Electronic Supporting Information

Ammonia N–H Activation by a *N,N′*–Diamidocarbene

*Todd W. Hudnall, Jonathan P. Moerdyk and Christopher W. Bielawski**

Department of Chemistry & Biochemistry, The University of Texas, Austin, Texas 78712 (USA)

E-mail: bielawski@cm.utexas.edu

General Considerations. All procedures were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glove box unless otherwise noted. *N,N′*–bis(2,4,6-trimethylphenyl)formamidine, 1,3-bis(2,6-di-*iso*-propylphenyl)-5,5-dimethyl-4,6-dioxopyrimidium triflate ([**1**H][OTf]), 1,3-bis(2,6-di-*iso*-propylphenyl)-4,6-diketo-5,5-dimethyl-pyrimidinyl-2-ylidene (**1**) and 2-chloro-1,3-dimesityl-5,5-dimethyl-4,6-diketopyrimidine (**2**·HCl) were synthesized using previously reported procedures.[1-3] Dimethylmalonyl dichloride and 2,4,6-trimethylaniline were obtained from TCI America and used as received. Triethylorthoformate was purchased from Alfa Aesar and used as received. Sodium bis(trimethylsilyl)amide (NaHMDS) and 2,6-di-*iso*-propylaniline were purchased from ACROS and were used as received. Benzene was dried over molecular sieves and distilled prior to use. Dichloromethane (CH_2Cl_2) and hexanes were dried and degassed by a Vacuum Atmospheres Company solvent purification system and stored over molecular sieves in a nitrogen-filled glove box. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX FTIR spectrophotometer. UV–visible spectra were recorded using a Perkin Elmer Lambda 35 UV–vis spectrophotometer. High resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (CI). NMR spectra were recorded on Varian UNITY+ 300, Varian Mercury 400, and Varian INOVA 500 spectrometers. Chemical shifts (δ) are given in ppm and are referenced to the residual protio solvent (^{1}H: $CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm; C_7H_8, 2.09 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm, C_7D_8, 128.3 ppm). Elemental analyses were performed at Midwest Microlab, LLC (Indianapolis, IN). Melting points were obtained using a Mel-Temp apparatus and are uncorrected.

Synthesis of 2-chloro-1,3-bis(2,6-di-*iso*-propylphenyl)-4,6-diketo-5,5-dimethylpyrimidine (1·HCl). Dimethylmalonyl dichloride (0.75 mL, 5.60 mmol, 1.05 equiv.) was added dropwise to a stirred solution of *N,N′*–di-*iso*-propylphenylformamidine (1.95 g, 5.35 mmol) and triethylamine (1.1 mL, 8.0 mmol, 1.5 equiv.) in CH_2Cl_2 (30 mL) at 0 °C. The solution was stirred at 0 °C for 1 h whereupon the volatiles were removed under reduced pressure. The resulting solid was taken up into a mixture of hexanes:CH_2Cl_2 (2:1 v:v) (24 mL) and passed through a plug of Celite. After removal of the residual solvent, the residue was washed a mixture of hexanes:CH_2Cl_2 (2:1 v:v) (18 mL). Removal of the volatiles under reduced pressure afforded the desired product as a white solid (2.56 g, 96% yield). m.p. = 163–165 °C (dec.) ^{1}H NMR ($CDCl_3$, 300.15 MHz): 1.12 (d, ^3J = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.32 (d, ^3J = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.33 (s, 6H, CH(CH_3)$_2$), 1.76 (s, 6H, C(CH_3)$_2$), 3.07 (sept., ^3J = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 6.85 (s, 1H, NC*H*N), 7.27 (s, 2H, Ar-*H*), 7.39 (d of d, *J* = 8.4 Hz, 2H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 75.47 MHz): 8.56, 23.07, 24.00, 24.64, 29.20, 45.71, 47.85, 90.15, 124.63, 130.00, 132.11, 146.80, 171.71. IR (KBr): ν_{CO} = 1708, 1685 cm^{-1}. HRMS [M+H]$^+$ calcd. for $C_{30}H_{42}ClN_2O_2$: 497.2935; Found: 497.2942. Anal. Calcd. for $C_{30}H_{41}ClN_2O_2$: C, 72.48; H, 8.31; N, 5.64; Found: C, 72.49; H, 8.41; N, 5.41.

Synthesis of 2-chloro-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (2·HCl). Dimethylmalonyl dichloride (0.75 mL, 5.60 mmol, 1.05 equiv.) was added dropwise to a stirred solution of *N,N′*-dimesitylformamidine (1.5 g, 5.35 mmol) and triethylamine (1.1 mL, 8.0 mmol, 1.5 equiv.) in CH_2Cl_2 (30 mL) at 0 °C. The solution was stirred at 0 °C for 1 h whereupon the residual solvent was removed under reduced pressure. The resulting solid was taken up into a mixture of hexanes:CH_2Cl_2 (2:1 v:v) (24 mL) and passed through a plug of Celite. The residue was washed with a mixture of hexanes:CH_2Cl_2 (2:1 v:v) (18 mL). Removal of the volatiles under reduced pressure afforded **2**·HCl as a white solid (2.04 g, 92% yield). Single crystals suitable for

X-ray diffraction analysis were grown from the slow vapor diffusion of *n*-pentane into a concentrated solution of **2**·HCl in CH_2Cl_2. Spectroscopic and melting point data were in accord with the reported literature values.[3]

Synthesis of *N,N'*-dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene (2). A vial was charged with **2**·HCl (600 mg, 1.45 mmol), NaHMDS (267 mg, 1.46 mmol), benzene (25 mL) and a stir bar. The solution was stirred at ambient temperature for 30 min and then filtered through a PTFE filter. After removing the residual solvent under reduced pressure, the solid residue was washed with cold hexanes, decanted, and then dried under vacuum to afford the desired product as a white solid (462 mg, 85% yield). Slow diffusion of hexanes into toluene saturated with **2** afforded crystals suitable for X-ray diffraction analysis. m.p. = 166–168 °C (dec.) ^{1}H NMR (C_6D_6, 300.14 MHz): δ 1.48 (s, 6H, C(C*H*$_3$)$_2$), 2.11 (s, 18H, Ar-C*H*$_3$), 6.78 (s, 4H, Ar-*H*). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.24, 20.95, 24.49, 51.07, 129.60, 134.56, 137.69, 138.70, 170.19, 277.73. IR (KBr): ν_{CO} = 1709 cm^{-1}. HRMS: $[M+H]^+$ calcd. for $C_{24}H_{29}N_2O_2$: 377.2229; Found: 377.2228.

Synthesis of 2-oxomethylene-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (3). An 8 mL vial was charged with C_7D_8 (1 mL) and **2** (39.2 mg, 0.104 mmol) and then transferred to a Wilmad QPV high pressure NMR tube. Three freeze-pump-thaw cycles were performed and the tube's headspace was filled with CO (g) (15 psi). Upon mixing, the solution turned purple in color, indicating the formation of **3** which was spectroscopically characterized but not isolated. The K_{eq} for equilibrium for **2** + CO (15 psi) ⇌ **3** was determined as previously described.[2] ^{1}H NMR (C_7D_8, 499.87 MHz): δ 1.70 (s, 6H, C(C*H*$_3$)$_2$), 1.88 (s, 6H, Ar-C*H*$_3$), 2.04 (s, 12H, Ar-C*H*$_3$), 6.38 (s, 4H, Ar-*H*). ^{13}C NMR (C_7D_8, 125.71 MHz): δ 18.37, 21.01, 21.97, 48.54, 91.70, 129.84, 131.816, 135.39, 137.09, 139.05, 167.98, 246.41. IR (C_7H_8, CaF_2): $\nu_{CC=O}$ = 2092 cm^{-1}; $\nu_{C=O}$ = 1681 cm^{-1}. UV–Vis (C_7H_8): λ_{max} = 543 nm.

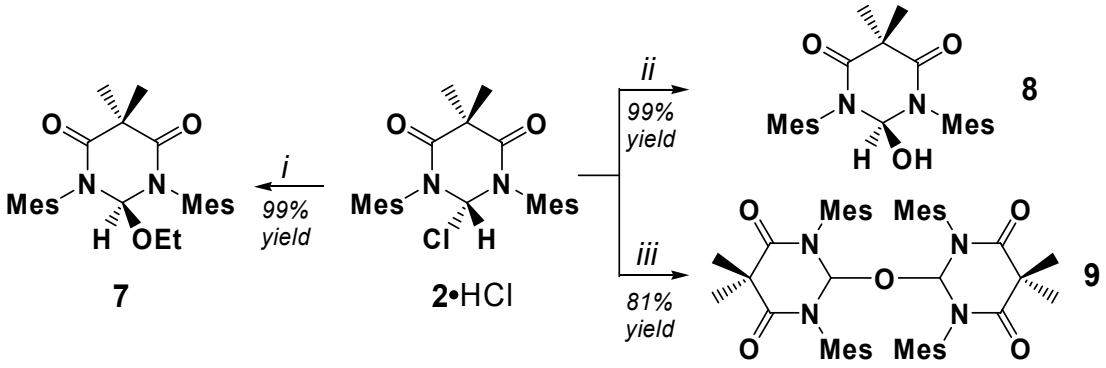
Synthesis of 2-((2,6-dimethylphenylimino)methylene)-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (4). An 8 mL vial was charged with benzene (2 mL), 2,6-dimethylphenylisocyanide (26 mg, 0.198 mmol), **2** (74 mg, 0.198 mmol) and a stir bar. The resulting mixture was stirred at ambient temperature for 1 h. Removal of the residual solvent under reduced pressure afforded the desired product as a bright, orange solid (96 mg, 96% yield). Evaporation to dryness of a pentane solution of **4** afforded crystals suitable for X-ray diffraction analysis. m.p. = 153–154 °C. ^{1}H NMR (C_6D_6, 300.14 MHz): δ 1.63 (s, 6H, C(C*H*$_3$)$_2$), 1.84 (s, 6H, Ar-C*H*$_3$), 1.96 (s, 6H, Ar-C*H*$_3$), 2.21 (s, 12H, Ar-C*H*$_3$), 6.60 (s, 4H, Ar-*H*), 6.61-6.71 (m, 3H, Ar-*H*). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 17.91, 18.28, 20.79, 23.72, 47.96, 106.27, 126.80, 128.49, 129.73, 130.95, 132.90, 136.44, 138.56, 139.47, 167.84, 202.68. IR (KBr): $\nu_{C=N}$ = 1978 cm^{-1}; ν_{CO} = 1696, 1662 cm^{-1}. HRMS: $[M+H]^+$ calcd. for $C_{33}H_{38}N_3O_2$: 508.2957; Found: 508.2964. Anal. Calcd. for $C_{33}H_{37}N_3O_2$: C, 78.07; H, 7.35; N, 8.28; Found: C, 77.77; H, 7.19; N, 8.26.

Synthesis of 2-amino-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (5). A 25 mL Schlenk flask was charged with **2** (53 mg, 0.14 mmol) and a stir bar, and then placed under an atmosphere of ammonia gas. The reaction vessel was then cooled to –78 °C. After approximately 3 mL of ammonia had condensed, the reaction mixture was slowly warmed to ambient temperature over 12 h. The residue, which was later determined to be the desired product, was isolated as a white solid (55 mg, 99% yield). Single crystals suitable for X-ray diffraction

analysis were grown from a concentrated solution of hexanes:CH_2Cl_2 (2:1 v:v) at –30 °C. m.p. = 162–163 °C. ^{1}H NMR (C_6D_6, 300.14 MHz): δ 1.15 (d, ^3J = 6.30 Hz, 2H, NH_2), 1.79 (s, 3H, CCH_3), 1.81 (s, 3H, CCH_3), 2.05 (s, 6H, Ar-CH_3), 2.10 (s, 6H, Ar-CH_3), 2.21 (s, 6H, Ar-CH_3), 5.22 (t, ^3J = 6.60 Hz, 1H, CHNH$_2$), 6.70 (s, 2H, Ar-H), 6.73 (s, 2H, Ar-H). ^{13}C NMR (C_6D_6, 75.47 MHz): 18.46, 19.27, 20.86, 46.82, 79.11, 129.81, 129.92, 134.34, 135.36, 137.61, 137.99, 170.31. IR (KBr): ν_{NH} = 3415.7, 3339.4 cm^{-1}; ν_{CO} = 1672.4, 1645.6 cm^{-1}. HRMS: [M+H]$^+$ calcd. for $C_{24}H_{32}N_3O_2$: 394.2495; Found: 394.2495. Anal. Calcd. for $C_{24.5}H_{32}Cl_1N_3O_2$ ($C_{24}H_{31}N_3O_2 \cdot 0.5CH_2Cl_2$): C, 67.49; H, 7.40; N, 9.64; Found: C, 67.21; H, 7.36; N, 9.49.

Synthesis of 2-amino-1,3-bis(2,6-diisopropylphenyl)- 4,6-diketo-5,5-dimethylpyrimidine (6). Compound **1** was prepared in situ from [**1**H][OTf] (100 mg, 0.164 mmol) and NaHMDS (30 mg, 0.164 mmol, 1 equiv.) in toluene (1 mL) using a previously reported procedure.[2] The resulting solution was then frozen in N_2 (liq.) and the reaction atmosphere was removed under vacuum. The reaction vessel was then placed under an atmosphere of ammonia gas. After approximately 3 mL of ammonia had condensed, the reaction mixture was slowly warmed to ambient temperature over 12 h. Recrystallization of the remaining residue from a mixture of CH_2Cl_2 and hexanes at –20 °C afforded the desired product as a white solid (65 mg, 83% yield). m.p. = 181–182 °C. ^{1}H NMR (C_6D_6, 300.14 MHz): δ 0.94 (d, ^3J = 5.70 Hz, 2H, NH_2), 1.14 (s, 3H, CCH_3), 1.16 (s, 3H, CCH_3), 1.21 (s, 6H, Ar-CH_3), 1.23 (s, 6H, Ar-CH_3), 1.30 (s, 3H, Ar-CH_3), 1.33 (s, 3H, Ar-CH_3), 1.79 (s, 3H, Ar-CH_3), 1.83 (s, 3H, Ar-CH_3), 3.13 (sept., ^3J = 6.90 Hz, 2H, CH(CH$_3$)$_2$), 3.26 (sept., ^3J = 6.90 Hz, 2H, CH(CH$_3$)$_2$), 5.33 (t, ^3J = 6.15 Hz, 1H, NCHN), 7.09 (d of t, ^3J = 7.50 Hz, 4H, Ar-H), 7.15-7.23 (m, 2H, Ar-H). ^{13}C NMR (C_6D_6, 75.47 MHz): 23.24, 23.48, 23.58, 24.98, 25.18, 26.52, 29.44, 29.54, 46.61, 80.63, 124.17, 124.67, 129.37, 133.77, 146.12, 148.87, 171.58. IR (KBr): ν_{NH} = 3454, 3351 cm^{-1}; ν_{CO} = 1677, 1649 cm^{-1}. HRMS: [M+H]$^+$ calcd. for $C_{30}H_{44}N_3O_2$: 478.3434; Found: 478.3431. Anal. Calcd. for $C_{30}H_{43}N_3O_2$: C, 75.43; H, 9.07; N, 8.80; Found: C, 75.52; H, 9.06; N, 8.72.

Compound **2**·HCl was reported[3] to be moisture sensitive and to react with methanol. Additional studies are summarized in Scheme S1.



Scheme S1. Synthesis of compounds **7**, **8** and **9**. Conditions: *i*) CH_3CH_2OH (excess), 25 °C, 15 min.; *ii*) H_2O (excess), CH_2Cl_2, 25 °C, 15 min.; *iii*) H_2O (0.5 equiv.), CH_2Cl_2, 25 °C, 15 min.

Synthesis of 2-ethoxy-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (7). An 8 mL vial was charged with **2**·HCl (100 mg, 0.242 mmol), ethanol (3 mL) and a stir bar. The resulting solution was stirred for 15 min at ambient temperature. Subsequent removal of the solvent under reduced pressure afforded **7** as a white powder (101 mg, 99% yield). Evaporation of toluene from a

concentrated toluene solution of **7** afforded single crystals suitable for X-ray diffraction analysis (see Figure S1). m.p. = 190–191 °C (dec.) ^{1}H NMR ($CDCl_3$, 300.15 MHz): δ 0.70 (t, ^3J = 7.05 Hz, 3H, OCH_2CH_3), 1.56 (s, 3H, CCH_3), 1.82 (s, 3H, CCH_3), 2.26 (s, 12H, Ar-CH_3), 2.28 (s, 6H, Ar-CH_3), 2.85 (q, ^3J = 7.05 Hz, 2H, OCH_2), 5.36 (s, 1H, NC*H*N), 6.91 (s, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 125.6 MHz): δ 14.71, 18.20, 18.55, 20.89, 21.15, 28.07, 46.81, 68.22, 96.46, 129.41, 129.78, 133.19, 134.36, 138.10, 138.18, 170.69. IR (KBr): ν_{CO} = 1701, 1669 cm^{-1}. HRMS: $[M+H]^+$ calcd. for $C_{26}H_{35}N_2O_3$: 423.2648; Found: 423.2651. Anal. Calcd. for $C_{26}H_{34}N_2O_3$: C, 73.90; H, 8.11; N, 6.63; Found: C, 73.66; H, 8.07; N, 6.75.

Synthesis of 2-hydroxy-1,3-dimesityl-4,6-diketo-5,5-dimethylpyrimidine (8). A 20 mL vial was charged with CH_2Cl_2 (3 mL), **2**·HCl (100 mg, 0.242 mmol), water (0.25 mL, 13.9 mmol) and a stir bar. The mixture was stirred under ambient conditions for 15 min. Subsequent removal of the residual solvent under reduced pressure afforded **8** as a white powder (95 mg, 99% yield). m.p. = 161–162 °C. ^{1}H NMR ($CDCl_3$, 300.15 MHz): δ 1.37 (s, 3H, CCH_3), 1.65 (s, 3H, CCH_3), 2.03 (s, 6H, Ar-CH_3), 2.09 (s, 6H, Ar-CH_3), 2.25 (s, 6H, Ar-CH_3), 4.01 (d, ^3J = 4.50 Hz, 1H, O*H*), 5.53 (d, ^3J = 4.50 Hz, 1H, NC*H*N), 6.81 (s, 4H, Ar-*H*). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 18.00, 18.57, 20.90, 27.66, 46.65, 88.49, 129.23, 129.67, 132.92, 134.68, 137.89, 138.18, 170.99. IR (KBr): ν_{OH} = 3305 cm^{-1}; ν_{CO} = 1692, 1648 cm^{-1}. HRMS: $[M+H]^+$: calcd for $C_{24}H_{31}N_2O_3$: 395.2335; Found: 395.2335. Anal. Calcd. for $C_{24}H_{32}N_2O_4$ (8·H_2O): C, 69.88; H, 7.82; N, 6.79; Found: C, 69.39; H, 7.70; N, 6.81.

Synthesis of di-*N,N'*-dimesityl-4,6-diketo-5,5-dimethylpyrimidinyl ether, [(2·H)$_2$(μ–O)] (9). A 20 mL vial was charged with benzene (1 mL), **2** (54 mg, 0.143 mmol), water (1.3 μL, 1.3 mg, 0.072 mmol, 0.5 equiv.) and a stir bar, and then stirred open to the atmosphere for 2 min. Removal of the residual solvent followed by recrystallization from a mixture of hexanes:CH_2Cl_2 (2:1 v:v) afforded **9** as a white solid (45 mg, 81% yield). Single crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of *n*-pentane into a toluene solution saturated with **9** (see Figure S2). m.p. = 122–123 °C. ^{1}H NMR (C_6D_6, 300.14 MHz): 1.35 (s, 6H), 1.37 (s, 3H), 1.70 (s, 6H), 1.75 (s, 6H), 1.98 (s, 6H), 2.02 (s, 6H), 2.12 (s, 6H), 2.60 (s, 6H), 6.33 (s, 2H), 6.38 (s, 6H), 6.49 (s, 6H), 6.76 (s, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): 17.55, 17.73, 19.43, 19.71, 20.69, 20.80, 21.67, 27.93, 47.89, 92.16, 129.39, 129.97, 130.31, 130.40, 131.33, 135.19, 135.70, 136.16, 137.02, 137.89, 138.79, 138.89, 139.82, 170.97, 171.38. IR (KBr): ν_{CO}: 1704, 1679 cm^{-1}. HRMS: $[M–H]^+$: calcd for $C_{48}H_{57}N_4O_5$: 769.4329; Found: 769.4317. Anal. Calcd. for $C_{48}H_{58}N_4O_5$: C, 74.77; H, 7.58; N, 7.27; Found: C, 74.40; H, 7.39; N, 7.32.

X-Ray Crystallography. Single crystals of **2**·HCl were obtained by slow vapor diffusion of *n*-pentane into a saturated CH_2Cl_2 solution. This compound crystallized in the primitive monoclinic space group $P2_{1/c}$ with four molecules in the asymmetric unit. Colorless single crystals of **2** were grown by slow diffusion of hexanes vapor into a saturated toluene solution. This compound crystallized in the primitive monoclinic space group $P2_{1/c}$ with four molecules in the asymmetric unit. The NH_3 adduct **5** was crystallized at –30 °C from a concentrated hexanes:CH_2Cl_2 (2:1 v:v) solution as colorless, elongated blocks. This compound crystallized in the centrosymmetric monoclinic space group $C_{2/c}$ with 8 molecules in the asymmetric unit and solvated with 0.5 molecules of CH_2Cl_2. Single crystals of **7** were grown by slow evaporation of a concentrated toluene solution. This compound crystallized in the primitive monoclinic space group $P2_{1/n}$ with 4 molecules in the asymmetric unit. Ether **9** was crystallized by slow vapor diffusion *n*-pentane into a saturated toluene solution. This compound crystallized in the primitive monoclinic space group $P2_{/c}$ with two crystallographically independent molecules and two interstitial molecules of toluene in the unit cell. Additionally, one highly disordered toluene molecule was removed via the SQUEEZE application. Despite our best efforts, only low quality crystals of **9** were obtained. As a result, the respective crystallographic data was used only to provide additional support for the general structure of this compound. All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150 K using an Oxford Cryostream low temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using DENZO-SMN.[4] The structures were solved by direct methods which successfully located most of the non-hydrogen atoms. Subsequent refinements on F_2 using the SHELXTL/PC package (version 5.1)[5] allowed location of the remaining non-hydrogen atoms. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **2**·HCl, **2**, **5**·0.5(CH_2Cl_2), **7** and **9**·(C_7H_8) were assigned as 770147, 770148, 770149, 770150 and 770151, respectively.

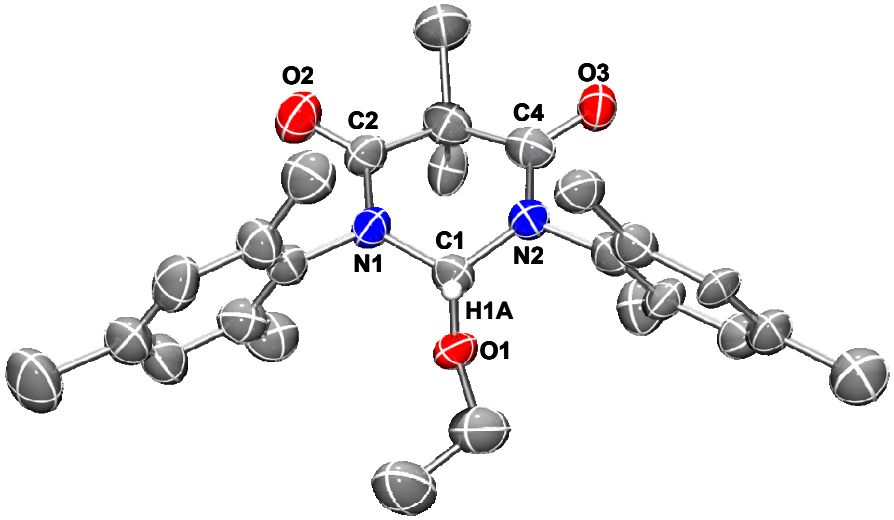


Figure S1. POV-Ray representation of **7** (50% ellipsoids, H atoms except for H1A have been omitted for clarity). Key bond distances (Å) and angles (°): C1–O1, 1.415(4); C1–N1, 1.448(4); N1–C2, 1.369(5); C1–N2, 1.455(4); N2–C4, 1.370(5); C2–O2, 1.214(4); C4–O3, 1.222(4); N1–C1–N2 = 112.6(3); N1–C1–O1 = 110.4(3); N2–C1–O1 = 110.7(3); N1–C2–O2 = 121.3(3); N2–C4–O3 = 121.5(3).

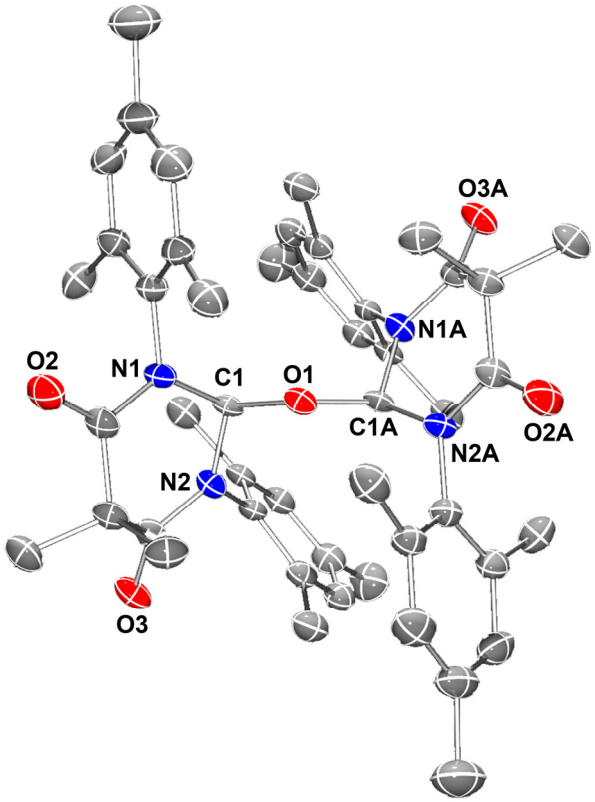


Figure S2. POV-Ray representation of **9** (50% ellipsoids, H atoms and solvent molecules have been omitted for clarity).

Table S1. Crystal Data, Data Collection, and Structure Refinement for **2**·HCl, **2**, **5**·(0.5 CH_2Cl_2), **7**, and **9**·(C_7H_8).

	2·HCl	**2**	**5**·(0.5 CH_2Cl_2)	**7**	**9**·(C_7H_8)[b]
Formula	$C_{24}H_{29}ClN_2O_2$	$C_{24}H_{28}N_2O_2$	$C_{24.50}H_{32}ClN_3O$	$C_{26}H_{34}N_2O_3$	$C_{55}H_{66}N_4O_5$
M_r	412.94	376.48	435.98	422.55	863.12
crystal size (mm^3)	0.28 × 0.22 × 0.08	0.30 × 0.21 × 0.14	0.62 × 0.13 × 0.11	0.50 × 0.18 × 0.06	0.39 × 0.11 × 0.1
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1/c}$	$P2_{1/c}$	$C_{2/c}$	$P2_{1/n}$	$P2_c$
a (Å)	8.3918(12	17.7632(14)	15.7619(11)	15.690(3)	13.884(3)
b (Å)	17.082(2)	16.2017(12)	25.7674(18)	8.4031(16)	15.417(3)
c (Å)	15.992(2)	7.6426(6)	11.6636(9)	18.318(4)	24.502(5)
α (°)	90	90	90	90	90
β (°)	102.394(2)	97.686(2)	92.970(2)	92.840(4)	99.35(3)
γ (°)	90	90	90	90	90
V ($Å^3$)	2239.0(6)	2179.7(3)	4730.7(6)	2412.1(8)	5175.0(18)
Z	4	4	8	4	4
ρ_{calc} (g cm^{-3})	1.225	1.147	1.224	1.164	1.108
μ (mm^{-1})	0.192	0.073	0.187	0.076	0.071
F(000)	880	808	1864	912	1856
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
scan mode	ω	ω	ω	ω	ω
hkl range	-9 → +9 -20 → +20 -19 → +19	-21 → +21 -19 → +19 -9 → +9	-18 → +18 -30 → +30 -13 → +13	-17 → +17 -9 → +9 -20 → +20	-16 → +16 -18 → +18 0 → +29
measd reflns	19164	18370	20564	18117	17760
unique reflns [R_{int}]	3926 [0.0315]	3830 [0.0307]	4162 [0.0373]	3782 [0.1109]	9109 [0.1121]
refinement reflns	3926	3830	4162	3782	9109
refined parameters	262	253	287	280	578
GOF on F^2	1.006	1.008	1.008	1.006	1.004
R1[a] (all data)	0.0544 (0.0608)	0.0586 (0.0701)	0.0578 (0.0700)	0.0749 (0.1223)	0.0823 (0.2052)
wR2[b] (all data)	0.1696 (0.1772)	0.1543 (0.1640)	0.1528 (0.1637)	0.1384 (0.1623)	0.1618 (0.1888)
ρ_{fin} (max/min)	0.420	0.380	0.680	0.331	0.286
(e $Å^{-3}$)	-0.313	-0.363	-0.573	-0.254	-0.261

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$ [b] Squeeze was used to remove a disordered solvent molecule.

References

1 E. Despagnet-Ayoub and R. H. Grubbs, *J. Am. Chem. Soc*., 2004, **126**, 10198.

2 T. W. Hudnall and C. W. Bielawski, *J. Am. Chem. Soc*., 2009, **131**, 16039.

3 V. César, N. Lugan and G. Lavigne, *Eur. J. Inorg. Chem.*, 2010, **3**, 361.

4 Z. Otwinowski and W. Minor, in *Macromolecular Crystallography, Part A*, **Vol. 276** (Eds.: C. W. Carter Jr., R. M. Sweets), Academic Press, 1997, 307–326.

5 G. M Sheldrick, SHELXTL/PC package (version 5.1) program for the refinement of crystal structure, University of Gottingen, Germany ed., 2003.