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Synthesis of CF_3-Substituted Olefins by Julia–Kocienski Olefination Using 2-[(2,2,2-Trifluoroethyl)sulfonyl]benzo[*d*]thiazole as Trifluoromethylation Agent

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A modified Julia–Kocienski protocol was investigated for the synthesis of CF_3-substituted terminal olefins. By employing a simple one-step procedure, aldehydes were converted into the corresponding CF_3-substituted olefins using 2-[(2,2,2-trifluoroethyl)sulfonyl]benzo[*d*]thiazole as the trifluoromethylation agent. This sulfone was prepared on a gram scale in two steps from inexpensive and commercially available trifluoroethanol. The Julia–Kocienski olefination tolerated various functional groups, and the trifluoromethylated olefins were obtained in good yields. However, the *E*/*Z* selectivity was strongly substrate dependent, and only moderate selectivities could be achieved.

Introduction

In recent years, the trifluoromethylation of aromatic and nonaromatic compounds has drawn a lot of attention.[1] Because of its unique biological and chemical behavior, the trifluoromethyl group has an important role in many pharmaceutical and agrochemical compounds.[2] To date, many reactions have been reported dealing with the direct trifluoromethylation of various compounds. The most common trifluoromethyl sources are trimethyl- and triethyl(trifluoromethyl)silane (Ruppert–Prakash reagent),[3] sodium trifluoromethanesulfinate (Langlois reagent),[4] electrophilic sulfonium salts (Umemoto/Yagupolskii reagents),[5] and hypervalent iodine agents (Togni's reagents).[6] In contrast to these quite expensive sources of CF_3, trifluoroethanol is a low cost chemical alternative (see Figure 1).

Inspired by the simplicity of the Julia–Kocienski olefination,[8] we envisioned the synthesis of trifluoromethylated olefins by using a trifluoromethyl-substituted sulfone, which should be easily accessible from trifluoroethanol. Although various examples show that Julia–Kocienski conditions can be applied to the synthesis of monofluorinated olefins,[9] trifluoromethylated olefins have never been prepared using this method. Herein, we describe a new approach towards trifluoromethylated olefins through a modified Julia–Kocienski protocol.

Results and Discussion

In general, trifluoromethyl-substituted olefins are accessible through metal-mediated cross-coupling reactions.[10] However, most of these reactions require high temperature, expensive sources of CF_3, or prefunctionalized substrates such as vinyl sulfonates,[10a] halides,[10b] or boronic acids.[10c] Furthermore, the decomposition of metallic CF_3-substituted intermediates often leads to perfluoroethylated byproducts.[10b] In contrast to these routes, standard olefination protocols tolerate various functional groups and

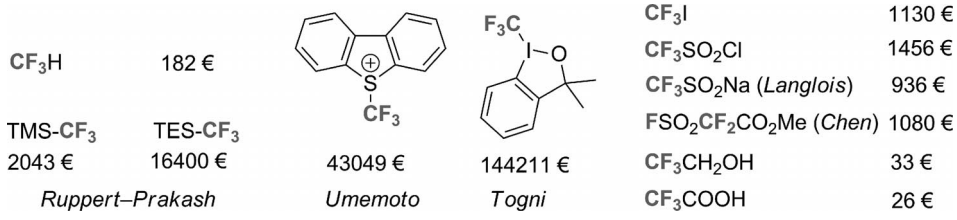

Figure 1. Commercially available (price per mole) sources of CF_3 (TMS = trimethylsilyl, TES = triethylsilyl).[7]

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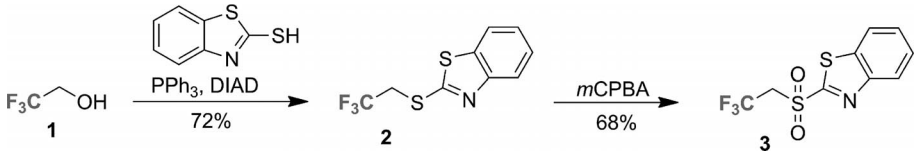


Scheme 1. Synthesis of 2-[(2,2,2-trifluoroethyl)sulfonyl]benzo[*d*]thiazole (**3**, DIAD = diisopropyl azodicarboxylate).

allow for the synthesis of olefins by starting from simple carbonyl compounds. To the best of our knowledge, the synthesis of trifluoromethyl-substituted olefins through a Julia–Kocienski olefination has never before been reported.

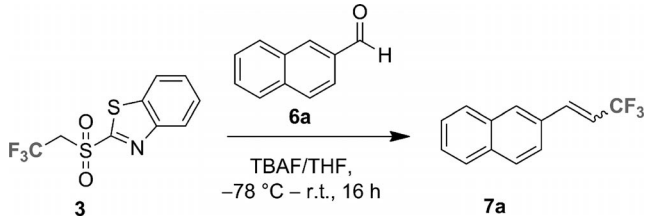
Because the one-step Julia–Kocienski olefination of carbonyl compounds requires electron-poor aromatic sulfones,[8,9] we explored the synthesis of sulfone **3**, which should be a suitable substrate for the synthesis of CF_3-substituted terminal olefins. As shown in Scheme 1, the synthesis of sulfone **3** could be achieved by a two-step procedure. First, trifluoroethanol was converted into sulfide **2** by using Mitsunobu reaction conditions. Subsequently, the oxidation of **2** by treatment with *meta*-chloroperoxybenzoic acid (*m*CPBA) afforded the corresponding sulfone **3** in 68% yield. Altogether, **3** could be synthesized on a gram scale in 49% overall yield. Additionally, sulfide **2** was also accessible in similar yields by starting from commercially available trifluoroethyl iodide (see Exp. Section).

After the synthesis of the CF_3-substituted sulfone, this substrate was subjected to standard Julia–Kocienski conditions.[8,9,11] Generally, the one-step Julia–Kocienski olefination is carried out with a strong metallic base. The first attempts using standard bases such as lithium hexamethyldisilazide (LiHMDS), NaHMDS, KO*t*Bu, or NaH did not result in conversion into the desired product. When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used, the 12% conversion into the corresponding trifluoromethylated olefin was determined by ^{19}F NMR spectroscopy. However, when DBU was employed as the base, the further optimization of the reaction conditions such as changing the solvent, temperature, or reaction time did not lead to an improvement in the yield. Therefore, we started a search for a modified reaction protocol.

Various examples show that deprotonation at the α position to a CF_3 group rapidly leads to a β-fluoro elimination[12] to give difluorovinylic compounds, which are no longer able to undergo reactions with carbonyl compounds (see Scheme 2). In contrast, highly fluorinated olefins can regioselectively add nucleophiles such as fluoride. This can be explained by the repulsive interactions between the lone pairs of the fluorine substituent and the π orbital of the sp^2-hybridized carbon.[13] Recently, we used this concept for the silver-mediated methoxycarbonyltetrafluoroethylation of arenes.[13a]

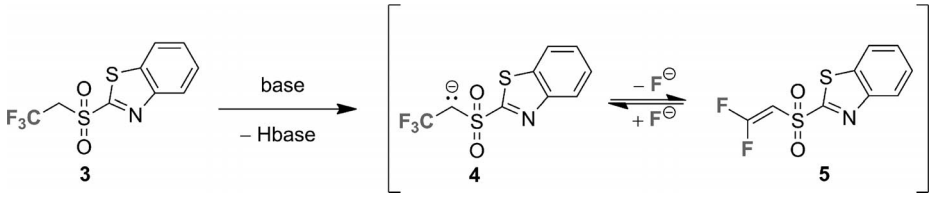
Thus, we assumed that adding an excess amount of a fluoride source (e.g., KF) would shift the equilibrium towards nucleophilic compound **4**. However, the addition of KF to a mixture of sulfone **3**, aldehyde **6**, and DBU did not affect the reaction. Inspired by the work of Ishibashi and co-workers,[14] we then investigated using the fluoride source tetra-*n*-butylammonium fluoride (TBAF) as the base in our olefination reaction. As shown in Table 1, using 10 equiv. of TBAF [1 M in tetrahydrofuran (THF)] considerably improved the yield of the reaction to 59% (see Table 1, Entry 1), whereas using only 5 equiv. of TBAF led to 50% yield (see Table 1, Entry 2). Interestingly, the addition of DBU as a stronger base reduced the yield significantly to 31% (see Table 1, Entry 3). Finally, increasing the amount of the aldehyde to 2 and 3 equiv. increased the yield to 90 and 99% (see Table 1, Entries 4 and 5), respectively.

Table 1. Optimization of the reaction conditions.[a]

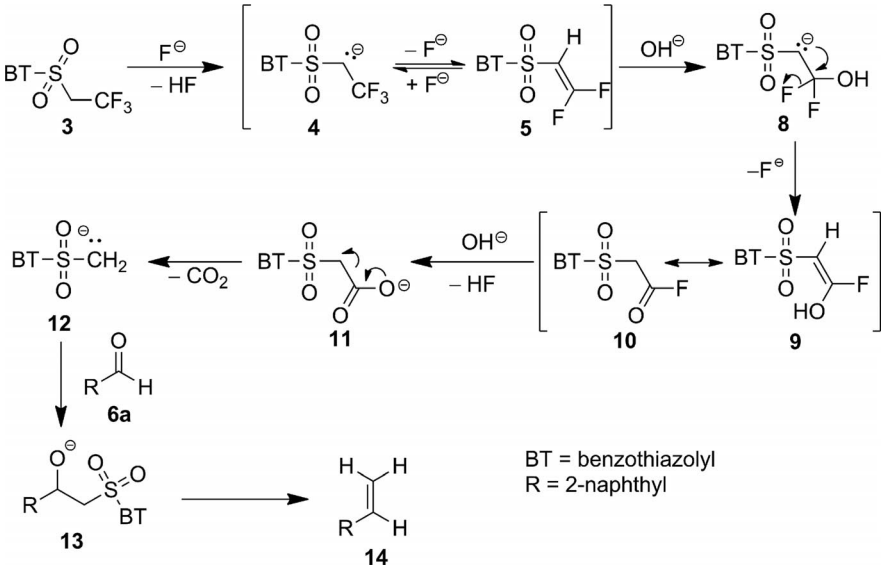


Entry	Sulfone [equiv.]	Aldehyde [equiv.]	TBAF [equiv.]	% Yield[b]
1	1.0	1.0	10	59
2	1.0	1.0	5	50
3[c]	1.0	1.0	10	31
4	1.0	2.0	10	90
5	1.0	3.0	10	99

[a] Reagents and conditions: sulfone **3**, aldehyde **6a**, TBAF (1 M in THF), 16 h, –78 °C to room temp. [b] Yields determined by ^{19}F NMR analysis with 2-fluoronitrobenzene as the internal standard. [c] Addition of 1.00 equiv. of DBU.



Scheme 2. Lability of carbanions next to a CF_3 group.



Scheme 3. Proposed mechanism for the generation of byproduct **14** as a result of the presence of water.

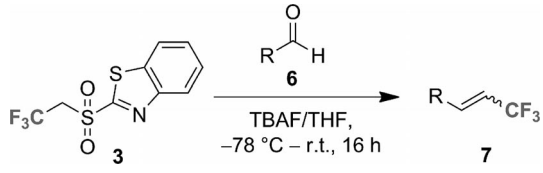
It is important to note that when the TBAF solution contained trace amounts of water, nonfluorinated olefin **14** could also be obtained as a byproduct (see Scheme 3). As previously mentioned, difluorovinylic compounds can rapidly undergo a reaction with nucleophiles. Therefore, we assumed that water could act as a nucleophile and attack the fluorinated double bond of **5** to generate sulfone **11**, which can be converted into sulfone **12** upon decarboxylation. Using the same reaction conditions as those for CF_3-substituted sulfone **3**, sulfone **12** can be converted into olefin **14**, which can be difficult to separate from fluorinated olefin **7a**.

Although Ishibashi et al. avoided the formation of side products by adding molecular sieves to the reaction mixture,[14] we suppressed this side reaction by storing the commercially available TBAF solution over molecular sieves (4 Å) for at least 3 d at 4 °C. Commercially available TBAF solutions contain approximately 5% of water for the stability of the TBAF salt. Without additional water, the stability of TBAF decreases as a result of the decomposition of the salt through an E2 elimination (Hofmann elimination) to generate TBA[HF_2].[15] Nevertheless, this decomposition did not affect the olefination reaction in any way, as there were no observed differences between reactions using TBAF solutions that were stored for three days over molecular sieves compared to those stored for up to two weeks. In addition, anhydrous THF has also stabilizing effects on TBAF salts leading to a slower decomposition compared to the pure anhydrous TBAF salt.[16]

Although 3 equiv. of aldehyde **6a** were necessary to obtain a nearly quantitative yield, GC–MS analysis of the reaction mixture showed that beside olefin **14** (in the presence of water) no other byproducts were formed during the reaction. Therefore, the remaining aldehyde could be recovered after the reaction.

With our optimized conditions in hand, we then explored the scope of the reaction. As shown in Table 2, the Julia–Kocienski trifluoromethylation of aldehydes mostly occurred in good to very good yields under very mild conditions. Furthermore, additional transformations of the products are possible as various functional groups were tolerated in the trifluoromethylation reaction. On the other hand, the *E*/*Z* selectivity appeared to be strongly dependent on the substrate. This reveals one drawback of the Julia–Kocienski olefination as electronically and sterically similar reactants can lead to different *E*/*Z* selectivities. In general, the reaction mechanism of the Julia–Kocienski olefination

Table 2. Scope of the Julia–Kocienski trifluoromethylation.[a]



Entry	R	% Yield[b]	*E*/*Z*[c]
1	2-naphthyl (**a**)	80	38:62
2	3-$PhOC_6H_4$ (**b**)	73	30:70
3	3-$NO_2C_6H_4$ (**c**)	78	23:77
4	4-PhC_6H_4 (**d**)	83	36:64
5	4-$NO_2C_6H_4$ (**e**)	92	100:0
6	1-naphthyl (**f**)	73	58:42
7	4-*t*BuC_6H_4 (**g**)	75	46:54
8	2-BrC_6H_4 (**h**)	61	76:24
9	4-$MeOOCC_6H_4$ (**i**)	56	27:73
10	4-$MeOC_6H_4$ (**j**)	45	44:56
11	2-(4-ClC_6H_4)SC_6H_4 (**k**)	83	65:35
12[d]	1-nonyl (**l**)	76	22:78
13	4-BrC_6H_4 (**m**)	61	46:54
14	2,6-ClC_6H_3 (**n**)	74	100:0

[a] Reagents and conditions: sulfone **3** (0.36 mmol), aldehyde **6** (1.08 mmol), TBAF (1 M in THF, 3.60 mmol), 16 h, –78 °C to room temp. [b] Isolated yields of an inseparable *E*/*Z* mixture of the products. [c] *E*/*Z* selectivity was determined by ^{19}F NMR of the crude mixture after removing the solvent. [d] Yield determined by ^{19}F NMR analysis using 2-fluoronitrobenzene as internal standard.

seems to be well understood, but this is often insufficient to explain the obtained *E*/*Z* ratios.[8c]

When ketones, instead of aldehydes, were subjected to our optimized reaction conditions, only trace amounts of the corresponding CF_3-substituted olefins could be detected by ^{19}F NMR analysis (data not shown). An explanation for this is that the strong electron-withdrawing effect of the CF_3 group in combination with the electron-withdrawing effect of the sulfonyl group could reduce the nucleophilicity and, therefore, the reactivity of carbanion **4**.

Conclusions

In summary, we reported the first synthesis of trifluoromethyl-substituted olefins by using a Julia–Kocienski olefination. Starting from commercially available, inexpensive trifluoroethanol, the required sulfone **3** was accessible on a gram scale through a simple two-step procedure. The olefination reaction takes place under mild conditions, tolerates various functional groups, and provides good yields. However, the *E*/*Z* selectivity is only moderate in most cases. Therefore, further studies will deal with investigations toward reaction conditions that provide greater selectivity.

Experimental Section

General Methods: The NMR spectroscopic data were recorded in solution with a Bruker AM 400, a Bruker Avance 300, or a Bruker DRX 500 spectrometer. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to the residual solvent peaks. All coupling constants (*J*) are absolute values and are reported in Hertz (Hz). The signals are described as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), dq (doublet of quartet), dd (doublet of doublet), or br. s (broad singlet). The spectra were interpreted according to first-order analysis. The signals of ^{13}C NMR spectra were analyzed by DEPT. MS (EI) (electron impact mass spectrometry) and MS (FAB) were performed by using a Finnigan MAT 95 (70 eV). In cases where the MS (EI) spectra could not be measured because of the high volatility of the compound, the GC–MS spectra were used for the characterization. IR data were recorded with a FT-IR Bruker alpha. Solvents, reagents, and chemicals were purchased from Aldrich, ABCR, and Acros. TBAF (1 M in THF) was purchased from Aldrich and stored for at least 3 d over molecular sieves (4 Å) at 4 °C. The molecular sieves were activated by heating them in vacuo for 2 h. All solvents, reagents, and chemicals were used as purchased unless stated otherwise.

General Procedure for the Olefination Reaction: A vial equipped with a septum and a stirring bar was charged with TBAF (1 M in THF, 3.60 mL, 3.60 mmol, 10.0 equiv.) and then cooled to –78 °C under argon. The vial was then opened, and **6a** (166 mg, 1.08 mmol, 3.00 equiv.) and sulfone **3** (100 mg, 0.36 mmol, 1.00 equiv.) were rapidly added. The reaction vessel was closed, and the solution was stirred for 16 h as it was slowly warmed to room temperature. The mixture was then filtered through a short pad of silica (ethyl acetate). Finally, the solvent was removed in vacuo, and the crude product was purified by flash column chromatography.

Synthesis of Sulfone 3

2-[(2,2,2-Trifluoroethyl)thio]benzo[*d*]thiazole (2) by Method A (from CF_3CH_2I): A 100 mL flask equipped with a septum and a stirring bar was charged with 2-mercaptobenzothiazole (5.00 g, 29.9 mmol, 1.00 equiv.). The flask was closed, and absolute *N*,*N*-dimethylformamide (DMF, 80 mL) was added. Then, DBU (6.26 mL, 41.9 mmol, 1.40 equiv.) and trifluoroethyl iodide (7.11 mL, 71.8 mmol, 2.50 equiv.) were added under argon by a syringe. The reaction mixture was stirred at room temperature for 16 h under argon. Saturated NH_4Cl solution was then added, and the resulting mixture was extracted with ethyl acetate (2×). The organic layer was then washed with a saturated NH_4Cl solution and dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 20:1) to give the product (6.00 g, 80%) as a colorless liquid; R_f = 0.28 (cyclohexane/ethyl acetate, 20:1).

2-[(2,2,2-Trifluoroethyl)thio]benzo[*d*]thiazole (2) by Method B (from CF_3CH_2OH): A 150 mL flask equipped with a septum and a stirring bar was charged with 2-mercaptobenzothiazole (5.00 g, 29.9 mmol, 1.00 equiv.). The flask was closed, and absolute THF (150 mL) was added. Then, trifluoroethanol (3.61 mL, 32.9 mmol, 1.10 equiv.) and DIAD (6.53 mL, 32.9 mmol, 1.10 equiv.) were slowly added under argon by a syringe. The reaction mixture was then stirred at room temperature for 40 h under argon. The solvent was removed in vacuo, and the crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 20:1) to give the product (5.38 g, 72%) as a colorless liquid; R_f = 0.28 (cyclohexane/ethyl acetate, 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.16 (q, ^3J = 9.6 Hz, 2 H, CH_2), 7.32–7.36 (m, 1 H, Ar-6-H), 7.43–7.47 (m, 1 H, Ar-5-H), 7.77 (d, ^3J = 7.9 Hz, 1 H, Ar-4-H), 7.92 (d, ^3J = 8.2 Hz, 1 H, Ar-7-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.4 (–, q, ^2J = 34.4 Hz, CH_2), 124.7 (q, ^1J = 276.4 Hz, C_{quat}, CF_3), 121.2 (+, CH-4), 121.9 (+, CH-7), 124.8 (+, CH-6), 126.3 (+, CH-5), 135.6 (C_{quat}, C-7′), 152.5 (C_{quat}, C-3′), 162.8 (C_{quat}, C-2) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –66.4 (s, 3 F, CF_3) ppm. IR (film): $\tilde{\nu}$ = 3443 (vw), 3064 (vw), 3001 (vw), 2951 (vw), 2131 (vw), 2049 (vw), 1610 (vw), 1467 (w), 1430 (w), 1310 (w), 1273 (w), 1243 (w), 1134 (w), 1089 (w), 1018 (vw), 999 (w), 844 (vw), 756 (w), 726 (vw), 705 (vw), 679 (vw), 638 (w), 535 (vw), 427 (vw) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 249 (100) $[M]^+$, 180 (28) $[M – CF_3]^+$. HRMS: calcd. for $C_9H_6F_3NS_2$ $[M]^+$ 248.9894; found 248.9892.

2-[(2,2,2-Trifluoroethyl)sulfonyl]benzo[*d*]thiazole (3): A 250 mL flask equipped with a septum and a stirring bar was charged with sulfide **2** (5.38 g, 22.09 mmol, 1.00 equiv.). The flask was closed, and absolute dichloromethane (100 mL) was added under argon. Then, the solution was cooled to 0 °C, and *m*CPBA (15.3 g, 86.48 mmol, 4.00 equiv.) was added in small portions (5× 3 g approximately). The reaction was stirred for 16 h and then slowly warmed to room temperature. The mixture was then quenched with saturated $NaHCO_3$ solution, and the resulting solution was extracted with dichloromethane (3×). The combined organic layers were washed with saturated $NaHCO_3$ solution and dried with $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by flash column chromatography (dichloromethane) to give the product (4.20 g, 68%) as a white solid; R_f = 0.65 (dichloromethane). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.43 (q, ^3J = 8.8 Hz, 2 H, CH_2), 7.62–7.70 (m, 2 H, Ar-5-H, Ar-6-H), 8.03–8.05 (m, 1 H, Ar-4-H), 8.22–8.25 (m, 1 H, Ar-7-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.2 (–, q, ^2J = 32.3 Hz, CH_2), 120.9 (q, ^1J = 278.3 Hz, C_{quat}, CF_3), 122.4 (+, CH-4), 125.6 (+, CH-7), 128.0 (+, CH-6), 128.6 (+, CH-5), 136.9 (C_{quat}, C-7′), 152.3 (C_{quat}, C-3′), 164.2 (C_{quat}, C-2) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –60.7 (s, 3 F,

CF_3) ppm. IR [attenuated total reflectance (ATR)]: $\tilde{\nu}$ = 2989 (vw) 2945 (w), 1463 (w), 1392 (vw), 1349 (m), 1319 (m), 1266 (w), 1244 (m), 1137 (m), 1087 (w), 1069 (m), 1025 (w), 868 (w), 852 (w), 779 (w), 761 (m), 725 (m), 695 (w), 670 (w), 606 (m), 592 (m), 565 (m), 539 (w), 512 (m), 481 (m), 430 (m), 405 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 281 (100) $[M]^+$, 198 (25) $[M - CH_2CF_3]^+$, 134 (79) $[M - C_2H_2F_3O_2S]^+$. HRMS: calcd. for $C_9H_6F_3NO_2S_2$ $[M]^+$ 280.9792; found 280.9790.

General Procedure for Trifluoromethylation of Aldehydes Using the Julia–Kocienski Olefination: A vial equipped with a septum and a stirring bar was charged with TBAF (1 M in THF, 3.60 mmol, 10.0 equiv.) and then cooled to –78 °C under argon. Then, the aldehyde (1.08 mmol, 3.00 equiv.) and sulfone **3** (0.36 mmol) were rapidly added. The reaction vessel was closed, and the solution was stirred for 16 h as it was slowly warmed to room temperature. The solution was filtered through a short pad of silica (ethyl acetate). Finally, the solvent was removed in vacuo, and the crude product was purified by flash column chromatography. Note: The *E*/*Z* product ratios were determined by ^1H and ^{19}F NMR spectroscopy.

(*E*/*Z*)-2-(3,3,3-Trifluoroprop-1-en-1-yl)naphthalene (7a): After flash column chromatography (cyclohexane), the product (64 mg, 80%; *E*/*Z* isomers, 1:2.35) was obtained as a white solid; R_f = 0.45 (cyclohexane). The spectroscopic data were only analyzed for the major *Z* isomer. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.86 (dq, ^3J = 12.6 Hz, ^3J = 9.0 Hz, 1 H, $CHCF_3$), 7.10 (d, ^3J = 12.6 Hz, 1 H, CH), 7.48–7.55 (m, 3 H, Ar-H), 7.81–7.91 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.1 (+, q, ^2J = 35.0 Hz, $CHCF_3$), 122.7 (q, ^1J = 271.3 Hz, C_{quat}, CF_3), 126.0 (+, q, ^5J = 2.8 Hz, CH-1), 126.5 (+, CH-4), 126.9 (+, CH-3), 127.6 (+, CH-6), 128.0 (+, CH-8), 128.4 (+, CH-7), 129.1 (+, CH-5), 131.1 (C_{quat}, C-2), 132.9 (C_{quat}, C-4′), 133.3 (C_{quat}, C-8′), 139.7 (+, q, ^3J = 5.9 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.3 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3064 (vw), 1664 (m), 1650 (m), 1596 (w), 1571 (w), 1508 (w), 1439 (w), 1418 (w), 1362 (w), 1314 (w), 1294 (m), 1276 (m), 1257 (m), 1233 (m), 1201 (w), 1163 (m), 1091 (s), 975 (m), 966 (m), 906 (m), 892 (w), 869 (m), 848 (w), 817 (m), 749 (m), 734 (m), 668 (m), 621 (w), 595 (vw) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 222 (100) $[M]^+$, 153 (9) $[M - CF_3]^+$. HRMS: calcd. for $C_{13}H_9F_3$ $[M]^+$ 222.0656; found 222.0653.

(*E*/*Z*)-1-Phenoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7b): After flash column chromatography (cyclohexane/ethyl acetate, 30:1), the product (69 mg, 73%; *E*/*Z* isomers, 1:3) was obtained as a colorless liquid; R_f = 0.60 (cyclohexane/ethyl acetate, 50:1). The spectroscopic were only analyzed for the major *Z* isomer. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.70 (dq, ^3J = 12.6 Hz, ^3J = 8.9 Hz, 1 H, $CHCF_3$), 6.81 (d, ^3J = 12.6 Hz, 1 H, CH), 6.94–7.16 (m, 6 H, Ar-H), 7.23–7.37 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.7 (+, q, ^2J = 35.0 Hz, $CHCF_3$), 119.0 (+, CH-2′, CH-6′), 119.1 (+, CH-2), 119.3 (+, CH-6), 122.7 (q, ^1J = 271.5 Hz, C_{quat}, CF_3), 123.6 (+, CH-4), 129.6 (+, CH-4′), 129.8 (+, CH-3′, CH-5′), 129.9 (+, CH-5), 135.3 (C_{quat}, C-3), 139.0 (+, q, ^3J = 5.8 Hz, CH), 156.7 (C_{quat}, C-1), 157.3 (C_{quat}, C-1′) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.5 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3041 (vw), 1666 (w), 1578 (m), 1487 (m), 1444 (w), 1309 (w), 1273 (m), 1242 (m), 1214 (s), 1112 (s), 1023 (w), 968 (m), 887 (w), 853 (w), 792 (m), 687 (s), 579 (w), 483 (w), 429 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 264 (100) $[M]^+$. HRMS: calcd. for $C_{15}H_{11}F_3O$ $[M]^+$ 264.0762; found 264.0765.

(*E*/*Z*)-1-Nitro-3-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7c): After flash column chromatography (cyclohexane/ethyl acetate, 5:1), the product (61 mg, 78%; *E*/*Z* isomers, 1:7.2) was obtained as a colorless liquid; R_f = 0.48 (cyclohexane/ethyl acetate, 5:1). The spectroscopic data were only analyzed for the major *Z* isomer. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.97 (dq, ^3J = 12.5 Hz, ^3J = 8.7 Hz, 1 H, $CHCF_3$), 7.00 (d, ^3J = 12.5 Hz, 1 H, CH), 7.55–7.61 (m, 1 H, Ar-H), 7.71 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 8.21–8.23 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.0 (+, q, ^2J = 35.0 Hz, $CHCF_3$), 122.4 (q, ^1J = 271.9 Hz, C_{quat}, CF_3), 123.7 (+, CH-2, CH-6), 129.4 (+, CH-5), 134.5 (+, q, ^5J = 2.6 Hz, CH-4), 135.2 (C_{quat}, C-3), 137.0 (+, q, ^3J = 5.8 Hz, CH), 148.1 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.7 (s, 3 F, CF_3) ppm. IR (film): $\tilde{\nu}$ = 3091 (vw), 1714 (w), 1671 (w), 1618 (w), 1533 (s), 1483 (w), 1409 (w), 1355 (s), 1315 (m), 1279 (m), 1227 (m), 1190 (m), 1131 (s), 973 (w), 918 (w), 870 (vw), 850 (w), 810 (w), 792 (w), 764 (w), 725 (w), 678 (w), 578 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 217 (100) $[M]^+$, 171 (11) $[M - NO_2]^+$. HRMS: calcd. for $C_9H_6NO_2F_3$ $[M]^+$ 217.0351; found 217.0349.

(*E*/*Z*)-4-(3,3,3-Trifluoroprop-1-en-1-yl)-1,1′-biphenyl (7d): After flash column chromatography (cyclohexane), the product (74 mg, 83%; *E*/*Z* isomers, 1:2) was obtained as a white solid; R_f = 0.23 (cyclohexane). Data for *E* isomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 6.26 (dq, ^3J = 16.1 Hz, ^3J = 6.5 Hz, 1 H, $CHCF_3$), 7.21 (dq, ^3J = 16.1 Hz, ^4J = 2.1 Hz, 1 H, CH), 7.36–7.42 (m, 1 H, Ar-H), 7.44–7.57 (m, 4 H, Ar-H), 7.60–7.67 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.7 (+, q, ^2J = 33.8 Hz, $CHCF_3$), 123.6 (q, ^1J = 268.7 Hz, C_{quat}, CF_3), 127.0 (+, CH-2′, CH-6′), 127.5 (+, CH-3′, CH-5′), 127.8 (+, CH-4′), 128.0 (+, CH-3, CH-5), 128.9 (+, Ar-H-2, Ar-H-6), 132.3 (C_{quat}, C-1), 137.2 (+, q, ^3J = 6.8 Hz, CH), 140.1 (C_{quat}, C-4), 142.8 (C_{quat}, C-1′) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.1 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 5.80 (dq, ^3J = 12.6 Hz, ^3J = 9.1 Hz, 1 H, $CHCF_3$), 6.96 (d, ^3J = 12.6 Hz, 1 H, CH), 7.36–7.42 (m, 1 H, Ar-H), 7.44–7.57 (m, 4 H, Ar-H), 7.60–7.67 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.8 (+, q, ^2J = 35.1 Hz, $CHCF_3$), 122.7 (q, ^1J = 271.2 Hz, C_{quat}, CF_3), 127.0 (+, CH-2′, CH-6′), 127.1 (+, CH-3′, CH-5′), 127.7 (+, CH-4′), 128.8 (+, CH-3, CH-5), 129.5 (+, q, ^5J = 2.5 Hz, CH-2, CH-6), 132.5 (C_{quat}, C-1), 139.2 (+, q, ^3J = 5.9 Hz, CH), 140.2 (C_{quat}, C-4), 141.9 (C_{quat}, C-1′) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.4 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3034 (w), 1651 (m), 1606 (w), 1520 (vw), 1486 (m), 1450 (w), 1427 (w), 1405 (w), 1333 (w), 1310 (m), 1268 (m), 1226 (m), 1175 (m), 1105 (s), 1004 (m), 976 (m), 913 (w), 872 (m), 838 (m), 821 (m), 773 (m), 762 (s), 738 (m), 720 (w), 689 (s), 672 (m), 586 (m), 569 (m), 490 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 248 (100) $[M]^+$. HRMS: calcd. for $C_{15}H_{11}F_3$ $[M]^+$ 248.0813; found 248.0811.

(*E*)-1-Nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7e): After flash column chromatography (cyclohexane/ethyl acetate, 8:1), the product (72 mg, 92%) was obtained as a white solid; R_f = 0.45 (cyclohexane/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.36 (dq, ^3J = 16.2 Hz, ^3J = 6.3 Hz, 1 H, $CHCF_3$), 7.21 (dq, ^3J = 16.2 Hz, ^4J = 2.0 Hz, 1 H, CH), 7.62 (d, ^3J = 8.8 Hz, 1 H, Ar-2-H, Ar-6-H), 8.26 (d, ^3J = 8.8 Hz, 2 H, Ar-3-H, Ar-5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.7 (+, q, ^2J = 34.4 Hz, $CHCF_3$), 122.9 (q, ^1J = 269.6 Hz, C_{quat}, CF_3), 124.2 (+, CH-3, CH-5), 128.3 (+, CH-2, CH-6), 135.4 (+, q, ^3J = 6.7 Hz, CH), 139.4 (C_{quat}, C-4), 148.5 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.9 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3114 (vw), 2920 (vw), 2851 (vw), 1668 (w), 1604 (w), 1518 (m), 1416 (w), 1376 (vw), 1346 (m), 1310 (m), 1270 (m), 1207 (m), 1100 (s), 974 (m), 957 (m), 867 (m), 823 (m), 745 (m), 698 (m), 686 (m), 630 (w), 576 (vw), 527 (w), 488 (w), 449 (w), 413 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 217 (90) $[M]^+$, 171 (11) $[M - NO_2]^+$, 151 (100). HRMS: calcd. for $C_9H_6NO_2F_3$ $[M]^+$ 217.0351; found 217.0352.

(*E*/*Z*)-1-(3,3,3-Trifluoroprop-1-en-1-yl)naphthalene (7f): After flash column chromatography (cyclohexane), the product (58 mg, 73%; *E*/*Z* isomers, 1.2:1) was obtained as a colorless liquid; R_f = 0.60 (pentane). Data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (dq, ^3J = 15.8 Hz, ^3J = 6.5 Hz, 1 H, $CHCF_3$), 7.48–7.63 (m, 4 H, Ar-H), 7.66 (d, ^3J = 7.1 Hz, 1 H, Ar-H), 7.85–7.92 (m, 2 H, Ar-H), 7.97 (dq, ^3J = 15.8 Hz, ^4J = 2.1 Hz, 1 H, CH), 8.06 (d, ^3J = 8.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.8 (+, q, ^2J = 33.6 Hz, *C*HCF$_3$), 123.1 (+, CH-3), 123.2 (q, ^1J = 269.3 Hz, C_{quat}, CF_3), 124.8 (+, CH-8), 125.4 (+, CH-7), 126.3 (+, CH-2), 126.9 (+, CH-6), 128.7 (+, CH-4), 130.2 (+, CH-5), 130.9 (C_{quat}, C-4′), 131.02 (C_{quat}, C-5′), 133.6 (C_{quat}, C-1), 135.2 (+, q, ^3J = 6.7 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.4 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.08 (dq, ^3J = 12.2 Hz, ^3J = 8.3 Hz, 1 H, $CHCF_3$), 7.48–7.63 (m, 5 H, Ar-H), 7.85–7.92 (m, 3 H, Ar-H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.6 (+, q, ^2J = 33.7 Hz, *C*CF$_3$), 122.7 (q, ^1J = 271.9 Hz, C_{quat}, CF_3), 124.3 (+, CH-3), 125.2 (+, CH-8), 126.1 (+, CH-7), 126.4 (q, ^5J = 2.9 Hz, CH-2), 126.5 (+, CH-6), 128.6 (+, CH-4), 129.1 (+, CH-5), 131.1 (C_{quat}, C-4′), 131.4 (C_{quat}, C-5′), 133.2 (C_{quat}, C-1), 138.3 (+, q, ^3J = 5.7 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.7 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3062 (vw), 1660 (w), 1592 (vw), 1509 (w), 1396 (w), 1373 (vw), 1351 (w), 1304 (s), 1272 (s), 1211 (w), 1108 (s), 1083 (m), 1036 (w), 965 (m), 913 (w), 881 (w), 867 (w), 792 (m), 770 (s), 731 (w), 673 (m), 590 (m), 529 (w), 501 (w), 460 (w), 429 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 222 (24) $[M]^+$, 153 (100) $[M - CF_3]^+$. HRMS: calcd. for $C_{13}H_9F_3$ $[M]^+$ 222.0656; found 222.0653.

(*E*/*Z*)-1-*tert*-butyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7g): After flash column chromatography (cyclohexane), the product (62 mg, 75%; *E*/*Z* isomers, 1:1) was obtained as a colorless liquid; R_f = 0.70 (cyclohexane). Data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, CH_3), 6.17 (dq, ^3J = 16.1 Hz, ^3J = 6.6 Hz, 1 H, $CHCF_3$), 7.13 (dq, ^3J = 16.1 Hz, ^4J = 2.2 Hz, CH), 7.37–7.44 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2 (+, CH_3), 34.7 [C_{quat}, *C*(CH_3)$_3$], 114.9 (+, q, ^2J = 33.7 Hz, *C*HCF$_3$), 123.7 (q, ^1J = 268.8 Hz, C_{quat}, CF_3), 125.9 (+, CH-2, CH-6), 127.3 (+, CH-3, CH-5), 130.6 (C_{quat}, C-4), 137.4 (+, q, ^3J = 6.7 Hz, CH), 153.5 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.0 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, CH_3), 6.17 (dq, ^3J = 12.7 Hz, ^3J = 9.2 Hz, 1 H, $CHCF_3$), 6.90 (d, ^3J = 12.7 Hz, CH), 7.37–7.44 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2 (+, CH_3), 34.7 [C_{quat}, *C*(CH_3)$_3$], 116.9 (+, q, ^2J = 35.0 Hz, *C*HCF$_3$), 123.1 (q, ^1J = 270.8 Hz, C_{quat}, CF_3), 125.3 (+, CH-2, CH-6), 129.0 (+, q, ^5J = 2.6 Hz, CH-3, CH-5), 130.6 (C_{quat}, C-4), 139.5 (+, q, ^3J = 5.9 Hz, CH), 152.4 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.4 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 2940 (vw), 1663 (vw), 1607 (w), 1579 (vw), 1513 (w), 1465 (vw), 1424 (vw), 1339 (vw), 1310 (vw), 1253 (w), 1173 (w), 1107 (w), 1033 (vw), 972 (vw), 875 (vw), 834 (vw), 810 (vw), 670 (vw), 569 (vw), 547 (vw), 513 (vw), 455 (vw) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 228 (19) $[M]^+$, 213 (100) $[M - CH_3]^+$. HRMS: calcd. for $C_{13}H_{15}F_3$ $[M]^+$ 228.1125; found 228.1128.

(*E*)-1-Bromo-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7h): After flash column chromatography (cyclohexane), the product (55 mg, 61%; *E*/*Z* isomers, 6.1:1) was obtained as a colorless liquid; R_f = 0.73 (pentane). The spectroscopic data were only analyzed for the major *E* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.16 (dq, ^3J = 16.1 Hz, ^3J = 6.4 Hz, 1 H, $CHCF_3$), 7.22–7.26 (m, 1 H, CH), 7.32–7.36 (m, 1 H, Ar-5-H), 7.51–7.57 (m, 2 H, Ar-3-H, Ar-4-H), 7.60–7.64 (m, 1 H, Ar-6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.5 (+, q, ^2J = 34.0 Hz, *C*HCF$_3$), 123.1 (q, ^1J = 269.4 Hz, C_{quat}, CF_3), 124.7 (C_{quat}, C-1), 127.6 (+, CH-3), 127.8 (+, CH-4), 131.1 (+, CH-5), 133.4 (+, CH-6), 136.6 (+, q, ^5J = 6.9 Hz, CH) 139.9 (C_{quat}, C-2) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.6 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 2963 (vw), 1660 (w), 1469 (w), 1440 (w), 1313 (m), 1285 (m), 1268 (m), 1205 (w), 1186 (w), 1108 (s), 1028 (s), 966 (s), 880 (w), 791 (m), 749 (s), 696 (m), 654 (w), 581 (m), 467 (w), 446 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 250 (19) $[M]^+$, 189 (100). HRMS: calcd. for $C_9H_6BrF_3$ $[M]^+$ 249.9605; found 249.9606.

(*E*/*Z*)-Methyl 4-(3,3,3-Trifluoroprop-1-en-1-yl)benzoate (7i): After flash column chromatography (cyclohexane/ethyl acetate, 20:1), the product (46 mg, 56%; *E*/*Z* isomers, 1:4) was obtained as a colorless liquid; R_f = 0.28 (cyclohexane/ethyl acetate, 20:1). The spectroscopic data were only analyzed for the major *Z* isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3 H, $COOCH_3$), 5.86 (dq, ^3J = 12.6 Hz, ^3J = 8.8 Hz, 1 H, $CHCF_3$), 6.97 (d, ^3J = 12.6 Hz, 1 H, CH), 7.44 (d, ^3J = 8.3 Hz, 1 H, Ar-3-H, Ar-5-H), 8.03 (d, ^3J = 8.3 Hz, 2 H, Ar-2-H, Ar-6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.2 (+, CH_3), 119.9 (+, q, ^2J = 35.0 Hz, *C*HCF$_3$), 122.5 (q, ^1J = 271.5 Hz, C_{quat}, CF_3), 128.7 (+, q, ^5J = 2.4 Hz, CH-3, CH-5), 129.5 (+, CH-2, CH-6), 130.4 (C_{quat}, C-1), 138.1 (C_{quat}, C-4), 138.5 (+, q, ^3J = 5.7 Hz, CH), 166.5 (C_{quat}, CO) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.6 (s, 3 F, CF_3) ppm. IR (film): $\tilde{\nu}$ = 2956 (w), 1726 (s), 1658 (w), 1612 (w), 1570 (w), 1510 (w), 1438 (m), 1405 (m), 1283 (s), 1227 (m), 1181 (m), 1129 (s), 1020 (w), 972 (w), 886 (w), 852 (w), 789 (w), 767 (w), 733 (w), 695 (w), 567 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 230 (48) $[M]^+$, 199 (100) $[M - OMe]^+$. HRMS: calcd. for $C_{11}H_9O_2F_3$ $[M]^+$ 230.0555; found 230.0554.

(*E*/*Z*)-1-Methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7j): After flash column chromatography (cyclohexane/ethyl acetate, 50:1), the product (33 mg, 45%; *E*/*Z* isomers, 1.4:1) was obtained as a colorless oil; R_f = 0.30 (cyclohexane/ethyl acetate = 50:1). Data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 6.02–6.13 (m, 1 H, $CHCF_3$), 6.87–6.92 (m, 2 H, Ar-2-H, Ar-6-H), 7.09 (d, ^3J = 16.0 Hz, 1 H, CH), 7.39–7.41 (m, 2 H, Ar-3-H, Ar-5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3 (+, CH_3), 113.4 (+, q, ^2J = 33.6 Hz, *C*HCF$_3$), 114.3 (+, CH-2, CH-6), 123.8 (q, ^1J = 268.5 Hz, C_{quat}, CF_3), 126.1 (C_{quat}, C-4), 129.0 (+, CH-3, CH-5), 137.1 (+, q, ^3J = 6.8 Hz, CH), 161.0 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –62.9 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, OCH_3), 5.58–5.72 (m, 1 H, $CHCF_3$), 6.82 (d, ^3J = 12.6 Hz, 1 H, CH), 6.87–6.92 (m, 2 H, Ar-2-H, Ar-6-H), 7.39–7.41 (m, 2 H, Ar-3-H, Ar-5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2 (+, CH_3), 113.8 (+, CH-2, CH-6), 115.6 (+, q, ^2J = 35.0 Hz, *C*HCF$_3$), 123.2 (q, ^1J = 270.9 Hz, C_{quat}, CF_3), 126.1 (C_{quat}, C-4), 130.9 (+, q, ^5J = 2.7 Hz, CH-3, CH-5), 139.1 (+, q, ^3J = 6.0 Hz, CH), 160.3 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.6 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 2964 (w), 1664 (w), 1651 (w), 1610 (vw), 1513 (w), 1465 (vw), 1406 (w), 1365 (w), 1334 (w), 1312 (m), 1271 (m), 1228 (w), 1202 (w), 1179 (m), 1105 (s), 1018 (w), 972 (m), 948 (vw), 877 (w), 834 (w), 814 (w), 744 (vw), 649 (w), 610 (vw), 572 (m), 542 (w), 442 (vw) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 202 (100) $[M]^+$, 187 (23) $[M - CH_3]^+$. HRMS: calcd. for $C_{10}H_9OF_3$ $[M]^+$ 202.0606; found 202.0605.

(*E*/*Z*)-(4-Chlorophenyl)[2-(3,3,3-trifluoroprop-1-en-1-yl)phenyl]sulfane (7k): After flash column chromatography (cyclohexane/ethyl acetate, 30:1), the product (94 mg, 83%; *E*/*Z* isomers, 1.5:1) was obtained as a colorless oil; R_f = 0.43 (cyclohexane/ethyl acetate, 20:1). Data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.13 (dq, ^3J = 16.0 Hz, ^3J = 6.5 Hz, 1 H, $CHCF_3$), 7.11–7.16 (m, 2 H,

Ar-H), 7.22–7.27 (m, 2 H, Ar-H), 7.31–7.44 (m, 3 H, Ar-H), 7.54–7.57 (m, 1 H, Ar-H), 7.71 (dq, ^3J = 16.0 Hz, ^4J = 2.2 Hz, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.2 (+, q, ^2J = 33.9 Hz, *C*HCF$_3$), 123.1 (q, ^1J = 269.3 Hz, C_{quat}, CF_3), 127.2 (+, CH-3), 128.6 (+, CH-5), 129.4 (+, CH-3′, CH-5′), 131.4 (+, CH-2′, CH-6′), 130.5 (+, CH-4), 133.1 (C_{quat}, C-4′), 133.9 (+, CH-6), 134.2 (C_{quat}, C-1′), 134.8 (C_{quat}, C-2), 135.3 (+, q, ^3J = 6.9 Hz, CH), 135.6 (C_{quat}, C-1) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.5 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (dq, ^3J = 12.3 Hz, ^3J = 8.5 Hz, 1 H, CHCF$_3$), 7.11–7.16 (m, 3 H, CH, Ar-H), 7.22–7.27 (m, 2 H, Ar-H), 7.31–7.44 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.5 (+, d, ^2J = 34.2 Hz, *C*HCF$_3$), 122.6 (q, ^1J = 271.8 Hz, C_{quat}, CF_3), 127.9 (+, CH-5), 129.3 (+, CH-3′, CH-5′), 129.7 (+, CH-4), 130.1 (+, q, ^5J = 3.4 Hz, CH-3), 131.2 (+, CH-2′, CH-6′), 132.7 (+, CH-6), 132.9 (C_{quat}, C-4′), 133.4 (C_{quat}, C-2), 134.0 (C_{quat}, C-1′), 136.3 (C_{quat}, C-1), 137.5 (+, q, ^3J = 5.7 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.7 (s, 3 F, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3060 (vw), 1658 (w), 1586 (vw), 1474 (m), 1437 (w), 1408 (w), 1390 (w), 1314 (m), 1270 (m), 1216 (m), 1181 (m), 1111 (s), 1090 (s), 1057 (m), 1038 (m), 1011 (s), 967 (m), 882 (w), 813 (m), 750 (m), 665 (w), 582 (m), 549 (w), 471 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 314 (100) $[M]^+$, 245 (61) $[M - CF_3]^+$. HRMS: calcd. for $C_{15}H_{10}SClF_3$ $[M]^+$ 314.0143; found 314.0143.

(*E*/*Z*)-1-Bromo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7m): After flash column chromatography (cyclohexane), the product (55 mg, 61%; *E*/*Z* isomers, 1:1.3) was obtained as a colorless liquid; R_f = 0.70 (cyclohexane). Data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (dq, ^3J = 16.1 Hz, ^3J = 6.4 Hz, 1 H, CHCF$_3$), 7.11 (dq, ^3J = 16.1 Hz, ^4J = 2.1 Hz, 1 H, CH), 7.32 (d, ^3J = 8.4 Hz, 2 H, Ar-3-H, Ar-5-H), 7.49–7.55 (m, 2 H, Ar-2-H, Ar-6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.5 (+, q, ^2J = 34.0 Hz, *C*HCF$_3$), 123.3 (q, ^1J = 269.1 Hz, C_{quat}, CF_3), 124.2 (C_{quat}, C-1), 129.0 (+, CH-3, CH-5), 132.2 (+, CH-2, CH-6), 132.3 (C_{quat}, C-4), 136.5 (+, q, ^3J = 6.7 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –63.4 (s, 3 F, CF_3) ppm. Data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (dq, ^3J = 12.6 Hz, ^3J = 8.9 Hz, 1 H, CHCF$_3$), 6.86 (d, ^3J = 12.6 Hz, 1 H, CH), 7.26 (d, ^3J = 8.4 Hz, 2 H, Ar-3-H, Ar-5-H), 7.49–7.55 (m, 2 H, Ar-2-H, Ar-6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.7 (+, q, ^2J = 34.9 Hz, *C*HCF$_3$), 122.6 (q, ^1J = 271.4 Hz, C_{quat}, CF_3), 123.4 (C_{quat}, C-1), 130.5 (+, q, ^5J = 2.6 Hz, CH-3, CH-5), 131.6 (+, CH-2, CH-6), 132.5 (C_{quat}, C-4), 138.4 (+, q, ^3J = 5.8 Hz, CH) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –57.6 (s, 3 F, CF_3) ppm. IR (film): $\tilde{\nu}$ = 3441 (w), 2924 (vw), 1658 (w), 1590 (w), 1489 (w), 1403 (w), 1330 (w), 1313 (w), 1276 (w), 1223 (w), 1177 (w), 1125 (m), 1073 (m), 1011 (w), 972 (w), 875 (vw), 828 (w), 805 (w), 779 (vw), 746 (vw), 695 (vw), 565 (vw), 496 (vw), 451 (vw) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 250 (100) $[M]^+$, 171 (34) $[M - Br]^+$. HRMS: calcd. for $C_9H_6BrF_3$ $[M]^+$ 249.9605; found 249.9603.

(*E*)-1,3-Dichloro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (7n): After flash column chromatography (cyclohexane), the product (64 mg, 74%) was obtained as a colorless oil; R_f = 0.72 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.42 (dq, ^3J = 16.5 Hz, ^3J = 6.2 Hz, 1 H, CHCF$_3$), 7.22–7.30 (m, 2 H, CH, Ar-5-H), 7.39 (d, ^3J = 7.9 Hz, 2 H, Ar-4-H, Ar-6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8 (q, ^1J = 269.9 Hz, C_{quat}, CF_3), 124.5 (+, q, ^2J = 33.9 Hz, *C*HCF$_3$), 128.8 (+, CH-4, CH-6), 129.9 (+, CH-5), 130.9 (C_{quat}, C-2), 131.4 (+, q, ^3J = 7.3 Hz, CH), 134.7 (C_{quat}, C-1, C-3) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = –64.7 (s, 3 F, CF_3) ppm. IR (film): $\tilde{\nu}$ = 3442 (vw), 2926 (vw), 1668 (w), 1580 (w), 1558 (w), 1432 (m), 1313 (s), 1275 (m), 1183 (m), 1128 (s), 968 (m), 885 (m), 839 (w), 776 (m), 721 (w), 688 (w), 610 (w), 415 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 240 (100) $[M]^+$, 205 (33) $[M - Cl]^+$. HRMS: calcd. for $C_9H_5Cl_2F_3$ $[M]^+$ 239.9715; found 239.9713.

2-Vinylnaphthalene (14): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.45 (d, ^3J = 10.8 Hz, 1 H, CH_2), 5.88 (d, ^3J = 17.6 Hz, 1 H, CH_2), 6.85–6.93 (m, 1 H, CH), 7.44–7.47 (m, 2 H, Ar-H), 7.63–7.66 (m, 1 H, Ar-H), 7.75 (s, 1 H, Ar-H), 7.79–7.83 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.2 (–, CH_2), 123.1 (+, CH-3), 125.9 (+, CH-1), 126.2 (+, CH-8), 126.4 (+, CH-6), 127.6 (+, CH-4), 128.0 (+, CH-7), 128.1 (+, CH-5), 133.1 (C_{quat}, C-4′), 133.5 (C_{quat}, C-8′) 135.0 (C_{quat}, C-2), 136.9 (+, *C*HCH$_2$) ppm. IR (ATR): $\tilde{\nu}$ = 3054 (w), 2961 (w), 2917 (w), 2849 (w), 1807 (vw), 1662 (vw), 1623 (w), 1593 (w), 1572 (w), 1506 (w), 1438 (w), 1415 (w), 1360 (w), 1259 (m), 1113 (m), 1016 (m), 992 (m), 966 (w), 950 (w), 895 (m), 861 (m), 819 (s), 748 (s), 697 (w), 668 (w), 595 (vw), 470 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 154 (100) $[M]^+$. HRMS: calcd. for $C_{12}H_{10}$ $[M]^+$ 154.0783; found 154.0782.

Supporting Information (see footnote on the first page of this article): Copies of NMR spectra.

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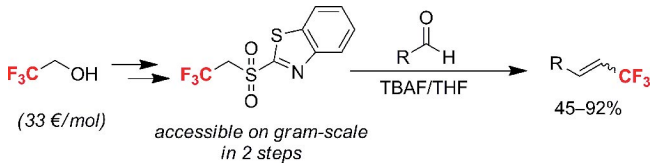

By employing a two-step procedure, it was possible to synthesize an α-trifluoromethyl-substituted sulfone on a gram scale by starting from inexpensive and commercially available trifluoroethanol. This substrate could then be used in a modified Julia–Kocienski olefination to prepare trifluoromethyl-substituted terminal olefins).

Keywords: Synthetic methods / Olefination / Fluorine / Aldehydes / Sulfur

