Electronic Supplementary Information


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I. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by column chromatography on flash silica gel (300–400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 500 spectrometer (500 MHz for $^1$H NMR; 125 MHz for $^{13}$C NMR) and a Mercury Plus 400 spectrometer (400 MHz for $^1$H NMR), with TMS as the internal standard. All shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

II. Typical Procedures and Analytical Data for 3, 3’ and 7

General procedure (taking 3aa as an example):

To a solution of $2a$ (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1$E$,6$E$)-1,7-bis(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) in DMSO (5.0 mL) was added K$_2$CO$_3$ (17.3 mg, 0.125 mmol) at room temperature. After 1a was consumed as indicated by TLC, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, evaporated in vacuo, and the residue was purified by column chromatography (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V) to give 3aa (283 mg, 95 %, 0.475 mmol) as a yellowish solid. Reaction time 8.5 h.

3aa, yellowish solid, m.p. 148–150 °C.

$^1$H NMR (500 MHz, DMSO): $\delta$ 3.00–3.04 (m, 1H), 3.07–3.14 (m, 2H), 3.20–3.24 (m, 2H), 3.32
(dd, J = 11.0, 3.5 Hz, 1H), 4.16 (d, J = 3.5 Hz, 1H), 4.39 (dd, J = 6.0, 3.5 Hz, 1H), 4.48 (d, J = 3.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.36 (m, 4H), 7.44 (m, 4H), 7.78 (s, 1H). ^{13}C NMR (125 MHz, DMSO): δ 36.8, 36.9, 48.1, 58.6, 60.3, 68.3, 112.6, 127.6, 128.2, 128.9, 129.3(2C), 129.4, 130.2, 131.1, 132.5, 132.7, 138.6, 143.0, 145.3, 163.2, 179.4, 179.8, 192.5. HRMS (ESI-TOF) Calcd for C_{30}H_{23}Cl_{3}NO_{2}S_{2}^{+} ([M+H]^+) 598.0230. Found 598.0156.

3aa', yellowish solid, m.p. 153–155 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.05–3.22 (m, 5H), 3.43 (dd, J = 12.4, 2.4 Hz, 1H), 4.04 (d, J = 4.8 Hz, 1H), 4.43 (d, J = 4.0 Hz, 1H), 4.50 (d, J = 4.0 Hz, 1H), 4.90 (s, 1H), 7.00 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.22–7.31 (m, 8H). ^{13}C NMR (125 MHz, DMSO): δ 36.8, 36.9, 48.1, 58.4, 60.3, 67.7, 112.6, 127.5, 127.9, 128.8, 129.1, 129.2, 130.0, 131.0, 131.2, 132.4, 132.5, 137.7, 143.0, 145.3, 163.3, 179.4, 180.3, 192.0. HRMS (ESI-TOF) Calcd for C_{30}H_{23}Cl_{3}NO_{2}S_{2}^{+} ([M+H]^+) 598.0230. Found 598.0162.

3ba, 3ba', 3ba/3ba'=1.5/1.0. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1,7-bis(3-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1b (223 mg, 0.5 mmol) gave 3ba, 3ba' (239 mg, 80 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 12.0 h.

3ba, yellowish solid, m.p. 141–143 °C.

$^1$H NMR (500 MHz, DMSO): δ 2.98–3.06 (m, 1H), 3.07–3.18 (m, 2H), 3.18–3.27 (m, 2H), 3.29–3.33 (m, 1H), 4.15 (d, J = 3.5 Hz, 1H), 4.40 (dd, J = 7.5, 2.5 Hz, 1H), 4.54 (d, J = 3.5 Hz, 1H), 7.23 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.34–7.38 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.90 (s, 1H). ^{13}C NMR (125 MHz, DMSO): δ 36.8, 36.9, 47.9, 58.4, 67.5, 68.0, 112.6, 126.1, 126.8, 127.2, 127.6, 127.9, 128.2, 128.5, 129.2 (2C), 130.9, 131.0, 132.6, 133.5, 133.7, 141.2, 142.9, 148.8, 163.2, 179.6, 180.2, 192.0. HRMS (ESI-TOF) Calcd for
C₃₀H₂₃Cl₃NO₂S₂⁺ ([M+H]⁺) 598.0230. Found 598.0216.

3ba’, yellowish solid, m.p. 146–148 °C.

¹H NMR (500 MHz, DMSO): δ 2.88–2.94 (m, 1H), 2.95–3.01 (m, 2H), 3.23–3.30 (m, 2H), 3.62 (dd, J = 13.5, 3.5 Hz, 1H), 4.18 (d, J = 3.5 Hz, 1H), 4.37 (dd, J = 5.0, 3.5 Hz, 1H), 4.58 (d, J = 3.5 Hz, 1H), 7.16–7.19 (m, 3H), 7.29–7.33 (m, 3H), 7.36–7.39 (m, 6H), 8.28 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 36.8, 36.9, 40.6, 47.9, 58.4, 67.5, 112.6, 126.1, 126.8, 127.2, 127.6, 127.8, 127.9, 128.5, 128.6, 129.2, 130.9, 131.0, 132.6, 133.6, 133.7, 141.2, 142.9, 148.8, 163.2, 179.6, 180.2, 192.0. HRMS (ESI-TOF) Calcd for C₃₀H₂₃Cl₃NO₂S₂⁺ ([M+H]⁺) 598.0230. Found 598.0255.

3ca, yellowish solid, m.p. 154–156 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1,7-bis(2-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1c (223 mg, 0.5 mmol) gave 3ca (254 mg, 85 %) after purification by column chromatography on silica gel (Et₃N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 16.0 h.

¹H NMR (500 MHz, DMSO): δ 2.80–3.08 (m, 3H), 3.19–3.44 (m, 2H), 3.78 (d, J = 11.2 Hz, 1H), 4.44 (s, 1H), 4.60 (m, 1H), 4.71 (s, 1H), 7.12–7.16 (m, 1H), 7.25–7.35 (m, 6H), 7.39 (d, J = 8.5 Hz, 2H), 7.46–7.48 (m, 2H), 7.53–7.55 (m, 1H), 8.36 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 36.8, 38.6, 40.4, 45.3, 60.3, 67.2, 112.7, 127.3, 128.1, 128.4, 129.1, 129.2, 129.9 (2C), 130.4, 132.6, 132.8, 133.5, 135.6, 142.9, 163.1, 179.3, 180.2, 191.9. HRMS (ESI-TOF) Calcd for C₃₀H₂₃Cl₃NO₂S₂⁺ ([M+H]⁺) 598.0230. Found 598.0231.

3da, yellowish solid, m.p. 198–200 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1,7-bis(4-bromophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1d (268 mg, 0.5 mmol) gave 3da (319 mg, 93 %) after purification by column chromatography on silica gel (Et₃N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 8.0 h.

¹H NMR (500 MHz, DMSO): δ 3.01–3.04 (m, 1H), 3.07–3.14 (m, 2H), 3.19–3.24 (m, 2H), 3.33
(d, J = 12.5 Hz, 1H), 4.16 (s, 1H), 4.38 (d, J = 4.5 Hz, 1H), 4.49 (s, 1H), 7.21 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.80 (s, 1H). 13C NMR (125 MHz, DMSO): δ 36.8 (2C), 40.3, 48.0, 58.7, 68.2, 112.5, 119.6, 121.1, 127.5, 128.1, 129.2, 129.7, 130.6, 131.8, 132.2, 132.7, 139.0, 142.9, 145.7, 163.1, 179.4, 179.7, 192.4. HRMS (ESI-TOF) Calcd for C30H23Br2ClNO2S2+ ([M+H]+) 685.9220. Found 685.9216.

3ea, yellowish solid, m.p. 135–137 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-4-(1,3-dithiolan-2-ylidene)-1,7-diphenylhepta-1,6-diene-3,5-dione 1e (189 mg, 0.5 mmol) gave 3ea (254 mg, 96 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 10.0 h. 1H NMR (500 MHz, CDCl3): δ 3.05–3.11 (m, 2H), 3.16 (dd, J = 11.5, 5.0 Hz, 1H), 3.23–3.34 (m, 2H), 3.72 (t, J = 12.5 Hz, 1H), 4.13 (d, J = 12.5 Hz, 1H), 4.40 (d, J = 4.5 Hz, 1H), 4.44 (s, 1H), 4.47 (m, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.32–7.40 (m, 6H), 7.38 (t, J = 7.5 Hz, 2H). 13C NMR (125 MHz, DMSO): δ 37.0 (2C), 41.3, 48.5, 59.4, 68.8, 112.9, 127.0, 127.6, 128.0, 128.2, 128.3, 128.5, 129.2, 129.4, 129.5, 132.8, 139.8, 143.5, 146.7, 163.8, 179.3, 180.2, 193.0. HRMS (ESI-TOF) Calcd for C30H25ClNO2S2+ ([M+H]+) 530.1010. Found 530.1000.

3fa, yellowish solid, m.p. 117–119 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-4-(1,3-dithiolan-2-ylidene)-1,7-di-p-tolylhepta-1,6-diene-3,5-dione 1f (203 mg, 0.5 mmol) gave 3fa (251 mg, 90 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 13.0 h. 1H NMR (500 MHz, DMSO): δ 2.28 (s, 3H), 2.29 (s, 3H), 2.96–3.05 (m, 2H), 3.08 (dd, J = 11.0, 5.0 Hz, 1H), 3.11–3.16 (m, 2H), 3.22 (dd, J = 10.5, 5.0 Hz, 1H), 4.10 (d, J = 3.5 Hz, 1H), 4.29 (d, J = 6.5 Hz, 1H), 4.41 (d, J = 3.5 Hz, 1H), 7.12 (s, 4H), 7.17 (d, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 7.32 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H), 7.80 (s, 1H). 13C NMR (125 MHz, DMSO): δ 37.0 (2C), 41.3, 48.5, 59.4, 68.8, 112.9, 127.0, 127.6, 128.0, 128.2, 128.3, 128.5, 129.2, 129.4, 129.5, 132.8, 139.8, 143.5, 146.7, 163.8, 179.3, 180.2, 193.0. HRMS (ESI-TOF) Calcd for C30H25ClNO2S2+ ([M+H]+) 530.1010. Found 530.1000.
Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.67 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 25.8, 25.9, 36.8 (2C), 43.1, 47.9, 51.5, 71.3, 113.6, 127.7, 128.6, 128.7, 128.9, 129.0, 129.1, 129.3, 129.9, 130.3, 130.6, 132.1, 138.0, 146.7, 163.2, 179.0, 179.4, 192.1. HRMS (ESI-TOF) Calcd for C$_{32}$H$_{29}$ClNO$_2$S$_2$ $^{+}$ ([M+H]$^{+}$) 558.1323. Found 558.1410.

3ga, yellowish solid, m.p. 146–148 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetophenone (1.2 equiv, 107 mg) and (1E,6E)-4-(1,3-dithiolan-2-ylidene)-1,7-bis(4-methoxyphenyl)hepta-1,6-diene-3,5-dione 1g (219 mg, 0.5 mmol) gave 3ga (268 mg, 91 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 24.0 h.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.95–3.01 (m, 1H), 3.02–3.06 (m, 2H), 3.09–3.16 (m, 2H), 3.39 (d, $J$ = 12.0 Hz, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 3.96 (d, $J$ = 5.5 Hz, 1H), 4.37 (d, $J$ = 2.5 Hz, 1H), 4.47 (s, 1H), 5.18 (s, 1H), 6.81 (d, $J$ = 8.0 Hz, 2H), 6.85 (d, $J$ = 8.0 Hz, 2H), 6.99 (d, $J$ = 8.0 Hz, 2H), 7.09 (d, $J$ = 8.0 Hz, 2H), 7.18–7.25 (m, 4H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 36.7, 37.6, 48.5, 55.5 (2C), 55.8, 58.4, 68.6, 112.6, 114.2, 114.6, 115.0, 124.2, 127.5, 128.0, 128.3, 129.1, 129.4, 130.8, 131.6, 138.7, 143.3, 161.8, 178.6, 179.8, 192.7. HRMS (ESI-TOF) Calcd for C$_{32}$H$_{29}$ClNO$_4$S$_2$ $^{+}$ ([M+H]$^{+}$) 590.1221. Found 590.1239.

3ha, yellowish solid, m.p. 146–148 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetophenone (1.2 equiv, 107 mg) and (1E,6E)-4-(1,3-dithiolan-2-ylidene)-1,7-di(thiophen-2-yl)hepta-1,6-diene-3,5-dione 1h (195 mg, 0.5 mmol) gave 3ha (243 mg, 90 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 13.0 h.

$^1$H NMR (500 MHz, DMSO): $\delta$ 2.97–3.02 (m, 1H), 3.08–3.13 (m, 2H), 3.17–3.21 (m, 1H), 3.25–3.30 (m, 1H), 3.42 (d, $J$ = 13.0, 2.0 Hz, 1H), 4.42 (d, $J$ = 3.0 Hz, 1H), 4.57 (d, $J$ = 3.5 Hz, 1H), 4.66 (dd, $J$ = 7.0, 3.0 Hz, 1H), 6.94–6.96 (m, 2H), 6.98–7.00 (m, 1H), 7.03 (d, $J$ = 3.5 Hz, 1H), 7.32 (d, $J$ = 4.0 Hz, 1H), 7.37 (d, $J$ = 8.5 Hz, 2H), 7.45–7.48 (m, 3H), 8.06 (s, 1H). $^{13}$C NMR
δ 36.4, 36.5, 46.4, 60.4, 63.6, 65.7, 111.4, 123.6, 124.1, 126.2, 126.6, 127.4, 128.2, 129.3, 129.4, 132.2, 132.9, 141.7, 142.6, 150.7, 162.9, 180.0, 180.1, 191.9.

HRMS (ESI-TOF) Calcd for C_{26}H_{21}ClNO_{2}S_{4}^{+} ([M+H]^{+}) 542.0138. Found 542.0145.

3ia, 3ia', yellowish solid, m.p. 174–176 °C, 3ia/3ia'=3.3/1.0. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-4-(1,3-dithiolan-2-ylidene)-1,7-di(pyridin-3-yl)hepta-1,6-diene-3,5-dione 1i (190 mg, 0.5 mmol) gave 3ia, 3ia' (210 mg, 79 %) after purification by column chromatography on silica gel (Et_{3}N/EtOAc/PE = 0.05/1/4, V/V/V). Reaction time 15.0 h.

δ 3.00–3.05 (m, 1H), 3.06–3.18 (m, 2H), 3.20–3.26 (m, 2H), 3.38 (d, J = 2.0 Hz, 1H), 4.21 (d, J = 4.0 Hz, 1H), 4.45 (d, J = 5.0 Hz, 1H), 4.59 (d, J = 4.5 Hz, 1H), 7.33–7.38 (m, 3Η), 7.42 (dd, J = 7.5, 4.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 8.42–8.45 (m, 2H), 8.50 (dd, J = 5.0, 1.5 Hz, 1H), 8.57 (s, 1H).

3ia', 1H NMR (500 MHz, DMSO): δ 3.08–3.11 (m, 1H), 3.13–3.17 (m, 1H), 3.20–3.27 (m, 2H), 3.37–3.39 (m, 2H), 4.20 (d, J = 4.0 Hz, 1H), 4.49 (d, J = 5.5 Hz, 1H), 4.59 (d, J = 4.0 Hz, 1H), 7.35–7.37 (m, 3Η), 7.42 (dd, J = 7.5, 5.0 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 7.5 Hz, 1H), 8.07 (s, 1H), 8.41–8.46 (m, 2H), 8.50 (d, J = 4.0 Hz, 1H), 8.56 (s, 1H).

3ia, 3ia', 13C NMR (125 MHz, DMSO): δ 36.8, 36.9, 38.5, 38.6, 40.3, 40.4, 47.8, 47.9, 56.4, 56.8, 67.4, 68.0, 112.4, 112.5, 124.2 (2C), 124.3, 127.5 (2C), 127.9, 128.3, 129.2, 129.3, 132.6, 132.7, 134.5, 134.7, 134.8, 134.9 (2C), 135.3 (2C), 135.7, 135.8, 141.4, 141.5, 142.7, 142.8, 148.0, 148.1, 149.1, 149.2, 149.5, 149.6, 162.8, 163.0, 179.5 (2C), 179.9, 180.7, 192.0, 192.2. HRMS (ESI-TOF) Calcd for C_{28}H_{23}ClN_{3}O_{2}S_{2}^{+} ([M+H]^{+}) 532.0915. Found 532.0913.

3ja, 3ja', yellowish solid, m.p. 204–206 °C, 3ja/3ja'=1.2/1.0. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg), (3E,8E)-6-(1,3-dithiolan-2-ylidene)-2,2,10,10-tetramethylundeca-3,8-diene-5,7-dione 1j (169 mg, 0.5 mmol) and DBU (2.0 equiv, 0.159 mL) gave 3ja, 3ja' (218 mg, 89 %) after
puriﬁcation by column chromatography on silica gel (Et₃N/EtOAc/PE = 0.05/1/4, V/V/V). Reaction time 24.0 h.

¹H NMR (500 MHz, DMSO): δ 0.90 (d, J = 21.5 Hz, 1H), 0.95 (d, J = 14.0 Hz, 1H), 2.66 (t, J = 3.5 Hz, 1H), 2.84–2.93 (m, 4H), 2.95 (d, J = 10.0 Hz, 2H), 3.05 (dd, J = 13.5, 3.5 Hz, 1H), 3.09–3.17 (m, 4H), 3.19–3.31 (m, 4H), 4.47 (s, 1H), 4.56 (s, 1H), 7.25–7.29 (m, 4H), 7.40–7.43 (m, 4H), 7.79 (s, 1H), 7.81 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 27.5, 28.2, 28.9, 29.5, 34.7, 35.2, 36.0, 36.1, 36.8, 36.9, 37.4, 37.8, 44.0, 45.2, 46.2, 46.5, 60.3, 60.5, 61.5, 61.7, 110.0, 110.1, 127.7, 127.9, 128.4, 129.1, 129.2, 130.0, 131.2 (2C), 144.0, 144.2, 164.8, 165.0, 176.7, 179.8, 180.8, 181.9, 193.1, 194.0. HRMS (ESI-TOF) Calcd for C₂₆H₃₃ClNO₂S₂⁺ ([M+H]⁺) 490.1636. Found 490.1652.

3ka, yellowish solid, m.p. 156–158 °C.
3ka’, yellowish solid, m.p. 146–148 °C, 3ka/3ka’=9.0/1.0.

Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-7-(4-methoxyphenyl)hepta-1,6-diene-3,5-dione 1k (221 mg, 0.5 mmol) gave 3ka, 3ka’ (264 mg, 89 %) after puriﬁcation by column chromatography on silica gel (Et₃N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 13.0 h.

3ka, ¹H NMR (500 MHz, DMSO): δ 3.01–3.04 (m, 1H), 3.07–3.15 (m, 2H), 3.17–3.32 (m, 2H), 3.30 (dd, J = 12.5, 2.0 Hz, 1H), 3.74 (s, 3H), 4.10 (d, J = 3.5 Hz, 1H), 4.39 (dd, J = 5.0, 3.0 Hz, 1H), 4.43 (d, J = 3.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.43–7.47 (m, 4H), 7.70 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 36.8 (2C), 48.1, 55.5, 55.6, 58.4, 68.7, 113.0, 114.3, 127.7, 128.0, 128.3, 129.2 (2C), 129.3, 130.2, 132.5, 138.6, 138.8, 143.3, 158.1, 162.7, 179.0, 179.8, 192.5. HRMS (ESI-TOF) Calcd for C₃₁H₂₆Cl₂NO₃S₂⁺ ([M+H]⁺) 594.0726. Found 594.0718.

3ka’, ¹H NMR (500 MHz, DMSO): δ 2.87–3.01 (m, 3H), 3.22–3.31 (m, 2H), 3.61 (dd, J = 13.0, 3.0 Hz, 1H), 3.74 (s, 3H), 4.11 (d, J = 3.5 Hz, 1H), 4.33 (dd, J = 5.0, 3.5 Hz, 1H), 4.49 (d, J = 3.0 Hz, 1H), 6.90 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.22–7.29 (m, 4H), 7.39 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 8.16 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 36.8, 36.9, 40.9, 48.2, 55.5, 58.3, 68.2, 113.0, 114.3, 127.7, 127.8, 128.3, 129.2 (2C), 130.2, 132.4 (2C), 137.8, 138.6, 143.4, 158.3, 163.0, 179.5, 180.2, 192.0. HRMS (ESI-TOF) Calcd for C₃₁H₂₆Cl₂NO₃S₂⁺ ([M+H]⁺) 594.0726. Found 594.0727.
3la, yellowish solid, m.p. 168–170 °C.
3la', yellowish solid, m.p. 158–160 °C, 3la/3la' = 5.4/1.0.

Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-7-(1-methyl-1H-indol-3-yl)hepta-1,6-diene-3,5-dione 11 (233 mg, 0.5 mmol) gave 3la, 3la' (286 mg, 93 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/4, V/V/V). Reaction time 8.0 h.

3la, 1H NMR (500 MHz, DMSO): δ 3.05–3.13 (m, 3H), 3.17–3.25 (m, 2H), 3.29 (d, $J = 8.5$ Hz, 1H), 3.75 (s, 3H), 4.41 (m, 2H), 4.50 (s, 1H), 6.98 (d, $J = 7.5$ Hz, 1H), 7.11 (s, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.34–7.45 (m, 10H), 7.66 (s, 1H).

3la', 1H NMR (500 MHz, DMSO): δ 2.87–2.97 (m, 3H), 3.22–3.30 (m, 2H), 3.65 (dd, $J = 12.0$, 2.0 Hz, 1H), 3.75 (s, 3H), 4.46 (s, 1H), 4.44 (d, $J = 2.0$ Hz, 1H), 4.59 (s, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.21–7.23 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.41–7.45 (m, 5H), 7.54 (d, $J = 7.5$ Hz, 1H), 8.28 (s, 1H).

3ma, yellowish solid, m.p. 132–134 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)octa-1,6-diene-3,5-dione 1m (175 mg, 0.5 mmol) gave 3ma (188 mg, 75 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/6, V/V/V). Reaction time 15.0 h.

1H NMR (500 MHz, DMSO): δ 1.37 (d, $J = 7.0$ Hz, 3H), 2.86 (dd, $J = 13.0$, 6.0 Hz, 1H),
2.91–3.06 (m, 3H), 3.25–3.32 (m, 2H), 3.41 (dd, $J = 13.0$, 3.0 Hz, 1H), 4.16 (dd, $J = 6.0$, 3.0 Hz, 1H), 4.34 (d, $J = 3.0$ Hz, 1H), 7.14 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 8.01 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 21.8, 36.7, 36.9, 40.4, 48.1, 48.6, 66.2, 114.3, 127.7, 128.0, 129.0, 129.1, 130.1, 132.2, 132.3, 128.0, 143.6, 161.8, 179.3, 180.1, 192.0. HRMS (ESI-TOF) Calcd for C$_{25}$H$_{22}$Cl$_2$NO$_2$S$_2$ $^+$ ([M+H]$^+$) 502.0464. Found 502.0495.

3na, yellowish solid, m.p. 120–122 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a ($E$)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and ($1E,6E$)-1,7-bis(4-chlorophenyl)-4-(1,3-dithian-2-ylidene)hepta-1,6-diene-3,5-dione 1n (230 mg, 0.5 mmol) gave 3na (269 mg, 88 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 10.0 h.

$^1$H NMR (500 MHz, DMSO): δ 2.01–2.08 (m, 2H), 2.61–2.71 (m, 4H), 3.15 (dd, $J = 12.5$, 7.5 Hz, 1H), 3.26 (dd, $J = 12.5$, 2.0 Hz, 1H), 4.16 (d, $J = 4.5$ Hz, 1H), 4.36 (d, $J = 5.0$ Hz, 1H), 4.49 (d, $J = 4.5$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 4H), 7.43–7.47 (m, 4H), 7.78 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 24.7, 30.3, 30.4, 40.9, 47.8, 58.5, 68.5, 112.5, 128.3, 128.8, 129.1, 129.2, 129.5, 130.2, 131.1, 132.3, 132.7, 136.9, 138.6, 142.7, 144.8, 163.3, 174.4, 179.9, 192.9. HRMS (ESI-TOF) Calcd for C$_{31}$H$_{25}$Cl$_3$NO$_2$S$_2$ $^+$ ([M+H]$^+$) 612.0387. Found 612.0399.

3oa, yellowish solid, m.p. 112–114 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a ($E$)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and ($1E,6E$)-4-(1,3-dithian-2-ylidene)-1,7-di-p-tolylhepta-1,6-diene-3,5-dione 1o (210 mg, 0.5 mmol) gave 3oa (234 mg, 82 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 15.0 h.

$^1$H NMR (500 MHz, DMSO): δ 2.03–2.09 (m, 2H), 2.28 (s, 3H), 2.29 (s, 3H), 2.63–2.70 (m, 4H),
3.12 (dd, J = 13.0, 7.5 Hz, 1H), 3.21 (dd, J = 13.0, 3.0 Hz, 1H), 4.08 (d, J = 4.5 Hz, 1H), 4.26 (dd, J = 7.5, 3.0 Hz, 1H), 4.41 (d, J = 4.5 Hz, 1H), 7.12 (s, 4H), 7.17 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.63 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 21.2 (2C), 24.7, 30.3, 30.4, 41.0, 48.1, 58.7, 68.8, 112.5, 127.4, 128.2 (2C), 129.2, 129.4 (2C), 129.7, 129.9, 132.5, 135.5, 136.7 (2C), 143.1, 163.8, 173.6, 179.9, 193.3. HRMS (ESI-TOF) Calcd for C₃₃H₃₁ClNO₂S₂⁺ ([M+H]⁺) 572.1479. Found 572.1481.

3pa, yellowish solid, m.p. 132–134 °C.
3pa', yellowish solid, m.p. 136–138 °C, 3pa/3pa' = 1.5/1.0.
Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-1,7-bis(4-chlorophenyl)-4-(1,3-dithiepan-2-ylidene)hepta-1,6-diene-3,5-dione 1p (238 mg, 0.5 mmol) gave 3pa (256 mg, 82 %) after purification by column chromatography on silica gel (Et₃N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 15.0 h.

3pa, ¹H NMR (500 MHz, DMSO): δ 1.68–1.87 (m, 4H), 2.58–2.85 (m, 4H), 3.22 (dd, J = 16.5, 3.0 Hz, 1H), 3.32 (d, J = 7.0 Hz, 1H), 4.13 (d, J = 6.0 Hz, 1H), 4.40 (dd, J = 7.0, 3.0 Hz, 1H), 4.59 (d, J = 6.0 Hz, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.44–7.45 (m, 6H), 8.09 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 30.1, 30.4, 33.6, 33.8, 39.1, 46.7, 57.7, 69.4, 111.6, 128.5, 128.8, 129.1, 129.3, 129.7, 130.0, 131.3, 132.2, 132.8, 137.8, 141.5, 142.3, 144.0, 154.9, 166.4, 179.4, 197.7. HRMS (ESI-TOF) Calcd for C₃₂H₂₇Cl₂NO₂S₂⁺ ([M+H]⁺) 626.0543. Found 626.0562.

3pa', ¹H NMR (500 MHz, DMSO): δ 1.58–1.79 (m, 4H), 2.46–2.73 (m, 4H), 3.26–3.32 (m, 2H), 4.16 (d, J = 2.6 Hz, 1H), 4.35 (s, 1H), 4.65 (s, 1H), 7.21–7.25 (m, 2H), 7.26–7.29 (m, 2H), 7.34–7.39 (m, 4H), 7.43–7.45 (m, 2H), 7.46–7.51 (m, 2H), 8.46 (s, 1H). ¹³C NMR (125 MHz, DMSO): δ 30.0, 30.6, 33.0, 33.8, 38.8, 47.4, 57.0, 68.8, 112.5, 128.2, 128.9, 129.0, 129.4, 129.8, 131.4, 132.0, 132.8, 138.0, 141.7, 142.4, 144.4, 154.2, 165.9, 178.5, 198.9. HRMS (ESI-TOF) Calcd for C₃₂H₂₇Cl₂NO₂S₂⁺ ([M+H]⁺) 626.0543. Found 626.0560.
3qa, yellowish solid, m.p. 184–186 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-4-(bis(ethylthio)methylene)-1,7-bis(4-fluorophenyl)hepta-1,6-diene-3,5-dione 1q (222 mg, 0.5 mmol) gave 3qa (238 mg, 80 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 8.0 h.

$^1$H NMR (500 MHz, DMSO): δ 0.97 (m, 3H), 1.08 (m, 3H), 2.44 (m, 2H), 2.61 (m, 2H), 3.15 (dd, $J = 18.0, 3.5$ Hz, 1H), 3.50 (dd, $J = 18.0, 8.0$ Hz, 1H), 4.06 (d, $J = 5.0$ Hz, 1H), 4.49 (dd, $J = 8.0$, 3.5 Hz, 1H), 4.63 (d, $J = 5.0$ Hz, 1H), 7.12 (t, $J = 8.5$ Hz, 2H), 7.19–7.25 (m, 4H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 2H), 7.48–7.50 (m, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 8.5$ Hz, 2H), 8.12 (s, 1H).

$^{13}$C NMR (125 MHz, DMSO): δ 14.8 (2C), 28.2, 28.6, 38.7, 45.5, 56.7, 69.5, 111.8, 115.5 (d), 116.0 (d), 128.3, 129.4, 129.6 (d), 130.2 (d), 132.8, 134.3, 141.2 (d), 142.4, 143.5, 148.5, 160.7 (d), 162.7 (d), 167.7, 177.6, 199.2.

HRMS (ESI-TOF) Calcd for C$_{32}$H$_{29}$ClF$_2$NO$_2$S$_2$+ ([M+H]$^+$) 596.1291. Found 596.1303.

3ra, yellowish solid, m.p. 100–102 °C. Following the procedure for the synthesis of 3aa, the reaction of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and (1E,6E)-4-(bis(ethylthio)methylene)-1,7-diphenylhepta-1,6-diene-3,5-dione 1r (204 mg, 0.5 mmol) gave 3ra (243 mg, 87 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 6.5 h.

$^1$H NMR (500 MHz, DMSO): δ 0.90 (m, 3H), 1.06 (m, 3H), 2.32 (m, 2H), 2.56 (m, 2H), 3.19 (dd, $J = 17.5$ Hz, 1H), 3.50 (dd, $J = 18.0, 6.5$ Hz, 1H), 4.07 (s, 1H), 4.49 (s, 1H), 4.66 (d, $J = 2.5$ Hz, 1H), 7.22–7.24 (m, 3H), 7.28–7.31 (m, 5H), 7.36–7.39 (m, 2H), 7.44–7.46 (m, 4H), 8.21 (s, 1H).

$^{13}$C NMR (125 MHz, DMSO): δ 14.8, 14.9, 28.1, 28.8, 39.2, 45.1, 45.1, 57.4, 69.5, 111.7, 126.9, 127.6, 127.7, 128.0, 128.2, 128.8, 129.1, 129.4, 132.8, 138.2, 142.7, 143.6, 145.2, 148.4, 167.7, 177.6, 199.2.

HRMS (ESI-TOF) Calcd for C$_{32}$H$_{31}$ClNO$_2$S$_2$+ ([M+H]$^+$) 560.1479. Found 560.1488.
3ab, yellowish solid, m.p. 147–149 °C. Following the procedure for the synthesis of 3aa, the reaction of 2b (E)-2-(benzylideneamino)acetonitrile (1.2 equiv, 86.4 mg), and (1E,6E)-1,7-bis(4-chlorophenyl)-4(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) gave 3ab (262 mg, 93 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 25.0 h.

$^1$H NMR (500 MHz, DMSO): δ 3.00–3.03 (m, 1H), 3.06–3.15 (m, 2H), 3.18–3.24 (m, 2H), 3.34 (dd, J = 12.0, 2.5 Hz, 1H), 4.21 (d, J = 4.0 Hz, 1H), 4.42 (dd, J = 12.0, 3.0 Hz, 1H), 4.48 (d, J = 4.0 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 7.30–7.33 (m, 3H), 7.36–7.41 (m, 6H), 7.46 (d, J = 8.5 Hz, 2H), 7.83 (s, 1H).

$^{13}$C NMR (125 MHz, DMSO): δ 36.7, 36.8, 40.3, 48.1, 58.7, 69.1, 112.6, 126.1, 127.6, 128.2, 128.8, 129.3(2C), 130.2, 131.0, 132.5, 138.6, 144.0, 145.6, 163.3, 179.2, 179.7, 192.4. HRMS (ESI-TOF) Calcd for C$_{30}$H$_{24}$Cl$_2$NO$_2$S$_2$+ ([M+H]$^+$) 564.0620. Found 564.0611.

3ac, yellowish solid, m.p. 141–143 °C. Following the procedure for the synthesis of 3aa, the reaction of 2c (E)-2-(3-methylbenzylidene)amino)acetonitrile (1.2 equiv, 94.8 mg), and (1E,6E)-1,7-bis(4-chlorophenyl)-4(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) gave 3ac (260 mg, 90 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/5, V/V/V). Reaction time 43.0 h.

$^1$H NMR (500 MHz, DMSO): δ 2.30 (s, 3H), 2.98–3.03 (m, 1H), 3.07 (dd, J = 11.0, 4.5 Hz, 1H), 3.11–3.24 (m, 4H), 4.17 (d, J = 4.0 Hz, 1H), 4.39 (d, J = 5.5 Hz, 1H), 4.42 (d, J = 4.0 Hz, 1H), 7.18 (s, 4H), 7.24 (d, J = 8.0 Hz, 2H), 7.35 (s, 4H), 7.45 (d, J = 8.5 Hz, 2H), 7.81 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 21.3, 36.8, 36.9, 40.4, 48.1, 58.9, 69.1, 112.7, 126.2, 127.7, 128.9, 129.4(2C), 129.9, 130.3, 131.1, 132.5, 137.5, 138.7, 141.1, 145.7, 163.3, 179.2, 179.9, 192.5. HRMS (ESI-TOF) Calcd for C$_{31}$H$_{26}$Cl$_2$NO$_2$S$_2$+ ([M+H]$^+$) 578.0777. Found 578.0783.
3ad, yellowish solid, m.p. 144–146 °C. Following the procedure for the synthesis of 3aa, the reaction of 2d (E)-2-((2,2-dimethylpropylidene)amino)acetonitrile (1.2 equiv, 74.4 mg), (1E,6E)-1,7-bis(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) and DBU (2.0 equiv, 0.159 mL) gave 3ad (258 mg, 95 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/6, V/V/V). Reaction time 12.0 h.

$^1$H NMR (400 MHz, CDCl₃): δ 0.83 (s, 9H), 3.03–3.13 (m, 3H), 3.18–3.26 (m, 3H), 3.49 (dd, $J = 12.4, 2.8$ Hz, 1H), 4.13 (d, $J = 3.6$ Hz, 1H), 4.37 (d, $J = 3.6$ Hz, 1H), 5.95 (s, 1H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.23–7.29 (m, 6H).

$^{13}$C NMR (125 MHz, DMSO): δ 26.5, 31.2, 34.4, 38.7, 49.5, 66.3, 91.6, 94.1, 113.0, 128.4, 129.2, 129.5, 132.2, 132.6, 134.2, 137.1, 138.9, 165.8, 168.5, 177.7, 185.1, 191.8. HRMS (ESI-TOF) Calcd for C$_{28}$H$_{28}$Cl$_2$NO$_2$S$_2$ + ([M+H])$^+$ 544.0933. Found 544.0921.

3ae, yellowish solid, m.p. 160–162 °C. Following the procedure for the synthesis of 3aa, the reaction of 2e (E)-2-((cyclohexylmethylene)amino)acetonitrile (1.2 equiv, 90.0 mg), (1E,6E)-1,7-bis(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) and DBU (2.0 equiv, 0.159 mL) gave 3ae (236 mg, 83 %) after purification by column chromatography on silica gel (Et$_3$N/EtOAc/PE = 0.05/1/6, V/V/V). Reaction time 18.0 h.

$^1$H NMR (500 MHz, DMSO): δ 0.87–0.95 (m, 2H), 1.04–1.18 (m, 3H), 1.35–1.42 (m, 1H), 1.52–1.73 (m, 5H), 2.87–2.94 (m, 3H), 3.16 (m, 1H), 3.23–3.26 (m, 2H), 3.55 (dd, $J = 13.0, 3.0$ Hz, 1H), 4.13 (d, $J = 3.5$ Hz, 1H), 4.23 (dd, $J = 5.5, 3.5$ Hz, 1H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.28–7.33 (m, 4H), 7.38 (d, $J = 8.5$ Hz, 2H), 7.86 (s, 1H).

$^{13}$C NMR (125 MHz, DMSO): δ 21.2, 21.3, 36.7, 40.7, 48.4, 58.8, 60.3, 65.4, 68.6, 112.6, 128.2, 129.2, 129.5, 132.4, 135.5, 136.7, 136.9, 163.5, 170.8, 178.7, 179.8, 192.7. HRMS (ESI-TOF) Calcd for C$_{30}$H$_{30}$Cl$_2$NO$_2$S$_2$ + ([M+H])$^+$ 570.1090. Found 570.1084.
General procedure (taking 7a as an example):
To a solution of 2a (E)-methyl 2-((4-chlorobenzylidene)amino)acetate (1.2 equiv, 127 mg) and (1E,6E)-1,7-bis(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)hepta-1,6-diene-3,5-dione 1a (223 mg, 0.5 mmol) in DMSO (5.0 mL) was added K₂CO₃ (34.6 mg, 0.5 mmol) at room temperature. After 1a was consumed as indicated by TLC, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL × 2). The combined organic layers were dried over anhydrous Na₂SO₄, evaporated in vacuo, and the residue was purified by column chromatography (Et₃N/EtOAc/PE = 0.05/1/4, V/V/V) to give 7a (207 mg, 63 %, 0.315 mmol) as a yellowish solid. Reaction time 6.5 h.

7a, yellowish solid, m.p. 150–152 °C.

¹H NMR (500 MHz, CDCl₃): δ 2.89 (d, J = 19.5 Hz, 1H), 2.99 (d, J = 4.5 Hz, 1H), 3.14–3.21 (m, 3H), 3.36–3.45 (m, 2H), 3.71 (d, J = 13.0 Hz, 1H), 3.75 (s, 3H), 3.77 (m, 1H), 4.27–4.36 (m, 2H), 6.80 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.19–7.26 (m, 6H).

¹³C NMR (125 MHz, CDCl₃): δ 37.1, 37.2, 45.3, 45.5, 52.9, 57.9, 66.9, 67.0, 70.1, 124.0, 128.2, 128.6, 128.7, 128.8, 128.9, 129.4, 133.4, 133.6 (2C), 134.1, 138.3, 138.4, 175.0, 187.3, 192.6, 196.6.

7b, yellowish solid, m.p. 116–118 °C. Following the procedure for the synthesis of 7a, the reaction of 2a (E)-methyl 2-((4-chlorobenzylidene)amino)acetate (1.2 equiv, 127 mg) and (1E,6E)-4-(1,3-dithiolan-2-yldiene)-1,7-di-p-tolylhepta-1,6-diene-3,5-dione 1f (203 mg, 0.5 mmol) gave 7b (185 mg, 60 %) after purification by column chromatography on silica gel (Et3N/EtOAc/PE = 0.05/1/4, V/V/V). Reaction time 12.0 h.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 2.22 (s, 3H), 2.29 (s, 3H), 2.90 (d, $J = 19.6$ Hz, 1H), 2.97 (d, $J = 4.8$ Hz, 1H), 3.14–3.21 (m, 3H), 3.34–3.41 (m, 2H), 4.30–4.41 (m, 2H), 6.74 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 7.05–7.12 (m, 4H), 7.17–7.24 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.0 (2C), 37.0, 37.1, 45.6, 45.7, 52.7, 58.3, 66.6, 67.4, 70.4, 124.5, 127.4, 127.9, 128.3, 128.4, 129.2, 129.3, 132.6, 133.2, 137.0, 137.1 (2C), 139.1, 175.5, 186.1, 193.5, 197.3. HRMS (ESI-TOF) Calcd for C$_{34}$H$_{33}$ClNO$_4$S$_2$ + ([M+H]$^+$) 618.1534. Found 618.1573.

To a solution of 2a (E)-2-(4-chlorobenzylideneamino)acetonitrile (1.2 equiv, 107 mg) and 4-chlorochalcone (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (121 mg, 0.5 mmol) in DMSO (5.0 mL) was added K$_2$CO$_3$ (34.5 mg, 0.25 mmol) at room temperature under oxygen atmosphere. After enone was consumed, the resulting mixture was poured into ice-water (20 mL) and extracted with diethyl ether (20 mL $\times$ 2). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, evaporated in vacuo, and the residue was purified by column chromatography (EtOAc/PE = 1/10, V/V) to give 4-chloro-N-(2-(4-chlorophenyl)-4-oxo-4-phenylbutanoyl) benzamide (191 mg, 90%). Reaction time 12.0 h.

Colorless crystals, m.p. 215–217 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.29 (dd, $J = 18.0$, 3.5
Hz, 1H), 4.08 (dd, $J = 18.0$, 11.0 Hz, 1H), 5.41 (dd, $J = 11.0$, 3.5 Hz, 1H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.41 (m, 4H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.96 (d, $J = 7.5$ Hz, 2H), 8.68 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 43.9, 46.2, 128.1, 128.2, 128.7, 129.1, 129.2, 130.0, 133.5, 133.7, 135.8, 136.0, 139.7, 164.0, 174.7, 197.6. HRMS (ESI-TOF) Calcd for C$_{23}$H$_{18}$Cl$_2$NO$_3$ $^{+}$ ([M+H]$^+$) 426.0658. Found 426.0657.
III. $^1$H-$^1$H COSY spectrum of 3ma
IV. Crystal data and OPTEP drawing of compound 3aa' and 7a

Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97¹ and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic.

(1) Crystal data and OPTEP drawing of compound 3aa' (CCDC1002968)

ORTEP drawing:

Crystal data:

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Absorption coefficient (mm⁻¹) 0.455
F(000) 1419.9
Theta range for data collection (deg) 1.9 to 25.0
Reflections collected/unique 5589/3667
Goodness-of-fit on F² 1.029
Final R indices [I > 2σ (I)] R1=0.057, WR2 =0.125
R indices (all data) R1=0.096, WR2 =0.146

(2) Crystal data and ORTEP drawing of compound 7a (CCDC 1003600)

ORTEP drawing:

Crystal data:
Empirical formula C₃₂H₂₆Cl₃NO₄S₂
Formula weight 659.04
Crystal system Triclinic
Space group P-1
a (Å) 10.069(5)
b (Å) 13.141(5)
c (Å) 18.165(5)
α (deg) 110.735(5)
β (deg) 93.826(5)
γ (deg) 107.061(5)
Volume (Å³) 2109.5(14)
Z 2
Calculated density (mg/m³) 1.597
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<td>Final R indices [I &gt; 2σ (I)]</td>
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<td>R indices (all data)</td>
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V. Copies of $^1$H NMR and $^{13}$C NMR spectra
$\text{3ac}$