

Supporting Information

Synthesis of Tetrahydro-2H-Thiopyran 1,1-Dioxides via [1+1+1+1+1] Annulation: An Unconventional Usage of Tethered C–S Synthon

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1. General information

All the materials and solvents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ¹H spectra were recorded in CDCl₃ and DMSO-d₆ on 600/400 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ¹³C spectra were recorded in CDCl₃ and DMSO-d₆ on 150/100 MHz NMR spectrometers and resonances (δ) are given in ppm. ¹⁹F spectra were recorded in CDCl₃ and DMSO-d₆ on 376 MHz NMR using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) on a TOF mass analyzer. The X-ray crystal-structure determinations of **3o** and **3u** were obtained on a Bruker SMART APEX CCD system. Sulfoxonium ylides **1** were known compounds, and prepared according to the reported procedures.¹ Rongalite **2** was commercially available (CAS No: 149-44-0) and purchased from TCI corporation.

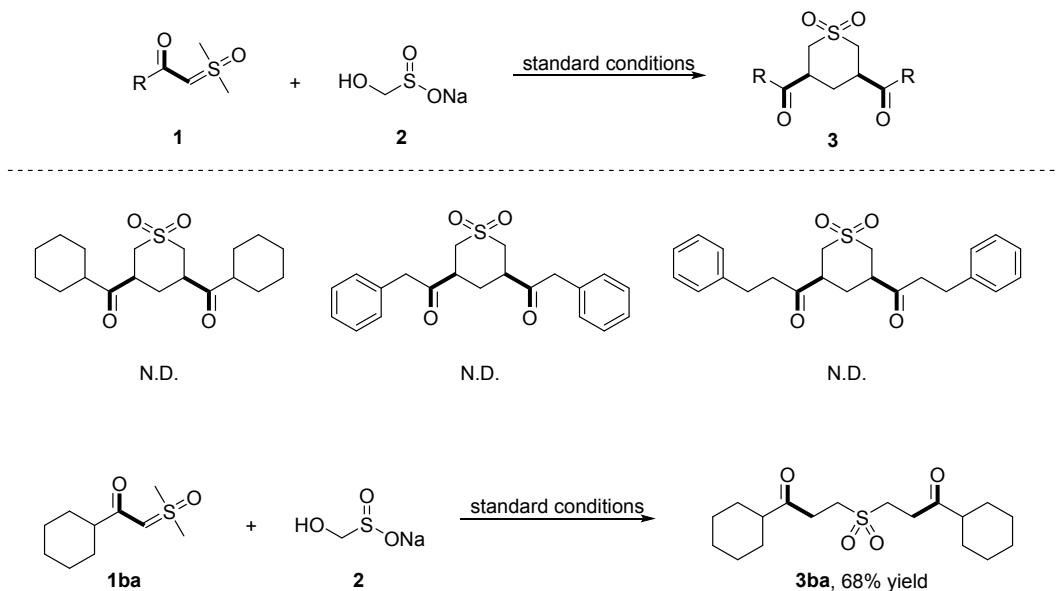
2. General procedure for the synthesis of tetrahydro-2H-thiopyran 1,1-dioxides

Under air atmosphere, a 35 mL oven dried reaction tube equipped with a magnetic stir bar was charged with the mixture of sulfoxonium ylide **1** (0.20 mmol), rongalite **2** (0.60 mmol), NaOAc (2.5 equiv.) and DMSO (2.0 mL). The mixture was stirred at 90 °C (metal heating block) for 6 hours. After cooling to room temperature, the mixture was quenched with water (25 mL), extracted with EtOAc (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether) to afford the corresponding products **3**.

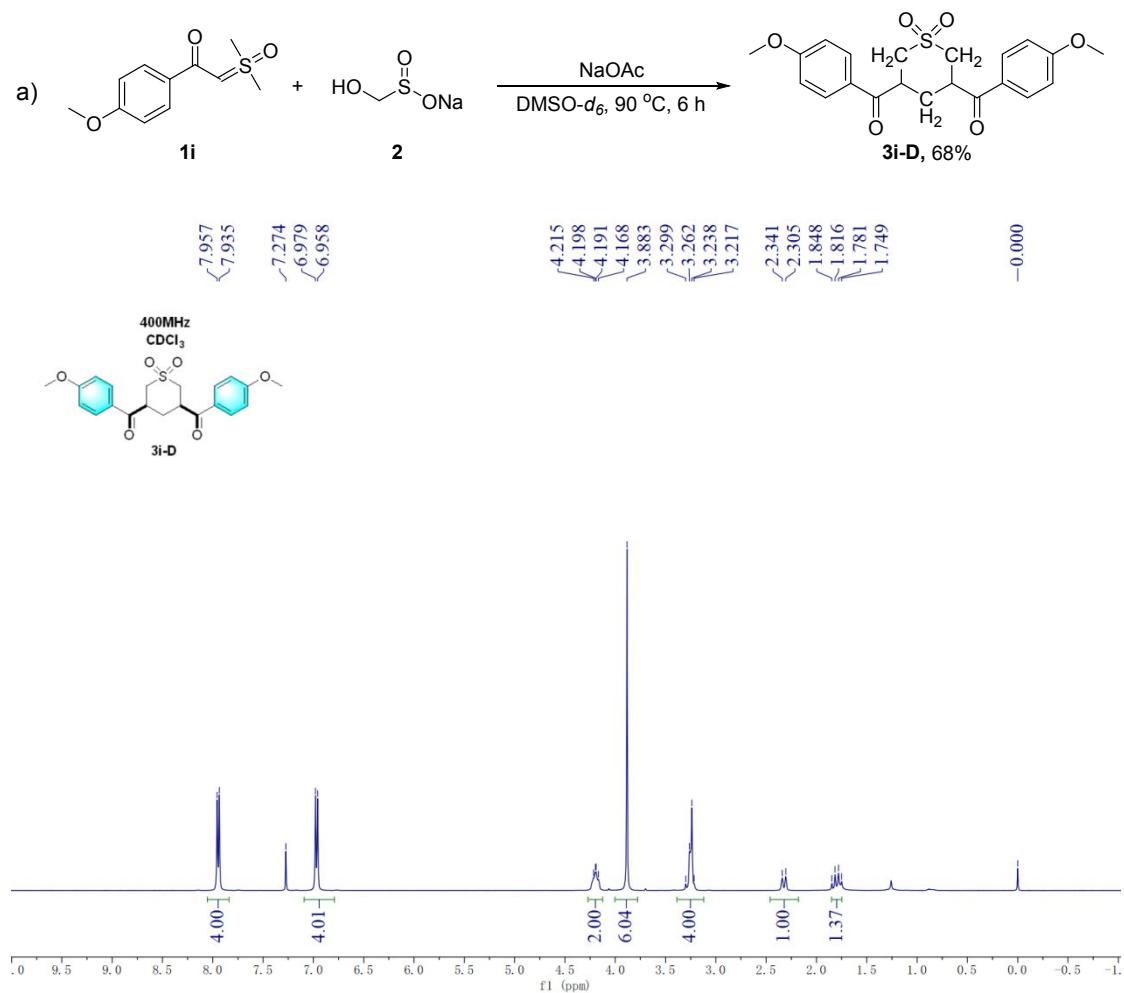
3. Scale-up experiment procedure for the synthesis of **3d**

Under air atmosphere, a 50 mL oven dried reaction tube equipped with a magnetic stir bar was charged with the mixture of sulfoxonium ylide **1d** (2.0 mmol), rongalite **2** (3.0 equiv), NaOAc (2.5 equiv) and DMSO (20 mL). The mixture was stirred at 90 °C (metal heating block) for 6 hours. After cooling to room temperature, the mixture was quenched with water (200 mL), extracted with EtOAc (3 × 200 mL), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:3) to afford the corresponding products **3d** (247 mg, 53% yield).

4. Further explorations

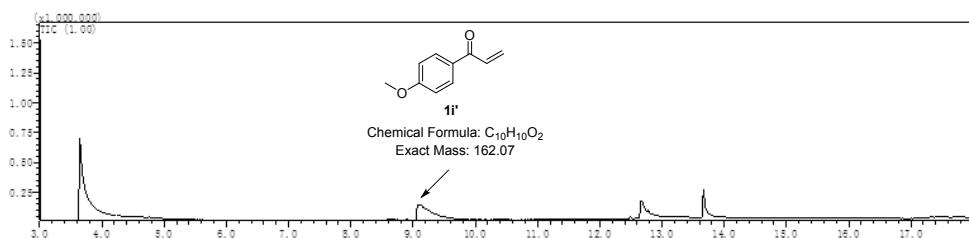
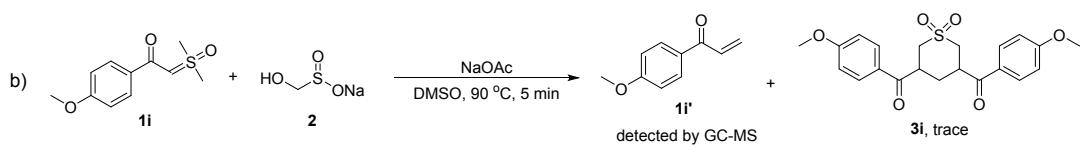
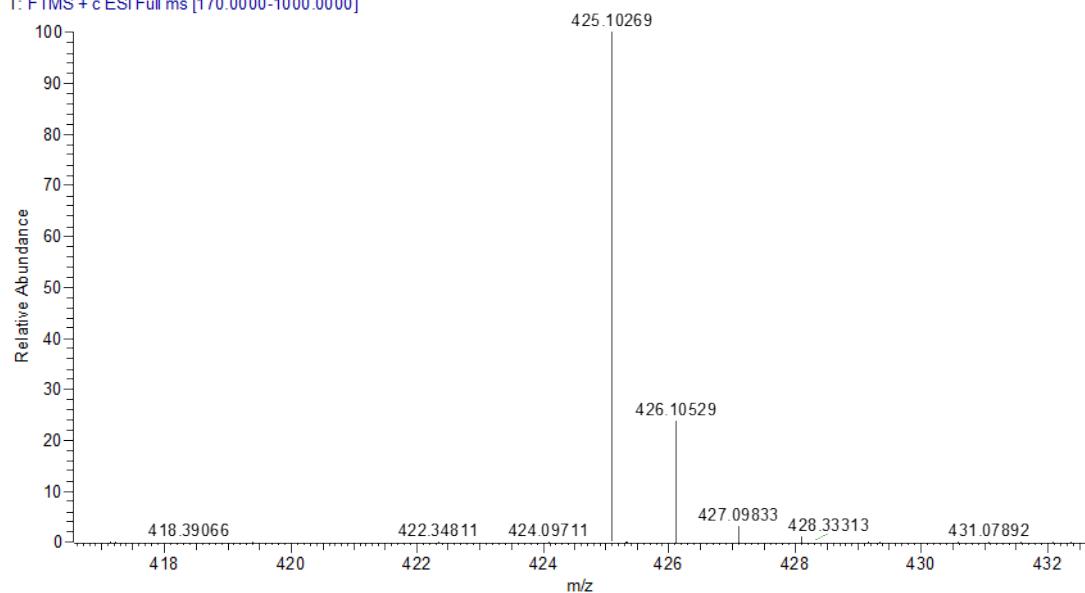


5. Mechanistic study

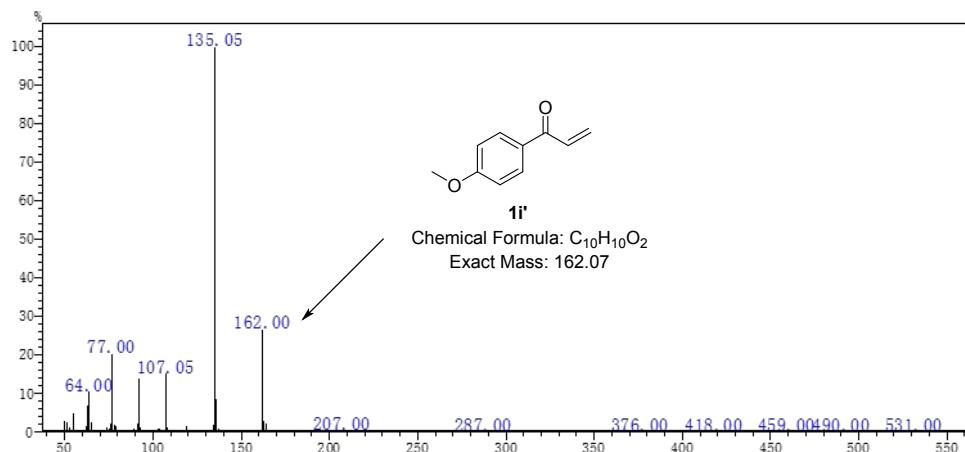


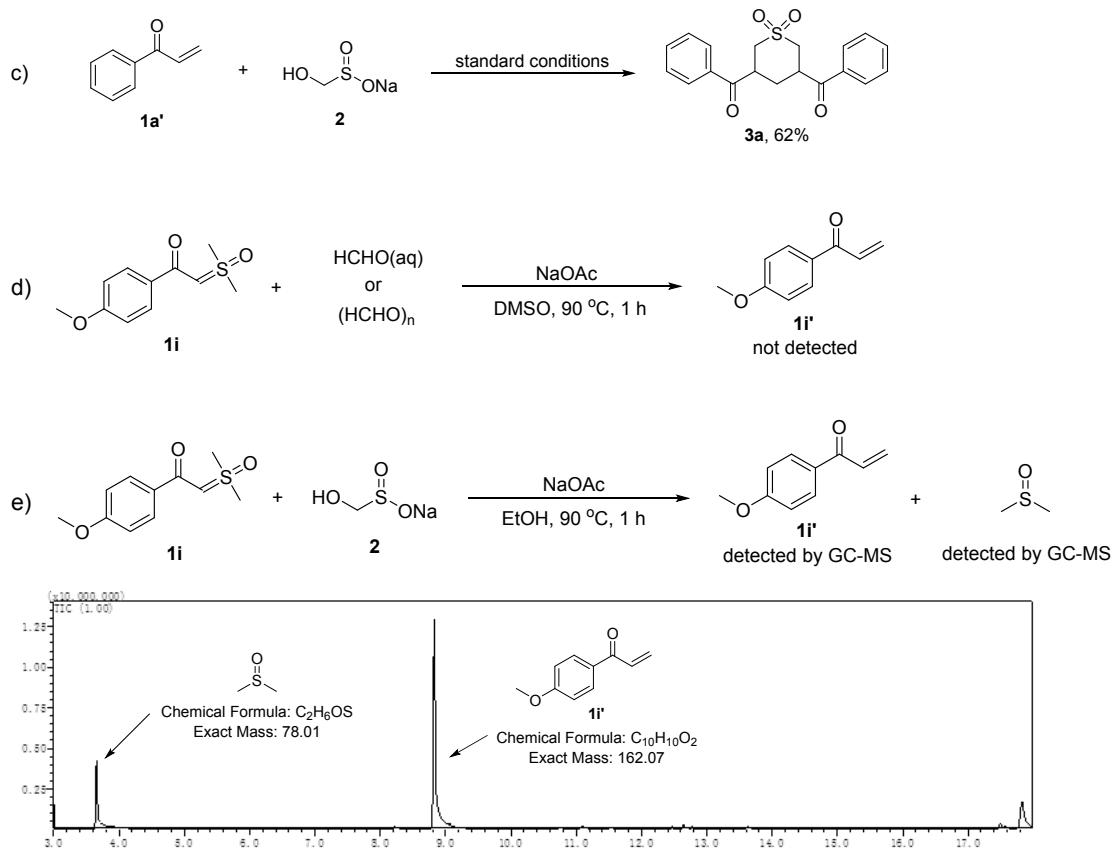
3i-D. HRMS (ESI) m/z calcd for $C_{21}H_{22}O_6SNa^+$ ($M+Na$)⁺ 425.1029, found 425.1027.

20220802_2_CXL_1577 #32 RT: 0.17 AV: 1 NL: 1.42E9
T: FTMS + c ESI Full ms [170.0000-1000.0000]

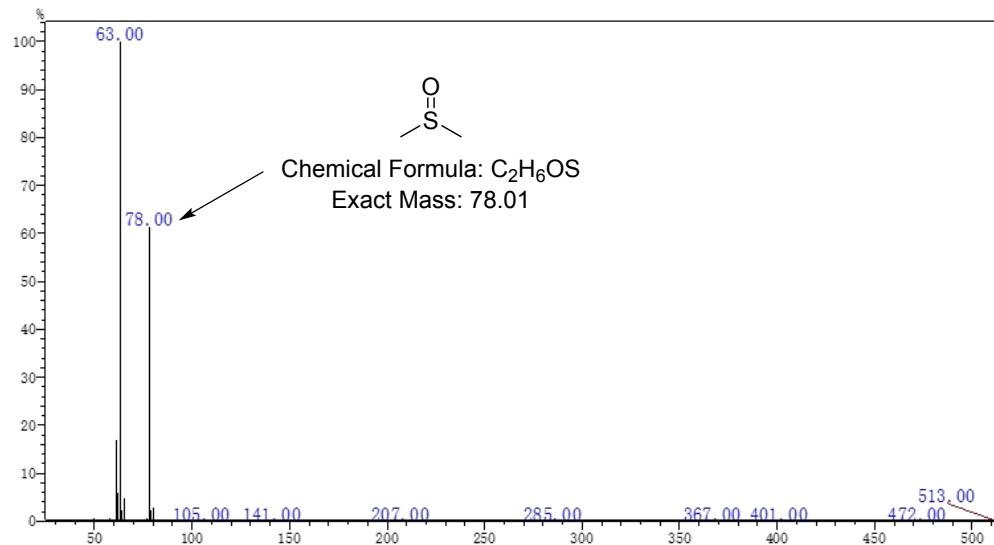


Retention time: 9.155 min

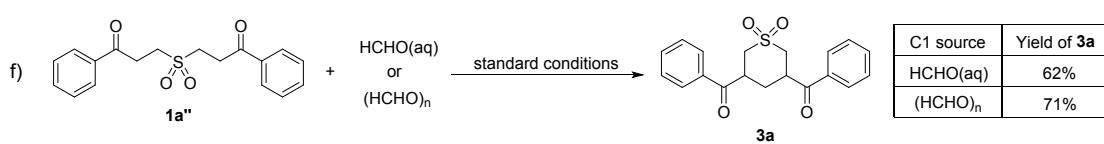
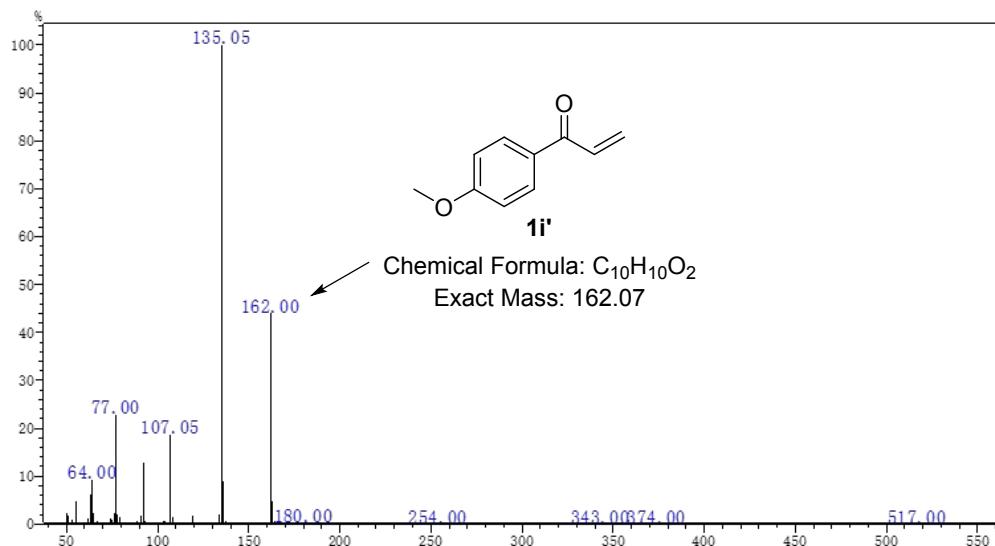




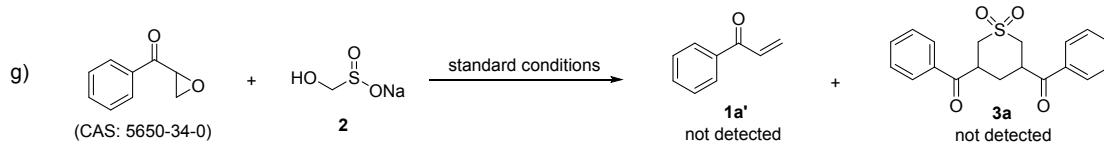
Retention time: 3.655 min



Retention time: 8.925 min



Note: **1a''** was synthesis according to the previous literature report.²



6. Characterization data for compounds



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diylbis(phenylmethanone) (3a):

Yield 74%; 25.3 mg; white solid; mp 171–174 °C; R_f 0.35 (EtOAc/petroleum ether = 1:3); ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, J = 7.8 Hz, 4H), 7.63 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.8 Hz, 4H), 4.26 (t, J = 12.0 Hz, 2H), 3.27 (d, J = 13.2 Hz, 4H), 2.39 (d, J = 14.4 Hz, 1H), 1.79 (q, J = 13.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 197.3, 134.2, 134.1, 129.2, 128.4, 52.5, 42.1, 31.2. HRMS (ESI) m/z calcd for C₁₉H₁₈O₄SnA⁺ (M+Na)⁺ 365.0818, found 365.0819.



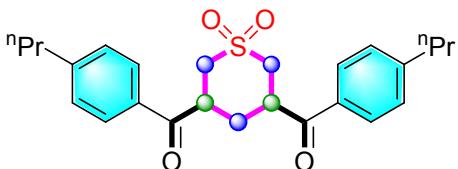
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis(p-tolylmethanone) (3b):

Yield 72%; 26.6 mg; white solid; mp 181-183 °C; R_f 0.32 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, DMSO- d_6) δ 8.00 (d, J = 8.0 Hz, 4H), 7.37 (d, J = 8.0 Hz, 4H), 4.32 (t, J = 12.0 Hz, 2H), 3.47 (s, 2H), 3.31 (d, J = 13.6 Hz, 2H), 2.39 (s, 6H), 2.19 (d, J = 13.6 Hz, 1H), 1.58 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 197.7, 144.4, 131.9, 129.6, 128.8, 51.4, 41.9, 31.4, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 393.1131, found 393.1132.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-ethylphenyl)methanone) (3c):

Yield 66%; 26.3 mg; white solid; mp 167-170 °C; R_f 0.30 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.0 Hz, 4H), 7.32 (d, J = 8.0 Hz, 4H), 4.24 (dt, J = 12.0, 7.2 Hz, 2H), 3.25 (d, J = 7.6 Hz, 4H), 2.71 (q, J = 7.6 Hz, 4H), 2.37 (d, J = 14.4 Hz, 1H), 1.77 (q, J = 12.8 Hz, 1H), 1.26 (t, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, CDCl₃) δ 196.9, 151.4, 131.9, 128.7, 128.6, 52.5, 42.0, 31.4, 28.9, 15.0. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 421.1444, found 421.1445.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-propylphenyl)methanone) (3d):

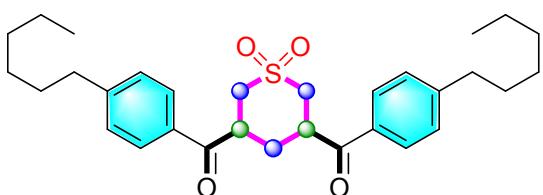
Yield 77%; 32.8 mg; white solid; mp 150-153 °C; R_f 0.25 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 4.24 (dt, J = 12.4, 7.6 Hz, 2H), 3.25 (d, J = 7.6 Hz, 4H), 2.75–2.54 (m, 4H), 2.37 (d, J = 14.4 Hz, 1H), 1.78 (q, J = 12.8 Hz, 1H), 1.66 (h, J = 7.4 Hz, 4H), 0.94 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl₃) δ 196.9, 149.9, 131.9, 129.2, 128.6, 52.5, 42.0, 37.9, 31.4, 24.0, 13.7. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{30}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 449.1757, found 449.1758.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-(tert-butyl)phenyl)methanone)

(3e):

Yield 62%; 28.1 mg; white solid; mp 247-251 °C; R_f 0.32 (EtOAc/petroleum ether = 1:6); ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.8 Hz, 4H), 7.52 (d, J = 8.4 Hz, 4H), 4.24 (dt, J = 12.0, 7.2 Hz, 2H), 3.26 (d, J = 8.0 Hz, 4H), 2.38 (d, J = 14.4 Hz, 1H), 1.83–1.73 (m, 1H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 158.2, 131.6, 128.5, 126.1, 52.6, 42.1, 35.2, 31.4, 30.9. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{34}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 477.2070, found 477.2072.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-hexylphenyl)methanone) (3f):

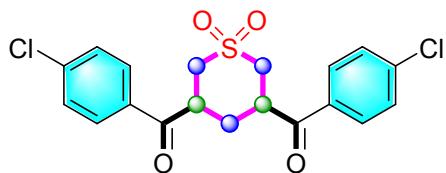
Yield 64%; 32.6 mg; white solid; mp 115-118 °C; R_f 0.40 (EtOAc/petroleum ether = 1:6); ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 4H), 7.30 (d, J = 8.4 Hz, 4H), 4.23 (dt, J = 12.4, 7.2 Hz, 2H), 3.25 (d, J = 7.6 Hz, 4H), 2.79–2.57 (m, 4H), 2.37 (d, J = 14.4 Hz, 1H), 1.85–1.76 (m, 1H), 1.62 (p, J = 7.7 Hz, 4H), 1.37–1.25 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.9, 150.2, 131.9, 129.1, 128.6, 52.6, 42.0, 36.0, 31.6, 31.4, 30.9, 28.8, 22.5, 14.0. HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{42}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 533.2696, found 533.2699.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-fluorophenyl)methanone)

(3g):

Yield 68%; 25.7 mg; white solid; mp 196-198 °C; R_f 0.27 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (dd, J = 8.8, 5.2 Hz, 4H), 7.20 (t, J = 8.4 Hz, 4H), 4.20 (dd, J = 11.2, 5.6 Hz, 2H), 3.26 (d, J = 7.6 Hz, 4H), 2.32 (d, J = 14.4 Hz, 1H), 1.82 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.7, 166.3 (d, J = 256.0 Hz, $^1\text{J}_{\text{CF}}$), 131.2 (d, J = 10.0 Hz, $^3\text{J}_{\text{CF}}$), 130.6 (d, J = 3.0 Hz, $^4\text{J}_{\text{CF}}$), 116.4 (d, J = 22.0 Hz, $^2\text{J}_{\text{CF}}$), 52.5, 42.0, 31.1. ^{19}F NMR (376 MHz, CDCl_3) δ -102.48 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 401.0630, found 401.0631.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-chlorophenyl)methanone) (3h):

Yield 59%; 24.2 mg; white solid; mp 212-214 °C; R_f 0.33 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.09 (d, *J* = 8.4 Hz, 4H), 7.62 (d, *J* = 8.4 Hz, 4H), 4.40–4.23 (m, 2H), 3.42 (t, *J* = 12.8 Hz, 2H), 3.30 (s, 2H), 2.16 (d, *J* = 13.2 Hz, 1H), 1.58 (q, *J* = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d*₆) δ 197.2, 138.7, 133.1, 130.6, 129.1, 51.2, 42.0, 30.9. HRMS (ESI) m/z calcd for C₁₉H₁₆Cl₂O₄SNa⁺ (M+Na)⁺ 433.0039, found 433.0038.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-methoxyphenyl)methanone) (3i):

Yield 75%; 30.1 mg; white solid; mp 167-170 °C; R_f 0.25 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.8 Hz, 4H), 6.97 (d, *J* = 9.2 Hz, 4H), 4.27–4.08 (m, 2H), 3.88 (s, 6H), 3.25 (d, *J* = 10.4 Hz, 4H), 2.33 (d, *J* = 14.4 Hz, 1H), 1.80 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ 195.7, 164.3, 130.8, 127.0, 114.3, 55.6, 52.6, 41.8, 31.6. HRMS (ESI) m/z calcd for C₂₁H₂₂O₆SNa⁺ (M+Na)⁺ 425.1029, found 425.1029.



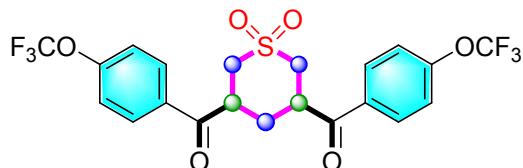
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-ethoxyphenyl)methanone) (3j):

Yield 74%; 31.8 mg; white solid; mp 155-158 °C; R_f 0.28 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 4.19 (t, *J* = 10.8 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 4H), 3.25 (d, *J* = 10.8 Hz, 4H), 2.33 (d, *J* = 14.4 Hz, 1H), 1.79 (q, *J* = 12.8 Hz, 1H), 1.45 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl₃) δ 195.7, 163.7, 130.8, 126.8, 114.7, 63.9, 52.6, 41.8, 31.6, 14.5. HRMS (ESI) m/z calcd for C₂₃H₂₆O₆SNa⁺ (M+Na)⁺ 453.1342, found 453.1339.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-(trifluoromethyl)phenyl)methane (3k):

Yield 65%; 31.1 mg; white solid; mp 195-198 °C; R_f 0.36 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 4H), 7.80 (d, J = 8.0 Hz, 4H), 4.27 (t, J = 12.0 Hz, 2H), 3.28 (q, J = 14.0 Hz, 4H), 2.34 (d, J = 14.4 Hz, 1H), 1.84 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.3, 136.8, 135.6 (q, J = 33.0 Hz, $^2J_{\text{CF}}$), 128.9, 126.3 (q, J = 3.0 Hz, $^3J_{\text{CF}}$), 123.2 (q, J = 271.0 Hz, $^1J_{\text{CF}}$), 52.3, 42.4, 30.5. ^{19}F NMR (376 MHz, CDCl_3) δ -63.30 (s, 6F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_6\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 501.0566, found 501.0569.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-(trifluoromethoxy)phenyl)methane (3l):

Yield 57%; 29.1 mg; white solid; mp 165-168 °C; R_f 0.31 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 4.23 (t, J = 9.6 Hz, 2H), 3.27 (d, J = 10.0 Hz, 4H), 2.32 (d, J = 14.4 Hz, 1H), 1.84 (q, J = 13.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.7, 153.4, 132.3, 130.6, 120.8, 120.2 (q, J = 258.0 Hz, $^1J_{\text{CF}}$), 52.4, 42.1, 30.8. ^{19}F NMR (376 MHz, CDCl_3) δ -57.62 (s, 6F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_6\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 533.0464, found 533.0461.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-((trifluoromethyl)thio)phenyl)methane (3m):

Yield 55%; 29.8 mg; white solid; mp 197-200 °C; R_f 0.39 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.0 Hz, 4H), 7.79 (d, J = 8.0 Hz, 4H), 4.23 (t, J = 12.0 Hz, 2H), 3.26 (q, J = 14.0 Hz, 4H), 2.34 (d, J = 14.4 Hz, 1H), 1.84 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 135.9, 135.5, 131.8, 129.2, 129.1 (q, J = 307.0 Hz, $^1J_{\text{CF}}$), 52.4, 42.3, 30.7. ^{19}F NMR (376 MHz, CDCl_3) δ -41.39 (s, 6F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_6\text{O}_4\text{S}_3\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ 565.0007, found 565.0002.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis(m-tolylmethanone) (3n):

Yield 66%; 24.4 mg; white solid; mp 164-167 °C; R_f 0.30 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 4H), 7.40 (dt, J = 11.6, 7.6 Hz, 4H), 4.25 (dt, J = 12.0, 7.2 Hz, 2H), 3.25 (d, J = 8.0 Hz, 4H), 2.42 (s, 7H), 1.79–1.68 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 139.1, 134.9, 134.2, 128.9, 125.6, 52.5, 42.2, 31.5, 21.3. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 393.1131, found 393.1130.



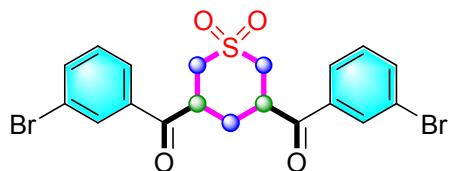
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-fluorophenyl)methanone) (3o):

Yield 62%; 23.4 mg; white solid; mp 158-161 °C; R_f 0.25 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.52 (td, J = 8.0, 5.6 Hz, 2H), 7.34 (td, J = 8.0, 2.0 Hz, 2H), 4.22 (t, J = 11.6 Hz, 2H), 3.27 (d, J = 11.6 Hz, 4H), 2.37 (d, J = 14.4 Hz, 1H), 1.85–1.74 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.1 (d, J = 3.0 Hz, $^4J_{\text{CF}}$), 163.0 (d, J = 248.0 Hz, $^1J_{\text{CF}}$), 136.2 (d, J = 6.0 Hz, $^3J_{\text{CF}}$), 130.9 (d, J = 7.0 Hz, $^3J_{\text{CF}}$), 124.1 (d, J = 3.0 Hz, $^4J_{\text{CF}}$), 121.4 (d, J = 21.0 Hz, $^2J_{\text{CF}}$), 115.3 (d, J = 22.0 Hz, $^2J_{\text{CF}}$), 52.4, 42.3, 31.0. ^{19}F NMR (376 MHz, CDCl_3) δ -110.30 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 401.0630, found 401.0630.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-chlorophenyl)methanone) (3p):

Yield 54%; 22.1 mg; white solid; mp 173–176 °C; R_f 0.31 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.93 (t, J = 1.6 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 4.21 (t, J = 11.6 Hz, 2H), 3.27 (d, J = 11.6 Hz, 4H), 2.35 (d, J = 14.4 Hz, 1H), 1.83–1.71 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.0, 135.7, 134.2, 130.5, 128.6, 126.5, 52.3, 42.3, 31.1. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 433.0039, found 433.0041.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-bromophenyl)methanone) (3q):

Yield 50%; 24.9 mg; white solid; mp 183–186 °C; R_f 0.26 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 4.21 (t, J = 11.6 Hz, 2H), 3.27 (d, J = 11.2 Hz, 4H), 2.35 (d, J = 14.4 Hz, 1H), 1.80–1.70 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.0, 137.1, 135.9, 131.5, 130.7, 126.9, 123.6, 52.3, 42.3, 31.1. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{Br}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 522.9008, found 522.9012.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-methoxyphenyl)methanone) (3r):

Yield 76%; 30.5 mg; white solid; mp 72–75 °C; R_f 0.27 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 7.6 Hz, 2H), 7.51–7.35 (m, 4H), 7.15 (dd, J = 8.4, 2.4 Hz, 2H), 4.24 (t, J = 10.0 Hz, 2H), 3.85 (s, 6H), 3.26 (d, J = 10.8 Hz, 4H), 2.40 (d, J = 14.4 Hz, 1H), 1.79–1.69 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 160.2, 135.5, 130.1, 120.8, 120.5, 112.8, 55.5, 52.5, 42.3, 31.4. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 425.1029, found 425.1031.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-(trifluoromethoxy)phenyl)methanone) (3s):

Yield 63%; 32.1 mg; white solid; mp 114-117 °C; R_f 0.29 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.74 (m, 4H), 7.68–7.41 (m, 4H), 4.38–4.15 (m, 2H), 3.30 (d, J = 7.6 Hz, 4H), 2.38 (d, J = 14.4 Hz, 1H), 1.78 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 149.9, 135.9, 130.8, 126.7, 126.5, 120.9, 120.3 (q, J = 257.0 Hz, $^1J_{\text{CF}}$), 52.2, 42.3, 31.1. ^{19}F NMR (376 MHz, CDCl_3) δ -57.92 (s, 6F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_6\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 533.0464, found 533.0461.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((2-fluorophenyl)methanone) (3t):

Yield 69%; 26.1 mg; white solid; mp 143-146 °C; R_f 0.32 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (t, J = 6.8 Hz, 2H), 7.59 (td, J = 8.4, 2.8 Hz, 2H), 7.34–7.11 (m, 4H), 4.10 (t, J = 12.4 Hz, 2H), 3.33 (d, J = 14.0 Hz, 2H), 3.20 (t, J = 13.2 Hz, 2H), 2.52 (d, J = 14.0 Hz, 1H), 1.59 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 161.5 (d, J = 254.0 Hz, $^1J_{\text{CF}}$), 135.7 (d, J = 9.0 Hz, $^3J_{\text{CF}}$), 131.2, 125.0, 123.4 (d, J = 10.0 Hz, $^3J_{\text{CF}}$), 116.9 (d, J = 24.0 Hz, $^2J_{\text{CF}}$), 52.2, 46.7, 30.4. ^{19}F NMR (376 MHz, CDCl_3) δ -109.95 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 401.0630, found 401.0631.



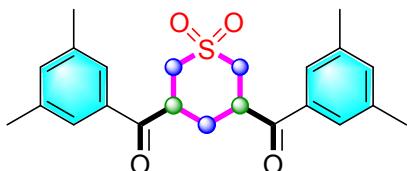
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((2-ethoxyphenyl)methanone) (3u):

Yield 80%; 34.4 mg; white solid; mp 133-136 °C; R_f 0.37 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, J = 7.6, 1.6 Hz, 2H), 7.54–7.41 (m, 2H), 7.09–6.88 (m, 4H), 4.29–4.08 (m, 6H), 3.33 (d, J = 14.0 Hz, 2H), 3.10 (t, J = 13.2 Hz, 2H), 2.40 (d, J = 14.0 Hz, 1H), 1.64 (q, J = 12.4 Hz, 1H), 1.46 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 200.3, 157.6, 134.3, 130.8, 126.2, 120.8, 112.0, 64.2, 52.5, 46.5, 30.1, 14.4. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 453.1342, found 453.1344.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-fluoro-2-methylphenyl)methano ne) (3v):

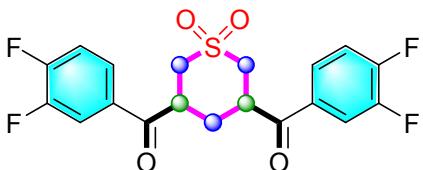
Yield 70%; 28.4 mg; white solid; mp 207–210 °C; R_f 0.30 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 7.69 (dd, J = 9.6, 5.6 Hz, 2H), 7.10–6.90 (m, 4H), 4.02 (t, J = 12.4 Hz, 2H), 3.38–3.00 (m, 4H), 2.47 (s, 6H), 2.22 (d, J = 14.4 Hz, 1H), 1.73–1.62 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.0, 164.5 (d, J = 254.0 Hz, $^1J_{\text{CF}}$), 143.7 (d, J = 9.0 Hz, $^3J_{\text{CF}}$), 131.0 (d, J = 3.0 Hz, $^4J_{\text{CF}}$), 130.8 (d, J = 9.0 Hz, $^3J_{\text{CF}}$), 119.6 (d, J = 21.0 Hz, $^2J_{\text{CF}}$), 113.2 (d, J = 22.0 Hz, $^2J_{\text{CF}}$), 52.4, 44.4, 30.4, 21.7. ^{19}F NMR (376 MHz, CDCl_3) δ -105.55 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{F}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 429.0943, found 429.0939.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3,5-dimethylphenyl)methanone)

(3w):

Yield 74%; 29.4 mg; white solid; mp 129–132 °C; R_f 0.42 (EtOAc/petroleum ether = 1:6); ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 4H), 7.24 (s, 2H), 4.25 (dt, J = 12.4, 7.2 Hz, 2H), 3.24 (d, J = 8.0 Hz, 4H), 2.38 (s, 13H), 1.68 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 138.8, 135.8, 134.3, 126.2, 52.4, 42.2, 31.6, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 421.1444, found 421.1444.

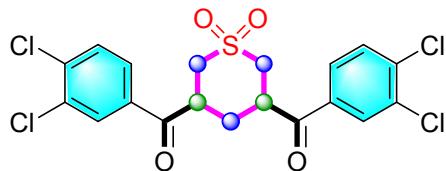


(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3,4-difluorophenyl)methanone)

(3x):

Yield 52%; 21.5 mg; white solid; mp 110–113 °C; R_f 0.29 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.29–8.12 (m, 2H), 8.07–7.91 (m, 2H), 7.63

(q, $J = 8.4$ Hz, 2H), 4.34 (t, $J = 12.0$ Hz, 2H), 3.43 (t, $J = 12.8$ Hz, 4H), 2.16 (d, $J = 13.2$ Hz, 1H), 1.55 (q, $J = 12.4$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 196.1, 152.9 (dd, $J = 253.0, 12.0$ Hz), 149.7 (dd, $J = 247.0, 13.0$ Hz), 132.0 (t, $J = 4.0$ Hz), 126.5 (dd, $J = 8.0, 3.0$ Hz), 118.1 (dd, $J = 17.0, 12.0$ Hz), 51.0, 41.9, 31.0. ^{19}F NMR (376 MHz, CDCl₃) δ -126.66 (d, $J = 18.8$ Hz, 2F), -134.14 (d, $J = 18.8$ Hz, 2F). HRMS (ESI) m/z calcd for C₁₉H₁₄F₄O₄SNa⁺ (M+Na)⁺ 437.0441, found 437.0442.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3,4-dichlorophenyl)methanone)

(3y):

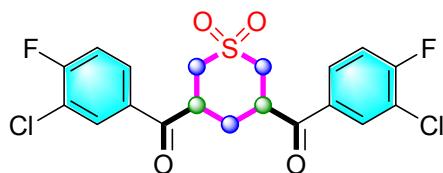
Yield 44%; 21.0 mg; white solid; mp 190-194 °C; R_f 0.30 (EtOAc/petroleum ether = 1:5); ^1H NMR (400 MHz, CDCl₃) δ 8.04 (d, $J = 2.0$ Hz, 2H), 7.79 (dd, $J = 8.4, 2.0$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 4.26–4.09 (m, 2H), 3.26 (d, $J = 10.8$ Hz, 4H), 2.30 (d, $J = 14.4$ Hz, 1H), 1.78 (q, $J = 12.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ 195.1, 139.2, 134.2, 133.6, 131.3, 130.4, 127.3, 52.2, 42.2, 31.0. HRMS (ESI) m/z calcd for C₁₉H₁₄Cl₄O₄SNa⁺ (M+Na)⁺ 502.9230, found 502.9231.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((4-fluoro-3-methylphenyl)methano

ne) (3z):

Yield 58%; 23.5 mg; white solid; mp 169-172 °C; R_f 0.38 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl₃) δ 7.91–7.78 (m, 4H), 7.11 (t, $J = 8.8$ Hz, 2H), 4.24 (dt, $J = 12.0, 6.0$ Hz, 2H), 3.27 (d, $J = 10.4$ Hz, 4H), 2.34 (s, 7H), 1.75 (q, $J = 12.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ 196.0, 164.8 (d, $J = 254.0$ Hz, $^1\text{J}_{\text{CF}}$), 132.3 (d, $J = 7.0$ Hz, $^3\text{J}_{\text{CF}}$), 130.3 (d, $J = 3.0$ Hz, $^4\text{J}_{\text{CF}}$), 128.4 (d, $J = 10.0$ Hz, $^3\text{J}_{\text{CF}}$), 126.2 (d, $J = 18.0$ Hz, $^2\text{J}_{\text{CF}}$), 115.8 (d, $J = 23.0$ Hz, $^2\text{J}_{\text{CF}}$), 52.3, 42.0, 31.4, 14.5 (d, $J = 3.0$ Hz, $^3\text{J}_{\text{CF}}$). ^{19}F NMR (376 MHz, CDCl₃) δ -106.76 (s, 2F). HRMS (ESI) m/z calcd for C₂₁H₂₀F₂O₄SNa⁺ (M+Na)⁺ 429.0943, found 429.0945.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-chloro-4-fluorophenyl)methanone)

e) (3aa):

Yield 47%; 21.0 mg; white solid; mp 175-178 °C; R_f 0.32 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (dd, J = 7.2, 2.4 Hz, 2H), 7.89 (ddd, J = 8.4, 4.4, 2.4 Hz, 2H), 7.32–7.26 (m, 2H), 4.26–4.10 (m, 2H), 3.27 (q, J = 7.6, 6.2 Hz, 4H), 2.30 (d, J = 14.4 Hz, 1H), 1.88–1.73 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.7, 161.7 (d, J = 258.0 Hz, $^1\text{J}_{\text{CF}}$), 131.5 (d, J = 1.0 Hz, $^4\text{J}_{\text{CF}}$), 131.3 (d, J = 4.0 Hz, $^3\text{J}_{\text{CF}}$), 128.9 (d, J = 8.0 Hz, $^3\text{J}_{\text{CF}}$), 122.8 (d, J = 18.0 Hz, $^2\text{J}_{\text{CF}}$), 117.5 (d, J = 22.0 Hz, $^2\text{J}_{\text{CF}}$), 52.3, 42.1, 31.0. ^{19}F NMR (376 MHz, CDCl_3) δ -104.64 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{F}_2\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 468.9850, found 468.9852.



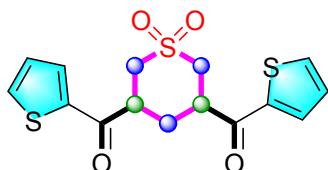
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((3-fluoro-4-methoxyphenyl)methanone) (3ab):

Yield 58%; 25.4 mg; white solid; mp 168-170 °C; R_f 0.34 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, CDCl_3) δ 7.85–7.63 (m, 4H), 7.04 (t, J = 8.4 Hz, 2H), 4.15 (dt, J = 14.8, 7.2 Hz, 2H), 3.98 (s, 6H), 3.25 (d, J = 7.6 Hz, 4H), 2.30 (d, J = 14.4 Hz, 1H), 1.81 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.9 (d, J = 2.0 Hz, $^4\text{J}_{\text{CF}}$), 152.9 (d, J = 11.0 Hz, $^2\text{J}_{\text{CF}}$), 152.3 (d, J = 248.0 Hz, $^1\text{J}_{\text{CF}}$), 127.2 (d, J = 5.0 Hz, $^3\text{J}_{\text{CF}}$), 125.9 (d, J = 3.0 Hz, $^3\text{J}_{\text{CF}}$), 116.1 (d, J = 19.0 Hz, $^2\text{J}_{\text{CF}}$), 112.7 (d, J = 1.0 Hz, $^4\text{J}_{\text{CF}}$), 56.4, 52.6, 41.8, 31.4. ^{19}F NMR (376 MHz, CDCl_3) δ -132.68 (s, 2F). HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{F}_2\text{O}_6\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 461.0841, found 461.0840.



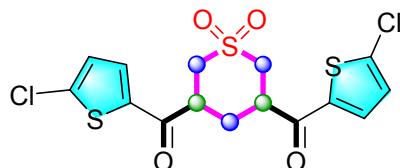
(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis(naphthalen-2-ylmethanone) (3ac):

Yield 60%; 26.5 mg; white solid; mp 211–216 °C; R_f 0.26 (EtOAc/petroleum ether = 1:4); ^1H NMR (400 MHz, DMSO- d_6) δ 9.08 (s, 2H), 8.38–8.19 (m, 2H), 8.09–7.84 (m, 6H), 7.66 (q, J = 5.7, 3.6 Hz, 4H), 4.64 (t, J = 12.0 Hz, 2H), 3.56 (t, J = 12.8 Hz, 2H), 3.44 (d, J = 13.6 Hz, 2H), 2.43 (d, J = 13.2 Hz, 1H), 1.64 (q, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 198.0, 135.2, 132.3, 131.5, 130.9, 129.7, 129.0, 128.6, 127.6, 127.0, 123.8, 51.3, 42.3, 32.6. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{22}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$) $^+$ 465.1131, found 465.1132.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis(thiophen-2-ylmethanone) (3ad):

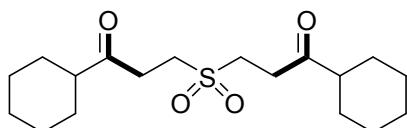
Yield 64%; 22.7 mg; white solid; mp 179–183 °C; R_f 0.27 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, DMSO- d_6) δ 8.30 (d, J = 3.2 Hz, 2H), 8.07 (d, J = 4.4 Hz, 2H), 7.38–7.24 (m, 2H), 4.20 (t, J = 12.0 Hz, 2H), 3.46 (t, J = 12.8 Hz, 2H), 3.33 (s, 2H), 2.26 (d, J = 13.2 Hz, 1H), 1.79–1.64 (m, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.2, 141.8, 136.3, 134.4, 129.1, 51.0, 43.0, 32.5. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_4\text{S}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 376.9946, found 376.9947.



(1,1-dioxidotetrahydro-2H-thiopyran-3,5-diyl)bis((5-chlorothiophen-2-yl)methanone)

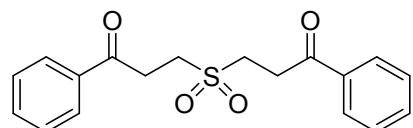
(3ae):

Yield 56%; 23.6 mg; white solid; mp 186–189 °C; R_f 0.29 (EtOAc/petroleum ether = 1:3); ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 4.0 Hz, 2H), 7.03 (d, J = 4.0 Hz, 2H), 4.09–3.84 (m, 2H), 3.40–3.12 (m, 4H), 2.33 (d, J = 14.4 Hz, 1H), 2.04–1.85 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 188.8, 142.0, 139.8, 132.5, 128.1, 52.3, 42.7, 31.6. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{Cl}_2\text{O}_4\text{S}_3\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 444.9167, found 444.9170.



3,3'-sulfonylbis(1-cyclohexylpropan-1-one) (3ba):

Yield 68%; 23.3 mg; white solid; mp 146–149 °C; R_f 0.38 (EtOAc/petroleum ether = 1:3); ^1H NMR (600 MHz, CDCl_3) δ 3.27 (t, J = 7.2 Hz, 4H), 3.02 (t, J = 7.2 Hz, 4H), 2.41 (t, J = 11.4 Hz, 2H), 2.14–1.58 (m, 10H), 1.29 (dtd, J = 51.5, 24.3, 12.1 Hz, 10H). ^{13}C NMR (150 MHz, CDCl_3) δ 209.5, 50.7, 47.7, 32.3, 28.4, 25.6, 25.4. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 365.1757, found 365.1753.



3,3'-sulfonylbis(1-phenylpropan-1-one) (1a''):

White solid; mp 173–176 °C; R_f 0.22 (EtOAc/petroleum ether = 1:2); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 7.6 Hz, 4H), 7.62 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 4H), 3.67–3.59 (m, 4H), 3.59–3.51 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.6, 135.7, 133.9, 128.8, 128.2, 48.2, 30.9. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{SNa}^+$ ($\text{M}+\text{Na}$)⁺ 353.0818, found 353.0815.

7. Crystallographic data and molecular structure of compounds **3o** and **3u**.

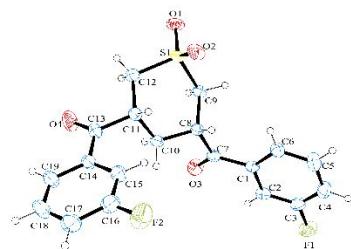


Figure 1. Molecular structure of **3o** with 30% probability ellipsoids (ORTEP)

Crystal Data for Compound **3o**: CCDC 2201136 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 20 mg of pure **3o** was completely dissolved in the mixed solvent of 3 mL CH_2Cl_2 and 1 mL MeOH, and then 2 mL of

n-hexane was added slowly. After a week of solvent evaporation, some colorless transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo K α radiation (0.71073 Å) at room temperature.

Bond precision:	C-C = 0.0026 Å	Wavelength=0.71073	
Cell:	a=16.870 (3)	b=5.4798 (9)	c=18.573 (3)
	alpha=90	beta=91.413 (2)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1716.4 (5)	1716.5 (5)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C19 H16 F2 O4 S	C19 H16 F2 O4 S	
Sum formula	C19 H16 F2 O4 S	C19 H16 F2 O4 S	
Mr	378.38	378.38	
Dx, g cm ⁻³	1.464	1.464	
Z	4	4	
μ (mm ⁻¹)	0.232	0.232	
F000	784.0	784.0	
F000'	784.98		
h, k, lmax	25, 8, 27	24, 8, 27	
Nref	5913	5442	
Tmin, Tmax	0.946, 0.955	0.675, 0.746	
Tmin'	0.933		
Correction method= # Reported T Limits: Tmin=0.675 Tmax=0.746			
AbsCorr = MULTI-SCAN			
Data completeness= 0.920		Theta(max)= 31.935	
R(reflections)= 0.0498 (4193)		wR2 (reflections)= 0.1607 (5442)	
S = 1.034		Npar= 235	

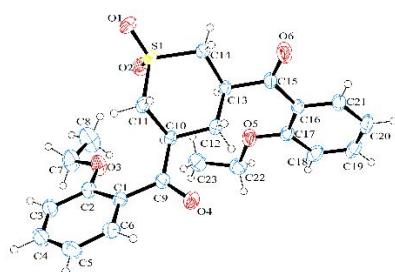


Figure 2. Molecular structure of **3u** with 30% probability ellipsoids (ORTEP)

Crystal Data for Compound **3u**: CCDC 2201137 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 20 mg of pure **3u** was completely dissolved in the mixed solvent of 3 mL CH₂Cl₂ and 1 mL MeOH, and then 2 mL of n-hexane was added slowly. After a week of solvent evaporation, some colorless

transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo K α radiation (0.71073 Å) at room temperature.

Bond precision:	C-C = 0.0025 Å	Wavelength=0.71073	
Cell:	a=13.476 (2)	b=15.227 (2)	c=10.6526 (17)
	alpha=90	beta=105.604 (2)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	2105.3(5)	2105.3(6)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H26 O6 S	C23 H26 O6 S	
Sum formula	C23 H26 O6 S	C23 H26 O6 S	
Mr	430.50	430.50	
Dx, g cm ⁻³	1.358	1.358	
Z	4	4	
Mu (mm ⁻¹)	0.191	0.191	
F000	912.0	912.0	
F000'	912.96		
h, k, lmax	20, 22, 15	19, 21, 15	
Nref	7243	6813	
Tmin, Tmax	0.955, 0.972	0.686, 0.746	
Tmin'	0.944		
Correction method= # Reported T Limits: Tmin=0.686 Tmax=0.746			
AbsCorr = MULTI-SCAN			
Data completeness= 0.941		Theta(max)= 31.892	
R(reflections)= 0.0512(4623)		wR2 (reflections)=	0.1847(6813)
S = 1.197	Npar= 273		

8. References

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2. Messinger, P.; Vietinghoff-Scheel, R. V. *Arch. Pharm. Med. Chem.* **1985**, *318*, 806.

9.¹H, ¹³C and ¹⁹F NMR spectras

