Supplementary Material (ESI) for Chemical Communications

Supporting Experimental Information for

Catalytic Production of Sulfur Heterocycles (Dihydrobenzodithiins): A New Application of Ligand-Based Alkene Reactivity

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General. All experiments were conducted under inert atmosphere (nitrogen or argon), using glovebox (MBraun Unilab) or Schlenk-type techniques, except where noted. Benzene-1,2-dithiol (97%, Alfa Aesar), iodine (≥99%, Aldrich), bromine (reagent grade, Aldrich), 3,5-bis(trifluoromethyl)bromobenzene (BTBB) (99%, Aldrich), 1,2-dichloroethane (99.8%, Aldrich), triethylamine (99%, Aldrich), tributylphosphine (97%, Aldrich), tris(pentafluorophenyl)borane (95%, Aldrich), molybdenum(IV) sulfide (99%, <2 micron powder, Aldrich), HBF_4 (54 wt. % in diethyl ether, Aldrich), Vazo 52® (Dupont), ethylene (99.5%, BOC Canada), 1-hexene (≥99%, Aldrich), cyclohexene (99%, Aldrich), *cis*-2-pentene (98%, Aldrich), *trans*-2-pentene (99%, Aldrich), allyl alcohol (99%, Aldrich) and 2,6-di-tert-butyl-4-methylphenol (BHT) (99%, Aldrich) were obtained from commercial sources, as indicated. NMR (deuterated) solvents were purchased from Cambridge Isotopes or Aldrich. Silica gel (Alfa Aesear) was dried under vacuum at 100°C for >3 h, where noted. Acetonitrile-d_3 (CD_3CN), chloroform-d ($CDCl_3$), chloroform, pentane, triethylamine and the liquid alkenes were dried over activated molecular sieves (3Å, Aldrich) and deoxygenated with argon or nitrogen purges. Dichloromethane-d_2 (CD_2Cl_2) was dried over calcium hydride and vacuum-transferred prior to use. Benzene-d_6 (C_6D_6) was dried over sodium/benzophenone and vacuum-transferred from the purple ketyl prior to use. $Mo(tfd)_2(bdt)$ was made using the literature procedure.[1] BPTS ($[S_2(C_6H_4)]_2$) has been reported previously,[2] but was prepared using a new procedure (see below) for the present study. Most of the NMR spectra were obtained on Bruker Avance III 400 MHz (^1H, ^{13}C, ^{19}F) or Unity/Inova Varian 500 MHz instruments (^{19}F NMR VT experiments). Residual proton (^1H NMR) or carbon (^{13}C NMR) peaks from the solvent were used as reference: ^1H (δ, ppm, benzene-d_6, 7.16, chloroform-d, 7.26; dichloromethane-d_2, 5.32); ^{13}C ((δ, ppm, chloroform-d, 77.23). For ^{19}F HMR spectra, BTBB (see above) was used as an internal standard (at -64.00 ppm); with BTBB at -64.00 ppm, external trifluoroacetic acid occurs at -76.52 ppm (in $CDCl_3$) or -76.42 ppm (in CD_2Cl_2). 1D NOESY NMR experiments were recorded on a Unity/Inova Varian 500 MHz instrument. Spectra were collected at room temperature (RT, 20-25°C), except where noted. Mass spectrometry (EI) was performed at Advanced Instrumentation for Molecular Structure (AIMS), Toronto, ON, Canada on a Waters GC TOF instrument.

Synthesis of BPTS ($[S_2(C_6H_4)]_2$). Benzene-1,2-dithiol (500 mg, 3.52 mmol) was added, in $CHCl_3$ (1.5 mL x 3) washings, to a 25 mL round-bottom flask containing I_2 (952 mg, 3.75 mmol) and $CHCl_3$ (8 mL) (and a stir bar). When the dithiol was added to the iodine solution, the color changed slightly from violet-red to brown-red. The flask was sealed with a septum. The mixture was stirred for 5 min and then NEt_3 (1.0 mL, 730 mg, 7.2 mmol) was added slowly (dropwise, over ca. 10 min) through the septum while vigorously stirring the solution. When addition of the amine was complete, the solution

was orange with a small amount of insoluble viscous oil (polymer, see below). The mixture was stirred at ca. 30°C for 2 h. The solution was placed on a dry (not suspended in solvent) silica gel column (16 g of dry silica [70-230 mesh], inner column diameter: 2 cm). Once the orange solution was absorbed on the silica, additional $CHCl_3$ (enough to collected 25 mL of light yellow eluent) was passed through the column. Note that an orange band remained on the column. From the light yellow eluent, the solvent volume was reduced to ca. 8 mL under vacuum, causing a small amount of light yellow solid to precipitate from solution. More material was precipitated by the addition of pentane (or diethyl ether) (80 mL, added slowly, with stirring). The suspension was cooled (-35°C) overnight. The solid was recovered by filtration (15 mL glass frit funnel) and washed with pentane (or ether) (ca. 3 mL x 3) and then dried under vacuum (overnight at RT, do not heat). Yield (light yellow solid): 55-70% based on benzene-1,2-dithiol. ^{1}H NMR (400 MHz, C_6D_6) δ 6.65 (m, 2H, Ar, byproduct, ca. 6%), 6.69 (m, 2H, Ar, byproduct) 6.70-6.81 (m, 4H, Ar, BPTS), 7.27 (m, 2H, Ar, byproduct), 7.41-7.51(m, 4H, Ar, BPTS). Trace pentane (or ether) was also observed in the ^{1}H spectrum. See Figure S1, below, for a representative NMR spectrum (aryl region). Also, see below for comments/discussion of the NMR data and the possible constitution of the byproduct. *m/z* (EI, reporting M^+ and base peaks and all peaks in between with intensities ≥ 10%) 280.0 (M^+, 21%), 216.0 (28%), 142.0 (12%), 141.0 (10%), 140.0 ($S_2(C_6H_4)$, 100%). HRMS calcd for $C_{12}H_8S_4$ (M^+) 279.9509, found 279.9507.

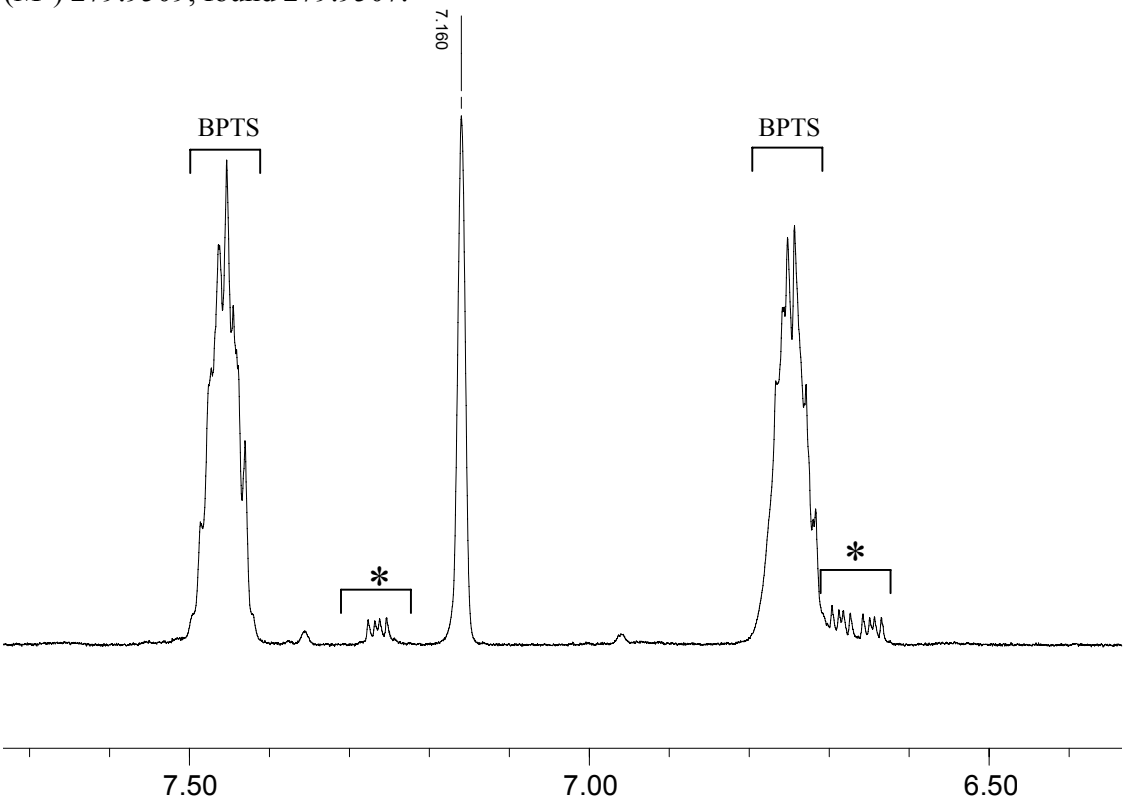

Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum for BPTS, as isolated. The possible identity of the unavoidable byproduct (labeled '*' in the above spectrum) is discussed below.

Comments on BPTS: In the report containing the original synthesis of BPTS,[2] it was noted that the molecular weights of the products were concentration-dependent in molten camphor and carbon disulfide. The authors also noted the propensity of BPTS to undergo polymerization when concentrated in solution and/or heated. Their synthesis, which used iodine to oxidize benzene-1,2-dithiol under high-dilution conditions in benzene, yielded ca. 50% oxidized product by mass, but approximately half of this material was insoluble in molten camphor (i.e., presumably high molecular weight species). An isolated yield for soluble/tractable material was not given.

Thus, the oxidation products of benzene-1,2-dithiol are highly reactive, particularly toward oligomerization/polymerization, and it is difficult to isolate soluble material with well-defined molecular weight, even under high dilutions conditions. Further, ^{1}H NMR data for BPTS in the literature are sparse and possibly in error. For example, BPTS is reported to be one of several products in the reaction between o-benzyne and elemental sulfur.[3] The reported ^{1}H NMR data indicate a doublet of a doublet for BPTS at 8.66 ppm (in $CDCl_3$), corresponding to four protons. Presumably, there is another signal to account for the other four protons, possibly obscured by resonances from other products in the mixture. In our various attempts to oxidize benzene-1,2-dithiol to BPTS, we did not observe ^{1}H NMR chemical shifts above 8 ppm (in $CDCl_3$ or C_6D_6) for any products, although it is possible that the reported shift at 8.66 ppm corresponds to another conformer of BPTS we have not observed. Rotational isomerism is possible for BPTS between C_{2h} (chair) and D_2 (twist-boat) forms (Figure S2, A and B; both forms are present for $[S_2(C_6F_4)]_2$ at 300 K in toluene)[4], although crystallographically characterised BPTS showed the chair isomer[5] and X-ray diffraction studies revealed only one type of crystal morphology in solid samples of BPTS.[2]

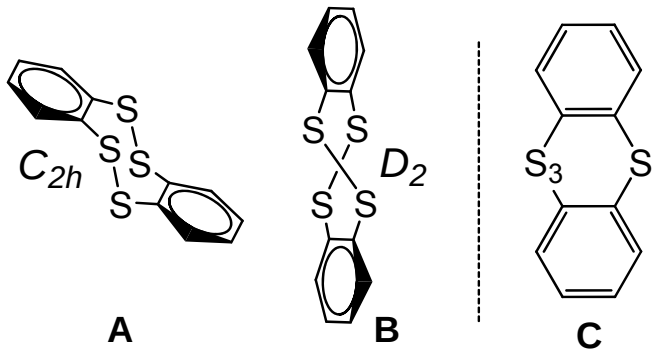

Figure S2. Conformational isomers of BPTS (A and B) and a possible structural isomer (C).

When we attempted to oxidize the dithiol (initially ca. 0.09 M) with Br_2 (1 equiv), in ethanol or dichloromethane, the majority of the isolated material was intractable/insoluble (in chlorinated, aromatic or aliphatic solvents and in EtOH, MeOH or acetone) polymer. Further, we found that evaporation (to dryness) of $CHCl_3$ or CH_2Cl_2 solutions containing BPTS resulted in considerable polymerization of the polysulfide to insoluble material, consistent with the observation that BPTS "polymerized

readily" at high concentration.[2] Our best results for the synthesis of BPTS, in terms of yield of soluble product and purity by ^{1}H NMR, were obtained using iodine as the oxidant (with amine present) in chloroform, as described above.

The material we isolated was consistently contaminated with 5-10% of an unidentified species with apparently lower symmetry than BPTS (in chair or twist-boat forms), characterised by four equal-intensity multiplets in the ^{1}H NMR spectrum (see Figure S1[6]). While we refer to BPTS as the *dimer* of highly reactive $S_2(C_6H_4)$ (observed by MS, see above), the presence of higher oligomers (e.g., trimer or tetramer) is a possibility, given the molecular weight dependence on concentration and the propensity of BPTS to polymerize.[2] Thus, the byproduct could be a higher oligomer of the dithietene with a less symmetrical structure than BPTS. Alternatively, this species could be a structural isomer of BPTS, with one trisulfide and one monosulfide linkage connecting the two aryl rings (i.e., a 1,2,3,6-tetrathiocin; see Figure S2, C), which would be consistent with our ^{1}H NMR data showing a species with four non-equivalent environments for aryl protons. The analogous perfluorinated 1,2,3,6-tetrathiocin forms upon photolysis of the 1,2,5,6-tetrathiocin isomer of $[S_2(C_6F_4)]_2$. This *trans*formation is reversible for $[S_2(C_6F_4)]_2$: the 1,2,3,6-tetrathiocin isomer slowly reverts to the 1,2,5,6-tetrathiocin in polar solvents.[4]

Procedures for isolated yields of DHBDs

Synthesis of DHBD(H,H) (see Table 1 in main text for structure). $Mo(tfd)_2(bdt)$ (10 mg, 0.015 mmol), BPTS (42 mg, 0.15 mmol) and $CHCl_3$ (1.5 mL) were combined in a 25 mL solvent bomb (Pyrex vessel sealable with a Teflon valve and a vacuum adaptor side-arm) (with a stir bar). CD_3CN (40 μL) was added. In air: the bomb was quickly opened and ethylene gas was allowed to bubble gently through the solution for ca. 1.5 min. The bomb was resealed under ethylene. The bomb was placed in an oil bath (68°C) and the solution was allowed to reflux, under ethylene, for 22.3 h. The solvent/volatiles were removed under vacuum (at RT), affording dark brown oily residue. From this residue, the product was distilled into the side-arm of the bomb, by heating the body of the bomb (but not the side-arm) in an oil bath at 100°C under vacuum. The bomb was sealed to sequester the distilled product in the side-arm. In air, using undried solvent: The clear/colorless oil that condensed in the side-arm of the bomb was extracted with dichloromethane (1 mL x 3), after removing the silicone grease from the ground-glass joint of the side-arm. The solvent was removed, in vacuo (RT), from the combined extracts, affording clear, colorless oil. Yield: 35 mg, 69 % based on BPTS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (s, 4H, $(CH_2)_2$), 6.99 (m, 2H, Ar), 7.15 (m, 2H, Ar). See the ^{1}H NMR spectrum below (Figure S3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 29.42, 125.41, 129.04, 131.55. *m/z* (EI) (reporting all peaks with *m/z* ≥ 140.0 and with intensities ≥ 10%) 168.0 (M^+, 69%), 153.0 (base peak, 100%), 140.0 (35%). HRMS calcd for $C_8H_8S_2$ (M^+) 168.0067, found 168.0071.

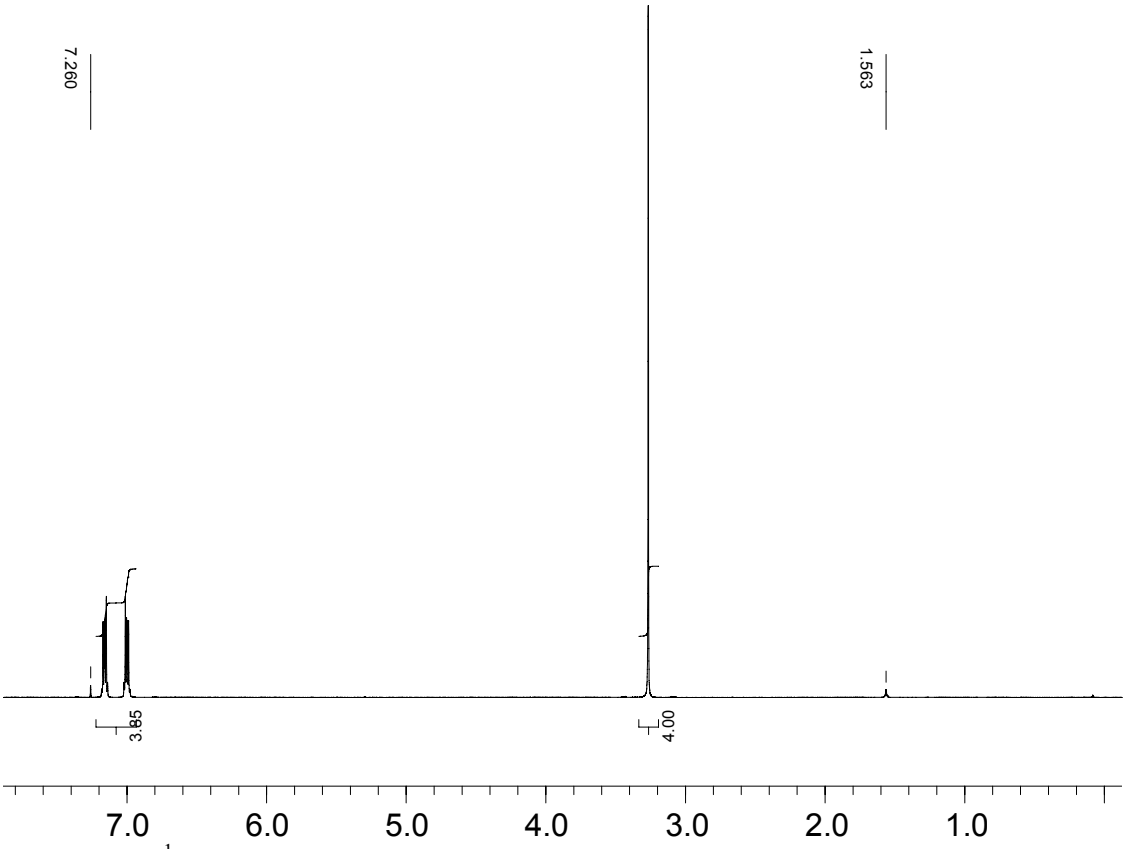

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for purified (by vacuum distillation) DHBD(H,H).

Synthesis of DHBD(H,^{n}Bu). $Mo(tfd)_2(bdt)$ (10 mg, 0.015 mmol) and 1-hexene (36 μL, 24 mg, 0.28 mmol) were combined in $CHCl_3$ (1.5 mL) and this solution was transferred to a 25 mL bomb containing BPTS (40 mg, 0.14 mmol). Acetonitrile-d_3 (35 μL) was added. The vessel was sealed under nitrogen and heated to reflux in an oil bath (65^{o}C) for 45 h. The solvent/volatiles were removed under vacuum (at RT), affording dark green-brown oily residue. From this residue, the product was distilled into the side-arm of the bomb, by heating the body of the bomb (but not the side-arm) in an oil bath at 140^{o}C under vacuum. The bomb was sealed to sequester the distilled product in the side-arm. In air, using undried solvent: The clear/colorless oil that condensed in the side-arm of the bomb was extracted with dichloromethane (1 mL x 3), after removing the silicone grease from the ground-glass joint of the side-arm. The solvent was removed, in vacuo (RT), from the combined extracts, affording clear, faintly green-blue (lightly tainted with trace catalyst residue) oil. Yield: 42 mg, 67 % based on BPTS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3), 1.30-1.58 (m, 4H, (CH_2)$_2$), 1.76 (q, $^{3}J_{HH}$ = 7.7 Hz, 2H, CH_2), 2.98 (dd, $^{2}J_{HH}$ = 13.1 Hz, $^{3}J_{HH}$ = 8.3 Hz, 1H, SC$H^{a}H^{b}$, *cis* to ^{n}Bu), 3.22 (dd, $^{2}J_{HH}$ = 13.1 Hz, $^{3}J_{HH}$ = 3.2 Hz, 1H, SCH$^{a}H^{b}$, *trans* to ^{n}Bu), 3.47 (m, 1H, SCH(^{n}Bu)), 6.99 (m, 2H, Ar), 7.16 (m, 2H, Ar). See the ^{1}H NMR spectrum in Figure S4, below. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.13, 22.65, 29.13, 34.56, 35.62, 43.54, 125.01, 125.44, 128.68, 128.77, 131.50, 132.11. *m/z* (EI) (reporting M^{+} and base peaks and all peaks in between with intensities ≥ 10%) 224.1 (M^{+}, 52%), 167.0 (41%), 153.0 (47%), 142.0

(32%), 140.0 (15%), 135.0 (12%), 134.0 (base peak, 100%). HRMS calcd for $C_{12}H_{16}S_2$ (M^+) 224.0693, found 224.0691.

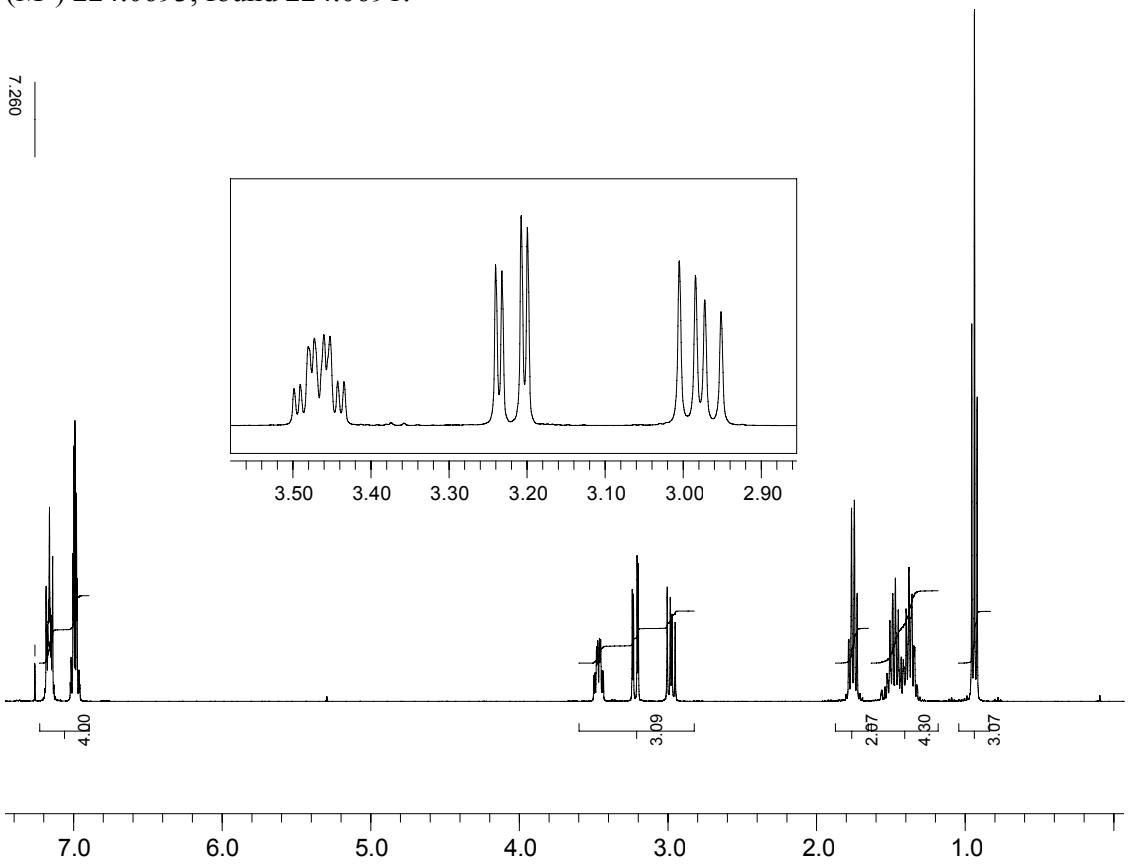

Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for purified (by vacuum distillation) DHBD(H,^{n}Bu). The inset shows an expanded view of the resonances associated with the aliphatic (i.e., attached to sp^3 carbon) ring protons.

Synthesis of DHBD(C_2H_4,C_2H_4). Note: this compound has been reported previously.[7] A procedure analogous to that used in the synthesis of DHBD(H,^{n}Bu) (see above; same solvents/concentrations) was used here, using cyclohexene as the alkene, with the following modifications: the catalyst/alkene/tetrasulfide mixture was heated (65^{o}C) for 18 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 160^{o}C. Yield (oily white solid at RT): 31 mg, 50 % based on BPTS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (m, 2H, CH_2), 1.70-1.92 (ov m, 4H, CH_2), 2.01 (m, 2H, CH_2), 3.57 (m, 2H, SC*H*R (x2)), 6.97 (m, 2H, Ar), 7.16 (m, 2H, Ar). Note: ^{1}H NMR spectra of the crude material, before distillation, show contaminants with broad aliphatic and aryl resonances, probably indicating polymeric byproduct (see below for discussion). See the ^{1}H NMR spectrum of the purified product in Figure S5, below. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 23.25, 31.16, 44.06, 125.07, 128.55, 131.29. *m/z* (EI) (reporting M^+ and base peaks and all peaks in between with intensities ≥ 10%) 222.1 (M^+, 61%), 179.0 (32%), 166.0 (24%), 153.0 (44%), 142.0 (31%), 141.0 (21%), 140.0 (100%). HRMS calcd for $C_{12}H_{14}S_2$ (M^+) 222.0537, found 222.0537.

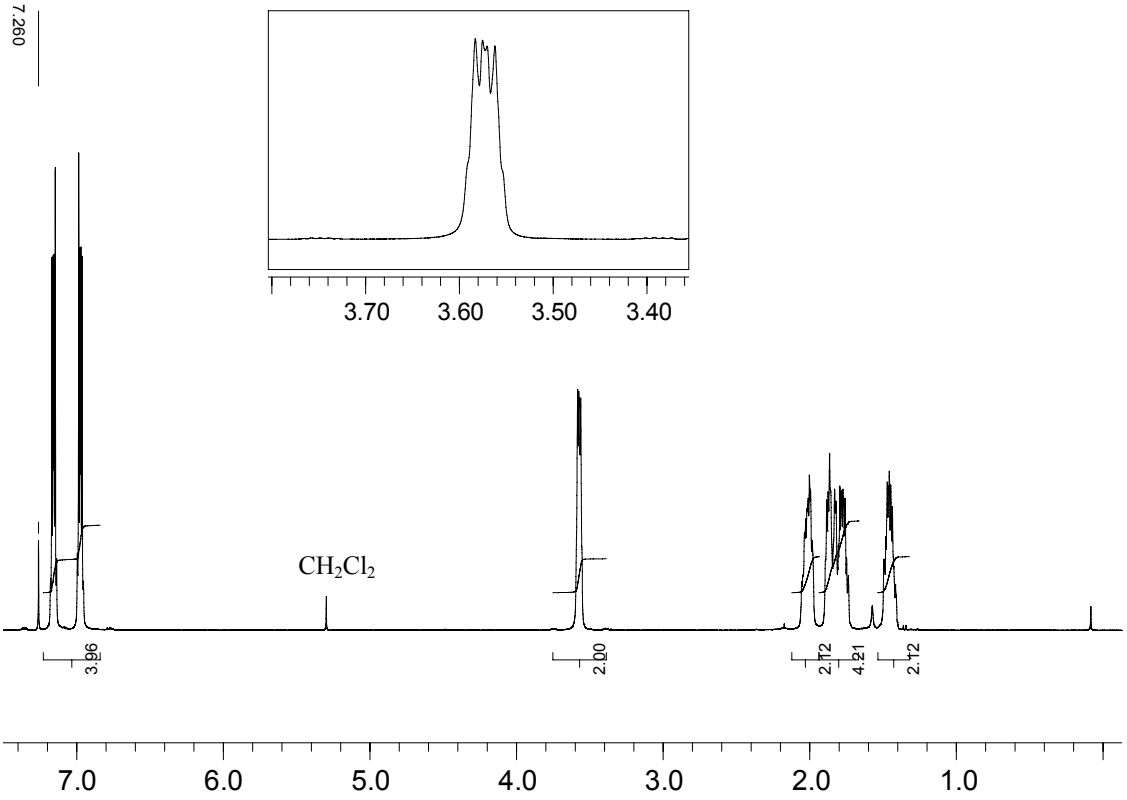

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) for purified (by vacuum distillation) DHBD(C_2H_4,C_2H_4). The inset shows an expanded view of the resonances associated with the aliphatic ring protons.

Synthesis of DHBD(H,CH_2OH). Complex **1** (10.2 mg, 0.015 mmol) was dissolved in $CHCl_3$ (1.5 mL) and the resulting deep green solution was added to a bomb containing BPTS (51 mg, 0.18 mmol). Allyl alcohol (19 μL, 16 mg, 0.28 mmol) and then CD_3CN (40 μL) were added. The vessel was sealed and heated in an oil bath (68^{o}C, reflux) for 2 h and 20 min. Note: the color of the solution changed from deep green to brown-green to brown-purple during this time. The solvent/volatiles were removed under reduced pressure, giving dark brown-purple oily residue. In air: this residue was redissolved in dichloromethane (3 mL) and then isopropanol (3 mL) was added. The volume of the resulting suspension was reduced by ca. ½ (to ca. 3 mL). The concentrated suspension was placed on a silica gel column (17 g of silica [230-400 mesh], suspended in isopropanol, inner column diameter: 2 cm). The reaction vessel was washed twice with isopropanol (1.5 mL) and these washings were also placed on the column. Isopropanol (20 mL) was passed through the column (pressurized to increase the flow rate) producing clear/colorless eluent (discarded). An additional 20 mL of isopropanol were passed through the column, giving very faintly green tinted eluent (kept). Note that a dark green-brown colored band remained on the bottom of the column. From the second 20 mL fraction, the solvent was removed under vacuum, yielding viscous (slightly green-brown) oil. This oil was redissolved in dichloromethane (ca. 5 mL) and the solvent was

removed, again, under vacuum. Yield: 32 mg, 58% based on ally alcohol (excess of BPTS used to avoid difficulties in separating the product and unreacted alkene). ^{1}H NMR (400 MHz, C_6D_6, sample filtered through Celite) δ 0.94 (t, $^{3}J_{HH}$ = 5.6 Hz, 1H, OH), 2.59-2.72 (ov m, 2H, $H^{A \text{ and } B}$), 3.13 (m, 1H, H^{C}), 3.31(m, 1H, $H^{D \text{ or } E}$), 3.44 (m, 1H, $H^{D \text{ or } E}$), 6.69 (m, 2H, Ar), 7.10 (m, 2H, Ar). Figure S6, below, shows the ^{1}H NMR spectrum of the product. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, sample filtered through Celite) δ 30.62, 45.48, 64.93, 125.55, 126.27, 129.33, 129.81, 132.09, 132.85. *m/z* (EI) (reporting M^+ and base peaks and all peaks in between with intensities ≥ 10%) 198.0 (M^+, 35%), 180.0 (16%), 167.0 (45%), 153.0 (53%), 142.0 (23%), 140.0 (17%), 135.0 (12%), 134.0 (base peak, 100%). HRMS calcd for $C_9H_{10}OS_2$ (M^+) 198.0173, found 198.0177.

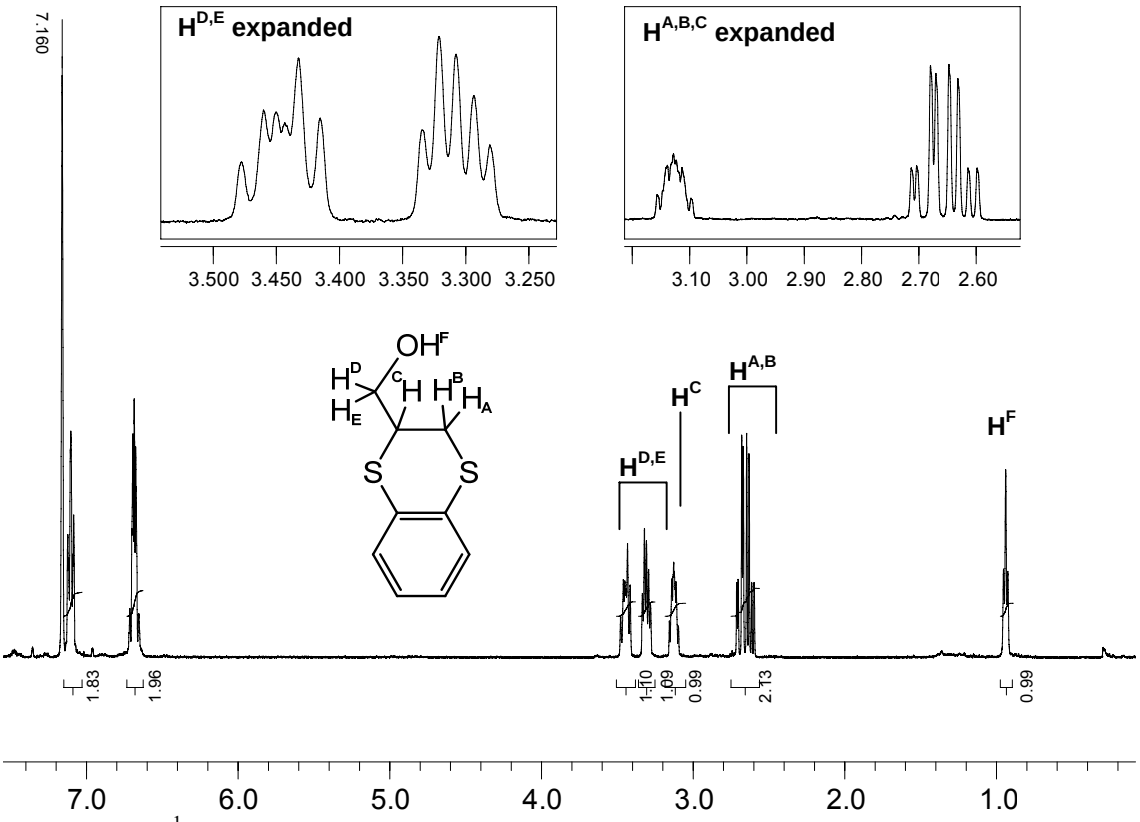

Figure S6. ^{1}H NMR (400 MHz, C_6D_6) spectrum for DHBD(H,CH_2OH), purified by column chromatography. The insets show expanded views of the resonances associated with the diastereotopic protons $H^{D,E}$ and aliphatic ring protons ($H^{A,B,C}$). Also shown is the structure of DHBD(H,CH_2OH), with the proton labeling scheme.

Synthesis of DHBD(*cis*-Et,Me). A procedure analogous to that used in the synthesis of DHBD(H,^{n}Bu) (see above; same solvents/concentrations) was used here, using *cis*-2-pentene as the alkene, with the following modifications: no CD_3CN was used; the catalyst/alkene/tetrasulfide mixture was heated (65^{o}C) for 21 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 170^{o}C. Yield (blue-tinted oil): 23 mg, 38 % based on BPTS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3), 1.39 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $SCHCH_3$), 1.62 (ov m, diastereotopic

C*H*HMe), 1.69 (ov m, diastereotopic CH*H*Me), 3.38 (m, 1H, SC*H*^{C}Et, *cis* to H^{A}, see below), 3.57 (dq, $^{3}J_{HH}$ = 6.9 Hz, $^{3}J_{HH}$ = 2.6 Hz, 1H, SC*H*^{A}Me, *cis* to H^{C}), 6.96 (m, 2H, Ar), 7.11(m, 2H, Ar). See Table 1 below for full ^{1}H NMR details: all coupling constants and chemical shifts are assigned for the [SCHMeCHEtS] spin system. Note: ^{1}H NMR spectra of the crude material, before distillation, show contaminants with broad aliphatic and aryl resonances, probably indicating polymeric byproduct (see below for discussion). Figures S7 and S8, below, show the ^{1}H NMR spectrum of the product, compared with the simulated spectrum. Simulating the spectrum (data in Table S1) gave accurate coupling constant information, which was used for assigning the product as the *cis* isomer. See discussion below. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 12.11, 17.50, 25.11, 39.51, 49.35, 124.91, 125.00, 128.32, 128.51, 129.96, 130.66. *m/z* (EI) (reporting M^+ and base peaks and all peaks in between with intensities ≥ 10%) 210.1 (M^+, 61%), 181.0 (80%), 167.0 (56%), 166 (33%), 153.0 (75%), 149.0 (11%), 148.0 (36%), 147.0 (31%), 142.0 (25%), 141.0 (29%), 140.0 (base peak, 100%). HRMS calcd for $C_{11}H_{14}S_2$ (M^+) 210.0537, found 210.0533.

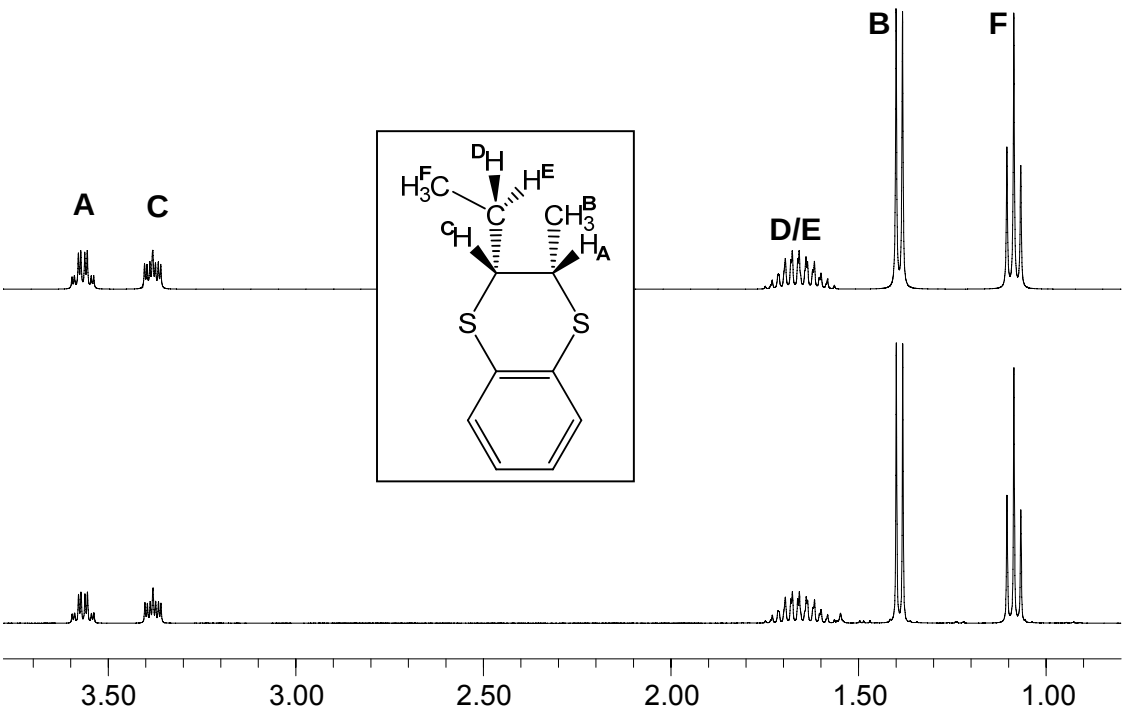

Figure S7. Comparison of experimental (bottom) and simulated (top) ^{1}H NMR (400 MHz, $CDCl_3$, for experimental spectrum) spectra for DHBD(*cis*-Et,Me). The aromatic region is not shown. The inset shows the structure of DHBD(*cis*-Et,Me) and the proton labeling scheme. See Figure S8, below, for expanded views of the A/C and D/E regions.

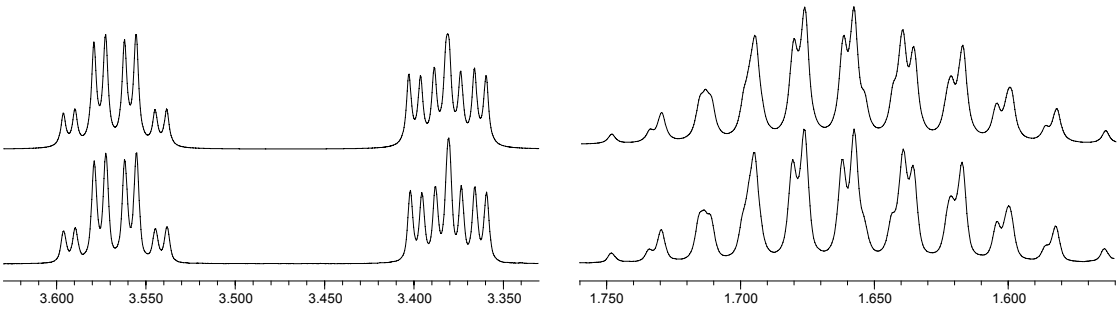

Figure S8. Expanded views of ring protons A and C (*cis*) (left side; experimental spectrum on bottom, simulated spectrum on top) and diastereotopic protons D and E (right side; experimental spectrum on bottom, simulated spectrum on top). See Table S1, below, for the simulation parameters (coupling constants, etc.).

Table S1. ^{1}H NMR parameters for DHBD(*cis*-Et,Me) used to simulate the experimental spectrum (aromatic protons not included). The coupling constant J_{AC} (in bold) was used to identify the product as the *cis* isomer (see below for discussion).

Environment	Number of protons	Chemical shift (ppm)	Coupling constants (Hz)
A (see Fig. S7)	1	3.567	J_{AB} = 6.85
B	3	1.391	**J_{AC} = 2.61**
C	1	3.381	J_{CD} = 9.20
D	1	1.624	J_{CE} = 5.50
E	1	1.691	J_{DE} = -14.00
F	3	1.086	J_{DF} = J_{EF} = 7.38
Line width (for simulation): 1.3		Spectral frequency: 400 MHz	

Synthesis of DHBD(*trans*-Et,Me). A procedure analogous to that used in the synthesis of DHBD(H,^{n}Bu) (see above; same solvents/concentrations) was used here, using *trans*-2-pentene as the alkene, with the following modifications: 40 μL of CD_3CN were used (instead of 35 μL); the catalyst/alkene/tetrasulfide mixture was heated (68^{o}C) for 22.3 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 150^{o}C. Yield (oil): 50 mg, 80 % based on BPTS. Note: in contrast to the reaction that gives DHBD(*cis*-Et,Me) (see above), no polymeric byproduct was formed in the present reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J_{HH} = 7.4 Hz, 3H, CH_2CH_3), 1.48 (d, 6.8 Hz, 3H, $SCHCH_3$), 1.70 (ov m, 1H, diastereotopic C*H*HMe), 1.80 (ov m, 1H, diastereotopic CH*H*Me), 2.93 (m, 1H, $SCH^{A}Et$, *trans* to H^{C}, see below), 2.93 (m, 1H, $SCH^{C}Me$, *trans* to H^{A}), 7.00 (m, 2H, Ar), 7.18 (m, 2H, Ar). See Table 2 below for full ^{1}H NMR details: all coupling constants and chemical shifts are assigned for the [SCHMeCHEtS] spin system. Figures S9 and S10, below, show the ^{1}H NMR spectrum of the product, compared with the simulated spectrum. The simulated spectrum was used for assigning the product as the *trans* isomer. See discussion below. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 11.46, 22.72, 29.13, 41.16, 50.64, 125.16, 125.19, 128.81, 128.98,

130.70, 131.00. *m/z* (EI) (reporting all peaks with *m/z* ≥ 140.0 and with intensities ≥ 10%) 210.1 (M^+ and base peak, 100%), 181.0 (74%), 167.0 (25%), 166.0 (11%), 153.0 (24%), 148.0 (18%), 142.0 (14%), 140.0 (73%). HRMS calcd for $C_{11}H_{14}S_2$ (M^+) 210.0537, found 210.0535.

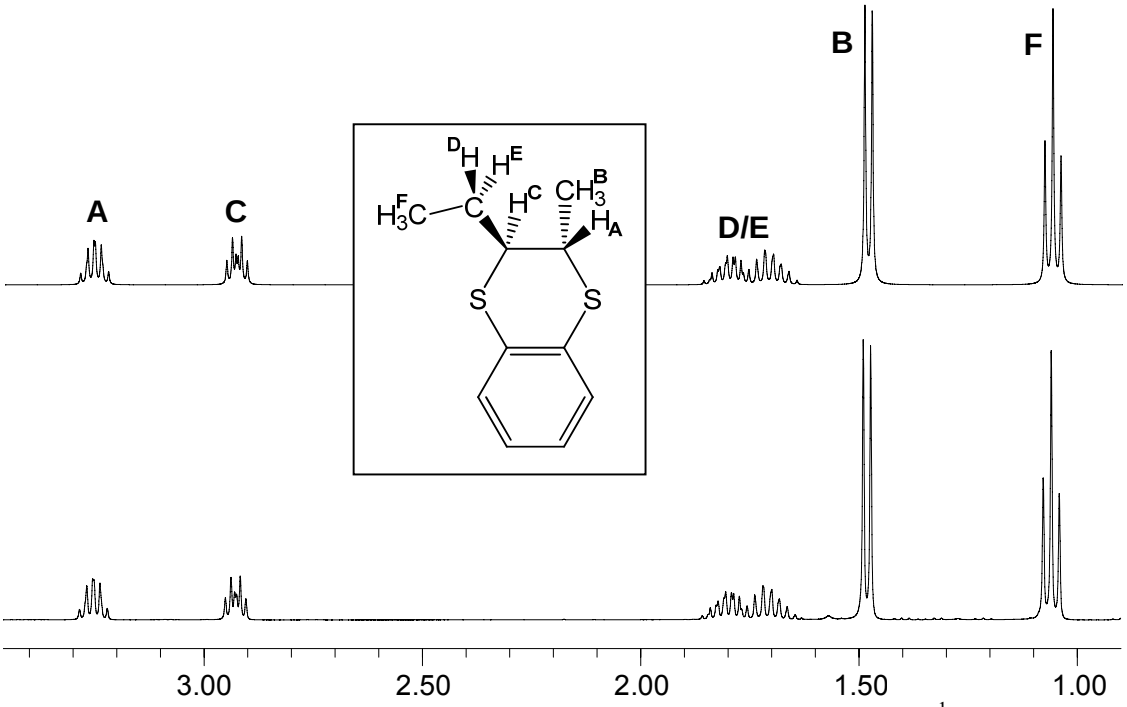

Figure S9. Comparison of experimental (bottom) and simulated (top) ^{1}H NMR (400 MHz, $CDCl_3$, for experimental spectrum) spectra for DHBD(*trans*-Et,Me). The aromatic region is not shown. The inset shows the structure of DHBD(*trans*-Et,Me) and the proton labeling scheme. See Figure S10, below, for expanded views of the A/C and D/E regions.

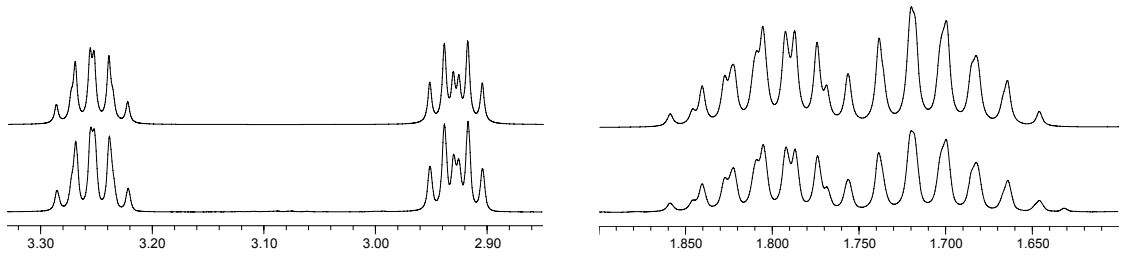

Figure S10. Expanded views of ring protons A and C (*trans*) (left side; experimental spectrum on bottom, simulated spectrum on top) and diastereotopic protons D and E (right side; experimental spectrum on bottom, simulated spectrum on top). See Table S2, below, for the simulation parameters (i.e., coupling constants, etc.).

Table S2. ^{1}H NMR parameters for DHBD(*trans*-Et,Me) used to simulate the experimental spectrum (aromatic protons not included). The coupling constant J_{AC} (in bold) identifies the product as the *trans* isomer (see below for discussion).

Environment	Number of protons	Chemical shift (ppm)	Coupling constants (Hz)
A (see Fig. S9)	1	3.254	$J_{AB} = 6.76$
B	3	1.482	$\mathbf{J_{AC} = 5.30}$
C	1	2.928	$J_{CD} = 8.50$
D	1	1.704	$J_{CE} = 5.05$
E	1	1.804	$J_{DE} = -14.00$
F	3	1.060	$J_{DF} = J_{EF} = 7.36$
Line width (for simulation): 1.6		Spectral frequency: 400 MHz	

Comments on distinguishing the *cis* and *trans* isomers: As stated in the main text, we observed diastereospecificity in the DHBD-forming reactions when 1,2-disubstituted alkenes were used. Specifically, the reaction of BPTS with *cis*-2-pentene [catalyzed by **1** {$Mo(S_2C_2(CF_3)_2)_2(S_2C_6H_4)$}] produces DHBD(*cis*-Et,Me) (i.e., Et and Me groups *cis* in product) and none of the *trans* isomer (although polymeric byproduct is formed). Similarly, BPTS reacts with *trans*-2-pentene, in the presence of complex **1**, to cleanly (no polymeric byproduct produced) furnish only DHBD(*trans*-Et,Me) and none of the *cis* isomer.

To distinguish between the *cis* and *trans* isomers, the vicinal coupling constants J_{AC} (see Figures S7 and S9, above and Figure S11 below) are used, as the observed coupling constant between protons A and C should be significantly different for DHBD(*cis*-Et,Me) and DHBD(*trans*-Et,Me). Extracting the experimental coupling constants from the ^{1}H NMR data is not trivial and, for the *trans* isomer in particular, we found it necessary to simulate (using Mestrec®) the experimental ^{1}H NMR spectrum to ensure correct determination of the relevant coupling constants. The parameters used in the simulations are given above, in Tables S1 and S2. The simulation was performed to maximize the fit between the experimental and simulated spectra (see Figures S8 and S10).

For both the *cis* and *trans* dihydrodithiins, two major conformations of the six-membered dihydrodithiin ring are relevant here (Figure S1; this is neglecting conformers arising from folding along the S---S axis, or rotational isomerism of the Et group – which should have little bearing on J_{AC}). In the *cis* isomer, DHBD(*cis*-Et,Me), protons A and C should be separated by a dihedral angle of ca. 60^o in both conformers [Figure S11(a) and (b)]. For the *trans* form, one conformer [Figure S11(c)] places protons A and C at a dihedral angle of ca. 180^o, and, in the other conformer [Figure S11(d)], the dihedral angle is ca. 60^o. Thus, the dihedral angle between protons A and C is ca. 60^o for *cis* isomer, corresponding to an expected coupling constant (J_{AC}) of 2.5 Hz according to the Haasnoot-de Leeuw-Altona equation (a version of the Karplus relationship that includes substituent effects),[8] regardless of which conformer is more stable (since both conformers place H^A and H^B at a 60^o dihedral angle). On the other hand, for the *trans* isomer, the

observed (effective) coupling constant will be a weighted (by relative population) average of the vicinal coupling constants for pure forms (c) and (d) (Figure S11). The predicted (from torsion angles)[8] coupling constants are 10 Hz and 2.5 Hz for (c) and (d), respectively. While a 50 % (c)/50 % (d) population distribution should yield a 6.3 Hz effective (averaged) coupling constant, it can be expected that structure (c) should be very slightly disfavored in equilibrium, due to the *gauche*-dialkyl effect. The observed coupling constant for the *trans*-isomer thus should be *significantly higher than 2.5 Hz but slightly lower than 6.3 Hz.* In contrast, the vicinal hydrogen-hydrogen coupling constant for the *cis*-isomer should be *very close to 2.5 Hz*. The observed coupling constants for the two different isolated isomers of DHBD(Et,Me) are 2.61 Hz and 5.30 Hz, which safely allows assignment as *cis*- and *trans*-, respectively.

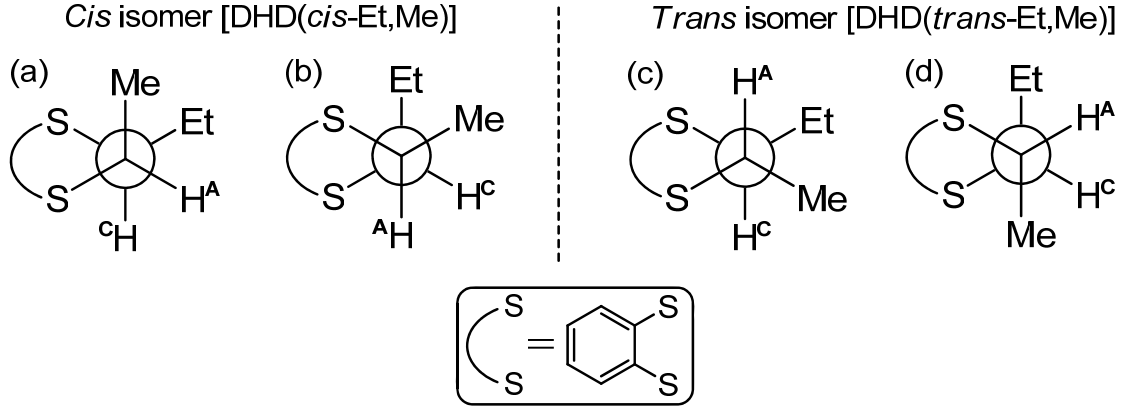

Figure S11. Left: two ring conformers of DHBD(*cis*-Et,Me). Right: two ring conformers of DHBD(*trans*-Et,Me).

Additional confirmation of our assignments of DHBD(*cis*-Et,Me) and DHBD(*trans*-Et,Me) was obtained from 1D NOESY NMR experiments. Specifically, we selectively irradiated the doublet CH_3 signal (labeled "B" in Figures S7 and S9, see Tables S1 and S2 for chemical shifts) for both the *cis* and *trans* isomers, while observing the response of H^c (Figures 7 and 9). The key results are summarized in Figure S12. When CH^B_3 was irradiated, a greater (by a factor of 2.8)[9] NOE response was observed for H^c in the *trans* isomer, compared to the *cis* isomer, as expected on the basis of the Newman projections shown in Figure S11. That is, for the *trans* isomer, the dihedral angle between H^c and the methyl group is ca. 60^o in both conformers [Figure S11(c and d)]. On the other hand, in the *cis* isomer, one conformer [Figure S11(a)] separates H^c and the methyl group by a dihedral angle of ca. 180^o, meaning that these environments are separated by a greater distance, on average, than the corresponding environments in the *trans* isomer.

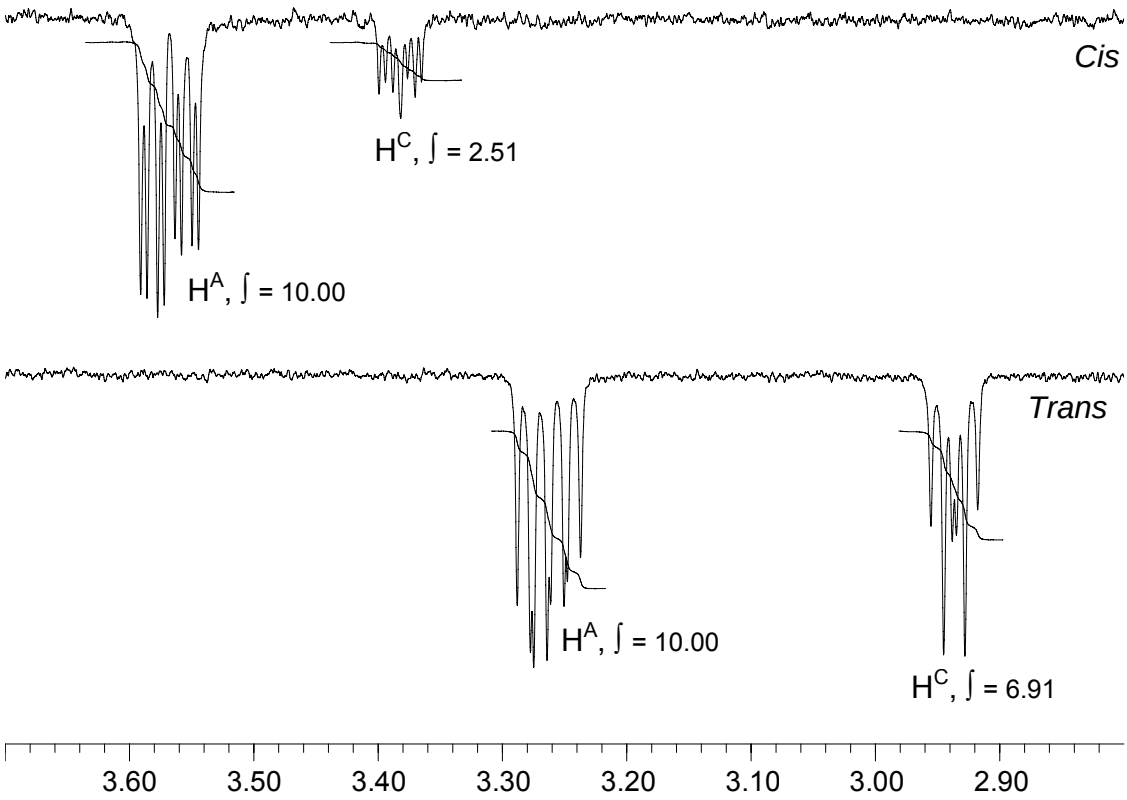

Figure S12. 1D NOESY NMR (500 MHz, $CDCl_3$) spectra showing the H^a/H^c regions for DHBD(*cis*-Et,Me) (top) and DHBD(*trans*-Et,Me) (bottom) and the relevant integrals.[9] Experimental details are described above.

Thus, from the combined evidence of relative coupling constants (J_{AC}) and NOESY NMR experiments, we can confidently distinguish DHBD(*cis*-Et,Me) and DHBD(*trans*-Et,Me). Also, concerted synfacial alkene addition to complex **1** is expected (and symmetry-allowed[1]), so *cis*-alkenes should yield *cis*-DHBDs and *trans*-alkenes should give *trans*-DHBDs.

DHBD-forming reactions observed by NMR spectroscopy

Synthesis of DHBD(H,H) for NMR yield. Note: this compound has been reported previously[10] and is commercially available. A $CDCl_3$ solution (1.0 mL) containing $Mo(tfd)_2(bdt)$ (5.0 mg, 0.0073 mmol) and 3,5-bis(trifluormethyl)bromobenzene (BTBB) (4.0 μL, 6.8 mg, 0.023 mmol) was added to a 25 mL bomb containing BPTS (20 mg, 0.071 mmol) and a stir bar. CD_3CN (25 μL) was added and then ethylene gas was added to the vessel by allowing the gas to gently bubble through the solution for ca. 2 min. The vessel was sealed under ethylene. Note: within 5 min of adding the ethylene, the color of the solution changed from green-blue to brown-green. The mixture was heated to reflux in an oil bath (64°C) for 20.5 h. A portion of the resulting brown-yellow solution was placed in a J. Young NMR tube. Product proton integrations, relative to BTBB (internal standard) were used to determine the concentration/NMR yield of the product

[DHBD(H,H)]. NMR yield: 80%, based on BPTS. See above (procedures for isolated yields) for ^{1}H, ^{13}C NMR and mass spectrometry data for this compound.

Synthesis of DHBD(H,^{n}Bu) for NMR yield. A $CDCl_3$ solution (0.50 mL) containing $Mo(tfd)_2(bdt)$ (5.1 mg, 0.0074 mmol) and BTBB (9.0 μL, 15 mg, 0.050 mmol) was added to a J. Young NMR tube (sealable with Teflon valve) containing BPTS (22 mg, 0.079 mmol). CD_3CN (20 μL) and 1-hexene (19 μL, 13 mg, 0.15 mmol) were added and the tube was sealed under nitrogen. The mixture was heated to reflux in an oil bath (68°C) for 2 h. NMR yield (based on ^{1}H integration vs. BTBB, see above): 96%, based on BPTS. See above for NMR (etc.) data for this product. Note: a parallel experiment, with identical conditions to those described above, except CD_3CN was not added, gave an NMR yield of 12% for DHBD(H,^{n}Bu) (2 h at 68°C, reflux). These experiments were used to calculate the TOFs reported in the manuscript {using TOF = [(moles of DHBD produced)/(moles of catalyst)]/time}. Note: when $Mo(tfd)_2(bdt)$ is first reacted with excess 1-hexene, to form **2**(H,^{n}Bu) quantitatively (in <2 min), the resulting **2**(H,^{n}Bu)/1-hexene mixture reacts with BPTS (aside from order of addition, otherwise same conditions as above) to form DHBD(H,^{n}Bu) catalytically. Thus, catalysis proceeds regardless of whether the catalyst starts in its alkene adduct form [**2**(H,^{n}Bu)], or alkene-free form (complex **1**), as expected from our mechanistic proposal (see main text).

Synthesis of DHBD(C_2H_4,C_2H_4) for NMR yield. The procedure was analogous to the one used for the synthesis (for NMR yield) of DHBD(H,^{n}Bu) (above), with the following modifications: the reaction was conducted in C_6D_6 (instead of $CDCl_3$); 1,2-dichloroethane was used as an internal standard (instead of BTBB); the reaction mixture was heated, in a J. Young NMR tube, at 65°C for 16.8 h. NMR yield of DHBD(C_2H_4,C_2H_4) (based on ^{1}H integration vs. 1,2-dichloroethane): 71%, based on BPTS. See above for NMR (etc.) data for this product. Note: the crude product was contaminated with polymeric material, which was not volatile (i.e., did not transfer under vacuum at 160°C). This material has a ^{1}H NMR spectral profile similar to that seen for the polymer produced in the synthesis of DHBD(*cis*-Et,Me) (see below).

Synthesis of DHBD(*cis*-Et,Me) for NMR yield. The procedure was analogous to the one used for the synthesis (for NMR yield) of DHBD(H,^{n}Bu) (above), with the following modifications: the reaction was conducted in CD_2Cl_2 (instead of $CDCl_3$) to minimize the amount of polymeric byproduct (see below); the reaction mixture was heated, in a J. Young NMR tube, at 65°C for 17.8 h, with the NMR tube completely submerged in the oil bath (i.e., heated under autogenic pressure). NMR yield of DHBD(*cis*-Et,Me) (based on ^{1}H integration vs. BTBB): 55%, based on BPTS. See above for NMR (etc.) data for this product. Note: the crude product was contaminated with polymeric material, which was not volatile (i.e., did not transfer under vacuum at 170°C). ^{1}H NMR (for polymeric contaminants only) (400 MHz, CD_2Cl_2) δ 0.80-1.78 (br ov m), 1.98-2.36 (br ov m), 2.88-4.04 (br ov m), 6.46-7.76 (br ov m). See Figure S13, below, for a possible polymeric structure of the byproduct produced here and in the synthesis of DHBD(C_2H_4,C_2H_4).

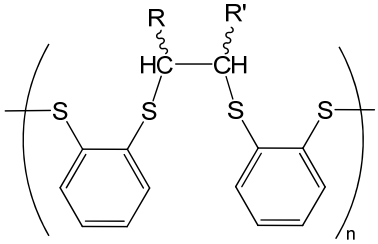

Figure S13. Suggested structure for the polymeric byproduct observed in catalytic reactions between BPTS and *internal cis* alkenes [i.e., cyclohexene (R=R'=C_2H_4) or *cis*-2-pentene (R=Me, R'=Et)].

Note: polymeric byproducts were not observed in the catalyzed reactions between BPTS and terminal alkenes (ethylene and 1-hexene). Also, some polymeric material was formed in mixtures containing BPTS and internal alkenes, even in the absence of Mo(tfd)$_2$(bdt) (see control experiments, below). Interestingly, however, the reaction of *trans*-2-pentene with BPTS (with Mo(tfd)$_2$(bdt) catalyst) cleanly affords DHBD(*trans*-Et,Me) and polymeric byproduct is not produced.

Synthesis of DHBD(*trans*-Et,Me) for NMR yield. The procedure was analogous to the one used for the synthesis (for NMR yield) of DHBD(H,^{n}Bu) (above), with the following modifications: 9.0 μL (0.052 mmol) of BTBB (instead of 4.0 μL); the alkene/BPTS/catalyst reaction mixture was heated (68^{o}C, reflux) for 18.7 h. NMR yield of DHBD(*trans*-Et,Me) (based on ^{1}H integration vs. BTBB): 94%, based on BPTS. See above for NMR (etc.) data for this product. No polymeric byproduct was observed in this reaction.

Synthesis of DHBD(H,CH$_2$OH) for NMR yield. The procedure was analogous to the one used for the synthesis (for NMR yield) of DHBD(H,^{n}Bu) (above), with the following modifications: 9.0 μL (0.052 mmol) of BTBB (instead of 4.0 μL); the alkene/BPTS/catalyst reaction mixture was heated (68^{o}C, reflux) for 3 h to obtain near-complete consumption of BPTS. NMR yield of DHBD(H,CH$_2$OH) (based on ^{1}H integration vs. BTBB): 89%, based on BPTS. See above for NMR (etc.) data for this product.

Observation of the catalyst resting state

The resting state of the catalyst, in reactions between ethylene or 1-hexene and BPTS, was assessed by ^{19}F NMR spectroscopy. In both cases, the resting form is the corresponding alkene adduct of Mo(tfd)$_2$(bdt) [i.e., **2**(R,R')].

Mo(tfd)$_2$(bdt) (compound **1**) is known to react with ethylene rapidly and cleanly to form **2**(H,H), its intraligand (at bdt) ethylene adduct.[1] This fully characterised complex is major species observed by ^{19}F NMR (two singlets for C_s-symmetric adduct) in the catalytic reactions between ethylene and BPTS early in the reaction (also present when reaction is complete, along with various catalyst decomposition products) when CD_3CN was not present. For the present study, we showed, in a stoichiometric experiment, that

2(H,H) is converted back to $Mo(tfd)_2(bdt)$, releasing free DHBD(H,H), upon treatment with excess BPTS (see below for experimental details).

The reactions involving 1-hexene gave much more complex spectra for the catalyst resting state, due to the C_1 symmetry of the adduct. When CD_3CN was *not* used, the major species observed (by ^{19}F NMR) is the 1-hexene adduct of $Mo(tfd)_2(bdt)$ (**2**(H,^{n}Bu), Figure S14) as (we propose) the exo isomer only (see below).

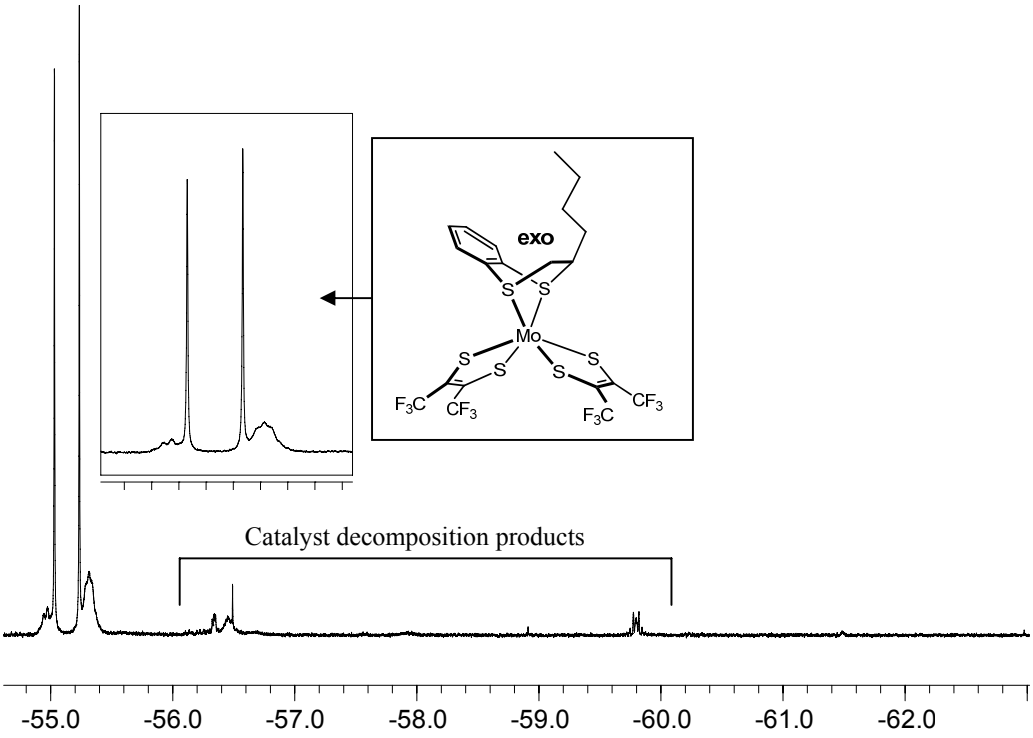

Figure S14. ^{19}F NMR (377 MHz, $CDCl_3$, 23^{o}C) spectrum showing the resting state of the catalyst in a reaction between 1-hexene and BPTS (with $Mo(tfd)_2(bdt)$ as precatalyst, no CD_3CN). The inset shows an expanded view of the resonances associated with $Mo(tfd)_2$(bdt(1-hexene).

The above spectrum (Figure S14) was obtained after heating a 1-hexene/BPTS/$Mo(tfd)_2(bdt)$ mixture (initial concentrations: 0.28 M/0.15 M/15 mM; in $CDCl_3$) for 22 h at reflux. At this stage, the reaction to give DHBD(H,^{n}Bu) was ca. 60% complete (the reaction is faster when CD_3CN is present). In addition to **2**(H,^{n}Bu), some minor products arising from catalyst decomposition are observed (labeled in Figure S14, <5% by integration). A ^{19}F NMR spectrum of the same mixture, taken at an earlier point during the reaction (after ca. 1 h) is identical to the spectrum shown here, except the catalyst decomposition peaks were not detectable. Thus, the catalyst has a finite lifetime, slowly decomposing to (presumably) inactive species.

We propose the ^{19}F NMR spectrum shown in Figure S14 represents only the exo isomer of **2**(H,^{n}Bu). The endo isomer appears unlikely to form on steric grounds, given the

size/length of the alkyl (^{n}Bu) chain (i.e., there would be significant steric conflict between the trifluoromethyl groups and the dangling alkyl chain). The complexity of the spectrum is likely explained by higher order coupling between the fluorine atoms of the CF_3 groups, where C-CF_3 bond rotation is impeded by steric constraint caused by the metal-bound alkyl-substituted DHBD.

Preliminary variable temperature (VT) NMR experiments show that the spectra for **2**(H,^{n}Bu) are temperature-dependent (Figure S15) and also field-dependent, as expected for higher order spectra.

Reactivity studies support our assignment of the ^{19}F NMR data: **2**(H,^{n}Bu) is converted to Mo(tfd)$_2$(bdt) (**1**), releasing DHBD(H,^{n}Bu), when treated with excess BPTS (see below for experimental details). Note that fully-characterised **2**(H,H)[1] is also converted to **1** and free DHBD(H,H).

Note: When CD_3CN was present in catalytic runs, the ^{19}F NMR spectra of the equilibrium mixture showed **2**(H,^{n}Bu), as well as a new species, characterised by one sharp singlet (-55.4 ppm in $CDCl_3$), which is reasonably assigned as $(CD_3CN)_2Mo(tfd)_2$. We found that having CD_3CN present accelerated the catalytic reactions between alkenes and BPTS, possibly because $(CD_3CN)_2Mo(tfd)_2$ is more reactive toward BPTS than **2**(R,R').

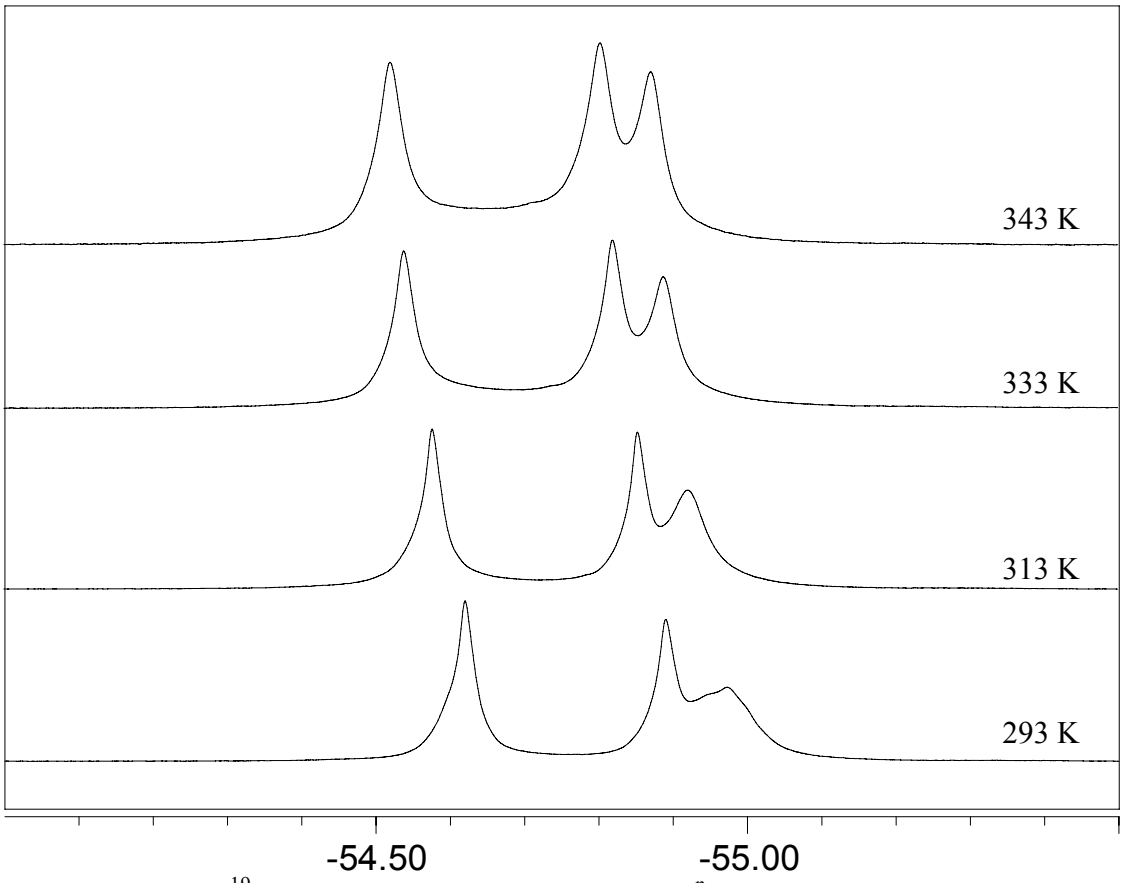

Figure S15. VT ^{19}F NMR (470 MHz, C_6D_6) for **2**(H,^{n}Bu) where $[Mo(tfd)_2(bdt)]_0$ = [1-hexene]$_0$ = 0.03 M.

Reaction of 2(H,H) with BPTS to generate Mo(tfd)$_2$(bdt) and DHBD(H,H). $Mo(tfd)_2(bdt)$ (9.9 mg, 0.014 mmol) and BTBB (2.5 μL, 4.2 mg, 0.015 mmol) were combined in CD_2Cl_2 (0.7 mL). The tube was opened in air and ethylene was added by allowing the gas to gently pass through the solution for ca. 1 min. The tube was quickly resealed under an ethylene atmosphere. Ca. 10 min after adding the ethylene, ^{1}H and ^{19}F NMR spectra were obtained to verify quantitative conversion to **2**(H,H) (see ref. 1 for NMR data for this compound). Excess ethylene was removed by purging the solution with argon for ca. 1.5 min. Note: approximately 0.1 mL of solvent was lost to evaporation from purging with ethylene and argon. A ^{1}H NMR spectrum was collected to confirm removal of excess ethylene. BTPS (10 mg, 0.036 mmol) was added, with an additional 0.1 mL of CD_2Cl_2, to the NMR tube. The entire tube was submerged in an oil bath and heated at 70^{o}C (under autogenic pressure) for 18.8 h. Another ^{19}F NMR spectrum was collected, which showed 83% yield (by integration relative to BTBB) of $Mo(tfd)_2(bdt)$ (singlet, -56.03 in CD_2Cl_2), based the original concentration of the molybdenum trisdithiolene. The ^{1}H NMR spectrum showed complete consumption of **2**(H,H) and clean production of DHBD(H,H) (singlet, 3.26 ppm in CD_2Cl_2), as well as unreacted BPTS.

Reaction of 2(H,^{n}Bu) with BPTS to generate Mo(tfd)$_2$(bdt) and DHBD(H,^{n}Bu). Mo(tfd)$_2$(bdt) (25 mg, 0.036 mmol) was combined with $CDCl_3$ (0.6 mL) and 1-hexene (5.0 μL, 3.4 mg, 0.040 mmol). After 45 min, ^{1}H and ^{19}F NMR spectra were obtained to verify conversion to **2**(H,^{n}Bu) (see above for discussion). BPTS (12 mg, 0.043 mmol) was then added and the tube was resealed. The tube was heated in an oil bath at 66^{o}C for 20.5 h. A ^{19}F NMR spectrum shows reasonably clean conversion to Mo(tfd)$_2$(bdt) (singlet, -56.0 ppm in $CDCl_3$) (see Figure S16); the ^{1}H NMR spectrum shows DHBD(H,^{n}Bu) (see data above) and unreacted BPTS. ^{19}F NMR (377 MHz, $CDCl_3$) (for **2**(H,^{n}Bu)) δ -54.66 to -54.34 (br ov m), -54.42 [s (apparently)], -54.30 to -54.07 (br ov m), -54.23 [s (apparently)].

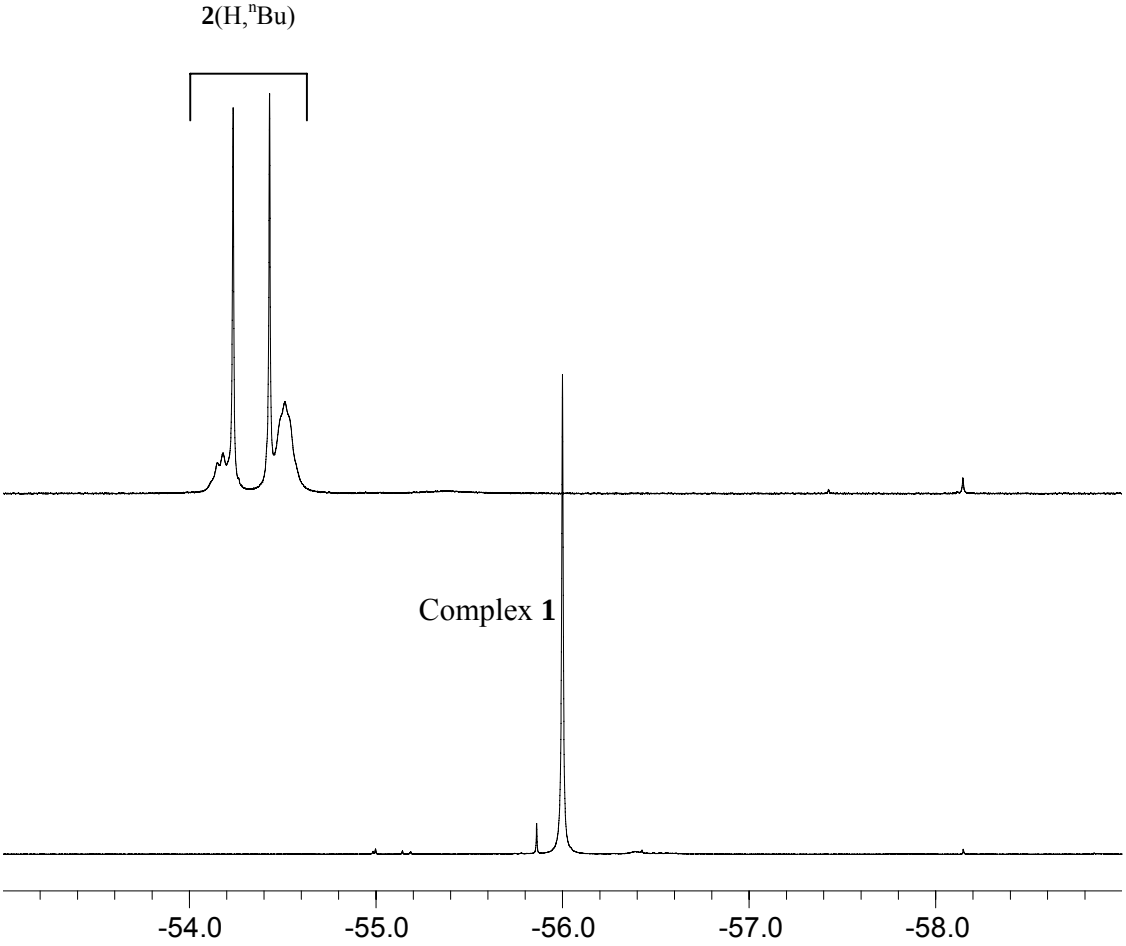

Figure S16. ^{19}F NMR (377 MHz, $CDCl_3$) spectra for (top) **2**(H,^{n}Bu) and (bottom) the same sample treated with excess BPTS to generate Mo(tfd)$_2$(bdt) [and DHBD(H,^{n}Bu)].

Control Experiments

For all alkene/BPTS reactions described here, control experiments were conducted without Mo(tfd)$_2$(bdt). Details as follows:

BPTS + excess ethylene (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(H,H) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ was not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 66°C for 48.5 h, affording no DHBD(H,H). A ^1H NMR spectrum showed unreacted starting materials.

BPTS + 2 equiv 1-hexene (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 66°C for 45 h, affording no DHBD(H,^{n}Bu). A ^1H NMR spectrum showed unreacted starting materials.

BPTS + 2 equiv cyclohexene (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(C_2H_4,C_2H_4) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 66°C for 21.5 h, affording no DHBD(C_2H_4,C_2H_4). A ^1H NMR spectrum showed unreacted starting materials and some polymeric material (ca. 10 %), as seen above in the syntheses of DHBD(*cis*-Et,Me) and DHBD(C_2H_4,C_2H_4).

BPTS + 2 equiv *cis*-2-pentene (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(*cis*-Et,Me) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ was not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 65°C for 23.5 h, affording no DHBD(*cis*-Et,Me) [or DHBD(*trans*-Et,Me)]. A ^1H NMR spectrum showed unreacted starting materials and some polymeric material (ca. 30 %), as seen above in the syntheses of DHBD(*cis*-Et,Me) and DHBD(C_2H_4,C_2H_4).

BPTS + 2 equiv *trans*-2-pentene (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ was not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 66°C for 22.3 h, affording no DHBD(*trans*-Et,Me) [or DHBD(*cis*-Et,Me)]. A ^1H NMR spectrum showed unreacted starting materials and very broad peaks in the aromatic and aliphatic regions, indicating some polymerized material (ca. 15-20%).

BPTS + 2 equiv allyl alcohol (no catalyst). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ was not added to the reaction mixture. The BPTS/alkene solution (in $CDCl_3$) was heated at 66°C for 22.3 h, affording no DHBD(H,CH_2OH). A ^1H NMR spectrum showed only unreacted starting materials.

We screened a cross-section of other potential catalysts/conditions for the reaction between BPTS and 1-hexene, including a Lewis acid, Lewis bases, a Brønsted acid, molybdenum sulfide and photolytic conditions. The reaction between BPTS and *cis*-2-pentene was examined in the presence of a radical initiator. All of these experiments failed to produce DHBDs. Further, the catalytic reaction between BPTS and 1-hexene (with $Mo(tfd)_2(bdt)$ present, 5 mol %) was conducted in the presence 2,6-di-tert-butyl-4-

methylphenol (BHT) to verify that the catalysis proceeds, to form DHBD(H,^{n}Bu), even in the presence of a radical inhibitor (i.e., to rule out a radical pathway). Details as follows:

BPTS + 2 equiv 1-hexene (with NEt_3). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. Instead, triethylamine (1.1 μL, 0.75 mg, 0.0074 mmol) was added. Note: when the amine was added, the solution became cloudy with very fine white-yellow precipitate, possibly indicating partial base-induced polymerization of BPTS. The BPTS/alkene/amine solution (in $CDCl_3$) was heated at 66^{o}C for 23 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials.

BPTS + 2 equiv 1-hexene (with PBu_3). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except at ½ the concentration. $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. Instead, tributylphosphine ($P(^{n}Bu)_3$) (18 μL, 15 mg, 0.072 mmol) was added. The BPTS/alkene/phosphine solution (in $CDCl_3$) was heated at 65^{o}C for 20.5 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterised by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(*cis*-Et,Me).

BPTS + 2 equiv 1-hexene (with $B(C_6F_5)_3$). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. Instead, tris(pentafluorophenyl)borane (4.4 mg, 0.0085 mmol) was added. The BPTS/alkene/borane solution (in $CDCl_3$) was heated at 66^{o}C for 22 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterised by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(*cis*-Et,Me).

BPTS + 2 equiv 1-hexene (with HBF_4). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. Instead, HBF_4 (54 wt. % in diethyl ether) (1.0 μL, 0.0073 mmol) was added. The BPTS/alkene/acid solution (in $CDCl_3$) was heated at 66^{o}C for 16 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 10-15%), characterised by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(*cis*-Et,Me).

BPTS + 2 equiv 1-hexene (with MoS_2). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except $Mo(tfd)_2(bdt)$ and CD_3CN were not added to the reaction mixture. Instead, MoS_2 (11 mg, 0.069 mmol) was added. The BPTS/alkene/MoS_2 mixture (in $CDCl_3$) was heated at 66^{o}C for 16 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials.

BPTS + 2 equiv 1-hexene (photolytic conditions). The procedure was analogous to the one used for the synthesis of DHBD(H,^{n}Bu) (for NMR yield, see above), except Mo(tfd)$_2$(bdt) and CD_3CN were not added to the reaction mixture. The BPTS/alkene solution was taped to a fluorescent light tube (with aluminum foil backing to maximize light exposure) and irradiated for 17 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterised by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(*cis*-Et,Me).

BPTS + 2 equiv *cis*-2-pentene (with Vazo 52® radical initiator). The procedure was analogous to the one used for the synthesis of DHBD(*cis*-Et,Me) (for NMR yield, see above), except Mo(tfd)$_2$(bdt) was not added to the reaction mixture. Instead, Vazo 52® (11 mg, 0.069 mmol) was added. The BPTS/alkene/Vazo 52® mixture (in $CDCl_3$) was heated at 66^{o}C for 18.5 h, affording no DHBD(H,^{n}Bu). A ^{1}H NMR spectrum showed unreacted starting materials.

BPTS + 2 equiv 1-hexene [catalyst: Mo(tfd)$_2$(bdt)/CD_3CN; with BHT radical trap]. A $CDCl_3$ solution (0.5 mL) containing Mo(tfd)$_2$(bdt) (5.0 mg, 0.0073 mmol) and BTBB (9.0 μL, 15 mg, 0.051 mmol) was added to a J. Young NMR tube containing BPTS (21 mg, 0.075 mmol) and 2,6-di-tert-butyl-4-methylphenol (BHT) (10 mg, 0.045 mmol). 1-Hexene (Aldrich, 99 %) (20 μL, 13.5 mg, 0.16 mmol) and then CD_3CN (20 μL) were added and the tube was sealed under nitrogen. The mixture was heated in an oil bath (68^{o}C, reflux) for 3.25 h, giving clean conversion to DHBD(H,^{n}Bu) (95% ^{1}H NMR yield, based on product integration relative to BTBB). Also visible in the ^{1}H NMR spectrum (400 MHz, $CDCl_3$): unchanged BHT [δ 1.43 (s, 18H, C(CH_3)$_3$ x 2), 2.27 (s, 3H, CH_3), 5.02 (s, 1H, OH). Note: the aryl BHT peak (at ca. 7 ppm) is obscured by one of the aryl resonances of DHBD(H,^{n}Bu)].

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[6] Three multiplets, for the byproduct, are visible in C_6D_6 (see Figure S1) and four muliplets can be seen in $CDCl_3$ (spectrum not shown).
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[9] The integrals were calibrated against the NOE signals for H^A; these integrals should be very similar for the *cis* and *trans* isomers because, in both cases, H^A and CH^B_3 are held in rigid proximity (i.e., they share a geminal carbon and should be held at approximately the same distance) and the coupling constants, J_{AB}, are nearly equal (Tables 1 and 2), meaning that distortion of the signal for H^A, caused by direct J-coupling between the A and B environments, should be comparable in both cases.
[10] See, for example: A. B. Pierini, M. T. Baumgartner and R. A. Rossi, *J. Org. Chem.* 1987, **52**, 1089.