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Supporting Information

The Role of Non-innocent Solvent Molecules in Organocatalyzed Asymmetric Michael Addition

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LIST OF ITEMS IN SUPPORTING INFORMATION

Full Citation for Ref. 53

Gaussian03 : Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

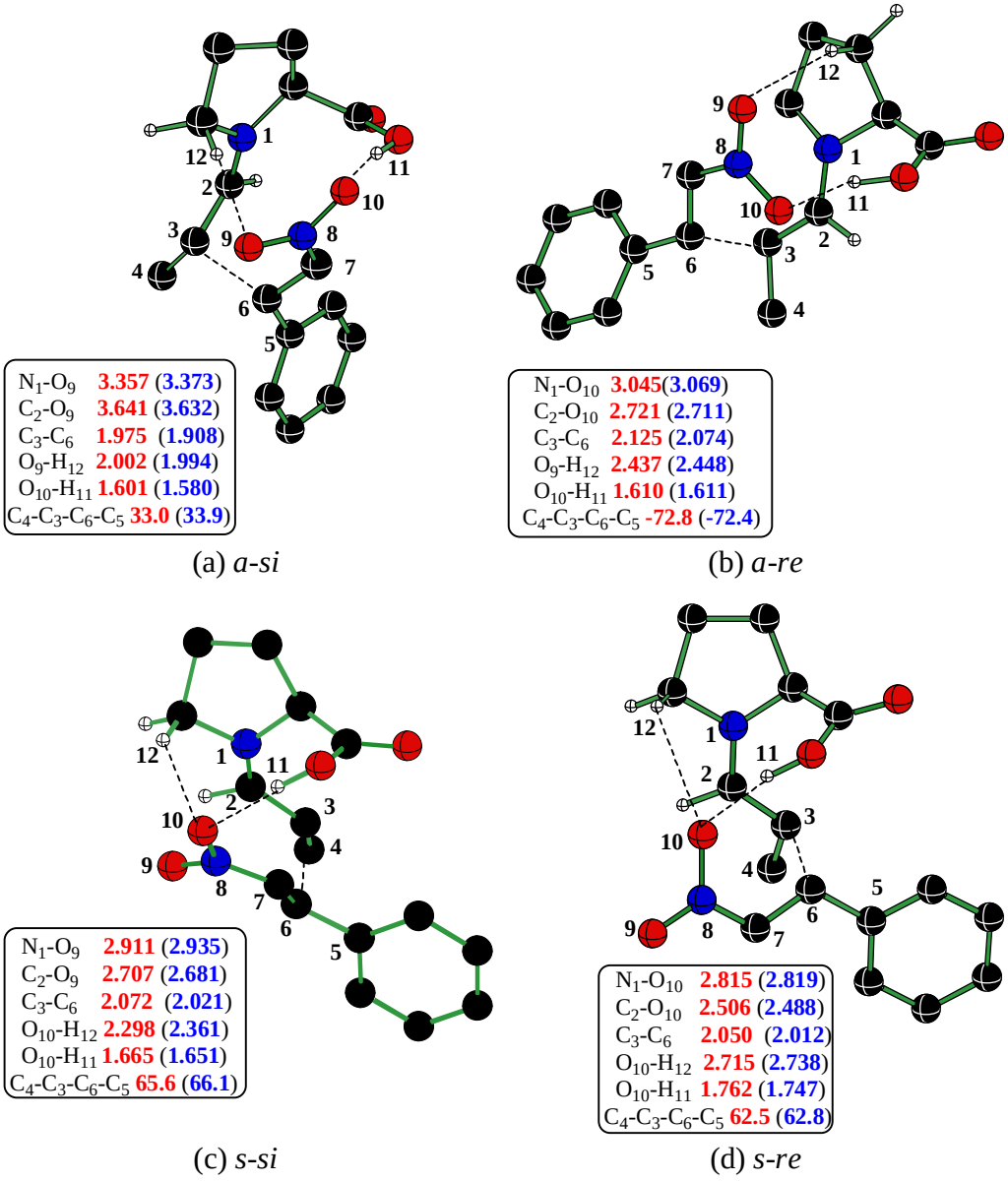


Figure S1. The mPW1PW91/6-31G* optimized transition state geometries for four stereochemical modes of addition for enamines derived from proline and propanal (**1**) to nitrostyrene. The values in parentheses refer to the optimized bond lengths at the B3LYP/6-31G* level of theory. Only selected hydrogens are shown for sake of clarity. Angles are given in degrees and distances in ? . [Atom colors: Black = C, Red = O, Blue = N].

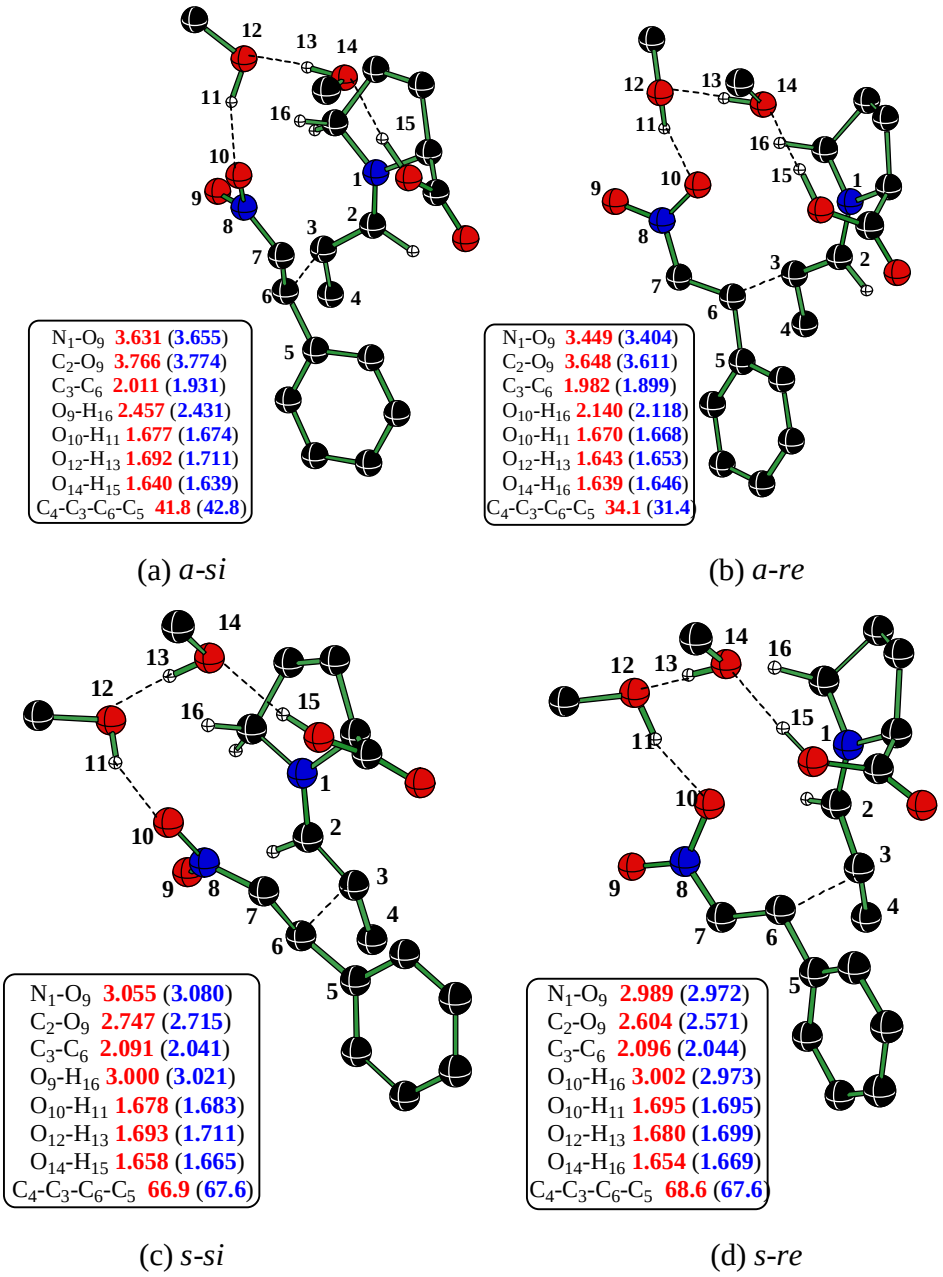
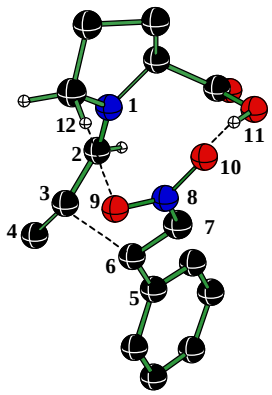
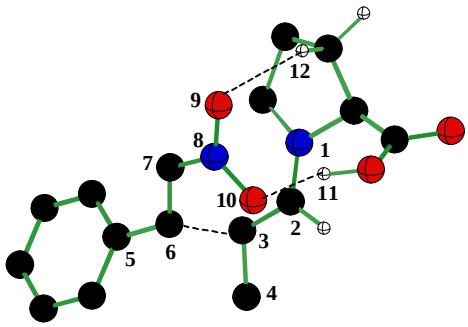


Figure S2. The mPW1PW91/6-31G* optimized transition state geometries for four stereochemical modes of methanol assisted addition of enamines (**C_2** model) derived from proline and propanal (**1**) to nitrostyrene. The values in parentheses refer to the optimized bond lengths at the B3LYP/6-31G* level of theory. Only selected hydrogens are shown for sake of clarity. Angles are given in degrees and distances in ? . [Atom colors: Black = C, Red = O, Blue = N].



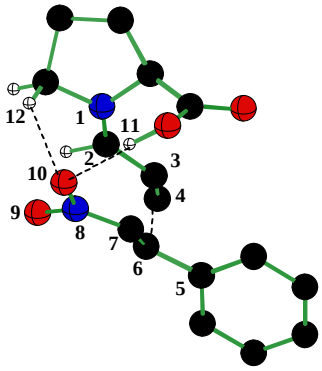
N_1 -0.37 (-0.36)	N_1-C_2 1.410
C_2 0.22 (0.17)	C_2-C_3 1.284
C_3 -0.36 (-0.26)	C_3-C_6 0.524
C_6 -0.22 (-0.17)	C_6-C_7 1.242
C_7 0.01 (-0.17)	C_7-N_8 1.274
N_8 0.20 (0.44)	N_8-O_9 1.340
O_9 -0.37 (-0.51)	N_8-O_{10} 1.227
O_{10} -0.44 (-0.57)	O_{10}-H_{11} 0.137

(a) *a-si*



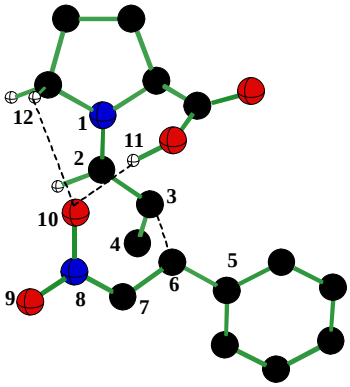
N_1 -0.41 (-0.39)	N_1-C_2 1.328
C_2 0.21 (0.15)	C_2-C_3 1.363
C_3 -0.38 (-0.29)	C_3-C_6 0.412
C_6 -0.20 (-0.15)	C_6-C_7 1.350
C_7 0.04 (-0.16)	C_7-N_8 1.200
N_8 0.22 (0.46)	N_8-O_9 1.397
O_9 -0.35 (-0.47)	N_8-O_{10} 1.245
O_{10} -0.41 (-0.55)	O_{10}-H_{11} 0.107

(b) *a-re*



N_1 -0.37 (-0.40)	N_1-C_2 1.313
C_2 0.18 (0.14)	C_2-C_3 1.361
C_3 -0.35 (-0.27)	C_3-C_6 0.446
C_6 -0.21 (-0.15)	C_6-C_7 1.313
C_7 0.02 (-0.15)	C_7-N_8 1.226
N_8 0.20 (0.45)	N_8-O_9 1.359
O_9 -0.35 (-0.48)	N_8-O_{10} 1.248
O_{10} -0.42 (-0.56)	O_{10}-H_{11} 0.125

(c) *s-si*



N_1 -0.30 (-0.40)	N_1-C_2 1.303
C_2 0.17 (0.14)	C_2-C_3 1.334
C_3 -0.41 (-0.27)	C_3-C_6 0.463
C_6 -0.26 (-0.16)	C_6-C_7 1.314
C_7 0.09 (-0.15)	C_7-N_8 1.217
N_8 0.23 (0.47)	N_8-O_9 1.420
O_9 -0.35 (-0.44)	N_8-O_{10} 1.224
O_{10} -0.45 (-0.59)	O_{10}-H_{11} 0.097

(d) *s-re*

Figure S3. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States of Four Stereochemical Modes of Addition of Enamines Derived from Proline and Propanal (**1**) to Nitrostyrene Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

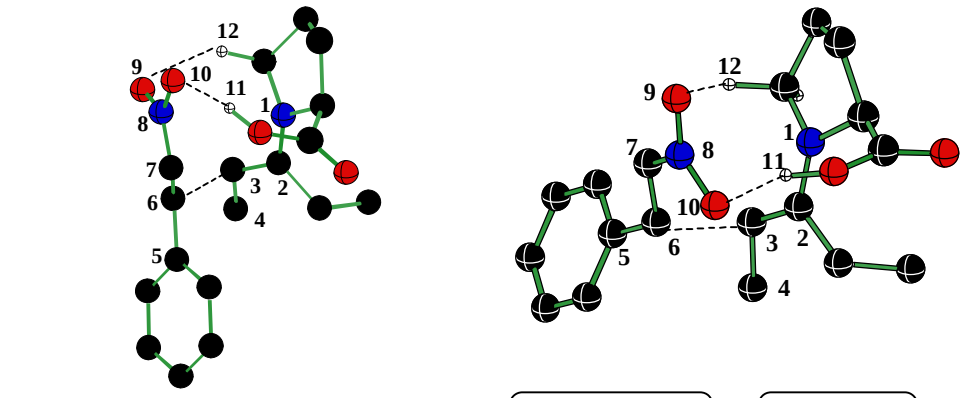


Figure S4. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States for Four Stereochemical Modes of Addition of Enamines Derived from Proline and 3-Pentanone (**2**) to Nitrostyrene Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

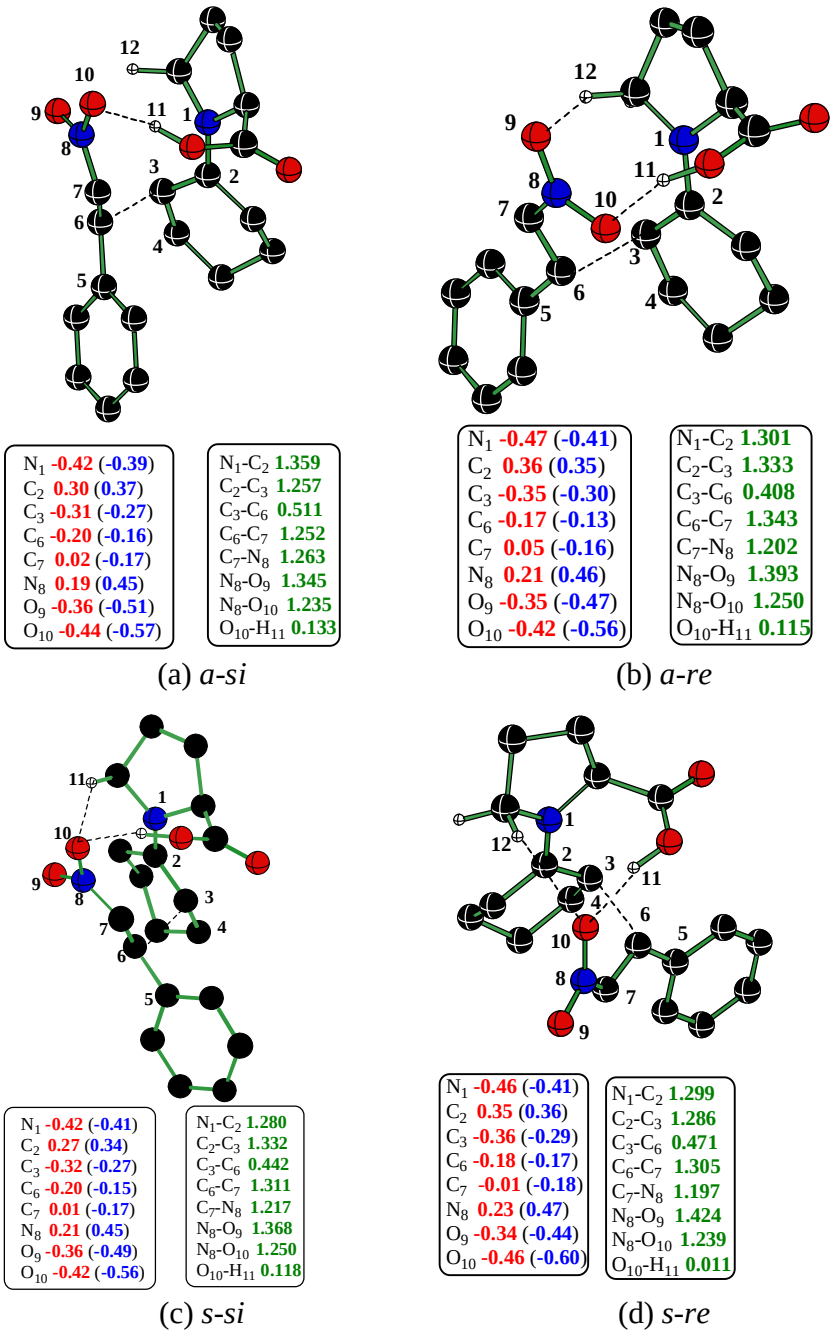


Figure S5. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States of Four Stereochemical Modes of Addition of Enamines Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

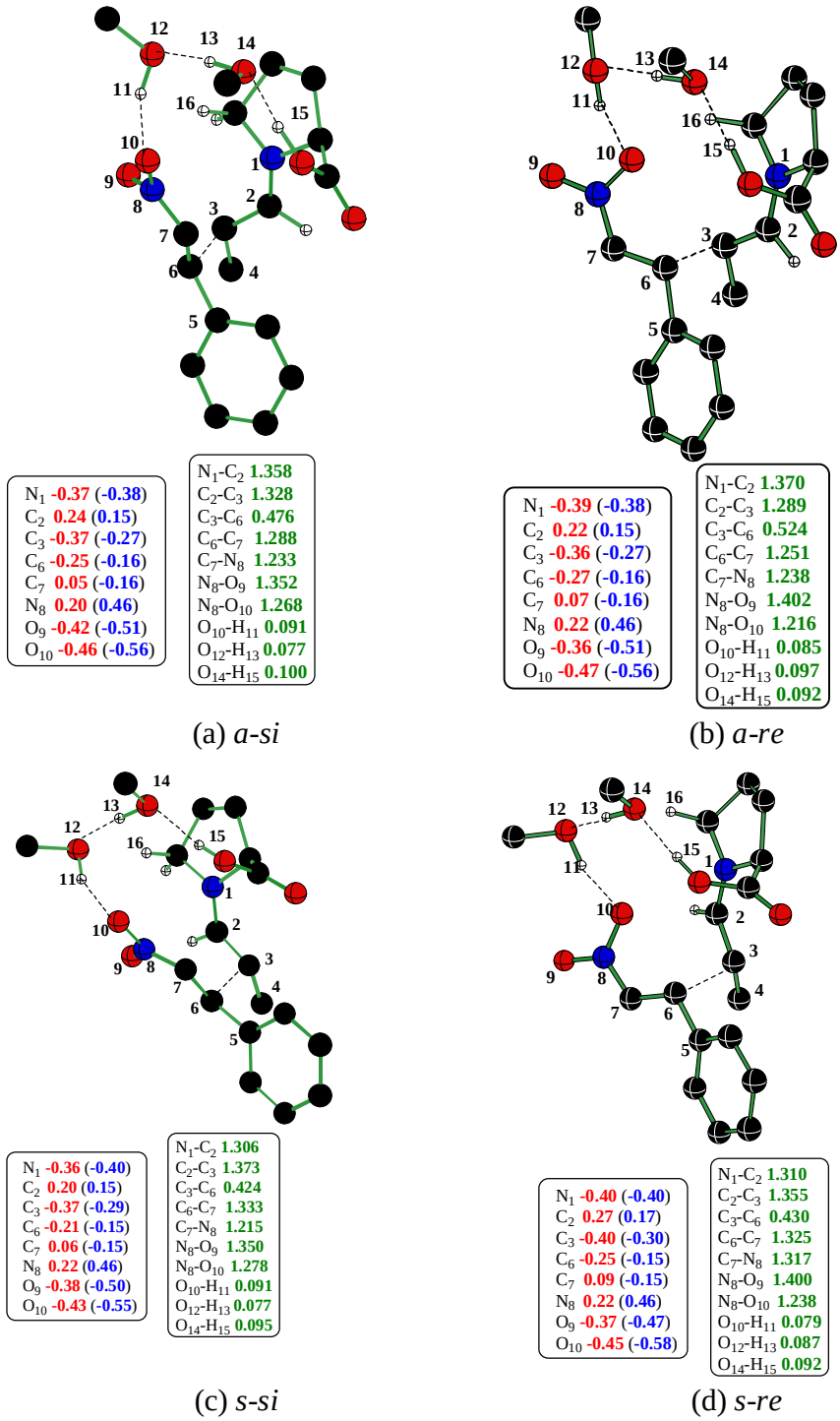


Figure S6. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States for Four Stereochemical Modes of Addition of Enamines Derived from Proline and Propanal (**1**) to Nitrostyrene Using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

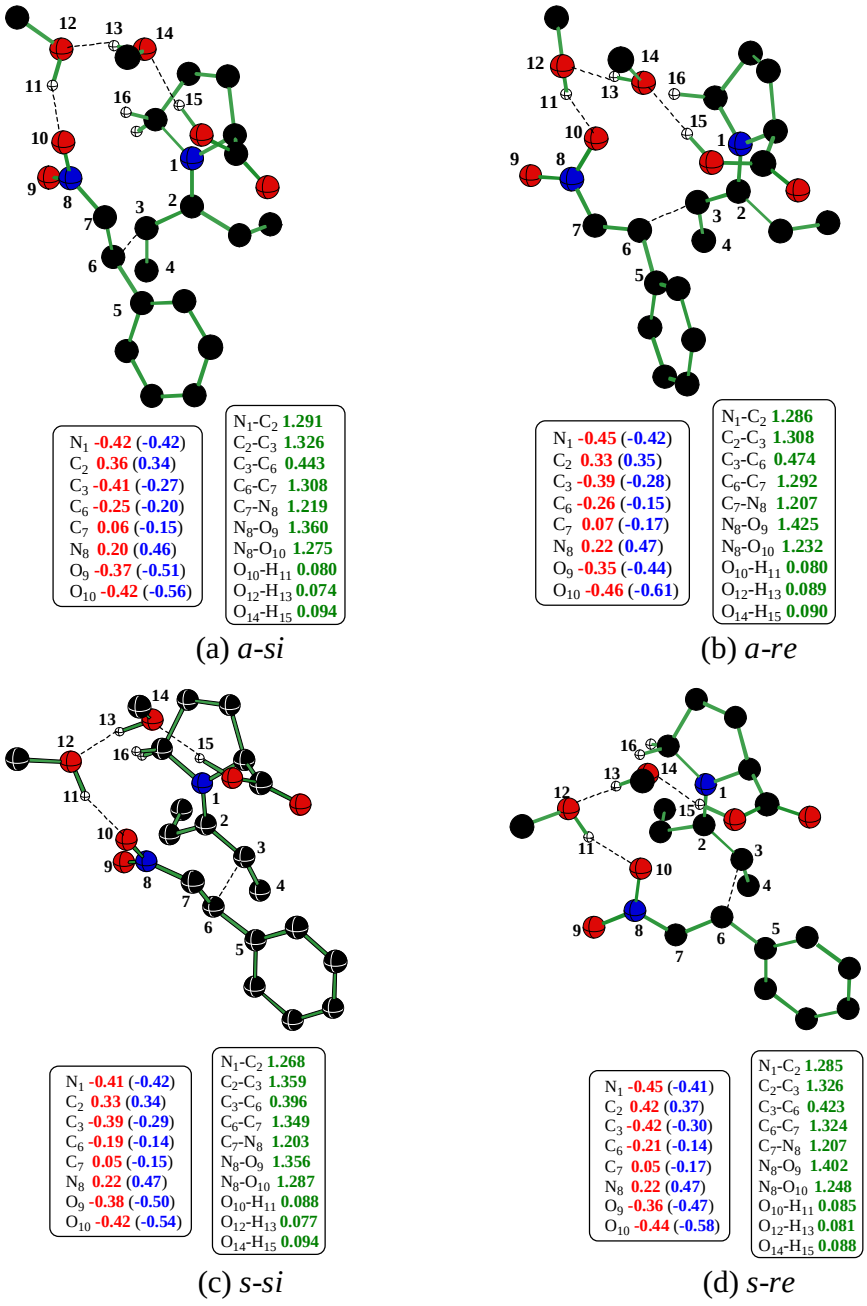


Figure S7. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States of Four Stereochemical Modes of Addition of Enamines Derived from Proline and 3-Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{C_2}$ model) Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

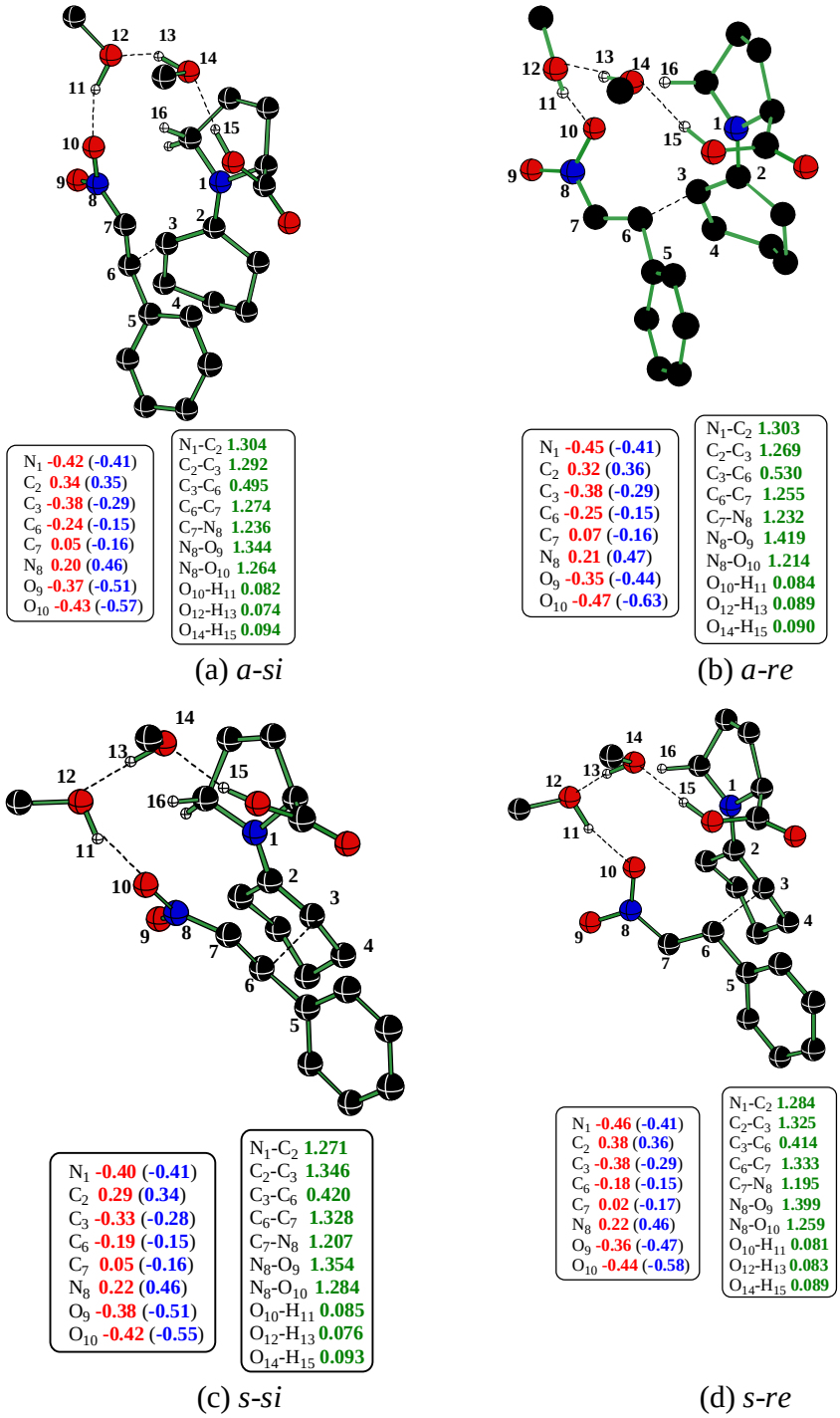


Figure S8. Bond Order (in green) for Representative Bonds, Natural (in blue) and Mulliken Charges (in red) for Selected Atoms of Transition States of Four Stereochemical Modes of Addition of Enamines Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

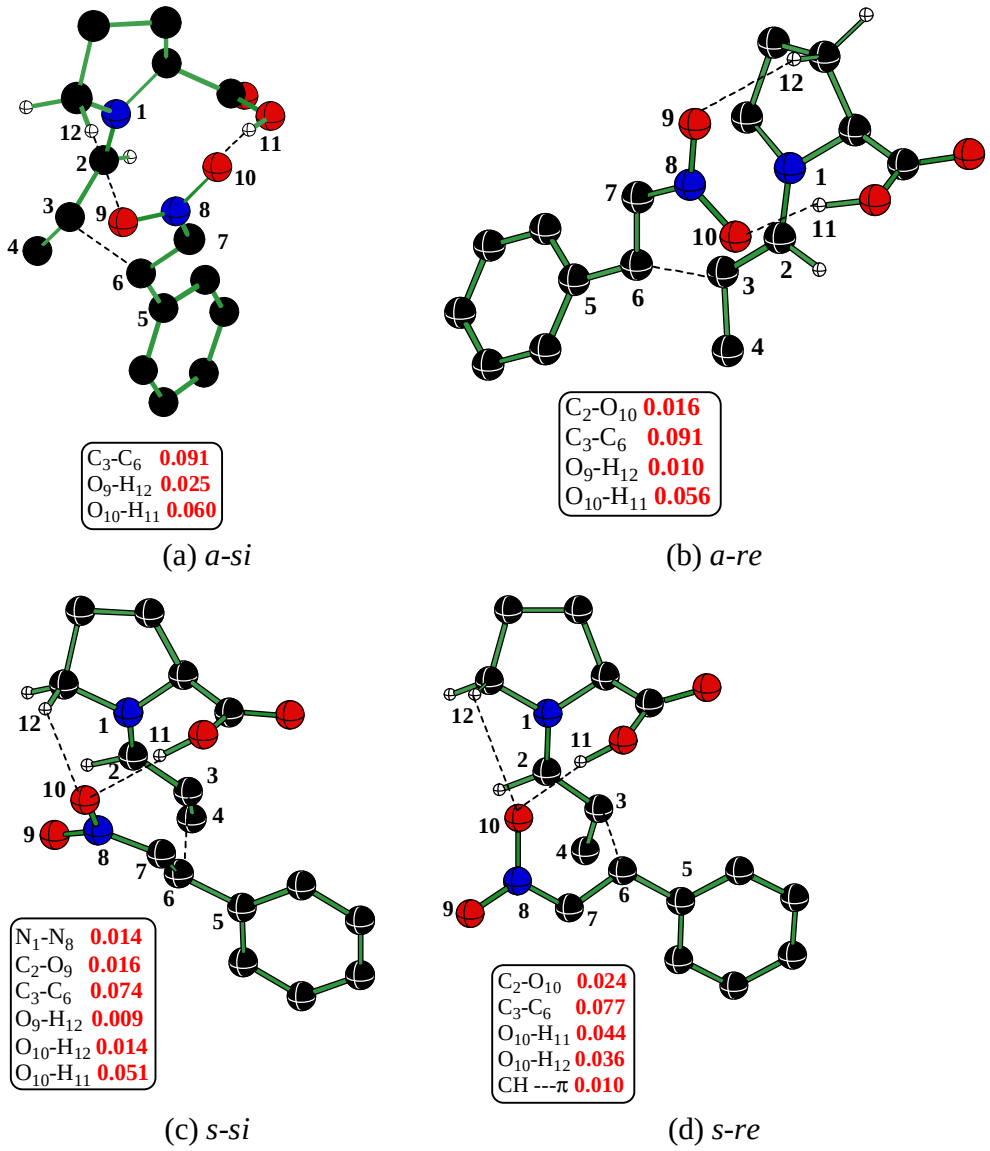


Figure S9. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States for Four Stereochemical Modes of Addition of Enamines Derived from Proline and Propanal (**1**) to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

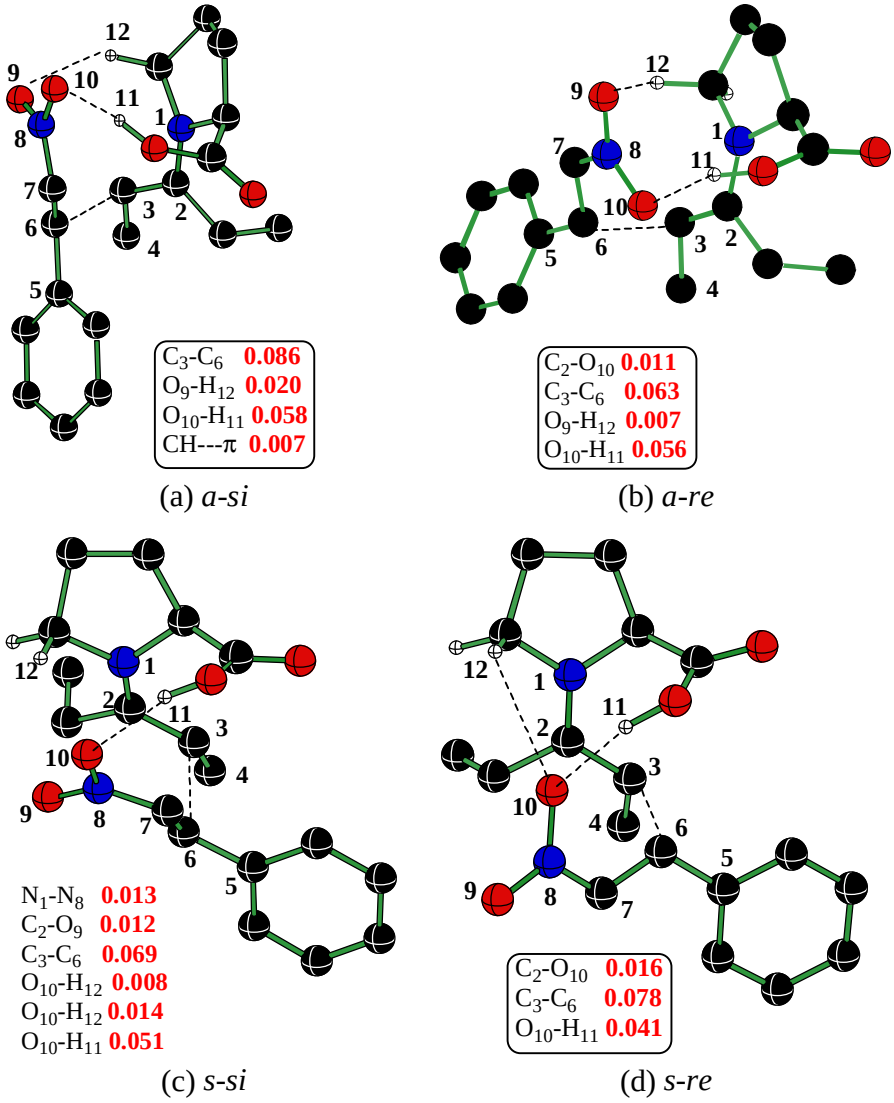


Figure S10. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States for Four Stereochemical Modes of Addition of Enamines Derived from Proline and 3-Pentanone (**2**) to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

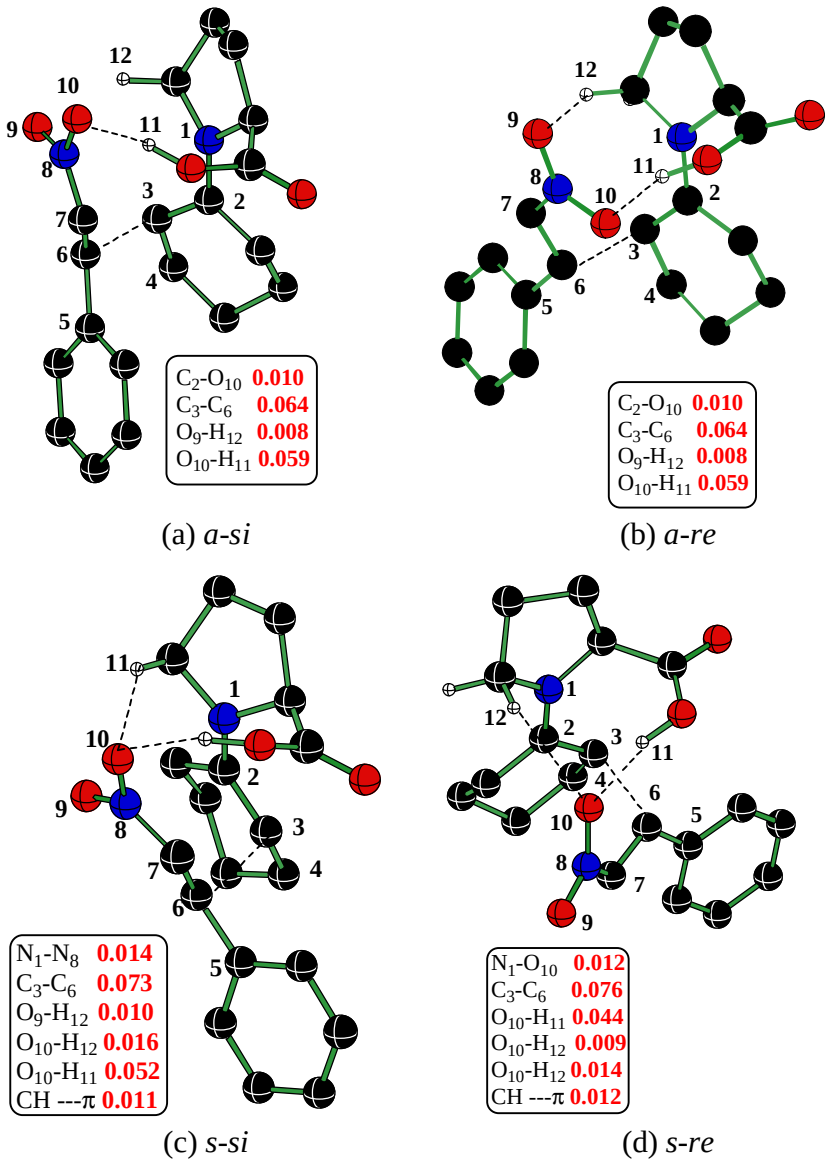


Figure S11. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States for Four Stereochemical Modes of Addition of Enamines Derived from Proline and Cyclohexanone (**3)** to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

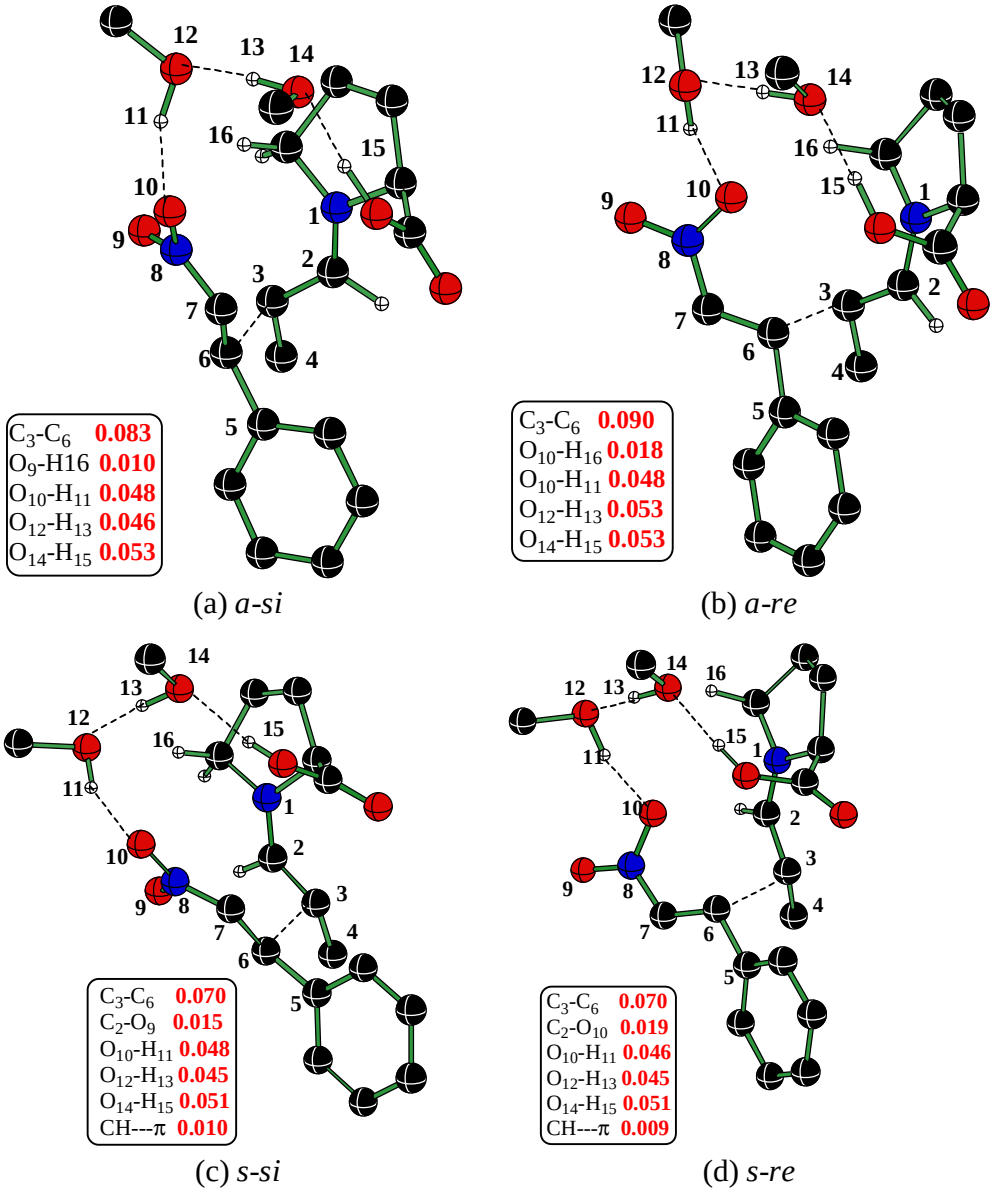


Figure S12. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States of Solvent-Assisted pathway (**C_2** model) for Four Stereochemical Modes of Addition of Enamines Derived from Proline and Propanal (**1**) to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

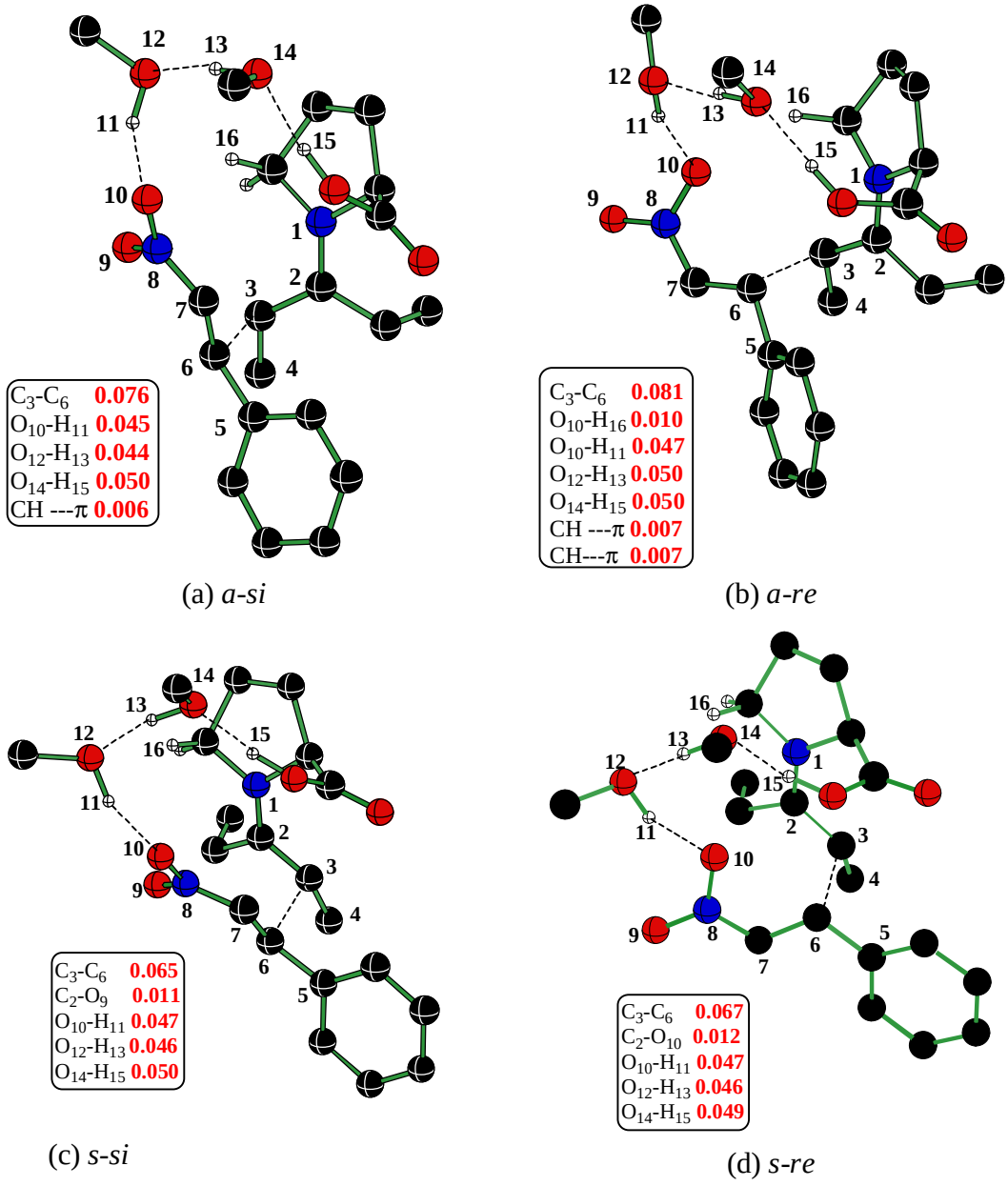


Figure S13. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States of Solvent-Assisted pathway (**C_2** model) for Four Stereochemical Modes of Addition of Enamines Derived from Proline and 3-Pentanone (**2**) to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

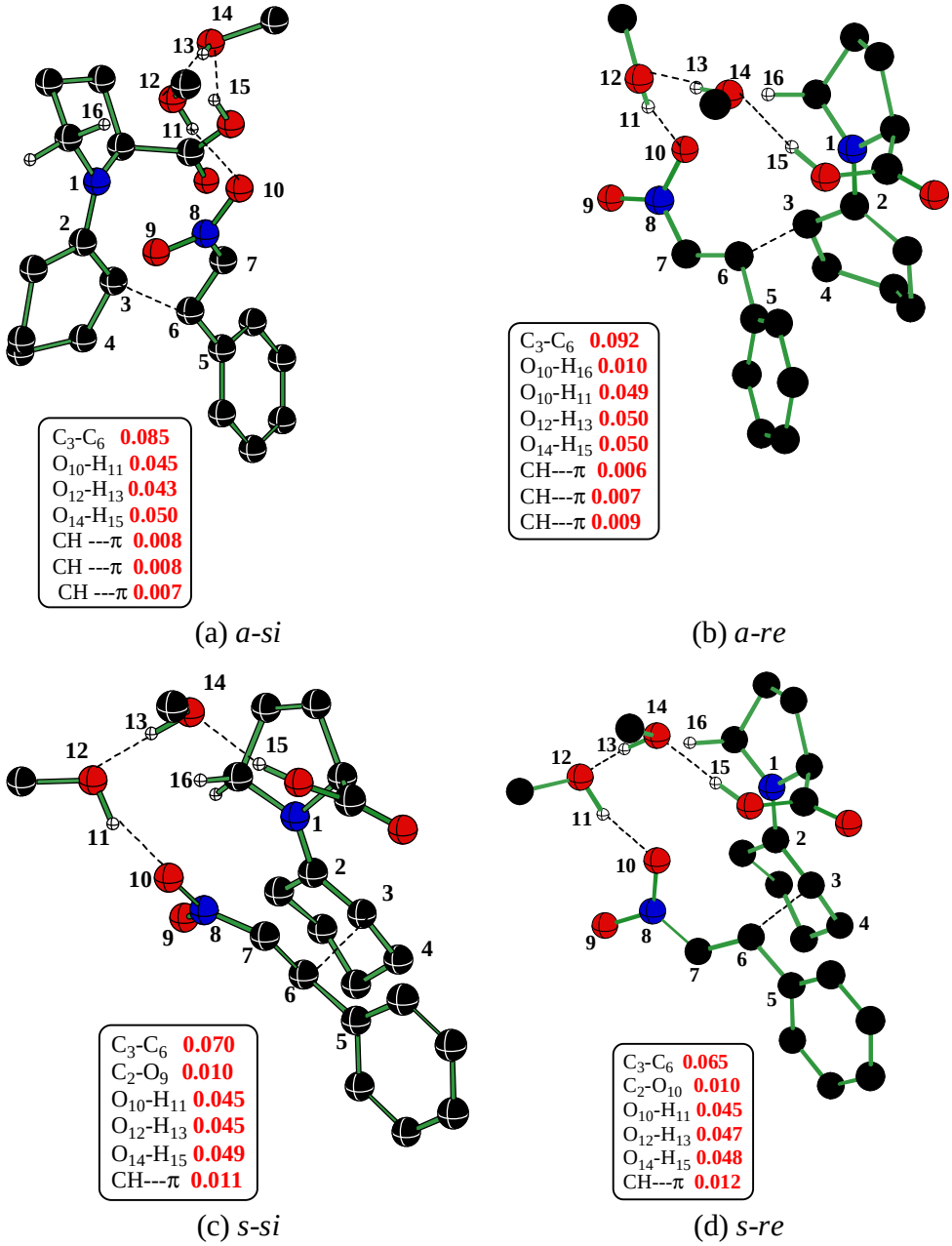


Figure S14. Summary of Electron Densities at the Bond Critical Points Obtained Using the Atoms in Molecule (AIM) Analyses on Transition States of Solvent-Assisted pathway (**C_2** model) for Four Stereochemical Modes of Addition of Enamines Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Performed Using the Wave Functions Generated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory

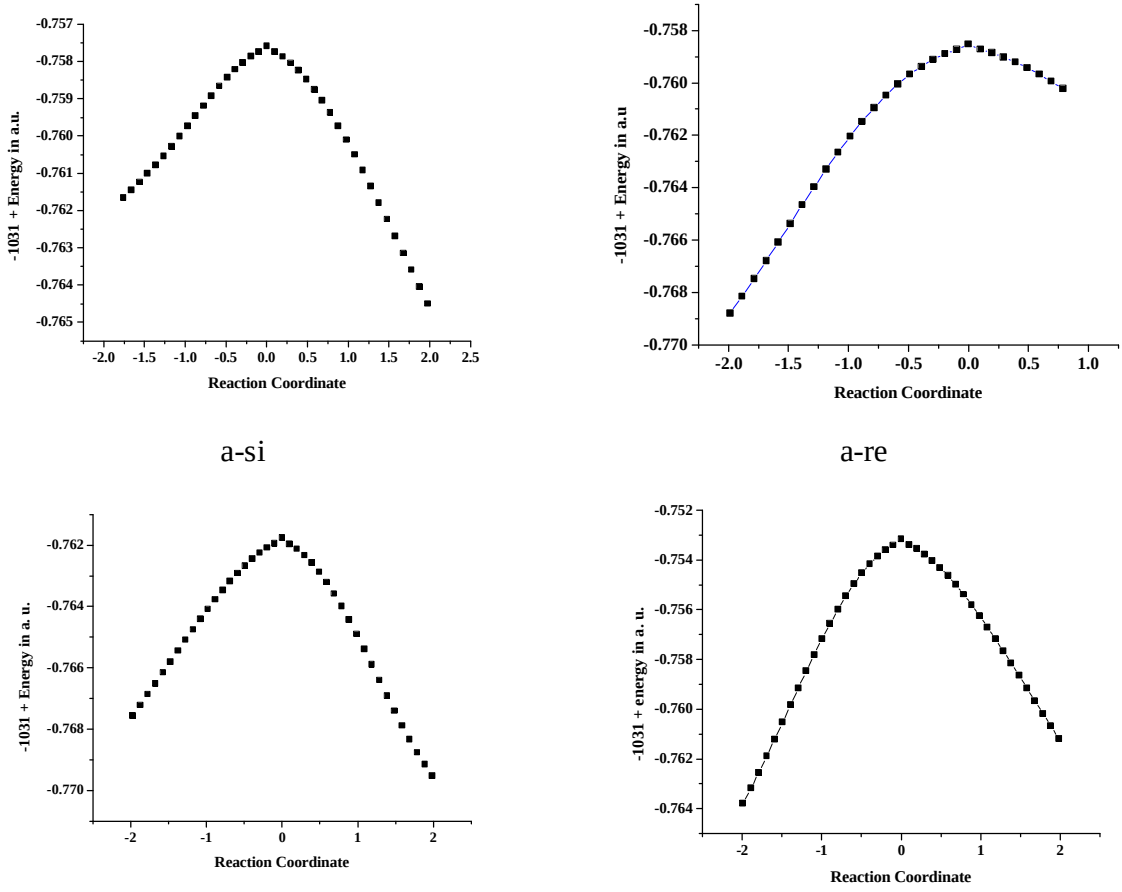
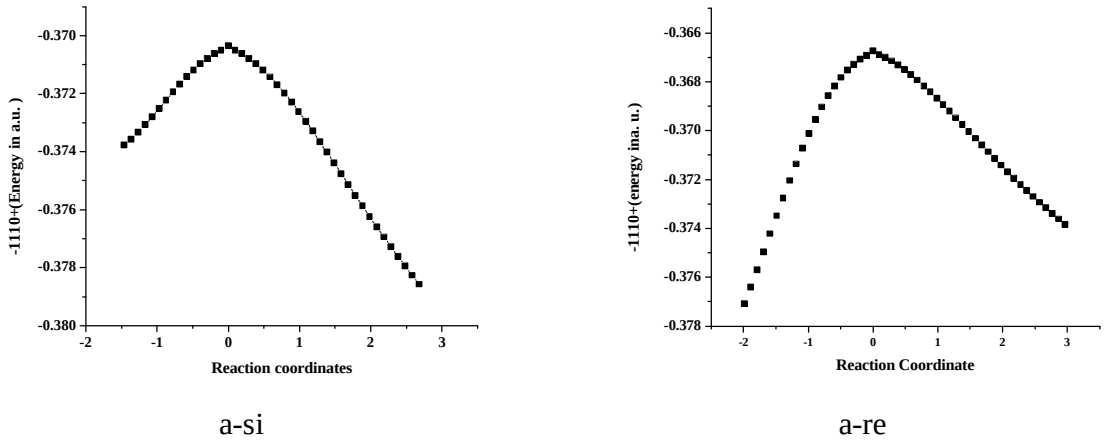
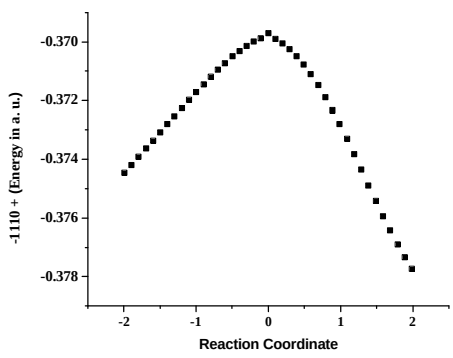


Figure S15. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Unassisted Pathway for the proline catalyzed Michael additon of Propanal (**1**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.





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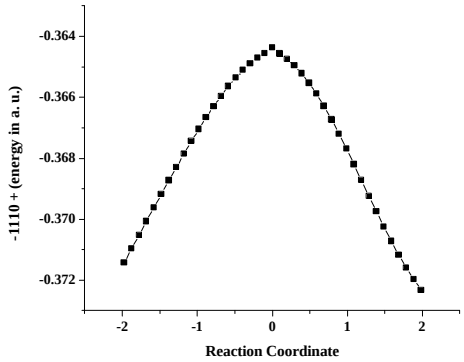

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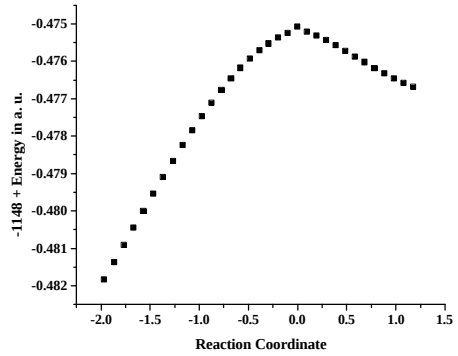
Figure S16. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Unassisted pathway for the proline catalyzed Michael additon of 3-Pentanone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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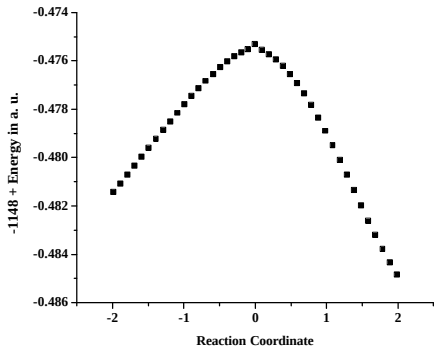

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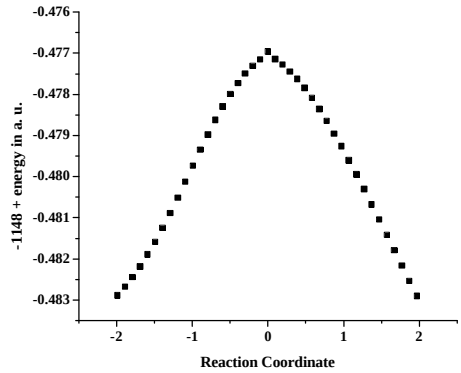

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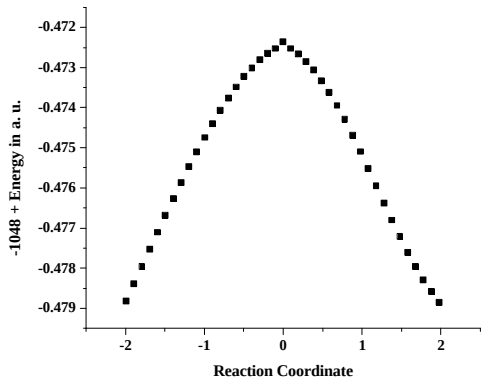

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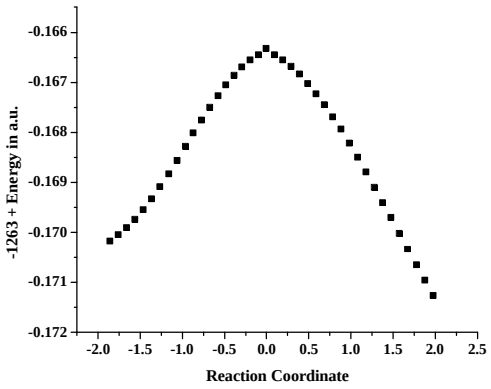
Figure S17. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Unassisted Pathway for the proline catalyzed Michael additon of Cyclohexanone (**3**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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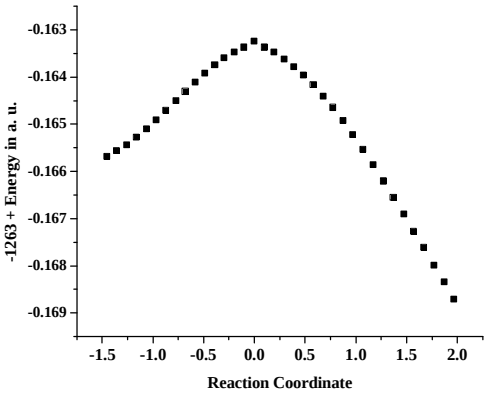

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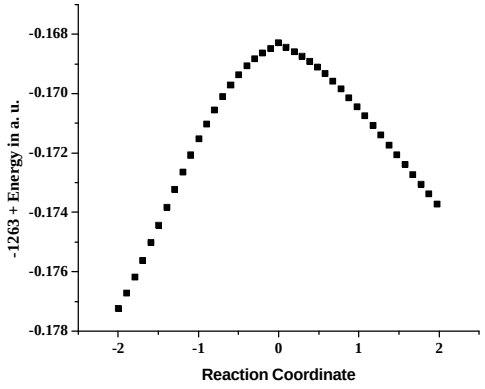

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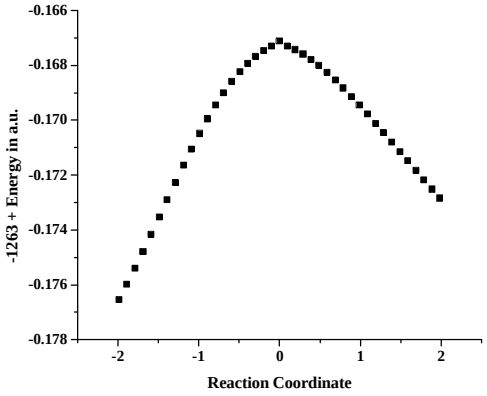

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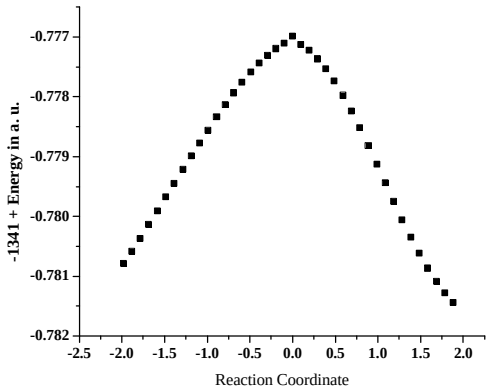
Figure S18. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway-$\mathbf{C_2}$ for the proline catalyzed Michael additon of Propanal (**1**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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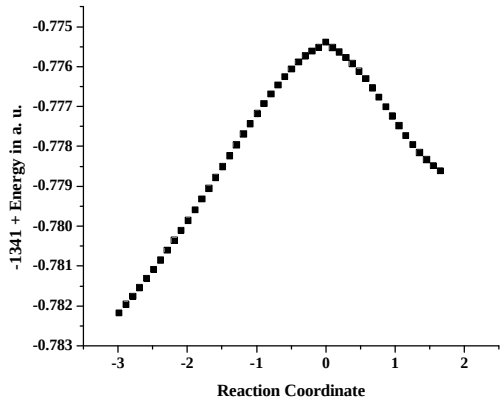

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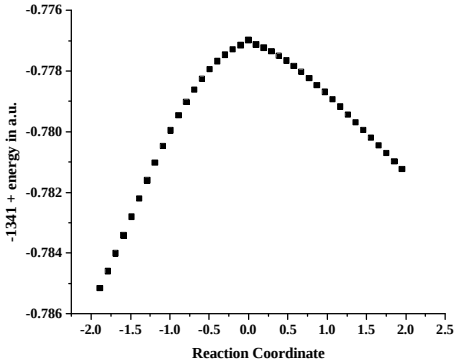

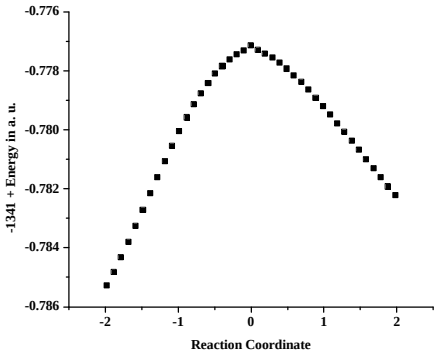

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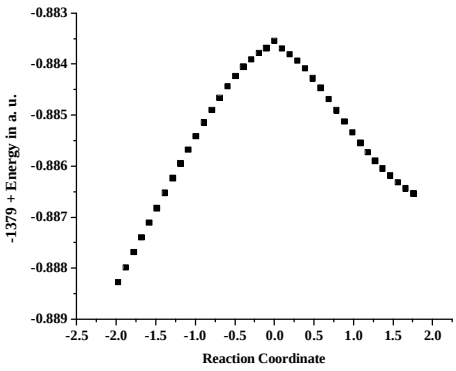
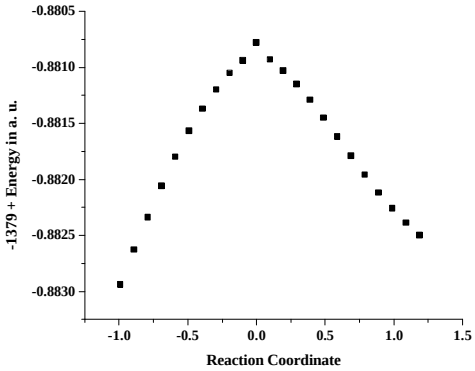
Figure S19. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway ($\mathbf{C_2}$ model) for the proline catalyzed Michael additon of 3-Pentanone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.





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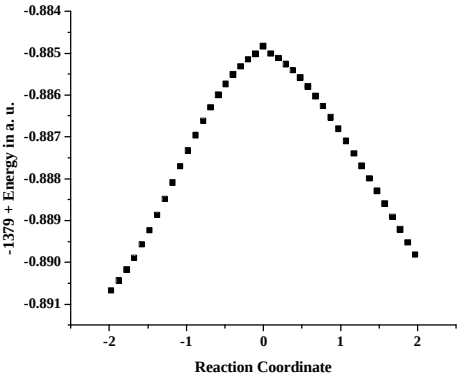
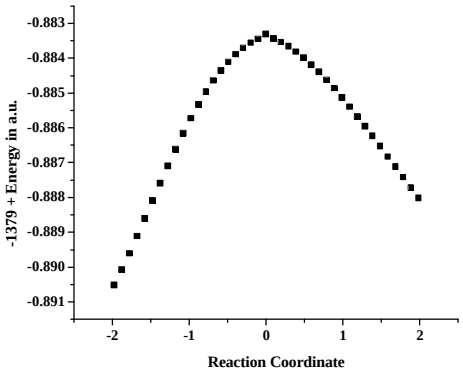
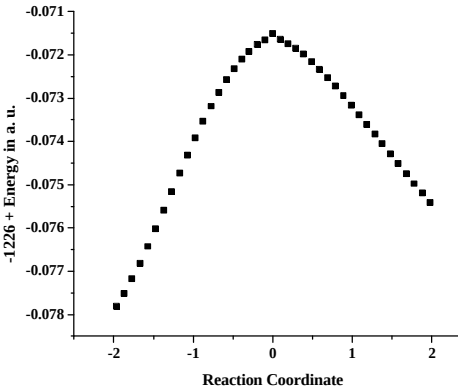




s-si s-re

Figure S20. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway ($\mathbf{C_2}$ model) for the proline catalyzed Michael additon of Cyclohexanone (**3**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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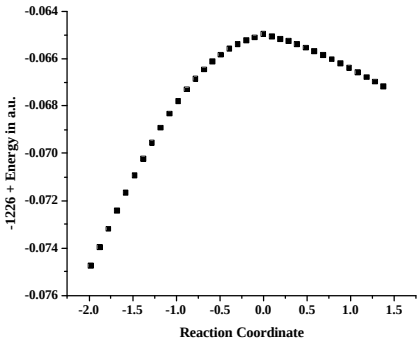

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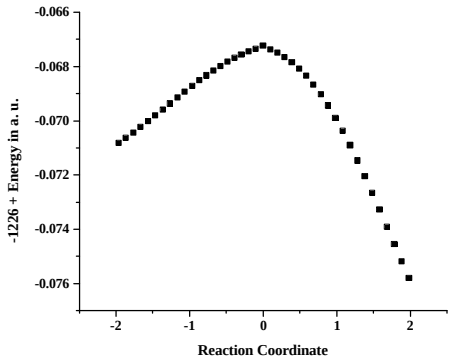

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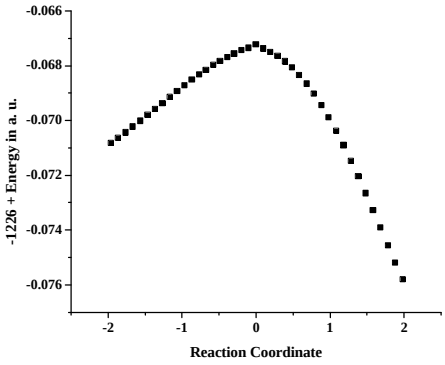
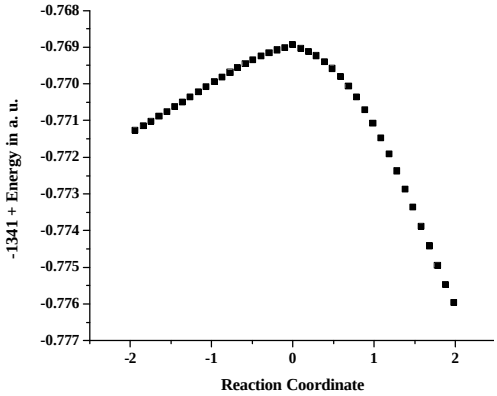


s-re

Figure S21. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway ($\mathbf{L_1}$ model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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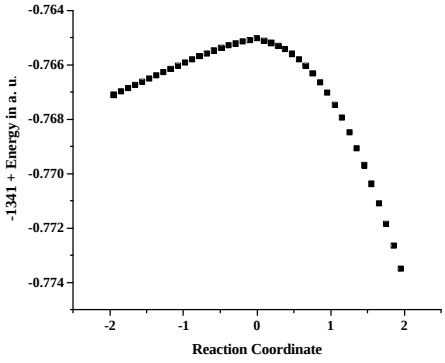

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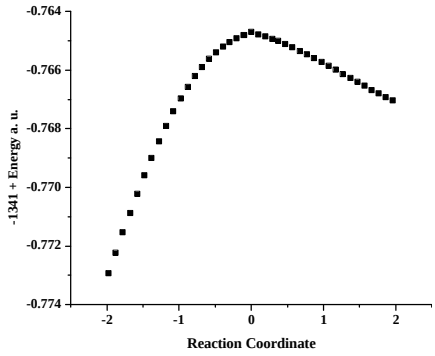

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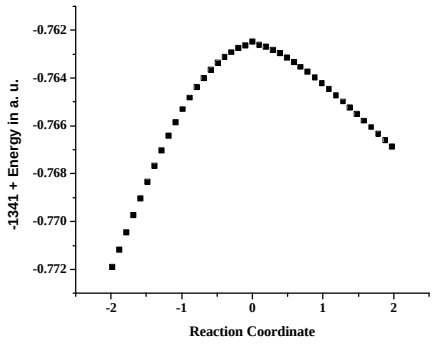
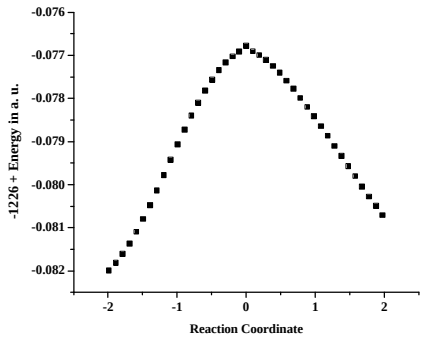


s-re

Figure S22. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway (**L_2** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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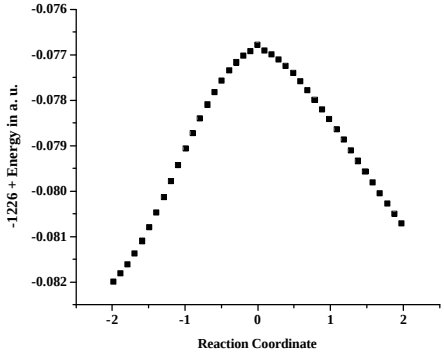

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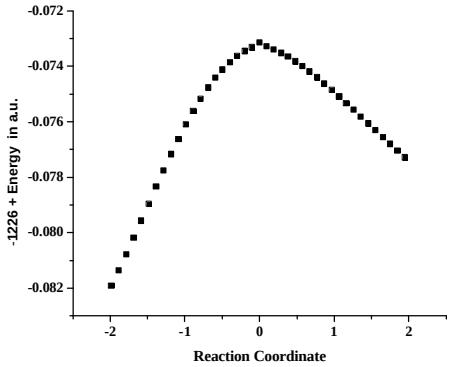

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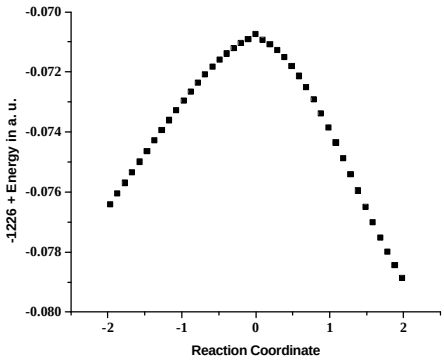
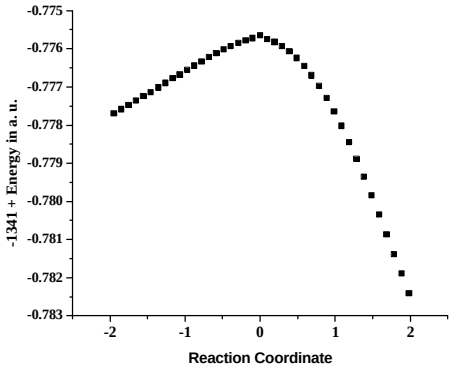


s-re

Figure S23. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway (**C_1** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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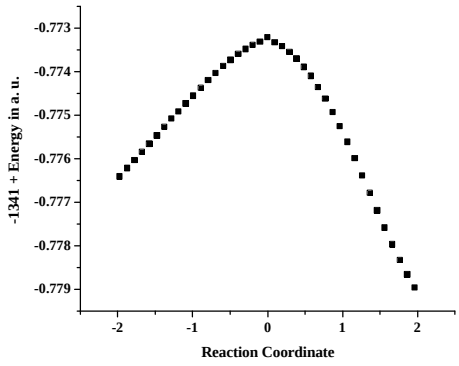

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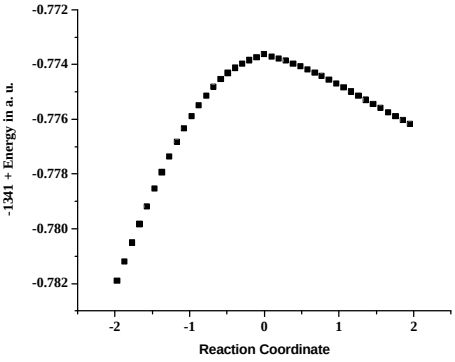

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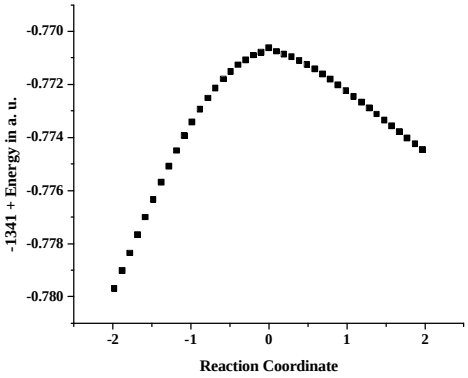
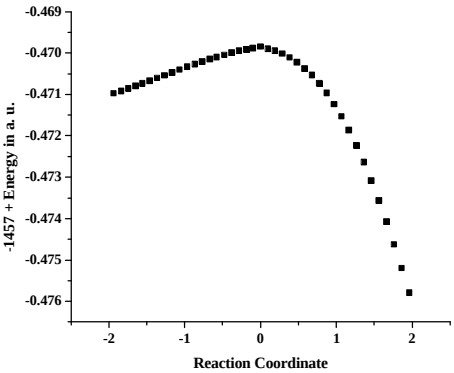


s-re

Figure S24. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway (**L_1C_1** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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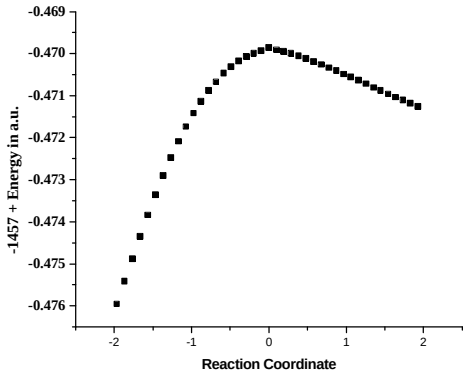
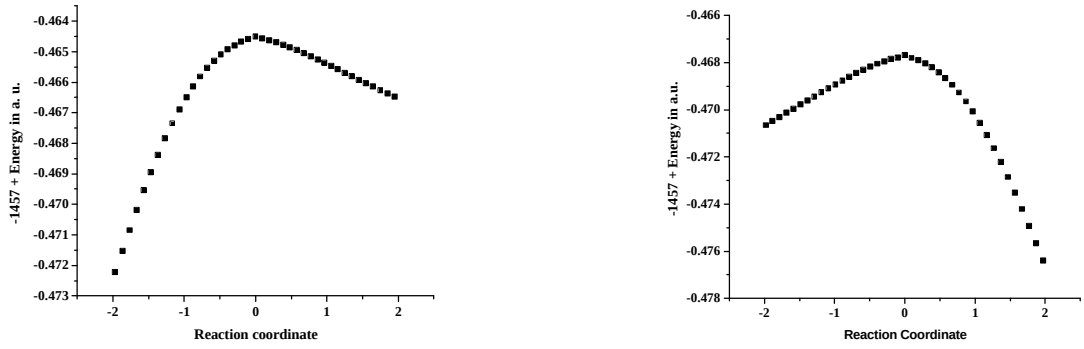
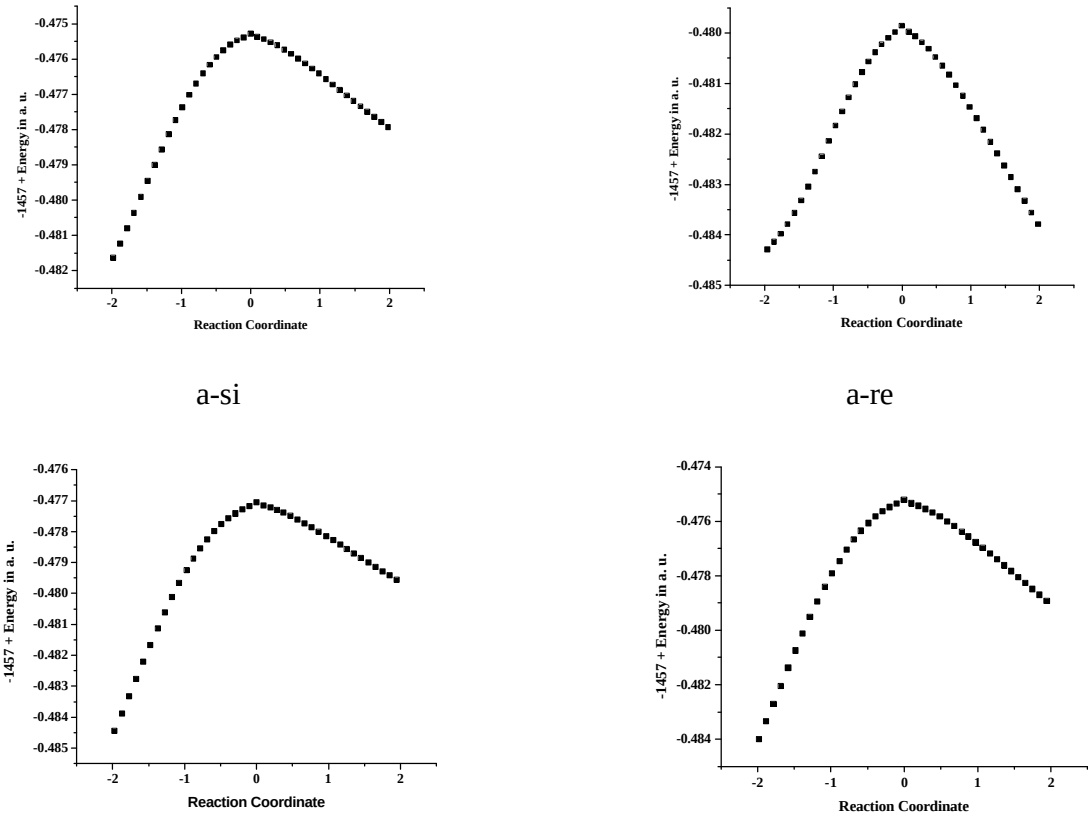


a-re



s-si s-re

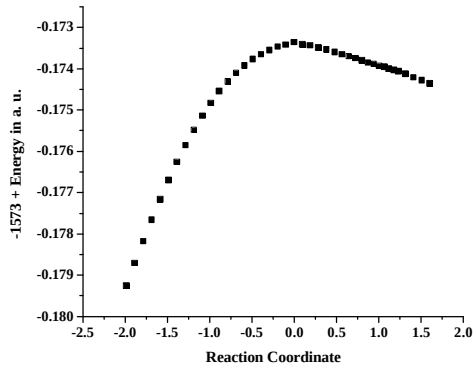
Figure S25. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway (**L_2C_1** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



a-si a-re

s-si s-re

Figure S26. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway (**L_1C_2** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.



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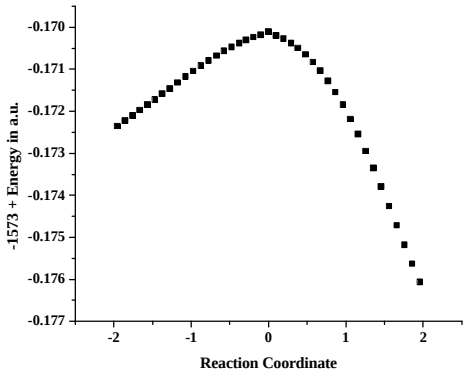

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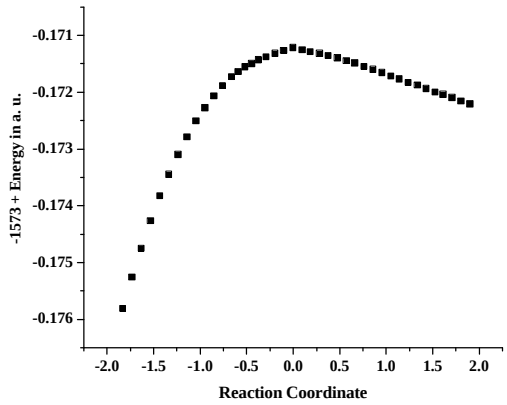

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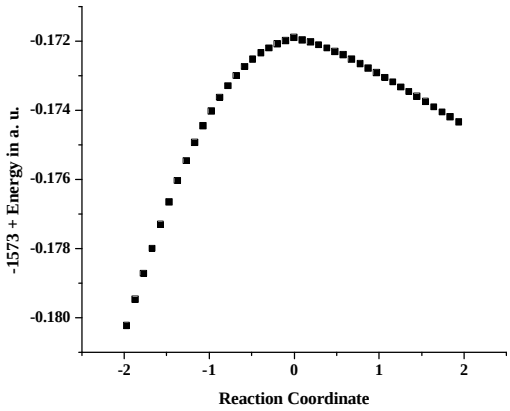
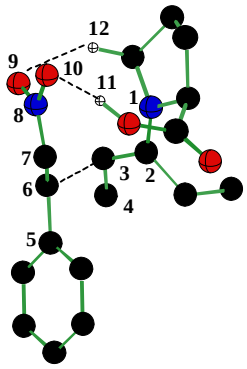


s-re

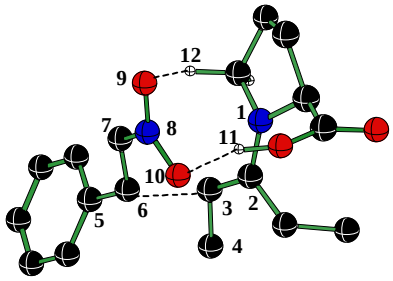
Figure S27. Intrinsic Reaction Coordinate (IRC) Plots for Transition States in the Solvent-assisted Pathway(**L_2C_2** model) for the proline catalyzed Michael additon of 3-Penatnone (**2**) to Nitrostyrene Generated at the mPW1PW91/6-31G* Level of Theory.

Table S1. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *a-si* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene in the Unassisted Pathway Computed at the mPW1PW91 Level of Theory in Combination with Different Basis Sets



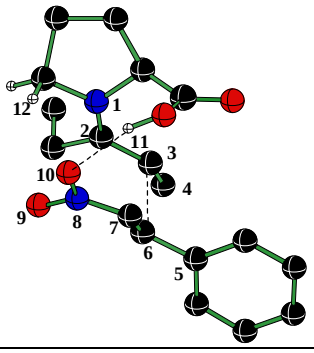
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	3.442	3.431	3.492	3.478	3.461
C_2-O_9	3.750	3.742	3.804	3.799	3.763
C_3-C_6	2.003	2.025	2.033	2.055	2.065
O_9-H_{12}	2.111	2.114	2.157	2.143	2.181
O_{10}-H_{11}	1.609	1.544	1.625	1.555	1.659
C_4-C_3-C_6-C_5	41.4	40.7	40.6	38.6	40.5

Table S2. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *a-re* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Unassisted Pathway Computed at the mPW1PW91 Level of Theory in Combination with Different Basis Sets



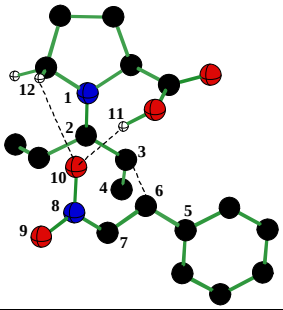
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_{10}	3.073	3.038	3.076	3.074	3.044
C_2-O_{10}	2.912	2.930	2.978	2.987	2.960
C_3-C_6	2.155	2.164	2.164	2.175	2.168
O_9-H_{12}	3.143	3.122	3.152	3.126	3.179
O_{10}-H_{11}	1.611	1.566	1.603	1.556	1.621
C_4-C_3-C_6-C_5	- 56.4	- 55.5	- 55.5	- 55.0	- 56.4

Table S3. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *s-si* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Unassisted Pathway Computed at the mPW1PW91 Level of Theory in Combination with Different Basis Sets



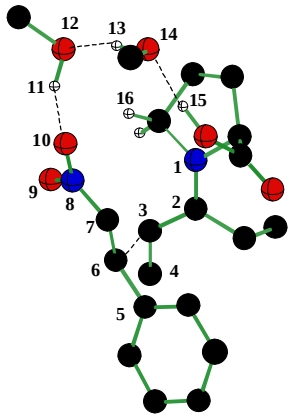
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	2.959	2.965	2.992	2.997	2.954
C_2-O_9	2.840	2.853	2.866	2.881	2.841
C_3-C_6	2.106	2.119	2.117	2.132	2.128
O_{10}-H_{12}	2.298	2.296	2.364	2.357	2.354
O_{10}-H_{11}	1.658	1.604	1.673	1.614	1.706
C_4-C_3-C_6-C_5	54.8	54.7	55.3	55.3	55.7

Table S4. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *s-re* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Unassisted Pathway Computed at the mPW1PW91 Level of Theory in Combination with Different Basis Sets



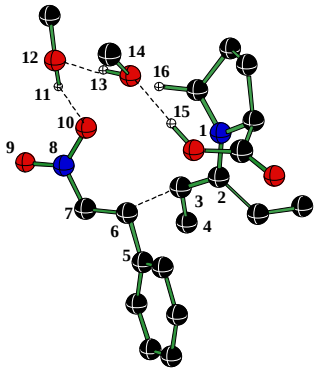
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	2.898	2.894	2.936	2.933	2.922
C_2-O_9	2.712	2.723	2.762	2.768	2.750
C_3-C_6	2.053	2.062	2.077	2.084	2.092
O_{10}-H_{12}	2.689	2.656	2.758	2.742	2.737
O_{10}-H_{11}	1.716	1.669	1.725	1.687	1.755
C_4-C_3-C_6-C_5	51.0	50.5	50.1	50.0	51.1

Table S5. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *a-si* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91 Level of Theory in Combination with Different Basis Sets



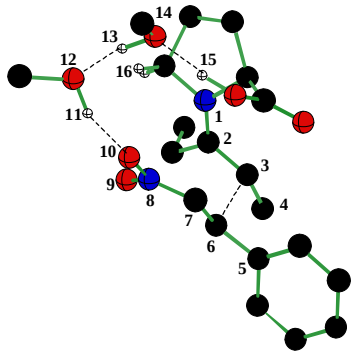
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	3.794	3.782	3.934	3.895	3.919
C_2-O_9	3.910	3.903	3.998	3.977	3.973
C_3-C_6	2.055	2.061	2.089	2.094	2.111
O_9-H_{16}	2.653	2.643	2.838	2.806	2.848
O_{10}-H_{11}	1.703	1.673	1.706	1.670	1.730
O_{12}-H_{13}	1.704	1.679	1.709	1.671	1.728
O_{14}-H_{15}	1.661	1.625	1.685	1.642	1.699
C_4-C_3-C_6-C_5	55.5	55.1	58.7	57.4	59.3

Table S6. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *a-re* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91 Level of Theory in Combination of Different Basis Sets.



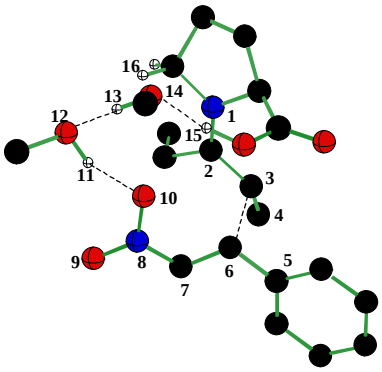
	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	3.804	3.808	3.888	3.881	3.868
C_2-O_9	3.906	3.903	3.962	3.965	3.940
C_3-C_6	2.024	2.038	2.061	2.072	2.075
O_9-H_{16}	2.424	2.432	2.584	2.532	2.549
O_{10}-H_{11}	1.669	1.636	1.694	1.663	1.708
O_{12}-H_{13}	1.661	1.625	1.681	1.644	1.693
O_{14}-H_{15}	1.660	1.616	1.684	1.635	1.694
C_4-C_3-C_6-C_5	58.4	59.1	60.1	60.0	60.5

Table S7. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *s-si* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91 Level of Theory in Combination of Different Basis Sets.

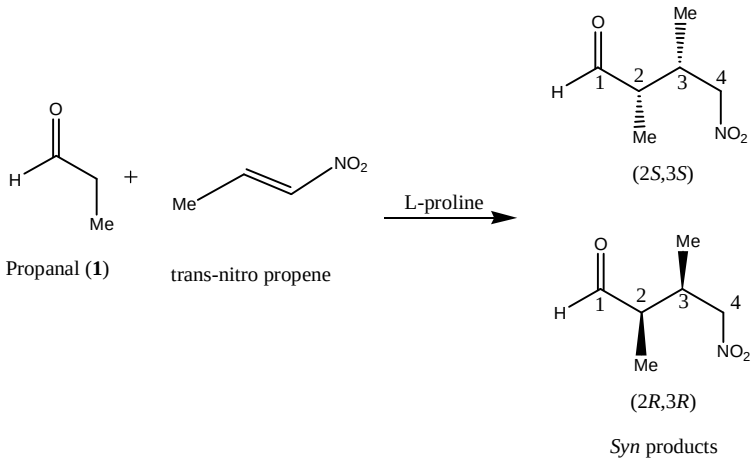


	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	3.119	3.120	3.170	3.175	3.104
C_2-O_9	2.887	2.891	2.921	2.928	2.896
C_3-C_6	2.135	2.138	2.146	2.151	2.154
O_9-H_{16}	3.036	3.033	3.134	3.140	3.038
O_{10}-H_{11}	1.693	1.657	1.698	1.661	1.717
O_{12}-H_{13}	1.692	1.666	1.693	1.661	1.713
O_{14}-H_{15}	1.662	1.630	1.688	1.644	1.707
C_4-C_3-C_6-C_5	56.1	56.1	56.9	57.0	56.8

Table S8. Selected Bond Distances (Å) and Dihedral Angles (in degrees) for *s-re* Mode of Addition of Proline Enamines Derived from 3-Pentanone (**2**) to Nitrostyrene using Solvent-Assisted Pathway (**C_2** model) Computed at the mPW1PW91 Level of Theory in Combination of Different Basis Sets.



	6-31G*	6-31G**	6-31+G*	6-31+G**	mPW1K/6-31+G*
N_1-O_9	3.116	3.111	3.199	3.195	3.166
C_2-O_{10}	2.829	2.829	2.902	2.904	2.884
C_3-C_6	2.121	2.125	2.130	2.134	2.147
O_{10}-H_{16}	3.111	3.117	3.193	3.173	3.132
O_{10}-H_{11}	1.680	1.644	1.700	1.671	1.761
O_{12}-H_{13}	1.694	1.663	1.698	1.664	1.711
O_{14}-H_{15}	1.673	1.635	1.694	1.644	1.708
C_4-C_3-C_6-C_5	58.0	58.1	59.3	59.2	59.5



Propanal (**1**) trans-nitro propene

Syn products

Scheme S1. Michael addition of propanal (**1**) to nitropropene (Model electrophile).

Table S9. Activation Parameter [a] (in kcal/mol) at the various levels of theory for the Michael Reaction between Proline Enamines Derived propanal (**1**) with trans-nitro propene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using Transition states in the Unassisted Pathway

Model		Mode of approach				%de	%ee [c]
		a-si	*a-re*	*s-si*	*s-re*		
		$\Delta H^{\ddagger}$ (gas-phase)					
	M1	11.8(2.4)	10.5(1.1)	9.4(0.0)	13.8(4.4)	*syn* (97)	2R,3R (73)
	M2	13.6(1.8)	12.1(0.3)	11.8(0.0)	15.8(4.0)	*syn* (90)	2R,3R (24)
	M3	15.3(1.7)	13.6(0.0)	13.8(0.2)	16.2(2.4)	*syn* (89)	2S,3S (17)
	M4	14.1(2.0)	12.3(0.2)	12.1(0.0)	16.4(4.3)	*syn* (93)	2R,3R (17)
ua	*M5*	16.9(2.1)	14.8(0.1)	14.7(0.0)	18.2(3.5)	*syn* (94)	2R,3R (8)
	M6	19.1(2.3)	16.8(0.0)	17.4(0.6)	19.1(2.3)	*syn* (97)	2S,3S (47)
	M7	15.8(3.0)	13.6(0.8)	12.8(0.0)	17.9(5.1)	*syn* (99)	2R,3R (59)
	M8[b]	17.8(2.9)	15.8(0.9)	14.9(0.0)	19.3(4.4)	*syn* (99)	2R,3R (59)
		$\Delta G^{\ddagger}$ (gas-phase)					
	M1	27.4(1.9)	25.5(0.0)	25.5(0.0)	28.6(3.1)	*syn* (92)	Nil
	M2	29.3(2.2)	27.1(0.0)	27.7(0.6)	30.4(3.3)	*syn* (95)	2S,3S (47)
	M3	30.9(2.4)	28.5(0.0)	29.6(1.1)	30.8(2.3)	*syn* (97)	2S,3S (73)
	M4	30.1(2.8)	27.3(0.0)	28.1(0.8)	31.1(3.8)	*syn* (98)	2S,3S (59)
ua	*M5*	32.9(3.1)	29.8(0.0)	30.8(1.0)	33.2(3.4)	*syn* (99)	2S,3S (67)
	M6	35.1(3.3)	31.8(0.0)	33.6(1.8)	34.2(2.4)	*syn* (99)	2S,3S (91)
	M7	32.5(3.1)	29.4(0.0)	29.7(0.5)	33.4(4.0)	*syn* (99)	2S,3S (40)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states.[b] The activation energy ($\Delta E^{\ddagger}$) computed at the B2PLYP/6-31G*//mPW1PW91/6-31G* [c] See Scheme S1 for the numbering of stereocenters.
M1 : mPW1PW91/6-31G*//6-31G*
M2 : mPW1PW91/6-311G**//6-31G*
M3 : mPW1PW91/6-311+G**//6-31G*
M4 : B3LYP/6-31G*//6-31G*
M5 : B3LYP/6-311G**//6-31G*
M6 : B3LYP/6-311+G**//6-31G*
M7 : CBS-4M
M8 : B2PLYP/6-31G*//mPW1PW91/6-31G*

Table S10. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamines Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States in the Unassisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
			$\Delta H^{\ddagger}$ (gas-phase)			
M1	9.2(0.9)	11.2(2.9)	8.3(0.0)	11.8(3.6)	*Syn* (64)	4R,5S (98)
M2	10.8(0.7)	12.6(2.5)	10.1(0.0)	12.7(2.6)	*Syn* (53)	4R,5S (97)
M3	11.5(0.0)	13.2(2.7)	11.8(0.2)	13.1(2.6)	*Anti* (16)	4S,5S (97)
M4	10.8(0.6)	12.5(2.5)	10.2(0.0)	12.8(2.6)	*Syn* (46)	4R,5S (97)
M5	8.4(0.8)	10.8(3.2)	7.6(0.0)	11.4(3.8)	*Syn* (58)	4R,5S (99)
M6	10.6(0.7)	12.4(2.5)	9.9(0.0)	12.5(2.6)	*Syn* (53)	4R,5S (97)
M7	10.3(0.0)	12.3(2.0)	11.5(1.2)	13.1(2.8)	*Syn* (76)	4R,5S (98)
M8	9.9(0.0)	11.7(1.8)	9.9(0.0)	12.6(2.7)	*Nil*	*Nil*
M9	12.3(0.0)	13.9(1.6)	12.6(0.3)	13.8(1.5)	*Anti*(24)	4S,5S (85)
M10	9.7(0.9)	11.7(2.9)	8.8(0.0)	12.1(3.3)	*Syn* (64)	4R,5S (98)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters.
M1 : mPW1PW91/6-31G*//6-31G*
M2 : mPW1PW91/6-311G**//6-31G*
M3 : mPW1PW91/6-31+G*//6-31+G*
M4 : mPW1PW91/6-311G**//6-31+G*
M5 : mPW1PW91/6-31G**//6-31G**
M6 : mPW1PW91/6-311G**//6-31G**
M7 : mPW1PW91/6-31+G**//6-31+G**
M8 : mPW1PW91/6-311G**//6-31+G**
M9 : mPW1PW91/6-311+G**//6-31G*
M10 : mPW1PW91/cc-PVDZ//6-31G*

Table S11. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamines Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States in the Unassisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
			$\Delta G^{\ddagger}$ (gas-phase)			
M1	26.1(0.2)	26.7(0.8)	25.9(0.0)	28.3(2.4)	*Syn* (64)	4R,5S (58)
M2	27.7(0.0)	28.1(0.4)	27.7(0.0)	29.2(1.5)	*Nil*	*Nil*
M3	28.1(0.0)	28.5(0.4)	29.0(0.9)	29.4(1.3)	*Anti* (16)	4S,5S (80)
M4	27.3(0.0)	27.8(0.5)	27.3(0.0)	29.1(1.8)	*Nil*	*Nil*
M5	25.4(0.2)	26.4(1.2)	25.2(0.0)	27.9(2.7)	*Syn* (16)	4R,5S (76)
M6	27.6(0.1)	27.9(0.4)	27.5(0.0)	29.1(1.6)	*Syn* (08)	4R,5S (32)
M7	27.2(0.0)	27.9(0.7)	28.7(1.6)	29.3(2.1)	*Anti* (53)	4S,5S (94)
M8	26.7(0.0)	27.3(0.6)	27.1(0.3)	28.8(2.1)	*Anti* (24)	4S,5S (94)
M9	29.2(0.0)	29.4(0.2)	30.2(1.0)	30.4(1.2)	*Anti* (16)	4S,5S (77)
M10	26.7(0.3)	27.2(0.8)	26.4(0.0)	28.7(2.3)	*Syn* (24)	4R,5S (59)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters.
M1 : mPW1PW91/6-31G*//6-31G*
M2 : mPW1PW91/6-311G**//6-31G*
M3 : mPW1PW91/6-31+G*//6-31+G*
M4 : mPW1PW91/6-311G**//6-31+G*
M5 : mPW1PW91/6-31G**//6-31G**
M6 : mPW1PW91/6-311G**//6-31G**
M7 : mPW1PW91/6-31+G**//6-31+G**
M8 : mPW1PW91/6-311G**//6-31+G**
M9 : mPW1PW91/6-311+G**//6-31G*
M10 : mPW1PW91/cc-PVDZ//6-31G*

Table S12. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamines Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States in the Unassisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
	$\Delta E^{\ddagger}$ (solvent-phase)					
M1	7.9(0.0)	9.4(1.5)	10.3(2.4)	10.6(2.7)	*Anti* (85)	4S,5S (97)
M2	9.2(0.0)	10.4(1.2)	12.0(2.8)	11.4(2.2)	*Anti* (76)	4S,5S (95)
M3	9.7(0.0)	10.5(0.7)	13.4(3.7)	11.2(1.5)	*Anti* (53)	4S,5S (99)
M4	9.1(0.0)	9.9(0.8)	11.7(2.6)	11.3(2.2)	*Anti* (59)	4S,5S (95)
M5	7.6(0.0)	9.0(1.4)	9.8(2.2)	10.5(2.9)	*Anti* (82)	4S,5S (76)
M6	9.5(0.0)	10.3(0.8)	12.0(2.5)	11.5(2.0)	*Anti* (59)	4S,5S (93)
M7	9.5(0.0)	10.6(1.1)	13.3(3.8)	11.3(1.8)	*Anti* (72)	4S,5S (90)
M8	9.1(0.0)	10.2(1.1)	11.7(2.6)	11.3(2.2)	*Anti* (72)	4S,5S (95)
M9	10.5(0.0)	11.6(1.1)	14.5(4.0)	12.1(1.6)	*Anti* (72)	4S,5S (87)
M10	8.2(0.0)	9.7(1.5)	10.5(2.3)	10.9(2.7)	*Anti* (85)	4S,5S (97)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition state. [b] See Scheme 2 for numbering of the stereocenters.
M1 : PCM/mPW1PW91/6-31G*//6-31G*
M2 : PCM/mPW1PW91/6-311G**//6-31G*
M3 : PCM/mPW1PW91/6-31+G*//6-31+G*
M4 : PCM/mPW1PW91/6-311G**//6-31+G*
M5 : PCM/mPW1PW91/6-31G**//6-31G**
M6 : PCM/mPW1PW91/6-311G**//6-31G**
M7 : PCM/mPW1PW91/6-31+G**//6-31+G**
M8 : PCM/mPW1PW91/6-311G**//6-31+G**
M9 : PCM/mPW1PW91/6-311+G**//6-31G*
M10 : PCM/mPW1PW91/cc-PVDZ//6-31G*

Table S13. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamines Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States Model-$\mathbf{C_2}$ in the Solvent-assisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
			$\Delta H^{\ddagger}$ (gas-phase)			
M1	- 13.5(0.8)	- 12.7(2.5)	- 15.2(0.0)	- 15.0(0.2)	*Syn* (16)	4R,5S (97)
M2	- 11.5(1.2)	- 11.2(1.5)	- 12.8(0.0)	- 12.7(0.1)	*Syn* (08)	4R,5S (85)
M3[c]	- 6.0(1.2)	- 7.2(0.3)	- 6.7(0.8)	- 7.5(0.0)	*Anti* (24)	4R,5R (76)
M4[c]	- 11.1(1.4)	- 11.6(0.9)	- 12.5(0.0)	- 12.3(0.2)	*Syn* (16)	4R,5S (64)
M5	- 14.0(1.6)	- 13.2(2.4)	- 15.6(0.0)	- 15.4(0.2)	*Syn* (16)	4R,5S (96)
M6	- 11.8(0.3)	- 11.5(0.6)	- 12.1(0.0)	- 12.0(0.1)	*Syn* (08)	4R,5S (46)
M7[c]	- 6.2(1.1)	- 6.7(0.6)	- 6.8(0.5)	- 7.3(0.0)	*Anti* (40)	4R,5R (73)
M8[c]	- 11.9(1.3)	- 11.3(1.9)	- 13.2(0.0)	-12.9(0.3)	*Syn* (24)	4R,5S (92)
M9	- 4.7(1.1)	- 5.6(0.2)	- 5.1(0.7)	- 5.8(0.0)	*Anti* (16)	4R,5R (72)
M10	–14.5(1.9)	–13.7(2.7)	–16.4(0.0)	–15.9(0.5)	*Syn* (39)	4R,5S (97)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters. [c] Thermal corrections to enthalpy are taken from the frequency calculation at the mPW1PW91/6-31G*.
M1 : mPW1PW91/6-31G*//6-31G*
M2 : mPW1PW91/6-311G**//6-31G*
M3 : mPW1PW91/6-31+G*//6-31+G*
M4 : mPW1PW91/6-311G**//6-31+G*
M5 : mPW1PW91/6-31G**//6-31G**
M6 : mPW1PW91/6-311G**//6-31G**
M7 : mPW1PW91/6-31+G**//6-31+G**
M8 : mPW1PW91/6-311G**//6-31+G**
M9 : mPW1PW91/6-311+G**//6-31G*
M10 : mPW1PW91/cc-pVDZ//6-31G*

Table S14. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamine Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States Model-$\mathbf{C_2}$ in the Solvent-assisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
			$\Delta G^{\ddagger}$ (gas-phase)			
M1	23.4(1.2)	22.9(0.7)	22.6(0.4)	22.2(0.0)	*Anti* (32)	4R,5R (77)
M2	25.4(1.0)	24.5(0.1)	25.0(0.5)	24.4(0.0)	*Anti* (08)	4R,5R(68)
M3[c]	30.4(1.0)	29.4(0.0)	30.7(1.3)	29.7(0.3)	*Syn* (24)	4S,5R (79)
M4[c]	25.2(0.2)	25.0(0.0)	25.0(0.0)	24.9(0.1)	*Nil*	*Nil*
M5	22.8(1.0)	22.6(0.8)	22.2(0.4)	21.8(0.0)	*Anti* (32)	4R,5R (67)
M6	24.9(0.5)	24.3(0.0)	25.1(0.8)	24.6(0.3)	*Syn* (24)	4S,5R (59)
M7[c]	29.5(1.6)	27.9(0.0)	30.1(2.1)	29.5(1.6)	*Syn* (87)	4S,5R (94)
M8[c]	23.8(0.6)	23.2(0.0)	23.7(0.5)	23.8(0.6)	*Syn* (46)	4S,5R (40)
M9	32.2(2.2)	30.0(0.0)	32.7(2.7)	31.4(1.4)	*Syn* (83)	4S,5R (98)
M10	22.4(1.2)	22.0(0.8)	21.4(0.2)	21.2(0.0)	*Anti* (16)	4R,5R (76)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters. [c] Thermal corrections to free energy are taken from the frequency calculation at the mPW1PW91/6-31G*.
M1 : mPW1PW91/6-31G*//6-31G*
M2 : mPW1PW91/6-311G**//6-31G*
M3 : mPW1PW91/6-31+G*//6-31+G*
M4 : mPW1PW91/6-311G**//6-31+G*
M5 : mPW1PW91/6-31G**//6-31G**
M6 : mPW1PW91/6-311G**//6-31G**
M7 : mPW1PW91/6-31+G**//6-31+G**
M8 : mPW1PW91/6-311G**//6-31+G**
M9 : mPW1PW91/6-311+G**//6-31G*
M10: mPW1PW91/cc-PVDZ//6-31G*

Table S15. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1PW91 level of theory for the Michael Reaction between Proline Enamines Derived from Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States Model-$\mathbf{C_2}$ in the Solvent-assisted pathway

	Mode of approach				%de	%ee [b]
	a-si	*a-re*	*s-si*	*s-re*		
	$\Delta E^{\ddagger}$ (Solvent-phase)					
M1	- 4.7(1.2)	- 5.9(0.0)	- 5.0(0.9)	- 5.4(0.4)	*Syn* (32)	4S,5R (64)
M2	- 2.6(1.6)	- 4.2(0.0)	- 2.4(1.8)	- 2.9(1.3)	*Syn* (80)	4S,5R (90)
M3	3.9(2.1)	1.8(0.0)	5.1(3.3)	3.4(1.6)	*Syn* (87)	4S,5R (99)
M4	- 3.0(0.7)	- 3.7(0.0)	- 2.6(0.9)	- 3.2(0.5)	*Syn* (40)	4S,5R (64)
M5	- 5.1(1.1)	- 6.2(0.0)	- 5.3(0.9)	- 5.7(0.5)	*Syn* (40)	4S,5R (64)
M6	- 2.8(1.5)	- 4.3(0.0)	- 2.4(1.9)	- 3.1(1.2)	*Syn* (77)	4S,5R (92)
M7	4.2(2.5)	1.7(0.0)	5.2(3.5)	3.8(2.1)	*Syn* (94)	4S,5R (99)
M8	- 3.1(1.0)	- 4.1(0.0)	- 2.9(1.2)	- 3.4(0.7)	*Syn*(53)	4S,5R (76)
M9	5.8(3.5)	2.3(0.0)	6.9(4.6)	5.6(3.3)	*Syn* (99)	4S,5R (99)
M10	–6.9(1.0)	–7.9(0.0)	–7.6(0.3)	–7.6(0.3)	*Syn* (24)	4S,5R (24)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters.
M1 : PCM/mPW1PW91/6-31G*//6-31G*
M2 : PCM/mPW1PW91/6-311G**//6-31G*
M3 : PCM/mPW1PW91/6-31+G*//6-31+G*
M4 : PCM/mPW1PW91/6-311G**//6-31+G*
M5 : PCM/mPW1PW91/6-31G**//6-31G**
M6 : PCM/mPW1PW91/6-311G**//6-31G**
M7 : PCM/mPW1PW91/6-31+G**//6-31+G**
M8 : PCM/mPW1PW91/6-311G**//6-31+G**
M9 : PCM/mPW1PW91/6-311+G**//6-31G*
M10 PCM/mPW1PW91/cc-PVDZ//6-31G*

Table S16. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1K/6-31+G* levels of theory for the Michael Reaction between Proline Enamines Derived from 3-Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States in the various pathway

Model[a]	Mode of approach				%de	%ee [b]
	a-si	a-re	s-si	s-re		
			$\Delta H^{\ddagger}$ (gas-phase)			
UA	12.5(0.0)	14.5 (2.0)	12.5 (0.0)	13.8 (1.3)	*Nil*	Nil
C_1	0.8 (0.0)	2.4 (1.6)	3.2 (2.4)	2.9 (2.1)	*Anti (87)*	4S,5S (94)
C_2	–5.9(1.7)	–6.3 (1.3)	–6.9(0.7)	–7.6 (0.0)	*Anti (53)*	4R,5R (89)
			$\Delta G^{\ddagger}$ (gas-phase)			
UA	29.4 (0.0)	30.2 (0.8)	29.8 (0.4)	30.4(1.0)	*Anti (59)*	4S,5S (68)
C_1	27.5 (0.0)	28.8 (1.3)	29.6 (2.1)	29.5(2.0)	*Anti (80)*	4S,5S (99)
C_2	29.6(1.0)	28.6(0.0)	29.9(1.3)	29.2(0.6)	*Syn (47)*	4S,5R (80)
			$\Delta E^{\ddagger}$ (solvent-phase)[c]			
UA	11.2 (0.0)	12.4 (1.2)	14.8 (3.2)	12.4(1.2)	*Anti (77)*	4S,5S (77)
C_1	5.8 (1.0)	4.8 (0.0)	9.6 (4.8)	8.8 (4.0)	*Syn (68)*	4S,5R (99)
C_2	5.4 (2.5)	2.9 (0.0)	5.9 (3.0)	4.4 (1.5)	*Syn (85)*	4S,5R (98)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters. [c] Activation parameter obtained at the $PCM_{(MeOH)}$/mPW1K/6-31+G*//mPW1K/6-31+G*.

Table S17. The Computed Activation Parameters [a] (in kcal/mol) at the mPW1K/6-311G**//6-31+G* levels of theory for the Michael Reaction between Proline Enamines Derived from 3-Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using the Transition States in the various pathway

Model[a]	Mode of approach				%de	%ee [b]
	a-si	a-re	s-si	s-re		
			$\Delta H^{\ddagger}$ (gas-phase)			
UA	12.2(0.8)	14.2(2.0)	11.4(0.0)	13.7(2.3)	*Syn(59)*	4R,5S (93)
C1	–1.3(0.0)	0.8(2.1)	0.2(1.5)	1.1(2.4)	*Anti (85)*	4S,5S (96)
C2	–9.8(1.4)	–9.4(1.8)	–11.2(0.0)	–11.1(0.1)	*Syn (08)*	4R,5S (91)
			$\Delta G^{\ddagger}$ (gas-phase)			
UA	29.0(0.3)	29.8(1.1)	28.7(0.0)	30.4(1.3)	*Syn (24)*	4R,5S (73)
C1	25.4(0.0)	27.1(1.7)	27.1(1.7)	27.6(2.2)	*Anti (89)*	4S,5S (95)
C2	25.7(0.2)	25.5(0.0)	25.6(0.2)	25.7(0.2)	*Syn (16)*	4S,5R (16)
			$\Delta E^{\ddagger}$ (solvent-phase)[c]			
UA	10.8(0.0)	12.0(1.2)	13.6(2.8)	12.8(2.0)	*Anti (76)*	4S,5S (93)
C1	3.1(0.2)	2.9(0.0)	6.6(4.7)	6.3(4.4)	*Syn (16)*	4S,5R (99)
C2	–0.2(1.3)	–1.5(0.0)	–0.2(1.3)	–0.8(0.7)	*Syn (80)*	4S,5R (80)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] See scheme 2 for numbering of stereocenters. [c] Activation parameter obtained at the $PCM_{(MeOH)}$/mPW1K/6-311G**//mPW1K/6-31+G*.

Table S18. Computed Solute-solvent Interactions Energies (in kcal/mol) Obtained at the $PCM_{(methanol)}$/mPW1PW91/6-311G**//mPW1PW91/6-31G* (*M_1*) and $PCM_{(methanol)}$/B3LYP/6-311G**//B3LYP/6-31G* (*M2*) Level of Theory for Michael Reaction of 3-Propanal (**1**), 3-Pentanone (**2**), or Cyclohexanone (**3**) with Nitrostyrene Catalyzed by Proline Using Unassisted pathway.

		Mode of approach			
		a-si	*a-re*	*s-si*	*s-re*
1	*M_1*	21.6	22.9	20.4	24.9
	M_2	27.8	25.8	22.5	27.0
2	*M_1*	26.7	25.8	21.9	25.6
	M_2	25.3	24.7	21.6	26.1
3	*M_1*	26.7	25.0	21.8	26.1
	M_2	28.3	25.9	22.9	26.8

Table S19. Computed Solute-Solvent Interactions Energies (in kcal/mol) Obtained at the $PCM_{(methanol)}$/mPW1PW91/6-311G**//mPW1PW91/6-31G* (*M_1*) and $PCM_{(methanol)}$/B3LYP/6-311G**//B3LYP/6-31G* (*M2*) Level of Theory for Michael Reaction of 3-Propanal (**1**), 3-Pentanone (**2**), or Cyclohexanone (**3**) with Nitrostyrene Catalyzed by Proline Using Solvent-assisted Pathway (**C_2**)

		Mode of approach			
		a-si	*a-re*	*s-si*	*s-re*
1	M_1	21.1	23.6	19.9	21.0
	M_2	23.5	25.1	20.5	21.5
2	M_1	16.7	20.0	18.8	19.3
	M_2	18.8	21.8	19.0	20.2
3	M_1	20.0	23.8	19.4	20.3
	M_2	21.8	26.3	22.9	21.3

Table S20. The Enthalpies of Activation [a] (in kcal/mol) at the mPW1PW91 (*M1*) and B3LYP (*M2*) levels of theory for the Michael Reaction between Proline Enamines Derived 3-Pentanone (**2**) with Nitrostyrene Along with the Corresponding Diastereomeric and Enantiomeric Excess Obtained by Using Different Methanol-Assisted Transition State Models

Model[a]		Mode of approach				%de	%ee [d]
		a-si	*a-re*	*s-si*	*s-re*		
		$\Delta H^{\ddagger}$ (gas-phase)[b]					
UA [c]	*M1*	10.8 (0.7)	12.6 (2.5)	10.1 (0.0)	12.7 (2.6)	*Syn* (53)	4R,5S (90)
	M2	14.9 (0.7)	15.7 (1.5)	14.2 (0.0)	17.0 (2.8)	*Syn* (53)	4R,5S (90)
L_1	*M1*	0.8 (0.0)	4.3 (3.5)	2.2 (1.4)	1.3 (0.5)	*Anti* (40)	4S,5S (83)
	M2	3.9 (0.0)	6.7 (2.8)	5.4 (1.5)	4.5 (0.6)	*Anti* (46)	4S,5S (85)
L_2	*M1*	- 4.4 (0.3)	- 4.7 (0.0)	- 2.3 (2.4)	- 4.5 (0.2)	*Syn* (17)	4S,5R (96)
	M2	- 2.2 (1.1)	- 3.3 (0.0)	- 0.1 (3.2)	- 2.2 (1.1)	*Syn* (73)	4S,5R (99)
		$\Delta H^{\ddagger}$ (gas-phase)[b]					
C_1	*M1*	- 2.8 (0.0)	- 0.6 (2.2)	- 1.1 (1.7)	- 0.1 (2.7)	*Anti* (89)	4S,5S (99)
	M2	0.8 (0.0)	3.1 (2.3)	1.9 (0.8)	4.2 (3.4)	*Anti* (59)	4S,5S (99)
L_1C_1	*M1*	- 11.4(0.0)	- 10.1(1.3)	- 10.8(0.6)	- 9.3 (2.1)	*Anti* (46)	4S,5S (94)
	M2	- 9.2 (0.0)	- 7.6 (1.6)	- 8.9 (0.3)	- 6.7 (2.5)	*Anti* (25)	4S,5S(97)
L_2C_1	*M1*	- 17.5 (0.5)	- 18.0 (0.0)	- 14.6(3.4)	- 16.7 (1.3)	*Syn* (40)	4S,5R (99)
	M2	- 16.2 (0.0)	- 15.9 (0.3)	- 13.2(3.0)	- 14.9 (1.3)	*Anti* (25)	4S,5S (80)
		$\Delta H^{\ddagger}$ (gas-phase)[b]					
C_2	*M1*	- 11.5 (1.3)	- 11.2 (1.6)	- 12.8 (0.0)	- 12.7 (0.1)	*Syn* (08)	4R,5S (87)
	M2	- 8.6 (1.5)	- 8.0 (2.1)	- 10.1 (0.0)	- 8.9 (1.2)	*Syn* (77)	4R,5S (94)
L_1C_2	*M1*	- 20.5 (0.3)	- 18.9 (1.9)	- 18.3 (2.5)	- 20.8 (0.0)	*Anti* (92)	4R,5R(25)
	M2	- 16.9 (1.7)	- 16.5 (2.1)	- 16.6 (2.0)	- 18.6 (0.0)	*Anti* (93)	4R,5R (88)
L_2C_2	*M1*	- 28.4 (0.0)	- 26.0 (2.4)	- 28.2 (0.2)	- 28.0 (0.4)	*Anti* (17)	4S,5S (32)
	M2	- 27.4 (0.0)	- 24.6 (2.8)	- 27.3 (0.1)	- 26.9 (0.5)	*Anti* (08)	4S,5S (40)

[a] Activation barriers are with respect to isolated reactants; values in parentheses indicate relative barriers with respect to the lowest energy transition states. [b] Activation parameter are obtained at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and B3LYP/6-311G**//B3LYP/6-31G* levels of theory. [c] UA refers to the unassisted pathway. [d] See Scheme2 (in the text) for the numbering of stereocenters.

Table S21. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Propanal (**1**) to Nitrostyrene. The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1031.7575762 (-1032.0159641) (-1032.0506009) NImag=1(-338.80 cm^{-1})				*a-re* Et =-1031.7585311 (-1032.0173004) (-1032.0494855) NImag= 1(-345.69 cm^{-1})			
6	3.643656	-0.975784	0.356370	6	-3.147270	1.182054	-0.011362
6	2.426678	-0.287170	0.307184	6	-2.808524	-0.145779	0.281842
6	2.448615	1.092952	0.062972	6	-3.825691	-1.108190	0.280441
6	3.654378	1.759664	-0.118932	6	-5.143031	-0.753625	0.007168
6	4.859443	1.062782	-0.061158	6	-5.464552	0.569107	-0.278521
6	4.850688	-0.307525	0.179238	6	-4.461033	1.536478	-0.287036
6	1.156047	-1.025184	0.528073	6	-1.424678	-0.549787	0.606987
6	0.224773	-0.408260	1.406410	6	-0.567063	-0.709824	-1.330404
7	-0.903505	-1.044307	1.781154	6	-0.659662	0.268005	1.446242
8	-1.056815	-2.266612	1.560633	7	0.548830	-0.173880	1.896905
8	-1.850384	-0.371897	2.326716	8	1.270041	0.545535	2.603390
6	0.383375	-1.396454	-1.250996	6	0.812968	-0.704685	-1.103629
6	-0.447387	-0.271846	-1.424869	7	1.549578	0.378897	-0.889680
7	-1.695272	-0.201008	-1.007760	6	3.016432	0.411359	-0.787322
6	-2.426668	1.080150	-0.856437	6	3.228051	1.659373	0.070899
6	-3.779940	0.645824	-0.297671	6	2.211666	2.639902	-0.525147
6	-3.985395	-0.734360	-0.916690	6	1.053991	1.755476	-1.026178
6	-2.595625	-1.353155	-0.817167	6	3.795448	-0.819138	-0.300347
6	-1.624553	2.099304	-0.027585	8	3.337067	-1.574937	0.676650
8	-1.649280	2.009784	1.287285	8	4.870054	-1.021483	-0.815868
8	-1.009508	2.967197	-0.608895	8	0.909375	-1.341924	1.539912
1	-4.299189	-0.649112	-1.962575	1	2.655451	3.186152	-1.361737
1	-4.729211	-1.328988	-0.383393	1	1.870780	3.373610	0.207470
1	-3.726005	0.552806	0.789757	1	2.982798	1.429769	1.112276
1	-4.563157	1.364169	-0.546378	1	4.257207	2.017009	0.016240
1	-2.535958	1.532811	-1.846624	1	3.419363	0.592136	-1.791149
1	-2.383802	-2.094961	-1.590360	1	0.809054	1.953543	-2.077566
1	-2.417948	-1.814195	0.162744	1	0.146566	1.874444	-0.437738
1	1.285821	-2.093711	0.692294	1	-0.915167	1.272094	1.748662
1	0.277460	0.635204	1.673315	1	-1.264939	-1.615379	0.737410
1	1.521380	1.657360	0.015315	1	-3.581706	-2.139482	0.517382
1	3.651061	2.828662	-0.305315	1	-5.917972	-1.513066	0.019484
1	5.799399	1.586408	-0.202140	1	-6.490769	0.846984	-0.495134
1	5.784141	-0.858683	0.231314	1	-4.704299	2.569954	-0.511685
1	3.643024	-2.043781	0.555398	1	-2.372997	1.943667	-0.029021
1	-0.145704	-2.306187	-0.972219	1	2.449811	-1.329936	1.072729
1	-1.855867	1.089861	1.673727	1	-1.001187	0.219798	-1.689148
6	1.532761	-1.603076	-2.205573	1	1.348459	-1.646430	-1.039719
1	2.024333	-0.660342	-2.459150	6	-1.186546	-1.968859	-1.878186
1	2.289141	-2.263310	-1.772756	1	-2.260304	-2.000940	-1.673061
1	1.183975	-2.066645	-3.134850	1	-1.064928	-2.037695	-2.965223
1	-0.008625	0.674881	-1.736787	1	-0.729409	-2.860076	-1.436406
s-si Et =-1031.7617621 (-1032.0197464) (-1032.0482244) NImag=1(-347.46 cm^{-1})				*s-re* Et =-1031.7531558 (-1032.0120641) (-1032.045215) NImag= 1(-387.32 cm^{-1})			
6	0.312661	-0.759906	-1.421466	6	0.132985	0.129686	1.352957
6	-0.983158	-1.207985	-1.150099	6	-1.171987	0.635902	1.211628
7	-1.992533	-0.461992	-0.703479	7	-2.263557	-0.001951	0.792551
6	-2.136782	0.989403	-0.905702	6	-2.314542	-1.386004	0.346037
6	-3.648962	1.241447	-0.709566	6	-3.823644	-1.642635	0.101264
6	-4.302795	-0.133453	-0.854961	6	-4.534610	-0.501092	0.831409

6	-3.254083	-1.063714	-0.265387
6	-1.307833	1.911432	0.004992
8	-1.533214	1.885014	1.311972
8	-0.557333	2.718876	-0.494763
1	-4.470571	-0.375167	-1.909616
1	-5.260238	-0.197319	-0.333907
1	-3.823436	1.634575	0.295334
1	-4.019139	1.979051	-1.423738
1	-1.811465	1.222795	-1.922762
1	-3.316577	-2.094005	-0.617718
1	-3.262593	-1.077316	0.832929
1	-1.790195	0.990099	1.694540
6	1.192624	-0.937578	0.445715
6	0.321474	-0.406672	1.410849
1	1.212415	-2.022294	0.389433
1	0.412384	0.580466	1.833949
6	2.496994	-0.270223	0.232956
6	2.613174	1.124775	0.156564
6	3.859083	1.716708	-0.007764
6	5.006858	0.931554	-0.100468
6	4.901790	-0.454164	-0.034617
6	3.654761	-1.049879	0.123691
1	1.726584	1.750524	0.207123
1	3.932967	2.797651	-0.067741
1	5.977788	1.399155	-0.228504
1	5.789842	-1.073802	-0.106668
1	3.575659	-2.131579	0.182940
7	-0.806174	-1.091780	1.743912
8	-0.970379	-2.261286	1.343347
8	-1.710158	-0.502706	2.427386
1	0.447938	0.317044	-1.507433
6	1.177882	-1.600820	-2.325062
1	2.238306	-1.397033	-2.155983
1	1.004984	-2.669300	-2.158653
1	0.969981	-1.391840	-3.380170
1	-1.197157	-2.270024	-1.207967

6	-3.562494	0.659758	0.673413
6	-1.554429	-1.691172	-0.946894
8	-1.402958	-0.706680	-1.830133
8	-1.207949	-2.822284	-1.183881
1	-4.659910	-0.738871	1.892333
1	-5.518893	-0.284101	0.411653
1	-4.036430	-1.589303	-0.970685
1	-4.115929	-2.635230	0.445105
1	-1.910167	-2.045841	1.119604
1	-3.660906	1.428514	1.442604
1	-3.647073	1.146652	-0.305312
1	-1.446430	0.211821	-1.453665
6	1.155361	0.589458	-0.363702
1	0.474919	0.003246	-0.964868
6	1.125144	1.971512	-0.619319
1	0.236860	-0.950889	1.259870
7	-0.046157	2.576307	-0.963624
8	-0.089751	3.787264	-1.202202
8	-1.116174	1.872493	-0.967070
6	2.451926	-0.096703	-0.159276
6	2.542625	-1.459230	-0.475234
6	3.739208	-2.148536	-0.321079
6	4.868352	-1.489121	0.157318
6	4.791532	-0.136642	0.480006
6	3.594446	0.553053	0.326453
1	1.666700	-1.978166	-0.856255
1	3.790120	-3.201168	-0.579706
1	5.804100	-2.025512	0.277106
1	5.667640	0.384787	0.852017
1	3.551581	1.605885	0.585180
1	1.951844	2.653657	-0.500210
1	-1.359844	1.656157	1.530340
6	0.958601	0.762481	2.450445
1	0.588671	0.488959	3.444815
1	2.001257	0.443574	2.387614
1	0.933695	1.854711	2.373689

Table S22. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), for Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and 3-Pentanone (**2**) to Nitrostyrene. The values in the parenthesis implies single-point energies evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1110.3703456 (-1110.6474702) (-1110.6756777) NImag=1(-323.91 cm^{-1})			
6	-3.731188	-0.930028	0.442198
6	-2.515319	-0.583705	-0.160157
6	-2.527997	0.401259	-1.158400
6	-3.715477	1.017148	-1.534752
6	-4.916305	0.662812	-0.923691
6	-4.920606	-0.316035	0.064907
6	-1.275571	-1.288624	0.248550
6	-0.329722	-1.593625	-0.757963
7	0.739815	-2.370089	-0.471833
8	0.794170	-3.026090	0.588970
8	1.733016	-2.380182	-1.278442
6	-0.404250	-0.251664	1.724574
6	-1.508876	0.204858	2.643275
6	0.420433	0.677413	1.043826

a-si (II) (TS without H-bonding) Et = -1110.3593266 (-1110.6378766) (-1110.669237) Nimag = 1(-344.46 cm^{-1})			
6	-0.614943	1.146956	-0.496849
6	0.746310	0.954653	-0.146078
7	1.425340	-0.109662	-0.625329
6	2.681812	-0.606042	-0.028513
6	2.948795	-1.948060	-0.743110
6	1.578418	-2.379273	-1.253062
6	0.916187	-1.063885	-1.632516
6	3.888017	0.299041	-0.244421
8	3.898185	0.980485	-1.412139
8	4.817516	0.344697	0.511697
1	3.641576	-1.801691	-1.579325
1	3.396527	-2.662747	-0.053022
1	2.524791	-0.752204	1.045277
1	-0.167542	-1.123140	-1.607570

6 -0.090091 2.035129 0.650676 6 0.308070 3.091553 1.692903 7 1.649072 0.307585 0.659885 6 2.477290 1.053566 -0.317079 6 3.847189 0.368724 -0.234965 6 3.896693 -0.146067 1.197326 6 2.481574 -0.667520 1.400994 6 1.924867 1.099808 -1.753996 8 1.759178 -0.029404 -2.414149 8 1.708317 2.176099 -2.266548 1 4.115209 0.669063 1.895760 1 4.641492 -0.931316 1.341385 1 3.887161 -0.473555 -0.931492 1 4.650251 1.062337 -0.490526 1 2.553841 2.097534 -0.003597 1 2.168891 -0.677228 2.446098 1 2.366228 -1.678020 0.998663 1 -2.135566 0.986306 2.208384 1 -2.164535 -0.634983 2.889938 1 -1.103008 0.581601 3.589244 1 -1.447385 -2.097458 0.955879 1 -0.292307 -1.098232 -1.714624 1 -1.605280 0.689739 -1.651911 1 -3.702425 1.774313 -2.312034 1 -5.842499 1.143708 -1.221019 1 -5.851459 -0.607752 0.540487 1 -3.744851 -1.705878 1.202118 1 0.128486 -1.126311 2.091998 1 -1.177838 1.996112 0.569705 1 0.285908 2.336736 -0.329424 1 1.394679 3.172366 1.790149 1 -0.074527 4.070421 1.392693 1 -0.100006 2.855507 2.679090 1 1.845600 -0.900878 -1.901345	1 1.218887 -0.729606 -2.636136 1 3.032670 0.876669 -1.837662 6 -1.601964 -0.041773 0.768639 6 -0.992439 -1.298322 0.960215 6 -1.269237 2.497791 -0.327616 1 -0.930860 3.209915 -1.087568 1 -2.351468 2.400187 -0.438257 1 -1.076198 2.940414 0.653336 1 -1.467027 0.643461 1.603217 1 -1.333151 -2.224521 0.523197 6 -2.978798 -0.054014 0.202389 6 -3.308117 -0.810439 -0.928700 6 -4.607838 -0.831940 -1.419773 6 -5.606774 -0.093195 -0.789824 6 -5.293720 0.666129 0.333100 6 -3.990752 0.688441 0.820772 1 -2.539804 -1.393227 -1.429581 1 -4.842238 -1.426541 -2.297018 1 -6.621583 -0.109327 -1.173571 1 -6.064771 1.243257 0.833317 1 -3.754206 1.276941 1.702245 7 0.137510 -1.397232 1.724019 8 0.602541 -0.346796 2.237564 8 0.701623 -2.501717 1.863557 1 -0.930853 0.658099 -1.413407 6 1.437659 1.919008 0.784807 1 2.257358 1.431126 1.312023 1 0.720724 2.183221 1.565123 6 1.946396 3.194517 0.097806 1 2.386276 3.853642 0.851145 1 2.722826 2.979712 -0.638981 1 1.144170 3.745461 -0.397438 1 1.022789 -2.853483 -0.440520 1 1.638163 -3.068278 -2.098693
a-re Et = -1110.3667367 (-1110.644317) (-1110.6737191) NImag= 1(-326.62 cm^{-1})	*a-re* (*II*) Et = -1110.3663982 (-1110.64363916) (-1110.67249220) NImag= 1(-331.8 cm^{-1})
6 -3.456860 -0.900347 0.762205 6 -3.000950 -0.158533 -0.335617 6 -3.921436 0.628147 -1.037878 6 -5.261051 0.660946 -0.665270 6 -5.701055 -0.083789 0.424539 6 -4.793050 -0.863650 1.138538 6 -1.593245 -0.204560 -0.781627 6 -0.696845 1.084190 0.694355 6 -1.481065 2.366173 0.548750 6 -0.943459 -1.438863 -0.824498 7 0.272861 -1.558886 -1.433263 8 0.896631 -2.628836 -1.379502 6 0.681748 1.040618 0.404253 6 1.312232 2.144708 -0.402979 6 2.056666 3.163768 0.469304 7 1.444773 0.031464 0.859166 6 2.911899 -0.101275 0.740017 6 3.127630 -1.572938 1.100907 6 2.172957 -1.758343 2.273597 6 0.955588 -0.915908 1.886252 6 3.689549 0.249464 -0.540434 8 3.278916 -0.166146 -1.722086 8 4.752450 0.809009 -0.394487 8 0.739467 -0.543973 -2.038547	6 3.316538 -1.144524 -0.473250 6 2.980716 -0.092515 0.390155 6 3.991324 0.797856 0.774887 6 5.296928 0.636073 0.323523 6 5.615135 -0.416059 -0.529360 6 4.618951 -1.305853 -0.926640 6 1.614112 0.094158 0.914074 6 0.658424 1.193102 -0.683955 6 1.304160 2.550342 -0.582851 6 0.835680 -1.012815 1.256063 7 -0.373443 -0.787520 1.844532 8 -1.165970 -1.760210 2.027620 6 -0.729341 1.022026 -0.493155 6 -1.584343 2.144670 0.032712 6 -2.279714 2.915627 -1.095542 7 -1.302021 -0.148981 -0.839191 6 -2.745052 -0.478281 -0.830674 6 -2.724568 -1.995882 -1.007504 6 -1.645016 -2.180617 -2.066244 6 -0.600917 -1.120592 -1.706912 6 -3.672652 -0.048545 0.322806 8 -3.471249 -0.504340 1.542070 8 -4.648642 0.611022 0.043232 8 -0.697743 0.376750 2.142730

1 2.625948 -1.373621 3.192338 1 1.904541 -2.802853 2.443426 1 2.832238 -2.200829 0.254229 1 4.171864 -1.773713 1.345970 1 3.378170 0.527596 1.506488 1 0.551516 -0.355160 2.737249 1 0.157182 -1.528727 1.470646 1 -1.570509 2.697211 -0.491904 1 -2.495864 2.222053 0.923301 1 -1.037694 3.193407 1.114894 1 -1.289520 -2.340428 -0.342476 1 -1.323493 0.491648 -1.568922 1 -3.584066 1.205200 -1.893517 1 -5.961091 1.269851 -1.228061 1 -6.745016 -0.056070 0.719015 1 -5.128211 -1.443596 1.992414 1 -2.756118 -1.504295 1.331332 1 2.328569 -0.482528 -1.779059 1 -1.029857 0.458186 1.515017 1 0.519013 2.653173 -0.952951 1 1.982046 1.742397 -1.162308 1 2.944386 2.729626 0.934393 1 2.393053 3.998756 -0.150567 1 1.414246 3.565404 1.258223	1 -2.056352 -1.986648 -3.061335 1 -1.219131 -3.186126 -2.072578 1 -2.428146 -2.465379 -0.064961 1 -3.702102 -2.381136 -1.303692 1 -3.206292 -0.017969 -1.711456 1 -0.215740 -0.606057 -2.595061 1 0.245043 -1.547481 -1.170920 1 1.142758 3.023925 0.390890 1 2.383555 2.456046 -0.724597 1 0.937160 3.245257 -1.347387 1 1.038007 -2.041309 1.001191 1 1.465234 0.967483 1.540457 1 3.750074 1.613587 1.449677 1 6.066092 1.332533 0.641098 1 6.632432 -0.542739 -0.884836 1 4.858662 -2.127409 -1.594008 1 2.550723 -1.842838 -0.797258 1 -2.606768 -0.976910 1.707355 1 1.119041 0.544216 -1.420808 1 -0.942839 2.819152 0.600100 1 -2.321459 1.780099 0.746022 1 -3.035969 2.305033 -1.593670 1 -2.793380 3.786418 -0.680058 1 -1.565705 3.268953 -1.845562
a-re (*III*) Et = -1110.3643453 (-1110.6424412) (-1110.675343) NImag= 1(-331.8 cm^{-1})	*a-re(IV)* TS without H-bonding Et = -1110.3524262 (-1110.63145) (-1110.6657406) Nimag = 1(-359.93 cm^{-1})
6 -3.637802 0.705154 -0.450129 6 -2.538677 0.204837 0.260562 6 -2.750314 -0.868397 1.134808 6 -4.013729 -1.430080 1.289774 6 -5.093021 -0.927715 0.570104 6 -4.900103 0.145202 -0.297225 6 -1.176935 0.794661 0.152729 6 -0.333561 0.026863 -1.473553 6 -1.393918 -0.569686 -2.369226 6 -1.085993 2.208267 0.053953 7 0.065335 2.870642 0.335116 8 0.109088 4.104082 0.258696 6 0.655427 -0.813265 -0.887203 6 0.288282 -2.180213 -0.379087 6 0.714011 -3.270625 -1.373189 7 1.907669 -0.387299 -0.717925 6 2.841872 -0.931718 0.281224 6 4.070751 -0.011900 0.171083 6 4.004250 0.506448 -1.262068 6 2.511360 0.734266 -1.453345 6 2.297352 -0.964149 1.715806 8 1.564444 0.054609 2.139892 8 2.572127 -1.897688 2.431726 8 1.123058 2.213406 0.646090 1 4.376704 -0.245810 -1.965603 1 4.577730 1.424254 -1.405599 1 3.970450 0.823765 0.870738 1 4.988926 -0.549127 0.412587 1 3.105994 -1.963404 0.035114 1 2.189837 0.702824 -2.496216 1 2.191193 1.676061 -0.989757 1 -2.160491 0.173588 -2.597406 1 -0.957153 -0.888985 -3.322774 1 -1.899736 -1.429108 -1.923494	6 0.551182 -0.041295 -1.075881 6 -0.812369 -0.222537 -0.696499 6 -1.417980 -1.595506 -0.785498 7 -1.583780 0.815303 -0.288807 6 -2.836857 0.597421 0.466373 6 -3.107415 1.943211 1.163592 6 -1.713306 2.534498 1.323078 6 -1.043896 2.157633 0.009502 6 -4.030620 0.233977 -0.407044 8 -3.958338 0.661065 -1.683722 8 -5.005628 -0.316312 0.024041 1 -1.190116 2.046298 2.150123 1 -1.718870 3.613529 1.493339 1 -3.725420 2.587985 0.528487 1 -3.637851 1.789865 2.103586 1 -2.672962 -0.185813 1.210138 1 0.039878 2.138642 0.083686 1 -1.317136 2.853339 -0.794023 1 -3.059566 1.003080 -1.829219 1 -2.223596 -1.715065 -0.061997 1 -0.636264 -2.299850 -0.477604 6 1.577477 -0.247178 0.560686 1 1.040004 0.520499 1.111933 6 1.421566 -1.518007 1.163462 1 0.820385 0.989288 -1.295799 7 0.279899 -1.759937 1.877915 8 0.123503 -2.833106 2.474842 8 -0.607229 -0.852931 1.879540 6 2.946663 0.186832 0.160623 6 3.265246 1.548947 0.201139 6 4.534137 2.003964 -0.139360 6 5.514483 1.099002 -0.535044 6 5.213960 -0.259708 -0.582390 6 3.944371 -0.711040 -0.239415

1 -1.883563 2.849778 -0.286135 1 -0.507754 0.374238 0.894004 1 -1.918851 -1.247150 1.722578 1 -4.154720 -2.253784 1.982162 1 -6.080071 -1.362358 0.689661 1 -5.738202 0.551242 -0.854567 1 -3.508366 1.546082 -1.123980 1 1.413269 0.804018 1.493746 1 0.066368 0.953244 -1.874022 1 -0.792205 -2.222989 -0.230644 1 0.745161 -2.384824 0.592912 1 1.794781 -3.262907 -1.539499 1 0.440730 -4.254681 -0.984087 1 0.223694 -3.140340 -2.341392	1 2.511051 2.262129 0.524865 1 4.758471 3.064695 -0.089396 1 6.506604 1.448914 -0.800900 1 5.972782 -0.974202 -0.884982 1 3.729686 -1.773524 -0.280861 1 2.120019 -2.338440 1.127888 6 1.181377 -0.996145 -2.065886 1 2.244648 -0.768907 -2.164659 1 1.093803 -2.039135 -1.750227 1 0.737603 -0.900626 -3.061384 6 -1.932399 -1.990327 -2.179015 1 -1.149522 -1.963534 -2.938070 1 -2.317259 -3.012411 -2.134422 1 -2.751392 -1.346491 -2.506406
s-si Et = -1110.3697226 (-1110.6468445) (-1110.6735793) NImag=1(-326.50 cm^{-1})	*s-si(II)* Et = -1110.3559058 (-1110.6349382) (-1110.666055) NImag=1(-372.54 cm^{-1})
6 -0.294566 1.013883 -0.874467 6 0.994650 1.257939 -0.367922 7 1.895779 0.257774 -0.292688 6 1.885755 -0.921251 -1.185136 6 3.342999 -1.436664 -1.162664 6 4.159256 -0.290602 -0.570868 6 3.183257 0.349254 0.403823 6 0.920315 -2.076015 -0.860701 8 1.087173 -2.753761 0.267605 8 0.115999 -2.426713 -1.695473 1 4.439247 0.429953 -1.346684 1 5.072612 -0.634519 -0.080786 1 3.410127 -2.316619 -0.518249 1 3.666320 -1.733503 -2.162076 1 1.592332 -0.581747 -2.181340 1 3.431308 1.379464 0.643013 1 3.098623 -0.207856 1.347611 1 1.399681 -2.213886 1.057261 6 -1.277285 0.411589 0.887592 6 -0.536971 -0.624112 1.472776 6 -1.154353 2.123209 -1.427233 1 -0.715710 2.563300 -2.330255 1 -2.135213 1.730015 -1.700064 1 -1.318477 2.935932 -0.713025 1 -1.169465 1.385120 1.357100 1 -0.750588 -1.671354 1.335059 6 -2.628588 0.110565 0.366760 6 -2.899764 -1.046651 -0.376692 6 -4.190292 -1.309157 -0.819385 6 -5.229219 -0.426296 -0.530594 6 -4.968750 0.729436 0.199333 6 -3.676614 0.998497 0.637314 1 -2.097887 -1.734350 -0.629624 1 -4.384028 -2.207319 -1.396741 1 -6.235593 -0.636627 -0.878077 1 -5.770883 1.423912 0.427735 1 -3.476321 1.899587 1.209740 7 0.615004 -0.343710 2.146743 8 0.909054 0.829620 2.438006 8 1.401554 -1.303585 2.443539 1 -0.434176 0.060856 -1.378385 6 1.379607 2.637828 0.105588 1 1.927530 2.588020 1.045544 1 0.465758 3.189296 0.332400	6 -2.652910 -1.304114 -0.855910 6 -2.557010 0.001943 -0.361206 6 -3.678475 0.552219 0.271591 6 -4.856656 -0.176061 0.392629 6 -4.937367 -1.471692 -0.110433 6 -3.828729 -2.035138 -0.735347 6 -1.276784 0.745906 -0.531856 6 -1.301293 2.159674 -0.552765 7 -0.182798 2.813889 -0.977191 8 0.814448 2.095868 -1.303391 8 -0.137246 4.052009 -1.009720 6 -0.168932 0.059347 0.907060 6 -0.873024 0.465148 2.183876 6 1.156355 0.524426 0.661883 6 1.679366 1.748632 1.361039 6 2.394154 1.393254 2.672185 7 2.040911 -0.206775 -0.061861 6 1.699856 -1.503585 -0.657301 6 2.925181 -1.838794 -1.521422 6 3.400933 -0.464944 -1.978336 6 3.199949 0.408593 -0.745522 6 1.457939 -2.606774 0.370606 8 2.103405 -2.458920 1.537501 8 0.792369 -3.575820 0.122299 1 2.767798 -0.094401 -2.789822 1 4.436759 -0.463933 -2.324498 1 3.691710 -2.326334 -0.908349 1 2.662733 -2.517817 -2.333498 1 0.806104 -1.436422 -1.281959 1 2.954075 1.436797 -1.009614 1 4.077809 0.397022 -0.089139 1 -0.971495 1.550644 2.272649 1 -1.879394 0.042194 2.194799 1 -0.355862 0.093029 3.073630 1 -0.652734 0.337881 -1.322698 1 -2.090749 2.797881 -0.190340 1 -3.635952 1.559145 0.672176 1 -5.715734 0.272192 0.881532 1 -5.857709 -2.038549 -0.014640 1 -3.877488 -3.044634 -1.130235 1 -1.792588 -1.756254 -1.342829 1 -0.326064 -0.991354 0.675018 1 0.841142 2.418884 1.562398 1 2.358324 2.303111 0.714875

6 2.180419 3.397997 -0.957943 1 2.417282 4.405351 -0.604402 1 3.124044 2.894461 -1.189663 1 1.618611 3.492886 -1.891366	1 3.285296 0.783486 2.486763 1 2.723257 2.306320 3.175275 1 1.748123 0.846274 3.363130 1 2.516707 -1.578296 1.540611
s-re Et = -1110.3643569 (-1110.6428551) (-1110.67458) NImag = 1(-364.0 cm^{-1})	*s-re(II)* Et = -1110.3637042 (-1110.642429) (-1110.670737) NImag=1(-326.50 cm^{-1})
6 0.169138 -0.143793 -1.126019 6 -1.135920 -0.623667 -0.839132 6 -1.409218 -2.100785 -0.921530 7 -2.152566 0.188242 -0.513555 6 -2.058787 1.647045 -0.463672 6 -3.497010 2.113142 -0.136741 6 -4.374227 0.914359 -0.484953 6 -3.490340 -0.271984 -0.128498 6 -1.126359 2.236156 0.597002 8 -1.002273 1.586448 1.750303 8 -0.627440 3.320597 0.415485 1 -4.600767 0.898206 -1.555829 1 -5.318858 0.908125 0.062702 1 -3.576774 2.334168 0.931921 1 -3.750009 3.022465 -0.682982 1 -1.720720 2.029557 -1.431170 1 -3.762662 -1.174716 -0.673607 1 -3.505282 -0.502863 0.944028 1 -1.154434 0.602867 1.704264 1 -2.110499 -2.394141 -0.139845 1 -0.474144 -2.618485 -0.687067 6 1.251444 -0.353452 0.606088 1 0.700123 0.440318 1.088840 6 1.098094 -1.613780 1.216651 1 0.257680 0.938728 -1.204852 7 -0.056895 -1.923398 1.874948 8 -0.173765 -3.003719 2.461958 8 -1.038376 -1.105198 1.828178 6 2.598878 0.095422 0.181378 6 2.851875 1.472228 0.115308 6 4.104102 1.949994 -0.253033 6 5.127189 1.059301 -0.566220 6 4.888075 -0.311655 -0.509345 6 3.635688 -0.789477 -0.142417 1 2.059344 2.172943 0.364981 1 4.281142 3.019976 -0.289788 1 6.106242 1.430351 -0.851790 1 5.680620 -1.012827 -0.750642 1 3.465633 -1.860347 -0.108833 1 1.829549 -2.405912 1.225170 6 0.997347 -0.872210 -2.162047 1 1.986781 -0.418092 -2.232593 1 1.140099 -1.928582 -1.915383 1 0.541761 -0.816829 -3.156788 6 -1.917293 -2.552577 -2.296050 1 -1.193996 -2.343658 -3.086987 1 -2.101467 -3.630071 -2.285502 1 -2.854373 -2.055700 -2.566000	6 -3.030282 -0.635575 -0.477537 7 -1.833032 0.082538 0.002872 6 -1.461863 1.187487 -0.897207 6 -2.680897 1.313657 -1.826277 6 -3.211626 -0.113401 -1.898035 6 -1.089160 -0.327053 1.054818 6 -1.769080 -1.161776 2.105782 6 -2.521361 -0.281875 3.112635 6 -1.205964 2.511777 -0.181787 8 -0.460695 3.342302 -0.628295 6 0.251138 0.106983 1.182625 6 0.953387 0.051758 2.518388 8 -1.922693 2.729024 0.933492 6 1.302893 -1.110717 0.006041 6 0.635688 -1.422067 -1.194200 7 -0.436378 -2.267984 -1.159946 8 -0.793236 -2.717707 -0.036798 6 2.608840 -0.407193 -0.115343 6 2.751413 0.764764 -0.867738 6 3.990789 1.380672 -0.994436 6 5.110826 0.837292 -0.369675 6 4.980769 -0.322246 0.388365 6 3.738453 -0.934640 0.519532 8 -1.057726 -2.542874 -2.205529 1 -2.601561 -0.721458 -2.570918 1 -4.251465 -0.164068 -2.227736 1 -3.424340 1.980975 -1.374660 1 -2.397734 1.733897 -2.792255 1 -0.566117 0.950698 -1.470062 1 -2.827487 -1.709673 -0.459791 1 -3.894837 -0.414737 0.160363 1 2.010222 0.295789 2.389763 1 0.537400 0.775886 3.227052 1 0.899028 -0.938396 2.980044 1 0.872905 -1.011405 -2.163964 1 1.286853 -1.914528 0.738751 1 3.642511 -1.843036 1.107083 1 5.847046 -0.752068 0.881057 1 6.077789 1.319794 -0.468124 1 4.079908 2.291620 -1.577291 1 1.884810 1.213238 -1.346031 1 -2.399973 1.913877 1.157690 1 0.504448 1.001477 0.620357 1 -1.018268 -1.762290 2.619982 1 -2.454956 -1.872283 1.645498 1 -3.348862 0.256107 2.635558 1 -2.955083 -0.899222 3.904051 1 -1.865345 0.454892 3.584427

Table S23. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene. The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si				*a-si(II)*			
Et =-1148.4782822 (-1148.7614342) (-1148.794807) NImag=1(-327.70 cm^{-1})				Et =-1148.4750759 (-1148.7580464) (-1148.7927497) NImag=1(-308.14 cm^{-1})			
6	3.556838	-1.045304	-0.691250	6	3.552726	-0.781359	-0.912072
6	2.390177	-0.859968	0.061676	6	2.329914	-0.813781	-0.230496
6	2.522447	-0.381696	1.374163	6	2.354588	-0.779664	1.171155
6	3.772045	-0.076947	1.899416	6	3.558614	-0.704562	1.860654
6	4.920448	-0.247924	1.129071	6	4.766372	-0.663665	1.166637
6	4.808623	-0.741036	-0.167008	6	4.759650	-0.706510	-0.223360
6	1.081139	-1.217194	-0.537952	6	1.064989	-0.929522	-1.006036
6	0.078742	-1.729566	0.322257	6	0.058966	-1.761121	-0.434697
7	-1.010510	-2.346419	-0.186005	7	-1.042303	-2.082764	-1.138779
8	-1.056317	-2.689928	-1.387073	8	-1.102002	-1.881984	-2.372344
8	-2.023920	-2.540734	0.571597	8	-2.066694	-2.543664	-0.518993
6	0.390645	0.362118	-1.577242	6	0.335521	0.813110	-1.434507
6	1.543093	1.184228	-2.126646	6	1.441652	1.780334	-1.840535
6	-0.515707	0.990888	-0.681728	6	-0.476028	1.158917	-0.315555
6	0.002147	2.036533	0.258875	6	0.094762	1.918756	0.846053
7	-1.775466	0.569174	-0.586802	7	-1.732242	0.715229	-0.246868
6	-2.718885	0.964092	0.486083	6	-2.541873	0.726399	0.991613
6	-4.011501	0.236696	0.105943	6	-3.952513	0.363704	0.512609
6	-3.963592	0.232874	-1.416070	6	-3.981592	0.894359	-0.914287
6	-2.502422	-0.092175	-1.695382	6	-2.602538	0.508024	-1.430065
6	-2.254610	0.674716	1.925529	6	-2.021163	-0.203187	2.103670
8	-2.049784	-0.576482	2.287590	8	-1.967825	-1.500307	1.872098
8	-2.138865	1.595301	2.702680	8	-1.723576	0.269644	3.178050
1	-4.228418	1.218169	-1.814811	1	-4.110762	1.982148	-0.921760
1	-4.631551	-0.507812	-1.859886	1	-4.775523	0.449131	-1.517225
1	-3.985964	-0.791861	0.475924	1	-4.076735	-0.722671	0.505701
1	-4.885004	0.738127	0.526488	1	-4.714004	0.792353	1.166455
1	-2.872594	2.046354	0.444074	1	-2.528516	1.731095	1.422810
1	-2.142185	0.314405	-2.642426	1	-2.246746	1.141568	-2.243374
1	-2.321164	-1.172597	-1.692949	1	-2.579341	-0.531548	-1.766664
1	1.175638	-1.776414	-1.465372	1	1.240386	-1.125186	-2.062748
1	0.030457	-1.525188	1.379592	1	0.022886	-2.016436	0.611658
1	1.645358	-0.253307	1.999868	1	1.427746	-0.816703	1.734509
1	3.849384	0.290446	2.917606	1	3.553084	-0.682324	2.945632
1	5.895351	-0.010150	1.541842	1	5.705159	-0.606661	1.707833
1	5.697195	-0.898038	-0.769977	1	5.694014	-0.689341	-0.775117
1	3.480554	-1.453190	-1.695074	1	3.556984	-0.839953	-1.996913
1	-0.088729	-0.259753	-2.329585	1	-0.238580	0.419832	-2.271501
1	0.554221	1.540933	1.068753	1	0.158024	1.279305	1.734411
1	-2.118055	-1.291481	1.570038	1	-2.101158	-1.825189	0.917095
1	-0.809045	2.583378	0.741535	1	-0.631657	2.697205	1.115593
6	0.944051	2.996126	-0.478976	6	1.449926	2.563599	0.534920
6	2.077609	2.239471	-1.159904	1	1.594832	3.412673	1.209627
1	2.355403	0.521682	-2.442837	1	2.258161	1.855850	0.739510
1	1.190160	1.678596	-3.043075	6	1.520362	3.000471	-0.922460
1	1.340345	3.722286	0.237507	1	1.269293	2.099585	-2.874156
1	0.369230	3.566439	-1.219856	1	2.412946	1.274019	-1.835478
1	2.724333	2.935548	-1.704445	1	0.691777	3.687402	-1.141643
1	2.700280	1.763300	-0.396751	1	2.446329	3.551283	-1.114678
a-re				*a-re(II)*			
Et = -1148.4773665 (-1148.7607456) (-1148.792993)				Et =-1148.4753125 (-1148.7583703) (-1148.791428)			

NImag= 1(-346.52 cm^{-1})				NImag= 1(-353.6 cm^{-1})			
6	-3.376214	-1.282208	0.656633	6	-3.363576	-1.239403	0.691371
6	-2.920936	-0.407452	-0.339099	6	-2.945762	-0.398331	-0.348612
6	-3.852215	0.427277	-0.969060	6	-3.906192	0.386987	-0.996577
6	-5.200046	0.377776	-0.628812	6	-5.246294	0.324686	-0.627728
6	-5.638389	-0.499155	0.358422	6	-5.646984	-0.516740	0.404769
6	-4.720548	-1.327382	1.001696	6	-4.699821	-1.298226	1.064215
6	-1.505399	-0.362375	-0.758534	6	-1.535272	-0.343101	-0.792253
6	-0.638087	0.719662	0.876683	6	-0.659472	0.765280	0.769298
6	-1.469781	1.978236	1.024109	6	-1.476688	2.047287	0.871714
6	-0.822700	-1.572451	-0.915077	6	-0.853003	-1.555850	-0.945334
7	0.408258	-1.595524	-1.497561	7	0.384225	-1.576495	-1.510835
8	1.099140	-2.626429	-1.459088	8	1.078233	-2.605730	-1.463442
6	0.740887	0.844730	0.596844	6	0.727919	0.848018	0.508149
6	1.266566	2.091749	-0.074274	6	1.323096	2.075576	-0.134293
7	1.620663	-0.132106	0.873648	7	1.586988	-0.133087	0.835502
6	3.089531	-0.011085	0.723390	6	3.058459	0.005772	0.747796
6	3.584524	-1.417544	1.070334	6	3.572720	-1.344595	1.260652
6	2.640345	-1.829154	2.190291	6	2.542584	-1.718082	2.315605
6	1.293571	-1.327720	1.682290	6	1.236605	-1.321833	1.640173
6	3.751994	0.464828	-0.581979	6	3.787598	0.348041	-0.564737
8	3.292075	0.096892	-1.756352	8	3.329672	-0.046348	-1.733367
8	4.774333	1.102657	-0.462146	8	4.856587	0.902214	-0.446622
8	0.825467	-0.531656	-2.054892	8	0.811343	-0.507449	-2.052919
1	2.914370	-1.326804	3.123877	1	2.699412	-1.135506	3.229696
1	2.627840	-2.905734	2.372152	1	2.557949	-2.778032	2.578062
1	3.455105	-2.072859	0.202607	1	3.559041	-2.073100	0.443062
1	4.638824	-1.404656	1.349680	1	4.593967	-1.255635	1.632171
1	3.455318	0.694933	1.477126	1	3.370701	0.796112	1.439164
1	0.608096	-1.055655	2.489164	1	0.443943	-1.076142	2.350136
1	0.822832	-2.084237	1.053851	1	0.896269	-2.124603	0.983237
1	-1.133227	-2.515461	-0.492216	1	-1.164589	-2.496092	-0.517228
1	-1.252345	0.411214	-1.475139	1	-1.304734	0.421644	-1.526696
1	-3.515273	1.109445	-1.743982	1	-3.600116	1.035735	-1.812003
1	-5.907128	1.026243	-1.135813	1	-5.976673	0.934785	-1.149116
1	-6.688629	-0.536390	0.628491	1	-6.690943	-0.563972	0.696803
1	-5.054665	-2.010667	1.775792	1	-5.004753	-1.954895	1.872673
1	-2.670797	-1.928487	1.170514	1	-2.634317	-1.849144	1.216999
1	2.378285	-0.319860	-1.783969	1	2.385222	-0.387550	-1.768467
1	-0.912354	-0.068974	1.570499	1	-0.948624	0.002745	1.483658
1	1.258410	1.910004	-1.155664	1	1.823773	1.791448	-1.062902
1	2.310973	2.260576	0.198250	1	2.108143	2.455932	0.533222
6	0.455175	3.346877	0.244824	6	0.313871	3.186473	-0.406457
6	-1.035848	3.094740	0.083905	6	-0.642644	3.319768	0.767521
1	-1.388120	2.336944	2.060958	1	-2.032224	2.030442	1.815148
1	-2.526997	1.739437	0.877214	1	-2.242968	2.076209	0.087011
1	-1.252236	2.820117	-0.956646	1	-0.069781	3.480007	1.690396
1	-1.606988	4.004640	0.295194	1	-1.300138	4.186507	0.645802
1	0.795003	4.158473	-0.405823	1	0.856534	4.117101	-0.596555
1	0.658579	3.663362	1.275577	1	-0.253137	2.961213	-1.317759
s-si Et = -1148.478284 (-1148.7610853) (-1148.789123) NImag=1(-326.97 cm^{-1})				*s-si(II)* Et =-1148.4769599 (-1148.7598037) (-1148.7882584) NImag=1(-334.44 cm^{-1})			
6	-0.320239	0.880473	-0.838089	6	-0.319919	0.880150	-0.819280
6	0.944471	1.267921	-0.355120	6	0.958717	1.247681	-0.344308
7	1.946266	0.371084	-0.286208	7	1.954915	0.350037	-0.304576
6	2.106333	-0.740657	-1.251618	6	2.072246	-0.795202	-1.237260
6	3.623279	-1.043354	-1.238292	6	3.578618	-1.138348	-1.232478
6	4.263770	0.159277	-0.546123	6	4.262384	0.084237	-0.625891
6	3.195565	0.564572	0.455010	6	3.233299	0.574471	0.379528
6	1.300576	-2.032496	-1.018638	6	1.240662	-2.062186	-0.957948

8	1.555433	-2.764599	0.057500	8	1.504760	-2.776038	0.125988
8	0.542790	-2.418301	-1.881146	8	0.459111	-2.447686	-1.799960
1	4.442184	0.972337	-1.257998	1	4.439460	0.851944	-1.386686
1	5.213406	-0.089967	-0.067839	1	5.219107	-0.158532	-0.158622
1	3.808433	-1.950447	-0.657539	1	3.748714	-2.013684	-0.600903
1	3.995099	-1.215375	-2.250035	1	3.926359	-1.381480	-2.238201
1	1.775222	-0.378891	-2.227375	1	1.738481	-0.453107	-2.219685
1	3.287363	1.581745	0.824468	1	3.355445	1.619242	0.651716
1	3.170544	-0.099851	1.331003	1	3.225977	-0.020690	1.303669
1	1.797566	-2.248956	0.887477	1	1.756022	-2.242935	0.947911
6	-1.149688	0.103022	0.902513	6	-1.153840	0.140660	0.888092
6	-0.287143	-0.887732	1.398298	6	-0.305804	-0.854940	1.414178
6	-1.283290	1.924529	-1.359679	6	-1.252017	1.944782	-1.379079
1	-1.137874	1.039679	1.452217	1	-1.147989	1.079696	1.434181
1	-0.394644	-1.938354	1.183435	1	-0.426057	-1.907925	1.219273
6	-2.483501	-0.322069	0.417983	6	-2.492500	-0.287682	0.412147
6	-2.652815	-1.447980	-0.399728	6	-2.665168	-1.413808	-0.404063
6	-3.923840	-1.836648	-0.804050	6	-3.938432	-1.805717	-0.798195
6	-5.044805	-1.112031	-0.403133	6	-5.058262	-1.084049	-0.388690
6	-4.887003	0.011740	0.401825	6	-4.897420	0.038832	0.416347
6	-3.614955	0.406759	0.802819	6	-3.622923	0.436710	0.807695
1	-1.788323	-2.013295	-0.736356	1	-1.802312	-1.978923	-0.745423
1	-4.038622	-2.709355	-1.438688	1	-4.055915	-2.678957	-1.431657
1	-6.035503	-1.420337	-0.721205	1	-6.050565	-1.394919	-0.699281
1	-5.753566	0.583124	0.718822	1	-5.762933	0.607282	0.741388
1	-3.495460	1.280652	1.436907	1	-3.501107	1.308041	1.445056
7	0.825064	-0.549723	2.109610	7	0.812522	-0.508690	2.104558
8	1.002686	0.613612	2.512103	8	0.996732	0.666234	2.474520
8	1.701482	-1.450870	2.334339	8	1.693479	-1.404845	2.343069
1	-0.361240	-0.065051	-1.373879	1	-0.366529	-0.068822	-1.346820
6	1.150271	2.673415	0.163909	6	1.214331	2.645276	0.171486
1	0.932866	2.688868	1.236791	1	1.550593	2.604389	1.208252
1	2.199228	2.960522	0.054253	1	2.038425	3.067058	-0.422655
6	0.280956	3.698462	-0.567866	6	-0.002512	3.559767	0.049287
6	-1.173669	3.256504	-0.628057	6	-0.680834	3.358617	-1.297244
1	-1.077592	2.080812	-2.428247	1	0.321037	4.596395	0.185083
1	-2.304459	1.535935	-1.308213	1	-0.712694	3.347291	0.857046
1	0.658824	3.835812	-1.589115	1	0.053387	3.518386	-2.097976
1	0.378846	4.665688	-0.064286	1	-1.478606	4.092201	-1.450129
1	-1.571265	3.162812	0.390542	1	-2.212315	1.911575	-0.851641
1	-1.785085	4.011381	-1.133093	1	-1.484449	1.690203	-2.418646
s-re Et =-1148.4723658 (-1148.7566916) (-1148.7890888) NImag= 1(-335.03 cm^{-1})				*s-re (II)* Et =-1148.4686631 (-1148.787317) (-1148.752974) NImag= 1(-362.4 cm^{-1})			
6	0.147282	-0.100032	-1.087314	6	0.178302	-0.168967	-1.071014
6	-1.093970	-0.731966	-0.819280	6	-1.104647	-0.732427	-0.803198
6	-1.072675	-2.225248	-0.735331	6	-1.250188	-2.231332	-0.748893
7	-2.225499	-0.049486	-0.592919	7	-2.195246	0.003142	-0.592114
6	-2.340397	1.405030	-0.747245	6	-2.258924	1.462593	-0.731035
6	-3.825799	1.707305	-0.449037	6	-3.744991	1.805872	-0.474553
6	-4.530935	0.366947	-0.625104	6	-4.484766	0.482072	-0.646397
6	-3.492467	-0.635420	-0.143801	6	-3.479474	-0.540508	-0.139830
6	-1.491988	2.279657	0.180072	6	-1.414196	2.298289	0.236265
8	-1.330196	1.887950	1.438818	8	-1.297809	1.884154	1.490206
8	-1.093505	3.349875	-0.213498	8	-0.984783	3.365499	-0.134345
1	-4.760388	0.185566	-1.680012	1	-4.705862	0.294299	-1.701951
1	-5.462451	0.301797	-0.059212	1	-5.424616	0.449527	-0.091790
1	-3.928526	2.048455	0.585444	1	-3.863303	2.166373	0.551410
1	-4.204382	2.497122	-1.098978	1	-4.087112	2.594389	-1.145750
1	-2.067646	1.683444	-1.769196	1	-1.946244	1.740754	-1.740985
1	-3.645794	-1.621684	-0.579722	1	-3.647207	-1.535928	-0.548458

1	-3.470406	-0.746531	0.947349
1	-1.411109	0.904912	1.596124
1	-0.538468	-2.468491	0.198354
6	1.089838	-0.058779	0.750748
1	0.473935	0.773933	1.059117
6	0.942956	-1.204571	1.560038
1	0.108562	0.977994	-1.234634
7	-0.201250	-1.423603	2.282260
8	-0.248117	-2.352868	3.093881
8	-1.230209	-0.699211	2.074310
6	2.450116	0.384008	0.360292
6	2.655993	1.746086	0.101800
6	3.914540	2.225075	-0.241677
6	4.992962	1.349823	-0.338806
6	4.801884	-0.006730	-0.089333
6	3.543090	-0.485833	0.254848
1	1.819661	2.435673	0.181934
1	4.053087	3.285095	-0.428064
1	5.976989	1.722186	-0.604657
1	5.637297	-0.696057	-0.159354
1	3.416361	-1.545756	0.448399
1	1.714652	-1.931925	1.756065
6	1.077807	-0.777676	-2.082173
1	-2.066902	-2.659932	-0.647605
6	-0.296693	-2.862580	-1.892870
6	1.113875	-2.295073	-1.953711
1	0.738021	-0.510509	-3.093428
1	2.083541	-0.360493	-1.983715
1	1.650756	-2.576004	-1.040377
1	1.669732	-2.726211	-2.792902
1	-0.274953	-3.947443	-1.747503
1	-0.820619	-2.679619	-2.839606

1	-3.457907	-0.624605	0.953830
1	-1.361756	0.890503	1.633741
1	-1.530340	-2.519874	0.269627
6	1.084383	-0.067780	0.699833
1	0.482850	0.772991	1.015185
6	0.954727	-1.194715	1.554057
1	0.168173	0.905673	-1.242982
7	-0.198974	-1.439935	2.225634
8	-0.282744	-2.397504	3.004812
8	-1.230529	-0.700924	2.014943
6	2.452463	0.376615	0.326968
6	2.663991	1.736300	0.062963
6	3.928801	2.211323	-0.262354
6	5.007328	1.333817	-0.337602
6	4.810780	-0.020922	-0.084763
6	3.545135	-0.495892	0.241478
1	1.828510	2.428689	0.128191
1	4.072462	3.270171	-0.451570
1	5.996072	1.703650	-0.589264
1	5.646026	-0.711923	-0.138088
1	3.411720	-1.554651	0.438410
1	1.731345	-1.915191	1.754446
6	1.062946	-0.904939	-2.079216
1	-2.091685	-2.512070	-1.396075
6	-0.004703	-2.981694	-1.215133
6	0.561765	-2.300350	-2.450346
1	2.082265	-0.979826	-1.687864
1	1.140424	-0.285405	-2.979509
1	1.379485	-2.884091	-2.884079
1	-0.219806	-2.235894	-3.219230
1	0.743704	-2.990134	-0.417101
1	-0.273130	-4.023805	-1.413103

Table S24. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Propanal (**1**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1263.1663156 (-1263.5056011) (-1263.5333137) NImag=1(-304.02 cm^{-1})			*a-re* Et = -1263.1631043 (-1263.5024845) (-1263.532496) NImag= 1(-298.53 cm^{-1})		
6	-4.203454	-1.444170	-0.287070	6	3.992577	1.245837	-0.268142
6	-3.027117	-0.691542	-0.385367	6	2.836893	0.473559	-0.438954
6	-3.091347	0.577043	-0.976933	6	2.947116	-0.748132	-1.115907
6	-4.299066	1.070057	-1.456796	6	4.173956	-1.185717	-1.602328
6	-5.462288	0.309573	-1.357000	6	5.315458	-0.409904	-1.421485
6	-5.410460	-0.951516	-0.771750	6	5.219092	0.808838	-0.755031
6	-1.754771	-1.266335	0.116075	6	1.503112	0.903396	0.053112
6	-0.622894	-1.173097	-0.720579	6	1.305332	0.102357	1.854557
7	0.490336	-1.897366	-0.445997	6	2.667436	0.075787	2.499997
8	0.572525	-2.585499	0.595006	6	1.213252	2.280899	0.217135
8	1.464702	-1.829352	-1.256452	7	-0.081956	2.691155	0.217665
6	-1.442604	-0.499059	1.949153	8	-0.375571	3.892145	0.296841
6	-2.784464	-0.514600	2.634471	6	0.694969	-1.120437	1.517532
6	-0.851107	0.734838	1.660255	7	-0.607550	-1.347393	1.489535
7	0.445202	0.935229	1.472605	6	-1.199751	-2.519112	0.807794
6	0.960273	2.223199	0.956990	6	-2.707628	-2.338654	1.005878
6	2.463046	2.184762	1.254101	6	-2.816923	-1.452604	2.250113
6	2.606504	1.121919	2.349317	6	-1.627184	-0.507631	2.120073
6	1.530175	0.100226	2.002467	6	-0.644391	-2.585347	-0.625560
6	0.480334	2.389138	-0.496123	8	-1.127848	-1.780858	-1.551418
8	1.182064	1.879571	-1.484881	8	0.295085	-3.317848	-0.851176
8	-0.583107	2.941870	-0.687106	8	-0.995868	1.797478	0.127735
1	2.411614	1.555602	3.335608	1	-2.723305	-2.050451	3.162613
1	3.598677	0.667522	2.362713	1	-3.765332	-0.913710	2.295367
1	3.041684	1.901846	0.372856	1	-3.161529	-1.828645	0.153097
1	2.817300	3.167822	1.571002	1	-3.202910	-3.304467	1.124581
1	0.468603	3.029949	1.507265	1	-0.838737	-3.427560	1.298126
1	1.164242	-0.462459	2.862540	1	-1.253156	-0.148402	3.082228
1	1.883674	-0.616599	1.258013	1	-1.823536	0.365549	1.485365
1	-3.433279	0.287919	2.273224	1	3.156775	1.049661	2.409970
1	-3.304343	-1.461750	2.462187	1	2.584122	-0.154317	3.567820
1	-2.671045	-0.398706	3.718143	1	3.320582	-0.671269	2.041904
1	-1.862633	-2.237626	0.596623	1	1.928445	3.070603	0.383753
1	-0.544646	-0.528008	-1.581517	1	0.682341	0.382634	-0.430578
1	-2.200667	1.193011	-1.061055	1	2.063854	-1.360347	-1.277668
1	-4.328571	2.055782	-1.909712	1	4.233117	-2.132288	-2.129596
1	-6.402976	0.698897	-1.733118	1	6.273304	-0.749208	-1.802595
1	-6.309195	-1.554932	-0.692654	1	6.101670	1.425314	-0.616836
1	-4.166342	-2.434566	0.157826	1	3.936827	2.202896	0.239619
1	-0.755595	-1.290916	2.240742	1	-1.923121	-1.208046	-1.327358
1	2.033529	1.394684	-1.262332	1	0.630684	0.845247	2.271581
8	3.523735	0.734806	-1.444431	8	-3.336207	-0.392597	-1.485577
1	3.693820	-0.100472	-0.937479	1	-3.349231	0.585833	-1.278597
6	3.661876	0.444186	-2.826860	6	-3.812325	-0.562370	-2.809401
1	4.694031	0.162371	-3.064597	1	-4.873987	-0.300411	-2.880988
1	2.983416	-0.357932	-3.134700	1	-3.248089	0.046944	-3.523639
1	3.412477	1.351156	-3.380166	1	-3.692291	-1.614249	-3.075752
8	3.766133	-1.542594	-0.054679	8	-3.295498	2.213041	-1.058227
1	2.914443	-1.905393	-0.416542	1	-2.397843	2.282213	-0.639792
6	4.779591	-2.520326	-0.145271	6	-4.225726	2.839375	-0.201785
1	5.707452	-2.075837	0.222029	1	-4.313826	2.329613	0.767870
1	4.544102	-3.393853	0.473762	1	-3.947629	3.882802	-0.018944

1 4.940326 -2.857320 -1.177406 1 -1.480652 1.588582 1.416364	1 -5.201689 2.819468 -0.692267 1 1.306695 -1.923475 1.109291
s-si Et = -1263.1700629 (-1263.5087355) (-1263.5344231) NImag=1(-327.17 cm^{-1})	*s-si(II)* Et = -1263.1683013 (-1263.5060636) (-1263.5322362) NImag=1(-337.24 cm^{-1})
6 1.505458 1.154076 -1.333678 6 0.175484 1.103151 -1.751331 7 -0.902383 1.367726 -1.010652 6 -0.890149 2.204475 0.202326 6 -2.347327 2.683805 0.342264 6 -2.940605 2.521263 -1.058855 6 -2.253816 1.263299 -1.573555 6 -0.324773 1.502625 1.448925 8 -1.027329 0.549909 2.027813 8 0.752544 1.846282 1.888400 1 -2.681779 3.376446 -1.692144 1 -4.027978 2.424225 -1.041867 1 -2.897089 2.053993 1.045380 1 -2.383778 3.710594 0.711605 1 -0.208756 3.041853 0.024859 1 -2.191915 1.208704 -2.662011 1 -2.743388 0.348793 -1.225313 1 -1.915203 0.318347 1.624369 6 1.828323 -0.806298 -0.680020 6 0.755282 -1.285481 0.082520 6 2.561462 1.334174 -2.395194 1 2.680587 2.390503 -2.661307 1 3.534845 0.975439 -2.050528 1 2.302462 0.791108 -3.310652 1 1.845033 -1.167090 -1.705049 1 0.729032 -1.344055 1.158571 6 3.155045 -0.685543 -0.033731 6 3.319267 -0.112868 1.234902 6 4.577228 -0.064508 1.822863 6 5.688804 -0.583021 1.161168 6 5.537463 -1.146657 -0.101804 6 4.280758 -1.191128 -0.696363 1 2.466463 0.319020 1.750248 1 4.690090 0.386312 2.803621 1 6.668564 -0.542542 1.626434 1 6.396694 -1.552482 -0.626284 1 4.163480 -1.640607 -1.678302 7 -0.384736 -1.682622 -0.546845 8 -0.498081 -1.560072 -1.786327 8 -1.320868 -2.168864 0.153733 1 1.702262 1.629783 -0.375118 8 -3.499322 -0.164280 1.548444 8 -3.753557 -1.643619 -0.664235 1 -3.706018 -0.711497 0.748207 1 -2.820034 -1.973323 -0.574492 6 -3.681478 -0.983890 2.691897 1 -3.372799 -0.406447 3.564864 1 -4.735164 -1.261797 2.810699 1 -3.070198 -1.891149 2.637023 6 -4.615439 -2.724181 -0.946635 1 -5.636409 -2.337523 -0.984264 1 -4.380533 -3.176244 -1.917478 1 -4.566580 -3.505293 -0.177284 1 -0.045075 0.764586 -2.758123	6 -1.313992 0.926841 1.425735 6 0.039410 0.848696 1.759090 7 1.074693 1.310810 1.056729 6 0.950268 2.278354 -0.044066 6 2.373909 2.837914 -0.204263 6 3.009082 2.633626 1.171254 6 2.438805 1.290498 1.608202 6 0.360379 1.700331 -1.340645 8 1.036068 0.768695 -1.980701 8 -0.691784 2.131633 -1.762546 1 2.695656 3.422048 1.863737 1 4.100094 2.625467 1.131771 1 2.925908 2.259475 -0.948471 1 2.351677 3.880571 -0.526714 1 0.247858 3.059794 0.263687 1 2.390704 1.168168 2.692312 1 3.008278 0.453026 1.200899 1 1.871539 0.430471 -1.533531 6 -1.753584 -0.898210 0.506740 6 -0.800930 -1.289693 -0.441011 6 -2.288827 0.933347 2.580008 1 -2.356227 1.926971 3.037129 1 -3.294213 0.657802 2.252950 1 -1.981719 0.231878 3.363613 1 -1.686306 -1.411598 1.461973 1 -0.915389 -1.192040 -1.508603 6 -3.128074 -0.639878 0.016219 6 -3.371157 0.156007 -1.111476 6 -4.669021 0.338578 -1.572739 6 -5.742608 -0.265672 -0.921234 6 -5.512033 -1.051759 0.203386 6 -4.214505 -1.231694 0.671861 1 -2.545036 0.650949 -1.614383 1 -4.842667 0.961000 -2.444650 1 -6.754257 -0.119810 -1.286268 1 -6.341431 -1.526064 0.718349 1 -4.036329 -1.853023 1.544937 7 0.391062 -1.815490 -0.048196 8 0.673145 -1.846764 1.192496 8 1.193380 -2.245863 -0.897939 1 -1.575113 1.557836 0.578920 8 3.351930 -0.186938 -1.229445 8 3.408414 -1.828088 0.940399 1 3.344055 -0.857614 -0.498499 1 2.439003 -1.956661 1.077262 6 3.745794 -0.838159 -2.427687 1 3.705801 -0.100593 -3.231522 1 4.773342 -1.211208 -2.348327 1 3.072808 -1.665852 -2.670268 6 3.979772 -3.103174 0.719831 1 5.022095 -2.956186 0.427321 1 3.961880 -3.709397 1.634028 1 3.455007 -3.643712 -0.075247 1 0.317369 0.353938 2.684528
s-re Et =-1263.1671158 (-1263.5056609)	

(-1263.5331574) (NImag= 1(-345.61 cm^{-1})	
6 1.150288 -0.504663 1.580789 6 -0.226855 -0.393119 1.816475 7 -1.209163 -1.160576 1.346962 6 -1.017114 -2.397653 0.590921 6 -2.441031 -2.969667 0.462332 6 -3.186508 -2.372900 1.656666 6 -2.608522 -0.966164 1.743865 6 -0.325244 -2.218391 -0.765590 8 -0.795502 -1.303995 -1.597672 8 0.625072 -2.910159 -1.055572 1 -2.962151 -2.932957 2.570433 1 -4.269029 -2.367386 1.515275 1 -2.900581 -2.618921 -0.465096 1 -2.429570 -4.060761 0.449576 1 -0.366386 -3.069898 1.160123 1 -2.651002 -0.536896 2.747432 1 -3.108612 -0.283434 1.052509 1 -1.630294 -0.824202 -1.314930 6 1.554795 0.787953 -0.018422 1 0.786207 0.311355 -0.616598 6 1.280688 2.120165 0.334103 1 1.485098 -1.407627 1.073506 7 -0.010812 2.531598 0.448597 8 -0.301352 3.715288 0.673032 8 -0.915046 1.638585 0.340793 6 2.938750 0.398241 -0.368478 6 3.142375 -0.697232 -1.219310 6 4.426004 -1.075847 -1.593882 6 5.531628 -0.372900 -1.123011 6 5.344453 0.712106 -0.270563 6 4.061669 1.092867 0.104693 1 2.289387 -1.261858 -1.583688 1 4.560239 -1.924762 -2.256391 1 6.533743 -0.669275 -1.416202 1 6.199887 1.265859 0.103156 1 3.936269 1.940448 0.770234 1 2.009123 2.884874 0.550516 6 2.060308 0.009523 2.669988 1 3.089740 0.090213 2.311960 1 1.741180 0.999546 3.012449 1 2.068229 -0.657800 3.539405 1 -3.274794 0.740341 -1.028328 8 -3.149800 -0.175987 -1.398060 8 -3.417773 2.213742 -0.234845 1 -2.486641 2.225250 0.101627 6 -3.618784 -0.198335 -2.732850 1 -3.414582 -1.189677 -3.142023 1 -4.699332 -0.018385 -2.774992 1 -3.110164 0.543979 -3.359485 6 -3.647157 3.414015 -0.945591 1 -4.685910 3.408440 -1.283699 1 -3.491659 4.286715 -0.302606 1 -2.992466 3.511016 -1.821427 1 -0.569362 0.390869 2.484118	

Table S25. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et =-1341.7769929 (-1342.1349609) (-1342.1572755) NImag=1(-285.99 cm^{-1})				*a-re* Et =-1341.7753852 (-1342.134044) (-1342.1599366) NImag= 1(-293.56 cm^{-1})			
6	3.908945	-1.905424	-0.224200	6	-3.486335	1.736017	0.350092
6	2.739580	-1.296669	0.249678	6	-2.290687	1.081445	0.676548
6	2.819058	-0.518126	1.413596	6	-2.322794	0.087183	1.663118
6	4.029254	-0.360823	2.077671	6	-3.513086	-0.245636	2.300408
6	5.183878	-0.974584	1.596111	6	-4.695213	0.406301	1.960859
6	5.119848	-1.748695	0.441827	6	-4.676713	1.399227	0.984406
6	1.466361	-1.520559	-0.469613	6	-0.997721	1.422264	0.036813
6	0.280277	-1.656225	0.271691	6	-0.904405	0.453579	-1.737344
7	-0.849869	-2.104077	-0.337612	6	-2.092138	0.915892	-2.536808
8	-0.872195	-2.344921	-1.562593	6	-0.734367	2.774496	-0.263020
8	-1.896839	-2.227421	0.366116	7	0.542227	3.173370	-0.535695
6	1.260586	-0.044498	-1.884765	8	0.818283	4.368871	-0.672817
6	2.510427	-0.117060	-2.722349	6	-0.740863	-0.895325	-1.358182
6	0.940093	1.092473	-1.121919	6	-1.926332	-1.801727	-1.174703
6	2.011766	2.033120	-0.639732	6	-2.198353	-2.616497	-2.447886
6	2.140832	3.251235	-1.564594	7	0.489068	-1.386020	-1.116986
7	-0.336110	1.324798	-0.762356	6	0.763328	-2.668533	-0.444617
6	-0.745147	2.319186	0.253848	6	2.285647	-2.846511	-0.579494
6	-2.214129	2.643509	-0.071494	6	2.647009	-2.001968	-1.798644
6	-2.432571	2.082468	-1.478502	6	1.720713	-0.800412	-1.671826
6	-1.513266	0.869419	-1.517764	6	0.281538	-2.702244	1.013177
6	-0.464677	1.768619	1.664773	8	0.698392	-1.741395	1.829192
8	-1.264931	0.848912	2.169001	8	-0.473299	-3.566973	1.391000
8	0.515453	2.144969	2.272939	8	1.436076	2.268046	-0.646058
1	-2.127396	2.808308	-2.239427	1	2.432256	-2.545031	-2.724994
1	-3.471811	1.804386	-1.663969	1	3.699460	-1.711035	-1.810735
1	-2.894952	2.160916	0.632439	1	2.796647	-2.446264	0.299766
1	-2.391237	3.719293	-0.010917	1	2.548946	-3.900894	-0.680547
1	-0.123345	3.209702	0.161297	1	0.232018	-3.479226	-0.949440
1	-1.217857	0.583452	-2.526322	1	1.497935	-0.332054	-2.632103
1	-1.985505	0.007133	-1.044238	1	2.118328	-0.029362	-1.008525
1	3.408178	0.210920	-2.193186	1	-2.145116	2.008925	-2.498418
1	2.682608	-1.147684	-3.047551	1	-1.994600	0.636007	-3.592024
1	2.415615	0.488550	-3.631386	1	-3.042791	0.520425	-2.170864
1	1.541062	-2.205904	-1.311479	1	-1.464195	3.568374	-0.279100
1	0.155486	-1.388123	1.308528	1	-0.142037	0.891485	0.445144
1	1.938335	-0.017598	1.803181	1	-1.404379	-0.420512	1.942782
1	4.067929	0.246863	2.975879	1	-3.512694	-1.016222	3.064405
1	6.126810	-0.850154	2.118853	1	-5.624997	0.146043	2.456423
1	6.011278	-2.236616	0.060622	1	-5.592251	1.917859	0.717908
1	3.861642	-2.524245	-1.115329	1	-3.487812	2.515350	-0.404684
1	0.416587	-0.578561	-2.315129	1	1.465773	-1.181717	1.511703
1	2.961098	1.496604	-0.611320	1	0.018367	0.965601	-1.995000
1	1.816909	2.353098	0.386030	1	-2.800063	-1.193479	-0.935235
1	1.210146	3.825384	-1.612820	1	-1.787686	-2.481064	-0.331390
1	2.926406	3.917804	-1.198510	1	-1.346751	-3.250535	-2.711877
1	2.398449	2.952845	-2.584582	1	-3.064306	-3.265855	-2.294994
1	-2.102478	0.623315	1.666708	1	-2.407470	-1.965935	-3.300994
8	-3.693467	0.197635	1.451242	8	2.943474	-0.430718	1.599078
1	-3.922113	-0.322520	0.639767	1	3.190715	0.454686	1.215060
6	-4.022557	-0.597118	2.579985	6	3.351853	-0.436463	2.956718
1	-5.103910	-0.767955	2.635875	1	4.444171	-0.403141	3.039720

1 -3.501122 -1.559464 2.555649 1 -3.709935 -0.049116 3.470350 8 -4.087424 -1.302604 -0.744433 1 -3.289498 -1.853014 -0.538905 6 -5.177589 -2.140649 -1.060166 1 -6.049517 -1.504773 -1.229518 1 -4.985213 -2.715209 -1.973940 1 -5.411395 -2.842855 -0.249535	1 2.930232 0.410015 3.509867 1 2.993036 -1.363075 3.408087 8 3.641686 1.977424 0.725836 1 2.853677 2.320853 0.233788 6 4.785928 2.156954 -0.080631 1 4.697875 1.650263 -1.050861 1 4.978475 3.220361 -0.261703 1 5.641207 1.737397 0.453863
s-si Et = -1341.7775155 (-1342.1350957) (-1342.1594584) (NImag=1(-296.3 cm^{-1})	*s-si(II)* Et =-1341.7769898 (-1342.133734) (-1342.1585245) NImag=1(-310.37 cm^{-1})
6 1.501561 1.437032 0.349029 6 0.211794 1.855576 -0.015634 7 -0.881964 1.369165 0.610178 6 -0.840640 0.794599 1.972490 6 -2.277397 0.947852 2.509213 6 -2.919835 1.992679 1.600463 6 -2.261575 1.729197 0.253638 6 -0.315344 -0.648821 2.076126 8 -1.050884 -1.641035 1.615854 8 0.753739 -0.859822 2.610508 1 -2.678341 3.005770 1.939992 1 -4.006645 1.897039 1.555561 1 -2.826727 0.008044 2.425420 1 -2.266465 1.235929 3.562380 1 -0.132659 1.385823 2.559906 1 -2.280865 2.601316 -0.394788 1 -2.737255 0.907783 -0.291494 1 -1.938565 -1.414324 1.211076 6 1.802431 -0.206716 -0.979148 6 0.739370 -1.112555 -0.926863 6 2.707514 2.305988 0.089035 1 2.682290 3.223397 0.688896 1 3.617821 1.768451 0.359994 1 2.807185 2.605106 -0.959387 1 1.795988 0.452501 -1.842881 1 0.724940 -2.024189 -0.351982 6 3.140351 -0.660839 -0.541905 6 3.331395 -1.403520 0.631279 6 4.601356 -1.847943 0.978647 6 5.697983 -1.562561 0.167366 6 5.519390 -0.819768 -0.995743 6 4.251145 -0.367148 -1.342720 1 2.489435 -1.608052 1.285674 1 4.735338 -2.417557 1.892694 1 6.687185 -1.913459 0.443797 1 6.366993 -0.590881 -1.633964 1 4.113534 0.208476 -2.253544 7 -0.405971 -0.856732 -1.622288 8 -0.538200 0.206097 -2.263486 8 -1.325489 -1.724839 -1.600685 1 1.578160 0.835430 1.250334 6 0.031326 2.873141 -1.115206 1 -0.817349 2.611846 -1.746447 1 0.901461 2.820408 -1.771836 6 -0.106203 4.299695 -0.570427 1 -0.210698 5.009887 -1.395636 1 -0.983435 4.408003 0.075135 1 0.769956 4.592188 0.014219 8 -3.540993 -1.592546 0.806004 8 -3.747162 -0.695341 -1.701411	6 1.291803 1.471828 0.010523 6 -0.045931 1.726819 -0.344373 7 -1.071029 1.431788 0.481398 6 -0.884178 1.132305 1.914434 6 -2.280026 1.320090 2.533630 6 -2.992150 2.254358 1.562407 6 -2.474875 1.790064 0.208191 6 -0.288018 -0.246577 2.243492 8 -0.973013 -1.325262 1.925174 8 0.769026 -0.316113 2.835057 1 -2.699918 3.295196 1.739198 1 -4.079769 2.186674 1.631633 1 -2.809011 0.365522 2.571850 1 -2.206625 1.711420 3.550128 1 -0.170657 1.854062 2.323919 1 -2.535226 2.570491 -0.546816 1 -3.026391 0.922900 -0.161232 1 -1.821857 -1.187087 1.403614 6 1.752047 -0.410921 -0.885118 6 0.834340 -1.420251 -0.581571 6 2.395551 2.337934 -0.550249 1 2.345818 3.358961 -0.153983 1 3.368831 1.932044 -0.270471 1 2.373152 2.409650 -1.642626 1 1.651657 0.022947 -1.876098 1 0.980418 -2.177524 0.171552 6 3.141174 -0.600705 -0.408470 6 3.425322 -0.983526 0.909445 6 4.738965 -1.203214 1.306237 6 5.786781 -1.048635 0.400761 6 5.514679 -0.663000 -0.908477 6 4.202137 -0.433710 -1.306924 1 2.618149 -1.085908 1.629100 1 4.944906 -1.494161 2.331345 1 6.810549 -1.223484 0.715959 1 6.323842 -0.539013 -1.621228 1 3.991900 -0.136798 -2.330432 7 -0.357621 -1.504485 -1.235290 8 -0.672909 -0.595848 -2.066857 8 -1.125115 -2.457667 -1.010708 1 1.466673 1.151504 1.033954 6 -0.364804 2.364291 -1.674481 1 -1.290547 1.950476 -2.076088 1 0.410942 2.069133 -2.383782 6 -0.436987 3.894696 -1.609760 1 -0.679497 4.299588 -2.596330 1 -1.202696 4.243286 -0.909980 1 0.515032 4.328201 -1.294977 8 -3.319375 -1.355630 0.773960 8 -3.379180 -0.753884 -1.868325

1 -3.738533 -1.271832 -0.110614 1 -2.818665 -0.985439 -1.900102 6 -3.756452 -2.994545 0.828176 1 -3.462048 -3.358862 1.813768 1 -4.815111 -3.230785 0.669551 1 -3.152701 -3.506136 0.070829 6 -4.601587 -1.084713 -2.753985 1 -5.619949 -0.797162 -2.482729 1 -4.336269 -0.577311 -3.689053 1 -4.580045 -2.168309 -2.927251	1 -3.327955 -1.224397 -0.209815 1 -2.407919 -0.746511 -2.054247 6 -3.702617 -2.694055 1.050372 1 -3.635157 -2.839591 2.130216 1 -4.737879 -2.874825 0.738825 1 -3.039713 -3.408737 0.553807 6 -3.965892 -1.727970 -2.709457 1 -5.011783 -1.839814 -2.413972 1 -3.937822 -1.413753 -3.760236 1 -3.460290 -2.695250 -2.615630
s-re Et =-1341.7771385 (-1342.1349224) (-1342.1602479) NImag= 1(-322.21 cm^{-1})	
6 1.156681 -0.374597 1.386459 6 -0.219718 -0.161601 1.629397 6 -0.655951 1.070885 2.377950 7 -1.174607 -1.025601 1.242246 6 -0.901475 -2.338922 0.646765 6 -2.289104 -2.992556 0.518601 6 -3.124936 -2.289364 1.582647 6 -2.606021 -0.858699 1.535942 6 -0.170111 -2.319541 -0.700647 8 -0.649755 -1.560331 -1.670203 8 0.811514 -3.010337 -0.864925 1 -2.938954 -2.723969 2.570489 1 -4.196664 -2.343940 1.381457 1 -2.710135 -2.784933 -0.468261 1 -2.227792 -4.074648 0.646435 1 -0.252247 -2.909606 1.318917 1 -2.745152 -0.339594 2.483483 1 -3.091425 -0.271690 0.751198 1 -1.513089 -1.088004 -1.482515 1 -1.618537 1.417581 1.999403 1 0.058688 1.866650 2.147311 6 1.616826 0.720814 -0.370485 1 0.913743 0.127405 -0.942973 6 1.261364 2.074942 -0.252387 1 1.422021 -1.347581 0.980422 7 -0.043956 2.438000 -0.406161 8 -0.391724 3.627305 -0.380727 8 -0.896959 1.505768 -0.553171 6 3.035245 0.349412 -0.566012 6 3.337374 -0.869820 -1.188572 6 4.656574 -1.236963 -1.428091 6 5.699938 -0.398219 -1.046630 6 5.414379 0.812139 -0.419364 6 4.096635 1.181252 -0.179858 1 2.532094 -1.536806 -1.482197 1 4.867198 -2.183133 -1.916058 1 6.729658 -0.684983 -1.235139 1 6.220609 1.472961 -0.116903 1 3.895622 2.126499 0.312833 1 1.928265 2.900553 -0.063177 6 2.174623 0.165353 2.363560 1 3.182915 -0.019250 1.988372 1 2.075459 1.244225 2.520103 1 2.099880 -0.323453 3.341652 6 -0.720756 0.878543 3.898161 1 0.253609 0.617821 4.316041 1 -1.052224 1.805622 4.373748 1 -1.422729 0.088649 4.182747	

1	-3.306569	0.328121	-1.439128
8	-3.088026	-0.589661	-1.748827
8	-3.480886	1.860534	-0.739768
1	-2.503125	1.991434	-0.640688
6	-3.342550	-0.668332	-3.139337
1	-3.013830	-1.650832	-3.482856
1	-4.413089	-0.563429	-3.351634
1	-2.791424	0.095789	-3.700085
6	-4.034546	2.982619	-1.395023
1	-5.112239	2.823839	-1.477625
1	-3.858374	3.899928	-0.822610
1	-3.622362	3.121693	-2.402840

Table S26. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1379.8835518 (-1380.2472712) (-1380.2735435) NImag=1(-291.89 cm^{-1})				*a-si (II)* Et = -1379.883306 (-1380.2470597) (-1380.273237) NImag=1(-293.67 cm^{-1})			
6	3.706694	-1.995440	0.132528	6	3.721385	-2.000342	-0.266142
6	2.526963	-1.319146	0.469256	6	2.563763	-1.382315	0.224756
6	2.533165	-0.497090	1.605241	6	2.606179	-0.806355	1.503101
6	3.687176	-0.346800	2.364111	6	3.775532	-0.838539	2.253909
6	4.857268	-1.016420	2.010110	6	4.922149	-1.448492	1.749506
6	4.862029	-1.845945	0.893505	6	4.889963	-2.033992	0.487242
6	1.313709	-1.519611	-0.357898	6	1.335121	-1.399818	-0.598835
6	0.077067	-1.645926	0.312315	6	0.103328	-1.626609	0.041401
7	-1.012977	-2.093894	-0.358133	7	-0.991197	-1.948179	-0.696022
8	-0.960511	-2.351549	-1.580067	8	-0.944384	-1.984634	-1.943255
8	-2.105746	-2.197218	0.280647	8	-2.079581	-2.163612	-0.080950
6	1.202268	-0.099588	-1.763027	6	1.245607	0.310228	-1.725920
6	2.480053	-0.137966	-2.584724	6	2.555875	0.429032	-2.477729
6	0.861544	1.076928	-1.061910	6	0.855234	1.325362	-0.829345
6	1.919653	2.055478	-0.623719	6	1.908550	2.181749	-0.178496
7	-0.413516	1.320132	-0.720567	7	-0.438770	1.487930	-0.501924
6	-0.822733	2.372182	0.234286	6	-0.923705	2.277022	0.650395
6	-2.273797	2.719680	-0.147212	6	-2.382124	2.631740	0.312325
6	-2.483258	2.064325	-1.515405	6	-2.531688	2.288169	-1.172569
6	-1.593816	0.831198	-1.450041	6	-1.578044	1.116312	-1.354892
6	-0.593233	1.865932	1.670107	6	-0.661478	1.468735	1.935505
8	-1.429058	0.979106	2.177425	8	-1.503203	0.513798	2.284007
8	0.378860	2.238340	2.292534	8	0.349328	1.678434	2.571319
1	-2.149588	2.726966	-2.320645	1	-2.219588	3.128882	-1.800571
1	-3.524858	1.794145	-1.698683	1	-3.553668	2.014471	-1.441217
1	-2.983399	2.311267	0.575156	1	-3.086784	2.047663	0.907277
1	-2.415905	3.802006	-0.168631	1	-2.576980	3.685362	0.522848
1	-0.168059	3.236872	0.123799	1	-0.321661	3.179185	0.756860
1	-1.301095	0.450060	-2.426490	1	-1.245024	0.978164	-2.382283
1	-2.088852	0.028825	-0.902513	1	-2.043322	0.190009	-1.015940
1	1.447503	-2.238434	-1.164847	1	1.441635	-1.931034	-1.542210
1	-0.105766	-1.368348	1.337992	1	-0.076671	-1.538433	1.100889
1	1.638877	0.040915	1.901746	1	1.728413	-0.320576	1.918265
1	3.669070	0.298179	3.236596	1	3.787378	-0.383730	3.239116
1	5.756589	-0.896300	2.605598	1	5.832879	-1.471762	2.339286
1	5.762835	-2.384084	0.616026	1	5.773515	-2.522855	0.089205
1	3.710951	-2.665497	-0.722426	1	3.697696	-2.473157	-1.243725
1	0.367120	-0.633670	-2.211577	1	0.444761	-0.142194	-2.306900
1	1.912791	2.161847	0.466054	1	2.310989	1.660621	0.697580

1 -2.251269 0.751944 1.650609 8 -3.827427 0.308939 1.376847 1 -4.048311 -0.195227 0.553325 6 -4.176800 -0.508312 2.484046 1 -5.259582 -0.675042 2.519780 1 -3.659022 -1.472016 2.445772 1 -3.875789 0.019874 3.390266 8 -4.238059 -1.167618 -0.842924 1 -3.461040 -1.749080 -0.640348 6 -5.363138 -1.964202 -1.144103 1 -6.212455 -1.295925 -1.303389 1 -5.204306 -2.546249 -2.059649 1 -5.612975 -2.656683 -0.329995 1 1.626782 3.039733 -1.018835 6 3.319139 1.710925 -1.133113 6 3.254122 1.179049 -2.557632 1 3.942922 2.608349 -1.073225 1 3.780137 0.961623 -0.482967 1 2.759233 1.917421 -3.202735 1 4.259713 1.028876 -2.963330 1 2.226747 -0.404462 -3.616885 1 3.137539 -0.937074 -2.220668	1 -2.337210 0.398764 1.740899 8 -3.918984 0.012047 1.404948 1 -4.112994 -0.345547 0.501904 6 -4.264717 -0.989082 2.349404 1 -5.341745 -1.191927 2.327540 1 -3.713929 -1.917254 2.165733 1 -4.001661 -0.612050 3.339126 8 -4.239377 -1.042198 -1.055121 1 -3.443414 -1.621021 -0.939810 6 -5.325090 -1.813156 -1.521779 1 -6.194879 -1.156113 -1.592722 1 -5.120959 -2.225939 -2.516804 1 -5.569314 -2.641633 -0.844320 1 1.476862 3.108526 0.202684 6 3.040010 2.504221 -1.158329 6 3.629896 1.231812 -1.747143 1 2.933073 -0.572015 -2.720114 1 2.347359 0.903755 -3.447298 1 4.444556 1.469999 -2.439396 1 4.062934 0.631396 -0.941526 1 3.807876 3.081399 -0.633183 1 2.654778 3.146007 -1.961339
a-re Et = -1379.8807824 (-1380.24553) (-1380.2759758) NImag= 1(-295.24 cm^{-1})	*a-re (II)* Et = -1379.881875 (-1380.2455464) (-1380.275198) NImag= 1(-308.50 cm^{-1})
6 -3.288083 1.592881 0.887962 6 -2.060519 0.918913 0.957539 6 -1.967937 -0.201955 1.792808 6 -3.068464 -0.648015 2.516697 6 -4.286291 0.020097 2.422828 6 -4.389305 1.145769 1.610036 6 -0.861953 1.362713 0.200449 6 -0.874492 0.537519 -1.583202 6 -2.150261 0.918036 -2.317469 6 -0.709055 2.756608 -0.010541 7 0.489458 3.263016 -0.402372 8 0.672269 4.482104 -0.485404 6 -0.602960 -0.834852 -1.352341 6 -1.717142 -1.833076 -1.208356 7 0.658984 -1.268612 -1.203573 6 1.018082 -2.631186 -0.775448 6 2.545557 -2.684738 -0.937612 6 2.823869 -1.662149 -2.034714 6 1.836208 -0.545464 -1.723980 6 0.560359 -2.972636 0.648538 8 0.898619 -2.131843 1.619761 8 -0.088326 -3.967113 0.866046 8 1.422368 2.432397 -0.692022 1 2.614732 -2.087263 -3.022003 1 3.856812 -1.308066 -2.029249 1 3.036669 -2.369891 -0.012976 1 2.878900 -3.695368 -1.179690 1 0.534572 -3.366321 -1.425349 1 1.549203 0.027901 -2.606394 1 2.217021 0.157623 -0.982033 1 -1.482310 3.496653 0.117858 1 0.056760 0.867141 0.508171 1 -1.020878 -0.724616 1.888853 1 -2.968957 -1.517766 3.158036 1 -5.146138 -0.327462 2.986387 1 -5.329731 1.683286 1.540714	6 -3.111814 1.939897 0.600808 6 -1.934824 1.197363 0.773622 6 -1.847855 0.341212 1.879814 6 -2.905137 0.222093 2.776883 6 -4.071899 0.955394 2.584911 6 -4.168922 1.817076 1.494327 6 -0.773186 1.325565 -0.138267 6 -1.009074 0.039372 -1.691500 6 -2.363672 0.278937 -2.326072 6 -0.531465 2.591970 -0.712893 7 0.694855 2.889211 -1.227908 8 0.967940 4.039185 -1.591015 6 -0.711334 -1.235874 -1.159344 6 -1.826172 -2.098284 -0.637998 7 0.556044 -1.667266 -1.065361 6 0.981602 -2.853017 -0.303693 6 2.498272 -2.911982 -0.535577 6 2.666287 -2.274253 -1.911282 6 1.661081 -1.130700 -1.882481 6 0.588281 -2.794314 1.177000 8 0.963490 -1.724179 1.872656 8 -0.050845 -3.684244 1.682378 8 1.552401 1.947454 -1.313657 1 2.408302 -2.987493 -2.701184 1 3.682946 -1.919317 -2.091036 1 3.021638 -2.307855 0.210407 1 2.865368 -3.938069 -0.474352 1 0.503614 -3.752182 -0.703972 1 1.282458 -0.869844 -2.873079 1 2.065394 -0.222985 -1.433014 1 -1.235099 3.407904 -0.751866 1 0.127168 0.827352 0.211567 1 -0.937055 -0.225846 2.049532 1 -2.811048 -0.444588 3.627951 1 -4.897866 0.862989 3.282690 1 -5.071417 2.400181 1.340472

1 -3.388602 2.480431 0.272366 1 1.581009 -1.437759 1.385787 1 -0.000670 1.116946 -1.869061 1 -1.725797 -2.261573 -0.200091 8 2.945768 -0.519910 1.576702 1 3.147560 0.394411 1.237342 6 3.326267 -0.569579 2.941398 1 4.413303 -0.482592 3.051309 1 2.848148 0.225560 3.524056 1 3.009747 -1.535275 3.339378 8 3.507209 1.953839 0.813562 1 2.746700 2.318022 0.290736 6 4.709658 2.291648 0.156249 1 4.762413 1.876107 -0.858702 1 4.831617 3.378502 0.092439 1 5.537298 1.884665 0.741589 1 -1.488127 -2.675308 -1.876311 6 -3.095963 -1.265433 -1.550773 6 -2.999777 -0.288238 -2.714345 1 -1.881330 1.494202 -3.209086 1 -2.749533 1.594125 -1.697090 1 -2.550588 -0.793440 -3.580051 1 -3.995787 0.042873 -3.024959 1 -3.516361 -0.755881 -0.678795 1 -3.766795 -2.097658 -1.785069	1 -3.207834 2.617712 -0.240732 1 1.626394 -1.119987 1.434539 1 -0.185708 0.511562 -2.219567 1 -2.120343 -1.745425 0.359431 8 3.011359 -0.182162 1.334882 1 3.247099 0.660440 0.858320 6 3.671108 -0.179811 2.586647 1 4.759429 -0.143565 2.461776 1 3.358386 0.665356 3.212024 1 3.407520 -1.104436 3.103540 8 3.763860 2.076455 0.110013 1 3.045444 2.187436 -0.561277 6 3.785975 3.244444 0.907983 1 3.928108 4.138771 0.292149 1 2.863877 3.369377 1.491025 1 4.627429 3.160100 1.599410 1 -1.501806 -3.132351 -0.510210 6 -3.038658 -2.026625 -1.573290 6 -3.491033 -0.584978 -1.761417 1 -2.777105 -2.472531 -2.541439 1 -3.846264 -2.634243 -1.152864 1 -2.612512 1.344274 -2.245907 1 -2.267698 0.082834 -3.403280 1 -3.820782 -0.188953 -0.796469 1 -4.355333 -0.541216 -2.432853
s-si Et = -1379.885563 (-1380.2488813) (-1380.2741884) NImag=1(-298.75 cm^{-1})	*s-si (II)* Et = -1379.8848448 (-1380.2481188) (-1380.2736599) NImag=1(-309.61 cm^{-1})
6 -1.592449 1.130799 -0.643195 6 -0.393970 1.788342 -0.319781 7 0.786655 1.315296 -0.767795 6 0.929239 0.611484 -2.061881 6 2.362716 0.946209 -2.533237 6 2.839409 2.067017 -1.605724 6 2.101575 1.767645 -0.310246 6 0.624994 -0.897478 -2.024506 8 1.491750 -1.726515 -1.478150 8 -0.401291 -1.310208 -2.524965 1 2.537400 3.047826 -1.988169 1 3.923547 2.066525 -1.476958 1 3.020214 0.081970 -2.425036 1 2.362551 1.232426 -3.586903 1 0.179346 1.021497 -2.741787 1 2.020113 2.615220 0.364064 1 2.581568 0.964738 0.256549 1 2.329220 -1.341945 -1.087213 6 -1.643571 -0.302081 0.892327 6 -0.459459 -1.051995 0.927853 6 -2.906393 1.878360 -0.579281 1 -1.733743 0.431840 1.688309 1 -0.324402 -2.012681 0.458142 6 -2.899047 -1.009409 0.547922 6 -2.978373 -1.908368 -0.524605 6 -4.163690 -2.585227 -0.784207 6 -5.286756 -2.379122 0.014946 6 -5.220329 -1.482777 1.076968 6 -4.036718 -0.799627 1.336888 1 -2.117697 -2.059859 -1.169506 1 -4.210988 -3.276123 -1.619908 1 -6.209624 -2.911199 -0.192950 1 -6.089301 -1.313817 1.705047	6 -1.517760 1.131754 -0.625837 6 -0.282701 1.749495 -0.342252 7 0.869365 1.258372 -0.833537 6 0.946671 0.477049 -2.090033 6 2.379509 0.712098 -2.608748 6 2.872086 1.942288 -1.848967 6 2.192674 1.799400 -0.495278 6 0.575748 -1.012812 -1.979103 8 1.403477 -1.848380 -1.387008 8 -0.460455 -1.404832 -2.475764 1 2.537841 2.863689 -2.337904 1 3.960293 1.973988 -1.765474 1 3.022866 -0.138727 -2.375516 1 2.379263 0.843321 -3.692752 1 0.204060 0.890231 -2.777558 1 2.101905 2.742236 0.037543 1 2.720035 1.103755 0.165262 1 2.253614 -1.476322 -1.008351 6 -1.661529 -0.246520 0.899340 6 -0.509874 -1.047930 0.994825 6 -2.795694 1.957680 -0.593341 1 -1.742967 0.505521 1.679172 1 -0.402479 -2.031605 0.567718 6 -2.937036 -0.926561 0.563048 6 -3.041080 -1.839490 -0.494800 6 -4.243798 -2.489838 -0.742503 6 -5.360210 -2.243154 0.054472 6 -5.268696 -1.334911 1.104009 6 -4.067134 -0.678877 1.352014 1 -2.184455 -2.026243 -1.135713 1 -4.309714 -3.192413 -1.567165 1 -6.296687 -2.754510 -0.144504 1 -6.131239 -1.135681 1.732083

1 -3.985705 -0.106352 2.171753 7 0.627835 -0.603967 1.618560 8 0.628163 0.512552 2.176847 8 1.640628 -1.360083 1.678521 1 -1.539138 0.383643 -1.430834 6 -0.425012 2.988506 0.598138 1 -0.316147 2.636056 1.629420 8 3.935640 -1.266280 -0.636263 8 3.997084 -0.191998 1.819514 1 4.070059 -0.863197 0.259227 1 3.078121 -0.514795 2.005371 6 4.343006 -2.622574 -0.560895 1 4.126122 -3.087720 -1.523942 1 5.419868 -2.698689 -0.370178 1 3.797779 -3.164602 0.219714 6 4.836420 -0.497402 2.911006 1 5.847580 -0.170997 2.657233 1 4.519613 0.033177 3.816861 1 4.861985 -1.573070 3.128593 1 0.429299 3.639669 0.398418 6 -1.708578 3.808621 0.448286 6 -2.947200 2.928891 0.523619 1 -3.072449 2.368625 -1.549611 1 -3.727122 1.164365 -0.465063 1 -2.992220 2.443156 1.506612 1 -3.855859 3.533170 0.432444 1 -1.725237 4.580613 1.224698 1 -1.696867 4.332609 -0.516162	1 -3.995511 0.020249 2.180626 7 0.579366 -0.594905 1.670699 8 0.599185 0.557171 2.156471 8 1.573213 -1.370197 1.797139 1 -1.497175 0.373293 -1.403117 6 -0.223676 2.979935 0.532894 1 0.424461 2.792354 1.390225 8 3.849323 -1.423734 -0.557138 8 3.888038 -0.134866 1.779962 1 3.983425 -0.949175 0.303078 1 2.982037 -0.476241 2.006399 6 4.204577 -2.782904 -0.359831 1 3.984262 -3.319852 -1.283946 1 5.275064 -2.880594 -0.144978 1 3.627915 -3.234963 0.454391 6 4.739971 -0.267240 2.895940 1 5.735860 0.070616 2.599987 1 4.398104 0.354130 3.732159 1 4.813297 -1.306480 3.241409 1 0.239329 3.784143 -0.057975 6 -1.597267 3.450867 1.001860 6 -2.584971 3.405066 -0.153925 1 -1.951427 2.816693 1.822921 1 -1.502783 4.462446 1.409313 1 -3.543588 3.853283 0.126326 1 -2.189070 4.001789 -0.986523 1 -3.528351 1.484488 0.070337 1 -3.250423 1.928657 -1.589624
s-re Et = -1379.8833053 (-1380.2467511) (-1380.2732569) NImag= 1(-293.95 cm^{-1})	*s-re (II)* Et = -1379.8833787 (-1380.2468782) (-1380.272483) NImag= 1(-286.94 cm^{-1})
6 1.258192 -0.481649 1.245395 6 -0.029593 -0.110399 1.686369 6 -0.143989 1.207237 2.398248 7 -1.121141 -0.866959 1.470588 6 -1.060029 -2.237144 0.937410 6 -2.506668 -2.754742 1.037907 6 -3.149233 -1.870160 2.100377 6 -2.488990 -0.517444 1.872407 6 -0.514323 -2.385308 -0.491263 8 -1.090563 -1.709041 -1.468171 8 0.416357 -3.131643 -0.706658 1 -2.911720 -2.234757 3.105146 1 -4.235338 -1.817796 2.002995 1 -3.026376 -2.609705 0.088037 1 -2.525738 -3.818786 1.280375 1 -0.379302 -2.825240 1.560807 1 -2.487053 0.085005 2.779563 1 -2.979327 0.061363 1.083817 1 -1.910369 -1.184499 -1.232152 1 -0.029027 1.991052 1.636268 6 1.446812 0.547217 -0.623621 1 0.672726 -0.087965 -1.038234 6 1.101526 1.908527 -0.597979 1 1.355944 -1.474125 0.814295 7 -0.210476 2.282447 -0.696711 8 -0.523950 3.476046 -0.817752 8 -1.095623 1.374230 -0.641080 6 2.824338 0.142795 -0.976192 6 3.034007 -1.131231 -1.522789 6 4.307043 -1.539992 -1.901900	6 1.189011 -0.445000 1.149918 6 -0.158963 -0.242748 1.502505 6 -0.374178 0.949749 2.379150 7 -1.173647 -1.059517 1.174021 6 -0.981459 -2.347389 0.499674 6 -2.389753 -2.963756 0.463866 6 -3.093257 -2.327906 1.658650 6 -2.548600 -0.904352 1.668373 6 -0.357810 -2.270979 -0.898609 8 -0.914794 -1.474112 -1.793818 8 0.610501 -2.947304 -1.168776 1 -2.816576 -2.840679 2.585780 1 -4.181145 -2.350519 1.568402 1 -2.902452 -2.672182 -0.455928 1 -2.345304 -4.053478 0.506054 1 -0.292053 -2.963115 1.088130 1 -2.546718 -0.477838 2.672570 1 -3.118111 -0.236662 1.014827 1 -1.755148 -1.010164 -1.508757 1 0.108990 1.792953 1.867541 6 1.512786 0.713155 -0.625913 1 0.773630 0.122988 -1.154358 6 1.161687 2.054588 -0.432133 1 1.461457 -1.398511 0.707151 7 -0.156908 2.425479 -0.477441 8 -0.486712 3.617194 -0.418646 8 -1.023566 1.504142 -0.554833 6 2.918853 0.347026 -0.898246 6 3.186887 -0.853428 -1.571497 6 4.492702 -1.221610 -1.872196

6	5.396534	-0.688964	-1.736995	6	5.556504	-0.403046	-1.502080
6	5.203840	0.575609	-1.186442	6	5.304160	0.788840	-0.827572
6	3.931406	0.987110	-0.808105	6	3.999162	1.160426	-0.528333
1	2.191368	-1.805855	-1.646000	1	2.364109	-1.504860	-1.851816
1	4.446115	-2.527903	-2.329013	1	4.677739	-2.153002	-2.397585
1	6.390390	-1.008583	-2.033792	1	6.576223	-0.691122	-1.737229
1	6.046903	1.246045	-1.052562	1	6.126566	1.434289	-0.535557
1	3.802250	1.976238	-0.381215	1	3.825062	2.093844	-0.003788
1	1.788415	2.739598	-0.588677	1	1.840610	2.880396	-0.291967
6	2.458554	-0.090076	2.088340	6	2.188761	0.155557	2.121797
1	-3.645401	0.298755	-1.199352	1	-3.533354	0.398284	-1.229055
8	-3.496732	-0.666636	-1.383131	8	-3.349054	-0.500761	-1.606886
8	-3.667837	1.925287	-0.760730	8	-3.621656	1.909205	-0.466841
1	-2.680679	1.980668	-0.706740	1	-2.638353	2.019781	-0.450261
6	-3.913677	-0.941110	-2.707693	6	-3.715249	-0.497203	-2.974345
1	-3.672888	-1.983600	-2.923788	1	-3.416254	-1.456325	-3.400926
1	-4.995606	-0.802002	-2.818243	1	-4.799318	-0.383785	-3.093391
1	-3.396976	-0.309143	-3.439825	1	-3.210211	0.300855	-3.531351
6	-4.137096	2.957337	-1.603315	6	-4.203994	3.055552	-1.052005
1	-5.227746	2.899144	-1.627108	1	-5.286562	2.910253	-1.064507
1	-3.846001	3.941074	-1.219693	1	-3.978027	3.954634	-0.468188
1	-3.758292	2.862357	-2.629339	1	-3.859605	3.217972	-2.081400
1	-1.122952	1.360773	2.849360	1	-1.420685	1.223971	2.504192
6	0.966824	1.400970	3.434674	6	0.338714	0.756121	3.736972
6	2.328062	1.267131	2.767863	6	1.683592	0.029153	3.564241
1	0.863239	0.659659	4.237213	1	3.154098	-0.341438	2.001746
1	0.852490	2.387217	3.896465	1	2.359101	1.218812	1.898862
1	3.134017	1.397941	3.497824	1	2.423690	0.426100	4.267037
1	2.438804	2.066156	2.025394	1	1.567684	-1.034909	3.799057
1	3.364817	-0.127106	1.476398	1	0.488774	1.746030	4.179325
1	2.590182	-0.864614	2.858632	1	-0.309085	0.202287	4.424439

Table S27. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway (**L_1** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1226.0715115 (-1226.3891709) (-1226.414941) NImag=1(-297.7 cm^{-1})				*a-re* Et = -1226.0649675 (-1226.3834067) (-1226.410066) NImag= 1(-290.50 cm^{-1})			
6	-3.741415	-1.788316	0.434135	6	-3.307008	-1.698322	-0.225691
6	-2.703181	-1.085104	-0.190764	6	-2.944009	-0.344473	-0.234232
6	-3.039616	-0.121161	-1.153317	6	-3.925250	0.613007	0.054580
6	-4.368010	0.127947	-1.474002	6	-5.234644	0.230391	0.324288
6	-5.389079	-0.579387	-0.842162	6	-5.582691	-1.116947	0.322564
6	-5.071049	-1.540976	0.111655	6	-4.613133	-2.080528	0.049455
6	-1.304339	-1.405586	0.157287	6	-1.580279	0.110083	-0.559858
6	-0.323903	-1.353220	-0.848473	6	-0.602911	-0.204245	1.404157
7	0.923505	-1.820936	-0.613931	6	-1.387055	0.731868	2.288004
8	1.198161	-2.475117	0.408777	6	-0.876166	-0.540766	-1.571498
8	1.845847	-1.536531	-1.461668	7	0.310156	-0.063879	-2.041763
6	-0.753338	-0.133607	1.738581	8	0.951991	-0.701680	-2.885928
6	-1.962185	-0.048605	2.629725	6	0.764582	0.000253	1.156028
6	-0.240723	0.987736	1.056078	6	1.414835	1.301874	1.542511
6	-1.124340	2.145445	0.682330	6	2.101709	1.220205	2.911880
6	-1.064851	3.248134	1.750347	7	1.512804	-0.977179	0.602423
7	1.045824	0.998290	0.673870	6	2.978729	-0.979805	0.426476
6	1.635581	1.987549	-0.257550	6	3.181840	-2.169218	-0.516294
6	3.139445	1.690547	-0.199636	6	2.213176	-3.200603	0.048696
6	3.344381	1.159736	1.212481	6	1.013270	-2.364856	0.502698
6	2.114618	0.287743	1.414549	6	3.768793	0.231557	-0.094987
6	1.084359	1.968294	-1.692795	8	3.336987	0.938779	-1.124052
8	1.199795	0.864607	-2.414615	8	4.858054	0.423709	0.392885
8	0.598799	2.973667	-2.159373	8	0.760794	1.041822	-1.582199
1	3.368354	1.979160	1.939068	1	2.665143	-3.712112	0.903781
1	4.256552	0.568660	1.297889	1	1.927073	-3.959685	-0.682015
1	3.407619	0.910508	-0.917595	1	2.893541	-1.877630	-1.531362
1	3.724633	2.581944	-0.432855	1	4.222192	-2.498107	-0.524275
1	1.433410	2.996973	0.110181	1	3.447851	-1.200146	1.391928
1	1.815113	0.195411	2.460036	1	0.633075	-2.687919	1.479241
1	2.286567	-0.714253	1.014372	1	0.190909	-2.409429	-0.210418
1	-2.782402	0.523828	2.191041	1	-1.416090	1.752978	1.894510
1	-2.345979	-1.049407	2.846622	1	-2.418229	0.383578	2.372661
1	-1.708103	0.409394	3.593285	1	-0.978356	0.780513	3.304253
1	-1.188995	-2.223645	0.863089	1	-1.168479	-1.479143	-2.018215
1	-0.442516	-0.826182	-1.781180	1	-1.409881	1.173979	-0.436242
1	-2.259868	0.440226	-1.658178	1	-3.653161	1.663962	0.052781
1	-4.606597	0.875864	-2.223112	1	-5.983282	0.986581	0.537047
1	-6.425699	-0.383732	-1.096166	1	-6.603139	-1.417238	0.536899
1	-5.857956	-2.104094	0.602825	1	-4.876851	-3.133223	0.053689
1	-3.499090	-2.552350	1.166866	1	-2.558510	-2.459477	-0.426018
1	-0.000731	-0.838898	2.080838	1	2.381016	0.813188	-1.377281
1	-2.152324	1.791785	0.580946	1	-0.943248	-1.233728	1.419964
1	-0.842540	2.568712	-0.283725	1	0.649422	2.078506	1.554398
1	-0.050541	3.640741	1.866963	1	2.134703	1.622700	0.791011
1	-1.713579	4.079220	1.461926	1	2.953625	0.535774	2.900226
1	-1.396133	2.880946	2.725165	1	2.481203	2.206693	3.190213
1	1.558118	0.051248	-1.956637	1	1.409411	0.892139	3.692255
1	3.502802	-1.771332	-0.662174	1	-0.049069	2.580983	-0.859635
8	4.343159	-1.639232	-0.182949	8	-0.585444	3.203929	-0.337019
6	4.761946	-2.893113	0.297491	6	-0.816873	4.357630	-1.113968
1	5.055086	-3.575148	-0.514309	1	-1.352564	4.134987	-2.046849

1 5.639192 -2.730897 0.930025 1 3.988403 -3.389649 0.898073	1 -1.434615 5.033685 -0.518487 1 0.115031 4.879893 -1.367029
s-si Et = -1226.0672325 (-1226.3849045) (-1226.4108838) NImag=1(-291.9 cm^{-1})	*s-re* Et = -1226.0678369 (-1226.3866036) (-1226.4132355) NImag = 1(-332.16 cm^{-1})
6 1.025680 1.454343 0.249499 6 -0.312181 1.623967 -0.131679 7 -1.298339 0.965986 0.517262 6 -1.173866 0.523631 1.922187 6 -2.629182 0.434807 2.432968 6 -3.436926 1.264395 1.440015 6 -2.715757 1.000704 0.127874 6 -0.439956 -0.796400 2.204244 8 -0.929834 -1.926010 1.700016 8 0.491576 -0.811200 2.976006 1 -3.389261 2.329304 1.692504 1 -4.487155 0.968831 1.398362 1 -2.964733 -0.605556 2.410731 1 -2.701476 0.784303 3.464539 1 -0.605331 1.282957 2.464977 1 -2.902354 1.763627 -0.622344 1 -3.006155 0.036616 -0.306241 1 -1.388640 -1.841146 0.820860 6 1.526820 -0.264275 -0.994400 6 0.575434 -1.256614 -0.753351 6 2.093208 2.464029 -0.081325 1 1.959356 3.390583 0.489713 1 3.076473 2.065656 0.176131 1 2.118166 2.735034 -1.140975 1 1.391676 0.308386 -1.906718 1 0.706601 -2.069758 -0.058295 6 2.922718 -0.483995 -0.574299 6 3.247614 -1.085232 0.650470 6 4.575338 -1.311131 0.989651 6 5.599007 -0.943134 0.118119 6 5.287874 -0.336678 -1.095128 6 3.960072 -0.102030 -1.434305 1 2.463394 -1.355528 1.351549 1 4.811742 -1.773550 1.942337 1 6.634668 -1.123532 0.387368 1 6.078433 -0.044838 -1.778872 1 3.719246 0.366538 -2.384048 7 -0.663154 -1.170254 -1.317112 8 -0.916240 -0.331711 -2.195489 8 -1.570435 -1.970631 -0.900839 1 1.200280 0.917013 1.177686 6 -0.667742 2.534467 -1.281610 1 -1.439517 2.085846 -1.905713 1 0.207246 2.628687 -1.927054 6 -1.093032 3.925752 -0.798375 1 -1.317760 4.569584 -1.653186 1 -1.988039 3.880832 -0.170323 1 -0.302760 4.405429 -0.214426 1 -3.217791 -1.531387 -1.773334 8 -4.173179 -1.341639 -1.807790 6 -4.843590 -2.513222 -1.419321 1 -5.911793 -2.283471 -1.375370 1 -4.705313 -3.336116 -2.135747 1 -4.533048 -2.875238 -0.427801	6 -0.645233 0.363281 1.222246 6 0.761434 0.227890 1.143845 6 1.421672 -1.012386 1.682317 7 1.551270 1.177177 0.614076 6 1.063309 2.474607 0.149846 6 2.344162 3.260967 -0.208056 6 3.443778 2.553776 0.577019 6 3.017717 1.093947 0.523280 6 0.160409 2.450974 -1.081774 8 0.372668 1.497265 -1.989164 8 -0.638070 3.336074 -1.267466 1 3.460499 2.901755 1.615157 1 4.436305 2.709900 0.149541 1 2.539809 3.176744 -1.281621 1 2.234239 4.320013 0.028073 1 0.500539 2.969173 0.947689 1 3.423463 0.504916 1.343378 1 3.317987 0.599291 -0.406631 1 0.812236 0.686807 -1.636068 1 2.285388 -1.282869 1.069432 1 0.707629 -1.835140 1.578631 6 -1.442386 -0.654051 -0.478406 1 -1.014875 0.085590 -1.138654 6 -0.907375 -1.943361 -0.616902 1 -1.042786 1.341439 0.958197 7 0.357841 -2.113263 -1.092866 8 0.827846 -3.247177 -1.248862 8 1.078489 -1.085547 -1.337941 6 -2.890364 -0.459510 -0.267418 6 -3.461384 0.762498 -0.651041 6 -4.824499 0.988108 -0.504254 6 -5.643040 -0.001964 0.032883 6 -5.088394 -1.218687 0.423001 6 -3.725398 -1.445159 0.277106 1 -2.829613 1.537964 -1.076015 1 -5.247883 1.937651 -0.814909 1 -6.708175 0.172247 0.146112 1 -5.720209 -1.995685 0.841175 1 -3.310433 -2.397322 0.590096 1 -1.401889 -2.867616 -0.364706 6 -1.387036 -0.292347 2.363409 1 -2.462052 -0.149671 2.241778 1 -1.203245 -1.369876 2.418681 1 -1.109602 0.143092 3.330012 6 1.835780 -0.889914 3.154722 1 0.979911 -0.709022 3.808399 1 2.315963 -1.817244 3.477751 1 2.549162 -0.075064 3.311094 1 2.819511 -1.720255 -1.157172 8 3.718677 -1.746278 -0.776779 6 4.300098 -2.988162 -1.097547 1 5.259095 -3.048212 -0.575698 1 3.675793 -3.832579 -0.781303 1 4.493068 -3.091181 -2.174853

Table S28. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway (**L_2** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1341.7643281 (-1342.122819) (-1342.148708) NImag=1(-289.08 cm^{-1})				*a-si (II)* Et = -1341.7689298 (-1342.1478971) NImag=1(-253.99 cm^{-1})			
6	-3.860125	0.660025	-1.661204	6	3.777007	1.222134	-0.300270
6	-2.789164	0.650192	-0.757070	6	2.683526	0.428629	-0.675452
6	-3.071482	0.781823	0.611472	6	2.937029	-0.811074	-1.283357
6	-4.380483	0.915265	1.055023	6	4.239690	-1.236292	-1.508165
6	-5.434677	0.921543	0.143353	6	5.316187	-0.434618	-1.131854
6	-5.170139	0.796643	-1.217033	6	5.080546	0.796961	-0.528460
6	-1.413991	0.541639	-1.270453	6	1.324799	0.946292	-0.448925
6	-0.378927	1.219667	-0.609128	6	0.303182	0.610408	-1.347569
7	0.853449	1.273636	-1.155415	7	-0.921795	1.178281	-1.286306
8	1.097179	0.855084	-2.299899	8	-1.179686	2.160546	-0.551853
8	1.818975	1.738369	-0.424872	8	-1.862913	0.662331	-1.981303
6	-0.940089	-1.559707	-1.355499	6	0.738454	0.284499	1.549503
6	-2.216715	-2.212122	-1.806991	6	1.978291	0.465270	2.376569
6	-0.380320	-1.792371	-0.087542	6	0.184447	-0.967700	1.251561
6	-1.241170	-2.201012	1.076494	6	1.021497	-2.217131	1.285932
6	-1.294774	-3.729179	1.220095	6	0.938436	-2.896597	2.660744
7	0.935756	-1.600836	0.109995	7	-1.111042	-1.058436	0.890346
6	1.591059	-1.623797	1.435918	6	-1.742822	-2.284847	0.357265
6	3.089012	-1.579277	1.104350	6	-3.237837	-1.940044	0.326745
6	3.174458	-2.275545	-0.246780	6	-3.399649	-0.956116	1.477826
6	1.942281	-1.747544	-0.965326	6	-2.142392	-0.107496	1.362412
6	1.180843	-0.508706	2.406533	6	-1.220682	-2.769245	-1.003964
8	1.313884	0.754061	2.024757	8	-1.316176	-1.964880	-2.054548
8	0.794458	-0.788836	3.516922	8	-0.774236	-3.887508	-1.115694
1	3.123031	-3.363501	-0.129871	1	-3.429114	-1.481266	2.438642
1	4.084274	-2.010780	-0.786054	1	-4.295663	-0.344371	1.369668
1	3.432472	-0.546426	0.996504	1	-3.502358	-1.441807	-0.610246
1	3.678672	-2.052684	1.891391	1	-3.850404	-2.839056	0.416362
1	1.343918	-2.556190	1.950448	1	-1.560766	-3.117882	1.041638
1	1.554822	-2.433057	-1.721200	1	-1.819348	0.320347	2.313242
1	2.156316	-0.788890	-1.445237	1	-2.296402	0.708606	0.652217
1	-2.999106	-2.205981	-1.044899	1	2.787691	-0.216523	2.105161
1	-2.617269	-1.701296	-2.686953	1	2.345747	1.488562	2.267185
1	-2.040135	-3.254322	-2.100132	1	1.759934	0.320780	3.442012
1	-1.324855	0.499475	-2.352050	1	1.288376	1.936605	-0.003560
1	-0.466627	1.681598	0.362449	1	0.371666	-0.201869	-2.053241
1	-2.262708	0.783723	1.334865	1	2.113145	-1.452206	-1.580251
1	-4.578107	1.020260	2.116691	1	4.415404	-2.197215	-1.980570
1	-6.456270	1.028786	0.492930	1	6.332752	-0.769363	-1.310850
1	-5.983524	0.811483	-1.935089	1	5.912330	1.430416	-0.237894
1	-3.658274	0.582009	-2.725391	1	3.594355	2.189107	0.158208
1	-0.220992	-1.386068	-2.150644	1	0.036179	1.108333	1.631184
1	-2.250840	-1.814443	0.922823	1	2.059696	-1.954914	1.072841
1	-0.882215	-1.767695	2.012047	1	0.714957	-2.928173	0.516288
1	-0.300879	-4.153390	1.389432	1	-0.087320	-3.188711	2.903906
1	-1.922617	-3.999667	2.072949	1	1.553528	-3.800240	2.667350
1	-1.712841	-4.201354	0.327389	1	1.295448	-2.236222	3.455136
1	1.603977	0.920611	1.088665	1	-1.647736	-1.041971	-1.886399
1	3.437231	1.154860	-1.142089	1	-3.515073	1.198144	-1.290931
8	4.247409	0.649838	-1.343756	8	-4.353718	1.241723	-0.794892

6 4.700454 1.058117 -2.611746 1 5.047012 2.101885 -2.615504 1 5.549029 0.423421 -2.881351 1 3.928422 0.951223 -3.385319 1 1.138365 3.352912 0.464180 8 0.511351 3.913735 0.949746 6 1.084189 4.226586 2.197773 1 1.319662 3.332510 2.789161 1 1.997839 4.831592 2.100369 1 0.350304 4.818351 2.750812	6 -4.763361 2.586456 -0.761414 1 -5.033817 2.966899 -1.757440 1 -5.652621 2.646643 -0.128068 1 -3.994526 3.248472 -0.340462 1 -0.128523 3.271582 0.535877 8 0.540216 3.642553 1.138822 6 0.645231 5.026126 0.893338 1 0.938410 5.249872 -0.141655 1 -0.291257 5.558090 1.108686 1 1.417776 5.418603 1.558651
a-re Et = -1341.7650275 (-1342.1461924) (-1342.1236215) NImag= 1(-237.08 cm^{-1})	*s-si* Et = -1341.7588251(-1342.1465515) (-1342.1176485) NImag=1(-262.66 cm^{-1})
6 -3.307080 1.264659 -0.624055 6 -2.960017 0.041498 -0.030001 6 -3.941515 -0.953617 0.080729 6 -5.236211 -0.728616 -0.372900 6 -5.568127 0.490459 -0.956274 6 -4.598407 1.484614 -1.082220 6 -1.618925 -0.226902 0.502705 6 -0.591025 -0.921876 -1.446693 6 -1.379048 -2.165560 -1.759353 6 -0.878743 0.807572 1.059837 7 0.306081 0.579554 1.687701 8 0.984691 1.539523 2.119610 6 0.767031 -0.968009 -1.115232 6 1.431311 -2.294383 -0.849910 6 2.105320 -2.866072 -2.103828 7 1.503666 0.166963 -1.070222 6 2.971192 0.252986 -0.949334 6 3.183698 1.748878 -0.697792 6 2.184563 2.394929 -1.650480 6 0.996071 1.430733 -1.648446 6 3.774315 -0.557242 0.077667 8 3.345690 -0.701535 1.323067 8 4.867094 -0.948156 -0.258044 8 0.737403 -0.605903 1.830298 1 2.615241 2.472195 -2.653248 1 1.878408 3.389630 -1.323724 1 2.931879 1.976689 0.342728 1 4.220069 2.038548 -0.878866 1 3.423687 -0.017935 -1.910021 1 0.618552 1.239829 -2.660317 1 0.175458 1.819162 -1.047201 1 -1.391283 -2.875787 -0.926379 1 -2.414878 -1.903114 -1.984476 1 -0.984053 -2.693069 -2.636166 1 -1.128125 1.855291 0.974776 1 -1.448682 -1.234376 0.865659 1 -3.680852 -1.902635 0.538888 1 -5.985634 -1.506738 -0.271279 1 -6.577043 0.666581 -1.314837 1 -4.851132 2.434764 -1.541440 1 -2.560408 2.045118 -0.735901 1 2.395735 -0.472995 1.486393 1 -0.953799 -0.014859 -1.915832 1 0.674553 -2.990632 -0.485884 1 2.161420 -2.220227 -0.045015 1 2.951219 -2.254574 -2.428245 1 2.490897 -3.866241 -1.889614 1 1.402238 -2.946381 -2.937614	6 -1.570158 -1.610366 0.008591 6 -0.286592 -1.990639 -0.394743 7 0.792105 -1.690352 0.368170 6 0.698144 -1.487056 1.828783 6 2.112778 -1.806465 2.359639 6 2.762683 -2.622503 1.247325 6 2.182144 -1.992189 -0.008752 6 0.248770 -0.109637 2.335047 8 0.980832 0.958860 2.021921 8 -0.684668 -0.018734 3.097780 1 2.466584 -3.674936 1.314825 1 3.853016 -2.570931 1.266584 1 2.668995 -0.878168 2.517086 1 2.060073 -2.326334 3.317962 1 -0.043289 -2.187852 2.221295 1 2.223850 -2.652464 -0.870289 1 2.709507 -1.069823 -0.279744 1 1.470389 0.899384 1.162987 6 -1.645277 0.416814 -0.944134 6 -0.506924 1.102852 -0.528601 6 -2.818634 -2.271063 -0.507889 1 -2.945625 -3.273254 -0.080557 1 -3.696541 -1.687725 -0.223108 1 -2.834445 -2.377443 -1.596384 1 -1.600060 -0.028838 -1.932615 1 -0.479271 1.794711 0.297249 6 -2.972591 0.847887 -0.482399 6 -3.198227 1.296426 0.827896 6 -4.459584 1.731976 1.211089 6 -5.513966 1.729284 0.299078 6 -5.303576 1.277101 -1.000212 6 -4.044305 0.831519 -1.385000 1 -2.394742 1.277911 1.558187 1 -4.621417 2.070698 2.229011 1 -6.497344 2.072539 0.603455 1 -6.119806 1.269627 -1.715129 1 -3.880309 0.483334 -2.400504 7 0.700543 0.829254 -1.094812 8 0.806434 0.105960 -2.092390 8 1.749615 1.329988 -0.540525 1 -1.667180 -1.199687 1.009737 6 -0.085380 -2.745969 -1.686237 1 0.800696 -2.389633 -2.210055 1 -0.921788 -2.520224 -2.350084 6 -0.014714 -4.259942 -1.457145 1 0.105243 -4.780735 -2.411084 1 0.830308 -4.534817 -0.818571 1 -0.924697 -4.634830 -0.980748

1 -0.081851 -2.326143 1.856614 8 -0.638893 -3.103365 1.676490 6 -0.897373 -3.762195 2.896569 1 -1.419396 -3.118906 3.617791 1 -1.538999 -4.617827 2.674838 1 0.021015 -4.136261 3.367281 1 0.548971 3.141993 1.270124 8 0.149108 3.810931 0.681554 6 -0.019885 5.002004 1.415848 1 -0.649006 4.860755 2.305243 1 0.937910 5.433446 1.737193 1 -0.513951 5.723945 0.761367	1 3.329617 0.610302 -1.441075 8 4.231275 0.249125 -1.473905 6 5.057443 1.150799 -0.771366 1 6.094834 0.910717 -1.019297 1 4.861936 2.193699 -1.046616 1 4.944378 1.062662 0.321224 1 2.410539 3.090978 -0.950322 8 2.860447 3.950901 -0.973387 6 2.673982 4.552848 0.281988 1 1.615465 4.758356 0.502335 1 3.081086 3.953032 1.109453 1 3.203882 5.508574 0.267588
s-re Et = -1341.762487 (-1342.1216339) (-1342.1504095) NImag = 1(-305.12 cm^{-1})	
6 -1.215289 0.937106 1.093948 6 0.180219 1.121443 1.179415 6 0.970419 0.385867 2.228038 7 0.854591 1.944197 0.353969 6 0.207805 2.806856 -0.632847 6 1.352427 3.684482 -1.185088 6 2.412163 3.636130 -0.090035 6 2.301243 2.210321 0.429892 6 -0.456935 2.090102 -1.804763 8 0.097262 0.949900 -2.225066 8 -1.383872 2.593907 -2.388631 1 2.173900 4.347077 0.707977 1 3.413970 3.862928 -0.460288 1 1.746805 3.240643 -2.104742 1 0.998476 4.687889 -1.424362 1 -0.564942 3.414164 -0.151011 1 2.661236 2.102811 1.450912 1 2.858112 1.493088 -0.181958 1 0.649620 0.499879 -1.546787 1 1.963417 0.132673 1.847249 1 0.463428 -0.565886 2.415354 6 -1.499280 -0.860582 -0.129971 1 -1.098733 -0.334003 -0.983146 6 -0.717327 -1.927890 0.327187 1 -1.748455 1.595351 0.411229 7 0.612183 -1.976559 0.043632 8 1.281582 -2.972603 0.381445 8 1.180733 -0.996458 -0.533437 6 -2.968715 -0.941783 -0.127987 6 -3.682827 -0.125587 -1.018023 6 -5.069191 -0.185506 -1.080502 6 -5.769259 -1.058817 -0.251975 6 -5.073334 -1.871228 0.640391 6 -3.687084 -1.812425 0.704569 1 -3.142791 0.555168 -1.670633 1 -5.602634 0.448284 -1.781143 1 -6.852164 -1.107801 -0.301423 1 -5.612375 -2.554779 1.288280 1 -3.163042 -2.449728 1.408928 1 -1.070259 -2.779753 0.885925 6 -2.003485 0.584455 2.331260 1 -3.041755 0.374051 2.068934 1 -1.608500 -0.297675 2.844182 1 -2.013525 1.410591 3.051535 6 1.092942 1.157774 3.548462 1 0.118498 1.352640 4.001678	

1	1.684990	0.575672	4.259400
1	1.592747	2.121379	3.411190
1	2.974997	-1.006095	0.144879
8	3.764615	-0.599820	0.543545
6	4.592446	-1.631563	1.049002
1	5.561378	-1.184861	1.286078
1	4.183033	-2.072260	1.968720
1	4.734216	-2.431865	0.316070
1	2.723300	-3.420020	-0.847891
8	3.472761	-3.643699	-1.425938
6	3.506848	-2.708070	-2.475059
1	3.703274	-1.685177	-2.123680
1	4.321852	-2.998997	-3.142954
1	2.577136	-2.695178	-3.062532

Table S29. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{C_1}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1226.0767788 (-1226.39482579) (-1226.42007194) NImag=1(-289.95 cm^{-1})				*a-re* Et = -1226.073661 (-1226.39161008) (-1226.42108327) NImag= 1(-302.0 cm^{-1})		
6	3.675189	-1.124895	-0.116374	6	-3.626451	-0.010000	-0.129410
6	2.328417	-0.974879	0.239835	6	-2.326258	-0.019509	0.393656
6	2.028323	-0.417617	1.491315	6	-2.019511	-0.951551	1.393758
6	3.044535	-0.024294	2.353006	6	-2.979672	-1.845553	1.855681
6	4.379746	-0.178359	1.985055	6	-4.264938	-1.829731	1.322001
6	4.692247	-0.731995	0.747334	6	-4.584174	-0.907719	0.328349
6	1.279547	-1.422731	-0.699375	6	-1.279660	0.938735	-0.046358
6	0.075833	-1.950526	-0.208239	6	-0.447043	0.233256	-1.714691
7	-0.792319	-2.548532	-1.074880	6	-1.572852	-0.034643	-2.678144
8	-0.503656	-2.674550	-2.276928	6	-1.674513	2.260075	-0.351392
8	-1.923775	-2.935171	-0.645589	7	-0.758383	3.269622	-0.431146
6	0.834287	0.143544	-1.968191	8	-1.126594	4.417486	-0.697971
6	2.109775	0.410842	-2.723978	6	0.399299	-0.804438	-1.254937
6	0.266140	1.098164	-1.108795	6	-0.096477	-2.216801	-1.125754
6	1.109183	2.196650	-0.518280	6	0.268056	-3.036918	-2.372807
6	1.085877	3.454047	-1.400145	7	1.661396	-0.522734	-0.891348
7	-1.037145	1.020843	-0.764685	6	2.534160	-1.412029	-0.106917
6	-1.662091	1.906270	0.243194	6	3.827768	-0.598404	0.049839
6	-3.169772	1.699227	0.040528	6	3.861893	0.261263	-1.209057
6	-3.274999	1.321938	-1.433261	6	2.400787	0.646624	-1.404646
6	-2.071182	0.409260	-1.627246	6	1.966540	-1.842992	1.251692
6	-1.198146	1.663224	1.688294	8	1.447093	-0.905171	2.032509
8	-1.345264	0.453173	2.206108	8	2.015750	-3.001422	1.590238
8	-0.709571	2.567496	2.326261	8	0.480568	3.013423	-0.243890
1	-3.184936	2.210229	-2.067660	1	4.219674	-0.323224	-2.063116
1	-4.212923	0.819070	-1.677499	1	4.504184	1.137773	-1.104523
1	-3.530790	0.870340	0.654974	1	3.757785	0.044646	0.931759
1	-3.727194	2.598396	0.309724	1	4.693955	-1.251799	0.166701
1	-1.396735	2.945149	0.031960	1	2.725370	-2.338645	-0.656002
1	-1.714478	0.382099	-2.657358	1	2.140174	0.799249	-2.454721
1	-2.305328	-0.612419	-1.318247	1	2.128148	1.552747	-0.858882
1	2.901063	0.836342	-2.102012	1	-2.218279	0.847950	-2.727881
1	2.492096	-0.521559	-3.150409	1	-1.193499	-0.212740	-3.690580
1	1.941112	1.093440	-3.565022	1	-2.192979	-0.888269	-2.394131
1	1.651790	-1.929385	-1.586574	1	-2.681182	2.567013	-0.587204
1	-0.272790	-1.858765	0.807205	1	-0.371747	0.875866	0.543205
1	0.996189	-0.283114	1.797831	1	-1.021493	-0.969752	1.822277

1 2.789320 0.408262 3.314854 1 5.170885 0.129794 2.660960 1 5.728786 -0.864284 0.454016 1 3.924960 -1.570136 -1.074781 1 0.142067 -0.496901 -2.510391 1 2.135542 1.837890 -0.421888 1 0.784529 2.458364 0.489729 1 0.072491 3.850720 -1.512776 1 1.701007 4.236001 -0.947148 1 1.477170 3.251434 -2.400256 1 -1.891760 -0.200846 1.673192 8 -2.899780 -1.393654 1.257575 1 -2.548367 -2.016782 0.562610 6 -3.343210 -2.147071 2.372805 1 -4.224315 -2.743856 2.114075 1 -2.561511 -2.815386 2.751357 1 -3.613465 -1.443427 3.162185	1 -2.720108 -2.553351 2.636290 1 -5.014887 -2.527546 1.680301 1 -5.585535 -0.882669 -0.089682 1 -3.896567 0.705958 -0.898125 1 1.557670 0.041146 1.718210 1 0.073458 1.164137 -1.919837 1 -1.179954 -2.203738 -0.996903 1 0.312483 -2.711397 -0.242358 1 1.350534 -3.081661 -2.523518 1 -0.097162 -4.061156 -2.261928 1 -0.179820 -2.611800 -3.274662 8 1.732496 1.666591 1.666015 1 1.198037 2.190641 1.014116 6 1.633287 2.278010 2.942139 1 2.067542 3.282682 2.925418 1 0.593851 2.344626 3.282478 1 2.193335 1.661783 3.647527
s-si Et = -1226.0731497 (-1226.39067219) (-1226.41703883) NImag=1(-312.28 cm^{-1})	*s-re* Et = -1226.070735 (-1226.38909719) (-1226.41642226) NImag = 1(-340.47 cm^{-1})
6 0.853254 1.403432 0.451633 6 -0.429962 1.691750 -0.042068 7 -1.513240 1.013143 0.398082 6 -1.538410 0.312874 1.698933 6 -3.033375 0.210888 2.057092 6 -3.701049 1.288487 1.208769 6 -2.885146 1.253646 -0.075483 6 -0.835745 -1.055070 1.761441 8 -1.339891 -2.065245 1.076758 8 0.128580 -1.202470 2.481360 1 -3.609576 2.269942 1.686600 1 -4.760479 1.090839 1.032233 1 -3.424114 -0.771013 1.780205 1 -3.185501 0.338193 3.130699 1 -1.000524 0.931291 2.423243 1 -2.948514 2.180536 -0.639318 1 -3.200993 0.429552 -0.721113 1 -2.084269 -1.843083 0.443649 6 1.589674 -0.014365 -0.965444 6 0.685453 -1.054098 -1.198173 6 1.939639 2.451180 0.451501 1 1.717017 3.261906 1.155270 1 2.886511 2.006236 0.762406 1 2.100043 2.907100 -0.530693 1 1.613584 0.749807 -1.737761 1 0.749147 -2.039835 -0.766316 6 2.895690 -0.349142 -0.357383 6 3.003666 -1.191627 0.757567 6 4.253506 -1.518708 1.269286 6 5.412429 -1.015061 0.681870 6 5.315192 -0.171468 -0.420668 6 4.065816 0.163724 -0.931042 1 2.108222 -1.568995 1.242485 1 4.321279 -2.167792 2.136401 1 6.385847 -1.274605 1.085705 1 6.211676 0.227680 -0.884418 1 3.992901 0.818338 -1.794777 7 -0.382045 -0.857063 -2.024779 8 -0.614033 0.273305 -2.496120 8 -1.120586 -1.849817 -2.295730 1 0.903667 0.722707 1.296610	6 -0.563097 0.453848 -1.337461 6 0.776188 0.870996 -1.153270 6 1.086936 2.343526 -1.100387 7 1.799937 0.004029 -1.050757 6 1.685424 -1.437362 -1.306326 6 3.136619 -1.948770 -1.242913 6 3.974775 -0.716254 -1.562021 6 3.205048 0.400162 -0.870419 6 0.794313 -2.239814 -0.351038 8 0.974913 -2.103715 0.952911 8 -0.019325 -3.016978 -0.797482 1 4.004714 -0.540149 -2.642385 1 5.002004 -0.795937 -1.200201 1 3.363201 -2.299226 -0.231498 1 3.290726 -2.782753 -1.929619 1 1.252559 -1.590801 -2.299974 1 3.393781 1.374052 -1.319650 1 3.442168 0.451488 0.196999 1 1.665379 -1.439940 1.247315 1 1.901026 2.532516 -0.400808 1 0.213380 2.847621 -0.676389 6 -1.394374 0.406123 0.579148 1 -0.671780 -0.339271 0.890432 6 -1.284175 1.628452 1.267025 1 -0.703305 -0.605120 -1.542418 7 -0.096149 1.970063 1.847436 8 -0.002493 2.953475 2.589164 8 0.913195 1.249366 1.559445 6 -2.741490 -0.139338 0.290016 6 -2.897572 -1.524618 0.144938 6 -4.150987 -2.077688 -0.091481 6 -5.272345 -1.259488 -0.193019 6 -5.130684 0.119524 -0.058818 6 -3.878779 0.673813 0.177750 1 -2.030340 -2.174514 0.213895 1 -4.248817 -3.153465 -0.195595 1 -6.250717 -1.692041 -0.376697 1 -5.998335 0.766984 -0.137445 1 -3.788843 1.750573 0.274739 1 -2.081181 2.331512 1.448107 6 -1.523412 1.337039 -2.099491

6	-0.621415	2.796066	-1.051937
1	-1.363231	2.510815	-1.796857
1	0.309630	2.911178	-1.609487
6	-0.989357	4.129485	-0.390737
1	-1.099800	4.909160	-1.149770
1	-1.932777	4.065585	0.160675
1	-0.218836	4.454042	0.313389
1	-2.556504	-1.776299	-1.493983
8	-3.221871	-1.839009	-0.754534
6	-3.850537	-3.107505	-0.846855
1	-3.118050	-3.921975	-0.842665
1	-4.507573	-3.217987	0.018077
1	-4.455317	-3.176935	-1.757303

1	-2.522881	0.898599	-2.079365
1	-1.598371	2.342045	-1.672716
1	-1.236511	1.439034	-3.152054
6	1.407279	2.944387	-2.474093
1	0.574005	2.833251	-3.170964
1	1.618183	4.012384	-2.371541
1	2.283534	2.473924	-2.931614
1	2.127740	0.280228	2.231899
8	2.689060	-0.529867	2.197241
6	2.792675	-1.077308	3.501284
1	3.364414	-2.003745	3.425101
1	3.321983	-0.392180	4.172010
1	1.808927	-1.305345	3.926921

Table S30. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{L_1C_1}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1341.7756517 (-1342.1343602) (-1342.1557084) NImag=1(-240.6 cm^{-1})			
6	3.487501	-2.125817	0.275502
6	2.386299	-1.337900	0.639494
6	2.617333	-0.159842	1.366563
6	3.909086	0.211550	1.715199
6	4.994711	-0.582265	1.348222
6	4.779898	-1.753403	0.627954
6	1.036250	-1.783118	0.267181
6	-0.067514	-1.488621	1.067286
7	-1.270271	-2.072744	0.793728
8	-1.401550	-2.870701	-0.145608
8	-2.278155	-1.752053	1.506961
6	0.639323	-0.992501	-1.738856
6	1.685594	-1.667584	-2.581217
6	0.623566	0.385303	-1.507981
6	1.861463	1.213902	-1.729646
6	1.921697	1.752134	-3.166557
7	-0.502761	0.998858	-1.078347
6	-0.562543	2.425905	-0.701792
6	-2.066860	2.716986	-0.585257
6	-2.695857	1.725492	-1.559202
6	-1.856782	0.473301	-1.351198
6	0.229763	2.789029	0.563268
8	-0.049913	2.148783	1.691501
8	1.091106	3.636881	0.521160
1	-2.600644	2.083964	-2.589832
1	-3.749598	1.529828	-1.353682
1	-2.422270	2.506828	0.426775
1	-2.280678	3.762515	-0.815573
1	-0.123151	3.037028	-1.494923
1	-1.825800	-0.170704	-2.231270
1	-2.249712	-0.112712	-0.520359
1	2.702998	-1.340706	-2.351047
1	1.646571	-2.751108	-2.431453
1	1.514919	-1.495516	-3.650861
1	0.981458	-2.735153	-0.251958
1	-0.076423	-0.779336	1.878598

a-re Et = -1341.7732161 (-1342.1323447) (-1342.1580586) NImag= 1(-269.43 cm^{-1})			
6	2.756833	-2.529360	-0.182465
6	2.055029	-1.452905	0.379262
6	2.789483	-0.393714	0.931069
6	4.179476	-0.410998	0.924224
6	4.863243	-1.483694	0.358728
6	4.146368	-2.541991	-0.194572
6	0.580164	-1.410297	0.442300
6	-0.093493	-0.664138	-1.428226
6	0.538560	-1.569704	-2.446926
6	-0.133933	-2.607742	0.597234
7	-1.460129	-2.614653	0.912794
8	-2.082980	-3.679311	0.962742
6	0.226577	0.701212	-1.332128
6	1.556221	1.224029	-1.804176
6	1.463651	1.737908	-3.248310
7	-0.652285	1.571519	-0.797729
6	-0.327284	2.951695	-0.407663
6	-1.674626	3.521249	0.066724
6	-2.696334	2.724365	-0.737344
6	-2.104111	1.322273	-0.735893
6	0.753628	3.080389	0.671039
8	0.668432	2.285383	1.732885
8	1.638182	3.894469	0.558250
8	-2.066687	-1.505825	1.132879
1	-2.764086	3.108054	-1.760794
1	-3.695646	2.746289	-0.298601
1	-1.808554	3.321536	1.134421
1	-1.723286	4.600499	-0.087572
1	0.044461	3.515643	-1.267870
1	-2.420349	0.709458	-1.580101
1	-2.365014	0.782301	0.176315
1	0.362740	-2.613010	-2.165737
1	0.082068	-1.428316	-3.433671
1	1.616794	-1.426328	-2.550988
1	0.263748	-3.591846	0.405568
1	0.182996	-0.555738	0.975521

1 1.788527 0.479824 1.652028 1 4.067319 1.129342 2.271791 1 6.002398 -0.288043 1.623184 1 5.618000 -2.381331 0.343343 1 3.323087 -3.047870 -0.273879 1 -0.316295 -1.509013 -1.720072 1 2.739799 0.595625 -1.534763 1 1.918787 2.050326 -1.031931 1 1.062170 2.389082 -3.395366 1 2.825881 2.351591 -3.301590 1 1.939203 0.941542 -3.899443 1 -0.878663 1.586665 1.688710 8 -2.249865 0.841924 2.172265 1 -2.317912 -0.120873 1.957415 6 -2.562777 1.035992 3.540855 1 -3.619526 0.822738 3.732655 1 -1.947617 0.406437 4.193723 1 -2.365488 2.082725 3.777790 1 -3.770053 -1.736954 0.324467 8 -4.407669 -1.421287 -0.340862 6 -4.739034 -2.510874 -1.166264 1 -3.855154 -2.982423 -1.615561 1 -5.302205 -3.288576 -0.629154 1 -5.377052 -2.132928 -1.970083	1 2.265502 0.446007 1.378397 1 4.726894 0.416558 1.363460 1 5.948331 -1.497368 0.351136 1 4.671160 -3.384088 -0.634294 1 2.216109 -3.364018 -0.615258 1 -0.144504 1.707900 1.780867 1 -1.127901 -0.915993 -1.211106 1 2.293897 0.421937 -1.746806 1 1.927860 2.025460 -1.161996 1 0.743470 2.556040 -3.340482 1 2.438239 2.111516 -3.573298 1 1.157162 0.944201 -3.934357 8 -1.367614 0.760135 2.408658 1 -1.578520 -0.115058 2.004520 6 -1.291958 0.616129 3.817659 1 -2.262276 0.324330 4.232405 1 -0.540104 -0.124435 4.112717 1 -1.007962 1.585278 4.230617 1 -3.374870 -1.487800 -0.201642 8 -3.738265 -1.371782 -1.098439 6 -4.513290 -2.506353 -1.408621 1 -5.421031 -2.572836 -0.791794 1 -4.822300 -2.417505 -2.453550 1 -3.951893 -3.441412 -1.288775
s-si Et = -1341.7736336 (-1342.13176048) (-1342.1544754) NImag=1(-257.22 cm^{-1})	*s-re* Et = -1341.7706349 (-1342.12923239) (-1342.1544028) NImag = 1(-298.86 cm^{-1})
6 -1.049209 -0.893292 1.306098 6 0.337172 -1.060089 1.204712 7 1.166843 0.012171 1.228426 6 0.774338 1.282720 1.877689 6 2.106840 1.955538 2.256960 6 3.102743 0.802183 2.305683 6 2.637947 -0.079405 1.156536 6 -0.139720 2.224075 1.078229 8 0.319135 2.778260 -0.030372 8 -1.245061 2.491929 1.497972 1 3.023750 0.261731 3.255448 1 4.137113 1.130253 2.182975 1 2.407820 2.667733 1.484718 1 2.011630 2.502113 3.197410 1 0.195425 1.035876 2.772257 1 2.977185 -1.107861 1.228405 1 2.986481 0.313410 0.198162 1 1.220553 2.467074 -0.339093 6 -1.646052 -0.694471 -0.831187 6 -0.784124 0.156415 -1.521261 6 -1.955066 -2.005059 1.765645 1 -1.838227 -2.200891 2.838508 1 -2.999090 -1.728597 1.604064 1 -1.780003 -2.950713 1.243517 1 -1.442910 -1.752930 -0.957925 1 -0.982471 1.189483 -1.757588 6 -3.062973 -0.328252 -0.664996 6 -3.475926 0.976034 -0.357138 6 -4.828311 1.278901 -0.265800 6 -5.790609 0.294042 -0.481075 6 -5.392163 -1.005607 -0.779249 6 -4.039372 -1.314670 -0.862815 1 -2.741382 1.747431 -0.150246 1 -5.131511 2.290833 -0.017753	6 -0.956156 0.144916 1.453310 6 0.450576 0.056464 1.469088 6 1.110776 -1.206283 1.956218 7 1.242599 1.081858 1.098724 6 0.753399 2.440883 0.843429 6 2.034801 3.274034 0.651921 6 3.103241 2.478893 1.394756 6 2.711968 1.036795 1.103929 6 -0.188281 2.613989 -0.353487 8 0.177566 2.115396 -1.526110 8 -1.222382 3.230342 -0.230411 1 3.049455 2.674465 2.470850 1 4.115453 2.709439 1.056080 1 2.287458 3.330041 -0.411298 1 1.901309 4.293098 1.018810 1 0.180170 2.784923 1.710420 1 3.076949 0.342373 1.858246 1 3.078441 0.709306 0.126103 1 1.048912 1.628400 -1.550810 1 2.018207 -1.425483 1.389872 1 0.430971 -2.037231 1.747411 6 -1.532794 -0.719677 -0.472559 1 -0.969294 0.059712 -0.970455 6 -1.010928 -2.011188 -0.626521 1 -1.377924 1.123693 1.239793 7 0.304514 -2.167660 -0.940232 8 0.781599 -3.307277 -1.125624 8 1.034467 -1.137892 -0.992339 6 -2.989678 -0.501023 -0.425286 6 -3.496373 0.764073 -0.757558 6 -4.865441 1.001526 -0.760507 6 -5.755264 -0.016163 -0.427488 6 -5.265729 -1.275113 -0.087320 6 -3.897610 -1.514948 -0.083604

1	-6.845778	0.537757	-0.409502
1	-6.133590	-1.780365	-0.946232
1	-3.730899	-2.328303	-1.101508
7	0.419237	-0.311174	-1.959976
8	0.763548	-1.486370	-1.686825
8	1.163964	0.436230	-2.649708
1	-1.409759	0.100541	1.554148
6	0.936855	-2.441542	1.105592
1	1.792871	-2.456160	0.429681
1	0.197613	-3.103251	0.651174
6	1.331337	-2.988145	2.483308
1	1.743209	-3.996231	2.382300
1	2.092868	-2.366006	2.963860
1	0.473238	-3.041282	3.159036
1	2.204568	1.456790	-1.783498
8	2.581209	2.155212	-1.193470
6	2.951113	3.261030	-2.002384
1	2.104459	3.635943	-2.587736
1	3.300232	4.053271	-1.337944
1	3.764667	2.988786	-2.682499
1	2.578963	-1.721898	-1.621368
8	3.455437	-1.990976	-1.283963
6	3.981521	-2.949281	-2.167179
1	4.151523	-2.542498	-3.174258
1	4.946362	-3.273629	-1.768064
1	3.338626	-3.836412	-2.262877

1	-2.811734	1.568859	-1.008365
1	-5.236364	1.986571	-1.024183
1	-6.824508	0.169915	-0.430443
1	-5.951795	-2.073823	0.175889
1	-3.536160	-2.500631	0.188948
1	-1.547249	-2.938567	-0.505567
6	-1.785730	-0.672717	2.410911
1	-2.845441	-0.565290	2.171099
1	-1.546552	-1.739713	2.373988
1	-1.654854	-0.339188	3.447020
6	1.413518	-1.179068	3.459754
1	0.507156	-1.058060	4.057865
1	1.890474	-2.117739	3.753325
1	2.093939	-0.363607	3.724890
1	2.062585	-0.106019	-1.942300
8	2.391284	0.794804	-2.147657
6	2.484599	0.945483	-3.555811
1	2.820936	1.964439	-3.752950
1	3.215288	0.247153	-3.976941
1	1.516903	0.793313	-4.046889
1	2.524909	-3.115392	-0.412424
8	3.370559	-2.955712	0.049191
6	4.294314	-2.517320	-0.911079
1	5.248496	-2.351836	-0.402571
1	4.462915	-3.259667	-1.705257
1	3.997175	-1.571465	-1.388572

Table S31. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{L_2C_1}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1457.4698464 (-1457.86941248) (-1457. .8908839) NImag=1(-187.5 cm^{-1})			*a-re* Et = -1457.4698575 (-1457.86933692) (-1457.8924957) NImag= 1(-208.48 cm^{-1})		
6	-3.413211	1.765879	-1.405736	6	-1.880609	-3.389265	0.088798
6	-2.314158	1.394563	-0.616869	6	-1.498376	-2.163675	-0.477701
6	-2.500265	1.240962	0.766823	6	-2.360572	-1.555087	-1.402570
6	-3.746987	1.458568	1.336583	6	-3.563681	-2.155884	-1.752422
6	-4.829909	1.832356	0.541753	6	-3.933270	-3.369591	-1.178657
6	-4.659691	1.985817	-0.831263	6	-3.087893	-3.982983	-0.256510
6	-1.009705	1.202763	-1.252977	6	-0.215526	-1.516409	-0.173202
6	0.171575	1.457790	-0.564722	6	-0.574623	-0.358808	1.728323
7	1.360518	1.424116	-1.232221	6	-1.120580	-1.398286	2.660910
8	1.433970	1.108050	-2.425395	6	0.904923	-2.285848	0.137500
8	2.432250	1.698384	-0.578193	7	2.161094	-1.757728	0.159328
6	-0.968454	-0.972611	-1.960814	8	3.135236	-2.467075	0.425768
6	-2.091473	-0.983029	-2.957094	6	-1.337236	0.695401	1.220959
6	-1.016953	-1.647893	-0.744644	6	-2.841148	0.626339	1.192637
6	-2.333055	-2.109995	-0.175009	6	-3.442804	1.248193	2.460866
6	-2.682485	-3.527002	-0.651396	7	-0.739106	1.813377	0.750415
7	0.118177	-1.917928	-0.055808	6	-1.424688	2.866599	-0.011970
6	0.131298	-2.546194	1.278554	6	-0.339319	3.938588	-0.206704
6	1.604804	-2.922322	1.499103	6	0.567735	3.746018	1.004124
6	2.135992	-3.132198	0.084077	6	0.615739	2.231194	1.148567
6	1.436163	-2.037016	-0.709187	6	-2.031280	2.408050	-1.344280
6	-0.450529	-1.670992	2.398914	8	-1.273032	1.685007	-2.161347
8	0.053771	-0.457516	2.578026	8	-3.164953	2.707823	-1.635137

8 -1.355732 -2.083760 3.087087 1 1.848247 -4.119221 -0.293736 1 3.221175 -3.036599 0.017691 1 2.145025 -2.097148 1.968027 1 1.691164 -3.802607 2.139042 1 -0.488255 -3.447501 1.273485 1 1.295272 -2.299836 -1.759275 1 2.007715 -1.108570 -0.669602 1 -3.076596 -0.852673 -2.501579 1 -1.958081 -0.180142 -3.689392 1 -2.113410 -1.919854 -3.527946 1 -0.969729 1.343403 -2.327942 1 0.242543 1.714040 0.481143 1 -1.673586 0.932790 1.398971 1 -3.873731 1.329073 2.406187 1 -5.802610 2.001711 0.992058 1 -5.496491 2.281325 -1.455810 1 -3.279600 1.900218 -2.474892 1 0.011088 -0.772280 -2.384078 1 -3.116959 -1.417285 -0.487220 1 -2.329207 -2.089268 0.915456 1 -1.922669 -4.253096 -0.347697 1 -3.635888 -3.841749 -0.218777 1 -2.771157 -3.574716 -1.739851 1 0.909514 -0.262233 2.094447 8 2.428731 0.231355 1.757238 1 2.530319 0.752790 0.932866 6 3.013846 0.949572 2.840075 1 4.106526 0.898908 2.785351 1 2.690346 1.993619 2.842749 1 2.684251 0.465537 3.760932 1 3.748634 0.521659 -1.351329 8 4.255598 -0.293817 -1.507203 6 4.596944 -0.332853 -2.871235 1 3.718972 -0.263583 -3.527018 1 5.296178 0.468672 -3.152123 1 5.093782 -1.288815 -3.057851 1 2.092302 3.133421 0.626421 8 1.712014 3.600673 1.390074 6 1.438681 4.929862 1.016943 1 0.999439 5.427956 1.884186 1 2.345442 5.481285 0.731084 1 0.719800 4.994334 0.187894	8 2.330403 -0.507481 -0.087323 1 0.121566 4.199221 1.895666 1 1.561303 4.176171 0.863930 1 0.223993 3.739369 -1.123042 1 -0.778331 4.934727 -0.284699 1 -2.261232 3.273224 0.563690 1 0.832940 1.891653 2.161768 1 1.365997 1.798559 0.483007 1 -0.463305 -2.273922 2.664712 1 -1.149263 -1.025109 3.692089 1 -2.126899 -1.734557 2.399964 1 0.882245 -3.333004 0.395399 1 -0.033091 -0.585406 -0.693463 1 -2.077653 -0.610999 -1.859328 1 -4.212255 -1.672263 -2.475336 1 -4.874249 -3.837240 -1.449558 1 -3.368264 -4.929993 0.193150 1 -1.234542 -3.880833 0.808125 1 -0.316763 1.572464 -1.890614 1 0.489199 -0.175810 1.847530 1 -3.149226 -0.417716 1.113664 1 -3.252985 1.131369 0.316787 1 -3.165324 2.301391 2.562930 1 -4.533916 1.191267 2.423579 1 -3.104644 0.726139 3.359605 8 1.310423 1.288452 -1.882965 1 1.643378 0.567122 -1.309720 6 1.943255 1.183686 -3.156736 1 3.008171 0.976217 -3.025278 1 1.486301 0.394549 -3.765385 1 1.811664 2.139138 -3.666900 1 2.899674 0.149360 1.631239 8 2.816465 0.364961 2.575039 6 3.837186 -0.314839 3.271408 1 4.837158 0.060672 3.013619 1 3.675083 -0.141295 4.337974 1 3.818960 -1.396415 3.087083 1 4.055764 -0.316348 -0.944139 8 4.717288 -0.065728 -1.611206 6 5.395047 -1.234448 -2.003787 1 4.731935 -1.973081 -2.477669 1 6.152670 -0.941756 -2.735136 1 5.901708 -1.727738 -1.163379
s-si Et = -1457.4645014 (-1457.86326159) (-1457.8908346) NImag=1(-238.57 cm^{-1})	*s-re* Et = -1457.4676901(-1457.86687122) (-1457. 89153) NImag = 1(-270.53 cm^{-1})
6 2.018230 1.459692 -0.313231 6 0.766184 1.986225 -0.636503 7 -0.233065 2.022192 0.281254 6 0.040093 2.006260 1.734790 6 -1.194737 2.667588 2.374111 6 -1.823435 3.468846 1.238752 6 -1.567905 2.586941 0.025110 6 0.359180 0.635437 2.356940 8 -0.587149 -0.283192 2.412353 8 1.458139 0.430261 2.826727 1 -1.316484 4.432240 1.117210 1 -2.887278 3.659112 1.395106 1 -1.897690 1.908245 2.723121 1 -0.907252 3.275362 3.234288 1 0.940291 2.601984 1.911608	6 0.462093 -1.040607 1.477126 6 -0.807480 -0.438939 1.471753 6 -1.001674 0.903308 2.127769 7 -1.890392 -1.042107 0.935425 6 -1.908174 -2.442412 0.501850 6 -3.387648 -2.718214 0.173023 6 -4.144710 -1.688619 1.004922 6 -3.242165 -0.464609 0.930067 6 -1.015448 -2.795762 -0.692328 8 -1.090541 -2.042646 -1.782059 8 -0.290089 -3.763022 -0.649222 1 -4.235955 -2.025864 2.042677 1 -5.147466 -1.488019 0.621847 1 -3.572389 -2.543395 -0.891339 1 -3.654605 -3.753150 0.393452

1	-1.587266	3.142364	-0.908857
1	-2.304289	1.780599	-0.032606
1	-1.456312	-0.058171	1.964333
6	1.724533	-0.704520	-0.912463
6	0.513874	-1.193281	-0.428994
6	3.263765	1.809350	-1.081081
1	3.608918	2.822389	-0.840084
1	4.072910	1.126019	-0.814899
1	3.135197	1.761177	-2.166622
1	1.710918	-0.383302	-1.949340
1	0.396607	-1.805136	0.450991
6	2.993928	-1.258993	-0.421281
6	3.202998	-1.585927	0.926851
6	4.401371	-2.161357	1.327746
6	5.406612	-2.423216	0.398233
6	5.212792	-2.095492	-0.940445
6	4.018703	-1.510297	-1.344983
1	2.445303	-1.355469	1.668888
1	4.552761	-2.401680	2.374878
1	6.339718	-2.875523	0.718338
1	5.990525	-2.294551	-1.670553
1	3.865908	-1.261377	-2.391042
7	-0.638112	-0.921628	-1.103114
8	-0.654917	-0.162531	-2.082055
8	-1.718922	-1.486088	-0.709771
1	2.194024	1.197785	0.725620
6	0.513271	2.560831	-2.009585
1	-0.493955	2.323405	-2.350425
1	1.175747	2.060844	-2.717760
6	0.766067	4.071940	-2.056138
1	0.592299	4.453203	-3.066309
1	0.105808	4.618188	-1.375198
1	1.795690	4.312384	-1.778601
1	-2.676068	-0.574160	0.455546
8	-2.924486	-0.046316	1.247001
6	-3.914740	-0.770776	1.981183
1	-3.687038	-1.839664	1.988073
1	-3.917353	-0.379764	3.000378
1	-4.903061	-0.610122	1.538527
1	-2.193322	-3.084528	0.270468
8	-2.817122	-3.650355	0.751916
6	-3.708908	-4.189045	-0.202480
1	-4.148893	-3.418304	-0.847252
1	-3.223952	-4.939886	-0.843139
1	-4.511444	-4.686622	0.347757
1	-3.071035	-1.390203	-2.057302
8	-3.947968	-1.378376	-2.478399
6	-4.401715	-0.052287	-2.461018
1	-3.742389	0.628100	-3.020529
1	-5.386335	-0.032998	-2.935959
1	-4.514521	0.349378	-1.440883

1	-1.557189	-3.078743	1.320951
1	-3.381529	0.209129	1.773460
1	-3.404695	0.099936	0.006615
1	-1.726020	-1.274804	-1.744297
1	-1.733028	1.508825	1.588883
1	-0.058508	1.451661	2.053640
6	1.465598	-0.191575	-0.345877
1	0.677410	-0.635517	-0.940916
6	1.462181	1.205863	-0.282738
1	0.521094	-2.065043	1.120023
7	0.321149	1.879724	-0.579319
8	0.300469	3.142862	-0.566138
8	-0.730586	1.236824	-0.825301
6	2.727060	-0.943018	-0.300676
6	2.748296	-2.261179	-0.781914
6	3.928579	-2.993453	-0.790753
6	5.108601	-2.426725	-0.315985
6	5.100439	-1.121270	0.170620
6	3.922700	-0.385354	0.181323
1	1.831883	-2.716870	-1.144936
1	3.924361	-4.010080	-1.169900
1	6.030790	-2.998994	-0.323158
1	6.015919	-0.672855	0.542817
1	3.938454	0.629425	0.564246
1	2.288833	1.839034	0.007036
6	1.481389	-0.701506	2.533005
1	2.444886	-1.149200	2.280469
1	1.638619	0.375399	2.643705
1	1.190855	-1.096302	3.514001
6	-1.389888	0.788018	3.607279
1	-0.620784	0.276458	4.191012
1	-1.527112	1.786938	4.029201
1	-2.326316	0.237466	3.741853
1	-2.020304	0.754396	-1.925566
8	-2.635855	0.064954	-2.246346
6	-2.700019	0.122207	-3.663348
1	-3.365025	-0.678063	-3.990890
1	-3.111776	1.079810	-3.998445
1	-1.716409	-0.027956	-4.122141
1	1.925918	3.899999	0.062368
8	2.869778	3.995827	0.288214
6	3.512720	4.557362	-0.830635
1	4.580459	4.610615	-0.603896
1	3.387077	3.952330	-1.740148
1	3.161715	5.576222	-1.047174
1	-1.471182	3.493348	0.066525
8	-2.353145	3.591815	0.471021
6	-3.289131	3.656739	-0.572220
1	-3.114238	4.509516	-1.244691
1	-3.311663	2.741631	-1.182816
1	-4.277538	3.784954	-0.122132

Table S32. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{L_1C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1457.4732854 (-1457.8721362) (-1457.8955669) NImag=1(-260.23 cm^{-1})				*a-si(II)* Et = -1457.4752794 (-1457.8748465) (-1457.8947196) NImag=1(-258.97 cm^{-1})			
6	-4.002119	-1.607223	1.225203	6	3.959855	1.540382	-1.211133
6	-2.842022	-1.254939	0.521887	6	2.879086	0.649380	-1.150979
6	-2.867474	-1.310122	-0.880063	6	3.141229	-0.725112	-1.256424
6	-4.017408	-1.710418	-1.548574	6	4.441450	-1.185162	-1.419321
6	-5.162707	-2.061736	-0.836345	6	5.505928	-0.287606	-1.480039
6	-5.151765	-2.008830	0.554070	6	5.260972	1.078125	-1.375209
6	-1.633107	-0.878264	1.277321	6	1.514996	1.190066	-1.017131
6	-0.369330	-1.240431	0.794578	6	0.432702	0.539532	-1.618075
7	0.721507	-1.103589	1.593472	7	-0.769324	1.168667	-1.713578
8	0.640048	-0.602292	2.728786	8	-0.907779	2.344389	-1.285132
8	1.854291	-1.457842	1.130541	8	-1.733503	0.542488	-2.221341
6	-1.699921	1.228585	1.584844	6	1.113036	1.392844	1.089050
6	-3.040867	1.470943	2.221902	6	2.209865	2.294243	1.586053
6	-1.364179	1.714979	0.314226	6	1.001107	0.052588	1.479378
6	-2.428360	2.037611	-0.700842	6	2.200248	-0.708587	1.981754
6	-2.745474	3.538727	-0.719665	6	2.250210	-0.730867	3.515097
7	-0.070398	1.861240	-0.035037	7	-0.175063	-0.598503	1.377277
6	0.403121	2.090570	-1.417223	6	-0.332680	-2.059991	1.530915
6	1.763084	2.795960	-1.264574	6	-1.796988	-2.263198	1.966410
6	1.848988	3.174816	0.217029	6	-2.309043	-0.856673	2.289453
6	1.030920	2.092940	0.909443	6	-1.498676	0.037944	1.360734
6	0.389409	0.749339	-2.178867	6	0.092164	-2.755355	0.225271
8	1.379254	-0.105560	-2.019047	8	-0.711492	-2.702056	-0.821987
8	-0.569660	0.470334	-2.869871	8	1.180791	-3.285504	0.149525
1	1.395720	4.155014	0.396788	1	-2.098766	-0.592574	3.330791
1	2.876987	3.198381	0.583689	1	-3.383008	-0.753198	2.122557
1	2.590490	2.134215	-1.525681	1	-2.394139	-2.699202	1.163756
1	1.819034	3.664733	-1.923739	1	-1.851229	-2.940302	2.821354
1	-0.308493	2.726227	-1.943614	1	0.354829	-2.425754	2.292485
1	0.632226	2.405257	1.873768	1	-1.441613	1.071802	1.698069
1	1.623354	1.188362	1.062921	1	-1.919755	0.031754	0.349849
1	-3.881247	1.296274	1.545965	1	3.202159	1.839029	1.539467
1	-3.171986	0.808516	3.083000	1	2.241966	3.209407	0.986680
1	-3.122127	2.497180	2.600147	1	2.032006	2.604717	2.622859
1	-1.732965	-0.927013	2.358720	1	1.446756	2.274086	-1.018582
1	-0.158333	-1.583307	-0.205585	1	0.429884	-0.475593	-1.982058
1	-1.994922	-1.024088	-1.459103	1	2.334725	-1.448030	-1.192931
1	-4.017241	-1.745457	-2.633109	1	4.621559	-2.252407	-1.495700
1	-6.058059	-2.375226	-1.363468	1	6.520066	-0.651962	-1.608764
1	-6.036365	-2.285568	1.118623	1	6.081701	1.786367	-1.427175
1	-3.993211	-1.584052	2.310839	1	3.772119	2.607955	-1.146615
1	-0.881536	1.137574	2.294070	1	0.185452	1.914389	0.870923
1	-3.331067	1.478643	-0.450508	1	3.102617	-0.231357	1.597465
1	-2.130136	1.694909	-1.693851	1	2.208687	-1.725471	1.583324
1	-1.866287	4.136943	-0.978846	1	1.365892	-1.211376	3.944929
1	-3.523117	3.748798	-1.458958	1	3.130118	-1.284513	3.853798
1	-3.103187	3.882664	0.254775	1	2.307875	0.280752	3.926069
1	2.190677	0.175866	-1.493481	1	-1.629758	-2.323151	-0.689944
8	3.744733	0.313583	-1.016407	8	-3.271676	-2.148397	-0.872648
1	3.883466	0.257647	-0.036865	1	-3.656469	-1.236544	-0.889276
6	4.483914	-0.735583	-1.634977	6	-3.603633	-2.766524	-2.106529
1	5.556975	-0.607318	-1.452948	1	-4.688068	-2.886301	-2.202768

1 4.160000 -1.720134 -1.281208 1 4.305244 -0.667349 -2.709615 8 3.902616 0.144080 1.661771 1 3.155434 -0.494855 1.742107 6 5.002795 -0.324421 2.414351 1 5.826292 0.378330 2.270401 1 4.763391 -0.363220 3.483425 1 5.331659 -1.320115 2.091723 1 2.386393 -2.910112 0.047189 8 2.818227 -3.550682 -0.544311 6 1.913679 -3.848008 -1.580470 1 1.614620 -2.958008 -2.151098 1 2.414372 -4.538451 -2.264247 1 1.003045 -4.344752 -1.212477	1 -3.229092 -2.188364 -2.957577 1 -3.136740 -3.752841 -2.116700 8 -4.207611 0.319736 -1.264760 1 -3.394263 0.709828 -1.651683 6 -4.965728 1.307104 -0.592184 1 -5.764165 0.794227 -0.051190 1 -4.360243 1.879533 0.119153 1 -5.428274 2.000970 -1.305397 1 -1.982524 2.832687 0.077917 8 -2.355118 3.083346 0.945879 6 -2.362783 4.488722 1.027291 1 -2.753368 4.759116 2.011418 1 -1.356789 4.919453 0.928596 1 -3.008256 4.948573 0.266425
a-re Et =-1457.4731565 (-1457.8771032) (-1457.8969932) NImag = 1(-284.4 cm^{-1})	*a-re(II)* Et = -1457.4683898 (-1457.8671386) (-1457.8942058) NImag= 1(-280.59 cm^{-1})
6 -3.216832 -1.750520 0.331458 6 -1.927384 -1.319766 0.675530 6 -1.213960 -2.044388 1.640645 6 -1.769616 -3.168824 2.240044 6 -3.046392 -3.592816 1.881634 6 -3.767606 -2.878916 0.927264 6 -1.311011 -0.113342 0.088110 6 -0.478773 -0.667081 -1.745771 6 -1.605781 -1.281939 -2.526924 6 -2.127961 0.985884 -0.232522 7 -1.553608 2.197449 -0.461847 8 -2.251733 3.218105 -0.642981 6 0.649651 -1.400441 -1.339186 6 0.579032 -2.887789 -1.126939 6 1.058312 -3.645540 -2.373739 7 1.820005 -0.773770 -1.107255 6 2.954467 -1.363412 -0.376142 6 4.086464 -0.333883 -0.541269 6 3.696519 0.448539 -1.793286 6 2.178740 0.525605 -1.692577 6 2.615519 -1.667637 1.090744 8 2.159706 -0.674680 1.846062 8 2.724996 -2.789258 1.527918 8 -0.287283 2.276765 -0.488385 1 3.984496 -0.095989 -2.698586 1 4.158292 1.437438 -1.829229 1 4.112349 0.347138 0.312500 1 5.056854 -0.827697 -0.617299 1 3.231623 -2.322180 -0.820881 1 1.692391 0.630864 -2.664413 1 1.839528 1.347784 -1.057521 1 -2.471464 -0.612615 -2.504434 1 -1.331132 -1.415131 -3.579976 1 -1.922940 -2.252736 -2.138823 1 -3.205743 0.973445 -0.317194 1 -0.344511 0.153727 0.503770 1 -0.222927 -1.712232 1.935855 1 -1.202108 -3.711363 2.989030 1 -3.480515 -4.471740 2.347354 1 -4.767226 -3.197656 0.649668 1 -3.796648 -1.199566 -0.401402 1 2.287887 0.256242 1.500283 1 -0.283204 0.371526 -1.994133 1 -0.452710 -3.163230 -0.904339	6 3.538612 -2.233276 -0.288392 6 2.552402 -1.413446 0.277852 6 2.856388 -0.723661 1.460251 6 4.105851 -0.848790 2.056455 6 5.077859 -1.661202 1.479114 6 4.789427 -2.352822 0.304960 6 1.194920 -1.282273 -0.290406 6 1.292508 0.185917 -1.759391 6 2.469345 -0.182594 -2.620221 6 0.601242 -2.370641 -0.958968 7 -0.747926 -2.410567 -1.122619 8 -1.296536 -3.344433 -1.717928 6 1.251690 1.380565 -1.012199 6 2.510195 2.020535 -0.492692 6 2.958820 3.165753 -1.411638 7 0.075029 1.966668 -0.733754 6 -0.138373 2.950606 0.344721 6 -1.566262 3.479079 0.112478 6 -1.916561 3.044791 -1.311982 6 -1.161355 1.732979 -1.484569 6 0.088100 2.293827 1.718262 8 -0.714928 1.306829 2.079492 8 1.021046 2.633379 2.411899 8 -1.442141 -1.447224 -0.629930 1 -1.557534 3.776810 -2.042467 1 -2.992022 2.920973 -1.453773 1 -2.268751 3.022366 0.812099 1 -1.606636 4.561004 0.251076 1 0.599498 3.751301 0.268854 1 -0.916433 1.521092 -2.527438 1 -1.705025 0.871305 -1.083753 1 2.385075 -1.230170 -2.925191 1 2.492248 0.416886 -3.537919 1 3.429837 -0.059591 -2.114705 1 1.123316 -3.201729 -1.406294 1 0.501782 -0.732001 0.336411 1 2.102655 -0.093987 1.924739 1 4.315688 -0.313330 2.976509 1 6.053470 -1.760059 1.944017 1 5.539197 -2.994035 -0.147339 1 3.328395 -2.787698 -1.196767 1 -1.557289 1.175258 1.550757 1 0.338742 -0.111304 -2.182134 1 3.294955 1.264847 -0.440535

1 1.169612 -3.198258 -0.262570 1 2.096832 -3.404185 -2.619483 1 0.997552 -4.723006 -2.199456 1 0.444831 -3.408043 -3.246796 8 2.763400 1.851820 1.535301 1 2.247742 2.615314 1.159060 6 3.095084 2.179366 2.874387 1 3.808550 3.010453 2.911273 1 2.207552 2.449805 3.456789 1 3.555659 1.299934 3.327815 8 1.362973 3.951064 0.677913 1 0.574373 3.532897 0.255442 6 1.920955 4.873901 -0.233351 1 2.197718 4.404806 -1.186741 1 1.225493 5.695117 -0.439956 1 2.821245 5.290673 0.223405 1 -4.080127 2.826878 -0.797953 8 -4.951637 2.392741 -0.724661 6 -5.539115 2.841375 0.471911 1 -5.757497 3.918866 0.453992 1 -6.485822 2.308866 0.594875 1 -4.916010 2.635403 1.354332	1 2.374880 2.391993 0.525448 1 2.201502 3.952804 -1.476003 1 3.877234 3.614751 -1.024538 1 3.156973 2.809870 -2.426237 8 -3.173757 0.950702 1.242699 1 -3.491476 0.397613 0.488785 6 -3.754368 0.429409 2.437712 1 -4.840493 0.573475 2.429730 1 -3.518087 -0.632076 2.555398 1 -3.331933 0.990524 3.272986 8 -3.970656 -0.721519 -0.742742 1 -3.128096 -1.209781 -0.892810 6 -4.618299 -0.489381 -1.972720 1 -4.016993 0.128834 -2.653895 1 -4.859544 -1.430035 -2.480963 1 -5.551302 0.037772 -1.762496 1 -2.100727 -2.159893 1.057275 8 -2.492833 -2.629663 1.812241 6 -3.383925 -3.587464 1.286062 1 -3.783692 -4.155937 2.129546 1 -4.224791 -3.126102 0.750305 1 -2.885186 -4.286490 0.601964
s-si Et = -1457.4721957 (-1457.8693691) (-1457.8946211) NImag=1(-270.74 cm^{-1})	*s-re* Et = -1457.4752176 (-1457.8734863) (-1457.896482) NImag = 1(-294.54 cm^{-1})
6 -1.718096 -1.624621 -0.033618 6 -0.445712 -2.086843 -0.400408 7 0.615237 -1.998414 0.432538 6 0.474395 -1.705983 1.871029 6 1.802301 -2.168599 2.494836 6 2.348165 -3.183522 1.496465 6 1.932497 -2.598552 0.153691 6 0.142358 -0.245596 2.218769 8 1.015587 0.692725 1.916195 8 -0.894630 0.013262 2.793448 1 1.878021 -4.162266 1.641466 1 3.430269 -3.308398 1.571558 1 2.496942 -1.330539 2.577023 1 1.641478 -2.577157 3.494331 1 -0.366931 -2.288913 2.258563 1 1.855929 -3.358780 -0.620361 1 2.636377 -1.837640 -0.190113 1 1.849844 0.405260 1.430494 6 -1.842578 0.415606 -0.884508 6 -0.750043 1.210606 -0.545484 6 -2.957656 -2.236561 -0.636576 1 -3.112543 -3.261689 -0.279047 1 -3.840040 -1.662257 -0.349739 1 -2.932546 -2.274898 -1.730572 1 -1.814855 -0.019452 -1.878758 1 -0.746399 1.945330 0.243756 6 -3.171720 0.809642 -0.381191 6 -3.372517 1.215597 0.945989 6 -4.629952 1.630398 1.366427 6 -5.702640 1.650486 0.476882 6 -5.514457 1.243307 -0.840663 6 -4.259923 0.818995 -1.263774 1 -2.550419 1.177931 1.654866 1 -4.773126 1.936212 2.397705 1 -6.682048 1.977285 0.811342 1 -6.344155 1.254492 -1.540210	6 0.998333 -0.344172 1.393389 6 -0.345013 0.068677 1.495698 6 -0.669478 1.524832 1.712831 7 -1.382582 -0.792170 1.447885 6 -1.231875 -2.249193 1.394775 6 -2.671728 -2.781311 1.499705 6 -3.409796 -1.675542 2.245216 6 -2.783933 -0.406990 1.680863 6 -0.534779 -2.795586 0.145697 8 -0.942135 -2.368188 -1.038013 8 0.348632 -3.617079 0.252297 1 -3.218582 -1.742330 3.321466 1 -4.489797 -1.706101 2.087276 1 -3.100596 -2.895936 0.500582 1 -2.698956 -3.750784 2.000047 1 -0.621184 -2.583513 2.240443 1 -2.842552 0.426033 2.380070 1 -3.258713 -0.097633 0.746136 1 -1.736466 -1.759447 -1.037147 1 -1.608516 1.773966 1.213961 1 0.101523 2.134249 1.233144 6 1.577150 -0.083923 -0.708977 1 0.788033 -0.758592 -1.016838 6 1.386189 1.254982 -1.073390 1 1.173400 -1.417159 1.397117 7 0.134337 1.697627 -1.354314 8 -0.075622 2.905480 -1.629137 8 -0.826194 0.877097 -1.312208 6 2.929439 -0.667401 -0.687348 6 3.067754 -2.059683 -0.787431 6 4.326924 -2.646635 -0.817233 6 5.471448 -1.857486 -0.743136 6 5.348766 -0.474018 -0.635207 6 4.091803 0.116000 -0.605784 1 2.181697 -2.685361 -0.835609 1 4.411778 -3.725340 -0.899395

1	-4.113961	0.505693	-2.293469
7	0.432109	1.085843	-1.208365
8	0.574040	0.180920	-2.078216
8	1.380979	1.863509	-0.954084
1	-1.840128	-1.287602	0.991319
6	-0.231787	-2.726358	-1.751266
1	0.756536	-2.468680	-2.134254
1	-0.936524	-2.276368	-2.453461
6	-0.430135	-4.246831	-1.740716
1	-0.251624	-4.654659	-2.739646
1	0.253939	-4.748504	-1.049487
1	-1.447152	-4.515909	-1.446156
8	3.349483	0.267576	0.825294
8	3.304751	-0.162523	-1.865152
1	3.339753	0.237925	-0.164160
1	2.356537	0.020320	-2.056675
6	4.100741	1.400392	1.250208
1	4.155166	1.363527	2.339864
1	5.120368	1.355578	0.851327
1	3.625190	2.340610	0.954406
6	4.078877	0.701435	-2.674620
1	5.125456	0.576822	-2.388105
1	3.980393	0.445777	-3.736892
1	3.792083	1.749641	-2.534831
1	1.595323	3.330607	0.208000
8	1.994415	4.130751	0.590092
6	2.161873	5.050543	-0.457851
1	2.788823	4.659890	-1.272861
1	1.205151	5.374303	-0.894392
1	2.656501	5.933505	-0.044387

1	6.454607	-2.316756	-0.767771
1	6.235522	0.148877	-0.575211
1	4.017753	1.194487	-0.517993
1	2.140102	2.025366	-1.077359
6	2.082088	0.460976	2.069021
1	3.063846	0.073887	1.788702
1	2.053822	1.521212	1.799436
1	2.012153	0.389125	3.161061
6	-0.733598	1.919773	3.194174
1	0.227195	1.766814	3.689471
1	-0.986829	2.979779	3.279919
1	-1.485286	1.348863	3.748122
1	-3.384411	-0.224185	-1.476335
8	-3.254381	-1.205076	-1.511176
8	-3.374731	1.478495	-1.271862
1	-2.389608	1.527908	-1.346389
6	-3.447490	-1.632954	-2.847670
1	-3.205434	-2.696090	-2.893110
1	-4.489832	-1.497180	-3.159503
1	-2.792368	-1.098153	-3.545119
6	-3.959910	2.404713	-2.163415
1	-5.044545	2.324983	-2.062307
1	-3.661097	3.430640	-1.920769
1	-3.690010	2.203806	-3.208099
1	0.934725	3.832203	-0.403999
8	1.490112	4.061902	0.367046
6	1.318741	5.429344	0.643916
1	1.931188	5.668677	1.517074
1	1.647623	6.071273	-0.185994
1	0.275854	5.686745	0.880194

Table S33. The mPW1PW91/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent-Assisted Pathway ($\mathbf{L_2C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the mPW1PW91/6-311G**//mPW1PW91/6-31G* and PCM-mPW1PW91/6-311G**//mPW1PW91/6-31G* Level of Theory.

a-si Et = -1573.1733583 (-1573.61331648) (-1573.6312005) NImag=1(-197.25 cm^{-1})				*a-re* Et = -1573.170 1132 (-1573.60884173) (-1573.629875) NImag= 1(-234.7 cm^{-1})			
6	4.066420	0.693827	-0.810731	6	3.947374	0.237542	-0.808247
6	2.855168	0.004491	-0.977096	6	2.730902	-0.450606	-0.935914
6	2.899503	-1.347715	-1.352529	6	2.761096	-1.799013	-1.323782
6	4.117868	-1.980833	-1.557497	6	3.968010	-2.439626	-1.575515
6	5.313561	-1.282795	-1.393563	6	5.168049	-1.746490	-1.438149
6	5.284361	0.057258	-1.018731	6	5.152742	-0.407199	-1.054805
6	1.602840	0.745090	-0.787603	6	1.427783	0.193563	-0.725519
6	0.445231	0.396350	-1.480960	6	0.994988	-0.012265	1.413950
7	-0.648756	1.202620	-1.481480	6	2.285361	0.364764	2.081782
8	-0.648241	2.317127	-0.875173	6	1.265215	1.578469	-0.872636
8	-1.679924	0.813657	-2.075828	7	0.011722	2.084440	-0.959226
6	1.121841	0.649424	1.421683	8	-0.175985	3.338865	-0.953630
6	2.334249	1.277937	2.046528	6	0.463246	-1.309140	1.460083
6	0.810139	-0.705081	1.523163	6	1.347514	-2.507209	1.684961
6	1.870874	-1.717796	1.867942	6	1.352907	-2.909179	3.166211
6	1.868919	-2.050515	3.365331	7	-0.859944	-1.513171	1.313791
7	-0.449409	-1.148646	1.301228	6	-1.471380	-2.805980	0.958435
6	-0.818982	-2.570660	1.163385	6	-2.984913	-2.584863	1.145448
6	-2.307807	-2.638646	1.558312	6	-3.097484	-1.273934	1.928325
6	-2.621481	-1.259957	2.146966	6	-1.880967	-0.477059	1.476610
6	-1.662971	-0.332931	1.410563	6	-1.044592	-3.226120	-0.460171
6	-0.471750	-3.051222	-0.256019	8	-1.439157	-2.487935	-1.486090
8	-1.224291	-2.657746	-1.270691	8	-0.304165	-4.171711	-0.621626
8	0.521451	-3.721751	-0.444176	8	-0.980549	1.310707	-1.009416
1	-2.404402	-1.233948	3.219492	1	-3.039975	-1.458020	3.005932
1	-3.664826	-0.971706	2.003715	1	-4.031565	-0.747628	1.722763
1	-2.942503	-2.822692	0.689788	1	-3.485538	-2.474874	0.182165
1	-2.478650	-3.450516	2.268269	1	-3.438127	-3.432019	1.663854
1	-0.209993	-3.178319	1.831814	1	-1.100038	-3.588770	1.622425
1	-1.464178	0.596440	1.942667	1	-1.554002	0.261232	2.209448
1	-2.053911	-0.078593	0.418542	1	-2.045275	0.057488	0.534657
1	3.250920	0.702682	1.891454	1	2.642930	1.321138	1.687819
1	2.483726	2.277987	1.630054	1	2.144269	0.499008	3.161442
1	2.200460	1.400892	3.128859	1	3.080770	-0.369863	1.938003
1	1.731739	1.794107	-0.543069	1	2.046137	2.324007	-0.820490
1	0.288511	-0.534383	-2.003720	1	0.566489	-0.396440	-1.017264
1	1.986360	-1.922466	-1.464145	1	1.829399	-2.345967	-1.438274
1	4.131385	-3.027680	-1.842276	1	3.968796	-3.480088	-1.883231
1	6.262907	-1.782930	-1.556311	1	6.111545	-2.245503	-1.634587
1	6.209897	0.609726	-0.892433	1	6.084083	0.140729	-0.954920
1	4.042449	1.742725	-0.531344	1	3.954899	1.284838	-0.526015
1	0.294708	1.336964	1.274070	1	-2.170891	-1.821569	-1.329564
1	2.843477	-1.309891	1.590007	1	0.266492	0.791367	1.379903
1	1.747500	-2.625988	1.273712	1	2.362486	-2.262404	1.368021
1	0.911691	-2.471546	3.688050	1	1.032517	-3.353616	1.071443
1	2.649414	-2.782852	3.589301	1	0.348984	-3.169944	3.514632
1	2.057180	-1.158965	3.969688	1	1.997769	-3.779302	3.315584
1	-2.080666	-2.184142	-1.060549	1	1.724389	-2.098829	3.799347
8	-3.684935	-1.738989	-1.189541	8	-3.590686	-0.998269	-1.595852
1	-3.919246	-0.787110	-1.058524	1	-3.606000	-0.005532	-1.533635
6	-4.105329	-2.103334	-2.494832	6	-4.064330	-1.353238	-2.883957

1	-5.194549	-2.033897	-2.587639	1	-5.125939	-1.104887	-2.993888
1	-3.639613	-1.471712	-3.258633	1	-3.499717	-0.850644	-3.676863
1	-3.802106	-3.138327	-2.661270	1	-3.941649	-2.431763	-2.998362
8	-4.198926	0.887117	-1.164015	8	-3.549045	1.658316	-1.635675
1	-3.325827	1.195546	-1.483078	1	-2.587376	1.811624	-1.509030
6	-4.788514	1.851157	-0.311182	6	-4.261969	2.494962	-0.741480
1	-5.672985	1.392416	0.135966	1	-3.768635	2.561302	0.233989
1	-4.109076	2.170481	0.486800	1	-4.365533	3.506146	-1.153600
1	-5.111063	2.732878	-0.878866	1	-5.262080	2.073682	-0.613978
1	-1.653884	2.692490	0.624094	1	-1.257848	3.272261	0.640297
8	-1.957707	2.851466	1.536311	1	1.437720	4.317686	-0.964340
6	-1.627070	4.182261	1.875216	8	-1.601326	3.038281	1.521986
1	-1.821717	4.305577	2.943221	6	-1.482274	4.172109	2.347617
1	-0.570614	4.405215	1.683397	1	-2.069637	5.024914	1.979371
1	-2.242964	4.912428	1.331325	1	-1.864500	3.901038	3.334850
1	0.700962	3.496565	-0.406862	1	-0.439842	4.500291	2.464998
8	1.454559	4.000171	-0.048854	8	2.363323	4.577414	-0.795277
6	1.794654	5.007399	-0.974929	6	2.405512	5.187328	0.469513
1	0.979089	5.727612	-1.124020	1	3.447486	5.443372	0.678139
1	2.653570	5.546906	-0.569577	1	1.816679	6.115111	0.510036
1	2.077757	4.599531	-1.954963	1	2.051874	4.525301	1.275054
s-si Et = -1573.1712209 (-1573.61095229) (-1573.6310052) NImag=1(-174.00 cm^{-1})				*s-re* Et = -1573.1718951 (-1573.61041461) (-1573.6310695) NImag = 1(-248.80 cm^{-1})			
6	4.353867	0.545119	-1.084305	6	1.508675	-0.707572	1.318495
6	3.287030	-0.343148	-0.883417	6	0.149434	-0.903095	1.610537
6	3.545157	-1.721867	-0.851110	6	-0.605730	0.127440	2.413128
6	4.838901	-2.191783	-1.032906	7	-0.531819	-2.010502	1.240177
6	5.890504	-1.302466	-1.251314	6	0.082289	-3.158830	0.569489
6	5.645114	0.067506	-1.275596	6	-1.059717	-4.182364	0.459117
6	1.937564	0.218569	-0.756550	6	-1.951832	-3.844744	1.647434
6	0.850972	-0.416801	-1.342025	6	-1.898164	-2.323049	1.693428
7	-0.341631	0.221234	-1.514209	6	0.692140	-2.872040	-0.803982
8	-1.276211	-0.401598	-2.074713	8	-0.028407	-2.199210	-1.683660
8	-0.500763	1.413299	-1.132692	8	1.801614	-3.279143	-1.072291
6	1.746359	0.061550	1.557448	1	-1.538240	-4.266060	2.569827
6	2.948314	0.832599	2.023211	1	-2.972325	-4.215689	1.531233
6	0.445790	0.543388	1.663806	1	-1.611556	-4.025495	-0.472457
6	0.191150	2.011234	1.898818	1	-0.677330	-5.204489	0.464211
6	0.080389	2.328105	3.394477	1	0.904994	-3.546207	1.181020
7	-0.612943	-0.308575	1.587973	1	-2.065127	-1.938264	2.699154
6	-0.497187	-1.734427	1.953310	1	-2.637772	-1.861656	1.034395
6	-1.890294	-2.124120	2.495177	1	-0.973722	-1.978591	-1.421677
6	-2.609263	-0.793191	2.717636	1	-1.652884	0.143017	2.103130
6	-2.021247	0.095276	1.631534	1	-0.201305	1.117569	2.183084
6	-0.004515	-2.645667	0.817020	6	1.594991	0.520150	-0.604562
8	1.103274	-3.137280	0.867073	1	1.022858	-0.256794	-1.095935
8	-0.803528	-2.893253	-0.207677	6	0.919709	1.723174	-0.390451
8	-2.413935	3.096851	0.034788	1	2.040794	-1.545104	0.875127
6	-3.706194	3.348868	-0.468081	7	-0.434302	1.753442	-0.440484
8	-3.386634	-2.373842	-0.438257	8	-1.044773	2.854532	-0.277437
6	-3.730091	-3.453768	-1.288528	8	-1.082389	0.696914	-0.636227
8	-3.874488	-0.012768	-1.675000	6	3.042729	0.502921	-0.842817
6	-4.611727	0.073948	-2.878883	6	3.608490	-0.603340	-1.495719
1	-2.371567	-0.379479	3.703336	6	4.967557	-0.636996	-1.781327
1	-3.694163	-0.887022	2.636530	6	5.788259	0.427363	-1.417732
1	-2.443427	-2.715823	1.763771	6	5.241583	1.528482	-0.761677
1	-1.795326	-2.721961	3.403942	6	3.883775	1.567049	-0.475247
1	0.268573	-1.819637	2.728224	1	2.978949	-1.444014	-1.770880
1	-2.133857	1.159128	1.819477	1	5.385332	-1.499848	-2.289518
1	-2.487987	-0.109144	0.661422	1	6.849909	0.399737	-1.641806

1	-1.716128	-2.491687	-0.186077
1	3.043169	0.798602	3.116184
1	3.860034	0.394274	1.611453
1	2.926265	1.885987	1.730308
1	1.893135	1.295294	-0.649668
1	0.849647	-1.434873	-1.697645
1	2.740223	-2.420663	-0.644826
1	5.029088	-3.259589	-0.997416
1	6.898973	-1.677436	-1.394379
1	6.459107	0.765807	-1.441566
1	4.155260	1.612653	-1.107768
1	1.881989	-1.014677	1.510217
1	-0.705005	2.355312	1.384086
1	1.007759	2.581892	1.453723
1	-0.076027	3.400650	3.539729
1	-0.762925	1.803911	3.855510
1	0.985982	2.041868	3.936685
1	-3.662088	-1.532639	-0.878830
1	-2.915925	0.088417	-1.883043
1	-3.366228	-4.370599	-0.821852
1	-4.816993	-3.530999	-1.409025
1	-3.264245	-3.360521	-2.276506
1	-5.659313	-0.119979	-2.640079
1	-4.537767	1.074713	-3.320198
1	-4.278649	-0.661171	-3.621945
1	-1.971881	2.454924	-0.546274
1	-3.681185	3.871275	-1.435705
1	-4.291148	2.428460	-0.585167
1	-4.214652	3.997503	0.249408
1	0.724346	2.866176	-1.194664
8	1.406045	3.520111	-0.966712
6	0.787544	4.788314	-0.935508
1	0.573905	5.167356	-1.945554
1	-0.149843	4.776737	-0.365959
1	1.481972	5.482763	-0.455963

1	5.875364	2.360635	-0.472555
1	3.478145	2.430041	0.041677
1	1.373217	2.671341	-0.151926
6	2.355761	0.183876	2.190304
1	3.335859	0.333695	1.732542
1	1.909551	1.170085	2.351294
1	2.532753	-0.268824	3.173731
6	-0.507432	-0.086090	3.929674
1	0.525464	-0.018834	4.276604
1	-1.083601	0.685578	4.447259
1	-0.897333	-1.060090	4.240957
1	-3.065116	-1.184879	-1.017760
8	-2.605851	-1.801075	-1.636224
8	-3.586935	0.050025	0.080104
1	-2.800653	0.600140	-0.122221
6	-2.783760	-1.281460	-2.949143
1	-2.062403	-1.777969	-3.600479
1	-3.794133	-1.495759	-3.316578
1	-2.611579	-0.200850	-2.976983
6	-4.770925	0.819399	-0.077100
1	-5.605543	0.121372	-0.172373
1	-4.945884	1.447761	0.804943
1	-4.715397	1.454532	-0.964963
1	-0.250363	3.545544	1.269382
8	0.325192	3.622291	2.053113
6	-0.199790	4.619567	2.894680
1	0.449599	4.684963	3.771115
1	-0.219737	5.607858	2.413578
1	-1.217071	4.388251	3.242174
1	-2.432734	2.729699	-1.548592
8	-3.096414	2.610889	-2.253055
6	-3.071981	3.756050	-3.066926
1	-3.341071	4.671494	-2.519501
1	-2.091842	3.917077	-3.538379
1	-3.807892	3.611303	-3.861917

Table S34. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Propanal (**1**) to Nitrostyrene Using Unassisted Pathway . The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1031.9969962 (-1032.273592) (-1032.3096274) NImag=1(-307.01 cm^{-1})				*a-re* Et =-1031.999442 (-1032.2766162) (-1032.3096078) NImag= 1(-356.42 cm^{-1})			
6	3.671270	-0.981329	0.353200	6	-3.182880	1.174011	-0.056641
6	2.450317	-0.293304	0.285071	6	-2.836779	-0.149366	0.266663
6	2.475389	1.089506	0.032127	6	-3.856022	-1.115023	0.297823
6	3.686489	1.758279	-0.139911	6	-5.180380	-0.768437	0.027456
6	4.894778	1.061246	-0.063501	6	-5.508453	0.550061	-0.288434
6	4.883527	-0.311486	0.185611	6	-4.503744	1.520814	-0.329688
6	1.168315	-1.037740	0.497940	6	-1.439523	-0.544612	0.587163
6	0.253428	-0.409493	1.416305	6	-0.570259	-0.709116	-1.288837
7	-0.884856	-1.018304	1.796737	6	-0.691446	0.293708	1.444861
8	-1.075271	-2.249979	1.572290	7	0.522743	-0.116605	1.905825
8	-1.828740	-0.318590	2.357392	8	1.242612	0.629955	2.607790
6	0.381140	-1.401067	-1.202224	6	0.827991	-0.707612	-1.086021
6	-0.467163	-0.273776	-1.413848	7	1.582043	0.372810	-0.927644
7	-1.724543	-0.207001	-1.032326	6	3.060048	0.388931	-0.790964
6	-2.464197	1.084785	-0.860191	6	3.269961	1.647514	0.066140
6	-3.808882	0.642125	-0.268433	6	2.272572	2.642155	-0.557643
6	-4.027175	-0.749074	-0.878886	6	1.095504	1.767836	-1.053431
6	-2.627915	-1.369508	-0.817362	6	3.814607	-0.858773	-0.281980
6	-1.630526	2.106476	-0.048185	8	3.352652	-1.571592	0.733769
8	-1.640738	2.036117	1.272627	8	4.876451	-1.109099	-0.812978
8	-1.002801	2.953794	-0.656433	8	0.912623	-1.297237	1.559247
1	-4.374972	-0.671133	-1.916077	1	2.732694	3.166343	-1.401470
1	-4.752660	-1.344707	-0.319124	1	1.937991	3.394903	0.160445
1	-3.729649	0.555232	0.818437	1	3.002514	1.430171	1.105730
1	-4.601016	1.357101	-0.504992	1	4.305567	1.993071	0.026773
1	-2.594683	1.533932	-1.849812	1	3.480226	0.557132	-1.790030
1	-2.433221	-2.110208	-1.597395	1	0.839832	1.970641	-2.101937
1	-2.417072	-1.825199	0.159498	1	0.197746	1.892701	-0.450924
1	1.322224	-2.098499	0.698634	1	-0.968802	1.297805	1.730818
1	0.330146	0.633606	1.681189	1	-1.293319	-1.606847	0.760328
1	1.548751	1.655581	-0.027001	1	-3.608313	-2.141478	0.555810
1	3.684313	2.827652	-0.332079	1	-5.954419	-1.529952	0.065338
1	5.837190	1.585504	-0.196181	1	-6.538394	0.821289	-0.502722
1	5.817580	-0.862830	0.252248	1	-4.750797	2.549654	-0.577153
1	3.670117	-2.049323	0.558294	1	-2.410345	1.937952	-0.098308
1	-0.162787	-2.305638	-0.932892	1	2.464188	-1.302949	1.127409
1	-1.833508	1.113375	1.689513	1	-0.986245	0.213308	-1.688523
6	1.495862	-1.638992	-2.207683	1	1.354490	-1.653712	-1.008810
1	2.000350	-0.708531	-2.485487	6	-1.173630	-1.977538	-1.860990
1	2.251684	-2.316258	-1.798043	1	-2.255543	-2.004942	-1.698970
1	1.099325	-2.098267	-3.121334	1	-1.005100	-2.053631	-2.942806
1	-0.023860	0.675114	-1.715482	1	-0.737578	-2.868446	-1.393756
s-si Et =-1032.0017757 (-1032.2779349) (-1032.3072107) NImag=1(-351.61 cm^{-1})				*s-re* Et = -1031.9934454 (-1032.2708424) (-1032.3049882) NImag = 1(-389.86 cm^{-1})			
6	0.308555	-0.785777	-1.378104	6	0.141909	0.162825	1.352800
6	-1.009507	-1.226524	-1.126070	6	-1.182087	0.655216	1.213599
7	-2.031672	-0.472664	-0.724370	7	-2.270581	-0.001803	0.810853
6	-2.169891	0.994817	-0.910468	6	-2.312230	-1.389274	0.335665
6	-3.685710	1.254506	-0.691100	6	-3.831601	-1.665366	0.116474

6	-4.357559	-0.121580	-0.831921	6	-4.552843	-0.524900	0.856066
6	-3.301966	-1.072818	-0.271399	6	-3.587189	0.651394	0.704199
6	-1.312589	1.912629	-0.005022	6	-1.566503	-1.675553	-0.981156
8	-1.525678	1.899355	1.310076	8	-1.429361	-0.681762	-1.866428
8	-0.551989	2.706012	-0.522904	8	-1.223132	-2.809515	-1.230881
1	-4.555116	-0.353478	-1.885100	1	-4.678482	-0.769065	1.916950
1	-5.303799	-0.180988	-0.287317	1	-5.539825	-0.312132	0.436592
1	-3.842088	1.647361	0.317678	1	-4.062222	-1.622666	-0.953166
1	-4.061499	1.996763	-1.399775	1	-4.105938	-2.660481	0.472128
1	-1.858208	1.231169	-1.931475	1	-1.884991	-2.054311	1.092920
1	-3.378207	-2.098511	-0.638287	1	-3.687503	1.412916	1.481974
1	-3.286210	-1.099891	0.826713	1	-3.677353	1.146577	-0.270825
1	-1.771480	1.002193	1.716343	1	-1.445325	0.243037	-1.487047
6	1.210967	-0.941555	0.423561	6	1.154520	0.574120	-0.336306
6	0.355631	-0.410284	1.423727	1	0.486332	-0.017382	-0.946345
1	1.250894	-2.027730	0.396173	6	1.133203	1.961261	-0.633899
1	0.458751	0.579193	1.839714	1	0.239843	-0.921599	1.295520
6	2.524044	-0.269419	0.213491	7	-0.031371	2.574957	-0.984083
6	2.638565	1.129358	0.124446	8	-0.069612	3.788862	-1.259696
6	3.887912	1.724963	-0.036615	8	-1.127932	1.876372	-0.954088
6	5.041769	0.940282	-0.114042	6	2.463410	-0.110708	-0.140920
6	4.938982	-0.448950	-0.035726	6	2.556323	-1.477703	-0.455931
6	3.688691	-1.048098	0.119839	6	3.758869	-2.166284	-0.308634
1	1.750274	1.754801	0.164608	6	4.893538	-1.501992	0.161538
1	3.959346	2.806975	-0.104980	6	4.815274	-0.145397	0.483010
1	6.013711	1.409780	-0.239248	6	3.611785	0.543460	0.336647
1	5.829987	-1.068108	-0.095656	1	1.678224	-2.000386	-0.829799
1	3.613026	-2.130622	0.188429	1	3.810024	-3.220587	-0.566291
7	-0.778659	-1.078061	1.760239	1	5.832524	-2.036771	0.275557
8	-0.966416	-2.255917	1.348584	1	5.693794	0.379883	0.847943
8	-1.691217	-0.473967	2.450589	1	3.569265	1.597809	0.593352
1	0.432100	0.289100	-1.505183	1	1.973579	2.632776	-0.544934
6	1.147353	-1.638308	-2.313175	1	-1.381672	1.672649	1.535063
1	2.212935	-1.426976	-2.186666	6	0.943337	0.808118	2.473834
1	0.987313	-2.707197	-2.126709	1	0.548840	0.538857	3.461653
1	0.896108	-1.443078	-3.363042	1	1.988677	0.490660	2.437598
1	-1.224605	-2.289001	-1.176587	1	0.917879	1.901189	2.390607

Table S35. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Unassisted Pathway . The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1110.6261298 (-1110.92281077) (-1110.95588907) NImag=1(-304.9 cm^{-1})				*a-si (II)* Et = -1110.6071035 (-1110.9056829) (-1110.941439) NImag=1(-349.91 cm^{-1})			
6	-3.770821	-0.924237	0.462139	6	0.556100	-0.085385	-1.033776
6	-2.554209	-0.559726	-0.137072	6	-0.827353	-0.262988	-0.657167
6	-2.581356	0.421262	-1.144360	6	-1.459270	-1.631653	-0.785222
6	-3.781267	1.016055	-1.531415	7	-1.603668	0.790647	-0.284286
6	-4.981966	0.643890	-0.922275	6	-2.877026	0.587700	0.469951
6	-4.972790	-0.331828	0.074862	6	-3.117798	1.928159	1.208045
6	-1.294005	-1.246047	0.287187	6	-1.708833	2.506865	1.357369
6	-0.368388	-1.580907	-0.756050	6	-1.056814	2.141855	0.023914
7	0.701347	-2.361439	-0.497547	6	-4.085504	0.267543	-0.411376
8	0.781213	-3.031477	0.570585	8	-4.012961	0.716596	-1.691053
8	1.694234	-2.374732	-1.333348	8	-5.075128	-0.268376	0.014793
6	-0.426096	-0.244889	1.687839	1	-1.177159	2.003336	2.171172
6	-1.500142	0.253281	2.640317	1	-1.703326	3.585356	1.540988
6	0.440719	0.692675	1.028187	1	-3.742629	2.594885	0.601072
6	-0.055417	2.057691	0.615013	1	-3.632000	1.757292	2.155673
6	0.344430	3.130078	1.654718	1	-2.730772	-0.216157	1.193807
7	1.676481	0.314221	0.686367	1	0.027954	2.127365	0.077061
6	2.546731	1.027651	-0.302158	1	-1.350277	2.843199	-0.769150
6	3.889148	0.275387	-0.219167	1	-3.105117	1.039349	-1.845539
6	3.921151	-0.246922	1.219103	1	-2.266684	-1.755501	-0.064123
6	2.477584	-0.699991	1.438627	1	-0.695089	-2.363866	-0.503691
6	1.992279	1.105800	-1.747796	6	1.609135	-0.235874	0.546920
8	1.767589	-0.012165	-2.418489	1	1.087806	0.539095	1.104672
8	1.830288	2.201628	-2.250497	6	1.475914	-1.504207	1.190964
1	4.191438	0.553307	1.918986	1	0.799872	0.944002	-1.290236
1	4.624745	-1.072677	1.354713	7	0.324883	-1.765854	1.877560
1	3.887807	-0.566724	-0.918061	8	0.164012	-2.839203	2.495680
1	4.723816	0.933256	-0.474285	8	-0.595617	-0.866150	1.832422
1	2.667623	2.065651	0.017237	6	2.986241	0.201622	0.142899
1	2.170264	-0.680546	2.486183	6	3.303447	1.568620	0.177084
1	2.304397	-1.707148	1.047315	6	4.574091	2.026990	-0.169109
1	-2.127115	1.038489	2.210413	6	5.559429	1.120624	-0.563063
1	-2.161744	-0.572527	2.920607	6	5.261216	-0.242756	-0.604123
1	-1.055916	0.639511	3.566340	6	3.989276	-0.697049	-0.256744
1	-1.484956	-2.075875	0.967042	1	2.547605	2.282716	0.498719
1	-0.346880	-1.077342	-1.709760	1	4.795368	3.090057	-0.124753
1	-1.661911	0.720636	-1.639263	1	6.551489	1.472421	-0.832330
1	-3.777589	1.768545	-2.315260	1	6.022213	-0.957825	-0.904888
1	-5.916322	1.107071	-1.227101	1	3.777710	-1.761298	-0.293928
1	-5.901399	-0.637852	0.549066	1	2.195013	-2.308576	1.175815
1	-3.775479	-1.695459	1.228484	6	1.164526	-1.041604	-2.052330
1	0.110169	-1.102605	2.088672	1	2.226595	-0.815609	-2.173590
1	-1.143236	2.029432	0.525829	1	1.081666	-2.088012	-1.744150
1	0.335572	2.348313	-0.362703	1	0.697493	-0.936912	-3.037510
1	1.432269	3.208325	1.755315	6	-1.993718	-1.974515	-2.195463
1	-0.034284	4.106826	1.337741	1	-1.210706	-1.959823	-2.956622
1	-0.070824	2.908530	2.642823	1	-2.417148	-2.983818	-2.172817
1	1.824675	-0.909978	-1.924279	1	-2.789184	-1.291841	-2.505958
a-re Et = -1110.6242292 (-1110.92146213) (-1110.95292843) NImag= 1(-343.6 cm^{-1})				*a-re (II)* Et = -1110.6204426 (-1110.9183167) (-1110.952648) NImag= 1(-263.39 cm^{-1})			

6	-3.500635	-0.891771	0.766366	6	-3.662511	0.686711	-0.489026
6	-3.028498	-0.140942	-0.323793	6	-2.572247	0.180957	0.239155
6	-3.946541	0.642533	-1.041042	6	-2.810655	-0.869712	1.139687
6	-5.296668	0.664126	-0.691203	6	-4.089653	-1.403529	1.303875
6	-5.751899	-0.089558	0.391296	6	-5.159564	-0.895191	0.567206
6	-4.847669	-0.866781	1.120234	6	-4.940618	0.155289	-0.327137
6	-1.604013	-0.174309	-0.748006	6	-1.186734	0.746328	0.118591
6	-0.700278	1.044056	0.702248	6	-0.350000	0.024025	-1.436922
6	-1.477466	2.348273	0.627626	6	-1.371087	-0.602296	-2.378003
6	-0.967971	-1.431482	-0.818365	6	-1.103038	2.182918	0.055406
7	0.248559	-1.562930	-1.419482	7	0.038667	2.852915	0.345725
8	0.876598	-2.645602	-1.367583	8	0.076558	4.099610	0.305312
6	0.696709	1.029419	0.416707	6	0.672172	-0.822560	-0.867697
6	1.308908	2.151323	-0.394638	6	0.309470	-2.187877	-0.330679
6	2.052832	3.185929	0.475530	6	0.725902	-3.305027	-1.313550
7	1.479004	0.041366	0.882946	7	1.924570	-0.390317	-0.732174
6	2.957247	-0.101829	0.722475	6	2.888378	-0.909462	0.274467
6	3.177572	-1.582116	1.077364	6	4.109325	0.029752	0.135122
6	2.241560	-1.774641	2.272885	6	4.017525	0.539006	-1.308317
6	1.002683	-0.947167	1.897998	6	2.512967	0.743290	-1.489446
6	3.710465	0.259589	-0.580881	6	2.354971	-0.936688	1.723781
8	3.282637	-0.165549	-1.759495	8	1.604206	0.073036	2.155242
8	4.771668	0.835852	-0.451761	8	2.659232	-1.866020	2.440995
8	0.736043	-0.534734	-2.023215	8	1.126006	2.190396	0.629372
1	2.704242	-1.380589	3.184657	1	4.398906	-0.210926	-2.011874
1	1.985530	-2.822469	2.450788	1	4.573016	1.467679	-1.463685
1	2.864792	-2.208359	0.234432	1	4.010198	0.869605	0.831274
1	4.227806	-1.783558	1.301791	1	5.038350	-0.496341	0.365938
1	3.437269	0.526273	1.480962	1	3.161957	-1.940157	0.034486
1	0.580670	-0.411169	2.756424	1	2.181283	0.697500	-2.529276
1	0.223466	-1.570706	1.462156	1	2.179490	1.679644	-1.024445
1	-1.556005	2.741558	-0.392659	1	-2.144947	0.125865	-2.632869
1	-2.496494	2.189780	0.987495	1	-0.890273	-0.910599	-3.315186
1	-1.029340	3.135690	1.246938	1	-1.873559	-1.474275	-1.950884
1	-1.327151	-2.330363	-0.338938	1	-1.915718	2.820451	-0.258349
1	-1.349555	0.509664	-1.551943	1	-0.549392	0.334698	0.894484
1	-3.599063	1.226314	-1.889559	1	-1.989022	-1.254171	1.739291
1	-5.991922	1.270235	-1.265544	1	-4.249133	-2.209351	2.015251
1	-6.802465	-0.071198	0.667518	1	-6.156984	-1.307085	0.693625
1	-5.193429	-1.454177	1.966546	1	-5.769048	0.565946	-0.898127
1	-2.806486	-1.496082	1.344928	1	-3.514180	1.509577	-1.182539
1	2.325988	-0.488086	-1.804340	1	1.423693	0.829765	1.511967
1	-1.004814	0.421713	1.537670	1	0.054926	0.938714	-1.860048
1	0.505027	2.651174	-0.938087	1	-0.770029	-2.228729	-0.170888
1	1.979057	1.758276	-1.158691	1	0.776963	-2.378780	0.639453
1	2.950896	2.761984	0.933419	1	1.807643	-3.308971	-1.483174
1	2.372968	4.024350	-0.151105	1	0.445718	-4.279817	-0.902334
1	1.412470	3.583064	1.270517	1	0.231861	-3.190206	-2.283388
a-re (II) (without H-bonding) Et = -1110.6141063 (-1110.9122106) (-1110.945815) NImag=1(-332.04 cm^{-1})				*s-si* Et = -1110.6261066 (-1110.92268724) (-1110.95080050) NImag=1(-338.25 cm^{-1})			
6	-0.626124	1.110141	-0.473129	6	-0.289313	1.010489	-0.842111
6	0.757549	0.939084	-0.126850	6	1.024902	1.258509	-0.356116
7	1.460670	-0.100346	-0.631770	7	1.933517	0.263882	-0.307872
6	2.727029	-0.599720	-0.021414	6	1.909325	-0.944340	-1.184808
6	3.002066	-1.951357	-0.732534	6	3.369845	-1.475143	-1.155849
6	1.630728	-2.389999	-1.257010	6	4.204841	-0.333531	-0.559866
6	0.963378	-1.072048	-1.648223	6	3.229110	0.342456	0.400758
6	3.939621	0.311832	-0.216198	6	0.925079	-2.091238	-0.843063
8	3.988413	0.985820	-1.399414	8	1.082923	-2.762510	0.297022
8	4.848943	0.372859	0.568442	8	0.117158	-2.440528	-1.681562

1 3.704873 -1.808128 -1.562383 1 3.443141 -2.663545 -0.033375 1 2.550388 -0.745656 1.048909 1 -0.120113 -1.135482 -1.639089 1 1.280651 -0.736051 -2.647846 1 3.137643 0.878644 -1.859999 6 -1.627591 -0.021291 0.745389 6 -1.042783 -1.304333 0.953756 6 -1.264782 2.486418 -0.351063 1 -0.875864 3.181897 -1.103655 1 -2.343025 2.406661 -0.510079 1 -1.109301 2.938242 0.633824 1 -1.510666 0.643312 1.600537 1 -1.403673 -2.222930 0.514898 6 -3.019029 -0.033549 0.187461 6 -3.353049 -0.771275 -0.959517 6 -4.661049 -0.796125 -1.440635 6 -5.664377 -0.079382 -0.784441 6 -5.347080 0.661730 0.354407 6 -4.036053 0.687212 0.831693 1 -2.583774 -1.337476 -1.479760 1 -4.897673 -1.376115 -2.328739 1 -6.684012 -0.098410 -1.159118 1 -6.119901 1.221238 0.874564 1 -3.797694 1.261130 1.723639 7 0.090863 -1.423616 1.705383 8 0.585638 -0.364734 2.215748 8 0.650997 -2.544359 1.846203 1 -0.911629 0.634834 -1.407670 6 1.440389 1.922138 0.802392 1 2.254296 1.440723 1.344724 1 0.713470 2.202255 1.568295 6 1.967764 3.194169 0.101335 1 2.412712 3.853817 0.853596 1 2.745166 2.964083 -0.631658 1 1.172884 3.751565 -0.401179 1 1.068083 -2.866950 -0.449797 1 1.701717 -3.078478 -2.104269	1 4.513878 0.373027 -1.339537 1 5.104468 -0.692494 -0.052181 1 3.424459 -2.357219 -0.511975 1 3.693601 -1.774335 -2.156029 1 1.618814 -0.615876 -2.185517 1 3.494815 1.372247 0.624676 1 3.119489 -0.198712 1.351452 1 1.376940 -2.216610 1.100538 6 -1.292292 0.443077 0.850704 6 -0.572158 -0.600783 1.482900 6 -1.118358 2.133915 -1.440736 1 -0.657429 2.533502 -2.353028 1 -2.107530 1.758382 -1.712242 1 -1.265953 2.972434 -0.751711 1 -1.208453 1.412268 1.335671 1 -0.797341 -1.646730 1.350442 6 -2.654740 0.127326 0.339420 6 -2.923847 -1.037998 -0.400246 6 -4.220152 -1.315950 -0.829904 6 -5.268063 -0.440710 -0.532220 6 -5.010501 0.722835 0.193860 6 -3.712855 1.006874 0.618992 1 -2.118474 -1.721189 -0.657393 1 -4.410966 -2.219607 -1.402261 1 -6.277229 -0.662682 -0.868536 1 -5.818025 1.410822 0.429530 1 -3.516746 1.912438 1.188061 7 0.580582 -0.329113 2.153493 8 0.899341 0.857843 2.424941 8 1.370596 -1.303298 2.467976 1 -0.415503 0.069002 -1.370899 6 1.414777 2.647019 0.113982 1 1.989358 2.597285 1.038003 1 0.503168 3.191884 0.367385 6 2.189431 3.424199 -0.969585 1 2.423982 4.432397 -0.611949 1 3.134285 2.930528 -1.223566 1 1.607369 3.521755 -1.891970
s-si(II)(without H-bonding) Et = -1110.6103846 (-1110.9091252) (-1110.940734) NImag=1(-373.45 cm^{-1})	*s-re* Et = -1110.6202785 (-1110.91838936) (-1110.95138960) NImag = 1(-359.10 cm^{-1})
6 -2.686383 -1.308104 -0.830279 6 -2.575366 0.005567 -0.346957 6 -3.695770 0.575651 0.279486 6 -4.886696 -0.139264 0.404078 6 -4.981986 -1.442072 -0.088410 6 -3.874646 -2.026050 -0.705536 6 -1.277288 0.735932 -0.521250 6 -1.304770 2.161135 -0.592902 7 -0.177795 2.809062 -0.999568 8 0.845870 2.071251 -1.269527 8 -0.123824 4.055720 -1.073887 6 -0.169438 0.114137 0.905006 6 -0.848575 0.545295 2.198966 6 1.180866 0.553807 0.653410 6 1.749347 1.755668 1.375200 6 2.476342 1.358999 2.678338 7 2.054104 -0.214251 -0.056006 6 1.681728 -1.511612 -0.662803 6 2.898532 -1.869041 -1.545259 6 3.416283 -0.497711 -1.989561	6 0.171586 -0.198978 -1.112111 6 -1.158278 -0.656268 -0.824462 6 -1.460040 -2.137419 -0.894598 7 -2.163899 0.182012 -0.526775 6 -2.045713 1.652736 -0.470560 6 -3.489756 2.146609 -0.168590 6 -4.389390 0.952048 -0.508517 6 -3.523144 -0.252259 -0.140543 6 -1.113929 2.241321 0.604934 8 -1.011001 1.608270 1.776742 8 -0.602312 3.322619 0.410489 1 -4.619157 0.930593 -1.580092 1 -5.334728 0.964868 0.040836 1 -3.578531 2.388785 0.895680 1 -3.721965 3.050768 -0.735120 1 -1.687588 2.026248 -1.434465 1 -3.809572 -1.155060 -0.678876 1 -3.539776 -0.473234 0.934745 1 -1.139995 0.613250 1.748875 1 -2.165835 -2.410477 -0.109298

6 3.242051 0.373551 -0.742525 6 1.418670 -2.622659 0.361359 8 2.082621 -2.509184 1.532848 8 0.720688 -3.572806 0.110763 1 2.793955 -0.099748 -2.798132 1 4.453330 -0.524054 -2.336117 1 3.655120 -2.389927 -0.945338 1 2.609595 -2.528179 -2.366638 1 0.785300 -1.419499 -1.279958 1 3.029149 1.411549 -0.995746 1 4.119321 0.326720 -0.085148 1 -0.941503 1.633306 2.273281 1 -1.856740 0.125817 2.237461 1 -0.313039 0.185540 3.084591 1 -0.670332 0.307738 -1.315763 1 -2.108810 2.803853 -0.269544 1 -3.642767 1.586424 0.671806 1 -5.742582 0.324809 0.886899 1 -5.910579 -1.997657 0.009635 1 -3.933998 -3.040036 -1.091234 1 -1.829462 -1.776971 -1.309632 1 -0.320391 -0.947125 0.720204 1 0.934614 2.446818 1.601236 1 2.437399 2.302794 0.731560 1 3.348351 0.725734 2.472469 1 2.838548 2.257884 3.187818 1 1.824324 0.821429 3.373291 1 2.526789 -1.640123 1.548280	1 -0.534667 -2.671624 -0.658698 6 1.250998 -0.338253 0.570232 1 0.718332 0.469456 1.050801 6 1.112861 -1.582818 1.246790 1 0.254889 0.880004 -1.237408 7 -0.034086 -1.885604 1.918865 8 -0.140890 -2.946308 2.563898 8 -1.048576 -1.079551 1.826434 6 2.613629 0.100425 0.148272 6 2.877626 1.478833 0.069990 6 4.139568 1.946478 -0.293787 6 5.162756 1.044248 -0.590645 6 4.913079 -0.328221 -0.522732 6 3.650799 -0.795825 -0.160410 1 2.087371 2.188270 0.306278 1 4.323722 3.016358 -0.339236 1 6.147836 1.406716 -0.871733 1 5.703721 -1.038024 -0.751026 1 3.473996 -1.866399 -0.117911 1 1.864053 -2.356102 1.294189 6 0.967289 -0.951788 -2.171141 1 1.960845 -0.510137 -2.269561 1 1.102408 -2.009055 -1.920505 1 0.485823 -0.897093 -3.155029 6 -1.983693 -2.600622 -2.269674 1 -1.260074 -2.414744 -3.067794 1 -2.184466 -3.676503 -2.241520 1 -2.916008 -2.093440 -2.542956
s-re(II) Et = -1110.6182125 (-1110.9165707) (-1110.945402) NImag = 1(-334.73 cm^{-1})	

6 -3.068961 -0.643094 -0.478846 7 -1.861265 0.076908 0.014582 6 -1.491626 1.198052 -0.889004 6 -2.716175 1.325247 -1.824118 6 -3.250596 -0.108578 -1.902335 6 -1.103079 -0.366046 1.045447 6 -1.780825 -1.208930 2.101832 6 -2.529432 -0.333770 3.129354 6 -1.228662 2.522523 -0.162793 8 -0.466752 3.349412 -0.597579 6 0.259134 0.060066 1.165627 6 0.942515 0.011341 2.523986 8 -1.955413 2.748485 0.956298 6 1.314626 -1.089350 0.017740 6 0.666246 -1.406338 -1.209944 7 -0.407739 -2.247175 -1.202584 8 -0.790585 -2.706355 -0.072067 6 2.633576 -0.387540 -0.104135 6 2.775826 0.807378 -0.827644 6 4.021798 1.419630 -0.955416 6 5.149754 0.849985 -0.360487 6 5.020809 -0.332917 0.368419 6 3.772246 -0.941754 0.499834 8 -1.026088 -2.518052 -2.265805 1 -2.641154 -0.714205 -2.579623 1 -4.292574 -0.155411 -2.231113 1 -3.461060 1.993847 -1.373869 1 -2.429193 1.746794 -2.790064 1 -0.596996 0.962034 -1.463326 1 -2.859338 -1.715652 -0.467934 1 -3.932891 -0.426447 0.162541 1 1.994232 0.288752 2.415977 1 0.490475 0.714428 3.233601 1 0.910575 -0.987058 2.972791 1 0.921610 -0.984456 -2.171309 1 1.325480 -1.921991 0.719585 1 3.678695 -1.866484 1.063996 1 5.891504 -0.783485 0.837342 1 6.120156 1.328613 -0.459519 1 4.109525 2.346211 -1.516047 1 1.906438 1.275773 -1.283290 1 -2.456826 1.942580 1.175840 1 0.483174 0.987056 0.644201 1 -1.027919 -1.816128 2.606599 1 -2.474696 -1.912681 1.642016 1 -3.355621 0.217011 2.661056 1 -2.964662 -0.963523 3.912325 1 -1.868242 0.392944 3.612360	

Table S36. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Using Unassisted Pathway . The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =-1148.7364504 (-1149.039627) (-1149.076129) NImag=1(-298.91 cm^{-1})				*a-si* (II) Et = -1148.7324905 (-1149.03559473) (-1149.07286969) NImag=1(-220.8 cm^{-1})			
6	3.602881	-1.020362	-0.717802	6	3.621967	-0.910395	-0.804358
6	2.434959	-0.825582	0.038124	6	2.421278	-0.786387	-0.086276
6	2.576005	-0.364639	1.359903	6	2.503013	-0.483506	1.284044
6	3.834225	-0.089816	1.892861	6	3.737631	-0.303172	1.906176
6	4.983713	-0.273388	1.120309	6	4.921639	-0.423632	1.174370
6	4.863332	-0.746354	-0.186643	6	4.859371	-0.731463	-0.184429
6	1.109825	-1.158269	-0.572420	6	1.118521	-1.032897	-0.791815
6	0.125083	-1.726508	0.306007	6	0.144554	-1.781599	-0.025788
7	-0.962073	-2.350073	-0.190554	7	-0.949065	-2.285978	-0.619086
8	-1.029513	-2.682317	-1.409389	8	-1.032541	-2.373990	-1.880696
8	-1.977648	-2.572088	0.587829	8	-1.969286	-2.635690	0.110666
6	0.399288	0.361375	-1.538295	6	0.371570	0.518848	-1.499233
6	1.516571	1.241722	-2.106658	6	1.438385	1.484610	-2.048268
6	-0.541935	0.998367	-0.652089	6	-0.521470	1.059065	-0.493491
6	-0.036969	2.046385	0.303948	6	0.006122	1.986981	0.570882
7	-1.803727	0.583481	-0.594036	7	-1.784282	0.650600	-0.436682
6	-2.776832	0.934695	0.489304	6	-2.689801	0.860687	0.734600
6	-4.048523	0.167473	0.086622	6	-4.032154	0.266955	0.269190
6	-3.990168	0.172909	-1.443038	6	-4.013399	0.492903	-1.244687
6	-2.510972	-0.100416	-1.720578	6	-2.568059	0.157749	-1.614184
6	-2.305416	0.641312	1.936128	6	-2.183151	0.261007	2.071746
8	-2.060120	-0.609464	2.291452	8	-1.985362	-1.043701	2.154370
8	-2.221547	1.565482	2.720761	8	-2.029760	1.003707	3.021577
1	-4.291211	1.149708	-1.841036	1	-4.249063	1.536845	-1.485351
1	-4.627946	-0.591953	-1.893863	1	-4.719222	-0.149466	-1.777891
1	-3.994890	-0.862298	0.452110	1	-4.057828	-0.805775	0.483194
1	-4.941407	0.641611	0.501931	1	-4.871207	0.743936	0.781836
1	-2.959774	2.012725	0.457283	1	-2.785488	1.935241	0.915867
1	-2.158804	0.327587	-2.662112	1	-2.214531	0.677429	-2.507205
1	-2.287780	-1.173570	-1.720106	1	-2.420001	-0.917224	-1.757570
1	1.221619	-1.736614	-1.487752	1	1.287166	-1.478049	-1.772571
1	0.089468	-1.528663	1.365831	1	0.124941	-1.791017	1.052758
1	1.700154	-0.228264	1.987272	1	1.598469	-0.397771	1.878744
1	3.916540	0.262733	2.917376	1	3.773973	-0.074920	2.967943
1	5.963663	-0.060244	1.538187	1	5.882603	-0.286091	1.662271
1	5.750325	-0.911012	-0.792420	1	5.772534	-0.840509	-0.763262
1	3.521266	-1.410256	-1.729492	1	3.584044	-1.171280	-1.859401
1	-0.083151	-0.231421	-2.312360	1	-0.176667	0.012860	-2.290738
1	0.536783	1.552971	1.101264	1	0.128571	1.445090	1.517619
1	-2.099522	-1.340327	1.571750	1	-2.053333	-1.618199	1.299981
1	-0.854673	2.570594	0.800969	1	-0.765624	2.738310	0.780371
6	0.882847	3.041252	-0.436320	6	1.326729	2.679888	0.167334
6	2.034092	2.316095	-1.138708	1	1.381993	3.646904	0.679042
1	2.346148	0.611932	-2.445999	1	2.180120	2.089249	0.514635
1	1.124112	1.731960	-3.010453	6	1.417422	2.854888	-1.350691
1	1.267100	3.768874	0.287379	1	1.274945	1.613940	-3.124918
1	0.287589	3.607356	-1.166362	1	2.437008	1.048560	-1.940145
1	2.651544	3.034206	-1.691717	1	0.557731	3.442580	-1.705032
1	2.682029	1.858097	-0.384701	1	2.316865	3.421199	-1.617889
a-re Et =-1148.7372111 (-1149.0409092) (-1149.073897)				*a-re* (II) Et =-1148.7346942 (-1149.03814967) (-1149.07215754)			

NImag= 1(-354.65 cm^{-1})				NImag= 1(-354.65 cm^{-1})		
6	-3.426132	-1.262729	0.679139	6	-3.400196	-1.212753	0.721783
6	-2.952487	-0.399780	-0.324316	6	-2.972038	-0.385426	-0.330459
6	-3.877730	0.426290	-0.983159	6	-3.933773	0.379260	-1.009351
6	-5.234868	0.380509	-0.663602	6	-5.282830	0.310144	-0.659355
6	-5.690619	-0.484551	0.331864	6	-5.693056	-0.517863	0.385594
6	-4.780025	-1.304498	1.003732	6	-4.745595	-1.278603	1.076146
6	-1.521903	-0.359492	-0.724105	6	-1.546365	-0.324627	-0.756655
6	-0.636605	0.682857	0.865107	6	-0.661522	0.741432	0.760583
6	-1.463122	1.950557	1.071067	6	-1.474298	2.037140	0.912912
6	-0.854871	-1.593554	-0.884571	6	-0.877964	-1.559974	-0.923042
7	0.378727	-1.641210	-1.455619	7	0.356722	-1.603365	-1.488128
8	1.075787	-2.682803	-1.384480	8	1.052093	-2.647259	-1.430158
6	0.754818	0.837026	0.582974	6	0.740640	0.844452	0.498949
6	1.242880	2.093577	-0.117180	6	1.315000	2.081866	-0.163597
7	1.661590	-0.108684	0.880803	7	1.616871	-0.115095	0.843881
6	3.140565	0.039528	0.701449	6	3.100358	0.037620	0.733804
6	3.684316	-1.342161	1.108200	6	3.644629	-1.291208	1.297211
6	2.729386	-1.770991	2.222900	6	2.598179	-1.685436	2.339750
6	1.370594	-1.343681	1.665017	6	1.291623	-1.340853	1.624525
6	3.772661	0.474268	-0.643424	6	3.813446	0.343393	-0.607396
8	3.297590	0.043967	-1.797263	8	3.336082	-0.082056	-1.763867
8	4.787708	1.138060	-0.567561	8	4.888604	0.900142	-0.516347
8	0.818812	-0.579369	-2.037083	8	0.806516	-0.529881	-2.043842
1	2.956675	-1.236897	3.153377	1	2.712780	-1.087172	3.251787
1	2.759847	-2.844610	2.428147	1	2.641632	-2.742895	2.615239
1	3.606202	-2.029453	0.257838	1	3.678799	-2.039191	0.496569
1	4.731713	-1.274987	1.410144	1	4.653925	-1.159119	1.691680
1	3.489880	0.791400	1.416985	1	3.400489	0.860561	1.391120
1	0.631283	-1.129258	2.440802	1	0.460502	-1.146271	2.305761
1	0.984528	-2.116990	0.997578	1	1.019237	-2.145925	0.936788
1	-1.176136	-2.523792	-0.439641	1	-1.201434	-2.491768	-0.483037
1	-1.278249	0.391164	-1.468668	1	-1.332108	0.418545	-1.518746
1	-3.529376	1.097624	-1.764091	1	-3.621577	1.017630	-1.832083
1	-5.934662	1.021225	-1.193084	1	-6.011524	0.903723	-1.204562
1	-6.746549	-0.519217	0.585109	1	-6.742309	-0.570520	0.662452
1	-5.126438	-1.978536	1.782486	1	-5.056519	-1.924348	1.892973
1	-2.729443	-1.903948	1.212859	1	-2.673810	-1.807723	1.269810
1	2.377805	-0.376978	-1.799034	1	2.383078	-0.421134	-1.784998
1	-0.877488	-0.096734	1.582326	1	-0.920658	-0.007629	1.501362
1	1.188889	1.899865	-1.196322	1	1.802379	1.794435	-1.099052
1	2.295880	2.278005	0.107295	1	2.107775	2.475809	0.488115
6	0.428794	3.351147	0.226214	6	0.286982	3.188618	-0.424218
6	-1.073032	3.088450	0.124966	6	-0.648524	3.321838	0.775717
1	-1.330568	2.293456	2.109504	1	-1.981956	2.014680	1.884540
1	-2.526306	1.713427	0.970323	1	-2.278034	2.067541	0.167081
1	-1.333429	2.827524	-0.910338	1	-0.054382	3.497892	1.684001
1	-1.640653	3.992776	0.374521	1	-1.318500	4.182128	0.663084
1	0.738261	4.161066	-0.443945	1	0.819989	4.123274	-0.629924
1	0.671207	3.677667	1.247003	1	-0.297444	2.955013	-1.323924
s-si (II) Et =-1148.7367595 (-1149.0396051) (-1149.069070) NImag=1(-331.21 cm^{-1})				*s-si* Et =-1148.73494082 (-1149.03780209) (-1149.07286969) NImag=1(-332.72 cm^{-1})			
6	-0.315448	0.877257	-0.798235	6	-0.312859	0.877515	-0.782127
6	0.974965	1.269382	-0.336779	6	0.996224	1.243395	-0.335908
7	1.985142	0.381220	-0.302800	7	1.993506	0.346579	-0.326904
6	2.127331	-0.763921	-1.255179	6	2.085382	-0.839148	-1.234944
6	3.646549	-1.094478	-1.232461	6	3.592877	-1.212435	-1.224991
6	4.314672	0.102837	-0.539193	6	4.310861	0.007609	-0.632691
6	3.244866	0.554811	0.450177	6	3.287582	0.556157	0.358701
6	1.290551	-2.045725	-1.008672	6	1.223532	-2.090285	-0.924845

8 1.534733 -2.783024 0.073006 8 0.521666 -2.417397 -1.874133 1 4.528614 0.903662 -1.257230 1 5.251135 -0.169652 -0.044504 1 3.810149 -2.004447 -0.648573 1 4.019537 -1.275889 -2.243739 1 1.806033 -0.408368 -2.236540 1 3.362175 1.576644 0.801031 1 3.186897 -0.094723 1.335730 1 1.762569 -2.271713 0.921038 6 -1.168705 0.131965 0.873563 6 -0.325972 -0.877817 1.409619 6 -1.248965 1.942904 -1.363999 1 -1.176713 1.057817 1.443091 1 -0.449327 -1.927116 1.195157 6 -2.514152 -0.301349 0.396788 6 -2.686179 -1.430119 -0.423743 6 -3.962440 -1.826006 -0.819258 6 -5.087002 -1.105934 -0.407107 6 -4.927179 0.020362 0.400769 6 -3.650054 0.421986 0.793211 1 -1.821858 -1.992981 -0.767309 1 -4.078050 -2.700073 -1.454266 1 -6.080071 -1.419140 -0.717672 1 -5.794741 0.587889 0.726670 1 -3.530674 1.296308 1.428757 7 0.791144 -0.554837 2.114770 8 0.998041 0.622634 2.506226 8 1.670136 -1.476212 2.348375 1 -0.344907 -0.052349 -1.361987 6 1.179476 2.681360 0.189030 1 0.926264 2.697085 1.254505 1 2.233471 2.962350 0.114375 6 0.333237 3.719011 -0.569976 6 -1.132861 3.293544 -0.651618 1 -1.009504 2.077497 -2.429803 1 -2.279474 1.576248 -1.334185 1 0.731643 3.846243 -1.586384 1 0.436197 4.688550 -0.068577 1 -1.552044 3.225338 0.361692 1 -1.724073 4.047711 -1.184476	8 1.476185 -2.792491 0.175843 8 0.432048 -2.473935 -1.765117 1 4.521390 0.754242 -1.407792 1 5.256142 -0.255628 -0.150000 1 3.744053 -2.085015 -0.583736 1 3.934591 -1.474193 -2.229731 1 1.756652 -0.512596 -2.224376 1 3.437619 1.605420 0.600943 1 3.253143 -0.013352 1.298571 1 1.716566 -2.250955 1.007338 6 -1.176310 0.181597 0.856038 6 -0.350895 -0.826868 1.435612 6 -1.219100 1.963788 -1.380587 1 -1.192540 1.115158 1.413187 1 -0.487628 -1.880679 1.254592 6 -2.525040 -0.260004 0.386951 6 -2.696766 -1.393962 -0.425910 6 -3.973624 -1.796855 -0.812699 6 -5.099056 -1.078952 -0.399148 6 -4.939851 0.050944 0.403292 6 -3.661971 0.459215 0.787364 1 -1.832869 -1.958329 -0.767951 1 -4.088921 -2.675183 -1.441929 1 -6.092378 -1.397674 -0.703357 1 -5.807940 0.616154 0.731810 1 -3.543140 1.334928 1.421162 7 0.772583 -0.487002 2.114685 8 0.986012 0.708314 2.451317 8 1.656067 -1.399282 2.376369 1 -0.353131 -0.057236 -1.335040 6 1.275002 2.653755 0.159233 1 1.629869 2.625616 1.190367 1 2.093727 3.057285 -0.457084 6 0.062495 3.586517 0.040331 6 -0.631584 3.380722 -1.305753 1 0.401739 4.621436 0.162522 1 -0.642552 3.390354 0.858204 1 0.098688 3.534083 -2.113451 1 -1.426443 4.120070 -1.457098 1 -2.190394 1.951475 -0.872999 1 -1.432766 1.700499 -2.423422
s-re Et = -1148.7308483 (-1149.03531646) (-1149.06896882) NImag = 1(-332.67 cm^{-1})	*s-re* (II) Et =-1148.7265821 (-1149.0307969) (-1149.064242) NImag = 1(-345.19 cm^{-1})
6 0.150714 -0.161575 -1.055738 6 -1.120164 -0.765172 -0.779536 6 -1.127193 -2.264130 -0.653833 7 -2.244142 -0.055671 -0.600721 6 -2.335624 1.413694 -0.767178 6 -3.824308 1.744615 -0.473109 6 -4.559542 0.409744 -0.633726 6 -3.535929 -0.616436 -0.149158 6 -1.465791 2.297029 0.148122 8 -1.317741 1.943620 1.426336 8 -1.044703 3.350048 -0.280545 1 -4.803126 0.224420 -1.686306 1 -5.488816 0.367236 -0.059118 1 -3.920735 2.101693 0.557543 1 -4.188893 2.533161 -1.134946 1 -2.060365 1.673373 -1.793591 1 -3.707565 -1.601031 -0.584056	6 0.170340 -0.262813 -1.033210 6 -1.157599 -0.757484 -0.757896 6 -1.400207 -2.254467 -0.700300 7 -2.211871 0.044531 -0.588812 6 -2.192691 1.519173 -0.713863 6 -3.678537 1.942829 -0.526548 6 -4.485949 0.651387 -0.710235 6 -3.548718 -0.426754 -0.168854 6 -1.351172 2.313954 0.304155 8 -1.282314 1.875393 1.560221 8 -0.889753 3.382390 -0.037686 1 -4.691031 0.467023 -1.771082 1 -5.441557 0.672548 -0.179440 1 -3.821575 2.330041 0.487420 1 -3.950395 2.735815 -1.226218 1 -1.819770 1.787347 -1.706128 1 -3.758887 -1.414634 -0.576906

1	-3.510266	-0.723953	0.942980
1	-1.385622	0.958386	1.620273
1	-0.582764	-2.494572	0.275984
6	1.100449	-0.036911	0.710822
1	0.507718	0.814557	1.013564
6	0.963700	-1.148038	1.593438
1	0.115428	0.906640	-1.264810
7	-0.176604	-1.346328	2.324456
8	-0.224426	-2.241427	3.189745
8	-1.231842	-0.639034	2.070430
6	2.476112	0.391097	0.318410
6	2.696726	1.750662	0.037596
6	3.965268	2.214345	-0.307266
6	5.039868	1.326231	-0.383486
6	4.834364	-0.028271	-0.113262
6	3.565348	-0.491898	0.231539
1	1.865589	2.449854	0.100723
1	4.114118	3.271284	-0.510661
1	6.029978	1.686172	-0.649571
1	5.664799	-0.727168	-0.167746
1	3.427106	-1.548705	0.439923
1	1.748753	-1.850948	1.826973
6	1.042055	-0.891051	-2.068596
1	-2.129330	-2.675342	-0.538918
6	-0.381563	-2.952459	-1.814285
6	1.046559	-2.414813	-1.915580
1	0.680350	-0.634849	-3.076438
1	2.060220	-0.496831	-2.005163
1	1.599950	-2.697087	-1.011037
1	1.572575	-2.870204	-2.763301
1	-0.381300	-4.034665	-1.639564
1	-0.919187	-2.783068	-2.757649

1	-3.562880	-0.502340	0.926104
1	-1.331706	0.872035	1.685986
1	-1.738518	-2.516659	0.306845
6	1.107513	-0.077301	0.654461
1	0.518186	0.766597	0.983468
6	1.013795	-1.186989	1.558398
1	0.184905	0.796062	-1.286191
7	-0.135504	-1.449921	2.228675
8	-0.212153	-2.393868	3.041061
8	-1.200779	-0.737341	1.972572
6	2.477880	0.382185	0.265344
6	2.672737	1.745394	-0.016019
6	3.933235	2.233429	-0.356138
6	5.025505	1.366438	-0.428342
6	4.846458	0.008995	-0.156861
6	3.584984	-0.478788	0.184304
1	1.829778	2.430390	0.047629
1	4.062449	3.293206	-0.558261
1	6.009297	1.745968	-0.690783
1	5.690834	-0.673360	-0.206138
1	3.467512	-1.537118	0.398163
1	1.814291	-1.876651	1.777326
6	1.015119	-1.086669	-2.028929
1	-2.229897	-2.483804	-1.384513
6	-0.184989	-3.091964	-1.119116
6	0.446242	-2.474592	-2.365640
1	2.028177	-1.204816	-1.632660
1	1.126914	-0.499422	-2.948484
1	1.243709	-3.112415	-2.763412
1	-0.315457	-2.397329	-3.155206
1	0.545986	-3.127189	-0.304277
1	-0.512431	-4.121930	-1.299894

Table S37. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Propanal (**1**) to Nitrostyrene Using Solvent Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1263.4722614 (-1263.83418605) (-1263.86515688) NImag=1(-282.56 cm^{-1})				*a-re* Et = -1263.4684617 (-1263.83071557) (-1263.86233948) NImag= 1(-251.79 cm^{-1})		
6	-4.210747	-1.450691	-0.231650	6	4.051394	1.239048	-0.207678
6	-3.032986	-0.693361	-0.332314	6	2.904761	0.454523	-0.410512
6	-3.098332	0.565023	-0.954332	6	3.031988	-0.731657	-1.152748
6	-4.306478	1.043292	-1.460277	6	4.265929	-1.121868	-1.673033
6	-5.470475	0.277826	-1.356606	6	5.397895	-0.333015	-1.461494
6	-5.418338	-0.973330	-0.741406	6	5.284929	0.850132	-0.728778
6	-1.753708	-1.255156	0.201585	6	1.556039	0.835054	0.119625
6	-0.629734	-1.213620	-0.681578	6	1.347478	0.010575	1.817286
7	0.485886	-1.930488	-0.411805	6	2.698734	-0.109027	2.503305
8	0.601294	-2.583081	0.666634	6	1.238817	2.225437	0.296251
8	1.452943	-1.904733	-1.259118	7	-0.057700	2.621763	0.261819
6	-1.407719	-0.475792	1.933839	8	-0.381403	3.826829	0.361394
6	-2.725624	-0.460908	2.689223	6	0.684814	-1.201965	1.464568
6	-0.808070	0.775599	1.653041	7	-0.621351	-1.394822	1.469702
7	0.488475	0.977573	1.482484	6	-1.271434	-2.531951	0.749008
6	1.017177	2.262685	0.932383	6	-2.776156	-2.320861	0.995700
6	2.534952	2.194095	1.179919	6	-2.838046	-1.452823	2.266534
6	2.696020	1.144188	2.296962	6	-1.617391	-0.535901	2.140272
6	1.582082	0.131851	2.015939	6	-0.738505	-2.558362	-0.704581
6	0.480068	2.431737	-0.509895	8	-1.255161	-1.748007	-1.615086
8	1.139760	1.912041	-1.529858	8	0.214170	-3.272933	-0.955887
8	-0.588564	2.996727	-0.658397	8	-0.971617	1.707890	0.112911
1	2.553302	1.604040	3.281878	1	-2.753172	-2.072463	3.166996
1	3.677723	0.664923	2.279311	1	-3.768808	-0.883687	2.335526
1	3.076036	1.883628	0.283838	1	-3.244573	-1.788657	0.164562
1	2.920504	3.176290	1.466718	1	-3.286726	-3.280682	1.112368
1	0.561491	3.080603	1.497870	1	-0.920259	-3.465322	1.198504
1	1.226109	-0.390128	2.906565	1	-1.218639	-0.208466	3.104618
1	1.894198	-0.620010	1.287828	1	-1.791555	0.354837	1.521206
1	-3.393167	0.327841	2.327815	1	3.221617	0.852290	2.488582
1	-3.250003	-1.415838	2.578169	1	2.573674	-0.404600	3.552045
1	-2.558731	-0.301232	3.761552	1	3.341552	-0.847714	2.015417
1	-1.880549	-2.232867	0.668290	1	1.942573	3.016098	0.508096
1	-0.577439	-0.604297	-1.571272	1	0.757487	0.343456	-0.429316
1	-2.209676	1.183908	-1.045957	1	2.157456	-1.352361	-1.336439
1	-4.335022	2.019566	-1.936425	1	4.338054	-2.039570	-2.250320
1	-6.409949	0.654397	-1.752212	1	6.359338	-0.634106	-1.868704
1	-6.315894	-1.580524	-0.658422	1	6.158411	1.475741	-0.565055
1	-4.175273	-2.431584	0.236550	1	3.982908	2.167242	0.351684
1	-0.710212	-1.245903	2.259731	1	-2.039478	-1.164047	-1.364028
1	1.994402	1.406654	-1.344270	1	0.696018	0.736079	2.299055
8	3.448431	0.692494	-1.593449	8	-3.449952	-0.321448	-1.463657
1	3.642065	-0.108854	-1.037356	1	-3.428231	0.657103	-1.239593
6	3.454068	0.283343	-2.965334	6	-3.972789	-0.449777	-2.785789
1	4.456662	-0.045931	-3.267089	1	-5.038569	-0.188955	-2.812149
1	2.732258	-0.522634	-3.137827	1	-3.432973	0.188076	-3.496225
1	3.174909	1.152572	-3.566026	1	-3.857191	-1.493428	-3.090248
8	3.742899	-1.505392	-0.054174	8	-3.266285	2.289122	-1.031698
1	2.898081	-1.901962	-0.413646	1	-2.346718	2.273172	-0.644283
6	4.775297	-2.481488	-0.066225	6	-4.092151	3.013573	-0.129885
1	5.692634	-2.003632	0.290797	1	-4.244812	2.479761	0.821096
1	4.535586	-3.320158	0.600724	1	-3.654579	3.994201	0.091360

1 4.958823 -2.878723 -1.074721 1 -1.438223 1.624049 1.390112	1 -5.066745 3.158892 -0.605758 1 1.261439 -1.999930 0.998236
s-si Et = -1263.4769248 (-1263.8380606) (-1263.8643444) NImag = 1(-340.5 cm^{-1})	*s-si(II)* Et = -1263.4754374 (-1263.83567309) (-1263.86246717) NImag=1(-346.23 cm^{-1})
6 1.459954 1.132012 -1.329401 6 0.111821 1.109141 -1.739326 7 -0.957449 1.412066 -1.000681 6 -0.936192 2.230175 0.240426 6 -2.406823 2.679616 0.418274 6 -3.028040 2.544104 -0.982722 6 -2.325250 1.311827 -1.556252 6 -0.325896 1.520002 1.471846 8 -0.994678 0.534965 2.052252 8 0.753686 1.887727 1.896844 1 -2.803591 3.426059 -1.594481 1 -4.113868 2.421756 -0.946282 1 -2.930582 2.022029 1.116795 1 -2.454128 3.697303 0.815009 1 -0.276460 3.085017 0.062361 1 -2.272260 1.303627 -2.647959 1 -2.792985 0.373585 -1.238981 1 -1.888020 0.283190 1.663552 6 1.838160 -0.776097 -0.710170 6 0.781292 -1.309139 0.065293 6 2.488217 1.361863 -2.423530 1 2.551008 2.423260 -2.694929 1 3.485050 1.048501 -2.100341 1 2.233542 0.803215 -3.332764 1 1.860578 -1.150528 -1.731174 1 0.780924 -1.392135 1.140798 6 3.176734 -0.662207 -0.065549 6 3.348099 -0.100476 1.211822 6 4.612433 -0.055890 1.796423 6 5.725013 -0.566929 1.122627 6 5.567452 -1.119517 -0.148778 6 4.304159 -1.160599 -0.739203 1 2.497390 0.323078 1.738402 1 4.728903 0.384683 2.782953 1 6.708191 -0.529685 1.584191 1 6.425639 -1.519144 -0.682572 1 4.183940 -1.601049 -1.726080 7 -0.369101 -1.696317 -0.546425 8 -0.515215 -1.531628 -1.793347 8 -1.303837 -2.212856 0.161679 1 1.665101 1.634213 -0.386001 8 -3.464744 -0.251279 1.624782 8 -3.731901 -1.631251 -0.671063 1 -3.687259 -0.754424 0.797395 1 -2.798065 -1.973103 -0.574670 6 -3.539620 -1.171580 2.717336 1 -3.219831 -0.639530 3.616590 1 -4.569793 -1.521994 2.862013 1 -2.877692 -2.030948 2.557832 6 -4.594855 -2.693448 -1.050655 1 -5.613996 -2.297802 -1.094585 1 -4.330188 -3.085380 -2.041801 1 -4.572368 -3.522978 -0.329693 1 -0.119765 0.776371 -2.745768	6 1.290293 0.899230 -1.416191 6 -0.076768 0.836107 -1.754580 7 -1.108366 1.331196 -1.068771 6 -0.990487 2.300828 0.048305 6 -2.429658 2.837337 0.223790 6 -3.080990 2.630229 -1.153064 6 -2.485366 1.299603 -1.619340 6 -0.369881 1.727723 1.343057 8 -1.021057 0.777208 1.995117 8 0.683687 2.179860 1.750666 1 -2.798038 3.435544 -1.841412 1 -4.172261 2.594966 -1.098456 1 -2.964237 2.247036 0.972173 1 -2.420582 3.880556 0.550070 1 -0.305895 3.096306 -0.264197 1 -2.436386 1.199208 -2.706992 1 -3.034253 0.440728 -1.226007 1 -1.861344 0.423018 1.561447 6 1.773492 -0.876829 -0.530963 6 0.831852 -1.312838 0.428919 6 2.247056 0.949232 -2.598428 1 2.261521 1.945593 -3.057869 1 3.269770 0.716700 -2.289568 1 1.955285 0.232410 -3.376224 1 1.721720 -1.408293 -1.478403 1 0.965495 -1.236467 1.496809 6 3.155607 -0.621049 -0.032504 6 3.397704 0.172360 1.102572 6 4.698101 0.354057 1.569726 6 5.776899 -0.248283 0.916814 6 5.548214 -1.031762 -0.214874 6 4.248051 -1.210938 -0.688501 1 2.570582 0.663709 1.608448 1 4.869040 0.972902 2.446452 1 6.788853 -0.103641 1.285608 1 6.379840 -1.504452 -0.730711 1 4.073324 -1.829526 -1.565602 7 -0.363159 -1.835561 0.046454 8 -0.669007 -1.835835 -1.206955 8 -1.164727 -2.292792 0.901678 1 1.546667 1.556616 -0.587841 8 -3.345632 -0.218011 1.275536 8 -3.409097 -1.829781 -0.940611 1 -3.338384 -0.877710 0.530533 1 -2.434406 -1.949940 -1.080524 6 -3.694636 -0.908413 2.479018 1 -3.653504 -0.182940 3.295808 1 -4.715283 -1.307297 2.415294 1 -2.991778 -1.722592 2.684723 6 -3.973353 -3.122995 -0.743470 1 -5.013478 -2.989556 -0.430815 1 -3.964792 -3.705718 -1.675155 1 -3.430247 -3.679011 0.030222 1 -0.356675 0.335620 -2.676773
s-re Et = -1263.47387 (-1263.83508767)	

(-1263.86306312) NImag=1(-355.14 cm^{-1})	
6 1.147455 -0.439295 1.568231 6 -0.245490 -0.339599 1.799938 7 -1.219060 -1.139821 1.365628 6 -1.030371 -2.396734 0.616146 6 -2.465913 -2.959730 0.478797 6 -3.229514 -2.336894 1.659105 6 -2.631446 -0.931178 1.753633 6 -0.311599 -2.240588 -0.738928 8 -0.778651 -1.350763 -1.610227 8 0.656692 -2.928995 -0.991961 1 -3.036600 -2.895397 2.582638 1 -4.309784 -2.314341 1.493256 1 -2.909756 -2.621094 -0.461307 1 -2.462934 -4.052445 0.485621 1 -0.393425 -3.067864 1.202544 1 -2.674473 -0.504307 2.759625 1 -3.113506 -0.234299 1.062144 1 -1.617542 -0.859623 -1.350197 6 1.582577 0.763168 -0.027117 1 0.845744 0.270487 -0.652182 6 1.280364 2.121111 0.253601 1 1.483831 -1.370876 1.115403 7 -0.016282 2.521219 0.332310 8 -0.339658 3.717155 0.506028 8 -0.917650 1.597566 0.248334 6 2.988159 0.393151 -0.351702 6 3.227367 -0.722214 -1.174084 6 4.527253 -1.084369 -1.523438 6 5.615201 -0.344980 -1.055476 6 5.393240 0.759598 -0.230727 6 4.093971 1.123534 0.119647 1 2.390529 -1.313605 -1.535898 1 4.688027 -1.947290 -2.163952 1 6.628272 -0.627579 -1.329123 1 6.232784 1.341509 0.140359 1 3.942154 1.985583 0.762338 1 1.999256 2.903428 0.442058 6 2.030255 0.079755 2.691366 1 3.073282 0.142925 2.368287 1 1.711998 1.079215 3.010878 1 1.997109 -0.577853 3.569462 1 -3.306819 0.677534 -1.060778 8 -3.156860 -0.223510 -1.463275 8 -3.465088 2.123497 -0.182845 1 -2.505725 2.164365 0.077134 6 -3.569377 -0.191901 -2.827250 1 -3.299873 -1.151082 -3.277076 1 -4.656080 -0.057092 -2.908252 1 -3.068060 0.607985 -3.388239 6 -3.829313 3.367516 -0.770108 1 -4.895037 3.321637 -1.013684 1 -3.661632 4.195774 -0.070872 1 -3.264875 3.574285 -1.690603 1 -0.596660 0.458537 2.446627	

Table S38. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1342.09916821 (-1342.48096357) (-1342.50602061) NImag=1(-286.6 cm^{-1})				*a-re* Et = -1342.0970055 (-1342.47960314) (-1342.50740453) NImag= 1(-273.0 cm^{-1})		
6	3.928135	-1.908981	-0.258693	6	-3.537618	1.705442	0.309574
6	2.760106	-1.284405	0.209029	6	-2.331825	1.064358	0.642333
6	2.840034	-0.524579	1.389807	6	-2.347878	0.110875	1.674087
6	4.047490	-0.399684	2.074906	6	-3.530198	-0.195595	2.348017
6	5.200407	-1.028353	1.597808	6	-4.721922	0.443256	2.001775
6	5.136496	-1.784914	0.427380	6	-4.720165	1.396259	0.980999
6	1.482226	-1.472985	-0.538751	6	-1.038422	1.380107	-0.038953
6	0.295301	-1.666965	0.225214	6	-0.925324	0.421127	-1.716514
7	-0.834971	-2.115920	-0.375606	6	-2.113483	0.817611	-2.571655
8	-0.877825	-2.326545	-1.620834	6	-0.780525	2.753618	-0.339277
8	-1.885940	-2.276487	0.345105	7	0.490980	3.169561	-0.596142
6	1.253151	-0.034407	-1.853816	8	0.764007	4.377812	-0.736387
6	2.485750	-0.053780	-2.740445	6	-0.722633	-0.945825	-1.346541
6	0.918920	1.130961	-1.103934	6	-1.894332	-1.877717	-1.143092
6	1.992804	2.083362	-0.626248	6	-2.163467	-2.724233	-2.407841
6	2.114622	3.308553	-1.558828	7	0.520457	-1.405751	-1.119306
7	-0.359341	1.358673	-0.754360	6	0.841151	-2.688538	-0.435004
6	-0.788708	2.349667	0.278765	6	2.376662	-2.817581	-0.566619
6	-2.275988	2.638410	-0.033616	6	2.719739	-1.956379	-1.789142
6	-2.498682	2.071740	-1.446881	6	1.750110	-0.779349	-1.673386
6	-1.545684	0.877391	-1.507648	6	0.350216	-2.741410	1.027831
6	-0.474264	1.801380	1.693538	8	0.712742	-1.754124	1.850450
8	-1.240633	0.848115	2.205474	8	-0.362905	-3.647575	1.401452
8	0.501887	2.211726	2.293886	8	1.413288	2.263541	-0.690694
1	-2.228456	2.810566	-2.210535	1	2.534675	-2.507807	-2.718651
1	-3.532715	1.761346	-1.617356	1	3.762480	-1.627432	-1.791283
1	-2.936195	2.139343	0.679048	1	2.871000	-2.404086	0.316550
1	-2.477305	3.711296	0.028973	1	2.672039	-3.864664	-0.670280
1	-0.189418	3.254495	0.177959	1	0.337649	-3.513978	-0.944225
1	-1.252643	0.606556	-2.521554	1	1.518729	-0.321388	-2.636949
1	-1.989015	0.000498	-1.034517	1	2.112782	0.006863	-1.007711
1	3.398152	0.259382	-2.225455	1	-2.182606	1.910737	-2.596345
1	2.654530	-1.069093	-3.115210	1	-1.989068	0.477270	-3.607256
1	2.353663	0.592286	-3.617584	1	-3.066038	0.428899	-2.200781
1	1.570967	-2.181983	-1.361792	1	-1.523559	3.536077	-0.363398
1	0.187050	-1.428817	1.272015	1	-0.184078	0.893135	0.426664
1	1.962240	-0.017201	1.779649	1	-1.424218	-0.386067	1.959779
1	4.084784	0.192258	2.985282	1	-3.515784	-0.932910	3.146012
1	6.139544	-0.929783	2.135545	1	-5.643734	0.204890	2.525481
1	6.024598	-2.284218	0.049089	1	-5.641065	1.905207	0.708609
1	3.882704	-2.513175	-1.161293	1	-3.553581	2.454733	-0.476184
1	0.404883	-0.537280	-2.313780	1	1.461023	-1.158049	1.541713
1	2.946089	1.552917	-0.602752	1	-0.012452	0.925836	-2.019869
1	1.800427	2.409055	0.398147	1	-2.779380	-1.283371	-0.909100
1	1.183041	3.884502	-1.597847	1	-1.737975	-2.544159	-0.292408
1	2.904977	3.973478	-1.195493	1	-1.303930	-3.352459	-2.665738
1	2.365740	3.011737	-2.582393	1	-3.020042	-3.383028	-2.233285
1	-2.082400	0.595079	1.714643	1	-2.389862	-2.093031	-3.272679
8	-3.666965	0.123810	1.523399	8	2.924504	-0.361169	1.622517
1	-3.903089	-0.370946	0.694613	1	3.157128	0.530471	1.232992
6	-3.930799	-0.741331	2.631666	6	3.344979	-0.352836	2.987407
1	-5.004442	-0.956067	2.710822	1	4.439747	-0.323685	3.061711

1 -3.372322 -1.679980 2.541474 1 -3.609380 -0.219758 3.536536 8 -4.070676 -1.300720 -0.742455 1 -3.271836 -1.862995 -0.543204 6 -5.163549 -2.130857 -1.108448 1 -6.033179 -1.486765 -1.270127 1 -4.954940 -2.674871 -2.039365 1 -5.411248 -2.861650 -0.325201	1 2.930449 0.504656 3.531853 1 2.982989 -1.274014 3.450843 8 3.585809 2.071455 0.749567 1 2.792282 2.378882 0.230751 6 4.746506 2.290721 -0.039800 1 4.697057 1.774136 -1.009734 1 4.900864 3.361393 -0.225448 1 5.607449 1.907281 0.516066
s-si Et = -1342.1006377 (-1342.48193169) (-1342.50708115) NImag=1(-317.18 cm^{-1})	*s-si(II)* Et = -1342.1003425 (-1342.4807582) (-1342.506568) NImag=1(-327.6 cm^{-1})
6 1.455868 1.431879 0.317824 6 0.143002 1.858113 -0.019624 7 -0.937253 1.384954 0.638676 6 -0.880256 0.784757 2.005781 6 -2.329195 0.889181 2.543554 6 -3.005473 1.938309 1.651609 6 -2.337287 1.729963 0.292213 6 -0.306859 -0.650071 2.105001 8 -1.006470 -1.668238 1.626936 8 0.764259 -0.828337 2.655844 1 -2.799824 2.951941 2.016671 1 -4.089939 1.808173 1.601105 1 -2.850663 -0.065508 2.442357 1 -2.326373 1.158570 3.603267 1 -0.193118 1.393124 2.600461 1 -2.373674 2.624089 -0.325768 1 -2.789439 0.914167 -0.282680 1 -1.899194 -1.470217 1.208328 6 1.819494 -0.152806 -0.962948 6 0.775131 -1.104833 -0.944287 6 2.636648 2.361306 0.087678 1 2.576286 3.254337 0.722963 1 3.567085 1.847655 0.339483 1 2.722093 2.702530 -0.950031 1 1.820390 0.484849 -1.843778 1 0.788890 -2.025203 -0.382191 6 3.170144 -0.610780 -0.533617 6 3.371514 -1.354201 0.642505 6 4.647144 -1.802422 0.981347 6 5.741008 -1.519716 0.158998 6 5.553146 -0.776069 -1.006805 6 4.279082 -0.320715 -1.345341 1 2.534829 -1.560401 1.303979 1 4.786951 -2.373086 1.895545 1 6.732991 -1.872880 0.427946 1 6.396668 -0.549288 -1.653554 1 4.136171 0.253785 -2.257477 7 -0.376563 -0.868109 -1.629754 8 -0.542343 0.219512 -2.251759 8 -1.291262 -1.763929 -1.626634 1 1.542064 0.862908 1.238895 6 -0.058801 2.879574 -1.122799 1 -0.926061 2.622176 -1.730386 1 0.794372 2.818725 -1.801410 6 -0.177975 4.319084 -0.581883 1 -0.300328 5.021184 -1.413674 1 -1.041101 4.436766 0.083259 1 0.713677 4.616265 -0.021009 8 -3.495880 -1.705024 0.785764 8 -3.713287 -0.707714 -1.700602	6 1.271693 1.451752 0.009391 6 -0.082116 1.725326 -0.333043 7 -1.100778 1.439853 0.504537 6 -0.916006 1.113641 1.947656 6 -2.325335 1.271631 2.564785 6 -3.059253 2.207267 1.598804 6 -2.521780 1.783542 0.231455 6 -0.292448 -0.265166 2.268064 8 -0.956898 -1.361168 1.936789 8 0.766075 -0.317027 2.866730 1 -2.799746 3.254332 1.797439 1 -4.146395 2.107335 1.658988 1 -2.835279 0.305872 2.593646 1 -2.261136 1.655826 3.586226 1 -0.217168 1.842467 2.369357 1 -2.589645 2.582098 -0.504277 1 -3.050225 0.913483 -0.166065 1 -1.807380 -1.238435 1.407246 6 1.771699 -0.353343 -0.882569 6 0.866512 -1.403926 -0.613596 6 2.359013 2.379476 -0.513938 1 2.263572 3.388887 -0.093927 1 3.341878 2.001378 -0.225761 1 2.351951 2.475417 -1.605655 1 1.687707 0.067198 -1.881834 1 1.032504 -2.178015 0.119106 6 3.170542 -0.560754 -0.410270 6 3.458141 -0.965047 0.905176 6 4.775171 -1.200217 1.296602 6 5.824896 -1.039165 0.388553 6 5.550402 -0.632203 -0.917881 6 4.234351 -0.388690 -1.310649 1 2.652863 -1.076640 1.626373 1 4.981645 -1.509043 2.317854 1 6.849594 -1.225835 0.698700 1 6.359124 -0.503453 -1.632457 1 4.024332 -0.076822 -2.331018 7 -0.325058 -1.494303 -1.262877 8 -0.665114 -0.553736 -2.075680 8 -1.088980 -2.472892 -1.063764 1 1.441117 1.145672 1.037809 6 -0.407345 2.379463 -1.662637 1 -1.334990 1.968747 -2.064101 1 0.367407 2.092191 -2.376925 6 -0.485870 3.918458 -1.589229 1 -0.732488 4.323590 -2.576477 1 -1.254438 4.261515 -0.887627 1 0.465283 4.357460 -1.275111 8 -3.308501 -1.423523 0.765049 8 -3.374104 -0.734941 -1.878117

1 -3.703751 -1.348561 -0.118343 1 -2.781857 -1.004210 -1.903042 6 -3.624145 -3.128056 0.724308 1 -3.323092 -3.527229 1.695927 1 -4.665139 -3.418038 0.530907 1 -2.974809 -3.553248 -0.050346 6 -4.567255 -1.042499 -2.784602 1 -5.585745 -0.750657 -2.511287 1 -4.282632 -0.500663 -3.696507 1 -4.558756 -2.120133 -3.001932	1 -3.314767 -1.263242 -0.217428 1 -2.397177 -0.719363 -2.059916 6 -3.652258 -2.792595 0.996902 1 -3.584374 -2.969145 2.073657 1 -4.681427 -2.994473 0.672614 1 -2.962147 -3.466381 0.478207 6 -3.954212 -1.695834 -2.755153 1 -4.996869 -1.837874 -2.454694 1 -3.940015 -1.342936 -3.795878 1 -3.427052 -2.656073 -2.698283
s-re Et = -1342.0997292 (-1342.48120261) (-1342.50754514) NImag = 1(-331.8 cm^{-1})	
6 1.151391 -0.311038 1.375811 6 -0.241652 -0.100599 1.622515 6 -0.685675 1.155949 2.343005 7 -1.190157 -0.987945 1.271423 6 -0.919720 -2.327176 0.695981 6 -2.315607 -2.986219 0.586689 6 -3.163054 -2.246818 1.628079 6 -2.636376 -0.812890 1.553837 6 -0.181548 -2.347231 -0.657658 8 -0.666581 -1.627097 -1.663496 8 0.809130 -3.038352 -0.792496 1 -2.993684 -2.658705 2.630113 1 -4.233938 -2.299985 1.414331 1 -2.732446 -2.814437 -0.409493 1 -2.253480 -4.064507 0.753197 1 -0.271807 -2.880924 1.383242 1 -2.779463 -0.272375 2.488981 1 -3.109435 -0.239548 0.750969 1 -1.525905 -1.135484 -1.492245 1 -1.647707 1.490210 1.951205 1 0.028734 1.947332 2.097318 6 1.641365 0.682266 -0.357210 1 0.958530 0.083043 -0.948221 6 1.285018 2.056523 -0.318483 1 1.407556 -1.306731 1.021547 7 -0.015554 2.416102 -0.501132 8 -0.374781 3.614269 -0.538965 8 -0.880359 1.464224 -0.606758 6 3.072793 0.316158 -0.548932 6 3.385518 -0.912299 -1.157603 6 4.711253 -1.275805 -1.390784 6 5.752228 -0.424238 -1.016993 6 5.456870 0.795336 -0.403900 6 4.132344 1.160484 -0.170606 1 2.584852 -1.588209 -1.445635 1 4.928630 -2.227727 -1.867701 1 6.785299 -0.707642 -1.200200 1 6.259258 1.466072 -0.107991 1 3.924901 2.111856 0.309784 1 1.957851 2.886442 -0.167895 6 2.152630 0.216512 2.393288 1 3.169446 0.017804 2.047321 1 2.063807 1.296883 2.550429 1 2.039591 -0.275021 3.367692 6 -0.761976 1.006348 3.876783 1 0.209589 0.757669 4.311358 1 -1.096563 1.950134 4.319965 1 -1.469297 0.226383 4.180504	

1	-3.322452	0.298309	-1.460441
8	-3.114394	-0.631154	-1.752271
8	-3.466722	1.852404	-0.762636
1	-2.478713	1.963539	-0.691651
6	-3.398425	-0.744240	-3.145151
1	-3.057937	-1.729654	-3.473495
1	-4.476645	-0.661914	-3.336353
1	-2.871815	0.019492	-3.732418
6	-4.016770	2.995676	-1.405807
1	-5.103744	2.872930	-1.434328
1	-3.778705	3.911626	-0.850917
1	-3.648315	3.111499	-2.435214

Table S39. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Cyclohexanone (**3**) to Nitrostyrene Using Solvent Assisted Pathway ($\mathbf{C_2}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1380. 207223 (-1380.59515760) (-1380.62363905) NImag=1(-250.25 cm^{-1})			*a-si II* Et = -1380.2080934 (-1380.5960502) (-1380.624659) NImag=1(-285.86 cm^{-1})		
6	3.708312	-2.022961	0.065949	6	3.726958	-1.996229	-0.268232
6	2.531567	-1.333737	0.402553	6	2.558781	-1.376683	0.206525
6	2.529679	-0.558315	1.575508	6	2.579269	-0.820208	1.498565
6	3.670767	-0.466323	2.370791	6	3.733768	-0.875175	2.278635
6	4.837539	-1.148752	2.016167	6	4.889760	-1.488339	1.789641
6	4.851140	-1.931873	0.861979	6	4.881284	-2.052347	0.513005
6	1.323150	-1.473131	-0.468526	6	1.337031	-1.375369	-0.649466
6	0.077245	-1.673275	0.210191	6	0.098691	-1.664810	-0.006380
7	-1.008430	-2.103534	-0.472292	7	-0.991751	-1.994091	-0.742043
8	-0.965857	-2.298208	-1.721091	8	-0.956359	-2.001076	-2.004454
8	-2.111624	-2.259476	0.172730	8	-2.087653	-2.250520	-0.121244
6	1.198843	-0.055950	-1.738723	6	1.210012	0.275844	-1.716384
6	2.469140	-0.037774	-2.600805	6	2.495653	0.433758	-2.527817
6	0.851193	1.132544	-1.019421	6	0.827504	1.331072	-0.833910
6	1.916375	2.106398	-0.560124	6	1.901972	2.185674	-0.199788
7	-0.424094	1.372732	-0.682611	7	-0.462804	1.516111	-0.508779
6	-0.845442	2.408978	0.306272	6	-0.943205	2.340705	0.639598
6	-2.315757	2.736067	-0.050917	6	-2.428640	2.639508	0.331002
6	-2.538861	2.091756	-1.431662	6	-2.607574	2.257534	-1.149673
6	-1.621013	0.870057	-1.404908	6	-1.623553	1.103622	-1.338286
6	-0.580886	1.880122	1.737888	6	-0.621679	1.588670	1.955402
8	-1.387187	0.954046	2.240938	8	-1.400708	0.581353	2.331988
8	0.391156	2.271484	2.355986	8	0.374981	1.885062	2.585124
1	-2.239043	2.775120	-2.234771	1	-2.342016	3.095914	-1.804227
1	-3.578046	1.796964	-1.597347	1	-3.627691	1.943311	-1.383870
1	-3.005230	2.306914	0.679681	1	-3.095200	2.043662	0.958262
1	-2.475459	3.817549	-0.057139	1	-2.652809	3.691906	0.525294
1	-0.208156	3.286995	0.198603	1	-0.366333	3.264400	0.688060
1	-1.339928	0.507235	-2.391850	1	-1.309153	0.958052	-2.370994
1	-2.085967	0.052111	-0.855629	1	-2.053987	0.171621	-0.972701
1	1.473639	-2.194358	-1.272961	1	1.468855	-1.934782	-1.575023
1	-0.097765	-1.454129	1.252069	1	-0.074034	-1.601939	1.056828
1	1.638706	-0.016205	1.877388	1	1.695554	-0.336080	1.904464
1	3.644507	0.141083	3.271308	1	3.725929	-0.437062	3.272871
1	5.725233	-1.074748	2.638525	1	5.787310	-1.530304	2.400695
1	5.747565	-2.478753	0.581849	1	5.770644	-2.542491	0.125761
1	3.720982	-2.655007	-0.818623	1	3.723317	-2.452691	-1.255069
1	0.358828	-0.535338	-2.238235	1	0.396644	-0.145506	-2.303935
1	1.931480	2.168053	0.533406	1	2.334105	1.647366	0.652776

1 -2.216314 0.712277 1.723372 8 -3.780777 0.211314 1.463590 1 -4.018386 -0.238738 0.610137 6 -4.043878 -0.716846 2.521237 1 -5.117509 -0.935382 2.588058 1 -3.485318 -1.647943 2.374511 1 -3.722854 -0.247385 3.454382 8 -4.239354 -1.122764 -0.861498 1 -3.460832 -1.724765 -0.697931 6 -5.383131 -1.901229 -1.184701 1 -6.232228 -1.219477 -1.291771 1 -5.244658 -2.436536 -2.133658 1 -5.621047 -2.635506 -0.401810 1 1.605062 3.104636 -0.905425 6 3.316602 1.800361 -1.115863 6 3.225792 1.298208 -2.557523 1 3.922856 2.711066 -1.050438 1 3.810582 1.046312 -0.494336 1 2.706515 2.046103 -3.174569 1 4.225379 1.173252 -2.989857 1 2.193902 -0.279380 -3.634649 1 3.150070 -0.833523 -2.275380	1 -2.239824 0.407858 1.805214 8 -3.809745 -0.073087 1.505735 1 -4.041789 -0.391102 0.594128 6 -4.049663 -1.153145 2.413030 1 -5.118170 -1.402789 2.446949 1 -3.471567 -2.040005 2.130377 1 -3.735865 -0.820517 3.405604 8 -4.232812 -1.021162 -1.008402 1 -3.448257 -1.630190 -0.926621 6 -5.353342 -1.745850 -1.495778 1 -6.209260 -1.064537 -1.513838 1 -5.177577 -2.111406 -2.516429 1 -5.603787 -2.604286 -0.856146 1 1.483822 3.104547 0.214396 6 3.011708 2.522845 -1.213859 6 3.593589 1.252898 -1.835536 1 2.878391 -0.557820 -2.800964 1 2.233256 0.919677 -3.479764 1 4.374597 1.506227 -2.562866 1 4.071305 0.654795 -1.052488 1 3.791622 3.098942 -0.702452 1 2.602292 3.172680 -2.000305
a-re Et = -1342.1006377 (-1380.59304244) (-1380.62608291) NImag= 1(-212.27 cm^{-1})	*a-re II* Et =-1380.2061713 (-1380.5941399) (-1380.625423) NImag= 1(-280.7 cm^{-1})
6 -3.350574 1.540930 0.854336 6 -2.104808 0.894068 0.933097 6 -1.977804 -0.186417 1.822123 6 -3.059515 -0.618611 2.590076 6 -4.294457 0.023998 2.488408 6 -4.433280 1.108882 1.620794 6 -0.913862 1.328762 0.130354 6 -0.886921 0.517599 -1.551115 6 -2.161513 0.837925 -2.347275 6 -0.783139 2.748093 -0.077478 7 0.403592 3.281827 -0.457041 8 0.570237 4.515343 -0.543440 6 -0.574687 -0.871797 -1.336054 6 -1.671719 -1.898671 -1.180518 7 0.697713 -1.272350 -1.205180 6 1.105453 -2.636143 -0.772784 6 2.642324 -2.641687 -0.929343 6 2.901006 -1.591404 -2.016553 6 1.871877 -0.502832 -1.708297 6 0.639230 -2.999992 0.652088 8 0.939648 -2.151192 1.638676 8 0.016608 -4.018635 0.853729 8 1.374178 2.459962 -0.740615 1 2.721695 -2.012147 -3.013144 1 3.922529 -1.202422 -1.991925 1 3.120057 -2.328569 0.003354 1 3.004338 -3.640236 -1.186409 1 0.647126 -3.379517 -1.431588 1 1.578017 0.071084 -2.588140 1 2.216989 0.203622 -0.952059 1 -1.576191 3.468030 0.051401 1 0.010454 0.887640 0.504203 1 -1.019627 -0.688725 1.925787 1 -2.931399 -1.455001 3.271819 1 -5.137910 -0.310515 3.086251 1 -5.385508 1.627061 1.543410	6 -3.210093 1.850816 0.542912 6 -2.005680 1.153366 0.742930 6 -1.879365 0.367837 1.901693 6 -2.923031 0.275038 2.824126 6 -4.115772 0.965305 2.606374 6 -4.253448 1.755375 1.462231 6 -0.847875 1.263592 -0.195117 6 -1.012494 -0.012963 -1.671080 6 -2.362695 0.135803 -2.370567 6 -0.621590 2.547997 -0.779251 7 0.606606 2.872692 -1.268296 8 0.876069 4.038975 -1.624386 6 -0.677248 -1.292357 -1.125330 6 -1.778562 -2.168763 -0.578524 7 0.600341 -1.691936 -1.036236 6 1.071835 -2.850158 -0.232179 6 2.593296 -2.889691 -0.490941 6 2.737385 -2.264083 -1.883804 6 1.704618 -1.136039 -1.866635 6 0.692726 -2.745810 1.258594 8 1.055508 -1.641544 1.921342 8 0.071009 -3.632690 1.799372 8 1.496827 1.935426 -1.341583 1 2.492450 -2.994463 -2.664191 1 3.745867 -1.887578 -2.074306 1 3.120639 -2.270691 0.240026 1 2.974328 -3.911868 -0.424026 1 0.602603 -3.769499 -0.594441 1 1.318777 -0.891772 -2.858958 1 2.086805 -0.216574 -1.421490 1 -1.344657 3.347582 -0.824558 1 0.064942 0.827599 0.205317 1 -0.949908 -0.163015 2.091682 1 -2.797639 -0.335234 3.714340 1 -4.929265 0.894745 3.323234 1 -5.175036 2.304184 1.286970

1 -3.479565 2.397172 0.199536 1 1.605401 -1.430806 1.419999 1 -0.024477 1.088582 -1.885100 1 -1.696789 -2.282764 -0.153793 8 2.948705 -0.471238 1.607072 1 3.121320 0.452088 1.263246 6 3.338887 -0.504909 2.980370 1 4.427609 -0.409207 3.082953 1 2.857255 0.295095 3.556263 1 3.029364 -1.470478 3.388242 8 3.419991 2.027978 0.830637 1 2.651245 2.365443 0.288945 6 4.626487 2.435127 0.200192 1 4.722514 2.031793 -0.818561 1 4.692551 3.529082 0.147459 1 5.461805 2.064794 0.802182 1 -1.403476 -2.763695 -1.803897 6 -3.063952 -1.381313 -1.584881 6 -2.958876 -0.408259 -2.760859 1 -1.880039 1.411216 -3.238174 1 -2.808322 1.498164 -1.759436 1 -2.465833 -0.908510 -3.607476 1 -3.955575 -0.113251 -3.108759 1 -3.535565 -0.877619 -0.735099 1 -3.694995 -2.241568 -1.834518	1 -3.336067 2.474080 -0.337298 1 1.704710 -1.031656 1.461781 1 -0.200315 0.449057 -2.224992 1 -2.096442 -1.779619 0.398680 8 3.079504 -0.075930 1.280686 1 3.253931 0.792999 0.815614 6 3.826203 -0.078113 2.495050 1 4.903045 -0.000730 2.297561 1 3.527458 0.744266 3.159111 1 3.626257 -1.023809 3.005687 8 3.692463 2.253080 0.080841 1 2.970539 2.285154 -0.603030 6 3.561042 3.426098 0.880423 1 3.481071 4.319934 0.250989 1 2.678707 3.386101 1.536522 1 4.456682 3.509307 1.503446 1 -1.429493 -3.187696 -0.401637 6 -2.987247 -2.171885 -1.537414 6 -3.483286 -0.748429 -1.802704 1 -2.699008 -2.655482 -2.481295 1 -3.782948 -2.784906 -1.098674 1 -2.656868 1.193046 -2.359610 1 -2.215672 -0.115640 -3.431633 1 -3.862682 -0.323300 -0.867869 1 -4.324800 -0.765961 -2.506144
s-si Et = -1380.2105649 (-1380.5982569) (-1380.624498) NImag=1(-306.72 cm^{-1})	*s-si* (*II*) Et = -1380.2095387 (-1380.59716414) (-1380.62338701) NImag=1(-320.4 cm^{-1})
6 -1.535552 1.133541 -0.612989 6 -0.317002 1.798692 -0.307561 7 0.856295 1.349300 -0.797809 6 0.981166 0.611829 -2.093488 6 2.436339 0.883790 -2.560841 6 2.943791 2.027026 -1.666111 6 2.192401 1.800734 -0.355672 6 0.614723 -0.893622 -2.057307 8 1.441105 -1.760040 -1.491095 8 -0.418447 -1.267044 -2.583145 1 2.675978 3.003544 -2.087136 1 4.028327 1.998440 -1.531013 1 3.062203 0.001189 -2.413691 1 2.455517 1.131541 -3.625579 1 0.254264 1.047922 -2.782595 1 2.123967 2.688277 0.268112 1 2.651720 1.020474 0.259839 1 2.290090 -1.410153 -1.082539 6 -1.662476 -0.265112 0.870500 6 -0.499532 -1.071675 0.948410 6 -2.834748 1.933344 -0.588214 1 -1.751317 0.451364 1.683648 1 -0.401335 -2.044646 0.493855 6 -2.935589 -0.965653 0.531665 6 -3.031143 -1.863182 -0.546246 6 -4.226602 -2.533373 -0.799674 6 -5.345086 -2.322189 0.011139 6 -5.263058 -1.427783 1.078848 6 -4.069142 -0.751927 1.332460 1 -2.175980 -2.022156 -1.197499 1 -4.284818 -3.222485 -1.637976 1 -6.274360 -2.848036 -0.191284 1 -6.126417 -1.255063 1.716043	6 1.461241 1.132773 0.611804 6 0.197218 1.751016 0.370040 7 -0.938372 1.258749 0.897804 6 -0.994675 0.414956 2.133001 6 -2.449003 0.566373 2.642976 6 -2.981505 1.828488 1.951583 6 -2.284159 1.801523 0.591541 6 -0.555076 -1.062525 1.987214 8 -1.335861 -1.921283 1.351496 8 0.487517 -1.423541 2.503081 1 -2.691098 2.730227 2.504341 1 -4.070664 1.824092 1.855637 1 -3.054930 -0.293202 2.347231 1 -2.467414 0.629710 3.734445 1 -0.280789 0.838929 2.844443 1 -2.207417 2.787828 0.139019 1 -2.787210 1.147702 -0.130115 1 -2.197321 -1.578123 0.960532 6 1.687385 -0.181330 -0.879347 6 0.556466 -1.028617 -1.039620 6 2.718361 2.016243 0.619145 1 1.775482 0.566447 -1.663804 1 0.479256 -2.031020 -0.649623 6 2.977643 -0.863234 -0.554939 6 3.092154 -1.793069 0.492663 6 4.302904 -2.442328 0.728464 6 5.418402 -2.178694 -0.070834 6 5.316987 -1.254887 -1.111128 6 4.107390 -0.600384 -1.346730 1 2.238655 -1.998315 1.132721 1 4.374917 -3.156960 1.544071 1 6.359560 -2.688216 0.118174 1 6.176714 -1.042515 -1.741226

1 -4.007460 -0.062321 2.171148 7 0.599341 -0.654620 1.634983 8 0.647351 0.492166 2.163461 8 1.594444 -1.455288 1.730764 1 -1.492388 0.419723 -1.430648 6 -0.346676 2.988163 0.637159 1 -0.285030 2.606156 1.662529 8 3.895024 -1.408860 -0.606914 8 3.932008 -0.227114 1.809156 1 4.034735 -0.967163 0.272496 1 3.020070 -0.579174 2.008016 6 4.199091 -2.795623 -0.438618 1 3.969787 -3.299415 -1.380761 1 5.264003 -2.937212 -0.212519 1 3.593278 -3.243252 0.358613 6 4.768053 -0.386110 2.945203 1 5.765839 -0.023317 2.680364 1 4.398704 0.202160 3.795987 1 4.850075 -1.437298 3.257066 1 0.530031 3.622451 0.487664 6 -1.611308 3.849219 0.466488 6 -2.879664 2.997868 0.511530 1 -2.952156 2.425311 -1.566268 1 -3.682597 1.247724 -0.497783 1 -2.966296 2.521070 1.497505 1 -3.770609 3.625367 0.388471 1 -1.621103 4.615034 1.251249 1 -1.565977 4.382873 -0.493439	1 4.030218 0.109668 -2.166929 7 -0.540687 -0.580252 -1.698879 8 -0.593632 0.610221 -2.126993 8 -1.528806 -1.378637 -1.874889 1 1.459884 0.394592 1.408062 6 0.108434 3.005775 -0.483126 1 -0.565759 2.834771 -1.323899 8 -3.790982 -1.593226 0.481326 8 -3.838923 -0.121254 -1.761567 1 -3.940554 -1.055299 -0.341299 1 -2.932329 -0.463293 -2.009331 6 -4.034066 -2.962690 0.148624 1 -3.794692 -3.562164 1.030331 1 -5.089490 -3.119879 -0.109142 1 -3.400067 -3.288008 -0.684819 6 -4.682260 -0.127487 -2.903714 1 -5.676682 0.203382 -2.588970 1 -4.312756 0.563060 -3.673606 1 -4.771591 -1.129294 -3.347616 1 -0.338717 3.796269 0.140202 6 1.471629 3.498185 -0.981630 6 2.483697 3.464885 0.163246 1 1.816742 2.871685 -1.813530 1 1.354555 4.511888 -1.382085 1 3.435607 3.919127 -0.135434 1 2.096141 4.068727 0.996582 1 3.488004 1.562325 -0.014660 1 3.137642 2.008310 1.632787
s-re Et = -1380.2086101 (-1380.59640746) (-1380.62384713) NImag = 1(-316.36 cm^{-1})	*s-re(II)* Et = -1380.208314 (-1380.5961662) (-1380.622596) NImag = 1(-307.3 cm^{-1})
6 1.219378 -0.294519 1.268632 6 -0.098349 0.099510 1.650457 6 -0.247011 1.497020 2.201308 7 -1.170553 -0.704991 1.530728 6 -1.091703 -2.139613 1.150140 6 -2.543955 -2.657240 1.282884 6 -3.218711 -1.664658 2.235956 6 -2.558717 -0.329393 1.888264 6 -0.507172 -2.449003 -0.246269 8 -1.070268 -1.903089 -1.317345 8 0.439293 -3.205920 -0.347178 1 -3.008443 -1.924186 3.280280 1 -4.303553 -1.628985 2.105847 1 -3.045113 -2.625018 0.312449 1 -2.558035 -3.689097 1.643035 1 -0.422249 -2.646048 1.852522 1 -2.566162 0.354090 2.737280 1 -3.039023 0.174393 1.042894 1 -1.891284 -1.344980 -1.164115 1 -0.087191 2.188375 1.362749 6 1.496110 0.452601 -0.645201 1 0.745570 -0.221349 -1.042000 6 1.149203 1.818278 -0.820640 1 1.334891 -1.339486 0.994267 7 -0.157391 2.173936 -0.998216 8 -0.483490 3.352174 -1.269653 8 -1.052552 1.260825 -0.850513 6 2.891857 0.019564 -0.930467 6 3.118256 -1.305275 -1.344503 6 4.403452 -1.744390 -1.658629	6 1.175350 -0.350209 1.155744 6 -0.189708 -0.144415 1.504918 6 -0.418268 1.079859 2.347498 7 -1.192821 -0.994362 1.225607 6 -1.000768 -2.322400 0.598846 6 -2.416096 -2.944554 0.588894 6 -3.139974 -2.241786 1.743468 6 -2.586784 -0.814950 1.696143 6 -0.366154 -2.318476 -0.806031 8 -0.924219 -1.576607 -1.756780 8 0.610674 -3.006630 -1.029453 1 -2.886210 -2.710936 2.701422 1 -4.227499 -2.262030 1.632900 1 -2.920530 -2.711845 -0.352711 1 -2.367795 -4.031109 0.696795 1 -0.314186 -2.909284 1.219092 1 -2.597077 -0.342392 2.679970 1 -3.140038 -0.173966 1.001939 1 -1.761828 -1.083965 -1.502306 1 0.063252 1.912259 1.819187 6 1.541892 0.654900 -0.626191 1 0.820902 0.047833 -1.160900 6 1.188165 2.022870 -0.544088 1 1.440964 -1.338948 0.791911 7 -0.126995 2.391832 -0.612370 8 -0.471509 3.593390 -0.639741 8 -1.004731 1.452373 -0.615947 6 2.959960 0.285175 -0.887090 6 3.236759 -0.942082 -1.515841 6 4.548649 -1.316151 -1.802148

6	5.490044	-0.873268	-1.559690	6	5.611272	-0.476687	-1.462216
6	5.281324	0.442205	-1.140358	6	5.351012	0.741927	-0.832016
6	3.996627	0.883493	-0.826928	6	4.039850	1.118761	-0.546746
1	2.280597	-1.994464	-1.416055	1	2.417710	-1.608381	-1.773552
1	4.553875	-2.770401	-1.983493	1	4.738983	-2.266919	-2.292767
1	6.491560	-1.215732	-1.806066	1	6.633926	-0.768649	-1.686002
1	6.119933	1.128770	-1.058999	1	6.170573	1.403572	-0.563922
1	3.856382	1.911069	-0.504580	1	3.860731	2.071051	-0.057024
1	1.841050	2.642601	-0.899090	1	1.873145	2.852959	-0.466287
6	2.376344	0.188954	2.147674	6	2.166152	0.265318	2.145722
1	-3.630277	0.149982	-1.265705	1	-3.538086	0.355134	-1.278545
8	-3.484585	-0.829855	-1.376392	8	-3.364556	-0.567395	-1.611507
8	-3.625674	1.817757	-0.931577	8	-3.602221	1.902585	-0.560959
1	-2.630673	1.858244	-0.930499	1	-2.611300	1.990446	-0.549313
6	-3.891134	-1.200895	-2.691802	6	-3.758315	-0.637070	-2.980120
1	-3.619320	-2.249302	-2.839113	1	-3.448582	-1.612420	-3.364188
1	-4.977706	-1.097886	-2.813150	1	-4.847954	-0.547257	-3.083276
1	-3.387454	-0.599513	-3.460149	1	-3.276788	0.143407	-3.584009
6	-4.124289	2.826745	-1.801410	6	-4.159127	3.056680	-1.178874
1	-5.216360	2.817804	-1.732699	1	-5.247217	2.941795	-1.180158
1	-3.757914	3.816785	-1.503879	1	-3.900637	3.965602	-0.621362
1	-3.835900	2.653304	-2.848284	1	-3.815783	3.179643	-2.215900
1	-1.248774	1.698511	2.578551	1	-1.467925	1.350222	2.457674
6	0.816229	1.813363	3.270938	6	0.285389	0.921494	3.726002
6	2.215129	1.614052	2.685832	6	1.634327	0.176867	3.588876
1	0.674798	1.164370	4.146449	1	3.129222	-0.244472	2.054887
1	0.677189	2.845424	3.613944	1	2.350757	1.321465	1.902048
1	2.985162	1.814602	3.440743	1	2.367993	0.586617	4.293285
1	2.367557	2.338472	1.875619	1	1.506446	-0.881123	3.851048
1	3.317657	0.091168	1.597979	1	0.437706	1.925084	4.139181
1	2.455564	-0.504453	2.999832	1	-0.373159	0.392167	4.424813

Table S40. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway (**L_1** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et = -1226.3615284 (-1226.7006648) (-1226.7276096) NImag=1(-312.67 cm^{-1})				*a-re* Et = -1226.3558732 (-1226.6959613) (-1226.7232295) NImag= 1(-315.90 cm^{-1})			
6	-3.794554	-1.751152	0.462975	6	-3.335541	-1.695120	-0.199278
6	-2.749414	-1.050038	-0.161627	6	-2.970161	-0.337724	-0.217652
6	-3.082951	-0.101797	-1.146230	6	-3.961966	0.624300	0.038178
6	-4.413022	0.134625	-1.487964	6	-5.280656	0.243384	0.285320
6	-5.440244	-0.570500	-0.855502	6	-5.629905	-1.107718	0.293508
6	-5.125840	-1.516970	0.120116	6	-4.651255	-2.076120	0.052763
6	-1.341950	-1.359456	0.211360	6	-1.589575	0.114313	-0.519496
6	-0.367429	-1.362459	-0.826368	6	-0.616616	-0.197471	1.372782
7	0.874103	-1.844451	-0.605250	6	-1.385288	0.727686	2.297642
8	1.163972	-2.492359	0.434837	6	-0.897645	-0.536617	-1.560537
8	1.802385	-1.584459	-1.482210	7	0.290211	-0.079269	-2.038516
6	-0.772267	-0.115035	1.704847	8	0.934053	-0.728167	-2.891588
6	-1.961719	0.028680	2.632995	6	0.774225	-0.000503	1.152694
6	-0.217109	1.018305	1.037152	6	1.425850	1.308285	1.541987
6	-1.085056	2.188108	0.635723	6	2.088366	1.239079	2.933900
6	-1.021261	3.316532	1.690265	7	1.528984	-0.989840	0.634011
7	1.078018	1.013067	0.693229	6	3.006456	-0.987503	0.422542
6	1.716221	1.977264	-0.256365	6	3.197570	-2.191453	-0.516734
6	3.216401	1.629993	-0.179323	6	2.234578	-3.226390	0.069970

6 3.395326 1.093185 1.242695 6 2.129270 0.262644 1.448099 6 1.168565 1.960793 -1.702681 8 1.237430 0.842005 -2.417703 8 0.727555 2.986813 -2.180112 1 3.449978 1.913842 1.968445 1 4.284567 0.466803 1.330952 1 3.468381 0.841127 -0.894356 1 3.831110 2.504771 -0.406425 1 1.540886 2.995261 0.101179 1 1.820528 0.189560 2.493150 1 2.259249 -0.746731 1.050906 1 -2.781296 0.607928 2.199801 1 -2.361293 -0.957803 2.888623 1 -1.667991 0.509513 3.575316 1 -1.250637 -2.197290 0.899214 1 -0.491673 -0.842823 -1.763322 1 -2.300827 0.454257 -1.655076 1 -4.647003 0.868837 -2.253910 1 -6.476259 -0.385865 -1.125548 1 -5.915502 -2.078343 0.611972 1 -3.557127 -2.502010 1.212408 1 -0.024947 -0.808923 2.080759 1 -2.117652 1.847532 0.532747 1 -0.788201 2.593768 -0.333728 1 -0.003201 3.703874 1.804513 1 -1.662775 4.146898 1.378889 1 -1.362900 2.971575 2.671182 1 1.563527 0.004263 -1.963009 1 3.457126 -1.814570 -0.684344 8 4.302396 -1.691060 -0.201889 6 4.700732 -2.958858 0.288214 1 5.008993 -3.641059 -0.520446 1 5.563992 -2.806009 0.945064 1 3.903986 -3.449406 0.865513	6 1.023711 -2.388690 0.511379 6 3.793551 0.229132 -0.119970 8 3.350993 0.934167 -1.153117 8 4.891738 0.420976 0.358839 8 0.768083 1.034135 -1.571076 1 2.691417 -3.722143 0.933725 1 1.950148 -3.999604 -0.648699 1 2.895169 -1.908932 -1.531531 1 4.239951 -2.518118 -0.534938 1 3.486790 -1.197545 1.384711 1 0.621833 -2.715929 1.477966 1 0.218878 -2.423427 -0.221930 1 -1.386315 1.764347 1.944544 1 -2.426150 0.401684 2.363285 1 -0.979265 0.722511 3.317535 1 -1.207379 -1.472619 -2.002655 1 -1.441403 1.184732 -0.428996 1 -3.691844 1.676819 0.028847 1 -6.034536 1.003258 0.472058 1 -6.655995 -1.406227 0.489572 1 -4.914489 -3.130350 0.063398 1 -2.583404 -2.459855 -0.376510 1 2.385320 0.814275 -1.399654 1 -0.939751 -1.232062 1.423645 1 0.666952 2.091697 1.526223 1 2.165967 1.612971 0.803732 1 2.928551 0.537785 2.950337 1 2.480283 2.225963 3.199507 1 1.376155 0.938672 3.709446 1 -0.046749 2.582957 -0.876106 8 -0.559771 3.220795 -0.339795 6 -0.753405 4.402304 -1.102392 1 -1.298857 4.212438 -2.038968 1 -1.347546 5.089771 -0.492915 1 0.197383 4.896400 -1.349831
s-si Et = -1226.3574284 (-1226.696541) (-1226.7237364) NImag=1(-311.3 cm^{-1})	*s-re* Et = -1226.3578989 (-1226.6984012) (-1226.7261202) NImag = 1(-338.83 cm^{-1})
6 0.993856 1.425036 0.273285 6 -0.362856 1.621963 -0.088744 7 -1.352906 0.969822 0.557929 6 -1.222957 0.432212 1.944440 6 -2.685291 0.288186 2.444223 6 -3.509464 1.178310 1.507500 6 -2.784798 1.023732 0.172226 6 -0.459681 -0.896344 2.156501 8 -0.936190 -2.017441 1.606982 8 0.479464 -0.924956 2.925786 1 -3.481956 2.223888 1.838006 1 -4.555793 0.867990 1.442831 1 -3.003526 -0.754046 2.347227 1 -2.764018 0.563736 3.499070 1 -0.670024 1.168223 2.533889 1 -2.976525 1.847006 -0.511084 1 -3.065334 0.094848 -0.339525 1 -1.373398 -1.919488 0.709566 6 1.558208 -0.188850 -0.981667 6 0.622639 -1.230929 -0.812821 6 2.039130 2.491265 0.008430 1 1.873113 3.378683 0.633280 1 3.032452 2.105998 0.250149	6 -0.643231 0.334891 1.219550 6 0.780520 0.208309 1.157010 6 1.445350 -1.033327 1.710452 7 1.569099 1.164636 0.636889 6 1.081208 2.463635 0.133773 6 2.372420 3.251052 -0.221033 6 3.473548 2.556605 0.587523 6 3.050132 1.088185 0.563434 6 0.183162 2.432268 -1.112748 8 0.402614 1.483063 -2.032640 8 -0.615368 3.323542 -1.297586 1 3.488175 2.928068 1.619079 1 4.468952 2.703815 0.159707 1 2.578257 3.154046 -1.292572 1 2.256763 4.313900 0.001486 1 0.510402 2.969705 0.918767 1 3.447104 0.520629 1.403318 1 3.358016 0.570020 -0.351648 1 0.808262 0.644563 -1.686423 1 2.310484 -1.306890 1.100860 1 0.732793 -1.858259 1.612850 6 -1.451559 -0.624071 -0.441793 1 -1.037961 0.109489 -1.117061

1	2.061380	2.824509	-1.034438
1	1.441103	0.393513	-1.891133
1	0.769089	-2.071225	-0.153416
6	2.961278	-0.427868	-0.563077
6	3.282306	-1.069578	0.647039
6	4.612161	-1.312011	0.984061
6	5.643062	-0.920592	0.125268
6	5.336487	-0.274482	-1.073140
6	4.006698	-0.023793	-1.409881
1	2.494768	-1.360986	1.337110
1	4.843881	-1.806089	1.923514
1	6.678539	-1.113541	0.392114
1	6.130938	0.035403	-1.746610
1	3.771394	0.474563	-2.347132
7	-0.613062	-1.141427	-1.374010
8	-0.889191	-0.246897	-2.209563
8	-1.522476	-1.987812	-1.000246
1	1.160984	0.888813	1.203493
6	-0.717154	2.571643	-1.218048
1	-1.513957	2.156829	-1.834346
1	0.147833	2.654658	-1.879585
6	-1.098839	3.973499	-0.701363
1	-1.321971	4.634755	-1.545272
1	-1.985259	3.942305	-0.057840
1	-0.285568	4.426344	-0.124935
1	-3.163084	-1.487442	-1.838367
8	-4.121489	-1.287288	-1.863134
6	-4.803283	-2.473446	-1.505531
1	-5.870846	-2.235676	-1.446491
1	-4.675537	-3.274385	-2.250917
1	-4.486871	-2.870513	-0.527397

6	-0.933368	-1.930305	-0.625444
1	-1.025801	1.324768	0.976120
7	0.324825	-2.116624	-1.108935
8	0.783478	-3.262035	-1.299391
8	1.079673	-1.082185	-1.328651
6	-2.911963	-0.432162	-0.245024
6	-3.484324	0.792290	-0.634529
6	-4.853414	1.015693	-0.501486
6	-5.678357	0.021118	0.027663
6	-5.123139	-1.197668	0.424055
6	-3.753935	-1.421661	0.292127
1	-2.850032	1.570666	-1.052931
1	-5.275765	1.965777	-0.816801
1	-6.746399	0.193130	0.129499
1	-5.757957	-1.977670	0.835679
1	-3.340567	-2.374399	0.609155
1	-1.450215	-2.849723	-0.397533
6	-1.372692	-0.292674	2.397482
1	-2.449161	-0.142830	2.291157
1	-1.196311	-1.370955	2.473816
1	-1.072841	0.163102	3.349335
6	1.861704	-0.905280	3.191459
1	1.005307	-0.725040	3.846783
1	2.343344	-1.833953	3.513913
1	2.576220	-0.089431	3.347391
1	2.808988	-1.699679	-1.150741
8	3.714093	-1.749102	-0.774375
6	4.285731	-2.989613	-1.156268
1	5.224936	-3.104970	-0.604730
1	3.629038	-3.836659	-0.917587
1	4.515820	-3.027287	-2.232641

Table S41. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway (**L_2** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =-1342.0880675 (-1342.4700789) (-1342.4980674) NImag=1(-308.15 cm^{-1})			*a-re* Et = -1342.0898716 (-1342.4720602) (-1342.481230) NImag= 1(-276.28 cm^{-1})		
6	-3.912142	0.574205 -1.662227	6	-3.337572	1.261639 -0.610337
6	-2.836393	0.574832 -0.757637	6	-2.985595	0.026951 -0.033597
6	-3.119786	0.723324 0.612921	6	-3.977828	-0.961743 0.090696
6	-4.432340	0.862774 1.057854	6	-5.284321	-0.720091 -0.332187
6	-5.490652	0.858440 0.145248	6	-5.620137	0.510676 -0.897968
6	-5.225774	0.716631 -1.217406	6	-4.641184	1.499219 -1.037075
6	-1.451481	0.459306 -1.275807	6	-1.625370	-0.258786 0.466821
6	-0.431327	1.207067 -0.629706	6	-0.610216	-0.877134 -1.426879
7	0.796150	1.301315 -1.174157	6	-1.387276	-2.121301 -1.803607
8	1.066888	0.872985 -2.324553	6	-0.899919	0.778811 1.074361
8	1.759570	1.816623 -0.438268	7	0.283444	0.560378 1.700267
6	-0.930990	-1.551090 -1.326322	8	0.960464	1.526927 2.162605
6	-2.181542	-2.288287 -1.756919	6	0.772409	-0.940403 -1.128027
6	-0.325606	-1.800521 -0.062291	6	1.432437	-2.281606 -0.885046
6	-1.162326	-2.207572 1.129280	6	2.078249	-2.854855 -2.163835
6	-1.187808	-3.742827 1.304219	7	1.519854	0.184503 -1.104194
7	0.993974	-1.614450 0.096660	6	2.998497	0.278229 -0.939528
6	1.700473	-1.601994 1.413352	6	3.197483	1.779448 -0.663229
6	3.192963	-1.523785 1.031327	6	2.210801	2.440236 -1.630031

6 3.257085 -2.219389 -0.330385 6 1.983204 -1.729085 -1.016987 6 1.284035 -0.485554 2.394007 8 1.365047 0.786334 2.007572 8 0.940755 -0.778545 3.520018 1 3.245803 -3.310162 -0.215317 1 4.141607 -1.922997 -0.896746 1 3.511378 -0.483173 0.916245 1 3.815966 -1.988288 1.799862 1 1.490377 -2.536411 1.940343 1 1.593307 -2.426582 -1.761532 1 2.146096 -0.760511 -1.497287 1 -2.961265 -2.303113 -0.990970 1 -2.610525 -1.820062 -2.648441 1 -1.949257 -3.328088 -2.023042 1 -1.382155 0.449968 -2.360869 1 -0.538990 1.679128 0.335685 1 -2.310207 0.737612 1.336523 1 -4.628588 0.981730 2.119717 1 -6.513192 0.970584 0.494747 1 -6.040388 0.722984 -1.936334 1 -3.712129 0.482101 -2.726802 1 -0.222121 -1.400295 -2.135289 1 -2.182346 -1.843413 0.987113 1 -0.793814 -1.753868 2.051861 1 -0.183776 -4.146989 1.471545 1 -1.802230 -4.003362 2.171739 1 -1.609912 -4.241680 0.426354 1 1.617038 0.982276 1.058406 1 3.385737 1.250579 -1.143696 8 4.206852 0.755124 -1.347354 6 4.653906 1.178719 -2.623350 1 5.002872 2.223637 -2.617652 1 5.500062 0.543715 -2.906889 1 3.871746 1.081928 -3.390122 1 1.000323 3.381472 0.483238 8 0.351561 3.902149 0.993406 6 0.927649 4.202038 2.254224 1 1.223721 3.299216 2.806279 1 1.804682 4.863778 2.167883 1 0.167029 4.729464 2.838978	6 1.010389 1.481316 -1.643533 6 3.794607 -0.551103 0.092593 8 3.355145 -0.715498 1.337660 8 4.894977 -0.934418 -0.242933 8 0.745855 -0.636739 1.813146 1 2.653587 2.520459 -2.629003 1 1.904322 3.434581 -1.298900 1 2.922761 1.992354 0.375852 1 4.237541 2.075458 -0.819710 1 3.466113 0.021003 -1.896638 1 0.616894 1.319014 -2.654505 1 0.204506 1.859680 -1.016676 1 -1.379792 -2.876314 -1.010406 1 -2.429916 -1.861232 -2.003086 1 -0.993117 -2.591814 -2.714320 1 -1.168714 1.823129 1.008056 1 -1.475891 -1.263766 0.844400 1 -3.717445 -1.918532 0.535159 1 -6.038995 -1.493590 -0.219578 1 -6.636808 0.699712 -1.231292 1 -4.895443 2.457921 -1.480760 1 -2.586919 2.038276 -0.730858 1 2.396430 -0.496208 1.504331 1 -0.951718 0.028145 -1.916039 1 0.680446 -2.974116 -0.503583 1 2.184177 -2.215606 -0.099808 1 2.914483 -2.239064 -2.509949 1 2.472048 -3.854983 -1.956539 1 1.354737 -2.939445 -2.981369 1 -0.080032 -2.350648 1.840802 8 -0.606573 -3.147977 1.633935 6 -0.802643 -3.886250 2.830927 1 -1.339022 -3.307077 3.597313 1 -1.407058 -4.762035 2.577060 1 0.146436 -4.236416 3.261781 1 0.535312 3.121788 1.305567 8 0.166406 3.795655 0.694587 6 -0.012099 5.003692 1.416995 1 -0.674600 4.878091 2.286484 1 0.941729 5.424739 1.768833 1 -0.473618 5.727045 0.737783
s-si Et =-1342.0824498 (-1342.4648587) (-1342.491279) NImag=1(-293.86 cm^{-1})	*s-re* Et =-1342.0862149 (-1342.4689892) (-1342.498926) NImag = 1(-320.82 cm^{-1})
6 -1.534683 -1.590527 -0.051085 6 -0.232328 -1.985346 -0.435728 7 0.832394 -1.735543 0.361327 6 0.722728 -1.517032 1.832892 6 2.141065 -1.827076 2.380448 6 2.811637 -2.654042 1.278016 6 2.239905 -2.042117 0.000567 6 0.250285 -0.136132 2.338038 8 0.978141 0.949294 2.047760 8 -0.698295 -0.065693 3.091347 1 2.525620 -3.710097 1.355602 1 3.902641 -2.591935 1.307913 1 2.689322 -0.892791 2.535624 1 2.081039 -2.340318 3.343605 1 -0.016523 -2.223478 2.219716 1 2.287973 -2.719642 -0.847987 1 2.765413 -1.121349 -0.281712	6 -1.199878 0.934497 1.091554 6 0.209573 1.123570 1.191892 6 0.989673 0.397902 2.266743 7 0.891696 1.937031 0.364041 6 0.264855 2.779083 -0.673326 6 1.431628 3.637804 -1.232721 6 2.484884 3.610355 -0.120362 6 2.352124 2.198507 0.449828 6 -0.398168 2.042932 -1.846083 8 0.150557 0.891702 -2.264396 8 -1.319356 2.556367 -2.439757 1 2.250746 4.353014 0.651543 1 3.494569 3.810331 -0.489047 1 1.832246 3.168372 -2.137946 1 1.087941 4.639274 -1.499925 1 -0.508702 3.406649 -0.219364 1 2.694946 2.124796 1.480191

1	1.458201	0.933947	1.174053
6	-1.684587	0.400264	-0.922329
6	-0.553573	1.131370	-0.513613
6	-2.766130	-2.297766	-0.577633
1	-2.852705	-3.310762	-0.162564
1	-3.665705	-1.751620	-0.283721
1	-2.778663	-2.389973	-1.668656
1	-1.645120	0.004224	-1.932517
1	-0.544677	1.813342	0.321398
6	-3.021095	0.824301	-0.452271
6	-3.250954	1.249119	0.869823
6	-4.516614	1.679577	1.260117
6	-5.572646	1.694986	0.344298
6	-5.358736	1.266787	-0.966722
6	-4.095103	0.827391	-1.358835
1	-2.448181	1.219203	1.601700
1	-4.679692	2.000550	2.285055
1	-6.557627	2.033536	0.653633
1	-6.174244	1.273754	-1.684603
1	-3.929916	0.499836	-2.382229
7	0.658718	0.887675	-1.074834
8	0.788673	0.154269	-2.079699
8	1.713787	1.409087	-0.507168
1	-1.644653	-1.236721	0.970044
6	-0.013428	-2.710054	-1.751374
1	0.895014	-2.357375	-2.238738
1	-0.827345	-2.444228	-2.429364
6	0.020717	-4.241450	-1.574327
1	0.153468	-4.726863	-2.546884
1	0.846176	-4.558652	-0.927336
1	-0.908749	-4.617399	-1.134609
1	3.284786	0.648188	-1.385563
8	4.184057	0.269112	-1.412322
6	5.029798	1.175246	-0.717073
1	6.063666	0.939140	-0.990315
1	4.820310	2.219072	-0.982623
1	4.939832	1.078000	0.378773
1	2.425305	3.126207	-0.990224
8	2.910209	3.971755	-1.030089
6	2.722967	4.617757	0.213773
1	1.666327	4.862206	0.411020
1	3.098231	4.026213	1.064286
1	3.284776	5.556720	0.181262

1	2.906090	1.450840	-0.128065
1	0.667972	0.403073	-1.576289
1	1.981735	0.125977	1.896638
1	0.470383	-0.543706	2.471718
6	-1.527724	-0.807005	-0.096013
1	-1.131318	-0.312494	-0.969474
6	-0.762678	-1.913710	0.340495
1	-1.714066	1.611523	0.412122
7	0.562537	-1.998882	0.056642
8	1.217088	-3.024194	0.381607
8	1.171712	-1.012384	-0.511591
6	-3.007039	-0.886415	-0.109607
6	-3.712592	-0.077252	-1.019448
6	-5.102460	-0.135072	-1.096827
6	-5.816303	-0.999179	-0.263783
6	-5.129787	-1.803947	0.648453
6	-3.739913	-1.746927	0.727604
1	-3.164183	0.595240	-1.675323
1	-5.626975	0.492109	-1.812184
1	-6.900058	-1.046514	-0.324856
1	-5.677612	-2.479604	1.299591
1	-3.225249	-2.377883	1.446113
1	-1.143846	-2.764924	0.883236
6	-1.996723	0.652196	2.353192
1	-3.040816	0.456884	2.099550
1	-1.622291	-0.218102	2.902068
1	-1.983879	1.508951	3.038922
6	1.118335	1.195740	3.582019
1	0.144526	1.413785	4.029178
1	1.698739	0.613233	4.304563
1	1.636225	2.149453	3.432047
1	2.953059	-1.042656	0.172494
8	3.757966	-0.646219	0.561020
6	4.589396	-1.698183	1.049046
1	5.581585	-1.272154	1.229883
1	4.212818	-2.109442	1.998196
1	4.670822	-2.514706	0.323470
1	2.656397	-3.449878	-0.854717
8	3.414661	-3.665074	-1.432457
6	3.456348	-2.705343	-2.472411
1	3.644192	-1.686945	-2.099550
1	4.281180	-2.983602	-3.136627
1	2.530855	-2.686848	-3.069797

Table S42. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway (**C_1** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =-1226.3659841 (-1226.7055201) (-1226.732758) NImag=1(-297.61 cm^{-1})			*a-re* Et = -1226.3625779 (-1226.702091) (-1226.734089) NImag= 1(-251.11 cm^{-1})		
6	3.749131	-1.042625	-0.167639	6	-3.658466	-0.009811	-0.171131
6	2.396596	-0.904145	0.185989	6	-2.358828	-0.024786	0.363478
6	2.090533	-0.386854	1.457506	6	-2.080726	-0.925260	1.405482
6	3.105501	-0.023828	2.341050	6	-3.066007	-1.783084	1.895488
6	4.446311	-0.167419	1.975105	6	-4.350317	-1.761361	1.349971
6	4.765085	-0.679458	0.716966	6	-4.642217	-0.870212	0.315305
6	1.342828	-1.325598	-0.779556	6	-1.278441	0.901773	-0.108575

6 0.171657 -1.951199 -0.271402 7 -0.701157 -2.544035 -1.131347 8 -0.451362 -2.608932 -2.361647 8 -1.820755 -2.995008 -0.682400 6 0.827340 0.196766 -1.931452 6 2.071212 0.567170 -2.720168 6 0.204087 1.147067 -1.074688 6 1.006801 2.276225 -0.467165 6 0.926140 3.557735 -1.327676 7 -1.099630 1.023861 -0.752277 6 -1.780114 1.866743 0.277871 6 -3.281016 1.570375 0.076277 6 -3.373055 1.192930 -1.406610 6 -2.113044 0.351532 -1.618925 6 -1.292214 1.641752 1.726951 8 -1.334986 0.411291 2.233686 8 -0.878452 2.580756 2.374967 1 -3.347623 2.089051 -2.038425 1 -4.279895 0.630939 -1.645886 1 -3.589448 0.718863 0.689403 1 -3.889076 2.435989 0.351555 1 -1.576060 2.919872 0.070179 1 -1.761837 0.351800 -2.651569 1 -2.281625 -0.683505 -1.311723 1 2.866990 0.994549 -2.103262 1 2.476347 -0.326614 -3.206559 1 1.840758 1.284793 -3.517472 1 1.739364 -1.825499 -1.662037 1 -0.141678 -1.917735 0.759765 1 1.056028 -0.262611 1.763983 1 2.845232 0.374282 3.317914 1 5.235110 0.115858 2.666668 1 5.804230 -0.802670 0.423678 1 4.005226 -1.454943 -1.140279 1 0.148126 -0.425662 -2.510839 1 2.049003 1.961554 -0.385319 1 0.676701 2.508474 0.546441 1 -0.103569 3.919638 -1.421247 1 1.517634 4.351351 -0.860053 1 1.316450 3.392662 -2.336493 1 -1.841407 -0.282735 1.703018 8 -2.794274 -1.524629 1.279864 1 -2.436020 -2.122931 0.557235 6 -3.193087 -2.326323 2.390748 1 -4.082729 -2.918892 2.144039 1 -2.392354 -3.005272 2.710748 1 -3.433891 -1.652282 3.217056	6 -0.465402 0.218471 -1.688473 6 -1.554213 -0.079252 -2.704177 6 -1.669196 2.249714 -0.399661 7 -0.753428 3.257236 -0.453410 8 -1.110639 4.424715 -0.705430 6 0.410299 -0.830330 -1.242544 6 -0.086122 -2.247644 -1.089652 6 0.277266 -3.097633 -2.328995 7 1.675422 -0.538505 -0.904735 6 2.573307 -1.409408 -0.099280 6 3.857845 -0.566143 0.051665 6 3.879030 0.294140 -1.216520 6 2.405618 0.651998 -1.425132 6 2.004372 -1.847198 1.266566 8 1.464566 -0.914708 2.051719 8 2.070901 -3.009283 1.604038 8 0.502981 2.991659 -0.255721 1 4.257535 -0.284027 -2.067814 1 4.500888 1.186791 -1.109821 1 3.777541 0.078553 0.932327 1 4.736296 -1.205352 0.169134 1 2.780515 -2.335046 -0.644266 1 2.147998 0.790729 -2.478478 1 2.106060 1.553788 -0.885901 1 -2.194507 0.803510 -2.806357 1 -1.126374 -0.285752 -3.692794 1 -2.189514 -0.924503 -2.425387 1 -2.674617 2.558125 -0.642626 1 -0.404697 0.855332 0.533940 1 -1.086035 -0.948267 1.843856 1 -2.827396 -2.465072 2.707135 1 -5.118950 -2.428719 1.730219 1 -5.641012 -0.839263 -0.112044 1 -3.908866 0.682490 -0.968954 1 1.564562 0.041088 1.747831 1 0.069749 1.131412 -1.933265 1 -1.169834 -2.232830 -0.961313 1 0.325205 -2.729999 -0.200271 1 1.361061 -3.151796 -2.477634 1 -0.094578 -4.118311 -2.194779 1 -0.169391 -2.689310 -3.240785 8 1.731049 1.669691 1.680552 1 1.192796 2.192954 1.020743 6 1.655718 2.308696 2.955568 1 2.114420 3.303799 2.917859 1 0.618644 2.406693 3.300844 1 2.206555 1.689234 3.668051
s-si Et =-1226.3634947 (-1226.7025774) (-1226.7299804) NImag=1(-330.74 cm^{-1})	*s-re* Et = -1226.3603215 (-1226.7002954) (-1226.7288495) NImag = 1(-346.73 cm^{-1})
6 0.846787 1.382767 0.417406 6 -0.455996 1.685275 -0.062187 7 -1.542451 1.035683 0.411135 6 -1.567055 0.316449 1.717449 6 -3.070384 0.208321 2.075053 6 -3.753828 1.277333 1.213584 6 -2.926447 1.260160 -0.071886 6 -0.854633 -1.056902 1.776171 8 -1.354699 -2.074671 1.086135 8 0.111325 -1.199798 2.501391 1 -3.688301 2.262209 1.691792	6 -0.572866 0.504071 -1.298017 6 0.788305 0.912213 -1.124928 6 1.111910 2.389436 -1.047146 7 1.807809 0.034862 -1.067539 6 1.688910 -1.417749 -1.342871 6 3.147745 -1.935072 -1.301381 6 3.996973 -0.692796 -1.589104 6 3.228114 0.418516 -0.873989 6 0.796293 -2.243615 -0.394708 8 0.996163 -2.157074 0.917871 8 -0.033479 -2.998785 -0.859682

1	-4.808843	1.057663	1.027710	1	4.036977	-0.492424	-2.666376
1	-3.451477	-0.781263	1.809586	1	5.022676	-0.785833	-1.221625
1	-3.224043	0.346529	3.148583	1	3.376618	-2.318152	-0.301552
1	-1.031934	0.933298	2.444863	1	3.295517	-2.749293	-2.015027
1	-2.999190	2.189386	-0.631597	1	1.249207	-1.551040	-2.336307
1	-3.219885	0.431097	-0.723011	1	3.424261	1.401262	-1.300623
1	-2.092946	-1.857163	0.438609	1	3.455124	0.443252	0.197211
6	1.611319	0.009979	-0.939618	1	1.683805	-1.494548	1.233175
6	0.731292	-1.066574	-1.186835	1	1.929404	2.559206	-0.346220
6	1.910497	2.468805	0.448677	1	0.243153	2.894136	-0.614373
1	1.647437	3.269226	1.152178	6	-1.402945	0.387206	0.548140
1	2.862097	2.046919	0.779132	1	-0.703530	-0.377948	0.866274
1	2.080445	2.934023	-0.528708	6	-1.296010	1.584637	1.308510
1	1.645643	0.748711	-1.737223	1	-0.702900	-0.544816	-1.555997
1	0.828423	-2.050068	-0.754279	7	-0.112884	1.904378	1.906471
6	2.932986	-0.324639	-0.340715	8	-0.013873	2.853698	2.708546
6	3.051719	-1.161245	0.783056	8	0.915095	1.197048	1.570371
6	4.309402	-1.488836	1.286670	6	-2.768144	-0.146058	0.264732
6	5.467130	-0.991127	0.682880	6	-2.941079	-1.532176	0.106629
6	5.360035	-0.153990	-0.428563	6	-4.205895	-2.072098	-0.124313
6	4.102743	0.180808	-0.931031	6	-5.323414	-1.240122	-0.207582
1	2.160210	-1.537682	1.277348	6	-5.165700	0.139702	-0.060792
1	4.384116	-2.133661	2.158158	6	-3.902170	0.680635	0.170203
1	6.445163	-1.250451	1.079370	1	-2.079917	-2.192453	0.161477
1	6.253748	0.239600	-0.905565	1	-4.315482	-3.147289	-0.237500
1	4.024060	0.828633	-1.800849	1	-6.309012	-1.661683	-0.386394
7	-0.347841	-0.902206	-2.000843	1	-6.028322	0.797800	-0.124702
8	-0.626617	0.235877	-2.469552	1	-3.800895	1.756424	0.277671
8	-1.073449	-1.924185	-2.268725	1	-2.102405	2.267194	1.527790
1	0.887133	0.731120	1.285313	6	-1.509206	1.407536	-2.087523
6	-0.647852	2.783376	-1.090437	1	-2.512915	0.976687	-2.097871
1	-1.400340	2.493057	-1.823156	1	-1.587308	2.411214	-1.656319
1	0.279837	2.882554	-1.657681	1	-1.190270	1.512973	-3.131739
6	-1.003454	4.140240	-0.449271	6	1.440515	3.020600	-2.415676
1	-1.111501	4.903793	-1.227122	1	0.606447	2.935105	-3.117255
1	-1.946543	4.096034	0.107523	1	1.661515	4.085208	-2.285410
1	-0.226205	4.475968	0.244213	1	2.314927	2.553354	-2.883429
1	-2.528489	-1.795323	-1.516085	1	2.123058	0.226194	2.239009
8	-3.218909	-1.835038	-0.788809	8	2.707923	-0.573832	2.190770
6	-3.883379	-3.095248	-0.893820	6	2.850612	-1.129625	3.498325
1	-3.170331	-3.928836	-0.874907	1	3.454769	-2.035919	3.406549
1	-4.561503	-3.187438	-0.040836	1	3.365083	-0.428489	4.166821
1	-4.471264	-3.149473	-1.818428	1	1.879614	-1.394681	3.936171

Table S43. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway (**L_1C_1** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =- -1342.0992523 (-1342.4814904) (-1342.5049131) NImag=1(-282.04 cm^{-1})				*a-re* Et = -1342.0963584 (-1342.4791526) (-1342.5047043) NImag= 1(-283.98 cm^{-1})			
6	3.569125	-2.106277	0.141523	6	2.889401	-2.398640	-0.205551
6	2.454151	-1.340279	0.524277	6	2.136022	-1.353707	0.358559
6	2.667976	-0.204219	1.327317	6	2.825751	-0.279507	0.947801
6	3.954160	0.146061	1.731975	6	4.219740	-0.250751	0.973754
6	5.052897	-0.626581	1.345311	6	4.954138	-1.292909	0.405446
6	4.855939	-1.755116	0.548663	6	4.282875	-2.366457	-0.183945

6 1.102969 -1.766021 0.091092 6 0.001029 -1.572603 0.952871 7 -1.196088 -2.151800 0.664899 8 -1.346897 -2.879612 -0.345016 8 -2.206819 -1.905918 1.434975 6 0.681425 -0.871948 -1.760100 6 1.730073 -1.437824 -2.694970 6 0.598512 0.513823 -1.487467 6 1.808942 1.405057 -1.664004 6 1.849231 2.033791 -3.074915 7 -0.557354 1.058310 -1.051077 6 -0.696340 2.471084 -0.591014 6 -2.220459 2.665123 -0.431695 6 -2.817922 1.680509 -1.444376 6 -1.899715 0.465547 -1.321739 6 0.108743 2.822901 0.679043 8 -0.079455 2.093183 1.779961 8 0.899541 3.742759 0.660761 1 -2.776735 2.095686 -2.458707 1 -3.851196 1.405508 -1.219957 1 -2.539044 2.388865 0.577477 1 -2.499254 3.707126 -0.609319 1 -0.311443 3.142509 -1.363382 1 -1.853623 -0.132775 -2.233265 1 -2.233314 -0.180077 -0.510221 1 2.745259 -1.100903 -2.465214 1 1.725933 -2.531833 -2.639144 1 1.519431 -1.175741 -3.740124 1 1.077540 -2.707325 -0.451837 1 0.004662 -0.931261 1.819446 1 1.831271 0.418003 1.631788 1 4.097405 1.028447 2.349362 1 6.054193 -0.350014 1.663855 1 5.702154 -2.366523 0.247174 1 3.420725 -2.994666 -0.466899 1 -0.263400 -1.406237 -1.807105 1 2.711344 0.810366 -1.507428 1 1.835518 2.203317 -0.921012 1 0.969467 2.657904 -3.265030 1 2.735952 2.668692 -3.169780 1 1.892950 1.269681 -3.857000 1 -0.874895 1.477607 1.779677 8 -2.202344 0.644709 2.258111 1 -2.256525 -0.310141 1.983610 6 -2.479659 0.745148 3.654627 1 -3.534504 0.525120 3.858939 1 -1.852158 0.064394 4.244044 1 -2.265777 1.772901 3.958594 1 -3.722914 -1.793508 0.298931 8 -4.378257 -1.455124 -0.345030 6 -4.702192 -2.520733 -1.220656 1 -3.809765 -2.976211 -1.672402 1 -5.273784 -3.317313 -0.717245 1 -5.330846 -2.111800 -2.019241	6 0.646666 -1.359185 0.386857 6 -0.044349 -0.679029 -1.402445 6 0.609754 -1.529999 -2.470501 6 -0.010656 -2.603870 0.582947 7 -1.323606 -2.679135 0.930120 8 -1.899408 -3.782035 1.013738 6 0.185259 0.724688 -1.336968 6 1.491286 1.320800 -1.810911 6 1.375791 1.834371 -3.263658 7 -0.748888 1.543240 -0.818639 6 -0.511288 2.955178 -0.422645 6 -1.898781 3.442481 0.054054 6 -2.879025 2.566422 -0.734378 6 -2.194797 1.199346 -0.732080 6 0.572481 3.154753 0.654815 8 0.546087 2.361570 1.730092 8 1.407193 4.023185 0.526489 8 -1.996895 -1.585640 1.153029 1 -2.989366 2.937744 -1.760210 1 -3.872285 2.523999 -0.279901 1 -2.012460 3.252864 1.126739 1 -2.018557 4.514986 -0.117582 1 -0.178182 3.535725 -1.287391 1 -2.482216 0.558057 -1.565462 1 -2.398594 0.652033 0.189991 1 0.472824 -2.588084 -2.222315 1 0.133332 -1.367768 -3.445791 1 1.682034 -1.346814 -2.583087 1 0.437645 -3.566937 0.390777 1 0.232183 -0.540780 0.963344 1 2.265156 0.535532 1.398716 1 4.729655 0.587059 1.441302 1 6.040339 -1.271385 0.423926 1 4.845251 -3.185071 -0.625062 1 2.387418 -3.244740 -0.664333 1 -0.229431 1.730016 1.797480 1 -1.072790 -0.976325 -1.216274 1 2.269445 0.557519 -1.755094 1 1.819882 2.141944 -1.169591 1 0.617501 2.619260 -3.355961 1 2.334772 2.254552 -3.583178 1 1.109939 1.027667 -3.953595 8 -1.396529 0.707593 2.426677 1 -1.560748 -0.187057 2.028627 6 -1.342636 0.587533 3.848813 1 -2.312081 0.268799 4.250079 1 -0.571331 -0.124621 4.168666 1 -1.098027 1.573889 4.250674 1 -3.262850 -1.655245 -0.215046 8 -3.603204 -1.600636 -1.131758 6 -4.282953 -2.812963 -1.419090 1 -5.236196 -2.894383 -0.873293 1 -4.505773 -2.819758 -2.491325 1 -3.675051 -3.695041 -1.177575
s-si Et =-1342.0979429 (-1342.4796314) (-1342.5038768) NImag=1(-297.22 cm^{-1})	*s-re* Et = -1342.094229 (-1342.4763463) (-1342.5024566) NImag = 1(-318.1 cm^{-1})
6 1.078080 0.878369 1.250197 6 -0.323023 1.084823 1.191289 7 -1.185165 0.045443 1.286072 6 -0.811828 -1.259374 1.910062	6 -0.954197 0.126923 1.432169 6 0.468823 0.045402 1.470416 6 1.130164 -1.218388 1.979090 7 1.260257 1.077139 1.115065

6	-2.161442	-1.899512	2.316215
6	-3.133110	-0.717218	2.395331
6	-2.667730	0.178978	1.248799
6	0.058189	-2.222904	1.071276
8	-0.444861	-2.752756	-0.037732
8	1.166074	-2.531028	1.467770
1	-3.030387	-0.194037	3.354111
1	-4.177719	-1.020144	2.281781
1	-2.494804	-2.600881	1.546398
1	-2.060143	-2.453903	3.253127
1	-0.203952	-1.041258	2.792627
1	-2.972154	1.215306	1.357049
1	-3.042825	-0.177563	0.286004
1	-1.336659	-2.396169	-0.337853
6	1.699390	0.661961	-0.797382
6	0.846036	-0.195003	-1.521496
6	1.997402	1.977730	1.747777
1	1.854862	2.165850	2.820137
1	3.040433	1.683372	1.609095
1	1.851544	2.930754	1.227798
1	1.525317	1.718850	-0.976395
1	1.052652	-1.230142	-1.744775
6	3.124108	0.278103	-0.643307
6	3.524444	-1.027067	-0.304830
6	4.877650	-1.349291	-0.224624
6	5.854315	-0.383014	-0.480287
6	5.468995	0.917332	-0.809341
6	4.115811	1.245382	-0.882856
1	2.780875	-1.783684	-0.072841
1	5.169680	-2.360729	0.044328
1	6.908070	-0.641086	-0.417582
1	6.219862	1.677228	-1.008670
1	3.819752	2.257981	-1.145713
7	-0.349998	0.261307	-1.979592
8	-0.712100	1.450593	-1.710070
8	-1.095479	-0.501393	-2.679357
1	1.402244	-0.114774	1.545850
6	-0.885582	2.487415	1.054007
1	-1.759598	2.496716	0.400921
1	-0.139021	3.105339	0.550996
6	-1.229021	3.116124	2.420600
1	-1.610664	4.132257	2.274378
1	-1.999870	2.546157	2.951711
1	-0.352742	3.177248	3.074034
1	-2.270753	-1.319323	-1.772214
8	-2.702568	-1.976226	-1.161897
6	-3.191591	-3.055445	-1.961261
1	-2.395546	-3.495825	-2.574342
1	-3.582569	-3.818242	-1.282821
1	-4.002946	-2.715502	-2.615902
1	-2.516224	1.667757	-1.652968
8	-3.409867	1.903203	-1.320709
6	-4.024963	2.744023	-2.277597
1	-4.166648	2.242608	-3.247671
1	-5.012321	3.018935	-1.891558
1	-3.457984	3.672024	-2.453852

6	0.775385	2.447982	0.831327
6	2.068488	3.281361	0.650743
6	3.140596	2.479854	1.397628
6	2.742350	1.030934	1.115633
6	-0.158573	2.618622	-0.383034
8	0.225227	2.134472	-1.564060
8	-1.202237	3.227442	-0.263760
1	3.094667	2.682586	2.474209
1	4.153652	2.703428	1.052040
1	2.324671	3.344178	-0.412074
1	1.934587	4.299738	1.023711
1	0.192997	2.799574	1.688921
1	3.108014	0.338283	1.871406
1	3.097392	0.697281	0.135044
1	1.090709	1.630265	-1.585646
1	2.035922	-1.449179	1.414335
1	0.448419	-2.051425	1.785723
6	-1.556118	-0.688930	-0.430186
1	-1.006289	0.078398	-0.961504
6	-1.044881	-1.995714	-0.623661
1	-1.361179	1.116405	1.239361
7	0.265232	-2.163338	-0.942983
8	0.743376	-3.311991	-1.156923
8	1.016229	-1.125731	-0.969579
6	-3.024314	-0.472870	-0.401288
6	-3.534158	0.788896	-0.758412
6	-4.908060	1.022122	-0.780924
6	-5.801337	0.003903	-0.442627
6	-5.309531	-1.251215	-0.077116
6	-3.936456	-1.486635	-0.053880
1	-2.849747	1.593210	-1.014242
1	-5.279525	2.002944	-1.064771
1	-6.872481	0.186190	-0.461349
1	-5.996249	-2.050065	0.189805
1	-3.575180	-2.468335	0.236801
1	-1.597110	-2.916884	-0.519877
6	-1.774678	-0.655047	2.442846
1	-2.838798	-0.545259	2.220701
1	-1.545322	-1.725615	2.438141
1	-1.617577	-0.285807	3.464454
6	1.439777	-1.172978	3.490288
1	0.535873	-1.040629	4.092279
1	1.912712	-2.113194	3.791233
1	2.127962	-0.358530	3.744251
1	2.059112	-0.143635	-1.941207
8	2.429155	0.745546	-2.154597
6	2.560412	0.871327	-3.572375
1	2.947791	1.872585	-3.775931
1	3.267748	0.132061	-3.966804
1	1.595297	0.754831	-4.081783
1	2.482925	-3.142249	-0.416190
8	3.336023	-2.991684	0.044674
6	4.256565	-2.533007	-0.923025
1	5.216506	-2.375206	-0.418888
1	4.418249	-3.263614	-1.732019
1	3.952104	-1.578637	-1.382421

Table S44. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway ($\mathbf{L_2C_1}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =-1457.8274386 (-1458.2525397) (-1458.2755193) NImag=1(-254.4 cm^{-1})				*a-re* Et= - 1457.8272984 (-1458.2522985) (-1458.2770998) NImag= 1(-257.09 cm^{-1})		
6	-3.510352	1.697548	-1.379799	6	-1.863273	-3.417199	0.098910
6	-2.401321	1.310580	-0.605879	6	-1.491950	-2.181560	-0.462344
6	-2.575870	1.145707	0.782051	6	-2.340612	-1.601797	-1.423425
6	-3.818590	1.368227	1.369491	6	-3.518263	-2.238169	-1.812158
6	-4.911075	1.756671	0.588390	6	-3.876507	-3.461826	-1.243100
6	-4.753156	1.920892	-0.788617	6	-3.044616	-4.047989	-0.286115
6	-1.093870	1.116930	-1.262281	6	-0.228848	-1.491007	-0.113594
6	0.087963	1.452975	-0.571961	6	-0.586140	-0.383052	1.693792
7	1.277116	1.470300	-1.228521	6	-1.142809	-1.389467	2.673365
8	1.381465	1.135444	-2.429646	6	0.917720	-2.263939	0.173996
8	2.350121	1.809850	-0.565762	7	2.169684	-1.736012	0.172674
6	-0.979148	-0.950224	-1.929426	8	3.167022	-2.441107	0.424558
6	-2.117133	-1.045451	-2.920664	6	-1.351983	0.704885	1.214208
6	-0.957568	-1.698113	-0.734869	6	-2.862949	0.634736	1.176653
6	-2.243287	-2.231059	-0.139722	6	-3.480659	1.252917	2.450566
6	-2.551407	-3.658649	-0.643536	7	-0.747483	1.826624	0.768428
7	0.210127	-1.950599	-0.103225	6	-1.422601	2.901678	-0.002370
6	0.313881	-2.607811	1.230157	6	-0.321565	3.971078	-0.186104
6	1.825561	-2.875970	1.399031	6	0.597486	3.753734	1.021595
6	2.334153	-3.016968	-0.041295	6	0.630586	2.230741	1.154435
6	1.527467	-1.962743	-0.800283	6	-2.037837	2.452220	-1.343869
6	-0.308707	-1.805328	2.393915	8	-1.288144	1.723204	-2.174876
8	0.082742	-0.544847	2.581982	8	-3.173620	2.766912	-1.626920
8	-1.147447	-2.319941	3.104106	8	2.335277	-0.465020	-0.082442
1	2.120767	-4.019566	-0.431275	1	0.167270	4.207888	1.922219
1	3.405889	-2.825817	-0.134950	1	1.597217	4.170874	0.874609
1	2.314296	-2.021507	1.873333	1	0.233488	3.782351	-1.110612
1	1.995511	-3.762396	2.015774	1	-0.753640	4.973118	-0.244564
1	-0.235843	-3.553190	1.213572	1	-2.255896	3.309203	0.576775
1	1.373870	-2.217964	-1.850893	1	0.859725	1.877342	2.160237
1	2.027211	-0.994501	-0.758486	1	1.359726	1.793633	0.469164
1	-3.104895	-0.956878	-2.458925	1	-0.475916	-2.257057	2.726815
1	-2.030584	-0.249434	-3.668671	1	-1.190535	-0.966191	3.685545
1	-2.090569	-1.995395	-3.471229	1	-2.142181	-1.749086	2.413019
1	-1.072452	1.322160	-2.328660	1	0.897873	-3.311136	0.435686
1	0.133436	1.736046	0.468795	1	-0.046106	-0.589567	-0.684555
1	-1.743204	0.830149	1.404276	1	-2.067647	-0.652701	-1.878011
1	-3.933911	1.233990	2.441256	1	-4.154023	-1.775991	-2.562114
1	-5.878660	1.929762	1.051396	1	-4.795354	-3.957188	-1.544462
1	-5.595109	2.227967	-1.403039	1	-3.313730	-5.001810	0.159426
1	-3.388438	1.842026	-2.450157	1	-1.228421	-3.889838	0.841947
1	-0.017334	-0.740428	-2.387577	1	-0.325400	1.596654	-1.918084
1	-3.063339	-1.564270	-0.414968	1	0.469760	-0.183797	1.850198
1	-2.210239	-2.241354	0.950413	1	-3.168840	-0.409910	1.093135
1	-1.756793	-4.362019	-0.372224	1	-3.271251	1.144735	0.301749
1	-3.482711	-4.016433	-0.192898	1	-3.214938	2.310350	2.555331
1	-2.667077	-3.687432	-1.731419	1	-4.572162	1.184032	2.403018
1	0.917157	-0.261193	2.094405	1	-3.144771	0.732022	3.352407
8	2.400303	0.338969	1.762546	8	1.306349	1.299620	-1.899701
1	2.474041	0.873596	0.936493	1	1.638978	0.571002	-1.326205
6	2.932342	1.094474	2.861896	6	1.977927	1.224013	-3.168441

1 4.028896 1.085185 2.834770 1 2.567377 2.125735 2.842017 1 2.595859 0.604127 3.778911 1 3.715740 0.667624 -1.289357 8 4.252295 -0.128757 -1.473614 6 4.597770 -0.099997 -2.847457 1 3.717241 -0.000101 -3.497658 1 5.294983 0.719273 -3.086525 1 5.100066 -1.045161 -3.079740 1 1.924049 3.214908 0.632848 8 1.518387 3.673948 1.394891 6 1.256417 5.017664 1.031310 1 0.784400 5.501885 1.891496 1 2.174338 5.574355 0.786878 1 0.567982 5.094870 0.175496	1 3.033785 0.984028 -3.010998 1 1.517688 0.466442 -3.816449 1 1.883359 2.201471 -3.648143 1 2.863751 0.159063 1.654866 8 2.760578 0.334799 2.609901 6 3.770936 -0.388127 3.299748 1 4.772105 0.037347 3.131869 1 3.547670 -0.321146 4.369190 1 3.793366 -1.446740 3.008075 1 4.051927 -0.285149 -0.946657 8 4.721776 -0.053728 -1.619439 6 5.369761 -1.252077 -2.007517 1 4.684095 -1.974300 -2.478738 1 6.137947 -0.984087 -2.740119 1 5.858943 -1.756337 -1.161319
s-si Et =-1457.8221377 (-1458.2464624) (-1458.2759191) NImag=1(-280.8 cm^{-1})	*s-re* Et = -1457.8245758 (-1458.2494103) (-1458.2749937) NImag = 1(-298.78 cm^{-1})
6 1.991948 1.437022 -0.320064 6 0.736555 1.993379 -0.651134 7 -0.257503 2.069512 0.266458 6 -0.007867 2.045753 1.738895 6 -1.263981 2.702254 2.361535 6 -1.903234 3.487978 1.210016 6 -1.610493 2.612911 -0.008735 6 0.314504 0.668523 2.368296 8 -0.629924 -0.261681 2.418482 8 1.414621 0.473887 2.850090 1 -1.424001 4.467720 1.094810 1 -2.975394 3.647409 1.353367 1 -1.956796 1.935985 2.717562 1 -0.989866 3.326016 3.216446 1 0.885610 2.646732 1.929669 1 -1.625259 3.172292 -0.940800 1 -2.323594 1.786175 -0.081196 1 -1.496499 -0.053642 1.948725 6 1.769730 -0.658843 -0.886209 6 0.559641 -1.200877 -0.412092 6 3.249299 1.838472 -1.064105 1 3.543834 2.868349 -0.821805 1 4.079005 1.190270 -0.772228 1 3.149257 1.776244 -2.153044 1 1.755729 -0.383345 -1.936978 1 0.465878 -1.824357 0.463400 6 3.045552 -1.225933 -0.394354 6 3.261320 -1.536183 0.961060 6 4.458709 -2.122169 1.364785 6 5.458279 -2.410309 0.431248 6 5.258510 -2.099090 -0.914540 6 4.064965 -1.504851 -1.321877 1 2.508721 -1.290532 1.704493 1 4.612705 -2.351174 2.415550 1 6.388988 -2.869906 0.752589 1 6.029784 -2.318502 -1.647775 1 3.909249 -1.270880 -2.372143 7 -0.599018 -0.958651 -1.077817 8 -0.646188 -0.176842 -2.057333 8 -1.680120 -1.561635 -0.684855 1 2.163039 1.221264 0.729745 6 0.493461 2.549038 -2.042253 1 -0.514847 2.312934 -2.381810	6 0.481640 -1.040018 1.454469 6 -0.813367 -0.455756 1.478962 6 -1.020586 0.876380 2.169617 7 -1.892171 -1.068375 0.946113 6 -1.904787 -2.467138 0.459349 6 -3.392674 -2.744350 0.129318 6 -4.162172 -1.725010 0.976830 6 -3.258199 -0.492257 0.935781 6 -1.007558 -2.789236 -0.751984 8 -1.107039 -2.031496 -1.845195 8 -0.258791 -3.743961 -0.717532 1 -4.267687 -2.082014 2.008098 1 -5.161515 -1.516690 0.584855 1 -3.578782 -2.560458 -0.934069 1 -3.654340 -3.784274 0.339679 1 -1.547200 -3.122943 1.259700 1 -3.408089 0.166295 1.789393 1 -3.404566 0.087319 0.018309 1 -1.742651 -1.259784 -1.799026 1 -1.750967 1.490886 1.639265 1 -0.079427 1.430818 2.115778 6 1.471014 -0.211431 -0.293878 1 0.710399 -0.649194 -0.928423 6 1.462365 1.202050 -0.253016 1 0.533706 -2.065258 1.098494 7 0.321840 1.868996 -0.554667 8 0.285576 3.146809 -0.561722 8 -0.743078 1.208769 -0.785914 6 2.757655 -0.940858 -0.273430 6 2.808483 -2.247015 -0.795838 6 4.008439 -2.954168 -0.829594 6 5.180442 -2.375171 -0.338645 6 5.143443 -1.082460 0.189583 6 3.945714 -0.371869 0.225197 1 1.901599 -2.712402 -1.172310 1 4.025966 -3.959494 -1.241250 1 6.116389 -2.926742 -0.365718 1 6.050504 -0.623949 0.573993 1 3.940253 0.631613 0.639448 1 2.291713 1.837251 0.025063 6 1.470840 -0.745952 2.566157 1 2.439209 -1.193989 2.330430 1 1.632678 0.325641 2.721300

1	1.156686	2.031775	-2.738069
6	0.754858	4.066695	-2.120166
1	0.590420	4.422057	-3.142933
1	0.088151	4.631856	-1.458926
1	1.783950	4.312720	-1.840220
1	-2.665831	-0.607321	0.407745
8	-2.949321	-0.055386	1.178346
6	-3.972839	-0.772456	1.896723
1	-3.751187	-1.843706	1.912762
1	-3.997634	-0.374413	2.914820
1	-4.948395	-0.604499	1.425500
1	-2.183739	-3.133886	0.324026
8	-2.837181	-3.690806	0.784849
6	-3.698763	-4.228739	-0.212301
1	-4.099441	-3.454903	-0.880827
1	-3.193121	-4.990903	-0.826323
1	-4.531263	-4.713637	0.307456
1	-3.012598	-1.485853	-2.055549
8	-3.891095	-1.457673	-2.482766
6	-4.334372	-0.119281	-2.429801
1	-3.668911	0.568043	-2.976980
1	-5.323415	-0.079292	-2.898394
1	-4.434584	0.258219	-1.397208

1	1.140674	-1.173807	3.521840
6	-1.422411	0.729016	3.652253
1	-0.657813	0.205557	4.233876
1	-1.561498	1.722077	4.091092
1	-2.362438	0.177675	3.769308
1	-2.011421	0.781343	-1.915922
8	-2.651853	0.112780	-2.249752
6	-2.752942	0.226415	-3.671379
1	-3.447717	-0.545837	-4.009955
1	-3.148906	1.207955	-3.957886
1	-1.783671	0.070321	-4.161747
1	1.908105	3.914706	0.054326
8	2.855104	4.037425	0.272980
6	3.478980	4.593529	-0.870599
1	4.549658	4.670679	-0.656012
1	3.353867	3.968204	-1.768638
1	3.105358	5.603047	-1.102687
1	-1.479877	3.477788	0.110050
8	-2.366911	3.564345	0.517361
6	-3.308335	3.609798	-0.534799
1	-3.145432	4.464648	-1.210691
1	-3.312953	2.690690	-1.142792
1	-4.300800	3.723628	-0.085226

Table S45. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway (**L_1C_2** model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =- 1457.829161 (-1458.253949) (-1458.2784126) NImag=1(-283.7 cm^{-1})			
6	-4.032977	-1.539453	1.260146
6	-2.870753	-1.189831	0.551528
6	-2.896497	-1.269030	-0.853201
6	-4.046762	-1.688756	-1.518550
6	-5.193839	-2.036295	-0.800142
6	-5.183278	-1.960189	0.593011
6	-1.654447	-0.789076	1.307437
6	-0.392417	-1.233857	0.834700
7	0.707102	-1.119897	1.619362
8	0.658631	-0.581405	2.755671
8	1.840378	-1.529584	1.154295
6	-1.648272	1.230256	1.558989
6	-2.971633	1.564096	2.218591
6	-1.303736	1.748856	0.283623
6	-2.373117	2.100445	-0.727716
6	-2.665184	3.616457	-0.737760
7	-0.008975	1.880698	-0.061726
6	0.480900	2.097677	-1.456085
6	1.871948	2.756903	-1.298310
6	1.972155	3.131020	0.192503
6	1.111095	2.077503	0.891166
6	0.413194	0.752598	-2.226997
8	1.367226	-0.151170	-2.061915
8	-0.555557	0.519651	-2.928235
1	1.561189	4.131110	0.373194
1	3.001107	3.109977	0.560564

a-si(II) Et = -1457.8315884 (-1458.2569535) (-1458.2782318) NImag= 1(-283.5 cm^{-1})			
6	3.930658	1.600326	-1.213142
6	2.856291	0.697700	-1.127638
6	3.132458	-0.677860	-1.234551
6	4.437583	-1.127754	-1.422568
6	5.494884	-0.217984	-1.507753
6	5.236785	1.149160	-1.402362
6	1.478857	1.229533	-0.964092
6	0.405648	0.574086	-1.615575
7	-0.798043	1.188675	-1.739246
8	-0.965668	2.373763	-1.299753
8	-1.757311	0.554724	-2.285276
6	1.057524	1.403764	1.046170
6	2.107660	2.349564	1.593599
6	0.964147	0.062848	1.497550
6	2.181651	-0.654552	2.041730
6	2.215079	-0.622774	3.585061
7	-0.197429	-0.612745	1.404388
6	-0.329777	-2.089074	1.583189
6	-1.816321	-2.319622	1.951674
6	-2.371325	-0.915374	2.251569
6	-1.547558	-0.000628	1.343499
6	0.180809	-2.809981	0.312497
8	-0.558310	-2.771951	-0.790828
8	1.274252	-3.343645	0.315731
1	-2.207075	-0.645138	3.301093
1	-3.441315	-0.833848	2.043222

1 2.675338 2.067127 -1.563427 1 1.956272 3.627465 -1.954492 1 -0.207256 2.762128 -1.977724 1 0.721548 2.406139 1.854377 1 1.669066 1.152215 1.046104 1 -3.835454 1.410138 1.565930 1 -3.113957 0.934012 3.103212 1 -2.991347 2.605904 2.564234 1 -1.762763 -0.868330 2.387694 1 -0.205870 -1.613213 -0.157966 1 -2.023691 -0.992070 -1.437731 1 -4.044612 -1.743135 -2.603671 1 -6.087841 -2.364682 -1.323275 1 -6.067245 -2.233621 1.162870 1 -4.026399 -1.498876 2.346424 1 -0.826218 1.162139 2.267005 1 -3.286261 1.559816 -0.473536 1 -2.088584 1.761670 -1.726045 1 -1.778760 4.200435 -1.010067 1 -3.450394 3.838235 -1.467826 1 -3.005562 3.966323 0.242385 1 2.192412 0.089598 -1.529540 8 3.756295 0.170390 -1.051102 1 3.891948 0.142123 -0.067274 6 4.455628 -0.940227 -1.634442 1 5.532331 -0.858191 -1.438378 1 4.075985 -1.897085 -1.257365 1 4.293530 -0.890494 -2.714273 8 3.871308 0.108644 1.648872 1 3.134180 -0.549796 1.735177 6 4.937620 -0.251123 2.518057 1 5.740448 0.478699 2.378420 1 4.618959 -0.222570 3.568410 1 5.331815 -1.252979 2.297561 1 2.274147 -3.006958 0.071233 8 2.644387 -3.663485 -0.551909 6 1.696732 -3.843297 -1.589630 1 1.464413 -2.907073 -2.118911 1 2.129325 -4.545708 -2.309720 1 0.751806 -4.278482 -1.223933	1 -2.365200 -2.768649 1.121220 1 -1.896548 -2.998182 2.805226 1 0.325584 -2.416918 2.389246 1 -1.522358 1.035594 1.678385 1 -1.935168 -0.020452 0.320135 1 3.120065 1.936457 1.571807 1 2.117867 3.272426 1.003430 1 1.883691 2.638148 2.628936 1 1.415444 2.313964 -1.012894 1 0.427176 -0.439843 -1.984680 1 2.333974 -1.409539 -1.158178 1 4.626377 -2.194777 -1.500322 1 6.511090 -0.573080 -1.656017 1 6.049742 1.866824 -1.473503 1 3.734805 2.667551 -1.148370 1 0.112364 1.900861 0.846723 1 3.077356 -0.167258 1.653273 1 2.220322 -1.685824 1.684648 1 1.342766 -1.121543 4.022117 1 3.111782 -1.135890 3.947549 1 2.235056 0.404014 3.964339 1 -1.491017 -2.401045 -0.720508 8 -3.121240 -2.242650 -1.015066 1 -3.554122 -1.354064 -0.940550 6 -3.322646 -2.693131 -2.358728 1 -4.390806 -2.833400 -2.563896 1 -2.902983 -1.983392 -3.080763 1 -2.811044 -3.653393 -2.460440 8 -4.162782 0.228662 -1.186706 1 -3.383203 0.653021 -1.617452 6 -4.993717 1.202270 -0.561650 1 -5.754479 0.663212 0.010990 1 -4.424091 1.850330 0.115511 1 -5.505235 1.823951 -1.310115 1 -2.054146 2.804039 0.066218 8 -2.430931 3.038835 0.942647 6 -2.446546 4.452427 1.046617 1 -2.832506 4.704939 2.039279 1 -1.441882 4.890138 0.946252 1 -3.100906 4.919683 0.295523
a-re Et =-1457.8242756 (-1458.2489097) (-1458.277329) NImag=1(-284.69 cm^{-1})	*a-re(II)* Et = -1457.8282014 (-1458.253226) (-1458.2794377) NImag = 1(-291.6 cm^{-1})
6 3.574238 -2.223027 -0.326484 6 2.586256 -1.407183 0.251817 6 2.881375 -0.762395 1.465988 6 4.122481 -0.925562 2.080290 6 5.095993 -1.733676 1.490405 6 4.816632 -2.382000 0.285262 6 1.229485 -1.233844 -0.338569 6 1.310697 0.190940 -1.739078 6 2.493464 -0.119431 -2.634099 6 0.616763 -2.342561 -0.993618 7 -0.733659 -2.397407 -1.120959 8 -1.302480 -3.344774 -1.701345 6 1.246919 1.411459 -1.001238 6 2.501451 2.061063 -0.462552 6 2.966026 3.214967 -1.378770 7 0.060196 1.983981 -0.741645 6 -0.182710 2.985048 0.335274 6 -1.629417 3.480101 0.093560	6 -3.190709 -1.859992 0.335083 6 -1.908309 -1.394068 0.675358 6 -1.188755 -2.080370 1.669319 6 -1.730764 -3.199667 2.300055 6 -3.001320 -3.657310 1.946029 6 -3.728804 -2.982419 0.962996 6 -1.303056 -0.184041 0.054537 6 -0.480170 -0.685479 -1.707843 6 -1.562959 -1.347211 -2.534699 6 -2.158165 0.915295 -0.240831 7 -1.619355 2.145272 -0.446474 8 -2.345632 3.165418 -0.612731 6 0.701906 -1.386727 -1.338061 6 0.684238 -2.883055 -1.124452 6 1.170414 -3.634601 -2.384034 7 1.851204 -0.716234 -1.129327 6 3.037956 -1.266388 -0.421269 6 4.124157 -0.177904 -0.593120

6 -1.969676 3.023552 -1.335020 6 -1.181845 1.722229 -1.502118 6 0.062645 2.354042 1.727206 8 -0.697736 1.327349 2.097719 8 0.972720 2.752530 2.426059 8 -1.435105 -1.425918 -0.603481 1 -1.631396 3.760903 -2.072210 1 -3.042946 2.870251 -1.475572 1 -2.321743 3.013622 0.797450 1 -1.692731 4.563753 0.220912 1 0.535940 3.801450 0.244982 1 -0.929121 1.512162 -2.544001 1 -1.702791 0.848499 -1.096827 1 2.422466 -1.155143 -2.982962 1 2.495241 0.521498 -3.525104 1 3.457824 -0.002809 -2.132649 1 1.138978 -3.168018 -1.453452 1 0.541156 -0.720258 0.324890 1 2.126446 -0.139957 1.940768 1 4.323912 -0.425031 3.023272 1 6.063193 -1.862726 1.968464 1 5.565365 -3.019617 -0.177111 1 3.371887 -2.744481 -1.257108 1 -1.540297 1.156056 1.573400 1 0.366224 -0.087914 -2.194112 1 3.289029 1.308440 -0.400570 1 2.352584 2.436290 0.552401 1 2.210897 4.005450 -1.449601 1 3.881128 3.659624 -0.974892 1 3.178848 2.862667 -2.393120 8 -3.164164 0.908380 1.275326 1 -3.492324 0.363256 0.515839 6 -3.735250 0.365427 2.479152 1 -4.821372 0.521439 2.489892 1 -3.505797 -0.701337 2.569345 1 -3.291463 0.909022 3.316918 8 -3.982793 -0.757460 -0.729990 1 -3.123946 -1.229305 -0.874048 6 -4.630592 -0.539379 -1.972951 1 -4.038437 0.096013 -2.649809 1 -4.842643 -1.487008 -2.484923 1 -5.579845 -0.035602 -1.769005 1 -2.093590 -2.183551 1.064876 8 -2.493331 -2.680540 1.804241 6 -3.383435 -3.626792 1.229181 1 -3.775412 -4.240500 2.046577 1 -4.229750 -3.144351 0.717786 1 -2.877156 -4.283205 0.507473	6 3.673187 0.610977 -1.830093 6 2.148323 0.618369 -1.706326 6 2.743972 -1.619204 1.053047 8 2.225238 -0.670902 1.838276 8 2.946680 -2.740347 1.467379 8 -0.338435 2.263661 -0.466479 1 3.973404 0.097571 -2.751214 1 4.086659 1.622890 -1.854876 1 4.138836 0.488583 0.272968 1 5.113917 -0.629070 -0.699327 1 3.347949 -2.202414 -0.891966 1 1.642658 0.714838 -2.669600 1 1.778217 1.411795 -1.052018 1 -2.450540 -0.705560 -2.547441 1 -1.242133 -1.475757 -3.576473 1 -1.863389 -2.326850 -2.152782 1 -3.235221 0.870983 -0.325171 1 -0.364999 0.117532 0.511996 1 -0.204541 -1.722294 1.961454 1 -1.159371 -3.710109 3.070426 1 -3.424764 -4.529757 2.436294 1 -4.722449 -3.325886 0.687979 1 -3.776081 -1.340794 -0.417569 1 2.290783 0.276906 1.511188 1 -0.307819 0.349352 -1.986614 1 -0.334925 -3.192778 -0.887170 1 1.300075 -3.175870 -0.271409 1 2.200893 -3.367767 -2.643161 1 1.138943 -4.713779 -2.203251 1 0.539029 -3.416668 -3.251032 8 2.703459 1.900247 1.554365 1 2.160912 2.655192 1.188671 6 3.043984 2.234068 2.900868 1 3.750323 3.073676 2.931305 1 2.155581 2.497098 3.488178 1 3.516357 1.356818 3.349941 8 1.228126 3.985376 0.746019 1 0.454624 3.536664 0.314326 6 1.742410 4.953249 -0.159058 1 2.022692 4.512920 -1.127218 1 1.012130 5.752375 -0.340073 1 2.634286 5.394538 0.295497 1 -4.153481 2.721088 -0.825017 8 -5.026564 2.276098 -0.782763 6 -5.677680 2.749637 0.381332 1 -5.919512 3.822705 0.320851 1 -6.618023 2.197515 0.481467 1 -5.086059 2.585688 1.295899
s-si Et =-1457.8291968 (-1458.252012) (-1458.278529) NImag=1(-299.6 cm^{-1})	*s-re* Et = -1457.8315624 (-1458.2554245) (-1458.2791921) NImag = 1(-311.9 cm^{-1})
6 -1.700399 -1.605968 -0.051071 6 -0.415782 -2.085824 -0.412824 7 0.636336 -2.018255 0.432293 6 0.503666 -1.721111 1.886399 6 1.849006 -2.170697 2.502446 6 2.417132 -3.171909 1.490471 6 1.974652 -2.598097 0.143531 6 0.147488 -0.259542 2.246871 8 1.007631 0.702369 1.952275 8 -0.896962 -0.025380 2.827032	6 0.994489 -0.293269 1.361628 6 -0.377888 0.077404 1.472534 6 -0.753106 1.530151 1.690280 7 -1.384309 -0.821272 1.442572 6 -1.196773 -2.288454 1.379736 6 -2.629993 -2.861289 1.485765 6 -3.408456 -1.770465 2.227620 6 -2.811436 -0.477343 1.669699 6 -0.481142 -2.823569 0.126361 8 -0.901705 -2.417262 -1.068228

1	1.978703	-4.166388	1.638102
1	3.504512	-3.264797	1.556008
1	2.527935	-1.320218	2.593553
1	1.696409	-2.593983	3.498728
1	-0.326553	-2.317429	2.276756
1	1.904418	-3.363405	-0.626601
1	2.654843	-1.820575	-0.212500
1	1.847551	0.437903	1.455683
6	-1.870325	0.367513	-0.873211
6	-0.781183	1.199788	-0.549809
6	-2.935792	-2.277589	-0.625504
1	-3.042467	-3.305012	-0.253530
1	-3.833085	-1.732558	-0.325156
1	-2.931164	-2.325367	-1.720269
1	-1.854149	-0.032351	-1.883329
1	-0.795929	1.943752	0.231494
6	-3.206529	0.778904	-0.373222
6	-3.409794	1.192687	0.955777
6	-4.668306	1.621711	1.372672
6	-5.741747	1.647734	0.478118
6	-5.552112	1.233006	-0.840940
6	-4.296101	0.795904	-1.260304
1	-2.589641	1.155222	1.667714
1	-4.811042	1.934666	2.403345
1	-6.720395	1.984994	0.808876
1	-6.380367	1.249015	-1.544307
1	-4.150687	0.479020	-2.290231
7	0.403253	1.089673	-1.205109
8	0.566393	0.162949	-2.073008
8	1.355544	1.888663	-0.957729
1	-1.819788	-1.301567	0.984079
6	-0.199386	-2.723129	-1.773198
1	0.788898	-2.461395	-2.154520
1	-0.906532	-2.272601	-2.473258
6	-0.390963	-4.253762	-1.774117
1	-0.210548	-4.648896	-2.779523
1	0.299413	-4.758613	-1.089285
1	-1.407020	-4.533449	-1.481428
8	3.354581	0.314244	0.840852
8	3.304647	-0.148745	-1.866003
1	3.336524	0.282293	-0.151446
1	2.348124	0.023757	-2.050231
6	4.095024	1.472041	1.256670
1	4.163737	1.435970	2.347168
1	5.110894	1.443674	0.842449
1	3.594647	2.401314	0.962830
6	4.063438	0.728064	-2.693466
1	5.113453	0.637139	-2.400181
1	3.975159	0.450927	-3.753252
1	3.744264	1.770609	-2.571101
1	1.562707	3.352856	0.195987
8	1.972509	4.155133	0.574088
6	2.172525	5.058593	-0.494919
1	2.796784	4.636923	-1.298756
1	1.225611	5.397532	-0.945775
1	2.685868	5.937359	-0.090637

8	0.425735	-3.623638	0.241937
1	-3.229656	-1.833722	3.307667
1	-4.486809	-1.829658	2.056684
1	-3.051731	-2.995093	0.485211
1	-2.629655	-3.829587	1.992278
1	-0.579037	-2.607008	2.226209
1	-2.897484	0.352169	2.370254
1	-3.282690	-0.178387	0.729541
1	-1.700154	-1.809141	-1.075215
1	-1.696784	1.747489	1.184377
1	0.000171	2.168049	1.220213
6	1.600704	-0.075285	-0.662471
1	0.847370	-0.772485	-1.007140
6	1.387151	1.259643	-1.082314
1	1.190989	-1.361925	1.406827
7	0.133086	1.675123	-1.380498
8	-0.108064	2.885289	-1.684314
8	-0.826607	0.828006	-1.321390
6	2.978661	-0.625094	-0.642022
6	3.158072	-2.015917	-0.755686
6	4.436906	-2.569376	-0.786408
6	5.562573	-1.748271	-0.699409
6	5.399862	-0.366285	-0.578186
6	4.122878	0.190013	-0.547939
1	2.290366	-2.666713	-0.816015
1	4.551565	-3.645863	-0.879932
1	6.559437	-2.180439	-0.724679
1	6.269469	0.281808	-0.508914
1	4.019786	1.266357	-0.451506
1	2.129924	2.041502	-1.094008
6	2.034271	0.539081	2.095664
1	3.036197	0.176379	1.853799
1	1.990961	1.600283	1.829757
1	1.917838	0.457281	3.184209
6	-0.846411	1.927984	3.179352
1	0.115265	1.815027	3.686316
1	-1.141078	2.979624	3.254944
1	-1.583537	1.332334	3.729683
1	-3.377604	-0.277490	-1.495582
8	-3.236304	-1.258888	-1.548059
8	-3.373925	1.439547	-1.238804
1	-2.384758	1.477337	-1.336142
6	-3.411564	-1.662975	-2.905570
1	-3.142205	-2.719991	-2.971434
1	-4.456608	-1.544293	-3.221136
1	-2.763579	-1.093870	-3.584647
6	-3.968105	2.411656	-2.090469
1	-5.052095	2.357661	-1.952719
1	-3.630181	3.423099	-1.831688
1	-3.738906	2.230719	-3.150247
1	0.834230	3.830467	-0.418519
8	1.353880	4.075172	0.378684
6	1.170474	5.456811	0.623045
1	1.743430	5.712044	1.520422
1	1.538861	6.082975	-0.204705
1	0.116161	5.719407	0.805453

Table S46. The B3LYP/6-31G* Optimized Geometries (in Cartesian coordinates), Total Electronic Energies (in hartree/particle), of Transition States of Different Stereochemical Modes of Addition of Enamine Derived from Proline and Pentanone (**2**) to Nitrostyrene Using Solvent Assisted Pathway ($\mathbf{L_2C_1}$ model). The Values in the Parenthesis Implies Single-point Energies Evaluated at the B3LYP/6-311G**//B3LYP/6-31G* and PCM-B3LYP/6-311G**//B3LYP/6-31G* Level of Theory.

a-si Et =- 1573.5638247 (-1574.0313014) (-1574.04 99657) NImag=1(-252.7 cm^{-1})				*a-re* Et = -1573.5594382 (-1574.0261836) (-1574.0488607) NImag= 1(-265.4 cm^{-1})			
6	4.043361	0.768634	-0.814243	6	3.991140	0.326254	-0.792261
6	2.835614	0.059286	-0.950362	6	2.796808	-0.406504	-0.920137
6	2.895434	-1.295347	-1.328874	6	2.876284	-1.745084	-1.347085
6	4.122116	-1.911462	-1.564513	6	4.106987	-2.332217	-1.635620
6	5.313517	-1.193170	-1.428453	6	5.284459	-1.594262	-1.497827
6	5.270042	0.149968	-1.052114	6	5.220957	-0.264065	-1.076389
6	1.564239	0.782681	-0.723344	6	1.462342	0.183490	-0.669300
6	0.417106	0.430657	-1.469310	6	1.044424	-0.037494	1.378472
7	-0.681731	1.221718	-1.509662	6	2.321763	0.319028	2.105501
8	-0.721836	2.350002	-0.892270	6	1.248570	1.575995	-0.845052
8	-1.702493	0.825750	-2.150222	7	-0.014702	2.035869	-0.980233
6	1.079670	0.672072	1.363956	8	-0.259014	3.298167	-0.972993
6	2.245565	1.351427	2.049005	6	0.486957	-1.342260	1.442903
6	0.792585	-0.699622	1.532600	6	1.369875	-2.554284	1.648505
6	1.885215	-1.672251	1.922806	6	1.392710	-2.976090	3.133907
6	1.880409	-1.952361	3.440836	7	-0.838572	-1.526164	1.309932
7	-0.453349	-1.177226	1.322748	6	-1.481474	-2.822951	0.961138
6	-0.793958	-2.624220	1.210179	6	-2.996413	-2.583693	1.178830
6	-2.304750	-2.710195	1.543614	6	-3.088122	-1.243567	1.931809
6	-2.668314	-1.321014	2.099766	6	-1.857711	-0.466951	1.460113
6	-1.699366	-0.378155	1.383305	6	-1.076584	-3.250440	-0.471971
6	-0.373214	-3.147647	-0.183572	8	-1.488504	-2.515131	-1.501629
8	-1.071022	-2.769605	-1.251440	8	-0.338164	-4.201776	-0.638752
8	0.623798	-3.834522	-0.301025	8	-0.990777	1.220403	-1.080052
1	-2.498244	-1.276083	3.181539	1	-3.036426	-1.401148	3.015339
1	-3.710952	-1.053579	1.908691	1	-4.015023	-0.708302	1.710586
1	-2.896132	-2.921135	0.650138	1	-3.518669	-2.500665	0.224283
1	-2.491686	-3.514516	2.260221	1	-3.440208	-3.413781	1.734692
1	-0.203642	-3.195087	1.926186	1	-1.104897	-3.607228	1.619668
1	-1.535703	0.560875	1.911005	1	-1.520348	0.284351	2.174755
1	-2.059531	-0.144388	0.375760	1	-2.012418	0.047469	0.504858
1	3.197503	0.830562	1.908293	1	2.678011	1.297732	1.767160
1	2.350682	2.368155	1.658000	1	2.148378	0.397679	3.187131
1	2.070242	1.437888	3.130042	1	3.129770	-0.399685	1.946094
1	1.697058	1.843275	-0.535957	1	2.001713	2.347080	-0.758920
1	0.291332	-0.503755	-1.995342	1	0.634984	-0.426394	-1.015772
1	1.989234	-1.885096	-1.425161	1	1.964448	-2.326108	-1.464935
1	4.144769	-2.958816	-1.852047	1	4.143616	-3.364162	-1.973409
1	6.267897	-1.678372	-1.614332	1	6.244720	-2.050005	-1.723411
1	6.189881	0.719174	-0.948128	1	6.131848	0.319786	-0.976088
1	4.011398	1.818228	-0.534517	1	3.962567	1.366180	-0.482007
1	0.224782	1.328807	1.236251	1	-2.211274	-1.834971	-1.339826
1	2.848293	-1.244644	1.639840	1	0.316782	0.767324	1.392021
1	1.793943	-2.607649	1.366308	1	2.383758	-2.311158	1.325367
1	0.936378	-2.401279	3.769512	1	1.043272	-3.393869	1.031589
1	2.688293	-2.646864	3.693479	1	0.392788	-3.245589	3.491415
1	2.029936	-1.033797	4.017327	1	2.042853	-3.847624	3.261503
1	-1.942317	-2.292747	-1.096536	1	1.771421	-2.173129	3.774476
8	-3.536540	-1.849406	-1.327164	8	-3.641953	-0.999419	-1.567162
1	-3.823697	-0.927781	-1.104492	1	-3.646667	-0.001961	-1.519386
6	-3.799148	-2.045752	-2.720158	6	-4.170581	-1.368486	-2.841433
1	-4.873776	-1.972015	-2.926215	1	-5.243453	-1.144680	-2.900454

1 -3.259916 -1.313614 -3.332242 1 -3.454992 -3.050396 -2.977739 8 -4.161305 0.758746 -1.086909 1 -3.318851 1.110120 -1.456476 6 -4.816539 1.741574 -0.289357 1 -5.670781 1.254331 0.189788 1 -4.155033 2.149825 0.484661 1 -5.195491 2.565069 -0.910811 1 -1.720206 2.663329 0.617091 8 -2.017072 2.805727 1.539679 6 -1.702397 4.148522 1.891151 1 -1.861233 4.250092 2.969213 1 -0.657912 4.396775 1.661372 1 -2.356426 4.871950 1.380380 1 0.605803 3.534734 -0.409311 8 1.338267 4.060417 -0.026256 6 1.650804 5.113869 -0.924937 1 0.807068 5.805720 -1.063921 1 2.484499 5.675023 -0.492493 1 1.960761 4.744388 -1.914006	1 -3.654416 -0.850118 -3.658810 1 -4.026209 -2.445369 -2.960956 8 -3.555517 1.668977 -1.670052 1 -2.579236 1.775867 -1.566490 6 -4.203408 2.558583 -0.762400 1 -3.686577 2.599869 0.204192 1 -4.253037 3.573281 -1.180547 1 -5.225933 2.198195 -0.612793 1 -1.239386 3.196298 0.672753 1 1.318077 4.326442 -0.946171 8 -1.548114 2.935749 1.565671 6 -1.475428 4.076726 2.404118 1 -2.130651 4.892002 2.061584 1 -1.806743 3.772048 3.401804 1 -0.451621 4.471803 2.488769 8 2.225592 4.638193 -0.742917 6 2.187435 5.229667 0.540245 1 3.207927 5.534210 0.794692 1 1.549119 6.126964 0.573499 1 1.835749 4.533749 1.320558
s-si Et =- 1573.5618622 (-1574.0290521) (-1574.0503161) NImag=1(-245.86 cm^{-1})	*s-re* Et = -1573.5625697 (-1574.0285686) (-1574.0498774) NImag = 1(-285.7 cm^{-1})
6 4.383969 0.658468 -1.047950 6 3.336248 -0.255493 -0.836156 6 3.628232 -1.631707 -0.816618 6 4.933558 -2.073457 -1.019499 6 5.965472 -1.157793 -1.245878 6 5.687122 0.209958 -1.258999 6 1.963535 0.274364 -0.682229 6 0.912358 -0.371356 -1.359253 7 -0.292146 0.222142 -1.557584 8 -1.189393 -0.407702 -2.202330 8 -0.528650 1.397213 -1.107236 6 1.708856 0.088877 1.504742 6 2.875218 0.889620 2.042650 6 0.377644 0.523913 1.670179 6 0.080886 1.988469 1.921699 6 0.001192 2.301935 3.429997 7 -0.649273 -0.362678 1.634910 6 -0.480097 -1.811672 1.944837 6 -1.867092 -2.272998 2.466644 6 -2.635082 -0.973666 2.755995 6 -2.082743 -0.003619 1.712479 6 0.056117 -2.678242 0.781463 8 1.171745 -3.159301 0.849899 8 -0.716460 -2.905345 -0.275676 8 -2.514193 2.996528 0.061850 6 -3.818073 3.251339 -0.436527 8 -3.307647 -2.395424 -0.523894 6 -3.638829 -3.460192 -1.415384 8 -3.768056 0.001644 -1.715451 6 -4.531707 0.123515 -2.911572 1 -2.412485 -0.602714 3.763600 1 -3.717467 -1.101566 2.669258 1 -2.397965 -2.844644 1.702989 1 -1.752486 -2.912151 3.346239 1 0.282559 -1.894972 2.722817 1 -2.221733 1.043424 1.965699 1 -2.548441 -0.161934 0.733213 1 -1.637525 -2.511509 -0.269766	6 1.490329 -0.699977 1.305427 6 0.118524 -0.902990 1.611648 6 -0.634336 0.126163 2.433706 7 -0.560294 -2.012939 1.244759 6 0.038770 -3.170299 0.542720 6 -1.122154 -4.184194 0.425519 6 -2.019824 -3.847239 1.619340 6 -1.944788 -2.320844 1.690186 6 0.654602 -2.878818 -0.836530 8 -0.066193 -2.208966 -1.728138 8 1.769809 -3.286910 -1.097781 1 -1.620930 -4.290636 2.539573 1 -3.046998 -4.199412 1.490358 1 -1.669602 -4.016365 -0.507671 1 -0.749312 -5.211442 0.424919 1 0.857630 -3.574550 1.148173 1 -2.109927 -1.948370 2.700943 1 -2.670573 -1.835639 1.032463 1 -1.009553 -1.964231 -1.467304 1 -1.681102 0.152556 2.122171 1 -0.224161 1.117889 2.221719 6 1.629453 0.479147 -0.553248 1 1.065947 -0.276357 -1.085312 6 0.953704 1.705524 -0.381495 1 2.013223 -1.553996 0.882640 7 -0.396114 1.748058 -0.443786 8 -1.013492 2.867489 -0.310759 8 -1.061109 0.677910 -0.617019 6 3.085905 0.469767 -0.801623 6 3.653959 -0.624924 -1.480684 6 5.015694 -0.649717 -1.774846 6 5.838926 0.411766 -1.394022 6 5.290879 1.500982 -0.711941 6 3.930165 1.530474 -0.417040 1 3.025120 -1.461425 -1.771663 1 5.432915 -1.502059 -2.303909 1 6.900684 0.391275 -1.624894 1 5.924269 2.330627 -0.409706

1	2.916945	0.842090	3.139451	1	3.525023	2.383877	0.117987
1	3.816222	0.479305	1.668419	1	1.417736	2.653400	-0.159629
1	2.838360	1.946581	1.760626	6	2.343846	0.141046	2.237186
1	1.906275	1.353559	-0.607763	1	3.340069	0.276558	1.809145
1	0.971562	-1.373826	-1.753933	1	1.920413	1.134343	2.418956
1	2.841242	-2.351813	-0.611045	1	2.479945	-0.350602	3.209713
1	5.147036	-3.138647	-0.995811	6	-0.545199	-0.110316	3.957073
1	6.981410	-1.509432	-1.404915	1	0.486345	-0.053965	4.313643
1	6.483377	0.928876	-1.432238	1	-1.121132	0.661269	4.478241
1	4.163410	1.722910	-1.063728	1	-0.946326	-1.085614	4.254876
1	1.875421	-0.983722	1.497096	1	-3.094493	-1.129434	-1.035553
1	-0.842112	2.302340	1.435769	8	-2.648001	-1.738634	-1.673883
1	0.863827	2.588555	1.454190	8	-3.580650	0.106657	0.119701
1	-0.187527	3.370819	3.575054	1	-2.769055	0.625335	-0.090625
1	-0.812991	1.751258	3.915790	6	-2.809409	-1.162397	-2.978759
1	0.930599	2.049855	3.950967	1	-2.072585	-1.630543	-3.636401
1	-3.574149	-1.539674	-0.951964	1	-3.814211	-1.370478	-3.369225
1	-2.804387	0.074321	-1.946409	1	-2.644460	-0.079315	-2.956744
1	-3.269950	-4.388113	-0.971517	6	-4.738376	0.936091	-0.023408
1	-4.725994	-3.540235	-1.545719	1	-5.605578	0.275401	-0.114042
1	-3.165303	-3.330896	-2.397215	1	-4.875883	1.568142	0.864896
1	-5.580421	-0.050589	-2.654872	1	-4.660096	1.571366	-0.911008
1	-4.441539	1.130215	-3.340349	1	-0.258687	3.520336	1.275842
1	-4.227725	-0.609175	-3.671862	8	0.290703	3.579161	2.085380
1	-2.062635	2.370738	-0.536736	6	-0.211874	4.629340	2.891282
1	-3.797964	3.790270	-1.397141	1	0.405627	4.674549	3.793862
1	-4.395921	2.327160	-0.567889	1	-0.154111	5.608134	2.390049
1	-4.327242	3.886680	0.294982	1	-1.256264	4.464424	3.199947
1	0.630185	2.879842	-1.102463	1	-2.382528	2.706025	-1.601196
8	1.258726	3.583503	-0.849869	8	-3.044807	2.581884	-2.312819
6	0.553625	4.817119	-0.888943	6	-2.993694	3.717340	-3.155139
1	0.392452	5.166887	-1.921251	1	-3.253513	4.648718	-2.626949
1	-0.422330	4.746495	-0.389876	1	-2.004344	3.853151	-3.619320
1	1.164309	5.563956	-0.371380	1	-3.725386	3.566954	-3.955331