

Catalytic Conjugate Addition of Acyl Anion Equivalents Promoted by Fluorodesilylation

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SUPPORTING INFORMATION

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General Experimental

All reactions were performed in flame-dried, glassware under an atmosphere of dry argon unless otherwise noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, ACS grade, BHT stabilized), and dichloromethane (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Methanol and ethanol were distilled from magnesium turnings under a nitrogen atmosphere. Solvents for filtration, transfers, chromatography, and recrystallization were purchased from Fisher (certified ACS grade) and used as received. "Brine" refers to a saturated solution of sodium chloride in distilled water. Column chromatography was performed using Merck grade 9385, 60 Å silica gel. Visualization was accomplished by UV light, iodine vapor, potassium permanganate solution, or phosphomolybdic acid solution. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F₂₅₄ indicator. R_f values reported were measured using a 10 × 2 cm TLC plate in a developing chamber containing the solvent system described. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples unless otherwise noted.

¹H, ¹³C and ¹⁹F NMR spectra were recorded on Varian Unity-400 or 500 MHz (400 or 500 MHz, ¹H; 126 MHz, ¹³C; 470 MHz, ¹⁹F) spectrometers. Spectra are referenced to residual chloroform (δ = 7.26 ppm, ¹H; 77.16 ppm, ¹³C), residual methanol (δ = 3.31 ppm, ¹H; 49.0 ppm, ¹³C), toluene (δ = 2.09 ppm, ¹H; 20.4 ppm, ¹³C) or THF (δ = 3.58 ppm, ¹H; 73.78 ppm, ¹³C). Neat trichlorofluoromethane (0.00 ppm) was used as an external reference for ¹⁹F NMR. Chemical shifts are reported in parts per million, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), sext (sextet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz, and integration is provided. Assignments were obtained by reference to COSY, HMQC, and HMBC correlations. Elemental analysis was performed by the University of Illinois Microanalysis Laboratory or Robertson Microlit Laboratories. Mass spectrometry (MS) was performed by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnagin-MAT C5 spectrometer. Chemical Ionization (CI) spectra were performed with methane reagent gas on a Micromass 70-VSE spectrometer. Electrospray Ionization (ESI) spectra were performed on a Micromass Q-ToF Ultima spectrometer. Data are reported in the form of *m/z* (intensity relative to the base peak = 100). Infrared spectra (IR) were recorded in KBr pellets on a Perkin-Elmer FT-IR system and peaks were reported in cm⁻¹ with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T); w (weak, 67–100% T). Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are corrected. Analytical supercritical fluid chromatography (SFC) was performed on an Agilent 1100 HPLC equipped with an Aurora Systems A-5 supercritical CO₂

adapter for supercritical fluid chromatography and a UV detector (220 nm or 254 nm) using a Diacel Chiralcel AS column.

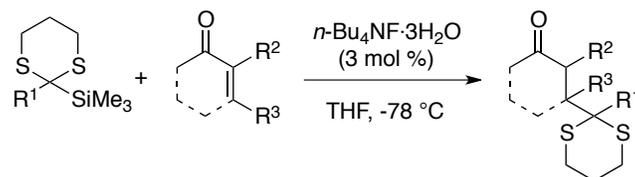
The following commercial reagents were used as received. 1,3-Propanedithiol (99%), iodine (>99.8%, ACS grade), chromone (99%), coumarin ($\geq 99\%$), methyl cinnamate (99%), ammonium chloride ($\geq 99.5\%$, ACS grade) and tetrabutylammonium bromide (99%) were purchased from Aldrich. Chloroform (ACS grade), trichloroacetic acid (ACS grade), sodium bicarbonate (ACS grade), magnesium sulfate (anhydrous, certified), sodium chloride (ACS grade), sodium thiosulfate (anhydrous, certified), sodium hydroxide (ACS grade) and potassium permanganate (ACS grade) were purchased from Fisher. Sodium sulfate (anhydrous) was purchased from EMD Millipore. 4,4-Dimethyl-2-cyclohexen-1-one (95%) was purchased from Oakwood Chemical. (*R*)-(-)-Carvone (98%) and 3-phenylpropionaldehyde (95%) were purchased from Alfa Aesar. Sodium periodate (99%) was purchased from Acros Organics. The following commercial reagents were purified prior to use. Chlorotrimethylsilane (>98%, Aldrich), 2-tolualdehyde (>98%, Fluka), 2-cyclohexen-1-one ($\geq 95\%$, Aldrich), 2-cyclopenten-1-one (98%, Aldrich), 2-cyclohepten-1-one (80% tech. grade, Aldrich), *trans*-cinnamaldehyde (99%, Aldrich), and 3-methyl-2-cyclohexen-1-one (98%, Aldrich) were distilled to a constant boiling point and stored under Ar. Boron trifluoride diethyl etherate ($\geq 99.5\%$, Aldrich) was diluted in excess anhydrous diethyl ether, and fractionally distilled under reduced pressure over CaH₂. *n*-Butyl lithium in hexanes (Aldrich) was filtered and titrated by the method of Gilman¹ prior to use. Chalcone was recrystallized from ethanol prior to use. Tetrabutylammonium fluoride trihydrate ($\geq 97\%$, Fluka) was used as received, dissolved in anhydrous THF to give a colorless 0.2 M solution, and stored at rt under Ar in a Teflon-sealed Schlenk flask.

Literature Preparations

The following compounds were prepared by literature methods and characterization matched the data previously reported: 2-phenyl-1,3-dithiane,² 2-phenyl-2-trimethylsilyl-1,3-dithiane (**1a**),³ and 2-(4-cyanophenyl)-1,3-dithiane.⁴

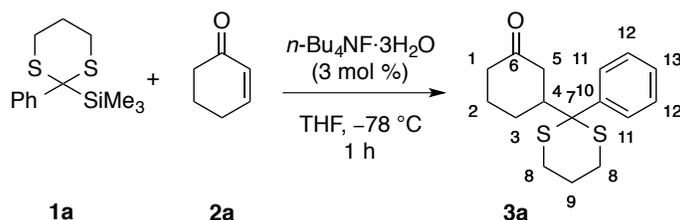
Experimental Procedures

I. General Procedure: TBAF Catalyzed Conjugate Addition of Dithiane Nucleophile



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added the silyldithiane (1.5 equiv). The flask was evacuated and backfilled with Ar twice, then Michael acceptor (1.0 equiv) and THF (0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to $-78\text{ }^{\circ}\text{C}$ (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (3 mol %) was added as a freshly prepared solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at $-78\text{ }^{\circ}\text{C}$. Reaction progress was monitored by disappearance of Michael acceptor by TLC or ^1H NMR analysis. Upon complete consumption of Michael acceptor, the reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with 5.0 mL of 2 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was stirred at rt for 1.5 h. The reaction mixture was transferred to a separatory funnel with diethyl ether and was neutralized with sat. NaHCO_3 (aq). The aqueous layer was extracted with diethyl ether once and the combined organic layer was washed with distilled water twice and brine once. The solution was dried over MgSO_4 or Na_2SO_4 , concentrated, and dried at room temperature under reduced pressure (0.1 mm Hg). Purification by column chromatography yielded the desired compound.

Preparation of 3-(2-Phenyl-1,3-dithian-2-yl)cyclohexan-1-one (**3a**)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added silyldithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclohexen-1-one **2a** (96 mg, 97 μL , 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to $-78\text{ }^{\circ}\text{C}$ (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL , 3 mol %) was added dropwise as a freshly prepared solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. Reaction progress was monitored by disappearance of **2a** by TLC (4:1

hexanes/TBME). The reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was stirred for 1.5 h at rt. The reaction mixture was transferred with 30 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1×30 mL). The combined organic layer was washed with distilled water (2×25 mL) and saturated brine (1×30 mL), dried over MgSO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, $25\text{ }^{\circ}\text{C}$). The colorless oil was dried under vacuum (0.1 mm Hg, $25\text{ }^{\circ}\text{C}$) for 1 h to yield 428 mg of a thick colorless oil. Purification by flash chromatography (30 g SiO_2 , 170 mm \times 25 mm, 10 mL fractions, hexanes/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 282 mg (96%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling ethanol (10 mL), cooled to room temperature, then cooled to $-20\text{ }^{\circ}\text{C}$ for 48 h. The shiny white plates were collected by vacuum filtration, washed with ice-cold ethanol, and dried under reduced pressure at rt (0.1 mm Hg) for 2 h to yield 180 mg (62%) as shiny white crystals.

Data for 3a:

m.p.: 124–126 $^{\circ}\text{C}$ (from EtOH)

^1H NMR: (500 MHz, CDCl_3)
7.89 (d, $J = 7.4$ Hz, 2 H, HC(11)), 7.38 (t, $J = 7.8$ Hz, 2 H, HC(12)), 7.26 (t, $J = 7.3$ Hz, 1 H, HC(13)), 2.69–2.64 (m, 4 H, $\text{H}_2\text{C}(8)$), 2.61 (ddt, $J = 14.0, 3.4, 2.3$ Hz, 1 H, $\text{H}_2\text{C}(5)$), 2.33–2.23 (m, 2 H, $\text{H}_2\text{C}(1)$, $\text{H}_2\text{C}(4)$), 2.22–2.18 (m, 1 H, $\text{H}_2\text{C}(3)$), 2.18–2.08 (m, 2 H, $\text{H}_2\text{C}(1)$, $\text{H}_2\text{C}(5)$), 2.02 (ddt, $J = 12.2, 6.2, 3.2$ Hz, 1 H, $\text{H}_2\text{C}(2)$), 1.95–1.85 (m, 2 H, $\text{H}_2\text{C}(9)$), 1.50 (ddd, $J = 13.0, 4.3, 3.0$ Hz, 1 H, $\text{H}_2\text{C}(2)$), 1.47–1.37 (m, 1 H, $\text{H}_2\text{C}(3)$).

^{13}C NMR: (126 MHz, CDCl_3)
211.0 (C(6)), 139.2 (HC(1)), 130.3 (HC(11)), 128.7 (HC(12)), 127.3 (HC(13)), 63.8 (C(7)), 50.6 (HC(4)), 43.3 ($\text{H}_2\text{C}(5)$), 41.2 ($\text{H}_2\text{C}(1)$), 27.7 ($\text{H}_2\text{C}(8)$), 27.7 ($\text{H}_2\text{C}(8)$), 26.5 ($\text{H}_2\text{C}(3)$), 25.4 ($\text{H}_2\text{C}(9)$), 24.7 ($\text{H}_2\text{C}(2)$).

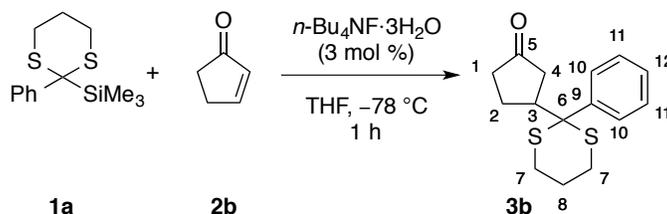
IR: (KBr)
2940 (m), 2898 (m), 2857 (w), 1705 (s), 1486 (m), 1420 (m), 1344 (m), 1264 (m), 1222 (m), 1046 (w), 914 (w), 761 (w), 706 (s).

LRMS: (EI, 70 eV)
51.0 (3), 55.1 (3), 77.1 (7), 91.1 (5), 106.0 (4), 115.0 (9), 121.0 (24), 122.0 (4), 128.1 (6), 129.1 (7), 149.0 (3), 149.1 (3), 157.1 (2), 160.0 (3), 161.0 (3), 185.1 (2), 195.0 (100), 196.0 (12), 197.0 (10), 292.1 (6).

Analysis: C₁₆H₂₀OS₂ (292.45)
 calcd: C, 65.71 H, 6.89
 found: C, 65.77 H, 6.97

TLC: *R_f* 0.28 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 3-(2-Phenyl-1,3-dithian-2-yl)cyclopentan-1-one (**3b**)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclopenten-1-one **2b** (82 mg, 84 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a freshly prepared solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at -78 °C for 1 h. Reaction progress was monitored by disappearance of **2b** by TLC (4:1 hexanes/TBME). The reaction was quenched at -78 °C with 2.5 mL of 2.0 M Cl₃CCO₂H in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was stirred at rt for 1 h. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over MgSO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 Mm Hg, 25 °C) for 1 h to yield 492 mg of a white solid. Adsorption of the crude material onto celite and purification by flash chromatography (30 g SiO₂, 170 mm \times 25 mm, 10 mL fractions, hexanes/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 264 mg (95%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of warm TBME (10 mL), cooled to room temperature, placed in a closed diffusion container with pentane and let crystallize at room temperature for 2 d. The fine white needles were collected by vacuum filtration, washed with pentane, and dried under reduced pressure at rt (0.1 mm Hg) for 2 h to yield 184 mg (66%) as fluffy white crystals.

Data for **3b**:

m.p.: 126–128 °C (from TBME/pentane)

¹H NMR: (500 MHz, CDCl₃)
 7.98 (d, *J* = 7.7 Hz, 2 H, HC(10)), 7.41 (t, *J* = 7.8 Hz, 2 H, HC(11)), 7.29 (t, *J* = 7.3 Hz, 1 H, HC(12)), 2.77–2.57 (m, 5 H, H₂C(7), HC(3)), 2.32 (d, *J* = 9.7 Hz, 2 H, H₂C(4)), 2.23–2.12 (m, 1 H, H₂C(1)), 2.11–1.97 (m, 2 H, H₂C(1), H₂C(2)), 1.96–1.77 (m, 3 H, H₂C(8), H₂C(2)).

¹³C NMR: (126 MHz, CDCl₃)
 217.4 (C(5)), 139.5 (C(9)), 130.0 (HC(10)), 128.9 (HC(11)), 127.4 (HC(12)), 62.7 (C(6)), 49.9 (HC(3)), 40.8 (H₂C(4)), 38.6 (H₂C(1)), 27.6 (H₂C(7)), 27.5 (H₂C(7)), 25.3 (H₂C(8)), 24.4 (H₂C(2)).

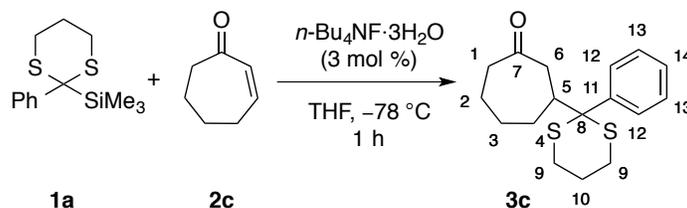
IR: (KBr)
 2933 (w), 2989 (m), 2829 (w), 1732 (s), 1483 (m), 1441 (m), 1392 (m), 1275 (m), 1240 (m), 1160 (m), 1124 (m), 1049 (w), 907 (w), 730 (w), 706 (m).

LRMS: (EI, 70 eV):
 55.1 (4), 77.1 (8), 91.1 (4), 106.0 (5), 115.1 (16), 121.0 (28), 129.1 (13), 143.1 (6), 148.0 (5), 162.0 (9), 171.1 (5), 176.0 (8), 204.1 (2), 195.0 (100), 278.1 (14).

Analysis: C₁₅H₁₈OS₂ (278.43)
 calcd: C, 64.71 H, 6.52
 found: C, 64.56 H, 6.61

TLC: *R_f* 0.31 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 3-(2-Phenyl-1,3-dithian-2-yl)cycloheptan-1-one (3c)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclohepten-1-one **2c** (110 mg, 112 μL, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL, 3 mol %) was added dropwise as a freshly prepared solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at -78 °C for 1 h. Reaction progress was monitored by disappearance of enone by TLC (4:1 hexanes/TBME). The reaction was quenched at -78 °C with 6.0 mL of 2.0 M Cl₃CCO₂H in THF

resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 × 30 mL). The combined organics was washed with distilled water (2 × 25 mL) and saturated brine (1 × 30 mL), dried over MgSO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 1 h to yield 428 mg of a thick colorless oil. Purification by flash chromatography (33 g SiO₂, 180 mm × 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 297 mg (97%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling ethanol (10 mL), cooled to room temperature, and then crystallized at -20 °C for 2 d. The shiny white plates were collected by vacuum filtration, washed with ice-cold ethanol, and dried under reduced pressure at rt (0.1 mm Hg) for 2 h to yield 189 mg (62%) as fluffy white crystals.

Data for 3c:

m.p.: 96–97 °C (from EtOH)

¹H NMR: (500 MHz, CDCl₃)
7.91 (d, *J* = 7.5 Hz, 2 H, HC(12)), 7.39 (t, *J* = 7.8 Hz, 2 H, HC(13)), 7.27 (t, *J* = 7.3 Hz, 1 H, HC(14)), 2.77 (dt, *J* = 15.2, 2.4 Hz, 1 H, H₂C(6)), 2.69–2.57 (m, 4 H, H₂C(9)), 2.48 (ddd, *J* = 13.9, 12.3, 3.7 Hz, 1 H, H₂C(1)), 2.42–2.33 (m, 3 H, H₂C(1), H₂C(6), H₂C(4)), 2.25 (ddt, *J* = 13.0, 9.9, 2.3 Hz, 1 H, HC(5)), 2.00–1.79 (m, 4 H, H₂C(2), H₂C(10), H₂C(3)), 1.45 (tdd, 14.9, 12.0, 2.9 Hz, 1 H, H₂(2)), 1.33 (dtt, *J* = 14.8, 12.0, 2.7 Hz, 1 H, H₂C(3)), 1.10 (dddd, *J* = 14.6, 12.5, 10.2, 2.6 Hz, 1 H, H₂C(4)).

¹³C NMR: (126 MHz, CDCl₃)
213.5 (C(7)), 139.4 (C(11)), 130.1 (HC(13)), 128.6 (HC(13)), 127.3 (HC(14)), 64.8 (C(8)), 48.4 (HC(5)), 45.6 (H₂C(6)), 43.5 (H₂C(1)), 31.7 (H₂C(4)), 29.4 (H₂C(3)), 27.7 (H₂C(9)), 27.6 (H₂C(9)), 25.2 (H₂C(10)), 25.1 (H₂C(2)).

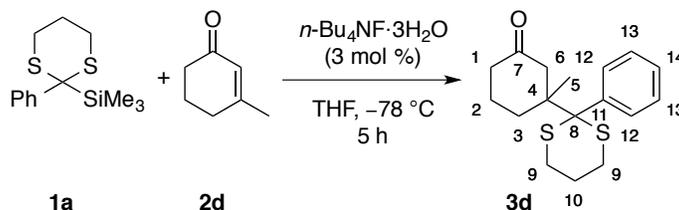
IR: (KBr)
2926 (s), 2898 (s), 2850 (m), 1698 (s), 1483 (m), 1441 (s), 1420 (m), 1344 (w), 1268 (m), 1240 (w), 1202 (w), 1163 (w), 1035 (w), 758 (m), 706 (s).

LRMS: (EI, 70 eV)
51.0 (2), 55.1 (5), 77.1 (7), 91.1 (6), 106.0 (4), 115.1 (10), 121.0 (26), 129.1 (7), 141.1 (3), 149.1 (3), 174.1 (2), 195.0 (100), 306.1 (6).

Analysis: C₁₇H₂₂OS₂ (306.49)
 calcd: C, 66.62 H, 7.24
 found: C, 66.36 H, 7.31

TLC: R_f 0.32 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 3-Methyl-3-(2-phenyl-1,3-dithian-2-yl)cyclohexan-1-one (**3d**)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 3-methyl-2-cyclohexen-1-one **2d** (110 mg, 113.5 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned yellow upon addition of fluoride and was stirred at -78 °C for 5 h. Reaction progress was monitored by disappearance of enone by ¹H NMR (10 μ L aliquot in CDCl₃, monitor alkenyl peak of enone at 5.85 ppm). The reaction appeared to stall at nearly complete conversion and was quenched at -78 °C with 6.0 mL of 2.0 M Cl₃CCO₂H in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over Na₂SO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 1 h to yield 404 mg of a colorless oil. Adsorption of the crude material on celite and purification by flash chromatography (31 g SiO₂, 175 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 247 mg (80%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling methanol (5 mL), cooled to room temperature, and then crystallized at -20 °C. The small crystals were collected by vacuum filtration, washed with ice-cold methanol, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 202 mg (66%) as small white crystals.

Data for 3d:

m.p.: 106–108 °C (from MeOH)

¹H NMR: (500 MHz, CDCl₃)

7.97 (d, *J* = 7.9 Hz, 2 H, HC(12)), 7.40 (t, *J* = 7.8 Hz, 2 H, HC(13)), 7.27 (t, *J* = 7.2 Hz, 1 H, HC(14)), 2.79 (br d, *J* = 13.8 Hz, 1 H, H₂C(5)), 2.71–2.63 (m, 2 H, H₂C(9)), 2.62–2.50 (m, 2 H, H₂C(9)), 2.35 (br d, *J* = 13.5 Hz, 1 H, H₂C(5)), 2.28 (br d, *J* = 14.0 Hz, 1 H, H₂C(1)), 2.25–2.08 (m, 2 H, H₂C(1), H₂C(3)), 1.94 (ddt, *J* = 13.5, 6.6, 3.2 Hz, 1 H, H₂C(2)), 1.86–1.79 (m, 3 H, H₂C(3), H₂C(10)), 1.70 (tdt, *J* = 13.5, 9.1, 4.2 Hz, 1 H, H₂C(1)), 1.04 (s, 3 H, H₃C(7)).

¹³C NMR: (126 MHz, CDCl₃)

211.9 (O=C(6)), 137.1 (C(11)), 132.3 (HC(12)), 128.2 (HC(13)), 127.1 (HC(14)), 70.4 (C(8)), 49.3 (H₂C(5)), 47.4 C(4), 40.9 (H₂C(1)), 31.4 (H₂C(3), 28.1 (H₂C(9)), 28.1 (H₂C(9)), 25.2 (H₂C(10)), 21.7 (H₂C(2)), 20.0 (H₃C(7)).

IR: 3052 (w), 2961 (s), 2989 (s), 1705 (s), 1587 (m), 1476 (m), 1441 (s), 1386 (s), 1347 (m), 1313 (s), 1275 (s), 1233 (s), 1153 (m), 1108 (m), 1073 (m), 1035 (m), 907 (m), 848 (m), 796 (m), 765 (m), 733 (s), 706 (s), 678 (m), 626 (m).

LRMS: (EI, 70 eV)

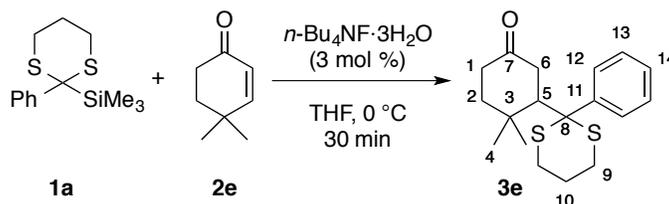
51.0 (3), 55.0 (7), 55.1 (6), 77.0 (7), 91.0 (5), 105.0 (2), 105.9 (4), 115.0 (5), 120.9 (38), 121.9 (4), 122.9 (2), 127.0 (2), 128.0 (5), 129.0 (7), 194.9 (100), 195.9 (13), 196.9 (10), 197.9 (1), 306.0 (3.4).

Analysis: C₁₇H₂₂OS₂ (306.49)

calcd: C, 66.62 H, 7.24

found: C, 66.49 H, 7.31

TLC: *R_f* 0.32 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 4,4-Dimethyl-3-(2-phenyl-1,3-dithian-2-yl)cyclohexanone (3e)

To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 4,4-dimethyl-2-cyclohexen-1-one **2e** (124 mg, 132 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and

cooled to 0 °C (ice bath). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at 0 °C for 30 min. Reaction progress was monitored by disappearance of enone by ^1H NMR (15 μ L aliquot in CDCl_3 , monitor alkenyl peaks of enone at 5.66 and 5.81 ppm). Complete conversion was observed at 30 min and the reaction was quenched at 0 °C with 5.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 1 h to yield 567 mg of a white solid. Adsorption of the crude material on celite and purification by flash chromatography (31 g SiO_2 , 175 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 288 mg (89%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling isopropyl alcohol (5 mL), cooled to room temperature, and then crystallized at -20 °C. The crystals were collected by vacuum filtration, washed with ice-cold isopropanol, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 222 mg (69%) as plate-like white crystals.

Data for 3e:

m.p.: 148–150 °C (from *i*-PrOH)

^1H NMR: (500 MHz, CDCl_3)

7.98 (d, $J = 7.7$ Hz, 2 H, HC(12)), 7.37 (t, $J = 7.7$ Hz, 2 H, HC(13)), 7.27 (t, $J = 7.4$ Hz, 1 H, HC(14)), 3.12 (ddd, $J = 15.7, 3.8, 1.8$ Hz, 1 H, $\text{H}_2\text{C}(5)$), 2.91 (dd, $J = 15.6, 12.9$ Hz, 1 H, $\text{H}_2\text{C}(5)$), 2.79 (ddd, $J = 14.2, 9.6, 6.2$ Hz, 1 H, $\text{H}_2\text{C}(9)$), 2.63 (dt, $J = 14.1, 3.6$ Hz, 1 H, $\text{H}_2\text{C}(9)$), 2.59–2.54 (m, 2 H, $\text{H}_2\text{C}(9)$), 2.39 (ddd, $J = 15.6, 12.9, 6.4$ Hz, 1 H, $\text{H}_2\text{C}(1)$), 2.29 (dd, $J = 12.8, 3.9$ Hz, 1 H, HC(4)), 2.21 (dtd, $J = 15.6, 4.5, 2.0$ Hz, 1 H, $\text{H}_2\text{C}(1)$), 1.87–1.80 (m, 2 H, $\text{H}_2\text{C}(10)$), 1.54 (td, $J = 13.2, 12.7, 4.8$ Hz, 1 H, $\text{H}_2\text{C}(2)$), 1.44 (ddd, $J = 13.9, 6.2, 4.2$ Hz, 1 H, $\text{H}_2\text{C}(2)$), 1.13 (s, 3 H, $\text{H}_3\text{C}(7)$), 0.55 (s, 3 H, $\text{H}_3\text{C}(7)$).

^{13}C NMR: (126 MHz, CDCl_3)

211.9 (O=C(6)), 141.3 (C(11)), 131.0 (HC(12)), 128.5 (HC(13)), 127.3 (HC(14)), 65.1 (C(8)), 58.0 (HC(4)), 43.4 ($\text{H}_2\text{C}(2)$), 41.8 ($\text{H}_2\text{C}(5)$), 37.8 ($\text{H}_2\text{C}(1)$), 36.5 (C(3)), 31.1 ($\text{H}_3\text{C}(7)$), 28.0 ($\text{H}_2\text{C}(9)$), 28.0 ($\text{H}_2\text{C}(9)$), 24.9 ($\text{H}_2\text{C}(10)$), 22.6 ($\text{H}_3\text{C}(7)$).

IR: 3045 (w), 2940 (s), 2905 (s), 1705 (s), 1479 (m), 1444 (m), 1420 (m), 1368 (m), 1344 (m), 1299 (m), 1278 (m), 1240 (w), 1153 (m), 1122 (w), 1014 (m), 903 (w), 855 (m), 754

(s), 702 (s).

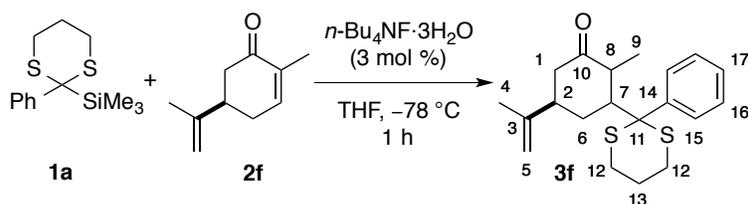
LRMS: (EI, 70 eV)

51.0 (6), 55.1 (13), 69.0 (15), 77.0 (13), 91.0 (10), 106.0 (12), 115.0 (23), 121.0 (34), 122.0 (5), 128.0 (6), 129.0 (8), 142.1 (5), 149.0 (8), 157.1 (8), 158.1 (7), 176.0 (6), 177.0 (8), 195.0 (100), 196.0 (14), 197.0 (11), 320.1 (7), 321.1 (2), 322.1 (1).

Analysis: C₁₈H₂₄OS₂ (320.51)

calcd: C, 67.45 H, 7.55

found: C, 66.29 H, 7.68

TLC: *R_f* 0.29 (silica gel, hexanes/TBME 4:1, UV/I₂)**Preparation of (5*R*)-2-Methyl-3-(2-phenyl-1,3-dithian-2-yl)-5-(prop-1-en-2-yl)cyclohexanone (3f)**

To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then (*R*)-(-)-carvone **2f** (150 mg, 157 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) was added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at -78 °C for 1 h. Reaction progress was monitored by disappearance of enone as indicated by ¹H NMR (15 μ L aliquot in CDCl₃, disappearance of peak at 6.75 ppm). Complete conversion was observed after 1 h and the reaction was quenched at -78 °C with 6.0 mL of 2.0 M Cl₃CCO₂H in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over Na₂SO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 1 h to yield 340 mg of a colorless thick oil. Adsorption of the crude material on celite and purification by flash chromatography (31 g SiO₂, 175 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 341 mg (98%, mixture of 3 diastereomers dr 12:3:1). For

characterization a second column was performed for partial separation of the diastereomers ((31 g SiO₂, 175 mm × 25 mm, 10 mL fractions, 10 % TBME in hexanes). The following fractions were collected: fraction 9-13 (diastereomer 1, R_f = 0.32, 9:1 hexanes/TBME), fractions 14-17 (mixture of diastereomer 1 & 2, R_f = 0.32, R_f = 0.29, 9:1 hexanes/TBME), and fractions 18-32 (mixture of diastereomer 1 & 3, R_f = 0.32, R_f = 0.20, 9:1 hexanes/TBME). Fractions 9-13 (enriched in the major diastereomer 1) yielded 180 mg, 52% as a white solid and was used for the following characterization.

Data for 3f:

m.p.: 100–104 °C (after column)

¹H NMR: (500 MHz, CDCl₃)

7.93 (d, *J* = 7.6 Hz, 2 H, HC(15)), 7.40 (t, *J* = 7.9 Hz, 2 H, HC(16)), 7.28 (t, *J* = 7.3 Hz, 1 H, HC(17)), 4.84 (br s, minor diastereomer, H₂C(5)), 4.81–4.76 (m, 2 H, H₂C(5)), 4.61 (br s, minor diastereomer, H₂C(5)), 2.91–2.72 (m, 1 H, H₂C(12)), 2.70–2.56 (m, 3 H, H₂C(12)), 2.45 (t, *J* = 14.4 Hz, 1 H, H₂C(1)), 2.35 (br d, *J* = 12.9 Hz, 1 H, H₂C(6)), 2.27 (dd, *J* = 7.1, 3.9 Hz, 1 H, HC(8)), 2.22–2.09 (m, 3 H, H₂C(1), HC(2), HC(7)), 2.04 (dd, *J* = 13.1, 11.7 Hz, 1 H, H₂C(6)), 1.91–1.81 (m, 2 H, H₂C(13)), 1.76 (s, 3 H, H₃C(4)), 1.54 (s, minor diastereomer, H₃C(4)), 1.26 (d, *J* = 7.2 Hz, minor diastereomer, H₃C(9)), 1.21 (d, *J* = 7.1 Hz, 3 H, H₃C(9)).

¹³C NMR: (126 MHz, CDCl₃)

213.5 (O=C(10)), 147.3 (C(3)), 140.6 (C(14)), 129.5 (HC(15)), 128.8 (HC(16)), 127.3 (HC(17)), 110.3 (H₂C(5)), 63.8 (C(11)), 53.5 (HC(7)), 47.5 (HC(8)), 44.5 (HC(2)), 42.3 (H₂C(1)), 28.4 (H₂C(12)), 27.7 (H₂C(12)), 27.3 (H₂C(6)), 25.1 (H₂C(13)), 20.6 (H₃C(4)), 14.2 (H₃C(9)).

IR: (KBr)

3073 (w), 3059 (w), 2961 (m), 2933 (m), 2898 (m), 2850 (m), 1708 (s), 1642 (m), 1590 (w), 1479 (m), 1441 (m), 1420 (m), 1379 (m), 1240 (m), 1018 (m), 889 (m), 744 (m), 702 (s).

LRMS: (EI, 70 eV)

106.0 (7), 121.0 (18), 129.1 (8), 195.0 (100), 196.0 (12), 197.0 (10), 346.1 (8).

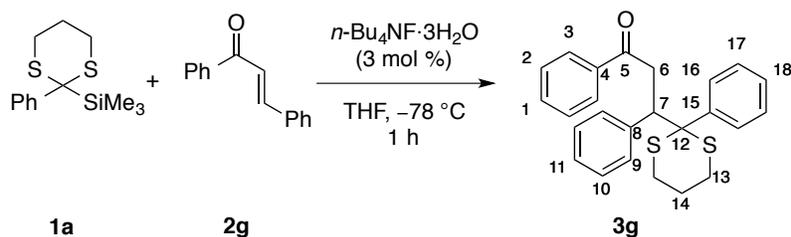
HRMS: C₂₀H₂₇OS₂ ([M+H]⁺, Q-TOF MS ES⁺):

calcd: 347.1503

found: 347.1513

TLC: R_f 0.41 (major diastereomer, silica gel, hexanes/TBME 4:1, UV/I₂)

R_f 0.35 (minor diastereomer, silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 1,3-Diphenyl-3-(2-phenyl-1,3-dithian-2-yl)propan-1-one (**3g**)

To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv) and *trans*-chalcone **2g** (208 mg, 1.0 mmol, 1.0 equiv). The flask was evacuated and backfilled with Ar twice, then THF (12.5 mL, 0.08 M) was added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to $-78\text{ }^{\circ}\text{C}$ (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL , 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. Reaction progress was monitored by disappearance of enone as indicated by TLC (4:1 hexanes/TBME). Complete conversion was observed after 1 h and the reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in loss of color to pale yellow. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O ($1 \times 30\text{ mL}$). The combined organics was washed with distilled water ($2 \times 25\text{ mL}$) and saturated brine ($1 \times 30\text{ mL}$), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, $25\text{ }^{\circ}\text{C}$). The colorless oil was dried under vacuum (0.1 mm Hg, $25\text{ }^{\circ}\text{C}$) for 2 h to yield 565 mg of a colorless oil/solid. Adsorption of the crude material on celite and purification by flash chromatography (32 g SiO_2 175 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a pale yellow solid, 370 mg (91%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of warm chloroform ($\sim 5\text{ mL}$), cooled to room temperature, and placed in a closed diffusion container with pentane and let crystallize at room temperature for one week. The small white needles were collected by vacuum filtration, washed with pentane, and dried under reduced pressure at rt (0.1 mm Hg) for 12 h to yield 309 mg (76%) as small white needles.

Data for **3g**:

m.p.: 136–138 $^{\circ}\text{C}$ (from CHCl_3 /pentane)

$^1\text{H NMR}$: (500 MHz, CDCl_3)

7.84 (d, $J = 7.2\text{ Hz}$, 2 H, HC(3)), 7.77 (d, $J = 7.5\text{ Hz}$, 2 H, HC(16)), 7.50 (t, $J = 7.4\text{ Hz}$, 1 H, HC(1)), 7.40 (t, $J = 7.7\text{ Hz}$, 2 H, HC(2)), 7.31 (t, $J = 7.4\text{ Hz}$, 2 H, HC(17)), 7.27–7.20

(m, 1 H, HC(18)), 7.14–7.04 (m, 3 H, HC(9), HC(11)), 6.94 (d, $J = 7.0$ Hz, 2 H, HC(10)), 4.00 (dd, $J = 10.5, 3.1$ Hz, 1 H, HC(7)), 3.94 (dd, $J = 17.2, 3.1$ Hz, 1 H, H₂C(6)), 3.61 (dd, $J = 17.2, 10.5$ Hz, 1 H, H₂C(6)), 2.71–2.58 (m, 4 H, H₂C(13)), 1.96–1.83 (m, 2 H, H₂C(14)).

¹³C NMR: (126 MHz, CDCl₃)
 197.9 (C(5)), 139.5 (C(15)), 138.2 (C(8)), 137.1 (C(4)), 133.0 (HC(1)), 130.5 (HC(16)), 130.2 (HC(10)), 128.6 (HC(2)), 128.3 (HC(17)), 128.2 (HC(3)), 127.3 (HC(9)), 127.2 (HC(11)), 127.2 (HC(18)), 64.7 (C(12)), 53.4 (HC(7)), 40.3 (H₂C(6)), 27.9 (H₂C(13)), 27.7 (H₂C(13)), 24.9 ((H₂C(14)).

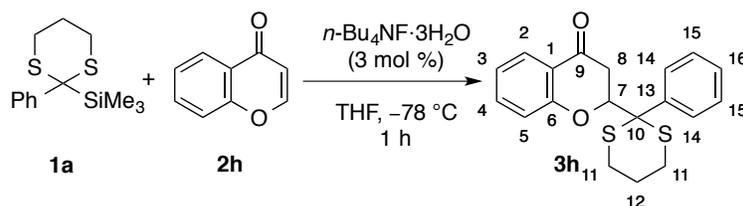
IR: (KBr)
 3052 (m), 3024 (m), 2891 (m), 2926 (m), 1680 (s), 1597 (m), 1576 (w), 1483 (m), 1444 (s), 1403 (m), 1344 (m), 1275 (s), 1073 (w), 983 (m), 907 (w), 751 (s), 699 (s), 595 (m).

LRMS: (EI, 70 eV)
 51.0 (6), 77.1 (23), 78.1 (3), 91.1 (4), 103.1 (3), 105.0 (27), 106.0 (3), 115.1 (4), 121.0 (30), 122.0 (3), 165.1 (2), 178.1 (5), 179.1 (3), 191.1 (4), 192.1 (2), 193.1 (6), 195.0 (100), 196.0 (22), 197.0 (16), 297.1 (9), 298.2 (12), 299.1 (4), 405.1 (5).

Analysis: C₁₆H₂₀OS₂ (404.59)
 calcd: C, 74.22 H, 5.98
 found: C, 74.27 H, 5.94

TLC: R_f 0.38 (silica gel, hexanes/TBME 4:1, UV/I₂/KMnO₄)

Preparation of 2-(2-Phenyl-1,3-dithian-2-yl)chroman-4-one (3h)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv) and chromone **2h** (146 mg, 1.0 mmol, 1.0 equiv). The flask was evacuated and backfilled with Ar twice, then THF (12.5 mL, 0.08 M) was added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78°C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL , 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned bright yellow upon addition of fluoride and was stirred at -78°C for 1 h over which the reaction color changed to orange. Reaction progress was monitored by disappearance of

enone as indicated by TLC (4:1 hexanes/TBME). Complete conversion was observed after 1 h and the reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1×30 mL). The combined organics was washed with distilled water (2×25 mL) and saturated brine (1×30 mL), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, $25\text{ }^{\circ}\text{C}$). The colorless oil was dried under vacuum (0.1 mm Hg, $25\text{ }^{\circ}\text{C}$) for 1 h to yield 404 mg of a colorless oil/solid mixture. Adsorption of the crude material on celite and purification by flash chromatography (32 g SiO_2 , 175 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 5:1) yields the desired compound as a white solid, 297 mg (87%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling ethanol (10 mL), cooled to room temperature, and then crystallized at $-20\text{ }^{\circ}\text{C}$ for 2 d. The small white needles were collected by vacuum filtration, washed with ice-cold ethanol, and dried under reduced pressure at rt (0.1 mm Hg) for 2 h to yield 164 mg (48%) as small white needles.

Data for 3h:

m.p.: 140–141 $^{\circ}\text{C}$ (from EtOH)

^1H NMR: (500 MHz, CDCl_3)

8.02 (d, $J = 7.4$ Hz, 2 H, HC(14)), 7.79 (dd, $J = 7.8$ Hz, 1.5 Hz, 1 H, HC(2)), 7.46 (ddd, $J = 8.5, 7.2, 1.7$ Hz, 2 H, HC(4)), 7.42 (t, $J = 7.8$ Hz, 2 H, HC(15)), 7.31 (t, $J = 7.3$ Hz, 1 H, HC(16)), 7.07 (d, $J = 7.5$ Hz, 1 H, HC(5)), 6.99 (t, $J = 7.5$ Hz, 1 H, HC(3)), 4.73 (dd, $J = 12.8, 3.5$ Hz, 1 H, HC(7)), 2.93–2.61 (m, 6 H, $\text{H}_2\text{C}(8)$, $\text{H}_2\text{C}(11)$), 2.11–1.87 (m, 2 H, $\text{H}_2\text{C}(12)$).

^{13}C NMR: (126 MHz, CDCl_3)

129.0 (C(9)), 161.2 (C(1)), 137.2 (C(13)), 136.2 (HC(4)), 130.4 (HC(14)), 128.9 (HC(15)), 128.0 (HC(16)), 126.9 (HC(2)), 121.9 (HC(3)), 121.0 (C(6)), 118.2 (HC(5)), 84.0 (HC(7)), 62.3 (C(10)), 38.9 ($\text{H}_2\text{C}(8)$), 27.6 ($\text{H}_2\text{C}(11)$), 27.4 ($\text{H}_2\text{C}(11)$), 25.0 ($\text{H}_2\text{C}(12)$).

IR: (KBr)

3059 (w), 2933 (m), 2898 (m), 2850 (m), 1684 (s), 1604 (s), 1583 (m), 1465 (s), 1309 (s), 1226 (s), 1150 (m), 1122 (m), 893 (m), 768 (s), 706 (m).

LRMS: (EI, 70 eV)

63.1 (4), 771. (6), 92.0 (5), 106.0 (4), 115.1 (10), 121.0 (26), 131.1 (3), 147.0 (5), 178.1 (1), 195.0 (100), 207.1 (2), 236.1 (4).

LRMS: (CI+)

73.0 (4), 91.1 (3), 107.0 (9), 121.0 (41), 135.0 (10), 149.1 (9), 195.0 (70), 207.1 (12),
221.1 (4), 237.1 (100), 265.1 (10), 343.1 (65), 371.1 (12), 383.1 (2).

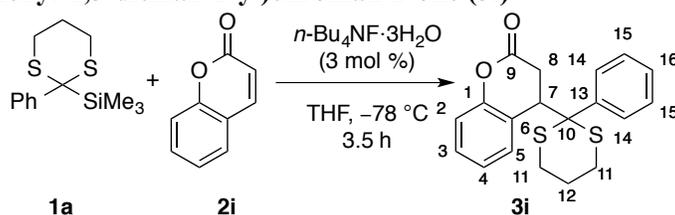
Analysis: C₁₉H₁₈OS₂ (342.07)

calcd: C, 66.63 H, 5.30

found: C, 66.40 H, 5.38

TLC: R_f 0.29 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 4-(2-Phenyl-1,3-dithian-2-yl)chroman-2-one (**3i**)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv) and coumarin **2i** (146 mg, 1.0 mmol, 1.0 equiv). The flask was evacuated and backfilled with Ar twice, then THF (12.5 mL, 0.08 M) was added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned pale yellow upon addition of fluoride and was stirred at -78 °C for 3.5 h over which the reaction color changed to orange. Reaction progress was monitored by disappearance of enone as indicated by TLC (4:1 hexanes/TBME). Complete conversion was observed after 3.5 h and the reaction was quenched at -78 °C with 6.0 mL of 2.0 M Cl₃CCO₂H in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 × 30 mL). The combined organics was washed with distilled water (2 × 25 mL) and saturated brine (1 × 30 mL), dried over Na₂SO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 1 h to yield 404 mg of a colorless oil/solid mixture. Adsorption of the crude material on celite and purification by flash chromatography (32 g SiO₂, 175 mm × 25 mm, 10 mL fractions, 4:1 hexane:ethyl acetate isocratic elution) yields the desired compound as a white solid, 266 mg (78%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling ethanol (10 mL), cooled to room temperature, and then crystallized at -20 °C for 2 d. The small white needles were collected by vacuum filtration, washed with

ice-cold ethanol, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 118 mg (35%) as small white crystals.

Data for 3i:

m.p.: 194–195 °C (from EtOH)

¹H NMR: (500 MHz, CDCl₃)

7.65 (br d, *J* = 6.8 Hz, 2 H, HC(14)), 7.36–7.19 (m, 4 H, HC(4), HC(15), HC(16)), 7.02–6.98 (m, 2 H, HC(3), HC(5)), 6.88 (d, *J* = 8.0 Hz, 1 H, HC(2)), 3.55 (d, *J* = 8.1 Hz, 1 H, H₂C(8)), 3.53 (dd, *J* = 17.2, 1.0 Hz, 1 H, HC(7)), 2.75–2.61 (m, 4 H, H₂C(8), H₂C(11)), 2.52 (ddd, *J* = 14.4, 8.7, 6.4 Hz, 1 H, H₂C(11)), 1.89 (dq, *J* = 9.5, 5.4, 4.0 Hz, 2 H, H₂C(12)).

¹³C NMR: (126 MHz, CDCl₃)

167.0 (C(9)), 152.5 (C(1)), 137.1 (C(13)), 131.4 (HC(5)), 130.3 (HC(14)), 129.7 (HC(4)), 128.7 (HC(16)), 128.3 (HC(15)), 123.3 (HC(3)), 119.2 (C(6)), 117.0 (HC(2)), 63.8 (C(10)), 47.8 (HC(7)), 31.0 (H₂C(8)), 27.7 (H₂C(11)), 27.5 (H₂C(11)), 24.6 (H₂C(12)).

IR: (KBr)

3059 (w), 2940 (m), 2891 (m), 1757 (s), 1604 (m), 1583 (w), 1483 (m), 1451 (s), 1417 (m), 1340 (m), 1247 (s), 1212 (s), 1160 (s), 1111 (m), 1039 (m), 994 (w), 896 (m), 772 (s), 740 (m), 699 (m).

LRMS: (EI, 70 eV)

51.0 (5), 63.1 (5), 77.1 (12), 91.1 (9), 118.0 (6), 121.0 (43), 122.0 (5), 123.0 (3), 165.1 (6), 195.1 (100), 196.1 (14), 197.1 (10), 207.1 (8), 208.1 (6), 209.1 (1), 342.2 (1).

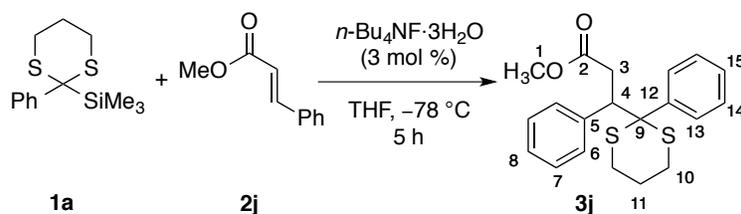
Analysis: C₁₉H₁₈OS₂ (342.07)

calcd: C, 66.63 H, 5.30

found: C, 66.40 H, 5.33

TLC: *R_f* 0.22 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of Methyl 3-Phenyl-3-(2-phenyl-1,3-dithian-2-yl)propanoate (3j)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-phenyl-1,3-dithiane **1a** (403 mg, 1.5 mmol, 1.5 equiv) and methyl *trans*-cinnamate **2j** (162 mg, 1.0 mmol, 1.0 equiv). The

flask was evacuated and backfilled with Ar twice, then THF (12.5 mL, 0.08 M) was added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to $-78\text{ }^{\circ}\text{C}$ (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μL , 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned dim yellow upon addition of fluoride and was stirred at $-78\text{ }^{\circ}\text{C}$ for 5 h. Reaction progress was monitored by disappearance of enone as indicated by TLC (4:1 hexanes/TBME). Complete conversion was observed after 5 h and the reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O ($1 \times 30\text{ mL}$). The combined organics was washed with distilled water ($2 \times 25\text{ mL}$) and saturated brine ($1 \times 30\text{ mL}$), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, $25\text{ }^{\circ}\text{C}$). The colorless oil was dried under vacuum (0.1 mm Hg, $25\text{ }^{\circ}\text{C}$) for 2 h to yield 517 mg of a colorless oil. Adsorption of the crude material on celite and purification by flash chromatography (33 g SiO_2 , 180 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1) yields the desired compound as sticky colorless oil, 317 mg (88%).

Data for 3j:

^1H NMR: (500 MHz, CDCl_3)
7.72 (d, $J = 7.4\text{ Hz}$, 2 H, HC(13)), 7.30 (t, $J = 7.5\text{ Hz}$, 2 H, HC(14)), 7.25 (t, $J = 8.0\text{ Hz}$, 1 H, HC(15)), 7.17 (t, $J = 7.1\text{ Hz}$, 1 H, HC(8)), 7.13 (t, $J = 7.3\text{ Hz}$, 2 H, HC(7)), 6.91 (d, $J = 7.3\text{ Hz}$, 2 H, HC(6)), 3.76 (dd, $J = 3.6, 11.5\text{ Hz}$, 1 H, HC(4)), 3.44 (s, 3 H, $\text{H}_3\text{C}(1)$), 3.29 (dd, $J = 3.7, 16.1\text{ Hz}$, 1 H, $\text{H}_2\text{C}(3)$), 2.79 (dd, $J = 11.6, 16.1\text{ Hz}$, 1 H, $\text{H}_2\text{C}(3)$), 2.67–2.57 (m, 4 H, $\text{H}_2\text{C}(10)$), 1.89–1.80 (m, 2 H, $\text{H}_2\text{C}(11)$).

^{13}C NMR: (126 MHz, CDCl_3)
172.3 (O=C(2)), 138.8 (C(12)), 137.4 (C(5)), 130.7 (HC(13)), 130.2 (HC(6)), 128.3 (HC(14)), 127.5 (HC(8)), 127.4 (HC(7)), 127.3 (HC(15)), 63.9 (C(9)), 54.1 (HC(4)), 51.7 ($\text{H}_3\text{C}(1)$), 35.9 ($\text{H}_2\text{C}(3)$), 27.8 ($\text{H}_2\text{C}(10)$), 27.7 ($\text{H}_2\text{C}(10)$), 24.9 ($\text{H}_2\text{C}(11)$).

IR: (KBr)
3024 (m), 2940 (m), 2885 (m), 1725 (s), 1587 (w), 1479 (m), 1431 (s), 1424 (s), 1358 (s), 1337 (s), 1261 (s), 1222 (s), 1163 (s), 1143 (s), 1087 (w), 865 (m), 778 (m), 699 (s).

LRMS: (EI, 70 eV)
77.0 (3), 105.0 (3), 115.1 (5), 121.0 (78), 122.0 (13), 123.0 (5), 178.1 (12), 195.0 (100), 196.0 (28), 198.0 (18), 223.1 (7), 237.1 (10), 252.1 (16), 253.1 (8), 327.1 (45), 328.1 (10), 329.1 (5), 358.1 (15), 359.1 (5).

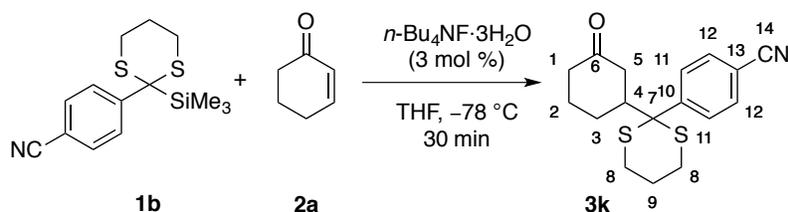
HRMS: (ESI, $[M+H]^+$):

calcd: 359.1139

found: 359.1142

TLC: R_f 0.38 (silica gel, hexanes/TBME 4:1, UV/I₂)

Preparation of 4-(2-(3-Oxocyclohexyl)-1,3-dithian-2-yl)benzonitrile (3k)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 4-cyano-1,3-trimethylsilyldithiane **1b** (440 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclohexenone **2a** (96 mg, 97 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled in a dry ice/isopropanol bath (I.T. = -73 °C). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned yellow then bright orange upon addition of fluoride and was stirred at -78 °C for 30 min. Reaction progress was monitored by disappearance of enone as indicated by TLC (7:3 hexanes/EtOAc). Complete conversion was observed after 30 min and the reaction was quenched at -70 °C with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in loss of color. The cooling bath was removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 3 h to yield 472 mg of a yellow oil. Adsorption of the crude material on celite and purification by flash chromatography (36 g SiO_2 , 195 mm \times 25 mm, 10 mL fractions, 15 % EtOAc in hexane isocratic elution (800 mL)) yields the desired compound as a colorless foam, 358 mg (quant.). The solid was dissolved in a minimum of boiling ethanol (5 mL), cooled to room temperature, and then crystallized at -20 °C for 18 h. The small white needles were collected by vacuum filtration, washed with ice-cold ethanol and ice-cold pentane, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 283 mg (89%) as a white powder.

Data for 3k:

m.p.: 130–131 °C (from EtOH)

¹H NMR: (500 MHz, CDCl₃)
 8.08 (d, *J* = 8.5 Hz, 2 H, HC(11)), 7.71 (d, *J* = 8.5 Hz, 2 H, HC(12)), 2.70 (dt, *J* = 14.5, 3.7 Hz, 1 H, H₂C(8)), 2.61–2.50 (m, 3 H, H₂C(5), H₂C(8)), 2.32 (ddt, *J* = 14.9, 4.0, 2.0 Hz, 1 H, H₂C(1)), 2.28–2.08 (m, 4 H, H₂C(1), H₂C(2), HC(4), H₂C(5)), 2.04 (ddt, *J* = 12.6, 6.0, 3.0 Hz, 1 H, H₂C(3)), 1.98–1.87 (m, 2 H, H₂C(9)), 1.54–1.38 (m, 2 H, H₂C(2), H₂C(3)).

¹³C NMR: (126 MHz, CDCl₃)
 210.1 (O=C(6)), 145.7 (C(13)), 132.5 (HC(12)), 131.1 (HC(11)), 118.7 (NC(14)), 111.4 (C(10)), 63.2 (C(7)), 50.4 (HC(4)), 43.2 (H₂C(5)), 41.1 (H₂C(1)), 27.7 H₂C(8)), 27.6 H₂C(8)), 26.5 (H₂C(2)), 25.0 (H₂C(9)), 24.5 (H₂C(3)).

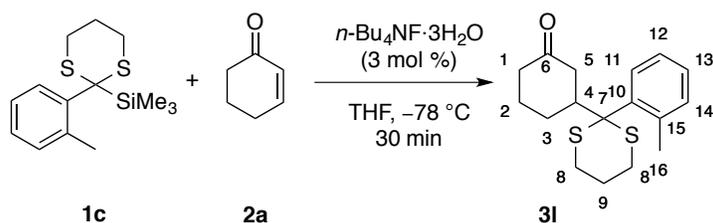
IR: (KBr)
 2940 (m), 2905 (m), 2857 (m), 2216 (m), 1705 (s), 1597 (m), 1493 (m), 1448 (w), 1403 (w), 1396 (w), 1271 (m), 1226 (m), 851 (m), 810 (w), 782 (w), 754 (w).

LRMS: (EI, 70 eV)
 74.0 (4), 102.0 (5), 106.0 (7), 127.1 (4), 140.1. (9), 146.0 (46), 154.1 (7), 186.0 (4), 220.0 (100), 221.0 (21), 222.0 (13), 317.1 (8).

Analysis: C₁₇H₁₉NOS₂ (317.47)
 calcd: C, 64.32 H, 4.41
 found: C, 63.98 H, 4.40

TLC: *R_f* 0.15 (silica gel, hexanes/EtOAc 85:15, UV/I₂)

Preparation of 3-(2-(*o*-Tolyl)-1,3-dithian-2-yl)cyclohexanone (**3l**)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added 2-(*o*-tolyl)-1,3-trimethylsilyldithiane **1c** (424 mg, 1.5 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclohexenone **2a** (96 mg, 97 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled in a dry ice/isopropanol bath (I.T. = -73 °C). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned yellow then brown red upon addition of fluoride and was stirred at -78 °C for 30 min. Reaction progress was monitored by

disappearance of enone as indicated by TLC (4:1 hexanes/TBME). Complete conversion was observed after 30 min and the reaction was quenched at $-70\text{ }^{\circ}\text{C}$ with 6.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et_2O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1×30 mL). The combined organics was washed with distilled water (2×25 mL) and saturated brine (1×30 mL), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, $25\text{ }^{\circ}\text{C}$). The colorless oil was dried under vacuum (0.1 mm Hg, $25\text{ }^{\circ}\text{C}$) for 3 h to yield 482 mg of a yellow oil. Adsorption of the crude material on celite and purification by flash chromatography (32 g SiO_2 , 170 mm \times 25 mm, 10 mL fractions, hexane/TBME gradient: 20:1 (100 mL) to 15:1 (100 mL) to 10:1 (400 mL) to 4:1 (100 mL)) yields the desired compound as white solid, 287 mg (93%). An analytically pure sample was prepared by recrystallization. The solid was dissolved in a minimum of boiling ethanol (10 mL), cooled to room temperature, and then crystallized at $-20\text{ }^{\circ}\text{C}$ for 18 h. The shiny white plates were collected by vacuum filtration, washed with ice-cold ethanol, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 213 mg (69%) as a white powder.

Data for 3I:

m.p.: 112–113 $^{\circ}\text{C}$ (from EtOH)

^1H NMR: (500 MHz, d_6 -DMSO)
8.03 (d, $J = 7.8$ Hz, 1 H, HC(11)), 7.30–7.16 (m, 3 H, HC(12), HC(13), HC(14)), 2.85–2.75 (br m, 2 H, $\text{H}_2\text{C}(8)$), 2.68–2.57 (br m, 5 H, HC(4), $\text{H}_2\text{C}(5)$, $\text{H}_2\text{C}(8)$), 2.58 (s, 3 H, $\text{H}_3\text{C}(16)$), 2.30 (td, $J = 14.0, 6.4$ Hz, 1 H, $\text{H}_2\text{C}(1)$), 2.11 (ddt, $J = 14.5, 4.4, 2.2$ Hz, 1 H, $\text{H}_2\text{C}(1)$), 1.95–1.82 (m, 2 H, $\text{H}_2\text{C}(2)$, $\text{H}_2\text{C}(3)$), 1.77–1.60 (m, 3 H, $\text{H}_2\text{C}(3)$, $\text{H}_2\text{C}(9)$), 1.52–1.35 (br m, 1 H, $\text{H}_2\text{C}(2)$).

^{13}C NMR: (126 MHz, d_6 -DMSO)
209.7 (O=C(6)), 137.4 (C(10)), 136.4 (C(15)), 134.2 (HC(14)), 132.4 (HC(11)), 127.3 (HC(12)), 125.5 (HC(13)), 64.4 (C(7)), 46.0 (HC(4)), 43.3 ($\text{H}_2\text{C}(5)$), 40.4 ($\text{H}_2\text{C}(1)$), 27.4 ($\text{H}_2\text{C}(8)$), 27.3 ($\text{H}_2\text{C}(8)$), 26.3 (br, $\text{H}_2\text{C}(3)$), 24.2 ($\text{H}_2\text{C}(2)$), 23.8 ($\text{H}_2\text{C}(9)$), 23.8 ($\text{H}_3\text{C}(16)$).

IR: (KBr)
3045 (w), 2940 (s), 2905 (s), 2864 (s), 1708 (s), 1472 (s), 1444 (s), 1420 (s), 1351 (m), 1278 (s), 1254 (s), 1226 (s), 1184 (m), 1163 (w), 1094 (w), 907 (m), 855 (m), 747 (s), 723 (m), 678 (w).

LRMS: (EI, 70 eV)
55.1 (5), 91.0 (10), 105.0 (5), 106.0 (15), 115.0 (9), 115.0 (9), 119.0 (5), 128.0 (12), 129.0 (16), 134.0 (10), 135.0 (56), 136.0 (13), 141.0 (5), 142.0 (6), 143.0 (8), 161.0 (8),

209.0 (100), 210.0 (14), 211.0 (10), 231.0 (7), 232.0 (8), 306.0 (30), 307.0 (6).

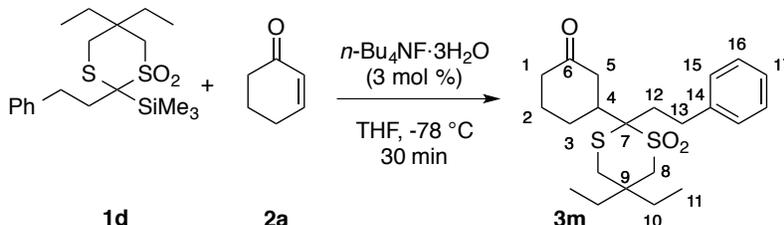
Analysis: C₁₇H₂₂OS₂ (306.11)

calcd: C, 66.62 H, 7.24

found: C, 66.50 H, 7.29

TLC: *R_f* 0.20 (silica gel, hexanes/TBME 9:1, UV/I₂)

Preparation of 3-(5,5-Diethyl-1,1-dioxido-2-phenethyl-1,3-dithian-2-yl)cyclohexan-1-one (3m)



To a flame-dried, 25-mL Schlenk flask with septum and stir bar was added trimethylsilylphenethyldithiane 1,1-dioxide **1d** (577 mg, 1.5 mmol, 1.5 equiv) The flask was evacuated and backfilled with Ar twice, then 2-cyclohexenone **2a** (96 mg, 97 μ L, 1.0 mmol, 1.0 equiv) and THF (12.5 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (150 μ L, 3 mol %) was added dropwise as a solution in THF (0.2 M). The reaction turned pale yellow upon addition of fluoride and was stirred at -78 °C for 30 min. Reaction progress was monitored by disappearance of enone as indicated by TLC (4:1 hexanes/EtOAc). Complete conversion was observed after 30 min and the reaction was quenched at -78 °C with 6.0 mL of 2.0 M Cl₃CCO₂H in THF resulting in loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 50 mL of Et₂O to a 125-mL separatory funnel containing 35 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 \times 30 mL). The combined organics was washed with distilled water (2 \times 25 mL) and saturated brine (1 \times 30 mL), dried over Na₂SO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The colorless oil was dried under vacuum (0.1 mm Hg, 25 °C) for 3 h to yield 482 mg of a yellow oil. Adsorption of the crude material on celite and purification by flash chromatography (32 g SiO₂, 170 mm \times 25 mm, 10 mL fractions, hexane/acetone gradient (200 mL each): 20:1 to 10:1 to 4:1 to 2:1) yields the desired compound as white solid, 401 mg (98%). The solid was dissolved in a minimum of boiling isopropanol (10 mL), cooled to room temperature to start crystallization, and then cooled to -20 °C for 24 h. The small white crystals were collected by vacuum filtration, washed with room temperature pentane, and dried under reduced pressure at 55 °C (0.1 mm Hg) for 18 h to yield 279 mg (68%) as a white powder.

Data for 3m:

m.p.: 193–194 °C (from *i*-PrOH)

¹H NMR: (500 MHz, CDCl₃)

7.32 (t, *J* = 7.5 Hz, 2 H), 7.28–7.18 (m, 3 H), 3.06–2.59 (m, 8H), 2.55–2.09 (m, 7 H), 2.06–1.76 (m, 3 H), 1.69–1.33 (m, 3 H), 0.84 (ddd, *J* = 12.1, 8.5, 6.3 Hz, 6 H).

¹³C NMR: (126 MHz, CDCl₃)

209.6, 209.2, 140.7, 140.7, 128.9, 128.5, 126.7, 72.7, 72.3, 58.2, 57.8, 44.3, 43.9, 43.5, 42.5, 42.4, 42.1, 41.4, 41.1, 33.6, 33.5, 33.0, 32.7, 30.7, 30.5, 27.7, 27.6, 25.4, 25.2, 7.4, 7.3.

IR: (KBr)

2968 (s), 2095 (m), 1725 (s), 1705 (s), 1493 (m), 1451 (m), 1292 (s), 1264 (s), 1226 (m), 1115 (s), 848 (w), 778 (m), 747 (m), 699 (s).

LRMS: (EI, 70 eV)

65.0 (32), 69.1 (30), 79.1 (28), 91.0 (89), 97.1 (35), 115.1 (52), 117.1 (62), 129.1 (35), 143.1 (31), 155.1 (43), 169.1 (27), 188.1 (20), 195.1 (34), 211.1 (40), 213.1 (51), 245.1 (88), 247.1 (100), 248.1 (68), 253.2 (50), 293.1 (10), 344.2 (38), 374.2 (18), 408.2 (8), 409.2 (4).

Analysis: C₂₂H₃₂O₃S₂ (408.61)

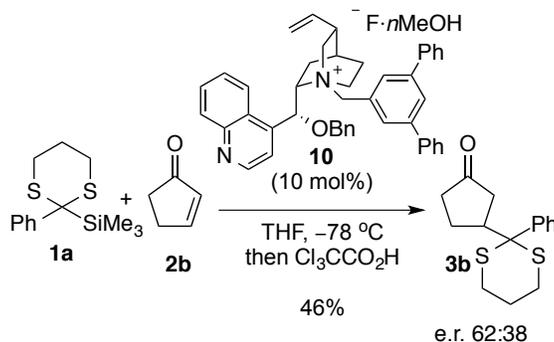
calcd: C, 64.67 H, 7.89

found: C, 64.76 H, 8.12

TLC: *R_f* 0.25 (silica gel, hexanes/acetone 4:1, UV/I₂)

R_f 0.26 (silica gel, hexanes/acetone 4:1, UV/I₂)

Reaction of 2-Phenyl-2-trimethylsilyl-1,3-dithiane and Cyclopenten-2-one Using Chiral Ammonium Fluoride Catalyst (3b)



To a flame-dried, 10-mL Schlenk flask with septum and stir bar was added silyl phenyl dithiane **1a** (100.7 mg, 0.375 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then 2-cyclopentenone **2b** (21 mg, 21 μL, 0.25 mmol, 1.0 equiv) and THF (3.0 mL, 0.08 M) were added by

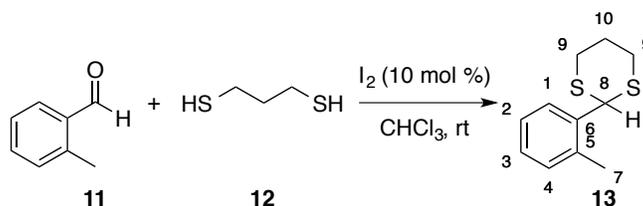
syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78 °C (dry ice/acetone). To a flame-dried, dram vial was added fluoride catalyst **10** (4.8 mg, 0.0075 mmol, 3 mol %) and 0.25 mL THF. The fluoride salt was then added dropwise as a solution in THF via canula. The vial was rinsed with an additional 0.25 mL and transferred via canula. The reaction turned bright yellow upon addition of fluoride and was stirred at -78 °C for 1 h. Reaction progress was monitored by disappearance of enone as indicated by TLC (85:15 hexanes/EtOAc). Complete conversion was observed after 1 h and the reaction was quenched at -78 °C with 3.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in loss of color. The cooling bath was then removed and the reaction was warmed to rt and stirred for 1 h 30 min. The reaction mixture was transferred with 20 mL of Et_2O to a 60-mL separatory funnel containing 10 mL of sat. NaHCO_3 (aq) solution. The aqueous layer was separated and extracted with Et_2O (1×20 mL). The combined organics was washed with distilled water (2×15 mL) and saturated brine (1×20 mL), dried over Na_2SO_4 , filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C) and dried under vacuum (0.1 mm Hg, 25 °C) for 3 h to yield a yellow oil. Adsorption of the crude material on celite and purification by flash chromatography (SiO_2 , 170 mm \times 15 mm, 5 mL fractions, hexane/TBME gradient: 20:1 (150 mL) to 15:1 (150 mL) to 10:1 (200 mL)) yields the desired compound as a white solid, 63.3 mg (46%). The characterization data matched that previously observed for the addition with using TBAF.

Data for **3b**:

SFC: t_R 6.37 min (37.8%); t_R 8.45 min (62.2%) (Chiralpak AS, 10% MeOH in CO_2 , 2.5 mL/min, 220 nm, 40 °C)

II. Synthesis of Aryl Silyl Dithiane Substrates

Preparation of 2-Tolyl-1,3-dithiane (**13**)



2-Tolualdehyde **11** (2.40 g, 2.31 mL, 20.0 mmol, 1.0 equiv), 1,3-propanedithiol **12** (2.60 g, 2.41 mL, 24.0 mmol, 1.2 equiv), and chloroform (100 mL, 0.2 M) were added under argon to a flame-dried, 250 mL two-necked round bottom flask fitted with an Ar inlet, stir bar, and internal temperature probe. The mixture was stirred at room temperature (25 °C) and iodine (508 mg, 2.0 mmol, 0.10 equiv) was added in one portion as a solid. Upon addition of iodine the reaction mixture turned from colorless to yellow to deep red over 1 min and the internal temperature increased to 35 °C. After stirring for 10 min,

the reaction was complete by TLC (20:1 hexanes/TBME). The reaction was quenched by addition of 40 mL of 0.2 M aqueous $\text{Na}_2\text{S}_2\text{O}_3$ at room temperature resulting in a biphasic yellow heterogeneous mixture. The reaction was stirred at rt for 20 min and then transferred to a 500 mL separatory funnel containing 100 mL of 10% aqueous NaOH. The organic layer was separated, and the aqueous layer was extracted with 100 mL CHCl_3 . The combined organics were washed with 10 % aqueous NaOH (1×100 mL), saturated aqueous NaCl (1×100 mL), and dried over Na_2SO_4 . The pale yellow solution was concentrated by rotary evaporation (40 °C, 15 Mm Hg) and dried at room temperature under reduced pressure (0.1 mm Hg) for 4 h to give a white solid (4.33 g). The solid was dissolved in 40 mL of boiling EtOH and the insoluble solid was removed by hot filtration through a cotton plug. The filtrate was heated again to give a colorless solution, which crystallized slowly upon cooling to room temperature for 1 h and then -20 °C for 14 h to yield thin colorless crystals (3.51 g, 83%). A second recrystallization from EtOH yielded an additional 400 mg (9.5%) with a melting point of 86–87 °C.

Data for 13:

m.p.: 89–90 °C (from EtOH)

^1H NMR: (500 MHz, CDCl_3)

7.59 (dd, $J = 7.4, 1.7$ Hz, 1 H, HC(1)), 7.25–7.12 (m, 3 H, HC(2,3,4)), 5.33 (s, 1 H, HC(8)), 3.09 (ddd, $J = 14.9, 12.7, 2.4$ Hz, 2 H, $\text{H}_2\text{C}(9)$), 2.92 (dt, $J = 14.5, 4.1$ Hz, 2 H, $\text{H}_2\text{C}(9)$), 2.45 (s, 3 H, $\text{H}_3\text{C}(7)$), 2.18 (dtt, $J = 13.7, 4.4, 2.5$ Hz, 1 H, $\text{H}_2\text{C}(10)$), 1.95 (dtt, $J = 14.0, 12.6, 3.0$ Hz, 1 H, $\text{H}_2\text{C}(10)$).

^{13}C NMR: (126 MHz, CDCl_3)

137.3 C(5), 135.1 C(6), 130.6 HC(3), 128.3 HC(2), 128.0 HC(1), 126.8 HC(4), 48.4 HC(8), 32.6 $\text{H}_2\text{C}(9)$, 25.4 $\text{H}_2\text{C}(10)$, 19.2 $\text{H}_3\text{C}(7)$.

IR: (KBr)

2933 (s), 2878 (s), 2822 (m), 1483 (s), 1458 (s), 1417 (s), 1379 (w), 1275 (s), 1181 (s), 1035 (m), 907 (m), 872 (m), 754 (s), 671 (s).

LRMS: (EI, 70 eV):

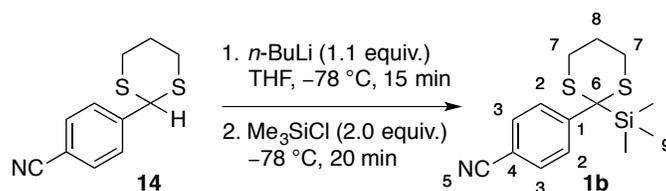
51.0 (3), 65.1 (3), 77.1 (6), 91.1 (13), 105.0 (40), 115.1 (2), 135.0 (100), 145.1 (7), 153.0 (3), 195.0 (3), 210.1 (37).

Analysis: $\text{C}_{11}\text{H}_{14}\text{S}_2$ (210.36)

calcd: C, 62.81 H, 6.71

found: C, 63.16 H, 6.69

TLC: R_f 0.29 (silica gel, hexanes/TBME 20:1, UV/ I_2)

Preparation of 2-(4-Cyanophenyl)-2-trimethylsilyl-1,3-dithiane (**1b**)

To a flame-dried, 25-mL Schlenk flask with stir bar, septum, and internal temperature probe was added dithiane **14** (443 mg, 2.0 mmol, 1.0 equiv) and THF (9.5 mL, 0.21 M). The reaction was stirred under Ar and cooled to -78 °C (dry ice/*i*-PrOH) for 30 min. To a flame-dried, 25-mL conical flask with Ar inlet and septum was added *n*-BuLi (0.86 mL, 2.2 mmol, 2.57 M in hexane, 1.1 equiv). The *n*-BuLi was cooled to -78 °C (dry ice/*i*-PrOH) and added dropwise over 3 min *via* canula while maintaining the internal temperature below -65 °C. Over the course of the addition the reaction mixture changed from bright yellow to orange-red. The reaction was stirred at -78 °C for an additional 15 min in which the reaction turned brown. Chlorotrimethylsilane (0.51 mL, 4.0 mmol, 2.0 equiv) was then added slowly to the reaction flask by syringe over 5 min while maintaining the internal temperature below -70 °C. The reaction mixture was stirred at -78 °C for an additional 20 min, over which the color of the reaction diminished to yellow. The reaction was quenched at -70 °C with the addition of 6 mL saturated ammonium chloride while maintaining the internal temperature below -50 °C, then allowed to warm to rt. The reaction mixture was transferred to a 125-mL separatory funnel with 30 mL of dichloromethane and 30 mL distilled water. The aqueous layer was extracted with 30 mL of dichloromethane twice and the combined organic layer was washed with 30 mL saturated brine. The solution was dried over MgSO₄, concentrated (10 mm Hg, 25 °C), and dried at room temperature under reduced pressure (0.1 mm Hg) for 12 h to yield the crude material as a pink solid. The solid was dissolved in a minimum of boiling ethanol (5 mL), cooled to room temperature and then crystallized slowly at rt, followed by cooling to -20 °C. The needle-like crystals were collected by vacuum filtration, washed with ice-cold EtOH, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 340 mg (58%) as a white powder. (Note: Compound **1b** is light-sensitive and will discolor to pink if stored for long periods of time).

Data for **1b**:

m.p.: 114–116 °C (from EtOH)

¹H NMR:(500 MHz, CDCl₃)

8.05 (d, *J* = 8.6 Hz, 2 H, HC(2)), 7.66 (d, *J* = 8.6 Hz, 2 H, HC(3)), 2.66 (td, *J* = 13.7, 13.1, 2.7 Hz, 2 H, H₂C(7)), 2.47 (dt, *J* = 14.4, 3.9 Hz, 2 H, H₂C(7)), 2.03 (dt, *J* = 12.6, 3.2 Hz, 1 H, H₂C(8)), 1.93 (ddd, *J* = 13.8, 6.8, 3.3 Hz, 1 H, H₂C(8)), 0.07 (s, 9 H,

(H₃C(9))₃Si).

¹³C NMR: (126 MHz, CDCl₃)
147.6 (C(1)), 132.2 (HC(3)), 130.4 (HC(2)), 119.3 (C(4)), 109.1 (NC(5)), 47.9 (C(6)),
25.5 (H₂C(7)), 24.9 (H₂C(8)), 3.9 ((H₃C(9))₃Si).

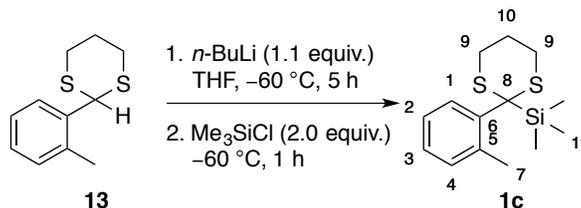
IR: 2954 (m), 2898 (m), 2222 (s), 1597 (m), 1490 (s), 1403 (m), 1247 (s), 1143 (m), 1018
(w), 1004 (m), 914 (s), 889 (m), 841 (s), 744 (m), 692 (w), 622 (w).

LRMS: (EI, 70 eV)
51.3 (4), 53.3 (3), 58.2 (4), 59.3 (3), 69.0 (3), 73.2 (100), 74.1 (12.0), 75.1 (5), 102.1 (25),
103.1 (5), 146.1 (33), 147.1 (3), 160.0 (5), 175.2 (4), 188.1 (5), 219.1 (15), 220.1 (10),
221.1 (2), 293.2 (13), 294.2 (3), 295.2 (2).

Analysis: C₁₄H₁₉NS₂Si (293.52)
calcd: C, 57.29 H, 6.52 N, 4.77
found: C, 57.23 H, 6.60 N, 4.68

TLC: R_f 0.22 (silica gel, hexanes/EtOAc 9:1, UV/I₂)

Preparation of 2-(*o*-Tolyl)-2-trimethylsilyl-1,3-dithiane (1c)



To a flame-dried, 25-mL Schlenk flask with stir bar, argon inlet, and internal temperature probe was added dithiane **13** (0.631 g, 3.0 mmol, 1.0 equiv) and THF (7.5 mL, 0.4 M). The reaction was stirred under Ar and cooled to -64 °C (*i*-PrOH/cryocool) for 15 min, then *n*-BuLi (1.28 mL, 3.3 mmol, 2.57 M in hexane, 1.1 equiv) was added dropwise by syringe over 5 min maintaining the internal temperature below -60 °C. Over the course of the addition the reaction mixture changed from colorless to red to pale yellow. The reaction was maintained at -60 °C and stirred for 5 h, over which the reaction became bright neon yellow. Chlorotrimethylsilane (0.84 mL, 2.0 mmol, 2.0 equiv) was then added dropwise over 5 min by syringe maintaining the internal temperature below -58 °C. The reaction was stirred at 60 °C for an additional 1 h over which the reaction lost its color and a white precipitate forms. The reaction was quenched at -60 °C with 5 mL saturated aqueous ammonium chloride, removed from the bath, and warmed to room temperature. The reaction mixture was transferred to a 250 mL separatory funnel with 40 mL dichloromethane. The aqueous layer was extracted with 25 mL of dichloromethane twice and the combined organic layer was washed with 40 mL saturated brine. The solution was dried over MgSO₄,

concentrated (15 mm Hg, 25 °C), cooled to -20 °C for 10 min to solidify, and dried at room temperature under reduced pressure (0.1 mm Hg) for 3 h to give 830 mg of a pale yellow waxy solid. ¹H NMR (CDCl₃) indicates approximately 5% of unreacted starting dithiane. The solid was dissolved in a minimum of boiling EtOH (10 mL), cooled to room temperature, and let crystallize at -20 °C for 18 h. The small white crystals were collected by vacuum filtration, washed with cold (0 °C) EtOH and pentane, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 256 mg (30%) as small white crystals. The remaining material (551 mg) was purified by flash chromatography (34 g SiO₂, 180 mm × 25 mm, 10 mL fractions, 30:1 hexane/TBME) to yield the desired compound as a white solid, 472 mg (56%).

Data for 1c:

m.p.: 55–56 °C (from EtOH)

¹H NMR: (500 MHz, CDCl₃)

8.13 (d, *J* = 8.3 Hz, 1 H, HC(1)), 7.21 (t, *J* = 7.2 Hz, 1 H, HC(3)), 7.17-7.09 (m, 2 H, HC(2), HC(4)), 2.80 (ddd, *J* = 14.4, 13.1, 2.9 Hz, H₂C(9)), 2.66 (s, 3H, H₃C(7)), 2.52 (dt, *J* = 14.5, 3.8 Hz, 2 H, H₂C(9)), 2.05 (dq, *J* = 12.8, 3.4 Hz, 1 H, H₂C(10)), 1.86 (ddt, *J* = 13.6, 6.8, 3.3 Hz, 1 H, H₂C(10)), 0.12 (s, 9 H, ((H₃C(11))₃Si)).

¹³C NMR: (126 MHz, CDCl₃)

138.0 (C(6)), 137.3 (C(5)), 134.1 (HC(4)), 133.1 (HC(1)), 126.2 (HC(3)), 126.2 (HC(2)), 48.7 (C(8)), 26.3 (H₂C(9)), 25.9 (H₃C(7)), 24.9 (H₂C(24.9)), -2.5 ((H₃C(11))₃Si).

IR: (KBr)

2954 (m), 2905 (m), 1472 (m), 1271 (w), 1240 (m), 917 (m), 889 (m), 841 (s), 747 (m).

LRMS: (EI, 70 eV):

73.1 (38), 74.1 (4), 91.0 (10), 115.0 (4), 118.1 (7), 134.0 (16), 135.0 (100), 136.0 (14), 137.0 (7), 148.0 (3), 149.0 (5), 161.0 (4), 177.0 (40), 178.0 (6), 193.0 (4), 207.0 (4), 209.0 (76), 210.0 (14), 211.0 (10), 239.0 (9), 267.0 (8), 282.0 (33), 283.0 (8), 284.0 (5).

Analysis: C₁₄H₂₂S₂Si (282.54)

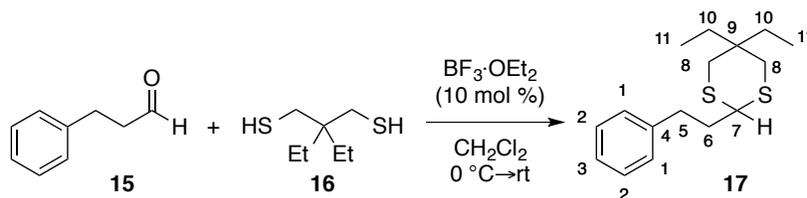
calcd: C, 59.51 H, 7.85

found: C, 59.23 H, 7.81

TLC: *R_f* 0.51 (silica gel, hexanes/TBME 20:1, UV/I₂)

III. Synthesis of Alkylsilyldithiane Dioxide Substrates

Preparation of 5,5-Diethyl-2-phenethyl-1,3-dithiane (17)



To a flame-dried, 250 mL two-neck round bottom flask fitted with an Ar inlet, stir bar, and internal temperature probe was added 3-phenylpropionaldehyde **15** (1.49 g, 1.37 mL, 11.1 mmol, 1.0 equiv) and 60 mL of dichloromethane. The colorless solution was stirred at room temperature (25 °C) and 2,2-diethyl-1,3-dithiol **16** (2.00 g, 12.17 mmol, 1.1 equiv) was added by cannula in 30 mL of dichloromethane to give a pale yellow solution. The reaction flask was then fitted with an internal temperature probe and cooled in an ice-water bath (I.T. = 0 °C). Boron trifluoride diethyl etherate (158 mg, 137 μ L, 1.11 mmol, 0.10 equiv) was added dropwise by syringe over 2 min while maintaining the internal temperature below 3 °C. The ice bath was removed and the turbid yellow solution was stirred at room temperature for 1 h, after which the reaction was complete by TLC (9:1 hexanes/EtOAc). The reaction was quenched at rt with 40 mL of distilled water. The reaction was stirred at rt for 10 min and then transferred to a 250 mL separatory funnel containing 25 mL of sat. aqueous NaHCO₃. The organic layer was separated, and the aqueous layer was extracted twice with 30 mL CH₂Cl₂. The combined organics were washed with 2 M aqueous NaOH (3 \times 50 mL), saturated aqueous NaCl (1 \times 50 mL), and dried over MgSO₄. The pale yellow solution was concentrated by rotary evaporation (40 °C, 15 Mm Hg) to give a yellow oil which solidified upon cooling to -20 °C (3.05 g). The solid was adsorbed onto celite and purified by flash chromatography (122 g SiO₂, 160 mm \times 40 mm, 20 mL fractions, hexane/TBME gradient: 100:0 (900 mL) to 30:1 (300 mL) to 25:1 (500 mL)) to yield 2.34 g (75%) of a white crystalline solid. Trailing fractions that were visibly yellow were collected separately, containing 0.35 g (11%) as a yellow solid. The material after column purification contained a minor contaminant visible in the ¹H NMR (dd at 4.59 ppm, integration of 0.05, see included ¹H NMR spectra). This material was used directly in the next step without further purification. An analytically pure sample was prepared by recrystallization of a small portion of material (218 mg). The solid was dissolved a minimum of boiling EtOH, filtered hot through filter paper, allowed to cool to rt, then cooled to -20 °C for 18 h to yield 117 mg (54%) as a white fluffy crystals.

Data for **17**:

m.p.:	44–45 °C (from EtOH)
¹ H NMR:	(500 MHz, CDCl ₃)
	7.32–7.25 (m, 2 H, HC(1)), 7.23–7.15 (m, 3 H, HC(2), HC(3)), 3.86 (t, <i>J</i> = 7.0 Hz, 1 H,

HC(7)), 2.82 (dd, $J = 8.8, 6.8$ Hz, 2 H, H₂C(5)), 2.64 (d, $J = 14.0$ Hz, 2 H, H₂C(8)), 2.56 (d, $J = 14.0$ Hz, 2 H, H₂C(8)), 2.09 (dt, $J = 9.4, 7.2$ Hz, 2 H, H₂C(6)), 1.80 (q, $J = 7.5$ Hz, 2 H, H₂C(10)), 1.35 (d, $J = 7.5$ Hz, 2 H, H₂C(10)), 0.83 (t, $J = 7.5$ Hz, 1 H, H₃C(11)), 0.78 (t, $J = 7.5$ Hz, 1 H, H₃C(11)).

¹³C NMR: (126 MHz, CDCl₃)
141.1 (C(4)), 128.6 (HC(2)), 128.6 (HC(1)), 126.2 (HC(3)), 46.7 (HC(7)), 39.2 (H₂C(8)), 36.5 (H₂C(6)), 33.0 (H₂C(5)), 31.1 (C(9)), 30.7 (H₂C(10)), 23.6 (H₂C(10)), 7.4 (H₃C(11)), 7.1 (H₃C(11)).

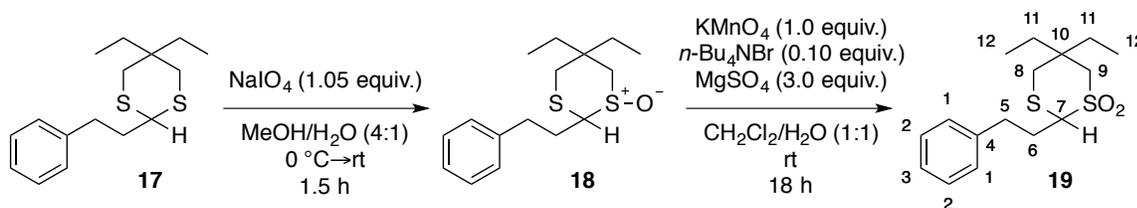
IR: (KBr)
3024 (w), 2954 (s), 2905 (s), 2871 (s), 1597 (w), 1493 (m), 1451 (s), 1424 (m), 1375 (w), 1302 (s), 1264 (m), 1195 (m), 1146 (m), 1111 (m), 862 (2), 785 (m), 751 (s), 699 (s).

LRMS: (EI, 70 eV):
55.1 (19), 63.0 (13), 78.0 (11), 91.1 (59), 97.1 (23), 101.0 (5), 115.1 (15), 117.1 (40), 118.1 (6), 129.1 (17), 149.0 (7), 159.1 (5), 175.1 (100), 176.1 (10), 177.1 (9), 189.1 (916), 190.1 (9), 280.1 (57), 281.1 (10), 282.1 (6).

Analysis: C₁₆H₂₄S₂ (280.49)
calcd: C, 68.51 H, 8.62
found: C, 68.62 H, 8.73

TLC: *R_f* 0.65 (silica gel, hexanes/EtOAc 9:1, UV/I₂)

Preparation of 5,5-Diethyl-2-phenethyl-1,3-dithiane-1,1-dioxide (19)



To a 250 mL 3-neck round bottom flask fitted with a large stir bar, septum, Ar inlet, temperature probe, and 25-mL addition funnel, was added dithiane **17** (2.162 g, 7.71 mmol, 1.0 equiv). The flask was evacuated and backfilled with Ar once. Methanol (59 mL, [0.13 M]) was added to give a heterogeneous white solution. The reaction was stirred and warmed in a warm water bath until starting dithiane went into solution (I.T. = 45 °C), then was cooled to rt. The addition funnel was charged with sodium periodate (1.733 g, 8.10 mmol, 1.05 equiv) as a solution in water (15.4 mL). The reaction flask was stirred vigorously and cooled in an ice-water bath (0 °C) in which starting dithiane formed a finely dispersed white slurry. Aqueous periodate solution was added dropwise by addition funnel over a period of 15 min while maintaining the internal temperature below 5 °C. An immediate white precipitate formed. The ice-

bath was then removed and the pale yellow heterogeneous mixture was stirred at room temperature for 1.5 h. Reaction progress was monitored by TLC for consumption of dithiane (9:1 hexanes/EtOAc; $R_f = 0.58$, UV/PMA) and appearance of sulfoxide (2% EtOH in CHCl_3 ; $R_f = 0.42$, KMnO_4). The reaction mixture was filtered through a Celite plug, washed with an excess of CHCl_3 (200 mL), and concentrated by rotary evaporation to an approximate volume of 10 mL. The resulting solution was transferred to a 250 mL separatory funnel with EtOAc (30 mL) and distilled water (30 mL). Attempted extraction resulted in an inseparable emulsion which separated into distinct layers with addition of solid NaCl. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×30 mL). The combined organic extracts were dried over Na_2SO_4 , filtered (cotton plug), and concentrated by rotary evaporation (25 °C, 15 Mm Hg). The resulting oil was diluted with hexanes to give a precipitate and concentrated again, to give 2.24 g of crude sulfoxide **18** as an orange powder (98%). This crude material was used directly in the next step.

To a 250 mL 1-neck round bottom flask fitted with a large stir bar, septum, and Ar inlet, was added crude sulfoxide **18** (7.71 mmol, 1.0 equiv). The flask was evacuated and backfilled with Ar twice. Anhydrous magnesium sulfate (2.784 g, 23.13 mmol, 3.0 equiv), tetrabutylammonium bromide (0.249 g, 0.771 mmol, 0.1 equiv), dichloromethane (31 mL, [0.25 M]) and distilled water (31 mL, [0.25 M]) were added sequentially. The reaction was stirred under Ar at rt to give a yellow biphasic mixture. At room temperature, potassium permanganate (1.218 g, 7.71 mmol, 1.0 equiv) was added in one portion, in which the solution turns deep purple. The reaction was stirred rigorously (1100 rpm) at rt for 18 h, over which time the reaction turned brown and sulfoxide **18** was completely consumed by TLC (1:1 hexanes/EtOAc). The reaction was quenched at rt by the addition of excess $\text{Na}_2\text{S}_2\text{O}_5$ (15.5 g). Complete loss of color was observed within 10 min to give a cloudy white biphasic mixture. The reaction was transferred to a 250 mL separatory funnel with CHCl_3 (40 mL) and distilled water (20 mL). The organic layer was separated, and the aqueous layer was extracted with CHCl_3 (3×40 mL). The combined organic layer was washed with brine (1×60 mL), dried over MgSO_4 , filtered (cotton plug), and concentrated by rotary evaporation (25 °C, 15 Mm Hg). Subsequent evacuation under high vacuum (0.1 mm Hg, 25 °C) for 1 h yield a thick, colorless oil (2.783 g). Adsorption of the crude material on celite and purification by flash chromatography (59 g SiO_2 , 170 mm \times 35 mm, 20 mL fractions, hexanes/EtOAc gradient: 10:1 (700 mL) to 4:1 (400 mL) to 2:1 (150 mL) to 1:1 (200 mL)) yields the desired compound as a white solid, 1.998 g (83% over 2 steps). An analytically pure sample was prepared by recrystallization. The solid (223 mg) was dissolved in a minimum of boiling chloroform (5 mL), cooled to room temperature, and then crystallized in a slow diffusion chamber with pentane at rt for 2 d. The colorless rod-like crystals were collected by vacuum filtration, washed with room temperature pentane, crushed, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 162 mg (73%) as a white powder.

Data for 18:

¹H NMR: (500 MHz, CDCl₃)
7.29 (t, $J = 7.5$ Hz, 2 H), 7.25–7.17 (m, 3 H), 3.44 (dd, $J = 9.6, 3.8$ Hz, 1 H), 3.21 (dd, $J = 12.6, 2.4$ Hz, 1 H), 2.98 (ddd, $J = 14.4, 9.9, 4.9$ Hz, 1 H), 2.80 (ddd, $J = 13.9, 9.7, 7.1$ Hz, 1 H), 2.71–2.63 (m, 1 H), 2.64 (d, $J = 14.2$ Hz, 1 H), 2.40–2.35 (m, 1 H), 2.35 (d, $J = 12.7$ Hz, 1 H), 2.02 (dtd, $J = 14.5, 9.7, 5.0$ Hz, 1 H), 1.90 (dq, $J = 14.9, 7.5$ Hz, 1 H), 1.78 (dq, $J = 14.6, 7.4$ Hz, 1 H), 1.39 (dq, $J = 14.5, 7.5$ Hz, 2 H), 0.86 (td, $J = 7.5, 3.8$ Hz, 6 H).

¹³C NMR: (126 MHz, CDCl₃)
140.3, 128.7, 128.6, 126.4, 66.0, 63.0, 45.0, 39.2, 32.0, 31.6, 30.4, 25.6, 7.5, 7.2.

LRMS: (TOF-MS, ESI+)
297.1 (100, [M+1]⁺), 298.1 (20), 299.1 (15), 319.0 (10, [M+Na]⁺).

HRMS: (ESI, [M+H]⁺):
calcd: 297.1347
found: 297.1342

Data for 19:

m.p.: 89–92 °C (from CHCl₃/pentane)

¹H NMR: (500 MHz, CDCl₃)
7.30 (t, $J = 7.5$ Hz, 2 H, HC(1)), 7.25–7.19 (m, 3 H, HC(2), HC(3)), 3.73 (dd, $J = 9.8, 4.3$ Hz, 1 H, HC(7)), 3.01 (d, $J = 14.9$ Hz, 1 H, H₂C(9)), 3.02–2.93 (m, 1 H, H₂C(5)), 2.79 (dt, $J = 14.0, 8.2$ Hz, 1 H, H₂C(5)), 2.70 (d, $J = 14.8$ Hz, 1 H, H₂C(9)), 2.65–2.49 (m, 3 H, H₂C(6), H₂C(8)), 2.04–1.94 (m, 2 H, H₂C(6), H₂C(11)), 1.89 (dq, $J = 14.7, 7.5$ Hz, 1 H, H₂C(11)), 1.44 (sept, $J = 7.1$ Hz, 2 H, H₂C(11)), 0.85 (q, $J = 7.5$ Hz, 6 H, H₃C(12)).

¹³C NMR: (126 MHz, CDCl₃)
139.8 (C(4)), 128.8 (HC(1)), 128.6 (HC(2)), 126.6 (HC(3)), 62.9 (HC(7)), 59.4 (H₂C(9)), 43.7 (C(10)), 37.6 (H₂C(8)), 32.0 (H₂C(5)), 31.0 (H₂C(11)), 26.3 (H₂C(6)), 24.6 (H₂C(11)), 7.5 (H₃C(12)), 7.2 (H₃C(12)).

IR: (KBr)
3017 (m), 940 (s), 2968 (s), 2878 (s), 1597 (w), 1497 (m), 1455 (s), 1410 (m), 1389 (m), 1316 (s), 1299 (s), 1268 (s), 1250 (s), 1202 (m), 1184 (m), 1146 (s), 1108 (s), 917 (m), 862 (s), 782 (m), 745 (s), 706 (s).

LRMS: (EI, 70 eV):
55.1 (13), 73.0 (14), 83.1 (8), 91.1 (84), 92.1 (15), 101.0 (9), 115.1 (28), 117.1 (69),

118.1 (15), 143.1 (100), 144.1 (10), 156.1 (22), 157.1 (66), 170.1 (9), 248.2 (50), 249.2 (10), 250.2 (5), 278.1 (15), 279.1 (5), 312.1 (16), 313.1 (4).

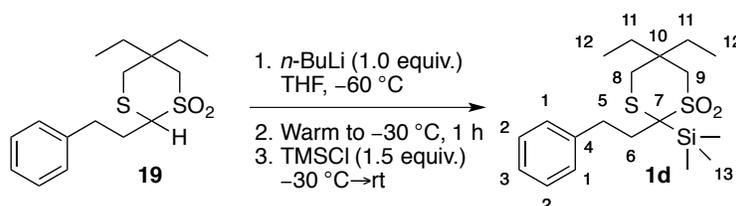
Analysis: C₁₆H₂₄O₂S₂ (312.49)

calcd: C, 61.50 H, 7.74

found: C, 61.40 H, 7.67

TLC: R_f 0.09 (silica gel, hexanes/EtOAc 9:1, UV/I₂)

Preparation of 5,5-Diethyl-2-phenethyl-2-(trimethylsilyl)-1,3-dithiane 1,1-dioxide (**1d**)



To a flame-dried, 100 mL Schlenk flask fitted with a stir bar and septum was added phenethyl dithiane dioxide **19** (1.776 g, 5.68 mmol, 1.0 equiv) and THF (14.2 mL, [0.40 M]). The reaction was stirred at room temperature, fitted with an internal temperature probe, and cooled to -63 °C in a dry ice/isopropanol bath. To the colorless, homogenous solution was added a 2.43 M solution of *n*-BuLi in hexanes (2.34 mL, 5.68 mmol, 1.0 equiv) dropwise by syringe over 8 min, maintaining the internal temperature below -60 °C. After addition, the yellow solution was allowed to warm to -30 °C slowly over 1 h (by no further addition of dry ice to bath). After 1 h, chlorotrimethylsilane (1.08 mL, 8.52 mmol, 1.5 equiv) was added dropwise by syringe while maintaining the internal temperature below -25 °C. The reaction was allowed to stir at -30 °C for 5 additional minutes resulting in complete loss of color. The bath was then removed and the reaction was stirred at rt for 30 min. The reaction was quenched at rt by the addition of 10 mL of NH₄Cl (aq). The reaction mixture was transferred to a 250 mL separatory funnel containing 40 mL of distilled water, extracted with CH₂Cl₂ (3 × 40 mL), washed with brine (1 × 60 mL), dried over MgSO₄, and filtered (cotton plug). The colorless solution was concentrated by rotary evaporation (25 C, 15 Mm Hg) to give a crude white solid (2.16 g). The solid was adsorbed onto celite and purified by flash chromatography (56 g SiO₂, 160 mm × 30 mm, 20 mL fractions, 10:1 hexane/EtOAc isocratic elution (900 mL)) to yield 2.05 g (93%) as a white crystalline solid. An analytically pure sample was prepared by recrystallization. The solid (256 mg) was dissolved in a minimum of boiling acetone (10 mL), cooled to room temperature, and then crystallized at -20 °C for 18 h. The small white crystals were collected by vacuum filtration, washed with ice-cold acetone, and dried under reduced pressure at rt (0.1 mm Hg) for 18 h to yield 198 mg (77%) as a white powder.

Data for **1d**:

m.p.: 152–153 °C (from acetone)

¹H NMR: (500 MHz, CDCl₃)
 7.32 (t, *J* = 7.4 Hz, 2 H, HC(1)), 7.26–7.19 (m, 3 H, HC(2), HC(3)), 3.05–2.95 (m, 2 H, (H₂C(5))), 2.93 (d, *J* = 14.6 Hz, 1 H, H₂C(9)), 2.73 (d, *J* = 15.0 Hz, 1 H, H₂C(9)), 2.69 (d, *J* = 14.7 Hz, 1 H, H₂C(8)), 2.52 (ddd, *J* = 14.8 Hz, 12.3, 5.3 Hz, 1 H, H₂C(6)), 2.33 (ddd, *J* = 14.8 Hz, 12.7 Hz, 4.9 Hz, 1 H, H₂C(6)), 2.23 (d, *J* = 14.7 Hz, 1 H, H₂C(8)), 2.09 (dq, *J* = 14.8, 7.4 Hz, 1 H, H₂C(11)), 1.92 (dq, *J* = 14.7, 7.4 Hz, 1 H, H₂C(11)), 1.38 (ddt, *J* = 16.8, 14.4, 7.1 Hz, 2 H, H₂C(11)), 0.83 (dt, *J* = 14.7, 7.4 Hz, 6 H, H₃C(12)), 0.42 (s, 9 H, (H₃C(13))₃Si).

¹³C NMR: (126 MHz, CDCl₃)
 141.5 (C(4)), 128.8 (HC(1)), 128.4 (HC(2)), 126.5 (HC(3)), 59.1 (C(7)), 55.4 (H₂C(9)), 43.9 (C(10)), 35.5 (H₂C(5)), 32.6 (H₂C(6)), 31.9 (H₂C(11)), 31.4 (H₂C(8)), 24.3 (H₂C(11)), 7.6 (H₃C(12)), 7.0 (H₃C(12)), -0.2 ((H₃C(13))₃Si).

IR: (KBr)
 3080 (m), 2961 (s), 2871 (s), 1597 (m), 1492 (m), 1451 (s), 1403 (s), 1382 (m), 1299 (s), 1250 (s), 1202 (m), 1177 (m), 1139 (s), 1111 (s), 848 (s), 751 (s), 699 (s).

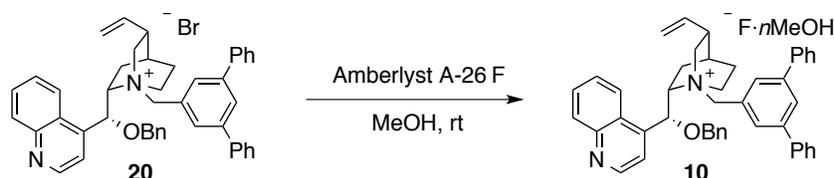
LRMS: (EI, 70 eV):
 55.1 (11), 65.0 (5), 73.0 (95), 74.0 (8), 91.1 (77), 97.1 (6), 115.1 (33), 117.1 (62), 130.1 (7), 147.0 (8), 153.0 (19), 157.1 (8), 162.1 (5), 221.1 (13), 229.1 (35), 248.2 (9), 251.1 (68), 252.1 (12), 253.1 (9), 293.1 (100), 294.1 (21), 295.1 (15), 369.1 (6), 384.2 (10).

Analysis: C₁₉H₃₂O₂S₂Si (384.67)
 calcd: C, 59.33 H, 8.39
 found: C, 59.13 H, 8.40

TLC: *R_f* 0.33 (silica gel, hexanes/EtOAc 9:1, UV/I₂)

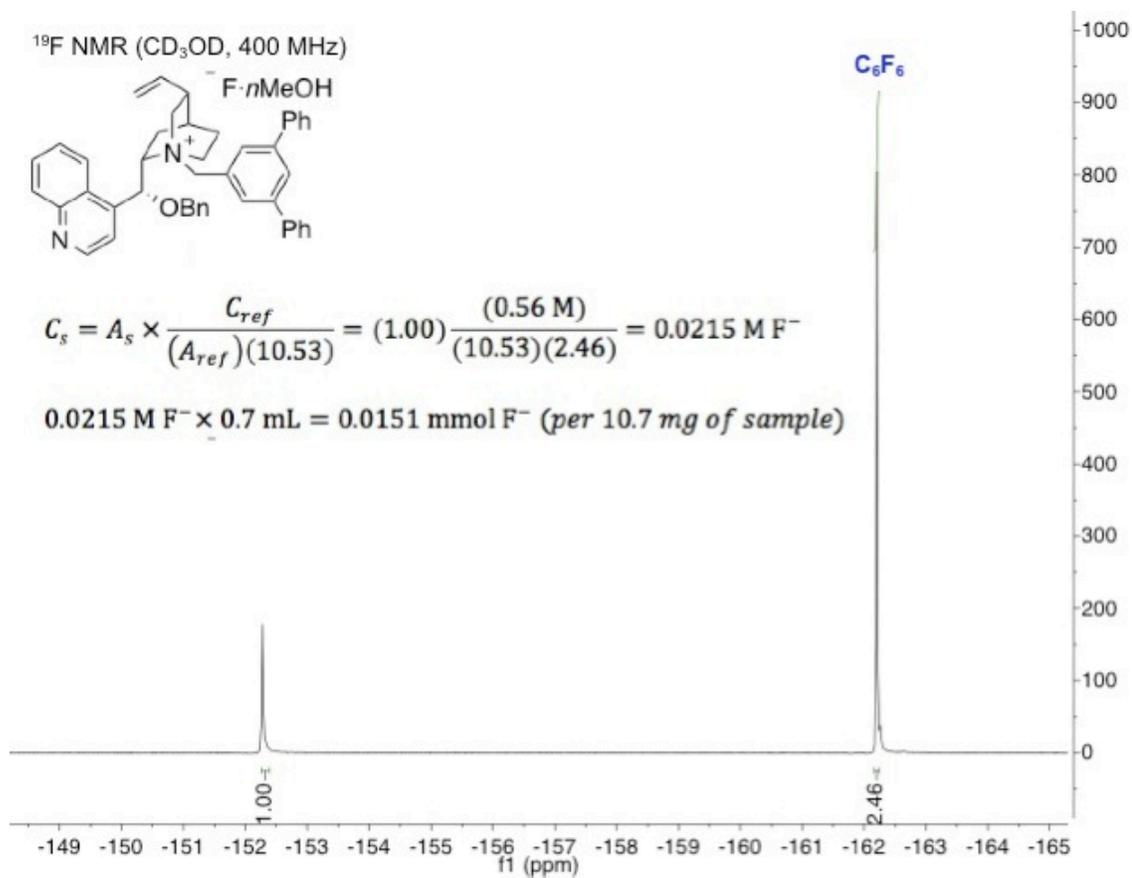
IV. Synthesis of Chiral Quaternary Ammonium Fluoride Catalyst

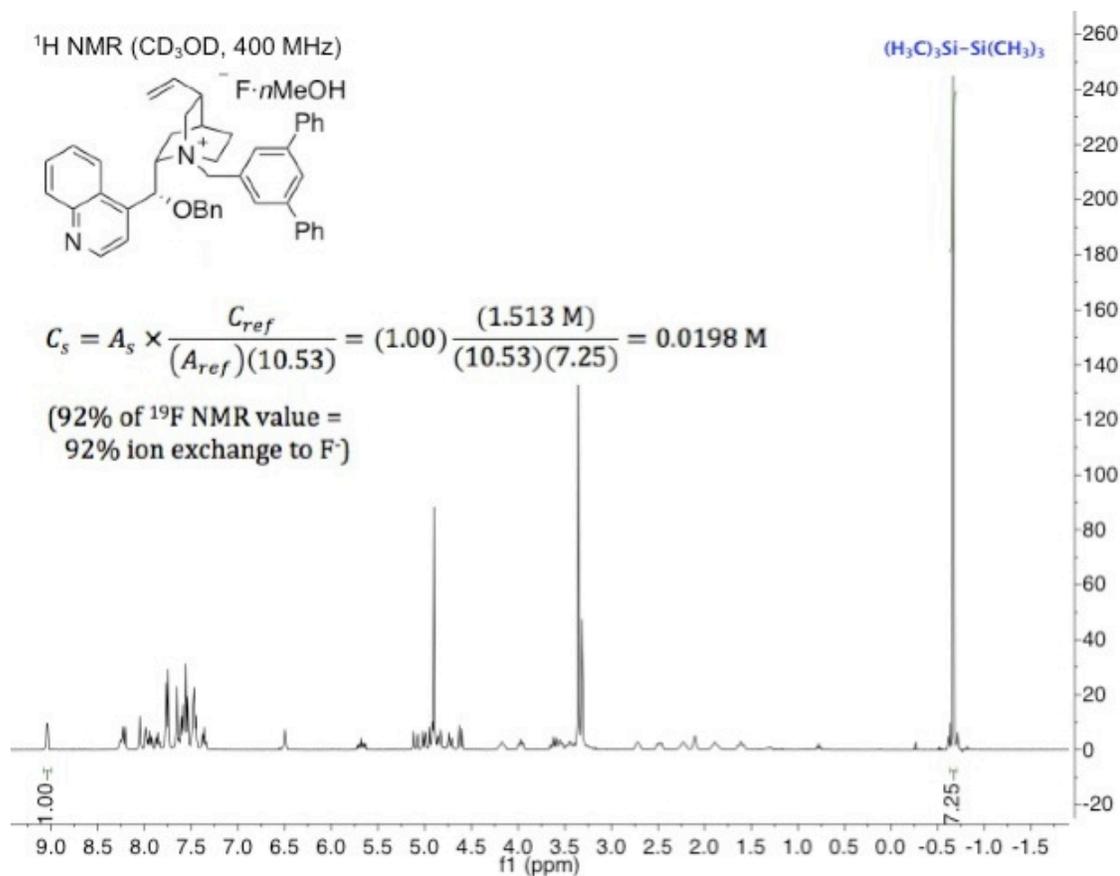
Preparation of 9-Benzyloxy-1-[(3,5-diphenyl)phenylmethyl-(8*S*,9*R*)-cinchonidinium Fluoride (10)



completely yellow). Excess acid was removed by H₂O (600 mL) until the effluent pH was equal to 6 (pH paper, resin returns to original pink color), upon which the column was rinsed with methanol (30 mL). Cinchonidinium bromide **20** was dissolved in 5 mL methanol and was passed through the resin dropwise over a 2 h period. Absence of remaining bromide salt was tested qualitatively by precipitation with 0.1 M aqueous AgNO₃ and 1.0 M aqueous HNO₃. The collected fractions were concentrated by rotary evaporation without heat and dried under vacuum (0.1 mm Hg) for 14 h at room temperature to give **13** as a free-flowing pale yellow powder (>100% mass recovery due to retained methanol solvate). Fluoride salt was stored in an inert atmosphere of argon (to prevent absorption of atmospheric moisture). The catalyst was also stored at -20 °C to slow decomposition by Hoffman elimination.

Characterization of fluoride salt **10** by quantitative ¹H and ¹⁹F NMR was as follows. A sample of fluoride salt (10.7 mg) was accurately weighed into a 528 pp NMR tube under dry argon upon which 0.7 mL of CD₃OD was added. Proton signals were integrated in reference to an internal standard contained within a sealed capillary (hexamethyldisilane, C₆H₁₈Si₂, ¹H NMR, -0.63 ppm) via ¹H NMR spectroscopy using the following parameters: at = 4.665, d1 = 30.0, pw90 = 10.0, pw=pw90, nt=8. Fluoride signals were integrated in reference to an internal standard contained within the sealed capillary (hexafluorobenzene, C₆F₆, ¹⁹F NMR, -162.9 ppm) via ¹⁹F NMR spectroscopy using the following parameters: at = 2.621, d1 = 22.5, pw90 = 22.8, pw=pw90, nt=20. Relaxation (t1) times for each proton or fluorine in both the standard and a representative sample were measured, and the delay (d1) time is set to be greater than the longer t1. A solution of each standard was prepared of known concentration in CDCl₃ (1.513 M hexamethyldisilane, 0.729 M hexafluorobenzene) and contained in a sealed melting point capillary. Due to the differences in diameter of the NMR tube and the melting point capillary, a smaller portion of the standard solution is irradiated relative to the bulk NMR sample. A correction value (10.53) was applied to account for this.⁵

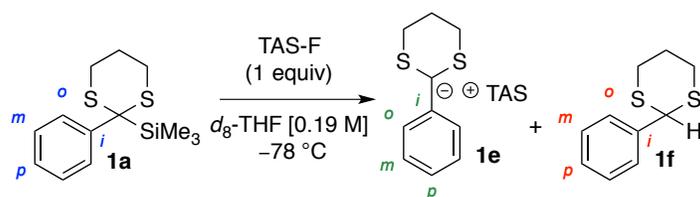


**Data for 10:****¹H NMR:**(400 MHz, CD₃OD)

9.04 (d, $J = 4.5$ Hz, 1 H), 8.32–8.13 (m, 2 H), 8.05 (t, $J = 1.7$ Hz, 1 H), 7.98 (d, $J = 4.5$ Hz, 1 H), 7.94 (t, $J = 7.6$ Hz, 1 H), 7.86 (t, $J = 7.6$ Hz, 1 H), 7.76 (d, $J = 7.1$ Hz, 4 H), 7.68–7.54 (m, 8 H), 7.50–7.44 (m, 4 H), 7.36 (t, $J = 7.4$ Hz, 1 H), 6.50 (s, 1 H), 5.68 (ddd, $J = 17.3, 10.4, 7.0$ Hz, 1 H), 5.10 (d, $J = 17.2$ Hz, 1 H), 5.01 (d, $J = 10.5$ Hz, 1 H), 4.93 (d, $J = 11.5$ Hz, 1 H), 4.84 (d, $J = 12.2$ Hz, 1 H), 4.73 (d, $J = 12.2$ Hz, 1 H), 4.62 (d, $J = 11.5$ Hz, 1 H), 4.24–4.14 (m, 1 H), 3.97 (t, $J = 9.1$ Hz, 1 H), 3.70–3.50 (m, 2 H), 3.44 (ddd, $J = 14.9, 10.4, 4.5$ Hz, 1 H), 2.81–2.65 (m, 1 H), 2.55–2.39 (m, 1 H), 2.32–2.14 (m, 1 H), 2.10 (br s, 1 H), 1.97–1.78 (m, 1 H), 1.72–1.49 (m, 1 H).

¹⁹F NMR:(376 MHz, CD₃OD)

-152.3 (br s).

V. ^{13}C NMR Analysis of Nucleophile Generation

To an oven dried 5 mm NMR tube was added tri(dimethylamino)sulfonium difluorotrimethylsilicate (TAS-F, 35.8 mg, 0.13 mmol, 1.0 equiv) under an Ar atmosphere in a dry box. The NMR tube was capped with a septum, sealed with Parafilm, and removed from the dry box and flushed with Ar on a Schlenk line. To the NMR tube was added 0.5 mL d_8 -THF to give a heterogeneous pale yellow solution (TAS-F is not fully soluble). To a flame-dried, dram vial was added **1a** (69.8 mg, 0.26 mmol, 2.0 equiv), backfilled with Ar twice, and dissolved in 0.4 mL THF to give a colorless, homogeneous solution. The NMR spectrometer (500 MHz) was cooled to an internal temperature of -78 °C (calibrated by relative chemical shifts of pure methanol sample), and locked onto d_8 -THF sample of TAS-F. The NMR tube containing TAS-F was removed from the spectrometer, cooled to -78 °C ($\text{CO}_2(\text{s})/\text{acetone}$ bath), then **1a** was added by syringe as a solution in THF (0.2 mL, 0.13 mmol, 1.0 equiv). The solution within the NMR tube immediate turned neon yellow but did not fully mix. The NMR tube was removed from the cooling bath, inverted once (to fully mix, upon which the solution turned bright red), and added to the NMR spectrometer (maintained at -78 °C). Acquisition of a ^{13}C NMR spectrum was performed immediately. Spectra are show in Figures S-1 and S-2.

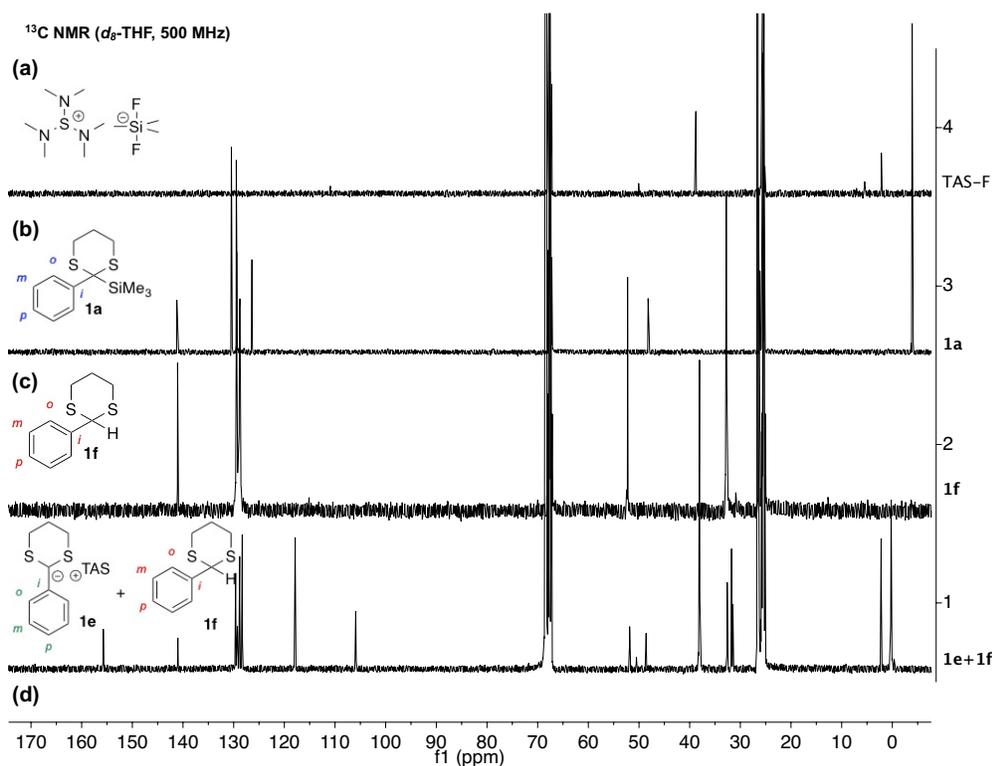


Figure S-1. ^{13}C NMR in d_8 -THF of (a) TAS-F reference spectrum, (b) starting silyl dithiane **1a** reference spectrum, (c) dithiane **1f** reference spectrum, and (d) immediate acquisition after addition **1a** to TAS-F (mixture of **1e** and **1f**).

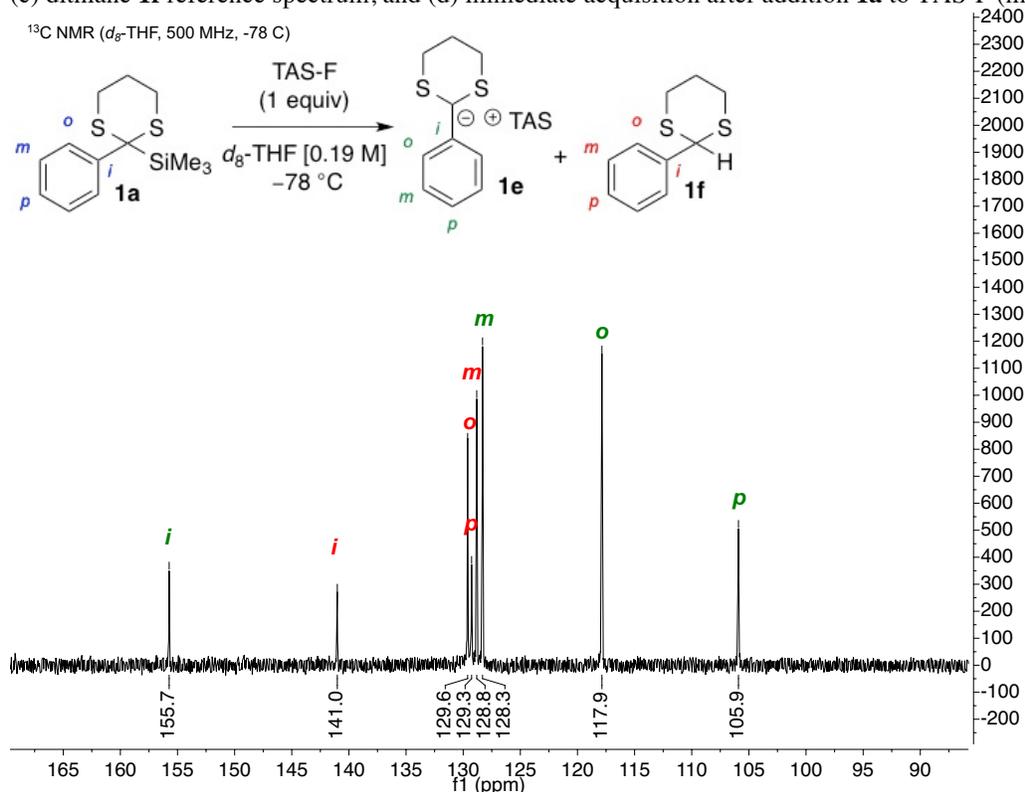
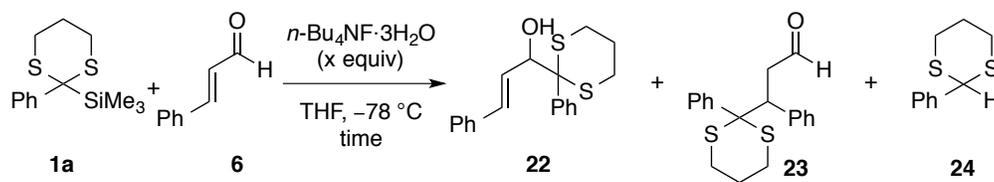


Figure S-2. ^{13}C NMR of aryl region in d_8 -THF (immediate acquisition) after addition **1a** to TAS-F (mixture of **1e** and **1f**).

VI. Additions to *trans*-Cinnamaldehyde



To a flame-dried, 10-mL Schlenk flask with septum and stir bar was added silyldithiane **1a** (200 mg, 0.75 mmol, 1.5 equiv). The flask was evacuated and backfilled with Ar twice, then *trans*-cinnamaldehyde **6** (66 mg, 63 μL , 0.5 mmol, 1.0 equiv) and THF (6.0 mL, 0.08 M) were added by syringe. The reaction was stirred under Ar, fitted with an internal temperature probe, and cooled to -78°C (dry ice/acetone). Tetrabutylammonium fluoride trihydrate (see Table S1 for equiv) was added dropwise as a freshly prepared solution in THF (0.2 M) and was stirred at -78°C for the specified amount of time (see Table S1). The reaction was quenched at -78°C with 5.0 mL of 2.0 M $\text{Cl}_3\text{CCO}_2\text{H}$ in THF resulting in complete loss of color. The cooling bath was then removed and the reaction was stirred for at

rt. The reaction mixture was transferred with 20 mL of Et₂O to a 60-mL separatory funnel containing 15 mL of sat. NaHCO₃ (aq) solution. The aqueous layer was separated and extracted with Et₂O (1 × 20 mL). The combined organic layer was washed with distilled water (2 × 20 mL) and saturated brine (1 × 20 mL), dried over MgSO₄, filtered (cotton plug), and concentrated *via* rotary evaporation (15 mm Hg, 25 °C). The crude yellow oil was purified by flash chromatography (30 g SiO₂, 170 mm × 25 mm, 10 mL fractions, hexanes/TBME gradient (200 mL each): 20:1 to 15:1 to 10:1 to 4:1 to 2:1). Multiple products were isolated in the following order of elution (monitor by TLC in 9:1 hexanes/TBME): recovered silyl dithiane **1a** (*R_f* 0.72), phenyl dithiane **24** (*R_f* 0.39), recovered **6** and 1,4-adduct **23** (coelute, *R_f* 0.19) and 1,2-adduct **22** (*R_f* 0.08).

Table S1. Addition of Silyl Phenyl Dithiane to *trans*-Cinnamaldehyde With Varying Fluoride Loading^a

entry	equiv of <i>n</i> -Bu ₄ NF·3H ₂ O ^b	time (h)	yield (mg, %) ^c				
			22	23	24	recovered 1a	recovered 6
1	0.03	1	11 mg, 6%	-	-	187 mg, 94%	68 mg, quant.
2	0.03	7	15 mg, 9%	-	-	185 mg, 93%	56 mg, 89%
3	0.10	1	131 mg, 80%	12% ^d	39 mg, 17%	-	10% ^d
4	1.0	1	125 mg, 76%	7% ^d	57 mg, 38%	-	5% ^d

^aAll reactions were performed on a 0.50 mmol scale in THF [0.08 M] at -78 °C with 1.5 equiv of **1a**, followed by quenching with 5 mL of 2 M Cl₃CCO₂H in THF. ^bEquivalents based upon **6**. ^cIsolated yield of chromatographically homogenous material. ^dApproximate yield estimated by relative integration in ¹H NMR (CDCl₃) in co-eluted fraction containing **23** and recovered **6** after chromatography.

Data for 22:

¹H NMR: (400 MHz, CDCl₃)

7.98 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34–7.11 (m, 6H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.01 (dd, *J* = 15.8, 6.5 Hz, 1H), 4.52 (t, *J* = 5.6 Hz, 1H), 2.75–2.58 (m, 4H), 2.43 (br d, *J* = 5.2 Hz, 1H), 1.91 (hept, *J* = 4.5 Hz, 2H).

TLC: *R_f* 0.08 (silica gel, hexanes/TBME 9:1, UV/KMnO₄)

Data for 23:

¹H NMR: (400 MHz, CDCl₃)
9.49 (dd, $J = 2.6, 1.1$ Hz, 1H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.37–7.21 (m, 3H), 7.21–7.11 (m, 3H), 6.89 (d, $J = 8.4$ Hz, 2H), 3.82 (dd, $J = 10.9, 4.0$ Hz, 1H), 3.35 (ddd, $J = 17.3, 4.0, 1.1$ Hz, 1H), 2.92 (ddd, $J = 17.3, 10.8, 2.5$ Hz, 1H), 2.63 (ddd, $J = 8.0, 4.9, 2.8$ Hz, 4H), 1.86 (dddd, $J = 9.8, 8.3, 5.4, 3.1$ Hz, 2H).

TLC: R_f 0.19 (silica gel, hexanes/TBME 9:1, UV/IKMnO₄)

Data for 24:

¹H NMR: (400 MHz, CDCl₃)
7.47 (d, $J = 7.0$ Hz, 2H), 7.37–7.27 (m, 3H), 5.17 (s, 1H), 3.07 (ddd, $J = 14.6, 12.8, 2.4$ Hz, 2H), 2.91 (ddd, $J = 14.5, 4.3, 2.9$ Hz, 2H), 2.18 (dtt, $J = 13.9, 4.6, 2.5$ Hz, 1H), 1.94 (dtt, $J = 14.2, 12.4, 3.1$ Hz, 1H).

TLC: R_f 0.39 (silica gel, hexanes/TBME 9:1, UV/KMnO₄)

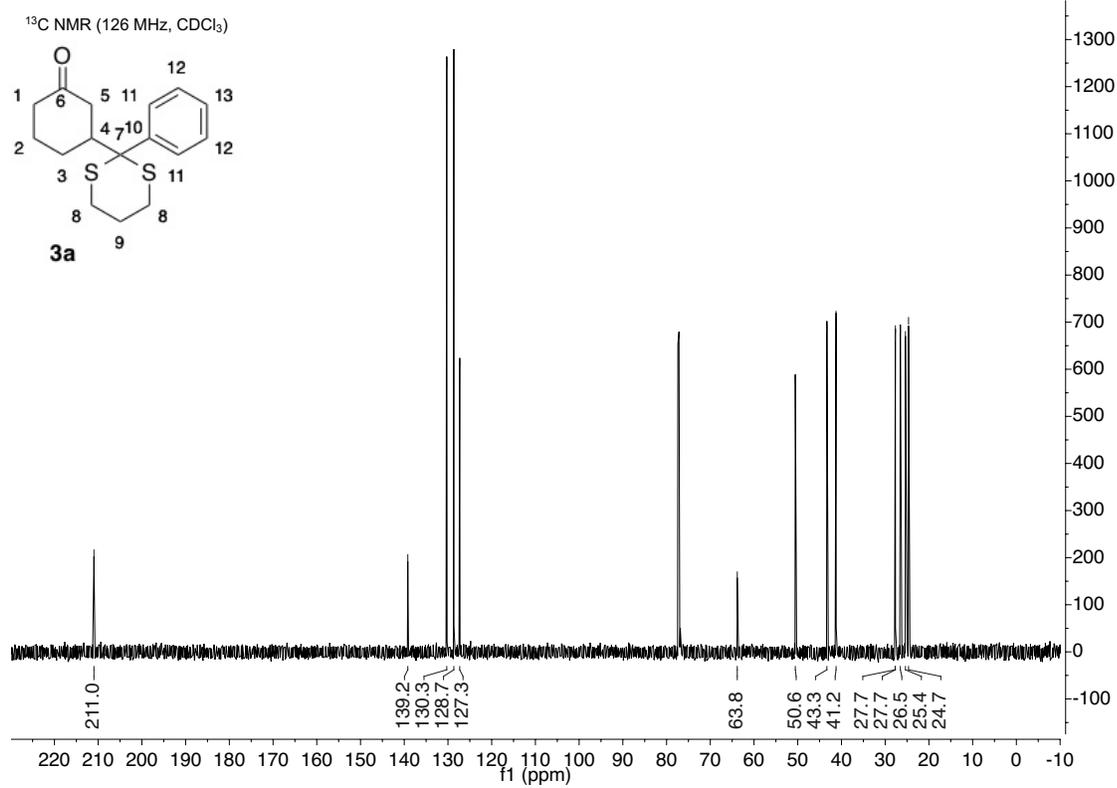
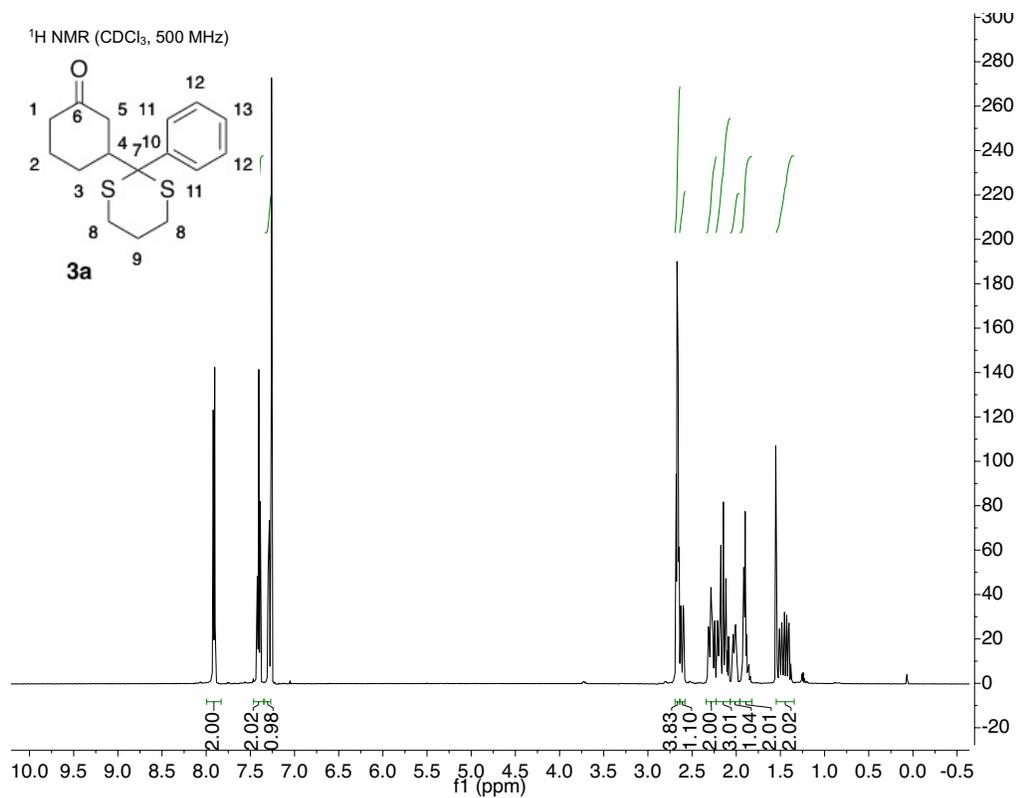
Data for 1a:

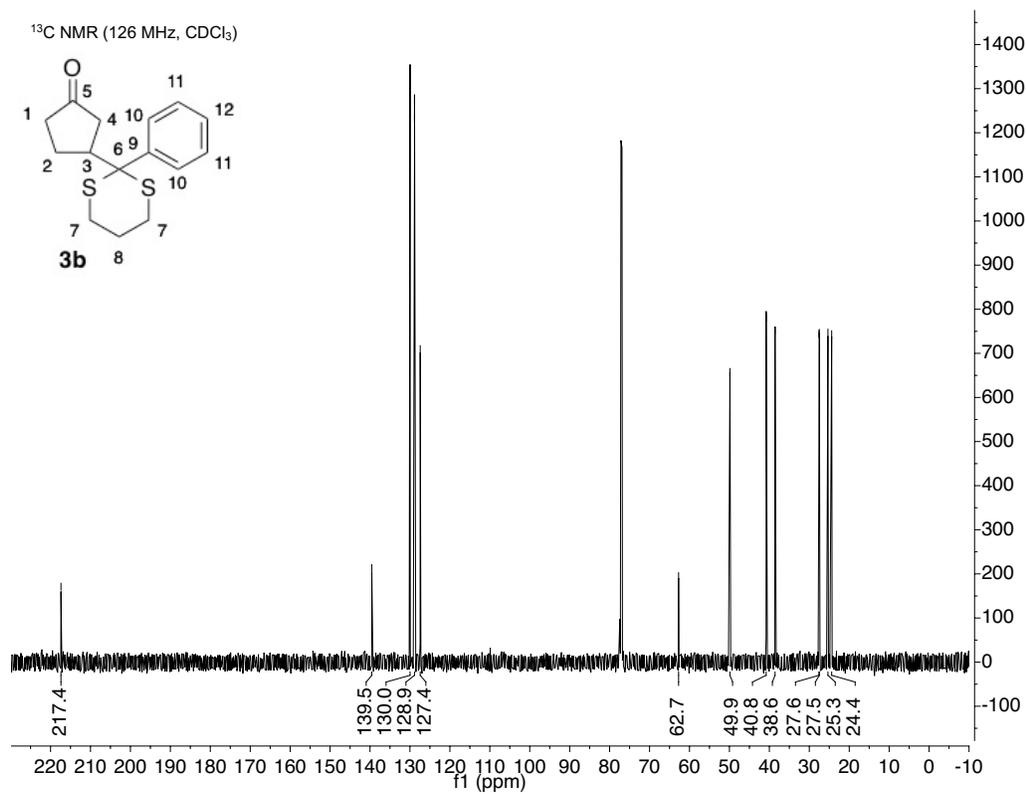
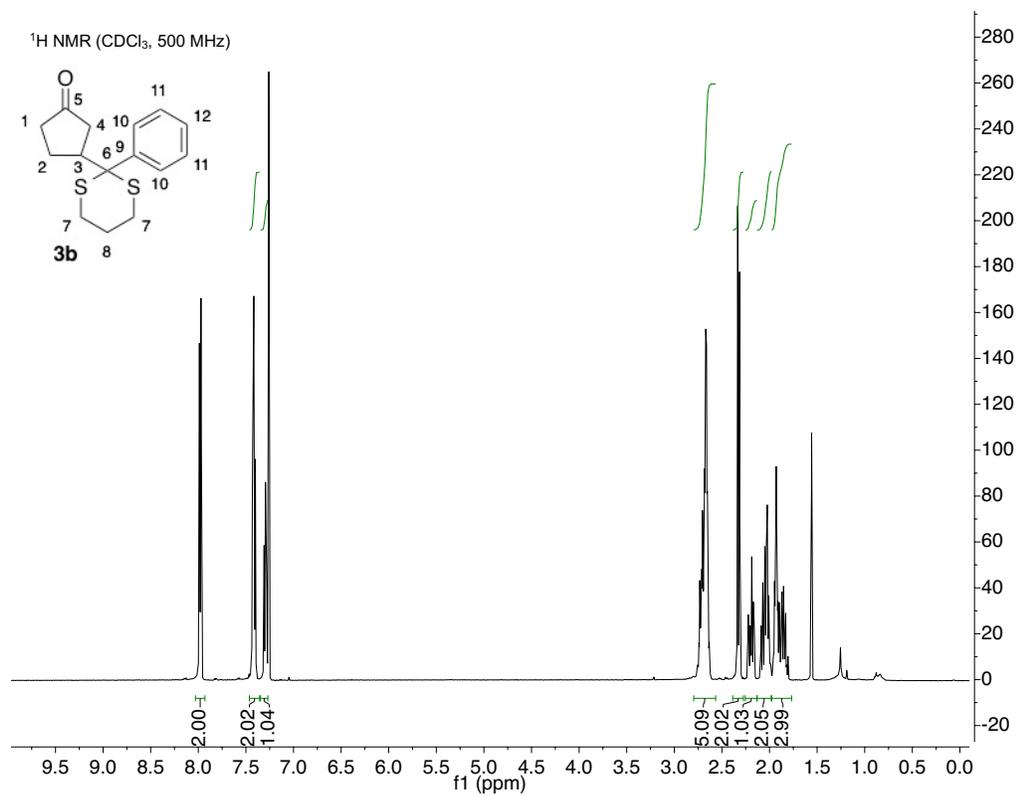
¹H NMR: (400 MHz, CDCl₃)
7.90 (dd, $J = 8.5, 1.1$ Hz, 2H), 7.37 (td, $J = 7.5, 1.9$ Hz, 2H), 7.18 (dtt, $J = 7.6, 6.9, 1.2$ Hz, 1H), 2.77 (tdd, $J = 12.7, 2.8, 1.0$ Hz, 2H), 2.43 (dddd, $J = 13.3, 4.1, 3.2, 1.1$ Hz, 2H), 2.03 (qt, $J = 12.7, 3.2$ Hz, 1H), 1.89 (dtt, $J = 10.8, 4.0, 2.0$ Hz, 1H), 0.06 (s, 9H).

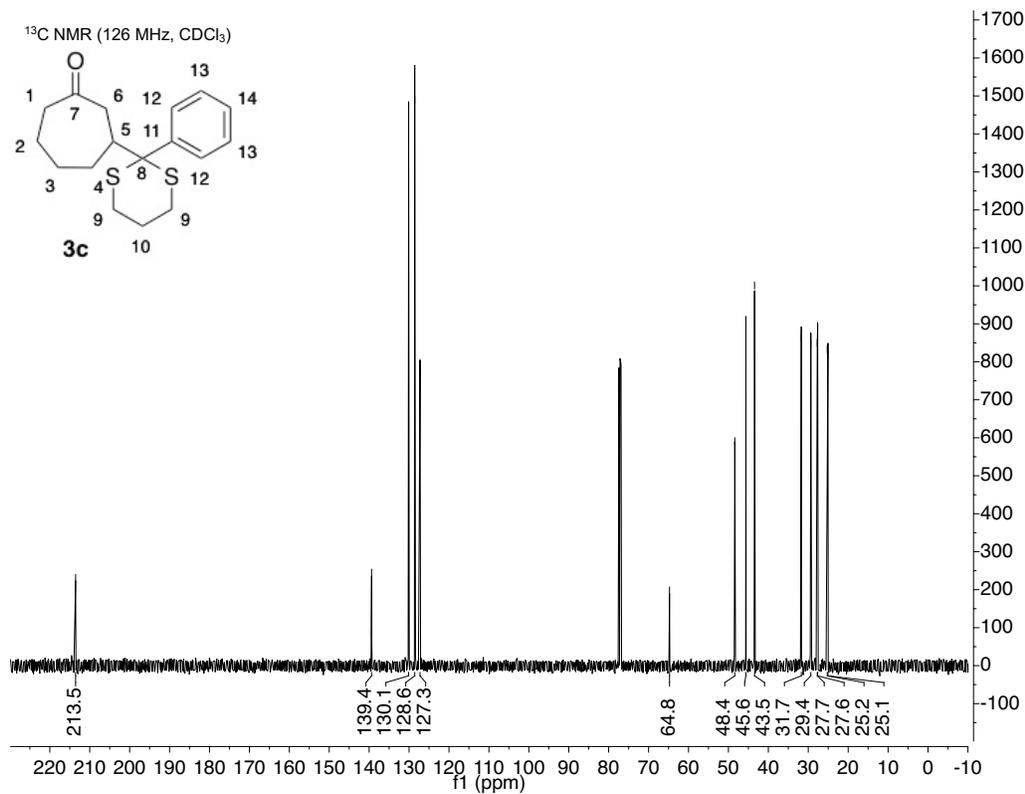
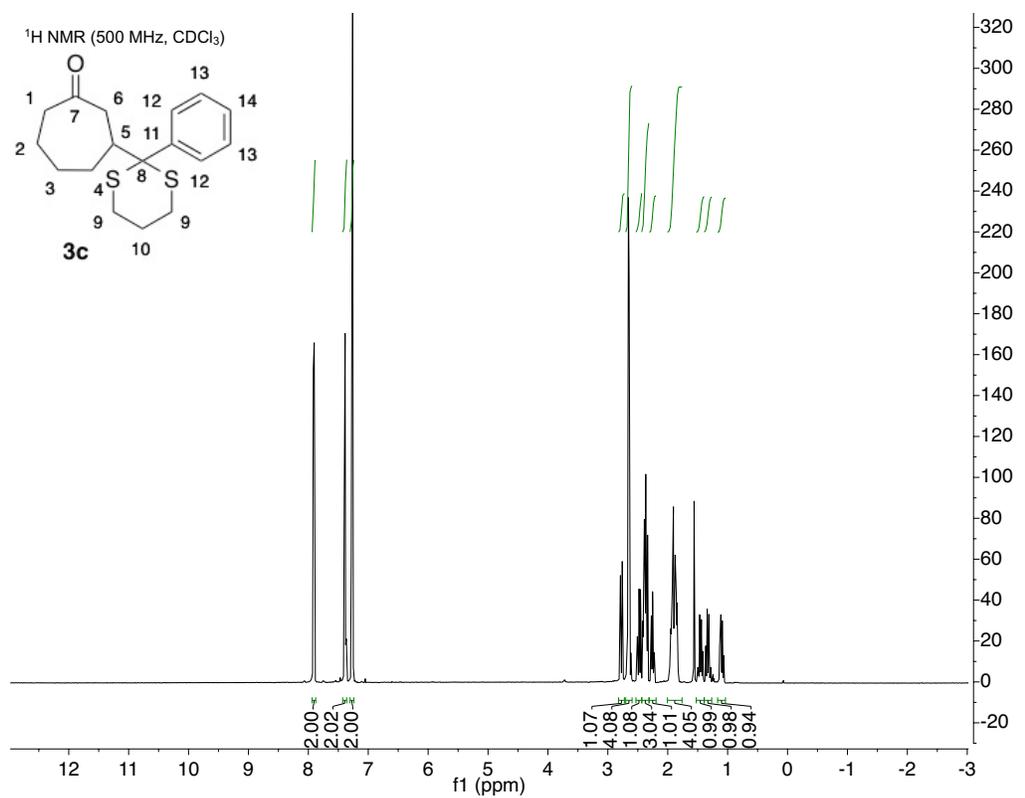
TLC: R_f 0.72 (silica gel, hexanes/TBME 9:1, UV/IKMnO₄)

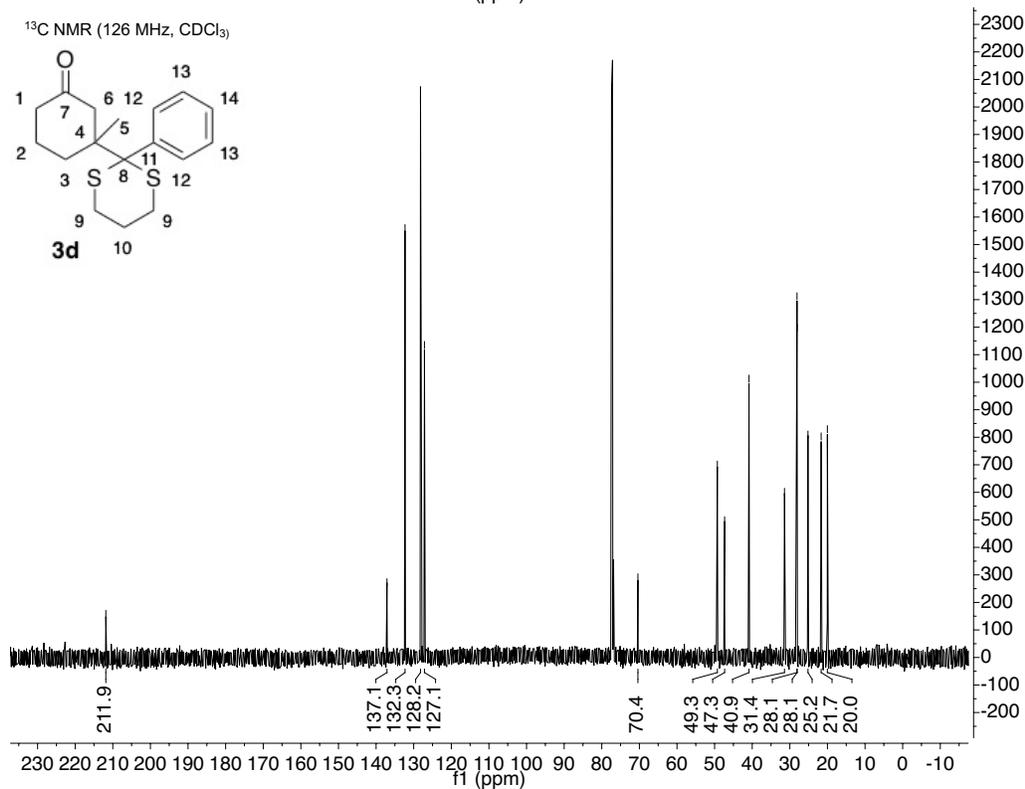
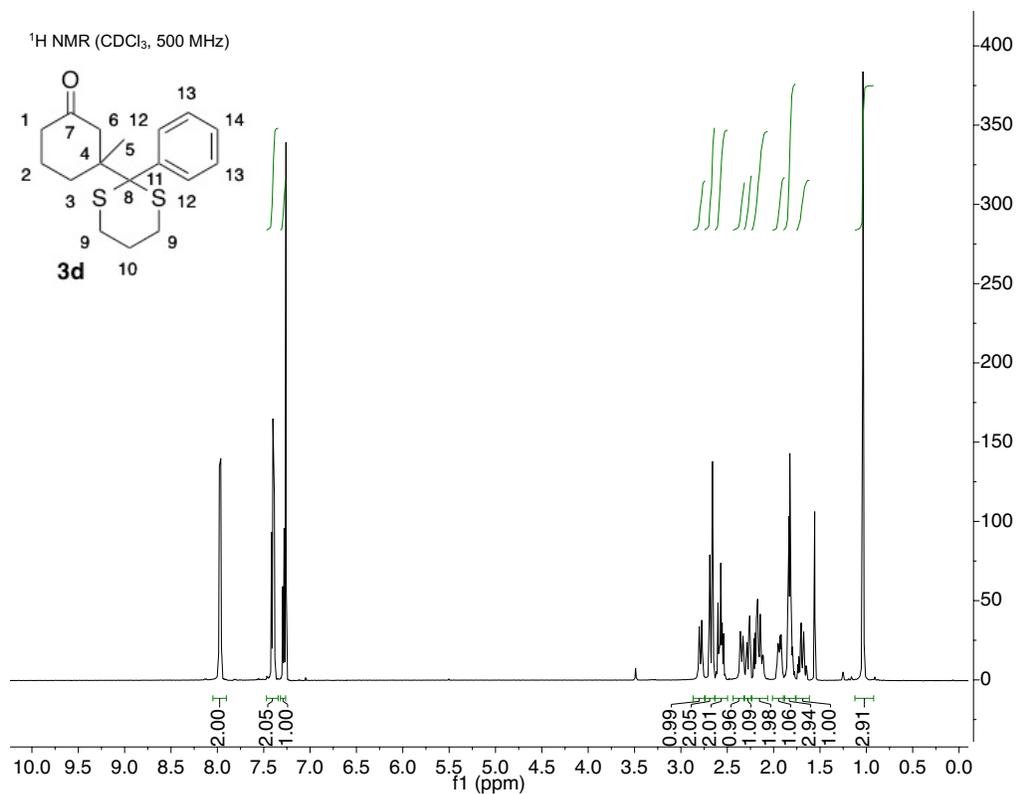
References

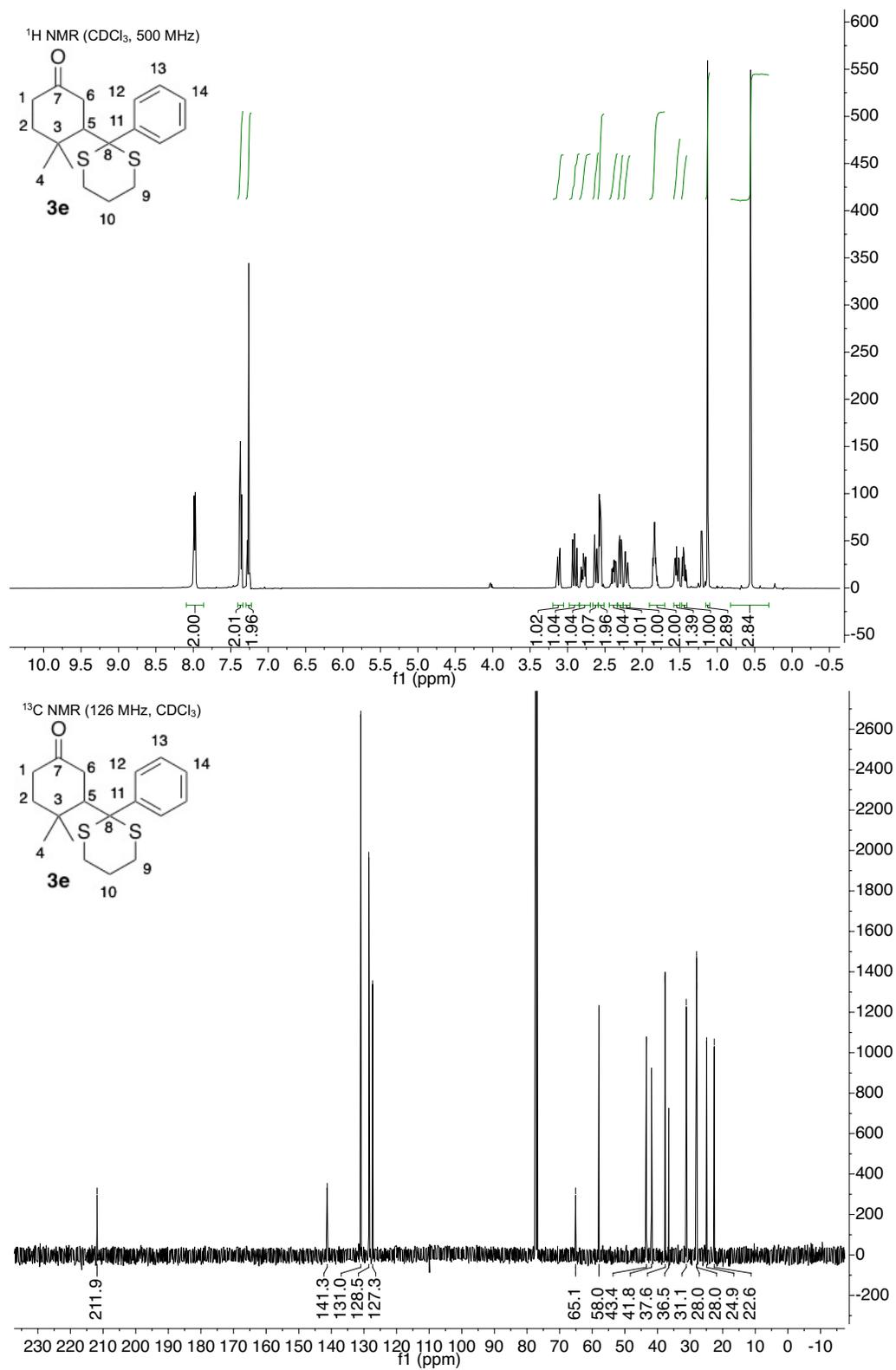
1. Gilman, H.; Cartledge, J. K.; Sims, S.-Y. *J. Organomet. Chem.* **1963**, *1*, 8–14. 2.
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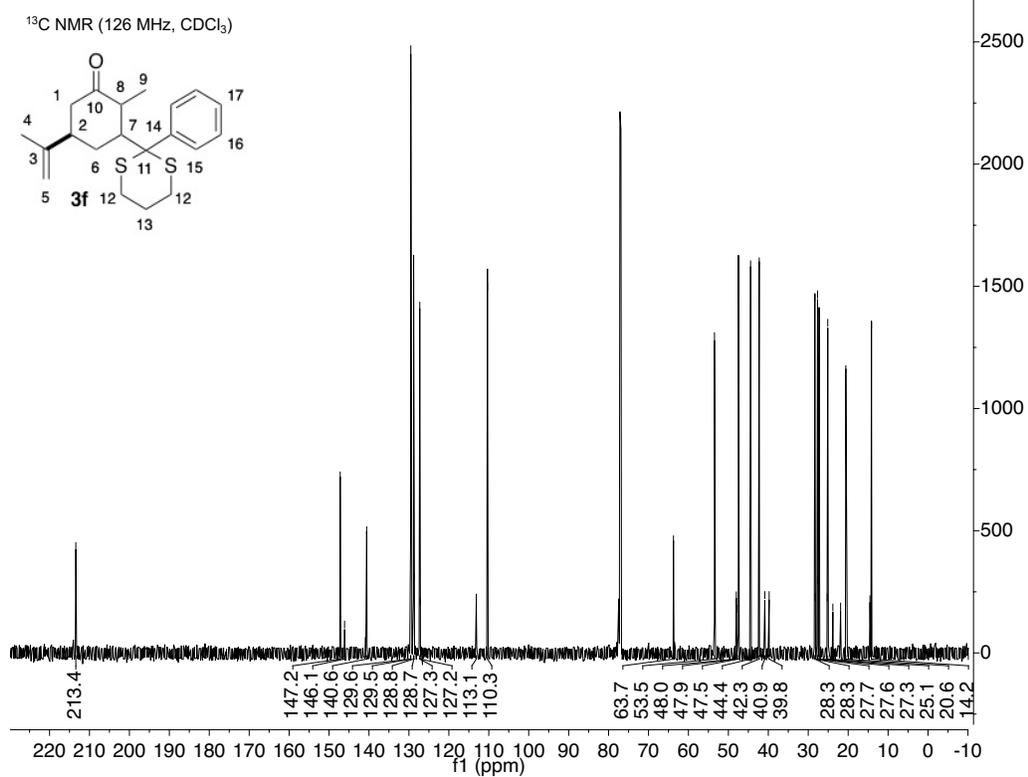
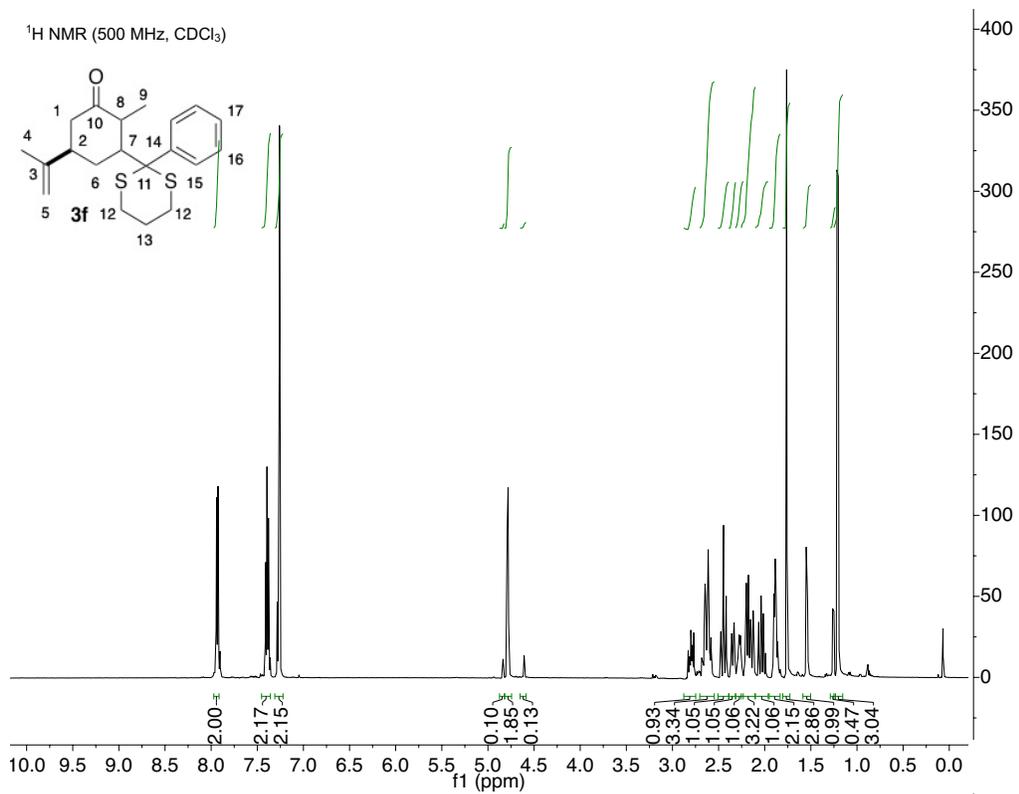


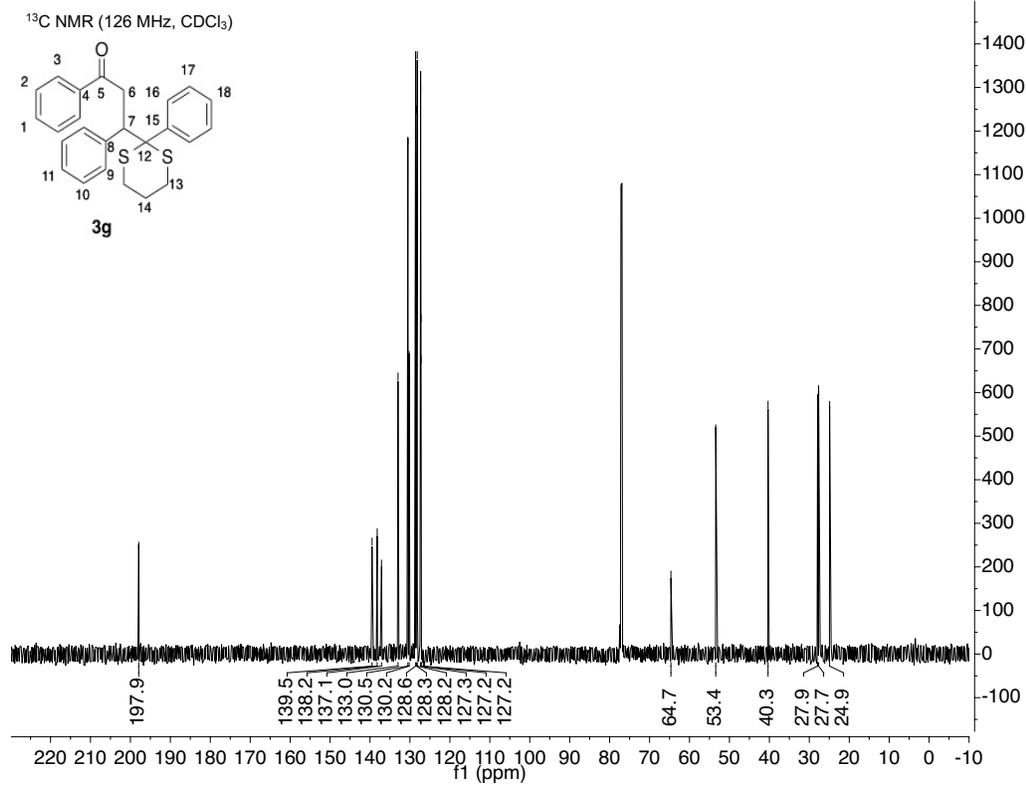
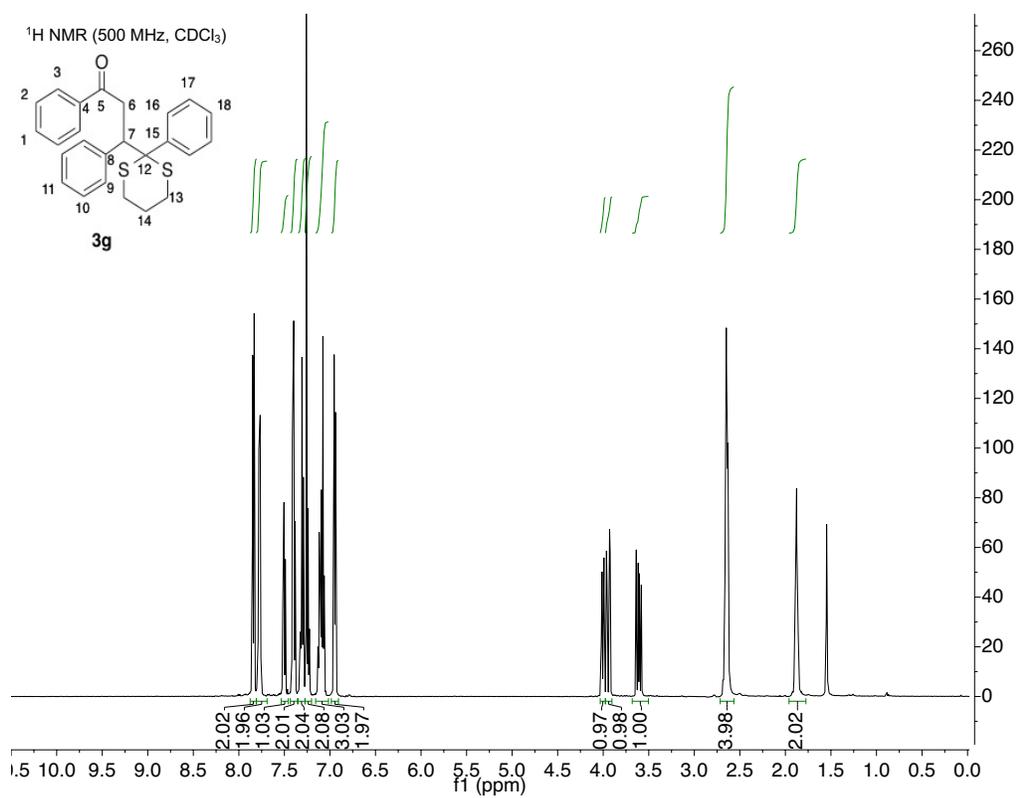


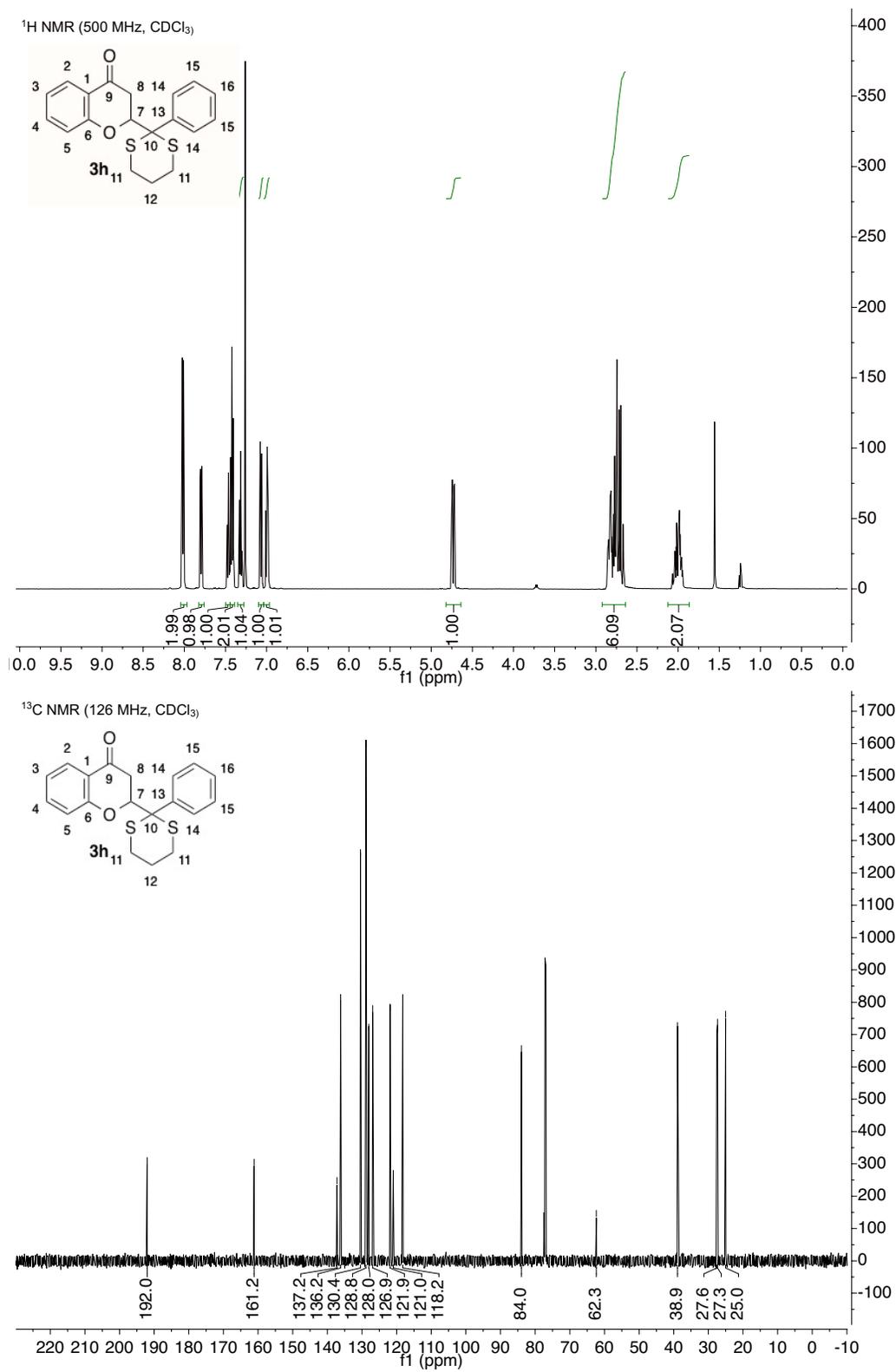


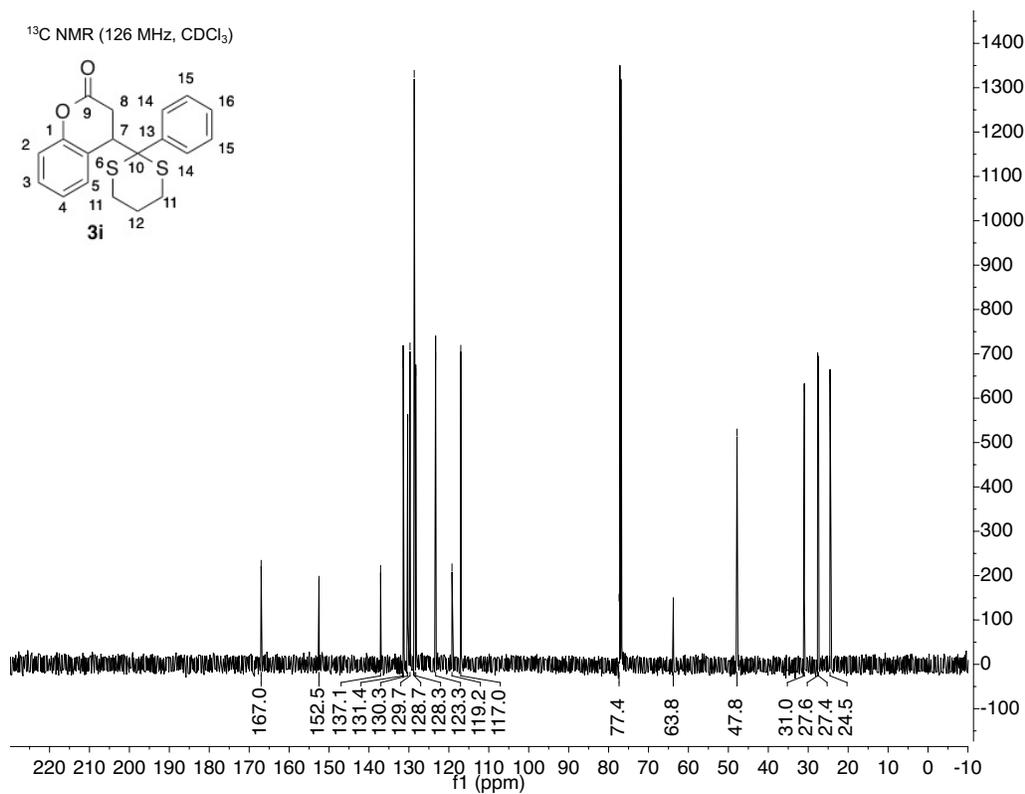
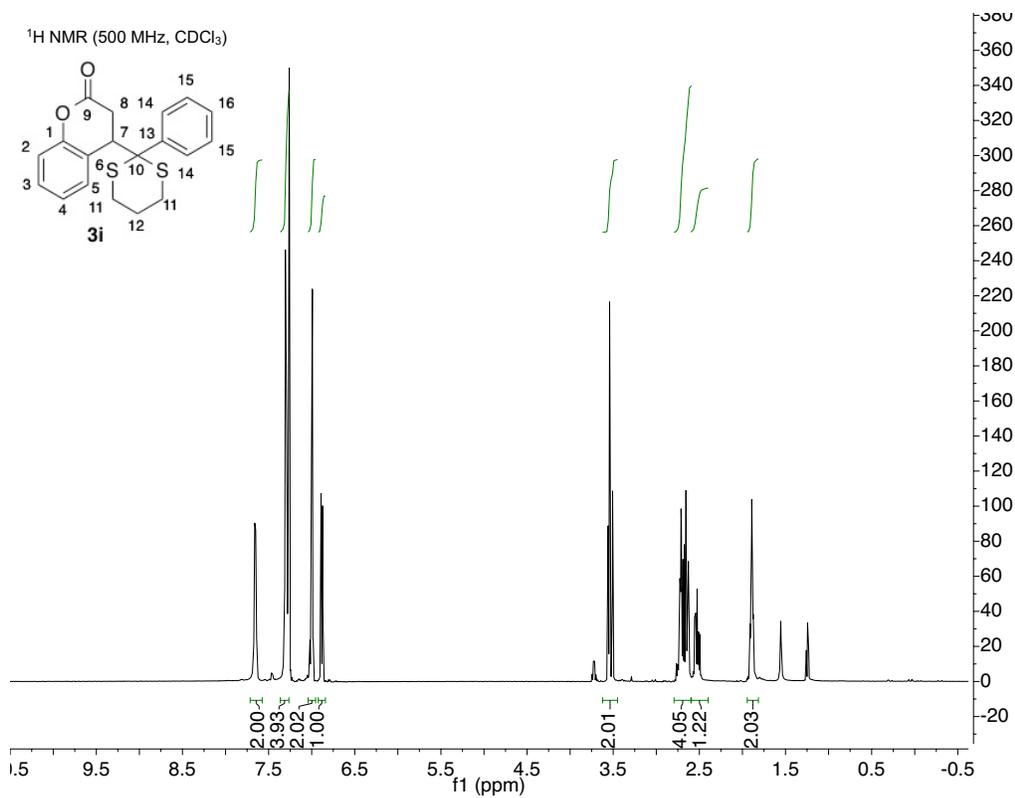


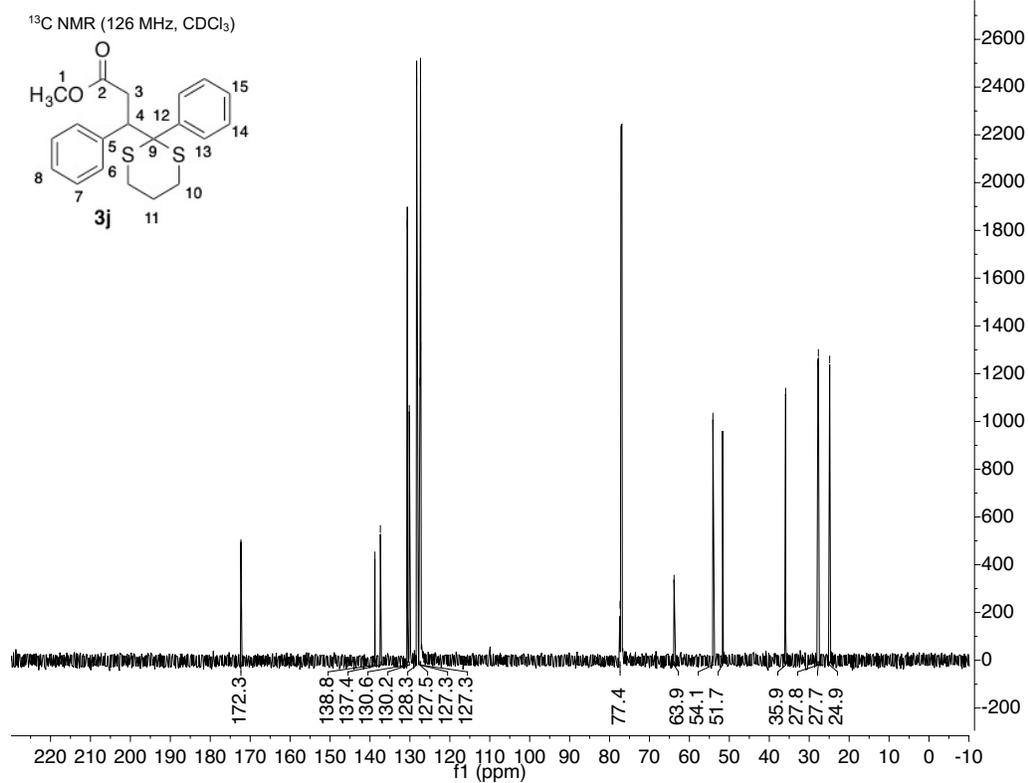
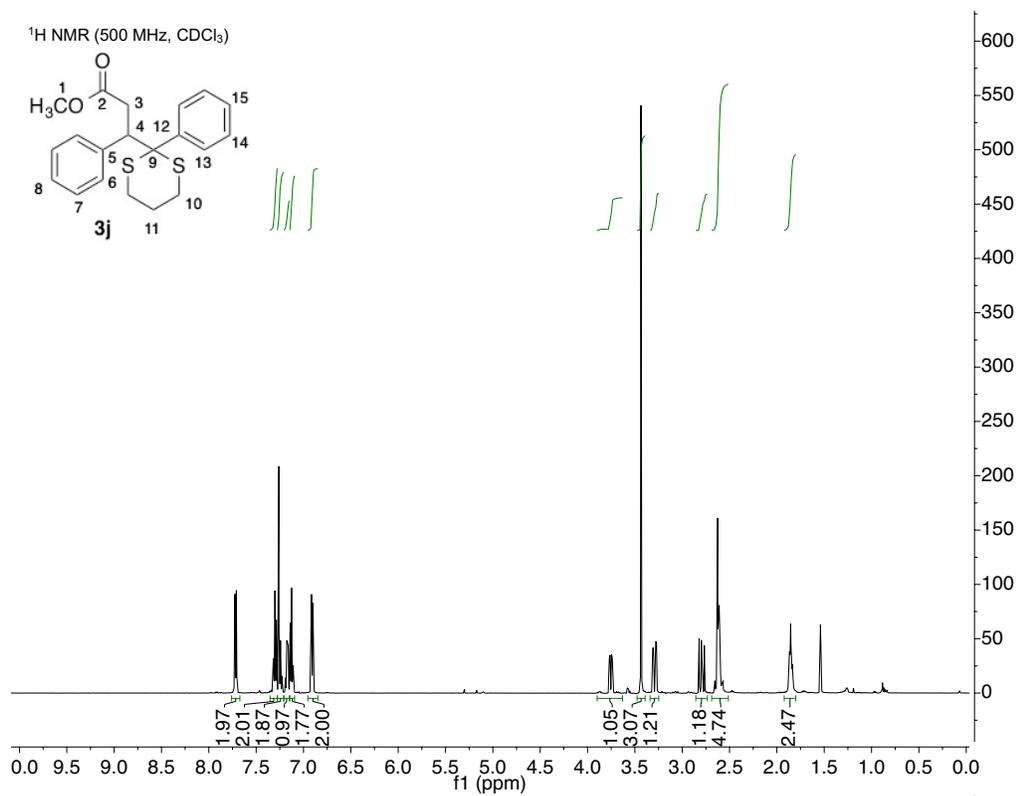


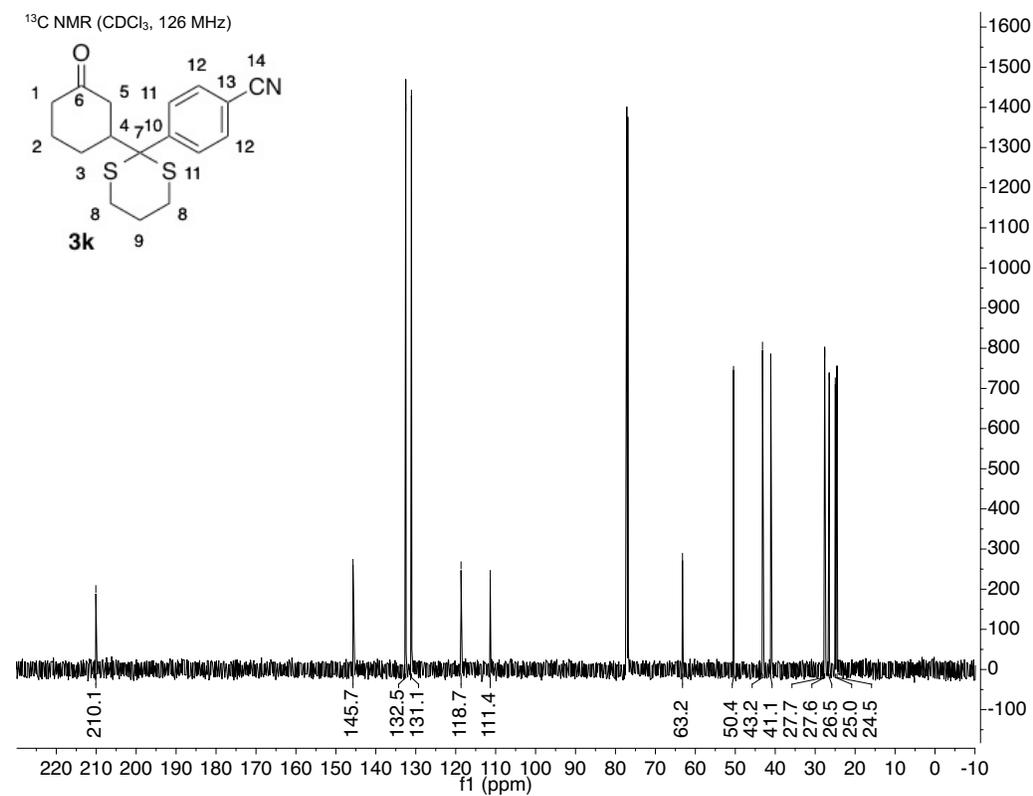
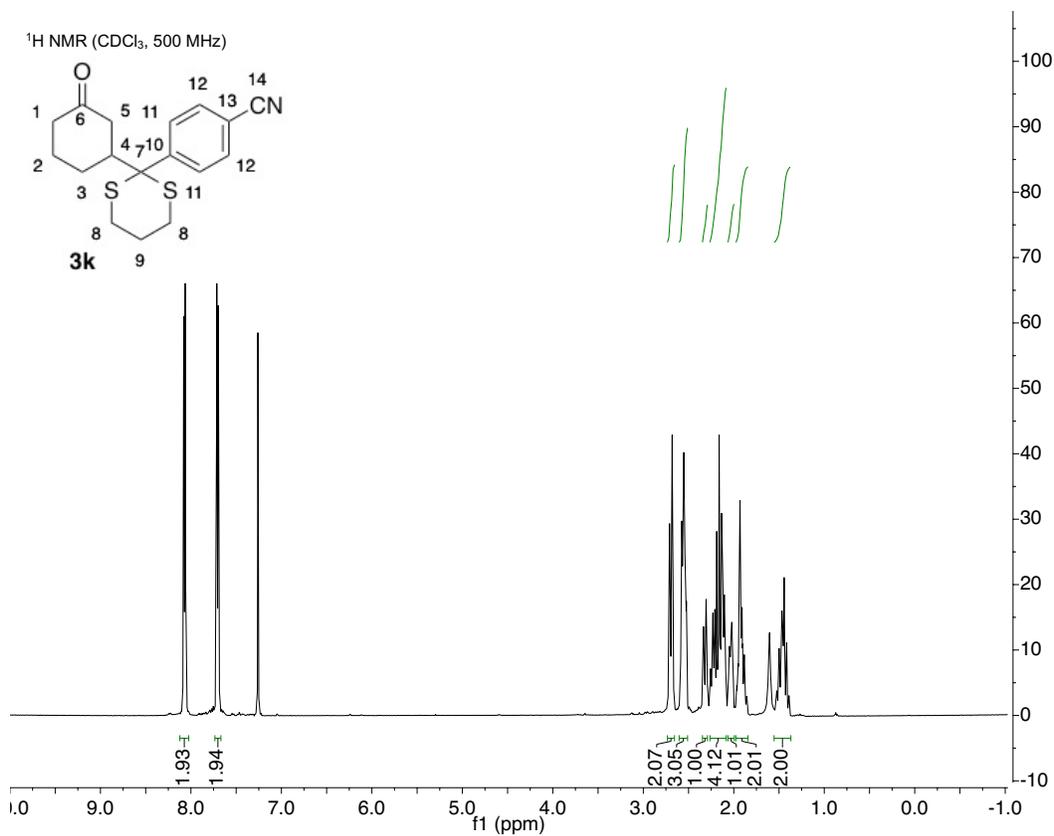


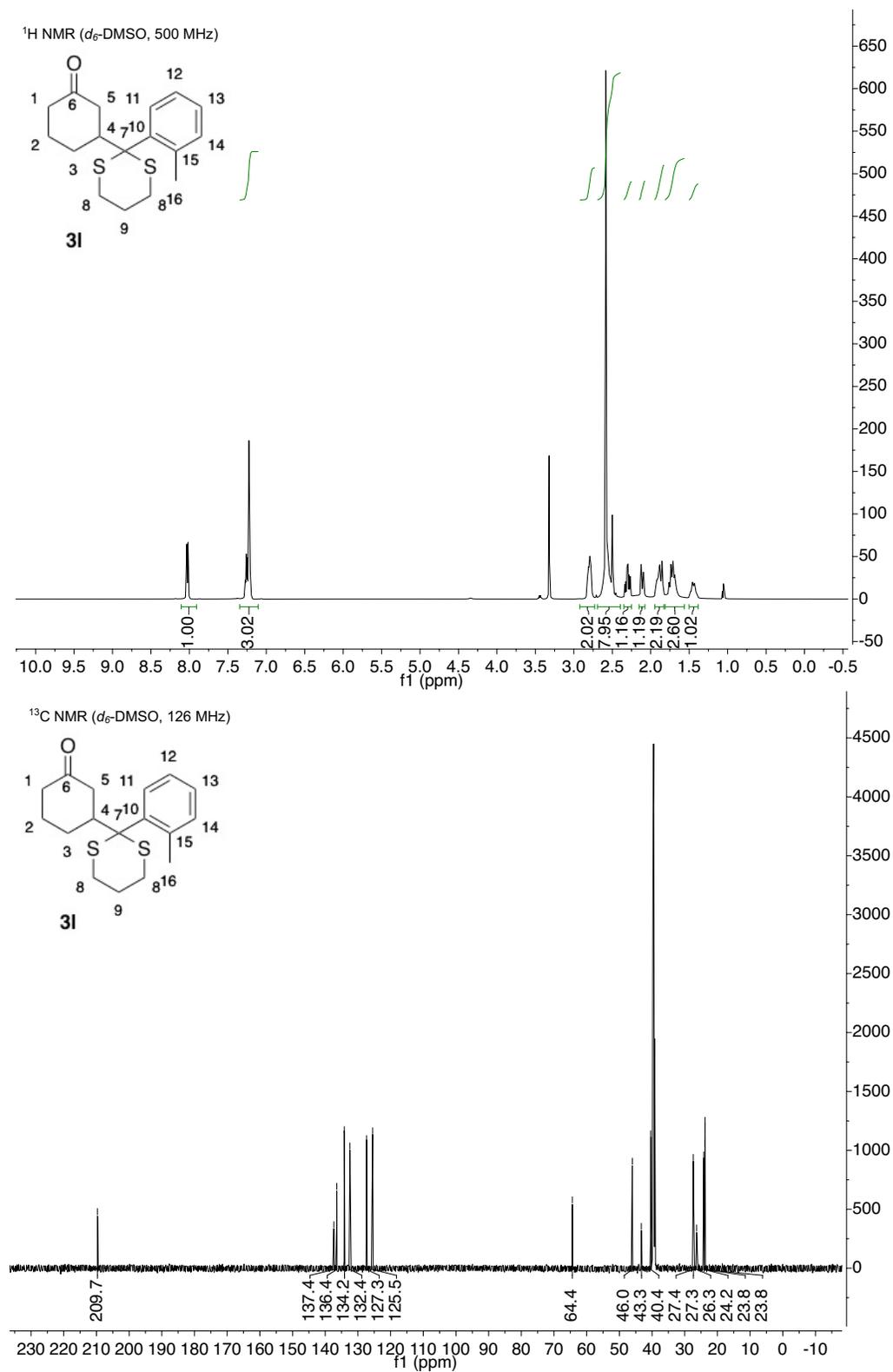


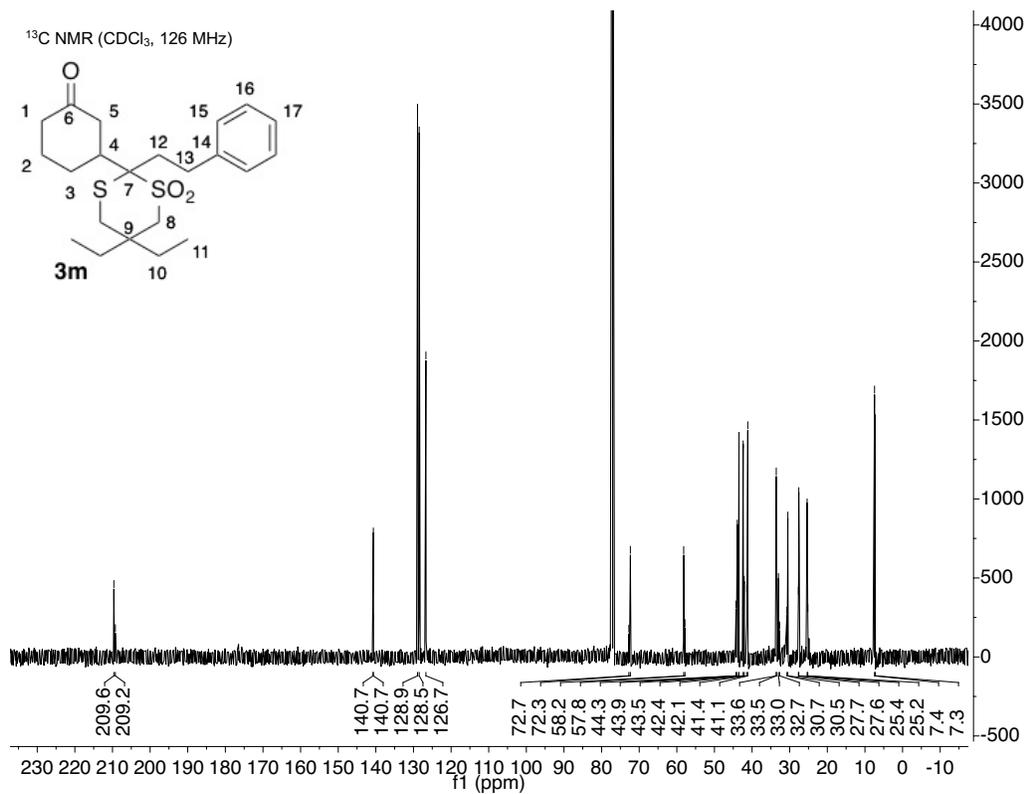
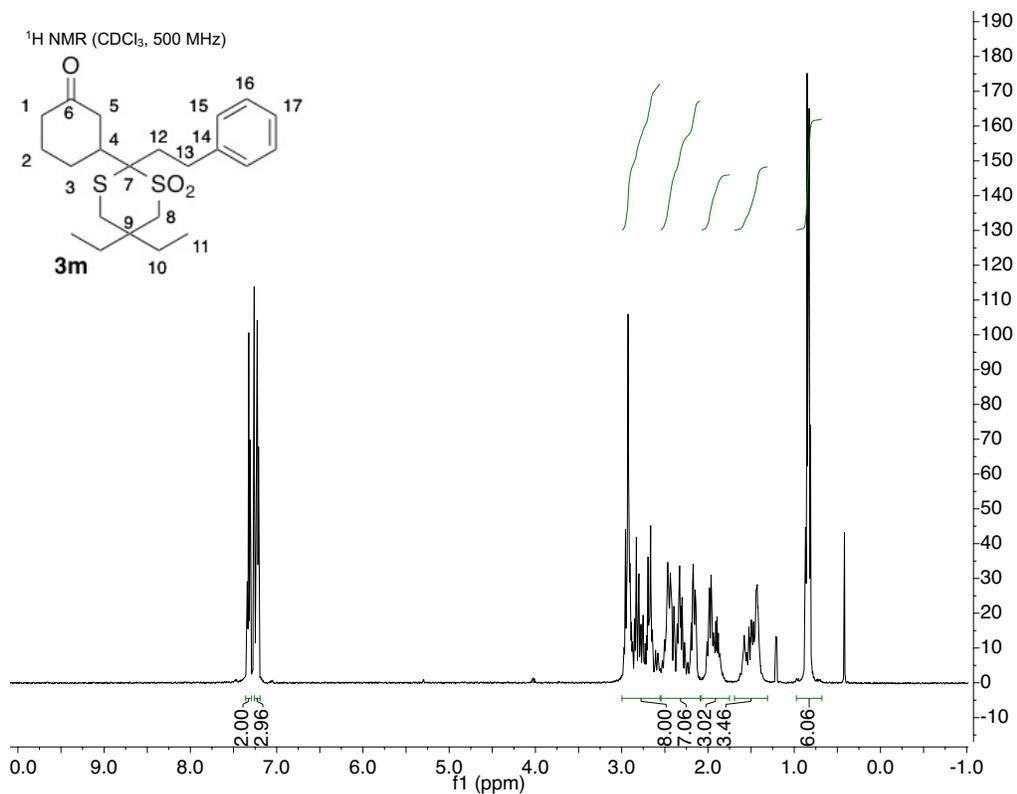


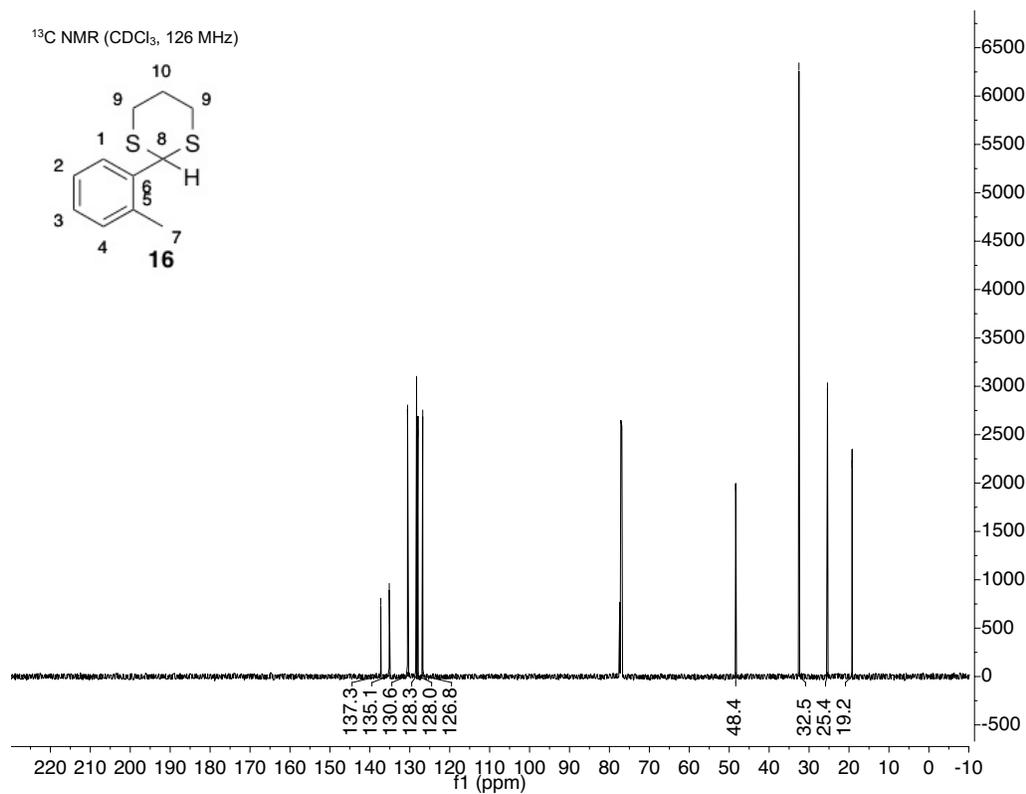
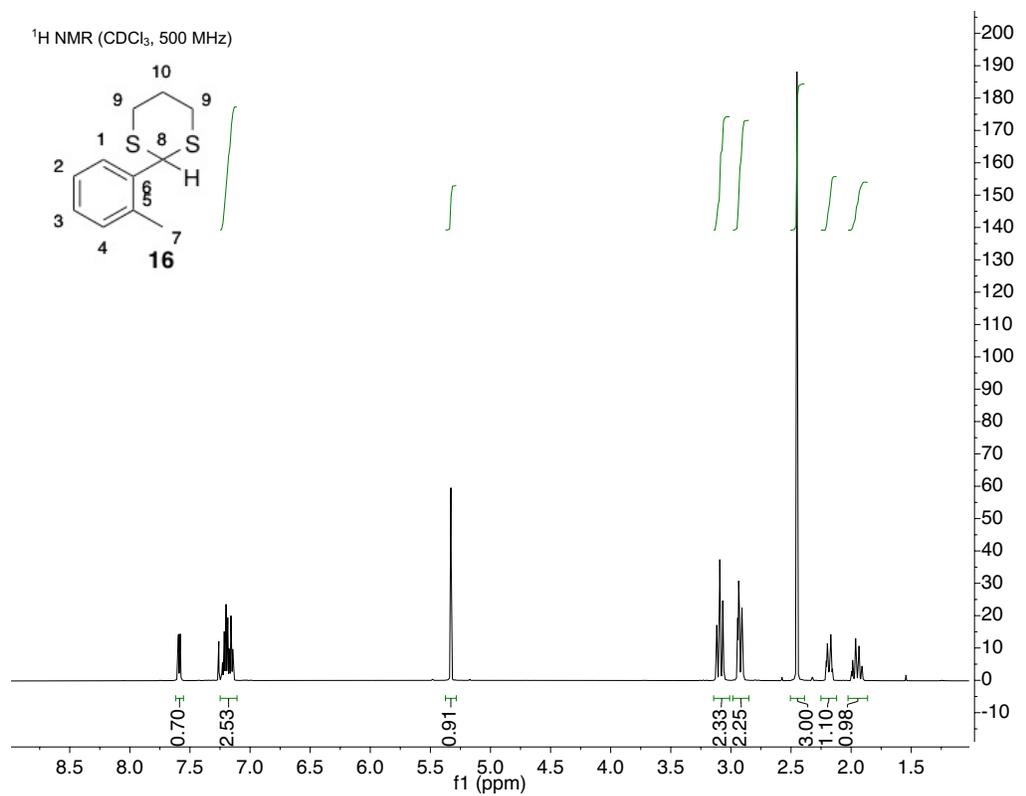


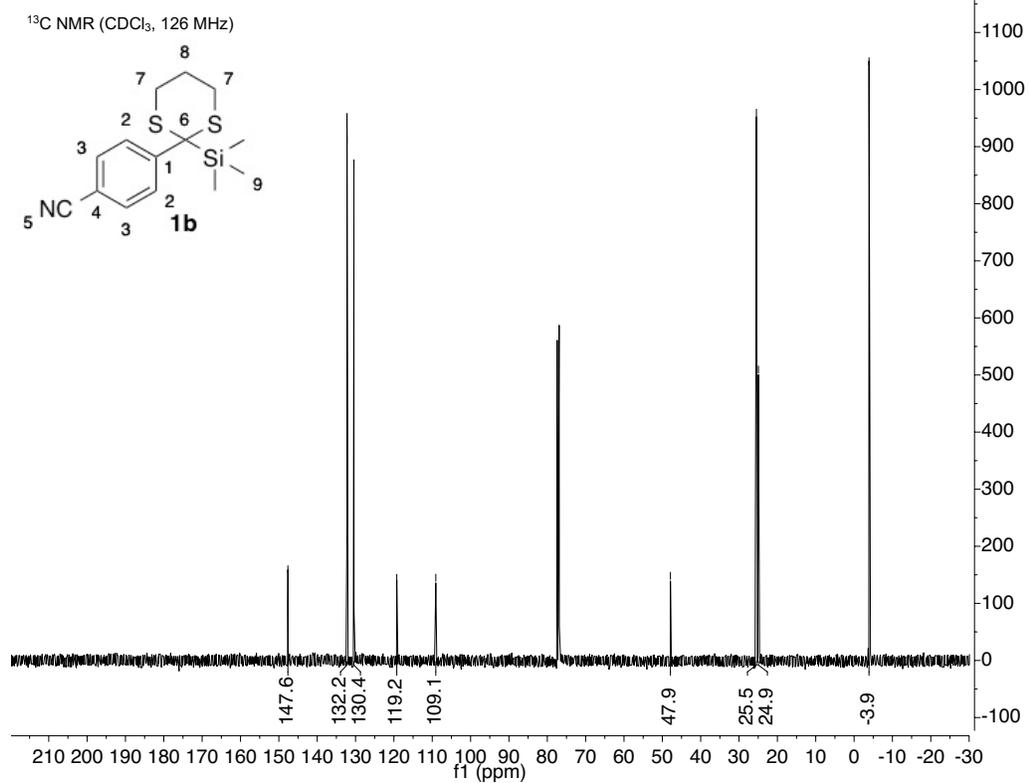
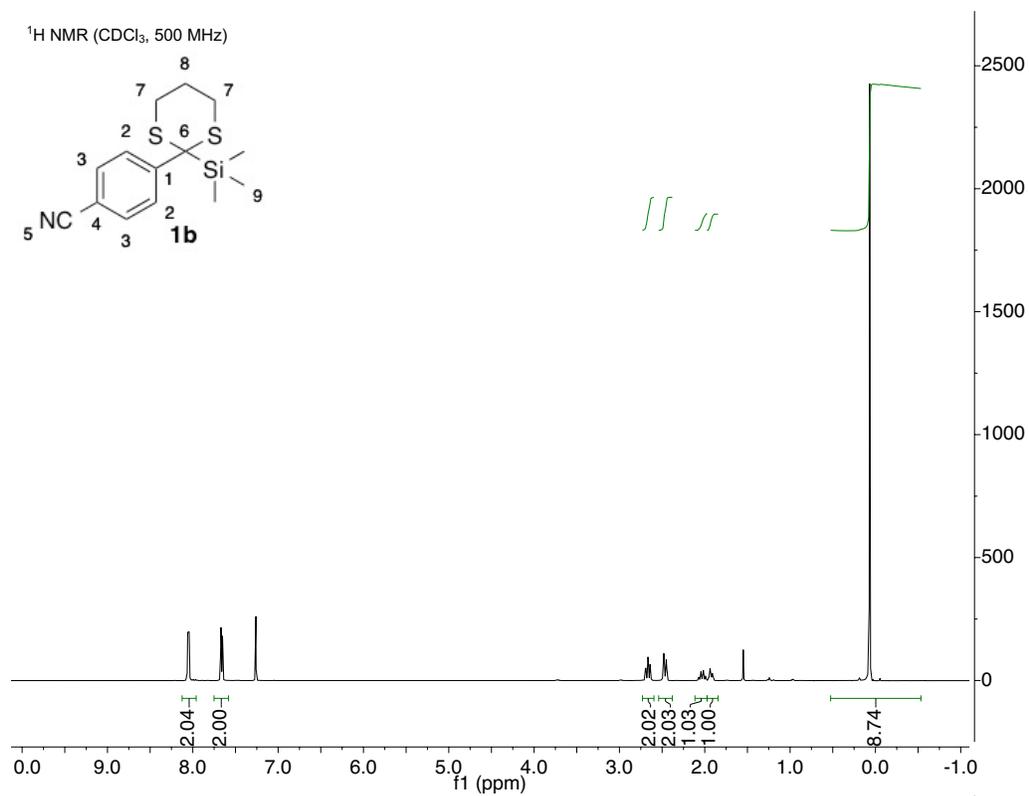


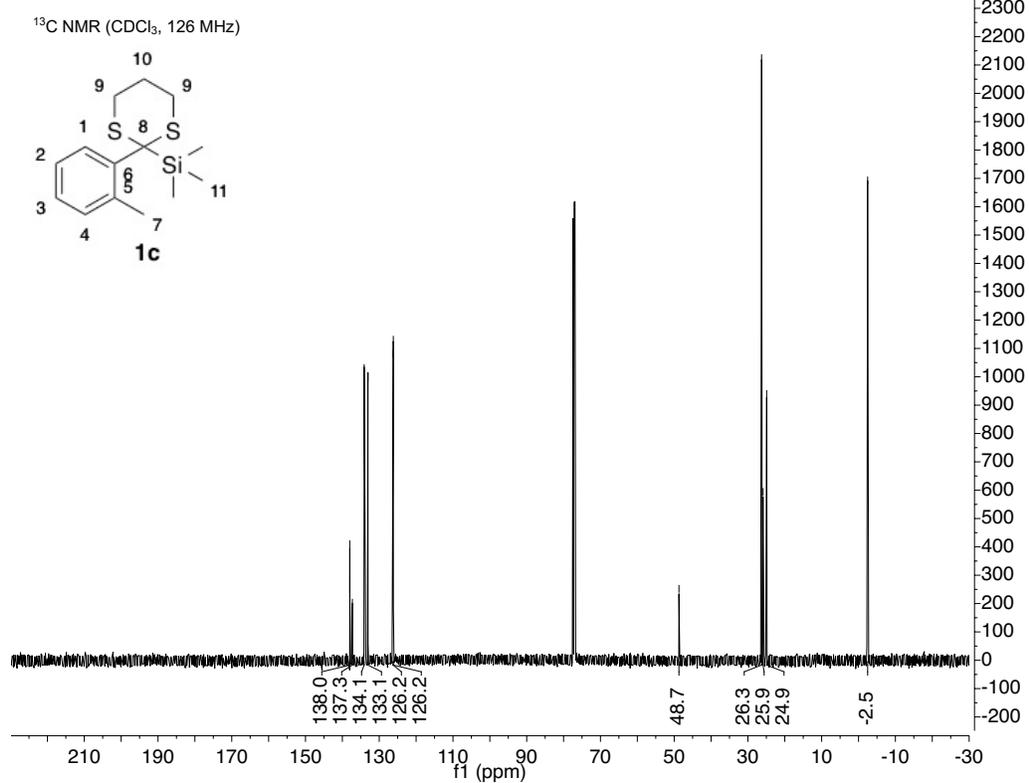
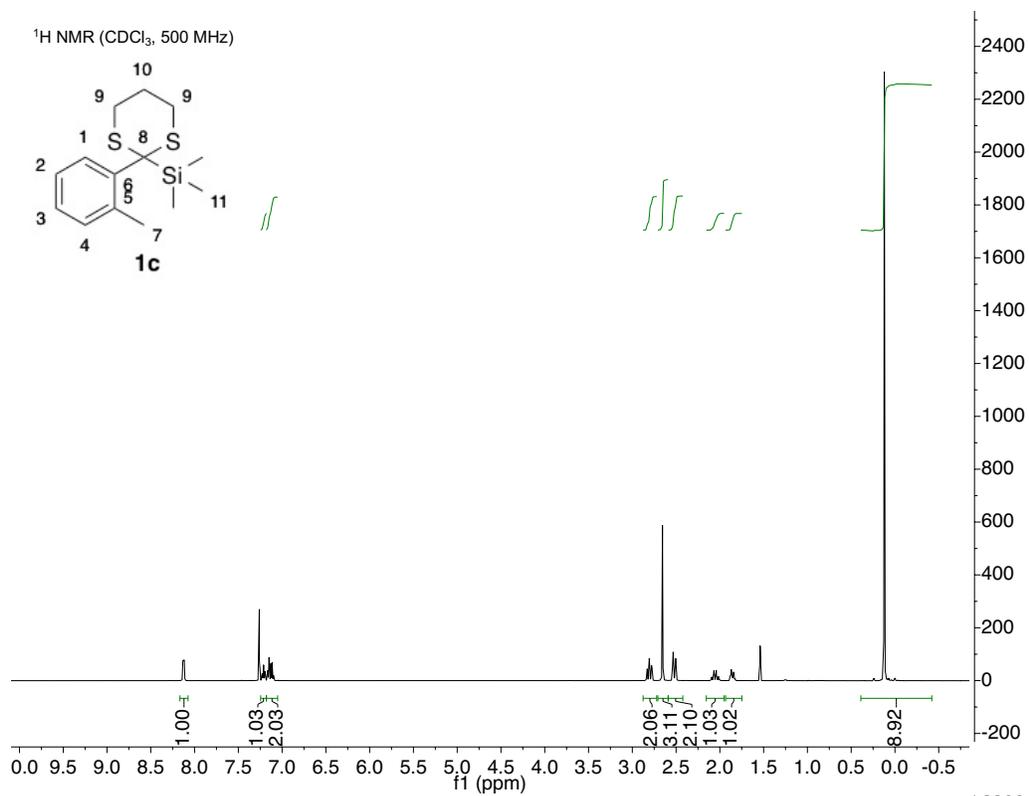


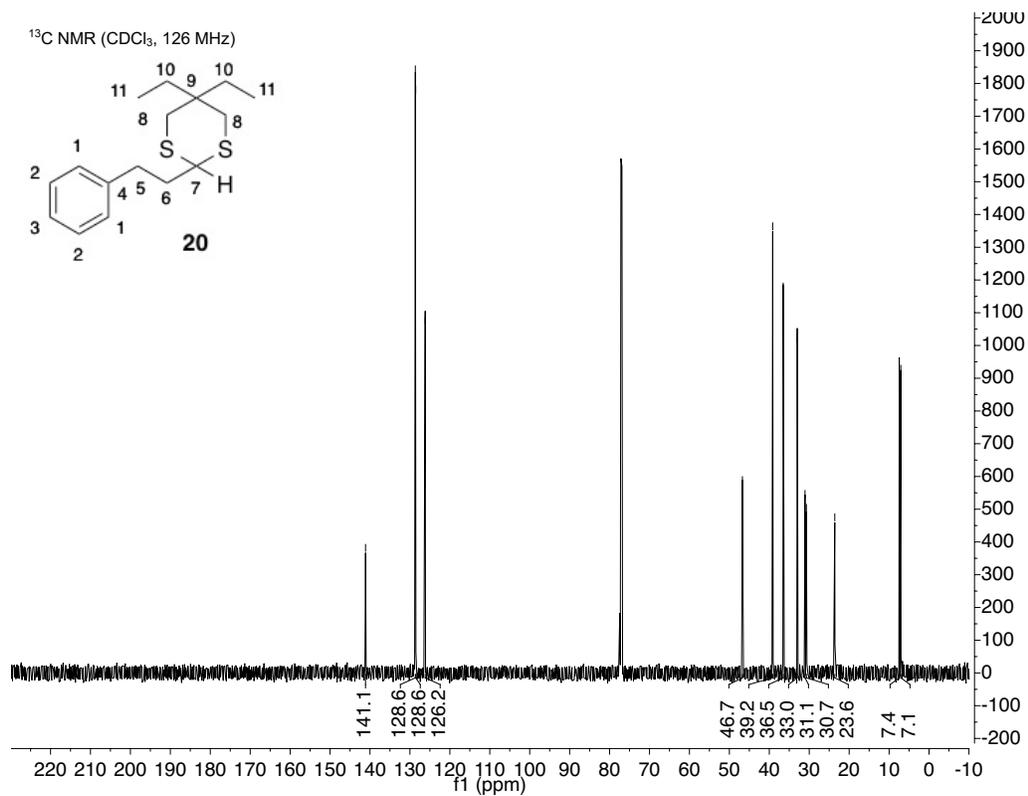
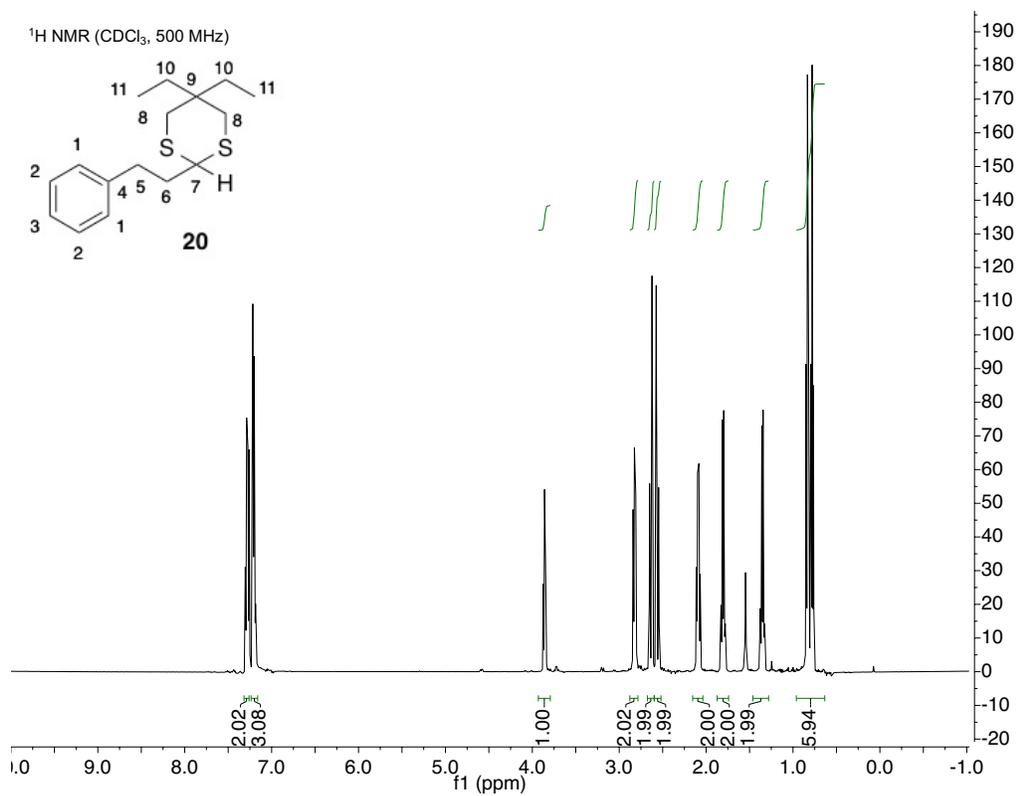


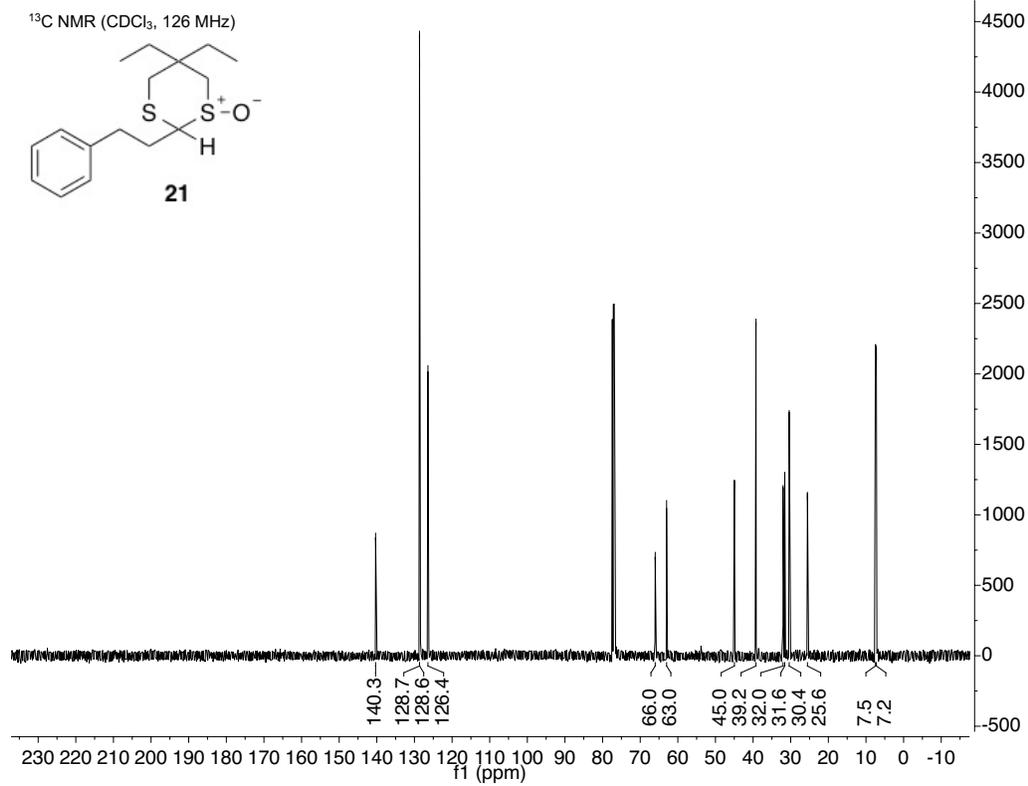
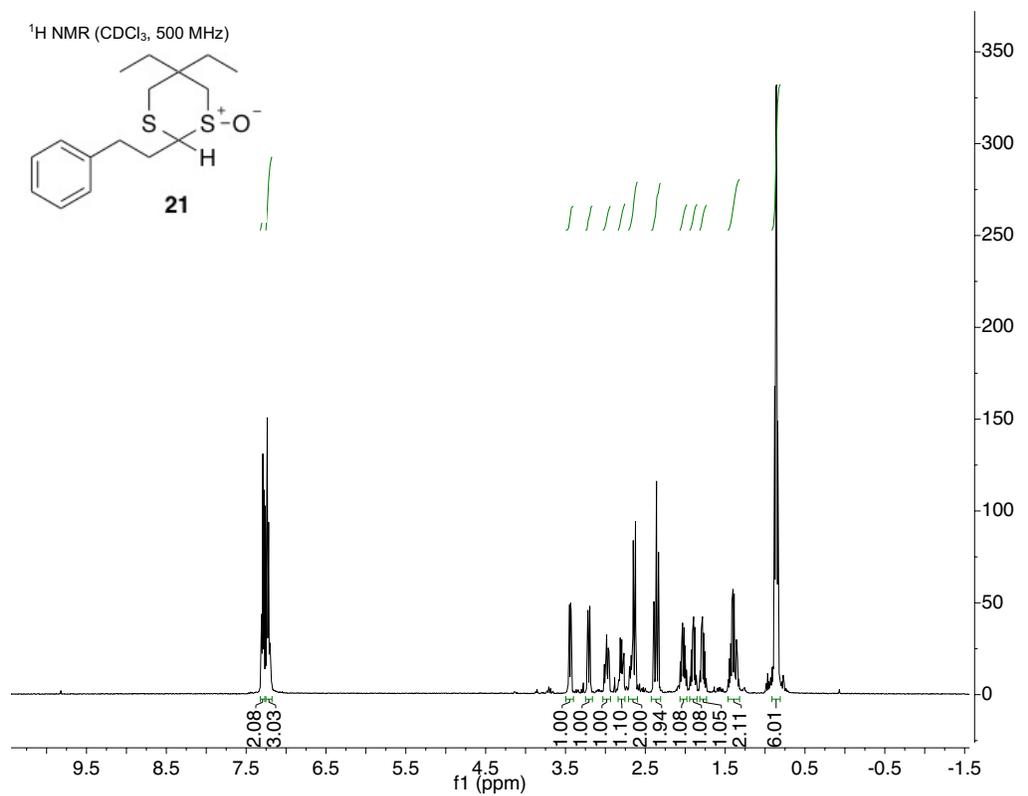


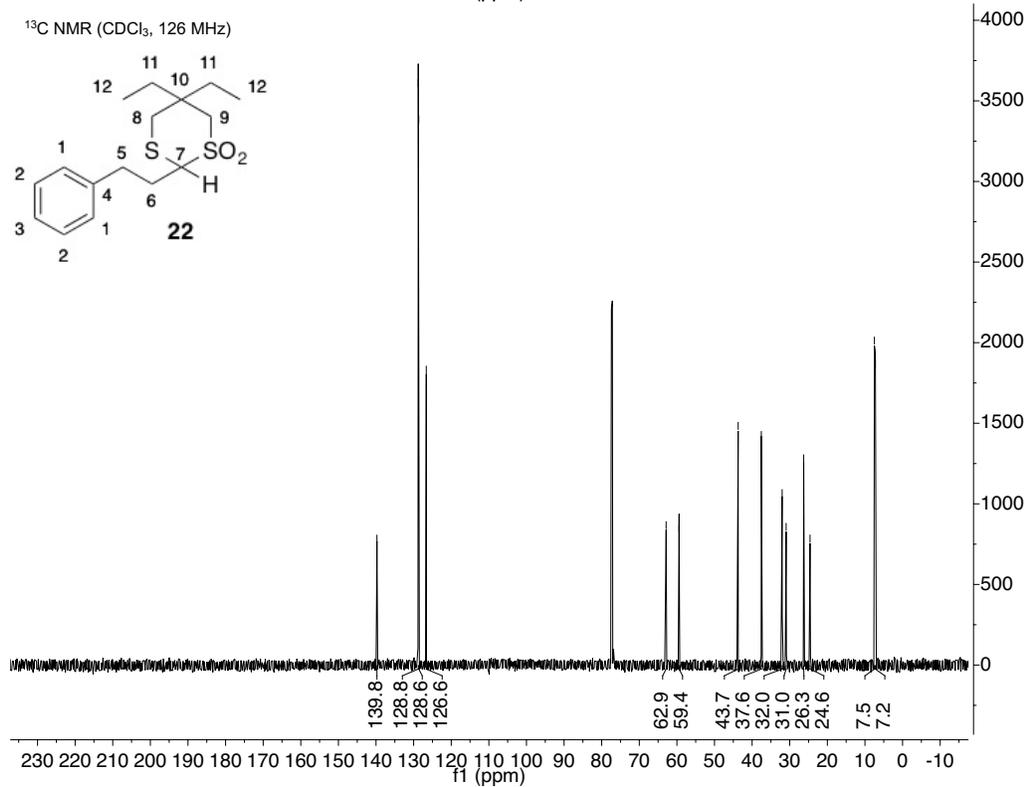
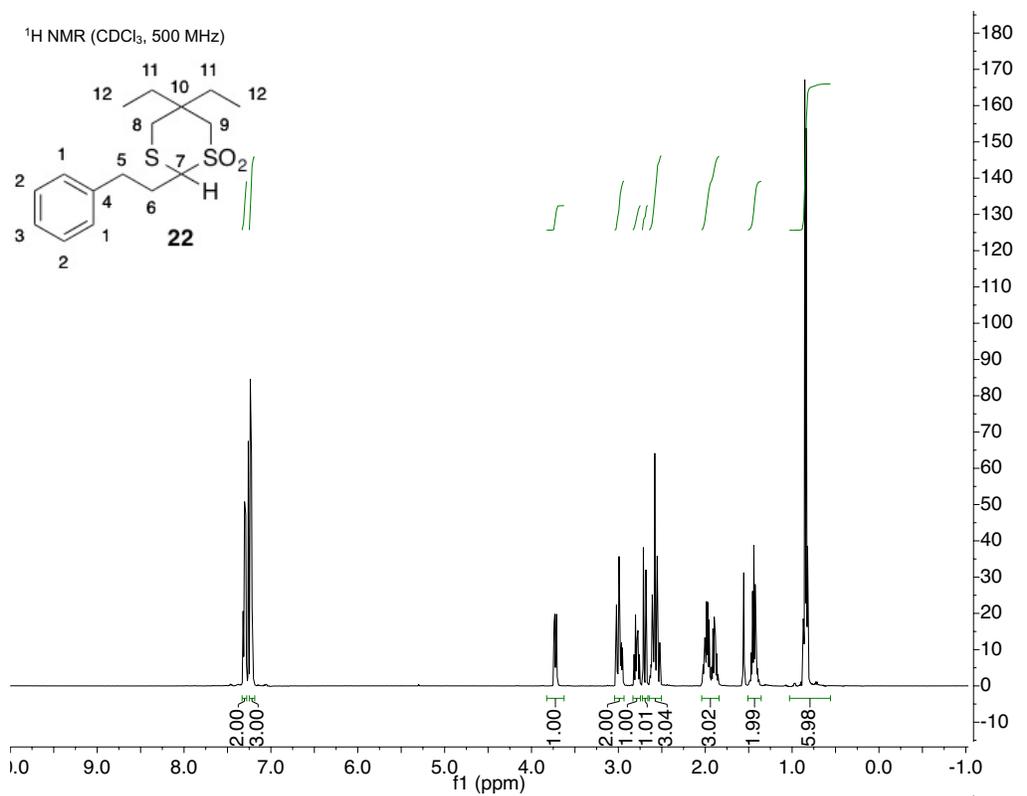


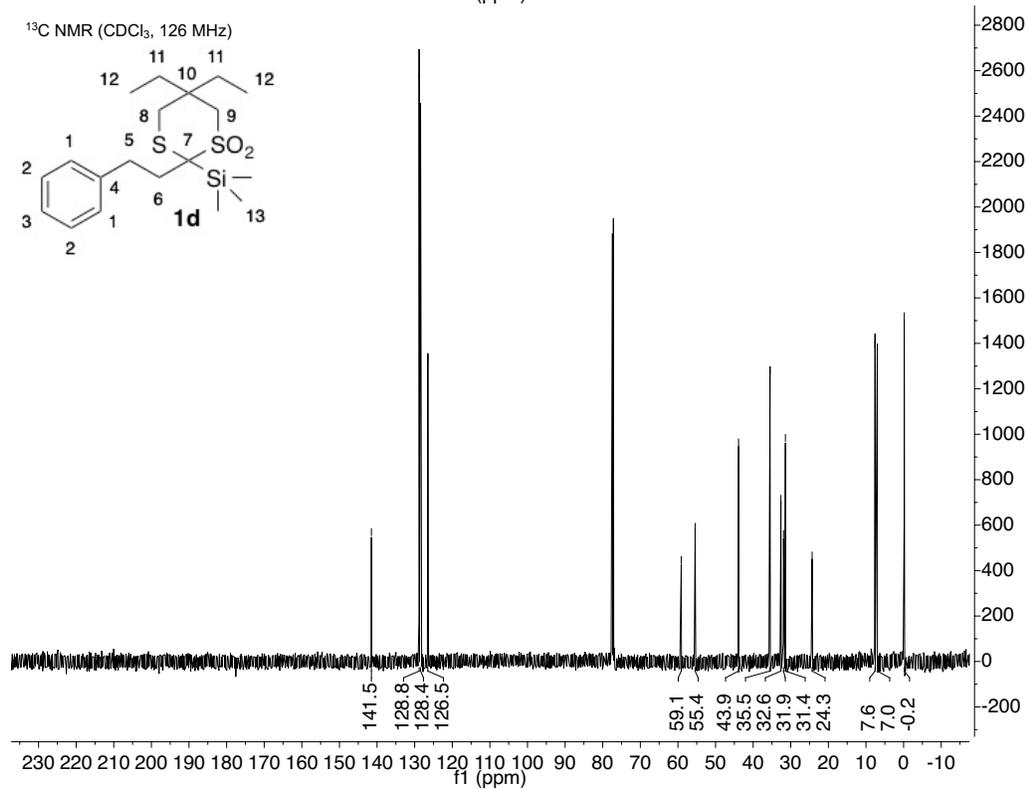
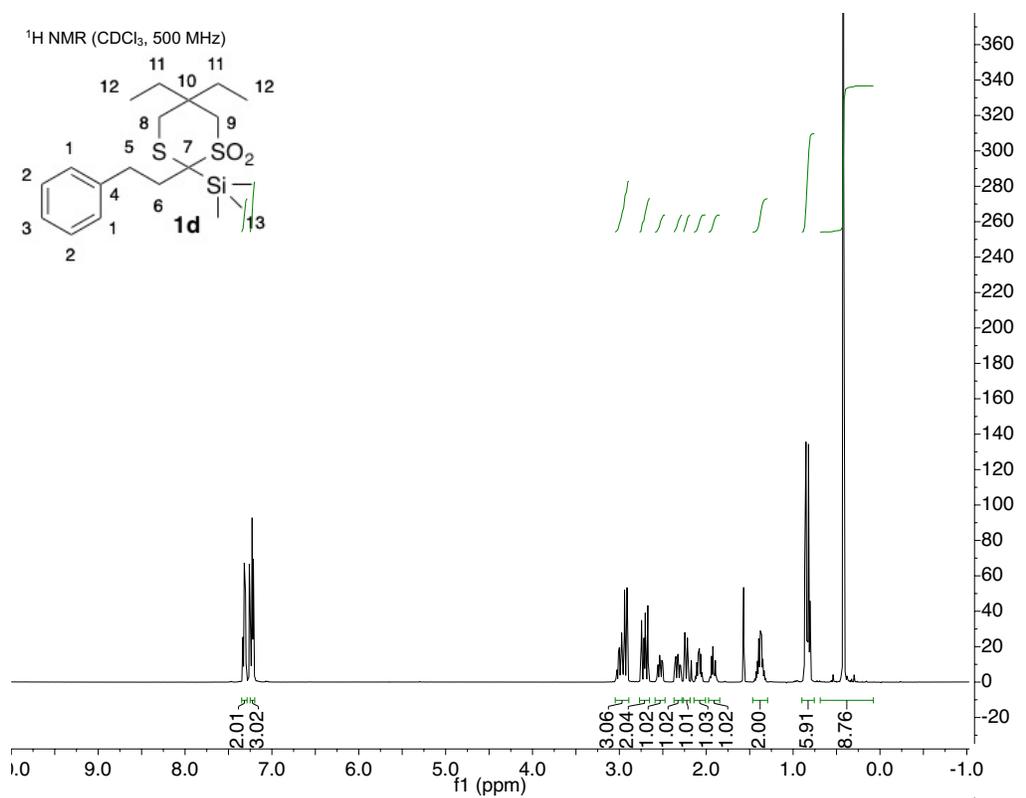




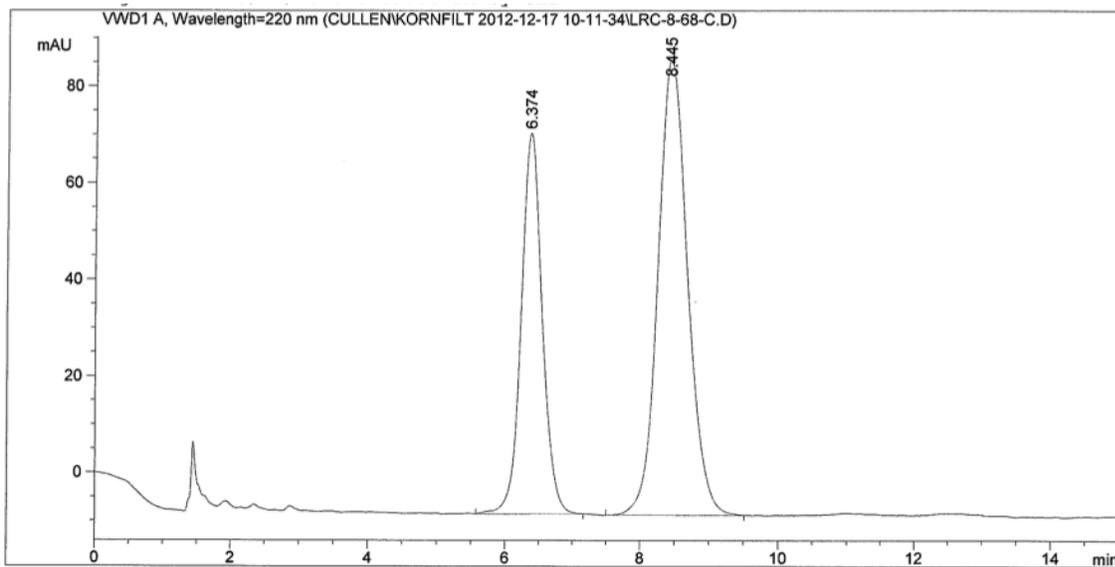




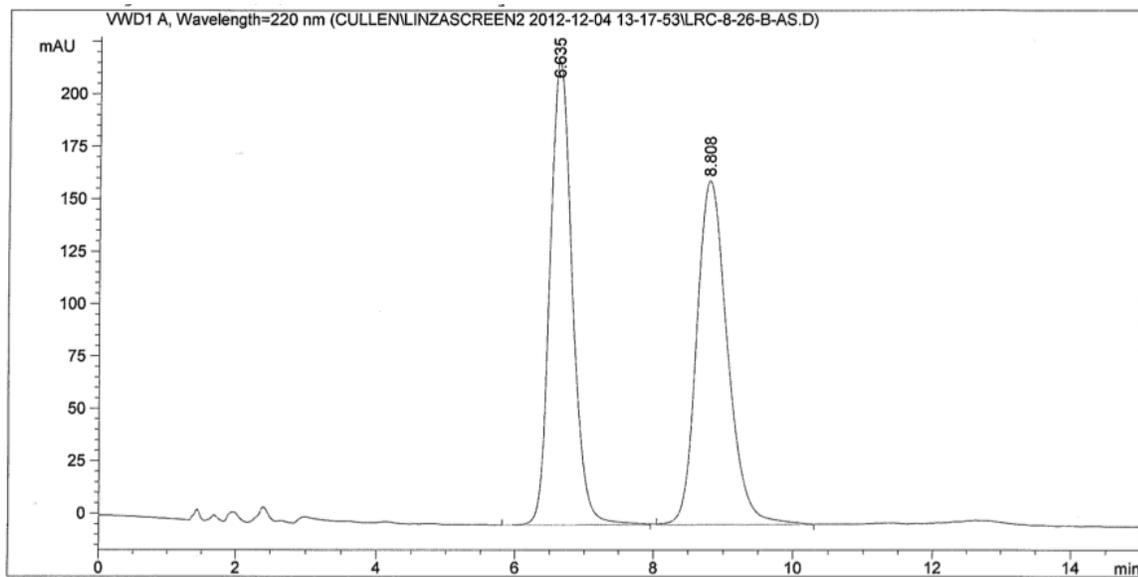




CSP-SFC Data for 3b:



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.374	VB	0.3283	1717.32507	78.88125	37.7581
2	8.445	BB	0.4594	2830.90894	94.31438	62.2419



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.635	VB	0.3471	4953.91406	221.27209	49.6112
2	8.808	BB	0.4674	5031.56787	163.88202	50.3888

