Supporting Information


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1. General Information

Reaction temperatures are reported as the ones of the heat transfer medium surrounding the vessel unless otherwise stated.

The following solvents DCM, MeCN, PhMe and THF were purified by passing through a Pure Solv™ column drying system from Innovative Technology, Inc. Additional anhydrous solvents (≤50 ppm water) were purchased from Acros Organics, Sigma-Aldrich or Alfa Aesar and stored over molecular sieves under a nitrogen atmosphere. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, TCI Chemicals and Fluorochem, and used as received, unless otherwise stated.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck) and they were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm) and/or by staining. For staining the TLC plates were dipped into a solution of KMnO4 (1 g KMnO4, 6 g K2CO3 and 0.1 g KOH in 100 mL H2O) and developed with a heat gun if necessary. Flash chromatography was performed using Geduran® Silica Gel 60 (0.040 - 0.063 nm) or Iatrobeads 6RS - 8060 silica gel with appropriate mixtures of cyclohexane and ethyl acetate and compressed air.

NMR spectra were recorded at room temperature on a Bruker AV 300 or or 500 MHz spectrometer running at 300 or 500 MHz for 1H, 75 or 126 MHz for 13C, 282 or 471 MHz for 19F in solvents as indicated. Chemical shifts (δ) for 1H- and 13C-NMR spectra are given in ppm relative to tetramethylsilane (TMS) using the residual solvent signals as references for 1H and 13C NMR spectra (CDCl3: δH = 7.26 ppm, δC = 77.16 ppm, (CD3)2CO: δH = 2.05 ppm, δC = 29.84, 206.26 ppm, C6D6: δH = 7.16 ppm, δC = 134.19, 129.26, 128.25, 125.96 ppm, CD2Cl2: δH = 5.32 ppm, δC = 53.84 ppm).[1] 19F-NMR spectra are not externally calibrated and chemical shifts is given relative to CCl3F as received from the automatic data processing. 13C-NMR and 19F-NMR spectra were acquired on a broadband decoupled mode. Chemical shifts are generally reported with two (1H) or one (all other nuclei) digits after the decimal point. NMR-data are reported as follows: chemical shift (multiplicity [s = singlet, d = doublet,
t = triplet, q = quartet, p = quintuplet, hept = heptuplet, m = multiplet, br = broad), coupling constants (J, Hz) and integration). All spectra were processed using the MestReNova program.

High-Resolution Mass Spectra (HRMS) were recorded on an Agilent Technologies 6120 Quadrupole LC/MS coupled with an SFC Agilent Technologies 1260 Infinity Series instrument for the ESI-MS (Electrospray Ionization) or on an Agilent Technologies 5977B MSD coupled with an Agilent Technologies 7820A GC System for the EI-MS (Electron Ionization mass spectroscopy). MassWorks software version 4.0.0.0 (Cerno Bioscience) was used for the formula identification. MassWorks is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra. Obtained data are expressed in mass/charge (m/z) units.

UV-Vis measurements were acquired on an Agilent 8453 UV-Vis Spectrophotometer controlled by UV-Visible ChemStation Software. Emission spectra were recorded on a JASCO Spectrofluorometer FP-8600 equipped with a TC-815 Peltier thermostated single cell holder (water-cooled) controlled by Spectra Manager Version 2.10.01. Time resolved emission spectra were carried out using an Edinburg Instruments FS5 Spectrofluorometer, and a 450 nm EPL laser.

Cyclic Voltammetry (CV) experiments were acquired on an IVIUM Technologies CompactStat controlled by IviumSoft version 2.124 offering a compliance voltage of up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 1 A current range. HPLC grade acetone solvent was used for all measurements. Tetra-n-butylammonium hexafluorophosphate was used as supporting electrolyte at 0.1 M concentration. All cyclic voltammetry experiments were performed using a conventional three-electrode system, containing a coiled Pt wire acting as counter electrode, an Ag/AgCl saturated solution as reference electrode and a glassy carbon working electrode (A = 0.071 cm²) at 20 mV/s scan rate. All the electrodes were
purchased from Metrohm. Redox-active species were dissolved at 1.0 nM concentration and these solutions were throughout the measurements.

A custom-made temperature-controlled photoreactor setup was used for the photocatalytic reactions (Figure S1). The irradiation takes place at the desired wavelengths (365, 385, 420, 450 or 540 nm) using 380 mW single LEDs, located 1 cm beneath the base of the vial. Reaction temperature is kept at 20-25 °C using a recirculating chiller.

Figure S1. Experimental setup employed during photocatalytic reactions.

2. Synthesis and Characterization of Substrates

2.1. General Procedure and Characterization of Sulfides SI-1

General procedure A for the synthesis of sulfides SI-1:

Compounds SI-1a-c were prepared following a slightly modified procedure reported in the literature.\[^3\] 1-(2-bromophenyl)ethan-1-one (1 equiv) was added to a stirred solution of the corresponding sodium alkanethiolate (1.1 equiv) in THF (1.3M) and heated to 75 °C for 12 h. After this time, the reaction was cooled to room temperature, diluted with dichloromethane and washed with water (3x) and brine. The organic phase was dried over anhydrous MgSO₄ and concentrated under reduced
pressure. Then, the solid residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure products SI-1.

**General procedure B for the synthesis of sulfides SI-1:**

Compounds SI-1d-s were prepared following a slightly modified procedure reported in the literature.\[3\] The corresponding thiol (1.05 equiv) was added dropwise over 0.25 h to a stirred suspension of NaH (1.2 equiv) in THF or DMF (2 mL/mmol of thiol) at 0 °C (icebath). Afterwards, a solution of the bromide/chloride/fluoride compound (1 equiv) in THF or DMF (0.5 mL/mmol) was added and the reaction was heated to 75 °C for 12 h. After this time, the reaction was cooled to room temperature, diluted with dichloromethane and washed with water (3x) and brine. The organic phase was dried over anhydrous MgSO4 and concentrated under reduced pressure. Then, the solid residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure products SI-1.

**1-(2-(methylthio)phenyl)ethan-1-one (SI-1a)**

Following the general procedure A, the reaction of 1-(2-bromophenyl)ethan-1-one (2.1 mmol, 0.28 mL) and sodium methanethiolate (2.3 mmol, 160.1 mg) in THF (1.6 mL) at 75 ºC afforded the product SI-1a (88%, 305.3 mg) as a pale orange solid. \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.71 (dd, \(J = 7.9, 1.3\) Hz, 1H), 7.37 – 7.29 (m, 1H), 7.17 (d, \(J = 7.9\) Hz, 1H), 7.04 (t, \(J = 7.5\) Hz, 1H), 2.46 (s, 3H), 2.27 (s, 3H). Spectral data is in accordance with the literature.\[4\]

**1-(2-(isopropylthio)phenyl)ethan-1-one (SI-1b)**

Following the general procedure A, the reaction of 1-(2-bromophenyl)ethan-1-one (2 mmol, 0.27 mL) and sodium 2-propanethiolate (2.2 mmol, 215.9 mg) in THF (1.5 mL) at 75 ºC afforded the product SI-1b (75%, 292.3 mg) as a yellow oil. \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.65 (dd, \(J = 7.7, 1.0\) Hz, 1H), 7.46 – 7.36 (m, 2H), 7.21 (ddd, \(J = 7.7, 6.7, 1.8\) Hz, 1H), 3.46 (hept, \(J = 6.6\) Hz, 1H), 2.60 (s, 3H), 2.27 (s, 3H). Spectral data is in accordance with the literature.\[4\]

\(\text{SiPr}\)
1-(2-( tert-butylthio)phenyl) ethan-1-one (SI-1c)

Following the general procedure A, the reaction of
1-(2-bromophenyl)ethan-1-one (2 mmol, 0.27 mL) and sodium
2-methyl-2-propanethiolate (2.2 mmol, 246.8 mg) in THF (1.5 mL) at
75 °C afforded the product SI-1c (68%, 284.4 mg) as a yellow oil. \(^1\text{H NMR (300 MHz, CDCl}_3\)} \(\delta\) 7.58 (t, \(J = 8.3\) Hz, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 2.29 (s, 3H),
1.22 (s, 9H). Spectral data is in accordance with the literature.[5]

1-(2-( benzylthio)phenyl) ethan-1-one (SI-1d)

Following the general procedure B, the reaction of
1-(2-bromophenyl)ethan-1-one (2 mmol, 0.27 mL), NaH (60%, 2.4
mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in THF (5.5
mL) at 75 °C afforded the product SI-1d (71%, 342.8 mg) as a white solid. \(^1\text{H NMR (300 MHz, CDCl}_3\)} \(\delta\) 7.78 (d, \(J = 7.7\) Hz, 1H), 7.40 (d, \(J = 3.6\) Hz, 2H), 7.39 (d, \(J = 6.5\)
Hz, 2H), 7.34 – 7.17 (m, 4H), 4.13 (s, 2H), 2.59 (s, 3H). Spectral data is in accordance
with the literature.[6]

1-(2-( phenylthio)phenyl) ethan-1-one (SI-1e)

Following the general procedure B, the reaction of
1-(2-bromophenyl)ethan-1-one (2 mmol, 0.27 mL), NaH (60%, 2.4
mmol, 96 mg) and thiophenol (2.1 mmol, 0.21 mL) in THF (5.5 mL) at
75 °C afforded the product SI-1e (72%, 330.0 mg) as a yellow solid. \(^1\text{H NMR (300 MHz, CDCl}_3\)} \(\delta\) 7.83 (dd, \(J = 7.7, 1.6\) Hz, 1H), 7.56 – 7.52 (m, 2H), 7.43 – 7.40 (m, 3H),
7.28 – 7.14 (m, 2H), 6.89 (dd, \(J = 8.0, 1.2\) Hz, 1H), 2.67 (s, 3H). Spectral data is in
accordance with the literature.[7]

1-(2-(benzylthio)-4-fluorophenyl) ethan-1-one (SI-1f)

Following the general procedure B, the reaction of
1-(2-bromo-4-fluorophenyl)ethan-1-one (2.8 mmol, 600.0 mg), NaH
(60%, 3.4 mmol, 134.4 mg) and benzyl mercaptan (3.0 mmol, 0.35
mL) in THF (7.7 mL) at 75 °C afforded the product SI-1f (64%, 463.7 mg) as a white
solid. \(^1\text{H NMR (300 MHz, CDCl}_3\)} \(\delta\) 7.84 (dd, \(J = 8.7, 6.0\) Hz, 1H), 7.43 – 7.37 (m, 2H),
7.35 – 7.24 (m, 3H), 7.08 (dd, \( J = 10.5, 2.4 \) Hz, 1H), 6.84 (ddd, \( J = 8.7, 7.6, 2.4 \) Hz, 1H), 4.08 (s, 2H), 2.56 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 197.5, 164.8 (d, \( J = 255.0 \) Hz), 145.8 (d, \( J = 8.9 \) Hz), 135.5, 133.6 (d, \( J = 10.1 \) Hz), 130.7 (d, \( J = 2.6 \) Hz), 129.2, 128.8, 127.6, 113.0 (d = 25.1 Hz), 110.8 (d, \( J = 22.0 \) Hz), 37.7, 28.1; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \( \delta \) -105.6.

1-(2-(benzylthio)-4-methoxyphenyl)ethan-1-one (SI-1g)

Following the general procedure B, the reaction of 1-(2-bromo-4-methoxyphenyl)ethan-1-one (2.4 mmol, 408.1 mg), NaH (60%, 2.9 mmol, 115.2 mg) and benzyl mercaptan (2.5 mmol, 0.3 mL) in DMF (6.6 mL) at 75 ºC afforded the product SI-1g (63%, 412.9 mg) as a white solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.71 (d, \( J = 8.7 \) Hz, 1H), 7.41 – 7.34 (m, 2H), 7.29 – 7.15 (m, 3H), 6.79 (d, \( J = 2.4 \) Hz, 1H), 6.57 (dd, \( J = 8.7, 2.4 \) Hz, 1H), 4.02 (s, 2H), 3.68 (s, 3H), 2.45 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 197.1, 162.5, 144.8, 136.3, 133.7, 129.1, 128.6, 127.3, 127.1, 111.3, 108.8, 55.5, 37.3, 27.7.

1-(2-(benzylthio)-5-methoxyphenyl)ethan-1-one (SI-1h)

Following the general procedure B, the reaction of 1-(2-bromo-5-methoxyphenyl)ethan-1-one (2 mmol, 458.1 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in THF (5.5 mL) at 75 ºC afforded the product SI-1h (60%, 327.5 mg) as a yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.33 – 7.19 (m, 6H), 7.11 (d, \( J = 2.8 \) Hz, 1H), 6.91 (dd, \( J = 8.7, 2.8 \) Hz, 1H), 4.02 (s, 2H), 3.80 (s, 3H), 2.53 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 200.7, 157.6, 140.9, 136.9, 131.9, 128.9, 128.3, 127.2, 127.0, 117.0, 114.5, 55.3, 39.6, 29.4.

1-(2-(benzylthio)-5-bromophenyl)ethan-1-one (SI-1i)

Following the general procedure B, the reaction of 1-(2-fluoro-5-bromophenyl)ethan-1-one (2 mmol, 434.1 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in THF (5.5 mL) at 75 ºC afforded the product SI-1i (57%, 367.3 mg) as a pale yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.84 (d, \( J = 2.2 \) Hz, 1H), 7.48 (dd, \( J = 8.5, 2.2 \) Hz,
1H), 7.34 – 7.17 (m, 6H), 4.09 (s, 2H), 2.56 (s, 3H); \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 198.1, 139.5, 137.1, 135.7, 134.6, 133.1, 128.9, 128.5, 128.5, 127.4, 117.6, 37.8, 28.4.

1-(2-(benzylthio)-5-(trifluoromethyl)phenyl)ethan-1-one (SI-1j)

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i) 1) MeMgBr, Et\(_2\)O, 0 °C; 2) PCC, silica gel, DCM, rt.

Compound SI-2 was prepared following a previously reported procedure\(^{[8]}\) and spectral data is in accordance with the literature.\(^{[9]}\)

Following the general procedure B, the reaction of 1-(2-bromo-5-(trifluoromethyl)ethan-1-one (SI-2) (1.7 mmol, 453.9 mg), NaH (60%, 2 mmol, 81.6 mg) and benzyl mercaptan (1.9 mmol, 0.22 mL) in DMF (4.7 mL) at 75 °C afforded the product SI-1j (43%, 224.6 mg) as a pale yellow solid. \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J\) = 0.8 Hz, 1H), 7.57 (dd, \(J\) = 8.5, 1.5 Hz, 1H), 7.46 (d, \(J\) = 8.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.20 (m, 3H), 4.13 (s, 2H), 2.59 (s, 3H); \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 197.9, 146.4 (q, \(J\) = 1.0 Hz), 135.5, 134.6, 129.0, 128.7, 128.2 (q, \(J\) = 3.5 Hz), 127.6, 127.4 (q, \(J\) = 3.8 Hz), 126.4, 126.0 (q, \(J\) = 33.3 Hz), 123.8 (q, \(J\) = 271.8 Hz), 37.5, 28.1; \(^{19}F\) NMR (282 MHz, CDCl\(_3\)) \(\delta\) -62.3.

1-(6-(benzylthio)benzo[d][1,3]dioxol-5-yl)ethan-1-one (SI-1k)

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i) 1) MeMgBr, Et\(_2\)O, 0 °C; 2) PCC, silica gel, DCM, rt.

Compound SI-3 was prepared following a previously reported procedure\(^{[8]}\) and spectral data is in accordance with the literature.\(^{[10]}\)
Following the general procedure B, the reaction of 1-(6-bromobenzo[d][1,3]dioxol-5-yl)ethan-1-one (SI-3) (1.2 mmol, 291.7 mg), NaH (60%, 1.4 mmol, 57.6 mg) and benzyl mercaptan (1.3 mmol, 0.15 mL) in DMF (3.3 mL) at 75 ºC afforded the product SI-1k (57%, 195.8 mg) as a pale brown solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40 – 7.24 (m, 5H), 7.22 (s, 1H), 6.88 (s, 1H), 6.01 (s, 2H), 4.06 (s, 2H), 2.50 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 197.6, 151.1, 145.1, 136.3, 129.2, 128.7, 127.4, 110.2, 107.4, 102.2, 38.6, 28.6.

1-(3-(benzyloxy)-2-(benzylthio)phenyl)ethan-1-one (SI-1l)

![Chemical structure]

$\text{i)}$ K$_2$CO$_3$, BnBr, DMF, rt; $\text{ii)}$ 1) MeMgBr, Et$_2$O, 0 ºC; 2) PCC, silica gel, DCM, rt; $\text{iii)}$ HSBn, NaH, DMF, 75 ºC.

Compounds SI-4 and SI-5 were prepared following previously reported procedures$^{[8,11]}$ and spectral data is in accordance with the literature.$^{[12]}$

Following the general procedure B, the reaction of 1-(3-(benzyloxy)-2-bromophenyl)ethan-1-one (SI-5) (0.7 mmol, 213.6 mg), NaH (60%, 0.84 mmol, 33.6 mg) and benzyl mercaptan (0.74 mmol, 0.09 mL) in DMF (1.9 mL) at 75 ºC afforded the product SI-1l (61%, 150.0 mg) as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45 – 7.39 (m, 2H), 7.37 – 7.25 (m, 3H), 7.22 – 7.15 (m, 1H), 7.12 – 7.03 (m, 3H), 7.00 – 6.94 (m, 2H), 6.91 (dd, $J = 8.2, 0.7$ Hz, 1H), 6.74 (dd, $J = 7.6, 0.7$ Hz, 1H), 5.08 (s, 2H), 3.95 (s, 2H), 2.20 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 203.9, 159.7, 149.1, 138.1, 136.6, 130.0, 129.0, 128.8, 128.4, 128.2, 127.4, 127.1, 118.8, 118.6, 113.8, 71.1, 39.3, 31.3.
1-(1-(benzylthio)naphthalen-2-yl)ethan-1-one (SI-1m)

![Chemical structure of SI-1m]

Compound SI-6 was prepared following a previously reported procedure and spectral data is in accordance with the literature.

Following the general procedure B, the reaction of 1-(1-bromonaphthalen-2-yl)ethan-1-one (SI-6) (2 mmol, 498.2 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in DMF (5.5 mL) at 75 ºC afforded the product SI-1m (62%, 364.3 mg) as a pale yellow solid.

1H NMR (300 MHz, CDCl3) δ 8.60 (d, J = 8.0 Hz, 1H), 8.07 – 7.77 (m, 2H), 7.56 (pd, J = 6.9, 1.1 Hz, 2H), 7.31 (d, J = 8.4 Hz, 1H), 7.22 – 7.03 (m, 3H), 7.09 – 6.88 (m, 2H), 3.96 (s, 2H), 2.49 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 204.6, 146.9, 137.4, 134.1, 129.9, 128.8, 128.5, 128.3, 127.6, 127.4, 127.2, 127.0, 126.4, 122.7, 42.2, 31.6.

1-(3-(benzylthio)furan-2-yl)ethan-1-one (SI-1n)

![Chemical structure of SI-1n]

Compound SI-7 was prepared following a previously reported procedure and spectral data is in accordance with the literature.

Following the general procedure B, the reaction of 1-(3-bromofuran-2-yl)ethan-1-one (SI-7) (3.45 mmol, 652.1 mg), NaH (60%, 4.1 mmol, 166 mg) and benzyl mercaptan (3.6 mmol, 0.47 mL) in DMF (9.5 mL) at 75 ºC afforded the product SI-1n (87%, 696.9 mg) as a yellow solid.

1H NMR (300 MHz, CDCl3) δ 7.33 (d, J = 1.9 Hz, 1H), 7.33 – 7.08 (m, 5H), 6.41 (d, J = 1.9 Hz, 1H), 4.06 (s, 2H), 2.35 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 186.7, 146.8,
1-(3-(benzylthio)thiophen-2-yl)ethan-1-one (SI-1o)

Following the general procedure B, the reaction of 1-(3-bromothiophen-2-yl)ethan-1-one (2 mmol, 408.1 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in DMF (5.5 mL) at 75 ºC afforded the product SI-1o (83%, 412.9 mg) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 5.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.32 – 7.20 (m, 3H), 7.03 (d, $J$ = 5.2 Hz, 1H), 4.19 (s, 2H), 2.47 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 189.8, 143.7, 136.2, 132.1, 131.4, 128.9, 128.7, 127.6, 127.3, 38.1, 28.8.

1-(2-(benzylthio)pyridin-3-yl)ethan-1-one (SI-1p)

Compound SI-8 was prepared following a previously reported procedure$^{[8]}$ and spectral data is in accordance with the literature.$^{[15]}$

Following the general procedure B, the reaction of 1-(2-bromopyridin-3-yl)ethan-1-one (1 mmol, 110.4 mg), NaH (60%, 1.2 mmol, 48 mg) and benzyl mercaptan (1.05 mmol, 0.13 mL) in THF (2.8 mL) at 75 ºC afforded the product SI-1p (45%, 108.7 mg) as a pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.58 (dd, $J$ = 4.7, 1.8 Hz, 1H), 8.04 (dd, $J$ = 7.8, 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 – 7.17 (m, 3H), 7.09 (dd, $J$ = 7.8, 4.7 Hz, 1H), 4.44 (s, 2H), 2.57 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 197.6, 161.4, 151.7, 138.4, 138.0, 129.5, 129.0, 128.4, 126.9, 118.3, 34.9, 27.7.
1-(2-(benzylthio)quinolin-3-yl)ethan-1-one (SI-1q)

Following the general procedure B, the reaction of 1-(2-chloroquinolin-3-yl)ethan-1-one (0.8 mmol, 187.5 mg), NaH (60%, 1 mmol, 38.4 mg) and benzyl mercaptan (0.84 mmol, 0.10 mL) in DMF (2.2 mL) at 75 ºC afforded the product SI-1q (96%, 225.8 mg) as a pale yellow solid. 

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.40 (s, 1H), 7.97 (d, $J = 8.3$ Hz, 1H), 7.79 – 7.70 (m, 2H), 7.53 (d, $J = 7.1$ Hz, 2H), 7.44 (t, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.25 – 7.17 (m, 1H), 4.56 (s, 2H), 2.64 (s, 3H); 

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.5, 158.7, 148.4, 139.6, 138.4, 132.4, 129.5, 128.8, 128.3, 127.9, 127.7, 126.8, 125.9, 124.0, 35.0, 27.7.

2-(benzylthio)benzaldehyde (SI-1r)

Following the general procedure B, the reaction of 2-bromobenzaldehyde (2 mmol, 370.0 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in THF (5.5 mL) at 75 ºC afforded the product SI-1r (75%, 341.1 mg) as a white solid. 

$^1$H NMR (300 MHz, CDCl$_3$) δ 10.25 (s, 1H), 7.79 (d, $J = 7.4$ Hz, 1H), 7.44 (dt, $J = 7.4$, 3.8 Hz, 2H), 7.33 – 7.17 (m, 6H), 4.11 (s, 2H). Spectral data is in accordance with the literature.[16]

(2-(benzylthio)phenyl)(phenyl)methanone (SI-1s)

Following the general procedure B, the reaction of (2-bromophenyl)(phenyl)methanone (2 mmol, 522.2 mg), NaH (60%, 2.4 mmol, 96 mg) and benzyl mercaptan (2.1 mmol, 0.25 mL) in THF (5.5 mL) at 75 ºC afforded the product SI-1s (63%, 385.4 mg) as a pale yellow solid. 

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 (d, $J = 8.3$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.28 (t, $J = 7.7$ Hz, 3H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.15 – 7.06 (m, 6H), 3.91 (s, 2H); 

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.6, 140.7, 137.3, 136.8, 135.3, 133.0, 131.1, 130.3, 130.0, 128.8, 128.7, 128.3, 127.0, 125.9, 39.6.
2.2. General Procedure and Characterization of Selenides

SI-10

General procedure for the synthesis of selenides SI-10:

Compounds SI-10a and SI-10b were prepared following a reported procedure in the literature. The corresponding 2-aminoacetophenone or 2-amino-5-chlorobenzaldehyde (1.1 equiv) and an aqueous HCl solution (2M) were added to an Erlenmeyer flask. The solution was cooled to 0 °C and a water solution of NaNO₂ (1 equiv, 2M) was added dropwise. At 0 °C, sodium acetate (2.5 equiv) was added, followed by the addition of acetate buffer solution until pH 4.3. The KSeCN (1.5 equiv) was then added under vigorous agitation and the solution was kept 1 h at 0 °C. Then, sodium acetate was added until pH 5.5. The resulting solution was extracted with dichloromethane (3x) and the combined organic phases were dried over anhydrous MgSO₄. The solvent was removed in vacuum and the residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure products SI-9a or SI-9b.

To a two necked round-bottomed flask under nitrogen, compound SI-9a or SI-9b (1 equiv) and methanol (5 mL/mmol) were added. The solution was cooled to 0 °C and benzylbromide (4 equiv) was added, followed by the slow addition of NaBH₄ (1.1 equiv). The solution was stirred 2h at 0 °C. The solvent was removed in vacuum and the residue was diluted in ethyl acetate followed by addition of saturated aqueous solution of NH₄Cl. After phase separation, the aqueous phase was extracted with ethyl acetate (2 x) and the combined organic phases were dried over MgSO₄. The solvent was removed in vacuum and the residue was subjected to flash.
chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure products SI-10a or SI-10b.

1-(2-(benzylselanyl)phenyl)ethan-1-one (SI-10a)

Following the general procedure, the reaction of 1-(2-selenocyanatophenyl)ethan-1-one (SI-9a) (2 mmol, 448.2 mg), NaBH₄ (2.2 mmol, 83.2 mg) and benzyl bromide (8.8 mmol, 1.05 mL) in MeOH (10 mL) at 0 °C afforded the product SI-10a (71%, 411.7 mg) as a pale brown solid. ^1H NMR (300 MHz, CDCl₃) δ 7.93 (dd, J = 7.8, 1.4 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.42 (dd, J = 11.9, 7.2 Hz, 3H), 7.35 – 7.20 (m, 4H), 4.11 (s, 2H), 2.62 (s, 3H). Spectral data is in accordance with the literature.[17]

2-(benzylselanyl)-5-chlorobenzaldehyde (SI-10b)

Following the general procedure, the reaction of 5-chloro-2-selenocyanatobenzaldehyde (SI-9b) (2 mmol, 489.0 mg), NaBH₄ (2.2 mmol, 83.2 mg) and benzyl bromide (8.8 mmol, 1.05 mL) in MeOH (10 mL) at 0 °C afforded the product SI-10b (76%, 469.3 mg) as an yellow oil. ^1H NMR (300 MHz, CDCl₃) δ 10.05 (s, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.43 (dd, J = 8.4, 2.4 Hz, 1H), 7.26 – 7.20 (m, 5H), 4.10 (s, 2H); ^13C NMR (75 MHz, CDCl₃) δ 191.5, 136.6, 134.5, 133.8, 133.7, 133.1, 132.3, 129.7, 129.0, 128.7, 127.3, 31.5.

2.3. General Procedure and Characterization of α-Imino-oxy Acids 1

Compound SI-11 was prepared following a reported procedure in the literature and spectral data is in accordance with the literature.[18]
General procedure for the synthesis of oximes 1:

Compounds 1a-u were prepared following a slightly modified procedure reported in the literature.[18] A solution of ketone (1.0 equiv) in MeOH or EtOH (0.2M) was treated with 2-(aminoxy)-2-methylpropanoic acid hydrochloride (SI-11) (1.2 equiv) and sodium acetate (2.4 equiv) and heated to reflux until completion by TLC analysis. The mixture was then allowed to cool to room temperature and water was added. The resulting aqueous solution was extracted with EtOAc (3x) and the combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum to provide the product. Then, the residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure products 1.

2-methyl-2-(((1-(2-(methylthio)phenyl)ethylidene)amino)oxy)propanoic acid (1a)

Following the general procedure, the reaction of SI-1a (0.9 mmol, 149.6 mg), SI-11 (1.08 mmol, 168.0 mg) and sodium acetate (2.2 mmol, 177.2 mg) in EtOH (4.5 mL) at reflux afforded the product 1a (57%, 137.3 mg) as a white solid. 

$^1$H NMR (300 MHz, CDCl₃) δ 10.02 (bs, 1H), 7.35 – 7.22 (m, 3H), 7.18 – 7.11 (m, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 1.62 (s, 6H); 

$^{13}$C NMR (75 MHz, CDCl₃) δ 179.5, 157.5, 137.7, 136.5, 129.1, 128.8, 126.8, 124.9, 81.3, 24.4, 16.8, 16.0; 

HRMS m/z (ESI): calcd. for C₁₃H₁₆NO₃S (M-H)⁻ 266.0856, found 266.0862.

2-(((1-(2-(isopropylthio)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1b)

Following the general procedure, the reaction of SI-1b (1 mmol, 194.0 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1b (75%, 22.7 mg) as a yellow oil. 

$^1$H NMR (300 MHz, CDCl₃) δ 8.20 (bs, 1H), 7.44 (d, $J = 7.7$ Hz, 1H), 7.35 – 7.25 (m, 1H), 7.22 (d, $J = 4.1$ Hz, 2H), 3.40 – 3.21 (m, 1H), 2.28 (s, 3H), 1.59 (s, 6H), 1.22 (d, $J = 6.6$ Hz, 6H); 

$^{13}$C NMR (75 MHz, CDCl₃) δ 177.0, 160.0, 139.8, 134.5, 132.7, 129.2, 129.1, 126.8, 81.7, 38.7, 24.5, 23.0, 17.3; 

HRMS m/z (ESI): calcd. for C₁₅H₂₀NO₃S
2-(((1-(2-(tert-butylthio)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1c)

Following the general procedure, the reaction of $\text{SI-1c}$ (0.3 mmol, 66.0 mg), $\text{SI-11}$ (0.36 mmol, 56.0 mg) and sodium acetate (0.72 mmol, 59.1 mg) in EtOH (1.5 mL) at reflux afforded the product 1c (60%, 55.9 mg) as a pale yellow solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.63 – 7.54 (m, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.25 (m, 1H), 2.29 (s, 3H), 1.58 (s, 6H), 1.22 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 178.0, 160.8, 144.3, 139.4, 131.4, 129.7, 129.2, 128.9, 81.5, 47.9, 31.3, 24.6, 18.8; HRMS m/z (ESI): calcd. for C$_{16}$H$_{22}$NO$_3$S (M-H)$^-$ 308.1326, found 308.1336.

2-(((1-(2-(benzylthio)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1d)

Following the general procedure, the reaction of $\text{SI-1d}$ (0.4 mmol, 100.2 mg), $\text{SI-11}$ (0.48 mmol, 74.7 mg) and sodium acetate (0.96 mmol, 78.7 mg) in EtOH (2 mL) at reflux afforded the product 1d (96%, 132.8 mg) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.91 (bs, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.24 (m, 8H), 4.09 (s, 2H), 2.29 (s, 3H), 1.65 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 179.4, 158.3, 139.1, 137.4, 134.9, 131.1, 129.1, 129.0, 128.9, 128.4, 127.1, 126.5, 81.3, 39.5, 24.4, 16.7; HRMS m/z (ESI): calcd. for C$_{19}$H$_{20}$NO$_3$S (M-H)$^-$ 342.1169, found 342.1162.

2-methyl-2-(((1-(2-(phenylthio)phenyl)ethylidene)amino)oxy)propanoic acid (1e)

Following the general procedure, the reaction of $\text{SI-1e}$ (1 mmol, 228.3 mg), $\text{SI-11}$ (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1e (34%, 111.0 mg) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.32 (bs, 1H), 7.39 – 7.24 (m, 9H), 2.36 (s, 3H), 1.61 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 177.3, 157.1, 137.3, 134.7, 134.1, 131.2, 130.5, 128.3, 128.2, 128.2, 126.2, 125.9, 80.5, 23.3, 15.4; HRMS m/z (ESI): calcd. for C$_{18}$H$_{18}$NO$_3$S (M-H)$^-$ 328.1013,
found 328.1017.

2-(((1-(2-(benzylthio)-4-fluorophenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1f)

Following the general procedure, the reaction of **SI-1f** (0.4 mmol, 99.2 mg), **SI-11** (0.48 mmol, 74.7 mg) and sodium acetate (0.96 mmol, 78.7 mg) in EtOH (2 mL) at reflux afforded the product **1f** (88%, 126.9 mg) as a white solid. **1H NMR** (300 MHz, CDCl₃) δ 9.99 (bs, 1H), 7.27 – 7.16 (m, 6H), 6.99 (dd, J = 9.5, 2.5 Hz, 1H), 6.83 (td, J = 8.3, 2.5 Hz, 1H), 4.03 (s, 2H), 2.20 (s, 3H), 1.57 (s, 6H); **13C NMR** (75 MHz, CDCl₃) δ 179.0, 162.7 (d, J = 250.1 Hz), 157.3, 138.3 (d, J = 8.1 Hz), 136.6, 134.1 (d, J = 3.3 Hz), 130.7 (d, J = 8.8 Hz), 128.9, 128.7, 127.5, 116.5 (d, J = 23.7 Hz), 113.0 (d, J = 21.6 Hz), 81.5, 39.1, 24.4, 16.5; **19F NMR** (282 MHz, CDCl₃) δ -111.98 (syn isomer), -112.59 (anti isomer); **HRMS** m/z (ESI): calcd. for C₁₉H₁₉FNO₃S (M-H)- 360.1064, found 360.1050.

2-(((1-(2-(benzylthio)-4-methoxyphenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1g)

Following the general procedure, the reaction of **SI-1g** (0.5 mmol, 149.6 mg), **SI-11** (0.6 mmol, 93.3 mg) and sodium acetate (1.2 mmol, 98.4 mg) in EtOH (2.5 mL) at reflux afforded the product **1g** (70%, 143.0 mg) as a white solid. **1H NMR** (300 MHz, CDCl₃) δ 9.89 (bs, 1H), 7.30 – 7.20 (m, 5H), 7.17 (d, J = 8.5 Hz, 1H), 6.82 (d, J = 2.5 Hz, 1H), 6.71 (dd, J = 8.5, 2.5 Hz, 1H), 4.04 (s, 2H), 3.71 (s, 3H), 2.23 (s, 3H), 1.59 (s, 6H); **13C NMR** (75 MHz, CDCl₃) δ 178.6, 159.9, 158.3, 137.2, 136.8, 130.8, 130.2, 129.0, 128.6, 127.3, 115.8, 111.9, 81.4, 55.4, 39.3, 24.5, 16.8; **HRMS** m/z (ESI): calcd. for C₂₀H₂₂NO₄S (M-H)- 372.1264, found 372.1264.
2-(((1-(2-(benzylthio)-5-methoxyphenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1h)

Following the general procedure, the reaction of SI-1h (1 mmol, 272.2 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1h (71%, 266.5 mg) as a white solid. 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 – 7.05 (m, 6H), 6.88 – 6.59 (m, 2H), 3.91 (s, 2H), 3.78 (s, 3H), 2.20 (s, 3H), 1.58 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 178.1, 159.2, 159.1, 142.2, 137.8, 135.8, 128.9, 128.9, 128.3, 126.9, 124.2, 114.7, 81.4, 55.4, 41.2, 24.3, 17.1; HRMS m/z (ESI): calcd. for C$_{20}$H$_{22}$NO$_4$S (M-H)$^-$ 372.1264, found 372.1259.

2-(((1-(2-(benzylthio)-5-bromophenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1i)

Following the general procedure, the reaction of SI-1i (1 mmol, 320.0 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1i (74%, 313.8 mg) as a brown oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.30 (m, 2H), 7.26 – 7.17 (m, 5H), 7.12 (d, $J = 9.0$ Hz, 1H), 3.99 (s, 2H), 2.19 (s, 3H), 1.57 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 178.3, 157.1, 140.6, 136.9, 134.1, 132.5, 131.9, 131.8, 128.8, 128.5, 127.2, 120.2, 81.5, 39.4, 24.3, 16.4; HRMS m/z (ESI): calcd. for C$_{19}$H$_{19}$BrNO$_3$S (M-H)$^-$ 420.0264, found 420.0277.

2-(((1-(2-(benzylthio)-5-(trifluoromethyl)phenyl)ethylidene)amino)oxy)-2-methyl propanoic acid (1j)

Following the general procedure, the reaction of SI-1j (0.6 mmol, 179.8 mg), SI-11 (0.7 mmol, 112.0 mg) and sodium acetate (1.4 mmol, 118.1 mg) in EtOH (3 mL) at reflux afforded the product 1j (89%, 211.8 mg) as a white solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 10.12 (bs, 1H), 7.49 – 7.43
(m, 2H), 7.40 – 7.34 (m, 1H), 7.31 – 7.24 (m, 5H), 4.10 (s, 2H), 2.26 (s, 3H), 1.61 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 179.4, 156.3, 141.1 (q, $J$ = 1.2 Hz), 137.8, 136.3, 128.8, 128.7, 128.6, 127.7 (q, $J$ = 32.8 Hz), 127.4, 125.6 (q, $J$ = 3.5 Hz), 125.4 (q, $J$ = 3.6 Hz), 123.9 (q, $J$ = 271.9 Hz), 81.6, 38.5, 24.3, 16.0; $^9$F NMR (282 MHz, CDCl$_3$) δ -62.43 (syn isomer), -62.48 (anti isomer); HRMS m/z (ESI): calcd. for C$_{26}$H$_{19}$F$_3$NO$_3$S (M-H)$^-$ 410.1032, found 410.1026.

2-(((1-(6-(benzylthio)benzo[d][1,3]dioxol-5-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (1k)

Following the general procedure, the reaction of SI-1k (0.1 mmol, 37.5 mg), SI-11 (0.12 mmol, 18.7 mg) and sodium acetate (0.24 mmol, 19.7 mg) in EtOH (0.5 mL) at reflux afforded the product 1k (81%, 41.0 mg) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.26 – 7.13 (m, 5H), 6.79 (s, 1H), 6.68 (s, 1H), 5.94 (s, 2H), 3.93 (s, 2H), 2.15 (s, 3H), 1.56 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 178.0, 158.9, 148.1, 147.2, 137.5, 134.6, 128.8, 128.4, 127.1, 126.6, 113.4, 109.2, 101.7, 81.4, 41.1, 24.4, 17.2; HRMS m/z (ESI): calcd. for C$_{20}$H$_{19}$F$_3$NO$_3$S (M-H)$^-$ 386.1057, found 386.1096.

2-(((1-(3-(benzyloxy)-2-(benzylthio)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1l)

Following the general procedure, the reaction of SI-1l (0.3 mmol, 99.9 mg), SI-11 (0.36 mmol, 56.0 mg) and sodium acetate (0.72 mmol, 59.1 mg) in EtOH (1.5 mL) at reflux afforded the product 1l (59%, 75.6 mg) as a white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.63 (bs, 1H), 7.58 – 7.51 (m, 2H), 7.48 – 7.38 (m, 3H), 7.32 – 7.24 (m, 1H), 7.22 – 7.15 (m, 3H), 7.11 – 7.06 (m, 2H), 7.00 (dd, $J$ = 8.3, 0.9 Hz, 1H), 6.84 (dd, $J$ = 7.6, 1.0 Hz, 1H), 5.18 (s, 2H), 4.06 (s, 2H), 2.07 (s, 3H), 1.60 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 177.7, 160.2, 159.8, 143.9, 138.3, 136.7, 129.6, 129.0, 128.8, 128.4, 128.3, 128.2, 127.4, 127.0, 121.6, 113.2, 81.5, 71.1, 39.1, 24.5, 17.6; HRMS m/z (ESI): calcd. for C$_{26}$H$_{26}$NO$_4$S (M-H)$^-$ 448.1577, found 448.1596.
2-(((1-(1-(benzylthio)naphthalen-2-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (1m)

Following the general procedure, the reaction of SI-1m (1 mmol, 292.0 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1m (78%, 305.3 mg) as a yellow solid.

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \] \( \delta \) 8.60 (d, \( J = 7.8 \) Hz, 1H), 7.88 – 7.81 (m, 2H), 7.56 (pd, \( J = 6.8, 1.5 \) Hz, 2H), 7.30 (d, \( J = 8.4 \) Hz, 1H), 7.21 – 7.09 (m, 3H), 6.97 (dd, \( J = 6.8, 2.9 \) Hz, 2H), 3.93 (s, 2H), 2.19 (s, 3H), 1.61 (s, 6H); \( ^{13}C \text{ NMR (75 MHz, CDCl}_3 \] \( \delta \) 177.3, 160.0, 141.5, 137.2, 134.5, 133.4, 129.8, 129.2, 128.4, 128.0, 127.8, 126.9, 126.6, 126.2, 126.0, 125.5, 81.0, 41.2, 24.0, 17.4; HRMS m/z (ESI): calcd. for C_{23}H_{22}NO_3S (M-H)^- 392.1326, found 392.1328.

2-(((1-(3-(benzylthio)furan-2-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (1n)

Following the general procedure, the reaction of SI-1n (1.3 mmol, 302.0 mg), SI-11 (1.56 mmol, 240.5 mg) and sodium acetate (3.1 mmol, 256.0 mg) in EtOH (6.5 mL) at reflux afforded the product 1n (81%, 349.6 mg) as a yellow solid. \( ^1H \text{ NMR (300 MHz, CDCl}_3 \] \( \delta \) 7.38 (d, \( J = 1.9 \) Hz, 1H), 7.35 – 7.20 (m, 5H), 6.40 (d, \( J = 1.9 \) Hz, 1H), 4.05 (s, 2H), 2.23 (s, 3H), 1.60 (s, 6H); \( ^{13}C \text{ NMR (75 MHz, CDCl}_3 \] \( \delta \) 178.0, 150.0, 145.2, 142.7, 137.2, 128.6, 128.4, 127.1, 118.8, 113.2, 81.8, 38.1, 24.1, 11.7. HRMS m/z (ESI): calcd. for C_{17}H_{18}NO_4S (M-H)^- 332.0962, found 332.0960.

2-(((1-(3-(benzylthio)thiophen-2-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (1o)

Following the general procedure, the reaction of SI-1o (0.6 mmol, 149.2 mg), SI-11 (0.72 mmol, 112.1 mg) and sodium acetate (1.44 mmol, 118.1 mg) in EtOH (3 mL) at reflux afforded the product 1o (84%, 176.3 mg) as a white solid. \( ^1H \text{ NMR (300 MHz, CDCl}_3 \] \( \delta \) 8.62 (d, \( J = 8.4 \) Hz, 1H), 7.89 – 7.81 (m, 2H), 7.56 (pd, \( J = 6.8, 1.5 \) Hz, 2H), 7.30 (d, \( J = 8.4 \) Hz, 1H), 7.21 – 7.09 (m, 3H), 6.97 (dd, \( J = 6.8, 2.9 \) Hz, 2H), 3.93 (s, 2H), 2.20 (s, 3H), 1.61 (s, 6H); \( ^{13}C \text{ NMR (75 MHz, CDCl}_3 \] \( \delta \) 177.8, 160.0, 141.5, 137.2, 134.5, 133.4, 129.8, 129.2, 128.4, 128.0, 127.8, 126.9, 126.6, 126.2, 126.0, 125.5, 81.0, 41.2, 24.0, 17.4; HRMS m/z (ESI): calcd. for C_{23}H_{22}NO_3S (M-H)^- 392.1326, found 392.1328.
2-(((1-(2-(benzylthio)pyridin-3-yl)ethylidene)amino)oxy)-2-methylpropanoic acid

(1p)

Following the general procedure, the reaction of SI-1p (0.2 mmol, 56.3 mg), SI-11 (0.24 mmol, 37.4 mg) and sodium acetate (0.48 mmol, 39.4 mg) in EtOH (1 mL) at reflux afforded the product 1p (77%, 61.7 mg) as a yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 9.92 (bs, 1H), 8.45 (dd, \(J = 4.8, 1.7\) Hz, 1H), 7.46 (dd, \(J = 7.6, 1.7\) Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.18 (m, 3H), 7.00 (dd, \(J = 7.6, 4.8\) Hz, 1H), 4.41 (s, 2H), 2.23 (s, 3H), 1.62 (s, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 179.0, 157.3, 155.2, 148.7, 138.2, 135.9, 131.2, 129.2, 128.3, 126.9, 119.0, 81.7, 35.2, 24.4, 15.2; HRMS m/z (ESI): calcd. for C\(_{18}\)H\(_{19}\)N\(_2\)O\(_3\)S (M-H)\(^-\) 343.1111, found 343.1099.

2-(((1-(2-(benzylthio)quinolin-3-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (1q)

Following the general procedure, the reaction of SI-1q (0.7 mmol, 200.0 mg), SI-11 (0.8 mmol, 130.7 mg) and sodium acetate (1.68 mmol, 137.8 mg) in EtOH (3.5 mL) at reflux afforded the product 1q (80%, 215.1 mg) as a white solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 10.87 (bs, 1H), 7.98 (d, \(J = 8.3\) Hz, 1H), 7.87 (s, 1H), 7.77 – 7.63 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.38 (m, 1H), 7.35 – 7.18 (m, 3H), 4.57 (s, 2H), 2.34 (s, 3H), 1.68 (s, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 179.3, 157.4, 155.4, 147.4, 138.5, 135.1, 131.2, 129.2, 128.4, 127.9, 127.8, 126.9, 125.7, 125.3, 81.8, 35.1, 24.5, 15.7; HRMS m/z (ESI): calcd. for C\(_{22}\)H\(_{21}\)N\(_2\)O\(_3\)S (M-H)\(^-\) 393.1278, found 393.1285.
2-(((2-(benzylthio)benzylidene)amino)oxy)-2-methylpropanoic acid (1r)

Following the general procedure, the reaction of SI-1r (1 mmol, 228.1 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1r (88%, 290.9 mg) as a white solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 11.29 (bs, 1H), 8.63 (s, 1H), 7.73 (dd, \(J = 7.4, 1.8\) Hz, 1H), 7.32 (dd, \(J = 7.7, 1.4\) Hz, 1H), 7.28 – 7.05 (m, 7H), 3.98 (s, 2H), 1.60 (s, 6H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 179.6, 148.3, 136.9, 135.6, 133.1, 132.7, 130.1, 128.8, 128.4, 127.3, 127.2, 81.6, 40.3, 24.0; HRMS m/z (ESI): calcd. for C\(_{18}\)H\(_{18}\)NO\(_3\)S (M-H\(^-\)) 328.1013, found 328.1015.

2-((((2-(benzylthio)phenyl)(phenyl)methylene)amino)oxy)-2-methylpropanoic acid (1s)

Following the general procedure, the reaction of SI-1s (1 mmol, 304.1 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in MeOH (5 mL) at reflux afforded the product 1s (67%, 272.8 mg) as a yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.45 – 7.25 (m, 9H), 7.24 – 7.10 (m, 5H), 4.00 (d, \(J = 9.8\) Hz, 2H), 1.55 (d, \(J = 4.4\) Hz, 6H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 176.2, 157.6, 137.1, 135.6, 134.8, 133.7, 131.6, 129.9, 129.1, 129.0, 128.9, 128.4, 128.4, 127.3, 127.2, 127.0, 82.7, 39.1, 24.3; HRMS m/z (ESI): calcd. for C\(_{24}\)H\(_{22}\)NO\(_3\)S (M-H\(^-\)) 404.1326, found 404.1325.

2-(((1-(2-(benzylselanyl)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1t)

Following the general procedure, the reaction of SI-10a (1 mmol, 289.2 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in MeOH (5 mL) at reflux afforded the product 1t (76%, 295.5 mg) as a pale yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.57 – 7.47 (m, 1H), 7.37 – 7.20 (m, 8H), 4.08 (s, 2H), 2.26 (s, 3H), 1.63 (s, 6H); \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 177.7, 159.0, 139.0, 138.0,
132.6, 131.1, 129.2, 128.9, 128.7, 128.4, 126.8, 126.5, 81.5, 32.3, 24.5, 16.1; HRMS m/z (ESI): calcd. for C$_{19}$H$_{20}$NO$_3$Se (M-H)$^-$ 390.0614, found 390.0623.

2-(((2-(benzylselanyl)-5-chlorobenzylidene)amino)oxy)-2-methylpropanoic acid (1u)

Following the general procedure, the reaction of SI-10b (1 mmol, 309.7 mg), SI-11 (1.2 mmol, 186.7 mg) and sodium acetate (2.4 mmol, 196.9 mg) in MeOH (5 mL) at reflux afforded the product 1u (65%, 268.2 mg) as a yellow solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.53 (s, 1H), 7.75 (d, $J$ = 2.4 Hz, 1H), 7.45 (d, $J$ = 8.3 Hz, 1H), 7.33 – 7.16 (m, 6H), 4.04 (s, 2H), 1.68 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 178.6, 149.3, 137.6, 136.8, 135.6, 134.2, 130.0, 129.4, 128.5, 127.3, 127.1, 82.0, 33.1, 24.1; HRMS m/z (ESI): calcd. for C$_{18}$H$_{17}$ClNO$_3$Se (M-H)$^-$ 410.0068, found 410.0072.

Procedure for the synthesis of oxime 1a$'$:

Compound SI-12 was prepared following a reported procedure in the literature.$^{[18]}$

Compound 1a$'$ was prepared following a slightly modified procedure reported in the literature.$^{[18]}$ A solution of ketone (1.0 equiv) in EtOH (0.2M) was treated with 2-(aminooxy)propanoic acid hydrochloride (SI-12) (1.2 equiv), sodium acetate (2.4 equiv) and heated to reflux until completion by TLC analysis. The mixture was then allowed to cool to room temperature and water was added. The resulting aqueous solution was extracted with EtOAc (3x) and the combined organic layers were dried over anhydrous MgSO$_4$, filtered and concentrated under vacuum to provide the product. Then, the residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure product 1a$'$. 

S24
2-(((1-(2-(methylthio)phenyl)ethylidene)amino)oxy)propanoic acid (1a’)

Following the procedure, the reaction of SI-1a (1 mmol, 166.2 mg), SI-12 (1.2 mmol, 168.6 mg) and sodium acetate (2.4 mmol, 196.9 mg) in EtOH (5 mL) at reflux afforded the product 1a’ (78%, 198.0 mg) as a yellow oil. \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.19 (s, 1H), 7.27 – 7.00 (m, 4H), 4.77 (q, \(J = 7.0\) Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 1.51 (d, \(J = 7.0\) Hz, 3H); \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 178.4, 158.4, 137.5, 136.6, 129.2, 128.8, 127.1, 125.1, 21.4, 16.9, 16.8, 16.3; HRMS m/z (ESI): calcd. for C\(_{12}\)H\(_{14}\)NO\(_3\)S (M-H)\(^{-}\) 252.0700, found 252.0704.

**Procedure for the synthesis of oxime 1a”**: 

![Chemical structure of compound SI-1a](image1.png)

Compound 1a” was prepared following a slightly modified procedure reported in the literature.\(^{[19]}\) A solution of SI-1a (0.8 mmol, 139.2 mg, 1.0 equiv) in EtOH (0.5 M) was treated with hydroxylamine hydrochloride (1.3 mmol, 93.1 mg, 1.6 equiv), sodium acetate (1.7 mmol, 137.4 mg, 2.0 equiv) and heated to reflux for 12 h. The mixture was then allowed to cool to room temperature and concentrated under vacuum to provide the product SI-13 as a white solid, which was used for the next step without purification. Then, SI-13 was added dropwise to a stirred suspension of NaH 60% in mineral oil (2.5 mmol, 60.3 mg, 3.0 equiv) in dry THF (1.5 M) at 0 °C (ice bath) under inert atmosphere and the mixture was stirred for 15 min. Afterwards, a solution of 2-bromo-2-phenylacetic acid (0.9 mmol, 198.1 mg, 1.1 equiv) in dry THF (0.5 M) was added and the reaction was heated to 75 °C for 12 h. After this time, the reaction was cooled to room temperature and concentrated hydrochloric acid was added until pH 2. The resulting solution was extracted with EtOAc (3x) and the combined organic layers were dried over MgSO\(_4\), filtered and concentrated under vacuum to provide the
product. Then, the residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure product 1a″.

2-(((1-(2-(methylthio)phenyl)ethylidene)amino)oxy)-2-phenylacetic acid (1a″)

Following the procedure, the reaction of SI-1a (0.8 mmol, 139.2 mg) afforded the product 1a″ (40% for two reaction steps, 106.5 mg) as white solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 11.00 (bs, 1H), 7.66 – 7.58 (m, 2H), 7.47 – 7.40 (m, 3H), 7.37 – 7.26 (m, 3H), 7.23 – 7.16 (m, 1H), 5.81 (s, 1H), 2.41 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 176.7, 159.1, 137.6, 136.5, 134.7, 129.3, 129.1, 128.9, 128.7, 127.7, 127.2, 125.1, 83.2, 16.9, 16.6; HRMS m/z (ESI): calcd. for C$_{17}$H$_{16}$NO$_3$S (M-H)⁻ 314.0856, found 314.0856.

3. Optimization of the Reaction Conditions

General procedure for the optimization of the reaction conditions of the synthesis of isothiazoles 2:

In an oven-dried glass vial equipped with a stirring bar, 2-methyl-2-(((1-(2-(methylthio)phenyl)ethylidene)amino)oxy)propanoic acid (1a, 0.05 mmol, 13.4 mg, 1 equiv), the base (0.05 mmol, 1 equiv), the photocatalyst (2.5·10⁻³ mmol, 0.05 equiv) and the respective solvent (0.67 mL) were added under air. Then, the vial was closed with a PTFE/rubber septum perforated several times to enable the air enter into the reaction. Afterwards, the mixture was stirred and irradiated at 450 nm using 380 mW single LEDs in a custom-made temperature-controlled system (see Figure S1) for 16h at 20 °C. Then, the volatiles were removed and yield was determined by $^1$H-NMR analysis using 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) as internal standard.
Table S1. Optimization of reaction conditions with 1a.

![Optimization of reaction conditions with 1a](image)

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<td>PC1</td>
<td>Na₂HPO₄</td>
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4. Optimization of the \(\alpha\)-Imino-oxy Acid Structure

*General procedure for the optimization of the \(\alpha\)-imino-oxy acid structure in the synthesis of isothiazoles 2:*

In an oven-dried glass vial equipped with a stirring bar, the corresponding \(\alpha\)-imino-oxy acid 1 (0.05 mmol, 1 equiv), NaOAc (0.05 mmol, 4.1 mg, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate, (2.5·10\(^{-3}\) mmol, 1.05 mg, 0.05 equiv) and acetone (0.67 mL) were added under air. Then, the vial was closed with a PTFE/rubber septum perforated several times to enable the air enter into the reaction. Afterwards, the mixture was stirred and irradiated at 450 nm using 380 mW single LEDs in a custom-made temperature-controlled system (see Figure S1) for 16h at 20 °C. Then, the volatiles were removed and yield was determined by \(^1\)H-NMR analysis using 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) as internal standard.

\[\text{Table:}
\begin{array}{cccc}
\text{Run} & \text{Photocatalyst (PC)} & \text{Additive (NaOAc)} & \text{Solvent (Acetone)} & \text{Yield (\%)} \\
13 & \text{PC1} & \text{NaHCO}_3 & \text{Acetone} & 23 \\
14 & \text{PC1} & \text{NaOAc} & \text{Acetone} & 56 \\
15 & \text{PC2} & \text{NaOAc} & \text{Acetone} & 35 \\
16 & \text{PC3} & \text{NaOAc} & \text{Acetone} & 31 \\
17 & \text{PC4} & \text{NaOAc} & \text{Acetone} & 32 \\
18 & \text{PC5} & \text{NaOAc} & \text{Acetone} & 44 \\
19\text{[b]} & \text{PC1} & \text{NaOAc} & \text{Acetone} & 54 \\
20\text{[c]} & \text{PC1} & \text{NaOAc} & \text{Acetone} & 4 \\
21 & - & \text{NaOAc} & \text{Acetone} & 0 \\
22 & \text{PC1} & - & \text{Acetone} & 0. \\
23\text{[d]} & \text{PC1} & \text{NaOAc} & \text{Acetone} & 0. \\
\end{array}\]

[a] The yield was determined from the crude \(^1\)H-NMR. [b] Oxygen was used instead air. [c] Argon was used instead air. [d] The reaction was performed in the dark. DCE = 1,2-Dichloroethane. DCM = Dichloromethane, THF = Tetrahydrofuran, DMF = N,N-Dimethylformamide.
Table S2. Optimization of α-imino-oxy acid structure.

![Chemical structure of 1 and 2a](image)

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<th>R₃</th>
<th>yield (%)&lt;sup&gt;[a]&lt;/sup&gt;</th>
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<td>Me</td>
<td>Bn</td>
<td>85 (81)&lt;sup&gt;[b]&lt;/sup&gt;</td>
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<tr>
<td>8&lt;sup&gt;[c]&lt;/sup&gt;</td>
<td>Me</td>
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</table>

<sup>[a]</sup>The yield was determined from the crude ¹H-NMR.  
<sup>[b]</sup>Isolated yield in 0.1 mmol scale in parentheses.  
<sup>[c]</sup>The reaction was performed with a blue LED spot of 40W instead of 380 mW single LEDs.

5. General Procedure and Characterization of Isothiazoles 2

![Chemical structure of 1 and 2](image)

**General procedure for the synthesis of isothiazoles 2:**

In an oven-dried glass vial equipped with a stirring bar, 1 (0.1 mmol, 1 equiv), NaOAc (0.1 mmol, 8.2 mg, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate, (5·10⁻³ mmol, 2.1 mg, 0.05 equiv) and acetone (1.33 mL) were
added under air. Then, the vial was closed with a PTFE/rubber septum perforated several times to enable the air enter into the reaction. Afterwards, the mixture was stirred and irradiated at 450 nm using 380 mW single LEDs in a custom-made temperature-controlled system (see Figure S1) for 16h at 20 ºC. Then, the volatiles were removed and the analytically pure product 2 was obtained by flash chromatography (latrobeads silica gel; cyclohexane/EtOAc).

3-methylbenzo[d]isothiazole (2a)

Following the general procedure, the reaction of 1d (0.1 mmol, 34.0 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2a (81%, 11.9 mg) as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 – 7.90 (m, 2H), 7.56 – 7.49 (m, 1H), 7.48 – 7.40 (m, 1H), 2.76 (s, 3H). Spectral data is in accordance with the literature.[20]

6-fluoro-3-methylbenzo[d]isothiazole (2b)

Following the general procedure, the reaction of 1f (0.1 mmol, 35.4 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2b (82%, 13.4 mg) as a white solid. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 7.05 (dd, $J$ = 8.8, 4.9 Hz, 1H), 6.86 (dd, $J$ = 8.5, 2.2 Hz, 1H), 6.70 (td, $J$ = 8.7, 2.2 Hz, 1H), 2.26 (s, 3H); $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 162.6 (d, $J$ = 249.6 Hz), 162.1, 154.2 (d, $J$ = 10.4 Hz), 132.4, 124.9 (d, $J$ = 10.2 Hz), 113.6 (d, $J$ = 25.4 Hz), 105.9 (d, $J$ = 25.6 Hz), 17.0; $^{19}$F NMR (282 MHz, C$_6$D$_6$) $\delta$ -113.77; HRMS m/z (ESI): calcd. for C$_8$H$_6$FNS (M)$^+$ 167.0205, found 167.0200.

6-methoxy-3-methylbenzo[d]isothiazole (2c)

Following the general procedure, the reaction of 1g (0.1 mmol, 37.1 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2c (89%, 15.8 mg) as a white solid. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 7.26 (d, $J$ = 8.8 Hz, 1H), 6.87 (dd, $J$ = 8.8, 2.2 Hz, 1H), 6.74 (d, $J$ = 2.2 Hz, 1H), 3.23 (s, 3H),
2.36 (s, 3H); $^{13}$C NMR (75 MHz, C$_6$D$_6$) δ 162.1, 160.0, 155.1, 130.3, 124.2, 115.9, 101.1, 55.1, 17.1; HRMS m/z (ESI): calcd. for C$_9$H$_{10}$NOS (M+H)$^+$ 180.0478, found 180.0480.

**5-methoxy-3-methylbenzo[d]isothiazole (2d)**

Following the general procedure, the reaction of 1h (0.1 mmol, 37.3 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2d (75%, 13.4 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 7.96 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 2.3 Hz, 1H), 7.23 (dd, J = 8.8, 2.3 Hz, 1H), 3.93 (s, 3H), 2.67 (s, 3H); $^{13}$C NMR (75 MHz, (CD$_3$)$_2$CO) δ 163.1, 159.1, 146.0, 137.5, 121.7, 120.0, 105.4, 56.2, 17.6; HRMS m/z (ESI): calcd. for C$_9$H$_{10}$NOS (M+H)$^+$ 180.0478, found 180.0482.

**5-bromo-3-methylbenzo[d]isothiazole (2e)**

Following the general procedure, the reaction of 1i (0.1 mmol, 42.0 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2e (68%, 15.6 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 8.28 (s, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 2.73 (s, 3H); $^{13}$C NMR (75 MHz, (CD$_3$)$_2$CO) δ 163.2, 152.1, 137.9, 131.2, 127.4, 122.9, 119.2, 17.5; HRMS m/z (ESI): calcd. for C$_8$H$_6$BrNS (M)$^+$ 227.9477, found 226.9404.

**3-methyl-5-(trifluoromethyl)benzo[d]isothiazole (2f)**

Following the general procedure, the reaction of 1j (0.1 mmol, 40.6 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2f (71%, 15.2 mg) as a white solid. $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.28 – 8.22 (m, 1H), 8.07 (d, J = 8.5 Hz, 1H), 7.74 (dd, J = 8.5, 1.4 Hz, 1H), 2.78 (s, 3H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 163.9, 155.8, 135.4, 127.6 (q, J = 32.6 Hz), 125.0 (q, J = 272.0 Hz), 124.2 (q, J = 3.2 Hz), 121.5 (q, J = 4.3 Hz), 121.4, 17.8; $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$) δ -61.17; HRMS m/z (ESI): calcd. for C$_9$H$_6$F$_3$NS (M)$^+$ 217.0173, found
3-methyl-[1,3]dioxolo[4',5':4,5]benzo[1,2-d]isothiazole (2g)

Following the general procedure, the reaction of 1k (0.1 mmol, 36.0 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2g (66%, 11.8 mg) as a white solid. $^1$H NMR (300 MHz, C$_6$D$_6$) δ 6.77 (s, 1H), 6.65 (s, 1H), 5.25 (s, 2H), 2.27 (s, 3H); $^{13}$C NMR (75 MHz, C$_6$D$_6$) δ 161.4, 149.8, 148.7, 147.4, 130.8, 102.0, 101.2, 98.6, 17.1; HRMS m/z (ESI): calcd. for C$_9$H$_8$NO$_2$S (M+H)$^+$ 194.0270, found 194.0265.

7-(benzyloxy)-3-methylbenzo[d]isothiazole (2h)

Following the general procedure, the reaction of 1l (0.1 mmol, 44.8 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2h (88%, 22.4 mg) as a white solid. $^1$H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.55 (dd, J = 8.0, 0.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.33 (m, 4H), 6.98 (d, J = 7.6 Hz, 1H), 5.29 (s, 2H), 2.71 (s, 3H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 163.7, 152.6, 143.0, 137.9, 137.0, 129.2, 128.7, 128.0, 127.0, 116.4, 108.8, 71.1, 17.9; HRMS m/z (ESI): calcd. for C$_{15}$H$_{14}$NOS (M+H)$^+$ 256.0791, found 256.0800.

3-methylnaphtho[2,1-d]isothiazole (2i)

Following the general procedure, the reaction of 1m (0.1 mmol, 39.3 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2i (70%, 14.3 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 8.24 – 8.17 (m, 1H), 8.16 – 8.10 (m, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.76 – 7.68 (m, 2H), 2.79 (s, 3H); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 164.7, 153.9, 133.9, 133.1, 130.0, 129.1, 128.4, 127.4, 127.3, 126.1, 121.6, 17.7; HRMS m/z (ESI): calcd. for C$_{12}$H$_9$NS (M+H)$^+$ 199.0456, found 199.0465.
3-methylfuro[2,3-d]isothiazole (2j)

Following the general procedure, the reaction of 1n (0.1 mmol, 33.3 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2j (32%, 4.5 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 7.91 (dd, $J$ = 3.7, 2.1 Hz, 1H), 7.01 (dd, $J$ = 3.7, 2.1 Hz, 1H), 2.50 (d, $J$ = 3.7 Hz, 3H); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 152.0, 148.3, 146.4, 135.3, 107.4, 15.8; HRMS m/z (ESI): calcd. for C$_6$H$_6$NOS (M+H)$^+$ 140.0165, found 140.0169.

3-methylthieno[2,3-d]isothiazole (2k)

Following the general procedure, the reaction of 1o (0.1 mmol, 35.0 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2k (36%, 5.6 mg) as a brown oil. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 7.89 (d, $J$ = 5.1 Hz, 1H), 7.48 (d, $J$ = 5.1 Hz, 1H), 2.57 (s, 3H). Spectral data is in accordance with the literature.[21]

3-methylisothiazolo[5,4-b]pyridine (2l)

Following the general procedure, the reaction of 1p (0.1 mmol, 34.2 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2l (86%, 12.8 mg) as a white solid. $^1$H NMR (300 MHz, C$_6$D$_6$) δ 8.40 (dd, $J$ = 4.5, 1.4 Hz, 1H), 7.19 (dd, $J$ = 8.2, 1.4 Hz, 1H), 6.52 (dd, $J$ = 8.2, 4.5 Hz, 1H), 2.19 (s, 3H). Spectral data is in accordance with the literature.[22]

3-methylisothiazolo[5,4-b]quinoline (2m)

Following the general procedure, the reaction of 1q (0.1 mmol, 39.2 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2m (69%, 13.8 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) δ 12 (s, 1H), 8.22 (d, $J$ = 8.3 Hz, 1H), 8.13 (d, $J$ = 8.7 Hz, 1H), 7.99 – 7.90 (m, 1H), 7.72 – 7.64 (m, 1H), 2.83 (s, 3H); $^{13}$C NMR (75 MHz, (CD$_3$)$_2$CO) δ 171.3, 163.9, 149.2, 133.9, 132.8, 130.6, 129.3, 127.5, 126.9, 125.7, 18.3; HRMS m/z (ESI): calcd. for
C_{11}H_{9}N_{2}S (M+H)^+ 201.0481, found 201.0481.

**Benzo[d]isothiazole (2n)**

Following the general procedure, the reaction of 1r (0.1 mmol, 32.9 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2n (27%, 3.6 mg) as a white solid. ¹H NMR (300 MHz, (CD₃)₂CO) δ 8.93 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.45 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H). Spectral data is in accordance with the literature.[23]

**3-phenylbenzo[d]isothiazole (2o)**

Following the general procedure, the reaction of 1s (0.1 mmol, 28.3 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2o (85%, 17.9 mg) as a white solid. ¹H NMR (300 MHz, (CD₃)₂CO) δ 8.27 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.93 (dd, J = 8.0, 1.5 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.63 – 7.52 (m, 3H); ¹³C NMR (75 MHz, (CD₃)₂CO) δ 165.1, 154.6, 136.3, 134.7, 130.4, 129.9, 129.7, 128.8, 126.4, 125.7, 121.4; HRMS m/z (ESI): calcd. for C₁₃H₁₀NS (M+H)^+ 212.0528, found 212.0534.

**3-methylbenzo[d][1,2]selenazole (2p)**

Following the general procedure, the reaction of 1t (0.1 mmol, 39.0 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2p (82%, 16.1 mg) as a white solid. ¹H NMR (300 MHz, (CD₃)₂CO) δ 8.19 (d, J = 8.0 Hz, 1H), 8.03 (dd, J = 8.0, 1.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.51 (ddd, J = 8.0, 7.1, 1.2 Hz, 1H), 2.65 (s, 3H); ¹³C NMR (75 MHz, (CD₃)₂CO) δ 167.6, 153.0, 139.4, 128.8, 126.9, 125.9, 125.2, 20.1; HRMS m/z (ESI): calcd. for C₈H₈NS (M+H)^+ 197.9816, found 197.9819.

**5-chlorobenzo[d][1,2]selenazole (2q)**

Following the general procedure, the reaction of 1u (0.1 mmol, 41.1 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 2q
(60%, 13.0 mg) as a white solid. \textsuperscript{1}H NMR (300 MHz, (CD\textsubscript{3})\textsubscript{2}CO) δ 9.47 (s, 1H), 8.27 (d, \(J = 8.6\) Hz, 1H), 8.24 (d, \(J = 2.0\) Hz, 1H), 7.57 (dd, \(J = 8.6, 2.0\) Hz, 1H); \textsuperscript{13}C NMR (75 MHz, (CD\textsubscript{3})\textsubscript{2}CO) δ 160.6, 151.7, 142.2, 132.0, 129.1, 126.7, 126.6; HRMS m/z (ESI): calcd. for C\textsubscript{7}H\textsubscript{4}ClNSe (M)\textsuperscript{+} 216.9197, found 216.9202.

6. Synthesis of Brassilexin Derivative 4

Following the general procedure for the synthesis of sulfides, benzyl mercaptan (0.53 mmol, 0.06 mL, 1.05 equiv) was added dropwise for 0.25 h to a stirred suspension of Na\textsubscript{H} (60%, 0.6 mmol, 24 mg, 1.2 equiv) in DMF (1.1 mL) at 0 °C (ice bath). Afterwards, a solution of the 3-acetyl-2-chloro-1-methyl-1\textsubscript{H}-indole (0.5 mmol, 103.8 mg, 1 equiv) in DMF (0.25 mL) was added and the reaction was heated to 75 °C for 12 h. After this time, the reaction was cooled to room temperature, diluted with dichloromethane and washed with water (3x) and brine. The organic phase was dried over MgSO\textsubscript{4} and concentrated under reduced pressure. Then, the solid residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure product 1-(2-(benzylthio)-1-methyl-1\textsubscript{H}-indol-3-yl)ethan-1-one.

1-(2-(benzylthio)-1-methyl-1\textsubscript{H}-indol-3-yl)ethan-1-one (SI-1t)

Following procedure, the reaction of 3-acetyl-2-chloro-1-methyl-1\textsubscript{H}-indole (0.5 mmol, 103.8 mg), Na\textsubscript{H} (60%, 0.6 mmol, 24 mg) and benzyl mercaptan (0.53 mmol, 0.06 mL) in DMF (1.35 mL) at 75 °C afforded the product SI-1t (89%, 131.2 mg) as a pale yellow solid. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 8.39 – 8.26 (m, 1H), 7.35 – 7.23 (m, 4H), 7.19 (d, \(J = 7.6\) Hz, 2H), 6.99 (d, \(J = 7.6\) Hz, 2H), 4.04 (s, 2H), 3.52 (s, 3H), 2.74 (s, 3H); \textsuperscript{13}C
NMR (75 MHz, CDCl₃) δ 194.8, 137.4, 137.1, 135.8, 128.7, 128.6, 127.6, 126.5, 123.9, 122.6, 122.5, 121.4, 109.9, 42.4, 30.6, 28.4.

Following the general procedure for the synthesis of oximes, a solution of 1-(2-(benzylthio)-1-methyl-1H-indol-3-yl)ethan-1-one (SI-1t, 0.44 mmol, 131.2 mg, 1 equiv) in EtOH (2.2 mL) was treated with 2-(aminooxy)-2-methylpropanoic acid hydrochloride (SI-11, 0.53 mmol, 82.2 mg, 1.2 equiv), sodium acetate (1.06 mmol, 86.6 mg, 2.4 equiv) and heated to reflux until completion by TLC analysis. The mixture was then allowed to cool to room temperature and water was added. The resulting aqueous solution was extracted with EtOAc (3x) and the combined organic layers were dried over anhydrous MgSO₄, filtered and concentrated under vacuum to provide the product. Then, the residue was subjected to flash chromatography (silica gel, cyclohexane/EtOAc) to give the analytically pure product 3.

2-(((1-(2-(benzylthio)-1-methyl-1H-indol-3-yl)ethylidene)amino)oxy)-2-methylpropanoic acid (3)

Following the procedure, the reaction of SI-1t (0.44 mmol, 131.2 mg), SI-11 (0.53 mmol, 82.2 mg) and sodium acetate (1.06 mmol, 86.6 mg) in EtOH (2.2 mL) at reflux afforded the product 3 (84%, 145.7 mg) (75% for two steps) as a yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J = 8.0 Hz, 1H), 7.32 – 7.11 (m, 6H), 6.95 (dd, J = 7.4, 1.8 Hz, 2H), 3.88 (s, 2H), 3.49 (s, 3H), 2.39 (s, 3H), 1.65 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 176.6, 155.8, 137.6, 137.3, 129.7, 128.7, 128.5, 127.4, 125.5, 123.5, 121.0, 120.5, 118.3, 110.0, 81.5, 42.6, 29.8, 24.6, 16.4; HRMS m/z (ESI): calcd. for C₂₂H₂₃N₂O₃S (M-H)- 395.1435, found 395.1241.

Following the general procedure for the synthesis of isothiazoles, in an oven-dried glass vial equipped with a stirring bar, 3 (0.1 mmol, 39.6 mg, 1 equiv), NaOAc (0.1 mmol, 8.2 mg, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate, (5·10⁻³ mmol, 2.1 mg, 0.05 equiv) and acetone (1.33 mL) were added under air. Then, the vial was closed with a PTFE/rubber septum perforated several
times to enable the air enter into the reaction. Afterwards, the mixture was stirred and irradiated at 450 nm using 380 mW single LEDs in a custom-made temperature-controlled system (see Figure S1) for 16h at 20 °C. Then, the volatiles were removed and the analytically pure product 4 was obtained by flash chromatography (Iatrobeads silica gel; cyclohexane/EtOAc).

3,8-dimethyl-8H-isothiazolo[5,4-b]indole (4)

Following the procedure, the reaction of 3 (0.1 mmol, 39.6 mg), NaOAc (0.1 mmol, 8.2 mg) and photocatalyst PC1 (5 mol%, 2.1 mg) in acetone (1.33 mL) irradiated at 450 nm afforded the product 4 (71%, 14.4 mg) as a white solid. $^1$H NMR (300 MHz, (CD$_3$)$_2$CO) $\delta$ 7.90 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.36 (ddd, J = 8.2, 7.8, 1.3 Hz, 1H), 7.30 – 7.18 (m, 1H), 3.94 (s, 3H), 2.72 (d, J = 1.3 Hz, 3H); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) $\delta$ 161.4, 157.3, 144.7, 123.9, 123.0, 120.7, 120.2, 118.9, 109.8, 32.2, 17.9; HRMS m/z (ESI): calcd. for C$_{11}$H$_{10}$N$_2$S (M+H)$^+$ 202.0565, found 202.0559.

7. Flow Setup for the Synthesis of Isothiazoles 2

General procedure for the optimization of the reaction conditions for the flow setup:

In a coil (V = 18 mL) made of perfluoroalkoxy (PFA) tubing (i.d. = 1.6 mm) irradiated with a blue LED spot (40 W), 2-(((1-(2-(benzylthio)phenyl)ethylidene)amino)oxy)-2-methylpropanoic acid (1d, 0.15 mmol, 36.3 mg, 1 equiv), NaOAc (0.15 mmol, 12.3 mg, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate and acetone (2 mL) were injected at 20 °C. Then, the volatiles were removed and yield was determined by $^1$H-NMR analysis using nitromethane (8 µL, 0.15 mmol) as the internal standard. O$_2$ gas was employed in a segmented flow fashion and a BPR (1.6 bar) was added at the end of the coil to increase the pressure of the system.
Table S3. Optimization of reaction conditions for the flow setup.

<table>
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<tr>
<th>entry</th>
<th>conditions[a]</th>
<th>PC1 (mol%)</th>
<th>tR (min)</th>
<th>conv. (%)[b]</th>
<th>yield (%)[b]</th>
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<td>No oxygen</td>
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<td>80</td>
<td>50</td>
<td>13</td>
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<td></td>
<td>Acetone sat.</td>
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<tr>
<td></td>
<td>with O₂</td>
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<td></td>
<td>BPR (1.6 bar)</td>
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<tr>
<td>2</td>
<td>O₂</td>
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<td>80</td>
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<td>O₂</td>
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<td>82</td>
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</table>

[a] Segmented flow (2 mm slugs) was made by passing oxygen gas and reaction solution through a T-union (1.25 mm thru-hole; 17.5 µl swept volume). [b] The yield was determined from the crude 'H-NMR. BPR = black pressure regulator

General procedure for the synthesis of isothiazoles 2 in the flow setup:

The corresponding oxime derivative 1 (0.33 mmol, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate (0.017 mmol, 6.8 mg, 0.05 equiv) and acetone (4.4 mL) were mixed at 20 ºC and passed through a packed bed reactor filled with NaOAc (Figure S2a). Afterwards, reaction solution and O₂ gas, used in a segmented flow fashion, were mixed through a T-union (Figure S2b), controlling the gas slugs (2 mm) with a micrometric valve. Compounds 1b, 1c and 1g were injected consecutively (separated by 4 mL of acetone) in the coil (V = 18 mL) made of perfluoroalkoxy (PFA) tubing (i.d. = 1.6 mm) and irradiated with a blue LED spot (40 W) (Figure S3). After 2 h, isothiazoles 2 were collected in different vials. Then, the volatiles were removed and yield was determined by 'H-NMR analysis using
nitromethane (17.7 µL, 0.33 mmol) as the internal standard: 2b (55%; 0.18 mmol), 2c (58%; 0.19 mmol) and 2g (44%; 0.14 mmol). In all the transformations the throughput of the reaction is ≈ 140 times higher than in conventional conditions and around 15% of starting material is recovered in all the cases.

Figure S2. a) Packed bed reactor filled with NaOAc and b) T-union with a micrometric valve employed in flow setup.

Figure S3. Coil of PFA with liquid and gas slugs employed in flow setup.

8. Mechanistic Studies

8.1. Cyclic Voltammetry of α-Imino-oxy Acids 1

Electrochemical studies of substrates 1a-d, 1a´ and 1a´´ were performed employing
1 nM solution of the corresponding α-imino-oxy acid 1 freshly prepared in HPLC grade acetone along with 1 nM sodium acetate and 0.1 M supporting electrolyte (tetrabutylammonium hexafluorophosphate) solutions. Nitrogen was passed through each sample before measurements to avoid the influence of oxygen reduction.

![Cyclic voltammetry of α-imino-oxy acids](image)

**Figure S4.** Cyclic voltammetry of α-imino-oxy acids 1a, 1a´ and 1a´´.

**Table S4.** Oxidation potentials of α-imino-oxy acids 1a, 1a´ and 1a´´.

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<th>α-Imino-oxy acids</th>
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<tr>
<td><img src="image" alt="Structure 1a´" /></td>
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<tr>
<td><img src="image" alt="Structure 1a´´" /></td>
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Figure S5. Cyclic voltammetry of α-imino-oxy acids 1a-d.

Table S5. Oxidation potentials of α-imino-oxy acids 1a-d.

<table>
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<th>α-Imino-oxy acids</th>
<th>$E_{1/2}^{ox}$ (V) vs SCE</th>
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<tbody>
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<tr>
<td><img src="image" alt="结构式1b" /></td>
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<tr>
<td><img src="image" alt="结构式1d" /></td>
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</table>
8.2. Fluorescence Quenching Studies

Emission intensities and time resolved emission spectra were recorded using an Edinburg Instruments FS5 Spectrofluorometer, and a 450 nm EPL laser.

For the steady-state and time resolved fluorescence quenching studies, increasing concentrations of quencher were added to a solution 3.7 mM of PC1 in acetone ($\lambda_{\text{exc}} = 450$ nm).
a)  

![Graph 1](Image1)

![Graph 2](Image2)

![Graph 3](Image3)

![Graph 4](Image4)

$K_q = 4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$

b)  

![Graph 1](Image5)

![Graph 2](Image6)

![Graph 3](Image7)

![Graph 4](Image8)

$K_q = 6.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
8.3. Radical Trapping Experiments

Table S6. Radical Trapping Experiments.

**Figure S7.** Fluorescence quenching studies. a) Quenching studies of PC1 with 1d: (1) Steady state luminescence quenching spectrum and (2) Stern-Volmer plot of the steady state; (3) Time resolved luminescence quenching and (4) Stern-Volmer plot to obtain $K_q$; b) Quenching studies of PC1 with 1d + NaOAc: (1) Steady state luminescence quenching spectrum and (2) Stern-Volmer plot of the steady state; (3) Time resolved luminescence quenching and (4) Stern-Volmer plot to obtain $K_q$; c) Quenching studies of PC1 with NaOAc: (1) Steady state luminescence quenching spectrum and (2) Stern-Volmer plot of the steady state; (3) Time resolved luminescence quenching and (4) Stern-Volmer plot to obtain $K_q$. 

$K_q = 0 \text{ M}^{-1} \text{s}^{-1}$
Following the general procedure for the synthesis of isothiazoles 2, in an oven-dried glass vial equipped with a stirring bar, 2-methyl-2-(((1-(2-(methylthio)phenyl)ethylidene)amino)oxy)propanoic acid (1a, 0.05 mmol, 13.4 mg, 1 equiv), the NaOAc (0.05 mmol, 4.1 mg, 1 equiv), photocatalyst PC1, 9-mesityl-10-methyl acridinium perchlorate, (2.5·10⁻³ mmol, 1 mg, 0.05 equiv), the corresponding radical scavenger (0.25 mmol, 5 equiv) and acetone (0.67 mL) were added under air. Then, the vial was closed with a PTFE/rubber septum perforated several times to enable the air enter into the reaction. Afterwards, the mixture was stirred and irradiated at 450 nm using 380 mW single LEDs in a custom-made temperature-controlled system (see Figure S1) for 16h at 20 ºC. Then, the volatiles were removed and yield was determined by ¹H-NMR analysis using 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) as internal standard.

9. References


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<th>entry</th>
<th>Radical scavenger</th>
<th>yield (%)(^{[a]})</th>
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<tr>
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<td>85</td>
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<tr>
<td>2</td>
<td>TEMPO</td>
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<td>3</td>
<td>BHT</td>
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\(^{[a]}\) The yield was determined from the crude ¹H-NMR.
10. NMR Spectra

10.1. NMR Spectra of Sulfides SI-1
S57
10.2. NMR Spectra of Selenides SI-10
10.3. NMR Spectra of α-Imino-oxy Acids 1

[Diagram of NMR spectra with chemical structures and peak assignments]
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<th>f1 (ppm)</th>
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<th>2.16</th>
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The chemical structure shown in the image is of a compound with chemical functionalities and possible functional groups depicted. The peaks in the spectra are indicative of specific chemical shifts in the NMR analysis, which are crucial for identifying the molecular structure and its properties.
10.4. NMR Spectra of Isothiazoles 2
10.5. NMR Spectra of Brassilexin Derivative 4