

A Synthetic Approach to a Novel Class of Fluorine Bearing Reversible Addition Fragmentation Chain Transfer (RAFT) Agents: F-RAFT

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SUPPORTING INFORMATION

Computational Procedures

Standard ab initio molecular orbital calculations were performed using GAUSSIAN 03¹ and Molpro 2000.6² software. Calculations were performed at a high level of theory chosen on the basis of a recent assessment studies for radical addition to C=S bonds, both in prototypical systems and also RAFT-related systems.³ Geometries of the reactants products and transition structures were optimized at the B3-LYP/6-31G(d) level of theory and improved energies were calculated using G3(MP2)-RAD.⁴ Rate coefficients (at 333 K) were calculated via standard transition state theory in conjunction with the rigid rotor / harmonic oscillator approximation using the B3-LYP/6-31G(d) geometries and (scaled⁵) frequencies and the G3(MP2)-RAD barriers.⁶

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- 1 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.
 - 2 Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. *MOLPRO 2000.6*; University of Birmingham: Birmingham, 1999
 - 3 (a) Coote, M. L.; Wood, G. P. F.; Radom, L. *J. Phys. Chem. A* **2002**, *106*, 12124–12138. (b) Coote, M. L. *J. Phys. Chem. A* **2005**, *109*, 1230–1239. (c) Coote, M. L.; Henry, D. J. *Macromolecules* **2005**, *39*, 1415–1433.
 - 4 Henry, D. J.; Sullivan, M. B.; Radom, L. *J. Chem. Phys.* **2003**, *118*, 4849–4860.
 - 5 Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
 - 6 Full details of the formulae used in these calculations are provided in the Supporting Information of: Coote, M. L.; Radom, L. *Macromolecules* **2004**, *37*, 590–596.

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

S=C(F)SCH₃

1\1\GINC-SC26\FOpt\RB3LYP\6-31G(d)\C2H3F1S2\MLC501\25-May-2004\0\# B3
LYP/6-31G* OPT FREQ SCF=TIGHT MAXDISK=402653184\raft_z=f_r=me-c1-6dub
3\0,1\S,0.6732495754,0.,-1.5951188068\C,0.6539442516,0.,0.0289884936\
F,1.785438625,0.,0.7564633643\S,-0.6766528731,0.,1.1663944045\C,-2.118
3749953,0.,0.0535320972\H,-2.9969946804,0.,0.7038462211\H,-2.115457859
8,-0.8932702421,-0.5737748037\H,-2.1154578598,0.8932702421,-0.57377480
37\Version=DEC-AXP-OSF/1-G03RevB.03\State=1-A\HF=-974.2219532\RMSD=5
.980e-09\RMSF=3.562e-05\Dipole=-1.0976782,0.,0.3076847\PG=CS [SG(C2H1F
1S2),X(H2)]\@

•CH₂Ph

1\1\GINC-SC89\FOpt\UB3LYP\6-31G(d)\C7H7(2)\MLC501\18-Jul-2002\1\# UB3
LYP/6-31G* FOPT=(TIGHT,MAXCYC=100,Z-MATRIX) MAXDISK=131072000 FREQ
SCF
=(TIGHT,MAXCYC=100)\bz_rad-c2v-6dub3 (guess from dave)\0,2\C,C,1,B1\
C,2,B2,1,A1\C,2,B2,1,A1,3,-180.,0\C,3,B3,2,A2,1,-180.,0\C,4,B3,2,A2,1,
180.,0\H,1,B4,2,A3,3,0,0\H,1,B4,2,A3,7,-180.,0\H,3,B5,2,A4,5,180.,0\H
,4,B5,2,A4,6,-180.,0\H,5,B6,3,A5,2,180.,0\H,6,B6,4,A5,2,-180.,0\X,2,1.
,1,90.,3,90.,0\C,2,B7,13,90.,1,180.,0\X,14,1.,2,90.,13,0.,0\H,14,B8,15
,90.,2,180.,0\B1=1.40658309\B2=1.4269787\B3=1.38585898\B4=1.08519274\
B5=1.08733663\B6=1.08707607\B7=2.83514342\B8=1.08628629\A1=121.3932742
5\A2=121.13892253\A3=121.22638869\A4=118.71171974\A5=119.70158608\Ver
sion=DEC-AXP-OSF/1-G98RevA.11.3\State=2-B1\HF=-270.9151435\S2=0.783683
\S2-1=0.\S2A=0.750769\RMSD=5.840e-09\RMSF=5.706e-07\Dipole=0.,0.,0.052
5474\PG=C02V [C2(H1C1C1C1),SGV(C4H6)]\@

•CH(Ph)CH₃

1\1\GINC-SC30\FOpt\UB3LYP\6-31G(d)\C8H9(2)\MLC501\25-May-2004\0\# B3L
YP/6-31G* OPT FREQ MAXDISK=268435456\EtPh-cs-6dub3\0,2\H,2.076652979
1,-1.7071221701,0.\C,1.8330785143,-0.6472341403,0.\C,2.9648478287,0.33
29041964,0.\C,0.4615044195,-0.296422334,0.\C,-2.3017509074,0.350177759
9,0.\C,-0.5414638247,-1.3098262805,0.\C,0.01601966,1.0572057614,0.\C,-
1.3371627939,1.3659918739,0.\C,-1.8898621213,-0.9905058968,0.\H,-0.229
1124677,-2.3517513472,0.\H,0.7487305703,1.8588289809,0.\H,-1.649403422
1,2.4074639039,0.\H,-2.6317608755,-1.785156805,0.\H,-3.3593148857,0.59
85933381,0.\H,3.930913811,-0.179956881,0.\H,2.94101482,0.9926776704,0.
8806011513\H,2.94101482,0.9926776704,-0.8806011513\Version=DEC-AXP-OS
F/1-G03RevB.03\State=2-A\HF=-310.2333536\S2=0.779917\S2-1=0.\S2A=0.75
0613\RMSD=8.432e-09\RMSF=3.493e-05\Dipole=0.1484688,0.0260889,0.\PG=CS
[SG(C8H7),X(H2)]\@

•C(CH₃)₂CN

1\1\GINC-SC69\FOpt\UB3LYP\6-31G(d)\C4H6N1(2)\MLC501\19-Jul-2002\1\#P
UB3LYP/6-31G* FOPT=(Z-MATRIX,TIGHT,MAXCYC=100) FREQ
MAXDISK=131072000
SCF=(TIGHT,MAXCYC=100)\me2ccn-c2vb-6dub3\0,2\C,C,1,b1\X,2,1.,1,90.\N

,2,b2,3,90.,1,180.,0\C,1,b3,2,a2,3,0.,0\C,1,b3,2,a2,3,180.,0\H,5,b4,1,
a3,2,0.,0\H,6,b4,1,a3,2,0.,0\H,5,b5,1,a4,7,d1,0\H,5,b5,1,a4,7,-d1,0\H,
6,b5,1,a4,8,d1,0\H,6,b5,1,a4,8,-d1,0\|b1=1.39173287\b2=1.17666605\b3=1
.50156142\b4=1.09243341\b5=1.09976071\|a2=120.24203494\|a3=112.14994686\
a4=110.62200038\d1=121.09506187\|Version=DEC-AXP-OSF/1-G98RevA.11.3\St
ate=2-B1\HF=-210.7373225\S2=0.765669\S2-1=0.\S2A=0.750113\RMSD=8.850e-
09\RMSF=1.667e-06\Dipole=0.,0.,-1.623572\PG=C02V [C2(C1C1N1),SGV(C2H2)
,X(H4)]\|@

CH₃SC•(F)SCH₂Ph

1\1\GINC-SC64\FOpt\UB3LYP\6-31G(d)\C9H10F1S2(2)\MLC501\08-Feb-2005\0\
B3LYP/6-31G* OPT MAXDISK=268435456\|rrad_z=f_r=bz-a1b1c3-6dub3.com\
0,2\C,-1.5136034022,-0.031467307,0.1113687682\S,-2.6458718156,-0.88337
20036,-0.8949930098\S,-0.8608398296,1.5297718896,-0.3149842014F,-1.57
56438353,-0.3025559488,1.4522309625\C,-4.2565322424,-0.5282128085,-0.0
622993251\C,0.6697388339,1.563834948,0.7552322365\H,-4.9964630942,-1.1
88536116,-0.5216817746\H,-4.5484601548,0.5140176525,-0.2103222061\H,-4
.1774474444,-0.754187307,1.0024080191\H,0.3351539866,1.4129209182,1.78
38332562\H,1.0204312311,2.5953599695,0.6577128882\C,1.7306065625,0.574
7654699,0.3584730318\C,1.7007923138,-0.7350572128,0.857615279\C,2.7601
437566,0.941139805,-0.518259018\H,0.9027907579,-1.0308562758,1.5328561
842\H,2.7924200265,1.9540557845,-0.9137516677\C,2.6810218592,-1.656033
0296,0.4877805126\C,3.7416311043,0.0217293085,-0.8870469162\H,2.646001
5521,-2.6676166488,0.8834747583\H,4.536188496,0.3227299061,-1.56468543
55\C,3.7042866933,-1.2805983612,-0.3845644261\H,4.4690526097,-1.997887
3957,-0.6700881613\|Version=DEC-AXP-OSF/1-G03RevB.03\State=2-A\HF=-124
5.1379942\S2=0.75568\S2-1=0.\S2A=0.750023\RMSD=8.940e-09\RMSF=4.967e-0
6\Dipole=-0.0163509,0.1894396,0.323868\PG=C01 [X(C9H10F1S2)]\|@

CH₃SC•(F)SCH(CH₃)Ph

1\1\GINC-LC83\FOpt\UB3LYP\6-31G(d)\C10H12F1S2(2)\MLC501\06-Feb-2005\0\
B3LYP/6-31G* OPT MAXDISK=402653184\|rrad_z=f_r=1PhEt-a1b2c3-6dub3\
0,2\C,-2.191858006,0.4502552443,0.4220516602\S,-2.2625380152,1.4373195
677,1.871750262\S,-0.8188265117,0.4808917491,-0.6302458224\F,-2.947437
2258,-0.688338011,0.4699365385\C,-4.0023792444,1.1753570392,2.38455926
32\C,0.4543928542,-0.6870312457,0.1889911387\H,-4.1880042826,0.1191740
322,2.5839408073\H,-4.1423693163,1.7541786985,3.3005320082\H,-4.686636
6619,1.5387126784,1.6143325491\H,0.5758729625,-0.2968527195,1.20360659
77\C,-0.0647353436,-2.1242741821,0.2460911862\C,1.7479543033,-0.507015
0639,-0.568693115\H,-1.002014051,-2.177047082,0.8052693591\H,-0.248595
91,-2.5265538951,-0.754570707\H,0.6755898373,-2.764207654,0.7422294453
\C,1.9119299816,-1.0077653354,-1.8694989243\C,2.8155597045,0.184602066
1,0.0209254364\H,1.0939170404,-1.5349404354,-2.3526205041\H,2.70023919
88,0.5869149324,1.0248149596\C,3.11424575,-0.8310658429,-2.5537624737\
C,4.0206681653,0.35731361,-0.6595060004\H,3.2230345013,-1.2255438164,-
3.5605938537\H,4.8384072572,0.8901656375,-0.1815169845\C,4.1739065093,
-0.1510015674,-1.9503919019\H,5.1112188425,-0.0165876792,-2.4835211737
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S2-1=0.\S2A=0.750026\RMSD=8.412e-09\RMSF=6.318e-06\Dipole=0.0458689,-0
.2651083,0.5472406\PG=C01 [X(C10H12F1S2)]\|@

CH₃SC•(F)SC(CH₃)₂CN

1\1\GINC-LC60\FOpt\UB3LYP\6-31G(d)\C6H9F1N1S2(2)\MLC501\06-Feb-2005\0\
\# B3LYP/6-31G* OPT MAXDISK=402653184\\rrad_z=f_r=mcn-a2b1c2-6dub3\\0,
2\C,-0.9134774371,-1.0737174345,0.1841407306\S,-1.2408597808,-0.877263
7323,1.8928036739\S,0.5423284116,-0.9458858803,-0.7016465697\F,-2.0881
209535,-1.0869843621,-0.5029857515\C,0.4306616681,-0.8570862568,2.6247
566158\C,0.71085958,0.919547555,-1.2495062891\H,0.9704564866,0.0445114
714,2.3305436075\H,0.2712772858,-0.853336266,3.7060664279\H,0.98764918
72,-1.7521479637,2.3416410148\C,0.9825412872,1.7033429155,-0.046829466
3\C,-0.5766770692,1.3845042271,-1.9406388817\C,1.9243923461,0.93111197
18,-2.1922556738\H,-1.4399446953,1.3081808216,-1.2759042651\H,-0.76262
34676,0.7648625972,-2.8226351821\H,-0.474081186,2.4292271047,-2.257692
4877\H,2.8282121456,0.5749889652,-1.6893102257\H,1.7256905182,0.291798
9149,-3.0579709662\H,2.108740063,1.9508703524,-2.5478456103\N,1.200630
2716,2.3068684563,0.9233519386\\Version=x86-Linux-G03RevB.03\State=2-A
\HF=-1184.9514909\S2=0.756645\S2-1=0.\S2A=0.75003\RMSD=2.657e-09\RMSF=
3.246e-06\Dipole=0.4192358,-0.2267913,-0.6436795\PG=C01 [X(C6H9F1N1S2)
J\@