Supporting Information

Regioselective Hydrosilylations of Propiolate Esters with Tris(trimethylsilyl)silane

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General Methods. Melting points are uncorrected. IR spectra were recorded in the FT-mode. ^1H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 100.6 MHz. ^1H Chemical shifts are reported in ppm relative to Me_4Si . ^{13}C Chemical shifts are reported in ppm relative to CDCl_3 (77.1 ppm). Chemical shifts (^{19}F) are reported relative to CFCl_3 . ^{13}C multiplicities were determined by DEPT and HSQC. Mass spectra were recorded at an ionizing voltage of 70 eV by EI or FAB. All reactions were carried out under a nitrogen atmosphere.

(Z)-Methyl 3-[tris(trimethylsilyl)silyl]propenoate (3a): ($R_f = 0.7$ (hexane-EtOAc = 20 : 1)): Colorless crystal; mp 30-31 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (s, 27H), 3.70 (s, 3H), 6.59 (d, 1H, $J = 13.9$ Hz), 6.74 (d, 1H, $J = 13.9$ Hz). NOE was observed between δ 6.59 and 6.74.; ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.4 (-Si(CH₃)₃), 51.2 (-OCH₃), 134.4 (-SiCH=CH-CO₂-), 148.7 (-SiCH=CH-CO₂-), 167.1 (-C(O)O-); IR (neat) 2949, 2894, 1723, 1583, 1435, 1362, 1244, 1213, 1178, 834 cm⁻¹; MS (EI) m/z 332 (M⁺), 317 (M⁺-CH₃), 259 (M⁺-Si(CH₃)₃), 73 (Si⁺(CH₃)₃); exact mass M⁺ 332.1483 (calcd for C₁₃H₃₂O₂Si₄ 332.1479); Anal. Calcd for C₁₃H₃₂O₂Si₄: C, 46.93; H, 9.69. Found: C, 46.87; H, 9.77.

NMR spectra of (Z)-ethyl 3-[tris(trimethylsilyl)silyl]propenoate (**3b**) were in accord with the reported data.^{3a}

(Z)-2,2,2-Trifluoroethyl 3-[tris(trimethylsilyl)silyl]propenoate (3c): ($R_f = 0.6$ (hexane)): Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (s, 27H), 4.50 (q, 2H, $J_{\text{F-H}} = 8.6$ Hz), 6.64 (d, 1H, $J = 13.9$ Hz), 6.97 (d, 1H, $J = 13.9$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.3 (-SiCH₃), 59.8 (q, $J_{\text{C-F}} = 36.6$ Hz, -OCH₂CF₃), 123.1 (q, $J_{\text{C-F}} = 277.0$ Hz, -CF₃), 132.3 (-SiCH=CH-CO₂-), 153.7 (-SiCH=CH-CO₂-), 164.6 (-C(O)O-); ^{19}F NMR (376.3 MHz, CDCl_3) δ -74.2 (t, $J_{\text{F-H}} = 8.6$ Hz); IR (neat) 2950, 2895, 1738, 1581, 1283, 1245, 1152, 836 cm⁻¹; MS (EI) m/z 400 (M⁺), 385 (M⁺-CH₃), 327 (M⁺-Si(CH₃)₃), 301 (M⁺-OCH₂CF₃), 73 (Si⁺(CH₃)₃); exact mass M⁺ 400.1342 (calcd for C₁₄H₃₁F₃O₂Si₄ 400.1353); Anal. Calcd for C₁₄H₃₁F₃O₂Si₄: C, 41.96; H, 7.80. Found: C, 41.67; H, 7.67.

(Z)-4-Tris[trimethylsilyl]silyl]but-3-en-2-one (3d): ($R_f = 0.2$ (hexane-EtOAc = 20 : 1)): Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (s, 27H), 2.21 (s, 3H), 6.64 (d, 1H, $J = 13.3$ Hz), 6.99 (d, 1H, $J = 13.3$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.5 (-Si(CH₃)₃), 30.8 (-C(O)CH₃), 141.2 (-SiCH=CH-C(O)-), 147.8 (-SiCH=CH-C(O)-), 197.7 (-C(O)-); IR (neat) 2949, 2894, 1691, 1558, 1366, 1243, 1184, 834 cm⁻¹; MS (EI) m/z 316 (M⁺), 301 (M⁺-CH₃), 243 (M⁺-Si(CH₃)₃), 73 (Si⁺(CH₃)₃); exact mass M⁺ 316.1533 (calcd for C₁₃H₃₂O₂Si₄ 316.1530).

(Z)-3-[Tris(trimethylsilyl)silyl]propenoic acid (3e): ($R_f = 0.5$ (hexane-EtOAc = 5 : 1)): Colorless crystal; mp 82-84 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.18 (s, 27H), 6.66 (d, 1H, $J = 13.9$ Hz), 6.96 (d, 1H, $J = 13.9$ Hz).

= 13.9 Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.4 (-Si(CH₃)₃), 134.0 (-SiCH=CH-CO₂-), 153.1 (-SiCH=CH-CO₂-), 172.0 (-C(O)O-); IR (KBr) 3073 (broad), 2950, 2894, 1691, 1584, 1413, 1254, 835 cm⁻¹; MS (EI) m/z 318 (M⁺), 303 (M⁺-CH₃), 245 (M⁺-Si(CH₃)₃), 73 (Si⁺(CH₃)₃); exact mass M⁺ 318.1334 (calcd for C₁₂H₃₀O₂Si₄ 318.1323); Anal. Calcd for C₁₂H₃₀O₂Si₄: C, 45.22; H, 9.49. Found: C, 45.10; H, 9.45.

[2] B3LYP/6-31G*-optimized geometries

Figure S1. UB3LYP/6-31G*-optimized structure of **X** in Scheme 1.
 ΔG is relative to $(\text{MeSi}_3)\text{Si-H}$ and triplet O_2 ($T = 298.15 \text{ K}$).

Figure S2. UB3LYP/6-31G*-optimized structure of **Z** in Scheme 1.
 ΔG is relative to $(\text{MeSi}_3)\text{Si-H}$ and triplet O_2 ($T = 298.15 \text{ K}$).

Figure S5. B3LYP/6-31G* SCRF-optimized structure of ionic intermediate **B** (R = Me) in Scheme 3.

Figure S6. B3LYP/6-31G* SCRF-optimized structure of **1b**.

Figure S7. B3LYP/6-31G* SCRF-optimized structure of **1b-AlCl₃**.

Figure S8. B3LYP/6-31G* SCRF-optimized structure of **1b-AlEtCl₂**.

Figure S9. B3LYP/6-31G* SCRF-optimized structure of **1b-AlEt₂Cl**.

[3] Cartesian coordinates and total energy

(Details of computational methods and results in GAUSSIAN format)

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-----
# UB3LYP/ 6-31G* 6d SCF=(DIRECT,PASS) optcyc=330 scfcyc=300 iop(1/8=2)
pop=none opt=(readfc,noeig,nofreeze) geom=allcheck guess=check
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```

(Me3Si)3SiH---O2, structure #X in Figure S1 and Scheme 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.131786	0.002222	-0.329910
2	14	0	-2.188218	-1.146862	-0.633562
3	1	0	0.528945	0.014105	-1.682384
4	14	0	-0.427035	2.280045	0.272007
5	14	0	1.359158	-1.143389	1.122990
6	6	0	-0.867888	2.432822	2.116805
7	6	0	-1.825175	3.078178	-0.742938
8	6	0	1.174091	3.251079	-0.062001
9	1	0	-0.073329	2.034359	2.758690
10	1	0	-1.790584	1.891734	2.356965
11	1	0	-1.018491	3.484585	2.392379
12	1	0	-2.793769	2.605234	-0.543012
13	1	0	-1.634423	3.004575	-1.819868
14	1	0	-1.919592	4.143302	-0.494250
15	1	0	1.451672	3.205152	-1.121466
16	1	0	2.016723	2.858544	0.518064
17	1	0	1.048178	4.308414	0.205111
18	6	0	-3.342701	-0.882232	0.856426
19	6	0	-3.058223	-0.517818	-2.203866
20	6	0	-1.892233	-3.016378	-0.832145
21	1	0	-4.280972	-1.434905	0.718047
22	1	0	-3.600659	0.175108	0.990238
23	1	0	-2.886746	-1.233201	1.789681
24	1	0	-2.433268	-0.670097	-3.091442
25	1	0	-3.291143	0.551169	-2.142381
26	1	0	-4.001432	-1.056370	-2.363492
27	1	0	-1.444204	-3.454991	0.067163
28	1	0	-1.225072	-3.230791	-1.675100
29	1	0	-2.840172	-3.538101	-1.017648
30	6	0	0.470209	-1.670452	2.721684
31	6	0	2.835109	-0.041276	1.603434
32	6	0	2.043170	-2.694413	0.259182
33	1	0	-0.349552	-2.371036	2.522527
34	1	0	0.049719	-0.808906	3.253701
35	1	0	1.171652	-2.169480	3.402818
36	1	0	3.387153	0.297613	0.719296
37	1	0	3.535804	-0.599725	2.237921
38	1	0	2.520457	0.847178	2.163652
39	1	0	2.607900	-2.427377	-0.641504
40	1	0	1.244259	-3.382127	-0.040059
41	1	0	2.721412	-3.240478	0.927797
42	8	0	3.315192	0.273401	-2.810505
43	8	0	4.123775	-0.189497	-2.031029

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SCF Done: E(UB+HF-LYP) = -1668.23789713 A.U. after 1 cycles
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies= -1667.952723
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# UB3LYP/ 6-31G* 6d SCF=(DIRECT,PASS) optcyc=330 scfcyc=300 iop(1/8=2)
pop=none opt=(readfc,noeig,nofreeze,ts) geom=allcheck guess=check
-----
```

(Me3Si)3Si--H--O=O, TS structure #Y in Figure 1 and Scheme 1
imaginary frequency=1409.8535 icm^{-1}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	14	0	0.064005	-0.014362	0.094574
2	14	0	1.888892	-1.528662	0.016985
3	1	0	-0.419203	0.065191	1.922465
4	14	0	0.603505	2.264872	-0.284790
5	14	0	-2.020647	-0.773552	-0.753267
6	6	0	0.566973	2.662484	-2.146069
7	6	0	2.341848	2.647417	0.383021
8	6	0	-0.649477	3.376984	0.610138
9	1	0	-0.423821	2.483554	-2.579776
10	1	0	1.289763	2.056805	-2.704586
11	1	0	0.816281	3.718435	-2.314492
12	1	0	3.113689	2.058548	-0.125919
13	1	0	2.417401	2.441771	1.456832
14	1	0	2.581515	3.707964	0.231563
15	1	0	-0.678337	3.163308	1.684588
16	1	0	-1.664342	3.242621	0.219582
17	1	0	-0.380381	4.433847	0.484748
18	6	0	2.819830	-1.348261	-1.633665
19	6	0	3.089386	-1.165853	1.444634
20	6	0	1.284842	-3.323735	0.175997
21	1	0	3.662288	-2.051241	-1.673289
22	1	0	3.225135	-0.338107	-1.764231
23	1	0	2.169361	-1.560182	-2.490077
24	1	0	2.598556	-1.278059	2.418132
25	1	0	3.492699	-0.148584	1.390669
26	1	0	3.936783	-1.863079	1.415754
27	1	0	0.636649	-3.612669	-0.659479
28	1	0	0.725401	-3.482977	1.104759
29	1	0	2.141255	-4.010565	0.182123
30	6	0	-1.849782	-1.228530	-2.594517
31	6	0	-3.327563	0.590703	-0.566133
32	6	0	-2.586280	-2.300851	0.220102
33	1	0	-1.115093	-2.027669	-2.747993
34	1	0	-1.538656	-0.368612	-3.198940
35	1	0	-2.811837	-1.582072	-2.988404
36	1	0	-3.438709	0.878637	0.484992
37	1	0	-4.302858	0.233697	-0.921869
38	1	0	-3.074326	1.489122	-1.140914
39	1	0	-2.694956	-2.060848	1.283375
40	1	0	-1.877535	-3.131474	0.130341
41	1	0	-3.559619	-2.649981	-0.148462
42	8	0	-0.760574	0.152816	3.019099
43	8	0	-2.047717	0.028977	3.063205

SCF Done: E(UB+HF-LYP) = -1668.18860348 A.U. after 1 cycles
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies= -1667.902697

UB3LYP/ 6-31G* 6d SCF=(DIRECT,PASS) optcyc=330 scfcyc=300 iop(1/8=2)
pop=none opt=(readfc,noeig) geom=allcheck guess=check

(Me3Si)3Si---H-O-O·, structure #Z in Figure S2 and Scheme 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	0.135772	-0.019219	0.002876
2	14	0	2.310832	-0.918884	0.266222
3	1	0	-0.883309	0.288567	2.154193
4	14	0	-0.035914	2.295630	-0.479370
5	14	0	-1.580625	-1.461006	-0.773182
6	6	0	0.059999	2.590234	-2.357412
7	6	0	1.386430	3.240406	0.356319
8	6	0	-1.684664	2.983398	0.164917
9	1	0	-0.757640	2.088216	-2.887382
10	1	0	1.004066	2.223527	-2.775843
11	1	0	-0.010088	3.663738	-2.577410
12	1	0	2.366769	2.923855	-0.018516
13	1	0	1.381362	3.101397	1.443390
14	1	0	1.289968	4.316078	0.159152
15	1	0	-1.802475	2.817646	1.241406
16	1	0	-2.540652	2.518324	-0.336066
17	1	0	-1.738791	4.064766	-0.016531
18	6	0	3.374596	-0.516506	-1.260052
19	6	0	3.145245	-0.179359	1.805034
20	6	0	2.225796	-2.807363	0.463766

21	1	0	4.384679	-0.930131	-1.140255
22	1	0	3.475075	0.564559	-1.411235
23	1	0	2.945523	-0.942478	-2.174141
24	1	0	2.584570	-0.414255	2.716903
25	1	0	3.228910	0.911137	1.737411
26	1	0	4.158721	-0.584678	1.922397
27	1	0	1.765323	-3.287184	-0.407657
28	1	0	1.649590	-3.098507	1.349367
29	1	0	3.236247	-3.221975	0.574299
30	6	0	-1.094710	-2.190439	-2.464300
31	6	0	-3.206332	-0.500722	-0.959915
32	6	0	-1.840218	-2.877496	0.462602
33	1	0	-0.166952	-2.771644	-2.407586
34	1	0	-0.952030	-1.406870	-3.217106
35	1	0	-1.884919	-2.861445	-2.826524
36	1	0	-3.521888	-0.080648	0.001094
37	1	0	-4.002053	-1.170587	-1.310985
38	1	0	-3.121546	0.319171	-1.682617
39	1	0	-2.162609	-2.487292	1.434008
40	1	0	-0.926992	-3.463385	0.615471
41	1	0	-2.618663	-3.561326	0.099616
42	8	0	-1.411851	0.479706	2.993304
43	8	0	-2.612893	-0.045054	2.787165

SCF Done: E(UB+HF-LYP) = -1668.19154667 A.U. after 1 cycles
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies= -1667.902704

ub3lyp / 6-31g* 6d optcyc=300 scfcyc=300 scf=(direct,pass) iop(1/8=2)
) opt=noeig pop=none

(Me3Si)3SiCH=C·CO2Me, compound #A(R=Me) in Figure S3 and Scheme 2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.046432	-0.160792	-1.580635
2	6	0	-0.768062	0.083647	-1.627768
3	6	0	-3.261758	-0.599940	-0.972785
4	8	0	-3.418247	-1.744726	-0.569007
5	8	0	-4.293393	0.285977	-0.877244
6	6	0	-4.133851	1.594805	-1.434611
7	1	0	-0.301989	0.291109	-2.598464
8	1	0	-3.865445	1.543219	-2.495565
9	1	0	-3.374627	2.170834	-0.895449
10	1	0	-5.105851	2.078446	-1.324615
11	14	0	0.467323	0.026884	-0.133627
12	14	0	-0.647724	-0.054819	1.973823
13	14	0	1.776721	2.003800	-0.367177
14	14	0	1.718785	-1.956194	-0.560205
15	6	0	3.394769	1.866979	0.623163
16	6	0	0.813675	3.525833	0.247447
17	6	0	2.208310	2.288612	-2.199304
18	6	0	0.635587	0.361520	3.318256
19	6	0	-2.050520	1.226242	2.073002
20	6	0	-1.358206	-1.776845	2.330415
21	6	0	2.942577	-2.309049	0.853656
22	6	0	2.707314	-1.781960	-2.177935
23	6	0	0.525439	-3.421980	-0.736967
24	1	0	4.023926	1.047194	0.257463
25	1	0	3.207669	1.692324	1.688765
26	1	0	3.976483	2.793745	0.535601
27	1	0	0.576089	3.458047	1.315395
28	1	0	-0.130158	3.649484	-0.296526
29	1	0	1.404748	4.438534	0.096964
30	1	0	1.308605	2.409747	-2.814159
31	1	0	2.790468	1.460394	-2.619004
32	1	0	2.805618	3.202999	-2.309734
33	1	0	0.175790	0.279828	4.311683
34	1	0	1.024191	1.381872	3.219441
35	1	0	1.489874	-0.325094	3.293827
36	1	0	-2.881481	0.974736	1.405363
37	1	0	-1.704325	2.235638	1.823156
38	1	0	-2.451907	1.256161	3.094406
39	1	0	-0.566984	-2.531120	2.416495
40	1	0	-2.050878	-2.095750	1.544339
41	1	0	-1.907405	-1.765748	3.281076

42	1	0	2.427664	-2.459242	1.809806
43	1	0	3.663049	-1.493610	0.986445
44	1	0	3.512135	-3.222997	0.640720
45	1	0	2.057152	-1.547755	-3.028960
46	1	0	3.222887	-2.723381	-2.408256
47	1	0	3.469429	-0.996693	-2.112325
48	1	0	-0.265425	-3.212513	-1.465468
49	1	0	0.034061	-3.660259	0.212554
50	1	0	1.065237	-4.317994	-1.069972

SCF Done: E(UB+HF-LYP) = -1822.51098970 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -1822.162080

rb3lyp / 6-31g* 6d optcyc=300 scfcyc=300 scf=(direct,pass) iop(1/8=2
) opt=noeig pop=none

(Z)-(Me3Si)3SiCH=CHCO2Me, compound #3a in Figure S4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	0	0	0.002643	-0.042171	0.017809
2	6	0	-2.202427	-0.371132	-1.647791
3	6	0	-0.856075	-0.424492	-1.564638
4	6	0	-3.057118	0.045734	-0.516077
5	8	0	-2.618430	0.335885	0.582000
6	8	0	-4.404788	0.107691	-0.686098
7	6	0	-5.026307	-0.192620	-1.937530
8	1	0	-0.380927	-0.774098	-2.484545
9	1	0	-4.863513	-1.235686	-2.230779
10	1	0	-4.678904	0.475036	-2.733527
11	1	0	-6.093535	-0.030721	-1.776455
12	14	0	0.388377	-0.058632	-0.152217
13	14	0	0.069423	1.992443	1.042207
14	14	0	2.445583	0.028960	-1.371655
15	14	0	0.395485	-1.977750	1.273388
16	6	0	3.967808	-0.102061	-0.236831
17	6	0	2.574172	1.650034	-2.367491
18	6	0	2.550914	-1.392227	-2.641157
19	6	0	1.792947	2.697829	1.460627
20	6	0	-0.836726	3.257459	-0.048519
21	6	0	-0.835878	1.809626	2.699553
22	6	0	1.548090	-1.663251	2.755614
23	6	0	1.048967	-3.503153	0.338740
24	6	0	-1.339282	-2.387231	1.921814
25	1	0	-2.688176	-0.653344	-2.577870
26	1	0	3.991303	-1.057151	0.301082
27	1	0	3.994325	0.700788	0.508118
28	1	0	4.889927	-0.035763	-0.828719
29	1	0	2.609211	2.533653	-1.720528
30	1	0	1.721655	1.772434	-3.046449
31	1	0	3.485832	1.651486	-2.979259
32	1	0	1.750170	-1.341408	-3.388883
33	1	0	2.499603	-2.378922	-2.168169
34	1	0	3.503338	-1.333211	-3.184221
35	1	0	1.678376	3.621351	2.043636
36	1	0	2.384324	2.943577	0.571901
37	1	0	2.378926	1.999101	2.069926
38	1	0	-1.859616	2.929998	-0.258915
39	1	0	-0.324166	3.413945	-1.004801
40	1	0	-0.892541	4.227669	0.462070
41	1	0	-0.316580	1.119204	3.374851
42	1	0	-1.855698	1.447522	2.553865
43	1	0	-0.878351	2.785527	3.201677
44	1	0	1.193283	-0.833359	3.377042
45	1	0	2.572364	-1.431867	2.441592
46	1	0	1.591658	-2.556292	3.392869
47	1	0	0.451537	-3.719472	-0.554542
48	1	0	1.006607	-4.388194	0.987164
49	1	0	2.090377	-3.376155	0.021897
50	1	0	-2.013589	-2.664564	1.104092
51	1	0	-1.789811	-1.535224	2.438795
52	1	0	-1.290375	-3.234555	2.618476

SCF Done: E(RB+HF-LYP) = -1823.17915976 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -1822.830460

```

-----
# rb3lyp / 6-31g* 6d optcyc=300 scfcyc=300 scf=(direct,pass) iop(1/8=2
) scrf=dipole opt=noeig pop=none
-----

```

(Me3Si)3Si+ H2C=C=CO2Me-, compound #B in Figure S5 and Scheme 3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.115650	-0.276963	-0.644008
2	6	0	0.064044	-0.134150	-1.152469
3	6	0	-2.404331	-0.501558	-0.325262
4	8	0	-3.323888	0.428564	-0.276265
5	8	0	-2.864721	-1.734665	0.000898
6	6	0	-1.944033	-2.826944	-0.022130
7	1	0	0.354231	-0.209670	-2.199439
8	13	0	-5.111148	0.346618	-0.136265
9	17	0	-5.772678	-0.367164	1.806663
10	17	0	-5.815739	2.389169	-0.393850
11	17	0	-5.984045	-0.881929	-1.708648
12	1	0	-1.122500	-2.655975	0.682058
13	1	0	-1.535452	-2.973649	-1.027348
14	1	0	-2.519504	-3.702209	0.280051
15	14	0	2.936055	0.107357	0.048663
16	14	0	2.413344	-0.196928	2.363368
17	14	0	3.507086	2.320257	-0.681359
18	14	0	3.857487	-1.731740	-1.189596
19	6	0	5.398650	2.360707	-0.638335
20	6	0	2.773147	3.611025	0.492845
21	6	0	2.849061	2.590147	-2.436308
22	6	0	3.932089	0.402022	3.322589
23	6	0	0.881154	0.846619	2.762212
24	6	0	2.074541	-2.021036	2.742099
25	6	0	5.518821	-2.036945	-0.334667
26	6	0	4.095846	-1.249238	-3.000981
27	6	0	2.720402	-3.238873	-1.042431
28	1	0	0.980424	0.116263	-0.496311
29	1	0	5.850993	1.652904	-1.341328
30	1	0	5.807295	2.158860	0.357735
31	1	0	5.737093	3.364406	-0.927568
32	1	0	3.136460	3.485319	1.518667
33	1	0	1.677771	3.579123	0.508796
34	1	0	3.074245	4.613366	0.162592
35	1	0	1.754112	2.555809	-2.473624
36	1	0	3.241873	1.851781	-3.143008
37	1	0	3.163836	3.580390	-2.789373
38	1	0	3.752169	0.274265	4.398073
39	1	0	4.150255	1.461550	3.150449
40	1	0	4.832681	-0.171855	3.078079
41	1	0	0.018838	0.561896	2.147870
42	1	0	1.069067	1.914364	2.607451
43	1	0	0.604189	0.705689	3.814861
44	1	0	2.951026	-2.648645	2.547364
45	1	0	1.235035	-2.418105	2.160003
46	1	0	1.825735	-2.133113	3.805202
47	1	0	5.407357	-2.336165	0.713184
48	1	0	6.186031	-1.169376	-0.374774
49	1	0	6.031873	-2.857188	-0.854328
50	1	0	3.147519	-1.048228	-3.512571
51	1	0	4.589274	-2.073582	-3.531360
52	1	0	4.737995	-0.368710	-3.110360
53	1	0	1.727510	-3.047653	-1.465443
54	1	0	2.596323	-3.557114	-0.002070
55	1	0	3.163820	-4.077376	-1.593966

```

-----
SCRF input: a0= 6.17 angstrom, dielectric constant= 8.93
SCF Done: E(RB+HF-LYP) = -3446.40040819 A.U. after 10 cycles
-----

```

```

-----
# rb3lyp / 6-31g* 6d optcyc=300 scfcyc=300 iop(1/8=2) opt=noeig scf=(d
irect,pass) scrf
-----

```

HC=CCO2Et, compound #1b in Figure S6

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.474227	0.592609	-0.000006
2	6	0	-2.066388	1.646182	0.000127
3	8	0	-1.408682	-1.745937	0.000142
4	6	0	-0.801225	-0.695516	-0.000114
5	8	0	0.544640	-0.683198	-0.000162
6	6	0	1.275814	0.573257	-0.000304
7	1	0	-2.586259	2.579645	0.000228
8	1	0	0.996221	1.150345	0.886934
9	1	0	0.996816	1.149805	-0.888084
10	6	0	2.753344	0.232416	0.000281
11	1	0	3.019528	-0.349070	-0.887850
12	1	0	3.019557	-0.346374	0.890159
13	1	0	3.342568	1.155046	-0.001130

SCRF input: a0= 3.80 angstrom, dielectric constant= 8.93

SCF Done: E(RB+HF-LYP) = -344.516446689 A.U. after 9 cycles

HC=CCO2Et---AlCl3, compound #1b-AlCl3 in Figure S7

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.555639	1.453340	-0.000597
2	6	0	-1.728544	2.649531	0.013055
3	8	0	-0.295753	-0.541546	-0.019102
4	6	0	-1.415025	0.032684	-0.017340
5	8	0	-2.465473	-0.727617	-0.032369
6	6	0	-3.843743	-0.164083	-0.027961
7	1	0	-1.871744	3.710522	0.025559
8	13	0	1.528658	-0.157865	0.001438
9	17	0	2.477133	-2.085211	0.011428
10	17	0	1.932660	0.941955	-1.790258
11	17	0	1.895025	0.942643	1.800523
12	1	0	-3.949594	0.426297	-0.940945
13	1	0	-3.922698	0.489310	0.843689
14	6	0	-4.800109	-1.332135	0.027886
15	1	0	-4.653574	-1.920696	0.937629
16	1	0	-4.684684	-1.981186	-0.844413
17	1	0	-5.823994	-0.944323	0.032511

SCRF input: a0= 4.78 angstrom, dielectric constant= 8.93

SCF Done: E(RB+HF-LYP) = -1967.81169861 A.U. after 1 cycles

HC=CCO2Et---AlEtCl2, compound #1b-AlEtCl2 in Figure S8

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.738189	1.384266	-0.000316
2	6	0	1.940869	2.575281	-0.000392
3	8	0	0.394623	-0.551127	0.000320
4	6	0	1.533583	-0.031064	0.000040
5	8	0	2.555298	-0.836537	0.000142
6	6	0	3.950870	-0.331821	-0.000094
7	1	0	2.112158	3.631205	-0.000532
8	13	0	-1.460485	-0.146235	0.000153
9	6	0	-2.339689	-1.907404	0.000268
10	17	0	-1.769585	1.036043	1.793236
11	17	0	-1.769356	1.035715	-1.793184
12	1	0	4.072827	0.286660	0.892247
13	1	0	4.072683	0.286192	-0.892779
14	6	0	4.858527	-1.540485	0.000144
15	6	0	-3.879199	-1.877981	-0.000512
16	1	0	-1.984550	-2.470337	0.876063
17	1	0	-1.983684	-2.470904	-0.874810
18	1	0	-4.269078	-1.356084	-0.884181
19	1	0	-4.269941	-1.354531	0.881859
20	1	0	-4.318781	-2.887464	0.000165
21	1	0	4.699501	-2.154338	-0.890602

22	1	0	4.700162	-2.153474	0.891603
23	1	0	5.898746	-1.199201	-0.000407

SCRF input: a0= 4.76 angstrom, dielectric constant= 8.93

SCF Done: E(RB+HF-LYP) = -1586.76774320 A.U. after 7 cycles

HC=CCO2Et--AlEt2Cl, compound #1b-AlEt2Cl in Figure S9

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.681567	1.221669	-0.626217
2	6	0	1.865091	2.330695	-1.068243
3	8	0	0.361239	-0.567349	0.145749
4	6	0	1.484879	-0.095218	-0.094871
5	8	0	2.527063	-0.849479	0.158534
6	6	0	3.899218	-0.373509	-0.086870
7	1	0	2.001773	3.315485	-1.461450
8	13	0	-1.561655	-0.226974	0.175900
9	6	0	-2.278170	-2.046329	-0.160512
10	6	0	-1.840159	0.666855	1.927050
11	17	0	-1.901379	1.109382	-1.538163
12	1	0	4.048700	0.535387	0.501607
13	1	0	3.984436	-0.131969	-1.149531
14	6	0	4.833988	-1.488618	0.327803
15	6	0	-3.809836	-2.135211	-0.304430
16	1	0	-1.950419	-2.712363	0.653137
17	1	0	-1.808798	-2.448990	-1.070568
18	1	0	-4.170409	-1.507027	-1.129054
19	1	0	-4.323450	-1.795092	0.605742
20	1	0	-4.159152	-3.160437	-0.502232
21	1	0	4.652918	-2.392548	-0.260601
22	1	0	4.716204	-1.726205	1.388754
23	1	0	5.867330	-1.168988	0.159393
24	6	0	-1.162009	2.032745	2.140161
25	1	0	-1.527003	-0.025650	2.724744
26	1	0	-2.928100	0.782034	2.065511
27	1	0	-0.068742	1.957456	2.072543
28	1	0	-1.386387	2.467352	3.124975
29	1	0	-1.477772	2.758868	1.381607

SCRF input: a0= 5.19 angstrom, dielectric constant= 8.93

SCF Done: E(RB+HF-LYP) = -1205.71332082 A.U. after 1 cycles

expl2 std1h

SAMPLE			DEC. & VT	
date	Nov 10 2003	dfrq	399.936	
solvent	CDCl3	dn	H1	
file	/export/home/~	dpwr	20	
nmr1/data/liu/TIM-	dof		0	
SSCO2Me_beta_H.fid	dm		nmn	
ACQUISITION				
sfrq	399.937	dmf	200	
tn	H1	dseq		
at	3.744	dres	1.0	
np	44928	homo	n	
sw	5999.3	PROCESSING		
fb	3000	wtfile		
bs	16	proc	ft	
tpwr	61	fn	not used	
pw	5.5	match	f	
d1	1.256			
tof	600.0	werr	react	
nt	16	wexp	procp1ot	
ct	16	wbs		
alock	n	wnt		
gain	not used			
FLAGS				
il	n			
in	n			
dp	y			
hs	nm			
DISPLAY				
sp	-380.9			
wp	4375.3			
vs	232			
sc	0			
wc	380			
hzmm	11.51			
is	500.00			
rfl	3292.3			
rfp	2903.5			
th	20			
ins	100.000			
nm	cdc	ph		

1H NMR (CDCl3, 400 MHz) □
(Z)-(Me3Si)3SiCH=CHCO2Me □
3a

expl3 std13c

SAMPLE			DEC. & VT		
date	Nov 10 2003	dfreq	399.936		
solvent	CDCl3	dn		H1	
file	/export/home/~	dpwr		42	
nmr1/data/liu/TIM-		dof		0	
SSCO2Me_beta.C.fid	dm			yyy	
ACQUISITION					
sfrq	100.574	dmf		11056	
tn	C13	dseq		garpl	
at	1.199	dres		1.0	
np	59968	homo		n	
sw	25000.0	PROCESSING			
fb	14000	lb		1.00	
bs	16	wfile			
tpwr	52	proc		ft	
pw	4.3	fn		not used	
dl	0.801	match		f	
tof	1000.0				
nt	100000	werf		react	
ct	3040	wexp		procp1ot	
alock		n	wbs		
gain	not used	wrt			
FLAGS					
il		n			
in		n			
dp		y			
hs		nn			
DISPLAY					
sp	-1994.2				
wp	25000.0				
vs	227				
sc	0				
wc	380				
hzmm	65.79				
is	500.00				
rfl	9747.6				
rfp	7753.5				
th	6				
lms	500.000				
nm	no	ph			

13C NMR (CDCl3, 100.6 MHz) □
(Z)-(Me3Si)3SiCH=CHCO2Me □
3a

041-TE-C.C.

expl2 std1h

SAMPLE				DEC. & VT	
date	Jan 12 2004	dfreq		399.936	
solvent	CDCl3	dn		H1	
file	/export/home/~	dpwr		20	
nmr1/data/liu/TFE-	dm	doe		0	
t_3-TTMS-acrylate-	dm			nmn	
-cid_H.fid	dmm			c	
ACQUISITION					
sfrq	399.937	dseq		200	
tn	H1	dres		1.0	
at	3.744	homo		n	
np	44928	PROCESSING			
sw	5999.3	wtfile			
fb	3000	proc		ft	
bs	16	fn		not used	
tpwr	61	math		f	
pw	5.5				
dl	1.256	wer		react	
tof	600.0	wexp		procp1ot	
nt	16	wbs			
ct	16	wnt			
alock	n				
gain	not used				
FLAGS					
il	n				
ln	n				
dp	y				
hs	nm				
DISPLAY					
sp	-177.6				
wp	3776.0				
vs	214				
sc	0				
wc	380				
hzmm	9.94				
is	500.00				
rfl	3292.3				
rfp	2901.9				
th	38				
ins	100.000				
nm cdc ph					

1H NMR (CDCl3, 400 MHz) □
(Z)-(Me3Si)3SiCH=CHCO2CH2CF3 □
3c

exp2 std13c

SAMPLE			DEC. & VT		
date	Jun 9 2004	dfreq	399.936		
solvent	CDCl3	dn		H1	
file	exp	dpwr	42		
ACQUISITION					
sfreq	100.574	dm		yyy	0
tn	Cl3	dmn		w	
at	1.199	dmf	11056		
np	59968	dseq	garpl		
sw	25000.0	dres	1.0		
fb	14000	homo	n		
bs	16	PROCESSING			
tpwr	52	lb	1.00		
pw	4.3	wtfile			
dl	0.801	proc	ft		
tof	1000.0	fn	not used		
nt	20000	match	f		
ct	20000				
alock	n	werf	react		
gain	not used	wexp	procp1ot		
FLAGS					
il	n	wnf			
in	n				
dp	y				
hs	nn				
DISPLAY					
sp	-1391.9				
wp	25000.0				
vs	945				
sc	0				
wc	380				
hzmm	1.82				
is	500.00				
rfl	9745.3				
rfp	7753.5				
th	20				
ins	500.000				
nm	no	ph			

13C NMR (CDCl3, 100.6 MHz) □
(Z)-(Me3Si)3SiCH=CHCO2CH2CF3 □
3c

expl2 std1h

SAMPLE			DEC. & VT	
date	Nov 5 2003	dfrq	399.936	
solvent	CDCl3	dn	H1	
file	/export/home/~	dpwr	20	
nmr1/data/liu/TIM-	dof		0	
SSCO2Me_alfa_h1104-	dm		nmn	
	.fid	dmm	c	
ACQUISITION				
sfrq	399.937	dseq	200	
tn	H1	dres	1.0	
at	3.744	homo	n	
np	44928			PROCESSING
sw	5999.3	wfile		
fb	3000	proc	ft	
bs	16	fn	not used	
tpwr	61	match	f	
pw	5.5			
dl	1.256	werr	react	
tof	600.0	wexp	procp1ot	
nt	16	wbs		
ct	16	wnt		
alock	n			
gain	not used			
FLAGS				
il	n			
in	n			
dp	y			
hs	nn			
DISPLAY				
sp	-80.1			
wp	4079.2			
vs	214			
sc	0			
wc	380			
hzmm	10.74			
is	583.16			
rfl	3292.3			
rfp	2903.5			
th	4			
ins	100.000			
nm	cdc	ph		

1H NMR (CDCl3, 400 MHz) □
H2C=C(CO2Me)(Si(SiMe3)3) □
4a

expl3 std13c

SAMPLE

DEC. & VT

date

Nov 7 2003

dfrq

399.936

solvent

CDCl3

dn

H1

file

/export/home/~

dpwr

42

nmr1/data/liu/TIM-

dof

0

SSCO2Me_alfa_c1108-

dm

yyy

w

ACQUISITION

.fid

dum

w

sfrq

100.574

dseq

11056

tn

Cl3

dres

garpl

at

1.199

homo

1.0

np

59968

PROCESSING

n

sw

25000.0

lb

1.00

fb

14000

wfile

bs

16

proc

ft

tpwr

52

fn

not used

pw

4.3

match

f

dl

0.801

tof

1000.0

werr

react

nt

1e+06

wexp

procp1ot

ct

27008

wbs

alock

n

wit

gain

not used

FLAGS

il

n

in

n

dp

y

hs

nn

DISPLAY

sp

-1993.4

wp

25000.0

vs

214

sc

0

wc

380

hzmm

65.79

is

500.00

rfl

9746.8

rfp

7753.5

th

6

ins

500.000

nm

no

ph

13C NMR (CDCl3, 100.6 MHz) □
H2C=C(CO2Me)(Si(SiMe3)3) □
4a

expl2 std1h

SAMPLE			DEC. & VT	
date	Nov 12 2003	dfreq	399.936	
solvent	CDCl3	dn	H1	
file	/export/home/~	dpwr	20	
nmr1/data/liu/Eth~	doe		0	
yl_2-TTMS-acrylat~	dm		nmn	
	e_H.fid	dmm	c	
ACQUISITION				
sfrq	399.937	dseq	200	
tn	H1	dres	1.0	
at	3.744	homo	n	
np	44928	PROCESSING		
sw	5999.3	wtfile		
fb	3000	proc	ft	
bs	16	fn	not used	
tpwr	61	math	f	
pw	5.5			
dl	1.256	werr	react	
tof	600.0	wexp	procplot	
nt	16	wbs		
ct	16	wnt		
alock	n			
gain	not used			
FLAGS				
il	n			
in	n			
dp	y			
hs	nm			
DISPLAY				
sp	-380.9			
wp	4383.1			
vs	214			
sc	0			
wc	380			
hzmm	11.53			
is	500.00			
rfl	3292.3			
rfp	2903.5			
th	20			
ins	100.000			
nm	cdc	ph		

1H NMR (CDCl3, 400 MHz) ☐
H2C=C(CO2Et)(Si(SiMe3)3) ☐
4b

expl3 std13c

SAMPLE			DEC. & VT		
date	Nov 12 2003	dfreq	399.936		
solvent	CDCl3	dn	H1		
file	/export/home/~ dpwr	42			
vmwr1/data/liu/Eth~	dof	0			
yl_2-TTMS-acrylat~	dm	yyy			
	e_c.fid	dmm	w		
ACQUISITION					
sfrq	100.574	dseq	11056		
tn	Cl3	dres	garpl		
at	1.199	homo	1.0		
np	59968	PROCESSING			
sw	25000.0	lb	1.00		
fb	14000	wfile			
bs	16	proc	ft		
tpwr	52	fn	not used		
pw	4.3	match	f		
dl	0.801				
tof	1000.0	werr	react		
nt	20000	wexp	procp1ot		
ct	1680	wbs			
alock	n	wit			
gain	not used				
FLAGS					
il	n				
in	n				
dp	y				
hs	nn				
DISPLAY					
sp	-1393.4				
wp	25000.0				
vs	214				
sc	0				
wc	380				
hzmm	28.10				
is	500.00				
rfl	9746.8				
rfp	7753.5				
th	8				
ins	500.000				
nm	no	ph			

13C NMR (CDCl3, 100.6 MHz) □
H2C=C(CO2Et)(Si(SiMe3)3) □
4b

expl2 std1h

SAMPLE		DEC. & VT	
date	Feb 9 2004	dfreq	399.936
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	20
nmr1/data/liu/TFE-	dmf	dmf	0
t-alfatTMS-acryla-	dm	dm	nmn
te_H.fid	dmn	c	200
ACQUISITION			
sfrq	399.937	dseq	1.0
tn	H1	dres	n
at	3.744	homo	
np	44928	PROCESSING	
sw	5999.3	wtfile	
fb	3000	proc	ft
bs	16	fn	not used
tpwr	61	math	f
pw	5.5		
dl	1.256	werf	react
tof	600.0	wexp	procp1ot
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nm		
DISPLAY			
sp	-168.4		
wp	3720.9		
vs	214		
sc	0		
wc	380		
hzmm	9.79		
is	500.00		
rfl	3292.5		
rfp	2903.5		
th	20		
ins	100.000		
nm cdc	ph		

¹H NMR (CDCl₃, 400 MHz) □
H₂C=C(CO₂CH₂CF₃)Si(SiMe₃)₃ □
4c

expl3 std13c

SAMPLE			DEC. & VT	
date	Feb 13 2004	dfreq	399.936	
solvent	CDCl3	dn	H1	
file	/export/home/~	dpwr	42	
vmwr1/data/liu/TFE-	dm	dot	0	
t_alfaTMS-acryla~	dm	yyy	yyy	
te060_C.fid	dmm	w	w	
ACQUISITION				
sfrq	100.574	dseq	11056	
tn	C13	dres	garpl	
at	1.199	homo	n	
np	59968	PROCESSING		
sw	25000.0	lb	1.00	
fb	14000	wtfile		
bs	16	proc	ft	
tpwr	52	fn	not used	
pw	4.3	math	f	
d1	0.801			
tof	1000.0	werr	react	
nt	10000	wexp	procplot	
ct	10000	wbs		
alock	n	wnt		
gain	not used			
FLAGS				
il	n			
ln	n			
dp	y			
hs	nm			
DISPLAY				
sp	-1994.2			
wp	25000.0			
vs	214			
sc	0			
wc	380			
hzmm	1.56			
is	500.00			
rfl	9747.6			
rfp	7753.5			
th	20			
ins	500.000			
nm	no	ph		

13C NMR (CDCl3, 100.6 MHz) ☐
H2C=C(CO2CH2CF3)(Si(SiMe3)3) ☐
4c