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Supporting Information for

Use of spin traps to measure the addition and fragmentation rate coefficients of small molecule RAFT-adduct radicals

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Experimental Procedures

RAFT agent - *tert*-butyl dithiobenzoate, TB, was synthesized and characterized as described before[1]. 2-Methyl-2-nitrosopropane (MNP) was used as received. All the reaction mixtures were prepared in the dark by dissolving of given amounts of MNP and a RAFT agent in benzene, solutions were poured in the ampule with inner diammeter 2.2 mm, degassed and sealed. The ESR spectra were detected at room temperature by ESR spectroscopy using a RE-1307 instrument, equipped with a universal X-band (9.4 GHz) cavity using 100 kHz field modulation, 30 mW microwave power and amplitude in field modulation 0.03 G. Data processing was carried out using the EPR (v. 2.3) software package. The amount of paramagnetic centers was determined by comparison of the integral of the ESR signal of the sample with that of a carbon black standard of known spin number.

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[1] Chernikova E., Morozov A., Leonova E., Garina E., Golubev V., Bui C., Charleux B., *Macromolecules*. 2004, **37**, 6329

Fig. S1. ESR-spectrum of DTBN adduct (A_N=14.50±0.05 G) observed on irradiation by visible light of the system MNP–benzene at 20^{o}C.

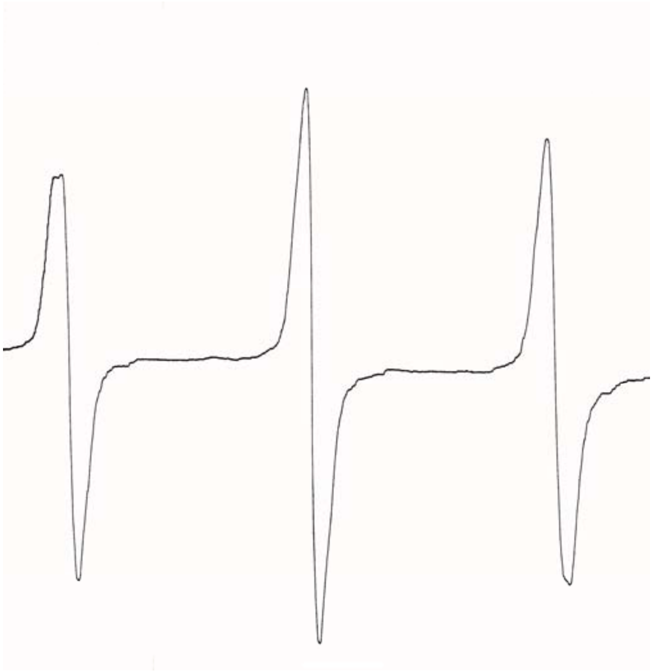

Fig. S2. ESR-spectrum of intermediate radical observed on heating the system TB–AIBN–styrene (A_{oH} = 3.65G, A_{mH} = 1.34 G, A_{pH} = 3.99 G, $A_{\delta H}$ = 0.42 G) at 90^{o}C.

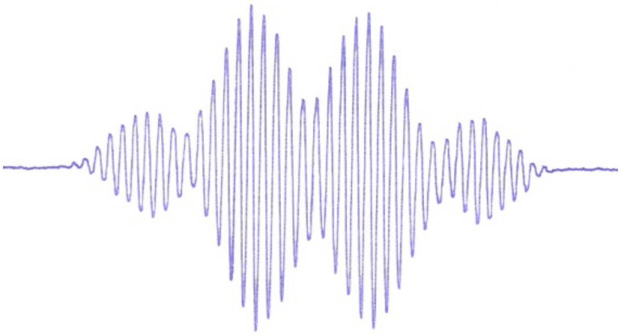

Fig. S3. Kinetic curves of accumulation and consumption of intermediate radical Int (1) and DTBN (2) in the system TB–MNP–benzene after switch-off of MNP photolysis: [TB] × 10^2 = 1 (a), 3 (b), 9 (c), [MNP] = 10^{-2} mol/L at 20°C.

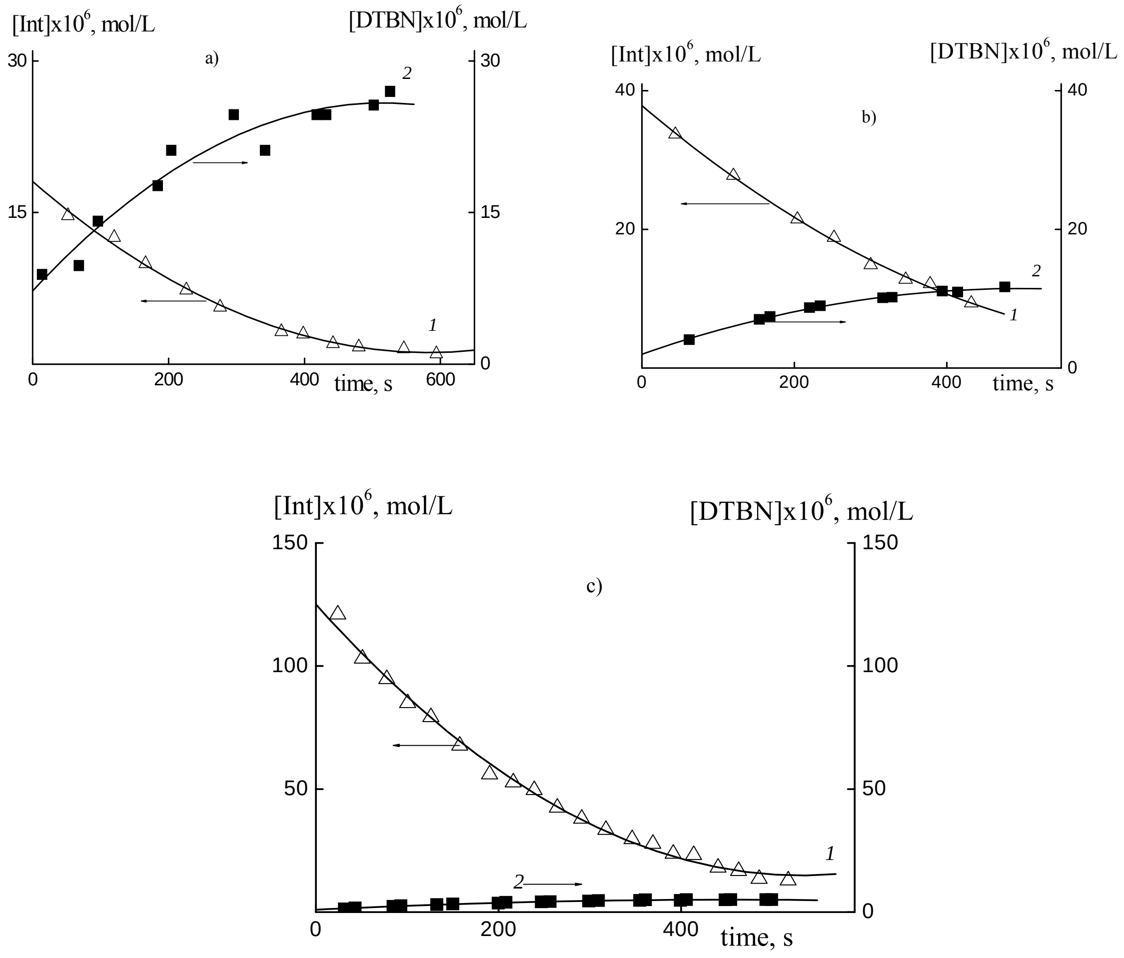

Table S1. Values of addition rate coefficients determined under various TB concentrations.

[TB]×10^2, mol/L	[MNP] ×10^2, mol/L	k_{ad}×10^{-6}, L mol^{-1} s^{-1}	average k_{ad}, L mol^{-1} s^{-1}
1	1	5.0	(5±1)×10^6
1		4.2	
3		4.2	
3		4.7	
6		5.3	
6		5.1	
9		5.5	

Computational Procedures

Standard ab initio molecular orbital theory and density functional theory calculations were performed using Gaussian 03[2] and Molpro 2006.1[3] software, using a high-level of theory, previously shown to reproduce experimental equilibrium constants for addition-fragmentation in RAFT polymerization to within chemical accuracy.[4] Geometries of all species were optimised at the B3-LYP/6-31G(d) level of theory and scaled frequency calculations were also performed at that level; this level has been previously shown to reproduce geometries and frequencies obtained via high-level ab initio methods.[5] Conformations of all species were systematically screened at the B3-LYP/6-31G(d) level of theory. Improved energies were then obtained using our W1-ONIOM method, as defined and evaluated in our previous papers.[6] In the present work the system was sufficiently small to allow for a two-layer approach where the reaction of $\bullet CH_3$ with $S=C(H)SCH_3$ was treated at W1[7]; the substituent effects of the remaining system were treated at the G3(MP2)-RAD[8] level. Partition functions and associated thermodynamic quantities (at 293.15 K) were calculated using the standard textbook formulae for an ideal gas under the rigid-rotor / harmonic oscillator approximation. These harmonic oscillator values were then corrected by treating all low frequency torsional modes as hindered internal rotations using the torsional eigenvalue summation (TES) method, applied to rotational potentials calculated from relaxed B3-LYP/6-31G(d) scans at 60° resolution. Full details of this method are provided in a recent publication.[9] The gas-phase calculations were corrected for solvent effects in benzene, using a thermodynamic cycle in which the solvation energies were modelled using the PCM-UAHF method[10] at the HF/6-31G(d) level of theory. All solvation energy

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[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *Gaussian 03, Revision B.03*. Gaussian, Inc.: Pittsburgh PA, **2003**.

[3] MOLPRO, version 2006.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel and G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer and M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni and T. Thorsteinsson , see http://www.molpro.net .

[4] C.Y.Lin, M.L.Coote, *Aust. J Chem.* 2009, **62**, 1479.

[5] Coote, M. L.; Wood, G. P. F.; Radom, L. *J. Phys. Chem. A* **2002,** *106*, 12124–12138.

[6] (a) (a) E. I. Izgorodina, M. L. Coote, *J. Phys. Chem. A* 2006, **110**, 2486. (b) E. I. Izgorodina, D. R. B. Brittain, J. L. Hodgson, E. H. Krenske, C. Y. Lin, M. Namazian, M. L. Coote, *J. Phys. Chem. A* 2007, **111**, 10754. (c) C. Y. Lin, J. L. Hodgson, M. Namazian, M. L. Coote, *J. Phys. Chem. A*, 2009, **113**, 3690.

[7] J. M. L. Martin, G. J. De Oliveira, *J. Chem. Phys.* 1999, **111**, 1843.

[8] D. J. Henry, S. B. Sullivan, L. Radom, *J. Chem. Phys.* 2003, **118**, 4849

[9] C. Y. Lin, E. I. Izgorodina, M. L. Coote, *J. Phys. Chem. A* 2008**,** **112**, 1956.

[10] (a) M. T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* 1997, **107**, 3032. (b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* 1998, **286**, 253. (c) B. Mennucci, J. Tomasi, *J. Chem. Phys.* 1997, **106**, 5151.

calculations were performed using the SCFVAC keyword in Gaussian so that the solvation energy instead of the total free energy in the solvent, could be extracted and combined with higher-level calculations of the free energy in gas phase so as to calculate the solution phase free energy of reaction, $\Delta G(soln)$ via equation 1.

$$\Delta G(soln) = \Delta G(g) + \Delta G(solv) + \Delta nRT \ln(RT/P^{o}) \qquad (1)$$

This equation includes the correction term $\Delta nRT \ln(RT/P^{\circ})$, where P° is the standard pressure in the gas-phase calculations, Δn is the change in the number of moles of solvated species on reaction and is equal to one in this case. This term is needed to account for the passage from 1 atm (g) to 1 mol/L (soln). The equilibrium constant K of the reaction was then calculated using the equation 2.

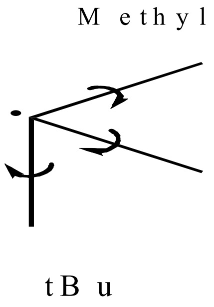
$$K(T) = (c^{o})^{\Delta n}\exp(-\Delta G(soln)/RT) \qquad (2)$$

where c° is the standard unit of concentration and is equal to 1 mol/L in solution.

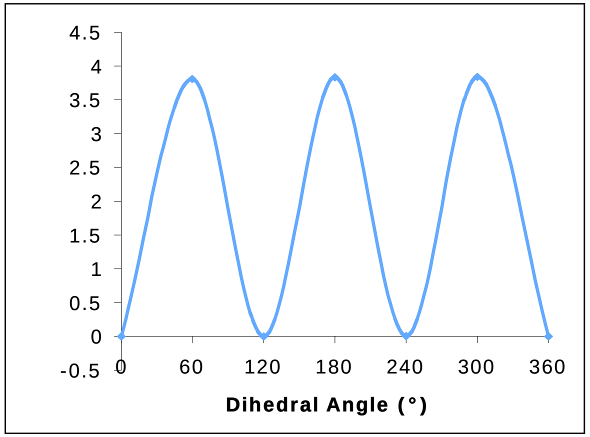
Table S2 Total Energies, Entropies, Thermal Corrections and Solvation Energies (units are Hartrees unless otherwise noted).

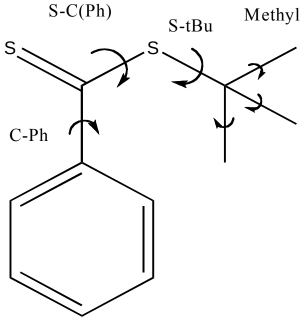
mol	Entropy at 293K (J/mol K)	Thermal correction at 293 K	Zero point vibrational energy	High level correction	B3LYP/6-31G*	ROMP2/6-31G*	ROMP2/GTMP2Large	URCCSD(T)/6-31G*	G3(MP2)-RAD E (no ZPVE)	W1 E (no ZPVE)	ONIOM E (no ZPVE)	ONIOM G at 293K	ΔGsolv (kcal/mol) COSMORS in benzene at 293.15 K	ΔGsolv (kcal/mol) UAHF-PCM in benzene at 293.15 K
tBu-SC(Ph)StBu	628.63830	0.02125	0.33736	-0.44638	-1381.80467	-1378.60278	-1379.48566	-	-	-	-1382.02889	-1382.74047	-10.45	2.26
S=C(Ph)StBu	489.96990	0.01467	0.21799	-0.32946	-1223.98214	-1221.38650	-1222.04634	-1221.55881	-1222.54810	-	-1225.34516	-1225.16720	-8.16	-0.20
r.tBu	326.61070	0.00715	0.11499	-0.11693	-157.79832	-157.17694	-157.39216	-157.24870	-157.58084	-	-157.63923	-157.55356	-2.27	-0.15
tBu-SC(Ph)SMe	-	-	-	-0.36166	-1263.86535	-1261.09811	-1261.82407	-1261.29482	-1262.38245	-	-	-	-	-
S=C(Ph)SMe	-	-	-	-0.24474	-1106.04526	-1103.88538	-1104.38813	-1104.01131	-1104.75879	-	-	-	-	-
r.tBu	-	-	-	-0.11693	-157.79832	-157.17694	-157.39216	-157.24870	-157.58084	-	-	-	-	-
Me-SC(H)SMe	-	-	-	-0.14512	-914.86617	-913.27196	-913.60526	-913.35926	-913.83768	-916.82254	-	-	-	-
S=C(H)SMe	-	-	-	-0.11292	-875.08805	-873.56611	-873.83292	-873.63116	-874.01089	-876.93905	-	-	-	-
r.Me	-	-	-	-0.0322	-39.84264	-39.66850	-39.73046	-39.69102	-39.78518	-39.84358	-	-	-	-

Table S3. Rotational potentials (B3LYP/6-31G(d)), entropy (S) and thermal correction (TC) from hindered rotor and harmonic oscillator of individual functional groups and estimated low-mode vibrational frequencies for corresponding rotations used for calculation of the propagation rate coefficients.



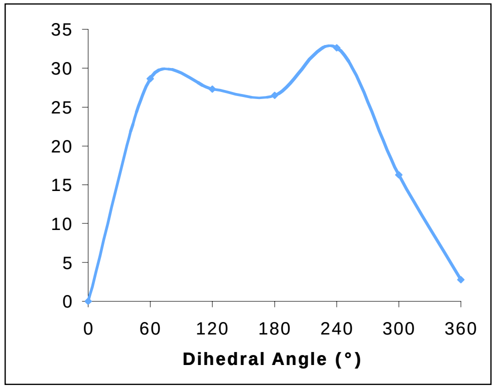
Methyl rotation
Estfreq = 127.3437 cm^{-1}
S HO = 12.3442 J/mol K
S HR = 13.6382 J/mol K
TC HO = 1.7552 kJ/mol
TC HR = 1.7540 kJ/mol

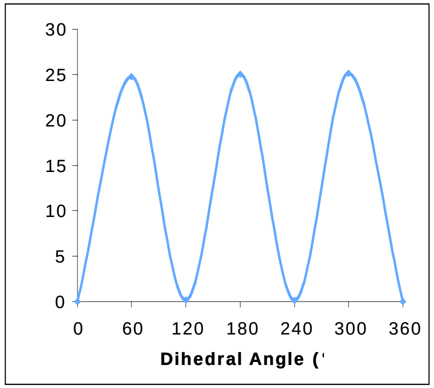


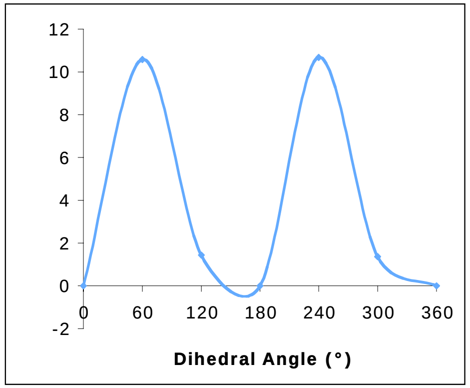


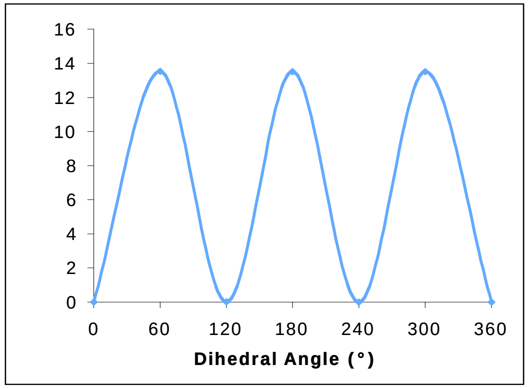
S=C(Ph)-StBu

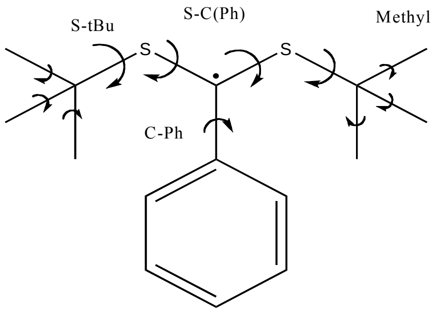
S-C(Ph) rotation	S-tBu rotation	C-Ph rotation	Methyl rotation
Estfreq = 43.9270 cm^{-1}	Estfreq = 61.2654 cm^{-1}	Estfreq = 32.9093 cm^{-1}	Estfreq = 265.0848 cm^{-1}
S HO = 21.0755 J/mol K	S HO = 18.0601 J/mol K	S HO = 23.4695 J/mol K	S HO = 6.6783 J/mol K
S HR = 21.5320 J/mol K	S HR = 18.5719 J/mol K	S HR = 24.6371 J/mol K	S HR = 7.8430 J/mol K
TC HO = 2.1843 kJ/mol	TC HO = 2.0789 kJ/mol	TC HO = 2.2460 kJ/mol	TC HO = 1.1873 kJ/mol
TC HR = 2.2354 kJ/mol	TC HR = 2.2570 kJ/mol	TC HR = 2.4572 kJ/mol	TC HR = 1.3961 kJ/mol





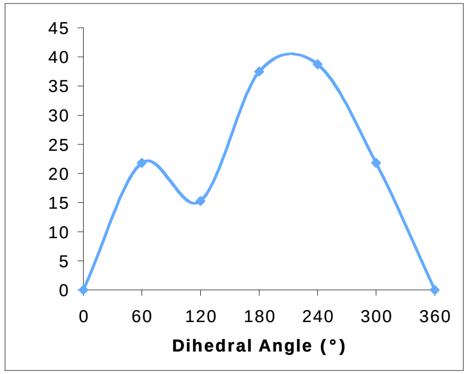


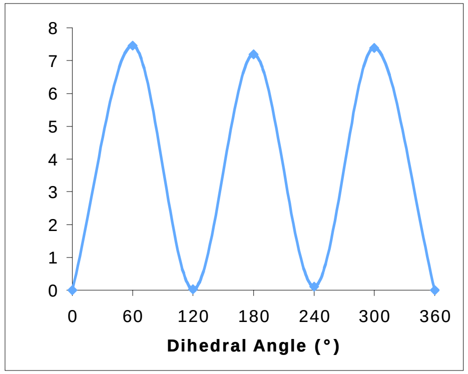


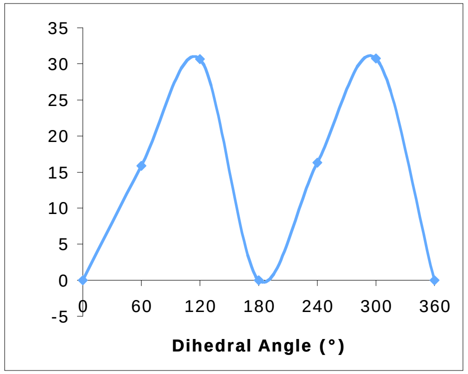


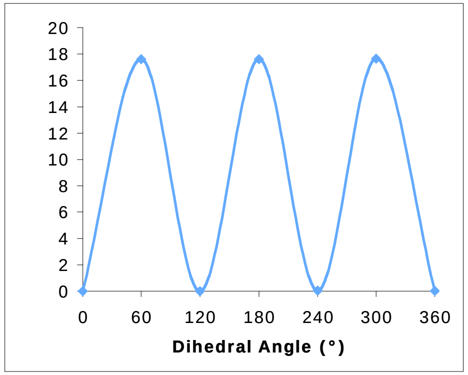
tBu-SC(Ph)-tBu

S-C(Ph) rotation	S-tBu rotation	C-Ph rotation	Methyl rotation
Estfreq = 40.2998 cm^{-1}	Estfreq = 61.2654 cm^{-1}	Estfreq = 49.2041 cm^{-1}	Estfreq = 305.4744 cm^{-1}
S HO = 21.7896 J/mol K	S HO = 18.3247 J/mol K	S HO = 20.1364 J/mol K	S HO = 5.6744 J/mol K
S HR = 22.4474 J/mol K	S HR = 15.6969 J/mol K	S HR = 20.4534 J/mol K	S HR = 6.4862 J/mol K
TC HO = 2.2045 kJ/mol	TC HO = 2.0896 kJ/mol	TC HO = 2.1552 kJ/mol	TC HO = 1.0516 kJ/mol
TC HR = 2.3185 kJ/mol	TC HR = 2.2101 kJ/mol	TC HR = 2.2552 kJ/mol	TC HR = 1.2077 kJ/mol









Appendix S1. B3-LYP/6-31G(d) Optimized Geometries

tBuS-C(Ph)StBu

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 2.4671173446,0.2767552157\C,1.5348440038,-2.2506830787,-0.137611128\C,
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 0.7577491277\C,0.6740062096,-2.6824587376,-1.3278730777\C,-2.606046917
 ,0.9940155397,-0.5953462604\C,-2.5303013294,-1.1838918078,0.4630353556
 \H,-2.1041514768,1.8715197944,-0.985132828\H,-1.9689053908,-2.00661673
 82,0.8894205696\C,-3.9913163178,0.9165493821,-0.6421652467\C,-3.916159
 4362,-1.2489657771,0.4148717164\C,-4.662363413,-0.2026680165,-0.137959
 8562\H,-4.4212430672,-2.1280025532,0.8073019503\H,-4.5558458782,1.7406
 03067,-1.0711862946\H,-5.7467525974,-0.2584476964,-0.175133412\C,1.550
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```

S=C(Ph)StBu

```
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 LYP/6-31G* Opt INT(grid=ultrafine) FREQ=noraman maxdisk=402653184\\RAF
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```

r.tBu

```
 1\1\GINC-SC115\FOpt\UB3LYP\6-31G(d)\C4H9(2)\MLC501\06-Mar-2003\0\\#N B
 3LYP/6-31G(D) OPT=TIGHT FREQ MAXDISK=26214400\\Bu_rad Cs\\0,2\H,-1.134
 0543532,1.7616707466,0.\C,-1.3291518262,0.6720547343,0.\C,-0.063598760
 4,-0.1288255571,0.\C,0.6742610965,-0.3163631938,1.2896997828\C,0.67426
 10964,-0.3163631938,-1.2896997829\H,-1.9400616179,0.4675010949,0.88858
 77545\H,-1.940061618,0.4675010949,-0.8885877544\H,1.2835911529,0.56875
 54926,1.555440113\H,-0.0116451147,-0.4829080616,2.1301907067\H,1.36782
 79377,-1.165692268,1.2415727567\H,1.2835911528,0.5687554926,-1.5554401
 131\H,-0.0116451148,-0.4829080615,-2.1301907067\H,1.3678279377,-1.1656
 92268,-1.2415727567\\Version=DEC-AXP-OSF/1-G98RevA.11.3\State=2-A'\HF=
 -157.7983276\S2=0.75402\S2-1=0.\S2A=0.750012\RMSD=4.543e-09\RMSF=2.179
 e-06\Dipole=0.0334859,0.0680061,0.\PG=CS [SG(C2H1),X(C2H8)]\\@
```

tBu-SC(Ph)SMe

```
 1\1\GINC-AC56\FOpt\UB3LYP\6-31G(d)\C12H17S2(2)\CYL509\20-Feb-2007\0\\#
  B3LYP/6-31G* OPT INT(GRID=ULTRAFINE)\\tBu-DB-me\\0,2\C,0.5040585171,0
 .3244503307,0.1847811121\S,1.9868536605,0.6018988427,-0.7496331997\S,0
 .2136245897,-1.2376958758,0.9583062751\C,-0.4602086786,1.4001449263,0.
 2859528913\C,-0.1682521617,-2.4964140696,-0.4228624922\C,3.2980831366,
 -0.1854946719,0.2564980477\C,-0.1318195473,2.7371117017,-0.07470337\C,
 -1.7836284706,1.1700873611,0.7541590987\H,0.8742689221,2.9630699568,-0
 .4092088002\H,-2.067534019,0.1659583488,1.0461118481\C,-1.0669904385,3
 .7597961148,0.0139356217\C,-2.7083236521,2.2014189956,0.8437187151\C,-
 2.3639130202,3.5055299828,0.471740998\H,-0.7782751772,4.7693845147,-0.
 2673722197\H,-3.7110681208,1.9865030301,1.2044831193\H,-3.0912940142,4
 .3094115824,0.5421826666\C,1.1179904916,-2.9577078073,-1.1182774403\C,
 -0.8090478614,-3.6652921052,0.3407291306\C,-1.1518236195,-1.8956877566
 ,-1.4299103162\H,-1.7439713167,-3.3655013453,0.8248759869\H,-0.1353864
 185,-4.0618955453,1.1089717142\H,-1.0318471702,-4.4797687614,-0.360273
 0063\H,-2.0827037395,-1.5843193952,-0.9459801787\H,-1.3980863518,-2.64
 6148823,-2.192971879\H,-0.723359482,-1.0273436853,-1.9396221937\H,1.82
 40846052,-3.3886242654,-0.4005013786\H,1.6089151036,-2.1315391554,-1.6
 401975695\H,0.8781949989,-3.7311459419,-1.8609253522\H,4.2224991216,-0
 .0679293445,-0.3156861615\H,3.3972495232,0.3201851966,1.2197206265\H,3
 .0939133584,-1.2452018508,0.4130515916\\Version=IA64L-G03RevC.02\State
 =2-A\HF=-1263.8653536\S2=0.77163\S2-1=0.\S2A=0.750352\RMSD=8.959e-09\R
 MSF=3.660e-06\Dipole=0.0886283,-0.4080502,-0.194378\PG=C01 [X(C12H17S2
 )]\\@
```

S=C(Ph)SMe

```
 1\1\GINC-AC1\FOpt\RB3LYP\6-31G(d)\C8H8S2\CYL509\05-Jun-2007\0\\# B3LYP
 /6-31G* OPT FREQ=NORAMAN INT(GRID=ULTRAFINE) MAXDISK=402653184\\sample
 \\0,1\C,0.7437083228,0.3340690534,-0.2106730953\S,1.7162708837,-0.0919
 427153,1.2026421506\S,1.3185450201,1.1937086345,-1.5011776233\C,-0.660
 2467244,-0.1423567218,-0.1041339448\C,3.3799383413,0.4925216684,0.7629
 527295\C,-0.9886773644,-1.3373785353,0.5638927992\C,-1.697164441,0.608
 7692509,-0.6880875068\H,-0.2029058173,-1.9516708653,0.9914686379\H,-1.
 4486595794,1.5291226006,-1.2052601209\C,-2.3127747374,-1.7641335134,0.
 644388622\C,-3.0187011778,0.185090541,-0.5942883823\C,-3.3323165249,-1
 .003303924,0.0709747177\H,-2.5454563262,-2.6971349922,1.1500379071\H,-
 3.8072734049,0.7841250427,-1.0411914263\H,-4.364752987,-1.3355136502,0
 .1378292242\H,3.7293636837,0.0043831761,-0.1492459788\H,4.0212411763,0
 .2245531325,1.6070261785\H,3.3787946279,1.574213934,0.6157475065\\Vers
 ion=IA64L-G03RevC.02\State=1-A\HF=-1106.0452603\RMSD=9.256e-09\RMSF=1.
 142e-05\Dipole=-0.2243171,-0.4402424,0.6391674\PG=C01 [X(C8H8S2)]\\@
```

Me-SC(H)SMe

```
 1\1\GINC-AC29\FOpt\UB3LYP\Gen\C3H7S2(2)\CYL509\20-Feb-2008\0\\#B3LYP/G
 EN 6D INT(GRID=ULTRAFINE) OPT FREQ=NORAMAN MAXDISK=1342177280\\CH3SCHS
```

```
 CH3.freq\\0,2\S,-0.6882309216,1.625949055,-0.2302971907\C,-0.604720119
 9,1.5711078656,1.6029992764\H,0.4361492434,1.5969963754,1.9361945197\H
 ,-1.1024599709,0.6844325708,2.000367826\H,-1.126003578,2.4657472605,1.
 9552062312\C,0.2456888881,0.2399852127,-0.7175294799\H,0.6910030919,0.
 3169943529,-1.70742147\S,-0.0347888506,-1.3639906191,-0.0635584324\C,1
 .5450313227,-2.1760497057,-0.5050091566\H,1.4566899765,-3.2240894674,-
 0.2055881155\H,2.3813213504,-1.7129462715,0.0250580372\H,1.715615695,-
 2.1287300303,-1.5848908976\\Version=IA64L-G03RevC.02\State=2-A\HF=-914
 .8661692\S2=0.755421\S2-1=0.\S2A=0.750021\RMSD=4.482e-09\RMSF=8.561e-0
 6\Dipole=0.5848833,-0.3016247,0.2564161\PG=C01 [X(C3H7S2)]\\@
```

S=C(H)SMe

```
 1\1\GINC-AC18\FOpt\RB3LYP\Gen\C2H4S2\CYL509\07-Jan-2008\0\\#B3LYP/GEN
 OPT FREQ=NORAMAN MAXDISK=1342177280\\SCHSCH3.1.freq\\0,1\S,0.158221240
 3,0.,-1.055574083\C,0.0121496708,0.,0.664183356\S,-1.3937103601,0.,1.4
 767510964\H,0.970997075,0.,1.1823430971\C,1.962836935,0.,-1.2981699525
 \H,2.4112707329,-0.8940256164,-0.8716931472\H,2.4112707329,0.894025616
 4,-0.8716931472\H,2.1243677418,0.,-2.3738694386\\Version=IA64L-G03RevC
 .02\State=1-A'\HF=-875.0880467\RMSD=4.455e-09\RMSF=3.095e-05\Dipole=1.
 4091687,0.,-0.6606179\PG=CS [SG(C2H2S2),X(H2)]\\@
```

r.Me

```
 1\1\GINC-AC28\FOpt\UB3LYP\Gen\C1H3(2)\CYL509\20-Feb-2008\0\\#B3LYP/GEN
  6D INT(GRID=ULTRAFINE) OPT FREQ=NORAMAN MAXDISK=1342177280\\CH3.freq\
 \0,2\H,-0.1617164304,-0.3245651343,-1.0209889129\C,0.0002146569,0.0003
 717968,-0.0001517853\H,0.8958563892,-0.3023331803,0.5291021344\H,-0.73
 54279002,0.6246675337,0.4927974904\\Version=IA64L-G03RevC.02\State=2-A
 1\HF=-39.8426447\S2=0.753502\S2-1=0.\S2A=0.750006\RMSD=5.766e-09\RMSF=
 2.535e-05\Dipole=-0.0006374,-0.0011039,0.0004507\PG=C03V [C3(C1),3SGV(
 H1)]\\@
```

Appendix S2. CALCULATION OF TERMINATION RATE COEFFICIENT

$$\frac{d[DTBN]}{dt} = k_{rT}[MNP][r]$$

$$\frac{d[Int]}{dt} = k_{ad}[TB][r] - k_{fr}[Int] - k_t''[Int]^2$$

$$\frac{d[r]}{dt} = -k_{rT}[MNP][r] - k_{ad}[TB][r] + k_{fr}[Int] = 0$$

$$[r] = \frac{k_{fr}[Int]}{k_{rT}[MNP] + k_{ad}[TB]}$$

$$\frac{\frac{d[DTBN]}{dt}}{\frac{d[Int]}{dt}} = \frac{k_{rT}[MNP][r]}{k_{ad}[TB][r] - k_{fr}[Int] - k_t''[Int]^2} = \frac{\frac{k_{rT}[MNP]k_{fr}[Int]}{k_{rT}[MNP] + k_{ad}[TB]}}{\frac{k_{ad}[TB]k_{fr}[Int]}{k_{rT}[MNP] + k_{ad}[TB]} - k_{fr}[Int] - k_t''[Int]^2} =$$

$$= \frac{k_{rT}[MNP]k_{fr}[Int]}{k_{ad}[TB]k_{fr}[Int] - k_{fr}[Int]k_{rT}[MNP] - k_{ad}[TB]k_{fr}[Int] - k_t''[Int]^2(k_{rT}[MNP] + k_{ad}[TB])} =$$

$$= \frac{k_{rT}[MNP]k_{fr}[Int]}{-k_{fr}[Int]k_{rT}[MNP] - k_t''[Int]^2(k_{rT}[MNP] + k_{ad}[TB])}$$

$$\frac{\frac{d[Int]}{dt}}{\frac{d[DTBN]}{dt}} = \frac{-k_{fr}[Int]k_{rT}[MNP] - k_t''[Int]^2(k_{rT}[MNP] + k_{ad}[TB])}{k_{rT}k_{fr}[MNP][Int]} = \frac{-k_{fr}k_{rT}[MNP] - k_t''[Int](k_{rT}[MNP] + k_{ad}[TB])}{k_{rT}k_{fr}[MNP]}$$

$$\left(\frac{\frac{d[Int]}{dt}}{\frac{d[DTBN]}{dt}}\right)k_{rT}k_{fr}[MNP] + k_{fr}k_{rT}[MNP] = -k_t''[Int](k_{rT}[MNP] + k_{ad}[TB])$$

$$k_{fr}k_{rT}[MNP]\left(\frac{d[Int]/dt}{d[DTBN]/dt} + 1\right) = -k_t''[Int](k_{rT}[MNP] + k_{ad}[TB])$$

$$k_t'' = \frac{-\left(\frac{d[Int]/dt}{d[DTBN]/dt} + 1\right)k_{fr}k_{rT}[MNP]}{[Int](k_{rT}[MNP] + k_{ad}[TB])}$$