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Nucleophilic *gem*-Difluoro(phenylsulfanyl)methylation of Carbonyl Compounds with $PhSCF_2H$ in the Presence of a Phosphazene as a Base

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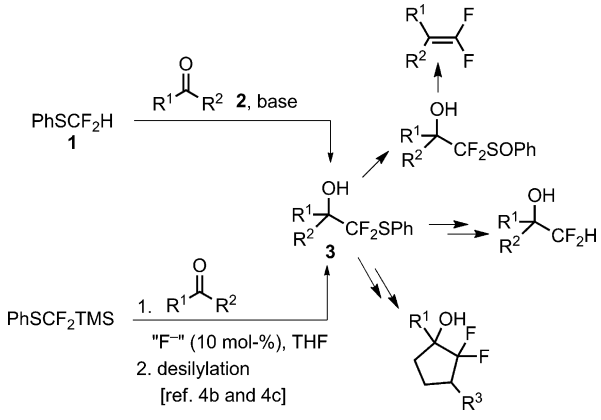
Direct nucleophilic *gem*-difluoro(phenylsulfanyl)methylation of carbonyl compounds has been achieved by use of difluoro(phenylsulfanyl)methane ($PhSCF_2H$) and the phosphazene base P_4-*t*Bu in THF. Non-enolizable aldehydes and ketones are suitable substrates to undergo nucleophilic *gem*-difluoro(phenylsulfanyl)methylation, providing α-*gem*-difluoromethylated adducts in good yields. In addition, this methodology is also applicable with cyclic imides and acid anhydrides.

Introduction

Tremendous efforts are being directed towards the development of new methods for the introduction of fluorine-containing groups into organic compounds, due to the enormous range of applications of fluorinated compounds in agrochemistry, pharmaceutical chemistry, and materials sciences.[1] Fluoride-induced nucleophilic fluoroalkylation with (fluoroalkyl)silanes (e.g., CF_3TMS, the Rupert–Prakash reagent),[2] $PhSO_2CF_2TMS$,[3] and $PhSCF_2TMS$ is one of the most commonly used methods for the synthesis of fluorinated compounds. We and others have demonstrated the synthetic utility of $PhSCF_2TMS$ as a *gem*-difluoromethyl carbanion ($PhSCF_2^-$) equivalent that can react with various electrophiles through initial activation by a fluoride ion.[4] Despite the successful results obtained with use of $PhSCF_2TMS$ as a difluoromethylating reagent, direct nucleophilic difluoromethylation with difluoro(phenylsulfanyl)methane ($PhSCF_2H$, **1**, readily available from thiophenol[5]) on treatment with a suitable base to generate $PhSCF_2^-$, which acts as the true nucleophilic difluoroalkylating species, remains highly desirable. The challenge of such a transformation lies in the facile nature of α-elimination of a fluoride ion from $PhSCF_2^-$. We had previously disclosed that $PhSCF_2MgBr$, generated from $PhSCF_2Br$ through a bromine/magnesium exchange reaction, was highly unstable and rapidly underwent α-elimination to give the corresponding carbenoid, which could be trapped with nucleophiles.[6] It has previously been reported that sulfoxide- and sulfone-stabilized fluorinated carbanions – $PhSOCHF^-$,[7] $PhSOCF_2^-$,[8] and $PhSO_2CF_2^-$[9] – could be generated from their corresponding hydrofluorocarbon precursors. The preparation of $PhSCF_2^-$ from $PhSCF_2H$ (**1**) by employment of a base, such as *t*BuOK, KOH, or $N(TMS)_3$/TMAF, in DMF was only recently disclosed by Hu and co-workers.[10,9c]

A phosphazene base – P_4-*t*Bu, a strong non-metallic or Schwesinger base[11] – was introduced by Shibata and co-workers as an organo-superbase for the direct generation of a stable form of CF_3^- from CHF_3 in THF.[12] Inspired by their finding and in continuation of our ongoing research into developing the synthetic methodology for the synthesis of fluorinated compounds, we have investigated the use of P_4-*t*Bu as a base for the direct generation of $PhSCF_2^-$ from **1** and its use for nucleophilic *gem*-difluoro(phenylsulfanyl)-methylation of carbonyl compounds **2** (Scheme 1). Notably, *gem*-difluoromethylated adducts **3** are useful synthetic precursors that can be converted into various fluorinated com-



Scheme 1. Nucleophilic *gem*-difluoro(phenylsulfanyl)methylation of carbonyl compounds.

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pounds, such as 1,1-difluoroalkenes, *gem*-difluoromethylenated cyclopentanols, and α-*gem*-(difluoromethyl) alcohols. Syntheses of **3** through the fluoride-catalyzed nucleophilic addition of $PhSCF_2TMS$ to carbonyl compounds had previously been reported.[4b,4c]

Results and Discussion

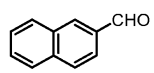
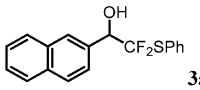
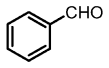
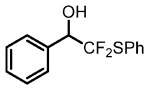
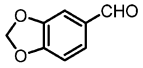
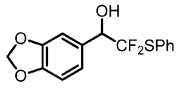
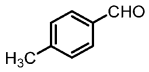
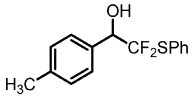
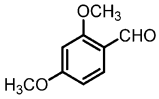
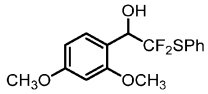
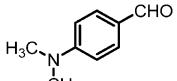
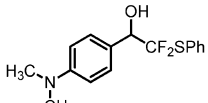
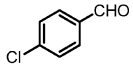
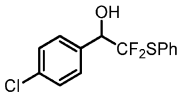
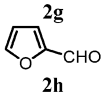
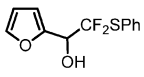
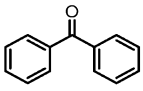
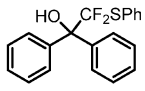
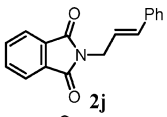
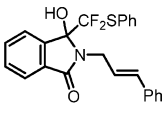
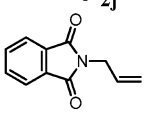
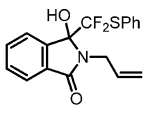
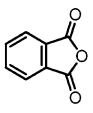
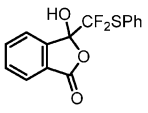
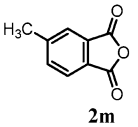
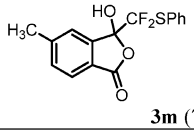
To begin with, the optimal reaction conditions for the generation of $PhSCF_2^-$ from **1** in the presence of P_4-*t*Bu as base were examined, together with its subsequent nucleophilic addition to 2-naphthaldehyde (**2a**). To our delight, it was initially found that upon addition of a solution of P_4-*t*Bu (0.8 M in hexane, 1.5 equiv.) to a mixture of **1** (1.5 equiv.) and **2a** in dry THF at –20 °C followed by further stirring at –20 °C for 1 h, the expected adduct **3a** was obtained in 67% yield. Significant improvements in the yields were observed when the reaction was performed at elevated temperatures. P_4-*t*Bu-mediated reactions between **1** and **2a** carried out at 0 °C and at room temperature, each for 1 h, provided **3a** in 92% and 85% yields, respectively. Attempts to perform the reaction with use of a catalytic quantity of P_4-*t*Bu (10 mol-%) were unsatisfactory; a low yield (34% yield) of **3a** was obtained and a longer reaction time (7 h) was required.

With the optimized reaction conditions in hand, the scope of the carbonyl compounds was next examined. The results are summarized in Table 1. In most cases, aromatic aldehydes underwent the P_4-*t*Bu-induced direct nucleophilic addition of $PhSCF_2^-$ derived from **1** to provide the expected adducts **3** in good to high yields. Benzaldehyde (**2b**) and aromatic aldehydes **2c**–**2h**, with either electron-donating or electron-withdrawing groups on their benzene rings, readily underwent the reaction to give the corresponding adducts **3b**–**3h** in 77–96% yields (Table 1, Entries 2–8). Benzophenone (**2i**) was also a good substrate, providing adduct **3i** in high yield (Table 1, Entry 9). It is worth noting that the reaction was found to be sensitive to aldehyde or ketone substrates bearing enolizable α-protons. Under standard reaction conditions, 3-phenylpropanal and acetophenone failed to provide the expected products.

After having succeeded with non-enolizable carbonyl compounds as substrates, we then expanded the substrate scope to imide and acid anhydride substrates. Gratifyingly, the same treatment of symmetrical phthalimides **2j** and **2k** worked well and provided the corresponding adducts **3j** and **3k** in 92% and 74% yields, respectively (Table 1, Entries 10 and 11). Symmetrical acid anhydride **2l** gave **3l** in 94% yield (Table 1, Entry 12). Interestingly, high chemoselectivity (95:5) as determined by ^{19}F NMR was observed when unsymmetrical acid anhydride **2m** was employed as a substrate, leading to product **3m** in 75% yield (Table 1, Entry 13). It is worth mentioning that a fluoride-catalyzed nucleophilic addition of $PhSCF_2TMS$ to **2m** gave **3m** as a 1:1 mixture with its regioisomer.[4p]

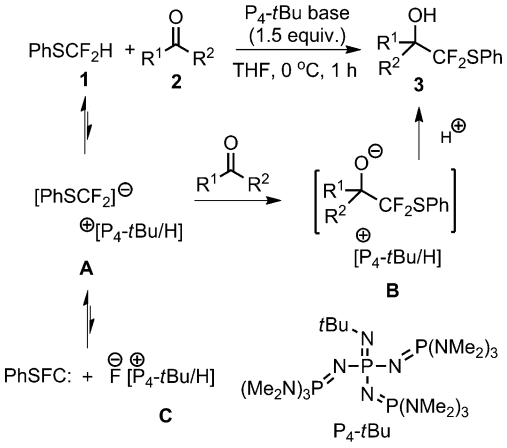
At this point, the mechanism for the reactions between **1** and carbonyl compounds mediated by P_4-*t*Bu as base should be addressed (Scheme 2). On the basis of relevant work reported by Shibata, it is proposed that deprotonation of **1** with P_4-*t*Bu base could lead to the formation of an ion pair of $[PhSCF_2]^-$ and $[P_4\text{-}t\text{Bu/H}]^+$ (**A**).[12a] Unlike

Table 1. Synthesis of compounds **3**.

Entry[a]	Substrate **2**	Adduct **3** (% yield)[b]
1	 **2a**	 **3a** (92)
2	 **2b**	 **3b** (80)
3	 **2c**	 **3c** (77)
4	 **2d**	 **3d** (79)
5	 **2e**	 **3e** (96)
6	 **2f**	 **3f** (87)
7	 **2g**	 **3g** (90)
8	 **2h**	 **3h** (79)
9	 **2i**	 **3i** (95)
10	 **2j**	 **3j** (92)
11	 **2k**	 **3k** (74)
12	 **2l**	 **3l** (94)
13	 **2m**	 **3m** (75, 95:5)[c]

[a] Reaction conditions: P_4-*t*Bu (1.5 equiv.) was added to a mixture of **2** (0.1 mmol) and **1** (1.5 equiv.) in THF at 0 °C. [b] Isolated yields. [c] The ratio was determined by ^{19}F NMR spectroscopy.

$PhSCF_2MgBr$, which proved to be unstable and rapidly collapsed to yield PhSCF carbenoid,[6] the $[PhSCF_2]^-$ component of **A** seems to be stable under the reaction conditions (0 °C in THF)[13] and readily reacted with various non-enolizable carbonyl compounds **2** to give the corresponding adducts **3** via alkoxide anions **B**. The exceptional stability of the $[PhSCF_2]^-$ component of **A** is believed to be attributable to the destabilization of the ion pair of F^- and $[P_4\text{-}t\text{Bu/H}]^+$ (**C**) upon α-elimination of **A**. In addition, formation of a sterically demanding $[P_4\text{-}t\text{Bu/H}]^+$ counterion also prevents the α-elimination process in the $[PhSCF_2]^-$ part of **A**. The observed results emphasize the crucial roles of P_4-*t*Bu as a base in a direct generation of the fluorinated carbanion from its corresponding hydrofluorocarbon.



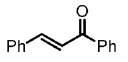
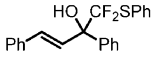
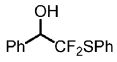
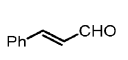
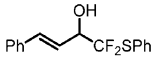
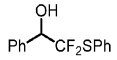
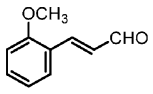
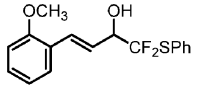
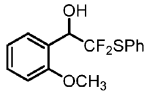
Scheme 2. Proposed mechanism for the reactions between **1** and carbonyl compounds **2** mediated by P_4-*t*Bu base.

Encouraged by the above results, we next investigated the reactions of **1** with activated carbonyl compounds mediated by P_4-*t*Bu base (Table 2). To our surprise, treatment of **1** with chalcone (**2n**) in the presence of P_4-*t*Bu led to the formation of benzaldehyde adduct **3b** as major product (60% yield) and the expected adduct **3n** as a minor product (27% yield) (Table 2, Entry 1). An improved yield of **3n** (from 27% to 70% yield) was obtained when compound **1** and P_4-*t*Bu were premixed at 0 °C for 30 min prior to the addition of chalcone (**2n**, Table 2, Entry 2).

Cinnamaldehyde (**2o**) did not give the expected product **3o**; benzaldehyde adduct **3b** was obtained as a sole product in 95% yield (Table 2, Entry 3). The modified reaction sequence as for **2n** was also applied to cinnamaldehyde (**2o**). Unfortunately, adduct **3b** was isolated in 80% yield as a sole product (Table 2, Entry 4).

Finally, 2-methoxycinnamaldehyde (**2p**) yielded the desired adduct **3p** in 53% yield together with the competing adduct **3p′** in 39% yield (Table 2, Entry 5).

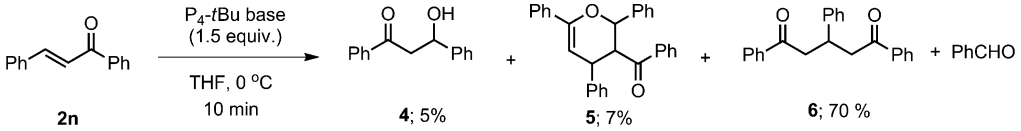
Table 2. Reactions between **1** and α,β-unsaturated carbonyl compounds mediated by P_4-*t*Bu.

Entry[a]	Substrate **2**	Adduct **3** (% yield)[b]	
1			
	2n	**3n** (27)	**3b** (60)
2[c]	**2n**	**3n** (70)	**3b** (18)
3			
	2o	**3o** (0)	**3b** (95)
4[c]	**2o**	**3o** (0)	**3b** (80)
5			
	2p	**3p** (53)	**3p'** (39)

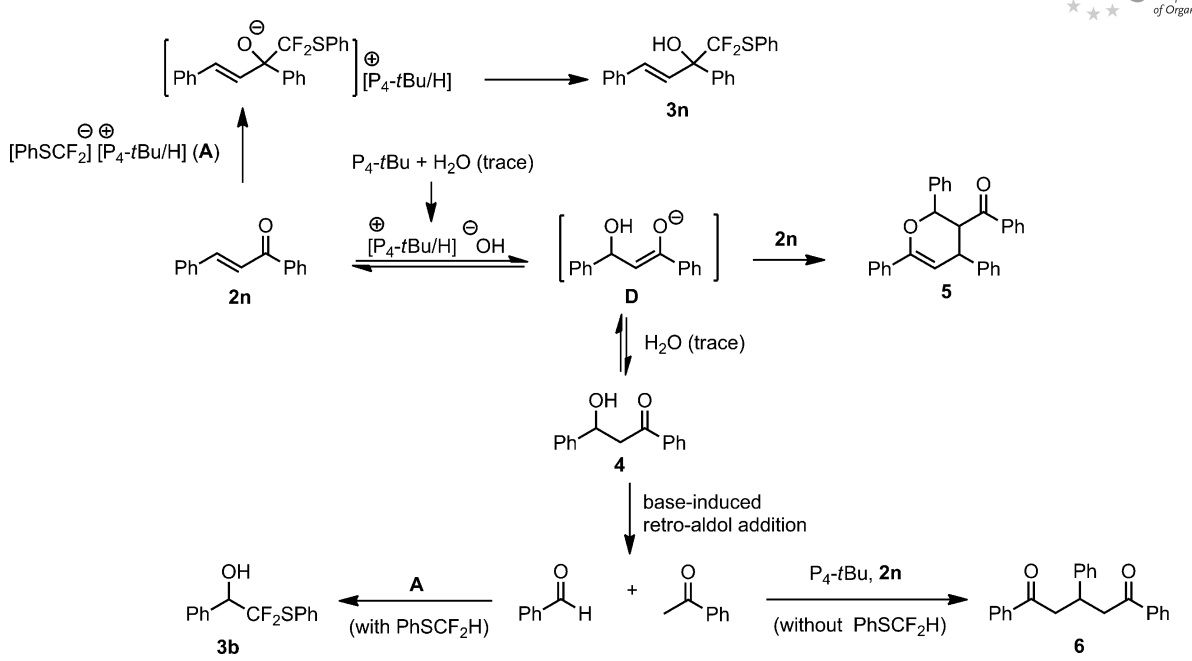
[a] Reaction conditions: P_4-*t*Bu (1.5 equiv.) was added to a mixture of **2** (0.1 mmol) and **1** (1.5 equiv.) in THF at 0 °C. [b] Isolated yields. [c] Compound **2** was added to a mixture of **1** and P_4-*t*Bu in THF cooled to 0 °C.

From the results obtained, it is believed that the in situ generation of the aldehyde occurred under the standard reaction conditions. In order to confirm our hypothesis, chalcone (**2n**) was treated with P_4-*t*Bu (1.5 equiv.) in dry THF at 0 °C without addition of compound **1** (Scheme 3). After the reaction mixture had been allowed to stir for 10 min, TLC revealed that chalcone (**2n**) had been completely consumed and that newly formed spots had appeared. The formation of benzaldehyde was observed and confirmed by TLC and ^{1}H NMR analyses of the crude mixture. After purification of the crude mixture by preparative thin-layer chromatography, compounds **4**, **5**, and **6** were isolated in 5%, 7%, and 70% yields, respectively (see the Supporting Information).

On the basis of the observed control experiments, a plausible reaction mechanism for the reactions between $PhSCF_2H$ and α,β-unsaturated carbonyl compounds in the presence of P_4-*t*Bu as a base was proposed (Scheme 4). It is believed that base-induced retro-aldol reactions of the substrates **2n**–**2p** took place and that the existence of trace amount of water played a crucial role. As a consequence, instead of 1,2-addition of $[PhSCF_2]^-$ of **A** to, for example, **2n**, leading to the desired product **3n**, the substrate **2n** was attacked by the hydroxide ion in a conjugate fashion to give the intermediate **D**. The hydroxide ion should originate



Scheme 3. The reaction between chalcone **2n** and P_4-*t*Bu.



Scheme 4. Proposed mechanism for reactions between **1** and α,β-unsaturated carbonyl compounds in the presence of P_4-*t*Bu.

from phosphazenium hydroxide,[14] which would be readily generated upon deprotonation of H_2O (pK_a = 15.7 in water) with P_4-*t*Bu (pK_b = 42.7 in MeCN). Next, the intermediate **D** could either react with a second equivalent of **2n** or be protonated, leading to the observed compound **5** and the aldol adduct **4**. A base-induced retro-aldol reaction of **4** would provide the corresponding benzaldehyde and acetophenone. In the absence of **1**, the resulting acetophenone could undergo base-catalyzed conjugate addition to **2n** to yield the observed compound **6**. However, under the standard reaction conditions, the readily formed benzaldehyde could competitively react with the $[PhSCF_2]^-$ component of **A** to give the observed product **3b**.

Conclusions

In conclusion, the direct generation of "naked $PhSCF_2^-$" from difluoro(phenylsulfanyl)methane ($PhSCF_2H$) was achieved by using phosphazene (P_4-*t*Bu) as a base. The generated $PhSCF_2^-$ is stable in THF at 0 °C and promptly reacted with various non-enolizable carbonyl compounds such as aromatic aldehydes and ketones, as well as with cyclic imides and acid anhydrides. This synthetic methodology proved potentially useful as a direct route to α-*gem*-difluoromethylated adducts, which are useful synthetic precursors for further synthetic conversion into a variety of fluorinated compounds.

Experimental Section

General: All reactions were performed under argon. Glassware, needles, and syringes were oven-dried and then kept in a desiccator before use. THF was distilled from sodium/benzophenone ketyl. A solution of P_4-*t*Bu (0.8 M in hexane) was purchased from Sigma–Aldrich. Preparative TLC plates were produced with Merck silica gel 60 PF_{254} (Art 7747). Column chromatography was performed with Merck silica gel 60 PF_{254} (Art 7734). Other common solvents [hexanes, ethyl acetate (EtOAc), and dichloromethane (CH_2Cl_2)] were distilled before use. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ with a Bruker 400 (400 MHz) spectrometer. Tetramethylsilane, $CDCl_3$, and trichlorofluoromethane were used as internal standards in ^1H, ^{13}C, and ^{19}F NMR spectra, respectively. The IR spectra were recorded with an ALPHA FT-IR spectrometer. The mass spectra were recorded with a Thermo Finnigan Polaris Q mass spectrometer. The high-resolution mass spectra were recorded with an HR-TOF-MS Micromass model VQTOF2 mass spectrometer.

General Procedure A for the Synthesis of Compounds 3a–3m: A solution of P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol, 1.5 equiv.) was added dropwise to a solution mixture of a compound **2** (0.1 mmol, 1 equiv.) and $PhSCF_2H$ (**1**, 24 mg, 0.15 mmol, 1.5 equiv.) in dry THF (0.5 mL), cooled to 0 °C. After having been stirred at 0 °C for 1 h, the reaction mixture was quenched with HCl (1 N) and then extracted with EtOAc (3× 10 mL). The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4.

2,2-Difluoro-1-(naphthalen-2-yl)-2-(phenylsulfanyl)ethanol (3a):[4b,4c,10] Treatment of 2-naphthaldehyde (**2a**, 16 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3a** (30 mg, 92%) as a white solid after column chromatography (SiO_2, 10% EtOAc in hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1 H, Ar*H*), 7.81–7.70 (m, 3 H, Ar*H*), 7.53–7.47 (m, 3 H, Ar*H*), 7.47–7.37 (m, 2 H, Ar*H*), 7.35–7.28 (m, 1 H, Ar*H*), 7.28–7.20 (m, 2 H, Ar*H*), 5.08 (t, J = 9.4 Hz, 1 H, C*H*), 2.86 (s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5 (2× CH), 133.7 (C), 132.9 (C), 132.6 (C), 129.9 (CH), 129.1 (2× CH), 129.1 (t, J = 283.2 Hz, CF_2), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.6 (CH), 126.6 (CH), 126.4 (CH), 125.8 (C), 125.0 (CH), 76.3 (t, J = 26.6 Hz, CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.9 (dd, J = 209.2, 7.7 Hz, 1 F), –84.2 (dd, J = 209.2, 11.7 Hz, 1 F) ppm.

2,2-Difluoro-1-phenyl-2-(phenylsulfanyl)ethanol (3b):[4b,4c,10] Treatment of benzaldehyde (**2b**, 11 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3b** (22 mg, 80%) as a pale yellow oil after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.1 Hz, 2 H, Ar*H*), 7.46–7.40 (m, 2 H, Ar*H*), 7.39–7.23 (m, 6 H, Ar*H*), 4.94 (t, J = 9.5 Hz, 1 H, C*H*), 2.79 (d, J = 3.5 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5 (2× CH), 135.2 (C), 129.9 (CH), 129.2 (CH), 129.1 (2× CH), 128.9 (t, J = 283.0 Hz, CF_2), 128.4 (2× CH), 127.8 (2× CH), 125.8 (C), 76.2 (t, J = 26.9 Hz, CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.3 (d, J = 208.2 Hz, 1 F), –84.9 (dd, J = 208.2, 11.5 Hz, 1 F) ppm.

1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2-difluoro-2-(phenylsulfanyl)ethanol (3c): Treatment of piperonaldehyde (**2c**, 16 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3c** (25 mg, 77%) as a pale yellow oil after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.7 Hz, 2 H, Ar*H*), 7.37–7.30 (m, 1 H, Ar*H*), 7.30–7.25 (m, 2 H, Ar*H*), 6.92 (s, 1 H, Ar*H*), 6.85 (d, J = 8.3 Hz, 1 H, Ar*H*), 6.73 (d, J = 8.3 Hz, 1 H, Ar*H*), 5.90 (s, 2 H, CH_2), 4.83 (dd, J = 10.7, 8.3 Hz, 1 H, C*H*), 2.69 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3 (C), 147.8 (C), 136.4 (2× CH), 129.9 (CH), 129.1 (2× CH), 128.9 (C), 128.8 (t, J = 283.2 Hz, CF_2), 125.9 (C), 121.8 (CH), 108.1 (CH), 108.0 (CH), 101.3 (CH_2), 76.0 (t, J = 26.6 Hz, CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.8 (d, J = 209.0 Hz, 1 F), –84.6 (dd, J = 209.0, 10.3 Hz, 1 F) ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3449, 1503, 1488, 1422, 1247, 1036, 923, 788, 748 cm^{-1}. MS: *m*/*z* (%) = 310 (5) $[M]^+$, 308 (35), 272 (33), 151 (100), 150 (58), 149 (40), 123 (32), 93 (28), 65 (44). HRMS (ESI-TOF): calcd. for $C_{15}H_{12}F_2O_3SNa$ $[M + Na]^+$ 333.0373; found 333.0365.

2,2-Difluoro-2-(phenylsulfanyl)-1-(*p*-tolyl)ethanol (3d):[4c,10] Treatment of *p*-tolualdehyde (**2d**, 13 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3d** (24 mg, 79%) as a white solid after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.5 Hz, 2 H, Ar*H*), 7.38–7.22 (m, 5 H, Ar*H*), 7.13 (d, J = 7.5 Hz, 2 H, Ar*H*), 4.89 (t, J = 9.5 Hz, 1 H, C*H*), 2.63 (br. s, 1 H, O*H*), 2.69 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.9 (C), 136.5 (2× CH), 132.3 (C), 129.8 (CH), 129.1 (2× CH), 129.0 (2× CH), 128.9 (t, J = 283.1 Hz, CF_2), 127.7 (2× CH), 125.9 (C), 76.1 (t, J = 26.5 Hz, CH), 21.3 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.6 (d, J = 207.9 Hz, 1 F), –84.7 (dd, J = 207.9, 11.1 Hz, 1 F) ppm.

1-(2,4-Dimethoxyphenyl)-2,2-difluoro-2-(phenylsulfanyl)ethanol (3e):[4c] Treatment of 2,4-dimethoxybenzaldehyde (**2e**, 17 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3e** (32 mg, 96%) as a white solid after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 6.9 Hz, 2 H, Ar*H*), 7.37–7.19 (m, 4 H, Ar*H*), 6.45 (dd, J = 8.5, 2.3 Hz, 1 H, Ar*H*), 6.41 (d, J = 2.3 Hz, 1 H, Ar*H*), 5.15 (dd, J = 12.8, 7.8 Hz, 1 H, C*H*), 3.77 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.47 (d, J = 7.2 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4 (C), 158.8 (C), 136.4 (2× CH), 131.2 (CH), 130.4 (CH), 129.6 (t, J = 284.2 Hz, CF_2), 128.9 (2× CH), 126.5 (C), 115.9 (C), 104.8 (CH), 99.0 (CH), 73.0 (t, J = 26.6 Hz, CH), 55.7 (CH_3), 55.4 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.5 (dd, J = 204.2, 8.1 Hz, 1 F), –84.4 (dd, J = 204.2, 12.2 Hz, 1 F) ppm.

1-[4-(Dimethylamino)phenyl]-2,2-difluoro-2-(phenylsulfanyl)ethanol (3f):[9] Treatment of 4-(dimethylamino)benzaldehyde (**2f**, 15 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3f** (27 mg, 87%) as a brown oil after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.45–7.30 (m, 5 H, Ar*H*), 6.74 (d, J = 8.4 Hz, 2 H, Ar*H*), 4.91 (t, J = 9.4 Hz, 1 H, C*H*), 2.97 (s, 6 H, 2× CH_3), 2.57 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9 (C), 136.4 (2× CH), 130.1 (C), 129.7 (2× CH), 129.2 (t, J = 283.2 Hz, CF_2), 129.0 (2× CH), 128.7 (2× CH), 126.3 (C), 112.1 (CH), 76.2 (t, J = 26.1 Hz, CH), 40.5 (2× CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –82.2 (dd, J = 205.9, 5.8 Hz, 1 F), –84.1 (dd, J = 205.9, 8.1 Hz, 1 F) ppm.

1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylsulfanyl)ethanol (3g):[4b,10] Treatment of *p*-chlorobenzaldehyde (**2g**, 15 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3g** (29 mg, 90%) as a white solid after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.39–7.22 (m, 7 H, Ar*H*), 4.89 (dd, J = 10.9, 7.7 Hz, 1 H, C*H*), 2.79 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5 (2× CH), 135.1 (C), 133.6 (C), 130.0 (CH), 129.2 (4× CH), 128.7 (t, J = 283.2 Hz, CF_2), 128.6 (2× CH), 125.5 (C), 75.5 (t, J = 26.9 Hz, CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.1 (dd, J = 210.6, 6.6 Hz, 1 F), –85.2 (dd, J = 210.6, 9.6 Hz, 1 F) ppm.

2,2-Difluoro-1-(furan-2-yl)-2-(phenylsulfanyl)ethanol (3h):[4c] Treatment of 2-furaldehyde (**2h**, 10 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3h** (21 mg, 79%) as a brown oil after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.1 Hz, 2 H, Ar*H*), 7.44–7.26 (m, 4 H, Ar*H*), 6.45 (d, J = 3.3 Hz, 1 H, Ar*H*), 6.35 (dd, J = 3.3, 1.8 Hz, 1 H, Ar*H*), 4.94 (dd, J = 16.4, 8.7 Hz, 1 H, C*H*), 2.71 (d, J = 7.0 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5 (C), 143.3 (CH), 136.6 (2× CH), 130.1 (CH), 129.2 (2× CH), 127.9 (t, J = 283.6 Hz, CF_2), 125.6 (C), 110.7 (CH), 110.1 (CH), 70.6 (t, J = 28.1 Hz, CH) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –83.1 (dd, J = 207.2, 8.1 Hz, 1 F), –84.6 (dd, J = 207.2, 9.0 Hz, 1 F) ppm.

2,2-Difluoro-1,1-diphenyl-2-(phenylsulfanyl)ethanol (3i):[4b,4c,10] Treatment of benzophenone (**2i**, 19 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3i** (34 mg, 95%) as a colorless solid after column chromatography (SiO_2, 10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.51 (m, 4 H, Ar*H*), 7.50–7.45 (m, 2 H, Ar*H*), 7.34–7.19 (m, 9 H, Ar*H*), 3.06 (s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3 (2× C), 136.7 (2× CH), 131.2 (t, J = 291.2 Hz, CF_2), 129.8 (CH), 129.0 (2× CH), 128.3 (3× CH), 128.0 (4× CH), 127.8 (3× CH), 126.4 (C), 81.7 (t, J = 22.7 Hz, C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –77.3 (s, 2 F) ppm.

2-(*E*)-Cinnamyl-3-[difluoro(phenylsulfanyl)methyl]-3-hydroxyisoindolin-1-one (3j):[4n] Treatment of **2j** (27 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) in dry THF (0.5 mL) at 0 °C as described in General Procedure A gave **3j** (40 mg, 92%) as a white solid after column chromatography (SiO_2, 25% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (t, J = 7.4 Hz, 2 H, Ar*H*), 7.53–7.41 (m, 2 H, Ar*H*), 7.33–7.22 (m, 5 H, Ar*H*), 7.21–7.09 (m, 5 H, Ar*H*), 6.53 (d, J = 15.9 Hz, 1 H, C*H*), 6.26 (dt, J = 15.9, 6.6 Hz, 1 H,

C*H*), 4.38 (dd, *J* = 15.6, 6.6 Hz, 1 H, CH*H*), 4.31 (s, 1 H, O*H*), 4.00 (dd, *J* = 15.6, 6.6 Hz, 1 H, C*H*H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1 (C), 142.1 (C), 136.7 (2× CH), 136.6 (C), 133.1 (CH), 132.7 (CH), 131.6 (2× C), 130.9 (CH), 130.1 (CH), 129.0 (2× CH), 128.5 (2× CH), 128.5 (t, *J* = 290.3 Hz, CF_2), 127.7 (CH), 126.5 (2× CH), 124.9 (CH), 124.2 (CH), 123.6 (CH), 91.0 (t, *J* = 25.7 Hz, C), 42.1 (CH_2) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.6 (d, *J* = 210.6 Hz, 1 F), –82.6 (d, *J* = 210.6 Hz, 1 F) ppm.

2-Allyl-3-[difluoro(phenylsulfanyl)methyl]-3-hydroxyisoindolin-1-one (3k):[4n] Treatment of **2k** (19 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3k** (26 mg, 74%) as a white solid after column chromatography (SiO_2, 25% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.77 (m, 1 H, Ar*H*), 7.75–7.69 (m, 1 H, Ar*H*), 7.64–7.54 (m, 2 H, Ar*H*), 7.46–7.37 (m, 3 H, Ar*H*), 7.36–7.29 (m, 2 H, Ar*H*), 6.08–6.59 (m, 1 H, C*H*), 5.35 (d, *J* = 17.1 Hz, 1 H, C*H*H), 5.22 (dd, *J* = 10.2, 1.2 Hz, 1 H, CH*H*), 4.47 (dd, *J* = 15.8, 5.3 Hz, 1 H, C*H*H), 3.96 (dd, *J* = 15.8, 7.1 Hz, 1 H, CH*H*), 3.80 (s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8 (C), 141.8 (C), 136.7 (CH), 133.8 (CH), 132.7 (CH), 131.6 (C), 131.0 (CH), 130.1 (CH), 129.1 (2× CH), 128.5 (t, *J* = 290.2 Hz, CF_2), 124.9 (C), 124.1 (CH), 124.0 (CH), 123.7 (CH), 118.1 (CH_2), 91.1 (t, *J* = 25.5 Hz, C), 42.6 (CH_2) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.6 (d, *J* = 211.9 Hz, 1 F), –82.3 (d, *J* = 211.9 Hz, 1 F) ppm.

3-[Difluoro(phenylsulfanyl)methyl]-3-hydroxyisobenzofuran-1(3*H*)-one (3l):[4p] Treatment of **2l** (15 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3l** (29 mg, 94%) as a white solid after column chromatography (SiO_2, 20% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 7.78–7.63 (m, 3 H, Ar*H*), 7.57 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.46–7.41 (m, 1 H, Ar*H*), 7.40–7.34 (m, 2 H, Ar*H*), 4.96 (br., 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (C), 143.0 (2× C), 136.8 (2× CH), 134.9 (CH), 131.9 (CH), 130.4 (CH), 129.2 (2× CH), 127.4 (C), 126.3 (t, *J* = 287.3 Hz, CF_2), 125.8 (CH), 124.5 (CH), 103.0 (t, *J* = 30.7 Hz, C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –84.6 (d, *J* = 214.3 Hz, 1 F), –86.9 (d, *J* = 214.3 Hz, 1 F) ppm.

3-[Difluoro(phenylsulfanyl)methyl]-3-hydroxy-5-methylisobenzofuran-1(3*H*)-one (3m):[4p] Treatment of **2m** (16 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3m** (24 mg, 75%), with a 95:5 ratio of the isomers as determined by ^{19}F NMR, as a colorless solid after column chromatography (SiO_2, 15% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.49 (d, *J* = 7.3 Hz, 2 H, Ar*H*), 7.44 (s, 1 H, Ar*H*), 7.40–7.33 (m, 2 H, Ar*H*), 7.32–7.25 (m, 2 H, Ar*H*), 4.76 (br., 1 H, O*H*), 2.41 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (C), 146.5 (C), 143.4 (C), 136.8 (2× CH), 132.9 (CH), 130.3 (CH), 129.1 (2× CH), 126.4 (t, *J* = 287.3 Hz, CF_2), 125.4 (CH), 124.8 (CH), 124.7 (C), 124.6 (C), 102.8 (t, *J* = 30.5 Hz, C), 22.1 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –84.5 (d, *J* = 213.8 Hz, 1 F), –87.1 (d, *J* = 213.8 Hz, 1 F) ppm.

General Procedure B for Reactions between 1/P_4-*t*Bu and α,β-Unsaturated Carbonyl Compounds: P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol, 1.5 equiv.) was added dropwise to a solution of **1** (24 mg, 0.15 mmol, 1.5 equiv.) in dry THF (0.2 mL), cooled to 0 °C. The reaction mixture was allowed to stir for 30 min, and then a solution of an α,β-unsaturated carbonyl compound **2** (0.1 mmol, 1.0 equiv.) in dry THF (0.3 mL) was added dropwise at 0 °C. After the complete consumption of **2** (1 h), the reaction mixture was quenched with HCl (1 N) and then extracted with EtOAc (3× 10 mL). The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4.

(*E*)-1,1-Difluoro-2,4-diphenyl-1-(phenylsulfanyl)but-3-en-2-ol (3n): Treatment of chalcone (**2n**, 21 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure B gave **3n** as a pale yellow oil (26 mg, 70%) and **3b** (5 mg, 18%) after column chromatography (SiO_2, 5% EtOAc in hexanes). **3n:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.49 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 7.37–7.16 (m, 11 H, Ar*H*), 6.84 (d, *J* = 16.0 Hz, 1 H, C*H*), 6.79 (d, *J* = 16.0 Hz, 1 H, C*H*), 2.84 (s, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6 (C), 136.6 (2× CH), 136.0 (C), 132.5 (CH), 130.5 (t, *J* = 289.6 Hz, CF_2), 129.8 (CH), 129.0 (2× CH), 128.7 (2× CH), 128.4 (CH), 128.3 (CH), 128.1 (2× CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.9 (2× CH), 126.1 (C), 73.6 (t, *J* = 23.7 Hz, C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.3 (d, *J* = 205.7 Hz, 1 F), –82.1 (d, *J* = 205.7 Hz, 1 F) ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3461, 1449, 1265, 1059, 971, 744 cm^{-1}. MS: *m*/*z* (%) = 368 (1) [M]$^+$, 327 (11), 209 (100), 191 (25), 131 (40), 103 (47), 77 (29). HRMS (ESI-TOF): calcd. for $C_{22}H_{18}F_2OSNa$ [M + Na]$^+$ 391.0944; found 391.0933.

Treatment of **2n** (21 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3n** (10 mg, 27%) and **3b** (16 mg, 60%).

(*E*)-1,1-Difluoro-4-(2-methoxyphenyl)-1-(phenylsulfanyl)but-3-en-2-ol (3p)[4e] **and 2,2-Difluoro-1-(2-methoxyphenyl)-2-(phenylsulfanyl)-ethanol (3p′):** Treatment of 2-methoxycinnamaldehyde (**2p**, 17 mg, 0.1 mmol) with **1** (24 mg, 0.15 mmol) and P_4-*t*Bu base (0.8 M in hexane, 190 μL, 0.15 mmol) as described in General Procedure A gave **3p** as a pale yellow oil (18 mg, 53%) and **3p′** (12 mg, 39%) after column chromatography (SiO_2, 10% EtOAc in hexanes).

Compound 3p: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.38–7.21 (m, 4 H, Ar*H*), 7.25–7.16 (m, 1 H, Ar*H*), 7.07 (d, *J* = 16.1 Hz, 1 H, C*H*), 6.88 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 6.82 (d, *J* = 8.2 Hz, 1 H, Ar*H*), 6.23 (dd, *J* = 16.1, 6.6 Hz, 1 H, C*H*), 4.54 (br., 1 H, C*H*), 3.80 (s, 3 H, CH_3), 2.33 (d, *J* = 5.2 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1 (C), 136.6 (2× CH), 130.5 (CH), 129.9 (CH), 129.6 (CH), 129.1 (2× CH), 129.0 (t, *J* = 281.6 Hz, CF_2), 127.4 (CH), 125.9 (C), 124.8 (C), 122.9 (CH), 120.7 (CH), 110.9 (CH), 75.6 (t, *J* = 26.8 Hz, CH), 55.5 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –82.9 (dd, *J* = 209.8, 7.7 Hz, 1 F), –84.7 (dd, *J* = 209.8, 8.1 Hz, 1 F) ppm.

Compound 3p′: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 6.9 Hz, 2 H, Ar*H*), 7.38–7.21 (m, 5 H, Ar*H*), 6.94 (dt, *J* = 7.5, 0.8 Hz, 1 H, Ar*H*), 6.87 (d, *J* = 8.3 Hz, 1 H, Ar*H*), 5.27–5.12 (m, 1 H, C*H*), 3.81 (s, 3 H, CH_3), 3.71 (d, *J* = 7.9 Hz, 1 H, O*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7 (C), 136.4 (2× CH), 130.2 (CH), 129.8 (CH), 129.7 (CH), 129.3 (t, *J* = 287.7 Hz, CF_2), 128.9 (2× CH), 126.4 (C), 123.3 (C), 120.9 (CH), 111.3 (CH), 73.6 (t, *J* = 26.7 Hz, CH), 55.7 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.1 (dd, *J* = 205.4, 8.1 Hz, 1 F), –84.8 (dd, *J* = 205.4, 13.5 Hz, 1 F) ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3474, 1602, 1493, 1463, 1439, 1245, 1047, 1024, 981, 963, 733 cm^{-1}. MS: *m*/*z* (%) = 297 (1) [M + H]$^+$, 259 (92), 137 (100), 107 (95), 77 (45). HRMS (ESI-TOF): calcd. for $C_{15}H_{14}F_2O_2SNa$ [M + Na]$^+$ 319.0580; found 319.0574.

Reaction of Chalcone (2n) with P_4-*t*Bu Base: A solution of P_4-*t*Bu base (0.8 M in hexane, 0.95 mL, 0.75 mmol, 1.5 equiv.) was added dropwise to a solution of compound **2n** (104 mg, 0.5 mmol, 1 equiv.) in dry THF (2.5 mL), cooled to 0 °C. After having been stirred at 0 °C for 10 min, the reaction mixture was quenched with

HCl (1 N) and then extracted with EtOAc (3× 25 mL). The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. The crude mixture was purified by preparative thin-layer chromatography (SiO_2, 50% CH_2Cl_2 in hexanes, multiple runs) to provide compounds **4**, **5**, and **6**.

Compound 4: This compound was obtained as a pale yellow oil (6 mg, 5%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 2 H, Ar*H*), 7.56–7.47 (m, 1 H, Ar*H*), 7.44–7.35 (m, 4 H, Ar*H*), 7.34–7.28 (m, 2 H, Ar*H*), 7.27–7.20 (m, 1 H, Ar*H*), 5.29 (t, *J* = 6.0 Hz, 1 H, C*H*), 3.52 (s, 1 H, O*H*), 3.31 (d, *J* = 6.0 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2 (C), 142.9 (C), 136.6 (C), 133.7 (CH), 128.7 (2× CH), 128.6 (2× CH), 128.2 (2× CH), 127.7 (CH), 125.7 (2× CH), 70.0 (CH), 47.4 (CH_2) ppm.

Compound 5: This compound was obtained as a white solid (7 mg, 7%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 2 H, Ar*H*), 7.33–7.22 (m, 5 H, Ar*H*), 7.21–7.00 (m, 11 H, Ar*H*), 6.99–6.92 (m, 2 H, Ar*H*), 5.61 (d, *J* = 2.2 Hz, 1 H, C*H*), 5.22 (d, *J* = 10.0 Hz, 1 H, C*H*), 4.32 (dd, *J* = 10.0, 2.2 Hz, 1 H, C*H*), 3.89 (dd, *J* = 10.0, 10.0 Hz, 1 H, C*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9 (C), 152.2 (C), 142.7 (C), 138.4 (C), 138.3 (C), 135.0 (C), 132.3 (CH), 128.7 (2× CH), 128.4 (CH), 128.2 (5× CH), 127.8 (2× CH), 127.7 (2× CH), 127.5 (2× CH), 127.3 (2× CH), 127.0 (CH), 124.8 (2× CH), 101.8 (CH), 80.9 (CH), 56.1 (CH), 44.9 (CH) ppm. HRMS (ESI-TOF): calcd. for $C_{30}H_{24}O_2Na$ $[M + Na]^+$ 439.1674; found 439.1672.

Compound 6:[15] This compound was obtained as a colorless oil (57 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.9 Hz, 4 H, Ar*H*), 7.48 (t, *J* = 7.4 Hz, 2 H, Ar*H*), 7.42–7.33 (m, 4 H, Ar*H*), 7.27–7.17 (m, 4 H, Ar*H*), 7.16–7.07 (m, 1 H, Ar*H*), 4.00 (quin, *J* = 7.0 Hz, 1 H, C*H*), 3.43 (dd, *J* = 16.7, 7.0 Hz, 2 H, CH_2), 3.29 (dd, *J* = 16.7, 7.0 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6 (2× C), 143.8 (C), 136.9 (2× C), 133.1 (2× CH), 128.6 (2× CH), 128.5 (4× CH), 128.1 (4× CH), 127.5 (2× CH), 126.7 (CH), 44.9 (2× CH_2), 37.2 (CH) ppm.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for all reported compounds.

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[13] Attempts to record ^{19}F NMR spectra of $[PhSCF_2]^-/[P_4\text{-}t\text{Bu/H}]^+$ (**A**) were made, according to a referee's suggestion. However, a mixture of $PhSCF_2H$ and P_4-*t*Bu in non-deuterated dry THF with $[D_6]$benzene as an internal standard showed no change in chemical shift of $PhSCF_2H$ in ^{19}F NMR analysis. However, upon addition of 2-naphthaldehyde to the mixture of $PhSCF_2H$ and P_4-*t*Bu, the corresponding adduct **3a** was readily formed as observed in ^{19}F NMR analysis (see the Supporting Information). These observations are similar to those observed on ^{19}F NMR analysis of a mixture of CF_3H and P_4-*t*Bu reported by Mikami and co-workers; see ref.[12b]

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