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Copper-Catalyzed Aminotrifluoromethylation of Unactivated Alkenes with (TMS)CF_3: Construction of Trifluoromethylated Azaheterocycles

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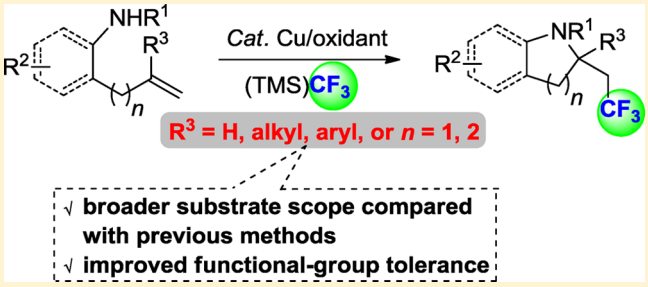
Supporting Information

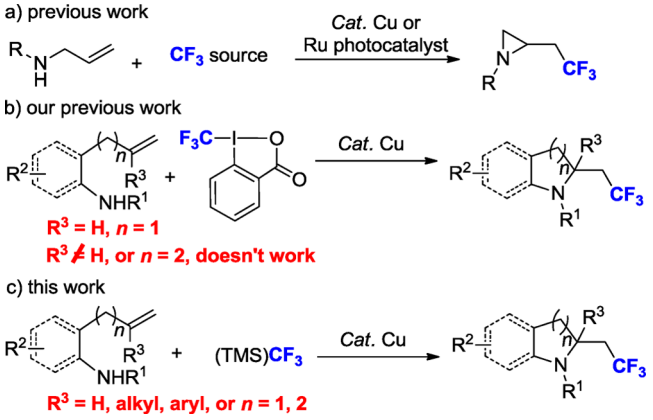
ABSTRACT: The first example of a copper(I)-catalyzed intramolecular aminotrifluoromethylation of unactivated alkenes using (TMS)CF_3 (trimethyl(trifluoromethyl)silane) as the CF_3 source is described. A broad range of electronically and structurally varied substrates undergo convenient and step-economical transformations for the concurrent construction of a five- or six-membered ring and a C−CF_3 bond toward different types of trifluoromethyl azaheterocycles. The methodology not only circumvents use of expensive electrophilic CF_3 reagents or the photoredox strategy but also expands the scope to substrates that are difficult to access by the existing methods. Mechanistic studies are conducted, and a plausible mechanism is proposed.



INTRODUCTION

Trifluoromethyl-containing azaheterocycles have been recognized as important building blocks in many bioactive compounds because the presence of a CF_3 group in such biologically active compounds enhances the lipophilicity, metabolic stability, and bioavailability.[1] Toward this end, much attention has been recently paid to the development of new methods for the synthesis of trifluoromethyl azaheterocycles.[2] From the point of high atom and step economy, intramolecular difunctionalization-type trifluoromethylation of unactivated alkenes with nitrogen-based nucleophiles (i.e., aminotrifluoromethylation) has been proven as an attractive but underexploited strategy for providing easy access to structurally diverse three- or five-membered CF_3-containing compounds.[3,4] In this context, Cho and co-workers have developed elegant visible-light-induced intramolecular trifluoromethylation of terminal allylic amines in the presence of a Ru complex as a photocatalyst to produce CF_3-containing aziridines (Scheme 1a).[3a] Very recently, Sodeoka[3b] and our group[4a] have independently reported intramolecular aminotrifluoromethylation of alkenes with diverse nitrogen-based nucleophiles in the presence of a copper catalyst with electrophilic Togni's reagent as the CF_3 source to give trifluoromethylated aziridines, pyrrolidines, or indolines (Scheme 1a,b). Although significant progress has been made, these reactions have encountered several major restrictions. For example, the aminotrifluoromethylation of alkenes is almost limited to not only monosubstituted terminal alkenes but also the formation of three- or five-membered azaheterocycles, thus limiting their synthetic value and making them less applicable to large-scale synthesis. It is noteworthy that recent work from our laboratory has demonstrated that the development of a catalytic method that leads to the six-membered CF_3-containing azaheterocycles with Togni's reagent remains a formidable challenge[4a] and that the overall transformation can be achieved in a stepwise fashion.[5] Therefore, the development of a convenient and step-economical strategy for expanding aminotrifluoromethylation of unactivated alkenes associated with the aforementioned challenges is still highly desirable.

Scheme 1. Transition-Metal-Catalyzed Aminotrifluoromethylation of Unactivated Alkenes



Recently, the Ruppert−Prakash reagent (trimethyl(trifluoromethyl)silane, (TMS)CF_3), which is a commercially available compound, has been widely used as a CF_3 source in organic synthesis to construct CF_3-containing diverse molecules.[6−8] In this area, we have also developed a mild and general

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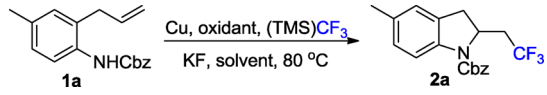
$PhI(OAc)_2$-mediated direct carbotrifluoromethylation of activated alkenes using $(TMS)CF_3$ under metal-free conditions, thus offering a complementary method to transition-metal-catalyzed methods.[4b] However, to our knowledge, there has been no report on the direct difunctionalization of unactivated alkenes, such as aminotrifluoromethylation, with nucleophilic $(TMS)CF_3$ as the CF_3 source. In light of all of these findings[6−8] and as a part of our continued interest in the area of trifluoromethylation, herein, we further report the Cu(I)-catalyzed oxidative aminotrifluoromethylation of unactivated alkenes using nucleophilic $(TMS)CF_3$ as the CF_3 source (Scheme 1c), which expands the scope and efficiency of aminotrifluoromethylation and avoids the use of expensive electrophilic CF_3 reagents or photocatalysts. Significantly, this efficient approach provides a useful alternative to the known aminotrifluoromethylation methods and proves especially valuable for the simultaneous formation of a five- or six-membered ring and a $C-CF_3$ bond, which should facilitate late-stage introduction of versatile CF_3-containing azaheterocycle moieties into complex scaffolds for diversity-oriented synthetic strategies.

RESULTS AND DISCUSSION

Our prior observation[4a] that substrates bearing *gem*-disubstituted alkenes or longer chain groups have displayed less or no efficiency in the presence of electrophilic CF_3 reagents as shown in Scheme 1b and the possibility that nucleophilic $(TMS)CF_3$ could be used as a CF_3 source in the presence of an appropriate oxidant for the aminotrifluoromethylation of simple alkenes inspired by the high reactivity of such reagents toward unactivated alkenes[8] and other transformations[7] led us to further expand the substrate scope of such reactions. To do so and further improve the product yield in our previous report,[4a] we initiated these investigations by examining the reaction of *N*-[(benzyloxy)carbonyl]-2-allylaniline **1a** by using $(TMS)CF_3$ as the CF_3 source in the presence of CuI (25 mol %), $AgNO_3$ as the oxidant, and KF as the base or initiator. We found that CuI could catalyze this reaction in DMF at 80 °C for 16 h to form the desired product **2a** in 58% yield (Table 1, entry 1). Encouraged by this result, we turned our attention to screen different copper catalysts, and $Cu(CH_3CN)_4BF_4$ was found to provide **2a** in 62% yield (Table 1, entries 1−7). The product yield could be further improved to 68% by reducing the catalyst loading of $Cu(CH_3CN)_4BF_4$ from 25 to 15 mol % (Table 1, entry 8). Among different organic solvents examined, it turned out that the reaction with DMF gave the best result (Table 1, entries 8−13). Further investigation revealed that $AgNO_3$ behaved as the most efficient oxidant among the screened oxidants (Table 1, entries 14−16) and a negative result was obtained by lowering the amount of $AgNO_3$ (Table 1, entry 17). In contrast, control experiments demonstrated that the reaction did not occur in the presence of a Cu catalyst or $AgNO_3$ alone (Table 1, entries 18 and 19), unambiguously revealing that a copper catalyst in combination with $AgNO_3$ is essential for this reaction. It should be noted that the product yield was remarkably improved under the current system as compared to our previous result.[4a]

With an optimized set of reaction conditions in hand, we next turned our attention to assessing the scope of aminotrifluoromethylation of alkenes. As can be seen in Table 2, regardless of the position and nature of the substituent, various 2-allylaniline derivatives reacted efficiently with $(TMS)CF_3$ to afford the desired products in moderate to good yields. Reactions of 2-allylaniline derivatives **1a−1f** having electron-donating and -neutral substituents on the aryl ring at the different positions

Table 1. Screening of the Reaction Conditions[a]



1a 2a

entry	Cu	oxidant	solvent	time (h)	yield[b] (%)
1	CuI	$AgNO_3$	DMF	16	58
2	CuBr	$AgNO_3$	DMF	16	35
3	CuTc[c]	$AgNO_3$	DMF	16	60
4	$CuOTf{\cdot}0.5C_6H_6$	$AgNO_3$	DMF	16	55
5	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	DMF	16	62
6	$Cu(OTf)_2$	$AgNO_3$	DMF	16	*d*
7	$Cu(CH_3CN)_4PF_6$	$AgNO_3$	DMF	16	61
8	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	DMF	16	68
9	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	DMSO	4	65
10	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	NMP	8	63
11	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	EtOAc	16	*d*
12	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	CH_3OH	16	*d*
13	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	dioxane	16	*d*
14	$Cu(CH_3CN)_4BF_4$	AgF	DMF	16	14
15	$Cu(CH_3CN)_4BF_4$	Ag_2CO_3	DMF	16	*d*
16	$Cu(CH_3CN)_4BF_4$	$PhI(OAc)_2$	DMF	16	9
17[e]	$Cu(CH_3CN)_4BF_4$	$AgNO_3$	DMF	16	38
18	$Cu(CH_3CN)_4BF_4$		DMF	16	*d*
19		$AgNO_3$	DMF	16	*d*

[a]Reaction conditions (unless otherwise mentioned): **1a** (0.05 mmol), solvent (0.3 mL), $(TMS)CF_3$ (4.0 equiv), oxidant (1.0 equiv), KF (4.0 equiv), Cu catalyst loading (entries 1−7, 25 mol %; entries 8−18, 15 mol %), under argon. Cbz = (benzyloxy)carbonyl. [b]Determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. [c]CuTc = copper(I) thiophene-2-carboxylate. [d]A trace amount of product was observed. [e]A 0.5 equiv sample of $AgNO_3$ was used..

worked well, furnishing **2a−2f** in 46−61% yields. Notably, electron-withdrawing substituents, including F, Cl, and Br, at the different aryl positions proved to be well-tolerated under the standard reaction conditions, giving the corresponding products **2g−2j** in good yields. These results are significant since aryl halides are reactive and, thus, are difficult to retain in many copper-catalyzed trifluoromethylation reactions,[7d,9] which offers opportunities for further modifications at these positions.[10] Interestingly, a good yield of **2k** containing three rings was achieved when the phenyl moiety was exchanged for a naphthyl group under similar reaction conditions. It is more encouraging to note that products that are more difficult to prepare via Cu(I)-catalyzed aminotrifluoromethylation with Togni's reagent,[4a] such as **1l** and **1m**, which contain *gem*-disubstituted alkenes bearing a methyl or phenyl group, can also be accessed by using this method. Furthermore, the protocol could be extended to the reaction of pentenylcarbamates **1n−1p** for the synthesis of highly substituted trifluoromethylated pyrrolidines **2n−2p**, and the product yields were relatively insensitive to the nature of the substitution on the carbon backbone. Most importantly, a variety of substituents on the nitrogen atom, including Boc and Ts, are compatible under the reaction conditions, giving the desired products **2q** and **2r** in 60% and 47% yields, respectively.

To further investigate the scope of application, we tested the use of more challenging 2-allylbenzylamine derivatives as substrates since the expected six-membered products could not be obtained with the previous Cu-catalyzed aminotrifluoromethylation with Togni's reagent.[4a] We were delighted to find that when **3a** was employed under the current reaction system in the

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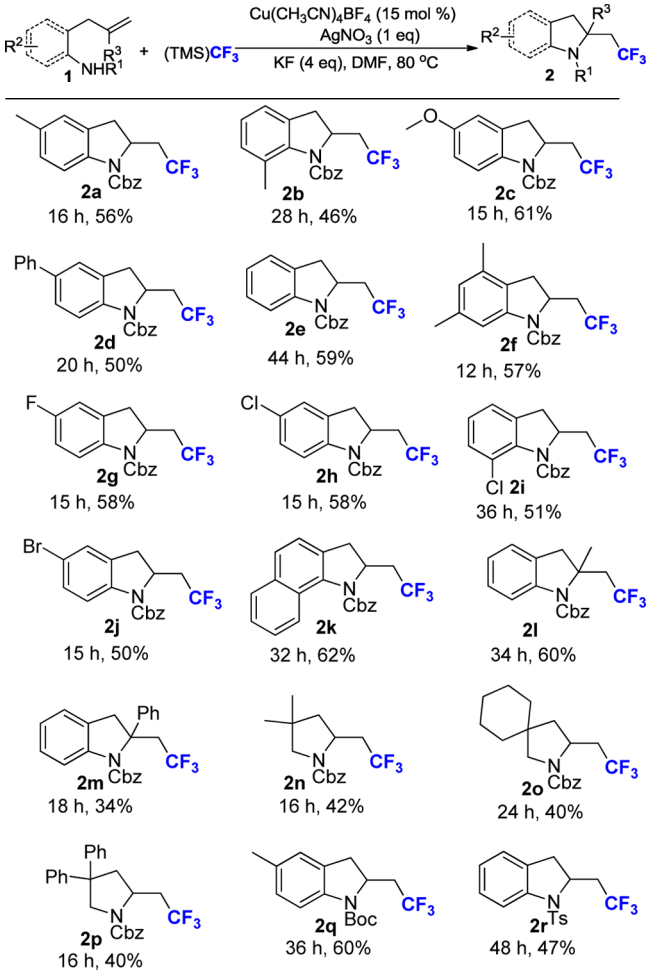
Table 2. Aminotrifluoromethylation of Alkenes To Form a Five-Membered Ring[a]



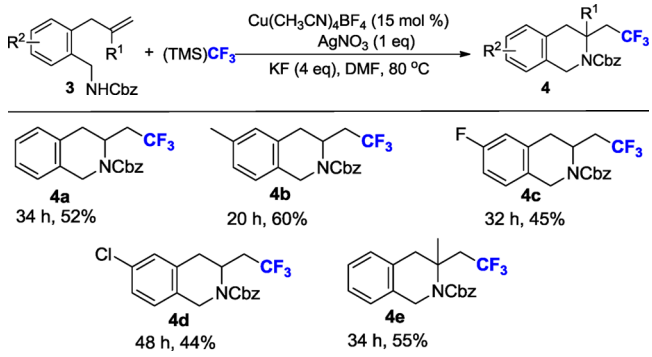
[a]Reaction conditions (unless otherwise mentioned): **1** (0.5 mmol), $(TMS)CF_3$ (4.0 equiv), KF (4.0 equiv), $Cu(CH_3CN)_4BF_4$ (15 mol %), $AgNO_3$ (1.0 equiv) in DMF, under argon. Yields are based on the starting alkene. Boc = (*tert*-butyloxy)carbonyl. Ts = *p*-tolylsulfonyl.

presence of $(TMS)CF_3$, the desired trifluoromethylated product **4a** with the formation of a six-membered ring was obtained in 52% yield (Table 3). With regard to the scope of such substrates, monosubstituted and *gem*-disubstituted alkenes bearing electron-donating and electron-withdrawing groups on the aryl ring also proved to be suitable substrates (**3b**−**3e**), furnishing the corresponding products **4b**−**4e** in 44−60% yields. Given the broad substrate scope, this approach is clearly complementary to the previous metal-catalyzed and photoredox trifluoromethylated methods.[3,4a]

It is interesting to note that the current protocol in the presence of $(TMS)CF_3$ could be extended to direct intramolecular carbotrifluoromethylation of alkenes. Thus, our preliminary result showed that, under conditions similar to those of the aminotrifluoromethylation reaction detailed above, the reaction of *N*-methyl-*N*-phenylacrylamide **3f** gave trifluoromethylated product **4f** in 40% yield (Scheme 2).

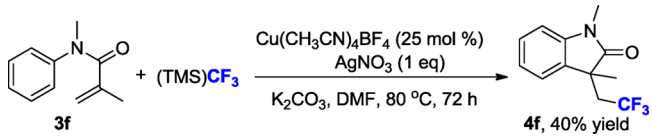
Preliminary mechanistic investigations on this reaction have been carried out (Scheme 3). First, under the standard conditions but with the addition of 1.0 or 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), the yield of the reaction between **1a** and $(TMS)CF_3$ significantly dropped (eq 1).

Table 3. Aminotrifluoromethylation of Alkenes To Form a Six-Membered Ring[a]



[a]Reaction conditions (unless otherwise mentioned): **1** (0.5 mmol), $(TMS)CF_3$ (4.0 equiv), KF (4.0 equiv), $Cu(CH_3CN)_4BF_4$ (15 mol %), $AgNO_3$ (1.0 equiv) in DMF, under argon. Yields are based on the starting alkene.

Scheme 2. Direct Intramolecular Carbotrifluoromethylation of Alkenes



However, neither an allylic−TEMPO adduct nor a TEMPO−CF_3 adduct was observed, as judged by ^{19}F and ^{1}H NMR analysis of the crude product. It is also noteworthy that no TEMPO−CF_3 adduct was observed in the reaction mixture of $(TMS)CF_3$, KF, $AgNO_3$, $Cu(CH_3CN)_4BF_4$ (15 mol %), and TEMPO in the absence of **1a** (eq 2). Collectively, these results reveal that the CF_3 radical or the allylic radical is unlikely involved as the reactive species under the current reaction conditions, which is in agreement with the observation involving oxidative trifluoromethylation of unactivated alkenes with $(TMS)CF_3$ reported by Qing and co-workers.[8a] Moreover, the reaction was found to be mostly inhibited by 2,6-di-*tert*-butyl-4-methylphenol (BHT) under the standard conditions (eq 3). These control experiments suggest that the involvement of an in situ generated $CuCF_3$ or $AgCF_3$ intermediate followed by a single-electron transfer (SET) radical pathway is possible; this is also described in recent reports involving such reagents for trifluoromethylation reactions with the SET pathway.[7g,k,11] To gain some further insights into this hypothesis, under the standard reaction conditions, we examined the aminotrifluoromethylation reaction of **1a** with $CuCF_3$ or $AgCF_3$ in situ generated from $(TMS)CF_3$, $Cu(CH_3CN)_4BF_4$ or $AgNO_3$, and KF according to the reported procedures.[7g,i] Interestingly, no detectable amount of the product **2a** was observed with $CuCF_3$ as the reagent (eq 4), whereas the product **2a** was observed with $AgCF_3$ as the reagent in 57% yield determined by ^{19}F NMR (eq 5). These observations clearly indicated that the reaction should proceed with the intermediacy of $AgCF_3$, which is presumably in situ generated from $AgNO_3$ and $(TMS)CF_3$ assisted by KF.

On the basis of the above experimental observations and the previous investigation on copper-catalyzed hydroamination or aminotrifluoromethylation of alkenes,[4,8,11] a plausible mechanism for our methodology was proposed (Scheme 4), which first involves outer-sphere attack of the nitrogen atom on the Cu(I)−alkene complex **A** to generate the neutral alkyl−copper complex

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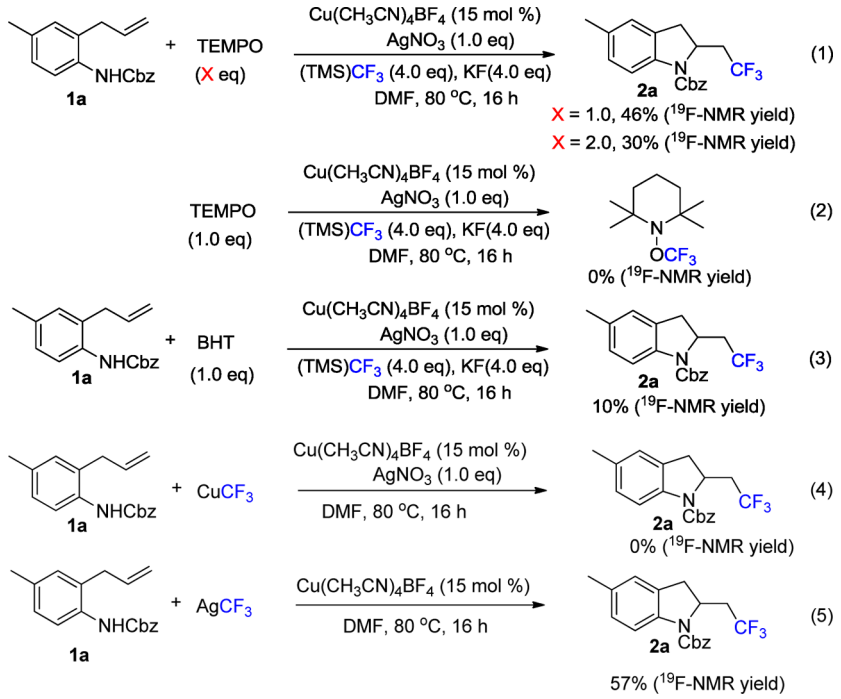
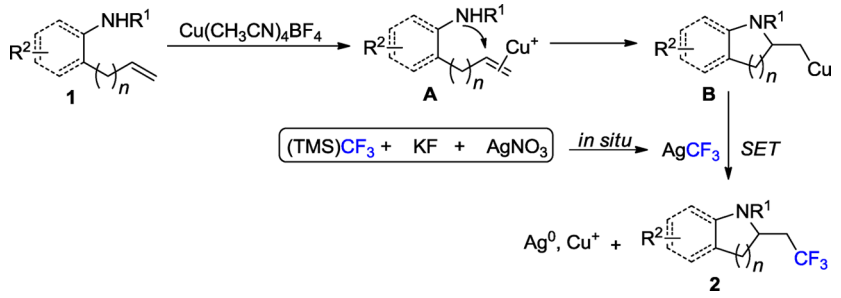
Scheme 3. Mechanistic Studies



Scheme 4. Proposed Mechanism for the Aminotrifluoromethylation Reaction of Unactivated Alkenes



B.[12] Second, the reaction of $(TMS)CF_3$, $AgNO_3$, and KF in situ generates $AgCF_3$, which then reacts with intermediate **B** via single-electron transfer[13] to produce the final product **2** and regenerate the cationic copper catalyst and silver. It is worth noting that a silver mirror was observed at the end of most of the aminotrifluoromethylation reactions. On the other hand, an alternative catalytic mechanism, which proceeds by the formation of an α-CF_3-alkyl radical intermediate initiated from alkene[8] followed by the subsequent coupling of this intermediate and the carbamate nitrogen atom,[4a] cannot be ruled out at the present stage. Therefore, rigorous investigations are necessary to unambiguously elucidate the detailed mechanism.

CONCLUSION

In summary, we have demonstrated the first example of a copper(I)-catalyzed aminotrifluoromethylation of unactivated alkenes with nucleophilic $(TMS)CF_3$ as the CF_3 source. The methodology furnishes a diverse collection of synthetically valuable trifluoromethylated azaheterocyles under mild reaction conditions. Furthermore, it has significant advantages over the conventional aminotrifluoromethylation because this approach not only circumvents the use of expensive electrophilic CF_3 reagents or the photoredox strategy, but also expands the substrate scope to substrates that are difficult to access by known methods, thus reflecting the synthetic utility of this method in medicinal chemistry and material science related fields.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under Ar using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. KF was activated in a muffle furnace at high temperature. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using silica gel 60 (particle size 0.040−0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on a 400 MHz spectrometer for ^1H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR ($CFCl_3$ as the external reference (0 ppm)) in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. The chemical shifts are expressed in parts per million, and coupling constants are given in hertz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (Hz), integration. High-resolution mass spectrometry (HRMS) was conducted on a TOF mass spectrometer.

Synthesis of Carbamate Substrates. Carbamate substrates **1a**,[4a] **1c**,[14] **1e**,[14] **1g**,[14] and **1h**[4a] were synthesized according to the procedures previously reported. The 2-allylaniline substrate[15] was synthesized according to the procedures previously reported.

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*Synthesis of Substrates **1b**, **1f**, **1i**, **1k**, and **1j**.* To a stirred solution of 2-allylaniline substrates (2.0 mmol) and pyridine (0.3 mL, 4.0 mmol) in CH_2Cl_2 (8 mL) was added CbzCl (0.3 mL, 2.4 mmol) in an ice−water bath, and the solution was left to warm to room temperature and stirred for an additional 4−8 h. After complete conversion (monitored by TLC), the reaction was quenched with H_2O (10 mL), and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were brined, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 80:1 to 30:1) to give **1**.

*Data for benzyl (2-allyl-6-methylphenyl)carbamate (**1b**):* 450 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.07 (m, 8H), 6.28 (s, 1H), 5.93−5.89 (m, 1H), 5.21 (s, 2H), 5.06 (d, J = 9.6 Hz, 1H), 5.00 (d, J = 17.2 Hz, 1H), 3.37 (d, J = 5.6 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 136.8, 136.6, 136.5, 133.6, 129.1, 128.6, 128.2, 127.7, 127.5, 116.0, 67.1, 36.9, 18.4; HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2$ $[M + Na]^+$ 304.1313, found 304.1309.

*Data for benzyl (2-allyl-3,5-dimethylphenyl)carbamate (**1f**):* 461 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.37 (m, 6H), 6.87 (s, 1H), 6.63 (br s, 1H), 6.00−5.91 (m, 1H), 5.25 (s, 2H), 5.10 (d, J = 10.4 Hz, 1H), 4.94 (d, J = 17.2 Hz, 1H), 3.38 (d, J = 4.8 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 136.9, 136.5, 136.3, 135.8, 135.0, 128.5, 128.2, 128.2, 127.6, 125.1, 121.2, 115.6, 66.9, 31.5, 21.1, 19.9; HRMS (ESI) m/z calcd for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1651, found 296.1643.

*Data for benzyl (2-allyl-6-chlorophenyl)carbamate (**1i**):* 453 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.17 (m, 8H), 6.41 (br s, 1H), 5.96−5.87 (m, 1H), 5.28 (m, 4H), 3.41−3.33 (m, 2H); HRMS (ESI) m/z calcd for $C_{17}H_{16}ClNNaO_2$ $[M + Na]^+$ 324.0767, found 324.0763.

*Data for benzyl (2-allyl-4-bromophenyl)carbamate (**1j**):* 609 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (br s, 1H), 7.48−7.33 (m, 6H), 7.30 (d, J = 2.4 Hz, 1H), 6.66 (br s, 1H), 5.91 (ddt, J = 17.2, 10.0, 6.0 Hz, 1H), 5.20−5.17 (m, 3H), 5.06 (dd, J = 17.2, 1.6 Hz, 1H), 3.31 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 136.0, 135.2, 134.8, 132.8, 131.2, 130.4, 128.7, 128.5, 128.8, 123.5, 117.5, 117.2, 67.2, 36.1; HRMS (ESI) m/z calcd for $C_{17}H_{16}BrNNaO_2$ $[M + Na]^+$ 368.0262, found 368.0257.

*Data for benzyl (2-allylnaphthalen-1-yl)carbamate (**1k**):* 546 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.55−7.09 (m, 8H), 6.66 (s, 1H), 6.01−5.97 (m, 1H), 5.30−5.05 (m, 4H), 3.56 (d, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.3, 136.2, 134.8, 133.1, 131.2, 129.8, 128.6, 128.4, 128.1, 128.0, 127.8, 126.7, 125.6, 122.7, 116.2, 67.3, 36.7; HRMS (ESI) m/z calcd for $C_{21}H_{20}NO_2$ $[M + H]^+$ 318.1494, found 318.1488.

*Synthesis of Benzyl (3-Allyl-[1,1′-biphenyl]-4-yl)carbamate (**1d**).* To a solution of **1j** (346.2 mg, 1.0 mmol), phenylboronic acid (183.0 mg, 1.5 mmol), K_2CO_3 (414.0 mg, 3.0 mmol), and 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl (X-Phos; 9.5 mg, 0.02 mmol) in CH_3CN/H_2O (6 mL/4 mL) was added $Pd(OAc)_2$ (2.3 mg, 0.01 mmol). The flask and its contents were put under reduced pressure and then backfilled with argon three times. The mixture was stirred at 60 °C for 12 h under an argon atmosphere, then cooled, and extracted with CH_2Cl_2, and the combined organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed in vacuo to afford a crude product, which was purified by flash chromatography (eluent petroleum ether:EtOAc = 60:1) to **1d** as a white solid: 268 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (br s, 1H), 7.61−7.34 (m, 12H), 6.75 (br s, 1H), δ 6.01 (ddt, J = 17.2, 10.4, 6.0 Hz, 1H), 5.25 (s, 2H), 5.20 (dd, J = 10.0, 1.2 Hz, 1H), 5.12 (dd, J = 17.2, 1.2 Hz, 1H), 3.44 (d, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 140.6, 137.4, 136.2, 135.7, 135.4, 128.9, 128.8, 128.7, 128.4, 127.2, 127.0, 126.2, 122.2, 117.1, 67.1, 36.7; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_2$ $[M + H]^+$ 344.1651, found 344.1645.

*Synthesis of Carbamate Substrates **1l** and **1m**.* The 2-allylaniline substrate[16] was synthesized according to the procedures previously reported. Benzyl (2-(2-methylallyl)phenyl)carbamate (**1l**) and benzyl (2-(2-phenylallyl)phenyl)carbamate (**1m**) were obtained by the procedure for the compounds **1b**, **1f**, **1i**, **1j**, and **1k**.

*Data for benzyl (2-(2-methylallyl)phenyl)carbamate (**1l**):* 239 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.46−7.36 (m, 5H), 7.32−7.28 (m, 1H), 7.18 (d, J = 6.8 Hz, 1H), 7.13−7.09 (m, 1H), 6.87 (br s, 1H), 5.25 (s, 2H), 4.94 (s, 1H), 4.74 (s, 1H), 3.36 (s, 2H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 143.8, 136.5, 136.3, 130.8, 128.6, 128.3, 128.3, 127.6, 124.3, 121.9, 112.5, 66.9, 41.3, 22.4; HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_2$ $[M + Na]^+$ 304.1313, found 304.1309.

*Data for benzyl (2-(2-phenylallyl)phenyl)carbamate (**1m**):* 282 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (br s, 1H), 7.46−7.28 (m, 12H), 7.20 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.64 (s, 1H), 5.48 (s, 1H), 5.20 (s, 2H), 4.86 (s, 1H), 3.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 145.7, 140.7, 136.2, 136.1, 130.9, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.7, 126.0, 124.7, 114.4, 67.1, 37.9; HRMS (ESI) m/z calcd for $C_{23}H_{21}NNaO_2$ $[M + Na]^+$ 366.1470, found 366.1463.

*Synthesis of Carbamate Substrates **1n**−**1p**.* Carbamate substrates **1n**−**1p** were synthesized according to the procedures previously reported.[17]

*Synthesis of tert-Butyl (2-Allyl-4-methylphenyl)carbamate (**1q**).* To a stirred solution of **1a** (441.6 mg, 3.0 mmol) in tetrahydrofuran (10 mL) were added di-*tert*-butyl dicarbonate (786.0 mg, 3.6 mmol) and triethylamine (TEA; 6.3 mL, 9.0 mmol). The reaction mixture was refluxed for 12 h, during which time a white precipitate formed. The solvent was removed in vacuo, and ethyl acetate (10 mL) was added to the residue. The mixture was washed with 1 M citric acid (aq) (3 × 10 mL), brined, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 60:1) to give **1q** as a white solid: 608 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.04 (dd, J = 8.0, 1.6 Hz, 1H), 6.96 (d, J = 1.6 Hz, 1H), 6.35 (s, 1H), 5.95 (ddt, J = 17.2, 10.4, 6.0 Hz, 1H), 5.15 (dq, J = 10.0, 1.6 Hz, 1H), 5.06 (dq, J = 17.2, 1.6 Hz, 1H), 3.33 (d, J = 6.0 Hz, 2H), 2.29 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 136.1, 133.8, 133.8, 130.6, 129.5, 127.9, 122.6, 116.4, 80.2, 36.5, 28.4, 20.8; HRMS (ESI) m/z calcd for $C_{15}H_{21}NNaO_2$ $[M + Na]^+$ 270.1470, found 270.1465.

*Synthesis of Carbamate Substrates **3a**−**3e**.* Carbamate substrate **3a**[18] was synthesized according to the procedures previously reported. 2-Iodo-4-methylbenzonitrile[19] was prepared according to a literature procedure. To a suspension of $Pd_2(dba)_3$ (183.1 mg, 0.2 mmol), triphenylphosphine (419.7 mg, 1.6 mmol), and lithium chloride (1.3 g, 30.0 mmol) in DMF (30 mL) was added 2-iodo-4-methylbenzonitrile (2.4 mg, 10.0 mmol) at room temperature under an argon atmosphere. After 15 min, allylindium reagent which is generated from allyl iodide (2.5 g, 15.0 mmol) and indium (1.1 g, 10.0 mmol) in DMF (5 mL) was added, and the mixture was stirred at 100 °C for 8 h. The reaction mixture was quenched with $NaHCO_3$ (satd aq). The aqueous layer was extracted with EtOAc (3 × 50 mL), and the combined organics were washed with water and brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 80:1) to afford 2-allyl-4-methylbenzonitrile (1.1 g, 68%).

*Synthesis of Benzyl (2-Allyl-4-methylbenzyl)carbamate (**3b**).* To a suspension of $LiAlH_4$ (LAH; 425.4 mg, 11.2 mmol) in THF (15 mL) at 0 °C was slowly added a solution of 2-allyl-4-methylbenzonitrile (440.2 mg, 2.8 mmol) in THF (10.0 mL). After being stirred for 3 h at 0 °C, the reaction mixture was quenched by slow, sequential addition of water (0.5 mL) in Na_2SO_4 (3.0 g). The reaction mixture was warmed to room temperature, stirred for an additional 30 min, filtered, and concentrated in vacuo to give the crude (2-allyl-4-methylphenyl)methanamine, which directly reacted with CbzCl without further purification to afford **3b**: 414 mg, 50% yield, two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−732 (m, 5H), 7.22 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 6.02−5.94 (m, 1H), 5.15-.501 (m, 5H), 4.38 (d, J = 5.6 Hz, 2H), 3.42 (d, J = 6.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 137.7, 137.6, 137.1, 136.6, 133.1, 130.8, 128.9, 128.5, 128.1, 127.4, 115.9, 66.7, 42.4, 36.9, 21.0; HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2$ $[M + Na]^+$ 318.1470, found 318.1467.

*Synthesis of Benzyl (2-Allyl-4-fluorobenzyl)carbamate (**3c**).* 2-Bromo-5-fluorobenzonitrile (400.0 mg, 2.0 mmol) was treated with

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allyltributyltin (0.81 mL, 2.6 mmol) and palladium tetrakis-(triphenylphosphine) (462.2 mg 0.4 mmol) in degassed, dry toluene (10 mL), and the mixture was refluxed for 24 h.[20] When cooled, the crude mixture was directly filtered through SiO_2, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 80:1) to give 2-allyl-5-fluorobenzonitrile (177.3 mg, 55%) as a liquid. **3c** was obtained by the procedure for the compound **3b**: 185 mg, 65% yield, two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (m, 5H), 7.27−7.23 (m, 1H), 6.90 (d, J = 9.2 Hz, 2H), 5.93 (ddt, J = 17.2, 10.4, 6.0 Hz, 1H), 5.12−4.98 (m, 5H), 4.35 (d, J = 5.6 Hz, 2H), 3.40 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 244.4 Hz), 156.2, 140.3 (d, J = 7.1 Hz), 136.4, 136.1, 131.9, 130.5 (d, J = 8.4 Hz), 128.6, 128.2, 128.2, 116.8, 116.7 (d, J = 21.2 Hz), 113.4 (d, J = 21.0 Hz), 66.9, 42.1, 36.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.85 (dd, J = 14.9, 8.8 Hz); HRMS (ESI) m/z calcd for $C_{18}H_{18}FNNaO_2$ $[M + Na]^+$ 322.1219, found 322.1214.

*Synthesis of Carbamate Substrates **3d** and **3e**.* 2-Allyl-4-chlorobenzonitrile and 2-(2-methylallyl)benzonitrile were prepared according to a literature procedure.[21] **3d** and **3e** were obtained by the procedure for the compound **3b**.

*Data for benzyl (2-allyl-4-chlorobenzyl)carbamate (**3d**):* 196 mg, 62% yield, two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 5H), 7.26−7.17 (m, 3H), 5.92(ddt, J = 17.2, 10.4, 6.0 Hz, 1H), 5.12−4.97 (m, 5H), 4.35 (d, J = 5.6 Hz, 2H), 3.39 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 139.7, 136.4, 136.0, 134.8, 133.5, 130.0, 129.9, 128.6, 128.2, 128.2, 126.8, 116.9, 67.0, 42.1, 36.7; HRMS (ESI) m/z calcd for $C_{18}H_{18}ClNNaO_2$ $[M + Na]^+$ 338.0924, found 338.0917.

*Data for benzyl [2-(2-methylallyl)benzyl]carbamate (**3e**):* 171 mg, 58% yield, two steps; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.19 (m, 9H), 5.22 (s, 1H), 5.16 (s, 2H), 4.88 (s, 1H), 4.55 (s, 1H), 4.41 (d, J = 6.0 Hz, 2H), 3.40 (s, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 144.8, 137.4, 136.5, 130.6, 128.6, 128.4, 128.0, 127.6, 126.7, 111.9, 66.6, 42.5, 41.0, 22.7; HRMS (ESI) m/z calcd for $C_{19}H_{21}NNaO_2$ $[M + Na]^+$ 318.1470, found 318.1463.

Experiments To Remove the Cbz Group. A solution of **2o** (35.5 mg, 0.1 mmol) in CH_3OH (5.0 mL) was stirred in the presence of 10% $Pd(OH)_2/C$ (60.0 mg) under H_2 (H_2 balloon) at room temperature for 24 h. The catalyst was filtered through Celite and washed with EtOAc, the filtrate was concentrated in vacuo, and the residue was purified by silica gel column chromatography (eluent CH_2Cl_2:CH_3OH = 100:1 to 30:1) to give 3-(2,2,2-trifluoroethyl)-2-azaspiro[4.5]decane (**5**) (18 mg, 81%) as a liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (s, 1H), 2.75−2.85 (m, 2H), 2.38−2.17 (m, 4H), 1.89 (s, 1H), 1.44−1.41 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6 (q, J = 275.3 Hz), 58.2, 52.1, 45.3, 43.0, 40.5 (q, J = 26.6 Hz), 38.4, 37.0, 26.1, 24.0, 23.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.31 (s, 3F); HRMS (ESI) m/z calcd for $C_{11}H_{19}F_3N$ $[M + H]^+$ 222.1470, found 222.1461. The present spectrum (^{1}H, ^{13}C, ^{19}F NMR and HRMS) is consistent with our previously reported spectrum.[4a]

General Procedure: Copper-Catalyzed Intramolecular Aminotrifluoromethylation of Unactivated Alkenes with (TMS)CF_3. Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (116.0 mg, 2.0 mmol, 4.0 equiv), $Cu(CH_3CN)_4BF_4$ (26.0 mg, 0.075 mmol, 15 mol %), carbamate substrates (0.5 mmol, 1.0 equiv), $AgNO_3$ (85.0 mg, 0.5 mmol, 1.0 equiv), DMF (superdry, 3.0 mL), and (TMS)CF_3 (0.3 mL, 2.0 mmol, 4.0 equiv). The sealed tube was then stirred at 80 °C. Upon completion (monitored by TLC), solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 80:1 to 15:1) to give the desired products. *Note: The reaction is water-sensitive; the reagents and Schlenk tube must be dried prior to use.*

*Data for benzyl 5-methyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2a**):*[4a] 98 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (br s, 1H), 7.48−7.36 (m, 5H), 7.02 (s, 2H), 5.34 (s, 2H), 4.80−4.78 (m, 1H), 3.40 (dd, J = 16.4, 9.6 Hz, 1H), 2.97 (d, J = 16.4 Hz, 1H), 2.66 (br s, 1H), 2.40−2.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (br s), 138.7 (br s), 136.1, 133.0, 129.2, 128.7, 128.5, 128.4, 128.2, 126.0 (q, J = 275.9 Hz), 125.8, 115.3, 67.5, 54.3, 38.2 (br s), 33.7 (br s), 20.8; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.86 (br s, 3F, minor), −63.24 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{19}H_{18}F_3NNaO_2$ $[M + Na]^+$ 372.1187, found 372.1182.

*Data for benzyl 7-methyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2b**):* 80 mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.34 (m, 5H), 7.08−7.02 (m, 3H), 5.27 (q, J = 12.4 Hz, 2H), 5.02 (dd, J = 14.8, 7.2 Hz, 1H), 3.47 (dd, J = 16.0, 8.0 Hz, 1H), 2.66 (d, J = 16.0 Hz, 1H), 2.50−2.39 (m, 1H), 2.31−2.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 139.6, 136.0, 131.9, 130.3, 128.9, 128.6, 128.3, 128.2, 125.8 (q, J = 275.7 Hz), 125.2, 122.3, 67.8, 56.6, 38.4 (q, J = 27.0 Hz), 35.1, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.44 (t, J = 10.6 Hz, 3F); HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NO_2$ $[M + H]^+$ 350.1368, found 350.1362

*Data for benzyl 5-methoxy-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2c**):* 111 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br s, 1H), 7.46−7.33 (m, 5H), 6.76 (s, 2H), 5.31 (s, 2H), 4.79 (s, 1H), 3.77 (s, 3H), 3.40 (dd, J = 16.4, 9.6 Hz, 1H), 2.95 (d, J = 16.4 Hz, 1H), 2.62 (br s, 1H), 2.39−2.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 152.1 (br s), 136.0, 134.8 (br s), 130.3 (br s), 128.7, 128.4, 128.2, 125.9 (q, J = 275.8 Hz), 116.0, 112.5, 111.3, 67.4 (br s), 55.6, 54.2 (br s), 38.4 (br s), 34.2 (br s); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.87 (br s, 3F, minor), −63.27 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{19}H_{18}F_3NNaO_3$ $[M + Na]^+$ 388.1136, found 388.1128.

*Data for benzyl 5-phenyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2d**):* 103 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.66−7.27 (m, 12H), 5.36 (s, 2H), 4.89−4.84 (m, 1H), 3.51 (dd, J = 16.4, 9.6 Hz, 1H), 3.08 (d, J = 16.4 Hz, 1H), 2.88−2.64 (m, 1H), 2.46−2.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (br s), 140.7, 136.8, 135.8, 128.9, 128.8, 128.5, 128.3, 127.1, 126.9, 126.9, 125.9 (q, J = 273.7 Hz), 123.9, 115.7, 67.8 (br s), 54.6 (br s), 38.5 (br s), 34.0 (br s); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.88 (br s, 3F, minor), −63.28 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{24}H_{20}F_3NNaO_2$ $[M + Na]^+$ 434.1344, found 434.1337.

*Data for benzyl 2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2e**):* 99 mg, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (br s, 1H), 7.47−7.35 (m, 5H), 7.20 (d, J = 7.2 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 5.33 (s, 2H), 4.83−4.78 (m, 1H), 3.43 (dd, J = 16.8, 9.6 Hz, 1H), 3.00 (d, J = 16.4 Hz, 1H), 2.64 (br s, 1H), 2.40−2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (br s), 140.9 (br s), 135.9, 128.7, 128.4, 128.3, 127.9, 125.9 (q, J = 275.7 Hz), 125.1, 123.4, 115.5, 67.6 (br s), 54.2 (br s), 38.3 (br s), 33.9 (br s); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.92 (br s, 3F, minor), −63.28 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3NNaO_2$ $[M + Na]^+$ 358.1031, found 358.1026.

*Data for benzyl 4,6-dimethyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2f**):* 103 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.25 (m, 6H), 6.70 (s, 1H), 5.33 (s, 2H), 4.85−4.79 (m, 1H), 3.26 (dd, J = 16.4, 9.6 Hz, 1H), 2.88 (d, J = 16.4 Hz, 1H), 2.65 (br s, 1H), 2.39−2.27 (m, 4H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (br s), 141.0 (br s), 138.0, 136.0, 134.2, 128.7, 128.4, 128.2, 125.9 (q, J = 275.8 Hz), 125.3, 124.7, 113.7, 67.5 (br s), 54.4 (br s), 38.7 (br s), 32.6 (br s), 21.6, 18.6, 18.5; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.91 (br s, 3F, minor), −63.27 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{20}H_{20}F_3NNaO_2$ $[M + Na]^+$ 386.1344, found 386.1337.

*Data for benzyl 5-fluoro-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2g**):* 102 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (br s, 1H), 7.45−7.34 (m, 5H), 6.90 (s, 1H), 6.88 (s, 1H), 5.31 (s, 2H), 4.81 (s, 1H), 3.41 (dd, J = 16.8, 9.6 Hz, 1H), 2.97 (d, J = 16.8 Hz, 1H), 2.63 (br s, 1H), 2.40−2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, J = 241.8 Hz), 152.2 (br s), 137.3 (br s), 135.7, 130.8 (br s), 128.7, 128.5, 128.3, 125.6 (q, J = 275.9 Hz), 116.2 (d, J = 8.3 Hz), 114.2 (d, J = 23.1 Hz), 112.4 (d, J = 23.9 Hz), 67.7 (br s), 54.5 (br s), 38.4 (br s), 33.9 (br s); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.91 (br s, 3F, minor), −63.29 (br s, 3F, major), −119.91 (br s, 1F, major), −120.29 (br s, 1F, minor); HRMS (ESI) m/z calcd for $C_{18}H_{15}F_4NNaO_2$ $[M + Na]^+$ 376.0937, found 376.0931.

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*Data for benzyl 5-chloro-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2h**):*[4a] 107 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br s, 1H), 7.42−7.35 (m, 5H), 7.14 (br s, 2H), 5.29 (s, 2H), 4.81−4.76 (m, 1H), 3.39 (dd, J = 16.8, 9.6 Hz, 1H), 2.96 (d, J = 16.8 Hz, 1H), 2.64 (br s, 1H), 2.38−2.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 139.8, 135.8, 131.1, 128.8, 128.6, 128.4, 128.3, 127.9, 125.8 (q, J = 275.8 Hz), 125.3, 116.5, 67.9, 54.6, 38.1, 33.6; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.93 (br s, 3F, minor), −63.27 (br s, 3F, major); HRMS (APCI) m/z calcd for $C_{17}H_{16}ClF_3N$ $[M - CO_2 + H]^+$ 326.0923, found 326.0856.

*Data for benzyl 7-chloro-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2i**):* 94 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.33 (m, 5H), 7.26 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 5.31 (s, 2H), 4.99 (td, J = 8.4, 5.2 Hz, 1H), 3.51 (dd, J = 16.0, 8.4 Hz, 1H), 2.78 (d, J = 16.0 Hz, 1H), 2.59−2.48 (m, 1H), 2.37−2.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 138.4, 135.6, 134.6, 129.7, 128.6, 128.4, 126.2, 125.7 (q, J = 275.7 Hz), 124.7, 123.4, 68.2, 57.4 (q, J = 2.6 Hz), 38.5 (q, J = 27.0 Hz), 35.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.38 (t, J = 10.6 Hz, 3F); HRMS (ESI) m/z calcd for $C_{18}H_{15}ClF_3NNaO_2$ $[M + Na]^+$ 392.0641, found 392.0633.

*Data for benzyl 5-bromo-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2j**):* 104 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (br s, 1H), 7.46−7.28 (m, 7H), 5.33 (s, 2H), 4.84−4.79 (m, 1H), 3.43 (dd, J = 16.8, 9.6 Hz, 1H), 3.00 (d, J = 16.8 Hz, 1H), 2.63 (br s, 1H), 2.41−2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (br s), 140.3 (br s), 135.6, 131.3, 130.8, 128.7, 128.6, 128.3, 128.2, 125.7 (q, J = 275.7 Hz), 116.9, 115.8, 67.9 (br s), 54.5 (br s), 38.2 (br s), 33.6 (br s); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −62.86 (br s, 3F, minor), −63.26 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{18}H_{15}BrF_3NNaO_2$ $[M + Na]^+$ 436.0136, found 436.0130.

*Data for benzyl 2-(2,2,2-trifluoroethyl)-2,3-dihydro-1H-benzo[g]indole-1-carboxylate (**2k**):* 119 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.92 (m, 1H), 7.87−7.82 (m, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.52−7.33 (m, 8H), 5.39 (d, J = 12.4 Hz, 1H), 5.25 (d, J = 12.4 Hz, 1H), 5.19 (q, J = 7.2 Hz, 1H), 3.67 (dd, J = 16.0, 8.0 Hz, 1H), 2.82 (d, J = 16.0 Hz, 1H), 2.62−2.48 (m, 1H), 2.36−2.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 136.6, 135.9, 134.0, 128.6, 128.3, 128.2, 126.6, 125.9 (q, J = 275.8 Hz), 125.5, 125.2, 124.8, 122.5, 68.0, 57.4 (q, J = 3.8 Hz), 38.7 (q, J = 26.9 Hz), 35.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.28 (t, J = 10.5 Hz, 3F); HRMS (ESI) m/z calcd for $C_{22}H_{19}F_3NO_2$ $[M + H]^+$ 386.1368, found 386.1364.

*Data for benzyl 2-methyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2l**):* 105 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.34 (m, 6H), 7.13 (d, J = 7.6 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 5.31 (dd, J = 18.4, 12.0 Hz, 2H),3.46 (d, J = 16.4 Hz, 1H), 3.05 (d, J = 16.4 Hz, 1H), 2.89 (br s, 2H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 141.6 (br s), 135.8, 128.8, 128.5, 128.4, 127.9, 126.0 (q, J = 275.8 Hz), 124.7, 123.2, 115.8, 67.6, 63.9, 42.7, 41.1 (br s), 26.5 (br s); ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.83 (s, 3F); HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3NO_2$ $[M + H]^+$ 350.1368, found 350.1361.

*Data for benzyl 2-phenyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2m**):* 70 mg, 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 8.16 (d, J = 6.4 Hz, 1H, major), 7.67 (s, 1H, minor), 7.56−6.98 (m, 13H, major + minor), 6.74 (d, J = 14.4 Hz, 1H, major + minor), 5.32−4.93 (m, 2H, major + minor), 3.95 (br s, 1H, minor), 3.76 (d, J = 17.2 Hz, 1H, major + minor), 3.56−3.45 (m, 1H, major), 3.39 (d, J = 16.8 Hz, 1H, major + minor), 3.05−2.94 (m, 1H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 152.7, 147.4, 143.2, 135.3, 129.1, 128.6, 128.5 (major), 128.5 (minor), 128.3, 128.0, 127.8, 127.3, 127.1 (overlap), 126.0, 124.2 (overlap), 123.4 (major), 123.1 (minor), 115.3, 67.2 (major), 66.2 (minor), 46.5, 45.1, 41.6 (q, J = 26.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −60.54 (br s, 3F, minor), −60.93 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{24}H_{21}F_3NO_2$ $[M + H]^+$ 412.1524, found 412.1518.

*Data for benzyl 4,4-dimethyl-2-(2,2,2-trifluoroethyl)pyrrolidine-1-carboxyl-ate (**2n**):* 66 mg, 42% yield; ^{1}H NMR (400 MHz, DMSO, observed as a mixture of rotamers, major and minor) δ 7.40−7.31 (m, 5H, major + minor), 5.11−5.09 (m, 2H, major + minor), 4.03−3.95 (m, 1H, major + minor), 3.35−3.33 (m, 1H, major + minor), 3.06−2.96 (m, 2H, major + minor), 2.84−2.75 (m, 1H, minor), 2.48−2.36 (m, 1H, major + minor), 1.96−1.91 (m, 1H, major + minor), 1.64−1.59 (m, 1H, major + minor), 1.06 (s, 3H, major + minor), 0.93 (s, 3H, major + minor); ^{13}C NMR (100 MHz, DMSO, observed as a mixture of rotamers, major and minor) δ 154.8 (major), 154.7 (minor), 137.4 (major), 137.4 (minor), 128.9, 128.3, 127.9, 127.0 (q, J = 275.3 Hz), 66.8 (minor), 66.4 (major), 58.9 (minor), 58.7 (major), 52.4 (major), 51.8 (minor), 46.1 (minor), 45.1 (major), 38.6 (q, J = 25.6 Hz, minor), 37.2 (q, J = 25.6 Hz, major), 37.8 (major), 37.5 (minor), 26.1, 25.7; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −63.26 (t, J = 11.6 Hz, 3F, major), −63.50 (t, J = 11.6 Hz, 3F, minor); ^{1}H NMR (500 MHz, DMSO, 60 °C) δ 7.51−7.43 (m, 5H), 5.28−5.19 (dd, J = 18.5, 10.5, Hz, 2H), 4.18−4.12 (m, 1H), 3.49 (d, J = 10.5 Hz, 1H), 3.15 (d, J = 10.5 Hz, H), 3.07 (br s, 1H), 2.63−2.45 (m, 1H), 2.09 (dd, J = 12.5, 7.5 Hz, 1H), 1.76 (dd, J = 12.5, 8.5 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (126 MHz, DMSO, 60 °C) δ 154.9, 137.4, 128.8, 128.3, 127.9, 127.0 (q, J = 278.1 Hz), 66.7, 59.1, 52.3, 45.6, 37.6, 26.2, 25.9; HRMS (ESI) m/z calcd for $C_{16}H_{20}F_3NNaO_2$ $[M + Na]^+$ 338.1344, found 338.1339.

*Data for benzyl 3-(2,2,2-trifluoroethyl)-2-azaspiro[4.5]decane-2-carboxylate (**2o**):* 71 mg, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 7.37−7.32 (m, 5H, major + minor), 5.21−5.09 (m, 2H, major + minor), 4.09−4.02 (m, 1H, major + minor), 3.69 (d, J = 10.8 Hz, 1H, major), 3.58 (d, J = 10.8 Hz, 1H, minor), 3.25−3.13 (m, 1H, minor), 2.96 (d, J = 11.2 Hz, 1H, major + minor), 2.92−2.80 (m, 1H, major), 2.18−2.00 (m, 2H, major + minor), 1.49−1.38 (m, 11H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 155.3 (major), 155.1 (minor), 136.8 (major), 136.4 (minor), 128.6, 128.2 (minor), 128.1 (major), 127.8, 126.3 (q, J = 275.3 Hz), 67.3 (minor), 66.9 (major), 56.7 (minor), 56.5 (major), 51.8 (major), 51.2 (minor), 44.5 (minor), 43.3 (major), 41.6 (major), 41.4 (minor), 39.6 (q, J = 25.1 Hz, minor), 38.1 (q, J = 26.4 Hz, major), 36.3, 34.4 (minor), 34.3 (major), 26.1, 23.8, 22.9 (minor), 22.8 (major); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −63.24 (t, J = 10.9 Hz, 3F, major), −63.62 (t, J = 10.9 Hz, 3F, minor); HRMS (ESI) m/z calcd for $C_{19}H_{24}F_3NNaO_2$ $[M + Na]^+$ 378.1657, found 378.1653.

*Data for benzyl 4,4-diphenyl-2-(2,2,2-trifluoroethyl)pyrrolidine-1-carboxylate (**2p**):* 88 mg, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$ observed as a mixture of rotamers, major and minor) δ 7.44−7.16 (m, 15H, major + minor), 5.35−5.11(m, 2H, major + minor), 4.73 (dd, J = 11.6, 2.0 Hz, 1H, major), 4.59 (dd, J = 11.6, 1.6 Hz, 1H, minor), 4.01−3.91 (m, 1H, major + minor), 3.73 (d, J = 11.6 Hz, 1H, major + minor), 3.28−3.15 (m, 1H, minor), 3.08−3.00 (m, 1H, major + minor), 2.97−2.84 (m, 1H, major), 2.59−2.49 (m, 1H, major + minor), 2.18−2.01 (m, 1H, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 155.0 (minor), 154.8 (major), 145.0 (major), 144.9 (minor), 144.2 (major), 144.2 (minor), 136.7 (major), 136.4 (minor), 128.8 (minor), 128.8 (major), 128.7 (minor), 128.7 (major), 128.6, 128.3 (minor), 128.2 (major), 128.1, 127.7, 126.8, 126.7, 126.3 (minor), 126.2 (major), 126.1 (q, J = 275.6 Hz), 67.3 (major), 67.2 (minor), 55.6 (minor), 55.6 (major), 53.0 (major), 52.9 (minor), 52.0 (q, J = 3.2 Hz, major), 51.5 (q, J = 3.0 Hz, minor), 44.7 (minor), 43.5 (major), 39.0 (q, J = 26.3 Hz, minor), 37.6 (q, J = 26.7 Hz, major); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ −63.08 (t, J = 11.3 Hz, 3F, major), −63.41 (t, J = 11.3 Hz, 3F, minor); HRMS (ESI) m/z calcd for $C_{26}H_{25}F_3NO_2$ $[M + H]^+$ 440.1837, found 440.1835.

*Data for tert-butyl 5-methyl-2-(2,2,2-trifluoroethyl)indoline-1-carboxylate (**2q**):* 95 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (br s, 1H), 7.01−6.96 (m, 2H), 4.69 (br s, 1H), 3.38 (dd, J = 16.4, 9.6 Hz, 1H), 2.90 (d, J = 16.4 Hz, 1H), 2.64 (br s, 1H), 2.33−2.25 (m, 4H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 (br s), 139.1 (br s), 132.6, 129.0 (br s), 128.2, 126.0 (q, J = 275.7 Hz), 125.6, 115.1, 81.5 (br s), 55.3, 54.2, 38.6 (br s), 34.1 (br s), 28.4, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ

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−62.98 (br s, 3F, minor), −63.63 (br s, 3F, major); HRMS (ESI) m/z calcd for $C_{16}H_{20}F_3NNaO_2$ $[M + Na]^+$ 338.1344, found 338.1335.

*Data for tosyl-2-(2,2,2-trifluoroethyl)indoline (**2r**):*[4a] 84 mg, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.26−7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.07−7.03 (m, 2H), 4.47−4.40 (m, 1H), 2.97−2.87 (m, 2H), 2.77 (dd, J = 16.4, 2.8 Hz, 1H), 2.51−2.40 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.9, 134.4, 130.8, 129.9, 128.3, 127.3, 125.8 (q, J = 275.9 Hz), 125.4, 125.3, 117.4, 57.0 (q, J = 3.3 Hz), 40.8 (q, J = 26.6 Hz), 34.39, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.08 (s, 3F); HRMS (ESI) m/z calcd for $C_{17}H_{17}F_3NO_2S$ $[M + H]^+$ 356.0932, found 356.0922.

*Data for benzyl 3-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**4a**):* 91 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.33 (m, 5H), 7.25−7.12 (m, 4H), 5.22 (s, 2H), 5.05−4.85 (m, 2H), 4.39 (dd, J = 17.6, 11.2 Hz, 1H), 3.17 (d, J = 16.0 Hz, 1H), 2.78 (dd, J = 24.0, 16.0 Hz, 1H), 2.40−2.28 (m, 1H), 2.12−2.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 155.2 (minor), 155.0 (major), 136.5 (major), 136.3 (minor), 132.0 (major), 131.8 (minor), 131.7 (minor), 131.3 (major), 129.4 (minor), 129.2 (major), 128.6, 128.2, 128.1, 127.2 (major), 127.1 (minor), 126.9 (major), 126.9 (minor), 126.4 (minor), 126.2 (major), 126.0 (q, J = 275.5 Hz), 67.7 (major), 67.6 (minor), 45.0 (major), 44.8 (minor), 43.0, 35.7 (q, J = 26.8 Hz), 33.6 (minor), 33.1 (major); ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.83 (t, J = 10.5 Hz, 3F); HRMS (ESI) m/z calcd for $C_{19}H_{18}F_3KNO_2$ $[M + K]^+$ 388.0927, found 388.0937.

*Data for benzyl 6-methyl-3-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**4b**):* 109 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.32 (m, 5H), 7.08−6.96 (m, 3H), 5.21 (s, 2H), 5.04−4.88 (m, 1H), 4.84 (t, J = 18.0, 1H), 4.34 (dd, J = 16.8, 9.2 Hz, 1H), 3.12 (d, J = 15.6 Hz, 1H), 2.73 (dd, J = 24.0, 16.0 Hz, 1H), 2.39−2.26 (m, 4H), 2.11- 2.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 155.3 (major), 155.0 (minor), 136.9 (minor), 136.8 (major), 136.5 (major), 136.4 (minor), 131.6 (minor), 131.2 (major), 130.0 (major), 129.8 (minor), 129.0 (major), 128.8 (minor), 128.6, 128.2, 128.1, 127.8 (major), 127.7 (minor), 126.3 (minor), 126.1 (major), 126.1 (q, J = 275.6 Hz), 67.7 (major), 67.5 (minor), 45.0 (minor), 44.9 (major), 42.9, 35.8 (q, J = 26.8 Hz), 33.6 (major), 33.1 (minor), 21.1; ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, A and B) δ −63.92 (t, J = 10.9 Hz, 3F, A), −64.14 (t, J = 10.9 Hz, 3F, B); HRMS (ESI) m/z calcd for $C_{20}H_{20}F_3NNaO_2$ $[M + Na]^+$ 386.1344, found 386.1337.

*Data for benzyl 6-fluoro-3-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**4c**):* 83 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.32 (m, 5H), 7.15−706 (m, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.87 (t, J = 10.0 Hz, 1H), 5.20 (s, 2H), 5.04−4.79 (m, 2H), 4.34 (dd, J = 16.8, 11.6 Hz, 1H), 3.14 (dd, J = 16.0, 3.6 Hz, 1H), 2.75 (dd, J = 25.6, 16.0 Hz, 1H), 2.39−2.26 (m, 1H), 2.10−1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 161.7 (d, J = 244.5 Hz), 155.2 (major), 155.0 (minor), 136.4 (major), 136.3 (minor), 128.6, 128.3, 128.2, 128.1 (minor), 128.0 (major), 127.9 (minor), 127.8 (major), 125.9 (q, J = 275.3 Hz), 115.9 (t, J = 20.8 Hz), 114.3 (d, J = 7.9 Hz), 114.1 (d, J = 5.4 Hz), 67.8 (major), 67.7 (minor), 44.7 (major), 44.6 (minor), 42.6 (major), 42.5 (minor), 35.7 (q, J = 27.2 Hz), 33.7 (major), 33.2 (minor); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, A and B) δ −63.91 (t, J = 11.7 Hz, 3F, A), −64.14 (t, J = 12.0 Hz, 3F, B), −115.18 to −115.24 (m, 1F, A), −115.32--115.36 (m, 1F, B); HRMS (ESI) m/z calcd for $C_{19}H_{17}F_4NNaO_2$ $[M + Na]^+$ 390.1093, found 390.1087.

*Data for benzyl 6-chloro-3-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**4d**):* 84 mg, 44% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.03 (m, 8H), 5.20 (s, 2H), 5.03−4.80 (m, 2H), 4.32 (dd, J = 17.2, 12.8 Hz, 1H), 3.15−3.10 (m, 1H), 2.74 (dd, J = 26.0, 16.0 Hz, 1H), 2.34−2.26 (m, 1H), 2.07−2.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, observed as a mixture of rotamers, major and minor) δ 155.1 (major), 154.9 (minor), 136.4 (minor), 136.2 (major), 133.7 (minor), 133.2 (major), 132.8 (minor), 132.8 (major), 130.5 (major), 130.3 (minor), 129.3 (major), 129.1 (minor), 128.6, 128.3, 128.2, 127.8 (major), 127.6 (minor), 127.3 (major), 127.2 (minor), 125.9 (q, J = 275.9 Hz), 67.9 (minor), 67.7 (major), 44.7 (major), 44.5 (minor), 42.6 (minor), 42.5 (major), 35.7 (q, J = 26.4 Hz), 33.5 (major), 33.0 (minor); ^{19}F NMR (376 MHz, $CDCl_3$, observed as a mixture of rotamers, A and B) δ −63.93 (t, J = 10.8 Hz, 3F, A), −64.16 (t, J = 10.8 Hz, 3F, B); HRMS (ESI) m/z calcd for $C_{19}H_{17}ClF_3NNaO_2$ $[M + Na]^+$ 406.0798, found 406.0792.

*Data for benzyl 3-methyl-3-(2,2,2-trifluoroethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (**4e**):* 100 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.21 (m, 9H), 5.21 (dd, J = 20.4, 12.4 Hz, 2H), 4.79 (d, J = 14.8 Hz, 1H), 4.47 (d, J = 14.8 Hz, 1H), 3.33 (d, J = 14.8 Hz, 1H), 2.92−2.67 (m, 3H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 136.5, 135.2, 135.2, 128.6, 128.1, 128.0, 127.9, 127.6, 127.0, 126.2 (q, J = 276.3 Hz), 125.6, 67.2, 56.1, 46.0, 41.4, 40.1 (br s), 26.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −59.78 (t, J = 11.6 Hz, 3F); HRMS (ESI) m/z calcd for $C_{20}H_{20}F_3NNaO_2$ $[M + Na]^+$ 386.1344, found 386.1337.

Direct Intramolecular Carbotrifluoromethylation of Alkenes. An oven-dried vessel equipped with a magnetic stir bar was charged with activated KF (138.0 mg, 1.0 mmol, 10.0 equiv), $Cu(CH_3CN)_4BF_4$ (8.5 mg, 0.025 mmol, 25 mol %), **3f** (17.5 mg, 0.1 mmol, 1.0 equiv), $AgNO_3$ (17.0 mg, 0.1 mmol, 1.0 equiv), DMF (superdry, 1.0 mL), and $(TMS)CF_3$ (0.15 mL, 1.0 mmol, 10.0 equiv). The sealed vessel was then stirred at 80 °C for 72 h. DMF was removed in vacuo, and the residue was purified by silica gel column chromatography (eluent petroleum ether:EtOAc = 90:1 to 40:1) to give the desired products. The present spectrum (^{1}H, ^{13}C and ^{19}F NMR) is consistent with our previously reported spectrum.[4b]

Experiments for the Mechanism Study. *Note: The reaction is water-sensitive; the reagents and Schlenk tube must be dried prior to use.*

Reaction of TEMPO with $(TMS)CF_3$.[8a] Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (23.2 mg, 0.4 mmol), $Cu(CH_3CN)_4BF_4$ (5.1 mg, 0.015 mmol), $AgNO_3$ (17.0 mg, 0.1 mmol), TEMPO (15.6 mg, 0.1 mmol), DMF (superdry, 0.6 mL), and $(TMS)CF_3$ (59 μL, 0.4 mmol). The sealed tube was then stirred at 80 °C for 16 h and cooled to room temperature, and α,α,α-trifluorotoluene (internal standard, 14.6 mg, 0.1 mmol) was added. ^{19}F NMR analysis of this reaction mixture showed that TEMPO−CF_3 was formed in 0% yield.

*Reaction of TEMPO and $(TMS)CF_3$ with **1a**.*[8a] Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (11.6 mg, 0.2 mmol), **1a** (14.0 mg, 0.05 mmol), $Cu(CH_3CN)_4BF_4$ (2.6 mg, 0.0075 mmol), $AgNO_3$ (8.5 mg, 0.05 mmol), TEMPO (7.8 mg, 0.05 mmol, or 15.6 mg, 0.1 mmol), DMF (superdry, 0.3 mL), and $(TMS)CF_3$ (29.5 μL, 0.2 mmol). The sealed tube was then stirred at 80 °C for 16 h and cooled to room temperature, and α,α,α-trifluorotoluene (internal standard, 7.3 mg, 0.05 mmol) was added. ^{19}F NMR analysis of this reaction mixture showed that **2a** was formed in 46% yield (TEMPO, 1.0 equiv) and 30% yield (TEMPO, 2.0 equiv).

*Reaction of BHT and $(TMS)CF_3$ with **1a**.* Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (11.6 mg, 0.2 mmol), **1a** (14.0 mg, 0.05 mmol), $Cu(CH_3CN)_4BF_4$ (2.6 mg, 0.0075 mmol), $AgNO_3$ (8.5 mg, 0.05 mmol), BHT (11.0 mg, 0.05 mmol), DMF (superdry, 0.3 mL), and $(TMS)CF_3$ (29.5 μL, 0.2 mmol). The sealed tube was then stirred at 80 °C for 16 h and cooled to room temperature, and α,α,α-trifluorotoluene (internal standard, 7.3 mg, 0.05 mmol) was added. ^{19}F NMR analysis of this reaction mixture showed that **2a** was formed in 10% yield.

Reaction of $CuCF_3$[7i] *with **1a**.* Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (2.9 mg, 0.05 mmol), $(TMS)CF_3$ (7.4 μL, 0.05 mmol), $Cu(CH_3CN)_4BF_4$ (17.1 mg, 0.05 mmol), and DMF (superdry, 0.3 mL). The sealed tube was then stirred at 25 °C for 30 min, and **1a** (14.0 mg, 0.05 mmol), $AgNO_3$ (8.5 mg, 0.05 mmol), and $Cu(CH_3CN)_4BF_4$ (2.6 mg, 0.0075 mmol) were added under argon. The sealed tube was then stirred at 80 °C for an additional 16 h and cooled to room temperature, and α,α,α-trifluorotoluene (internal standard, 7.3 mg, 0.05 mmol) was added. ^{19}F NMR analysis of this reaction mixture showed that **2a** was formed in 0% yield.

Reaction of $AgCF_3$[7g] *with **1a**.* Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with activated KF (11.6 mg, 0.2 mmol), $(TMS)CF_3$ (29.5 μL, 0.2 mmol),

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$AgNO_3$ (34.0 mg, 0.2 mmol), and DMF (superdry, 0.3 mL). The sealed tube was then stirred at 25 °C for 30 min, and **1a** (14.0 mg, 0.05 mmol) and $Cu(CH_3CN)_4BF_4$ (2.6 mg, 0.0075 mmol) were added under argon. The sealed tube was then stirred at 80 °C for an additional 16 h and cooled to room temperature, and α,α,α-trifluorotoluene (internal standard, 7.3 mg, 0.05 mmol) was added. ^{19}F NMR analysis of this reaction mixture showed that **2a** was formed in 57% yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Compound characterization, including ^{1}H, ^{13}C, and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Eq 4 and 5 were missing from Scheme 3 in the version published ASAP July 16, 2014; the correct version reposted July 18, 2014.