Visible-light mediated regioselective chlorosulfonylation of acrylamides

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Abstract Herein, 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.

Keywords Acrylamides, difunctionalization of alkenes, photocatalysis, chlorosulfonylation, α-chloro sulfones

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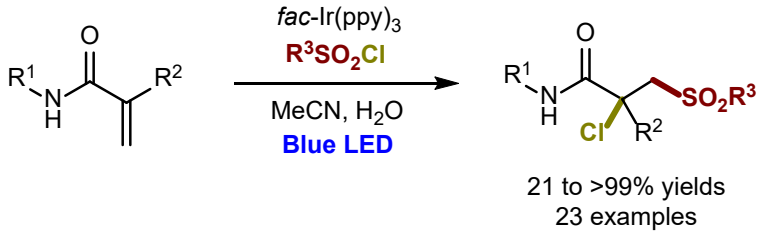
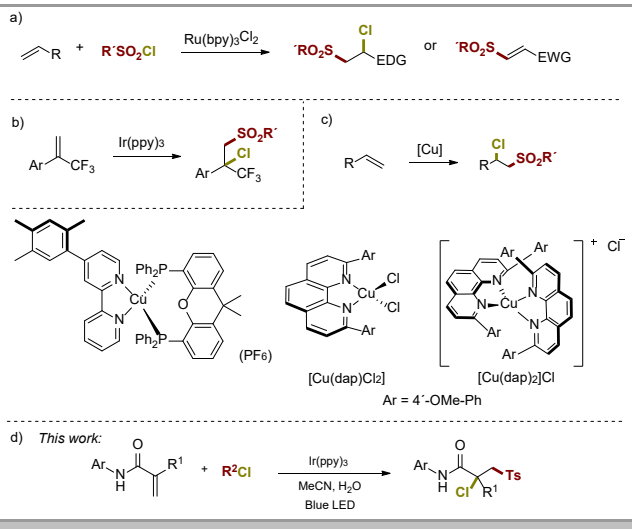


Sulfonyl group-containing compounds constitute an important class of therapeutic agents in medicinal chemistry since this group can not only form hydrogen bonding interactions with biological targets but also fit specific conformations that can interact with active sites. Some studies suggest that the 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 has 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 to 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]

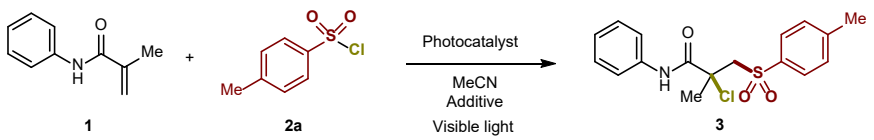
Recently, the difunctionalization of alkenes has emerged as a powerful strategy for the formation of C(sp^3)-sulfonylated compounds via radical processes.[11] In the last years, a few photoredox chlorosulfonylation of alkenes have been reported using sulfonyl chloride as the sulfonyl radical source.[12] 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 to amides with a quaternary center in α position (Scheme 1d).

We initiated our studies by monitoring the reaction of acrylamide **1** and tosylchloride **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



Scheme 1 Chlorosulfonylation of alkenes

Table 1 Optimization of the reaction conditions

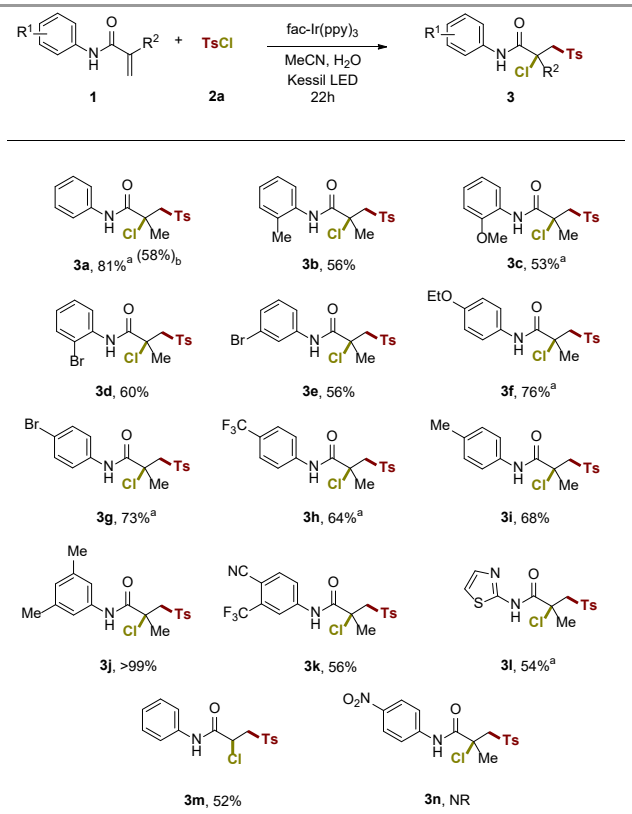


Entry	Photocatalyst	Solvent	Light	Time (h)	Yield (%)[b]
1	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	MeCN:H_2O (9:1)	2 Kessil LED (40 W)	16	16
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	MeCN:H_2O (9:1)	2 Kessil LED (40 W)	16	6
3	*fac*-Ir(ppy)$_3$	MeCN:H_2O (9:1)	2 Kessil LED (40 W)	16	18
4	*fac*-Ir(ppy)$_3$	MeCN:H_2O (9:1)	LED 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 eq.), tosyl chloride (2.5 eq.), photocatalyst (1 mol %), solvent (0.1 M), LED (455 nm) at room temperature.
[b] Yield determined by 1H NMR using 1,3,5-trimethoxybenzene as internal standard.
[c] Isolated yield.
[d] 5 eq. of H_2O were added.

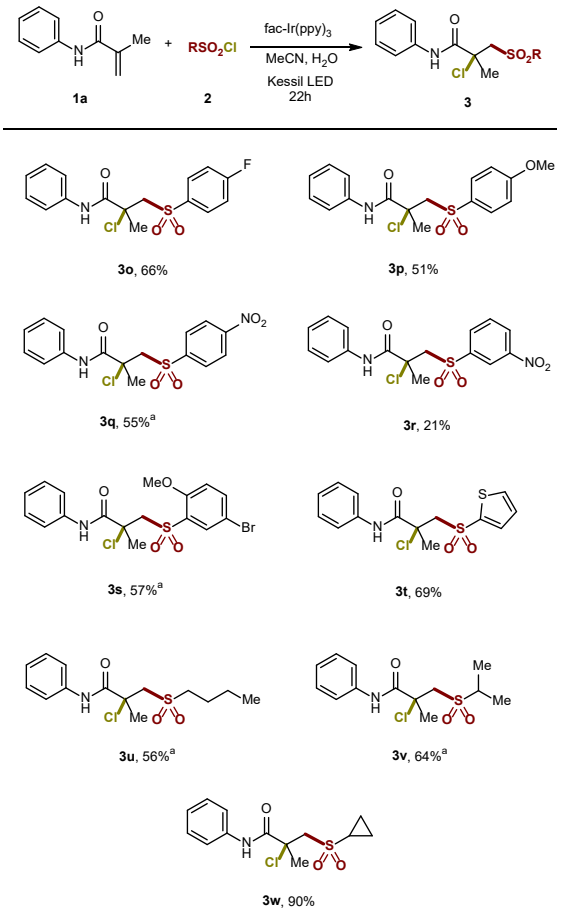
2 Kessil LED lights the yield of the desired product was found to be very low (Table 1, entries 1-3). Instead with light emitting diodes (7.2 W m^{-1}) the product yield was increased up to 44% (Table 1, entry 4). When the amount of water is increased until a 5:1 mixture (MeCN/H_2O), the yield dropped to 19% (Table 1, entry 5) while a decrease (20:1, MeCN/H_2O) leads to better yield (Table 1, 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 (Table 1 entry 7-8). When the reaction was carried out in absence of water, the yield drops to 57 % showing its beneficial effect in the reaction (Table 1 entry 9).

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 electrowithdrawing groups (Br, CF_3) and electron-donating groups (Me, OMe, OEt) were used to afford chlorosulfonylation products **3b-3i** with 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 tertiary centre in 52% yield. The limitation was found for *N*-(4-nitrophenyl)methacrylamide 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.



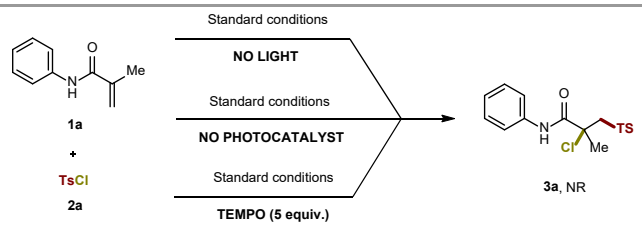
Scheme 2 Substrate scope for acrylamides. Reaction conditions: **1** (1.0 eq.), **2a** (2.0 eq.), fac-Ir(ppy)$_3$ (1 mol %), MeCN (0.1 M), H_2O (5 eq.) under argon and irradiation with a Kessil LED (40 W) at room temperature for 22 h. Isolated yields are shown. NR: No reaction. [a]2.5 eq. of **2a** were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

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 derivate 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 in 57% yield (**3s**). 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-propane sulfonyl chloride afforded **3u** and **3v** in 56 and 64% yield, respectively. Remarkably, product **3w** synthesized from cyclopropane sulfonyl chloride was isolated in 90% yield.



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

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.



Scheme 4 Control experiments

The mechanistic proposal is illustrated in Figure 1. 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-chloro sulfonyl acrylamide.

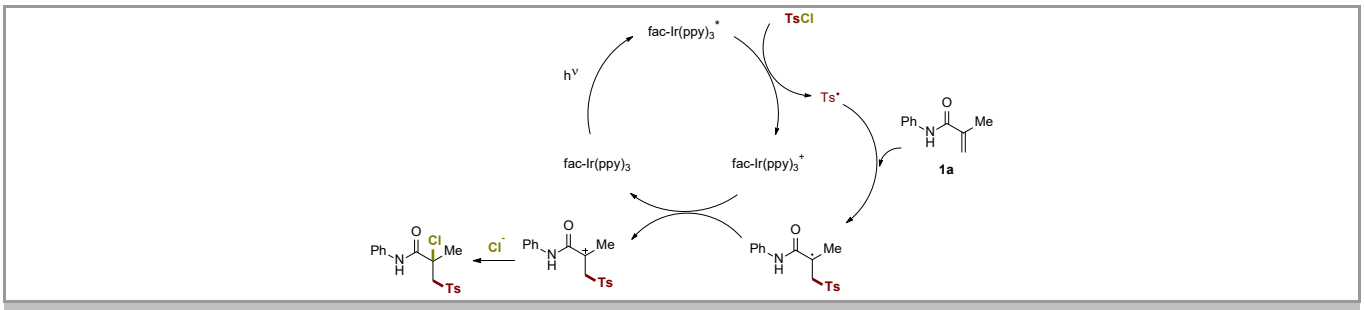


Figure 1 Mechanistic proposal

In conclusion, we have developed the synthesis of quaternary substituted acyclic α-chloro sulfonyl 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.

Procedures

All manipulations of air and moisture sensitive species were performed under argon atmosphere unless otherwise stated. Glassware was dried with a heat gun under vacuum. Triethylamine was dried over calcium hydride, distilled under vacuum and stored over molecular sieves (3 Å) under inert atmosphere. Dry 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 room temperature. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane, with calibration the residual chloroform signals (δ(H) = 7.26 ppm for ^{1}H NMR and δ(C) = 77.2 ppm 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; quin, quintet; sex, sextet; sep, septet; bs, 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.

Acrylamides 1: General procedure[17]

To a round-bottom flask was added the solution of corresponding aniline 1 (1.0 eq) in anhydrous DCM (0.1 M) and triethylamine (2.0 eq). The mixture was stirred at 0 ºC and added acyl chloride 2 (1.5 eq) slowly under argon atmosphere. The resulting solution was stirred at room temperature until no starting material is observed by TLC, quenched with H_2O (50 mL) and extracted with DCM (×3). The combined organic layers were washed with brine (×3), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on a silica gel using DCM and ethyl acetate (AcOEt) (1:0∼9:1, v/v) as the eluent to give corresponding substrates **1**.

N-Phenylmethacrylamide (1a)[18]

General procedure was followed to afford **3a** as a white solid (1.47 g, 85% yield).

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

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

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

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.36 (bs, 1H), 77.24-7.16 (m, 2H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 5.84- 5.75 (m, 1H), 5.47 (dd, *J* = 1.6, 0.8 Hz, 1H), 2.29 (s, 3H), 2.09 (dd, *J* = 1.6, 0.9 Hz, 3H).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

^{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 (0.74 g, 90% yield).

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

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

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

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

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

To a solution of methacrylamide (1.7 eq.) in anhydrous DMF (0.1 M) was added 4-cyano-3-trifluoromethylphenyl fluoride (1.0 eq) at room temperature. The solution was cooled in a NaCl/ice (1/3) bath to -20ºC. To this cooled solution was added sodium hydride (2.5 eq), portionwise, while keeping the reaction temperature below 70ºC. The reaction mixture was allowed to cool to room temperature and stirred for 4 h under an argon atmosphere. Water was added followed by 18% HCl (7.0 eq) and hexane. The resulted slurry was allowed to stir overnight. The solid was filtered, washed with water (x3) and hexane (x3) and concentrated under vacuum. The residue was purified by flash chromatography on a silica gel using DCM and AcOEt (1:0∼9:1, v/v) as the eluent to give the titled compound **1k** as a pale-yellow solid (0.46 g, 69% yield).

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

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

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

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

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

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

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

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

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

General procedure of photoredox reaction

To an oven-dried Schlenk tube (10 ml size) equipped with a stirring bar was added the acrylamide **1** (0.1 mmol, 1.0 eq), sulfonyl chloride **2** (0.2-0.25 mmol, 2.0-2.5 eq) and *fac*-Ir(ppy)$_3$ (1.0 mol %). Then, 1 mL of a mixture of dry MeCN/distilled H_2O (0.5 mmol, 5 eq), previously degasified over 15 minutes 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 room temperature. 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 the desired product **3**.

Scale experiment

To an oven-dried Schlenk tube (100 ml size) equipped with a stirring bar was added the acrylamide **1a** (1 g, 6.2 mmol, 1.0 eq), sulfonyl chloride **2a** (15.5 mmol, 2.5 eq) and *fac*-Ir(ppy)$_3$ (1.0 mol %). Then, 60 mL of a mixture of dry MeCN/distilled H_2O (31.0 mmol, 5 eq), previously degasified over 15 minutes 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 room temperature. 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 1.26 g of **3a** as a white solid (58% yield).

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

White solid. M.p. 51-53 ºC; yield: 27.1 mg (81%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{18}ClNNaO_3S$ $[M+Na]^+$: 374.0594; Found: 374.0581.

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

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

White solid. M.p. 54-55 ºC; yield: 20.4 mg (56%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{18}H_{20}ClNNaO_3S$ $[M+Na]^+$: 388.0750; Found: 388.0749.

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

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

Pale yellow solid. M.p. 97-100 ºC; yield: 20.4 mg (53%).

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

^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 148.6, 145.1, 137.3, 129.8 (2C), 128.5 (2C), 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 calculated for $C_{18}H_{20}ClNNaO_4S$ $[M+Na]^+$: 404.0699; Found: 404.0699.

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{17}BrClNNaO_3S$ [M+Na]+: 451.9699; Found: 451.9705.

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

***N*-(3-bromophenyl)-2-chloro-2-methyl-3-tosylpropanamide (3e)**

White solid. M.p. 112-114 ºC; yield: 24.0 mg (56%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{17}BrClNNaO_3S$ $[M+Na]^+$: 451.9699; Found: 451.9705.

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{19}H_{22}ClNNaO_4S$ $[M+Na]^+$: 418.0856; Found: 418.0858.

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

***N*-(4-bromophenyl)-2-chloro-2-methyl-3-tosylpropanamide (3g)**

Yellow solid. M.p. 55-57 ºC; yield: 29.9 mg (73%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{17}BrClNNaO_3S$ [M+Na]+: 451.9699; Found: 451.9698.

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

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

White solid. M.p. 56-58 ºC; yield: 25.7 mg (64%).

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{18}H_{17}ClF_3NNaO_3S$ $[M+Na]^+$: 442.0467; Found: 442.0469.

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

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

White solid. M.p. 80-82 ºC: yield: 24.9 mg (68%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{18}H_{20}ClNNaO_3S$ $[M+Na]^+$ 388.0750; Found: 388.0753.

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{19}H_{22}ClNNaO_3S$ $[M+Na]^+$: 402.0907; Found: 402.0906.

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

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

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

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

^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.3, 145.6, 141.2, 137.5, 136.0, 134.3 (q, $^2J_{C\text{-}F}$= 32.9 Hz) 130.2 (2C), 128.2 (2C), 122.8, 118.2 (q, $^3J_{C\text{-}F}$= 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 calculated for $C_{19}H_{16}ClF_3N_2NaO_3S$ $[M+Na]^+$: 467.0420; Found: 467.0427.

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

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

White solid. M.p. 54-56 ºC; yield: 19.2 mg (54%).

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

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

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

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{16}H_{16}ClNNaO_3S$ $[M+Na]^+$: 360.0437; Found: 360.0442.

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

2-Chloro-3-((4-fluorophenyl)sulfonyl)-2-methyl-*N*-phenyl propanamide (3o)

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

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

^{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, 2C), 129.3 (2C), 125.6, 120.7 (2C), 116.7 (d, $^2J_{C-F}$= 22.7 Hz, 2C), 66.4, 65.7, 31.2.

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

HRMS (ESI): m/z calculated for $C_{16}H_{15}ClFNNaO_3S$ $[M+Na]^+$: 378.0343; Found: 378.0345.

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{18}ClNNaO_4S$ $[M+Na]^+$: 390.0543; Found: 390.0546.

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

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

Brown solid. M.p. 135-136 ºC; yield: 21.1 mg (55%).

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

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

HRMS (ESI-TOF): exact m/z calculated for $C_{16}H_{15}ClN_2NaO_5S$ $[M+Na]^+$: 405.0288; Found: 405.0285.

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

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

Yellow solid. Decomposition at 150 ºC; yield: 8.3 mg (21%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{16}H_{15}ClN_2NaO_5S$ $[M+Na]^+$: 405.0288; Found: 405.0291.

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

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

White solid. M.p. 122-124 ºC; yield: 25.5 mg (57%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{17}H_{17}BrClNNaO_4S$ $[M+Na]^+$: 467.9648; Found: 467.9652.

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

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

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

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

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

HRMS (ESI-TOF): m/z calculated for $C_{14}H_{14}ClNNaO_3S_2$ $[M+Na]^+$: 366.0001; Found: 366.0005.

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

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

White solid. M.p. 94-96 ºC; yield: 17.7 mg (56%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{14}H_{20}ClNNaO_3S$ $[M+Na]^+$: 340,0750; Found: 340.0753.

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

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 (bs, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.10 (d, *J* = 14.4 Hz, 1H), 3.58 (d, *J* = 14.4 Hz, 1H), 3.23 (hept, *J* = 6.9 Hz, 1H), 2.00 (s, 3H), 1.41 (d, *J* = 2.1 Hz, 3H), 1.38 (d, *J* = 2.1 Hz, 3H).

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

HRMS (ESI-TOF): m/z calculated for $C_{13}H_{18}ClNNaO_3S$ $[M+Na]^+$: 326.0594; Found: 326.0594.

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

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

White solid. M.p. 108-110 ºC; yield: 27.0 mg (90%).

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

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

HRMS (ESI-TOF): m/z calculated for $C_{13}H_{16}ClNNaO_3S$ $[M+Na]^+$: 324.0437; Found: 324.0437.

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

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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