Electronic Supplementary Information

# A Mild, Efficient and Catalyst-Free Thermoreversible Ligation System Based on Dithiooxalates

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## Content

# 1. Materials and Methods

## a) Materials

Stabilized *tert*-butyl acrylate was freed from inhibitor via a short column of basic aluminum oxide. Cyclopentadiene was freshly cracked at 180 °C from dicyclopentadiene. All other chemicals were used as supplied by the manufacturers.

## b) Characterization Techniques

SEC of polymeric samples was carried out on a Polymer Laboratories/Varian PL-GPC 50 Plus system, comprising an autosampler, a Polymer Laboratories 5.0 µm bead-size guard column (50 x 7.5 mm²), followed by three PL columns and a differential refractive index detector. Measurements were performed in THF at 35 °C with a flow rate of 1 ml·min$^{-1}$. The SEC system was calibrated using linear poly(methyl methacrylate) standards ranging from 800 g·mol$^{-1}$ to 1.6·10$^{6}$ g·mol$^{-1}$ (MHKS parameters: $K = 12.8 \cdot 10^{-5}$ dL g$^{-1}$, $\alpha = 0.69$)[1] or polystyrene standards ranging from 500 g·mol$^{-1}$ to 2.5·10$^{6}$ g·mol$^{-1}$ ($K = 14.1 \cdot 10^{-5}$ dL g$^{-1}$, $\alpha = 0.70$).[2]

The temperature dependent SEC (TD SEC) experiments were carried out on a PL GPC 220 high temperature chromatograph (Agilent Technologies, US), using DMAc (+ 3 g/L LiCl) as a solvent at a flow rate of 1 mL/min on an ABOA DMAc-phil column (AppliChrom, Germany).

$^{1}$H NMR spectra were measured on a Bruker Avance III 400 spectrometer with a CryoProbe at 400 MHz in $CDCl_3$ for standard measurements and toluene-$d_8$ in a pressure tube for measurements at elevated temperatures (HT NMR). After the stabilization of an adjusted temperature within minutes, the establishment of the equilibrium was ensured by repeated additional measurements with 16 scans before and after the actual measurement with 128 scans until (typically immediately)

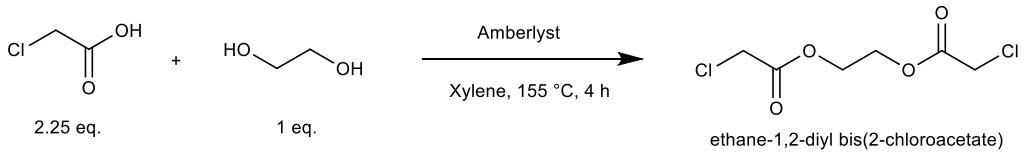
no difference could be determined in the measured data anymore. The recyclability of the samples was checked after cooling to ambient temperature overnight. A baseline correction was applied.

Mass spectra were recorded on a Q-Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range of 74-1822 via premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The samples were dissolved with a concentration of 0.05 $mg \cdot mL^{-1}$ in a mixture of THF and MeOH (3:2) containing 100 µmol of sodium triflate and infused with a flow of 5 $\mu L \cdot min^{-1}$.

UV/Vis measurements were carried out on a Varian Cary 50 Bio spectrophotometer. Spectra were recorded between 300 and 800 nm and kinetics were measured at 500 nm in acetonitrile or toluene in a 10 mm path length cell with a baseline correction regarding the solvent.

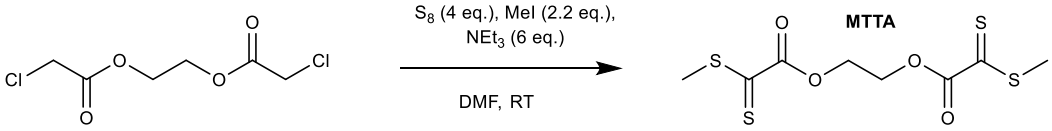
Additional UV/Vis measurements of single spectra under similar conditions were carried out on an OceanOptics USB4000 spectrometer with a USB-ISS-UV-Vis detecting unit.

## c) Synthesis of MTTA




A literature procedure was adopted and refined to generate the desired dithiooxalate dilinker.[3, 4] Ethylene glycol (124.1 g, 2.0 mol) and chloracetic acid (472.5 g, 5.0 mol) were dissolved in 1 L

xylol, Amberlyst-15 (16.0 g) was added and the reaction mixture was heated to 165 °C under reflux in a Dean-Stark apparatus for 4 h. After cooling, Amberlyst was separated via decantation and the reaction mixture was washed three times with saturated sodium carbonate solution (2x250 mL, 1x70 mL) and two times with brine (250 mL). The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The product was further purified via vacuum distillation at 170 °C, yielding crystalline ethane-1,2-diyl bis(2-chloroacetate) (357.1 g, 83 %).




Subsequently, triethylamine (282 g, 2.79 mol) was added to a suspension of sulphur (60 g, 1.86 mol) in DMF (1.1 L) under nitrogen. Slowly, a solution of ethane-1,2-diyl bis(2-chloroacetate) (100 g, 0.47 mol) in 100 mL DMF (dry) was added dropwise over 1 h to allow the reaction mixture to reach 40 °C. The mixture was stirred for an additional 3 h at ambient temperature and then cooled to 10 °C. Methyl iodide (145 g, 64 mL, 1.02 mol) was added dropwise within 1 h while keeping the temperature of the reaction mixture ≤ 10 °C, whereafter the mixture was stirred for an additional 2 h at 10 °C. The crude mixture was diluted with methyl *tert*-butyl ether (5 L) and the emerging yellow-orange precipitate was filtered-off via a short column of silica. The filtrate was washed two times each with 0.5 M sulphuric acid (1.6 L), water (1.6 L) and a 4:1 mixture of brine and saturated sodium hydrogen carbonate solution (1.2 L). The organic phase was dried over magnesium sulfate und the solvent was removed under reduced pressure to yield the dark violet oily solid product (119.7 g, 83 %). Further purification can be achieved via flash chromatography (cyclohexane/ethylacetate 8:1, silica, $R_f$ = 0.38). Although the product seems to be stable under

ambient conditions and also – at least for limited time scales – at elevated temperatures, a storage in the freezer is recommended due to its reactivity and literature reports of smaller, fully liquid dithiooxalate species.[5]

ESI-MS $(M+Na)^+$ $C_8H_{10}O_4S_4+Na^+$ theoretical: 320.9360 Da, experimental: 320.9370 Da

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.64 (s, 4H, -O-C*H*$_2$-), 2.68 (s, 6H, -S-C*H*$_3$).

$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm) = 215.75 (-*C*=S), 160.02 (-*C*=O), 64.20 (-O-*C*H$_2$-), 19.75 (-*C*H$_3$).

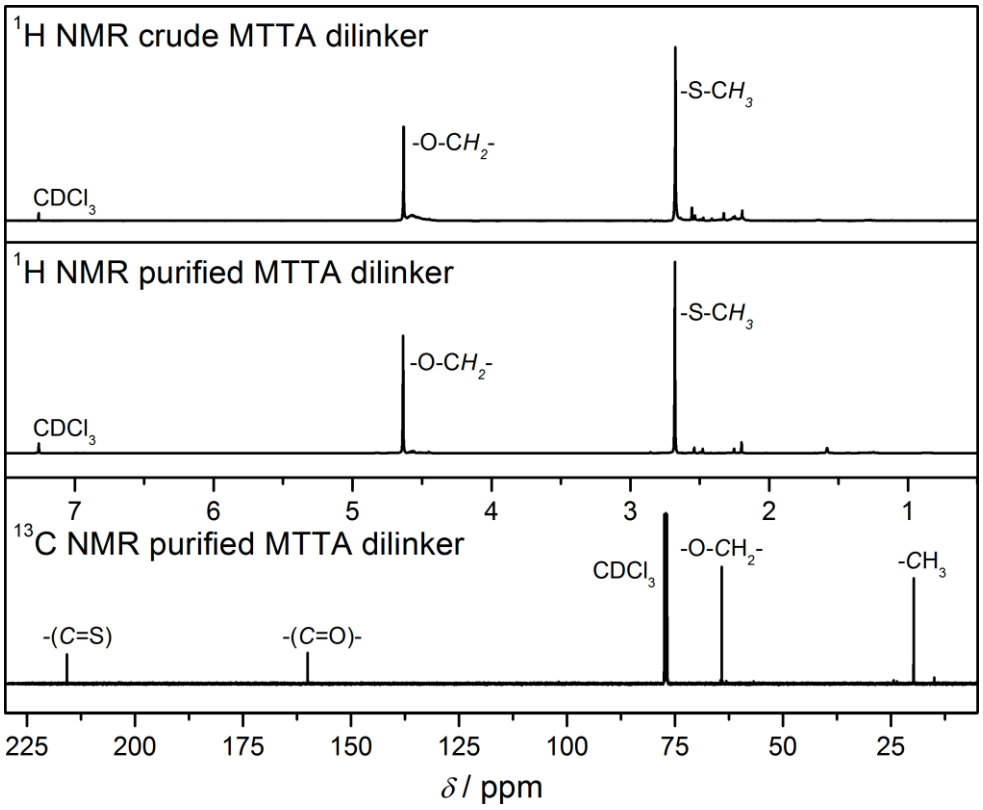



**Fig. S1.** $^1$H NMR (400 MHz, $CDCl_3$) of **MTTA** before (top) and after (middle) column chromatography and $^{13}$C NMR (bottom, 100 MHz, $CDCl_3$) of **MTTA**.

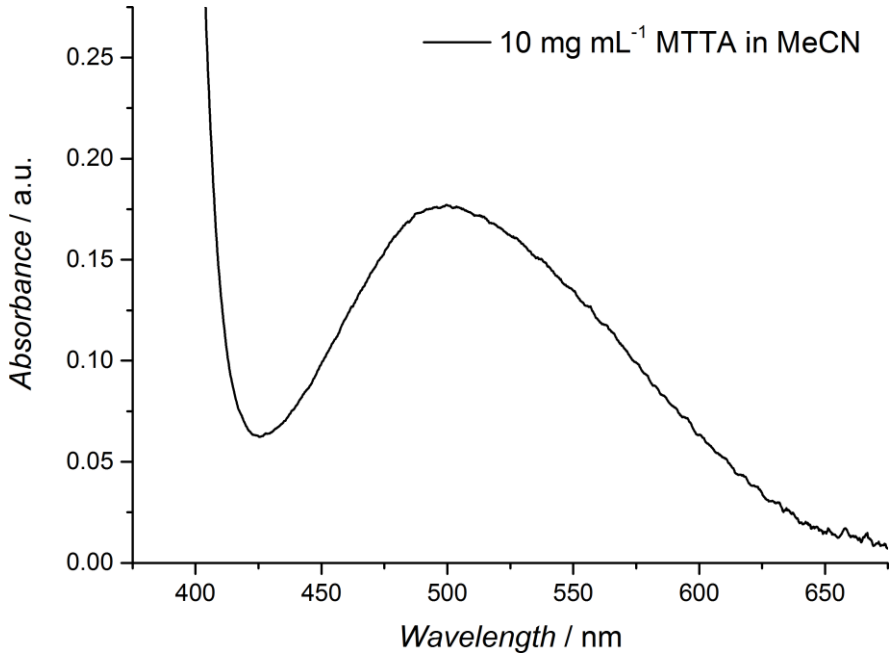



**Fig. S2.** UV/Vis spectra of the characteristic C=S double bond absorbance of MTTA (10 mg $mL^{-1}$ in MeCN) at 500 nm.

### d) Synthesis of $Cp_2P^tBuA$

Synthesis of $Cp_2P^tBuA$ was carried out according to a literature procedure earlier established by us.[6, 7] $M_n$ = 6000 g $mol^{-1}$, $Đ$ = 1.12 (PMMA calibration, K = 19.70 · $10^{-5}$ dL $g^{-1}$, α = 0.66).[8]

### e) Synthesis of Diels–Alder adducts of MTTA with diverse Dienes

#### MTTA + Cp

In a typical procedure, MTTA (20 mg, 0.67 mmol ≙ 0.13 mmol dithiooxalate end-groups) was dissolved in 1 mL acetonitrile, transferred into a UV/Vis cuvette and heated to the desired reaction temperature (25 or 50 °C). Cyclopentadiene (depending on the desired reaction conditions 1.2 eq.,

13.3 µL, 0.16 mmol or 5.0 eq., 55.4 µL, 0.67 mmol) was added and the reaction mixture was shaken to guarantee good intermixture. The reaction process was tracked immediately in a UV/Vis spectrometer via the decreasing C=S double bond absorbance at 500 nm. Subsequently, the solvent and the excess of cyclopentadiene was evaporated and the slightly yellow product was characterized without further purification.

ESI-MS $(M+Na)^+$ $C_{18}H_{22}O_4S_4+Na^+$ theoretical: 453.0299 Da, experimental: 453.0315 Da

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) = 6.54 (dd, 1 H, $H^a$), 6.43 (dd, 1 H, $H^{a'}$), 6.15 (dd, 1 H, $H^b$), 6.04 (dd, 1 H, $H^{b'}$), 4.53-4.20 (m, 4 H, $H^c$), 4.16 (s, 1 H, $H^d$), 4.05 (s, 1 H, $H^{d'}$), 3.90 (s, 1 H, $H^c$), 3.60 (s, 1 H, $H^{c'}$), 2.33-2.19 (m, 6 H, $H^{f,f'}$), 2.01-1.68 (m, 3 H, $H^g$), 1.58-1.22 (m, 3 H, $H^{g'}$).

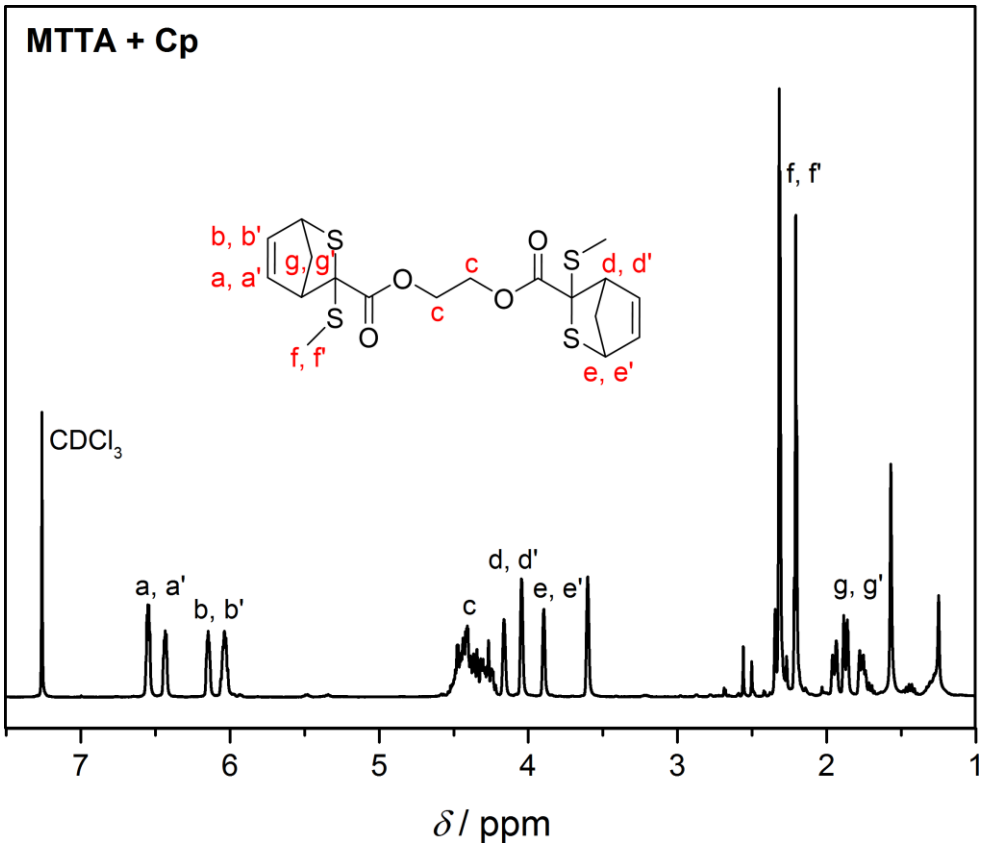



**Fig. S3.** $^1$H NMR (400 MHz, $CDCl_3$) of the DA adduct of MTTA and cyclopentadiene.

**MTTA + 2,3-Dimethyl-1,3-butadiene**

ESI-MS $(M+Na)^+$ $C_{20}H_{30}O_4S_4+Na^+$ theoretical: 485.0925 Da, experimental: 485.0941 Da

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) = 4.50-4.31 (m, 4H, $H^a$), 3.28+2.84 (ABX, 2H, $H^b$), 2.88+2.44 (ABX, 2H, $H^c$), 2.18 (s, 6 H, $H^d$), 1.72 (s, 6 H, $H^e$), 1.69 (s, 6 H, $H^{e'}$).

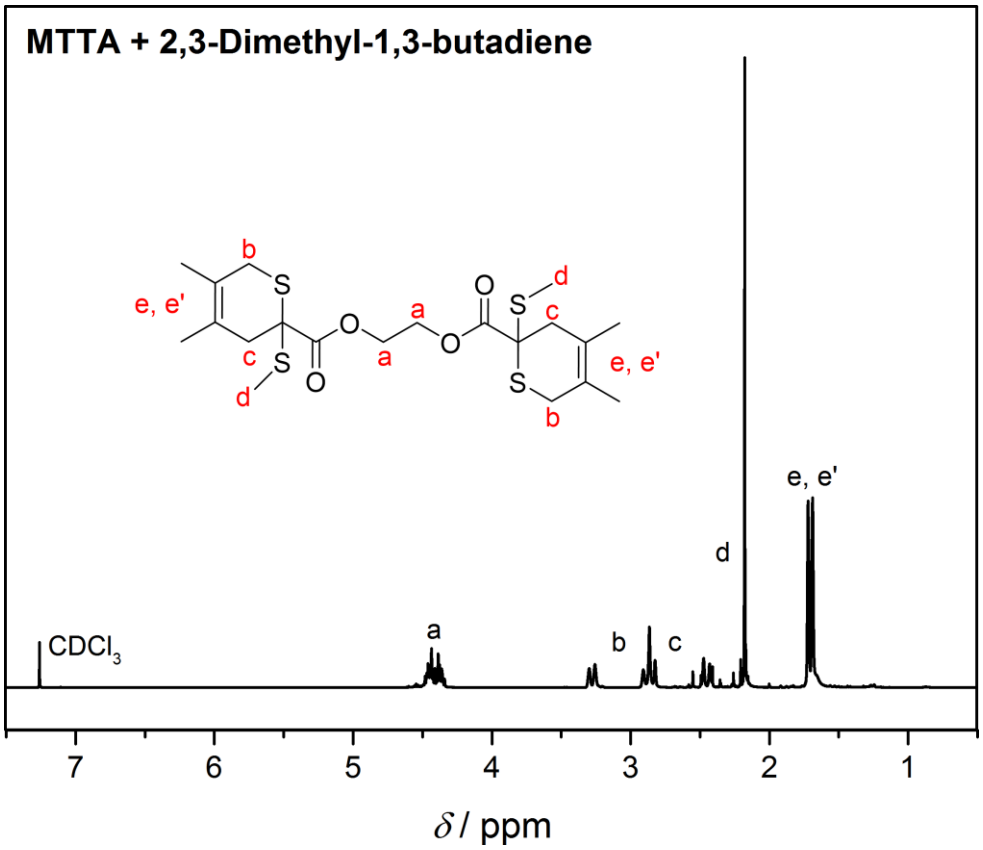



**Fig. S4.** $^1$H NMR (400 MHz, $CDCl_3$) of the DA adduct of MTTA and 2,3-dimethyl-1,3-butadiene.

**MTTA + Sorbic Alcohol**

ESI-MS $(M+Na)^+$ $C_{20}H_{30}O_6S_4+Na^+$ theoretical: 517.0823 D Da, experimental: 517.0843 Da

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) = 5.92-5.59 (m, 4 H, $H^a$), 4.53-4.29 (m, 4 H, $H^b$), 4.11-3.53 (m, 6 H, $H^{c,c',d,d'}$), 3.22-2.68 (m, 2 H, $H^{e,e'}$), 2.24-2.16 (m, 6 H, $H^{f,f'}$), 1.39-1.12 (m, 6 H, $H^{g,g'}$).

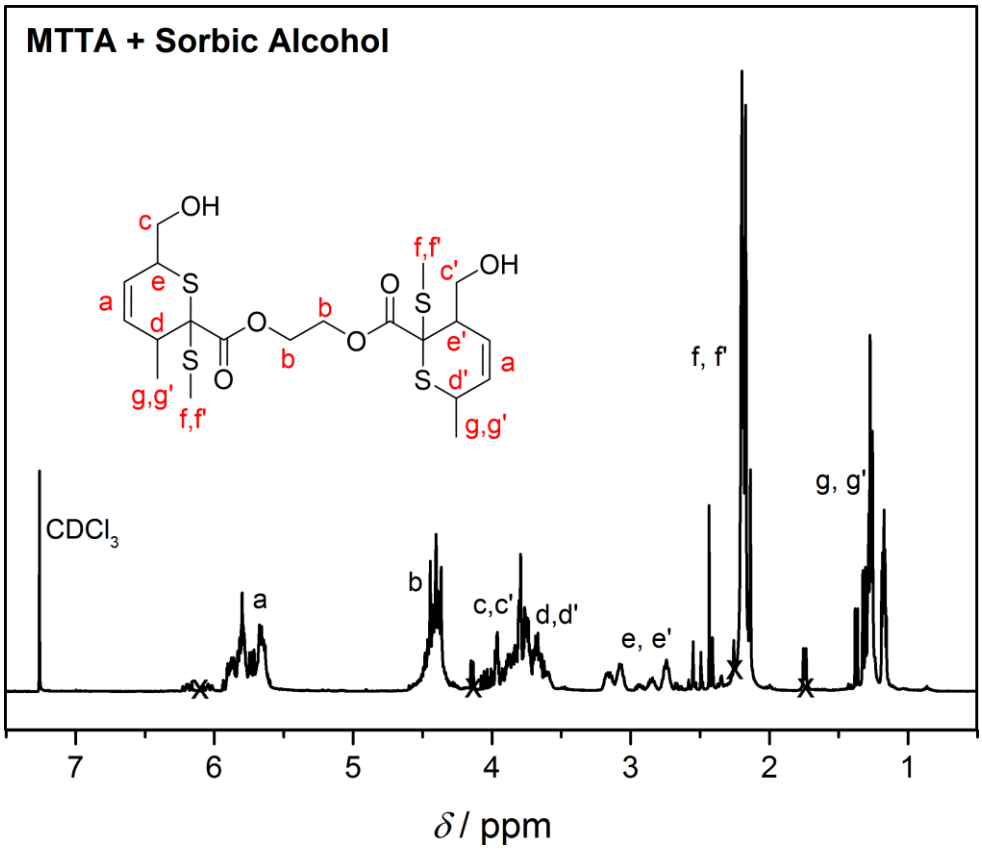



**Fig. S5.** $^1$H NMR (400 MHz, $CDCl_3$) of the DA adduct of MTTA and sorbic alcohol; x: residual sorbic alcohol.

**MTTA + Ethyl Sorbate**

ESI-MS $(M+Na)^+$ $C_{24}H_{34}O_8S_4+Na^+$ theoretical: 601.1034 Da, experimental: 601.1062 Da

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) = 5.97-5.76 (m, 4 H, $H^a$), 4.48-4.35 (m, 4 H, $H^b$), 4.25-4.10 (m, 4 H, $H^{c,c'}$), 4.13-3.95 (m, 2 H, $H^{d,d'}$), 3.71-3.52 (m, 2 H, $H^{e,e'}$), 2.19+2.16 (s, 6 H, $H^{f,f'}$), 1.39-1.19 (m, 12 H, $H^{g,g',h}$).

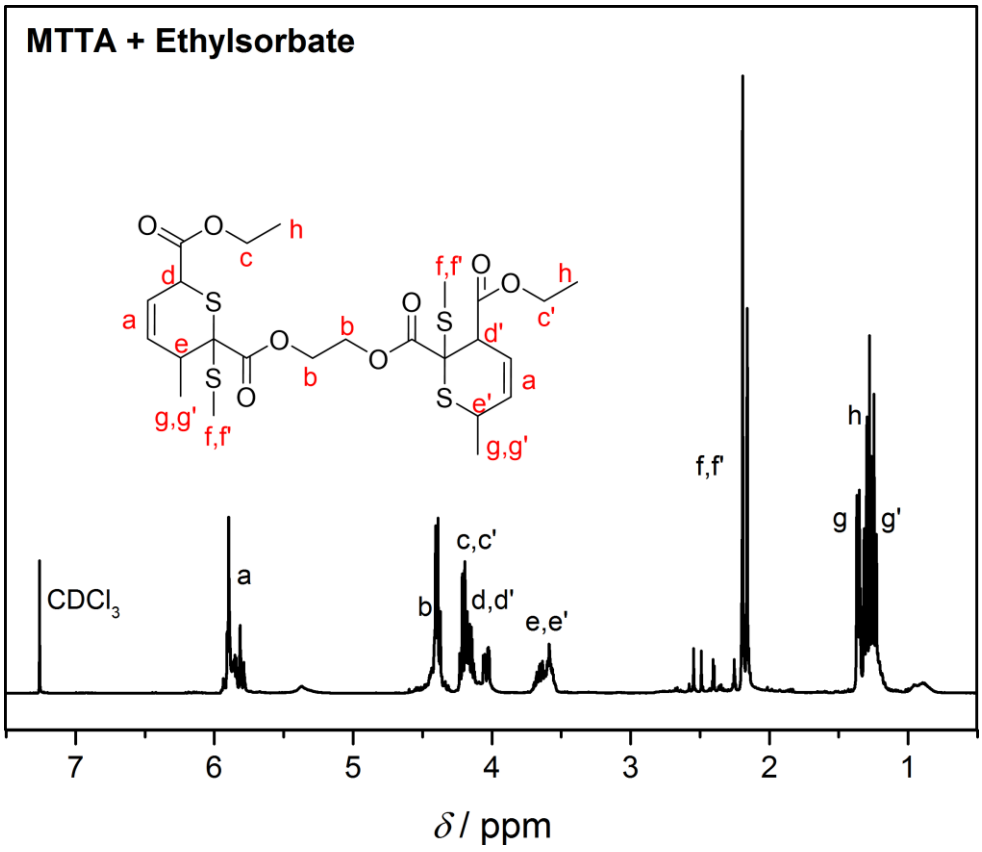



**Fig. S6.** $^1$H NMR (400 MHz, $CDCl_3$) of the DA adduct of MTTA and ethyl sorbate.

**MTTA + IPDI-SA**

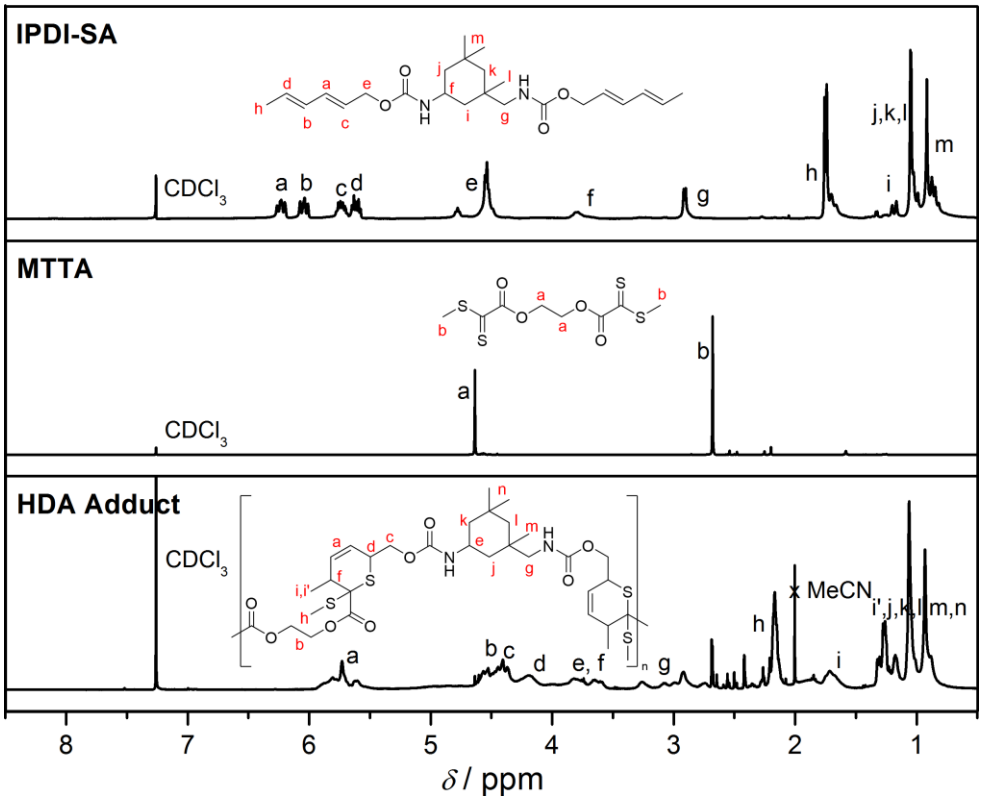



**Fig. S7.** $^{1}$H NMR (400 MHz, $CDCl_3$) of IPDI-SA (top), MTTA (middle) and their step-growth adduct (bottom).

Isophorone bis(sorbic carbamate) (IPDI-SA) was provided by Evonik Industries. From Fig. S7, it can be seen that all diene groups of the IPDI-SA have reacted in a Diels–Alder reaction with the MTTA dilinker. The implied step-growth behavior is evidenced via SEC in Fig. S8. The degree of polymerization is calculated as:

$$DP_n = \frac{M_n(DA-Polymer)}{(M_n(Macromonomer) + M(Dilinker))/2} \qquad \textbf{Equation S1}$$

Although the employed SEC calibration via polystyrene standards is likely inadequate for the material at hand, the method allows for a convenient visualization of the step-growth. The

assumedly low $DP_n$ as well as the residual starting material visible in the SEC trace (Fig. S8) are probably a result of a non-functional IPDI species and is not arising due to limited reactivity, as no dienes can be identified via NMR anymore (Fig. S7).

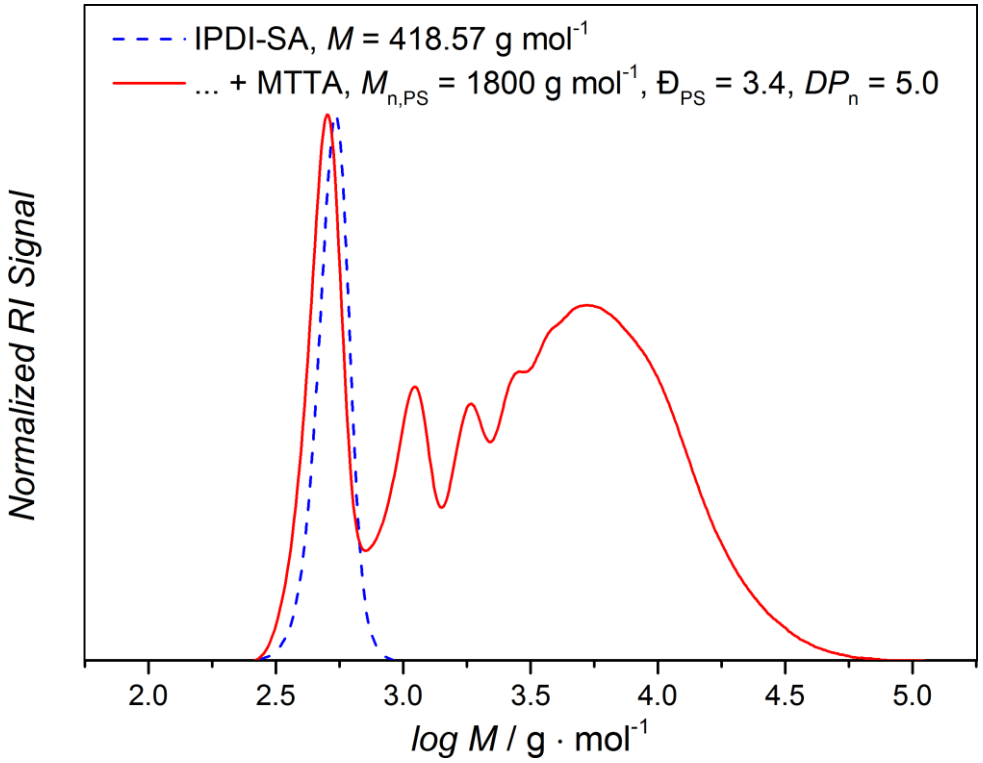



**Fig. S8.** SEC trace of IPDI-SA and its step-growth adduct with equimolar amounts of MTTA (20 mg $mL^{-1}$ in MeCN), measured in THF at 35 °C.

## 2. Evaluation of UV/Vis Kinetics

For an evaluation of the reaction rates, the time dependent reactant concentrations were calculated via the known starting concentrations and the normalized time dependent absorbance of the C=S double bond at 500 nm, which decreases with ongoing hetero Diels–Alder reaction of the thiocarbonyl species with dienes. Via the time dependent reactant concentrations and the

assumption of a 2nd order reaction ($A + B \rightarrow C$) without retro reaction at the given reaction temperatures (as computationally predicted), reaction rate coefficients $k$ are accessible via standard textbook equations:[9] for $[A]_0 \neq [B]_0$, $k$ is the slope of $ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) \cdot \frac{1}{([B]_0-[A]_0)}$ vs. $t$, whereas for $[A]_0 = [B]_0$, $k$ is the slope of $\frac{1}{[A]} - \frac{1}{[A]_0}$ vs. $t$. A typical graph can be seen in Fig. S9.

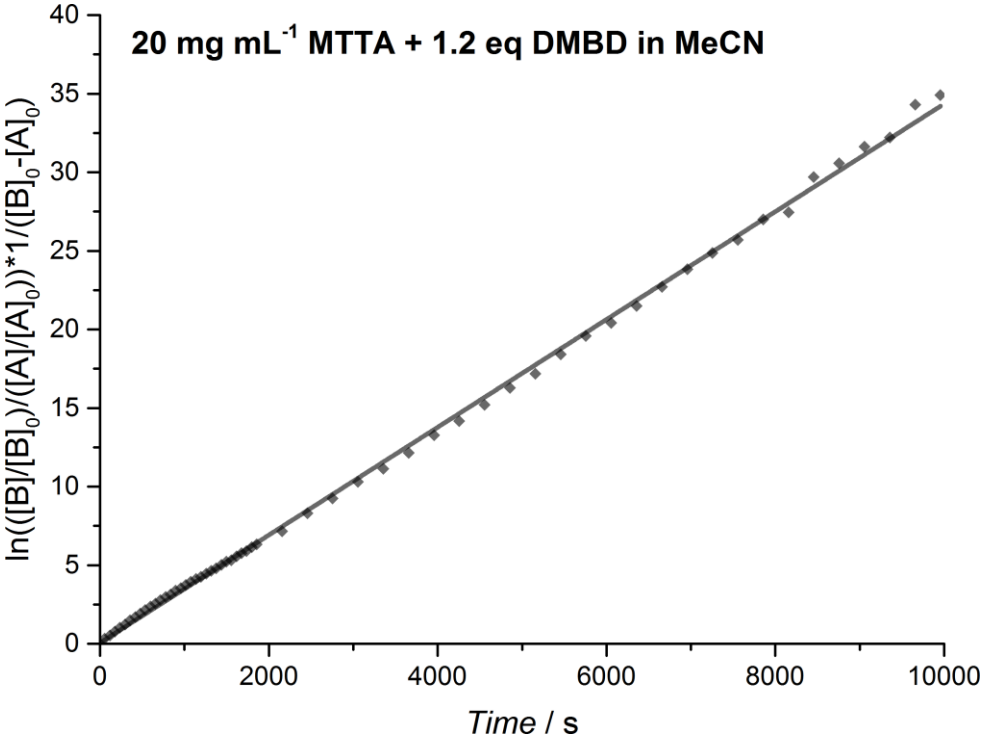



**Fig. S9.** Linear fit to determine k as the slope of $\boldsymbol{ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) \cdot \frac{1}{([B]_0-[A]_0)}}$ **vs.** $\boldsymbol{t}$ for the Diels–Alder reaction of 1.2 eq. DMBD with MTTA (20 mg mL$^{-1}$ in MeCN).

The activation energies ($E_a$) were determined via the subtraction of the two logarithmic forms of the Arrhenius equations for the rate coefficients as determined for 25 °C (298.15 K) and 50 °C (323.15 K) with $R$ being the universal gas constant:[9] $E_a = R \cdot \ln\left(\frac{k_1}{k_2}\right) \cdot \frac{T_1 \cdot T_2}{T_1 - T_2}$.

## 3. TD SEC Investigations

40 mg of the MTTA-P$^t$BuA DA polymer were dissolved in 125 µL DMAc (+ 3 g/L LiCl, c(MTTA) = 13.5 mg mL$^{-1}$). High concentrations are necessary in order to observe repolymerization reactions within reasonable time frames. It is, however, not possible to directly measure at such concentrations in the SEC instrument. Hence, a small volume (< 10 µL) of the concentrated solution was diluted in 1 mL DMAc (+ 3 g/L LiCl) and then measured. To achieve readily comparable chromatograms, all measurements were performed at 70 °C. At this temperature, DMAc has a sufficiently low viscosity and the temperature is low enough to avoid significant rDA reaction during the analysis. As no kinetics were measured via TD SEC, relatively long repolymerization times were chosen to assure high conversions even at lower concentrations in comparison to the UV/Vis experiments. In order to maximize the stability of the MTTA linker at high temperatures, the concentrated solution was kept under nitrogen atmosphere. The entire analysis scheme is summarized in the following table:

| | **Concentrated Solution** | **Sample Name** |
|---|---|---|
| 1. | At ambient temperature | *DA adduct MTTA + $Cp_2P^tBuA$* |
| 2. | 30 min at 100 °C | *1. rDA (100 °C)* |
| 3. | 1 d at ambient temperature | *1.DA* |
| 4. | 30 min at 100 °C | *2. rDA (100 °C)* |
| 5. | 1 d at ambient temperature | *2.DA* |
| 6. | 30 min at 120 °C | *3. rDA (120 °C)* |
| 7. | 2 d at ambient temperature | *3.DA* |

Averaging a broad molar mass distribution (MMD) always comes along with the risk of not taking into account or underestimating small changes in particular areas of the chromatogram. In theory, the dispersity $Đ_M$ of any step-growth polymer increases with the monomer conversion from 1.0 to 2.0. Hence, the broadness of a distribution is due to the nature of the polymerization reaction. Both dispersity and degree of polymerization (and thus the number averaged molar mass ($M_n$)) are related to the conversion:

$$DP_n = \frac{1}{1 - X}$$ **Equation S2** (Carothers Equation)

$$Đ_M = 1 + DP_n$$ **Equation S3**

These correlations clearly state that with an increase in monomer conversion (DA reaction), both $M_n$ and $Đ_M$ have to increase and vice versa. Consequently, those values can be monitored to follow the progress of the thermoreversible (r)DA reaction. In Fig. S10, $M_n$, the monomer conversion $X$ (as obtained from Equation S2) and $Đ_M$ are displayed.

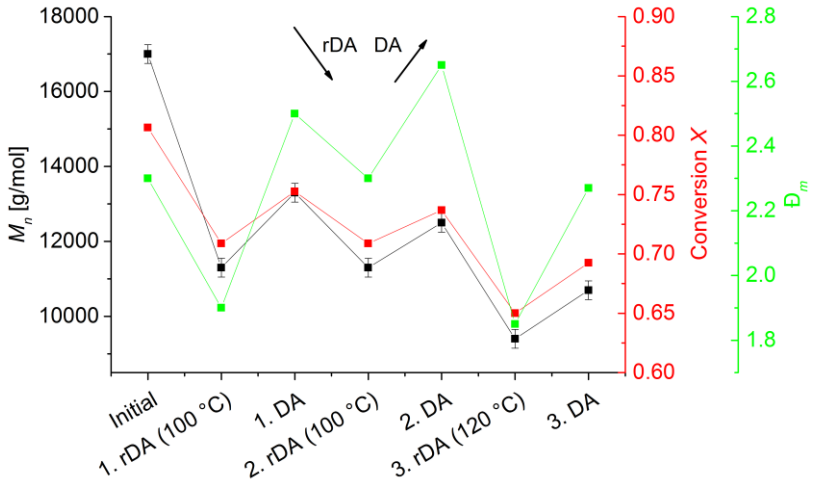



**Fig. S10.** Evolution of $M_n$, $X$ and $Đ_M$ during multiple rDA/DA cycles.

As consistent trends can be observed, the data set appears to be reliable. The accuracy (in terms of reproducibility) of the $M_n$ determination is high (±250 g/mol), but only molar masses relative to polystyrene standards were calculated. Accordingly, the data does not allow to calculate reliable quantitative conversions, but enables displaying qualitative trends, as all measurements were performed under identical conditions.

# 4. Computational Methodology & Data

### General Methodology

Gibbs free energies for the Diels–Alder reactions between a monofunctional MTTA species ($MTTA_{half}$) and several dienes were determined via standard *ab initio* calculations. The reactions between the difunctional full MTTA ($MTTA_{full}$) and two successive cyclopentadiene molecules and two successive sorbic alcohol molecules were also modelled. The reactants and products were considered in their optimized minimum energy conformations in the presence of a solvent field (acetonitrile), modeled using the SMD/M05-2X/6-31G(d) method.[10-13] As an example, in the Diels–Alder reaction of $MTTA_{half}$ with one sorbic alcohol molecule, there are four structural isomers (Fig. S11, top row).

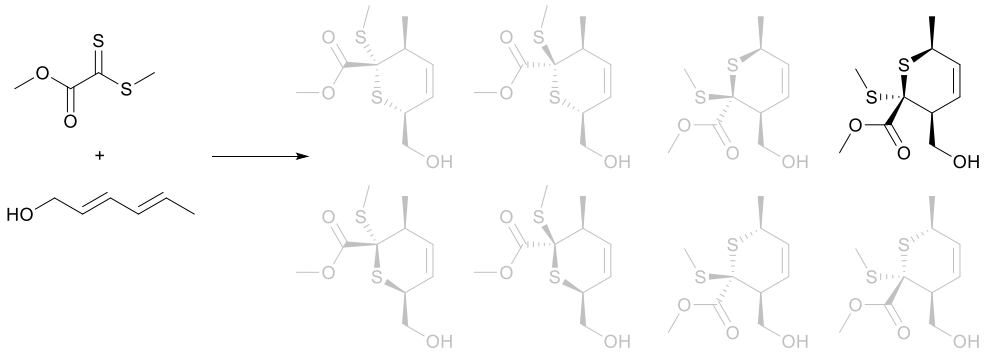



**Fig. S11.** Screened isomers and ring conformations for the reaction of $MTTA_{half}$ with sorbic alcohol, highlighted: lowest energy geometry.

For systems where the ring formed by the Diels–Alder reaction is flexible, multiple ring conformations can also be adopted (Fig. S11, bottom row). These can place different substituents in axial and equatorial positions around the ring, allowing different intramolecular interactions to form within the molecule and resulting in different stabilities for the conformers. Two possible "chair-like" ring conformations were investigated for each structural isomer (shown with the sulfur "up" or "down" in Fig. S11). Chemical knowledge and previous experience indicates that "boat-like" conformations are likely to be higher in energy. Additionally, bond rotation leads to different molecular conformations. In our study, we screened for conformers with the bonds (a) (Fig. S12) being rotated in increments of 120°, (b) (Fig. S12) being rotated in increments of 60° and (c) not being rotated due to experience from other studies showing that their configuration as described in Fig. S12 are consistently more stable.

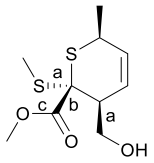



**Fig. S12.** Bond rotation conformer screening with (a) being rotated in increments of 120°, (b) of 60° and (c) not being rotated due to previous studies.

For systems with the conformational spaces containing a very large number of potential structures, an Energy-Directed Tree Search algorithm (EDTS) was employed to select which conformers to investigate in detail.[14]

Partition functions and hence entropies and thermal corrections to the energies were calculated using standard textbook formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator rigid rotor approximation ($T$ = 298 K). Justification for the use of solution phase properties for this purpose can be found in reference [15]. Vibrational frequencies were scaled

using recommended scaling factors for the calculation of zero point energies, thermal corrections and entropies.[16] The quasi-harmonic oscillator approximation was also applied to minimize the potentially large effects of errors in very low frequency vibrations.[15] Approximate M05-2X solution-phase Gibbs free energies ($G°_{soln}$) could hence be calculated and compared by the EDTS algorithm to identify the most stable conformation for each species.

In order to calculate equilibrium constants and $T_{20\%\ \text{debonding}}$, more accurate values of $G°_{soln}$ were determined at a range of temperatures for the most stable conformation of each species. These were obtained using accurate Gibbs free energies calculated in the gas phase, which were combined with free energies of solvation via standard thermodynamic cycles. Gas phase energies were calculated using the high-level composite G3(MP2) level of theory.[17] All geometries were re-optimized in the gas phase using M05-2X/6-31G* for this purpose, and gas phase vibrational frequencies were also calculated. Gas phase partition functions and hence entropies and thermal corrections to the energies were determined at the temperatures of interest, as described above, and combined with the G3(MP2) energies to give $G^o_{gas}(T)$. Temperature dependent free energies of solvation ($\Delta G_{solv}(T)$) in acetonitrile were determined based on the solution phase geometries using COSMO(RS)[18, 19]. It was also important to consider the geometric relaxation associated with solvation; this was approximated as the energy difference between the gas and solution phase geometries, calculated in the solution phase ($E_{relax}$).[20, 21] Solution phase free energies could hence be calculated according to Equation S4:

$$G^o_{soln}(T) = G^o_{gas}(T) + \Delta G_{solv}(T) - E_{relax} + \Delta G^o_{conc}(T) \qquad \textbf{Equation S4}$$

where $\Delta G^o_{conc}(T)$ is a phase change correction.[22] All calculations were carried out using the Gaussian 09,[23] Molpro 2012.1[24, 25] or ADF 2014.01[26] software packages.

For each reaction, the equilibrium constants were calculated as a function of temperature using the Gibbs free energies via the standard textbook equation. These equilibrium constants were then used to calculate the extent of debonding, and hence the temperature for 20 % debonding ($T_{20\%\ \text{debonding}}$) as follows. For the reactions modelled as 1-step processes (i.e. diene + $\text{MTTA}_{\text{half}}$), Equation S5 was used:[27]

$$\%debonding = \left(1 - \frac{2K[A]_0 + 1 - \sqrt{4K[A]_0 + 1}}{2K[A]_0}\right) \times 100\% \qquad \textbf{Equation S5}$$

where: $[A]_0$ is the starting concentration of the Diels–Alder product (diene-$\text{MTTA}_{\text{half}}$). For the small molecule NMR experiments, the appropriate value of $[A]_0$ is 0.05 M (i.e., twice the concentration of diene-MTTA-diene product), and hence $T_{20\%\ \text{debonding}}$ occurs when $\log(K) = 2.6$. For the reactions modelled as (more experimentally realistic) 2-step processes, it is necessary to solve Equations S6 and S7 simultaneously for pairs of $K_1$ and $K_2$ (i.e. each system at each temperature) to yield the values of $x$ and [Cp].[28]

$$\frac{1}{K_1} = \frac{(2x - [\text{Cp}])[\text{Cp}]}{[A']_0 - x} \qquad \textbf{Equation S6}$$

$$\frac{1}{K_2} = \frac{([\text{Cp}] - x)[\text{Cp}]}{2x - [\text{Cp}]} \qquad \textbf{Equation S7}$$

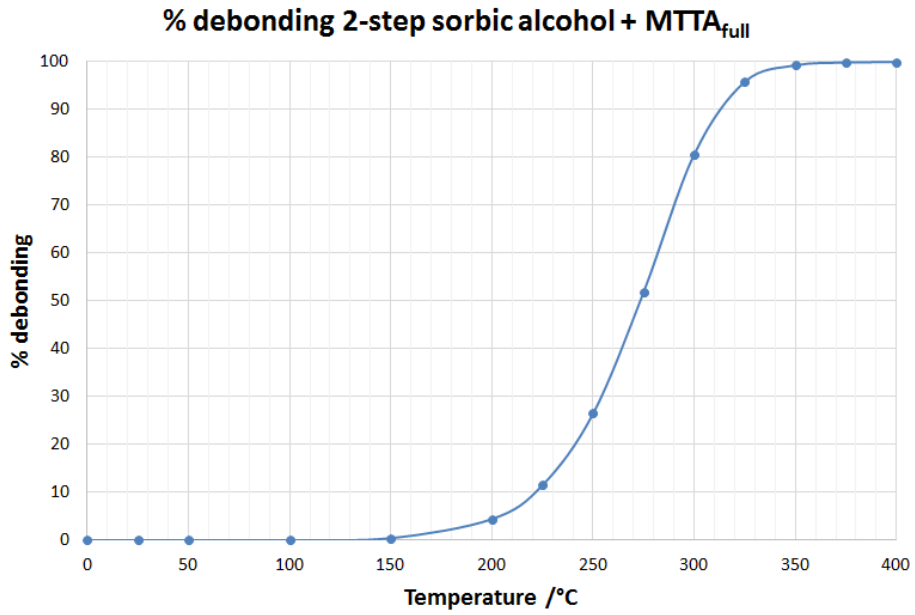
In these equations, $K_1$ is the equilibrium constant for the first reaction of the diene with MTTA, and $K_2$ is the equilibrium constant for the second reaction. Both are defined in the bonding (Diels–Alder) direction, as is K in equation S3 above. The value of $[A']_0$ is the starting concentration of the doubly reacted MTTA (i.e. the diene-MTTA-diene product) and has the value 0.025 M. [Cp]

is the concentration of the diene (either cyclopentadiene or sorbic alcohol depending on the system) and $x$ is defined such that the concentration of the doubly reacted MTTA at equilibrium [A'] = $[A']_0 - x$. The extent of debonding is given by:

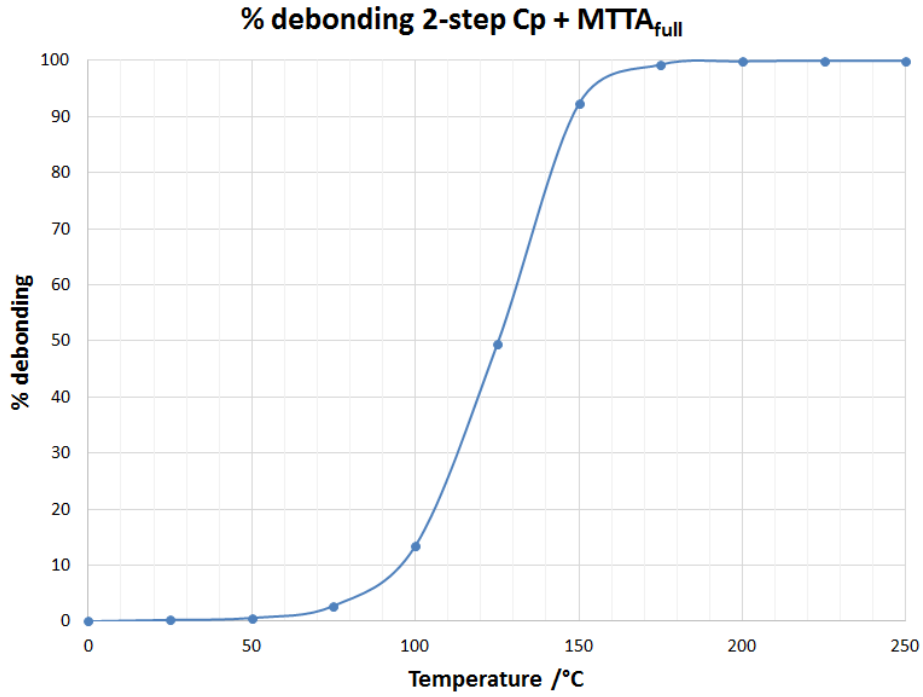
$$\%debonding = \frac{[\mathrm{Cp}]}{2[A']_0} \times 100\% \qquad \textbf{Equation S8}$$

For each system, %debonding was calculated as a function of temperature to identify $T_{20\ \%\ \mathrm{debonding}}$.

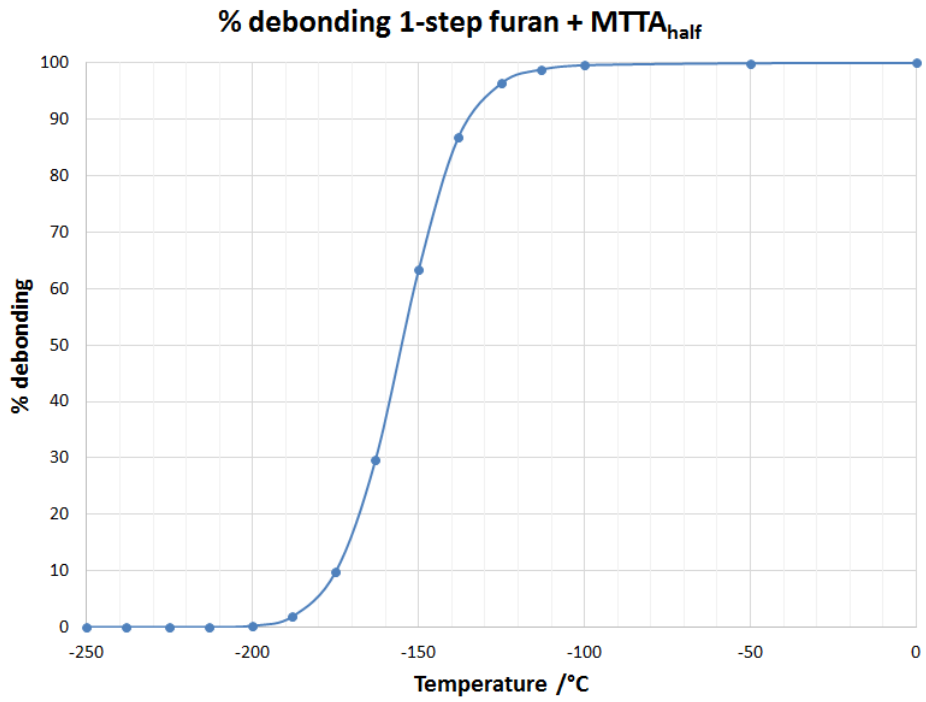
## % Debonding Curves



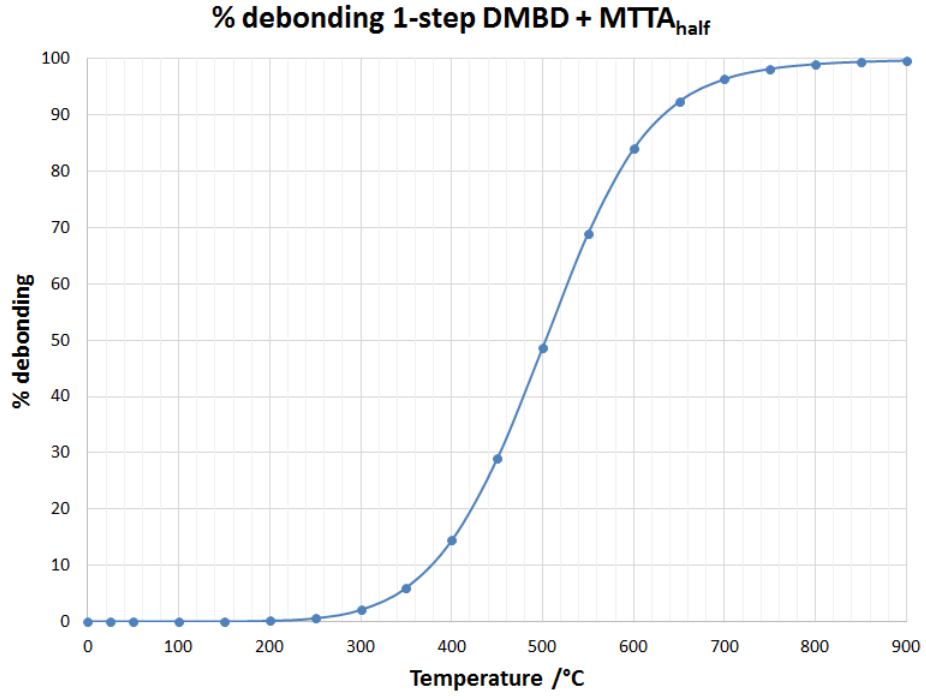

$T_{20\%\ debonding}$ = 240°C



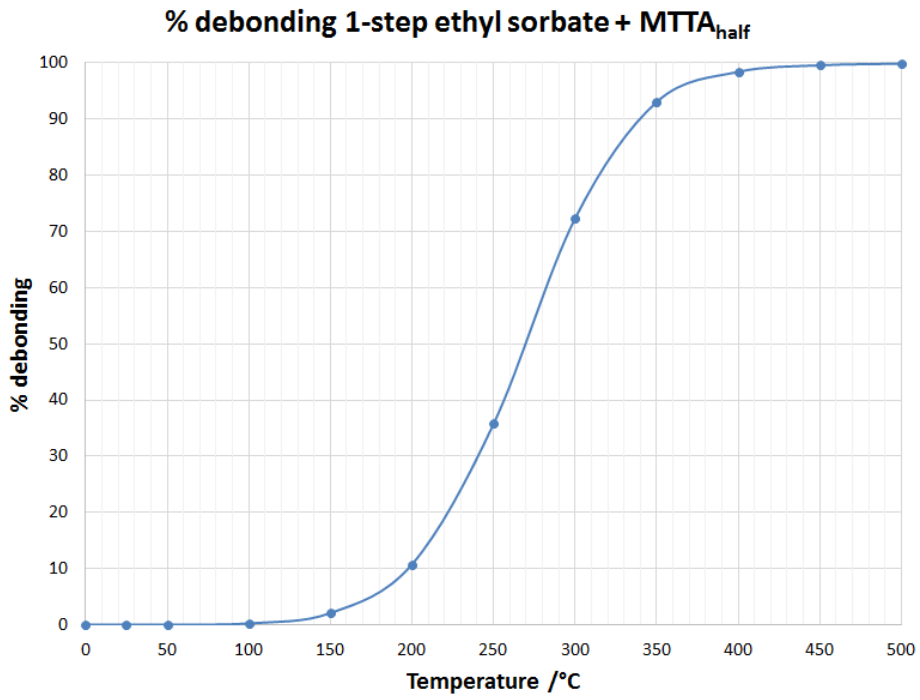

$T_{20\%\ debonding}$ = 105 °C




$T_{20\%\ debonding}$ = **-169 °C**




$T_{20\%\ debonding}$ = **427 °C**

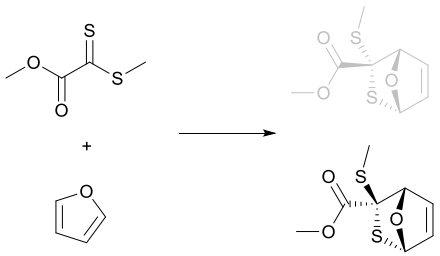



$T_{20\%\ \text{debonding}}$ = 225 °C

**Detailed Computational Data**

**Furan**

Furan + $MTTA_{half}$ ($T_{logK=2.6}$ = **-169 °C**)



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T (°C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| -250 | 31.1 | -13.8 | -25.8 | -164.8 | 7.1 |
| -225 | 12.8 | -11.8 | -26.5 | -185.4 | 5.1 |
| -200 | 7.2 | -10.1 | -27.0 | -193.8 | 3.5 |
| -150 | 1.3 | -3.0 | -27.6 | -200.3 | 1.1 |
| -100 | -1.1 | 3.7 | -27.9 | -202.1 | -0.8 |
| -50 | -2.5 | 10.8 | -27.9 | -202.3 | -2.3 |
| 0 | -3.5 | 18.1 | -27.8 | -201.7 | -3.5 |
| 25 | -3.8 | 21.8 | -27.7 | -201.3 | -3.9 |
| 50 | -4.1 | 25.5 | -27.5 | -200.8 | -4.4 |
| 100 | -4.6 | 33.0 | -27.1 | -199.8 | -5.1 |
| 150 | -5.0 | 40.5 | -26.7 | -198.6 | -5.7 |
| 200 | -5.3 | 48.0 | -26.1 | -197.4 | -6.2 |
| 250 | -5.5 | 55.5 | -25.6 | -196.2 | -6.6 |

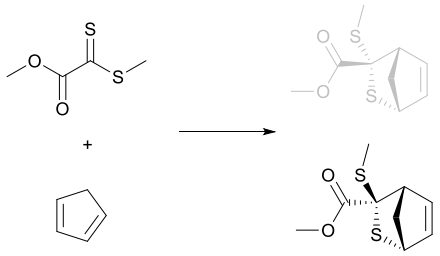
Components of Solution Free Energy Calculations– values in $E_h$ unless otherwise specified

| Species | Entropy (298K) / J mol$^{-1}$ K$^{-1}$ | $H^{298}$-$H^0$ | *ZPVE* | *HLC* | *E*[M05-2X/ 6-31G* SMD, gas geom] | *E*[M05-2X/ 6-31G* SMD, sol geom] | *E*[MP2/ 6-31G*] | *E*[MP2/ G3MP2Large] | *E*[CCSD(T)/ 6-31G*] |
|---|---|---|---|---|---|---|---|---|---|
| Furan | 273.3 | 0.004733 | 0.068875 | -0.122369 | -229.998527 | -229.998551 | -229.309880 | -229.561891 | -229.363438 |
| MTTA half | 402.6 | 0.010476 | 0.097745 | -0.216499 | -1102.771496 | -1102.771707 | -1100.815553 | -1101.328463 | -1100.911710 |
| Furan – MTTA half | 474.6 | 0.014218 | 0.170380 | -0.338868 | -1332.783794 | -1332.784513 | -1330.137845 | -1330.903460 | -1330.287758 |

| Species | $E^0$ [G3MP2,CC] | $H^{298}$ [G3MP2,CC] | $G_{gas}$ (298K) [G3MP2,CC] | $\Delta G_{solv}$ (298K) [COSMO(RS)] | $E_{relax}$ [M06-2X/ 6-31G*, SMD] | $G°_{sol}$ (298K) [G3MP2,CC] |
|---|---|---|---|---|---|---|
| Furan | -229.668943 | -229.664210 | -229.695248 | -0.006368 | -0.000024 | -229.698573 |
| MTTA half | -1101.543374 | -1101.532898 | -1101.578621 | -0.012714 | -0.000211 | -1101.588105 |
| Furan – MTTA half | -1331.221861 | -1331.207643 | -1331.261541 | -0.020586 | -0.000718 | -1331.278390 |

**Cyclopentadiene**

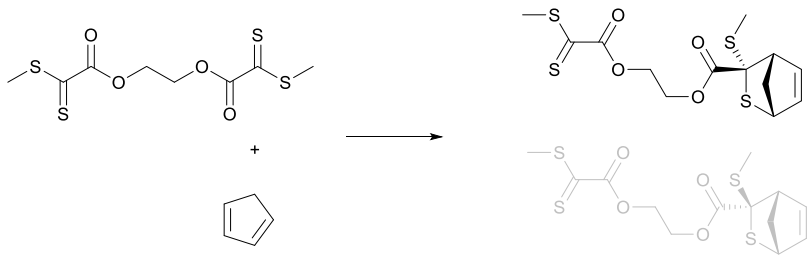
Cp + $MTTA_{half}$ (***T*****$_{logK=2.6}$ = 166 °C)**



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T ($^{o}$C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 9.1 | -47.6 | -98.5 | -206.6 | 1.7 |
| 25 | 7.7 | -43.8 | -98.5 | -206.6 | 1.2 |
| 50 | 6.5 | -40.0 | -98.5 | -206.4 | 0.7 |
| 100 | 4.5 | -32.4 | -98.3 | -205.9 | -0.2 |
| 150 | 3.0 | -24.7 | -98.0 | -205.2 | -0.9 |
| 200 | 1.9 | -17.0 | -97.6 | -204.4 | -1.5 |
| 250 | 0.9 | -9.3 | -97.2 | -203.5 | -2.1 |

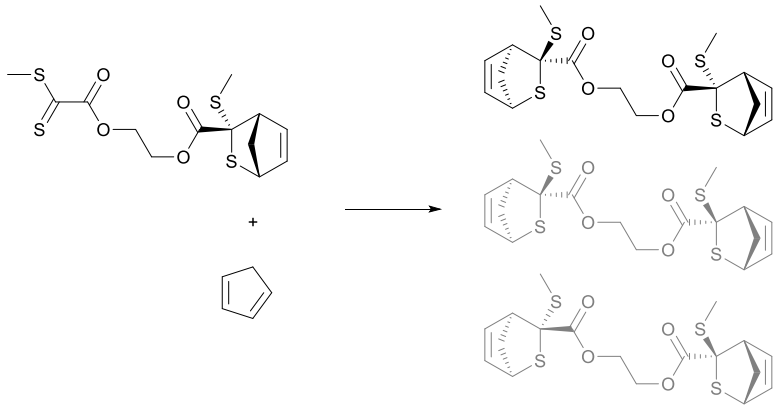
Cp + $MTTA_{full}$ ($T_{logK=2.6}$ = 113 °C)



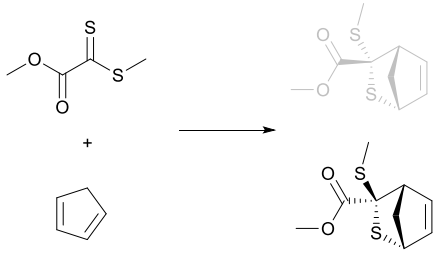
Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T ($^{o}$C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 9.0 | -46.9 | -108.7 | -214.5 | 10.0 |
| 25 | 7.2 | -41.3 | -106.9 | -214.6 | 9.3 |
| 50 | 5.7 | -35.4 | -104.9 | -214.6 | 8.7 |
| 100 | 3.2 | -22.9 | -100.1 | -214.3 | 7.6 |
| 150 | 1.2 | -9.5 | -94.4 | -213.7 | 6.7 |
| 200 | -0.5 | 4.7 | -88.0 | -212.9 | 6.0 |
| 250 | -1.9 | 19.5 | -80.8 | -212.1 | 5.3 |

Cp + Cp-MTTA$_{full}$ (***T*$_{logK=2.6}$ = 87 °C)**



ONIOM Core (Cp-MTTA$_{half}$):



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T (ºC ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 7.4 | -38.5 | -93.5 | -209.1 | 4.8 |
| 25 | 5.8 | -32.9 | -91.6 | -209.1 | 4.1 |
| 50 | 4.4 | -27.1 | -89.5 | -209.0 | 3.6 |
| 100 | 2.1 | -14.8 | -84.7 | -208.5 | 2.6 |
| 150 | 0.2 | -1.6 | -78.9 | -207.9 | 1.7 |
| 200 | -1.4 | 12.3 | -72.4 | -207.1 | 1.0 |
| 250 | -2.7 | 26.8 | -65.2 | -206.2 | 0.4 |

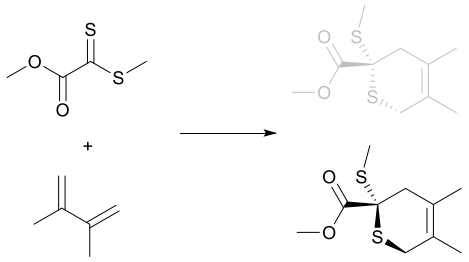
Components of Solution Free Energy Calculations– values in $E_h$ unless otherwise specified

| Species | Entropy (298K) / J mol$^{-1}$ K$^{-1}$ | $H^{298}$-$H^0$ | *ZPVE* | *HLC* | *E*[M05-2X/ 6-31G* SMD, gas geom] | *E*[M05-2X/ 6-31G* SMD, sol geom] | *E*[MP2/ 6-31G*] | *E*[MP2/ G3MP2Large] | *E*[CCSD(T)/ 6-31G*] |
|---|---|---|---|---|---|---|---|---|---|
| Cp | 280.9 | 0.005225 | 0.090763 | -0.122369 | -194.080257 | -194.080278 | -193.425083 | -193.647864 | -193.494232 |
| MTTA half | 402.6 | 0.010476 | 0.097745 | -0.216499 | -1102.771496 | -1102.771707 | -1100.815553 | -1101.328463 | -1100.911710 |
| MTTA | 576.2 | 0.019177 | 0.177408 | -0.423585 | -2204.360345 | -2204.360849 | -2200.474347 | -2201.480435 | -2200.659468 |
| Cp – MTTA - half | 477.0 | 0.014411 | 0.194153 | -0.338868 | -1296.894881 | -1296.895043 | -1294.288452 | -1295.024835 | -1294.447126 |
| Cp – MTTA (as product) | 636.9 | 0.022724 | 0.274385 | -0.545954 | -2398.487115 | -2398.487761 | -2393.954324 | -2395.184495 | |
| Cp – MTTA (as reactant) | 636.9 | 0.022724 | 0.274385 | -0.545954 | -2398.487115 | -2398.487761 | -2393.954324 | -2395.184495 | |
| Cp – MTTA-CP | 703.2 | 0.026632 | 0.370795 | -0.668323 | -2592.609090 | -2592.609820 | -2587.428620 | -2588.882540 | |

| Species | $E^0$ [G3MP2,CC] | $H^{298}$ [G3MP2,CC] | $G_{gas}$ (298K) [G3MP2,CC] | $\Delta G_{solv}$ (298K) [COSMO(RS)] | $E_{relax}$ [M06-2X/ 6-31G*, SMD] | $G°_{sol}$ (298K) [G3MP2,CC] |
|---|---|---|---|---|---|---|
| Cp | -193.748619 | -193.743394 | -193.775294 | -0.005554 | -0.000021 | -193.777808 |
| MTTA half | -1101.543374 | -1101.532898 | -1101.578621 | -0.012714 | -0.000211 | -1101.588105 |
| MTTA | -2201.310414 | -2201.291237 | -2201.356670 | -0.026363 | -0.000504 | -2201.379510 |
| Cp – MTTA half | -1295.328224 | -1295.313813 | -1295.367977 | -0.017812 | -0.000162 | -1295.382607 |
| Cp – MTTA (as product) | -2395.098225 | -2395.075501 | -2395.147830 | -0.028377 | -0.000646 | -2395.172542 |
| Cp – MTTA (as reactant) | -2394.812236 | -2394.789511 | -2394.861841 | -0.028377 | -0.000646 | -2394.886553 |
| Cp – MTTA-CP | -2588.594573 | -2588.567941 | -2588.647796 | -0.032355 | -0.000730 | -2588.676402 |

**2,3-Dimethly-1,3-butadiene**

DMBD + $MTTA_{half}$ (***T*****$_{logK=2.6}$ = 427 °C)**



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T (°C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 17.5 | -91.3 | -133.2 | -188.4 | -3.4 |
| 25 | 15.4 | -88.1 | -133.1 | -188.2 | -4.0 |
| 50 | 13.7 | -84.8 | -133.1 | -188.0 | -4.5 |
| 100 | 10.9 | -78.2 | -132.9 | -187.6 | -5.5 |
| 150 | 8.8 | -71.4 | -132.7 | -187.0 | -6.2 |
| 200 | 7.1 | -64.7 | -132.4 | -186.4 | -6.9 |
| 250 | 5.8 | -57.9 | -132.1 | -185.7 | -7.4 |
| 300 | 4.7 | -51.1 | -131.7 | -184.9 | -7.9 |
| 350 | 3.7 | -44.3 | -131.2 | -184.1 | -8.3 |

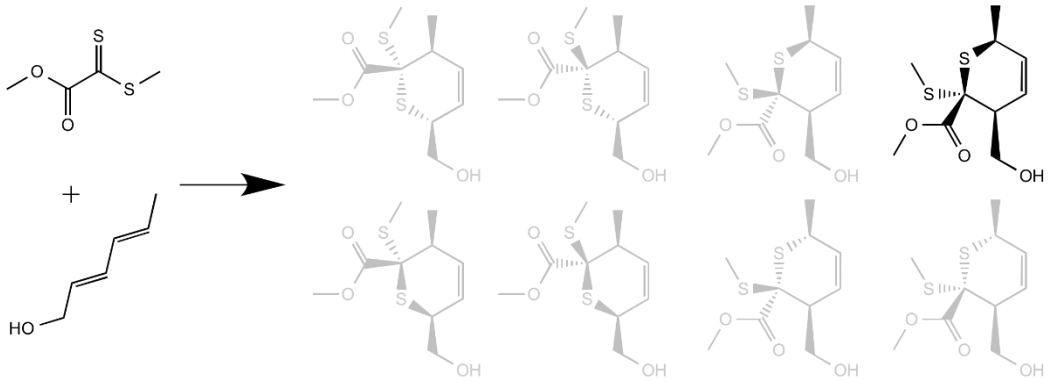
Components of Solution Free Energy Calculations– values in $E_h$ unless otherwise specified

| Species | Entropy (298K) / J mol$^{-1}$ K$^{-1}$ | $H^{298}$-$H^0$ | *ZPVE* | *HLC* | *E*[M05-2X/ 6-31G* SMD, gas geom] | *E*[M05-2X/ 6-31G* SMD, sol geom] | *E*[MP2/ 6-31G*] | *E*[MP2/ G3MP2Large] | *E*[CCSD(T)/ 6-31G*] |
|---|---|---|---|---|---|---|---|---|---|
| DMBD | 332.3 | 0.008107 | 0.139527 | -0.160021 | -234.586554 | -234.586578 | -233.762827 | -234.059894 | -233.857046 |
| MTTA half | 402.6 | 0.010476 | 0.097745 | -0.216499 | -1102.771496 | -1102.771707 | -1100.815553 | -1101.328463 | -1100.911710 |
| DMBD – MTTA half | 546.7 | 0.018040 | 0.241647 | -0.376520 | -1337.419616 | -1337.420174 | -1334.639905 | -1335.449314 | -1334.823870 |

| Species | $E^0$ [G3MP2,CC] | $H^{298}$ [G3MP2,CC] | $G_{gas}$ (298K) [G3MP2,CC] | $\Delta G_{solv}$ (298K) [COSMO(RS)] | $E_{relax}$ [M06-2X/ 6-31G*, SMD] | $G°_{sol}$ (298K) [G3MP2,CC] |
|---|---|---|---|---|---|---|
| DMBD | -234.174607 | -234.166501 | -234.204230 | -0.004580 | -0.000023 | -234.205768 |
| MTTA half | -1101.543374 | -1101.532898 | -1101.578621 | -0.012714 | -0.000211 | -1101.588105 |
| DMBD – MTTA half | -1335.768151 | -1335.750112 | -1335.812190 | -0.018814 | -0.000559 | -1335.827427 |

**Sorbic Alcohol**

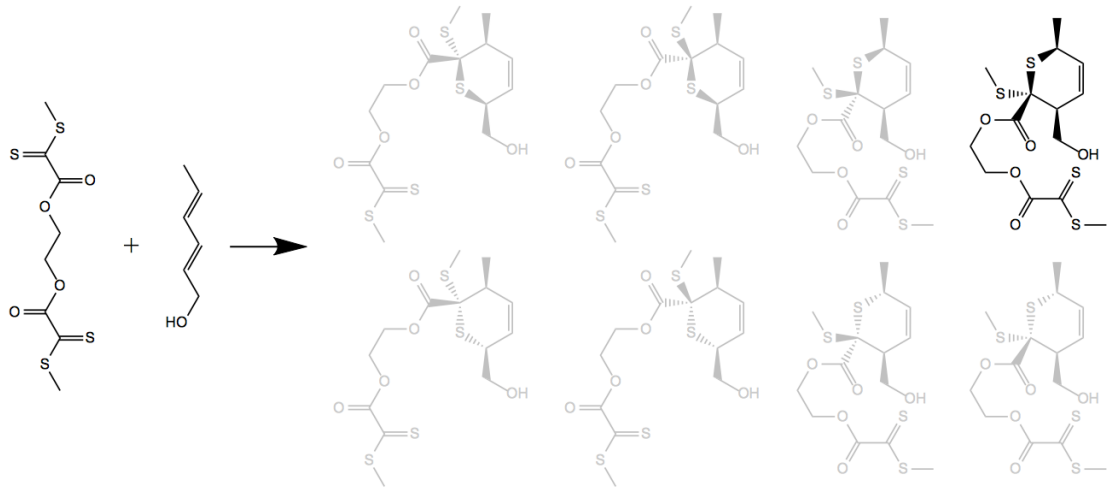
Sorbic Alcohol + $MTTA_{half}$ ($T_{logK=2.6}$ = 240 °C)



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T (°C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 12.0 | -62.9 | -134.0 | -234.9 | 10.8 |
| 25 | 10.4 | -59.6 | -134.1 | -235.2 | 9.1 |
| 50 | 9.1 | -56.0 | -134.1 | -235.3 | 7.6 |
| 100 | 6.8 | -48.5 | -134.1 | -235.1 | 5.2 |
| 150 | 5.0 | -40.4 | -133.9 | -234.6 | 3.4 |
| 200 | 3.5 | -31.9 | -133.6 | -233.9 | 2.1 |
| 250 | 2.3 | -23.3 | -133.2 | -233.1 | 1.0 |
| 300 | 1.3 | -14.5 | -132.7 | -232.3 | 0.1 |
| 350 | 0.5 | -5.7 | -132.2 | -231.4 | -0.6 |
| 400 | -0.2 | 3.1 | -131.7 | -230.6 | -1.2 |

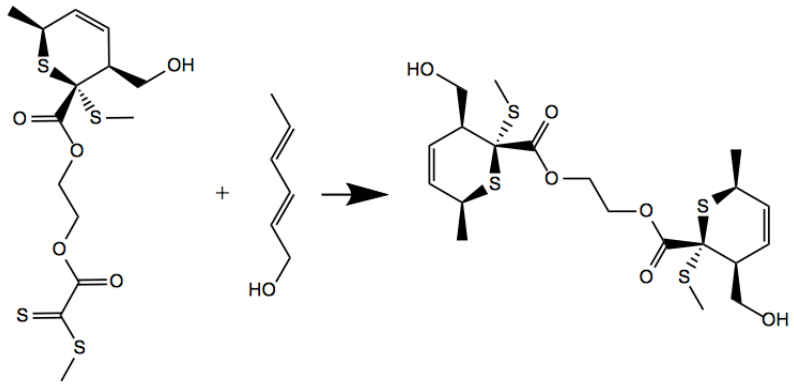
Sorbic Alcohol + $MTTA_{full}$ ($T_{logK=2.6}$ = **340 °C**)



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T ($^{o}$C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 16.8 | -87.6 | -162.5 | -243.0 | 15.3 |
| 25 | 14.8 | -84.2 | -162.6 | -243.3 | 13.5 |
| 50 | 13.0 | -80.6 | -162.6 | -243.3 | 11.9 |
| 100 | 10.2 | -72.9 | -162.5 | -243.1 | 9.3 |
| 150 | 8.0 | -64.5 | -162.3 | -242.6 | 7.4 |
| 200 | 6.2 | -55.8 | -162.0 | -241.8 | 5.9 |
| 250 | 4.7 | -46.8 | -161.6 | -241.0 | 4.8 |
| 300 | 3.4 | -37.7 | -161.1 | -240.1 | 3.9 |
| 350 | 2.4 | -28.5 | -160.6 | -239.2 | 3.1 |
| 400 | 1.5 | -19.3 | -160.0 | -238.3 | 2.4 |

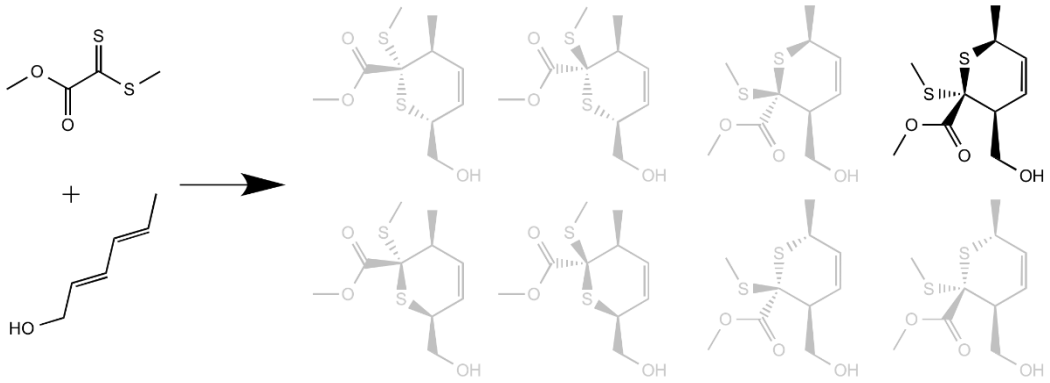
Sorbic Alcohol + Sorbic Alcohol-MTTA$_{full}$ ($T_{logK=2.6}$ = 114 °C)



Conformational/isomer searching not performed – isomer and conformation chosen based on the strong preference of SA-MTTA$_{half}$ and SA-MTTA$_{full}$ for the given structure.

The debonding temperature of the first sorbic alcohol from the SA-MTTA$_{full}$–SA adduct is much lower than for the cleavage of the second sorbic alcohol as the SA-MTTA$_{full}$ adduct is stabilized via strong hydrogen bonding interactions.

ONIOM Core (Sorbic Alcohol-MTTA$_{half}$):



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T ($^{o}$C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 7.2 | -37.5 | -116.1 | -242.8 | 8.2 |
| 25 | 5.9 | -33.9 | -116.2 | -243.0 | 6.6 |
| 50 | 4.9 | -30.0 | -116.2 | -243.1 | 5.3 |
| 100 | 3.1 | -21.9 | -116.1 | -242.9 | 3.0 |
| 150 | 1.6 | -13.3 | -115.9 | -242.3 | 1.4 |
| 200 | 0.5 | -4.4 | -115.6 | -241.6 | 0.1 |
| 250 | -0.5 | 4.7 | -115.2 | -240.8 | -0.9 |
| 300 | -1.3 | 13.9 | -114.7 | -239.9 | -1.7 |
| 350 | -1.9 | 23.2 | -114.2 | -239.0 | -2.4 |
| 400 | -2.5 | 32.4 | -113.6 | -238.2 | -3.0 |

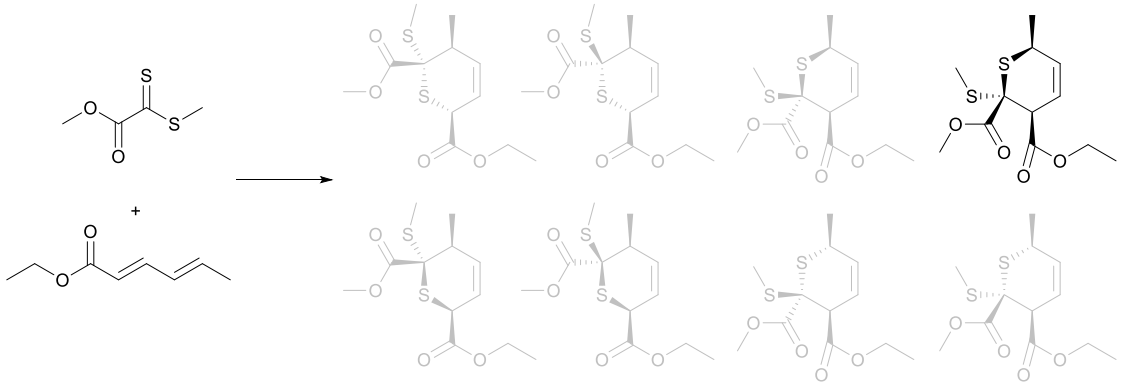
Components of Solution Free Energy Calculations– values in $E_h$ unless otherwise specified

| Species | Entropy (298K) / J mol$^{-1}$ K$^{-1}$ | $H^{298}$-$H^0$ | *ZPVE* | *HLC* | *E*[M05-2X/ 6-31G* SMD, gas geom] | *E*[M05-2X/ 6-31G* SMD, sol geom] | *E*[MP2/ 6-31G*] | *E*[MP2/ G3MP2Large] | *E*[CCSD(T)/ 6-31G*] |
|---|---|---|---|---|---|---|---|---|---|
| SA | 376.8 | 0.009635 | 0.143924 | -0.188260 | -309.792225 | -309.792439 | -308.786687 | -309.169559 | -308.886143 |
| MTTA half | 403.9 | 0.010523 | 0.097640 | -0.216499 | -1102.770887 | -1102.771697 | -1100.815552 | -1101.328457 | -1100.911714 |
| MTTA | 576.2 | 0.019177 | 0.177408 | -0.423585 | -2204.360345 | -2204.360849 | -2200.474347 | -2201.480435 | -2200.659468 |
| SA – MTTA half | 545.5 | 0.018238 | 0.247853 | -0.404759 | -1412.616091 | -1412.618356 | -1409.660602 | -1410.560199 | -1409.849476 |
| SA - MTTA | 709.7 | 0.026826 | 0.327454 | -0.611845 | -2514.216669 | -2514.217497 | -2509.331850 | -2510.724004 | -2509.608480 |
| SA - MTTA - SA | 843.4 | 0.034651 | 0.477532 | -0.800105 | -2824.049170 | -2824.054470 | -2818.167199 | -2819.948908 | |

| Species | $E^0$ [G3MP2,CC] | $H^{298}$ [G3MP2,CC] | $G_{gas}$ (298K) [G3MP2,CC] | $\Delta G_{solv}$ (298K) [COSMO(RS)] | $E_{relax}$ [M06-2X/ 6-31G*, SMD] | $G°_{sol}$ (298K) [G3MP2,CC] |
|---|---|---|---|---|---|---|
| SA | -309.313351 | -309.303716 | -309.346501 | -0.010945 | -0.000215 | -309.354212 |
| MTTA half | -1101.543478 | -1101.532955 | -1101.578818 | -0.012773 | -0.000810 | -1101.587762 |
| MTTA | -2201.911733 | -2201.892556 | -2201.957988 | -0.026363 | -0.000504 | -2201.980829 |
| SA - MTTA half | -1410.905979 | -1410.887741 | -1410.949685 | -0.020259 | -0.002265 | -1410.964660 |
| SA - MTTA | -2511.285025 | -2511.258199 | -2511.338789 | -0.032184 | -0.000828 | -2511.367127 |
| SA - MTTA - SA | -2820.065009 | -2820.030359 | -2820.126136 | -0.040603 | -0.005300 | -2820.158420 |

**Ethylsorbate**

Ethyl sorbate + $MTTA_{half}$ **($T_{logK=2.6}$ = 225 °C)**



Key thermodynamic parameters and equilibrium constants in acetonitrile as a function of temperature, using M05-2X/6-31G* geometries and frequencies.

| T ($^{o}$C ) | log K | ΔG*soln kJ mol$^{-1}$ | ΔH(g) kJ mol$^{-1}$ | ΔS(g) J mol$^{-1}$ K$^{-1}$ | ΔΔG*solv kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 12.2 | -63.8 | -122.5 | -231.1 | 2.6 |
| 25 | 10.4 | -59.6 | -122.5 | -231.1 | 1.9 |
| 50 | 8.9 | -55.2 | -122.4 | -231.0 | 1.3 |
| 100 | 6.5 | -46.5 | -122.2 | -230.5 | 0.3 |
| 150 | 4.7 | -37.7 | -121.9 | -229.7 | -0.5 |
| 200 | 3.2 | -28.9 | -121.5 | -228.8 | -1.2 |
| 250 | 2.0 | -20.1 | -121.1 | -227.8 | -1.8 |

Components of Solution Free Energy Calculations– values in $E_h$ unless otherwise specified

| Species | Entropy (298K) / J mol$^{-1}$ K$^{-1}$ | $H^{298}$-$H^0$ | *ZPVE* | *HLC* | *E*[M05-2X/ 6-31G* SMD, gas geom] | *E*[M05-2X/ 6-31G* SMD, sol geom] | *E*[MP2/ 6-31G*] | *E*[MP2/ G3MP2Large] | *E*[CCSD(T)/ 6-31G*] |
|---|---|---|---|---|---|---|---|---|---|
| Ethylsorbate | 442.2 | 0.012656 | 0.182196 | -0.263564 | -462.450496 | -462.450663 | -461.017407 | -461.555792 | -461.146024 |
| MTTA half | 402.6 | 0.010476 | 0.097745 | -0.216499 | -1102.771496 | -1102.771707 | -1100.815553 | -1101.328463 | -1100.911710 |
| Ethsorb – MTTA half | 613.7 | 0.021663 | 0.285046 | -0.480063 | -1565.271285 | -1565.271840 | -1561.886457 | -1562.941204 | -1562.104558 |

| Species | $E^0$ [G3MP2,CC] | $H^{298}$ [G3MP2,CC] | $G_{gas}$ (298K) [G3MP2,CC] | $\Delta G_{solv}$ (298K) [COSMO(RS)] | $E_{relax}$ [M06-2X/ 6-31G*, SMD] | $G°_{sol}$ (298K) [G3MP2,CC] |
|---|---|---|---|---|---|---|
| Ethylsorbate | -461.765776 | -461.753121 | -461.803335 | -0.011957 | -0.000167 | -461.812273 |
| MTTA half | -1101.543374 | -1101.532898 | -1101.578621 | -0.012714 | -0.000211 | -1101.588316 |
| Ethsorb – MTTA half | -1563.354322 | -1563.332659 | -1563.402348 | -0.023942 | -0.000555 | -1563.423272 |

## Molecular Gas Phase Geometries

Sorbalc – M05-2X

```
 1\1\GINC-R41\FOpt\RM052X\Gen\C6H10O1\ROOT\02-Dec-2015\0\\#M052X/gen 6D
  SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=671088640\\a1 b
 3 c3\\0,1\C,-6.6931052609,1.9839842681,0.7412792194\C,-5.4724118052,1.
 1173100314,0.6941830631\C,-5.2633524218,0.0559867077,1.4795727479\C,-4
 .0637276052,-0.7704438649,1.4182229562\C,-3.8460171286,-1.8278927979,2
 .2058060482\C,-2.6144637785,-2.6866176312,2.1327851928\O,-1.8199809301
 ,-2.434688758,0.9897518415\H,-2.3788038151,-2.5915273216,0.2180884579\
 H,-7.3934036518,1.6339800874,1.5006227551\H,-7.2074711513,1.9906585322
 ,-0.2235464739\H,-6.4293901963,3.0203299334,0.969015254\H,-4.709655875
 4,1.3839611289,-0.0333027241\H,-6.0165182788,-0.2223671653,2.212992260
 3\H,-3.3060072777,-0.4914399222,0.691917429\H,-4.5854636729,-2.1081621
 452,2.9515565793\H,-1.9690607967,-2.4932259996,2.9927841831\H,-2.90320
 23536,-3.7443380832,2.1875272103\\Version=ES64L-G09RevD.01\State=1-A\H
 F=-309.7801827\RMSD=7.394e-09\RMSF=1.217e-05\Dipole=-0.687576,-0.07909
 36,-0.0651558\Quadrupole=-4.422078,2.3245857,2.0974923,0.0740582,-0.28
 96286,-1.6388745\PG=C01 [X(C6H10O1)]\\@
```

MTTA_half – M05-2X

```
 1\1\GINC-R42\FOpt\RM052X\Gen\C4H6O2S2\ROOT\27-Jan-2016\0\\# M052X/Gen
 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=1073741824\\u
 u.M052X\\0,1\C,0.339587294,1.0985392283,-0.6999772702\C,0.3263870022,0
 .0262148892,0.3813103638\O,1.5509970003,1.569307427,-0.9533825394\O,-0
 .6695908259,1.4640098525,-1.2539309261\S,1.6626642649,-0.4923174655,1.
 1513068592\S,-1.3063317174,-0.5091873141,0.6219856501\C,-1.0704031415,
 -1.7448820271,1.9145034126\H,-2.0594699825,-2.1431273098,2.1344804692\
 H,-0.6400686187,-1.2871989987,2.8036116388\H,-0.4115970368,-2.53831976
 31,1.5657799351\C,1.591761065,2.5828385279,-1.9696574444\H,2.636885474
 1,2.8594446704,-2.0573135108\H,1.2122457466,2.1830080008,-2.9077832845
 \H,0.9849504756,3.4344582822,-1.6688263537\\Version=ES64L-G09RevD.01\S
 tate=1-A\HF=-1102.7601919\RMSD=6.392e-09\RMSF=1.245e-05\Dipole=0.02285
 36,-0.0426739,0.0469823\Quadrupole=-4.3155964,3.1483046,1.1672918,5.41
 72288,-5.9043315,-4.1758342\PG=C01 [X(C4H6O2S2)]\\@
```

SA-MTTA_half – M05-2X

```
 1\1\GINC-R37\FOpt\RM052X\Gen\C10H16O3S2\ROOT\27-Jan-2016\0\\# M052X/Ge
 n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=1610612736\
 \21uu.M052X\\0,1\C,-4.8824599914,-4.272014071,-1.6210468883\C,-3.97782
 91201,-3.5374690641,-0.6298436094\C,-2.8731751003,-4.4226170209,-0.136
 0926473\C,-1.604953657,-4.0704195423,0.055147032\C,-0.981274927,-2.729
 2318269,-0.2266188343\C,-0.07444103,-2.8303976291,-1.4887850134\O,1.23
 20450369,-2.3577170635,-1.2700125897\S,-3.370862716,-2.0383816666,-1.4
 748505823\C,-2.0295414869,-1.6022871882,-0.3137142557\S,-2.6075261371,
 -1.2983380531,1.4166337843\C,-3.8739773267,-0.018080761,1.1922882328\C
 ,-1.3731348157,-0.3071864566,-0.7693618388\O,-0.1933317261,-0.05887814
 01,-0.6494843118\O,-2.2460520741,0.5631432971,-1.2746669344\C,-1.68426
 15475,1.8261228723,-1.6699300429\H,-4.5745874267,-3.2058750919,0.22525
 17796\H,-3.1764956521,-5.4384528516,0.102231021\H,-0.9066035687,-4.820
 1924013,0.4120669453\H,-0.3062565804,-2.4869757729,0.6001148575\H,-4.3
```

056465797,-4.6140151556,-2.4810158179\H,-5.6879911177,-3.6252751473,-1
.97243085\H,-5.3292645539,-5.1408033748,-1.1337160012\H,-3.4356669294,
0.9636426267,1.0294466153\H,-4.4546948757,-0.0084856042,2.1136885742\H
,-4.5214688489,-0.2780822392,0.3559540749\H,1.1416451451,-1.4280593343
,-1.0151989007\H,-2.5172072733,2.4010522837,-2.0602982427\H,-0.9250528
011,1.670196161,-2.4328688168\H,-1.2366400222,2.3176518148,-0.80871162
31\H,0.0255963073,-3.8779005778,-1.7710121861\H,-0.5665056038,-2.32144
90213,-2.32793193\\Version=ES64L-G09RevD.01\State=1-A\HF=-1412.5995433
\RMSD=5.426e-09\RMSF=2.176e-06\Dipole=-1.4724735,0.6188776,-0.0286912\
Quadrupole=-8.0444976,11.1937868,-3.1492892,2.5541876,-0.6148958,-2.26
07403\PG=C01 [X(C10H16O3S2)]\\@

MTTA_full - M05-2X
1\1\GINC-R45\FOpt\RM052X\Gen\C8H10O4S4\ROOT\02-Dec-2015\0\\#M052X/gen
6D SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=2147483648\\a
1 b3 c3\\0,1\C,0.3735125428,1.0742883577,-0.7324481243\C,0.3661422848,
0.0914654189,0.42959116\O,1.5442333419,1.6757026456,-0.8984188154\O,-0
.5992812749,1.2699184347,-1.4200762543\S,1.6186963984,-0.0997341781,1.
4497366507\S,-1.1584792352,-0.7355801493,0.4577533425\C,-0.92399717,-1
.8280554353,1.8736235687\H,-1.8417096382,-2.4069065697,1.9623865012\H,
-0.7538791237,-1.2465778286,2.7780403995\H,-0.0742311779,-2.4878345953
,1.7066566636\C,1.595174417,2.599602829,-1.9968222431\C,3.0146820243,3
.0887826856,-2.0846880607\H,1.2911836023,2.0919541452,-2.9108728305\H,
0.910648958,3.426221252,-1.8046665973\O,3.8081789135,1.9759672296,-2.5
259148501\H,3.1013968649,3.9018662385,-2.8059179728\H,3.378729621,3.43
17049138,-1.1174860288\C,5.1133768073,2.2085316659,-2.5728706424\O,5.6
310155148,3.2613215914,-2.2880638217\C,5.9195016519,1.0004944329,-3.02
79962589\S,5.2428558997,-0.3879334457,-3.5384514157\S,7.6093332598,1.3
74394307,-2.9099442335\C,8.3384927891,-0.176250114,-3.4729725164\H,9.4
170706236,-0.0386277748,-3.4193664059\H,8.0284957528,-0.9969736355,-2.
8282993687\H,8.0341973722,-0.3896999662,-4.4961389841\\Version=ES64L-G
09RevD.01\State=1-A\HF=-2204.3366704\RMSD=3.413e-09\RMSF=1.079e-05\Dip
ole=0.1271522,-0.3487588,0.1125322\Quadrupole=1.9828462,-0.3144999,-1.
6683463,-3.1377759,-9.3173673,-4.6913647\PG=C02 [X(C8H10O4S4)]\\@

SA-MTTA_full - M05-2X
1\1\GINC-R41\FOpt\RM052X\Gen\C14H20O5S4\ROOT\02-Dec-2015\0\\# M052X/Ge
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=2684354560\
\21uuu.M052X\\0,1\C,-4.4484800857,-4.0818227537,-1.570029262\C,-3.7849
059052,-3.0795547202,-0.6227295093\C,-2.7062011524,-3.7364876185,0.188
827244\C,-1.5035485699,-3.2411347323,0.4739658877\C,-0.9497028542,-1.9
250899863,-0.0065252977\C,0.0495341545,-2.199674151,-1.1460983755\O,0.
7913518882,-1.0608324592,-1.5309188366\S,-3.1839212639,-1.6942117329,-
1.6483814797\C,-2.0680243028,-0.9421586451,-0.4107703474\S,-2.95004522
23,-0.4430045432,1.1246853301\C,-3.8973167344,0.9603347941,0.472809903
1\C,-1.4736010717,0.2992511151,-1.0659608632\O,-1.7389271242,0.6855150
172,-2.1737208132\O,-0.635960462,0.9407030043,-0.233330539\C,0.2112276
595,1.8972170491,-0.8749979817\H,-4.5376747914,-2.6817914044,0.0638288
952\H,-2.9785963351,-4.7058964384,0.5986412598\H,-0.8269950399,-3.8355
826253,1.0793178513\H,-0.3939394527,-1.4544937169,0.8125357036\H,-3.71
33311269,-4.4994266511,-2.258898513\H,-5.2393582822,-3.6042263536,-2.1
504824367\H,-4.8912695521,-4.8975006389,-0.9946110594\H,-3.2522773068,
1.8183296799,0.2858698326\H,-4.6332051582,1.2231576983,1.2308711293\H,
-4.4096288115,0.6674416324,-0.4434807161\H,1.3701939999,-0.8206059292,

-0.790514924\C,1.2987445348,2.2221491795,0.1129594845\H,-0.3540127812,
2.7951989745,-1.1276437695\H,0.6131872334,1.4554278683,-1.78571454\H,0
.7140794997,-3.0101400713,-0.8243638804\H,-0.4958234725,-2.5372744088,
-2.0263572717\O,2.0296676672,0.9971489216,0.3447196598\H,1.9812622209,
2.9752348041,-0.2793351827\H,0.8920158929,2.56562192,1.0626844247\C,3.
016157609,1.0952042675,1.2263711198\O,3.3495362431,2.1172591215,1.7726
632511\C,3.7115581553,-0.2330963096,1.4961637219\S,3.1893039034,-1.660
0552908,0.9028134354\S,5.0818934688,0.0404439663,2.5124702869\C,5.7265
55473,-1.6358121157,2.679347196\H,6.6127724044,-1.5555151896,3.3062894
064\H,4.9872490351,-2.2810265683,3.1507508971\H,5.9885408163,-2.040634
9596,1.7032206783\\Version=ES64L-G09RevD.01\State=1-A\HF=-2514.1868257
\RMSD=6.241e-09\RMSF=2.886e-06\Dipole=0.9392289,-0.3942941,1.2329835\Q
uadrupole=10.0474316,3.971597,-14.0190286,-3.3907534,1.6691794,-4.5311
211\PG=C01 [X(C14H20O5S4)]\\@

SA-MTTA_full-SA - M05-2X
1\1\GINC-R38\FOpt\RM052X\Gen\C20H30O6S4\ROOT\18-Jan-2016\0\\# M052X/Ge
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=3489660928\
\21uuu21.M052X\\0,1\C,3.3399188563,-1.1840501878,-1.853660844\C,2.3662
530766,-0.9637203134,-0.6935693836\C,2.6773318992,0.2975945815,0.05438
00309\C,1.7957939067,1.1816322467,0.5133275365\C,0.2997362301,1.148613
4311,0.3410691145\C,-0.1267366759,2.2300651788,-0.6956137802\O,-1.1337
897659,3.0882310321,-0.2180642021\S,0.6900227256,-0.9792424681,-1.4115
281724\C,-0.2162725351,-0.2642501819,0.0041884346\S,-0.0801239843,-1.2
496544764,1.5642279639\C,-0.5955940907,-2.9090483516,1.0399995434\C,-1
.6974524271,-0.221840253,-0.3374023196\O,-2.4618674631,0.6586365708,-0
.0105657009\O,-2.0930046846,-1.3018925544,-1.0156065583\C,-3.474264766
3,-1.3232667383,-1.4068770246\H,2.4319514564,-1.8099782832,-0.00283053
61\H,3.7339709491,0.4640624632,0.2456404865\H,2.1643595112,2.058479066
8,1.0353286671\H,-0.1593874436,1.4518557081,1.2873224514\H,3.296555346
9,-0.3448742967,-2.5492610361\H,3.102999107,-2.1014778447,-2.395524047
1\H,4.3582712631,-1.2656690718,-1.4687596104\H,-1.6770957056,-2.993782
8725,0.9631932179\H,-0.232344177,-3.5908648455,1.8076870551\H,-0.13426
9223,-3.1569899372,0.0848953025\H,-1.8957717485,2.5247218905,-0.021734
5585\H,-3.7119282512,-0.3987988505,-1.9309036501\H,-4.1049681322,-1.40
19993811,-0.521181485\H,0.7306631787,2.864468338,-0.9175300204\H,-0.40
92530862,1.737466617,-1.6350887663\C,1.8120803066,-1.1521624715,-6.176
7250945\C,0.4066159132,-1.6657121073,-6.4981598337\C,0.4516353552,-2.8
832618981,-7.3714656785\C,-0.3068796466,-3.9693960224,-7.2521651587\C,
-1.3373526994,-4.2475810467,-6.1892976906\C,-0.7840756959,-5.313208386
7,-5.1971041395\O,-1.6545242211,-6.4026577505,-5.0125231608\S,-0.41855
66571,-1.9582234407,-4.8984768593\C,-1.8242910763,-2.9581988337,-5.499
1430476\S,-2.899729724,-2.0887504457,-6.7282880145\C,-3.3239793932,-0.
5451010675,-5.8731408435\C,-2.7225240129,-3.2936352913,-4.3188720311\O
,-3.3117986294,-4.34080573,-4.1685973058\O,-2.835136749,-2.2761782433,
-3.4615318436\C,-3.6409573956,-2.5241459783,-2.299382503\H,-0.15416574
22,-0.8805316626,-7.0144972372\H,1.1673580007,-2.8314352771,-8.1874515
813\H,-0.1617956966,-4.7830551645,-7.9550846859\H,-2.2039542666,-4.714
305252,-6.6681687605\H,2.3912042801,-1.9252490517,-5.6698634279\H,1.76
99505839,-0.2690351472,-5.5366222956\H,2.3254237789,-0.8819207813,-7.1
015495196\H,-4.1117577692,-0.6907288991,-5.1376669006\H,-3.671972755,0
.1384992331,-6.6462903686\H,-2.4384138841,-0.1310446756,-5.3926735374\
H,-2.473330114,-6.0338250331,-4.6516605218\H,-3.2964160606,-3.43545275
67,-1.8130293268\H,-4.6823272179,-2.6513299425,-2.5957212352\H,0.13794

68821,-5.7284562114,-5.6024342604\H,-0.522619041,-4.8230168809,-4.2503
012449\\Version=ES64L-G09RevD.01\State=1-A\HF=-2824.0158541\RMSD=7.712
e-09\RMSF=1.868e-06\Dipole=0.429175,0.0528948,-0.1514725\Quadrupole=19
.3440965,-21.6024617,2.2583652,-0.5566607,-4.5390917,-16.4199278\PG=C0
1 [X(C20H30O6S4)]\\@

Cp
1\1\GINC-R95\FOpt\RM052X\Gen\C5H6\ROOT\13-Jan-2016\0\\# M052X/Gen 6D S
CF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=671088640\\cp.smd
.acetonitrile\\0,1\C,-3.2325664467,0.8025580063,-0.0008649936\C,-3.278
7033873,2.1452289005,0.0007877044\C,-1.828467364,0.366888826,-0.000265
6634\C,-1.0303576146,1.4475500492,0.0017473281\C,-1.8777540918,2.68832
07226,0.0026167137\H,-4.081686646,0.1333067175,-0.0024017229\H,-4.1655
011883,2.7621536795,0.0008394617\H,-1.5074284644,-0.6654889501,-0.0013
02975\H,0.049896482,1.4539218046,0.0026384455\H,-1.6840706319,3.313846
3385,0.881648834\H,-1.6826349841,3.3160573438,-0.8745197155\\Version=E
S64L-G09RevD.01\State=1-A'\HF=-194.0721845\RMSD=4.182e-09\RMSF=4.354e-
05\Dipole=0.0521367,0.1680802,0.0002542\Quadrupole=0.848976,1.6945217,
-2.5434976,0.2900188,0.0031384,0.0055727\PG=CS [SG(C5H4),X(H2)]\\@

MTTA_half-Cp
1\1\GINC-R89\FOpt\RM052X\Gen\C9H12O2S2\ROOT\13-Jan-2016\0\\#M052X/gen
6D SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=1610612736\\a
1 b1\\0,1\C,-6.3267887386,1.8908052102,0.0324635622\O,-5.5908462206,0.
8677880036,-0.6501725309\C,-4.3636988878,1.2203012642,-1.0307027116\C,
-3.6502841297,0.1342377147,-1.8142692999\O,-3.8881842819,2.3164488293,
-0.8381832268\C,-2.1017374016,0.3544758216,-1.8119187934\C,-1.65314424
08,0.4660943619,-0.3653162717\S,-3.9088586302,-1.5533688667,-1.1123268
42\C,-2.0571706617,-1.734615459,-0.9210702055\C,-1.6416215914,-0.76417
35355,0.1582748221\C,-1.5421889159,-1.0286408187,-2.1789937766\S,-4.35
72708792,0.1118992785,-3.5094450983\C,-4.2552617368,1.8748099854,-3.95
14744718\H,-5.799134919,2.191082267,0.9355081495\H,-6.4527195022,2.757
0144835,-0.6147514465\H,-1.8238422037,1.1843191795,-2.4567618885\H,-1.
5063072731,1.4020515361,0.1518328867\H,-1.8101866857,-2.7838100714,-0.
7876956334\H,-1.4834024259,-1.0351271908,1.1926941137\H,-1.9438567602,
-1.4358501882,-3.1053279905\H,-0.4519752051,-1.0120258103,-2.205428532
5\H,-4.9180163876,2.4830168944,-3.338486761\H,-4.5756291518,1.93597476
45,-4.9908477895\H,-3.2380575309,2.2537207268,-3.8718718442\H,-7.28614
56386,1.4451026193,0.2736125806\\Version=ES64L-G09RevD.01\State=1-A\HF
=-1296.8777593\RMSD=4.652e-09\RMSF=1.946e-05\Dipole=0.2797138,0.424577
1,0.2165292\Quadrupole=1.858252,-2.5569563,0.6987043,-6.5352577,-1.677
8042,-2.9903915\PG=C01 [X(C9H12O2S2)]\\@

MTTA_full-Cp
1\1\GINC-R66\FOpt\RM052X\Gen\C13H16O4S4\ROOT\10-Mar-2016\0\\# M052X/Ge
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=2684354560\
\1uuup.M062X\\0,1\C,2.3776661186,-1.7316480122,-0.8569464866\C,3.75428
88459,-1.0665339599,-0.7670165947\C,4.1739476964,-1.4340465041,0.63302
79785\C,3.07064515,-1.5350490311,1.3814962316\C,1.8763255439,-1.216218
2411,0.505214853\S,3.2888922806,0.7478395729,-0.733440996\C,1.82080474
4,0.3367940135,0.3151791727\S,1.9559140858,1.2971765951,1.8615618429\C
,0.3508459612,0.878853247,2.6080297869\C,0.5665327677,0.7169793757,-0.
463303879\O,-0.2407034673,-0.0845157786,-0.8728080373\O,0.4736133781,2
.0399805442,-0.6497412281\C,-0.6358150962,2.5058188701,-1.4307672481\H

,5.199773944,-1.4814913382,0.9697624142\H,3.0245660609,-1.6889921489,2
.4494436151\H,0.9106826889,-1.5962611852,0.8303874683\H,-0.4824526442,
1.1848639293,1.9760778935\H,0.2981058608,1.4270812654,3.5480347965\H,0
.2748310033,-0.1871099217,2.820250743\H,1.7786300055,-1.4013267424,-1.
7024344308\H,2.4640887528,-2.8190338932,-0.8520273053\C,-1.803659134,2
.8396072452,-0.5258340426\H,-0.9095719438,1.7579719785,-2.170325025\H,
-0.2875279514,3.4119408998,-1.9229140713\O,-2.2629685463,1.6684956778,
0.1703676636\H,-1.4937427559,3.5223463405,0.2609921503\H,-2.6200799778
,3.2672044988,-1.1062935932\C,-2.9356249461,0.7993969288,-0.5809783608
\O,-3.2777359343,1.0019735329,-1.7202838043\C,-3.261592269,-0.49759430
31,0.1426807051\S,-2.9196267543,-0.7663184275,1.7115317022\S,-4.030348
6005,-1.579892709,-0.9690416261\C,-4.2971450362,-3.0183405561,0.085290
6857\H,-4.7783535432,-3.7662992804,-0.5425785426\H,-3.3464768253,-3.39
36130597,0.4603783939\H,-4.9380996578,-2.7607013941,0.9266318608\H,4.4
590001952,-1.2381080289,-1.575534686\\Version=ES64L-G09RevD.01\State=1
-A\HF=-2398.4606296\RMSD=6.703e-09\RMSF=5.362e-06\Dipole=-0.3165817,-0
.6125306,0.074261\Quadrupole=-2.5362494,7.6804347,-5.1441853,-3.176870
6,-3.719142,-1.9499393\PG=C01 [X(C13H16O4S4)]\\@

Cp-MTTA_full-Cp
1\1\GINC-R37\FOpt\RM052X\Gen\C18H22O4S4\ROOT\10-Mar-2016\0\\# M052X/Ge
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=3221225472\
\1uuu1-gas\\0,1\C,2.3472890043,-1.6632627333,-1.7098688948\C,3.7834754
156,-1.1393102826,-1.629975226\C,4.3024965265,-1.8703461268,-0.4191312
356\C,3.274157951,-2.078346153,0.4100935183\C,2.0358032964,-1.46734208
86,-0.2134076333\S,3.5007190773,0.639231875,-1.1097373189\C,2.11788264
54,0.0842336786,-0.0103774688\S,2.5370715701,0.6112403759,1.6854070764
\C,1.0077699747,0.1315262761,2.5432340004\C,0.8375318668,0.7386310351,
-0.5215140986\O,-0.022727008,0.1463607562,-1.1299241981\O,0.7924756352
,2.0462142837,-0.2442564593\C,-0.3654386501,2.7619111406,-0.6998004442
\H,5.3473429673,-2.0693975104,-0.2277656246\H,3.3209406102,-2.48823753
16,1.4082199656\H,1.0729130126,-1.8435130622,0.1271235581\H,0.13689161
73,0.6313839387,2.1204706165\H,1.128456791,0.4452117654,3.5796438495\H
,0.8549151669,-0.9465312255,2.5174565591\H,1.7027944572,-1.0934510025,
-2.3739230823\H,2.3298331075,-2.7220381854,-1.9727477997\C,-1.38136291
92,2.8510964806,0.4187036391\H,-0.784074749,2.2763225564,-1.5762595113
\H,-0.0132736814,3.7610685359,-0.950444163\H,-0.9168981451,3.243715052
3,1.3201227658\H,-2.2145503715,3.4831251619,0.1133189083\H,4.384442217
,-1.1534921406,-2.5346294229\C,-2.7489572468,-1.8547857958,-1.20638900
66\C,-2.5462998291,-2.6898952989,0.0624375648\C,-3.9478773669,-3.17226
93797,0.3377565223\C,-4.7979024443,-2.2429522917,-0.1097523068\C,-3.98
62470371,-1.1011768925,-0.6852202031\S,-2.175449463,-1.3576310067,1.32
46852209\C,-3.4056042555,-0.2608372982,0.5004702644\S,-4.6493514376,0.
2290677373,1.7590368394\C,-5.8331344841,1.1352645989,0.7149613618\O,-1
.874199781,1.5564055768,0.7973956787\H,-4.1880605422,-4.0588624821,0.9
072504544\H,-5.8706469044,-2.2327357737,0.0194000411\H,-4.4844648362,-
0.4500387844,-1.3981396386\H,-5.3464133467,1.9327779503,0.1566623488\H
,-6.564838349,1.567900023,1.3961117068\H,-6.3450786148,0.4642403865,0.
0262878239\H,-1.9018475628,-1.2143518254,-1.4468124432\H,-3.0109949204
,-2.486784128,-2.0561494851\H,-1.741978392,-3.4202159678,0.0691224412\
C,-2.7911993934,1.0276270283,-0.0246446853\O,-3.165665179,1.5711027543
,-1.0388923756\\Version=ES64L-G09RevD.01\State=1-A\HF=-2592.5786512\RM
SD=8.209e-09\RMSF=3.173e-06\Dipole=-0.6246519,-0.4391293,-0.4230322\Qu
adrupole=-0.4143145,6.9056769,-6.4913625,-7.8210012,-1.2335413,1.98500

66\PG=C01 [X(C18H22O4S4)]\\@

DMBD.gas
1\1\GINC-R421\FOpt\RM052X\Gen\C6H10\ROOT\10-Dec-2015\0\\#M052X/gen 6D
SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=671088640\\a4\\0
,1\C,-1.3023354109,0.3841677425,0.0689189768\C,0.1781586493,0.42135503
72,0.0457290102\C,-1.9730267158,-0.7669813807,-0.0504225881\C,0.848840
1564,1.5725645532,0.1645419127\C,-2.0449589163,1.6853742238,0.23153540
13\C,0.9207897465,-0.8798982394,-0.1164777805\H,-1.4765273252,-1.72023
68064,-0.1687705554\H,-3.0556585195,-0.7813451082,-0.0320183365\H,0.35
23316443,2.5258762032,0.2823977062\H,1.9314712509,1.5869326526,0.14609
93903\H,-1.8078230919,2.3764280867,-0.5806780729\H,-1.7748537291,2.176
588938,1.1691998582\H,-3.1206700695,1.5134543586,0.2321602424\H,0.6512
194415,-1.3710278601,-1.054349368\H,0.6831114709,-1.5709905406,0.69553
44176\H,1.9965129033,-0.7080523635,-0.1164549382\\Version=ES64L-G09Rev
D.01\State=1-A\HF=-234.5808313\RMSD=3.441e-09\RMSF=1.007e-04\Dipole=-0
.0000007,0.0000045,-0.0000392\Quadrupole=1.1980414,1.1856961,-2.383737
5,-0.3442759,-0.1066359,0.4198462\PG=C02 [X(C6H10)]\\@

MTTA_DMBD_gas
1\1\GINC-R159\FOpt\RM052X\Gen\C10H16O2S2\ROOT\10-Dec-2015\0\\#M052X/ge
n 6D SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=1610612736\
\a3 b4\\0,1\C,-0.6626635085,0.3546413273,-0.0947754119\C,-0.6214121768
,-0.9471466517,-0.3967282752\C,0.6506590621,-1.7580877001,-0.515971832
6\C,0.5616167844,1.197500083,0.1601845595\S,2.1316810316,0.5613237392,
-0.4843232587\C,1.9101302207,-1.1489297327,0.0979646897\C,-1.929801167
8,1.154185187,0.0833785401\C,-1.839275119,-1.7923378878,-0.6760122858\
S,1.7650759073,-1.3076245237,1.9292562869\C,3.323789291,-0.5516720778,
2.4703243608\C,3.1645300264,-1.9111752167,-0.2993950529\O,2.9247519732
,-3.2136843866,-0.4858156586\O,4.2604019434,-1.4132831656,-0.39430357\
C,4.0907420896,-3.9984670992,-0.7727272639\H,0.850514255,-1.9522251477
,-1.5748496003\H,0.4840257786,-2.7368626937,-0.0556177755\H,0.66292877
09,1.3788193773,1.2342370126\H,0.4365392598,2.1709558247,-0.3209298438
\H,-2.8205471295,0.5369644183,0.1682021536\H,-2.0681648855,1.850358456
8,-0.749517969\H,-1.858117351,1.7567316838,0.9934983699\H,-2.732092006
1,-1.2075920446,-0.8823333455\H,-2.0472845512,-2.4581022163,0.16709579
9\H,-1.6525924212,-2.4298011926,-1.5449661918\H,3.4305702047,0.4379883
529,2.0291912858\H,4.1815397085,-1.1643884831,2.2024099502\H,3.2563824
692,-0.4665394807,3.553997783\H,3.731509218,-5.0139176123,-0.904842736
1\H,4.7913442202,-3.9398407056,0.0579692075\H,4.5738141019,-3.63402043
12,-1.6768699268\\Version=ES64L-G09RevD.01\State=1-A\HF=-1337.4026027\
RMSD=6.170e-09\RMSF=4.962e-06\Dipole=-0.5405137,-0.5082772,0.069252\Qu
adrupole=-1.2482681,3.8145867,-2.5663186,-6.5729672,2.7879455,4.34516\
PG=C01 [X(C10H16O2S2)]\\@

Furan_gas
1\1\GINC-R37\FOpt\RM052X\Gen\C4H4O1\ROOT\15-Jan-2016\0\\# M052X/Gen 6D
SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=671088640\\fur_
gas\\0,1\C,-2.7073533774,0.9387992975,0.\C,-1.7263277283,-0.1078173492
,0.\C,-0.5204352366,0.5111833361,0.\C,-2.0117325619,2.1021790223,0.\O,
-0.6769117686,1.858952105,0.\H,-3.7792994389,0.8330385725,0.\H,-1.9009
680763,-1.1707190225,0.\H,0.4949116247,0.1559971358,0.\H,-2.3005734369
,3.1383369025,0.\\Version=ES64L-G09RevD.01\State=1-A'\HF=-229.9919863\
RMSD=9.215e-09\RMSF=7.069e-05\Dipole=-0.183923,-0.1724229,0.\Quadrupol

e=1.3768417,1.5793612,-2.9562029,-1.5618955,0.,0.\PG=CS [SG(C4H4O1)]\\
@

MTTA_Furan_gas

1\1\GINC-R154\FOpt\RM052X\Gen\C8H10O3S2\ROOT\18-Jan-2016\0\\#M052X/gen
6D SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt(maxstep=2) maxdisk=1
610612736\\a6 b2\\0,1\C,-6.2958388109,2.3744348777,-0.5323784973\O,-5.
0933729406,1.7845836738,-0.0196542108\C,-4.1472341817,1.5676573471,-0.
9286606982\C,-2.8567641326,1.026828753,-0.3297433253\O,-4.2654458954,1
.8378158773,-2.1027140686\C,-2.0761941071,0.2179799608,-1.4326957713\C
,-0.6904988141,-0.1035261096,-0.9178221436\S,-3.1705253314,-0.20487929
64,0.9939594823\C,-2.3198556346,-1.4685599286,-0.1274521378\C,-0.84817
65145,-1.1429033461,-0.0995600052\O,-2.7281133947,-1.0486405451,-1.402
979754\S,-1.9242066141,2.4358002652,0.3714454624\C,-1.6371459188,3.416
1469282,-1.136649593\H,-6.0770122963,3.3469047034,-0.9694947867\H,-6.7
337312183,1.7282140742,-1.2901629691\H,-2.1846494108,0.6753037452,-2.4
096352794\H,0.1974222528,0.483757023,-1.0910673803\H,-2.6586455966,-2.
4723270265,0.1005229997\H,-0.1270580014,-1.6051141278,0.5569092327\H,-
2.5696035625,3.6423879666,-1.6497371314\H,-0.9565678604,2.9076744021,-
1.8190479369\H,-1.1738295056,4.3446437417,-0.8057625422\H,-6.955829510
4,2.4735550409,0.322974054\\Version=EM64L-G09RevC.01\State=1-A\HF=-133
2.7649922\RMSD=8.046e-09\RMSF=4.499e-06\Dipole=0.3317748,0.2370064,-0.
1011068\Quadrupole=5.5140404,3.379361,-8.8934014,-2.8945111,-2.0696868
,-4.1783347\PG=C01 [X(C8H10O3S2)]\\@

Etsorbat_trans_gas

1\1\GINC-R922\FOpt\RM052X\Gen\C8H12O2\ROOT\18-Jan-2016\0\\#M052X/gen 6
D SCF=Tight IOP(2/17=4) INT(grid=ultrafine) Opt maxdisk=1073741824\\a1
b1 c1\\0,1\C,-7.4714180937,0.2553437993,0.010359397\C,-6.0958875327,0
.8417454439,-0.0247220369\C,-4.9626967937,0.1310510229,0.0266173026\C,
-3.6497636091,0.7495511868,-0.0108233129\C,-2.4932832908,0.0747542991,
0.038193015\C,-1.2161218724,0.8112481656,-0.0072876158\O,-0.1662391272
,-0.0292407491,0.0525657779\C,1.1235705322,0.606508781,0.0139761801\C,
2.1611852275,-0.4920136441,0.0915546822\H,-8.0358784965,0.6419333059,0
.8629997924\H,-7.4354224429,-0.8317874521,0.0836042428\H,-8.0303106693
,0.5240121312,-0.8899299055\H,-6.0251534175,1.9239998421,-0.0972463528
\H,-5.0053975986,-0.9521126967,0.099294262\H,-3.6001690063,1.831985901
9,-0.0834397112\H,-2.4486355184,-1.0043014143,0.1108803418\H,1.1962405
771,1.3019434685,0.8501985447\H,1.2021082449,1.1833265945,-0.907598291
2\H,2.0487163833,-1.0581196902,1.0163651746\H,3.1629822731,-0.06122530
42,0.0657949431\H,2.0545649537,-1.1773078166,-0.7495187106\O,-1.098040
7226,2.0143748243,-0.0878077191\\Version=ES64L-G09RevD.01\State=1-A\HF
=-462.4376286\RMSD=6.144e-09\RMSF=5.884e-06\Dipole=-0.4963756,-0.58486
69,0.0378193\Quadrupole=9.8225177,-5.2147389,-4.6077787,-1.5738652,0.1
518467,0.0361871\PG=C01 [X(C8H12O2)]\\@

MTTA_Etsorb.M052X

1\1\GINC-R37\FOpt\RM052X\Gen\C12H18O4S2\ROOT\28-Jan-2016\0\\# M052X/Ge
n 6D SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=2147483648\
\etso2.M052X\\0,1\C,-3.7392191056,-0.034641288,1.1106635654\C,-2.56919
57389,-0.2914081839,0.15829513\C,-2.439759036,0.814373174,-0.847177281
1\C,-1.3137940909,1.3787477108,-1.2748885601\C,0.0804537283,1.00564183

47,-0.8246136916\C,0.6504076125,2.0994402041,0.0734263628\O,1.19136594
62,1.9277766159,1.1374256284\O,0.4971049282,3.3016988773,-0.4945018733
\S,-1.0803622127,-0.5048402766,1.1890876038\C,0.1598076549,-0.36387645
55,-0.140557432\S,-0.0438639659,-1.6289412109,-1.4683550109\C,0.279003
3185,-3.1416024457,-0.5185321113\C,1.5239667445,-0.6068057104,0.494962
4023\O,1.6953681159,-1.210452489,1.5226868894\O,2.5126040635,-0.147565
1548,-0.2818754423\C,3.8172862087,-0.2693327857,0.2993828134\H,-2.7419
640102,-1.2286821714,-0.378768335\H,-3.3800601997,1.1583981523,-1.2700
485515\H,-1.3624197419,2.1804138651,-2.0003822921\H,0.7317557073,0.982
6883489,-1.7049352195\H,-3.5926709058,0.9011096006,1.6512436304\H,-3.8
36158152,-0.844861633,1.8348205649\H,-4.6700406806,0.0312494452,0.5436
1606\H,1.334895001,-3.247721979,-0.2785454147\H,-0.0381481092,-3.97038
20624,-1.1494829391\H,-0.3078070686,-3.1318486578,0.3990191436\C,1.011
9430514,4.4128980128,0.2701845308\H,4.5024493003,0.1453393604,-0.43328
75866\H,4.0455415011,-1.3146233879,0.4963712705\H,3.8520359781,0.29380
58252,1.2302702087\C,0.7257403473,5.6660782595,-0.5265918208\H,0.52130
03475,4.4187343055,1.2426892792\H,2.0786583254,4.2582863924,0.42986982
72\H,1.0961714132,6.5396604286,0.0112341338\H,1.2163888815,5.621734470
1,-1.4989751007\H,-0.3467781571,5.7820630083,-0.6826593818\\Version=ES
64L-G09RevD.01\State=1-A\HF=-1565.2495177\RMSD=7.592e-09\RMSF=3.761e-0
6\Dipole=-0.0542131,0.8547623,-0.9050254\Quadrupole=6.6080285,5.994519
4,-12.6025479,1.7958794,-1.4503935,1.2072471\PG=C01 [X(C12H18O4S2)]\\@

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