Electronic Supplementary Material (ESI) for Chemical Science.

The Hydrogen Atom Transfer Reactivity of Sulfinic Acids

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Supporting Information

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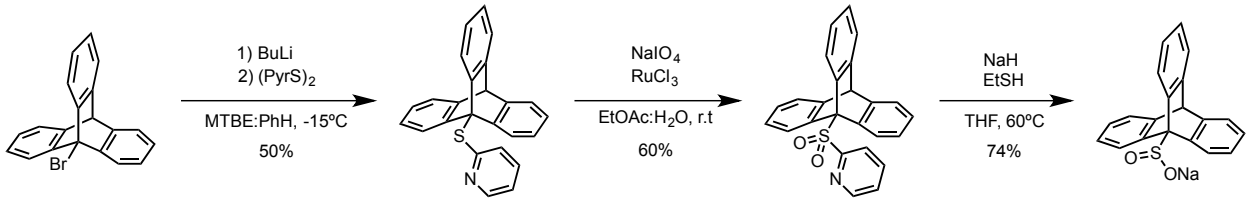
Synthetic Procedures

Synthesis of 9-triptycenesulfinic acid



2-(9,10-[1,2]benzenoanthracen-9(10H)-ylthio)pyridine.

9-Bromotriptycene (4.0 g, 12.0 mmol) was dissolved in dry MTBE (95 mL) and benzene (145 mL) and cooled to -15 °C under nitrogen. After stirring for 15 minutes, BuLi (5.8 mL, 14.5 mmol) was added dropwise. The solution was warmed to 0 °C over 30 minutes and 2,2'-dithiopyridine was added all at once and the resulting yellow solution was stirred overnight. The reaction was quenched with water (100 mL) and added to EtOAc (150 mL) in a separatory funnel. The organic phase was washed with water and brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude solid was purified by column chromatography using 10% EtOAc/hexanes as the eluent to yield the product as a white solid (2.10 g, 50%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.49 (ddd, *J* = 4.8, 1.8, 0.8 Hz, 1H), 7.51-7.43 (m, 6H), 7.29-7.25 (m, 1H), 7.07-6.94 (m, 7H), 6.67 (d, *J* = 8.2 Hz, 1H), 5.46 (s, 1H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 158.5, 149.3, 145.4, 142.9, 135.8, 125.9, 125.0, 124.6, 123.8, 123.6, 119.7, 62.1, 54.1. HRMS (EI, [M^+]): m/z calcd for $C_{25}H_{17}NS$: 363.1082, found 363.1079.

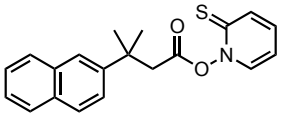
2-(9,10-[1,2]benzenoanthracen-9(10H)-ylsulfonyl)pyridine.

2-(9,10-[1,2]benzenoanthracen-9(10H)-ylthio)pyridine (1.50 g, 4.30 mmol) was added to a 1:1 mixture of EtOAc and water (16 mL) and cooled to 0 °C under N_2. $RuCl_3$ (44.4 mg, 0.21 mmol) was added and the solution was stirred for 10 minutes before $NaIO_4$ (5.50 g, 26.0 mmol) was added portion wise and the mixture was vigorously stirred at room temperature overnight. The solution was diluted with ethyl acetate (100 mL) and washed with water and brine. The organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo. The crude yellow solid was purified by column chromatography using a gradient of 10-20% EtOAc/hexanes as the eluent to yield the product as a white

solid (1.10 g, 60%). ^{1}H NMR (400 MHz; CD_3CN): δ 8.41 (dt, *J* = 8.1, 1.0 Hz, 1H), 8.36 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.24-8.18 (m, 2H), 7.80 (dt, *J* = 7.9, 0.5 Hz, 2H), 7.64 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H), 7.53-7.49 (m, 3H), 7.13-7.08 (m, 4H), 6.97-6.93 (m, 2H), 5.60 (s, 1H). ^{13}C NMR (101 MHz; acetone-d_6): δ 162.4, 149.8, 147.3, 146.4, 141.6, 140.8, 140.2, 128.8, 127.2, 126.85, 126.66, 125.35, 125.24, 124.99, 124.91, 124.2, 122.8, 78.8, 54.9. HRMS (EI, [M^+]): m/z calcd for $C_{25}H_{17}NO_2S$: 395.0980, found 395.0985.

Sodium 9,10-[1,2]benzenoanthracene-9(10H)-sulfinate.

2-(9,10-[1,2]benzenoanthracen-9(10H)-ylsulfonyl)pyridine (1.00 g, 2.53 mmol) was dissolved in dry THF (12 mL), cooled to 0 °C and purged with N_2 in a sealed tube. NaH (30.4 mg, 7.59 mmol) was added portion wise followed by EtSH (violent gas evolution) and the tube was sealed quickly. The solution was stirred at 70 °C overnight after which the reaction was quenched with methanol (5 mL) and concentrated. The crude product was purified by column chromatography using a gradient of 10-20% MeOH:DCM to yield the product as a off white solid (63.0 mg, 74%). ^{1}H NMR (400 MHz; CD_3OD): δ 8.26 (br, 3H), 7.36-7.34 (m, 3H), 7.01-6.94 (m, 6H), 5.32 (s, 1H). ^{13}C NMR (151 MHz; CD_3OD): δ 148.1, 143.9, 126.5, 126.2, 125.5, 123.8, 75.9, 55.8. HRMS (ESI, [M-H+]): m/z calculated for $C_{20}H_{13}O_2S$: 317.0642, found 317.0652.



2-thioxopyridin-1(2H)-yl 3-methyl-3-(naphthalen-2-yl)butanoate. 3-methyl-3-(naphthalen-2-yl)butanoic acid[1, 2] (0.600 g, 2.60 mmol) was dissolved in dry benzene (15 mL) in an over-dried round bottom flask and purged with N_2 for 5 minutes. DMF (1 drop) and thionyl chloride (0.283 mL, 3.9 mmol) were added dropwise and the solution was heated at reflux for 2 hours. Excess thionyl chloride was removed by rotary evaporation and the crude acyl chloride was dissolved in benzene (2 mL) and added dropwise to a stirred suspension of 2-mercaptopyridine sodium salt (0.500 g, 3.38 mmol) and DMAP (0.050 g, 0.40 mmol) in benzene (10 mL). The solution was stirred at room temperature for 1 hour in the dark after which it was concentrated and the crude yellow solid was purified by column chromatography using 50% EtOAc/hexanes as the

eluent to yield the product as a yellow solid (0.53 g, 61%). ^{1}H NMR (600 MHz; $CDCl_3$): δ 7.86-7.81 (m, 4H), 7.60 (ddd, *J* = 8.7, 4.8, 1.8 Hz, 2H), 7.50-7.45 (m, 2H), 7.07 (ddd, *J* = 8.7, 7.0, 1.6 Hz, 1H), 6.75 (d, *J* = 7.0 Hz, 1H), 6.34 (td, *J* = 6.9, 1.7 Hz, 1H), 3.15 (s, 2H), 1.68 (s, 6H). ^{13}C NMR (151 MHz; $CDCl_3$): δ 175.9, 166.6, 144.2, 137.5, 137.3, 133.5, 133.3, 132.1, 128.2, 128.2, 127.5, 126.4, 126.0, 124.5, 124.2, 112.5, 45.2, 37.9, 29.1.

***N-Hydroxy-N-methylbenzamide.*[3]** A suspension of N-methylhydroxylamine hydrochloride (2.02 g, 24 mmol) in THF/H_2O (40 mL, 10:1) at 0 °C was treated with $NaHCO_3$ (4.06 g, 48 mmol) and stirred for 10 min, then benzoyl chloride (2.81 mL, 24 mmol) was added dropwise over 10 min. The reaction was stirred overnight without cooling. After dilution with 50 mL of DCM and H_2O the solution was extracted three times with DCM and washed with brine. The yellow oil was purified by column chromatography (20% EtOAc/hexanes to 100% EtOAc) to give a pale yellow oil (2.50 g, 69%). ^{1}H NMR (400 MHz; DMSO-d_6): δ 9.99 (s, 1H), 7.63-7.56 (m, 2H), 7.48-7.37 (m, 3H), 3.24 (s, 3H).

***2,4-Dimethyl-2,4-diphenyl-3-pentanone.*[4]** 1,3-diphenylpropan-2-one (2.00 g, 9.5 mmol), dissolved in 30 mL of dry THF was added dropwise over 15 min to a suspension of NaH (2.28 g, 95 mmol) in 30 mL of dry THF under N_2 at 0 °C. After 30 min of stirring, MeI (14.2 g, 100 mmol) was added dropwise and after 30 min the reaction was heated to reflux for 3 h. After cooling and addition of water the mixture was extracted three times with EtOAc, washed with brine, and dried over $MgSO_4$ and concentrated in vacuo. To also convert remaining trimethylated product the procedure was repeated once more with a third of the reagents. Finally the product was recrystallized from hexanes to give white needles (1.18 g, 46%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.26-7.24 (m, 2H), 7.23-7.17 (m, 6H), 1.29 (s, 12H).

Procedure to Determine BDEs Through REqEPR

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMXplus (X-band) spectrometer equipped with an ER 4119HS cavity. The (composite) spectra were fitted and the radical concentration was determined using the quantitative EPR package of the Bruker Xenon software. To generate the radicals 5% (v/v) di-*tert*-butyl peroxide was added to the solutions in benzene (with or without 10% v/v t-BuOH) under nitrogen and the EPR cavity irradiated with a Hamamatsu LC5 Hg−Xe lamp (150 W) via a 3.5 mm quartz light guide. REqEPR experiments with sulfonyl radicals were performed under continuous irradiation.

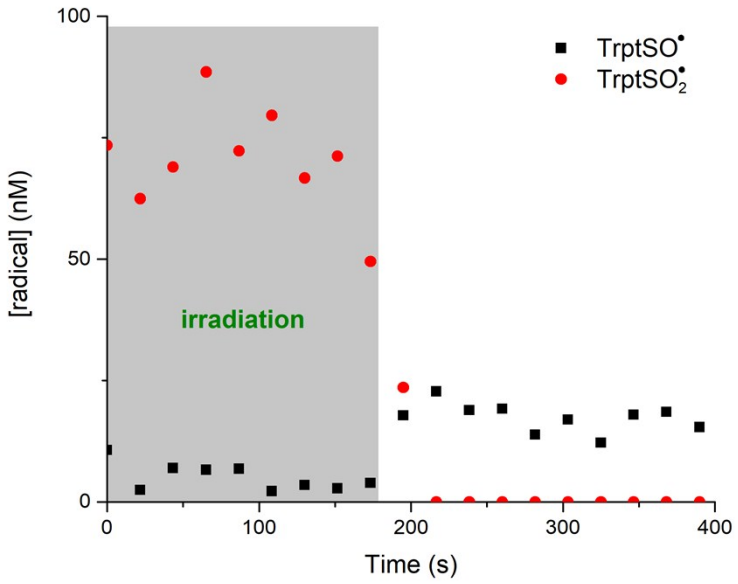


Figure S1. Concentrations of sulfinyl and sulfonyl radicals, determined during and after the irradiation of $TrptSO_2H$ (4 mM) and 5% (v/v) di-*tert*-butyl peroxide in benzene with 10% (v/v) *t*-BuOH at 25 °C.

During the REqEPR experiments the concentrations of nitroxide and sulfonyl radical were recorded over time under continuous irradiation, which was necessary due to the decay of the sulfonyl radicals. Data after reaching “stable” conditions were processed and averaged. In total 5 concentrations (54 data points) were averaged for $TrptSO_2H$ and 4 concentrations (75 data points) were averaged for $PhSO_2H$.

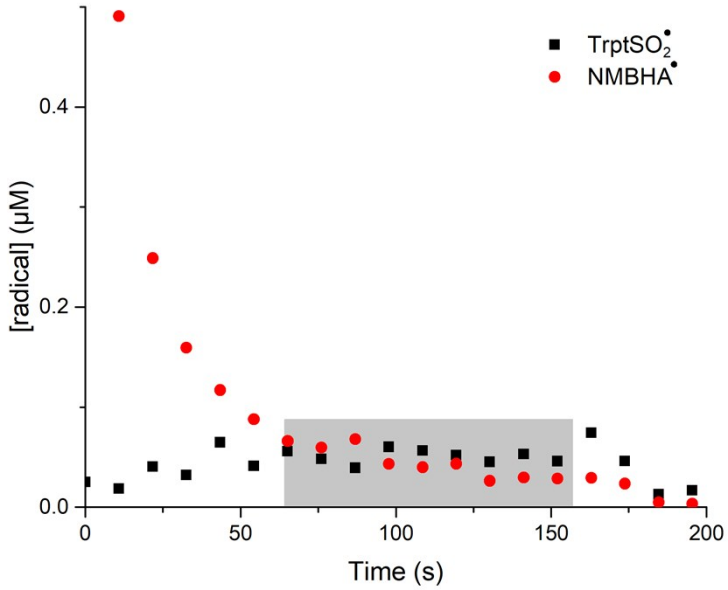


Figure S2. Concentrations of nitroxide and sulfonyl radical, determined during the irradiation of $TrptSO_2H$ (4 mM) and NMBHA (0.5 mM) and 5% (v/v) di-*tert*-butyl peroxide in benzene with 10% (v/v) *t*-BuOH at 25 °C. The grey area represents the region of useful data.

Assuming a negligible reaction entropy for the H-atom exchange and given the known BDE of NMBHA, the BDE for sulfinic acid can be determined. As all involved compounds are relative strong hydrogen bond donors it is important to take this influence on the apparent BDE into account. For this purpose we also re-examined the BDE of NMBHA as at the time no correction had been made.[5] The important properties to know is the hydrogen bond acidity α_2^H of the analytes as well as the hydrogen bond basicity β_2^H of the solvent system. This influence has been quantified previously[6] and can be expressed by the following equation:

$$\Delta H\left(\frac{kcal}{mol}\right) = -20.56\ \alpha_2^H\beta_2^H + 0.59$$

The β_2^H for benzene is 0.14 and for and the mixture of benzene/*t*-BuOH 9:1, which was necessary to solubilize NMBHA and $TrptSO_2H$, was determined as 0.34. This was achieved via the via the ^{19}F NMR method we have described previously.[7] The α_2^H values

for phenols have been studied previously.[7] We employed a value of α_2^H = 0.24 for BHT,[8] while NMBHA was determined to have α_2^H = 0.45 (via ^{1}H NMR shifts in $CDCl_3$ and DMSO-d_6).[9]

Using these values we obtained a new, solvent corrected, BDE for NMBHA of 78.0 ± 0.2 kcal/mol. Referencing this value and employing an α_2^H = 0.64 for sulfinic acid (see manuscript) we can determine an O-H BDE of 77.6 kcal/mol for 9-triptycenesulfinic acid. For phenylsulfinic acid a similar correction (in benzene) is necessary, finally yielding a BDE of 78.3 kcal/mol. Both values are in very good agreement with the CBS-QB3 calculations. The direct experimental error from the processed data is 0.2 kcal/mol, although including the error for the reference NMBHA and the solvent effect a more appropriate error is ± 1.0 kcal/mol.

LFP – Details and Results

Table S1. Summary of rate constants (k_H) for HAT by cumyl radicals, determined via photolysis of dicumylketone.

	k_H (M^{-1} s^{-1})	
Solvent	**$PhSO_2H$**	**TrptSOH**
isooctane	-	$(1.2 \pm 0.2) \times 10^7$
chlorobenzene	$(1.7 \pm 0.2) \times 10^6$	$(5.0 \pm 0.4) \times 10^6$
benzene	$(1.0 \pm 0.2) \times 10^6$	$(2.9 \pm 0.4) \times 10^6$
anisole	$(2.3 \pm 0.3) \times 10^5$	$(6.1 \pm 0.8) \times 10^5$

Table S2. Summary of rate constants (k_H) for HAT by benzophenone triplet.

	k_H (M^{-1} s^{-1})		
Solvent	**$PhSO_2H$**	**$TrptSO_2H$**	**TrptSOH**
chlorobenzene	$(2.3 \pm 0.6) \times 10^9$	-	-
benzene	$(1.7 \pm 0.3) \times 10^9$	-	$(2.3 \pm 0.1) \times 10^9$
acetonitrile	$(6.5 \pm 0.1) \times 10^7$	$(1.8 \pm 0.1) \times 10^8$	$(8.6 \pm 0.1) \times 10^8$
ethyl acetate	$(2.0 \pm 0.1) \times 10^7$	-	$(5.0 \pm 0.1) \times 10^8$

Table S3. Summary of rate constants (k_H) for HAT by cumyloxyl radicals, determined via photolysis of dicumylperoxide.

	k_H (M^{-1} s^{-1})	
Solvent	**$PhSO_2H$**	**TrptSOH**
isooctane	-	$(2.3 \pm 0.5) \times 10^9$
chlorobenzene	-	$(1.6 \pm 0.1) \times 10^9$
benzene	$(6.9 \pm 1.3) \times 10^8$	$(1.4 \pm 0.2) \times 10^9$
anisole	-	$(6.9 \pm 0.2) \times 10^8$
acetonitrile	-	$(3.6 \pm 0.1) \times 10^8$
ethyl acetate	-	$(2.3 \pm 0.3) \times 10^8$
dimethyl sulfoxide	-	$(5.2 \pm 1.0) \times 10^7$

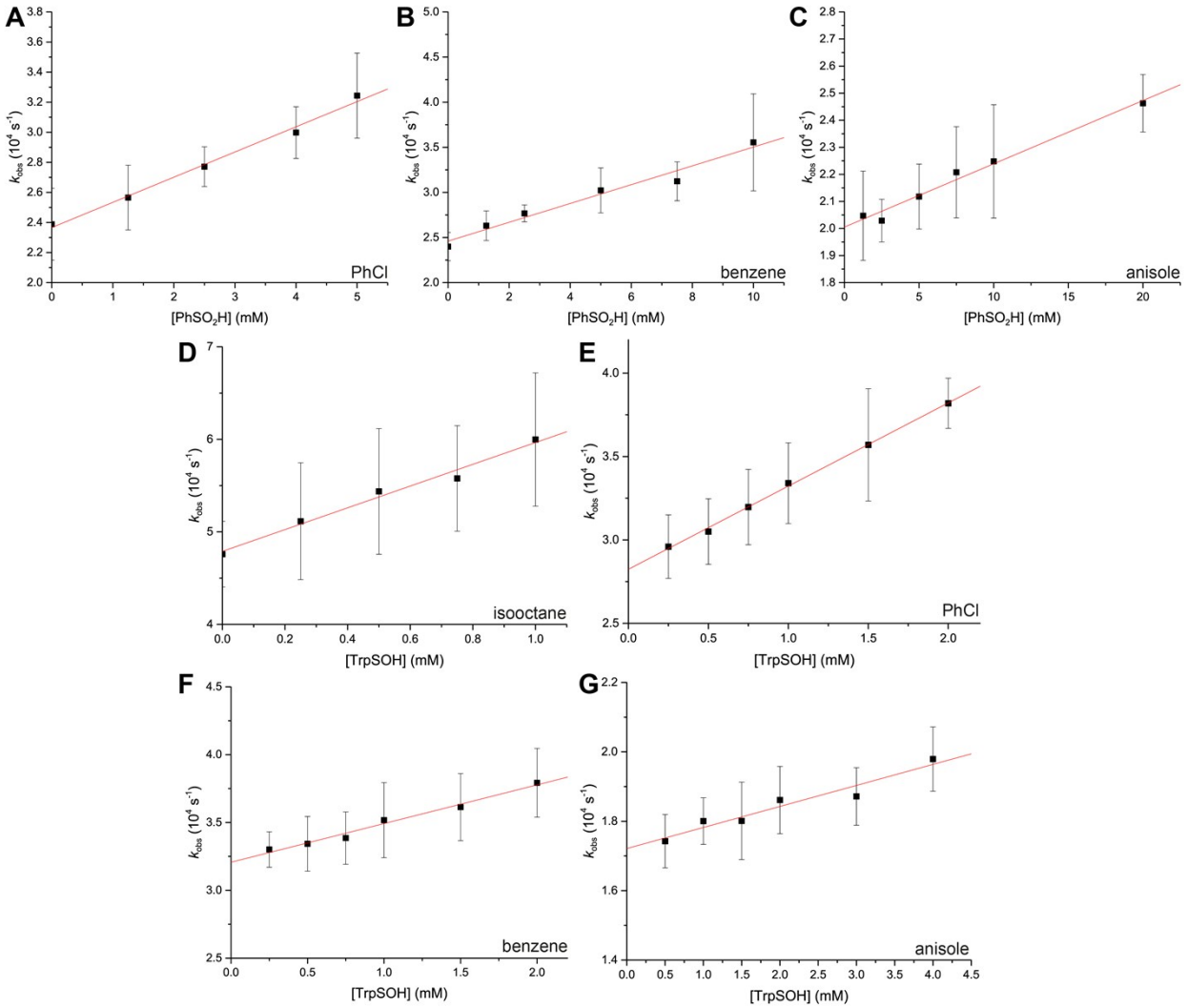


Figure S3. Dependence of the pseudo-first-order rate on the concentration of $PhSO_2H$ (A-C) and TrpSOH (D-G) upon photolysis of dicumylketone (2 mM) at 25 °C in PhCl (A, E), benzene (B, F), anisole (C, G), and isooctane (D).

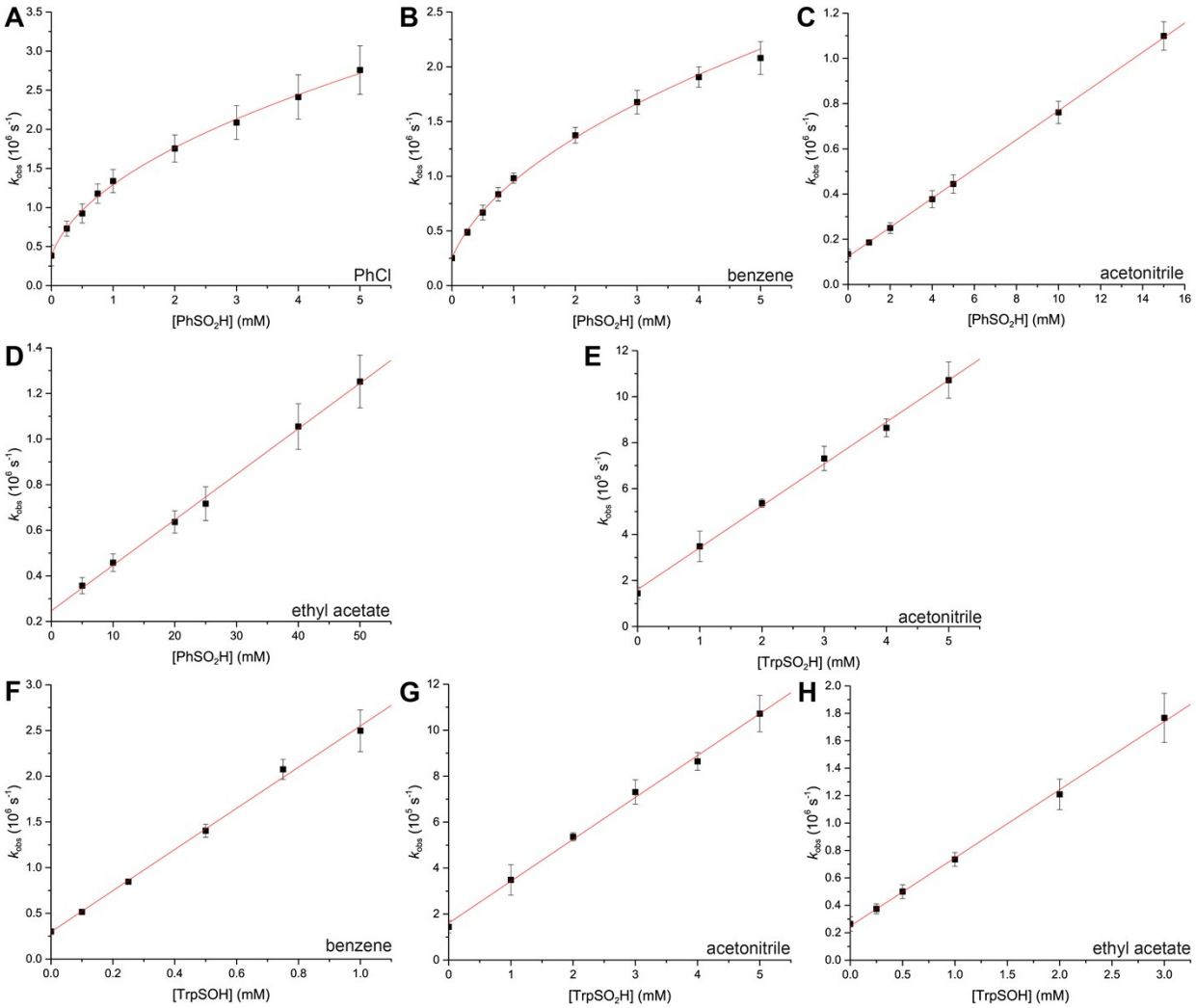


Figure S4. Dependence of the pseudo-first-order rate on the concentration of $PhSO_2H$ (A-D), $TrptSO_2H$ (E), and TrpSOH (F-H) upon photolysis of benzophenone (2 mM) at 25 °C in chlorobenzene (A), benzene (B, F), acetonitrile (C, E, G), and ethyl acetate (D, H).

Generation of cumylperoxyl radicals

LFP experiments (308 nm) were performed under oxygen atmosphere in benzene with between 1 and 3 mM of dicumylketone and the appearance of sulfonyl radical (from sulfinic acid) was monitored at 350 nm. The concentration of $PhSO_2H$ was varied between 1 and 20 mM. No appearance of signal could be observed (also at longer timescales eg. 250 µs). A higher concentration of dicumylketone let to a decrease in radical production because of optical density.

Performing equivalent experiments under nitrogen atmosphere were successful in determining HAT kinetics of cumyl radicals indirectly in a concentration range of 1-5 mM of $PhSO_2H$.

Transient Absorption Experiments with PhSSPh

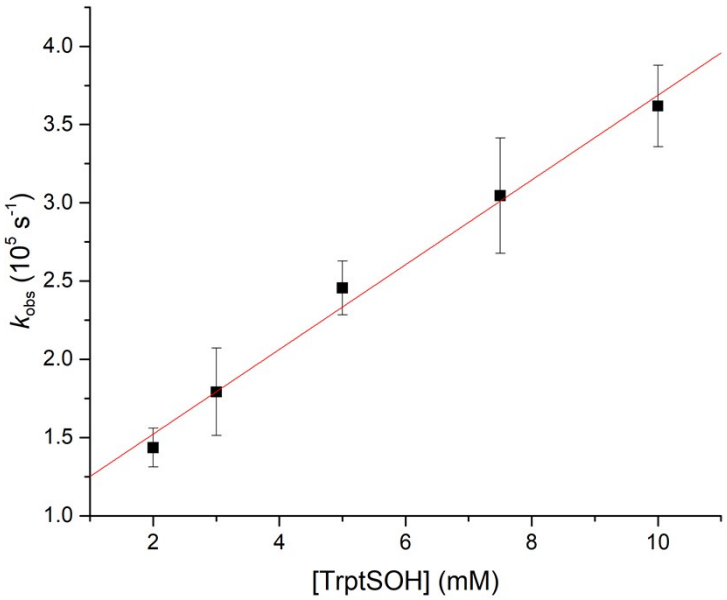


Figure S5. Dependence of the pseudo-first-order rate on the concentration of TrptSOH upon photolysis of diphenyl disulfide in acetonitrile at 25 °C.

As the phenylthiyl radical has a visible absorption (observed at 460 nm) and is easily produced by photolysis of diphenyldisulfide (0.2 mM), it is a convenient probing molecule. While for TrptSOH HAT activity with PhS$^{\bullet}$ can be observed (k = (2.7 ± 0.4) × 10^7 M^{-1} s^{-1} in acetonitrile – single experiment), no reactivity could be discerned for $PhSO_2H$. This is also corroborated when calculating the corresponding TS via CBS-QB3. For $PhSO_2H$ $\Delta G^{\ddagger}$ = 15.1 kcal/mol corresponding to a rate constant of to k = 1.2 × 10^3 M^{-1} s^{-1}, in addition the reaction is only exergonic by 4.6 kcal/mol. In contrast for sulfenic acids ΔG° ~ -14 kcal/mol and the rate constant predicted near the diffusion limit.

Estimation of the Kinetics of Addition of the Tosyl Radical to Oxygen

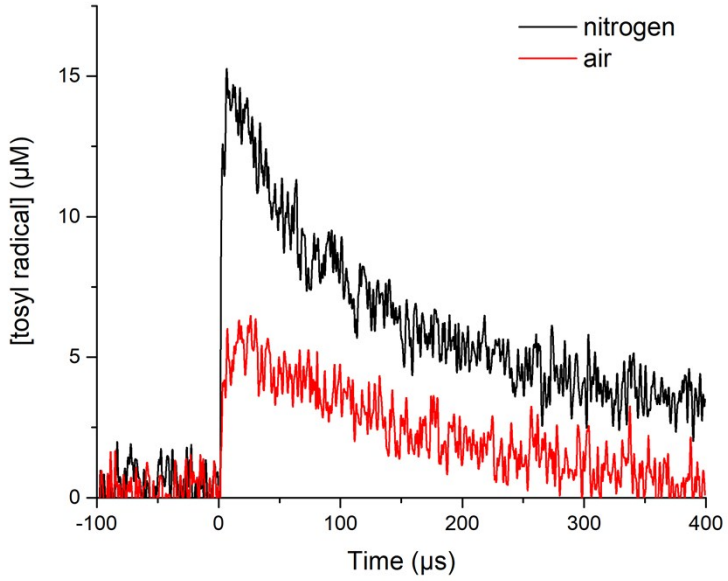


Figure S6. Decays for the tosyl radical (335 nm, ε = 1200 M^{-1} cm^{-1})[10] under nitrogen (black) and air (red) generated from a solution of 0.2 mM p-toluenesulphonyl iodide[11] in benzene at 25 °C.

The following rate constants were determined for the (apparent) disproportionation reaction in second order:

nitrogen: k_{RSO_2} = (7.3 ± 0.5) × 10^8 M^{-1} s^{-1}

air: k_{obs} = (1.0 ± 0.2) × 10^9 M^{-1} s^{-1}

Under the assumption that the difference in second order rate is caused by the reaction with oxygen the following equation can be constructed:

$$k_{obs}[RSO_2]^2 = k_{RSO_2}[RSO_2]^2 + k_{O_2}[RSO_2][O_2]$$

As [RSO_2•] is ~ 6 μM at the begin of the decay we can estimate the rate constant k_{O_2} = (9 ± 4) × 10^5 M^{-1} s^{-1}.

Co-autoxidations in Organic Solutions

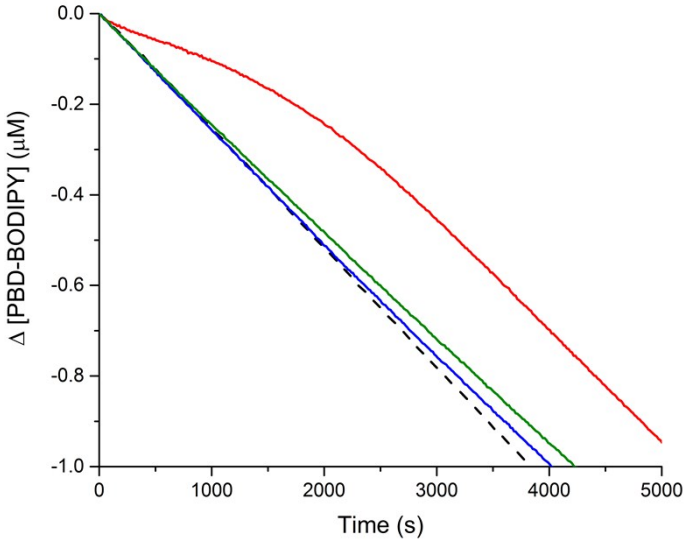


Figure S7. Thermally initiated (AIBN, 6 mM) co-autoxidations of THF (3.1 M) and PBD-BODIPY (10 μM) at 37 °C in PhCl inhibited by 10 μM of TrptSOH (red), $TrptSO_2H$ (blue) or $PhSO_2H$ (green). Reaction progress was monitored via absorbance at 588 nm (ε = 128 100 M^{-1} cm^{-1}).[12]

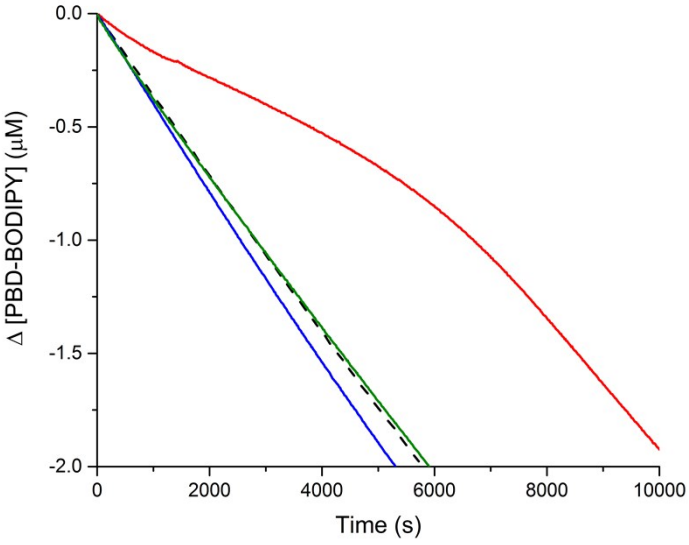


Figure S8. Thermally initiated (AIBN, 6 mM) co-autoxidations of dioxane (2.9 M) and PBD-BODIPY (10 μM) at 37 °C in PhCl inhibited by 10 μM of TrptSOH (red), $TrptSO_2H$ (blue) or $PhSO_2H$ (green). Reaction progress was monitored via absorbance at 587 nm (ε = 123 000 M^{-1} cm^{-1}).[12]

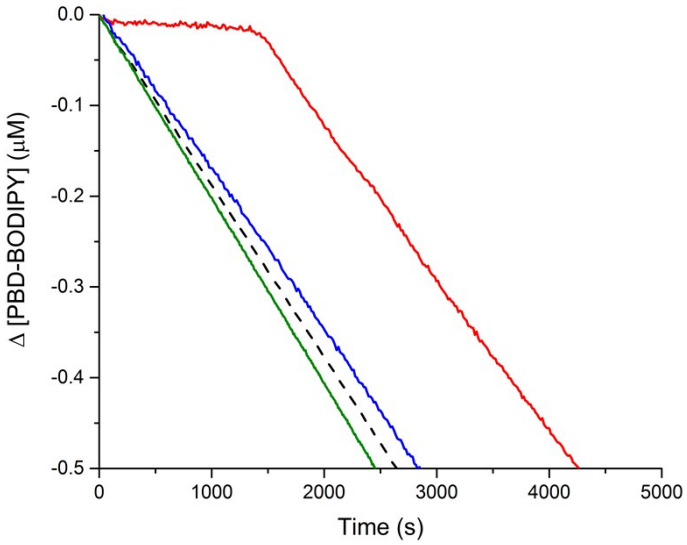


Figure S9. Thermally initiated (AIBN, 6 mM) co-autoxidations of styrene (4.3 M) and PBD-BODIPY (10 μM) in PhCl at 37 °C inhibited by 10 μM of TrptSOH (red), $TrptSO_2H$ (blue) or $PhSO_2H$ (green). Reaction progress was monitored via absorbance at 591 nm (ε = 139 000 M^{-1} cm^{-1}).[13]

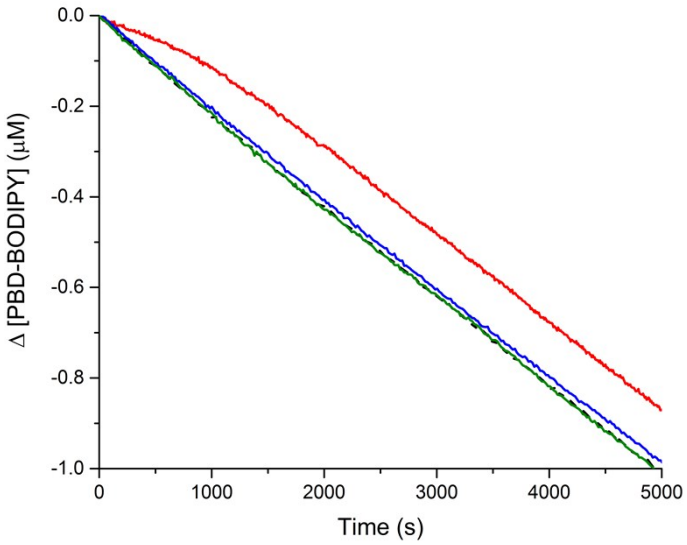


Figure S10. Thermally initiated (AIBN, 6 mM) co-autoxidations of styrene (4.3 M) and PBD-BODIPY (10 μM) in MeCN at 37 °C inhibited by 10 μM of TrptSOH (red), $TrptSO_2H$ (blue) or $PhSO_2H$ (green). Reaction progress was monitored via absorbance at 585 nm (ε = 127 860 M^{-1} cm^{-1}).[13]

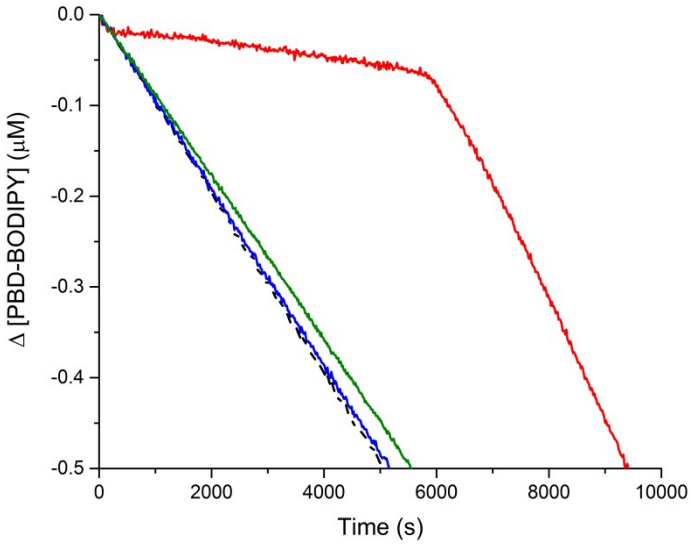


Figure S11. Thermally initiated (AIBN, 6 mM) co-autoxidations of hexadecene (2.8 M) and PBD-BODIPY (10 μM) at 37 °C in PhCl inhibited by 10 μM of TrptSOH (red), $TrptSO_2H$ (blue) or $PhSO_2H$ (green). Reaction progress was monitored via absorbance at 588 nm (ε = 148 700 M^{-1} cm^{-1}).[12]

Summary of Rate Constants for Peroxyl Radicals

Table S4. Summary of rate constants (k_{inh}) and stoichiometry (n) during inhibited co-autoxidations (6 mM AIBN) at 37 °C.

	TrptSOH	
Substrate/Solvent	k_{inh} (M^{-1} s^{-1})	n
THF/PhCl	$(1.2 \pm 0.2) \times 10^5$	0.6 ± 0.1
Dioxane/PhCl	$(2.7 \pm 0.4) \times 10^5$	0.7 ± 0.1
Styrene/PhCl	$(3.6 \pm 0.7) \times 10^6$	0.5 ± 0.05
Styrene/MeCN	$(2.5 \pm 0.6) \times 10^5$	0.5 ± 0.03
Hexadecene/PhCl	$(1.8 \pm 0.4) \times 10^6$	0.7 ± 0.1

Naphthyl-Neophyl Clock to Measure Alkyl Radical Kinetics

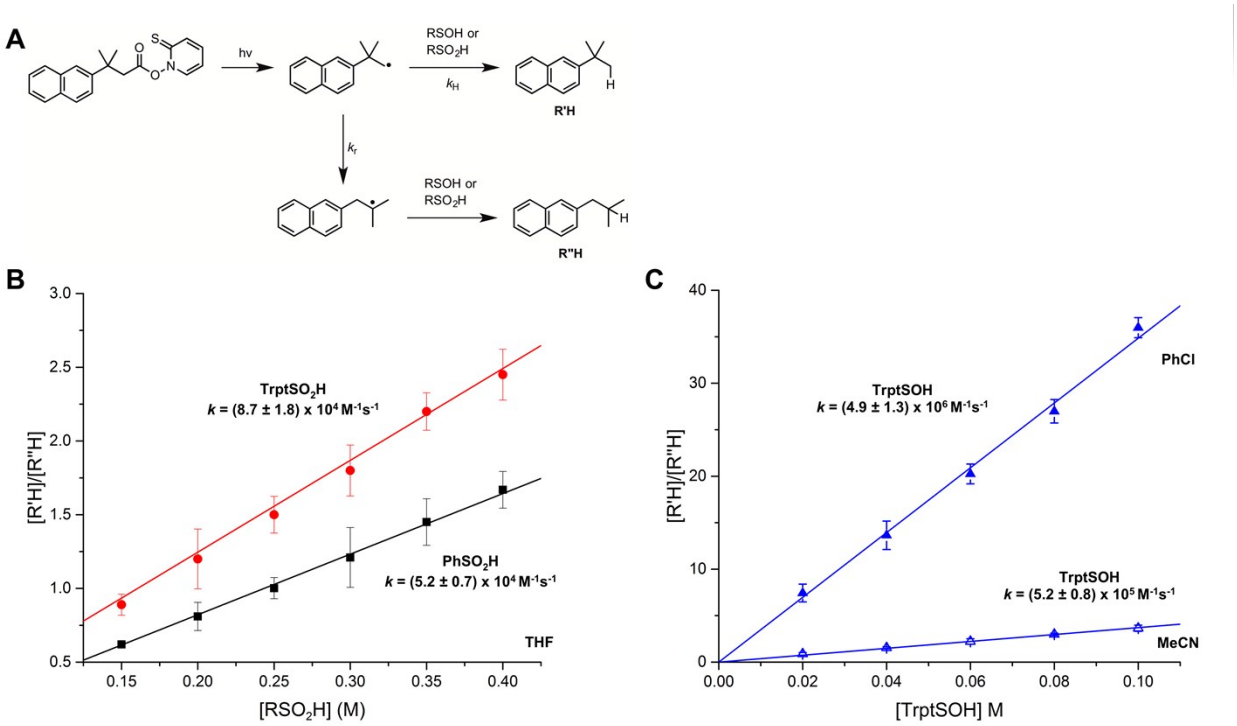
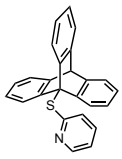
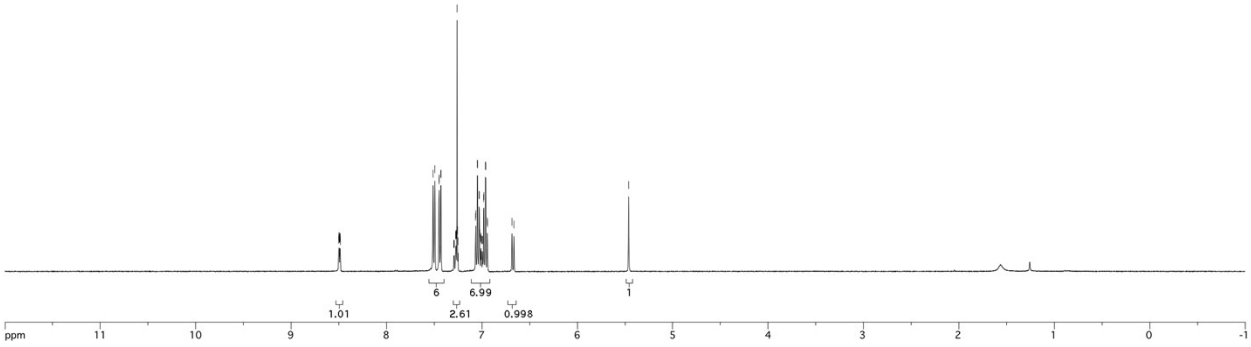


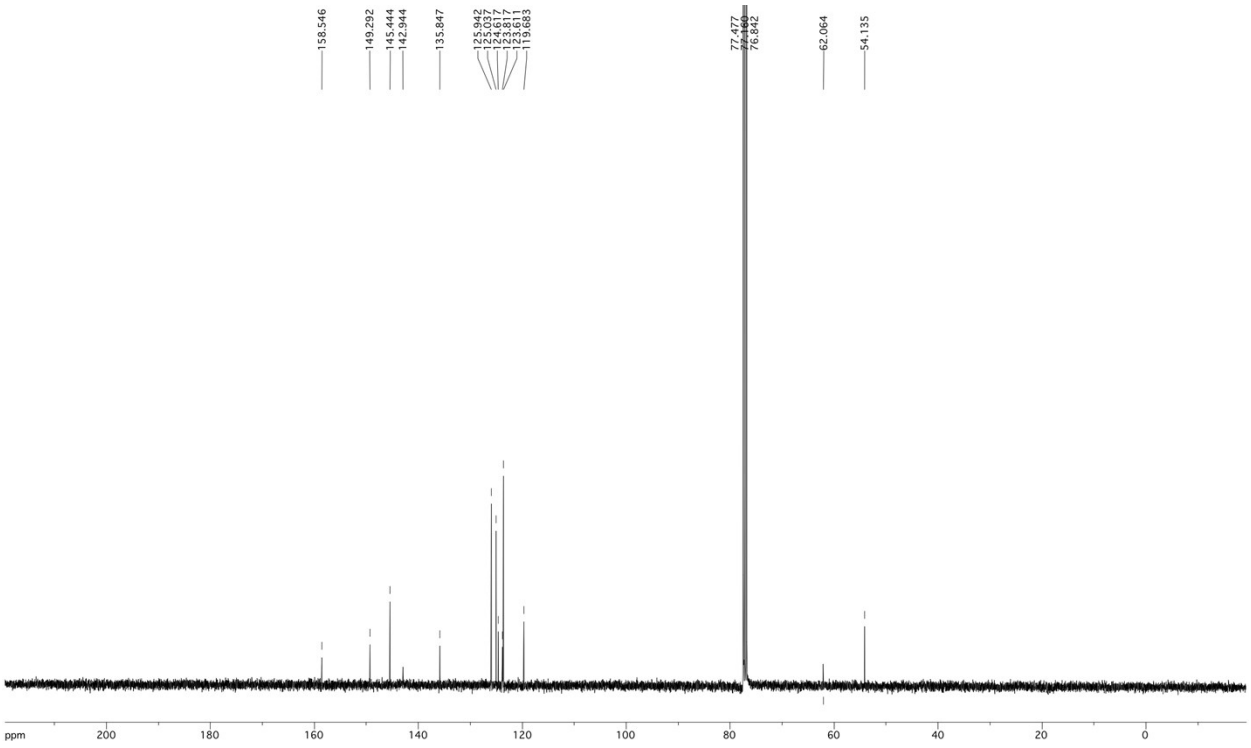
Figure S12. Photolytic generation of the 2-methyl-2-(2-naphthyl)-1-propyl radical as a radical clock to obtain the rate constant for HAT from sulfinic acids and sulfenic to alkyl radicals (A). Ratio of reduced (R'H) to rearranged and reduced (R"H) products as a function of the concentration of $TrptSO_2H$ (red) or $PhSO_2H$ (blue) during photocleavage of the radical precursor in THF at 25 °C (B). Ratio of reduced (R'H) to rearranged and reduced (R"H) products as a function of the concentration of TrptSOH during photocleavage of the radical precursor in chlorobenzene or acetonitrile at 25 °C (C).

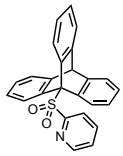
^{1}H and ^{13}C NMR Spectra



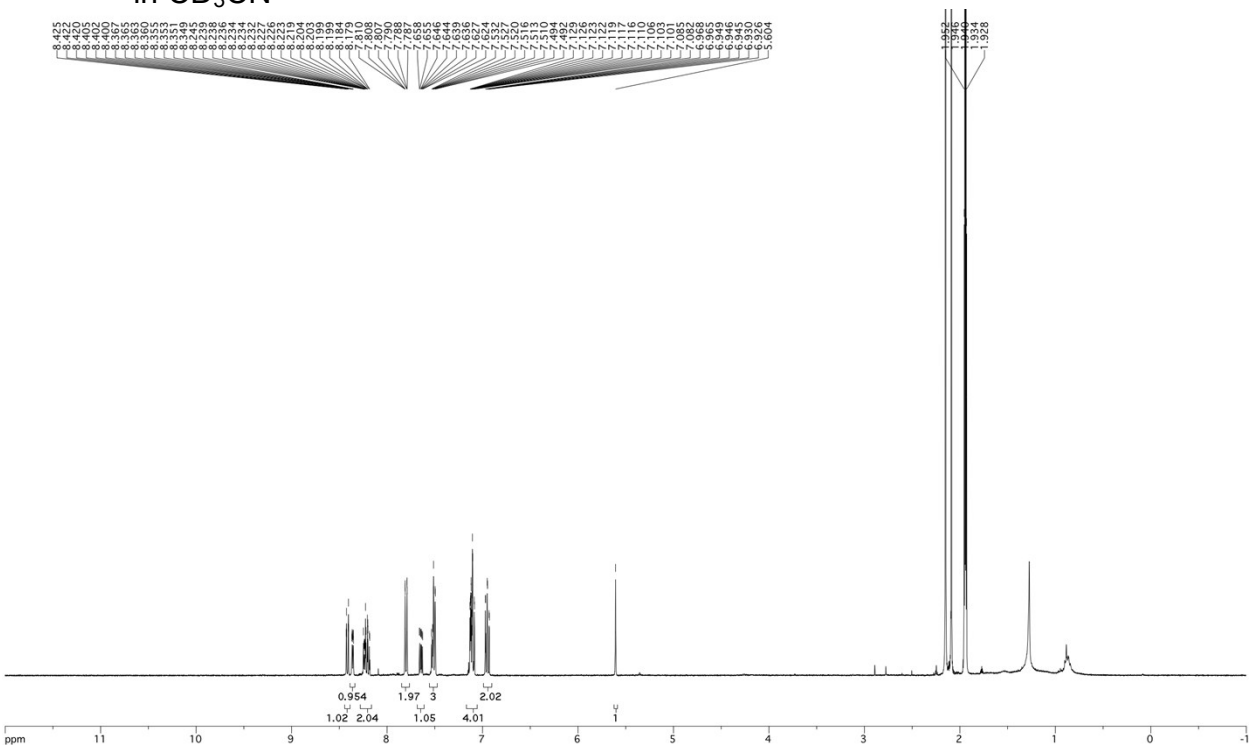
in $CDCl_3$



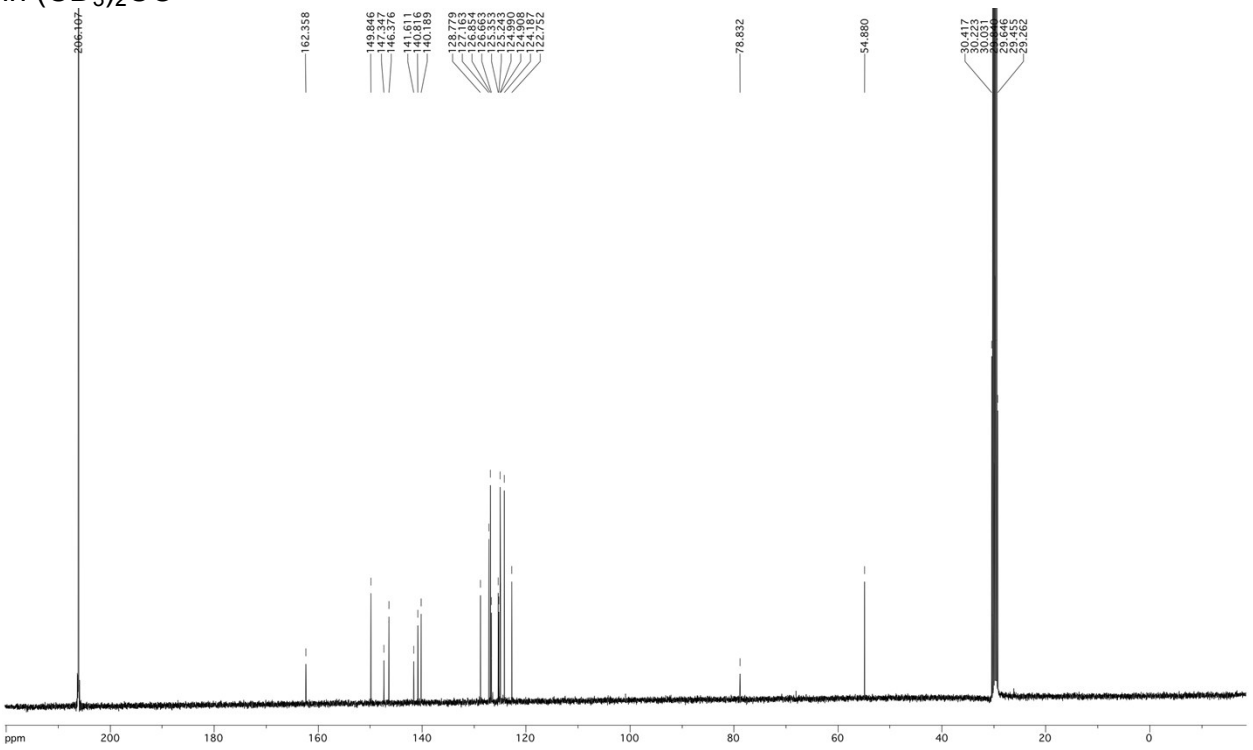


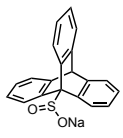


in CD_3CN



in $(CD_3)_2CO$

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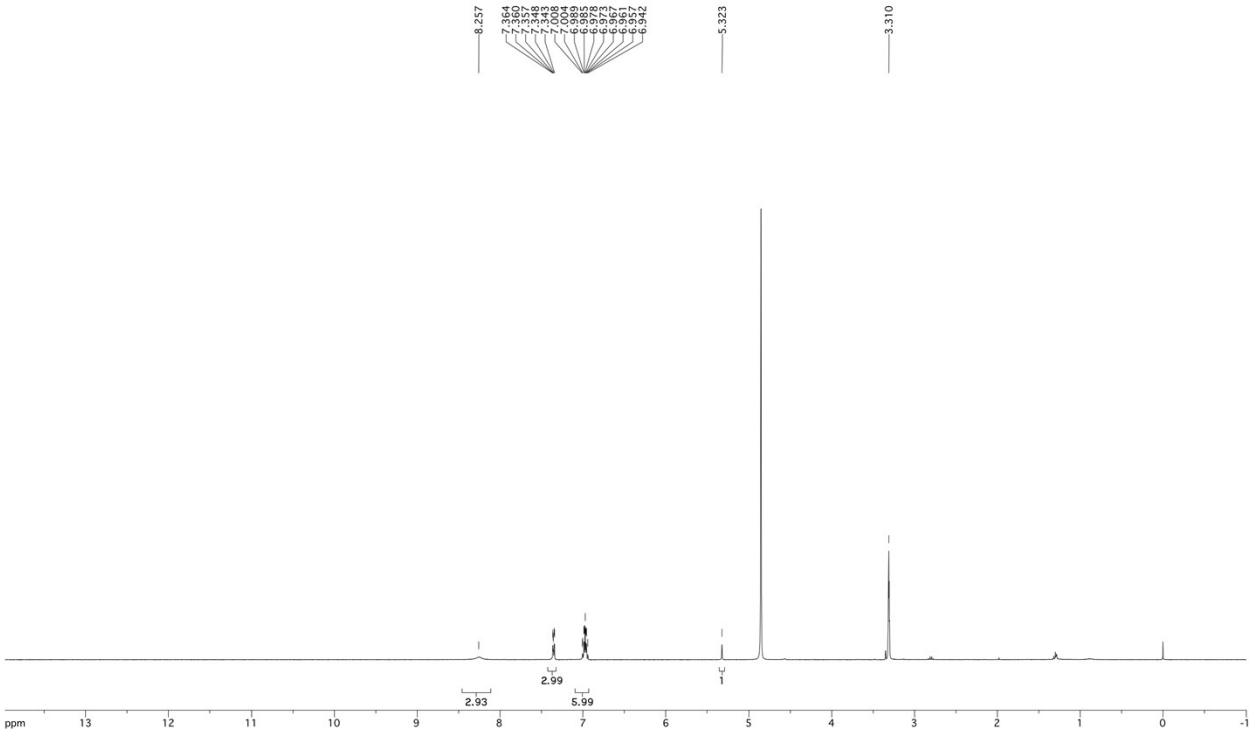
ONa

in CD_3OD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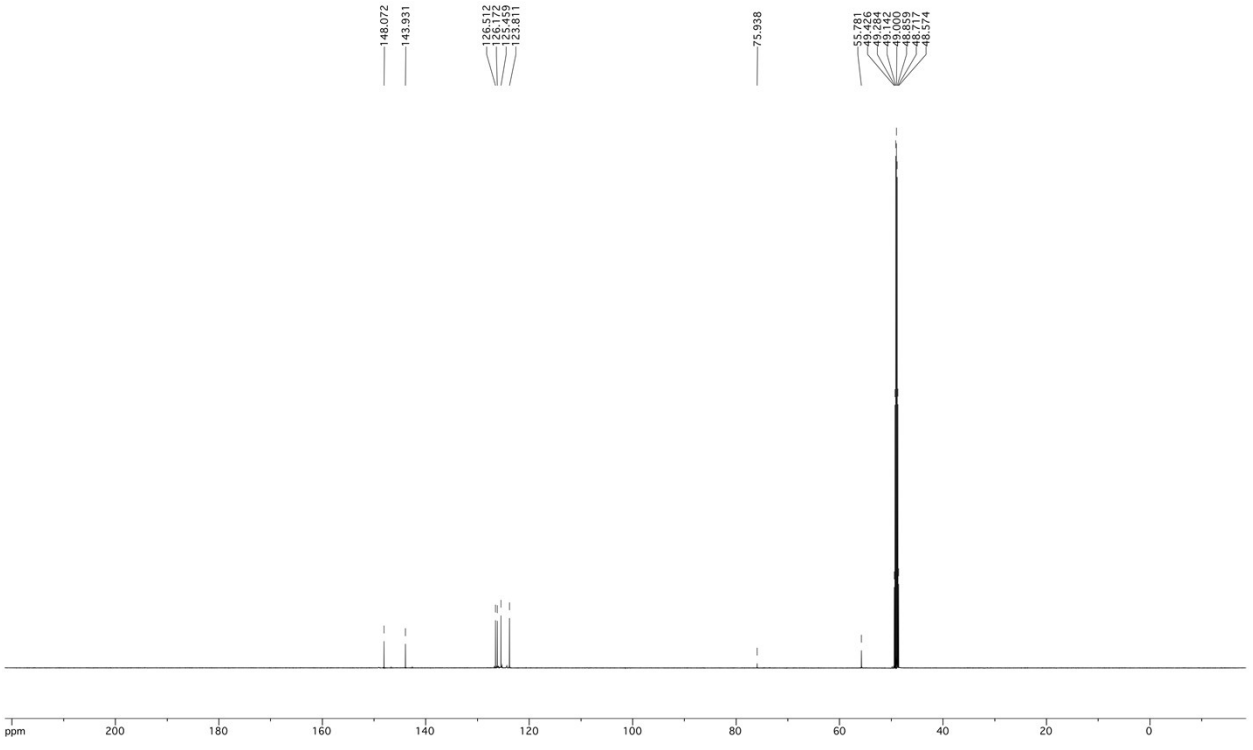
7.360
7.357
7.348
7.346
7.343
7.008
7.004
6.989
6.985
6.978
6.973
6.967
6.963
6.957
6.951
6.942
5.323
3.310
2.93
2.99
1
5.99
ppm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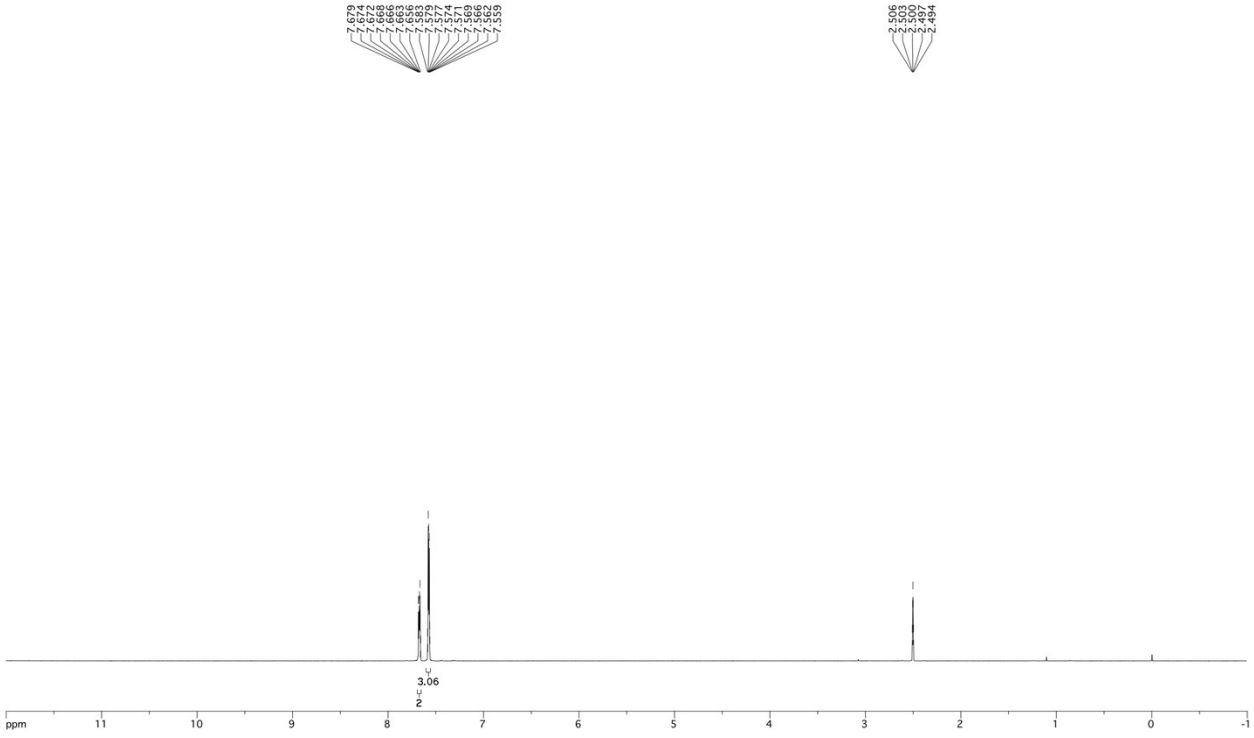
143.931
126.512
125.772
125.456
123.811
75.938
55.781
49.426
49.284
49.142
49.000
48.859
48.717
48.574
ppm


in $(CD_3)_2SO$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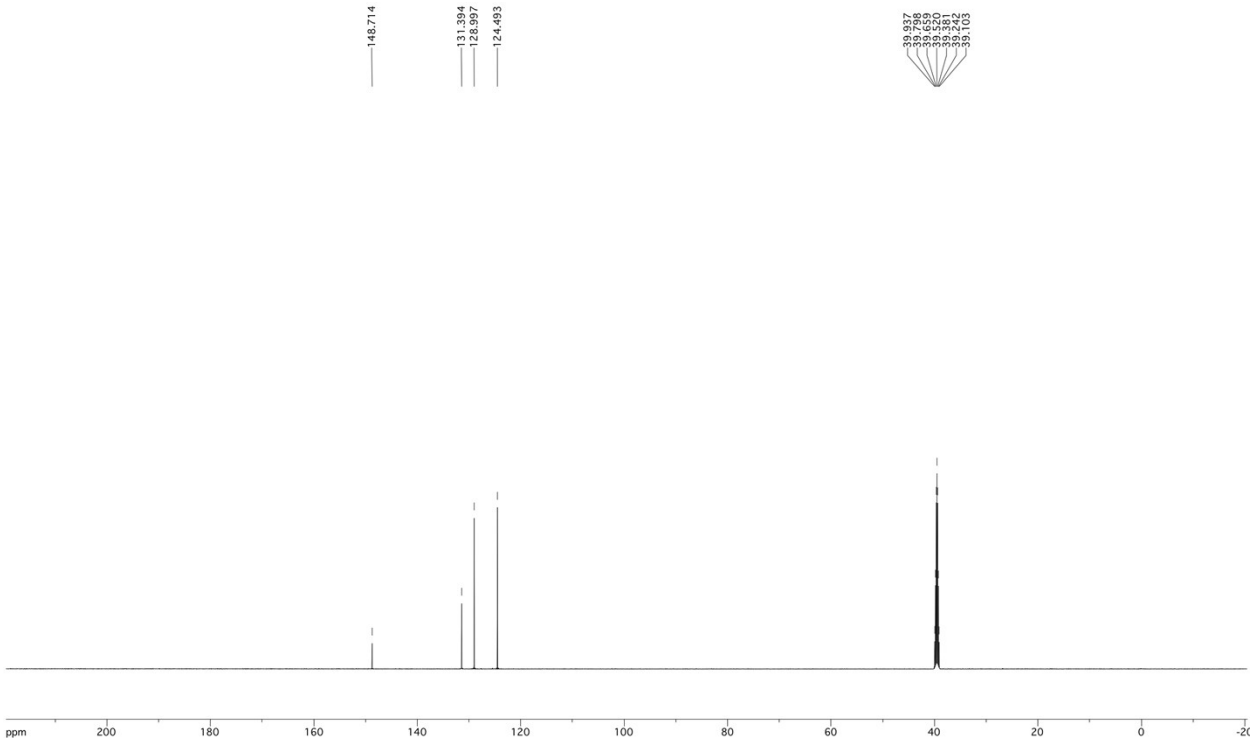
7.674
7.672
7.668
7.666
7.656
7.583
7.579
7.577
7.574
7.571
7.569
7.566
7.562
7.559
2.506
2.503
2.500
2.497
2.494
3.06
2.00
ppm
11
10
9
8
7
6
5
4
3
2
1
0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39.937
39.788
39.659
39.520
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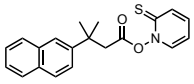
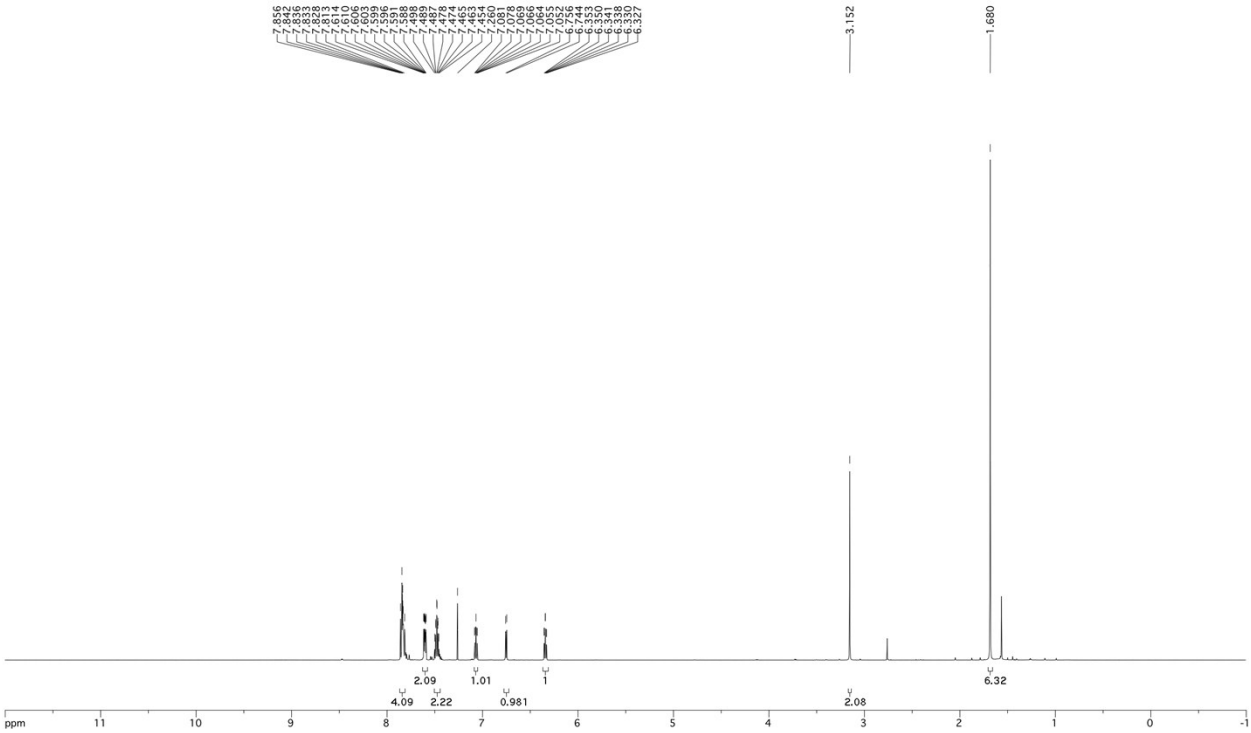
39.241
39.102
38.963
ppm
200
180
160
140
120
100
80
60
40
20
0



in $CDCl_3$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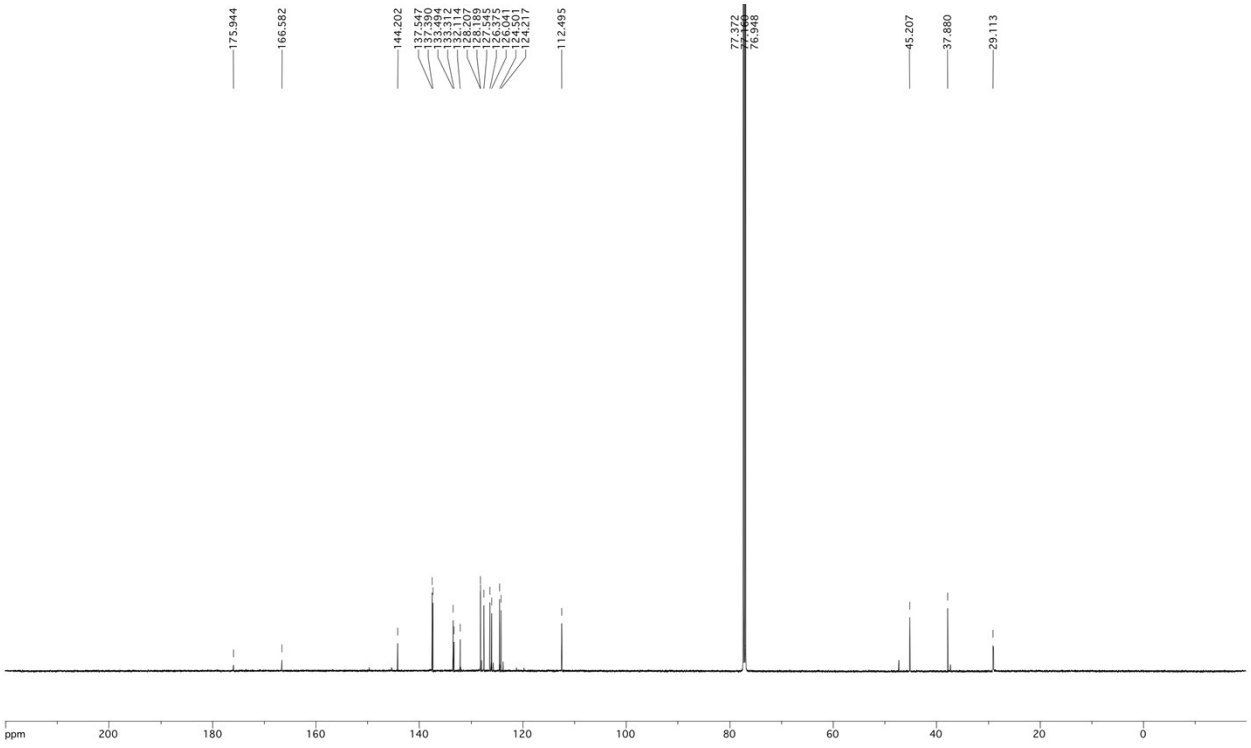
7.833
7.828
7.823
7.614
7.610
7.606
7.603
7.599
7.596
7.591
7.588
7.488
7.480
7.487
7.478
7.474
7.465
7.463
7.454
7.260
7.081
7.078
7.069
7.066
7.064
7.055
7.052
6.756
6.744
6.353
6.350
6.341
6.338
6.330
6.327
3.152
1.680
2.09
2.22
1.01
1
0.981
6.32
4.09
2.08
ppm


175.944
166.582
144.202
137.547
137.390
133.494
133.312
132.114
132.007
128.189
127.545
127.375
126.041
124.501
124.217
112.495
77.372
77.166
76.948
45.207
37.880
29.113
ppm

Computational Data

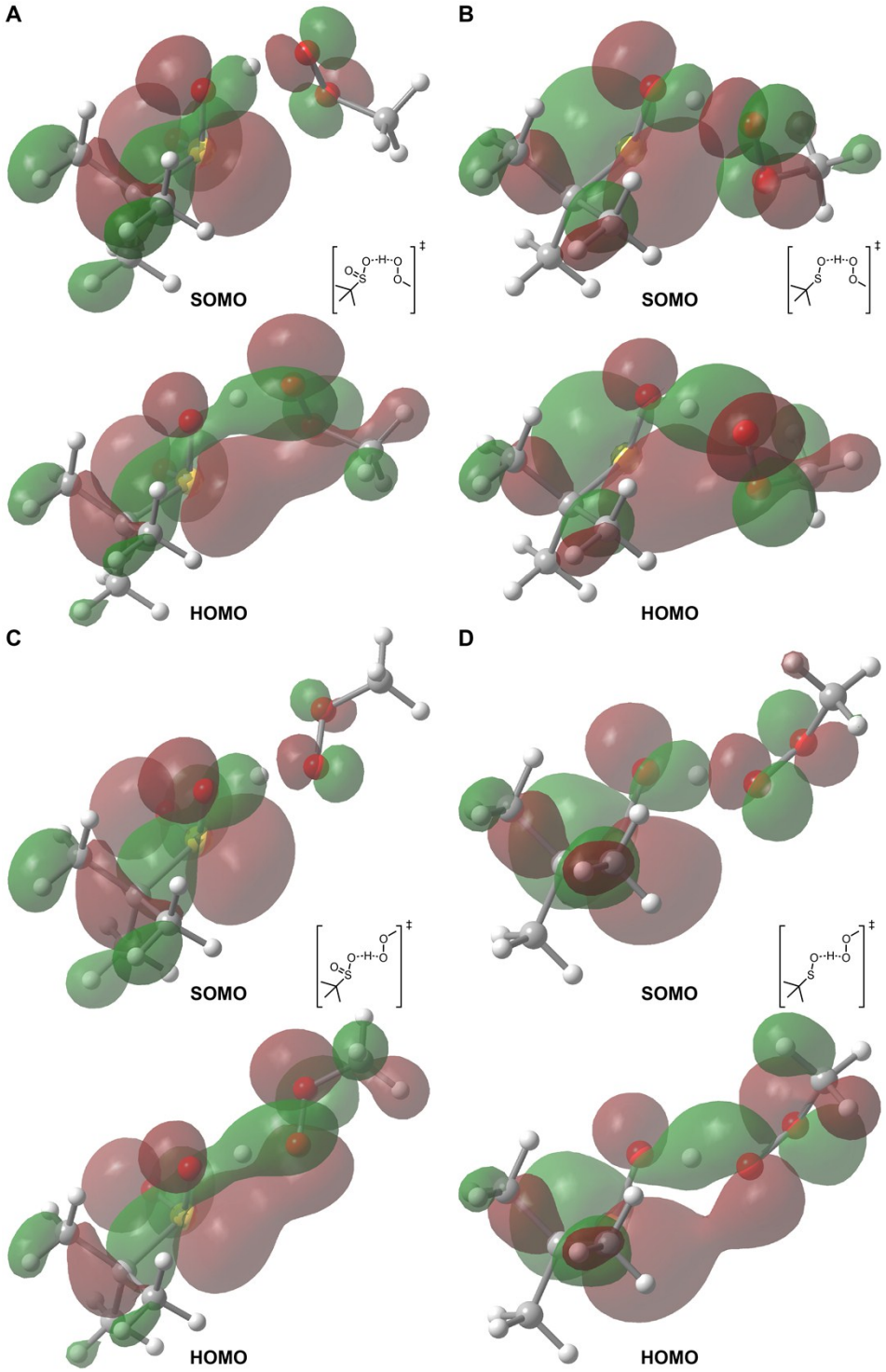


Figure S13. Calculated (CBS-QB3) TS structures for HAT between model sulfenic and sulfinic acid and model peroxyl radical (MeOO$^{\bullet}$) and associated free energy barriers and rate constants estimated using transition state theory, SOMO and HOMO visualized.

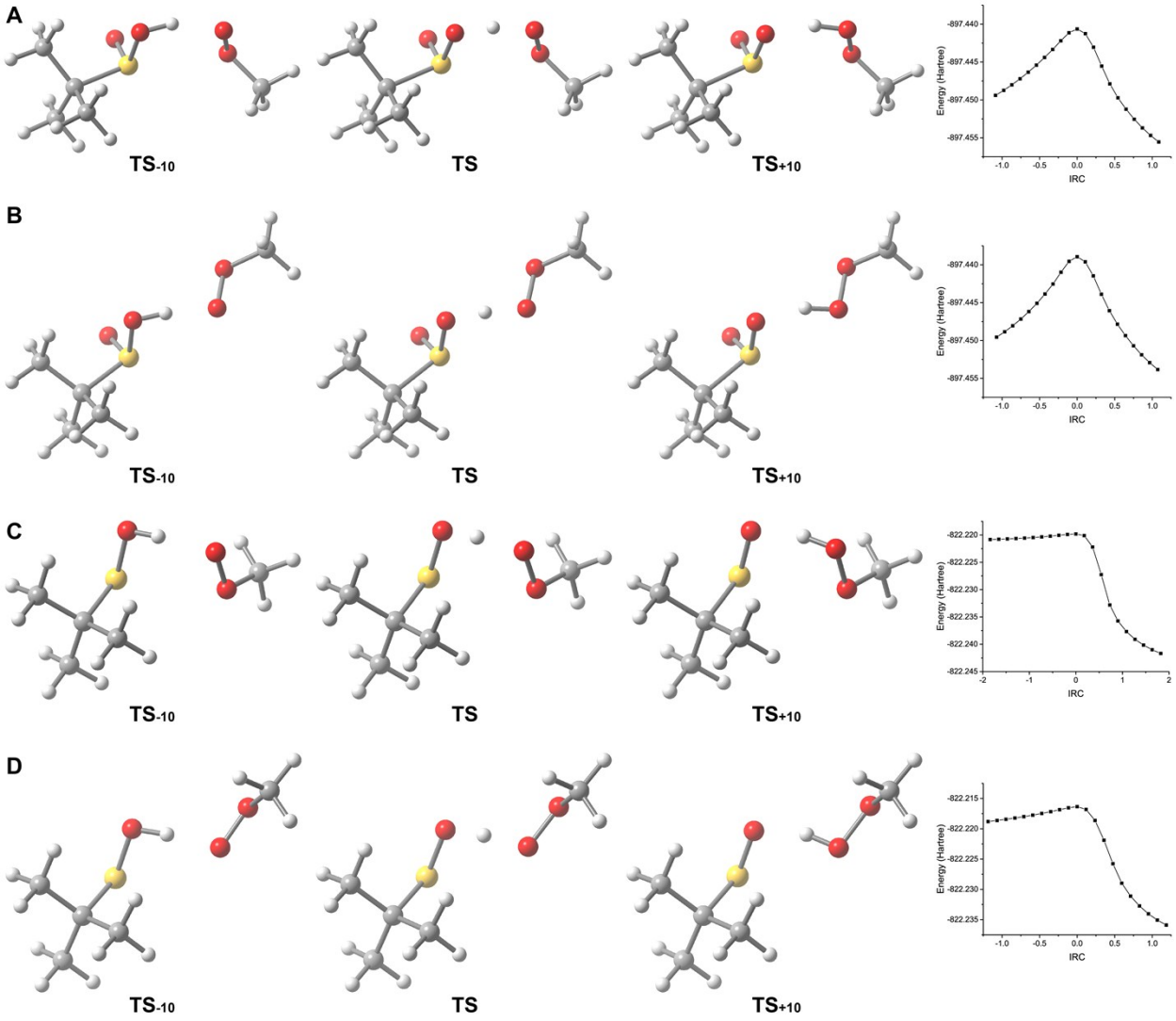
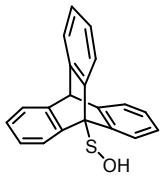


Figure S14. Calculated (CBS-QB3) structures for HAT between model sulfenic and sulfinic acid and model peroxyl radical (MeOO$^{\bullet}$) as well as corresponding IRC energy diagrams. Visualized are the TS as well as structures preceding and following the TS by 10 steps (stepsize = 0.1 Bohr).

Optimized Gaussian Structures and CBS-QB3 Energies

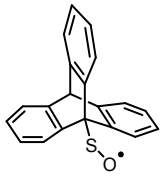
TrptSOH



CBS-QB3 Enthalpy= -1241.996261 CBS-QB3 Free Energy= -1242.056530

```
0 1
 S                  0.62950700    0.07043500    2.57309600
 O                  2.31774400    0.10013200    2.49552800
 C                  0.18417100    0.01794200    0.80103000
 C                 -0.58333200   -0.05865100   -1.68524300
 H                 -0.90862800   -0.09175900   -2.72516000
 C                 -1.33885200   -0.17097800    0.64442600
 C                 -1.74034100   -0.20605800   -0.70049600
 C                 -3.07736700   -0.36929100   -1.02886500
 H                 -3.38326500   -0.39786500   -2.06941700
 C                 -4.02689600   -0.49852000   -0.01063700
 H                 -5.07359500   -0.62644600   -0.26221500
 C                 -3.63067900   -0.46494500    1.32120000
 H                 -4.36740800   -0.56717100    2.10966600
 C                 -2.28213100   -0.30130800    1.65516100
 H                 -1.99224500   -0.28249500    2.69952700
 C                  0.50504600    1.31133700    0.02091700
 C                  0.10693200    1.25057700   -1.32303500
 C                  0.82078900   -1.14043300    0.00109100
 C                  0.40189700   -1.16754400   -1.33709000
 C                  1.08827800    2.47062500    0.51394200
 H                  1.33497600    2.55934200    1.56617100
 C                  0.32046700    2.32699800   -2.17138600
 H                  0.00594300    2.27436400   -3.20846900
 C                  1.30741000    3.55548200   -0.34126700
 H                  1.76359300    4.45942700    0.04602100
 C                  0.93337400    3.48247500   -1.67830300
 H                  1.10484900    4.32615800   -2.33705700
 C                  1.69997800   -2.10693900    0.47193600
 H                  2.03811600   -2.08730500    1.49822200
 C                  0.86156900   -2.14957600   -2.20268400
 H                  0.52872400   -2.16625500   -3.23531800
 C                  1.74969200   -3.11869800   -1.72983200
 H                  2.11446100   -3.88959500   -2.39931300
 C                  2.16295400   -3.09522600   -0.40188900
 H                  2.85123900   -3.84875500   -0.03600900
 H                  2.59142500    1.00672800    2.30572400
```

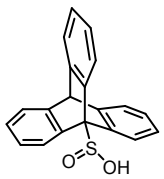
TrptSO•



CBS-QB3 Enthalpy= -1241.385689 CBS-QB3 Free Energy= -1241.446231

```
0 2
 S                -2.62746500   -0.46387600    0.00000000
 O                -2.81075600   -1.96475200    0.00000000
 C                -0.81432600   -0.13434900    0.00000000
 C                 1.70533700    0.47371900    0.00000000
 H                 2.76551300    0.72692800    0.00000000
 C                -0.56202800    1.38782100    0.00000000
 C                 0.80517600    1.70304600    0.00000000
 C                 1.22313300    3.02510300    0.00000000
 H                 2.28188100    3.26184400    0.00000000
 C                 0.27110700    4.04862000    0.00000000
 H                 0.59171400    5.08415400    0.00000000
 C                -1.08397100    3.73983700    0.00000000
 H                -1.82199200    4.53363500    0.00000000
 C                -1.50767700    2.40667100    0.00000000
 H                -2.56920300    2.19131500    0.00000000
 C                -0.06641500   -0.69006300    1.22993600
 C                 1.29453600   -0.34709400    1.21861000
 C                -0.06641500   -0.69006300   -1.22993600
 C                 1.29453600   -0.34709400   -1.21861000
 C                -0.58430500   -1.45402400    2.26717000
 H                -1.62388800   -1.75324500    2.27088500
 C                 2.13020600   -0.75456100    2.24770400
 H                 3.18141100   -0.48619800    2.23540100
 C                 0.26133000   -1.86307500    3.30340000
 H                -0.14050800   -2.46053600    4.11366800
 C                 1.60736600   -1.51498500    3.29743300
 H                 2.25521400   -1.83752600    4.10460800
 C                -0.58430500   -1.45402400   -2.26717000
 H                -1.62388800   -1.75324500   -2.27088500
 C                 2.13020600   -0.75456100   -2.24770400
 H                 3.18141100   -0.48619800   -2.23540100
 C                 1.60736600   -1.51498500   -3.29743300
 H                 2.25521400   -1.83752600   -4.10460800
 C                 0.26133000   -1.86307500   -3.30340000
 H                -0.14050800   -2.46053600   -4.11366800
```

TrptSO$_2$H



CBS-QB3 Enthalpy= -1317.140039 CBS-QB3 Free Energy= -1317.202009

```
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 S                 0.96445100   -0.58511300   -2.28114900
```
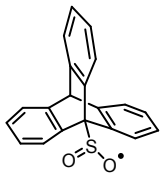

O	1.36085500	-2.17197500	-1.93965800
O	2.18928900	0.22440800	-2.41747700
C	0.23429900	-0.14940200	-0.61500600
C	-0.87240700	0.47640400	1.64251800
H	-1.33342200	0.74362200	2.59334700
C	-0.99857200	-1.02197800	-0.28257000
C	-1.58399200	-0.67177800	0.94334400
C	-2.71141000	-1.33242600	1.40834800
H	-3.15211400	-1.05367500	2.35971000
C	-3.27587400	-2.35212500	0.63888400
H	-4.15799400	-2.87279300	0.99380500
C	-2.70692600	-2.69560000	-0.58203600
H	-3.14527200	-3.48491300	-1.18184700
C	-1.56655000	-2.03499000	-1.04913100
H	-1.13418300	-2.33418000	-1.99330900
C	1.20879900	-0.26049100	0.57604300
C	0.58250100	0.04950900	1.79478900
C	-0.27324200	1.30839800	-0.58633500
C	-0.87254900	1.63019100	0.64247700
C	2.56672400	-0.56980100	0.55754800
H	3.09569400	-0.69553300	-0.37778300
C	1.29073400	-0.00520400	2.98573100
H	0.79910900	0.23727800	3.92200300
C	3.27524000	-0.62926000	1.76296500
H	4.33176100	-0.87057600	1.74524600
C	2.64213600	-0.36119900	2.97025000
H	3.19956400	-0.40675600	3.89880500
C	-0.19183300	2.26542900	-1.59032500
H	0.29917900	2.05124100	-2.53055900
C	-1.39636500	2.89494600	0.86088400
H	-1.85687000	3.13747200	1.81282700
C	-1.32492600	3.85356100	-0.15392700
H	-1.73272100	4.84451000	0.01002600
C	-0.72578500	3.53905600	-1.36786300
H	-0.66221400	4.28571800	-2.15097300
H	1.81708700	-2.23850200	-1.08535800

TrptSO$_2$•



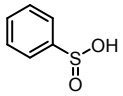
CBS-QB3 Enthalpy= -1316.520376 CBS-QB3 Free Energy= -1316.582936

0 2

S	2.25674300	1.17282800	0.00000000
O	2.35399200	1.89950000	1.27051500
O	2.35399200	1.89950000	-1.27051500
C	0.60037700	0.26659700	0.00000000
C	-1.66770600	-0.94409700	0.00000000
H	-2.62921400	-1.45697200	0.00000000
C	0.43061600	-0.64159900	1.23131200
C	-0.81379600	-1.29276600	1.21432900
C	-1.16250200	-2.16924300	2.23051400
H	-2.12556700	-2.66821900	2.21175800
C	-0.26389000	-2.40592700	3.27392600
H	-0.53058500	-3.08992900	4.07145100
C	0.96908000	-1.76460800	3.28932100

H	1.66504900	-1.94586500	4.10012400
C	1.32361700	-0.87648400	2.26903900
H	2.27691600	-0.36802000	2.31166100
C	-0.58115800	1.25322600	0.00000000
C	-1.80930400	0.57335200	0.00000000
C	0.43061600	-0.64159900	-1.23131200
C	-0.81379600	-1.29276600	-1.21432900
C	-0.54686200	2.64024100	0.00000000
H	0.39442500	3.17499700	0.00000000
C	-3.00024200	1.28458400	0.00000000
H	-3.94833800	0.75729700	0.00000000
C	-1.74979400	3.35181700	0.00000000
H	-1.72606500	4.43521100	0.00000000
C	-2.96797600	2.68125400	0.00000000
H	-3.89569600	3.24193900	0.00000000
C	1.32361700	-0.87648400	-2.26903900
H	2.27691600	-0.36802000	-2.31166100
C	-1.16250200	-2.16924300	-2.23051400
H	-2.12556700	-2.66821900	-2.21175800
C	-0.26389000	-2.40592700	-3.27392600
H	-0.53058500	-3.08992900	-4.07145100
C	0.96908000	-1.76460800	-3.28932100
H	1.66504900	-1.94586500	-4.10012400

$PhSO_2H$

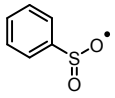


CBS-QB3 Enthalpy= -779.808964 CBS-QB3 Free Energy= -779.851846

0 1

C	-2.07554500	1.24041300	0.27880600
C	-2.84886600	0.09026500	0.13171700
C	-2.24532000	-1.13054500	-0.17478000
C	-0.86459100	-1.20441300	-0.33275700
C	-0.10237500	-0.04702700	-0.17603200
C	-0.69234900	1.17745900	0.11875200
S	1.70094700	-0.11651200	-0.42011900
O	2.17140900	1.26122600	-0.18832200
O	2.05481700	-1.07129600	0.91512800
H	-2.54840500	2.18743200	0.51257100
H	-3.92503700	0.14400100	0.25071800
H	-2.85058300	-2.02218400	-0.29117000
H	-0.38533800	-2.14888800	-0.56613700
H	-0.06244400	2.05396400	0.21599900
H	1.72113300	-0.62648200	1.71122800

$PhSO_2^{\bullet}$



CBS-QB3 Enthalpy= -779.188467 CBS-QB3 Free Energy= -779.230967

0 2

S	-0.14498200	-1.71918400	0.00000000
O	0.38866500	-2.18270100	1.28520400

O	0.38866500	-2.18270100	-1.28520400
C	-0.08871400	0.09140600	0.00000000
C	-0.09682600	0.76414100	1.21976900
C	-0.09682600	2.15630100	1.21042300
C	-0.09903000	2.84916700	0.00000000
C	-0.09682600	2.15630100	-1.21042300
C	-0.09682600	0.76414100	-1.21976900
H	-0.08335800	0.20566300	2.14670100
H	-0.09050400	2.69852600	2.14865000
H	-0.10092700	3.93303700	0.00000000
H	-0.09050400	2.69852600	-2.14865000
H	-0.08335800	0.20566300	-2.14670100

tert-BuSOH

CBS-QB3 Enthalpy= -630.958987 CBS-QB3 Free Energy= -631.000322

0 1

S	0.96312700	-0.81679200	-0.01806700
O	2.06273300	0.47277900	0.11035400
H	2.31178300	0.71140400	-0.79044800
C	-0.65925900	0.08175600	0.00081900
C	-0.75607400	1.02495600	-1.20368700
H	-1.71881200	1.54723100	-1.19937300
H	0.02878200	1.78461900	-1.16728400
H	-0.66674800	0.47658900	-2.14438100
C	-0.79151300	0.85864900	1.31598000
H	-1.72416300	1.43351100	1.32524400
H	-0.79347400	0.18097800	2.17218900
H	0.04178200	1.55396700	1.43455700
C	-1.70311000	-1.04069600	-0.09297000
H	-2.70742000	-0.60761700	-0.05936000
H	-1.61009400	-1.60079900	-1.02733100
H	-1.61379600	-1.74144000	0.74157800

tert-BuSO•

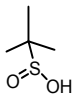
CBS-QB3 Enthalpy= -630.352256 CBS-QB3 Free Energy= -630.393921

0 2

S	0.51173100	-1.16329100	0.00000000
O	-0.78578900	-1.94371900	0.00000000
C	0.03808900	0.64692500	0.00000000
C	-0.78578900	0.91613000	1.26438000
H	-1.13698900	1.95312400	1.26798400
H	-1.65600000	0.25765300	1.30066700
H	-0.19433900	0.75403800	2.16921800
C	-0.78578900	0.91613000	-1.26438000
H	-1.13698900	1.95312400	-1.26798400
H	-0.19433900	0.75403800	-2.16921800
H	-1.65600000	0.25765300	-1.30066700
C	1.36361000	1.41533800	0.00000000

H	1.16776500	2.49183800	0.00000000
H	1.96238800	1.18689600	0.88633300
H	1.96238800	1.18689600	-0.88633300

tert-$BuSO_2H$



CBS-QB3 Enthalpy= -706.108573 CBS-QB3 Free Energy= -706.152201

0 1

S	-0.92589900	-0.16834000	-0.53899500
O	-1.47732300	-1.28369500	0.26062200
O	-1.56236000	1.26196700	0.07162600
H	-1.70818900	1.12632100	1.02202500
C	0.85752800	0.03255100	0.04508900
C	0.87109900	0.13797800	1.56877000
H	0.28738500	-0.67173600	2.01321600
H	1.89778700	0.06280900	1.93883500
H	0.47051700	1.09625400	1.90999000
C	1.55490200	-1.24739200	-0.43428900
H	1.47295400	-1.36727600	-1.51914800
H	2.61937300	-1.20092500	-0.18577300
H	1.12656400	-2.13130500	0.04145100
C	1.42301900	1.27520200	-0.64535300
H	2.47867100	1.39634500	-0.38317400
H	1.36001100	1.19037700	-1.73436100
H	0.88748900	2.17637000	-0.34241800

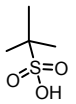
tert-$BuSO_2^{\bullet}$

CBS-QB3 Enthalpy= -705.490439 CBS-QB3 Free Energy= -705.534391

0 2

S	1.02117400	0.00000000	-0.35884500
O	1.55160700	-1.27340100	0.14666100
O	1.55160800	1.27340100	0.14666100
C	-0.88766000	0.00000000	0.02506900
C	-0.98454500	-0.00001400	1.55053300
H	-2.04220000	-0.00001700	1.83515600
H	-0.51389300	-0.88752900	1.97638200
H	-0.51389300	0.88749100	1.97639800
C	-1.44106600	-1.27237200	-0.60617000
H	-2.51428700	-1.33387100	-0.39801000
H	-1.31040800	-1.27367600	-1.69111300
H	-0.95957500	-2.16115400	-0.19728000
C	-1.44106100	1.27238700	-0.60614500
H	-1.31040300	1.27371100	-1.69108800
H	-2.51428200	1.33388600	-0.39798500
H	-0.95956800	2.16115800	-0.19723700

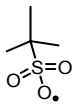
tert-$BuSO_3H$



CBS-QB3 Enthalpy= -781.277017 CBS-QB3 Free Energy= -781.321987

```
0 1
S                  0.83821800   -0.16226800   -0.07101000
 O                  1.30530200    0.09337000   -1.41537600
 O                  1.34359500    1.10444600    0.83944700
 H                  1.82015700    1.70201900    0.24558700
 C                 -0.99040200    0.03742300    0.00632300
 C                 -1.35656500    1.39438000   -0.60614500
 H                 -0.98518100    1.48007800   -1.62827800
 H                 -2.44561500    1.49048600   -0.62685200
 H                 -0.95688000    2.21886000   -0.01330300
 C                 -1.55925800   -1.12319500   -0.82674700
 H                 -1.26571000   -2.08836300   -0.41134800
 H                 -2.65063900   -1.06065700   -0.81692900
 H                 -1.22042500   -1.07074200   -1.86287700
 C                 -1.41991400   -0.06326900    1.47533800
 H                 -2.50915600    0.01980300    1.52957800
 H                 -1.12375700   -1.01931900    1.90782200
 H                 -0.98447500    0.73912000    2.07279100
 O                  1.20948300   -1.35869500    0.63184800
```

tert-$BuSO_3^{\bullet}$



CBS-QB3 Enthalpy= -780.608433 CBS-QB3 Free Energy= -780.654740

```
0 2
S                 -0.85925100    0.00002500   -0.00000300
 O                 -1.32610700    1.34424800   -0.38155600
 O                 -1.32606800   -1.00255800   -0.97334600
 C                  0.97380000   -0.00000500    0.00001000
 C                  1.42934400    0.35866600   -1.42175300
 H                  1.07283900    1.34717900   -1.71600300
 H                  2.52218400    0.36574800   -1.44962700
 H                  1.07290100   -0.37205200   -2.14964300
 C                  1.42939400    1.05193400    1.02151300
 H                  1.07272900    0.81261300    2.02468300
 H                  2.52223800    1.07238100    1.04173200
 H                  1.07314300    2.04770400    0.75253200
 C                  1.42929900   -1.41065000    0.40026200
 H                  2.52213200   -1.43840800    0.40786500
 H                  1.07301900   -1.67559500    1.39710200
 H                  1.07257000   -2.15971500   -0.30859800
 O                 -1.32616900   -0.34167900    1.35487800
```

tert-butyl radical

CBS-QB3 Enthalpy= -157.425524 CBS-QB3 Free Energy= -157.462444

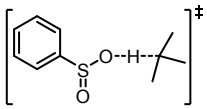
```
0 2
 C                  0.00001200   -0.00003700   -0.14928700
 C                 -1.13936400   -0.95436600    0.01501900
 C                  1.39621300   -0.50948600    0.01473600
 H                 -1.36709400   -1.14542200    1.07940200
 H                 -0.92133500   -1.92825200   -0.43495800
 H                 -2.06000800   -0.56867600   -0.43453000
 H                  1.67570700   -0.61107100    1.07907900
 H                  1.52256800   -1.49965800   -0.43479600
 H                  2.13046400    0.16629100   -0.43542600
 C                 -0.25685800    1.46386100    0.01484300
 H                  0.53744900    2.06834700   -0.43473500
 H                 -1.20929200    1.76198800   -0.43512700
 H                 -0.30847700    1.75661200    1.07922500
```

tert-Butane

CBS-QB3 Enthalpy= -158.077849 CBS-QB3 Free Energy= -158.111186

```
0 1
 C                  0.00000000    0.00000000    0.37225800
 C                  0.00000000    1.46129200   -0.09577300
 C                  1.26551600   -0.73064600   -0.09577300
 H                  0.00000000    0.00000000    1.47022700
 H                  0.00000000    1.51929200   -1.18993700
 H                  0.88410000    1.99527900    0.26499300
 H                 -0.88410000    1.99527900    0.26499300
 H                  1.31574600   -0.75964600   -1.18993700
 H                  2.17001200   -0.23198600    0.26499300
 H                  1.28591200   -1.76329300    0.26499300
 C                 -1.26551600   -0.73064600   -0.09577300
 H                 -1.28591200   -1.76329300    0.26499300
 H                 -2.17001200   -0.23198600    0.26499300
 H                 -1.31574600   -0.75964600   -1.18993700
```

$PhSO_2H$ H-abstraction by *tert*-butyl radical TS

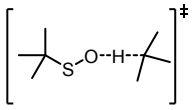


TS freq.: -1582.62 cm^{-1}
CBS-QB3 Enthalpy= -937.237245 CBS-QB3 Free Energy= -937.297834

```
0 2
 C                 -2.93675900   -0.45203400    1.25594700
 C                 -3.34070400   -1.31830400    0.24160100
 C                 -2.72517000   -1.26993100   -1.01007300
 C                 -1.70354900   -0.35489600   -1.25031800
 C                 -1.30213900    0.49897300   -0.22364500
```

C	-1.91530200	0.46839400	1.02483200
S	-0.02185600	1.76016400	-0.54525800
O	0.34844300	2.28621400	0.78648400
O	1.11881000	0.87432600	-1.20512700
H	-3.41687900	-0.49068700	2.22723500
H	-4.13837500	-2.02960900	0.42343800
H	-3.04164600	-1.94396600	-1.79801100
H	-1.21423000	-0.31175200	-2.21650600
H	-1.57947100	1.15237300	1.79473600
H	1.64398100	0.00931100	-0.48337200
C	3.73882200	-0.23887400	0.12817900
H	3.75356300	0.74437700	0.60334800
H	4.07528000	-0.12816600	-0.90546100
C	2.36330300	-0.87019500	0.20473100
C	2.20263300	-2.15389400	-0.58282700
H	2.79898000	-2.95380900	-0.11973100
H	1.16278500	-2.48901900	-0.60026900
H	2.54928800	-2.04169000	-1.61318000
C	1.74564700	-0.87903700	1.58873700
H	1.72390200	0.12242000	2.02189500
H	0.72544800	-1.26888800	1.57376800
H	2.33823300	-1.52572300	2.25244700
H	4.47011600	-0.87333600	0.64995900

tert-BuSOH H-abstraction by *tert*-butyl radical TS



TS freq.: -1692.93 cm^{-1}
CBS-QB3 Enthalpy= -788.388783 CBS-QB3 Free Energy= -788.448835

0 2

S	-0.91188100	-1.15284800	0.30074000
H	1.19318700	-0.36829100	-0.37122600
C	-2.10567600	0.23927600	-0.01670400
C	2.45681500	0.15291200	0.05056400
C	2.24565100	0.50784700	1.50306900
H	1.53056900	1.32530200	1.62405800
H	1.88732200	-0.34773000	2.08222900
O	0.27452500	-0.89759100	-0.79545000
C	-1.43814700	1.58819600	0.26892200
H	-0.57078500	1.73493000	-0.37821900
H	-2.14183100	2.40525400	0.07520600
H	-1.11162700	1.65662400	1.30915000
C	-2.57647400	0.16245100	-1.47381200
H	-3.11133100	-0.77050900	-1.66483300
H	-3.24656200	0.99903600	-1.70094700
H	-1.72305000	0.20958600	-2.15306200
C	-3.26023100	-0.02377800	0.95986400
H	-2.92510900	0.01822200	1.99990200
H	-4.03458400	0.73779300	0.82570700
H	-3.71877300	-1.00076600	0.78440900
C	2.69235300	1.32036600	-0.88098600
H	3.68493500	1.76197200	-0.70072000
H	2.66141400	1.01178800	-1.92942400
H	1.95508500	2.11418400	-0.73440700
C	3.34047900	-1.04997300	-0.19512000
H	3.03851800	-1.90327500	0.41743900
H	3.31710700	-1.35869700	-1.24339500

```
 H                  4.38657300   -0.81691000    0.05682400
 H                  3.19422000    0.83400100    1.95829600
```

tert-BuO•

CBS-QB3 Enthalpy= -232.559991 CBS-QB3 Free Energy= -232.597221

```
0 2
 O                 -0.51504300    1.35749900    0.00000000
 C                 -0.06471700    0.05489400    0.00000000
 C                 -0.51504300   -0.67961200    1.27723900
 H                 -0.18332600   -0.13225500    2.16166200
 H                 -1.60556800   -0.74508500    1.30469300
 H                 -0.11054400   -1.69502700    1.31475700
 C                 -0.51504300   -0.67961200   -1.27723900
 H                 -0.18332600   -0.13225500   -2.16166200
 H                 -0.11054400   -1.69502700   -1.31475700
 H                 -1.60556800   -0.74508500   -1.30469300
 C                  1.48764400    0.22435400    0.00000000
 H                  1.94050400   -0.77022900    0.00000000
 H                  1.81084000    0.76741200   -0.88873800
 H                  1.81084000    0.76741200    0.88873800
```

tert-Butanol

CBS-QB3 Enthalpy= -233.227909 CBS-QB3 Free Energy= -233.264675

```
0 1
 O                 -0.48653800    1.36731600    0.00000000
 C                  0.00169900    0.01261900    0.00000000
 C                 -0.48653800   -0.70694000    1.26469500
 H                 -0.16787500   -0.15928600    2.15447800
 H                 -1.58016300   -0.76856600    1.27614400
 H                 -0.09557500   -1.72686300    1.32338500
 C                 -0.48653800   -0.70694000   -1.26469500
 H                 -0.16787500   -0.15928600   -2.15447800
 H                 -0.09557500   -1.72686300   -1.32338500
 H                 -1.58016300   -0.76856600   -1.27614400
 C                  1.52451200    0.14733300    0.00000000
 H                  2.00503600   -0.83417700    0.00000000
 H                  1.85226800    0.69819500   -0.88444200
 H                  1.85226800    0.69819500    0.88444200
 H                 -1.44885700    1.33225500    0.00000000
```

MeOO•

CBS-QB3 Enthalpy= -189.954731 CBS-QB3 Free Energy= -189.985244

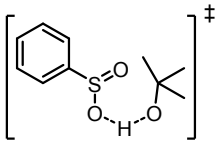
```
0 2
 C                  1.09605800   -0.18318200    0.00000000
 H                  1.87467600    0.57860400    0.00000800
 H                  1.14883700   -0.80072600    0.89698200
 H                  1.14884100   -0.80070700   -0.89699400
 O                 -0.15733600    0.54388500    0.00000000
 O                 -1.18625200   -0.27864500    0.00000000
```

MeOOH

CBS-QB3 Enthalpy= -190.589542 CBS-QB3 Free Energy= -190.620447

```
0 1
 C                  1.12961700   -0.22363900    0.02672600
 H                  1.97292200    0.47126800    0.02466300
 H                  1.14400300   -0.82582300    0.94203000
 H                  1.18954600   -0.87767300   -0.84877800
 O                 -0.01619300    0.60684200   -0.03138200
 O                 -1.16412700   -0.28550700   -0.09072700
 H                 -1.64161500    0.00338800    0.69860100
```

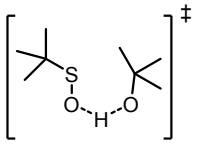
$PhSO_2H$ + *tert*-$BuO^{\bullet}$ TS



TS freq.: -1156.36 cm^{-1}
CBS-QB3 Enthalpy = -1012.376400 CBS-QB3 Free Energy= -1012.438625

```
0 2
 S                 -0.53043300    1.85129200   -0.05562700
 O                  0.11774400    1.85327800    1.27683700
 O                  0.45755600    1.41803500   -1.21298200
 H                  0.98165100    0.45531200   -1.09817600
 O                  1.54325400   -0.69223800   -0.83259800
 C                  2.65377100   -0.70706300    0.00650900
 C                  2.20281200   -0.86694300    1.47377200
 H                  1.63265700    0.01624800    1.77020400
 H                  1.56451200   -1.74674700    1.57655900
 H                  3.06966600   -0.97658800    2.13116100
 C                  3.41648700   -1.99735200   -0.43978500
 H                  3.72301500   -1.90940300   -1.48270700
 H                  4.30163500   -2.11160100    0.19050800
 H                  2.77466800   -2.87152400   -0.32798400
 C                  3.54115600    0.53058800   -0.18710600
 H                  4.44884300    0.45849300    0.41750300
 H                  3.82794700    0.63347000   -1.23634700
 H                  3.00132400    1.43077000    0.11352900
 C                 -1.68545800    0.44595600   -0.03361500
 C                 -2.05440900   -0.09973700    1.19211200
 C                 -2.24085500   -0.00465300   -1.23044700
 C                 -2.98239500   -1.13916700    1.21504900
 H                 -1.60563900    0.28018500    2.10128400
 C                 -3.16653600   -1.04298900   -1.19479500
 H                 -1.93805900    0.43567200   -2.17289000
 C                 -3.53724200   -1.60834700    0.02588700
 H                 -3.27015100   -1.58183400    2.16179100
 H                 -3.59654600   -1.41241000   -2.11861700
 H                 -4.26102100   -2.41506100    0.04867400
```

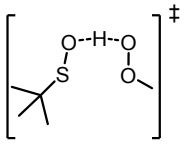
tert-BuSOH + *tert*-BuO• TS



TS freq.: -396.84 cm^{-1}
CBS-QB3 Enthalpy = -863.528387 CBS-QB3 Free Energy= -863.590026

```
0 2
 S                  1.06762400   -0.69445100   -0.76224100
 H                 -0.42902300   -1.01373400    0.63449400
 C                  2.37939700    0.31328300    0.08533600
 O                 -1.24679900    0.17107200    0.45724600
 C                 -2.56719100    0.15974400   -0.00120000
 O                  0.42849600   -1.58161600    0.43735300
 C                  1.75761800    1.14455000    1.21150000
 H                  1.29726200    0.50029300    1.96214800
 H                  2.54004700    1.73431600    1.70084900
 H                  0.98765000    1.81748100    0.83319800
 C                  3.43573900   -0.65564900    0.63531500
 H                  3.91993200   -1.21606400   -0.16780100
 H                  4.20518200   -0.09534900    1.17701100
 H                  2.97881700   -1.36749700    1.32526300
 C                  2.95246400    1.20237100   -1.02649200
 H                  2.20113900    1.89514800   -1.41399500
 H                  3.78080900    1.79461400   -0.62669700
 H                  3.34069400    0.60934300   -1.85974100
 C                 -3.46532300   -0.00238200    1.25181000
 H                 -4.52052900    0.01990800    0.96461100
 H                 -3.25885700   -0.95478900    1.74545300
 H                 -3.27026700    0.80543100    1.95916900
 C                 -2.81059600   -0.99377300   -0.98923900
 H                 -2.16530200   -0.88153100   -1.86447000
 H                 -2.58227000   -1.95414000   -0.51968400
 H                 -3.84959200   -1.01790500   -1.33041600
 C                 -2.84597300    1.52291300   -0.66545700
 H                 -2.66211600    2.33144100    0.04487600
 H                 -2.18396600    1.65992700   -1.52367800
 H                 -3.88197500    1.58234000   -1.01096500
```

tert-BuSOH + MeOO• TS syn

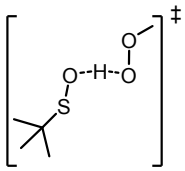


TS freq.: -473.63 cm^{-1}
CBS-QB3 Enthalpy = -820.915623 CBS-QB3 Free Energy= -820.969459

```
0 2
 O                 -0.35654700   -1.58688300   -0.17904800
 H                 -1.14468600   -1.20584200    0.41768100
 C                 -3.29704000    0.63272600   -0.59088600
 H                 -3.24670300    1.59073400   -1.10871300
 H                 -3.16032600   -0.19548400   -1.28849300
 H                 -4.24438400    0.52601500   -0.05895900
```

O	-2.18533500	-0.53080400	1.04044100
O	-2.22105300	0.65183800	0.36158000
C	1.64871300	0.25602800	0.13058800
S	0.34045600	-0.39484100	-1.02045200
C	2.35463300	1.35068200	-0.68130100
H	1.66983500	2.16099900	-0.94568400
H	3.16406500	1.77987900	-0.08351000
H	2.79392300	0.95320100	-1.60055100
C	2.60272600	-0.89345400	0.47769400
H	3.35890300	-0.54675200	1.18990700
H	2.05587000	-1.72108000	0.93296200
H	3.11354400	-1.26834200	-0.41224700
C	0.99137400	0.82939900	1.39134000
H	1.76531200	1.19895500	2.07243600
H	0.31646900	1.65175800	1.14830400
H	0.41192100	0.06791900	1.91570300

tert-BuSOH + MeOO• TS anti

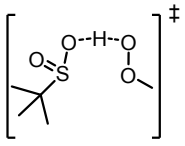


TS freq.: -1094.21 cm^{-1}
CBS-QB3 Enthalpy = -820.905338 CBS-QB3 Free Energy= -820.961411

0 2

S	0.85329400	-1.14391900	-0.29519200
O	-0.37562900	-0.90302400	0.71434500
O	-2.10820900	0.21398500	-0.50441100
O	-3.32674300	-0.36825100	-0.28455400
H	-1.21261300	-0.45398000	0.16873100
C	-4.22179100	0.59850200	0.27321500
H	-5.17531500	0.08034600	0.38044300
H	-3.85289300	0.93161100	1.24659200
H	-4.31942400	1.44974000	-0.40427200
C	1.95055700	0.32438500	0.01250300
C	3.16032400	0.10363400	-0.90489500
H	2.86777700	0.07725200	-1.95807900
H	3.87066900	0.92560000	-0.77575600
H	3.68143000	-0.82792500	-0.66718200
C	2.35524200	0.33266800	1.49163000
H	2.95968900	1.21972900	1.70870000
H	1.47002300	0.35407400	2.12984800
H	2.94072300	-0.55357400	1.74704600
C	1.18878500	1.60285700	-0.35817000
H	1.81291000	2.47917100	-0.15306900
H	0.91819200	1.61153100	-1.41622700
H	0.27208800	1.69517900	0.22756200

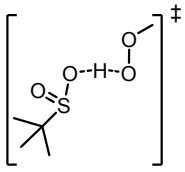
tert-BuSO_2H + MeOO• TS syn



TS freq.: -1606.69 cm^{-1}
CBS-QB3 Enthalpy = -896.048552 CBS-QB3 Free Energy= -896.105357

```
0 2
 S                 -0.18329600   -0.45328400    0.16239700
 O                 -0.41877000   -1.90748200    0.23301400
 O                  0.31384000    0.03535400   -1.24679400
 H                  1.46744600    0.07642900   -1.27120400
 C                 -1.92046400    0.36068800    0.12539200
 O                  2.68315700    0.24095800   -1.06948400
 O                  2.79187100   -0.28896100    0.19345000
 C                  3.63953000    0.55012600    0.98583000
 H                  3.66265800    0.08631800    1.97171200
 H                  4.63837200    0.57401100    0.54530100
 H                  3.22415800    1.55842400    1.03420500
 C                 -1.70393000    1.86743300    0.01674200
 H                 -1.19900200    2.12922400   -0.91324000
 H                 -2.67496200    2.37297600    0.03812000
 H                 -1.11326100    2.24964600    0.85429700
 C                 -2.65854100   -0.22683400   -1.07630600
 H                 -2.69160400   -1.31597600   -1.01479500
 H                 -3.68624600    0.15137500   -1.08538000
 H                 -2.17422000    0.05522200   -2.01168900
 C                 -2.56686500   -0.03904800    1.45191200
 H                 -2.00322700    0.34427100    2.30718400
 H                 -3.57635500    0.38108600    1.50057200
 H                 -2.64017700   -1.12359600    1.54365400
```

tert-$BuSO_2H$ + $MeOO^{\bullet}$ TS anti



TS freq.: -1742.44 cm^{-1}
CBS-QB3 Enthalpy = -896.042882 CBS-QB3 Free Energy= -896.101106

```
0 2
 S                  0.44641200   -0.49084900   -0.30578500
 O                  0.62089700   -1.91651500    0.04108900
 O                 -0.39130200    0.30779900    0.74526700
 H                 -1.45449700    0.44654900    0.25466200
 C                  2.15862900    0.32573400   -0.02215100
 O                 -2.48428400    0.61729300   -0.37642800
 O                 -3.36814500   -0.31350800    0.11284100
 C                  1.99594900    1.80904800   -0.34091800
 H                  1.28534900    2.28361200    0.33615400
 H                  2.96440500    2.30832900   -0.23228100
 H                  1.65529900    1.96414300   -1.36848400
 C                  2.52808900    0.06399100    1.43703300
 H                  2.53602300   -1.00660900    1.64828800
 H                  3.52902100    0.46422600    1.63020000
 H                  1.82241000    0.54787500    2.11330300
 C                  3.10056200   -0.38053800   -0.99648600
 H                  2.79489000   -0.22649700   -2.03502400
 H                  4.10983200    0.02685900   -0.88001500
 H                  3.13711100   -1.45323800   -0.80175300
 C                 -4.69626900    0.18964900   -0.03659700
```

```
 H                -4.90736400    0.37372000   -1.09264900
 H                -5.34330200   -0.59516400    0.35484300
 H                -4.81086600    1.11193000    0.53788100
```

PhS•

CBS-QB3 Enthalpy= -628.910084 CBS-QB3 Free Energy= -628.947151

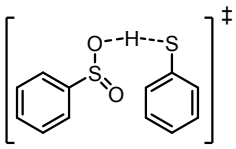
```
0 2
 C                 0.00000000    0.00000000   -2.23137611
 C                 0.00000000   -1.21271391   -1.53451120
 C                 0.00000000   -1.21800602   -0.14939220
 C                 0.00000000   -0.00000000    0.57708589
 C                -0.00000000    1.21800602   -0.14939220
 C                -0.00000000    1.21271391   -1.53451120
 H                 0.00000000    0.00000000   -3.31546411
 H                 0.00000000   -2.14988087   -2.07920928
 H                 0.00000000   -2.14899207    0.40354772
 H                -0.00000000    2.14899207    0.40354772
 H                -0.00000000    2.14988087   -2.07920928
 S                 0.00000000    0.00000000    2.29996189
```

PhSH

CBS-QB3 Enthalpy= -629.536732 CBS-QB3 Free Energy= -629.575407

```
0 1
 S                 2.28881889   -0.08321411    0.00000000
 C                 0.50622890    0.00087900    0.00000000
 C                -0.19632603    1.20936605    0.00000000
 C                -0.20018418   -1.20648195    0.00000000
 C                -1.58857803    1.20509913    0.00000000
 H                 0.33831503    2.15231701    0.00000000
 C                -1.59144418   -1.19999687    0.00000000
 H                 0.33672376   -2.14853499    0.00000000
 C                -2.29350710    0.00374718    0.00000000
 H                -2.12183897    2.14923917    0.00000000
 H                -2.12710924   -2.14266783    0.00000000
 H                -3.37704410    0.00536924    0.00000000
 H                 2.51271497    1.24002788    0.00000000
```

$PhSO_2H$ + PhS• TS

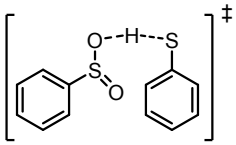


TS freq.: -1468.84 cm^{-1}
CBS-QB3 Enthalpy = -1408.712426 CBS-QB3 Free Energy= -1408.774886

```
0 2
 S                -1.27027700    1.43625400   -1.02284800
 O                -0.55912600    2.20640600    0.02392200
 O                -0.40594300    0.42302600   -1.79647700
 H                 0.24624700   -0.49631700   -1.06459000
 C                -2.46895600    0.38556200   -0.13208300
 C                -2.76304800    0.67483000    1.19646400
```

C	-3.12165500	-0.63285700	-0.82441900
C	-3.71972100	-0.09585800	1.85422200
H	-2.23504900	1.47510000	1.69921700
C	-4.07698700	-1.39325300	-0.15604200
H	-2.87384200	-0.83600900	-1.85936200
C	-4.37543700	-1.12465700	1.18017500
H	-3.94931500	0.10658700	2.89405900
H	-4.58588700	-2.19593900	-0.67707600
H	-5.12136900	-1.71860500	1.69572600
S	1.06894000	-1.62425400	-0.46272600
C	2.50509900	-0.72519100	-0.01974000
C	3.74830200	-1.39060000	-0.03197800
C	2.44592900	0.62135000	0.39635000
C	4.89609600	-0.73360000	0.38498700
H	3.79352700	-2.41969100	-0.36745900
C	3.60541000	1.27072700	0.79510600
H	1.50062700	1.15028500	0.39628900
C	4.83086000	0.59998300	0.79663600
H	5.84641500	-1.25501600	0.37983100
H	3.55352400	2.30768400	1.10641300
H	5.73172000	1.11583800	1.10850300

tert-BuSOH + PhS• TS



TS freq.: -1458.08 cm^{-1}
CBS-QB3 Enthalpy = -1259.878512 CBS-QB3 Free Energy= -1259.940940

0 2

S	-1.46102300	0.04483700	-1.11628100
H	-0.21925500	1.90205900	-0.32136600
C	-2.49973300	-0.60302300	0.28553600
S	1.16986900	2.24024800	0.44217300
O	-1.26966300	1.58137700	-0.78845600
C	1.90928300	0.66678900	0.17196300
C	2.33855600	-0.11339600	1.26390200
C	2.11753300	0.17136800	-1.13138200
C	2.96237100	-1.33660900	1.05633900
H	2.18000200	0.26115800	2.26789700
C	2.72950200	-1.06174900	-1.33071000
H	1.81599700	0.77608300	-1.97791500
C	3.15706400	-1.81813800	-0.24076400
H	3.29665900	-1.92044800	1.90689000
H	2.88353400	-1.42713700	-2.33990600
H	3.64295800	-2.77428600	-0.39844100
C	-1.72536100	-0.44785100	1.59891700
H	-1.47869800	0.59839500	1.78917200
H	-2.34137900	-0.80720200	2.42987300
H	-0.79619900	-1.02121900	1.58549700
C	-3.81229900	0.18965400	0.31851500
H	-4.38679900	0.04851700	-0.60001100
H	-4.42462200	-0.14573900	1.16184700
H	-3.61430800	1.25606200	0.44003900
C	-2.73350600	-2.07894700	-0.06370300
H	-1.79410400	-2.63629700	-0.11074600
H	-3.35634800	-2.53920800	0.70875000

```
 H                 -3.25212000   -2.19170500   -1.01989100
```

O_2

CBS-QB3 Enthalpy= -150.161251 CBS-QB3 Free Energy= -150.184523

```
0 3
 O                  0.00000000    0.00000000    0.60281700
 O                  0.00000000    0.00000000   -0.60281700
```

$MeSO_2^{\bullet}$

CBS-QB3 Enthalpy= -587.802595 CBS-QB3 Free Energy= -587.836703

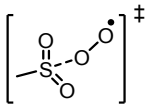
```
0 2
 S                  0.28431400    0.19915100    0.00000000
 O                 -0.17133300    0.74686800    1.28110900
 O                 -0.17133300    0.74686800   -1.28110900
 C                 -0.17133300   -1.57887100    0.00000000
 H                  0.24068000   -2.02352900   -0.90329600
 H                  0.24068000   -2.02352900    0.90329600
 H                 -1.26105500   -1.61602600    0.00000000
```

$MeSO_2H$

CBS-QB3 Enthalpy= -588.424080 CBS-QB3 Free Energy= -588.458321

```
0 1
 S                 -0.16471300   -0.16721300   -0.42035100
 O                 -0.71241600   -1.27207800    0.38146200
 O                 -0.61990400    1.32150500    0.25986500
 H                 -1.51766200    1.50064100   -0.05045200
 C                  1.54171300    0.07527200    0.14625900
 H                  2.09576500   -0.82342800   -0.12483200
 H                  1.96255500    0.95676500   -0.33657100
 H                  1.50303200    0.19439000    1.22929700
```

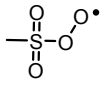
$MeSO_2^{\bullet}$ + O_2 TS



TS freq.: -132.52 cm^{-1}
CBS-QB3 Enthalpy = -737.961367 CBS-QB3 Free Energy= -738.003697

```
0 2
 S                 -0.54950500   -0.20719400   -0.00217200
 O                 -1.30163900   -0.94762200   -1.00536600
 O                 -0.31018800   -0.71738000    1.33884800
 C                 -1.26988200    1.45689600    0.13510700
 H                 -0.63671300    2.03443400    0.80517800
 H                 -1.30358300    1.88370300   -0.86515900
 H                 -2.27284600    1.33235300    0.54570400
 O                  1.69730800    0.34239500   -0.67325800
 O                  2.49258200   -0.01198900    0.18207400
```

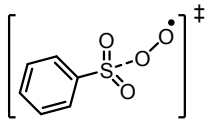
$MeS(O)_2OO^{\bullet}$



CBS-QB3 Enthalpy = -737.986159 CBS-QB3 Free Energy= -738.025794

```
0 2
 S                -0.48743500   -0.13071900    0.06624100
 O                -1.35886000   -0.75359100   -0.88375000
 O                -0.47448000   -0.44289200    1.46346700
 C                -0.41549800    1.63837100   -0.16576000
 H                 0.46795200    2.00084600    0.35605600
 H                -0.37378500    1.83902700   -1.23423800
 H                -1.32593400    2.04041500    0.27894000
 O                 1.16111200   -0.55152200   -0.58629500
 O                 2.11269100    0.04563000    0.07332200
```

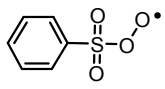
$PhSO_2^{\bullet} + O_2$ TS



TS freq.: -104.32 cm^{-1}
CBS-QB3 Enthalpy = -929.348716 CBS-QB3 Free Energy= -929.399501

```
0 2
 S                 1.09898100   -0.61592600    0.36174900
 O                 1.27686800   -2.03971700    0.10173200
 O                 1.61399600    0.04769600    1.55206300
 O                 2.22178000    0.76015200   -1.32859500
 O                 2.94228200    1.57875100   -0.78536500
 C                -0.63304700   -0.19452500    0.15727300
 C                -1.43823000   -1.01670600   -0.62944900
 C                -1.11114700    0.97920400    0.73830700
 C                -2.76849100   -0.65547300   -0.82080500
 H                -1.03075900   -1.92145500   -1.06127800
 C                -2.44394800    1.32414300    0.53597000
 H                -0.45569700    1.58910800    1.34613800
 C                -3.26822700    0.51103900   -0.24202800
 H                -3.41451800   -1.28696000   -1.41907600
 H                -2.83879100    2.22582800    0.98887900
 H                -4.30479200    0.78713900   -0.39692500
```

$PhS(O)_2OO^{\bullet}$

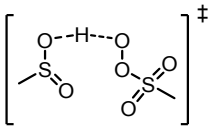


CBS-QB3 Enthalpy = -929.371766 CBS-QB3 Free Energy= -929.420032

```
0 2
 S                 1.28451300    0.36554600   -0.38180500
 O                 1.66127300    1.74334100   -0.25873100
 O                 1.78538500   -0.52680100   -1.38538600
 O                 1.87252300   -0.30821900    1.21939900
```

O	1.70628300	-1.59264400	1.30535800
C	-0.46160200	0.16037300	-0.19182200
C	-1.19826200	1.18979700	0.39488700
C	-1.05184300	-1.02957200	-0.61790400
C	-2.56909100	1.01715700	0.55237900
H	-0.70439300	2.10092000	0.70587500
C	-2.42387900	-1.18524900	-0.44795500
H	-0.44711600	-1.80156200	-1.07362800
C	-3.17750100	-0.16664300	0.13445500
H	-3.16155600	1.80669000	0.99861000
H	-2.90355300	-2.10059900	-0.77279400
H	-4.24624000	-0.29478200	0.26146100

$MeSO_2H + MeS(O)_2OO^{\cdot}$ TS

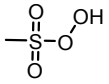


TS freq.: -746.25 cm^{-1}
CBS-QB3 Enthalpy = -1259.878512 CBS-QB3 Free Energy= -1259.940940

0 2

S	1.90283600	-0.04266700	0.25925300
O	3.00700200	0.32778600	1.15246700
O	1.62853400	1.02935800	-0.88048100
H	0.69779200	1.50320200	-0.69243000
C	2.50656600	-1.37094300	-0.83400200
H	2.79988300	-2.19676900	-0.18808100
H	1.68213000	-1.64248900	-1.48995600
H	3.35799400	-0.97273700	-1.38517900
O	-0.59550400	1.84978400	-0.27267700
O	-0.82555500	0.92534800	0.71334100
S	-1.69345100	-0.44656200	0.09297400
O	-0.98369600	-0.94248200	-1.05500900
O	-1.91332300	-1.24284500	1.26388800
C	-3.18400800	0.37302100	-0.43809400
H	-3.77768300	-0.37545200	-0.96241600
H	-3.69904700	0.74272600	0.44609500
H	-2.88623300	1.18111100	-1.10332200

$MeS(O)_2OOH$



CBS-QB3 Enthalpy = -738.637045 CBS-QB3 Free Energy= -738.675689

0 1

H	-2.23753300	-0.52397100	0.59254300
O	-2.06088600	0.16116300	-0.07246900
O	-0.94729500	-0.42223100	-0.78937500
S	0.46200700	-0.15083900	0.07481400
O	0.20788900	-0.49967500	1.44553400
O	1.44700000	-0.81477600	-0.72551800
C	0.61906500	1.61813500	-0.06626400
H	1.47613300	1.90836400	0.54113200
H	0.77864500	1.86099300	-1.11475400
H	-0.29740800	2.06337100	0.31626000

References

1. M. Ghosal, S. Das and D. Mukherjee, *Synth. Commun.*, 1989, **19**, 3275-3282.
2. A. K. Saha, S. Das and D. Mukherjee, *Synth. Commun.*, 1993, **23**, 1821-1828.
3. G. X. Ortiz, B. N. Hemric and Q. Wang, *Org. Lett.*, 2017, **19**, 1314-1317.
4. L. Valgimigli, J. T. Banks, J. Lusztyk and K. U. Ingold, *J. Org. Chem.*, 1999, **64**, 3381-3383.
5. R. Amorati, M. Lucarini, V. Mugnaini, G. F. Pedulli, F. Minisci, F. Recupero, F. Fontana, P. Astolfi and L. Greci, *J. Org. Chem.*, 2003, **68**, 1747-1754.
6. P. Mulder, H.-G. Korth, D. A. Pratt, G. A. DiLabio, L. Valgimigli, G. F. Pedulli and K. U. Ingold, *J. Phys. Chem. A*, 2005, **109**, 2647-2655.
7. L. A. Farmer, E. A. Haidasz, M. Griesser and D. A. Pratt, *J. Org. Chem.*, 2017, **82**, 10523-10536.
8. G. Litwinienko and K. U. Ingold, *J. Org. Chem.*, 2003, **68**, 3433-3438.
9. M. H. Abraham, R. J. Abraham, J. Byrne and L. Griffiths, *J. Org. Chem.*, 2006, **71**, 3389-3394.
10. H. T. Ho, O. Ito, M. Iino and M. Matsuda, *J. Phys. Chem.*, 1978, **82**, 314-319.
11. G. L. Edwards, C. A. Muldoon and D. J. Sinclair, *Tetrahedron*, 1996, **52**, 7779-7788.
12. J.-P. R. Chauvin, M. Griesser and D. A. Pratt, *J. Am. Chem. Soc.*, 2017, **139**, 6484-6493.
13. E. A. Haidasz, A. T. M. Van Kessel and D. A. Pratt, *J. Org. Chem.*, 2016, **81**, 737-744.