Supporting Information

**Regio- and stereoselective synthesis of 2-cyclopentenones via a hydrogenolysis-terminated Heck cyclization of $\beta$-alkylthio dienones**

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I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 25ºC on a Varian 500 MHz and 125 MHz, and using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Melting points were uncorrected. The compound 2a with dimension 0.40 $\times$ 0.35 $\times$ 0.30 mm, was glued on a glass fiber. Data were collected at 293K using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073\AA$) and Bruker APEX CCD area-detector in the range 3.09° $< \theta < 25.00°$. Substrates 1 were prepared following the known procedure.$^1$ 1$'$a,$^2$ 1$'$e,$^3$ 1$'$f,$^4$ 1$'$g,$^5$ 1$'$h,$^6$ 1$'$i,$^6$ 1$'$j,$^7$ 1$'$k,$^8$ 1$'$l,$^9$ 1$'$m,$^9$ 1$'$n,$^9$ 1$'$o,$^9$ 1$'$p,$^9$ 1$'$q,$^9$ 1$'$r,$^9$ 1$'$s,$^9$ 1$'$t,$^9$ 1$'$v,$^9$ 1$'$w,$^9$ 1$'$x,$^4$ and 1$'$y$^{10}$ are known compounds.

II. Synthetic procedures/analytical data of compounds 1

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General procedure for the synthesis of ketene dithioacetals of 1a-u and 1y (taking 1a as an example): To a well-stirred suspension of 1-(4-methoxyphenyl)propan-2-one (15.4 mL, 100 mmol), K₂CO₃ (34.5 g, 250 mmol) and DMF (50 mL) at room temperature was added CS₂ (6.6 mL, 110 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 0.5 h, EtBr (16.4 mL, 220 mmol) was added dropwise within 15 min. The mixture was allowed to warm to room temperature and stirred for 24 h, and then poured into ice-water (100 mL) under stirring and extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was washed with water (3 × 25 mL), dried over MgSO₄ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 60/1, v/v) to give 4,4-bis(ethylthio)-3-(4-methoxyphenyl)but-3-en-2-one 1a' (23.7 g, 80%) as a yellow liquid. Then, to a stirred solution of 1a' (296 mg, 1.0 mmol) and benzaldehyde (0.12 mL, 1.2 mmol) in EtOH (3 mL) was added NaOH (80 mg, 2.0 mmol) in one portion at room temperature. After 1a' was consumed as indicated by TLC, the resulting mixture was quenched by ice-water (20 mL). The precipitate was collected by filtration, washed with water (3 × 15 mL) and dried at ambience to give 1a (353 mg, 92%) as a yellow crystal.

General procedure for the synthesis of ketene dithioacetals 1v-x (taking 1v as an example): To a well-stirred suspension of anhydrous t-BuOK (4.94 g, 44 mmol) and butan-2-one (1.79 mL, 20 mmol) in 40 mL of anhydrous DMF were added CS₂ (1.32 mL, 20 mmol) at 0 ºC. After the reaction mixture was stirred at 0 °C for 1.5 h, MeI (2.49 mL, 40 mmol) was added dropwise within 30 min. The mixture was allowed to warm to room temperature and stirred for 5 h, and then poured into saturated aqueous NH₄Cl (100 mL) under stirring. The resulting mixture was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was washed with water (3 × 15 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate: 80/1, v/v) to give 3-methyl-4,4-bis(methylthio)but-3-en-2-one 1'f (705 mg, 20%) as a light yellow liquid. Then, to a stirred solution of 1'f (176 mg, 1.0 mmol) and benzaldehyde (0.12 mL, 1.2 mmol) in EtOH (3 mL) was added NaOH (80 mg, 2.0 mmol) in one portion at room temperature. After 1'f was consumed as indicated by TLC, the resulting mixture was quenched by ice-water (20 mL) under stirring. The precipitate was collected by filtration, washed with water (15 mL × 3) and dried at ambience to give 1v (198 mg, 75%) as a light yellow crystal.

Procedure for the synthesis of ketene dithioacetal 1z: To a well-stirred suspension of pentane-2,4-dione (10.2 mL, 100 mmol), K₂CO₃ (34.5 g, 250 mmol) and DMF (50 mL) at room temperature was added CS₂ (6.6 mL, 110 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 0.5 h, EtBr (16.4 mL, 220 mmol) was added dropwise within 15 min. The mixture was
allowed to warm to room temperature and stirred for 16.0 h, and then poured into ice-water (200 mL) under stirring and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The combined organic phase was washed with water (3 × 25 mL), dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 20/1, v/v) to give 3-(bis(ethylthio)methylene)pentane-2,4-dione (20.8 g, 90%) as a yellow liquid. Then to a solution of 3-(bis(ethylthio)methylene)pentane-2,4-dione (1.16 g, 5.0 mmol) in 20 mL of CH$_2$Cl$_2$ was added concentrated H$_2$SO$_4$ (1.1 mL, 20 mmol) at 0°C. The mixture was allowed to warm to room temperature and stirred for 10 h, and then poured onto saturated NaCl ice-water (50 mL) under stirring. The mixture was neutralized with aqueous Na$_2$CO$_3$, and extracted with CH$_2$Cl$_2$ (3 × 15 mL). The combined organic phase was washed with water (3 × 10 mL), dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 30/1, V/V) to give 4,4-bis(ethylthio)but-3-en-2-one $\mathbf{1i}$ (855 mg, 90%) as a white solid. Then, to a stirred solution of $\mathbf{1i}$ (190 mg, 1.0 mmol) and 4-chlorobenzaldehyde (154 mg, 1.1 mmol) in EtOH (3 mL) was added NaOH (80 mg, 2.0 mmol) in one portion at room temperature. After $\mathbf{1i}$ was consumed as indicated by TLC, the resulting mixture was quenched by ice-water (20 mL) under stirring. The precipitate was collected by filtration, washed with water (3 × 15 mL) and dried at ambience to give $\mathbf{1z}$ (281 mg, 90%) as a yellow crystal.

**Procedure for the synthesis of ketene dithioacetal $\mathbf{1aa}$**: The procedure for the synthesis of $\mathbf{1aa}$ is the same as that of $\mathbf{1a}$.

**Procedure for the synthesis of ketene dithioacetal $\mathbf{1ab}$**: To a stirred solution of $\mathbf{1'd}$ (284 mg, 1.0 mmol) and benzophenone (182 mg, 1.0 mmol) in tBuOH (5.0 mL) was added tBuOK (448 mg, 4.0 mmol) in one portion at room temperature. The reaction mixture was stirred for 15 min at room temperature and then heated to 50°C to stir for additional 7 h. After $\mathbf{1'd}$ was consumed (monitored...
by TLC), the reaction mixture was poured into ice water (30 mL), neutralized with diluted hydrochloric acid, extracted with CH₂Cl₂ (3 × 15 mL). The combined organic extracts were washed with water (3 × 15 mL), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel chromatography (eluent, petroleum ether/ethyl acetate: 20/1, v/v) to give 1ab (166 mg, 37%) as a yellow crystal.

General procedure for the synthesis of ketene dithioacetals 1ac–ae: General procedure for the synthesis of 1ac–ae is the same as that of 1a.

4,4-Bis(ethylthio)-3-(2-methoxyphenyl)but-3-en-2-one(1'b)

Yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 1.13 (t, J = 7.5 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H), 2.28 (s, 3H), 2.60 (q, J = 7.5 Hz, 2H), 2.91 (q, J = 7.5 Hz, 2H), 3.79 (s, 3H), 6.88-6.90 (m, 1H), 6.94-6.98 (m, 1H), 7.22-7.24 (m, 1H), 7.30-7.33 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 200.7, 156.7, 143.9, 140.7, 131.1, 129.6, 127.6, 120.5, 110.7, 55.3, 30.0, 28.5 (2C), 14.6, 14.5. HRMS (ESI-TOF) calcd for C₁₅H₂₁O₂S₂⁺ ([M+H⁺]) 297.0977, found 297.0983.

3-(4-Chlorophenyl)-4,4-bis(ethylthio)but-3-en-2-one(1'c)

White solid. mp 62-63 °C. ¹H NMR (500 MHz, CDCl₃) δ 1.15 (t, J = 7.0 Hz, 3H), 1.32 (t, J = 7.0 Hz, 3H), 2.29 (s, 3H), 2.68 (q, J = 7.5 Hz, 2H), 2.89 (q, J = 7.5 Hz, 2H), 7.23 (dd, J = 2.0, 6.5 Hz, 2H), 7.34 (dd, J = 2.0, 6.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 200.9, 147.9, 136.7, 134.8, 134.0, 130.4 (2C), 128.5 (2C), 30.4, 28.4, 28.2, 14.6, 14.5. HRMS (ESI-TOF) calcd for C₁₄H₁₈ClO₂S₂⁺ ([M+H⁺]) 301.0482, found 301.0484.
4,4-Bis(ethylthio)-3-(4-fluorophenyl)but-3-en-2-one (1'd)

Yellow solid. mp 40-41 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.15 (t, $J = 7.5$ Hz, 3H), 1.32 (t, $J = 7.5$ Hz, 3H), 2.29 (s, 3H), 2.67 (q, $J = 7.5$ Hz, 2H), 2.88 (q, $J = 7.5$ Hz, 2H), 7.05 (t, $J = 8.5$ Hz, 2H), 7.26-7.29 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 201.2, 162.3 (d, $J = 247$ Hz, 1C), 148.2, 135.9, 132.2 (d, $J = 3.4$ Hz, 1C), 130.8 (d, $J = 8.1$ Hz, 2C), 115.3 (d, $J = 21.4$ Hz, 2C), 30.3, 28.3, 28.0, 14.6, 14.5. HRMS (ESI-TOF) calcd for C$_{14}$H$_{18}$FOS$_2$ $^+$ ([M+H]$^+$) 285.0778, found 285.0778.

(E)-1,1-Bis(ethylthio)-2-(4-methoxyphenyl)-5-p-tolylpenta-1,4-dien-3-one (1c)

Yellow solid. mp 82-83 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.22 (t, $J = 7.5$ Hz, 3H), 1.26 (t, $J = 7.5$ Hz, 3H), 2.36 (s, 3H), 2.73 (q, $J = 7.5$ Hz, 2H), 2.84 (q, $J = 7.5$ Hz, 2H), 3.80 (s, 3H), 6.77 (d, $J = 16.5$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 16.5$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 194.7, 159.3, 147.8, 144.6, 140.9, 134.1, 131.9, 130.5 (2C), 129.6 (2C), 128.9, 128.3 (2C), 126.1, 113.7 (2C), 55.2, 28.6, 27.9, 21.5, 14.8, 14.6. HRMS (ESI-TOF) calcd for C$_{23}$H$_{27}$O$_2$S$_2$ $^+$ ([M+H]$^+$) 399.1447, found 399.1454.

(E)-5-(Benzo[d][1,3]dioxol-5-yl)-1,1-bis(ethylthio)-2-(4-methoxyphenyl)penta-1,4-dien-3-one (1d)

Yellow solid. mp 60-61 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.21 (t, $J = 7.5$ Hz, 3H), 1.27 (t, $J = 7.5$ Hz, 3H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.84 (q, $J = 7.5$ Hz, 2H), 3.81 (s, 3H), 5.99 (s, 2H), 6.63 (d, $J = 16.0$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.87-6.89 (m, 2H), 6.97-6.99 (m, 2H), 7.33-7.35 (m, 2H),
7.44 (d, J = 16.0 Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 194.4, 159.3, 149.8, 148.3, 147.8, 144.3, 134.2, 130.5 (2C), 129.1, 128.9, 125.1, 124.9, 113.7 (2C), 108.6, 106.6, 101.6, 55.2, 28.6, 27.9, 14.8, 14.6. **HRMS** (ESI-TOF) calcd for C\(_{23}\)H\(_{25}\)O\(_4\)S\(_2\)^{+} ([M+H]^{+}) 429.1187, found 429.1187.

**(E)-5-(2-Chlorophenyl)-1,1-bis(ethylthio)-2-(4-methoxyphenyl)penta-1,4-dien-3-one**(1f)

Yellow solid. mp 65-66 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.23 (t, \(J\) = 7.5 Hz, 3H), 1.26 (t, \(J\) = 7.5 Hz, 3H), 2.73 (q, \(J\) = 7.5 Hz, 2H), 2.85 (q, \(J\) = 7.5 Hz, 2H), 3.80 (s, 3H), 6.77 (d, \(J\) = 16.5 Hz, 1H), 6.89 (d, \(J\) = 9.0 Hz, 2H), 7.27-7.29 (m, 2H), 7.36-7.40 (m, 3H), 7.60-7.62 (m, 1H), 7.97 (d, \(J\) = 16.5 Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 194.8, 159.4, 147.3, 140.3, 135.2, 134.7, 132.8, 131.2, 130.5 (2C), 130.2, 129.3, 128.8, 127.5, 127.1, 113.7 (2C), 55.2, 28.7, 27.9, 14.8, 14.5. **HRMS** (ESI-TOF) calcd for C\(_{22}\)H\(_{24}\)ClO\(_2\)S\(_2\)^{+} ([M+H]^{+}) 419.0901, found 419.0902.

**(E)-1,1-Bis(ethylthio)-2-(4-methoxyphenyl)-6,6-dimethylhepta-1,4-dien-3-one**(1h)

Yellow solid. mp 57-58 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.05 (s, 9H), 1.19 (t, \(J\) = 7.0 Hz, 3H), 1.27 (t, \(J\) = 7.5 Hz, 3H), 2.70 (q, \(J\) = 7.0 Hz, 2H), 2.81 (q, \(J\) = 7.5 Hz, 2H), 3.80 (s, 3H), 6.10 (d, \(J\) = 16.0 Hz, 1H), 6.80 (d, \(J\) = 16.0 Hz, 1H), 6.86 (d, \(J\) = 8.5 Hz, 2H), 7.28 (d, \(J\) = 8.5 Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 195.8, 159.8, 159.2, 148.0, 132.6, 130.2 (2C), 128.8, 126.0, 113.5 (2C), 55.1, 33.9, 28.5 (3C), 28.4, 27.6, 14.7, 14.5. **HRMS** (ESI-TOF) calcd for C\(_{20}\)H\(_{29}\)O\(_2\)S\(_2\)^{+} ([M+H]^{+}) 365.1603, found 365.1605.

**(E)-1,1-Bis(ethylthio)-2-(2-methoxyphenyl)-5-phenylpenta-1,4-dien-3-one**(1i)

Yellow solid. mp 76-77 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.18 (t, \(J\) = 7.5 Hz, 3H), 1.30 (t, \(J\) = 7.5 Hz, 3H), 2.70 (q, \(J\) = 7.0 Hz, 2H), 2.81 (q, \(J\) = 7.5 Hz, 2H), 3.80 (s, 3H), 6.10 (d, \(J\) = 16.0 Hz, 1H), 6.80 (d, \(J\) = 16.0 Hz, 1H), 6.86 (d, \(J\) = 8.5 Hz, 2H), 7.28 (d, \(J\) = 8.5 Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 195.8, 159.8, 159.2, 148.0, 132.6, 130.2 (2C), 128.8, 126.0, 113.5 (2C), 55.1, 33.9, 28.5 (3C), 28.4, 27.6, 14.7, 14.5. **HRMS** (ESI-TOF) calcd for C\(_{20}\)H\(_{29}\)O\(_2\)S\(_2\)^{+} ([M+H]^{+}) 365.1605, found 365.1605.
(E)-5-(Benzo[d][1,3]dioxol-5-yl)-1,1-bis(ethylthio)-2-(2-methoxyphenyl)penta-1,4-dien-3-one(1j)

Yellow solid. mp 128-129 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.17 (t, \(J = 7.5\) Hz, 3H), 1.29 (t, \(J = 7.5\) Hz, 3H), 2.64 (q, \(J = 7.5\) Hz, 2H), 2.86 (q, \(J = 7.5\) Hz, 2H), 3.79 (s, 3H), 6.71 (d, \(J = 16.0\) Hz, 1H), 6.97 (d, \(J = 8.0\) Hz, 1H), 6.92-6.95 (m, 2H), 6.96-6.98 (m, 1H), 7.29-7.36 (m, 5H), 7.48-7.50 (m, 2H), 7.71 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 193.4, 156.6, 143.8, 142.6, 139.6, 135.2, 130.8, 129.9, 129.6, 128.8 (2C), 128.1 (2C), 127.0, 126.9, 120.5, 110.9, 55.3, 28.7, 28.2, 14.8, 14.7. HRMS (ESI-TOF) calcd for C\(_{22}\)H\(_{25}\)O\(_2\)S\(_2\)\(^{+}\) ([M+H]\(^{+}\)) 385.1290, found 385.1289.

(E)-5-(4-Chlorophenyl)-1,1-bis(ethylthio)-2-(2-methoxyphenyl)penta-1,4-dien-3-one(1k)

Yellow solid. mp 118-119 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.17 (t, \(J = 7.5\) Hz, 3H), 1.30 (t, \(J = 7.5\) Hz, 3H), 2.64 (q, \(J = 7.5\) Hz, 2H), 2.88 (q, \(J = 7.5\) Hz, 2H), 3.77 (s, 3H), 6.86-6.90 (m, 2H), 6.97 (t, \(J = 7.5\) Hz, 1H), 7.29-7.34 (m, 4H), 7.42 (d, \(J = 8.5\) Hz, 2H), 7.64 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 193.1, 156.6, 143.5, 140.7, 140.3, 135.7, 133.7, 130.9, 129.7, 129.2 (2C), 129.1 (2C), 127.4, 127.0, 120.6, 110.9, 55.3, 28.8, 28.3, 14.8, 14.6. HRMS (ESI-TOF) calcd for C\(_{22}\)H\(_{24}\)ClO\(_2\)S\(_2\)\(^{+}\) ([M+H]\(^{+}\)) 429.1189, found 429.1188.

(E)-2-(4-Chlorophenyl)-1,1-bis(ethylthio)-5-phenylpenta-1,4-dien-3-one(1l)

Yellow solid. mp 118-119 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.17 (t, \(J = 7.5\) Hz, 3H), 1.30 (t, \(J = 7.5\) Hz, 3H), 2.64 (q, \(J = 7.5\) Hz, 2H), 2.88 (q, \(J = 7.5\) Hz, 2H), 3.77 (s, 3H), 6.86-6.90 (m, 2H), 6.97 (t, \(J = 7.5\) Hz, 1H), 7.29-7.34 (m, 4H), 7.42 (d, \(J = 8.5\) Hz, 2H), 7.64 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 193.1, 156.6, 143.5, 140.7, 140.3, 135.7, 133.7, 130.9, 129.7, 129.2 (2C), 129.1 (2C), 127.4, 127.0, 120.6, 110.9, 55.3, 28.8, 28.3, 14.8, 14.6. HRMS (ESI-TOF) calcd for C\(_{22}\)H\(_{24}\)ClO\(_2\)S\(_2\)\(^{+}\) ([M+H]\(^{+}\)) 419.1158, found 419.1152.
Yellow solid. mp 138-139 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.22 (t, $J = 7.5$ Hz, 3H), 1.28 (t, $J = 7.5$ Hz, 3H), 2.73 (q, $J = 7.5$ Hz, 2H), 2.87 (q, $J = 7.5$ Hz, 2H), 6.84 (d, $J = 16.0$ Hz, 1H), 7.32-7.38 (m, 7H), 7.49-7.51 (m, 2H), 7.54 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.7, 146.2, 144.4, 137.2, 135.1, 134.4, 133.9, 130.5, 130.4 (2C), 128.9 (2C), 128.5 (2C), 128.3 (2C), 126.7, 28.6, 28.1, 14.7, 14.6. HRMS (ESI-TOF) calcd for C$_{21}$H$_{22}$ClO$_2$S$_2$ $^+$ ([M+H]$^+$) 389.0795, found 389.0802.

(E)-5-(Benzo[d][1,3]dioxol-5-yl)-2-(4-chlorophenyl)-1,1-bis(ethylthio)penta-1,4-dien-3-one(1m)

Yellow solid. mp 149-150 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.5$ Hz, 3H), 1.28 (t, $J = 7.5$ Hz, 3H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.86 (q, $J = 7.5$ Hz, 2H), 5.99 (s, 2H), 6.65 (d, $J = 16.0$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 2H), 7.31-7.35 (m, 4H), 7.45 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.7, 149.9, 148.4, 146.5, 144.4, 136.8, 135.2, 133.9, 130.5 (2C), 128.9, 128.5 (2C), 125.0, 124.8, 108.6, 106.6, 101.6, 28.6, 28.2, 14.8, 14.7. HRMS (ESI-TOF) calcd for C$_{22}$H$_{22}$ClO$_3$S$_2$ $^+$ ([M+H]$^+$) 433.0693, found 433.0701.

(E)-2,5-Bis(4-chlorophenyl)-1,1-bis(ethylthio)penta-1,4-dien-3-one(1n)

Yellow solid. mp 120-121 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.5$ Hz, 3H), 1.28 (t, $J = 7.0$ Hz, 3H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.87 (q, $J = 7.0$ Hz, 2H), 6.80 (d, $J = 16.0$ Hz, 1H), 7.33-7.35 (m, 6H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.2, 146.0, 142.6, 138.0, 136.4, 135.1, 134.0, 133.0, 130.6 (2C), 129.4 (2C), 129.2 (2C), 128.5 (2C), 127.1, 28.7, 28.3, 14.8, 14.7. HRMS (ESI-TOF) calcd for C$_{21}$H$_{21}$Cl$_2$O$_2$S$_2$ $^+$ ([M+H]$^+$) 423.0405,
found 423.0409.

**(E)-2-(4-Chlorophenyl)-1,1-bis(ethylthio)-5-(furan-2-yl)penta-1,4-dien-3-one**(1o)

Yellow solid. mp 87-88 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.20 (t, $J = 7.5$ Hz, 3H), 1.30 (t, $J = 7.5$ Hz, 3H), 2.71 (q, $J = 7.5$ Hz, 2H), 2.88 (q, $J = 7.5$ Hz, 2H), 6.47 (dd, $J = 2.0$, 3.5 Hz, 1H), 6.64 (d, $J = 3.0$ Hz, 1H), 6.73 (d, $J = 15.5$ Hz, 1H), 7.27-7.32 (m, 5H), 7.47 (d, $J = 1.5$ Hz, 1H). 13C NMR (125 MHz, CDCl$_3$) $\delta$ 193.0, 151.2, 146.3, 145.1, 137.8, 135.3, 133.9, 130.6 (2C), 130.0, 128.5 (2C), 124.1, 115.9, 112.6, 28.7, 28.3, 14.7, 14.6. HRMS (ESI-TOF) calcd for C$_{19}$H$_{20}$ClO$_2$S$_2$ $^+$ ([M+H]$^+$) 379.0588, found 379.0587.

**(E)-1,1-Bis(ethylthio)-2-(4-fluorophenyl)-5-phenylpenta-1,4-dien-3-one**(1p)

Yellow solid. mp 125-126 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.22 (t, $J = 7.5$ Hz, 3H), 1.28 (t, $J = 7.5$ Hz, 3H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.86 (q, $J = 7.5$ Hz, 2H), 6.84 (d, $J = 16.0$ Hz, 1H), 7.03-7.06 (m, 2H), 7.37-7.40 (m, 5H), 7.49-7.51 (m, 2H), 7.55 (d, $J = 16.0$ Hz, 1H). 13C NMR (125 MHz, CDCl$_3$) $\delta$ 193.9, 162.3 (d, $J = 247.0$ Hz, 1C), 146.5, 144.4, 136.7, 134.5, 132.7, 131.0 (d, $J = 8.1$ Hz, 2C), 130.5, 128.9 (2C), 128.3 (2C), 126.8, 115.3 (d, $J = 21.5$ Hz, 2C), 28.7, 28.1, 14.8, 14.7. HRMS (ESI-TOF) calcd for C$_{21}$H$_{22}$FOS$_2$ $^+$ ([M+H]$^+$) 373.1091, found 373.1086.

**(E)-5-(Benzo[d][1,3]dioxol-5-yl)-1,1-bis(ethylthio)-2-(4-fluorophenyl)penta-1,4-dien-3-one**(1q)

Yellow solid. mp 134-136 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J = 7.5$ Hz, 3H), 1.28 (t, $J = 7.5$ Hz, 3H), 2.72 (q, $J = 7.5$ Hz, 2H), 2.86 (q, $J = 7.5$ Hz, 2H), 6.00 (s, 2H), 6.65 (d, $J = 16.0$ Hz,
1H), 6.80 (d, J = 8.0 Hz, 1H), 6.98-7.06 (m, 4H), 7.36-7.39 (m, 2H), 7.46 (d, J = 16.0 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 193.9, 162.3 (d, J = 247.0 Hz, 1C), 149.9, 148.4, 146.8, 144.4, 136.3, 132.7, 131.0 (d, J = 8.1 Hz, 2C), 129.0, 125.0 (d, J = 3.5 Hz, 2C), 115.3 (d, J = 21.4 Hz, 2C), 108.6, 106.6, 28.6, 28.1, 14.8, 14.7. HRMS (ESI-TOF) calcd for C22H22FO3S2+ ([M+H]+) 417.0989, found 417.0983.

(E)-5-(4-Chlorophenyl)-1,1-bis(ethylthio)-2-(4-fluorophenyl) penta-1,4-dien-3-one(1r)

Yellow solid. mp 123-125 °C. 1H NMR (500 MHz, CDCl3) δ 1.21 (t, J = 7.5 Hz, 3H), 1.28 (t, J = 7.5 Hz, 3H), 2.72 (q, J = 7.5 Hz, 2H), 2.84 (q, J = 7.5 Hz, 2H), 6.80 (d, J = 16.0 Hz, 1H), 7.03-7.07 (m, 2H), 7.33-7.39 (m, 4H), 7.42 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 16.0 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 193.5, 162.4 (d, J = 247.1 Hz, 1C), 146.3, 142.5, 137.5, 136.4, 133.1, 132.7, 131.0 (d, J = 8.1 Hz, 2C), 129.4 (2C), 129.2 (2C), 127.1, 115.3 (d, J = 21.4 Hz, 2C), 28.7, 28.2, 14.8, 14.7. HRMS (ESI-TOF) calcd for C21H21ClFOS2+ ([M+H]+) 407.0701, found 407.0698.

(E)-1,1-bis(ethylthio)-2-(4-fluorophenyl)-5-(furan-2-yl)penta-1,4-dien-3-one(1s)

Yellow solid. mp 59-60 °C. 1H NMR (500 MHz, CDCl3) δ 1.20 (t, J = 7.5 Hz, 3H), 1.30 (t, J = 7.5 Hz, 3H), 2.71 (q, J = 7.5 Hz, 2H), 2.88 (q, J = 7.5 Hz, 2H), 6.46 (dd, J = 2.0 Hz, 1H), 6.64 (d, J = 3.5 Hz, 1H), 6.74 (d, J = 15.5 Hz, 1H), 7.02-7.06 (m, 2H), 7.31 (d, J = 15.5 Hz, 1H), 7.35-7.37 (m, 2H), 7.47 (d, J = 1.0 Hz, 1H). 13C NMR (125 MHz, CDCl3) δ 193.2, 162.3 (d, J = 247.1 Hz, 1C), 151.2, 146.6, 145.0, 137.2, 132.8 (d, J = 3.4 Hz, 1C), 131.0 (d, J = 8.1 Hz, 2C), 129.9, 124.1, 115.8, 115.3 (d, J = 21.4 Hz, 2C), 112.6, 28.7, 28.2, 14.7, 14.6. HRMS (ESI-TOF) calcd for C19H20FO2S2+ ([M+H]+) 363.0883, found 363.0883.

(E)-2-(4-Chlorophenyl)-1,1-bis(methylthio)-5-phenylpenta-1,4-dien-3-one(1t)
Yellow solid. mp 134-135 °C. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 2.26 (s, 3H), 2.37 (s, 3H), 6.82 (d, \(J = 16.5\) Hz, 1H), 7.34-7.38 (m, 7H), 7.50-7.51 (m, 2H), 7.54 (d, \(J = 16.5\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 193.1, 144.2, 143.7, 141.7, 135.2, 134.5, 134.1, 130.6 (3C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 126.6, 18.1, 17.4. HRMS (ESI-TOF) calcd for C\textsubscript{19}H\textsubscript{18}ClO\textsubscript{2}S\textsubscript{2} \([\text{M+H}]^+\) 361.0482, found 361.0478.

\textbf{(E)-2,5-Bis(4-chlorophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one(1u)}

Yellow solid. mp 114-115 °C. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 2.26 (s, 3H), 2.38 (s, 3H), 6.77 (d, \(J = 16.0\) Hz, 1H), 7.32-7.36 (m, 6H), 7.42 (d, \(J = 8.5\) Hz, 2H), 7.49 (d, \(J = 16.0\) Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 192.6, 143.4, 142.6, 142.3, 136.4, 135.1, 134.2, 133.0, 130.6 (2C), 129.5 (2C), 129.2 (2C), 128.7 (2C), 126.9, 18.2, 17.5. HRMS (ESI-TOF) calcd for C\textsubscript{19}H\textsubscript{17}Cl\textsubscript{2}O\textsubscript{2}S\textsubscript{2} \([\text{M+H}]^+\) 395.0092, found 395.0085.

\textbf{1,1-Bis(ethylthio)-2-(4-fluorophenyl)-5,5-diphenylpenta-1,4-dien-3-one (1ab)}

Yellow solid. mp 99-100 °C. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 1.11 (t, \(J = 7.5\) Hz, 3H), 1.31 (t, \(J = 7.5\) Hz, 3H), 2.61 (q, \(J = 7.5\) Hz, 2H), 2.91 (q, \(J = 7.5\) Hz, 2H), 6.72 (s, 1H), 6.97 (t, \(J = 8.0\) Hz, 2H), 7.07-7.10 (m, 2H), 7.15 (d, \(J = 8.0\) Hz, 2H), 7.21 (d, \(J = 8.0\) Hz, 2H), 7.28-7.36 (m, 6H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 192.9, 162.2 (d, \(J = 246.5\) Hz, 1C), 153.0, 147.8, 141.4, 138.8, 132.9 (d, \(J = 3.4\) Hz, 1C), 131.3 (d, \(J = 8.1\) Hz, 2C), 129.9 (2C), 129.2, 128.4 (2C), 128.3, 128.2 (3C) 127.9 (2C), 126.2, 114.8 (d, \(J = 21.5\) Hz, 2C), 28.8, 28.3, 14.8, 14.7. HRMS (ESI-TOF) calcd for C\textsubscript{27}H\textsubscript{28}FOS\textsubscript{2} \([\text{M+H}]^+\) 449.1404, found 449.1400.
(E)-1,1-Bis(ethylthio)-2,4,5-triphenylpenta-1,4-dien-3-one (1ac)

Yellow solid. mp 114-115 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.21 (t, $J$ = 7.0 Hz, 3H), 1.26 (t, $J$ = 7.0 Hz, 3H), 2.73 (q, $J$ = 7.0 Hz, 2H), 2.85 (q, $J$ = 7.0 Hz, 2H), 7.01 (d, $J$ = 7.0 Hz, 2H), 7.12-7.20 (m, 5H), 7.25-7.35 (m, 6H), 7.43 (d, $J$ = 7.5 Hz, 2H), 7.67 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 196.0, 148.8, 142.2, 141.0, 136.2, 135.6, 134.6, 133.2, 130.7 (2C), 129.8 (2C), 129.3, 128.9 (2C), 128.5 (2C), 128.2 (2C), 128.1 (2C), 128.0, 127.8, 28.5, 27.7, 14.9, 14.6. HRMS (ESI-TOF) calcd for C$_{27}$H$_{27}$O$_2$S$_2$ + ([M+H]$^+$) 431.1498, found 431.1499.

(E)-5-(Benzo[d][1,3]dioxol-5-yl)-1,1-bis(ethylthio)-2,4-diphenylpenta-1,4-dien-3-one (1ad)

Yellow solid. mp 86-87 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.20 (t, $J$ = 7.0 Hz, 3H), 1.26 (t, $J$ = 7.5 Hz, 3H), 2.72 (q, $J$ = 7.0 Hz, 2H), 2.84 (q, $J$ = 7.5 Hz, 2H), 5.88 (s, 2H), 6.31 (d, $J$ = 1.5 Hz, 1H), 6.64-6.70 (m, 2H), 7.14-7.16 (m, 2H), 7.29-7.37 (m, 6H), 7.41 (t, $J$ = 7.0 Hz, 2H), 7.59 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 195.9, 149.0, 148.8, 147.5, 142.2, 139.1, 136.3, 135.7, 132.8, 129.7 (2C), 128.9 (2C), 128.8, 128.7 (2C), 128.1 (2C), 128.0, 127.9, 127.1, 109.6, 108.2, 101.3, 28.4, 27.6, 14.9, 14.7. HRMS (ESI-TOF) calcd for C$_{29}$H$_{27}$O$_3$S$_2$ + ([M+H]$^+$) 475.1396, found 475.1400.

(E)-5-(4-Chlorophenyl)-1,1-bis(ethylthio)-2,4-diphenylpenta-1,4-dien-3-one (1ae)

Yellow solid. mp 94-95 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.19 (t, $J$ = 7.0 Hz, 3H), 1.25 (t, $J$ = 7.0 Hz, 3H), 2.72 (q, $J$ = 7.0 Hz, 2H), 2.84 (q, $J$ = 7.0 Hz, 2H), 6.95 (d, $J$ = 8.5 Hz, 2H), 7.10-7.14 (m, 4H), 7.30-7.36 (m, 6H), 7.40 (d, $J$ = 7.5 Hz, 2H), 7.60 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 195.8, 148.5, 141.4, 140.4, 136.1, 135.3, 135.2, 133.5, 133.1, 131.8 (2C), 129.7 (2C), 128.9 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 128.1, 128.0, 28.5, 27.7, 14.9, 14.6. HRMS (ESI-TOF) calcd
for C$_{27}$H$_{26}$ClO$_2$S$_2$ ([M+H]$^+$) 465.1114, found 465.1117.

III. Synthetic procedures/analytical data of compounds 2

General procedure for the synthesis of cyclopentenones 2 (taking 2a as an example): To a starting 1a (192 mg, 0.5 mmol) in a dried flask under N$_2$ were added triphenylsilane (262 mg, 1.0 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 0.05 mmol) and anhydrous DMF (5.0 mL) at room temperature. After the reaction mixture was stirred for 0.5 h at room temperature, it was heated to 90°C and stirred for 10 h. After 1a was consumed (monitored by TLC), the reaction mixture was poured into ice water (30 mL), extracted with CH$_2$Cl$_2$ (3 × 15 mL). The combined organic extracts were washed with water (3 × 15 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel chromatography (eluent, petroleum ether/ethyl acetate: 15/1, v/v) to give 2a (148 mg, 92%) as a light yellow crystal.

3-(Ethylthio)-2-(4-methoxyphenyl)-4-phenylcyclopent-2-enone (2a)

![Chemical structure of 3-(Ethylthio)-2-(4-methoxyphenyl)-4-phenylcyclopent-2-enone (2a)]

Light yellow solid. mp 159-160 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.08 (t, $J = 7.5$ Hz, 3H), 2.41 (dd, $J = 2.0$, 18.5 Hz, 1H), 2.47-2.51 (m, 1H), 2.78-2.81 (m, 1H), 3.12 (dd, $J = 7.5$, 18.5 Hz, 1H), 3.84 (s, 3H), 4.35 (t, $J = 6.0$ Hz, 1H), 6.98 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 7.5$ Hz, 2H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 201.8, 172.7, 158.9, 142.0, 137.2, 130.1 (2C), 128.9 (2C), 127.0, 126.5 (2C), 123.2, 113.3 (2C), 54.9, 46.5, 45.8, 24.6, 13.8. HRMS (ESI-TOF) calcd for C$_{20}$H$_{21}$O$_2$S$^+$ ([M+H]$^+$) 325.1257, found 325.1255.

3-(Ethylthio)-2,4-bis(4-methoxyphenyl)cyclopent-2-enone (2b)

![Chemical structure of 3-(Ethylthio)-2,4-bis(4-methoxyphenyl)cyclopent-2-enone (2b)]

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.08 (t, $J = 8.0$ Hz, 3H), 2.37 (d, $J = 18.0$ Hz, 1H), 2.48-2.53 (m, 1H), 2.75-2.80 (m, 1H), 3.09 (dd, $J = 7.5$, 18.0 Hz, 1H), 3.78 (s, 3H), 3.81 (s, 3H),
4.30 (t, J = 7.0 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 202.3, 173.0, 159.2, 158.7, 137.4, 134.2, 130.3 (2C), 127.8 (2C), 123.5, 114.5 (2C), 113.6 (2C), 55.2, 55.1, 46.2, 46.1, 24.8, 14.1. HRMS (ESI-TOF) calcd for C\(_{21}\)H\(_{23}\)O\(_3\)S\(^+\) ([M+H\(^+\)]) 355.1362, found 355.1366.

3-(Ethylthio)-2-(4-methoxyphenyl)-4-p-tolylcyclopent-2-enone (2c)

![3-(Ethylthio)-2-(4-methoxyphenyl)-4-p-tolylcyclopent-2-enone (2c)](image)

Yellow solid. mp 91-92 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.06 (t, J = 7.0 Hz, 3H), 2.33 (s, 3H), 2.37 (dd, J = 2.0, 18.5 Hz, 1H), 2.47-2.51 (m, 1H), 2.76-2.82 (m, 1H), 3.08 (dd, J = 7.5, 18.5 Hz, 1H), 3.81 (s, 3H), 4.29 (dd, J = 2.0, 7.5 Hz, 1H), 6.96-6.98 (m, 2H), 7.12-7.17 (m, 4H), 7.51 (dd, J = 2.0, 7.5 Hz, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 202.1, 172.9, 159.1, 139.2, 137.4, 136.9, 130.3 (2C), 129.8 (2C), 126.6 (2C), 123.5, 113.5 (2C), 55.1, 46.5, 46.1, 24.8, 20.9, 14.0. HRMS (ESI-TOF) calcd for C\(_{21}\)H\(_{23}\)O\(_2\)S\(^+\) ([M+H\(^+\)]) 339.1413, found 339.1417.

4-(Benzo[d][1,3]dioxol-5-yl)-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2d)

![4-(Benzo[d][1,3]dioxol-5-yl)-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2d)](image)

White solid. mp 55-56 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.20 (t, J = 7.0 Hz, 3H), 2.41 (dd, J = 1.5, 18.0 Hz, 1H), 2.55-2.58 (m, 1H), 2.81-2.85 (m, 1H), 3.09 (dd, J = 7.5, 18.0 Hz, 1H), 3.84 (s, 3H), 4.26 (t, J = 7.0 Hz, 1H), 5.98 (d, J = 2.5 Hz, 2H), 6.71-6.75 (m, 2H), 6.80 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 202.0, 172.7, 159.2, 148.3, 146.7, 137.6, 135.9, 130.3 (2C), 123.3, 120.1, 113.6 (2C), 108.7, 106.8, 101.1, 55.2, 46.6, 46.1, 24.9, 14.1. HRMS (ESI-TOF) calcd for C\(_{21}\)H\(_{21}\)O\(_4\)S\(^+\) ([M+H\(^+\)]) 369.1155, found 369.1157.

4-(4-Chlorophenyl)-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2e)

![4-(4-Chlorophenyl)-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2e)](image)
Yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 1.76 (t, *J* = 7.0 Hz, 3H), 2.37 (dd, *J* = 0.5, 18.5 Hz, 1H), 2.45-2.49 (m, 1H), 2.74-2.78 (m, 1H), 3.10 (dd, *J* = 7.5, 18.5 Hz, 1H), 3.81 (s, 3H), 4.30 (d, *J* = 7.0 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.7, 172.0, 159.3, 140.9, 137.9, 133.1, 130.4 (2C), 129.4 (2C), 128.3 (2C), 123.3, 113.7 (2C), 55.2, 46.3, 45.9, 25.0, 14.1. **HRMS** (ESI-TOF) calcd for C₁₉H₂₁ClO₂S⁺ ([M+H⁺]⁺) 359.0867, found 359.0863.

**4-(2-Chlorophenyl)-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2f)**

![Chemical Structure](image)

White solid. mp 99-100 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.11 (t, *J* = 7.5 Hz, 3H), 2.30 (d, *J* = 18.5 Hz, 1H), 2.37-2.41 (m, 1H), 2.73-2.77 (m, 1H), 3.18 (dd, *J* = 7.5, 18.5 Hz, 1H), 3.84 (s, 3H), 4.85 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.5, 171.9, 159.3, 139.9, 137.9, 133.3, 130.3 (2C), 129.6, 128.6, 127.9, 127.7, 127.0, 123.4, 113.7 (2C), 55.2, 44.6, 42.9, 24.8, 14.1. **HRMS** (ESI-TOF) calcd for C₂₀H₂₁ClO₂S⁺ ([M+H⁺]⁺) 359.0869, found 359.0865.

**3-(Ethylthio)-4-(furan-2-yl)-2-(4-methoxyphenyl)cyclopent-2-enone (2g)**

Yellow solid. mp 69-70 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.16 (t, *J* = 7.5 Hz, 3H), 2.61 (dd, *J* = 2.0, 18.0 Hz, 1H), 2.66-2.70 (m, 1H), 2.84-2.88 (m, 1H), 3.01 (dd, *J* = 2.0, 18.0 Hz, 1H), 3.83 (s, 3H), 4.43 (dd, *J* = 2.0, 7.5 Hz, 1H), 6.24 (d, *J* = 3.5 Hz, 1H), 6.36 (dd, *J* = 1.5, 3.0 Hz, 1H), 6.95-6.98 (m, 2H), 7.38 (d, *J* = 1.0 Hz, 1H), 7.44-7.46 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.7, 169.4, 159.3, 154.2, 142.0, 137.6, 130.4 (2C), 123.3, 113.6 (2C), 110.6, 106.2, 55.2, 42.8, 40.3, 24.9, 14.3. **HRMS** (ESI-TOF) calcd for C₁₈H₁₉O₃S⁺ ([M+H⁺]⁺) 315.1049, found 315.1043.

**4-Tert-butyl-3-(ethylthio)-2-(4-methoxyphenyl)cyclopent-2-enone (2h)**
Yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 1.05 (d, J = 10.5 Hz, 12H), 2.45-2.65 (m, 4H), 2.92 (d, J = 12.0 Hz, 1H), 3.82 (s, 3H), 6.92 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.5 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 204.0, 172.0, 159.3, 139.4, 130.7 (2C), 124.1, 113.6 (2C), 55.2, 54.0, 40.8, 35.4, 27.9 (3C), 27.8, 14.0. **HRMS** (ESI-TOF) calcd for C₁₈H₂₅O₂S⁺ ([M+H]⁺) 305.1570, found 305.1578.

3-(Ethylthio)-2-(2-methoxyphenyl)-4-phenyleclopent-2-enone (2i)

Yellow oil. **¹H NMR** (500 MHz, CDCl₃) δ 1.01 (t, J = 7.5 Hz, 3H), 2.40-2.45 (m, 2H), 2.65-2.69 (m, 1H), 3.12 (dd, J = 7.5, 18.0 Hz, 1H), 3.84 (s, 3H), 4.33 (t, J = 6.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.01 (q, J = 8.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.28-7.38 (m, 6H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.8, 174.9, 157.1, 142.3, 136.7, 130.7, 129.8, 129.0, 127.2 (2C), 126.9, 120.6, 120.4 (2C), 111.9, 55.5, 47.7, 45.9, 24.6, 14.1. **HRMS** (ESI-TOF) calcd for C₂₀H₂₁O₂S⁺ ([M+H]⁺) 325.1257, found 325.1251.

4-(Beno[d][1,3]dioxol-5-yl)-3-(ethylthio)-2-(2-methoxyphenyl)cyclopent-2-enone (2j)

White solid. mp 127-128 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.05 (t, J = 7.5 Hz, 3H), 2.38 (dd, J = 1.5, 18.0 Hz, 1H), 2.45-2.52 (m, 1H), 2.67-2.73 (m, 1H), 3.09 (dd, J = 7.5, 18.5 Hz, 1H), 3.84 (s, 3H), 4.27 (t, J = 6.0 Hz, 1H), 5.96 (d, J = 4.5 Hz, 2H), 6.79 (s, 2H), 6.82 (s, 1H), 6.96 (d, J = 8.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.20 (q, J = 7.5 Hz, 1H), 7.34 (m, 1H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.8, 175.0, 157.1, 148.4, 146.7, 136.6, 136.1, 130.7, 129.8, 120.6, 120.5, 120.4, 111.0, 108.5, 107.0, 101.1, 55.5, 47.4, 46.0, 24.6, 14.1. **HRMS** (ESI-TOF) calcd for C₂₁H₂₁O₄S⁺ ([M+H]⁺) 369.1155, found 369.1159.
4-(4-Chlorophenyl)-3-(ethylthio)-2-(2-methoxyphenyl)cyclopent-2-enone (2k)

Yellow oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.02 (t, $J = 7.5$ Hz, 3H), 2.35-2.44 (m, 2H), 2.62-2.69 (m, 1H), 3.11 (dd, $J = 7.5$, 18.0 Hz, 1H), 3.84 (s, 3H), 4.31 (d, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 7.20-7.22 (m, 1H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.34-7.37 (m, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 201.4, 174.3, 157.0, 140.9, 132.9, 130.6, 129.8, 129.5, 129.2 (2C), 128.3 (2C), 120.4, 120.3, 110.1, 55.5, 47.0, 45.7, 24.6, 14.0. HRMS (ESI-TOF) calcd for C$_{20}$H$_{20}$ClO$_2$S$^+$ ([M+H]$^+$) 359.0867, found 359.0861.

2-(4-Chlorophenyl)-3-(ethylthio)-4-phenylcyclopent-2-enone (2l)

Yellow solid. mp 151-152 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.08 (t, $J = 7.5$ Hz, 3H), 2.42 (dd, $J = 2.0$, 18.5 Hz, 1H), 2.47-2.53 (m, 1H), 2.77-2.82 (m, 1H), 3.13 (dd, $J = 2.0$, 18.5 Hz, 1H), 4.36 (dd, $J = 2.0$, 7.5 Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.37-7.34 (m, 4H), 7.50 (dd, $J = 2.0$, 7.5 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 201.5, 174.4, 142.0, 136.8, 133.9, 130.5 (2C), 129.6, 129.3 (2C), 128.5 (2C), 127.5, 126.8 (2C), 47.2, 46.1, 25.1, 14.1. HRMS (ESI-TOF) calcd for C$_{19}$H$_{18}$ClO$_2$S$^+$ ([M+H]$^+$) 329.0761, found 329.0765.

4-(Benzo[d][1,3]dioxol-5-yl)-2-(4-chlorophenyl)-3-(ethylthio)cyclopent-2-enone (2m)

White solid. mp 142-143 °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.12 (t, $J = 7.5$ Hz, 3H), 2.40 (d, $J = 18.5$ Hz, 1H), 2.55-2.59 (m, 1H), 2.81-2.85 (m, 1H), 3.09 (dd, $J = 2.5$, 18.5 Hz, 1H), 4.28 (d, $J = 7.5$ Hz, 1H), 5.98 (s, 2H), 6.69 (s, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 201.4, 174.3, 148.4, 146.9, 136.7, 135.6, 133.8, 130.4 (2C), 129.6, 128.4 (2C), 120.2, 108.8, 106.8, 101.2, 46.8, 46.1, 25.0,
14.1. **HRMS** (ESI-TOF) calcd for C_{20}H_{18}ClO_{3}S^{+} ([M+H]^+) 373.0660, found 373.0664

2,4-Bis(4-chlorophenyl)-3-(ethylthio)cyclopent-2-enone (2n)

![Structure](image)

Yellow solid. mp 97-98 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.09 (t, J = 7.5 Hz, 3H), 2.42 (d, J = 18.5 Hz, 1H), 2.46-2.50 (m, 1H), 2.75-2.80 (m, 1H), 3.11 (dd, J = 7.5, 18.5 Hz, 1H), 4.33 (d, J = 7.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.1, 173.7, 140.4, 137.0, 133.9, 133.2, 130.4 (2C), 128.1 (2C), 129.5, 129.9 (2C), 132.4 (2C), 129.8 (2C), 46.4, 45.8, 25.1, 14.0. **HRMS** (ESI-TOF) calcd for C_{19}H_{17}Cl_{2}O_{3}S⁺ ([M+H]^+) 363.0372, found 363.0378.

2-(4-Chlorophenyl)-3-(ethylthio)-4-(furan-2-yl)cyclopent-2-enone (2o)

![Structure](image)

Yellow solid. mp 70-71°C. **¹H NMR** (500 MHz, CDCl₃) δ 1.17 (t, J = 7.5 Hz, 3H), 2.62 (d, J = 2.0, 18.5 Hz, 1H), 2.67-2.71 (m, 1H), 2.85-2.89 (m, 1H), 3.01 (dd, J = 7.5, 18.5 Hz, 1H), 4.45 (dd, J = 2.0, 7.5 Hz, 1H), 6.24 (d, J = 3.0 Hz, 1H), 6.36-6.37 (m, 1H), 7.39 (q, J = 8.0 Hz, 3H), 7.46 (t, J = 8.0 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.1, 171.1, 153.8, 142.1, 136.8, 133.9, 130.5 (2C), 129.5, 128.4 (2C), 110.7, 106.4, 42.8, 40.6, 25.1, 14.2. **HRMS** (ESI-TOF) calcd for C_{17}H_{16}ClO_{2}S⁺ ([M+H]^+) 319.0554, found 319.0556.

3-(Ethylthio)-2-(4-fluorophenyl)-4-phenylcyclopent-2-enone (2p)

![Structure](image)

White solid. mp 145-146 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.08 (t, J = 7.5 Hz, 3H), 2.42 (dd, J = 2.0, 18.5 Hz, 1H), 2.47-2.51 (m, 1H), 2.78-2.82 (m, 1H), 3.13 (dd, J = 7.5, 18.5 Hz, 1H), 4.36 (dd, J = 2.0, 7.5 Hz, 1H), 7.12-7.16 (m, 2H), 7.25-7.29 (m, 2H), 7.29-7.32 (m, 1H), 7.37-7.39 (m, 2H), 7.39-7.56 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.7, 174.0, 162.2 (d, J = 246.6 Hz, 1C), 142.0,
137.0, 130.9 (d, J = 8.1 Hz, 2C), 129.3 (2C), 127.4, 127.1 (d, J = 3.4 Hz, 1C), 126.8 (2C), 115.2 (d, J = 21.5 Hz, 2C), 47.1, 46.1, 24.9, 14.1. **HRMS (ESI-TOF)** calcd for C_{19}H_{18}FO_{3}S^+ ([M+H]^+) 313.1057, found 313.1058.

**4-(Benzo[d][1,3]dioxol-5-yl)-3-(ethylthio)-2-(4-fluorophenyl)cyclopent-2-enone (2q)**

![Image of 4-(Benzo[d][1,3]dioxol-5-yl)-3-(ethylthio)-2-(4-fluorophenyl)cyclopent-2-enone (2q)]

Yellow solid. mp 146-147 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.12 (t, J = 7.5 Hz, 3H), 2.38 (dd, J = 1.5, 18.5 Hz, 1H), 2.55-2.58 (m, 1H), 2.79-2.84 (m, 1H), 3.08 (dd, J = 7.5, 18.0 Hz, 1H), 4.27 (t, J = 6.5 Hz, 1H), 5.97 (d, J = 1.5 Hz, 2H), 6.49-6.47 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H), 7.51-7.54 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.6, 173.9, 162.2 (d, J = 246.1 Hz, 1C), 148.4, 146.9, 136.9, 135.7, 130.9 (d, J = 8.0 Hz, 2C), 127.1 (d, J = 2.9 Hz, 1C), 120.1, 115.1 (d, J = 21.5 Hz, 2C), 108.8, 106.8, 101.2, 46.8, 46.1, 24.9, 14.1. **HRMS (ESI-TOF)** calcd for C_{20}H_{18}FO_{3}S^+ ([M+H]^+) 357.0955, found 357.0954.

**4-(4-Chlorophenyl)-3-(ethylthio)-2-(4-fluorophenyl)cyclopent-2-enone (2r)**

![Image of 4-(4-Chlorophenyl)-3-(ethylthio)-2-(4-fluorophenyl)cyclopent-2-enone (2r)]

Yellow solid. mp 136-137 °C. **¹H NMR** (500 MHz, CDCl₃) δ 1.10 (t, J = 7.5 Hz, 3H), 2.38 (dd, J = 1.5, 18.5 Hz, 1H), 2.46-2.50 (m, 1H), 2.76-2.80 (m, 1H), 3.11 (dd, J = 7.5, 18.5 Hz, 1H), 4.33 (dd, J = 1.5, 7.5 Hz, 1H), 7.11-7.15 (m, 2H), 7.20 (t, J = 7.0 Hz, 2H), 7.36 (t, J = 7.0 Hz, 2H), 7.52-7.54 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 201.3, 173.2, 162.3 (d, J = 247.0 Hz, 1C), 140.5, 137.2, 133.2, 130.9 (d, J = 8.1 Hz, 2C), 129.5 (2C), 128.2 (2C), 126.9 (d, J = 3.4 Hz, 1C), 115.2 (d, J = 21.5 Hz, 2C), 46.4, 45.8, 25.0, 14.0. **HRMS (ESI-TOF)** calcd for C_{19}H_{17}ClFO_{3}S^+ ([M+H]^+) 347.0667, found 367.0664.

**3-(Ethylthio)-2-(4-fluorophenyl)-4-(furan-2-yl)cyclopent-2-enone (2s)**
Yellow solid. mp 99-100 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 1.17 (t, $J = 7.5$ Hz, 3H), 2.64 (dd, $J = 2.0$, 18.0 Hz, 1H), 2.67-2.71 (m, 1H), 2.85-2.89 (m, 1H), 3.02 (dd, $J = 7.5$, 18.0 Hz, 1H), 3.45 (dd, $J = 2.0$, 7.5 Hz, 1H), 6.24 (d, $J = 3.0$ Hz, 1H), 6.36-6.37 (m, 1H), 7.12 (t, $J = 9.0$ Hz, 2H), 7.38 (d, $J = 1.0$ Hz, 1H), 7.47-7.50 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 201.2, 170.7, 162.3 (d, $J = 246.5$ Hz, 1C), 153.9, 142.1, 136.9, 131.0 (d, $J = 8.1$ Hz, 2C), 127.0, 115.2 (d, $J = 21.5$ Hz, 2C), 110.6, 106.3, 42.8, 40.5, 24.9, 14.2. HRMS (ESI-TOF) calcd for C$_{17}$H$_{16}$FO$_2$S$^+$ ([M+H]$^+$) 303.0850, found 303.0859.

2-(4-Chlorophenyl)-3-(methylthio)-4-phenylcyclopent-2-enone (2t)

Yellow solid. mp 55-56°C. $^1$H NMR (500 MHz, CDCl$_3$) δ 2.11 (s, 3H), 2.41 (dd, $J = 1.5$, 18.5 Hz, 1H), 3.13 (dd, $J = 7.5$, 18.5 Hz, 1H), 4.37 (dd, $J = 1.5$, 7.5 Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.35-7.41 (m, 4H), 7.51 (d, $J = 7.5$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 201.5, 174.8, 141.6, 136.8, 133.8, 130.3 (2C), 129.5, 129.3 (2C), 128.4 (2C), 127.5, 126.7 (2C), 46.8, 46.1, 13.9. HRMS (ESI-TOF) calcd for C$_{18}$H$_{16}$ClO$_2$S$^+$ ([M+H]$^+$) 315.0605, found 315.0609.

2,4-Bis(4-chlorophenyl)-3-(methylthio)cyclopent-2-enone (2u)

White solid. mp 152-153 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 2.11 (s, 3H), 2.36 (d, $J = 18.5$ Hz, 1H), 3.11 (dd, $J = 2.5$, 18.5 Hz, 1H), 4.34 (d, $J = 7.0$ Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.9, 173.9, 140.2, 137.1, 133.9, 133.3, 130.3 (2C), 129.5 (2C), 129.3, 128.4 (2C), 128.1 (2C), 46.1, 45.9, 13.9. HRMS (ESI-TOF) calcd for C$_{18}$H$_{15}$Cl$_2$OS$^+$ ([M+H]$^+$) 349.0215, found 349.0213.

2-Methyl-3-(methylthio)-4-phenylcyclopent-2-enone (2v)
4-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-3-(methylthio)cyclopent-2-enone (2w)

Light yellow solid. mp 79-80 °C. 

$^1$H NMR (500 MHz, CDCl$_3$) δ 1.85 (s, 3H), 2.11 (s, 3H), 2.25 (dd, $J = 2.0$, 18.5 Hz, 1H), 2.98 (dd, $J = 7.5$, 18.5 Hz, 1H), 4.24-4.26 (m, 1H), 7.17 (q, $J = 7.0$ Hz, 2H), 7.25-7.33 (m, 1H), 7.32-7.35 (m, 2H). 

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 203.3, 172.4, 142.0, 135.6, 129.1 (2C), 127.3, 126.8 (2C), 46.9, 45.8, 13.4, 8.7. HRMS (ESI-TOF) calcd for C$_{13}$H$_{15}$OS$^+$ ([M+H]$^+$) 219.0838, found 219.0837.

2-Butyl-3-(methylthio)-4-phenylcyclopent-2-enone (2x)

Light yellow oil. 

$^1$H NMR (500 MHz, CDCl$_3$) δ 0.95 (s, $J = 7.0$ Hz, 3H), 1.26-1.43 (m, 2H), 1.49 (q, $J = 7.5$ Hz, 2H), 2.09 (s, 3H), 2.23-2.31 (m, 2H), 2.35-2.40 (m, 1H), 2.96 (dd, $J = 7.0$, 18.0 Hz, 1H), 4.24 (d, $J = 7.0$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.5$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 2H). 

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 203.1, 172.2, 142.1, 140.4, 129.2 (2C), 127.2, 126.7 (2C), 46.7, 45.9, 29.3, 23.6, 22.8, 13.9, 13.3. HRMS (ESI-TOF) calcd for C$_{16}$H$_{21}$OS$^+$ ([M+H]$^+$) 261.1308, found 261.1304.

2-Benzoyl-4-(4-chlorophenyl)-3-(ethylthio)cyclopent-2-enone (2y)
Yellow solid. mp 142-143 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.10 (t, \(J = 7.0\) Hz, 3H), 2.45 (dd, \(J = 2.0, 18.5\) Hz, 1H), 2.52-2.56 (m, 1H), 2.75-2.79 (m, 1H), 3.16 (dd, \(J = 8.0, 18.0\) Hz, 1H), 4.39 (dd, \(J = 2.0, 8.0\) Hz, 1H), 7.21 (dd, \(J = 7.0, 6.5\) Hz, 2H), 7.36-7.39 (m, 2H), 7.49 (t, \(J = 7.5\) Hz, 2H), 7.59 (dd, \(J = 2.0, 8.0\) Hz, 1H), 7.85 (dd, \(J = 2.0, 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 199.3, 192.0, 184.1, 139.7, 136.9, 136.6, 133.7, 133.6, 129.6 (2C), 129.5 (2C), 128.5 (2C), 128.4 (2C), 48.0, 46.2, 26.2, 13.5. HRMS (ESI-TOF) calcd for C\(_{20}\)H\(_{18}\)ClO\(_2\)S\(^+\) ([M+H\(^+\)]) 357.0711, found 357.0719.

\(\text{4-(4-Chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-1-(4-methoxyphenyl)butan-2-one(2aa')}\)

Yellowish liquid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.49 (t, \(J = 7.5\) Hz, 2H), 2.84 (t, \(J = 7.5\) Hz, 2H), 3.21 (t, \(J = 7.0\) Hz, 2H), 3.46 (t, \(J = 7.0\) Hz, 2H), 3.84 (s, 3H), 6.92 (d, \(J = 8.5\) Hz, 2H), 6.98 (d, \(J = 8.5\) Hz, 2H), 7.09 (d, \(J = 8.5\) Hz, 2H), 7.16 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 194.7, 159.3, 143.4, 140.1, 132.1, 131.5, 130.9 (2C), 129.8 (2C), 128.3 (2C), 126.0, 114.4 (2C), 55.2, 41.9, 39.8, 33.5, 29.8. HRMS (ESI-TOF) calcd for C\(_{20}\)H\(_{20}\)ClO\(_2\)S\(_2\)\(^+\) ([M+H\(^+\)]) 391.0588, found 391.0585.

\(\text{5-(Ethylthio)-4-(4-fluorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (2'ab)}\)

Light yellow solid. mp 128-129 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.32 (t, \(J = 7.5\) Hz, 3H), 2.79 (q, \(J = 7.5\) Hz, 2H), 6.66 (s, 1H), 7.05-7.13 (m, 4H), 7.20-7.22 (m, 2H), 7.29-7.31 (m, 2H), 7.35-7.40 (m, 6H), 7.78(s, 1H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 189.5, 162.1 (d, \(J = 246.0\) Hz, 1C), 152.1, 148.5, 141.0, 139.1, 146.4, 134.9, 131.2 (d, \(J = 8.1\) Hz, 2C), 129.6 (2C), 129.0, 128.4 (2C), 128.3
(2C), 128.2 (2C), 127.8, 124.8, 115.2 (d, \( J = 21.5 \) Hz, 2C), 29.0, 15.4. \textbf{HRMS} (ESI-TOF) calcd for C\textsubscript{25}H\textsubscript{22}FOS\textsuperscript{+} ([M+H]\textsuperscript{+}) 389.1370, found 389.1374.

\textbf{3-(Ethylthio)-2,4,5-triphenylcyclopent-2-enone(2ac)}

Light yellow liquid. \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \( \delta \) 1.06 (t, \( J = 7.5 \) Hz, 3H), 2.44-2.48 (m, 1H), 2.75-2.79 (m, 1H), 3.55 (d, \( J = 2.0 \) Hz, 1H), 4.31 (d, \( J = 2.0 \) Hz, 1H), 7.17 (d, \( J = 7.5 \) Hz, 2H), 7.24-7.39 (m, 9H), 7.44 (d, \( J = 7.5 \) Hz, 2H). \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \( \delta \) 201.1, 173.3, 141.4, 139.6, 137.6, 131.2, 129.4 (2C), 129.2 (2C), 129.0 (2C), 128.7, 128.2 (2C), 127.6, 127.5 (2C), 127.2, 126.9 (2C), 63.2, 57.4, 25.1, 14.1. \textbf{HRMS} (ESI-TOF) calcd for C\textsubscript{25}H\textsubscript{23}OS\textsuperscript{+} ([M+H]\textsuperscript{+}) 371.1464, found 371.1460.

\textbf{4-(Benzo[d][1,3]dioxol-5-yl)-3-(ethylthio)-2,5-diphenylcyclopent-2-enone(2ad)}

Yellow solid. mp 149-150 °C. \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \( \delta \) 1.11 (t, \( J = 7.5 \) Hz, 3H), 2.53-2.57 (m, 1H), 2.79-2.83 (m, 1H), 3.52 (d, \( J = 2.0 \) Hz, 1H), 4.22 (d, \( J = 2.0 \) Hz, 1H), 5.98 (d, \( J = 2.0 \) Hz, 2H), 6.70 (t, \( J = 1.5 \) Hz, 2H), 6.80 (d, \( J = 8.0 \) Hz, 1H), 7.17 (d, \( J = 7.0 \) Hz, 2H), 7.24-7.37 (m, 4H), 7.45 (t, \( J = 8.0 \) Hz, 2H), 7.59 (t, \( J = 7.0 \) Hz, 2H). \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \( \delta \) 201.1, 173.2, 148.5, 147.1, 139.6, 137.6, 135.2, 131.2, 129.2 (2C), 129.0 (2C), 128.2 (3C), 127.5 (2C), 127.2, 120.3, 108.9, 106.9, 101.2, 63.2, 57.2, 25.1, 14.2. \textbf{HRMS} (ESI-TOF) calcd for C\textsubscript{26}H\textsubscript{23}O\textsubscript{3}S\textsuperscript{+} ([M+H]\textsuperscript{+}) 415.1362, found 415.1362.

\textbf{4-(4-Chlorophenyl)-3-(ethylthio)-2,5-diphenylcyclopent-2-enone(2ae)}
Light yellow liquid. \(^1\text{H} \text{NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 1.09 (t, \(J = 7.5\) Hz, 3H), 2.44-2.48 (m, 1H), 2.74-2.78 (m, 1H), 3.50 (d, \(J = 2.0\) Hz, 1H), 4.28 (d, \(J = 2.0\) Hz, 1H), 7.16 (d, \(J = 7.5\) Hz, 2H), 7.19 (d, \(J = 8.0\) Hz, 2H), 7.29 (t, \(J = 7.5\) Hz, 1H), 7.34-7.38 (m, 5H), 7.45 (d, \(J = 7.5\) Hz, 2H), 7.59 (d, \(J = 7.5\) Hz, 2H). \(^1\text{C} \text{NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 200.8, 172.5, 139.9, 139.3, 137.9, 133.4, 131.0, 129.6 (2C), 129.2 (2C), 129.1 (2C), 128.3, 128.3 (2C), 128.2 (2C), 127.5 (2C), 127.4, 63.1, 56.8, 25.2, 14.1. \text{HRMS} \text{ (ESI-TOF)} \text{calcd for C}_{25}\text{H}_{22}\text{ClOS}^{+} ([M+H]^{+}) 405.1074, \text{found} 405.1078.

IV. Crystal data and ORTEP drawing of compound 2a

\text{Crystal data for 2a: C}_{20}\text{H}_{20}\text{O}_{2}\text{S}, \text{colorless,} M = 324.42, \text{monoclinic,} \text{space group} P21/c, a = 19.0155(8) Å, b = 8.2100(3) Å, c = 11.6450(5) Å, \(V\) = 1735.83(12) Å\(^3\), \(\alpha = 90.00, \beta = 107.291(4), \gamma = 90.00, Z = 4, T = 293(2) K, F000 = 688, 6642 \text{reflections collected,} 3048 \text{unique with} R(\text{int}) = 0.0206, R1 = 0.0427, wR2 = 0.1047 (I > 2\sigma(I)). \text{CCDC 901005 (2a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via} \text{www.ccdc.cam.uk/data_request/cif.}

Fig. ORTEP diagram of 2a.

V. References

8 Y. Zhao, S. Yang, C. Di, X. Han, Q. Liu, *Chem. Commun.*, 2010, **46**, 7614.
VI. Copies of $^1$H NMR and $^{13}$C NMR spectra of compounds 1', 1 and 2
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