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Difunctionalization of Alkenes via the Visible-Light-Induced Trifluoromethylarylation/1,4-Aryl Shift/Desulfonylation Cascade Reactions

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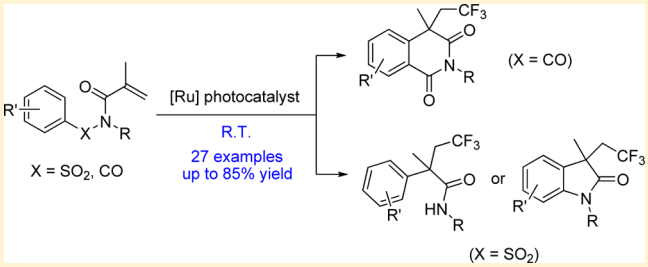
Supporting Information

ABSTRACT: A novel visible-light-induced trifluoromethylarylation/1,4-aryl shift/desulfonylation cascade reaction using CF_3SO_2Cl as CF_3 source was described. The protocol provides an efficient approach for the synthesis of α-aryl-β-trifluoromethyl amides and/or CF_3-containing oxindoles as well as the isoquinolinediones under benign conditions.



INTRODUCTION

The trifluoromethyl moiety is one of the prevalent and important groups in functional molecular agrochemicals, pharmaceuticals and materials, due to its biological activities and physical properties.[1−4] In recent years, extensive efforts have been made to explore the incorporation of trifluoromethyl moiety into organic molecules that include nucleophilic, electrophilic, and radical trifluoromethylation pathways.[5−14,48−55] Among these oxidative difunctionalizations of alkenes, radical transformation has been proven to be an attractive strategy to build CF_3 containing molecules and has attracted considerable attention. For example, Nevado and coworkers reported an efficient and complementary method for Cu and tetrabutylammonium iodide catalyzed intramolecular aryltrifluoromethylation/1,4-aryl migration/desulfonylation reaction.[15] Subsequently the Liu group also developed carbotrifluoromethylation of alkenes using the combination of $TMSCF_3$/KF/$PhI(OAc)_2$.[16] Despite these advances, there is still a great demand to develop the alternative, promising and environmentally friendly protocol for trifluoromethylation of alkenes under mild conditions.

In the past few years, visible-light photoredox catalysis has been regard as an ecofriendly and effective strategy for the advantages of convenience, availability and safety.[17−28] Recently, visible-light-mediated radical difunctionalization of alkenes to introduce the trifluoromethyl group serves as a feasible and efficient method.[29−39] However, when the various transformations involving hydrotrifluoromethylation,[29,34] halotrifluoromethylation,[30,32] aminotrifluoromethylation,[31,35] and oxytrifluoromethylation[35,38] have been well documented, the visible-light-induced carbotrifluoromethylation of alkenes is quite rare. With our continuous efforts devoted to photochemical reactions,[40−45] herein we developed a trifluoromethylation initiated desulfonylation followed by either C−N or C−H bond formation using CF_3SO_2Cl as CF_3 resource under mild photocatalytic conditions.

RESULTS AND DISCUSSION

Our preliminary investigation was started from tosyl amide **1a** as model substrate for the screening of reaction conditions (Table 1). In presence of $Ru(bpy)_3Cl_2$, Togni's reagent **2c**, and K_2HPO_4 in MeCN, to our delight, compound **1a** was transformed to product **3a** in 36% yield through an aryltrifluoromethylation/desulfonylation cascade reaction when 5 W blue LEDs were used as light source (Table 1, entry 1). Subsequently, the examination of solvents showed that the reaction in DMSO, DMF, or CH_2Cl_2 did not improve the yield (entries 4−6). Furthermore, the change of photocatalyst and base showed the same result (entries 2 and 3). The CF_3I also showed the low yield (entry 13). However, when the oxidant **2c** was replaced by CF_3SO_2Cl, the yield was increased to 80% (entry 7). Further experiments showed that both light and photocatalyst were essential for the reaction (entries 9 and 10). In addition, no reaction was observed under air atmosphere or without CF_3SO_2Cl (entry 11 and 12).

With the optimized conditions in hand, we set out to evaluate the scope of the reaction. Therefore, a range of substrates containing various substituents which directly bound to the N atom, such as butyl, isopropyl and methyl, were submitted to the reaction conditions, which led to the corresponding products (Scheme 1, **3a**−**3k**, **3k**′). Both the electron-withdrawing and electron-donating groups at the *para* position of the aromatic ring of **1** were tolerant with the reaction conditions to achieve the corresponding products in moderate to good yields (Scheme 1, **3b**−**3g**, **3h** and **3j**). When

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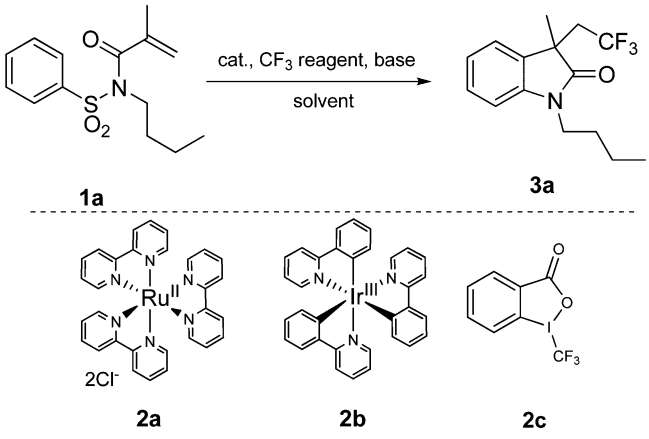
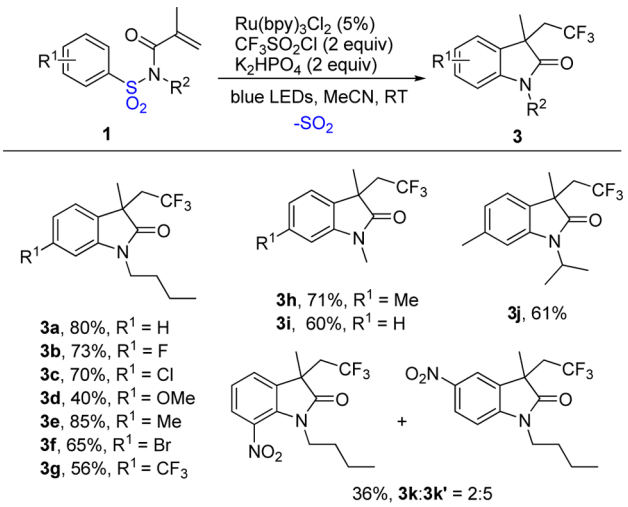
Table 1. Screening of the Optimal Reaction Conditions[a]



entry	catalyst	solvent	CF_3 reagent	yields (%)[b]
1	**2a**	MeCN	**2c**	36
2[c]	**2a**	MeCN	**2c**	32
3	**2b**	MeCN	**2c**	34
4	**2a**	DMSO	**2c**	15
5	**2a**	DMF	**2c**	34
6	**2a**	CH_2Cl_2	**2c**	35
7	**2a**	MeCN	CF_3SO_2Cl	80
9[d]	**2a**	MeCN	CF_3SO_2Cl	0
10	–	MeCN	CF_3SO_2Cl	0
11[e]	**2a**	MeCN	CF_3SO_2Cl	0
12	**2a**	MeCN	–	0
13	**2a**	MeCN	CF_3I	35

[a]Reaction conditions: **1a** (0.1 mmol), catalyst **2** (0.005 mmol), base (K_2HPO_4, 0.2 mmol), oxidant (0.2 mmol), solvent (anhydrous 2 mL), 5 W blue LEDs light, rt, under N_2 atmosphere. [b]Isolated yield. [c]Base (KF, 0.2 mmol). [d]In the dark. [e]Under air.

Scheme 1. Scope of α,β-Unsaturated Imide Alkenes 1[a,b]

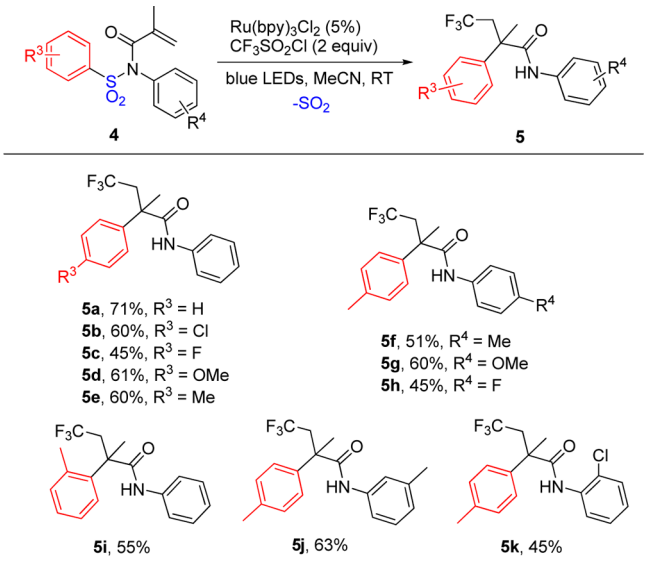


[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.005 mmol), CF_3SO_2Cl (0.2 mmol), K_2HPO_4 (0.2 mmol), anhydrous MeCN (2 mL), 5 W blue LEDs light, rt, under N_2 atmosphere. [b]Isolated yield.

the substituent at the *meta* position of aromatic ring of **1** was replaced by NO_2, the regioisomers was obtained with a ratio of 2:5 (Scheme 1, **3k**, **3k′**). However, a very complex product was observed for the *ortho* substituted substrates that might be owing to the effect of the steric hindrance.[46]

Interestingly, if the substituents on N atom were changed from alkyl to aryl groups, a unique 1,4-aryl shift was observed rather than the radical cyclization. For example, the reaction of **4a** under the standard reaction conditions led to the product **5a** through a trifluoromethylation/1,4-aryl shift/desulfonylation cascade reaction. Such a result represents the first example of visible light photocatalytic approach on the above transformations and triggers us to investigate it in details, although the similar results have recently reported by Nevado and coworkers under metal-catalytic conditions.[15] Further investigation revealed that the reaction could conduct well in the absence of K_2HPO_4 to give the product in 71% yield (Scheme 2). To investigate the scope of the reaction, the effect of

Scheme 2. Scope of α,β-Unsaturated Imide Alkenes 4[a,b]



[a]Reaction conditions: **4** (0.1 mmol), **2a** (0.005 mmol), CF_3SO_2Cl (0.2 mmol), anhydrous MeCN (2 mL), 5 W blue LEDs light, rt, under N_2 atmosphere. [b]Isolated yield.

substituents of the sulfonamide group was examined, which led to the corresponding products in moderate to good yields (Scheme 2, **5a**–**5e**, **5i**). Next we also studied the influence of substituents of the aryl group that directly bounded to the N atom. Electron-donating groups at the *para* or *meta* position were well compatible with the reaction to form the products **5f**, **5g**, **5j** in good yields. In contrast, the present of electron-withdrawing groups decreased the efficiency of the reaction (**5h**, **5k**).

With our continuous studies on the application of this protocol, we also prepared amide **6a** and subjected it to the reaction conditions, and trifluoromethylated isoquinolinedione **7a** was obtained smoothly in 70% yield (Scheme 3). Substrates bearing methyl and F groups at the *para* position of the aryl ring or having different substituents at N atoms were also tolerant with the reaction conditions, providing the desired products **7b**–**7e**.

Upon the basis of the above results, a plausible mechanism of the protocol was proposed in Scheme 4. The photocatalyst $[Ru(bpy)_3]^{2+}$ was activated by visible light to the excited state $[Ru(bpy)_3]^{2+*}$, which then reduced CF_3SO_2Cl to generate CF_3 radical after release of a Cl^- and SO_2 The CF_3 radical was trapped by **1**, **4** (X = SO_2) or **6** (X = CO) to give the intermediate **B** after formation of a new $C(sp^3)$–CF_3 bond.

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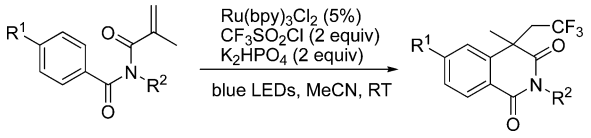
Scheme 3. Trifluoromethylation of α,β-Unsaturated Imide Alkenes 6[a,b]



6	7
6a, R^1 = H, R^2 = Me	**7a**, 70%
6b, R^1 = Me, R^2 = Me	**7b**, 60%
6c, R^1 = F, R^2 = Me	**7c**, 50%
6d, R^1 = H, R^2 = Butyl	**7d**, 43%
6e, R^1 = H, R^2 = Bn	**7e**, 54%

[a]Reaction conditions: **6** (0.1 mmol), **2a** (0.005 mmol), CF_3SO_2Cl (0.2 mmol), K_2HPO_4 (0.2 mmol), anhydrous MeCN (2 mL), 5 W blue LEDs light, rt, under N_2 atmosphere. [b]Isolated yield.

Arylmigration/desulfonylation cascade reaction occurred to form the intermediate **C** when X is SO_2, due to the instability of intermediate **B**.[15] Cyclization of amidyl radical to the aryl ring of intermediate **C** led to the final product **3** if the substituent R on the N atom was alkyl (R = alkyl), a process that seems prefer to be trapped by the aromatic ring.[15] In contrast, **5** was obtained through the direct hydrogen abstraction from the medium, which might be owing to the stability of nitrogen radical when R was aryl group.[5,6] For X = CO, the intramolecular radical cyclization of **B** led to the intermediate **A**, which produced isoquinolinedione **7** after oxidation and deprotonation.

CONCLUSION

In summary, we have developed the visible-light-induced trifluoromethylarylation/1,4-aryl shift/desulfonylation cascade reactions. It provides a practical and effective method for the synthesis of trifluoromethyl oxindoles and α-aryl-β-trifluoromethyl amides. In addition, the trifluoromethyl isoquinolinedione could also be obtained in this protocol. The method described in this paper is highlighted by its operational simplicity (under light), low catalyst loading (5% catalyst), and less additives (the base KH_2PO_4 was not need for the trifluoromethylation of **4**).

EXPERIMENTAL SECTION

General Methods. Amide **1**, **4** and **6** were synthesized according to previous literature,[2j,3,4] and the NMR spectroscopys were consisted with those data. ^1H NMR and ^{13}C NMR spectra were obtained at 400 and 100 MHz; HRMS (ESI) spectra were obtained using a QTOF mass spectrometer. GC−MS analysis was obtained by quadrupole analyzer. The starting materials were purchased from commercial sources used without additional purification.

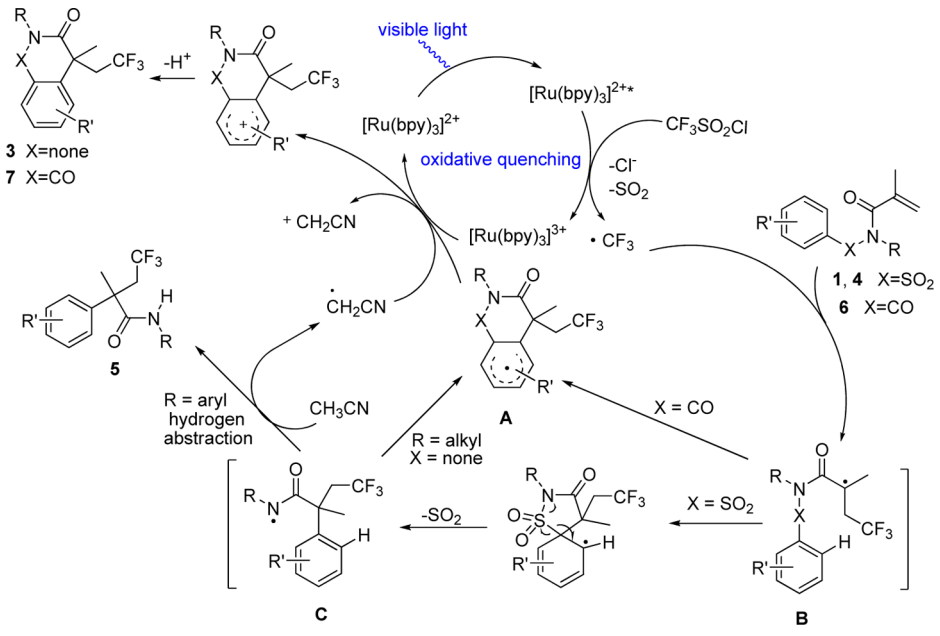
Characterization of New Substrates. *N-Butyl-N-(phenylsulfonyl)methacrylamide (**1a**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.91 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 5.28 (s, 1H), 5.11 (s, 1H), 3.77−3.73 (m, 2H), 1.93 (s, 3H), 1.69−1.62 (m, 2H), 1.36−1.27 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.5, 141.0, 139.6, 133.7, 129.1, 128.3, 119.3, 47.4, 31.9, 20.1, 19.8, 13.7; GC−MS (EI, QMS, m/z) 281.1 (1%), 225.1, 140.0, 124.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) $(M + Na)^+$ calcd for $C_{14}H_{19}NO_3SNa^+$, 304.0978, found 304.0977.

*N-Butyl-N-(4-fluorophenylsulfonyl)methacrylamide (**1b**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.98 (s, 2H), 7.21 (t, J = 8.1 Hz, 2H), 5.33 (s, 1H), 5.17 (s, 1H), 3.76 (t, J = 7.5 Hz, 2H), 1.95 (s, 3H), 1.67−1.64 (m, 2H), 1.34−1.29 (m, 2H), 0.92 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.3, 165.7 (d, J = 256.5 Hz), 140.7, 135.4 (d, J = 3.1 Hz), 131.3 (d, J = 9.7 Hz), 119.4, 116.3 (d, J = 22.6 Hz), 47.7, 32.1, 20.0, 19.7, 13.7; GC−MS (EI, QMS, m/z) 299.1 (1%), 244.1, 159.1, 124.2, 95.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) $(M + Na)^+$ calcd for $C_{14}H_{18}FNO_3SNa^+$, 322.0884, found 322.0894.

*N-Butyl-N-(4-chlorophenylsulfonyl)methacrylamide (**1c**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.90 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 5.34 (s, 1H), 5.17 (s, 1H), 3.78−3.75 (m, 2H), 1.96 (s, 3H), 1.68−1.64 (m, 2H), 1.35−1.29 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.4, 140.7, 140.4, 137.9, 129.9, 129.3, 119.6, 47.7, 32.1, 20.0, 19.8, 13.7; GC−MS (EI, QMS, m/z) 315.1 (1%), 175.0, 124.0, 111.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) $(M + Na)^+$ calcd for $C_{14}H_{18}ClNO_3SNa^+$, 338.0588, found 338.0600.

*N-Butyl-N-(4-methoxyphenylsulfonyl)methacrylamide (**1d**).* Colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (d, J = 8.4 Hz, 2H),

Scheme 4. Proposed Mechanism



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6.98 (d, J = 8.4 Hz, 2H), 5.28 (s, 1H), 5.13 (s, 1H), 3.88 (s, 3H), 3.76−3.73 (m, 2H), 1.93 (s, 3H), 1.67−1.62 (m, 2H), 1.34−1.27 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.4, 163.7, 140.9, 130.9, 130.6, 118.9, 114.1, 55.8, 47.3, 32.0, 20.0, 19.8, 13.7; GC−MS (EI, QMS, m/z) 311.1 (1%), 247.2, 171.1, 155.0, 124.2 (100%), 69.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{15}H_{21}NO_4SNa^+$, 334.1083, found 334.1088.

*N-(4-Bromophenylsulfonyl)-N-butylmethacrylamide (**1f**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.82 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 5.34 (s, 1H), 5.17 (s, 1H), 3.78−3.74 (m, 2H), 1.96 (s, 3H), 1.69−1.62 (m, 2H), 1.36−1.27 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.3, 140.6, 138.5, 132.3, 129.9, 128.9, 119.6, 47.7, 32.1, 20.0, 19.7, 13.7; GC−MS (EI, QMS, m/z) 361.1 (1%), 359.1 (1%), 220.9, 219.0, 157.0, 155.0, 124.2, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{14}H_{18}BrNO_3SNa^+$, 382.0083, found 382.0094.

*N-Butyl-N-(4-(trifluoromethyl)phenylsulfonyl)methacryla-mide (**1g**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.10 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 5.37 (s, 1H), 5.21 (s, 1H), 3.79 (t, J = 7.6 Hz, 2H), 1.97 (s, 3H), 1.69−1.67 (m, 2H), 1.36−1.30 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.4, 143.0, 140.5, 135.3 (q, J = 33.1 Hz), 129.0, 126.2, 123.2 (q, J = 273.0 Hz), 119.9, 47.9, 32.2, 20.0, 19.7, 13.7; GC−MS (EI, QMS, m/z) 349.1 (1%), 294.1, 229.1, 209.0, 145.0, 124.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{15}H_{18}F_3NO_3SNa^+$, 372.0852, found 372.0868.

*N-Butyl-N-(3-nitrophenylsulfonyl)methacrylamide (**1k**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.79 (s, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.33 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 8.1 Hz, 1H), 5.39 (s, 1H), 5.22 (s, 1H), 3.84−3.80 (m, 2H), 1.96 (s, 3H), 1.72−1.64 (m, 2H), 1.37−1.28 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.3, 148.1, 141.5, 140.2, 134.31, 130.3, 128.2, 123.7, 120.1, 48.3, 32.4, 20.0, 19.7, 13.7; GC−MS (EI, QMS, m/z) 326.1 (1%), 271.1, 253.0, 186.0, 124.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{14}H_{18}N_2O_5SNa^+$, 349.0829, found 349.0821.

*N-(4-Chlorophenylsulfonyl)-N-phenylmethacrylamide (**4b**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.85 (d, J = 8.0 Hz, 2H), 7.51−7.41 (m, 5H), 7.15 (d, J = 7.0 Hz, 2H), 5.44 (s, 1H), 5.31 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.1, 140.6, 139.2, 137.1, 136.6, 131.0, 129.9, 129.6, 129.5, 129.1, 125.3, 19.2; GC−MS (EI, QMS, m/z) 335.0 (1%), 159.0, 144.1, 111.1, 91.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{16}H_{14}ClNO_3SNa^+$, 358.0275, found 358.0281.

*N-(4-Fluorophenylsulfonyl)-N-phenylmethacrylamide (**4c**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.96−7.93 (m, 2H), 7.43−7.41 (m, 3H), 7.22−7.14 (m, 4H), 5.43 (s, 1H), 5.30 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.1, 165.9 (d, J = 256.5 Hz), 139.2, 137.1, 134.1 (d, J = 3.0 Hz), 132.4 (d, J = 9.8 Hz), 129.9, 129.5, 129.5, 125.1, 116.0 (d, J = 22.4 Hz), 19.2; GC−MS (EI, QMS, m/z) 319.1 (1%), 291.1, 144.1, 95.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{16}H_{14}FNO_3SNa^+$, 342.0571, found 342.0579.

*N-(4-Methoxyphenylsulfonyl)-N-phenylmethacrylamide (**4d**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (d, J = 8.3 Hz, 2H), 7.41−7.39 (m, 3H), 7.16 (d, J = 6.9 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 5.38 (s, 1H), 5.26 (s, 1H), 3.90 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.0, 163.8, 139.4, 137.3, 131.7, 130.0, 129.5, 129.3, 129.2, 124.3, 113.8, 55.7, 19.3; GC−MS (EI, QMS, m/z) 331.1 (1%), 267.1, 171.1, 144.1 (100%), 69.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{17}H_{17}NO_4SNa^+$, 354.0770, found 354.0762.

*N-(4-Methoxyphenyl)-N-tosylmethacrylamide (**4g**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.79 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.36 (s, 1H), 5.23 (s, 1H), 3.83 (s, 3H), 2.44 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.1, 160.3, 144.8, 139.7, 135.4, 131.3, 129.6, 129.5, 129.3, 124.0, 114.5, 55.6, 21.8, 19.4; GC−MS (EI, QMS, m/z) 345.1 (1%), 281.1, 174.0, 91.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{18}H_{19}NO_4SNa^+$, 368.0927, found 368.0921.

*N-(4-Fluorophenyl)-N-tosylmethacrylamide (**4h**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.77 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.14−7.04 (m, 4H), 5.36 (s, 1H), 5.27 (s, 1H), 2.45 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 170.9, 163.0 (d, J = 250.7 Hz), 145.1, 139.5, 135.2, 133.2 (d, J = 3.3 Hz), 131.9 (d, J = 8.9 Hz), 129.5, 129.5, 124.5, 116.4 (d, J = 22.9 Hz), 21.8, 19.5; GC−MS (EI, QMS, m/z) 333.1 (1%), 269.1, 162.1, 109.1, 91.1, 69.1 (100%); HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{17}H_{16}FNO_3SNa^+$, 356.0727, found 356.0728.

*N-Phenyl-N-(o-tolylsulfonyl)methacrylamide (**4i**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.07 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.43−7.35 (m, 4H), 7.30 (d, J = 7.0 Hz, 3H), 5.39 (s, 1H), 5.27 (s, 1H), 2.55 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.2, 139.6, 139.0, 137.4, 136.7, 133.8, 132.6, 131.9, 130.3, 129.5, 129.4, 126.3, 124.1, 21.0, 19.4; GC−MS (EI, QMS, m/z) 315.1 (1%), 144.1, 91.1, 69.1 (100%), 41.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{17}H_{17}NO_3SNa^+$, 338.0821, found 338.0819.

*N-m-Tolyl-N-tosylmethacrylamide (**4j**).* White solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.79 (d, J = 8.3 Hz, 2H), 7.31−7.21 (m, 4H), 7.01 (s, 1H), 6.89 (d, J = 7.4 Hz, 1H), 5.36 (s, 1H), 5.23 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 171.1, 144.8, 139.5, 139.4, 137.1, 135.6, 130.9, 130.2, 129.5, 129.3, 129.0, 127.0, 124.2, 21.8, 21.4, 19.4; GC−MS (EI, QMS, m/z) 329.0 (1%), 301.1, 265.1, 158.1 (100%), 91.1, 69.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{18}H_{19}NO_3SNa^+$, 352.0978, found 352.0980.

*4-Fluoro-N-methacryloyl-N-methylbenzamide (**6c**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.57−7.52 (m, 2H), 7.13−7.09 (m, 2H), 5.31 (s, 1H), 5.20 (s, 1H), 3.41 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 175.2, 173.2, 164.9 (d, J = 254.1 Hz), 143.0, 133.4 (d, J = 3.1 Hz), 131.0 (d, J = 8.9 Hz), 122.3, 116.1 (d, J = 22.1 Hz), 33.7, 18.8. GC−MS (EI, QMS, m/z) 221.1, 206.1, 164.0, 136.1, 123.0, 95.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{12}H_{13}FNO_2^+$, 222.0925, found 222.0921.

*N-Butyl-N-methacryloylbenzamide (**6d**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49−7.46 (m, 3H), 7.42−7.39 (m, 2H), 5.28 (s, 1H), 5.11 (s, 1H), 3.94−3.91 (m, 2H), 1.73−1.70 (m, 2H), 1.61 (s, 3H), 1.45−1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 175.2, 174.3, 144.0, 138.1, 131.9, 128.9, 128.6, 122.2, 46.5, 31.0, 20.4, 18.6, 13.9. GC−MS (EI, QMS, m/z) 245.2, 230.1, 216.2, 203.1, 160.1, 105.1, 77.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{20}NO_2^+$, 246.1489, found 246.1481.

*N-Benzyl-N-methacryloylbenzamide (**6e**).*[47] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.53−7.44 (m, 5H), 7.41−7.29 (m, 5H), 5.21 (s, 1H), 5.12 (s, 2H), 5.09 (s, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.9, 174.0, 143.7, 137.9, 137.4, 132.0, 129.0, 128.9, 128.7, 128.6, 127.8, 122.6, 49.8, 18.6. GC−MS (EI, QMS, m/z) 279.1, 210.1, 174.1, 105.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{18}H_{18}NO_2^+$, 280.1332, found 280.1325.

General Procedure for Trifluoromethylation of 1a−1k. In a 10 mL bottom flask, the magnetic stir bar was added. Then it was charged with substrate **1** (0.1 mmol), CF_3SO_2Cl (0.2 mmol), CH_3CN (2.0 mL), $Ru(bpy)_3Cl_2$ (0.005 mmol) and K_2HPO_4 (0.2 mmol). The mixture was charged with N_2 three times under −78 °C and then was irradiated under blue LEDs (5 W). After the substrate was consumed (monitored by TLC), the mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **3**.

Characterization of 3a−3k and 3k′. *1-Butyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3a**).* 22.8 mg, 80% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.34−7.28 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 3.84−3.77 (m, 1H), 3.71−3.64 (m, 1H), 2.92−2.80 (m, 1H), 2.72−2.61 (m, 1H), 1.70−1.66 (m, 2H), 1.46−1.39 (m, 5H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.5, 142.5, 131.4, 128.5, 125.4 (q, J = 278.2 Hz), 123.8, 122.5, 108.9, 44.4, 40.8 (q, J = 28.4 Hz), 40.1, 29.4, 25.4, 20.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.1; GC−MS (EI, QMS, m/z) 285.1, 242.1, 214.1, 130.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{19}F_3NO^+$, 286.1413, found 286.1418.

*1-Butyl-6-fluoro-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3b**).* 22.1 mg, 73% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$)

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δ_H 7.22−7.19 (m, 1H), 6.79−6.73 (m, 1H), 6.64 (d, J = 8.9 Hz, 1H), 3.81−3.74 (m, 1H), 3.67−3.60 (m, 1H), 2.92−2.78 (m, 1H), 2.71−2.58 (m, 1H), 1.70−1.62 (m, 2H), 1.43−1.38 (m, 5H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.8, 163.3 (d, J = 244.7 Hz), 144.0 (d, J = 11.4 Hz), 126.5 (d, J = 3.1 Hz), 125.3 (q, J = 278.3 Hz), 124.8 (d, J = 9.8 Hz), 108.7 (d, J = 22.3 Hz), 97.6 (d, J = 27.5 Hz), 44.1, 40.7 (q, J = 28.3 Hz), 40.3, 29.3, 25.5, 20.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.1, −111.9; GC−MS (EI, QMS, m/z) 303.1, 260.1, 232.1, 148.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{18}F_4NO^+$, 304.1319, found 304.1312.

1-Butyl-6-chloro-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3c**). 22.4 mg, 70% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.19 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 6.90 (s, 1H), 3.81−3.74 (m, 1H), 3.68−3.62 (m, 1H), 2.91−2.79 (m, 1H), 2.70−2.61 (m, 1H), 1.70−1.64 (m, 2H), 1.44−1.38 (m, 5H), 0.99 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.4, 143.7, 134.4, 129.6, 125.2 (q, J = 278.5 Hz), 124.7, 122.4, 109.6, 44.2, 40.6 (q, J = 28.4 Hz), 40.2, 29.3, 25.4, 20.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.9; GC−MS (EI, QMS, m/z) 319.2, 276.1, 248.1, 164.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{18}ClF_3NO^+$, 320.1024, found 320.1024.

1-Butyl-6-methoxy-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3d**). 12.6 mg, 40% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.17 (d, J = 8.2 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 6.49 (s, 1H), 3.86 (s, 3H), 3.80−3.73 (m, 1H), 3.67−3.60 (m, 1H), 2.87−2.75 (m, 1H), 2.68−2.57 (m, 1H), 1.70−7.63 (m, 2H), 1.45−1.36 (m, 5H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 179.1, 160.4, 143.7, 125.5 (q, J = 278.2 Hz), 124.4, 123.2, 106.0, 97.0, 55.7, 44.0, 40.8 (q, J = 28.2 Hz), 40.1, 29.4, 25.5, 20.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.8; GC−MS (EI, QMS, m/z) 315.2, 300.1, 272.1, 244.2, 232.2, 190.1, 176.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{16}H_{21}F_3NO_2^+$, 316.1519, found 316.1521.

1-Butyl-3,6-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3e**).[15] 27.2 mg, 85% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.16 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 3.82−3.75 (m, 1H), 3.70−3.62 (m, 1H), 2.86−2.80 (m, 1H), 2.67−2.61 (m, 1H), 2.42 (s, 3H), 1.69−1.67 (m, 2H), 1.44−1.40 (m, 5H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.8, 142.6, 138.7, 128.4, 125.5 (q, J = 278.3 Hz), 123.5, 123.0, 109.7, 44.2, 40.8 (q, J = 28.2 Hz), 40.0, 29.5, 25.5, 22.0, 20.2, 13.9; GC−MS (EI, QMS, m/z) 299.1, 256.1, 228.1, 144.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{16}H_{20}F_3NONa^+$, 322.1389, found 322.1391.

6-Bromo-1-butyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3f**). 23.5 mg, 65% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.23 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 7.04 (s, 1H), 3.81−3.74 (m, 1H), 3.67−3.60 (m, 1H), 2.91−2.79 (m, 1H), 2.70−2.58 (m, 1H), 1.69−1.64 (m, 2H), 1.43−1.38 (m, 5H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.3, 143.7, 130.2, 125.3,125.2 (q, J = 278.3 Hz) 125.1, 122.2, 112.3, 44.2, 40.6 (q, J = 28.4 Hz), 40.2, 29.3, 25.4, 20.2, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.9; GC−MS (EI, QMS, m/z) 356.1, 363.1, 322.1, 320.1, 307.1, 292.0, 213.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{18}BrF_3NO^+$, 364.0518, found 364.0519.

1-Butyl-3-methyl-3-(2,2,2-trifluoroethyl)-6-(trifluoromethy-l)-indolin-2-one (**3g**). 21.0 mg, 56% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 (s, 2H), 7.10 (s, 1H), 3.87−3.80 (m, 1H), 3.74−3.67 (m, 1H), 2.93−2.84 (m, 1H), 2.75−2.66 (m, 1H), 1.70−1.66 (m, 2H), 1.47−1.39 (m, 5H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.1, 143.2, 135.1, 131.1 (q, J = 32.4 Hz), 125.2 (q, J = 278.2 Hz), 124.1, 124.0 (q, J = 272.2 Hz), 119.6 (q, J = 4.1 Hz), 105.5 (q, J = 3.8 Hz), 44.4, 40.6 (q, J = 28.6 Hz), 40.3, 29.3, 25.4, 20.2, 13.8; GC−MS (EI, QMS, m/z) 353.2, 334.1, 310.1, 297.1, 282.1, 198.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{16}H_{17}F_6NNaO^+$, 376.1107, found 376.1116.

1,3,6-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3h**).[15] 18.2 mg, 71% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.14 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.71 (s, 1H), 3.22 (s, 3H), 2.82−2.73 (m, 1H), 2.68−2.59 (m, 1H), 2.40 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 179.0, 143.0, 138.8, 128.2, 125.4 (q, J = 278.1 Hz), 123.5, 123.3, 109.5, 44.3, 40.8 (q, J = 28.0 Hz), 26.5, 25.2, 22.0; GC−MS (EI, QMS, m/z) 257.1, 222.1, 174.1, 159.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{13}H_{15}F_3NO^+$, 258.1100, found 258.1108.

1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3i**).[15] 14.5 mg, 60% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.36−7.28 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.26 (s, 3H), 2.91−2.79 (m, 1H), 2.73−2.62 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.6, 143.0, 131.2, 128.7, 125.4 (q, J = 278.2 Hz), 123.7, 122.8, 108.6, 44.5, 40.8 (q, J = 28.1 Hz), 26.6, 25.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{12}H_{13}F_3NO^+$, 244.0944, found 244.0949.

1-Isopropyl-3,6-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (**3j**).[15] 17.3 mg, 61% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.15 (d, J = 7.4 Hz, 1H), 7.00−6.88 (m, 2H), 4.67−4.59 (m, 1H), 2.90−2.78 (m, 1H), 2.67−2.59 (m, 1H), 2.41 (s, 3H), 1.51−1.49 (m, 6H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.6, 141.8, 138.4, 128.6, 125.4 (q, J = 278.3 Hz), 123.6, 122.7, 111.2, 44.1, 44.0, 40.9 (q, J = 27.8 Hz), 25.6, 22.1, 19.4, 19.2; GC−MS (EI, QMS, m/z) 285.1, 270.1, 242.1, 160.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{19}F_3NO^+$, 286.1413, found 286.1418.

1-Butyl-3-methyl-7-nitro-3-(2,2,2-trifluoroethyl)indolin-2-one (**3k**). 5 mg, 14% yield, yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.67 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 7.3 Hz, 1H), 7.16 (t, J = 7.9 Hz, 1H), 3.99−3.91 (m, 1H), 3.81−3.73 (m, 1H), 2.98−2.86 (m, 1H), 2.74−2.63 (m, 1H), 1.44 (s, 3H), 1.41−1.36 (m, 2H), 1.32−1.26 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 179.0, 136.3, 135.2, 134.9, 127.5, 124.9 (q, J = 277.7 Hz), 124.8, 122.3, 43.3, 42.4, 40.9 (q, J = 28.4 Hz), 29.7, 25.9, 19.9, 13.8; GC−MS (EI, QMS, m/z) 330.1, 287.1, 259.1, 229.1, 213.1, 145.1, 130.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{18}F_3N_2O_3^+$, 331.1264, found 331.1270.

1-Butyl-3-methyl-5-nitro-3-(2,2,2-trifluoroethyl)indolin-2-one (**3k′**). 7 mg, 22% yield, yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.29 (dd, J = 8.7, 2.1 Hz, 1H), 8.15 (d, J = 1.9 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 3.88−3.81 (m, 1H), 3.74−3.66 (m, 1H), 2.98−2.86 (m, 1H), 2.78−2.66 (m, 1H), 1.70−1.62 (m, 2H), 1.46−1.35 (m, 5H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 178.5, 148.3, 143.4, 132.0, 125.9, 124.9 (q, J = 278.2 Hz), 119.7, 108.5, 44.3, 40.7 (q, J = 27.8 Hz), 40.6, 29.3, 25.4, 20.2, 13.8; GC−MS (EI, QMS, m/z) 330.1, 287.1, 259.1, 229.1, 213.1, 145.1, 130.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{15}H_{18}F_3N_2O_3^+$, 331.1264, found 331.1259.

General Procedure for Trifluoromethylation of 4a−4k. In a 10 mL bottom flask, the magnetic stir bar was added. Then it was charged with substrate **4** (0.1 mmol), CF_3SO_2Cl (0.2 mmol), CH_3CN (2.0 mL), $Ru(bpy)_3Cl_2$ (0.005 mmol). The mixture was charged with N_2 three times under −78 °C and then was irradiated under blue LEDs (5 W). After the substrate was consumed (monitored by TLC), the mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **5**.

Characterization of 5a−5k. *4,4,4-Trifluoro-2-methyl-N,2-diphenylbutanamide* (**5a**).[15] 21.7 mg, 71% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.47−7.28(m, 9H), 7.12 (t, J = 7.0 Hz, 1H), 6.80 (s, 1H), 3.30−3.18 (m, 1H), 2.96−2.84 (m, 1H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.5, 140.9, 137.6, 129.3, 129.1, 128.3, 127.0, 126.6 (q, J = 278.2 Hz), 125.2, 120.1, 49.0, 42.2 (q, J = 27.1 Hz), 22.8; GC−MS (EI, QMS, m/z) 307.2, 288.1, 188.1, 120.1, 105.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{17}H_{17}F_3NO^+$, 308.1257, found 308.1259.

2-(4-Chlorophenyl)-4,4,4-trifluoro-2-methyl-N-phenylbutanamide (**5b**). 20.4 mg, 60% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44−7.29 (m, 8H), 7.13 (t, J = 7.1 Hz, 1H), 6.78 (s, 1H), 3.27−3.15 (m, 1H), 2.91−2.79 (m, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 172.9, 139.4, 137.3, 134.4, 129.5, 129.2, 128.4, 126.4 (d, J = 278.2 Hz), 125.0, 120.2, 48.6, 42.3 (q, J = 27.1 Hz), 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.1; GC−MS (EI, QMS, m/z) 341.1, 222.1, 187.1, 157.1, 120.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{17}H_{16}ClF_3NO^+$, 342.0867, found 342.0877.

4,4,4-Trifluoro-2-(4-fluorophenyl)-2-methyl-N-phenylbutanamide (**5c**). 14.6 mg, 45% yield, white solid: ^{1}H NMR (400 MHz,

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$CDCl_3$) δ_H 7.46−7.42 (m, 2H), 7.36−7.29 (m, 4H), 7.17−7.11 (m, 3H), 6.78 (s, 1H), 3.27−3.15 (m, 1H), 2.92−2.80 (m, 1H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.2, 162.4 (d, J = 248.5 Hz), 137.4, 136.6 (d, J = 3.4 Hz), 129.2, 128.8 (d, J = 8.0 Hz), 126.4 (d, J = 278.0 Hz), 125.0, 120.1, 116.3 (d, J = 21.4 Hz), 48.5, 42.4 (q, J = 27.1 Hz), 22.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.1, −113.6; GC−MS (EI, QMS, m/z) 325.2, 205.1, 141.1, 120.1, 92.1, 77.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{17}H_{16}F_4NO^+$, 326.1163, found 326.1169.

4,4,4-Trifluoro-2-(4-methoxyphenyl)-2-methyl-N-phenylbutanamide (**5d**).[15] 20.5 mg, 61% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39−7.28 (m, 6H), 7.11 (t, J = 7.2 Hz, 1H), 7.00−6.97 (m, 2H), 6.85 (s, 1H), 3.86 (s, 3H), 3.26−3.14 (m, 1H), 2.92−2.80 (m, 1H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.9, 159.3, 137.6, 132.5, 129.4, 128.3, 126.6 (q, J = 278.3 Hz), 124.7, 120.0, 114.6, 55.4, 48.4, 42.1 (q, J = 27.1 Hz), 23.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.1; GC−MS (EI, QMS, m/z) 337.2, 217.2, 203.1, 135.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{18}H_{19}F_3NO_2^+$, 338.1362, found 338.1369.

4,4,4-Trifluoro-2-methyl-N-phenyl-2-p-tolylbutanamide (**5e**).[15] 19.2 mg, 60% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35−7.25 (m, 8H), 7.11 (t, J = 7.0 Hz, 1H), 6.82 (s, 1H), 3.25−3.16 (m, 1H), 2.94−2.82 (m, 1H), 2.40 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.8, 138.1, 137.7, 137.6, 130.0, 129.1, 126.6 (q, J = 278.1 Hz), 126.9, 124.7, 120.0, 48.7, 42.13 (q, J = 27.0 Hz), 22.9, 21.2; GC−MS (EI, QMS, m/z) 321.2, 202.2, 187.1, 137.1, 119.2; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{18}H_{18}F_3NONa^+$, 344.1233, found 344.1236.

4,4,4-Trifluoro-2-methyl-N,2-di-p-tolylbutanamide (**5f**).[15] 17.0 mg, 51% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 (d, J = 7.8 Hz, 2H), 7.26−7.21 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 6.77 (s, 1H), 3.27−3.15 (m, 1H), 2.93−2.81 (m, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.7, 138.0, 137.9, 135.0, 134.4, 130.0, 129.6, 126.6 (q, J = 278.4 Hz), 126.9, 120.2, 48.6, 42.2 (q, J = 27.4 Hz), 22.9, 21.2, 21.0; GC−MS (EI, QMS, m/z) 335.2, 201.2, 187.1, 134.2, 119.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{19}H_{21}F_3NO^+$, 336.1570, found 336.1587.

4,4,4-Trifluoro-N-(4-methoxyphenyl)-2-methyl-2-p-tolylbutanamide (**5g**). 21.0 mg, 60% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.34−7.32 (m, 2H), 7.26−7.23 (m, 4H), 6.83 (d, J = 9.0 Hz, 2H), 6.75 (s, 1H), 3.79 (s, 3H), 3.27−3.15 (m, 1H), 2.92−2.80 (m, 1H), 2.40 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.7, 156.8, 138.0, 137.9, 130.6, 129.9, 126.9, 126.5 (q, J = 278.4 Hz), 122.1, 114.2, 55.6, 48.5, 42.2 (q, J = 26.9 Hz), 22.9, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.0; GC−MS (EI, QMS, m/z) 351.2, 201.2, 149.1, 122.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{19}H_{21}F_3NO_2^+$, 352.1519, found 352.1534.

4,4,4-Trifluoro-N-(4-fluorophenyl)-2-methyl-2-p-tolylbutanamide (**5h**). 15.2 mg, 45% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.31−7.22 (m, 6H), 6.96 (t, J = 8.6 Hz, 2H), 6.78 (s, 1H), 3.24−3.12 (m, 1H), 2.90−2.77 (m, 1H), 2.37 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.8, 159.7 (d, J = 244.0 Hz), 138.2, 137.7, 133.5 (d, J = 2.5 Hz), 130.0, 126.8, 126.4 (q, J = 278.4 Hz), 122.1 (d, J = 7.8 Hz), 115.7 (d, J = 22.8 Hz), 48.6, 42.1 (q, J = 26.8 Hz), 22.9, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.1, −117.6; GC−MS (EI, QMS, m/z) 339.2, 201.2, 187.1, 161.1, 137.1, 119.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{18}H_{18}F_4NO^+$, 340.1319, found 340.1324.

4,4,4-Trifluoro-2-methyl-N-phenyl-2-o-tolylbutanamide (**5i**). 17.6 mg, 55% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.58−7.55 (m, 1H), 7.35−7.25 (m, 7H), 7.14−7.11 (m, 1H), 6.86 (s, 1H), 3.15−3.05 (m, 2H), 2.33 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.9, 137.5, 137.5, 137.5, 132.6, 129.1, 128.7, 127.9, 126.8, 126.7 (q, J = 277.6 Hz), 124.8, 124.0, 120.2, 48.7, 39.2 (q, J = 26.6 Hz), 25.9, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.7; GC−MS (EI, QMS, m/z) 321.2, 201.2, 187.1, 161.1, 120.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{18}H_{19}F_3NO^+$, 322.1413, found 322.1420.

4,4,4-Trifluoro-2-methyl-N-m-tolyl-2-p-tolylbutanamide (**5j**). 21.1 mg, 63% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.31−7.28 (m, 2H), 7.23−7.21 (m, 2H), 7.18−7.13 (m, 2H), 7.08 (d, J = 8.2 Hz, 1H), 6.90 (d, J = 7.4 Hz, 1H), 6.76 (s, 1H), 3.24−3.12 (m, 1H), 2.90−2.78 (m, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.7, 139.1, 138.1, 137.8, 137.5, 130.0, 128.9, 126.9, 126.6 (q, J = 278.2 Hz), 125.5, 120.6, 117.1,48.7, 42.1 (q, J = 26.8 Hz), 22.9, 21.5, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −59.0; GC−MS (EI, QMS, m/z) 335.2, 202.2, 134.2, 119.2, 91.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{19}H_{21}F_3NO^+$, 336.1570, found 336.1576.

N-(2-Chlorophenyl)-4,4,4-trifluoro-2-methyl-2-p-tolylbutanamide (**5k**).[15] 16.0 mg, 45% yield, yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.29 (d, J = 8.1 Hz, 1H), 7.53 (s, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 4H), 7.03 (t, J = 7.7 Hz, 1H), 3.30−3.18 (m, 1H), 2.98−2.86 (m, 1H), 2.40 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 173.8, 138.1, 137.4, 134.4, 130.0, 129.1, 127.8, 126.8, 126.6 (q, J = 278.2 Hz), 124.9, 123.3, 121.5, 49.0, 41.9 (q, J = 26.9 Hz), 22.8, 21.2; GC−MS (EI, QMS, m/z) 355.2, 320.2, 201.2, 187.1 119.2; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{18}H_{18}ClF_3NO^+$, 356.1024, found 356.1026.

General Procedure for Trifluoromethylation of 6a−6e. In a 10 mL bottom flask, the magnetic stir bar was added. Then it was charged with substrate **6** (0.1 mmol), CF_3SO_2Cl (0.2 mmol), CH_3CN (2.0 mL), $Ru(bpy)_3Cl_2$ (0.005 mmol) and K_2HPO_4 (0.2 mmol). The mixture was charged with N_2 three times under −78 °C and then was irradiated under blue LEDs (5 W). After the substrate was consumed (monitored by TLC), the mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **7**.

Characterization of 7a−7e. *2,4-Dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione* (**7a**).[16] 18.9 mg, 70% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.31 (dd, J = 7.9, 1.0 Hz, 1H), 7.69 (td, J = 7.8, 1.4 Hz, 1H), 7.53−7.49 (m, 1H), 7.45 (d, J = 7.9 Hz, 1H), 3.43−3.32 (m, 4H), 2.88−2.77 (m, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.7, 163.9, 140.5, 133.9, 129.4, 128.2, 125.8, 125.0 (q, J = 278.8 Hz), 124.4, 44.5 (q, J = 27.6 Hz), 43.7, 31.3, 27.5; GC−MS (EI, QMS, m/z) 271.1, 214.1, 145.1, 131.1, 115.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{13}H_{13}F_3NO_2^+$, 272.0898, found 272.0894.

2,4,6-Trimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (**7b**).[16] 17.1 mg, 60% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.18 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 9.8 Hz, 1H), 7.21 (s, 1H), 3.41−3.30 (m, 4H), 2.86−2.75 (m, 1H), 2.48 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.9, 163.9, 144.9, 140.5, 129.4, 129.3, 126.1, 125.1 (q, J = 278.8 Hz), 121.9, 44.5 (q, J = 27.5 Hz), 43.6, 31.3, 27.5, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.6; GC−MS (EI, QMS, m/z) 285.1, 228.1, 159.1, 145.1, 115.1; HRMS (ESI, Q-TOF, m/z) (M + H)$^+$ calcd for $C_{14}H_{15}F_3NO_2^+$, 286.1055, found 286.1050.

6-Fluoro-2,4-dimethyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3-(2H,4H)-dione (**7c**). 14.4 mg, 50% yield, white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.34 (t, J = 7.1 Hz, 1H), 7.21 (t, J = 8.2 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 3.42−3.33 (m, 4H), 2.81−2.70 (m, 1H), 2.48 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.2, 166.2 (d, J = 256.2 Hz), 162.9, 143.5 (d, J = 8.6 Hz), 132.5 (d, J = 9.8 Hz), 124.9 (q, J = 278.7 Hz), 120.9 (d, J = 1.9 Hz), 116.3 (d, J = 22.1 Hz), 112.8 (d, J = 23.4 Hz), 44.6 (q, J = 27.7 Hz), 43.9, 31.2, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.7, −103.2; GC−MS (EI, QMS, m/z) 289.1, 232.1, 163.1, 149.1, 133.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{13}H_{11}F_4NNaO_2^+$, 312.0618, found 312.0622.

2-Butyl-4-methyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3(2H,4H)-dione (**7d**). 13.4 mg, 43% yield, colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.30 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 4.06−4.01 (m, 2H), 3.44−3.33 (m, 1H), 2.88−2.77 (m, 1H), 1.67−1.58 (m, 5H), 1.43−1.38 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.4, 163.6, 140.5, 133.8, 129.5, 128.1, 125.8, 125.1 (q, J = 279.0 Hz), 124.5, 44.3 (q, J = 27.5 Hz), 43.7, 40.7, 31.5, 29.7, 20.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.4; GC−MS (EI, QMS, m/z) 313.2, 298.1, 284.1, 258.1, 230.2, 214.1, 145.1; HRMS (ESI, Q-TOF, m/z) (M + Na)$^+$ calcd for $C_{16}H_{18}F_3NO_2Na^+$, 336.1182, found 336.1175.

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*2-Benzyl-4-methyl-4-(2,2,2-trifluoroethyl)isoquinoline-1,3-(2H,4H)-dione (**7e**).* 18.7 mg, 54% yield, yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.32 (d, J = 7.9 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.52−7.43 (m, 4H), 7.34−7.26 (m, 3H), 5.29−5.20 (m, 2H), 3.47−3.36 (m, 1H), 2.90−2.79 (m, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 174.5, 163.6, 140.5, 136.9, 134.0, 129.6, 128.7, 128.6, 128.2, 127.6, 125.8, 125.1 (q, J = 279.0 Hz), 124.4, 44.1, 44.0, 44.0 (q, J = 28.0 Hz), 31.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F −61.2; GC−MS (EI, QMS, m/z) 347.2, 236.1, 214.1, 145.1, 131.1, 41.2; HRMS (ESI, Q-TOF, m/z) $(M + Na)^+$ calcd for $C_{19}H_{16}F_3NO_2Na^+$, 370.1025, found 370.1020.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00677.

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Notes

The authors declare no competing financial interest.

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