Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Non-radiative Relaxation of UV Photoexcited Phenylalanine Residues: Probing the Role of Conical Intersections by Chemical Substitution

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Supporting Information

S1. UV Spectroscopy and pump-probe experiment on conformer A

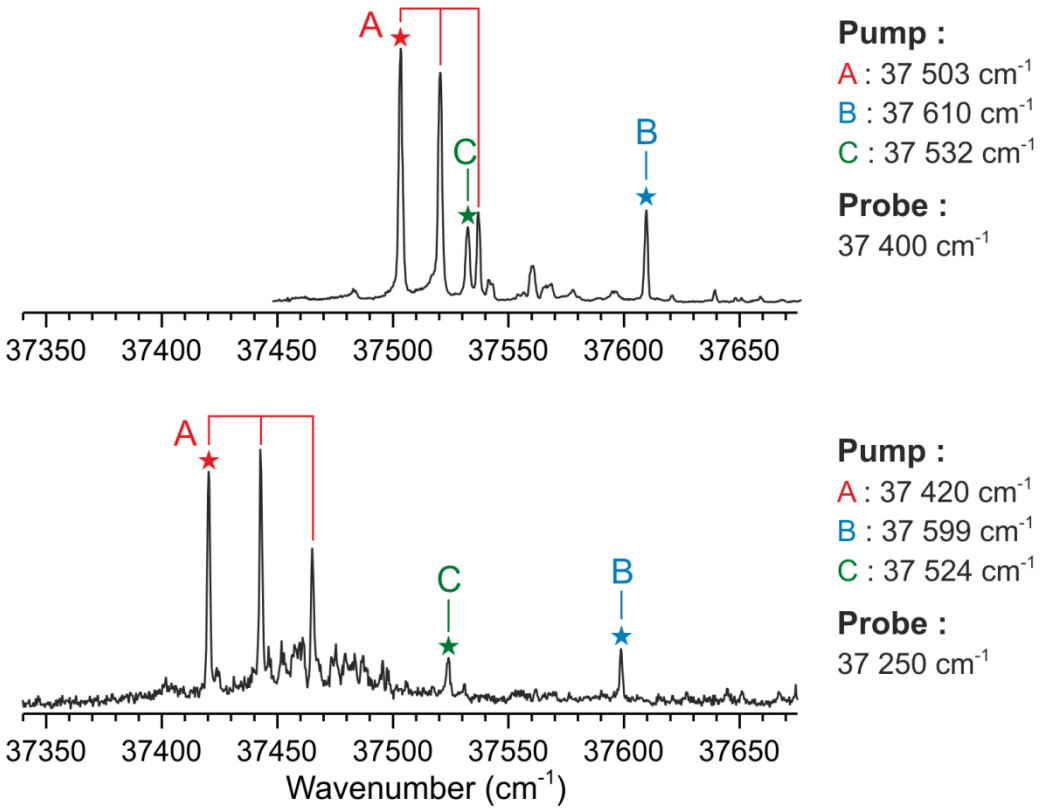

Figure S1-1. NAPA (top) and NAPMA (bottom) UV spectra.[1] Stars mark the origin transition of each conformer where the pump-probe experiments presented on Figure 2 and S1-2 have been done.

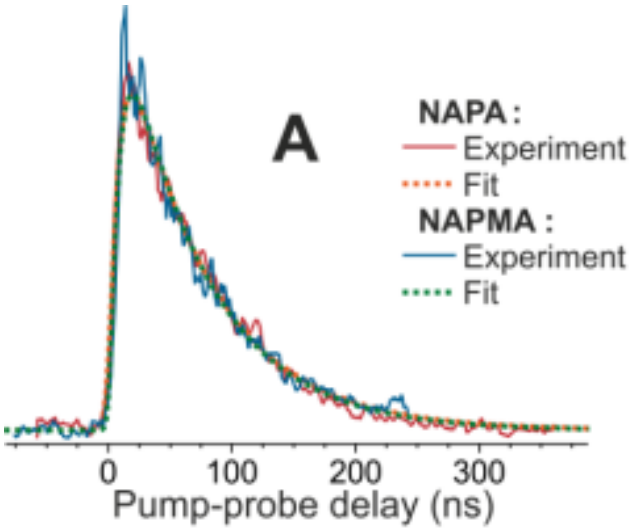

Figure S1-2. Pump-probe nanosecond signal obtained after pumping the origin transition of conformers A of NAPMA (blue) and NAPA (red). Best fits (dotted lines) provide a lifetime of 67 ns (precision: ± 3 ns) for NAPMA A, in contrast with 70 ns for NAPA.

S2. Computational details

To enable a direct comparison with NAPA, the same strategy with the same methods and the same levels of calculations were used for the ground and excited states.[2] Specifically, in modeling the experimental abundances, the ground state geometries and ZPEs of the three NAPMA conformers were calculated at the MP2(FC)/6-311+G(2d,p) level. Coupled cluster doubles (CC2) method,[3] using Dunning's cc-pVDZ basis set[4] and accelerated with the resolution-of-identity (RI) approximation,[5] was used in describing the excited state minima, ZPEs and investigating the LIPs. The experimental origin bands (see Table S2-1) have been recomputed using the RI-CC2 method with the TZVP basis set for the computation of all geometries and corresponding excitation energies. The smaller cc-pVDZ basis set has been used for the computation of the ZPE corrections. The MP2 calculations were performed with Gaussian 09[6] and RI-CC2 with the Turbomole 6.31[7].
In the ground state, the relative stability of the NAPMA conformers resembles that of NAPA (see Table S2-1), which is consistent with the apparent experimental abundances. Regarding the first ππ* state, the calculated ZPE-corrected adiabatic excitation energies match the experimental transitions of the three conformers[1,8] (see Table S2-1) within 0.12 eV. Likewise, the experimentally observed redshift of conformer A with respect to B (and C) of 0.022 eV (0.013 eV) is qualitatively reproduced by the calculated values of 0.043 eV (0.035 eV).

Table S2-1. Relative ZPE-corrected ground state energies (in kcal mol^{-1}) for the three observed NAPA and NAPMA conformers, and the calculated and experimental excitation energies (in eV) to the lowest-lying phenyl ππ* excited state of NAPMA. The Cartesian geometries and drawings of all the NAPMA structures are given in Appendix S3.

	Ground state		Excitation energies to ππ* state	
Conf.	NAPA [a]	NAPMA	Calc.	Exp.
A β_L(a)	0.00	0.00	4.742	4.640
B γ_L(g+)	0.38	1.09	4.784	4.662
C γ_L(g–)	1.01	1.75	4.777	4.653

[a] values are taken from reference 2.

For the three conformers, A, B, C, the first singlet excited state of ππ* character was optimized and the corresponding adiabatic minima, $M_{\pi\pi^*}$, were located. Several minima have been optimized on the nπ* surface with excitations localized on the second peptide group and denoted, $M_{n\pi^*}$ (see Table S2-2). Hessian matrices were calculated for each adiabatic minimum at the RI-CC2/cc-pVDZ level of theory.

Table S2-2. Energy of the ππ* and nπ* excited state minima (in eV) of NAPMA B and NAPA B calculated relative to their corresponding ππ* minimum ($M_{\pi\pi^*}$), geometrical root-mean square deviations (in Å) of nπ* minima from ππ* minimum and their structurally most distinct geometrical parameters. Torsion angles ϑ_N, ϑ_C and ω_2 (see Figure 3 in text) and C=O bond distance, d(C=O), are given in degrees and Å respectively. The Cartesian geometries and drawings of all the NAPMA structures are given in Appendix S4.

	NAPMA B						NAPA B					
	ΔE	RMSD	ϑ_N	ϑ_C	ω_2	d(C=O)	ΔE	RMSD	ϑ_N	ϑ_C	ω_2	d(C=O)
$M_{\pi\pi^*}$	0.00	0.00	–178.5	–178.1	1.6	1.24	0.00	0.00	–159.8	–178.5	–6.9	1.24
M_{IIb}	–0.72	0.55	–146.1	–127.0	61.6	1.33	–0.71	0.34	–123.2	–132.9	33.2	1.38
M_{IIc}	–0.68	0.79	137.4	132.8	9.2	1.48	–0.72	0.52	125.9	134.9	3.5	1.45
M_{IId}	–0.63	0.38	–135.9	–136.2	–7.1	1.48	–0.69	0.25	–124.7	–136.9	–1.62	1.45
M_{IIe}	–0.62	0.33	136.9	–132.6	50.0	1.48	–0.64	0.24	129.4	–132.8	56.9	1.46
M_{IIf}	–0.67	0.75	–136.2	129.6	–41.5	1.48	–0.69	0.58	–127.4	130.2	–44.9	1.46
M_{IIg}	–0.74	0.54	140.2	126.7	–61.7	1.33	–0.73	0.53	120.5	131.1	–36.8	1.38

Having optimized the geometry of the nπ*local minima, linearly interpolated paths (LIPs) between the $M_{\pi\pi^*}$ and each of the $M_{n\pi^*}$, minima have been constructed, e.g. the LIP between $M_{\pi\pi^*}$ and M_{IId} (see the left part of Figure S2). The geometries along the LIPs are obtained by interpolating in internal coordinates between the two minima. The characters of electronic states are tracked by monitoring the canonical orbital contributions or changes in electron densities respectively for each discrete point along the LIP. This enables construction of smooth potential energy curves of the same well-defined electronic character, and pinpointing parts of LIP where these curves intersect or come close together. An intersection of two curves is interpreted as a conical intersection (CI) between two electronic states, not as avoided crossing. Regions in configuration space of such close approaching electronic states are always most likely to be associated with the true CI regions.[9] To explore how the systems reach the electronic ground state once they have crossed to their nπ* state consecutive constrained optimizations on the first excited (nπ*) state were performed keeping the C=O bond fixed while other internal coordinates were allowed to relaxed.[2] Starting from a corresponding $M_{n\pi^*}$ minimum, the C=O bond length was increased in small fixed steps until the first excited state crossed to the ground electronic state. An almost barrierless pathway to the electronic ground state was found for all structures (see for example the right part of Figure S2).

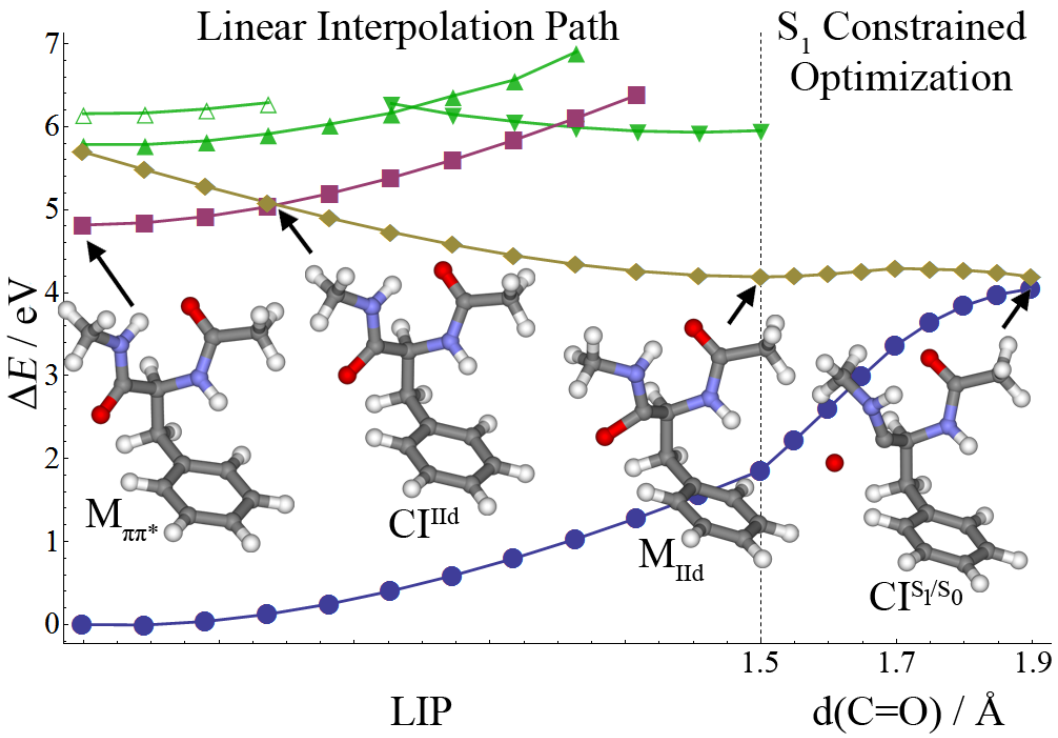

Figure S2. Relative RI-CC2/cc-pVDZ energies of the ground (blue cycles) and the four lowest excited states (ΔE) along the LIP involving the readjustment of the peptide backbone from $M_{\pi\pi^*}$ to minimum M_{IId} (left) in NAPMA conformer B ($\gamma_L(g+)$) followed by the constrained optimization at fixed C=O distances (to the right of the figure). The vertical dashed line separates the two computational approaches. The insets show the geometries along the relaxation path: $M_{\pi\pi^*}$, CI^{IId}, M_{IId} and $CI^{S1/S0}$.

The sequential penalty constrained optimization method of Levine *et al.* has been used to locate the minimum energy conical intersections (MECI).[10] The method does not require the knowledge of the derivative coupling vector not available in RI-CC2 calculations. Instead the minimum of an objective function is sought. Basically, the method minimizes the average energy of the two electronic states subject to the constraint that the energy difference between them vanishes. The default initial values of

0.025 Hartree and 3.5 were set for parameters α and σ, and the optimization of the MECI were started from the CI^{IIb} and CI^{IIc} geometries. CI geometries were converged to the default energy gap threshold value of 0.001 Hartree (0.02 eV). This method has also been used to locate the CI intersection with minimal distance from the initially excited $M_{\pi\pi^*}$ minimum, the so called minimum distance CI (MDCI). In the MDCI optimization the deviation from the reference $M_{\pi\pi^*}$ structure in mass-weighted Cartesian coordinates is minimized with the constraint that the gap between the two states vanishes.
All located CI geometries, oriented relative to the minimum Mππ* so to satisfy the Eckart conditions,[11] have been expressed in terms of the ππ* normal modes. The ratio of the potential energy of each mode, V_i, to its zero point energy

$$\frac{V_i}{ZPE_i} = \frac{\omega_i^2 Q_{i,CI}^2/2}{\omega_i/2}$$

was taken as an estimate of the Q_i mode excitation. In the experiment the vibrationless level of the ππ* is excited. Hence a particular CI geometry is accessible to the ground state wave function if $V_i/ZPE_i < 1$ for all normal modes.

Semi-classically, when $V_i/ZPE_i > 1$ for one of the normal modes, the probability to reach the CI geometry every time the particle "hits" the wall is given by:

$$P_i = \left|\Psi\left(Q_i^{CI}\right)\right|^2 = e^{2S}$$

where S is the action integral through the barrier:

$$S = -\frac{1}{\hbar}\int_{Q_i^0}^{Q_i^{CI}} p\left(Q_i\right) dQ_i ,$$

and Q_i^0 and Q_i^{CI} are the displacements at the classical turning point and the CI geometry, respectively. In normal mode coordinates and atomic units the above equation reads

$$S = -\int_{Q_i^0}^{Q_i^{CI}} \sqrt{2\left(\omega_i^2 Q_i^2 - \omega_i/2\right)}\, dQ_i = -\int_{Q_i^0}^{Q_i^{CI}} \sqrt{2\left(V_i - ZPE_i\right)}\, dQ_i .$$

Changing to $\rho_i = Q_i/Q_i^0$, using $\alpha = \sqrt{V_i/ZPE_i}$ and $Q_i^{CI} = Q_i^0\,\alpha_i$ one obtains

$$P_i = e^{-2\int_1^{\alpha_i}\sqrt{\rho_i^2-1}\,d\rho_i},$$

$$P_i = e^{-\alpha_i\sqrt{\alpha_i^2-1}}\left(\alpha_i + \sqrt{\alpha_i^2-1}\right).$$

Thus for a normal mode Q_i with $\alpha_i = \sqrt{3}$ the probability to reach the CI geometry is $P_i \approx 1/4$ every time the particle is at the classical turning point. For n modes in the tunneling regime the total probability to reach the CI is given by:

$$P = \prod_i^n P_i .$$

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S3. Cartesian geometries of the NAPMA A, B and C conformer ground state structures

Note. All geometries are obtained on a MP2/6-311+G(2d,p) level of theory. All coordinate values are in Angstroms (Å).

Table S3-1. NAPMA A.

C	3.55768397	-1.14407824	-0.25596468
C	2.16801542	-1.15950393	-0.12251260
C	1.41430107	0.00000000	-0.35136484
C	2.08019899	1.17155179	-0.72986960
C	3.46865808	1.19039252	-0.87070766
C	4.21201208	0.03383191	-0.62538333
C	-0.06293616	0.00000005	-0.08372987
C	-0.35136493	-0.00000002	1.43509472
N	-1.76769735	-0.02321907	1.70216202
C	-2.48443943	-1.17296639	1.59055177
O	-1.95618847	-2.24118760	1.28245078
C	0.21568685	1.26178109	2.06953230
N	1.50343921	1.18315982	2.47767321
O	-0.46726366	2.28209064	2.17639927
C	-3.96386706	-1.05867765	1.87812908
H	-2.19967957	0.86479280	1.92658220
H	0.10046130	-0.89460927	1.87489691
H	-0.53755917	0.88405901	-0.52084238
H	-0.53947428	-0.89219478	-0.49870380
H	1.50345617	2.07631421	-0.90827672
H	3.96982087	2.10631224	-1.16941285
H	5.29223542	0.04687829	-0.73163507
H	4.12810753	-2.05082077	-0.07836840
H	1.65778613	-2.07904828	0.15729431
H	2.03460679	0.37748827	2.17409507
H	-4.27412849	-0.04400666	2.13070348
H	-4.51573389	-1.39818373	1.00083371
H	-4.20879238	-1.72680190	2.70469159
C	2.22696516	2.38373271	2.86311819
H	1.63931246	2.93940548	3.59215081
H	3.17655978	2.09327206	3.31010895
H	2.41355109	3.03002750	2.00095483

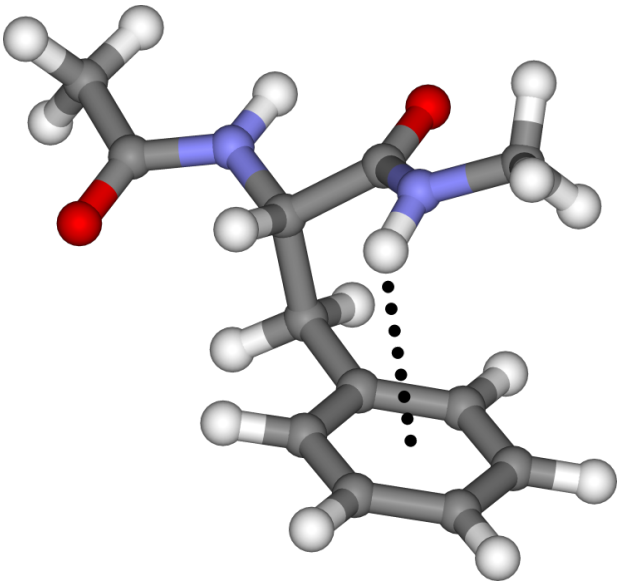

Figure S3-1. NAPMA conformer A ground state minimum.

Table S3-2. NAPMA B.

C	3.56269187	-1.13588493	-0.52779514
C	2.18764335	-1.17330570	-0.29417140
C	1.42279147	-0.00000001	-0.36671298
C	2.06951203	1.20365135	-0.68359909
C	3.44702271	1.24290626	-0.91325877
C	4.19830996	0.07023011	-0.83239954
C	-0.05607846	0.00000009	-0.06866555
C	-0.36671305	-0.00000006	1.43537853
N	0.51181807	0.93911609	2.11710362
C	0.18763117	1.57765761	3.26583958
O	-0.86489478	1.35184465	3.87418868
C	-0.31186862	-1.41913000	2.03297499
N	-0.48835803	-1.46369764	3.36947354
O	-0.15699121	-2.42532710	1.33939327
C	1.19048645	2.59045245	3.76373723
H	1.42028652	1.10393963	1.69993287
H	-1.39067581	0.35821745	1.59373210
H	-0.50794337	0.89347598	-0.50916609
H	-0.53551029	-0.87827942	-0.50507342
H	1.48329968	2.11686759	-0.76365032
H	3.92764324	2.18433189	-1.16205138
H	5.26856379	0.09423555	-1.01233202
H	4.14031159	-2.05369251	-0.47217834
H	1.69394877	-2.10754057	-0.04714867
H	-0.76272534	-0.60393203	3.83855806
H	1.47369964	2.32933156	4.78395650
H	2.08455206	2.64966202	3.14156312
H	0.70687878	3.56804277	3.79243799
C	-0.54766732	-2.74097544	4.05743411
H	-0.65313805	-2.55636084	5.12545224
H	-1.39142319	-3.33966551	3.70694504
H	0.36667422	-3.30781339	3.87875172

Table S3-3. NAPMA C.

C	3.42634006	-1.15225969	-1.08996559
C	2.04392874	-1.12769990	-0.88857379
C	1.41463314	-0.00000006	-0.34960479
C	2.20155794	1.11157574	-0.02194514
C	3.58116226	1.09451937	-0.22161675
C	4.19861209	-0.04091000	-0.75265604
C	-0.06502831	0.00000005	-0.07485609
C	-0.34960482	0.00000002	1.42446093
N	0.37561300	-1.08932482	2.06754449
C	0.80018184	-1.00641618	3.35378909
O	0.45234886	-0.08591156	4.10029657
C	-1.85627477	-0.12339694	1.69645695
N	-2.20714170	0.17922493	2.96525380
O	-2.65757573	-0.46833821	0.82891621
C	1.72728494	-2.10235605	3.81951905
H	0.76807410	-1.81078161	1.47775385
H	0.01211907	0.92881613	1.87902066
H	-0.54868938	0.87951719	-0.50879010
H	-0.54676105	-0.87188555	-0.52639812
H	1.72853637	1.99998540	0.39039776
H	4.17511525	1.96622013	0.03567283
H	5.27276042	-0.05518568	-0.90797309
H	3.89614981	-2.03492906	-1.51324601
H	1.44205020	-1.98966804	-1.16959915
H	-1.45250399	0.31511380	3.63310605
H	1.34534170	-2.51181933	4.75470936
H	1.84094877	-2.90484489	3.08952643
H	2.70543288	-1.66174459	4.02025255
C	-3.57638337	-0.00259598	3.41236248
H	-3.66010840	0.35817471	4.43643964
H	-4.25561730	0.56376709	2.77478807
H	-3.87157159	-1.05391656	3.37269714

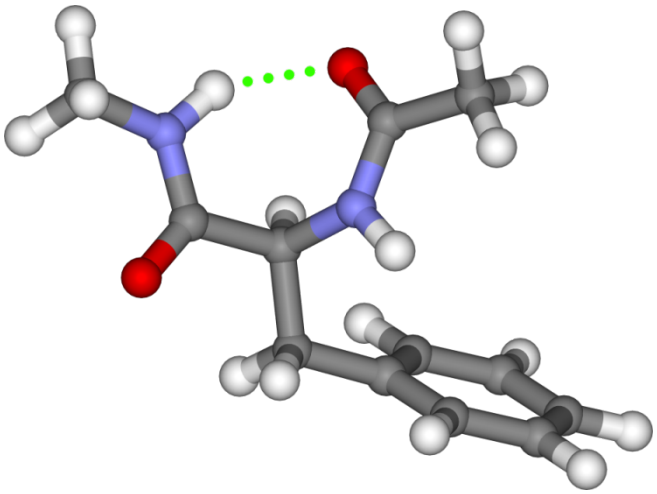

Figure S3-2. NAPMA conformer C ground state minimum

S4. Cartesian geometries of the relevant NAPMA B (1-7) and NAPA B (8-14) excited states minima structures

Note. All geometries are obtained on a RI-CC2/cc-pVDZ level of theory. All coordinate values are in Angstroms (Å).

Table S4-1. NAPMA B ππ* excited state minimum ($M_{\pi\pi^*}$).

C	0.0130748	0.0514015	1.3966765
C	1.2529700	-0.0147692	2.1395283
C	2.5075725	-0.0910924	1.4088792
C	2.5108152	-0.0741262	-0.0328195
C	1.2701739	-0.0137719	-0.7573696
C	0.0227293	0.0463893	-0.0451101
C	1.2722404	-0.0577999	3.6388736
C	1.1476001	-1.4884371	4.2107502
C	-0.3248725	-1.9555014	4.2520589
O	-1.2660953	-1.2605352	3.8315246
N	1.9973369	-2.3938236	3.4460539
C	2.5468067	-3.5227348	3.9797273
C	3.4967213	-4.2762950	3.0698103
N	-0.4647794	-3.1817716	4.8284257
O	2.2829497	-3.9166869	5.1341714
H	2.1965687	-2.1371307	2.4786238
H	1.5195566	-1.5132616	5.2524557
H	2.2243801	0.3691239	4.0007574
H	0.4376907	0.5312432	4.0517915
H	3.4532222	-0.0592129	1.9609177
H	3.4601078	-0.1026233	-0.5755128
H	1.2800460	-0.0081925	-1.8508258
H	-0.9213658	0.0877131	-0.5945085
H	-0.9258282	0.0785252	1.9528916
H	0.3870899	-3.6319877	5.1785663
H	3.0585223	-5.2579888	2.8323289
H	3.7176406	-3.7402060	2.1347659
H	4.4325716	-4.4567479	3.6190847
C	-1.7603214	-3.8181144	4.9756920
H	-1.7801978	-4.7965669	4.4690457
H	-2.0135874	-3.9643546	6.0384038
H	-2.5063503	-3.1550344	4.5167314

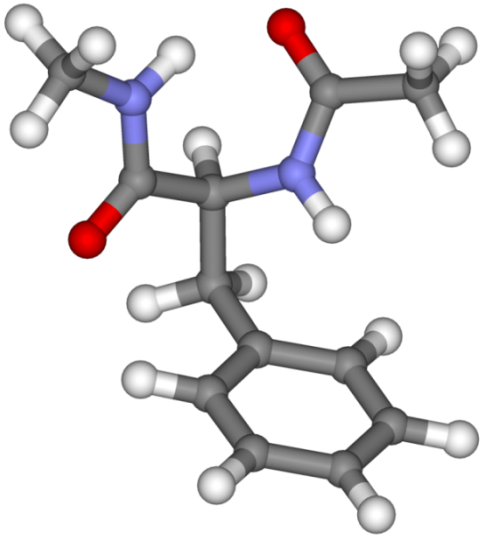

Figure S4-1. NAPMA B $M_{\pi\pi^*}$ excited state minimum.

Table S4-2. NAPMA B IIb nπ* excited state minimum (M_{IIb}).

C	-2.1140881	-1.0621349	-0.1018378
C	-1.5945703	-0.1085700	0.8034537
C	-2.1069335	1.2050079	0.7757572
C	-3.1191220	1.5655849	-0.1343348
C	-3.6302417	0.6103696	-1.0286271
C	-3.1273510	-0.7047176	-1.0059956
C	-0.4625371	-0.4804886	1.7291256
C	0.8810286	-0.4749654	0.9830688
C	0.8739550	-1.5536726	-0.0771100
O	0.7297094	-2.8345898	0.2477854
N	1.1591150	0.8338642	0.4194255
C	2.4463010	1.2313244	0.1572573
C	2.5665782	2.5630101	-0.5617229
N	2.1033203	-1.5753071	-0.8927808
O	3.4404450	0.5572774	0.4799315
H	0.3894242	1.3040617	-0.0538908
H	1.6999770	-0.6911148	1.7016865
H	-0.4067999	0.2206476	2.5786714
H	-0.6055771	-1.4999497	2.1248937
H	-1.7193363	1.9470730	1.4842332
H	-3.5112007	2.5878486	-0.1377168
H	-4.4210460	0.8849677	-1.7337273
H	-3.5278573	-1.4547272	-1.6958327
H	-1.7179082	-2.0835273	-0.0815153
H	2.9805717	-1.5212889	-0.3503409
H	2.7577691	2.3752547	-1.6308394
H	1.6621914	3.1822368	-0.4646483
H	3.4324105	3.1045126	-0.1560977
C	2.1359527	-2.3419157	-2.1274611
H	2.8752580	-1.8772224	-2.7996929
H	2.4145623	-3.3931836	-1.9582696
H	1.1355694	-2.2999700	-2.5792577

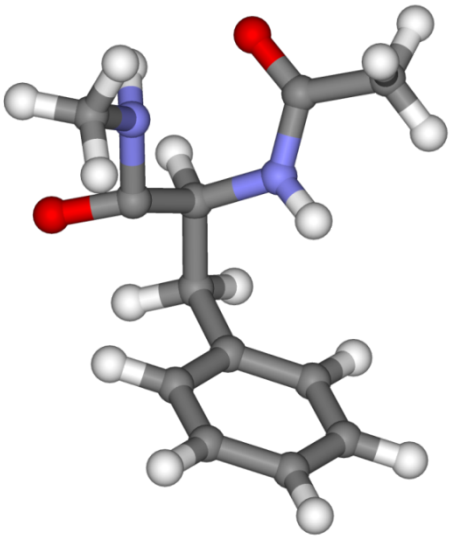

Figure S4-2. NAPMA B M_{IIb} excited state minimum.

Table S4-3. NAPMA B IIc nπ* excited state minimum (M_{IIc}).

C	-2.2413862	-1.1127876	-0.0597174
C	-1.5815234	-0.1607412	0.7487980
C	-2.0144705	1.1847725	0.7079722
C	-3.0757540	1.5698252	-0.1253475
C	-3.7240069	0.6126217	-0.9313722
C	-3.3110762	-0.7273935	-0.8899134
C	-0.4035799	-0.5665829	1.5998600
C	0.9114407	-0.4460300	0.8192596
C	0.9221700	-1.3213875	-0.4191087
O	-0.1089793	-0.9129513	-1.3940645
N	1.1311039	0.9469317	0.4124735
C	2.4229256	1.3813429	0.1835017
C	2.5237694	2.7365144	-0.4923788
N	2.1296674	-1.5057086	-1.0822768
O	3.4263131	0.7412455	0.5374129
H	0.4212089	1.2954456	-0.2347892
H	1.7683430	-0.7243827	1.4560553
H	-0.3390067	0.0717296	2.4972060
H	-0.5104882	-1.6154570	1.9237152
H	-1.5179207	1.9254158	1.3451545
H	-3.4043536	2.6140120	-0.1435147
H	-4.5550087	0.9125446	-1.5773148
H	-3.8169966	-1.4780358	-1.5049391
H	-1.9344333	-2.1626199	-0.0101379
H	2.9308033	-1.2656229	-0.4915449
H	3.0297714	2.6132784	-1.4628842
H	1.5446765	3.2133844	-0.6470242
H	3.1554950	3.3904441	0.1270582
C	2.2659072	-1.1007268	-2.4802238
H	2.3055211	-0.0030009	-2.6140628
H	3.1839197	-1.5457505	-2.8916490
H	1.3969480	-1.4764688	-3.0414074

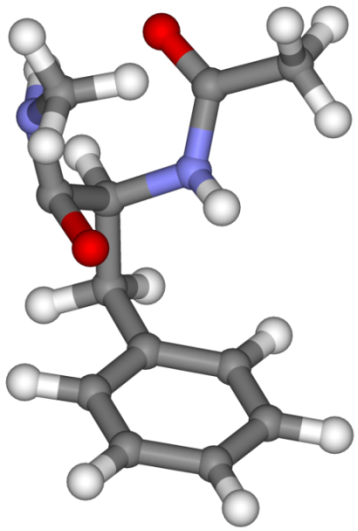

Figure S4-3. NAPMA B M_{IIc} excited state minimum.

Table S4-4. NAPMA B IId nπ* excited state minimum (M_{IId}).

C	-2.2070937	-0.8874976	-0.1566233
C	-1.7063441	0.1032830	0.7175175
C	-2.3195100	1.3742157	0.7283388
C	-3.4120827	1.6552481	-0.1136584
C	-3.9033668	0.6633711	-0.9786406
C	-3.2995247	-0.6081534	-0.9935771
C	-0.4956862	-0.1706279	1.5792985
C	0.8025360	-0.1479788	0.7536384
C	0.8356602	-1.3170079	-0.2103527
O	0.3569829	-2.5533949	0.4458737
N	0.9048581	1.1360092	0.0708867
C	2.0796786	1.6070155	-0.4498439
C	1.9795747	2.9442101	-1.1592963
N	1.9696523	-1.5895289	-0.9610188
O	3.1606127	0.9975584	-0.3418128
H	0.0288361	1.5428805	-0.2544464
H	1.6759517	-0.2325032	1.4356558
H	-0.4178478	0.5844412	2.3792182
H	-0.5652441	-1.1666461	2.0519312
H	-1.9473691	2.1444550	1.4147605
H	-3.8806090	2.6443634	-0.0873118
H	-4.7551931	0.8761443	-1.6319797
H	-3.6818240	-1.3866823	-1.6615354
H	-1.7371838	-1.8783974	-0.1640141
H	2.6265370	-0.7986418	-0.9350178
H	2.2000005	2.7951200	-2.2277297
H	0.9935227	3.4198439	-1.0525440
H	2.7536556	3.6110913	-0.7520612
C	2.5874785	-2.9126553	-0.8757683
H	3.3225014	-3.0111306	-1.6877462
H	3.0895906	-3.0989392	0.0912313
H	1.8087191	-3.6799441	-1.0069933

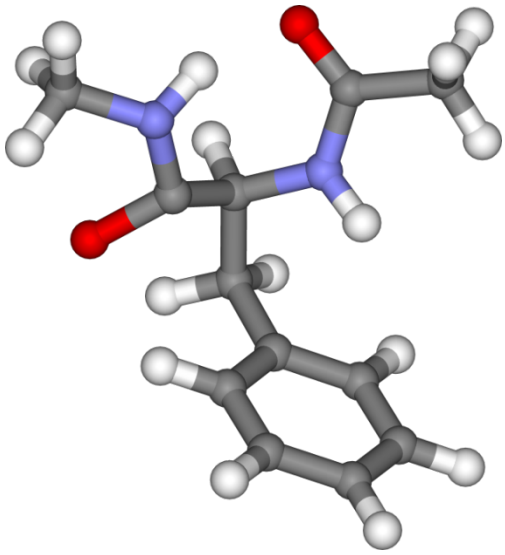

Figure S4-4. NAPMA B M_{IId} excited state minimum.

Table S4-5. NAPMA B IIe nπ* excited state minimum (M_{IIe}).

C	-2.0141332	-0.8302394	-0.4166579
C	-1.5370338	-0.1056804	0.6984492
C	-2.1192522	1.1464074	0.9934187
C	-3.1570247	1.6664069	0.1977023
C	-3.6257432	0.9369328	-0.9077279
C	-3.0523246	-0.3126300	-1.2084606
C	-0.3862325	-0.6237769	1.5328500
C	0.9657200	-0.4806762	0.8094359
C	1.0954553	-1.4969197	-0.3125615
O	0.3286447	-2.7289070	-0.0415671
N	1.0980641	0.8974458	0.3470358
C	2.2741255	1.4244293	-0.1129450
C	2.1860667	2.8588642	-0.6011808
N	2.3736638	-1.8308748	-0.7336055
O	3.3492265	0.7964736	-0.1152807
H	0.2298448	1.3677033	0.0940014
H	1.7891774	-0.6739390	1.5272985
H	-0.3348776	-0.0661574	2.4826155
H	-0.5183596	-1.6947565	1.7682198
H	-1.7648236	1.7112308	1.8640307
H	-3.6006022	2.6360022	0.4459765
H	-4.4357587	1.3351989	-1.5265835
H	-3.4166413	-0.8885567	-2.0652744
H	-1.5649941	-1.8031051	-0.6503130
H	2.9709611	-0.9959438	-0.7780037
H	2.4251542	2.8820967	-1.6756660
H	1.1992662	3.3160412	-0.4359323
H	2.9538069	3.4495435	-0.0798139
C	2.5260564	-2.8083558	-1.8037415
H	2.1575184	-2.4396821	-2.7801213
H	3.5902007	-3.0671800	-1.8987000
H	1.9668611	-3.7189813	-1.5408688

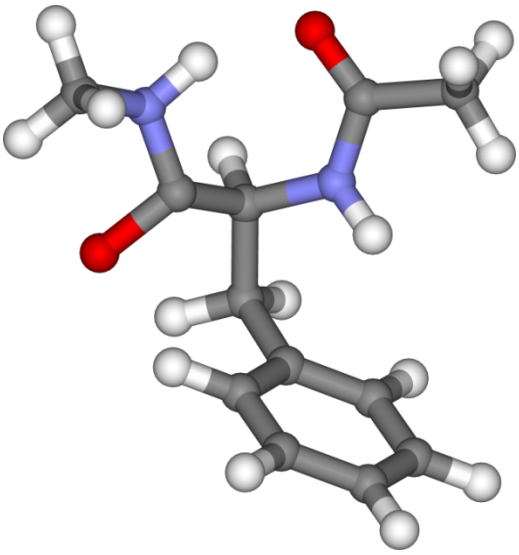

Figure S4-5. NAPMA B M_{IIe} excited state minimum.

Table S4-6. NAPMA B IIf nπ* excited state minimum (M_{IIf}).

C	-0.0220340	0.1465529	1.4985999
C	1.2354971	0.0478494	2.1342454
C	2.3900829	-0.1241749	1.3354831
C	2.2876557	-0.2028368	-0.0609075
C	1.0267816	-0.1076824	-0.6841755
C	-0.1241712	0.0743277	0.0964698
C	1.3412684	0.0882622	3.6390581
C	1.3105865	-1.3233220	4.2373402
C	0.0198619	-2.0445709	3.9003461
O	-0.1474111	-2.2130718	2.4443003
N	2.4256527	-2.1289472	3.7312757
C	2.9112059	-3.1335877	4.5630469
C	3.6574835	-4.2289482	3.8253078
N	-0.1756036	-3.2753296	4.5209291
O	2.7638852	-3.1225697	5.7910018
H	2.2574547	-2.4281307	2.7662399
H	1.4272004	-1.2866872	5.3337160
H	2.2843830	0.5717905	3.9443080
H	0.5012123	0.6629863	4.0648970
H	3.3689823	-0.1901354	1.8223105
H	3.1897469	-0.3320879	-0.6676736
H	0.9488783	-0.1638470	-1.7744520
H	-1.1051664	0.1595220	-0.3812000
H	-0.9182526	0.3073367	2.1067077
H	-0.0871140	-3.2075694	5.5370654
H	2.9241589	-4.9745754	3.4749301
H	4.1974726	-3.8352301	2.9506811
H	4.3575704	-4.7210600	4.5131500
C	-1.2625312	-4.1304340	4.0538043
H	-1.1640328	-5.1198878	4.5231084
H	-2.2642440	-3.7199876	4.2825250
H	-1.1683355	-4.2420197	2.9640626

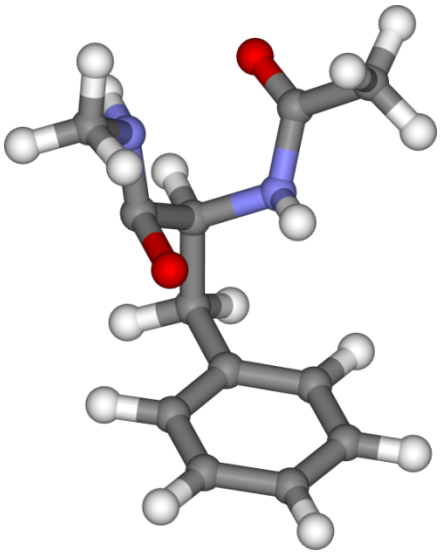

Figure S4-6. NAPMA B M_{IIf} excited state minimum.

Table S4-7. NAPMA B IIg nπ* excited state minimum (M_{IIg}).

C	-2.0174652	-0.8522717	-0.3662842
C	-1.5883032	-0.0935807	0.7453185
C	-2.1890343	1.1618854	0.9806048
C	-3.2004415	1.6501331	0.1326224
C	-3.6221420	0.8845782	-0.9673077
C	-3.0297535	-0.3685152	-1.2105408
C	-0.4658207	-0.5829285	1.6323144
C	0.9085925	-0.4562448	0.9481180
C	1.0578063	-1.4007942	-0.2383482
O	0.7852468	-1.0157531	-1.4794185
N	1.0865643	0.9430868	0.5448234
C	2.2430255	1.3344994	-0.0790014
C	2.1601635	2.6647045	-0.7992419
N	2.4332320	-1.9319806	-0.3876106
O	3.2933403	0.6609652	-0.0461423
H	0.2333217	1.3878504	0.2019257
H	1.7026846	-0.7150862	1.6725037
H	-0.4511219	0.0034281	2.5677621
H	-0.6128709	-1.6434687	1.8946700
H	-1.8698632	1.7545006	1.8463853
H	-3.6592842	2.6232789	0.3350683
H	-4.4102430	1.2583591	-1.6283439
H	-3.3533330	-0.9698841	-2.0659684
H	-1.5545384	-1.8231022	-0.5642884
H	3.1319592	-1.1617078	-0.3791561
H	1.8419172	2.4724973	-1.8372133
H	1.4357574	3.3467758	-0.3292975
H	3.1557013	3.1274197	-0.8187877
C	2.6714127	-3.0646202	-1.2660399
H	2.8361751	-2.7537360	-2.3088706
H	3.5674517	-3.5954090	-0.9052969
H	1.7979678	-3.7297598	-1.2188053

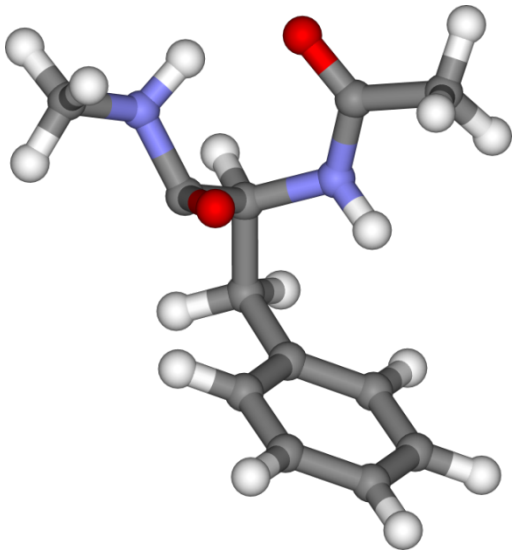

Figure S4-7. NAPMA B M_{IIg} excited state minimum.

Table S4-8. NAPA B ππ* excited state minimum ($M_{\pi\pi^*}$).

C	-2.1252717	-1.1546159	-0.2226251
C	-1.4713441	-0.2826615	0.7293417
C	-1.9349089	1.0883775	0.8621547
C	-3.0483759	1.5583897	0.0760321
C	-3.6857968	0.6814654	-0.8690932
C	-3.2248664	-0.6720585	-1.0206385
C	-0.2951474	-0.7452156	1.5369858
C	1.0498089	-0.5759332	0.7973685
C	1.2975704	-1.7314188	-0.2001655
O	0.5385732	-2.7046127	-0.3087644
N	1.1010772	0.7390793	0.1722200
C	2.2692556	1.4061498	-0.0572559
C	2.1185112	2.8033248	-0.6258816
N	2.4460980	-1.5724348	-0.9158344
O	3.3857242	0.8992651	0.1719711
H	0.2109399	1.1618115	-0.0921014
H	1.8863566	-0.6115673	1.5215295
H	-0.2436729	-0.1626483	2.4735101
H	-0.3952562	-1.8139177	1.7858947
H	-1.4967595	1.7307338	1.6337328
H	-3.4106788	2.5826595	0.2023664
H	-4.5254285	1.0463043	-1.4671186
H	-3.7060896	-1.3379560	-1.7416317
H	-1.7538018	-2.1751941	-0.3353733
H	2.7395599	-2.3517642	-1.4963761
H	3.1136449	-0.8520683	-0.6304265
H	2.5028856	2.8104427	-1.6577124
H	1.0781531	3.1613156	-0.6236561
H	2.7442935	3.4879346	-0.0348836

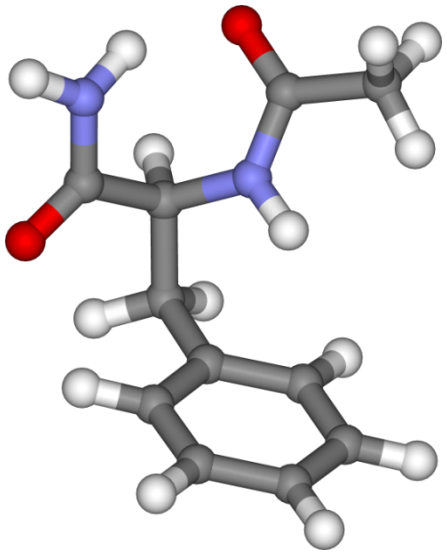

Figure S4-8. NAPA B $M_{\pi\pi^*}$ excited state minimum.

Table S4-9. NAPA B IIb nπ* excited state minimum (M_{IIb}).

C	-2.0710079	-1.0323881	-0.2022098
C	-1.5678491	-0.1272217	0.7592886
C	-2.1114537	1.1725455	0.8201167
C	-3.1397784	1.5646740	-0.0575728
C	-3.6349389	0.6568083	-1.0086910
C	-3.0996247	-0.6434017	-1.0756759
C	-0.4173462	-0.5278243	1.6501587
C	0.9184000	-0.4323210	0.8960325
C	0.9368428	-1.4163059	-0.2450883
O	0.7860441	-2.7549114	0.0447886
N	1.1586968	0.9208466	0.4339294
C	2.4444299	1.3482369	0.1783934
C	2.5338368	2.6961717	-0.5110960
N	2.0533078	-1.3447090	-1.1472043
O	3.4441780	0.6827201	0.4898223
H	0.3913168	1.3706418	-0.0635912
H	1.7523961	-0.6911897	1.5819539
H	-0.3695385	0.1180135	2.5422971
H	-0.5315591	-1.5738024	1.9843057
H	-1.7336468	1.8775548	1.5700987
H	-3.5562588	2.5750893	0.0071629
H	-4.4376838	0.9568293	-1.6893331
H	-3.4857796	-1.3567780	-1.8107803
H	-1.6542363	-2.0450905	-0.2529732
H	2.0729734	-2.1822416	-1.7380872
H	2.9431410	-1.2352645	-0.6336886
H	2.5656000	2.5342368	-1.6010837
H	1.6751686	3.3427689	-0.2752528
H	3.4679020	3.1886045	-0.2095565

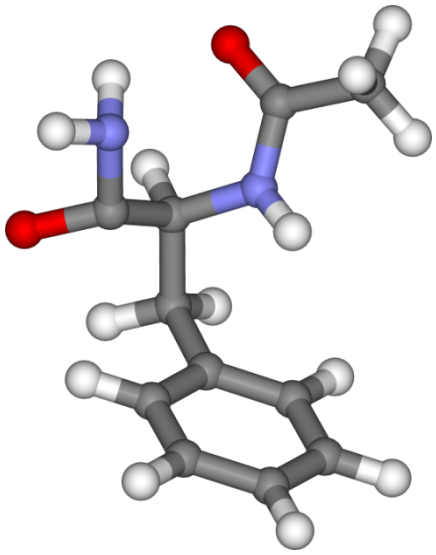

Figure S4-9. NAPA B M_{IIb} excited state minimum.

Table S4-10. NAPA B IIc nπ* excited state minimum (M_{IIc}).

C	-2.1727516	-1.0776932	-0.1511492
C	-1.5602108	-0.1595182	0.7303811
C	-2.0173641	1.1779516	0.7457780
C	-3.0576672	1.5893442	-0.1026235
C	-3.6577264	0.6669588	-0.9817388
C	-3.2191655	-0.6661090	-0.9976391
C	-0.3974672	-0.5859326	1.5928841
C	0.9317702	-0.4414269	0.8376569
C	0.9678739	-1.3032222	-0.4052338
O	0.0348943	-0.9008114	-1.4405521
N	1.1339737	0.9645963	0.4656173
C	2.4087144	1.4194811	0.1941637
C	2.4584432	2.7870988	-0.4605052
N	2.2033169	-1.5659527	-1.0077349
O	3.4317699	0.7728658	0.4753283
H	0.3921828	1.3420458	-0.1269793
H	1.7797056	-0.7244375	1.4837321
H	-0.3497620	0.0307938	2.5061461
H	-0.5070780	-1.6423964	1.8893346
H	-1.5590373	1.8920016	1.4396096
H	-3.4056451	2.6270011	-0.0755025
H	-4.4708996	0.9866082	-1.6406473
H	-3.6876898	-1.3908297	-1.6705585
H	-1.8485543	-2.1233157	-0.1474804
H	2.1833158	-1.3609468	-2.0131947
H	2.9713320	-1.0706861	-0.5382504
H	2.4789021	2.6573238	-1.5553257
H	1.5866654	3.4038901	-0.1962335
H	3.3846474	3.2938208	-0.1581487

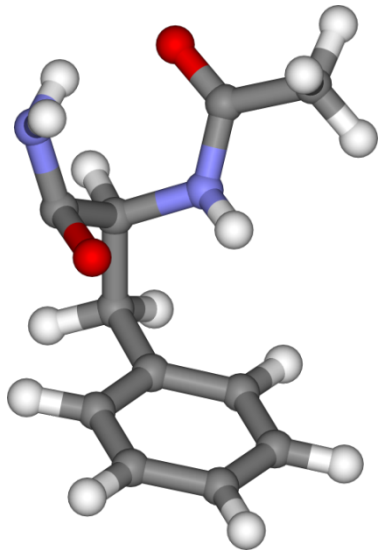

Figure S4-10. NAPA B M_{IIc} excited state minimum.

Table S4-11. NAPA B IId nπ* excited state minimum (M_{IId}).

C	-2.2065394	-0.9057577	-0.1211360
C	-1.7132995	0.1060500	0.7330548
C	-2.3311093	1.3741496	0.7148738
C	-3.4219590	1.6320895	-0.1366200
C	-3.9052389	0.6200028	-0.9825787
C	-3.2966691	-0.6492938	-0.9685177
C	-0.4994089	-0.1451500	1.5959296
C	0.7913468	-0.1206740	0.7607008
C	0.8143638	-1.2851396	-0.1991989
O	0.4759849	-2.5475893	0.4296489
N	0.9050677	1.1565997	0.0738939
C	2.1046894	1.6262795	-0.3948009
C	2.0310794	2.9430192	-1.1436897
N	1.9047195	-1.4802496	-1.0541197
O	3.1789991	1.0250197	-0.2133139
H	0.0416198	1.5515496	-0.2959269
H	1.6716095	-0.2163939	1.4325596
H	-0.4237189	0.6189168	2.3870793
H	-0.5583258	-1.1368897	2.0786394
H	-1.9633594	2.1604394	1.3851196
H	-3.8949789	2.6193893	-0.1330560
H	-4.7550787	0.8155098	-1.6437995
H	-3.6730890	-1.4431396	-1.6215095
H	-1.7352795	-1.8959095	-0.1053640
H	2.6621793	-0.8140058	-0.8424978
H	2.2362794	2.7556692	-2.2093894
H	1.0558297	3.4419990	-1.0439797
H	2.8232692	3.6041490	-0.7639408
H	2.2334394	-2.4511093	-1.0252397

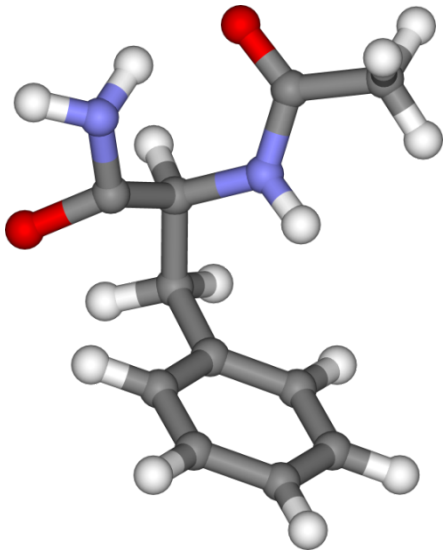

Figure S4-11. NAPA B M_{IId} excited state minimum.

Table S4-12. NAPA B IIe nπ* excited state minimum (M_{IIe}).

C	-1.9954721	-0.8634388	-0.3975012
C	-1.5280433	-0.1123577	0.7039472
C	-2.1152370	1.1446717	0.9661103
C	-3.1482485	1.6436617	0.1511018
C	-3.6070796	0.8880303	-0.9408870
C	-3.0287541	-0.3666626	-1.2088673
C	-0.3820538	-0.6093471	1.5574527
C	0.9737858	-0.4764114	0.8405656
C	1.1151695	-1.5124853	-0.2592444
O	0.3646328	-2.7423020	-0.0001337
N	1.1108488	0.8930860	0.3555853
C	2.2943370	1.4152305	-0.0922207
C	2.2108786	2.8411465	-0.6057978
N	2.4017991	-1.8586793	-0.6634607
O	3.3687975	0.7876876	-0.0683971
H	0.2456177	1.3610995	0.0889263
H	1.7932102	-0.6583950	1.5665463
H	-0.3390497	-0.0319961	2.4956334
H	-0.5127200	-1.6755175	1.8132040
H	-1.7689065	1.7297798	1.8265240
H	-3.5960517	2.6174470	0.3740307
H	-4.4133589	1.2701393	-1.5745907
H	-3.3857257	-0.9632162	-2.0545558
H	-1.5424399	-1.8402114	-0.6068151
H	2.4266398	-2.4665971	-1.4820346
H	3.0057748	-1.0312844	-0.7322643
H	2.4233301	2.8416052	-1.6862762
H	1.2330189	3.3118873	-0.4261923
H	2.9974867	3.4324588	-0.1145988

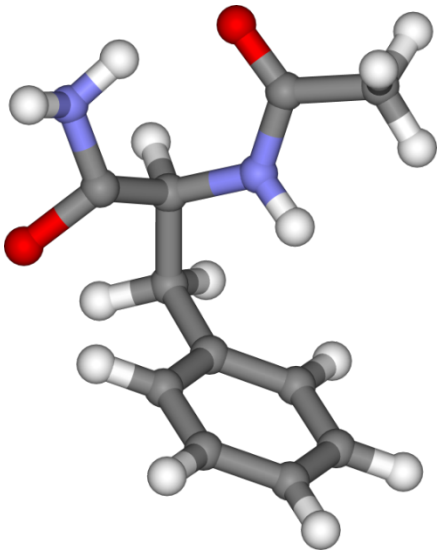

Figure S4-12. NAPA B M_{IIe} excited state minimum.

Table S4-13. NAPA B IIf nπ* excited state minimum (M_{IIf}).

C	-1.5149153	-1.5858256	-1.3656674
C	-0.2606294	-1.4321882	-0.7347935
C	0.6289862	-2.5314951	-0.7122888
C	0.2693753	-3.7536005	-1.2985649
C	-0.9873186	-3.8971774	-1.9208815
C	-1.8735388	-2.8108073	-1.9594263
C	0.1086078	-0.1321168	-0.0636093
C	-0.2495914	-0.1529450	1.4273771
C	-1.7363557	-0.3576138	1.6403510
O	-2.2154029	-1.6260600	1.0886576
N	0.4506550	-1.2383939	2.1190646
C	0.7740894	-1.0385068	3.4587217
C	0.9949849	-2.3252339	4.2304928
N	-2.2027556	-0.2589004	2.9552425
O	0.8874741	0.0842605	3.9631992
H	0.0205189	-2.1458771	1.9184169
H	0.0641829	0.7820090	1.9212268
H	1.1922675	0.0518425	-0.1534970
H	-0.4272659	0.7078207	-0.5379668
H	1.6071819	-2.4148749	-0.2338193
H	0.9690309	-4.5954134	-1.2776200
H	-1.2646680	-4.8501055	-2.3822679
H	-2.8466081	-2.9116766	-2.4500260
H	-2.1990093	-0.7323743	-1.4134633
H	-3.1857254	-0.5208294	3.0411221
H	-2.0221842	0.6595613	3.3653894
H	0.0169764	-2.6860560	4.5904966
H	1.4427676	-3.1070319	3.5981141
H	1.6374883	-2.1251273	5.0979287

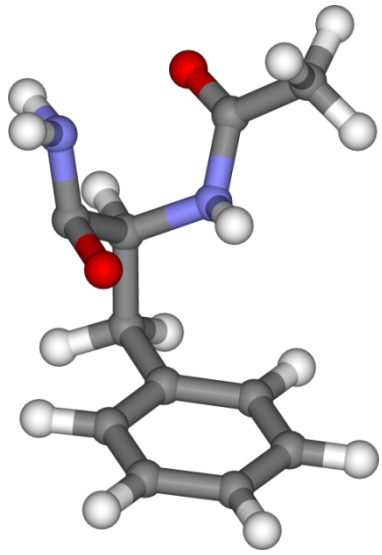

Figure S4-13. NAPA B M_{IIf} excited state minimum.

Table S4-14. NAPA B IIg nπ* excited state minimum (M_{IIg}).

C	-2.0325761	-0.9236096	-0.2984053
C	-1.5776817	-0.1064946	0.7600227
C	-2.1463615	1.1761421	0.9181762
C	-3.1483518	1.6339944	0.0432328
C	-3.5929691	0.8118215	-1.0063254
C	-3.0354522	-0.4691528	-1.1705822
C	-0.4550531	-0.5654644	1.6613781
C	0.9135164	-0.4432588	0.9649045
C	1.0315238	-1.3812644	-0.2221430
O	0.6600987	-0.9629250	-1.4702232
N	1.1009300	0.9544328	0.5666844
C	2.2753927	1.3461835	-0.0318487
C	2.2109385	2.6899874	-0.7293383
N	2.3395119	-1.9627162	-0.4404272
O	3.3138111	0.6614358	0.0083872
H	0.2561187	1.4031151	0.2087644
H	1.7176659	-0.7170043	1.6707349
H	-0.4367141	0.0451095	2.5807255
H	-0.5948352	-1.6198733	1.9504340
H	-1.8108025	1.8130981	1.7453807
H	-3.5828926	2.6287268	0.1850465
H	-4.3737398	1.1635655	-1.6876614
H	-3.3795175	-1.1163343	-1.9833623
H	-1.6037161	-1.9219891	-0.4282863
H	2.3505285	-2.4450644	-1.3457106
H	3.0531882	-1.2113628	-0.4044998
H	1.8663558	2.5262280	-1.7638688
H	1.5129968	3.3801508	-0.2318781
H	3.2168961	3.1284916	-0.7604963

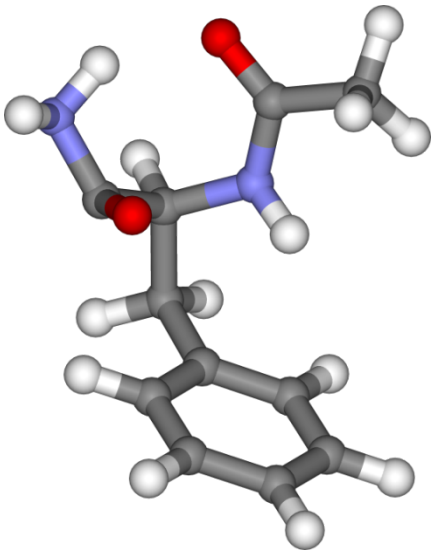

Figure S4-14. NAPA B M_{IIg} excited state minimum.

S5. Cartesian geometries of NAPMA B (1-9) and NAPA B (10-18) structures on the ππ*/nπ* conical intersection seam

Note. All geometries are obtained on a RI-CC2/cc-pVDZ level of theory. All coordinate values are in Angstroms (Å).

Table S5-1. NAPMA B type a nπ*/ππ* minimum energy conical intersection (MECI[a]).

C	0.0053121	-0.0069011	0.0017405
C	-0.0104939	-0.0157714	1.4294496
C	1.2176097	-0.0110311	2.1694994
C	2.4600393	-0.0054480	1.4468896
C	2.4717293	0.0056853	0.0191192
C	1.2437297	0.0031649	-0.7049608
C	1.2309797	-0.0456631	3.6743690
C	1.1564397	-1.4807796	4.2366188
N	2.1470694	-2.3117194	3.5671490
C	2.6581693	-3.4514690	4.1328288
O	2.3666593	-3.8206089	5.2865085
C	-0.2541989	-2.0499694	4.1237388
N	-0.3806309	-3.4133490	4.3183388
C	-1.7145295	-3.9461089	4.5542187
O	-1.2845096	-1.2939996	3.9291089
C	3.5965590	-4.2366888	3.2360491
H	2.2459794	-2.1741894	2.5609493
H	1.4408896	-1.4776696	5.3094085
H	2.1631994	0.4145029	4.0447489
H	0.3716389	0.5117209	4.0824989
H	3.4031290	0.0299125	2.0038494
H	3.4251990	0.0245958	-0.5169189
H	1.2536796	0.0164902	-1.7984595
H	-0.9393057	-0.0059586	-0.5494848
H	-0.9564907	-0.0402700	1.9772994
H	0.3809889	-3.8093589	4.8806586
H	3.0970791	-5.1724585	2.9365092
H	3.8909389	-3.6799390	2.3330493
H	4.4939087	-4.5062387	3.8119289
H	-1.7133695	-5.0279586	4.3576188
H	-2.0723694	-3.7663089	5.5851684
H	-2.4118193	-3.4490790	3.8647089

Table S5-2. NAPMA B type b ππ*/nπ* minimum energy conical intersection (MECI[b]).

C	0.0424448	0.1384880	-0.0622049
C	0.0032091	0.1248310	1.3653996
C	1.2073897	0.0036394	2.1293594
C	2.4637393	-0.0637216	1.4300596
C	2.4992893	-0.0435840	0.0037394
C	1.2897696	0.0492841	-0.7436338
C	1.1856597	-0.0743600	3.6309590
C	1.1916997	-1.5221096	4.1699088
N	2.2642294	-2.2771694	3.5134490
C	2.7965392	-3.4086590	4.0717989
O	2.4594993	-3.8323889	5.1945985

C	-0.1525100	-2.2115594	4.0128189
N	-0.3762689	-3.2655991	4.8789086
C	-1.4120896	-4.2358188	4.5554587
O	-1.0371897	-1.8379895	3.1428891
C	3.8571089	-4.0997288	3.2349191
H	2.4215393	-2.0902794	2.5212293
H	1.4401896	-1.5273596	5.2474585
H	2.0794194	0.4351409	4.0348789
H	0.2923109	0.4339779	4.0306989
H	3.3985190	-0.0699361	2.0016794
H	3.4615590	-0.0865597	-0.5154359
H	1.3246396	0.0718980	-1.8365295
H	-0.8892158	0.2322589	-0.6270428
H	-0.9511587	0.2006739	1.8907895
H	0.4942369	-3.6318090	5.2793385
H	3.5137590	-5.1162986	2.9855592
H	4.0956288	-3.5561490	2.3079994
H	4.7668787	-4.1996888	3.8461689
H	-1.0924397	-4.9612386	3.7829389
H	-1.6875495	-4.7866087	5.4661485
H	-2.2934694	-3.6989890	4.1764088

Table S5-3. NAPMA B ππ*/nπ* minimum distance conical intersection (MDCI).

C	-0.9831347	1.7475795	-2.9686092
C	-0.9930517	1.7524495	-1.5355896
C	0.2398929	1.6936895	-0.7973098
C	1.4866296	1.6235695	-1.5227096
C	1.4927496	1.6383895	-2.9553392
C	0.2580559	1.6926395	-3.6776790
C	0.2585659	1.6487395	0.7160228
C	0.1234100	0.2176979	1.2855896
N	0.9847917	-0.6890478	0.5198239
C	1.5323896	-1.8190995	1.0538397
O	1.2695296	-2.2147994	2.2086694
C	-1.2927796	-0.2658329	1.3396096
N	-1.4878596	-1.4844896	1.9081695
C	-2.7758092	-2.1116294	2.0549794
O	-2.3113694	0.4650059	0.9012537
C	2.4825593	-2.5735193	0.1413600
H	1.1763497	-0.4409559	-0.4478729
H	0.5288179	0.1896449	2.3375293
H	1.2033997	2.0798694	1.0772297
H	-0.5771948	2.2480094	1.1303997
H	2.4430093	1.6486595	-0.9630887
H	2.4521793	1.6138195	-3.5037690
H	0.2677559	1.6987195	-4.7826087
H	-1.9379995	1.7863595	-3.5264190
H	-1.9508195	1.7762895	-0.9786827
H	-0.6338798	-1.9139095	2.2534294
H	2.0434694	-3.5570090	-0.0978772
H	2.7032092	-2.0357394	-0.7943468
H	3.4197190	-2.7548092	0.6904138
H	-2.8123692	-3.0982391	1.5429496

H	-3.0449791	-2.2636294	3.1223591
H	-3.5398190	-1.4548896	1.5977496

Table S5-4. NAPMA B ππ*/nπ* IIb conical intersection (CI^{IIb}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIb} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4303303
C	1.2384417	0.0000000	2.1587255
C	2.4779071	-0.0055116	1.4247255
C	2.4728826	0.0076039	-0.0066995
C	1.2349652	0.0041603	-0.7182040
C	1.2590045	-0.0518041	3.6604658
C	1.1493830	-1.4914443	4.2047860
N	2.0898089	-2.3590333	3.5092569
C	2.6097322	-3.4840491	4.0854696
O	2.2894496	-3.8635270	5.2290039
C	-0.2945264	-2.0042969	4.1089488
N	-0.4433752	-3.2928122	4.6273915
C	-1.7123895	-3.9938501	4.5519841
O	-1.2831850	-1.2244834	3.9466119
C	3.6033169	-4.2472258	3.2307632
H	2.2917293	-2.1358381	2.5347302
H	1.4355787	-1.5103164	5.2747464
H	2.2007566	0.3872556	4.0334161
H	0.4125565	0.5176172	4.0775735
H	3.4257240	0.0559929	1.9712941
H	3.4197157	0.0259352	-0.5547421
H	1.2351463	0.0111615	-1.8119993
H	-0.9494821	-0.0034683	-0.5427112
H	-0.9374196	-0.0164043	1.9919032
H	0.3266365	-3.6397408	5.2126309
H	3.1472608	-5.2001258	2.9193918
H	3.9211421	-3.6891390	2.3373908
H	4.4818390	-4.4858401	3.8476334
H	-1.5597331	-5.0140807	4.1643431
H	-2.1981412	-4.0571732	5.5388264
H	-2.3615184	-3.4324400	3.8662312

Table S5-5. NAPMA B ππ*/nπ* IIc conical intersection (CI^{IIc}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIb} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4321057
C	1.2381806	0.0000000	2.1616122
C	2.4798260	-0.0036137	1.4274284
C	2.4742266	0.0094172	-0.0032678
C	1.2349411	0.0038820	-0.7163077
C	1.2603003	-0.0476264	3.6632801
C	1.2274699	-1.4882908	4.2131351
N	2.2232305	-2.3020454	3.5198419
C	2.8046163	-3.3907062	4.1130168
O	2.5265628	-3.7545295	5.2720474

C	-0.1756887	-2.1060691	4.1028604
N	-0.2927630	-3.3358695	4.6953620
C	-1.4037557	-4.2222772	4.3886237
O	-1.0470219	-1.5973020	3.2673366
C	3.8225180	-4.1231241	3.2603128
H	2.3445231	-2.1084729	2.5247844
H	1.5067594	-1.4946732	5.2827679
H	2.1796952	0.4386168	4.0337255
H	0.3873009	0.4826484	4.0772138
H	3.4266722	0.0600176	1.9749353
H	3.4207804	0.0289752	-0.5516753
H	1.2363808	0.0103943	-1.8100614
H	-0.9493702	-0.0043678	-0.5425332
H	-0.9385096	-0.0091789	1.9914038
H	0.5272146	-3.6530754	5.2219175
H	3.4486583	-5.1377645	3.0525897
H	4.0382592	-3.6120152	2.3102780
H	4.7516175	-4.2264088	3.8402084
H	-1.0820512	-5.0806920	3.7746627
H	-1.8630342	-4.6007031	5.3156420
H	-2.1501694	-3.6425553	3.8274631

Table S5-6. NAPMA B ππ*/nπ* IId conical intersection (CI^{IId}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IId} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4311093
C	1.2390155	0.0000000	2.1594461
C	2.4793680	-0.0050027	1.4246475
C	2.4738523	0.0091236	-0.0073493
C	1.2351462	0.0052066	-0.7188508
C	1.2644055	-0.0497945	3.6616306
C	1.1370110	-1.4854593	4.2145667
N	2.0481500	-2.3638154	3.4903547
C	2.5446108	-3.5187952	4.0234065
O	2.2102034	-3.9384862	5.1494027
C	-0.3185000	-1.9754533	4.1573146
N	-0.5343646	-3.2040202	4.7219938
C	-1.8755156	-3.6544571	5.0586059
O	-1.2749275	-1.1237851	3.8787362
C	3.5348958	-4.2632813	3.1492470
H	2.2607366	-2.1108413	2.5251891
H	1.4488759	-1.5080364	5.2773413
H	2.2157448	0.3744453	4.0272832
H	0.4312578	0.5366573	4.0831600
H	3.4273314	0.0583078	1.9707291
H	3.4205267	0.0282207	-0.5555447
H	1.2351385	0.0122513	-1.8125981
H	-0.9496334	-0.0046550	-0.5422661
H	-0.9377039	-0.0159613	1.9925963
H	0.3042778	-3.6769497	5.0768171
H	3.0949677	-5.2294680	2.8574426
H	3.8205683	-3.7049318	2.2453809
H	4.4329796	-4.4766283	3.7475119

H	-2.0239690	-4.6951080	4.7300040
H	-2.0679065	-3.5925181	6.1430577
H	-2.5906959	-3.0044060	4.5347669

Table S5-7. NAPMA B ππ*/nπ* IIe conical intersection (CI^{IIe}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIe} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4308273
C	1.2385555	0.0000000	2.1592061
C	2.4784256	-0.0053842	1.4239265
C	2.4729662	0.0086011	-0.0076243
C	1.2345598	0.0051473	-0.7190944
C	1.2669263	-0.0477345	3.6620580
C	1.1296490	-1.4802785	4.2215562
N	2.0107490	-2.3723070	3.4761259
C	2.4787370	-3.5504021	3.9836269
O	2.1487690	-3.9795868	5.1071483
C	-0.3346446	-1.9494007	4.2077815
N	-0.5477098	-3.1264448	4.8743773
C	-1.8760345	-3.7085337	4.9599410
O	-1.2860853	-1.1048591	3.8871479
C	3.4359993	-4.3081209	3.0840164
H	2.2165481	-2.1125899	2.5112676
H	1.4663101	-1.5051310	5.2761256
H	2.2235203	0.3691466	4.0222014
H	0.4407850	0.5473861	4.0851518
H	3.4265677	0.0563727	1.9698145
H	3.4197305	0.0270015	-0.5556950
H	1.2344302	0.0123544	-1.8128478
H	-0.9497801	-0.0042944	-0.5420761
H	-0.9376972	-0.0171893	1.9923942
H	0.3014619	-3.6360014	5.1420863
H	2.9687509	-5.2607855	2.7902959
H	3.7191257	-3.7470536	2.1810077
H	4.3392538	-4.5486555	3.6639951
H	-1.9780113	-4.5862805	4.2990796
H	-2.0962222	-4.0157852	5.9943915
H	-2.6013427	-2.9413581	4.6542057

Table S5-8. NAPMA B ππ*/nπ* IIf conical intersection (CI^{IIf}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIf} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4322214
C	1.2379782	0.0000000	2.1623094
C	2.4800361	-0.0031792	1.4282411
C	2.4745565	0.0102437	-0.0023825
C	1.2352670	0.0047180	-0.7159097
C	1.2610441	-0.0439619	3.6641025
C	1.2552511	-1.4832891	4.2181051
N	2.2566697	-2.2870394	3.5225091
C	2.8670156	-3.3517400	4.1358769

O	2.6428910	-3.6644445	5.3198004
C	-0.1392579	-2.1218065	4.1149040
N	-0.2144498	-3.3643359	4.6885239
C	-1.4380187	-4.1461208	4.6254530
O	-1.0258892	-1.6169131	3.2955540
C	3.8377280	-4.1220254	3.2621932
H	2.3274137	-2.1240629	2.5164907
H	1.5408419	-1.4828656	5.2860678
H	2.1723123	0.4584994	4.0328469
H	0.3796232	0.4732725	4.0769779
H	3.4263375	0.0591750	1.9764417
H	3.4212073	0.0299050	-0.5506118
H	1.2370777	0.0115634	-1.8096781
H	-0.9492132	-0.0045488	-0.5428207
H	-0.9386346	-0.0112868	1.9912493
H	0.5517152	-3.6049722	5.3244188
H	3.3774902	-5.0835540	2.9846931
H	4.1114003	-3.5766302	2.3465231
H	4.7423087	-4.3390913	3.8481833
H	-1.2127360	-5.1924237	4.3658268
H	-1.9841602	-4.1267534	5.5840250
H	-2.0733607	-3.7077890	3.8433782

Table S5-9. NAPMA B ππ*/nπ* IIg conical intersection (CI^{IIg}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIg} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4298942
C	1.2374792	0.0000000	2.1585262
C	2.4765609	-0.0070810	1.4239690
C	2.4719038	0.0060192	-0.0068402
C	1.2342871	0.0034842	-0.7182560
C	1.2629369	-0.0473365	3.6614249
C	1.1144692	-1.4792462	4.2198037
N	2.0206992	-2.3684518	3.4967705
C	2.4039174	-3.5784837	4.0027392
O	2.0371242	-3.9866471	5.1236887
C	-0.3436402	-1.9667777	4.1622210
N	-0.5572228	-3.1175612	4.9305155
C	-1.8856645	-3.6813944	5.0865319
O	-1.1552165	-1.5912023	3.2604754
C	3.3105365	-4.3964985	3.1049321
H	2.2182727	-2.1161765	2.5275277
H	1.4182027	-1.4996812	5.2832303
H	2.2220112	0.3640726	4.0226594
H	0.4410408	0.5552727	4.0805795
H	3.4245639	0.0522783	1.9704234
H	3.4189325	0.0226701	-0.5545547
H	1.2342435	0.0096403	-1.8120438
H	-0.9497123	-0.0052039	-0.5421307
H	-0.9385477	-0.0176479	1.9883266
H	0.2970846	-3.6152151	5.2188158
H	2.7292226	-5.2335731	2.6870609
H	3.7393599	-3.8079681	2.2800988

H	4.1196880	-4.8211008	3.7161957
H	-1.9780756	-4.6438738	4.5587568
H	-2.1094111	-3.8388216	6.1542396
H	-2.6046038	-2.9649404	4.6659260

Table S5-10. NAPA B type a ππ*/nπ* minimum energy conical intersection (MECI[a]).

C	0.0047388	0.0006019	-0.0000911
C	0.0019197	-0.0029385	1.4283396
C	1.2361197	-0.0024071	2.1588794
C	2.4732993	-0.0011605	1.4262896
C	2.4733693	0.0072131	-0.0026674
C	1.2384097	0.0033058	-0.7164448
C	1.2568096	-0.0499613	3.6617690
C	1.1357997	-1.4846296	4.2144288
N	2.0914294	-2.3486293	3.5381690
C	2.5895693	-3.4863090	4.1163888
O	2.2643494	-3.8524889	5.2613985
C	-0.2983749	-2.0032094	4.1345988
N	-0.4687479	-3.3550891	4.3891788
O	-1.3003696	-1.2198397	3.9448289
C	3.5636190	-4.2708888	3.2601291
H	2.2472194	-2.1758794	2.5452393
H	1.4225696	-1.4954496	5.2868385
H	2.2044694	0.3757759	4.0319189
H	0.4205349	0.5337839	4.0793789
H	3.4211090	0.0427881	1.9743194
H	3.4223490	0.0236619	-0.5475328
H	1.2395297	0.0078047	-1.8097195
H	-0.9448197	-0.0000814	-0.5434988
H	-0.9392377	-0.0194550	1.9838594
H	-1.4281396	-3.5847290	4.6470887
H	0.2508989	-3.7602189	4.9977386
H	3.0657491	-5.1833785	2.8948492
H	3.9361389	-3.6938690	2.4007193
H	4.4083288	-4.5811487	3.8919389

Table S5-11. NAPA B type b ππ*/nπ* minimum energy conical intersection (MECI[b]).

C	0.0415131	0.1249160	-0.0660246
C	-0.0072515	0.1088460	1.3615596
C	1.1956097	-0.0054446	2.1313494
C	2.4558593	-0.0574050	1.4365996
C	2.5000193	-0.0368774	0.0099843
C	1.2927196	0.0456869	-0.7427888
C	1.1745397	-0.0885860	3.6336390
C	1.1604197	-1.5342496	4.1804988
N	2.1975194	-2.3161893	3.5020890
C	2.7229992	-3.4587690	4.0442489
O	2.3816393	-3.8988189	5.1585386
C	-0.2137699	-2.1818194	4.0819989
N	-0.4332059	-3.2230491	4.9685486
O	-1.1364397	-1.7655795	3.2834591

C	3.7698789	-4.1539888	3.1958791
H	2.3593393	-2.1116694	2.5153693
H	1.4440496	-1.5343696	5.2499385
H	2.0787994	0.4043479	4.0339689
H	0.2890599	0.4306289	4.0376689
H	3.3865290	-0.0661054	2.0148594
H	3.4634190	-0.0924872	-0.5051149
H	1.3294296	0.0465160	-1.8355395
H	-0.8888328	0.1905959	-0.6364538
H	-0.9662897	0.1742190	1.8798995
H	-1.1871097	-3.8498389	4.6904287
H	0.4288259	-3.6795290	5.2869985
H	3.3504191	-5.0983186	2.8147092
H	4.1184588	-3.5425190	2.3504493
H	4.6215987	-4.4085388	3.8429289

Table S5-12. NAPA B ππ*/nπ* minimum distance conical intersection (MDCI).

C	-3.2286391	-0.6960538	-0.9956987
C	-2.1350794	-1.1425497	-0.1827969
C	-1.4929396	-0.2399799	0.7367648
C	-1.9624594	1.1239497	0.8224378
C	-3.0683791	1.5610296	0.0209451
C	-3.6953490	0.6537798	-0.8930937
C	-0.3045979	-0.6715938	1.5666896
C	1.0390297	-0.5251049	0.8186668
N	1.0852397	0.7795418	0.1578850
C	2.2525194	1.4446096	-0.0906005
O	3.3714791	0.9503787	0.1541470
C	1.3098796	-1.6620095	-0.1297010
N	2.4408593	-1.5586396	-0.8795448
O	0.5280549	-2.7149292	-0.2148689
C	2.0948294	2.8254792	-0.7011578
H	0.1978719	1.1857097	-0.1305660
H	1.8831595	-0.5094559	1.5632296
H	-0.2605689	-0.0641017	2.4833793
H	-0.4028789	-1.7358995	1.8585195
H	-1.5198896	1.8040795	1.5755296
H	-3.4401790	2.5968593	0.1117420
H	-4.5424787	0.9963327	-1.5120796
H	-3.7107390	-1.3955896	-1.7025595
H	-1.7564995	-2.1792794	-0.2664529
H	2.7570792	-2.3498793	-1.4122996
H	3.1025091	-0.8413488	-0.5858558
H	2.4797493	2.8045492	-1.7345495
H	1.0515297	3.1787491	-0.7092748
H	2.7177892	3.5308090	-0.1295620

Table S5-13. NAPA B ππ*/nπ* IIb conical intersection (CI^{IIb}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIb} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4312773

C	1.2391763	0.0000000	2.1599976
C	2.4796286	-0.0080348	1.4262933
C	2.4748325	0.0057958	-0.0058128
C	1.2359834	0.0033726	-0.7178467
C	1.2578136	-0.0536430	3.6614461
C	1.1350762	-1.4933553	4.2003383
N	2.0850246	-2.3611405	3.5209949
C	2.5855665	-3.4925577	4.1062350
O	2.2510507	-3.8589728	5.2486638
C	-0.3098479	-2.0014229	4.0938291
N	-0.4697529	-3.3215271	4.4758722
O	-1.2970638	-1.1985291	3.9749218
C	3.5697526	-4.2744402	3.2584141
H	2.2817155	-2.1512616	2.5424468
H	1.3995750	-1.5163068	5.2760373
H	2.2023650	0.3755308	4.0378391
H	0.4154747	0.5224126	4.0786254
H	3.4271446	0.0508287	1.9734036
H	3.4216053	0.0229433	-0.5538155
H	1.2363642	0.0103754	-1.8115672
H	-0.9492037	-0.0031297	-0.5429853
H	-0.9385859	-0.0125117	1.9915155
H	-1.4361344	-3.6306501	4.5583056
H	0.2581229	-3.7212198	5.0779238
H	3.0752606	-5.1881297	2.8924693
H	3.9457162	-3.6994674	2.3989321
H	4.4119887	-4.5817866	3.8945851

Table S5-14. NAPA B ππ*/nπ* IIc conical intersection (CI^{IIc}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIc} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4317264
C	1.2384110	0.0000000	2.1606078
C	2.4792983	-0.0058918	1.4267118
C	2.4741105	0.0072024	-0.0039152
C	1.2348720	0.0025288	-0.7164818
C	1.2581264	-0.0523852	3.6621921
C	1.1909559	-1.4949273	4.2019830
N	2.1880620	-2.3178757	3.5229887
C	2.7257399	-3.4333106	4.1074857
O	2.4083191	-3.8110654	5.2515783
C	-0.2238412	-2.0808814	4.0746605
N	-0.3658559	-3.3451815	4.5918891
O	-1.1009036	-1.5248810	3.2908751
C	3.7344194	-4.1811430	3.2575262
H	2.3352080	-2.1176104	2.5330254
H	1.4481132	-1.5120314	5.2773563
H	2.1871980	0.4109170	4.0371232
H	0.3959028	0.4942173	4.0774728
H	3.4263686	0.0543741	1.9742209
H	3.4206956	0.0254073	-0.5522248
H	1.2358315	0.0087081	-1.8102046
H	-0.9493213	-0.0034177	-0.5425894

H	-0.9390317	-0.0047047	1.9905515
H	-1.2519134	-3.8039574	4.3878962
H	0.4322127	-3.7285713	5.1065732
H	3.2701844	-5.1097823	2.8893043
H	4.0897576	-3.5918722	2.3990789
H	4.5868280	-4.4622711	3.8922722

Table S5-15. NAPA B ππ*/nπ* IId conical intersection (CI^{IId}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IId} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4318884
C	1.2399878	0.0000000	2.1602851
C	2.4809719	-0.0073390	1.4257917
C	2.4757537	0.0071920	-0.0068685
C	1.2361482	0.0039808	-0.7185927
C	1.2616586	-0.0534491	3.6618430
C	1.1219500	-1.4904653	4.2046762
N	2.0472915	-2.3695844	3.5033688
C	2.5385513	-3.5174963	4.0581297
O	2.1908657	-3.9188093	5.1859967
C	-0.3345355	-1.9740008	4.1266942
N	-0.5366766	-3.2633359	4.5508078
O	-1.2975649	-1.1272366	3.9466649
C	3.5327609	-4.2768947	3.2016723
H	2.2668471	-2.1308916	2.5363944
H	1.4063528	-1.5177057	5.2754180
H	2.2136222	0.3632282	4.0337100
H	0.4292948	0.5347648	4.0823710
H	3.4286763	0.0537193	1.9724143
H	3.4223377	0.0253346	-0.5551160
H	1.2361944	0.0108566	-1.8122966
H	-0.9493279	-0.0039531	-0.5426794
H	-0.9382319	-0.0120107	1.9927997
H	-1.4971036	-3.5012127	4.7896063
H	0.2468576	-3.7241052	5.0242011
H	3.0726369	-5.2238396	2.8789179
H	3.8604059	-3.7121958	2.3161520
H	4.4056271	-4.5271947	3.8220272

Table S5-16. NAPA B ππ*/nπ* IIe conical intersection (CI^{IIe}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIe} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4310065
C	1.2390219	0.0000000	2.1591806
C	2.4789074	-0.0076497	1.4242202
C	2.4738004	0.0061546	-0.0074699
C	1.2349440	0.0036509	-0.7189040
C	1.2641772	-0.0490856	3.6618224
C	1.1091271	-1.4809862	4.2149511
N	2.0026016	-2.3763289	3.4905644
C	2.4555948	-3.5556781	4.0097483

O	2.1026585	-3.9783653	5.1280862
C	-0.3588503	-1.9390051	4.1830273
N	-0.5769676	-3.1677350	4.7512066
O	-1.3100564	-1.0801745	3.9414166
C	3.4200233	-4.3231877	3.1262078
H	2.2222421	-2.1243147	2.5269581
H	1.4214626	-1.5083962	5.2774770
H	2.2234931	0.3569352	4.0263568
H	0.4420105	0.5523301	4.0836276
H	3.4269725	0.0515369	1.9704569
H	3.4205215	0.0232743	-0.5555527
H	1.2346804	0.0106681	-1.8126307
H	-0.9496157	-0.0031018	-0.5423172
H	-0.9382358	-0.0135836	1.9922118
H	-1.5453693	-3.4732478	4.7979128
H	0.2480332	-3.6777001	5.0793189
H	2.9333611	-5.2531990	2.7934368
H	3.7507479	-3.7511803	2.2465446
H	4.2943836	-4.6055206	3.7306789

Table S5-17. NAPA B ππ*/nπ* IIf conical intersection (CI^{IIf}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIf} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4329119
C	1.2389868	0.0000000	2.1629241
C	2.4814974	-0.0056215	1.4288157
C	2.4762201	0.0081676	-0.0025898
C	1.2360613	0.0036133	-0.7161332
C	1.2599425	-0.0461106	3.6643350
C	1.2322249	-1.4863659	4.2128825
N	2.2345787	-2.2979652	3.5305237
C	2.8310569	-3.3678689	4.1483760
O	2.5894370	-3.6806735	5.3283816
C	-0.1716126	-2.1058196	4.1013792
N	-0.2458479	-3.3951412	4.5644867
O	-1.0863242	-1.5309558	3.3825483
C	3.8035544	-4.1449308	3.2828802
H	2.3223159	-2.1363975	2.5259511
H	1.5025681	-1.4921135	5.2852709
H	2.1769587	0.4425949	4.0366371
H	0.3842590	0.4809606	4.0771386
H	3.4277949	0.0547390	1.9771478
H	3.4227576	0.0267682	-0.5509148
H	1.2376461	0.0103652	-1.8098583
H	-0.9490401	-0.0037714	-0.5430386
H	-0.9388359	-0.0080103	1.9918976
H	-1.1729652	-3.8122728	4.5671997
H	0.4510166	-3.6875166	5.2533129
H	3.3289478	-5.0922237	2.9814640
H	4.1065606	-3.5920869	2.3810218
H	4.6912016	-4.3894530	3.8835027

Table S5-18. NAPA B ππ*/nπ* IIg conical intersection (CI^{IIg}) obtained from the LIP connecting $M_{\pi\pi^*}$ and M_{IIg} minima.

C	0.0000000	0.0000000	0.0000000
C	0.0000000	0.0000000	1.4303818
C	1.2378297	0.0000000	2.1592049
C	2.4774404	-0.0078081	1.4252124
C	2.4729999	0.0054789	-0.0057529
C	1.2348745	0.0025642	-0.7175771
C	1.2587945	-0.0531286	3.6614532
C	1.1145895	-1.4900536	4.2050328
N	2.0545905	-2.3622786	3.5080075
C	2.4494724	-3.5646835	4.0270397
O	2.0600530	-3.9765955	5.1371997
C	-0.3366443	-1.9891587	4.1102899
N	-0.5558708	-3.1956973	4.7621765
O	-1.1647891	-1.5172820	3.2581821
C	3.3932420	-4.3651567	3.1517261
H	2.2656390	-2.1140914	2.5408188
H	1.3825016	-1.5153921	5.2780280
H	2.2135342	0.3596433	4.0315405
H	0.4306657	0.5409246	4.0805489
H	3.4251910	0.0506207	1.9721106
H	3.4199651	0.0220988	-0.5534485
H	1.2350944	0.0086358	-1.8113068
H	-0.9494307	-0.0039160	-0.5425088
H	-0.9391776	-0.0109217	1.9887058
H	-1.5217466	-3.5182034	4.7462290
H	0.2793823	-3.6656144	5.1315657
H	2.8299523	-5.1915541	2.6899183
H	3.8570582	-3.7591686	2.3590814
H	4.1747919	-4.8042467	3.7878155

S6. Zero point energy accessibility test of the relevant ππ*/nπ* conical intersection seam structures

Note. All figures display the ratio of potential energy along each *i*-th normal $M_{\pi\pi^*}$ mode, V_i, and its corresponding zero point energy, ZPE_i, necessary to reach the specific CI structure in NAPA (top) and NAPMA (bottom). For more details see the main text and Appendix S2.

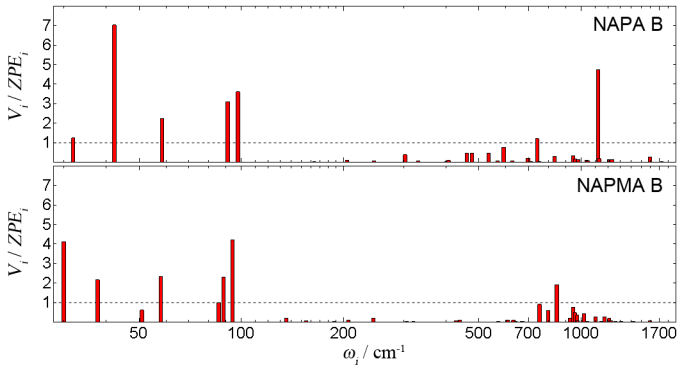

Figure S6-1. MECI[b]

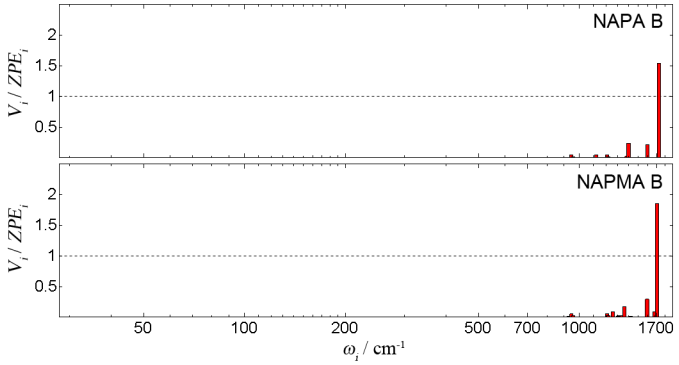

Figure S6-2. MDCI

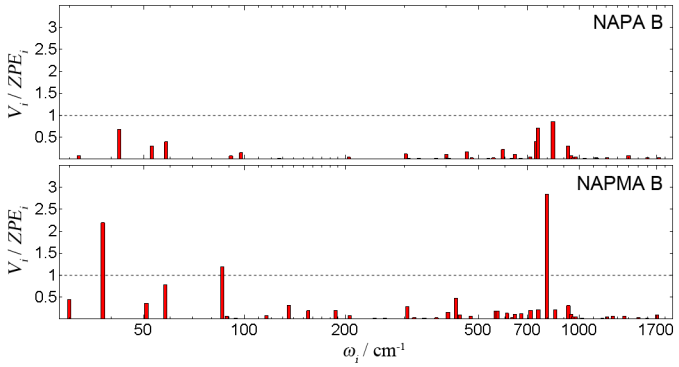

Figure S6-3. CI[IIb]

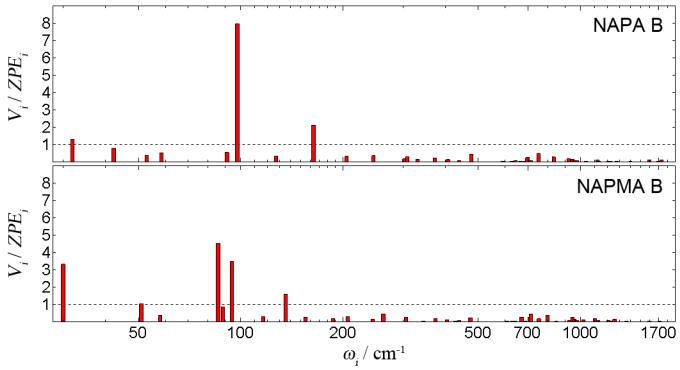

Figure S6-4. CI^{IIc}

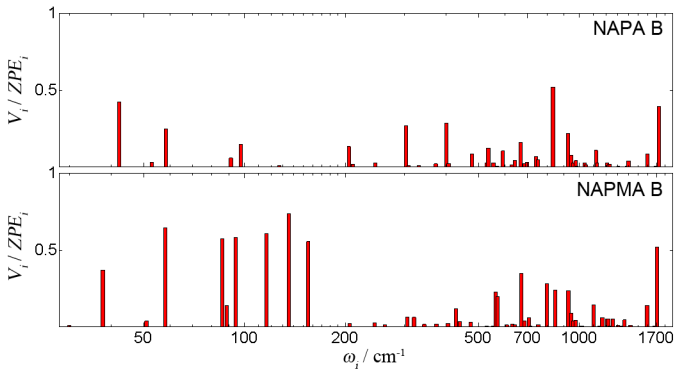

Figure S6-5. CI^{IId}

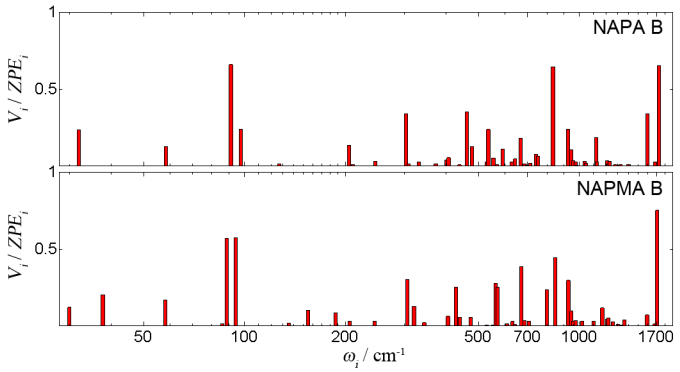

Figure S6-6. CI^{IIe}

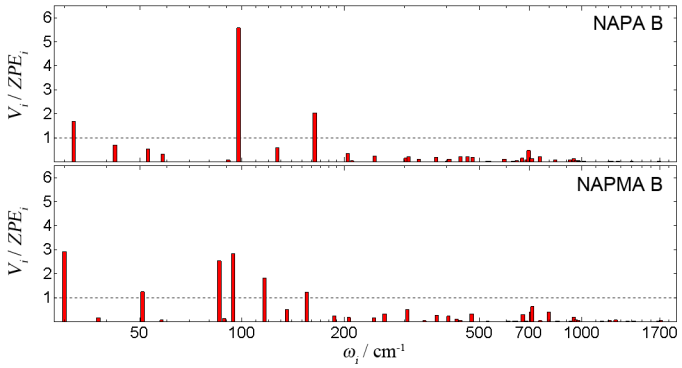

Figure S6-7. CI^{IIf}

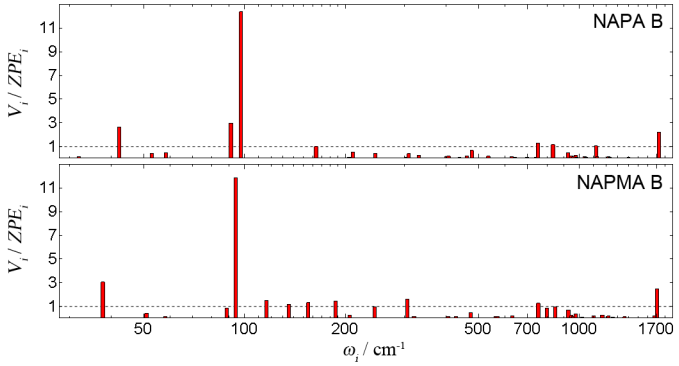

Figure S6-8. CI^{IIg}