Cu-Catalyzed Photoredox Chlorosulfonation of Alkenes and Alkynes

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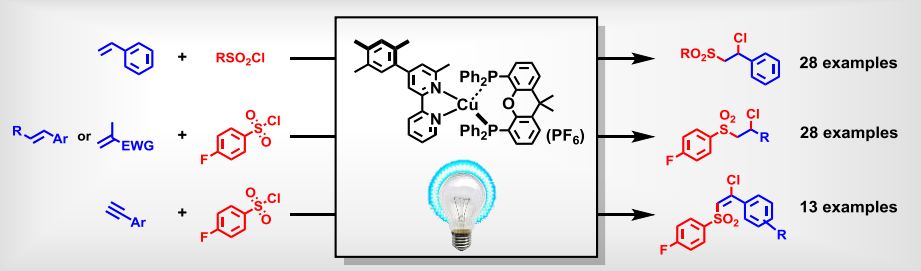
Supporting Information Placeholder



ABSTRACT: Visible-light photoredox chlorosulfonation of alkenes and alkynes is achieved using a Cu photocatalyst. The reactions occur under mild conditions, have broad scope and high functional group tolerance.

Sulfones are widely present in pharmaceutical compounds (Figure 1A).[1] Methods introducing the sulfone functional group into organic compounds are highly desirable. Traditionally, sulfones are made in two steps: first thiolation followed by oxidation.[2-3] Chlorosulfonation of alkenes and alkynes is an attractive method to introduce both sulfone and chloro functional groups into organic molecules using feedstock reagents.[4-9] Recently, photoredox catalysis was developed for efficient sulfonations of alkenes and heteroarenes using organic sulfonyl chlorides as sulfonating agents.[10-13] However, there were still only a few reports of photocatalytic chlorosulfonation of alkenes and alkynes.[14-17] Here we describe a broad-scope photoredox chlorosulfonation of terminal alkenes and alkynes, employing our recently developed Cu photocatalyst[18] **1** (Figure 1B).

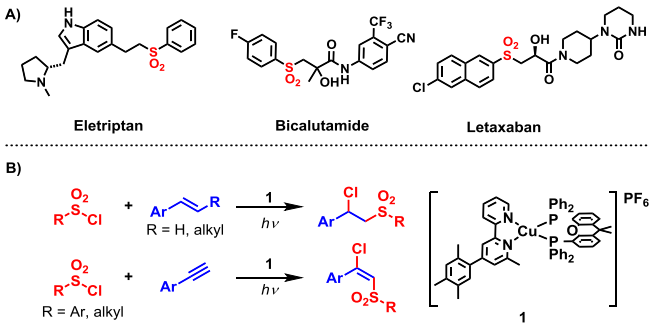
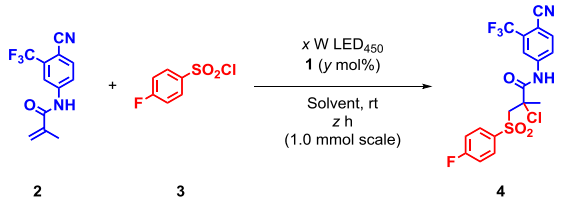


Figure 1. (A) Examples of sulfone-containing pharmaceutical compounds. (B) Cu-catalyzed chlorosulfonation of both alkenes and alkynes.

The chlorosulfonation of methacrylamide **2** using *para*-fluorobenzylsulfonyl chloride (**3**) yielding a *Bicalutamide* derivative **4** was the test reaction for the optimization of conditions (Table 1). Cu complex **1**, previously developed by us for chlorotrifluoromethylation of alkenes[18], was chosen as the catalyst. After an initial screening, we found that **4** could indeed be formed, albeit in low yields, when the reaction was conducted at room temperature in dichloromethane (DCM) using a 2 W LED light (Table 1, entries 1-3). A loading of 2.5 mol% of **1** gave the best result (Table 1, entry 2). The optimal ratio of **2**:**3** was 1:1 (SI, Table S1, entries 1-5). A 40 W light source improved the conversion to 70% and the yield to 59% (Table 1, entry 4). Various additives did not improve conversions or yields (SI, Table S1, entries 5-9). While acetonitrile (MeCN) alone was less effective as the solvent (Table 1, entry 5), a mixture of DCM and MeCN gave better yields (Table 1, entries 6-7). The reaction could be conducted at a 5 mmol scale (Table 1, entry 7). Control reactions showed that a high-energy light source (SI, Table S1, entry 10), **PC 1**, light and a N_2 atmosphere were all needed for the reaction to proceed smoothly (SI, Table S2, entries 1-3).

Table 1. Optimization of reaction conditions for chlorosulfonation.



2 3 4

Entry	*x*	*y*	Solvent	Time [h]	Conversion[a] (yield)[b] [%]
1	2	1	DCM (3 mL)	67.5	36 (n.d.)[c]
2	2	2.5	DCM (3 mL)	24	45 (33)
3	2	5	DCM (3 mL)	24	20 (n.d.)
4	40	2.5	DCM (3 mL)	24	70 (59)
5	40	2.5	MeCN (3 mL)	24	55 (47)
6	40	2.5	DCM+MeCN (1.5+1.5 mL)	24	90 (71)
7	40	2.5	DCM+MeCN (2.5+2.5 mL)	66	93 (86, 64[d])

[a]Determined by ^{1}H NMR. [b]Isolated yields. [c]n.r. = no reaction, n.d. = not determined. [d]Reaction performed in 5 mmol scale.

We further tested common Ru and Ir based **PC**s as well as organic **PC**s (SI, Table S3) in place of catalyst **1**. Organic **PC** 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine gave 43% yield at 50% conversion of starting material (SI, Table S2, entry 10). [Ir(dtbbpy)(ppy)$_2$][PF$_6$] gave 42% yield at full conversion of starting material (SI, Table S2, entry 13). All other tested Ru, Ir, and organic PCs gave no or only a trace amount of product. No reaction occurred when the radical initiator AIBN was used instead of a catalyst. The commonly used Cu **PC** [Cu(dap)$_2$]Cl (**5**, dap = 2,9-bis(4-anisyl)-1,10-phenanthroline) was a good catalyst, giving 89% yield at full conversion of starting material (SI, Table S2, entry 5). This result prompted us to compare the efficiencies of catalysts **1** and **5** for the reactions of several other substrates (SI, Figure S2). For all substrates examined, catalyst **1** was more efficient than **5**. Thus, catalyst **1** was used for the study of scope.

The scope of sulfonyl chlorides was first probed using styrene as the alkene partner (Figure 2). A large number of arylsulfonyl chlorides with various substituents at 4-, 3-, or 2-position of the aryl groups reacted in good yields (Figure 2, **8a-8p**). Both electron donating and withdrawing substituents were tolerated. For some unknown reason 2-fluorobenzylsulfonyl chloride did not react. For a very bulky aryl sulfonyl chloride with an isopropyl group at 2,4,6-positions of the aryl group, the yield was still 50% (Figure 2, **8q**). A heteroaryl suflonyl chloride was also successfully employed (Figure 2, **8r**). Interestingly, when trichloromethylsulfonyl chloride was used, extrusion of SO$_2$ was observed (Figure 2, **8s**). Alkylsulfonyl chlorides were suitable substrates as well (Figure 2, **8t-8y**). In some cases (**8b**, **8d**, **8f**, **8g** and **8s**), the catalyst loading could be lowered to 1.0 mol% under slightly modified conditions. Sulfamoyl chlorides were more challenging substrates, generally giving lower yields even when 5 equiv. of styrene was used (Figure 2, **8z-8ab**).

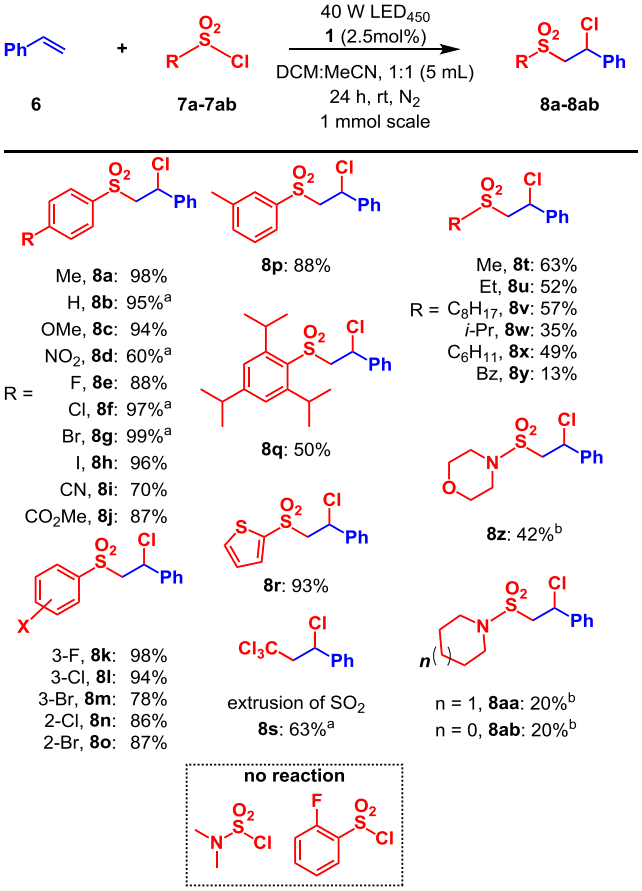


Figure 2. Substrate scope of sulfonyl chlorides. [a]2 W LED$_{450}$, **1** (1.0 mol%), DCM (3 mL), 24 h, rt, N$_2$ atm., 1 mmol scale. [b]5 equiv. of styrene.

We then probed the substrate scope of the alkenes using the arylsulfonyl chloride **3** as the reaction partner (Figure 3). Both electron-donating and electron-withdrawing substituents at the 4-position of styrenes reacted in good yields (Figure 3, **10a-10h**). The product from 4-methoxy styrene was unstable with respect to elimination of HCl, and an (*E*)-vinylsulfone (**10e**) was obtained after purification. Styrenes with a halogen group in 4-, 3- or 2-position all reacted in excellent yields (Figure 3, **10f-10n**). The reaction tolerated a 2,4,6-trisubstituted styrene (Figure 3, **10o**). Pyridyl- or naphtyl substrates also reacted well (Figure 3, **10p-10r**). A styrene substituted at the α-position was a viable substrate (Figure 3, **10s**). Internal styrenes also worked (Figure 3, **10t-10u**), but cinnamaldehyde was unreactive. Alkenes substituted by an electron-withdrawing group were reactive only when there was an additional Me-group at the 2-position of the alkenes (Table 1, **4**; Figure 3, **10v**). Unbranched, terminal alkenes substituted by an electron-withdrawing group underwent no reaction. Unactivated terminal alkyl alkenes gave low yields while internal alkyl alkenes gave no reaction (Figure 3, **10w-10y**). To our delight, a complex, *Estrone*-derived substrate reacted to give **10z** in 66% yield.

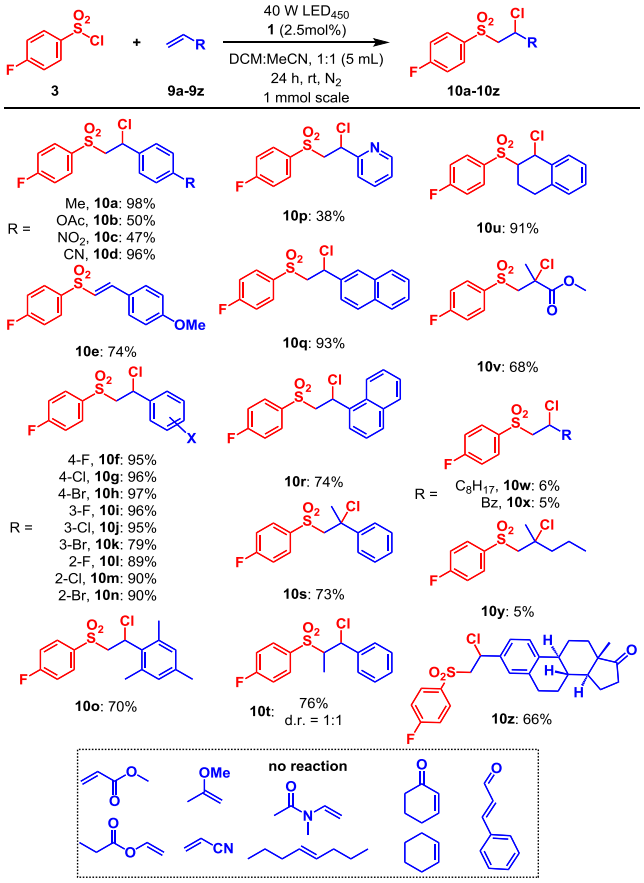


Figure 3. Substrate scope of alkenes.

Phenylacetylenes were also tested as substrates using the same optimized conditions (Figure 4). In contrast to the recently reported Ir-catalyzed chlorosulfonation of alkynes, which gave a mixture of (*E*)- and (*Z*)-alkenes[17], we obtained exclusively (*E*)-chlorosulfonylvinylbenzenes. The excellent *E*-selectivity might originate from an outer-sphere reaction mechanism where the radical termination step proceeds through the thermodynamically favored configuration. The yields were typically modest. Substituents at 4, 3-, or 2-positions were tolerated (Figure 4, **12a-12m**). A single crystal X-ray structure of **12d** was determined, confirming the connectivity and stereochemistry (Figure 4). Unactivated alkyl alkynes or internal aryl alkynes were not reactive.

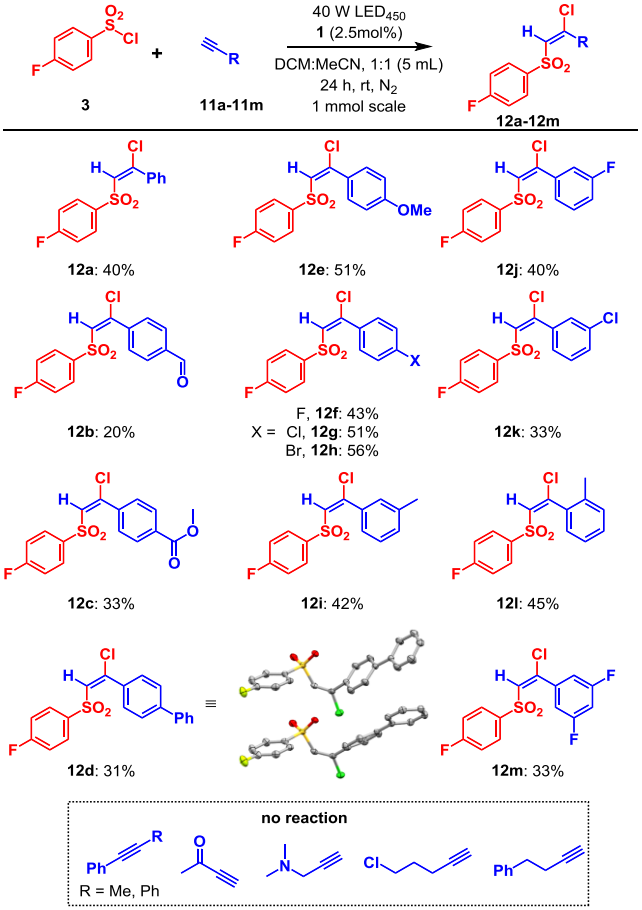


Figure 4. Substrate scope of alkynes. The single crystal X-ray structure of **12d** is displayed with ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity.

Overall, the chlorosulfonation of alkenes and alkynes tolerated various functional groups such as ester (**8j**), nitrile (**8i**), halogens (**8e-8h** and **8k-8o**), thiophene (**8r**) and amine (**8z-8ab**) in the sulfonyl chloride reagents, as well as ester (**10b**, **10v**, **12c**), F (**10f**, **10i**, **10l**, **12f**, **12j**, **12m**), Cl (**10g**, **10j**, **10m**, **12g**, **12k**) and Br (**10h**, **10k**, **10n**, **12h**) functional groups in the alkene and alkyne substrates.

In summary, a Cu-catalyzed photoredox chlorosulfonation of alkenes and alkynes has been developed. The method has broad substrate scope and high functional group tolerance. It can be used to prepare a wide range of organic sulfones from feedstock reagents under mild conditions.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from commercial suppliers and used without further purification. Complex **1**[18] and (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one[19] were prepared according to literature procedure. All photoredox reactions were carried out under an N_2 atmosphere using standard glovebox techniques and NMR spectra of known compounds agree with reports. The light sources were either a homemade device (700 mA or ca. 2 W as previously reported[18] from the mechanical and electrical workshop

of EPFL or LEDs purchased from Kessil Co., Ltd. (40 W max., product No. A160WE) cooled by table fans purchased from Galaxus Co., Ltd. (35 W max.). Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glovebox without exposure to air. NMR spectra were recorded on a Bruker Avance 400 Spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts were referenced internally to residual solvent peaks relative to TMS (δ = 0 ppm) and ^{19}F chemical shifts were externally referenced to $CFCl_3$ (δ = 0 ppm). High resolution mass spectra, X-ray structures and elemental analyses were determined by the respective EPFL facilities. X-ray quality crystals were grown by slow diffusion of Et_2O in DCM. The stereochemistry of compounds **12a-12m** were confirmed by one dimensional NOESY experiments which showed no NOE signal to the aryl moieties.

General Procedure A (GP A). A Schlenk flask (10 mL) was charged with a magnetic stirring bar and catalyst **1** (10.8 mg, 1.0 mol%). The Schlenk flask was then transferred into a glovebox where DCM (3 mL), sulfonyl chloride (1.0 mmol) and alkene (1.0 mmol) were added. The reaction mixture was then irradiated with a blue LED (λ_{max} = 450 nm, 700 mA, ca. 2 W as previously reported[18]) from a distance of ca. 1 cm and stirred at rt for 24 hours. After completion of the reaction, the flask was transferred out of the glovebox, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography. NMR spectra of known compounds agree with literature values and new compounds were further characterized by HRMS and/or elemental analysis.

General Procedure B (GP B). A screw-cap reaction vial (10 mL) was charged with a magnetic stirring bar and catalyst **1** (27 mg, 2.5 mol%) and transferred into a glovebox. Solvents (DCM:MeCN, 2.5:2.5 mL), sulfonyl chloride (1.0 mmol) and alkene/alkyne (1.0 mmol) were added and the screw-cap vial was closed and further sealed with electrical tape. The reaction vial was moved outside the glovebox, placed ca. 10 cm under a 40 W blue LED from Kessil Co., Ltd. and cooled with a fan. The reaction mixture was then stirred under irradiation for 24 hours. Afterwards the solvent mixture was removed under reduced pressure and the crude mixture was purified by column chromatography. NMR spectra of known compounds agree with literature values and new compounds were further characterized by HRMS and/or elemental analysis. One LED/fan setup was used for a maximum of three reactions at once to assure sufficient light-irradiation per reaction vial. A temperature increase from rt to ca. 30 °C could be measured with a regular thermometer over the course of 24 hours irradiation.

2-Chloro-N-(4-cyano-3-(trifluoromethyl)phenyl)-3-((4-fluorophenyl)sulfonyl)-2-methylpropanamide (4). GP B was applied (385 mg = 86%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 1.93 (s, 3H), 3.79 (d, $^{2}J_{H,H}$ = 14.73 Hz, 1H), 4.27 (d, $^{2}J_{H,H}$ = 14.69 Hz, 1H), 7.20-7.30 (m, 2H), 7.82-7.89 (m, 1H), 7.89-8.00 (m, 3H), 8.12 (s, 1H), 8.97 (s, 1H). $^{19}F\{^{1}H\}$ NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -62.49, -103.48. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 31.2, 65.9, 66.5, 105.8, 115.4, 117.1 (d, $^{2}J_{C,F}$ = 22.89 Hz), 118.4 (q, $^{3}J_{C,F}$ = 4.98 Hz), 122.7 (q, $^{1}J_{C,F}$ = 270.17 Hz), 123.2, 131.5 (d, $^{3}J_{C,F}$ = 9.85 Hz), 134.1 (q, $^{2}J_{C,F}$ = 32.76 Hz), 136.4, 137.0 (d, $^{4}J_{C,F}$ = 2.86 Hz), 141.6, 166.2 (d, $^{1}J_{C,F}$ = 256.34 Hz), 168.5. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{13}ClF_4N_2NaO_3S$ 471.0164; Found 471.0173.

1-((2-Chloro-2-phenylethyl)sulfonyl)-4-methylbenzene[15] (8a). GP B was applied (298 mg = 98%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.41 (s, 3H), 3.86 (dd, $^{2}J_{H,H}$ = 14.75 Hz, $^{3}J_{H,H}$ = 7.18 Hz, 1H), 3.95 (dd, $^{2}J_{H,H}$ = 14.75 Hz, $^{3}J_{H,H}$ = 6.74 Hz, 1H), 5.32 (t, $^{3}J_{H,H}$ = 6.94 Hz, 1H), 7.26-7.32 (m, 7H), 7.61 (d, $^{3}J_{H,H}$ = 8.40 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.7, 55.7, 64.2, 127.6, 128.5, 129.3, 129.5, 130.2, 136.7, 139.1, 145.6. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{15}ClNaO_2S$ 317.0373; Found 317.0383.

(1-Chloro-2-(phenylsulfonyl)ethyl)benzene (8b). GP A was applied (267 mg = 95%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.82-3.90 (m, 4H), 3.96 (dd, $^{2}J_{H,H}$ = 14.75 Hz, $^{3}J_{H,H}$ = 6.90 Hz, 1H), 5.34 (t, $^{3}J_{H,H}$ = 6.88 Hz, 1H), 6.91 (d, $^{3}J_{H,H}$ = 8.72 Hz, 2H), 7.25-7.32 (m, 5H), 7.69 (d, $^{3}J_{H,H}$ = 8.72 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.4, 55.8, 64.4, 114.5, 127.3, 129.0, 129.2, 130.5, 130.7, 138.8, 163.3. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{13}ClO_2SNa$ 303.0222; Found 303.0226.

1-((2-Chloro-2-phenylethyl)sulfonyl)-4-methoxybenzene (8c). GP B was applied (292 mg = 94%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.82-3.90 (m, 4H), 3.96 (dd, $^{2}J_{H,H}$ = 14.75 Hz, $^{3}J_{H,H}$ = 6.90 Hz, 1H), 5.34 (t, $^{3}J_{H,H}$ = 6.88 Hz, 1H), 6.91 (d, $^{3}J_{H,H}$ = 8.72 Hz, 2H), 7.25-7.32 (m, 5H), 7.69 (d, $^{3}J_{H,H}$ = 8.72 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.4, 55.8, 64.4, 114.5, 127.3, 129.0, 129.2, 130.5, 130.7, 138.8, 163.3. HRMS (ESI/QTOF) *m/z*: $[M-Cl]^+$ Calcd for $C_{15}H_{15}O_3S$ 275.0736; Found 275.0737.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-nitrobenzene (8d).[4] GP A was applied (195 mg = 60%, yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.87 (dd, $^{2}J_{H,H}$ = 15.09 Hz, $^{3}J_{H,H}$ = 7.20 Hz, 1H), 3.98 (dd, $^{2}J_{H,H}$ = 15.09 Hz, $^{3}J_{H,H}$ = 6.88 Hz, 1H), 5.30 (t, $^{3}J_{H,H}$ = 7.04 Hz, 1H), 7.15-7.22 (m, 5H), 7.81 (d, $^{3}J_{H,H}$ = 8.88 Hz, 2H), 8.16 (d, $^{3}J_{H,H}$ = 8.85 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.0, 64.2, 124.3, 127.4, 129.0, 129.2, 129.6, 129.8, 137.9, 144.8, 150.8. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+OH]^-$ Calcd for $C_{14}H_{15}ClNO_5S$ 342.0208; Found 342.0209.

1-((2-Chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (8e). GP B was applied (263 mg = 88%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.87 (dd, $^{2}J_{H,H}$ = 14.89 Hz, $^{3}J_{H,H}$ = 7.12 Hz, 1H), 3.97 (dd, $^{2}J_{H,H}$ = 14.89 Hz, $^{3}J_{H,H}$ = 6.84 Hz, 1H), 5.34 (t, $^{3}J_{H,H}$ = 6.96 Hz, 1H), 7.05-7.13 (m, 2H), 7.23-7.7.32 (m, 5H), 7.69-7.77 (m, 2H). $^{19}F\{^{1}H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.99. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.2, 64.3, 116.5 (d, $^{2}J_{C,F}$ = 22.74 Hz), 129.1, 129.4, 131.2 (d, $^{3}J_{C,F}$ = 9.69 Hz), 135.4 (d, $^{4}J_{C,F}$ = 3.08 Hz), 138.4, 165.9 (d, $^{1}J_{C,F}$ = 257.01 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}FO_2S$ 263.0537; Found 263.0535.

1-Chloro-4-((2-chloro-2-phenylethyl)sulfonyl)benzene (8f). GP B was applied (306 mg = 97%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.87 (dd, $^{2}J_{H,H}$ = 14.89 Hz, $^{3}J_{H,H}$ = 7.12 Hz, 1H), 3.97 (dd, $^{2}J_{H,H}$ = 14.89 Hz, $^{3}J_{H,H}$ = 6.84 Hz, 1H), 5.33 (t, $^{3}J_{H,H}$ = 6.98 Hz, 1H), 7.22-7.30 (m, 5H), 7.39 (d, $^{3}J_{H,H}$ =

8.56 Hz, 2H), 7.64 (d, $^3J_{H,H}$ = 8.56 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.2, 64.3, 127.3, 129.1, 129.4, 129.5, 129.8, 137.8, 138.3, 140.8. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{12}Cl_2NaO_2S$ 336.9827; Found 336.9830.

1-Bromo-4-((2-chloro-2-phenylethyl)sulfonyl)benzene (8g). GP B was applied (356 mg = 99%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.87 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.16 Hz, 1H), 3.97 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.80 Hz, 1H), 5.33 (t, $^3J_{H,H}$ = 6.98 Hz, 1H), 7.20-7.31 (m, 5H), 7.55 (s, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.1, 64.2, 127.3, 129.1, 129.3, 129.4, 129.8, 132.5, 138.2, 138.3. HRMS (LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}BrO_2S$ 322.9736; Found 322.9739.

1-((2-Chloro-2-phenylethyl)sulfonyl)-4-iodobenzene (8h). GP B was applied (390 mg = 96%, off-white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.86 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 7.20 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 6.52 Hz, 1H), 5.32 (t, $^3J_{H,H}$ = 6.62 Hz, 1H), 7.16-7.27 (m, 5H), 7.39 (d, $^3J_{H,H}$ = 7.76 Hz, 2H), 7.76 (d, $^3J_{H,H}$ = 7.88 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.1, 64.1, 102.0, 127.3, 129.1, 129.3, 129.5, 138.5. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}IO_2S$ 370.9597; Found 370.9598.

4-((2-Chloro-2-phenylethyl)sulfonyl)benzonitrile (8i)[14]. GP B was applied (214 mg = 70%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.91 (dd, $^2J_{H,H}$ = 15.05 Hz, $^3J_{H,H}$ = 7.24 Hz, 1H), 4.02 (dd, $^2J_{H,H}$ = 15.05 Hz, $^3J_{H,H}$ = 6.84 Hz), 5.35 (t, $^3J_{H,H}$ = 7.02 Hz, 1H), 7.20-7.32 (m, 5H), 7.70 (d, $^3J_{H,H}$ = 8.32 Hz, 2H), 7.80 (d, $^3J_{H,H}$ = 8.32 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.0, 64.0, 117.1, 117.6, 127.4, 129.0, 129.2, 129.6, 132.9, 137.9, 143.4. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{15}H_{12}NO_2S$ 270.0583; Found 270.0583.

Methyl 4-((2-Chloro-2-phenylethyl)sulfonyl)benzoate (8j). GP B was applied (295 mg = 87%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.81-4.11 (m, 5H), 5.35 (t, $^3J_{H,H}$ = 6.80 Hz, 1H), 7.14-7.33 (m, 5H), 7.79 (d, $^3J_{H,H}$ = 8.08 Hz, 2H), 8.07 (d, $^3J_{H,H}$ = 8.08 Hz, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 52.9, 55.1, 64.1, 127.3, 128.3, 129.1, 129.4, 130.3, 143.9, 138.2, 143.1, 165.5. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{15}ClNaO_4S$ 361.0272; Found 361.0275.

1-((2-Chloro-2-phenylethyl)sulfonyl)-3-fluorobenzene (8k). GP B was applied (293 mg = 98%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.89 (dd, $^2J_{H,H}$ = 14.87 Hz, $^3J_{H,H}$ = 7.30 Hz, 1H), 3.99 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.72 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 7.00 Hz, 1H), 7.21-7.29 (m, 6H), 7.35-7.47 (m, 2H), 7.50-7.57 (m, 1H). ^{19}F NMR$\{^1H\}$ (376.3 MHz, $CDCl_3$, ppm): δ = 109.13. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.1, 64.2, 115.7 (d, $^2J_{C,F}$ = 24.53 Hz), 121.2 (d, $^2J_{C,F}$ = 21.18 Hz), 124.0 (d, $^4J_{C,F}$ = 3.39 Hz), 127.3, 129.1, 129.5, 131.1 (d, $^3J_{C,F}$ = 7.56 Hz), 138.2, 141.3 (d, $^3J_{C,F}$ = 6.53 Hz), 162.3 (d, $^1J_{C,F}$ = 252.52 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}FO_2S$ 263.0537; Found 263.0534.

1-Chloro-3-((2-chloro-2-phenylethyl)sulfonyl)benzene (8l). GP B was applied (296 mg = 94%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.90 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.56 Hz, 1H), 3.99 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.56 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 7.06 Hz, 1H), 7.23-7.30 (m, 5H), 7.33-7.40 (m, 1H), 7.48-7.54 (m, 1H), 7.58-7.64 (m, 2H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.1, 64.2, 126.3, 127.3, 128.5, 129.1, 129.6, 130.2, 134.0, 135.5, 138.1, 141.0. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}ClO_2S$ 279.0241; Found 279.0241.

1-Bromo-3-((2-chloro-2-phenylethyl)sulfonyl)benzene (8m). GP B was applied (281 mg = 78%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.91 (dd, $^2J_{H,H}$ = 14.71 Hz, $^3J_{H,H}$ = 7.58 Hz, 1H), 3.99 (dd, $^2J_{H,H}$ = 14.75 Hz, $^3J_{H,H}$ = 6.42 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 6.80 Hz, 1H), 7.10-7.33 (m, 5H), 7.61-7.69 (m, 2H), 7.75 (s, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.1, 64.1, 123.2, 126.7, 127.3, 129.0, 129.6, 130.7, 131.2, 136.9, 138.0, 141.1. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}BrO_2S$ 322.9736; Found 322.9734.

1-Chloro-2-((2-chloro-2-phenylethyl)sulfonyl)benzene (8n). GP B was applied (271 mg = 86%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.22 (dd, $^2J_{H,H}$ = 15.05 Hz, $^3J_{H,H}$ = 6.96 Hz, 1H), 4.27 (dd, $^2J_{H,H}$ = 15.05 Hz, $^3J_{H,H}$ = 7.20 Hz), 5.34 (t, $^3J_{H,H}$ = 7.08 Hz, 1H), 7.16-7.22 (m, 3H), 7.23-7.31 (m, 3H), 7.40-7.48 (m, 2H), 7.78-7.85 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.4, 61.8, 127.2, 127.4, 129.0, 129.4, 131.7, 131.8, 132.5, 134.8, 136.8, 138.1. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}ClO_2S$ 279.0241; Found 279.0237.

1-Bromo-2-((2-chloro-2-phenylethyl)sulfonyl)benzene (8o). GP B was applied (313 mg = 87%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.25 (dd, $^2J_{H,H}$ = 15.02 Hz, $^3J_{H,H}$ = 6.84 Hz, 1H), 4.32 (dd, $^2J_{H,H}$ = 15.01 Hz, $^3J_{H,H}$ = 7.34 Hz, 1H), 5.35 (t, $^3J_{H,H}$ = 7.09 Hz, 1H), 7.16-7.22 (m, 3H), 7.24-7.30 (m, 2H), 7.30-7.39 (m, 2H), 7.62-7.68 (m, 1H), 7.82-7.87 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.4, 61.4, 120.9, 127.3, 128.0, 129.0, 129.4, 132.3, 134.8, 135.3, 138.1, 138.5. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{12}BrO_2S$ 322.9736; Found 322.9740.

1-((2-Chloro-2-phenylethyl)sulfonyl)-3-methylbenzene (8p). GP B was applied (259 mg = 88%, red solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.34 (s, 3H), 3.87 (dd, $^2J_{H,H}$ = 14.75 Hz, $^3J_{H,H}$ = 7.34 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 6.64 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 6.98 Hz, 1H), 7.22-7.29 (m, 5H), 7.29-7.38 (m, 2H), 7.44-7.49 (m, 1H), 7.52-7.59 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.3, 55.2, 64.1, 125.3, 127.3 128.6, 128.9, 129.1, 129.3, 134.7, 138.52, 139.1, 139.5. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{15}H_{15}O_2S$ 259.0787; Found 259.0784.

2-((2-Chloro-2-phenylethyl)sulfonyl)-1,3,5-triisopropyl benzene (8q). GP B was applied (204 mg = 50%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.25 (d, $^3J_{H,H}$ = 6.92 Hz, 6H), 1.27 (d, $^3J_{H,H}$ = 6.72 Hz, 6H), 1.28 (d, $^3J_{H,H}$ = 6.68 Hz, 6H), 2.90 (sept., $^3J_{H,H}$ = 6.93 Hz, 1H), 3.86 (dd, $^2J_{H,H}$ = 14.61 Hz, $^3J_{H,H}$ = 5.68 Hz, 1H), 4.01 (dd, $^2J_{H,H}$ = 14.61 Hz, $^3J_{H,H}$ = 7.52 Hz, 1H), 4.10 (sept., $^3J_{H,H}$ = 6.76 Hz, 2H), 5.49 (dd, $^2J_{H,H}$ = 7.48 Hz, $^3J_{H,H}$ = 5.72 Hz, 1H), 7.15 (s, 2H), 7.27-7.37 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 23.67, 23.70, 25.0, 25.2, 29.8, 34.4, 55.3, 66.2, 124.2, 129.1, 129.2, 132.9, 139.4, 151.1, 154.2. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{31}ClNaO_2S$ 429.1625; Found 429.1627.

2-((2-Chloro-2-phenylethyl)sulfonyl)thiophene (8r). GP B was applied (267 mg = 93%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.97 (dd, $^2J_{H,H}$ = 14.83 Hz, $^3J_{H,H}$ = 6.98 Hz, 1H), 4.06 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 6.80 Hz, 1H), 5.37 (t, $^3J_{H,H}$ = 6.86 Hz, 1H), 7.02 (dd, $^3J_{H,H}$ = 4.86 Hz, 3.90 Hz, 1H), 7.29-7.33 (m, 5H), 7.48 (dd, $^3J_{H,H}$ = 3.80 Hz, $^4J_{H,H}$ = 1.24 Hz, 1H), 7.66 (dd, $^3J_{H,H}$ = 4.95 Hz, $^4J_{H,H}$ = 1.22 Hz, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.2, 65.5, 127.3, 128.0, 129.1, 129.4, 134.7, 135.1, 138.6, 140.5. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{12}H_{11}O_2S_2$ 251.0195; Found 251.0191.

(1,3,3,3-Tetrachloropropyl)benzene (8s)[15]. GP A was applied (163 mg = 63%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.55 (dd, $^2J_{H,H}$ = 15.33 Hz, $^3J_{H,H}$ = 6.44 Hz, 1H), 3.63 (dd, $^2J_{H,H}$ = 15.33 Hz, $^3J_{H,H}$ = 5.44 Hz, 1H), 5.31 (t, $^3J_{H,H}$ = 5.92 Hz), 7.31-7.49 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 58.4, 62.9, 96.343 127.5, 129.1, 140.6.

(1-Chloro-2-(methylsulfonyl)ethyl)benzene (8t). GP B was applied (138 mg = 63%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76 (s, 3H), 3.64 (dd, $^2J_{H,H}$ = 15.15 Hz, $^3J_{H,H}$ = 5.86 Hz, 1H), 3.85 (dd, $^2J_{H,H}$ = 15.17 Hz, $^3J_{H,H}$ = 7.76 Hz, 1H), 5.39 (t, $^3J_{H,H}$ = 6.78 Hz), 7.34-7.48 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 42.8, 55.7, 63.7, 127.3, 129.4, 129.7, 138.7. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_9H_{11}O_2S$ 183.0474; Found 183.0472.

(1-Chloro-2-(ethylsulfonyl)ethyl)benzene (8u). GP B was applied (121 mg = 52%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.33 (t, $^3J_{H,H}$ = 7.44 Hz, 3H), 2.74-2.95 (m, 2H), 3.59 (dd, $^2J_{H,H}$ = 15.17 Hz, $^3J_{H,H}$ = 5.88 Hz, 1H), 3.82 (dd, $^2J_{H,H}$ = 15.19 Hz, $^3J_{H,H}$ = 7.70 Hz, 1H), 5.40 (dd, $^3J_{H,H}$ = 7.64 Hz, 5.96 Hz, 1H), 7.34-7.47 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 6.7, 49.0, 55.6, 60.9, 127.2, 129.4, 129.7, 138.9. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{10}H_{13}O_2S$ 197.0631; Found 197.0628.

(1-Chloro-2-(octylsulfonyl)ethyl)benzene (8v). GP B was applied (181 mg = 57%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.88 (t, $^3J_{H,H}$ = 6.90 Hz, 3H), 1.14-1.35 (m, 10H), 1.61-1.85 (m, 2H), 2.65-2.83 (m, 2H), 3.60 (dd, $^2J_{H,H}$ = 15.11 Hz, $^3J_{H,H}$ = 6.26 Hz, 1H), 3.79 (dd, $^2J_{H,H}$ = 15.13 Hz, $^3J_{H,H}$ = 7.44 Hz, 1H), 5.39 (t, $^3J_{H,H}$ = 6.84 Hz, 1H), 7.34-7.48 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 14.2, 21.9, 22.7, 28.4, 29.0, 31.8, 54.5, 55.6, 61.4, 127.3, 129.3, 129.6, 138.9. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{16}H_{25}O_2S$ 281.1570; Found 281.1565.

(1-Chloro-2-(isopropylsulfonyl)ethyl)benzene (8w). GP B was applied (86 mg = 35%, colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.32 (d, $^3J_{H,H}$ = 6.86 Hz, 3H), 1.36 (d, $^3J_{H,H}$ = 6.76 Hz, 3H), 2.99 (sept., $^3J_{H,H}$ = 6.83 Hz, 1H), 3.57 (dd, $^2J_{H,H}$ = 14.95 Hz, $^3J_{H,H}$ = 5.90 Hz, 1H), 3.84 (dd, $^2J_{H,H}$ = 14.97 Hz, $^3J_{H,H}$ = 7.60 Hz, 1H), 5.43 (t, $^3J_{H,H}$ = 6.72 Hz, 1H), 7.35-7.48 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 14.8. 15.4. 54.2. 55.5. 58.4. 127.2. 129.3. 129.6. 139.2. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{11}H_{15}O_2S$ 211.0787; Found 211.0782.

(1-Chloro-2-(cyclohexylsulfonyl)ethyl)benzene (8x). GP B was applied (141 mg = 49%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.98-1.27 (m, 3H), 1.42-1.56 (m, 2H), 1.60-1.71 (m, 1H), 1.80-1.90 (m, 2H), 1.93-2.05 (m, 1H), 2.05-2.16 (m, 1H), 2.50 (tt, $^3J_{H,H}$ = 12.12 Hz, 3.35 Hz, 1H), 3.59 (dd, $^2J_{H,H}$ = 14.97 Hz, $^3J_{H,H}$ = 6.60 Hz, 1H), 3.78 (dd, $^2J_{H,H}$ = 14.95 Hz, $^3J_{H,H}$ = 7.06 Hz, 1H), 5.40 (t, $^3J_{H,H}$ = 6.82 Hz, 1H), 7.31-7.51 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 24.7, 24.8, 25.0, 25.07, 25.08, 55.5, 58.3, 61.8, 127.3, 129.2, 129.5, 139.2. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{19}O_2S$ 251.1100; Found 251.1100.

(2-(Benzylsulfonyl)-1-chloroethyl)benzene (8y). GP B was applied (40 mg = 13%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.45 (dd, $^2J_{H,H}$ = 15.21 Hz, $^3J_{H,H}$ = 5.80 Hz, 1H), 3.76 (dd, $^2J_{H,H}$ = 15.19 Hz, $^3J_{H,H}$ = 7.82 Hz, 1H), 4.07 (d, $^2J_{H,H}$ = 13.97 Hz, 1H), 4.20 (d, $^2J_{H,H}$ = 13.97 Hz, 1H), 5.44 (d, $^3J_{H,H}$ = 7.82 Hz, 5.86 Hz, 1H), 7.29-7.50 (m, 10H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.8, 59.9, 60.9, 127.35, 127.36, 129.2, 129.32, 129.34, 129.7, 131.1, 138.8. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{15}H_{15}O_2S$ 259.0787; Found 259.0786.

4-((2-Chloro-2-phenylethyl)sulfonyl)morpholine (8z). GP B with 5 equiv. of Styrene was applied (122 mg = 42%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.07-3.15 (m, 2H), 3.15-3.22 (m, 2H), 3.58-3.70 (m, 5H), 3.74 (dd, $^2J_{H,H}$ = 14.61 Hz, $^3J_{H,H}$ = 6.72 Hz, 1H), 5.31 (t, $^3J_{H,H}$ = 6.72 Hz, 1H), 7.35-7.45 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 45.5, 55.7, 58.1, 64.7, 66.6, 127.2, 129.2, 129.5, 139.3. HRMS (APCI/QTOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{17}ClNO_3S$ 290.0612; Found 290.0614.

1-((2-Chloro-2-phenylethyl)sulfonyl)piperidine (8aa) GP B with 5 equiv. of Styrene was applied (58 mg = 20%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.44-1.64 (m, 6H), 3.03-3.20 (m, 4H), 3.63 (dd, $^2J_{H,H}$ = 14.53 Hz, $^3J_{H,H}$ = 6.80 Hz, 1H), 3.70 (dd, $^2J_{H,H}$ = 14.53 Hz, $^3J_{H,H}$ = 6.72 Hz, 1H), 5.31 (t, $^3J_{H,H}$ = 6.74 Hz, 1H), 7.32-7.45 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 23.8, 25.7, 46.4, 56.0, 58.2, 127.2, 129.1, 129.3, 139.6. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{19}ClNO_2S$ 288.0820; Found 288.0814.

1-((2-Chloro-2-phenylethyl)sulfonyl)pyrrolidine (8ab). GP B with 5 equiv. of Styrene was applied (55 mg = 20%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.73-1.85 (m, 4H), 3.12-3.23 (m, 2H), 3.23-3.33 (m, 2H), 3.70 (dd, $^2J_{H,H}$ = 14.74 Hz, $^3J_{H,H}$ = 6.70 Hz, 1H), 3.80 (dd, $^2J_{H,H}$ = 14.74 Hz, $^3J_{H,H}$ = 6.79 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 6.74 Hz, 1H), 7.31-7.46 (m, 5H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 25.9, 47.6, 56.2, 58.5, 127.2, 129.2, 129.3, 139.6. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{16}ClNNaO_2S$ 296.0482; Found 296.0488.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-4-methylbenzene (10a). GP B was applied (307 mg = 98%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.31 (s, 3H), 3.87 (dd, $^2J_{H,H}$ = 14.83 Hz, $^3J_{H,H}$ = 7.30 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 6.68 Hz, 1H), 5.31 (t, $^3J_{H,H}$ = 6.94 Hz, 1H), 6.98-7.18 (m, 6H), 7.64-7.77 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.19. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.2, 55.2, 64.3, 116.4 (d, $^2J_{C,F}$ = 22.85 Hz), 127.2, 129.7, 131.2 (d, $^3J_{C,F}$ = 9.69 Hz), 135.4 (d, $^4J_{C,F}$ = 5.44 Hz), 139.5, 165.9 (d, $^1J_{C,F}$ = 256.57 Hz). HRMS

(ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{14}ClFNaO_2S$ 335.0279; Found 335.0278.

4-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)phenyl acetate (10b). GP B was applied (178 mg = 50%, grey solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.30 (s, 3H), 3.86 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.32 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.72 Hz, 1H), 5.35 (t, $^3J_{H,H}$ = 7.02 Hz, 1H), 6.96-7.02 (m, 2H), 7.08-7.16 (m, 2H), 7.25-7.30 (m, 2H), 7.66-7.73 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.74. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.2, 54.6, 64.4, 116.7 (d, $^2J_{C,F}$ = 22.81 Hz), 122.3, 128.5, 131.2 (d, $^3J_{C,F}$ = 9.67 Hz), 135.3 (d, $^4J_{C,F}$ = 3.10 Hz), 135.8, 151.3, 166.0 (d, $^1J_{C,F}$ = 257.22 Hz), 169.1. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{16}H_{14}FO_4S$ 321.0591; Found 321.0591.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-4-nitrobenzene (10c). GP B was applied (162 mg = 47%, grey solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.80 (dd, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 7.20 Hz, 1H), 3.92 (d, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 6.68 Hz, 1H), 5.38 (t, $^3J_{H,H}$ = 6.92 Hz, 1H), 7.13-7.23 (m, 2H), 7.46 (d, $^3J_{H,H}$ = 8.28 Hz, 2H), 7.63 (d, $^3J_{H,H}$ = 8.24 Hz, 1H), 7.76-7.85 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -101.84. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 53.9, 64.0, 113.4, 116.9 (d, $^2J_{C,F}$ = 22.69 Hz), 128.2, 131.2 (d, $^3J_{C,F}$ = 9.70 Hz), 132.9, 135.2 (d, $^4J_{C,F}$ = 2.73 Hz), 143.4, 166.2 (d, $^1J_{C,F}$ = 257.99 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{11}FNO_4S$ 308.0387; Found 308.0383.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-4-isocyanobenzene (10d). GP B was applied (311 mg = 96%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.80 (dd, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 7.16 Hz, 1H), 3.93 (dd, $^2J_{H,H}$ = 14.71 Hz, $^3J_{H,H}$ = 6.70 Hz, 1H), 5.38 (t, $^3J_{H,H}$ = 6.92 Hz, 1H), 7.14-7.24 (m, 2H), 7.46 (d, $^3J_{H,H}$ = 8.36 Hz, 2H), 7.63 (d, $^3J_{H,H}$ = 8.40 Hz, 2H), 7.76-7.85 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -101.34. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 53.9, 64.0, 113.4, 116.9 (d, $^2J_{C,F}$ = 22.75 Hz), 118.0, 128.2, 131.2 (d, $^3J_{C,F}$ = 9.65 Hz), 132.9, 135.2 (d, $^4J_{C,F}$ = 3.06 Hz), 143.4, 166.2 (d, $^1J_{C,F}$ = 258.19 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{15}H_{11}FNO_2S$ 288.0489; Found 288.0485.

(*E*)-1-Fluoro-4-((4-methoxystyryl)sulfonyl)benzene (10e). GP B was applied (216 mg = 74%, off-white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.84 (s, 3H), 6.69 (d, $^3J_{H,H}$ = 15.33 Hz, 1H), 6.87-6.94 (m, 2H), 7.17-7.24 (m, 2H), 7.39-7.47 (m, 2H), 7.63 (d, $^3J_{H,H}$ = 15.33 Hz, 1H), 7.90-8.00 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -104.41. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.6, 114.7, 116.7 (d, $^2J_{C,F}$ = 22.62 Hz), 124.4, 125.0, 130.5 (d, $^3J_{C,F}$ = 9.45 Hz), 130.6, 137.4 (d, $^4J_{C,F}$ = 3.37 Hz), 142.6, 162.3, 165.6 (d, $^1J_{C,F}$ = 255.14 Hz). HRMS (APCI/QTOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}FO_3S$ 293.0642; Found 293.0647.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-4-fluorobenzene (10f). GP B was applied (301 mg = 95%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.86 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 7.40 Hz, 1H), 3.97 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 6.64 Hz, 1H), 5.37 (t, $^3J_{H,H}$ = 7.02 Hz, 1H), 6.96-7.05 (m, 2H), 7.12-7.20 (m, 2H), 7.25-7.33 (m, 2H), 7.72-7.81 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.59, -111.32. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.4, 64.4, 116.1 (d, $^2J_{C,F}$ = 21.97 Hz), 116.6 (d, $^2J_{C,F}$ = 22.74 Hz), 129.3 (d, $^3J_{C,F}$ = 8.57 Hz), 131.2 (d, $^3J_{C,F}$ = 9.63 Hz), 134.4 (d, $^4J_{C,F}$ = 3.52 Hz), 135.3 (d, $^4J_{C,F}$ = 3.32 Hz), 163.1 (d, $^1J_{C,F}$ = 249.90 Hz), 166.0 (d, $^1J_{C,F}$ = 257.39 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{11}F_2O_2S$ 281.0442; Found 281.0440.

1-Chloro-4-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl)benzene (10g). GP B was applied (320 mg = 96%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.85 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 7.40 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 6.64 Hz, 1H), 5.34 (t, $^3J_{H,H}$ = 7.02 Hz, 1H), 7.11-7.20 (m, 2H), 7.21-7.32 (m, 4H), 7.72-7.80 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.49. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.3, 64.2, 116.7 (d, $^2J_{C,F}$ = 22.76 Hz), 128.7, 129.3, 131.2 (d, $^3J_{C,F}$ = 9.87 Hz), 135.3 (d, $^4J_{C,F}$ = 3.04 Hz), 135.4, 136.9, 166.1 (d, 257.45 Hz). HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{11}Cl_2FNaO_2S$ 354.9733; Found 354.9729.

1-Bromo-4-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl)benzene (10h). GP B was applied (366 mg = 97%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.82 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 7.48 Hz, 1H), 3.93 (dd, $^2J_{H,H}$ = 14.81 Hz, $^3J_{H,H}$ = 6.60 Hz, 1H), 5.30 (t, $^3J_{H,H}$ = 7.04 Hz, 1H), 7.09-7.18 (m, 4H), 7.38-7.45 (m, 2H), 7.69-7.77 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.44. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.4, 64.2, 116.7 (d, $^2J_{C,F}$ = 22.74 Hz), 123.6, 129.0, 131.2 (d, $^3J_{C,F}$ = 9.85 Hz), 132.3, 135.3 (d, $^4J_{C,F}$ = 3.07 Hz), 137.4, 166.1 (d, $^1J_{C,F}$ = 257.51 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{11}BrFO_2S$ 340.9642; Found 340.9640.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-3-fluorobenzene (10i). GP B was applied (304 mg = 96%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.85 (dd, $^2J_{H,H}$ = 14.87 Hz, $^3J_{H,H}$ = 7.10 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.85 Hz, $^3J_{H,H}$ = 6.80 Hz, 1H), 5.35 (t, $^3J_{H,H}$ = 6.94 Hz, 1H), 6.94-7.05 (m, 2H), 7.06-12 (m, 1H), 7.13-7.21 (m, 2H), 7.24-7.35 (m, 1H), 7.75-7.83 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.57, -111.28. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.3, 64.2, 114.4 (d, $^2J_{C,F}$ = 22.73 Hz), 116.5 (d, $^2J_{C,F}$ = 21.47 Hz), 116.7 (d, $^2J_{H,H}$ = 23.06 Hz), 123.1 (d, $^4J_{C,F}$ = 2.98 Hz), 130.8 (d, $^3J_{C,F}$ = 8.46 Hz), 131.2 (d, $^3J_{C,F}$ = 9.82 Hz), 135.3 (d, $^4J_{C,F}$ = 3.20 Hz), 140.8 (d, $^3J_{C,F}$ = 7.33 Hz), 162.9 (d, $^1J_{C,F}$ = 248.06 Hz), 166.1 (d, $^1J_{C,F}$ = 257.32 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{11}F_2O_2S$ 281.0442; Found 281.0437.

1-Chloro-3-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl)benzene (10j). GP B was applied (317 mg = 95%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.84 (dd $^2J_{H,H}$ = 14.86 Hz, $^3J_{H,H}$ = 7.42 Hz, 1H), 3.94 (dd, $^2J_{H,H}$ = 14.86 Hz, $^3J_{H,H}$ = 6.60 Hz), 5.29 (t, $^3J_{H,H}$ = 7.00 Hz, 1H), 7.08-7.15 (m, 2H), 7.15-7.28 (m, 4H), 7.68-7.78 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.55. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.3, 64.1, 116.7 (d, $^2J_{C,F}$ = 22.69 Hz), 125.6, 127.6, 129.6, 130.4, 131.2 (d, $^3J_{C,F}$ = 9.73 Hz), 135.0, 135.2 (d, $^4J_{C,F}$ = 3.37 Hz), 140.2, 166.1 (d, $^1J_{C,F}$ = 257.83 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{14}H_{11}ClFO_2S$ 297.0147; Found 297.0142.

1-Bromo-3-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl) benzene (10k). GP B was applied (298 mg = 79%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.84 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.52 Hz, 1H), 3.94 (dd, $^2J_{H,H}$ = 14.87 Hz. $^3J_{H,H}$ = 6.54 Hz, 1H), 5.28 (t, $^3J_{H,H}$ = 7.02 Hz), 7.08-7.19 (m, 3H), 7.19-7.25 (m, 1H), 7.36 (s, 1H), 7.38-7.43 (m, 1H), 7.68-7.77 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.51. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.2, 64.0, 116.7 (d, $^2J_{C,F}$ = 22.90 Hz), 123.0, 126.1, 130.4, 130.6, 131.2 (d, $^3J_{C,F}$ = 10.07 Hz), 132.5, 135.1 (d, $^4J_{C,F}$ = 2.97 Hz), 140.4, 166.0 (d, $^1J_{C,F}$ = 257.16 Hz). HRMS (LTQ-Orbitrap) *m/z*: [M-Cl]$^+$ Calcd for $C_{14}H_{11}BrFO_2S$ 340.9642; Found 340.9641.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-2-fluoro-benzene (10l). GP B was applied (282 mg = 89%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.89 (d, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.56 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.64 Hz, 1H), 5.44 (t, $^3J_{H,H}$ = 7.08 Hz, 1H), 6.81-6.92 (m, 1H), 6.98-7.08 (m, 3H), 7.16-7.28 (m, 2H), 7.62-7.74 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.83, -115.39. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 49.6 (d, $J_{C,F}$ = 2.90 Hz), 62.7 (d, $J_{C,F}$ = 2.66 Hz), 116.3 (d, $^2J_{C,F}$ =21.38 Hz), 116.6 (d, $^2J_{C,F}$ = 22.74 Hz), 124.8 (d, $^4J_{C,F}$ = 3.61 Hz), 125.5 (d, $^3J_{C,F}$ = 11.95 Hz), 129.4 (d, $^4J_{C,F}$ = 3.20 Hz), 131.2 (d, $^3J_{C,F}$ = 9.63 Hz), 131.4 (d, $^3J_{C,F}$ = 8.68 Hz), 135.0 (d, $^3J_{C,F}$ = 3.22 Hz), 160.0 (d, $^1J_{C,F}$ = 250.35 Hz), 166.0 (d, $^1J_{C,F}$ = 256.99 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M-Cl]$^+$ Calcd for $C_{14}H_{11}F_2O_2S$ 281.0442; Found 281.0439.

1-Chloro-2-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl) benzene (10m). GP B was applied (300 mg = 90%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.82 (dd, $^2J_{H,H}$ = 14.99 Hz, $^3J_{H,H}$ = 7.30 Hz, 1H), 3.88 (dd, $^2J_{H,H}$ = 14.99 Hz, $^3J_{H,H}$ = 6.46 Hz, 1H), 5.71 (t, $^3J_{H,H}$ = 6.86 Hz, 1H), 7.03-7.11 (m, 2H), 7.11-7.21 (m, 2H), 7.22 (m, 1H), 7.29-7.35 (m, 1H), 7.77-7.82 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.69. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 51.5, 62.9, 116.7 (d, $^2J_{C,F}$ = 22.73 Hz), 127.7, 129.0, 130.3, 130.5, 131.4 (d, $^3J_{C,F}$ = 9.80 Hz), 132.9, 135.7, 135.8 (d, $^4J_{C,F}$ = 3.05 Hz), 166.1 (d, 257.33 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M-Cl]$^+$ Calcd for $C_{14}H_{11}ClFO_2S$ 297.0147; Found 297.0145.

1-Bromo-2-(1-chloro-2-((4-fluorophenyl)sulfonyl)ethyl) benzene (10n). GP B was applied (340 mg = 90%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.80-3.96 (m, 2H), 5.77 (t, $^3J_{H,H}$ = 6.80 Hz, 1H), 7.11-7.20 (m, 3H), 7.26 (t, $^3J_{H,H}$ = 7.48 Hz, 1H), 7.40 (d, $^3J_{H,H}$ = 7.80 Hz, 1H), 7.52 (d, $^3J_{H,H}$ = 7.96 Hz, 1H), 7.81-7.91 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.67. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 53.9, 63.1, 116.7 (d, $^2J_{C,F}$ = 22.84 Hz), 123.0, 128.3, 129.1, 130.7, 131.4, 131.5 (d, $^3J_{C,F}$ = 9.85 Hz), 133.5, 135.0 (d, $^4J_{C,F}$ = 3.37 Hz), 137.3, 166.1 (d, $^1J_{C,F}$ = 257.83 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M-Cl]$^+$ Calcd for $C_{14}H_{11}BrFO_2S$ 340.9642; Found 340.9640.

2-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-1,3,5-trimethylbenzene (10o). GP B was applied (239 mg = 70%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.21 (s, 3H), 2.27 (s, 3H), 2.44 (s, 3H), 3.98-4.11 (m, 2H), 5.88 (t, $^3J_{H,H}$ = 7.01 Hz, 1H), 6.61 (s, 1H), 6.81 (s, 1H), 6.98-7.11 (m, 2H), 7.60-7.72 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.18. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 20.60, 20.64, 20.9, 50.8, 62.4, 116.3 (d, $^2J_{C,F}$ = 22.85 Hz), 129.5, 131.0 (d, $^3J_{C,F}$ = 9.90 Hz), 131.1, 131.6, 134.8 (d, $^4J_{C,F}$ = 3.25 Hz), 136.7, 137.4, 139.2, 165.9 (d, $^1J_{C,F}$ = 256.95 Hz). HRMS (ESI/QTOF) *m/z*: [M-Cl]$^+$ Calcd for $C_{17}H_{18}FO_2S$ 305.1012; Found 305.1014.

2-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)pyridine (10p). GP B was applied (114 mg = 38%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.98 (dd, $^2J_{H,H}$ = 14.69 Hz, $^3J_{H,H}$ = 5.80 Hz, 1H), 4.46 (dd, $^2J_{H,H}$ = 14.67 Hz, $^3J_{H,H}$ = 7.62 Hz, 1H), 5.41 (dd, $^3J_{H,H}$ = 7.58 Hz, 5.82 Hz, 1H), 7.06-7.14 (m, 2H), 7.19 (ddd, $^3J_{H,H}$ = 7.50 Hz, 4.86 Hz, $^4J_{H,H}$ = 0.72 Hz, 1H), 7.36 (d, $^3J_{H,H}$ = 7.80 Hz, 1H), 7.67 (td, $^3J_{H,H}$ = 7.70 Hz, $^4J_{H,H}$ = 1.76 Hz, 1H), 7.73-7.79 (m, 2H), 8.40 (d, $^3J_{H,H}$ = 4.12 Hz, 1H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.16. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 54.8, 61.7, 116.5 (d, $^2J_{C,F}$ = 22.72 Hz), 123.2, 123.9, 131.2 (d, $^3J_{C,F}$ = 9.65 Hz), 135.5 (d, $^4J_{C,F}$ = 3.08 Hz), 137.3, 149.8, 156.0, 165.9 (d, $^1J_{C,F}$ = 256.91 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M+H]$^+$ Calcd for $C_{13}H_{12}ClFNO_2S$ 300.0256; Found 300.0254.

2-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)naphthalene (10q). GP B was applied (324 mg = 93%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.98 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 7.64 Hz, 1H), 4.86 (dd, $^2J_{H,H}$ = 14.89 Hz, $^3J_{H,H}$ = 6.52 Hz), 5.51 (t, $^3J_{H,H}$ = 7.06 Hz), 6.84-6.92 (m, 2H), 7.29 (dd, $^3J_{H,H}$ = 8.56 Hz, $^4J_{H,H}$ = 1.84 Hz), 7.48-7.55 (m, 2H), 7.59-7.66 (m, 2H), 7.67-7.73 (m, 2H), 7.74-7.81 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.09. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.6, 64.2, 116.3 (d, $^2J_{C,F}$ = 22.77 Hz), 123.9, 127.0, 127.1, 127.3, 127.8, 128.2, 128.3, 131.1 (d, $^3J_{C,F}$ = 9.64 Hz), 132.9, 133.5, 135.1 (d, $^4J_{C,F}$ = 3.10 Hz), 165.7 (d, $^1J_{C,F}$ = 256.99 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M]$^+$ Calcd for $C_{18}H_{14}ClFO_2S$ 348.0382; Found 348.0381.

1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)naphthalene (10r). GP B was applied (258 mg = 74%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.99-4.24 (m, 2H), 6.14 (br. s, 1H), 1.91-7.04 (m, 2H), 7.35 (t, $^3J_{H,H}$ = 7.74 Hz, 1H), 7.48-7.56 (m, 2H), 7.60 (t, $^3J_{H,H}$ = 7.54 Hz, 1H), 7.63-7.72 (m, 2H), 7.78 (d, $^3J_{H,H}$ = 8.20 Hz, 1H), 7.84 (d, $^3J_{H,H}$ = 8.04 Hz, 1H), 8.10 (d, $^3J_{H,H}$ = 8.52 Hz, 1H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.07. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 52.2 (br. s, FWHM = 94.59 Hz), 63.7, 116.3 (d, $^2J_{C,F}$ = 22.75 Hz), 122.5 (br. s, FWHM = 11.83 Hz), 125.2, 125.9 (br. s, FWHM = 31.52 Hz), 126.4, 127.3, 129.3, 129.8, 130.2, 131.0 (d, $^3J_{C,F}$ = 9.65 Hz), 133.5 (br. s, FWHM = 16.14 Hz), 134.0, 134.9 (br. s, FWHM = 9.72 Hz), 165.8 (d, $^1J_{C,F}$ = 256.89 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: [M]$^+$ Calcd for $C_{18}H_{14}ClFO_2S$ 348.0382; Found 348.0387.

1-((2-Chloro-2-phenylpropyl)sulfonyl)-4-fluorobenzene (10s). GP B was applied (228 mg = 73%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.38 (s, 3H), 4.01 (d, $^2J_{H,H}$ = 14.84 Hz, 1H), 4.18 (d, $^2J_{H,H}$ = 14.85 Hz, 1H), 6.93-7.03 (m, 2H), 7.17-7.24 (m, 3H), 7.33-7.40 (m, 2H), 7.46-7.53 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.73. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 29.9, 67.5, 70.0, 116.4 (d, $^2J_{C,F}$ = 22.46 Hz), 126.7, 128.4, 128.7, 130.8 (d, $^3J_{C,F}$ = 9.91 Hz), 136.1 (d, $^4J_{C,F}$ = 3.24 Hz), 141.0, 165.6 (d, $^1J_{C,F}$ = 256.19 Hz).

HRMS (APCI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{14}ClFNaO_2S$ 335.0279; Found 335.0274.

1-((1-Chloro-1-phenylpropan-2-yl)sulfonyl)-4-fluorobenzene (10t). GP B was applied (238 mg = 76%, d.r. 1:1, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.45 (s, 3H), 1.47 (s, 3H), 3.45-3.54 (m, 2H), 5.68 (s, 1H), 5.69 (s, 1H), 7.13-7.23 (m, 4H), 7.27-7.37 (m, 10H), 7.82-7.91 (m, 4H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.08. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 9.5, 60.0, 67.3, 116.5 (d, $^2J_{C,F}$ = 22.89 Hz), 127.3, 128.9, 128.9, 132.4 (d, $^3J_{C,F}$ = 9.86 Hz), 133.7 (d, $^4J_{C,F}$ = 3.19 Hz), 138.5, 166.9 (d, $^1J_{C,F}$ = 256.87). HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{14}ClFNaO_2S$ 335.0279; Found 335.0279.

1-Chloro-2-((4-fluorophenyl)sulfonyl)-1,2,3,4-tetrahydronaphthalene (10u). GP B was applied (296 mg = 91%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.17-2.30 (m, 1H), 2.54-2.66 (m, 1H), 2.83-2.96 (m, 1H), 2.96-3.08 (m, 1H), 3.81-3.90 (m, 1H), 5.57 (d, $^3J_{H,H}$ = 3.76 Hz, 1H), 7.01-7.13 (m, 1H), 7.17-7.28 (m, 4H), 7.30-7.40 (m, 1H), 7.84-7.97 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.54. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 20.1, 25.7, 54.1, 67.9, 116.8 (d, $^2J_{C,F}$ = 22.62 Hz), 127.1, 128.9, 129.1, 130.2, 131.8 (d, $^3J_{C,F}$ = 9.90 Hz), 133.5, 134.2 (d, $^4J_{C,F}$ = 3.29 Hz), 135.9, 166.2 (d, $^1J_{C,F}$ = 257.52 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{16}H_{14}FO_2S$ 289.0693; Found 289.0696.

Methyl 2-chloro-3-((4-fluorophenyl)sulfonyl)-2-methylpropanoate (10v). GP B was applied (200 mg = 68%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.03 (s, 3H), 3.77 (d, $^2J_{H,H}$ = 14.17 Hz, 1H), 3.84 (s, 3H), 4.12 (d, $^2J_{H,H}$ = 14.17 Hz, 1H), 7.19-7.31 (m, 2H), 7.88-7.99 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.44. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 27.0, 53.9, 62.4, 65.8, 116.9 (d, $^2J_{C,F}$ = 22.72 Hz). 131.2 (d, $^3J_{C,F}$ = 9.80 Hz), 136.5 (d, $^4J_{C,F}$ = 3.11 Hz), 166.2 (d, $^1J_{C,F}$ = 257.52 Hz), 169.3. HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{12}ClFNaO_4S$ 317.0021; Found 317.0023.

1-((2-Chlorodecyl)sulfonyl)-4-fluorobenzene (10w). GP B was applied (20 mg = 6%, pale yellow oil). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.88 (t, $^3J_{H,H}$ = 6.64 Hz, 3H), 1.27 (br. s., 10H), 1.36-1.56 (m, 2H), 1.70-1.84 (m, 1H), 1.87-2.00 (m, 1H), 3.47 (dd, $^2J_{H,H}$ = 14.75 Hz, $^3J_{H,H}$ = 5.74 Hz, 1H), 3.57 (dd, $^2J_{H,H}$ = 14.73 Hz, $^3J_{H,H}$ = 6.72 Hz, 1H), 4.27-4.36 (m, 1H), 7.22-7.30 (m, 2H), 7.91-7.99 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.71. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 14.2, 22.8, 25.9, 28.9, 29.3, 29.5, 31.9, 38.2, 54.6, 63.9, 116.8 (d, $^2J_{C,F}$ = 22.75 Hz), 131.3 (d, $^3J_{C,F}$ = 9.85 Hz), 135.7 (d, $^4J_{C,F}$ = 3.77 Hz), 166.2 (d, $^1J_{C,F}$ = 256.66 Hz). HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{24}ClFNaO_2S$ 357.1062; Found 357.1059.

1-((2-Chloro-3-phenylpropyl)sulfonyl)-4-fluorobenzene (10x). GP B was applied (16 mg = 5%, colorless oil). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.13 (dd, $^2J_{H,H}$ = 14.27 Hz, $^3J_{H,H}$ = 7.38 Hz, 1H), 3.24 (dd, $^2J_{H,H}$ = 14.25 Hz, $^3J_{H,H}$ = 6.04 Hz, 1H), 3.51 (d, $^3J_{H,H}$ = 1.68 Hz, 1H), 3.52 (s, 1H), 4.51 (quin., $^3J_{H,H}$ = 6.44 Hz, 1H), 7.18-7.36 (m, 8H), 7.87-7.97 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.61. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 44.2, 54.4, 62.6, 116.9 (d, $^2J_{C,F}$ = 22.72 Hz), 127.6, 128.9, 129.7, 131.3 (d, $^3J_{C,F}$ = 9.55 Hz), 135.6 (d, $^4J_{C,F}$ = 3.37 Hz), 135.8, 166.2 (d, $^1J_{C,F}$ = 257.06 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{15}ClFO_2S$ 313.0460; Found 313.0453.

1-((2-Chloro-2-methylpentyl)sulfonyl)-4-fluorobenzene (10y). GP B was applied (14 mg = 5%, colorless oil). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.97 (t, $^3J_{H,H}$ = 7.32 Hz, 3H), 1.48-1.62 (m, 2H), 1.88 (s, 3H), 1.95-2.11 (m, 2H), 3.57 (d, $^2J_{H,H}$ = 14.29 Hz, 1H), 3.64 (d, $^2J_{H,H}$ = 14.29 Hz, 1H), 7.21-7.30 (m, 2H), 7.90-7.99 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -102.96. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 14.0, 18.3, 30.7, 45.7, 67.2, 69.7, 116.8 (d, $^2J_{C,F}$ = 22.70 Hz), 131.0 (d, $^3J_{C,F}$ = 9.62 Hz), 137.0 (d, $^4J_{C,F}$ = 3.34 Hz), 166.1 (d, $^1J_{C,F}$ = 257.04 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M-Cl]^+$ Calcd for $C_{12}H_{16}FO_2S$ 243.0850; Found 243.0854.

(8*R*,9*S*,13*S*,14*S*)-3-(1-Chloro-2-((4-fluorophenyl)sulfonyl)ethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (10z). GP B was applied (314 mg = 66%, white solid). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.90-0.95 (m, 3H), 1.25 (s, 1H), 1.33-1.45 (m, 1H), 1.47-1.54 (m, 3H), 1.60-1.71 (m, 1H), 1.93-2.10 (m, 3H), 2.14 (dd, $^2J_{H,H}$ = 18.73 Hz, $^3J_{H,H}$ = 8.92 Hz, 1H), 2.19-2.29 (m, 1H), 2.33-2.43 (m, 1H), 2.52 (dd, $^2J_{H,H}$ = 18.87 Hz, $^3J_{H,H}$ = 8.70 Hz, 1H), 2.63-2.78 (m, 1H), 2.78-2.87 (m, 1H), 3.89 (dd, $^2J_{H,H}$ = 14.87 Hz, $^3J_{H,H}$ = 7.74 Hz, 1H), 3.96 (dd, $^2J_{H,H}$ = 14.85 Hz, $^3J_{H,H}$ = 6.44 Hz, 1H), 5.27 (t, $^3J_{H,H}$ = 7.06 Hz, 1H), 6.87 (s, 1H), 7.00-7.09 (m, 3H), 7.13-7.21 (m, 1H), 7.63-7.72 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.29. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 13.9, 21.7, 25.9, 26.4, 29.4, 31.7, 35.9, 38.1, 44.5, 48.0, 50.6, 55.1, 64.0, 116.3 (d, $^2J_{C,F}$ = 22.56 Hz), 124.9, 126.1, 127.7, 131.2 (d, $^3J_{C,F}$ = 9.55 Hz), 135.3 (d, $^4J_{C,F}$ = 3.37 Hz), 135.5, 137.4, 141.4, 165.1 (d, $^1J_{C,F}$ = 257.16 Hz). HRMS (ESI/QTOF) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{28}ClFNaO_3S$ 497.1324; Found 497.1322. Elemental analysis: Anal. Calcd for $C_{26}H_{28}ClFO_3S$: C, 65.74; H, 5.94; N, 0.00. Found: C, 65.97; H, 6.23; N, 0.00.

(*E*)-1-((2-Chloro-2-phenylvinyl)sulfonyl)-4-fluorobenzene (12a). GP B was applied (119 mg = 40%, off-white solid). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.97 (s, 1H), 7.05-7.16 (m, 2H), 7.30-7.41 (m, 4H), 7.41-7.49 (m, 1H), 7.56-7.64 (m, 2H). $^{19}F\{^1H\}$ NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -104.33. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.7 (d, $^2J_{C,F}$ = 22.82 Hz), 128.5, 129.1, 131.0 (d, $^3J_{C,F}$ = 9.78 Hz), 131.2, 131.4, 134.8, 137.0 (d, $^4J_{C,F}$ = 3.11 Hz), 148.9, 166.1 (d, $^1J_{C,F}$ = 255.87 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{12}FO_2S$ 263.0537; Found 263.0537.

(*E*)-4-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl) benzaldehyde (12b). GP B was applied (65 mg = 20%, white solid). ^1H NMR (400 MHz, CD_2Cl_2, ppm): δ = 7.01 (s, 3H), 7.10-7.20 (m, 2H), 7.50-7.60 (m, 2H), 7.61-7.74 (m, 2H), 7.85-8.00 (m, 2H), 10.07 (s, 1H). $^{19}F\{^1H\}$ NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.56. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 117.0 (d, $^2J_{C,F}$ = 22.96 Hz), 129.5, 129.8, 131.1 (d, $^3J_{C,F}$ = 9.77 Hz), 132.2, 136.8 (d, $^4J_{C,F}$ = 3.08 Hz), 138.0, 140.2, 147.0, 166.3

(d, $^1J_{C,F}$ = 256.6 Hz), 191.6. HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{11}ClFO_3S$ 325.0096; Found 325.0096.

Methyl (*E*)-4-(1-chloro-2-((4-fluorophenyl)sulfonyl)vinyl) benzoate (12c). GP B was applied (117 mg = 33%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 3.93 (s, 3H), 7.00 (s, 1H), 7.07-7.20 (m, 2H), 7.38-7.50 (m, 2H), 7.59-7.70 (m, 2H)-7.98-8.09 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.76. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 52.7, 116.9 (d, $^2J_{C,F}$ = 22.87 Hz), 129.2, 129.6, 131.1 (d, $^3J_{C,F}$ = 9.83 Hz), 132.1, 132.6, 136.8 (d, $^4J_{C,F}$ = 3.31 Hz), 138.9, 147.4, 166.3 (d, $^1J_{C,F}$ = 255.95 Hz), 166.3. HRMS (ESI/QTOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{13}ClFO_4S$ 355.0202; Found 355.0199.

(*E*)-4-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-1,1'-biphenyl (12d). GP B was applied (116 mg = 31%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.99 (s, 1H), 7.05-7.14 (m, 2H), 7.38-7.52 (m, 5H), 7.58-7.69 (m, 6H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -104.23. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.7 (d, $^2J_{C,F}$ = 22.96 Hz), 127.1, 127.6, 128.6, 129.4, 129.8, 131.1 (d, $^3J_{C,F}$ = 9.76 Hz), 131.4, 133.6, 137.0 (d, $^4J_{C,F}$ = 3.59 Hz), 140.2, 144.1, 148.6, 166.1 (d, $^1J_{C,F}$ = 255.66 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M]^+$ Calcd for $C_{20}H_{14}ClFO_2S$ 372.0382; Found 372.0390. CCDC 1889527 contains the supplementary crystallographic data for **12d**. This data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-4-methoxybenzene (12e). GP B was applied (167 mg = 51%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.85 (s, 3H), 6.79-6.87 (m, 2H), 6.88 (s, 1H), 7.02-7.14 (m, 2H), 7.32-7.43 (m, 2H), 7.60-7.70 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, $CDCl_3$, ppm): δ = -103.52 ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 55.6, 113.6, 116.4 (d, $^2J_{C,F}$ = 22.70 Hz), 126.4, 129.6, 130.7 (d, $^3J_{C,F}$ = 9.51 Hz), 131.1, 136.8 (d, $^4J_{C,F}$ = 3.13 Hz), 149.0, 161.9, 165.7 (d, $^1J_{C,F}$ = 256.21 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}ClFO_3S$ 327.0252; Found 327.0255.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-4-fluorobenzene (12f). GP B was applied (135 mg = 43%, off-white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.97 (s, 1H), 7.03-7.19 (m, 4H), 7.34-7.45 (m, 2H), 7.58-7.69 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.95, -108.98. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 115.7 (d, $^2J_{C,F}$ = 22.27 Hz), 116.8 (d, $^2J_{C,F}$ = 23.02 Hz), 130.8 (d, $^4J_{C,F}$ = 3.61 Hz), 131.0 (d, $^3J_{C,F}$ = 9.68 Hz), 131.6 (d, $^3J_{C,F}$ = 8.56 Hz), 136.9 (d, $^4J_{C,F}$ = 3.11 Hz), 147.7, 164.4 (d, $^1J_{C,F}$ = 251.65 Hz), 166.2 (d, $^1J_{C,F}$ = 255.95 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{10}ClF_2O_2S$ 315.0053; Found 315.0053.

(*E*)-1-Chloro-4-(1-chloro-2-((4-fluorophenyl)sulfonyl)vinyl) benzene (12g). GP B was applied (169 mg = 51%, yellow solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.96 (s, 1H), 7.08-7.20 (m, 2H), 7.24-7.46 (m, 4H), 7.56-7.72 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.83. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.8 (d, $^2J_{C,F}$ = 22.83 Hz), 128.8, 130.7, 131.1 (d, $^3J_{C,F}$ = 9.79 Hz), 131.8, 133.2, 136.8 (d, $^4J_{C,F}$ = 2.77 Hz), 137.4, 147.4, 166.2 (d, $^1J_{C,F}$ = 256.33 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{10}Cl_2FO_2S$ 330.9757; Found 330.9762.

(*E*)-1-Bromo-4-(1-chloro-2-((4-fluorophenyl)sulfonyl)vinyl) benzene (12h). GP B was applied (210 mg = 56%, yellow solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.96 (s, 1H), 7.12-7.19 (m, 2H), 7.2-7.30 (m, 2H), 7.52-7.58 (m, 2H), 7.62-7.69 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.81. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.9 (d, $^2J_{C,F}$ = 23.02 Hz), 125.7, 129.1, 130.8, 131.1 (d, $^3J_{C,F}$ = 9.79 Hz), 131.8 (d, $^4J_{C,F}$ = 3.62 Hz), 132.5, 133.7, 147.4, 166.2 (d, $^1J_{C,F}$ = 256.49 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{10}BrClFO_2S$ 374.9252; Found 374.9262.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-3-methylbenzene (12i). GP B was applied (131 mg = 42%, yellow solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 2.33 (s, 3H), 6.95 (s, 1H), 7.03-7.12 (m, 3H), 7.12-7.17 (m, 1H), 7.22-7.29 (m, 2H), 7.52-7.63 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -104.57. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 21.4, 116.6 (d, $^2J_{C,F}$ = 22.79 Hz), 126.3, 128.4, 129.4, 131.1 (d, $^3J_{C,F}$ = 9.85 Hz), 131.4, 131.9, 134.7, 137.0 (d, $^4J_{C,F}$ = 3.08 Hz), 138.6, 149.2, 166.1 (d, $^1J_{C,F}$ = 255.54 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}ClFO_2S$ 311.0303; Found 311.0307.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-3-fluorobenzene (12j). GP B was applied (126 mg = 40%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.98 (s, 1H), 7.02-7.09 (m, 1H), 7.09-7.22 (m, 4H), 7.31-7.43 (m, 1H), 7.61-7.70 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.86, -112.75. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.2 (d, $^2J_{C,F}$ = 23.68 Hz), 116.8 (d, $^2J_{C,F}$ = 22.84 Hz), 118.1 (d, $^2J_{C,F}$ = 21.07 Hz), 125.2 (d, $^4J_{C,F}$ = 3.24 Hz), 130.4 (d, $^3J_{C,F}$ = 8.24 Hz), 131.1 (d, $^3J_{C,F}$ = 9.80 Hz), 132.1, 136.5 (d, $^3J_{C,F}$ = 8.35 Hz), 136.8 (d, $^4J_{C,F}$ = 3.11 Hz), 146.8, 162.4 (d, $^1J_{C,F}$ = 247.69 Hz), 166.2 (d, $^1J_{C,F}$ = 256.13 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{10}ClF_2O_2S$ 315.0053; Found 315.0058.

(*E*)-1-Chloro-3-(1-chloro-2-((4-fluorophenyl)sulfonyl)vinyl) benzene (12k). GP B was applied (109 mg = 33%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.99 (s, 1H), 7.11-7.19 (m, 2H), 7.25-7.30 (m, 2H), 7.32-7.39 (m, 1H), 7.41-7.48 (m, 1H), 7.60-7.68 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.82. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 116.9 (d, $^2J_{C,F}$ = 23.03 Hz), 127.5, 128.9, 130.0, 131.12 (d, $^3J_{C,F}$ = 9.84 Hz), 131.13, 132.3, 134.4, 136.3, 136.7 (d, $^4J_{C,F}$ = 3.08 Hz), 146.8, 166.3 (d, $^1J_{C,F}$ = 256.56 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{10}Cl_2FO_2S$ 330.9757; Found 330.9758.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-2-methylbenzene (12l). GP B was applied (140 mg = 45%, white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 2.08 (s, 3H), 7.04 (s, 1H), 7.06-7.12 (m, 3H), 7.14-7.23 (m, 2H), 7.31-7.38 (m, 1H), 7.45-7.53 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -104.26. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 19.2, 116.6 (d, $^2J_{C,F}$ = 22.78 Hz), 125.6, 129.0, 130.7, 130.8, 131.2 (d, $^3J_{C,F}$ = 9.83 Hz), 132.9, 134.2, 136.4, 136.7 (d, $^4J_{C,F}$ = 3.69 Hz), 149.3, 166.2 (d, $^1J_{C,F}$ = 255.96 Hz). HRMS

(APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}ClFO_2S$ 311.0303; Found 311.0310.

(*E*)-1-(1-Chloro-2-((4-fluorophenyl)sulfonyl)vinyl)-3,5-difluorobenzene (12m). GP B was applied (110 mg = 33%, off-white solid). ^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ = 6.90-6.97 (m, 3H), 6.97-7.02 (m, 1H), 7.15-7.23 (m, 2H), 7.67-7.75 (m, 2H). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2, ppm): δ = -103.40, -108.92. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ = 106.5 (t, $^2J_{C,F}$ = 25.18 Hz), 112.5 (d, $^2J_{C,F}$ = 27.28 Hz), 117.0 (d, $^2J_{C,F}$ = 23.00 Hz), 131.1 (d, $^3J_{C,F}$ = 9.82 Hz), 132.7, 136.6 (d, $^4J_{C,F}$ = 3.36 Hz), 137.4 (t, $^3J_{C,F}$ = 10.15 Hz), 146.2, 162.7 (d, $^1J_{C,F}$ = 250.20 Hz), 162.8 (d, $^1J_{C,F}$ = 250.42 Hz), 166.4 (d, $^1J_{C,F}$ = 256.56 Hz). HRMS (APPI/LTQ-Orbitrap) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_9ClF_3O_2S$ 332.9958; Found 332.9962.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information (experimental procedure for photoredox catalysis and characterization data (X-ray and NMR) of synthesized compounds as PDF) is available free of charge on the ACS Publications website.

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Notes

The authors declare no conflict of interest.

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