Supplementary Material

Rearrangement and cyclisation reactions on the 1-arylpyrrol-2-iminyl – 2-aryliminopyrrol-1-yl radical energy surface

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Experimental

1-(*p*-Tolyl)pyrrole 6.
A mixture of *p*-toluidine (4.53 g, 42.3 mmol), 2,5-dimethoxytetrahydrofuran (6.01 g, 45 mmol) and glacial acetic acid (20 cm^3) was heated under reflux for 2 h. The volatiles were removed under reduced pressure, water (100 cm^3) was added and the reaction mixture extracted with dichloromethane (3 × 80 cm^3). The combined organic extracts were washed with water (80 cm^3), dried ($MgSO_4$) and concentrated to give crude **6** (5.71 g, 86%), mp 77-78 °C (lit.,[1] 81-82 °C) δ_H 7.30-7.19 (4H, m), 7.06 (2H, t, ^3J 2.2), 6.33 (2H, t, ^3J 2.2) and 2.37 (3H, s); δ_C 138.32 (quat), 135.22 (quat), 129.89, 120.39, 119.24, 109.90 and 20.72; *m/z* 157 (M^+, 100%), 115 (39) and 91 (30).

1-(*p*-Tolyl)pyrrole-2-carbaldehyde 7
A solution of 1-*p*-tolylpyrrole **6** (4.023 g, 25.6 mmol) in DMF (40 cm^3) was added to a solution of phosphoryl chloride (5.19 g, 33.2 mmol) in DMF (85 cm^3) and stirred for 1 h. A further portion of phosphoryl chloride (5.19 g, 33.2 mmol) in DMF (85 cm^3) was added and stirring continued for another hour. The reaction mixture was poured onto crushed ice, hydrolysed with dilute aqueous sodium hydroxide (2 M, 200 cm^3) and acidified to pH 6-7 with dilute hydrochloric acid (2 M, 20 cm^3). The mixture was then extracted with ether (3 × 250 cm^3) and the combined organic extracts were washed with water (200 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give crude aldehyde as an orange oil. Distillation removed remaining traces of DMF and the aldehyde crystallised as an orange solid. TLC showed that formylation had occurred at both the 2- and 3-positions and so the mixture was recrystallised from light petroleum (bp 40-60 °C) to yield only the 2-isomer **7** as white crystals (3.30 g, 70%), mp 54-56 °C (lit.,[2] 55 °C); δ_H 9.55 (1H, s), 7.25-7.23 (4H, m), 7.15-7.13 (2H, m), 7.05-7.03 (2H, m), 6.38 (1H, m) and 2.41 (3H, s) (spectrum consistent with literature data[3]); δ_C 178.99, 138.11 (quat), 136.08 (quat), 132.46 (quat), 130.90, 129.55, 125.71, 121.54, 110.56 and 21.00; *m/z* 185 (M^+, 100 %), 157 (55), 128 (36) and 92 (83).

***N,N*-(Dimethylamino)pyrrole 9**
2,5-Dimethoxytetrahydrofuran (11 g, 83 mmol) was added to a stirred solution of *N,N*-dimethylhydrazine (5 g, 83mmol) in acetic acid (15 cm^3) and heated at reflux for 2.5 h. The mixture was then quenched with sodium bicarbonate solution and extracted with dichloromethane (100 cm^3); the organic layer was washed with water (2 × 50 cm^3) and then brine (50 cm^3). The organic layer was then dried ($MgSO_4$) filtered and concentrated under vacuum. The residue was purified by distillation, bp 100-105 °C (15 Torr) [lit.,[4] 138-140 °C (767 Torr)], to give **9** as a pale yellow oil (4.9 g, 54%); δ_H 6.90 (2H, d, ^3J 2.2), 6.08 (2H, ^3J 2.2) and 2.87 (6H, s); δ_C 116.20 (2CH), 105.67 (2CH) and 48.27 ($2CH_3$).

FVP reactions
General conditions are given in the main paper.

FVP of *N,N*-(dimethylamino)pyrrole 9 – temperature profile
Due to its low boiling point (138-140 °C at atmospheric pressure) *N,N*-(dimethylamino)pyrrole **9** was frozen in the inlet system using an acetone/dry ice bath which remained in place around the inlet as the vacuum was applied. The cooling bath was then slowly removed allowing the *N,N*-(dimethylamino)pyrrole **9** to volatilise into the furnace tube in a controlled manner.

***T*$_f$ 550 °C**, (24.8 mg, T_i RT, *P* 2.3-2.4 × 10^{-2} Torr, *t* 16 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 97%)
***T*$_f$ 600 °C**, (21.5 mg, T_i RT, *P* 2.4-3.0 × 10^{-2} Torr, *t* 17 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 92%) and pyrrole **10** (*ca* 8%)

***T*f 650 °C**, (21.3 mg, *T*i RT, *P* 2.6-3.5 × 10^{-2} Torr, *t* 16 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 63%) and pyrrole **10** (*ca* 37%)
***T*f 700 °C**, (21.6 mg, *T*i RT, *P* 2.6-3.2 × 10^{-2} Torr, *t* 15 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 21%) and pyrrole **10** (*ca* 79%)
***T*f 750 °C**, (24.3 mg, *T*i RT, *P* 2.8-5.0 × 10^{-2} Torr, *t* 17 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 18%) and pyrrole **10** (*ca* 82%)
***T*f 800 °C**, (24.6 mg, *T*i RT, *P* 2.5-6.0 × 10^{-2} Torr, *t* 16 min) gave *N,N*-(dimethylamino)pyrrole **9** (*ca* 3%) and pyrrole **10** (*ca* 97%)
***T*f 850 °C**, (25.5 mg, *T*i RT, *P* 3.2-7.3 × 10^{-2} Torr, *t* 19 min) gave pyrrole **10** (*ca* 99%).

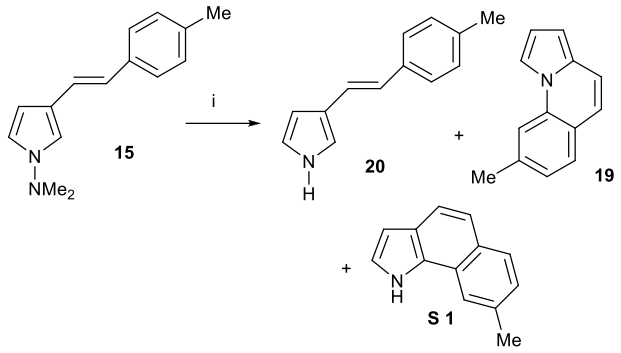
_N_-(Dimethylamino)-3-(2-_p_-tolylvinyl)pyrrole 15

Synthesised as described in the main paper for **13**, from *N*-(dimethylamino)pyrrole-3-carboxaldehyde **14** in 60% yield, *N*-(dimethylamino)-3-(2-*p*-tolylvinyl)pyrrole **15** had mp 70 °C; (Found: M^+ 226.1469. $C_{15}H_{18}N_2$ requires *M* 226.1470); δ_H 7.34 (2H, d, ^3J 8.1), 7.13 (2H, d, ^3J 8.1), 6.97 (1H, m), 6.94 (1H, d, ^3J 16.5), 6.84 (1H, t, ^3J 2.8), 6.75 (1H, d, ^3J 16.5), 6.31 (1H, t, ^3J 2.8), 2.85 (6H, s) and 2.65 (3H, s); δ_C 135.98 (quat), 135.45 (quat), 129.10 (2CH), 125.51 (2CH), 124.17 (CH), 121.24 (CH), 120.52 (quat), 117.80 (CH), 115.62 (CH), 103.12 (CH), 48.20 ($2CH_3$) and 21.04 (CH_3); *m/z* 226 (M^+, 100%) and 167 (66).

FVP of _N,N_-dimethylamino-3-(2-_p_-tolylvinyl)pyrrole 15

FVP of *N,N*-dimethylamino-3-(2-*p*-tolylvinyl)pyrrole **15** [116 mg (0.51 mmol) T_f 750 °C, T_i 140 °C, *P* 2.1-10 × 10^{-2} Torr, t 1 h) gave a mixture of products: 8-methylpyrrolo[1,2-*a*]quinoline **19** (4.6 mg, 5%); δ_H 7.71 (1H, s), 7.54 (1H, d, ^3J 7.9), 7.34 (1H, m), 7.27 (1H, d, ^3J 9.3), 7.15 (1H, d, ^3J 7.9), 6.97 (1H, d, ^3J 9.3), 6.80 (1H, t, ^3J 3.2), 6.52 (1H, m) and 2.56 (3H, s): 3-(2-*p*-tolylvinyl)pyrrole **20** (10.3 mg, 11%) (Found: M^+ 183.1047. $C_{13}H_{13}N$ requires *M* 183.1048); δ_H 8.16 (1H, br. s), 7.37 (2H, d, ^3J 8.1), 7.15 (2H, d, ^3J 8.1), 7.04 (1H, d, ^3J 16.2), 6.90 (1H, dd, ^3J 4.2), 6.81 (1H, d, ^3J 16.2), 6.80 (1H, dd, ^4J 2.6), 6.51 (1H, dd, ^3J 4.2, ^4J 2.6) and 2.36 (3H, s); δ_C 136.04 (quat), 135.40 (quat), 129.12 (2CH), 125.56 (2CH), 124.60 (CH), 123.10 (quat), 121.20 (CH), 119.01 (CH), 117.12 (CH), 105.45 (CH) and 20.82 (CH_3) (spectra consistent with literature data[5]); *m/z* 183 (M^+, 100%): a fraction which was tentatively identified as impure 8-methylbenzo[*g*]indole **S1** (trace) (Found: M^+ 181.0891. $C_{13}H_{11}N$ requires *M* 181.0892); δ_H 9.01 (1H, br. s), 7.85-7.80 (2H, m), 7.67 (1H, d, ^3J 8.5), 7.49 (1H, d, ^3J 8.5), 7.36-7.13 (2H, m), 6.12 (1H, m) and 2.39 (3H, s); *m/z* 181 (M^+, 100%) and 84 (92).

Formation of products from FVP of *N,N*-dimethylamino-3-(2-*p*-tolylvinyl)pyrrole 15



Scheme 9 (from main paper) *Reagents and conditions:* (i) FVP, 750 °C

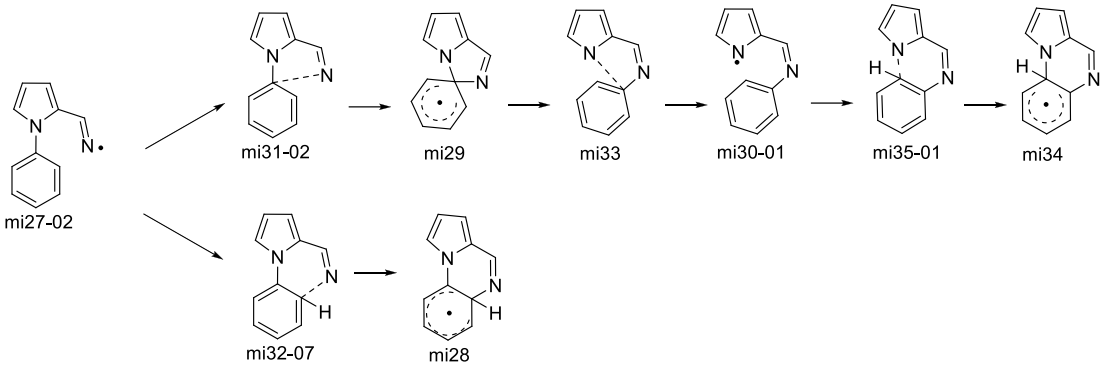
Three products were isolated, in low yield, from FVP of **15**. The product of hydrogen-capture by the pyrrol-1-yl radical, **20**, retains the carbon skeleton of the precursor. Similarly, the formation of 8-methylbenzo[*g*]indole **S1**, tentatively identified in trace amounts from an impure fraction, is consistent with delocalisation of the pyrrol-1-yl radical to the 2-position, followed by cyclisation. Clearly this is not a favourable process for the initial radical. Finally the formation of 8-methylpyrrolo[1,2-*a*]quinoline **19** requires rearrangement of the vinyl group from the 3-position to the 2-position of the pyrrole, followed by cyclisation. Such 1,5-shifts are well-known in the thermal chemistry of pyrroles,[6] and although the rearrangement is not normally quantitative at temperatures as low as 750 °C in our apparatus, they may well account for the formation of such a minor product (5%).

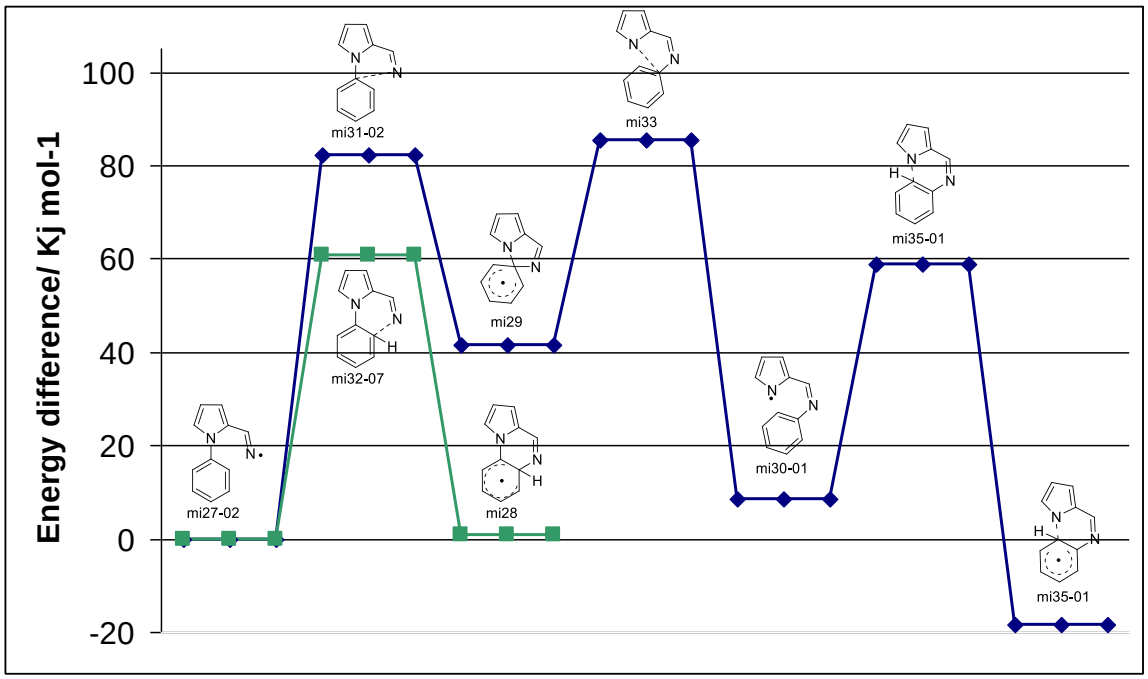
References

1. E. H. Huntress, T. E. Leslie and W. M. Hearon, *J. Am. Chem. Soc*., 1956, **78**, 419-423.
2. C. F. Candy, R. A. Jones and P. H. Wright, *J. Chem. Soc. (C)*, 1970, 2563-2567.
3. B. R. D'Arcy, K. G. Lewis and C. E. Mulquiney, *Aust. J. Chem*., 1985, **38**, 953-965.
4. G. R. Martinez, P. R. Grieco and G. V. Srinivasan, *J. Org. Chem*., 1981, **46**, 3760- 3761.
5. K. Ogawa, Eur. Pat. Appl., EP 575923, 1993.
6. J. M. Patterson, *Synthesis* 1976, 281-304

DFT calculations of energy surfaces[1]

1. The iminyl **1** (X = N) – pyrrol-1-yl **3** (X = N) energy surface





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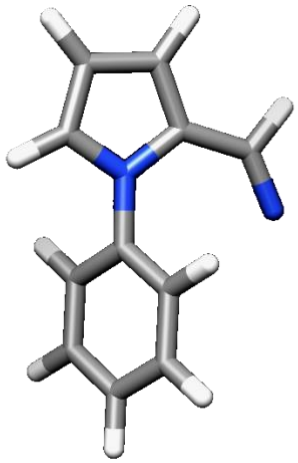

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C	0.597369	-0.304639	0.073369
C	1.348210	-1.109017	-0.792774
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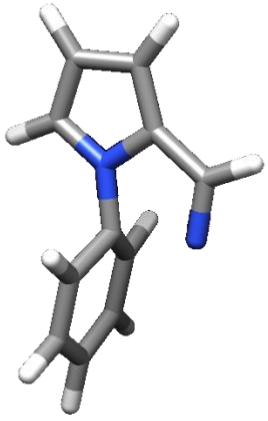
mi31-02



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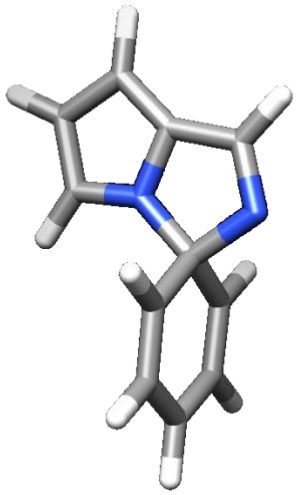
Calculated Negative Frequency = -586.6398 cm^{-1}

mi29



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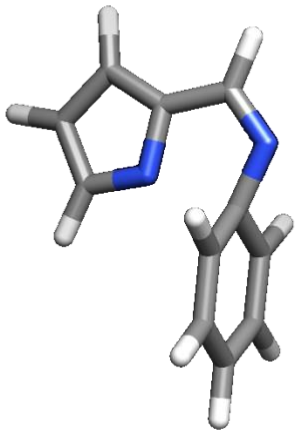
mi33



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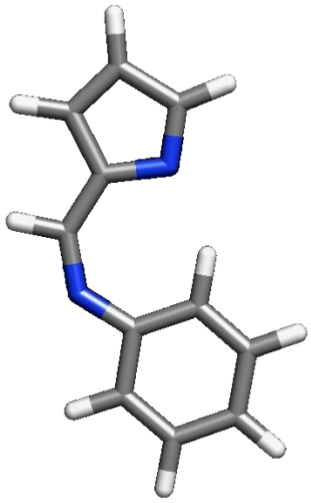
Calculated Negative Frequency = -289.7431 cm^{-1}

mi30-01



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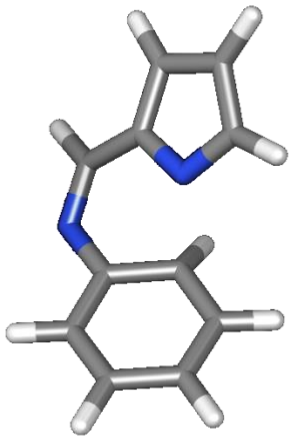
mi35-01



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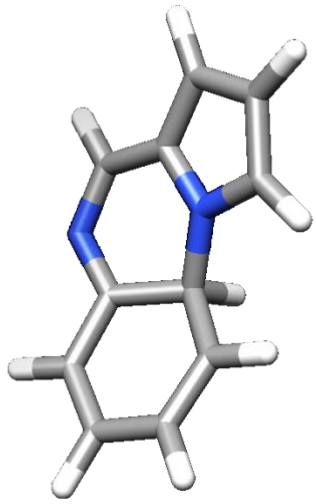
mi34



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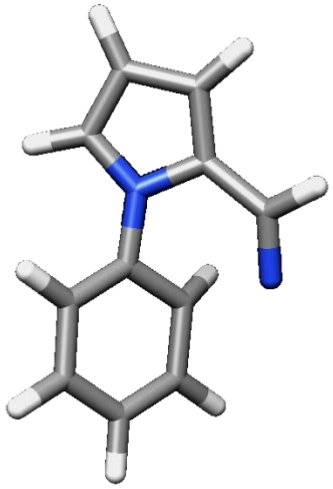
H	-1.611708	2.860859	0.057317

mi32-07



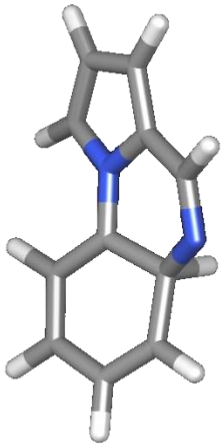
Energy = -534.0267681 Ha

Cartesian Coordinates

C	3.010825	0.314594	-0.151556
C	1.665107	0.662901	-0.136472
N	0.937338	-0.476961	0.189577
C	1.804066	-1.529139	0.365073
C	3.096322	-1.065081	0.175089
C	0.968373	1.889474	-0.498931
C	-0.476313	-0.463210	0.165578
C	-1.219186	-1.455559	-0.464243
C	-2.612362	-1.329120	-0.549678
C	-1.086635	0.728305	0.684168
C	-2.517572	0.810063	0.594333
C	-3.249829	-0.184564	-0.026951
N	-0.264156	2.177273	-0.334730
H	3.834159	0.988376	-0.377957
H	1.433188	-2.512206	0.641286
H	4.001527	-1.659733	0.269723
H	1.594658	2.657410	-0.993015
H	-0.710705	-2.313844	-0.907738
H	-3.198156	-2.109394	-1.038696
H	-0.611415	1.189758	1.554919
H	-3.015888	1.680201	1.025339
H	-4.336421	-0.094730	-0.096253

Calculated Negative Frequency = -552.9239 cm^{-1}

mi28

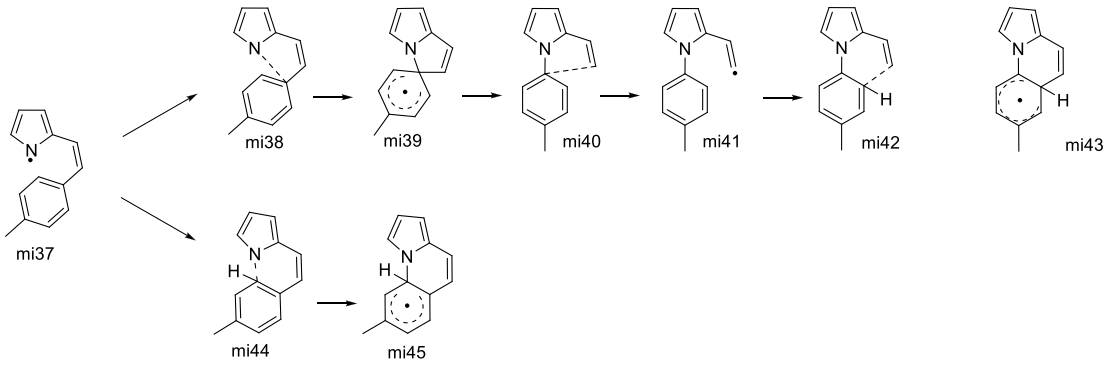


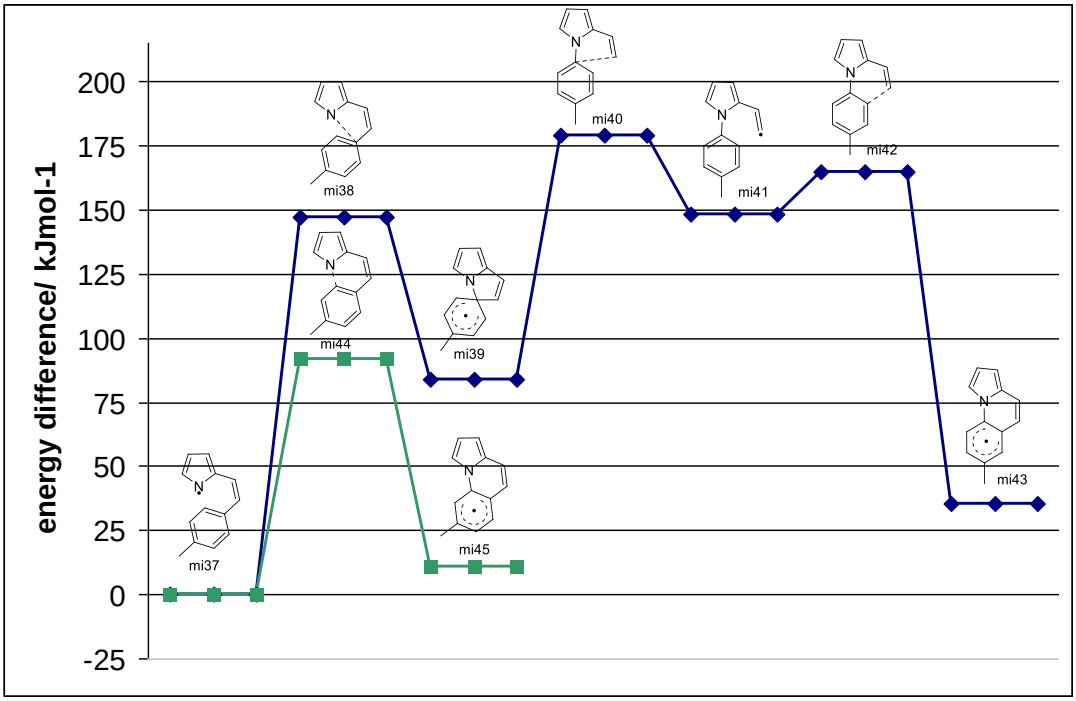
Energy = -534.0494495 Ha

Cartesian Coordinates

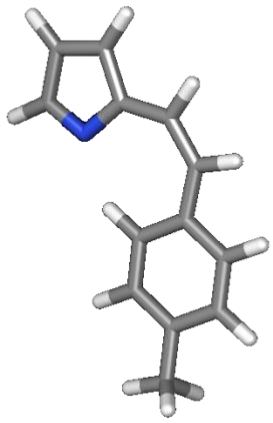
C	3.020963	0.362746	-0.142791
C	1.672684	0.691471	-0.086292
N	0.954726	-0.486981	0.121935
C	1.837200	-1.542163	0.186362
C	3.121116	-1.043190	0.038725
C	0.931069	1.918256	-0.283726
C	-0.445266	-0.469230	0.111625
C	-1.035956	0.880460	0.458853
C	-2.506874	0.945942	0.158304
C	-1.226247	-1.570765	-0.160910
C	-2.630057	-1.450749	-0.234761
C	-3.243292	-0.170297	-0.115863
N	-0.330831	2.062405	-0.085748
H	3.836868	1.065713	-0.293471
H	1.489274	-2.555673	0.359619
H	4.033291	-1.634051	0.069674
H	1.494710	2.791567	-0.640190
H	-0.922010	0.997640	1.569331
H	-2.958869	1.938150	0.211346
H	-0.757214	-2.535102	-0.367519
H	-3.235091	-2.330023	-0.459799
H	-4.320263	-0.081062	-0.279463

2. The vinyl **1** (X = CH) – pyrrol-1-yl **3** (X = CH) energy surface





mi37

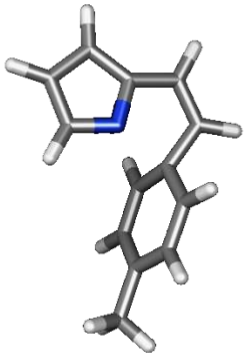


Energy = -557.3385771 Ha

Cartesian Coordinates

C	3.971925	0.453164	0.000349
C	2.513530	0.363405	-0.000010
N	2.119050	-0.967791	0.000268
C	3.240614	-1.668171	0.000006
C	4.434319	-0.832510	0.000170
C	-0.874761	0.895467	-0.000093
C	-2.127978	1.565715	-0.000115
C	-3.326192	0.866772	-0.000122
C	-0.893752	-0.520237	-0.000082
C	-2.104251	-1.208481	-0.000099
C	-3.340306	-0.541193	-0.000113
C	1.684203	1.503833	-0.000062
C	0.308740	1.728285	-0.000088
C	-4.644952	-1.295808	-0.000064
H	4.548418	1.377060	0.000541
H	3.218393	-2.760870	0.000027
H	5.466363	-1.179431	0.000227
H	-2.143885	2.659030	-0.000129
H	-4.271764	1.416031	-0.000144
H	0.056050	-1.057638	-0.000108
H	-2.090528	-2.301890	-0.000115
H	2.264816	2.432748	-0.000029
H	0.059853	2.795568	-0.000103
H	-4.484037	-2.383592	-0.000701
H	-5.252256	-1.041471	-0.885503
H	-5.251600	-1.042445	0.886112

mi38



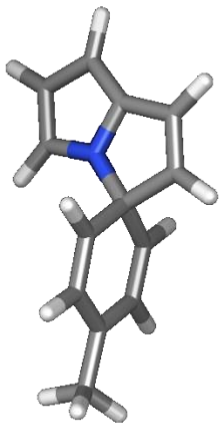
Energy = -557.2825262 Ha

Cartesian Coordinates

C	3.355660	-0.691058	0.167686
C	2.358208	0.269286	-0.010235
N	1.211791	-0.355979	-0.485523
C	1.412671	-1.691288	-0.484250
C	2.750135	-1.941006	-0.123497
C	2.148341	1.665632	0.261209
C	-1.107408	1.044235	-1.109915
C	-2.323955	0.403611	-1.062679
C	-2.755075	-0.296052	0.095921
C	-0.170018	0.964277	-0.004819
C	-0.674159	0.331494	1.198996
C	-1.906681	-0.294323	1.223361
C	0.851069	2.045510	0.173105
C	-4.083030	-1.002329	0.110907
H	4.376083	-0.515469	0.502615
H	0.660142	-2.387545	-0.850423
H	3.244734	-2.911485	-0.161698
H	2.968534	2.354963	0.468754
H	-0.804076	1.596708	-2.001281
H	-2.990244	0.452555	-1.928843
H	-0.035682	0.342043	2.083756
H	-2.239695	-0.785482	2.141583
H	0.511490	3.082106	0.213335
H	-4.880886	-0.368658	-0.311123
H	-4.377085	-1.294678	1.129677
H	-4.050402	-1.921136	-0.502419

Calculated Negative Frequency = -448.8027 cm^{-1}

mi39

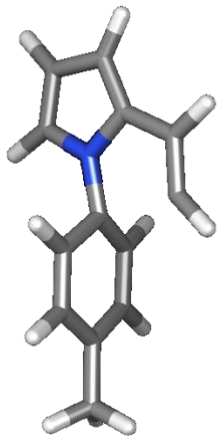


Energy =-557.3066668 Ha

Cartesian Coordinates

C	3.483010	-0.416578	-0.000064
C	2.395625	0.445722	0.000009
N	1.242886	-0.316255	0.000128
C	1.559039	-1.649554	0.000144
C	2.946163	-1.740386	0.000033
C	1.988872	1.839889	-0.000104
C	-0.806854	0.274047	-1.252264
C	-2.137314	-0.036665	-1.220485
C	-2.858721	-0.193746	0.000007
C	0.004730	0.505734	0.000020
C	-0.806928	0.274282	1.252296
C	-2.137401	-0.036437	1.220495
C	0.639858	1.912277	-0.000100
C	-4.311177	-0.577248	-0.000058
H	4.533608	-0.136768	-0.000160
H	0.794025	-2.420687	0.000254
H	3.514229	-2.668352	0.000037
H	2.676267	2.685474	-0.000181
H	-0.273605	0.382753	-2.199038
H	-2.670036	-0.179117	-2.165726
H	-0.273741	0.383166	2.199085
H	-2.670179	-0.178709	2.165731
H	0.018371	2.805689	-0.000154
H	-4.438479	-1.677074	-0.001102
H	-4.832213	-0.194465	-0.891901
H	-4.831863	-0.196137	0.892689

mi40



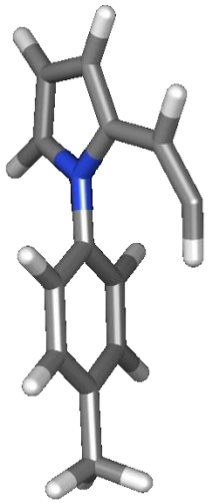
Energy = -557.2704077 Ha

Cartesian Coordinates

C	3.540535	-0.013799	-0.000046
C	2.302708	0.611522	-0.000001
N	1.326172	-0.369652	-0.000002
C	1.926297	-1.610655	-0.000046
C	3.297719	-1.419267	-0.000076
C	1.776755	1.964779	0.000064
C	-0.809122	-0.173533	-1.221496
C	-2.195501	-0.200168	-1.208144
C	-2.922829	-0.190729	0.000035
C	-0.079694	-0.051055	0.000035
C	-0.809100	-0.173739	1.221527
C	-2.195513	-0.200347	1.208175
C	0.451746	2.074149	0.000107
C	-4.430211	-0.185936	-0.000065
H	4.506687	0.485178	-0.000053
H	1.329790	-2.518523	-0.000057
H	4.045057	-2.209515	-0.000113
H	2.468663	2.817303	0.000080
H	-0.253467	-0.208585	-2.159892
H	-2.736890	-0.255451	-2.156607
H	-0.253452	-0.208955	2.159920
H	-2.736901	-0.255761	2.156627
H	-0.275884	2.883495	0.000161
H	-4.825606	0.846151	-0.003296
H	-4.837018	-0.684849	0.893306
H	-4.836915	-0.690257	-0.890475

Calculated Negative Frequency = -449.1627 cm^{-1}

mi41

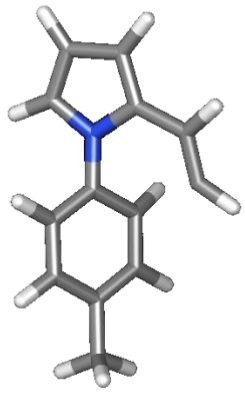


Energy = -557.2819893 Ha

Cartesian Coordinates

C	-3.472610	-0.042161	0.081226
C	-2.221364	0.554226	-0.048936
N	-1.272326	-0.461539	0.039960
C	-1.922221	-1.667958	0.218778
C	-3.283784	-1.438908	0.248350
C	-1.956456	1.967316	-0.311244
C	0.804900	0.293012	1.108942
C	2.197355	0.393744	1.109104
C	2.967157	-0.131833	0.059530
C	0.151016	-0.330426	0.040382
C	0.901810	-0.863914	-1.013534
C	2.294243	-0.767650	-0.996064
C	-0.832841	2.604301	-0.607465
C	4.471632	-0.003972	0.052149
H	-4.419250	0.491982	0.033834
H	-1.346724	-2.581427	0.339862
H	-4.053041	-2.196182	0.378533
H	-2.876916	2.569267	-0.267289
H	0.217403	0.695933	1.935322
H	2.696712	0.882728	1.949543
H	0.386576	-1.348098	-1.845151
H	2.869046	-1.191215	-1.823992
H	4.953310	-0.931937	-0.294476
H	4.862272	0.229935	1.053678
H	4.797782	0.803333	-0.626737
H	0.226087	2.411788	-0.760151

mi42



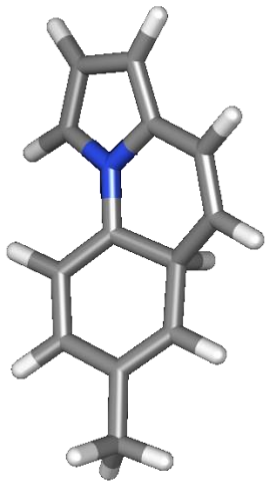
Energy = -557.2758494 Ha

Cartesian Coordinates

C	3.456492	0.183482	-0.136936
C	2.140397	0.628418	-0.144210
N	1.333663	-0.461343	0.181544
C	2.130669	-1.571944	0.377365
C	3.449002	-1.199271	0.198914
C	1.582895	1.923136	-0.506648
C	-0.082666	-0.419296	0.159195
C	-0.827951	-1.347663	-0.564683
C	-2.221023	-1.232934	-0.626383
C	-0.728421	0.670226	0.802180
C	-2.142895	0.745989	0.744198
C	-2.896314	-0.176658	0.019110
C	0.308818	2.280455	-0.360538
C	-4.399994	-0.069353	-0.067155
H	4.325207	0.800585	-0.356056
H	1.687764	-2.522529	0.660719
H	4.312132	-1.851060	0.309843
H	2.305950	2.625815	-0.949606
H	-0.315588	-2.150724	-1.097819
H	-2.792645	-1.970915	-1.194771
H	-0.200951	1.196712	1.597951
H	-2.648462	1.546346	1.290278
H	-4.787209	0.722888	0.590339
H	-4.887731	-1.016387	0.216964
H	-4.722375	0.162787	-1.096803
H	-0.225786	3.198368	-0.608299

Calculated Negative Frequency = -407.7119 cm^{-1}

mi43

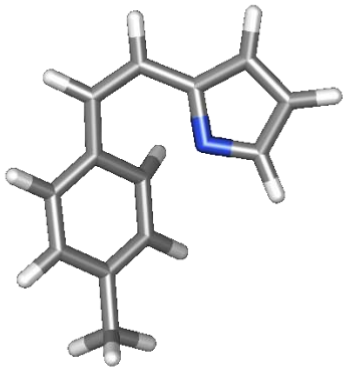


Energy = -557.3249804 Ha

Cartesian Coordinates

C	3.456488	0.288210	-0.211272
C	2.129001	0.678301	-0.123412
N	1.366191	-0.468599	0.126386
C	2.211766	-1.563014	0.184318
C	3.505137	-1.122055	-0.010868
C	1.455872	1.946690	-0.291624
C	-0.034777	-0.438422	0.151138
C	-0.645275	0.894448	0.525738
C	-2.123543	0.947853	0.241160
C	-0.821451	-1.539663	-0.109481
C	-2.225361	-1.433124	-0.156583
C	-2.873801	-0.161747	-0.029655
C	0.142532	2.070641	-0.025862
C	-4.368312	-0.079399	-0.230180
H	4.296255	0.954526	-0.394005
H	1.827300	-2.556007	0.393165
H	4.393809	-1.748499	0.004916
H	2.049652	2.793345	-0.642791
H	-0.532562	0.975084	1.642236
H	-2.602265	1.927698	0.327194
H	-0.353807	-2.501055	-0.330672
H	-2.821543	-2.322091	-0.371939
H	-4.735464	0.952034	-0.125527
H	-4.900223	-0.705837	0.506283
H	-4.656857	-0.445515	-1.230114
H	-0.377288	3.024194	-0.143952

mi44



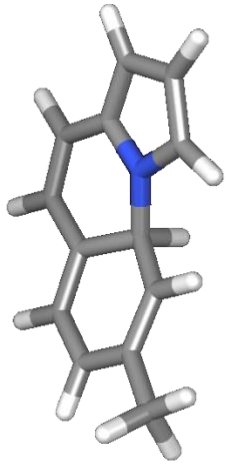
Energy = -557.303685 Ha

Cartesian Coordinates

C	-3.498161	-0.232776	-0.156683
C	-2.219679	0.369463	-0.028958
N	-1.252793	-0.626373	-0.127706
C	-1.874679	-1.804745	-0.229914
C	-3.283345	-1.608371	-0.274915
C	0.573833	1.312919	0.198113
C	1.811709	1.653685	-0.392742
C	2.834278	0.729022	-0.508478
C	0.420114	-0.020700	0.758976
C	1.511745	-0.941574	0.644003
C	2.685253	-0.596070	0.002694
C	-1.859159	1.733535	0.138646
C	-0.553692	2.190860	0.163780
C	3.830401	-1.568781	-0.121677
H	-4.451790	0.292549	-0.160498
H	-1.316231	-2.736185	-0.324600
H	-4.030850	-2.383514	-0.436435
H	1.935200	2.659100	-0.804298
H	3.769375	1.008897	-0.999615
H	-0.189524	-0.092522	1.662677
H	1.415082	-1.925899	1.108694
H	-2.674938	2.461277	0.138920
H	4.750153	-1.163310	0.332883
H	4.060246	-1.767488	-1.182724
H	3.603562	-2.529958	0.361917
H	-0.372437	3.262865	0.039937

Calculated Negative Frequency = -384.7188 cm^{-1}

mi45



Energy = -557.3344448 Ha

Cartesian Coordinates

C	-3.362922	-0.350878	-0.235863
C	-2.187768	0.388804	-0.055270
N	-1.144286	-0.515476	0.110554
C	-1.646981	-1.790231	0.068966
C	-3.016848	-1.719138	-0.159878
C	-1.911849	1.788598	-0.074258
C	0.477450	1.350033	0.120914
C	1.819982	1.729655	-0.056894
C	2.847318	0.801608	-0.096197
C	0.193635	-0.080748	0.557186
C	1.299731	-1.042138	0.206538
C	2.568013	-0.616295	-0.035693
C	-0.608853	2.243798	-0.027709
C	3.700975	-1.583805	-0.271476
H	-4.346612	0.072576	-0.425462
H	-1.010530	-2.659071	0.200054
H	-3.681100	-2.572361	-0.274728
H	2.038289	2.787650	-0.228959
H	3.875253	1.131818	-0.261607
H	1.087084	-2.111163	0.262866
H	0.135762	-0.049164	1.674731
H	-2.747176	2.478853	-0.199796
H	4.496827	-1.447290	0.481014
H	4.164319	-1.417628	-1.258987
H	3.362414	-2.629024	-0.223144
H	-0.395823	3.307557	-0.162051

References

1. 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, Gaussian03; Gaussian, Inc., Wallingford CT, 2004.

