

Bismuth (III)chloride Catalyzed One-Pot Synthesis of Thioenol Ethers from 1,3-dicabonyls/2-Oxindoles Under Ultrasonic Irradiation

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Supplementary Information

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1. General Information

The required starting materials, thiols and catalyst were purchased from Sigma Aldrich, Avra and SRL were used without further purification. All other reagents and solvents were received from commercial suppliers and used without further purification. All reactions were performed in the round bottom flask using Digital Ultrasonic Cleaner (Helix Bioscience Model; HBPS-20A) instrument. NMR spectra (^1H and ^{13}C) of all compounds were recorded with CDCl_3 using 500 MHz and 400 MHz instrument Model: AV III, Make Bruker. Chemical shift of ^1H and ^{13}C NMR were reported in parts per million from TMS at 0 ppm as the internal standard. Peak multiplicities are given as follow: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet; dd, doublet of doublet, and so on. The coupling constants (J values) are given in Hz. IR spectra were recorded on Thermo Scientific Nicolet iS5; Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High-resolution mass spectra were recorded using 2% Water: IPA as mobile phase under (ESI+) condition with a QTOF and Agilent, advanced version LC-MS, QTOF.

The general synthesis method A and B applied for all thio-enols derivatives. The progress of the reaction mixture was monitored over silica gel 60 coated TLC plate (precoated F254 Merck plates) under UV lamp (254 nm) irradiation. All compounds were purified using 100-200 mesh size silica gel by column chromatography (ethyl acetate: Hexane).

2. General experimental procedure

General procedure (A) for the synthesis of compounds 4a to 4z

A 10 mL dry round bottom flask was charged with 1,3-dicarbonyl compound **1** (1.0 mmol), DMF-DMA (**2**) (1.0 mmol), and bismuth chloride (20 mol%). The mixture was sonicated (Frequency 40 kHz) at rt. The reaction progress was monitored by TLC (thin-layer chromatography). Then thiol **3** (1.1 mmol) was added and again reaction mixture was sonicated at rt. After the completion of the reaction, water was added, and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with 0.1 N HCl aqueous solution, saturated sodium bicarbonate solution, brine, and water. The organic layer was dried over Na_2SO_4 , filtered, and concentrated, and the crude product was subjected to column

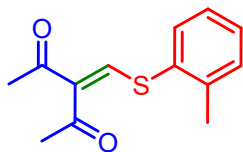
chromatography on silica gel (100-200 mesh size) with an ethyl acetate/hexane mixture to afford the pure product **4**.

General procedure (B) for the synthesis of compounds **6a** to **6h**:

To a 10 mL round bottom flask was added oxindole **5** (0.75 mmol), DMF-DMA (**2**) (1.5 mmol), and bismuth chloride (20 mol%) at rt. Then the mixture was sonicated at 40 °C. The progress of the reaction was monitored by TLC. Then thiol **3** (0.82 mmol) was added to the reaction mixture and again sonicated for the appropriate time (see Table 3) and was monitored by TLC. After completion of the reaction, dichloromethane was added filtered the crude reaction mixture to remove the bismuth chloride. The filtered residue was concentrated under reduced pressure and purified by column chromatography on silica gel (100-200 mesh size) using hexane and ethyl acetate (8.5:1.5) as an eluent to give the desired product.

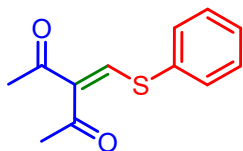
3. Characterization data of synthesized compounds

3-((*o*-tolyl thio) methylene) pentane-2,4-dione (**4a**)



The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 84% (198 mg); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 2.51 (s, 3H), 2.47 (s, 3H), 2.34 (s, 3H); ¹³C NMR (125 MHz, Chloroform-*d*) δ 197.4, 194.6, 162.2, 139.6, 135.5, 133.7, 132.5, 130.9, 129.5, 127.2, 30.7, 27.5, 20.7; IR (neat): 2945, 2883, 1707, 1587, 1465, 1367, 1033, 748 cm⁻¹; HRMS (ESI+) *m/z* [M+H]⁺ calcd for C₁₃H₁₄O₂S: 235.0793. Found: 235.0798.

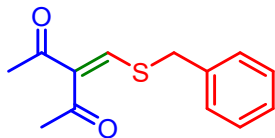
3-((phenyl thio) methylene) pentane-2,4-dione (**4b**)



The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 81% (179 mg); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.49 – 7.47 (m, 2H), 7.41 – 7.36 (m, 3H), 2.46 (s, 3H), 2.33 (s, 3H). ¹³C NMR (125 MHz, Chloroform-*d*) δ 197.4,

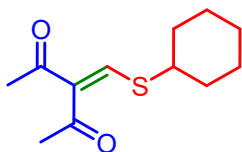
194.6, 161.9, 136.6, 133.6, 130.9, 129.6, 129.1, 30.7, 27.6; IR (neat): 2969, 2881, 1765, 1659, 1466, 1378, 953, 739 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}$: 221.0636. Found: 221.0641.

3-((benzyl thio) methylene) pentane-2,4-dione (4c)



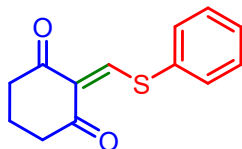
The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 84% (197 mg); ^1H NMR (500 MHz, Chloroform- d) δ 8.15 (s, 1H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.33 (dt, $J = 7.9, 1.9$ Hz, 3H), 4.02 (s, 2H), 2.44 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, Chloroform- d) δ 197.5, 194.6, 161.2, 136.3, 134.1, 129.3, 129.3, 128.1, 41.2, 31.0, 27.5; IR (neat): 3053, 2883, 1764, 1587, 1421, 1365, 1264, 955, 732 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$: 235.0793. Found: 235.0807.

3-((cyclohexyl thio) methylene) pentane-2,4-dione (4d)



The title compound was prepared according to the general procedure A. Light green liquid; Yield: 79% (179 mg); ^1H NMR (500 MHz, Chloroform- d) δ 8.31 (s, 1H), 2.93 (ddd, $J = 14.6, 10.8, 3.7$ Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.04 (s, 2H), 1.83 (d, $J = 13.2$ Hz, 2H), 1.66 (d, $J = 12.8$ Hz, 1H), 1.50 (q, $J = 10.9$ Hz, 2H), 1.39 (q, $J = 11.4$ Hz, 2H), 1.29 (dd, $J = 21.5, 9.5$ Hz, 1H). ^{13}C NMR (125 MHz, Chloroform- d) δ 197.4, 194.5, 160.2, 133.5, 49.2, 33.3, 30.8, 27.5, 25.5, 25.0; IR (neat): 3049, 2944, 1707, 1421, 1365, 1022, 732 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$: 227.1106. Found: 227.1110.

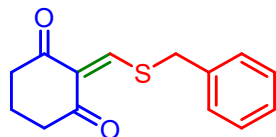
2-((phenyl thio) methylene) cyclohexane-1,3-dione (4e).



The title compound was prepared according to the general procedure A. Yellow solid; Yield: 78% (161 mg); M.p: 88-89 $^{\circ}\text{C}$; ^1H NMR (500 MHz, Chloroform- d) δ 8.83 (s, 1H), 7.53 (d, $J = 3.5$ Hz, 2H), 7.44 – 7.42 (m, 3H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.62 – 2.60 (t, 2H), 2.05 (dd,

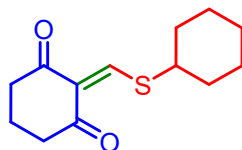
$J = 7.4, 5.6$ Hz, 2H). ^{13}C NMR (125 MHz, Chloroform- d) δ 197.6, 194.6, 165.3, 135.8, 130.9, 129.8, 129.5, 128.8, 38.3, 38.1, 18.5; IR (neat): 3053, 2888, 1764, 1421, 1264, 1077, 733 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$: 233.0558. Found: 233.0562

2-((benzyl thio) methylene) cyclohexane-1,3-dione (4f).



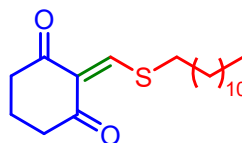
The title compound was prepared according to the general procedure A. Light Yellow liquid; Yield: 83 % (182 mg); ^1H NMR (500 MHz, Chloroform- d) δ 8.75 (s, 1H), 7.32 (d, 1H), 7.30 (d, $J = 3.0$ Hz, 3H), 7.29 (d, 1H), 4.10 (s, 2H), 2.56 (t, $J = 6.4$ Hz, 2H), 2.51 (t, $J = 6.4$ Hz, 2H), 1.98 – 1.92 (m, 2H); ^{13}C NMR (125 MHz, Chloroform- d) δ 197.3, 194.3, 165.1, 135.9, 129.1, 129.0, 128.9, 127.9, 42.4, 38.1, 37.8, 18.4; IR (neat): 3053, 2887, 1787, 1641, 1472, 1264, 1078, 731 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$: 247.0715 Found: 247.0735

2-((cyclohexyl thio) methylene) cyclohexane-1,3-dione (4g)



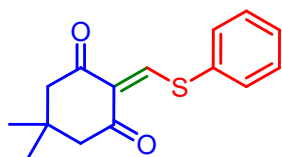
The title compound was prepared according to the general procedure A. Yellow solid; Yield: 77% (163 mg); M.p: 106-107 $^{\circ}\text{C}$; ^1H NMR (500 MHz, Chloroform- d) δ 8.81 (s, 1H), 2.96 (tt, $J = 11.0, 3.8$ Hz, 1H), 2.59 – 2.55 (m, 2H), 2.55 – 2.52 (m, 2H), 2.06 – 2.00 (m, 2H), 1.97 (tt, $J = 7.3, 5.8$ Hz, 2H), 1.79 (dt, $J = 13.2, 4.0$ Hz, 2H), 1.62 (ddd, $J = 12.6, 5.9, 2.9$ Hz, 1H), 1.52 – 1.44 (m, 2H), 1.39 – 1.30 (m, 2H), 1.30 – 1.19 (m, 1H); ^{13}C NMR (125 MHz, Chloroform- d) δ 197.3, 194.6, 164.8, 128.5, 50.2, 38.3, 37.9, 33.4, 25.7, 25.1, 18.5; IR (neat): 2969, 2881, 1764, 1466, 1378, 1128, 951, 816 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$: 239.1106. Found: 239.1107

2-((dodecyl thio) methylene) cyclohexane-1,3-dione (4h)



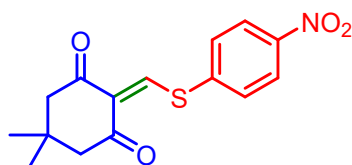
The title compound was prepared according to the general procedure A. Yellow solid; Yield: 80 % (231mg); M.p: 48 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 2.90 (t, J = 7.5 Hz, 2H), 2.61 (t, J = 6.4 Hz, 2H), 2.59 – 2.55 (m, 2H), 2.01 (p, J = 6.5 Hz, 2H), 1.72 (p, J = 7.5 Hz, 2H), 1.41 (p, J = 7.2 Hz, 2H), 1.25 (s, 16H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.4, 194.7, 167.2, 128.9, 38.7, 38.4, 38.0, 32.0, 30.3, 29.7, 29.6, 29.5, 29.4, 29.2, 28.5, 22.8, 18.6, 14.2; IR (neat): 2969, 2883, 1783, 1467, 1379, 1127, 954, 816 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{S}$: 325.2201. Found: 325.2227.

5,5-dimethyl-2-((phenyl thio) methylene) cyclohexane-1,3-dione (4i)



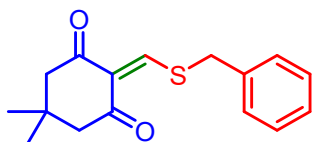
The title compound was prepared according to the general procedure A. Yellow solid; Yield: 82 % (152 mg); M.p: 92-93 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 7.51 (dd, J = 6.7, 2.9 Hz, 2H), 7.42 – 7.39 (m, 3H), 2.54 (s, 2H), 2.48 (s, 2H), 1.07 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.2, 194.1, 164.1, 135.7, 130.8, 129.6, 129.3, 127.3, 51.8, 51.7, 30.5, 28.5; IR (neat): 2971, 2883, 1787, 1467, 1379, 1162, 952, 810 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{S}$: 261.0949. Found: 261.0958.

5,5-dimethyl-2-(((4-nitrophenyl) thio) methylene) cyclohexane-1,3-dione (4j)



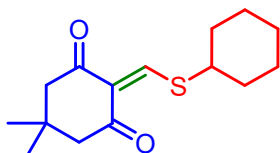
The title compound was prepared according to the general procedure A. Yellow solid; Yield: 72% (156 mg); M.p: 120 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.29 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 2.59 (s, 2H), 2.53 (s, 2H), 1.10 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.4, 194.0, 159.0, 148.0, 143.8, 130.7, 128.4, 124.6, 51.8, 51.7, 30.5, 28.5; IR (neat): 3053, 2981, 2883, 1786, 1642, 1421, 1365, 1264, 956, 731 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{S}$: 306.1035. Found: 306.1049.

2-((benzyl thio) methylene)-5,5-dimethylcyclohexane-1,3-dione (4k)



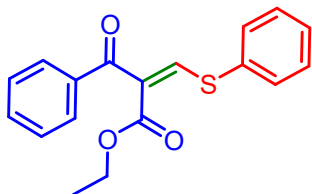
The title compound was prepared according to the general procedure A. Yellow solid; Yield: 81 % (158 mg); M.p: 110-112 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.33 (t, J = 6.2 Hz, 3H), 7.29 (d, J = 6.9 Hz, 1H), 4.13 (s, 2H), 2.48 (s, 2H), 2.44 (s, 2H), 1.04 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.2, 194.2, 164.4, 135.9, 129.2, 129.1, 128.1, 127.7, 51.9, 51.7, 42.6, 30.6, 28.6; IR (neat): 2969, 2882, 1763, 1466, 1378, 1128, 958, 816 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$: 275.1106. Found: 275.1121.

2-((cyclohexyl thio) methylene)-5,5-dimethylcyclohexane-1,3-dione (4l).



The title compound was prepared according to the general procedure A. Yellow solid; Yield: 79 % (149 mg); M.p: 118-119 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 3.03 – 2.95 (m, 1H), 2.49 (s, 2H), 2.45 (s, 2H), 2.06 (dt, J = 12.2, 3.8 Hz, 2H), 1.82 (dt, J = 13.1, 4.0 Hz, 2H), 1.65 (d, J = 5.7 Hz, 1H), 1.56 – 1.48 (m, 2H), 1.42 – 1.33 (m, 2H), 1.31 – 1.24 (m, 1H), 1.05 (s, 6H) ^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.2, 194.4, 164.1, 127.2, 52.1, 51.7, 50.3, 33.5, 30.5, 28.7, 25.8, 25.2; IR (neat): 3053, 2888, 1787, 1421, 1264, 1054, 732 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{S}$: 267.1419. Found: 267.1429.

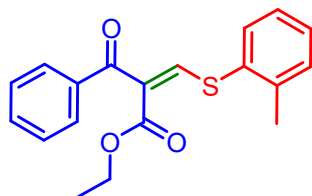
Ethyl (*E/Z*)-2-benzoyl-3-(phenyl thio) acrylate (4m)



The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 82% (133 mg); (*E/Z*: 7:3); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.99 (s, 1H), 7.79 – 7.76 (m, 4H), 7.57 – 7.50 (m, 6H), 7.45 (dd, J = 11.6, 7.9 Hz, 4H), 7.41 – 7.37 (m, 6H), 4.19 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.6, 191.7, 165.1, 164.4, 158.1, 155.8, 138.1,

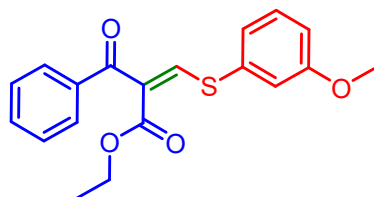
137.9, 135.1, 134.4, 132.8, 132.8, 131.4, 131.2, 129.7, 129.6, 129.1, 129.0, 129.0, 128.6, 128.4, 128.3, 126.7, 126.7, 61.2, 61.1, 13.9; IR (neat): 2969, 2882, 1763, 1466, 1378, 1127, 950 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{S}$: 313.0898. Found: 313.0909.

Ethyl (*E/Z*)-2-benzoyl-3-(*o*-tolyl thio) acrylate (4n)



The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 86% (146 mg); (*E/Z*: 6:4); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.86 (s, 1H), 7.82 – 7.75 (m, 4H), 7.58 – 7.51 (m, 2H), 7.49 (ddd, J = 10.9, 4.7, 2.3 Hz, 2H), 7.43 (dt, J = 17.1, 7.7 Hz, 4H), 7.29 – 7.20 (m, 6H), 4.20 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.5, 191.6, 165.0, 164.2, 158.5, 155.4, 139.9, 139.8, 138.1, 137.7, 134.0, 133.3, 132.9, 132.8, 132.7, 132.6, 130.9, 130.8, 129.5, 129.4, 128.9, 128.5, 128.3, 128.2, 127.2, 127.2, 126.8, 126.7, 61.0, 61.0, 20.9, 20.8, 13.8; IR (neat): 2969, 2882, 1763, 1658, 1466, 1378, 1127, 950, 816 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{S}$: 327.1055. Found: 327.1067.

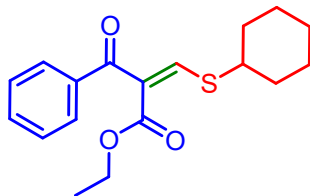
Ethyl (*E/Z*)-2-benzoyl-3-((3-methoxyphenyl) thio) acrylate (4o)



The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 85% (152 mg); (*E/Z*: 6:4); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.02 (s, 1H), 7.80 – 7.76 (m, 4H), 7.57 – 7.51 (m, 2H), 7.47 – 7.40 (m, 4H), 7.29 (dt, J = 11.0, 7.9 Hz, 2H), 7.09 (dtd, J = 7.0, 2.2, 1.0 Hz, 2H), 7.04 (dt, J = 4.2, 2.0 Hz, 2H), 6.90 (tdd, J = 9.1, 2.5, 0.9 Hz, 2H), 4.20 (q, J = 7.2 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.4, 191.5, 165.0, 164.2, 160.1, 157.6, 155.3, 138.0, 137.8, 135.9, 135.3, 132.7, 130.4, 130.4, 129.0, 128.5, 128.3, 128.2, 126.5, 123.3, 123.1, 116.4, 116.4, 114.8, 114.7, 61.1, 61.0, 55.4, 55.4, 13.8; IR

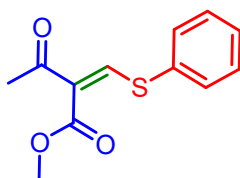
(neat): 2971, 2883, 1724, 1665, 1379, 1162, 954, 817 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{S}$: 343.1004. Found: 343.1019.

Ethyl (*E/Z*)-2-benzoyl-3-(cyclohexyl thio) acrylate (4p)



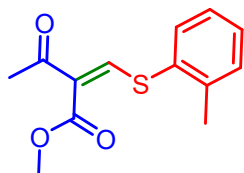
The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 79% (130 mg); (*E/Z*: 6:4); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.01 (s, 1H), 7.71 (ddd, $J = 8.4, 4.7, 1.4$ Hz, 4H), 7.50 (dt, $J = 7.3, 1.8$ Hz, 2H), 7.41 (d, $J = 7.7$ Hz, 4H), 4.09 (dq, $J = 12.7, 7.1$ Hz, 4H), 3.00 (td, $J = 10.8, 5.5$ Hz, 1H), 2.94 (ddt, $J = 10.9, 7.7, 4.0$ Hz, 1H), 2.05 – 2.01 (m, 4H), 1.81 – 1.76 (m, 4H), 1.63 – 1.59 (m, 2H), 1.52 – 1.42 (m, 4H), 1.38 – 1.31 (m, 4H), 1.27 – 1.20 (m, 2H), 1.03 (d, $J = 7.1$ Hz, 3H), 1.00 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.0, 192.0, 165.3, 164.5, 157.8, 154.6, 138.6, 138.0, 132.6, 132.4, 128.9, 128.5, 128.3, 128.2, 126.0, 125.7, 60.9, 60.7, 48.6, 48.4, 33.6, 25.7, 25.2, 13.9, 13.8; IR (neat): 2969, 2881, 1738, 1466, 1378, 1129, 953, 817 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{S}$: 319.1368. Found: 319.1382.

Methyl (*E/Z*)-3-oxo-2-((phenyl thio) methylene) butanoate (4q)



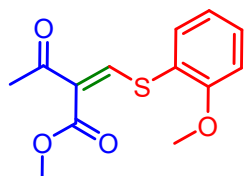
The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 86% (174 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.54 – 7.51 (m, 3H), 7.42 (dd, $J = 5.1, 2.0$ Hz, 2H), 3.79 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 164.7, 163.9, 136.8, 131.1, 129.7, 129.1, 123.9, 52.1, 30.4; IR (neat): 2944, 2832, 1654, 1448, 1113, 1021, 614 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3\text{S}$: 237.0585. Found: 237.0592.

Methyl (*E/Z*)-3-oxo-2-((o-tolyl thio) methylene) butanoate (4r)



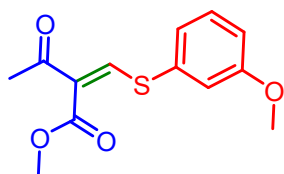
The title compound was prepared according to the general procedure A. Light yellow liquid; Yield: 84% (180 mg); (*E/Z*: 9:1) ^1H NMR (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 (d, J = 2.2 Hz, 1H), 3.77 (s, 3H), 2.58 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 164.8, 164.6, 139.9, 135.8, 132.9, 131.0, 129.7, 127.3, 124.0, 52.0, 30.5, 20.9; IR (neat): 2969, 2882, 1658, 1466, 1378, 1127, 950, 816 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}$: 251.0742. Found: 251.0744.

Methyl (*E/Z*)-2-(((2-methoxyphenyl) thio) methylene)-3-oxobutanoate (4s)



The title compound was prepared according to the general procedure A. Pale yellow liquid; Yield: 83% (190 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.47 (dd, J = 7.6, 1.7 Hz, 1H), 7.40 (ddd, J = 8.3, 7.5, 1.7 Hz, 1H), 7.00 (td, J = 7.5, 1.1 Hz, 1H), 6.96 (dd, J = 8.3, 1.1 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 165.3, 164.9, 158.4, 133.7, 131.2, 124.2, 123.5, 121.4, 111.7, 56.0, 52.0, 30.5; IR (neat): 2943, 2882, 1763, 1719, 1466, 1378, 1128, 951, 816, 737 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{S}$: 267.0691. Found: 267.0690.

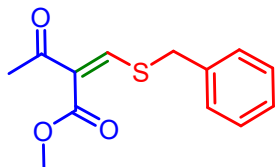
Methyl (*E/Z*)-2-(((3-methoxyphenyl) thio) methylene)-3-oxobutanoate (4t)



The title compound was prepared according to the general procedure A. Pale yellow liquid; Yield: 82% (187 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.03 (s, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.82 (s, 3H), 3.77 (d, J = 1.0 Hz, 3H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.6, 164.6, 163.4, 160.2, 137.8, 130.6, 123.8, 123.1, 116.5, 114.8, 55.5, 52.0, 30.6; IR (neat): 2969, 2882, 1763,

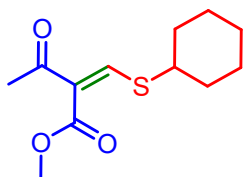
1466, 1378, 1127, 950, 816 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{S}$: 267.0691. Found: 267.0695.

Methyl (*E/Z*)-2-((benzyl thio) methylene)-3-oxobutanoate (4u)



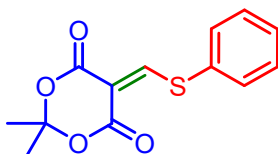
The title compound was prepared according to the general procedure A. Light orange liquid; Yield: 81% (174 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.37 – 7.35 (m, 1H), 7.34 (d, J = 0.9 Hz, 1H), 7.33 (d, J = 1.7 Hz, 1H), 7.32 – 7.27 (m, 2H), 4.03 (s, 2H), 3.77 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 164.7, 163.6, 136.4, 129.0, 129.0, 127.8, 124.0, 52.0, 41.9, 30.4; IR (neat): 2969, 2882, 1763, 1719, 1466, 1378, 1128, 951, 816, 737 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}$: 251.0742. Found: 251.0738.

Methyl (*E/Z*)-2-((cyclohexyl thio) methylene)-3-oxobutanoate (4v)



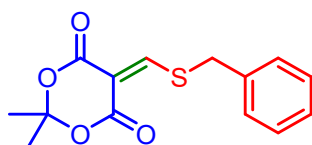
The title compound was prepared according to the general procedure A. Pale yellow liquid; Yield: 82% (170 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 3.75 – 3.74 (m, 3H), 2.86 – 2.80 (m, 1H), 2.45 – 2.44 (m, 3H), 1.98 (d, J = 12.8 Hz, 2H), 1.76 (d, J = 9.2 Hz, 2H), 1.59 (d, J = 12.5 Hz, 1H), 1.46 – 1.38 (m, 2H), 1.36 – 1.26 (m, 2H), 1.21 (d, J = 12.0 Hz, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.3, 164.9, 162.7, 123.3, 51.8, 49.3, 33.3, 30.4, 25.7, 25.2; IR (neat): 2969, 2881, 1764, 1659, 1378, 1129, 953, 817, 668 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{S}$: 243.1055. Found: 243.1059.

2,2-dimethyl-5-((phenyl thio) methylene)-1,3-dioxane-4,6-dione (4w)



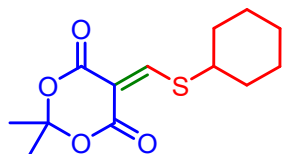
The title compound was prepared according to the general procedure A. White solid; Yield: 85 % (156 mg); M.p: 132-134 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 7.56 – 7.54 (m, 2H), 7.46 (dd, J = 5.2, 1.9 Hz, 3H), 1.76 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.6, 161.1, 160.4, 133.6, 131.0, 130.0, 129.9, 108.6, 105.3, 27.6; IR (neat): 2989, 1705, 1523, 1280, 926, 870, 790 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{O}_4\text{S}$: 265.0769. Found: 265.0792.

5-((benzyl thio) methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (4x)



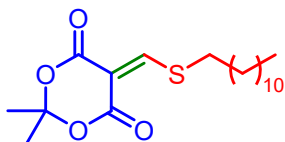
The title compound was prepared according to the general procedure A. White solid; Yield: 82 % (159 mg); M.p: 136 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 7.38 (d, J = 7.0 Hz, 2H), 7.34 (d, J = 7.2 Hz, 3H), 4.22 (s, 2H), 1.71 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.0, 161.2, 160.6, 135.1, 129.4, 129.1, 128.5, 108.9, 105.3, 41.9, 27.7; IR (neat): 3062, 2975, 2852, 1693, 1520, 1277, 871, 708 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}$: 279.0613. Found: 279.0630.

5-((cyclohexyl thio) methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (4y)



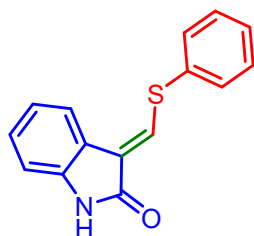
The title compound was prepared according to the general procedure A. White solid; Yield: 84 % (157 mg); M.p: 94 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.10 (s, 1H), 3.13 (tt, J = 11.0, 3.9 Hz, 1H), 2.12 – 2.07 (m, 2H), 1.84 (dt, J = 13.3, 4.0 Hz, 2H), 1.72 (s, 6H), 1.69 – 1.64 (m, 1H), 1.55 (ddd, J = 14.2, 11.2, 3.4 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.34 – 1.24 (m, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 169.7, 161.1, 160.9, 108.0, 105.0, 50.3, 33.4, 27.5, 25.6, 25.0; IR (neat): 2935, 2854, 1701, 1524. 995, 871, 708 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{O}_4\text{S}$: 271.1239. Found: 271.1255.

5-((dodecyl thio) methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (4z)



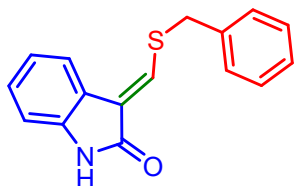
The title compound was prepared according to the general procedure A. White solid; Yield: 78% (193mg); M.p: 60 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 3.00 (t, J = 7.5 Hz, 2H), 1.77 (q, J = 7.5 Hz, 2H), 1.73 (s, 6H), 1.43 (dd, J = 10.5, 5.0 Hz, 2H), 1.31 – 1.24 (m, 16H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 171.9, 161.3, 160.9, 108.5, 105.0, 38.3, 32.0, 30.2, 29.7, 29.6, 29.5, 29.4, 29.1, 28.4, 27.6, 22.8, 14.2; IR (neat): 3053, 2981, 2960, 1787, 1421, 1264, 723, 663 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{32}\text{O}_4\text{S}$: 357.2334. Found: 357.2349.

(*E*)-3-((phenyl thio) methylene) indolin-2-one (6a)



The title compound was prepared according to the general procedure B. Yellow solid; Yield: 80% (152 mg); M.p: 182 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.98 (s, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.58 (dd, J = 8.0, 1.5 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.23 (t, J = 8.2 Hz, 1H), 7.10 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 167.8, 140.5, 140.2, 133.4, 131.2, 129.8, 129.0, 128.7, 124.0, 123.2, 122.8, 122.3, 109.8; IR (neat): 3136, 3068, 2884, 1686, 1461, 985, 729 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{ONS}$: 254.0639. Found: 254.0653.

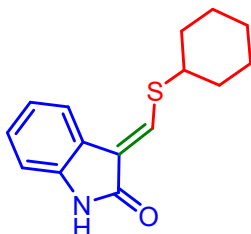
(*E*)-3-((benzyl thio) methylene) indolin-2-one (6b)



The title compound was prepared according to the general procedure B. Yellow solid; Yield: 79 % (159 mg); M.p: 152 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.86 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.39 (dd, J = 11.9, 7.0 Hz, 4H), 7.33 – 7.30 (m, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 4.25 (s, 2H); ^{13}C NMR (125 MHz,

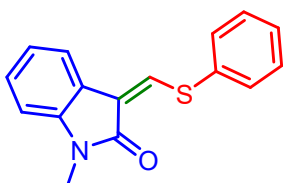
Chloroform-*d*) δ 167.2, 140.4, 139.7, 136.1, 129.0, 128.9, 128.2, 128.0, 123.9, 122.9, 122.7, 122.0, 109.4, 40.1; IR (neat): 3332, 2969, 2882, 1466, 1379, 950, 816 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{16}\text{H}_{13}\text{ONS}$:268.0796. Found:268.0800.

(*E*)-3-((cyclohexyl thio) methylene) indolin-2-one (6c)



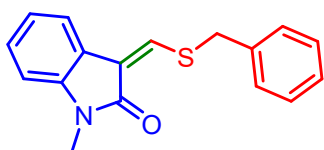
The title compound was prepared according to the general procedure B. Yellow solid; Yield: 75% (146 mg); M.p: 128 °C; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.94 (s, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 3.23 – 3.16 (m, 1H), 2.15 (dd, J = 9.1, 4.1 Hz, 2H), 1.85 (dt, J = 12.6, 3.7 Hz, 2H), 1.67 (dd, J = 8.6, 4.0 Hz, 1H), 1.58 (t, J = 13.6 Hz, 2H), 1.41 (d, J = 13.4 Hz, 2H), 1.36 – 1.27 (m, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 167.6, 140.6, 139.7, 128.0, 127.5, 123.8, 123.3, 122.1, 109.5, 48.8, 33.9, 25.9, 25.4; IR (neat): 3172, 2925, 2850, 1685, 1577, 1481, 1204, 743, 624 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{ONS}$:260.1109. Found:260.1109.

(*E/Z*)-1-methyl-3-((phenyl thiol) methylene)-2-one (6d)



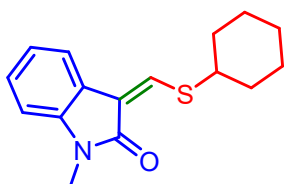
The title compound was prepared according to the general procedure B. Yellow liquid; Yield: 78% (142 mg); (*E/Z*: 7:3); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.75 (s, 1H), 7.66 (dt, J = 7.5, 0.8 Hz, 1H), 7.62 – 7.56 (m, 4H), 7.46 – 7.39 (m, 6H), 7.34 (dt, J = 7.4, 0.9 Hz, 1H), 7.30 (td, J = 7.7, 1.2 Hz, 1H), 7.24 (dd, J = 7.7, 1.2 Hz, 1H), 7.12 (td, J = 7.6, 1.0 Hz, 1H), 7.01 (td, J = 7.6, 0.9 Hz, 1H), 6.85 (dd, J = 7.8, 0.9 Hz, 2H), 3.31 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 166.2, 142.8, 140.2, 139.6, 133.3, 131.2, 129.6, 129.5, 128.8, 128.5, 128.4, 127.8, 123.6, 122.9, 122.1, 121.7, 118.5, 108.0, 107.8, 26.1, 25.8; IR (neat): 3136, 2995, 2361, 2252, 1630, 1373, 917, 750 cm^{-1} ; HRMS (ESI+) m/z $[M+H]^+$ calcd for $\text{C}_{16}\text{H}_{13}\text{ONS}$:268.0796. Found:268.0811.

(*E/Z*)-3-((benzyl thio) methylene)-1-methylindolin-2-one (6e)



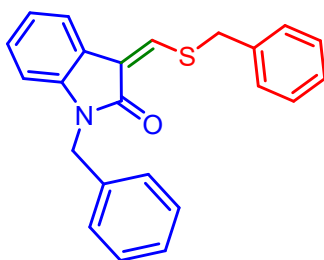
The title compound was prepared according to the general procedure B. Yellow liquid; Yield: 78% (150 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.54 (dt, J = 7.6, 0.9 Hz, 1H), 7.40 – 7.35 (m, 4H), 7.31 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 1.2 Hz, 1H), 7.05 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 4.25 (s, 2H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.1, 142.7, 141.5, 139.8, 139.5, 136.8, 136.3, 129.2, 129.1, 129.0, 128.2, 128.1, 127.8, 127.7, 123.7, 122.7, 122.1, 121.6, 118.3, 108.0, 107.8, 40.1, 39.9, 26.1, 25.9; IR (neat): 3057, 2980, 1787, 1422, 1267, 955, 733 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{ONS}$:282.0952. Found:282.0957.

(*E/Z*)-3-((cyclohexyl thio) methylene)-1-methylindolin-2-one (6f)



The title compound was prepared according to the general procedure B. Yellow liquid; Yield: 75% (138 mg); (*E/Z*: 9:1); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.57 (dt, J = 7.5, 0.8 Hz, 1H), 7.23 (dd, J = 7.8, 1.2 Hz, 1H), 7.06 (td, J = 7.6, 1.0 Hz, 1H), 6.84 – 6.77 (m, 1H), 3.25 (s, 3H), 3.19 (tt, J = 10.8, 3.8 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.84 (dd, J = 12.8, 5.0 Hz, 2H), 1.70 – 1.64 (m, 1H), 1.60 – 1.54 (m, 2H), 1.45 – 1.37 (m, 2H), 1.36 – 1.29 (m, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 166.2, 139.7, 127.8, 123.4, 122.4, 121.9, 121.4, 118.0, 107.5, 48.6, 33.7, 26.0, 25.8, 25.3; IR (neat): 3054, 2989, 2938, 1709, 1686, 1264, 730 cm^{-1} ; HRMS (ESI+) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{ONS}$:274.1265. Found:274.1270.

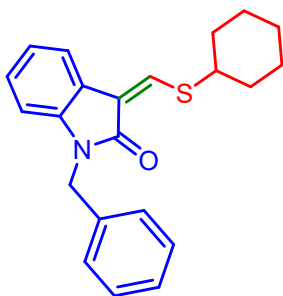
(*E/Z*)-1-benzyl-3-((benzyl thio) methylene) indolin-2-one (6g)



The title compound was prepared according to the general procedure B. Yellow liquid; Yield: 77% (123 mg); (*E/Z*: 7:3); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.62 (s, 1H), 7.55 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.44 – 7.42 (m, 1H), 7.41 – 7.39 (m, 4H), 7.38 (d, *J* = 1.0 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.33 (t, *J* = 1.9 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.30 – 7.28 (m, 2H), 7.28 (d, *J* = 2.6 Hz, 4H), 7.25 – 7.19 (m, 3H), 7.12 (d, *J* = 1.2 Hz, 1H), 7.10 (dd, *J* = 4.7, 1.2 Hz, 1H), 7.01 (td, *J* = 7.6, 1.1 Hz, 1H), 6.94 (d, *J* = 1.0 Hz, 1H), 6.70 (dt, *J* = 3.2, 0.8 Hz, 1H), 6.69 – 6.67 (m, 1H), 4.94 (s, 2H), 4.26 (s, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.2, 141.8, 140.6, 140.3, 139.9, 136.3, 136.2, 129.2, 129.2, 129.1, 129.0, 128.8, 128.8, 128.2, 128.1, 127.9, 127.6, 127.3, 123.7, 122.5, 122.2, 121.7, 118.4, 109.1, 108.8, 43.7, 43.6, 40.2; IR (neat): 3053, 2991, 1786, 1421, 1264, 731, 663 cm⁻¹

(i) P. Dahiya, A. Yadav, R. Budhwan, M. Rawat and R. K. Peddinti, Construction of arylthio/aryl amino methylene bonds by addition–elimination of nitroolefins with aromatic thiols and amines. *Org. Biomol. Chem.*, 2024, **22**, 7664–7670.

(*E/Z*)-1-benzyl-3-((cyclohexyl thio) methylene) indolin-2-one (6h)



The title compound was prepared according to the general procedure B. Yellow liquid; Yield: 77% (121 mg); (*E/Z*: 7:3); ¹H NMR (500 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.78 (s, 1H), 7.61 – 7.54 (m, 1H), 7.36 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.29 (d, *J* = 4.7 Hz, 5H), 7.24 (dd, *J* = 7.7, 2.4 Hz, 2H), 7.11 (qd, *J* = 7.8, 1.1 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.97 (td, *J* = 7.6, 1.0 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.98 (s, 2H), 4.97 (s, 2H), 3.21 (ddd, *J* = 14.4, 10.7, 3.6 Hz, 1H), 3.11 – 3.02 (m, 1H), 2.19 – 2.10 (m, 4H), 1.86 (ddt, *J* = 10.6, 6.7, 3.6 Hz, 4H), 1.66 (ddd, *J* = 20.9, 11.6, 3.2 Hz, 4H), 1.55 (d, *J* = 3.5 Hz, 1H), 1.47 – 1.38 (m, 4H), 1.36 – 1.29 (m, 3H); ¹³C NMR (125 MHz, Chloroform-*d*) δ 166.8, 140.3, 140.1, 136.4, 136.3, 128.6, 128.6, 127.7, 127.5, 127.4, 127.2, 123.4, 122.6, 122.5, 122.0, 121.5, 120.9, 118.0, 108.9, 108.6, 48.7, 48.5, 43.6, 43.4, 33.8, 33.7, 25.8, 25.8, 25.3, 25.3; IR (neat): 3053, 2981, 1787, 1597, 1421, 1364, 1264, 731 cm⁻¹; HRMS (ESI⁺) *m/z* [M+H]⁺ calcd for C₂₂H₂₃ONS:350.1578. Found:350.1585.

4. ^1H NMR and ^{13}C NMR spectra of synthesized compounds

