Highly diastereoselective addition of nitromethane anion to chiral α-amidoalkylphenyl sulfones. Synthesis of optically active α-amino acid derivatives.

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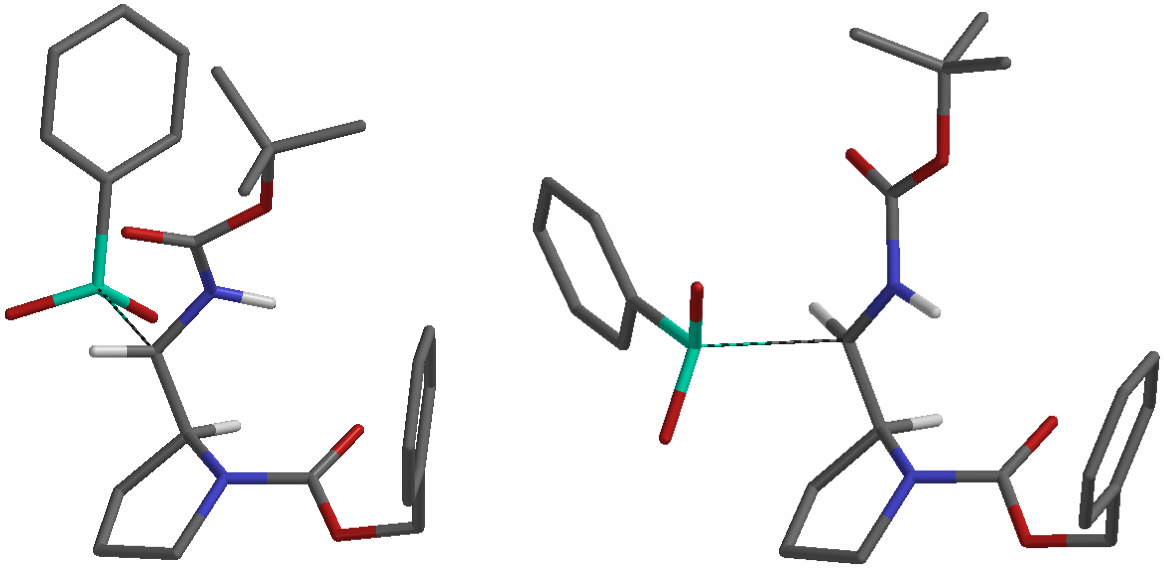
Supporting Information

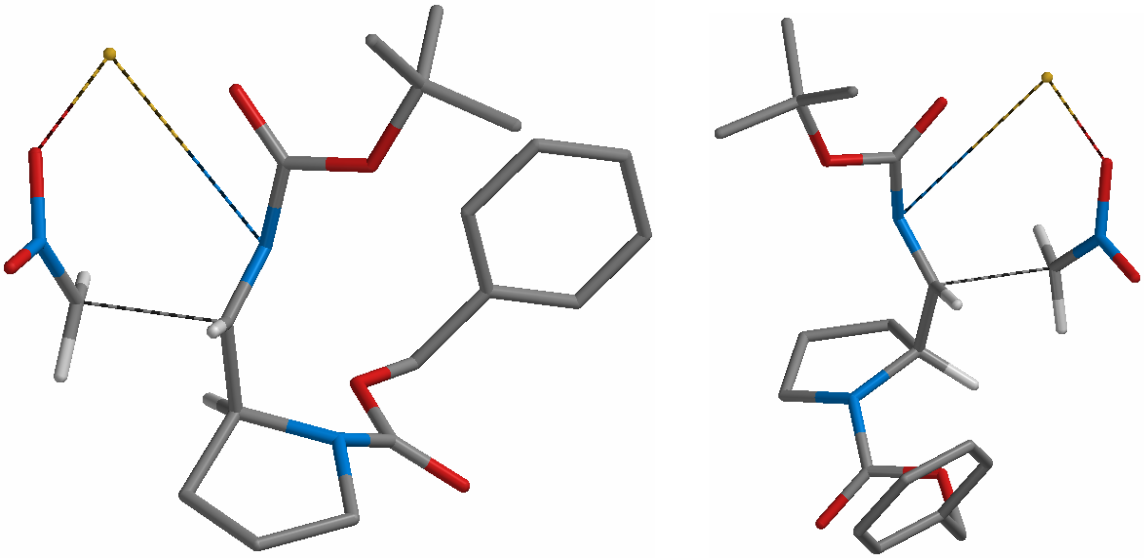
Figure 6. PM3 minimized structures of the transition states leading to sulfones **21**.



Si-(*S,S*)-**21-TS**
0.00 Kcal mol^{-1}

Re-(*S,R*)-**21-TS**
+ 3.07 Kcal mol^{-1}

Figure 7. PM3 minimized structures of the transition states leading to nitro derivatives **22.**



Si-(*S,S*)-**22-TS**
+ 7.39 Kcal mol^{-1}

Re-(*S,R*)-**22-TS**
0.00 Kcal mol^{-1}

COMPUTATIONAL CALCULATIONS

(*S*)-**7**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
           (Analytical Gradient)
  Model: RHF/AM1
  Number of shells:  52
    36 S shells
    16 P shells
  Number of basis functions:  84
  Number of electrons:  92
  Use of molecular symmetry disabled
  Molecular charge:   1
  Spin multiplicity:  1
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 102 degrees of freedom
  Initial Hessian option
   Hessian from MMFF94     calculation used.

  Heat of Formation:       -7.985 kcal/mol

36  84  52 156   1   1  84   0 RHF      AM1              OPT
C1
GEOMETRY
  1     2.0393748     2.0323872     6.3488068
  6     3.8074354     1.1781664     5.5708199
  1     5.5163451     1.9425696     6.5585923
  6     4.1116462     1.4020054     2.6746675
  1     5.7152070     2.6823996     2.0937608
  6     1.7406687     2.3851397     1.4487895
  8     3.6153892    -1.4751164     5.9700276
  8     4.6635754    -1.0874275     1.8381352
  6     4.9112473    -2.7903270     3.9895510
  6     7.6865766    -3.1850399     4.5883361
  1     8.6089397    -1.3514009     5.0704596
  1     8.6592797    -4.0276475     2.9172853
  1     7.8599204    -4.4942667     6.2345094
  6     3.5121961    -5.2241928     3.4118983
  1     1.5158198    -4.8234066     2.8699961
  1     3.5220131    -6.4444197     5.1346821
  1     4.4824380    -6.2276846     1.8309395
  1     1.1224498     4.3340493     2.0000933
  7     0.4063382     1.1413376    -0.2174401
  6    -1.8658233     2.2012339    -1.3906213
  8    -2.6225407     4.3269361    -0.8540183
  8    -2.8510686     0.5326173    -3.0094631
  6    -5.1834375     1.2221497    -4.4437528
  6    -7.3210583     1.6729687    -2.5986765
  1    -6.9794005     3.4174648    -1.4589484
```

1	-7.5390010	0.0261325	-1.2978006
1	-9.1186508	1.9207779	-3.6804821
6	-5.5940339	-1.1567676	-6.0055139
1	-7.3273088	-0.8885036	-7.1810451
1	-5.8608179	-2.8316438	-4.7516605
1	-3.9450566	-1.5065630	-7.2733002
6	-4.6385733	3.4989296	-6.0857074
1	-4.3365024	5.2247813	-4.9071358
1	-6.2910742	3.8372692	-7.3578704
1	-2.9292624	3.1636762	-7.2766023
1	0.9067496	-0.6285846	-0.7613116

Si-(*R,S*)-**5a-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
           (Analytical Gradient)
           (MM/Amide correction used)
  Model: RHF/PM3
  Number of shells:  75
    50 S shells
    25 P shells
  Number of basis functions: 125
  Number of electrons: 140
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Point Group = C1  Order =  1 Nsymop =  1
  This system has   144 degrees of freedom
  Found 1 amide linkage(s)

  Heat of Formation:     -167.591 kcal/mol

50 125  75 225   0   1 125   0 RHF      PM3              XOPT
C1
GEOMETRY
  1    -2.0551405     2.1865630     6.2882655
  6    -1.2109531     4.0391599     5.6878055
  1    -2.6472986     5.5286358     5.8913380
  6     0.0621681     3.9759595     3.0784277
  1    -0.2747052     5.7645870     2.0041169
  8     0.7571849     4.7243032     7.3774432
  8     2.7056721     3.9871875     3.5960216
  6     3.1489871     4.1172933     6.2765323
  6     5.0014633     6.2783902     6.8128744
  1     4.3088708     8.0981071     6.0989727
  1     6.8374179     5.9076424     5.9227259
  1     5.3129071     6.4799542     8.8534163
  6     4.1782157     1.5941315     7.2589969
  1     2.8595530     0.0243595     6.9328402
  1     4.5279274     1.6994080     9.3004293
  1     5.9694768     1.1152631     6.3305829
  6     0.2428091     0.5851154    -3.0102449
  8    -1.9324554     0.5649155    -3.7757747
  8     2.3558963     0.2089359    -4.4091047
  6     2.2355109    -0.4496557    -7.0695839
  6     0.8562190    -2.9523048    -7.4963177
  1    -1.1824476    -2.7954414    -7.1417475
  1     1.5987760    -4.4542052    -6.2724873
  1     1.0950502    -3.5718087    -9.4621146
  6     5.0377149    -0.7433791    -7.7658006
  1     5.2296716    -1.2486010    -9.7688193
  1     5.9579175    -2.2340615    -6.6531639
  1     6.0979756     1.0141041    -7.4596566
```

6	1.0551209	1.6672599	-8.6426827
1	-0.9832065	1.8559927	-8.3022355
1	1.3101442	1.2799334	-10.6651223
1	1.9367890	3.5019844	-8.2416788
6	-0.7385415	1.8261239	1.3772037
7	0.9902742	0.9189652	-0.4340967
1	2.8165422	1.2620463	-0.1042592
16	-1.7677102	-2.3086069	4.0393302
8	-2.9892285	-1.1821201	6.3222868
8	0.5193820	-3.8723917	4.4185009
1	-2.7282079	1.9501334	0.7635283
6	-3.9910906	-3.7987055	2.0642836
6	-7.5121103	-6.0608455	-1.1685431
6	-3.2847673	-5.8098156	0.5041728
6	-6.4894216	-2.9433295	1.9867595
6	-8.2381730	-4.0659151	0.3819126
6	-5.0331875	-6.9331872	-1.1008611
1	-1.3343109	-6.5196281	0.5614737
1	-7.0792161	-1.3831987	3.2225739
1	-10.1893491	-3.3767644	0.3403234
1	-4.4553245	-8.5092504	-2.3114883
1	-8.8887958	-6.9432390	-2.4373551

Re-(*R*,*R*)-**5a-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
           (Analytical Gradient)
           (MM/Amide correction used)
  Model: RHF/PM3
  Number of shells:  75
    50 S shells
    25 P shells
  Number of basis functions: 125
  Number of electrons: 140
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1

  Point Group = C1  Order =  1 Nsymop =  1
  This system has 144 degrees of freedom
  Found 1 amide linkage(s)

  Heat of Formation:     -170.491 kcal/mol

50 125  75 225   0   1 125   0 RHF      PM3              XOPT
C1
GEOMETRY
  1     2.0552989     0.2514191     5.8981529
  6     3.9987855     0.5451109     5.2133312
  1     5.0031980     1.7595334     6.5801935
  6     4.2100689     1.5152247     2.4748213
  1     5.1612014     3.3940724     2.3623214
  8     5.1371916    -1.8768511     5.1870019
  8     5.8599670    -0.2375072     1.2542102
  6     6.7541299    -2.0887437     3.0254385
  6     9.5172603    -1.5524551     3.7203580
  1     9.7568639     0.3362511     4.5435843
  1    10.7310676    -1.6647674     2.0436503
  1    10.2077198    -2.9355865     5.1026643
  6     6.4553297    -4.7312901     1.8828865
  1     4.4941146    -5.1307981     1.3361323
  1     7.0388153    -6.1868471     3.2397020
  1     7.6345383    -4.9315279     0.1876331
  6    -1.8906317    -1.1199674     0.2218578
  8    -3.5469370     0.2217468     1.1037780
  8    -2.1950937    -3.5015214    -0.6814515
  6    -4.6651589    -4.6746535    -0.8731307
  6    -5.8831744    -5.0438768     1.7209089
  1    -6.5018144    -3.2495501     2.5596896
  1    -4.5798801    -5.9505562     3.0560394
  1    -7.5571136    -6.2595939     1.5574791
  6    -4.0417141    -7.2597797    -2.0367241
  1    -5.7781448    -8.3627989    -2.3080535
  1    -2.7795657    -8.3686997    -0.8192011
```

1	-3.1233510	-7.0727065	-3.8885086
6	-6.4173640	-3.2078551	-2.6418990
1	-7.0036534	-1.3880271	-1.8345901
1	-8.1403105	-4.3036025	-3.0106907
1	-5.5124352	-2.8278582	-4.4707266
6	1.6864842	1.7040908	1.1678817
1	0.2965652	2.8735769	2.1924775
7	0.6855505	-0.3959795	-0.1498313
16	2.5058682	5.1603217	-2.3888727
6	-0.6243750	6.1580457	-2.8911596
6	-5.6535101	7.6398208	-3.5982310
6	-1.8024055	7.7860838	-1.1753071
6	-2.0037241	5.2891870	-4.9706808
6	-4.4991320	6.0261855	-5.3226468
6	-4.2985405	8.5220828	-1.5255534
1	-0.7372592	8.5032532	0.4562113
1	-1.1003321	4.0233007	-6.3475505
1	-5.5551104	5.3333717	-6.9621870
1	-5.1978467	9.7961063	-0.1648484
1	-7.6232807	8.2141852	-3.8708028
8	3.6239401	4.0191641	-4.6582646
8	3.9915303	7.0398561	-0.9728386
1	1.9063481	-1.7885907	-0.5246545

(*S*)-**8**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
          (Analytical Gradient)
  Model: RHF/AM1
  Number of shells:  51
    35 S shells
    16 P shells
  Number of basis functions:  83
  Number of electrons:  92
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Point Group = C1  Order =  1 Nsymop =  1
  This system has  99 degrees of freedom
  Initial Hessian option
   Hessian from MMFF94     calculation used.

  Heat of Formation:     -160.291 kcal/mol

35  83  51 153   0   1  83   0 RHF      AM1              OPT
C1
GEOMETRY
  1    -2.4136411     4.4896093    -0.5958008
  6    -4.1403242     3.8546997    -1.6358770
  1    -5.8287128     4.9663347    -1.0184696
  6    -4.5766867     0.9933575    -1.4738411
  1    -6.5238568     0.4906176    -0.7883705
  6    -2.5997771    -0.3711151     0.0752680
  8    -3.7947055     4.3673152    -4.2644773
  8    -4.4336285     0.1184165    -4.0263635
  6    -3.4270849     2.0620844    -5.6348198
  6    -4.9721116     2.1496221    -8.0550429
  1    -6.9985540     2.5147635    -7.6084465
  1    -4.8038049     0.3025351    -9.0544559
  1    -4.2423705     3.6981347    -9.2842544
  6    -0.6300429     1.6116698    -6.1281180
  1     0.4064750     1.4165041    -4.3025033
  1     0.1625789     3.2449954    -7.1984895
  1    -0.3869409    -0.1546738    -7.2503357
  1    -1.4457198    -1.7294678    -1.0428424
  7    -2.3782116     0.0276291     2.4595340
  6    -0.5498884    -1.2634250     3.9422276
  8    -0.9552464    -2.3328988     5.9750707
  8     1.8549064    -1.1105187     2.9827670
  6     3.9913804    -1.9785662     4.4674332
  6     4.1535791    -0.5495929     6.9523508
  1     2.5656901    -1.1007166     8.2293949
  1     4.0554552     1.5277603     6.6013998
  1     5.9820143    -1.0011279     7.9002665
```

6	6.2482112	-1.3301413	2.7872217
1	8.0202498	-1.9323930	3.7557191
1	6.3169670	0.7466306	2.4324038
1	6.0900655	-2.3282508	0.9373597
6	3.8372950	-4.8150132	4.8864452
1	5.6387288	-5.4936409	5.7461861
1	3.5383699	-5.8052187	3.0488917
1	2.2393430	-5.2859189	6.1825687

Re-(*S*,*R*)-**6a-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 105
    63 S shells
    42 SP shells
  Number of basis functions: 231
  Number of electrons:       158
  Number of heavy atoms:      21
  Number of hydrogens:        21
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   17.4 Mb
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 120 degrees of freedom

  E(HF)  =   -1026.2993355 a.u.

42 231 105 189   0   1 231   0 RHF      3-21G(*)        NOOPT
C1
GEOMETRY
  1     1.3247087     1.1409951     6.4067479
  6    -0.6377376     0.4150928     6.5051393
  1    -0.8105122    -0.7475617     8.2259521
  6    -1.5132399    -0.9551639     4.1026645
  1    -2.0397397    -2.9621184     4.4518908
  6     0.3212382    -0.6972714     1.8920147
  8    -2.2823900     2.5100911     6.8086576
  8    -3.8285741     0.2630753     3.4398278
  6    -4.0684040     2.6078890     4.7761178
  6    -6.7511403     2.7978400     5.8489287
  1    -7.1992588     1.2103699     7.1059598
  1    -8.1544046     2.8094233     4.3221186
  1    -6.9784428     4.5477647     6.9380093
  6    -3.4808047     4.8558322     3.0368080
  1    -1.5820844     4.7221966     2.2098455
  1    -3.5848215     6.6418374     4.0852095
  1    -4.8421809     4.9531100     1.4757105
  1     1.3891274     1.0865536     1.7263227
  7     0.1209818    -2.3611156     0.0925058
  6     1.4002745    -2.3213718    -2.2637365
  8     2.9738791    -3.9232646    -2.9302237
  8     0.5122117    -0.4891308    -3.7811070
  6     1.1831115    -0.2529028    -6.4367686
  6     3.9991666     0.2930478    -6.7860729
  1     5.1858899    -1.3521502    -6.3429993
  1     4.6289202     1.8688880    -5.5919529
  1     4.3832506     0.8139975    -8.7578290
  6    -0.3700992     2.0549585    -7.2632395
```

1	-0.0455398	2.4557331	-9.2728045
1	0.1465878	3.7570215	-6.1942880
1	-2.4064356	1.7467006	-7.0068307
6	0.3700761	-2.5697955	-7.9588007
1	0.5766489	-2.1961596	-9.9895049
1	-1.6177792	-3.0542106	-7.6122562
1	1.5156401	-4.2446449	-7.5212631
6	4.2901492	-1.8463770	3.7104327
1	3.8639838	-0.6358079	5.3244540
7	4.4839094	-4.3888209	4.0279004
8	5.3489067	-5.7887835	2.2115317
8	3.8502528	-5.5609992	5.9286524
3	5.0468390	-6.2963260	-1.1117933
1	5.2778353	-0.9084413	2.1680687

Si-(*S*,*S*)-**6a-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 105
    63 S shells
    42 SP shells
  Number of basis functions: 231
  Number of electrons:       158
  Number of heavy atoms:      21
  Number of hydrogens:        21
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   17.4 Mb
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 120 degrees of freedom

  E(HF)  =   -1026.3055773 a.u.

42 231 105 189   0   1 231   0 RHF      3-21G(*)        NOOPT
C1
GEOMETRY
  1    -2.2418744    -2.3214258     3.7717644
  6    -3.8447637    -0.9924507     3.8660676
  1    -5.5916053    -2.0926769     4.1426242
  6    -4.0004316     0.8788104     1.6480231
  1    -5.8389741     0.8055088     0.6212858
  6    -1.8286773     0.6728214    -0.2197394
  8    -3.5330765     0.5034078     6.0681221
  8    -3.9764688     3.3105189     2.8116386
  6    -3.2007836     3.1051914     5.3973090
  6    -4.9395929     4.7462687     7.0289431
  1    -6.9308663     4.1991864     6.8355804
  1    -4.7798006     6.7434046     6.4930773
  1    -4.4305357     4.5797903     9.0322916
  6    -0.4249460     3.8919850     5.7132342
  1     0.8364982     2.8053674     4.4753422
  1     0.2036584     3.5993656     7.6672507
  1    -0.1748357     5.8994829     5.2577068
  1    -0.5866952     2.3375893    -0.4282432
  7    -1.3142909    -1.5483062    -1.1537899
  6     0.7689050    -2.1317280    -2.7411683
  8     0.5925705    -2.7603812    -4.9887321
  8     2.9409595    -2.1696507    -1.4242670
  6     5.3298960    -3.0621180    -2.4508940
  6     5.1964224    -5.8449937    -3.2151601
  1     4.0300163    -6.1453541    -4.9059553
  1     4.4185582    -7.0208087    -1.6923909
  1     7.0975546    -6.5575204    -3.6445787
  6     7.1276513    -2.7528519    -0.1937678
```

1	9.0396621	-3.3715269	-0.7095190
1	6.5217089	-3.8852428	1.4365717
1	7.2557407	-0.7767435	0.4271151
6	6.2332900	-1.4161501	-4.6475307
1	8.1865140	-1.9073872	-5.1479106
1	6.2045672	0.6000978	-4.1576001
1	5.0790914	-1.6704047	-6.3548851
6	-3.7590753	2.7776302	-3.7158335
1	-4.5554272	4.1341653	-2.3912299
7	-5.3029891	1.2012357	-5.0257013
8	-4.3996929	-0.1596757	-6.8590129
8	-7.5603498	0.8552747	-4.6000904
3	-1.9397229	-2.3421175	-7.5673734
1	-1.9077888	3.2824123	-4.4585746

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SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
           (Analytical Gradient)
           (MM/Amide correction used)
  Model: RHF/PM3
  Number of shells:  72
    48 S shells
    24 P shells
  Number of basis functions: 120
  Number of electrons: 130
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1

  Point Group = C1  Order =  1 Nsymop =  1
  This system has 138 degrees of freedom

Heat of Formation:     -142.756 kcal/mol

  48 120  72 216   0   1 120   0 RHF      PM3              OPT
C1
GEOMETRY
  1    -5.2149944    -3.5998797    -5.9062380
  6    -4.6732854    -5.0351090    -4.4864826
  6    -2.6238202    -4.0476827    -2.6810651
  7    -3.4743875    -4.7470885    -0.0637430
  6    -5.9358693    -6.1257366    -0.1731563
  6    -6.9216991    -5.8174776    -2.8621291
  1    -3.9443553    -6.6568200    -5.5874948
  1    -0.7592818    -4.9343511    -3.1408272
  1    -7.2139104    -5.2826862     1.2511623
  1    -5.7094328    -8.1415984     0.3537731
  1    -8.4351558    -4.3761959    -2.9408065
  1    -7.7961202    -7.5814500    -3.5596977
  6    -1.7054393    -5.5074735     1.8209062
  8    -2.2549813    -6.6810071     3.7286291
  8     0.6946924    -4.7002623     1.3146874
  6     2.5078401    -4.6842201     3.3036370
  1     4.2812472    -4.8119977     2.2082543
  1     2.3552700    -6.3742846     4.5275597
  6     2.3942562    -2.2754648     4.7985473
  6     2.2286263     2.2045221     7.5640401
  6     1.6985103    -2.3165343     7.3404120
  6     3.0086863     0.0158195     3.6476074
  6     2.9144897     2.2484920     5.0276610
  6     1.6246518    -0.0790097     8.7178278
  1     1.1957408    -4.1107092     8.2479448
  1     3.5528146     0.0640235     1.6469927
  1     3.3798781     4.0434202     4.0850576
  1     1.0809000    -0.1172651    10.7138427
```

1	2.1612705	3.9641932	8.6497413
6	-2.4627025	-1.1966941	-2.8371099
1	-3.9498354	-0.0977328	-1.8779216
7	-0.6229773	-0.1916988	-4.0712138
6	-0.3006177	2.4818940	-4.3981782
8	-1.4366896	3.7753577	-5.9197253
8	1.5610032	3.2306129	-2.8175321
6	2.5313103	5.7945035	-2.8337265
6	4.6109402	5.6950832	-0.8119421
1	6.0898621	4.3224168	-1.2978230
1	3.8582758	5.1606721	1.0597989
1	5.5154360	7.5510127	-0.6154244
6	3.6912195	6.4957117	-5.3858424
1	5.0347117	5.0547551	-6.0364095
1	4.7213050	8.2903251	-5.2343455
1	2.2521305	6.7312288	-6.8623456
6	0.5088608	7.7075602	-2.0563378
1	1.3670976	9.5711195	-1.7471371
1	-0.4320853	7.1524492	-0.2926453
1	-0.9533862	7.9352571	-3.5107825

Re-(*S*,*R*)-**22-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
  Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 139
    81 S shells
    58 SP shells
  Number of basis functions: 313
  Number of electrons:       212
  Number of heavy atoms:      29
  Number of hydrogens:        26
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   29.3 Mb

  Point Group = C1  Order =  1 Nsymop =  1
  This system has 159 degrees of freedom

  E(HF)  =   -1346.9664263 a.u.

55 313 139 252   0   1 313   0 RHF      3-21G(*)        NOOPT
C1
GEOMETRY
  7    -4.5327131    -0.6417602     1.0555105
  6    -3.6173511    -3.0495044    -0.1537447
  1    -3.4617682    -4.6360896     1.2520352
  6    -0.9417649    -2.5588929    -1.1216271
  6    -6.7963505     0.3360876    -0.3233292
  6    -5.5935948    -3.7311878    -2.1572947
  6    -7.1655609    -1.3622375    -2.6226737
  1     0.4793275    -2.1599020     0.3595552
  7    -0.6548923    -1.7654792    -3.4667366
  6     1.5704295    -0.7632685    -4.5211033
  8     3.2965522    -1.9755284    -5.5617676
  8     1.4421682     1.7698383    -4.5358607
  6     3.2533771     3.3821315    -5.8226819
  6     5.9107105     3.1211784    -4.7137740
  1     6.7867298     1.2934187    -5.1703129
  1     5.9000016     3.3192826    -2.6480150
  1     7.1489136     4.6023314    -5.4749649
  6     2.2264845     6.0399439    -5.2666441
  1     3.4361873     7.4777887    -6.1457148
  1     2.1649509     6.4319694    -3.2295604
  1     0.3061843     6.2947480    -6.0114115
  6     3.2657077     2.9265330    -8.6768129
  1     4.3681590     4.4030260    -9.6309463
  1     1.3468610     2.9716374    -9.4655825
  1     4.1143390     1.1003021    -9.1817658
  6     0.2092019    -6.4869483    -1.0225621
  1    -0.6475764    -6.9449685    -2.8456806
```

7	2.7772228	-6.7637939	-0.7130602
8	4.2529379	-6.8575410	-2.6421046
8	3.8545635	-6.8612836	1.3348441
3	4.9945585	-5.0846429	-5.4766987
1	-1.0173432	-6.9086735	0.5904081
1	-6.5497815	-0.3925990	-4.3701470
1	-9.1815660	-1.8226149	-2.9168577
1	-8.4915924	0.3682404	0.9082421
1	-6.4096335	2.3215626	-0.8526238
1	-4.7128247	-4.4428773	-3.9141698
1	-6.7983884	-5.2973126	-1.4674390
6	-4.4797330	-0.3379575	3.7306700
8	-5.7872624	1.1466448	4.9193621
8	-2.6921505	-1.8274742	4.8510106
6	-2.0762915	-1.4166350	7.4382463
1	-1.3880962	-3.3148764	7.9726705
1	-3.7639817	-0.9690194	8.5900582
6	-0.0489204	0.5450282	7.7391975
6	3.7338932	4.1501436	8.3707414
6	-0.6600967	2.9675355	8.5790502
6	2.4609219	-0.0657658	7.2081811
6	4.3454917	1.7373317	7.5244106
6	1.2326679	4.7634278	8.8944966
1	-2.6357560	3.4554309	8.9747731
1	2.9432616	-1.9678462	6.5402211
1	6.3134078	1.2521533	7.1100286
1	0.7487052	6.6635172	9.5550172
1	5.2211079	5.5654481	8.6249375

Si-(*S,S*)-**22-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 139
    81 S shells
    58 SP shells
  Number of basis functions: 313
  Number of electrons:       212
  Number of heavy atoms:      29
  Number of hydrogens:        26
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   29.3 Mb
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 159 degrees of freedom

  E(HF)  =   -1346.9546481 a.u.

  55 313 139 252   0   1 313   0 RHF      3-21G(*)         NOOPT
C1
GEOMETRY
  7    -4.7096497    -0.5743427    -0.3490124
  6    -3.8715243    -2.6957122    -2.0569430
  1    -3.5451598    -4.4902922    -0.9924537
  6    -1.4129032    -1.8812234    -3.3478575
  6    -6.8246968     0.8489485    -1.5771412
  6    -6.0442505    -3.0185284    -3.9556994
  6    -7.4117664    -0.4887417    -4.0644447
  1    -1.6019143    -0.8524673    -5.1565197
  7     0.5728601    -1.6344803    -1.8629058
  6     2.8512302    -0.3873044    -2.4167701
  8     4.8407236    -1.4003029    -3.1573320
  8     2.7066013     2.0490399    -1.7173419
  6     4.8821853     3.7097073    -1.5080855
  6     6.7816695     2.7502717     0.4477958
  1     7.7646378     1.0338734    -0.1809303
  1     5.8603456     2.3214853     2.2703076
  1     8.2278619     4.1936555     0.8068968
  6     3.6890759     6.1830494    -0.5666595
  1     5.1491518     7.6338374    -0.3077784
  1     2.7272190     5.9275188     1.2551082
  1     2.2961912     6.9285712    -1.9121932
  6     6.1531096     4.1567667    -4.0656920
  1     7.5501611     5.6834157    -3.9099914
  1     7.1552157     2.4746846    -4.7597061
  6    -0.7176045    -5.3128351    -5.4715162
  1    -0.1166224    -6.3981950    -3.8207098
  7     0.9541454    -4.9505504    -7.4329427
```

8	3.3408267	-5.2547825	-7.1080906
8	0.3454564	-4.2594625	-9.5594106
3	5.9407614	-4.0802273	-5.2151054
1	-2.7086514	-5.5857546	-5.9617238
1	4.7779883	4.7165578	-5.5154158
1	-8.5095833	0.9631445	-0.3368960
1	-6.1745937	2.8149837	-1.8691999
1	-6.7556981	0.6434288	-5.6961834
1	-9.4667240	-0.7336625	-4.3433939
1	-5.3433820	-3.6286445	-5.8369701
1	-7.3351277	-4.5396359	-3.3264089
6	-4.8470482	-0.8975868	2.3252117
8	-6.1330401	0.4038426	3.7323409
8	-3.3108296	-2.7736285	3.2196257
6	-2.8596431	-2.9156557	5.8645199
1	-2.0956680	-4.8544597	6.0082753
1	-4.6492025	-2.8204740	6.9446524
6	-0.9669166	-1.0206211	6.8013655
6	2.5584410	2.4414734	8.6336920
6	1.2182749	-0.4986257	5.4221716
6	-1.3784349	0.1981969	9.1035493
6	0.3874754	1.9147442	10.0190778
6	2.9643964	1.2402171	6.3325033
1	1.5419039	-1.4397907	3.6029982
1	-3.1040509	-0.1828149	10.1844663
1	0.0588968	2.8637233	11.8277922
1	4.6586329	1.6710461	5.2067034
1	3.9392451	3.8046189	9.3503709

(*S*)-**26**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Geometry optimization
           (Analytical Gradient)
           (MM/Amide correction used)
  Model: RHF/PM3
  Number of shells:  73
    49 S shells
    24 P shells
  Number of basis functions: 121
  Number of electrons: 130
  Use of molecular symmetry disabled
  Molecular charge:   1
  Spin multiplicity:  1
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 141 degrees of freedom
  Initial Hessian option
   Hessian from MMFF94     calculation used.
  Found 1 amide linkage(s)

Heat of Formation:       11.980 kcal/mol

49 121  73 219   1   1 121   0 RHF      PM3             OPT
C1
GEOMETRY
  6     5.5515862     1.4159845    -1.4042096
  1     6.0979792     2.7069567     0.1919678
  6     3.3945360     2.6851194    -2.7678812
  6     6.7555549    -3.0521293    -1.1764062
  6     7.8311797     0.9777964    -3.1521896
  6     8.1820522    -1.8752352    -3.3824310
  1     3.7800461     3.4731937    -4.6726522
  7     1.1478962     2.9230433    -1.7481828
  6    -0.9905750     4.2324404    -3.0766762
  8    -0.7084666     5.1817650    -5.1317878
  8    -2.9854108     4.0660409    -1.5507327
  6    -5.4612669     5.1526195    -2.2497642
  6    -5.2718630     8.0101103    -2.5594279
  1    -4.2086847     8.5585515    -4.2558881
  1    -4.3758104     8.9125321    -0.9191370
  1    -7.1752544     8.8200186    -2.7449335
  6    -7.0601963     4.4748978     0.0620953
  1    -9.0100678     5.1321013    -0.2188732
  1    -6.3456449     5.3689609     1.7948671
  1    -7.1361663     2.4258579     0.3906150
  6    -6.4981044     3.8862367    -4.6209061
  1    -5.4339198     4.4016979    -6.3272977
  1    -8.4645638     4.4787463    -4.9284423
  1    -6.4963960     1.8173773    -4.4611106
  1     0.8559781     2.1945529     0.0358967
  1     8.0297292    -3.5035224     0.4253033
```

1	5.7729530	-4.8243229	-1.6928399
1	7.4516842	-2.5765358	-5.2138474
1	10.2039658	-2.4057456	-3.3526800
6	3.5455224	-1.2610100	1.9484334
8	4.0593096	-3.3332249	3.3155156
8	2.0432747	0.4065491	2.5817245
6	2.6450583	-3.8323820	5.5809365
1	2.4521753	-2.1060322	6.7447819
1	3.9700045	-5.1448878	6.5227446
1	7.5744838	1.8718556	-5.0273508
1	9.5357439	1.8804221	-2.3394175
7	4.7944510	-1.1493669	-0.4494298
6	0.1515339	-5.0481311	5.0327673
6	-4.4926771	-7.3632488	4.1488619
6	-2.0882492	-3.7372580	5.5005600
6	0.0589467	-7.5257249	4.1313492
6	-2.2608600	-8.6744704	3.6841416
6	-4.4038808	-4.8985083	5.0600827
1	-2.0229996	-1.7986922	6.2306026
1	1.8155879	-8.5706793	3.7949041
1	-2.3301817	-10.6216583	2.9832840
1	-6.1603060	-3.8744588	5.4504660
1	-6.3196875	-8.2782031	3.8125943

Re-(*S*,*R*)-**21-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 161
    93 S shells
    67 SP shells
     1 6D shells
  Number of basis functions: 367
  Number of electrons:       252
  Number of heavy atoms:      33
  Number of hydrogens:        30
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   38.9 Mb
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 183 degrees of freedom

E(HF)  =   -1871.7155125 a.u.

63 367 161 292   0   1 367   0 RHF      3-21G(*)        NOOPT
C1
GEOMETRY
  7    -4.4963700    -1.2266624     0.8205640
  6    -3.9216203    -1.2935554    -1.9631899
  6    -6.8891015     0.2185845     1.2775807
  6    -6.1605880     0.0244263    -3.2584799
  6    -7.4955963     1.5374927    -1.2052488
  6     3.2074423    -0.6358420    -2.2198874
  8     3.7082643    -0.1573981    -4.4172019
  8     4.8404240    -1.2537098    -0.3516717
  6     7.5581003    -1.0324829    -0.6854097
  6     8.5411836    -2.9011952    -2.6569533
  1     7.9659367    -2.3857005    -4.5834222
  1     7.8685974    -4.8287001    -2.2893751
  1    10.6150331    -2.9451083    -2.6227648
  6     8.5633225    -1.7502778     1.9399615
  1    10.6366856    -1.6751965     1.9565258
  1     8.0020852    -3.6729845     2.4846430
  1     7.8776952    -0.4539636     3.4091451
  6     8.3395901     1.6724736    -1.3297212
  1     7.7742865     2.2156173    -3.2509663
  1    10.4017349     1.8653182    -1.2153171
  1     7.5068492     3.0461810    -0.0155236
  6    -1.4101778    -0.1019959    -2.6294746
  1    -1.0959514     0.1659752    -4.6786007
  7     0.7050532    -0.6759262    -1.1847490
 16    -1.6242644     4.9053337    -2.2442257
  6    -1.2407099     5.6322621    -5.5050323
  6    -0.6847271     6.6313299   -10.6661757
  6    -3.1278409     4.9454774    -7.2184183
```

6	0.9332953	6.8161799	-6.4118825
6	1.2112089	7.3108958	-8.9791262
6	-2.8593777	5.4462012	-9.7807948
1	-4.8457986	3.9956568	-6.5163470
1	2.4339403	7.3620173	-5.0847823
1	2.9269614	8.2391672	-9.6682582
1	-4.3595683	4.9125374	-11.1013469
1	-0.4682904	7.0258381	-12.6861619
8	0.6130442	5.7935239	-0.7358305
8	-4.1858705	5.8286015	-1.3426644
1	0.4618574	-1.2964415	0.5809021
1	-8.4482685	-1.0389644	1.8908001
1	-6.5424201	1.5684200	2.8363063
1	-5.5514892	1.2668350	-4.8417387
1	-7.4352858	-1.3924408	-4.1190043
1	-6.7518249	3.5398307	-1.1817888
1	-9.5496490	1.6723654	-1.5354387
6	-3.9829210	-3.4535685	2.2515425
8	-2.4620533	-5.0797996	1.6230369
8	-5.2803918	-3.5346741	4.4725683
6	-4.6171935	-5.3968644	6.3062219
1	-6.4219663	-5.5597851	7.3452072
1	-4.1835428	-7.2462254	5.4303491
6	-2.5136865	-4.5133527	7.9909111
6	1.3688456	-2.9066475	11.1642527
6	-3.0229730	-2.8363617	9.9616169
6	-0.0540704	-5.3836402	7.6146686
6	1.8801951	-4.5791946	9.2018776
6	-1.0830149	-2.0359595	11.5422895
1	-4.9537632	-2.1458929	10.2583166
1	0.3516641	-6.6916292	6.0592006
1	3.8101345	-5.2633954	8.9004433
1	-1.4877514	-0.7158676	13.0836276
1	2.8950929	-2.2729979	12.4090658
1	-3.7904100	-3.3041394	-2.6346510

Si-(*S*,*S*)-**21-TS**

```
SPARTAN 'O2 Fast HF Program:  (PC/x86c)
Run type: Single point energy
  Model: RHF/3-21G(*)
  Number of shells: 161
    93 S shells
    67 SP shells
     1 6D shells
  Number of basis functions: 367
  Number of electrons:       252
  Number of heavy atoms:      33
  Number of hydrogens:        30
  Use of molecular symmetry disabled
  Molecular charge:   0
  Spin multiplicity:  1
  Memory model: direct   38.9 Mb
  Point Group = C1  Order =  1 Nsymop =  1
  This system has 183 degrees of freedom

  E(HF)  =   -1871.7203986 a.u.

  63 367 161 292   0   1 367   0 RHF      3-21G(*)        NOOPT
C1
GEOMETRY
  7    -0.8756945     4.9768729     2.0249943
  6    -0.4457392     3.3578957     4.3391458
  1     1.5879649     3.4215756     4.9311899
  6    -2.9185774     6.8654204     2.5171833
  6    -2.1434189     4.5026062     6.3948922
  6    -0.9656067    -2.1802352     0.0610069
  8    -3.1278330    -2.9698941     0.1731356
  8     0.7392577    -2.6783696    -1.7890814
  6     0.1427287    -4.3040268    -3.9141488
  6     2.6209663    -4.2962915    -5.4271649
  1     4.2315518    -4.9339072    -4.2853550
  1     3.0739560    -2.3937917    -6.1545451
  1     2.4682436    -5.5654312    -7.0610435
  6    -1.9795042    -3.2074923    -5.5404880
  1    -2.2069730    -4.3346452    -7.2675297
  1    -1.5645898    -1.2539737    -6.1179939
  1    -3.8063598    -3.2074587    -4.5570846
  6    -0.4781733    -6.9961826    -3.0684152
  1     0.9654133    -7.7453498    -1.7802991
  1    -0.5685841    -8.2602502    -4.7113517
  1    -2.3107576    -7.1097996    -2.1011763
  6    -1.1867913     0.6628564     3.7510705
  7     0.2595716    -0.6724020     1.9469680
  1     1.8993698     0.1291876     1.4553480
 16    -0.1760641    -1.7675637     8.0334703
  8    -2.5698834    -1.6354359     9.4751260
  8     2.0695071    -0.5137197     9.1303790
```

1	-3.2283962	0.2352818	3.7891735
6	0.4954384	-4.8622437	7.0075340
6	1.5401854	-9.7470790	5.2735541
6	2.9860050	-5.6325699	6.5807533
6	-1.4636164	-6.5769083	6.5602403
6	-0.9446704	-9.0028794	5.6980652
6	3.5049190	-8.0583844	5.7200348
1	4.5477119	-4.3141760	6.9486815
1	-3.4298778	-6.0057596	6.9053606
1	-2.4981346	-10.3271540	5.3555626
1	5.4652136	-8.6400518	5.4004592
1	1.9495007	-11.6590197	4.5949894
1	-4.2821944	6.7758792	0.9349029
6	1.2446471	5.6464385	0.5154067
8	3.2810832	4.5517399	0.5515753
8	0.7318403	7.5807517	-1.1133014
6	2.3712318	7.9741364	-3.2162851
1	2.0164534	9.9953833	-3.6020637
1	4.3865337	7.7356623	-2.7095066
6	1.6524885	6.3271000	-5.4131614
6	0.2780182	3.2537922	-9.4648346
6	-0.0166724	7.2219477	-7.2470164
6	2.6469361	3.8946575	-5.6273289
6	1.9424227	2.3581049	-7.6385481
6	-0.6917469	5.6895556	-9.2726039
1	-0.8012683	9.1325054	-7.0893884
1	3.9719405	3.1887674	-4.1959665
1	2.6916200	0.4200797	-7.7561933
1	-1.9968000	6.4002311	-10.7124081
1	-0.2696981	2.0421220	-11.0499509
1	-3.0498989	3.0318993	7.5762560
6	-4.0969344	6.1288788	5.0406966
1	-5.8773592	5.0683450	4.7537332
1	-4.6190785	7.8087560	6.1659857
1	-2.1717806	8.8218834	2.5599118
1	-1.0000429	5.6521329	7.7174478