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Versatile Access to Martin's Spirosilanes and Their Hypervalent Derivatives

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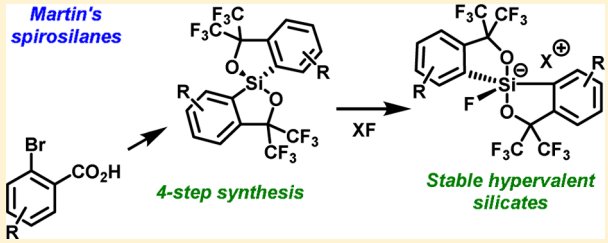
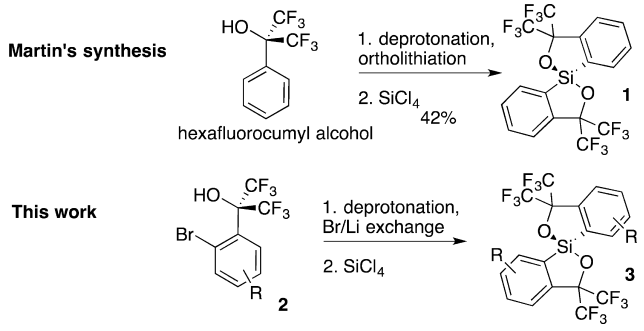
Supporting Information

ABSTRACT: A new route to Martin's spirosilanes has been devised. The original synthesis does not allow diversely substituted spirosilane derivatives to be synthesized, and thus their corresponding silicates. In this report, Martin's spirosilanes bearing alkyl, aryl, halogen, alkoxy, and trifluoromethyl substituents on the aryl ring have been prepared through a versatile four-step route. Addition of fluoride onto these Lewis acids as a prototypical reaction with a nucleophile yielded a library of stable fluorosilicates. Both sets of compounds have been characterized by X-ray crystallography.



Silicon, among a number of other elements, has the ability to become hypervalent. Penta- or hexacoordinate derivatives can be obtained by reaction of electrophilic tetravalent compounds with nucleophiles. The so-called 3 centers−4 electrons hypervalent bond emerged from years of controversy[1] and was finally accepted as the description of this particular bonding pattern.[2] This important structural alteration impacts the reactivity and properties of the silicon derivatives and allows a broad spectrum of applications. As the first discovered hypervalent silicon compound, by Gay-Lussac[3] in the beginning of the 19th century, hexafluorosilicate anion is still used in material sciences, health care, or photovoltaic devices.[4] Hypervalent silicates are now encountered in numbers of organic and organometallic transformations.[5] In 1979, Martin reported the preparation of bis(α,α-bis(trifluoromethyl) benzenemethanolato-(-2)C[2],O) silane **1** as a versatile precursor of stable pentavalent silicon derivatives (Scheme 1).[6]

Scheme 1. Synthetic Routes to Martin's Spirosilanes



Nucleophilic attack on the silicon atom of **1** triggers strain release and synergic stabilization provided by the electronegative bistrifluoro alkoxy ligands leads to a trigonal bipyramidal pentavalent adduct. Indeed, the trifluoromethyl groups withdraw electrons from the apical oxygen atoms that are themselves more able to accept extra electron density from the hypervalent O−Si−O bond.[7] Due to this particular environment, **1** behaves as a strong Lewis acid. For instance, it has been used not only as a catalyst in the polymerization of cyclohexene oxide,[8] but also in the reduction of carbonyl compounds through a hydridosiliconate derivative.[9] Recently, Martin's spirosilane **1** was engaged in the synthesis of hypervalent silicon species containing a Si−Si bond.[10] We have also shown that **1** could be used as a probe for the detection of NO[11] and fluoride.[12]

Martin's synthesis is still the most efficient way to prepare **1**.[6] Deprotonation of the commercially available hexafluorocumyl alcohol followed by ortholithiation using 2.2 equiv of *n*-BuLi in the presence of 10 mol % TMEDA afforded the corresponding dilithiated intermediate that reacts with silicon tetrachloride. After crystallization and sublimation, **1** is obtained in 42% yield.

This reliable preparation cannot be extended to analogues with substituted aryl moieties presumably because of the lack of regiocontrol in the ortholithiation step. In order to solve this, we developed a strategy based on orthobromo precursors **2**. Thus, deprotonation followed by bromide/lithium exchange would generate the corresponding dilithiated intermediates which should react with $SiCl_4$ to afford new Martin's spirosilane analogues **3** (Scheme 1).

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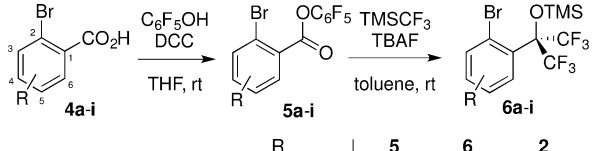
The major issue in the preparation of precursors **2** resides in the introduction of the 2-hydroxy-1,1,1,3,3,3-hexafluoro-propanyl group at the desired position. This reaction has been accomplished by using hexafluoroacetone (HFA) as an electrophile to trap Grignard reagents[13] or in aromatic electrophilic substitution.[14] However, due to its high toxicity and the difficulty handling this gaseous compound, we turned our attention to a reported method for the introduction of the two trifluoromethyl groups.[15] Commercially available ortho-bromo benzoic acids **4a–i** have been esterified with pentafluorophenol in the presence of DCC (dicyclohexylcarbodiimide) to afford esters **5a–i** in good to excellent yields (75–98%) (Scheme 2). These activated esters reacted with Ruppert-Prakash reagent ($TMSCF_3$) in the presence of a catalytic amount of TBAF.[16] Two successive nucleophilic additions of the trifluoromethyl anion occurred at the benzylic position to generate silyl ethers **6a–i** in high yields. When the aromatic ring was substituted by an electron withdrawing group (**5d**, **5e**, **5g**), the alcohol function was partially desilylated. Subsequent treatment with aqueous hydrochloric acid (6N) in THF was necessary to fully deprotect the alcohol group and obtain spirosilane precursors **2a–i** in good to excellent yields.

Scheme 2. Synthesis of Precursors 2a–i

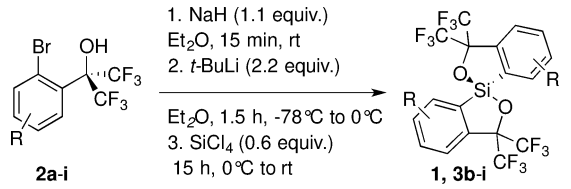


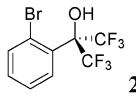
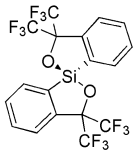
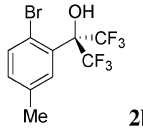
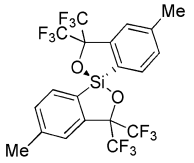
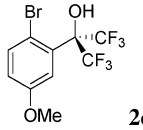
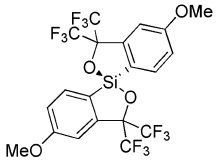
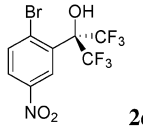
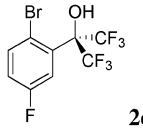
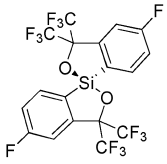
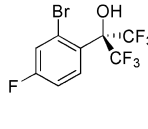
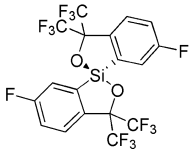
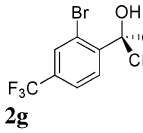
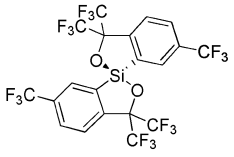
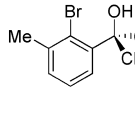
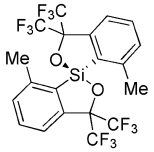
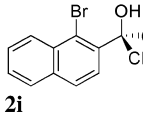
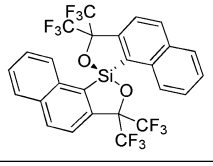
R	5	6	2
5-H , **a**	75%	84%	96%
5-Me , **b**	95%	82%	90%
5-OMe , **c**	92%	72%	88%
5-NO_2 , **d**	87%	75%[a]	75%
5-F , **e**	87%	70%[a]	92%
4-F , **f**	94%	82%	90%
4-CF_3 , **g**	97%	80%[a]	90%
3-Me , **h**	90%	86%	91%
Br , **i**	98%	72%	81%

[a]The alcohol function was partially desilylated after workup.

With this set of substrates in hand, we screened experimental conditions in order to optimize the preparation of the corresponding spirosilanes derivatives **3a–i**. First, we used an excess of *t*-BuLi to perform the deprotonation—bromide/lithium exchange sequence from **2a**.[17] All attempts were unsuccessful and only debrominated hexafluorocumyl alcohol was obtained. Therefore, we concluded that this was due to uncontrolled protonation of the arylithium intermediate. This observation was consistent with some very interesting work by Beak[18] who showed with different substrates bearing an acidic proton and an exchangeable halide that the faster deprotonation is followed by rapid halogen–lithium exchange to give a dilithiated intermediate. This intermediate then reacts in an intermolecular fashion with starting material and gets protonated. Thus, the desired dilithiated intermediate cannot form in satisfactory fashion. To overcome this issue, alcohols **2a–i** were initially deprotonated by an equimolar amount of sodium hydride to form the intermediate sodium alkoxide at rt (Table 1). The reaction mixture was cooled to −78 °C followed by the addition of *t*-BuLi (2.2 equiv). The solution was warmed to 0 °C to afford the corresponding dilithiated intermediate, and then, silicon tetrachloride was added

Table 1. Preparation of Spirosilanes 1 and 3b–i



Entry	Substrate	Product	Yield
1	 **2a**		**1**, 72%
2	 **2b**		**3b**, 71%
3	 **2c**		**3c**, 70%
4	 **2d**	-	-
5	 **2e**		**3e**, 67%
6	 **2f**		**3f**, 65%
7	 **2g**		**3g**, 73%
8	 **2h**		**3h**, 54%
9	 **2i**		**3i**, 80%

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dropwise at 0 °C to the reaction mixture. After workup, spirosilane derivatives **3** were obtained by crystallization.

Using this method, the reference Martin's spirosilane **1** was obtained in 72% overall yield as an analytically pure sample (Table 1, entry 1). Compound **2d** (Table 1, entry 4) did not allow the formation of the corresponding spirosilane, due to the incompatibility of the nitro group with *t*-BuLi, and led to the degradation of the starting material. The electronics of the aromatic ring did not exhibit particular influence on the formation of the spirosilane derivatives as **3b** (71%) and **3c** (70%) bearing an electron donating group (Me and OMe, respectively) and were isolated in comparable yields to **3g** (73%) substituted by a CF_3 electron withdrawing group (Table 1, entries 2 and 3 vs entry 7). However, steric hindrance seemed to play an important role. When **2h** was reacted to form spirosilane **3h**, the presence of the methyl group at the ortho position of the bromide affected the addition onto the silicon center and the yield decreased to 54% (Table 1, entry 8). Naphthyl precursor **2i** allowed access of **3i** in 80% yield, giving rise to a new class of spirosilanes (Table 1, entry 9). We confirmed the structures of **3b**, **3h**, and **3i** (Figure 1) by X-ray

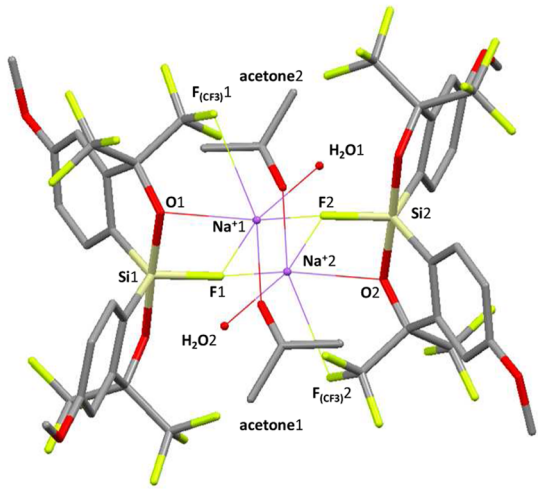
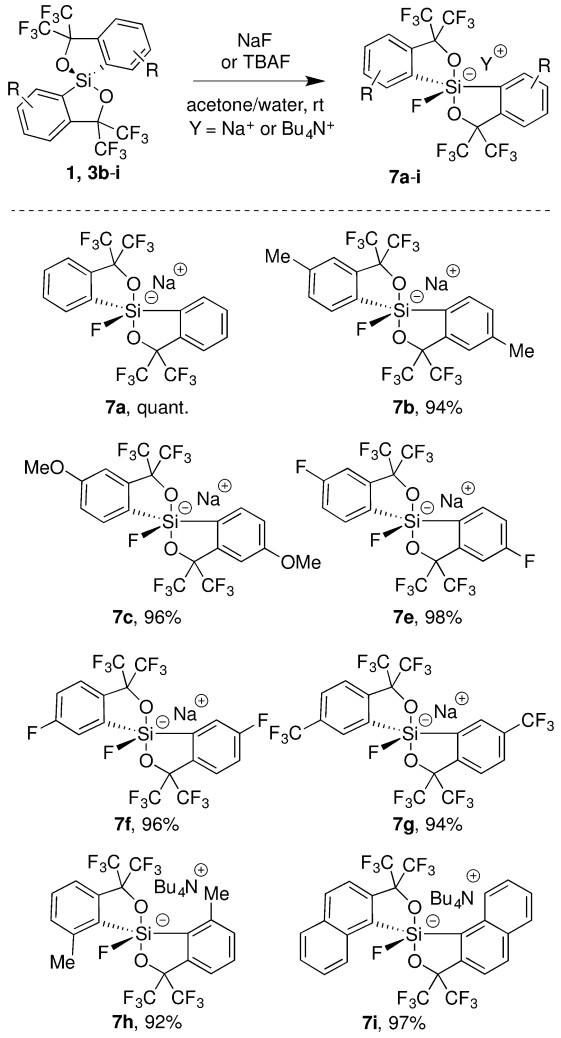


Figure 1. Crystal structure of fluorosilicate **7c**-(Na).

diffraction analysis. In order to generate stable hypervalent species from spirosilanes **1** and **3b–i**, we decided to choose nucleophiles that form a strong bond to silicon.

Due to its high affinity for silicon, we selected fluoride for that purpose,[19] and we investigated NaF and TBAF as sources of fluoride. Reactions of **1** and **3b–g** with NaF were run in acetone/water (1000/1) mixture at rt (Scheme 3). In less than 45 min, conversions were total and the corresponding fluorosilicates **7a–g** were obtained in excellent yields, higher than 94%. All products were isolated as stable solids. Their ^{29}Si NMR shifts were all around −80 ppm, consistent with a pentavalent silicon nucleus. Hypervalent compound **7c-(Na)** was crystallized in an acetone/cyclohexane mixture. The crystal structure was determined and showed a trigonal bipyramidal geometry of the silicon centers, which is in agreement with the reported structure of the fluorosilicate from **1** (Figure 1).[20] Both oxygen groups are at the apical position while the aromatic ring occupies the equatorial positions together with the fluorine atom. Of particular interest, the X-ray diffraction analysis shows a dimeric structure with two bridging sodium cations. Each of them are hexacoordinated with a water and

Scheme 3. Synthesis of Hypervalent Silicates 7a–i, 8b, 8c, 8i



acetone molecules (coming from the crystallization solvent), an oxygen atom of the hypervalent bond, and three fluorine atoms. Tetrabutylammonium fluorosilicates **7h** and **7i** were also accessible by treatment of the corresponding spirosilanes with TBAF in dichloromethane and were obtained in 92% and 97% yields, respectively. It is important to note that when **7h** had a sodium cation as counterion, the hypervalent compound was not stable enough to be isolated.

In conclusion, we have reported an efficient method to access diversely substituted Martin's spirosilane analogues. This four-step sequence relies on commercially available ortho-bromo benzoic acid derivatives and proceeds in high yields. The so-formed tetravalent spirosilanes serve as precursors for the preparation of fluorosilicates, obtained in excellent yields and high purity. Numerous applications such as anion sensing[12] and organocatalysis are currently under investigation in our laboratory.

■ EXPERIMENTAL SECTION

General Remarks. Reagents and chemicals were purchased from commercial sources and used as received. Unless otherwise noted, reactions were carried out under an argon atmosphere with magnetic stirring in redistilled solvents when necessary. Solvents were purified and dried by standard procedures: THF and Et_2O were distilled over sodium/benzophenone. *t*-Butyllithium was purchased from commercial sources as a 1.7 M solution in pentane and titrated before use.

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$SiCl_4$ was distilled before use. Infrared (IR) spectra were recorded on an ATR spectrophotometer and only the strongest or the structurally most important peaks were listed. Melting points were determined in open capillary tubes and are uncorrected. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded at room temperature at 400, 377, and 100 MHz, respectively, or at 300, 282, and 75 MHz, respectively. ^{29}Si NMR spectra were recorded at 119 MHz. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz (Hz). Abbreviations used for peak multiplicity are s (singlet); d (doublet); t (triplet); q (quartet); quat (quaternary); quint (quintet); sept (septet); m (multiplet); br (broad). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a ultraviolet lamp (λ = 254 nm) and $KMnO_4$ staining. Flash Column Chromatographies were conducted on silica Geduran Si 60 Å (40−63 μm). High resolution mass spectrometries were performed on a LTQ Orbitrap (ESI) and on a microTOF (ESI).

Procedure A: Preparation of Pentafluorophenyl Ester. To a stirred solution of carboxylic acid (1.00 equiv) and pentafluorophenol (1.12 equiv) in THF (0.27 M) was added *N,N′*-dicyclohexylcarbodiimide (1.13 equiv) at room temperature. The progress of the reaction was monitored by TLC (petroleum ether/Et_2O mixture). The *N,N′*-dicyclohexylurea was removed by filtration and the filtrate was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

*Perfluorophenyl 2-Bromobenzoate (**5a**).* Following the general procedure **A** with 2-bromobenzoic acid (14.81 g, 73.66 mmol), pentafluorophenol (15.18 g, 82.5 mmol) and *N,N′*-dicyclohexylcarbodiimide (17.17 g, 83.23 mmol) in 275 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 2% EtOAc) to afford **5a** (22.17 g, 60.4 mmol, 82%) as a white solid (mp 54 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 8.14−8.06 (m, 1H), 7.82−7.74 (m, 1H), 7.53−7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 143.1, 141.5, 140.3, 139.9, 138.4, 136.4, 135.3, 134.5, 132.7, 128.6, 127.7, 123.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ −151.9 − −152.1 (m, 2F), −157.5 (t, J = 21.7 Hz, 1F), −162.0 − −162.2 (m, 2F). IR: υ = 2950, 1781, 1556, 1345, 1274, 1256, 1145, 1021, 999, 975, 822 cm^{-1}. HRMS (ESI+) calc. for $C_{13}H_4BrF_5LiO_2$ $[M+Li]^+$ 372.9470; found 372.9467.

*Perfluorophenyl 2-Bromo-5-Methylbenzoate (**5b**).* Following the general procedure **A** with 2-bromo-5-methylbenzoic acid (16.93 g, 78.72 mmol), pentafluorophenol (16.23 g, 88.16 mmol) and *N,N′*-dicyclohexylcarbodiimide (18.35 g, 88.95 mmol) in 290 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 2% EtOAc) to afford **5b** (28.5 g, 74.79 mmol, 95%) as a white solid (mp 69 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 2.0 Hz 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 8.2, 2.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.70, 142.7, 141.1, 140.2, 139.4, 138.5, 136.9, 137.9, 135.4, 135.0, 133.2, 128.2, 120.0, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −151.9 − −152.3 (m, 2F), −157.7 (t, J = 21.6 Hz, 1F), −162.0 − −162.5 (m, 2F). IR: υ = 2929, 1773, 1520, 1286, 1243, 1186, 1068, 1007, 981, 822 cm^{-1}. HRMS (ESI+) calc. for $C_{14}H_6BrF_5NaO_2$ $[M + Na]^+$ 402.9364; found 402.9344.

*Perfluorophenyl 2-Bromo-5-methoxybenzoate (**5c**).* Following the general procedure **A** with 2-bromo-5-methoxybenzoic acid (1.99 g, 8.6 mmol), pentafluorophenol (1.77 g, 9.63 mmol), and *N,N′*-dicyclohexylcarbodiimide (2 g, 9.72 mmol) in 32 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **5c** (3.14 g, 7.91 mmol, 92%) as a white solid (mp 64 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 3.1 Hz, 1H), 7.04 (dd, J = 8.8, 3.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 158.9, 142.6, 141.1, 140.1, 139.3, 138.6, 136.8, 136.0, 129.1, 120.9, 117.7, 113.6, 56.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −151.8 − −152.0 (m, 2F), −157.5 (t, J = 21.5 Hz, 1F), −162.0 − −162.2 (m, 2F). IR: υ = 2948, 1774, 1519, 1474, 1283, 1245, 1206, 1078, 1006, 894, 824 cm^{-1}. HRMS (ESI+) calc. for $C_{14}H_6BrF_5NaO_3$ $[M + Na]^+$ 420.9292; found 420.9285.

*Perfluorophenyl 2-Bromo-5-nitrobenzoate (**5d**).* Following the general procedure **A** with 2-bromo-5-nitrobenzoic acid (1.23 g, 5 mmol), pentafluorophenol (1.03 g, 5.6 mmol), and *N,N′*-dicyclohexylcarbodiimide (1.17 g, 5.65 mmol) in 18 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **5d** (1.8 g, 4.37 mmol, 87%) as a pale yellow solid (mp 57 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 8.93 (d, J = 2.7 Hz, 1H), 8.32 (dd, J = 8.8, 2.7 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 147.1, 144.6, 143.1, 141.9, 139.6, 138.5, 124.5, 136.7, 130.7, 129.9, 128.3, 127.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ −151.6 − −151.9 (m, 2F), −156.3 (t, J = 21.7 Hz, 1F), −161.2 − −161.5 (m, 2F). IR: υ = 2981, 1760, 1496, 1254, 1236, 1176, 1054, 973, 851 cm^{-1}. HRMS (ESI−) calc. for $C_7H_3BrNO_4$ $[M - C_6F_5]^-$ 243.9251; found 243.9252.

*Perfluorophenyl 2-Bromo-5-fluorobenzoate (**5e**).* Following the general procedure **A** with 2-bromo-5-fluorobenzoic acid (2.37 g, 10.81 mmol), pentafluorophenol (2.23 g, 12.1 mmol), and *N,N′*-dicyclohexylcarbodiimide (2.52 g, 12.21 mmol) in 40 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 2% Et_2O) to afford **5e** (3.83 g, 9.95 mmol, 92%) as a white solid (mp 97 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J_{H-H} = 3.0 Hz, J_{H-F} = 8.5 Hz, 1H), 7.76 (dd, J_{H-H} = 8.8 Hz, J_{H-F} = 5.0 Hz, 1H), 7.23 (ddd, J_{H-H} = 8.8, 3.0 Hz, J_{H-F} = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (d, J = 250 Hz), 160.5, 142.7, 141.5, 140.2, 139.4, 138.7, 137.4, 136.8 (d, J = 7.5 Hz), 129.9 (d, J = 7.4 Hz), 122.0 (d, J = 22.1 Hz), 119.8 (d, J = 25.1 Hz), 117.9 (d, J = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.7 (q, J = 7.8 Hz, 1F, F8), −151.9 − −152.0 (m, 2F), −157.0 (t, J = 21.7 Hz, 1F), −161.7 − −161.9 (m, 2F). IR: υ = 1762, 1593, 1516, 1484, 1322, 1296, 1237, 1216, 1156, 1070, 1036, 1010, 992, 879, 867, 840 cm^{-1}. HRMS (ESI+) calc. for $C_{13}H_3BrF_6NaO_2$ $[M + Na]^+$ 406.9113; found 406.9129.

*Perfluorophenyl 2-Bromo-4-fluorobenzoate (**5f**).* Following the general procedure **A** with 2-bromo-4-fluorobenzoic acid (2.04 g, 9.33 mmol), pentafluorophenol (1.92 g, 10.45 mmol), and *N,N′*-dicyclohexylcarbodiimide (2.17 g, 10.54 mmol) in 35 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 3% Et_2O) to afford **5f** (3.37 g, 8.77 mmol, 94%) as a white solid (mp 76 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J_{H-H} = 8.8 Hz, J_{H-F} = 5.9 Hz, 1H), 7.53 (dd, J_{H-H} = 2.5 Hz, J_{H-F} = 8.2 Hz, 1H), 7.20 (ddd, J_{H-H} = 8.8, 2.5 Hz, J_{H-F} = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (d, J = 260 Hz), 160.6, 142.7, 141.2, 140.1, 139.4, 138.6, 136.8, 134.9 (d, J = 9.8 Hz), 125.3 (d, J = 10.2 Hz), 124.6 (d, J = 3.6 Hz), 123.0 (d, J = 24.8 Hz), 115.2 (d, J = 21.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −101.9 − −102.1 (m, 1F), −152.0 − −152.2 (m, 2F), −157.3 (t, J = 21.6 Hz, 1F), −161.9 − −162.1 (m, 2F). IR: υ = 1762, 1593, 1516, 1484, 1389, 1362, 1322, 1296, 1237, 1216, 1156, 1070, 1036, 1010, 992, 879, 867, 840 cm^{-1}. HRMS (ESI+) calc. for $C_{13}H_3BrF_6NaO_2$ $[M + Na]^+$ 406.9113; found 406.9128.

*Perfluorophenyl 2-Bromo-4-(trifluoromethyl)benzoate (**5g**).* Following the general procedure **A** with 2-bromo-4-(trifluoromethyl)-benzoic acid (1.28 g, 4.74 mmol), pentafluorophenol (977.4 mg, 5.31 mmol), and *N,N′*-dicyclohexylcarbodiimide (1.1 g, 5.35 mmol) in 18 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 1% Et_2O) to afford **5g** (2 g, 4.6 mmol, 97%) as a white solid (mp 60 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 2.2 Hz, 1H), 7.77−7.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 142.7, 141.4, 140.1, 139.5, 138.8, 137.0, 136.0 (q, J = 33 Hz), 132.9, 132.3, 132.1 (q, J = 3.7 Hz), 124.6 (q, J = 3.6 Hz), 123.6, 122.5 (q, J = 273 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.5 (s, 3F, F8), −151.8 − −152.0 (m,2F), −156.8 (t, J = 21.6 Hz, 1F), −161.6 − −161.8 (m, 2F). IR: υ = 1780, 1521, 1389, 1322, 1293, 1237, 1181, 1142, 1078, 1030, 999, 978 cm^{-1}. HRMS (ESI-) calc. for $C_8H_3BrF_3O_2$ $[M - C_6F_5]^-$ 266.9274; found 266.9272.

*Perfluorophenyl 2-Bromo-3-methylbenzoate (**5h**).* Following the general procedure **A** with 2-bromo-3-methylbenzoic acid (922.6 mg, 4.29 mmol), pentafluorophenol (883.5 g, 4.8 mmol), and *N,N′*-dicyclohexylcarbodiimide (1 g, 4.85 mmol) in 16 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **5h** (1.47 g, 3.86 mmol, 90%) as a white solid (mp 63 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J

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= 7.7 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4, 143.2, 141.4, 139.8, 138.1, 136.4, 125.2, 140.8, 135.1, 130.0, 129.4, 127.2, 124.6, 23.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ −152.0 − −152.3 (m, 2F), −157.7 − −158.1 (m, 1F), −162.2 − −162.6 (m, 2F). IR: υ = 2975, 1771, 1518, 1280, 1263, 1244, 1175, 1143, 1115, 1086, 997, 905, 884 cm^{-1}. HRMS (ESI+) calc. for $C_{14}H_6BrF_5NaO_2$ $[M + Na]^+$ 402.9369; found 402.9364.

*Perfluorophenyl 1-Bromo-2-naphthoate (**5i**).* Following the general procedure **A** with 1-bromo-2-naphthoic acid (1 g, 4 mmol), pentafluorophenol (824.6 mg, 4.48 mmol), and *N*,*N*′-dicyclohexylcarbodiimide (932.6 g, 4.52 mmol) in 15 mL of THF. The crude product was purified by flash column chromatography (petroleum ether 2% Et_2O) to afford **5h** (1.63 g, 3.92 mmol, 98%) as a white solid (mp 73 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56−8.50 (m, 1H), 7.98−7.87 (m, 3H), 7.76−7.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 142.7, 141.1, 140.1, 139.4, 138.6, 136.9, 136.0, 132.7, 129.3, 129.2, 128.8, 128.5, 128.3, 127.5, 126.2, 125.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −151.7 − −152.0 (m, 2F), −157.4 − −157.6 (t, J = 21.6 Hz, 1F), −161.9 − −162.2 (m, 2F). IR: υ = 2925, 1771, 1516, 1460, 1374, 1323, 1308, 1263, 1223, 1208, 1169, 1151, 1073, 1029, 994, 957, 866, 820 cm^{-1}. HRMS (ESI+) calc. for $C_{17}H_6BrF_5NaO_2$ $[M + Na]^+$ 438.9364; found 438.9355.

Procedure B: Preparation of Trimethyl [2,2,2-trifluoro-1-organyl-1-(trifluoromethyl)ethoxy] Silane. To a stirred solution of pentafluorophenyl ester **5** (1.00 equiv) in toluene (0.2 M) was added trimethyl(trifluoromethyl)silane (6.00 equiv). The reaction mixture was cooled to 0 °C in an ice bath and a solution of tetrabutylammonium fluoride (1 M in THF) (0.35 equiv) was added dropwise. The reaction mixture was allowed to reach room temperature and stirred for 18 h. The reaction was monitored by TLC (petroleum ether), and if necessary, additional trimethyl-(trifluoromethyl)silane could be added. Diethyl ether was added and the organic phase was washed with aqueous HCl (1 M). The aqueous phase was extracted with Et_2O (2 times). The combined etheral phases were washed with H_2O, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

*(2-(2-Bromophenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6a**).* Following the general procedure **B** with **5a** (18.52 g, 50.46 mmol), trimethyl(trifluoromethyl)silane (44.75 mL, 302.76 mmol) and tetrabutylammonium fluoride (17.66 mL, 17.66 mmol) in 190 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether 1% AcOEt) to afford **6a** (16.75 g, 42.39 mmol, 84%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 8.0, 1.5 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.39−7.30 (m, 1H), 7.26−7.21 (m, 1H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 131.1, 130.5, 130.1 (quint, J = 3.2 Hz), 127.2, 123.0 (q, J = 293 Hz), 122.5, 82.0 (quint, J = 30.0 Hz), 1.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.4 (s, 6F, F9). IR: υ = 2944, 1756, 1575, 1544, 1489, 1378, 1345, 1286, 1256, 1178, 1054, 1005, 989, 851 cm^{-1}. HRMS (ESI−) calc. for $C_9H_4BrF_6O$ $[M - TMS]^-$ 320.9355; found 320.9368.

*(2-(2-Bromo-5-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6b**).* Following the general procedure **B** with **5b** (850 mg, 2.23 mmol), trimethyl(trifluoromethyl)silane (1.98 mL, 13.38 mmol) and tetrabutylammonium fluoride (0.78 mL, 0.78 mmol) in 9 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether) to afford **6b** (7.50 g, 18.3 mmol, 82%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.1 Hz, 1H), 7.44 (s, 1H), 7.05 (dd, J = 8.1, 1.7 Hz, 1H), 2.33 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 137.1, 131.9, 130.8 (quint, J = 2.9 Hz), 130.1, 122.0 (q, J = 293 Hz), 119.1, 82.0 (quint, J = 32.3 Hz), 21.3, 1.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.4 (s, 6F). IR: υ = 2945, 1278, 1254, 1230, 1145, 1112, 1032, 981, 863, 867 cm^{-1}. HRMS (ESI-) calc. for $C_{10}H_6BrF_6O$ $[M - TMS]^-$ 334.9512; found 334.9501.

*(2-(2-Bromo-5-methoxyphenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6c**).* Following the general procedure **B** with **5c** (3.12 g, 7.87 mmol), trimethyl(trifluoromethyl)silane (6.98 mL, 47.22 mmol), and tetrabutylammonium fluoride (2.75 mL, 2.75 mmol) in 30 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether 2% Et_2O) to afford **6c** (2.41 g, 5.67 mmol, 72%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 6.81 (dd, J = 8.8, 2.8 Hz, 1H), 3.80 (s, 3H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 137.9, 131.1, 123.3 (q, J = 290 Hz), 117.1 (quint, J = 3.3 Hz), 116.1, 112.6, 81.8 (quint, J = 29.9 Hz), 55.6, 1.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.4 (s, 6F). IR: υ = 2962, 1601, 1470, 1403, 1192, 1057, 1027, 963, 846, 761 cm^{-1}. HRMS (ESI−) calc. for $C_{10}H_6BrF_6O$ $[M - TMS]^-$ 350.9461; found 350.9450.

*(2-(2-Bromo-5-nitrophenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6d**).* Following the general procedure **B** with **5d** (1.75 g, 4.24 mmol), trimethyl(trifluoromethyl)silane (3.76 mL, 25.44 mmol), and tetrabutylammonium fluoride (1.48 mL, 1.48 mmol) in 16 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether 1% Et_2O) to afford **6d** (1.4 g, 3.18 mmol, 75%) as an orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, J = 2.6 Hz, 1H), 8.11 (dd, J = 8.8, 2.6 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 131.0, 125.3, 125.1, 124.8, 123.2, 119.5 (q, J = 291 Hz), 81.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ −70.4 (s, 6F). IR: υ = 2973, 1580, 1481, 1432, 1376, 1176, 1089, 1060, 956, 882 cm^{-1}. HRMS (ESI-) calc. for $C_9H_3BrF_6O_3$ $[M - TMS]^-$ 365.9206; found 365.9212.

*(2-(2-Bromo-5-fluorophenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6e**).* Following the general procedure **B** with **5e** (2.55 g, 6.64 mmol), trimethyl(trifluoromethyl)silane (5.89 mL, 39.84 mmol), and tetrabutylammonium fluoride (2.32 mL, 2.32 mmol) in 25 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether then petroleum ether 15% Et_2O) to afford **6e** (1.92 g, 4.65 mmol, 70%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J_{H-H} = 8.9 Hz, J_{H-F} = 5.8 Hz, 1H), 7.42 (dd, J_{H-H} = 2.9 Hz, J_{H-F} = 10.8 Hz, 1H), 7.01 (ddd, J_{H-H} = 8.9, 2.9 Hz, J_{H-F} = 6.8 Hz, 1H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (d, J = 248 Hz), 138.6 (d, J = 7.6 Hz), 132.2, 122.7 (q, J = 293 Hz), 118.4 (d, J = 21.6 Hz), 117.9 (dquint, J_{C-F8} = 26.9 Hz, J_{C-F9} = 3.0 Hz, 116.7 (d, J = 3.6 Hz), 81.7 (t, J = 29.4 Hz), 1.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.5 (s, 6F), −113.2 (dt, J = 11.4, 6.2 Hz, 1F). IR: υ = 1585, 1474, 1395, 1226, 996, 960, 851, 761 cm^{-1}. HRMS (ESI−) calc. for $C_9H_3BrF_7O$ $[M - TMS]^-$ 338.9261; found 338.9252.

*(2-(2-Bromo-4-fluorophenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6f**).* Following the general procedure **B** with **5f** (1.48 g, 3.84 mmol), trimethyl(trifluoromethyl)silane (3.40 mL, 23.04 mmol), and tetrabutylammonium fluoride (1.34 mL, 1.34 mmol) in 14 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether then petroleum ether 15% Et_2O) to afford **6f** (1.31 g, 3.15 mmol, 82%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J_{H-H} = 9.2 Hz, J_{H-F} = 5.7 Hz, 1H), 7.30 (dd, J_{H-H} = 2.8 Hz, J_{H-F} = 8.3 Hz, 1H), 6.89 (ddd, J_{H-H} = 9.3, 2.8 Hz, J_{H-F} = 7.1 Hz, 1H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, J = 255 Hz), 131.5, 126.5, 124.5 (d, J = 24.0 Hz), 123.3 (d, J = 9.0 Hz), 122.8 (q, J = 291 Hz), 114.4 (d, J = 20.8 Hz), 81.7 (quint, J = 30.2 Hz), 1.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.6 (s, 6F), −110.0 (m, 1F). IR: υ = 2963, 1603, 1549, 1494, 1290, 1248, 1223, 1196, 1153, 1138, 1042, 965, 948, 913, 868, 849 cm^{-1}. HRMS (ESI−) calc. for $C_9H_3BrF_7O$ $[M - TMS]^-$ 338.9261; found 338.9250.

*(2-(2-Bromo-4-(trifluoromethyl)phenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6g**).* Following the general procedure **B** with **5g** (1.3 g, 3.00 mmol), trimethyl(trifluoromethyl)silane (2.66 mL, 18.00 mmol) and tetrabutylammonium fluoride (1.05 mL, 1.05 mmol) in 12 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether then petroleum ether 15% Et_2O) to afford **6g** (1.00 g, 2.16 mmol, 72%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 2.4 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.61 (dd, J = 8.6, 2.4 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.3 (q, J = 3.9 Hz), 133.1 (q, J = 34 Hz), 130.7 (quint, J = 3.1 Hz), 127.0, 124.0 (q, J = 3.4 Hz), 123.0, 122.7 (q, J = 273 Hz), 122.6 (q, J = 290 Hz), 81.9 (t, J = 29.9 Hz), 1.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.4 (s, 3F, F8), −70.4 (s, 6F, F9). IR: υ = 1390, 1334, 1286, 1247, 1219, 1199, 1140, 1089, 1051, 957, 943, 896,

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870, 849, 816 cm^{-1}. HRMS (ESI−) calc. for $C_{10}H_3BrF_9O$ [M − TMS]$^-$ 388.9229; found 388.9238.

*(2-(2-Bromo-3-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6h**).* Following the general procedure **B** with **5h** (1.40 g, 3.68 mmol), trimethyl(trifluoromethyl)silane (3.26 mL, 22.08 mmol), and tetrabutylammonium fluoride (1.29 mL, 1.29 mmol) in 14 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether 2% Et_2O) to afford **6h** (1.30 g, 3.17 mmol, 86%) as an orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J = 8.1 Hz, 1H), 7.37−7.31 (m, 1H), 7.27−7.20 (m, 1H), 2.49 (s, 3H), 0.20 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.9, 132.4, 130.7, 127.8, 126.6, 125.3, 123.1 (q, J = 293 Hz), 82.6 (quint, J = 29.8 Hz), 26.0, 1.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ −69.8 (s, 6F, F9). IR: υ = 1287, 1254, 1224, 1193, 1159, 1120, 1024, 979, 959, 871, 848 cm^{-1}. HRMS (ESI−) calc. for $C_{10}H_6BrF_6O$ [M − TMS]$^-$ 334.9512; found 334.9522.

*(2-(1-Bromonaphthalen-2-yl)-1,1,1,3,3,3-hexafluoropropan-2-yloxy)trimethylsilane (**6i**).* Following the general procedure **B** with **5i** (2.45 g, 5.96 mmol), trimethyl(trifluoromethyl)silane (5.28 mL, 35.76 mmol), and tetrabutylammonium fluoride (2.09 mL, 2.09 mmol) in 23 mL of toluene. The crude product was purified by flash column chromatography (petroleum ether 1% Et_2O) to afford **6i** (2.02 g, 4.53 mmol, 76%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72−8.65 (m, 1H), 7.86−7.80 (m, 2H), 7.76−7.70 (m, 1H), 7.69−7.57 (m, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 134.0, 129.1, 128.3, 128.2, 128.0, 128.0, 127.7, 125.5, 125.00, 123.2 (q, J = 289 Hz), 82.9 (quint, J = 29.7 Hz), 1.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −69.6 (s, 6F). IR: υ = 2966, 1197, 1154, 1007, 957, 855, 748 cm^{-1}. HRMS (ESI−) calc. for $C_{13}H_6BrF_6O$ [M − TMS]$^-$ 370.9512; found 370.9509.

Procedure C: Preparation of 1,1,1,3,3,3-Hexafluoro-2-arylpropan-2-ol. To a stirred solution of trimethyl[2,2,2-trifluoro-1-organyl-1-(trifluoromethyl)ethoxy]silane (1.00 equiv) in THF (0.2 M) was added 6 M HCl (half volume of THF). The reaction mixture was stirred overnight at room temperature. The mixture was diluted with H_2O and the product was extracted with Et_2O (2 times). The ethereal phases were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired product.

*2-(2-Bromophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2a**).* Following the general procedure **C** with **6a** (9.97 g, 25.24 mmol), in 125 mL of THF and 60 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 1% EtOAc, then 6% EtOAc) to afford **2a** (7.83 g, 24.23 mmol, 96%) as a white solid (mp 43 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.68 (m, 2H), 7.47−7.39 (m, 1H), 7.33 (td, J = 7.7, 1.6 Hz, 1H), 5.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 131.7, 130.7 (quint, J = 3.2 Hz), 128.0, 127.6, 122.7 (q, J = 289 Hz), 120.4, 80.3 (t, J = 29.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.6 (s, 6F). The spectroscopic data were consistent with those reported in the literature.[6b]

*2-(2-Bromo-5-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2b**).* Following the general procedure **C** with **6b** (974 mg, 2.38 mmol), in 12 mL of THF and 6 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2b** (730 mg, 2.17 mmol, 91%) as a white solid (mp 52 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 1H), 7.50 (s, 1H), 7.13 (dd, J = 8.2, 2.0 Hz, 1H), 5.41 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 136.4, 132.6, 131.2 (quint, J = 1.8 Hz), 124.1 (q, J = 282 Hz), 127.1, 116.9, 82.5 (quint, J = 32.3 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.6 (s, 6F, F9). IR: υ = 3578, 2880, 1727, 1670, 1429, 1338, 1220, 1082, 997, 912, 761, 706 cm^{-1}. HRMS calc. for $C_{10}H_6BrF_6O$ [M − H]$^-$ 334.9512; found 334.9501. The spectroscopic data were consistent with those reported in the literature.[17b]

*2-(2-Bromo-5-methoxyphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2c**).* Following the general procedure **C** with **6c** (2.46 g, 5.79 mmol), in 30 mL of THF and 15 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2c** (1.80 g, 5.10 mmol, 88%) as a white solid (mp 64 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.9 Hz, 1H), 7.26 (s, 1H), 6.88 (dd, J = 8.9, 2.9 Hz, 1H), 5.44 (s, 1H), 3.90−3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 137.2, 128.2, 122.7 (q, J = 290 Hz), 117.2 (quint, J = 3.4 Hz), 117.0, 110.3, 80.1 (quint, J = 30.4 Hz), 55.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.7 (s, 6F). IR: υ = 3484, 2926, 1601, 1474, 1374, 1219, 1048, 960, 820, 735 cm^{-1}. HRMS (ESI +) calc. for $C_{10}H_7BrF_6NaO_2$ [M + Na]$^+$ 374.9426; found 374.9444.

*2-(2-Bromo-5-nitrophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2d**).* Following the general procedure **C** with **6d** (796.8 mg, 1.81 mmol), in 9 mL of THF and 4.5 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 15% Et_2O) to afford **2d** (500 mg, 1.36 mmol, 75%) as a white solid (mp 67 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61(s, 1H), 8.16 (dd, J = 8.8, 2.6 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 5.00 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 128.4, 125.8, 125.4, 120.9, 119.4 (q, J = 290 Hz), 80.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.5 (s, 6F, F9). IR: υ = 3478, 2956, 1580, 1483, 1425, 1364, 1208, 1054, 988, 952, 819 cm^{-1}. HRMS (ESI−) calc. for $C_9H_3BrF_6NO_3$ [M − H]$^-$ 365.9206; found 365.9200.

*2-(2-Bromo-5-fluorophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2e**).* Following the general procedure **C** with **6e** (1.47 g, 3.56 mmol), in 18 mL of THF and 9 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2e** (1.12 g, 3.28 mmol, 92%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, J_{H-H} = 8.9 Hz, J_{H-F} = 5.6 Hz, 1H), 7.45 (d, J_{H-F} = 8.8 Hz, 1H), 7.09 (ddd, J_{H-H} = 8.9, 3.0 Hz, J_{H-F} = 6.8 Hz, 1H), 5.30 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, J = 250 Hz), 138.1 (d, J = 7.8 Hz), 129.3, 122.7 (q, J = 290 Hz), 119.2 (d, J = 21.9 Hz), 118.4 (d, J = 26.8 Hz), 114.8 (d, J = 3.6 Hz), 80.0 (t, J = 29.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.7 (s, 6F), −111.5 − −111.7 (m, 1F). IR: υ = 3496, 1587, 1476, 953, 848, 753 cm^{-1}. HRMS (ESI−) calc. for $C_9H_3BrF_7O$ [M − H]$^-$ 338.9261; found 338.9248.

*2-(2-Bromo-4-fluorophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2f**).* Following the general procedure **C** with **6f** (1.19 g, 2.28 mmol), in 11 mL of THF and 5.5 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2f** (700 mg, 2.05 mmol, 90%) as an orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (br s, 1H), 7.47 (dd, J_{H-H} = 2.8 Hz, J_{H-F} = 8.0 Hz, 1H), 7.15 (ddd, J_{H-H} = 9.4, 2.8 Hz, J_{H-F} = 7.0 Hz, 1H), 5.08 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7 (d, J = 256 Hz), 132.0, 124.0 (d, J = 24.6 Hz), 123.9, 122.8 (q, J = 287 Hz), 121.4 (d, J = 9.3 Hz), 115.3 (d, J = 21.0 Hz), 80.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −73.9 (s, 6F), −108.5 (s). IR: υ = 3503, 2359, 1604, 1582, 1496, 1207, 1155, 1105, 1040, 963, 938, 866, 819, 752 cm^{-1}. HRMS (ESI-) calc. for $C_9H_3BrF_7O$ [M − H]$^-$ 338.9261; found 338.9249.

*2-(2-Bromo-4-(trifluoromethyl)phenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2g**).* Following the general procedure **C** with **6g** (1.64 g, 3.55 mmol), in 18 mL of THF and 9 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 1% Et_2O then petroleum ether 10% Et_2O) to afford **2g** (1.25 g, 3.20 mmol, 90%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 0.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.70−7.66 (m, 1H), 5.24 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8 (q, J = 3.9 Hz), 133.7 (q, J = 33.8 Hz), 131.5, 131.2, 124.7, 122.5 (q, J = 273 Hz), 122.4 (q, J = 289 Hz), 121.2, 80.3 (t, J = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.5 (s, 3F), −73.5 (s, 6F). IR: υ = 3482, 2930, 1460, 1374, 1219, 1048, 1140, 1089, 1012, 964, 882, 876, 816 cm^{-1}. HRMS (ESI−) calc. for $C_{10}H_3BrF_9O$ [M − H]$^-$ 388.9229; found 388.9200.

*2-(2-Bromo-3-methylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2h**).* Following the general procedure **C** with **6h** (1.12 g, 2.93 mmol), in 15 mL of THF and 7.5 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2h** (900 mg, 2.67 mmol, 91%) as a white solid (mp 54 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz, 1H), 7.41−7.39 (m, 1H), 7.32 (t, J = 8.1 Hz, 1H), 5.82 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 133.1, 128.4 (quint, J = 3.1 Hz), 127.9, 127.5, 123.4, 122.8 (q, J = 293 Hz), 80.9 (quint, J = 29.9 Hz), 25.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.2 (s, 6F, F9). IR: υ = 3482, 2928, 1519, 1472, 1451, 1365, 1255, 1202, 1187, 1141, 1098, 1018, 971, 950,

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819 cm^{-1}. HRMS (ESI−) calc. for $C_{10}H_6BrF_6O$ $[M - H]^-$ 334.9512; found 334.9503.

*2-(1-Bromonaphthalen-2-yl)-1,1,1,3,3,3-hexafluoropropan-2-ol (**2i**).* Following the general procedure **C** with **6i** (1.91 g, 3.48 mmol), in 21 mL of THF and 10.5 mL of 6 M HCl. The crude product was purified by flash column chromatography (petroleum ether 5% Et_2O) to afford **2i** (1.30 g, 3.48 mmol, 81%) as a white solid (mp 65 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.54−8.49 (m, 1H), 7.92−7.84 (m, 2H), 7.79−7.73 (m, 1H), 7.72−7.62 (m, 2H), 5.94 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 133.1, 128.8, 128.7, 128.6, 128.2, 128.0, 126.0, 125.6 (quint, J = 3.3 Hz), 123.0, 122.9 (q, J = 289 Hz), 81.3 (quint, J = 30.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −72.8 (s, 6F). IR: υ = 3447, 1206, 1148, 1097, 994, 947, 861, 809, 745 cm^{-1}. HRMS (ESI−) calc. for $C_{13}H_6BrF_6O$ $[M - H]^-$ 370.9512; found 370.9495.

Procedure D: Preparation of Bis(α,α-bis(trifluoromethyl) arenemethanolato-(-2)C^2, O) Silanes. To a stirred solution of alcohol **2** (1.00 equiv) in diethyl ether (0.3 M) was added NaH (60%) (1.1 equiv) at room temperature. The mixture was stirred for 30 min and cooled to −78 °C. A solution of *t*BuLi (1.6 M in pentane) (2.20 equiv) was added dropwise and the reaction was warmed to 0 °C. Silicon tetrachloride (0.6 equiv) was added dropwise and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with H_2O and extracted with Et_2O (30 mL). The ethereal phase was washed with HCl (0.5 M) (3 × 20 mL), H_2O (20 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the crude product as an orange oil. The residue was crystallized with hexane to obtain the desired product.

Due to their high reactivity, attempts to characterize spirosilanes **3** by HRMS led to the observation of the corresponding hydroxy or methoxy adducts.

*3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′(3H,3′H)-spirobi-[2,l-benzoxasilole] (**1**).* Following the general procedure **D** with **2a** (1.75 g, 5.42 mmol), NaH (60%, 238.4 mg, 5.96 mmol), tBuLi (1.6 M, 7.45 mL, 11.92 mmol), and $SiCl_4$ (372.3 μL g, 3.25 mmol) in 6.5 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **1** (1.00 g, 1.95 mmol, 72%) as a white solid (mp 132 °C). ^1H NMR (400 MHz, acetone-d_6): δ 7.98−7.86 (m, 6H, arom.), 7.82−7.79 (m, 2H, arom.). ^{13}C NMR (100 MHz, acetone-d_6): δ = 142.0, 135.3, 134.2, 132.5, 130.0, 126.0, 124.9 (q, J = 285 Hz), 83.2. ^{19}F NMR (376 MHz, acetone-d_6): −76.5 (s, 12F, CF_3). ^{29}Si NMR (119 MHz, $CDCl_3$): δ 7.5. The spectroscopic data were consistent with those reported in the literature.[6b]

*5,5′-Dimethyl-3,3,3′,3′-tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo[c][1,2] oxasilole] (**3b**).* Following the general procedure **D** with **2b** (1.01 g, 3.01 mmol), NaH (60%, 132.4 mg, 3.31 mmol), tBuLi (1.6 M, 4.14 mL, 6.62 mmol), and $SiCl_4$ (206.2 μL g, 1.80 mmol) in 10 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3b** (0.58 g, 1.07 mmol, 71%) as a white solid (mp 154 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H), 2.51 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 142.3, 133.3, 132.7, 126.0 (quint, J = 1.8 Hz), 124.4, 123.8 (q, J = 282 Hz), 82.7 (quint, J = 31.6 Hz), 22.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −75.9 (q, J = 8.9 Hz, 6F), −76.3 (q, J = 8.9 Hz, 6F). ^{29}Si NMR (119 MHz, $CDCl_3$): δ 7.7. IR: υ = 2928, 1607, 1312, 1281, 1213, 1174, 1106, 1084, 979, 906, 852, 824 cm^{-1}. HRMS (ESI−) calc. for $C_{21}H_{15}F_{12}O_3Si$ $[M + CH_3O]^-$ 571.0604; found 571.0584.

*5,5′-Dimethoxy-3,3,3′,3′-tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo[c][1,2]oxasilole] (**3c**).* Following the general procedure **D** with **2c** (988.6 mg, 2.80 mmol), NaH (60%, 123.2 mg, 3.08 mmol), tBuLi (1.6 M, 3.85 mL, 6.16 mmol), and $SiCl_4$ (192.5 μL g, 1.68 mmol) in 9 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3c** (0.56 g, 0.98 mmol, 70%) as a white solid (mp 112 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.2 Hz, 2H), 7.26 (s, 2H), 7.15 (dd, J = 8.2, 2.2 Hz, 2H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 144.0, 134.6, 122.2 (q, J = 283 Hz), 118.3, 118.2, 110.8 (quint, J = 1.6 Hz), 82.4 (quint, J = 31.7 Hz), 55.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −75.9 (q, J = 9.0 Hz, 6F), −76.4 (q, J = 9.0 Hz, 6F). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 7.2. IR: υ = 2947, 1602, 1473, 1281, 1219, 1084, 1032, 980, 852, 744, 708, 689 cm^{-1}. HRMS (ESI−) calc. for $C_{21}H_{15}F_{12}O_5Si$ $[M + CH_3O]^-$ 603.0503; found 603.0520.

*5,5′-Difluoro-3,3,3′,3′-tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo[c][1,2]oxasilole] (**3e**).* Following the general procedure **D** with **2e** (518.4 g, 1.52 mmol), NaH (60%, 66.8 mg, 1.67 mmol), tBuLi (1.6 M, 2.09 mL, 3.34 mmol), and $SiCl_4$ (104.3 μL g, 0.91 mmol) in 5 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3e** (0.28 g, 0.51 mmol, 67%) as a white solid (mp 150 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J_{H-F} = 5.5 Hz, J_{H-H} = 8.3 Hz, 2H), 7.52 (d, J_{H-F} = 9.0 Hz, 2H), 7.37 (dt, J_{H-F} = 8.3 Hz, J_{H-H} = 8.3, 2.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1 (d, J = 256 Hz), 144.6, 135.6 (d, J = 9.2 Hz), 122.7, 122.4 (q, J = 288 Hz), 119.8 (d, J = 21.6 Hz), 113.5 (d, J = 26.4 Hz), 82.4 (t, J = 30.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −75.9 (q, J = 8.8 Hz, 6F), −76.4 (q, J = 8.8 Hz, 6F), −102.9 − −103.0 (m, 2F). ^{29}Si NMR (119 MHz, $CDCl_3$/Trifluorotoluene (1/4)): δ −50.1. IR: υ = 1345, 1274, 1215, 1160, 1106, 1080, 999, 978, 913, 871, 832, 743, 707, 672, 641, 614 cm^{-1}. HRMS (ESI−) calc. for $C_{19}H_9F_{14}O_3Si$ $[M + CH_3O]^-$ 579.0103; found 579.0088.

*6,6′-Difluoro-3,3,3′,3′-tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo[c][1,2] oxasilole] (**3f**).* Following the general procedure **D** with **2f** (692.2 mg, 2.03 mmol), NaH (60%, 89.2 mg, 2.23 mmol), tBuLi (1.6 M, 2.79 mL, 4.47 mmol), and $SiCl_4$ (140 μL g, 1.22 mmol) in 6.8 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3f** (0.36 g, 0.66 mmol, 65%) as a white solid (mp 131 °C). ^1H NMR (300 MHz, acetone-d_6): δ 7.75 (dd, J_{H-H} = 2.7 Hz, J_{H-F} = 8.7 Hz, 2H), 7.72−7.66 (s, 2H), 7.37−7.29 (td, J_{H-H} = 8.6, 2.7 Hz, J_{H-F} = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8 (d, J = 255 Hz), 137.3, 130.0 (d, J = 6.4 Hz), 127.8, 122. 0 (q, J = 284 Hz), 121.8 (q, J = 283 Hz), 121.5 (d, J = 23.6 Hz), 119.8 (d, J = 21.2 Hz), 82.6 (t, J = 32.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −76.0 (q, J = 8.8 Hz, 6F), −76.5 (q, J = 8.8 Hz, 6F), −108.2 (s, 2F). ^{29}Si NMR (119 MHz, $CDCl_3$): δ 4.9. IR: υ = 1581, 1514, 1471, 1273, 1213, 1103, 1068, 970, 928, 836 cm^{-1}. HRMS (ESI-) calc. for $C_{19}H_9F_{14}O_3Si$ $[M + CH_3O]^-$ 579.0103; found 579.0124.

*3,3,3′,3′,6,6′-Hexakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo-[c][1,2]oxasilole] (**3g**).* Following the general procedure **D** with **2g** (567 mg, 1.45 mmol), NaH (60%, 63.8 mg, 1.595 mmol), tBuLi (1.6 M, 1.99 mL, 3.19 mmol), and $SiCl_4$ (100 μL g, 0.87 mmol) in 4.8 mL of Et_2O. The crude product was purified by crystallization from hexane to afford 3g (0.34 g, 0.53 mmol, 73%) as a white solid (mp 162 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05−7.97 (m, 4H), 7.90 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 145.3, 134.3 (q, J = 33.0 Hz), 130.7, 130.5, 128.1, 126.4, 123.3 (q, J = 273 Hz), 121.8 (q, J = 288 Hz), 121.5 (q, J = 280 Hz), 82.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.1 (s, 6F), −75.6 (q, J = 8.6 Hz, 6F), −76.0 (q, J = 8.6 Hz, 6F). IR: υ = 1331, 1274, 1216, 1199, 1137, 1102, 1086, 1069, 982, 968, 921, 842, 754, 732, 709, 639, 620 cm^{-1}. HRMS (ESI−) calc. for $C_{21}H_9F_{18}O_3Si$ $[M + CH_3O]^-$ 679.0039; found 679.0015.

*7,7′-dimethyl-3,3,3′,3′-tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[benzo[c][1,2]oxasilole] (**3h**).* Following the general procedure **D** with **2h** (684.2 mg, 2.03 mmol), NaH (60%, 89.2 mg, 2.23 mmol), tBuLi (1.6 M, 2.79 mL, 4.47 mmol), and $SiCl_4$ (140 μL g, 1.22 mmol) in 6.8 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3h** (0.30 g, 0.55 mmol, 54%) as a white solid (mp 182 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.65−7.58 (m, 4H), 7.45−7.39 (m, 2H), 2.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.1, 142.0, 133.7, 132.0, 127.2, 122.9, 122.5 (q, J = 285 Hz), 122.0 (q, J = 286 Hz), 82.7, 22.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.3 (q, J = 9.0 Hz, 6F), −76.3 (q, J = 9.0 Hz, 6F). ^{29}Si NMR (119 MHz, $CDCl_3$): δ 8.2. IR: υ = 2927, 1591, 1467, 1308, 1278, 1254, 1210, 1158, 1136, 1110, 1075, 1044, 974, 906, 850 cm^{-1}. HRMS (ESI−) calc. for $C_{20}H_{13}F_{12}O_3Si$ $[M + HO]^-$ 557.0448; found 557.0436.

*3,3,3′,3′-Tetrakis(trifluoromethyl)-3H,3′H-1,1′-spirobi[naphtho-[1,2-c][1,2]oxasilole] (**3i**).* Following the general procedure **D** with **2i** (307.8 mg, 0.825 mmol), NaH (60%, 36.3 mg, 0.907 mmol), tBuLi (1.6 M, 1.14 mL, 1.82 mmol), and $SiCl_4$ (56.7 μL g, 0.495 mmol) in 2.75 mL of Et_2O. The crude product was purified by crystallization from hexane to afford **3i** (0.20 g, 0.33 mmol, 80%) as a white solid

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(mp 196 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.62−7.58 (m, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.43−7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 135.0, 134.7, 134.2, 128.8, 128.7, 128.5, 128.2 (d, J = 2.5 Hz), 127.7, 122.6 (q, J = 284 Hz), 122.1 (q, J = 284 Hz), 121.6 (quint, J = 1.7 Hz), 83.1 (quint, J = 31.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −74.7 (q, J = 9.2 Hz, 6F), −75.6 (q, J = 9.2 Hz, 6F). ^{29}Si NMR (119 MHz, $CDCl_3$): δ 9.4. IR: υ = 2930, 1281, 1204, 1157, 1100, 1040, 976, 744 cm^{-1}. HRMS (ESI−) calc. for $C_{27}H_{15}F_{12}O_3Si$ [M + CH_3O]$^-$ 643.0604; found 643.0580.

Procedure E-a: Preparation of Sodium bis[α,α-bis(trifluoromethyl)arenemethanolato(2-)-C^2,0]fluorosilicate. To a stirred solution of spirosilane **3** (1.00 equiv) in acetone (0.05 M) and 0.1% H_2O was added sodium fluoride (4.00 equiv). The progress of the reaction was monitored by ^{19}F NMR. The excess of sodium fluoride was filtered off and the filtrate was evaporated under reduced pressure to afford the pure product.

Procedure E-b: Preparation of Tetrabutylammonium bis[α,α-bis(trifluoromethyl)arenemethanolato(2-)-C^2,0]fluorosilicate. To a stirred solution of spirosilane **3** (1.00 equiv) in dichloromethane (0.05 M) was added TBAF (1 M in THF, 1.00 equiv). The progress of the reaction was monitored by ^{19}F NMR. The organic phase was washed with H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to afford the pure product.

*Sodium Bis[α,α-bis(trifluoromethyl)benzenemethanolato(2-)-C^2,0]fluoro silicate (**7a**).* Following the general procedure **E-a** with **3a** (307.4 mg, 0.60 mmol), in 12 mL of acetone and 12 μL of water, to afford **7a** (0.32 g, 0.58 mmol, 96%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.23−8.20 (m, 2H, arom.), 7.59−7.55 (m, 2H, arom.), 7.43−7.39 (m, 4H, arom.). ^{13}C NMR (100 MHz, acetone-d_6): δ = 142.8 (d, J = 16.0 Hz), 142.5, 138.1, 129.7, 129.2, 126.8 (q, J = 288 Hz), 124.3 (quint, J = 2.0 Hz), 81.0 (quint, J = 28.6 Hz). ^{19}F NMR (376 MHz, acetone-d_6): −75.7 − −75.8 (m, 6F, CF_3), −75.9 (q, J = 9.0 Hz, 6F, CF_3), −132.2 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −73.7 (d, J = 236 Hz). IR: υ = 1446, 1275, 1190, 1142, 1087, 969, 768, 739 cm^{-1}. HRMS (ESI−) calc. for $C_{18}H_8F_{13}O_2Si$ [M − Na]$^-$ 531.0091; found 531.0090.

*Sodium Bis[α,α-bis(trifluoromethyl)-5-methylbenzenemethanolato(2-)-C^2,0] fluoro silicate (**7b**).* Following the general procedure **E-a** with **3b** (97.3 mg, 0.18 mmol), in 3.6 mL of acetone and 3.6 μL of water, to afford **7b** (0.1 g, 0.17 mmol, 94%) as a white solid (mp >260 °C). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.08 (d, J = 7.5 Hz, 2H), 7.36 (s, 2H), 7.18 (d, J = 7.5 Hz, 2H), 2.36 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 143.0, 139.7 (d, J = 15.9 Hz), 139.3, 138.0, 130.2, 125.4 (q, J = 289 Hz), 124.8 (quint, J = 1.9 Hz), 81.0 (quint, J = 28.7 Hz), 21.6. ^{19}F NMR (282 MHz, acetone-d_6): δ −75.5 (m, 6F), −75.7 (t, J = 8.3 Hz, 6F), −132.1 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −77.0 (d, J = 226.9 Hz). IR: υ = 1701, 1609, 1272, 1207, 1162, 1082, 968, 851, 710, 668 cm^{-1}. HRMS (ESI−) calc. for $C_{20}H_{12}F_{13}O_2Si$ [M − Na]$^-$ 559.0404; found 559.0398.

*Sodium Bis[α,α-bis(trifluoromethyl)-5-methoxybenzenemethanolato(2-)-C^2,0] fluoro silicate (**7c**).* Following the general procedure **E-a** with **3c** (38.9 mg, 0.068 mmol), in 1.4 mL of acetone and 1.4 μL of water, to afford **7c** (0.04 g, 0.065 mmol, 96%) as a white solid (mp >260 °C). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.09 (d, J = 8.2 Hz, 2H), 7.06 (s, 2H), 6.97 (d, J = 8.2 Hz, 2H), 3.81 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 161.7, 139.1, 133.8 (d, J = 16.3 Hz), 125.3 (q, J = 289 Hz), 115.4, 115.2, 109.9 (quint, J = 1.6 Hz), 81.0 (quint, J = 28.6 Hz), 55.4. ^{19}F NMR (282 MHz, acetone-d_6): δ −75.7 − −75.9 (m, 6F), −75.9 − −76.0 (m, 6F), −132.1 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −77.2 (d, J = 225 Hz). IR: υ = 2938, 1701, 1599, 1473, 1270, 1213, 1165, 1080, 1032, 968, 851, 709 cm^{-1}. HRMS (ESI−) calc. for $C_{20}H_{12}F_{13}O_4Si$ [M − Na]$^-$ 591.0303; found 591.0320.

*Sodium Bis[α,α-bis(trifluoromethyl)-5-fluorobenzenemethanolato(2-)-C^2,0]fluoro silicate (**7e**).* Following the general procedure **E-a** with **3e** (29 mg, 0.053 mmol), in 1 mL of acetone and 1 μL of water, to afford **7e** (0.03 g, 0.05 mmol, 94%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.18 (dd, J_{H-F} = 6.5 Hz, J_{H-H} = 8.2 Hz, 2H), 7.22 (d, J_{H-F} = 9.8 Hz, 2H), 7.17 (ddd, J_{H-F} = 9.3 Hz, J_{H-H} = 8.2, 2.3 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 164.7 (d, J = 245 Hz), 144.8 (d, J = 7.6 Hz), 139.8 (d, J = 8.2 Hz), 138.5, 125.2 (q, J = 293 Hz), 125.0 (q, J = 288 Hz), 116.6 (d, J = 20.3 Hz), 111.1 (d, J = 22.9 Hz), 80.5 (t, J = 30.9 Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ −76.0 (td, J = 9.3, 3.5 Hz, 6F), −76.3 (q, J = 9.3 Hz, 6F), −115.0 (td, J = 9.5, 6.5 Hz, 2F), −132.1 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −79.3 (d, J = 228 Hz). IR: υ = 2938, 1375, 1325, 1289, 1167, 1044, 979, 835 cm^{-1}. HRMS (ESI−) calc. for $C_{18}H_6F_{15}O_2Si$ [M − Na]$^-$ 566.9903; found 566.9890.

*Sodium Bis[α,α-bis(trifluoromethyl)-4-fluorobenzenemethanolato(2-)-C^2,0]fluoro silicate (**7f**).* Following the general procedure **E-a** with **3f** (28 mg, 0.051 mmol), in 1 mL of acetone and 1 μL of water, to afford **7f** (0.03 g, 0.05 mmol, 97%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.71 (dd, J_{H-H} = 2.7 Hz, J_{H-F} = 9.0 Hz, 2H), 7.45−7.40 (m, 2H), 7.00 (td, J_{H-H} = 2.7 Hz, J_{H-F} = 8.5 Hz, 2H). ^{13}C NMR (150 MHz, acetone-d_6): δ 164.5 (d, J = 246 Hz), 125.7 (d, J = 17.6 Hz), 137.9, 126.1, 125. 0 (q, J = 293 Hz), 123.2 (d, J = 19.5 Hz), 117.1 (d, J = 23.6 Hz), 80.5 (t, J = 28.9 Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ −76.0 − −76.1 (m, 6F), −76.4 (q, J = 9.3 Hz, 6F), −116.7 (td, J = 8.8, 4.7 Hz, 2F), −132.3 (s, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −80.5 (d, J = 230 Hz). IR: υ = 2965, 1567, 1510, 1378, 1342, 1258, 1157, 1031, 995, 857, 753 cm^{-1}. HRMS (ESI−) calc. for $C_{19}H_9F_{14}O_3Si$ [M − Na + CH_3O]$^-$ 579.0103; found 579.0088.

*Sodium Bis[α,α-bis(trifluoromethyl)-4-trifluoromethylbenzenemethanolato(2-)-C^2,0]fluoro silicate (**7g**).* Following the general procedure **E-a** with **3g** (27.2 mg, 0.042 mmol), in 1 mL of acetone and 1 μL of water, to afford **7g** (0.03 g, 0.04 mmol, 95%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.54 (s, 2H), 7.80−7.73 (m, 4H). ^{13}C NMR (150 MHz, acetone-d_6): δ 146.3, 144.1 (q, J = 16.8 Hz), 134.6 (q, J = 3.9 Hz), 131.4 (q, J = 31.2 Hz), 127.1 (q, J = 3.9 Hz), 125.8 (q, J = 272 Hz), 125.2, 125.1 (dq, J = 287, 6.1 Hz), 124.8 (q, J = 285 Hz), 80.9 (t, J = 29.5 Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ −62.9 (s, 6F), −75.8 − −75.9 (m, 6F), −76.3 (q, J = 9.2 Hz, 6F), −132.9 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −79.8 (dt, J = 228, 5.4 Hz). IR: υ = 1330, 1269, 1216, 1193, 1137, 1087, 1072, 967, 928, 840, 762, 737, 709 cm^{-1}. HRMS (ESI−) calc. for $C_{20}H_6F_{19}O_2Si$ [M − Na]$^-$ 666.9839; found 666.9826.

*Tetrabutylammonium Bis[α,α-bis(trifluoromethyl)-3-methylbenzenemethanolato(2-)-C^2,0]fluoro silicate (**7h**).* Following the general procedure **E-b** with **3h** (77.8 mg, 0.144 mmol), in 3 mL of acetone and 3 μL of water, to afford **7h** (0.11 g, 0.14 mmol, 97%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.24 (d, J = 6.6 Hz, 2H), 7.13−7.06 (m, 4H), 3.47−3.41 (m, 8H), 2.56 (s, 6H), 1.88−1.77 (m, 8H), 1.43 (q, J = 7.4 Hz, 8H), 0.95 (t, J = 7.4 Hz, 12H). ^{13}C NMR (100 MHz, acetone-d_6): δ 151.7 (d, J = 68.5 Hz), 143.2 (d, J = 2.4 Hz), 135.5 (d, J = 4.3 Hz), 130.5, 126.9, 125.2 (q, J = 285 Hz), 124.9 (q, J = 285 Hz), 120.8, 79.6, 59.4, 59.3, 24.4, 22.8, 20.4, 20.3, 13.8. ^{19}F NMR (376 MHz, acetone-d_6): δ −75.7 (q, J = 8.9 Hz, 6F), −76.2 (q, J = 8.8 Hz, 6F), −99.5 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −81.6 (d, J = 328 Hz). IR: υ = 2967, 2880, 1456, 1381, 1284, 1239, 1211, 1182, 1142, 1113, 1050, 971, 881, 840, 783, 744, 727, 713 cm^{-1}. HRMS (ESI−) calc. for $C_{20}H_{12}F_{13}O_2Si$ [M − TBA]$^-$ 559.0404; found 559.0398.

*Sodium Bis[α,α-bis(trifluoromethyl)naphthalenemethanolato(2-)-C^2,0]fluoro silicate (**7i**).* Following the general procedure **E-a** with **3i** (95 mg, 0.155 mmol), in 3.1 mL of acetone and 3.1 μL of water, to afford **7i** (0.10 g, 0.15 mmol, 97%) as a white solid (mp >260 °C). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.71−8.65 (m, 2H), 7.89−7.84 (m, 2H), 7.82−7.77 (m, 2H), 7.63−7.57 (m, 2H), 7.49−7.43 (m, 4H). ^{13}C NMR (75 MHz, acetone-d_6): δ 152.9 (d, J = 67.5 Hz), 137.5 (d, J = 2.0 Hz), 135.4, 133.1, 132.8 (d, J = 4.4 Hz), 128.3, 128.1, 126.3, 125.4, 125.3 (q, J = 287 Hz), 124.8 (q, J = 285 Hz), 121.8, 80.5 (quint, J = 30.4 Hz). ^{19}F NMR (376 MHz, acetone-d_6): δ −75.3 (q, J = 9.0 Hz, 6F), −75.9 (q, J = 9.0 Hz, 6F), −94.3 (s, 1F, Si−F). ^{29}Si NMR (119 MHz, acetone-d_6): δ −80.9 (d, J = 322.6 Hz). IR: υ = 1698, 1623, 1508, 1281, 1189, 1129, 1041, 972, 815, 751, 679, 644 cm^{-1}. HRMS (ESI−) calc. for $C_{26}H_{12}F_{13}O_2Si$ [M − Na]$^-$ 631.0404; found 631.0424.

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■ ASSOCIATED CONTENT

Supporting Information

NMR spectra and X-ray diffraction data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The experiments were performed by HL, GS, VC, JPG, and CC. LEZ and LK participated to the design of experiments. Crystal structure determinations were determined by LMC. The manuscript was written by JPG and LF. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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