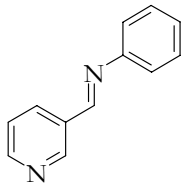
Supplementary Information

(A) Experimental Details

(*E*)-*N*-((pyridine-3-yl)methylene)benzenamine

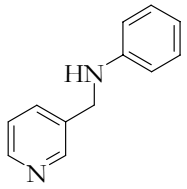


Aniline (2.05 g, 21 mmol) and 3-pyridine carboxaldehyde (2.35 g, 22 mmol) were dissolved in dry 1,2-dichloroethane (250 mL), and magnesium sulfate (3.0 g, 25 mmol) was added. The solution was placed under reflux for 6 hours whilst stirring. After this time the solution was filtered to remove the magnesium sulfate, and the solution concentrated under reduced pressure to yield the product as an orange oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.88 (1H, d, J = 1.9, Pyridyl-H); 8.56 (1H, dd, J = 4.6, 1.9, Pyridyl-H); 8.34 (1H, s, CH); 8.14 (1H, dt, J = 7.8; 1.9, Pyridyl-H); 7.32-7.08 (5H, m, Pyridyl-H (1H), Ar-H (4H)).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz, δ / ppm): 157.1; 152.0; 151.4; 150.9; 134.8; 131.8; 129.2; 126.5; 123.7; 120.8; 43.5.

_N_-((pyridin-3-yl)methyl)benzenamine



Imine was dissolved in methanol, and whilst stirring $NaBH_4$ (5.03 g, 13 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 hours. 50:50 HCl:H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product extracted, as a white crystalline solid (3.15 g, 17 mmol, 77 %) and recrystallised with dichloromethane and hexane.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 6.39 (1H, d, J=1.5, Py-H), 8.53 (1H, dd, J=5.0, 1.0, Py-H), 7.71 (1H, d, J=7.5, Py-H), 7.27 (1H, m, Ar-H), 7.20 (2H, t, J=8.0, Ar-H), 6.76 (1H, t, J=7.5, Py-H), 7.64 (2H, d, J=8.0, Ar-H), 4.36 (2H, s, CH_2), 4.19 (1H, bs, NH).

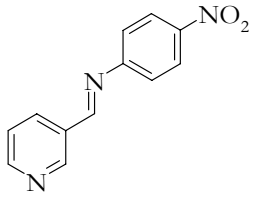
^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 149.4; 148.9; 147.9; 135.4; 135.2; 129.6; 123.8; 118.3; 113.2; 46.0.

ES+ MS: m/z = 185 [M^+]

Anal: Calculated for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21 %
Found: C, 78.15; H, 6.56; N, 15.20 %

IR: 3258 (s)

4-nitro-(*E*)-*N*-((pyridine-3-yl)methylene)benzenamine



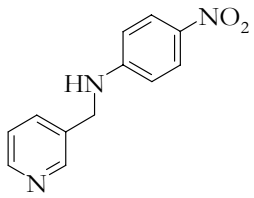
4-nitroaniline (13.60 g, 65 mmol) and 3-pyridinecarboxaldehyde (6.93 g, 65 mmol) were dissolved in dry 1,2-dichloroethane, and magnesium sulfate (5.00 g, mmol) was added. The solution was placed under reflux for 6 hours whilst stirring. After this time the solution was filtered to remove magnesium sulfate, and then concentrated under reduced pressure. The product was washed with ether, and the ether was removed under reduced pressure to yield the impure imine as dark yellow solid.

^{1}H-NMR (MeOD, 400 MHz, δ / ppm, J / Hz): 8.78 (1H, d, J=2.4, Pyridyl-H); 8.58 (1H, dd, J=4.8, 1.6, Pyridyl-H); 8.08 (2H, d, J=2.0, ArH); 7.53 (1H, dd, J=8.4, 5.6, Pyridyl-H); 7.45 (1H, s, Pyridyl-H); 6.77 (2H, d, J=2.0, ArH).

^{13}C{^{1}H}-NMR (MeOD, 125 MHz, δ / ppm): 152.2; 148.9; 148.7; 148.0; 135.3; 125.9; 125.6; 125.4; 124.1; 123.9; 112.6; 112.2; 111.9; 63.8.

ES+ MS: m/z = 228 [M^+]

4-nitro-*N*-((pyridine-3-yl)methyl)benzenamine



Imine (2.15 g, 7.18 mmol) was dissolved in methanol, and whilst stirring $NaBH_4$ (2.69 g, 71.8 mmol) was added until the solution ceased to effervesce. The solution was stirred for a further 2 hours. 50:50 HCl:H_2O was added until the solution was pH 3, and then 2 M NaOH was added until the solution was pH 9. The product was extracted using dichloromethane. The organic layer was dried over $MgSO_4$, and then filtered. The solvent was evaporated under reduced pressure, and the product, (0.54 g, 1.79 mmol, 25 %) re-crystallized from dichloromethane and hexane.

^{1}H-NMR ($CDCl_3$, 500 MHz, δ / ppm, J / Hz): 8.63 (1H, s, Pyridyl-H); 8.57 (1H, d, J=5.0, Pyridyl-H); 8.09 (2H, dd, J=7.0, 2.0, ArH); 7.67 (1H, dd, J=8.0, 2.0, Pyridyl-H); 7.30 (1H, dd, J=8.0, 5.0, Pyridyl-H); 6.59 (2H, dd, J=7.0; 2.0, ArH); 4.92 (1H, s, NH); 4.47 (2H, d, J=6.0, CH_2).

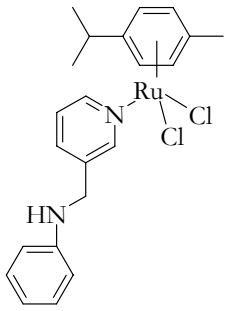
^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 207.3; 152.8; 149.6; 149.3; 135.2; 133.2; 126.6; 124.0; 111.72; 45.4; 31.2.

ES+ MS: m/z = 230 [M^+]

Anal: Calculated for $C_{12}H_{12}N_3O_2$: C, 62.60; H, 5.25; N, 18.25
Found: C, 62.40; H, 4.80; N, 18.38

IR: 3239 (s)

Ru(η^6-*p*-cymene)(*N*-((pyridin-3-yl)methyl)benzenamine)Cl_2 1a



$[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (0.77 g, 1.3 mmol) and *N*-((pyridin-3-yl)methyl)benzenamine (0.48 g, 2.6 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time an orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (1.08 g, 2.2 mmol, 85%)

^{1}H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.95 (1H, s, Pyridyl-H); 8.89 (1H, d, J = 5.6, Ar-H); 7.69 (1H, d, J = 8.0, Pyridyl-H); 7.10 (3H, m, Ar-H); 6.73 (1H, t, J = 8.0, Pyridyl-H); 6.57 (1H, d, J = 8.0, Pyridyl-H); 5.29 (2H, J = 4.8, Ar-H); 5.03 (2H, J = 4.8, Ar-H); 4.40 (1H, bs, NH); 4.58 (2H, s, CH_2); 2.85 (1H, h, J = 6.8, CH); 1.22 (6H, dd, J = 6.8, 1.6, CH_3).

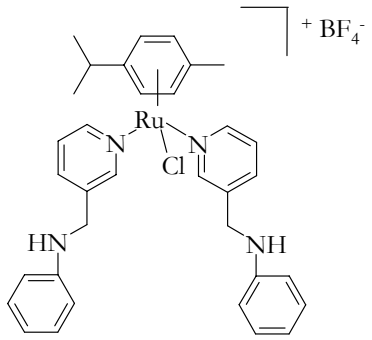
^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 154.1; 153.4; 147.1; 136.9; 136.5; 129.6; 124.5; 118.4; 113.4; 103.6; 97.41; 83.0; 82.4; 45.1; 31.5; 30.8; 22.5.

ES+ MS: m/z = 489 [M^+]

Anal:	Calculated for $C_{22}H_{26}N_2Cl_2Ru$:	C, 53.88; H, 5.34; N, 5.71
	Found:	C, 53.71; H, 5.34; N, 5.62

IR: 3352 (s)

[Ru(η^6-*p*-cymene)(*N*-((pyridin-3-yl)methyl)benzenamine)Cl]$^+BF_4^-$ 2a



Ru(η^6-*p*-cymene)(*N*-((pyridin-3-yl)methyl)benzenamine)Cl_2 (0.4 g, 0.8 mmol) and silver tetrafluoroborate (0.16 g, 0.8 mmol) were dissolved in 50:50 MeOH:Acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver (I) chloride was removed through celite and *N*-((pyridin-3-yl)methyl)benzenamine (0.15 g, 0.8 mmol) was added to the MeOH:Acetone solution and stirred for a further 4 hours. The solvent was removed under reduced pressure to yield a crude orange solid, which was re-crystallised from CH_2Cl_2 and C_6H_{14}. The orange solid was filtered and washed with C_6H_{14}, and dried in air (0.3 g, 0.4 mmol, 56 %)

^{1}H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.76 (2H, s, Pyridyl-H); 8.38 (2H, d, J = 5.8, Ar-H); 7.54 (2H, d, J = 7.6, Pyridyl-H); 7.0 (6H, m, Ar-H); 6.55 (2H, t, J = 7.6, Pyridyl-H); 6.42 (4H, d, J = 7.6, Pyridyl-H); 5.37 (2H, bs, NH); 5.29 (4H, q, J = 18.7, 6.2, Ar-H); 4.40 (2H, d, J =17.2, CH_2); 4.32 (2H, d, J =17.2, CH_2); 2.28 (1H, h, J = 6.8, CH); 0.83 (6H, d, J = 6.8, CH_3).

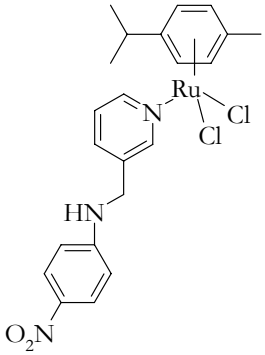
^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 154.1; 151.2; 147.1; 139.0; 138.1; 129.5; 125.1; 117.3; 112.9; 102.6; 102.4; 90.5; 81.2; 44.5; 30.9; 22.6; 17.6.

ES+ MS: m/z = 639 [M-BF_4^-]

Anal: Calculated for $C_{34}H_{38}N_4ClRuBF_4$: C, 56.25; H, 5.28; N, 7.72
Found: C, 55.86; H, 5.22; N, 7.63

IR: 3421 (s)

Ru(η^6-*p*-cymene)(4-nitro-*N*-((pyridin-3-yl)methyl)benzenamine)Cl_2 1b



[Ru(η^6-*p*-cymene)Cl_2]$_2$ (1.0 g, 1.6 mmol) and 4-nitro-*N*-((pyridin-3-yl)methyl)benzenamine (0.8 g, 3.2 mmol) were dissolved in toluene (100 mL), previously degassed for 1 h and left to stir at room temperature for 1 h. During this time a yellow/orange precipitate formed. The solid was collected by filtration, washed with toluene and dried in the air for 18 h (1.2 g, 2.24 mmol, 68 %).

^{1}H-NMR ($CDCl_3$, 400 MHz, δ / ppm, J / Hz): 8.76 (1H, d, J=6.4, Pyridyl-H); 7.95 (2H, d, J=8.8, ArH); 7.45 (1H, d, J=7.6, Pyridyl-H); 7.07 (1H, t, J=6.0, Pyridyl-H); 6.44 (2H, d, J=8.8); 5.94 (1H, s, NH); 5.30 (2H, d, J=5.6, ArH); 5.09 (2H, d, J=5.6, ArH); 4.15 (2H, s, CH_2); 2.81 (1H, q, J=6.8, CH); 1.61 (3H, s, CH_3); 1.18 (6H, d, J=6.8, CH_3).

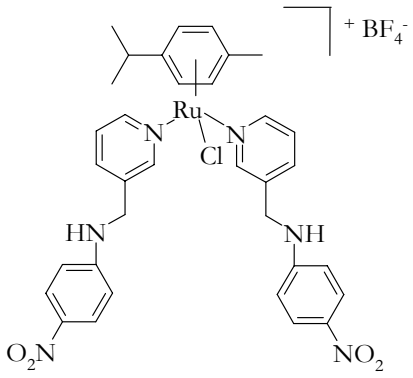
^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 153.4; 138.5; 136.8; 135.4; 126.5; 124.5; 111.8; 103.9; 97.3; 82.9; 82.6; 44.07; 31.2, 22.4; 18.4.

ES+ MS: m/z = 535 [M^+]

Anal: Calculated for $C_{22}H_{25}N_3O_2Cl_2Ru$: C, 49.35; H, 4.71; N, 7.85
Found: C, 50.39; H, 4.70; N, 8.92

IR: 3228 (s)

[Ru(η^6-*p*-cymene)(4-nitro-*N*-((pyridin-3-yl)methyl)benzenamine)Cl]$^+$$BF_4^-$ 2b



Ru(η^6-*p*-cymene)(4-nitro-*N*-((pyridin-3-yl)methyl)benzenamine)Cl_2 (0.3 g, 0.6 mmol), silver tetrafluoroborate (0.2 g, 0.9 mmol) and 4-nitro-*N*-((pyridin-3-yl)methyl)benzenamine(0.2 g, 0.8 mmol) were dissolved in 50:50 MeOH:Acetone (50 mL), previously degassed for 1 h and left to stir at room temperature for 20 min. The silver (I) chloride was removed through celite. The solvent volume was reduced under reduced pressure and the product recrystallised in the freezer from MeOH:Acetone:Diethyl Ether solution overnight. During this time an orange solid formed and was collected by filtration and washed with ether (0.1 g, 0.2 mmol, 33 %).

^{1}H-NMR ($CDCl_3$, 500 MHz, δ / ppm, J / Hz): 8.84 (2H, s, Pyridyl-H); 8.54 (2H, d, J=5.5, Pyridyl-H); 7.98 (4H, d, J=9.0, Ar); 7.63 (2H, d, J=8.0, Pyridyl-H); 7.12 (2H, t, J=5.5, Pyridyl-H); 6.67 (2H, s, NH); 6.49 (4H, d, J=9.0, Ar); 5.47 (2H, d, J=6.0, Ar(Ru)); 5.44 (2H, d, J=6.5, Ar(Ru)); 4.57 (2H, dd, J=7.0, 17.0, CH_2-NH); 4.49 (2H, dd, J=7.0, 17.0, CH_2-NH); 2.30 (1H, q, J=7.0, CH); 1.56 (3H, s, CH_3); 0.85 (6H, d, J=7.0, CH_3).

^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz, δ / ppm): 153.7; 152.6; 151.9; 138.4; 138.1; 137.4; 126.4; 125.2; 111.6; 102.8; 102.3; 90.2; 81.5; 44.2; 30.8; 22.4; 17.7.

ES+ MS: m/z = 729 [M-BF_4].

Anal: Calculated for $C_{34}H_{36}N_6O_4ClRuBF_4$: C, 50.04; H, 4.45; N, 10.30
Calculated for $C_{34}H_{36}N_6O_4ClRuBF_4 \cdot Me_2CO$: C, 50.16; H, 4.91; N, 9.75
Found: C, 50.41; H, 4.79; N, 9.25

IR: 3390 (s)

(B) Crystallography of Compound 3

Crystal data for **3**: $C_{16}H_{22}Cl_2N_2Ru$, M = 414.33, red block, 0.15 × 0.10 × 0.08 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 9.2102(3), b = 7.9958(3), c = 22.4459(8) Å, β = 98.992(2)°, V = 1632.67(10) $Å^3$, Z = 4, D_c = 1.686 g/cm^3, F_{000} = 840, KappaCCD, MoKα radiation, λ = 0.71070 Å, T = 120(2)K, $2\theta_{max}$ = 55.0º, 16294 reflections collected, 3714 unique (R_{int} = 0.0280). Final *GooF* = 1.030, *R1* = 0.0245, *wR2* = 0.0550, *R* indices based on 3282 reflections with I >2sigma(I) (refinement on F^2), 199 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.282 mm^{-1}.

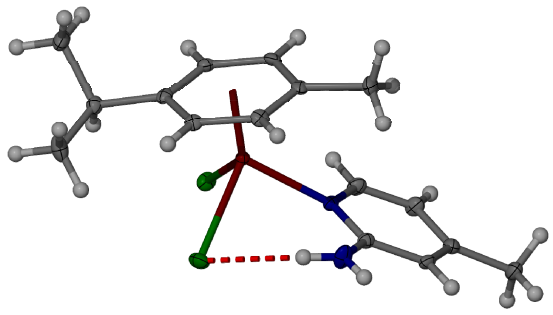
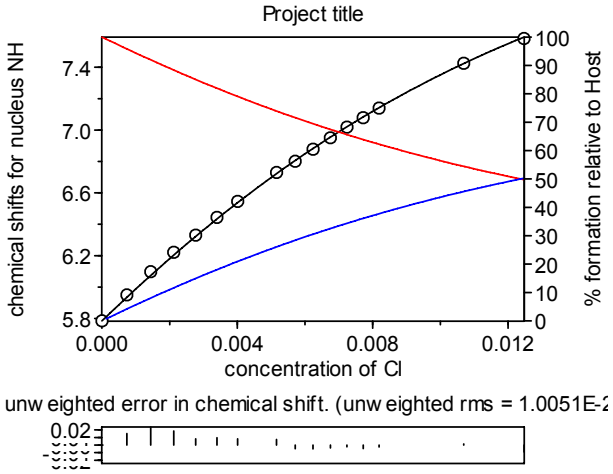


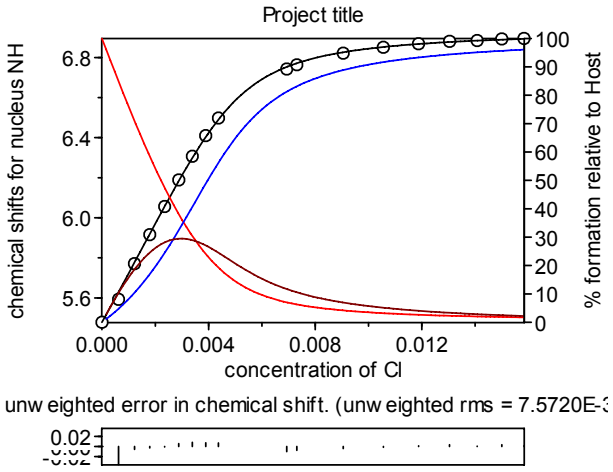
Figure S1: Molecular structure (50% ellipsoids) of [Ru(η^6-$C_6H_4MeCHMe_2$)Cl_2(2-apic)] (**3**). Hydrogen bond distance (Å): N(2)H···Cl(1) 3.162(2) Å

(C) Titration plots

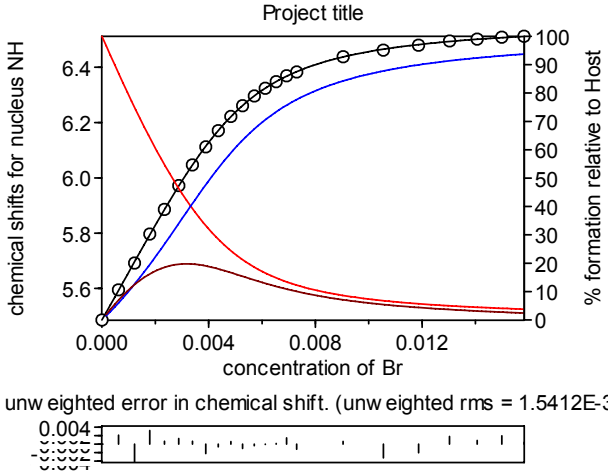
1b + Cl^-



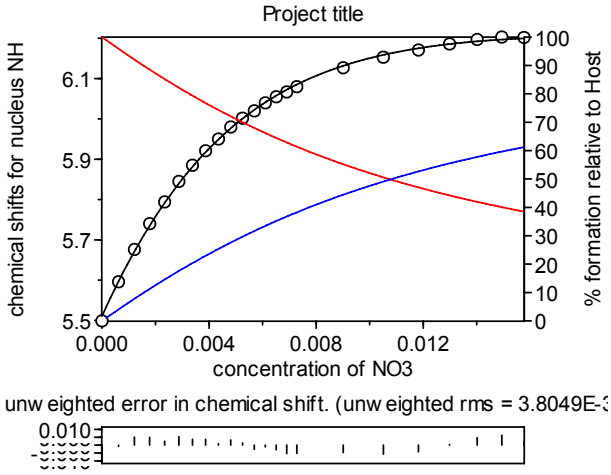
2a + Cl^-



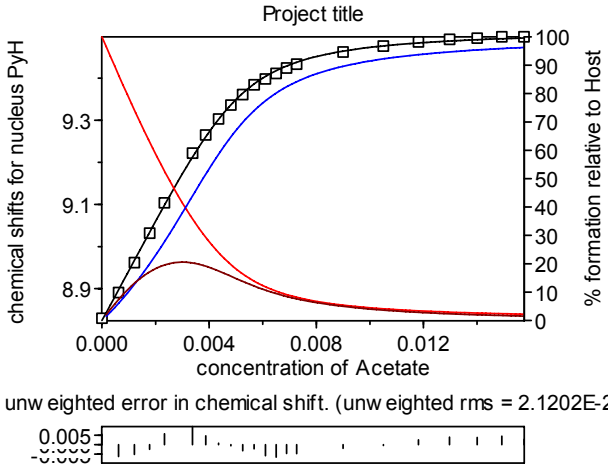
2a + Br^-



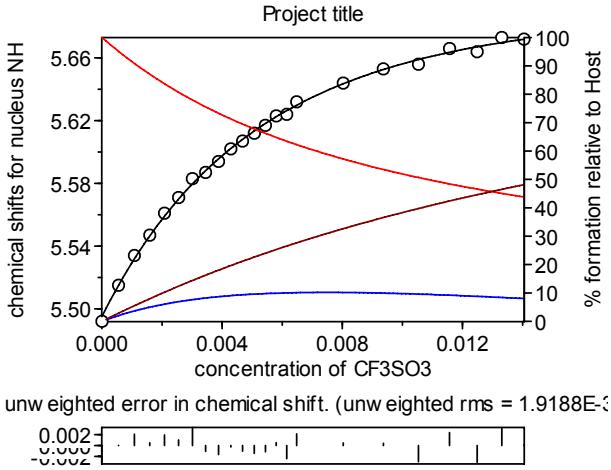
2a + NO_3^-



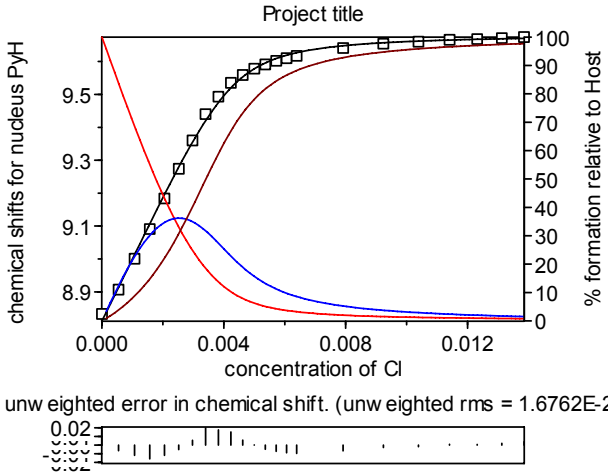
2a + $MeCO_2^-$



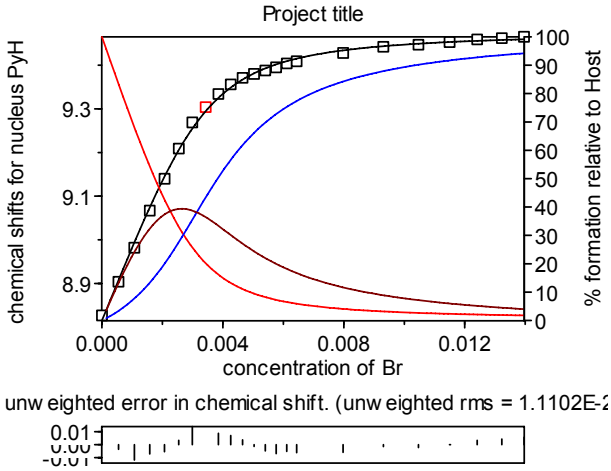
2a + $CF_3SO_3^-$



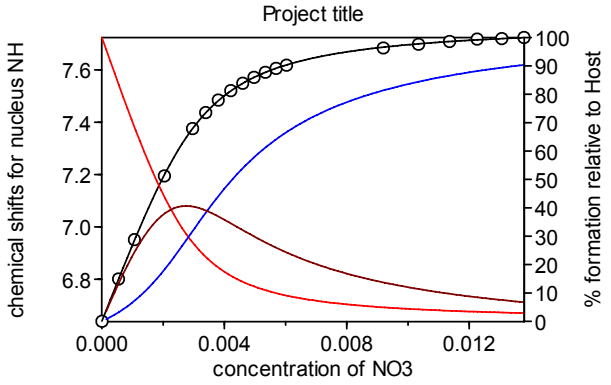
2b + Cl^-



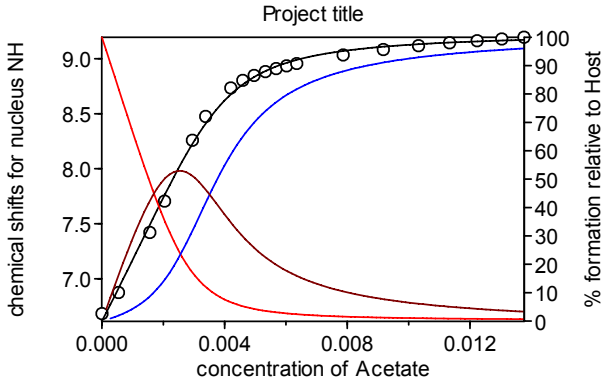
2b + Br^-



2b + NO_3^-



2b + $MeCO_2^-$



2b + $CF_3SO_3^-$