Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

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Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. If “dried solvents” were used these were obtained by different procedures. Toluene, EtOH, n-hexane, n-pentane and CH_2Cl_2 were prepared by using an MBraun Solvent Purification System MB-SPS 800 filled with Al_2O_3. Et_2O was dried over Na/benzophenone and THF was dried over K/benzophenone under argon. The $CDCl_3$ was dried over CaH_2 and d_8-THF over sodium prior to vacuum transfer onto 4 Å sieves followed by three freeze pump thaw degassing cycles. ^1H, $^{13}C\{^1H\}$, and ^7Li NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ chemical shifts are referenced to the residual proton resonance of the deuterated solvents and $^7Li\{^1H\}$ chemical shifts are referenced to an internal reference capillary containing LiO_3SCF_3 in d_6-acetone (alongside a PPh_3 ^{31}P reference and PhF ^{19}F reference). Epoxides and CS_2 were dried over calcium hydride at room temperature for 3 days, vacuum transferred followed by three freeze pump thaw degassing cycles and stored inside an argon filled glovebox prior to use. Alcohols and thiols were dried over 4Å molecular sieves. Phtalic thioanhydride was synthesized according to the literature procedure and then purified by recrystallisation from ^{t}BuOMe followed by recrystallisation from $CHCl_3$ and two sublimation under dynamic vacuum at 90°C and was stored inside an argon filled glovebox prior to use.[1] Cyclohexyl(di/tri)thiocarbonate were prepared according to the literature procedure.[2,3] Infrared spectra were measured using a Thermo-Nicolet Nexus 670 FTIR spectrometer with DuraSampl IR accessory in total reflection at room temperature.

Section S2: Reaction Schemes

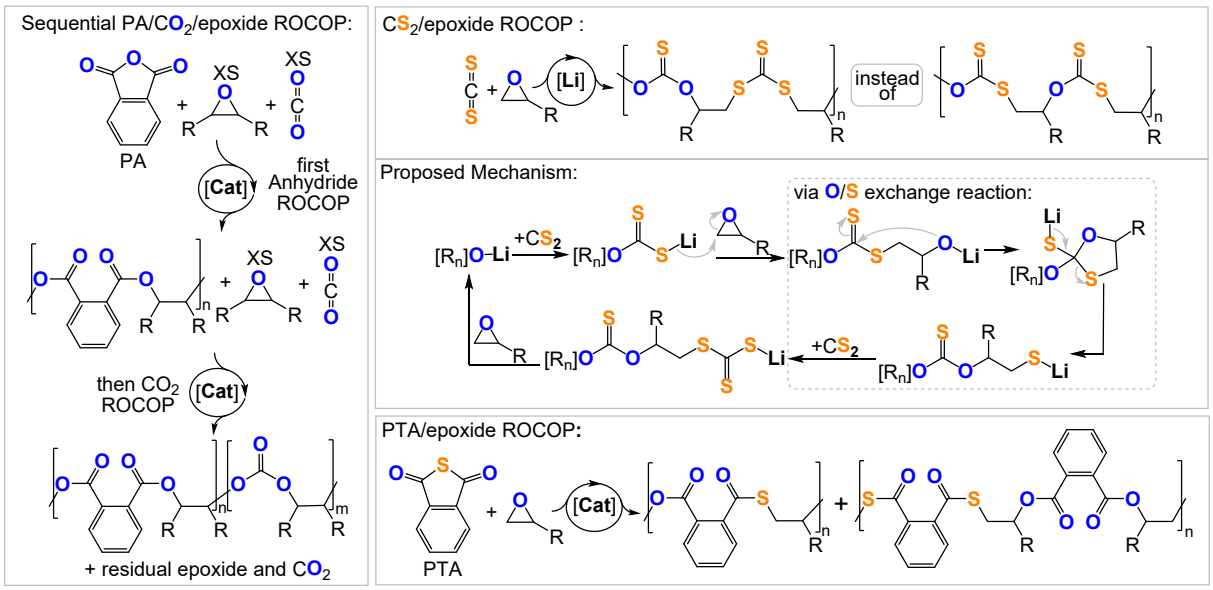
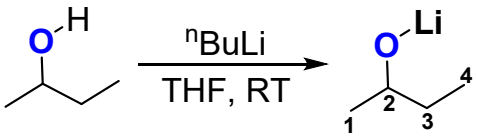


Figure S 1: ROCOP processes mentioned in the introduction of this paper.

Section S3: Synthesis and model experiment with A



Synthesis of A: In an oven dried Schlenk flask 2-Butanol (806.0mg, 10.87 mmol) was dissolved in THF (25 mL). ^{n}BuLi (4.35 mL of a 2.5 M solution, 1 eq.) was added dropwise at 0°C and the resulting solution was warmed to room temperature and stirred for another 30 min. All volatiles were removed in vacuum to yield A as a colourless solid (852.0 mg, 10.65 mmol, 98% yield). XRD quality crystals were grown from a saturated THF solution at -80°C.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 3.69 – 3.48 (m, 1H, H-2), 1.45 - 1.35 (m, 1H, H-3), 1.21 – 0.98 (m, 1H, H-3), 0.93 (d, *J* = 5.8 Hz, 3H, H-1), 0.76 (t, *J* = 7.5 Hz, 3H, H-4).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.51.

^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 70.84 (C-2), 37.89 (C-3), 27.39 (C-1), 11.53 (C-4).

Elemental analysis: calculated C 60.0%, H 11.3%; found: C 59.7%, H 11.1%.

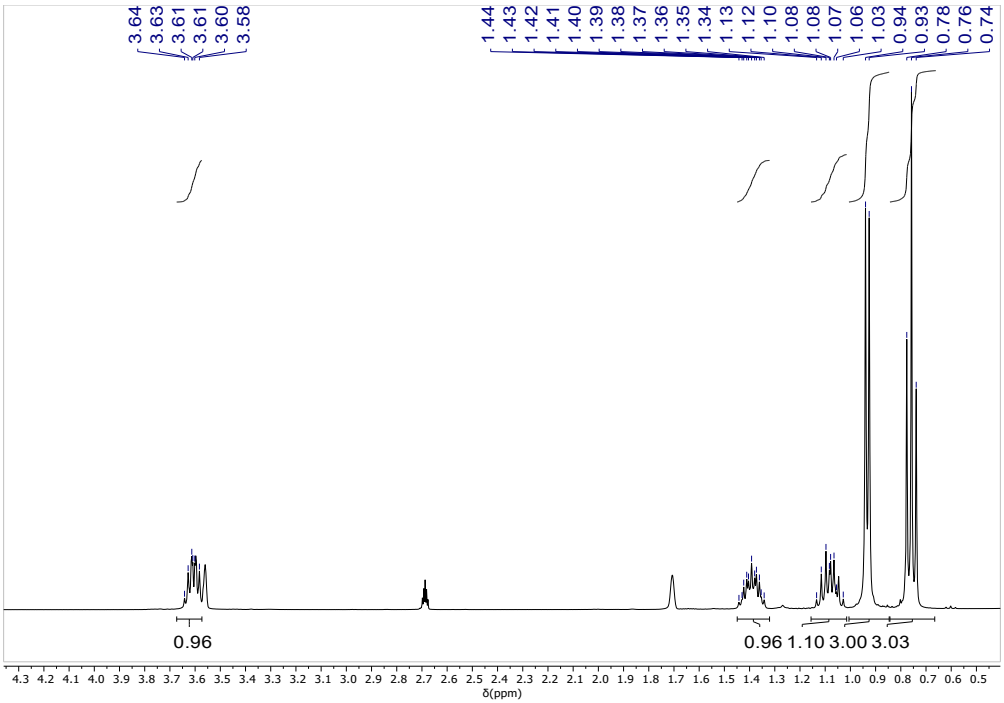


Figure S 2: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of A. D_6-Acetone signal from internal reference capillary.

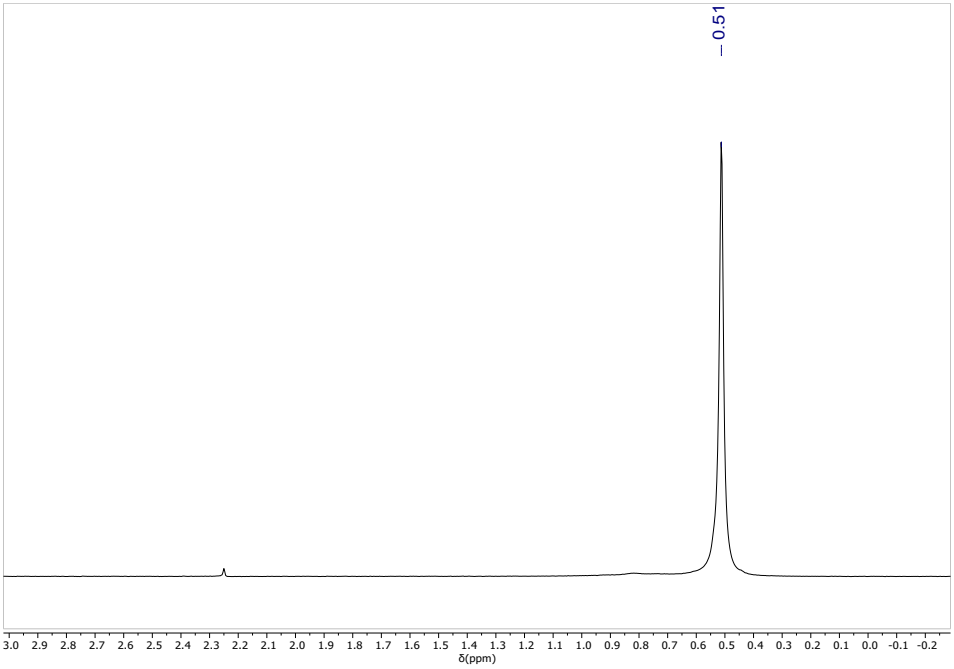


Figure S 3: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of A. Signal at 2.25 ppm corresponds to internal $LiSO_3CF_3$ standard.

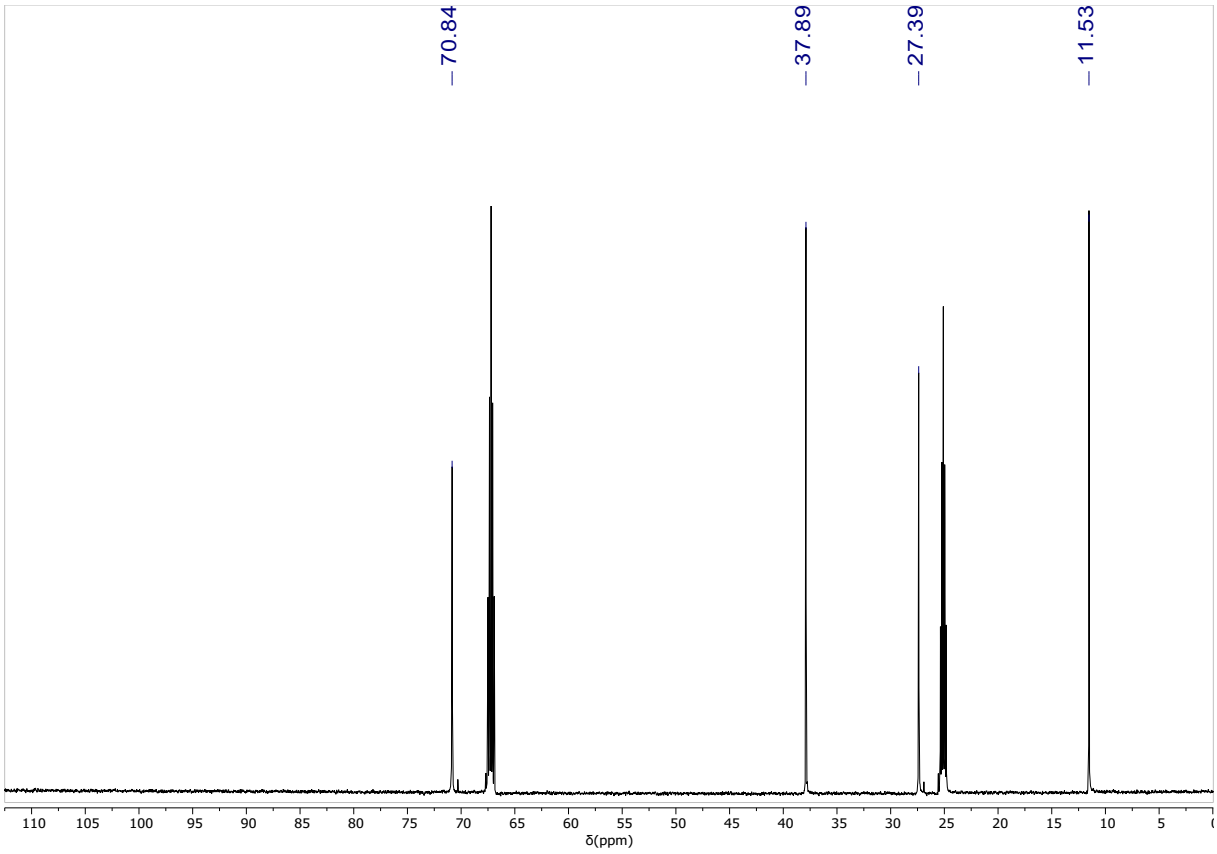
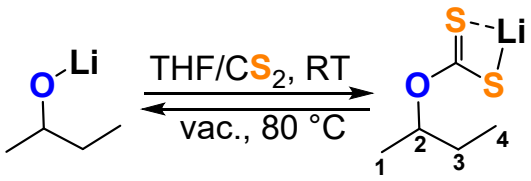


Figure S 4: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, d_8-THF, 25°C) of A.



CS_2 addition and removal experiment of DTC: A (20.0 mg, 0.25 mmol, 1 eq.) dissolved in d_8-THF (0.4 mL) and CS_2 (377.0 µL, 25 equiv.) was added resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. For FTIR analysis an aliquot was drop casted on the measurement window of the instrument and the solvent was let to evaporate immediately prior to analysis.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 5.37-5.25 (m, 1H, H-2), 1.83 – 1.41 (m, 2H. H-3), 1.20 (d, *J* = 6.2 Hz, 3H, H-1), 0.90 (t, *J* = 7.4 Hz, 3H, H-4).

$^{13}C\{^{1}H\}$ NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 231.15 (C=S), 79.28 (C-2), 28.89 (C-3), 18.51 (C-1), 9.94 (C-4).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.66.

FTIR [cm^{-1}]: $\tilde{\nu}$(C=S) = 1037.1

Afterwards all volatiles were removed in vacuum leaving a solid behind, which was then heated at 80°C under dynamic vacuum during which the initial yellow colour disappeared. The resulting solid was taken up in d_8-THF and analysed by NMR.

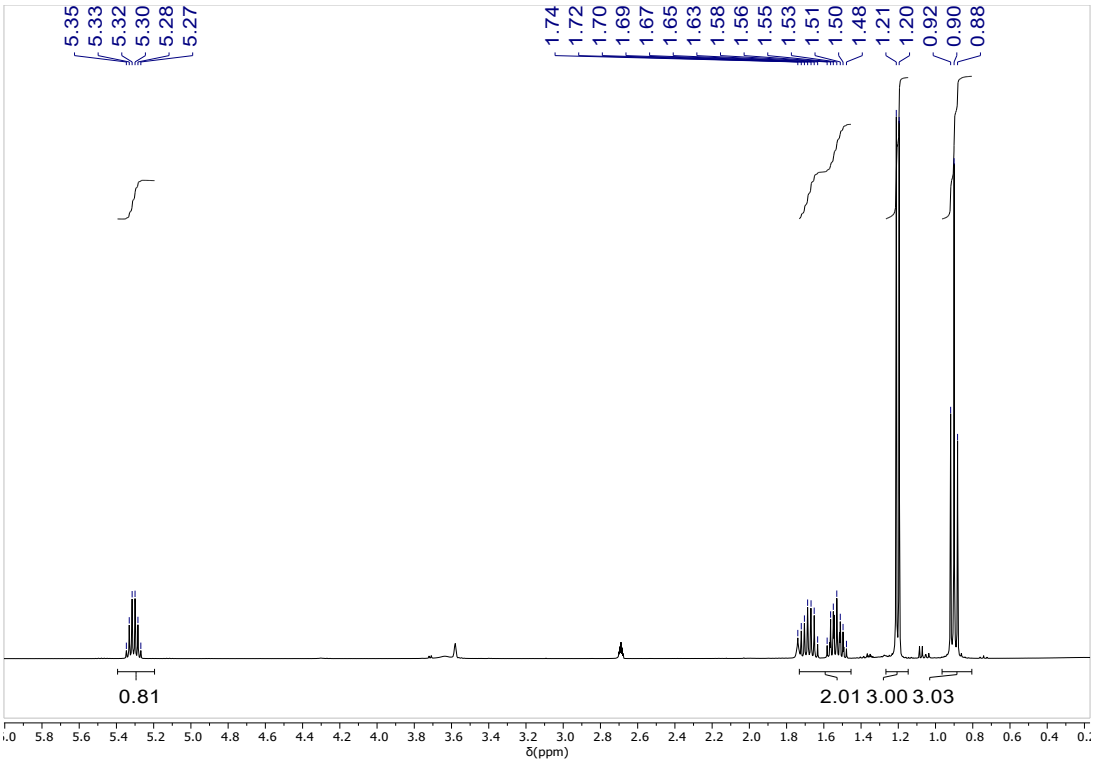


Figure S 5: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of DTC. D_6-Acetone signal from internal reference capillary.

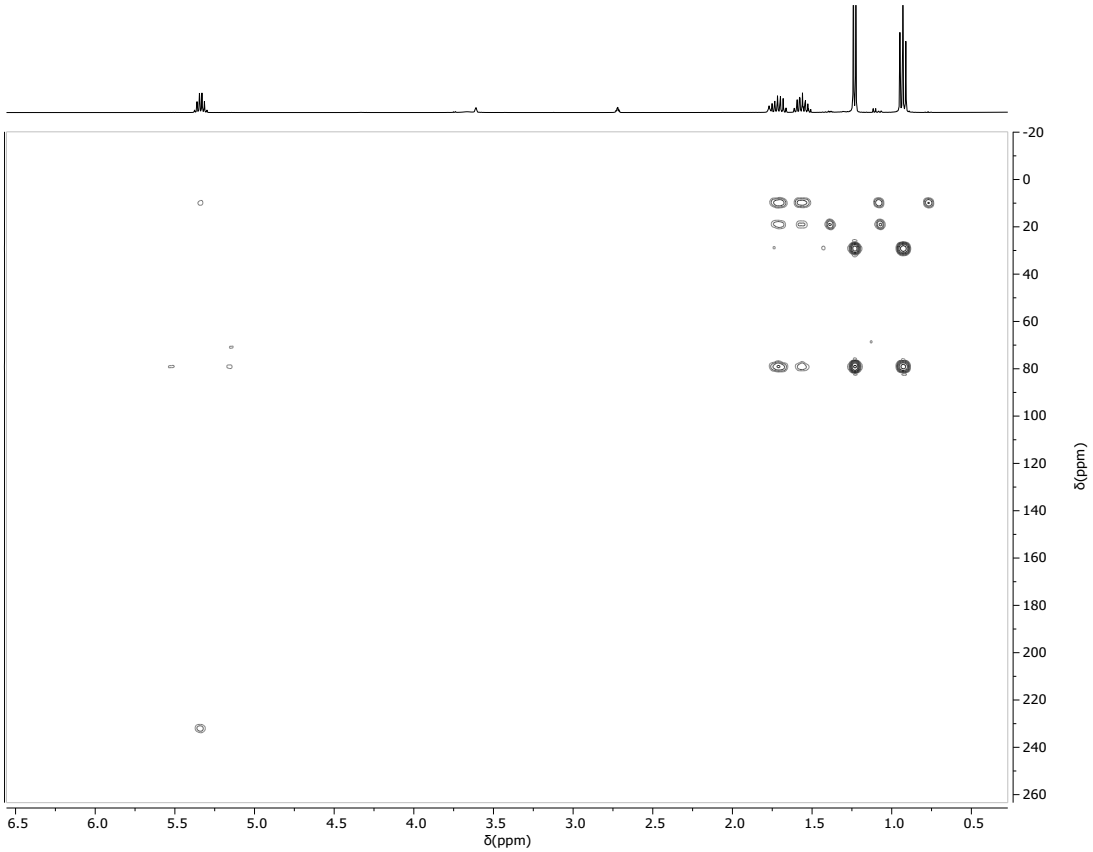


Figure S 6: ^{1}H-^{13}C HMBC NMR spectrum (d_8-THF, 25°C) of DTC.

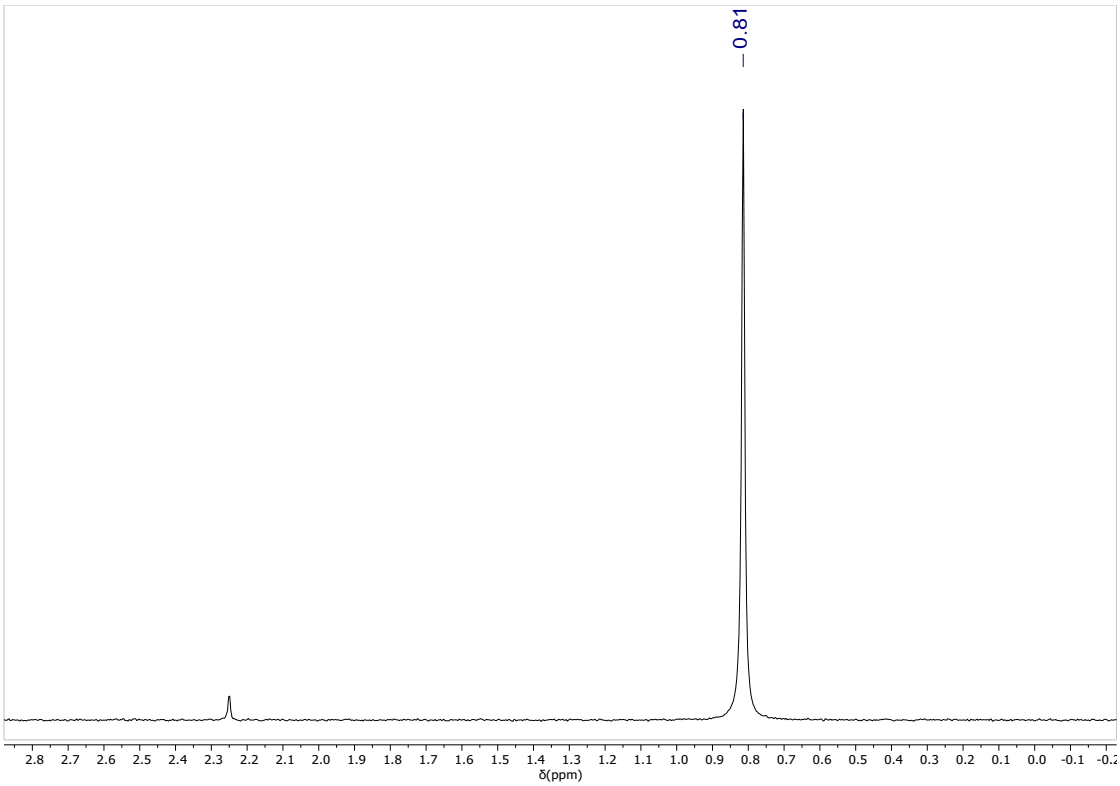


Figure S 7: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of DTC. Signal at 2.25 ppm corresponds to internal $LiSO_3CF_3$ standard.

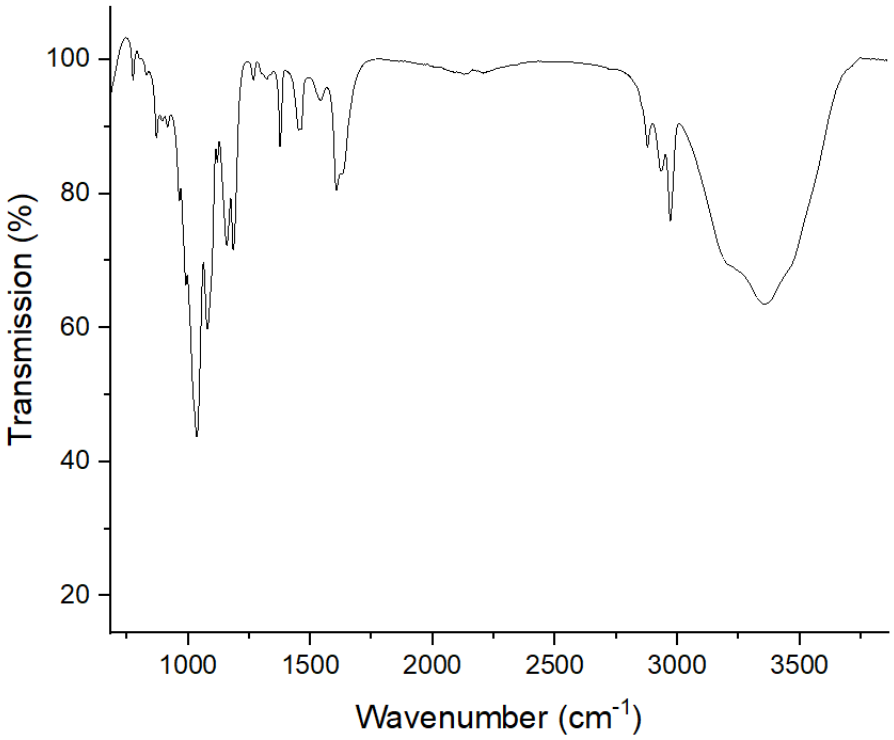


Figure S 8: Solid state FTIR spectrum of DTC. Resonance at ca. 1600 cm^{-1} from residual CS_2.

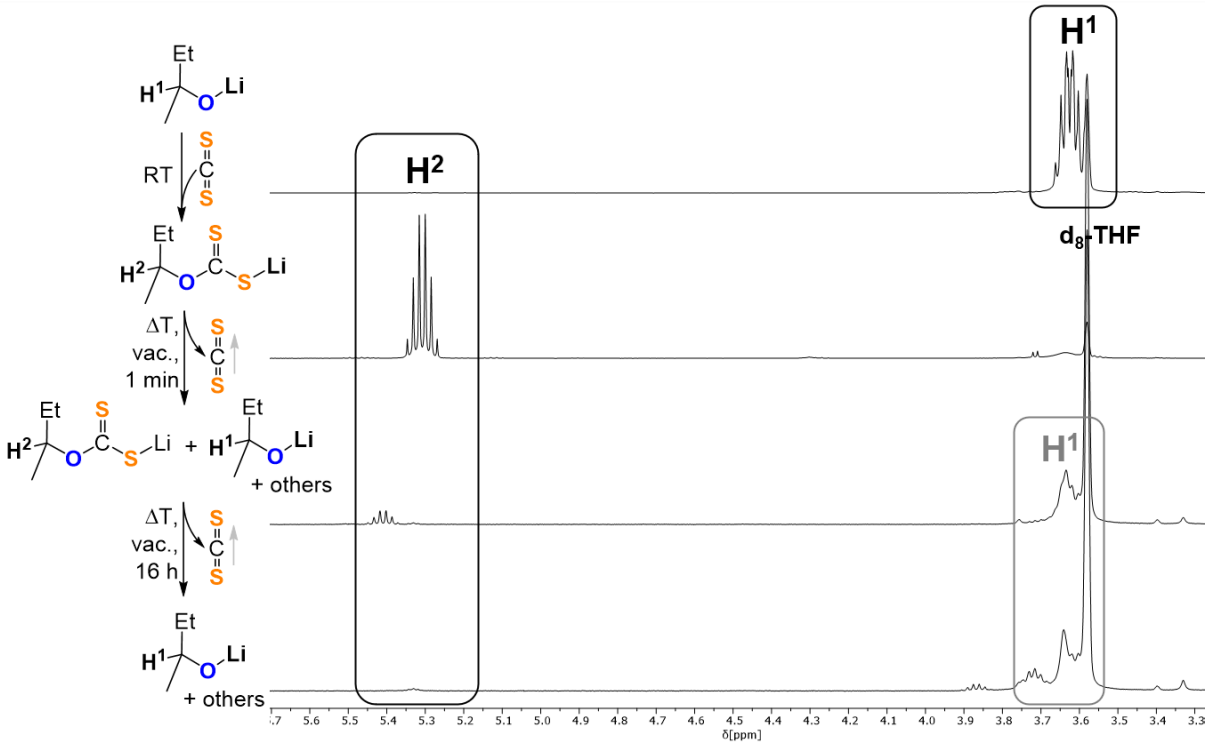


Figure S 9: Overlayed ^{1}H NMR spectra (400 MHz, d_8-THF, 25°C) of CS_2 addition and removal from A.

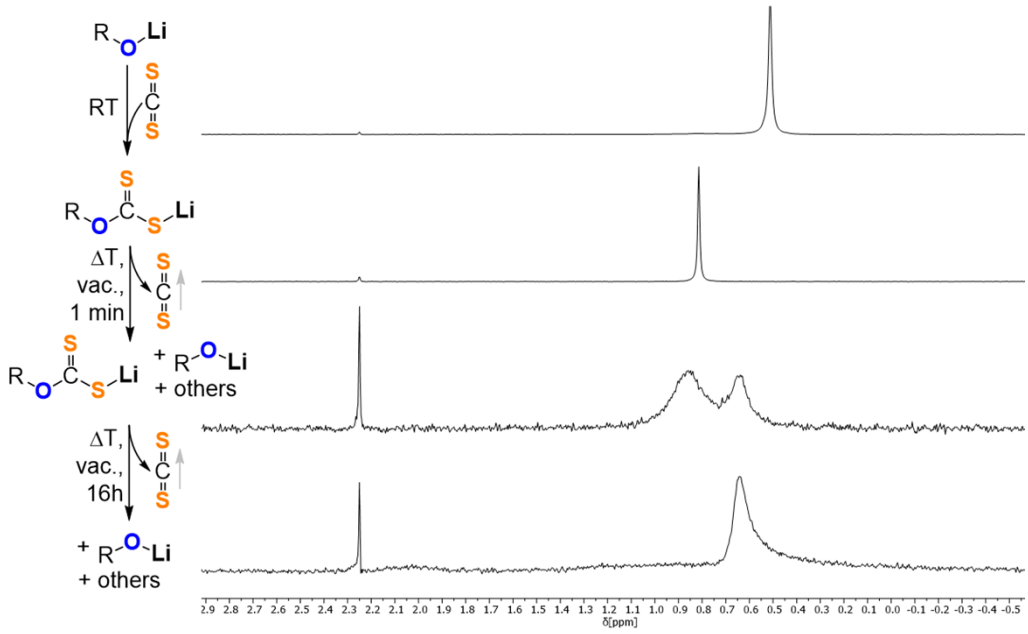
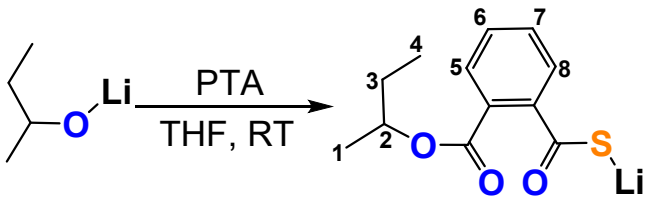


Figure S 10: Overlayed ^{7}Li NMR spectra (400 MHz, d_8-THF, 25°C) of CS_2 addition and removal from A. Signal at 2.25 ppm corresponds to internal $LiSO_3CF_3$ standard.



Synthesis of TC: A (20mg, 0.25 mmol, 1 eq.) and PTA (41.1 mg, 0.25 mmol, 1 eq.) were dissolved in d_8-THF (0.8 mL) resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. For FTIR analysis an aliquot was drop casted on the measurement window of the instrument and the solvent was let to evaporate immediately prior to analysis.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 7.90 (d, *J* = 7.7 Hz, 1H, H-8), 7.39 (d, *J* = 7.6 Hz, 1H, H-5), 7.32-7.26 (m, 1H, H-6), 7.24-7.16 (m, 1H, H-7), 4.98 (dt, *J* = 12.5, 6.2 Hz, 1H, H-2), 1.77 – 1.48 (m, 2H, H-3), 1.27 (d, *J* = 6.3 Hz, 3H, H-1), 0.93 (t, *J* = 7.5 Hz, 3H, H-4).

^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 218.02 (R(C=O)SLi), 169.07 (R(C=O)OR), 148.47 (C_q(R(C=O)SLi)), 131.50 – 125.25 (C-5, C-6, C-7, C-8, C_q(R(C=O)OR), 72.57 (C-2), 28.84 (C-3), 17.90 (C-1), 9.01 (C-4).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.65.

FTIR [cm^{-1}]: ṽ(C=O) = 1701.5, 1498.5.

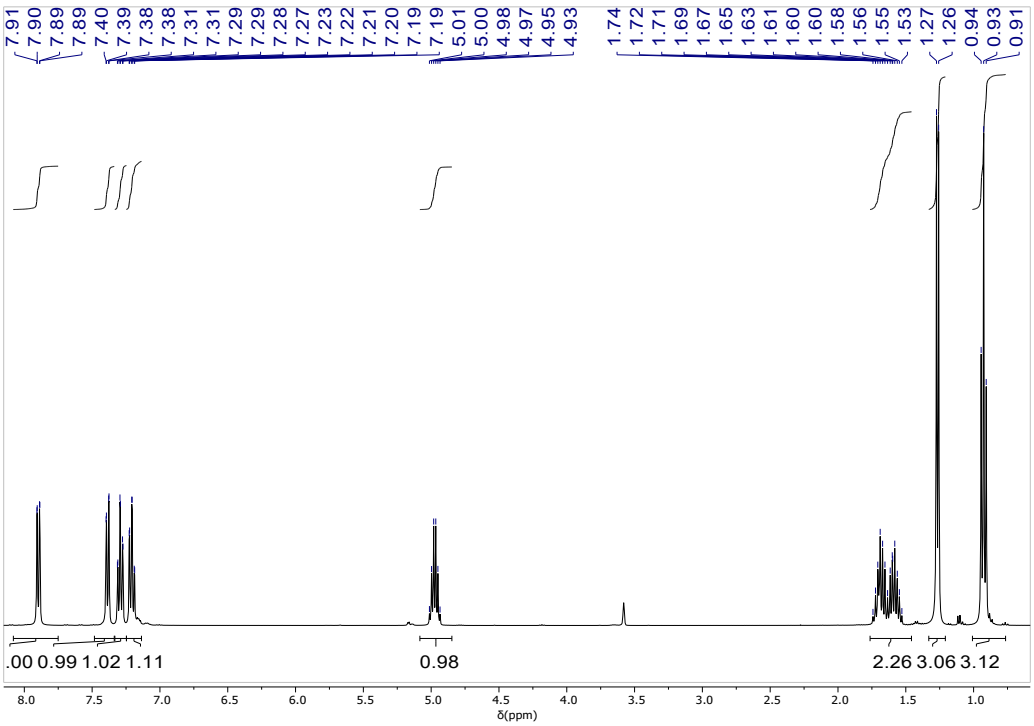


Figure S 11: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of TC.

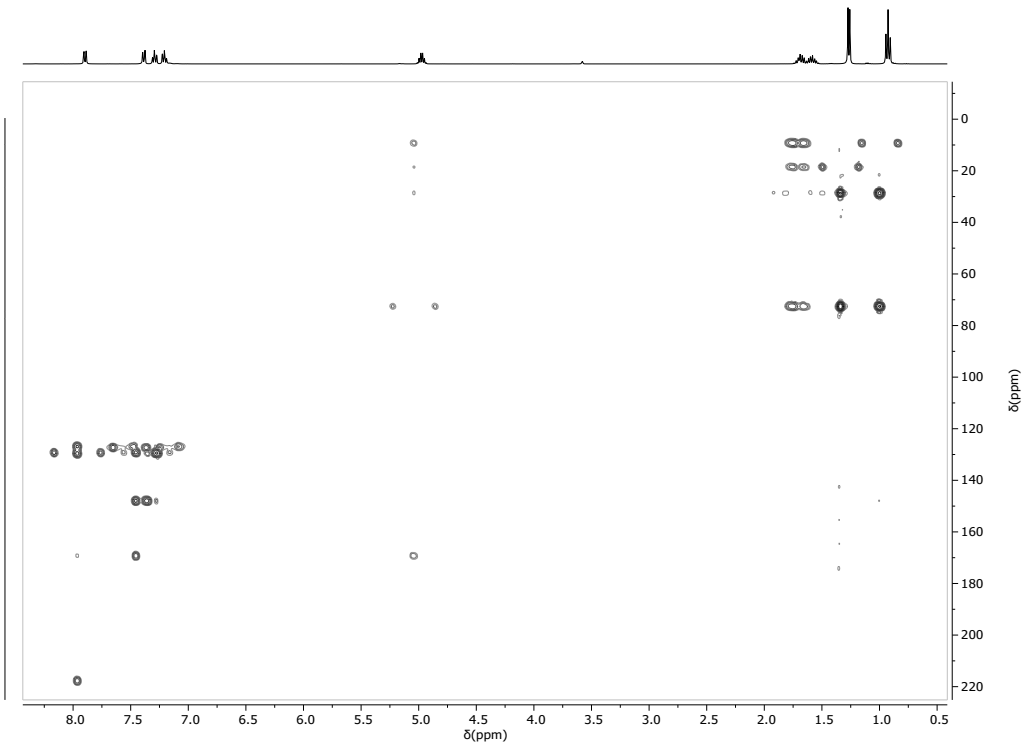


Figure S 12: ^{1}H-^{13}C HMBC NMR spectrum (d_8-THF, 25°C) of TC.

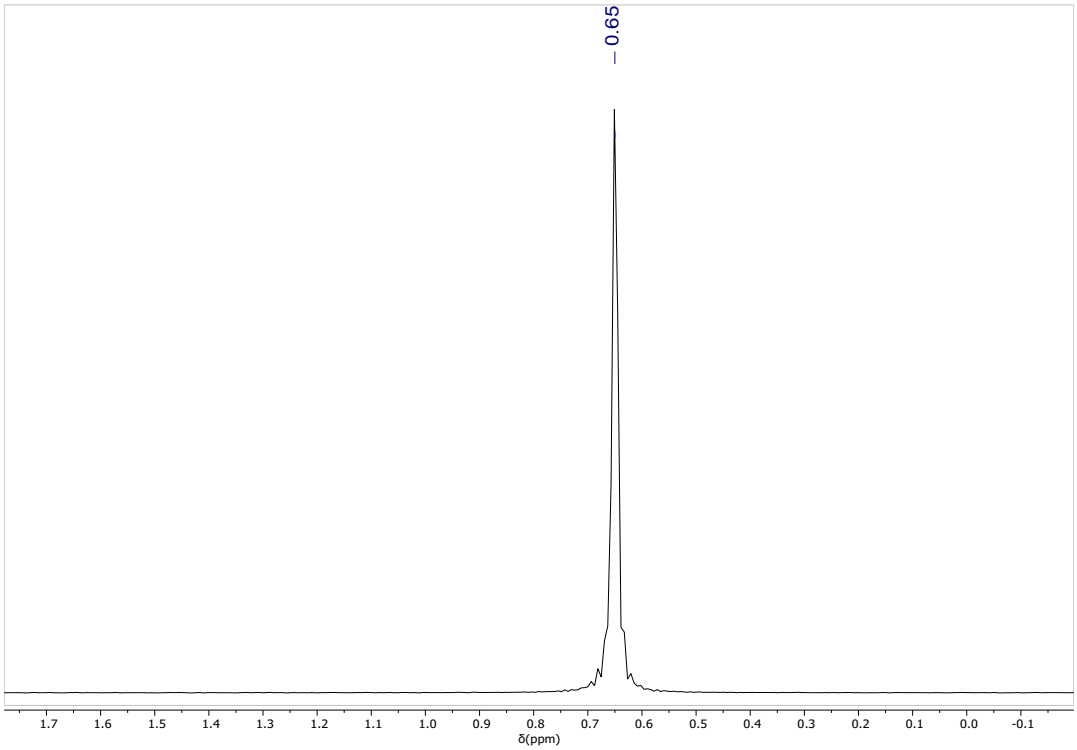


Figure S 13: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of TC.

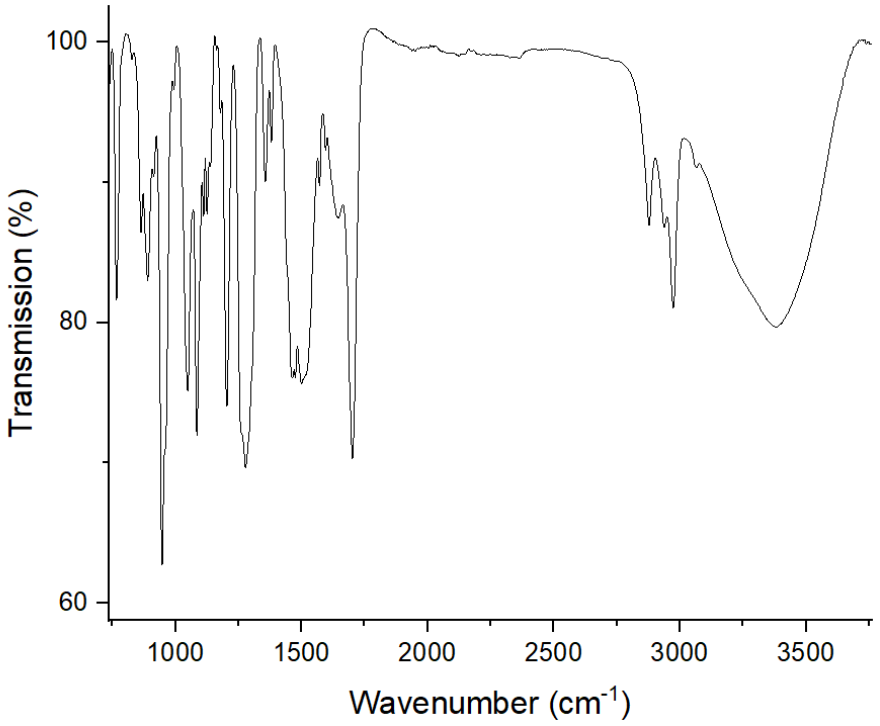
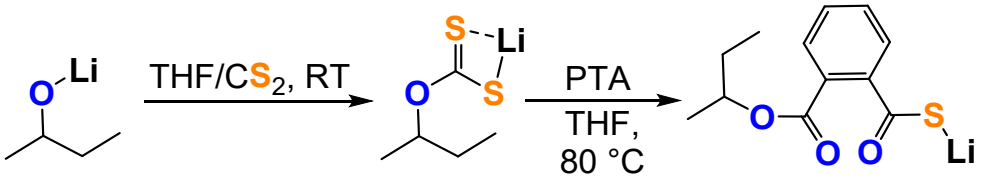


Figure S 14: Solid state FTIR spectrum of DTC



CS_2-PTA exchange: A (10.0 mg, 0.13 mmol, 1 eq.) dissolved in d_8-THF (0.6 mL) and CS_2 (377.0 µL, 50 equiv.) was added resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. Afterwards PTA (102.5 mg, 5 eq.) was added and after 30 minutes the mixture was analysed again by NMR. Afterwards the mixture was heated at 80°C overnight and then analysed by NMR. Note that this 10 CS_2:1 PTA ratio is also present during initial stages of ROTERP.

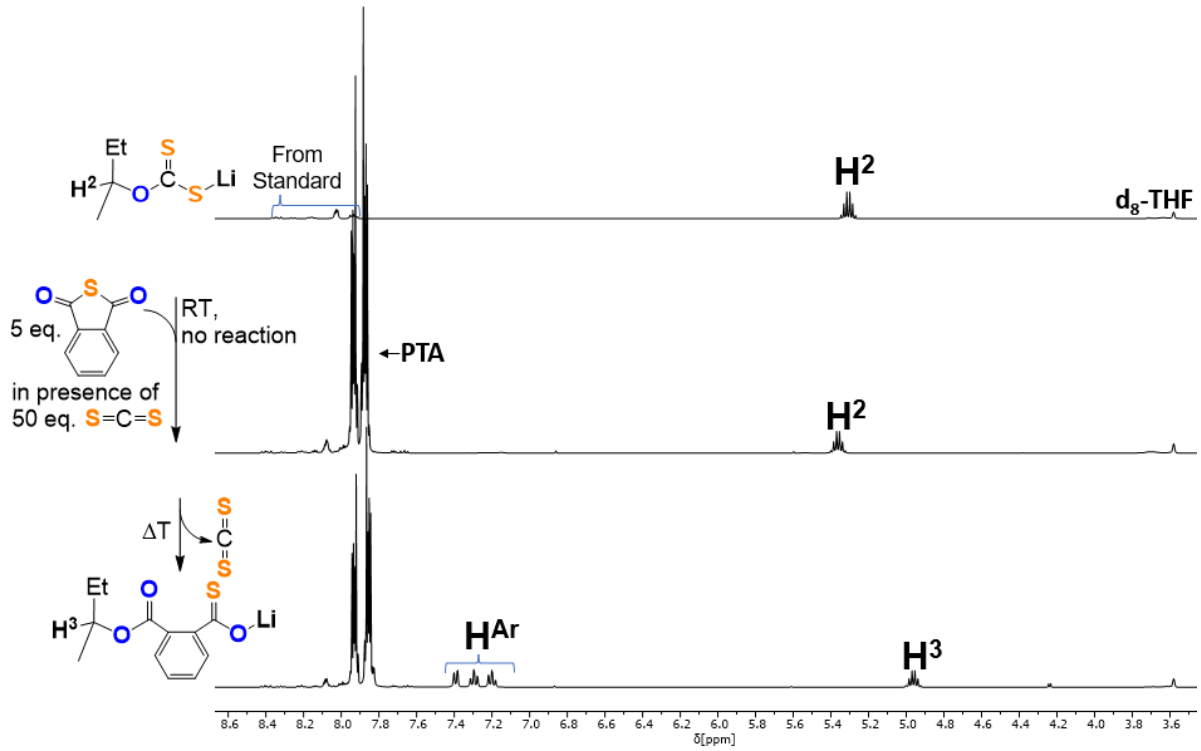
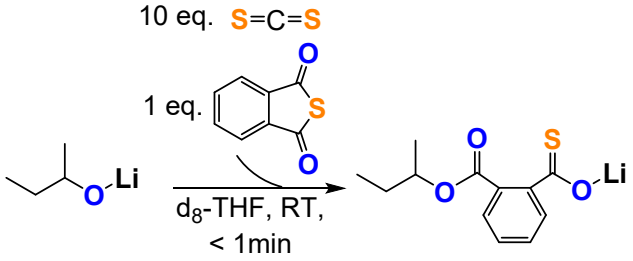


Figure S 15: Overlayed ^{1}H NMR (400 MHz, d_8-THF, 25°C) spectra of PTA/CS_2 exchange experiments starting from DTC.



CS_2-PTA competition: A (10.0 mg, 0.13 mmol, 1 eq.) dissolved in d_8-THF (0.6 mL) and CS_2 (75.4 µL, 10 equiv.) and PTA (20.5 mg, 1 eq.) was added resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR.

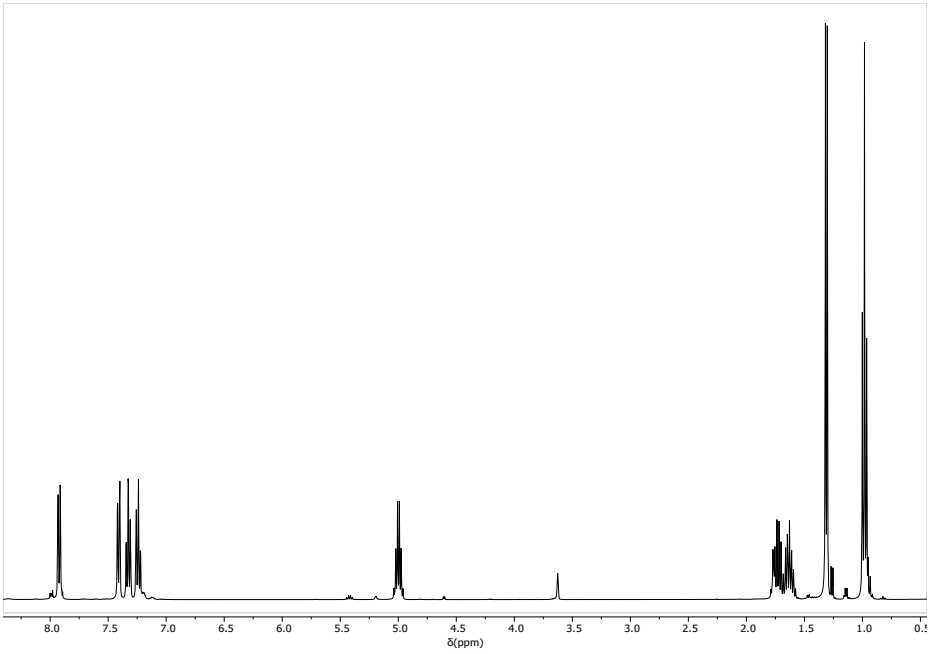
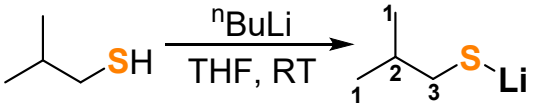


Figure S 16: ^{1}H NMR (400 MHz, d_8-THF, 25°C) spectra from PTA/CS_2 competition experiment.

Section S4: Model experiments from T



Synthesis of T·0.1THF: In an oven dried Schlenk flask 2-methyl-1-propanthiol (1.66 g, 18.41 mmol) was dissolved in THF (25 mL). ^{n}BuLi (7.36 mL of a 2.5 M solution, 1 eq.) was added dropwise at 0°C and the resulting solution warmed to room temperature and stirred for another 30 min. All volatiles were removed in vacuum to yield T·0.1THF as a colourless solid (1.82 g, 17.9 mmol, 97% yield). XRD quality crystals were grown from a saturated THF solution at -80°C.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 3.6 (m, 0.5H, THF), 2.26 (d, *J* = 6.6 Hz, 2H, H-3), 1.75 (m, 0.4 H, THF), 1.47 – 1.40 (m, 1H, H-2), 0.89 (d, *J* = 6.7 Hz, 6H, H-1).

^{13}C NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 68.02 (THF), 35.85 (C2), 35.50 (C3), 26.13 (THF), 22.80 (C1).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.24.

Elemental analysis T·0.1 THF: calculated C 51.2%, H 9.6%; found: C 51.5%, H 9.9%.

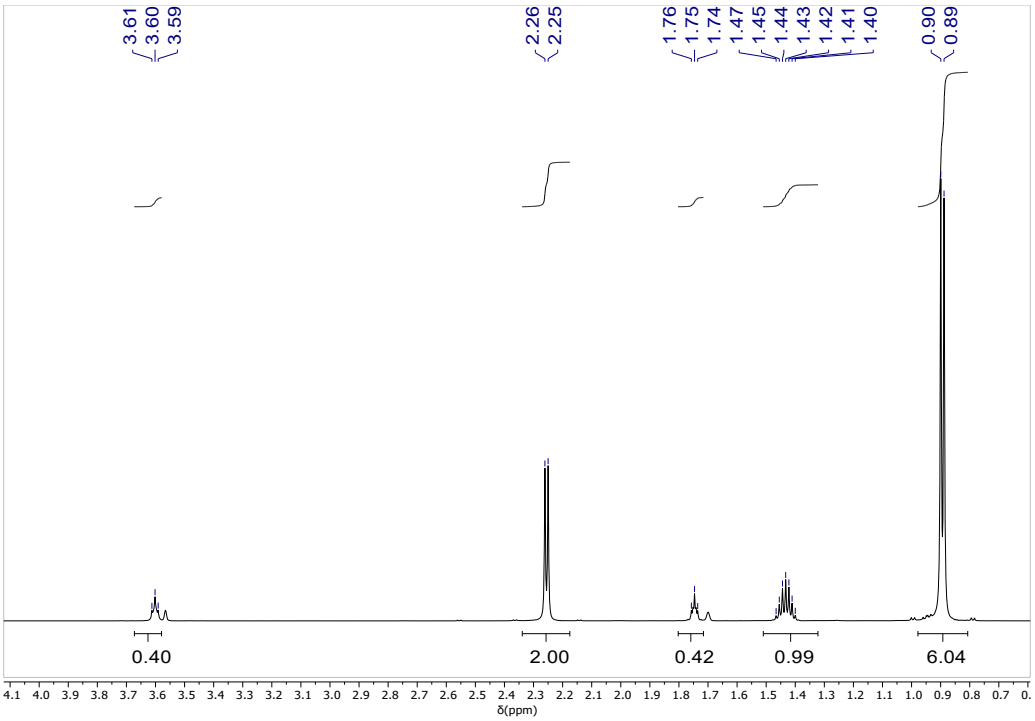


Figure S 17: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of T·0.1 THF. D_6-Acetone signal from internal $LiSO_3CF_3$ reference capillary.

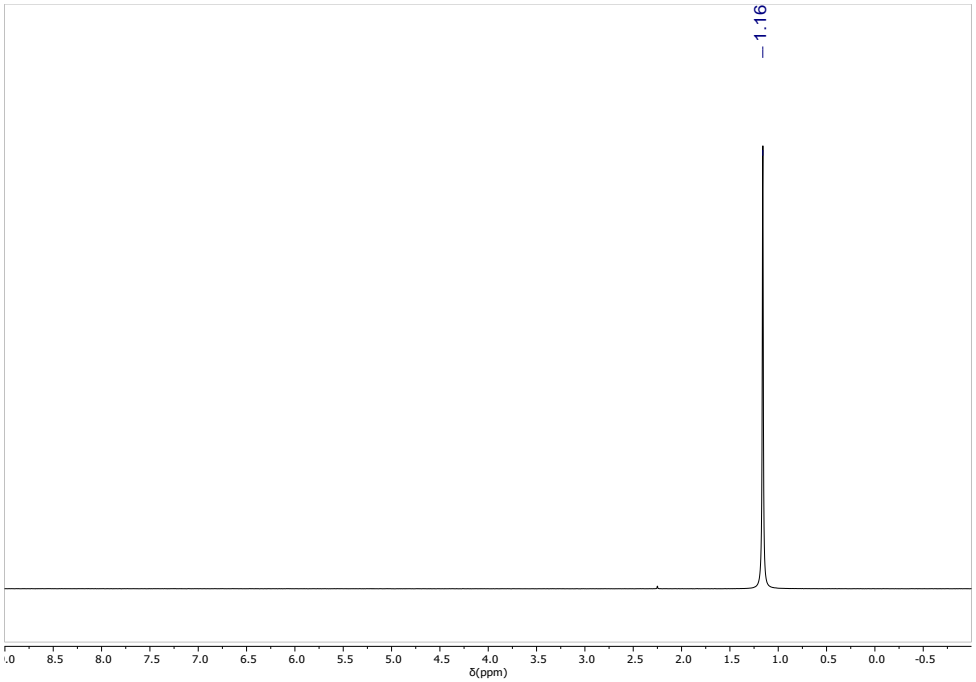


Figure S 18: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of T·0.1 THF. Signal at 2.25 ppm corresponds to internal $LiSO_3CF_3$ standard.

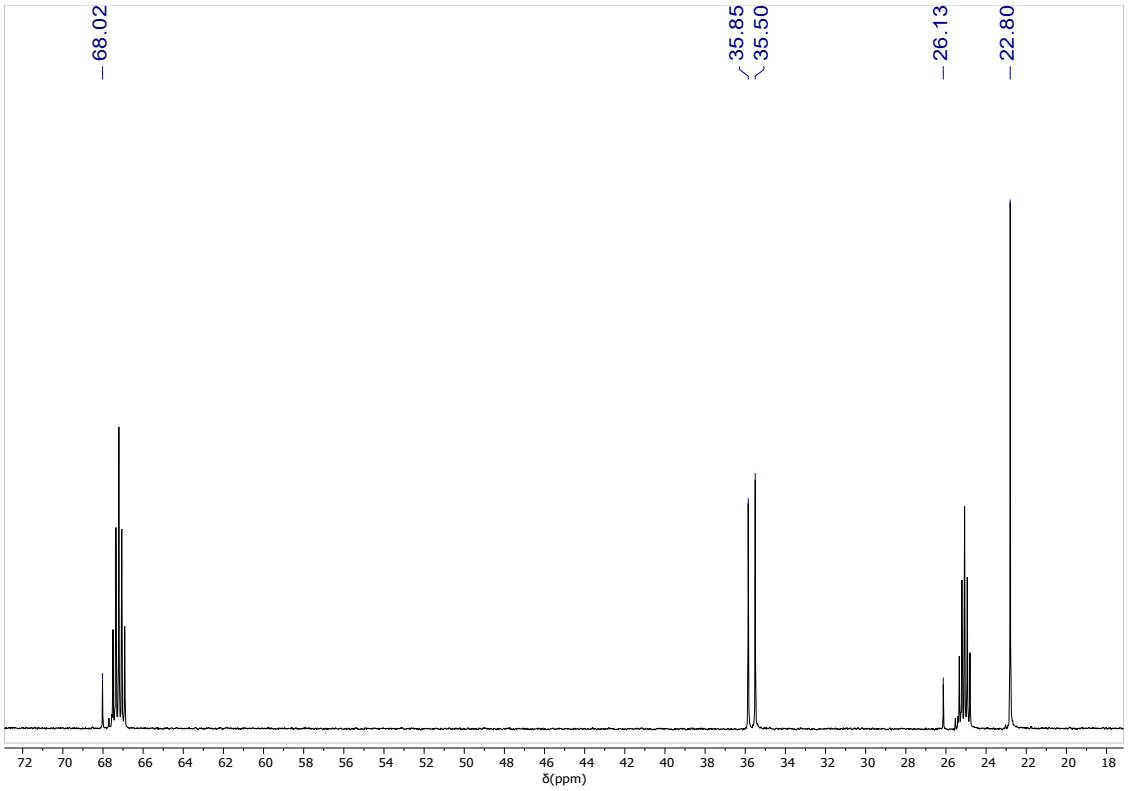
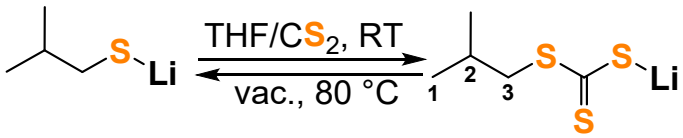


Figure S 19: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, d_8-THF, 25°C) of T·0.1 THF.



CS_2 addition and removal experiment of T: T·0.1 THF (20mg, 0.19 mmol, 1 eq.) dissolved in d_8-THF (0.4 mL) and CS_2 (292 µL, 25 equiv.) was added resulting in the immediate formation of a yellow solution. For FTIR analysis an aliquot was drop casted on the measurement window of the instrument and the solvent was let to evaporate immediately prior to analysis.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 3.00 (d, *J* = 6.8 Hz, 2H, H3), 2.00 – 1.85 (m, 1H, H2), 0.96 (d, *J* = 6.7 Hz, 6H, H1).

$^{13}C\{^{1}H\}$ NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 245.4 (C=S), 49.55 (C-3), 28.89 (C-2), 22.57 (C-1).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.66.

FTIR [cm^{-1}]: $\tilde{\nu}$(C=S) = 996.5.

Afterwards all volatiles were removed in vacuum leaving a solid behind, which was then heated at 80°C in vacuum during which the initial yellow colour disappeared. The resulting solid was taken up in d_8-THF and analysed by NMR.

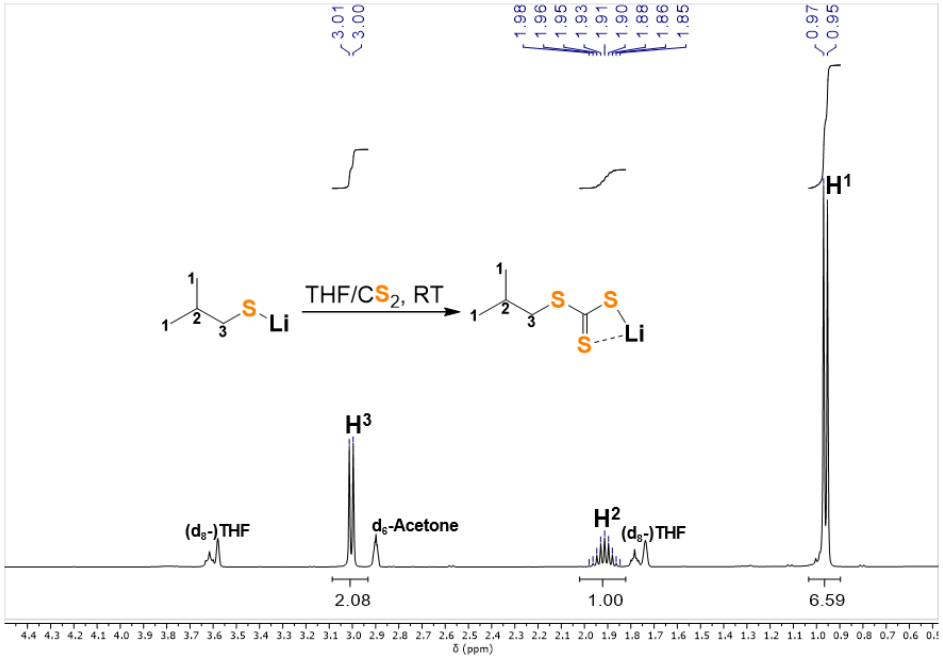


Figure S 20: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of TT. D_6-Acetone signal from internal $LiSO_3CF_3$ reference capillary.

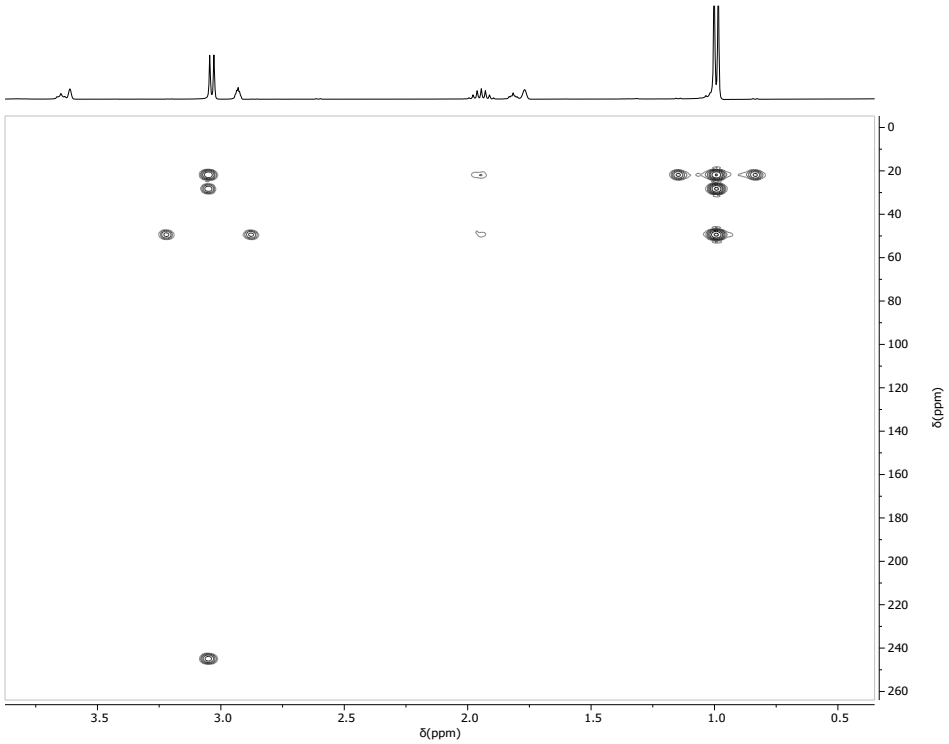


Figure S 21: ^{1}H-^{13}C HMBC NMR spectrum (d_8-THF, 25°C) of TT.

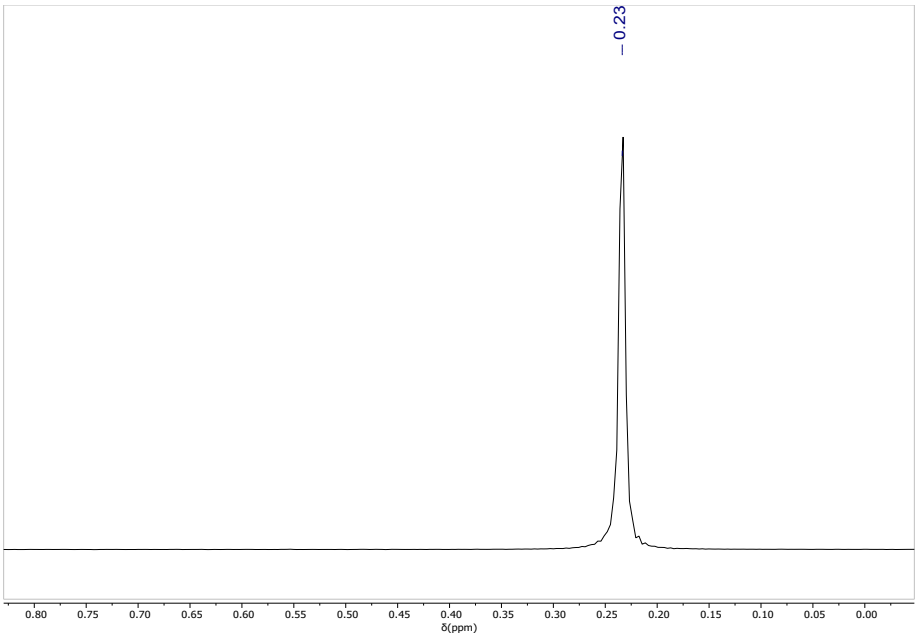


Figure S 22: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of TT.

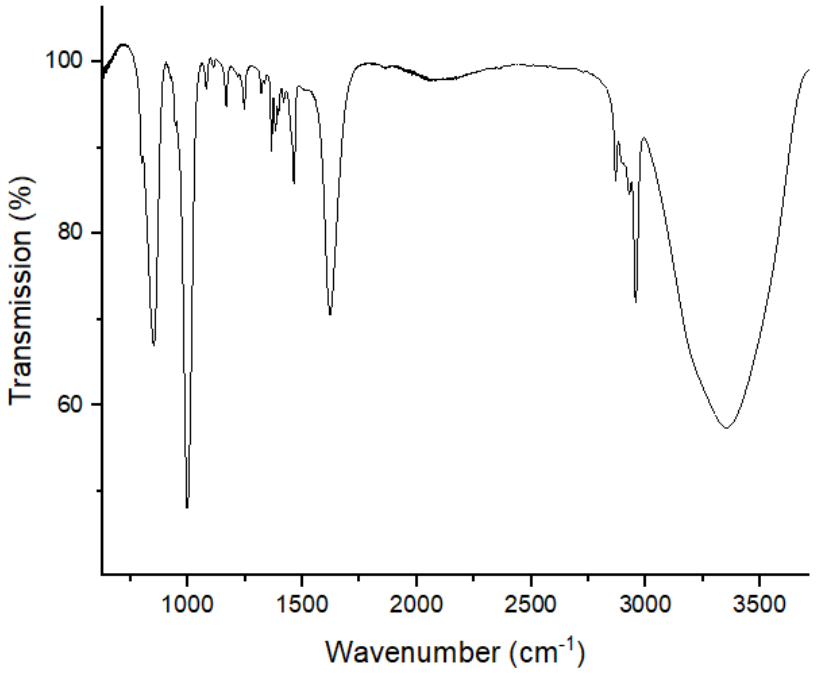


Figure S 23: Solid state FTIR spectrum of TT. Resonance at ca. 1600 cm^{-1} from residual CS_2.

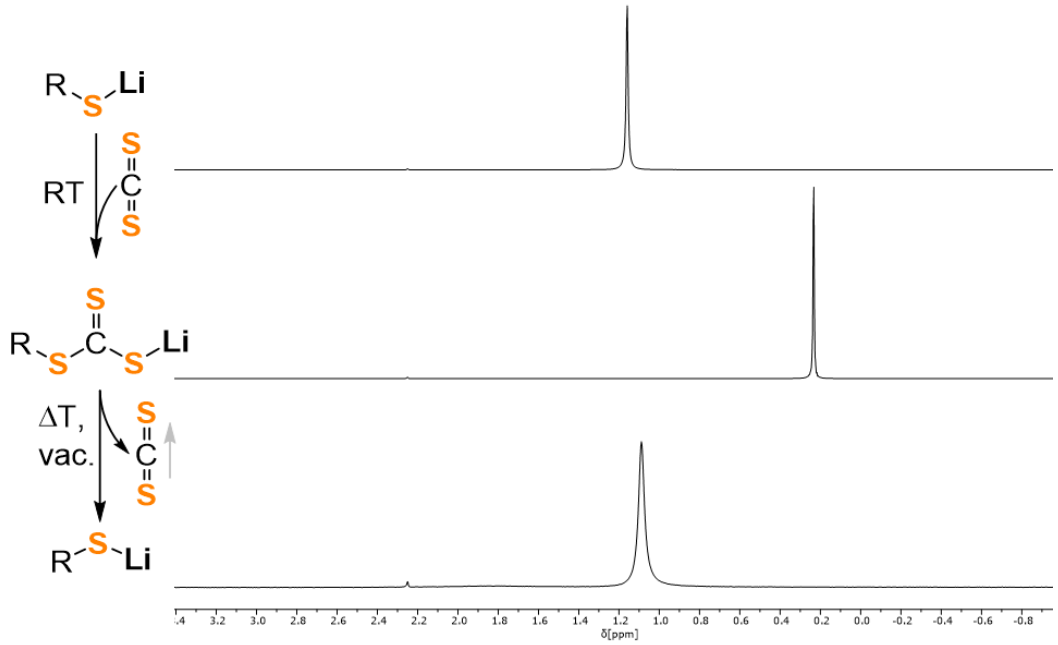


Figure S 24: Overlayed ^{7}Li NMR spectra (156 MHz, d_8-THF, 25°C) of CS_2 addition and removal from T. Signal at 2.25 ppm corresponds to internal $LiSO_3CF_3$ standard.

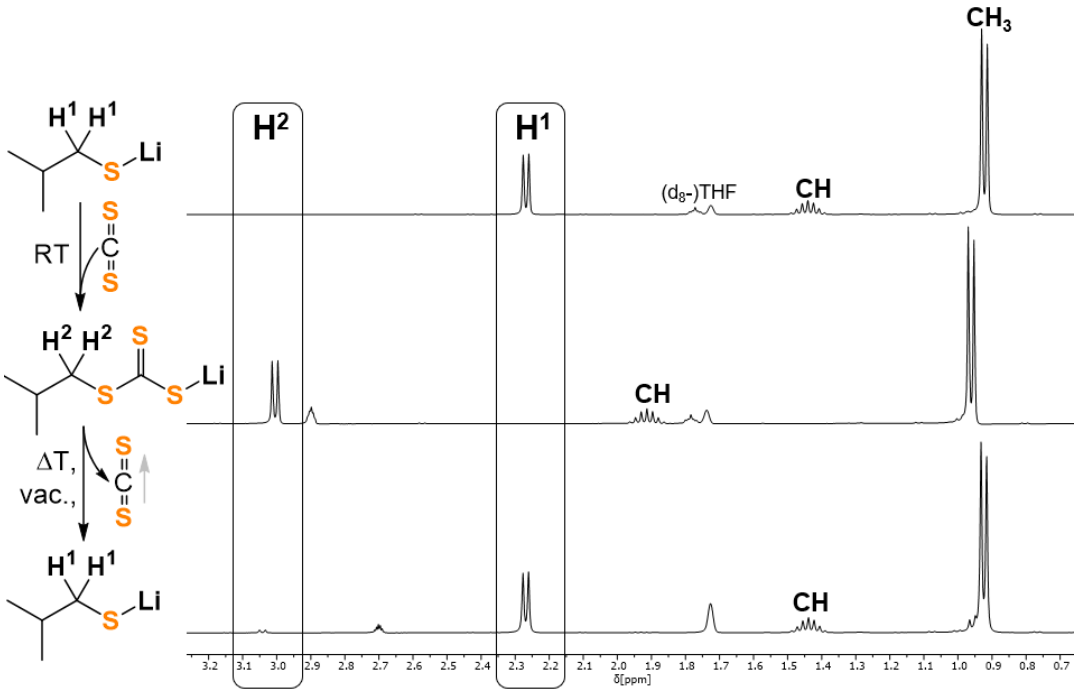
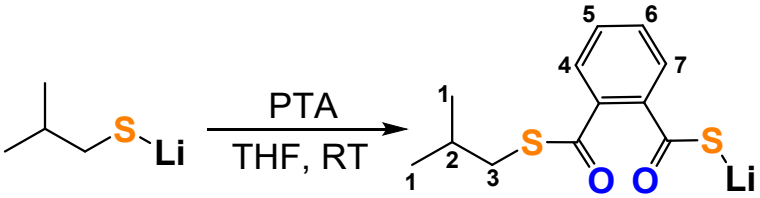


Figure S 25: Overlayed ^{1}H NMR spectra (400 MHz, d_8-THF, 25°C) of CS_2 addition and removal from T.



Synthesis of TC': T·0.1 THF (10.0 mg, 0.10 mmol, 1 eq.) and PTA (15.9 mg, 0.09 mmol, 1 eq.) were dissolved in d_8-THF (0.8 mL) resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. For FTIR analysis an aliquot was drop casted on the measurement window of the instrument and the solvent was let to evaporate immediately prior to analysis.

^{1}H NMR (400 MHz, d_8-THF, 25°C); δ(ppm): 8.17 – 7.99 (m, 1H, H7), 7.49 – 7.10 (m, 3H, H4/H5/H6), 2.85 (d, *J* = 6.7 Hz, 2H, H3), 1.90 – 1.80 (m, 1H, H2), 0.98 (d, *J* = 6.7 Hz, 6H, H1).

^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 25°C); δ(ppm): 218.02 (R(C=O)SLi), 169.07 (R(C=O)OR), 148.47 (C_q(R(C=O)SLi)), 131.50 – 125.25 (C-5, C-6, C-7, C-8, C_q(R(C=O)OR), 72.57 (C-2), 28.84 (C-3), 17.90 (C-1), 9.01 (C-4).

^{7}Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.65.

FTIR [cm^{-1}]: ṽ(C=O) = 1689.1, 1556.3.

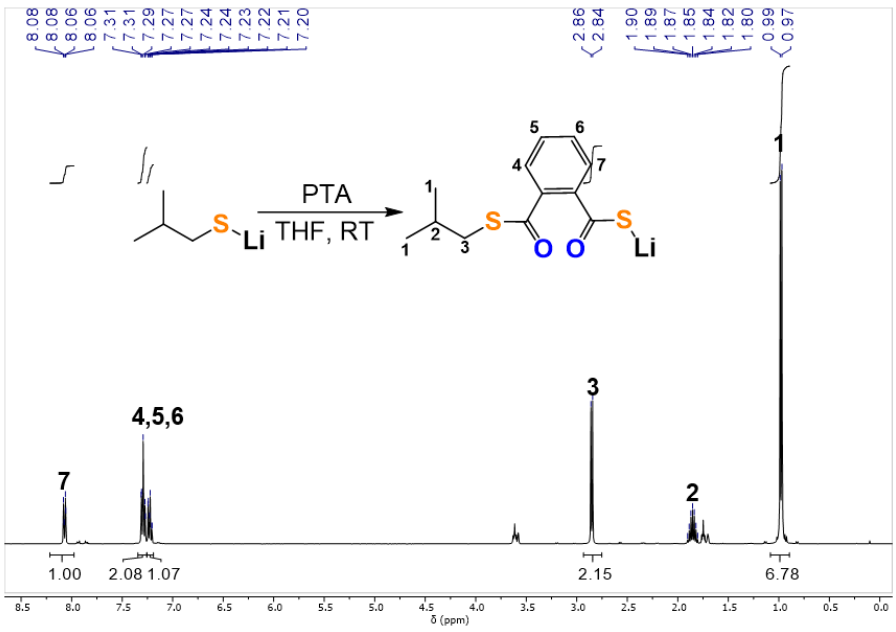


Figure S 26: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of TC'.

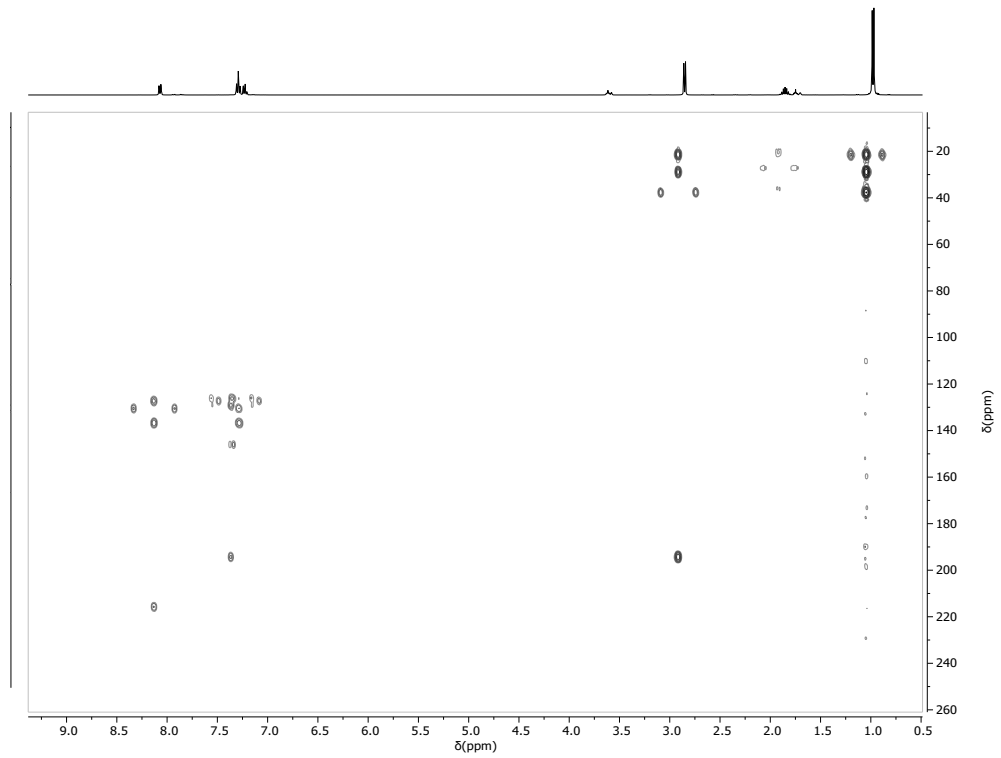


Figure S 27: ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, d_8-THF, 25°C) of TC'.

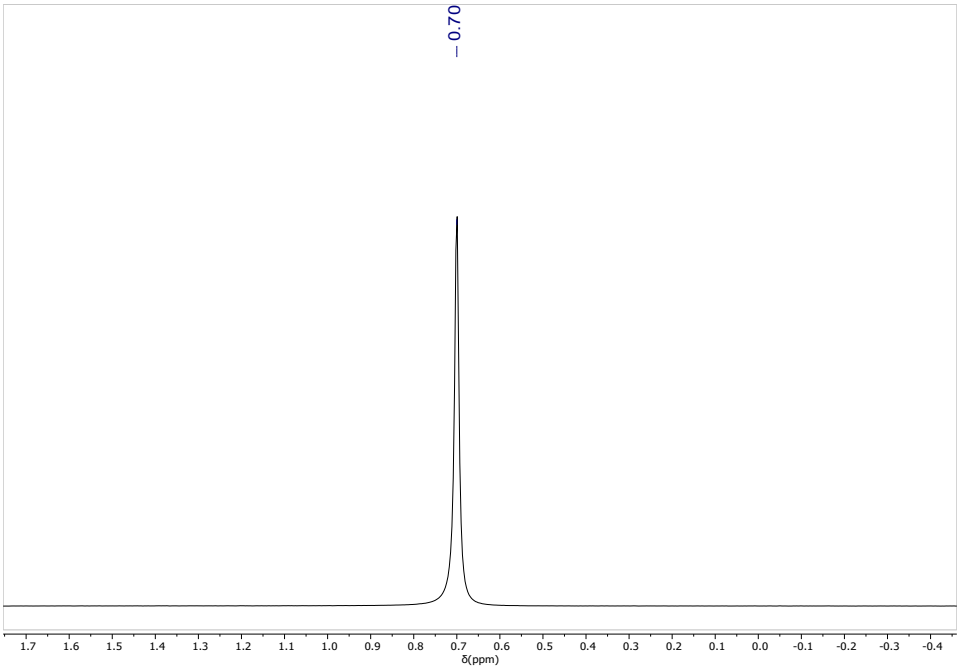


Figure S 28: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of TC'.

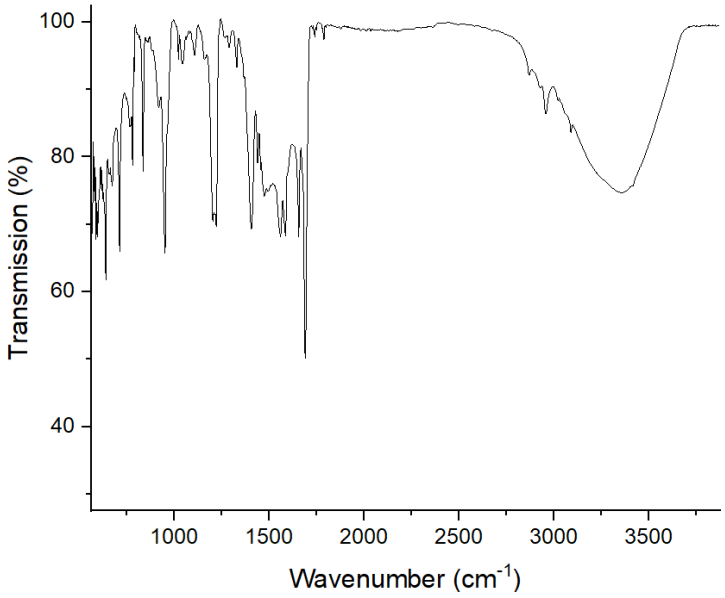


Figure S 29: Solid state FTIR spectrum of TC'.

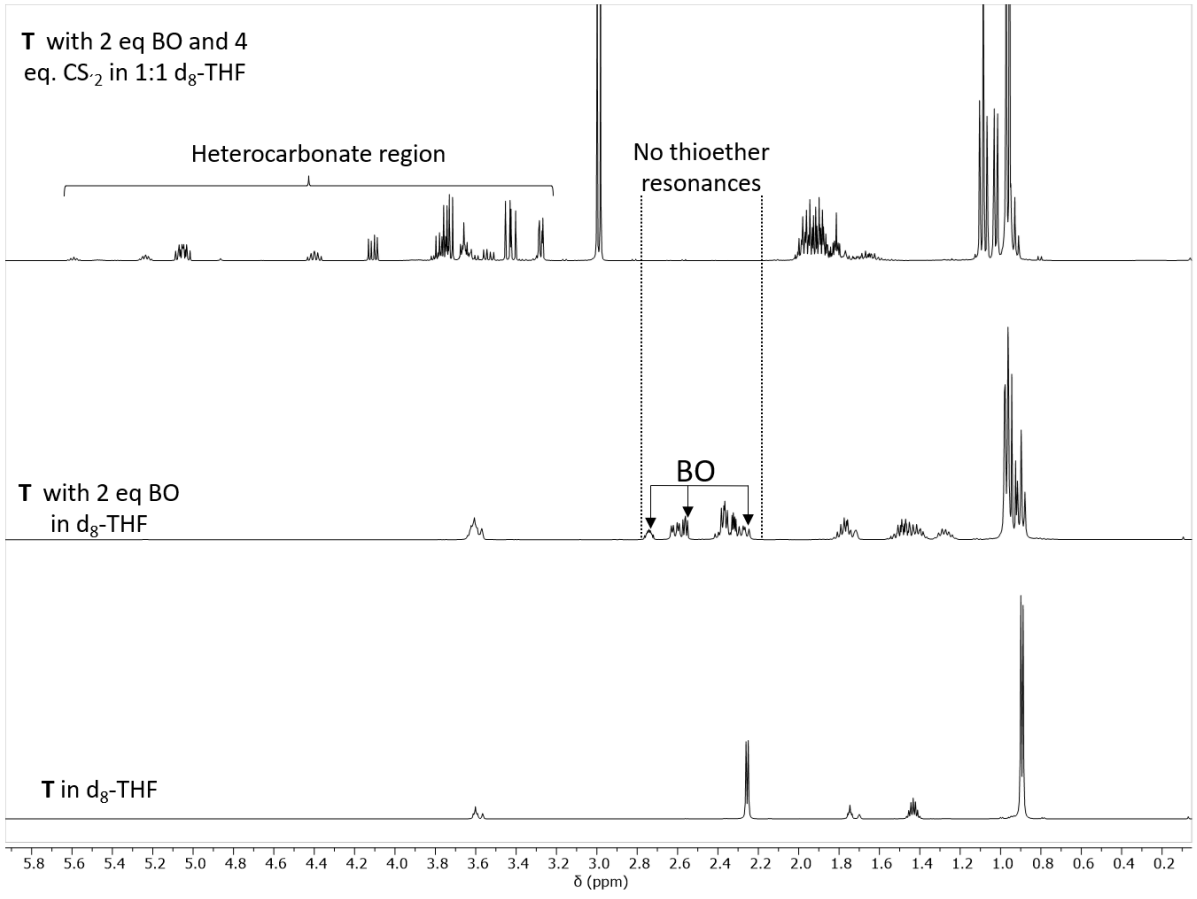
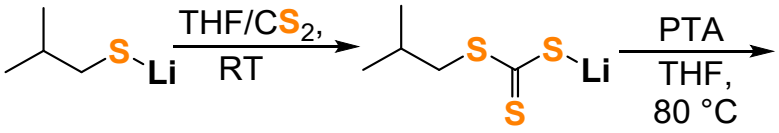


Figure S 30: Overlayed ^{1}H NMR spectra (400 MHz, d_8-THF, 25°C) of T reacted with BO in absence and presence of CS_2.



Attempted CS_2-PTA exchange: T·0.1 THF (10mg, 0.1 mmol, 1 eq.) dissolved in d_8-THF (0.6 mL) and CS_2 (292.8 µL, 50 equiv) was added resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. Afterwards PTA (79.6 mg, 05 eq.) was added and the mixture was heated at 80°C overnight and then analysed by NMR.

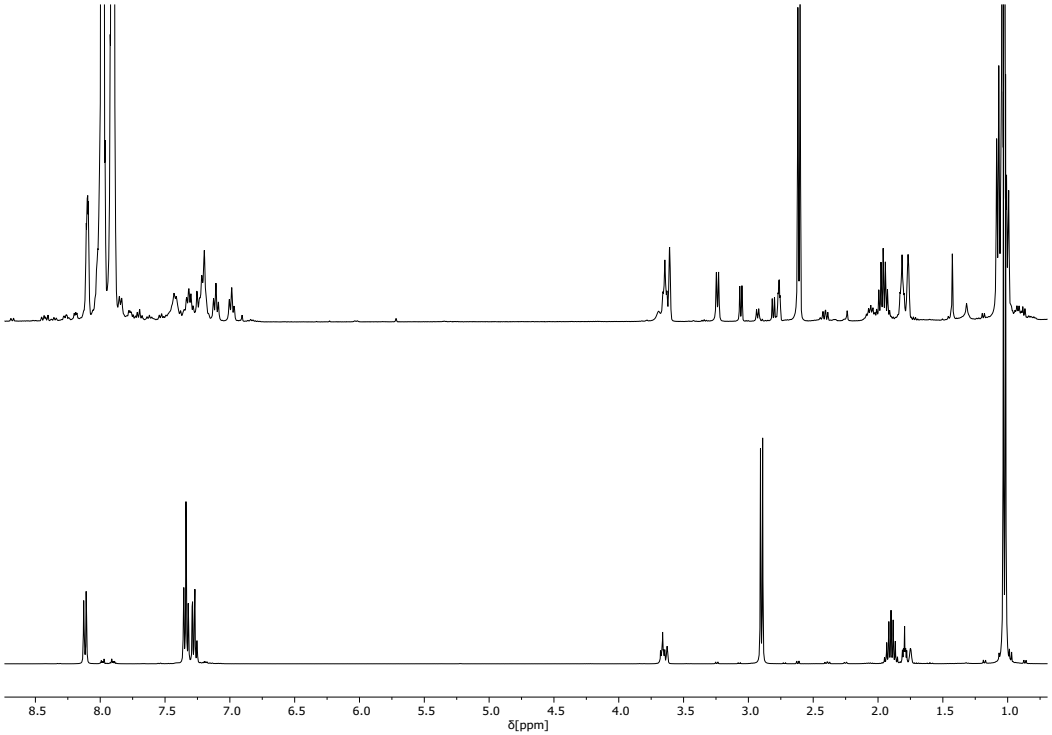
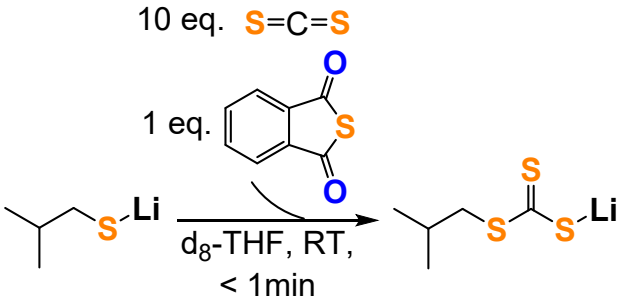


Figure S 31: Overlayed ^{1}H NMR spectra (400 MHz, d_8-THF, 25°C) of attempted PTA exchange from TT; (top) mixture obtained from attempted exchange; (bottom) ^{1}H NMR spectrum of TC'.



CS_2-PTA competition: T·0.1 THF (12.7 mg, 0.12 mmol, 1 eq.) dissolved in d_8-THF (0.3 mL) and CS_2 (74.4 µL, 10 equiv.) and PTA (20.2 mg, 1 eq.) in d_8-THF (0.3 mL) was added resulting in the immediate formation of a yellow solution. The mixture was analysed by NMR. In an analogous fashion the experiment was also conducted with lower amounts of CS_2 (1 eq., 2 eq. and 5 eq.).

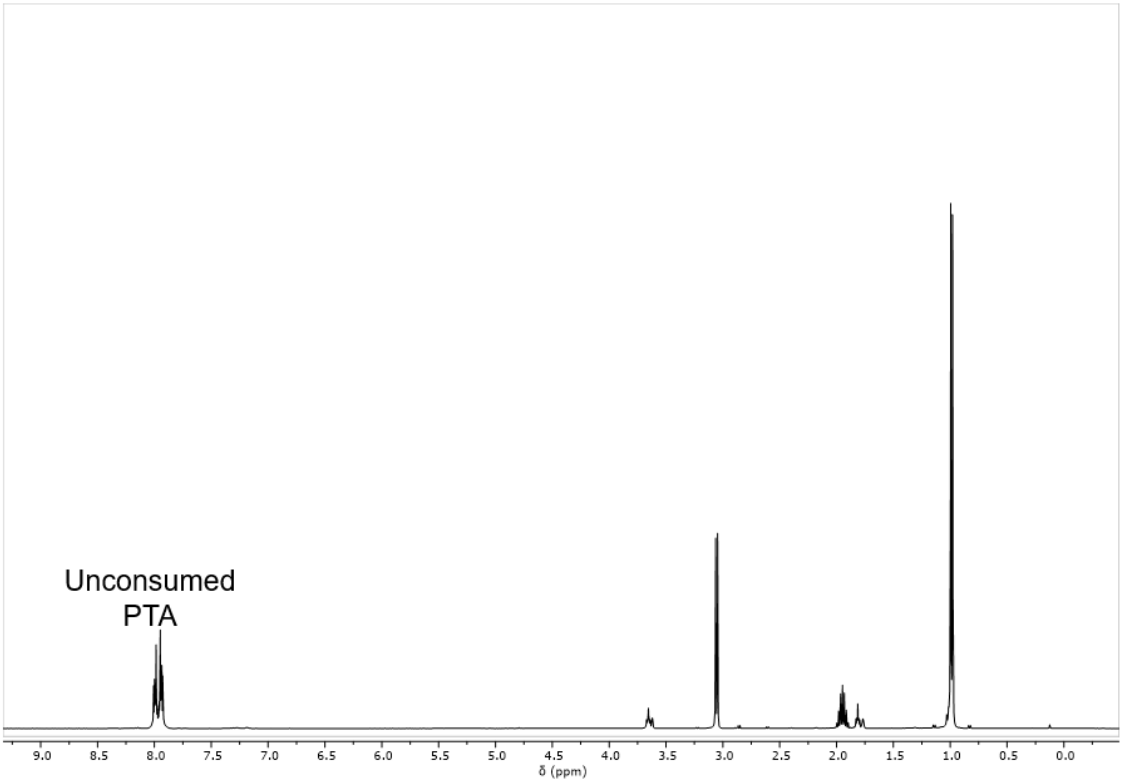


Figure S 32: ^{1}H NMR (400 MHz, d_8-THF, 25°C) spectra from PTA/CS_2 competition experiment.

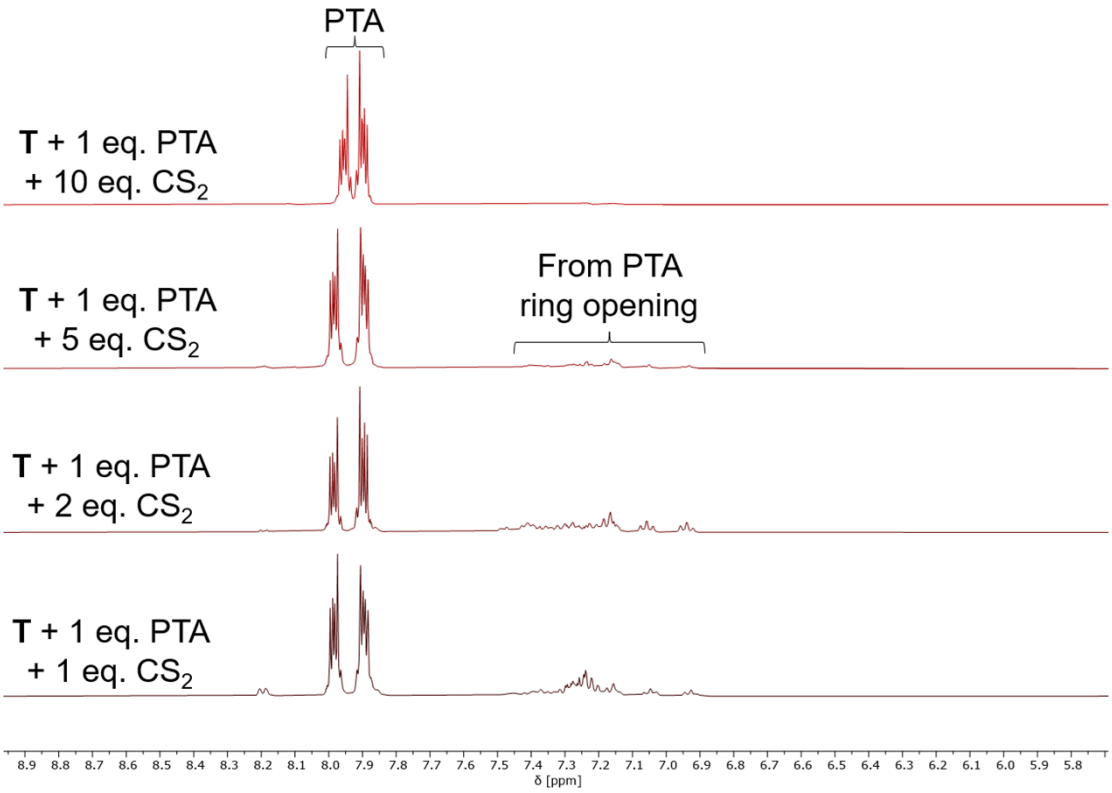
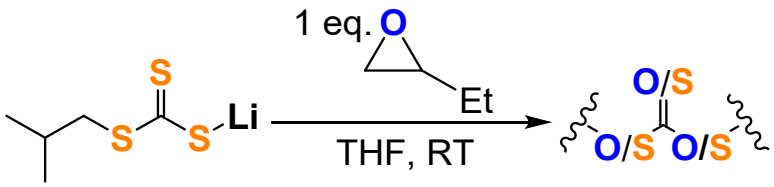


Figure S 33: Aromatic region of the ^{1}H NMR (400 MHz, d_8-THF, 25°C) spectra from PTA/CS_2 competition experiment with different relative amounts of PTA and CS_2.

Section S5: Model experiments for O/S scrambling and O/S exchange



O/S Scrambling from TT: In an oven dried J. Youngs NMR Tube T·0.1 THF (85.0 mg, 0.82 mmol, 1 eq.) dissolved in d_8-THF (0.6 mL) and CS_2 (50 µL,1 equiv) was added. The mixture was let react for 3 min and afterwards BO (72 µL, 1 eq.). Afterwards the mixture was analysed by NMR.

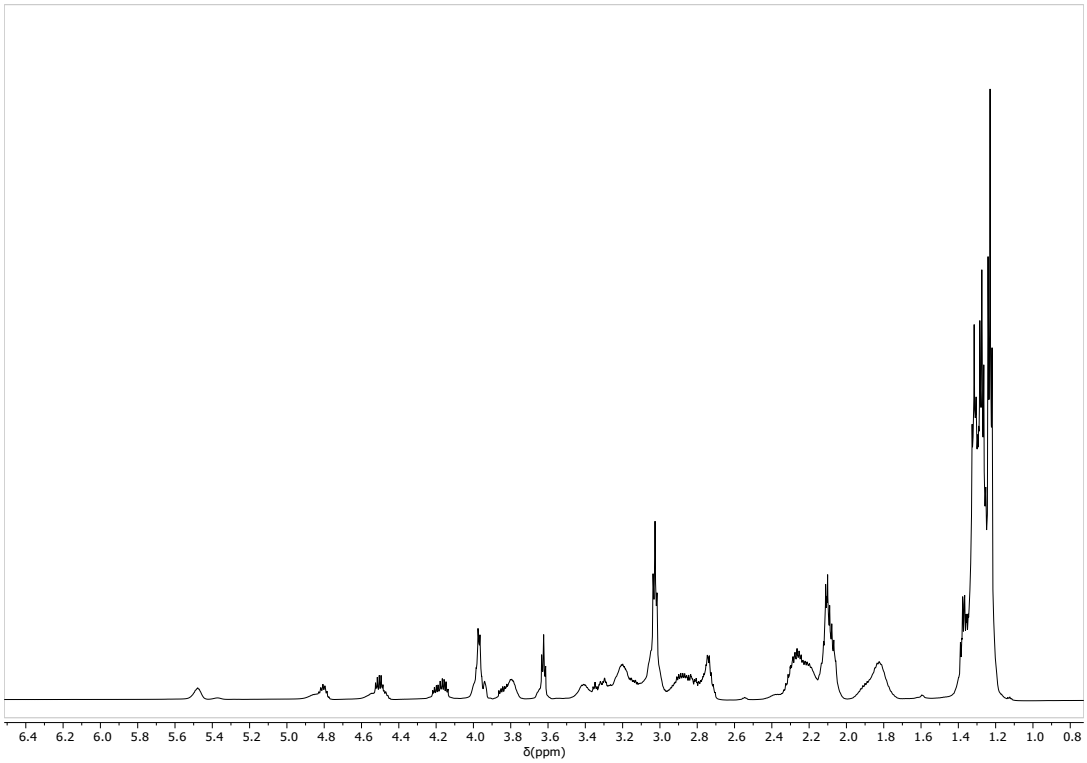


Figure S 34: ^{1}H- spectrum (400 MHz, d_8-THF, 25°C) of product mixture obtained from O/S scrambling from TT.

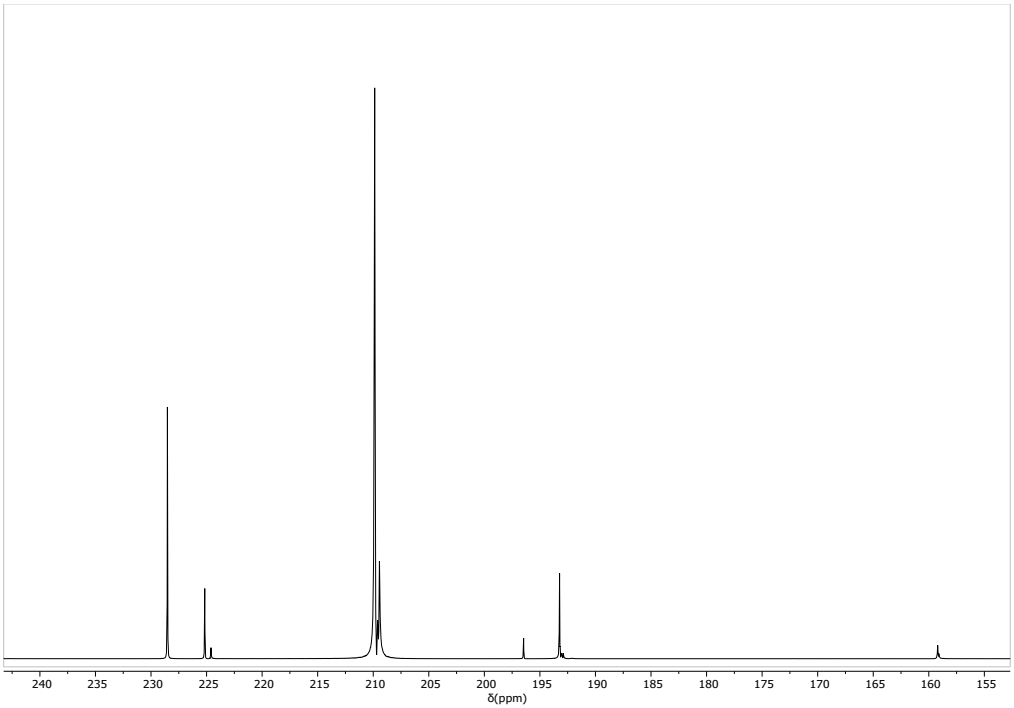
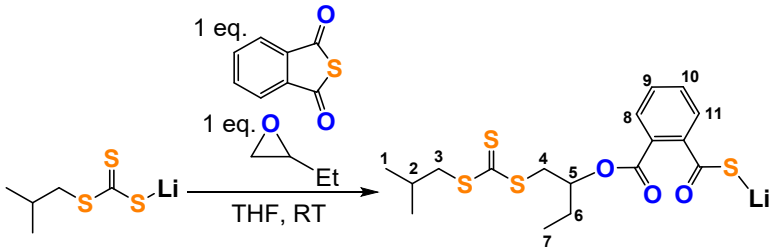


Figure S 35: Heterocarbonate region of ^{13}C NMR spectrum (151 MHz, d_8-THF, 25°C) of product mixture obtained from O/S Scrambling from TT



Attempted O/S scrambling in presence of PTA: T·0.1 THF (85mg, 0.82 mmol, 1 eq.) dissolved in d_8-THF (0.6 mL) and CS_2 (50 µL,1 eq.) was added. The mixture was let react for 1 min and afterwards BO (72 µL, 1 eq.). and PTA (135.0 mg, 1 eq.) in d_8-THF (0.3 mL) were added. Afterwards the mixture was analysed by NMR. For FTIR analysis an aliquot was drop casted on the measurement window of the instrument and the solvent was let to evaporate immediately prior to analysis.

^1H NMR (400 MHz, d_8-THF, 25°C): δ[ppm] = 7.91 (d, J = 6.9 Hz, 1H, H11), 7.43 (d, J = 7.6 Hz, 1H, H8), 7.38 – 7.30 (m, 1H, H9/10), 7.30 – 7.22 (t, J = 8.0 Hz, 1H, H9/10), 5.22 (p, J = 6.1 Hz, 1H, H5), 4.15 – 3.74 (m, 2H, H4), 3.36 (d, J = 6.7 Hz, 2H, H3), 2.05 –1.57 (m, H2, H6), 1.30 – 0.65 (m, 9H, H1, H7).

^{13}C NMR (151 MHz, d_8-THF, 25°C): δ[ppm] = 224.32, 217.11, 192.67, 168.57, 147.93, 129.41, 129.10, 127.40, 127.06, 73.58, 45.20, 39.38, 28.17, 26.20, 21.50, 9.38.

^7Li NMR (156 MHz, d_8-THF, 25°C); δ(ppm): 0.62.

FTIR [cm^{-1}]: ṽ(C=O) = 1700.0, 1494.3; ṽ(C=S) = 1054.0

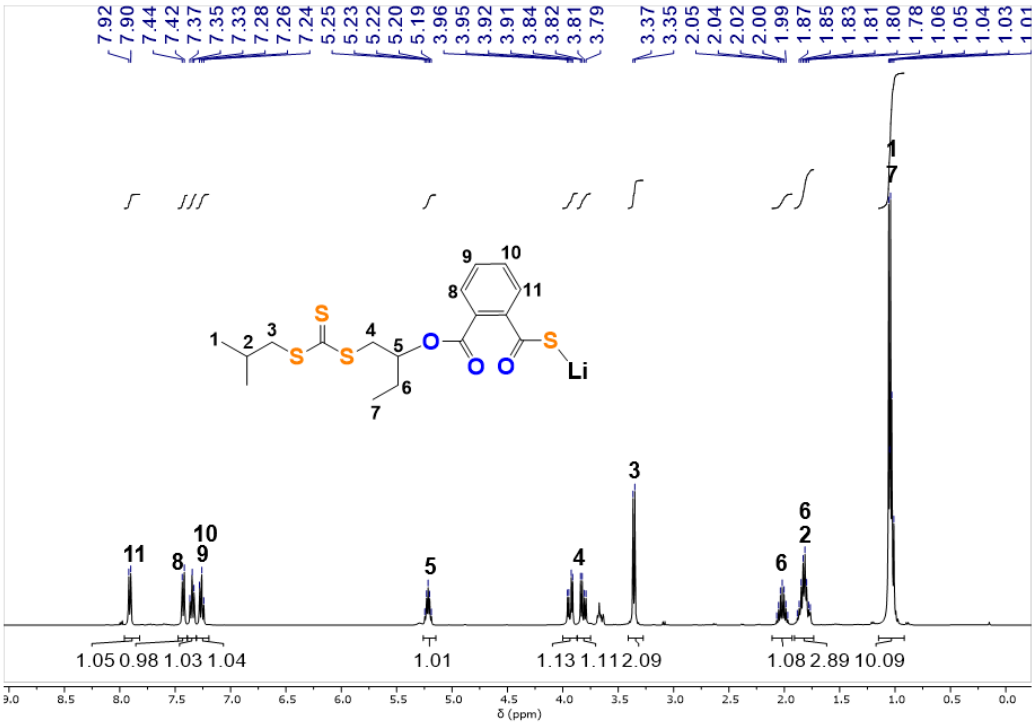


Figure S 36: ^{1}H NMR spectrum (400 MHz, d_8-THF, 25°C) of TC*.

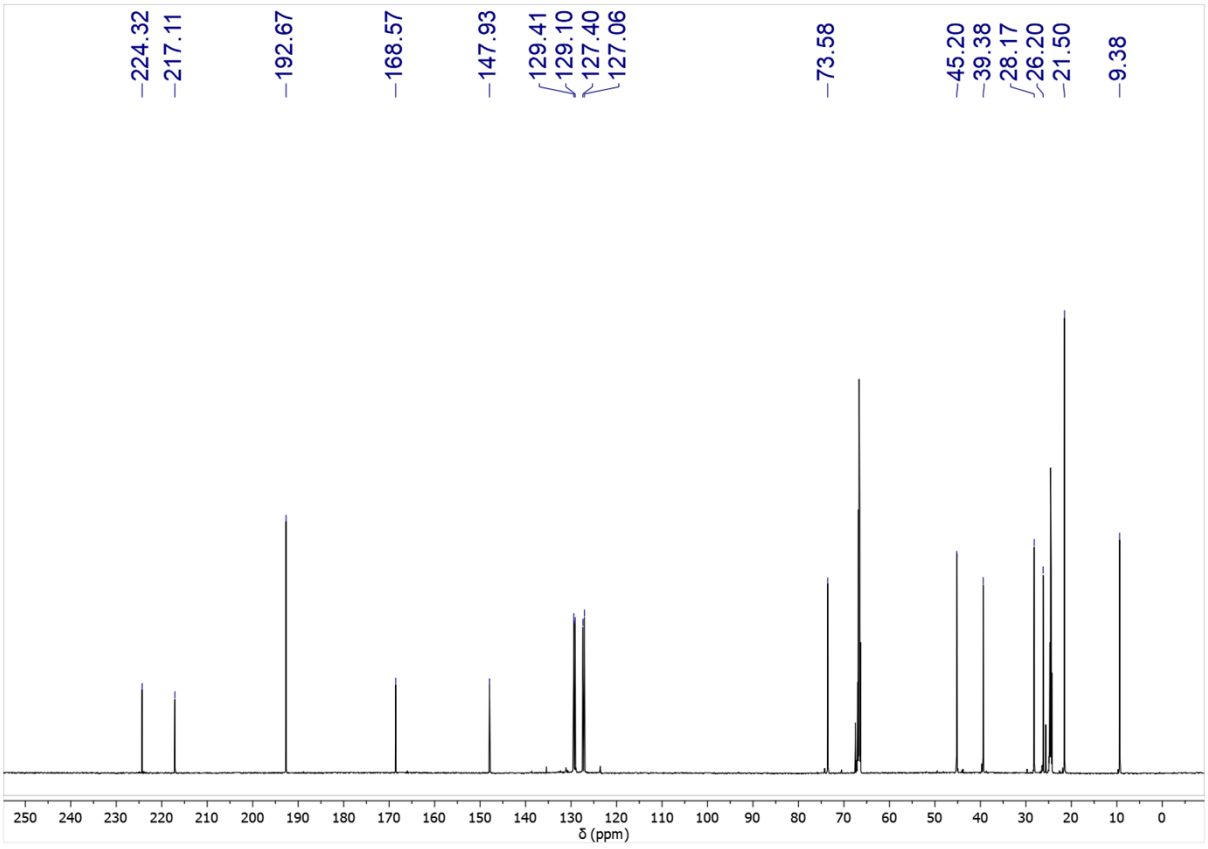


Figure S 37: ^{13}C NMR spectrum (151 MHz, d_8-THF, 25°C) of TC*.

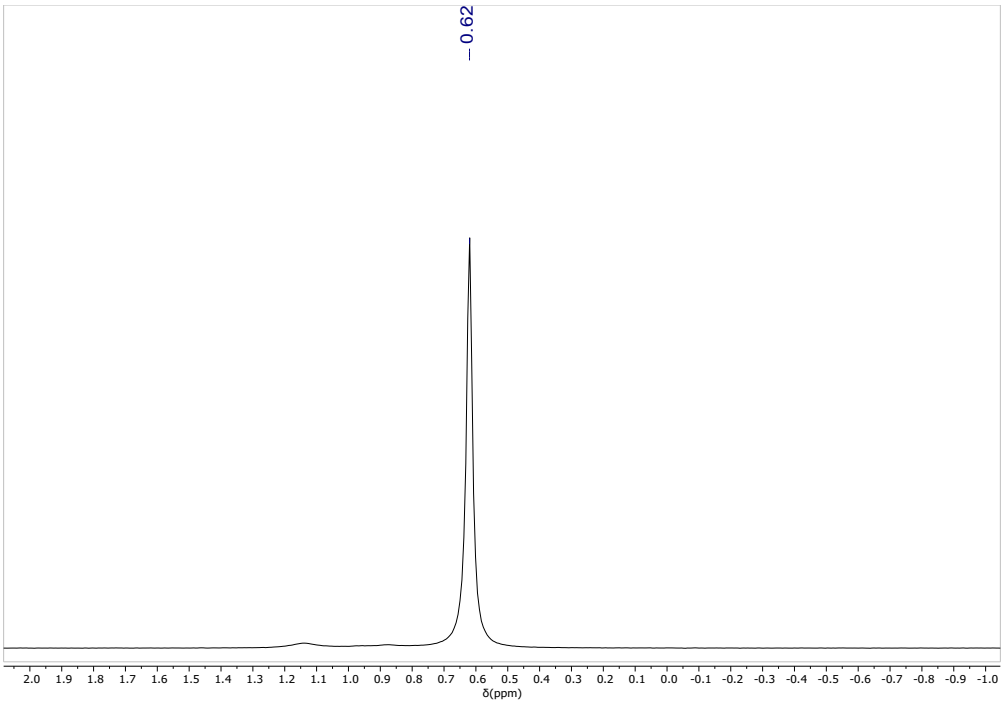


Figure S 38: ^{7}Li NMR spectrum (156 MHz, d_8-THF, 25°C) of TC*.

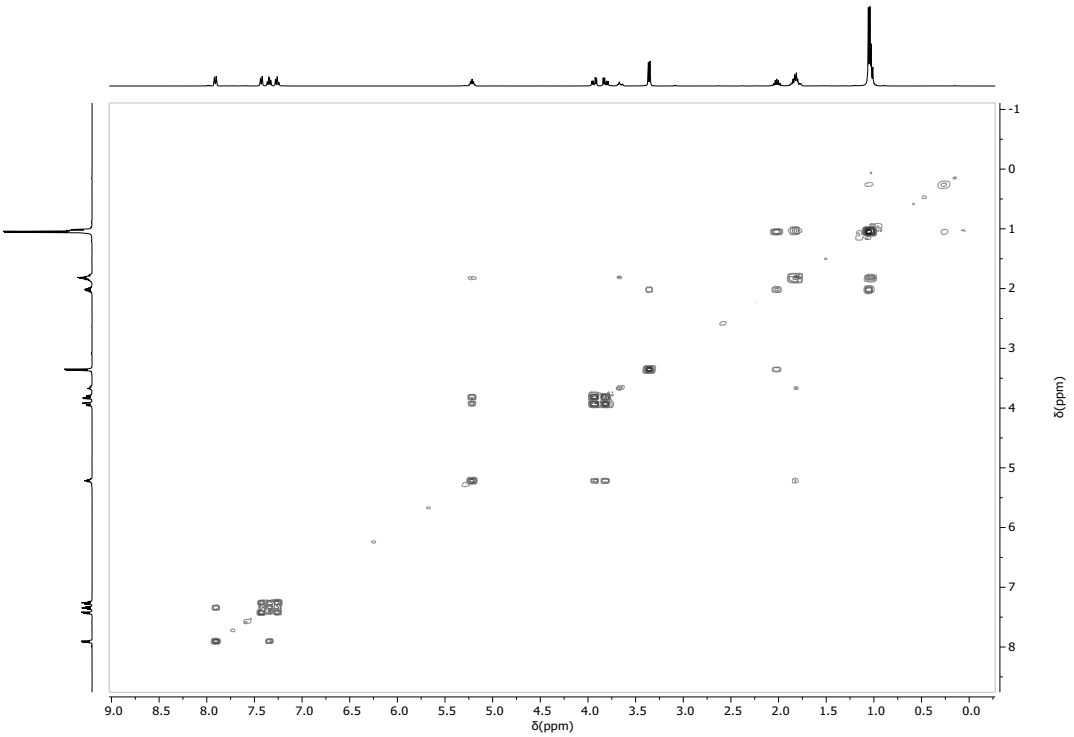


Figure S 39: ^{1}H-^{1}H COSY NMR spectrum (d_8-THF, 25°C) of TC*.

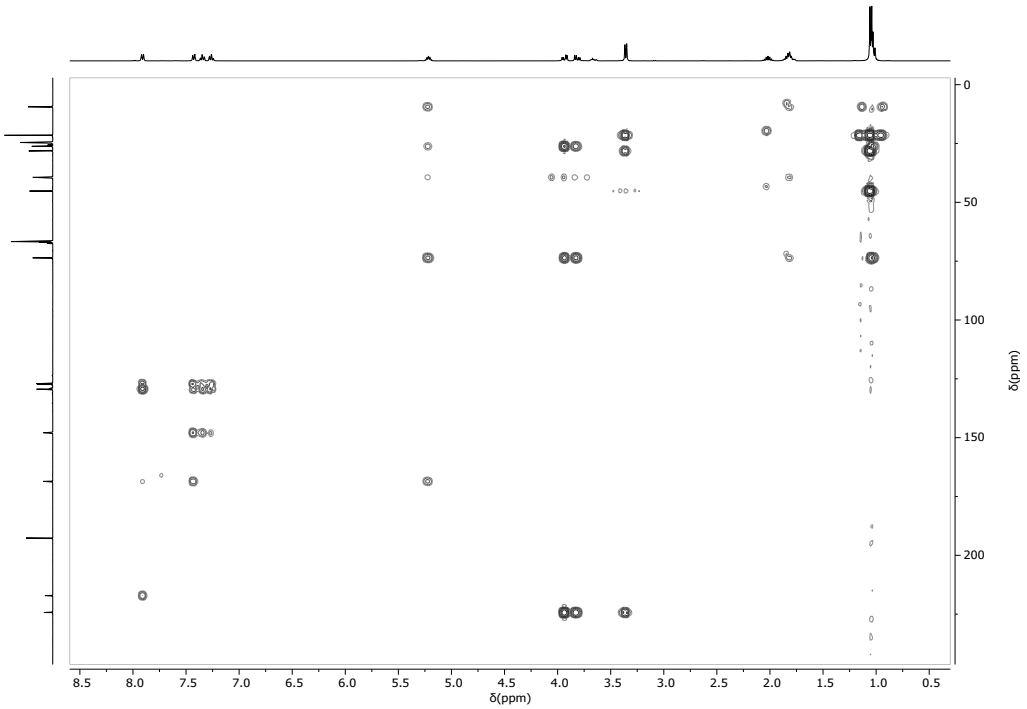


Figure S 40: ^{1}H-^{13}C HMBC NMR spectrum (d_8-THF, 25°C) of TC*.

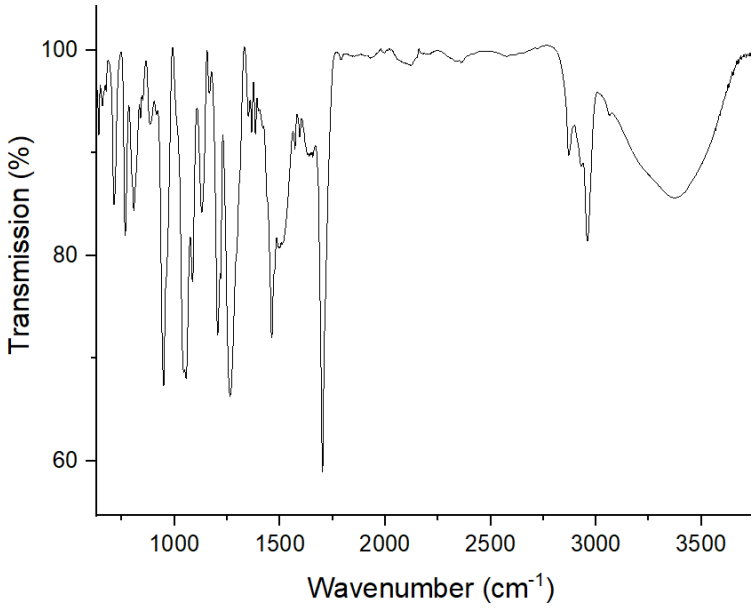
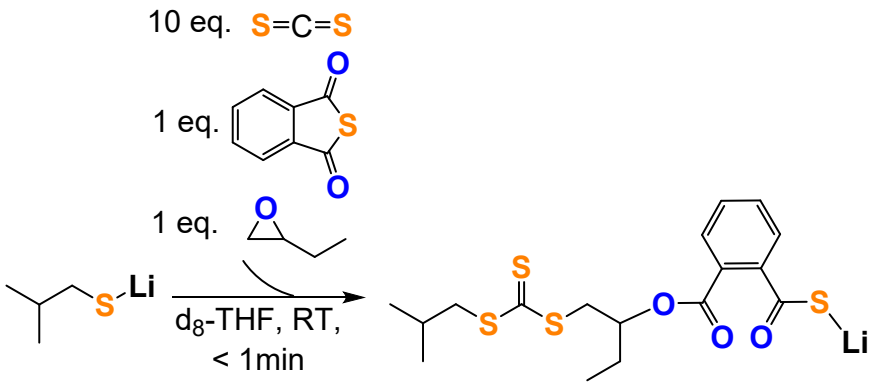
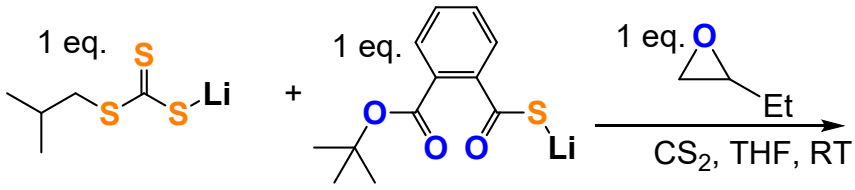


Figure S 41: Solid state FTIR spectrum of TC*.



Four component cascade: T·0.1 THF (85.0 mg, 0.82 mmol, 1 eq.) dissolved in d_8-THF (0.3 mL). CS_2 (496 µL,10 eq.), BO (72 µL, 1 eq.). and PTA (135.0 mg, 1 eq.) in d_8-THF (0.3 mL) were added. Afterwards the mixture was analysed by NMR.

Section S6: Resting state experiments



TT vs. TC competition experiment: T·0.1 THF (20.0 mg, 0.19 mmol, 1 eq.) and the ^{t}Bu derivative of TC·0.75 THF (57.8 mg, 1 eq.) were dissolved in d_8-THF (0.6 mL) and a CS_2 (117 µL,10 equiv) was added. Then BO (16.8 µL, 1 eq.). was added. Afterwards the mixture was analysed by NMR.

Polymerisation protocol for aliquot analysis: In an argon-filled glovebox, the appropriate amount of LiHMDS and BnOH were dissolved in butylene oxide and the mixture was transferred to a Schlenk flask equipped with a dried stirrer bar. CS_2 and/or PTA and/or additional toluene were then added and the vial was brought outside the glovebox, connected to a Schlenk line and placed in a pre-heated oil bath at 25°C. Aliquots (50 µl of the reaction mixture) were removed under a stream of argon at the specified times and analysed by ^{1}H NMR in $CDCl_3$.

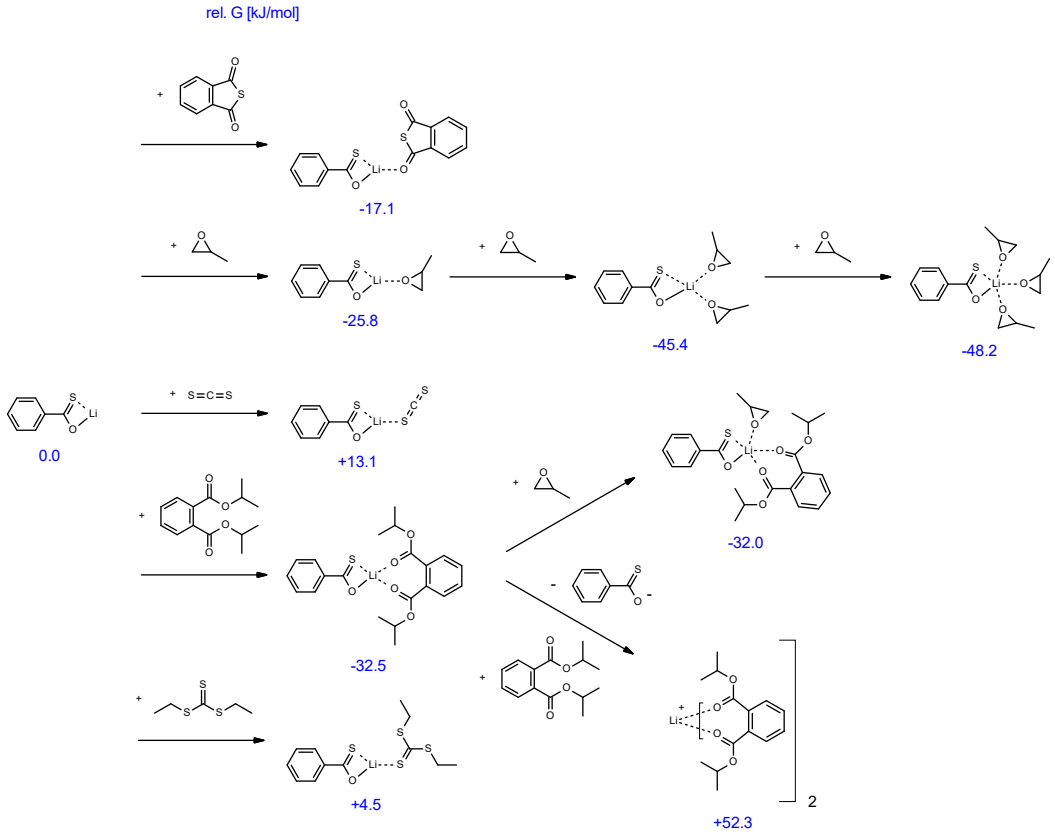
Section S7: Crystallography

Table S1. Crystallographic data.

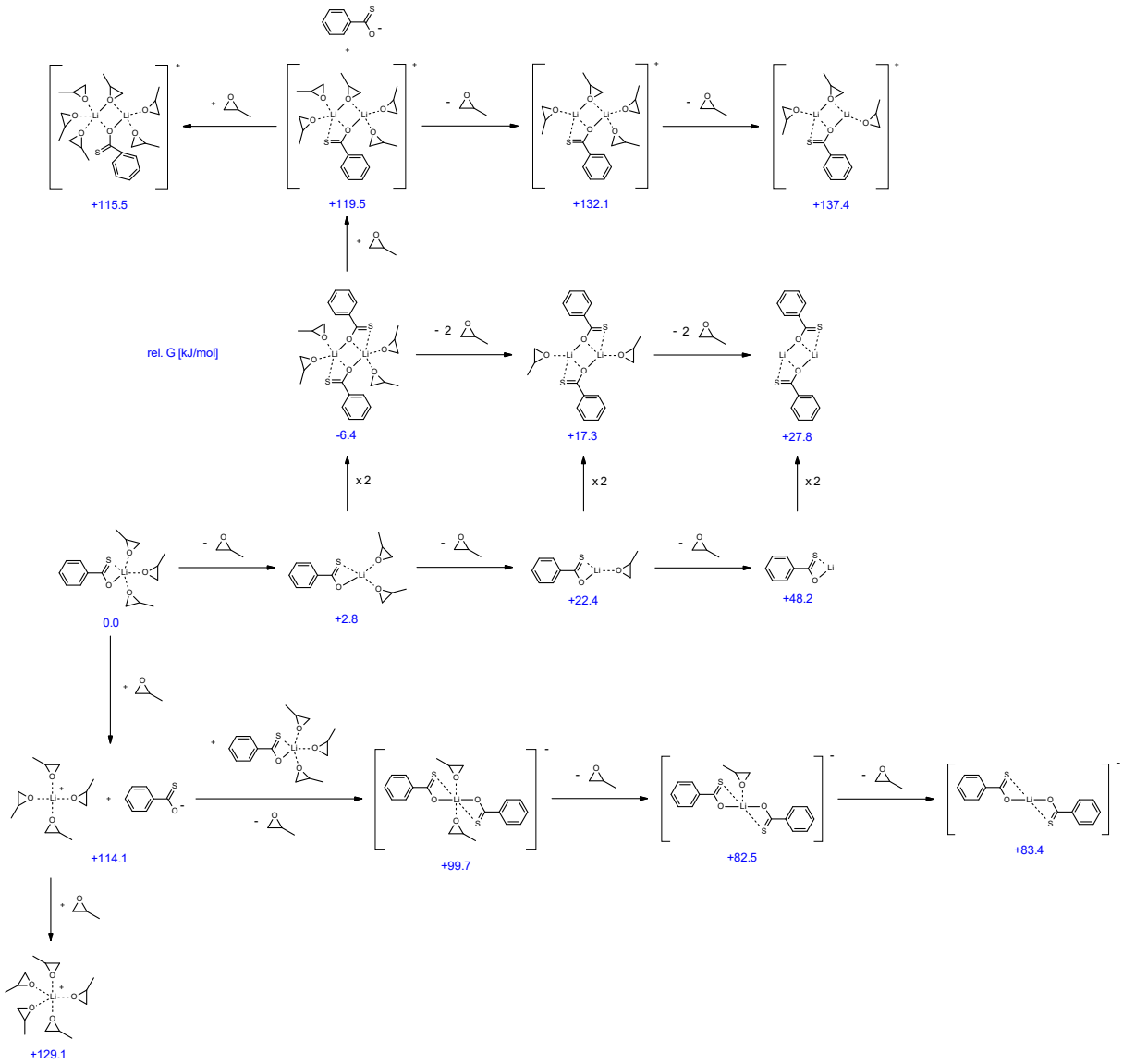
Compound	A	T
Empirical formula	$C_8H_{17}LiO_2$	$C_8H_{17}LiOS$
Formula weight	152.15	168.21
Temperature/K	100	100
Crystal system	tetragonal	triclinic
Space group	$I4_1/a$	P-1
a/Å	19.3447(15)	8.1843(17)
b/Å	19.3447(15)	11.066(3)
c/Å	10.3928(10)	13.037(3)
α/°	90	113.372(7)
β/°	90	102.438(7)
γ/°	90	98.398(8)
Volume/Å^3	3889.2(7)	1022.5(4)
Z	16	4
ρ_{calc}g/cm^3	1.039	1.093
μ/mm^{-1}	0.070	0.262
F(000)	1344.0	368.0
Crystal size/mm^3	0.501 × 0.453 × 0.433	0.6 × 0.47 × 0.35
Crystal shape	Block	Needle
Crystal color	Colorless	Colorless
Radiation	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
2Θ range for data collection/°	4.212 to 50.232	5.276 to 51.726
Index ranges	-10 ≤ h ≤ 19, -23 ≤ k ≤ 22, -11 ≤ l ≤ 12	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	3821	18312
Independent reflections	1711 [R_{int} = 0.0338, R_{sigma} = 0.0319]	3884 [R_{int} = 0.0850, R_{sigma} = 0.0684]
Data/restraints/parameters	1711/0/149	3884/0/234
Goodness-of-fit on F^2	1.033	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1476	R_1 = 0.0535, wR_2 = 0.1133
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1601	R_1 = 0.0772, wR_2 = 0.1221
Largest diff. peak/hole / e Å^{-3}	0.19/-0.14	0.34/-0.37

X-Ray data were collected on a BRUKER D8 Venture system. Data were collected at 100(2) K using graphite-monochromated Mo K_α radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard "*ψ-ω* scan techniques" and were scaled and reduced using Saint+software. The structures were solved by using Olex2,[4] the structure was solved with the XT[5] structure solution program using Intrinsic Phasing and refined with the XL refinement package[6,7] using Least Squares minimization. If it is noted, bond length and angles were measured with Diamond Crystal and Molecular Structure Visualization Version 4.6.2.[8] Drawings were generated with POV-Ray.[9]

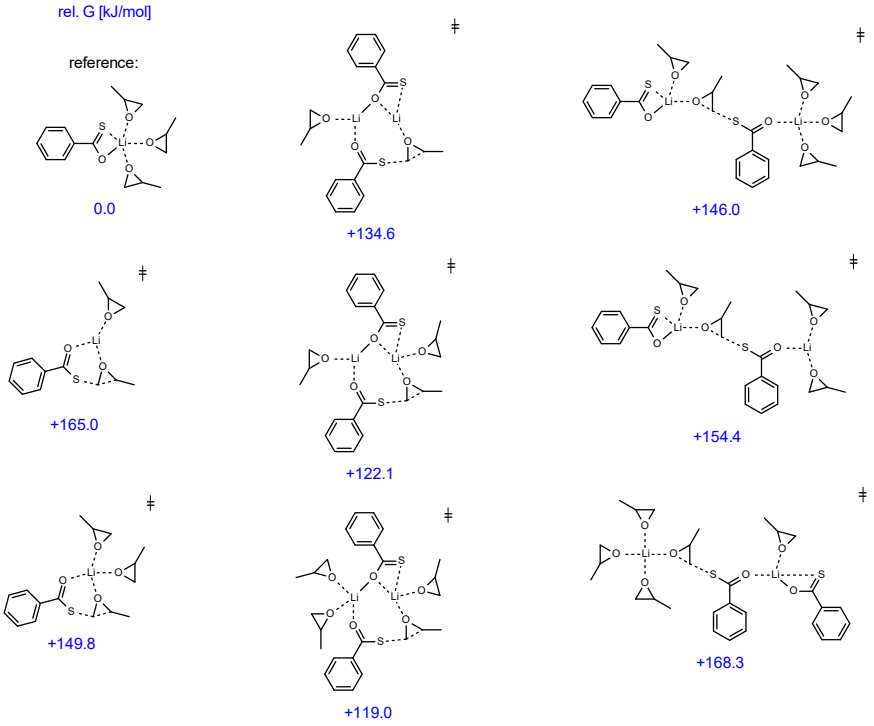
Section S8: Density functional theory
Coordination of Ligands for the Example of PhCOS-Li



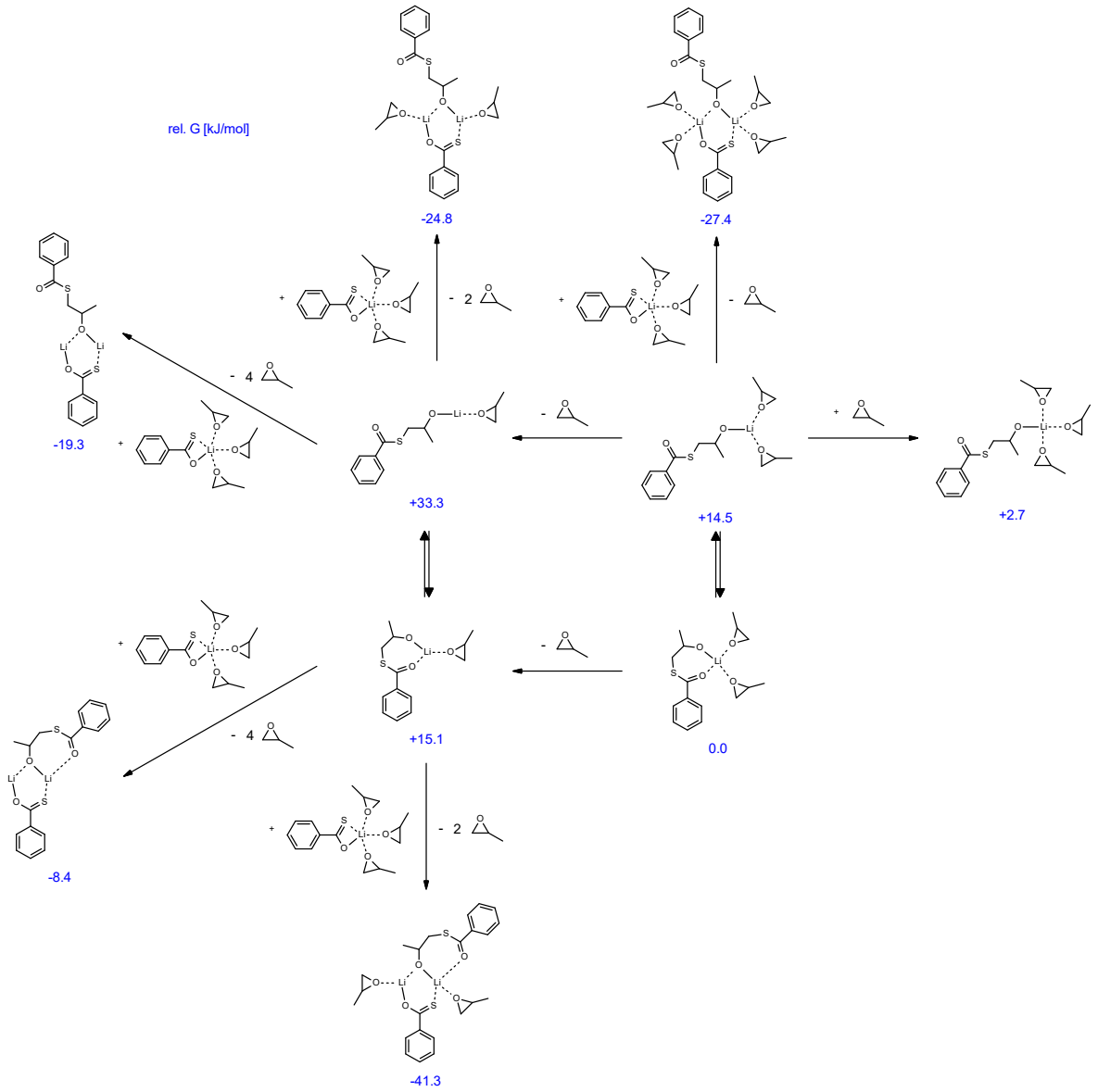
Speciation of I



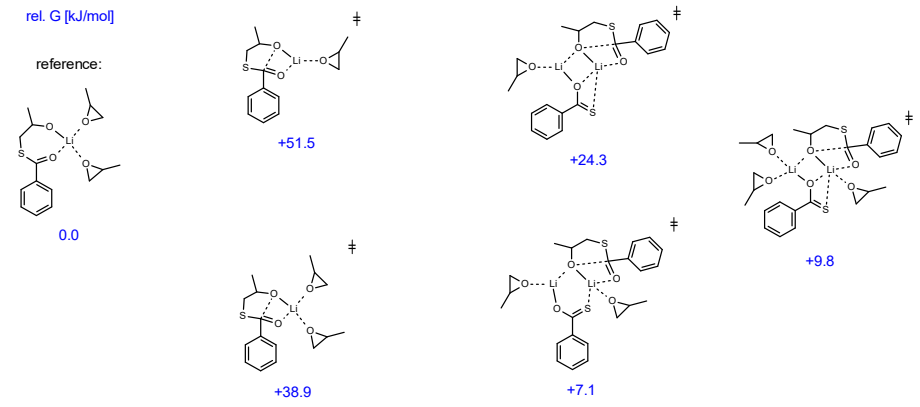
Speciation of TS^{I}



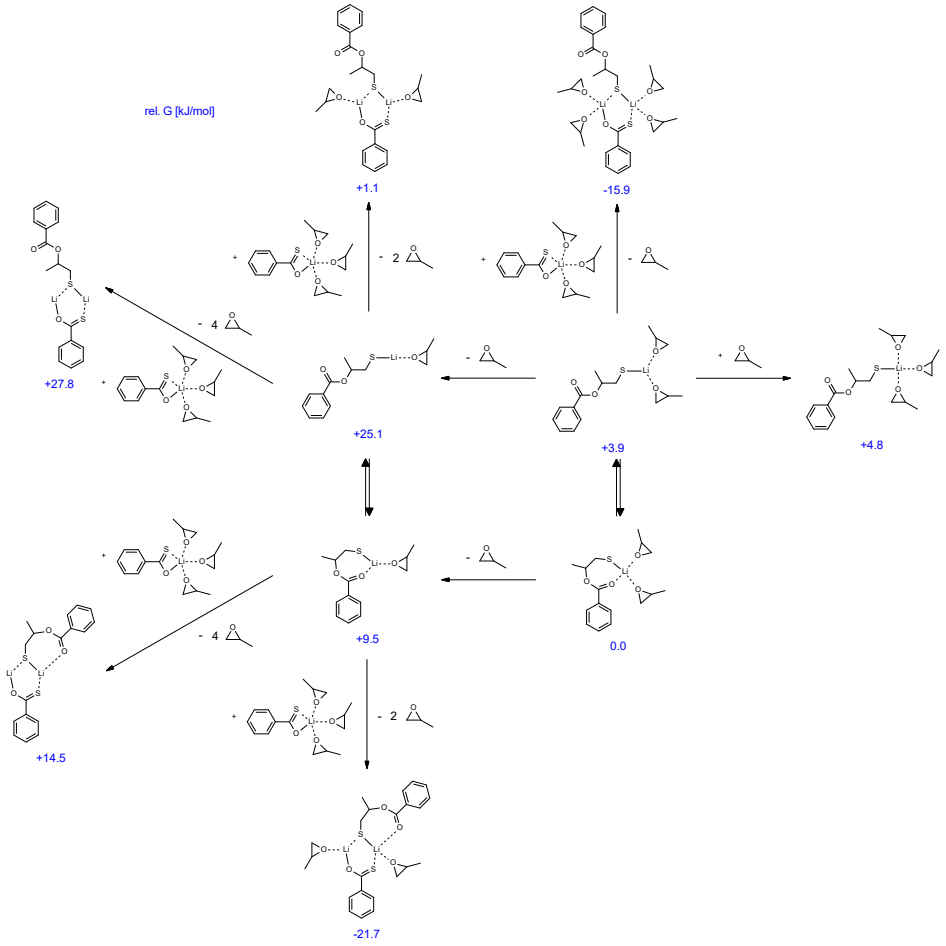
Speciation of II



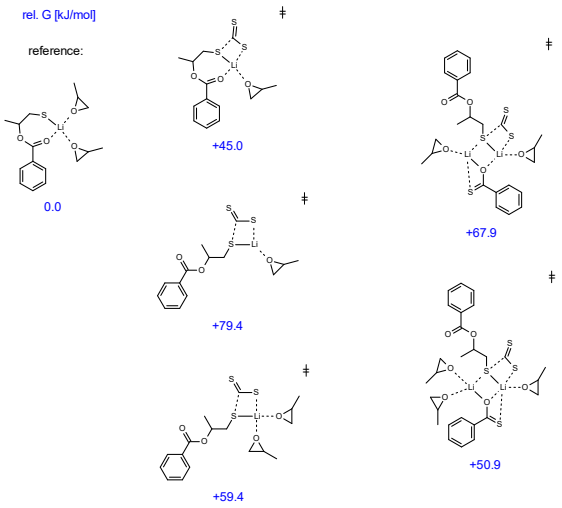
Speciation of TS^{II}



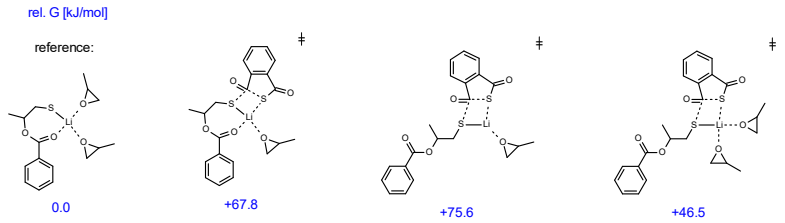
Speciation of III



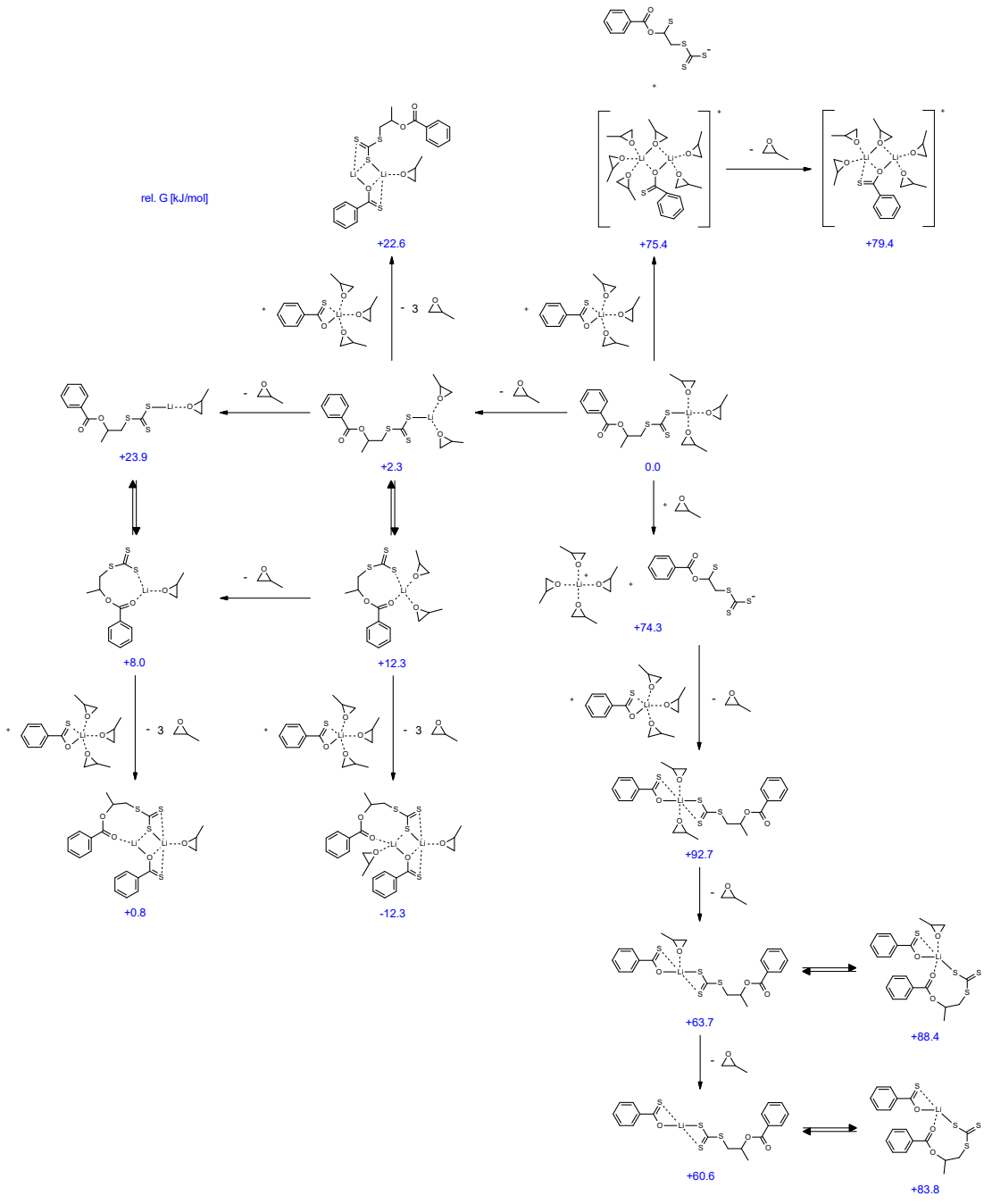
Speciation of TS^{III}



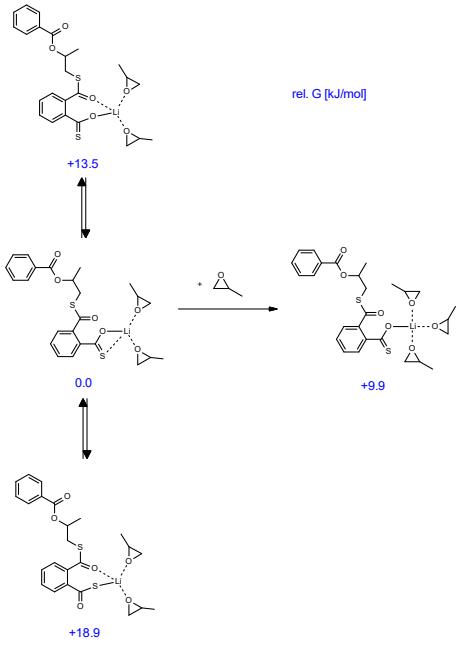
Speciation of TS^{III*}



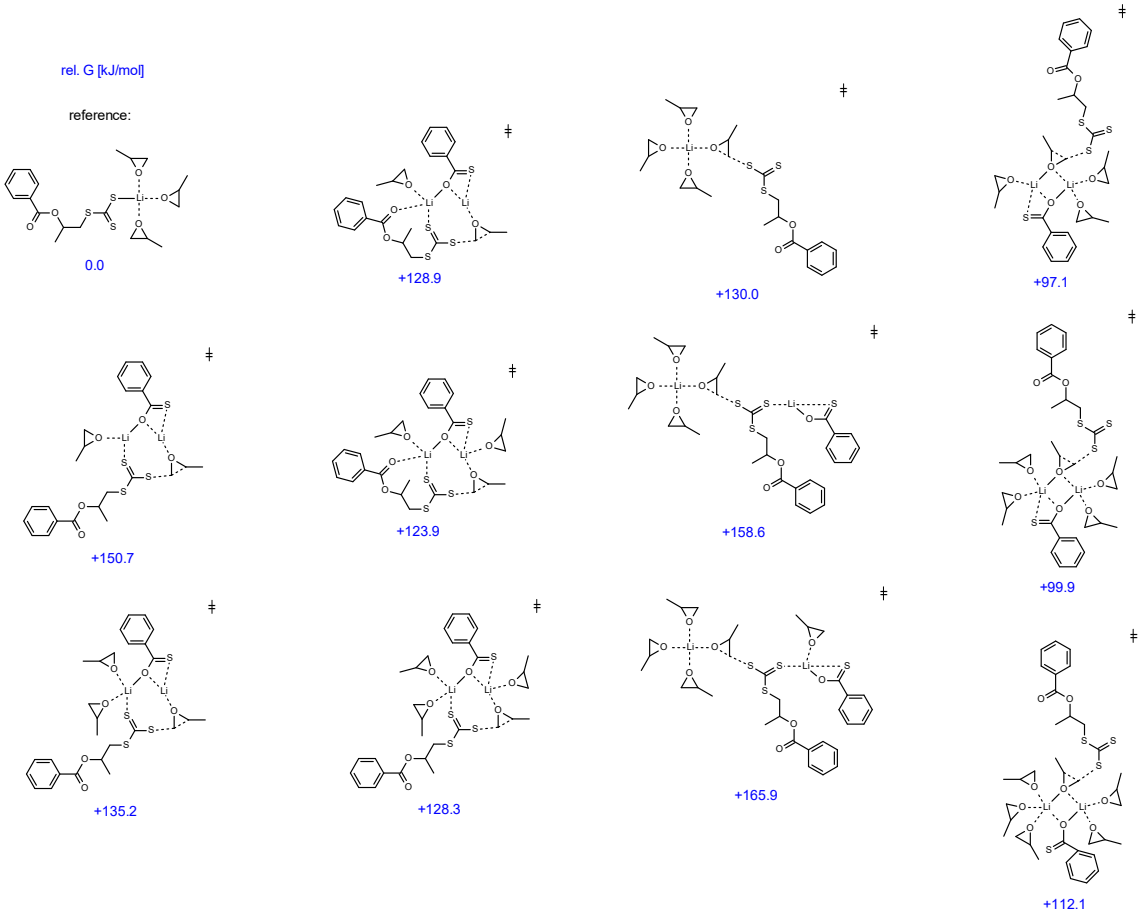
Speciation of IV



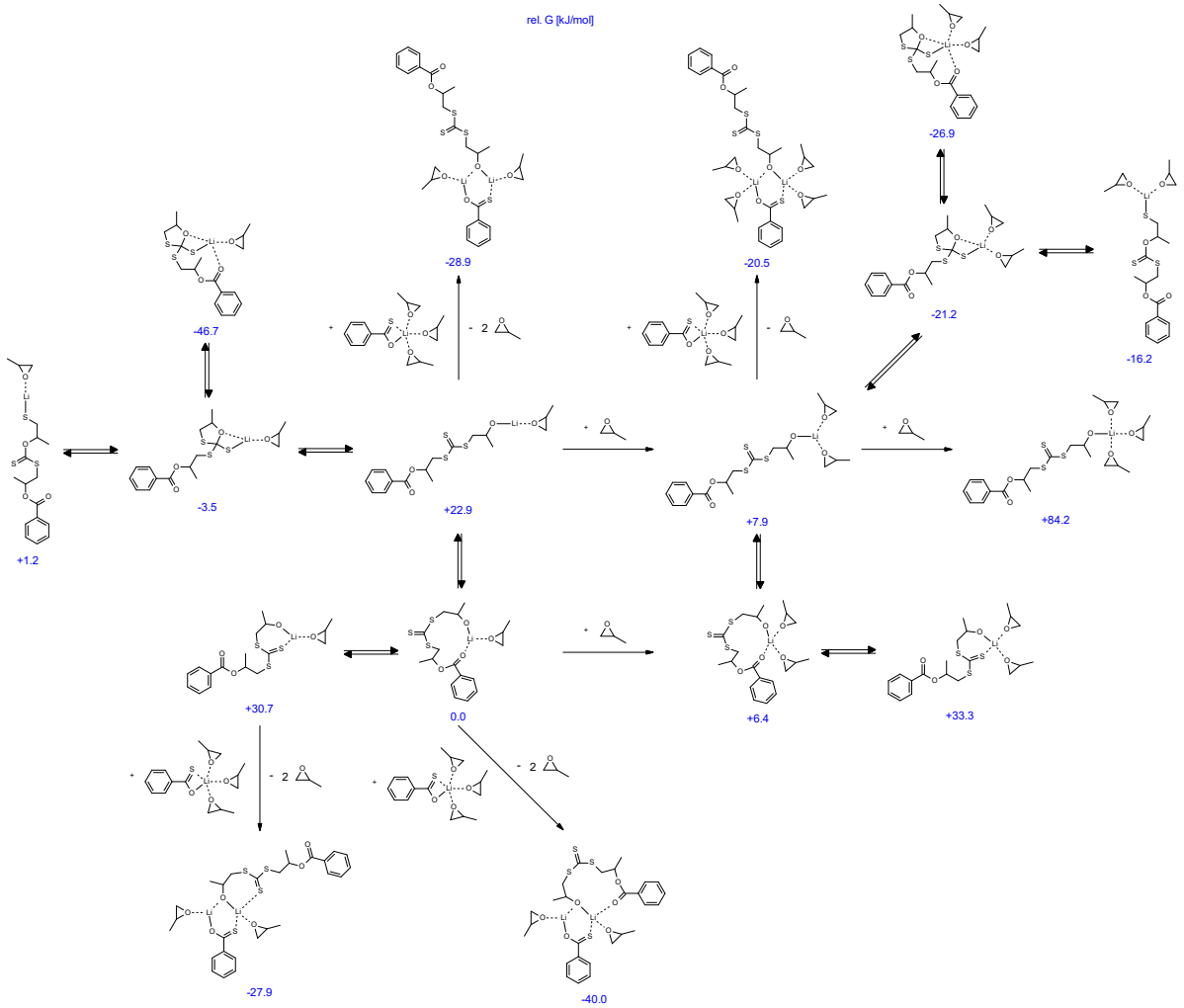
Speciation of IV*



Speciation of TS^{IV}



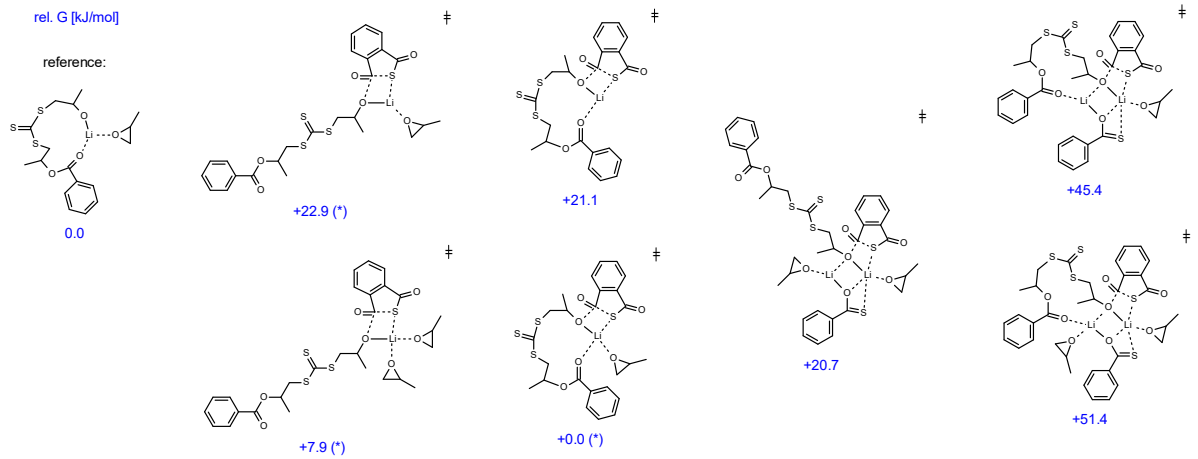
Speciation of V



Estimation of relative G of activation for CS_2 addition to model alkylsulfide species with:

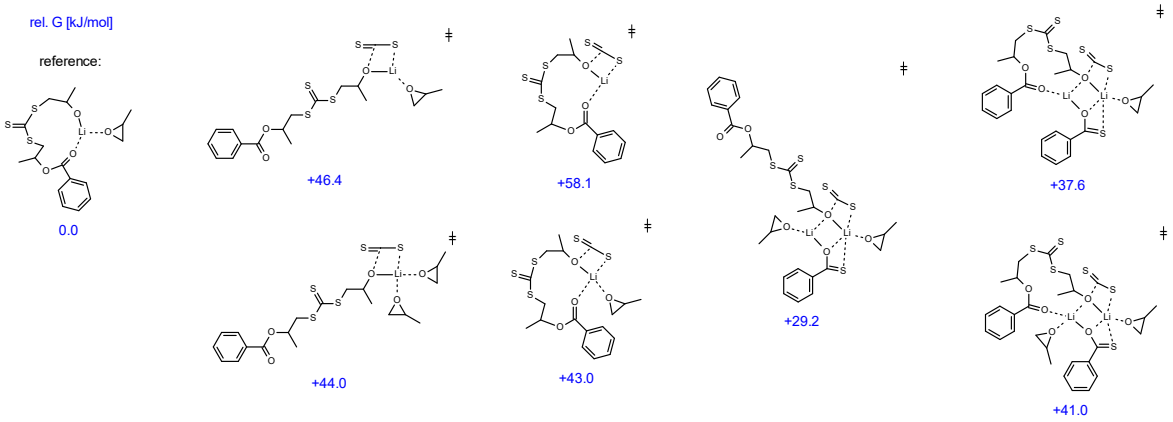
- 1 PO: rel. G = +1.2 kJ/mol + 19.9 kJ/mol (ΔG for analogous TS^{III}) = +21.1 kJ/mol
- 2 PO: rel. G = -16.2 kJ/mol + 41.1 kJ/mol (ΔG for analogous TS^{III}) = +24.9 kJ/mol

Speciation of TS^{V}



The (*) behind relative free energies of activation denote a barrierless reaction, confirmed by the absence of a maximum in the potential energy curve of PTA approach to the alkoxide. In these cases, the relative free energy of the “precursor” without PTA added (i.e. the entry from **Speciation of V**) was taken as an estimate of the maximal free energy barrier to be overcome. This was motivated by the fact that all three such species have free coordination sites and should thus allow for an exergonic PTA addition (see **Coordination of Ligands for the Example of PhCOS-Li**) as further ligand before reaction then takes place by just assuming a conformation that orients the alkoxide group and PTA appropriately.

Speciation of TS^{V*}



XYZ Structures of Species Discussed in Main Document (Figure 7)

PO
10
Energy = -193.1989662567
O 1.1767685 4.2324428 0.2258649
C 2.0766766 4.9650611 1.0906103
C 2.2646136 4.9932088 -0.3618139
H 2.7277908 4.3403021 1.6957706
H 1.6278326 5.8146461 1.5965007
H 1.9153959 5.8775957 -0.8903729
C 3.3407731 4.1988928 -1.0450940
H 2.9976620 3.8446501 -2.0208048
H 4.2220191 4.8272115 -1.2031994
H 3.6306279 3.3380291 -0.4383416

CS_2
3
Energy = -834.5503135825
S 2.8513642 4.0499780 0.1399243
C 3.2441961 4.5144100 -1.3001504
S 3.6365498 4.9784620 -2.7405039

PTA
15
Energy = -856.1265998262
O 0.3485930 0.2116118 0.4567921
C 1.5144801 0.5172530 0.3822365
S 2.8212588 -0.6524440 -0.1361936
C 2.1170508 1.8349705 0.6761967
C 4.1160219 0.6257337 0.0476810
C 3.5012294 1.8930090 0.4969595
C 4.2040418 3.0683188 0.7345241
C 3.4900783 4.1902928 1.1565617
C 2.1060408 4.1322084 1.3358314
C 1.4031965 2.9510545 1.0963937
H 5.2771289 3.1077119 0.5938073
H 4.0161638 5.1179768 1.3477529
H 1.5713157 5.0153315 1.6644622
H 0.3301477 2.9003606 1.2335904
O 5.2839424 0.4167808 -0.1764757

I[m]

45

Energy = -1330.590074881

C	-2.8518428	-3.9098729	2.6399563
C	-2.2368159	-2.5470473	2.7986140
O	-1.7255655	-2.0220843	1.7788050
S	-2.2425535	-1.7538479	4.3409639
Li	-0.8918500	-0.2731032	2.0021883
C	-2.7921945	-4.5315578	1.3844837
C	-3.3455294	-5.7935508	1.1921239
C	-3.9690897	-6.4521833	2.2519966
C	-4.0352056	-5.8410341	3.5044344
C	-3.4798333	-4.5797552	3.6967953
H	-2.3069609	-4.0108619	0.5677729
H	-3.2917330	-6.2645919	0.2164875
H	-4.4012079	-7.4357951	2.1030259
H	-4.5199696	-6.3487571	4.3312101
H	-3.5245469	-4.0964208	4.6659098
O	0.9090583	-0.1749698	2.8805280
C	1.5652410	-1.2841393	3.5512156
C	1.2427821	-0.0663050	4.2972189
H	2.5852478	-1.4529980	3.2213231
H	0.9402846	-2.1629648	3.6703169
H	0.3567987	-0.1041401	4.9247830
C	2.2792574	0.9605603	4.6473560
H	1.8496418	1.9654809	4.6254380
H	2.6511212	0.7732262	5.6585896
H	3.1200748	0.9185334	3.9519575
O	-1.8906287	1.4348233	2.3326044
C	-2.3050813	1.9996098	3.6049483
C	-3.3129362	1.5677013	2.6350941
H	-2.0825264	3.0570929	3.7053371
H	-2.0873371	1.3684018	4.4597174
H	-3.7788233	0.6030657	2.8189478
C	-4.0779644	2.5351691	1.7813088
H	-4.2860989	2.1020318	0.7995158
H	-5.0346299	2.7654863	2.2587426
H	-3.5198117	3.4641546	1.6497020
O	-0.3528929	0.0614905	0.0597172
C	-1.1750248	-0.3931846	-1.0485775
C	0.1359667	-1.0011539	-0.8117911
H	-1.2858757	0.3396548	-1.8414175
H	-2.0725907	-0.9230888	-0.7484538
H	0.1433049	-1.9663353	-0.3132221
C	1.3396676	-0.6665615	-1.6428479
H	2.2465746	-0.6882393	-1.0329818
H	1.4500472	-1.4061729	-2.4407712
H	1.2378746	0.3226605	-2.0938347

I[d]

70

Energy = -2274.778972372

C	-0.3505701	-1.4239536	-0.2301987
C	0.1898402	-0.0442949	-0.0055664
O	0.2336699	0.7460041	-0.9896466
S	0.7081169	0.4437438	1.5656161
Li	0.3240329	1.1219770	-2.9483835
C	-1.0950009	-1.6906190	-1.3878050
C	-1.6139833	-2.9619844	-1.6145418
C	-1.3846992	-3.9879113	-0.6985887
C	-0.6371398	-3.7333946	0.4519522
C	-0.1304592	-2.4597779	0.6873391
H	-1.2769942	-0.8965344	-2.1013937
H	-2.1979186	-3.1542264	-2.5082610
H	-1.7858800	-4.9793239	-0.8789519
H	-0.4512787	-4.5280987	1.1662207
H	0.4434121	-2.2509908	1.5825517
C	1.2674491	5.2270963	-3.2330149
C	1.0114016	3.7714118	-3.4804692
O	0.7299873	3.0393130	-2.4907103
S	1.0775020	3.1373277	-5.0835277
Li	0.8517921	2.6094008	-0.5459427
C	1.9068159	6.0348791	-4.1829989
C	2.1398144	7.3814903	-3.9248516
C	1.7233874	7.9451672	-2.7180372
C	1.0801586	7.1507316	-1.7697241
C	0.8603514	5.7992903	-2.0197522
H	2.2181725	5.5910107	-5.1211931
H	2.6443302	7.9930593	-4.6649003
H	1.8993256	8.9967992	-2.5191196
H	0.7504594	7.5859175	-0.8324384
H	0.3614210	5.1852327	-1.2805239
O	2.7365281	3.1154253	-0.0654856
O	-1.4962305	0.8035560	-3.7368771
C	3.3023496	3.3368559	1.2575253
C	3.7926707	2.2431003	0.4159956
C	-2.5151391	1.7926137	-4.0600130
C	-1.9765101	0.9137574	-5.1005829
H	2.6082934	3.0656925	2.0485430
H	4.7320184	2.3611231	-0.1149162
H	-2.1242534	2.8061925	-4.0277250
H	-1.2415713	1.3024851	-5.7972721
H	-2.5609585	0.0600945	-5.4288244
H	3.4685212	1.2284376	0.6223771
C	-3.8644096	1.5736825	-3.4417513
H	-4.6054214	2.1964397	-3.9506909
H	-4.1659552	0.5280598	-3.5272065
H	-3.8556203	1.8529548	-2.3850476
C	4.0627813	4.6176658	1.4393769
H	4.6698149	4.5574861	2.3471357
H	4.7209741	4.8018651	0.5882542
H	3.3760067	5.4613084	1.5456338
O	-0.4670212	3.7740630	0.4277326
O	1.5875236	-0.2624346	-3.6680488
C	1.7905999	-0.6457759	-5.0579732
C	2.8849548	-0.0545394	-4.2854076

C	-1.7871421	3.4053389	0.9204341
C	-0.7679073	3.9192424	1.8386259
H	-1.9380522	2.3290609	0.9146147
H	-0.2309709	3.2272421	2.4786129
H	-0.8233615	4.9514139	2.1696457
H	1.2691529	0.0178961	-5.7428295
H	3.1397250	0.9886652	-4.4393921
H	3.6647144	-0.6980037	-3.8901557
C	1.7117166	-2.1149061	-5.3528318
H	2.1469386	-2.3147308	-6.3361351
H	2.2574335	-2.6914301	-4.6035130
H	0.6711931	-2.4491180	-5.3687407
C	-2.9296846	4.2472712	0.4335188
H	-3.8090059	4.0661443	1.0577464
H	-2.6784220	5.3085173	0.4803492
H	-3.1868684	3.9906959	-0.5972394

TS^{I}
70
Energy = -2274.750191960
C -2.8054019 2.4703390 -2.3783090
C -3.1701924 1.0280035 -2.5057336
O -2.2961027 0.1528447 -2.2337275
S -4.7391471 0.5719437 -3.0585482
Li -3.2332017 -1.5110847 -2.9838741
C -1.4591552 2.8496756 -2.4725795
C -1.0958445 4.1891588 -2.3720167
C -2.0692624 5.1633767 -2.1541673
C -3.4105897 4.7928541 -2.0507991
C -3.7780484 3.4571921 -2.1731916
H -0.7021430 2.0952812 -2.6544638
H -0.0541141 4.4753912 -2.4658750
H -1.7851006 6.2063181 -2.0690877
H -4.1705133 5.5469289 -1.8782321
H -4.8191620 3.1646541 -2.1058132
C 2.9202426 1.0708995 -3.4115703
C 1.7605196 0.1189027 -3.4850469
O 0.9206501 0.1488759 -2.5648954
S 1.6715830 -0.9770276 -4.8398826
Li -0.5554202 -0.1244087 -1.3846950
C 3.1514891 1.7475547 -2.2061486
C 4.2106545 2.6405793 -2.0867900
C 5.0477353 2.8792115 -3.1767300
C 4.8210538 2.2166972 -4.3831722
C 3.7671332 1.3159925 -4.4994866
H 2.4927300 1.5551994 -1.3683914
H 4.3850603 3.1524328 -1.1467317
H 5.8718634 3.5783383 -3.0865541
H 5.4660073 2.4036372 -5.2346527
H 3.5885255 0.7988117 -5.4347950
O -0.6049833 -2.0790034 -0.9466687
O -2.4445252 -2.0710057 -4.6168287
C 0.4682275 -2.8877638 -0.3835617
C -0.8014548 -2.7332539 0.3315805
C -1.5914054 -1.1776247 -5.3155005
C -0.6119609 -1.9091970 -4.5111046
H 1.3036395 -2.2830606 -0.0402561
H -1.5253105 -3.5413828 0.3016813
H -1.7273768 -0.1315234 -5.0232787
H -0.4889792 -1.6638885 -3.4716894
H -0.2857103 -2.8781687 -4.8574229
H -0.8674400 -2.0560217 1.1763464
C -1.5784576 -1.3466165 -6.8184924
H -0.7834799 -0.7426170 -7.2647891
H -1.4171893 -2.3949113 -7.0833881
H -2.5343569 -1.0215460 -7.2382930
C 0.8187721 -4.1353176 -1.1395175
H 1.4108077 -4.7952901 -0.4995047
H -0.0830556 -4.6645178 -1.4530062
H 1.4154210 -3.8942558 -2.0228548
O -4.2338528 -2.9102574 -2.0017862
C -5.6366473 -3.1701741 -2.2903293
C -5.2417643 -2.6713456 -0.9720705
H -5.8674356 -4.2230754 -2.4138911

H	-6.0767271	-2.4903328	-3.0123518
H	-5.3886052	-1.6103320	-0.7884871
C	-5.1725480	-3.5602471	0.2340653
H	-4.3760086	-3.2360722	0.9083252
H	-6.1189189	-3.5063152	0.7791745
H	-4.9941413	-4.5973406	-0.0566829
O	-0.3961863	0.7102369	0.4203534
C	0.0618880	1.9345504	1.0604067
C	-1.3064399	1.4537172	1.2697688
H	0.1933747	2.7475109	0.3513115
H	-2.1316196	1.9222399	0.7438798
H	-1.5545467	0.9473863	2.1969730
C	1.1358950	1.7748355	2.0954449
H	1.2020757	2.6871452	2.6946189
H	0.9160059	0.9344913	2.7558133
H	2.1075918	1.6087816	1.6229935

II[d]

60

Energy = -2081.591172602

Li	-3.5111248	1.6582986	1.2472154
C	0.3941784	-1.1882627	0.5475812
C	-0.0091367	0.1429664	0.0276142
S	-1.0396179	0.1208011	-1.4300300
O	0.3336250	1.1851385	0.5800737
Li	-0.8243631	2.7657038	1.1194078
C	-1.1294211	1.9112166	-1.8453345
H	-1.1135168	1.9487094	-2.9365747
H	-0.2064560	2.3502595	-1.4636464
C	-2.3647296	2.6299669	-1.2653607
H	-2.2383891	3.6752070	-1.6133065
O	-2.3950229	2.5719004	0.1224415
C	-3.6565902	2.1034965	-1.8998001
H	-4.5084773	2.6773224	-1.5263138
H	-3.6354657	2.1880821	-2.9912404
H	-3.8081749	1.0513725	-1.6359955
C	0.3448394	-2.3512107	-0.2328075
C	0.7374102	-3.5700608	0.3093751
C	1.1772905	-3.6385954	1.6313678
C	1.2290843	-2.4832318	2.4122974
C	0.8437863	-1.2619137	1.8737730
H	0.0200126	-2.3035098	-1.2657691
H	0.7056238	-4.4652526	-0.3007486
H	1.4812127	-4.5907427	2.0517125
H	1.5681408	-2.5376839	3.4403724
H	0.8734795	-0.3584132	2.4703731
S	-1.1701007	2.4816041	3.5967333
O	-2.9391580	0.6892946	2.8028063
C	-2.1235949	1.0236152	3.6892395
C	-1.9875888	0.1241307	4.8841745
C	-2.8552282	-0.9715659	4.9977760
C	-2.7682645	-1.8336167	6.0857530
C	-1.8079589	-1.6160948	7.0742203
C	-0.9379307	-0.5308018	6.9681453
C	-1.0278654	0.3337361	5.8814981
H	-3.5962874	-1.1328468	4.2243812
H	-3.4477690	-2.6752664	6.1644965
H	-1.7378080	-2.2885373	7.9223019
H	-0.1878606	-0.3595197	7.7325194
H	-0.3554786	1.1785391	5.7913067
O	-5.4773272	1.4563274	1.2577754
C	-6.3181058	0.3662376	1.7165490
C	-6.6178965	1.0433868	0.4515778
H	-6.9046476	0.6049993	2.5977355
H	-5.8354623	-0.6050757	1.7085928
H	-6.3152476	0.5384155	-0.4615491
C	-7.7264865	2.0458514	0.3219287
H	-7.4543244	2.8321391	-0.3866160
H	-8.6253541	1.5483856	-0.0523047
H	-7.9537135	2.5003057	1.2883769
O	0.4342589	4.3314291	1.0026952
C	0.8280787	5.1938883	-0.1060021
C	0.1494405	5.7530280	1.0658936
H	0.2220561	5.0302583	-0.9935451

H	-0.9048206	6.0035677	1.0124363
H	0.7317861	6.2836008	1.8121089
C	2.3039989	5.3418857	-0.3301816
H	2.4898373	6.2000382	-0.9818566
H	2.8262872	5.4990921	0.6154528
H	2.7100837	4.4517708	-0.8174016

TS^{II}

60

Energy = -2081.575099738

Li	2.3813701	3.0843184	1.7062316
C	1.7172160	3.3857610	-1.3347547
O	1.8192384	3.0804781	-0.1104055
C	5.0358945	1.5162564	1.1930141
C	4.0410890	0.3901027	1.0965129
S	4.2330367	-0.9210427	2.4188548
O	3.5728835	0.0599255	-0.0124035
Li	1.8265961	1.0113833	-0.0263592
C	2.4238732	-1.0513139	2.6750750
H	2.2503780	-1.7171370	3.5209333
H	1.9700461	-1.4738292	1.7788692
C	1.9112083	0.3750409	2.9249605
H	0.8216065	0.3402623	2.7787204
O	2.4658455	1.2225078	1.9400342
C	2.2015212	0.8723785	4.3393234
H	1.8240978	1.8911394	4.4600331
H	1.7097081	0.2377095	5.0829732
H	3.2765499	0.8736364	4.5329064
C	5.6402286	1.8959070	2.3964818
C	6.5660515	2.9341093	2.4211825
C	6.8939540	3.6101908	1.2451316
C	6.2905203	3.2417057	0.0440559
C	5.3683546	2.1987199	0.0172786
H	5.3794804	1.3727853	3.3084865
H	7.0319182	3.2180292	3.3584099
H	7.6156906	4.4193877	1.2666176
H	6.5423635	3.7628299	-0.8730459
H	4.8988332	1.8991431	-0.9120667
O	2.6829025	4.6668173	2.7822212
O	0.1980799	-0.1405732	-0.0089872
C	3.6526599	5.7462234	2.8536216
C	3.3127360	4.9897648	4.0610187
H	3.2199770	6.7302064	2.7079529
H	4.5832454	5.5480912	2.3330048
H	4.0146398	4.2223991	4.3754803
C	2.4031931	5.5363031	5.1202284
H	1.8074952	4.7368023	5.5674943
H	3.0041018	5.9942164	5.9106081
H	1.7331813	6.2918927	4.7058701
C	-1.1431545	0.1759991	-0.4838609
C	-0.3574460	-0.8791987	-1.1273689
H	-1.1800715	1.1354072	-0.9930753
H	0.1288753	-0.6820274	-2.0770568
H	-0.5749180	-1.9177549	-0.8995341
C	-2.2631824	-0.1214428	0.4694463
H	-3.2136206	-0.1200340	-0.0716448
H	-2.1260778	-1.0988654	0.9361235
H	-2.3163866	0.6415815	1.2502521
S	1.5368949	2.1647019	-2.5339321
C	1.7404238	4.8349422	-1.7011036
C	1.5920370	5.7975953	-0.6924815
C	1.6085446	7.1537958	-1.0018021
C	1.7875645	7.5675235	-2.3217046
C	1.9416733	6.6168618	-3.3314267

C	1.9122452	5.2607633	-3.0244624
H	1.4514129	5.4745685	0.3314589
H	1.4819353	7.8891627	-0.2147391
H	1.8056233	8.6247482	-2.5624648
H	2.0841646	6.9338189	-4.3585047
H	2.0255168	4.5159081	-3.8033090

III[d]

45

Energy = -1330.611895219

C	-0.5499702	0.9340978	1.0060823
C	-0.0208651	0.0253221	-0.0478201
S	3.0088455	-1.5782683	-0.5737521
O	0.4008043	0.4387367	-1.1290460
Li	2.3939110	0.5753116	-1.4554388
O	3.3063348	2.0546234	-0.4729092
C	3.6877519	1.9200385	0.9319563
C	4.7101477	1.9180445	-0.1157548
H	3.4012361	0.9517500	1.3344218
H	5.1596167	0.9806614	-0.4269108
H	5.2939031	2.8156784	-0.2915306
C	3.4311826	3.1155435	1.8005252
H	3.9983183	3.0170661	2.7302588
H	3.7386600	4.0348684	1.2985482
H	2.3710611	3.1864018	2.0558282
C	1.5098310	-2.2163756	-1.4506063
H	1.7187057	-3.2165695	-1.8409380
H	1.2915081	-1.5788937	-2.3062457
C	0.2460641	-2.3718956	-0.6002529
H	-0.6187374	-2.4367064	-1.2675768
O	-0.0659919	-1.2473898	0.3129901
C	0.2958935	-3.5765123	0.3202357
H	-0.5995610	-3.6307715	0.9420527
H	0.3565068	-4.4860172	-0.2817934
H	1.1788318	-3.5195327	0.9608787
C	-1.0084835	0.4520077	2.2388480
C	-1.5030059	1.3382436	3.1897749
C	-1.5468001	2.7056379	2.9169661
C	-1.0929669	3.1887331	1.6894958
C	-0.5952298	2.3068921	0.7370598
H	-0.9765867	-0.6095903	2.4468850
H	-1.8563241	0.9629871	4.1434141
H	-1.9349853	3.3937741	3.6596650
H	-1.1280401	4.2509681	1.4763617
H	-0.2409326	2.6703106	-0.2199337
O	2.6227494	0.9729343	-3.3901418
C	2.1534631	2.1415021	-4.1151590
C	1.6421465	0.8133652	-4.4616201
H	2.9119558	2.5989688	-4.7418811
H	1.5427134	2.8202895	-3.5291897
H	0.6597256	0.5502560	-4.0794506
C	2.1100706	0.0610532	-5.6715941
H	2.1295564	-1.0135537	-5.4732279
H	1.4194171	0.2400884	-6.5002579
H	3.1082823	0.3865262	-5.9698486

TS^{III}

38

Energy = -1971.953348944

C	4.2268835	3.3539462	-0.9146332
C	2.9939529	3.3478936	-0.0908921
S	1.9961426	1.6444203	2.8839114
O	1.9978712	2.6840640	-0.3876085
Li	1.0337829	1.4226580	0.7072659
S	-0.2724247	-0.5790945	4.1384680
C	2.0898759	3.4605427	3.1135127
H	3.0329373	3.7279771	3.5967138
H	1.2760242	3.7268572	3.8027450
C	1.9068895	4.3067341	1.8619840
H	1.0250625	3.9879658	1.3057830
O	3.0760670	4.1302620	0.9776336
C	1.8441299	5.7957517	2.1618238
H	1.7512691	6.3705899	1.2386809
H	0.9723357	6.0006968	2.7868318
H	2.7398828	6.1222792	2.6952109
C	4.2698781	2.5402058	-2.0533558
C	5.4105907	2.5147156	-2.8468813
C	6.5130027	3.2997882	-2.5079875
C	6.4733879	4.1120161	-1.3742939
C	5.3346295	4.1420472	-0.5770311
H	3.4078494	1.9342927	-2.3048341
H	5.4419173	1.8835786	-3.7274675
H	7.4029014	3.2783474	-3.1270537
H	7.3302009	4.7218871	-1.1121516
H	5.3005140	4.7711935	0.3028527
O	-0.3052197	0.1962723	0.0742210
C	-0.3823299	-1.2546123	0.0893716
C	-0.5346900	-0.5280752	-1.1739845
H	-1.2653892	-1.6370976	0.5901342
H	0.5545366	-1.7505047	0.3183174
H	0.3293977	-0.4952639	-1.8313967
C	-1.8713164	-0.3095472	-1.8172987
H	-1.9008437	0.6590171	-2.3225083
H	-2.0447026	-1.0885849	-2.5645774
H	-2.6710154	-0.3508288	-1.0753687
C	-0.2398570	0.9959655	4.3584886
S	-0.6963123	2.4152794	4.9094407

TS^{III*}

60

Energy = -2186.734110961

C	5.6867917	0.3862111	0.2372407
C	4.4119349	0.8588410	0.8424679
S	-0.6147360	0.1485714	0.7456748
O	4.2808107	1.9402421	1.3958892
Li	-2.0619969	-1.7267883	-0.0260531
C	1.0977967	-0.3605185	0.3549184
H	1.2661660	-0.0263954	-0.6740240
H	1.1727440	-1.4472634	0.4056929
C	2.1075916	0.3027969	1.2843101
H	1.9992690	1.3863281	1.2413981
O	3.4194129	-0.0358282	0.7109804
C	2.0614355	-0.1896868	2.7200706
H	2.8239879	0.3060616	3.3231409
H	1.0826211	0.0343900	3.1503269
H	2.2212501	-1.2701728	2.7575406
C	5.8001308	-0.8738509	-0.3633859
C	7.0140246	-1.2738033	-0.9127938
C	8.1178813	-0.4223146	-0.8668068
C	8.0080898	0.8332997	-0.2685776
C	6.7973156	1.2371721	0.2826196
H	4.9416935	-1.5321733	-0.3957193
H	7.0999035	-2.2498521	-1.3766349
H	9.0625172	-0.7371464	-1.2960649
H	8.8658406	1.4951698	-0.2322997
H	6.7006222	2.2096570	0.7505098
O	-3.6238053	-2.1676455	1.0266432
C	-4.5249596	-1.4544756	1.9280688
C	-5.0572670	-2.2026138	0.7860333
H	-4.4471256	-0.3761066	1.8188912
H	-5.3728845	-1.6731774	-0.1064843
H	-5.5011883	-3.1781737	0.9537815
C	-4.5913832	-1.9737404	3.3331267
H	-5.4752183	-1.5624334	3.8284014
H	-4.6579658	-3.0631956	3.3424223
H	-3.7097175	-1.6638719	3.8995318
O	-1.1287589	-3.2512781	-0.7600992
C	-0.6562769	-3.6804137	-2.0636220
C	-1.5396008	-4.5522681	-1.2842185
H	0.4073759	-3.8921346	-2.0913503
H	-1.0557904	-3.1101859	-2.8954932
H	-2.5887394	-4.5679654	-1.5658120
C	-1.0333394	-5.7477625	-0.5343252
H	-1.6026532	-5.8921090	0.3872848
H	-1.1551493	-6.6412998	-1.1526380
H	0.0235832	-5.6326521	-0.2871999
C	-0.9619372	1.2775226	-1.0016823
O	0.0449241	1.4339427	-1.6847310
S	-2.4754926	0.0254769	-1.8959012
C	-3.7745910	1.0607771	-1.2481818
O	-4.9677469	0.8028844	-1.3215187
C	-3.2261064	2.2875462	-0.6221180
C	-1.8383631	2.4085088	-0.5353915
C	-4.0580783	3.3143111	-0.1630635
C	-3.4920617	4.4689598	0.3608775

C	-2.1008720	4.5989510	0.4235897
C	-1.2711140	3.5737977	-0.0217083
H	-5.1333696	3.2025838	-0.2372822
H	-4.1273143	5.2732255	0.7132552
H	-1.6619819	5.5065705	0.8226361
H	-0.1936802	3.6727300	0.0371622

IV^{m}

58

Energy = -2358.391157473

C	1.7310437	0.2541136	4.3044448
C	0.8370994	0.0861028	3.1266473
S	-1.4093241	-3.2958488	3.0667897
O	1.1724612	0.3194829	1.9760139
Li	-1.6654440	-6.5983204	-0.6502027
O	-0.6375428	-8.3466497	-0.6678351
C	-0.2258206	-9.0692260	-1.8684603
C	0.7724749	-8.4409612	-1.0005278
H	-0.4902313	-8.5340144	-2.7762163
H	1.2288181	-7.5023183	-1.2960189
H	1.3434158	-9.0570622	-0.3134532
C	-0.4776420	-10.5479132	-1.8639687
H	0.1099444	-11.0200822	-2.6562438
H	-0.1924953	-10.9880737	-0.9064531
H	-1.5328622	-10.7600102	-2.0540414
C	-2.2700234	-1.6894290	2.8720315
H	-2.7056862	-1.4555680	3.8448066
H	-3.0651161	-1.8504695	2.1410836
C	-1.3660039	-0.5638356	2.3994301
H	-0.8220704	-0.8575228	1.5019964
O	-0.3858316	-0.3538420	3.4697054
C	-2.1346649	0.7283730	2.1650012
H	-1.4550201	1.5271347	1.8638903
H	-2.8654360	0.5784162	1.3672116
H	-2.6631289	1.0328409	3.0713679
C	1.3123827	-0.0542156	5.6047945
C	2.1850532	0.1192543	6.6742235
C	3.4755597	0.6003441	6.4542176
C	3.8955408	0.9084815	5.1599654
C	3.0274111	0.7358613	4.0879521
H	0.3107367	-0.4278104	5.7735814
H	1.8589703	-0.1208831	7.6797928
H	4.1530467	0.7348531	7.2901736
H	4.8983884	1.2827389	4.9884397
H	3.3431107	0.9720948	3.0787791
O	-0.9654463	-5.8080958	-2.3262955
C	-1.5157067	-4.7893361	-3.2132856
C	-0.2628143	-4.5479662	-2.4944475
H	-2.4097418	-4.3312631	-2.7997051
H	-0.2676052	-3.9188162	-1.6106374
H	0.6797830	-4.6420201	-3.0240393
C	-1.5530980	-5.1407897	-4.6710336
H	-1.7095674	-4.2326660	-5.2599540
H	-0.6153422	-5.6039299	-4.9835388
H	-2.3773205	-5.8273126	-4.8799273
O	-3.5530298	-7.2223641	-0.6311206
C	-4.5411301	-6.8802340	0.3780160
C	-4.0723145	-8.2619403	0.2546548
H	-5.5078265	-6.6091418	-0.0334982
H	-4.1613209	-6.2483039	1.1729543
H	-3.3287352	-8.5957254	0.9735441
C	-4.8917437	-9.3334534	-0.4007316
H	-4.2490427	-10.0481756	-0.9209806
H	-5.4558146	-9.8778249	0.3617095

H	-5.5951639	-8.9020178	-1.1156905
C	-1.6853340	-4.1742280	1.5320354
S	-2.6166590	-3.5610937	0.2687859
S	-0.8946546	-5.6988781	1.5461714

IV[d]

63

Energy = -2916.173178536

C	-3.8244857	-2.6843035	-2.6318982
C	-2.4405756	-2.6382925	-2.1053613
S	-0.9771390	-5.4526529	-0.7711565
O	-2.1389165	-2.0598117	-1.0648454
Li	-1.1788651	-1.5596630	0.5227335
O	-0.1136244	0.0545006	0.1565075
C	0.9284828	0.6935213	0.9571710
C	1.2110589	0.2476579	-0.4093514
H	1.2744778	0.0543673	1.7651982
H	1.7669584	-0.6698621	-0.5720179
H	1.2394320	0.9774822	-1.2114999
C	0.7008385	2.1352437	1.3005171
H	1.6418943	2.5801173	1.6351430
H	0.3395851	2.6889984	0.4317442
H	-0.0251601	2.2282582	2.1119136
C	0.1766635	-4.7329926	-2.0013574
H	0.1347604	-5.4396439	-2.8330005
H	1.1815634	-4.7400008	-1.5780627
C	-0.1566842	-3.3217775	-2.4746015
H	-0.0242026	-2.6216685	-1.6541570
O	-1.5616522	-3.2708852	-2.8866379
C	0.6779397	-2.9225360	-3.6788067
H	0.4354601	-1.9048474	-3.9892157
H	1.7373426	-2.9619275	-3.4162595
H	0.5010846	-3.6025587	-4.5150174
C	-4.1425358	-3.3705145	-3.8108752
C	-5.4553507	-3.3853589	-4.2685292
C	-6.4526659	-2.7180329	-3.5572348
C	-6.1381195	-2.0348840	-2.3819815
C	-4.8283837	-2.0179142	-1.9184874
H	-3.3668691	-3.8875129	-4.3605393
H	-5.7016568	-3.9169980	-5.1803898
H	-7.4749927	-2.7305920	-3.9182801
H	-6.9151595	-1.5176281	-1.8310595
H	-4.5686844	-1.4924115	-1.0074096
C	-0.6483921	-4.6578738	0.7754475
S	-1.6629317	-5.1981046	2.0306993
S	0.5656610	-3.4649105	0.9600061
O	-1.8907071	-1.5829989	2.2923596
Li	-0.9314466	-3.1116238	3.2692811
O	0.3749035	-3.6203796	4.6731513
C	1.1662000	-4.8392788	4.6428973
C	0.0848169	-4.6948015	5.6202722
H	2.1934167	-4.6998300	4.9635063
H	1.0123152	-5.4429769	3.7550148
H	-0.8525939	-5.1954775	5.3925235
C	0.3372078	-4.3828675	7.0651610
H	-0.4596180	-3.7516497	7.4663843
H	0.3553244	-5.3128341	7.6400579
H	1.2940548	-3.8729098	7.1921885
C	-2.9192066	-1.4272915	3.0195107
S	-3.0557380	-2.2579047	4.5204210
C	-3.9902012	-0.5033657	2.5433676
C	-5.2982857	-0.5789878	3.0389276

C	-6.2842627	0.2759480	2.5586545
C	-5.9737663	1.2297889	1.5889156
C	-4.6715634	1.3222003	1.0985350
C	-3.6887381	0.4560266	1.5659160
H	-5.5314550	-1.3190670	3.7954081
H	-7.2964376	0.1988998	2.9398244
H	-6.7425188	1.8990063	1.2188415
H	-4.4232936	2.0678354	0.3514699
H	-2.6761951	0.5346287	1.1881650

IV² cation

76

Energy = -1917.676212165

C	-0.2979619	1.0192577	-3.7659367
C	0.0021858	2.1253637	-2.8041719
O	0.8295548	1.9074335	-1.8754949
S	-0.7595239	3.6682161	-2.9685194
Li	1.9361830	0.7731664	-0.5617682
C	-1.4432112	1.0339421	-4.5721206
C	-1.7096413	-0.0211968	-5.4383218
C	-0.8281259	-1.0997702	-5.5206412
C	0.3202475	-1.1183236	-4.7295075
C	0.5804694	-0.0706203	-3.8514210
H	-2.1196799	1.8778790	-4.5062447
H	-2.6052457	-0.0037884	-6.0494551
H	-1.0343307	-1.9198613	-6.1996328
H	1.0118545	-1.9510211	-4.7965811
H	1.4757772	-0.0780343	-3.2417635
Li	0.9503391	3.6764983	-0.8831207
O	-0.2013835	4.6110603	0.4935795
O	3.4470913	0.5392535	-1.9482192
C	-1.0590113	5.7777987	0.3136287
C	-1.6417590	4.4728911	0.6287270
C	4.2770725	1.5300065	-2.6172320
C	4.8886412	0.4510440	-1.8357093
H	-1.1047365	6.0935949	-0.7253382
H	-1.9676120	4.2696368	1.6436053
H	4.2063420	2.5075694	-2.1474483
H	5.2743172	0.6456970	-0.8412713
H	5.3197390	-0.3980386	-2.3567474
H	-2.1072215	3.8930718	-0.1614104
C	4.2563813	1.5141874	-4.1176443
H	5.1127302	2.0769672	-4.4997477
H	4.3149431	0.4914009	-4.4951369
H	3.3450571	1.9811742	-4.4979879
C	-0.9193776	6.8621354	1.3408806
H	-1.7835908	7.5296609	1.2832366
H	-0.8677879	6.4400284	2.3462171
H	-0.0211457	7.4574945	1.1588513
O	2.0322473	2.5541350	0.5902014
C	2.9633706	3.2433176	1.4917873
C	1.7982025	2.5418777	2.0299650
H	2.8766141	4.3213297	1.3979917
H	0.9256318	3.1074464	2.3343824
H	1.9287331	1.5655548	2.4825371
C	4.3560294	2.6972879	1.5754434
H	4.8322575	3.0760193	2.4840606
H	4.3474079	1.6073658	1.6057321
H	4.9512979	3.0296741	0.7214955
O	0.2478903	-0.2026685	0.2171040
C	-0.7334355	-1.0878129	-0.3815880
C	-1.1631956	0.1474115	0.2762385
H	-0.8480408	-2.0333372	0.1391277
H	-0.6945853	-1.1382803	-1.4644845
H	-1.4062437	0.9876285	-0.3683143
C	-1.7862771	0.1529220	1.6420591
H	-1.4990309	1.0499740	2.1969400

H	-2.8753976	0.1492298	1.5461950
H	-1.4812316	-0.7268270	2.2117596
O	2.4521969	4.8751086	-1.4620567
C	2.8051301	6.2407719	-1.1206385
C	2.4680310	5.8957065	-2.5034838
H	3.8464804	6.3681511	-0.8430242
H	2.0801790	6.7540363	-0.4974007
H	1.4677854	6.1436204	-2.8466376
C	3.5137121	5.7374535	-3.5668779
H	3.2175710	4.9702196	-4.2862516
H	3.6286171	6.6814042	-4.1069114
H	4.4758685	5.4648534	-3.1293412
O	3.1136548	-0.5144570	0.7005501
C	3.2383065	-1.9377468	0.4579354
C	2.7562891	-1.4560702	1.7539855
H	4.2632076	-2.2837669	0.3671468
H	2.5363643	-2.3383895	-0.2665694
H	1.6842581	-1.4865816	1.9236878
C	3.6308442	-1.4484433	2.9746101
H	3.3890727	-0.6020581	3.6228031
H	3.4658438	-2.3662591	3.5459094
H	4.6854269	-1.3933546	2.6975335

IV^{z} anion

27

Energy = -1771.298177878

C	1.4890338	-0.2441423	0.1164586
C	0.0730915	0.1422970	-0.1310264
S	-1.3124895	-0.4978432	-3.8884196
O	-0.4241655	1.1891566	0.2540104
C	-2.2683646	-1.1978087	-2.4880448
H	-2.0035349	-2.2560118	-2.4475731
H	-3.3241670	-1.0920083	-2.7412323
C	-2.0031800	-0.5213661	-1.1542289
H	-2.1268505	0.5568624	-1.2430539
O	-0.5985726	-0.7888802	-0.8285343
C	-2.8856097	-1.0748415	-0.0447524
H	-2.6493952	-0.5957644	0.9071305
H	-3.9339831	-0.8757497	-0.2790177
H	-2.7485124	-2.1541318	0.0559305
C	2.2906439	0.6254368	0.8653295
C	3.6206196	0.3070101	1.1158283
C	4.1584085	-0.8811938	0.6201709
C	3.3629955	-1.7506023	-0.1262251
C	2.0313004	-1.4365662	-0.3787585
H	1.8622300	1.5451478	1.2455311
H	4.2382422	0.9833369	1.6957197
H	5.1959043	-1.1290022	0.8150273
H	3.7808842	-2.6737414	-0.5113137
H	1.4126832	-2.1093243	-0.9584865
C	-2.3004733	0.8571562	-4.5244861
S	-3.7980632	1.2655252	-3.8508562
S	-1.5270547	1.6149301	-5.8461016

TS^{IV}

93

Energy = -3495.756133183

C	-4.1564155	-3.3546125	-6.5479161
C	-3.9237339	-1.9607011	-6.0508538
O	-2.8736892	-1.7346046	-5.3832977
S	-5.0719489	-0.7178177	-6.3696469
Li	-1.0794520	-2.1206754	-4.6818834
C	-5.0630071	-3.6264009	-7.5809795
C	-5.2507139	-4.9281053	-8.0333946
C	-4.5457452	-5.9812735	-7.4494132
C	-3.6467125	-5.7221155	-6.4155326
C	-3.4455142	-4.4178375	-5.9733058
H	-5.6129702	-2.8039534	-8.0229594
H	-5.9475263	-5.1222765	-8.8413809
H	-4.6972011	-6.9971038	-7.7977755
H	-3.1008357	-6.5385794	-5.9551420
H	-2.7450701	-4.2200386	-5.1709173
Li	-2.6620348	0.2190066	-4.8094017
O	-3.7375076	0.7596441	-3.1838349
O	0.3159895	-2.7449211	-5.9997461
C	-5.1468922	1.0672444	-2.9749851
C	-4.5801598	-0.1868757	-2.4747230
C	0.8538227	-2.3357930	-7.2898224
C	0.3046039	-3.6820039	-7.1052760
H	-5.7145635	1.0088963	-3.8991767
H	-4.3440618	-0.2811163	-1.4194947
H	1.9354930	-2.2360124	-7.2614136
H	0.9715772	-4.5277968	-6.9763925
H	-0.6843549	-3.9057822	-7.4925329
H	-4.7636872	-1.1103831	-3.0137529
C	0.1092734	-1.2607337	-8.0255874
H	0.4343556	-1.2440247	-9.0694226
H	-0.9669322	-1.4415151	-7.9968053
H	0.3168721	-0.2804882	-7.5899407
C	-5.4403804	2.2288217	-2.0713693
H	-6.4880604	2.1918307	-1.7600045
H	-4.8089567	2.1987862	-1.1813772
H	-5.2759730	3.1761022	-2.5911881
O	-0.8993867	-0.3058896	-4.0646602
C	0.1379585	0.5623860	-3.6356508
C	-0.4886000	0.2274222	-2.3525801
H	-0.0229932	1.5912823	-3.9680631
H	-1.3999014	0.7327261	-2.0751361
H	-0.2453421	-0.7153681	-1.8830453
C	1.5454107	0.0876765	-3.9150555
H	2.2679695	0.7411159	-3.4199169
H	1.6885909	-0.9327443	-3.5521163
H	1.7393124	0.1099598	-4.9899696
O	-1.0757308	-3.6822884	-3.4559812
C	-1.4024135	-4.0021880	-2.0810425
C	-0.1074580	-4.4012777	-2.6406587
H	-2.1875967	-4.7442139	-1.9778544
H	-1.4611945	-3.1445750	-1.4189579
H	0.7491404	-3.7844675	-2.3807801
C	0.1902914	-5.8110114	-3.0581748
H	0.8527800	-5.8225708	-3.9271234

H	0.6929163	-6.3349930	-2.2405419
H	-0.7290089	-6.3461774	-3.3038339
O	-2.1711866	1.7756639	-6.0153089
C	-2.4732640	1.9289819	-7.4271540
C	-2.7493420	3.0242801	-6.4948415
H	-3.2959508	1.3075428	-7.7671202
H	-1.5967335	1.9704791	-8.0653122
H	-2.0284106	3.8368977	-6.4602500
C	-4.1392808	3.3529319	-6.0355090
H	-4.1257352	3.7367266	-5.0124988
H	-4.5603151	4.1286665	-6.6815481
H	-4.7772350	2.4688579	-6.0806260
S	0.7463466	1.3146342	-0.5098259
C	1.5904164	-0.0209657	0.1768642
S	1.1004693	-1.6279178	0.1775050
S	3.1164425	0.5284057	0.9284469
C	3.8817798	-0.9930043	1.6018440
C	4.7155203	-1.7277127	0.5581347
O	5.0503166	-3.0062780	1.1998657
C	5.2177704	-4.0776754	0.4015169
C	5.5294281	-5.3134403	1.1703754
C	5.6009503	-5.3202306	2.5689544
C	5.8940051	-6.5015510	3.2426933
C	6.1185829	-7.6781229	2.5281082
C	6.0484943	-7.6742420	1.1346368
C	5.7544598	-6.4964625	0.4569551
O	5.1238642	-4.0340402	-0.8135929
H	5.4265441	-4.4058422	3.1213235
H	5.9478895	-6.5048587	4.3253852
H	6.3479133	-8.5970465	3.0561871
H	6.2232705	-8.5884847	0.5789791
H	5.6970627	-6.4814952	-0.6248507
H	3.0701759	-1.6306780	1.9536436
H	4.4937068	-0.6664719	2.4445246
H	4.1020328	-1.9531410	-0.3139941
C	5.9967840	-1.0141615	0.1635688
H	6.5503825	-1.5989264	-0.5722806
H	5.7549424	-0.0455312	-0.2802458
H	6.6286648	-0.8486257	1.0396410

V^d

73

Energy = -3109.383777888

Li	-1.8690246	0.4953862	-3.6297445
S	-1.1676613	6.6800712	-4.9838210
C	-2.4369167	5.5190697	-5.3662543
S	-1.9204301	3.8994010	-5.7457015
S	-4.0016570	6.0954075	-5.3367731
Li	-2.1095610	2.6713638	-2.1167333
C	-3.4699023	2.9215446	-5.7971264
H	-3.1747529	2.0326735	-6.3614770
H	-4.2064136	3.4913775	-6.3660862
C	-3.9633355	2.5250874	-4.3881600
H	-4.3442330	3.4498067	-3.9220055
O	-2.9603574	1.9590004	-3.6234735
C	-5.1596684	1.5772699	-4.5762652
H	-5.5673252	1.3097753	-3.5982759
H	-5.9581807	2.0335713	-5.1713846
H	-4.8329218	0.6576050	-5.0726134
S	-1.5866094	-1.3874780	-1.8582362
O	-0.8229457	1.1111970	-1.9453529
C	-0.7775673	0.0338749	-1.2903343
C	0.0086419	0.0188287	-0.0173353
C	0.7055135	1.1768134	0.3566242
C	1.4519473	1.2036932	1.5299100
C	1.5088013	0.0744189	2.3471876
C	0.8164194	-1.0813698	1.9840795
C	0.0724213	-1.1095695	0.8091791
H	0.6527146	2.0474057	-0.2857693
H	1.9904662	2.1028322	1.8085866
H	2.0903617	0.0944481	3.2624135
H	0.8576477	-1.9605065	2.6175663
H	-0.4670282	-2.0031856	0.5181345
O	-0.9594163	-0.2302153	-5.2621949
C	0.1436489	-1.1730680	-5.3118204
C	0.2771902	0.1438725	-5.9388491
H	-0.0488159	-2.0386747	-5.9374732
H	0.6069684	-1.3684763	-4.3512203
H	0.8364048	0.8952214	-5.3873782
C	0.1865712	0.3386286	-7.4236847
H	-0.2739350	1.3005343	-7.6633267
H	1.1920523	0.3298489	-7.8534955
H	-0.3987488	-0.4594390	-7.8840267
O	-3.2958953	2.6468102	-0.4478374
C	-4.7309637	2.9021959	-0.4634131
C	-4.2241620	1.5395930	-0.2904015
H	-5.0916215	3.1720833	-1.4523783
H	-4.2321564	0.8504254	-1.1282171
H	-4.2174131	1.0988160	0.7015306
C	-5.2676135	3.7117971	0.6805055
H	-6.3547635	3.6026739	0.7278173
H	-4.8406950	3.3755557	1.6274664
H	-5.0402680	4.7721023	0.5425811
C	0.4483774	5.7927509	-5.0165945
H	0.5403936	5.2482557	-5.9568466
H	1.1694251	6.6125821	-5.0276284
C	0.7173781	4.8595365	-3.8412094

H	-0.0290122	4.0700099	-3.7989446
O	0.6084618	5.6370579	-2.6078106
C	-0.3374465	5.2959627	-1.7216964
C	-0.3293164	6.1502425	-0.5103928
O	-1.1189623	4.3691299	-1.8893517
C	0.5408910	7.2400104	-0.3792804
C	0.5147158	8.0091166	0.7791198
C	-0.3727791	7.6943474	1.8084986
C	-1.2390446	6.6077390	1.6803685
C	-1.2198590	5.8369801	0.5240137
H	1.2287543	7.4808690	-1.1794213
H	1.1867603	8.8533726	0.8804259
H	-0.3889912	8.2950683	2.7109759
H	-1.9253526	6.3637680	2.4831218
H	-1.8825862	4.9873728	0.4097383
C	2.1222045	4.2810492	-3.9015856
H	2.2944394	3.6187399	-3.0514795
H	2.2425974	3.7021851	-4.8199985
H	2.8710246	5.0760478	-3.8912275

V^m

48

Energy = -2165.183466864

C	-1.3310886	-0.0599437	-0.3761470
C	0.1277778	-0.0896834	-0.1229443
S	3.9414178	-2.5669429	1.7139844
O	0.7691184	0.8813551	0.2658573
Li	1.6308187	2.2787016	1.2615932
C	2.2133432	-2.3669567	1.1064244
H	1.5969453	-1.9855451	1.9201048
H	1.8963198	-3.3866180	0.8811604
C	2.1149949	-1.4804570	-0.1374783
H	2.5557672	-0.5036918	0.0526805
O	0.6766876	-1.2825561	-0.3718295
C	2.6836393	-2.1120344	-1.3923993
H	2.5712404	-1.4367159	-2.2416928
H	3.7477024	-2.3115972	-1.2495256
H	2.1769109	-3.0543874	-1.6131514
C	-2.0333431	-1.2062271	-0.7709720
C	-3.4041309	-1.1347205	-0.9910041
C	-4.0785072	0.0744391	-0.8208626
C	-3.3810687	1.2174264	-0.4288617
C	-2.0112332	1.1520889	-0.2061275
H	-1.5076106	-2.1433029	-0.9005737
H	-3.9473943	-2.0219019	-1.2950223
H	-5.1476974	0.1260484	-0.9933283
H	-3.9053496	2.1568451	-0.2972099
H	-1.4611247	2.0345631	0.0970567
O	2.2309417	3.7197512	0.0229075
C	2.3620138	5.0414522	0.6431396
C	3.5495806	4.3058746	0.2085909
H	2.1317737	5.0009774	1.7044789
H	4.1643983	3.7973485	0.9440530
H	4.0378559	4.5804629	-0.7206208
C	1.7942383	6.1892279	-0.1367443
H	2.1779677	7.1290831	0.2700668
H	2.0740421	6.1231255	-1.1899158
H	0.7042783	6.2060567	-0.0571090
C	4.3169649	-1.1272734	2.6683195
S	3.0262341	0.0222518	2.8716374
S	5.8702776	-1.0175787	3.2687094
C	3.7688333	1.3705933	3.8669975
H	4.2073436	0.9408919	4.7684359
H	4.5470037	1.8337829	3.2569370
C	2.6057725	2.3522802	4.1333410
H	1.9617939	1.8693817	4.8978998
O	1.9071770	2.6115081	2.9751302
C	3.1850112	3.6231824	4.7758344
H	3.7297911	3.4047163	5.7010174
H	3.8629499	4.1194355	4.0746386
H	2.3692980	4.3121402	5.0099765

V^c

48

Energy = -2165.203942485

C	2.8024962	-2.7565349	3.5207385
C	1.5303040	-2.0108970	3.6661277
S	-3.0053483	-1.4084873	4.5417200
O	1.0154311	-1.3753031	2.7478105
Li	-0.4009423	-0.6630610	1.6583830
O	0.0653364	0.2211729	-0.0343484
C	-0.0805931	-0.4142475	-1.3444648
C	-0.9833897	0.6654827	-0.9422709
H	-0.4646932	-1.4276125	-1.2634466
H	-1.9862268	0.4234142	-0.6053568
H	-0.8240521	1.6652131	-1.3324557
C	1.0525778	-0.2030950	-2.3032226
H	0.7270381	-0.4687700	-3.3127843
H	1.3746367	0.8398686	-2.3013563
H	1.9013926	-0.8402317	-2.0424222
C	-1.4103439	-2.2937936	4.7032852
H	-1.2174884	-2.7257606	3.7168124
H	-1.5697539	-3.1002954	5.4210524
C	-0.2654124	-1.3854699	5.1493377
H	-0.2567561	-0.4805490	4.5466796
O	1.0064115	-2.0932145	4.8884648
C	-0.2683872	-1.0670192	6.6297816
H	0.5658302	-0.4125225	6.8875844
H	-1.2009140	-0.5568843	6.8807562
H	-0.2032062	-1.9828851	7.2215977
C	3.4381293	-2.7511015	2.2731333
C	4.6311788	-3.4417253	2.0975865
C	5.1953665	-4.1405928	3.1653176
C	4.5646738	-4.1482420	4.4096948
C	3.3707045	-3.4592791	4.5912679
H	2.9900963	-2.2051638	1.4518127
H	5.1210952	-3.4366621	1.1308070
H	6.1259650	-4.6796795	3.0277850
H	5.0038397	-4.6916841	5.2383340
H	2.8789538	-3.4641001	5.5554825
C	-2.8454950	-0.7102694	2.7859768
S	-4.4351925	0.2067714	2.5358172
S	-2.4843195	-1.9582476	1.5383736
C	-3.7117181	1.6464852	3.4016505
H	-4.2434238	2.5484428	3.1014913
H	-3.7848737	1.5114448	4.4805166
C	-2.2632044	1.6764976	2.9266413
H	-2.2188428	2.1270102	1.9320987
O	-1.8129312	0.2913190	2.7617581
C	-1.3235137	2.3935283	3.8777056
H	-1.6113910	3.4454881	3.9477577
H	-1.3693925	1.9491163	4.8738882
H	-0.2957376	2.3471494	3.5118818

TS^{V}

63

Energy = -3021.308734876

C	-1.3633924	0.1203254	-0.5055820
C	0.0123687	-0.0839191	0.0061616
S	3.5616704	1.1544284	3.1050624
O	0.9892910	-0.2741384	-0.7083291
Li	2.3487399	-0.3640888	-2.1127657
C	1.8575939	1.1576666	2.4063909
H	1.8161165	1.8588951	1.5733688
H	1.2433383	1.5504760	3.2183945
C	1.3830266	-0.2377672	1.9940682
H	2.0601771	-0.6663923	1.2570300
O	0.0803687	-0.0465445	1.3432590
C	1.1518149	-1.1816604	3.1571320
H	0.7974185	-2.1476463	2.7951400
H	2.0900422	-1.3378656	3.6936982
H	0.4163836	-0.7668105	3.8504237
C	-2.4642992	0.2044958	0.3571998
C	-3.7392348	0.3889228	-0.1656786
C	-3.9215883	0.4953874	-1.5447010
C	-2.8259210	0.4156992	-2.4046722
C	-1.5486504	0.2261504	-1.8896904
H	-2.3201584	0.1223312	1.4266530
H	-4.5911992	0.4499305	0.5015602
H	-4.9171931	0.6412485	-1.9487064
H	-2.9691652	0.5017390	-3.4757687
H	-0.6891493	0.1703192	-2.5470694
O	2.6478656	-2.3141311	-2.4533603
C	3.5605910	-2.6725930	-3.5386227
C	3.9081775	-2.9704811	-2.1483465
H	4.0227681	-1.7913019	-3.9752145
H	4.6250663	-2.3446377	-1.6269607
H	3.7939181	-3.9827591	-1.7748196
C	3.0664910	-3.7239117	-4.4874048
H	3.9045969	-4.1067037	-5.0761785
H	2.6102337	-4.5546768	-3.9456097
H	2.3306792	-3.3040369	-5.1783408
C	4.6777300	1.1437824	1.7368702
S	3.9731657	1.3226752	0.1538351
S	6.2970000	0.9788031	2.1027513
C	5.4163328	1.1870903	-0.9661518
H	6.1667992	1.9144702	-0.6562086
H	5.8179846	0.1779210	-0.8562494
C	4.9075183	1.4289940	-2.4015448
H	4.6757508	2.5112841	-2.4750761
O	3.7791164	0.6818913	-2.6746820
C	6.0650230	1.1331515	-3.3676570
H	6.9400206	1.7549126	-3.1519124
H	6.3527952	0.0803839	-3.2927129
H	5.7444560	1.3295388	-4.3919709
C	2.0968263	1.5252706	-3.9214799
O	1.3825420	0.5387978	-3.8079935
S	1.8301868	3.0583862	-2.9133942
C	2.9072830	4.0381608	-3.9885241
O	3.1516189	5.2134740	-3.8022347
C	2.9567318	1.8734764	-5.0741502

C	3.3958559	3.1987851	-5.1017268
C	4.2014786	3.6656349	-6.1394624
C	4.5451090	2.7847706	-7.1608649
C	4.0831406	1.4635614	-7.1456996
C	3.2834554	0.9977412	-6.1047821
H	4.5375574	4.6954642	-6.1502675
H	5.1671034	3.1263803	-7.9798033
H	4.3497413	0.7950672	-7.9561287
H	2.9244710	-0.0237241	-6.0893550

TS^{V*}
76
Energy = -3943.919255838
Li -8.0297304 -3.4132300 1.2583835
S -1.7133655 0.1414429 0.6625700
C -2.1941513 -1.5242384 1.0174691
S -3.7063350 -1.4439915 1.9330145
S -1.3652929 -2.8920934 0.5938866
Li -6.6524627 -1.1535000 1.3162360
C -4.2587269 -3.1915803 2.0149668
H -4.8701936 -3.2287124 2.9188379
H -3.3621384 -3.7980482 2.1491674
C -5.0663715 -3.6425057 0.7889075
H -4.4506191 -3.4421540 -0.1047970
O -6.2680948 -2.9357294 0.6696858
C -5.3055508 -5.1541876 0.8756475
H -5.8862465 -5.4798425 0.0090605
H -4.3617075 -5.7058394 0.8851975
H -5.8644234 -5.4069711 1.7821638
S -6.7300593 -0.6057778 3.8012955
O -8.4543772 -1.8074962 2.2534895
C -8.2461751 -1.3358914 3.4096370
C -9.3511544 -1.4124492 4.4104607
C -10.6260688 -1.8118296 3.9844233
C -11.6774545 -1.8970820 4.8908103
C -11.4665141 -1.5939237 6.2359234
C -10.2002826 -1.1987373 6.6692459
C -9.1506129 -1.1039718 5.7622459
H -10.7817024 -2.0440078 2.9379236
H -12.6614907 -2.1995399 4.5501992
H -12.2853743 -1.6639131 6.9435023
H -10.0324858 -0.9641062 7.7145441
H -8.1653111 -0.7947583 6.0907457
O -8.8444605 -5.0786727 1.7994368
C -9.2905586 -6.3029472 1.1597650
C -10.1636427 -5.6166794 2.1162893
H -8.7454907 -7.1846480 1.4799311
H -9.4752750 -6.2108801 0.0951248
H -10.9646574 -5.0094325 1.7039181
C -10.3519057 -6.1041566 3.5219001
H -10.4806825 -5.2631283 4.2077621
H -11.2506489 -6.7245820 3.5722994
H -9.4953996 -6.6987878 3.8445434
O -6.7892000 0.5314378 0.3084916
C -6.3670425 1.8671662 0.7179211
C -5.8709679 1.2796952 -0.5296548
H -5.7025255 1.8394661 1.5770244
H -4.8678022 0.8689032 -0.5751938
H -6.3013534 1.5965870 -1.4738239
C -7.4399246 2.9143820 0.7436779
H -6.9802264 3.9057324 0.7839586
H -8.0646387 2.8530805 -0.1494676
H -8.0695138 2.7954879 1.6288289
C -0.0113593 -0.0277990 0.0088344
H 0.0124530 -0.9194962 -0.6174713
H 0.1331999 0.8579007 -0.6108232
C 1.0498278 -0.1175380 1.0941158

H	0.8195309	-0.9182743	1.7954723
O	0.9940580	1.1494361	1.8224676
C	1.2490934	1.1268315	3.1451352
C	1.1312972	2.4719203	3.7678883
O	1.5402320	0.1123006	3.7570440
C	0.7650676	3.6038730	3.0292310
C	0.6614674	4.8393302	3.6598319
C	0.9223038	4.9527448	5.0252469
C	1.2881832	3.8268668	5.7634042
C	1.3926627	2.5899304	5.1380252
H	0.5619187	3.5139515	1.9699975
H	0.3769132	5.7142873	3.0866823
H	0.8406700	5.9172426	5.5141352
H	1.4912772	3.9145055	6.8246906
H	1.6754434	1.7086581	5.7012621
C	2.4415081	-0.3030278	0.5078554
H	3.1859293	-0.3323370	1.3054770
H	2.4860206	-1.2472599	-0.0391993
H	2.6841051	0.5122254	-0.1771622
C	-6.8610065	-2.6628656	-1.4044265
S	-8.4601593	-2.6060526	-1.2375572
S	-5.5084811	-2.6238731	-2.2307652

instead of **VI^m**, *starting and propagated polymeric model have been computed*

starting polymeric model

31
Energy = -1811.073838746

C	0.4988825	-1.0779613	-0.8584782
C	0.1307248	0.1496528	-0.1048083
S	2.0121353	3.4259139	3.2920675
O	-1.0161919	0.4902406	0.1331837
C	2.1718592	2.1114365	2.0320851
H	2.2744462	1.1655352	2.5635538
H	3.0988252	2.3444674	1.5063276
C	0.9823921	2.0679209	1.0764415
H	0.0561177	1.9327371	1.6336861
O	1.2111403	0.8493937	0.2945441
C	0.8901375	3.2565242	0.1363696
H	0.0334704	3.1487199	-0.5304282
H	0.7602423	4.1749726	0.7133480
H	1.8008888	3.3437986	-0.4609222
C	-0.5334025	-1.8907997	-1.3416243
C	-0.2348716	-3.0518626	-2.0453223
C	1.0951426	-3.4079832	-2.2708745
C	2.1264562	-2.6003676	-1.7915733
C	1.8330532	-1.4372738	-1.0871325
H	-1.5624029	-1.6042650	-1.1598936
H	-1.0366310	-3.6791765	-2.4176188
H	1.3275087	-4.3140429	-2.8193254
H	3.1597559	-2.8775743	-1.9664781
H	2.6320550	-0.8099359	-0.7139724
C	1.0439757	2.6591502	4.5663288
S	0.7525282	3.8576155	5.8221117
S	0.5179280	1.0904786	4.5852139
C	-0.1645659	2.9218361	7.0861002
H	-1.0998095	2.5549205	6.6690808
H	0.4458640	2.1001385	7.4546628
H	-0.3541610	3.6452495	7.8786986

propagated polymeric model

69

Energy = -3888.234679299

C	3.4100182	-4.4692950	3.9414966
C	2.2809928	-3.7889830	3.2536380
S	-2.3795394	-4.6432450	1.4226097
O	2.3892503	-2.7671215	2.5978140
C	-0.9311102	-5.0807748	2.4489592
H	-0.3529006	-5.8201579	1.8955786
H	-1.3555405	-5.5361046	3.3445377
C	-0.0761494	-3.8628885	2.7892387
H	0.2542836	-3.3670791	1.8767828
O	1.1086666	-4.4335837	3.4325109
C	-0.7379494	-2.8786922	3.7378785
H	-0.0649216	-2.0474519	3.9522069
H	-1.6454631	-2.4770861	3.2817446
H	-1.0077622	-3.3725352	4.6743470
C	3.2348904	-5.6591613	4.6590582
C	4.3244847	-6.2600016	5.2810360
C	5.5896037	-5.6793222	5.1919920
C	5.7665683	-4.4932409	4.4787337
C	4.6810789	-3.8893328	3.8547031
H	2.2525769	-6.1084365	4.7269931
H	4.1874193	-7.1814661	5.8352450
H	6.4368222	-6.1503153	5.6780223
H	6.7494839	-4.0413695	4.4098619
H	4.8060908	-2.9685423	3.2975780
C	-1.7297983	-4.6399482	-0.2271446
S	-3.0016261	-4.0333140	-1.2899147
S	-0.2199513	-5.1340224	-0.6860240
C	-2.3016512	-4.2488507	-2.9689426
H	-1.7410280	-5.1833728	-2.9742070
H	-3.1756386	-4.3445509	-3.6145455
C	-1.4107478	-3.1043300	-3.4209040
H	-0.6143632	-2.9269183	-2.7005039
O	-2.2622658	-1.9131947	-3.4516070
C	-0.8385836	-3.3586735	-4.8076208
H	-0.2026249	-4.2462403	-4.7828268
H	-1.6396554	-3.5204688	-5.5321212
H	-0.2320233	-2.5104314	-5.1282142
C	-1.6695328	-0.7272764	-3.2345673
C	-2.6175509	0.4126397	-3.3530513
O	-0.4835526	-0.5944688	-2.9858689
C	-2.2542243	1.6709179	-2.8430792
C	-3.0955074	2.7647764	-3.0398094
C	-4.2996716	2.6126195	-3.7232632
C	-4.6675892	1.3651508	-4.2208219
C	-3.8281600	0.2717755	-4.0390199
C	-0.9896766	1.9008009	-2.0652078
H	-2.8149860	3.7351616	-2.6468013
H	-4.9477208	3.4697144	-3.8650396
H	-5.6020393	1.2448534	-4.7561903
H	-4.0977934	-0.6958397	-4.4415956
O	-0.0572344	2.5649295	-2.4707341
O	-1.0823178	1.3634591	-0.8377691
C	0.0689742	1.4685073	0.0656916
C	-0.3993793	2.1997531	1.3149730

H	0.8452010	2.0349848	-0.4447876
S	-0.8952400	3.9370577	1.0213482
H	0.3918905	2.2075730	2.0652214
H	-1.2921945	1.7302953	1.7305027
C	0.5352995	0.0579663	0.3865173
H	1.4048998	0.0985377	1.0455861
H	-0.2561920	-0.5056954	0.8857102
H	0.8129392	-0.4615584	-0.5310795
C	0.6465254	4.8086450	1.0338738
S	2.1346185	4.1592329	1.3597491
S	0.3257461	6.4975498	0.6535762
C	1.9665782	7.2743462	0.7902552
H	1.7926516	8.3257953	0.5627198
H	2.3488386	7.1589705	1.8022716
H	2.6466891	6.8319802	0.0655279

Section S9: Bibliography

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