Table of Contents

Experimental Procedures ........................................................................................................... 3
General synthesis procedures ..................................................................................................... 3
General analytical procedures .................................................................................................... 3
Effect of metals on photospliccing .............................................................................................. 4
Procedures for radical studies .................................................................................................. 5
Presence of radical quencher during the irradiation of sulfonamide 1a ..................................... 5
Presence of radical starters with sulfonamide 1a ....................................................................... 5
Excess of toluene during the photosplicling of sulfonamide 2s ................................................ 6
Cross experiment ....................................................................................................................... 6
Compound 1ak ............................................................................................................................ 6
Compound 2ak ............................................................................................................................ 6
Modification of the linker .......................................................................................................... 8
Compound 1al .............................................................................................................................. 8
Compound 2a (=2al) .................................................................................................................. 8
Compound 1am .......................................................................................................................... 8
Compound 2a (=2am) ................................................................................................................ 8
Compound 1an .......................................................................................................................... 9
Compound 2a (=2an) ................................................................................................................ 9
Chemical synthesis procedures for SAR studies ....................................................................... 10
Compound 1d ............................................................................................................................ 10
Compound 2d ............................................................................................................................ 10
Compound 1e ............................................................................................................................ 10
Compound 2e ............................................................................................................................ 11
Compound 1f ............................................................................................................................ 11
Compound 2f ............................................................................................................................ 11
Compound 1g ............................................................................................................................ 11
Compound 2g ............................................................................................................................ 12
Compound 1h ............................................................................................................................ 12
Compound 2h ............................................................................................................................ 12
Compound 1j ............................................................................................................................ 13
Compound 2j ............................................................................................................................ 13
Compound 2k ............................................................................................................................ 13
Compound 1l ............................................................................................................................ 14
Compound 2l ............................................................................................................................ 14
Compound 1ao ......................................................................................................................... 14
Compound 1m ............................................................................................................................ 14
Compound 2m ............................................................................................................................ 15
Compound 1n ............................................................................................................................ 15
Compound 2n ............................................................................................................................ 15
Compound 1o ............................................................................................................................ 16
Compound 2o ............................................................................................................................ 16
Compound 2p ............................................................................................................................ 16
Compound 1r ............................................................................................................................ 16
Compound 2r ............................................................................................................................ 17
Compound 1v ............................................................................................................................ 17
Compound 2v ............................................................................................................................ 17
Compound 1w ............................................................................................................................ 18
Compound 2w ............................................................................................................................ 18
General synthesis procedures

All reagents were obtained from commercial suppliers (Sigma Aldrich, TCI, Alfa Aesar, etc.) and used without further purification unless otherwise explained. Reactions were carried out under inert gas (argon) by using the Schlenk technique in dried solvents. Dichloromethane (DCM), acetonitrile (MeCN), methanol (MeOH) and chloroform were used from a solvent purification system ( Innovative Technologies). Open column chromatographic separations were executed on silica gel (Kieselgel 60, 15-40 µm, Merck KGaA). Reaction progresses were monitored by thin layer chromatography (TLC) (silica gel on aluminium sheets 20 × 20 cm with fluorescent indicator 254 nm, Merck KgaA). GC-MS or HPLC-(HR)MS. Photoreactions were performed on a self-made photo reactor made from a milled aluminum block (16.9 × 31.9 × 0.03 cm, reaction volume ~15 mL) covered with a quartz glass slide. A SIMDOS 02 dosing pump from KNF was attached to the photo reactor. Flow rates (0.5-10 mL/min) were selected in the course of reaction optimization.

General analytical procedures

All 1D (1H, 13C, 19F, DEPT) and 2D NMR (1H-1H COSY, HSQC, NOESY, HMBC) have been recorded in deuterated solvents on a Bruker AVANCE II 300, AVANCE III 500 or 600 MHz instrument equipped with Bruker Cryo Platform. The chemical shifts are reported in ppm relative to the solvent residual signal (1H: δ (CHCl3) = 7.26 ppm, δ (CD2Cl2) = 5.32 ppm, δ (MeOH) = 3.31 ppm, δ (DMSO) = 2.50 ppm, δ (MeCN) = 1.94 ppm. 13C: δ (CDCl3) = 77.16 ppm, δ (CD2Cl2) = 52.84 ppm, δ (MeOD) = 49.00 ppm, δ (DMSO-d6) = 39.52 ppm, δ (CD3CN) = 1.32 ppm or 118.26 ppm. 19F: δ (PhCF3) = -62.61 ppm as an external standard). Following abbreviations are used for multiplicities of resonance signals: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, br = broad.

Experimental Procedures

Surveyor HPLC system (Thermo Fisher Scientific, Bremen). HPLC conditions using Exactive: C18 column (Thermo Fisher Accucore C18, 2.6 µm, 100 × 2.1 mm) and gradient elution (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH)) starting with 5:95 for 1 min, going up to 99:1 in 16 min, then 99:1 for 15 min; flow rate 0.2 mL/min; injection volume: 3 µL). HPLC conditions using Q Exactive: C18 column (Thermo Fisher Accucore C18, 2.6 µm, 100 × 2.1 mm) and gradient elution (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH)) starting with 5:95, going up to 98:2 in 10 min, then 98:2 for 12 min; flow rate 0.2 mL/min; injection volume: 3 µL). HPLC conditions using Q Exactive-HF-X: C18 column (Phenomenex Kinetex C18, 1.7 µm, 50 × 2.1 mm) and gradient elution (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH)) starting with 5:95, going to 100:0 in 4.5 min, then 100:0 for 2 min; flow rate 0.7 mL/min; injection volume: 2 µL). HPLC conditions using LTO: C18 column (Phenomenex Kinetex XB-C18, 2.6 µm, 100 × 3 mm) and gradient elution (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH)) 10:90 for 1 min, going up to 100:0 in 8 min, then 100:0 for 4 min; flow rate 0.6 mL/min; injection volume: 5 µL) or (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH) 48:52 for 11 min; flow rate 0.6 mL/min; injection volume: 5 µL). HPLC conditions for regioisomer separation using Q Exactive: C18 column (Thermo Fisher Accucore C18, 2.6 µm, 100 × 2.1 mm) and isotropic elution (MeCN (0.1 % (v/v) HCOOH)/H2O (0.1 % (v/v) HCOOH)) with 50:50 for 20 min, then 100:0 for 10 min; flow rate 0.2 mL/min; injection volume: 3 µL). UV-vis spectra were recorded with a UV-1800 UV-vis-spectrometer from Shimadzu using fused quartz glass cuvettes with 1 cm path length. The samples were measured at 20 °C in MeCN. The emission spectrum of the light source was recorded with a specbos 1211 UV broadband radiometer from JETI Technische Instrumente GmbH. The spectral range is from 230 nm to 1000 nm, the optical bandwidth is 4.5 nm and the wavelength resolution is 1 nm.
Effect of metals on photosplicing

Methyl 4-(((4-methylphenyl)sulfonamido)methyl)benzoate (1a) (500.2 mg, 1.57 mmol) was dissolved in MeOH (250.6 mL). 10 mL of this solution were transferred into 18 tubes with ~5 mol% of different metal salts (see Table S1), mixed gently and stored at room temperature for 24 h. In some cases, the metal salts were not completely soluble. These samples were centrifuged to remove the solid. All samples were measured by HPLC-MS. All samples were loaded on the photo reactor (reduced light intensity (only 2 Philips TUV 15 W tubes), 5 mL/min) and irradiated until 75 mL of the solution were collected. 2 µL of each 18 solutions were mixed with MeOH (98 µL) and were measured by HPLC as triplicates. The results are shown in Figure S1.

Table S1: Used additives with molar mass, amount in mg, mol% and solubility.

| Number | Substance        | Amount   | Mol% | Solubility          |
|--------|------------------|----------|------|---------------------|
| 1      | No additive      | -        | -    | -                   |
| 2      | RuCl₂(PPh₃)₃    | 3.036 mg | 5.1  | Not completely soluble |
| 3      | RuCl₃           | 0.637 mg | 4.9  | Good                |
| 4      | RhCl(PPh₃)₃     | 2.926 mg | 5.1  | Not completely soluble |
| 5      | Rh₂(OAc)₄       | 0.791 mg | 5.7  | Good                |
| 6      | Cu(OAc)₂·H₂O    | 0.668 mg | 5.3  | Good                |
| 7      | CuOAc           | 0.461 mg | 6.0  | Not completely soluble |
| 8      | Co(OAc)₂        | 0.567 mg | 5.1  | Good                |
| 9      | NiCl₂·6H₂O      | 0.514 mg | 3.5  | Good                |
| 10     | Fe(acac)₂       | 0.796 mg | 5.0  | Good                |
| 11     | FeCl₃·6H₂O      | 0.865 mg | 5.1  | Good                |
| 12     | Pd(PPh₃)₄      | 3.289 mg | 4.5  | Not completely soluble |
| 13     | Pd(OAc)₂       | 0.755 mg | 5.4  | Not completely soluble |
| 14     | PtCl₂          | 0.870 mg | 5.2  | Not completely soluble |
| 15     | IrClCOD        | 1.138 mg | 5.4  | Not completely soluble |
| 16     | K₂OsO₄         | 1.132 mg | 4.9  | Not completely soluble |

Figure S1. Ratio of sulfonamide 1a and biphenyl 2a after the photoreaction with different additives.
Procedures for radical studies

Presence of radical quencher during the irradiation of sulfonamide 1a

Sulfonamide 1a (20.6 mg, 64.6 μmol, 1 eq.) and 2,6-di-tert-butyl-4-methylphenol (BHT, 14.3 mg, 64.9 μmol, 1 eq.) were dissolved in MeOH (4 mL). Sulfonamide 1a (20.0 mg, 62.7 μmol, 1 eq.) and BHT (139.5 mg, 633.1 μmol, 10.1 eq.) were dissolved in MeOH (4 mL). BHT (50 mg, 227 μmol) was dissolved in MeOH (10 mL). The prepared solutions were loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The crude products were analyzed by HPLC-HRMS in comparison with 1a and 2a and the results are shown in Figure S2.

![Figure S2](image)

**Figure S2.** PDA traces from the addition of BHT as a radical quencher to sulfonamide 1a with BHT, 1a and 2a for comparison.

Presence of radical starters with sulfonamide 1a

A stock solution of sulfonamide 1a in benzene (3.1 mmol/L) was prepared. To aliquots of the stock solution (1 mL each) were added: a) 2,2’-azobis(2 methylpropionitrile) (AIBN, 0.38 mg, 2.3 μmol, 0.74 eq.) and tributylstannane (TBS, 1.1 mg, 1 μL, 3.8 μmol, 1.2 eq.), b) AIBN (0.38 mg, 2.3 μmol, 0.74 eq.) or c) benzoyl peroxide (DBPO, 0.64 mg, 2.64 μmol, 0.84 eq.). The resulting mixtures were stirred and heated to 70 °C for 25 h. 500 μL of a washing solution (saturated aqueous solution of NH₄F (300 μL), saturated aqueous solution of NaHCO₃ (300 μL) and water (3 mL)) was added to each reaction mixture and stirred vigorously. The organic layer was separated and the solvent was removed under a flow of nitrogen. The residue was analyzed by HPLC-HRMS in comparison with sulfonamide 1a and biphenyl 2a. The results are shown in Figure S3.

![Figure S3](image)

**Figure S3.** PDA traces from the reaction of radical initiators to sulfonamide 1a in comparison with 1a and irradiated 1a.
Excess of toluene during the photosplicing of sulfonamide 2s

A solution of sulfonamide 2s (18.9 mg, 61.9 µmol) in a mixture of MeCN and toluene (v/v = 1:1) (4 mL) was prepared. The solution was loaded on the photo reactor with a flow rate of 1 mL/min (MeCN/toluene (v/v = 1:1)) and irradiated with UV light at room temperature. The solvent fraction containing the photoproducts was collected and the solvent was removed under reduced pressure. The crude product was analyzed by HPLC-HRMS in comparison with 1s, 2s and 2a. The results are shown in Figure S4.

Figure S4. PDA traces from the reaction of 1s in toluene/methanol in comparison with 1s and 2a.

Cross experiment

Compound 1ak. Ethyl 4-(((4-ethylphenyl)sulfonamido)methyl)benzoate. A solution of ethyl 4-((aminomethyl)benzoate (105.4 mg, 0.49 mmol, 1 eq.). N,N-disopropylamine (139 mg, 1.07 mmol, 2.2 eq., 183 µL) and 4-ethylbenzenesulfonyl chloride (100 mg, 0.49 mmol, 1 eq.) was stirred for 1 h at room temperature. The solution was washed with water (2 mL), aqueous hydrochloric acid (1 M, 2 mL) and brine (2 mL). The organic solvent was removed under reduced pressure and purified by column chromatography (silica, Rf=0.5, DCM/ethyl acetate 20:1) to give the title compound (154 mg, 0.44 mmol, 91%) as a white powder.

1H NMR (300 MHz, CDCl3): δ = 1.21-1.30 (t, JHH = 7.6 Hz, 3H, H3C-CH2-C), 1.33-1.42 (t, JHH = 7.1 Hz, 3H, H3C-CH2-O), 2.65-2.77 (q, JHH = 7.6, 2H, H3C-CH2-C), 4.15-4.22 (d, JHH = 6.3 Hz, 2H, N-C=H2), 4.29 - 4.41 (q, JHH = 7.1 Hz, 2H, H3C-CH2-O), 5.02-5.11 (t, JHH = 6.4 Hz, 1H, NH), 7.22-7.33 (m, 4H, CH2-CH2-C-(CH3)2 & N-CH2-C-(CH3)2), 7.71-7.79 (d, JHH = 8.4 Hz, 2H, SO2-C-(CH3)2), 7.88-7.95 (m, 2H, CO2-C-(CH3)2) ppm. 13C NMR (75 MHz, CDCl3): δ = 14.4 (1C, H3C-CH2-O), 15.3 (1C, H3C-CH2-C), 28.9 (1C, H3C-CH2-C), 47.0 (1C, N-CH2), 61.2 (1C, H3C-CH2-O), 127.4 (2C, N-CH2-C-(CH3)2), 127.7 (2C, H3C-CH2-C-(CH3)2), 128.7 (2C, SO2-C-(CH3)2), 130.0 (2C, CO2-C-(CH3)2), 130.1 (1C, C=CO2), 137.1 (1C, C=SO2), 141.5 (1C, N-CH2-C), 149.9 (1C, H3C-CH2-C), 166.3 (1C, C=CO2) ppm. HRMS (ESI+) calcd. for C18H12O3S+: 348.1264; found: 348.1262.

Compound 2ak. Ethyl 4′-ethyl-[1,1′-biphenyl]-4-carboxylate. A solution of ethyl 4-(((4-ethylphenyl)sulfonamido)methyl)benzoate (1ak) (19.9 mg, 57 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 5 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.7, DCM) to yield the title compound (7.8 mg, 31 µmol, 54%).
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 1.23–1.34$ (t, $^3$J$_{HH} = 7.6$ Hz, 3H, H$_3$C-CH$_2$-C), 1.36–1.47 (t, $^3$J$_{HH} = 7.1$ Hz, 3H, H$_3$C-CH$_2$-O), 2.64–2.79 (q, $^3$J$_{HH} = 7.6$ Hz, 2H, H$_3$C-CH$_2$-C), 4.33–4.49 (q, $^3$J$_{HH} = 7.1$ Hz, 2H, H$_3$C-CH$_2$-O), 7.27–7.36 (m, 2H, CO$_2$C-(CH-CH$_2$)-C), 7.52–7.60 (m, 2H, CO$_2$C-(CH-CH$_2$)-C), 7.61–7.70 (m, 2H, CO$_2$C-(CH-CH$_2$)-C), 8.05–8.15 (m, 2H, CO$_2$C-(CH-CH$_2$)-C) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 14.5 (1C, H$_3$C-CH$_2$-O), 15.7 (1C, H$_3$C-CH$_2$-C), 28.7 (1C, H$_3$C-CH$_2$-C), 61.1 (1C, H$_3$C-CH$_2$-O), 126.9 (2C, CO$_2$C-(CH-CH$_2$)-C), 127.3 (2C, H$_3$C-CH$_2$-C-(CH-CH$_2$)-C), 128.6 (2C, H$_3$C-CH$_2$-C-(CH-CH$_2$)-C), 129.1 (1C, H$_3$C-CH$_2$-C-(CH-CH$_2$)-C), 130.2 (2C, CO$_2$C-(CH-CH$_2$)-C), 137.5 (1C, CO$_2$C-(CH-CH$_2$)-C), 144.6 (1C, H$_3$C-CH$_2$-C), 145.6 (1C, CO$_2$C), 166.7 (1C, CO$_2$C) ppm. HRMS (ESI$^+$) calcd. for C$_{17}$H$_{19}$O$_2$: 255.1380; found: 255.1379.

A solution of methyl 4-(((4-methylphenyl)sulfonamido)methyl)benzoate (1a) (10 mg, 31 µmol, 1 eq.) and ethyl 4-(((4-ethylphenyl)sulfonamido)methyl)benzoate (1ak) (10.8 mg, 31 µmol, 1 eq.) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and was analyzed by HPLC-HRMS. No mixed products were detected as shown in Figure S5.

Figure S5. PDA traces from the irradiation of a mixture of 1a and 1ak in comparison with the crude products from the irradiation 1a and 1ak.
Modification of the linker

![Chemical Structure]

**Compound 1al.** Methyl 4-((5,6-dimethylphenyl)sulfonamido)methylbenzoate. A solution of methyl 4-(((5-methylphenyl)sulfonamido)methyl)benzoate (1al) (68.8 mg, 0.22 mmol, 1 eq.) and K₂CO₃ (59.5 mg, 0.43 mmol, 1.5 eq.) was suspended in MeCN (3 mL) and dimethylsulfate (40.8 mg, 30.6 μL, 0.32 mmol, 1.5 eq.) was added. The solution was heated to 80 °C and stirred for 19 h. The solvent was removed under reduced pressure and the residue was dissolved in DCM (2 mL) and was washed with NaHCO₃ solution. The organic phase was dried over Na₂SO₄ and was removed under reduced pressure to yield the title product (72 mg, 0.22 mmol, 99%).

\[ ^1H\, NMR\, (300\, MHz,\, CDCl₃)\, δ = 2.46\, (s, 3H, -C-CH₃), 2.59\, (s, 3H, -N-(CH₃)₃), 3.39\, (s, 3H, -O-CH₃), 4.18\, (s, 2H, -N-(CH₃)₂-H), 7.37\, (t, 3JNMe = 7.8\, Hz, 4H, H₃C-C-(CH)=O & -CH₂-C-(CH)=O), 7.77-7.80\, (m, 2H, -SO₂-C-(CH)=O), 8.04-8.07\, (m, 2H, -C(=O)-O-C-(CH)=O) ppm. \]

\[ ^13C\, NMR\, (75\, MHz,\, CDCl₃)\, δ = 21.7\, (1C, C-CH₃), 34.8\, (1C, -N(CH₃)₂), 52.3\, (1C, -O-CH₃), 54.0\, (1C, -N-(CH₃)₂-H), 127.6\, (2C, -CH₂-C-(CH)=O), 128.3\, (2C, -SO₂-C-(CH)=O), 129.9\, (1C, -C(=O)-O), 130.0\, (2C, H₃C-C-(CH)=O), 130.1\, (2C, -C(=O)-O-C-(CH)=O), 134.3\, (1C, -SO₂-C), 141.1\, (1C, H₃C-C), 143.8\, (1C, -CH₂-C), 166.9\, (1C, -C(=O)-O) ppm. HRMS (ESI⁺) calcd. for C₁₃H₁₃NO₃S⁺: m/z = 334,1108. \]

**Compound 2a (=2al).** Methyl 4'-methyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-(((5,6-dimethylphenyl)sulfonamido)methyl)benzoate (1al) (21.7 mg, 0.65 mmol) in MeCN (3 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduc was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, R₁=0.75. DCM) to yield the title compound (8 mg, 0.35 μmol, 54%).

NMR and HRMS spectra are equivalent to those of biphenyl 2a.³

![Chemical Structure]

**Compound 1am.** Methyl 4-(((5-methylphenyl)sulfonamido)propan-2-yl)benzoate. A solution of 4-methylbenzenesulfonyl chloride (42 mg, 0.22 mmol, 1 eq.), methyl 4-((2-aminopropan-2-yl)benzoate hydrochloride (50 mg, 0.22 mmol, 1 eq.) and N,N-disopropylethylamine (62.6 mg, 82 μL, 0.48 mmol, 2.2 eq.) in DCM (2 mL) was stirred for 3 h at room temperature. The solution was washed with water (2 mL), aqueous hydrochloric acid (1 M, 2 mL) and brine (2 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The residue was purified by open column chromatography (silica, R₁=0.22. DCM) to yield the title compound (36 mg, 0.10 mmol, 47%) as white crystals.

\[ ^1H\, NMR\, (500\, MHz,\, CDCl₃)\, δ = 1.57-1.69\, (s, 6H, (CH₃)₂-C-N), 2.29-2.44\, (s, 3H, CH₃-C), 3.84-3.95\, (s, 3H, CH₃-O-C), 5.30-5.45\, (s, 1H, NH), 7.08-7.16\, (d, 3JNMe = 7.8\, Hz, 2H, CH₃-C-(CH)=O), 7.31-7.38\, (d, 3JNMe = 8.7\, Hz, 2H, C(CH₃)₂-C-(CH)=O), 7.47-7.56\, (d, 3JNMe = 8.2\, Hz, 2H, CO-C-(CH)=O), 7.77-7.85\, (d, 3JNMe = 8.6\, Hz, 2H, CO-C-(CH)=O) ppm. \]

\[ ^13C\, NMR\, (126\, MHz,\, CDCl₃)\, δ = 21.5\, (1C, CH₃-C), 29.9\, (2C, CH₂-C), 52.2\, (1C, CH₃-O), 58.5\, (1C, CH₃-C), 125.8\, (2C, CH₃-C-(CH)=O), 127.0\, (2C, C(CH₃)₂-C-(CH)=O), 128.8\, (1C, C=O), 129.4\, (2C, CO-C-(CH)=O), 129.5\, (2C, CO-C-(CH)=O), 139.6\, (1C, CH₃-C), 143.0\, (1C, C=O), 150.1\, (1C, CH₃-C-C), 166.9\, (1C, C=O) ppm. HRMS (ESI⁺) calcd. for C₁₈H₁₆NO₃S⁺: 348.1264; found: 348.1267. \]

**Compound 2a (=2am).** Methyl 4'-methyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-(((5-methylphenyl)sulfonamido)propan-2-yl)benzoate (1am) (19.8 mg, 0.57 mmol) in MeCN (5 mL) was loaded on the photo reactor with a
flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCM) to yield the title compound (8 mg, 0.35 mol, 62%). NMR and HRMS spectra are equivalent to those of biphenyl 2a.¹

\[
\text{Me} - \text{SO} - \text{NH} - \text{Ph} - \text{C} - \text{O} - \text{Me}
\]

**Compound 1an.** Methyl 4'-{1-[(4-methylphenyl)sulfonamido]cyclopropyl}benzoate. A solution of 4-methylbenzenesulfonyl chloride (30 mg, 0.16 mmol, 1 eq.), methyl-4-(1-aminocyclopropyl)benzoate (30 mg, 0.16 mmol, 1 eq.) and N,N-diisopropylethylamine (24.3 mg, 32.8 µL, 0.19 mmol, 1.2 eq.) in DCM (4 mL) was stirred for 12 h at room temperature and DMAP (20 mg, 0.16 mmol, 1 eq.) was added. After 1 h the solution was washed with water (3 mL),NaHCO₃ solution (3 mL) and aqueous hydrochloric acid (1 m, 3 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The residue was purified by open column chromatography (silica, Rf=0.15, DCM) to yield the title compound (18.3 mg, 0.05 mmol, 34%) as white crystals. 

¹H-NMR (300 MHz, CDCl₃) δ = 1.19 – 1.09 (m, 2H, -CHH-CHH-), 1.45 – 1.35 (m, 2H, -CHH-CHH-), 2.33 (s, 3H, -C-CH₃), 5.60 (s, 1H, -NH), 3.89 (s, 3H, -O-CH₃), 7.19 – 7.04 (m, 4H, H₂C-C(CH₃)₂- & -NH-C-(CH₂)₂-), 7.59–7.48 (m, 2H, -SO₂-C-(CH₃)₂), 7.80–7.72 (m, 2H, -C═O)-C-(CH₂)₂) ppm. ¹³C-NMR (75 MHz, CDCl₃) δ = 17.1 (2C, -NH-(CH₂)₂), 21.5 (1C, -C-CH₃), 37.8 (1C, -NH-C-), 52.2 (1C, -O-CH₃), 126.3 (2C, -NH-C-(CH₂)₂), 127.2 (2C, -SO₂-C-(CH₂)₂), 128.4 (1C, -C═O-), 129.5 (2C, -C═O)-C-(CH₂)₂, 129.6 (2C, H₂C-C-(CH₂)₂), 138.4 (1C, H₂C-C-), 143.5 (1C, -NH-C-), 146.7 (1C, -SO₂-C-), 166.9 (1C, -C═O-O-) ppm. HRMS (ESI⁺) calcd. for C₁₈H₂₄NO₄S⁺: 346.1108; found: 346.1112. HRMS (ESI⁻) calcd. for C₁₈H₁₈NO₄S⁻: 344.0962; found: 344.0965.

\[
\text{Me} - \text{C} - \text{O} - \text{Me}
\]

**Compound 2a (=2an).** Methyl 4'-methyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-(1-[(4-methylphenyl)sulfonamido]cyclopropyl)benzoate (1an) (7.7 mg, 0.022 mmol) in MeCN (5 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCM) to yield the title compound (1.0 mg, 4.4 µmol, 20%). NMR and HRMS spectra are equivalent to those of biphenyl 2a.³
Chemical synthesis procedures for SAR studies

1a, 1b, 1c, 1h, 1q, 1s, 11, 1u, 2a, 2b, 2c, 2h, 2q, 2s, 2t and 2u are known compounds. 3

**Compound 1d.** Methyl 4-(((4-chlorophenyl)sulfonamido)methyl)benzoate. A solution of 4-chlorobenzenesulfonoyl chloride (211.1 mg, 1 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-disopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (20 mL), aqueous hydrochloric acid (1 M, 20 mL) and brine (20 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was obtained as white a solid (335.4 mg, 0.99 mmol, 99%) and was subjected to further purification.

1H NMR (600 MHz; CDCl3): δ = 3.90 (s, 3H, -OCH3), 4.20 (d, 2H, 3JHH = 5.7 Hz, -CH2Z), 5.00 (s, 1H, -NH), 7.27 (d, 2H, 3JHH = 8.2 Hz, -CH2-C-CH3), 7.64 (d, 2H, 3JHH = 8.6 Hz, -C(Cl)-CH3), 7.57 (d, 2H, 3JHH = 8.6 Hz, -CH-C(SO2)-), 7.93 (d, 2H, 3JHH = 8.2 Hz, -CH(C(OOMe)) ppm. 13C NMR (150.9 MHz; CDCl3): δ = 47.0 (1C, -CH2Z), 52.4 (1C, -OCH3), 127.8 (2C, -CH2-C-CH3), 128.7 (2C, -CH-C(SO2)-), 129.6 (2C, -C(Cl)-CH3), 130.0 (1C, -C(COOME)), 130.2 (2C, -CH-C(COOME)-), 138.5 (1C, -C-SO2), 139.6 (1C, -C(Cl)-), 141.2 (1C, -CH2-C), 166.8 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C13H13ClNO4S: 340.0405; found: 340.0408. 

**Compound 2d.** Methyl 4′-chloro-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4-(((4-chlorophenyl)sulfonamido)methyl)benzoate (1d) (21.5 mg, 63.3 µmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.68, DCM) to yield the title compound (13.5 mg, 57.4 µmol, 86%).

1H NMR (300 MHz; CDCl3): δ = 3.94 (s, 3H, -OCH3), 7.42 – 7.45 (m, 2H, -C(Cl)-CH3), 7.53 – 7.56 (m, 2H, -C(Cl)-CH3), 7.60 – 7.64 (m, 2H, -CH-CH(C(OOMe)) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 52.3 (1C, -OCH3), 127.0 (2C, -CH-CH(C(OOMe))), 128.7 (2C, -C(Cl)-CH3), 129.2 (2C, -C(Cl)-CH3), 129.3 (1C, -C(COOME)), 130.3 (2C, -CH(C(COOME))), 134.5 (1C, -C(Cl)-), 138.6 (1C, -C-CH-CH(C(OOMe))), 144.5 (1C, -C-CH-CH(C(COOME))), 167.0 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C13H12ClO2: 247.0520; found: 247.0520.

**Compound 1e.** Methyl 4-(((4-hydroxyphenyl)sulfonamido)methyl)benzoate. A suspension of methyl 4-(((4-benzyloxyphenyl)sulfonamido)methyl)benzoate (1w) (100 mg, 0.243 mmol, 1 eq.) and palladium on carbon (26 mg, 5 mol%, 5% loading) in MeOH (2 mL) was hydrogenated for 1 h. The suspension was filtered off and the solvent was removed under reduced pressure. The crude product (0.235 mg, 0.35 mmol, 97%) was used without further purification.

1H NMR (500 MHz; DMSO-D6): δ = 3.83 (s, 3H, -OCH3), 4.00 (d, 2H, 3JHH = 6.4 Hz, -CH2Z), 6.88 (d, 2H, 3JHH = 8.7 Hz, -C(OH)-CH3), 7.39 (d, 2H, 3JHH = 8.3 Hz, -CH2-C-CH3), 7.62 (d, 2H, 3JHH = 8.7 Hz, -CH-C(SO2)-), 7.87 (d, 2H, 3JHH = 8.3 Hz, -CH-C(COOME)-), 8.02 (d, 2H, 3JHH = 6.4 Hz, -NH), 10.41 (s, 1H, -OH) ppm. 13C NMR (125.8 MHz; DMSO-D6): δ = 45.7 (1C, -CH2Z), 52.1 (1C, -OCH3), 115.5 (2C, -C(OH)-CH3), 127.7 (2C, -CH2-C-CH3), 128.4 (1C, -C(COOME)), 128.9 (2C, -CH-C(SO2)-), 129.1 (2C, -CH-C(COOME)-), 130.5 (1C, -C(SO2)-), 143.7 (1C, -CH2-C), 161.0 (1C, -C(OH)), 166.1 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C13H14NO5S2: 322.0744; found: 322.0737. HRMS (ESI+) calcd. for C13H14NO4S2: 320.0598; found: 320.0598.
Compound 2e. Methyl 4′-hydroxy-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4′-((4-hydroxyphenyl)sulfonamido)methyl)benzoate (1e) (22.5 mg, 70.1 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduc was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, R=0.18 DCM) to yield the title compound (12.1 mg, 53.1 µmol, 76%).

1H NMR (500 MHz; CDCl3): δ = 3.86 (s, 3H, -OCH3), 6.88 (d, 2H, J=8.6 Hz, -C(OH)-CH3), 7.58 (d, 2H, J=8.6 Hz, -CH-C(COOMe)-), 7.89 (d, 2H, J=8.5 Hz, -CH-CH-CH(COOMe)-). 11C NMR (125.8 MHz; CDCl3): δ = 52.0 (1C, -OCH3), 115.9 (2C, -C(OH)-CH3), 126.0 (2C, -CH-CH-C(COOMe)-), 127.3 (1C, -C(COOMe)-), 128.2 (2C, -C(OH)-CH-CH3), 129.4 (1C, -C(OH)-CH-CH-CH-C), 129.7 (2C, -CH-C(COOMe)-), 144.7 (1C, -C-CH-CH-CH(COOMe)-), 158.0 (1C, -C(OH)-), 166.1 (1C, -COOME) ppm. HRMS (ESI) calcd. for C19H14O3S: 227.0714; found: 227.0719.

\[
\text{Me} \quad \text{SO} \quad \text{NH} \quad \text{CN}
\]

Compound 1f. N-(4-Cyanobenzyl)-4-methylbenzenesulfonamide. A solution of 4-methylbenzenesulfonyl chloride (190.6 mg, 1 mmol, 1 eq.) and 4-(aminomethyl)benzonitrile hydrochloride (168.6 mg, 1 mmol, 1 eq.) in 1,4-dioxane (3 mL) was prepared and N,N-disopropylethylamine (284.4 mg, 383.2 µL, 2.2 eq.) was added. The solution was stirred for 24 h at room temperature. The mixture was diluted with aqueous hydrochloric acid (1 M, 30 mL) and ethyl acetate (50 mL). The separated organic phase was washed with brine (30 mL). The organic layer was washed with sodium sulfate, filtered, and the solvent was removed under reduced pressure. This provided the title compound as a white powder (282 mg, 0.98 mmol, 98%).

1H NMR (300 MHz; CDCl3): δ = 2.43 (s, 3H, -CH3), 4.16 (m, 2H, -CH3), 5.38 (s, 1H, -NCH3), 7.26-7.29 (m, 2H, -C(CH3)-CH3), 7.31 - 7.34 (m, 2H, -CH3-C-CH3), 7.51 - 7.54 (m, 2H, -CH-C(CN)-), 7.69 - 7.72 (m, 2H, -CH-CH-CH3) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 21.5 (1C, -CH3), 46.5 (1C, -CH2), 111.5 (1C, -C-CN), 118.5 (1C, -CN), 127.0 (2C, -CH-CH3), 128.3 (2C, -CH-CH2), 129.8 (2C, -CH(CH2)-), 132.3 (2C, -CH-C(CN)), 136.5 (1C, -C(CH3)), 142.0 (1C, -CH2-C), 143.9 (1C, -SO2) ppm. HRMS (ESI) calcd. for C19H17N2O2S*: 287.0849; found: 287.0840. HRMS (ESI) calcd. for C19H17N2O2S: 286.0703; found: 285.0703.

\[
\text{Me} \quad \text{CN}
\]

Compound 2f. 4′-Methyl-[1,1′-biphenyl]-4-carbonitrile. A solution of 4′-(4-cyanobenzyl)-4-methylbenzenesulfonamide (1f) (27.6 mg, 96.4 µmol) in MeOH (30 mL) was loaded on the photo reactor with a flow rate of 1.0 mL/min (MeOH) and irradiated with UV light (254 nm) at 8 °C. The solvent fraction containing the photoproduce was collected and the solvent was removed under reduced pressure. The residue was purified by preparative HPLC to yield the title compound (13.7 mg, 70.9 µmol, 74%).

1H NMR (500 MHz; CDCl3): δ = 2.42 (s, 3H, -CH3), 7.27 – 7.31 (m, 2H, -CH3-C-CH3), 7.47 - 7.51 (m, 2H, -CH-CH-C(CN)), 7.65 - 7.73 (m, 4H, -CH-CH-C(CN)) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.2 (1C, -CH3), 110.5 (1C, -C-CN), 119.0 (1C, -CN), 127.0 (2C, -CH-CH-C(CH3)), 127.4 (2C, -CH-CH-C-CN), 129.8 (2C, -CH-CH3), 132.5 (2C, -CH-C-CN), 136.3 (1C, -CH-CH-C-CH2), 138.7 (1C, -CH3), 145.6 (1C, -CH-CH-C-CN) ppm. HRMS (ESI) calcd. for C19H17N2O2S+: 287.0849; found: 287.0840. HRMS (ESI) calcd. for C19H17N2O2S: 286.0703; found: 285.0703.

\[
\text{Me} \quad \text{O} \quad \text{SO} \quad \text{NH} \quad \text{BnO} \quad \text{O} \quad \text{fBu} \quad \text{Bn}
\]

Compound 1g. tert-Butyl 3,5-bis(benzoyloxy)-4-((2-methylphenyl)sulfonamido)methyl benzoate. A solution of tert-butyl 3,5-bis(benzoyloxy)-4-((o-tolytsulfonyl)-imino)methyl)benzoate (85 mg, 0.15 mmol, 1 eq.) in dried THF was prepared under argon. Freshly prepared lithium methoxide (0.23 mg, 6 µmol, 0.04 eq.) and trimethoxysilane (63.6 mg, 0.52 mmol, 47 µL, 3.5 eq.) were added at 0 °C and the mixture was allowed to warm up to room temperature within 3 hours. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from MeOH/water (v/v = 1:1) to provide the title compound as white crystals (44 mg, 76.7 µmol, 52%).

1H NMR (300 MHz; CD3OD): δ = 1.55 (s, 9H, -CH(CH3)), 2.41 (s, 3H, -CH3), 4.24 (s, 2H, -CH2-NH), 5.07 (s, 4H, -O-CH2-Ph), 7.08 – 7.14 (m, 2H, Me-C6H4-SO2-), 7.12 (s, 2H, -C(OBn)-CH3), 7.33 – 7.44 (m, 12H, Me-C6H4-SO2- and -O-CH2-C6H3), 7.76 (dd, 1H, 8.7 Hz, 8.5 Hz).
Compound 2g. tert-Butyl 2,6-bis(benzyloxy)-2'-methyl-[1,1'-biphenyl]-4-carboxylate. A solution of tert-butyl 3,5-bis(benzyloxy)-4-(((2-methylphenyl)sulfonamido)methyl)benzoate (1g) (12.0 mg, 20.9 µmol) in MeOH (5 mL, containing 0.01 M NH₃) was loaded on the photo reactor with a flow rate of 0.1 mL/min (MeOH, containing 0.01 M NH₃) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rₛ=0.79, DCM) to yield the title compound (6.8 mg, 14.1 µmol, 67%).

Compound 11. Methyl 4-((N-(4-methoxybenzyl)sulfamoyl)benzoate. A solution of methyl 4-((chlorosulfonyl)benzoate (234.7 mg, 1 mmol, 1 eq.), (4-methoxyphenyl)methanamine (137.2 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (142.1 mg, 191.6 µL, 1.1 mmol, 1.1 eq.) in DCM (4 mL) was stirred for 16 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) which provided the title compound as a white powder (273 mg, 0.81 mmol, 81%).

Compound 2i. Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-((N-(4-methoxybenzyl)sulfamoyl)benzoate (1I) (20.6 mg, 62.3 µmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 0.1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rₛ=0.66, DCM) to yield the title compound (9.1 mg, 37.6 µmol, 61%).

NMR and HRMS spectra are equivalent to those of biphenyl 2i.³
Compound 1j. N-(2,6-Dimethoxybenzyl)-4-methylbenzenesulfonamide. A solution of 4-methylbenzenesulfonyl chloride (190.6 mg, 1 mmol, 1 eq.), (2, 6-dimethoxyphenyl)methanamine (167.2 mg, 1 mmol, 1 eq.) and N,N-disopropylethylamine (142.1 mg, 191.6 µL, 1.1 mmol, 1.1 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (20 mL), aqueous hydrochloric acid (1 M, 20 mL) and brine (20 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 3:2) to provide the title compound as white crystals (257 mg, 80.0 µmol, 80%).

1H NMR (500 MHz; CDCl3): δ = 2.36 (s, 3H, -CH3), 3.71 (s, 6H, -OCH3), 4.25 (d, 2H, 3J_H-H = 6.3 Hz, -CH2-C6H4), 5.17 (t, 1H, 3J_H-H = 6.3 Hz, -CH2), 6.38 (d, 2H, 3J_H-H = 8.4 Hz, -C(OMe)-CH3), 7.10 (t, 1H, 3J_H-H = 8.4 Hz, CH-CH2-CH3), 7.15 (d, 2H, 3J_H-H = 8.4 Hz, -C(Me)-CH2-CH3), 7.64 (d, 2H, 3J_H-H = 8.4 Hz, -C(Me)-CH2-CH3) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.5 (1C, CH3), 36.5 (1C, CH3), 55.7 (2C, -OCH3), 103.6 (2C, -C(OMe)-CH3), 112.8 (1C, -CH2-C6H4), 127.2 (2C, -C(Me)-CH2-CH3), 129.1 (2C, -C(Me)-CH3), 137.4 (1C, -C(Me)-), 142.8 (1C, -C-SO2-), 158.1 (2C, -C(OMe)-) ppm. HRMS (ESI+) calcd. for C18H18NO3S+: 322.1108; found: 322.1108. HRMS (ESI+) calcd. for C18H18NO3S+: 320.0951; found: 320.0966.

Compound 2j. 2,6-Dimethoxy-4′-methyl-1,1′-biphenyl. A solution of N-(2,6-dimethoxybenzyl)-4-methylbenzenesulfonamide (1j) (26.0 mg, 80.9 µmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, R = 0.88, DCM) to yield the title compound (10.6 mg, 46.5 µmol, 57%).

1H NMR (500 MHz; CDCl3): δ = 2.40 (s, 3H, -CH3), 3.74 (s, 6H, -OCH3), 6.66 (d, 2H, 3J_H-H = 8.4 Hz, -C(OMe)-CH3), 7.22–7.28 (m, 5H, -C(Me)-CH2-CH3 and –CH-CH2-CH3) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.5 (1C, -CH3), 56.1 (2C, -OCH3), 104.4 (2C, -C(OMe)-CH3), 119.7 (1C, -C-C(OMe)-), 128.6 (1C, -CH2-CH3), 128.7 (2C, -C(OMe)-CH3), 130.9 (2C, -C(Me)-CH2-CH3), 131.2 (1C, -CH-C-C-C(OMe)-), 136.4 (1C, -C(Me)-), 157.9 (2C, -C(OMe)-) ppm. HRMS (ESI+) calcd. for C18H17O2S+: 229.1223; found: 229.1231.

Compound 2k. 4-Methoxy-4′-methyl-1,1′-biphenyl. A solution of 4-methoxy-N-(4-methylbenzyl)benzenesulfonamide (Alfa Aesar, H56245, 1k) (20.2 mg, 69.3 µmol) in MeCN (5 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (DCM) to yield the title compound (4.3 mg, 21.7 µmol, 36%).

1H NMR (300 MHz; CD2Cl2): δ = 2.37 (s, 3H, -CH3-C6H4), 3.83 (s, 3H, -OCH3), 6.95 – 9.98 (m, 2H, -OCH2-C6H4), 7.23 (d, 2H, 3J_H-H = 8.0 Hz, CH3-C(=CH2)), 7.45 (d, 2H, 3J_H-H = 8.0 Hz, CH2-C(=CH2)=(CH2)), 7.50 – 7.53 (m, 2H, -OCH2-C(=CH2)=(CH2)) ppm. 13C NMR (75.5 MHz; CD2Cl2): δ = 21.3 (1C, -CH3-C6H4), 55.8 (1C, -O-C6H4), 114.7 (2C, -CH3-C(=CH2)), 126.9 (2C, CH3-C(=CH2)=(CH2)), 128.3 (2C, CH2-C(=CH2)=O-C6H4), 130.0 (2C, CH3-C(=CH2)), 134.0 (1C, -CH3-C(=CH2)=O-C6H4), 137.0 (1C, CH3-C6H4), 138.3 (1C, CH3-C(=CH2)=(CH2)=C), 159.6 (1C, CH3-O-C6H4) ppm. HRMS (ESI+) calcd. for C18H18O2: 299.1117; found: 299.1117.
**Compound 11.** Methyl 4-(((4-acetylphenyl)sulfonylamido)methyl)benzoate. A solution of 4-acetylbenzenesulfonyl chloride (218.7 mg, 1 mmol, 1 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-disopropylethyamine (284.4 mg, 383.2 µL, 2.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was obtained as a solid (200.3 mg, 0.58 mmol, 58%) and used without further purification.

1H NMR (300 MHz; CDCl3): δ = 2.59 (s, 3H, -CO-CH3), 3.84 (s, 3H, -OCH3), 4.18 (d, 2H, JHN= 6.3 Hz, -CH2-), 6.28 (t, 1H, JHH= 6.3 Hz, -NH), 7.31 (d, 2H, JHH= 8.5 Hz, -CH2-C-CH3), 7.84 − 7.89 (m, 4H, -CH-C-COOCH3 and -CH-C-SO2CH2), 8.01 − 8.04 (m, 2H, Me-C-C-CH3) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 27.3 (1C, -CO-CH3), 47.2 (1C, -CH2-), 52.7 (1C, -OCH3), 128.1 (2C, -CH-C-SO2CH2), 128.9 (2C, -CH2-C-CH3), 129.9 (2C, Me-C-C-CH3), 130.4 (2C, -CH-C-COOCH3), 130.4 (1C, -C(COOCH3)), 141.0 (1C, Me-C-C-CH3), 143.4 (1C, -CH=CH-C-), 145.2 (1C, -SO2CH3), 167.4 (1C, -COOME), 198.2 (1C, -CO-CH3) ppm. HRMS (ESI⁺) calcd. for C17H18NO5S+: 348.0900; found: 348.0903. HRMS (ESI⁻) calcd. for C17H18NO5S⁻ : 346.0755; found: 346.0757.

**Compound 21.** Methyl 4'-acetyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-(((4-acetylphenyl)sulfonylamido)methyl)benzoate (1) (19.8 mg, 57.1 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 2 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.81, DCM) to yield the title compound (5.0 mg, 20.1 µmol, 35%).

1H NMR (300 MHz; CDCl3): δ = 2.65 (s, 3H, -CO-CH3), 3.85 (s, 3H, -OCH3), 7.68 − 7.73 (m, 4H, -CH-C-C-CH3), 8.05 (d, 2H, JHH= 8.3 Hz, Me-C-C-CH3), 8.13 (d, 2H, JHH= 8.3 Hz, -CH-C-COOCH3) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 26.8 (1C, -CO-CH3), 52.4 (1C, -CH2-), 127.4 (2C, -CH-C-C-CH3), 127.6 (2C, -CH-C-C-CH3), 129.1 (2C, Me-C-C-CH3), 129.9 (1C, -C(COOCH3)), 130.4 (2C, -CH-C-COOCH3), 136.7 (1C, Me-C-C-CH3), 144.4 (1C, Me-C-C-C-CH-C-C-CH3), 144.6 (1C, Me-C-C-CH-C-C-CH3), 166.9 (1C, -COOME), 197.8 (1C, -CO-Me) ppm. HRMS (ESI⁺) calcd. for C19H16O4+: 295.1016; found: 255.1015.

**Compound 1ao.** N-(4-(Hydroxymethyl)(benzyl))-4-methylbenzenesulphonamide. A solution of 4-methylbenzenesulfonyl chloride (190.6 mg; 1 mmol; 1 eq.), (4-(aminomethyl)phenyl)ethanol (137.2 mg; 1 mmol; 1 eq.) and N,N-disopropylethyamine (142.1 mg; 191.6 µL; 1.1 mmol; 1.1 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. The solution was diluted with ethyl acetate (20 mL) washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (245.7 mg; 0.84 mmol; 84%).

1H NMR (500 MHz; CDCl3): δ = 2.42 (s, 3H; -CH3); 3.17 (t, 1H; 3JHH= 5.9 Hz; -OH); 4.00 (d, 2H; 3JHH= 6.4 Hz; -NH-CH2-); 4.52 (d; 2H; 3JHH= 5.9 Hz; -CH2-OH); 5.93 (t; 1H; 3JHH= 6.4 Hz; -NH); 7.18 (d; 2H; 3JHH= 8.0 Hz; -NH-CH2-CH2-); 7.24 (d; 2H; 3JHH= 8.0 Hz; -CH2-OH); 7.36 (d; 2H; 3JHH= 8.2 Hz; -C(=CH2)-CH3); 7.71 (d; 2H; 3JHH= 8.2 Hz; -C(=CH2)-CH3-COO-CH3) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.4 (1C, -CH3); 47.4 (1C, -CH2-OH); 64.3 (1C, -NH-CH2-); 127.7 (2C, -CH2-CH2-OH); 127.8 (2C, -C(=CH2)-CH2-); 128.7 (2C, -NH-CH2-CH2-); 130.6 (2C, -C(=CH2)-CH2-); 137.0 (1C, -CH2-C-); 138.4 (1C, -C-SO2); 142.3 (1C, -CH2-OH); 144.5 (1C, -CH2-COO-CH3) ppm. HRMS (ESI⁺) calcd. for C21H16NO3S+: 329.0924; found: 329.0924. HRMS (ESI⁻) calcd. for C21H16NO3S⁻ : 309.0852; found: 309.0852.

**Compound 1m.** N-(4-Formylbenzyl)-4-methylbenzenesulphonamide. A solution of N-(4-(hydroxymethyl)(benzyl))-4-methylbenzenesulfonylamine (1ao) (100 mg, 0.34 mmol; 1 eq.) and pyridinium chlorochromate (109.9 mg, 0.51 mmol; 1.5 eq.) in MeCN (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The residue
was dissolved, filtered and purified by open column chromatography (silica, Rf=0.49, chloroform/MeOH 95:5) to yield the title compound (96.8 mg, 0.33 mmol, 97%) as a white amorphous solid.

\[ \text{Compound (2C,3H,74%) as slightly yellow crystals.} \]

\[ \text{chloride (381.3 mg, 0.33 mmol, 0.20 mL), aqueous hydrochloric acid (0.5 M),} \]

under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.76, DCM) to yield the title compound (3.7 mg, 18.9 µmol, 31%).

\[ \text{Compound 1n. N-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide (1m) (17.5 mg, 60.5 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 1.5 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.43, DCM) to give the title compound (454.4 mg, 1.49 mmol, 74%) as slightly yellow crystals.} \]

\[ \text{Compound 2n. 5-(p-tolyl)benzo[d][1,3]dioxole. A solution of ethyl N-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide (1m) (19.98 mg, 65.4 µmol) in MeCN (3 mL) was loaded on the photo reactor with a flow rate of 0.5 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.87, DCM) to yield the title compound (4 mg, 18.9 µmol, 29%).} \]

\[ \text{\( ^1 \text{H NMR (500 MHz; CDCl}_3): \delta = 2.38 (s, 3H, -CH}_3) \text{, 5.99 (s, 2H, -O-CH}_2=O) \text{, 6.87 (d, 1H, \text{J}_{HH} = 7.9 Hz, -C(O)-CH}_3) \text{, 7.08 - 7.01 (m, 2H, -CH=CH-CH=CH-)} \text{, 7.22 (d, 2H, \text{J}_{HH} = 8.3 Hz, Me-C=CH-CH=CH-)} \text{, 7.41 (d, 2H, \text{J}_{HH} = 8.2 Hz, Me-C=CH-CH=CH-)} \text{ ppm.} \]

\[ \text{\( ^{13} \text{C NMR (151 MHz, CDCl}_3): \delta = 21.2 (C1, -CH}_3) \text{, 101.2 (C1, -O-CH}_2=O) \text{, 107.7 (C1, -C=CH=CH-)} \text{, 108.7 (C1, -C=CH=CH-)} \text{, 120.5 (C1, -C=CH=CH-)} \text{, 126.9 (2C, -CH=CH-CH=CH-)} \text{, 129.6 (2C, -CH=CH-CH=CH-)} \text{, 135.7 (C1, -CH} \text{3) \text{, 136.8 (C1, -C(O)-CH=CH=CH-)} \text{, 138.2 (C1, -C(O)-CH=CH=CH-)} \text{, 146.9 (C1, -C(O)-CH=CH=CH-)} \text{, 148.2 (C1, -C(O)-CH=CH=CH-)} \text{ ppm.} \]

\[ \text{HRMS (ESI') calcd. for C}_{12}\text{H}_{12}\text{O}_2S: 213.0910, found: 213.0910.} \]
Compound 1o. Methyl 4-(((3-cyanophenyl)sulfonamido)methyl)benzoate. A solution of 3-cyanobenzenesulfonyl chloride (201.6 mg, 1 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and triethylamine (253 mg, 347.5 µL, 2.5 mmol, 2.5 eq.) in 1,4-dioxane (12 mL) was stirred for 12 h at room temperature. The mixture was diluted with ethyl acetate (50 mL) and washed with aqueous hydrochloric acid (2 M, 25 mL) and water (50 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by preparative HPLC to provide the title compound (100 mg, 0.3 mmol, 30%).

\[\text{Compound 1o} \]

1H NMR (500 MHz; CDCl₃): δ = 3.96 (s, 3H, -OCH₃), 7.56–7.61 (m, 1H, CH=CH-C=C≡N), 7.62–7.66 (m, 2H, -CH=CH-C=C≡N), 7.82–7.87 (m, 1H, -CH=CH-C=C≡N), 7.90 (m, 1H, -C=CH-C≡N), 8.13–8.17 (m, 2H, -CH=CH-C≡N) ppm. 13C NMR (125.8 MHz; CDCl₃): δ = 52.3 (1C, -OCH₃), 113.3 (1C, -C≡C), 118.5 (1C, -C≡N), 127.1 (2C, -CH=CH-C≡N), 130.1 (1C, -C≡C≡N), 130.4 (2C, -CH=CH-C≡N), 130.8 (1C, -C=CH-C≡N), 131.5 (1C, -C≡C≡C≡N), 131.6 (1C, -C=CH-C≡C≡N), 141.3 (1C, -C=CH-C≡C≡N), 143.1 (1C, -C=CH-C≡C≡N), 166.6 (1C, -C≡C≡N) ppm. HRMS (ESI⁺) calcd. for C₁₅H₁₂NO₂S⁺: 331.0747; found: 331.0738. HRMS (ESI⁺) calcd. for C₁₆H₁₂NO₂S⁻: 329.0602; found: 329.0600.

Compound 2o. Methyl 3'-cyano-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-(((3-cyanosulfonamido)methyl)benzoate (1o) (20.3 mg, 61.4 µmol) in MeOH (20 mL) was loaded on the photo reactor with a flow rate of 1.0 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoprodast was collected and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica, Rf=0.78, DCM) to yield the title compound (3.0 mg, 12.6 µmol, 21%).

\[\text{Compound 2o} \]

1H NMR (500 MHz; CDCl₃): δ = 2.56 (s, 3H, -OCH₃), 7.61 (m, 1H, CH=CH-C≡C≡N), 7.82–7.88 (m, 1H, -CH=CH-C≡C≡N), 8.17 (m, 1H, -C=CH-C≡N), 8.3–8.35 (m, 2H, -CH=CH-C≡N) ppm. 13C NMR (125.8 MHz; CDCl₃): δ = 120.8 (1C, -OCH₃), 124.8 (1C, -C≡N), 130.1 (1C, -C≡C≡N), 130.4 (2C, -CH=CH-C≡N), 130.8 (1C, -C≡C≡C≡N), 131.5 (1C, -C≡C≡C≡C≡N), 141.3 (1C, -C≡C≡C≡C≡N), 143.1 (1C, -C≡C≡C≡C≡C≡N), 166.6 (1C, -C≡C≡C≡N) ppm. HRMS (ESI⁺) calcd. for C₁₅H₁₀N₂O₂⁺: 238.0683; found: 238.0685.

Compound 2p. 1,1'-Biphenyl. A solution of N-benzybenzensulfonylamide (Alfa Aesar, H55588, 1p) (20.5 mg, 82.9 µmol) in MeOH (5 mL) was loaded on the photo reactor with a flow rate of 1.5 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoprodast was collected and the solvent was removed under reduced pressure. The residue was purified by filtration over silica (DCM) to yield the title compound (traces). GCMS (EI, 70 eV): 154 (100).

\[\text{Compound 2p} \]

Compound 1f. Methyl 4-(((2,4-difluorophenyl)sulfonamido)methyl)benzoate. A solution of 2,4-difluorobenzenesulfonyl chloride (212.2 mg, 134 µL, 1 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-disopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by
recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (316.5 mg, 0.93 mmol, 93%).

1H NMR (500 MHz; CDCl3): δ = 3.90 (s, 3H, -OCH3), 4.27 (d, 2H, 1H J = 6.4 Hz, -CH2-), 5.21 (t, 1H, 2H J = 5.9 Hz, -NH-), 6.89-6.93 (m, 1H, -CF-CH-CF-), 6.95 - 6.99 (m, 1H, -CF-CH-CH3), 7.29 (d, 2H, 2H J = 8.1 Hz, -CH2-C-CH3), 7.86 - 7.90 (m, 1H, -CF-CH-C-), 7.93 (d, 2H, 2H J = 8.1 Hz, -CH(COOMe)) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 47.1 (1C, -CH2-), 52.4 (1C, -OCH3), 105.7 (t, 1C, 13JCF = 25.5 Hz, -CF-CH-CF-), 112.1 (dd, 1C, 2H JCF = 21.9 Hz, 13JCF = 3.3 Hz, -CF-CH-CF-), 124.7 (dd, 1C, 2H JCF = 14.0 Hz, 13JCF = 4.0 Hz, -C-SO2-), 127.8 (2C, -CH2-C-CH3), 130.0 (1C, -C(COOMe)), 131.0 (2C, -CH2-C(COOMe)) ppm. HRMS (ESI+) calcd. for C34H29NO5F2S2+: 546.1605; found: 546.1598.

**Compound 2r.** Methyl 2′,4′-difluoro-[1,1′-biphenyl]-4-carboxylate. A solution of 4-(((2,4-difluorophenyl)sulfonylamido)methyl)benzoate (1r) (19.5 mg, 57.2 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 2 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoprocess was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCm) to yield the title compound (11.2 mg, 45.2 µmol, 79%).

1H NMR (500 MHz; CDCl3): δ = 3.94 (s, 3H, -OCH3), 6.91 - 7.00 (m, 2H, -CF-CH-CF- and -CF-CH-CH3), 7.41 - 7.45 (m, 1H, -CF-CH-C-), 7.57 (m, 2H, -CH2-CH(COOOMe)), 8.10 (d, 2H, 2H J = 8.3 Hz, -CH(COOOMe)) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 52.3 (1C, -OCH3), 104.7 (t, 1C, 13JCF = 25.9 Hz, -CF-CH-CF-), 111.9 (dd, 1C, 13JCF = 21.3 Hz, 13JCF = 3.7 Hz, -CF-CH-CF-), 124.4 (m, 1C, -CF-CH-C), 129.0 (m, 2C, -CH2-CH(COOOMe)), 129.5 (1C, -C(COOMe)), 129.9 (2C, -CH2-C(COOOMe)), 131.6 (m, 1C, -CF-CH-C), 139.7 (1C, -C(COC-C)), 159.9 (dd, 1C, 13JCF = 250.1 Hz, 13JCF = 12.3 Hz, -CF-C-), 162.9 (dd, 1C, 13JCF = 251.5 Hz, 13JCF = 12.2 Hz, -CF-CH-C-), 167.0 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C14H11NO2F2S2+. 249.0722; found: 249.0725.

**Compound 1v.** Methyl 4-(((4-cyanophenyl)sulfonylamido)methyl)benzoate. A solution of 4-cyanobenzenesulfonyl chloride (201.6 mg, 1 mmol, 1 eq.) and triethylamine (253 mg, 347.5 µL, 2.5 mmol, 2.5 eq.) in 1,4-dioxane (12 mL) was stirred for 12 h at room temperature. The mixture was diluted with ethyl acetate (50 mL) and washed with aqueous hydrochloric acid (2 m, 25 mL) and water (50 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by preparative HPLC to provide the title compound (252 mg, 0.77 mmol, 77%).

1H NMR (300 MHz; CDCl3): δ = 3.90 (s, 3H, -OCH3), 4.24 (d, 2H, 2H J = 5.7 Hz, -CH2-), 5.34 (s, 1H, -NH-), 7.25 (d, 2H, 2H J = 7.9 Hz, -CH2-C-CH3), 7.76 (m, 2H, 2H J = 8.1 Hz, -C(CN)-CH3), 7.89 - 7.94 (m, 4H, -CH2-C(SO2)- and -CH2-C(COOMe)-) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 47.0 (1C, -CH2-), 52.4 (1C, -OCH3), 116.6 (1C, -C(CN)-), 117.3 (1C, -CN-), 127.8 (4C, -CH2-C and -CH2-C(SO2)2), 130.1 (1C, -C(COOMe)), 130.1 (2C, -CH2-C(COOMe)), 133.1 (2C, -C(CN)-CH3), 140.9 (1C, -CH2-C), 144.4 (1C, -C(SO2)-), 166.9 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C14H11N2O6S: 321.0747; found: 321.0739. HRMS (ESI+) calcd. for C14H11N2O6S: 321.0692; found: 321.0600.

**Compound 2v.** Methyl 4′-cyano-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4-(((4-cyano)sulfonylamido)methyl)benzoate (1v) (21.9 mg, 66.3 µmol) in MeOH (20 mL) was loaded on the photo reactor with a flow rate of 1.0 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoprocess was collected and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica, Rf=0.68, chloroform/MeOH 49:1) to yield the title compound (10.1 mg, 42.6 µmol, 64%).

1H NMR (500 MHz; CD2Cl2): δ = 3.92 (s, 3H, -OCH3), 7.68 - 7.72 (m, 2H, -CH2-CH-C(C-Ο)-), 7.73 - 7.79 (m, 4H, -CH-CH-C-C≡N), 8.11 - 8.15 (m, 2H, -CH-C(C-Ο)-) ppm. 13C NMR (125.8 MHz; CD2Cl2): δ = 52.7 (1C, -OCH3), 112.4 (1C, -C-CN), 119.2 (1C, CN), 127.8 (2C, -CH2-CH-C(C-Ο)-), 128.5 (2C, -CH2-CH-C-C≡N), 130.7 (2C, -CH2-CH-C(C-Ο)-), 130.9 (1C, -C-C≡N), 133.3 (2C, -CH2-C-C≡N).
Compound 1w. N-(4-Acetylbenzyl)-4-methylbenzenesulfonamide. A solution of 4-methylbenzenesulfonyl chloride (190.7 mg, 1 mmol, 1 eq.), 1-(4-aminomethyl)phenylethan-1-one hydrochloride (185.7 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (284.4 mg, 383.2 μL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 2 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 mL, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered, and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (214.4 mg, 0.71 mmol, 71%).

1H NMR (500 MHz; CDCl3): δ = 2.43 (s, 3H, -CH3), 1.26 (s, 3H, -C(O)-CH3), 7.28 (d, 2H, 3JMe = 6.0 Hz, -C(Me)-CH3), 7.53 (d, 2H, 3JMe = 8.0 Hz, -C(Me)-CH3), 7.67 (d, 2H, 3JMe = 8.4 Hz, -CH2-CH(COMe)-), 8.02 (d, 2H, 3JMe = 8.4 Hz, -CH2-CH(COMe)-) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.3 (1C, -CH3), 26.8 (1C, -C(O)-CH3), 127.1 (2C, -CH2-CH(COMe)-), 127.3 (2C, -C(Me)-CH)3, 129.1 (2C, -CH2-CH(COMe)-), 138.4 (1C, -C=C=CH-C(COMe)-), 145.9 (1C, -C=C=CH-C(COMe)-), 197.9 (1C, -CO- ) ppm. HRMS (ESI) calcd. for C18H16NO3S+: 304.0997; found: 304.0997.

Compound 2w. 1-(4-Methyl[1,1′-biphenyl]-4-yl)ethan-1-one. A solution of N-(4-acetylbenzyl)-4-methylbenzenesulfonamide (1w) (18.6 mg, 64.3 μmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with ultraviolet light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.56, DCM) to yield the title compound (7.6 mg, 38.7 μmol, 60%).

1H NMR (500 MHz; CDCl3): δ = 2.41 (s, 3H, -CH3), 1.26 (s, 3H, -C(O)-CH3), 7.28 (d, 2H, 3JMe = 8.0 Hz, -C(Me)-CH3), 7.53 (d, 2H, 3JMe = 8.0 Hz, -C(Me)-CH3), 7.67 (d, 2H, 3JMe = 8.4 Hz, -CH2-CH(COMe)-), 8.02 (d, 2H, 3JMe = 8.4 Hz, -CH2-CH(COMe)-) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 21.3 (1C, -CH3), 26.8 (1C, -C(O)-CH3), 127.1 (2C, -CH2-CH(COMe)-), 127.3 (2C, -C(Me)-CH)3, 129.1 (2C, -CH2-CH(COMe)-), 138.4 (1C, -C=C=CH-C(COMe)-), 145.9 (1C, -C=C=CH-C(COMe)-), 197.9 (1C, -CO- ) ppm. HRMS (ESI) calcd. for C18H16NO3S+: 304.1117; found: 304.1115.

Compound 1x. Methyl 4-(((4-benzyloxy)phenyl)sulfonylamido)methylbenzoate. A solution of 4-((benzyloxy)benzenesulfonyl chloride (282.8 mg, 1 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (284.4 mg, 383.2 μL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 2 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 mL, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered, and the solvent was evaporated. The crude product (395.8 mg, 0.96 mmol, 96%) was used without further purification.

1H NMR (500 MHz; CDCl3): δ = 3.89 (s, 3H, -OCH3), 4.17 (d, 2H, 3JMe = 6.3 Hz, -NH-CH2), 4.95 (t, 1H, 3JMe = 6.3 Hz, -NH-CH2), 5.12 (s, 2H, -OCH2), 7.03 (dd, 2H, 3JMe = 6.9 Hz, -CH2-OCH3), 7.27 (d, 2H, 3JMe = 8.2 Hz, -CH2-OCH3), 7.35 - 7.44 (m, 5H, -OCH2-C6H5), 7.78 (d, 2H, 3JMe = 8.9 Hz, -CH2-O(C2H5)), 7.93 (d, 2H, 3JMe = 8.2 Hz, -CH2-O(COMe)) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 47.0 (1C, -NH-CH2), 52.3 (1C, -OCH2), 79.5 (1C, -OCH2), 115.3 (2C, -O(OCH3)-CH2), 127.6 (2C, -O(OCH3)-CH2), 128.5 (1C, -OCH2-C6H5), 128.9 (2C, -OCH2-C6H5), 138.9 (2C, -CH2-O(C2H5)), 138.9 (1C, -C(OCH3)-), 139.1 (1C, -O-CH2-C6H5), 162.3 (1C, -C(O)-), 166.8 (1C, -COOMe) ppm. HRMS (ESI) calcd. for C23H21NO5S: 412.1206; found: 412.1208. HRMS (ESI) calcd. for C23H22O6S: 410.1086; found: 410.1086.
Compound 2x. Methyl 4′-(benzloxy)-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4-(((4-(benzloxy)phenyl)sulfonyl)amino)methyl)benzoate (1x) (22.4 mg, 54.4 μmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduce was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.76, DCM) to yield the title compound (9.5 mg, 29.8 μmol, 55%).

1H NMR (500 MHz; CDCl3): δ = 3.94 (s, 3H, -OCH3), 5.13 (s, 2H, -O-CH2-), 7.07 (d, 2H, 3JHH = 8.7 Hz, -C(O-CH2)CH2-), 7.26 - 7.47 (m, 5H, -O-CH2-CH3), 7.57 (d, 2H, 3JHH = 8.7 Hz, -C(O-CH2CH2-CH3), 7.62 (d, 2H, 3JHH = 8.4 Hz, -CH-CH2(COOMe)-), 8.08 (d, 2H, 3JHH = 8.4 Hz, -CH-CH2(COOMe)-) ppm. 13C NMR (125.8 MHz; CDCl3): δ = 52.2 (1C, -OCH3), 70.2 (1C, -O-CH2-), 115.4 (2C, -C(O-CH2-CH3)), 126.6 (2C, -C=CH2(COOMe)-), 127.6 (2C, -C=CH2), 128.1 (1C, -C(O-CH2-CH3)), 128.5 (2C, -C=CH2(COOMe)-), 128.8 (2C, -C=CH2), 130.2 (2C, -C=CH2(COOMe)-), 132.8 (1C, -C(O-CH2-CH2-CH3)), 136.9 (1C, -O-CH2-CH3), 145.3 (1C, -C=CH2(COOMe)-), 159.2 (1C, -C(O-CH2-CH3)), 167.2 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C21H19O2S: 319.1329; found: 319.1325.

Compound 1y. Methyl 4-(((4-dimethylamino)phenyl)sulfonyl)amino)methyl)benzoate. A solution of 4-(dimethylamino)benzenesulfonyl chloride (219.7 mg, 1 mmol, 1 eq.), methyl 4-(aminomethyl)benzene hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-disopropylethylamine (284.4 mg, 383.2 μL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 2 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (260 mg, 0.75 mmol, 75%).

1H NMR (300 MHz; CDCl3): δ = 3.05 (s, 6H, -N(CH3)2), 3.89 (s, 3H, -OCH3), 4.14 (d, 2H, 3JHH = 6.4 Hz, -NCH2-), 4.79 (t, 1H, 3JHH = 6.4 Hz, -NCH2-), 6.66 - 6.69 (m, 2H, -C(N(CH3)2)-CH2-), 7.27 - 7.30 (m, 2H, -CH2-C=CH2-), 7.67 - 7.70 (m, 2H, -N(CH3)2)-CH2-CH3), 7.91 - 7.94 (m, 2H, -CH=CH2(COOMe)-) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 40.3 (2C, -C(N(CH3)2)-), 46.9 (1C, -CH2-), 52.3 (1C, -OCH3), 111.3 (2C, -C(N(CH3)2)-CH2-), 125.0 (1C, -C(SO2)-), 127.8 (2C, -CH=CH2-C=CH2-), 129.1 (2C, -C(N(CH3)2)-CH2-), 129.6 (1C, -C(OOMe)-), 130.0 (2C, -C=CH2(COOMe)-), 142.1 (1C, -CH2-C=CH2), 152.9 (1C, -C(N(CH3)2)-), 166.9 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C17H17N2O3S+: 349.1217; found: 349.1211. HRMS (ESI+) calcd. for C17H15N2O3S+: 347.1071; found: 347.1067.

Compound 2y. Methyl 4′-(dimethylamino)-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4′-(dimethylamino)phenyl)sulfonyl)amino)methyl)benzoate (1y) (21.1 mg, 60.6 μmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 0.5 mL/min (MeCN) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduce was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCM) to yield the title compound (5.5 mg, 21.6 mg, 36%).

1H NMR (300 MHz; CDCl3): δ = 3.04 (s, 6H, -N(CH3)2), 3.95 (s, 3H, -OCH3), 6.86 - 6.88 (m, 2H, -C(N(CH3)2)-CH2-), 7.57 - 7.66 (m, 4H, -C(N(CH3)2)-CH2-CH2-CH2-CH3) and -CH-CH2(COOMe)-), 8.06 - 8.09 (m, 2H, -CH=CH2(COOMe)-) ppm. 13C NMR (75.5 MHz; CDCl3): δ = 40.8 (2C, -C(N(CH3)2)-), 52.1 (1C, -OCH3), 113.0 (2C, -C(N(CH3)2)-CH2-), 126.0 (2C, -C=CH2-CH2-CH2-CH3), 127.6 (1C, -C(COOMe)-), 128.1 (2C, -C(N(CH3)2)-CH2-CH3), 130.2 (2C, -C=CH2(COOMe)-), 130.4 (1C, -C(N(CH3)2)-CH2-CH2-C=CH2), 145.6 (1C, -C=CH2(COOMe)-), 150.5 (1C, -C(N(CH3)2)-), 167.3 (1C, -COOMe) ppm. HRMS (ESI+) calcd. for C19H18O2N: 256.1332; found: 256.1332.
Compound 1z. 4-Methoxy-N-(3-(trifluoromethyl)benzyl)benzenesulfonamide. A solution of 4-methoxybenzenesulfonyl chloride (200 mg, 0.97 mmol, 1 eq.), (3-(trifluoromethyl)phenyl)methanamine (170 mg, 137.8 µL, 0.97 mmol, 1 eq.) and N,N-diisopropylethylamine (150.1 mg, 202.3 µL, 1.16 mmol, 1.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. The solution was washed with water (4 mL), aqueous hydrochloric acid (1 M, 4 mL) and brine (4 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was obtained as white a solid (254.5 mg, 0.74 mmol, 76%) and used without further purification.

1H NMR (500 MHz, CDCl3) δ = 3.81 - 3.91 (s, 3H, O-CH3), 4.14 - 4.25 (d, 3JCH3 = 4.2 Hz, 2H, NH-CH2), 4.91 - 5.07 (s, 1H, NH), 6.89 - 7.00 (m, 2H, O-C(=CH2)), 7.34 - 7.45 (m, 3H, CH-CH-CH-CH3), 7.45 - 7.53 (d, 3JCH3 = 7.4 Hz, 1H, CF3-C-CH-CH3), 7.72 - 7.81 (m, 2H, O-C-(CH3)2) ppm. 13C NMR (126 MHz, CDCl3) δ = 46.8 (1CH, CH2-NH), 55.8 (1C, O-CH3), 114.5 (2C, O-C-(CH3)2), 120.31 - 127.82 (1C, q, 3JCF = 272.4 Hz, CF3), 124.58 - 124.70 (1C, q, 3JCF = 3.7 Hz, CF3-C-CH3), 124.74-124.86 (1C, q, 3JCF = 3.7 Hz, CF3-C-CH3), 129.3 (1C, CF3-C-CH-CH3), 128.4 (2C, O-C-(CH3)2), 130.66-131.55 (1C, q, 3JCF = 32.0 Hz, C-CH3), 131.3 (1C, CH2-CH-CH3), 131.4 (1C, CH2-CH3), 163.2 (1C, CH2-C), 272.4 (1C, O-CH3), 272.6 (1C, O-CH3), 320.0951; found: 320.0949. HRMS (ESI+ calcd. for C19H16F3NO2S+: 346.0719; found: 346.0721. HRMS (ESI-) calcd. for C19H16F3NO2S-: 344.0574; found: 344.0576.

Compound 2z. 4-Methoxy-3-(trifluoromethyl)-1,1′-biphenyl. A solution of 4-methoxy-N-(3-(trifluoromethyl)benzyl)benzenesulfonamide (1z) (20 mg, 57.9 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 2 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.80, DCM) to yield the title compound (4.7 mg, 18.5 µmol, 32%).

1H NMR (500 MHz, CDCl3) δ = 7.76 - 7.82 (s, 1H, C-CH-C-F3), 7.68 - 7.75 (d, 3JCH3 = 7.1 Hz, 1H, CH-CH-C-CH3), 7.48 - 7.60 (m, 4H, CH-CH-C-CH-F3 & C-C(CH2)3), 6.93 - 7.05 (m, 2H, O-C(CH2)3), 3.80 - 3.92 (s, 3H, O-CH3) ppm. 13C NMR (126 MHz, CDCl3) δ = 55.5 (1C, O-CH3), 114.6 (2C, O-CH3), 123.38 - 123.50 (1C, q, 3JCF = 3.9 Hz, CF3-C-CH-CH3), 123.52 - 123.66 (1C, q, 3JCF = 3.9 Hz, CF3-C-CH-CH3), 120.99 - 127.85 (1C, q, 3JCF = 272.6 Hz, CF3), 128.4 (2C, C-C(CH2)3), 129.3 (1C, CF3-C-CH-CH3), 130.1 (1C, CF3-C-CH-CH3), 130.76 - 131.72 (1C, q, 3JCF = 31.6 Hz, C-CH3), 132.4 (1C, F3-C-CH-C-CH3), 141.7 (1C, F3-C-CH-C-CH3), 159.9 (1C, C-CH2-C) ppm. 19F NMR (471 MHz, CDCl3): -62.5 (s, 3F) ppm. HRMS (ESI+) calcd. for C19H16F3NO2: 293.0835; found: 253.0835. HRMS (ESI-) calcd. for C19H16F3NO2-: 251.0689; found: 251.0689.

Compound 1aa. Methyl 4-[[4-(methylbenzyl)sulfonyl]benzoyl]benzoate. A solution of 4-tolylmethanamine (50 mg, 53 µL, 0.41 mmol, 1.1 eq.), methyl 4-(chlorosulfonyl)benzoate (88 mg, 0.38 mmol, 1 eq.) and N,N-diisopropylethylamine (73 mg, 98 µL, 0.57 mmol, 1.5 eq.) in DCM (2 mL) was stirred at 1 h at room temperature. The solution was washed with water (2 mL), NaHCO3 solution (2 mL) and aqueous hydrochloric acid (1 M, 2 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The residue was purified by open column chromatography (silica, Rf=0.20, DCM) to yield the title compound (104 mg, 0.33 mmol, 87%) as a white solid.

1H NMR (500 MHz, CDCl3) δ = 2.27 - 2.32 (s, 3H, O-CH3), 3.95 - 3.99 (s, 3H, O-CH3), 4.10 - 4.15 (d, 3JCH3 = 5.8 Hz, 2H, -CH2-), 4.77 - 4.83 (d, 3JCH3 = 6.2 Hz, 1H, NH), 7.02 - 7.10 (m, 4H, CH-CH-C-CH3), 7.28 - 7.34 (m, 3H, CH-CH-C-CH3), 8.11 - 8.17 (d, 3JCH3 = 8.5 Hz, 2H, C-CH(C=O)) ppm. 13C NMR (126 MHz, CDCl3) δ = 21.2 (1C, CH3-C), 47.3 (1C, CH2-C), 52.8 (1C, CH3-C), 127.3 (2C, CH-C-CH3), 128.0 (2C, CH-CH-C-CH3), 130.4 (2C, CH-CH-C-CH3), 141.7 (1C, CH2-C), 144.4 (1C, CH-CH3), 165.8 (1C, O-(CH3)-C) ppm. HRMS (ESI+) calcd. for C19H16O2N2S: 320.0951; found: 320.0949. HRMS (ESI-) calcd. for C19H16O2N2S-: 318.0806; found: 318.0805.

Compound 2a (=2aa). Methyl 4′-methyl-[1,1′-biphenyl]-4-carboxylate. A solution of methyl 4-[[4-(methylbenzyl)sulfonyl]benzoyl]benzoate (1aa) (20.2 mg, 0.063 mmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 5 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed.
under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCM) to yield the title compound (4.7 mg, 0.021 μmol, 33%) as a white solid.

NMR and HRMS spectra are equivalent to those of biphenyl 2a.3

**Compound 1ab.** Methyl 4-(((4-(methylthio)phenyl)sulfonamido)methyl)benzoate. A solution of 4-(methylthio)benzenesulfonyl chloride (227.2 mg, 1 mmol, 1 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (284.4 mg, 383.2 μL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 2 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (307 mg, 0.88 mmol, 88%).

**Compound 2ab.** Methyl 4-((4-(methylthio)phenyl)sulfonamido)methyl)benzoate (1ab) (25.0 mg, 71.2 μmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.40, DCM) and recrystallization from diethyl ether/petrol ether (v/v = 1:1) to yield the title compound (4.8 mg, 18.6 μmol, 26%).

**Compound 1ac.** Methyl 4-(((4-formylphenyl)sulfonamido)methyl)benzoate. A solution of 4-formylbenzenesulfonyl chloride (204.6 mg, 1 mmol, 1 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (284.4 mg, 383.2 μL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (291.7 mg, 0.88 mmol, 88%).
**Compound 2ac.** Methyl 4'-formyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-((4-formylphenyl)sulfonamido)methyl]benzoate (1ac) (18.0 mg, 54.1 µmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 2 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silia, Rf=0.65, DCM) to yield the title compound (2.4 mg, 10 µmol, 18%).

1H NMR (300 MHz, CDCl₃) δ = 3.96 (s, 3H, -OCH₃), 7.69 – 7.72 (m, 2H, -CH=CH₂), 7.77 – 7.80 (m, 2H, -CH=CH₂), 7.97 – 8.00 (m, 2H, -OCH=CH₂), 8.10 – 8.16 (m, 2H, -CH=COOMe), 10.08 (s, 1H, -CHO); ppm. 13C NMR (75 MHz, CDCl₃): δ = 38.6 (1C, -OCH₃), 127.5 (2C, -CH=CH₂), 128.1 (2C, -CH=CH₂), 130.2 (1C, -COOMe), 130.4 (2C, -CH=COOMe), 130.5 (2C, -OCH=CH₂), 136.0 (1C, -OCH=CH₂), 144.2 (1C, -OCH=CH₂), 146.0 (1C, -COOMe), 166.9 (1C, -COOMe), 191.2 (1C, -CHO) ppm. HRMS (ESI⁺) calcd. for C₁₉H₁₃O₃S: 241.0859; found: 241.0857.

**Compound 1ad.** Methyl 4-((2,4,6-trimethylphenyl)sulfonamido)methyl]benzoate. A solution of 2,4,6-trimethylbenzenesulfonyl chloride (218.7 mg, 1 mmol, 1 eq.), methyl 4-[(aminomethyl]benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-disopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (10 mL), aqueous hydrochloric acid (1 M, 10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by recrystallization from ethanol/water (v/v = 1:1) to provide the title compound as a white crystalline compound (287.5 mg, 0.83 mmol, 83%).

1H NMR (300 MHz, CDCl₃) δ = 2.27–2.33 (s, 3H, -HC=CH₂-C-C), 2.59–2.66 (s, 6H, -H₂C=CH₂-C-C), 3.87–3.93 (s, 3H, -OCH₃), 4.10–4.19 (d, JHH = 5.3, 2H, -CH₃), 4.73–4.90 (s, 1H, -NH), 6.91–6.98 (s, 2H, -H₂C=CH₂-C-C), 7.19–7.26 (d, JHH = 8.7, 2H, -CH=CH₂-C-C), 7.87–7.97 (d, JHH = 8.3, 2H, -CH=CH₂-C-C) ppm. 13C NMR (75 MHz, CDCl₃): δ = 21.1 (1C, -OCH₃), 127.5 (2C, -CH=CH₂-C-C), 128.1 (2C, -CH=CH₂-C-C), 130.0 (1C, -COOMe), 132.2 (2C, -CH₂=CH₂-C-C), 133.6 (1C, -H₂C=CH₂-C-C), 139.2 (2C, -H₂C=CH₂-C-C), 141.7 (1C, -CH₂-C-C), 142.7 (1C, -C=O) ppm. HRMS (ESI⁺) calcd. for C₂₈H₃ₕNO₅S: 384.1264; found: 348.1265.

**Compound 2ad.** Methyl 2',4'-6'-trimethyl-[1,1'-biphenyl]-4-carboxylate. A solution of methyl 4-((2,4,6-trimethylphenyl)sulfonamido)methyl]benzoate (1ad) (20.5 mg, 82.9 µmol) in MeOH (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min (MeOH) and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproducts was collected and the solvent was removed under reduced pressure. The desired photoprodut was observed by HPLC-HRMS and GCMS in traces.

HRMS (ESI⁺) calcd. for C₂₉H₂₃O₃: 255.1380; found: 255.1382; GCMS (EI, 70 eV) m/z (%): 254 (100), 239 (9), 223 (29), 195 (52), 180 (30), 165 (35), 152 (11).

**Compound 1ae.** Methyl 6-((4-methylphenyl)sulfonamido)methyl]nicotinate. A solution of methyl 6-[[aminomethyl]nicotinate hydrochloride (95.3 mg; 0.47 mmol; 1 eq.) in 1,4-dioxan (500 µL) was added to a suspension of 4-methylbenzenesulfonyl chloride (101.3 mg; 0.53 mmol; 1 eq.) and N,N-disopropylethylamine (153 mg; 2.07 µL; 1.19 mmol; 2.5 eq.) 1,4-dioxan (500 µL). The
mixure was sonicated for 5 h at room temperature. After dilution with ethyl acetate (30 mL) the solution was washed with NH₄Cl solution (30 mL, saturated) and brine (30 mL). The organic layer was dried with Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was crystallized from ethanol/water (v/v = 3/2) to provide the title compound as a white crystalline solid (75.4 mg; 0.235 mmol; 50%).

1H NMR (500 MHz; CDCl₃): δ = 2.38 (s; 3H; C-CH₃); 3.95 (s; 3H; -OCH₃); 4.34 (d; 2H; 3J_HH = 5.7 Hz; -CH₂-); 5.94 (t; 1H; 3J_HH = 5.5 Hz; -NH); 7.22–7.27 (m; 2H; -CH=CH₂); 7.31–7.35 (m; 2H; -CH₂-CH₂-); 7.70–7.76 (m; 2H; -CH=CH₂-SO₂-); 8.21–8.27 (m; 1H; -CH=CH-C=C(=O)-); 9.01–9.06 (m; 1H; -CH=CH-N=); ppm. 13C NMR (125.8 MHz; CDCl₃): δ = 21.5 (1C; C-CH₃); 47.2 (1C; -CH₂-); 52.5 (1C; -OCH₃); 121.8 (1C; -CH₂-C-); 125.3 (1C; -C(=O)-); 127.2 (2C; -SO₂-C-CH₂-); 128.7 (2C; -CH=CH₂-C-); 136.4 (1C; -SO₂-C-); 138.3 (1C; -CH-CH₂-); 143.6 (1C; -CH=CH₂); 149.7 (1C; -CH=CH-N=); 159.1 (1C; -CH=CH-); 165.1 (1C; -C=O-) ppm. HRMS (ESI⁺) calcd. for C₁₀H₈O₂N₂S²: 321.0904; found: 321.0901.

Compound 2af. Methyl-4-((pyridin-3-sulfonamido)methyl)benzoate. A solution of methyl-4-((pyridin-3-sulfonamido)methyl)nicotinate (1af) (20.1 mg, 62.7 µmol) in MeCN (50 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the product was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rₐ=0.22, DCN with 1% N,N-diisopropylethylamine) to yield the title compound (5.2 mg; 22.9 µmol; 37%) as a white solid.

1H NMR (300 MHz; CDCl₃): δ = 2.42 (s; 3H; C-CH₃); 3.97 (s; 3H; -OCH₃); 7.29–7.33 (m; 2H; -CH=CH₂-C-); 7.78–7.82 (m; 1H; -CH=CH-C=C(=O)-); 7.95–8.00 (m; 2H; -CH=CH=CH₂-C-); 8.32–8.37 (m; 1H; -CH=CH-C(O)=O); 9.25–9.29 (m; 1H; -CH=CH-N=) ppm. 13C NMR (125.8 MHz; CDCl₃): δ = 21.5 (1C; C-CH₃); 52.3 (1C; -OCH₃); 119.7 (1C; -CH=CH-C=C(=O)-); 124.0 (1C; -C(=O)=O)-; 127.3 (2C; -CH=CH₂-C-); 129.7 (2C; -CH=CH₂-C-); 135.0 (1C; -CH=CH-C=O); 143.1 (1C; -CH=CH-N=); 145.0 (1C; -CH=CH-); 150.6 (1C; -CH=CH-N=); 160.7 (1C; -C=O-); 165.7 (1C; -C=O-) ppm. HRMS (ESI⁺) calcd. for C₁₀H₈O₂N₂: 228.1019; found: 228.1016.

Compound 1af. Methyl-4-((pyridin-3-sulfonamido)methyl)benzoate. A solution of pyridazine-3-sulfonamide chloride (194.6 mg; 1 mmol; 1 eq.), methyl-4-((aminomethyl)benzoate hydrochloride (201.7 mg, 1 mmol, 1 eq.) and N,N-diisopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2 eq.) in DCN (4 mL) was stirred for 1 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with water (20 mL), aqueous hydrochloric acid (1 M, 20 mL) and brine (20 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was used without further purification (135.6 mg; 0.44 mmol; 44%).

1H NMR (300 MHz; CDCl₃): δ = 3.90 (s; 3H; -OCH₃); 4.27 (d; 2H; 3J_HH = 6.1 Hz; -CH₂-); 5.42 (t; 1H; 3J_HH = 6.1 Hz; -NH₂); 7.13–7.19 (m; 2H; -SO₂-C-CH₃); 7.27 (d; 2H; δ_HH = 8.3 Hz; -CH=CH₂-C-); 7.43 (dd; 1H; δ_HH = 7.9 Hz; 3J_HH = 4.8 Hz; -CH=CH-); 7.93 (d; 2H; 3J_HH = 8.3 Hz; -CH=CH-COMe); 8.09 (dd; 1H; 3J_HH = 8.0 Hz; 3J_HH = 1.9 Hz; -CH=CH-); 8.77 (dd; 1H; 3J_HH = 4.8 Hz; 3J_HH = 1.4 Hz; -CH=N-CH₂-); 9.03 (d; 1H; 3J_HH = 2.0 Hz; -CH=CH-N=) ppm. 13C NMR (75.5 MHz; CDCl₃): δ = 47.0 (1C; -CH₂-); 52.4 (1C; -OCH₃); 123.9 (1C; -CH=CH₂-C-); 127.2 (2C; -CH=CH₂-C-); 130.1 (1C; -COOME); 130.2 (2C; -CH=CH-COMe); 134.9 (1C; -CH=CH₂-C-); 137.0 (1C; -C=O); 141.0 (1C; -CH₂-C-); 148.0 (1C; -CH=CH₂-C-); 153.3 (1C; -CH=CH₂-C-); 166.7 (1C; -COOME) ppm. HRMS (ESI⁺) calcd. for C₁₀H₈O₂N₂S: 307.0747; found: 307.0743. HRMS (ESI⁺) calcd. for C₁₀H₈O₂N₂S⁻: 305.0602; found: 305.0598.

Compound 2af. Methyl-4-((pyridin-3-sulfonamido)methyl)benzoate. A solution of methyl-4-((pyridin-3-sulfonamido)methyl)benzoate (1af) (17.0 mg; 56.0 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the product was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rₐ=0.45, chloroform/MeOH 95:5) to yield the title compound (10 mg; 46.9 µmol; 85%) as a white solid.

1H NMR (300 MHz; CDCl₃): δ = 3.95 (s; 3H; -OCH₃); 7.40 (dd; 1H; 3J_HH = 7.9 Hz; 3J_HH = 4.9 Hz; -CH=CH-CH-N-); 7.64–7.68 (d; 2H; 3J_HH = 8.4 Hz; -CH=CH-C(COOMe)-); 7.89–7.93 (m; 1H; -CH=CH-CH-N-); 8.12–8.16 (dd; 2H; 3J_HH = 8.4 Hz; -CH=CH-C(OOME)-); 8.63 (d; 1H; 3J_HH = 3.8 Hz; -CH=CH-N=); 8.88 (s; 1H; -N=CH₃-C-); ppm. 13C NMR (75.5 MHz; CDCl₃): δ = 52.4 (1C; -OCH₃); 123.8 (1C; -CH=CH-CH-N-); 127.2 (2C; -CH=CH-C(COOMe)-); 129.9 (1C; -COOME); 130.5 (2C; -CH=CH-C(OOME)-); 134.7 (1C; -CH=CH-CH-N-); 135.7 (1C; -N=CH₃-C-); 142.3 (1C; -CH=CH-C(OOME)-); 148.4 (1C; -N=CH₃-C-); 149.3 (1C; -CH=CH-CH-N-); 166.9 (1C; -COOME) ppm. HRMS (ESI⁺) calcd. for C₁₅H₁₂N₂O₄: 214.0863; found: 214.0861.
**Compound 1ag.** 4-Methyl-N-(pyridin-2-yl-methyl)benzensulfonamide. A solution of 4-methylbenzenesulfonyl chloride (190.6 mg; 1 mmol; 1 eq.), pyridin-2-ylmethanimine (108.1 mg; 10 μL; 1 mmol; 1 eq.) and N,N-dimethylpropylnamine (142.1 mg; 191.6 μL; 1.1 mmol; 1.1 eq.) in 1.4-dioxan (2 mL) was prepared and stirred for 12 h at room temperature. After dilution with ethyl acetate (20 mL) the solution was washed with NH₄Cl solution (30 mL, saturated) and brine (30 mL). The organic layer was dried with Na₂SO₄, filtered and the solvent was evaporated under reduced pressure. The crude product was used without further purification (247 mg; 94% yield).

1H NMR (300 MHz; CDCl₃): δ = 2.38 (s; 3H; CH₃); 4.22 (d; 2H; δJHH = 5.4 Hz; CH₂); 6.03 (s; 1H; NH); 7.14–7.18 (m; 2H; N-C-H); N-CH₃; 7.26 (d; 2H; δJHH = 8.2 Hz; CH₂-C(CH₃); 7.61 (dt; δJHH = 7.7 Hz; δJHH = 1.7 Hz; N-CH-C-H); 7.70 (d; 2H; δJHH = 8.2 Hz; SO₂-C(CH₃)); 8.43 (m; 2H; N-CH) ppm. 13C NMR (75.5 MHz; CDCl₃): δ = 21.6 (1C; CH₃); 47.7 (1C; CH₂); 122.3 (1C; N-C-H); 123.0 (1C; N-C-H); 127.5 (2C; SO₂-C(CH₃); 130.0 (2C; CH₃-C(CH₂); 137.1 (1C; N-C-H-C-H); 137.2 (1C; SO₂-C); 143.9 (1C; C₆H₅); 149.2 (1C; N-C); 158.5 (1C; N-C) ppm. HRMS (ESI⁺) calcd. for C₁₇H₁₂N₂O₅S⁺: 283.0849; found: 263.0847.

**Compound 2ag.** 2-((p-Tolyl)pyridine. A solution of 4-methyl-N-(pyridin-2-yl-methyl)benzensulfonamide (1ag) (23.3 mg; 88.8 μmol) in MeCN (50 mL) was loaded on the photo reactor with a flow rate of 2 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduction was collected and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica, Rf=0.20, DCM with 1% N,N-dimethylpropylnamine) to yield the title compound (2.4 mg; 14.2 μmol; 16%) as a white solid.

1H NMR (500 MHz; CDCl₃): δ = 2.41 (s; 3H; C-CH₃); 7.22–7.28 (m; 1H; N=CH-CH₂); 7.28–7.32 (m; 2H; -CH₂-C-CH₃); 7.72–7.75 (m; 1H; -CH₂-N=C); 7.76–7.82 (m; 1H; CH₂-C=CH₃); 7.89–7.93 (m; 2H; -CH₂-C=N); 8.66–8.73 (m; 1H; -CH₂-C-N) ppm. 13C NMR (125.8 MHz; CDCl₃): δ = 21.3 (1C; CH₃); 120.6 (1C; CH₃-C-N); 121.9 (1C; N=CH-C-H); 126.9 (2C; CH₂-C-C-H); 129.6 (1C; -CH₂-C-CH₃); 135.7 (1C; -C-C-N); 137.5 (1C; -CH₂-C=C-N); 139.4 (1C; -CH₂); 148.9 (1C; -CH=CH₂); 157.1 (1C; -C-C=CH₃) ppm. HRMS (ESI⁺) calcd. for C₂₁H₁₇N₂O₅S⁺: 270.0964; found: 270.0964.

**Compound 1ah.** Methyl 4-(((1-methyl-1H-imidazole)-4-sulfamidomethyl)benzozate. A solution of 1-methyl-1H-imidazole-4-sulfonyl chloride (100 mg, 0.55 mmol, 1 eq.) methyl 4 (aminomethyl)benzozate hydrochloride (123 mg, 0.61 mmol, 1.1 eq.) and N,N-dimethylpropylnamine (157.4 mg, 1.22 μL, 1.22 mmol, 2.2 eq.) in DCM (3 mL) was stirred for 2 h at room temperature. The solution was washed with water (3 mL), aqueous hydrochloric acid (0.5 M, 3 mL) and water (3 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was obtained as white a solid (70.5 mg, 0.23 mmol, 41%) and used without further purification.

1H NMR (300 MHz, CDCl₃) δ = 3.66 – 3.75 (s, 3H, N-CH₃); 3.87 – 3.94 (s, 3H, O-CH₃); 4.16 – 4.35 (d, δJHH = 4.2, 2H, N-CH₂); 5.89 – 6.21 (s, 1H, NH); 7.34 – 7.41 (m, 3H, CH₂-C-C-H & NeMe₆-C); 7.45 – 7.51 (s, 1H, N=CH-CH₂); 7.91 – 7.98 (d, δJHH = 8.3, 2H, CH₂-C-COMe) ppm. 13C NMR (75 MHz, CDCl₃) δ = 34.2 (1C, N-CH₂); 47.1 (1C, N-CH₃); 52.3 (1C, O-CH₃); 124.2 (1C, N=CH-C); 128.0 (2C, CH₂-C-C-H); 129.6 (1C, COOMe-C); 129.9 (2C, CH₂-C-COMe); 139.2 (1C, N-CH₃); 140.2 (1C, SO₂-C); 142.1 (1C, CH₂-C), 166.9 (1C, COOMe) ppm. HRMS (ESI⁺) calcd. for C₁₅H₁₄N₂O₅S⁺: 310.0856; found: 310,0845.

**Compound 2ah.** Methyl 4-((1-methyl-1H-imidazole-4-yl)benzozate. A solution of methyl 4-(((1-methyl-1H-imidazole)-4-sulfamidomethyl)benzozate (1ah) (14.5 mg; 46.9 μmol) in MeCN (15 mL) was loaded on the photo reactor with a flow rate of 0.7 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduction was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.20, ethyl acetate) to yield the title compound (5.9 mg; 27.3 μmol; 58%) as a white solid.

1H NMR (300 MHz, CDCl₃) δ = 3.73 – 3.78 (s, 3H, N-CH₃); 3.89 – 3.93 (s, 3H, O-CH₃); 7.27 – 7.29 (d, δJHH = 1.3, 1H, NeMe₆-C-C); 7.58 – 7.63 (m, 1H, N=CH-N); 7.79 – 7.86 (m, 2H, CH₂-C-COMe), 8.01 – 8.08 (m, 2H, CH₂-C-C-COMe) ppm. 13C NMR (75 MHz, CDCl₃) δ = 33.9 (N-CH₃); 52.1 (O-CH₃); 117.5 (1C, N-C-H); 124.6 (2C, CH₂-C-COMe); 128.4 (1C, C-COMe), 130.2 (2C, C-COMe).
Compound 1ai. Methyl 4-((thiophene-2-sulfonamido)methyl)benzoate. A solution of thiophene-2-sulfonyl chloride (100 mg, 0.55 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (116 mg, 0.58 mmol, 1 eq.) and N,N-dimethylpropylamine (155 mg, 210 µL, 1.21 mmol, 2.2 eq.) in DCM (2 mL) was stirred for 2 h at room temperature. After dilution with DCM (8 mL) the solution was washed with water (4 mL), aqueous hydrochloric acid (1 M, 4 mL) and water (4 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated under reduced pressure. The residue was purified by open column chromatography (silica, R=0.13, DCM) to yield the title compound (162 mg; 0.52 mmol; 95%) as a crystalline solid.

\(^1H\) NMR (300 MHz; CDCl\(_3\)): \(\delta = 3.84-3.98\) (s, 3H, -OCH\(_3\)), 4.22-4.36 (d, 2H, \(J_{HH} = 6.3\) Hz, -CH\(_2\)-), 4.87-5.02 (t, 1H, \(J_{HH} = 6.3\) Hz, -NH), 7.04-7.12 (dd, 1H, \(J_{HH} = 5.0, 3.8\), S-CH-CH-CH), 7.27-7.37 (d, 2H, \(J_{HH} = 8.2\) Hz, -CH-CH-C-COO), 7.56-7.65 (m, 2H, S-CH-CH-CH), 7.89-8.01 (d, 2H, \(J_{HH} = 8.2\) Hz, CH-CH-C-COOMe) ppm. \(^13C\) NMR (75.5 MHz; CDCl\(_3\)): \(\delta = 47.3\) (1C, -CH\(_2\)-), 52.3 (1C, -OCH\(_3\)), 127.6 (1C, S-CH-CH-CH), 127.8 (2C, CH-CH-C-COO), 130.0 (1C, -C-COO), 130.2 (2C, CH-CH-C-CH), 132.4 & 132.6 (2C, S-CH-CH-CH), 140.9 (1C, CH-CH), 141.3 (1C, -C-SO\(_2\)), 166.8 (1C, -COOMe) ppm. HRMS (ESI\(^+\)) calcd. for C\(_{13}\)H\(_8\)NO\(_3\)S\(_2\): 312.0359; found: 312.0357. HRMS (ESI\(^+\)) calcd. for C\(_{13}\)H\(_8\)NO\(_3\)S\(_2\): 310.0213; found: 310.0212.

Compound 2ai. Methyl 4-((thiophen-2-yl)benzyl)benzoate. A solution of methyl 4-((thiophene-2-sulfonamido)methyl)benzoate (1ai) (20.5 mg; 65.8 µmol) in MeCN (10 mL) was loaded on the photo reactor with a flow rate of 4 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduction was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, R=0.80, DCM) to yield the title compound (4.5 mg; 20.6 µmol; 31%) as a white solid.

\(^1H\) NMR (300 MHz; CDCl\(_3\)): \(\delta = 3.93\) (s, 3H, -OCH\(_3\)), 7.10-7.13 (dd, 1H, \(J_{HH} = 5.1, 3.6\), S-CH-CH-CH), 7.33-7.45 (m, 2H, S-CH-CH-CH), 7.64-7.73 (d, 2H, \(J_{HH} = 8.5\) Hz, CH-CH-C-COO), 7.97-8.08 (d, 2H, \(J_{HH} = 8.5\) Hz, CH-CH-C-COOMe) ppm. \(^13C\) NMR (75.5 MHz; CDCl\(_3\)): \(\delta = 52.3\) (1C, -OCH\(_3\)), 124.6 & 126.4 (2C, S-CH-CH-CH), 125.7 (2C, CH-CH-C-COO), 128.5 (1C, S-CH-CH), 128.9 (1C, C-SO\(_2\)), 130.4 (2C, CH-CH-C-COO), 138.8 (1C, S-C-C), 143.2 (1C, S-C), 166.9 (1C, -COOMe) ppm. HRMS (ESI\(^+\)) calcd. for C\(_{13}\)H\(_8\)NO\(_3\)S\(_2\): 219.0474; found: 219.0477.

Compound 1aj. Methyl 4-((benzo[b]thiophene-2-sulfonamido)methyl)benzoate. A solution of benzo[b]thiophene-2-sulfonyl chloride (50 mg, 0.21 mmol, 1 eq.), methyl 4-((aminomethyl)benzoate hydrochloride (47.7 mg, 0.24 mmol, 1.1 eq.) and N,N-dimethylpropylamine (61.1 mg, 0.32 µL, 0.47 µmol, 2.2 eq.) in DCM (3 mL) was stirred for 3 h at room temperature. The mixture was washed with water (3 mL) and aqueous hydrochloric acid (0.5 M, 3 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated under reduced pressure. The residue was purified by open column chromatography (silica, R=0.26, chloroform/ethyl acetate 19:1) to yield the title compound (72.1 mg, 0.21 mmol, 93%) as a white solid.

\(^1H\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.89\) (s, 3H, -OCH\(_3\)), 4.32 (d, 2H, \(J_{HH} = 6.2\) Hz, -NH-CH\(_2\)), 5.11 (1H, \(J_{HH} = 6.3\) Hz, -NH), 7.36 - 7.29 (m, 2H, -CH-CH-C-C(O)-O), 7.54 - 7.42 (m, 2H, -CH-CH-CH-CH-C), 7.89 - 7.83 (m, 3H, -CH-CH-CH-CH-C), 7.95 - 7.89 (m, 2H, -CH-CH-C-C(O)-O) ppm. \(^13C\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 47.3\) (1C, -NH-CH\(_2\)), 52.3 (1C, -OCH\(_3\)), 122.8 (1C, S-CH-CH), 125.7 (1C, -S-C-CH-CH), 125.8 (1C, -S-C-CH-CH), 127.5 (1C, -S-C-CH-CH), 127.8 (2C, -C(O)=C(CH-CH)), 129.8 (1C, -C(O)=C), 129.8 (1C, -S-C-CH-CH), 130.0 (2C, -C(O)=C(CH-CH)), 137.6 (-S-C-SO\(_2\)), 140.6 (1C, -S-C-C), 141.2 (1C, -S-C-C), 141.8 (1C, -NH-CH\(_2\)-C), 166.8 (1C, -C(O)=O) ppm. HRMS (ESI\(^+\)) calcd. for C\(_{13}\)H\(_8\)NO\(_3\)S\(_2\): 362.0515, found: 362.0520.
Compound 2aj. Methyl 4-(benzo[b]thiophen-2-yl)benzoate. A solution of methyl 4-(benzo[b]thiophene-2-sulfonamido)methyl)benzoate (1a) (21.1 mg, 58.4 μmol) in MeCN (3 mL) was loaded on the photo reactor with a flow rate of 1 mL/min and irradiated with UV light (254 nm) at room temperature. The solvent fraction containing the photoproduct was collected and the solvent was removed under reduced pressure. The residue was purified by open column chromatography (silica, Rf=0.75, DCM) to yield the title compound (2,8 mg, 10,4 μmol, 18%) as a faintly red solid.

$^1$H-NMR (300 MHz, CDCl$_3$) δ = 8.12 – 8.06 (m, 2H, -CH-C-C(=O)-O-), 7.88 – 7.75 (m, 4H, -CH-CH-CH-C-CH-C-C-C-CH-), 7.66 (d, 1H, $^3$J$_{HH}$ = 6.0 Hz, -S-C-CH-C-), 7.42 – 7.31 (m, 2H, -CH-CH-CH-CH-), 3.95 (s, 3H, -O-CH$_3$) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$) δ = 166.8 (1C, -C(=O)-O-), 142.9 (1C, -CH-CH-CH-C-S-C-), 140.6 (1C, -CH-CH-CH-C-S-C-), 140.0 (1C, -CH-CH-CH-C-S-C-), 138.7 (1C, -S-C-CH-CH-C-), 130.4 (2C, -C(=O)-C-CH-), 129.7 (1C, -C(=O)-C-CH-), 126.3 (2C, -C(=O)-C-CH-), 125.1 (1C, -S-C-CH-CH-), 124.9 (1C, -S-C-CH-CH-CH-), 124.1 (1C, -S-C-CH-CH-CH-CH-), 122.5 (1C, -S-C-CH-CH-CH-), 121.2 (1C, -S-C-CH-C-), 52.4 (1C, -O-CH$_3$) ppm. HRMS (ESI$^+$) calcd. for C$_{16}$H$_{13}$O$_2$S$: 269.0631, found: 269.0634.
Computational details

The ground state potential energy surface of \( 1a, 1p \) and \( 1aa \) were sampled by means of relaxed scans and conformer analysis. All ground state density functional theory (DFT) calculations were carried out using the range-separated exchange correlation functional CAM-B3LYP\(^4\) and the all-electron def2-TZVP triple-\( \zeta \) basis set\(^5\). Dispersion interactions were taken into account by Grimme’s D3-model with Becke-Johnson damping\(^6\).\(^7\). Relaxed scans were performed with Gaussian 16, Revision B.01\(^8\) at the DFT level (CAM-B3LYP/def2-TZVP) by varying the central (C-N-S-C)-dihedral angle in the sulfonamide-linker from -180° to 180° in 37 steps while equilibrating the remaining degrees of freedom at each step.

Possible conformers of the biaryl substrates were generated by the simulated annealing procedure as implemented in Grimme’s extended tight binding code GFN-xTB 5.8 using the GFN2-parametrization. Effects of solvation (acetonitrile) on the conformer geometries were taken into account by the generalized Born solvent area (GBSA) continuum solvation model\(^9\). Improved energies\(^10\) for the conformers (generated by xTB) were calculated with the domain-based local pair natural orbital coupled cluster approach with triples corrections (DLPNO–CCSD(T)) as implemented in ORCA 4.0.1\(^11\)-\(^12\). The def2-QZVPP and the corresponding auxiliary basis sets were utilized\(^13\)-\(^15\). Solvent effects (acetonitrile, \( \varepsilon = 36.6, n = 1.344 \)) on the coupled cluster single point energies were taken into account by the conductor-like polarizable continuum model (CPCM)\(^16\)-\(^17\). Tight criteria were used for the self-consistent-field convergence and the truncation threshold in the DLPNO procedure (TightPNO, \( T_{\text{CutPNO}} = 10^{-6} \), \( T_{\text{CutPNO}} = 10^{-7}, T_{\text{CutMKN}} = 10^{-4} \))\(^18\). To visualize the correlation between the conformer bonding parameters and their coupled cluster energies, a principal component analysis was conducted using a set of eight internal coordinates as features.

Transition state (TS) optimizations, subsequent vibrational analysis and reaction path calculations were carried out at the DFT level, while the nature of the first-order saddle points was confirmed by vibrational analysis. Minimum energy paths were obtained by calculating the intrinsic reaction coordinate (IRC) using the Hessian predictor-corrector method as implemented in Gaussian\(^19\)-\(^20\) to verify that the optimized TS connects the presumed educt and product of the biaryl coupling reaction. The exact Hessian was recalculated every seventh IRC step. Equally spaced geometries were sampled from both sides of the IRC every sixth step, yielding reaction paths for the subsequent excited state calculations.

All excited-state calculations were carried out in Gaussian 16 using time-dependent DFT (TDDFT) and along the sampled IRC-images. The same basis set and dispersion correction model as for the preliminary ground state DFT calculations was applied. This computational setup allows a balanced description of local as well as of charge transfer excitations among the \( \pi \)-systems of educt and product states.\(^21\) Vertical excitation energies and oscillator strengths for the six lowest singlet excited states were calculated for the sampled geometries along the IRC. Solvent effects (acetonitrile) on the vertical excitation energies and oscillator strengths were taken into account by CPCM. Excited state characters were interpreted in terms of natural transition orbitals (NTOs)\(^22\) as calculated by Multiwfn 3.5\(^23\).
Ground state calculations

Conformational analysis

Definition of internal coordinates for the PCA

![Figure S6](image)

**Figure S6**: Atom labels used in defining the internal coordinates for the principal component analysis (PCA) of 1a, 1p and 1aa.

**Table S2**: Definition of the eight internal coordinates used as features in the PCA.

| Internal coordinate type | Indices          |
|--------------------------|------------------|
| Distance                 | C6-C7            |
| Distance                 | C5-C1            |
| Angle                    | C5-S4-N3         |
| Angle                    | S4-N3-C2         |
| Angle                    | N3-C2-C1         |
| Angle                    | C5-N3-C2         |
| Dihedral                 | C5-S4-N3-C2      |
| Dihedral                 | S4-N3-C2-C1      |
**Conformers of 1p**

Figure S7: Conformers of 1p obtained at the GFN2-xTB/GBSA (acetonitrile) level of theory.

Figure S8: Scatter plot of the DLPNO-CCSD(T)/def2-QZVPP/CPCM (acetonitrile) energies for the first two principal components of the PCA for 1p. All energies are given in relation to the minimum energy (conformer 8).
Conformers of 1a

Figure S9: Conformers of 1a obtained at the GFN2-xTB/GBSA (acetonitrile) level of theory.
Figure S10: Scatter plot of the DLPNO-CCSD(T)/def2-QZVPP/CPCM (acetonitrile) energies for the first two principal components of the PCA for 1a. All energies are given in relation to the minimum energy (conformer 2). Conformers with energies above 30 kJ/mol (conformers 17, 26, 28 and 32) were excluded.
Figure S11: Conformers of 1aa obtained at the GFN2-xTB/GBSA (acetonitrile) level of theory.
Figure S12: Scatter plot of the DLPNO-CCSD(T)/def2-QZVPP/PCM (acetonitrile) energies for the first two principal components of the PCA for 1a. All energies are given in relation to the minimum energy (conformer 6). Conformers with energies above 30 kJ/mol (conformers 28-36) were excluded.
Frontier molecular orbitals

Figure S13: Isocontour plots and energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for linear and horseshoe conformations of 1a, 1p and 1aa as obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.
Intrinsic Reaction Coordinate of 1p

**Figure S14:** Selected bond lengths over the course of the IRC for 1p as obtained at the CAM-B3LYP/def2-TZVP level of theory.

Intrinsic Reaction Coordinate of 1a

**Figure S15:** Selected bond lengths over the course of the IRC for 1a as obtained at the CAM-B3LYP/def2-TZVP level of theory.
Figure S16: Selected bond lengths over the course of the IRC for 1aa as obtained at the CAM-B3LYP/def2-TZVP level of theory.
Excited state calculations

Comparison between experimental and calculated spectrum

Figure S17: Comparison between experimental (dashed line) and calculated spectrum of 1p, 1a and 1aa as obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.
Nomenclature

Figure S18: π-orbitals located on the S-linked phenyl residue (green) are denoted by a S-subscript (π_S), whereas π-orbitals located on the CH2-NH-linked phenyl residue (blue) are given a N-subscript (π_N).

TDDFT spectrum of 1p, horseshoe

Table S3: Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs of 1p for a horseshoe conformation at the educt side of the IRC obtained at the CAM-B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

| State | λ/nm | ΔE/eV | f   | Transition Weight/% |
|-------|------|-------|-----|---------------------|
| S1    | 230.5| 5.38  | 0.0125 | π_S → π_S 67 |
|       |      |       |       | π_S → π_S 33 |
| S2    | 226.6| 5.47  | 0.0007 | π_N → π_N 52 |
|       |      |       |       | π_N → π_N 48 |
| S3    | 213.3| 5.81  | 0.1169 | π_S → π_S 86 |
| S4    | 206.1| 6.02  | 0.0550 | π_N → π_S, π_N, σ_CC 74 |
|       |      |       |       | π_N → π_N 19 |
| S5    | 200.2| 6.19  | 0.0028 | π_N → π_S 87 |
| S6    | 194.6| 6.37  | 0.0172 | π_N → π_S 94 |
Table S4: Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs for a linear form of 1p (linear minimum of the relaxed scan) obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.

| State | λ/nm | ΔE/eV | f    | Transition          | Weight/% |
|-------|------|-------|------|---------------------|----------|
| S₁    | 229.3| 5.41  | 0.0122| \( \pi_S \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 63       |
|       |      |       |      | \( \pi_S \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 37       |
| S₂    | 226.0| 5.49  | 0.0001| \( \pi_N \rightarrow \pi_N \) \( \pi_N \rightarrow \pi_N \) | 54       |
|       |      |       |      | \( \pi_N \rightarrow \pi_N \) \( \pi_N \rightarrow \pi_N \) | 45       |
| S₃    | 210.5| 5.89  | 0.2619| \( \pi_S \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 83       |
| S₄    | 204.1| 6.08  | 0.0350| \( \pi_N \rightarrow \pi_N \) \( \pi_N \rightarrow \pi_N \) | 68       |
|       |      |       |      | \( \pi_N \rightarrow \pi_N \) \( \pi_N \rightarrow \pi_N \) | 30       |
| S₅    | 189.0| 6.56  | 0.5052| \( \pi_N \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 57       |
| S₆    | 183.6| 6.75  | 0.4564| \( \pi_S \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 63       |
|       |      |       |      | \( \pi_S \rightarrow \pi_S \) \( \pi_S \rightarrow \pi_S \) | 36       |

Figure S19: Leading NTO pairs for the horseshoe conformation of 1p.

**TDDFT spectrum of 1p, linear**
Figure S20: Leading NTO pairs for the linear form of 1p.
**TDDFT spectrum of 1a, horseshoe**

**Table S5:** Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs of 1a for a horseshoe conformation at the educt side of the IRC obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.

| State | λ/nm | ΔE/eV | f     | Transition | Weight/% |
|-------|------|-------|-------|------------|----------|
| S₁    | 242.1| 5.12  | 0.0157| π_N → π_N  | 74       |
|       |      |       |       | π_N → π_N  | 25       |
| S₂    | 234.1| 5.30  | 0.0664| π_S → π_S, σ_CC | 57 |
|       |      |       |       | π_S → π_S  | 28       |
| S₃    | 229.7| 5.40  | 0.3611| π_N → π_N  | 70       |
|       |      |       |       | π_N → π_N  | 16       |
| S₄    | 227.8| 5.44  | 0.0158| n_O → π_N  | 98       |
| S₅    | 216.5| 5.73  | 0.2116| π_S, π_N → π_S | 58 |
| S₆    | 195.9| 6.33  | 0.0444| π_S → π'_N, σ_CC | 82 |

**Figure S21:** Leading NTO pairs for the horseshoe conformation of 1a.
**TDDFT spectrum of 1a, linear**

**Table S6:** Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs for a linear form of 1a (linear minimum of the relaxed scan) obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.

| State | λ/nm  | ΔE/eV | f    | Transition                  | Weight/% |
|-------|-------|-------|------|-----------------------------|----------|
| S₁    | 240.4 | 5.16  | 0.0212 | π_{N} → π_{N}  \π_{N} → π_{N} | 74/26    |
| S₂    | 231.9 | 5.35  | 0.0063 | π_{S} → π_{S}  \π_{S} → π_{S} | 53/47    |
| S₃    | 228.2 | 5.43  | 0.0767 | n_{O} → π_{N}             | 97       |
| S₄    | 227.7 | 5.44  | 0.5335 | π_{N} → π_{N}             | 90       |
| S₅    | 215.6 | 5.75  | 0.2402 | π_{S} → π_{S}             | 83       |
| S₆    | 193.5 | 6.41  | 0.0721 | p_{N} → π_{N}  \π_{N} → π_{N} | 79/20    |

Figure S22: Leading NTO pairs for the linear form of 1a.
Comparison of excited states along the IRC for 1a and 1p

Table S7: Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs of 1aa for a horseshoe conformation at the educt side of the IRC obtained at the CAM-B3LYP/def2-TZVP/CPCM (acetonitrile) level of theory.

| State | λ/nm | ΔE/eV | f    | Transition             | Weight/% |
|-------|------|-------|------|------------------------|----------|
| S1    | 246.0| 5.04  | 0.0338 | π_S → π^*_S          | 81       |
| S2    | 235.6| 5.26  | 0.0124 | π_O → π^*_S          | 99       |
| S3    | 233.0| 5.32  | 0.0086 | π_O → π^*_S          | 92       |
| S4    | 230.2| 5.39  | 0.0100 | π_N → π^*_N          | 64       |
| S5    | 225.6| 5.50  | 0.0086 | π_N → π^*_N          | 98       |
| S6    | 211.0| 5.88  | 0.0022 | π_N → π^*_S          | 98       |
| S7    | 207.3| 5.98  | 0.1010 | π_N → π^*_N          | 68       |
| S8    | 195.9| 6.33  | 0.0293 | σ_CG → π^*_S         | 90       |

Figure S23: Comparison between excited states of 1a and 1p along their respective IRCs as obtained at the TDDFT level of theory (CAM-B3LYP/def2-TZVP/CPCM (acetonitrile)).
Figure S24: Leading NTO pairs for the horseshoe conformation of 1aa.
**TDDFT spectrum of 1aa, linear**

**Table S8:** Calculated low-lying excited singlet states, excitation wavelengths (λ/nm), excitation energies (ΔE/eV), oscillator strengths and leading NTO pairs of 1aa for a linear conformation (linear minimum of the relaxed scan) obtained at the CAM-B3LYP/def2-TZVP/PCM (acetonitrile) level of theory.

| State | λ/nm | ΔE/eV | f   | Transition  | Weight/% |
|-------|------|-------|-----|-------------|----------|
| S₁    | 245.4| 5.05  | 0.0405 | πₓ → πₓ*   | 81       |
| S₂    | 235.3| 5.27  | 0.0049 | n₀ → πₓ*     | 99       |
| S₃    | 232.2| 5.34  | 0.4409 | πₓ → πₓ*     | 76       |
| S₄    | 230.0| 5.39  | 0.1631 | πₓ → πₓ*     | 50       |
| S₅    | 211.0| 5.88  | 0.0347 | πₓ → πₓ*     | 28       |
| S₆    | 207.8| 5.97  | 0.0959 | πₓ → πₓ*     | 95       |

**Figure S25:** Leading NTO pairs for the linear form of 1aa.
Video of the mechanism

Figure S26: Video of charge density difference in the S1 along the calculated IRC of 1aa. Blue isosurfaces denote regions of charge density decrease, whereas red isosurfaces denote regions of charge density increase.
Figure S27: $^1$H NMR spectrum of 1d.

Figure S28: $^{13}$C NMR spectrum of 1d.
Figure S29: $^1$H NMR spectrum of 2d.

Figure S30: $^{13}$C NMR spectrum of 2d.
Figure S31: $^1$H NMR spectrum of 1e.

Figure S32: $^{13}$C NMR spectrum of 1e.
Figure S33: $^1$H NMR spectrum of 2e.

Figure S34: $^{13}$C NMR spectrum of 2e.
Figure S35: $^1$H NMR spectrum of 1f.

Figure S36: $^{13}$C NMR spectrum of 1f.
Figure S37: $^1$H NMR spectrum of 2f.

Figure S38: $^{13}$C NMR spectrum of 2f.
Figure S39: $^1$H NMR spectrum of 1g.

Figure S40: $^{13}$C NMR spectrum of 1g.
Figure S41: $^1$H NMR spectrum of 2g.

Figure S42: $^{13}$C NMR spectrum of 2g.
Figure S45: $^1$H NMR spectrum of 2i.

Figure S46: $^{13}$C NMR spectrum of 2i.
Figure S47: $^1$H NMR spectrum of 1.

Figure S48: $^{13}$C NMR spectrum of 1.
Figure S49: $^1$H NMR spectrum of J.

Figure S50: $^{13}$C NMR spectrum of J.
Figure S51: $^1$H NMR spectrum of 2k.

Figure S52: $^{13}$C NMR spectrum of 2k.
Figure S53: $^1$H NMR spectrum of 1l.

Figure S54: $^{13}$C NMR spectrum of 1l.
Figure S55: $^1$H NMR spectrum of 2I.

Figure S56: $^{13}$C NMR spectrum of 2I.
Figure S57: $^1$H NMR spectrum of 1m.

Figure S58: $^{13}$C NMR spectrum of 1m.
Figure S59: $^1$H NMR spectrum of 2m.

Figure S60: $^{13}$C NMR spectrum of 2m.
Figure S61: $^1$H NMR spectrum of 1n.

Figure S62: $^{13}$C NMR spectrum of 1n.
Figure S63: $^1$H NMR spectrum of 2n.

Figure S64: $^{13}$C NMR spectrum of 2n.
Figure S65: $^1$H NMR spectrum of 10.

Figure S66: $^{13}$C NMR spectrum of 10.
Figure S67: $^1$H NMR spectrum of 2o.

Figure S68: $^{13}$C NMR spectrum of 2o.
Figure S69: $^1$H NMR spectrum of 1r.

Figure S70: $^{13}$C NMR spectrum of 1r.
Figure S71: $^1$H NMR spectrum of 2r.

Figure S72: $^{13}$C NMR spectrum of 2r.
Figure S73: $^1$H NMR spectrum of 1v.

Figure S74: $^{13}$C NMR spectrum of 1v.
Figure S75: $^1$H NMR spectrum of 2v.

Figure S76: $^{13}$C NMR spectrum of 2v.
Figure S77: $^1$H NMR spectrum of 1w.

Figure S78: $^{13}$C NMR spectrum of 1w.
Figure S79: $^1$H NMR spectrum of 2w.

Figure S80: $^{13}$C NMR spectrum of 2w.
Figure S81: $^1$H NMR spectrum of 1x.

Figure S82: $^{13}$C NMR spectrum of 1x.
Figure S83: $^1$H NMR spectrum of 2x.

Figure S84: $^{13}$C NMR spectrum of 2x.
Figure S85: $^1$H NMR spectrum of 1y.

Figure S86: $^{13}$C NMR spectrum of 1y.
Figure S87: ¹H NMR spectrum of 2y.

Figure S88: ¹³C NMR spectrum of 2y.
Figure S89: $^1$H NMR spectrum of 1z.

Figure S90: $^{13}$C NMR spectrum of 1z.
Figure S91: $^1$H NMR spectrum of 2z.

Figure S92: $^{13}$C NMR spectrum of 2z.
Figure S93: ^1^H NMR spectrum of 1aa.

Figure S94: ^1^C NMR spectrum of 1aa.
Figure S95: $^1$H NMR spectrum of 1ab.

Figure S96: $^{13}$C NMR spectrum of 1ab.
Figure S97: $^1$H NMR spectrum of 2ab.

Figure S98: $^{13}$C NMR spectrum of 2ab.
Figure S99: $^1$H NMR spectrum of 1ac.

Figure S100: $^{13}$C NMR spectrum of 1ac.
Figure S101: $^1$H NMR spectrum of 2ac.

Figure S102: $^{13}$C NMR spectrum of 2ac.
Figure S103: $^1$H NMR spectrum of 1ad.

Figure S104: $^{13}$C NMR spectrum of 1ad.
Figure S105: $^1$H NMR spectrum of 1ae.

Figure S106: $^{13}$C NMR spectrum of 1ae.
Figure S107: $^1$H NMR spectrum of 2ae.

Figure S108: $^{13}$C NMR spectrum of 2ae.
Figure S109: $^1$H NMR spectrum of 1af.

Figure S110: $^{13}$C NMR spectrum of 1af.
Figure S11: $^1$H NMR spectrum of 2af.

Figure S12: $^{13}$C NMR spectrum of 2af.
Figure S113: $^1$H NMR spectrum of 1a.

Figure S114: $^{13}$C NMR spectrum of 1a.
Figure S115: $^1$H NMR spectrum of 2ag.

Figure S116: $^{13}C$ NMR spectrum of 2ag.
Figure S117: $^1$H NMR spectrum of 1ah.

Figure S118: $^{13}$C NMR spectrum of 1ah.
Figure S119: $^1$H NMR spectrum of 2ah.

Figure S120: $^{13}$C NMR spectrum of 2ah.
Figure S121: $^1$H NMR spectrum of 1ai.

Figure S122: $^{13}$C NMR spectrum of 1ai.
Figure S123: $^1$H NMR spectrum of 2ai.

Figure S124: $^{13}$C NMR spectrum of 2ai.
Figure S125: $^1$H NMR spectrum of 1aj.

Figure S126: $^{13}$C NMR spectrum of 1aj.
Figure S127: $^1$H NMR spectrum of 2aj.

Figure S128: $^{13}$C NMR spectrum of 2aj.
Figure S129: $^1$H NMR spectrum of 1ak.

Figure S130: $^{13}$C NMR spectrum of 1ak.
Figure S131: $^1$H NMR spectrum of 2ak.

Figure S132: $^{13}$C NMR spectrum of 2ak.
Figure S133: $^1$H NMR spectrum of 1a.

Figure S134: $^{13}$C NMR spectrum of 1a.
Figure S135: $^1$H NMR spectrum of 1am.

Figure S136: $^{13}$C NMR spectrum of 1am.
Figure S137: $^1$H NMR spectrum of 1an.

Figure S138: $^{13}$C NMR spectrum of 1an.
Figure S139: $^1$H NMR spectrum of 1aO.

Figure S140: $^{13}$C NMR spectrum of 1aO.