of **1a**, column chromatography (hexane) provided 5.18 g (79% yield) of **1b**: oil; ^1H NMR (CDCl_3) δ 7.68-7.24 (m, 10H), 1.86 (q, $J=7.4$ Hz, 2H), 1.24 (t, $J=7.4$ Hz, 3H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -66.40 (s, 3F); MS, *m/z* (relative intensity) 328 (M^+ , 7), 219(85), 179(7), 141(5), 109 (100), 77(5), 65(11); IR (neat) 3060, 2980, 2940, 1582, 1473, 1439, 1249, 1253, 1181, 1102, 750, 690 cm^{-1} .

Preparation of 1,1-difluoro-2-phenylthiopropene (2a). A mixture of TiCl_4 (3.80 g, 20 mmol) and LiAlH_4 (1.14 g, 30 mmol) in dry THF (100 mL) was stirred at room temperature for 1 hours and then heated to boiling. 2, 2-Bis(phenylthio)-1,1,1-trifluoropropane (3.14 g, 10 mmol) in THF (5 mL) was added under reflux and the reaction mixture was kept boiling for further 3 hours. After cooling,

the reaction mixture was poured on ice water, neutralized with conc. HCl and extracted with ether. The ether solution was dried and then chromatographed (hexane) to provide 1.45 g (78% yield) of **2a**: oil; ^1H NMR (CDCl_3) δ 7.33-7.17 (m, 5H), 1.83 (t, $J=3.5$ Hz, 3H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -82.63 (d, $J=28.5$ Hz, 1F), -83.06 (d, $J=28.5$ Hz, 1F); MS, *m/z* (relative intensity) 186 (M^+ , 100), 165(30), 127(65), 121(16), 109(24), 77(35), 65(26), 59(81), 51(49), 29(16); IR (neat) 3067, 2929, 1718, 1587, 1483, 1443, 1267, 1109, 1031, 913, 743, 691 cm^{-1} .

Preparation of 1,1-difluoro-2-phenylthio-1-butene (2b). After the reaction of 2,2-bis(phenylthio)-1,1,1-trifluorobutane (3.28 g, 10 mmol) with a mixture of TiCl_4 (3.80 g, 20 mmol) and LiAlH_4 (1.14 g, 30 mmol) in dry THF (100 mL) according to the procedure for the preparation of **2a**, column chromatography (hexane) provided 1.50 g (75% yield) of **2b**: oil; ^1H NMR (CDCl_3) δ 7.33-7.17 (m, 5H), 2.33-2.06 (m, 2H), 1.06 (t, $J=7.4$ Hz, 3H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -82.31 (d, $J=28.7$ Hz, 1F), -82.88 (d, $J=28.7$ Hz, 1F); MS, *m/z* (relative intensity) 200 (M^+ , 97), 171(12), 165(27), 127(19), 110(23), 91(13), 73(100), 65(13), 51(16); IR (neat) 3075, 2973, 2934, 1711, 1583, 1477, 1440, 1259, 1117, 964, 739, 690 cm^{-1} .

Preparation of 3-bromo-3,3-difluoro-2-phenylthiopropene (3a) and 3-bromo-1,1-difluoro-2-phenylthiopropene (3b). A mixture of 1,1-difluoro-2-phenylthiopropene (0.93 g, 5 mmol), N-bromosuccinimide (1.07 g, 6 mmol), 10 mol% AIBN and CH_3CN (50 mL) was heated to reflux for 3 hours. After cooling and evaporation of solvent, the reaction mixture was chromatographed (hexane) to provide 1.09 g (82% yield) of **3a** and **3b**: oil. **3a**: ^1H NMR (CDCl_3) δ 7.58-7.26 (m, 5H), 6.00 (m, 1H), 5.24 (m, 1H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -46.54 (s, 2F); MS, *m/z* (relative intensity) 266 ($\text{M}^+ + 2$, 21), 264 (M^+ , 21), 185(44), 165(100), 135(22), 109(40), 91(23), 77(35), 65(38), 51(24); IR (neat) 3062, 1702, 1606, 1583, 1478, 1384, 1228, 1085, 920, 783, 747, 691 cm^{-1} . **3b**: ^1H NMR (CDCl_3) δ 7.82-7.24 (m, 5H), 4.06-3.99 (m, 2H); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -43.31 (s, 1F), -43.79 (s, 1F); MS, *m/z* (relative intensity) 266 ($\text{M}^+ + 2$, 31), 264 (M^+ , 30), 185(54), 165(100), 135(18), 109(34), 91(16), 65(20); IR (neat) 3059, 1700, 1578, 1476, 1439, 1286, 1247, 1153, 1067, 967, 867, 742, 689 cm^{-1} .

Preparation of 1-bromo-1,1-difluoro-2-phenylthio-2-butene (3c). A mixture of 1,1-difluoro-2-phenylthio-1-butene (1.00 g, 5 mmol), N-bromosuccinimide (1.07 g, 6 mmol), 10 mol% AIBN and CH_3CN (50 mL) was heated to reflux for 3 hours. After cooling and evaporation of solvent, the reaction mixture was chromatographed (hexane) to provide 1.12 g (86% yield) of **3c** (*E:Z* = 4:1): oil; ^1H NMR (CDCl_3) δ 7.33-7.15 (m, 10H, *E* and *Z* isomer), 7.04 (q, $J=6.6$ Hz, 1H, *E*-isomer), 6.44 (q, $J=7.6$ Hz, 1H, *Z*-isomer), 2.11-1.84 (m, 6H, *E* and *Z* isomer); ^{19}F NMR (CDCl_3 , internal standard CFCl_3) δ -39.58 (s, 2F, *Z* isomer), -45.72 (s, 2F, *E* isomer); MS, *m/z* (relative intensity) 280 ($\text{M}^+ + 2$, 45), 278 (M^+ , 43), 199(38), 179(100), 146(28), 109(34), 77(9), 65(15); IR (neat) 3075, 2923, 2847, 1626, 1583, 1479, 1440, 1216, 1136, 1094, 992, 944, 799, 739, 689 cm^{-1} .

Preparation of 3,3-difluoro-3-trimethylsilyl-2-phenylthiopropene (5). *n*-BuLi (2.5 M solution in hexane) (1.2 mL, 3.0 mmol) was added to a solution of a mix-

ture of 3-bromo-3,3-difluoro-2-phenylthiopropene and 3-bromo-1,1-difluoro-2-phenylthiopropene (0.264 g, 1.0 mmol), $(\text{CH}_3)_3\text{SiCl}$ (0.162 g, 1.5 mmol) and TMEDA (0.116 g, 1.0 mmol) in 10 mL of mixed solvent (pentane:ether:THF=1:1:4) at -90°C dropwise and then the reaction mixture was stirred at -90°C for 3 hours. After quenching with saturated NaCl solution, extraction with ether and drying with anhy. MgSO_4 , the reaction mixture was chromatographed (hexane) to provide 0.106 g (41% yield) of **5**: oil; $^1\text{H NMR}$ (CDCl_3) δ 7.43-7.16 (m, 5H), 5.43 (m, 1H), 4.82 (s, 1H), 0.20 (s, 9H); $^{19}\text{F NMR}$ (CDCl_3 , internal standard CFCl_3) δ -109.36 (s, 2F); MS, m/z (relative intensity) 258 (M^+ , 9), 182(30), 165(34), 147(13), 73(100), 45(16); IR (neat) 3076, 2960, 1644, 1583, 1478, 1440, 1263, 1081, 1015, 944, 799, 741, 691 cm^{-1} .

Preparation of 2,2-difluoro-1-phenyl-2-phenylthio-3-buten-1-ol (6). A solution of a mixture of 3-bromo-3,3-difluoro-2-phenylthiopropene and 3-bromo-1,1-difluoro-2-phenylthiopropene (0.264 g, 1.0 mmol), $\text{Zn}(\text{Cu})$ (0.26 g, 4.0 mmol) and benzaldehyde (0.127 g, 1.2 mmol) in dry THF (5 mL) was heated to reflux for 3 hours. After cooling and quenching with 5% HCl solution, extraction with ether and drying with anhy. MgSO_4 , the reaction mixture was chromatographed (ethyl acetate:n-hexane=1:4) to provide 0.190 g (65% yield) of **6**: oil; $^1\text{H NMR}$ (CDCl_3) δ 7.42-7.18 (m, 5H), 5.57 (s, 1H), 5.26-5.05 (m, 2H), 2.47 (d, $J=4.1$ Hz, 1H); $^{19}\text{F NMR}$ (CDCl_3 , internal standard CFCl_3) δ -107.75 (d, $J=10.4$ Hz, 1F), -108.05 (d, $J=11.4$ Hz, 1F); MS, m/z (relative intensity) 292 (M^+ , 34), 186(48), 107(100), 79(65), 77(39); IR (neat) 3442, 3076, 1715, 1593, 1480, 1454, 1445, 1393, 1262, 1087, 799, 741, 691 cm^{-1} .

Preparation of 3-diethylphosphonyl-1,1-difluoro-2-phenylthiopropene (7). A solution of a mixture of 3-bromo-3,3-difluoro-2-phenylthiopropene and 3-bromo-1,1-difluoro-2-phenylthiopropene (0.264 g, 1.0 mmol) and triethylphosphite (0.249 g, 1.5 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 50 hours. After quenching with saturated NaCl solution, extraction with CH_2Cl_2 and drying with anhy. MgSO_4 , the reaction mixture was chromatographed (ethyl acetate:n-hexane=1:1) to provide 0.277 g (86% yield) of **7**: oil; $^1\text{H NMR}$ (CDCl_3) δ 7.32-7.22 (m, 5H), 4.12 (dq, $J=7.4, 7.2$ Hz, 4H), 2.70 (dt, $J=20.0, 1.8$ Hz, 2H), 1.32 (t, $J=7.2$ Hz, 6H); $^{19}\text{F NMR}$ (CDCl_3 , internal standard CFCl_3) δ -77.97 (t, $J=13.8$ Hz, 1F), -78.70 (t, $J=16.3$ Hz, 1F); MS, m/z (relative intensity) 322 (M^+ , 50), 182(26), 165(100), 135(32), 109(38), 81(32), 65(26), 29(21); IR (neat) 3058, 2983, 2908, 1711, 1583, 1478, 1440, 1392, 1271, 1028, 823, 744, 691 cm^{-1} .

Preparation of 1,1-difluoro-3-phenylsulfonyl-2-phenylthiopropene (8). A solution of 3-bromo-3,3-difluoro-2-phenylthiopropene (0.264 g, 1.0 mmol) and sodium benzenesulfinate (0.246 g, 1.5 mmol) in dry DMF (15 mL) was stirred at room temperature for 12 hours. After quenching with saturated NaCl solution, extraction with ether and drying with anhy. MgSO_4 , the reaction mixture was chromatographed (ethyl acetate:n-hexane=1:4) to provide 0.267 g (82% yield) of **8**: oil; $^1\text{H NMR}$ (CDCl_3) δ 7.94-7.20 (m, 10H), 3.85 (t, $J=2.1$ Hz, 2H); $^{19}\text{F NMR}$ (CDCl_3 , internal standard CFCl_3) δ -74.24 (s, 1F), -74.47 (s, 1F); MS, m/z

(relative intensity) 326 (M^+ , 40), 182(54), 165(100), 135(87), 109(26), 77(25); IR (neat) 3064, 2927, 1704, 1584, 1478, 1328, 1289, 1167, 1086, 1011, 689 cm^{-1} .

Preparation of 3-diethylphosphonyl-3,3-difluoro-2-phenylthiopropene (9). Diethyl phosphite (0.138 g, 1.0 mmol) was added to a solution of sodium (0.034 g, 1.5 mmol) in toluene (3 mL) and then the reaction mixture was stirred at room temperature for 0.5 hour. 1,1-Difluoro-3-phenylsulfonyl-2-phenylthiopropene (0.228 g, 0.7 mmol) in toluene (1 mL) was added to the reaction mixture and then the reaction mixture was stirred at room temperature for 24 hours. After quenching with saturated NaCl solution, extraction with CH_2Cl_2 and drying with anhy. MgSO_4 , the reaction mixture was chromatographed (ethyl acetate:n-hexane=1:1) to provide 0.079 g (35% yield) of **9**: oil; $^1\text{H NMR}$ (CDCl_3) δ 7.51-7.30 (m, 5H), 5.96 (m, 1H), 5.26 (m, 1H), 4.31 (dq, $J=7.4, 7.2$ Hz, 4H), 1.31 (t, $J=7.2$ Hz, 6H); $^{19}\text{F NMR}$ (CDCl_3 , internal standard CFCl_3) δ -105.62 (d, $J=111.4$ Hz, 2F); MS, m/z (relative intensity) 322 (M^+ , 87), 273(12), 246(18), 184(100), 165(67), 134(14), 109(61), 91(30), 81(39), 77(31), 29(15).

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