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Visible-Light-Mediated Regioselective Chlorosulfonylation of Acrylamides

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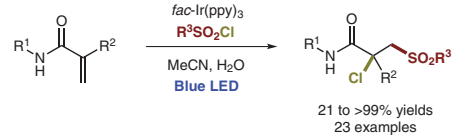

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Abstract A one-step chlorosulfonylation of acrylamides via a photocatalytic redox process is described. This reaction provides α-chlorosulfonylamides with a quaternary center with high regioselectivity via radical process. It is amenable to a broad range of substrates and the products are obtained in moderate to good yields.

Key words acrylamides, difunctionalization of alkenes, photocatalysis, chlorosulfonylation, α-chlorosulfones

Sulfonyl group-containing compounds constitute an important class of therapeutic agents in medicinal chemistry since this group can not only form hydrogen bonding interactions with biological targets but also fits specific conformations that can interact with active sites. Some studies suggest that the sulfonyl group is a key functional group for the ligands binding at human receptors, which could be involved in central neural system pathologies.[1] Additionally, the sulfonyl derivatives have been used in the development of anti-Alzheimer[2] and anti-HIV agents.[3] In the last years, a large number of sulfonamides have been reported as pharmaceuticals and some studies suggest that they present potential application in the treatment of diabetes and its complications,[4] and bacterial infections.[5]

The thiolation followed by oxidation of a sulfide or sulfoxide with strong oxidant is the traditional method to access sulfone derivatives.[6] Other methods[7] include Friedel–Crafts type sulfonylation of arenes,[8] alkylation of sulfinate salts,[9] and addition reactions to alkenes and alkynes.[10]

Recently, the difunctionalization of alkenes has emerged as a powerful strategy for the formation of C(sp^3)-sulfonylated compounds via radical processes.[11] In the last years, a few photoredox chlorosulfonylation of alkenes have been reported using sulfonyl chloride as the sulfonyl radical source.[12] Visible-light induced chemoselective process provided access α-chloro and vinyl sulfone derivatives (Scheme 1a).[13] A similar difunctionalization has been applied to α-CF_3 styrenes using $Ir(ppy)_3$ as photocatalyst (Scheme 1b).[14] Reiser[15] and Hu's[16] groups reported a visible-light-mediated photocatalyzed protocol for styrene derivatives, unactivated olefins, and alkynes using Cu photocatalysts (Scheme 1c). Here we report a visible-light-mediated regioselective chlorosulfonylation of acrylamides to access amides with a quaternary center in α-position (Scheme 1d).

We initiated our studies by monitoring the reaction of acrylamide **1** and tosyl chloride (**2a**) under various photocatalytic conditions. With 1 mol% of iridium catalyst such as $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ ($E_{Ir(IV)/Ir(III)^*}$ = –0.89 V vs SCE), $[Ir(dtbbpy)(ppy)_2]PF_6$ ($E_{Ir(IV)/Ir(III)^*}$ = –0.96 V vs SCE) or *fac*-$Ir(ppy)_3$ ($E_{Ir(IV)/Ir(III)^*}$ = –1.73 V vs SCE) in a 9:1 mixture of acetonitrile and water under irradiation with 2 Kessil LED lights the yield of the desired product was found to be very low (Table 1, entries 1–3). Instead with light emitting diodes (7.2 W m^{-1}) the product yield was increased up to 44% (entry 4). When the amount of water is increased until a 5:1 mixture ($MeCN/H_2O$), the yield dropped to 19% (entry 5) while a decrease (20:1, $MeCN/H_2O$) leads to better yield (entry 6). The optimal conditions were found for 5 equivalents of water with 82% yield of **3a**. The use of LED strip or Kessil LED light led to similar yields (entries 7, 8). When the reaction was carried out in the absence of water, the yield drops to 57% showing its beneficial effect in the reaction (entry 9).

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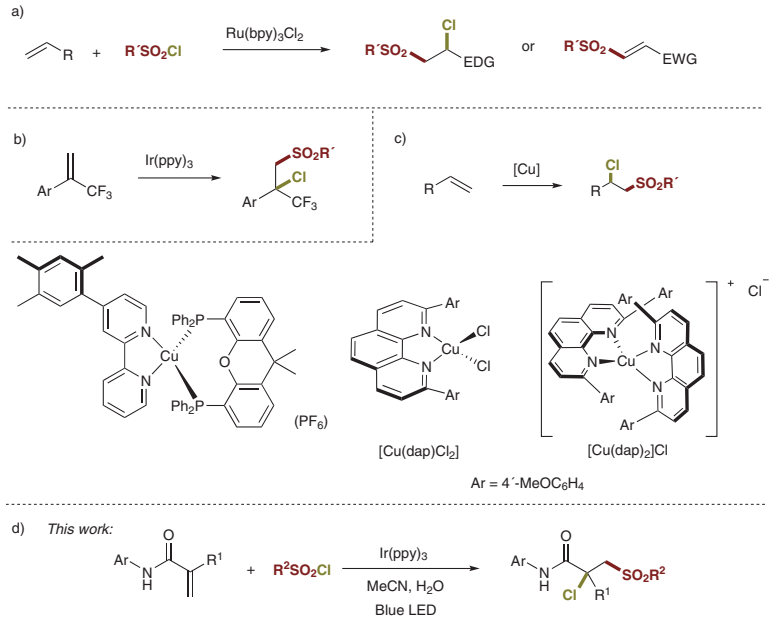
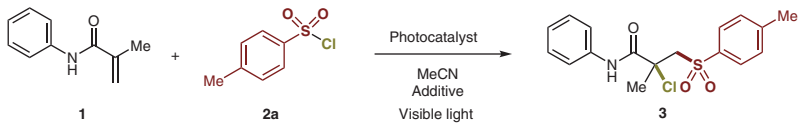


Scheme 1 Chlorosulfonylation of alkenes

Table 1 Optimization of the Reaction Conditions[a]



Entry	Photocatalyst	Solvent	Light	Time (h)	Yield (%)[b]
1	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	$MeCN:H_2O$ (9:1)	2 Kessil LED (40 W)	16	16
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	$MeCN:H_2O$ (9:1)	2 Kessil LED (40 W)	16	6
3	*fac*-$Ir(ppy)_3$	$MeCN:H_2O$ (9:1)	2 Kessil LED (40 W)	16	18
4	*fac*-$Ir(ppy)_3$	$MeCN:H_2O$ (9:1)	LED strip (33 W)	22	44[c]
5	*fac*-$Ir(ppy)_3$	$MeCN:H_2O$ (5:1)	LED strip (33 W)	22	19
6	*fac*-$Ir(ppy)_3$	$MeCN:H_2O$ (20:1)	LED strip (33 W)	22	54[c]
7	*fac*-$Ir(ppy)_3$	MeCN[d]	LED strip (33 W)	22	82[c]
8	*fac*-$Ir(ppy)_3$	MeCN[d]	1 Kessil LED (40 W)	22	81
9	*fac*-$Ir(ppy)_3$	MeCN	1 Kessil LED (40 W)	22	57

[a] Reaction conditions: Acrylamide **1** (1.0 equiv), tosyl chloride (**2a**; 2.5 equiv), photocatalyst (1 mol%), solvent (0.1 M), LED (455 nm) at rt.
[b] Yield determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.
[c] Isolated yield.
[d] Five equiv of H_2O were added.

After optimizing the reaction conditions, we evaluated the substrate scope and generality of the developed method with a variety of acrylamides and sulfonyl chlorides. First, we investigated the scope of acrylamides with *p*-toluenesulfonyl chloride (Scheme 2). A number of acrylamides with different substitution on the benzene ring on *ortho*-, *meta*- or *para*- position containing electron-withdrawing groups (Br, CF_3) and electron-donating groups (Me, OMe, OEt) were used to afford chlorosulfonylation products **3b–i** in moderate to good yields showing functional group tolerance. The reaction between disubstituted arylacrylamides **1j** and **1k** and tosyl chloride afforded the desired products **3j** and **3k** in quantitative and 56% yield, respectively. *N*-(Thiazol-2-yl)methacrylamide was found to be compatible with the reaction conditions allowing the isolation of **3l** in 54% yield. The reaction with the *N*-phenylacrylamide furnished **3m**, which contains no tertiary center in 52% yield. The limitation was found for *N*-(4-nitrophenyl)methacrylamide,

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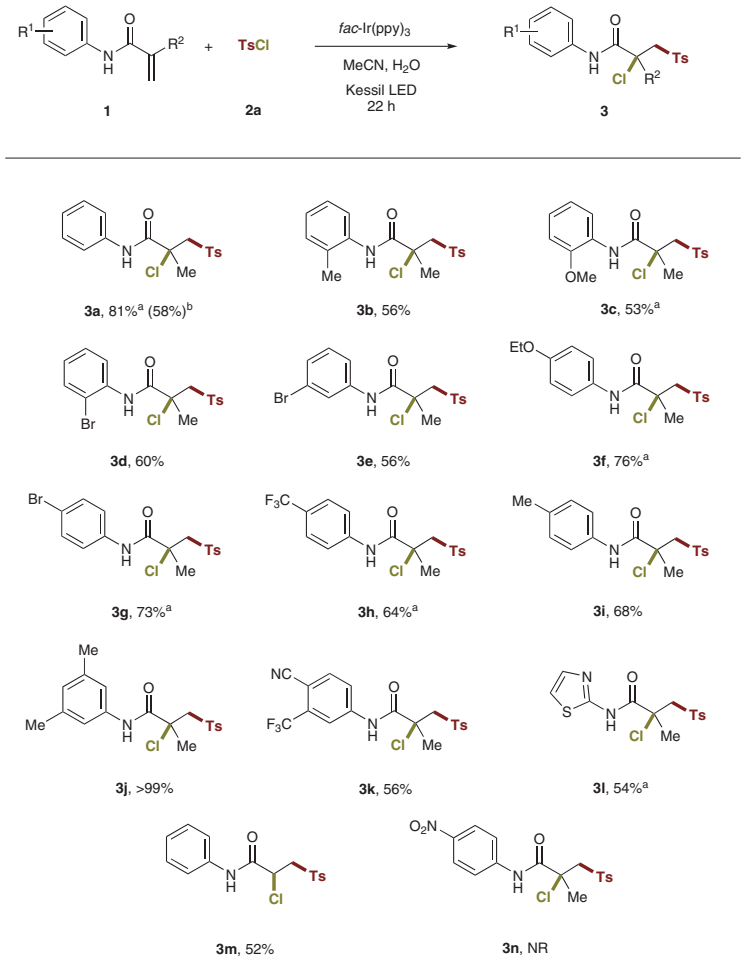

Scheme 2 Substrate scope for acrylamides. *Reagents and conditions*: **1** (1.0 equiv), **2a** (2.0 equiv), *fac*-Ir(ppy)$_3$ (1 mol%), MeCN (0.1 M), H_2O (5 equiv) under argon and irradiation with a Kessil LED (40 W) at rt for 22 h. Isolated yields are shown. NR: No reaction. [a] 2.5 equiv of **2a** were used. [b] One gram-scale experiment.

which did not yield to product **3n**. To demonstrate the scalability of the reaction, one gram scale experiment with **1a** was run and **3a** was isolated in 58% yield.

Next, we examined the scope of sulfonyl chlorides under the optimal conditions (Scheme 3). We observed that both electron-rich and electron-poor sulfonyl chlorides **2o–p** underwent the coupling with **1a** in good yields. The reaction with *p*-nitro derivative afforded **3q** in 55% yield while *m*-nitro derivative showed lower reactivity giving 21% yield of **3r**. The reaction with disubstituted sulfonyl chloride also afforded the desired product **3s** in 57% yield. Heterocyclic sulfonyl chlorides were tolerated and the thiophene derivative **3t** can be isolated in 69% yield. Aliphatic sulfonyl chlorides were also suitable substrates for this transformation. 1-Butane- and 2-propanesulfonyl chloride afforded **3u** and **3v** in 56 and 64% yield, respectively. Remarkably, product **3w** synthesized from cyclopropanesulfonyl chloride was isolated in 90% yield.

Control experiments proved that both light and catalyst are necessary in the chlorosulfonylation reaction (Scheme 4). In the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), starting material was exclusively observed, which points towards a radical mechanism.

The mechanistic proposal is illustrated in Scheme 5. The catalytic cycle begins with the visible-light irradiation of photocatalyst. Then, the sulfonyl radical is generated by S–Cl bond cleavage via reductive SET.[6] Subsequent addition of the sulfonyl radical to the double bond of the acrylamide affords a tertiary radical, which undergoes a SET process with the oxidized catalyst to regenerate it. Finally, the carbocation is trapped with the halide leading to the α-chlorosulfonyl acrylamide.

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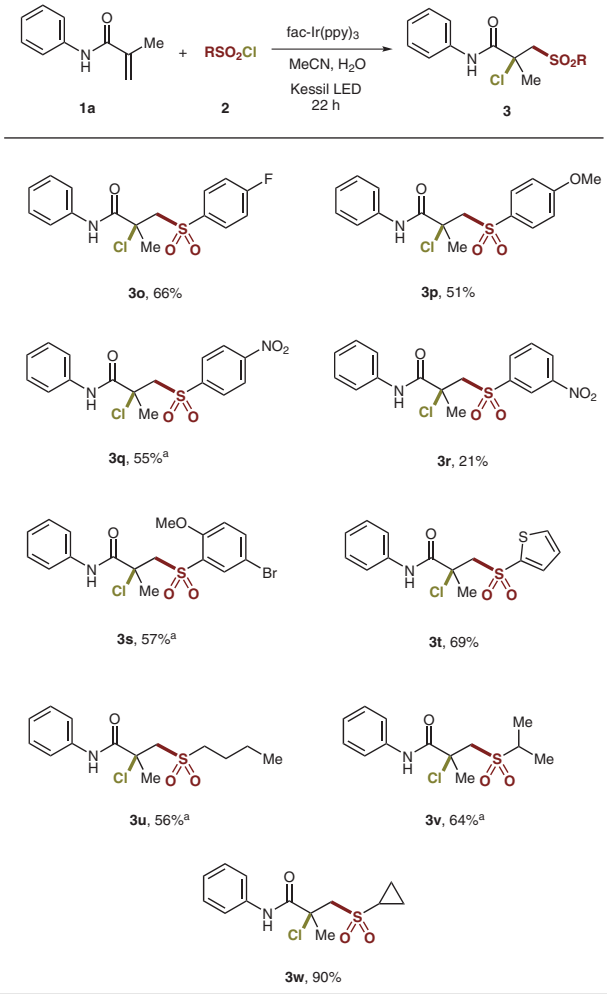
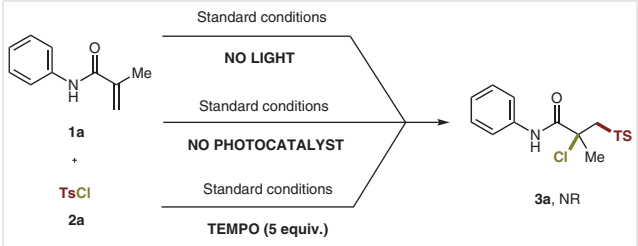


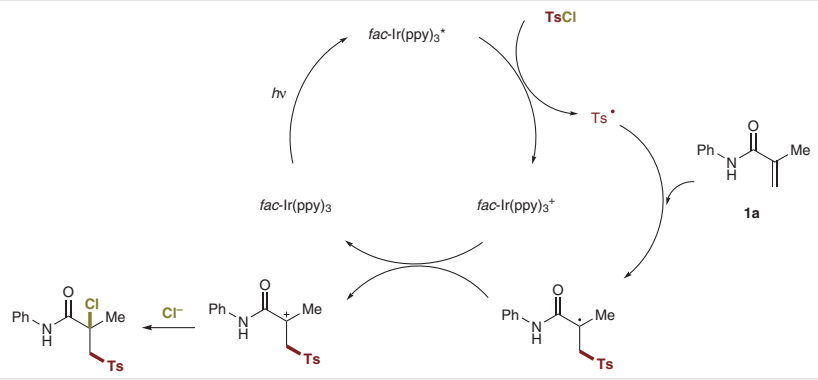
Scheme 3 Substrate scope for sulfonyl chlorides. *Reagents and conditions*: **1** (1.0 equiv), **2a** (2.0 equiv), *fac*-Ir(ppy)$_3$ (1 mol%), MeCN (0.1 M), H_2O (5 equiv) under argon and irradiation with a Kessil LED (40 W) at rt for 22 h. Isolated yields are shown. [a] 2.5 equiv of **2** were used.



Scheme 4 Control experiments

In conclusion, we have developed the synthesis of quaternary substituted acyclic α-chlorosulfonyl amides by photoredox chlorosulfonylation of *N*-arylacrylamides. The products are obtained in moderate to good yields and the transformation is amenable to a broad range of substrates.

All manipulations of air and moisture sensitive species were performed under argon atmosphere, unless otherwise stated. Glassware were dried with a heat gun under vacuum. NEt_3 was dried over CaH_2, distilled under vacuum and stored over molecular sieves (3 Å) under inert atmosphere. Anhydrous solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. Starting materials sourced from commercial suppliers were used as received, unless otherwise stated. Reactions were monitored using analytical TLC plates (Scharlab; silica gel 60 F254, 0.20 mm) visualized by UV-light at 254 nm. Silica gel grade 60 (230–400 mesh, Silicycle Inc.) was used for column chromatography. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on either Mercury VX-300, Bruker 400, or Unity 500 MHz Varian spectrometers at rt. Chemical shifts are given in ppm (δ) downfield from TMS, with calibration the residual $CHCl_3$ signals (δ_H = 7.26 for ^{1}H NMR and δ_C = 77.2 for ^{13}C NMR). Coupling constants (*J*) are in hertz (Hz) and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; br s, broad singlet; dd, double doublet; ddd, double doublet of doublets; tt, triple triplet and m, multiplet. High-resolution analyses (HRMS) were performed on an Agilent 6210 time of-flight LC/MS. IR spectra were recorded on an Agilent Cart 630 FTIR spectrometer.



Scheme 5 Mechanistic proposal

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Acrylamides 1; General Procedure[17]

To a round-bottomed flask were added a solution of the corresponding aniline (11.0 mmol, 1.0 equiv) in anhyd DCM (0.1 M) and NEt_3 (2.0 equiv). The mixture was stirred at 0 °C and the respective acyl chloride (1.5 equiv) was added slowly under argon atmosphere. The resulting solution was stirred at rt until no starting material was observed by TLC. The reaction mixture was quenched with H_2O (50 mL) and extracted with DCM (3 ×). The combined organic layers were washed with brine (3 ×), dried (anhyd Na_2SO_4), and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using DCM and EtOAc (1:0 → 9:1, v/v) as the eluent to give the corresponding acrylamide **1**.

***N*-Phenylmethacrylamide (1a)**[18]

General procedure was followed to afford **1a** as a white solid; yield: 1.47 g (85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.50 (m, 2 H), 7.47 (br s, 1 H), 7.38–7.30 (m, 2 H), 7.16–7.07 (m, 1 H), 5.97–5.63 (m, 1 H), 5.47 (dd, *J* = 1.6, 0.7 Hz, 1 H), 2.07 (dd, *J* = 1.6, 0.9 Hz, 3 H).

***N*-(*o*-Tolyl)methacrylamide (1b)**[19]

General procedure was followed to afford **1b** as a white solid; yield: 0.55 g (67%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.0 Hz, 1 H), 7.36 (br s, 1 H), 7.24–7.16 (m, 2 H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1 H), 5.84–5.75 (m, 1 H), 5.47 (dd, *J* = 1.6, 0.8 Hz, 1 H), 2.29 (s, 3 H), 2.09 (dd, *J* = 1.6, 0.9 Hz, 3 H).

***N*-(2-Methoxyphenyl)methacrylamide (1c)**[19]

General procedure was followed to afford **1c** as a brown oil; yield: 0.53 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.43 (dd, *J* = 8.0, 1.8 Hz, 1 H), 8.24 (br s, 1 H), 7.06 (td, *J* = 7.7, 1.8 Hz, 1 H), 6.98 (td, *J* = 7.7, 1.6 Hz, 1 H), 6.89 (dd, *J* = 8.0, 1.6 Hz, 1 H), 5.84–5.83 (m, 1 H), 5.55– 5.36 (m, 1 H), 3.90 (s, 3 H), 2.08 (dd, *J* = 1.6, 0.9 Hz, 3 H).

***N*-(2-Bromophenyl)methacrylamide (1d)**[20]

General procedure was followed to afford **1d** as a brown oil; yield: 0.14 g (20%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 8.1 Hz, 1 H), 8.15 (br s, 1 H), 7.55 (d, *J* = 8.1 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 6.99 (t, *J* = 7.8 Hz, 1 H), 5.93 (s, 1 H), 5.53 (s, 1 H), 2.11 (s, 3 H).

***N*-(3-Bromophenyl)methacrylamide (1e)**[21]

General procedure was followed to afford **1e** as a white solid; yield: 0.77 g (99%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (t, *J* = 1.9 Hz, 1 H), 7.58–7.39 (m, 2 H), 7.26–7.23 (m, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 5.87–5.68 (m, 1 H), 5.51–5.48 (m, 1 H), 2.06 (dd, *J* = 1.6, 0.9 Hz, 3 H).

***N*-(4-Ethoxyphenyl)methacrylamide (1f)**[22]

General procedure was followed to afford **1f** as a pale-red solid; yield: 1.27 g (85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 9.0 Hz, 2 H), 7.37 (br s, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 5.78–5.77 (m, 1 H), 5.43 (dd, *J* = 1.7, 0.8 Hz, 1 H), 4.02 (q, *J* = 7.0 Hz, 2 H), 2.06 (dd, *J* = 1.6, 0.9 Hz, 2 H), 1.40 (t, *J* = 7.0 Hz, 3 H).

***N*-(4-Bromophenyl)methacrylamide (1g)**[23]

General procedure was followed to afford **1g** as a white solid; yield: 1.26 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 4 H), 5.79 (br s, 1 H), 5.48–5.49 (m, 1 H), 2.06 (dd, *J* = 1.6, 0.9 Hz, 1 H).

***N*-(4-(Trifluoromethyl)phenyl)methacrylamide (1h)**[19]

General procedure was followed to afford **1h** as a white solid; yield: 0.35 g (99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 8.6 Hz, 2 H + br s, 1 H), 5.85–5.75 (m, 1 H), 5.53–5.52 (m, 1 H), 2.08 (dd, *J* = 1.6, 0.9 Hz, 3 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.2.

***N*-(*p*-Tolyl)methacrylamide (1i)**[18]

General procedure was followed to afford **1i** as a white solid; yield: 0.74 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.4 Hz, 2 H + br s, 1 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 5.85–5.70 (m, 1 H), 5.44 (dd, *J* = 1.7, 0.8 Hz, 1 H), 2.32 (s, 3 H), 2.06 (dd, *J* = 1.6, 0.9 Hz, 3 H).

***N*-(3,5-Dimethylphenyl)methacrylamide (1j)**[24]

General procedure was followed to afford **1j** as a white solid; yield: 0.81 g (99%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (br s, 1 H), 7.20 (s, 2 H), 6.77 (s, 1 H), 5.85–5.64 (m, 1 H), 5.44 (d, *J* = 2.1 Hz, 1 H), 2.30 (s, 6 H), 2.06 (dd, *J* = 1.5, 0.9 Hz, 3 H).

***N*-(4-Cyano-3-(trifluoromethyl)phenyl)methacrylamide (1k)**[25]

To a solution of methacrylamide (4.5 mmol, 1.7 equiv) in anhyd DMF (0.1 M) was added 4-cyano-3-trifluoromethylphenyl fluoride (1.0 equiv) at rt. The solution was cooled in a NaCl/ice (1/3) bath to –20 °C. To this cooled solution was added NaH (2.5 equiv), portionwise, while keeping the reaction temperature below 70 °C. The reaction mixture was allowed to cool to rt and stirred for 4 h under an argon atmosphere. H_2O was added followed by aq 18% HCl (7.0 equiv) and hexane. The resulted slurry was allowed to stir overnight. The solid was filtered, washed with H_2O (3 ×) and hexane (3 ×) and concentrated under vacuum. The residue was purified by flash chromatography on a silica gel using DCM and EtOAc (1:0 → 9:1, v/v) as the eluent to give the titled compound **1k** as a pale-yellow solid; yield: 0.46 g (69%).

***N*-(Thiazol-2-yl)methacrylamide (1l)**[26]

General procedure was followed to afford **1l** as a pale-yellow solid; yield: 0.46 g (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.62 (br s, 1 H), 7.43 (d, *J* = 3.6 Hz, 1 H), 6.99 (d, *J* = 3.6 Hz, 1 H), 5.96 (q, *J* = 1.0 Hz, 1 H), 5.64 (q, *J* = 1.6 Hz, 1 H), 2.11 (dd, *J* = 1.6, 1.0 Hz, 3 H).

***N*-Phenylmethacrylamide (1m)**[27]

General procedure was followed to afford **1m** as a brown solid; yield: 1.13 g (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2 H), 7.37–7.31 (m, 2 H), 7.13 (t, *J* = 7.4 Hz, 1 H), 6.44 (dd, *J* = 16.9, 1.3 Hz, 1 H), 6.25 (dd, *J* = 16.9, 10.2 Hz, 1 H), 5.78 (dd, *J* = 10.2, 1.3 Hz, 1 H).

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N-(4-Nitrophenyl)methacrylamide (1n)[28]

General procedure was followed to afford **1n** as a pale-yellow solid; yield: 0.94 g (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 9.2 Hz, 2 H), 7.76 (d, *J* = 9.2 Hz, 2 H), 7.74 (br s, 1 H), 5.85 (d, *J* = 0.9 Hz, 1 H), 5.58 (d, *J* = 1.6 Hz, 1 H), 2.09 (dd, *J* = 1.6, 0.9 Hz, 2 H).

Chlorosulfonylation of Acrylamides 1; General Procedure

To an oven-dried Schlenk tube (10 mL size) equipped with a stirring bar were added the acrylamide **1** (0.1 mmol, 1.0 equiv), sulfonyl chloride **2** (0.2–0.25 mmol, 2.0–2.5 equiv) and *fac*-Ir(ppy)$_3$ (1.0 mol%). Then, a mixture of anhyd MeCN/distilled H_2O (1 mL, 0.5 mmol, 5 equiv), previously degasified over 15 min by positive flow of argon, was added. The resulting solution was deoxygenated by three freeze-pump-thaw cycles. The reaction mixture was irradiated with a Kessil LED (40W, λ_{max} = 455 nm), under argon at rt. After 22 h, the mixture was filtered on Celite and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to give the desired product **3**.

Gram-Scale Experiment

To an oven-dried Schlenk tube (100 mL size) equipped with a stirring bar were added the acrylamide **1a** (1 g, 6.2 mmol, 1.0 equiv), sulfonyl chloride **2a** (15.5 mmol, 2.5 equiv) and *fac*-Ir(ppy)$_3$ (1.0 mol%). Then, a mixture of anhyd MeCN/distilled H_2O (60 mL, 31.0 mmol, 5 equiv), previously degasified over 15 min by positive flow of argon, was added. The resulting solution was deoxygenated by three freeze-pump-thaw cycles. The reaction mixture was irradiated with a Kessil LED (40W, λ_{max} = 455 nm), under argon at rt. After 22 h, the reaction mixture was filtered on Celite and concentrated under vacuum. The residue was purified by flash chromatography on a silica gel to give **3a** as a white solid; yield: 1.26 g (58%).

2-Chloro-2-methyl-N-phenyl-3-tosylpropanamide (3a)

White solid; mp 51–53 °C; yield: 27.1 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (br s, 1 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.50 (d, *J* = 7.4 Hz, 2 H), 7.36 (t, *J* = 7.9 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 4.23 (d, *J* = 14.6 Hz, 1 H), 3.73 (d, *J* = 14.6 Hz, 1 H), 2.37 (s, 3 H), 1.93 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.2, 145.2, 137.5, 137.0, 130.0 (2 C), 129.2 (2 C), 128.4 (2 C), 125.5, 120.6 (2 C), 66.4, 65.5, 31.2, 21.7.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{18}ClNO_3SNa$ [M + Na]$^+$: 374.0594; found: 374.0581.

IR: 3358, 2927, 1683, 1597, 1533, 1444, 1321, 1144, 1086, 756, 574 cm^{-1}.

2-Chloro-2-methyl-N-(o-tolyl)-3-tosylpropanamide (3b)

White solid; mp 54–55 °C; yield: 20.4 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (br s, 1 H), 7.86–7.73 (m, 3 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.25–7.19 (m, 2 H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1 H), 4.25 (d, *J* = 14.5 Hz, 1 H), 3.73 (d, *J* = 14.5 Hz, 1 H), 2.39 (s, 3 H), 2.33 (s, 3 H), 1.96 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.3, 145.2, 137.8, 135.0, 130.7, 130.0 (2 C), 129.8, 128.3 (2 C), 127.0, 126.0, 122.9, 66.9, 65.5, 31.4, 21.8, 17.7.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{20}ClNO_3SNa$ [M + Na]$^+$: 388.0750; found: 388.0749.

IR: 3412, 3364, 2924, 2359, 2341, 1685, 1521, 1457, 1321, 1146, 1086, 755, 669, 574 cm^{-1}.

2-Chloro-N-(2-methoxyphenyl)-2-methyl-3-tosylpropanamide (3c)

Pale yellow solid; mp 97–100 °C; yield: 20.4 mg (53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (br s, 1 H), 8.20 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.25 (d, *J* = 7.2 Hz, 2 H), 7.09 (td, *J* = 7.8, 1.6 Hz, 1 H), 6.95 (td, *J* = 7.8, 1.4 Hz, 1 H), 6.90 (dd, *J* = 8.1, 1.4 Hz, 1 H), 4.20 (d, *J* = 14.6 Hz, 1 H), 3.92 (s, 3 H), 3.76 (d, *J* = 14.6 Hz, 1 H), 2.33 (s, 3 H), 1.95 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 148.6, 145.1, 137.3, 129.8 (2 C), 128.5 (2 C), 126.9, 124.8, 121.1, 119.6, 110.2, 66.4, 65.3, 56.1, 31.0, 21.7.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{20}ClNO_4SNa$ [M + Na]$^+$: 404.0699; found: 404.0699.

IR: 3394, 2920, 1681, 1599, 1530, 1487, 1463, 1290, 1142, 1116, 1027, 887, 751, 574 cm^{-1}.

N-(2-Bromophenyl)-2-chloro-2-methyl-3-tosylpropanamide (3d)

Colorless oil; yield: 26.0 mg (60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.13 (br s, 1 H), 8.24 (dd, *J* = 8.2, 1.6 Hz, 1 H), 7.81 (d, *J* = 8.3 Hz, 2 H), 7.57 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.38–7.30 (m, 1 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.04 (ddd, *J* = 8.0, 7.5, 1.6 Hz, 1 H), 4.24 (d, *J* = 14.6 Hz, 1 H), 3.74 (d, *J* = 14.6 Hz, 1 H), 2.34 (s, 3 H), 1.96 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 145.3, 137.3, 135.1, 132.5, 130.0 (2 C), 128.6 (2 C), 128.5, 126.2, 121.8, 114.5, 66.5, 65.5, 31.2, 21.7.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{17}BrClNO_3SNa$ [M + Na]$^+$: 451.9699; found: 451.9705.

IR: 3356, 2924, 1692, 1595, 1530, 1439, 1323, 1146, 1086, 1025, 755 cm^{-1}.

N-(3-Bromophenyl)-2-chloro-2-methyl-3-tosylpropanamide (3e)

White solid; mp 112–114 °C; yield: 24.0 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (br s, 1 H), 7.82–7.76 (m, 3 H), 7.39 (ddd, *J* = 8.1, 2.0, 1.0 Hz, 1 H), 7.33–7.28 (m, 3 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 4.22 (d, *J* = 14.6 Hz, 1 H), 3.71 (d, *J* = 14.6 Hz, 1 H), 2.39 (s, 3 H), 1.92 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 145.3, 138.2, 137.4, 130.4, 130.0 (2 C), 128.4, 128.3 (2 C), 123.5, 122.8, 119.1, 66.3, 65.4, 31.2, 21.8.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{17}BrClNO_3SNa$ [M + Na]$^+$: 451.9699; found: 451.9705.

IR: 3354, 2928, 1687, 1590, 1526, 1477, 1321, 1144, 1086, 777, 680, 574 cm^{-1}.

2-Chloro-N-(4-ethoxyphenyl)-2-methyl-3-tosylpropanamide (3f)

Brown oil; yield: 28.5 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.44 (br s, 1 H), 7.80 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 9.0 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 4.21 (d, *J* = 14.6 Hz, 1 H), 4.02 (q, *J* = 7.0 Hz, 2 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 2.38 (s, 3 H), 1.92 (s, 3 H), 1.40 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.1, 156.7, 145.13, 137.6, 129.9 (2 C), 129.8, 128.3 (2 C), 122.6 (2 C), 114.9 (2 C), 66.4, 65.5, 63.8, 31.2, 21.7, 14.9.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{19}H_{22}ClNO_4SNa$ [M + Na]$^+$: 418.0856; found: 418.0858.

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IR: 3356, 2980, 1675, 1597, 1510, 1317, 1231, 1142, 1086, 1043, 736, 572, 524 cm^{-1}.

N-(4-Bromophenyl)-2-chloro-2-methyl-3-tosylpropanamide (3g)

Yellow solid; mp 55–57 °C; yield: 29.9 mg (73%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (br s, 1 H), 7.79 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 8.9 Hz, 2 H), 7.42 (d, *J* = 8.9 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 4.21 (d, *J* = 14.6 Hz, 1 H), 3.71 (d, *J* = 14.6 Hz, 1 H), 2.39 (s, 3 H), 1.92 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.4, 145.3, 137.56, 136.1, 132.2 (2 C), 130.0 (2 C), 128.3 (2 C), 122.3 (2 C), 118.3, 66.4, 65.5, 31.2, 21.8.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{17}BrClNO_3SNa$ [M + Na]$^+$: 451.9699; found: 451.9698.

IR: 3360, 2924, 1687, 1524, 1593, 1524, 1489, 1396, 1321, 1144, 1086, 818, 574 cm^{-1}.

2-Chloro-2-methyl-3-tosyl-N-[4-(trifluoromethyl)phenyl]propenamide (3h)

White solid; mp 56–58 °C; yield: 25.7 mg (64%).

^{1}H NMR (500 MHz, $CDCl_3$): d = 8.71 (br s, 1 H), 7.79 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.8 Hz, 2 H), 7.62 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 4.23 (d, *J* = 14.6 Hz, 1 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 2.39 (s, 3 H), 1.94 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.6, 145.4, 137.5, 130.0 (2 C), 128.3 (2 C), 126.4 (q, $^3J_{C,F}$ = 3.8 Hz, 2 C), 120.3 (2 C), 66.4, 65.6, 31.2, 21.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –61.0.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{17}ClF_3NO_3SNa$ [M + Na]$^+$: 442.0467; found: 442.0469.

IR: 3349, 2924, 1690, 1601, 1530, 1321, 1142, 1116, 1068, 842, 574 cm^{-1}.

2-Chloro-2-methyl-N-(p-tolyl)-3-tosylpropanamide (3i)

White solid; mp 80–82 °C: yield: 24.9 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1 H), 7.80 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 4.22 (d, *J* = 14.6 Hz, 1 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 2.38 (s, 3 H), 2.33 (s, 3 H), 1.93 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 145.2, 137.6, 135.2, 134.4, 130.0 (2 C), 129.7 (2 C), 128.4 (2 C), 120.7 (2 C), 66.5, 65.5, 31.2, 21.7, 21.1.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{18}H_{20}ClNO_3SNa$ [M + Na]$^+$: 388.0750; found: 388.0753.

IR: 3356, 2922, 2851, 1681, 1597, 1523, 1405, 1321, 1144, 1086, 814, 568, 552, 512 cm^{-1}.

2-Chloro-N-(3,5-dimethylphenyl)-2-methyl-3-tosylpropanamide (3j)

Colorless oil; yield: 37.7 mg (>99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (br s, 1 H), 7.81 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.13 (s, 2 H), 6.81 (s, 1 H), 4.21 (d, *J* = 14.6 Hz, 1 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 2.38 (s, 3 H), 2.31 (s, 6 H), 1.93 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.0, 145.2, 138.92 (2 C), 137.6, 136.8, 130.0 (2 C), 128.4 (2 C), 127.2, 118.3 (2 C), 66.5, 65.4, 31.2, 21.7, 21.5 (2 C).

HRMS (ESI-TOF): *m*/*z* calcd for $C_{19}H_{22}ClNO_3SNa$ [M + Na]$^+$: 402.0907; found: 402.0906.

IR: 3358, 2920, 1683, 1597, 1545, 1454, 1321, 1142, 1086, 842 cm^{-1}.

2-Chloro-N-[4-cyano-3-(trifluoromethyl)phenyl]-2-methyl-3-tosylpropanamide (3k)

Yellow oil; yield: 25.0 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (br s, 1 H), 8.07 (d, *J* = 2.2 Hz, 1 H), 7.92 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 7.79 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 7.9 Hz, 2 H), 4.22 (d, *J* = 14.6 Hz, 1 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 2.43 (s, 3 H), 1.93 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.3, 145.6, 141.2, 137.5, 136.0, 134.3 (q, $^2J_{C,F}$ = 32.9 Hz) 130.2 (2 C), 128.2 (2 C), 122.8, 118.2 (q, $^3J_{C,F}$ = 5.0 Hz), 115.4, 66.2, 65.7, 31.2, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.1.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{19}H_{16}ClF_3N_2O_3SNa$ [M + Na]$^+$: 467.0420; found: 467.0427.

IR: 3340, 2231, 1696, 1592, 1523, 1429, 1321, 1177, 1133, 1085, 1051, 904, 840, 816, 736 cm^{-1}.

2-Chloro-2-methyl-N-(thiazol-2-yl)-3-tosylpropanamide (3l)

White solid; mp 54–56 °C; yield: 19.2 mg (54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.17 (br s, 1 H), 7.78 (d, *J* = 8.3 Hz, 2 H), 7.51 (d, *J* = 3.5 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 3.5 Hz, 1 H), 4.18 (d, *J* = 14.6 Hz, 1 H), 3.82 (d, *J* = 14.6 Hz, 1 H), 2.38 (s, 3 H), 1.97 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 157.6, 145.4, 138.0, 137.1, 130.0 (2 C), 128.4 (2 C), 114.6, 65.3, 65.0, 30.5, 21.8.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{14}H_{16}ClN_2O_3S_2$ [M + H]$^+$: 359.0291; found: 359.0291.

IR: 2924, 2359, 1681, 1537, 1321, 1291, 1150, 1086, 568 cm^{-1}.

2-Chloro-N-phenyl-3-tosylpropanamide (3m)

Yellow oil; yield: 17.5 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (br s, 1 H), 7.83 (d, *J* = 8.3 Hz, 2 H), 7.46 (dd, *J* = 8.6, 1.0 Hz, 2 H), 7.39–7.30 (m, 4 H), 7.17 (tt, *J* = 7.5, 1.4 Hz, 1 H), 4.85 (dd, *J* = 7.6, 4.6 Hz, 1 H), 4.20 (dd, *J* = 14.8, 4.6 Hz, 1 H), 3.67 (dd, *J* = 14.8, 7.6 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.8, 145.7, 136.67, 136.2, 130.2 (2 C), 129.3 (2 C), 128.4 (2 C), 125.6, 120.3 (2 C), 66.0, 52.3, 29.9.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{16}ClNO_3SNa$ [M + Na]$^+$: 360.0437; found: 360.0442.

IR: 3336, 2924, 2853, 1701, 1677, 1601, 1549, 1500, 1446, 1321, 1148, 1086, 814, 758, 691, 520 cm^{-1}.

2-Chloro-3-((4-fluorophenyl)sulfonyl)-2-methyl-N-phenylpropanamide (3o)

Yellow oil; yield: 23.0 mg (66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (br s, 1 H), 8.00–7.91 (m, 2 H), 7.51 (dd, *J* = 8.6, 1.1 Hz, 2 H), 7.37 (t, *J* = 7.9 Hz, 2 H), 7.23–7.14 (m, 3 H), 4.27 (d, *J* = 14.6 Hz, 1 H), 3.75 (d, *J* = 14.6 Hz, 1 H), 1.94 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.2, 166.4 (d, $^1J_{C,F}$ = 255.9 Hz), 136.8, 136.7 (d, $^4J_{C,F}$ = 3.1 Hz), 131.3 (d, $^3J_{C,F}$ = 9.7 Hz, 2 C), 129.3 (2 C), 125.6, 120.7 (2 C), 116.7 (d, $^2J_{C,F}$ = 22.7 Hz, 2 C), 66.4, 65.7, 31.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –102.9.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{15}ClFNO_3SNa$ [M + Na]$^+$: 378.0343; found: 378.0345.

IR: 3358, 2342, 2357, 1683, 1597, 1534, 1493, 1444, 1325, 1237, 1146, 1084, 840, 757, 572 cm^{-1}.

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2-Chloro-3-[(4-methoxyphenyl)sulfonyl]-2-methyl-*N*-phenylpropenamide (3p)

Yellow oil; yield: 19.0 mg (51%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (br s, 1 H), 7.85 (d, *J* = 8.9 Hz, 2 H), 7.50 (dd, *J* = 8.5, 1.0 Hz, 2 H), 7.35 (t, *J* = 7.9 Hz, 2 H), 7.18 (ddd, *J* = 8.5, 4.6, 1.6 Hz, 1 H), 6.93 (d, *J* = 8.9 Hz, 2 H), 4.24 (d, *J* = 14.6 Hz, 1 H), 3.80 (s, 3 H), 3.72 (d, *J* = 14.6 Hz, 1 H), 1.93 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 164.1, 137.0, 131.9 (2 C), 130.7 (2 C), 129.2, 125.4, 120.6 (2 C), 114.9 (2 C), 66.5, 65.6, 55.8, 31.3.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{18}ClNO_4SNa$ [M + Na]$^+$: 390.0543; found: 390.0546.

IR: 3356, 2928, 1677, 1593, 1530, 1496, 1442, 1321, 1139, 1086, 1023, 835, 576 cm^{-1}.

2-Chloro-2-methyl-3-[(4-nitrophenyl)sulfonyl]-*N*-phenylpropanamide (3q)

Brown solid; mp 135–136 °C; yield: 21.1 mg (55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (br s, 1 H), 8.33 (d, *J* = 8.9 Hz, 2 H), 8.13 (d, *J* = 8.9 Hz, 2 H), 7.48 (dd, *J* = 8.5, 1.0 Hz, 2 H), 7.39–7.36 (m, 2 H), 7.22–7.18 (m, 1 H), 4.36 (d, *J* = 14.7 Hz, 1 H), 3.79 (d, *J* = 14.7 Hz, 1 H), 1.95 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 151.0, 145.9, 136.6, 129.9 (2 C), 129.3 (2 C), 125.8, 124.5 (2 C), 120.6 (2 C), 66.2, 65.6, 31.3.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{15}ClN_2O_5SNa$ [M + Na]$^+$: 405.0288; found: 405.0285.

IR: 3384, 1683, 1599, 1530, 1349, 1332, 1310, 1146, 1083, 855, 758, 740, 691 cm^{-1}.

2-Chloro-2-methyl-3-[(3-nitrophenyl)sulfonyl]-*N*-phenylpropanamide (3r)

Yellow solid; mp 150 °C (dec.); yield: 8.3 mg (21%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (t, *J* = 2.0 Hz, 1 H), 8.53 (br s, 1 H), 8.45–8.41 (m, 1 H), 8.29–8.24 (m, 1 H), 7.73 (t, *J* = 8.0 Hz, 1 H), 7.51–7.46 (m, 2 H), 7.39–7.35 (m, 2 H), 7.23–7.17 (m, 1 H), 4.37 (d, *J* = 14.7 Hz, 1 H), 3.82 (d, *J* = 14.7 Hz, 1 H), 1.96 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 142.6, 134.0, 131.2, 130.8, 129.4, 129.3 (2 C), 128.5, 125.8, 123.8, 120.5 (2 C), 66.2, 65.6, 31.4.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{16}H_{15}ClN_2O_5SNa$ [M + Na]$^+$: 405.0288; found: 405.0291.

IR: 3373, 3088, 1681, 1601, 1532, 1444, 1351, 1331, 1159, 1120, 880, 758 cm^{-1}.

3-[(5-Bromo-2-methoxyphenyl)sulfonyl]-2-chloro-2-methyl-*N*-phenylpropanamide (3s)

White solid; mp 122–124 °C; yield: 25.5 mg (57%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (br s, 1 H), 7.99 (d, *J* = 2.5 Hz, 1 H), 7.60 (dd, *J* = 8.8, 2.5 Hz, 1 H), 7.48 (dd, *J* = 8.7, 1.2 Hz, 2 H), 7.38–7.31 (m, 2 H), 7.20–7.13 (tt, *J* = 7.4, 1.2 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 1 H), 4.39 (d, *J* = 14.9 Hz, 1 H), 4.01 (d, *J* = 14.9 Hz, 1 H), 3.98 (s, 3 H), 1.96 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 156.5, 138.5, 136.9, 132.7, 129.9, 129.2 (2 C), 125.5, 120.5 (2 C), 114.4, 113.0, 66.5, 63.6, 56.9, 31.1.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{17}H_{17}BrClNO_4SNa$ [M + Na]$^+$: 467.9648; found: 467.9652.

IR: 3355, 2939, 1683, 1597, 1528, 1476, 1440, 1318, 1271, 1135, 1060, 1013, 883, 755, 691, 518 cm^{-1}.

2-Chloro-2-methyl-*N*-phenyl-3-(thiophen-2-ylsulfonyl)propanamide (3t)

Colorless oil; yield: 24.0 mg (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (br s, 1 H), 7.72 (dd, *J* = 3.8, 1.2 Hz, 1 H), 7.69 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.53 (d, *J* = 7.7 Hz, 2 H), 7.36 (t, *J* = 7.9 Hz, 2 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 7.10 (dd, *J* = 4.9, 3.9 Hz, 1 H), 4.36 (d, *J* = 14.6 Hz, 1 H), 3.89 (d, *J* = 14.6 Hz, 1 H), 1.97 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 141.7, 136.9, 134.8, 134.6, 129.2 (2 C), 128.1, 125.6, 120.7 (2 C), 66.8, 66.5, 31.1.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{14}H_{14}ClNO_3S_2Na$ [M + Na]$^+$: 366.0001; found: 366.0005.

IR: 3362, 1683, 1599, 1532, 1444, 1325, 1142, 1016, 757, 691, 596 cm^{-1}.

3-(Butylsulfonyl)-2-chloro-2-methyl-*N*-phenylpropanamide (3u)

White solid; mp 94–96 °C; yield: 17.7 mg (56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (br s, 1 H), 7.53 (d, *J* = 7.8 Hz, 2 H), 7.36 (t, *J* = 7.8 Hz, 2 H), 7.21–7.15 (m, 1 H), 4.10 (d, *J* = 14.8 Hz, 1 H), 3.60 (d, *J* = 14.8 Hz, 1 H), 3.14–3.04 (m, 2 H), 1.99 (s, 3 H), 1.89–1.75 (m, 2 H), 1.46 (sext, *J* = 7.4 Hz, 2 H), 0.94 (t, *J* = 9.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 136.8, 129.3 (2 C), 125.6, 120.8 (2 C), 66.6, 62.3, 56.1, 31.2, 23.9, 21.8, 13.7.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{14}H_{20}ClNO_3SNa$ [M + Na]$^+$: 340,0750; found: 340.0753.

IR: 3355, 2961, 2933, 1979, 1597, 1530, 1442, 1318, 1127, 754, 691, 507 cm^{-1}.

2-Chloro-3-(isopropylsulfonyl)-2-methyl-*N*-phenylpropanamide (3v)

Yellow oil; yield: 19.5 mg (64%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (br s, 1 H), 7.53 (d, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.9 Hz, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 4.10 (d, *J* = 14.4 Hz, 1 H), 3.58 (d, *J* = 14.4 Hz, 1 H), 3.23 (hept, *J* = 6.9 Hz, 1 H), 2.00 (s, 3 H), 1.41 (d, *J* = 2.1 Hz, 3 H), 1.38 (d, *J* = 2.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6, 136.9, 129.3 (2 C), 125.6, 120.9 (2 C), 66.4, 58.9, 56.0, 31.3, 15.4, 15.2.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{13}H_{18}ClNO_3SNa$ [M + Na]$^+$: 326.0594; found: 326.0594.

IR: 3355, 2984, 2935, 2361, 1679, 1597, 1531, 1444, 1312, 1123, 881, 755, 691 cm^{-1}.

2-Chloro-3-(cyclopropylsulfonyl)-2-methyl-*N*-phenylpropanamide (3w)

White solid; mp 108–110 °C; yield: 27.0 mg (90%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (br s, 1 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.36 (t, *J* = 7.9 Hz, 2 H), 7.20–7.15 (m, 1 H), 4.22 (d, *J* = 14.7 Hz, 1 H), 3.70 (d, *J* = 14.7 Hz, 1 H), 2.61 (tt, *J* = 8.0, 4.8 Hz, 1 H), 1.99 (s, 3 H), 1.32–1.24 (m, 2 H), 1.04 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5, 136.9, 129.2 (2 C), 125.6, 120.8 (2 C), 66.6, 63.7, 32.7, 31.1, 5.6, 5.5.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{13}H_{16}ClNO_3SNa$ [M + Na]$^+$: 324.0437; found: 324.0437.

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IR: 3356, 2359, 1681, 1597, 1531, 1444, 1321, 1131, 885, 757, 576, 507 cm^{-1}.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0042-1751424.

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