Supplementary Material

Tautomerization in Naphthalenediimines: A Keto-Enamine

Schiff-base Macrocycle

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Experimental Section

Materials. 1,4-Bis(hydroxymethyl)-2,3-dimethoxynaphthalene (**3**),¹ 1,2-propyloxy-4,5-diaminobenzene (**6**),² 3,6-diformyl-1,2-dihydroxybenzene,³ and *N*-(*tert*-butyloxycarbonyl)-1,2-diaminobenzene were prepared by literature methods.⁴ Other reagents were obtained from standard suppliers.

Equipment. ¹H and ¹³C NMR spectra were recorded on either a Brüker AV-300 or AV-400 spectrometer. ¹³C NMR spectra were recorded using a proton decoupled pulse sequence. ¹H and ¹³C NMR spectra were calibrated to the residual protonated solvent at δ 7.24 and δ 77.00, respectively, in CDCl₃ and δ 2.50 and δ 29.84, respectively, in DMSO-*d*₆. Carbonyl and vinyl peaks of all compounds were assigned through the use of ¹³C APT and HMBC pulse sequences. UV-vis spectra were obtained on a Varian Cary 5000 UV-vis/near-IR spectrophotometer using a 1 cm quartz cuvette. IR spectra were obtained as KBr discs with a Bomems MB-series spectrometer. EI spectra were obtained using a double focusing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of: source temperature 200°C and ionization energy 70eV. MALDI-TOF mass spectra were obtained in a dithranol matrix (cast from THF) on a Brüker Biflex IV instrument where spectra were acquired in the positive reflection mode with delay extraction. Melting points were obtained on a Fisher-John's melting point apparatus.

1,4-Diformyl-2,3-dimethoxynaphthalene (4). Compound **3** (2.22 g, 9.1 mmol) was dissolved in 600 mL of dichloromethane and pyridinium chlorochromate (7.84 g, 36.4 mmol) was added slowly with stirring resulting in a dark brown solution. Stirring was

continued for 2h at room temperature. The solution was filtered through a plug of silica washing with dichloromethane to give a yellow solution. Rotary evaporation of the solid afforded 1.86 g (7.6 mmol, 84% yield) of yellow solid which was nearly pure **4** by ^1H NMR spectroscopy. Compound **4** could be purified further by vacuum sublimation.

Data for 4. ^{13}C NMR (100.6 MHz, CDCl_3) δ 192.0, 158.2, 128.7, 128.5, 127.8, 124.8, 63.0 ppm; ^1H NMR (400 MHz, CDCl_3) δ 10.83 (s, 2H, $\text{CH}=\text{O}$), 9.01 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 3.6$ Hz, 2H, aromatic CH), 7.59 (dd, $^3J_{\text{HH}} = 6.6$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, 2H, aromatic CH), 4.09 (s, 6H, OCH_3) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 356 (8.7×10^3), 264 (1.4×10^4), 227 (2.5×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). EI-MS: $m/z = 244$ (M^+). IR (KBr): $\nu = 3351$, 3101, 2944, 2874, 2767, 1688, 1612, 1572, 1503, 1455, 1431, 1399, 1370, 1346, 1326, 1241, 1205, 1181, 1161, 1109, 1073, 1036, 1020, 883, 803, 771, 574, 513, 461 cm^{-1} . Mp. 101-102 $^\circ\text{C}$. Anal. Calc'd for **4** ($\text{C}_{14}\text{H}_{12}\text{O}_4$): C, 68.85; H, 4.95. Found: C, 68.45; H, 5.02.

1,4-Diformyl-2,3-dihydroxynaphthalene (5). Under an atmosphere of nitrogen 1.77 g (7.25 mmol) of compound **4** was dissolved in 120 mL of dry dichloromethane and cooled in an ice/water bath. While stirring, BBr_3 (3.1 mL, 32.6 mmol) was added, the solution then turning orange in color. This solution was stirred for 12 h after slowly warming to room temperature. The reaction was quenched with water (50 mL) and the product was extracted with dichloromethane (3 x 50 mL). The combined organic fractions were dried over MgSO_4 then filtered. The solvent was removed by rotary evaporation to yield 1.25 g (5.75 mmol, 80% yield) of yellow solid. Compound **5** could be further purified by vacuum sublimation.

Data for 5. ^{13}C NMR (100.6 MHz, CDCl_3) δ 194.3, 154.9, 126.7, 126.1, 119.9, 115.3 ppm; ^1H NMR (300 MHz, CDCl_3) δ 12.95 (s, 2H, H-bonded OH), 10.88 (s, 2H, CH=O), 8.37 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, 2H, aromatic CH), 7.57 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 3.3$ Hz, 2H, aromatic CH) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 388 (8.78×10^3), 227 (5.06×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). EI-MS: $m/z = 216$ (M^+). IR (KBr): $\nu = 3302, 2360, 2348, 1680, 1640, 1603, 1555, 1515, 1446, 1410, 1374, 1305, 1225, 1016, 923, 855, 746, 661, 601, 512, 456 \text{ cm}^{-1}$. Mp. decomposition $> 180^\circ\text{C}$.

Macrocycle 2. Under a nitrogen atmosphere, 1,4-diformyl-2,3-dihydroxynaphthalene (**5**) (150 mg, 0.69 mmol) and 1,2-dipropoxy-4,5-diaminobenzene (**6**) (156 mg, 0.69 mmol) were dissolved in 30 mL of degassed CHCl_3 and stirred at reflux for 12 h. The solvent was then reduced to 5 mL and the product precipitated from 25 mL of MeCN to yield deep red solid (127 mg, 46% yield).

Data for macrocycle 2. ^{13}C NMR (75.5 MHz, $\text{DMSO}-d_6$) δ 162.0 (C=O), 155.6 (CH-NH), 148.8, 130.6, 126.1, 124.6, 121.0, 111.5, 104.6, 70.5, 22.2, 10.5 ppm; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 15.57 (b, 6H, NH), 9.58 (b, 6H CH-NH), 8.38 (b, 6H, aromatic CH), 7.48 (b, 6H, aromatic CH), 7.39 (b, 6H, aromatic CH), 4.13 (b, 12H, OCH_2), 1.79 (b, 12H, CH_2CH_3), 1.04 (b, 18H, CH_2CH_3) ppm. UV-Vis (CH_2Cl_2) λ_{max} (ϵ) = 441 (4.97×10^4), 319 (2.93×10^4), 233 (7.04×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). MALDI-TOF-MS: $m/z = 1213.8$ ($\text{M}+\text{H}^+$); 1236.0 ($\text{M}+\text{Na}^+$); 1251.9 ($\text{M}+\text{K}^+$). IR (KBr): $\nu = 3431, 2964, 2936, 2872, 1616, 1548, 1370, 1318, 1258, 1177, 1012, 807, 743, 694 \text{ cm}^{-1}$. Mp. $> 270^\circ\text{C}$.

Anal. Calc'd for $2 \cdot 4\text{H}_2\text{O}$ ($\text{C}_{72}\text{H}_{80}\text{N}_6\text{O}_{16}$): C, 67.27; N, 6.54; H, 6.27. Found: C, 67.37; N, 6.88; H, 6.08.

Synthesis of model compounds (7-9). 100 mg of either 3,6-diformyl-1,2-dihydroxybenzene or 1,4-diformyl-2,3-dihydroxynaphthalene (**5**) was dissolved in 50 mL of EtOH to give a yellow solution. Two molar equivalents of the appropriate amine (either 4-methoxyaniline or *N*-(*tert*-butyloxycarbonyl)-1,2-diaminobenzene) was added, turning the solution deep red in color. The mixture was stirred at reflux for 12h and, after cooling, an orange precipitate formed. The product was isolated by filtration and was dried under vacuum.

Data for 7. Yield: 82%. ^{13}C NMR (75.5 MHz, CDCl_3) δ 159.7 (CH=N), 159.2 (COCH_3), 150.3 (C-OH), 141.0, 122.5, 120.9, 120.5, 114.7, 55.6 (CH_3) ppm; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 13.42 (s, 2H, OH), 8.97 (s, 2H, CH=N), 7.45 (d, $^3J_{\text{HH}} = 8.7$ Hz, 4H, aromatic CH), 7.20 (s, 2H, aromatic CH), 7.04 (d, $^3J_{\text{HH}} = 8.7$ Hz, 4H, aromatic CH), 3.80 (s, 6H, OCH_3) ppm; ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s, 2H, CH=N), 7.38 (d, $^3J_{\text{HH}} = 8.4$ Hz, 4H, aromatic CH), 7.12 (s, 2H, aromatic CH), 6.95 (d, $^3J_{\text{HH}} = 8.8$ Hz, 4H, aromatic CH), 3.83 (s, 6H, OCH_3) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 390 (4.37×10^4), 300 (1.08×10^4), 236 (2.76×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). EI-MS: $m/z = 376$ (M^+). IR (KBr): $\nu = 3447, 3033, 2924, 2843, 1733, 1612, 1580, 1548, 1435, 1362, 1322, 1306, 1246, 1205, 1165, 1105, 1024, 855, 835, 815, 791, 758, 694, 618, 570 \text{ cm}^{-1}$. Mp. slow decomposition $> 120^\circ\text{C}$. Anal. Calc'd for **7** ($\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4$): C, 70.20; N, 7.44; H, 5.36. Found: C, 70.24; N, 7.84; H, 5.42.

Data for 8. Yield: 63%. ^{13}C NMR (100.6 MHz, CDCl_3) δ 168.7 ($\text{C}=\text{O}$), 158.4 (COCH_3), 150.8 ($\text{C}=\text{C}-\text{N}$), 135.5, 126.4, 124.3, 120.7, 119.2, 114.9, 109.8, 55.5 (CH_3) ppm; ^1H NMR (400 MHz, CDCl_3) δ 15.68 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H, NH), 9.02 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H, $\text{CH}-\text{N}$), 7.84 (dd, $^3J_{\text{HH}} = 6.2$ Hz, $^4J_{\text{HH}} = 3.4$ Hz, 2H, aromatic CH), 7.33 (d, 8.8 Hz, 4H, aromatic CH), 7.27 (dd, $^3J_{\text{HH}} = 6.0$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, 2H, aromatic CH), 6.97 (d, $^3J_{\text{HH}} = 8.8$ Hz, 4H, aromatic CH), 3.82 (s, 6H, OCH_3) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 459 (2.92×10^4), 303 (1.80×10^4), 243 (3.90×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). EI-MS: $m/z = 426$ (M^+). IR (KBr): $\nu = 3439, 3061, 3040, 2995, 2843, 1737, 1624, 1551, 1511, 1467, 1435, 1403, 1322, 1298, 1254, 1189, 1125, 1028, 968, 823, 755, 694, 557 \text{ cm}^{-1}$. Mp. 243-257 $^\circ\text{C}$ (dec.). Anal. Calc'd for **8** ($\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4$): C, 73.23; N, 6.57; H, 5.20. Found: C, 73.20; N, 6.88; H, 5.20.

Data for 9. Yield: 74%. ^{13}C NMR (75.5 MHz, CDCl_3) δ 158.5 ($\text{C}=\text{O}$), 158.1 ($\text{C}=\text{C}-\text{N}$), 152.7 ($\text{C}=\text{O}$ – from boc), 136.7, 132.3, 128.2, 126.4, 125.3, 123.7, 120.5, 120.2, 119.1, 112.6, 81.1 ($\text{C}-\text{CH}_3$), 28.3 (CH_3) ppm; ^1H NMR (400 MHz, CDCl_3) δ 14.65 (s, 2H, NH), 9.30 (s, 2H, $\text{CH}-\text{N}$), 8.15 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, aromatic CH), 8.10 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, 2H, aromatic CH), 7.43 (dd, $^3J_{\text{HH}} = 6.4$ Hz, $^4J_{\text{HH}} = 3.2$ Hz, 2H, aromatic CH), 7.32 (m, 2H, aromatic CH), 7.20 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, aromatic CH), 7.14 (m, 2H, aromatic CH), 7.06 (s, 2H, NH – from boc), 1.51 (s, 18H, CCH_3) ppm. UV-vis (CH_2Cl_2) λ_{max} (ϵ) = 439.5 (2.77×10^4), 271 (2.40×10^4), 237.5 (6.25×10^4) nm ($\text{L mol}^{-1} \text{ cm}^{-1}$). EI-MS: $m/z = 596$ (M^+). IR (KBr): $\nu = 3451, 3033, 2984, 2928, 2856, 1729, 1620, 1600, 1548, 1515, 1491, 1451, 1370, 1326, 1250, 1157, 1052, 1028, 747, 698 \text{ cm}^{-1}$. Mp. 200-

230 °C (dec.). Anal. Calc'd for **9** (C₃₄H₃₆N₂O₆): C, 68.44; N, 9.39; H, 6.08. Found: C, 68.05; N, 9.56; H, 6.18.

Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of **4**

Figure S2. ^{13}C NMR spectrum (400 MHz, CDCl_3) of **4**

Figure S3. ^1H NMR spectrum (300 MHz, CDCl_3) of **5**

Figure S4. ^{13}C NMR spectrum (400 MHz, CDCl_3) of **5**

Figure S5. ^1H NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of macrocycle **2** ($\text{R} = \text{OC}_3\text{H}_7$)

Figure S6. ^{13}C NMR spectrum (300 MHz, $\text{DMSO-}d_6$) of macrocycle **2** ($\text{R} = \text{OC}_3\text{H}_7$)

Figure S7. MALDI-MS spectrum (dithranol matrix, THF) of macrocycle **2**. Inset: calculated isotope distribution of [M+H]⁺ ion

Figure S8. ^1H NMR spectrum (300 MHz, $\text{DMSO}-d_6$) of model compound **7**

Figure S9. ^{13}C NMR spectrum (300 MHz, CDCl_3) of model compound **7**

Figure S10. ^1H NMR spectrum (400 MHz, CDCl_3) of model compound **8**

Figure S11. ^{13}C NMR spectrum (400 MHz, CDCl_3) of model compound **8**

Figure S12. ^1H NMR spectrum (400 MHz, CDCl_3) of model compound **9**

Figure S13. ^{13}C NMR spectrum (400 MHz, CDCl_3) of model compound **9**

Figure S14. ^{13}C APT NMR spectrum (400 MHz, CDCl_3) of model compound **9**

X-ray Diffraction Study of 5. Crystals of **5** suitable for X-ray diffraction were grown from CH₂Cl₂. All measurements were made on a Brüker X8 diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069 \text{ \AA}$). The data were collected at a temperature of $-100.0 \pm 0.1 \text{ }^{\circ}\text{C}$ to a maximum 2θ value of 52.98° . Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 12s exposures. Of the 8268 reflections that were collected, 5263 were unique ($R_{\text{int}} = 0.0542$); equivalent reflections were merged. The twinned data was collected and integrated using the Brüker SAINT software package.⁵ Data were corrected for absorption effects using the multi-scan technique (SADABS),⁶ with max and min transmission coefficients of 0.980 and 0.613, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located through difference mapping and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 5263 reflections and 266 variable parameters and converged (largest parameter shift was 0.000 times its esd).⁸ Further details are available in the supplementary CIF file.

Crystal data: yellow prism ($0.50 \times 0.25 \times 0.17 \text{ mm}^3$), $a = 10.126(5) \text{ \AA}$, $b = 14.618(5) \text{ \AA}$, $c = 18.704(5) \text{ \AA}$, $V = 2768.6(18) \text{ \AA}^3$, space group Pccn (orthorhombic), $Z = 12$, mol wt. = 216.18, $T = -100(1) \text{ }^{\circ}\text{C}$, $\mu(\text{Mo-K}_{\alpha}) = 1.18 \text{ cm}^{-1}$, 8268 observed reflections, 266 variables, $R_1 = 0.0435$, $wR_2 = 0.0981$, GOF = 0.683.

X-ray Diffraction Study of 8. Crystals of **8** suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of **8** in EtOH. All measurements were

made on a Brüker X8 diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). The data were collected at a temperature of $-100.0 \pm 0.1^\circ\text{C}$ to a maximum 2θ value of 50.10° . Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 45 s exposures. Of the 21437 reflections that were collected, 3569 were unique ($R_{\text{int}} = 0.0456$); equivalent reflections were merged. Data were collected and integrated using the Brüker SAINT software package.⁵ Data were corrected for absorption effects using the multi-scan technique (SADABS),⁶ with max and min transmission coefficients of 0.976 and 0.861, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.⁷ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located through difference mapping and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 3569 reflections and 377 variable parameters and converged (largest parameter shift was 0.001 times its esd).⁸ Further details are available in the supplementary CIF file.

Crystal data: orange prism ($0.50 \times 0.30 \times 0.25 \text{ mm}^3$), $a = 11.649(5) \text{ \AA}$, $b = 7.4767(16) \text{ \AA}$, $c = 23.829(8) \text{ \AA}$, $\beta = 103.823(13)^\circ$, $V = 2015.3(12) \text{ \AA}^3$, space group $P2_1/n$ (monoclinic), $Z = 4$, mol wt. = 426.46, $T = -100(1)^\circ\text{C}$, $\mu(\text{Mo-K}\alpha) = 0.96 \text{ cm}^{-1}$, 21437 observed (3569 unique) reflections, 377 variables, $R_1 = 0.0385$, $wR_2 = 0.0857$, GOF = 0.990.

X-ray Diffraction Study of 9. Crystals of **9** suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of **9** in EtOH. All measurements were made on a Brüker X8 diffractometer with graphite monochromated Mo-K α radiation ($\lambda =$

0.71069 Å). The data were collected at a temperature of -100.0 ± 0.1 °C to a maximum 2θ value of 43.02° . Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 60 s exposures. Of the 23286 reflections that were collected, 4922 were unique ($R_{\text{int}} = 0.1550$); equivalent reflections were merged. Data were collected and integrated using the Brüker SAINT software package.⁵ Data were corrected for absorption effects using the multi-scan technique (SADABS),⁶ with max and min transmission coefficients of 0.997 and 0.751, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.⁷ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to C34, C51 and C52 were included in calculated positions but not refined. All other hydrogen atoms were located through difference mapping and refined isotropically. The final cycle of full-matrix least-squares refinement on F^2 was based on 4922 reflections and 611 variable parameters and converged (largest parameter shift was 0.024 times its esd (for H21C)).⁸ Further details are available in the supplementary CIF file.

Crystal data: red needle ($0.35 \times 0.07 \times 0.03$ mm³), $a = 11.0671(13)$ Å, $b = 11.9912(12)$ Å, $c = 14.8146(15)$ Å, $\alpha = 101.064(5)^\circ$, $\beta = 93.762(4)^\circ$, $\gamma = 95.581(4)^\circ$, $V = 1913.16(56)$ Å³, space group P-1 (triclinic), $Z = 2$, mol wt. = 688.80, $T = -100(1)$ °C, $\mu(\text{Mo-K}\alpha) = 0.84$ cm⁻¹, 23286 observed (4922 unique) reflections, 266 variables, $R_1 = 0.0596$, $wR_2 = 0.0996$, GOF = 0.957.

Computation Details. We undertook an *ab initio* study to determine whether structures of compounds **8** and **9** determined from single crystal X-ray diffraction studies were consistent with the enol-imine or keto-enamine tautomer. In addition, we hoped that the calculations would help establish which isomer is likely to be most stable. *Ab initio* DFT calculations were performed on a PC with a dual Xeon 2.80 GHz (1 GB RAM) using Spartan '04 for Windows (Wavefunction Inc., Irvine, CA). Both the keto and enol isomers of **10** were geometry minimized using B3LYP with a 6-31G(d,p) basis set. For each molecule, the calculation was started with different possible orientations of the peripheral benzene rings until the minimum energies were determined. Although we do not know for certain that the geometries are the absolute minima, they likely are. Bond lengths and bond angles of both **8** and **9** agree closely with the calculated structure of **10** (keto), which is the more stable tautomer (0 K, vacuum).

Energies of B3LYP/6-31G(d,p) minimized structures:

10 (enol) E = -1185.3867337 Hartree

10 (keto) E = -1185.3878286 Hartree

Estimation of Equilibrium Constant. The ^{13}C NMR spectra of **10(keto)** and **10(enol)** were calculated using Gaussian '03 on a Linux cluster of IBM machines with Intel Xeon processors. Calculations were performed on the optimized structures (B3LYP/6-31G(d,p)) using the same method. It was determined that the theoretical chemical shift (^{13}C) of the C=O resonance for **10(keto)** is 174 ppm, and the shift of the C-OH resonance for **10(enol)** is 153 ppm. To determine the extent of tautomerization in model compound **8**, we undertook a variable temperature ^{13}C NMR experiment. ^{13}C NMR data were determined at various temperatures in CDCl_3 . We noted that the resonance assigned to the carbonyl/enol C (~ 168 ppm) was temperature sensitive.

Consider the following equilibrium for compound **8**:

Calculated ^{13}C C-O resonance: A = 153 ppm
B = 174 ppm

At a given temperature the equilibrium constant will be:

$$K = \frac{1-x}{x}$$

Where x = mole fraction of A at equilibrium, and
 $1-x$ = mole fraction of B at equilibrium

At a given temperature, the observed chemical shift ($^{13}\text{C}_{\text{obs}}$) is a weighted average of the shifts for each isomer:

$$^{13}\text{C}_{\text{obs}} = xA + (1-x)B \quad \rightarrow \quad \text{Therefore, } x = \frac{^{13}\text{C}_{\text{obs}} - B}{A - B}, \text{ and } K \text{ can be calculated.}$$

Since $-R \ln K = \Delta H \left(\frac{1}{T} \right) - \Delta S$ at equilibrium, a plot of $-R \ln K$ versus $\frac{1}{T}$ at varying temperatures should be linear with slope of ΔH and intercept of $-\Delta S$. This is indeed observed, Figure S15.

Figure S15. Plot of $-R\ln K$ vs. $1/T$ as determined by VT ^{13}C NMR experiment for **8** in CDCl_3 ($R = 0.99$ for best-fit line).

From the slope and intercept, we extract the following thermodynamic parameters for the equilibrium of $\text{A} \rightleftharpoons \text{B}$ in CDCl_3 :

$$\Delta H = -11.8(6) \text{ kJ mol}^{-1}$$

$$\Delta S = -30(2) \text{ J mol}^{-1} \text{ K}^{-1}$$

Based on these numbers, we calculate that there is 22% of the enol isomer (isomer A above) at room temperature and only 1% at -100°C . Note that this is an estimate and is based on two important assumptions: (1) the ^{13}C shift of the $\text{C}=\text{O}/\text{C}-\text{OH}$ would be the same in **10** and **8**; and (2) the calculated values of the ^{13}C shifts are accurate (they seem quite reasonable). It is well-known that the equilibrium constants for tautomerization are strongly solvent dependent. But, we believe that we can say that the crystal structures depict almost exclusively the keto form of **8** and **9**.

Figure S16. Calculated Structure of **10** (enol) as viewed from (a) the top and (b) the side.

Figure S17. Calculated Structure of **10** (keto) as viewed from (a) the top and (b) the side.

Table S1. Atomic Coordinates Calculated for **10** (enol)

Atom #	Atom Type	X	Y	Z
1	H	1.249	-4.906	-0.067
2	C	0.701	-3.969	-0.039
3	H	2.468	-2.804	-0.118
4	C	1.386	-2.771	-0.064
5	C	-1.386	-2.771	0.048
6	C	0.715	-1.524	-0.031
7	C	-0.701	-3.969	0.022
8	C	-0.715	-1.524	0.017
9	C	1.43	-0.259	-0.046
10	H	-1.249	-4.906	0.048
11	H	-2.468	-2.804	0.1
12	C	0.719	0.949	-0.035
13	C	-0.718	0.949	0.019
14	C	-1.43	-0.259	0.034
15	O	-1.298	2.143	0.047
16	H	-2.292	1.978	0.096
17	O	1.299	2.143	-0.064
18	H	2.293	1.977	-0.112
19	C	2.878	-0.205	-0.057
20	H	3.432	-1.144	-0.018
21	C	-2.878	-0.204	0.052
22	H	-3.432	-1.144	0.022
23	N	-3.528	0.917	0.11
24	N	3.529	0.916	-0.117
25	C	-4.934	0.944	0.053
26	C	-7.735	1.115	0
27	C	-5.684	0.073	-0.756
28	C	-5.602	1.921	0.809
29	C	-6.992	1.995	0.79
30	C	-7.075	0.162	-0.777
31	H	-5.176	-0.642	-1.395
32	H	-5.014	2.602	1.416
33	H	-7.496	2.747	1.39
34	H	-7.643	-0.51	-1.414
35	H	-8.819	1.183	-0.023
36	C	4.934	0.944	-0.05
37	C	7.735	1.116	0.023
38	C	5.679	0.078	0.769
39	C	5.607	1.917	-0.806
40	C	6.997	1.992	-0.778
41	C	7.069	0.167	0.799
42	H	5.166	-0.634	1.408
43	H	5.024	2.594	-1.422
44	H	7.505	2.74	-1.379
45	H	7.633	-0.501	1.444
46	H	8.818	1.184	0.052

Table S2. Atomic Coordinates Calculated for **10** (keto)

Atom #	Atom Type	X	Y	Z
1	H	1.243	-4.968	0.147
2	C	0.693	-4.034	0.081
3	H	2.446	-2.859	0.285
4	C	1.37	-2.826	0.15
5	C	-1.371	-2.824	-0.135
6	C	0.709	-1.583	0.068
7	C	-0.694	-4.033	-0.076
8	C	-0.71	-1.582	-0.047
9	C	1.454	-0.31	0.097
10	H	-1.245	-4.966	-0.147
11	H	-2.447	-2.858	-0.264
12	C	0.757	0.962	0.098
13	C	-0.756	0.963	-0.036
14	C	-1.454	-0.308	-0.066
15	O	-1.325	2.071	-0.098
16	O	1.327	2.068	0.18
17	C	2.846	-0.285	0.08
18	H	3.409	-1.209	0.014
19	C	-2.845	-0.282	-0.072
20	H	-3.411	-1.206	-0.042
21	N	-3.579	0.839	-0.116
22	N	3.581	0.834	0.138
23	H	2.995	1.681	0.233
24	H	-2.991	1.687	-0.18
25	C	4.978	0.941	0.044
26	C	7.76	1.273	-0.091
27	C	5.79	-0.096	-0.44
28	C	5.569	2.15	0.443
29	C	6.949	2.311	0.373
30	C	7.172	0.074	-0.496
31	H	5.351	-1.022	-0.797
32	H	4.939	2.953	0.815
33	H	7.392	3.252	0.686
34	H	7.79	-0.735	-0.874
35	H	8.837	1.4	-0.143
36	C	-4.977	0.944	-0.045
37	C	-7.762	1.275	0.046
38	C	-5.561	2.16	-0.434
39	C	-5.797	-0.101	0.406
40	C	-7.18	0.069	0.441
41	C	-6.942	2.32	-0.385
42	H	-4.925	2.969	-0.781
43	H	-5.364	-1.032	0.755
44	H	-7.804	-0.746	0.794
45	H	-7.38	3.266	-0.69
46	H	-8.839	1.401	0.082

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