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Photomediated C–H trifluoromethoxylations enabled by bis(trifluoromethyl)peroxide

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We describe a photomediated protocol for the trifluoromethoxylation of benzylic, aldehydic, and non-activated C–H bonds, using bis(trifluoromethyl)peroxide (BTMP, (F₃CO)₂) as the key reagent. Under catalyst-free conditions in acetone, this reaction proceeds with selective functionalization of benzylic methylene groups. Furthermore, by using tetrabutylammonium decatungstate as a photocatalyst, the scope extends to include both non-activated methylene C(sp³)–H and formyl C(sp²)–H bonds. The methodology was successfully applied to 24 examples including odorants, pharmaceuticals, and natural products and was demonstrated on gram scale. Finally, by using [¹³C]-BTMP, the corresponding trifluoromethoxy groups can be site-specifically labeled with ¹³C.

Introduction

The strategic incorporation of fluorine into agrochemicals and pharmaceuticals has become critical for optimizing their metabolic stability, lipophilicity, and conformational properties.^{1–8} However, increasing concerns over the persistence of many fluorinated compounds have led the EU to initiate a ban on per- and polyfluoroalkyl substances (PFAS).⁹ Notably, compounds bearing trifluoromethoxy (–OCF₃) groups are exempt from this regulation, as they degrade under biological conditions into non-persistent molecules.¹⁰

Despite the well-established benefits of incorporating fluorine into drug design, trifluoromethoxy (–OCF₃) groups remain significantly underrepresented in approved pharmaceuticals. While 68% of fluoro-pharmaceuticals contain a C–F bond and 22% feature a C–CF₃ moiety, only 2% bear a C–OCF₃ group (Scheme 1).¹¹ This scarcity is particularly pronounced for C(sp³)–OCF₃ containing compounds. The limited utilization of this valuable functional group can be largely attributed to the lack of efficient and broadly applicable synthetic methods for accessing trifluoromethoxylated molecules. Direct C–H functionalization strategies for the installation of trifluoromethoxy groups offer a particularly promising route to streamline access to OCF₃-containing targets in drug discovery.^{12–22}

Although numerous methods have been reported for the C–H trifluoromethoxylation of aromatic compounds,^{9–27} the corresponding transformations on aliphatic C–H bonds remain largely unexplored.²⁸ Only one method has been reported for the

benzylic C–H trifluoromethoxylation, developed by Xu, Tang, and coworkers, which requires the use of silver salts in catalytic to stoichiometric amounts depending on the substrate.²⁹ Moreover, no general procedure exists for the trifluoromethoxylation of non-activated alkanes, significantly restricting access to trifluoromethoxylated alkyl derivatives.

Hopkinson and Riedel recently demonstrated the use of bis(trifluoromethyl)peroxide (BTMP, (F₃CO)₂) for trifluoromethoxylation of arenes, silyl enol ethers, and allyl silanes.^{30–35} Despite being a peroxide, BTMP remains remarkably stable up to 200 °C, is an easy to handle gas, and can be prepared in large quantities from abundant starting materials.^{36,37} Its two –OCF₃ units provide superior atom economy compared to other trifluoromethoxylation reagents.^{30,31} Here, we report that BTMP is a versatile reagent for the direct C–H trifluoromethoxylation of benzylic positions, non-activated alkanes, and aldehydes.

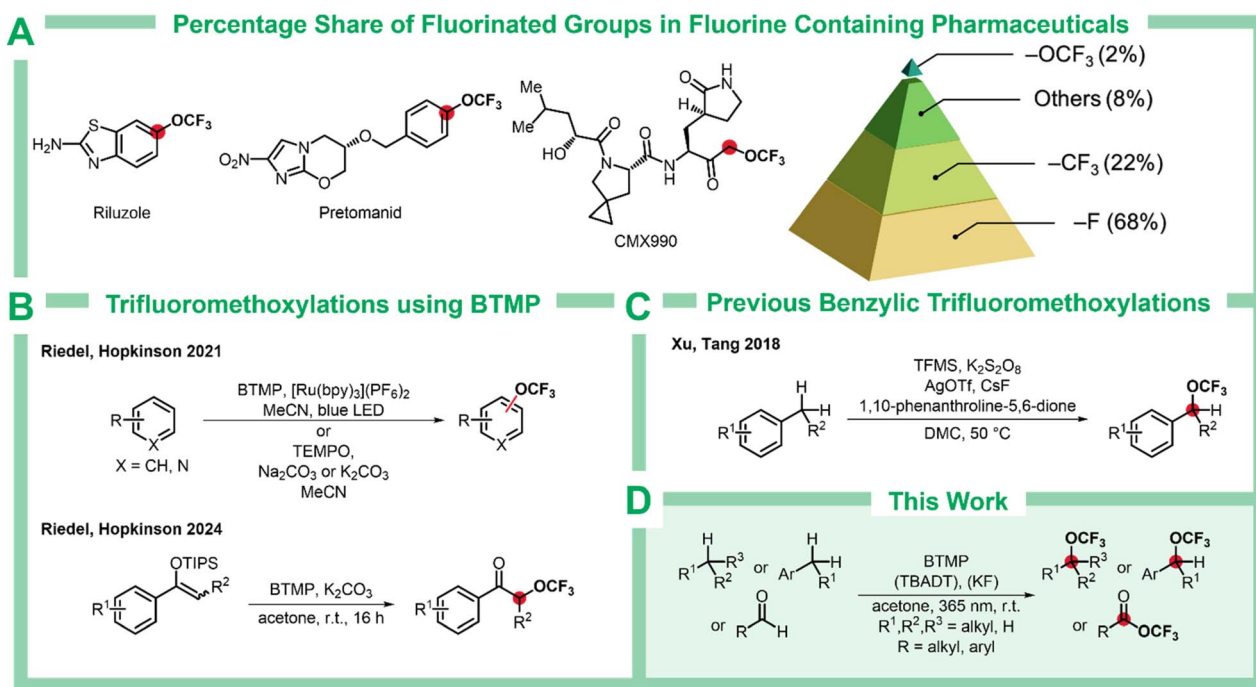
Results and discussion

To investigate the C–H trifluoromethoxylation of benzylic positions using BTMP, we selected ethylbenzene (**1a**) as a model substrate for screening. Given the established versatility of decatungstate catalysis in photochemical C–H functionalizations,^{37–42} tetrabutylammonium decatungstate (TBADT) was selected as the catalyst. Subsequent reaction with BTMP was expected to yield the corresponding trifluoromethyl ether **2a**. Initial experiments involved irradiating a solution of ethylbenzene (**1a**) and TBADT in acetonitrile under UV light for 18 h. This reaction provided **2a** in a yield of 18% (Table 1, entry 1). To optimize the reaction conditions, acetone was investigated as an alternative solvent, which significantly improved the yield of **2a** to 55% (Table 1, entry 2).

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Scheme 1 (A) Percentage share of fluorinated groups in fluorine containing substrates in pharmaceutical industry and some examples. (B) Previous trifluoromethoxylations using BTMP. (C) Benzylic C–H trifluoromethoxylation by Xu, Tang, and coworkers. (D) C–H trifluoromethoxylation of benzylic, non-activated, and aldehydic C–H bonds. Bpy = 2,2′-bipyridine, TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, TFMS = trifluoromethyl 4-fluorobenzenesulfonate, Tf = trifluoromethanesulfonyl, DMC = dimethyl carbonate, TBADT = tetrabutylammonium decatungstate.

Table 1 Optimization and Control Experiments

Entry	X (mol%)	Solvent	Conc. (M)	Time [h]	Yield ^a (%)
1	5	MeCN	0.24	18	18
2	5	Acetone	0.24	18	55
3	5	Acetone/HFIP (10 : 1)	0.24	18	34
4 ^b	5	Acetone	0.24	18	29
5	5	Acetone	0.48	18	46
6	10	Acetone	0.24	18	31
7 ^c	5	Acetone	0.24	18	38
8	5	Acetone	0.24	2	60
9	5 ^d	Acetone	0.24	2	27
10 ^e	5	Acetone	0.24	4	Traces
11	—	Acetone	0.24	4	66

^a Determined by ¹⁹F NMR spectroscopy using α,α,α -trifluorotoluene (PhCF₃) as internal standard. ^b Performed with 1.00 equivalent KF as additive. ^c Using 4 equivalents BTMP. ^d Using NaDT instead of TBADT. ^e Reaction conducted under exclusion of light.

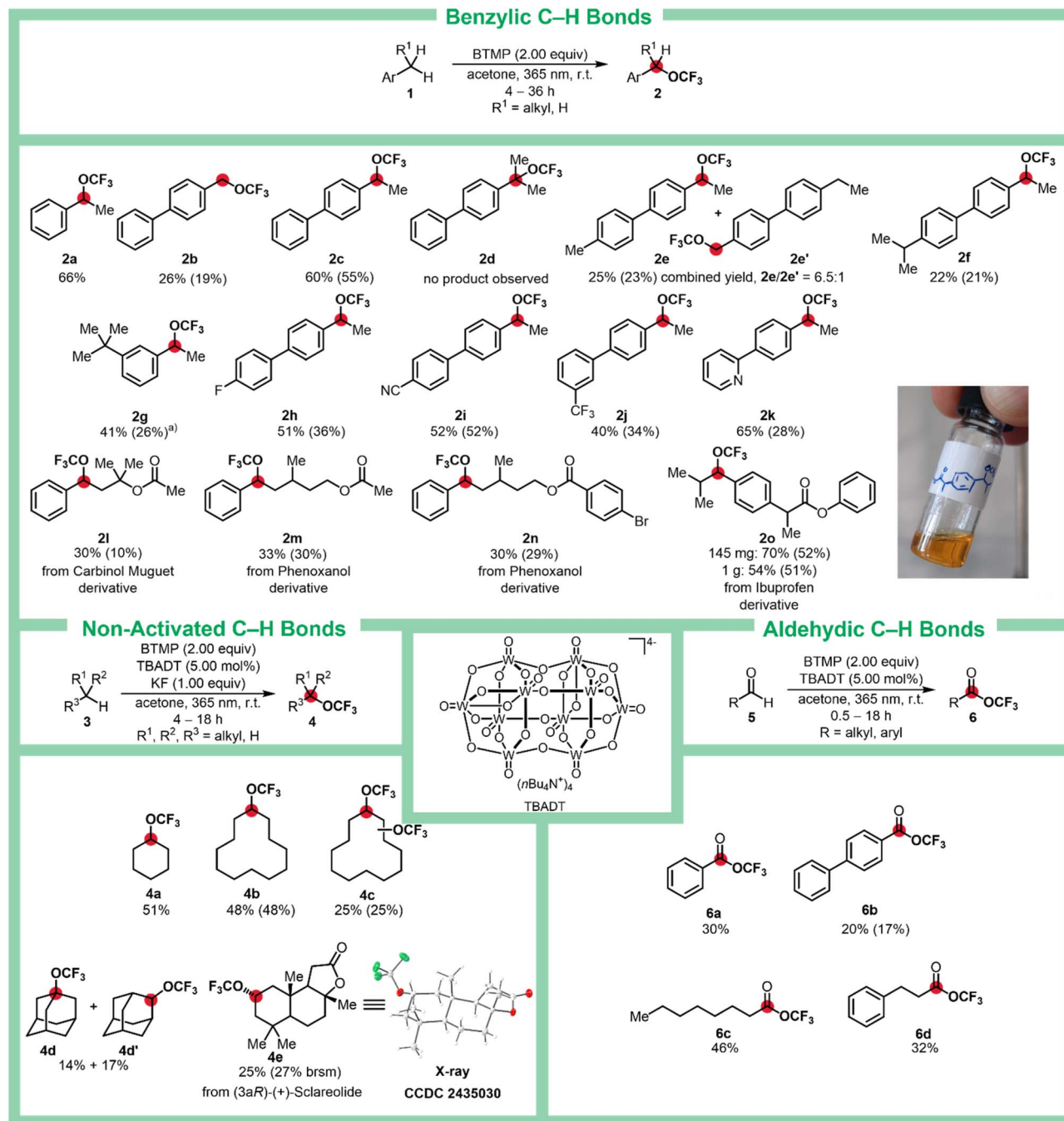
Addition of hexafluoroisopropanol (HFIP) resulted in a reduced yield of 34% (Table 1, entry 3). Similarly, KF as an additive showed no improvement (Table 1, entry 4).

Changing the reaction molarity or catalyst loading also diminished yields (Table 1, entries 5 and 6). Also, increasing the amount of BTMP to 4 equivalents lead to a decreased yield of 38% (Table 1, entry 7). Shortening the reaction time to 2 h significantly increased the yield to 60% (Table 1, entry 8). Longer reaction times resulted in further decomposition of the substrate. The substitution of TBADT with sodium decatungstate (NaDT) resulted in a lower yield (Table 1, entry 9). Control experiments conducted under exclusion of light yielded only trace amounts of **2a** (Table 1, entry 10). Surprisingly, performing the reaction in the absence of a catalyst gave the highest yield of 66% (Table 1, entry 11).

With the optimized conditions established, the trifluoromethoxylation protocol was explored over a range of benzylic substrates (Scheme 2). First, the effect of primary, secondary, and tertiary benzylic positions on the reaction outcome was investigated. For a substrate with a benzylic methyl group, the corresponding trifluoromethoxy derivative **2b** was obtained in 19% yield. In contrast, a substrate with a benzylic methylene group showed a significant improvement, yielding **2c** in 55%. However, when a tertiary benzylic substrate was employed, no formation of **2d** was observed.

The selectivity for benzylic methylene groups was demonstrated through competition experiments using biphenyl derivatives with ethyl/methyl or ethyl/isopropyl substituents, as exemplified by **2e** and **2f**, respectively. Starting from 4-ethyl-4′-methyl-1,1′-biphenyl, trifluoromethoxylation yielded **2e** and its constitutional isomer **2e′** in a 6.5 : 1 ratio, with a combined yield





Scheme 2 Scope of trifluoromethyl ethers **2**, **4**, and **6**, by C–H trifluoromethoxylation using BTMP. All yields were determined by ^{19}F NMR spectroscopy using α, α, α -trifluorotoluene (PhCF_3) as internal standard. Isolated yields are given in parenthesis. (a) Obtained as a 2 : 1 mixture with the starting material determined by ^1H NMR spectroscopy.

of 23%, demonstrating a strong preference for the methylene group over the methyl group. In the presence of a tertiary benzylic C–H bond, functionalization occurred exclusively in the secondary benzylic position, yielding **2f** with an isolated yield of 21%.

The protocol was shown to exhibit tolerance for functional groups such as *tert*-butyl (**2g**, 26% yield), fluorine (**2h**, 36% yield), cyano (**2i**, 52% yield), and trifluoromethyl (**2j**, 34% yield) substituents. A pyridinyl group was also tolerated, affording **2k**

in 28% yield. Furthermore, the stability of aliphatic and benzylic esters under the reaction conditions was demonstrated by the synthesis of trifluoromethoxylated derivatives of the odorants Carbinol Muguet (**2l**, 10% yield), phenoxanol (**2m**, 30% yield), and **2n** (29% yield).

Notably, the Ibuprofen derivative **1o** was selectively functionalized at the secondary benzylic position, affording trifluoromethyl ether **2o** in 52% yield. To showcase the scalability



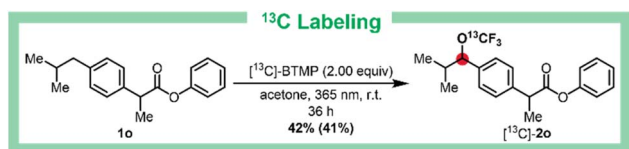
of the trifluoromethoxylation protocol, **2o** was also prepared on a gram scale, achieving a comparable yield of 51%.

The benzylic trifluoromethoxylation using BTMP offers a significant improvement in the atom economy.⁴³ For instance, the synthesis of compound **2c** requires a total reagent-to-substrate mass ratio of 2 : 1 with BTMP (55% yield), compared to the 15 : 1 ratio reported in the method by Xu, Tang, and coworkers (58% yield) (see SI, chapter 3).²⁹

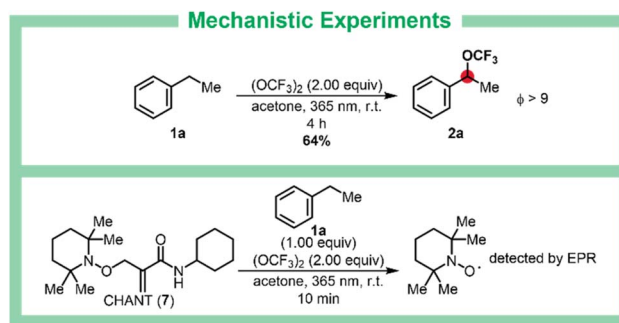
Next, we focused on the functionalization of non-activated and aldehydic C–H bonds (see SI, chapter 7, for screening details). Using TBADT and KF in acetone, we obtained trifluoromethylcyclohexyl ether (**4a**) in 51% yield, as determined by ¹⁹F NMR. With cyclododecane as the substrate, **4b** was isolated as a colorless liquid in 48% yield. Notably, **4b** could undergo a second functionalization under the same reaction conditions, affording the double-functionalized product **4c** in 25% yield. Additionally, adamantane was C–H trifluoromethylated at both the secondary and tertiary positions, yielding **4d** and **4d'** in 14% and 17% ¹⁹F NMR yield, respectively. The protocol was also successfully applied to the natural product (3aR)-(+)-sclareolide, providing the corresponding trifluoromethylether **4e** as a single diastereomer in 25% yield. The structure of **4e** was unambiguously confirmed by single-crystal X-ray diffraction, with crystals of **4e** obtained through slow evaporation of a solution in a dichloromethane–cyclohexane mixture.

Expanding the scope of C–H activated groups to aldehydes enabled the preparation of trifluoromethyl esters **6a–6d**, providing a novel approach to access these compounds.⁴⁴ For benzaldehyde, the corresponding ester **6a** was obtained in 30% ¹⁹F NMR yield. Using the heavier analog **5b**, trifluoromethyl ester **6b** was isolated in 17% yield. Aliphatic aldehydes were also successfully transformed, as evidenced by the formation of **6c** (46% ¹⁹F NMR yield) and **6d** (32% ¹⁹F NMR yield).

Stable-isotope-labeled substrates are crucial in chemical, biomedical, and environmental research, offering powerful tools for monitoring drugs in biological systems, tracking metabolic processes, and accelerating drug discovery.^{45–49} To this end, we developed a synthesis of ¹³C-labeled bis(trifluoromethyl)peroxide (¹³[C]-BTMP) from commercially available ¹³CO and F₂ (see SI, chapter 2). This reagent enables simultaneous C–H trifluoromethoxylation and ¹³C-labeling of various compounds in a single step using our C–H trifluoromethoxylation protocol. As an example, the ¹³C-labeled ibuprofen derivative [¹³C]-**2o** was prepared in 41% isolated yield using [¹³C]-BTMP (Scheme 3). For a deeper mechanistically



Scheme 3 One step trifluoromethoxylation and ¹³C labeling of ibuprofen derivative **1o**. Yield was determined by ¹⁹F NMR spectroscopy using α,α,α -trifluorotoluene (PhCF₃) as internal standard. Isolated yield is given in parenthesis.

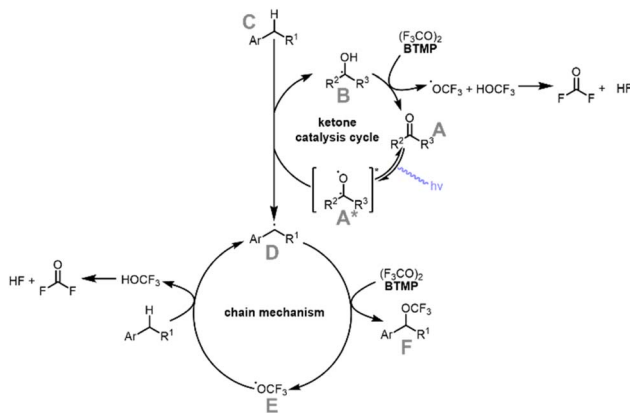


Scheme 4 Mechanistic Experiments. Yield was determined by ¹⁹F NMR spectroscopy using α,α,α -trifluorotoluene (PhCF₃) as internal standard. CHANT = *N*-cyclohexyl-2-((2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)acrylamide, TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

insight into the catalyst-free benzylic trifluoromethoxylation, quantum yield experiment and EPR spectroscopy were conducted (Scheme 4).⁵⁰ The quantum yield of $\Phi > 9$ indicates a chain reaction process.⁵¹ Notably, neither UV/Vis spectra of the reaction mixture nor of acetone mixed with BTMP shows significant difference to the UV/Vis spectra of pure acetone. But when mixing acetone with BTMP and irradiating the mixture for 4 h, mesityl oxide as well as phorone could be detected by HRMS. During the irradiation process, there must be the formation of these two species from acetone. We cannot exclude the existence of traces of mesityl oxide or phorone at the beginning of the reaction mixture even though we could not detect any in HRMS or UV/Vis before starting irradiation. This leak of absorption hints quite efficient radical chain process. The release of TEMPO from *N*-cyclohexyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)acrylamide (**7**) (CHANT)⁵² (proven by EPR) under standard reaction conditions shows formation of a radical species (see SI, chapter 8).

On the base of these observations, a plausible reaction mechanism suggests a radical chain propagation pathway for the trifluoromethoxylation of benzylic C–H bonds (Scheme 5).

The proposed reaction mechanism begins with the excitation of acetone or traces of mesityl oxide or phorone (A) by UV light irradiation, potentially forming the excited state A*.



Scheme 5 Plausible reaction mechanism.



subsequent hydrogen atom transfer (HAT) step may lead to the formation of the intermediate B, which is hypothesized to reduce BTMP. This reduction could trigger mesolytic cleavage, forming an OCF₃ radical and HOCF₃. The HOCF₃ is proposed to further decompose to fluorophosgene and HF. Acetone appears to be regenerated in the process, possibly completing the catalytic cycle. In parallel, a benzylic radical (D) could be generated, which is proposed to react with BTMP to yield the functionalized product F and another OCF₃ radical (E). This radical could propagate the chain reaction by abstracting a hydrogen atom from another benzylic C–H bond, regenerating radical D and maintaining the reaction cycle.

Conclusion

In conclusion, we have developed a C–H trifluoromethoxylation protocol utilizing BTMP as an OCF₃ source, enabling the functionalization of benzylic, non-activated, and aldehydic positions. Notably, trifluoromethoxylation of benzylic positions was achieved even in the absence of a catalyst. For non-activated and aldehydic C–H bonds, the use of TBADT as a catalyst expanded the scope of the methodology. The protocol was successfully applied to 24 examples, delivering products in moderate to good yields, and its scalability was demonstrated by performing the reaction on a gram scale.

Additionally, we synthesized a ¹³C-labeled peroxide ([¹³C]-BTMP), which facilitates simultaneous C–H trifluoromethoxylation and ¹³C labeling in a single step, as exemplified by the preparation of the Ibuprofen derivative [¹³C]-**2o**. Finally, mechanistic studies suggest the possibility of a radical chain mechanism.

Author contributions

K. S., M. K., S. R., and M. C. conceived the methodology. K. S. carried out the synthetic experiments. P. G. and T. D. prepared BTMP. M. W. performed XRD measurement. K. S., M. K., S. R., and M. C. wrote the manuscript.

Conflicts of interest

K. S., M. K., P. G., S. R., and M. C. are inventors of a pending patent related to this work, submitted by Freie Universität Berlin (25174771.3). The authors declare that they have no other competing interests.

Data availability

CCDC 2435030 (**4e**) contains the supplementary crystallographic data for this paper.⁵³

Supplementary information: The data supporting this article have been included as part of the SI. See DOI: <https://doi.org/10.1039/d5sc04945h>.

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Notes and references

- 1 S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330.
- 2 T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2013, **52**, 8214–8264.
- 3 K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881–1886.
- 4 T. Fujiwara, D. O'Hagan and J. Fluor, *Chem*, 2014, **167**, 16–29.
- 5 A. Harsanyi and G. Sandford, *Green Chem.*, 2015, **17**, 2081–2086.
- 6 N. A. Meanwell, *J. Med. Chem.*, 2018, **61**, 5822–5880.
- 7 H. Mei, J. Han, S. Fustero, M. Medio-Simon, D. M. Sedgwick, C. Santi, R. Ruzzicone and V. A. Soloshonok, *Chem.–Eur. J.*, 2019, **25**, 11797–11819.
- 8 X. Huang, T. Besset, P. Jubault and S. Couve-Bonnaire, *Adv. Synth. Catal.*, 2023, **365**, 2467–2486.
- 9 BAuA (DE), RIVM (NL), KEM (SE), NEA (NO) and DEPA (DK), *Annex XV Restriction Report Per- and Polyfluoroalkyl Substances (PFAS)*, Helsinki, 2023.
- 10 T. Frömel and T. P. Knepper, *J. Fluorine Chem.*, 2015, **177**, 80–89.
- 11 M. Inoue, Y. Sumii and N. Shibata, *ACS Omega*, 2020, **5**, 10633–10640.
- 12 A. Tlili, F. Toulgoat and T. Billard, *Angew. Chem., Int. Ed.*, 2016, **55**, 11726–11735.
- 13 T. Besset, P. Jubault, X. Pannecoucke and T. Poisson, *Org. Chem. Front.*, 2016, **3**, 1004–1010.
- 14 S. Barata-Vallejo, S. M. Bonesi and A. Postigo, *Chem.–Eur. J.*, 2022, **28**, e202201776.
- 15 Q. Wang, X. Zhang, A. E. Sorochinsky, G. Butler, J. Han and V. A. Soloshonok, *Symmetry*, 2021, **13**, 2380.
- 16 K. N. Lee, J. W. Lee and M. Y. Ngai, *Tetrahedron*, 2018, **74**, 7127–7135.
- 17 P. Chen and G. Liu, *Synthesis*, 2013, **45**, 2919–2939.
- 18 G. Landelle, A. Panossian and F. R. Leroux, *Curr. Top. Med. Chem.*, 2014, **14**, 941–951.
- 19 A. Turksoy, T. Scattolin, S. Bouayad-Gervais and F. Schoenebeck, *Chem.–Eur. J.*, 2020, **26**, 2183–2186.
- 20 G. Chen, P. Chen and G. Liu, *J. Am. Chem. Soc.*, 2015, **137**, 15648–15651.
- 21 M. Zhou, C. Ni, Y. Zeng and J. Hu, *J. Am. Chem. Soc.*, 2018, **140**, 6801–6805.
- 22 C. Delobel, A. Panossian, G. Hanquet, F. R. Leroux, F. Toulgoat and T. Billard, *Beilstein J. Org. Chem.*, 2024, **20**, 2434–2441.



- 23 W. Zheng, C. A. Morales-Rivera, J. W. Lee and M. Y. Ngai, *Angew. Chem., Int. Ed.*, 2018, **57**, 9645–9649.
- 24 W. Zheng, J. W. Lee, C. A. Morales-Rivera, P. Liu and M. Y. Ngai, *Angew. Chem., Int. Ed.*, 2018, **57**, 13795–13799.
- 25 J. W. Lee, S. Lim, D. N. Maienshein, P. Liu and M. Y. Ngai, *Angew. Chem., Int. Ed.*, 2020, **59**, 21475–21480.
- 26 B. J. Jelier, P. F. Tripet, E. Pietrasiak, I. Franzoni, G. Jeschke and A. Togni, *Angew. Chem., Int. Ed.*, 2018, **57**, 13784–13789.
- 27 A. V. Nyuchev, T. Wan, B. Cendón, C. Sambigiagio, J. J. C. Struijs, M. Ho, M. Gulías, Y. Wang and T. Noël, *Beilstein J. Org. Chem.*, 2020, **16**, 1305–1312.
- 28 X. Qi, P. Chen and G. Liu, *Angew. Chem., Int. Ed.*, 2017, **56**, 9517–9521.
- 29 H. Yang, F. Wang, X. Jiang, Y. Zhou, X. Xu and P. Tang, *Angew. Chem., Int. Ed.*, 2018, **57**, 13266–13270; for calculation see SI chapter 3.
- 30 S. Dix, P. Golz, J. R. Schmid, S. Riedel and M. N. Hopkinson, *Chem.–Eur. J.*, 2021, **27**, 11554–11558.
- 31 L. M. Maas, C. Fasting, P. Voßnacker, N. Limberg, P. Golz, C. Müller, S. Riedel and M. N. Hopkinson, *Angew. Chem., Int. Ed.*, 2024, **63**, e202317770.
- 32 For previous applications of (F₃CO)₂ under drastic conditions with limited substrate scope, see ref. 33 and 34.
- 33 H. L. Roberts, *J. Chem. Soc.*, 1964, 4538–4540.
- 34 M. S. Toy and R. S. Stringham, *J. Fluorine Chem.*, 1976, **7**, 375–383.
- 35 W. J. Peláez and G. A. Argüello, *Tetrahedron Lett.*, 2010, **51**, 5242–5245.
- 36 J. H. Nissen, T. Drews, B. Schröder, H. Beckers, S. Steinhauer and S. Riedel, *Chem.–Eur. J.*, 2019, **25**, 14721–14727.
- 37 J. H. Nissen, T. Stücker, T. Drews, S. Steinhauer, H. Beckers and S. Riedel, *Angew. Chem., Int. Ed.*, 2019, **58**, 3584–3588.
- 38 P. P. Singh, S. Sinha, P. Gahtori, S. Tivari and V. Srivastava, *Org. Biomol. Chem.*, 2024, **22**, 2523–2538.
- 39 B. C. Hong and R. R. Indurmuddam, *Org. Biomol. Chem.*, 2024, **22**, 3799–3842.
- 40 M. D. Tzikaris, I. N. Lykakis and M. Orfanopoulos, *Chem. Soc. Rev.*, 2009, **38**, 2609–2621.
- 41 P. Bellotti, H.-M. Huang, T. Faber and F. Glorius, *Chem. Rev.*, 2023, **123**, 4237–4352.
- 42 G. Laudadio, Y. Deng, K. van der Wal, D. Ravelli, M. Nuño, M. Fagnoni, D. Guthrie, Y. Sun and T. Noël, *Science*, 2020, **369**, 92–96.
- 43 B. M. Trost, *Science*, 1991, **254**, 1471–1477.
- 44 H. Zhu, C. Gao, T. Yu, C. Xu and M. Wang, *Angew. Chem., Int. Ed.*, 2024, **63**, e202400449.
- 45 H. K. Fasshuber, J.-P. Demers, V. Chevelkov, K. Giller, S. Becker and A. Lange, *J. Magn. Reson.*, 2015, **252**, 10–19.
- 46 K.-J. Booy, P. Wiegerinck, J. Vader, F. Kaspersen, D. Lambregts, H. Vromans and E. Kellenbach, *J. Pharm. Sci.*, 2005, **94**, 458–463.
- 47 W. Wiechert, *Metab. Eng.*, 2001, **3**, 195–206.
- 48 V. Silvestre, V. M. Mboula, C. Jouitteau, S. Akoka, R. J. Robins and G. S. Remaud, *J. Pharm. Biomed. Anal.*, 2009, **50**, 336–341.
- 49 M. S. Ledovskaya, V. V. Voronin, K. S. Rodygin and V. P. Ananikov, *Org. Chem. Front.*, 2020, **7**, 638–647.
- 50 See SI chapter 8 for quantum yield experiments and EPR spectra. Additionally there is a proposed mechanism for trifluoromethoxylation using TBADT.
- 51 See SI for further details.
- 52 P. J. H. Williams, G. A. Boustead, D. E. Heard, P. W. Seakins, A. R. Rickard and V. Chechik, *J. Am. Chem. Soc.*, 2022, **144**, 15969–15976.
- 53 K. Shakeri, M. Kleoff, P. Golz, T. Drews, M. Weber, S. Riedel and M. Christmann, CCDC [2435030]: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2mqvcl](https://doi.org/10.5517/ccdc.csd.cc2mqvcl).

