Supporting Information for

Spectral Tuning in Visual Pigments: An ONIOM(QM:MM) Study on Bovine Rhodopsin and its Mutants

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Contents

1. Abbreviations

WT: Wild Type Enzyme
PSB(R): Protonated Schiff-Base (Retinal)
SB(R): Deprotonated Schiff-Base (Retinal)
B3LYP(ME//ME): TD-B3LYP:AMBER-ME calculations on B3LYP:AMBER-ME geometries
B3LYP(EE//ME): TD-B3LYP:AMBER-EE calculations on B3LYP:AMBER-ME geometries
B3LYP(ME//EE): TD-B3LYP:AMBER-EE calculations on B3LYP:AMBER-EE geometries

2. AMBER Charges and Parameters for 11-*cis*-retinal and Attached Lys296

AMBER force field is derived for RESP charges calculated at the HF/6-31G* level. Hence, we calculated RESP charges for the model part (both for SBR and PSBR, see Figure 2 of the paper for the model part and indexing of its atoms) at the same level by fitting point charges of all protein atoms to the electrostatic potential. We used the resulting RESP charges shown in Table 2.1 in our pure AMBER and hybrid ONIOM(QM:AMBER) calculations with a modification for the Schiff-base terminal due to excess link atom for force-field calculations (see footnote of Table 2.1). The RESP charges of hydrogen atoms attached the same C atom were averaged.

Table 2.1. RESP charges of model part for both PSBR and SBR calculated at HF/6-31G* level along with atom types

Atom Index	Atom Type	PSBR	SBR	Atom Index	Atom Type	PSBR	SBR
C6	CM	0.00449	-0.01483	C8	CA	-0.05066	-0.06693
C1	CT	0.00256	-0.00649	H	HA	0.10702	0.12494
C16	CT	0.00154	-0.00234	C9	CA	-0.05141	-0.07765
H	HC	0.01228	0.00911	C19	CT	0.00179	-0.01897
H	HC	0.01228	0.00911	H	HC	0.04429	0.02453
H	HC	0.01228	0.00911	H	HC	0.04429	0.02453
C17	CT	-0.01344	-0.01886	H	HC	0.04429	0.02453
H	HC	0.00070	-0.00312	C10	CA	-0.07518	-0.10232
H	HC	0.00070	-0.00312	H	HA	0.02535	0.01643
H	HC	0.00070	-0.00312	C11	CA	-0.04160	-0.05948
C5	CM	0.03438	0.01428	H	HA	0.15666	0.15711
C18	CT	-0.00550	-0.01434	C12	CA	-0.19867	-0.31224
H	HC	0.00664	0.00098	H	HA	0.13259	0.09108
H	HC	0.00664	0.00098	C13	CA	-0.11583	-0.13365
H	HC	0.00664	0.00098	C20	CT	0.02796	0.02643
C2	CT	0.00558	0.00183	H	HC	0.05765	0.05995
H	HC	0.01363	0.01029	H	HC	0.05765	0.05995
H	HC	0.01363	0.01029	H	HC	0.05765	0.05995
C3	CT	-0.00649	-0.01163	C14	CA	0.04429	0.13197
H	HC	-0.00803	-0.01322	H	HA	0.13363	0.33794
H	HC	-0.00803	-0.01322	C15	CA	0.39916	0.20567
C4	CT	0.00292	-0.00930	H	HA	0.12354	-0.05957
H	HC	0.01361	0.00247	N[a]	N2	-0.34790	-0.40132
H	HC	0.01361	0.00247	H_{PSB}[a]	H	0.31707	-
C7	CA	-0.03367	-0.06291				
H	HA	0.01673	-0.00830	SUM		+1.00000	0.00000

[a] NH (NH_2) moiety of SBR (PSBR) in QM/MM calculations must be arranged as N (NH) for pure force-field calculations, in other words, link atom charge must be distributed to the remaining. We performed additional calculations extending the model part to the full Lys296 for PSBR. The resulting RESP charge of N atom was assigned to N and the remaining charge that completes overall charge of the model system to 1 was assigned to H_{PSB}. For SBR, additional calculations were not performed. Summation of the charges of N and link atom was assigned to the charge of N simply.

There are also no standard charges for side-chain bound Lys atoms. Even in its presence, the charges must be redistributed as N terminal atoms are in the model part to make total charge outside the model part integer (0). Except CD and CE atoms and H atoms attached to them, standard AMBER charges for the charged Lys were used. Although ONIOM(QM:MM) calculations with electronic embedding are not suffering from overpolarization problem due to MM charges at QM/MM border next to the link atom seen in conventional QM/MM methods (ref 44 of the paper), the charge on CE atom was set to zero to be at the safer side analogous to previous ONIOM calculations performed by other groups (refs 9 and 10 of the paper). The remaining charge that complete the total charge to zero is distributed to CD atom and attached hydrogens to it as well as hydrogens attached to CE atom with a ratio of 1:2 for H:C for making CH_2 group charges unchanged (see Table 2.2). Our ONIOM test calculations with the modification of these charges and giving some values to the CE atom charges show that geometries and excitation energies are not much sensitive to those charges. During the RESP charge calculation of model part, Lys296 charges were treated as in Table 2.2.

Table 2. RESP charges of the atoms of side-chain bound Lys outside the model part.

Atom Index	Atom Type	RESP
N	N	-0.3479
H	H	0.2747
CA	CT	-0.2400
HA	H1	0.1426
CB	CT	-0.0094
HB	HC	0.0362
HB	HC	0.0362
CG	CT	0.0187
HG	HC	0.0103
HG	HC	0.0103
CD	CT	-0.1744
HD	HC	-0.0012
HD	HC	-0.0012
CE[b]	CT	0.0000
HE[b]	H1	0.0502
HE[b]	H1	0.0502
C	C	0.7341
O	O	-0.5894
SUM		0.0000

The missing AMBER bond parameters for retinal and its connection to Lys296 were taken as follows.

HrmBnd1	N2	CA	HA	20.0	122.0
HrmBnd1	N2	CA	CA	30.0	118.0
HrmBnd1	CM	CT	CT	25.0	114.0
HrmBnd1	CM	CA	HA	20.0	114.0
HrmBnd1	CM	CA	CA	25.0	132.0
HrmBnd1	CT	CM	CA	25.0	120.0
HrmBnd1	CT	CM	CT	25.0	110.0

3. Vertical Excitation Energies and Oscillator Strengths

Vertical excitation energies from ground state singlet to first ($S_0 \rightarrow S_1$) and second ($S_0 \rightarrow S_2$) lowest energy singlet states as well as their oscillator strengths *f* (in parenthesis) calculated at different ONIOM(TD-DFT:MM) levels for wild type bovine rhodopsin with PSBR are given in this section for both WT enzyme and some of its mutants.

3.1. WT Enzyme with PSBR

Table 3.1.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	534.86 (1.1440)[b]	541.02 (1.2029)	532.53 (1.2385)
TD-B3LYP:MM-ME	503.82 (1.1440)	515.70 (1.2029)	509.52 (1.2385)
TD-B3LYP:MM-EE[c]	504.97 (1.2602)	516.18 (1.2861)	509.16 (1.3110)
TD-BLYP	577.56 (0.7510)	577.66 (0.8226)	565.60 (0.8810)
TD-BLYP:MM-ME	542.58 (0.7510)	549.31 (0.8226)	540.26 (0.8810)
TD-BLYP:MM-EE	543.31 (0.8458)	550.56 (0.8894)[d]	540.63 (0.9391)

[a] Experiment: 500 nm
[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 559.82 nm (0.8180)
[c] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 503.28 nm (0.9976) /514.73 nm (1.0966).
[d] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 571.64 nm (0.6483).

Table 3.1.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	407.03 (0.3882)[b]	412.53 (0.3179)	405.97 (0.2766)
TD-B3LYP:MM-ME	386.37 (0.3882)	393.61 (0.3179)	389.12 (0.2766)
TD-B3LYP:MM-EE[c]	388.84 (0.3019)	397.02 (0.2660)	392.29 (0.2311)
TD-BLYP	463.32 (0.6495)	473.70 (0.5699)	468.29 (0.5149)
TD-BLYP:MM-ME	440.77 (0.6495)	452.62 (0.5699)	449.63 (0.5149)
TD-BLYP:MM-EE	447.38 (0.6048)	459.29 (0.5484)[d]	455.77 (0.4931)

[a] Experiment: 380 nm
[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 410.00 nm (0.6780)
[c] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 381.13 nm (0.5273)/389.62 (0.4722).
[d] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 443.00 nm (0.8226).

TD-B3LYP:MM-EE//B3LYP:MM-ME level $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ vertical excitation energy (*f*)

(a) turning the charge of Glu113 off: 535.20 nm (1.1196) / 409.17 nm (0.3871)

(b) including all Glu113 atoms into the model system: 498.62 nm (0.8728) / 385.24 nm (0.2200), which is similar to TD-B3LYP:MM-ME//B3LYP:MM-ME result of 500.15 nm (1.3528) / 386.79 nm (0.2703) with Glu113 in the model part. When Glu113 is included in the model part, no further geometry relaxation was performed.

3.2. WT Enzyme with SBR and Protonated Glu113

Hydrogen atom of PSBR was moved to OE2 atom of Glu113. When it is moved to OE1, the structure is 1.8 kcal/mol less stable but gives almost the same excitation energies.

Table 3.2.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	400.45 (1.2058)[a]	419.68 (1.1842)	415.49 (1.2604)
TD-B3LYP:MM-ME	399.40 (1.2058)	418.03 (1.1842)	415.29 (1.2604)
TD-B3LYP:MM-EE[b]	412.32 (1.1285)	430.35 (1.1267)	426.81 (1.1910)
TD-BLYP	463.57 (0.6609)	482.56 (0.6436)	472.24 (0.7667)
TD-BLYP:MM-ME	458.56 (0.6609)	475.15 (0.6436)	470.21 (0.7667)
TD-BLYP:MM-EE	480.71 (0.6085)	496.92 (0.6056)[c]	488.09 (0.7097)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 407.51 nm (1.2124)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 428.8 nm (1.0684) /447.31 nm (1.0970)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 513.21 nm (0.6137).

Table 3.2.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	324.07 (0.1011)[a]	336.36 (0.3513)	335.57 (0.0178)
TD-B3LYP:MM-ME	307.20 (0.1011)	332.95 (0.3513)	311.86 (0.0178)
TD-B3LYP:MM-EE[b]	325.34 (0.4423)	339.03 (0.4340)	334.27 (0.3796)
TD-BLYP	416.79 (0.0027)	428.98 (0.0044)	439.98 (0.0002)
TD-BLYP:MM-ME	372.73 (0.0027)	383.25 (0.0044)	390.64 (0.0002)
TD-BLYP:MM-EE	381.04 (0.7909)	395.66 (0.8065)[c]	391.44 (0.7285)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 333.56 nm (0.0006)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 333.64 nm (0.4692)/346.84 nm (0.4519)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 403.16 nm (0.0607).

3.3. WT Enzyme with SBR and Deprotonated Glu113

Table 3.3.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	398.96 (1.1368)[a]	418.10 (1.1645)	411.85 (1.1951)
TD-B3LYP:MM-ME	366.40 (1.1368)	385.87 (1.1645)	381.81 (1.1951)
TD-B3LYP:MM-EE[b]	382.18 (1.4682)	400.64 (1.4788)	396.67 (1.4706)
TD-BLYP	466.41 (0.5823)	484.10 (0.6131)	473.34 (0.6780)
TD-BLYP:MM-ME	409.88 (0.0003)	426.80 (0.6131)	434.77 (0.0008)
TD-BLYP:MM-EE	472.64 (0.0018)	482.56 (0.0013)[c]	503.90 (0.0017)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 396.27 nm (1.0999)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 379.75 nm (1.4087)/399.22 nm (1.4656)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 455.30 nm (0.0026).

Table 3.3.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	327.65 (0.0013)[a]	337.71 (0.3974)	342.19 (0.0021)
TD-B3LYP:MM-ME	314.79 (0.0013)	334.27 (0.3974)	328.50 (0.0021)
TD-B3LYP:MM-EE[b]	348.57 (0.0010)	356.16 (0.0007)	364.80 (0.0008)
TD-BLYP	424.63 (0.0003)	436.11 (0.0003)	451.19 (0.0008)
TD-BLYP:MM-ME	406.20 (0.5823)	418.31 (0.0003)	421.45 (0.6780)
TD-BLYP:MM-EE	421.76 (1.1784)	440.18 (1.1596)[c]	434.91 (1.2331)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 322.77 nm (0.3088)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 340.76 nm (0.0012) /344.22 nm (0.0014)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 443.86 nm (0.3954).

3.4. E122Q Mutant with PSBR

The results in the following were obtained with a Q122 conformation whose NH_2 moiety was oriented towards one of the methyl groups attached to C1 atom of the chromophore (Conformation A).

Table 3.4.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	532.89 (1.1584)[b]	539.09 (1.2275)	533.40 (1.2278)
TD-B3LYP:MM-ME	502.70 (1.1584)	511.78 (1.2275)	507.11 (1.2278)
TD-B3LYP:MM-EE[c]	496.99 (1.3068)	511.02 (1.3235)	506.54 (1.3157)
TD-BLYP	577.32 (0.7520)	573.83 (0.8557)	567.05 (0.8691)
TD-BLYP:MM-ME	536.76 (0.7520)	543.06 (0.8557)	537.92 (0.8691)
TD-BLYP:MM-EE	535.87 (0.8718)	542.98 (0.9444)	538.08 (0.9464)

[a] Experiment: 480 nm
[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 565.84 nm (0.7724)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 491.52 nm (1.0237)/505.15 nm (1.1475)

Table 3.4.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	404.26 (0.4146)[a]	412.02 (0.2951)	406.74 (0.2845)
TD-B3LYP:MM-ME	384.37 (0.4146)	391.00 (0.2951)	387.64 (0.2845)
TD-B3LYP:MM-EE[b]	385.65 (0.2939)	394.65 (0.2257)	391.23 (0.2213)
TD-BLYP	459.71 (0.6896)	474.00 (0.5417)	468.73 (0.5234)
TD-BLYP:MM-ME	433.75 (0.6896)	450.52 (0.5417)	447.50 (0.5234)
TD-BLYP:MM-EE	442.49 (0.6175)	458.51 (0.4945)	455.05 (0.4828)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 410.13 nm (0.7284)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 374.88 nm (0.5137)/384.07 nm (0.4189)

When O=C–NH_2 plane of Q112 is rotated by ca. 90˚ (Conformation B), less consistent results with experiment is obtained: TD-B3LYP//B3LYP:MM-ME, 543.90 nm (1.0039) → B3LYP(ME//ME), 509.07 nm (1.0039) → B3LYP(EE//ME), 512.16 nm (1.1217) → TD-B3LYP//B3LYP:MM-EE, 566.39 nm (0.7764) → B3LYP(EE//EE), 513.46 nm (0.9093)

3.5. E122Q Mutant with SBR and Protonated Glu113

The results in this section were obtained on Conformation A (see Section 3.4).

Table 3.5.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	401.99 (1.2058)[a]	421.64 (1.2264)	414.33 (1.2715)
TD-B3LYP:MM-ME	394.66 (1.2058)	415.17 (1.2264)	409.31 (1.2715)
TD-B3LYP:MM-EE[b]	406.20 (1.2222)	425.50 (0.0763)	418.54 (1.2722)
TD-BLYP	464.51 (0.6651)	481.62 (0.7032)	471.20 (0.7780)
TD-BLYP:MM-ME	449.27 (0.6651)	467.52 (0.7032)	460.89 (0.7780)
TD-BLYP:MM-EE	466.52 (0.6962)	483.23 (0.7305)[c]	474.95 (0.7822)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 407.21 nm (1.2063)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 417.98 nm (1.1653) /436.87 nm (1.1997)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 495.91 nm (0.6973).

Table 3.5.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	325.14 (0.0894)[a]	337.03 (0.0694)	336.02 (0.0131)
TD-B3LYP:MM-ME	307.83 (0.0894)	331.83 (0.0694)	314.95 (0.0131)
TD-B3LYP:MM-EE[b]	322.51 (0.3551)	336.65 (0.3324)	332.70 (0.2915)
TD-BLYP	418.40 (0.0033)	431.66 (0.0057)	440.32 (0.0003)
TD-BLYP:MM-ME	378.14 (0.0033)	389.99 (0.0057)	398.07 (0.0003)
TD-BLYP:MM-EE	379.24 (0.7328)	394.97 (0.7157)[c]	392.04 (0.6449)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 333.90 nm (0.0032)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 328.09 nm (0.3998) /341.74 nm (0.3801)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 399.57 nm (0.7604).

3.6. E122Q Mutant with SBR and Deprotonated Glu113

The results in this section were obtained on Conformation A (see Section 3.4).

Table 3.6.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	398.93 (1.1248)[a]	417.67 (1.1927)	412.21 (1.2151)
TD-B3LYP:MM-ME	361.52 (1.1248)	381.55 (1.1927)	378.47 (1.2151)
TD-B3LYP:MM-EE[b]	382.30 (1.4663)	400.76 (1.5140)	397.76 (1.4843)
TD-BLYP	467.45 (0.5663)	482.48 (0.6367)	472.74 (0.6980)
TD-BLYP:MM-ME	397.45 (0.5663)	419.81 (0.6367)	414.69 (0.6980)
TD-BLYP:MM-EE	486.16 (0.0017)	490.39 (0.0012)[c]	519.91 (0.0018)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 396.82 nm (1.1051)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 379.00 nm (1.4578) / 417.32 nm (1.3038)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 467.09 nm (0.0007).

Table 3.6.2. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	328.15 (0.0006)[a]	337.23 (0.3920)	343.07 (0.0013)
TD-B3LYP:MM-ME	318.18 (0.0006)	333.04 (0.3920)	332.30 (0.0013)
TD-B3LYP:MM-EE[b]	353.92 (0.0010)	359.05 (0.0007)	371.31 (0.0012)
TD-BLYP	425.42 (0.0004)	436.00 (0.7833)	452.99 (0.0011)
TD-BLYP:MM-ME	416.87 (0.0004)	423.70 (0.7833)	443.23 (0.0011)
TD-BLYP:MM-EE	419.87 (1.2621)	437.10 (1.3142)[c]	434.01 (1.3125)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 323.46 nm (0.3683)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 344.94 (0.0009) /336.14 nm (0.2707)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 435.09 nm (1.2106).

3.7. E113Q Mutant with SBR

Table 3.7.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths) when Gln is oriented to form an H-bond with SBR (Conformation A).

	Geometry[e]		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	398.97 (1.2113)[b]	418.45 (1.2753)	414.63 (1.2455)
TD-B3LYP:MM-ME	396.28 (1.2113)	414.69 (1.2753)	411.52 (1.2455)
TD-B3LYP:MM-EE[c]	408.13 (1.1563)	423.27 (1.2507)	422.01 (1.2044)
TD-BLYP	461.60 (0.6680)	477.35 (0.7546)	472.13 (0.7597)
TD-BLYP:MM-ME	453.63 (0.6680)	468.72 (0.7546)	465.61 (0.7597)
TD-BLYP:MM-EE	474.42 (0.6307)	483.33 (0.7352)[d]	482.28 (0.7223)

[a] Experiment: 384 nm
[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 407.09 nm (1.1940)
[c] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 425.39 nm (1.0722) /434.82 nm (1.2009)
[d] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 496.29 nm (0.7047).
[e] The results are almost the same when including Q113 in the model part on geometries optimized without including it in the model part (TD-B3LYP:MM-**ME**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**EE**: 405.98 nm (1.2706) → 412.46 nm (1.2746) → 396.64 nm (1.2990)).

Table 3.7.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) when Gln is oriented to form an H-bond with SBR (Conformation A).

	Geometry[d]		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	324.00 (0.0515)[a]	334.98 (0.3056)	337.51 (0.0070)
TD-B3LYP:MM-ME	304.49 (0.0515)	335.49 (0.3056)	314.69 (0.0070)
TD-B3LYP:MM-EE[b]	323.34 (0.4197)	335.77 (0.3393)	333.00 (0.3475)
TD-BLYP	417.87 (0.0018)	425.70 (0.0028)	443.18 (0.0002)
TD-BLYP:MM-ME	374.36 (0.0018)	392.96 (0.0028)	398.26 (0.0002)
TD-BLYP:MM-EE	378.93 (0.7873)	394.67 (0.7162)[c]	390.90 (0.6933)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 332.41 nm (0.0008)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 331.74 nm (0.4650) /339.63 nm (0.3994)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 397.24 nm (0.7715).
[d] The results are almost the same when including Q113 in the model part on geometries optimized without including it in the model part (TD-B3LYP:MM-**ME**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**EE**: 323.02 nm (0.3828) → 324.06 nm (0.3588) → 324.28 nm (0.3084)).

Table 3.7.3. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths) when side chain NH_2 group and carbonyl O moieties of Q113 are oriented towards its backbone carbonyl O and SBR-N, respectively (Conformation B).

	Geometry[e]		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	397.92 (1.1096)[b]	416.26 (1.1498)	416.45 (1.1899)
TD-B3LYP:MM-ME	389.58 (1.1096)	408.13 (1.1498)	408.64 (1.1899)
TD-B3LYP:MM-EE[c]	397.27 (1.1231)	415.66 (1.1628)	415.45 (1.2035)
TD-BLYP	466.28 (0.5554)	482.36 (0.6002)	476.53 (0.7051)
TD-BLYP:MM-ME	449.61 (0.5554)	466.78 (0.6002)	463.39 (0.7051)
TD-BLYP:MM-EE	464.69 (0.5597)	480.89 (0.6046)[d]	474.71 (0.7111)

[a] Experiment: 384 nm

[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 397.75 nm (1.1549)

[c] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 409.17 nm (1.0315) /427.54 nm (1.0496)

[d] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 500.09 nm (0.5369).

[e] The results are almost the same when including Q113 in the model part on geometries optimized without including it in the model part (TD-B3LYP:MM-**ME**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**EE**: 390.30 nm (1.2740) → 394.67 nm (1.2618) → 404.80 nm (1.1594)).

Table 3.7.4. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) when side chain NH_2 group and carbonyl O moieties of Q113 are oriented towards its backbone carbonyl O and SBR-N, respectively (Conformation B).

	Geometry[d]		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	323.75 (0.3244)[a]	336.26 (0.3860)	339.15 (0.0298)
TD-B3LYP:MM-ME	321.61 (0.3244)	335.71 (0.3860)	332.91 (0.0298)
TD-B3LYP:MM-EE[b]	323.65 (0.3043)	336.22 (0.3779)	340.00 (0.0186)
TD-BLYP	412.49 (0.0006)	422.03 (0.0015)	442.70 (0.0012)
TD-BLYP:MM-ME	400.22 (0.0006)	409.03 (0.0015)	429.82 (0.0012)
TD-BLYP:MM-EE	413.27 (0.0004)	422.78 (0.0007)[c]	444.95 (0.0010)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 323.56 nm (0.2613)

[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 325.84 nm (0.0936) /338.10 nm (0.5060)

[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 425.95 nm (0.0004).

[d] The results are almost the same when including Q113 in the model part on geometries optimized without including it in the model part (TD-B3LYP:MM-**ME**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**ME** → TD-B3LYP:MM-**EE**//B3LYP:MM-**EE**: 322.48 nm (0.2689) → 321.74 nm (0.2722) → 322.41 nm(0.4019)).

When side chain NH_2 and carbonyl O moieties of Q113 are oriented, respectively, towards Gly90 and SBR-N, vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are calculated as follows (Conformation C): TD-B3LYP//B3LYP:MM-ME, 391.38 nm (1.2220) / 320.62 nm (0.0470) B3LYP(ME//ME), 388.87 nm (1.2220) / 311.19 nm (0.0470) → B3LYP(EE//ME), 396.99 nm (1.1605) / 321.13 nm (0.4417) → TD-B3LYP//B3LYP:MM-EE, 394.57 nm (1.2427) / 328.35 nm (0.0010) → B3LYP(EE//EE), 422.04 nm (1.0043) / 336.27 nm (0.4781).

3.8. E113Q Mutant with PSBR

Table 3.8.1. Calculated vertical $S_0 \rightarrow S_1$ excitation energies in nm (oscillator strengths) on Conformation B (see Section 3.7)

	Geometry		
Excitation[a]	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	535.78 (1.1463)[b]	546.32 (1.1169)	532.47 (1.2454)
TD-B3LYP:MM-ME	520.58 (1.1463)	530.79 (1.1169)	519.67 (1.2454)
TD-B3LYP:MM-EE[c]	526.40 (1.1658)	535.79 (1.1372)	524.52 (1.2575)
TD-BLYP	577.10 (0.7593)	586.01 (0.7400)	566.64 (0.8704)
TD-BLYP:MM-ME	561.33 (0.7593)	570.04 (0.7400)	553.66 (0.8704)
TD-BLYP:MM-EE	567.36 (0.7716)	575.32 (0.7515)[d]	558.72 (0.8758)

[a] Experiment: 496 nm
[b] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 535.95 nm (1.1154)
[c] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 530.20 nm (1.1219) /534.36 nm (1.2228)
[d] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 571.77 nm (0.8217).

Table 3.8.2. Calculated vertical $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) on Conformation B (see Section 3.7)

	Geometry		
Excitation	B3LYP:MM-ME	BLYP:MM-ME	DFTB:MM-ME
TD-B3LYP	407.54 (0.3659)[a]	417.48 (0.3397)	405.38 (0.2887)
TD-B3LYP:MM-ME	397.70 (0.3659)	407.34 (0.3397)	396.92 (0.2887)
TD-B3LYP:MM-EE[b]	401.24 (0.3569)	410.22 (0.3325)	400.12 (0.2865)
TD-BLYP	464.66 (0.6283)	477.38 (0.5856)	467.16 (0.5493)
TD-BLYP:MM-ME	454.07(0.6283)	466.41 (0.5856)	457.71 (0.5493)
TD-BLYP:MM-EE	458.31 (0.6308)	469.94 (0.5912)[b]	461.86 (0.0067)

[a] TD-B3LYP excitation energy of the isolated QM region at B3LYP:MM-EE geometry: 407.42 nm (0.4127)
[b] TD-B3LYP:MM-EE excitation energies on B3LYP:MM-EE/BLYP:MM-EE geometries: 404.19 nm (0.4077) /409.05 nm (0.3182)
[c] TD-BLYP:MM-EE excitation energy on BLYP:MM-EE geometry: 469.73 nm (0.5978).

3.9. G90D Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows

a) With Deprotonated Asp90

TD-B3LYP//B3LYP:MM-ME, 544.22 nm (1.0260) / 405.88 nm (0.5367) → B3LYP(ME//ME), 493.02 nm (1.0260) / 378.20 nm (0.5367) → B3LYP(EE//ME), 490.38 nm (1.2549) / 380.63 nm (0.3437) → TD-B3LYP//B3LYP:MM-EE, 586.66 nm (0.6506) / 411.69 nm (0.7652) → B3LYP(EE//EE), 475.26 nm (0.9720) / 362.78 nm (0.5233)

b) With Protonated Asp90

TD-B3LYP//B3LYP:MM-ME, 544.03 nm (1.0197) / 406.81 nm (0.5468) → B3LYP(ME//ME), 501.20 nm (1.0197) / 384.65 nm (0.5468) → B3LYP(EE//ME), 503.07 nm (1.1827) / 387.52 nm (0.4227) → TD-B3LYP//B3LYP:MM-EE, 573.85 nm (0.7478) / 407.80 nm (0.7445) → B3LYP(EE//EE), 501.58 nm (0.9496) / 377.94 nm (0.5850)

3.10. A292S Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows when

a) side chain –OH unit of S292 forms an H-bond with carbonyl O of Met288 (Conformation A).

TD-B3LYP//B3LYP:MM-ME, 542.44 nm (1.0277) / 405.60 nm (0.5468) → B3LYP(ME//ME), 499.67 nm (1.0277) / 383.43 nm (0.5468) → B3LYP(EE//ME), 503.07 nm (1.1827) / 386.36 nm (0.4226) → TD-B3LYP//B3LYP:MM-EE, 570.90 nm (0.7237) / 409.10 nm (0.8049) → B3LYP(EE//EE), 501.43 nm (0.9396) / 381.23 nm (0.6300)

b) side chain –OH unit of S292 is oriented towards –OH unit of Ser186 (Conformation B).

TD-B3LYP//B3LYP:MM-ME, 541.79 nm (1.0210) / 406.08 nm (0.5396) → B3LYP(ME//ME), 501.81 nm (1.0210) / 385.22 nm (0.5396) → B3LYP(EE//ME), 504.43 nm (1.1697) / 388.00 nm (0.4283) → TD-B3LYP//B3LYP:MM-EE, 570.23 nm (0.7139) / 409.71 nm (0.8045) → B3LYP(EE//EE), 506.51 nm (0.9057) / 384.51 nm (0.6517)

c) side chain –OH unit of S292 forms an H-bond with a water molecule (Conformation C).

TD-B3LYP//B3LYP:MM-ME, 537.25 nm (1.0603) / 401.26 nm (0.5602) → B3LYP(ME//ME), 496.19 nm (1.0603) / 378.79 nm (0.5602) → B3LYP(EE//ME), 499.02 nm (1.2138) / 381.66 nm (0.4479) → TD-B3LYP//B3LYP:MM-EE, 566.77 nm (0.7461) / 407.14 nm (0.7936) → B3LYP(EE//EE), 499.65 nm (0.9507) / 378.61 nm (0.6317)

3.11. A269T Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows when

a) side chain methyl moiety of T269 is oriented towards C1 (one of methyl group attached to it) and C2 atoms of the chromophore and side chain –OH unit forms an H-bond with Leu266 (Conformation A).

TD-B3LYP//B3LYP:MM-ME, 546.81 nm (0.9454) / 408.01 nm (0.6076) → B3LYP(ME//ME), 500.36 nm (0.9454) / 385.80 nm (0.6076) → B3LYP(EE//ME), 503.54 nm (1.1167) / 387.68 nm (0.4747) → TD-B3LYP//B3LYP:MM-EE, 574.29 nm (0.6908) / 410.48 nm (0.8133) → B3LYP(EE//EE), 503.35 nm (0.8988) / 382.70 nm (0.6404)

b) side chain methyl moiety of T269 as in a and side chain –OH unit forms an H-bond with Trp265 (Conformation B).

TD-B3LYP//B3LYP:MM-ME, 541.88 nm (1.0279) / 405.81 nm (0.5264) → B3LYP(ME//ME), 500.31 nm (1.0279) / 383.85 nm (0.5264) → B3LYP(EE//ME), 502.22 nm (1.1740) / 386.18 nm (0.4144) → TD-B3LYP//B3LYP:MM-EE, 567.89 nm (0.7430) / 407.08 nm (0.7890) → B3LYP(EE//EE), 497.98 nm (0.9527) / 378.10 nm (0.6197)

c) side chain methyl moiety of T269 as in a and side chain –OH unit is oriented towards backbone carbonyl O (Conformation C).

TD-B3LYP//B3LYP:MM-ME, 543.19 nm (0.9788) / 406.48 nm (0.5971) → B3LYP(ME//ME), 499.12 nm (0.9788) / 384.83 nm (0.5971) → B3LYP(EE//ME), 502.34 nm (1.1471) / 387.02 nm (0.4658) → TD-B3LYP//B3LYP:MM-EE, 571.24 nm (0.6966) / 410.44 nm (0.8133) → B3LYP(EE//EE), 506.23 nm (0.8919) / 385.20 nm (0.6522)

d) side chain methyl moiety of T269 is oriented towards Leu266 side chain and side chain –OH unit as in c (Conformation D)

TD-B3LYP//B3LYP:MM-ME, 542.25 nm (1.0096) / 406.10 nm (0.5657) → B3LYP(ME//ME), 501.48 nm (1.0096) / 385.37 nm (0.5657) → B3LYP(EE//ME), 504.11 nm (1.1558) / 387.53 nm (0.4555) → TD-B3LYP//B3LYP:MM-EE, 567.99 nm (0.7440) / 408.75 nm (0.7709) → B3LYP(EE//EE), 505.50 nm (0.9197) / 382.72 nm (0.6262)

3.12. D83N Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows: TD-B3LYP//B3LYP:MM-ME, 533.53 nm (1.1601) / 405.40 nm (0.4176) → B3LYP(ME//ME), 500.67 nm (1.1601) / 384.60 nm (0.4176) → B3LYP(EE//ME), 503.06 nm (1.2845) / 387.63 nm (0.3230) → TD-B3LYP//B3LYP:MM-EE, 570.40 nm (0.7147) / 409.74 nm (0.8111) → B3LYP(EE//EE), 502.39 nm (0.9234) / 382.12 nm (0.6410)

3.13. W265Y Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows: TD-B3LYP//B3LYP:MM-ME, 536.17 nm (1.0586) / 404.46 nm (0.5286) → B3LYP(ME//ME), 495.33 nm (1.0586) / 382.26 nm (0.5286) → B3LYP(EE//ME), 503.07 nm (1.1827) / 384.35 nm (0.3957) →

TD-B3LYP//B3LYP:MM-EE, 573.46 nm (0.6804) / 411.05 nm (0.8033) → B3LYP(EE//EE), 497.11 nm (0.9079) / 380.15 nm (0.6115)

3.14. H211C Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows: TD-B3LYP//B3LYP:MM-ME, 543.36 nm (0.9915) / 406.13 nm (0.5712) → B3LYP(ME//ME), 499.15 nm (0.9915) / 383.51 nm (0.5712) → B3LYP(EE//ME), 501.35 nm (1.1628) / 385.91 nm (0.4390) → TD-B3LYP//B3LYP:MM-EE, 572.86 nm (0.6922) / 410.17 nm (0.8198) → B3LYP(EE//EE), 501.13 nm (0.9155) / 381.74 nm (0.6399)

3.15. E181Q Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows

a) when OE2 atom of E181 is replaced with NH_2 moiety (Conformation A).

TD-B3LYP//B3LYP:MM-ME, 541.20 nm (1.1601) / 405.16 nm (0.5261) → B3LYP(ME//ME), 498.95 nm (1.1601) / 382.83 nm (0.5261) → B3LYP(EE//ME), 500.76 nm (1.1884) / 385.46 nm (0.4073) → TD-B3LYP//B3LYP:MM-EE, 570.83 nm (0.7221) / 408.78 nm (0.7798) → B3LYP(EE//EE), 499.24 nm (0.9343) / 378.79 nm (0.6097)

b) when OE1 atom of E181 is replaced with NH_2 moiety (Conformation B).

TD-B3LYP//B3LYP:MM-ME, 543.28 nm (1.0049) / 406.79 nm (0.5332) → B3LYP(ME//ME), 499.95 nm (1.0049) / 384.10 nm (0.5332) → B3LYP(EE//ME), 501.93 nm (1.1633) / 386.39 nm (0.4121) → TD-B3LYP//B3LYP:MM-EE, 570.37 nm (0.7193) / 408.30 nm (0.7889) → B3LYP(EE//EE), 500.39 nm (0.9271) / 379.60 nm (0.6244)

3.16. E113D Mutant with PSBR

Calculated vertical $S_0 \rightarrow S_1$ / $S_0 \rightarrow S_2$ excitation energies in nm (oscillator strengths) are as follows: TD-B3LYP//B3LYP:MM-ME, 533.22 nm (1.1663) / 406.10 nm (0.3760) → B3LYP(ME//ME), 503.49 nm (1.1663) / 386.33 nm (0.3760) → B3LYP(EE//ME), 504.94 nm (1.2775) / 388.90 nm (0.2947) → TD-B3LYP//B3LYP:MM-EE, 556.96 nm (0.8401) / 408.22 nm (0.7157) → B3LYP(EE//EE), 498.73 nm (1.0433) / 379.14 nm (0.5426)

4. Geometry Parameters of 11-*cis*-retinal

Indexing of C atoms (1-15) are as in Figure 2 of the paper. A and B correspond to chain A and B in the X-ray structures.

	1U19-A	1U19-B	1F88-A	1F88-B	1HZX-A	1HZX-B	1L9H-A	1L9H-B	1JFP
Bond Lengths (Å)									
1-6	1.6	1.61	1.52	1.53	1.5	1.55	1.55	1.55	1.54
5-6	1.43	1.44	1.36	1.35	1.38	1.34	1.41	1.41	1.36
6-7	1.51	1.52	1.48	1.48	1.5	1.52	1.52	1.49	1.46
7-8	1.36	1.36	1.36	1.36	1.38	1.38	1.38	1.36	1.34
8-9	1.47	1.46	1.48	1.48	1.49	1.49	1.48	1.46	1.46
9-10	1.37	1.37	1.36	1.36	1.35	1.37	1.35	1.35	1.35
10-11	1.46	1.46	1.48	1.49	1.47	1.48	1.49	1.49	1.45
11-12	1.39	1.39	1.36	1.37	1.36	1.37	1.37	1.37	1.35
12-13	1.49	1.49	1.49	1.49	1.49	1.5	1.48	1.49	1.47
13-14	1.35	1.38	1.33	1.34	1.36	1.37	1.35	1.37	1.35
14-15	1.43	1.45	1.48	1.48	1.49	1.5	1.5	1.51	1.48
15-N	1.33	1.34	1.46	1.46	1.35	1.36	1.35	1.37	1.28
N-C(Leu296)	1.48	1.48	1.46	1.47	1.47	1.48	1.47	1.48	1.47
N···O(Glu113)	3.45	3.28	3.22	3.35	3.6	3.57	3.13	3.04	3.35
Bond Angles (°)									
1-6-7	119.2	119.4	113.5	114.5	111.8	114.2	124	124.2	117.2
5-6-7	121.4	120.8	122.7	121.6	125	123.3	117.4	116.6	120.3
6-7-8	131.8	132.3	118.8	116	121.6	118.7	119.5	117.3	123.3
7-8-9	131.2	130.5	128.9	130.8	130.6	130.8	132.1	132.2	127.4
8-9-10	115.4	115.1	123.5	123.9	123	123.6	117.4	116.8	117.9
9-10-11	125.7	126	128.1	126.8	127.4	127.4	124.9	125.4	127.5
10-11-12	122.3	123	127.9	129.4	130	131.5	129.2	128	128.5
11-12-13	131.7	131.6	133.5	135.5	139.6	139.4	138.6	137.5	131.2
12-13-14	112.9	112.7	121.4	122.8	118.4	120.1	114.2	115.1	118.2
13-14-15	127.4	128.4	123.5	124.2	129.1	127.4	125	126	123.7
14-15-N	118.3	119.2	118.5	117.5	118.3	120.1	117.9	119	125.2
15-N-C	135.2	134.5	130.6	132.5	132.6	132.4	134.4	135.4	128.2
Dihedral Angles (°)									
1-6-7-8	148	146.4	120.1	120.7	122.9	127.2	104	96.6	-94.3
5-6-7-8	-30.3	-31.9	-59.4	-58.6	-56.6	-52.8	-77.4	-84.4	85.9
6-7-8-9	-174.8	-176.8	179.6	179.8	169.2	170.6	-172.9	-178.5	176
7-8-9-10	171.5	167	-179.7	-179.8	-152.7	-160.2	-149.3	-146.6	-161.6
8-9-10-11	-176	-176.4	179.3	179	176.4	172.6	179.8	180	-175.3
9-10-11-12	173.2	173.9	179.1	177.8	157.8	158.3	162.5	162.8	-157.2
10-11-12-13	-40.8	-36.1	-0.74	-1.7	7.9	7.9	0	0.1	8
11-12-13-14	-173.5	178.6	170.5	157	156.2	151.6	171.5	150.1	-168.5
12-13-14-15	171	171.2	179.4	179.5	-144.3	-144.6	172.1	157.7	-175.2
13-14-15-N	164.6	178.6	-179.6	-179.9	-99	-114.3	135.5	-175.8	165.4

14-15-N-C	-167.9	-166	179.5	-179.8	-167.7	-178.1	-178.9	-148.3	-154
15-N-C-C	55	47.7	53.8	35.09	-76.5	-4.4	74.2	37.7	-175.9

In the following tables, only QM level and embedding scheme of ONIOM(QM:MM) calculations will be shown.

	WT enzyme with PSBR					WT enzyme with SBR and protonated Glu113				
	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me	b3lyp-me	b3lyp-ee	Blyp-me	blyp-ee	dftb-me
Bond Lengths (Å)										
1-6	1.548	1.546	1.561	1.559	1.53	1.544	1.544	1.557	1.557	1.528
5-6	1.37	1.359	1.386	1.375	1.377	1.356	1.356	1.37	1.37	1.363
6-7	1.448	1.464	1.45	1.465	1.439	1.472	1.472	1.476	1.475	1.46
7-8	1.371	1.36	1.386	1.377	1.378	1.353	1.355	1.367	1.37	1.362
8-9	1.424	1.441	1.428	1.441	1.424	1.45	1.45	1.45	1.45	1.444
9-10	1.396	1.379	1.409	1.396	1.402	1.366	1.368	1.385	1.388	1.375
10-11	1.401	1.42	1.408	1.42	1.402	1.437	1.435	1.435	1.432	1.432
11-12	1.395	1.379	1.405	1.394	1.397	1.361	1.365	1.38	1.384	1.365
12-13	1.406	1.427	1.415	1.43	1.407	1.455	1.452	1.457	1.453	1.448
13-14	1.417	1.397	1.426	1.411	1.42	1.366	1.372	1.384	1.39	1.372
14-15	1.38	1.397	1.388	1.402	1.388	1.455	1.442	1.458	1.445	1.454
15-N	1.336	1.322	1.349	1.338	1.336	1.286	1.292	1.302	1.308	1.28
N-C(Leu296)	1.466	1.469	1.473	1.475	1.479	1.485	1.482	1.495	1.491	1.496
N···O(Glu113)	2.807	2.731	2.804	2.737	2.818	2.84	2.677	2.842	2.672	2.862
Bond Angles (˚)										
1-6-7	117.6	117.2	117.8	117.3	118.4	116.8	117	117.1	116.9	117.5
5-6-7	121.3	121.4	121.3	121.5	121.4	121.5	121.4	121	121.5	121.4
6-7-8	123.7	123	123.9	123.3	122.8	123	122.8	121.8	122.4	122.1
7-8-9	128.3	129	128.5	129	126.6	128.7	129.1	130.1	130.2	127.1
8-9-10	117.1	117.3	117.1	117.3	118	118.2	117.9	116.6	116.6	118.8
9-10-11	125	124.8	125.3	125.2	123.5	125.3	125.3	126.7	126.6	122.4
10-11-12	128.8	129.8	128.6	129.6	127.2	129.9	130	129.5	129.4	128.9
11-12-13	130.3	130.6	130.6	131.1	129.1	132.4	131.8	132.8	132	131.1
12-13-14	117.5	116.8	117.2	116.3	117.5	116.4	116.9	116.7	117.3	116.1
13-14-15	125.6	123.7	124	124.4	123.8	126.5	126.4	127	126.7	125.9
14-15-N	125.4	124	125.4	123.7	123	121.1	121.4	121	121.4	121.6
15-N-C	124.3	123	124.1	122.9	124	115.8	116.2	115.5	116.2	118
Dihedral Angles (˚)										
1-6-7-8	142.9	138.2	114.3	140.6	148.1	134.3	134.9	132.6	134.8	143.1
5-6-7-8	-40.8	-45.5	-39.3	-43.4	-37.3	-48.6	-48.6	-49.1	-48	-41.6
6-7-8-9	178.3	177.4	178.2	177.1	179.3	176.5	176.1	175.6	177.5	177.7
7-8-9-10	170.7	175.9	169.9	175.5	166.9	177.1	178.8	175.4	175.7	172.8
8-9-10-11	169.4	170.6	169.7	169.8	169.1	171.1	170.2	169.8	170.4	171.5
9-10-11-12	174.8	173.6	172.3	173	174.7	170.3	172.2	174.5	175	167
10-11-12-13	-24.1	-18.6	-23.9	-19.2	-24.6	-12	-14.4	-13	-16.1	-13.6
11-12-13-14	175.3	174.2	176.1	175.7	176.5	173.6	172.4	174	172.9	177
12-13-14-15	180	179.4	178.4	178.1	177.6	-179.1	177.5	-179.9	177.3	180

13-14-15-N	171.1	172.4	171.8	173.4	172	165.5	171.9	167.8	172.6	163.3
14-15-N-C	175.6	174.2	175.9	174.7	177	177.1	177.6	176.5	176.6	177.3
15-N-C-C	96.1	92	94.2	89.9	93.4	95.8	94.9	97.1	96.9	93.7
	WT enzyme with SBR and deprotonated Glu113					E113Q with SBR (Conformation A)				
	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me	b3lyp-me	b3lyp-ee	Blyp-me	blyp-ee	dftb-me
Bond Lengths (Å)										
1-6	1.546	1.545	1.558	1.558	1.528	1.544	1.544	1.56	1.559	1.528
5-6	1.358	1.356	1.372	1.369	1.363	1.356	1.356	1.37	1.37	1.363
6-7	1.475	1.479	1.478	1.481	1.463	1.471	1.472	1.473	1.474	1.46
7-8	1.355	1.356	1.371	1.371	1.363	1.353	1.355	1.369	1.371	1.361
8-9	1.453	1.453	1.453	1.454	1.447	1.45	1.45	1.452	1.452	1.445
9-10	1.368	1.367	1.386	1.385	1.376	1.366	1.368	1.383	1.385	1.375
10-11	1.443	1.441	1.442	1.439	1.436	1.438	1.436	1.438	1.436	1.433
11-12	1.362	1.362	1.379	1.38	1.367	1.361	1.364	1.378	1.381	1.365
12-13	1.456	1.457	1.456	1.457	1.449	1.455	1.453	1.456	1.454	1.449
13-14	1.396	1.366	1.386	1.382	1.375	1.365	1.371	1.381	1.385	1.372
14-15	1.455	1.455	1.457	1.455	1.455	1.456	1.444	1.456	1.447	1.456
15-N	1.282	1.281	1.298	1.297	1.277	1.284	1.291	1.3	1.305	1.278
N-C(Leu296)	1.478	1.479	1.488	1.488	1.49	1.483	1.481	1.493	1.491	1.495
N···O(Glu113)	3.371	3.76	3.358	3.961	3.41	-	-	-	-	-
N···N(Gln113)	-	-	-	-	-	2.965	2.861	3.013	2.912	2.981
Bond Angles (˚)										
1-6-7	118.4	118.7	118.5	118.2	119.2	116.8	117.2	115.6	115.8	117.3
5-6-7	120.8	120.7	120.9	121.2	120.8	121.4	121.3	122.8	122.6	121.6
6-7-8	122.2	121.4	122.2	122.2	121.6	123.1	122.5	125.4	125	122.5
7-8-9	129.1	130.1	129.6	129.9	126.9	128.7	129.5	128.1	128.4	126.7
8-9-10	117.8	117.2	117.7	117.4	118.7	118.2	117.6	118.7	118.3	118.8
9-10-11	126.4	127.1	126.8	127	124.5	125.2	125.3	125.1	125.3	122.8
10-11-12	130.1	129.4	129.9	130.1	128.8	130	129.9	129.9	129.8	128.7
11-12-13	132.2	131.9	132.4	132.9	131	132.3	131.4	132.2	131.7	131.1
12-13-14	117.9	116.9	117.9	116.2	118	116.5	117.1	116.4	116.9	116.4
13-14-15	124.7	126	124.9	127.1	123.9	126.2	126.3	127.1	127.2	125.8
14-15-N	121.4	119.6	121.4	119.1	122	120.8	121	120.2	120.1	121.4
15-N-C	116.5	116.6	116.1	116.3	118.9	116.3	116.5	115.9	116	118.7
Dihedral Angles (˚)										
1-6-7-8	136.2	133.5	137.6	136.2	143	135	135.3	138.4	138.2	143.2
5-6-7-8	-47.5	-49.4	-46.2	-47.4	-42.4	-47.9	-47.9	-45.1	-46	-41.6
6-7-8-9	172.2	172.2	172.4	173.6	174.9	176.4	176.2	-178.3	-179.8	179.1
7-8-9-10	179.9	-178.8	179.1	179.6	174.1	176.7	178.5	172.1	174.1	171.9
8-9-10-11	169	168.8	168.3	169.5	170	172	171.2	175.1	173.8	173
9-10-11-12	168.9	170.1	170.1	172.4	167.7	168.9	170.8	166.7	170.6	122.4
10-11-12-13	-12.4	-12.7	-13.8	-12.4	-13.3	-11.2	-14	-12.2	-14	-12.6
11-12-13-14	173	172.5	173.9	177.2	173.2	174.7	173.5	172.7	171.2	175.7
12-13-14-15	-179.6	177.8	-179.3	176.3	178.9	-178.2	177.9	-177.5	177.9	179.5
13-14-15-N	168.6	170.6	169	172.5	167.1	163.4	172.2	163.5	170.2	163.6
14-15-N-C	179.3	179	179.5	179.5	178.7	177.8	177.9	177.9	177.5	176.1

15-N-C-C	97.3	98.8	97.3	92.4	97.6	95.8	94.4	93.4	93.3	96.1

	E113Q with SBR (Conformation B)					E113Q with PSBR				
	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me
Bond Lengths (Å)										
1-6	1.544	1.544	1.557	1.557	1.528	1.548	1.547	1.559	1.56	1.531
5-6	1.357	1.355	1.371	1.37	1.363	1.369	1.367	1.385	1.383	1.376
6-7	1.475	1.476	1.478	1.48	1.461	1.447	1.45	1.452	1.453	1.44
7-8	1.354	1.355	1.369	1.37	1.361	1.371	1.37	1.384	1.385	1.378
8-9	1.451	1.453	1.452	1.453	1.446	1.424	1.427	1.43	1.431	1.424
9-10	1.366	1.368	1.384	1.385	1.375	1.395	1.393	1.41	1.407	1.401
10-11	1.44	1.438	1.439	1.437	1.436	1.401	1.402	1.408	1.408	1.402
11-12	1.361	1.363	1.378	1.38	1.366	1.395	1.395	1.409	1.407	1.396
12-13	1.456	1.456	1.456	1.456	1.45	1.407	1.409	1.418	1.418	1.408
13-14	1.364	1.369	1.38	1.386	1.372	1.412	1.413	1.423	1.423	1.416
14-15	1.451	1.453	1.452	1.455	1.452	1.38	1.384	1.392	1.393	1.388
15-N	1.283	1.284	1.299	1.299	1.278	1.338	1.336	1.352	1.35	1.338
N-C(Leu296)	1.479	1.479	1.489	1.489	1.491	1.465	1.467	1.474	1.475	1.477
N···N(Gln113)	3.317	3.469	3.336	3.413	3.391	2.921	2.863	2.888	2.885	2.968
Bond Angles (˚)										
1-6-7	118.2	118.1	118.1	118.4	117.7	117.1	117.1	117.4	117.2	117.4
5-6-7	120.8	120.9	121	120.8	121.6	121.7	121.7	121.4	121.9	121.8
6-7-8	121.8	121.9	122.1	121.6	122.4	124.2	123.9	123.5	124.4	123.5
7-8-9	129.3	129.3	129.5	130.1	126.7	128.1	128.3	129.2	128.4	126.1
8-9-10	117.6	117.2	117.5	116.9	118.7	116.9	116.9	115.8	117	118.2
9-10-11	126.6	126.6	126.9	127.1	124	125.1	125	126.6	125.4	123.3
10-11-12	128.8	129.7	128.7	129.2	127.5	127.9	128.4	127.5	128.6	127
11-12-13	131.3	132.1	131.4	131.8	129.7	129.3	129.7	129.8	130.4	128.8
12-13-14	116.9	116.7	116.9	116.9	117.3	117.3	117.3	117.7	117	116.6
13-14-15	127.3	127.5	127.6	127.5	126.3	125	124.9	125	125.5	125.6
14-15-N	119.6	119.3	119.5	119.5	120.3	123.9	124	123.7	124	121.2
15-N-C	116.3	116.5	115.8	115.8	118.8	124.6	123.8	125	123.7	124.3
Dihedral Angles (˚)										
1-6-7-8	133.9	134	135.7	134.9	142.6	143.7	143	142.5	145.5	148.7
5-6-7-8	-48.8	-49.3	-47.4	-48.4	-42.4	-40.6	-41.8	-41.6	-39.7	-37
6-7-8-9	172.7	173.8	173	173	178	179.8	179.4	178.6	179.4	-179
7-8-9-10	179.5	179.1	178.2	178.9	174.2	171.1	172.7	169	172.2	168.1
8-9-10-11	168.7	170.9	168.4	168.9	170.9	171	171.4	171.2	171	171.2
9-10-11-12	170.4	171.2	171.8	172.8	166.1	173.5	174.2	175.3	174.1	172.8
10-11-12-13	-12.8	-11	-13.8	-13.4	-14.4	-23.1	-22.4	-22.5	-23.2	-22.5
11-12-13-14	169.8	172.2	171	172.8	171	173.3	174	171.9	175.8	176.2
12-13-14-15	178.2	178	178.2	178	175.4	178	178.1	179.9	175.9	174
13-14-15-N	173.2	174.1	173.3	173.9	174.4	176.5	177.3	175.8	178.1	177.7
14-15-N-C	179.6	179.1	179.9	179.2	178.1	178.5	177	177.6	177.4	179.4

15-N-C-C	97.1	92.9	95.5	95.1	95.5	93.6	92.5	95.4	89.6	88.6

b3lyp-me and b3lyp-ee bond lengths of Conformation C are as follows in the order given in the table:

b3lyp-me: 1.545/1.355/1.475/1.352/1.452/1.365/1.437/1.361/1.457/1.364/1.453/1.285/1.484/-
b3lyp-ee: 1.544/1.355/1.475/1.353/1.453/1.368/1.434/1.365/1.453/1.371/1.445/1.290/1.480/-

	E122Q with PSBR					E122Q with SBR and protonated Glu113				
	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me
Bond Lengths (Å)										
1-6	1.548	1.546	1.561	1.56	1.53	1.545	1.547	1.558	1.56	1.528
5-6	1.369	1.359	1.385	1.375	1.376	1.356	1.357	1.371	1.372	1.363
6-7	1.448	1.468	1.45	1.466	1.44	1.473	1.475	1.475	1.477	1.46
7-8	1.371	1.359	1.386	1.376	1.378	1.353	1.335	1.368	1.37	1.362
8-9	1.427	1.445	1.43	1.443	1.424	1.45	1.451	1.45	1.451	1.445
9-10	1.396	1.377	1.409	1.396	1.402	1.368	1.37	1.385	1.388	1.375
10-11	1.403	1.423	1.408	1.422	1.402	1.436	1.435	1.435	1.433	1.433
11-12	1.395	1.377	1.406	1.394	1.397	1.363	1.366	1.38	1.383	1.365
12-13	1.407	1.428	1.415	1.431	1.407	1.456	1.453	1.456	1.453	1.449
13-14	1.416	1.396	1.426	1.411	1.419	1.366	1.372	1.384	1.389	1.372
14-15	1.38	1.398	1.389	1.403	1.388	1.456	1.443	1.457	1.445	1.455
15-N	1.336	1.322	1.349	1.337	1.336	1.286	1.292	1.302	1.308	1.28
N-C(Leu296)	1.466	1.469	1.473	1.476	1.479	1.485	1.482	1.495	1.491	1.497
N···O(Glu113)	2.811	2.73	2.808	2.733	2.817	2.842	2.678	2.821	2.676	2.866
Bond Angles (˚)										
1-6-7	117.2	116.9	117.4	116.8	118.4	116.5	116.7	116.6	116.8	117
5-6-7	121.7	121.8	121.9	122.1	121.5	121.6	121.6	121.7	121.7	121.7
6-7-8	124.8	123.4	124.7	124.2	122.9	122.8	122.6	122.8	122.6	122.9
7-8-9	127.5	128.2	128.1	128.5	126.5	129.5	129.8	130	130.1	126.5
8-9-10	117.5	117.6	117.1	117.5	118	117.2	116.9	116.9	116.7	119.2
9-10-11	125	124.8	125.5	125	123.6	125.5	125.6	125.9	126.1	122.5
10-11-12	129.3	130.3	128.5	129.6	127	130.3	130.4	130	130	129
11-12-13	130.8	130.9	130.6	130.7	128.9	132.8	132.2	132.6	132.1	131.33
12-13-14	117.3	116.5	117.4	116.8	117.5	116.4	116.9	116.7	117.1	116.2
13-14-15	123.7	123.9	123.7	123.7	123.7	126.9	126.6	126.8	126.7	126.1
14-15-N	125.3	123.8	125.3	124.1	122.8	120.9	121.5	121.3	121.5	121.6
15-N-C	124.4	123.2	124.3	122.9	124.2	116	116.3	115.4	115.9	118.1
Dihedral Angles (˚)										
1-6-7-8	143.8	137.3	145.2	141.2	147.9	133.2	133.1	134.8	134.5	143.2
5-6-7-8	-40.8	-45.9	-39.4	-42.9	-37.8	-48.8	-48.5	-47.1	-47.3	-41.7
6-7-8-9	178.7	178	179.1	178.9	179.2	178.1	177.6	178.7	177.6	179
7-8-9-10	171.1	177.3	170.9	175.1	168.6	176.5	177.1	174.2	175.4	172.2
8-9-10-11	170.4	170.2	169.7	170.6	168.1	172.3	171.3	172.4	171	172.5
9-10-11-12	175.3	174.7	174.8	174.7	176.1	171.7	173.7	172.1	175.1	166
10-11-12-13	-22.6	-17.8	-24.7	-20.3	-24.9	-12.2	-14.3	-13.9	-16.1	-12.8
11-12-13-14	174.6	174.2	174.5	174.3	175.9	176.3	174.9	176.9	175.8	174.9
12-13-14-15	-179.9	180	-179.1	-179.3	179.6	-179.9	176.9	179.8	176.7	179.4

13-14-15-N	170.9	171.7	170.5	171.8	171.4	165.4	171.1	166.4	171.8	164.1
14-15-N-C	176.3	175.3	176.9	174.9	178.7	176.3	176.5	175.8	176.4	176.1
15-N-C-C	94.5	91	96.7	91.1	94.3	94.1	93.4	93.7	93.3	94.5

b3lyp-me and b3lyp-ee bond lengths of Conformation C for PSBR are as follows in the order given in the table:

b3lyp-me: 1.548/1.368/1.452/1.370/1.427/1.395/1.403/1.393/1.407/1.414/1.379/1.335/1.465/2.804
b3lyp-ee: 1.548/1.362/1.465/1.361/1.443/1.380/1.419/1.378/1.426/1.397/1.395/1.323/1.468/2.739

	E122Q with SBR and deprotonated Glu113					E181Q (Conform. A)		E181Q (Conform. B)	
	b3lyp-me	b3lyp-ee	blyp-me	blyp-ee	dftb-me	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee
Bond Lengths (Å)									
1-6	1.545	1.546	1.559	1.56	1.529	1.547	1.545	1.548	1.545
5-6	1.357	1.357	1.372	1.371	1.363	1.368	1.358	1.368	1.358
6-7	1.476	1.48	1.478	1.483	1.463	1.45	1.468	1.451	1.468
7-8	1.355	1.356	1.371	1.371	1.363	1.37	1.36	1.37	1.359
8-9	1.453	1.452	1.453	1.455	1.447	1.427	1.445	1.427	1.445
9-10	1.368	1.368	1.386	1.385	1.377	1.394	1.379	1.394	1.378
10-11	1.443	1.441	1.442	1.439	1.436	1.403	1.421	1.403	1.421
11-12	1.362	1.362	1.38	1.38	1.367	1.393	1.378	1.393	1.378
12-13	1.456	1.457	1.455	1.457	1.449	1.407	1.427	1.407	1.428
13-14	1.369	1.365	1.387	1.382	1.376	1.415	1.397	1.415	1.396
14-15	1.456	1.456	1.457	1.455	1.456	1.38	1.396	1.38	1.397
15-N	1.282	1.281	1.297	1.297	1.277	1.336	1.323	1.336	1.322
N-C(Leu296)	1.478	1.479	1.487	1.488	1.49	1.467	1.468	1.466	1.469
N···O(Glu113)	3.334	3.794	3.378	3.93	3.396	2.825	2.738	2.821	2.745
Bond Angles (˚)									
1-6-7	118.5	118.4	118.3	117.7	118.9				
5-6-7	120.8	120.9	121.1	121.6	121				
6-7-8	122	121.4	122.6	122.6	121.9				
7-8-9	129.3	129.9	129.3	129.6	126.8				
8-9-10	117.8	117.3	117.9	117.6	118.8				
9-10-11	126.4	126.9	126.6	126.9	124.3				
10-11-12	130.2	129.6	130.3	130.2	129.1				
11-12-13	132.3	132.2	132.6	133.1	131.1				
12-13-14	117.9	116.7	117.8	116	118.2				
13-14-15	124.7	126.3	124.9	127.4	123.9				
14-15-N	121.4	119.3	121.4	118.8	122				
15-N-C	116.7	116.9	116	116.6	119				
Dihedral Angles (˚)									
1-6-7-8	135.2	132.4	138	134.7	142.7				
5-6-7-8	-47.9	-49.5	-45.9	-47.6	-42.5				
6-7-8-9	172.7	173.7	172.9	175.8	175.6				
7-8-9-10	179.9	-179.2	179.4	179	173.6				
8-9-10-11	169	168.8	168.7	169.7	170.2				
9-10-11-12	168.7	170.6	170.4	172.2	168.3				
10-11-12-13	-12.6	-13	-13.5	-12.7	-13.6				

11-12-13-14	172.8	173	175	177	173.6
12-13-14-15	-179.6	178.2	180	176.4	178.8
13-14-15-N	168.5	170.7	169.2	172.1	166.9
14-15-N-C	179.1	179.3	179.3	179.4	178.4
15-N-C-C	98.1	98.7	95.8	92.7	98

Bond Lengths (Å)	G90D with PSBR				H211C with PSBR		D83N with PSBR	
	protonated Asp90		deprotonated Asp90					
	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee
1-6	1.548	1.548	1.55	1.547	1.548	1.545	1.547	1.545
5-6	1.369	1.359	1.368	1.357	1.368	1.358	1.369	1.358
6-7	1.452	1.466	1.452	1.471	1.452	1.468	1.449	1.468
7-8	1.37	1.359	1.37	1.357	1.37	1.359	1.371	1.359
8-9	1.428	1.444	1.428	1.45	1.427	1.444	1.426	1.445
9-10	1.395	1.377	1.395	1.374	1.394	1.379	1.396	1.378
10-11	1.404	1.42	1.405	1.431	1.403	1.42	1.402	1.42
11-12	1.394	1.376	1.396	1.373	1.392	1.377	1.395	1.378
12-13	1.407	1.429	1.408	1.437	1.407	1.426	1.407	1.427
13-14	1.415	1.394	1.416	1.388	1.414	1.396	1.417	1.397
14-15	1.38	1.394	1.381	1.406	1.379	1.395	1.38	1.396
15-N	1.336	1.325	1.336	1.314	1.335	1.323	1.336	1.323
N-C(Leu296)	1.467	1.468	1.467	1.47	1.465	1.467	1.466	1.467
N···O(Glu113)	2.844	2.794	2.863	2.767	2.8	2.732	2.812	2.735

Bond Lengths (Å)	A292S with PSBR						W265Y with PSBR	
	Conformation A		Conformation B		Conformation C			
	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee
1-6	1.548	1.545	1.547	1.546	1.548	1.546	1.547	1.545
5-6	1.369	1.358	1.369	1.359	1.368	1.359	1.367	1.358
6-7	1.451	1.468	1.451	1.468	1.451	1.468	1.448	1.465
7-8	1.37	1.359	1.37	1.36	1.37	1.36	1.37	1.358
8-9	1.427	1.444	1.427	1.444	1.428	1.445	1.427	1.444
9-10	1.394	1.379	1.394	1.38	1.395	1.379	1.394	1.377
10-11	1.403	1.42	1.403	1.419	1.404	1.421	1.404	1.422
11-12	1.392	1.378	1.393	1.379	1.394	1.378	1.393	1.376
12-13	1.407	1.426	1.407	1.425	1.408	1.427	1.406	1.428
13-14	1.415	1.397	1.415	1.398	1.414	1.397	1.414	1.395
14-15	1.379	1.395	1.379	1.396	1.38	1.396	1.379	1.397
15-N	1.335	1.324	1.335	1.323	1.335	1.323	1.335	1.321

N-C(Leu296)	1.465	1.467	1.465	1.468	1.465	1.468	1.465	1.467
N···O(Glu113)	2.806	2.737	2.797	2.728	2.806	2.732	2.809	2.736

Bond Lengths (Å)	A269T with PSBR							
	Conformation A		Conformation B		Conformation C		Conformation D	
	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee	b3lyp-me	b3lyp-ee
1-6	1.544	1.543	1.548	1.545	1.545	1.543	1.547	1.544
5-6	1.365	1.357	1.367	1.358	1.366	1.358	1.366	1.357
6-7	1.452	1.467	1.449	1.467	1.451	1.467	1.452	1.466
7-8	1.368	1.358	1.368	1.359	1.368	1.359	1.369	1.359
8-9	1.427	1.443	1.427	1.446	1.426	1.442	1.428	1.444
9-10	1.393	1.378	1.393	1.378	1.393	1.379	1.393	1.379
10-11	1.403	1.421	1.403	1.422	1.403	1.419	1.403	1.421
11-12	1.391	1.377	1.392	1.376	1.391	1.377	1.392	1.378
12-13	1.407	1.426	1.407	1.427	1.407	1.425	1.407	1.427
13-14	1.413	1.396	1.415	1.396	1.413	1.397	1.414	1.397
14-15	1.379	1.396	1.38	1.396	1.379	1.394	1.38	1.397
15-N	1.335	1.323	1.336	1.322	1.335	1.324	1.335	1.323
N-C(Leu296)	1.465	1.467	1.466	1.467	1.464	1.467	1.465	1.469
N···O(Glu113)	2.807	2.736	2.814	2.733	2.807	2.732	2.81	2.738

E113D		
Bond Lengths (Å)	b3lyp-me	b3lyp-ee
1-6	1.548	1.546
5-6	1.370	1.359
6-7	1.447	1.465
7-8	1.372	1.360
8-9	1.424	1.442
9-10	1.396	1.379
10-11	1.401	1.419
11-12	1.395	1.378
12-13	1.406	1.426
13-14	1.419	1.398
14-15	1.379	1.395
15-N	1.337	1.323
N-C(Leu296)	1.468	1.469
N···O(Asp113)	2.883	2.814

5. Average BLA Values

Structure	Average BLA (Å) of B3LYP:MM-EE geometry	B3LYP(EE//EE) First Vertical Excitation Energy (nm)
WT	0.064	503
WT with SBR and protonated Glu113	0.099	429
WT with SBR and protonated Glu113	0.109	380
E113Q with SBR (Conformation A)	0.100	425
E113Q with SBR (Conformation B)	0.106	409
E113Q with SBR (Conformation C)	0.102	422
E113Q with PSBR	0.035	530
E113D with PSBR	0.063	499
E122Q with PSBR (Conformation A)	0.067	492
E122Q with PSBR (Conformation B)	0.063	514
E122Q with SBR and protonated Glu113	0.103	418
E122Q with SBR and deprotonated Glu113	0.109	379
G90D with PSBR and protonated Asp90	0.066	502
G90D with PSBR and deprotonated Asp90	0.079	475
W265Y with PSBR	0.067	497
A292S with PSBR (Conformation A)	0.065	501
A292S with PSBR (Conformation B)	0.064	507
A292S with PSBR (Conformation C)	0.065	500
A269T with PSBR (Conformation A)	0.066	503
A269T with PSBR (Conformation B)	0.067	498
A269T with PSBR (Conformation C)	0.064	506
A269T with PSBR (Conformation D)	0.066	506
H211C with PSBR	0.065	501
D83N with PSBR	0.066	502
E181Q (Conformation A)	0.066	499
E181Q (Conformation A)	0.067	500