C–H···O Non-Classical Hydrogen Bonding in the Stereomechanics of Organic Transformations: Theory and Recognition

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Supplementary Information

Table of Contents

General Information

Geometries from structures reproduced in the manuscript are reported here. While some molecular structural data was available in supporting information of the original report, some structures were recomputed due to a lack of supporting information. For these recomputed geometries, the structures were computed according to the methods used in the original report.

Molecular Geometries for Structures Reproduced in Figure 1

Original Report: S. Bahmanyar and K. N. Houk, *J. Am. Chem. Soc.*, 2001, **123**, 12911–12912.

Method: B3LYP/6-31G(d)

TS-*(S,S)*-major

41
Hajos-Parrish-6-SS.pdb

C	-1.27800	-0.57200	-0.77900
C	-0.99900	1.44100	0.89900
H	0.52800	1.04800	2.41200
H	-0.96600	0.13700	2.64000
C	-2.27100	1.71100	-1.24200
C	3.46200	-1.55100	-0.45900
O	-3.75100	0.62900	1.47000
C	-3.19200	0.18200	0.48900
H	-0.26300	2.04000	0.35600
C	-2.51000	-1.38200	-1.27600
C	-0.74600	-1.59100	0.67400
H	-0.44000	-2.52400	0.21400
N	1.48600	-0.75200	0.63600
C	-1.89200	0.71400	-0.11500
C	-0.25600	0.49500	1.88800
C	0.26200	-0.70100	1.13900
O	-0.27100	-0.45400	-1.58900
H	-1.59000	-1.71300	1.35000
H	1.97100	-2.80300	0.56400
C	2.01600	-1.93700	-0.10600
C	2.51000	0.30600	0.71700
H	1.40000	-2.12100	-0.98400
H	-2.29600	-2.45300	-1.33800
H	-2.71500	-1.04100	-2.29600
C	-3.66600	-1.03600	-0.31800
H	-4.59700	-0.78400	-0.83900
H	-3.00900	1.29300	-1.93500
H	-1.61800	2.12800	1.48600
H	-2.69300	2.62600	-0.81200
C	3.82500	-0.47700	0.57600
H	2.44700	0.83000	1.67200
H	4.63700	0.18300	0.26800
H	3.50000	-1.12800	-1.46800
H	4.09000	-0.93400	1.53700
H	4.12900	-2.41700	-0.43300
C	2.41100	1.39800	-0.39500
H	-3.91900	-1.84000	0.38300
H	-1.37500	1.96100	-1.81600
O	3.24100	2.28600	-0.34800
O	1.47600	1.32000	-1.31500
H	0.77100	0.52200	-1.32400

TS-*(R,R)*-minor

41
Hajos-Parrish-6-RR

C	3.28300	1.40900	-0.86500
C	2.07400	2.01200	-0.12000
H	2.38500	2.55100	0.78300
C	1.22900	0.79600	0.35800
H	1.49100	2.71500	-0.72100
C	2.26300	-0.35200	0.57000
H	1.15500	0.19200	-2.01600
O	0.32300	0.92300	1.27000
C	2.98200	-0.11500	1.92500
C	3.27200	-0.09700	-0.54500
C	-2.03700	-1.91900	0.53800
H	0.14500	-2.95700	-0.44400
C	-2.54700	0.11600	-0.72900
C	1.64100	-1.75000	0.58600
C	-2.74200	1.49500	-0.00400
C	0.67900	-2.01700	-0.60100
C	-0.24600	-0.84700	-0.80200
C	0.38000	0.33700	-1.26800
C	-3.81000	-0.74800	-0.57500
N	-1.47500	-0.83000	-0.30100
H	1.27500	-2.12600	-1.51300
H	-0.24100	1.20900	-1.45300
H	-2.35800	0.37500	-1.77600
H	1.09200	-1.86500	1.52800
H	3.68200	-0.93300	2.13100
H	2.23100	-0.06700	2.71800
H	3.54700	0.82200	1.93900
H	2.43300	-2.50700	0.56600
H	-1.48900	-1.97300	1.48200
H	-1.93300	-2.87600	0.01400
H	-4.14700	-2.42900	0.82000
H	-4.69500	-0.11600	-0.51300
C	-3.51600	-1.54500	0.70100
H	-3.91200	-1.42300	-1.43400
H	-3.65500	-0.90900	1.58300
H	3.24400	1.53500	-1.95300
H	4.24000	1.83700	-0.54400
O	3.93600	-0.93900	-1.11400
O	-3.82200	2.02800	-0.19500
O	-1.77500	2.06000	0.66600
H	-0.88500	1.52400	0.89200

Molecular Geometries for Structures Reproduced in Figure 2

. **Original Report:** D. Suarez, J. Gonzalez, T. L. Sordo, and J. A. Sordo, *J. Org. Chem.*, 1994, **59**, 8058–8064.

Method: MP2/6-31G(d)//HF/6-31G(d)

TS-*meta-endo*

16
meta-endo.log

C	-1.33011	-0.00208	0.28766
C	-0.37727	-0.34019	1.28850
H	-0.04808	0.43720	1.95760
C	-1.22910	1.19475	-0.41170
H	-1.75798	1.28904	-1.34261
C	-0.23747	2.09851	-0.11592
H	0.02501	2.86226	-0.82230
H	-0.53717	-1.27970	1.79186
H	0.13607	2.24506	0.87317
C	-2.19983	-1.09468	-0.25883
H	-1.57082	-1.73267	-0.87567
H	-2.62439	-1.69882	0.53403
H	-2.99944	-0.69935	-0.87254
S	1.35240	-0.54375	0.18112
O	1.53042	0.89013	-0.16175
O	0.96721	-1.37273	-0.94821

TS-*meta-exo*

16
meta-exo.log

C	-1.47464	-0.24740	0.26362
C	-0.33919	-0.92809	0.76336
H	0.14381	-0.50988	1.62918
C	-1.48719	1.13927	0.16360
H	-2.26936	1.60932	-0.40419
C	-0.36449	1.87204	0.47151
H	-0.27688	2.88812	0.13821
H	-0.39731	-2.00376	0.80790
H	0.34347	1.57872	1.21693
C	-2.56672	-1.04644	-0.39550
H	-2.16611	-1.56339	-1.26389
H	-2.95125	-1.80120	0.28172
H	-3.38583	-0.41931	-0.72241
S	1.34797	-0.47415	-0.44639
O	0.98889	0.90203	-0.85758
O	2.35927	-0.51808	0.58998

TS-*para-endo*

16
para-endo.log

C	-0.76201	-1.13079	0.55945
C	0.45637	-1.04641	1.25963
H	0.55178	-0.34620	2.07200
C	-1.54149	-0.03861	0.21106
C	-1.15557	1.19533	0.69799
H	-1.54284	2.09786	0.26474
H	0.97853	-1.97237	1.43061
H	-0.69725	1.31100	1.65544
S	1.59928	0.09924	-0.12351
O	0.84647	1.36198	0.07577
O	1.38239	-0.49743	-1.42275
H	-0.95577	-2.05519	0.04314
C	-2.55172	-0.14639	-0.91260
H	-3.39514	0.51699	-0.75840
H	-2.09394	0.10136	-1.86525
H	-2.93817	-1.15659	-0.98350

TS-*para-endo*

16
para-exo.log

C	1.01064	1.24383	-0.04413
C	-0.32403	1.51684	0.29420
H	-0.67328	1.24142	1.27383
C	1.67790	0.06833	0.26843
C	0.95798	-0.91395	0.92314
H	1.32776	-1.92102	0.96469
H	-0.73902	2.44821	-0.05173
H	0.16731	-0.69774	1.60970
S	-1.56078	-0.07671	-0.52563
O	-0.56320	-1.16972	-0.49702
O	-2.52817	-0.15863	0.54701
H	1.48493	1.90025	-0.75529
C	3.01788	-0.26128	-0.35462
H	2.94568	-1.14014	-0.98798
H	3.37592	0.55883	-0.96594
H	3.77183	-0.45825	0.40084

Molecular Geometries for Structures Reproduced in Table 3

. **Original Report:** I. Washington and K. N. Houk, *Angew. Chem., Int. Ed.* 2001, **40**, 4485-4488.

Method: B3LYP/6-31+G(d,p)//B3LYP/6-31G(d)

Note: Only the X=H case is reproduced here.

TS-*cis*-major

28
cis-equat.log

C	1.17357	-1.20823	0.94798
C	1.16697	0.14533	1.18298
C	1.96544	1.13792	0.37680
C	2.43021	0.52166	-0.95544
C	3.01190	-0.88423	-0.75483
C	1.96724	-1.84365	-0.15925
H	0.66314	0.52456	2.07058
H	0.64170	-1.86597	1.63164
H	1.57322	0.47263	-1.63840
H	3.17488	1.18058	-1.41856
H	3.38383	-1.28596	-1.70443
H	3.87694	-0.82557	-0.07933
H	1.26330	-2.17642	-0.93395
H	2.45023	-2.75314	0.22274
H	2.86255	1.36315	0.98077
C	1.19821	2.45407	0.17670
H	0.92176	2.90446	1.13769
H	1.81617	3.17804	-0.36658
H	0.28156	2.27571	-0.39265
C	-2.93844	-0.10238	-0.07634
O	-2.72658	-0.35008	1.12311
O	-2.00362	0.01521	-0.96779
O	-0.45197	-0.26067	-0.01914
H	-1.08126	-0.38260	0.75755
C	-4.35139	0.07979	-0.60673
H	-4.35529	0.34155	-1.66611
H	-4.90784	-0.85088	-0.45507
H	-4.84980	0.86257	-0.02660

TS-*trans*-minor

28
trans-equat.log

C	-1.15687	0.66322	0.78358
C	-0.89966	-0.59139	1.28234
C	-1.49936	-1.83958	0.70089
C	-2.06992	-1.60589	-0.70549
C	-2.89518	-0.31306	-0.75271
C	-2.04827	0.92738	-0.40466
H	-0.35216	-0.68774	2.21738
H	-0.75999	1.53003	1.30891
H	-1.23999	-1.53900	-1.41814
H	-2.68494	-2.46303	-1.00350
H	-3.34425	-0.17786	-1.74411
H	-3.72969	-0.38772	-0.03920
H	-1.38158	1.14185	-1.25260
H	-2.29309	-2.18409	1.38343
C	3.09637	0.15815	-0.07978
O	2.80645	0.64955	1.02563
O	2.22936	-0.36125	-0.89049
O	0.62559	-0.17232	0.00350
H	1.20525	0.26235	0.70403
C	4.53110	0.14328	-0.58254
H	5.17565	-0.28154	0.19275
H	4.62911	-0.42825	-1.50705
H	4.85455	1.17523	-0.75552
C	-2.92232	2.17093	-0.16739
H	-2.30995	3.06040	0.02113
H	-3.54625	2.37335	-1.04506
H	-3.58874	2.03024	0.69236
H	-0.74049	-2.63030	0.69067

Molecular Geometries for Structures Reproduced in Figure 4

. **Original Report:** M. N. Paddon-Row, C. D. Anderson, and K. N. Houk, *J. Org. Chem.*, 2009, **74**, 861–868.

Method: B3LYP/6-31G(d)/PCM(DCM)//B3LYP/6-31G(d)

TS-*re*-major

70
TS-re-1.xyz

C	0.996672	2.330545 -2.620652
N	0.747743	1.013333 -1.902992
C	2.088780	0.488572 -1.419651
C	1.755340	-0.368700 -0.168956
O	0.651282	0.335934 0.420229
B	-0.198866	0.978883 -0.527021
C	2.887599	1.776995 -1.203397
C	1.320250	-1.814380 -0.496145
C	2.937610	-0.393984 0.803925
C	-0.814243	2.376568 -0.061709
C	5.149292	-0.425626 2.533058
C	4.114506	-1.066755 0.443146
C	2.876162	0.252137 2.041873
C	3.977072	0.232247 2.902879
C	5.214937	-1.076406 1.298300
H	4.168867	-1.599055 -0.503680
H	1.962891	0.758208 2.332388
H	3.914400	0.733864 3.864662
H	6.120450	-1.599580 1.004362
H	6.004616	-0.437949 3.202351
C	0.453250	-4.467427 -0.918877
C	0.991728	-2.649952 0.585401
C	1.207172	-2.337609 -1.789255
C	0.776795	-3.652785 -2.000674
C	0.563729	-3.958881 0.379508
H	1.096099	-2.268584 1.597147
H	1.467958	-1.744091 -2.661438
H	0.709000	-4.037381 -3.014495
H	0.335701	-4.591319 1.233499
H	0.133430	-5.492665 -1.081533
H	0.321185	0.345286 -2.546894
H	2.556476	-0.096826 -2.214754
H	3.959786	1.580469 -1.145956
H	2.583642	2.257144 -0.267767
C	2.492982	2.631336 -2.416953

H 0.354579 3.083990 -2.166658
H 0.718188 2.220119 -3.670899
H 3.068046 2.328639 -3.299019
H 2.669750 3.698070 -2.258045
C -1.886156 4.854759 0.791073
C -0.280348 3.062852 1.042894
C -1.904918 2.972409 -0.726688
C -2.435095 4.195756 -0.312127
C -0.807353 4.284369 1.468802
H 0.557419 2.627402 1.580414
H -2.350834 2.469812 -1.583402
H -3.273255 4.635182 -0.846792
H -0.376608 4.790889 2.328481
H -2.296151 5.806411 1.117811
H -4.414059 -2.079737 3.212330
C -4.554960 -1.503695 2.299338
C -5.094523 -2.161105 1.203587
C -3.994822 -0.193513 2.276534
H -5.521212 -1.600496 0.377757
H -5.533934 -3.142484 1.357905
C -3.366129 -2.678702 0.144270
C -3.971296 0.612919 1.179538
H -3.480712 0.138337 3.175765
C -2.970001 -1.607189 -0.672285
H -3.905627 -3.500605 -0.319268
H -2.725443 -2.976294 0.967256
H -3.451896 1.565531 1.189888
H -4.548680 0.394317 0.287963
C -1.886919 -0.816320 -0.253174
O -1.353652 0.067378 -1.028073
H -1.407134 -0.996099 0.707935
C -3.619874 -1.342134 -2.007618
H -4.520624 -1.948278 -2.139798
H -3.888869 -0.287064 -2.128425
H -2.931793 -1.587198 -2.826072

TS-*si*-major

71
TS-si-8.xyz
C 0.766224 2.363984 -2.634623
N 0.720025 1.043378 -1.884916
C 2.119670 0.764790 -1.367580
C 1.900751 -0.144342 -0.132787
O 0.706799 0.401206 0.446939
B -0.228850 0.877339 -0.513288
C 2.666580 2.173041 -1.123665
C 1.670261 -1.629798 -0.487791
C 3.064500 -0.024775 0.854637
C -1.061591 2.170337 -0.092143
C 5.239688 0.215422 2.613377
C 4.322622 -0.537500 0.505917
C 2.905036 0.599716 2.095077
C 3.988016 0.714895 2.970738
C 5.404154 -0.411989 1.375951
H 4.457316 -1.052215 -0.442427
H 1.931412 0.983784 2.376073
H 3.849218 1.197416 3.934326
H 6.372963 -0.812618 1.091404
H 6.080710 0.307640 3.294450
C 1.209703 -4.374093 -0.958887
C 1.261588 -2.482880 0.550627
C 1.850205 -2.180848 -1.762370
C 1.621198 -3.542580 -1.997686
C 1.032557 -3.836510 0.320048
H 1.135101 -2.074053 1.548142
H 2.191610 -1.573555 -2.596080
H 1.782000 -3.948439 -2.992762
H 0.729196 -4.478985 1.142221
H 1.043124 -5.432483 -1.137224
H 0.429315 0.294444 -2.515229
H 2.705479 0.281755 -2.152559
H 3.754576 2.171387 -1.034524
H 2.253397 2.582517 -0.196733
C 2.162634 2.952780 -2.348303
H -0.038144 2.993821 -2.258465
H 0.594237 2.172768 -3.696225
H 2.827108 2.789489 -3.203618
H 2.114432 4.029888 -2.170170
C -2.482115 4.505546 0.649473
C -0.702499 2.914924 1.044546
C -2.157154 2.634548 -0.847080
C -2.856721 3.788801 -0.490300
C -1.404497 4.063943 1.418097
H 0.140345 2.585741 1.646194
H -2.468263 2.085706 -1.735244
H -3.690223 4.131296 -1.098413
H -1.106793 4.617006 2.304975
H -3.024542 5.403492 0.932028
H -4.532348 -2.755120 3.064913
C -4.435804 -1.875109 2.434587
C -5.151684 -1.838488 1.243909
H -4.263343 -0.952785 2.981063
C -2.501585 -2.076476 1.855821
C -5.178621 -0.720326 0.365224
H -5.598797 -2.763656 0.885354
C -2.009921 -0.991927 1.114502
H -2.187769 -2.136282 2.894626
H -2.589471 -3.035958 1.358911
C -4.517622 0.444919 0.607271
H -5.679483 -0.850934 -0.591275
C -1.873983 -1.054246 -0.294502
H -1.581263 -0.130395 1.607977
H -4.487516 1.240829 -0.128224
H -4.078721 0.681241 1.568980
O -1.187165 -0.249796 -1.031835
O -2.477143 -2.065234 -0.903705
C -2.279670 -2.251161 -2.321194
H -2.626450 -1.374908 -2.873580
H -1.224711 -2.442118 -2.529567
H -2.881072 -3.123061 -2.575014

Molecular Geometries for Structures Reproduced in Figure 6

. **Original Report:** (a) R. S. Paton and J. M. Goodman, *Org. Lett.*, 2006, **8**, 4299-4302. (b) R. S. Paton and J. M. Goodman, *J. Org. Chem.*, 2008, **73**, 1253–1263.

Method: B3LYP/6-31G(d,p)/PCM(Et_2O)//B3LYP/6-31G(d,p)

TS-in-*anti*-major

38
TS-Boat-anti-in.xyz
C 10.84539 -1.57710 -1.09195
C 10.14809 -1.37272 0.08703
H 10.34540 -2.11175 -1.89309
H 11.92565 -1.57149 -1.11614
C 8.69551 -1.77594 0.23112
C 7.76530 -0.55856 0.41152
H 8.38295 -2.39681 -0.61352
B 11.80435 0.23042 1.17065
C 13.12993 -0.56247 1.61818
H 13.03666 -0.92019 2.65059
H 13.34873 -1.43653 0.99158
H 14.00916 0.09218 1.58072
C 11.37655 1.50073 2.05943
H 11.12039 1.19334 3.08057
H 12.19204 2.22978 2.13608
H 10.50261 2.02717 1.65215
C 11.13908 0.67698 -1.18992
O 12.05847 0.70647 -0.30409
H 10.10197 0.86671 -0.90466
C 11.53085 0.94868 -2.61068
H 10.77538 0.58272 -3.30829
H 11.61305 2.03707 -2.73897
H 12.50329 0.50783 -2.83842
O 10.59207 -0.70936 1.11782
H 8.16774 0.03438 1.23901
O 7.84824 0.34728 -0.70297
C 7.33729 -0.11152 -1.94316
H 7.50688 0.69513 -2.66094
H 7.84945 -1.01235 -2.30752
H 6.25956 -0.31578 -1.90391
H 8.61376 -2.39431 1.13343
C 6.32427 -0.96064 0.75141
H 5.91388 -1.60452 -0.03755
H 6.36025 -1.58149 1.65514
C 5.40679 0.24316 0.98551
H 4.38942 -0.07826 1.22869
H 5.77368 0.85681 1.81530
H 5.36114 0.88542 0.10169

TS-in-*syn*-minor

38
TS-Boat-syn-in.xyz
C 10.79900 -1.48700 -1.01500
C 10.23300 -1.21000 0.21800
C 8.80500 -1.60500 0.52700
C 7.78700 -0.43500 0.57300
B 12.06400 0.35500 1.02200
C 13.39000 -0.51900 1.28400
C 11.87300 1.66000 1.94200
C 11.12100 0.76200 -1.26000
O 12.13300 0.80700 -0.48600
C 11.35000 0.96800 -2.72600
O 10.80000 -0.49900 1.15700
O 7.82600 0.33600 -0.63300
C 7.20600 -0.26800 -1.75100
C 7.95900 0.56400 1.72200
C 7.89500 -0.06100 3.11800
H 10.21200 -2.05600 -1.72800
H 11.87000 -1.49500 -1.15800
H 8.79500 -2.10700 1.50100
H 13.43300 -0.84600 2.33000
H 13.45700 -1.42100 0.66200
H 14.29200 0.07500 1.09300
H 11.72100 1.37700 2.99100
H 12.75900 2.30500 1.90700
H 11.01300 2.27400 1.64400
H 10.12200 0.97500 -0.87300
H 10.51300 0.58900 -3.31500
H 11.43100 2.04900 -2.90900
H 12.28300 0.50100 -3.04500
H 6.78800 -0.89500 0.66500
H 7.20500 0.47200 -2.55500
H 7.73900 -1.16300 -2.10200
H 6.16500 -0.55000 -1.53000
H 7.16200 1.30800 1.60600
H 8.90900 1.08900 1.60000
H 8.47200 -2.34200 -0.20900
H 7.88700 0.72100 3.88400
H 6.99100 -0.66600 3.25400
H 8.76500 -0.69500 3.31000

Molecular Geometries for Structures Reproduced in Figure 8

. **Original Report:** M. N. Grayson, S. C. Pellegrinet, and J. M. Goodman, *J. Am. Chem. Soc.*, 2012, **134**, 2716–2722.

Method: M06-2X/6-31G(d,p)//ONIOM(B3LYP/6-31G(d,p):UFF)

TS-*re*-major

155
TS-13-Re.xyz
C 0.863616 3.288595 0.000375
C 1.721780 2.170602 0.108055
C 3.007519 2.200812 -0.459047
C 3.431836 3.334857 -1.157876
H 4.434814 3.362850 -1.566756
C -3.109812 3.282007 1.645393
C -0.459695 3.250872 0.696768
C -1.350508 2.208025 0.372312
C -2.689778 2.259608 0.788298
H -4.146571 3.321273 1.959296
O 1.365191 1.097349 0.882224
P 0.135004 0.185163 0.332718
O -0.928830 1.176083 -0.422500
C 5.710558 -1.149900 -0.118983
C 5.419743 -0.358144 0.995264
C 4.545116 0.740412 0.909984
C 3.918479 1.031565 -0.335832
C 4.194447 0.215042 -1.472728
C 5.103827 -0.849607 -1.343507
H 5.899131 -0.588111 1.937852
H 5.344637 -1.454232 -2.206569
C -5.678793 -0.480305 -0.680893
C -5.189178 -0.601356 0.622757
C -4.172371 0.241346 1.107285
C -3.678630 1.281014 0.269748
C -4.173387 1.412987 -1.059093
C -5.149475 0.509835 -1.516725
H -5.603609 -1.365415 1.267111
H -5.525468 0.596940 -2.526816
C 4.335622 1.603115 2.155965
H 3.630407 2.433549 1.956945
C 3.727000 0.785567 3.304249
H 4.440603 0.023330 3.681369
H 3.457538 1.457999 4.146515
H 2.804216 0.270008 2.964006
C 5.646921 2.269318 2.591541
H 6.393737 1.517262 2.922355
H 6.073741 2.852799 1.747729
H 5.456546 2.967745 3.434400
C 6.688789 -2.305452 0.006063
H 7.073322 -2.357253 1.049273
C 6.002811 -3.646166 -0.281103
H 5.608802 -3.684492 -1.318781
H 6.724106 -4.480092 -0.145795
H 5.164425 -3.800500 0.429552
C 7.905609 -2.102246 -0.905161
H 7.617196 -2.140175 -1.976891
H 8.379052 -1.119439 -0.694320
H 8.658422 -2.897028 -0.715995
C 3.560035 0.471018 -2.842390
H 2.737795 1.210848 -2.760270
C 4.595355 1.048365 -3.815291
H 5.412613 0.319953 -4.004477
H 5.039817 1.976952 -3.402081
H 4.110799 1.298165 -4.783313
C 2.923584 -0.796489 -3.436992
H 3.692641 -1.510989 -3.797921
H 2.298241 -1.310928 -2.683810
H 2.277154 -0.525646 -4.298970
C -3.709218 2.527089 -2.000742
H -2.980366 3.197999 -1.505283
C -2.994429 1.952028 -3.230245
H -2.126997 1.336157 -2.913162
H -3.677775 1.323613 -3.839149
H -2.612786 2.777201 -3.868708
C -4.880058 3.428044 -2.415410
H -5.612376 2.880054 -3.044575
H -5.398904 3.815087 -1.512310
H -4.503078 4.296680 -2.996657
C -3.644476 0.015219 2.523387
H -2.736960 0.627799 2.703535
C -4.687112 0.440640 3.563282
H -4.962709 1.505845 3.416369
H -5.605818 -0.178707 3.483053
H -4.271171 0.328693 4.587344
C -3.221962 -1.446456 2.749660
H -4.102768 -2.114056 2.853925
H -2.606214 -1.812531 1.901736
H -2.622894 -1.524528 3.681615
C -6.784524 -1.403065 -1.164258
H -7.076644 -2.096351 -0.343965
C -8.040922 -0.609035 -1.542510
H -8.362465 0.024141 -0.687985
H -7.855590 0.042216 -2.422805
H -8.870551 -1.305547 -1.789054
C -6.310949 -2.273687 -2.333235
H -6.033512 -1.654157 -3.212106
H -5.431830 -2.874173 -2.022077
H -7.116413 -2.976214 -2.636056
C -0.859572 4.234248 1.636299
C -2.200335 4.244897 2.102479
C -2.618440 5.230261 3.010721
C -1.715376 6.187609 3.475407
C -0.389564 6.169104 3.042110
C 0.040616 5.200190 2.132834
H -3.641954 5.256162 3.365726
H -2.042710 6.942200 4.178937
H 0.309082 6.907382 3.414150
H 1.080248 5.206514 1.832854
C 1.255983 4.386904 -0.810138
C 2.562525 4.411615 -1.363337
C 2.979006 5.508393 -2.134702
C 2.103617 6.565103 -2.386078
C 0.804895 6.533073 -1.880056
C 0.377964 5.453361 -1.104050
H 3.977688 5.542134 -2.554092
H 2.428647 7.404953 -2.986521
H 0.123686 7.346835 -2.093092
H -0.644448 5.457568 -0.751942
O -0.405772 -0.594421 1.470612
O 0.709922 -0.593449 -0.900123
H 0.254123 -1.511347 -1.082433
B 0.226475 -4.131346 -1.064152
C -1.274464 -2.886140 -2.448735
C -1.548941 -4.438453 -2.513689
C -2.683313 -4.885574 -1.575764
H -2.671771 -5.977310 -1.517710
H -3.664004 -4.571870 -1.944859
H -2.547702 -4.495719 -0.564569

C -1.807194 -4.974644 -3.921947
H -0.954819 -4.796466 -4.579826
H -2.697375 -4.514352 -4.364319
H -1.973850 -6.054485 -3.873324
C -0.538676 -2.346277 -3.683146
H -1.190470 -2.329413 -4.561478
H 0.340391 -2.952503 -3.917048
H -0.210178 -1.321327 -3.488332
C -2.490272 -2.009836 -2.142254
H -3.218778 -2.058443 -2.958103
H -2.179058 -0.967114 -2.035021
H -2.980143 -2.306764 -1.213687
O -0.314563 -5.004113 -2.037944
O -0.360719 -2.800689 -1.317744
C 1.980514 -4.124236 -1.124936
H 2.226626 -3.776568 -2.128255
H 2.244321 -5.173888 -0.984584
C 2.366794 -3.245431 -0.062999
C 2.306644 -3.602101 1.274368
H 2.552841 -2.870149 2.037400
H 2.440397 -4.641309 1.558627
H 2.453931 -2.185158 -0.292710
C 0.225503 -3.735388 1.321000
O -0.038019 -4.565652 0.341550
H 0.021703 -2.677344 1.161437
C -0.453699 -5.009122 5.339303
C -0.369893 -3.649816 5.029240
C -0.136972 -3.245607 3.716297
C 0.011107 -4.207386 2.704863
C -0.079702 -5.571596 3.016726
C -0.311073 -5.967814 4.331186
H -0.636320 -5.322576 6.363128
H -0.493004 -2.904331 5.809200
H -0.089827 -2.191884 3.454519
H 0.017178 -6.303855 2.221750
H -0.386171 -7.024203 4.572030

TS-*re*-major

155
TS-13-Si.xyz
B -1.099212 -4.121921 -1.168283
C 1.160922 -3.921543 -1.845190
C 0.695396 -5.424782 -1.808971
C 1.077547 -6.144691 -0.503315
H 0.540427 -7.096258 -0.464748
H 2.150918 -6.353117 -0.451182
H 0.790588 -5.563886 0.376016
C 1.159056 -6.262570 -3.002047
H 0.781951 -5.864695 -3.945460
H 2.252364 -6.309163 -3.051031
H 0.782242 -7.283996 -2.896065
C 1.163648 -3.351543 -3.271750
H 2.051156 -3.658359 -3.833335
H 0.276650 -3.680037 -3.818931
H 1.137980 -2.261438 -3.228717
C 2.472085 -3.634097 -1.117927
H 3.319698 -4.093934 -1.635712
H 2.645340 -2.558232 -1.063848
H 2.440293 -4.008230 -0.094195
O -0.734361 -5.301318 -1.867263
O 0.090750 -3.254093 -1.114928
C -2.467876 -3.353826 -1.923658
H -2.113467 -3.057675 -2.911367
H -3.217236 -4.145252 -1.986523
C -2.807137 -2.266461 -1.051519
C -3.462302 -2.448134 0.148038
H -3.632730 -1.608517 0.804774
H -4.117633 -3.302870 0.281832
H -2.317627 -1.307635 -1.216597
C -1.809648 -3.439154 1.047369
O -1.602072 -4.421052 0.216805
H -1.150926 -2.572442 1.010872
C -3.383749 -4.296173 4.921199
C -2.648737 -3.130467 4.696165
C -2.143789 -2.858485 3.426181
C -2.377493 -3.754848 2.372424
C -3.104919 -4.932027 2.604258
C -3.606599 -5.197575 3.874816
H -3.778432 -4.507029 5.910905
H -2.465675 -2.435248 5.509958
H -1.560924 -1.961568 3.237044
H -3.259195 -5.628121 1.786158
H -4.169579 -6.108801 4.054275
C 1.398635 3.141639 -0.145975
C 2.039197 1.922826 0.183238
C 3.433240 1.798410 0.005300
C 4.170875 2.865755 -0.520445
H 5.246307 2.769220 -0.622866
C -2.714895 4.046751 0.639062
C -0.006062 3.382230 0.301592
C -1.011271 2.476817 -0.094440
C -2.370317 2.819321 0.058483
H -3.760448 4.319405 0.725579
O 1.369345 0.932418 0.863707
P 0.092404 0.215349 0.152101
O -0.669266 1.329775 -0.763998
C 5.473298 -1.871300 1.013876
C 4.949324 -1.053353 2.018409
C 4.293559 0.154168 1.718333
C 4.140410 0.538608 0.354415
C 4.701371 -0.274648 -0.676189
C 5.344954 -1.474543 -0.322078
H 5.076111 -1.350169 3.051357
H 5.771419 -2.099597 -1.094592
C -5.601785 0.221101 -1.154207
C -5.380737 0.495063 0.198254
C -4.316055 1.312316 0.621330
C -3.455010 1.891443 -0.360298
C -3.688094 1.631254 -1.742618
C -4.748946 0.783976 -2.109216
H -6.052959 0.069943 0.931979
H -4.935335 0.585270 -3.155576
C 3.836551 1.041126 2.878989
H 3.327042 1.953263 2.511761
C 2.828944 0.314261 3.782069
H 3.310210 -0.515705 4.340505
H 2.400073 1.026168 4.519281
H 1.995744 -0.102098 3.178393
C 5.038116 1.538887 3.692282
H 5.564809 0.698760 4.192083
H 5.754228 2.066003 3.025929
H 4.699563 2.254287 4.472072
C 6.211882 -3.146421 1.384906
H 6.221893 -3.262624 2.491825
C 5.508171 -4.383517 0.816655
H 5.499600 -4.366935 -0.293507
H 6.030248 -5.305383 1.150781
H 4.463222 -4.427528 1.188939
C 7.676199 -3.089141 0.932300
H 7.754875 -3.069652 -0.175292
H 8.166357 -2.180872 1.343778
H 8.224868 -3.979166 1.307826
C 4.682792 0.129993 -2.155840
H 4.146162 1.083250 -2.312279
C 6.107685 0.346986 -2.682215
H 6.678740 -0.605024 -2.704643
H 6.645657 1.073563 -2.036687
H 6.074570 0.759987 -3.713106
C 3.929496 -0.882803 -3.020003

H 4.367880 -1.899511 -2.946655
H 2.871496 -0.906408 -2.697843
H 3.948715 -0.568676 -4.085515
C -2.870734 2.288860 -2.856538
H -2.075656 2.938843 -2.443966
C -2.166894 1.237762 -3.727730
H -1.579563 0.539622 -3.095117
H -2.897297 0.647630 -4.319944
H -1.468576 1.736892 -4.432947
C -3.748951 3.210309 -3.713039
H -4.521241 2.636174 -4.266878
H -4.253467 3.960506 -3.067041
H -3.121653 3.754611 -4.451087
C -4.155607 1.576472 2.123911
H -3.261429 2.193903 2.332502
C -5.361578 2.347848 2.676286
H -5.528197 3.273818 2.086684
H -6.284229 1.731058 2.639927
H -5.175842 2.639597 3.732085
C -3.931687 0.283909 2.915991
H -4.788401 -0.414918 2.820402
H -3.010927 -0.211797 2.555136
H -3.789106 0.515161 3.993312
C -6.784335 -0.637134 -1.572090
H -7.327408 -0.989398 -0.666692
C -7.784491 0.176610 -2.402318
H -8.099513 1.081093 -1.839080
H -7.339928 0.492669 -3.369836
H -8.689196 -0.432883 -2.612624
C -6.331643 -1.889402 -2.333300
H -5.809889 -1.623739 -3.276690
H -5.649229 -2.493296 -1.701735
H -7.211021 -2.520273 -2.583761
C -0.364249 4.535204 1.049135
C -1.731994 4.878362 1.182138
C -2.100914 6.047229 1.866969
C -1.125918 6.861172 2.444819
C 0.221243 6.513150 2.351308
C 0.603573 5.358801 1.664468
H -3.143835 6.324629 1.965533
H -1.416384 7.757828 2.976929
H 0.972944 7.138995 2.814816
H 1.656237 5.110802 1.631863
C 2.123171 4.137655 -0.856114
C 3.525409 4.005649 -1.002420
C 4.265328 5.011609 -1.644445
C 3.620980 6.131646 -2.170309
C 2.235836 6.253108 -2.068532
C 1.488661 5.265513 -1.423034
H 5.340235 4.924862 -1.751401
H 4.195446 6.900804 -2.670201
H 1.737765 7.114879 -2.493827
H 0.414184 5.385678 -1.386259
O -0.745769 -0.423756 1.194857
O 0.655560 -0.715463 -0.989541
H 0.365599 -1.690707 -0.968148

Molecular Geometries for Structures Reproduced in Figure 9

. **Original Report:** H. Yang, S. Mahapatra, P. H.-Y. Cheong, and R. G. Carter, *J. Org. Chem.*, 2010, **75**, 7279–7290.

Method: SCS-MP2/cc-pV∞Z//B3LYP/6-31G(d)

TS-*re*-major

52
TS-Anti-Re.xyz
C 1.290423 -0.470026 -0.285804
H -1.730575 4.286185 -1.406021
H -1.836921 1.520675 2.186888
C -0.077845 1.125844 3.399027
H -1.244430 3.638326 -2.982389
C -2.522049 2.296677 -1.785014
H -2.375939 1.504444 -2.528243
H -3.542622 2.672396 -1.886080
H -1.157662 -0.071971 1.950187
H 0.006618 2.188003 3.668775
C 1.278613 1.366854 0.839156
H 1.784759 1.904055 0.042215
N -0.815971 1.925092 -0.173672
H 0.907426 -1.096218 0.523830
C -0.887731 0.981959 2.099702
C -0.125046 1.483705 0.889140
O 0.502812 -0.268998 -1.302011
C 2.085128 1.238158 2.118974
H -2.834553 2.309408 0.368650
C -2.272337 1.729612 -0.372110
C -0.222382 2.730080 -1.270995
C -2.779234 0.274593 -0.238089
H 1.882502 0.608914 4.18272
C 2.741613 -0.588646 -0.549537
H 1.233623 -0.545407 3.022870
O -3.956057 0.121594 0.082029
H -0.563671 -0.468226 -1.006699
H 0.476017 3.460654 -0.851088
C -1.441440 3.373037 -1.939680
H 0.320145 2.081315 -1.962421
C 1.322180 0.527312 3.243830
H 2.370147 2.246041 2.460142
H 3.029103 0.722815 1.906106
H -0.626180 0.635004 4.210549
C 5.484688 -0.881005 -1.052837
C 3.560241 -1.285911 0.351705
C 3.310340 -0.051703 -1.715705
C 4.672344 -0.195500 -1.962404
C 4.925120 -1.430361 0.101469
H 3.120449 -1.736729 1.237816
H 2.670023 0.458871 -2.428093
H 5.103596 0.219662 -2.869372
H 5.547503 -1.979255 0.802667
H 6.547259 -0.993989 -1.249905
N -1.858194 -0.681883 -0.542657
S -2.137274 -2.265522 -0.068173
O -2.432509 -2.319470 1.373153
O -0.979288 -3.015765 -0.578718
C -3.610610 -2.799292 -0.958496
H -4.421015 -2.122623 -0.685824
H -3.399591 -2.764126 -2.028923
H -3.822225 -3.823561 -0.642924

TS-*si*-minor

52
TS-Anti-Si.xyz
C -1.281792 -0.189636 -1.618613
H 3.211079 -3.318268 -2.036715
H 0.043167 -1.854598 2.379740
H -4.191424 -2.113079 1.617339
H 2.956669 -1.566757 -1.924518

C 3.136268 -2.515954 0.019427
H 4.101543 -2.044972 0.214148
H 3.169070 -3.537220 0.418027
H -0.761532 -0.428058 1.760803
H -3.164615 -3.366380 -0.151264
C -1.528630 -2.077241 -0.630687
H -1.299598 -2.616201 -1.545708
N 0.808548 -2.083420 -0.112028
C -2.118532 0.785023 -0.876461
C -0.756452 -1.525839 1.711433
C -0.464661 -1.949224 0.286593
O -0.002319 -0.059017 -1.819527
C -3.237339 -1.718636 1.247605
H 1.870495 -2.057860 1.730139
C 1.995281 -1.732029 0.696360
C 1.205934 -2.717387 -1.399585
C 2.342105 -0.218022 0.788599
H -2.034402 -3.163316 2.3235435
H -3.343203 -0.629759 1.197647
H -1.800748 -0.609495 -2.484466
O 3.206167 0.066211 1.619860
H 0.688511 0.297830 -1.018076
H 0.924779 -3.778896 -1.361843
C 2.724252 -2.529027 -1.457000
H 0.702099 -2.239656 -2.236385
H -3.656449 -1.851308 -0.876706
C -2.956311 -2.284915 -0.151082
H -2.301483 -1.665078 3.209911
C -2.104230 -2.072209 2.211774
C -3.809117 2.638444 0.390071
C -1.627018 1.616404 0.144028
C -3.465356 0.910948 -1.262043
C -4.306026 1.825717 -0.631492
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H -3.848720 0.301496 -2.077021
H -5.342459 1.913362 -0.945813
H -2.062669 3.176102 1.545287
H -4.459891 3.358816 0.878206
N 1.713443 0.606531 -0.087880
S 1.989618 2.270719 0.015512
O 1.500224 2.784266 1.305261
O 1.426169 2.819538 -1.225806
C 3.778482 2.499851 -0.038228
H 4.216083 1.976102 0.810287
H 4.148951 2.111509 -0.988843
H 3.946570 3.577667 0.022327

Molecular Geometries for Structure Reproduced in Figure 10

. **Original Report:** O. Pattawong, T. J. L. Mustard, R. C. Johnston, and P. H.-Y. Cheong, *Angew. Chem., Int. Ed.*, 2013, **52**, 1420–1423.

Method: SCS-MP2/def2-∞//B3LYP/6-31G(d)

TS-*si*-minor

71
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C 1.231968 -2.422213 1.071765
C -0.134150 -2.174076 1.168054
C 1.744160 0.007842 -1.863864
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C 0.734422 3.188551 -0.273065
C 2.112845 2.806316 -0.131319
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H 4.077023 2.569953 -1.009532
H 2.937208 3.462036 -2.020838
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C 5.510344 -2.884942 0.537210
H 3.659869 -4.019103 0.828446
H 3.844499 -2.664782 1.959473
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H 5.975177 -2.033585 1.047928
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C -3.201110 -1.386229 -0.288580
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C -2.801054 -2.224593 -1.484485
H -1.768382 -2.573950 -1.423073
H -3.432195 -3.121266 -1.561933
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H -4.504223 -0.109137 1.785285
C -6.879744 -0.982584 -1.136020
H -5.177445 -1.828729 -2.101968
C -7.387974 -0.324721 -0.016391
H -6.885815 0.493943 1.914486
H -7.536989 -1.236101 -1.965641
H -8.440931 -0.060477 0.04288