

Supporting Information

for

Photosensitized Oxidation of Alkyl Phenyl Sulfoxides. C-S Bond Cleavage in Alkyl Phenyl Sulfoxide Radical Cations

Enrico Baciocchi, Tiziana Del Giacco, Osvaldo Lanzalunga,

Paolo Mencarelli, Barbara Procacci

| | |
|--|-----|
| Stability of photoproducts in the steady-state photolysis of the 3-CN-NMQ ⁺ /1 and 3-CN-NMQ ⁺ /3 systems | S2 |
| Figure S1: Laser flash photolysis of the 3-CN-NMQ ⁺ /toluene/1 system | S3 |
| Figure S2: Laser flash photolysis of the 3-CN-NMQ ⁺ /toluene/2 system | S3 |
| Figure S3: Decay kinetics of PhSO [•] at 470 nm, LFP of the 3-CN-NMQ ⁺ /toluene/4 system | S4 |
| Figure S4: Decay kinetics of 1 ⁺⁺ at 560 nm, LFP of the 3-CN-NMQ ⁺ /toluene/1 system | S4 |
| Figure S5: Decay kinetics of 2 ⁺⁺ at 560 nm, LFP of the 3-CN-NMQ ⁺ /toluene/2 system | S5 |
| Figure S6: Decay kinetics of 5 ⁺⁺ at 560 nm, LFP of the 3-CN-NMQ ⁺ /toluene/5 system | S5 |
| C-S BDFEs for the sulfoxide and sulfide radical cations | S6 |
| C-H BDFE for benzyl phenyl sulfoxide radical cation | S7 |
| Cartesian coordinates, electronic energies, and zero-point vibrational energies obtained from DFT calculations | S8 |
| References for Supporting Information | S22 |

Stability of photoproducts in the steady-state photolysis of the 3-CN-NMQ⁺/1 and 3-CN-NMQ⁺/3 systems

A solution of 3-CN-NMQ⁺ (0.01 M) and sulfoxides **1** or **3** (0.01 M) in 2 mL of N₂-saturated CD₃CN was irradiated in a photoreactor equipped with 4 lamps (360 nm) at 25°C for several irradiation times. Reaction products were quantitatively analysed by ¹HNMR after addition of an internal standard. In the oxidation of **1**, after 20 min of irradiation, the products observed were benzylacetamide (5.6 %, referred to the initial amount of substrate) and benzyl alcohol (1.0 %). After 40 min of irradiation benzaldehyde (1.0 %) was formed together with benzylacetamide (11.3 %) and benzyl alcohol (1.8 %). In the oxidation of **3**, after 5 min of irradiation, the products observed were benzhydrol (16 % referred to the initial amount of substrate) and benzophenone (2.0 %). The yields of benzhydrol and benzophenone were respectively 32 % and 12 % after 15 min of irradiation, 24 % and 26 % after 30 min of irradiation, 10 % and 32 % after 1h of irradiation,

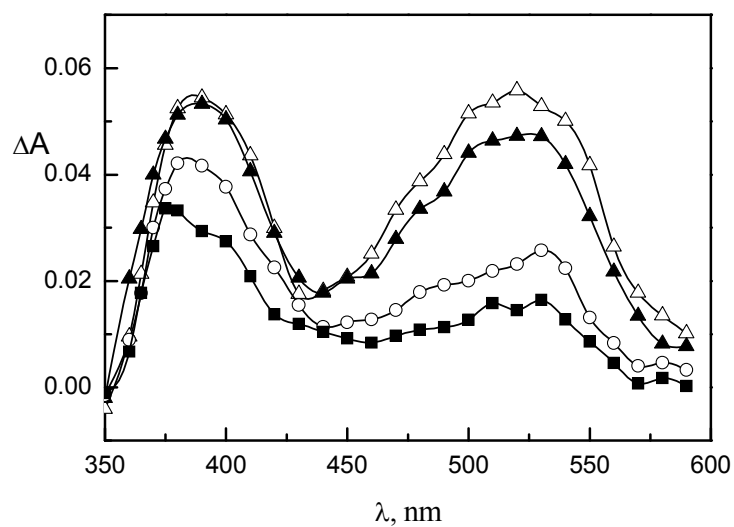


Figure S1 Time-resolved absorption spectra of the 3-CN-NMQ⁺ (1.0×10^{-2} M)/toluene (1 M)/**1** (1.0×10^{-2} M) system in N₂-saturated CH₃CN recorded 0.13 (Δ), 0.51 (\blacktriangle) 3.0 (\circ) and 6.4 (\blacksquare) μ s after the laser pulse ($\lambda_{\text{exc}} = 355$ nm).

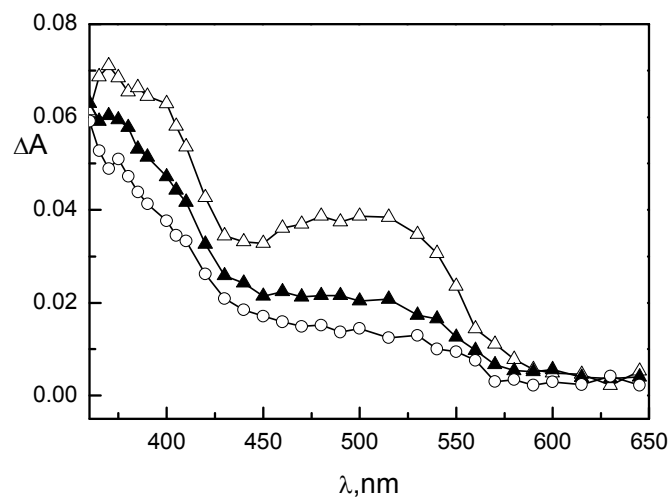


Figure S2 Time-resolved absorption spectra of the 3-CN-NMQ⁺ (1.0×10^{-2} M)/toluene (1 M)/**2** (1.0×10^{-2} M) system in N₂-saturated CH₃CN recorded 0.032 (Δ), 1.9 (\blacktriangle) and 6.4 (\circ) μ s after the laser pulse ($\lambda_{\text{exc}} = 355$ nm).

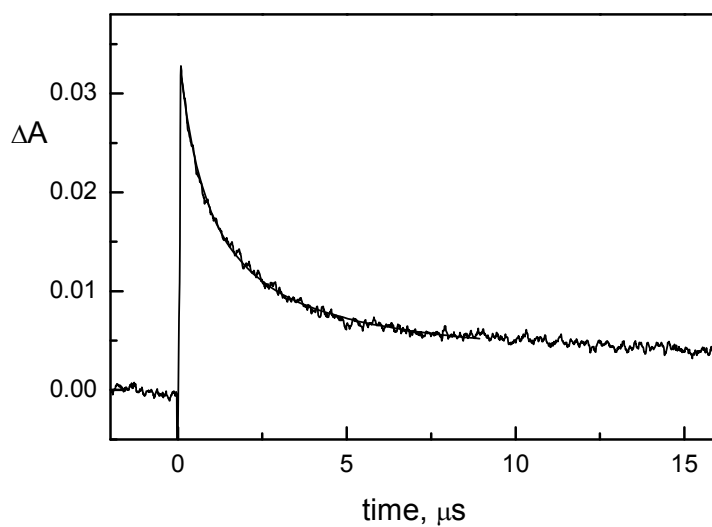


Figure S3 Decay kinetics of the radical PhSO^\bullet , generated by photolysis of the 3-CN-NMQ⁺ (1.0×10^{-2} M)/toluene (1 M)/4 (1.0×10^{-2} M) system, recorded in N₂-saturated CH₃CN at 470 nm ($\lambda_{\text{exc}} = 355$ nm).

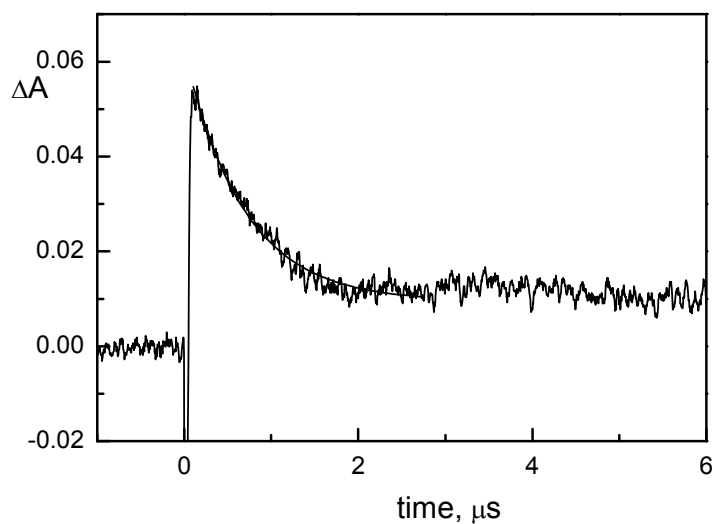


Figure S4 Decay kinetics of the radical cation $1^{\bullet+}$ generated by photolysis of the 3-CN-NMQ⁺ (1.0×10^{-2} M)/toluene (1 M)/1 (1.0×10^{-2} M) system, recorded in N₂-saturated CH₃CN at 560 nm ($\lambda_{\text{exc}} = 355$ nm).

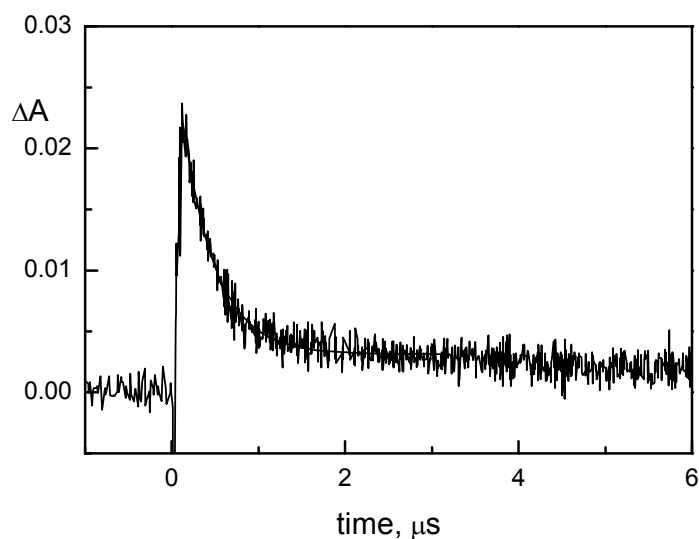


Figure S5 Decay kinetics of the radical radical cation $2^{+\bullet}$ generated by photolysis of the 3-CN-NMQ $^+$ (1.0×10^{-2} M)/toluene (1 M)/**2** (1.0×10^{-2} M) system, recorded in N_2 -saturated CH_3CN at 560 nm ($\lambda_{exc} = 355$ nm).

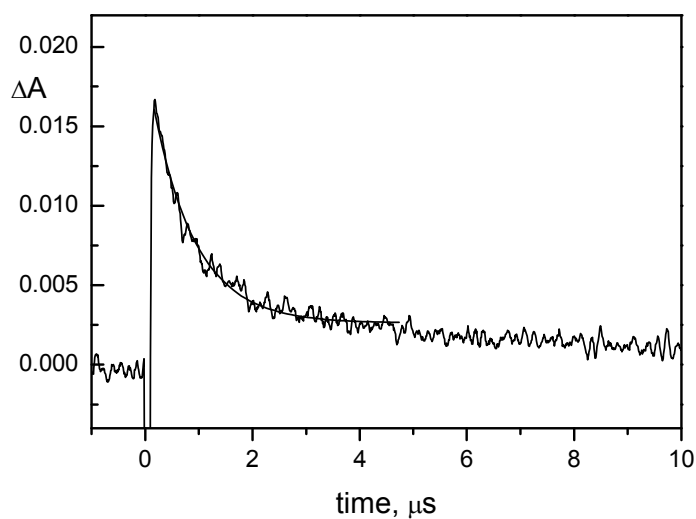
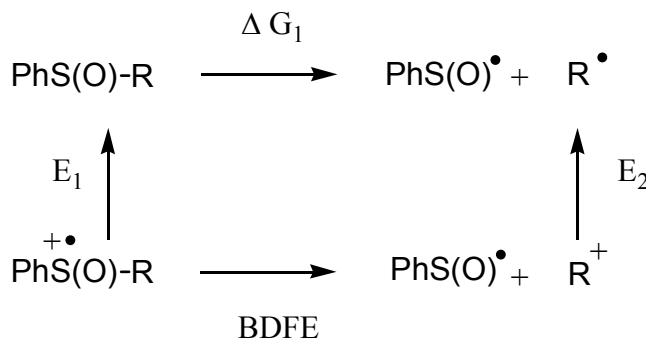


Figure S6 Decay kinetics of the radical radical cation $5^{+\bullet}$ generated by photolysis of the 3-CN-NMQ $^+$ (1.0×10^{-2} M)/toluene (1 M)/**5** (1.0×10^{-2} M) system, recorded in N_2 -saturated CH_3CN at 560 nm ($\lambda_{exc} = 355$ nm).

C-S BDFEs for the sulfoxide and sulfide radical cations

The C-S BDFE values for the sulfoxide radical cations $1^{+\bullet}$ - $5^{+\bullet}$, *t*-butyl phenyl sulfide and dimethylbenzyl phenyl sulphide were calculated by using the following thermochemical cycle Scheme S1):



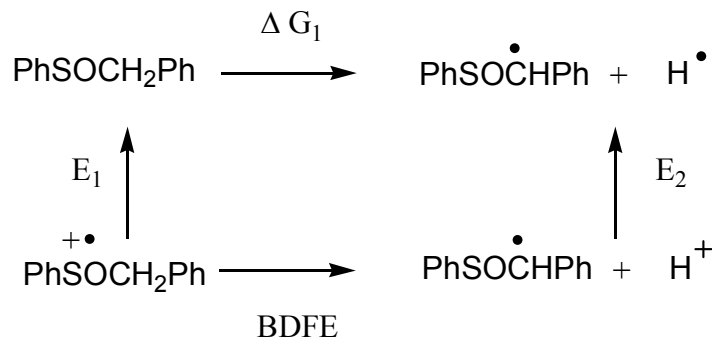
Scheme S1

$$\text{BDFE} = \Delta G_1 + F(E_2 - E_1)$$

E_1 values are the peak reduction potential of sulfoxide or sulfide radical cations. For sulfoxide radical cations $1^{+\bullet}$ - $5^{+\bullet}$ E_1 was taken as 2.0 V vs SCE (peak reduction potential of methyl phenyl sulfoxide radical cation^{S1}). E_1 values for sulfide radical cations are taken from the literature.^{S2} E_2 values, the reduction potential of the tertiary carbocations, are available in the literature.^{S3} ΔG_1 , the C-S bond dissociation free energies of the neutral sulfoxides and sulfides, have been determined from the C-S BDEs, obtained by DFT calculations, and applying an entropic correction ($T\Delta S^\circ$) of 10 kcal mol⁻¹. The latter value has been considered similar to the entropy change associated with the homolytic C-S bond cleavage of thioanisole.^{S2}

C-H BDFE for benzyl phenyl sulfoxide radical cation

The C-H BDFE value for benzyl phenyl sulfoxide radical cation $1^{+\bullet}$ was calculated by using the following thermochemical cycle (Scheme S2):



Scheme S2

$$\text{BDFE} = \Delta G_1 + F(E_2 - E_1)$$

E_1 is the peak reduction potential of benzyl phenyl sulfoxide radical cations (2.01 V vs SCE, see above). E_2 is the reduction potential of the proton (-2.0 V).^{S4} ΔG_1 , the C-H bond dissociation free energy of the neutral sulfoxide **1**, has been determined from the C-H BDE (88.8 kcal mol⁻¹),^{S5} and applying an entropic correction ($T\Delta S^\circ$) of 8 kcal mol⁻¹.^{S6}

Cartesian Coordinates, energies, ZPVE obtained from DFT calculations

Sulfoxide **1** PhSOCH₂Ph

conformer 1, E = -978.2157895 a.u., ZPVE = 0.2108760 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -2.33324400 | -2.06251500 | -0.23526000 |
| C | -2.77808900 | -1.07306700 | -0.20293200 |
| C | -3.85054500 | 1.49755600 | -0.02747000 |
| C | -2.02418800 | -0.02002200 | 0.29198700 |
| C | -4.08051300 | -0.82825600 | -0.62576800 |
| C | -4.61397500 | 0.45326800 | -0.54241800 |
| C | -2.54948300 | 1.26295700 | 0.39998300 |
| S | -0.34676700 | -0.37793600 | 0.87889800 |
| H | -4.68153300 | -1.64228200 | -1.01568300 |
| H | -5.63108700 | 0.63885600 | -0.86886500 |
| H | -1.95787500 | 2.06968400 | 0.82228800 |
| H | -4.27214800 | 2.49353400 | 0.04949300 |
| C | 0.52708900 | 0.35667500 | -0.58932100 |
| O | -0.16357500 | -1.87052700 | 0.76800200 |
| H | 0.17013900 | -0.23193700 | -1.43757100 |
| C | 2.00703300 | 0.28410600 | -0.41461500 |
| H | 0.17007400 | 1.38444600 | -0.68108800 |
| C | 4.77463200 | 0.13689500 | -0.04841800 |
| C | 2.73523000 | 1.41556700 | -0.04324400 |
| C | 2.68126800 | -0.92588800 | -0.59505700 |
| C | 4.05600000 | -0.99723700 | -0.41135400 |
| C | 4.11097600 | 1.34458200 | 0.13618100 |
| H | 2.22094600 | 2.36099000 | 0.10038200 |
| H | 2.11734700 | -1.81255600 | -0.86195800 |
| H | 4.56804400 | -1.94266900 | -0.55174900 |
| H | 4.66505100 | 2.23302700 | 0.41822900 |
| H | 5.84856000 | 0.07979600 | 0.09007100 |

Sulfoxide **1** PhSOCH₂Ph,

conformer 2, E = -978.2158586 a.u., ZPVE = 0.2110010 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -2.52647000 | 0.69667500 | -1.81482000 |
| C | -2.38316400 | 0.07317100 | -0.93729000 |
| C | -2.05131800 | -1.48590500 | 1.34915900 |
| C | -1.50678200 | 0.45934800 | 0.07054700 |
| C | -3.08518400 | -1.11812500 | -0.80006500 |
| C | -2.91783000 | -1.89677100 | 0.34205100 |
| C | -1.34019600 | -0.29790400 | 1.21933500 |
| S | -0.61582000 | 2.02718900 | -0.05632900 |
| H | -3.77184900 | -1.43272800 | -1.57805100 |
| H | -3.47333400 | -2.82172600 | 0.44978300 |
| H | -0.66450100 | 0.06192100 | 1.98805700 |
| H | -1.92931800 | -2.09088000 | 2.24069900 |

| | | | |
|---|------------|-------------|-------------|
| C | 0.72309900 | 1.45978000 | -1.23114500 |
| O | 0.05037500 | 2.25971700 | 1.27521700 |
| H | 0.21154200 | 1.21754700 | -2.16525200 |
| C | 1.54224900 | 0.33506000 | -0.70749500 |
| H | 1.30801900 | 2.37115800 | -1.37482500 |
| C | 3.05875800 | -1.78220700 | 0.30913000 |
| C | 1.35536700 | -0.96484500 | -1.18269400 |
| C | 2.49273000 | 0.56100900 | 0.29159100 |
| C | 3.24375200 | -0.49303400 | 0.79640400 |
| C | 2.11239900 | -2.01613100 | -0.68272400 |
| H | 0.61368600 | -1.15193300 | -1.95268800 |
| H | 2.62723000 | 1.56329300 | 0.68089900 |
| H | 3.97737000 | -0.30576800 | 1.57271600 |
| H | 1.96307700 | -3.01889000 | -1.06756400 |
| H | 3.65139100 | -2.60211700 | 0.69974000 |

Sulfoxide **2** PhSOCH(CH₃)Ph,

conformer 1, E = -1017.6885998 a.u., ZPVE = 0.238599 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 0.22906900 | -1.25567000 | -1.43929200 |
| C | 1.13732400 | -1.17862400 | -0.85178500 |
| C | 3.49048100 | -0.95937400 | 0.63074100 |
| C | 1.54890300 | 0.04818600 | -0.34234800 |
| C | 1.90914000 | -2.30615000 | -0.59575900 |
| C | 3.08150200 | -2.19769500 | 0.14595700 |
| C | 2.72559200 | 0.17465100 | 0.38279800 |
| S | 0.61789900 | 1.56107900 | -0.69557700 |
| H | 1.59742000 | -3.26940300 | -0.98382600 |
| H | 3.68412000 | -3.07910400 | 0.33532800 |
| H | 3.02741300 | 1.16126700 | 0.71963300 |
| H | 4.41256000 | -0.87392500 | 1.19509000 |
| C | -0.67100600 | 1.39866000 | 0.66913000 |
| O | 1.50155700 | 2.71012400 | -0.27221200 |
| H | -0.07507200 | 1.19616200 | 1.56307500 |
| C | -1.59000100 | 0.25161200 | 0.38503400 |
| C | -1.34047600 | 2.75906300 | 0.78436600 |
| C | -3.28550600 | -1.91839900 | -0.13701600 |
| C | -2.46853500 | 0.27771500 | -0.70235700 |
| C | -1.57118000 | -0.88175400 | 1.19982600 |
| C | -2.41566400 | -1.95575800 | 0.94663500 |
| C | -3.30724800 | -0.79876600 | -0.96222300 |
| H | -2.49759000 | 1.14527000 | -1.35303200 |
| H | -0.88733700 | -0.91962900 | 2.04148500 |
| H | -2.39159900 | -2.82411200 | 1.59573500 |
| H | -3.98180500 | -0.76204800 | -1.81057400 |
| H | -3.94434700 | -2.75594400 | -0.33733700 |
| H | -1.91264100 | 3.00920500 | -0.11239000 |
| H | -0.58997700 | 3.53541400 | 0.94225700 |
| H | -2.02901300 | 2.75405500 | 1.63277700 |

Sulfoxide **2** PhSOCH(CH₃)Ph,
conformer 2, E = -1017.6879761 a.u., ZPVE = 0.238544 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -1.74486700 | 2.11474700 | -0.78176200 |
| C | -2.43227100 | 1.33821700 | -0.45981900 |
| C | -4.20925900 | -0.66874400 | 0.30294200 |
| C | -2.02189100 | 0.01092400 | -0.39204700 |
| C | -3.74145300 | 1.65904300 | -0.12272000 |
| C | -4.62837400 | 0.65653200 | 0.26082500 |
| C | -2.89959100 | -0.99964100 | -0.02914000 |
| S | -0.33952500 | -0.45627700 | -0.87894400 |
| H | -4.07271300 | 2.69047700 | -0.16864700 |
| H | -5.65101500 | 0.90995500 | 0.51682200 |
| H | -2.53866400 | -2.02306000 | -0.02060200 |
| H | -4.90485500 | -1.44929100 | 0.59078200 |
| C | 0.54948500 | 0.22370700 | 0.63827300 |
| O | -0.27561700 | -1.96176400 | -0.77114200 |
| H | 0.17325700 | 1.24746700 | 0.72055800 |
| C | 2.01787000 | 0.25365200 | 0.32472200 |
| C | 0.17539300 | -0.60171900 | 1.85532900 |
| C | 4.75319500 | 0.33989600 | -0.26344100 |
| C | 2.66754600 | 1.47374800 | 0.13380100 |
| C | 2.75565000 | -0.92738900 | 0.20727000 |
| C | 4.11252400 | -0.88186300 | -0.08682500 |
| C | 4.02662100 | 1.51951500 | -0.15260600 |
| H | 2.10457800 | 2.39839800 | 0.21953300 |
| H | 2.25900400 | -1.88347000 | 0.32685200 |
| H | 4.67166900 | -1.80628200 | -0.18042100 |
| H | 4.51723200 | 2.47688100 | -0.28968500 |
| H | 5.81347000 | 0.37204100 | -0.48822100 |
| H | 0.78131900 | -0.29012500 | 2.70926900 |
| H | 0.35512900 | -1.66253000 | 1.66919900 |
| H | -0.87886200 | -0.47594400 | 2.10917500 |

Sulfoxide **2** PhSOCH(CH₃)Ph,
conformer 3, E = -1017.6865367 a.u., ZPVE = 0.238706 a.u.

| | | | |
|---|------------|-------------|-------------|
| H | 2.76703900 | -1.12305200 | 1.20420400 |
| C | 2.51917600 | -0.24645300 | 0.61446200 |
| C | 1.93326500 | 1.96721300 | -0.97449000 |
| C | 1.50510700 | -0.29895300 | -0.33620900 |
| C | 3.22823800 | 0.93785900 | 0.78225700 |
| C | 2.93294600 | 2.04331500 | -0.00949800 |
| C | 1.21464700 | 0.79054100 | -1.14581100 |
| S | 0.60317200 | -1.83753600 | -0.61533600 |
| H | 4.02169100 | 0.99173300 | 1.51933700 |
| H | 3.49446200 | 2.96237200 | 0.11670300 |
| H | 0.44298700 | 0.68907600 | -1.90134000 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.71458100 | 2.82645800 | -1.59865300 |
| C | -0.76664200 | -1.63738900 | 0.68143300 |
| O | -0.08281100 | -1.70086800 | -1.95154900 |
| H | -1.38511600 | -2.49121500 | 0.38697700 |
| C | -1.53735600 | -0.37729900 | 0.46381700 |
| C | -0.19413500 | -1.87456000 | 2.06558100 |
| C | -2.98885300 | 1.96781800 | -0.02872300 |
| C | -1.34762000 | 0.75808500 | 1.25576400 |
| C | -2.46156700 | -0.31659100 | -0.58445400 |
| C | -3.17829300 | 0.84743900 | -0.82995100 |
| C | -2.07204700 | 1.91870800 | 1.01535700 |
| H | -0.63337600 | 0.74057000 | 2.07069400 |
| H | -2.60191900 | -1.18558200 | -1.21642900 |
| H | -3.88979400 | 0.87717400 | -1.64779600 |
| H | -1.91808700 | 2.78776600 | 1.64556700 |
| H | -3.55496300 | 2.87393000 | -0.21472900 |
| H | 0.32240300 | -2.83629900 | 2.11387700 |
| H | -1.00178300 | -1.88781800 | 2.80173800 |
| H | 0.51240800 | -1.09598100 | 2.36038600 |

Sulfoxide **3** PhSOCH(Ph)₂

conformer 1, E = -1210.0377003 a.u., ZPVE = 0.290708 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 2.34594300 | 0.08295500 | 1.86095200 |
| C | 2.72440000 | -0.43933400 | 0.98871000 |
| C | 3.60913700 | -1.85372600 | -1.25035400 |
| C | 1.85825500 | -1.24663600 | 0.26779100 |
| C | 4.04698300 | -0.33407800 | 0.57274600 |
| C | 4.48716300 | -1.03494600 | -0.54498100 |
| C | 2.28671000 | -1.97003300 | -0.83988100 |
| S | 0.15774000 | -1.41684800 | 0.85342400 |
| H | 4.73557000 | 0.29633400 | 1.12423700 |
| H | 5.52045700 | -0.95256800 | -0.86324400 |
| H | 1.60265500 | -2.62547600 | -1.37080100 |
| H | 3.95778600 | -2.41126500 | -2.11252300 |
| O | 0.09474600 | -0.71120100 | 2.18646600 |
| C | -0.65427800 | -0.27530400 | -0.42743500 |
| C | -0.13513600 | 1.12480400 | -0.30399100 |
| C | -2.15011400 | -0.44409700 | -0.33796500 |
| H | -0.31060600 | -0.70276400 | -1.37376900 |
| C | -4.93733000 | -0.71423200 | -0.28715700 |
| C | -2.87754200 | -0.56622500 | -1.52344500 |
| C | -2.83777500 | -0.46925000 | 0.87808100 |
| C | -4.22140300 | -0.60546600 | 0.89875000 |
| C | -4.26015100 | -0.69462000 | -1.50114300 |
| H | -2.35463800 | -0.55139900 | -2.47487400 |
| H | -2.28749200 | -0.40072100 | 1.81021500 |
| H | -4.74066000 | -0.62925300 | 1.85052100 |
| H | -4.80777700 | -0.78415800 | -2.43288600 |

| | | | |
|---|-------------|-------------|-------------|
| H | -6.01643900 | -0.81801400 | -0.26605400 |
| C | 0.89521000 | 3.71980000 | -0.11037200 |
| C | 0.79170500 | 1.59657600 | -1.23715400 |
| C | -0.53350600 | 1.96911300 | 0.73440400 |
| C | -0.01804800 | 3.25564400 | 0.82953600 |
| C | 1.29891300 | 2.88594400 | -1.14693200 |
| H | 1.11554900 | 0.94654000 | -2.04390600 |
| H | -1.24480700 | 1.61972800 | 1.47081800 |
| H | -0.33490600 | 3.89954800 | 1.64252000 |
| H | 2.00974800 | 3.23839900 | -1.88614800 |
| H | 1.28865300 | 4.72769400 | -0.03681500 |

Sulfoxide **3** PhSOCH(Ph)₂

conformer 2, E = -1210.0377468 a.u., ZPVE = 0.290809 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 2.38792300 | 0.79766900 | -1.26258900 |
| C | 2.72682900 | -0.05331800 | -0.68271700 |
| C | 3.59818500 | -2.26101000 | 0.78307800 |
| C | 1.86541200 | -1.10948500 | -0.40453300 |
| C | 4.03063400 | -0.10346400 | -0.20315800 |
| C | 4.46504700 | -1.20258600 | 0.53112300 |
| C | 2.29230400 | -2.22166200 | 0.30835100 |
| S | 0.17128100 | -1.13927400 | -1.05413400 |
| H | 4.71000500 | 0.71572800 | -0.41049300 |
| H | 5.48526900 | -1.23910000 | 0.89673300 |
| H | 1.59912800 | -3.04319700 | 0.45754400 |
| H | 3.94221700 | -3.12494200 | 1.34102100 |
| O | -0.31899900 | -2.54905900 | -0.84469200 |
| C | -0.62671200 | -0.09003000 | 0.33909700 |
| C | -2.11659100 | -0.29163200 | 0.28726700 |
| C | -0.10485200 | 1.30918100 | 0.23710300 |
| H | -0.23191600 | -0.57068900 | 1.23744300 |
| C | 0.92171400 | 3.91331000 | 0.08527800 |
| C | -0.19597700 | 2.04486900 | -0.94930300 |
| C | 0.51729800 | 1.89704000 | 1.33953700 |
| C | 1.02130500 | 3.18939800 | 1.26822200 |
| C | 0.31378600 | 3.33602100 | -1.02386300 |
| H | -0.65974900 | 1.60159400 | -1.82399500 |
| H | 0.60585000 | 1.33376200 | 2.26265400 |
| H | 1.49727000 | 3.62982500 | 2.13731500 |
| H | 0.23582800 | 3.89129400 | -1.95214200 |
| H | 1.31726700 | 4.92119800 | 0.02732400 |
| C | -4.87755600 | -0.76959300 | 0.24257100 |
| C | -2.63803500 | -1.51390900 | 0.72608200 |
| C | -3.00175600 | 0.68872900 | -0.16545100 |
| C | -4.37111200 | 0.45161000 | -0.18474700 |
| C | -4.00502800 | -1.75144900 | 0.69850600 |
| H | -1.96074500 | -2.28676000 | 1.06847400 |
| H | -2.62674200 | 1.65374000 | -0.48311900 |
| H | -5.04374200 | 1.22876200 | -0.53082400 |

| | | | |
|---|-------------|-------------|------------|
| H | -4.38948900 | -2.70725600 | 1.03672500 |
| H | -5.94624500 | -0.95288900 | 0.22696400 |

Sulfoxide **3** PhSOCH(Ph)₂

conformer 3, E = -1210.0356546 a.u., ZPVE = 0.291024 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -2.44222000 | 1.65960200 | 1.04599900 |
| C | -1.66883600 | 2.10868700 | 0.43179900 |
| C | 0.39769400 | 3.22091900 | -1.07697300 |
| C | -0.35607200 | 1.69372500 | 0.60725500 |
| C | -1.94579100 | 3.08588600 | -0.51740400 |
| C | -0.91676600 | 3.63614500 | -1.27435200 |
| C | 0.68886100 | 2.25269500 | -0.12346000 |
| S | -0.03532300 | 0.48282200 | 1.90743800 |
| H | -2.96725100 | 3.41892300 | -0.66440800 |
| H | -1.13594100 | 4.39963300 | -2.01264200 |
| H | 1.71248600 | 1.93681900 | 0.04476200 |
| H | 1.20039000 | 3.65961100 | -1.65914900 |
| O | -1.35205300 | 0.23799900 | 2.59452000 |
| C | 0.30035100 | -1.09281000 | 0.85273300 |
| C | 1.64671500 | -0.97152800 | 0.18963900 |
| C | -0.90547700 | -1.47406400 | 0.05970600 |
| H | 0.39074800 | -1.79218500 | 1.69012700 |
| C | -3.22549500 | -2.24379900 | -1.31738700 |
| C | -1.71750200 | -2.50499900 | 0.53881700 |
| C | -1.29257000 | -0.81592900 | -1.11352500 |
| C | -2.43802900 | -1.20307000 | -1.79695300 |
| C | -2.86387400 | -2.89145900 | -0.14269900 |
| H | -1.44645400 | -3.00734600 | 1.46132300 |
| H | -0.70428400 | 0.01075100 | -1.49197800 |
| H | -2.71950500 | -0.68280800 | -2.70586300 |
| H | -3.47690000 | -3.69576800 | 0.24831900 |
| H | -4.11934200 | -2.54318500 | -1.85341600 |
| C | 4.21566200 | -0.75853100 | -0.92912200 |
| C | 2.76557000 | -0.71220200 | 0.99285300 |
| C | 1.84631200 | -1.14542600 | -1.18019500 |
| C | 3.11874800 | -1.03993000 | -1.73270000 |
| C | 4.03402500 | -0.60120900 | 0.44114400 |
| H | 2.64048800 | -0.60027000 | 2.06500700 |
| H | 1.00901400 | -1.38974400 | -1.82072400 |
| H | 3.24985700 | -1.18621000 | -2.79929100 |
| H | 4.88342400 | -0.39970600 | 1.08452900 |
| H | 5.20592800 | -0.67586900 | -1.36281600 |

Sulfoxide **3** PhSOCH(Ph)₂

conformer 4, E = -1210.0348275 a.u., ZPVE = 0.291033 a.u.

| | | | |
|---|-------------|------------|-------------|
| H | -2.67511400 | 0.33217300 | 0.65548200 |
| C | -2.18920300 | 1.20973800 | 0.24437000 |
| C | -0.91223500 | 3.50860500 | -0.69533500 |
| C | -0.89597900 | 1.52033800 | 0.64683400 |

| | | | |
|---|-------------|-------------|-------------|
| C | -2.83424700 | 2.04930000 | -0.65495500 |
| C | -2.19635100 | 3.19254900 | -1.12762600 |
| C | -0.25748900 | 2.67446200 | 0.20394600 |
| S | -0.09080300 | 0.48726800 | 1.88843100 |
| H | -3.84116000 | 1.81474200 | -0.98158000 |
| H | -2.70828000 | 3.84875800 | -1.82283600 |
| H | 0.73588200 | 2.92100500 | 0.56363100 |
| H | -0.42587500 | 4.41225500 | -1.04541100 |
| O | -1.20252300 | -0.17208100 | 2.66738300 |
| C | 0.64133100 | -0.93362900 | 0.80786900 |
| C | 1.92459700 | -0.49565300 | 0.16955600 |
| C | -0.41898900 | -1.60375600 | -0.01099000 |
| H | 0.88798400 | -1.59282500 | 1.64545900 |
| C | -2.47055500 | -2.89727500 | -1.42224700 |
| C | -1.37865600 | -2.37274700 | 0.66122500 |
| C | -0.49743900 | -1.51057300 | -1.40271500 |
| C | -1.51173300 | -2.15426800 | -2.10068200 |
| C | -2.39837000 | -3.00492500 | -0.03811100 |
| H | -1.32868800 | -2.45586300 | 1.73994500 |
| H | 0.24972600 | -0.95541100 | -1.95437000 |
| H | -1.54757200 | -2.07774200 | -3.18193800 |
| H | -3.13316500 | -3.59186300 | 0.50197800 |
| H | -3.26038300 | -3.39980700 | -1.96970600 |
| C | 4.39774400 | 0.26994600 | -0.92126700 |
| C | 1.99198200 | 0.44259900 | -0.86545000 |
| C | 3.12301500 | -1.02928700 | 0.65321800 |
| C | 4.34673000 | -0.65713600 | 0.11306900 |
| C | 3.21655100 | 0.81926500 | -1.40495700 |
| H | 1.08537300 | 0.89396900 | -1.24797500 |
| H | 3.09267600 | -1.75443400 | 1.46040300 |
| H | 5.26094200 | -1.09141700 | 0.50215600 |
| H | 3.24528800 | 1.54779900 | -2.20788800 |
| H | 5.35116700 | 0.56370400 | -1.34582200 |

Sulfoxide 4 PhSOC(CH₃)₂Ph

conformer 1, E = -1057.1587878 a.u., ZPVE = 0.266059 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -3.11551400 | 1.13175300 | 0.33861700 |
| C | -2.78399600 | 0.11480500 | 0.15598600 |
| C | -1.87390600 | -2.45675900 | -0.41594700 |
| C | -1.54108400 | -0.08358300 | -0.43024100 |
| C | -3.56852800 | -0.98872100 | 0.47115600 |
| C | -3.11297000 | -2.27252500 | 0.19025600 |
| C | -1.08226200 | -1.36086600 | -0.73894000 |
| S | -0.60161000 | 1.39265100 | -0.89955200 |
| H | -4.54073800 | -0.84445200 | 0.92945400 |
| H | -3.72927900 | -3.13138500 | 0.43202300 |
| H | -0.12323400 | -1.50211800 | -1.22419700 |
| H | -1.52411800 | -3.45674900 | -0.64692100 |

| | | | |
|---|-------------|-------------|-------------|
| O | -1.50425900 | 2.56699200 | -0.59818000 |
| C | 0.72579400 | 1.40726900 | 0.48779100 |
| C | 1.46287600 | 2.72357900 | 0.23896500 |
| C | 1.60695800 | 0.20179300 | 0.27636700 |
| C | -0.00202800 | 1.46919900 | 1.81667600 |
| C | 3.23757300 | -2.04619300 | -0.17188000 |
| C | 1.72787400 | -0.80258300 | 1.23903600 |
| C | 2.32409100 | 0.05477400 | -0.91844100 |
| C | 3.12572100 | -1.05628300 | -1.14263200 |
| C | 2.53826700 | -1.91143100 | 1.02033400 |
| H | 1.18972500 | -0.72268300 | 2.17506900 |
| H | 2.25068300 | 0.81376900 | -1.68931500 |
| H | 3.66706000 | -1.14706900 | -2.07799000 |
| H | 2.61945100 | -2.67357400 | 1.78764400 |
| H | 3.86752900 | -2.91192300 | -0.34303200 |
| H | 1.94844400 | 2.75455700 | -0.73813900 |
| H | 2.23521300 | 2.85027700 | 1.00247500 |
| H | 0.76505500 | 3.56112300 | 0.30250100 |
| H | 0.71064000 | 1.64771400 | 2.62753600 |
| H | -0.55784100 | 0.55595800 | 2.03458800 |
| H | -0.70951800 | 2.30160800 | 1.79705300 |

Sulfoxide **4** PhSOC(CH₃)₂Ph

conformer 2, E = -1057.1565849 a.u., ZPVE = 0.265974 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.76678800 | 0.71546900 | -1.89795100 |
| C | -1.51202500 | 0.62010700 | -1.11604500 |
| C | -3.43894000 | 0.25891000 | 0.87062000 |
| C | -1.50451400 | -0.51563600 | -0.31759000 |
| C | -2.48428700 | 1.58872900 | -0.90141700 |
| C | -3.44150100 | 1.41259600 | 0.09317900 |
| C | -2.47253100 | -0.71852600 | 0.66056400 |
| S | -0.27805400 | -1.79645500 | -0.65445100 |
| H | -2.49782700 | 2.48201600 | -1.51585800 |
| H | -4.20168500 | 2.16922200 | 0.25295700 |
| H | -2.48519700 | -1.63587100 | 1.24000000 |
| H | -4.19872700 | 0.11158800 | 1.63008000 |
| O | 0.27509600 | -1.50667500 | -2.02943100 |
| C | 1.09767400 | -1.29152500 | 0.59185200 |
| C | 0.57285200 | -1.64315600 | 1.97536000 |
| C | 1.44624000 | 0.15930100 | 0.39268300 |
| C | 2.24309900 | -2.23032700 | 0.21482300 |
| C | 2.09188900 | 2.86549100 | -0.01943500 |
| C | 1.11523800 | 1.13269100 | 1.34069300 |
| C | 2.10426900 | 0.57398300 | -0.77303300 |
| C | 2.41739100 | 1.91197700 | -0.97664900 |
| C | 1.43919900 | 2.46894700 | 1.14101700 |
| H | 0.60354900 | 0.85391700 | 2.25329300 |
| H | 2.34648900 | -0.14975100 | -1.53940300 |
| H | 2.92215400 | 2.20814600 | -1.88982000 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.17845200 | 3.20136000 | 1.89724200 |
| H | 2.34582000 | 3.90815400 | -0.17577800 |
| H | 0.30489400 | -2.70189900 | 2.02124500 |
| H | -0.30240300 | -1.05725800 | 2.25987400 |
| H | 1.35347800 | -1.46591100 | 2.72100300 |
| H | 1.95569400 | -3.27346300 | 0.37468500 |
| H | 3.10988100 | -2.01169900 | 0.84418900 |
| H | 2.53599800 | -2.11871200 | -0.82882700 |

Sulfoxide **4** PhSOC(CH₃)₂Ph

conformer 3, E = -1057.1549551 a.u., ZPVE = 0.266001 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 2.23847400 | -2.08603800 | 0.26540400 |
| C | 2.75761800 | -1.14595900 | 0.11124500 |
| C | 4.03563500 | 1.27455400 | -0.42338800 |
| C | 2.05358700 | -0.07825500 | -0.42980300 |
| C | 4.10620300 | -0.98809300 | 0.40808800 |
| C | 4.74305300 | 0.22132100 | 0.14817800 |
| C | 2.68684100 | 1.12517800 | -0.72438500 |
| S | 0.31968100 | -0.34387900 | -0.88791700 |
| H | 4.66408500 | -1.81510000 | 0.83333500 |
| H | 5.79701900 | 0.33838600 | 0.37435200 |
| H | 2.13857400 | 1.93447800 | -1.19495900 |
| H | 4.53752500 | 2.20903800 | -0.64824800 |
| O | 0.11835000 | -1.84022400 | -0.81512400 |
| C | -0.57771700 | 0.36555500 | 0.66113400 |
| C | -0.18665200 | -0.49455600 | 1.85289900 |
| C | -2.04369300 | 0.22255700 | 0.29625500 |
| C | -0.13518900 | 1.80767900 | 0.84720000 |
| C | -4.75427400 | -0.07418700 | -0.39109200 |
| C | -2.81708000 | 1.32462900 | -0.07992200 |
| C | -2.65637300 | -1.03641000 | 0.30735300 |
| C | -3.99465900 | -1.18149700 | -0.03267400 |
| C | -4.15858300 | 1.17990400 | -0.41453000 |
| H | -2.38146800 | 2.31556100 | -0.10588600 |
| H | -2.07436400 | -1.91402200 | 0.55509000 |
| H | -4.44366600 | -2.16852800 | -0.02064800 |
| H | -4.73733300 | 2.05341200 | -0.69436200 |
| H | -5.80048200 | -0.18840900 | -0.65229700 |
| H | 0.84311000 | -0.29336200 | 2.15538400 |
| H | -0.27120300 | -1.55752700 | 1.61937000 |
| H | -0.84644600 | -0.27277400 | 2.69620200 |
| H | -0.75307100 | 2.28339200 | 1.61434600 |
| H | -0.22726800 | 2.39936500 | -0.06784800 |
| H | 0.90252100 | 1.85146500 | 1.17907000 |

Sulfoxide **5** PhSOC(CH₃)₃

conformer 1, E = -864.8068043 a.u., ZPVE = 0.213549 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.96761200 | -2.03526300 | 0.60290600 |
| C | -1.50146800 | -1.12252600 | 0.35934500 |
| C | -2.82144600 | 1.21499800 | -0.39702400 |
| C | -0.84856200 | -0.14994000 | -0.38576000 |
| C | -2.81974900 | -0.90910500 | 0.74480000 |
| C | -3.47673900 | 0.25993900 | 0.37421800 |
| C | -1.50400000 | 1.00872800 | -0.79002100 |
| S | 0.84061400 | -0.49878500 | -0.93722700 |
| H | -3.33834900 | -1.66167800 | 1.32848800 |
| H | -4.50709100 | 0.42015800 | 0.67155500 |
| H | -1.00013200 | 1.73620800 | -1.41751800 |
| H | -3.34073100 | 2.11554400 | -0.70541200 |
| O | 1.08408900 | -1.95848400 | -0.62450700 |
| C | 1.84095100 | 0.45827500 | 0.35390500 |
| C | 3.28176000 | 0.11686400 | -0.01638200 |
| C | 1.49462700 | -0.06316900 | 1.73605000 |
| C | 1.56885700 | 1.94480500 | 0.19581500 |
| H | 3.53348500 | 0.46824000 | -1.02121900 |
| H | 3.45022700 | -0.96092500 | 0.02691000 |
| H | 0.55397700 | 2.20953800 | 0.49897300 |
| H | 1.72961600 | 2.27959900 | -0.83375000 |
| H | 2.26117400 | 2.50403800 | 0.83302700 |
| H | 3.96088200 | 0.60188700 | 0.69109700 |
| H | 1.56985800 | -1.15328300 | 1.76067100 |
| H | 0.48642100 | 0.22747600 | 2.03896600 |
| H | 2.20035400 | 0.34367100 | 2.46730900 |

Radical PhSO•

conformer 1, E = -706.2987951 a.u., ZPVE = 0.0924623 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.33084800 | -2.29285200 | 0.00000100 |
| C | -0.71264100 | -1.27646500 | 0.00000100 |
| C | -1.67651600 | 1.33987200 | -0.00000200 |
| C | 0.16680900 | -0.19146300 | -0.00000300 |
| C | -2.07980800 | -1.04050900 | 0.00000400 |
| C | -2.56305500 | 0.26537200 | 0.00000200 |
| C | -0.30692800 | 1.11943700 | -0.00000500 |
| S | 1.90439300 | -0.52340200 | -0.00000500 |
| H | -2.77012500 | -1.87637300 | 0.00000700 |
| H | -3.63196400 | 0.44578500 | 0.00000500 |
| H | 0.40499800 | 1.93717100 | -0.00000900 |
| H | -2.05638900 | 2.35543800 | -0.00000400 |
| O | 2.61836100 | 0.81347400 | 0.00001200 |

Radical PhCH₂•

conformer 1, E = -271.8637311 a.u., ZPVE = 0.1127646 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 0.79205200 | 2.15410900 | 0.00000000 |
| C | 0.25136900 | 1.21326400 | 0.00000000 |
| C | -1.12906700 | -1.20714900 | 0.00000000 |
| C | 0.99038000 | 0.00000000 | 0.00000000 |
| C | -1.12906800 | 1.20714800 | 0.00000000 |
| C | -1.83202700 | 0.00000000 | 0.00000000 |
| C | 0.25136900 | -1.21326400 | 0.00000000 |
| C | 2.39242100 | 0.00000000 | 0.00000000 |
| H | -1.67117900 | 2.14664800 | -0.00000100 |
| H | -2.91592200 | -0.00000100 | 0.00000100 |
| H | 0.79205300 | -2.15410900 | -0.00000100 |
| H | -1.67117900 | -2.14664900 | 0.00000000 |
| H | 2.95095800 | 0.92791000 | 0.00000000 |
| H | 2.95095700 | -0.92791100 | 0.00000100 |

Radical Ph(CH₃)CH•

conformer 1, E = -311.3386972 a.u., ZPVE = 0.1403100 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | 0.75223800 | 1.85063700 | 0.00007700 |
| C | 0.01971600 | 1.05134000 | -0.00000800 |
| C | -1.88209500 | -0.98511000 | 0.00000100 |
| C | 0.45976100 | -0.29739900 | -0.00004200 |
| C | -1.32787600 | 1.36120000 | 0.00001400 |
| C | -2.29011800 | 0.35099100 | 0.00000100 |
| C | -0.53955100 | -1.30555200 | -0.00000500 |
| C | 1.82622700 | -0.64716400 | -0.00006700 |
| H | -1.63848200 | 2.40067500 | 0.00006000 |
| H | -3.34488000 | 0.60068800 | 0.00001000 |
| H | -0.22930400 | -2.34578200 | -0.00000600 |
| H | -2.62405900 | -1.77642600 | 0.00000900 |
| C | 2.94587700 | 0.33290100 | -0.00003200 |
| H | 2.06942700 | -1.70507000 | 0.00044700 |
| H | 3.91296500 | -0.17133500 | -0.00385400 |
| H | 2.91743800 | 0.98707300 | 0.88098900 |
| H | 2.91300900 | 0.99229600 | -0.87691200 |

Radical (Ph)₂CH•

conformer 1, E = -503.6999395 a.u., ZPVE = 0.1936216 a.u.

| | | | |
|---|-------------|-------------|-------------|
| C | 1.29440600 | -0.44578800 | 0.02141000 |
| C | 0.00000100 | -1.05061900 | -0.00000400 |
| H | -4.92155700 | 1.01177800 | -0.05815300 |
| C | -1.29440600 | -0.44578800 | -0.02141200 |
| H | 0.00000000 | -2.13795700 | -0.00000700 |
| C | 3.91675000 | 0.60518800 | 0.05056600 |
| C | 2.41586100 | -1.24296300 | -0.30868900 |

| | | | |
|---|-------------|-------------|-------------|
| C | 1.54534800 | 0.89198900 | 0.40400400 |
| C | 2.83268900 | 1.40144300 | 0.41417000 |
| C | 3.69762500 | -0.72551000 | -0.30368800 |
| H | 2.25386900 | -2.28008500 | -0.58486700 |
| H | 0.72705700 | 1.51482200 | 0.74156000 |
| H | 2.99705100 | 2.42812000 | 0.72338600 |
| H | 4.53473200 | -1.35994200 | -0.57399600 |
| H | 4.92155700 | 1.01178000 | 0.05815700 |
| C | -3.91675000 | 0.60518700 | -0.05056300 |
| C | -1.54535000 | 0.89198900 | -0.40400700 |
| C | -2.41586000 | -1.24296300 | 0.30869000 |
| C | -3.69762400 | -0.72551000 | 0.30369200 |
| C | -2.83269000 | 1.40144200 | -0.41417000 |
| H | -0.72705900 | 1.51482200 | -0.74156300 |
| H | -2.25386700 | -2.28008500 | 0.58486900 |
| H | -4.53473000 | -1.35994200 | 0.57400400 |
| H | -2.99705300 | 2.42811900 | -0.72338700 |

Radical Ph (CH₃)₂C•

conformer 1, E = -350.8115652 a.u., ZPVE = 0.1677283 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.03636700 | -2.15717200 | 0.00036900 |
| C | -0.55836600 | -1.20776400 | 0.00011300 |
| C | -1.94099400 | 1.20233200 | -0.00017000 |
| C | 0.18666700 | -0.00000100 | -0.00021200 |
| C | -1.94099600 | -1.20233300 | 0.00025600 |
| C | -2.64761900 | 0.00000000 | 0.00008500 |
| C | -0.55836400 | 1.20776300 | -0.00028500 |
| C | 1.60973900 | -0.00000100 | -0.00031100 |
| H | -2.47866500 | -2.14467400 | 0.00053500 |
| H | -3.73153100 | 0.00000100 | 0.00018500 |
| H | -0.03636300 | 2.15716900 | -0.00045900 |
| H | -2.47866100 | 2.14467500 | -0.00026700 |
| C | 2.36914500 | -1.28822800 | -0.00027500 |
| C | 2.36913800 | 1.28823100 | 0.00047600 |
| H | 2.13247100 | -1.90440000 | -0.87708900 |
| H | 2.13762300 | -1.90122800 | 0.88022500 |
| H | 3.44566300 | -1.11248900 | -0.00367100 |
| H | 3.44566200 | 1.11249600 | 0.00007000 |
| H | 2.13525200 | 1.90214100 | 0.87967500 |
| H | 2.13481600 | 1.90349000 | -0.87764900 |

Radical (CH₃)₃C•

conformer 1, E = -158.4436820 a.u., ZPVE = 0.1144009 a.u.

| | | | |
|---|-------------|-------------|-------------|
| C | 1.22752300 | -0.82593100 | 0.01494400 |
| C | -0.00000500 | -0.00002200 | -0.15103600 |

| | | | |
|---|-------------|-------------|-------------|
| H | 1.01749600 | 1.87277100 | -0.43369800 |
| C | -1.32906000 | -0.65006800 | 0.01494500 |
| C | 0.10153800 | 1.47600200 | 0.01494100 |
| H | 1.47151700 | -0.98992400 | 1.07953300 |
| H | 2.10300100 | -0.34636700 | -0.43365600 |
| H | 1.11310300 | -1.81765300 | -0.43346200 |
| H | -1.59323500 | -0.77909200 | 1.07952700 |
| H | -1.35147500 | -1.64813100 | -0.43342800 |
| H | -2.13062500 | -0.05517500 | -0.43369700 |
| H | 0.12186800 | 1.76927400 | 1.07953100 |
| H | -0.75162900 | 1.99441800 | -0.43341700 |

t-butyl phenyl sulphide PhSC(CH₃)₃

conformer 1 E = -789.4643667 a.u., ZPVE = 0.2099230 a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.93985300 | 2.13943300 | -0.49811800 |
| C | -1.44640100 | 1.20471600 | -0.28755900 |
| C | -2.74700300 | -1.20313400 | 0.20329200 |
| C | -0.78153300 | 0.00000600 | -0.52641300 |
| C | -2.74701000 | 1.20312700 | 0.20330400 |
| C | -3.39828300 | -0.00000700 | 0.45229400 |
| C | -1.44639300 | -1.20471000 | -0.28757100 |
| S | 0.86408700 | 0.00001500 | -1.21240400 |
| H | -3.25453300 | 2.14430500 | 0.38464400 |
| H | -4.41432800 | -0.00001200 | 0.83116700 |
| H | -0.93984000 | -2.13942200 | -0.49814000 |
| H | -3.25452000 | -2.14431600 | 0.38462300 |
| H | 0.72491300 | 1.29030200 | 1.52251100 |
| C | 1.97141300 | -0.00000200 | 0.29336200 |
| C | 1.74285100 | -1.25370100 | 1.12763800 |
| C | 1.74291800 | 1.25372500 | 1.12761500 |
| C | 3.37823400 | -0.00004500 | -0.30016000 |
| H | 1.91810300 | -2.15678000 | 0.53860300 |
| H | 0.72484400 | -1.29021700 | 1.52253500 |
| H | 3.55032400 | 0.88641700 | -0.91591300 |
| H | 3.55027600 | -0.88652700 | -0.91589900 |
| H | 4.11560900 | -0.00005900 | 0.50865100 |
| H | 2.43128900 | -1.26062300 | 1.98022400 |
| H | 1.91821800 | 2.15678300 | 0.53856200 |
| H | 2.43135600 | 1.26062600 | 1.98020100 |

Radical PhS•

conformer 1, E = -630.9288596 a.u., ZPVE = 0.0891494a.u.

| | | | |
|---|-------------|-------------|-------------|
| H | -0.00362300 | 0.00196900 | -0.00796700 |
| C | 0.00768100 | -0.01036400 | 1.07543100 |
| C | 0.05687900 | 0.00664600 | 3.86649600 |

| | | | |
|---|-------------|-------------|------------|
| C | 0.49335600 | 1.12913800 | 1.75751400 |
| C | -0.44148000 | -1.11226900 | 1.77940800 |
| C | -0.41863400 | -1.10800200 | 3.17464000 |
| C | 0.50817000 | 1.11331600 | 3.17141200 |
| S | 1.05272000 | 2.50061600 | 0.88865800 |
| H | -0.81198100 | -1.98079000 | 1.24656200 |
| H | -0.77168900 | -1.97412100 | 3.72328300 |
| H | 0.88031700 | 1.98657200 | 3.69387400 |
| H | 0.07245800 | 0.00500200 | 4.95059900 |

References for Supporting Information

- S1. Baciocchi, E.; Del Giacco, T.; Gerini, M. F.; Lanzalunga, O. *J. Phys. Chem. A*. **2006**, *110*, 9940-9948.
- S2. Baciocchi, E.; Del Giacco, T.; Gerini, M. F.; Lanzalunga, O. *Org. Lett.* **2006**, *8*, 641-644.
- S3. Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.
- S4. Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287-294.
- S5. Bordwell, F. G.; Liu W.-Z. *J. Phys. Org. Chem.* **1998**, *11*, 397.
- S6. Baciocchi, E.; Del Giacco, T.; Elisei, F. *J. Am. Chem. Soc.* **1993**, *115*, 12290-12295.