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Oxy-trifluoromethylation of alkenes and its application to the synthesis of β-trifluoromethylstyrene derivatives

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ABSTRACT

Oxy-trifluoromethylation of di-substituted styrenes and dienes was achieved by using Cu/Togni's reagent system. Not only *gem*-di-substituted styrenes, but also a β-methylstyrene derivative were transformed to the corresponding oxy-trifluoromethylation products. 1,4-Addition products were obtained selectively in the reaction of mono-substituted dienes. These reactions provide a new approach for the synthesis of β-trifluoromethyl styrene derivatives.

1. Introduction

Introduction of a trifluoromethyl group into an organic framework often results in increased metabolic stability, lipophilicity, and bioactivity [1]. Therefore, development of new methodologies for construction of trifluoromethylated organic compounds is of interest not only in organic chemistry, but also in the fields of pharmaceutical and agrochemical science [1]. Indeed, many reports on trifluoromethylation, including C_{sp2}–CF_3 and C_{sp3}–CF_3 bond formation reactions, have appeared [2]. Among trifluoromethylation reactions, trifluoromethylation of alkenes, especially difunctionalization-type trifluoromethylation, is a topic of growing interest [3]. We have studied trifluoromethylation reactions of alkene, alkyne, and heteroaromatic compounds using Togni's reagent [4,5] and we reported the oxy-trifluoromethylation reaction of mono-substituted styrene type compounds catalyzed by copper ion in 2012 (Scheme 1) [5c]. Szabó independently reported the same type of trifluoromethylation [6] and Buchwald reported an intramolecular oxy-trifluoromethylation in the same year [7a]. Buchwald also developed an asymmetric version of his reaction in 2013 [7b].

The pioneering work by Fuchikami on oxy-trifluoromethylation using CF_3I and palladium catalyst was reported in 1987 [8]. TFA was employed by Uneyama as a trifluoromethyl source for electrochemical reactions [9], and Nagano reported oxy-trifluoromethylation of an alkene via iodo-trifluoromethylation [10]. Akita and Koike accomplished oxy-trifluoromethylation with a combination of Umemoto reagent [11] and photo-redox catalysis [12], and Studer described a radical reaction system using Togni's reagent with TEMPONa in 2012 [13]. Intramolecular and intermolecular oxy-trifluoromethylation reactions using Umemoto reagent, Togni's reagent, or Langlois reagent have recently been the main focuses of attention [14].

In our original paper, as well as Szabo's paper, only limited substrates, mainly mono-substituted styrene-type compounds, were examined as substrates for intermolecular oxy-trifluoromethylation using Cu/Togni's reagent system (Scheme 1) [5c,6]. We also reported two examples of reactions of dienes [5c]. Xu et al. investigated ligand effects in the diastereoselective reaction of dienes in 2013 [15]. However, the scope of substrates, such as di-substituted alkenes and dienes, in the original systems has not been fully established. In addition, although we originally reported a direct synthesis of β-trifluoromethylstyrene derivatives from styrenes, there were only two examples [5c,16]. In the present report, we describe the oxy-trifluoromethylation of di-substituted styrenes and diene derivatives as well as application of this reaction leading to the synthesis of β-trifluoromethyl styrene derivatives.

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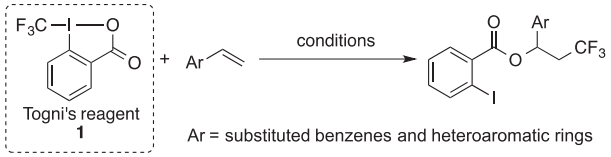
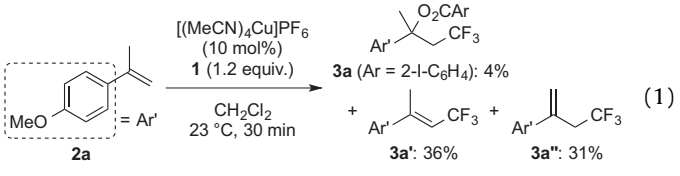


Sodeoka: $[(MeCN)_4Cu]PF_6$ (10 mol %), **1** (1.2 eqiv.), CH_2Cl_2, 23 °C, up to 95%
Szabó: CuI (10 mol %), **1** (1.5 equiv.), $CHCl_3$, 60 °C or 120 °C/mW, up to 86%

Scheme 1. Oxy-trifluoromethylation of mono-substituted styrene derivatives using the combination of copper salt and Togni's reagent.

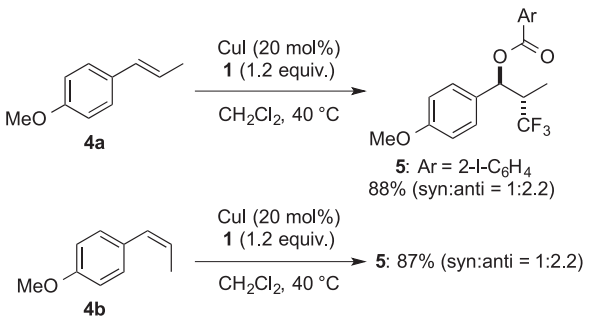
2. Results and discussion

In order to expand the substrate scope of our trifluoromethylation reaction system, we first focused on *gem*-di-substituted styrene derivative **2a**. The reaction with $[(MeCN)_4Cu]PF_6$, which was reported to be a better catalyst for mono-substituted styrene derivatives [5c], was found to provide a mixture of α-methyl-β-trifluoromethyl-4-methoxystyrene **3a′** and α-trifluoroethyl-4-methoxystyrene **3a″**, which would be generated via E1 reaction from **3a** (Eq. (1)). Therefore, we concluded that cationic copper species were not suitable for the reaction of *gem*-di-substituted styrene derivatives, and CuI was chosen as a catalyst for the oxy-trifluoromethylation to suppress the E1 reaction, because CuI has a lower Lewis acidity than $[(MeCN)_4Cu]PF_6$. Fortunately, the reaction using CuI proceeded smoothly at 40 °C and **3a** was obtained in 93% yield (Table 1). An *ortho*-substituent affected the reaction rate, but **3b** was obtained in high yield. The reaction of **3c** having a naphthalene ring also proceeded smoothly. However, an electron-withdrawing group, such as bromide, retarded the reaction, and **3d** was obtained in only 11% yield. In this case, 56% of the substrate was recovered, suggesting that this reaction system is not suitable for electron-deficient substrates. In contrast, cyclic-type substrate **2e** afforded the desired oxy-trifluoromethylation product **3e** in 46% yield, together with 42% yield of 4-trifluoroethyl-1,2-dihydronaphthalene **3e′**. The reaction of a β-methylstyrene derivative also proceeded, albeit with low diastereoselectivity (Scheme 2). The stereochemistry of the product was determined after hydrolysis of **5** to give a known material [17]. It is noteworthy that the *syn*/*anti* ratio was the same in the reactions using *trans*- and *cis*-isomers.



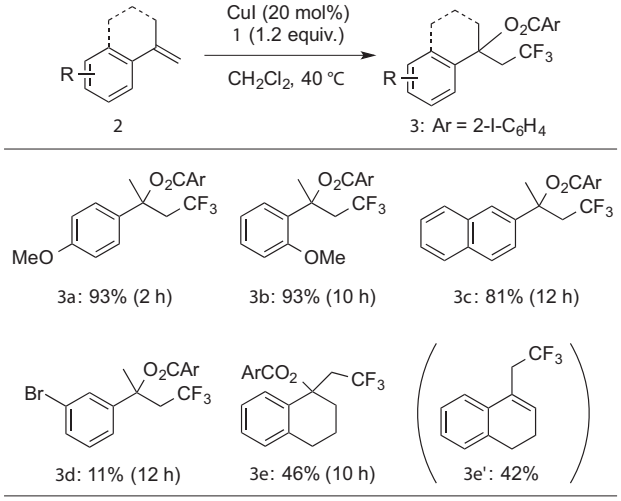
The yields were determined by ^{19}F NMR analysis using trifluoromethylbenzene.

We next examined the reactions of dienes [18]. A mixture of 1,4-addition product and the corresponding 1,2-addition product was generated when $[(MeCN)_4Cu]PF_6$ was used as a catalyst (Eq. (2)). To our delight, however, we found that the reaction of mono-substituted dienes exclusively afforded 1,4-adducts when CuI was used as a catalyst (Table 2, entries 1–5). 1,4-Adduct **7a** was produced from *trans*-1-phenyl-1,3-butadiene **6a** in 93% yield and no 1,2-addition product was detected (entry 1). Contrary to the reaction of mono-substituted styrene derivatives, dienes bearing an electron-withdrawing group, or an electron-donating group, provided the desired products. Although the reaction of **6b** bearing a methoxy group was faster than that of **6c** bearing a fluorine atom on the phenyl ring, the corresponding products **7b** and **7c** were obtained in 91% and 87% yields, respectively (entries 2 and 3). Surprisingly, aliphatic dienes **6d** and **6e** were also good substrates, affording **7d** and **7e**, respectively, in excellent yields (entries 4 and 5). Despite the sterically hindered nature of **6f**, compound **7f** was obtained in 83% yield (entry 6). Meanwhile, 1,2-oxy-trifluoromethylation occurred exclusively when terminally di-substituted diene was used as a substrate, and **8g** was obtained from 1,1-diphenyl-1,3-butadiene **6g** in 97% yield (entry 7). It should be noted that all compounds were obtained with excellent stereo- and regio-selectivity [19].

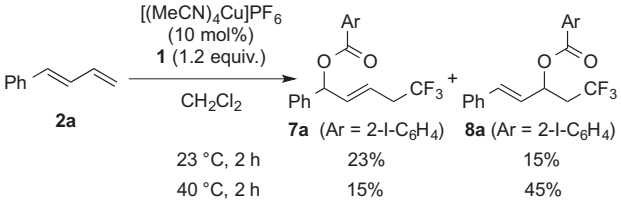


Scheme 2. Trifluoromethylation of *trans*- and *cis*-β-methylstyrene derivatives.

Table 1
Oxy-trifluoromethylation of *gem*-di-substituted styrene derivatives[a].



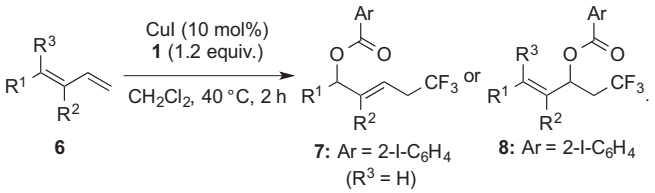
[a] The reactions were carried out with CuI (20 mol%) and Togni's reagent (1.2 equiv.) in CH_2Cl_2 (1 mL) at 40 °C on a 0.2 mmol scale.

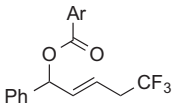
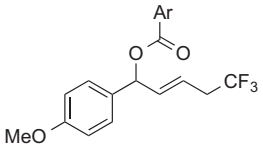
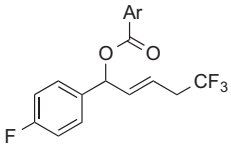
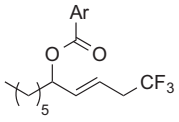
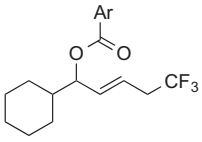
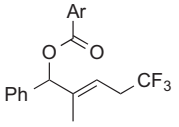
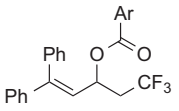


The yields were determined by ^{19}F NMR analysis using trifluoromethylbenzene.

The reaction character was completely changed by addition of a Brønsted acid. That is, the reaction in the presence of *p*-TsOH provided β-trifluoromethylstyrene derivatives instead of oxy-trifluoromethylation products. To demonstrate the utility of this reaction system, various substrates were examined (Table 3) [20]. Styrenes having oxygen functionality, such as a methoxy group, on the aryl ring reacted smoothly. Compounds **10a**, **10b** and **10c** were obtained in 90%, 87% and 62% yields, respectively. In addition, heteroaromatic compounds tolerated these reaction conditions (**10d**, **10e**). A diene derivative could be successfully transformed to trifluoromethylated diene under the same reaction conditions (**10f**).

Table 2
Oxy-trifluoromethylation of dienes[a].

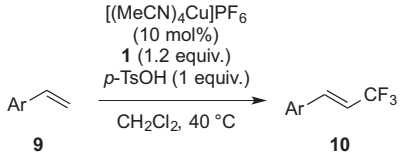


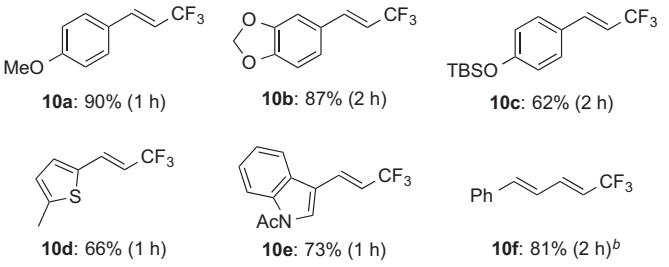
Entry	Product		Yield [%]
1		**7a**	93
2		**7b**	91
3[b]		**7c**	87
4[c]		**7d**	85
5[c]		**7e**	92
6		**7f**	83
7[d]		**8g**	97

[a] The reactions were carried out with catalyst (10 mol%) and Togni's reagent 2 (1.2 equiv.) in CH_2Cl_2 (1 mL) at 40 °C on a 0.2 mmol scale.
[b] Run for 6 h.
[c] Run for 1 h.
[d] Run with $[(MeCN)_4Cu]PF_6$ as the catalyst on a 1 mmol scale.

In general, styrene derivatives have a nature to polymerize under acidic conditions. In fact, β-trifluoromethyl-2-hydroxystyrene **10g** was not obtained in the presence of acid due to rapid polymerization. However, it was found that addition of Et_3N allowed **10g** to be obtained in 73% yield (Eq. (3)). The base presumably suppresses polymerization and activates the hydroxyl group to stabilize the benzylic cation. On the other hand, *p*-TsOH failed to accelerate the E1 reaction of a substrate bearing an amide moiety, such as **11h**. Therefore, triflic acid (TfOH) was tried, and the desired product **10h** was isolated in 99% yield (Eq. (4)). Although the transformation of oxy-trifluoromethylation product **11i** failed under the acidic conditions, it was found that **11i** could be converted to **10i** by treatment with sodium hexamethyldisilazide

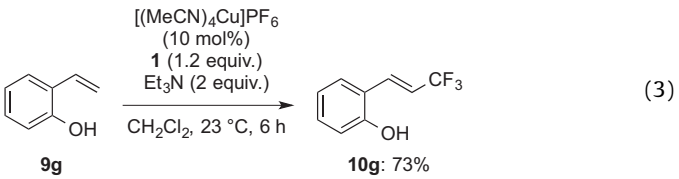
Table 3
Direct formation of β-trifluoromethylstyrene derivatives[a].

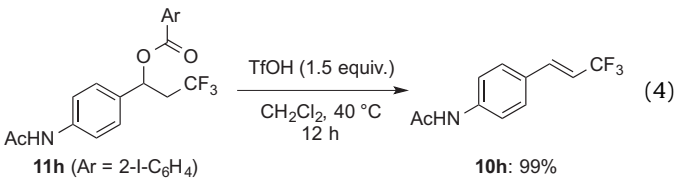


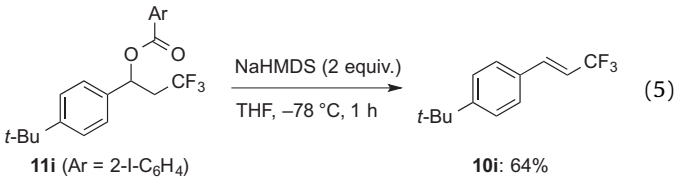


[a] The reactions were carried out with $[(MeCN)_4Cu]PF_6$ (10 mol%), **1** (1.2 equiv.) and p-TsOH (1.0 equiv.) in CH_2Cl_2 (1 mL) at 40 °C on a 0.2 mmol scale.
[b] Run with 10 mol% of CuI instead of $[(MeCN)_4Cu]PF_6$.

(NaHMDS) (Eq. (5)). Thus, we consider that a β-trifluoromethylstyrene derivative can be accessed if the oxy-trifluoromethylation product is obtained.







3. Conclusion

In this report, we describe oxy-trifluoromethylation of disubstituted styrene derivatives and dienes using Cu/Togni's reagent system, which was originally reported by our group and also at the same time by Szabó. It is noteworthy that the reactions of both *cis*- and *trans*-β-methylstyrene derivatives gave similar results. 1,4-Addition products were selectively obtained in the reaction of mono-substituted dienes using CuI, and various compounds having not only aryl but also aliphatic groups could be utilized as substrates. In addition, we succeeded in the synthesis of β-trifluoromethylstyrene derivatives under both acidic and basic conditions. We believe that these reactions provide a new approach for the synthesis of trifluoromethylated building blocks. Further studies, including detailed examination of the reaction mechanism, are ongoing in our laboratory.

4. Experimental

4.1. General

All reactions were carried out under a nitrogen atmosphere. Togni's reagent was prepared according to the literature [21]. Dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical Co., Inc. CuI and $[(CH_3CN)_4Cu]PF_6$ were obtained from commercial sources, and used as received. Other reagents were purified by usual methods.

^1H and ^{19}F NMR spectra were measured on a JEOL JNM-ECS-400 spectrometer at 400 and 376 MHz, respectively. ^{13}C NMR spectra were recorded on a JEOL JNM-ECS-400 spectrometer at 100 MHz. Chemical shifts were reported downfield from TMS (=0) or $CDCl_3$ for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$. For ^{19}F NMR, chemical shifts were reported in the scale relative to a $CFCl_3$ external standard (0 ppm). Infrared spectra were measured on a Thermo Nicolet iS5, and only diagnostic absorptions are listed below. ESI-MS was taken on Waters SYNAPT G2 MS. EI-MS was taken on a JEOL JMS-700V. Column chromatography was performed with silica gel N-60 (40–100 μm) purchased from Kanto Chemical Co., Inc. TLC analysis was performed on Silica gel 60 F_{254}-coated glass plates (Merck). Visualization was accomplished by means of ultraviolet (UV) irradiation at 254 nm or by spraying a solution of 12-molybdo(-VI)phosphoric acid in ethanol as the developing agent.

4.2. Typical procedure for oxy-trifluoromethylation of substituted styrene derivatives

CuI (7.6 mg, 20 mol%) and Togni's reagent **1** (76 mg, 1.2 equiv.) were added to a Schlenk tube which had been flame-dried under vacuum. The tube was evacuated and backfilled with nitrogen. CH_2Cl_2 (1 mL) and α-methyl-4-methoxystyrene **2a** (29.6 mg, 0.2 mmol) were added to the tube. The reaction mixture was stirred for 2 h at 40 °C, then diluted with EtOAc (5 mL) and quenched with aqueous saturated $NaHCO_3$. The mixture was extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 30/1) to give product **3a** (86.0 mg, 93%) as a colorless oil.

4.2.1. 4,4,4-Trifluoro-2-(4-methoxyphenyl)butan-2-yl 2-iodobenzoate (**3a**)

Colorless oil; 86.0 mg, 93%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3H), 2.95–3.24 (m, 2H), 3.81 (s, 3H), 6.92 (d, J = 7.4 Hz, 2H), 7.16 (dd, J = 7.8, 7.8 Hz, 1H), 7.37–7.44 (m, 3H), 7.84 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.5, 44.2 (q, J = 27.0 Hz), 55.2, 81.4 (br), 93.7, 113.9, 125.2 (q, J = 277.4 Hz), 125.7, 128.0, 130.8, 132.6, 134.9, 135.6, 141.3, 159.0, 164.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −60.4 (t, J = 10.4 Hz); IR (neat): 2959, 1612, 1583, 1514, 1369, 1289, 1183 cm^{-1}; HRMS (ESI^+): Calcd. for $[C_{18}H_{16}F_3IO_3+Na]^+$: m/z = 486.9994, Found: 487.0000.

4.2.2. 4,4,4-Trifluoro-2-(2-methoxyphenyl)butan-2-yl 2-iodobenzoate (**3b**)

Colorless oil; 86.8 mg, 93%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3H), 3.38–3.50 (m, 2H), 3.85 (s, 3H), 6.94 (d, J = 8.3 Hz, 1H), 7.00 (ddd, J = 1.4, 7.6, 8.3 Hz, 1H), 7.17 (ddd, J = 1.4, 7.8, 7.8 Hz, 1H), 7.31 (m, 1H), 7.45 (ddd, J = 0.9, 7.8, 7.8 Hz, 1H), 7.53 (dd, J = 1.4, 7.8 Hz, 1H), 7.87 (dd, J = 1.4, 7.8 Hz, 1H), 8.00 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.0, 40.4 (q, J = 27.0 Hz), 55.2, 81.7 (q, J = 2.9 Hz), 93.8, 111.4, 120.7, 125.6 (q, J = 278.4 Hz), 126.5, 127.9, 129.1, 129.6, 130.7, 132.3, 136.0, 141.1, 155.5, 164.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −60.4 (t, J = 10.4 Hz); IR (neat): 2939, 1721, 1581, 1439, 1387, 1368, 1316 cm^{-1}; HRMS (ESI^+): Calcd. for $[C_{18}H_{16}F_3IO_3+Na]^+$: m/z = 486.9994, Found: 486.9992.

4.2.3. 4,4,4-Trifluoro-2-(naphthalen-2-yl)butan-2-yl 2-iodobenzoate (**3c**)

Colorless oil; 78.3 mg, 81%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.09–3.21 (m, 1H), 3.29–3.41 (m, 1H), 7.18 (ddd, J = 1.8, 7.8, 7.8 Hz, 1H), 7.44–7.59 (m, 4H), 7.84–7.93 (m, 5H), 8.02 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 44.0 (q, J = 27.0 Hz), 81.5 (q, J = 1.9 Hz), 93.9, 122.2, 123.4, 125.3 (q, J = 278.4 Hz), 126.3, 126.4, 127.5, 128.0, 128.3, 128.6, 130.9, 132.6, 133.0, 135.5, 140.3, 141.3, 164.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −59.8 (t, J = 10.4 Hz); IR (neat): 3059, 1731, 1583, 1508, 1464, 1430, 1198 cm^{-1}; HRMS (ESI^+): Calcd. for $[C_{21}H_{16}F_3IO_2+Na]^+$: m/z = 507.0045, Found: 507.0040.

4.2.4. 2-(3-Bromophenyl)-4,4,4-trifluorobutan-2-yl 2-iodobenzoate (**3d**)

Colorless oil; 11.1 mg, 11%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 2.96–3.21 (m, 2H), 7.18 (ddd, J = 1.8, 7.8, 7.8 Hz, 1H), 7.24–7.28 (m, 1H), 7.37 (ddd, J = 1.8, 1.8, 7.8 Hz, 1H), 7.42–7.46 (m, 2H), 7.59 (dd, J = 1.8, 1.8 Hz, 1H), 7.81 (dd, J = 1.8, 7.8 Hz, 1H), 8.00 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 44.0 (q, J = 27.0 Hz), 80.7, 93.8, 122.9, 123.1, 125.0 (q, J = 278.4 Hz), 127.0, 128.1, 130.2, 130.8, 131.0, 132.8, 135.3, 141.4, 145.3, 164.8: ^{19}F NMR (376 MHz, $CDCl_3$): δ = −59.9 (t, J = 10.4 Hz). IR (neat): 2920, 1731, 1582, 1567, 1464, 1419, 1371, 1192 cm^{-1}; HRMS (EI^+): Calcd. for $[C_{17}H_{13}BrF_3IO_2]^+$: m/z = 511.9096, Found: 511.9088.

4.2.5. 1-(2,2,2-Trifluoroethyl)-1,2,3,4-tetrahydronaphthalen-1-yl 2-iodobenzoate (**3e**)

Colorless oil; 42.0 mg, 46%; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84–1.95 (m, 1H), 2.10–2.18 (m, 1H), 2.43–2.47 (m, 1H), 2.81–3.21 (m, 5H), 7.12–7.16 (m, 2H), 7.20–7.22 (m, 2H), 7.41 (dd, J = 7.8, 7.8 Hz, 1H), 7.46–7.48 (m, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 29.1, 30.5, 44.0 (q, J = 27.0 Hz), 81.2 (br), 93.8, 125.2 (q, J = 278.4 Hz), 125.5, 126.4, 127.9, 128.0, 129.3, 130.7, 132.5, 135.7, 136.7, 137.3, 141.3, 164.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −59.3 (t, J = 10.4 Hz); IR (neat): 2940, 1730, 1582, 1490, 1463, 1429, 1375, 1153 cm^{-1}; HRMS (ESI^+): Calcd. for $[C_{19}H_{16}F_3IO_2+Na]^+$: m/z = 483.0045, Found: 483.0038.

4.2.6. 4-(2,2,2-Trifluoroethyl)-1,2-dihydronaphthalene (**3e′**)

Colorless oil; 17.8 mg, 42%; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30–2.35 (m, 2H), 2.76–2.80 (m, 2H), 3.23 (dq, J = 0.9, 10.7 Hz, 2H), 6.12–1.14 (m, 1H), 7.13–7.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.34, 28.07, 36.90 (q, J = 29.9 Hz), 122.9, 126.2 (q, J = 277.4 Hz), 126.6, 126.8, 127.4, 127.9, 132.2, 133.8, 136.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −64.4 (t, J = 10.7 Hz); IR (neat): 2939, 1489, 1353, 1255, 1127 cm^{-1}; HRMS (EI^+): Calcd. for $[C_{12}H_{11}F_3]^+$: m/z = 212.0812, Found: 212.0814.

4.2.7. 3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-methylpropyl 2-iodobenzoate; syn/anti *mixture (1:2.2)* (**5**)

Colorless oil; 82.1 mg, 88%; ^1H NMR (400 MHz, $CDCl_3$): *syn*-isomer, δ = 1.00 (d, J = 6.9 Hz, 3H), 2.90–3.00 (m, 1H), 3.81 (s, 3H), 6.10 (d, J = 8.7 Hz, 1H), 6.89–6.92 (m, 2H), 7.12–7.15 (m, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.38–7.41 (m, 1H), 7.83 (dd, J = 1.4, 7.8 Hz, 1H), 7.98 (dd, J = 1.4, 7.8 Hz, 1H): *anti*-isomer, δ = 1.27 (d, J = 7.4 Hz, 3H), 2.65–2.74 (m, 1H), 3.81 (s, 3H), 6.37 (d, J = 3.7 Hz, 1H), 6.89–6.92 (m, 2H), 7.18 (ddd, J = 1.4, 7.8, 7.8 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.44 (ddd, J = 1.4, 7.8, 7.8 Hz, 1H), 7.89 (dd, J = 1.4, 7.8 Hz, 1H), 8.02 (dd, J = 1.4, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.0, 10.8, 42.8 (q, J = 25.1 Hz), 44.3 (q, J = 25.1 Hz), 55.4, 55.4, 73.3, 75.1, 94.3, 94.5, 114.1, 127.0 (q, J = 280.3 Hz), 127.1 (q, J = 280.3), 127.6, 128.0, 128.1, 129.0, 129.1, 129.7, 131.0, 132.9, 133.0, 134.4, 134.5, 141.6,

141.7, 159.6, 160.0, 164.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −68.9 (d, J = 8.7 Hz, *syn*), −69.8 (d, J = 8.7 Hz, *anti*); IR (neat): 1732, 1613, 1513, 1463, 1243, 1126, 1015, 833, 740 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{18}H_{16}F_3NO_3+Na]^+$: m/z = 486.9994, Found: 486.9989.

4.3. Typical procedure for the oxy-trifluoromethylation of diene derivatives

CuI (3.8 mg, 10 mol%) and Togni's reagent **1** (76 mg, 1.2 equiv.) were added to a Schlenk tube which had been flame-dried under vacuum. The tube was evacuated and backfilled with nitrogen. CH_2Cl_2 (1 mL) and 1-phenyl-1,3-butadiene **6a** (26.0 mg, 0.2 mmol) were added to the tube. The reaction mixture was stirred for 2 h at 40 °C, then diluted with EtOAc (5 mL) and quenched with aqueous saturated $NaHCO_3$. The mixture was extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 30/1) to give product **7a** (81.4 mg, 91%) as a colorless solid.

4.3.1. (E)-5,5,5-Trifluoro-1-phenylpent-2-en-1-yl 2-iodobenzoate (*7a*)

Colorless solid; 81.4 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84–2.94 (m, 2H), 5.89–5.86 (m, 1H), 6.07 (dd, J = 6.0, 15.2 Hz, 1H), 6.54 (d, J = 6.0 Hz, 1H), 7.16 (m, 1H), 7.33–7.47 (m, 6H), 7.84 (dd, J = 1.8, 7.8 Hz, 1H), 8.00 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.0 (q, J = 30.8 Hz), 76.6, 94.2, 121.6 (q, J = 3.9 Hz), 125.6 (q, J = 277.4 Hz), 127.3, 127.9, 128.5, 128.7, 131.0, 132.8, 134.8, 135.2, 138.0, 141.4, 165.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −66.0 (t, J = 10.4 Hz); IR (neat): 3034, 1727, 1583, 1429, 1242, 1130, 1092, 1014, 968, 737, 696 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{18}H_{14}F_3IO_2+Na]^+$: m/z = 468.9883, Found: 468.9880.

4.3.2. (E)-5,5,5-Trifluoro-1-(4-methoxyphenyl)pent-2-en-1-yl 2-iodobenzoate (*7b*)

Colorless oil; 86.7 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84–2.94 (m, 2H), 3.81 (s, 3H), 5.75–5.83 (m, 1H), 6.07 (dd, J = 6.0, 15.6 Hz, 1H), 6.50 (d, J = 6.0 Hz, 1H), 6.86–6.93 (m, 2 H), 7.14 (dd, J = 7.8 Hz, 1H), 7.34–7.43 (m, 3H), 7.80 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.0 (q, J = 29.9 Hz), 55.2, 76.2, 94.1, 114.0, 121.1 (q, J = 3.8 Hz), 125.6 (q, J = 276.5 Hz), 127.9, 128.9, 130.0, 130.9, 132.7, 134.9, 135.4, 141.4, 159.7, 165.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −66.0 (t, J = 10.4 Hz); IR (neat): 2960, 1729, 1607, 1583, 1464, 1429, 1175 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{19}H_{16}F_3IO_3+Na]^+$: m/z = 498.9994, Found: 498.9995.

4.3.3. (E)-5,5,5-Trifluoro-1-(4-fluorophenyl)pent-2-en-1-yl 2-iodobenzoate (*7c*)

Colorless oil; 80.6 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84–2.94 (m, 2H), 5.80 (dt, J = 7.3, 15.6 Hz, 1H), 6.03 (dt, J = 5.8, 15.6 Hz, 1H), 6.51 (d, J = 5.8 Hz, 1H), 7.05–7.18 (m, 3H), 7.39–7.45 (m, 3H), 7.78–7.81 (m, 1H), 7.98–8.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.9 (q, J = 29.9 Hz), 75.8, 94.0, 115.6 (d, J = 22.2 Hz), 121.7 (q, J = 2.9 Hz), 125.5 (q, J = 276.5 Hz), 127.9, 129.2 (d, J = 7.7 Hz), 130.9, 132.8, 133.8 (d, J = 2.9 Hz), 134.7, 135.0, 141.4, 162.7 (d, J = 247.6 Hz), 165.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −113.0 to −112.9 (m), −66.0 (t, J = 10.4 Hz); IR (neat): 2933, 1605, 1583, 1562, 1465, 1429, 1042 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{18}H_{13}F_4IO_2+Na]^+$: m/z = 486.9794, Found: 486.9799.

4.3.4. (E)-1,1,1-Trifluoroundec-3-en-5-yl 2-iodobenzoate (*7d*)

Colorless oil; 77.3 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H), 1.29–1.42 (m, 8H), 1.68–1.88 (m, 2H), 2.79–2.91 (m, 2H), 5.50 (dt, J = 6.4, 6.4 Hz, 1H), 5.73–5.85 (m, 2H), 7.14 (ddd, J = 1.8, 7.8, 7.8 Hz, 1H), 7.40 (ddd, J = 0.9, 7.8, 7.8 Hz, 1H), 7.77 (dd, J = 1.8, 7.8 Hz, 1H), 7.99 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.0, 28.9, 31.6, 34.1, 37.0 (q, J = 29.9 Hz), 75.4, 93.9, 121.4 (q, J = 3.8 Hz), 125.6 (q, J = 276.5 Hz), 127.9, 130.7, 132.5, 135.4, 135.5, 141.3, 165.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −66.1 (t, J = 10.4 Hz); IR (neat): 2928, 1727, 1465, 1430, 1347, 1285, 1043 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{18}H_{22}F_3IO_2+Na]^+$: m/z = 477.0514, Found: 477.0513.

4.3.5. (E)-1-Cyclohexyl-5,5,5-trifluoropent-2-en-1-yl 2-iodobenzoate (*7e*)

Colorless oil; 73.7 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02–1.29 (m, 5H), 1.66–1.86 (m, 6H), 2.76–2.94 (m, 2H), 5.32 (dd, J = 6.4, 6.4 Hz, 1H), 5.70–5.83 (m, 2H), 7.14 (ddd, J = 1.8, 7.8, 7.8 Hz, 1H), 7.41 (ddd, J = 0.9, 7.8, 7.8 Hz, 1H), 7.78 (dd, J = 1.4, 7.8 Hz, 1H), 7.99 (dd, J = 0.9, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.8, 25.8, 26.2, 28.5, 28.6, 37.0 (q, J = 29.9 Hz), 41.5, 79.4, 94.0, 122.1 (q, J = 3.8 Hz), 125.7 (q, J = 276.5 Hz), 127.9, 130.7, 132.5, 134.1, 135.3, 141.3, 165.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −66.1 (t, J = 10.4 Hz); IR (neat): 2927, 2854, 1583, 1464, 1450, 1429, 1281 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{18}H_{20}F_3IO_2+Na]^+$: m/z = 475.0358, Found: 475.0352.

4.3.6. (E)-5,5,5-Trifluoro-2-methyl-1-phenylpent-2-en-1-yl 2-iodobenzoate (*7f*)

Colorless oil; 76.8 mg, 83%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (s, 3H), 2.87–2.97 (m, 2H), 5.78 (t, J = 7.4 Hz, 1H), 6.46 (s, 1H), 7.14–7.18 (m, 1H), 7.32–7.43 (m, 6H), 7.85 (dd, J = 1.8, 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 32.7 (q, J = 29.9 Hz), 80.3, 94.2, 115.6 (q, J = 3.8 Hz), 126.1 (q, J = 276.5 Hz), 127.0, 127.9, 128.3, 128.5, 130.9, 132.8, 134.7, 137.5, 140.0, 141.5, 165.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −65.7 (t, J = 10.4 Hz); IR (neat): 2928, 1730, 1583, 1562, 1495, 1465, 1375, 1191 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{19}H_{16}F_3IO_2+Na]^+$: m/z = 483.0045, Found: 483.0040.

4.3.7. 5,5,5-Trifluoro-1,1-diphenylpent-1-en-3-yl 2-iodobenzoate (*8g*)

Colorless solid; 506.5 mg, 97% ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51–2.63 (m, 1H), 2.67–2.81 (m, 1H), 5.84–5.89 (m, 1H), 6.21 (d, J = 9.2 Hz, 1H), 7.12–7.16 (m, 1H), 7.24–7.31 (m, 7H), 7.36–7.45 (m, 4H), 7.74 (dd, J = 1.4, 7.8 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.7 (q, J = 27.9 Hz), 68.2 (q, J = 2.9 Hz), 93.9, 123.6, 125.2 (q, J = 277.4 Hz), 127.5, 127.9, 128.1, 128.3, 128.3, 128.6, 129.3, 130.8, 132.7, 135.0, 138.2, 140.8, 141.2, 146.9, 165.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.7 (t, J = 10.4 Hz); IR (neat): 3058, 3026, 1730, 1583, 1494, 1445, 1429, 1387, 1281, 1237, 1129, 1090, 1015, 759, 739, 697 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{24}H_{18}F_3IO_2+Na]^+$: m/z = 545.0196, Found: 545.0199.

4.4. Typical procedure for the synthesis of β-trifluoromethylstyrene derivatives

$[(MeCN)_4Cu]PF_6$ (7.5 mg, 10 mol%), p-TsOH·H_2O (38 mg, 1 equiv.) and Togni's reagent **1** (76 mg, 1.2 equiv.) were weighed and added to a Schlenk tube which had been flame-dried under vacuum. The tube was evacuated and backfilled with nitrogen. CH_2Cl_2 (1 mL) was added to the tube, followed by addition of 4-methoxystyrene **9a** (27 μL, 0.2 mmol). The reaction mixture was stirred for 1 h at 40 °C, then diluted with EtOAc (5 mL) and quenched with aqueous $NaHCO_3$. The mixture was extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 30/1) to give **10a** (36.6 mg, 90%) as a colorless solid.

*4.4.1. (E)-1-Methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**10a**)*

Colorless solid; 36.6 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 6.06 (dq, J = 6.9, 16.1 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 7.06–7.11 (m, 1H), 7.40 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 113.4 (q, J = 33.7 Hz), 114.3, 123.9 (q, J = 268.8 Hz), 126.0, 129.0, 137.1 (q, J = 6.7 Hz), 161.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.7 (d, J = 6.9 Hz); IR (neat) 3036, 2966, 2937, 2846, 1664, 1606, 1514, 1290, 1258, 1177, 1131, 1108, 1029, 974, 810 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_{10}H_9F_3O]^+$: m/z = 202.0605, Found: 202.0607.

*4.4.2. (E)-5-(3,3,3-Trifluoroprop-1-en-1-yl)benzo[d][1,3]dioxole (**10b**)*

White solid; 37.8 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00 (s, 2 H), 6.02 (dq, J = 6.9, 16.1 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.90–6.95 (m, 2H), 7.04 (ddd, J = 1.8, 1.8, 16.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.5, 106.2, 108.5, 113.8 (q, J = 33.7 Hz), 123.4, 123.8 (q, J = 268.8 Hz), 127.7, 137.2 (q, J = 6.7 Hz), 148.4, 149.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8 (d, J = 6.9 Hz); IR (neat): 2910, 1664, 1621, 1607, 1451, 1362, 1285, 1113 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_{10}H_7F_3O_2]^+$: m/z = 216.0398, Found: 216.0391.

*4.4.3. (E)-tert-Butyldimethylsiloxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**10c**)*

Colorless oil; 37.8 mg, 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (s, 6 H), 0.98 (s, 9H), 6.06 (dq, J = 6.9, 16.1 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.08 (dq, J = 2.3, 16.1 Hz, 1H), 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.4, 18.2, 25.6, 113.6 (q, J = 33.7 Hz), 120.5, 123.9 (q, J = 268.8 Hz), 126.6, 129.0, 137.1 (q, J = 6.7 Hz), 157.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8 (d, J = 6.9 Hz); IR (neat): 2957, 2932, 2860, 1421, 1391, 1363, 1205 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_{15}H_{21}F_3OSi]^+$: m/z = 302.1314, Found: 302.1312.

*4.4.4. (E)-2-Methyl-5-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (**10d**)*

Colorless oil; 25.2 mg, 66%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 5.87 (dq, J = 6.9, 15.6 Hz, 1H), 6.68–6.69 (m, 1H), 6.96 (d, J = 3.7 Hz, 1H), 7.15 (dq, J = 1.8, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.7, 113.0 (q, J = 33.7 Hz), 123.6 (q, J = 268.8 Hz), 126.2, 130.5, 130.8 (d, J = 6.7 Hz), 135.9, 143.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.7 (d, J = 6.9 Hz); IR (neat): 2927, 1731, 1542, 1475, 1350, 1305, 1206 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_8H_7F_3S]^+$: m/z = 192.0221, Found: 192.0220.

*4.4.5. 1-Acetyl-3-((E)-3,3,3-trifluoroprop-1-enyl)-1H-indole (**10e**)*

Colorless solid; 37.2 mg, 73%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 6.34 (dq, J = 6.9, 16.1 Hz, 1H), 7.21–7.27 (m, 1H), 7.35–7.45 (m, 2H), 7.59 (s, 1H), 7.75 (d, J = 7.4 Hz, 1H), 8.47 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 116.2 (q, J = 33.7 Hz), 116.9, 119.6, 123.6 (q, J = 268.8 Hz), 124.5, 126.1, 126.6, 127.6, 128.9 (q, J = 7.7 Hz), 136.4, 168.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.3 (d, J = 6.9 Hz); IR (neat): 3136, 3020, 2929, 1714, 1666, 1450, 1379, 1348, 1306, 1274, 1215, 1113, 1088, 1012, 970, 743 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{13}H_{10}F_3NO+Na]^+$: m/z = 276.0607, Found: 276.0609.

*4.4.6. ((1E,3E)-5,5,5-Trifluoropenta-1,3-dien-1-yl)benzene (**10f**)*

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.80 (dq, J = 6.9, 15.2 Hz, 1H), 6.73–6.93 (m, 3H), 7.29–7.38 (m, 3H), 7.43–7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.3 (q, J = 33.7 Hz), 123.5 (q, J = 268.8 Hz), 124.9, 127.0, 128.8, 128.9, 135.8, 137.5 (q, J = 7.7 Hz), 139.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.1 (d, J = 6.9 Hz); IR (neat): 3030, 2918, 1737, 1498, 1450, 1156, 1030 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_{11}H_9F_3]^+$: m/z = 198.0656, Found: 198.0654.

*4.5. Synthesis of (E)-2-(3,3,3-trifluoroprop-1-en-1-yl)phenol (**10g**)*

$[(MeCN)_4Cu]PF_6$ (7.5 mg, 10 mol%), Et_3N (40.5 mg, 2 equiv.) and Togni's reagent **1** (76 mg, 1.2 equiv.) were weighed and added to a Schlenk tube which had been flame-dried under vacuum. The tube was evacuated and backfilled with nitrogen. CH_2Cl_2 (1 mL) was added to the tube, followed by addition of 4-methoxystyrene **9g** (24.0 mg, 0.2 mmol). The reaction mixture was stirred for 6 h at 23 °C, then diluted with EtOAc (5 mL) and quenched with aqueous $NaHCO_3$. The mixture was extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **10g** (24.6 mg, 66%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.19 (s, 1H), 6.38 (ddq, J = 2.3, 6.9, 16.1 Hz, 1H), 6.77–6.79 (m, 1H), 6.94–6.98 (m, 1H), 7.21–7.26 (m, 1H), 7.35–7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.1, 116.9 (q, J = 33.7 Hz), 120.8, 121.2, 128.3 (q, J = 268.8 Hz), 129.1, 130.9, 132.7 (q, J = 6.7 Hz), 154.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.2 (d, J = 6.9 Hz); IR (neat): 3609, 3416, 1664, 1607, 1500, 1210, 1178 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_9H_7F_3O]^+$: m/z = 188.0449, Found: 188.0452.

*4.6. Synthesis of (E)-4-(3,3,3-trifluoroprop-1-en-1-yl)acetoaniline (**10h**)*

To a solution of **11h** (105 mg, 0.22 mmol) in CH_2Cl_2 (1.1 mL) was added TfOH (49.5 mg, 1.5 equiv.). The reaction mixture was stirred for 12 h at 40 °C, then diluted with CH_2Cl_2 (5 mL) and quenched with aqueous $NaHCO_3$. After extraction, the organic layer was dried over $MgSO_4$ and filtered, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give **10h** (49.7 mg, 99%) as a colorless oil. ^{1}H NMR (400 MHz, CD_3OD): δ = 2.13 (s, 3H), 6.36 (dq, J = 6.9, 16.1 Hz, 1H), 7.10–7.15 (m, 1H), 7.42 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ = 23.9, 115.4 (q, J = 33.7 Hz), 121.0, 125.5 (q, J = 267.8 Hz), 129.4, 130.4, 138.5 (d, J = 6.7 Hz), 141.7, 171.7; ^{19}F NMR (376 MHz, CD_3OD): δ = −64.5 (d, J = 6.9 Hz); IR (neat): 3305, 2967, 1458, 1414, 1371, 1208, 1181 cm^{-1}; HRMS (ESI$^+$): Calcd. for $[C_{11}H_{10}F_3NO+H]^+$: m/z = 230.0793, Found: 230.0793.

*4.7. Synthesis of (E)-1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**10i**)*

To a solution of **11i** (95.3 mg, 0.2 mmol) in THF (2 mL) was added a 1 M solution of NaHMDS in THF (0.4 mL, 2 equiv.) in −78 °C. The reaction mixture was stirred for 1 h, and then quenched with aqueous NH_4Cl. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give **10i** (29.2 mg, 64%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 6.16 (dq, J = 6.9, 16.1 Hz, 1H), 7.10–7.15 (m, 1H), 7.38–7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 34.8, 114.9 (q, J = 33.7 Hz), 123.8 (q, J = 268.8 Hz), 125.9, 127.3, 130.6, 137.4 (d, J = 6.7 Hz), 153.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.0 (d, J = 6.9 Hz); IR (neat): 2967, 1665, 1334, 1312, 1272, 1215, 1107 cm^{-1}; HRMS (EI$^+$): Calcd. for $[C_{13}H_{15}F_3]^+$: m/z = 228.1126, Found: 228.1127.

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