Supporting Information

NIS-initiated photo-induced oxidative decarboxylative sulfoximidation of cinnamic acids

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1. General information:

All the reagents were commercial grade and purified according to the established procedures. All the reactions were carried out in oven-dried glassware. The highest commercial quality reagents were purchased and were used without further purification unless otherwise stated. All the cinnamic acids used in this protocol were commercially purchased from Sigma Aldrich and BLD Pharma. Reactions were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel plates (60F₂₅₄) visualized under UV illumination at 254 nm. Organic extracts were dried over anhydrous sodium sulfate (Na₂SO₄). Solvents were removed using a rotary evaporator under reduced pressure. Column chromatography was performed to purify the crude product on silica gel 60-120 mesh using a mixture of hexane and ethyl acetate as eluent. The isolated compounds were characterized by spectroscopic [1 H, 13 C{1H} NMR, and IR] techniques and HRMS analysis. NMR spectra were recorded in deuterochloroform (CDCl₃). ¹H, ¹³C{¹H} were recorded in 400 (100), 500 (125) or 600 (150) MHz spectrometers and were calibrated using tetramethylsilane or residual undeuterated solvent for ¹H NMR, deuterochloroform for ¹³C NMR as an internal reference {Si(CH₃)₄: 0.00 ppm or CHCl₃: 7.260 ppm for ¹H NMR and 77.230 ppm for ¹³C{1H}. ¹⁹F NMR was calibrated without any internal standard in CDCl₃ in a 370 or 471 MHz spectrometer. The chemical shifts are quoted in δ units, parts per million (ppm). ¹H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), integration and coupling constant(s) J in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflection experiments. FT-IR spectra were recorded in neat and reported in the frequency of absorption (cm⁻¹). All UV experiments were performed in 1 mL quartz cuvettes of path length 1 cm at 25 °C in UV/Vis spectrometer in HPLC grade solvent.

2. Light information and reaction setup:

Philips 2 x 5 W blue LED (448 nm) bulb was used as the light source for this lightinduced reaction, and no filter was used. Borosilicate round bottom glass was used as the reaction vessel. The distance from the light source to the irradiation vessel was \sim 3-5 cm. A regular fan was used to ventilate the area to maintain the room temperature (27–30 °C). The reaction setup for this photochemical reaction and the corresponding images of the reaction mixture before the start of the reaction and after the completion of the reaction is shown below (Fig. S1).



(a)



(b) (c)

Fig. S1. (a) Photochemical Reaction Set-up (b) Before reaction (c) After reaction

3. Representative examples of bioactive sulfoximine derivatives



Fig. S2. Some biologically relevant sulfoximines.

4. General procedure:

4A. Procedure for the synthesis of starting substrates (a)

All the substrates were prepared according to the previously reported literature procedure.¹ In an oven-dried 50 mL round bottom flask, methylphenylsulfide **S** (5 mmol, 1 equiv, 620 mg), ammonium carbamate (7.5 mmol, 1.5 equiv, 585 mg) and phenyliodo diacetate (PIDA) (11.5 mmol, 2.3 equiv, 3.7 g) in 15 mL methanol are taken and stirred at room temperature for 3 hours. After the disappearance of the sulfides, as indicated by TLC, the reaction was stopped and the solvent was evaporated under reduced pressure. The compound was purified by column chromatography and separated in a 1:2 ratio of EtOAc:hexane to result in the product *S*-phenyl-*S*-methyl-sulfoximine (**a**) in 690 mg, 89% yield (Scheme S1).



Scheme S1. Preparation of *NH*-sulfoximines (a).

4B. Procedure for the synthesis of α -keto-N-acyl sulfoximines (1a)

Cinnamic acid (1) (0.4 mmol, 1 equiv, 59 mg), *NH*-sulfoximine (**a**) (0.4 mmol, 1 equiv, 62 mg), and *N*-iodosuccinimide (NIS) (0.08 mmol, 20 mol%, 18 mg) in 2 mL of DCM were added to an oven-dried 10 mL borosilicate vial and stirred at room temperature, approximately at a distance of $\sim 3-5$ cm from two 448 nm 5 W blue LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was added ethyl acetate (25 mL) and washed with saturated NaHCO₃ solution (1 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) solution followed by saturated brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, and then the solvent was evaporated under reduced pressure. The crude product obtained was purified over a column of silica gel using (3:1) of ethyl acetate in hexane to afford the α -keto-*N*-acyl sulfoximine (1**a**) in 82% yield. The identity and purity of the product was confirmed by spectroscopic analysis (Scheme S2).



Scheme S2. Preparation of α -keto-*N*-acyl sulfoximines (1a).

4C. Procedure for the synthesis of intermediate A.²

Intermediate **A** was prepared according to the previously reported literature procedure. In an oven-dried 10 mL round bottom flask, methylphenylsulfide **S** (1 mmol, 1equiv, 124 mg), ammonium carbonate (1.5 mmol, 1.5 equiv, 117 mg) and phenyliodo diacetate (PIDA) (2.3 mmol, 2.3 equiv, 741 mg) in 5 mL methanol were taken and stirred at room temperature for 1 hour. Then, 1.1 equiv of NIS (1.1 mmol, 248 mg) was added, and the stirring was continued for another 1 hour. After the completion of the reaction as indicated by TLC, the reaction was stopped and the precipitate was collected by vacuum filtration using a Büchner funnel, washed with a small amount of MeOH, and dried under reduced pressure (vacuum pump) to obtain pure product *N*-iodo-*S*-phenyl-*S*-methyl sulfoximine **A** in 83% yield (233 mg). The identity and purity of the product was confirmed by spectroscopic analysis and literature reports (Scheme S3).



Scheme S3. Preparation of *N*-iodo-*S*-phenyl-*S*-methyl sulfoximine (A).

4D. Procedure for the synthesis of intermediate D.³

A Schlenk flask equipped with a magnetic stir bar was charged with CuI (190 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol) and the *S*-aryl-*S*-methyl sulfoximine (**a**, 1.0 mmol) and purged with argon. Then, 5 mL dry toluene was added through a glass syringe, followed by *N*,*N*'-dimethylethylenediamine (213 mL, 2.0 mmol) and the (*E*)-(2-bromovinyl)benzene (1.5 mmol, 271 mg). After heating the mixture at 110 °C under stirring for 24 h, it was allowed to cool to room temperature, diluted with diethyl ether, and filtered through a thin pad of celite. The solvents were then removed under vacuum. The crude product obtained was purified over a column of silica gel using (5:2) of ethyl acetate in hexane to afford the essentially pure *N*-vinylsulfoximine (**D**) in 71% yield (182 mg) (Scheme S4).



Scheme S4. Preparation of intermediate D.

5. Optimization of reaction conditions:

COOH HN O + Me (1) (a) DCM, 36 h, rt 2 x 5 W blue LEDs (1a)			
entry	variation from optimal conditions ^a	yield (%) ^b	
1.	None	82	
2.	NCS, NBS, I ₂ (1 equiv) instead of NIS	Trace, 57, Trace	
3.	Without NIS	N.D.	
4.	50 mol% NIS	85	
5.	1 equiv NIS	80	
6.	DCE instead of DCM	34	
7.	CH ₃ CN instead of DCM	12	
8.	DMSO, DMF, EtOH, 1,2-dioxane instead of DCM	N.D.	
9.	2 x 5 W white LEDs	78	
10.	2 x 5 W green LEDs	25	
^{<i>a</i>} Reaction condition: 1 (0.4 mmol), a (0.4 mmol), NIS (0.08 mmol), DCM (2 mL) for 36 h in blue LED's (448 nm). ^{<i>b</i>} Isolated pure product. N.D. = not detected.			

Table S1. Optimization of the reaction conditions^{*a,b*}

A preliminary reaction was carried out between cinnamic acid (1, 1 equiv) and S-aryl-S-methyl sulfoximine (a, 1 equiv) in the presence of N-iodosuccinimide (NIS) (20 mol%), in DCM (2 mL) under the irradiation of 2 x 5 W blue LEDs at room temperature. Gratifyingly, a new product was isolated in 82% yield. The spectroscopic evidences (¹H and ¹³C{¹H} NMR and X-ray diffraction) revealed the structure of the product to be N-(methyl(oxo)(phenyl)- λ^{6} sulfaneylidene)-2-oxo-2-phenylacetamide (1a) Extensive optimization studies involving the selection of different reaction conditions were carried out. Initially, different catalysts such as *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), and molecular iodine (I_2) were screened. Both NCS and I_2 failed to result in the anticipated product, NBS resulted in **1a** with 47% yield (Table S1, entry 2). Moreover, the desired product was not formed at all in the absence of NIS (Table S1, entry 3). Further, to improve the yield, the reaction was carried out with different concentrations of NIS, such as 50 mol% and 1 equiv of NIS (Table S1, entries 4-5). However, there were no substantial changes in the yield, so all further reactions were carried out using 20 mol% of NIS. Next, different solvents such as DCE, CH₃CN, DMSO, DMF, EtOH, and 1,2-dioxane were screened in lieu of DCM. Except for DCE (34%) and CH₃CN (12%), the reaction did not proceed at all in other tested solvents (Table S1, entries 6-8). To check the effect of wavelength and intensity of light, the standard reaction was carried out in 2 x 5 W white (46 mW/cm²) and green (534 nm) LEDs. Both the lights failed to improve the reaction yield (Table 1, entries 9 and 10). Hence, the optimized condition for this reaction are the use of cinnamic acid (1 equiv), *NH*-sulfoximine (1 equiv), NIS (20 mol%) in DCM (2 mL) under 2 x 5 W blue LEDs (448 nm). For all the reactions, proper aeration was maintained using a fan.

6. Mechanistic investigations:

(a) Radical-trapping experiments:

In an oven-dried 10 mL borosilicate vial, cinnamic acid (1) (0.2 mmol, 1 equiv, 30 mg), *NH*-sulfoximine (**a**) (0.2 mmol, 1 equiv, 31mg), *N*-iodosuccinimide (0.04 mmol, 20 mol%. 9mg), and 1,1-diphenylethylene (1 equiv, 36 mg), were taken in DCM (1 mL) and was stirred at room temperature, approximately at a distance of \sim 3-5 cm from two 448 nm 5 W blue LED bulbs. A small aliquot of the reaction mixture was withdrawn at approximately 12 h and diluted with 60:40 acetonitrile:water mixture (1 mL) and subjected to HRMS. The HRMS analysis of this reaction aliquot shows HRMS values corresponding to diphenylethylene-sulfoximine adduct (**a'**). This observation infers the possible involvement of *N*-centered sulfoximine radical in the reaction (Scheme S5) (Fig. S3).



Scheme S5. Radical trapping experiments with 1,1-diphenylethylene.



Fig. S3 HRMS analysis of diphenylethylene-sulfoximine adduct (a').

(b) H₂O¹⁸-labelling experiment

In an oven-dried 10 mL borosilicate vial, cinnamic acid (1) (1 mmol, 1 equiv, 148 mg), *NH*-sulfoximine (**a**) (1 mmol, 1 equiv, 155 mg), *N*-iodosuccinimide (0.2 mmol, 20 mol%. 45 mg), and H₂O¹⁸ (1 mmol, 1 equiv, 20 mg) were taken in DCM (3 mL) and was stirred at room temperature, approximately at a distance of ~3-5 cm from two 448 nm 5 W blue LED bulbs. After completion of the reaction (monitored by TLC analysis), the mixture was admixed with 20 mL ethyl acetate and sequentially washed with aqueous NaHCO₃ (1 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) and brine solution (1 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by column chromatography over silica gel (60-120 mesh) using hexane and ethyl acetate (3:1) as eluent to afford *N*-[methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a') in 81% yield (Scheme S6). To confirm the origin of the two carbonyl oxygens present in the product, the isolated product was subjected to ¹³C NMR and HRMS analysis. The ¹³C NMR of 1a' shows two signals for the amidic carbonyl (δ 173.489 and 173.450 ppm) due to both labelled and unlabelled carbonyl groups of α -keto-*N*-acyl

sulfoximines (Fig. S4). Further, the HRMS analysis also confirms the formation of ¹⁸O-labeled α -keto-*N*-acyl sulfoximines (**1a'**) (Fig. S5). This observation confirms that out of the two oxygen in the product, one originates from water and the other oxygen might be originating from atmospheric oxygen. Further, from HRMS analysis the percentage abundance of ¹⁸O labelled product **1a'** is found to be 45% compared to ¹⁶O labelled product.



Fig. S4 ¹³C{¹H} spectra of ¹⁸O labelled α -keto-*N*-acylsulfoximines (1a').



Fig. S5 HRMS of ¹⁸O labelled α -keto-*N*-acylsulfoximines (1a').

(c) H₂O₂ Detection in the reaction mixture

Method-1: H₂O₂ detection by Mohr's Salt

In an oven-dried 10 mL borosilicate vial, cinnamic acid (1) (1 mmol, 1 equiv, 148 mg), *NH*-sulfoximines (**a**) (1 mmol, 1 equiv, 155 mg), *N*-iodosuccinimide (0.2 mmol, 20 mol%. 45 mg), and were taken in DCM (3 mL) and was stirred at room temperature, approximately at a distance of ~3-5 cm from two 448 nm 5 W blue LED bulbs. After around 16 hours, a 100 μ L solution of Mohr's Salt (10 mg in 100 μ L H₂O + 1 mL CH₃CN) was added to the reaction mixture. After some time a rapid setting of Fe(OH)₃ floc was observed (Fig. S6). The floc observed was because of the rapid oxidation of Fe(II) to Fe(III) due to the presence of hydrogen peroxide, H₂O₂ in the medium.



Fig. S6 (a) Reaction mixture before addition of Fe(II) solution; (b) Reaction mixture after addition of Fe(II) solution

Method-2: H₂O₂ detection by UV-vis experiment⁴

The above reaction mixture (5 μ L) was withdrawn at approximately 16 h and was dissolved in 1 mL of DCM and subjected to UV-vis spectroscopy. An absorption maximum of 507 nm was recorded. Another portion of the same reaction mixture was admixed with 5 μ L of TiCl₄ solution and was dissolved in 1 mL of DCM, and their UV absorption was recorded. Now, there was a shift from 507 nm to 495 nm upon addition of TiCl₄. This shift was due to the formation of peroxo complex of titanium (IV) (Fig. S7).



Fig. S7 UV absorption spectra for H_2O_2 detection in the medium.

7. UV-vis experiments:

A 0.1 mM 10 mL stock solution of cinnamic acid (1), S-aryl-S-methyl sulfoximine (a) and N-iodo-S-phenyl-S-methyl sulfoximine (A) were prepared separately in DCM. The UV absorption of cinnamic acid (1) (5 μ M in 1mL DCM) and S-aryl-S-methyl sulfoximine (a) (5 μ M in 1 mL DCM) and N-iodo-S-phenyl-S-methyl sulfoximine (A) were independently recorded. The absorption spectra for the substrates 1 and a did not show any notable absorption pattern at either blue or visible region (λ >350 nm). However, the absorption spectra of A, recorded under the same condition exhibited a remarkable progressive increase of absorbance around 480 nm, with a maximum in the region at 363 nm. This implied that intermediate A is serving as an energy-absorbing species in blue light and mediates the entire reaction in the absence of any photocatalyst (Fig. S8).



Fig. S8 UV-vis spectra of cinnamic acid (1), S-aryl-S-methyl sulfoximine (a), and (A) in DCM.

8. Scale up reaction procedure:

Cinnamic acid (1) (5.0 mmol, 1 equiv, 740 mg), *NH*-sulfoximine (**a**) (2.0 mmol, 1 equiv, 775 mg), and *N*-iodosuccinimide (NIS) (1.0 mmol, 20 mol%, 225 mg) in 10 mL of DCM were added to an oven-dried 25 mL borosilicate vial and stirred at room temperature, approximately at a distance of \sim 3–5 cm from two 448 nm 5 W blue LED bulbs. After completion of the reaction (monitored by TLC analysis), the reaction mixture was added ethyl acetate (40 mL) and washed with saturated NaHCO₃ solution (2 x 10 mL), 5% aqueous Na₂S₂O₃ (1 x 10 mL) solution followed by saturated brine solution (2 x 10 mL). The organic layer was dried over anhydrous Na₂SO₄, and then the solvent was evaporated under reduced pressure. The crude

product obtained was purified over a column of silica gel using (3:1) of ethyl acetate in hexane to afford the α -keto-*N*-acyl sulfoximine (1a) in 61% yield (875 mg) (Scheme S7).



Scheme S7. Scale up reaction condition for the synthesis of α -keto-*N*-acyl sulfoximines (1a).

9. Crystallographic information:

Crystallographic information of *N*-[methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a):

(i) Sample Preparation: The single crystal of compound 1a was prepared by the slow evaporation method for which 10 mg of the compound (1a) was dissolved in 1 mL of DCM in a clean and dry 10 mL glass vial. MeOH (0.5 mL) was added to this solution slowly with a dropper. The mouth of the glass vial was covered with a cap having a small hole and kept for slow evaporation at room temperature. Crystals of 1a were obtained after approximately 3-4 days as a transparent block-shaped crystal.

(ii) Data Collection: Diffraction data were collected at 292 K with MoK α radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART APEX CCD diffractometer equipped with graphite monochromator and Apex CD camera. The SMART software was used for data collection and for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT^{5,6} software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-973 software. All the non-H atoms were refined in the anisotropic approximation against F2 of all reflections.⁷

(iii) Crystallographic description of *N*-[methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a):

C₁₅H₁₃NO₃S, colourless block shaped crystal; crystal dimensions 0.06 x 0.05 x 0.05 mm, $M_r = 287.32$, Orthorhombicic, space group F d d 2; a = 13.0303(7), b = 43.234 (3), c = 10.2922 (7) Å, $a = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, V = 5798.1 (6) Å³, Z = 16, $\rho_{calcd} = 1.317$ g/cm³, $\mu = 0.229$ mm⁻¹, F(000) = 2400.0, reflection collected / unique = 2880 / 2269, refinement method = full-matrix least-squares on F^2 , final *R* indices [*I*> 2\s(*I*)]: $R_1 = 0.0532$, $wR_2 = 0.0856$, *R* indices (all data):

 $R_1 = 0.0758$, $wR_2 = 0.0947$, goodness of fit = 1.065. CCDC-2227206 for *N*-[methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.



Fig. S9 ORTEP diagram of *N*-[methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a) with 30% ellipsoid probability (CCDC 2227206).

10. Spectral data

N-[Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-phenylacetamide (1a):⁸



White solid (94 mg, 82%); purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.09–8.04 (m, 4H), 7.73 (t, 1H, J = 9.5 Hz), 7.67–7.58 (m, 3H), 7.47 (t, 2H, J = 9.5 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.3, 173.5, 137.9, 134.7, 134.4, 133.0, 130.4, 130.1, 128.9, 127.4, 45.1; IR (neat, cm⁻¹): 3019, 2924, 2853, 1682, 1631, 1597, 1448, 1405, 1208; HRMS (ESI): calculated for C₁₅H₁₃NO₃SNa [M + Na]⁺: 310.0508, found 310.0503.

N-[Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene]-2-oxo-2-(*p*-tolyl)acetamide (2a):⁹



White solid (89 mg, 74%); purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.08–8.06 (m, 2H), 7.94 (d, 2H, J= 8.4 Hz), 7.74–7.69 (m, 1H), 7.66–7.62 (m, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 3.47 (s, 3H), 2.41 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 190.1, 173.7, 145.6, 137.9, 134.6, 130.5, 130.4, 130.1, 129.6, 127.4, 45.0, 22.1; IR (neat, cm⁻¹): 3017, 2925, 2854, 1677, 1629, 1605, 1447, 1331, 1211; HRMS (ESI): calculated for C₁₆H₁₆NO₃S [M + H]⁺: 302.0845, found 302.0842.

N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(*m*-tolyl)acetamide (3a):⁹



Off white solid (87 mg, 72%), purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (d, 2H, J = 7.5 Hz), 7.84 (s, 2H), 7.72 (t, 1H, J = 9.0 Hz), 7.64 (t, 2H, J = 7.5 Hz), 7.41 (d, 1H, J = 7.5 Hz), 7.35 (t, 1H, J = 7.5 Hz), 3.48 (s, 3H), 2.39 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.6, 173.6, 138.7, 138.0, 135.3, 134.6, 132.9, 130.7, 130.1, 128.8, 127.7, 127.4, 45.0, 21.5; IR (neat, cm⁻¹): 3018, 2921, 2854, 1677, 1634, 1581, 1449, 1324, 1222; HRMS (ESI): calculated for C₁₆H₁₅NO₃SNa [M + Na]⁺: 324.0665, found 324.0670.

2-(3-Methoxyphenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (4a): ¹⁰



Yellow solid (85 mg, 67%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (d, 2H, J = 7.5 Hz), 7.73 (t, 1H, J = 7.5 Hz), 7.66–7.62 (m, 3H), 7.56 (s, 1H), 7.37 (t, 1H, J = 7.5 Hz), 7.15 (d, 1H, J = 8.5 Hz), 3.84 (s, 3H), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.2, 173.4, 160.0, 138.0, 134.6, 134.3, 130.1, 129.9, 127.4, 123.6, 121.6, 113.5, 55.7, 45.1; IR (neat, cm⁻¹): 3009, 2928, 2841, 1683, 1632, 1596, 1449, 1324, 1249; HRMS (ESI): calculated for C₁₆H₁₆NO₄S [M + H]⁺: 318.0795 found 318.0797.

2-(4-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (5a): ¹⁰



Light yellow solid (89 mg, 73%); purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (dd, 3H, $J_1 = 9.0$ Hz, $J_2 = 6.0$ Hz), 8.05 (s, 1H), 7.73 (t, 1H, J = 7.5 Hz), 7.64 (t, 2H, J = 7.5 Hz), 7.13 (t, 2H, J = 9.0 Hz), 3.47 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 188.6, 173.1, 166.6 (d, J = 255.2 Hz), 137.7, 134.7, 133.2 (d, J = 9.5 Hz), 130.1, 129.4 (d, J = 3.0 Hz), 127.3, 116.1 (d, J = 21.9 Hz), 45.0; ¹⁹F NMR (CDCl₃, 370 MHz): δ (ppm) –102.7; IR (neat, cm⁻¹): 3020, 2928, 1683, 1631, 1596, 1505, 1448, 1331, 1206; HRMS (ESI): calculated for C₁₅H₁₂FNO₃SNa [M + Na]⁺: 328.0414, found 328.0423.

2-(4-Chlorophenyl)-*N*-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (6a): ⁹



Pale yellow solid, (96 mg, 75% yield), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (400 MHZ, CDCl₃): δ 8.08–8.05 (m, 2H), 8.01–7.98 (m, 2H), 7.73 (t, 1H, J = 7.6 Hz), 7.65 (t, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.4 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (100 MHZ, CDCl₃): δ 188.9, 172.8, 141.0, 137.7, 134.7, 131.8, 131.4, 130.2, 129.2, 127.3, 45.0; IR (neat, cm⁻¹): 3016, 2925, 2851, 1681, 1630, 1586, 1447, 1329, 1205; HRMS (ESI): calculated for C₁₅H₁₂ClNO₃SNa [M + Na]⁺: 344.0119, found 344.0122.

2-(4-Bromophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (7a):⁹



White solid (96 mg, 66%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.07 (d, 2H, J = 8.0 Hz), 7.92 (d, 2H, J = 8.5 Hz), 7.73 (t, 1H, J = 7.5 Hz), 7.65 (t, 2H, J = 7.5 Hz), 7.61 (d, 2H, J = 8.5 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): 189.2, 172.8, 137.9, 134.7, 132.5, 132.3, 131.9, 130.2, 129.9, 127.4, 45.1; IR (neat, cm⁻¹): 3016, 2924, 2851, 1685, 1631, 1583, 1447, 1329, 1207; HRMS (ESI): calculated for C₁₅H₁₃BrNO₃S [M + H]⁺: 365.9794, found 365.9799.

2-(3-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxoacetamide (8a):



Yellow solid (87 mg, 71%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.06 (d, 2H, J = 8.5 Hz), 7.84 (d, 1H, J = 7.5 Hz), 7.73 (t, 2H, J = 7.0 Hz), 7.65 (t, 2H, J = 7.5 Hz), 7.44 (dd, 1H, $J_1 = 13.5$ Hz, $J_2 = 8.0$ Hz), 7.29 (t, 1H, J = 8.5 Hz), 3.48 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 188.9 (d, J = 2.3 Hz), 172.7, 162.8 (d, J = 247.0 Hz), 137.8, 135.1 (d, J = 6.5 Hz), 134.7, 130.6 (d, J = 7.5 Hz), 130.2, 127.4, 126.4 (d, J = 3.0 Hz), 121.5 (d, J = 21.5 Hz), 116.6 (d, J = 22.5 Hz), 45.0; ¹⁹F NMR (CDCl₃, 471 MHz): δ (ppm) –111.5; IR (neat, cm⁻¹): 2955, 2926, 2872, 1687, 1632, 1587, 1447, 1329, 1235; HRMS (ESI): calculated for C₁₅H₁₂FNO₃SNa [M + Na]⁺: 328.0414, found 328.0424.

2-(3-Chlorophenyl)-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (9a):⁹



Yellow solid (86 mg, 67%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.07 (d, 2H, J = 7.0 Hz), 8.02 (s, 1H), 7.94 (d, 1H, J = 8.0 Hz), 7.74 (t, 1H, J = 7.5 Hz), 7.66 (t, 2H, J = 7.5 Hz), 7.56 (d, 1H, J = 8.0 Hz), 7.41 (t, 1H, J = 8.0 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 187.8, 171.6, 136.8, 134.2, 133.8, 133.6, 133.5, 133.3, 129.2, 129.1, 127.7, 126.4, 44.0; IR (neat, cm⁻¹): 2958, 2925, 2851, 1687, 1632, 1571, 1447, 1326, 1196; HRMS (ESI): calculated for C₁₅H₁₂ClNO₃SNa [M + Na]⁺: 344.0119, found: 344.0105.

2-(3-Bromophenyl)-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (10a):⁸



Yellow solid (92 mg, 63%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (t, 1H, J = 2.0 Hz), 8.08–8.06 (m, 2H), 7.99–7.97 (m, 1H), 7.76–7.71 (m, 2H), 7.66 (t, 2H, J = 7.0 Hz), 7.35 (t, 1H, J = 7.5 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 188.7, 172.5, 137.8, 137.2, 134.9, 134.8, 133.1, 130.4, 130.2, 129.1, 127.4, 123.1, 45.1; IR (neat, cm⁻¹): 2955, 2921, 2849, 1688, 1635, 1563, 1456, 1328, 1198; HRMS (ESI): calculated for C₁₅H₁₃BrNO₃S [M + H]⁺: 365.9794, found: 365.9779.

N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl)

acetamide (11a): 10



Yellow solid (87 mg, 61%), purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.17 (d, 2H, J = 8.0 Hz), 8.07 (d, 2H, J = 7.0 Hz), 7.76–7.72 (m, 3H), 7.67 (d, 2H, J = 8.0 Hz), 3.49 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 189.0, 172.4, 137.7, 135.9, 135.6, 135.3, 134.8, 130.8, 130.2, 127.4, 125.9 (q, J = 14.5Hz), 45.1; ¹⁹F NMR (CDCl₃, 471 MHz): δ (ppm) –63.3; IR (neat, cm⁻¹): 2953, 2925, 2854, 1693, 1637, 1581, 1449, 1325, 1210; HRMS (ESI): calculated for C₁₆H₁₃F₃NO₃S [M + H]⁺: 356.0563, found 356.0565. N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-(3-(trifluoromethyl)phenyl) acetamide (12a):



Yellow solid (78 mg, 55%), purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.29 (s, 1H), 8.23 (d, 1H, J = 8.0 Hz), 8.06 (d, 2H, J =7.5 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.73 (t, 1H, J = 7.5 Hz), 7.65 (t, 2H, J = 8.0 Hz), 7.61 (t, 1H, J = 7.5 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 188.6, 172.3, 137.7, 134.8, 133.8, 133.7, 131.5 (q, J = 131.5 Hz), 130.6 (q, J = 14.0 Hz), 130.2, 129.5, 127.3, 127.1 (q, J = 15.5 Hz), 122.7, 45.0; ¹⁹F NMR (CDCl₃, 471 MHz): δ (ppm) –62.9; IR (neat, cm⁻¹): 3075, 3020, 2928, 1691, 1631, 1446, 1326, 1225; HRMS (ESI): calculated for C₁₆H₁₃F₃NO₃S [M + H]⁺: 356.0563, found 356.0565.

N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-(4-nitrophenyl)-2-oxoacetamide (13a): ¹¹



Yellow solid (76 mg, 57%), purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.29 (d, 2H, J = 8.5 Hz), 8.22 (d, 2H, J = 8.5 Hz), 8.06 (d, 2H, J = 8.0 Hz), 7.75 (t, 1H, J = 7.0 Hz), 7.66 (t, 2H, J = 8.0 Hz), 3.50 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 188.2, 171.8, 151.0, 137.8, 137.6, 134.9, 131.4, 130.2, 127.3, 123.9, 45.0; IR (neat, cm⁻¹): 3110, 3021, 2928, 1693, 1631, 1604, 1526, 1447, 1345, 1201; HRMS (ESI): calculated for C₁₅H₁₃N₂O₅S [M + H]⁺: 333.0540, found 333.0547. N-(Methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-(3-nitrophenyl)-2-oxoacetamide (14a):¹¹



Yellow solid (84 mg, 63%), purified over a column of silica gel (30% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.87 (s, 1H), 8.44 (d, 1H, J = 8.0 Hz), 8.40 (d, 1H, J =7.5 Hz), 8.08 (d, 2H, J = 8.0 Hz), 7.76 (t, 1H, J = 7.5 Hz), 7.69 (d, 3H, J = 7.5 Hz), 3.51 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 187.6, 171.6, 148.6, 137.6, 135.9, 134.9, 134.7, 130.3, 130.1, 128.4, 127.3, 125.2, 45.0; IR (neat, cm⁻¹): 3056, 2986, 2925, 1696, 1638, 1534, 1446, 1351, 1264; HRMS (ESI): calculated for C₁₅H₁₃N₂O₅S [M + H]⁺: 333.0540, found: 333.0536.

2-(3-Chloro-4-methoxyphenyl)-N-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-

oxoacetamide (15a):



Yellow solid (90 mg, 64%), purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.08 (dd, 3H, $J_1 = 11.6$ Hz, $J_2 = 7.6$ Hz), 7.99 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.73 (t, 1H, J = 7.6 Hz), 7.65 (t, 2H, J = 7.6 Hz), 6.96 (d, 1H, J = 8.8Hz), 3.97 (s, 3H), 3.47 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 187.9, 173.0, 159.9, 137.9, 134.7, 132.3, 131.4, 130.2, 127.4, 126.7, 123.4, 111.6, 56.7, 45.1; IR (neat, cm⁻¹): 3014, 2926, 2849, 1676, 1631, 1590, 1500, 1445, 1308, 1191; HRMS (ESI): calculated for C₁₆H₁₄ClNO₄SNa [M + Na]⁺: 374.0224, found 374.0233.

N-(Methyl(oxo)(*p*-tolyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1b):⁸



White solid (93 mg, 77%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.05 (d, 2H, J = 7.5 Hz), 7.94 (d, 2H, J = 8.5 Hz), 7.59 (t, 1H, J = 7.0 Hz), 7.46 (t, 2H, J = 8.0 Hz), 7.43 (d, 2H, J = 8.5 Hz), 3.46 (s, 3H), 2.47 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.4, 173.5, 145.9, 134.9, 134.3, 133.1, 130.7, 130.4, 128.8, 127.4, 45.2, 21.9; IR (neat, cm⁻¹): 2961, 2926, 2851, 1685, 1636, 1597, 1450, 1330, 1208; HRMS (ESI): calculated for C₁₆H₁₅NO₃SNa [M + Na]⁺: 324.0665, found 324.0662.

N-((4-Ethylphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1c):



Yellow solid (94 mg, 75%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.05 (d, 2H, J = 7.0 Hz), 7.97 (d, 2H, J = 8.5 Hz), 7.60 (t, 1H, J = 7.5 Hz), 7.48–7.44 (m, 4H), 3.47 (s, 3H), 2.77 (q, 2H, J = 7.5 Hz), 1.28 (t, 3H, J = 7.5 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.4, 173.5, 152.0, 134.9, 134.4, 133.0, 130.4, 129.6, 128.8, 127.5, 45.2, 29.1, 15.2; IR (neat, cm⁻¹): 3024, 2966, 1682, 1630, 1595, 1451, 1330, 1206; HRMS (ESI): calculated for C₁₇H₁₇NO₃SNa [M + Na]⁺: 338.0821, found 338.0824.





Yellow solid (85 mg, 67%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.05 (d, 2H, J = 7.5 Hz), 7.99 (d, 2H, J = 9.0 Hz), 7.59 (t, 1H, J = 7.0 Hz), 7.46 (t, 2H, J = 7.5 Hz), 7.08 (d, 2H, J = 9.0 Hz), 3.90 (s, 3H), 3.46 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.5, 173.5, 164.6, 134.4, 133.1, 130.4, 129.7, 129.0, 128.8, 115.4, 56.1, 45.5; IR (neat, cm⁻¹): 3014, 2927, 2846, 1682, 1631, 1592, 1496, 1449, 1310, 1207; HRMS (ESI): calculated for C₁₆H₁₅NO₄SNa [M + Na]⁺: 340.0614, found 340.0613.

N-((3-Methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1e):



Yellow solid (81 mg, 64%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.05 (d, 2H, J = 7.6 Hz), 7.64–7.58 (m, 2H), 7.56 (t, 1H, J = 3.2 Hz), 7.52 (d, 1H, J = 7.6 Hz), 7.47 (t, 2H, J = 7.6 Hz), 7.22 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 3.89 (s, 3H), 3.46 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 190.4, 173.5, 160.8, 139.1, 134.4, 133.0, 131.2, 130.4, 128.9, 121.2, 119.4, 111.9, 56.1, 45.1; IR (neat, cm⁻¹): 3015, 2927, 2839, 1682, 1631, 1596, 1482, 1429, 1206; HRMS (ESI): calculated for C₁₆H₁₅NO₄SK [M + K]⁺: 356.0353, found 356.0352.

N-((4-Fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1f):⁸



Light yellow solid (99 mg, 81%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.10 (dd, 2H, $J_1 = 8.8$ Hz, $J_2 = 4.8$ Hz), 8.05 (d, 2H, J = 7.2 Hz), 7.61 (t, 1H, J = 7.6 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.33 (t, 2H, J = 9.2 Hz), 3.49 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.2, 173.4, 166.5 (d, J = 256.8 Hz), 134.5, 133.92, 133.90, 133.0, 130.5, 130.4, 128.9, 117.5 (d, J = 23.0 Hz), 45.3; ¹⁹F NMR (CDCl₃, 370 MHz): δ (ppm) –101.9; IR (neat, cm⁻¹): 3057, 2955, 2924, 2854, 1683, 1636, 1592, 1493, 1375, 1263; HRMS (ESI): calculated for C₁₅H₁₂FNO₃SNa [M + Na]⁺: 328.0414; found 328.0421.





White solid (87 mg, 68%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.05–8.01 (m, 4H), 7.63–7.59 (m, 3H), 7.48 (t, 2H, J =8.0 Hz), 3.47 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 190.2, 173.4, 141.7, 136.4, 134.5, 132.8, 130.5, 130.4, 128.93, 128.91, 45.1; IR (neat, cm⁻¹): 3055, 2960, 2921, 2860, 1680, 1635, 1590, 1495, 1372, 1260; HRMS (ESI): calculated for C₁₅H₁₆ClN₂O₃S [M + NH₄]⁺: 959.9858, found: 359.9648.





Light yellow solid (95 mg, 78%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.04 (d, 2H, J = 7.0 Hz), 7.87 (d, 1H, J = 8.0 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.65 (t, 1H, J = 5.5 Hz), 7.60 (t, 1H, J = 7.0 Hz), 7.47 (t, 2H, J = 7.5 Hz), 7.42 (t, 1H, J = 8.0 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.1, 173.3, 162.9 (d, J = 252.8 Hz), 140.1 (d, J = 6.9 Hz), 134.5, 132.9, 132.0 (d, J = 7.8 Hz), 130.4, 128.9, 123.2, (d, J = 3.1 Hz), 122.0 (d, J = 21.4 Hz), 115.1 (d, J = 25.0 Hz), 45.0; ¹⁹F NMR (CDCl₃, 471 MHz): δ (ppm) –107.5; IR (neat, cm⁻¹): 3070, 3021, 2927, 1682, 1633, 1594, 1478, 1331, 1206; HRMS (ESI): calculated for C₁₅H₁₂FNO₃SNa [M + Na]⁺: 328.0414, found 328.0424.





Light yellow solid (91 mg, 71%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.05 (t, 3H, J = 7.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 7.69 (d, 1H, J = 8.0 Hz), 7.60 (q, 2H, J = 8.0 Hz), 7.48 (t, 2H, J = 7.5 Hz), 3.48 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.0, 173.3, 139.8, 136.5, 134.9, 134.5, 132.9, 131.4, 130.4, 128.9, 127.6, 125.5, 45.0; IR (neat, cm⁻¹): 3055, 2928, 2851, 1686, 1639, 1576, 1374, 1264, 1240, 1207; HRMS (ESI): calculated for C₁₅H₁₂ClNO₃SNa [M + Na]⁺: 344.0119, found 344.0122.





Light yellow solid (114 mg, 78%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.36 (d, 1H, J = 7.8 Hz), 8.04 (d, 2H, J = 6.6 Hz), 7.82 (d, 1H, J = 7.8 Hz), 7.63 (t, 1H, J = 7.8 Hz), 7.59 (t, 1H, J = 7.2 Hz), 7.55 (t, 1H, J = 7.8 Hz), 7.45 (t, 2H, J = 7.8 Hz), 3.64 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) 189.8, 172.4, 137.1, 136.2, 135.5, 134.4, 133.0, 132.1, 130.4, 128.9, 128.8, 119.7, 42.6; IR (neat, cm⁻¹): 3011, 2927, 2854, 1682, 1632, 1596, 1449, 1329, 1206; HRMS (ESI): calculated for C₁₅H₁₂BrNO₃SNa [M + Na]⁺: 387.9613, found 387.9623.

N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (1k):



Light yellow solid (87 mg, 61%), purified over a column of silica gel (28% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.22 (d, 2H, J = 8.5 Hz), 8.04 (d, 2H, J = 7.0 Hz), 7.92 (d, 2H, J = 8.5 Hz), 7.61 (t, 1H, J = 7.0 Hz), 7.48 (t, 2H, J = 7.5 Hz), 3.49 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.0, 173.3, 141.7, 136.5, 136.3, 134.6, 132.8, 130.4, 128.9, 128.2, 127.3 (q, J = 14.5 Hz), 44.9; ¹⁹F NMR (CDCl₃, 471 MHz): δ (ppm) –63.3; IR (neat, cm⁻¹): 3019, 2926, 2855, 1684, 1636, 1576, 1402, 1321, 1206; HRMS (ESI): calculated for C₁₆H₁₃F₃NO₃S [M + H]⁺: 356.0563, found 356.0567.

N-(Ethyl(oxo)(phenyl)- λ^6 -sulfaneylidene)-2-oxo-2-phenylacetamide (11):¹¹



Light yellow solid (71 mg, 59%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.04 (t, 3H, J = 8.5 Hz), 7.73 (t, 1H, J = 7.0 Hz), 7.64 (t, 2H, J = 7.5 Hz), 7.59 (t, 1H, J = 7.0 Hz), 7.54–7.41 (m, 3H), 3.66–3.54 (m, 2H), 1.33 (t, 3H, J = 7.5 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.5, 173.6, 135.6, 134.6, 134.4, 133.1, 130.4, 130.0, 128.8, 128.2, 51.5, 7.2; IR (neat, cm⁻¹): 3062, 2924, 2853, 1686, 1636, 1596, 1461, 1309, 1206; HRMS (ESI): calculated for C₁₆H₁₅NO₃SNa [M + Na]⁺: 324.0665, found 324.0666.





Light yellow solid (72 mg, 57%), purified over a column of silica gel (25% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.04 (t, 3H, J = 8.5 Hz), 7.72 (t, 1H, J = 7.5 Hz), 7.64 (t, 2H, J = 7.5 Hz), 7.60–7.50 (m, 2H), 7.46 (t, 2H, J = 7.5 Hz), 3.62–3.44 (m, 2H), 1.87–1.79 (m, 2H), 1.00 (t, 3H, J = 7.5 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.5, 173.5, 136.3, 134.5, 134.3, 133.1, 130.4, 130.0, 128.8, 128.1, 58.4, 16.3, 12.9; IR (neat, cm⁻¹): 3065, 2921, 2854, 1685, 1634, 1449, 1327, 1276, 1207; HRMS (ESI): calculated for C₁₇H₁₇NO₃SNa [M + Na]⁺: 338.0821, found 338.0825.

2-Oxo-*N*-(oxo(phenyl)(pyridin-2-yl)- λ^6 -sulfaneylidene)-2-phenylacetamide (1n):



Light yellow solid (63 mg, 45%), purified over a column of silica gel (35% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.69 (d, 1H, J = 5.5 Hz), 8.45 (d, 1H, J = 10.0 Hz), 8.19 (d, 2H, J = 11.5 Hz), 8.08 (d, 2H, J = 10.5 Hz), 8.02–7.98 (m, 1H), 7.66 (t, 1H, J = 9.0 Hz), 7.59–7.55 (m, 3H), 7.51–7.45 (m, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 190.1, 173.6, 157.4, 150.8, 138.7, 135.9, 134.6, 134.3, 133.2, 130.5, 129.6, 129.2, 128.8, 127.4, 123.9; IR (neat, cm⁻¹): 2955, 2918, 2869, 1690, 1642, 1578, 1459, 1377, 1190; HRMS (ESI): calculated for C₁₉H₁₄N₂O₃SNa [M + Na]⁺: 373.0617, found 373.0621.

(Iodoimino)(methyl)(phenyl)- λ^6 -sulfanone (A):²



White solid (233 mg, 83%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86–7.84 (m, 2H), 7.70–7.65 (m, 1H), 7.62–7.58 (m, 2H), 3.32 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 140.1, 133.9, 129.8, 128.5, 42.9; IR (neat, cm⁻¹): 3020, 2917, 1445, 1405, 1312, 1199, 1088.

(*E*)-Methyl(phenyl)(styrylimino)-λ⁶-sulfanone (D):³



Brown gummy solid (182 mg, 71%), purified over a column of silica gel (20% ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.96 (d, 2H, J = 7.5 Hz), 7.64 (d, 1H, J = 7.0 Hz), 7.59 (t, 2H, J = 7.0 Hz), 7.18 (d, 4H, J = 4.5 Hz), 7.08–7.05 (m, 1H), 6.91 (d, 1H, J = 13.5 Hz), 6.20 (d, 1H, J = 13.5 Hz), 3.22 (s, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ (ppm) 139.5,

138.1, 133.7, 130.0, 129.9, 128.8, 128.6, 125.7, 125.2, 118.4, 45.5; IR (neat, cm⁻¹): 3274, 3061, 2925, 2854, 1685, 1639, 1446, 1221; HRMS (ESI) calculated for $C_{15}H_{15}NOS [M + H]^+$: 258.0947, found 258.0953.

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12. Spectra of all compounds

N-[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxo-2-phenylacetamide (1a): ¹H NMR (500 MHz, CDCl₃)





N-[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxo-2-phenylacetamide (1a): ¹³C NMR (125 MHz, CDCl₃)

N-[Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene]-2-oxo-2-(*p*-tolyl)acetamide (2a): ¹H NMR (400 MHz, CDCl₃)













N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(*m*-tolyl)acetamide (3a): ¹³C NMR (125 MHz, CDCl₃)





2-(3-Methoxyphenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (4a): ¹³C NMR (125 MHz, CDCl₃)


2-(4-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (5a): ¹H NMR (500 MHz, CDCl₃)



2-(4-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (5a): ¹³C NMR (125 MHz, CDCl₃)







2-(4-Chlorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (6a): ¹H NMR (400 MHz, CDCl₃)







2-(4-Bromophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (7a): ¹H NMR (500 MHz, CDCl₃)







2-(3-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (8a): ¹H NMR (500 MHz, CDCl₃)









2-(3-Fluorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (8a): ¹³C NMR (125 MHz, CDCl₃)











2-(3-Chlorophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (9a): ¹³C NMR (125 MHz, CDCl₃)

2-(3-Bromophenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (10a): ¹H NMR (500 MHz, CDCl₃)







N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (11a): ¹H NMR (500 MHz, CDCl₃)

-3.492









N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (11a): ¹³C NMR (125 MHz, CDCl₃)

N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl) acetamide (11a): ¹⁹F NMR (471 MHz, CDCl₃)

---63.274





N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(3-(trifluoromethyl)phenyl) acetamide (12a): ¹H NMR (500 MHz, CDCl₃)







N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(3-(trifluoromethyl)phenyl) acetamide (12a): ¹³C NMR (125 MHz, CDCl₃)

N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-(3-(trifluoromethyl)phenyl) acetamide (12a): ¹⁹F NMR (471 MHz, CDCl₃)

--62.858





N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-(4-nitrophenyl)-2-oxoacetamide (13a): ¹H NMR (500 MHz, CDCl₃)



N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-(4-nitrophenyl)-2-oxoacetamide (13a): ¹³C NMR (125 MHz, CDCl₃)



N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-(3-nitrophenyl)-2-oxoacetamide (14a): ¹H NMR (500 MHz, CDCl₃)





N-(Methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-(3-nitrophenyl)-2-oxoacetamide (14a): ¹³C NMR (125 MHz, CDCl₃)

2-(3-Chloro-4-methoxyphenyl)-*N*-(methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxoacetamide (15a): ¹H NMR (400 MHz, CDCl₃)







N-(Methyl(oxo)(p-tolyl)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1b): ¹H NMR (500 MHz, CDCl₃)











N-((4-Ethylphenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1c): ¹H NMR (500 MHz, CDCl₃)





N-((4-Ethylphenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1c): ¹³C NMR (125 MHz, CDCl₃)

N-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1d): ¹H NMR (500 MHz, CDCl₃)





N-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1d): ¹³C NMR (125 MHz, CDCl₃)

N-((3-Methoxyphenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1e): ¹H NMR (400 MHz, CDCl₃)



N-((3-Methoxyphenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1e): ¹³C NMR (100 MHz, CDCl₃)



N-((4-Fluorophenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1f): ¹H NMR (400 MHz, CDCl₃)










N-((4-Fluorophenyl)(methyl)(oxo)- λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1f): ¹⁹F NMR (370 MHz, CDCl₃)





N-((4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1g): ¹H NMR (400 MHz, CDCl₃)



N-((4-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1g): ¹³C NMR (100 MHz, CDCl₃)



N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1h): ¹H NMR (500 MHz, CDCl₃)





N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1h): ¹³C NMR (125 MHz, CDCl₃)

N-((3-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1h): ¹⁹F NMR (471 MHz, CDCl₃)



N-((3-Chlorophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1i): ¹H NMR (500 MHz, CDCl₃)







N-((2-Bromophenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1j): ¹H NMR (600 MHz, CDCl₃)







N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1k): ¹H NMR (500 MHz, CDCl₃)

-3.493







N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1k): ¹³C NMR (125 MHz, CDCl₃)



N-(Methyl(oxo)(4-(trifluoromethyl)phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (1k):¹⁹F NMR (471 MHz, CDCl₃)

---63.300





-32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 f1 (ppm)

N-(Ethyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (11): ¹H NMR (500 MHz, CDCl₃)





N-(Ethyl(oxo)(phenyl)-λ⁶-sulfaneylidene)-2-oxo-2-phenylacetamide (11):¹³C NMR (125 MHz, CDCl₃)

2-Oxo-*N*-(oxo(phenyl)(propyl)-λ⁶-sulfaneylidene)-2-phenylacetamide (1m): ¹H NMR (500 MHz, CDCl₃)





2-Oxo-N-(oxo(phenyl)(propyl)-λ⁶-sulfaneylidene)-2-phenylacetamide (1m): ¹³CNMR (125 MHz, CDCl₃)

2-Oxo-*N*-(oxo(phenyl)(pyridin-2-yl)-λ⁶-sulfaneylidene)-2-phenylacetamide (1n): ¹H NMR (500 MHz, CDCl₃)





2-Oxo-N-(oxo(phenyl)(pyridin-2-yl)-λ⁶-sulfaneylidene)-2-phenylacetamide (1n): ¹³C NMR (125 MHz, CDCl₃)

(Iodoimino)(methyl)(phenyl)- λ⁶-sulfanone (A): ¹H NMR (400 MHz, CDCl₃)

 







(*E*)-Methyl(phenyl)(styrylimino)-λ⁶-sulfanone (D): ¹H NMR (500 MHz, CDCl₃)







(E)-Methyl(phenyl)(styrylimino)-λ⁶-sulfanone (D): ¹³C NMR (125 MHz, CDCl₃)

