SUPPLEMENTARY MATERIAL

Table 11. Total energies, zero point vibrational energies, enthalpies and Gibbs free energies (kcal/mol) of the optimized structures for the polar nucleophilic reaction of p-X-benzylamines (X=H, OCH_3, CF_3, NO_2, $N(CH_3)_2$, Cl, OH, Br, I , F) with flavin (t=10.9^o), calculated from PM3 method.

Table 11A

p-H	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	19.821	90.169	109.991	114.272	114.836	90.266
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	0.859	187.738	188.597	200.764	201.329	155.249
TS1	47.975	185.961	233.936	244.987	245.551	204.991
Adduct	33.551	189.983	223.534	234.838	235.403	194.181
TS2	38.230	187.990	226.221	237.769	238.333	195.683
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	194.546	77.225	271.772	271.777	271.780	271.750
E_b (E_{RC}-E_{E+S})	-5.112	3.437	-1.676	-1.931	-2.524	11.383
ΔE_1^* (E_{TS1} –E_{E+S})	42.004	1.660	43.663	42.291	41.698	61.125
ΔE_2^*(E_{TS2}-E_{adduct})	4.679	-1.993	2.687	2.931	2.930	1.502

Table 11B

p-OCH_3	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	-18.290	110.193	91.940	97.773	98.337	70.112
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-35.178	207.219	172.041	186.247	186.812	134.948
TS1	10.328	205.937	216.265	228.938	229.502	184.890
Adduct	-3.936	209.896	205.960	218.913	219.477	174.061
TS2	-0.466	208.147	207.681	220.768	221.332	174.941
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	152.257	97.323	249.581	249.586	249.588	249.557
E_b (E_{RC}-E_{E+S})	-3.038	2.894	-0.181	0.050	-0.542	11.236
ΔE_1^* (E_{TS1} –E_{E+S})	42.468	1.612	44.043	42.742	42.148	61.178
ΔE_2^*(E_{TS2}-E_{adduct})	3.470	-1.749	1.721	1.855	1.855	0.880

Table 11C

p-CF_3	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	-138.312	93.391	-44.920	-38.399	-37.806	-70.375
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-154.466	191.537	37.071	51.883	52.447	-2.295
TS1	-110.824	190.468	79.644	92.798	93.363	46.530
Adduct	-126.974	194.662	67.688	81.025	81.590	33.981
TS2	-117.594	192.100	74.507	88.253	88.817	39.325
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	44.759	81.722	126.480	126.486	126.488	126.456
E_b (E_{RC}-E_{E+S})	-2.304	4.014	1.709	1.858	1.236	14.480
ΔE_1^* ($E_{TS1} - E_{E+S}$)	41.338	2.945	44.282	42.773	42.152	63.305
ΔE_2^* (E_{TS2}-E_{adduct})	9.380	-2.562	6.819	7.228	7.227	5.344

Table 11D

p-NO_2	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	11.337	91.271	102.608	109.102	109.695	76.326
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-6.207	189.750	183.543	197.631	198.195	146.721
TS1	38.192	188.394	226.586	239.158	239.722	194.827
Adduct	20.621	192.707	213.328	226.042	226.607	181.320
TS2	33.210	190.109	223.318	236.411	236.975	190.030
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	198.307	79.467	277.774	277.780	277.782	277.751
E_b (E_{RC}-E_{E+S})	-3.694	4.347	0.653	0.105	-0.517	16.795
ΔE_1^* ($E_{TS1} - E_{E+S}$)	40.705	2.991	43.696	41.632	41.010	64.901
ΔE_2^* (E_{TS2}-E_{adduct})	12.589	-2.598	9.990	10.369	10.368	8.710

Table 11E

p-$N(CH_3)_2$	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	16.152	135.468	151.620	158.252	158.816	128.732
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-4.165	233.375	229.211	243.625	244.189	193.459
TS1	44.786	231.156	275.942	289.421	289.986	243.565
Adduct	30.469	235.123	265.592	279.342	279.906	232.705
TS2	33.504	233.366	266.869	280.783	281.347	233.152
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	181.188	127.714	308.903	315.665	316.229	286.217
E_b (E_{RC}-E_{E+S})	-6.467	-18.815	-2.691	-3.051	-3.644	11.127
ΔE_1^* (E_{TS1} –E_{E+S})	42.484	-21.034	44.040	42.745	42.153	61.223
ΔE_2^*(E_{TS2}-E_{adduct})	3.035	-1.757	1.277	1.441	1.441	0.447

Table 11F

p-Cl	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	13.144	84.435	97.579	102.538	103.103	76.623
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-3.623	181.418	177.795	191.750	191.687	141.939
TS1	41.247	180.197	221.144	233.214	233.778	191.224
Adduct	26.345	184.270	210.615	222.614	223.178	180.014
TS2	32.093	182.168	214.260	226.529	227.094	182.352
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	188.641	71.497	260.138	260.144	260.146	260.116
E_b (E_{RC}-E_{E+S})	-2.917	2.851	-0.066	0.788	-0.433	11.716
ΔE_1^* (E_{TS1} –E_{E+S})	41.953	1.630	43.283	42.252	41.658	61.001
ΔE_2^*(E_{TS2}-E_{adduct})	5.748	-2.102	3.645	3.915	3.916	2.338

Table 11G

p-OH	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	-25.362	93.621	68.259	73.216	73.780	47.931
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-42.313	190.631	148.318	161.820	162.195	112.914
TS1	3.285	189.321	192.605	204.399	204.963	162.718
Adduct	-11.018	193.264	182.245	194.324	194.888	151.883
TS2	-7.399	191.561	184.162	196.365	196.929	152.781
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	146.002	80.893	226.895	226.901	226.903	226.873
E_b (E_{RC}-E_{E+S})	-3.101	2.878	0.223	0.180	-0.602	11.383
ΔE_1^* (E_{TS1} –E_{E+S})	42.496	1.568	44.064	42.759	42.166	61.187
ΔE_2^*(E_{TS2}-E_{adduct})	3.619	-1.703	1.917	2.041	2.041	0.898

Table 11H

p-Br	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	27.592	84.199	111.791	116.903	117.467	90.127
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	10.800	181.712	191.972	205.463	206.027	155.262
TS1	55.621	179.954	235.575	247.509	248.074	204.702
Adduct	40.525	184.046	224.571	236.724	237.289	193.318
TS2	46.953	181.882	228.835	241.277	241.842	196.216
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	204.953	77.285	282.239	287.000	287.564	261.976
E_b (E_{RC}-E_{E+S})	-2.942	-3.381	-0.101	0.136	-0.457	11.535
ΔE_1^* (E_{TS1} –E_{E+S})	41.879	1.623	43.502	42.182	41.590	60.975
ΔE_2^*(E_{TS2}-E_{adduct})	6.428	-2.164	4.264	4.553	4.553	2.898

Table 11I

p-I	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	41.254	84.499	125.753	130.819	131.383	103.837
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	24.500	181.465	205.966	219.410	219.975	169.139
TS1	69.334	180.236	249.570	261.470	262.035	218.418
Adduct	54.395	184.311	238.705	250.828	251.392	207.201
TS2	60.334	182.228	242.562	254.953	255.518	209.715
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	216.632	77.558	294.190	298.908	299.472	273.650
E_b (E_{RC}-E_{E+S})	-2.904	2.834	-0.069	0.167	-0.425	11.702
ΔE_1^* ($E_{TS1} - E_{E+S}$)	41.930	1.605	43.535	45.227	41.635	60.981
ΔE_2^* (E_{TS2}-E_{adduct})	5.939	-2.083	3.857	4.125	4.126	2.514

Table 11J

p-F	E	ZPE	E+ZPE	E^T	H^T	G^T
Amine(S)	-23.705	85.963	62.258	66.947	67.512	41.917
FAD(E)	-13.850	94.132	80.282	88.424	89.017	53.600
Reactant complex	-40.555	182.959	142.404	155.450	156.015	107.306
TS1	4.589	181.723	186.312	197.806	198.370	156.623
Adduct	-126.996	185.791	175.459	187.183	187.747	145.394
TS2	-117.594	183.679	179.250	191.254	191.818	147.855
FAD^-	-90.640	101.643	11.003	19.027	19.619	-15.017
Immonium(P)	153.860	79.022	232.882	237.234	237.799	213.834
E_b (E_{RC}-E_{E+S})	-3.000	2.864	-0.136	0.079	-0.514	11.789
ΔE_1^* ($E_{TS1} - E_{E+S}$)	42.144	1.628	43.772	42.435	41.841	61.106
ΔE_2^* (E_{TS2}-E_{adduct})	9.402	-2.112	-3.791	-4.071	4.071	2.461