Tetrahedron 100 (2021) 132477

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Nucleophilic trifluoromethylation of azinium salts with $Zn(CF_3)_2 \cdot bpy$

Shitao Pan, Xiu Wang, Chuanfa Ni, Jinbo Hu*

Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Ling-Ling Road, Shanghai, 200032, China

ARTICLE INFO

Article history:
Received 10 August 2021
Received in revised form
19 September 2021
Accepted 22 September 2021
Available online 2 October 2021

Keywords:
(Trifluoromethyl)zinc reagent
Trifluoromethylation
Nucleophilic addition
Azinium salts

ABSTRACT

(Trifluoromethyl)zinc complexes have been widely used in metal-mediated trifluoromethylation reactions. However, direct nucleophilic addition with a (trifluoromethyl)zinc complex is rare. In this article, we describe an unprecedented trifluoromethylation of azinium salts using $Zn(CF_3)_2 \cdot bpy$ as CF_3 source, giving 1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinolines as products. The latter species were further transformed to 2-trifluoromethylquinolines under oxidative conditions. This work also shows that ligands play an important role in tuning the reactivity of (trifluoromethyl)zinc complexes.

© 2021 Elsevier Ltd. All rights reserved.

1. Introduction

Trifluoromethylated compounds have been widely used in materials and pharmaceuticals due to the unique properties of the trifluoromethyl group [1,2]. Various methods including nucleophilic trifluoromethylation [3], radical trifluoromethylation [4] and metal-catalyzed cross-couplings [5], have been developed for the introduction of CF_3 group into target molecules. Among them, nucleophilic addition of trifluoromethyl anion or its equivalent is a straightforward and efficient method. The commonly used nucleophilic trifluoromethylation reagents include $TMSCF_3$ [3a-d], $ArSO_2CF_3$ [3e-h], and HCF_3 [3i-l], among others (Scheme 1a). These reagents can release trifluoromethyl anion to participate many kinds of reactions under the activation with bases or reductants. However, the use of these reagents suffers from some limitations: 1) requirement of basic initiators; 2) poor chemoselectivity towards common reactive functionalities such as aldehydes [6]; 3) operational difficulty in handling gaseous reagents such as HCF_3. Therefore, it is of great interest to develop operationally simple and highly selective nucleophilic trifluoromethylation method for the efficient synthesis of functionalized trifluoromethyl-containing compounds.

$Zn(CF_3)_2 \cdot L_n$ has been widely used as a trifluoromethyl source in various trifluoromethylation reactions [7–9]. At present, different ligand-coordinated trifluoromethyl zinc complexes, such as $Zn(CF_3)_2 \cdot DMPU$ [7], $Zn(CF_3)_2 \cdot TMEDA$ [8], and $Zn(CF_3)_2 \cdot bpy$ [9], have been developed and employed in copper-catalyzed radical trifluoromethylation reactions [7,9] (Scheme 1b). However, the application of $Zn(CF_3)_2 \cdot L_n$ as trifluoromethyl anion sources in nucleophilic addition reactions was rarely investigated, probably due to the difficulty in activation of the $Zn-CF_3$ bond. As an exception, Mikami and co-workers reported the nucleophilic addition of $Zn(CF_3)_2 \cdot TMEDA$ to aryl aldehydes by using $n Bu_4NOAc$ as an additive [8]. Inspired by this result, we envisioned that tuning the ligand of the zinc complex may be a useful strategy to activate the $Zn-CF_3$ bond [8]. Herein, we describe the nucleophilic trifluoromethylation of azinium salts with $Zn(CF_3)_2 \cdot bpy$ in the absence of any additive (Scheme 1c). This method tolerates a wide range of functionalities including halogens, cyano, nitro, methyl ester and formyl groups. The compatibility with methyl ester and formyl groups further proved the high chemoselectivity of the $Zn(CF_3)_2 \cdot bpy$ reagent used in this transformation. Moreover, we found the important influence of the ligands derived from $Zn(CF_3)_2 \cdot L_n$ in tuning their reactivities.

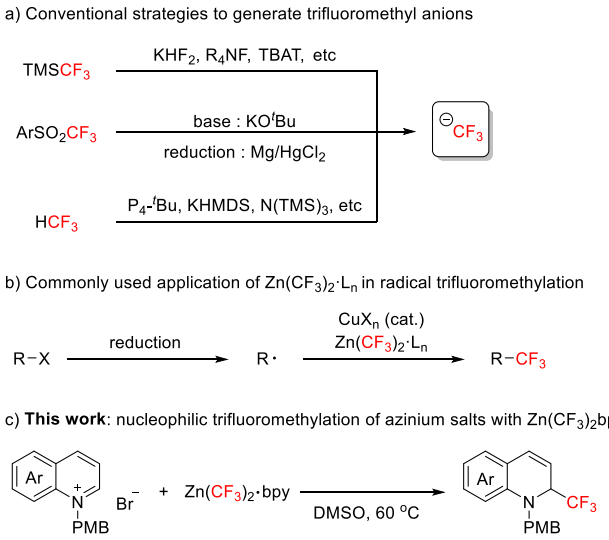
2. Results and discussion

2.1. Optimization of reaction conditions

At the onset of our exploration, we selected **1a** as the model substrate and $Zn(CF_3)_2 \cdot bpy$ (**2**) as the trifluoromethylation reagent. Initially, catalytic amount of CuF_2 (as the copper source) and 1,1′-

* Corresponding author.
E-mail address: jinbohu@mail.sioc.ac.cn (J. Hu).

https://doi.org/10.1016/j.tet.2021.132477
0040-4020/© 2021 Elsevier Ltd. All rights reserved.



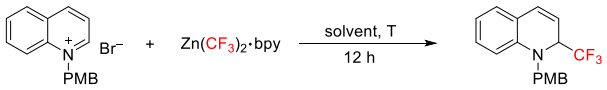
Scheme 1. Trifluoromethylation reactions. TBAT = tetrabutylammonium difluorotriphenylsilicate; bpy = 2,2′-bipyridine.

bis(diphenylphosphino)ferrocene (as the ligand) were added, affording the trifluoromethylation product **3a** in 69% yield (entry 1). To our surprise, we found that this reaction could proceed smoothly without the addition of CuF_2 and ligand, implying that **2** possesses enough nucleophilicity to attack **1a** to give the desired product (entry 2). Therefore, the direct nucleophilic trifluoromethylation reaction of **1a** and **2** was further evaluated in the absence of copper catalyst. A series of solvents including CH_3CN, THF, DMA, DMF and DMSO were screened (entries 2–6). A low yield (13%) of **3a** was observed in THF, probably owing to the low solubility of **1a** in the THF (entry 3). However, the reaction proceeded well in DMF, CH_3CN and DMSO, among which DMSO gave the best result, with product **3a** being formed in 78% yield (entry 6). Subsequently, the influence of the amount of **2** and the reaction temperature was examined. Increasing the amount of **2** to 2 or 2.5 equivalents led to no obvious improvement of the yield (entries 7–8). Meanwhile, raising temperature to 60 °C gave **3a** in 80% yield (entry 11), while the yield of the **3a** decreased to 67% when conducting the reaction at 70 °C. Finally, adjusting the concentration of the reaction in DMSO from 0.05 M to 0.1 M provided the highest yield (Table 1, entry 13). Finally, we could isolated the **3a** of 0.6 mmol scale in 71% yield (entry 13). Based on these results, we suggest that this reaction may proceed through a nucleophilic trifluoromethylation process using $Zn(CF_3)_2\cdot$bpy (**2**) as a trifluoromethy anion equivalent.

2.2. Scope and limitation

With the optimized conditions in hand (Table 1, entry 13), we then investigated the substrate scope of the present trifluoromethylation reaction. The results are summarized in Table 2. The introduction of an electron-poor functional group (such as nitro group) afforded the target product **3b** in 62% yield, while the product with the electron-donating group (such as methoxyl group) could be isolated in 69% yield (**3l**). Furthermore azinium salts with halogen substituents at 6-position gave the target products **3c**-**3f** in 46–67% yields. The steric effect was demonstrated by the comparison of halogens incorporated into aromatic ring at different positions. The substitution of chlorine atom at the 7-position gave the highest yield (**3k**) as compared with the substitution at 5-position (**3d**) and 4-position (**3g**). Interestingly, the methyl ester and formyl groups, which can be attacked by

Table 1
The optimization of reaction conditions for the trifluoromethylation of azinium salts **1a** with $Zn(CF_3)_2\cdot$bpy (**2**). [a]



1a (0.10 mmol) **2** **3a**

Entry	equiv. (2)	Solvent	T (°C)	Yield (%)
1[b]	1.5	CH_3CN	50	69
2	1.5	CH_3CN	50	76
3	1.5	THF	50	13
4	1.5	DMA	50	33
5	1.5	DMF	50	60
6	1.5	DMSO	50	78
7	2.0	DMSO	50	76
8	2.5	DMSO	50	76
9	1.5	DMSO	25	17
10	1.5	DMSO	40	62
11	1.5	DMSO	60	80
12	1.5	DMSO	70	67
13[c]	1.5	DMSO	60	81 (71)[d]

[a] The yield of **3a** was determined by ^{19}F NMR analysis of the reaction mixture using $PhCF_3$ as an internal standard.
[b] 0.2 equiv. of CuF_2 and 0.2 equiv. of 1,1′-bis(diphenylphosphino)ferrocene were added.
[c] 1.0 mL DMSO was used. PMB = 4-methoxybenzyl.
[d] Isolated yield of a reaction in 0.60-mmol scale.

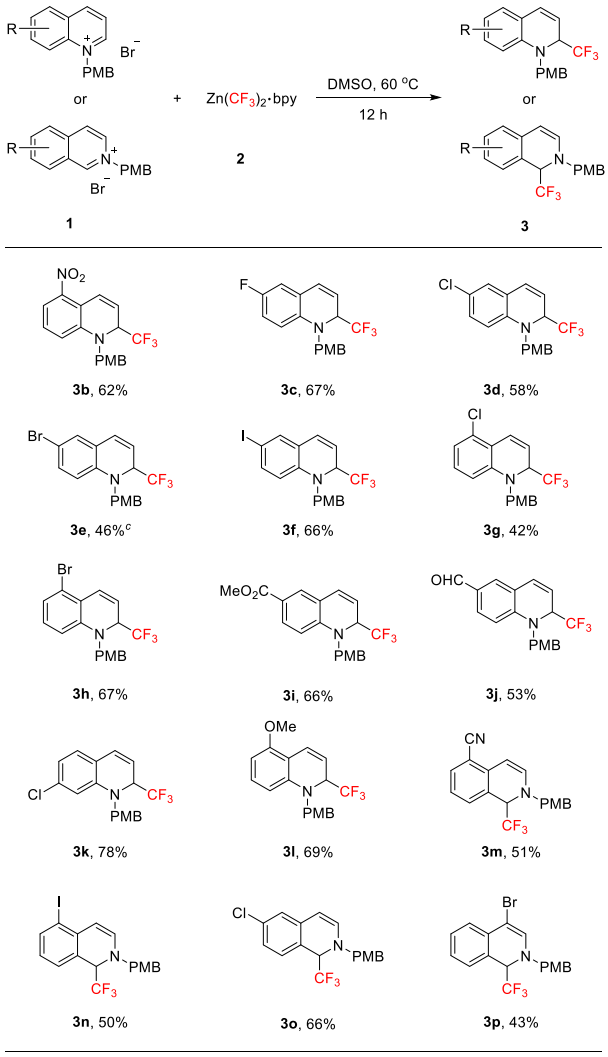
trifluoromethyl anions from $TMSCF_3$ [2c], were both tolerated under the current reaction conditions. Moreover, the formyl group, which has been known to be attacked by $Zn(CF_3)_2\cdot$TMEDA in moderate to good yields [8], remained untouched in our reactions. This result implies that the trifluoromethylzinc complexes ($Zn(CF_3)_2\cdot L_n$) bearing different ligands can exhibit very different reactivities. In addition to quinolinium salts, isoquinolinium salts are also amenable to this trifluoromethylation reaction (**3m**-**p**). We also attempted the trifluoromethylation of pyridinium salts; however, the corresponding product was not stable enough to be isolated by flash column chromatography.

To evaluate the synthetic potential of this method, the oxidation of the *in-situ* formed **3** by ceric ammonium nitrate (CAN) in methanol/H_2O to obtain the 2-trifluoromethylquinoline was examined (Table 3) [10]. As expected, the target products **4a-4g** could be obtained in moderate yields. In this oxidation process, halogen substituents (such as Br and I) were well tolerated, which are active reaction sites in metal-catalyzed cross-coupling reactions and potentially useful for further elaboration. One-pot trifluoromethylation and subsequent oxidation of isoquinolinium salts **1q** and **1r** were also examined. However, corresponding products **4h** and **4i** decomposed into complex mixtures during the oxidation process [11].

3. Conclusion

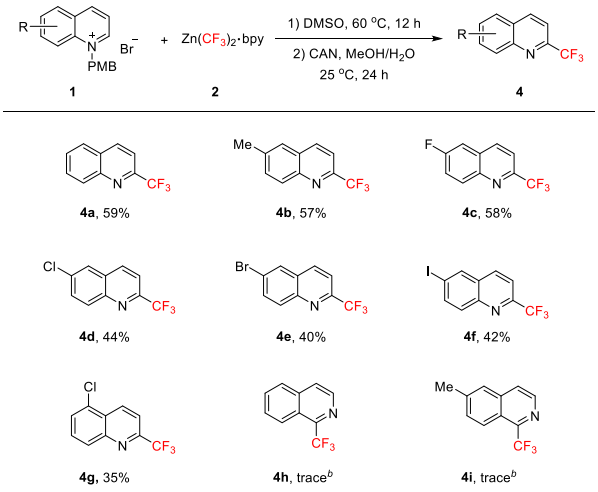
In summary, we have succeeded in the nucleophilic trifluoromethylation of azinium salts with $Zn(CF_3)_2\cdot$bpy under additive-free conditions. The reaction is amenable with a series of azinium salts bearing different functional groups. The trifluoromethylated products were able to be oxidized to remove the protection group 4-methoxybenzyl (PMB), which provided a new access to 2-trifluoromethylquinoline. Moreover, $Zn(CF_3)_2\cdot$bpy exhibited higher compatibility towards aldehydes and methyl esters than $Zn(CF_3)_2\cdot$TMEDA, which provides a new insight into the important role of ligand on the nucleophilic reactivity of the $Zn(CF_3)_2\cdot L_n$ complexes.

Table 2
Trifluoromethylation of azinium salts with $Zn(CF_3)_2 \cdot bpy$. [a,b].



[a] Reaction parameters: **1** (0.20 mmol), **2** (0.30 mmol), DMSO (2.0 mL).
[b] **1a** (0.60 mmol) and **2** (0.90 mmol) were used.
[c] **2** (0.40 mmol) was used.

Table 3
One-pot trifluoromethylation and subsequent oxidation. [a].



[a] Reaction conditions: **1** (0.50 mmol), **2** (0.75 mmol), CAN (2.20 mmol), DMSO (5.0 mL), MeOH (2.5 mL), H_2O (1.0 mL).
[b] The yield was determined by ^{19}F NMR analysis of the reaction mixture using $PhOCF_3$ as an internal standard.

4. Experimental section

4.1. General procedure for the synthesis of $Zn(CF_3)_2 \cdot bpy$

The typical procedures for the synthesis of $Zn(CF_3)_2 \cdot bpy$ are as follows [9b]: To an oven-dried 150-mL three-neck round-bottomed flask were added dry hexane (30 mL) and dry DMF (3.0 mL, 40 mmol) under N_2 atmosphere. At −78 °C, ICF_3 (ca. 19.6 g, 100 mmol) was bubbled into the solution. Diethylzinc (1.0 M in hexanes, 20 mL, 20 mmol) was then added dropwise with a syringe at −78 °C. With the addition of diethylzinc, white solid appeared gradually. After the addition, the reaction mixture was stirred at −20 °C for 24 h. The resulting mixture was filtered quickly, and the precipitate was washed with Et_2O (50–100 mL) and then dried under reduced pressure. Then the complex $Zn(CF_3)_2(DMF)_2$ was obtained as a light yellow solid. Yield: 4.68 g (67%).

$Zn(CF_3)_2(DMF)_2$ (4.68 g, 13.4 mmol) was added to an oven-dried flask under N_2 atmosphere. Anhydrous DMF (14 mL) was added and stirred for 10–15 min to dissolve the $Zn(CF_3)_2(DMF)_2$. 2,2′-Bipyridine (2.50 g, 16.0 mmol, 1.2 equiv) was then added. After the addition of 2,2′-bipyridine, the solution turned yellow quickly and the mixture was stirred for another 30–45 min. Dry Et_2O (150 mL) was then added into the reaction mixture and the mixture was stirred for another 15 min. The resulting mixture was filtered quickly, and the precipitate was washed with Et_2O (20 mL × 3) and dried under reduced pressure to afford $Zn(CF_3)_2 \cdot bpy$ as a light yellow solid. Yield: 2.76 g (58%).

4.2. General procedure for synthesis of azinium salts

The typical procedures for the synthesis of azinium salts are as follows: Into a 25 mL round-bottom flask were added quinoline (5.0–10.0 mmol), 4-methoxybenzyl bromide (1.0 equiv) and actone (5.0–10.0 mL). The reaction stirred at room temperature overnight. When the reaction was completed, the reaction mixture was filtrated. After drying under the reduced pressure, the product **1** could be afforded as solid.

4.2.1. 1-(4-methoxybenzyl)quinolin-1-ium bromide (**1a**)

Green solid. ^1H NMR (400 MHz, DMSO-d_6) δ 9.82 (d, J = 5.2 Hz, 1H), 9.40 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.9 Hz, 1H), 8.54 (d, J = 8.0 Hz, 1H), 8.28 (dt, J = 20.6, 7.1 Hz, 2H), 8.04 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.2 Hz, 2H), 6.35 (s, 2H), 3.74 (s, 3H). The characterization data are consistent with previous report [10].

4.2.2. 1-(4-methoxybenzyl)-5-nitroquinolin-1-ium bromide (**1b**)

Brown solid. ^1H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.58 (d, J = 8.3 Hz, 1H), 9.03 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 7.5 Hz, 1H), 8.51–8.31 (m, 2H), 7.46 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 7.3 Hz, 2H), 6.41 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.69, 151.44, 146.59, 143.06, 137.57, 134.08, 129.64, 127.09, 125.39, 124.96, 124.92, 122.49, 114.49, 60.72, 55.24. IR (film): 3016, 2989, 2978, 2949, 2835, 1610, 1596, 1512, 1336, 1242, 1023, 863, 839, 805 cm^{-1}. MS (EI) m/z $[M - Br]^+$: 295.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}N_2O_3^+$ $[M - Br]^+$: 295.1077, found 295.1078.

*4.2.3. 6-Fluoro-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1c**)*

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (d, J = 5.7 Hz, 1H), 9.34 (d, J = 8.4 Hz, 1H), 8.75 (dd, J = 9.8, 4.4 Hz, 1H), 8.46–8.38 (m, 1H), 8.38–8.30 (m, 1H), 8.27–8.16 (m, 1H), 7.45 (d, J = 8.3 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.36 (s, 2H), 3.74 (s, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ −108.08 (td, J = 8.5, 4.5 Hz). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.62 (d, J = 252.0 Hz), 159.51, 149.67, 147.15 (d, J = 5.1 Hz), 134.60, 131.41 (d, J = 11.1 Hz), 129.49, 125.29, 125.18 (d, J = 26.3 Hz), 123.42, 122.88 (d, J = 9.7 Hz), 114.38, 114.15 (d, J = 23.1 Hz), 59.74, 55.20. IR (film): 3088, 2986, 2928, 2834, 1596, 1535, 1514, 1481, 1387, 1306, 1269, 1159, 969, 887, 857, 838, 814 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 268.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}FNO^+$ [M − Br]$^+$: 268.1132, found 268.1132.

*4.2.4. 6-Chloro-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1d**)*

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.70 (dd, J = 5.9, 1.4 Hz, 1H), 9.27 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 2.4 Hz, 1H), 8.64 (d, J = 9.5 Hz, 1H), 8.34–8.24 (m, 2H), 7.41 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.28 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.59, 150.37, 147.01, 136.20, 135.50, 134.44, 130.79, 129.47, 129.25, 125.19, 123.66, 121.67, 114.45, 59.73, 55.21. IR (film): 3067, 2981, 2932, 2903, 2832, 1607, 1588, 1515, 1360, 1247, 1091, 1017, 981, 855, 840, 810 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 284.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}ClNO^+$ [M − Br]$^+$: 284.0837, found 284.0837.

*4.2.5. 6-Bromo-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1e**)*

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (dd, J = 5.9, 1.4 Hz, 1H), 9.26 (d, J = 8.4 Hz, 1H), 8.84 (d, J = 2.3 Hz, 1H), 8.55 (d, J = 9.5 Hz, 1H), 8.38 (dd, J = 9.4, 2.3 Hz, 1H), 8.31 (dd, J = 8.4, 5.8 Hz, 1H), 7.40 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.28 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.58, 150.41, 146.90, 138.04, 136.44, 132.53, 131.10, 129.46, 125.23, 123.62, 123.11, 121.57, 114.45, 59.67, 55.22. IR (film): 3048, 3008, 2952, 2933, 2834, 1610, 1585, 1513, 1375, 1300, 1251, 1179, 1026, 879, 803, 754 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 328.0. HRMS (EI) m/z calcd. for $C_{17}H_{15}BrNO^+$ [M − Br]$^+$: 328.0332, found 328.0333.

*4.2.6. 6-Iodo-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1f**)*

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (d, J = 5.2 Hz, 1H), 9.25 (d, J = 8.3 Hz, 1H), 9.00 (d, J = 1.7 Hz, 1H), 8.47 (dd, J = 9.3, 1.8 Hz, 1H), 8.39 (d, J = 9.3 Hz, 1H), 8.29 (dd, J = 8.4, 5.8 Hz, 1H), 7.41 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.29 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.56, 150.21, 146.60, 143.29, 138.77, 136.75, 131.25, 129.40, 125.30, 123.31, 120.88, 114.44, 97.53, 59.50, 55.21. IR (film): 2991, 2937, 2834, 1610, 1583, 1513, 1462, 1368, 1297, 1252, 1181, 1089, 1023, 808, 771, 746 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 376.0. HRMS (EI) m/z calcd. for $C_{17}H_{15}INO^+$ [M − Br]$^+$: 376.0193, found 376.0191.

*4.2.7. 5-Chloro-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1g**)*

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (d, J = 5.8 Hz, 1H), 9.30 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 2.3 Hz, 1H), 8.66 (d, J = 9.5 Hz, 1H), 8.39–8.23 (m, 2H), 7.43 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.32 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.59, 150.37, 147.01, 136.19, 135.50, 134.44, 130.79, 129.48, 129.25, 125.20, 123.66, 121.68, 114.45, 59.73, 55.22. IR (film): 3003, 2981, 2933, 2903, 1607, 1588, 1515, 1360, 1305, 1247, 1183, 1017, 890, 839, 809, 763 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 284.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}ClNO^+$ [M − Br]$^+$: 284.0837, found 284.0836.

*4.2.8. 5-Bromo-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1h**)*

Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (d, J = 5.7 Hz, 1H), 9.42 (d, J = 8.6 Hz, 1H), 8.65 (d, J = 8.9 Hz, 1H), 8.43–8.32 (m, 2H), 8.21–8.05 (m, 1H), 7.41 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.33 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.56, 150.85, 146.48, 138.74, 135.75, 134.01, 129.48, 128.76, 125.22, 123.89 (d, J = 2.3 Hz), 119.61, 114.41, 60.05, 55.21. IR (film): 3062, 2988, 2957, 2932, 2835, 1607, 1577, 1513, 1361, 1253, 1181, 1047, 1022, 798, 755 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 328.0. HRMS (EI) m/z calcd. for $C_{17}H_{15}BrNO^+$ [M − Br]$^+$: 328.0332, found 328.0332.

*4.2.9. 1-(4-methoxybenzyl)-6-(methoxycarbonyl)quinolin-1-ium bromide (**1i**)*

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 5.2 Hz, 1H), 9.56 (d, J = 8.4 Hz, 1H), 9.17 (s, 1H), 8.75 (d, J = 9.2 Hz, 1H), 8.59 (d, J = 9.1 Hz, 1H), 8.42–8.33 (m, 1H), 7.45 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.33 (s, 2H), 3.98 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.51, 159.61, 151.74, 149.20, 139.29, 133.94, 132.73, 130.23, 129.61, 129.59, 125.12, 123.45, 120.33, 114.45, 59.73, 55.21, 53.00. IR (film): 3020, 2987, 2941, 2837, 1727, 1612, 1586, 1512, 1464, 1367, 1284, 1250, 1233, 1110, 979, 819, 792 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 308.1. HRMS (EI) m/z calcd. for $C_{19}H_{18}NO_3^+$ [M − Br]$^+$: 308.1281, found 308.1281.

*4.2.10. 6-Formyl-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1j**)*

Yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H), 9.84 (d, J = 5.5 Hz, 1H), 9.56 (d, J = 8.3 Hz, 1H), 9.10 (d, J = 1.4 Hz, 1H), 8.79 (d, J = 9.2 Hz, 1H), 8.56 (dd, J = 9.2, 1.6 Hz, 1H), 8.39 (dd, J = 8.3, 5.9 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.35 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 191.71, 159.62, 151.91, 149.38, 139.84, 135.63, 134.29, 132.63, 129.84, 129.56, 125.16, 123.62, 120.65, 114.48, 59.87, 55.22. IR (film): 2965, 2931, 2901, 2832, 1695, 1593, 1515, 1465, 1249, 1180, 1024, 862, 838, 802 761 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 278.1. HRMS (EI) m/z calcd. for $C_{18}H_{16}NO_2^+$ [M − Br]$^+$: 278.1176, found 278.1177.

*4.2.11. 7-Chloro-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1k**)*

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 5.8 Hz, 1H), 9.41 (d, J = 8.0 Hz, 1H), 8.82 (s, 1H), 8.59 (d, J = 8.8 Hz, 1H), 8.30 (dd, J = 8.3, 5.9 Hz, 1H), 8.12 (dd, J = 8.8, 1.6 Hz, 1H), 7.46 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.34 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.62, 150.58, 147.75, 140.56, 137.99, 132.70, 130.71, 129.66, 128.60, 125.07, 122.79, 118.82, 114.50, 59.35, 55.21. IR (film): 3047, 3007, 2963, 2837, 1713, 1611, 1585, 1512, 1355, 1251, 1181, 1148, 1086, 1026, 848, 819, 746 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 284.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}ClNO^+$ [M − Br]$^+$: 284.0837, found 284.0838.

*4.2.12. 5-Methoxy-1-(4-methoxybenzyl)quinolin-1-ium bromide (**1l**)*

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (d, J = 5.3 Hz, 1H), 9.38 (d, J = 8.3 Hz, 1H), 8.16 (dt, J = 28.2, 8.5 Hz, 3H), 7.48 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 6.29 (s, 2H), 4.12 (s, 3H), 3.74 (s, 3H). The characterization data are consistent with previous report [11].

*4.2.13. 5-Cyano-2-(4-methoxybenzyl)isoquinolin-2-ium bromide (**1m**)*

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.49 (s, 1H), 9.01 (d, J = 7.0 Hz, 1H), 8.88 (t, J = 7.8 Hz, 2H), 8.65 (d, J = 6.9 Hz, 1H), 8.23 (t, J = 7.9 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 5.99 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.06, 151.11, 143.01, 137.12, 136.45, 135.94, 130.95, 130.92, 127.34, 125.69, 123.49, 115.42, 114.52, 109.29, 63.22, 55.28. IR (film): 3077, 2938, 2890, 2835, 2223, 1648, 1609, 1580, 1511, 1339, 1304, 1254, 1209, 928, 854, 831, 805 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 275.1. HRMS (EI) m/z calcd. for $C_{18}H_{15}N_2O^+$ [M − Br]$^+$: 275.1179, found 275.1179.

4.2.14. 5-Iodo-2-(4-methoxybenzyl)isoquinolin-2-ium bromide (**1n**)

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.87 (d, J = 7.0 Hz, 1H), 8.82 (d, J = 7.4 Hz, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.48 (d, J = 7.0 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H), 7.61 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 5.98 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.01, 150.61, 147.36, 138.53, 136.20, 132.31, 131.29, 130.82, 129.70, 128.15, 125.86, 114.53, 98.71, 62.81, 55.28. IR (film): 3035, 2994, 2932, 2878, 2834, 1638, 1606, 1512, 1355, 1334, 1248, 961, 852, 826, 793 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 376.0. HRMS (EI) m/z calcd. for $C_{17}H_{15}INO^+$ [M − Br]$^+$: 376.0193, found 376.0195.

4.2.15. 6-Chloro-2-(4-methoxybenzyl)isoquinolin-2-ium bromide (**1o**)

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 8.92 (d, J = 6.8 Hz, 1H), 8.61–8.49 (m, 3H), 8.12 (dd, J = 8.9, 2.0 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 5.94 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.99, 149.89, 141.97, 137.82, 135.68, 132.69, 131.92, 130.82, 126.36, 125.91, 125.87, 125.34, 114.51, 62.96, 55.26. IR (film): 3072, 3010, 2976, 2949, 2833, 1641, 1608, 1512, 1446, 1397, 1357, 1250, 1180, 1024, 892, 857 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 284.1. HRMS (EI) m/z calcd. for $C_{17}H_{15}ClNO^+$ [M − Br]$^+$: 284.0837, found 284.0837.

4.2.16. 4-Bromo-2-(4-methoxybenzyl)isoquinolin-2-ium bromide (**1p**)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 9.41 (s, 1H), 8.63 (d, J = 8.2 Hz, 1H), 8.49–8.30 (m, 2H), 8.18 (t, J = 7.5 Hz, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 5.90 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.06, 148.73, 137.76, 134.81, 134.74, 131.09, 130.71, 129.96, 126.50, 124.93, 124.66, 120.89, 113.49, 61.97, 54.26. IR (film): 3026, 2988, 2973, 2877, 1629, 1606, 1513, 1366, 1249, 1210, 1151, 1021, 898, 851, 822, 761 cm^{-1}. MS (EI) m/z [M − Br]$^+$: 328.0. HRMS (EI) m/z calcd. for $C_{17}H_{15}BrNO^+$ [M − Br]$^+$: 328.0332, found 328.0333.

4.2.17. 2-(4-methoxybenzyl)isoquinolin-2-ium bromide (**1q**)

White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.31 (s, 1H), 8.84 (d, J = 6.9 Hz, 1H), 8.60 (d, J = 6.8 Hz, 1H), 8.54 (d, J = 8.3 Hz, 1H), 8.36 (d, J = 8.3 Hz, 1H), 8.27 (t, J = 7.6 Hz, 1H), 8.09 (t, J = 7.5 Hz, 1H), 7.61 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 5.92 (s, 2H), 3.76 (s, 3H). The characterization data are consistent with previous report [12].

4.2.18. 2-(4-methoxybenzyl)-6-methylisoquinolin-2-ium bromide (**1r**)

Light yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 8.84 (d, J = 6.8 Hz, 1H), 8.46 (dd, J = 13.0, 7.7 Hz, 2H), 8.13 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.6 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 5.93 (s, 2H), 3.77 (s, 3H), 2.66 (s, 3H). The characterization data are consistent with previous report [12].

4.3. General procedure for trifluoromethylation of azinium salts

The typical procedures for the trifluoromethylation of azinium salts are as follows: Under N_2 atmosphere, into an oven-dried sealed tube were added azinium salts (**1**, 0.2 mmol), $Zn(CF_3)_2\cdot$bpy (**2**, 107.9 mg, 0.3 mmol) and DMSO (2.0 mL). The reaction tube was put into an oil bath at 60 °C and stirred for 12 h. When the reaction was completed, the reaction mixture was cooled to room temperature and added water (20 mL), extracted with dichloromethane (DCM) (3 × 20 mL). The organic layers were washed with water (3 × 30 mL), dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by fast column chromatography to afford product **3**.

4.3.1. 1-(4-Methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3a**)

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 8.4 Hz, 2H), 7.09 (td, J = 8.2, 1.2 Hz, 1H), 7.04–7.00 (m, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.76–6.66 (m, 3H), 5.60 (dd, J = 9.7, 6.0 Hz, 1H), 4.83 (d, J = 15.3 Hz, 1H), 4.50–4.42 (m, 1H), 4.38 (d, J = 15.4 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14, 143.36, 131.09, 129.60, 128.78, 128.73, 127.78, 125.36 (q, J = 291.2 Hz), 121.69, 118.19, 114.65, 114.25, 112.89, 58.32 (q, J = 29.8 Hz), 55.29, 53.99. ^{19}F NMR (376 MHz, $CDCl_3$): δ −77.49 (d, J = 7.0 Hz, 3F). MS (DART) m/z [M+H]$^+$: 320.1. HRMS (DART) m/z calcd. for $C_{18}H_{17}F_3NO^+$ [M+H]$^+$: 320.1257, found 320.1255.

4.3.2. 1-(4-Methoxybenzyl)-5-nitro-2-(trifluoromethyl)-1,2-dihydroquinoline (**3b**)

Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.24 (m, 2H), 7.20–7.12 (m, 3H), 6.93 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 5.85 (dd, J = 9.8, 6.5 Hz, 1H), 4.85 (d, J = 15.4 Hz, 1H), 4.58–4.40 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.44, 147.67, 144.31, 128.94, 128.74, 127.32, 125.59, 124.89 (q, J = 291.9 Hz), 118.32, 117.83, 115.64, 114.50, 114.14, 57.71 (q, J = 30.6 Hz), 55.41, 55.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.28 (d, J = 6.8 Hz, 3F). IR (film): 3002, 2933, 2838, 1644, 1609, 1558, 1422, 1346, 1205, 894, 837, 818, 801, 760 cm^{-1}. MS (DART) m/z [M+H]$^+$: 365.1. HRMS (DART) m/z calcd. for $C_{18}H_{16}F_3N_2O_3^+$ [M+H]$^+$: 365.1108, found 365.1101.

4.3.3. 6-Fluoro-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3c**)

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.82–6.72 (m, 2H), 6.65 (d, J = 9.7 Hz, 1H), 6.58 (dd, J = 8.9, 4.4 Hz, 1H), 5.68 (dd, J = 9.7, 6.1 Hz, 1H), 4.75 (d, J = 15.3 Hz, 1H), 4.45–4.40 (m, 1H), 4.36 (d, J = 15.4 Hz, 1H), 3.78 (d, J = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.25, 157.09, 154.74, 139.55, 130.35 (d, J = 2.2 Hz), 128.82, 128.56, 125.27 (q, J = 290.9 Hz), 122.79 (d, J = 8.0 Hz), 116.63, 115.68 (d, J = 22.4 Hz), 114.33, 113.95 (dd, J = 15.3, 7.7 Hz), 58.38 (q, J = 30.2 Hz), 55.38, 54.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.41 (d, J = 6.9 Hz, 3F), −127.77 (td, J = 8.6, 4.5 Hz, 1F). IR (film): 3049, 3001, 2935, 2837, 1648, 1611, 1582, 1512, 1495, 1398, 1248, 946, 923, 829 cm^{-1}. MS (DART) m/z [M+H]$^+$: 338.1. HRMS (DART) m/z calcd. for $C_{18}H_{16}F_4NO^+$ [M+H]$^+$: 338.1163, found 338.1158.

4.3.4. 6-Chloro-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3d**)

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.2 Hz, 2H), 7.08–6.96 (m, 2H), 6.85 (d, J = 8.3 Hz, 2H), 6.65 (d, J = 9.7 Hz, 1H), 6.58 (d, J = 8.6 Hz, 1H), 5.65 (dd, J = 9.7, 6.0 Hz, 1H), 4.77 (d, J = 15.4 Hz, 1H), 4.45 (p, J = 6.7 Hz, 1H), 4.37 (d, J = 15.4 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.27, 141.82, 130.18, 129.13, 128.74, 128.23, 127.27, 125.16 (q, J = 290.7 Hz), 123.08, 123.04, 116.19, 114.37, 114.24, 58.47 (q, J = 30.4 Hz), 55.39, 54.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.50 (d, J = 7.0 Hz). IR (film): 2984, 2967, 2933, 2833, 1612, 1512, 1489, 1463, 1303, 1248, 1208, 1035, 883, 855, 806 cm^{-1}. MS (DART) m/z [M+H]$^+$: 354.1. HRMS (DART) m/z calcd. for $C_{18}H_{16}ClF_3NO^+$ [M+H]$^+$: 354.0867, found 354.0865.

4.3.5. 6-Bromo-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3e**)

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 4H), 6.85 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 9.7 Hz, 1H), 6.53 (d, J = 8.6 Hz, 1H), 5.64 (dd, J = 9.7, 6.1 Hz, 1H), 4.76 (d, J = 15.4 Hz, 1H), 4.48–4.42 (m, 1H), 4.36 (d, J = 15.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.29, 142.28, 132.03, 130.11, 128.82, 128.73, 128.17, 125.13 (q, J = 290.6 Hz), 123.57, 116.11, 114.72, 114.38, 110.18, 58.48 (q, J = 30.0 Hz), 55.40, 54.21. ^{19}F NMR (376 MHz, $CDCl_3$)

δ −77.51 (d, *J* = 6.9 Hz, 3F). IR (film): 3006, 2963, 2928, 2842, 1611, 1512, 1463, 1399, 1303, 1172, 1125, 875, 850, 804, 765 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 398.0. HRMS (DART) *m/z* calcd. for $C_{18}H_{16}BrF_3NO^+$ $[M+H]^+$: 398.0362, found 398.0360.

4.3.6. 6-Iodo-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3f**)

Light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.44 (d, *J* = 8.6 Hz, 1H), 5.62 (dd, *J* = 9.4, 6.2 Hz, 1H), 4.76 (d, *J* = 15.5 Hz, 1H), 4.50−4.41 (m, 1H), 4.35 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.28, 142.94, 137.96, 135.91, 129.96, 128.71, 128.11, 125.14 (q, *J* = 290.5 Hz), 124.11, 115.82, 115.27, 114.38, 79.49, 58.46 (q, *J* = 29.7 Hz), 55.40, 54.07. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.52 (d, *J* = 6.8 Hz, 3F). IR (film): 3000, 2931, 2835, 1645, 1611, 1585, 1511, 1462, 1398, 1359, 1274, 1205, 871, 845, 802 cm^{-1}. MS (FI) *m/z* $[M]^+$: 445. HRMS (FI) *m/z* calcd. for $C_{18}H_{15}IF_3NO^+$ $[M]^+$: 445.0145, found 445.0148.

4.3.7. 5-Chloro-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3g**)

Light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.2 Hz, 2H), 7.05−6.98 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 9.7 Hz, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 5.66 (dd, *J* = 9.7, 6.0 Hz, 1H), 4.77 (d, *J* = 15.4 Hz, 1H), 4.48−4.42 (m, 1H), 4.37 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.28, 141.83, 130.19, 129.14, 128.74, 128.24, 127.28, 125.16 (q, *J* = 290.7 Hz), 123.08, 123.05, 116.20, 114.37, 114.25, 58.48 (q, *J* = 29.6 Hz), 55.40, 54.26. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.50 (d, *J* = 6.8 Hz). IR (film): 3006, 2958, 2933, 2838, 1611, 1512, 1489, 1463, 1303, 1248, 1125, 883, 855, 806, 722 689 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 354.1. HRMS (DART) *m/z* calcd. for $C_{18}H_{16}ClF_3NO^+$ $[M+H]^+$: 354.0867, found 354.0864.

4.3.8. 5-Bromo-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3h**)

Light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.12 (m, 3H), 6.96−6.89 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 1H), 5.69 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.81 (d, *J* = 15.3 Hz, 1H), 4.48−4.43 (m, 1H), 4.39 (d, *J* = 15.4 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.30, 144.79, 130.03, 129.85, 128.80, 128.14, 125.06 (q, *J* = 290.8 Hz), 123.05, 122.44, 120.97, 116.22, 114.38, 112.54, 58.05 (q, *J* = 30.3 Hz), 55.40, 54.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.38 (d, *J* = 7.2 Hz, 3F). IR (film): 2955, 2931, 2836, 1643, 1611, 1586, 1359, 1250, 1037, 957, 923, 867, 837, 820 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 398.0. HRMS (DART) *m/z* calcd. for $C_{18}H_{16}BrF_3NO^+$ $[M+H]^+$: 398.0362, found 398.0356.

4.3.9. Methyl 1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline-6-carboxylate (**3i**)

White solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.71 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 9.6 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 5.64 (dd, *J* = 9.7, 5.9 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 4.52 (m, 1H), 4.43 (d, *J* = 15.5 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99, 159.35, 147.14, 131.57, 130.86, 129.50, 128.71, 127.74, 125.01 (q, *J* = 290.2 Hz), 121.02, 119.75, 115.06, 114.43, 112.33, 58.63 (q, *J* = 30.2 Hz), 55.38, 54.05, 51.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.53 (d, *J* = 6.5 Hz, 3F). IR (film): 3032, 2954, 2838, 2721, 1711, 1648, 1605, 1433, 1328, 1250, 1172, 1034, 859, 825, 763 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 378.1. HRMS (DART) *m/z* calcd. for $C_{20}H_{19}F_3NO_3^+$ $[M+H]^+$: 378.1312, found 378.1306.

4.3.10. 1-(4-Methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline-6-carbaldehyde (**3j**)

Light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.69−7.52 (m, 2H), 7.17 (t, *J* = 6.6 Hz, 2H), 6.87 (q, *J* = 6.7, 5.3 Hz, 2H), 6.78 (dd, *J* = 9.1, 4.4 Hz, 2H), 5.74−5.66 (m, 1H), 4.93 (dt, *J* = 11.5, 5.8 Hz, 1H), 4.58 (q, *J* = 6.5 Hz, 2H), 4.53−4.42 (m, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.46, 159.46, 148.54, 132.60, 130.71, 129.28, 128.70, 127.52, 127.32, 124.86 (q, *J* = 289.8 Hz), 121.49, 115.59, 114.53, 112.74, 58.76 (q, *J* = 30.3 Hz), 55.41, 54.20. IR (film): 2931, 2837, 1682, 1650, 1600, 1513, 1406, 1329, 1248, 1036, 860, 813, 778, 761 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 348.1. HRMS (DART) *m/z* calcd. for $C_{19}H_{17}F_3NO_2^+$ $[M+H]^+$: 348.1206, found 348.1198.

4.3.11. 7-Chloro-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3k**)

Light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 11.0 Hz, 3H), 5.59 (dd, *J* = 9.6, 6.0 Hz, 1H), 4.77 (d, *J* = 15.2 Hz, 1H), 4.48−4.31 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.30, 144.39, 135.05, 130.31, 128.96, 128.61, 127.88, 125.18 (q, *J* = 290.6 Hz), 120.26, 118.24, 114.89, 114.38, 113.02, 57.66 (q, *J* = 29.9 Hz), 55.38, 53.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.36 (d, *J* = 6.8 Hz, 3F). IR (film): 2933, 2837, 1646, 1611, 1595, 1491, 1463, 1357, 1249, 1095, 956, 868, 838, 809 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 354.1. HRMS (DART) *m/z* calcd. for $C_{18}H_{16}ClF_3NO^+$ $[M+H]^+$: 354.0867, found 354.0860.

4.3.12. 5-Methoxy-1-(4-methoxybenzyl)-2-(trifluoromethyl)-1,2-dihydroquinoline (**3l**)

Orange liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.8 Hz, 3H), 7.03 (t, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 8.2 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 1H), 5.56−5.48 (m, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 4.49−4.26 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.08, 155.80, 144.22, 129.69, 128.97, 128.70, 125.45 (q, *J* = 290.8 Hz), 125.11, 114.23, 112.46, 110.63, 106.39, 100.72, 57.97 (q, *J* = 30.0 Hz), 55.62, 55.37, 54.31. ^{19}F NMR (376 MHz, Chloroform-*d*) δ −77.63 (d, *J* = 7.0 Hz). The characterization data are consistent with previous report [10].

4.3.13. 2-(4-Methoxybenzyl)-1-(trifluoromethyl)-1,2-dihydroisoquinoline-5-carbonitrile (**3m**)

Brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 7.5 Hz, 1H), 4.85 (q, *J* = 7.3 Hz, 1H), 4.49 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.65, 139.25, 137.44, 133.44, 132.62, 129.03, 128.15, 125.26 (q, *J* = 291.5 Hz), 124.80, 120.16, 117.92, 114.52, 105.55, 95.00, 60.08 (q, *J* = 30.5 Hz), 58.32, 55.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ −77.01 (d, *J* = 7.3 Hz, 3F). IR (film): 2933, 2838, 2219, 1618, 1586, 1565, 1458, 1376, 1321, 1251, 1009, 835, 795, 765 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 345.1. HRMS (DART) *m/z* calcd. for $C_{19}H_{16}F_3N_2O^+$ $[M+H]^+$: 345.1209, found 345.1203.

4.3.14. 5-Iodo-2-(4-methoxybenzyl)-1-(trifluoromethyl)-1,2-dihydroisoquinoline (**3n**)

Light red liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 5.62 (d, *J* = 7.6 Hz, 1H), 4.74 (q, *J* = 7.5 Hz, 1H), 4.54−4.39 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.54, 140.05, 137.65, 136.61, 129.03, 128.70, 128.66, 126.28, 125.63 (q, *J* = 292.9 Hz), 120.45, 114.44, 102.18, 95.00, 60.78 (q, *J* = 30.1 Hz), 57.97, 55.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.58 (d, *J* = 7.4 Hz, 3F). IR (film): 3006, 2958, 2933, 2846, 1609, 1585, 1512, 1441, 1374, 1303, 1170, 1033, 962, 757, 689 cm^{-1}. MS (DART) *m/z* $[M+H]^+$: 446.0. HRMS (DART) *m/z* calcd. for $C_{18}H_{16}F_3INO^+$ $[M+H]^+$: 446.0223, found 446.0219.

*4.3.15. 6-Chloro-2-(4-methoxybenzyl)-1-(trifluoromethyl)-1,2-dihydroisoquinoline (**3o**)*

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.2 Hz, 2H), 7.05–6.97 (m, 2H), 6.90–6.83 (m, 3H), 6.34 (d, J = 7.4 Hz, 1H), 5.36 (d, J = 7.5 Hz, 1H), 4.79 (q, J = 7.4 Hz, 1H), 4.50–4.37 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.53, 136.64, 135.82, 135.21, 129.53, 128.97, 128.90, 125.65 (q, J = 291.5 Hz), 125.02, 123.32, 118.00, 114.45, 97.53, 60.26 (q, J = 30.2 Hz), 58.20, 55.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.97 (d, J = 7.4 Hz, 3F). IR (film): 3001, 2963, 2930, 2838, 1688, 1621, 1593, 1512, 1487, 1362, 1321, 1251, 1034, 899, 806 cm^{-1}. MS (DART) m/z $[M+H]^+$: 354.1. HRMS (DART) m/z calcd. for $C_{18}H_{16}ClF_3NO^+$ $[M+H]^+$: 354.0867, found 354.0865.

*4.3.16. 4-Bromo-2-(4-methoxybenzyl)-1-(trifluoromethyl)-1,2-dihydroisoquinoline (**3p**)*

Light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.17–7.12 (m, 3H), 6.97 (d, J = 7.4 Hz, 1H), 6.84 (d, J = 8.2 Hz, 2H), 6.60 (s, 1H), 4.81 (q, J = 7.2 Hz, 1H), 4.50–4.35 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.61, 135.88, 132.46, 129.72, 129.13, 128.37, 128.13, 126.66, 125.35 (q, J = 291.5 Hz), 123.48, 120.36, 114.48, 92.15, 60.89 (q, J = 29.7 Hz), 58.23, 55.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.86 (d, J = 7.3 Hz, 3F). IR (film): 2963, 2941, 2842, 1614, 1512, 1484, 1453, 1304, 1250, 1173, 1034, 983, 878, 758, 689 cm^{-1}. MS (DART) m/z $[M+H]^+$: 398.0. HRMS (DART) m/z calcd. for $C_{18}H_{16}BrF_3NO^+$ $[M+H]^+$: 398.0362, found 398.0360.

4.4. General procedure for synthesis of 2-trifluoromethylquinoline/2-trifluoromethylisoquinoline

The typical procedures for the synthesis of 2-trifluoromethylquinoline are as follows: Under N_2 atmosphere, into an oven-dried sealed tube were added azinium salts (**1**) (0.50 mmol), $Zn(CF_3)_2\cdot$bpy (**2**) (269.7 mg, 0.75 mmol) and DMSO (5.0 mL). The sealed tube was immersed into 60 °C oil bath and stirred for 12 h. After completing the reaction, the reaction mixture was cooled to room temperature and added with 20 mL water, extracted with DCM (3 × 20 mL). The organic phase was washed with H_2O (3 × 30 mL), dried over Na_2SO_4, then concentrated under vacuum. The crude was then dissolved in MeOH (2.5 mL), and a solution of CAN (1.21 g, 2.20 mmol) in water (1.0 mL) was added dropwise at room temperature when stirring. After 24 h, the reaction mixture was then diluted with H_2O (10 mL), and the product was extracted with ether (3 × 10 mL). The combined organic phases were washed with H_2O, dried over Na_2SO_4, then concentrated under vacuum. Then the product **4** was purified by column chromatography.

*4.4.1. 2-(Trifluoromethyl)quinoline (**4a**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.85–7.81 (m, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.72–7.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.04 (q, J = 34.6 Hz), 147.29, 138.23, 130.93, 130.22, 128.97, 128.71, 127.80, 121.72 (q, J = 274.4 Hz), 116.88 (q, J = 2.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.99 (s, 3F). The characterization data are consistent with previous report [13].

*4.4.2. 6-Methyl-2-(trifluoromethyl)quinoline (**4b**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 9.1 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.66–7.62 (m, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.15 (q, J = 34.5 Hz), 145.92, 139.00, 137.39, 133.31, 129.83, 129.07, 126.54, 121.82 (q, J = 275.1 Hz), 116.89 (q, J = 2.3 Hz), 21.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.38 (s, 3F). The characterization data are consistent with previous report [13].

*4.4.3. 6-Fluoro-2-(trifluoromethyl)quinoline (**4c**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.6 Hz, 1H), 8.25 (dd, J = 9.3, 5.3 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.65–7.57 (m, 1H), 7.53 (dd, J = 8.6, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.68 (d, J = 252.0 Hz), 147.46 (qd, J = 34.9, 3.2 Hz), 144.35, 137.54 (d, J = 5.7 Hz), 132.90 (d, J = 9.5 Hz), 129.80 (d, J = 10.4 Hz), 121.60 (q, J = 274.4 Hz), 121.46 (d, J = 26.1 Hz), 117.64 (d, J = 3.8 Hz), 110.81 (d, J = 22.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.00 (s, 3F), −110.04 (td, J = 8.5, 5.3 Hz). The characterization data are consistent with previous report [13].

*4.4.4. 6-Chloro-2-(trifluoromethyl)quinoline (**4d**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 2.3 Hz, 1H), 7.76 (dd, J = 8.7, 3.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.26 (q, J = 35.2 Hz), 145.63, 137.33, 134.78, 132.03, 131.80, 129.49, 126.45, 121.51 (q, J = 275.4 Hz), 117.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.05 (s, 3F). The characterization data are consistent with previous report [13].

*4.4.5. 6-Bromo-2-(trifluoromethyl)quinoline (**4e**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.7 Hz, 1H), 8.13–8.03 (m, 2H), 7.90–7.87 (m, 1H), 7.76 (d, J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.37 (q, J = 34.9 Hz), 145.83, 137.25, 134.57, 131.85, 129.93, 129.86, 123.06, 121.51 (q, J = 275.5 Hz), 117.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.11 (s, 3F). The characterization data are consistent with previous report [13].

*4.4.6. 6-Iodo-2-(trifluoromethyl)quinoline (**4f**)*

Red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 2.0 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 8.05 (dd, J = 8.9, 2.0 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.46 (q, J = 34.5 Hz), 146.15, 139.77, 137.00, 136.57, 131.67, 130.37, 121.50 (q, J = 275.6 Hz), 117.68, 95.00. ^{19}F NMR (376 MHz, $CDCl_3$) δ −68.09 (s, 3F). The characterization data are consistent with previous report [13].

*4.4.7. 5-Chloro-2-(trifluoromethyl)quinoline (**4g**)*

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 7.88 (s, 1H), 7.76 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.26 (q, J = 34.6 Hz), 145.63, 137.34, 134.78, 132.04, 131.81, 129.49, 126.45, 121.50 (q, J = 275.1 Hz), 117.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ −67.61 (s, 3F). The characterization data are consistent with previous report [14].

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Xiu Wang reports financial support was provided by National Natural Science Foundation of China. Xiu Wang reports was provided by Ministry of Science and Technology of the People's Republic of China.

Acknowledgments

Financial support of this work by the National Natural Science Foundation of China (21632009), the Key Programs of the Chinese Academy of Sciences (KGZD-EW-T08), the Key Research Program of Frontier Sciences of CAS (QYZDJ-SSW-SLH049), and Shanghai Science and Technology Program (18JC1410601) is acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132477.

References

[1] (a) S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, Fluorine in medicinal chemistry, Chem. Soc. Rev. 37 (2008) 320–330;
(b) Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J.L. AceÇa, V.A. Soloshonok, K. Izawa, H. Liu, Next generation of fluorine-containing pharmaceuticals, compounds currently in phase II–III clinical trials of major pharmaceutical companies: new structural trends and therapeutic areas, Chem. Rev. 116 (2016) 422–518;
(c) T. Fujiwara, D. O'Hagan, Successful fluorine-containing herbicide agrochemicals, J. Fluor. Chem. 167 (2014) 16–29;
(d) F. Babudri, G.M. Farinola, F. Naso, R. Ragni, Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom, Chem. Commun. (2007) 1003–1022;
(e) R. Berger, G. Resnati, P. Metrangolo, E. Weber, J. Hulliger, Organic fluorine compounds: a great opportunity for enhanced materials properties, Chem. Soc. Rev. 40 (2011) 3496–3508;
(f) E.P. Gillis, K.J. Eastman, M.D. Hill, D.J. Donnelly, N.A. Meanwell, Applications of fluorine in medicinal chemistry, J. Med. Chem. 58 (2015) 8315–8359.

[2] For reviews, see:. (a) H. Xiao, Z. Zhang, Y. Fang, L. Zhu, C. Li, Radical trifluoromethylation, Chem. Soc. Rev. 50 (2021) 6308–6319;
(b) X. Ma, Q. Song, Recent progress on selective deconstructive modes of halodifluoromethyl and trifluoromethyl-containing reagents, Chem. Soc. Rev. 49 (2020) 9197–9219;
(c) X. Liu, C. Xu, M. Wang, Q. Liu, Trifluoromethyltrimethylsilane: nucleophilic trifluoromethylation and beyond, Chem. Rev. 115 (2015) 683–730;
For recent examples, see:. (d) C. Le, T.Q. Chen, T. Liang, P. Zhang, D.W.C. MacMillan, A radical approach to the copper oxidative addition problem: trifluoromethylation of bromoarenes, Science 360 (2018) 1010–1014;
(e) Z. Kuang, H. Chen, J. Qiu, Z. Ou, Y. Lan, Q. Song, Cu-catalyzed regio- and stereodivergent chemoselective sp^2/sp^3 1,3- and 1,4-diborylations of CF_3-containing 1,3-enynes, Inside Chem. 6 (2020) 2347–2363;
(f) C. Jiang, L. Wang, H. Zhang, P. Chen, Y.-L. Guo, G. Liu, Enantioselective copper-catalyzed trifluoromethylation of benzylic radicals via ring opening of cyclopropanols, Inside Chem. 6 (2020) 2407–2419;
(g) H. Jia, A.P. Häring, F. Berger, L. Zhang, T. Ritter, Trifluoromethyl thianthrenium triflate: a readily available trifluoromethylating reagent with formal CF_3^+, $CF_3\bullet$, and CF_3^- reactivity, J. Am. Chem. Soc. 43 (2021) 7623–7628.

[3] For examples, see:. (a) C. P Félix, N. Khatimi, A.J. Laurent, Stereoselective addition of CF_3SiMe_3 on azirines. Synthesis of (E)-aziridines, Tetrahedron Lett. 35 (1994) 3303–3304;
(b) G.K.S. Prakash, R. Mogi, G.A. Olah, Preparation of tri- and difluoromethylated amines from aldimines using (trifluoromethyl)trimethylsilane, Org. Lett. 8 (2006) 3589–3592;
(c) N.V. Kirij, L.A. Babadzhanova, V.N. Movchun, Y.L. Yagupolskii, W. Tyrra, D. Naumann, H.T.M. Fischer, H. Scherer, Trifluoromethylation of non-activated aldimines with trimethyl(trifluoromethyl)silane in the presence of tetramethylammonium fluoride: a closer look into the reaction route, J. Fluor. Chem. 129 (2008) 14–21;
(d) V.V. Levin, A.D. Dilman, P.A. Belyakov, M.I. Struchkova, V.A. Tartakovsky, Nucleophilic trifluoromethylation of imines under acidic conditions, Eur. J. Org Chem. 31 (2008) 5226–5230;
(e) G.K.S. Prakash, J. Hu, G.A. Olah, Alkoxide- and hydroxide-induced nucleophilic trifluoromethylation using trifluoromethyl sulfone or sulfoxide, Org. Lett. 5 (2003) 3253–3256;
(f) Y. Zhao, J. Zhu, C. Ni, J. Hu, Magnesium metal-mediated reductive trifluoromethylation of aldehydes with phenyl trifluoromethyl sulfone, Synthesis 11 (2010) 1899–1904;
(g) G.K.S. Prakash, Y. Wang, R. Mogi, J. Hu, T. Mathew, G.A. Olah, Nucleophilic perfluoroalkylation of imines and carbonyls: perfluoroalkyl sulfones as efficient perfluoroalkyl-transfer motifs, Org. Lett. 12 (2010) 2932–2935;
(h) K. Sakavuyi, K.S. Petersen, Nucleophilic trifluoromethylation of conjugate acceptors via phenyl trifluoromethyl sulfone, Tetrahedron Lett. 54 (2013) 6129–6132;
(i) G.K.S. Prakash, P.V. Jog, P.T.D. Batamak, G.A. Olah, Taming of fluoroform: direct nucleophilic trifluoromethylation of Si, B, S, and C centers, Science 338 (2012) 1324–3127;
(j) S. Large, N. Roques, B.R. Langlois, Nucleophilic trifluoromethylation of carbonyl compounds and disulfides with trifluoromethane and silicon-containing bases, J. Org. Chem. 65 (2000) 8848–8856;
(k) Y. Zhang, M. Fujiu, H. Serizawa, K. Mikami, Organocatalysis approach to trifluoromethylation with fluoroform, J. Fluor. Chem. 156 (2013) 367–371;
(l) H. Kawai, Z. Yuan, E. Tokunaga, N. Shibata, A sterically demanding organosuperbase avoids decomposition of a naked trifluoromethyl carbanion directly generated from fluoroform, Org. Biomol. Chem. 11 (2013) 1446–1450.

[4] For examples, see:. (a) D.A. Nagib, M.E. Scott, D.W.C. MacMillan, Enantioselective α-trifluoromethylation of aldehydes via photoredox organocatalysis, J. Am. Chem. Soc. 131 (2009) 10875–10877;
(b) N. Iqbal, J. Jung, S. Park, E.J. Cho, Controlled trifluoromethylation reactions of alkynes through visible-light photoredox catalysis, Angew. Chem. Int. Ed. 53 (2014) 539–552;
(c) R. Tomita, T. Koike, M. Akita, Photoredox-catalyzed stereoselective conversion of alkynes into tetrasubstituted trifluoromethylated alkenes, Angew. Chem. Int. Ed. 54 (2015) 12923–12927;
(d) R. Tomita, Y. Yasu, T. Koike, M. Akita, Combining photoredox-catalyzed trifluoromethylation and oxidation with DMSO: facile synthesis of α-trifluoromethylated ketones from aromatic alkenes, Angew. Chem. Int. Ed. 53 (2014) 7144–7148.

[5] For examples, see:. (a) M. Oishi, H. Kondoa, H. Amii, Aromatic trifluoromethylation catalytic in copper, Chem. Commun. (2009) 1909–1911;
(b) X.-S. Wang, L. Truesdale, J.-Q. Yu, Pd(II)-catalyzed ortho-trifluoromethylation of arenes using TFA as a promoter, J. Am. Chem. Soc. 132 (2010) 3648–3649;
(c) T. Liu, Q. Shen, Copper-catalyzed trifluoromethylation of aryl and vinyl boronic acids with an electrophilic trifluoromethylating reagent, Org. Lett. 13 (2011) 2342–2345;
(d) E.J. Cho, T.D. Senecal, T. Kinzel, Y. Zhang, D.A. Watson, S.L. Buchwald, The Palladium-catalyzed trifluoromethylation of aryl chlorides, Science 328 (2010) 1679–1681.

[6] X. Yang, G.C. Tsui, Silver-catalyzed trifluoromethylalkynylation of unactivated alkenes with hypervalent iodine reagents, Org. Lett. 21 (2019) 8625–8629.

[7] (a) Z. Liu, H. Shen, H. Xiao, Z. Wang, L. Zhu, C. Li, Copper-catalyzed ring-opening radical triflfluoromethylation of cycloalkanone oximes, Org. Lett. 21 (2019) 5201–5205;
(b) Z. Zhang, L. Zhu, C. Li, Copper-catalyzed carbotrifluoromethylation of unactivated alkenes driven by trifluoromethylation of alkyl radicals, Chin. J. Chem. 37 (2019) 452–456.

[8] K. Aikawa, W. Toya, Y. Nakamura, K. Mikami, Development of (trifluoromethyl)zinc reagent as trifluoromethyl anion and difluorocarbene sources, Org. Lett. 17 (2015) 4996–4999.

[9] (a) Z. Liu, H. Xiao, B. Zhang, H. Shen, L. Zhu, C. Li, Copper-catalyzed remote $C(sp^3)$-H trifluoromethylation of carboxamides and sulfonamides, Angew. Chem. Int. Ed. 58 (2019) 2510–2513;
(b) H. Xiao, Z. Liu, H. Shen, B. Zhang, L. Zhu, C. Li, Copper-catalyzed late-stage benzylic $C(sp^3)$–H trifluoromethylation, Inside Chem. 5 (2019) 940–949;
(c) H. Xiao, H. Shen, L. Zhu, C. Li, Copper-catalyzed radical amino-trifluoromethylation of alkenes, J. Am. Chem. Soc. 141 (2019) 11440–11445;
(d) H. Shen, H. Xiao, L. Zhu, C. Li, Copper-catalyzed radical bis(trifluoromethylation) of alkynes and 1,3-enynes, Synlett 31 (2020) 41–44;
(e) H. Zhang, H. Xiao, F. Jiang, Y. Fang, L. Zhu, C. Li, Copper-catalyzed ring-opening 1,3-aminotrifluoromethylation of arylcyclopropanes, Org. Lett. 23 (2021) 2268–2272.

[10] R. Loska, M. Majcher, M. Makosza, Synthesis of trifluoromethylated azines via nucleophilic oxidative substitution of hydrogen by trifluoromethyl carbanions, J. Org. Chem. 72 (2007) 5574–5580.

[11] R. Loska, M. Makosza, Synthesis of perfluoroalkyl-substituted azines via nucleophilic substitution of hydrogen with perfluoroisopropyl carbanions, J. Org. Chem. 72 (2007) 1354–1365.

[12] J.-H. Xu, S.-C. Zheng, J.-W. Zhang, X.-Y. Liu, B. Tan, Construction of tropane derivatives by the organocatalytic asymmetric dearomatization of isoquinolines, Angew. Chem. Int. Ed. 55 (2016) 11834–11839.

[13] T. Shirai, M. Kanai, Y. Kuninobu, 2-Position-selective C–H perfluoroalkylation of quinoline derivatives, Org. Lett. 20 (2018) 1593–1596.

[14] H. Keller, M. Schlosser, 2-(Trifluoromethyl)quinolines from anilines: a novel mode of isomerization and cyclization, Tetrahedron 52 (1996) 4637–4644.