Aza-Nazarov Reaction and the Role of Superelectrophiles.

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S-1	Index
S-2 to S-5	Experimental procedures and characterization data
S-6 to S-19	¹ H and ¹³ C NMR spectra
S-20	References to known compounds
S-21 to S-30	Computational methods, results, tables, and figures.

All reactions were performed with oven-dried glassware, and the moisture-sensitive reactions were setup under Ar. Trifluoromethanesulfonic acid was distilled under an Ar atmosphere prior to use. All commercially available compounds and anhydrous solvents were used as received. Imines were purchased from commercial suppliers, although salt **21** was prepared from 3,4-dihydroisoquinoline.¹ ¹H and ¹³C NMR spectra were recorded on Brüker 200 or 500 MHz spectrometer and low resolution mass spectra were obtained from a capillary GC (DB-5 column) equipped with a mass selective detector. High-resolution mass spectra were obtained from the Analytical Services Department at University of Illinois. Photolysis reactions were done using a 450 W medium pressure Hg vapor lamp (pyrex filter) and a photochemical reactor assembly from Ace Glass.

General procedure for the preparation of cyclization products: A 25 mL round-bottom flask containing 1.0 mmol imine in 5 mL CH₂Cl₂ is added 1.0 equivalent carboxylic acid chloride slowly. After stirring at room temperature for 2 hrs, 5 or more equivalents freshly distilled triflic acid is added (slowly). Evolution of HCl gas requires that the reaction flask have an outlet or vent. The reaction mixture is stirred at room temperature for at least 2 hrs. Then the reaction mixture is poured onto ice and extracted with CHCl₃. Following by washing with brine, the organic layer is dried over anhydrous Na₂SO₄. If necessary, the products are purified by flash column chromatography (hexanes:ether).

Alternatively, acylation of the imine can be done by reaction of 1.0 mmol of the imine with 1.0 mmol of the carboxylic acid chloride in 5 mL of anhydrous CH₃CN. After stirring 2 hrs at room temperature, the solvent is removed by vacuum. As described above, the triflic acid is then added and the reaction is later quenched. Product isolation is done as above.

5-Methoxy-2-methyl-3-phenyl-2,3-dihydro-isoindol-1-one (7b): White solid, mp: 110-114°C. ¹H NMR (CDCl₃, 200 MHz) δ 2.92 (s, 3H), 3.73 (s, 3H), 5.25 (s, 1H), 6.61-6.64 (m, 1H), 6.87-6.97 (m, 1H), 7.10-7.16 (m, 2H), 7.30-7.36 (m, 3H), 7.79 (d, 1H, *J* = 8.4 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ 27.4, 55.5, 66.3, 107.8, 114.8, 124.1, 124.7, 127.4, 128.6, 129.1, 137.0, 148.3, 162.9, 168.7. Low resolution mass spectra (EI): *m/z*: 253 (M⁺), 222, 176, 152, 118, 77. HRMS for C₁₆H₁₅O₂N, calcd: 253.1103, found: 253.1109.

5-Chloro-2-methyl-3-phenyl-2,3-dihydro-isoindol-1-one (7c): White solid, mp: 169-171°C. ¹H NMR (CDCl₃, 200 MHz) δ 2.97 (s, 3H), 5.33 (s, 1H), 7.14-7.17 (m, 3H), 7.36-7.46 (m, 4H), 7.81 (d, 1H, *J* = 8.1 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ 27.6, 66.2, 123.4, 124.7, 127.4, 129.0, 129.3, 130.2, 136.2, 138.0, 147.6, 167.6. Low resolution mass spectrum (EI), *m/z*: 257(M⁺), 222, 180, 118, 77.

4,6-Dimethoxy-2-methyl-3-phenyl-2,3-dihydro-isoindol-1-one (9a): White solid, mp: 123-125°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.88 (s, 3H), 3.59 (s, 3H), 3.84 (s, 3H), 5.26 (s, 1H), 6.48 (d, *J* = 1.1 Hz, 1 H), 6.99 (d, *J* = 1.1 Hz, 1 H), 7.10-7.12 (m, 2H), 7.24-7.33 (m, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.4, 55.5, 55.8, 64.6, 97.8, 102.7, 126.6, 127.7, 128.1, 128.5, 134.2, 136.5, 155.3, 162.0. Low resolution mass spectra (EI): *m/z*: 283 (M⁺), 252, 206, 118, 77. HRMS for C₁₇H₁₇O₃N, calcd: 283.1208, found: 283.1213.

4,6-Dichloro-2-methyl-3-phenyl-2,3-dihydro-isoindol-1-one (9b): White solid, mp: 174-175°C; ¹H NMR (CDCl₃, 500 MHz) δ 3.00 (s, 3H), 5.34 (s, 1H), 7.16-7.19 (m, 2H), 7.29-7.49 (m, 4H), 7.84 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.6, 66.2, 123.4, 124.7, 127.4 (two carbons), 129.0, 129.3, 130.2, 136.2, 138.0, 147.6, 167.7. Low resolution mass spectra (EI): *m/z*: 291 and 293 (M⁺), 256, 214, 118, 77.

4,5,6-Trimethoxy-2-methyl-3-phenyl-2,3-dihydro-isoindol-1-one (11): White solid, mp: 100-104°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.89 (s, 3H), 3.28 (s, 3H), 3.83 (s, 3H), 3.91 (s, 3H), 5.29 (s, 1H), 7.14 (d, 2H, *J* = 7.6 Hz), 7.22 (s, 1H), 7.27-7.33 (m, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.4, 56.4, 60.1, 60.8, 64.6, 101.8, 127.1, 127.7, 128.4, 128.8, 131.7, 136.9, 145.4, 148.3, 155.1, 168.3. Low resolution mass spectra (EI): *m/z*: 313 (M⁺), 282, 236, 118, 77. HRMS for C₁₈H₁₉O₄N, calcd: 313.1314, found: 313.1316.

2,3-Bis-(4-fluoro-phenyl)-4,5,6-trimethoxy-2,3-dihydro-isoindol-1-one (13): White solid, mp: 130-132°C. ¹H NMR (CDCl₃, 500 MHz) δ 3.38 (s, 3H), 3.88 (s, 3H), 3.94 (s, 3H), 6.00 (s, 1H), 6.92-6.99 (m, 4H), 7.16-7.19 (m, 2H), 7.26 (s, 1H), 7.44-7.47 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 56.4, 60.1, 60.9, 63.3, 102.1, 115.6 (d, *J*_{C-F} = 22.0 Hz), 124.8 (d, *J*_{C-F} = 7.9 Hz), 126.4, 129.3 (d, *J*_{C-F} = 8.1 Hz), 131.1, 133.1, 133.4, 146.1, 148.2, 155.6, 160.0 (d, *J*_{C-F} = 244 Hz), 162.4 (d, *J*_{C-F} = 246 Hz), 167.5. Low resolution mass spectra (EI): *m/z*: 411 (M⁺), 380, 316, 216, 109. HRMS for C₂₃H₁₉O₄NF₂, calcd: 411.1282, found: 411.1271.

2-Benzyl-4,5,6-trimethoxy-3-phenyl-2,3-dihydro-isoindol-1-one (15): White solid, mp: 132-134 °C. ¹H NMR (CDCl₃, 500 MHz) δ 3.23 (s, 3H), 3.66 (d, 1H, *J* = 14.9 Hz), 3.82 (s, 3H), 3.93 (s, 3H), 5.22 (s, 1H), 5.32 (d, 1H, *J* = 14.9 Hz), 7.10 (d, 2H, *J* = 6.4 Hz), 7.16 (d, 2H, *J* = 7.1 Hz), 7.22-7.35 (m, 7H). ¹³C NMR (CDCl₃, 125 MHz) δ 43.8, 56.4, 60.0, 60.8, 61.6, 102.0, 126.9, 127.5, 128.0, 128.4, 128.6, 128.7, 132.0, 136.9, 137.2, 145.6, 148.5, 155.2, 168.1. HRMS for C₂₄H₂₃O₄N, calcd: 389.1627, found: 389.1631.

5-Methyl-4-phenyl-4,5-dihydro-thieno[2,3-*c*]pyrrol-6-one (19): Yellow solid, mp: 112-115°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.95 (s, 3H), 5.30 (s, 1H), 6.82 (d, 1H, *J* = 4.8 Hz), 7.15-7.18 (m, 2H), 7.35-7.40 (m, 3H), 7.57-7.59 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 28.1, 65.3, 120.8, 127.3, 128.8, 129.1, 129.2, 134.9, 135.9, 155.9, 164.8. Low resolution mass spectra (EI): *m/z*: 229 (M⁺), 200, 171, 152, 118, 77. HRMS for C₁₃H₁₁ONS, calcd: 229.0561, found: 229.0558.

5,6-Dihydro-10,11,12-trimethoxyisoindolo[1,2-*a*]isoquinolin-8(12*bH*)-one (21): White solid, mp: 169-174°C. ¹H NMR (CDCl₃, 500 MHz) δ 3.65-3.72 (m, 2H), 3.96 (s, 3H), 4.01 (s, 3H), 4.10 (s, 3H), 5.70 (s, 1H), 7.21-7.31 (m, 5H), 7.71-7.74 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 28.9, 39.0, 56.4, 58.4, 60.7, 61.2, 101.8, 126.5, 126.8, 127.6, 128.3, 128.5, 128.8, 135.2, 135.3, 145.0, 148.5, 155.1, 167.7. Low resolution mass spectrum (EI): m/z: 325 (M⁺), 310, 294, 224, 139. HRMS for C₁₉H₁₉O₄N, calcd: 325.1314, found: 325.1312.

Compound 23: White solid, mp: 146-149°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.98-3.02 (m, 1H), 3.10-3.14 (m, 1H), 3.61-3.65 (m, 1H), 3.99 (s, 3H), 4.22-4.25 (m, 1H), 5.75 (s, 1H), 7.20-7.37 (m, 4H), 3.96 (s, 3H), 4.01 (s, 3H), 4.10 (s, 3H), 5.70 (s, 1H), 7.26-7.35 (m, 4H), 7.42-7.47 (m, 1H), 7.49 (d, *J* = 15.1 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 29.2, 30.1, 39.2, 56.7, 111.1, 120.7, 120.8, 122.0, 124.1, 125.9, 126.8 (two carbons), 127.4, 128.7, 134.7, 135.0, 135.3, 142.6, 162.6. Low resolution mass spectrum (EI): m/z: 288 (M-1), 259, 232, 217.

Compound 25: ¹H NMR (CDCl₃, 500 MHz) δ 3.05-3.11 (m, 1H), 3.33-3.39 (m, 1H), 3.63-3.68 (m, 1H), 4.66-4.71 (m, 1H), 6.12 (s, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 7.06-7.08 (m, 1H), 7.18-7.25 (m, 2H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.58-7.61 (m, 1H), 7.65-7.68 (m, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 6.5 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.4, 42.6, 59.6, 123.8, 124.5, 124.8, 126.1, 126.3, 126.4, 126.5, 127.1, 127.7, 128.1, 128.2, 128.7, 131.5, 132.8, 138.6, 143.6, 163.2. Low resolution mass spectrum (EI): m/z: 285 (M⁺), 284, 269, 127, 77.

1,4-Dimethyl-5-phenyl-4,5-dihydro-1H-pyrrolo[4,3,2-*de*]isoquinolin-3-one (27): Yellow solid, mp: 195-197°C. ¹H NMR (CDCl₃, 500 MHz) δ 2.84 (s, 3H), 3.35 (s, 3H), 5.06 (s, 1H), 7.15-7.18 (m, 2H), 7.24-7.38 (m, 6H), 8.06-8.10 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 27.1, 30.6, 62.0, 110.0, 120.6, 121.4, 121.5, 122.6, 127.9, 129.2, 129.3, 134.4, 141.7, 143.6, 155.0, 166.6. Low resolution mass spectra (EI): m/z: 276 (M⁺), 247, 158, 118, 77. HRMS for C₁₈H₁₆ON₂, calcd: 276.1263, found: 276.1258.

2-Methyl-3-phenyl-2,3-dihydro-dibenzo[*de,h*]isoquinolin-1-one (29): Yellow solid, 72-75°C. ¹H NMR (CDCl₃, 500 MHz) δ 3.22 (s, 3H), 5.92 (s, 1H), 7.22-7.27 (m, 3H), 7.31-7.39 (m, 4H), 7.53-7.56 (m, 1H), 7.68-7.72 (m, 1H), 7.86 (d, 1H, *J* = 8.1 Hz), 8.00 (d, 1H, *J* = 8.4 Hz), 8.56 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 34.3, 67.8, 118.2, 124.6, 125.0, 125.7, 126.1, 127.2, 127.8, 128.0, 128.2, 128.9, 129.0, 129.8, 131.8, 132.6, 132.7, 132.8, 143.0, 165.0. Low resolution mass spectra (EI): m/z: 323 (M⁺), 246, 203, 176. HRMS for C₂₃H₁₇ON, calcd: 323.1310, found: 323.1309.

2-Methyl-3-phenyl-2,3-dihydro-dibenzo[*e,g*]isoindol-1-one (32): Off-white solid, mp: 142-145 °C. ¹H NMR (CDCl₃, 500 MHz) δ 2.99 (s, 3H), 5.50 (s, 1H), 7.20-7.22 (m, 2H), 7.32-7.35 (m, 2H), 7.37-7.41 (m, 2H), 7.56-7.64 (m, 2H), 7.74-7.81 (m, 2H), 8.65-8.69 (m, 2H), 9.55 (dd, 1H, *J* = 15.7 Hz, 1.2 Hz). ¹³C NMR (CDCl₃, 125 MHz) δ 27.0, 65.6, 122.7, 123.5, 124.6, 125.0, 125.3, 126.1, 126.9, 127.3, 127.6, 128.1, 128.3, 128.8, 129.2, 130.8, 132.2, 137.1, 144.0, 169.4. Low resolution mass spectra (EI): *m/z*: 323 (M⁺), 294, 246, 176, 118, 77. HRMS for C₂₃H₁₂ON, calcd: 323.1310, found: 323.1308.

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

11

5-member 3,4,5-trimethoxy-N-Methyl-Phenylamide

^1H and ^{13}C NMR spectra:

5-member 3,4,5-trimethoxy-N-p-fluorophenyl-fluorophenylamide

^1H and ^{13}C NMR spectra:

15

5-member 3,4,5-trimethoxy-N-Benzyl-Phenylamide

5-member 3,4,5-trimethoxy-N-Benzyl-Phenylamide

^1H and ^{13}C NMR spectra:

5-member thiopheneamide

5-member thiopheneamide

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR:

COSY NMR:

^1H and ^{13}C NMR spectra:

^1H and ^{13}C NMR spectra:

Known compounds and literature citations:

Okura, K.; Inokawa, N.; Miura, M.; Nomura, M. *J. Chem. Res., Synop.* **1994**, 10, 372-373.

Nan'ya, Seiko; Ishida, Hirofumi; Butsugan, Yasuo. *J. Heterocyclic Chem.* **1994**, 31(6), 1725-1726.

Cohen, Theodore; Dinwoodie, A. H.; McKeever, L. Dennis. *J. Org. Chem.* **1962**, 27, 3385-3390.

Bouancheau, C.; Rudler, M.; Chelain, E.; Rudler, H.; Vaissermann, J.; Daran, J.-C. *J. Organomet. Chem.* **1995**, 496(1), 127-135.

Computational protocols: geometry optimizations were performed employing standard techniques at the B3LYP/6-311++G** level using the Gaussian 03 program.^{1,2,3} Optimized structures were subsequently checked by vibrational analysis with respect to being true minima on the potential energy surface, as shown by the absence of imaginary frequencies. Located transitions states were found to have a single imaginary frequency (given in Table S1). Energy differences correspond to conditions at 298 K and 1 atm, with thermal and zero-point corrections.

- (1) Calculations done using Gaussian 03, Revision **B.04**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
- (2) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785. (d) R. Fletcher *Practical Methods of Optimization*; Wiley: New York, 1980; vol. 1.
- (3) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, 72, 650.

Table S1: Thermodynamic parameters for calculated species (B3LYP/6-311++G**).

Structure	H(298K) (hartree)	S(298K) (cal/mol.K)	G(298K) (hartree)	IMAG Freq (cm ⁻¹)
42a	-403.595544	103.112	-403.644536	none
TS [42a->43a]	-403.558978	96.377	-403.604769	406i
43a	-403.583474	100.024	-403.630998	none
42b	-403.743195	101.886	-403.791604	none
TS [42b->43b]	-403.725667	97.105	-403.771805	291i
43b	-403.757842	99.174	-403.804963	none
40a	-517.943597	108.910	-517.995344	none
TS [40a->41a]	-517.900738	100.212	-517.948352	330i
41a	-517.908793	101.016	-517.956789	none
40b	-518.112496	108.133	-518.163873	none
TS [40b->41b]	-518.088142	100.705	-518.135990	279i
41b	-518.110400	101.813	-518.158774	none

Figure 1 shows the potential energy diagram for the reaction of 40b with H₂. The y-axis represents Gibbs free energy (G) in kcal/mol, and the x-axis represents the reaction coordinate (r, c). The reaction starts at 40b (0 kcal/mol), goes through a transition state (17.5 kcal/mol), and ends at 41b (3.2 kcal/mol). Chemical structures for 40b, the transition state, and 41b are shown with bond lengths in Å. The transition state is labeled 2+.

Structure 40b:

- C1-C2: 1.375
- C2-C3: 1.457
- C3-C4: 1.445
- C4-C5: 1.485
- C5-C6: 1.374
- C6-C1: 1.408
- C1-H1: 1.091
- C2-H2: 1.091
- C3-H3: 1.091
- C4-H4: 1.091
- C5-H5: 1.091
- C6-H6: 1.091
- H7-H8: 0.973
- H7-C7: 1.290
- H8-C8: 1.290
- C7-C8: 1.307
- C7-H9: 1.086
- C8-H10: 1.086

Transition State (2+):

- C1-C2: 1.392
- C2-C3: 1.436
- C3-C4: 1.445
- C4-C5: 1.410
- C5-C6: 1.408
- C6-C1: 1.391
- C1-H1: 1.291
- C2-H2: 1.291
- C3-H3: 1.291
- C4-H4: 1.291
- C5-H5: 1.291
- C6-H6: 1.291
- H7-H8: 0.974
- H7-C7: 1.349
- H8-C8: 1.349
- C7-C8: 1.491
- C7-H9: 1.406
- C8-H10: 1.406

Structure 41b:

- C1-C2: 1.364
- C2-C3: 1.465
- C3-C4: 1.511
- C4-C5: 1.473
- C5-C6: 1.471
- C6-C1: 1.422
- C1-H1: 1.091
- C2-H2: 1.091
- C3-H3: 1.091
- C4-H4: 1.091
- C5-H5: 1.091
- C6-H6: 1.091
- H7-H8: 0.973
- H7-C7: 1.296
- H8-C8: 1.296
- C7-C8: 1.564
- C7-H9: 1.469
- C8-H10: 1.469

Figure S-3

Figure S-4

Cartesian coordinates:

42a

C,-0.512600082,2.1097133038,2.0395311649
H,-0.6501930562,2.0102932196,3.1155934166
H,0.4219118714,2.6450385659,1.8511538255
H,-1.3194956087,2.7263054656,1.635771035
C,-0.5040762309,0.7549382037,1.382201625
C,-0.740794946,-0.397307522,2.028079057
H,-0.7964897988,-1.3580281663,1.5309669552
H,-0.9358549006,-0.3992030733,3.0941991961
C,-0.3732522506,0.7891872579,-0.0896373806
O,-0.6086341105,1.7072725312,-0.8088622835
N,0.103109983,-0.4869564915,-0.7959025296
C,1.1713116452,-1.0842543701,-0.3898511815
H,1.6020409379,-0.7063782556,0.5344383257
C,-0.5888713138,-0.8136979203,-2.069229355
H,-0.9211161339,-1.8507767444,-2.0385776985
H,-1.4426998249,-0.150566855,-2.169378051
H,0.0837847417,-0.6523533862,-2.9109813695
C,1.8606223675,-2.2009761478,-1.0641289069
H,1.364114886,-2.5678676861,-1.9586278959
H,2.87686585,-1.872022071,-1.3176496656
H,1.9903989027,-3.019542654,-0.346482236

TS [42a -> 43a]

C,0.5459138186,2.0826295896,1.8134563822
H,0.7555878681,1.8939441371,2.8647320948
H,1.4205770207,2.4969837542,1.3001432932
H,-0.2194163117,2.8708943615,1.7407814305
C,0.0177144324,0.9016031039,1.1096868012
C,-0.2590218918,-0.336710245,1.6613974099
H,-1.1310701177,-0.8972909786,1.3390234301
H,0.0753147995,-0.5682648891,2.669130369
C,-0.1769923345,0.9638544829,-0.3755186114
O,-0.4723943741,1.9305177831,-1.0236200429
N,0.0134441343,-0.3445554393,-0.8665085816
C,0.5671379418,-1.2427566606,0.0286315254
H,1.5723443287,-1.0230979886,0.3726175472
C,-0.5152562693,-0.7106910478,-2.1889280742
H,-1.5062985438,-1.1634689221,-2.1034919129
H,-0.5983816191,0.2143003344,-2.7588912846
H,0.1670930151,-1.3934844095,-2.6917394912
C,0.2470074771,-2.6959928949,-0.0738417171
H,-0.8029690639,-2.8939575657,-0.291093709
H,0.8550671839,-3.1290445475,-0.8789872856
H,0.5381784469,-3.2113854446,0.8429936368

Cartesian coordinates:

43a

N,-0.8147603339,-0.2389095565,0.426585386
C,-0.7005898654,1.2038598508,0.1992932579
C,0.773683114,1.362499107,-0.218422276
C,1.3499971683,0.0298181917,-0.2206391335
C,0.318925824,-0.9750743292,0.1795485099
C,-1.6999588508,1.7339450309,-0.8349978706
O,0.4899420478,-2.1706674597,0.2623412606
C,2.6965209565,-0.3738656216,-0.5461818499
C,-2.0397995962,-0.873916102,0.8862814891
H,-0.8731312068,1.7129011473,1.155063012
H,1.3552385379,2.01463984,0.4544865201
H,0.907901878,1.8301873299,-1.2073426777
H,2.6343080713,-1.1072625701,-1.3705830562
H,3.379441599,0.436399665,-0.7889946228
H,3.0768320093,-1.006671124,0.2738040612
H,-1.7969076061,-1.8787525791,1.22898897
H,-2.4761108156,-0.2898843222,1.6991954057
H,-2.7651012065,-0.9441015357,0.0694336104
H,-2.7262123321,1.5807726907,-0.4987939857
H,-1.5547525323,2.8079847881,-0.9689774364
H,-1.5703929431,1.2378964781,-1.8004003481

43b

C,1.6027074761,1.6995557649,1.8489016151
H,1.6874907413,1.6211268022,2.9318112985
H,2.6112494068,1.7238200953,1.4263603075
H,1.1175228588,2.6465108515,1.6009423944
C,0.8233411453,0.5270652349,1.3063687974
C,0.4769795011,-0.5595956024,2.0612782843
H,-0.000510508,-1.4483989501,1.6638903215
H,0.7250453651,-0.5860540102,3.1184260881
C,0.5500629354,0.498505674,-0.0940923787
O,1.1733428862,1.3367260383,-0.8391903873
N,-0.3617428873,-0.4099394888,-0.7307647793
C,-1.6131408982,-0.4577835096,-0.3309142579
H,-1.8734155608,0.2049620457,0.4928939975
C,0.1693858298,-1.2183624309,-1.8924542327
H,-0.2642884557,-0.8567724953,-2.8256112281
H,1.2544529097,-1.1315101905,-1.9106499858
H,-0.0929421987,-2.2627834931,-1.7296972746
C,-2.6699848488,-1.2773287334,-0.912546379
H,-2.3777653286,-1.9312475294,-1.7295470511
H,-3.1431552162,-1.8560204956,-0.1027437943
H,-3.4749702357,-0.5972332708,-1.2398701474
H,0.9406364996,1.377030371,-1.7865770633

Cartesian coordinates:

TS [42b -> 43b]

C,-2.7391323268,-0.6655542735,0.2968438994
C,-1.3263020196,-0.5741272689,-0.1337669253
C,-0.5449289505,-1.6187902382,-0.599319068
C,-0.598904566,0.687376434,-0.0367206068
O,-1.2392294578,1.802317656,-0.0811792983
N,0.7307824524,0.5412632495,0.0958715087
C,1.1550190721,-0.7435338263,0.4673202093
C,2.4770006673,-1.2738412926,0.0985426492
C,1.680098617,1.6692172616,-0.1514603881
H,-3.0950728453,-1.6946129501,0.3110731457
H,-2.9113120273,-0.1785919515,1.2626288046
H,-3.351084829,-0.1062054125,-0.4312023262
H,0.1985856431,-1.4680723444,-1.3798095058
H,-0.8632185909,-2.6492275992,-0.4602395177
H,0.6979914074,-1.1346329158,1.3701285963
H,1.3320391603,2.2563988373,-1.0017729763
H,1.7519170556,2.2769872109,0.7549664319
H,2.6624129724,1.263448958,-0.3784249815
H,2.8387050487,-0.9700022192,-0.8842829309
H,3.1989926527,-0.9436161609,0.8667972611
H,2.4701952593,-2.3650148773,0.1817649672
H,-0.7488953729,2.6212766535,0.1180682381

43b

C,-0.4251243946,-1.4622787567,0.5366482509
C,-0.2701396056,-1.0673801315,-0.9374698623
C,0.4435265158,0.724410509,0.4009242986
C,0.0022090531,-0.3312242916,1.3389199054
H,-1.4483447046,-1.7668788898,0.8251916023
H,0.1683649321,-2.3545385619,0.8216071745
H,0.4878724588,-1.6837214363,-1.4347104485
O,0.8779664041,1.8512590692,0.8638503147
C,0.0305264257,-0.1833397705,2.7685701028
H,1.0505586837,0.1160552709,3.0858276182
H,-0.5441956975,0.7236962402,3.0496499153
H,-0.3159784138,-1.0545253886,3.3205044559
N,0.3206381508,0.3058569798,-0.8354057831
C,0.7002591712,1.079680629,-2.0280989933
H,1.5823303462,1.6878962763,-1.8165660373
H,0.9312198922,0.38710264,-2.8362017613
H,-0.1369243876,1.7198674532,-2.3281096141
C,-1.5673375541,-1.0827852873,-1.759129536
H,-1.3891532514,-0.7668861327,-2.7875523653
H,-1.9363222459,-2.1102738988,-1.7951219572
H,-2.3357323042,-0.4485452312,-1.3104973897
H,1.134588735,2.5371828444,0.2208317747

Cartesian coordinates:

40a

C,0.335997539,-0.0598267431,1.1020443663
O,0.3939483682,-0.2355961314,2.2788427812
N,1.7005836043,0.1245815794,0.4100711207
C,1.9784465647,-0.5666098781,-0.6411739768
H,1.1597074901,-1.1555866356,-1.0482821075
C,2.6968898411,0.9374178102,1.1505253035
H,3.0098537287,1.7749637572,0.5269772796
H,2.2238182136,1.3012776255,2.0575064261
H,3.5544251594,0.3235424906,1.4220468661
C,3.2873967327,-0.6440274475,-1.3194577777
H,4.0491961578,0.0139473066,-0.9096872291
H,3.6370494483,-1.6835275085,-1.2739057803
H,3.1443778982,-0.4299158402,-2.3846991768
C,-0.8473174086,-0.0078210933,0.2413009805
C,-2.0128643173,-0.6252757254,0.7317952734
C,-0.8844687782,0.694808373,-0.977378174
C,-3.1866456415,-0.5651670122,-0.0047876464
H,-1.9789100803,-1.1460196801,1.6807054086
C,-2.070583434,0.7648156091,-1.6966590758
H,-0.0121651094,1.222283921,-1.3444270789
C,-3.2165284052,0.1284674793,-1.2167582197
H,-4.080635847,-1.0515616514,0.3655813032
H,-2.1064825535,1.3216698287,-2.6248766566
H,-4.1378428376,0.1809361496,-1.784885669

TS [40a -> 41a]

C,0.4225293247,0.1705091994,1.4357887505
O,0.4675749916,0.3845576407,2.617622384
N,1.4979290285,-0.2279032922,0.6187891361
C,1.1392659707,-0.6094450726,-0.6794325174
H,0.5445986958,-1.5173525499,-0.7402152718
C,2.8803133317,-0.0801723818,1.0883689696
H,3.3573217242,0.8004579019,0.6508914507
H,2.8297220151,0.0454102203,2.1693040186
H,3.4602078503,-0.9720568898,0.8530693433
C,2.1430740955,-0.4608075667,-1.7807159251
H,2.627781505,0.5162666526,-1.787031595
H,2.9183055538,-1.2257670837,-1.6529400325
H,1.6761928923,-0.6439067172,-2.7489358222
C,-0.7475228311,0.3053169475,0.5208417909
C,-2.0373084788,-0.0570444509,0.8543845942
C,-0.3712871891,0.5845809636,-0.8412970244
C,-2.971429886,-0.2159963446,-0.1751115664
H,-2.2900211794,-0.2850514453,1.8831437715
C,-1.3609724604,0.4254156203,-1.8607545579
H,0.3335399874,1.3958920989,-1.0160043186
C,-2.6296186974,0.0011355563,-1.5247692019
H,-3.9756190412,-0.5456872959,0.0678592059
H,-1.1262436029,0.6960175139,-2.8838979153
H,-3.3841486111,-0.1263153097,-2.2915657307

Cartesian coordinates:

41a

C,-0.3289671032,0.1975988241,-2.2247692795
C,-0.3290482407,0.2477681067,-0.852950048
C,0.899054295,0.2586274394,-0.0616950824
C,2.1476053126,-0.0282946037,-0.785201746
C,2.1304348678,-0.1096212582,-2.1503142645
C,0.9080430669,0.0187359767,-2.8605181644
C,0.4809172102,-0.4127633942,1.2998393446
N,-0.9711172685,-0.1899893197,1.2879502743
C,-1.5047101293,0.1455091366,0.0656439265
C,-1.8191385031,-0.4660471799,2.442217152
O,-2.6658495024,0.3036092309,-0.2351340918
C,1.1848822499,0.1478016532,2.5281097047
H,0.6847627464,-1.4865804998,1.2114527345
H,3.0822853961,-0.0741851578,-0.2360056395
H,3.0475424656,-0.2688213441,-2.7040763948
H,0.933257047,-0.0589661249,-3.9432285077
H,-1.2581704609,0.2201766348,-2.7822115981
H,-2.8546669341,-0.3636127832,2.1210324963
H,-1.6248901143,0.243162124,3.2495083698
H,-1.6500351503,-1.4830792683,2.8052571684
H,1.0379282081,1.3320812483,0.2145330983
H,0.8798938755,-0.3873079285,3.4286055862
H,0.9659851852,1.2100011852,2.6647241693
H,2.2662864778,0.022295101,2.4336600743

40b

C,-1.8005605361,0.0129630385,-2.7154924195
C,-1.8183106962,-0.0080137361,-1.3406432354
C,-0.5840683492,0.0946642061,-0.6121498893
C,0.6512988511,0.2393571145,-1.3287579049
C,0.6419333716,0.263393654,-2.7027960399
C,-0.577750056,0.1467147296,-3.3973631
H,-2.7248178861,-0.0760865302,-3.2733106128
H,-2.7517459619,-0.1202221317,-0.8037613062
H,1.5880248657,0.3763275609,-0.8028807422
H,1.5658637169,0.3886396268,-3.2538251761
H,-0.5733036111,0.1673952961,-4.4823205178
C,-0.63467628,0.0994227452,0.7818882498
O,-1.7705857364,0.2038682548,1.4030561888
N,0.5457490757,0.0379280532,1.6140266899
C,1.3140961362,-1.0187993826,1.5666164487
H,1.0064353003,-1.7964098544,0.8690026789
C,2.5105258139,-1.2487439052,2.375841264
H,2.7889258334,-0.4413205021,3.047607515
H,2.3556917517,-2.1780583069,2.9470746138
H,3.3446742337,-1.4915619083,1.700465692
C,0.7906827359,1.2095941582,2.5313237519
H,0.6919593049,0.8935790857,3.5700946041
H,1.7922800283,1.5936806571,2.3420199811
H,0.0643909683,1.9866981716,2.301626677
H,-1.7629621304,0.0575806922,2.3647675015

TS [40b -> 41b]

C,-2.0827030081,-0.0274647716,-2.2239717433
C,-2.036988558,0.1885808105,-0.8432908466
C,-0.792808554,0.377610517,-0.2477052336
C,0.4167480216,0.4277303067,-1.0360941745
C,0.3361909706,0.1677188506,-2.4192633288
C,-0.9067513809,-0.0648038193,-2.998076034
H,-3.0401997563,-0.2042819378,-2.7019492178
H,-2.9383648486,0.1346645328,-0.2436694872
H,1.2382477156,1.0621329853,-0.7084293014
H,1.2224286463,0.2427464527,-3.0391914819
H,-0.9803952662,-0.2320840269,-4.0670115094
C,-0.5639691306,0.3225229261,1.1705615248
O,-1.4648034162,0.7132790034,2.009113741
N,0.6604936842,-0.1404697691,1.4970825317
C,1.3006834757,-0.8504693398,0.4659651742
H,0.7154718003,-1.663036195,0.0514564799
C,2.7691635174,-0.9735491148,0.4051823589
H,3.3111514475,-0.0577033869,0.6445542779
H,3.0733578276,-1.7560562831,1.1212383894
H,3.0702185162,-1.3457964221,-0.5760660318
C,1.2902313112,0.1098733731,2.8255662364
H,1.0791188811,-0.7271744407,3.4947792288
H,2.3660960002,0.2027222398,2.6971912942
H,0.9118703613,1.0473350729,3.2328910526
H,-1.3128097745,0.5070893362,2.9484750568

41b

N,-1.3469449788,-0.0421714073,-0.8867058179
C,-1.346151159,0.0270202549,0.4226680806
C,0.0277933289,0.0641933775,0.9291631665
C,0.9040298439,-0.2967419087,-0.1938634395
C,0.0442787292,-0.051575209,-1.4765520844
C,2.323801985,0.0559880349,-0.041408887
C,2.7896477557,0.4788535168,1.1851168989
C,1.8997964275,0.6611993467,2.2615828817
C,0.495021857,0.4758599103,2.1422368908
O,-2.345244688,0.0953698839,1.2439627057
H,0.2267083236,0.9647644964,-1.838721701
C,-2.5394906236,-0.0566354613,-1.7517004939
H,3.0109927198,-0.1324669204,-0.8612650607
H,3.8459550363,0.6758452096,1.3289671813
H,2.2984164581,0.9905864858,3.2172688689
H,-0.1645154326,0.7132572483,2.9695227901
H,-3.4030541538,0.3394012634,-1.2164624608
H,-2.7479732174,-1.0757995093,-2.0833708598
H,-2.3549389672,0.5823545418,-2.615113633
H,0.9963099098,-1.4137778975,-0.1265310233
C,0.2157488593,-1.0668452803,-2.5949299513
H,-0.3941441048,-0.812677527,-3.4627876154
H,1.255008091,-1.0546629834,-2.9327320641
H,-0.029469924,-2.0808678277,-2.2694470103
H,-3.2355844053,0.08838471,0.8520332929