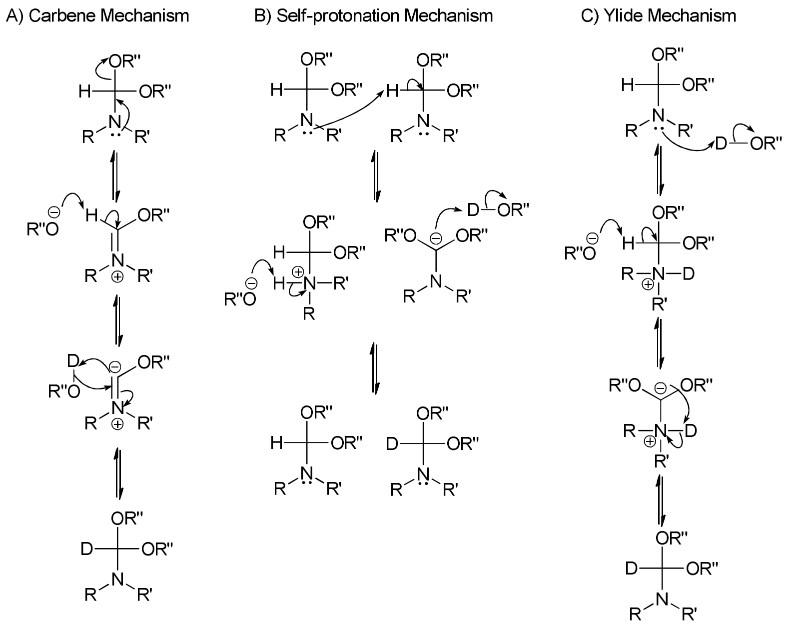
Electronic Supporting Information

1. Proposed mechanisms



A) Carbene Mechanism

B) Self-protonation Mechanism

C) Ylide Mechanism

Scheme 1 Mechanisms proposed for H-D exchange in *N,N*-dialkylated formamides.[1]

2. Synthesis

Unless otherwise stated, reactions were performed under air in glassware that was not predried. Inert conditions are defined as reactions performed under argon (zero grade) in vacuum-dried glassware using dry solvents and standard syringe techniques. Triethylamine was freshly distilled from calcium hydride. All other reagents and solvents were used as received from commercial suppliers. Degasification was performed by the standard freeze-pump-thaw technique, with three repetitions. Purification of products via flash chromatography was conducted using silica gel 60 (220-240 mesh). NMR spectra were recorded on a Varian Unity Inova 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer. ^{15}N-NMR spectra for structural elucidation and NMR-scale reactions were recorded on a Varian DirectDrive 600 (600 MHz for ^{1}H, 150 MHz for ^{13}C and 60 MHz for ^{15}N) equipped with a Varian inverse-detected triple-resonance HCN cold probe operating at 25K. *J* values are recorded in Hz. Infra-red (IR) spectra were obtained on a Brüker Tensor 27 spectrometer. High-Resolution ElectroSpray Mass Spectrometry (HRESIMS) was performed on a Waters Q-TOF Premier Tandem mass spectrometer.

N,1-Dimethyl-4-(methylamino)-1*H*-imidazole-5-carboxamide (**6**)

Caffeine (10.0 g, 51.5 mmol) was added to a solution of NaOH (2.40 g, 60 mmol) in H_2O (30 mL) and refluxed for two hours. The reaction was cooled with ice, HNO_3 (6.25 mL, 105 mmol) was added dropwise and the resulting white solid was filtered and washed with water. The precipitate was dissolved in a solution of K_2CO_3 (6.00 g, 43.4 mmol) in H_2O (20 mL), the resulting oil was extracted with $CHCl_3$ (3 x 20 mL) and the organic phase concentrated under reduced pressure to afford a white solid. Recrystalisation from EtOAc yielded **6** (3.22 g, 37%) as a white crystal.

Mp 85.7-85.9 ^oC (from EtOAc)(lit.,[2] 93 ^oC); ν_{max}/cm^{-1} 3377 (NH), 3114 (CH), 2954 (CH), 1607 (CO), 1574, 1536 (CN); δ_H (500 MHz; $CDCl_3$) 7.21 (1 H, s, C(2)*H*), 6.98 (1 H, br s, N(N)*H*), 3.87 (3 H, s, N(1)C*H*$_3$), 3.68 (1 H, br s, N(4)*H*), 2.94 (3 H, d, *J* 4.8, N(N)C*H*$_3$), 2.89 (3 H, s, N(4)C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 162.3 (*C*=O), 151.9 (*C*(4)), 137.3 (*C*(2)), 110.9 (*C*(5)), 34.9 (N(1)*C*H$_3$), 32.8 (N(4)*C*H$_3$), 25.7 (N(N)C*H*$_3$); HRESIMS (*m/z* 169.1086 $[M+H]^+$ calcd for $C_7H_{13}N_4O$, 169.1089, Δ = -1.8 ppm).

4-[Formyl(methyl)amino]-*N*,1-dimethyl-1*H*-imidazole-5-carboxamide (**3**)

Formic acid (2.21 mL, 58.6 mmol) and acetic anhydride (5.00 mL, 53.0 mmol) were heated together at 55 ^oC for two hours. The reaction was cooled, **6** (3.22 g, 19.1 mmol) was added and the reaction was stirred at room temperature for 12 hours. The reaction was concentrated under reduced pressure and the resulting pale yellow oil was crystallised from EtOAc to yield **3** (1.93 g, 51%) as a tan crystal.

Mp 145.0-146.1 ^oC (from EtOAc)(lit.,[2] 141-143 ^oC); δ_H (500 MHz; $CDCl_3$) Rotamer A- 8.26 (1 H, s, N(4)C*H*=O), 7.57 (1 H, br s, N(*N*)*H*), 7.39 (1 H, s, C(2)*H*), 3.82 (3 H, s, N(1)C*H*$_3$), 3.36 (3 H, s, N(4)C*H*$_3$), 2.84 (3 H, d, *J* 5.4, N(*N*)C*H*$_3$), Rotamer B- 8.29 (1 H, s, N(4)C*H*=O), 7.38 (1 H, s, C(2)*H*), 6.02 (1 H, br s, N(*N*)*H*), 3.91 (3 H, s, N(1)C*H*$_3$), 3.25 (3 H, s, N(4)C*H*$_3$), 2.93 (3 H, d, *J* 5.4, N(*N*)C*H*$_3$); δ_H (500 MHz; CD_3OD) Rotamer A- 8.28 (1 H, s, N(4)C*H*=O), 7.70 (1 H, s, C(2)*H*), 3.83 (3 H, s, N(1)C*H*$_3$), 3.37 (3 H, s, N(4)C*H*$_3$), 2.84 (3 H, s, N(*N*)C*H*$_3$), Rotamer B- 8.25 (1 H, s, N(4)C*H*=O), 7.67 (1 H, s, C(2)*H*), 3.82 (3 H, s, N(1)C*H*$_3$), 3.21 (3 H, s, N(4)C*H*$_3$), 2.86 (3 H, s, N(*N*)C*H*$_3$); δ_H (500 MHz; DMSO-d_6) Rotamer A- 8.20 (1H, s, N(4)C*H*=O), 7.69 (1 H, s, C(2)*H*), 7.46 (1 H, br s, N(*N*)*H*), 3.72 (3 H, s, N(1)C*H*$_3$), 3.26 (3 H, s, N(4)C*H*$_3$), 2.68 (3 H, d, *J* 4.8, N(*N*)C*H*$_3$), Rotamer B- 8.18 (1 H, s, N(4)C*H*=O), 7.96 (1 H, br s, N(*N*)*H*), 7.68 (1 H, s, C(2)*H*), 3.70 (3 H, s, N(1)C*H*$_3$), 3.07 (3 H, s, N(4)C*H*$_3$), 2.72 (3 H, d, *J* 4.5, N(*N*)C*H*$_3$); δ_H (500 MHz; D_2O) Rotamer A- 8.24 (1 H, s, N(4)C*H*=O), 7.67 (1 H, s, C(2)*H*), 3.76 (3 H, s, N(1)C*H*$_3$), 3.35 (3 H, s, N(4)C*H*$_3$), 2.83 (3 H, s, N(*N*)C*H*$_3$), Rotamer B- 8.22 (1H, s, N(4)C*H*=O), 7.64 (1 H, s, C(2)*H*), 3.75 (3 H, s, N(1)C*H*$_3$), 3.18 (3 H, s, N(4)C*H*$_3$), 2.86 (3 H, s, N(*N*)C*H*$_3$); δ_C (125 MHz; $CDCl_3$) Rotamer A- 164.3 (N(4)*C*H=O), 160.5 (C(5)*C*=O), 138.2 (*C*(2)), 136.5 (*C*(4)), 121.7 (*C*(5)), 37.4 (N(4)*C*H$_3$), 34.4 (N(1)*C*H$_3$), 26.4 (N(*N*)*C*H$_3$), Rotamer B- 163.8 (N(4)*C*H=O), 159.9 (C(5)*C*=O), 141.3 (*C*(4)), 138.4 (*C*(2)), 118.4 (*C*(5)), 35.3 (N(1)*C*H$_3$), 32.6 (N(4)*C*H$_3$), 26.3 (N(*N*)*C*H$_3$); δ_C (125 MHz; DMSO-d_6) Rotamer A- 163.2 (N(4)*C*H=O), 159.8 (C(5)*C*=O), 137.7 (*C*(2)), 136.9 (*C*(4)), 119.6 (*C*(5)), 35.9 (N(4)*C*H$_3$), 33.5 (N(1)*C*H$_3$), 25.8 (N(*N*)*C*H$_3$), Rotamer B- 162.5 (N(4)*C*H=O), 159.8 (C(5)*C*=O), 140.4 (*C*(4)), 138.0 (*C*(2)), 117.7 (*C*(5)), 33.8 (N(1)*C*H$_3$), 31.5 (N(4)*C*H$_3$), 25.8 (N(*N*)*C*H$_3$); δ_N (60 MHz; $CDCl_3$) Rotamer A- -129 (*N*(3)), -217 (*N*(1)), -258 (*N*(4)), -273 (*N*(*N*)), Rotamer B- -127 (*N*(3)), -215 (*N*(1)), -262 (*N*(4)), -281 (*N*(*N*)); HRESIMS (*m/z* 197.1033 $[M+H]^+$, calcd for $C_8H_{13}N_4O_2$, 197.1039, Δ = 3.0 ppm; *m/z* 219.0856 $[M+Na]^+$, calcd for $C_8H_{12}N_4O_2Na$, 219.0858, Δ = -0.9 ppm).

N-Methyl-2-(methylamino)benzamide (**8**)

N-methylisatoic anhydride (9 g, 50.8 mmol) was dissolved in H_2O (26.6 mL), aq. CH_3NH_2 (9.62 mL, 40% w/w., 124 mmol) was added and the reaction was stirred at 50 ^oC for 1 hour. The reaction was cooled, diluted with H_2O (50 mL) and extracted with EtOAc (50 mL x 2). The combined organic phases were washed with sat. aq. NH_4Cl (50 mL x 2), H_2O (50 mL x 2), brine (50 mL x 2), dried over $MgSO_4$, filtered and the filtrate concentrated under reduced pressure to yield **8** as a white powder (8.17 g, 98%).

ν_{max}/cm^{-1} 3358 (NH), 3007 (CH), 2938, 2903 (CH), 1629 (CO), 1518 (CC); δ_H (500 MHz; $CDCl_3$) 7.42 (1 H, br s, N(2)*H*), 7.31 (1 H, t, *J* 8.0, C(4)*H*, 7.30 (1 H, d, *J* 7.6, C(6)*H*), 6.66 (1 H, d, *J* 8.3, C(3)*H*), 6.56 (1

H, t, *J* 7.3, C(5)*H*), 6.12 (1 H, br s, N(*N*)*H*), 2.94 (3 H, d, *J* 4.9, N(*N*)C*H*$_3$), 2.85 (3 H, br s, N(*N*)C*H*$_3$); δ_C (125 MHz; CDCl$_3$) 170.7 (*C*=O), 150.5 (*C*(2)), 132.8 (*C*(4)), 127.2 (*C*(6)), 115.4 (*C*(1)), 114.6 (*C*(5)), 111.2 (*C*(3)), 29.8 (N(2)*C*H$_3$), 26.6 (N(*N*)*C*H$_3$); HRESIMS (*m/z* 187.0850 [M+Na]$^+$, calcd for $C_9H_{12}N_2ONa$, 187.0847, Δ = 1.6 ppm; *m/z* 165.1031 [M+H]$^+$, calcd for $C_9H_{13}N_2O$, 165.1028, Δ = 1.8 ppm).

N-Methyl-2-(*N*-methylformamido)benzamide (**4**)

Formic acid (1.15 mL, 30.42 mmol) and acetic anhydride (2.61 mL, 27.65 mmol) were heated together for 2 hours at 55 °C. The reaction was cooled, **8** was added and the reaction stirred at room temperature for 12 hours. The reaction was concentrated under reduced pressure and purified by flash chromatography to yield **4** as a white crystal (2.42 g, 86.2%).

Mp 87.1-87.6 °C (from EtOAc); δ_H (500 MHz; CDCl$_3$) Rotamer A- 8.27 (1 H, s, N(2)C*H*=O), 7.64 (1 H, dd, *J* 7.5 & 1.7, C(6)*H*), 7.51 (1 H, dt, *J* 7.8 & 1.7, C(4)*H*), 7.41 (1 H, dt, *J* 7.5 & 1.2, C(5)*H*), 7.20 (1 H, dd, *J* 7.8 & 1.0, C(3)*H*), 5.85 (1 H, br s, N(*N*)*H*), 3.26 (3 H, s, N(2)C*H*$_3$), 2.99 (3 H, s, N(*N*)C*H*$_3$), Rotamer B- 8.25 (1 H, s, N(2)C*H*=O), 7.55 (1 H, dd, *J* 7.6 & 1.2, C(6)*H*), 7.51 (1 H, dt, *J* 7.8 & 1.4, C(4)*H*), 7.41 (1 H, dt, *J* 7.5 & 1.2, C(5)*H*), 7.18 (1 H, dd, *J* 8.0 & 1.2, C(3)*H*), 6.30 (1 H, br s, N(*N*)*H*), 3.33 (3 H, s, N(2)C*H*$_3$), 2.93 (3 H, s, N(*N*)C*H*$_3$); δ_H (500 MHz; CD$_3$OD) Rotamer A- 8.15 (1 H, s, N(2)C*H*=O), 7.59–7.51 (2 H, m, C(4)*H* & C(6)*H*), 7.45 (1 H, dt, *J* 7.3 & 1.2, C(5)*H*), 7.37 (1 H, dd, *J* 7.9 & 0.9, C(3)*H*), 3.20 (3 H, s, N(2)C*H*$_3$), 2.87 (3 H, s, N(*N*)C*H*$_3$), Rotamer B- 8.19 (1 H, s, N(2)C*H*=O), 7.59–7.51 (2 H, m, C(4)*H* & C(6)*H*), 7.45 (1 H, dt, *J* 7.3 & 1.2, C(5)*H*), 7.32 (1 H, d, *J* 8.2, C(3)*H*), 3.37 (3 H, s, N(2)C*H*$_3$), 2.84 (3 H, s, N(*N*)C*H*$_3$); δ_H (500 MHz; D$_2$O) Rotamer A- 7.98 (1 H, s, N(2)C*H*=O), 7.50–7.45 (1 H, m, C(6)*H*, C(4)*H* or C(5)*H*), 7.42–7.34 (2 H, m, C(6)*H*, C(4)*H* or C(5)*H*), 7.25 (1 H, dd, *J* 8.0 & 0.7, C(3)*H*), 3.03 (3 H, s, N(2)C*H*$_3$), 2.73 (3 H, s, N(*N*)C*H*$_3$), Rotamer B- 8.04 (1 H, s, N(2)C*H*=O), 7.50–7.45 (1 H, m, C(6)*H*, C(4)*H* or C(5)*H*), 7.42–7.34 (2 H, m, C(6)*H*, C(4)*H* or C(5)*H*), 7.22 (1 H, d, *J* 8.1, C(3)*H*), 3.21 (3 H, s, N(2)C*H*$_3$), 2.71 (3 H, s, N(*N*)C*H*$_3$); δ_C (125 MHz; CDCl$_3$) Rotamer A- 167.6 (C(1)*C*=O), 162.6 (N(2)*C*=O), 139.4 (*C*(2)), 133.7 (*C*(1)), 131.5 (*C*(4)), 129.3 (*C*(6)), 128.1 (*C*(5)), 127.6 (*C*(3)), 33.8 (N(2)*C*H$_3$), 27.0 (N(*N*)*C*H$_3$), Rotamer B- 168.5 (C(1)*C*=O), 163.3 (N(2)*C*=O), 137.0 (*C*(2)), 136.2 (*C*(1)), 131.3 (*C*(4)), 128.7 (*C*(6)), 128.7 (*C*(5)), 127.8 (*C*(3)), 38.5 (N(2)*C*H$_3$), 26.7 (N(*N*)*C*H$_3$); HRESIMS (*m/z* 193.0983 [M+H]$^+$, calcd for $C_{12}H_{13}N_2O_2$, 193.0977, Δ = 3.1 ppm; *m/z* 215.0798 [M+Na]$^+$, calcd for $C_{12}H_{12}N_2O_2Na$, 215.0796, Δ = 0.9 ppm).

2-Methoxy-1,3-dimethyl-1,2,3,4-tetrahydroquinazolin-4-one (**9**)

Under inert conditions and with 3 Å molecular sieves, **4** (135 mg, 0.70 mmol) was dissolved in CH$_3$OH (25 mL) and the reaction stirred at room temperature for 12 hours. The reaction was filtered and the filtrate concentrated under reduced pressure to yield a colourless oil that was a mixture of **9** and **4** (1:1.35 ratio).

ν_{max}/cm^{-1} 3076 (CH), 2941, 2885 (CH), 1640 (CO), 1347 (CN), 1275 (CO); δ_H (500 MHz; CDCl$_3$) 7.96 (1 H, d, *J* 7.8, C(5)*H*), 7.41 (1 H, t, *J* 8.3, C(7)*H*), 6.85 (1 H, t, *J* 7.5, C(6)*H*), 6.67 (1 H, d, *J* 8.3, C(8)*H*), 5.77 (1 H, s, C(2)*H*), 3.13 (3 H, s, N(3)C*H*$_3$), 3.03 (3 H, s, N(1)C*H*$_3$), 2.93 (3 H, s, OC*H*$_3$); δ_C (125 MHz; CDCl$_3$) 163.0 (*C*(4)), 145.2 (*C*(8a)), 134.2 (*C*(7)), 128.3 (*C*(5)), 118.2 (*C*(6)), 113.5 (*C*(4a)), 110.2 (*C*(8)), 96.8 (*C*(2)), 49.3 (O*C*H$_3$), 34.6 (N(1)*C*H$_3$), 32.2 (N(3)*C*H$_3$); HRESIMS (*m/z* 207.1139 [M+H]$^+$, calcd for $C_{11}H_{15}N_2O_2$, 207.1134, Δ = 2.4 ppm; *m/z* 229.0945 [M+Na]$^+$, calcd for $C_{11}H_{14}N_2O_2Na$, 229.0953, Δ = 3.5 ppm).

1,3-Dimethyl-4-oxo-3,4-dihydroquinazolin-1-ium chloride (**11**)

Under inert conditions, **4** (400 mg, 2.08 mmol) was suspended in ethylchloroformate (8 mL, 84 mmol) and stirred overnight at 50 °C. The reaction was concentrated under reduced pressure and the resulting solid was rinsed with EtOAc (5 mL x 2). The liquid phase was decanted to yield **11** as a white solid (379 mg, 86 %).

ν_{max}/cm^{-1} 3059, 3029 (CH), 2983, 2955 (CH), 1709 (CO), 1661, 1602 (CN); δ_H (500 MHz; CDCl$_3$) 12.3 (1 H, s, C(2)*H*), 8.45 (1 H, d, *J* 8.6, C(8)*H*), 8.03 (1 H, t, *J* 7.3, C(6)*H*), 7.80 (1 H, t, *J* 7.5, C(7)*H*), 7.74 (1 H, d, *J* 8.1, C(5)*H*), 4.41 (3 H, s, N(3)C*H*$_3$), 3.98 (3 H, s, N(1)C*H*$_3$); δ_C (125 MHz; CDCl$_3$) 157.8 (*C*(8a)), 155.2 (*C*(2)), 138.2 (*C*(4)), 137.0 (*C*(5)), 130.1 (*C*(6)), 129.2 (*C*(8)), 119.7 (*C*(4a)), 117.3 (*C*(7)), 40.4 (N(3)CH$_3$), 36.3 (N(1)CH$_3$); HRESIMS (*m/z* 175.0874 $[M]^+$, calcd for $C_{10}H_{11}N_2O$, 175.0871, Δ = 1.7 ppm).

2-(1,3-Dimethyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-ylidene)-1,3-dimethyl-1,2,3,4-tetrahydroquinazolin-4-one (**13**)

Under inert conditions in an NMR tube, **11** (7.1 mg, 0.034 mmol) was dissolved in degassed $CDCl_3$ (0.55 mL), Ag_2O (15.6 mg, 0.067 mmol) was added and the reaction was allowed to proceed at room temperature for 2 hours. **13** was observed by both NMR and MS spectroscopy, but degraded quantitatively to **14** following exposure to air, or during storage (one day).

δ_H (600 MHz; $CDCl_3$) 7.87 (2 H, d, *J* 7.9, C(5)*H*), 7.38 (2 H, t, *J* 7.8, C(7)*H*), 6.81 (2 H, t, *J* 7.7, C(6)*H*), 6.65 (2 H, d, *J* 8.3, C(8)*H*), 3.13 (6 H, s, N(3)CH_3), 3.00 (6 H, s, N(1)CH_3); δ_C (150 MHz; $CDCl_3$) 161.8 (*C*(4)), 142.0 (*C*(8a)), 133.9 (*C*(7)), 128.3 (*C*(5)), 118.7 (*C*(6)), 112.2 (*C*(8)), 111.7 (*C*(4a)), 106.8 (*C*(2)), 32.3 (N(3)CH$_3$), 34.9 (N(1)CH$_3$); HRESIMS (*m/z* 419.1497 $[M + MeOH + K]^+$, calcd for $C_{21}H_{24}N_4O_3K$, 419.1485, Δ = -2.6 ppm; *m/z* 403.1755 $[M + MeOH + Na]^+$, calcd for $C_{21}H_{24}N_4O_3Na$, 403.1746, Δ = 2.2 ppm; *m/z* 379.1768 $[M + MeO]^-$, calcd for $C_{21}H_{23}N_4O_3$, 379.1770, Δ = -0.5 ppm).

1,3-Dimethyl-1,2,3,4-tetrahydroquinazoline-2,4-dione (**14**)

δ_H (500 MHz; $CDCl_3$) 8.22 (1 H, dd, *J* 7.8 & 1.7, C(5)*H*), 7.67 (1 H, ddd, *J* 8.5, 7.3 & 1.7, C(7)*H*), 7.26 (1 H, ddd, *J* 8.0, 7.2 & 1.0, C(6)*H*), 7.20 (1 H, d, *J* 8.3, C(8)*H*), 3.61 (3 H, s, N(1)CH_3), 3.49 (3 H, s, N(3)CH_3); δ_C (125 MHz; $CDCl_3$) 161.9 (*C*(4)), 151.2 (*C*(2)), 140.4 (*C*(8a)), 135.0 (*C*(7)), 128.9 (*C*(5)), 122.9 (*C*(6)), 115.4 (*C*(4a)), 113.5 (*C*(8)), 30.8 (N(1)CH$_3$), 28.5 (N(3)CH$_3$); HRESIMS (*m/z* found 213.0645 $[M + Na]^+$, calcd for $C_{10}H_{10}N_2O_2Na$, 213.0640, Δ = 2.3 ppm).

Diacetoxybis(1,3-dimethyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-ylidene) palladium(II) (**15**)

Under inert conditions in an NMR tube, **11** (7 mg, 0.033 mmol) was dissolved in degassed $CDCl_3$ (0.55 mL), Ag_2O (15.3 mg, 0.066 mmol) and $Pd(OAc)_2$ (7.5 mg, 0.033 mmol) were added and the reaction was allowed to proceed at room temperature for 24 hours. **15** was observed by NMR and MS spectroscopy, but degraded upon exposure to air or during storage (one day) to **14**.

δ_H (600 MHz; $CDCl_3$) Isomer A- 8.33 (2 H, dd, *J* 7.9 & 1.5, C(5)*H*), 7.84 (2 H, ddt, *J* 7.1, 2.5 & 1.7, C(7)*H*), 7.57 (2 H, dd, *J* 7.8 & 2.5, C(8)*H*), 7.55 (2 H, t, *J* 7.6, C(6)*H*), 5.00 (6 H, s, N(1)CH_3), 4.69 (6 H, s, N(3)CH_3), 1.95 (3 H, s, AcMe), 1.81 (3 H, s, AcMe), Isomer B- 8.23 (2 H, dd, *J* 8.6 & 1.5, C(5)*H*), 7.68 (2 H, ddd, *J* 9.0, 7.3 & 1.7, C(7)*H*), 7.34 (2 H, dt, *J* 7.6 & 1.4, C(6)*H*), 7.28 (2 H, dd, *J* 7.3 & 0.9, C(8)*H*), 4.99 (6 H, s, N(1)CH_3), 4.68 (6 H, s, N(3)CH_3), 1.89 (3 H, s, AcCH_3), 1.70 (3 H, s, AcCH_3); δ_C (150 MHz; $CDCl_3$) Isomer A- 199.1 (*C*(2)), 188.8 (Ac*C*=O), 188.4 (Ac*C*=O), 157.5 (*C*(4)), 138.8 (*C*(8a)), 134.1 (*C*(7)), 127.9 (*C*(5)), 126.5 (*C*(6)), 117.7 (*C*(4a)), 114.8 (*C*(8)), 43.5 (N(1)CH$_3$), 38.7 (N(3)CH$_3$), 22.2 (AcCH$_3$), 21.7 (AcCH$_3$), Isomer B- 199.2 (*C*(2)), 183.5 (Ac*C*=O), 176.4 (Ac*C*=O), 157.4 (*C*(4)), 138.3 (*C*(8a)), 134.2 (*C*(7)), 128.3 (*C*(5)), 126.1 (*C*(6)), 117.8 (*C*(4a)), 114.8 (*C*(8)), 43.8 (N(1)CH$_3$), 38.9 (N(3)CH$_3$), 21.5 (AcCH$_3$), 21.1 (AcCH$_3$); HRESIMS (*m/z* 451.0552 $[M - CH_3COOH - CH_3COO]^+$, calcd for $C_{20}H_{19}N_4O_2Pd$, 451.0548, Δ = 0.9 ppm; *m/z* 497.0606 $[M - CH_3COOH – CH_3COO + HCOOH]^+$, calcd for $C_{21}H_{21}N_4O_4Pd$, 497.0603, Δ = 0.6 ppm; *m/z* 571.0959 $[M + H]^+$, calcd for $C_{24}H_{27}N_4O_6Pd$, 571.0971, Δ = 2.1 ppm).

3. Kinetic Studies

Kinetic studies were recorded on a Varian DirectDrive 600 (600 MHz for ^1H) spectrometer equipped with a Varian inverse-detected triple-resonance HCN cold probe operating at 25 K. T_1 analysis of **3**, **4** and **11** were completed to ensure the pulse delay used in the kinetic studies was of a sufficient length to allow complete relaxation between pulses. The 90° pulse was calibrated prior to all kinetic experiments involving **3**, but not for other analytes due to their shorter half-life. Deuterated solvent (0.55 mL) was used in each experiment. The experiment timing began upon first contact between analyte and solvent. The time for each data point represents the midpoint of acquisition of each FID. The integrals for all carbon-bound proton resonances of the analyte were defined and the sum of these normalised to a value of 100. The value reported is the integral of the formyl, amidine or amide acetal resonance, depending on analyte, and represents the contribution of this resonance to the total integral of 100. Data was analysed and models were fitted using OriginPro 8 (OriginLab Corp.) software, version 8.0724.

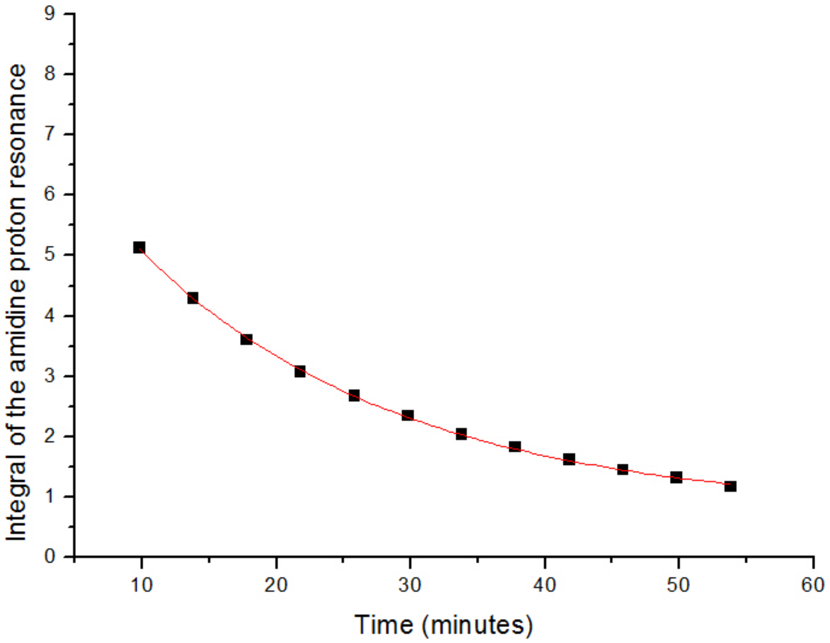
Effect of acid and base on the rate of exchange of **4**

In an NMR tube, **4** (6.0 mg, 0.0312 mmol) was dissolved in D_2O (0.55 mL), with triethylamine (12.4 µL, 0.089 mmol) or acetic acid-d_4 (5.4 µL, 0.088 mmol) also added. The reaction was followed by NMR spectroscopy, with acquisition times of 10 seconds, a d1 delay of 10 seconds, 12 acqusitions per data set and data sets acquired every thirty minutes. The integral of the exchanging resonance with time for each of the experiments is displayed in the text.

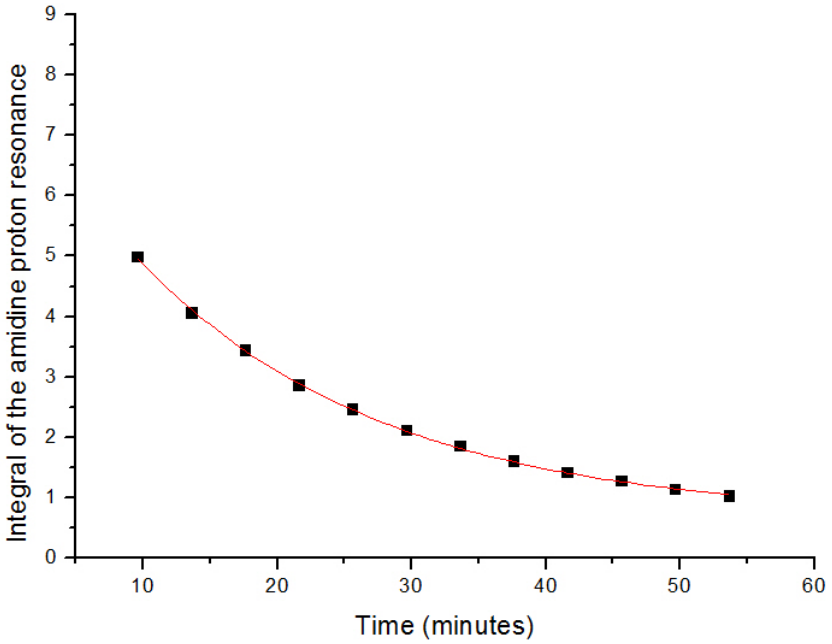
Relationship between concentration of base and rate of exchange of **11**

In an NMR tube, **11** (6.0 mg, 0.0312 mmol) was dissolved in D_2O (0.55 mL), with triethylamine added as an exogenous base. The concentrations range assayed were 0.01 mmol/L to 0.10 mmol/L. The reaction was followed by NMR spectroscopy, with acquisition times of 10 seconds, a d1 delay of 10 seconds, 12 acquisitions per data set and data sets were continually acquired continuously over 1 hour. The integral of the exchanging resonance with time for each of the experiments is displayed below.

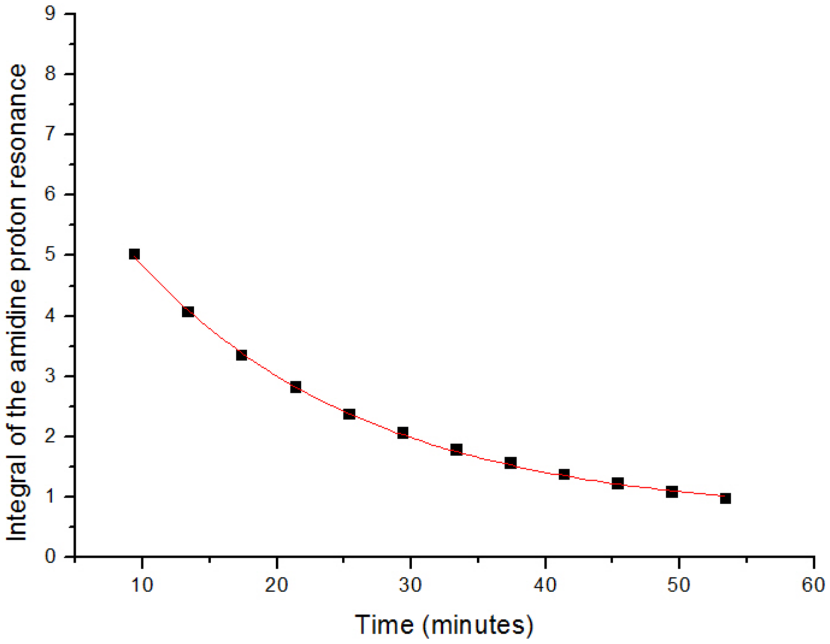
[Triethylamine] = 0.01 mmol/L



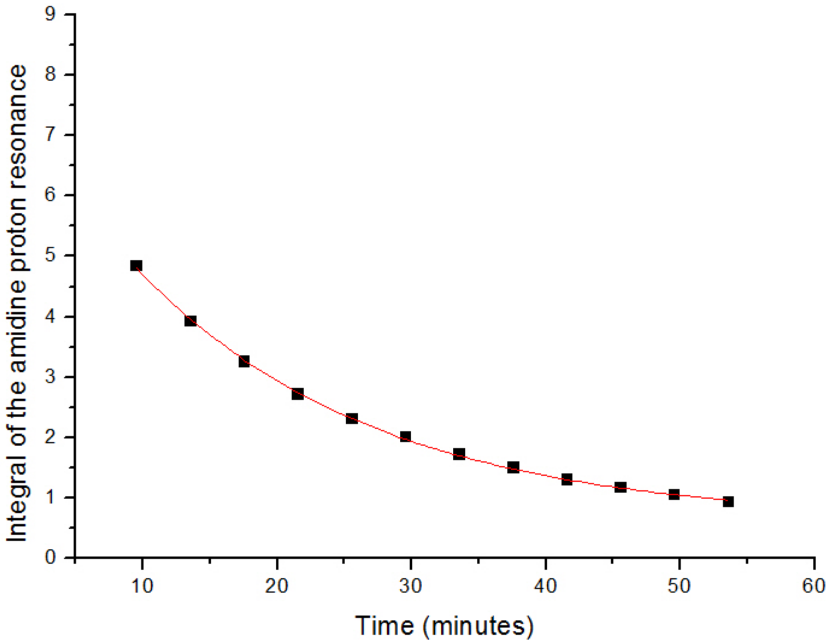
[Triethylamine] = 0.025 mmol/L



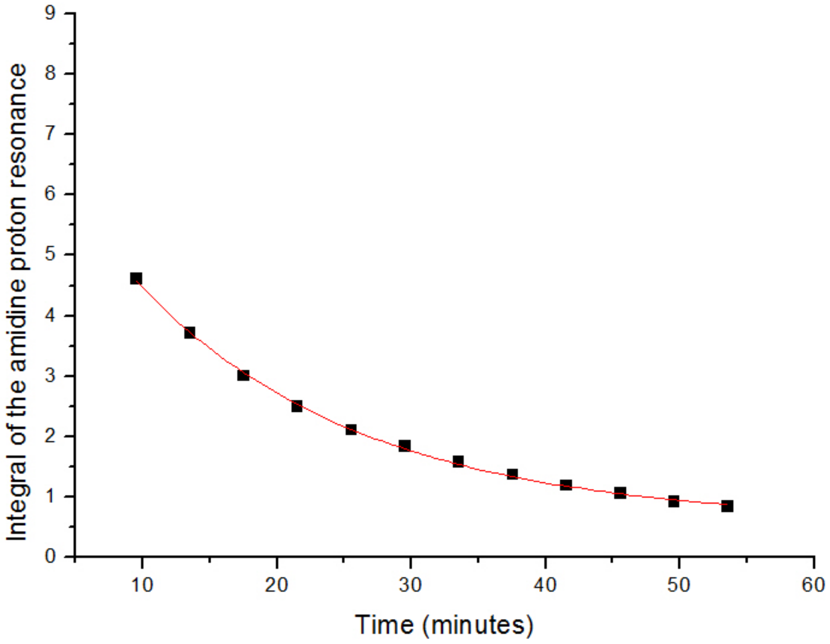
[Triethylamine] = 0.055 mmol/L



[Triethylamine] = 0.075 mmol/L



[Triethylamine] = 0.10 mmol/L



Exponential decay curves were fitted to these sets of data. According to the following manipulations of this model and inserting [concentration] = 0.5 and *t* = $t_{1/2}$, the half-life for the H-D exchange of **11** in each experiment could be obtained from the exponential rate, κ. The results of this are displayed below.

$$[concentration] = exp^{-\kappa . t} + c$$

$$\log([concentration]) = -\kappa . t + c'$$

$$\log(2) = \kappa . t_{1/2}$$

$$t_{1/2} = \log(2) / \kappa$$

[Triethylamine] (mmol/L)	Exponential rate, κ	r^2	Half-life (min)
0.01	-0.0553	0.999	12.5
0.025	-0.0586	0.999	11.8
0.055	-0.0622	0.999	11.1
0.075	-0.0602	0.999	11.5
0.10	-0.0649	0.999	10.7

The relationship between initial concentration and half-life was then examined. When the concentration of all other species in a reaction is constant, the rate law

$$rate = k[A]^N [B]^m$$

can be simplified to

$$-\frac{dA}{dt} = k'[A]^n$$

Integration of this and substitution of $A = A_o/2$ and $t = t_{1/2}$, yields the following equation.

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)kA_o^{n-1}}$$

Rearranging the logarithm of this results in the following equation, which specifies that a plot of $\log t_{1/2}$ against $\log A_o$ should describe a straight line of slope (1-n).

$$\log t_{1/2} = (1-n)\log A_o + C$$

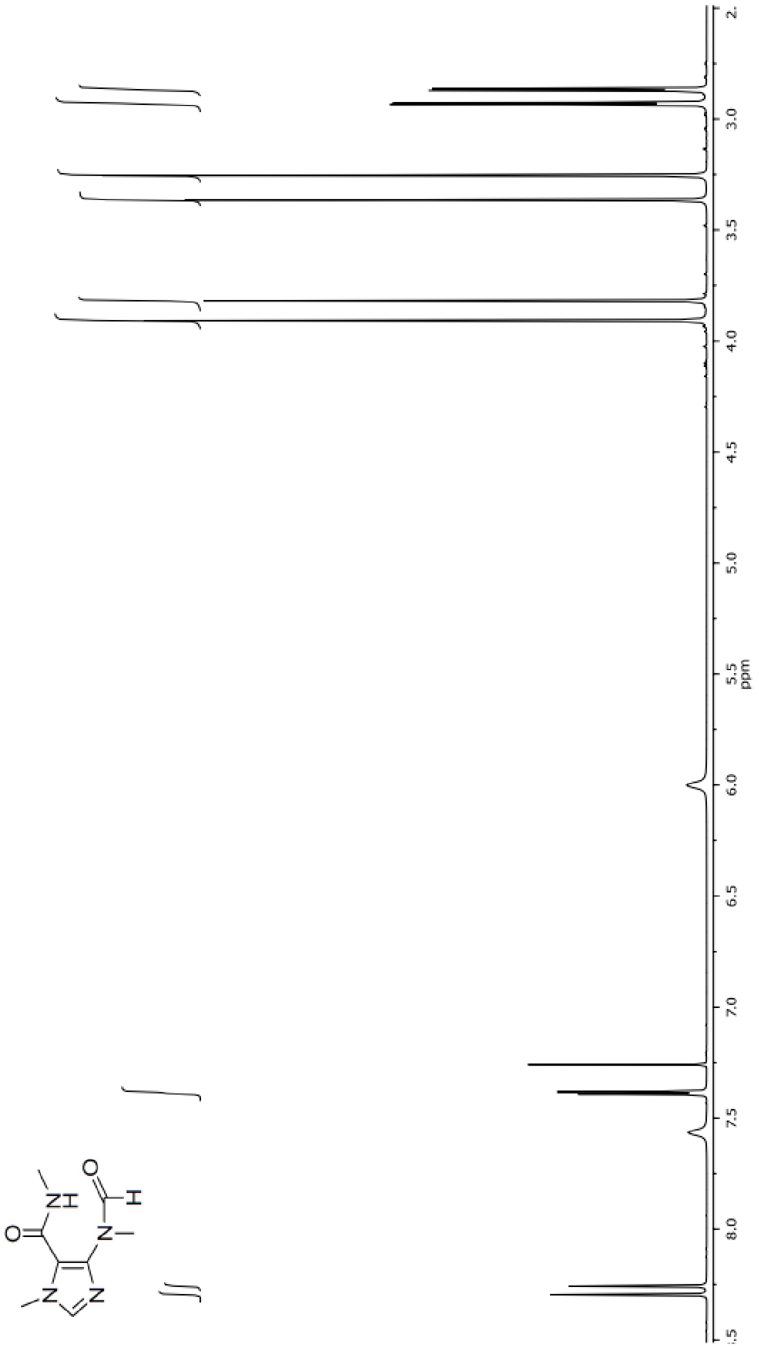
Applying a linear model to the graph of $\log t_{1/2}$ against $\log A_o$, as shown in the text, resulted in the following equation:

$$\log(t_{1/2}) = -0.060 * \log([triethylamine]) + 0.977$$
$$r^2 = 0.812$$

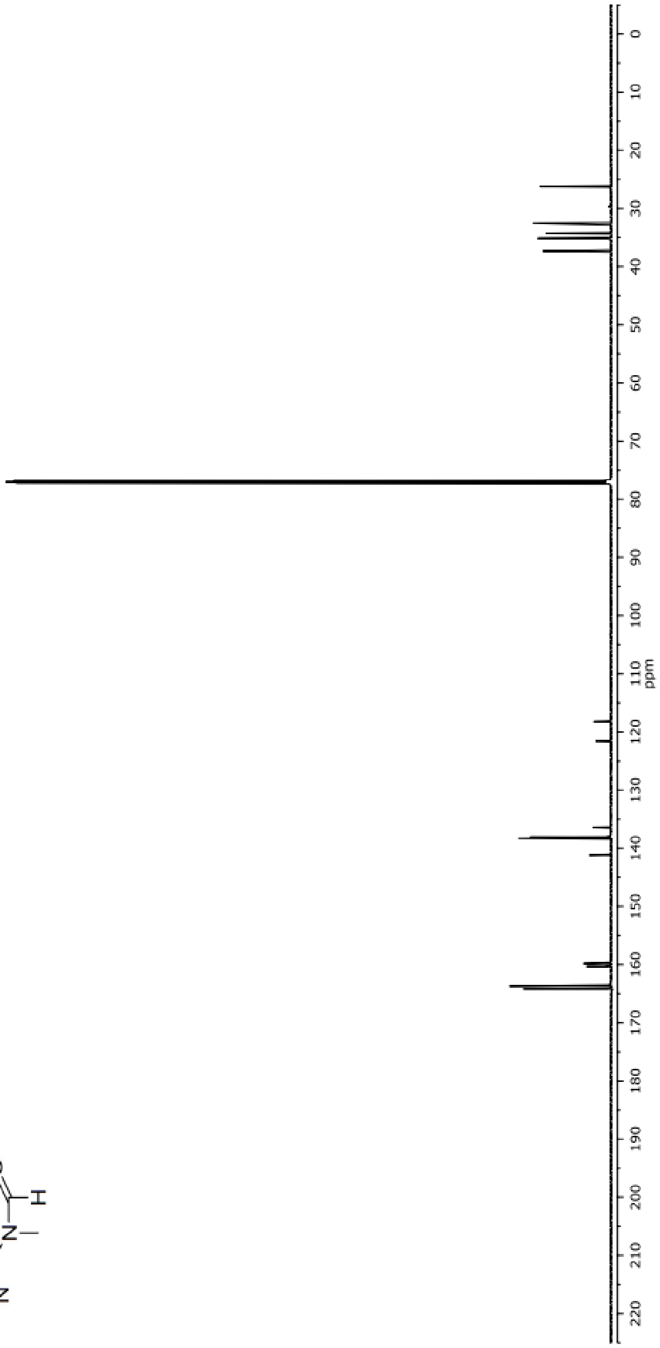
A gradient of -0.060 reveals that the order of triethylamine in the rate determining step of the H-D exchange of **11** is 1.06, or that the exchange is approximately first order with respect to the concentration of base.

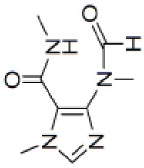
4. Compound Spectra

^{1}H-NMR spectra of **3** (600 MHz, $CDCl_3$)

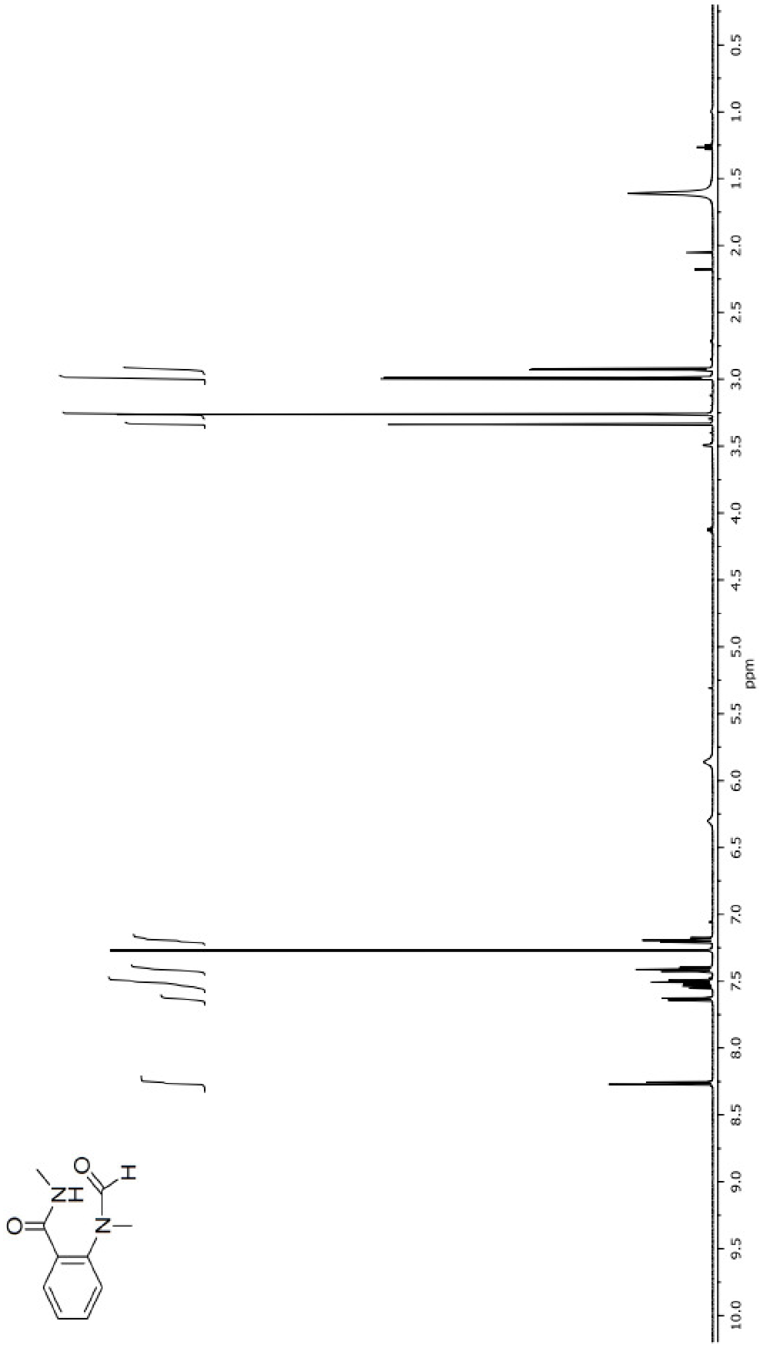


^{13}C-NMR spectrum of **3** (150 MHz, CDCl$_3$)

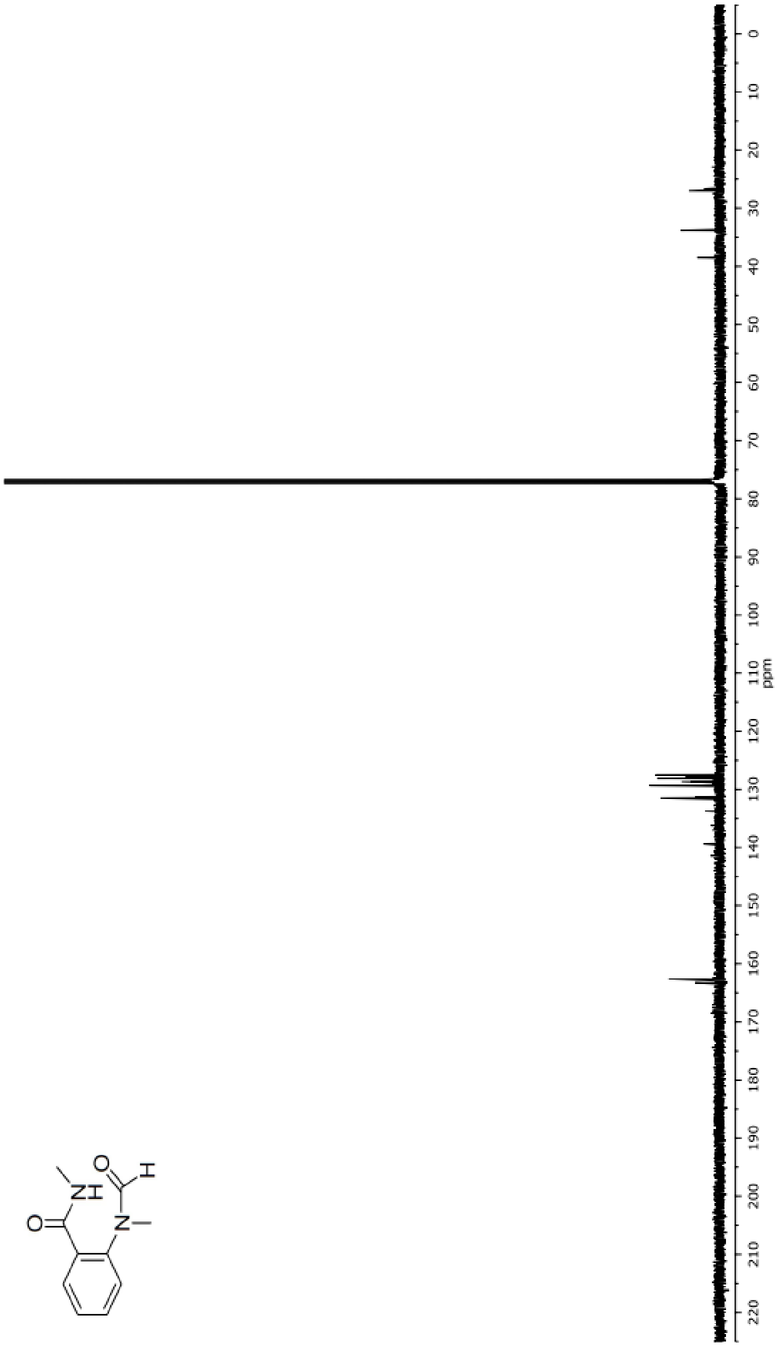




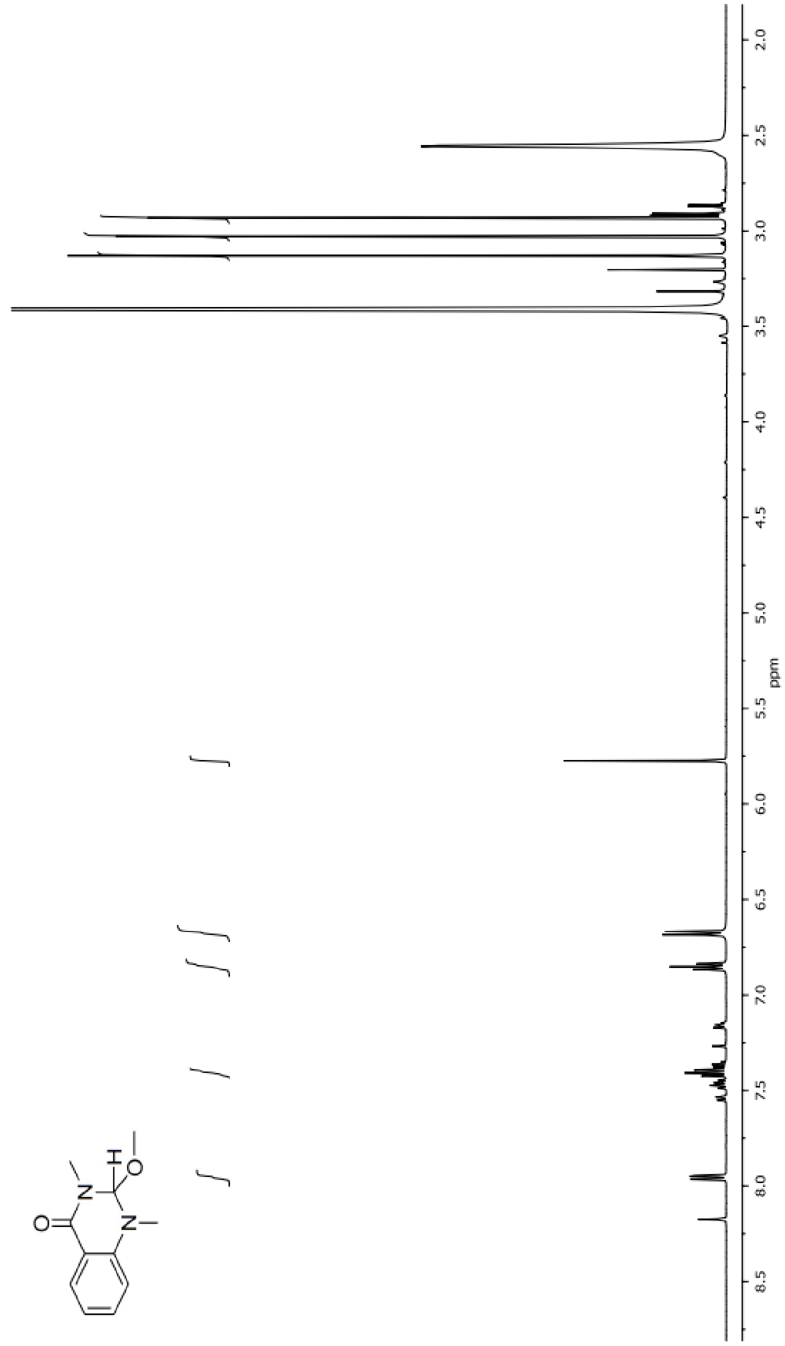
^{1}H-NMR spectrum of **4** (600 MHz, CDCl$_3$)



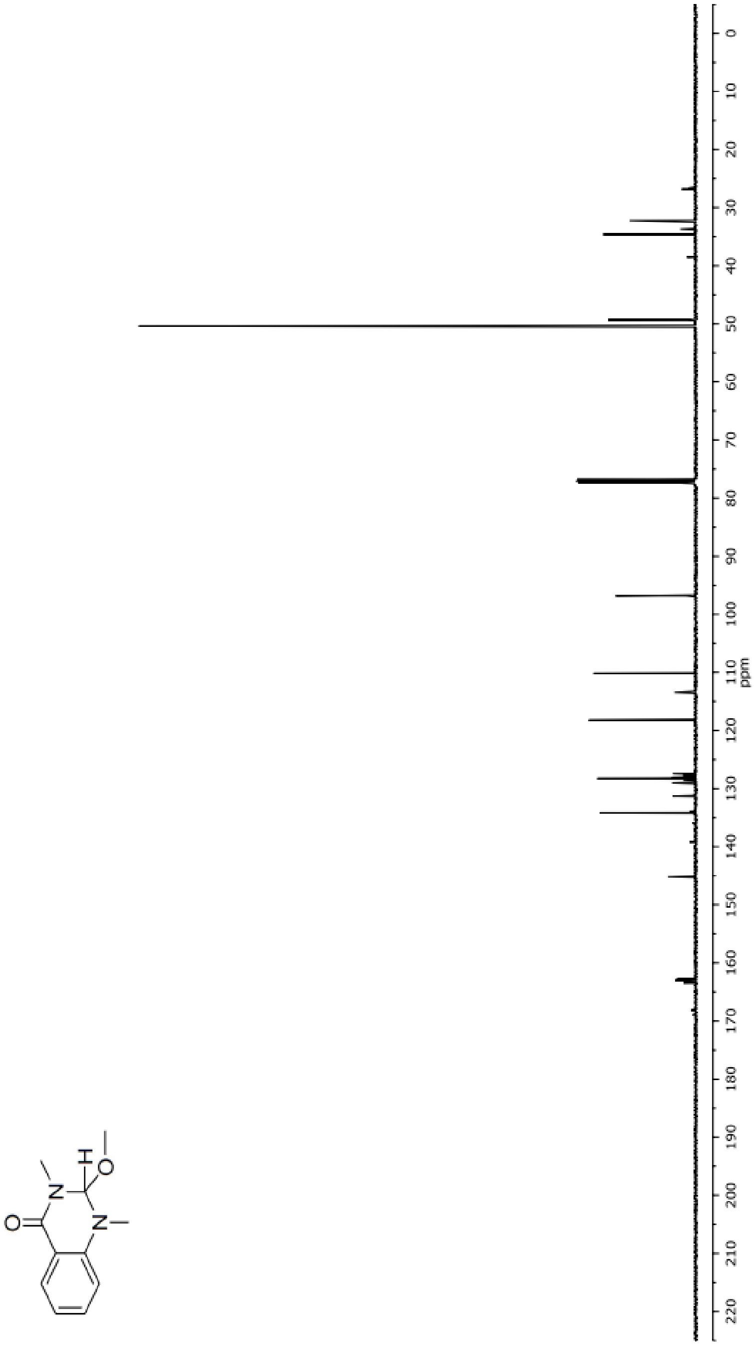
^{13}C-NMR spectrum of **4** (125 MHz, CDCl$_3$)



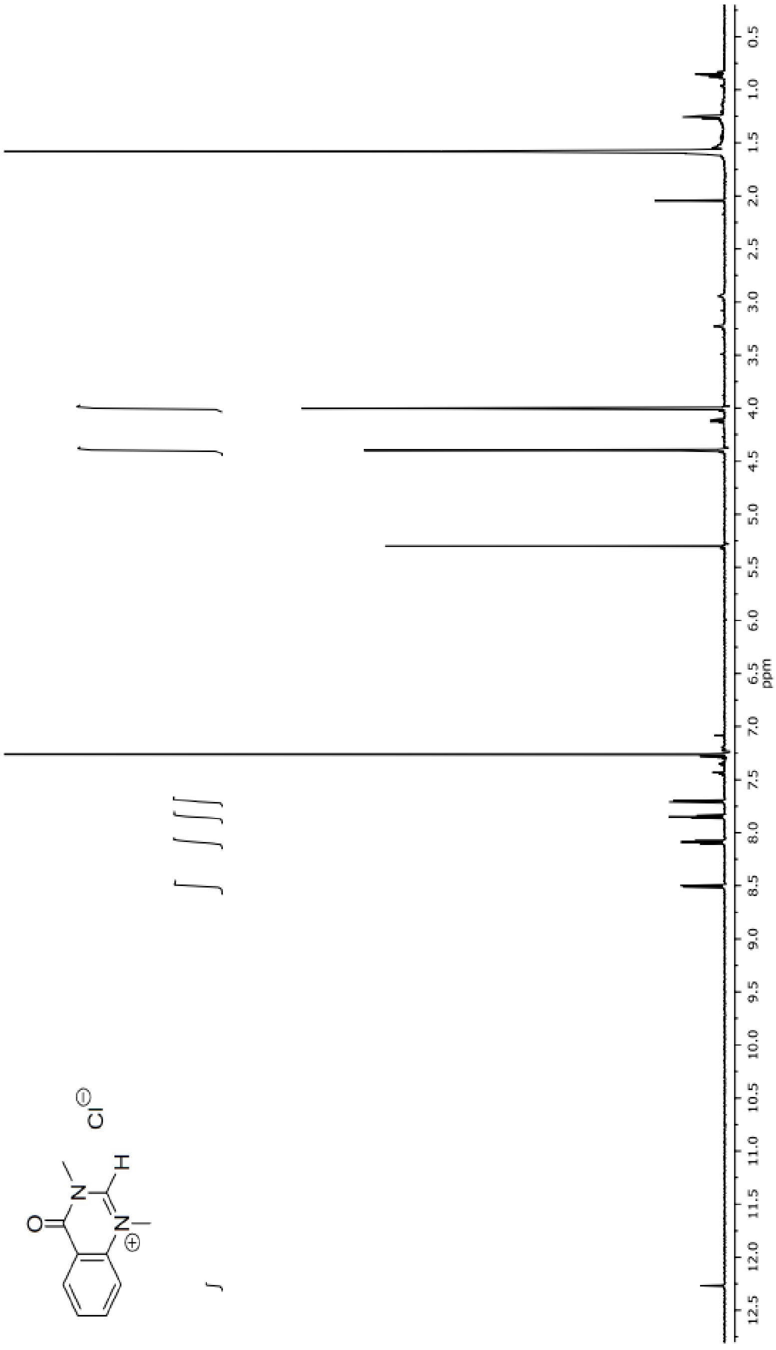
^{1}H-NMR spectrum of **9** (500 MHz, $CDCl_3$)



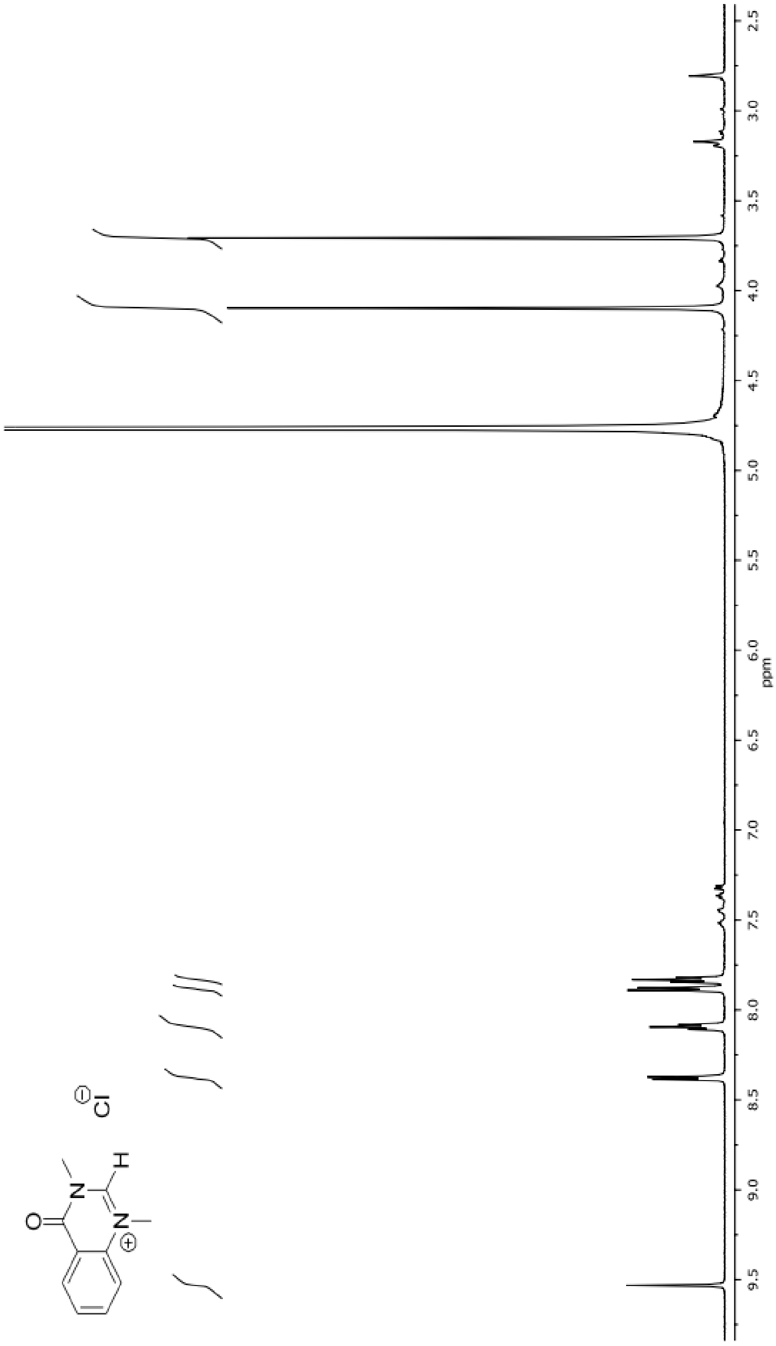
^{13}C-NMR spectrum of **9** (125 MHz, $CDCl_3$)



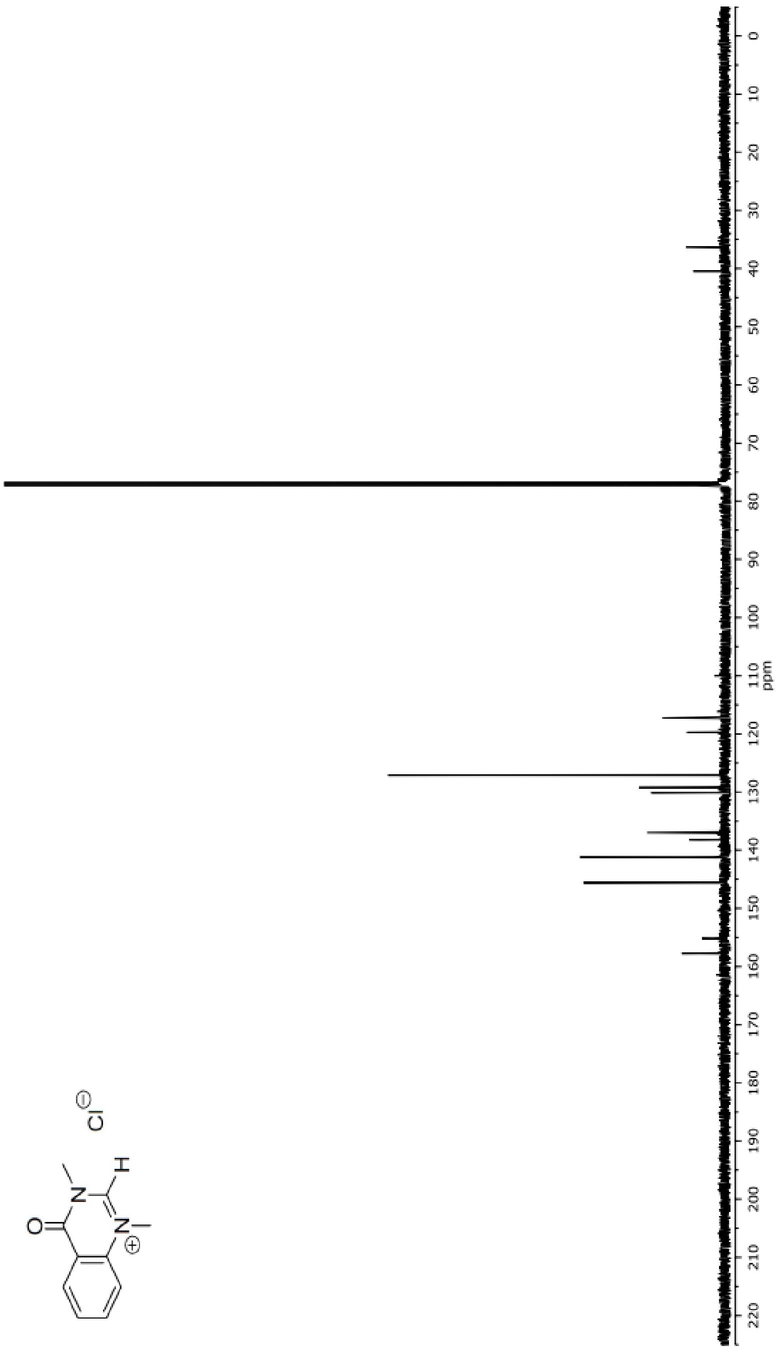
^{1}H-NMR spectrum of **11** (600 MHz, CDCl$_3$)



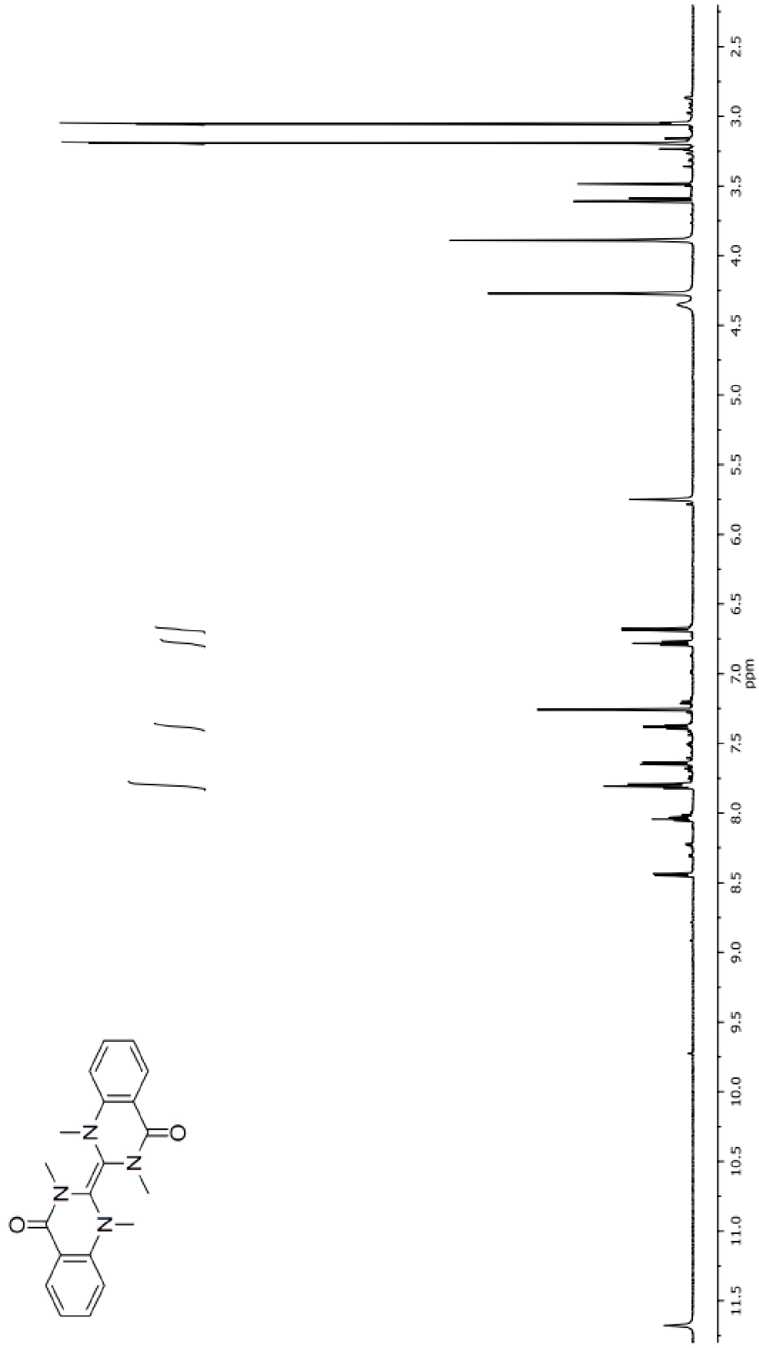
^{1}H-NMR spectrum of **11** (600 MHz, D_2O)



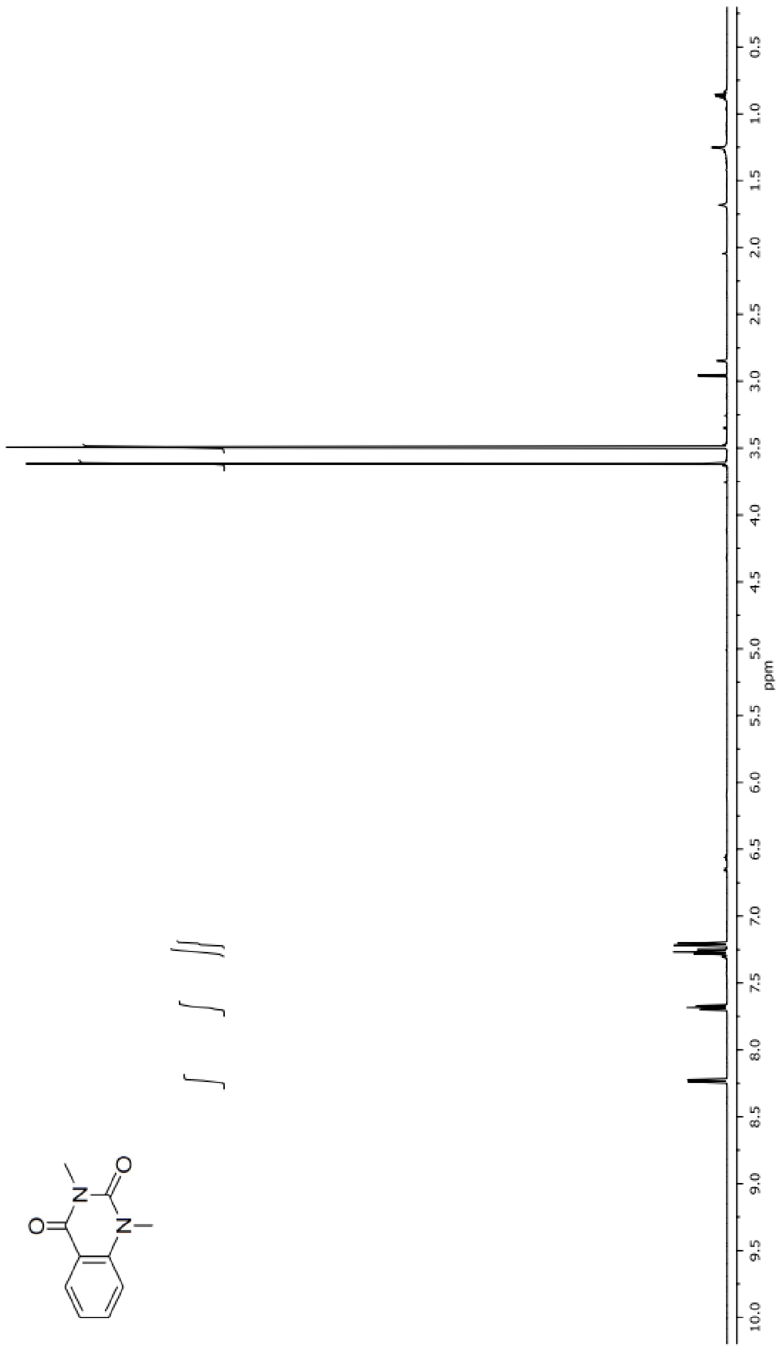
^{13}C-NMR spectrum of **11** with pyridine (125 MHz, $CDCl_3$)



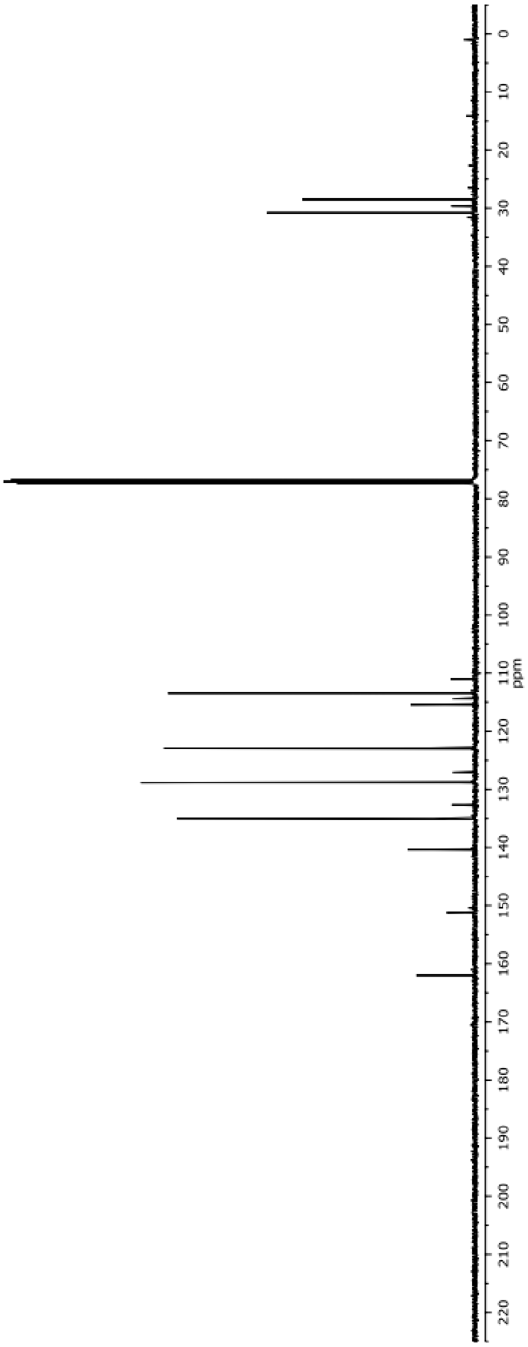
^{1}H-NMR spectrum of **13** (600 MHz, CDCl$_3$)

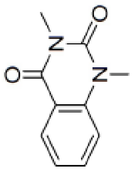


^{1}H-NMR spectrum of **14** (500 MHz, CDCl$_3$)

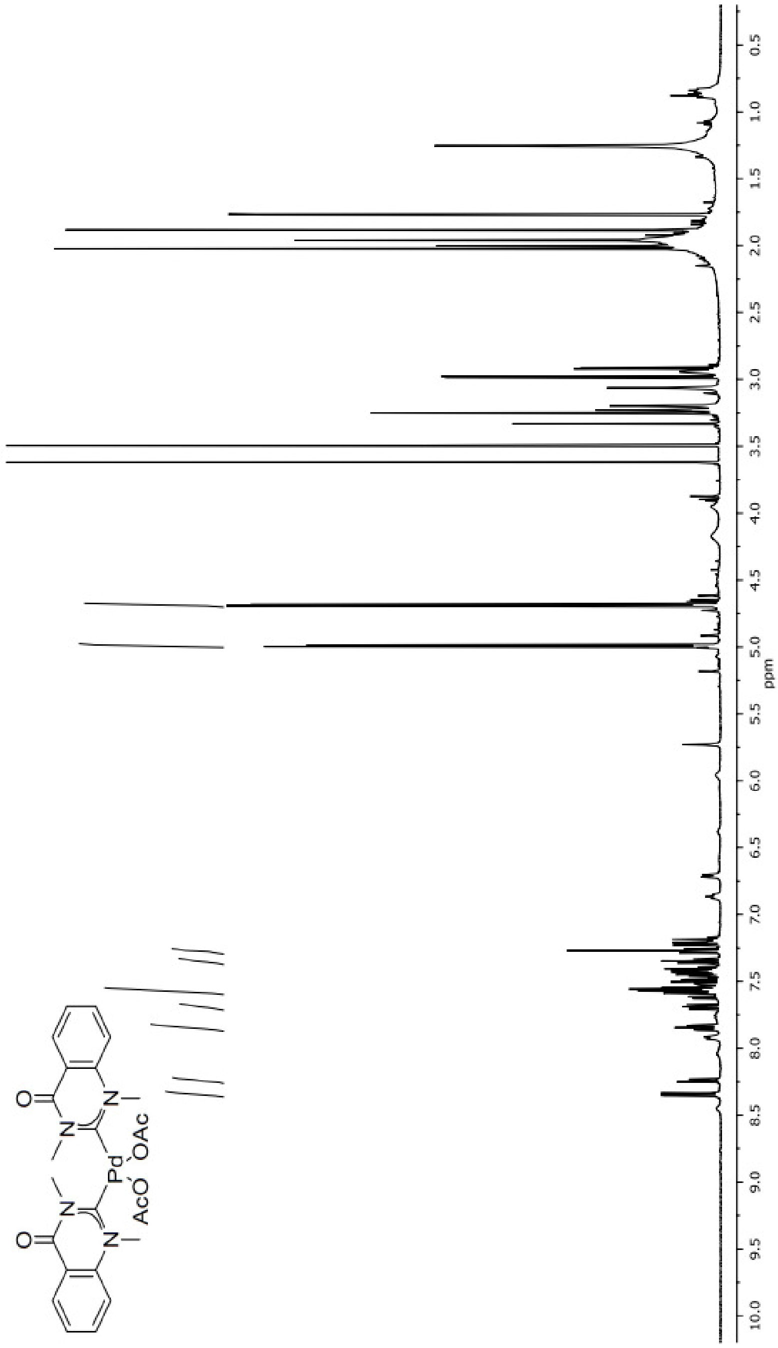


^{13}C-NMR spectrum of **14** (125 MHz, $CDCl_3$)

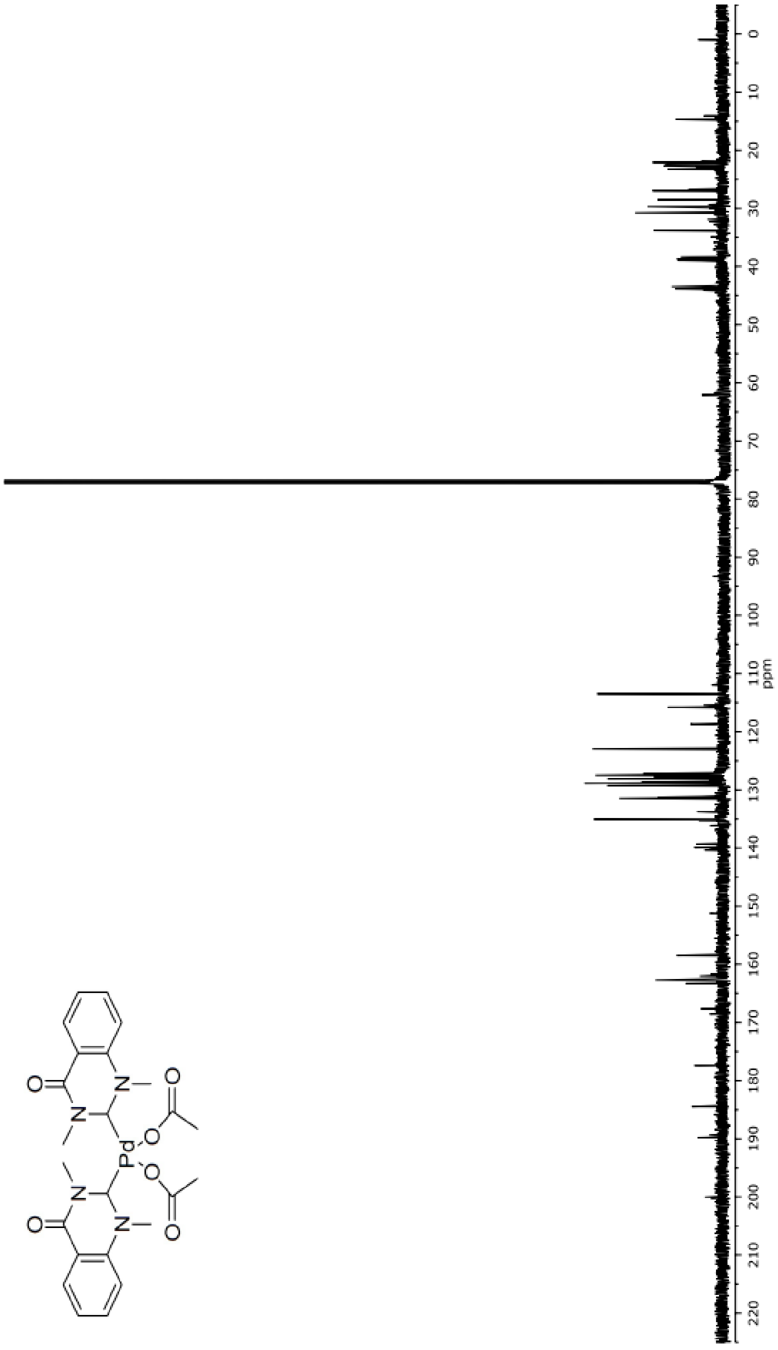




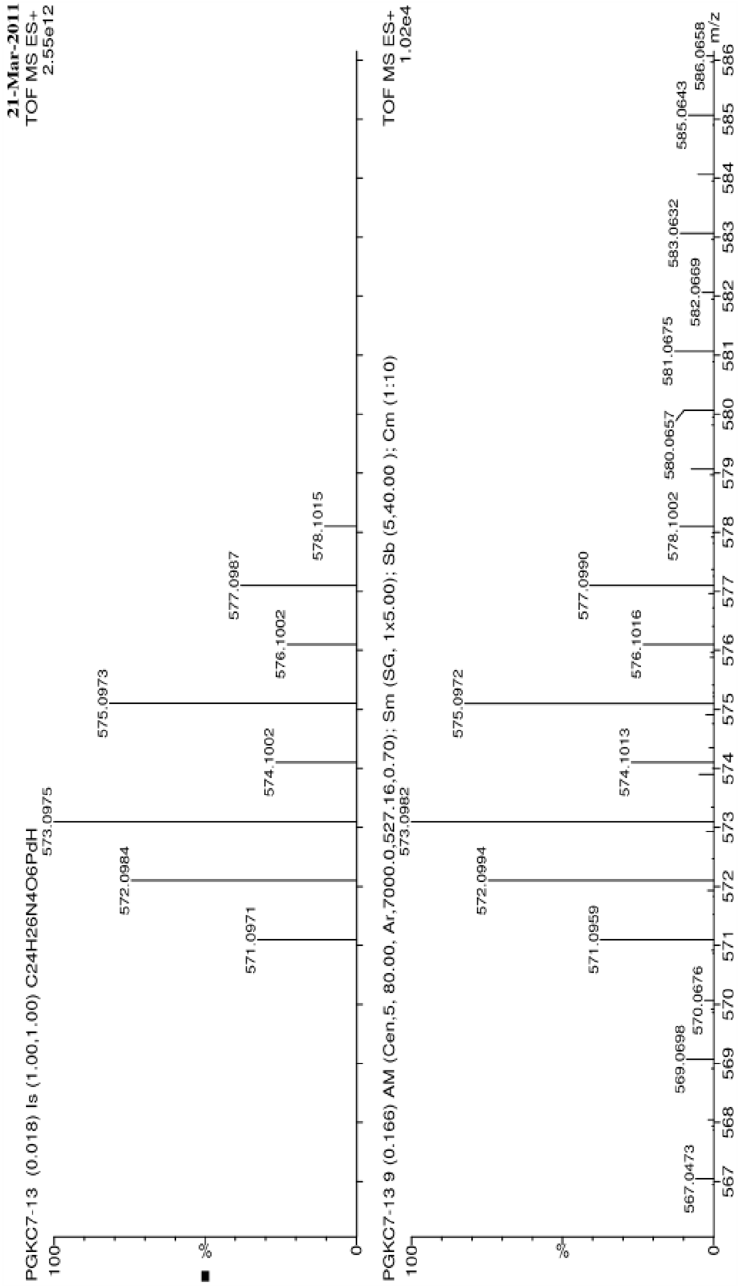
^{1}H-NMR spectrum of **15** (500 MHz, $CDCl_3$)



^{13}C-NMR spectrum of **15** (125 MHz, CDCl$_3$)



HRESIMS spectrum of **15** with $[M+H]^+$ predicted (top) and detected (bottom) clusters for this species



5. Computational and Structural Data

Five structurally and electronically related compounds whose p*K*a values had been determined experimentally were used to calibrate the computational results for compounds **3** and **11** of the present study. The five species are dimethylimidazole (DMI), dimethylbenzimidazole (DMBI) and diphenylethylbenzimidazole (DPEBI),[3] as well as as dichlorophenylimidazolium ($1H^+(a)$) and diisopropyltetrahydropyrimidinium ($3H^+(l)$),[4] (original naming schemes were retained for clarity).[3,4]
All molecular structures were fully optimized (see coordinates below) with the B3LYP hybrid density functional[5] using Pople's standard triple-ζ 6-311+G(d,p) basis set including one set of d-type polarization functions on all non-hydrogen atoms and one set of p-type polarization functions on hydrogen atoms. The basis set also includes diffuse s and p functions.
Solvent effects were included as an additional energy correction on the gas-phase structures using the polarizable conductor (C-PCM) model with water as the solvent.[6] All calculations were performed using the Gaussian09 suite of Computational Chemistry programmes.[7]
The thermodynamic cycle as outlined[8] was used for the calculation of the p*K*a values. For the proton and the hydrated proton, experimental values of -6.28 kcal/mol and -264.61 kcal/mol, respectively were used.[9]
After the theoretical p*K*a values were calculated, they were correlated to their respective experimentally measured values and a trend line was fitted with the ordinary least squares method ($R^2 = 0.995$). The trend line was then used to predict the experimental pKa values for **3** and **11**.

Obtained Structures

Structure of **3** (protonated):

C	0.000000	0.708723	0.000000
C	-1.100591	-0.135724	0.000000
C	0.290848	-1.989038	0.000000
C	1.353343	0.247173	0.000000
C	-1.885835	1.809548	0.000000
H	0.421515	-3.063097	0.000000
H	-2.565143	2.649075	0.000000
N	-0.536906	1.977518	0.000000
C	0.195836	3.251597	0.000000
H	0.820901	3.319336	0.889228
H	0.820901	3.319336	-0.889228
H	-0.532261	4.060565	0.000000
N	-2.263150	0.535291	0.000000
N	-0.947120	-1.514387	0.000000
C	-2.139236	-2.390362	0.000000
H	-2.732260	-2.180885	0.888864
H	-2.732260	-2.180885	-0.888864
H	-1.812911	-3.428134	0.000000
O	2.387679	0.865246	0.000000
N	1.377654	-1.218989	0.000000
C	2.725258	-1.828955	0.000000
H	3.266047	-1.499342	-0.885817
H	3.266047	-1.499342	0.885817
H	2.626900	-2.912400	0.000000

Structure of **3** (deprotonated):

C	0.000000	0.744158	0.000000
C	-1.124861	-0.094255	0.000000

C	0.257197	-1.978389	0.000000
C	1.329299	0.271781	0.000000
C	-1.962125	1.920342	0.000000
H	0.375867	-3.053145	0.000000
N	-0.567904	1.999827	0.000000
C	0.159097	3.261086	0.000000
H	0.790163	3.347779	0.886945
H	0.790163	3.347779	-0.886945
H	-0.591272	4.049482	0.000000
N	-2.272237	0.564025	0.000000
N	-0.969587	-1.478318	0.000000
C	-2.169146	-2.327576	0.000000
H	-2.764090	-2.100231	0.883491
H	-2.764090	-2.100231	-0.883491
H	-1.866773	-3.373803	0.000000
O	2.403123	0.850272	0.000000
N	1.345640	-1.209145	0.000000
C	2.679784	-1.822625	0.000000
H	3.229647	-1.497259	-0.882455
H	3.229647	-1.497259	0.882455
H	2.578901	-2.907145	0.000000

Structure of **11** (protonated):

C	-2.718266	1.480572	0.000000
C	-2.320116	0.149594	0.000000
C	-0.955704	-0.152837	0.000000
C	0.000000	0.882088	0.000000
C	-0.424124	2.216873	0.000000
C	-1.776751	2.515215	0.000000
H	-3.776298	1.713078	0.000000
H	-3.068861	-0.629925	0.000000
C	1.434742	0.591462	0.000000
H	0.328138	2.995650	0.000000
H	-2.105311	3.546886	0.000000
C	0.800257	-1.751715	0.000000
H	1.108377	-2.789409	0.000000
N	-0.495679	-1.492318	0.000000
N	1.744935	-0.821701	0.000000
O	2.336488	1.386441	0.000000
C	-1.456384	-2.615947	0.000000
H	-2.077888	-2.567006	0.893694
H	-2.077888	-2.567006	-0.893694
H	-0.903715	-3.552628	0.000000
C	3.177289	-1.187583	0.000000
H	3.651866	-0.768689	-0.885969
H	3.651866	-0.768689	0.885969
H	3.267355	-2.271989	0.000000

Structure of **11** (deprotonated):

C	-2.720409	1.419854	0.000000
C	-2.304797	0.096388	0.000000

C	-0.931424	-0.204946	0.000000
C	0.000000	0.847533	0.000000
C	-0.438917	2.177749	0.000000
C	-1.792237	2.468142	0.000000
H	-3.782216	1.639382	0.000000
H	-3.041916	-0.694110	0.000000
C	1.436277	0.553067	0.000000
H	0.311426	2.958663	0.000000
H	-2.132290	3.496685	0.000000
C	0.866256	-1.866668	0.000000
N	-0.443625	-1.520130	0.000000
N	1.742942	-0.823140	0.000000
O	2.316027	1.397253	0.000000
C	-1.402925	-2.631565	0.000000
H	-2.034812	-2.598483	0.891487
H	-2.034812	-2.598483	-0.891487
H	-0.820052	-3.547517	0.000000
C	3.177714	-1.150136	0.000000
H	3.658085	-0.727353	-0.883703
H	3.658085	-0.727353	0.883703
H	3.257826	-2.233072	0.000000

Structure of **DMI** (protonated):

C	0.000000	0.680330	-1.236252
C	0.000000	-0.680330	-1.236252
C	0.000000	0.000000	0.861640
N	0.000000	1.087468	0.084395
H	0.000000	1.382632	-2.052665
H	0.000000	-1.382632	-2.052665
H	0.000000	0.000000	1.939135
N	0.000000	-1.087468	0.084395
C	0.000000	2.482756	0.552248
H	0.893171	2.987481	0.185590
H	-0.893171	2.987481	0.185590
H	0.000000	2.490723	1.640254
C	0.000000	-2.482756	0.552248
H	-0.893171	-2.987481	0.185590
H	0.893171	-2.987481	0.185590
H	0.000000	-2.490723	1.640254

Structure of **DMI** (deprotonated):

C	0.000000	0.677380	-1.213634
C	0.000000	-0.677380	-1.213634
C	0.000000	0.000000	0.980094
N	0.000000	1.063890	0.122042
H	0.000000	1.378183	-2.032301
H	0.000000	-1.378183	-2.032301
N	0.000000	-1.063890	0.122042
C	0.000000	2.447119	0.571826
H	0.890469	2.971284	0.214450
H	-0.890469	2.971284	0.214450

H	0.000000	2.439249	1.659670
C	0.000000	-2.447119	0.571826
H	-0.890469	-2.971284	0.214450
H	0.890469	-2.971284	0.214450
H	0.000000	-2.439249	1.659670

Structure of **DMBI** (protonated):

C	0.000000	0.701829	-0.208721
C	0.000000	-0.701829	-0.208721
C	0.000000	-1.435682	-1.394578
C	0.000000	-0.704188	-2.574056
C	0.000000	0.704188	-2.574056
C	0.000000	1.435682	-1.394578
C	0.000000	0.000000	1.888830
H	0.000000	-2.517952	-1.402580
H	0.000000	-1.229824	-3.520779
H	0.000000	1.229824	-3.520779
H	0.000000	2.517952	-1.402580
H	0.000000	0.000000	2.967341
N	0.000000	1.099196	1.130484
N	0.000000	-1.099196	1.130484
C	0.000000	2.482734	1.616914
H	0.892767	2.995890	1.258611
H	-0.892767	2.995890	1.258611
H	0.000000	2.477157	2.705239
C	0.000000	-2.482734	1.616914
H	-0.892767	-2.995890	1.258611
H	0.892767	-2.995890	1.258611
H	0.000000	-2.477157	2.705239

Structure of **DMBI** (deprotonated):

C	0.000000	0.701908	-0.170807
C	0.000000	-0.701908	-0.170807
C	0.000000	-1.425890	-1.359791
C	0.000000	-0.700964	-2.551874
C	0.000000	0.700964	-2.551874
C	0.000000	1.425890	-1.359791
C	0.000000	0.000000	2.016552
H	0.000000	-2.509265	-1.365367
H	0.000000	-1.232079	-3.496577
H	0.000000	1.232079	-3.496577
H	0.000000	2.509265	-1.365367
N	0.000000	1.076403	1.171756
N	0.000000	-1.076403	1.171756
C	0.000000	2.452765	1.635950
H	0.890209	2.981259	1.282783
H	-0.890209	2.981259	1.282783
H	0.000000	2.433568	2.723561
C	0.000000	-2.452765	1.635950
H	-0.890209	-2.981259	1.282783
H	0.890209	-2.981259	1.282783

H	0.000000	-2.433568	2.723561

Structure of **DPEBI** (protonated):

C	0.132320	0.690978	-0.668802
C	-0.132320	-0.690978	-0.668802
C	-0.261844	-1.408479	-1.860155
C	-0.127103	-0.692351	-3.039213
C	0.127103	0.692351	-3.039213
C	0.261844	1.408479	-1.860155
C	0.000000	0.000000	1.423301
H	-0.443052	-2.473555	-1.867108
H	-0.218487	-1.211854	-3.985074
H	0.218487	1.211854	-3.985074
H	0.443052	2.473555	-1.867108
H	0.000000	0.000000	2.501784
N	0.209539	1.083642	0.672693
N	-0.209539	-1.083642	0.672693
C	0.543632	2.435587	1.227783
H	0.365745	2.324742	2.301621
C	-0.543632	-2.435587	1.227783
H	-0.365745	-2.324742	2.301621
C	2.032060	2.723320	1.022756
H	2.296652	3.659666	1.516051
H	2.634293	1.928278	1.466514
H	2.297378	2.802845	-0.032468
C	-0.431720	3.485334	0.703985
C	-1.801510	3.317930	0.942180
C	0.000000	4.631093	0.032362
C	-2.720683	4.266410	0.507101
H	-2.157905	2.442294	1.476232
C	-0.921388	5.584948	-0.402756
H	1.053569	4.800840	-0.151758
C	-2.281233	5.404103	-0.170271
H	-3.776995	4.123252	0.702007
H	-0.570663	6.470838	-0.918924
H	-2.995060	6.146617	-0.506564
C	-2.032060	-2.723320	1.022756
H	-2.296652	-3.659666	1.516051
H	-2.634293	-1.928278	1.466514
H	-2.297378	-2.802845	-0.032468
C	0.431720	-3.485334	0.703985
C	1.801510	-3.317930	0.942180
C	0.000000	-4.631093	0.032362
C	2.720683	-4.266410	0.507101
H	2.157905	-2.442294	1.476232
C	0.921388	-5.584948	-0.402756
H	-1.053569	-4.800840	-0.151758
C	2.281233	-5.404103	-0.170271
H	3.776995	-4.123252	0.702007
H	0.570663	-6.470838	-0.918924
H	2.995060	-6.146617	-0.506564

Structure of **DPEBI** (deprotonated):

C	0.257228	0.653726	-0.690702
C	-0.257228	-0.653726	-0.690702
C	-0.511389	-1.328697	-1.884127
C	-0.250267	-0.654768	-3.074632
C	0.250267	0.654768	-3.074632
C	0.511389	1.328697	-1.884127
C	0.000000	0.000000	1.495746
H	-0.884753	-2.343819	-1.892248
H	-0.436565	-1.154121	-4.018398
H	0.436565	1.154121	-4.018398
H	0.884753	2.343819	-1.892248
N	0.396209	1.004439	0.657035
N	-0.396209	-1.004439	0.657035
C	0.963787	2.258752	1.180852
H	0.813658	2.161926	2.259123
C	-0.963787	-2.258752	1.180852
H	-0.813658	-2.161926	2.259123
C	2.473885	2.322256	0.928144
H	2.914920	3.175356	1.448390
H	2.938565	1.413956	1.315911
H	2.717742	2.403079	-0.133506
C	0.162595	3.475651	0.714293
C	-1.230665	3.467061	0.862919
C	0.766582	4.619766	0.187408
C	-1.996631	4.566353	0.489807
H	-1.714164	2.587008	1.272535
C	0.000000	5.725086	-0.188252
H	1.841702	4.662928	0.063606
C	-1.382996	5.702285	-0.039970
H	-3.073695	4.538219	0.612808
H	0.489346	6.602383	-0.596894
H	-1.978849	6.559600	-0.332247
C	-2.473885	-2.322256	0.928144
H	-2.914920	-3.175356	1.448390
H	-2.938565	-1.413956	1.315911
H	-2.717742	-2.403079	-0.133506
C	-0.162595	-3.475651	0.714293
C	1.230665	-3.467061	0.862919
C	-0.766582	-4.619766	0.187408
C	1.996631	-4.566353	0.489807
H	1.714164	-2.587008	1.272535
C	0.000000	-5.725086	-0.188252
H	-1.841702	-4.662928	0.063606
C	1.382996	-5.702285	-0.039970
H	3.073695	-4.538219	0.612808
H	-0.489346	-6.602383	-0.596894
H	1.978849	-6.559600	-0.332247

Structure of **3H**$^{+}$(i) (protonated):

C	-0.638631	-0.000873	0.000000
H	-1.716349	0.119725	0.000000
N	-0.044906	-0.068656	1.176041
N	-0.044906	-0.068656	-1.176041
C	-0.854069	0.009354	2.433593
H	-1.894381	0.006221	2.097583
C	-0.854069	0.009354	-2.433593
H	-1.894381	0.006221	-2.097583
C	-0.623995	-1.229545	3.301552
H	-1.297327	-1.196762	4.160225
H	-0.826815	-2.149969	2.749426
H	0.396370	-1.271367	3.690390
C	-0.591894	1.319929	-3.179766
H	-1.271405	1.389798	-4.031706
H	-0.764550	2.187442	-2.539048
H	0.425623	1.373262	-3.574364
C	-0.591894	1.319929	3.179766
H	-1.271405	1.389798	4.031706
H	0.425623	1.373262	3.574364
H	-0.764550	2.187442	2.539048
C	-0.623995	-1.229545	-3.301552
H	-1.297327	-1.196762	-4.160225
H	0.396370	-1.271367	-3.690390
H	-0.826815	-2.149969	-2.749426
C	1.421335	-0.224615	1.254033
H	1.658284	-1.285850	1.373289
H	1.771875	0.296641	2.143942
C	1.421335	-0.224615	-1.254033
H	1.658284	-1.285850	-1.373289
H	1.771875	0.296641	-2.143942
C	2.073967	0.349503	0.000000
H	3.138497	0.110281	0.000000
H	1.982639	1.439090	0.000000

Structure of **3H**$^+$(i) (deprotonated):

C	-0.779046	0.026506	0.000000
N	-0.081165	-0.061110	1.149301
N	-0.081165	-0.061110	-1.149301
C	-0.844813	0.012476	2.411456
H	-1.883311	0.019617	2.078117
C	-0.844813	0.012476	-2.411456
H	-1.883311	0.019617	-2.078117
C	-0.620212	-1.225540	3.288834
H	-1.277993	-1.190346	4.161581
H	-0.842732	-2.139836	2.732614
H	0.408298	-1.288963	3.658174
C	-0.578008	1.316832	-3.174634
H	-1.235859	1.383644	-4.045998
H	-0.772765	2.179479	-2.533187
H	0.451643	1.382816	-3.540359
C	-0.578008	1.316832	3.174634

H	-1.235859	1.383644	4.045998
H	0.451643	1.382816	3.540359
H	-0.772765	2.179479	2.533187
C	-0.620212	-1.225540	-3.288834
H	-1.277993	-1.190346	-4.161581
H	0.408298	-1.288963	-3.658174
H	-0.842732	-2.139836	-2.732614
C	1.378887	-0.233165	1.242976
H	1.630221	-1.296693	1.347291
H	1.746335	0.273055	2.138744
C	1.378887	-0.233165	-1.242976
H	1.630221	-1.296693	-1.347291
H	1.746335	0.273055	-2.138744
C	2.046005	0.343506	0.000000
H	3.113831	0.109580	0.000000
H	1.942808	1.433104	0.000000

Structure of **1H**$^{+}$(a) (protonated):

C	1.998269	0.825440	0.679803
C	1.998269	0.825440	-0.679803
C	0.052669	0.021500	0.000000
N	0.772275	0.324183	1.089161
H	2.737291	1.161750	1.386295
H	2.737291	1.161750	-1.386295
H	-0.924303	-0.431118	0.000000
N	0.772275	0.324183	-1.089161
C	0.339824	0.145136	-2.454648
C	1.136808	-0.590873	-3.328533
C	-0.861329	0.713105	-2.872727
C	0.723638	-0.761332	-4.644793
H	2.060673	-1.042985	-2.987779
C	-1.278717	0.532439	-4.186867
H	-1.458019	1.309828	-2.192814
C	-0.483069	-0.201853	-5.065965
H	1.327070	-1.333396	-5.337233
H	-2.206945	0.969435	-4.530797
C	0.339824	0.145136	2.454648
C	1.136808	-0.590873	3.328533
C	-0.861329	0.713105	2.872727
C	0.723638	-0.761332	4.644793
H	2.060673	-1.042985	2.987779
C	-1.278717	0.532439	4.186867
H	-1.458019	1.309828	2.192814
C	-0.483069	-0.201853	5.065965
H	1.327070	-1.333396	5.337233
H	-2.206945	0.969435	4.530797
Cl	-1.000846	-0.420896	6.712090
Cl	-1.000846	-0.420896	-6.712090

Structure of **1H**$^{+}$(a) (deprotonated):

C	2.087536	0.501450	0.674600

C	2.087536	0.501450	-0.674600
C	-0.059512	0.013722	0.000000
N	0.778789	0.202359	1.066608
H	2.878267	0.727571	1.368214
H	2.878267	0.727571	-1.368214
N	0.778789	0.202359	-1.066608
C	0.349725	0.086984	-2.421110
C	1.235902	-0.340429	-3.410401
C	-0.968403	0.399351	-2.758996
C	0.815549	-0.440274	-4.734529
H	2.250265	-0.621221	-3.155395
C	-1.395322	0.290136	-4.077245
H	-1.648819	0.716935	-1.980595
C	-0.498367	-0.123994	-5.058269
H	1.500983	-0.774568	-5.502529
H	-2.416464	0.532335	-4.342378
C	0.349725	0.086984	2.421110
C	1.235902	-0.340429	3.410401
C	-0.968403	0.399351	2.758996
C	0.815549	-0.440274	4.734529
H	2.250265	-0.621221	3.155395
C	-1.395322	0.290136	4.077245
H	-1.648819	0.716935	1.980595
C	-0.498367	-0.123994	5.058269
H	1.500983	-0.774568	5.502529
H	-2.416464	0.532335	4.342378
Cl	-1.035114	-0.251651	6.727676
Cl	-1.035114	-0.251651	-6.727676

Regression Analysis:

	experiment	**theory**
DMI	23.0	22.53
DMBI	21.6	20.29
DPEBI	21.2	19.65
3H$^+$(l)	28.2	28.86
1H$^+$(a)	19.8	17.42
3	*30.0*	31.37
11	*19.8*	17.78

Table 1: Given are the experimental p*K*a values and the theoretically obtained p*K*a values for all species in the computational analysis. The experimental p*K*a values for **3** and **11** (in italics) have been computed as an interpolation (and extrapolation, respectively) from the results of the linear regression analysis of the other data points.

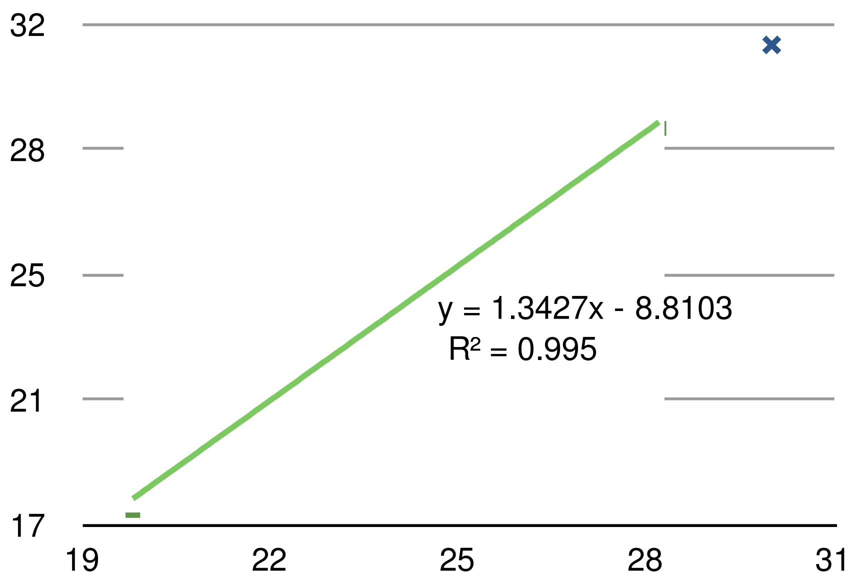


Figure 1: Graphical representation of the linear regression. The points used for calibration are given as green squares. The trend line is also given in green. The two predicted points are shown as blue check marks. Also given are the linear equation and the R^2 value.

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