Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for "Two-photon absorption of fluorescent protein chromophores incorporating non-canonical amino acids: TDDFT screening and classical dynamics"

M. Alaraby Salem[a] **and Alex Brown**[a*]

Table S1 Coordinates of the optimized models at the PBE0/6-31+G(d,p) level of theory in the gas phase.

Coordinates for Model Number 1a			
C	-2.004341	2.044783	0.000026
C	-0.745110	1.457117	0.000033
C	-0.612638	0.054944	0.000013
C	0.669150	-0.626807	0.000019
C	-1.774466	-0.731069	-0.000014
C	-3.037302	-0.133378	-0.000020
C	-3.155698	1.262783	0.000000
C	3.131168	-0.975476	0.000050
C	3.598382	1.220328	0.000106
C	1.917459	-0.105674	0.000048
C	-4.212836	-0.951833	-0.000046
N	4.161024	-0.033060	0.000089
N	2.304977	1.238482	0.000083
N	-5.167801	-1.613413	-0.000067
H	0.151245	2.067632	0.000054
H	-1.697179	-1.814411	-0.000029
H	0.639826	-1.715793	-0.000004
H	4.217340	2.110997	0.000135
H	5.142484	-0.261640	0.000099
H	-4.140390	1.718765	-0.000006
H	-2.091697	3.126949	0.000041
O	3.254725	-2.183013	0.000025
Coordinates for Model Number 1b			
C	-2.669828	0.350148	-0.000023
C	-1.274237	0.319087	-0.000006
C	-0.602774	-0.915019	-0.000028
C	0.844609	-1.027956	-0.000011
C	-1.364114	-2.097405	-0.000066
C	-2.753961	-2.059019	-0.000082
C	-3.417113	-0.837907	-0.000060
C	3.241065	-0.355063	0.000048
C	2.779450	1.842203	0.000110
C	1.779265	-0.050192	0.000032
C	-3.350363	1.611677	0.000000

N	3.801391	0.923178	0.000100
N	1.589696	1.335019	0.000072
N	-3.910944	2.629119	0.000019
H	-0.702029	1.240155	0.000024
H	-0.851822	-3.056129	-0.000084
H	-3.323106	-2.983389	-0.000112
H	1.251251	-2.038599	-0.000035
H	2.984492	2.907228	0.000148
H	4.791234	1.112035	0.000124
H	-4.501319	-0.792525	-0.000073
O	3.841875	-1.410056	0.000023
Coordinates for Model Number 2a			
C	-2.382542	0.051571	0.000094
C	-0.991872	-0.031375	0.000047
C	-0.205649	1.135977	0.000012
C	1.244558	1.118170	-0.000038
C	-0.854918	2.382560	0.000024
C	-2.243750	2.467023	0.000070
C	-3.007798	1.307005	0.000105
C	3.574994	0.250403	-0.000119
C	2.939021	-1.903626	-0.000098
C	2.096025	0.065595	-0.000067
C	-3.249785	-1.170363	0.000133
C	-2.594480	-2.528806	0.000123
N	4.030969	-1.069393	-0.000135
N	1.794334	-1.301497	-0.000057
H	-0.487289	-0.990847	0.000038
H	-0.256619	3.290393	-0.000004
H	1.738040	2.089581	-0.000056
H	3.058997	-2.981567	-0.000102
H	5.002631	-1.336190	-0.000169
H	-4.093013	1.340395	0.000141
H	-1.956509	-2.655953	-0.881072
H	-1.956458	-2.655943	0.881284
H	-3.373475	-3.291652	0.000150
H	-2.727314	3.439333	0.000079
O	4.262559	1.252160	-0.000142
O	-4.463720	-1.060596	0.000173
Coordinates for Model Number 2b			
C	-1.594319	2.245517	0.054927
C	-0.359102	1.612099	0.039753
C	-0.285121	0.204213	-0.001070
C	0.965875	-0.531420	-0.019660
C	-1.479094	-0.528822	-0.025012

C	-2.722921	0.104843	-0.009683
C	-2.774339	1.502254	0.030404
C	3.409547	-0.993011	-0.027753
C	3.977557	1.178966	0.036158
C	2.238125	-0.070178	-0.003598
C	-3.951646	-0.750123	-0.037273
C	-5.305287	-0.082975	-0.021817
N	4.481824	-0.099020	0.000090
N	2.686701	1.255346	0.035688
H	-1.640487	3.330194	0.086460
H	0.560244	2.187434	0.059063
H	-1.462264	-1.615130	-0.056561
H	0.883940	-1.617325	-0.051350
H	4.637148	2.039566	0.062573
H	5.451205	-0.373810	-0.005080
H	-3.730499	2.016361	0.042573
H	-5.428482	0.573113	-0.890401
H	-5.429176	0.533021	0.875550
H	-6.074486	-0.855371	-0.039214
O	3.481814	-2.205101	-0.062224
O	-3.855508	-1.964365	-0.071999

Coordinates for Model Number 3

C	-1.170720	-0.877053	-0.543579
C	0.192925	-0.693181	-0.363255
C	0.726344	0.601754	-0.212399
C	2.140312	0.868165	-0.032125
C	-0.152117	1.699465	-0.246914
C	-1.517360	1.523531	-0.425218
C	-2.009616	0.232593	-0.565547
C	4.583936	0.477726	0.209600
C	4.402642	-1.752992	0.026354
C	3.181939	0.005645	0.020789
C	-4.173226	-0.259826	0.209465
N	5.296048	-0.722760	0.199603
N	3.166337	-1.389509	-0.083228
H	-1.589262	-1.869638	-0.669973
H	0.863485	-1.545192	-0.344050
H	0.246531	2.704298	-0.135756
H	-2.198923	2.366686	-0.459185
H	2.423487	1.914751	0.075740
H	4.738767	-2.783490	-0.011809
H	6.295743	-0.792788	0.304566
O	5.047936	1.592659	0.342640
O	-3.371880	0.065860	-0.823905

F	-4.155392	0.659125	1.188817
F	-3.844059	-1.434137	0.774276
F	-5.414531	-0.353563	-0.255981
Coordinates for Model Number 4			
C	-1.850017	-1.008352	0.000038
C	-0.479634	-0.791376	0.000015
C	0.028156	0.522247	0.000046
C	1.442511	0.840590	0.000050
C	-0.884880	1.592234	0.000091
C	-2.252389	1.358400	0.000103
C	-2.769692	0.054788	0.000078
C	3.911215	0.549125	0.000049
C	3.803954	-1.693714	-0.000038
C	2.517764	0.017483	0.000019
N	4.667839	-0.623538	0.000010
N	2.549414	-1.381283	-0.000035
H	-2.231277	-2.025721	0.000028
H	0.215182	-1.624074	-0.000018
H	-0.507502	2.611969	0.000126
H	-2.916859	2.221520	0.000166
H	1.694943	1.900592	0.000091
H	4.176353	-2.712412	-0.000075
H	5.674938	-0.652087	0.000017
H	-4.954527	1.622812	-0.000635
H	-5.676045	-1.623235	0.000495
O	4.339427	1.686556	0.000098
O	-5.283516	0.721102	-0.000253
O	-4.716291	-1.546364	0.000542
B	-4.309587	-0.244123	0.000113
Coordinates for Model Number 5			
C	2.556015	-1.211939	0.000033
C	1.202508	-0.906217	0.000054
C	0.768063	0.434352	0.000020
C	-0.628394	0.817470	0.000040
C	1.738081	1.454029	-0.000036
C	3.095123	1.160997	-0.000058
C	3.477513	-0.172399	-0.000023
C	-3.107585	0.628305	0.000104
C	-3.092582	-1.618008	0.000170
C	-1.738785	0.041502	0.000089
N	-3.911293	-0.513559	0.000157
N	-1.826531	-1.355684	0.000133
H	2.905915	-2.238886	0.000059
H	0.461720	-1.698224	0.000097

H	1.417985	2.492692	-0.000063
H	3.849427	1.940536	-0.000102
H	-0.835365	1.887312	0.000013
H	-3.505466	-2.620920	0.000210
H	-4.918709	-0.500774	0.000182
O	-3.491584	1.781849	0.000079
F	4.789792	-0.466502	-0.000044
Coordinates for Model Number 6			
C	-0.816519	-0.519193	0.000507
C	0.569334	-0.491706	0.000271
C	1.255863	0.738138	-0.000270
C	2.701324	0.844889	-0.000530
C	0.503282	1.927974	-0.000570
C	-0.881620	1.896984	-0.000321
C	-1.555902	0.670675	0.000218
C	5.098300	0.180362	-0.000561
C	4.649835	-2.019309	0.000545
C	3.638924	-0.132255	-0.000215
C	-3.045721	0.708497	0.000485
C	-5.594086	-0.282195	0.001151
C	-6.548255	-1.464394	-0.000164
N	5.666664	-1.094665	-0.000031
N	3.457183	-1.518842	0.000462
H	-1.323793	-1.479728	0.000942
H	1.139579	-1.413752	0.000512
H	1.020640	2.884087	-0.000996
H	-1.465417	2.811904	-0.000537
H	3.110910	1.854595	-0.001038
H	4.861493	-3.083072	0.001029
H	6.657624	-1.276965	-0.000067
H	-5.730808	0.349374	0.882785
H	-5.730471	0.351217	-0.879225
H	-6.415172	-2.091824	-0.886850
H	-6.415326	-2.093634	0.885281
H	-7.579906	-1.098662	0.000103
O	5.695224	1.238162	-0.001140
O	-3.671033	1.750982	0.000468
S	-3.873311	-0.870320	0.000792
Coordinates for Model Number 7			
C	-0.486788	-0.513583	-0.013210
C	0.899096	-0.486516	-0.002924
C	1.586985	0.739154	-0.092247
C	3.032514	0.845173	-0.083714
C	0.835617	1.925637	-0.192120

C	-0.549233	1.895534	-0.199073
C	-1.225033	0.673049	-0.111435
C	5.428300	0.183812	0.013845
C	4.977193	-2.005936	0.217929
C	3.968705	-0.127761	0.021174
C	-2.715401	0.712486	-0.119274
C	-5.282238	-0.327287	-0.109726
C	-5.689103	-0.012137	1.322699
C	-6.142283	-1.417677	-0.737037
N	5.995044	-1.085233	0.145115
N	3.785317	-1.508195	0.150613
H	-0.996334	-1.469424	0.065844
H	1.468117	-1.405747	0.078143
H	1.354141	2.878468	-0.262806
H	-1.131624	2.808438	-0.271811
H	3.443284	1.850643	-0.170533
H	5.187579	-3.064701	0.324262
H	6.985617	-1.266336	0.179683
H	-5.327101	0.586113	-0.711956
H	-5.608137	-0.900790	1.957315
H	-5.068051	0.781280	1.745081
H	-6.731420	0.327829	1.342212
H	-5.864489	-1.604489	-1.778000
H	-6.060467	-2.360101	-0.184344
H	-7.192909	-1.109378	-0.711817
O	6.026304	1.237061	-0.077860
O	-3.335613	1.757909	-0.086444
S	-3.534490	-0.869236	-0.201942

Coordinates for Model Number 8

C	2.301627	-1.104416	0.000052
C	0.942094	-0.839654	0.000048
C	0.473653	0.488701	0.000001
C	-0.934591	0.836107	0.000000
C	1.414168	1.535647	-0.000045
C	2.775586	1.277652	-0.000042
C	3.226883	-0.049042	0.000007
C	-3.408851	0.570648	0.000036
C	-3.322852	-1.672156	0.000105
C	-2.018358	0.025065	0.000036
C	4.630370	-0.325955	0.000013
N	-4.176156	-0.595440	0.000082
N	-2.064388	-1.372205	0.000081
N	5.770902	-0.549425	0.000017
H	2.660057	-2.128737	0.000089

H	0.223531	-1.651522	0.000083
H	1.064666	2.564599	-0.000082
H	3.493119	2.091581	-0.000077
H	-1.169800	1.899701	-0.000032
H	-3.703823	-2.687688	0.000141
H	-5.183654	-0.615993	0.000095
O	-3.823146	1.711515	0.000003
Coordinates for Model Number 9			
C	1.726088	-1.194310	-0.000061
C	0.367394	-0.909306	-0.000080
C	-0.076342	0.425919	-0.000050
C	-1.472195	0.808823	-0.000052
C	0.894485	1.445168	-0.000010
C	2.249080	1.147717	0.000009
C	2.692816	-0.181046	-0.000017
C	-3.951882	0.628373	-0.000239
C	-3.945854	-1.618255	0.000039
C	-2.586067	0.036573	-0.000096
C	4.168339	-0.518600	-0.000001
C	4.866325	-0.003229	1.262754
C	4.866374	-0.003140	-1.262692
N	-4.760354	-0.510057	0.000202
N	-2.679139	-1.360525	-0.000165
H	-0.365388	-1.708905	-0.000115
H	0.571307	2.483677	0.000012
H	-1.677165	1.879271	-0.000050
H	-4.363358	-2.619291	0.000236
H	-5.767601	-0.492483	0.000829
H	2.970196	1.961288	0.000044
H	4.245474	-1.614089	-0.000038
H	4.387668	-0.389198	2.168003
H	5.917571	-0.311057	1.272445
H	4.840178	1.091101	1.310864
H	4.387752	-0.389044	-2.167988
H	4.840229	1.091193	-1.310726
H	5.917620	-0.310967	-1.272365
H	2.050061	-2.232865	-0.000083
O	-4.333682	1.783416	0.000207
Coordinates for Model Number 10			
C	1.458448	-0.996653	-0.000049
C	0.089605	-0.769091	-0.000011
C	-0.419834	0.543763	0.000020
C	-1.835284	0.853307	0.000044
C	0.492949	1.613746	0.000019

C	1.864608	1.396937	-0.000019
C	2.336655	0.086949	-0.000057
C	-4.301596	0.530779	0.000057
C	-4.164109	-1.710879	0.000010
C	-2.901864	0.018721	0.000035
N	-5.041919	-0.652876	0.000039
N	-2.913863	-1.380578	0.000006
H	1.845422	-2.010178	-0.000075
H	-0.602867	-1.603868	-0.000009
H	0.116983	2.633801	0.000045
H	2.556085	2.232676	-0.000024
H	-2.096056	1.911092	0.000068
H	-4.522178	-2.734678	-0.000009
H	-6.048566	-0.695350	0.000046
O	-4.745879	1.661923	0.000082
BR	4.202032	-0.230176	-0.000128

Coordinates for Model Number 11

C	-1.940372	-1.077351	-0.001470
C	-0.575118	-0.828797	0.000937
C	-0.096791	0.494895	-0.011569
C	1.312487	0.835729	-0.008171
C	-1.032222	1.548364	-0.027093
C	-2.393053	1.294003	-0.028703
C	-2.865040	-0.024026	-0.015692
C	3.785823	0.572682	0.012676
C	3.703648	-1.670507	0.043535
C	2.397327	0.025412	0.010067
C	-4.344201	-0.246155	-0.017251
C	-4.871927	-1.659639	-0.007970
N	4.555325	-0.591938	0.034786
N	2.445155	-1.372405	0.029948
H	-2.285620	-2.106798	0.008416
H	0.137031	-1.646327	0.012748
H	-0.674026	2.574778	-0.037383
H	-3.118591	2.101484	-0.039751
H	1.549829	1.898949	-0.020902
H	4.086725	-2.685111	0.060671
H	5.562728	-0.609855	0.042848
H	-4.533923	-2.198238	0.884194
H	-5.961690	-1.625636	-0.017888
H	-4.517076	-2.217199	-0.881660
O	4.200611	1.714054	-0.000156
O	-5.108454	0.703857	-0.025592

Coordinates for Model Number 12

C	2.039037	-0.688645	0.000057
C	0.659508	-0.570497	0.000036
C	0.043882	0.697438	0.000007
C	-1.388930	0.888425	-0.000018
C	0.872259	1.836231	0.000001
C	2.251896	1.726630	0.000022
C	2.843602	0.459642	0.000050
C	-3.820250	0.366913	-0.000037
C	-3.503484	-1.857043	0.000027
C	-2.385601	-0.030504	-0.000008
N	-4.463043	-0.872891	-0.000011
N	-2.283992	-1.425968	0.000030
N	4.810566	-0.665569	0.000089
N	4.250140	0.431443	0.000069
N	5.448749	-1.604624	0.000109
H	2.492269	-1.676604	0.000078
H	0.035581	-1.457755	0.000042
H	0.416813	2.823188	-0.000022
H	2.887330	2.606208	0.000016
H	-1.739453	1.920324	-0.000048
H	-3.777967	-2.906275	0.000053
H	-5.463138	-0.994883	-0.000021
O	-4.357616	1.457808	-0.000074

Coordinates for Model Number 13

C	2.229640	-0.886854	0.000030
C	0.853906	-0.697061	0.000015
C	0.298332	0.595103	-0.000093
C	-1.120718	0.861182	-0.000116
C	1.185158	1.692275	-0.000187
C	2.554605	1.515373	-0.000170
C	3.089054	0.219504	-0.000061
C	-3.577230	0.481221	-0.000075
C	-3.390676	-1.758485	0.000168
C	-2.170807	0.002209	-0.000023
C	5.036680	-1.140234	0.000014
N	-4.291378	-0.719261	0.000055
N	-2.148895	-1.397880	0.000128
H	2.623784	-1.896892	0.000112
H	0.188468	-1.553856	0.000089
H	0.778643	2.700701	-0.000273
H	3.235774	2.360204	-0.000241
H	-1.410813	1.911741	-0.000225
H	-3.726099	-2.789865	0.000279
H	-5.296777	-0.782158	0.000062

H	6.113041	-0.966055	-0.000004
H	4.762006	-1.710840	0.895720
H	4.761992	-1.710944	-0.895624
O	-4.052586	1.601977	-0.000199
O	4.437838	0.139479	-0.000054
Coordinates for Model Number 14			
C	-1.521775	-0.707662	0.000010
C	-0.138518	-0.583302	0.000012
C	0.477601	0.680497	-0.000009
C	1.909178	0.871876	-0.000008
C	-0.355447	1.818948	-0.000035
C	-1.732224	1.707453	-0.000037
C	-2.326045	0.438646	-0.000015
C	4.341181	0.355341	0.000019
C	4.029534	-1.870235	0.000076
C	2.909420	-0.044311	0.000020
C	-4.330115	-0.833708	-0.000010
C	-5.770133	-0.626608	-0.000023
C	-6.970187	-0.495048	-0.000035
N	4.986852	-0.883442	0.000057
N	2.809754	-1.440849	0.000056
H	-1.958326	-1.700114	0.000027
H	0.484831	-1.471060	0.000031
H	0.097826	2.807164	-0.000052
H	-2.373617	2.582715	-0.000056
H	2.258579	1.904367	-0.000031
H	4.306385	-2.918851	0.000106
H	5.987187	-1.002545	0.000066
H	-4.039338	-1.411215	-0.889314
H	-4.039352	-1.411197	0.889311
H	-8.030007	-0.368386	-0.000045
O	4.879061	1.447056	-0.000007
O	-3.681037	0.427592	-0.000018
Coordinates for Model Number 15			
C	-0.922225	-0.611953	0.011280
C	0.463593	-0.555251	0.015213
C	1.122723	0.685386	-0.074400
C	2.566085	0.822384	-0.077096
C	0.343797	1.855362	-0.168622
C	-1.039090	1.793407	-0.171533
C	-1.691036	0.557020	-0.080234
C	4.975621	0.207406	-0.014948
C	4.569932	-1.993021	0.162609
C	3.521720	-0.133128	0.006030

C	-3.183831	0.552097	-0.077159
C	-3.893584	-0.789975	0.014194
C	-5.411525	-0.697537	-0.042171
C	-6.111223	-0.012419	1.097921
N	5.568416	-1.052141	0.090305
N	3.367328	-1.518143	0.118333
H	-1.402612	-1.583253	0.078319
H	1.053745	-1.462032	0.086155
H	0.840864	2.819507	-0.239854
H	-1.642691	2.692624	-0.244209
H	2.955829	1.836675	-0.157428
H	4.802148	-3.048897	0.249940
H	6.562714	-1.214665	0.108050
H	-3.591294	-1.278671	0.950976
H	-3.565054	-1.431086	-0.810832
H	-5.877918	1.056740	1.056521
H	-7.188359	-0.162040	1.014278
H	-5.751639	-0.387905	2.062233
O	5.550875	1.273221	-0.098770
O	-3.808106	1.596200	-0.150621
O	-6.012226	-1.186878	-0.976301

Coordinates for Model Number 16a

C	-2.128383	-1.539240	0.000096
C	-0.797600	-1.143725	0.000072
C	-0.469768	0.224954	0.000070
C	0.889643	0.718414	0.000042
C	-1.510733	1.173594	0.000092
C	-2.837303	0.779506	0.000116
C	-3.145056	-0.588895	0.000118
C	3.374446	0.740466	-0.000007
C	3.553082	-1.499461	-0.000004
C	2.062996	0.039194	0.000019
N	4.273582	-0.328358	-0.000020
N	2.269191	-1.345585	0.000019
H	-2.382070	-2.597483	0.000098
H	-0.003201	-1.881018	0.000056
H	-1.288952	2.236955	0.000090
H	1.008625	1.801666	0.000039
H	4.051431	-2.462738	-0.000011
H	5.275889	-0.227149	-0.000041
H	-4.615610	-1.833772	0.000133
H	-4.675170	1.251658	0.000150
O	3.662284	1.922757	-0.000017
O	-4.477165	-0.881285	0.000141

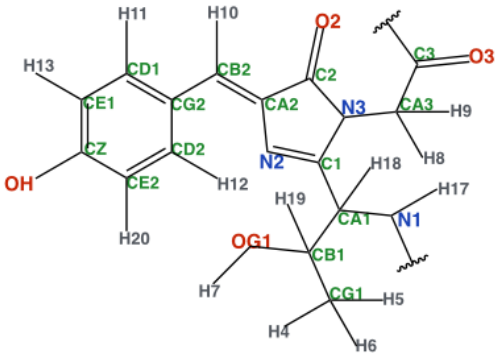
O	-3.824001	1.708450	0.000136
Coordinates for Model Number 16b			
C	2.388879	0.829189	0.000137
C	1.018223	0.642222	0.000096
C	0.478574	-0.659677	0.000030
C	-0.942016	-0.930477	-0.000008
C	1.354086	-1.759280	0.000005
C	2.730774	-1.572898	0.000045
C	3.248191	-0.283456	0.000112
C	-3.399603	-0.556890	-0.000029
C	-3.216621	1.682743	0.000085
C	-1.992593	-0.074061	0.000015
N	-4.115863	0.641276	0.000021
N	-1.974380	1.325453	0.000085
H	0.361734	1.505389	0.000117
H	0.948948	-2.766994	-0.000047
H	-1.227538	-1.981954	-0.000063
H	-3.554097	2.713451	0.000131
H	-5.121368	0.702650	0.000010
H	5.108200	-0.788084	0.000142
H	3.403120	-2.428043	0.000025
H	3.865607	2.021401	0.000220
O	-3.870359	-1.679219	-0.000093
O	4.578685	0.015551	0.000156
O	2.901647	2.083116	0.000200
Coordinates for Model Number 17			
C	-1.443721	-0.621977	-0.109757
C	-0.058642	-0.531950	-0.072378
C	0.588225	0.714875	-0.003500
C	2.022775	0.868677	0.043203
C	-0.217224	1.872954	0.025397
C	-1.595720	1.795360	-0.013291
C	-2.221720	0.543108	-0.081547
C	4.440733	0.291362	0.080727
C	4.077017	-1.922546	-0.049727
C	3.001093	-0.071415	0.021093
C	-4.271925	-0.673375	-0.185982
C	-5.732062	-0.372439	-0.258394
C	-6.644124	-0.934021	0.533012
N	5.057016	-0.961344	0.029337
N	2.868370	-1.463095	-0.057566
H	-1.906181	-1.601325	-0.157873
H	0.543581	-1.433924	-0.094545
H	0.259299	2.848780	0.079320

H	-2.215366	2.686007	0.009864
H	2.396964	1.890471	0.106978
H	4.328715	-2.976210	-0.100495
H	6.053867	-1.105171	0.048764
H	-6.030690	0.332951	-1.032452
H	-3.951268	-1.217349	-1.087705
H	-4.043508	-1.293207	0.691291
H	-7.702067	-0.717168	0.420764
H	-6.365122	-1.631928	1.319455
O	5.004391	1.367735	0.155316
O	-3.572877	0.563101	-0.111857
Coordinates for Model Number 18			
C	2.542622	-1.189107	-0.003976
C	1.193177	-0.892866	-0.003170
C	0.742111	0.444221	-0.001559
C	-0.648408	0.818073	-0.000208
C	1.718325	1.460083	-0.001021
C	3.070757	1.170319	-0.001334
C	3.508816	-0.164987	-0.002366
C	-3.127153	0.621202	0.000452
C	-3.109335	-1.626909	0.001688
C	-1.762430	0.039832	0.000963
N	-3.929463	-0.522939	0.000797
N	-1.844556	-1.358402	0.001964
N	4.850791	-0.465106	-0.049828
H	2.866453	-2.227267	-0.010277
H	0.458732	-1.691176	-0.002768
H	1.399245	2.499665	0.000659
H	3.800681	1.976113	-0.005803
H	5.132379	-1.396645	0.210128
H	-0.859826	1.887434	-0.000868
H	-3.519538	-2.630856	0.002193
H	-4.936626	-0.510310	0.000000
H	5.502754	0.256075	0.213851
O	-3.519861	1.774741	-0.000130
Coordinates for Model Number 19			
C	1.390565	0.702759	0.000410
C	3.872932	0.809039	0.000396
C	4.128517	-1.422606	-0.000246
C	2.584466	0.061422	0.000168
C	0.047037	0.165103	0.000241
C	-1.013231	1.061962	-0.000079
C	-0.235989	-1.235055	0.000372
C	-2.356852	0.627531	-0.000251

C	-1.531056	-1.679341	0.000192
C	-2.627125	-0.774851	-0.000117
C	-3.443914	1.539430	-0.000563
C	-3.973020	-1.212087	-0.000305
C	-4.740760	1.084189	-0.000736
C	-5.007343	-0.304135	-0.000605
N	4.808340	-0.226829	0.000320
N	2.840276	-1.314850	-0.000369
H	1.473239	1.789378	0.000834
H	4.660003	-2.368016	-0.000471
H	5.806726	-0.091930	0.000523
H	-0.810521	2.131107	-0.000190
H	0.594073	-1.932505	0.000619
H	-1.737555	-2.746928	0.000287
H	-3.233802	2.606191	-0.000665
H	-4.177996	-2.279805	-0.000206
H	-5.566149	1.790183	-0.000976
H	-6.036133	-0.652928	-0.000744
O	4.115306	2.000856	0.001007
Coordinates for Model Number 20			
C	-0.951254	0.385524	-0.058413
C	-3.391493	0.885348	-0.073680
C	-3.990238	-1.274647	0.112890
C	-2.242940	-0.041810	-0.007198
C	0.240059	-0.401838	-0.006253
C	1.622720	0.044696	0.004058
C	0.286806	-1.790970	-0.015331
C	2.430160	-1.113357	-0.022591
C	2.258236	1.305588	0.052117
C	3.825202	-1.093195	-0.053788
C	3.654539	1.331971	0.010784
C	4.419396	0.159705	-0.048538
N	-4.476828	0.006090	0.007114
N	-2.698421	-1.359440	0.110870
N	1.525623	2.486017	0.086500
N	1.578393	-2.200728	-0.027096
H	-0.851380	1.460349	-0.185990
H	-4.658758	-2.124897	0.190985
H	-5.441888	0.294571	-0.003779
H	-0.543579	-2.482261	-0.027042
H	1.875507	-3.162262	-0.050316
H	4.412760	-2.005425	-0.081766
H	4.159299	2.294792	0.036747
H	5.502105	0.240075	-0.075350

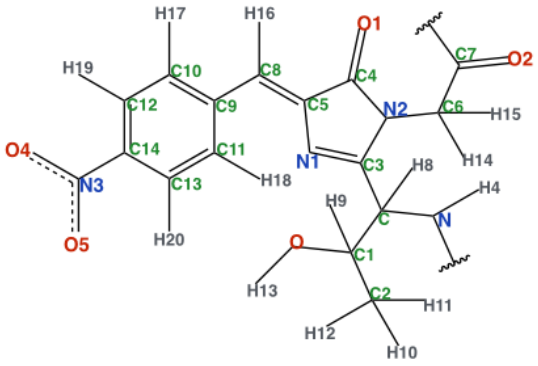
H	0.677464	2.462072	0.633195
H	2.073074	3.308444	0.294833
O	-3.457058	2.099991	-0.166379
Coordinates for Model Number 21			
C	-1.709938	0.781640	-0.000170
C	-4.192548	0.668746	-0.000389
C	-4.246741	-1.576278	-0.000369
C	-2.841014	0.037478	-0.000266
C	-0.324662	0.364402	-0.000041
C	0.667774	1.330106	0.000055
C	0.095330	-1.004454	-0.000005
C	2.028711	0.963833	0.000183
C	2.317290	-0.432837	0.000207
C	3.077450	1.916856	0.000284
C	3.684141	-0.842417	0.000338
C	4.381145	1.485942	0.000407
C	4.686511	0.108901	0.000435
N	-5.031119	-0.446152	-0.000448
N	-2.973174	-1.354717	-0.000263
N	1.348718	-1.383857	0.000113
H	-1.887651	1.857065	-0.000192
H	-4.691176	-2.565559	-0.000396
H	-6.037664	-0.401365	-0.000538
H	0.403985	2.386014	0.000032
H	-0.659550	-1.785644	-0.000078
H	2.836392	2.976096	0.000264
H	5.195247	2.204746	0.000485
H	5.727196	-0.208774	0.000536
H	4.878492	-2.319640	0.000450
O	-4.538142	1.834084	-0.000431
O	3.927013	-2.169781	0.000364
Coordinates for Model Number 22			
C	-1.893561	-1.060417	-0.000137
C	-0.530182	-0.809610	-0.000113
C	-0.048098	0.514483	-0.000001
C	1.363734	0.849715	0.000025
C	-0.975364	1.573941	0.000086
C	-2.340453	1.333755	0.000061
C	-2.779601	0.014080	-0.000050
C	3.835722	0.565418	-0.000015
C	3.732448	-1.676104	-0.000218
C	2.440134	0.029644	-0.000053
N	4.594076	-0.606236	-0.000127
N	2.475869	-1.367189	-0.000180

N	-4.218699	-0.250316	-0.000076
H	-2.283213	-2.072024	-0.000223
H	0.179108	-1.629436	-0.000182
H	-0.613284	2.598304	0.000174
H	-3.062961	2.141453	0.000126
H	1.607538	1.911251	0.000117
H	4.105854	-2.694443	-0.000312
H	5.601452	-0.634641	-0.000139
O	4.257018	1.703183	0.000086
O	-4.971051	0.712822	-0.000019
O	-4.579678	-1.417712	-0.000151



Atom Name	Atom type	Charge
N1	n	-0.373500
H17	hn	0.237600
CA1	c3	-0.005700
H18	h1	0.169400
CB1	c3	0.104500
H19	h1	0.179200
CG1	c3	-0.326300
H4	hc	0.089800
H5	hc	0.089800
H6	hc	0.089800
OG1	oh	-0.605100
H7	ho	0.385500
C1	cc	0.012200
N2	nd	-0.307100
N3	n	0.011000
C2	c	0.355800
O2	o	-0.629500
CA2	cd	-0.039300
CA3	c3	-0.047000
H8	h1	0.046500
H9	h1	0.046500
C3	c	0.589400
O3	o	-0.605400
CB2	ce	-0.072700
H10	ha	0.129100
CG2	ca	-0.077800
CD1	ca	-0.103300
H11	ha	0.129900
CD2	ca	-0.103300
H12	ha	0.129900
CE1	ca	-0.369800
H13	ha	0.127800
CE2	ca	-0.369800
H20	ha	0.127800
CZ	c	0.657000
OH	o	-0.672900

Table S2 Atom Types and charges for the *control* model mapped by the atom names. The lower-case letters refer to atom types as in the GAFF. The charges are computed by R.E.D. Server Development online tools as explained in the main text.



Atom Name	Atom type	Charge
C7	c	0.567500
O2	o	-0.541800
C6	c3	-0.113900
H14	h1	0.090300
H15	h1	0.090300
N2	n	0.029900
C4	c	0.410300
O1	o	-0.529000
C3	cc	0.226600
C	c3	-0.047700
N	n	-0.363100
H4	hn	0.312800
C1	c3	0.027100
C2	c3	-0.054400
H10	hc	0.030700
H11	hc	0.030700
H12	hc	0.030700
O	oh	-0.679800
H13	ho	0.473700
H9	h1	0.119200
H8	h1	0.167600
N1	nd	-0.377400
C5	cd	0.102100
C8	ce	-0.154600
H16	ha	0.139600
C9	ca	0.052700
C11	ca	-0.083300
H18	ha	0.129900
C13	ca	-0.191500
H20	ha	0.181200
C14	ca	0.032100
N3	no	0.773600
O4	o	-0.459200
O5	o	-0.459200
C12	ca	-0.191500
H19	ha	0.181200
C10	ca	-0.083300
H17	ha	0.129900

Table S3 Atom Types and charges for the *nitro* model mapped by the atom names. The lower-case letters refer to atom types as in the GAFF. The charges are computed by R.E.D. Server Development online tools as explained in the main text.

Additional Parameters for the interface atoms between the chromophore model parameterized with GAFF and the rest of the protein parameterized with FF12SB. The parameters are given in the frcmod format. Some are produced by ANTECHAMBER and the rest are assigned via comparison to parameters for similar atom types.

```
BOND
C-n         490.0    1.335
c-N         490.0    1.335

ANGLE
ce-cd-c      63.460    120.890
o -c -N      80.0      122.90
O -C -n      80.0      122.90
c -N -H      50.0      120.00
C -n -hn     50.0      120.00
C -n -c3     63.92     121.35
c3-c -N      67.86     115.15
CX-C -n      70.0      116.60
c -N -CX     50.0      121.90

DIHE
ca-ca-ce-ha    1    6.650       180.000          2.000
ca-ca-ce-cd    1    6.650       180.000          2.000
ca-ce-cd-c     1    1.000       180.000          2.000
ca-ce-cd-nd    1    1.000       180.000          2.000
ha-ce-cd-c     1    1.000       180.000          2.000
ha-ce-cd-nd    1    1.000       180.000          2.000
O -C -n -hn    1    2.50        180.000         -2.000
H -N -c -o     1    2.50        180.000         -2.000
H -N -c -o     1    2.00          0.000          1.000
CX-C -n -hn    1    2.5         180.000          2.000
O -C -n -c3    1    2.5         180.000          2.000
CX-C -n -hn    1    2.5         180.000          2.000
CX-C -n -c3    1    2.5         180.000          2.000
c3-c -N -H     1    2.5         180.000          2.000
c3-c -N -CX    1    2.5         180.000          2.000
o -c -N -CX    1    2.5         180.000          2.000
o -c -N -H     1    2.5         180.000          2.000

IMPROPER
ca-o -no-o          1.1          180.0         2.0
ca-ca-ca-no         1.1          180.0         2.0
ca-ca-ca-ha         1.1          180.0         2.0
ca-ca-ca-ce         1.1          180.0         2.0
ca-cd-ce-ha         1.1          180.0         2.0
```

```
c -ce-cd-nd          1.1          180.0          2.0
cd-n -c -o          10.5          180.0          2.0
c3-n -cc-nd          1.1          180.0          2.0
c3-n -c -o          10.5          180.0          2.0
c -c3-n -cc          1.1          180.0          2.0
```

Amber Input files used in the MD simulations. Minimization was done in two steps, heating in one step and density equilibration in 4 steps. Production was carried out in identical steps of 5 ns.

```
Minimization1
&cntrl
imin=1,
maxcyc=1000,
ncyc=100,
cut=10.0,
ntpr=100,
ntr=1,
restraintmask=':1-226',
restraint_wt=500,
/
Minimization2
&cntrl
imin=1,
maxcyc=1000,
ncyc=200,
cut=10.0,
ntpr=100,
/
Heating
&cntrl
imin=0,
irest=0,
ntx=1,
ntpr=1000,
ntwx=1000,
ntr=1,
restraint_wt=10.0,
restraintmask=?:1-226?,
nstlim=10000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntt=3,
gamma_ln=2.0,
tempi=0.0,
temp0=300.0,
```

```
ig=-1,
/
density1
&cntrl
imin=0,
irest=1,
ntx=7,
nstlim=25000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntp=1,
pres0=1.0,
taup=2.0,
ntpr=1000,
ntwx=1000,
ntt=3,
gamma_ln=2.0,
ioutfm=1,
temp0=300.0,
tempi=300.0,
ig=-1,
ntr=1,
restraintmask=':1-226',
restraint_wt=5.0,
/
density2
&cntrl
imin=0,
irest=1,
ntx=7,
nstlim=25000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntp=1,
pres0=1.0,
taup=2.0,
ntpr=1000,
ntwx=1000,
ntt=3,
gamma_ln=2.0,
ioutfm=1,
temp0=300.0,
tempi=300.0,
ig=-1,
```

```
ntr=1,
restraintmask=':1-226',
restraint_wt=2.0,
/
density3
&cntrl
imin=0,
irest=1,
ntx=7,
nstlim=25000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntp=1,
pres0=1.0,
taup=2.0,
ntpr=1000,
ntwx=1000,
ntt=3,
gamma_ln=2.0,
ioutfm=1,
temp0=300.0,
tempi=300.0,
ig=-1,
ntr=1,
restraintmask=':1-226',
restraint_wt=0.5,
/
density4
&cntrl
imin=0,
irest=1,
ntx=7,
nstlim=25000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntp=1,
pres0=1.0,
taup=2.0,
ntpr=1000,
ntwx=1000,
ntt=3,
gamma_ln=2.0,
ioutfm=1,
temp0=300.0,
```

```
tempi=300.0,
ig=-1,
ntr=1,
restraintmask=':1-226',
restraint_wt=0.1,
/
Production
&cntrl
imin=0,
irest=1,
ntx=7,
nstlim=2500000,dt=0.002,
ntc=2,ntf=2,
cut=8.0,
ntp=1,
pres0=1.0,
taup=2.0,
ntpr=1000,
ntwx=1000,
ioutfm=1,
ntt=3,
gamma_ln=2.0,
temp0=300.0,
tempi=300.0,
ig=-1,
ntr=0,
/
```

Model	δ^{TPA}(a.u.)
1a	42
1b	13
2a	15
2b	20
3	24
4	11
5	180
6	342
7	339
8	370
9	609
10	763
11	1049
12	1358
13	1751
14	1744
15	1879
16a	2046
16b	1882
17	2067
18	2540
19	2908
20	5738
21	5258
22	8834

Table S4 The δ^{TPA} values for the chromophore models as computed at the TDDFT/6-31+(d,p) Level of Theory in PCM (water)

Bond	Dynamics Average (DA)	Crystal Structure (CS)	DFT-optimized Structure (DF)	DA-CS	DA-DF	DF-CS
C1-N3	1.39	1.35	1.38	0.04	0.01	0.03
C2-CA2	1.46	1.46	1.46	0.00	0.01	0.00
C2-O2	1.22	1.30	1.24	0.08	0.02	0.06
CA2-CB2	1.37	1.47	1.39	0.10	0.01	0.08
CA2-N2	1.38	1.37	1.40	0.01	0.01	0.03
CB2-CG2	1.49	1.47	1.41	0.02	0.08	0.06
CD1-CE1	1.39	1.40	1.37	0.01	0.02	0.03
CD2-CG2	1.40	1.40	1.43	0.00	0.03	0.03
CE1-CZ	1.48	1.39	1.45	0.09	0.03	0.06
CE2-CD2	1.39	1.43	1.37	0.04	0.03	0.06
CG2-CD1	1.40	1.43	1.43	0.03	0.03	0.00
CZ-CE2	1.48	1.39	1.46	0.09	0.03	0.07
CZ-OH	1.21	1.39	1.25	0.18	0.04	0.14
N2-C1	1.34	1.38	1.30	0.04	0.05	0.08
N3-C2	1.34	1.34	1.40	0.00	0.07	0.06
maximum difference				0.18	0.08	0.14

Table S5 Comparison of average bond lengths (in Å) of the *control* chromophore over the dynamics trajectory (Dynamic Average) to the corresponding bond lengths of the chromophore in the crystal structure (PDB ID: 2Y0G) and to those of the same chromophore as optimized at the PBE0/6-31+(d,p) level of theory in the gas phase (DFT-optimized Structure). Bond lengths differences are given in absolute values. Atom names match the figure in Table S2

Bond	Dynamics Average (DA)	DFT-optimized Structure (DF)	DA-DF
C5-N1	1.38	1.40	0.02
C5-C8	1.38	1.35	0.02
N1-C3	1.34	1.29	0.05
C3-N2	1.39	1.37	0.02
N2-C4	1.34	1.40	0.06
C4-C5	1.47	1.49	0.03
C4-O1	1.22	1.21	0.01
C8-C9	1.49	1.45	0.03
C9-C10	1.39	1.41	0.01
C10-C12	1.40	1.39	0.01
C12-C14	1.40	1.39	0.01
C14-C13	1.40	1.39	0.01
C14-N3	1.50	1.46	0.03
C13-C11	1.40	1.39	0.01
C11-C9	1.40	1.41	0.01
N3-O4	1.22	1.22	0.00
N3-O5	1.22	1.22	0.00
maximum difference			0.06

Table S6 Comparison of average bond lengths (in Å) of the *nitro* chromophore over the dynamics trajectory (Dynamic Average) to the corresponding bond lengths of the same chromophore (Model 22) as optimized at the PBE0/6-31+(d,p) level of theory in the gas phase (DFT-optimized Structure). Bond lengths differences are given in absolute values. Atom names match the figure in Table S3

Model	PCM			Gas-phase		
	Energy(eV)	OS	TPA (GM)	Energy(eV)	OS	TPA (GM)
6	3.197	0.91	1	3.336	0.81	0
7	3.200	0.93	1	3.331	0.81	0
12	3.210	0.98	5	3.351	0.86	5
13	3.289	0.85	7	3.444	0.74	7
14	3.310	0.89	7	3.451	0.79	7
16a	3.218	0.58	8	3.348	0.42	8
18	3.137	0.93	9	3.352	0.79	10
19	3.138	0.55	11	3.250	0.33	11
20	2.689	0.36	15	2.826	0.28	17
22	2.965	0.64	29	3.257	0.61	22

Table S7 Comparison of PCM and Gas phase computations at the TDDFT/6-31+(d,p) Level of Theory for selected chromophore models.

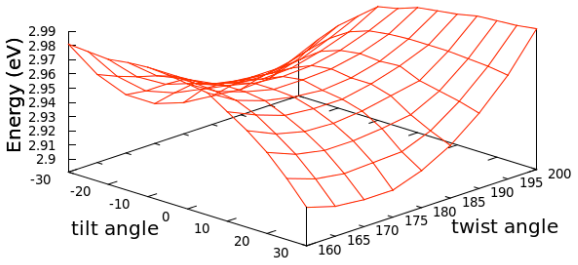


Fig. S1 Variation of Energy for various conformers of the nitro chromophore with the tilt and twist angles while fixing the methine bridge at 134°.

C						
N	1	1.39729				
C	2	1.29399	1	105.277		
N	3	1.37369	2	115.035	1	0
C	4	1.39566	3	108.2405	2	0
H	4	1.00778	3	127.2314	5	180
O	5	1.21326	4	126.7683	3	180
H	3	1.08464	2	123.9485	4	180
C	1	1.3532	2	128.768	5	180
H	9	1.08917	1	114.3677	2	180
C	9	1.45109	1	meth	2	tilt
C	11	1.40793	9	117.8361	1	twist
C	12	1.38606	11	121.2143	9	180
C	13	1.39083	12	118.3849	11	0
C	14	1.3927	13	122.0847	12	0
C	15	1.38626	14	119.0858	13	0
H	15	1.08406	14	119.4249	13	180
H	16	1.08407	15	120.4418	14	180
H	12	1.08647	13	119.4459	14	180
H	13	1.08369	14	119.7805	15	180
N	14	1.46318	13	118.8164	12	180
O	21	1.22216	14	117.5846	13	0
O	21	1.22193	14	117.593	13	180

Table S8 The z-matrix used in the conformational analysis of the nitro-chromophore. The entries: meth, tilt and twist refer to the methyl bridge, tilting and twisting angles referred to in the main text.

Table S9 Energy, OS, TPA (in GM) and the square of the x-component of the difference between permanent moments of excited and ground states (in atomic units) of various conformers of the nitro chromophore computed at the TDDFT/6-31+(d,p) Level of Theory in the gas phase (while fixing the methine bridge at 134°).

Tilt	Twist	Energy(eV)	OS	TPA	$(\Delta\mu_x)^2$
-30	160	2.981	0.509	26.62	6.452
-30	165	2.953	0.534	26.25	6.239
-30	170	2.932	0.556	25.78	6.011
-30	175	2.919	0.575	25.21	5.798
-30	180	2.913	0.593	24.55	5.613
-30	185	2.911	0.608	24.12	5.465
-30	190	2.909	0.620	24.16	5.358
-30	195	2.910	0.627	24.32	5.295
-30	200	2.917	0.630	24.56	5.273
-25	160	2.980	0.523	28.63	7.195
-25	165	2.956	0.548	28.12	6.890
-25	170	2.939	0.569	27.55	6.606
-25	175	2.931	0.589	26.82	6.355
-25	180	2.927	0.606	26.21	6.149

-25	185	2.923	0.619	26.07	5.994
-25	190	2.922	0.628	26.15	5.894
-25	195	2.926	0.633	26.34	5.844
-25	200	2.935	0.634	26.57	5.851
-20	160	2.979	0.539	30.11	7.796
-20	165	2.960	0.562	29.53	7.423
-20	170	2.948	0.583	28.78	7.095
-20	175	2.942	0.602	28.07	6.825
-20	180	2.935	0.617	27.78	6.615
-20	185	2.933	0.627	27.74	6.471
-20	190	2.933	0.633	27.86	6.394
-20	195	2.939	0.636	28.01	6.386
-20	200	2.949	0.635	28.32	6.444
-15	160	2.981	0.555	31.12	8.255
-15	165	2.965	0.577	30.36	7.840
-15	170	2.956	0.598	29.65	7.496
-15	175	2.946	0.614	29.25	7.228
-15	180	2.942	0.626	29.06	7.037
-15	185	2.940	0.633	29.07	6.916
-15	190	2.943	0.637	29.17	6.888
-15	195	2.951	0.637	29.40	6.947
-15	200	2.960	0.632	29.79	7.100
-10	160	2.982	0.572	31.65	8.578
-10	165	2.969	0.593	30.96	8.149
-10	170	2.957	0.610	30.46	7.809
-10	175	2.951	0.623	30.16	7.564
-10	180	2.947	0.632	30.02	7.414
-10	185	2.948	0.637	30.00	7.364
-10	190	2.953	0.638	30.09	7.418
-10	195	2.960	0.634	30.40	7.604
-10	200	2.971	0.626	30.73	7.921
-5	160	2.981	0.587	32.02	8.790
-5	165	2.968	0.606	31.35	8.378
-5	170	2.960	0.622	30.84	8.067
-5	175	2.955	0.632	30.55	7.870
-5	180	2.953	0.638	30.44	7.791
-5	185	2.954	0.639	30.48	7.842
-5	190	2.958	0.635	30.75	8.019
-5	195	2.965	0.627	31.15	8.339
-5	200	2.974	0.614	31.64	8.731

0	160	2.979	0.602	31.92	8.914
0	165	2.967	0.619	31.31	8.516
0	170	2.960	0.630	30.95	8.253
0	175	2.955	0.636	30.78	8.095
0	180	2.955	0.639	30.65	8.038
0	185	2.956	0.637	30.72	8.095
0	190	2.960	0.629	31.03	8.253
0	195	2.967	0.617	31.44	8.516
0	200	2.979	0.602	31.88	8.914
5	160	2.977	0.616	31.42	8.731
5	165	2.965	0.628	31.01	8.339
5	170	2.958	0.635	30.69	8.019
5	175	2.954	0.639	30.52	7.842
5	180	2.952	0.637	30.52	7.791
5	185	2.954	0.631	30.65	7.870
5	190	2.959	0.620	30.94	8.067
5	195	2.968	0.606	31.32	8.378
5	200	2.981	0.588	31.84	8.790
10	160	2.968	0.624	30.99	7.921
10	165	2.959	0.633	30.51	7.604
10	170	2.952	0.638	30.15	7.418
10	175	2.950	0.638	29.93	7.364
10	180	2.950	0.634	29.81	7.414
10	185	2.954	0.625	29.94	7.564
10	190	2.960	0.611	30.34	7.809
10	195	2.968	0.594	30.87	8.149
10	200	2.983	0.574	31.39	8.578
15	160	2.959	0.631	29.93	7.100
15	165	2.950	0.637	29.44	6.947
15	170	2.945	0.638	29.09	6.888
15	175	2.944	0.635	28.85	6.916
15	180	2.946	0.627	28.85	7.037
15	185	2.950	0.614	29.11	7.228
15	190	2.954	0.600	29.58	7.496
15	195	2.968	0.582	30.01	7.840
15	200	2.986	0.560	30.59	8.255
20	160	2.948	0.635	28.42	6.444
20	165	2.940	0.637	27.97	6.386
20	170	2.936	0.635	27.65	6.394

20	175	2.936	0.628	27.56	6.471
20	180	2.938	0.617	27.65	6.615
20	185	2.941	0.604	28.02	6.825
20	190	2.951	0.588	28.36	7.095
20	195	2.967	0.568	28.87	7.423
20	200	2.987	0.544	29.58	7.796
25	160	2.934	0.635	26.58	5.851
25	165	2.927	0.634	26.20	5.844
25	170	2.924	0.628	26.01	5.894
25	175	2.925	0.619	25.96	5.994
25	180	2.926	0.608	26.20	6.149
25	185	2.934	0.593	26.46	6.355
25	190	2.948	0.575	26.90	6.606
25	195	2.966	0.554	27.47	6.890
25	200	2.988	0.528	28.08	7.195
30	160	2.918	0.631	24.44	5.273
30	165	2.912	0.627	24.15	5.295
30	170	2.910	0.619	24.01	5.358
30	175	2.910	0.610	24.15	5.465
30	180	2.917	0.597	24.28	5.613
30	185	2.928	0.581	24.55	5.798
30	190	2.944	0.562	24.99	6.011
30	195	2.964	0.539	25.46	6.239
30	200	2.990	0.513	25.98	6.452