Supporting Information
for
Photocatalytic Difunctionalisation of Alkenes with N–SCN Sulfoximines

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1. General information

Unless otherwise noted, the reagents were purchased from commercial suppliers and used without purification. Reactions were tracked by thin layer chromatography (TLC) using TLC plates from Merck. Column chromatography was performed using silica gel 60 (63 - 200 µm) from Merck. $^1$H NMR spectra were recorded on an Agilent 400 or 600 MHz spectrometer in deuterated chloroform. The chemical shifts were given in ppm relative to the residual peak of the non-deuterated solvent was used as internal standard (CDCl$_3$ δ 7.26 ppm). $^1$H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad), coupling constants (in Hz), integration. $^{13}$C {$^1$H} NMR data were collected at 100 or 150 MHz with complete proton decoupling (CDCl$_3$ δ 77.16 ppm). IR spectra were recorded on a Perkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm$^{-1}$. Mass (MS) were acquired on a Finnigan SSQ 7000 spectrometer [electron ionization (EI), 70 eV. High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode. Visible light was provided by irradiation with blue-LEDs (5 W, 455 nm). The microwave reactor (CEM Discover) was purchased from CEM Company. The respective temperature (90 °C) was measured externally. N–Bromo sulfoximines 1 were prepared according to literature procedures.$^{[1]}$

2. Synthesis of N–SCN sulfoximines

2.1. Using N–Br sulfoximines 1 as starting materials

![Chemical structure](image)

The N–bromo sulfoximine 1 (0.2 mmol) and NH$_4$SCN (22.8 mg, 0.3 mmol, 1.5 equiv) was added to a 5.0 mL sealable reaction tube. Then, DCM (1.0 mL) was added and the reaction was stirred for 16 h at 25 ºC in the air atmosphere. The product was purified by flash column chromatography (ethyl acetate/ n-pentane = 1/4 to 1/1) to give the corresponding N–SCN sulfoximine 2.

Note: The N–SCN sulfoximines were transferred to the small glass bottle. Then, they were kept under vacuum until them were used in the next step.

2.2. Using N–H sulfoximines as starting materials

The N–H sulfoximine (0.2 mmol), NH$_4$SCN (22.8 mg, 0.3 mmol, 1.5 equiv) and NBS (0.24 mmol, 42.7 mg) were added to a 5.0 mL sealable reaction tube. Then, DCM (1.0 mL) was added and the reaction was stirred for 16 h at 25 °C in the air atmosphere. The isolation of 2 was performed as described under 2.1.
3. General method for the synthesis of 4 (as illustrated for 4aa)

Under argon, freshly prepared \( N\text{--}SCN \) sulfoximine 2a (31.8 mg, 0.15 mmol, 1.0 equiv), styrene 3a (78.2 mg, 0.75 mmol, 5.0 equiv) and \( \text{fac-}[\text{Ir}(ppy)_3] \) (1.0 mg, 1.0 mol%, 0.01 equiv) were added into a 5.0 mL sealable reaction tube. Then, DCM (3 mL, 0.05 M of \( N\text{--}SCN \) sulfoximine) was added, and the mixture was stirred under argon with blue-LED irradiation (5 W) at room temperature for 40 h. Subsequently, the product was purified by flash column chromatography (ethyl acetate/ \( n\text{-pentane} = 1/2 \)) to give 4aa in 72% yield. The diastereomeric ratio of 4 was determined by \(^1\text{H} \) NMR of the crude product mixture.

Note: In all reactions freshly prepared \( N\text{--}SCN \) sulfoximines were used.

4. Conversions of 4aa into thioether 5 and disulfide 6

\([(2\text{-(Benzylthio)-2-phenylethyl}i\text{mino})(\text{methyl})(\text{phenyl})\lambda^-\text{6-sulfanone (5)}\]

A mixture of 4aa (15.6 mg, 0.05 mmol), lithium aluminum hydride (5.4 mg, 0.14 mmol), benzylbromide (15.0 \( \mu \)L, 0.125 mmol) in THF (0.6 mL) was stirred in air at room temperature for 48 h. Purification by column chromatography (\( n\text{-pentane: ethyl acetate} = 2:1 \)) gave 14.8 mg (78%) of product 5 as a light yellow oil.

Note: The protocol followed a literature procedure applied for converting related compounds.\(^2\) Accordingly, we expected to isolate the corresponding dimerized disulfide. That product, however, remained undetected.

\(^1\text{H} \) NMR (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.80 (d, \( J = 7.7 \text{ Hz}, \) 1H), 7.56 (dd, \( J = 16.5, \) 7.5 Hz, 2H), 7.50 (t, \( J = 7.7 \text{ Hz}, \) 1H), 7.42 (t, \( J = 7.7 \text{ Hz}, \) 1H), 7.33 – 7.18 (m, 10H), 3.98 – 3.86 (m, 1H), 3.60 – 3.48 (m, 2H), 3.44 – 3.38 (m, 1H), 3.22 – 3.07 (m, 1H), 2.97 (s, 3H). \(^{13}\text{C} \) \(^1\text{H} \) NMR (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 141.2, 141.0, 139.3, 139.0, 138.3, 132.9, 132.7, 129.4, 129.3, 129.0, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.2, 127.1, 126.8, 126.8, 126.8, 52.0, 51.6, 49.5, 49.5, 45.0, 44.8, 35.7, 35.7. MS (EI, 70 eV): \( m/z \) (%) = 168.0 (78), 141.0 (53), 125.0 (16), 124.0 (12), 121.0 (14), 104.1 (12), 91.1 (100). MS (ESI) [M+Na]\(^+\): 404.11 (ESI) \( m/z \) [\( \text{C}_{22}\text{H}_{23}\text{NOS}_{2}\text{Na} \]^+: Calcd. 404.1119. found, 404.1096. IR (ATR): \( \nu \) = 3570, 3027, 2917, 2845, 2667, 2330, 2108, 1900, 1815, 1726, 1595, 1489, 1447, 1239, 1136, 1082, 974, 737, 696.
[(2-(Hexylthio)-2-phenylethyl)imino](methyl)(phenyl)-λ⁶-sulfanone (6)

A mixture of 4aa (15.6 mg, 0.05 mmol), 1-bromohexane (12.4 mg, 0.075 mmol), thiourea (4.6 mg, 0.06 mmol), K₃PO₄ (12.7 mg, 0.06 mmol), KI (12.4 mg, 0.075 mmol) and TBAH (49.0 mg, 0.075 mmol, 40% in water) in water (1.0 mL) was put into the cavity of the microwave reactor (with a power of 50 W at 90 °C for 10 min). Then, the reaction mixture was extracted by DCM (3 x 2.0 mL). The combined organic extract was concentrated, and the product was purified by column chromatography (n-pentane : ethyl acetate = 2:1) to give 6.5 mg (32%) of 6 as a light yellow oil.

Note: The protocol followed a procedure reported in the literature.[3]

¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.89 – 7.86 (m, 1H), 7.72 – 7.69 (m, 1H), 7.62 – 7.47 (m, 4H), 7.31 – 7.26 (m, 4H), 4.11 – 4.03 (m, 1H), 3.63 (dd, J = 12.7, 5.9 Hz, 0.5H), 3.51 (dd, J = 12.8, 6.8 Hz, 0.5H), 3.39 (dd, J = 12.8, 7.5 Hz, 0.5H), 3.27 (dd, J = 12.6, 8.7 Hz, 0.5H), 3.03 (d, J = 4.4 Hz, 3H), 2.35 – 2.29 (m, 1H), 2.19 – 2.15 (m, 1H), 1.51 – 1.42 (m, 2H), 1.28 – 1.23 (m, 4H), 1.20 – 1.17 (m, 2H), 0.87 – 0.85 (m, 3H).

¹³C NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 140.2, 132.9, 132.8, 129.4, 129.3, 128.7, 128.6, 128.5, 128.3, 128.2, 127.4, 57.9, 57.6, 48.2, 47.5, 45.0, 38.9, 38.7, 31.3, 28.9, 28.9, 28.1, 22.5, 14.0.

MS (EI, 70 eV): m/z (%) = 258.0 (52), 168.0 (80), 141.0 (100), 125.0 (16), 124.0 (13), 91.1 (33). MS (ESI) [M+H]+: 408.15 (ESI) (m/z) [C₂₁H₃₀NOS₃]+: Calcd. 408.1490. found, 408.1484.


5. Characterisation Data

Methyl(phenyl)(thiocyanatoimino)-λ⁶-sulfanone (2a)

Colorless oil, 38.2 mg, 90% yield, ¹H NMR (600 MHz, CDCl₃) δ 7.94 – 7.89 (m, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.9 Hz, 2H), 3.31 (s, 3H). ¹³C ¹H NMR (151 MHz, CDCl₃) δ 135.8, 134.8, 130.0, 128.6, 115.3, 43.8, 43.8. MS (EI, 70 eV): m/z (%) = 212.0 (100, M⁺), 186.0 (14), 156.0 (15), 140.1 (90), 125.0 (76), 97.1 (22), 77.2 (25). IR (ATR): ν =3524, 3008, 2918, 2326, 2193, 2132, 2053, 1925, 1740, 1571, 1448, 1321, 1217, 1091, 973, 744, 678. HRMS (ESI) (m/z) [M+Na]+: Calcd. [C₉H₈N₂O₂S₂Na]+: 234.9976, found, 234.9977.

(4-Methoxyphenyl)(methyl)(thiocyanatoimino)-λ⁶-sulfanone (2b)

Colorless oil, 25.1 mg, 52% yield, ¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, J = 8.8, 1.5 Hz, 2H), 7.10 (dd, J = 8.8, 1.5 Hz, 2H), 3.91 (d, J = 1.5 Hz, 3H), 3.28 (d, J = 1.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.6, 130.9, 126.4, 115.5, 115.2, 55.9, 44.2. MS (EI, 70 eV): m/z (%) = 242.0 (9, M⁺), 155.1 (100),
76.3 (3). \textbf{IR} (ATR): $\nu = 3492, 3002, 2914, 2666, 2299, 2054, 1910, 1638, 1546, 1447, 1400, 1322, 1219, 1101, 1007, 843, 743, 681$. \textbf{HRMS} (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_9$H$_{10}$N$_2$O$_2$S$_2$Na]$^+$: 265.0081, found, 265.0077.

**Methyl(thiocyanatoimino)(p-tolyl)-$\lambda^6$-sulfanone (2c)**

Colorless oil, 26.2 mg, 58% yield, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 3.29 (s, 3H), 2.48 (s, 3H). $^{13}$C $[^1$H$]$ NMR (151 MHz, CDCl$_3$) $\delta$ 146.1, 132.6, 130.6, 128.6, 115.4, 44.0, 21.8. \textbf{MS} (EI, 70 eV): $m/z$ (%) = 226.0 (18, M$^+$), 194.1 (18), 139.0 (64), 91.2 (29), 77.2 (23), 65.3 (57), 63.2 (41), 58.2 (13), 46.2 (100). \textbf{IR} (ATR): $\nu = 3893, 3745, 2922, 2344, 2095, 1746, 1597, 1397, 1215, 1091, 969, 795, 692$. \textbf{HRMS} (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_9$H$_{10}$N$_2$O$_2$S$_2$Na]$^+$: 249.0232, found, 249.0127.

**4-Bromophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (2d)**

Colorless oil, 44.1 mg, 76% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 – 7.73 (m, 4H), 3.29 (s, 3H). $^{13}$C $[^1$H$]$ NMR (101 MHz, CDCl$_3$) $\delta$ 134.8, 133.3, 130.4, 130.1, 115.0, 43.9. \textbf{MS} (EI, 70 eV): $m/z$ (%) = 289.9 (72, M$^+$), 219.9 (100), 218.0 (97), 204.9 (80), 202.9 (78), 156.9 (16), 155.0 (16), 75.2 (28), 50.2 (40). \textbf{IR} (ATR): $\nu = 3876, 2913, 2337, 2101, 1740, 1528, 1349, 1221, 1094, 975, 854, 728$. \textbf{HRMS} (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_8$H$_7$N$_2$O$_2$SBrNa]$^+$: 312.9081, found 312.9076

**4-Chlorophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (2e)**

Colorless oil, 31.9 mg, 65% yield, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.80 (m, 2H), 7.66 – 7.56 (m, 2H), 3.30 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.8, 134.2, 130.3, 130.0, 115.0, 43.9. \textbf{MS} (EI, 70 eV): $m/z$ (%) = 245.9 (85, M$^+$), 176.0 (41), 174.0 (85), 160.9 (52), 158.9 (100), 130.9 (19), 128.0 (20), 126.0 (12), 111.0 (19). \textbf{IR} (ATR): $\nu = 3542, 3299, 3016, 2923, 2661, 2310, 2134, 2055, 1915, 1573, 1472, 1395, 1318, 1218, 1085, 975, 829, 773, 685$. \textbf{HRMS} (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_8$H$_7$N$_2$O$_2$ClNa]$^+$: 268.9586, found 268.9581.

**4-Fluorophenyl)(methyl)(thiocyanatoimino)-$\lambda^6$-sulfanone (2f)**

Colorless oil, 31.1 mg, 68% yield, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.97 – 7.92 (m, 2H), 7.34 (t, $J = 8.5$ Hz, 2H), 3.32 (s, 3H). $^{13}$C $[^1$H$]$ NMR (151 MHz, CDCl$_3$) $\delta$ 166.4 ($J = 258$ Hz), 131.6 ($J = 16.5$ Hz), 131.5 ($J = 16.5$ Hz), 117.5 ($J = 22.5$ Hz), 115.1, 44.0. \textbf{MS} (EI, 70 eV): $m/z$ (%) = 230.0 (6, M$^+$), 158.0 (34), 143.0 (58), 110.1 (97), 95.2 (68), 83.1 (48), 75.2 (55), 63.2 (23), 59.2 (33), 50.2 (46), 46.2 (100). \textbf{IR} (ATR): $\nu = 3859, 3742, 3525, 3307, 3071, 3015, 2922, 2668, 2325, 2125, 1995, 1898, 1743, 1634, 1567, 1458, 1404, 1313, 1219, 1096, 974, 780, 680$. \textbf{HRMS} (ESI) ($m/z$) [M+Na]$^+$: Calcd. [C$_8$H$_7$N$_2$O$_2$FNa]$^+$: 252.9882, found 252.9878.
(3-Methoxyphenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2g)

Colorless oil, 24.7 mg, 51% yield, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.55 (td, $J = 8.1$, 1.9 Hz, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.39 (d, $J = 1.4$ Hz, 1H), 7.25 (d, $J = 8.3$ Hz, 1H), 3.90 (d, $J = 2.0$ Hz, 3H), 3.30 (d, $J = 1.9$ Hz, 3H). $^{13}$C $^1$H NMR (151 MHz, CDCl$_3$) δ 160.5, 136.9, 131.0, 121.4, 120.6, 115.3, 112.9, 55.9, 55.9, 43.9, 43.9. MS (EI, 70 eV): m/z (%) = 242.2 (7, M$^+$), 155.0 (19), 124.1 (11), 95.1 (13), 92.1 (40), 78.2 (13), 77.1 (50), 64.2 (58), 63.2 (81), 46.1 (100). IR (ATR): ν = 3743, 3625, 3303, 3073, 3015, 2924, 2666, 2320, 2134, 1993, 1904, 1741, 1570, 1461, 1405, 1318, 1220, 1097, 977, 778, 680. HRMS (ESI) (m/z) [M+Na$^+$]: Calcd. [C$_9$H$_{10}$N$_2$O$_2$S$_2$Na]$^+$ 265.0081, found 265.0079.

(3-Bromophenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2h)

Colorless oil, 40.1 mg, 69% yield, $^1$H NMR (600 MHz, CDCl$_3$) δ 8.07 (t, $J = 1.7$ Hz, 1H), 7.90 – 7.81 (m, 2H), 7.54 (t, $J = 8.0$ Hz, 1H), 3.33 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 137.9, 137.7, 131.5, 131.4, 127.1, 124.0, 114.9, 43.8, 43.8. MS (EI, 70 eV): m/z (%) = 289.9 (56, M$^+$), 219.9 (100), 218.0 (90), 204.9 (74), 202.9 (72), 156.9 (15), 155.0 (15), 75.2 (30), 50.2 (36). CHN-elemental analysis: Calcd. for C$_8$H$_7$N$_2$OS$_2$Br, C = 33.00, H = 2.42, N = 9.62, found C = 32.75, H = 2.55, N = 9.48. IR (ATR): ν = 3616, 3021, 2924, 2341, 2116, 1743, 1570, 1406, 1405, 1217, 1095, 968, 776, 689. HRMS (ESI) (m/z) [M+Na$^+$]: Calcd. [C$_8$H$_7$N$_2$OS$_2$BrNa]$^+$ 312.9081, found 312.9075.

(3-Chlorophenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2i)

Colorless oil, 32.4 mg, 66% yield, $^1$H NMR (600 MHz, CDCl$_3$) δ 7.92 (t, $J = 1.9$ Hz, 1H), 7.82 – 7.79 (m, 1H), 7.61 (t, $J = 7.9$ Hz, 1H), 3.33 (s, 3H). $^{13}$C $^1$H NMR (101 MHz, CDCl$_3$) δ 137.6, 136.3, 134.9, 131.2, 128.6, 126.6, 114.9, 43.8. MS (EI, 70 eV): m/z (%) = 176.1 (18), 174.1 (54), 161.1 (14), 159.1 (36), 131.1 (22), 128.2 (28), 126.1 (36), 113.1 (21), 111.1 (67), 99.2 (21), 45.3 (100). IR (ATR): ν = 3867, 3532, 3298, 3073, 3013, 2921, 2657, 2319, 2127, 2063, 1898, 1636, 1574, 1460, 1408, 1318, 1220, 1115, 976, 788, 678. HRMS (ESI) (m/z) [M+Na$^+$]: Calcd. [C$_8$H$_7$N$_2$OS$_2$ClNa]$^+$ 268.9586, found 268.9581.

(2-Bromophenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2j)

Colorless oil, 46.4 mg, 80% yield, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.70 – 7.48 (m, 2H), 3.54 (s, 3H). $^{13}$C $^1$H NMR (101 MHz, CDCl$_3$) δ 136.1, 135.8, 134.8, 133.4, 128.6, 120.7, 114.1, 41.9. MS (EI, 70 eV): m/z (%) = 289.9 (99, M$^+$), 220.0 (100), 218.0 (100), 204.9 (86), 202.9 (86), 139.1 (61), 75.2 (26). CHN-elemental analysis: Calcd. for C$_8$H$_7$N$_2$OS$_2$Br, C = 33.00, H = 2.42, N = 9.62, found C = 32.78, H = 2.54, N = 9.44. IR (ATR): ν = 3624, 3305, 3083, 3010, 2925, 2329, 2136, 2055, 1917, 1738, 1632, 1568, 1434, 1315, 1217, 1097, 1029,
(2-Chlorophenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2k)

Colorless oil, 30.1 mg, 61% yield, 1H NMR (600 MHz, CDCl3) δ 8.24 (dd, J = 8.0, 1.5 Hz, 1H), 7.69 (td, J = 7.8, 1.5 Hz, 1H), 7.65 – 7.57 (m, 2H), 3.53 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 136.0, 133.1, 133.0, 132.5, 132.4, 128.0, 114.2, 42.2, 42.2. MS (EI, 70 eV): m/z (%) = 245.9 (8, M+), 176.0 (6), 174.0 (18), 161.0 (10), 159.0 (27), 133.0 (6.2), 131.0 (18), 76.2 (12), 75.1 (64), 741.1 (19), 63.1 (34), 50.2 (68), 46.1 (100). MS (EI, 70 eV): m/z (%) = 246.2 (2, M+), 176.1 (18), 174.1 (74), 159.1 (41), 131.1 (27), 128.2 (38), 126.1 (36), 113.1 (21), 111.1 (100). CHN-elemental analysis: Calcd. for C8H7N2OS2Cl, C = 38.94, H = 2.86, N = 11.35, found C = 38.73, H = 3.02, N = 11.38. IR (ATR): ν = 3899, 3743, 3621, 3525, 3013, 2929, 2677, 2316, 2114, 1999, 1901, 1741, 1589, 1540, 1368, 1218, 1094, 975, 808, 763, 692. HRMS (ESI) (m/z) [M+Na]+: Calcd. [C8H7N2OS2ClNa]+ 268.9586, found 268.9583.

(3,5-Dichlorophenyl)(methyl)(thiocyanatoimino)-λ6-sulfanone (2l)

Colorless oil, 47.0 mg, 84% yield, 1H NMR (600 MHz, CDCl3) δ 7.79 (d, J = 1.8 Hz, 2H), 7.71 (t, J = 1.6 Hz, 1H), 3.35 (s, 3H). 13C {1H} NMR (151 MHz, CDCl3) δ 138.9, 137.1, 134.8, 126.9, 114.6, 43.8, 43.8. MS (EI, 70 eV): m/z (%) = 279.9 (18, M+), 209.9 (25), 207.9 (37), 194.9 (30), 192.9 (44), 163.9 (17), 161.9 (28), 147.1 (12), 145.0 (23), 111.0 (16), 109.0 (38), 75.1 (68), 46.2 (100). CHN-elemental analysis: Calcd. for C8H6N2OS2Cl2, C = 34.17, H = 2.15, N = 9.96, found C = 34.50, H = 2.25, N = 9.74. IR (ATR): ν = 3893, 3742, 3614, 2961, 2334, 2098, 1897, 1722, 1532, 1360, 1247, 1118, 1001, 864, 764. HRMS (ESI) (m/z) [M+Na]+: Calcd. [C8H6N2OS2Cl2Na]+ 302.9196, found 302.9193.

Diphenyl(thiocyanatoimino)-λ6-sulfanone (2m)

Colorless oil, 42.2 mg, 77% yield, 1H NMR (600 MHz, CDCl3) δ 8.00 – 7.95 (m, 4H), 7.65 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.8 Hz, 4H). 13C {1H} NMR (151 MHz, CDCl3) δ 137.6, 134.2, 129.7, 128.5, 115.2. MS (EI, 70 eV): m/z (%) = 274.0 (100, M+), 202.0 (93), 186.1 (15), 174.0 (34), 154.1 (74), 109.1 (38), 77.2 (23). CHN-elemental analysis: Calcd. for C13H10N2OS2, C = 56.91, H = 3.67, N = 10.21, found C = 56.76, H = 3.52, N = 9.96. IR (ATR): ν = 3751, 3457, 3079, 3015, 3933, 2651, 2450, 2281, 2138, 2090, 2037, 1990, 1941, 1739, 1623, 1577, 1445, 1367, 1220, 1085, 948, 727, 684. HRMS (ESI) (m/z) [M+Na]+: Calcd. [C13H10N2OS2Na]+ 297.0132, found 297.0128.
Ethyl(phenyl)(thiocyanatoimino)-\(\lambda^6\)-sulfanone (2n)

Colorless oil, 35.3 mg, 78% yield, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 – 7.83 (m, 2H), 7.76 – 7.69 (m, 1H), 7.67 – 7.61 (m, 2H), 3.51 – 3.28 (m, 2H), 1.28 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 134.7, 133.8, 129.9, 129.3, 115.4, 50.5, 7.1. MS (EI, 70 eV): \(m/z\) (%) = 226.0 (73, M\(^+\)), 154.0 (37), 126.0 (100), 125.0 (38), 78.2 (37), 77.2 (26). IR (ATR): \(\nu = 3854, 3745, 3462, 2930, 2314, 2061, 1901, 1741, 1547, 1450, 1365, 1218, 1099, 960, 734, 677\). HRMS (ESI) \((m/z)\) [M+Na\(^+\)]: Calcd. [C\(_9\)H\(_{10}\)N\(_2\)O\(_2\)S\(_2\)Na\(^+\)] 249.0132, found 249.0126.

Methyl(phenyl)((2-phenyl-2-thiocyanatoethyl)imino)-\(\lambda^6\)-sulfanone (4aa)

Light yellow oil, 34.2 mg, 72% yield. \(dr = 1:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 7.89 – 7.78 (m, 2H), 7.66 – 7.49 (m, 3H), 7.39 – 7.26 (m, 5H), 4.81 – 4.54 (m, 1H), 3.59 – 3.50 (m, 1H), 3.41 – 3.30 (m, 1H), 3.09 (d, \(J = 8.9\) Hz, 3H). \(^{13}\)C \(^{1\text{H}}\) NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 138.9, 138.6, 137.4, 137.3, 133.3, 133.3, 129.6, 129.6, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 112.3, 112.3, 56.9, 55.9, 48.5, 48.4, 45.1, 44.8. MS (EI, 70 eV): \(m/z\) (%) = 287.0 (20), 168.0 (100), 141.0 (61), 132.0 (19), 125.0 (19), 77.1 (19). MS (ESI) [M+H\(^+\)]: 317.08. HRMS (ESI) \((m/z)\) [C\(_{16}\)H\(_{17}\)N\(_2\)O\(_2\)S\(_2\)]\(^+\): Calcd. 317.0782, found, 317.0761. IR (ATR): \(\nu = 3522, 3011, 2926, 2838, 2607, 2337, 2143, 2092, 1907, 1785, 1607, 1510, 1448, 1238, 1139, 1029, 973, 892, 833, 743\).

Methyl(phenyl)((2-thiocyanato-2-(o-tolyl)ethyl)imino)-\(\lambda^6\)-sulfanone (4ab)

Light yellow oil, 18.8 mg, 38% yield, \(dr = 1:1\). \(^1\)H NMR (400 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 7.95 – 7.81 (m, 2H), 7.68 – 7.49 (m, 3H), 7.35 – 7.22 (m, 1H), 7.21 – 7.12 (m, 3H), 4.87 – 4.71 (m, 1H), 3.62 – 3.52 (m, 1H), 3.48 – 3.35 (m, 1H), 3.10 (d, \(J = 12.5\) Hz, 3H), 2.36 (d, \(J = 2.9\) Hz, 3H). \(^{13}\)C \(^{1\text{H}}\) NMR (101 MHz, CDCl\(_3\), mixture of diastereomers) \(\delta\) 139.2, 138.6, 136.6, 136.3, 135.1, 133.3, 133.2, 130.8, 130.8, 129.7, 129.6, 128.6, 128.4, 126.7, 126.7, 126.6, 126.5, 112.1, 52.8, 51.5, 48.3, 48.2, 45.1, 44.8. MS (EI, 70 eV): \(m/z\) (%) = 168.0 (100), 141.1 (63), 77.1 (18). MS (ESI) [M+H\(^+\)]: 331.09 (ESI) \((m/z)\) [C\(_{17}\)H\(_{19}\)N\(_2\)O\(_2\)S\(_2\)]\(^+\): Calcd. 331.0939, found, 331.0936. IR (ATR): \(\nu = 3533, 3019, 2924, 2849, 2334, 2147, 1997, 1911, 1736, 1591, 1450, 1235, 1140, 1087, 973, 887, 742, 688\).
Methyl(phenyl)((2-thiocyanato-2-(m-tolyl)ethyl)imino)-λ₆-sulfanone (4ac)

Light yellow oil, 25.3 mg, 51% yield, dr = 1:1. ¹H NMR (400 MHz, CDCl₃, mixture of diastereomers) δ 7.92 – 7.75 (m, 2H), 7.66 – 7.45 (m, 3H), 7.24 – 7.19 (m, 1H), 7.15 – 7.09 (m, 3H), 4.58 – 4.50 (m, 1H), 3.58 – 3.51 (m, 1H), 3.40 – 3.29 (m, 1H), 3.09 (d, J = 9.0 Hz, 3H), 2.31 (d, J = 5.2 Hz, 3H). ¹³C {¹H} NMR (101 MHz, CDCl₃, mixture of diastereomers) δ 139.0, 138.7, 138.6, 137.2, 133.3, 133.2, 129.7, 129.6, 129.6, 128.7, 128.6, 128.5, 128.4, 125.1, 124.8, 112.4, 57.0, 56.0, 48.6, 48.4, 45.1, 44.8, 21.4. MS (EI, 70 eV): m/z (%) = 168.0 (100), 141.1 (63), 125.0 (20), 77.1 (15). MS (ESI) [M+H]+: 331.09 (ESI) (m/z) [C₁₇H₁₉N₂O₃S₂]+: Calcd. 331.0939. found, 331.0915. IR (ATR): ν = 3526, 3019, 2847, 2671, 2330, 2142, 1999, 1895, 1602, 1446, 1237, 1140, 1085, 974, 881, 785, 742, 696.

Methyl(phenyl)((2-thiocyanato-2-(p-tolyl)ethyl)imino)-λ₆-sulfanone (4ad)

Light yellow oil, 25.7 mg, 52% yield, dr = 1:1. ¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.89 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.63 (q, J = 7.4 Hz, 1H), 7.56 (dt, J = 15.2, 7.7 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.21 (d, J = 8.1 Hz, 1H), 7.17 – 7.12 (m, 2H), 4.57 (ddd, J = 24.9, 8.6, 5.7 Hz, 1H), 3.60 – 3.50 (m, 1H), 3.40 – 3.31 (m, 1H), 3.11 (d, J = 12.9 Hz, 3H), 2.33 (d, J = 9.6 Hz, 3H). ¹³C {¹H} NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 139.0, 138.8, 138.6, 134.3, 134.2, 133.3, 133.3, 129.7, 129.6, 129.6, 129.5, 128.6, 128.4, 127.9, 127.7, 112.5, 112.5, 56.9 55.9, 48.6, 48.4, 45.1, 44.8, 21.2, 21.2. MS (EI, 70 eV): m/z (%) = 168.0 (100), 141.1 (46), 125.0 (11). MS (ESI) [M+H]+: 331.09 (ESI) (m/z) [C₁₇H₁₉N₂O₃S₂]+: Calcd. 331.0939. found, 331.0915. IR (ATR): ν = 3611, 3019, 2923, 2847, 2671, 2330, 2142, 1999, 1895, 1602, 1446, 1237, 1140, 1085, 892, 818, 740.

{2-[4-(tert-butyl)phenyl]-2-thiocyanatoethyl}imino(methyl)(phenyl)-λ₆-sulfanone (4ae)

Light yellow oil, 33.5 mg, 60% yield, dr = 1:1. ¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) δ 7.90 – 7.86 (m, 1H), 7.86 – 7.83 (m, 1H), 7.66 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, J = 8.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 4.61 – 4.54 (m, 1H), 3.58 – 3.52 (m, 1H), 3.41 – 3.32 (m, 1H), 3.12 (d, J = 11.9 Hz, 3H), 1.29 (d, J = 9.5 Hz, 9H). ¹³C {¹H} NMR (151 MHz, CDCl₃, mixture of diastereomers) δ 151.89, 138.94, 138.61, 134.23, 134.22, 133.31, 133.27, 129.64, 129.60, 128.61, 128.42, 127.62, 127.46, 125.81, 125.77, 112.56, 112.55, 56.78, 55.78, 48.68, 48.43, 45.08, 44.83, 34.64, 34.62, 31.24, 31.22. MS (EI, 70 eV): m/z (%) = 168.0 (100), 141.1 (65), 125.0 (19), 117.0 (16), 91.1 (12), 77.1 (12). MS (ESI) [M+Na]+: 395.12 (ESI) (m/z) [C₂₀H₂₄N₂O₃S₂Na]+: Calcd. 395.1227. found, 395.1216. IR (ATR): ν =
{[2-(4-Methoxyphenyl)-2-thiocyanatoethyl]imino}(methyl)(phenyl)-λ₆-sulfanone (4af)

Light yellow oil, 25.0 mg, 50% yield, \(dr = 1:1\). \(^1\)H NMR (400 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 7.91 – 7.83 (m, 2H), 7.65 – 7.53 (m, 3H), 7.27 (dd, \(J = 17.6, 8.2\) Hz, 2H), 6.86 (dd, \(J = 8.5, 6.4\) Hz, 2H), 4.63 – 4.54 (m, 1H), 3.79 (d, \(J = 6.0\) Hz, 3H), 3.58 – 3.50 (m, 1H), 3.42 – 3.31 (m, 1H), 3.11 (d, \(J = 8.1\) Hz, 3H). \(^{13}\)C \(^1\)H NMR (101 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 159.9, 133.3, 133.2, 129.6, 129.6, 129.3, 129.1, 128.6, 128.4, 114.2, 112.5, 56.8, 55.8, 55.3, 48.6, 48.4, 45.1, 44.8. MS (EI, 70 eV): \(m/z\) (%) = 287.0 (20), 168.0 (100), 141.0 (61), 132.0 (19), 125.0 (19), 91.1 (12), 77.1 (18). MS (ESI) [M+H]⁺: 347.09 (ESI) \(\left[\text{C}_{17}\text{H}_{19}\text{N}_{2}\text{O}_{2}\text{S}_{2}\right]^+\): Calcd. 347.0888. found, 347.0882.

IR (ATR): \(\nu\) = 3522, 3011, 2926, 2838, 2670, 2337, 2143, 2092, 1907, 1758, 1607, 1510, 1448, 1238, 1139, 1029, 973, 892, 833, 743, 687.

{[2-(4-Bromophenyl)-2-thiocyanatoethyl]imino}(methyl)(phenyl)-λ₆-sulfanone (4ag)

Light yellow oil, 39.0 mg, 66% yield, \(dr = 1:1\). \(^1\)H NMR (400 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 7.87 – 7.78 (m, 2H), 7.67 – 7.60 (m, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.45 (m, 2H), 7.27 – 7.18 (m, 2H), 4.59 – 4.46 (m, 1H), 3.55 – 3.48 (m, 1H), 3.38 – 3.25 (m, 1H), 3.08 (d, \(J = 10.1\) Hz, 3H). \(^{13}\)C \(^1\)H NMR (101 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 138.8, 138.6, 136.5, 133.4, 133.3, 132.0, 129.7, 129.6, 129.5, 128.5, 128.3, 122.9, 56.0, 55.0, 48.1, 45.1, 44.9. MS (EI, 70 eV): \(m/z\) (%) = 287.0 (20), 168.0 (100), 141.0 (77), 124.9 (28), 124.0 (11), 97.0 (11). MS (ESI) [M+Na]⁺: 416.97 (ESI) \(\left[\text{C}_{16}\text{H}_{15}\text{N}_{2}\text{O}_{2}\text{S}_{2}\text{Br}\text{Na}\right]^+\): Calcd. 416.9707. found, 416.9718. IR (ATR): \(\nu\) = 3786, 3458, 3060, 3019, 2924, 2848, 2663, 2501, 2327, 2144, 2083, 1994, 1957, 1739, 1586, 1485, 1445, 1405, 1368, 1228, 1140, 1075, 1008, 978, 889, 826, 783, 742, 688.

{[2-(4-Chlorophenyl)-2-thiocyanatoethyl]imino}(methyl)(phenyl)-λ₆-sulfanone (4ah)

Light yellow oil, 27.8 mg, 53% yield, \(dr = 1:1\). \(^1\)H NMR (600 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 7.85 (dd, \(J = 17.6, 7.5\) Hz, 2H), 7.67 – 7.61 (m, 1H), 7.57 (q, \(J = 7.6\) Hz, 2H), 7.33 – 7.25 (m, 4H), 4.60 – 4.52 (m, 1H), 3.56 – 3.49 (m, 1H), 3.39 – 3.28 (m, 1H), 3.10 (d, \(J = 15.0\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl₃, mixture of diastereomers) \(\delta\) 138.8, 138.6, 136.0, 135.9, 134.8, 133.4, 132.9, 129.7, 129.7, 129.4, 129.3, 129.1, 129.1, 128.5, 128.4, 112.0, 112.0, 56.0, 55.0, 48.3, 48.2, 45.1, 44.9. MS (EI, 70 eV): \(m/z\) (%) = 287.0 (100), 141.1 (45), 125.0 (25). MS (ESI) [M+Na]⁺: 373.02 (ESI) \(\left[\text{C}_{16}\text{H}_{15}\text{N}_{2}\text{O}_{2}\text{S}_{2}\text{Cl}\text{Na}\right]^+\):
{2-(4-Fluorophenyl)-2-thiocyanatoethyl}imino(methyl)(phenyl)-λ₆-sulfanone (4ai)

Light yellow oil, 25.0 mg, 50% yield, $dr = 1:1$. ¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) $\delta$ 7.89 – 7.81 (m, 2H), 7.68 – 7.61 (m, 1H), 7.57 (q, $J = 7.6$ Hz, 2H), 7.40 – 7.34 (m, 1H), 7.32 (dd, $J = 8.6$, 5.2 Hz, 1H), 7.03 (q, $J = 8.5$ Hz, 2H), 4.64 – 4.53 (m, 1H), 3.58 – 3.51 (m, 1H), 3.40 – 3.29 (m, 1H), 3.11 (d, $J = 12.9$ Hz, 3H). ¹³C {¹H} NMR (151 MHz, CDCl₃, mixture of diastereomers) $\delta$ 163.6, 163.6, 161.9, 161.9, 138.8, 138.6, 133.4, 133.4, 129.9, 129.9, 129.8, 129.7, 128.5, 128.4, 115.9, 115.8, 112.2, 112.1, 112.1, 56.5, 56.1, 48.5, 48.3, 45.1, 45.0. MS (EI, 70 eV): $m/z$ (%) = 168.0 (100), 141.1 (47), 125.0 (17). MS (ESI) [M+Na⁺]: 357.05 (ESI) ($m/z$) [C₁₆H₁₅N₂O₄S₂Na⁺]: Calcd. 357.0508. found, 357.0492.

IR (ATR): $\nu = 2918$, 2336, 2122, 1898, 1740, 1604, 1501, 1225, 976, 741.

{(2-(1,1'-Biphenyl)-4-yl)-2-thiocyanatoethyl}imino(methyl)(phenyl)-λ₆-sulfanone (4aj)

Light yellow oil, 24.1 mg, 41% yield, $dr = 1:1$. ¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) $\delta$ 7.93 – 7.79 (m, 2H), 7.64 (dd, $J = 14.4$, 7.2 Hz, 1H), 7.60 – 7.52 (m, 6H), 7.47 – 7.39 (m, 4H), 7.35 (dd, $J = 13.3$, 7.1 Hz, 1H), 4.71 – 4.57 (m, 1H), 3.68 – 3.49 (m, 1H), 3.47 – 3.37 (m, 1H), 3.13 (d, $J = 15.1$ Hz, 3H). ¹³C {¹H} NMR (151 MHz, CDCl₃, mixture of diastereomers) $\delta$ 141.8, 140.3, 140.3, 138.9, 138.6, 136.3, 133.4, 133.3, 129.7, 129.6, 128.8, 128.6, 128.5, 128.4, 128.3, 127.6, 127.5, 127.1, 112.4, 112.3, 56.7, 55.6, 48.5, 48.4, 45.1, 44.9. MS (EI, 70 eV): $m/z$ (%) = 168.0 (100), 141.1 (47), 125.0 (15), 77.1 (17), 58.1 (25). MS (ESI) [M+Na⁺]: 415.09 (ESI) ($m/z$) [C₂₂H₂₀N₂O₄S₂Na⁺]: Calcd. 415.09147. found, 415.08948. IR (ATR): $\nu = 3534$, 3029, 2922, 2853, 2148, 1724, 1599, 1483, 1447, 1407, 1236, 1138, 1083, 974, 839, 738, 691.

[(2-Mesityl-2-thiocyanatoethyl)imino](methyl)(phenyl)-λ₆-sulfanone (4ak)

Light yellow oil, 16.5 mg, 33% yield, $dr = 1:1$. ¹H NMR (600 MHz, CDCl₃, mixture of diastereomers) $\delta$ 7.94 (d, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 1H), 7.67 – 7.51 (m, 3H), 6.80 (dd, $J = 27.3$, 5.3 Hz, 2H), 5.33 – 5.14 (m, 1H), 3.71 – 3.55 (m, 1H), 3.44 – 3.37 (m, 1H), 3.18 – 3.17 (m, 3H), 2.44 – 2.26 (m, 6H), 2.22 – 2.21 (m, 3H). ¹³C {¹H} NMR (151 MHz, CDCl₃, mixture of diastereomers) $\delta$ 138.3, 137.4, 137.4, 137.1, 137.0, 133.5, 133.4, 131.4, 131.3, 129.8, 129.7, 129.6, 129.5, 129.5, 128.6, 128.4, 113.1, 113.0, 53.8, 52.4, 47.0, 46.2, 44.9, 44.7, 21.3, 21.3, 21.1, 20.9. MS (EI, 70 eV): $m/z$ (%) = 190.1 (10), 168.0 (79), 145.1 (16), 141.0 (100), 133.1 (26), 125.0 (67), 117.1 (32), 115.1 (33), 91.1 (47), 77.2 (67), 51.2 (54). MS (ESI)
[M+Na]^+: 359.12 (ESI) (m/z) [C_{19}H_{23}N_2O_2S_2]^+: Calcd. 359.1252. found, 359.1238. IR (ATR): \nu = 3523, 2926, 2336, 2144, 1912, 1727, 1606, 1452, 1229, 1137, 971, 858, 743, 678.

(4-Methoxyphenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-\lambda^6-sulfanone (4ba)

Light yellow oil, 42.0 mg, 81% yield, \textit{dr} = 1:1. $^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 7.77 (dd, \(J = 21.5, 8.8\) Hz, 2H), 7.39 – 7.29 (m, 5H), 7.01 (dd, \(J = 11.0, 8.8\) Hz, 2H), 4.62 – 4.56 (m, 1H), 3.87 (s, 3H), 3.56 – 3.52 (m, 1H), 3.42 – 3.31 (m, 1H), 3.08 (d, \(J = 15.7\) Hz, 3H).

$^{13}$C $\{^1$H\} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 163.5, 163.5, 137.5, 137.4, 130.7, 130.6, 130.0, 129.6, 128.9, 128.0, 127.9, 114.9, 114.8, 112.4, 112.4, 57.0, 56.0, 48.6, 48.4, 45.5, 45.2. MS (EI, 70 eV): \(m/z\) (%) = 198.0 (90), 171.0 (96), 154.9 (100), 139.0 (13), 91.1 (41), 77.1 (18), 63.1 (11). MS (ESI) [M+H]^+: 347.09 (ESI) (m/z) [C$_{17}$H$_{19}$N$_2$O$_2$S$_2$]^+: Calcd. 347.0888. found, 347.0873. IR (ATR): \(\nu = 3556, 3018, 2923, 2845, 2680, 2325, 2147, 1901, 1722, 1588, 1492, 1454, 1410, 1306, 1245, 1135, 1091, 1021, 973, 891, 834, 766, 699.

Methyl[(2-phenyl-2-thiocyanatoethyl)imino](p-tolyl)-\lambda^6-sulfanone (4ca)

Light yellow oil, 35.1 mg, 71% yield, \textit{dr} = 1:1. $^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 7.73 (dd, \(J = 20.3, 8.2\) Hz, 2H), 7.42 – 7.28 (m, 7H), 4.62 – 4.58 (m, 1H), 3.59 – 3.49 (m, 1H), 3.41 – 3.31 (m, 1H), 3.09 (d, \(J = 14.5\) Hz, 3H), 2.45 (d, \(J = 1.9\) Hz, 3H). $^{13}$C $\{^1$H\} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 144.3, 144.2, 137.4, 137.4, 135.8, 135.4, 130.3, 130.3, 128.9, 128.8, 128.5, 128.0, 127.9, 114.2, 114.7, 57.0, 56.0, 48.6, 48.4, 45.5, 45.2. MS (EI, 70 eV): \(m/z\) (%) = 182.0 (100), 155.0 (48), 139.0 (18), 91.1 (17). MS (ESI) [M+H]^+: 331.09 (ESI) (m/z) [C$_{17}$H$_{19}$N$_2$O$_2$S$_2$]^+: Calcd. 331.0939. found, 331.0924. IR (ATR): \(\nu = 3556, 3018, 2923, 2845, 2680, 2325, 2147, 1901, 1722, 1588, 1492, 1454, 1410, 1306, 1245, 1135, 1091, 1021, 973, 891, 834, 766, 699.

(4-Bromophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-\lambda^6-sulfanone (4da)

Light yellow oil, 39.1 mg, 66% yield, \textit{dr} = 1:1. $^1$H NMR (600 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 7.74 – 7.65 (m, 4H), 7.38 – 7.31 (m, 5H), 4.62 – 4.53 (m, 1H), 3.59 – 3.54 (m, 1H), 3.40 – 3.30 (m, 1H), 3.10 (d, \(J = 16.4\) Hz, 3H). $^{13}$C $\{^1$H\} NMR (151 MHz, CDCl$_3$, mixture of diastereomers) \(\delta\) 138.1, 137.8, 137.2, 137.1, 133.0, 132.9, 130.2, 130.0, 129.0, 128.9, 128.9, 128.7, 128.6, 128.0, 127.8, 112.2, 112.2, 56.7, 55.7, 48.5, 48.4, 45.1, 44.9. MS (EI, 70 eV): \(m/z\) (%) = 247.9 (100), 245.9 (98), 221.0 (60), 219.0 (59), 204.9 (27), 202.9 (26), 118.1 (26), 91.1 (43). MS (ESI) [M+Na]^+: 416.97 (ESI) (m/z)
(4-Chlorophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-λ₆-sulfanone (4ea)

Light yellow oil, 32.3 mg, 62% yield, \( dr = 1:1 \). \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.81 – 7.71 (m, 2H), 7.55 – 7.47 (m, 2H), 7.37 – 7.29 (m, 5H), 4.60 – 4.51 (m, 1H), 3.60 – 3.52 (m, 1H), 3.40 – 3.28 (m, 1H), 3.08 (d, \( J = 10.2 \text{ Hz}, 3\text{H} \)). \(^1\text{C} \{^1\text{H} \} \text{ NMR} \) (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 140.8, 140.0, 137.5, 137.2, 137.2, 130.1, 130.1, 130.0, 129.9, 129.0, 128.9, 128.9, 128.0, 127.8, 112.2, 112.2, 56.68, 56.67, 55.7, 48.5, 48.4, 45.1, 44.9. \( \text{MS} \) (EI, 70 eV): \( m/z \) (%): 203.9 (36), 201.9 (100), 176.9 (22), 174.9 (60), 159.9 (12), 158.9 (25), 118.0 (17), 91.1 (26). \( \text{MS} \) (ESI) \([\text{M}+\text{Na}]^+\): 373.02 (ESI) \( m/z \). \([\text{C}_{16}\text{H}_{15}\text{N}_{2}\text{OS}_{2}\text{ClNa}]^+\): Calcd. 373.0212. found, 373.0200. \( \text{IR} \) (ATR): \( \nu = 3543, 3067, 3027, 2923, 2844, 2563, 2324, 2149, 2055, 1925, 1811, 1728, 1576, 1466, 1393, 1238, 1141, 1082, 975, 889, 829, 769, 699.

(4-Fluorophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-λ₆-sulfanone (4fa)

Light yellow oil, 27.6 mg, 55% yield, \( dr = 1:1 \). \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.91 – 7.75 (m, 2H), 7.37 – 7.29 (m, 4H), 7.25 – 7.18 (m, 2H), 4.60 – 4.53 (m, 1H), 3.60 – 3.51 (m, 1H), 3.41 – 3.29 (m, 1H), 3.08 (d, \( J = 10.4 \text{ Hz}, 3\text{H} \)). \(^1\text{C} \{^1\text{H} \} \text{ NMR} \) (101 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 166.8, 164.3, 137.2, 137.2, 134.9, 134.6, 131.4, 131.3, 131.2, 131.1, 128.9, 128.9, 128.0, 127.8, 117.0, 117.0, 116.8, 116.7, 112.2, 112.1, 56.7, 55.7, 48.5, 48.4, 45.3, 45.0. \( \text{MS} \) (EI, 70 eV): \( m/z \) (%): 185.9 (100), 158.9 (47), 142.9 (15). \( \text{MS} \) (ESI) \([\text{M}+\text{H}]^+\): 335.07 (ESI) \( m/z \). \([\text{C}_{16}\text{H}_{16}\text{N}_{2}\text{OS}_{2}\text{F}]^+\): Calcd. 335.0688. found, 335.0674. \( \text{IR} \) (ATR): \( \nu = 3066, 3030, 2924, 2848, 2207, 2150, 2052, 1986, 1909, 1739, 1588, 1490, 1453, 1404, 1367, 1229, 1138, 1085, 981, 838, 765, 699.

(3-Methoxyphenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-λ₆-sulfanone (4ga)

Light yellow oil, 20.8 mg, 40% yield, \( dr = 1:1 \). \(^1\text{H} \text{NMR} \) (600 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 7.50 – 7.42 (m, 2H), 7.41 – 7.30 (m, 6H), 7.16 – 7.13 (m, 1H), 4.63 – 4.56 (m, 1H), 3.86 (d, \( J = 4.6 \text{ Hz}, 3\text{H} \)), 3.60 – 3.53 (m, 1H), 3.44 – 3.34 (m, 1H), 3.11 (d, \( J = 13.3 \text{ Hz}, 3\text{H} \)). \(^1\text{C} \{^1\text{H} \} \text{ NMR} \) (151 MHz, CDCl\(_3\), mixture of diastereomers) \( \delta \) 160.4, 160.4, 140.2, 139.9, 137.4, 137.3, 130.7, 130.6, 128.9, 128.9, 128.0, 127.9, 120.5, 120.3, 119.8, 119.6, 113.0, 112.3, 56.9, 55.9, 55.7, 48.6, 48.4, 45.1, 44.8. \( \text{MS} \) (EI, 70 eV): \( m/z \) (%): 198.0 (100), 171.0 (96), 155.0 (63), 148.0 (18), 121.0 (29), 108.0 (29), 91.1 (82), 77.1 (58). \( \text{MS} \) (ESI) \([\text{M}+\text{H}]^+\): 347.09 (ESI) \( m/z \). \([\text{C}_{17}\text{H}_{19}\text{N}_{2}\text{O}_{2}\text{S}_{2}]^+\): Calcd. 347.0888. found,
347.0877. **IR** (ATR): $\nu = 3589, 3018, 2925, 2846, 2331, 2147, 1892, 1772, 1593, 1470, 1239, 1138, 1084, 1034, 972, 864, 767, 692.$

(3-Bromophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)$\lambda^6$-sulfanone (4ha)

Light yellow oil, 26.0 mg, 44% yield, $dr = 1:1$. $^1H$ NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.98 (dt, $J = 16.7, 1.8$ Hz, 1H), 7.80 – 7.70 (m, 2H), 7.41 (q, $J = 8.0$ Hz, 1H), 7.35 – 7.30 (m, 5H), 4.59 – 4.53 (m, 1H), 3.61 – 3.52 (m, 1H), 3.41 – 3.30 (m, 1H), 3.09 (d, $J = 11.2$ Hz, 3H). $^{13}C$ $^1H$ NMR (101 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 141.2, 141.0, 137.1, 136.4, 136.3, 131.6, 131.3, 131.1, 131.1, 129.0, 128.9, 128.0, 127.8, 127.0, 126.9, 123.7, 123.6, 112.1, 112.1, 56.6, 55.6, 48.5, 48.3, 45.1, 44.9. MS (EI, 70 eV): $m/z$ (%) = 247.9 (100), 245.9 (99), 220.9 (40), 218.9 (41), 204.9 (10), 202.8 (9), 91.1 (13). MS (ESI) [M+Na]$^+$: 416.97 (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$O$_3$S$_2$BrNa]$^+$: Calcd. 416.9707. found, 416.9718. **IR** (ATR): $\nu = 3063, 3027, 2925, 2845, 2328, 2149, 1889, 1737, 1568, 1493, 1454, 1404, 1366, 1235, 1140, 1098, 979, 889, 834, 774, 732, 699, 678.

(3-Chlorophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)$\lambda^6$-sulfanone (4ia)

Light yellow oil, 22.6 mg, 43% yield, $dr = 1:1$. $^1H$ NMR (600 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 7.84 (dt, $J = 28.8, 1.6$ Hz, 1H), 7.72 (dd, $J = 27.1, 7.8$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 – 7.48 (m, 1H), 7.37 – 7.32 (m, 5H), 4.61 – 4.56 (m, 1H), 3.61 – 3.53 (m, 1H), 3.42 – 3.33 (m, 1H), 3.11 (d, $J = 17.2$ Hz, 3H). $^{13}C$ $^1H$ NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 141.1, 140.7, 137.1, 135.9, 135.9, 133.5, 133.5, 130.9, 130.9, 129.00, 128.9, 128.9, 128.7, 128.5, 128.0, 127.8, 126.7, 126.5, 112.2, 112.1, 56.6, 55.6, 48.5, 48.3, 45.1, 44.9. MS (EI, 70 eV): $m/z$ (%) = 222.2 (42), 204.0 (53), 202.0 (100), 177.0 (22), 175.0 (58), 159.0 (16), 118.1 (49), 104.1 (10), 91.1 (30). MS (ESI) [M+Na]$^+$: 373.02 (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$O$_3$ClNa]$^+$: Calcd. 373.0212. found, 373.0219. **IR** (ATR): $\nu = 3525, 3065, 3028, 2923, 2849, 2688, 2339, 2149, 2061, 1887, 1731, 1577, 1454, 1408, 1241, 1139, 1077, 975, 891, 840, 758, 696.

(2-Bromophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)$\lambda^6$-sulfanone (4ja)

Light yellow oil, 22.5 mg, 38% yield, $dr = 1:1$. $^1H$ NMR (400 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 8.21 – 8.17 (m, 1H), 7.81 – 7.73 (m, 1H), 7.56 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.30 (m, 5H), 4.62 – 4.57 (m, 1H), 3.53 – 3.44 (m, 1H), 3.36 – 3.28 (m, 4H). $^{13}C$ $^1H$ NMR (151 MHz, CDCl$_3$, mixture of diastereomers) $\delta$ 137.7, 137.7, 137.2, 137.2, 135.8, 135.7, 134.4, 133.3, 133.2, 128.9, 128.9, 128.5, 128.4, 128.0, 127.9, 120.7, 120.7, 112.3, 112.3, 56.5, 55.7, 48.6, 48.5, 42.7, 42.6. MS (EI, 70 eV): $m/z$ (%) = 393.9 (2, M$^+$), 247.9 (100), 245.9 (96), 220.9 (59), 218.9 (60), 204.9 (15), 202.8 (14). MS (ESI) [M+Na]$^+$: 416.97 (ESI) ($m/z$) [C$_{16}$H$_{15}$N$_2$O$_3$BrNa]$^+$: Calcd. 416.9707. found, 416.9712. **IR** (ATR): $\nu = 3533,
3028, 2923, 2845, 2693, 2148, 1992, 1940, 1734, 1569, 1492, 1441, 1235, 1141, 1093, 1025, 972, 878, 832, 758, 700.

(2-Chlorophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-λ<sup>6</sup>-sulfanone (4ka)

Light yellow oil, 27.3 mg, 52% yield, 

**1H NMR** (400 MHz, CDCl<sub>3</sub>, mixture of diastereomers) δ 8.17 – 8.09 (m, 1H), 7.55 – 7.52 (m, 2H), 7.49 – 7.43 (m, 1H), 7.35 – 7.26 (m, 5H), 4.58 – 4.53 (m, 1H), 3.54 – 3.44 (m, 1H), 3.36 – 3.24 (m, 4H).

**13C NMR** (101 MHz, CDCl<sub>3</sub>, mixture of diastereomers) δ 137.2, 136.1, 134.4, 132.9, 132.9, 132.3, 132.2, 132.1, 128.9, 127.9, 127.9, 127.8, 127.7, 112.2, 56.4, 55.7, 48.6, 48.6, 43.1, 42.3.

**MS** (EI, 70 eV): m/z (%) = 203.9 (38), 202.0 (100), 176.9 (27), 174.9 (66), 160.0 (10), 158.9 (12), 91.1 (16). **MS** (ESI) [M+Na]<sup>+</sup>: 373.02 (ESI) (m/z) [C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>ClNa]<sup>+</sup>; Calcd. 373.0212. found, 373.0198.

**IR** (ATR): ν = 3836, 3508, 3065, 2922, 2845, 2681, 2328, 2145, 1882, 1739, 1573, 1493, 1445, 1243, 1142, 1029, 969, 761, 700.

(3,5-Dichlorophenyl)(methyl)((2-phenyl-2-thiocyanatoethyl)imino)-λ<sup>6</sup>-sulfanone (4la)

Light yellow oil, 33.6 mg, 58% yield,

**1H NMR** (400 MHz, CDCl<sub>3</sub>, mixture of diastereomers) δ 7.72 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.37 – 7.29 (m, 5H), 4.59 – 4.50 (m, 1H), 3.63 – 3.53 (m, 1H), 3.42 – 3.31 (m, 1H), 3.09 (d, J = 13.6 Hz, 3H).

**13C {1H} NMR** (101 MHz, CDCl<sub>3</sub>, mixture of diastereomers) δ 142.6, 142.3, 136.9, 136.9, 136.6, 136.6, 133.3, 133.3, 129.1, 129.0, 128.9, 127.9, 127.8, 126.9, 126.7, 112.0, 111.9, 56.4, 55.3, 48.5, 48.2, 45.0, 44.9.

**MS** (EI, 70 eV): m/z (%) = 238.0 (63), 235.9 (100), 211.0 (31), 208.9 (50), 194.9 (9), 192.9 (15), 118.1 (21), 91.1 (31). **MS** (ESI) [M+H]<sup>+</sup>: 385.00 (ESI) (m/z) [C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Cl]<sup>+</sup>; Calcd. 385.0003. found, 384.9990. **IR** (ATR): ν = 3479, 3057, 2923, 2149, 1743, 1568, 1408, 1241, 1139, 980, 780, 699.

Diphenyl((2-phenyl-2-thiocyanatoethyl)imino)-λ<sup>6</sup>-sulfanone (4ma)

Light yellow oil, 25.6 mg, 46% yield. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.91 (m, 4H), 7.58 – 7.47 (m, 6H), 7.41 – 7.33 (m, 5H), 4.71 (dd, J = 8.2, 5.7 Hz, 1H), 3.67 – 3.58 (m, 2H).

**13C {1H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.1, 139.8, 137.6, 132.8, 129.3, 129.3, 128.9, 128.8, 128.5, 128.3, 128.1, 128.0, 112.4, 56.8, 48.2. **MS** (EI, 70 eV): m/z (%) = 230.1 (82), 203.1 (62), 186.1 (20), 154.1 (24), 125.0 (29), 121.0 (23), 118.1 (40), 109.0 (55), 104.1 (23), 97.1 (34), 91.1 (100), 89.1 (27), 78.2 (28), 77.2 (94), 65.2 (62). **MS** (ESI) [M+H]<sup>+</sup>: 379.09 (ESI) (m/z) [C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>]<sup>+</sup>; Calcd. 379.0939. found, 379.0920. **IR** (ATR): ν = 3596, 3061, 2920, 2846, 2334, 2149, 2055, 1901, 1739, 1585, 1447, 1365, 1245, 1142, 1083, 996, 896, 835, 728.
Ethyl(phenyl)((2-phenyl-2-thiocyanatoethyl)imino)-κ6-sulfanone (4na)

Light yellow oil, 27.2 mg, 55% yield, dr = 1:1. 1H NMR (600 MHz, CDCl3, mixture of diastereomers) δ 7.80 (dd, J = 20.3, 7.8 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.55 (dd, J = 16.6, 8.1 Hz, 2H), 7.40 – 7.30 (m, 5H), 4.66 – 4.59 (m, 1H), 3.62 – 3.55 (m, 1H), 3.43 – 3.38 (m, 1H), 3.25 – 3.11 (m, 2H), 1.24 (dt, J = 12.5, 7.4 Hz, 3H). 13C {1H} NMR (151 MHz, CDCl3, mixture of diastereomers) δ 137.5, 137.5, 137.2, 136.9, 133.3, 133.2, 129.6, 129.5, 129.3, 129.1, 128.8, 128.8, 128.1, 127.9, 112.5, 112.5, 57.3, 56.2, 51.1, 50.9, 48.4, 48.2, 7.2, 7.2. MS (EI, 70 eV): m/z (%) = 183.0 (21), 182.0 (100), 155.0 (61), 125.0 (14), 109.0 (14), 91.0 (12). MS (ESI) [M+Na]+: 353.08. (ESI) (m/z) [C17H18N2OS2Na]+: Calcd. 353.0758. found, 353.0746. IR (ATR): ν = 3905, 2928, 2677, 2336, 2096, 1743, 1448, 1226, 895, 725.

Methyl(phenyl)((2-phenyl-2-(phenylthio)ethyl)imino)-κ6-sulfanone (7)

Light yellow oil, 6.6 mg, 12% yield, yield, dr = 1:1. 1H NMR (600 MHz, CDCl3, mixture of diastereomers) δ 7.72 – 7.66 (m, 2H), 7.52 – 7.47 (m, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 – 7.16 (m, 7H), 7.12 – 7.07 (m, 1H), 4.29 (dd, J = 7.5, 6.5 Hz, 1H), 3.52 (dd, J = 13.0, 6.3 Hz, 1H), 3.29 (dd, J = 9.4, 3.6 Hz, 1H), 3.11 (s, 3H). 13C {1H} NMR (151 MHz, CDCl3, mixture of diastereomers) δ 143.5, 139.7, 136.9, 134.8, 132.7, 130.0, 129.0, 128.7, 128.6, 128.1, 127.1, 127.1, 125.4, 58.1, 45.0, 43.5. MS (EI, 70 eV): m/z (%) = 244.1 (100), 141.1 (82), 125.0 (27), 123.1 (27), 91.1 (17), 77.2 (49). MS (ESI) [M+H]+: 368.11 (ESI) (m/z) [C21H22NOS2]+: Calcd. 368.1143 found, 368.1127. IR (ATR): ν = 3440, 3061, 2923, 2858, 2662, 2322, 2101, 1995, 1908, 1729, 1581, 1448, 1355, 1313, 1226, 1129, 976, 847, 739, 693.

6. References

7. $^1$H and $^{13}$C$^1$H NMR spectra of compounds 2 and 4-7