Kinetics and mechanism of the racemic addition of trimethylsilyl cyanide to aldehydes catalysed by Lewis bases

Supplementary Information

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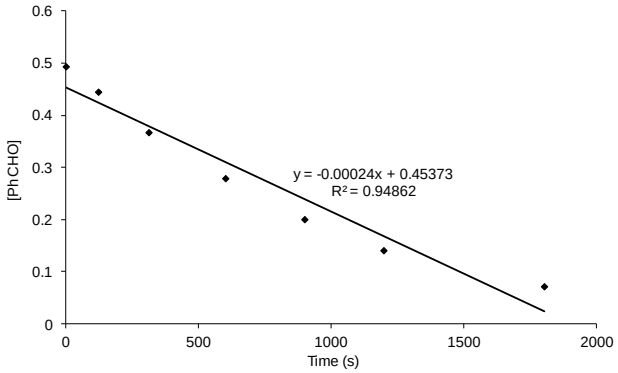
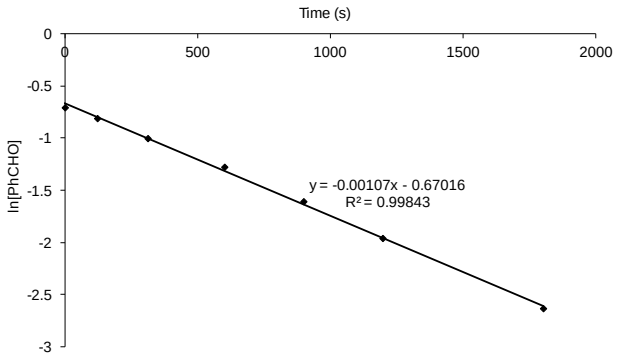
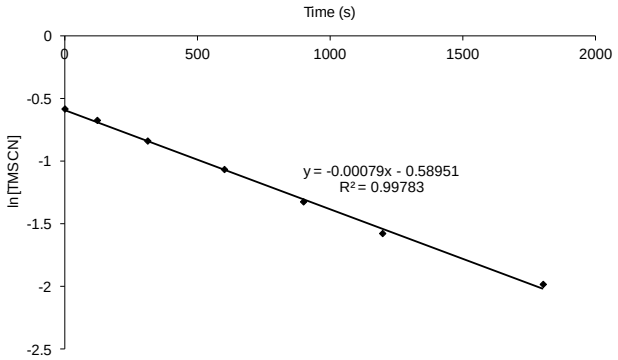
Zero order kinetics plot



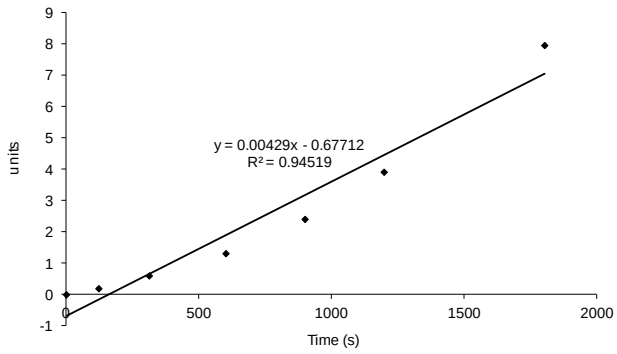
First order in [PhCHO] kinetics plot



First order in [Me_3SiCN] kinetics plot



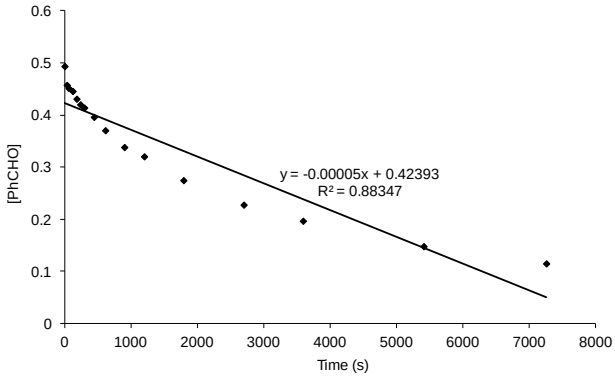
Second order kinetics plot



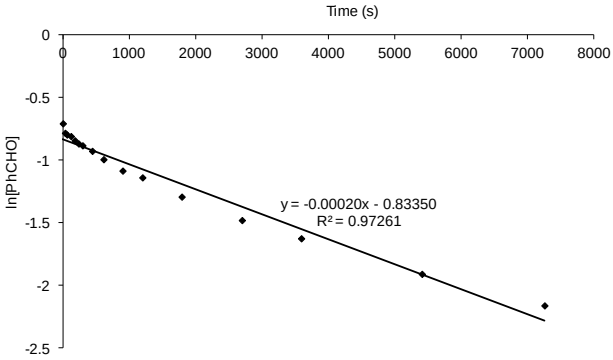
For the second order plot, the units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. In all cases the concentration of benzaldehyde was monitored.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NNCS 2

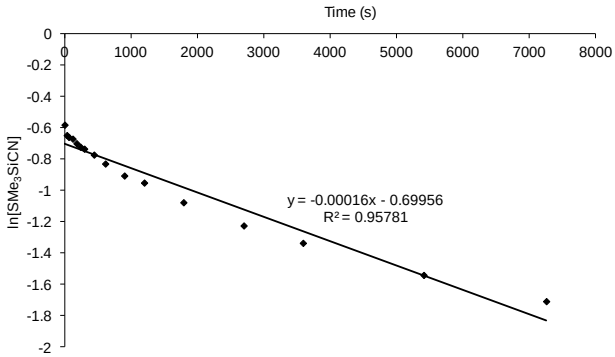
Zero order kinetics plot



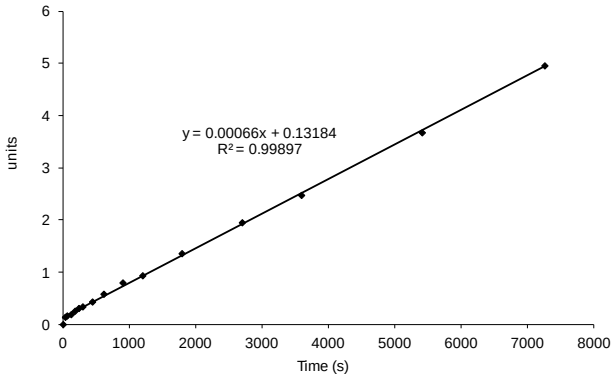
First order in [PhCHO] kinetics plot



First order in [Me_3SiCN] kinetics plot



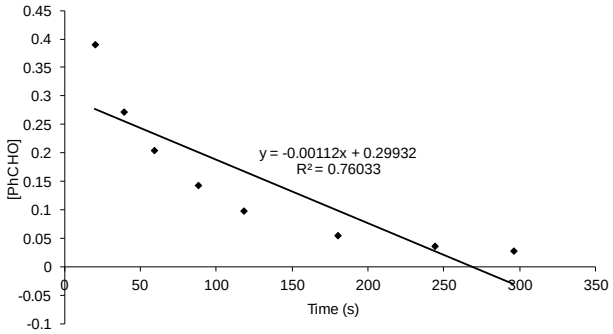
Second order kinetics plot



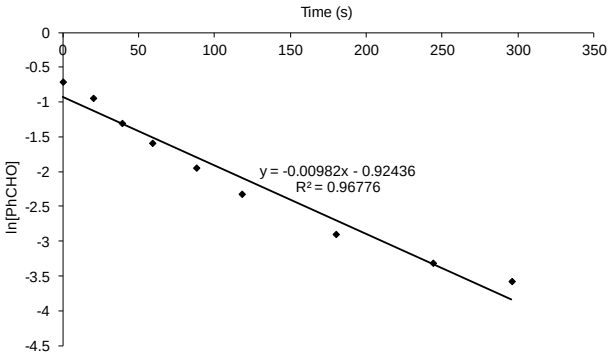
For the second order plot, the units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0–B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. In all cases the concentration of benzaldehyde was monitored.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NN_3 3

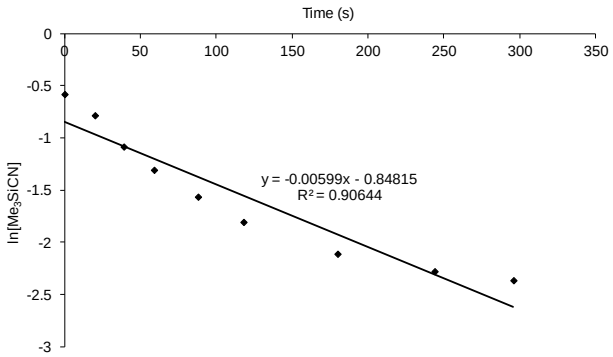
Zero order kinetics plot



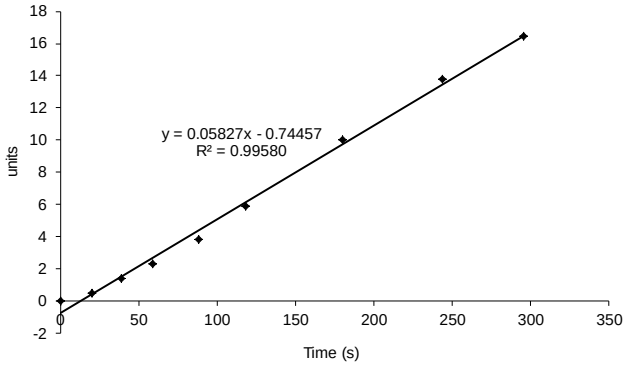
First order in [PhCHO] kinetics plot



First order in [Me_3SiCN] kinetics plot



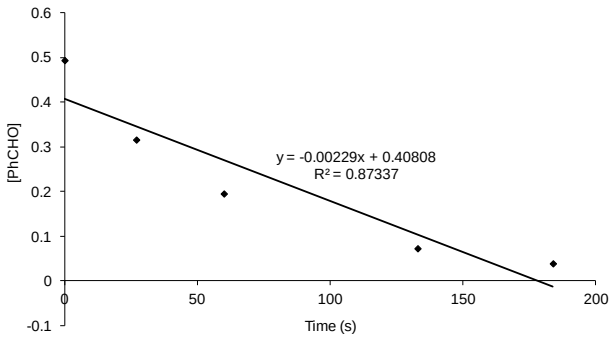
Second order kinetics plot



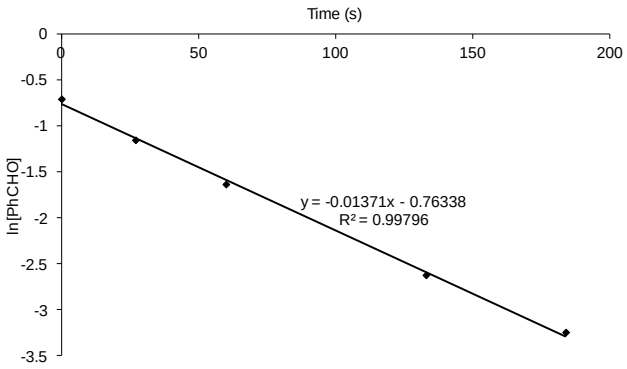
For the second order plot, the units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. In all cases the concentration of benzaldehyde was monitored.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NCN 3

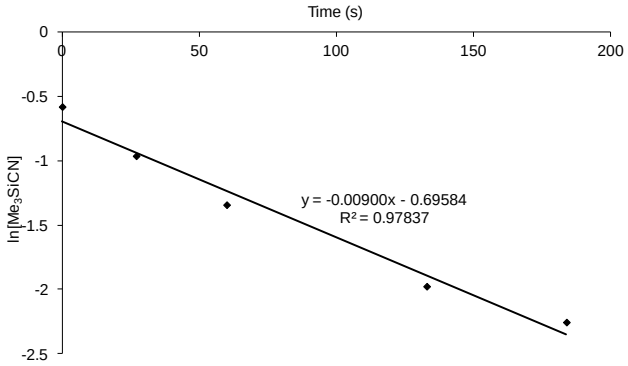
Zero order kinetics plot



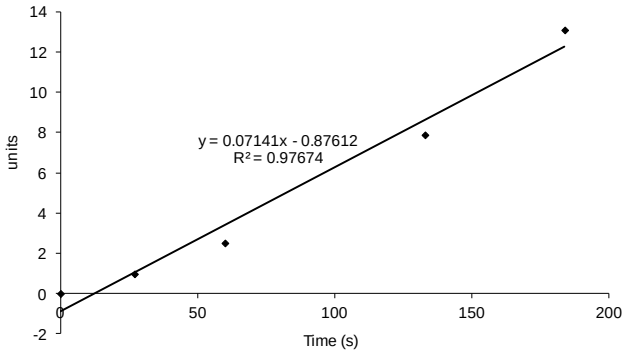
First order in [PhCHO] kinetics plot



First order in [Me_3SiCN] kinetics plot



Second order kinetics plot

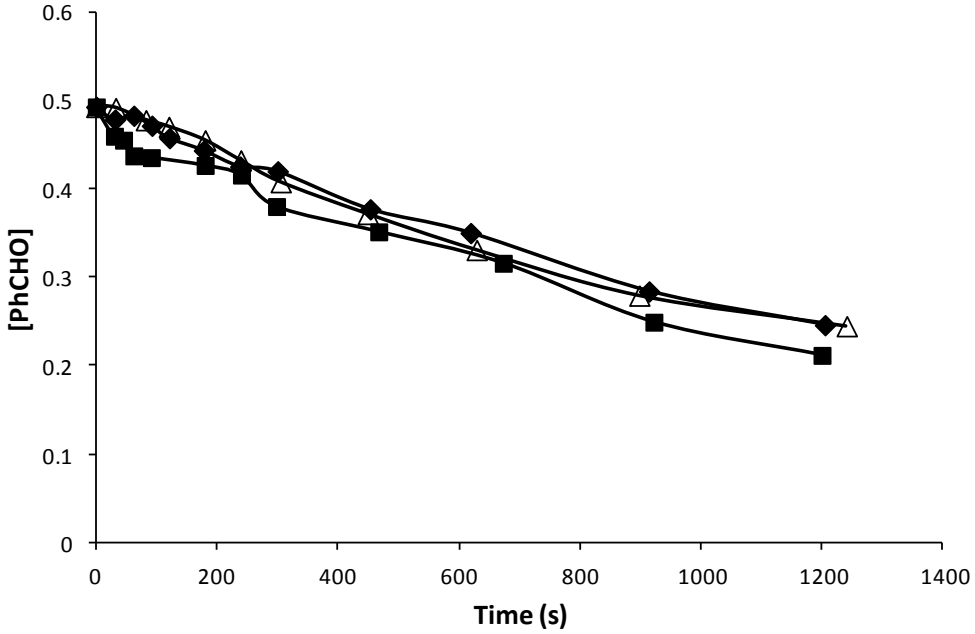


For the second order plot, the units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. In all cases the concentration of benzaldehyde was monitored.

Kinetic plots used to determine the reaction order with respect to [PhCHO] and [Me_3SiCN]

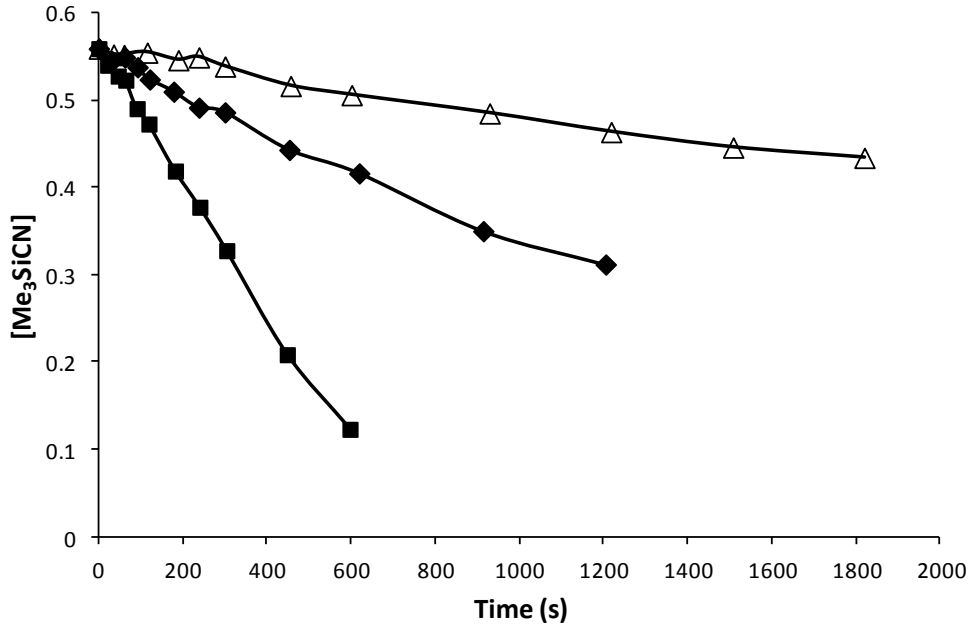
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Et_3N 1

Kinetic plot showing that the initial rate of reaction does not depend on the initial concentration of Me_3SiCN



Open triangles $[Me_3SiCN]_0$ = 0.28 M, filled diamonds $[Me_3SiCN]_0$ = 0.56 M, filled squares $[Me_3SiCN]_0$ = 1.12 M. In each case $[PhCHO]_0$ = 0.53 M and $[Et_3N]$ = 0.01 M.

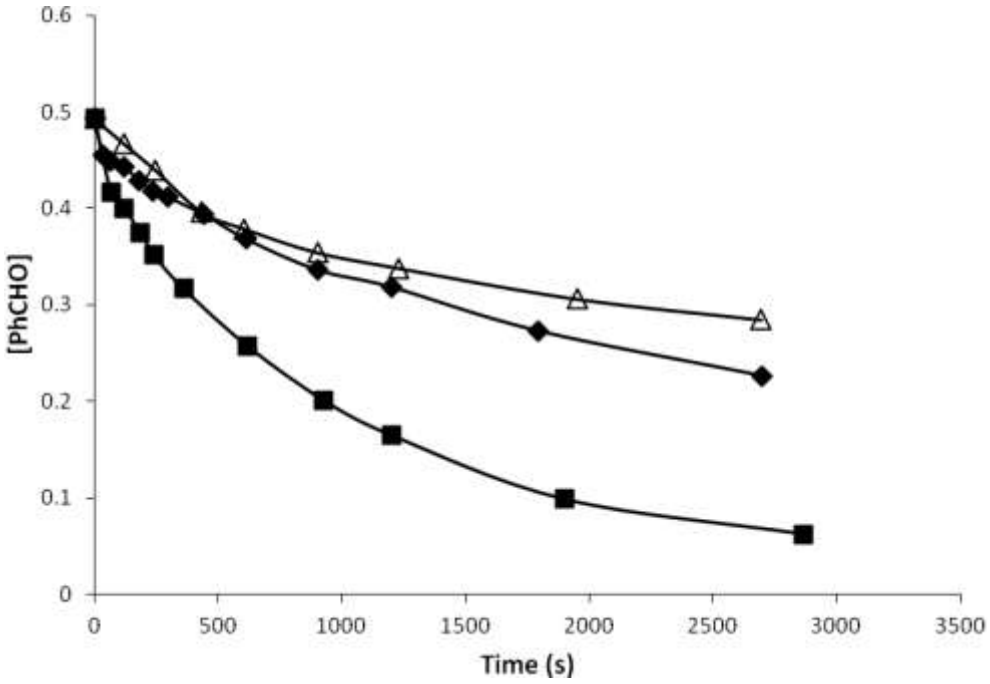
Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of PhCHO



Open triangles $[PhCHO]_0$ = 0.25 M, filled diamonds $[PhCHO]_0$= 0.49 M, filled squares $[PhCHO]_0$ = 0.99 M. In each case $[Me_3SiCN]_0$ = 0.56 M and $[Et_3N]$ = 0.01 M.

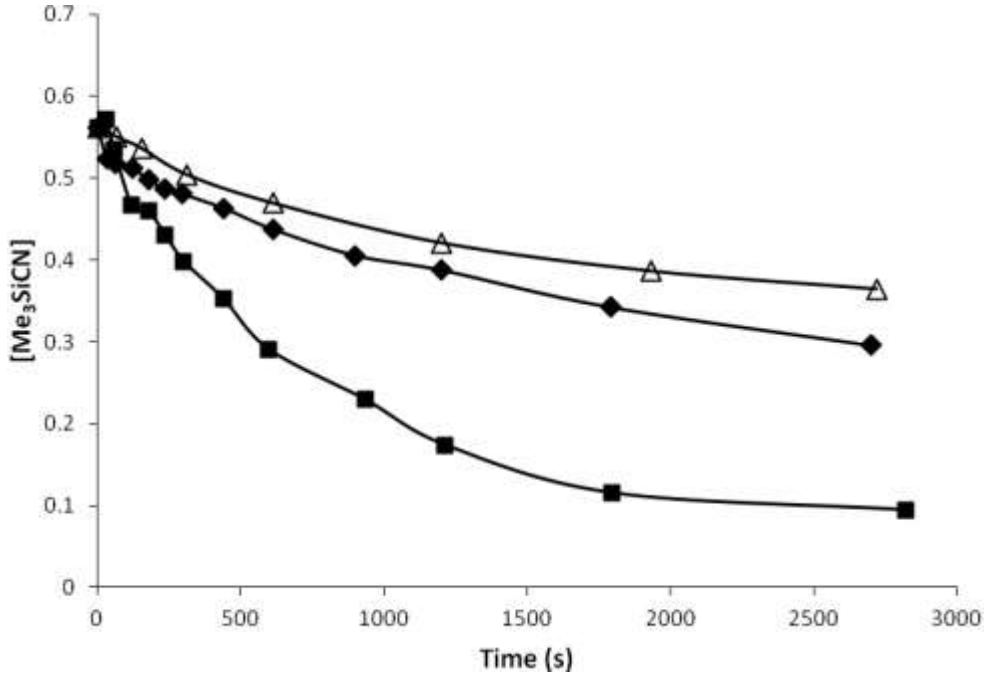
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NNCS 2

Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of Me_3SiCN



Open triangles $[Me_3SiCN]_0$ = 0.28 M, filled diamonds $[Me_3SiCN]_0$ = 0.56 M, filled squares $[Me_3SiCN]_0$ = 1.12 M. In each case $[PhCHO]_0$ = 0.53 M and $[Bu_4NNCS]$ = $9.4x10^{-3}$ M.

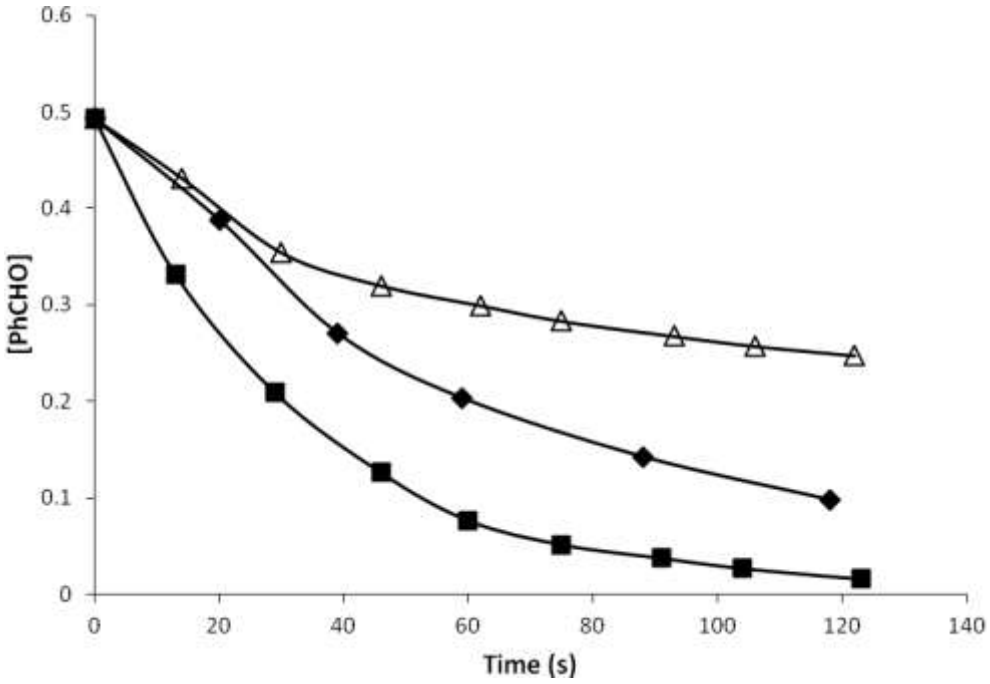
Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of PhCHO



Open triangles $[PhCHO]_0$ = 0.27 M, filled diamonds $[PhCHO]_0$= 0.53 M, filled squares $[PhCHO]_0$ = 1.06 M. In each case $[Me_3SiCN]_0$ = 0.56 M and $[Bu_4NNCS]$ = $9.4x10^{-}3$ M.

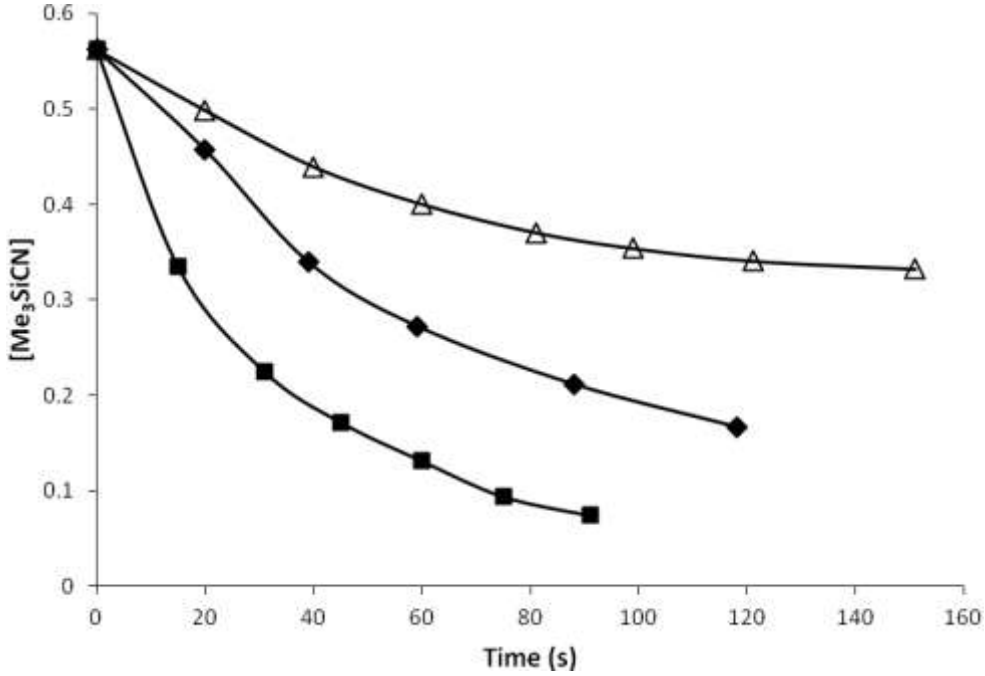
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NN_3 3

Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of Me_3SiCN



Open triangles $[Me_3SiCN]_0$ = 0.28 M, filled diamonds $[Me_3SiCN]_0$ = 0.56 M, filled squares $[Me_3SiCN]_0$ = 1.12 M. In each case $[PhCHO]_0$ = 0.53 M and $[Bu_4NN_3]$ = 2.3x10^{-}3 M.

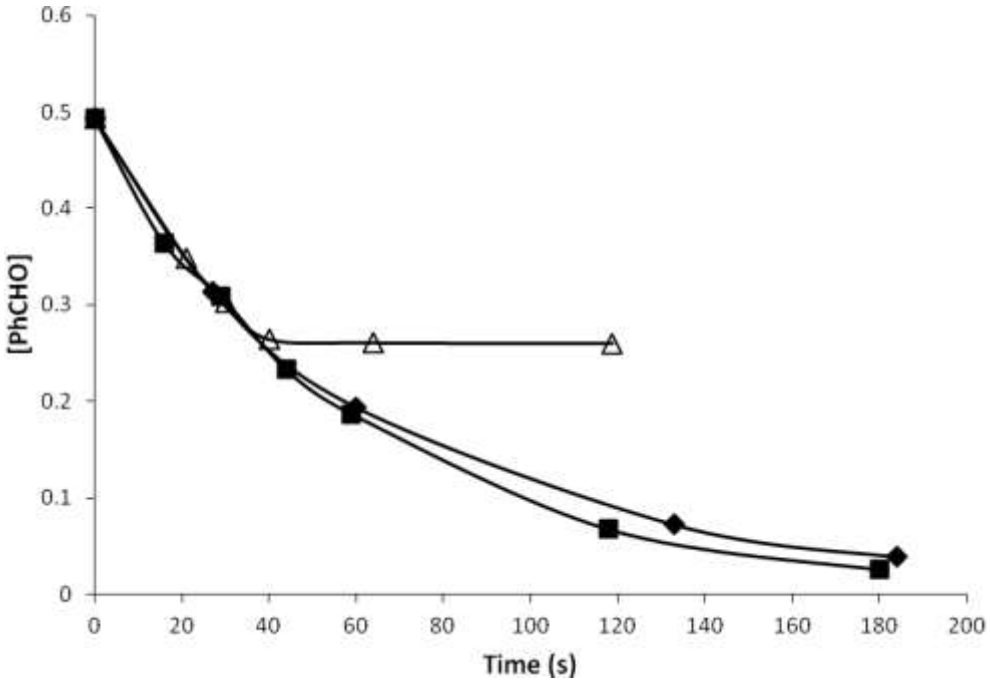
Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of PhCHO



Open triangles $[PhCHO]_0$ = 0.27 M, filled diamonds $[PhCHO]_0$= 0.53 M, filled squares $[PhCHO]_0$ = 1.06 M. In each case $[Me_3SiCN]_0$ = 0.56 M and $[Bu_4NN_3]$ = 2.3x10^{-}3 M.

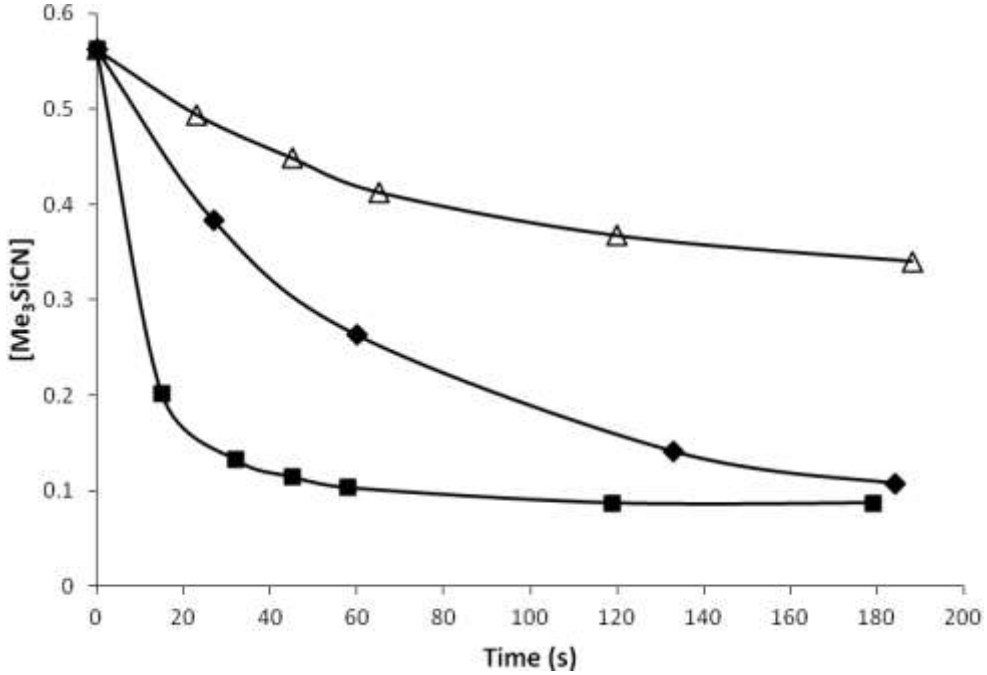
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NCN 4

Kinetic plot showing that the initial rate of reaction does not depend on the initial concentration of Me_3SiCN



Open triangles $[Me_3SiCN]_0$ = 0.28 M, filled diamonds $[Me_3SiCN]_0$ = 0.56 M, filled squares $[Me_3SiCN]_0$ = 1.12 M. In each case $[PhCHO]_0$ = 0.53 M and $[Bu_4NCN]$ = 2.3x10^{-}3 M.

Kinetic plot showing that the initial rate of reaction does depend on the initial concentration of PhCHO



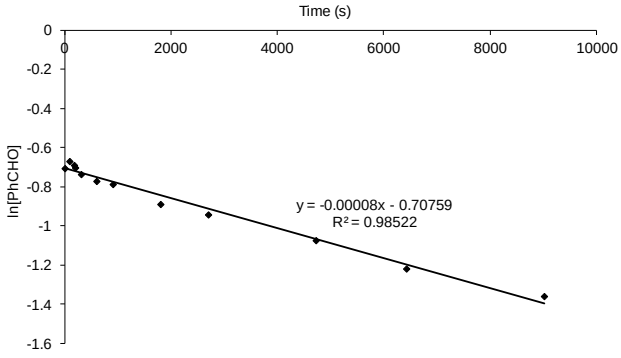
Open triangles $[PhCHO]_0$ = 0.27 M, filled diamonds $[PhCHO]_0$= 0.53 M, filled squares $[PhCHO]_0$ = 1.06 M. In each case $[Me_3SiCN]_0$ = 0.56 M and $[Bu_4NCN]$ = 2.3x10^{-3} M.

Kinetic plots used to determine the reaction order with respect to catalyst concentration

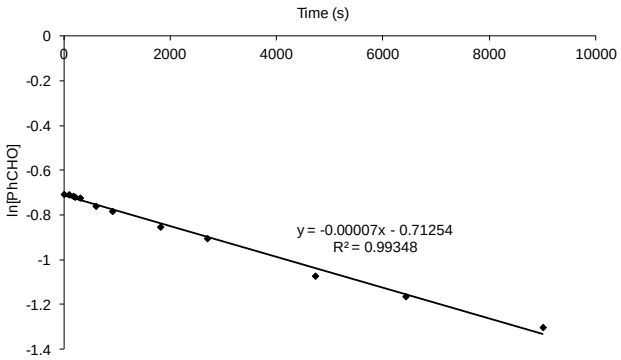
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Et_3N 1

[Et_3N] = 0.001 M (corresponds to 0.2 mol%)

Run 1

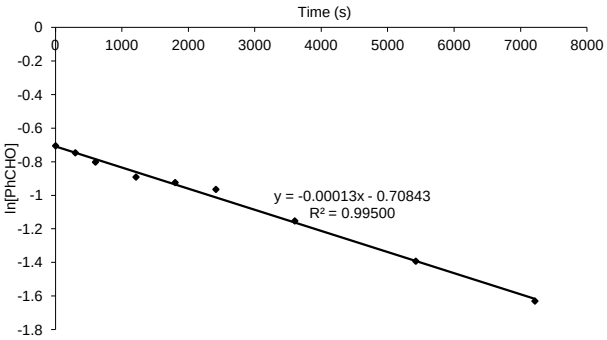


Run 2

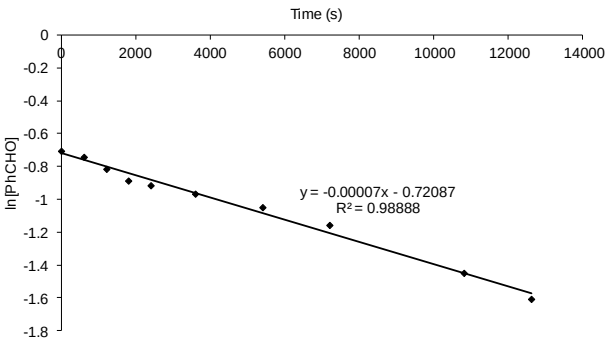


[Et_3N] = 0.002 M (corresponds to 0.4 mol%)

Run 1

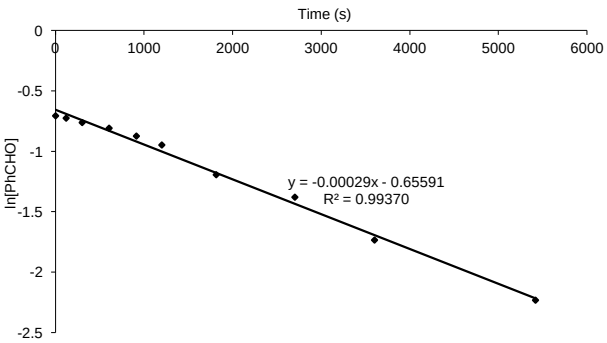


Run 2

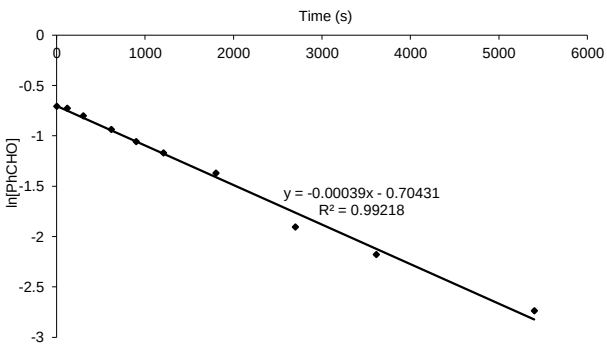


[Et_3N] = 0.004 M (corresponds to 0.8 mol%)

Run 1

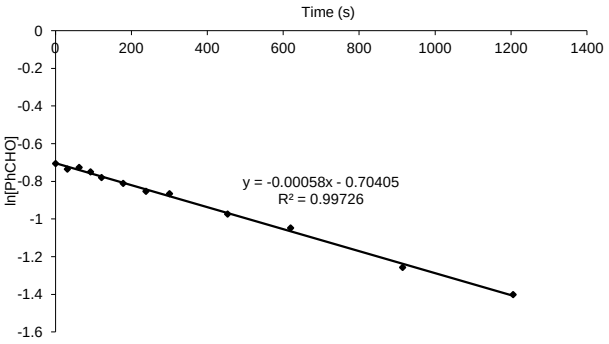


Run 2

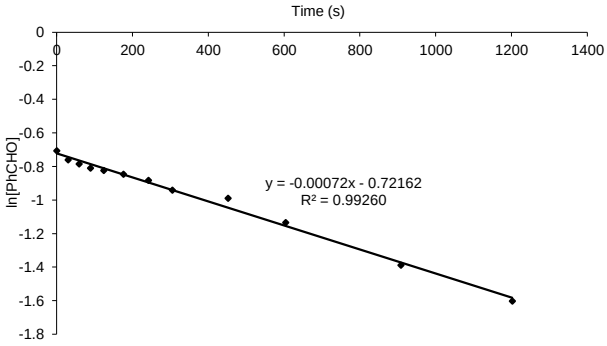


[Et_3N] = 0.01 M (corresponds to 2 mol%)

Run 1

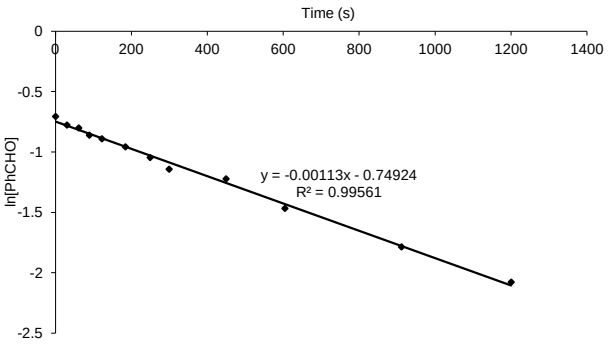


Run 2

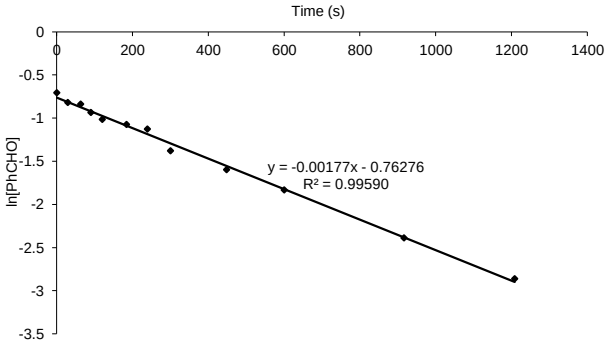


[Et_3N] = 0.02 M (corresponds to 4 mol%)

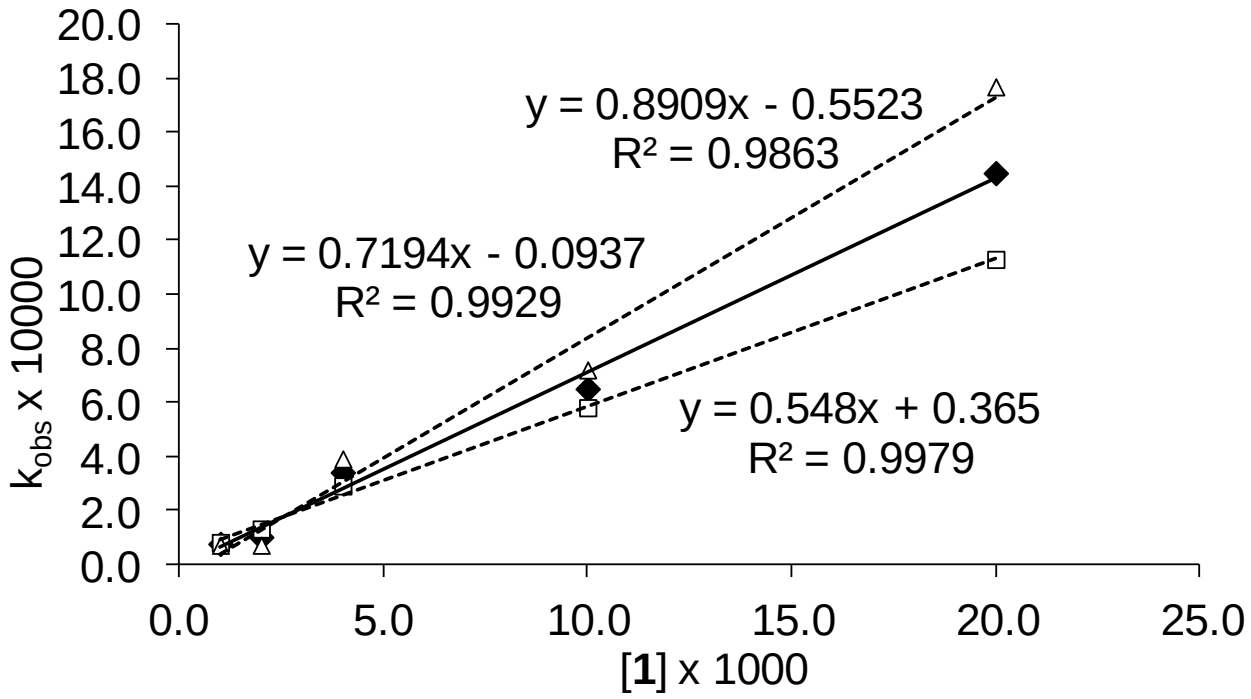
Run 1



Run 2



Plot of k_{obs} against [**1**]

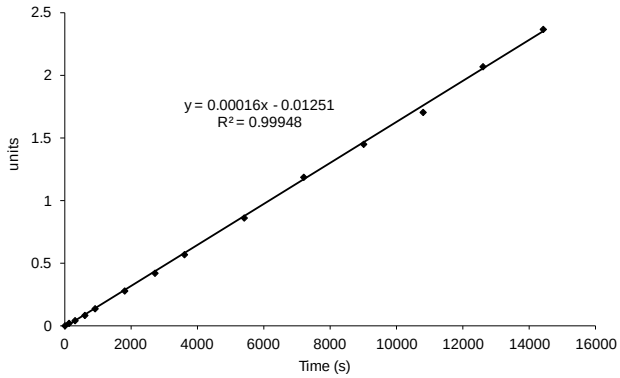


The dotted lines and empty data points show the rate data obtained from each of a duplicated series of kinetic experiments. The solid line and filled data points show the average of these two data sets and correspond to the data given in Figure 1 of the manuscript. The error in the rate constant was estimated from the difference in slopes of the three lines in this plot.

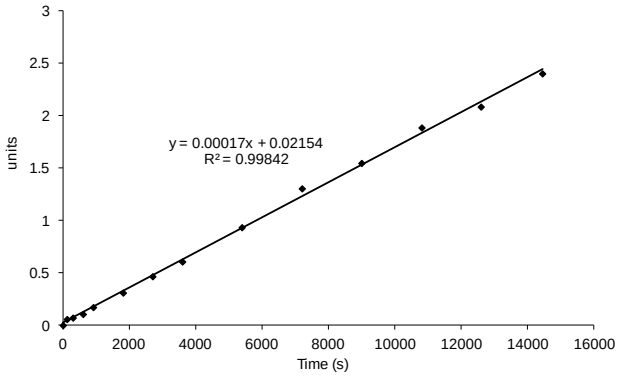
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NNCS 2

[Bu_4NNCS] = $2.5x10^{-4}$ M (corresponds to 0.05 mol%)

Run 1

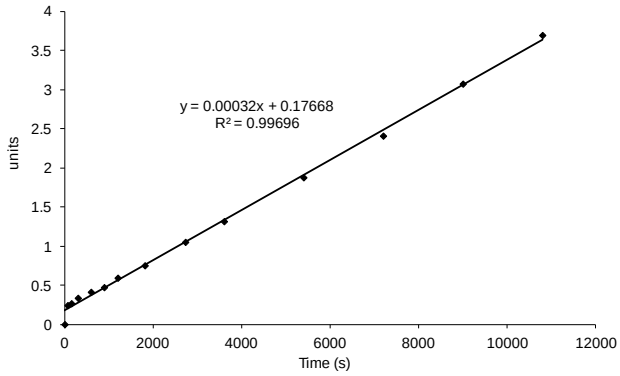


Run 2

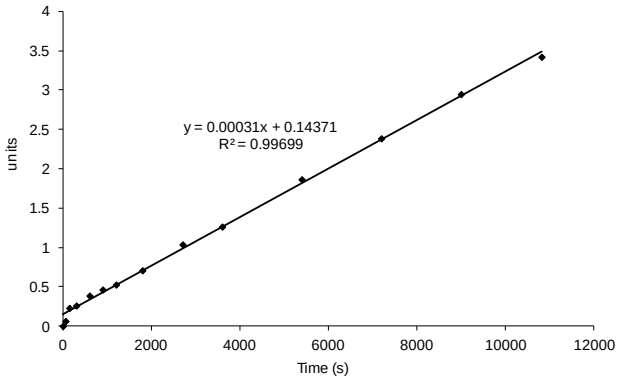


[Bu_4NNCS] = $5x10^{-4}$ M (corresponds to 0.1 mol%)

Run 1

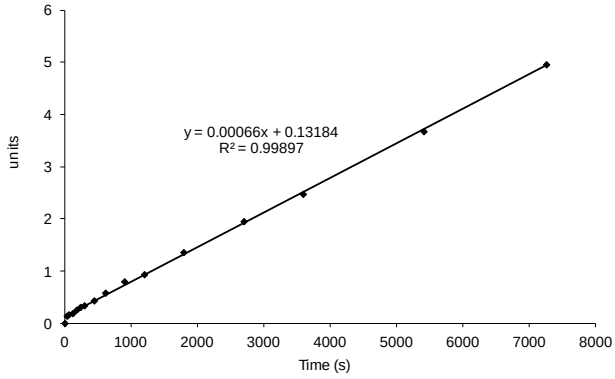


Run 2

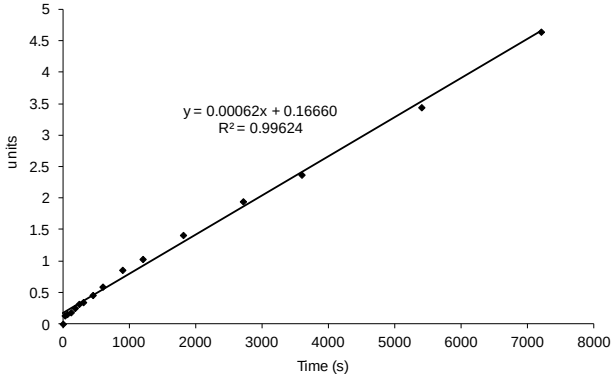


[Bu_4NNCS] = 0.001 M (corresponds to 0.2 mol%)

Run 1

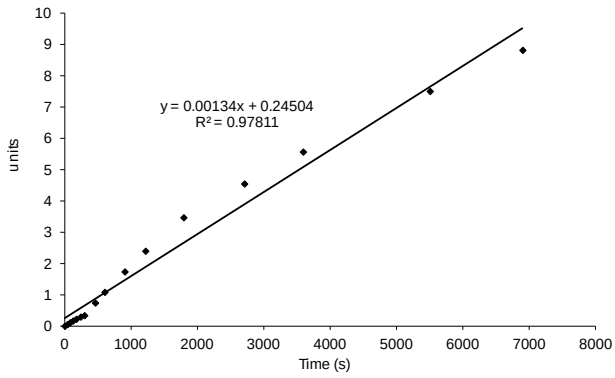


Run 2

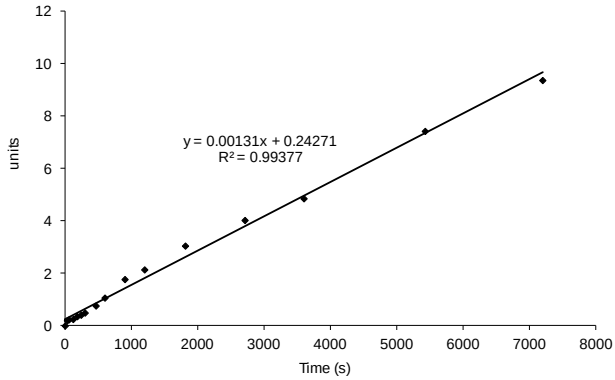


[Bu_4NNCS] = 0.002 M (corresponds to 0.4 mol%)

Run 1

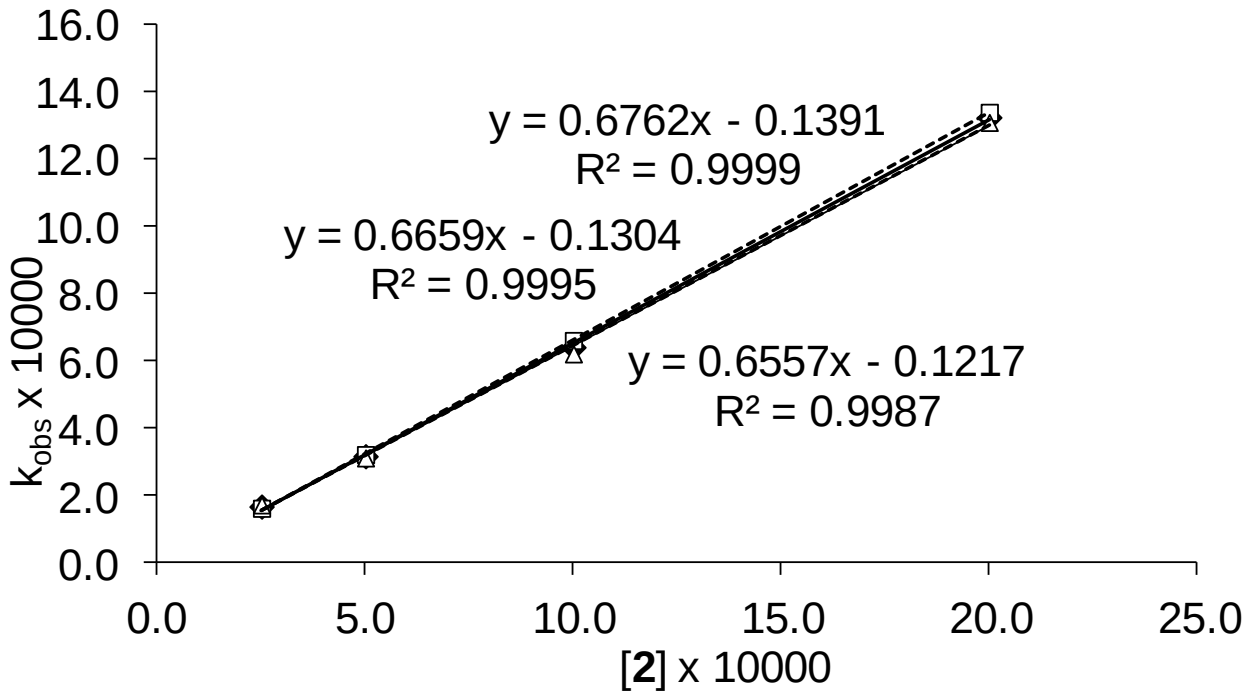


Run 2



The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Plot of k_{obs} against [**2**]

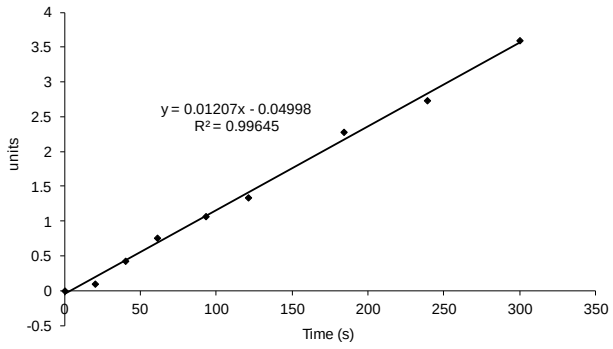


The dotted lines and empty data points show the rate data obtained from each of a duplicated series of kinetic experiments. The solid line and filled data points show the average of these two data sets and correspond to the data given in Figure 1 of the manuscript. The error in the rate constant was estimated from the difference in slopes of the three lines in this plot.

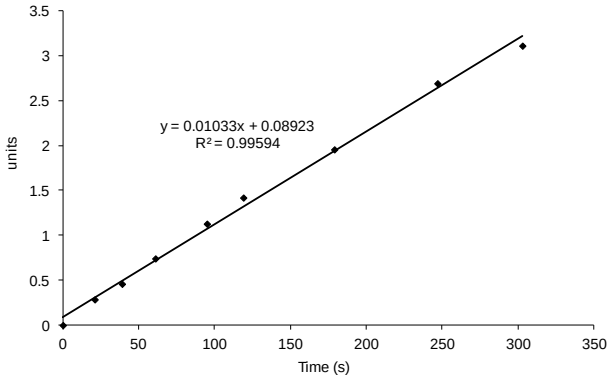
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NN_3 3

$[Bu_4NN_3] = 5x10^{-5}$ M (corresponds to 0.01 mol%)

Run 1

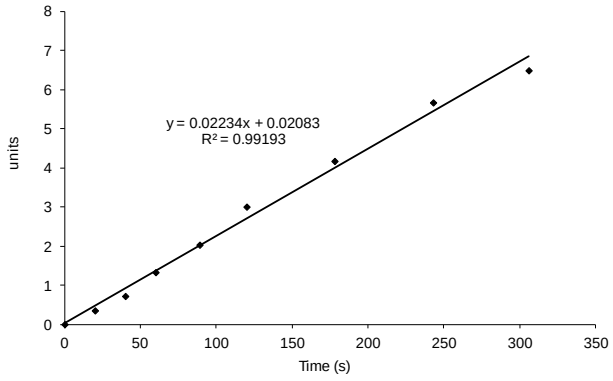


Run 2

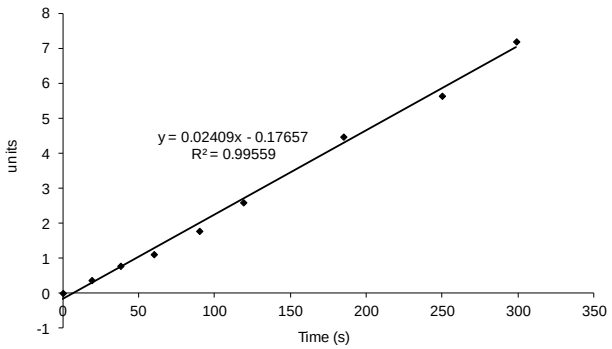


$[Bu_4NN_3] = 1x10^{-4}$ M (corresponds to 0.02 mol%)

Run 1

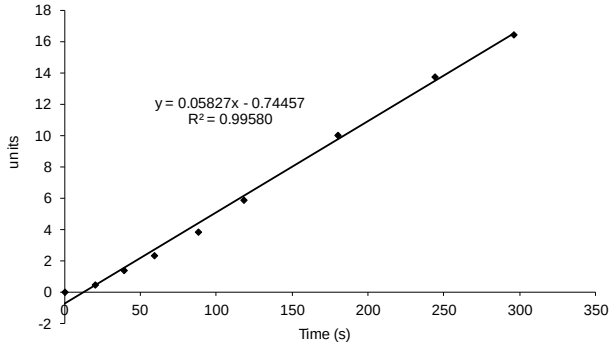


Run 2

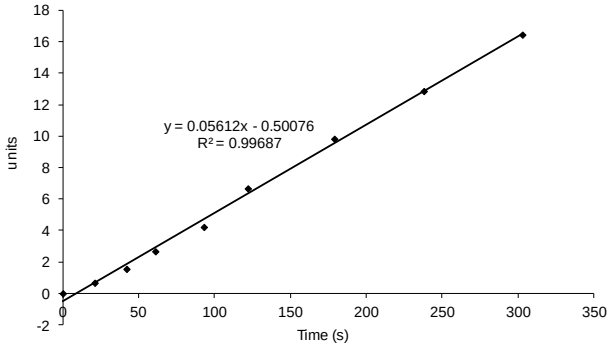


$[Bu_4NN_3] = 3x10^{-4}$ M (corresponds to 0.05 mol%)

Run 1

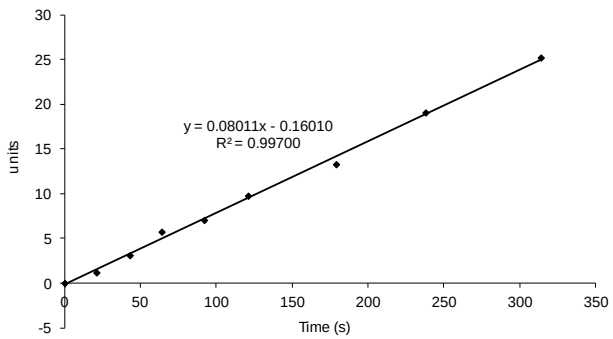


Run 2

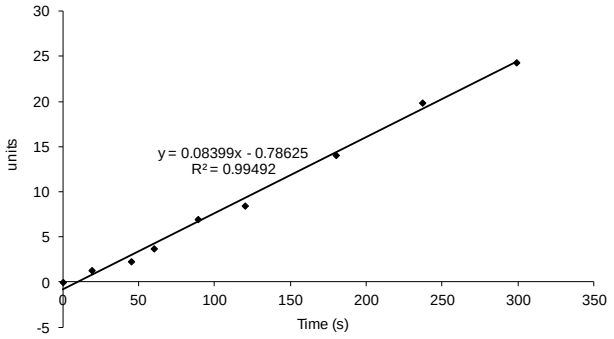


[Bu_4NN_3] = $4x10^{-4}$ M (corresponds to 0.07 mol%)

Run 1

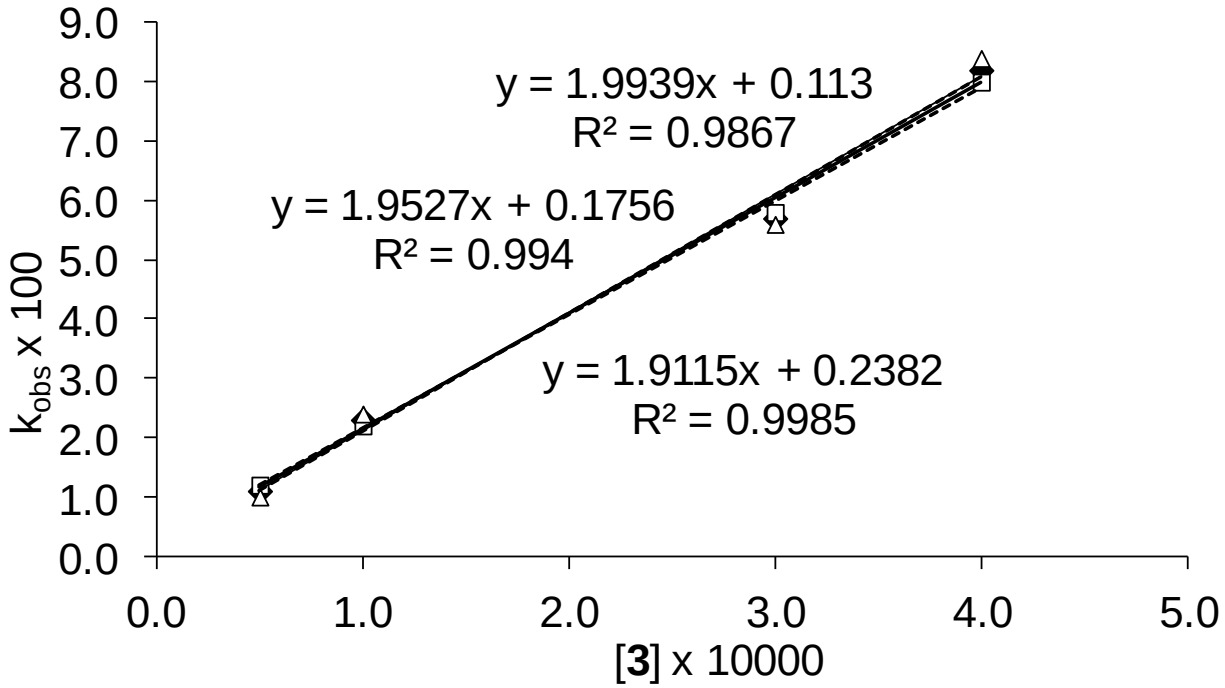


Run 2



The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Plot of k_{obs} against [**3**]

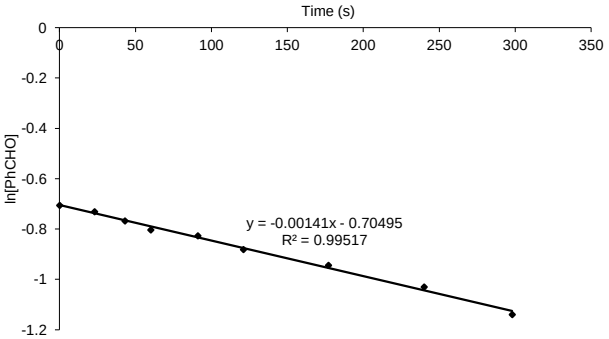


The dotted lines and empty data points show the rate data obtained from each of a duplicated series of kinetic experiments. The solid line and filled data points show the average of these two data sets and correspond to the data given in Figure 1 of the manuscript. The error in the rate constant was estimated from the difference in slopes of the three lines in this plot.

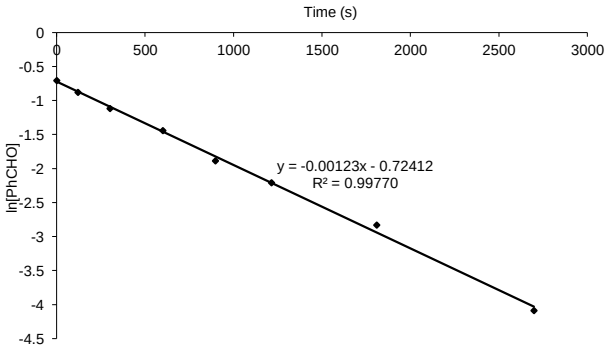
Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NCN 4

[Bu_4NCN] = $3x10^{-5}$ M (corresponds to 0.005 mol%)

Run 1

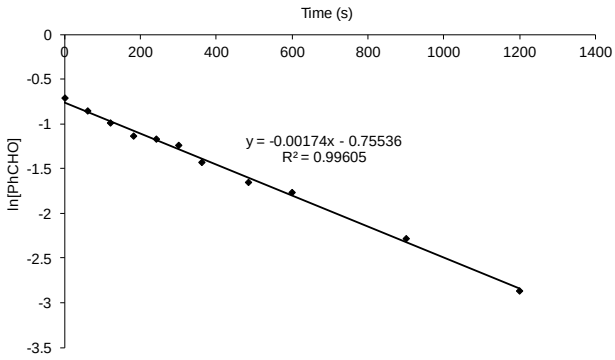


Run 2

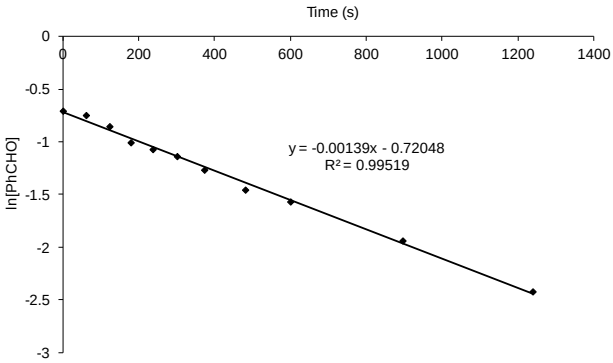


[Bu_4NCN] = $4x10^{-5}$ M (corresponds to 0.007 mol%)

Run 1

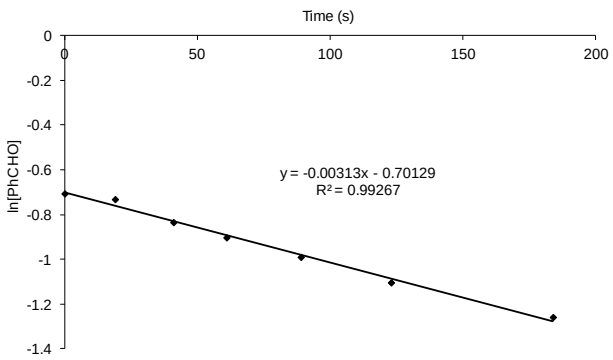


Run 2

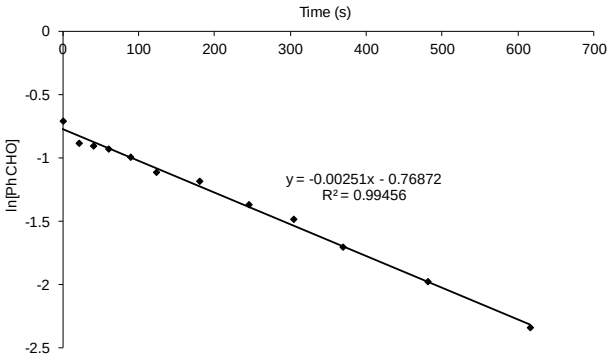


[Bu_4NCN] = $5x10^{-5}$ M (corresponds to 0.01 mol%)

Run 1

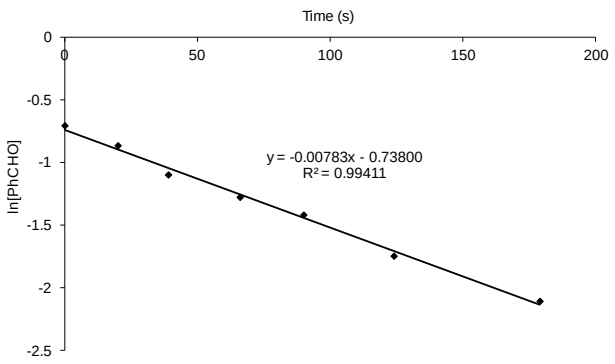


Run 2

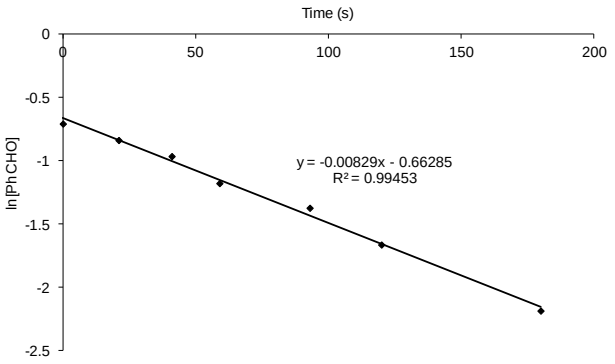


[Bu_4NCN] = $2x10^{-4}$ M (corresponds to 0.03 mol%)

Run 1

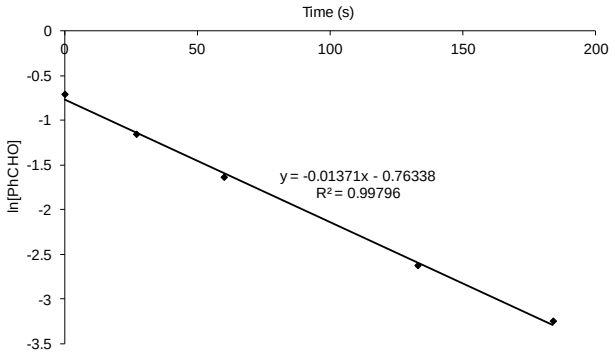


Run 2

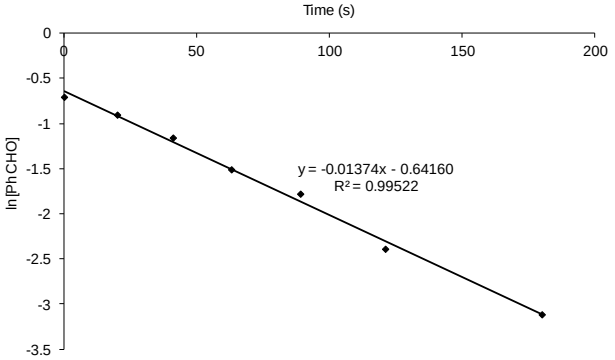


[Bu_4NCN] = $3x10^{-4}$ M (corresponds to 0.05 mol%)

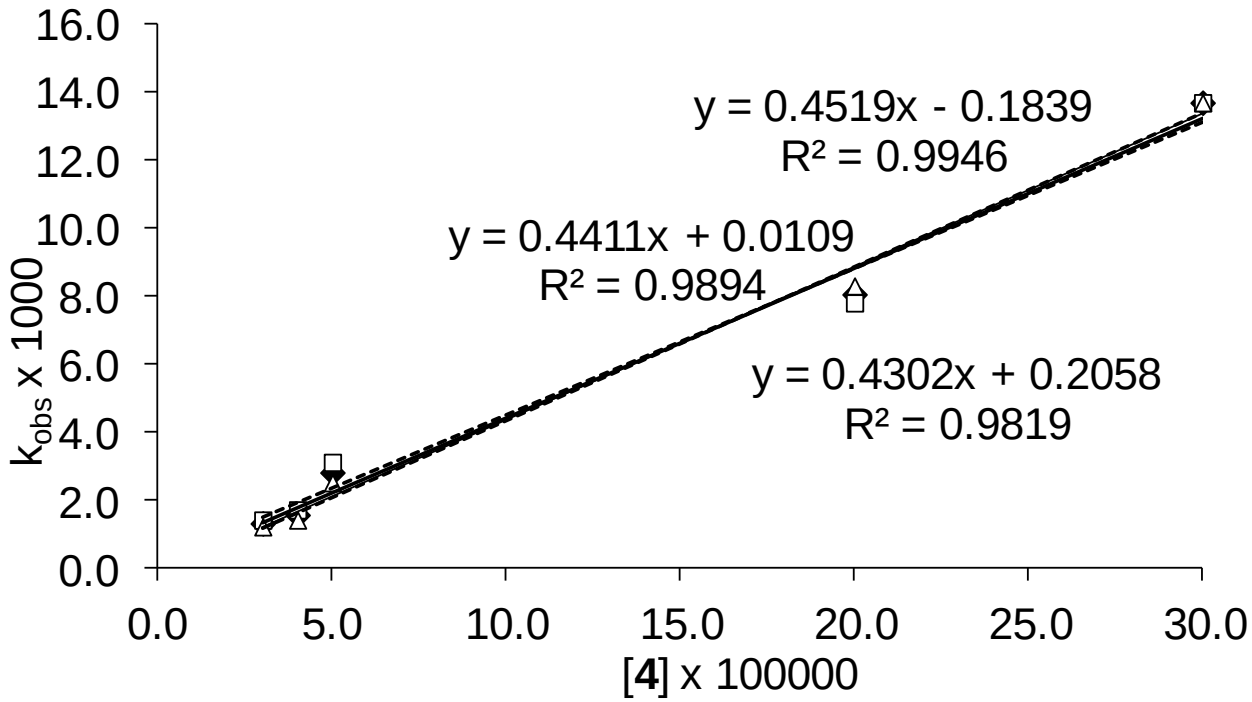
Run 1



Run 2



Plot of k_{obs} against [**4**]

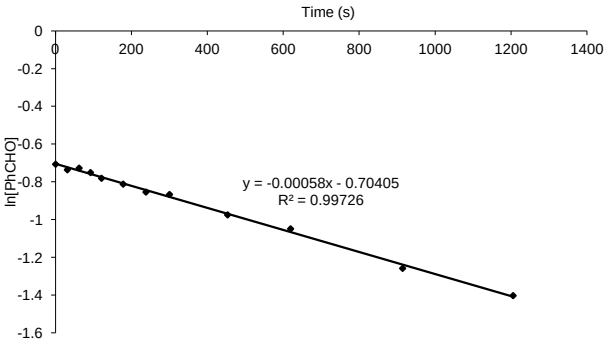


The dotted lines and empty data points show the rate data obtained from each of a duplicated series of kinetic experiments. The solid line and filled data points show the average of these two data sets and correspond to the data given in Figure 1 of the manuscript. The error in the rate constant was estimated from the difference in slopes of the three lines in this plot.

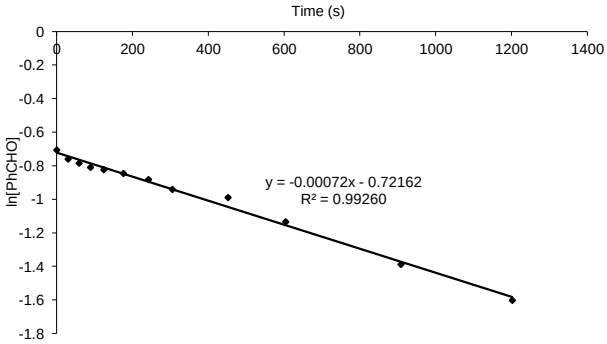
Kinetic plots used to construct the Hammett plots

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Et_3N 1

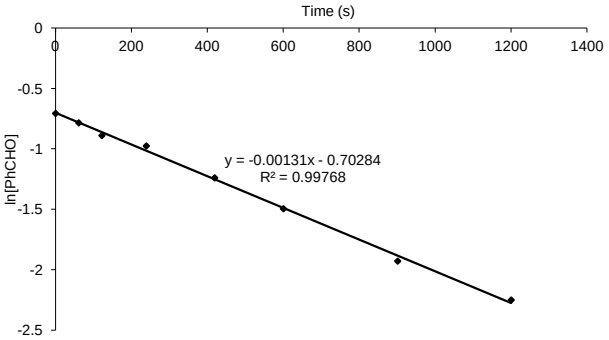
Benzaldehyde run 1



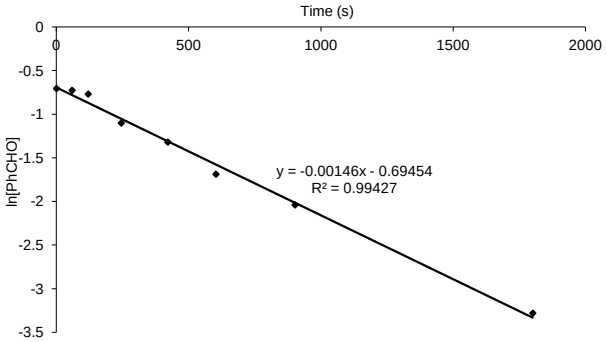
Benzaldehyde run 2



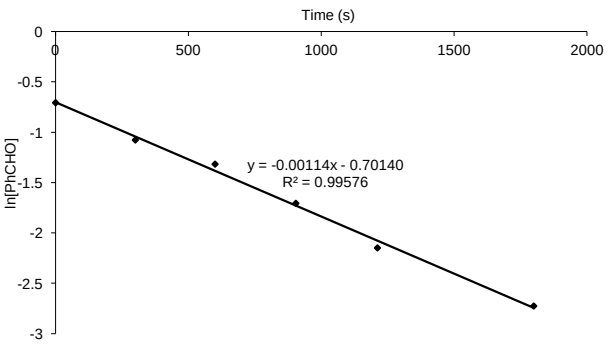
3-Chlorobenzaldehyde run 1



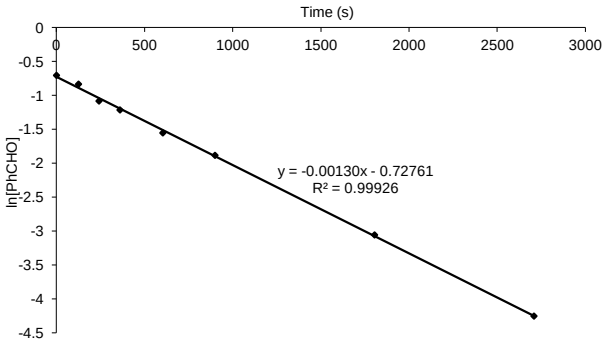
3-Chlorobenzaldehyde run 2



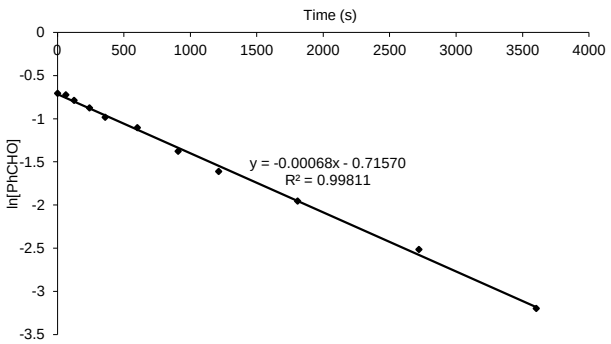
3-Fluorobenzaldehyde run 1



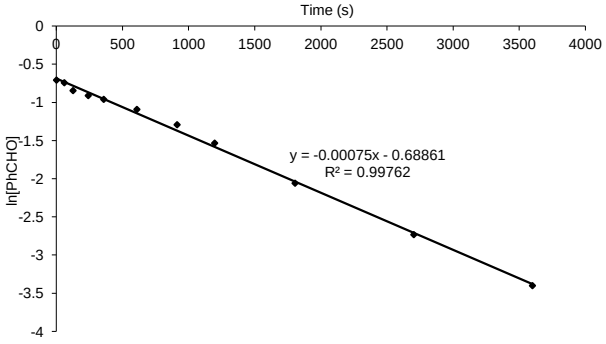
3-Fluorobenzaldehyde run 2



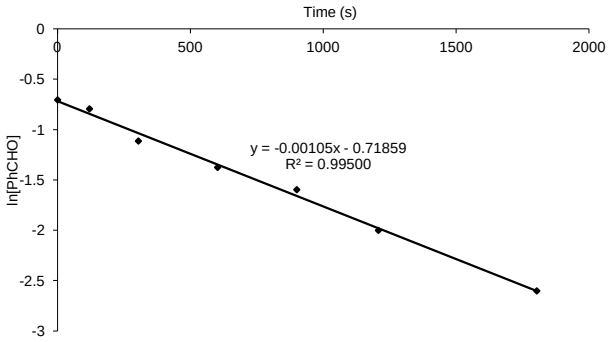
4-Chlorobenzaldehyde run 1



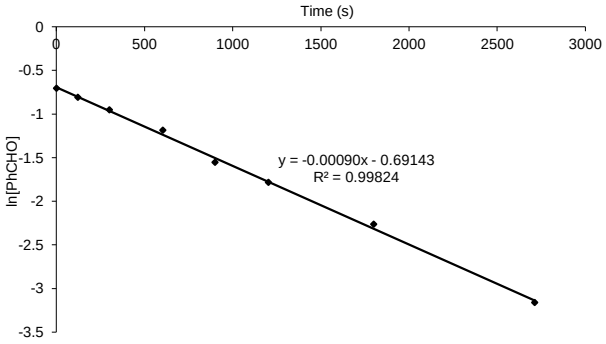
4-Chlorobenzaldehyde run 2



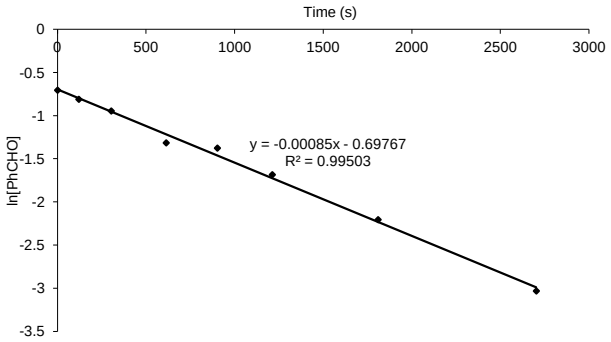
4-Fluorobenzaldehyde run 1



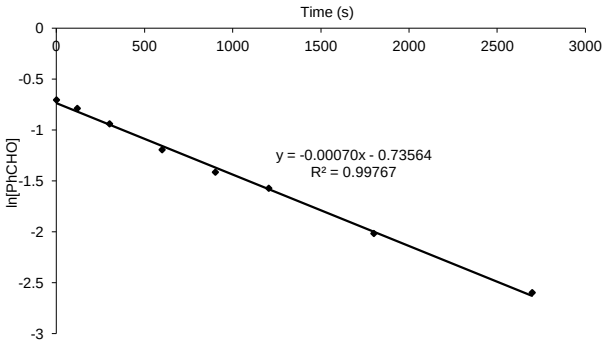
4-Fluorobenzaldehyde run 2



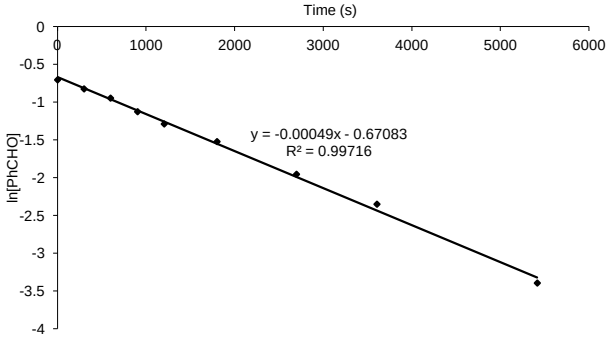
4-Thiomethylbenzaldehyde run 1



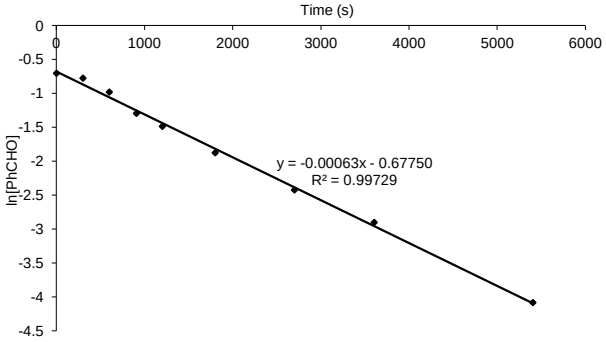
4-Thiomethylbenzaldehyde run 2



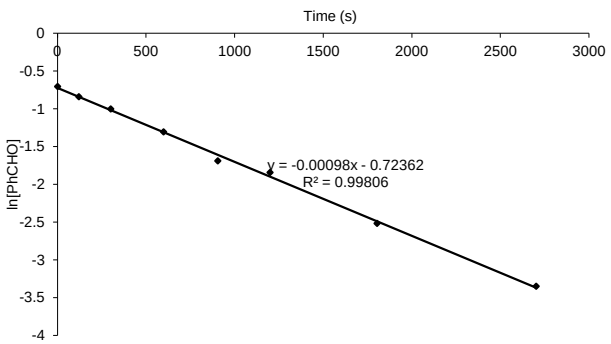
3-Methylbenzaldehyde run 1



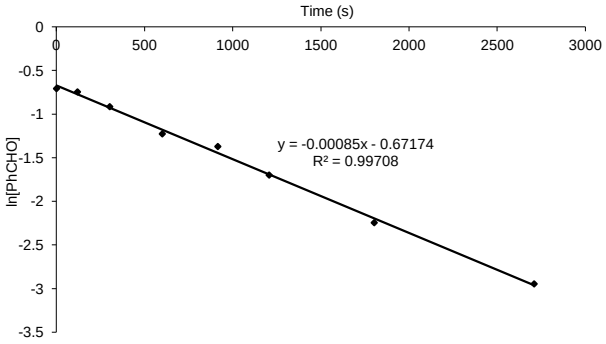
3-Methylbenzaldehyde run 2



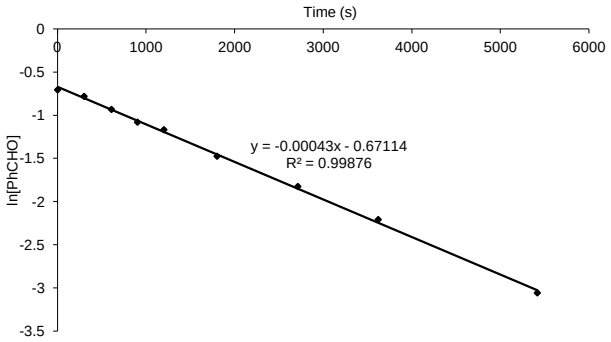
4-Methylbenzaldehyde run 1



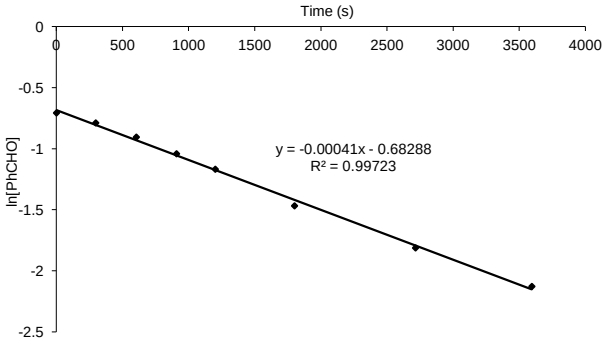
4-Methylbenzaldehyde run 2



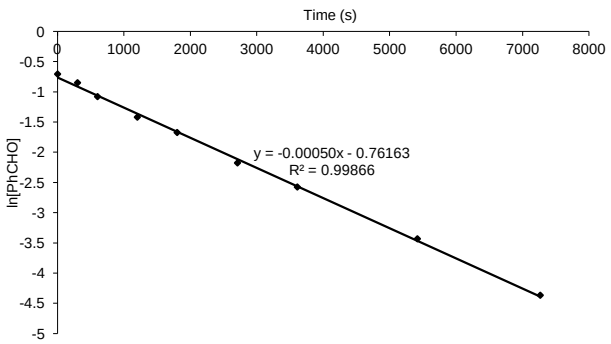
3,4-Dimethylbenzaldehyde run 1



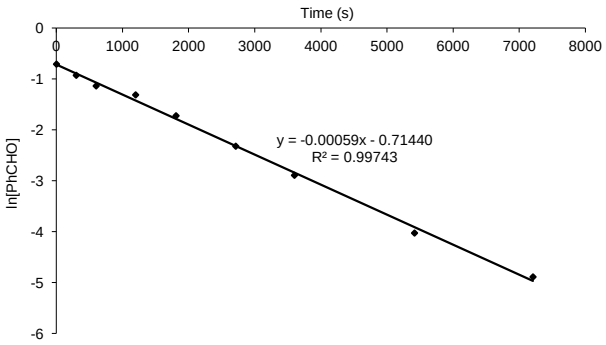
3,4-Dimethylbenzaldehyde run 2



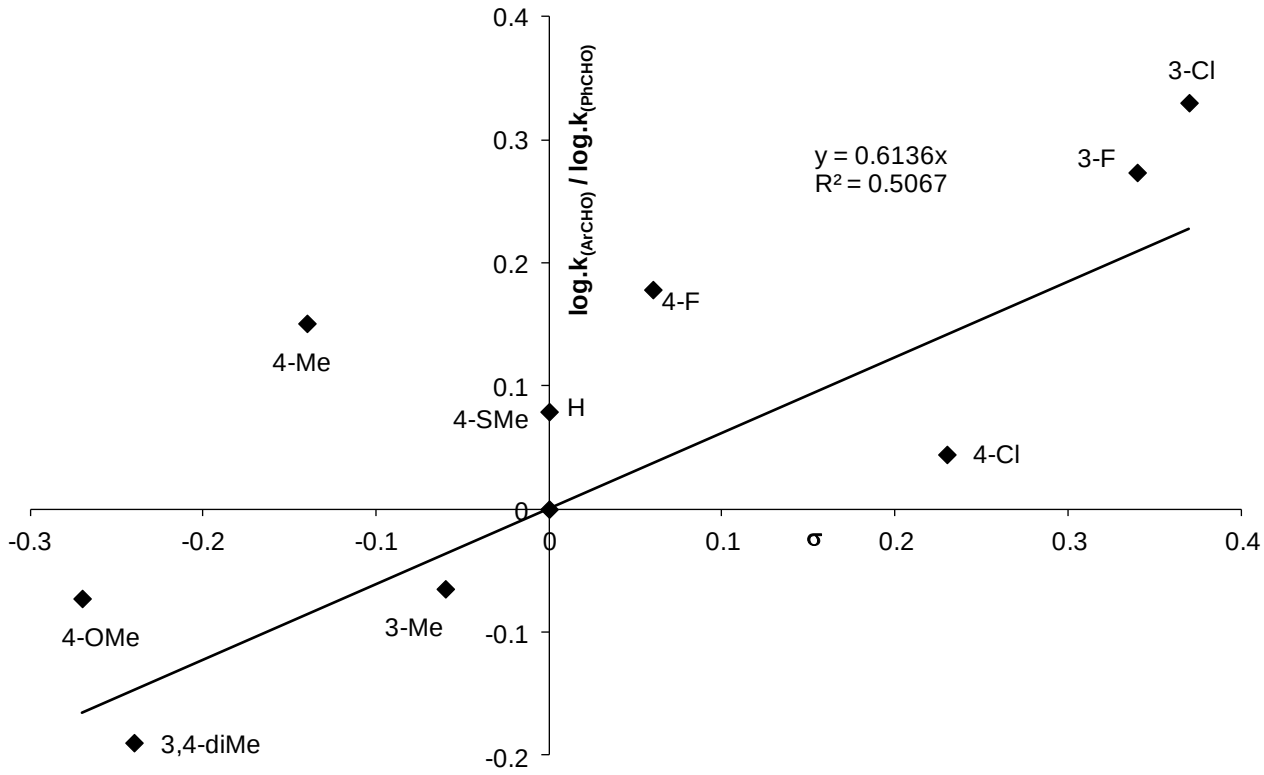
4-Methoxybenzaldehyde run 1



4-Methoxybenzaldehyde run 2



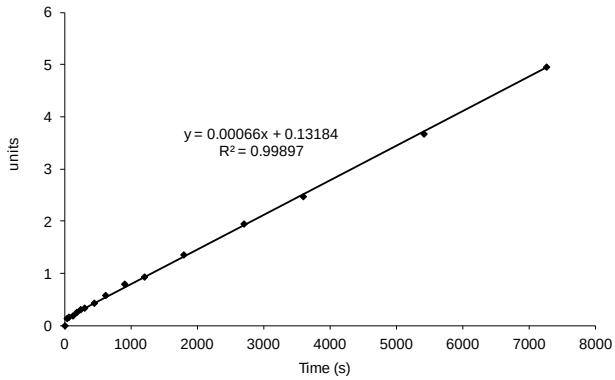
Hammett plot for the reaction catalysed by Et_3N 1



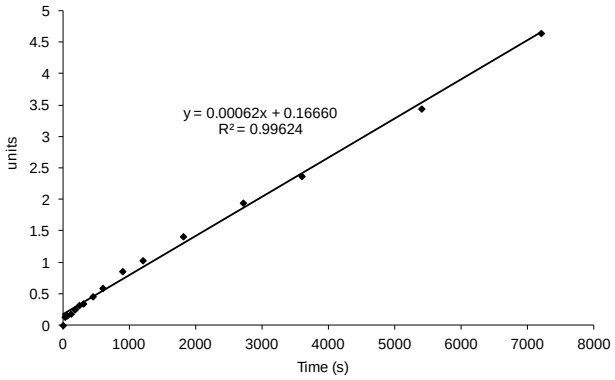
Only the average of two individual rate constants were used to construct this graph.

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Bu_4NNCS 2

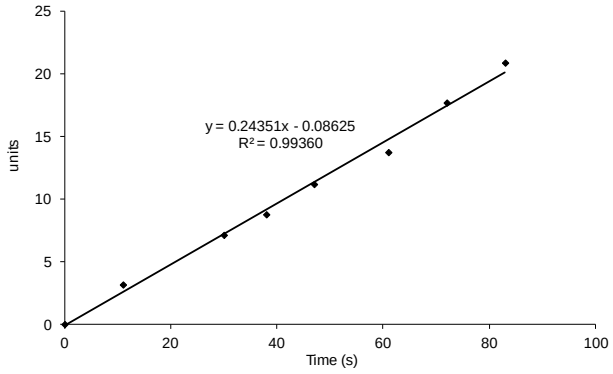
Benzaldehyde run 1



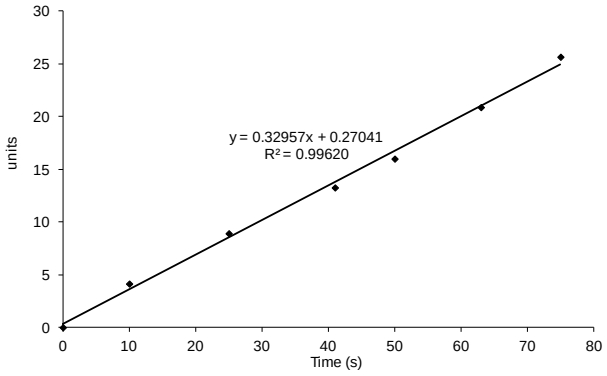
Benzaldehyde run 2



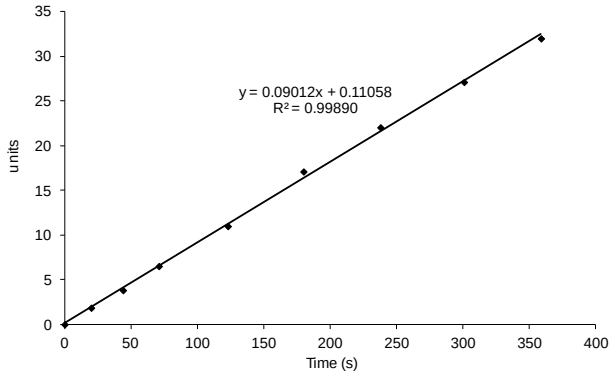
3,5-Difluororobenzaldehyde run 1



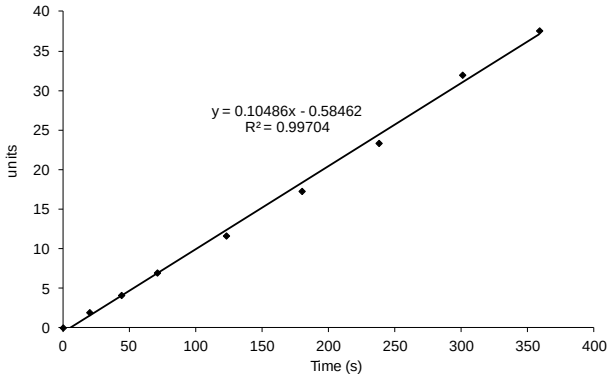
3,5-Difluororobenzaldehyde run 2



4-Trifluoromethylbenzaldehyde run 1

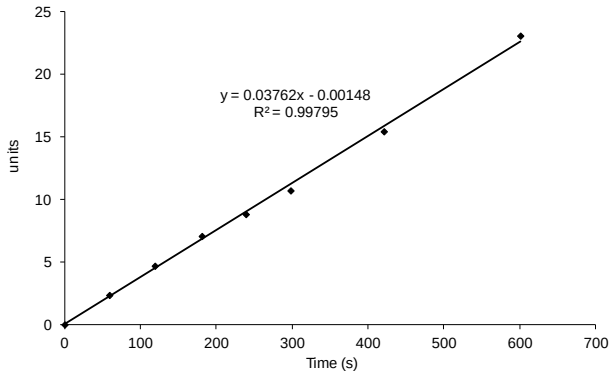


4-Trifluoromethylbenzaldehyde run 2

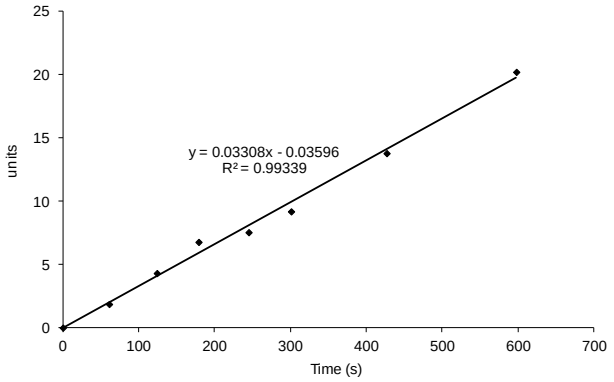


The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

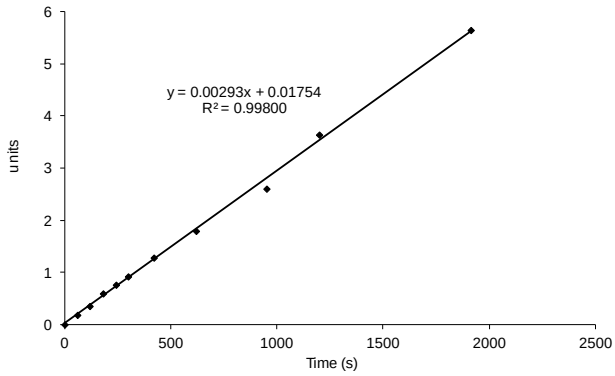
3-Chlorobenzaldehyde run 1



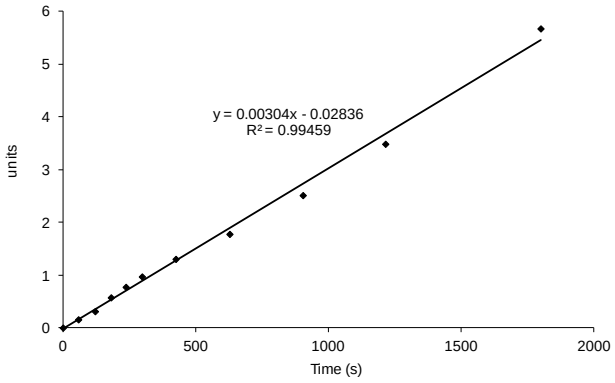
3-Chlorobenzaldehyde run 2



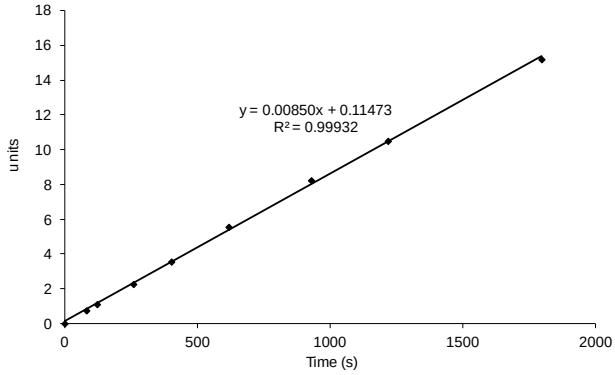
3-Fluorobenzaldehyde run 1



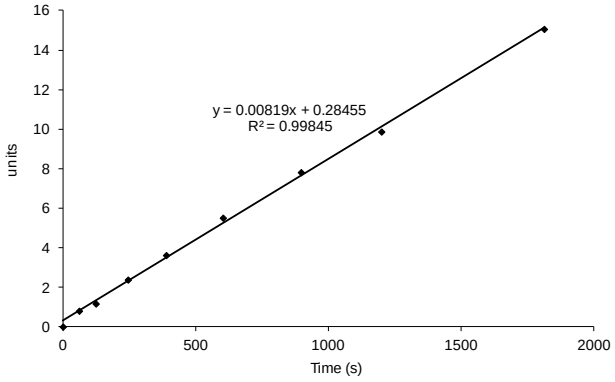
3-Fluorobenzaldehyde run 2



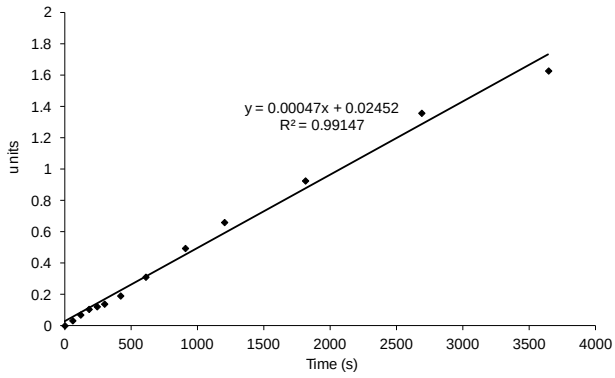
4-Chlorobenzaldehyde run 1



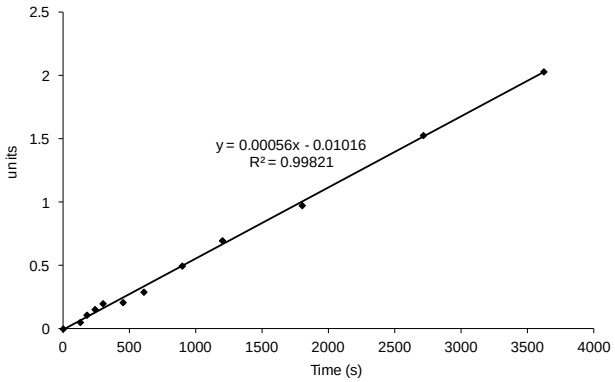
4-Chlorobenzaldehyde run 2



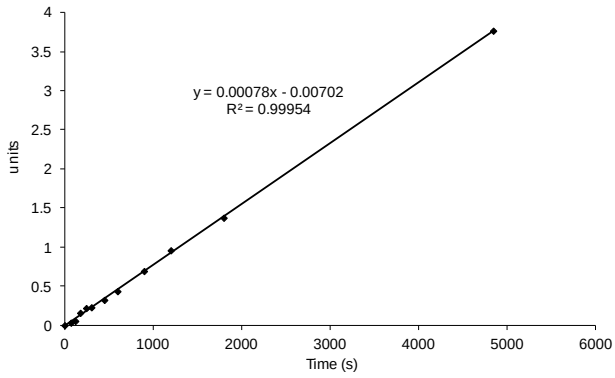
4-Fluorobenzaldehyde run 1



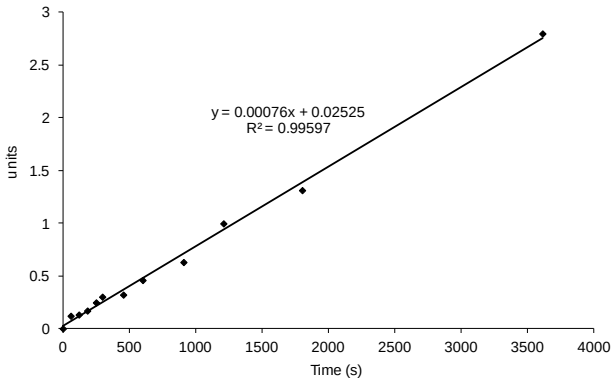
4-Fluorobenzaldehyde run 2



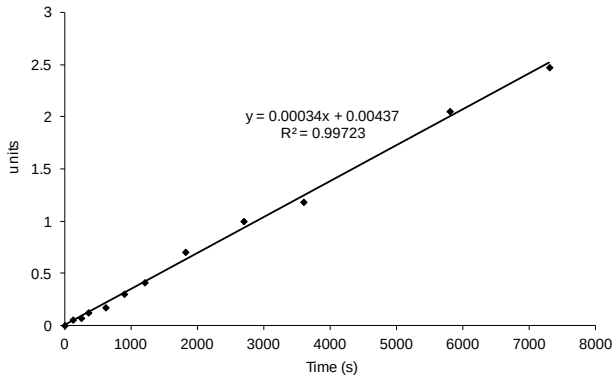
4-Thiomethylbenzaldehyde run 1



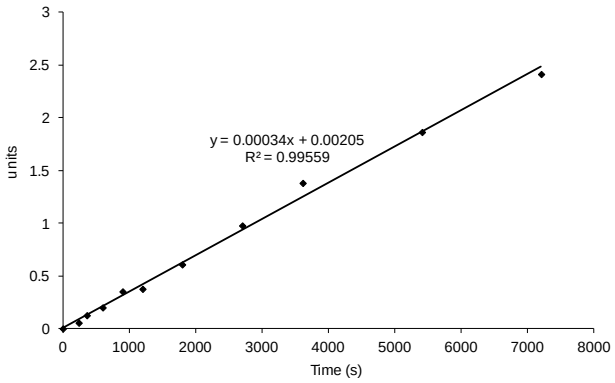
4-Thiomethylbenzaldehyde run 2



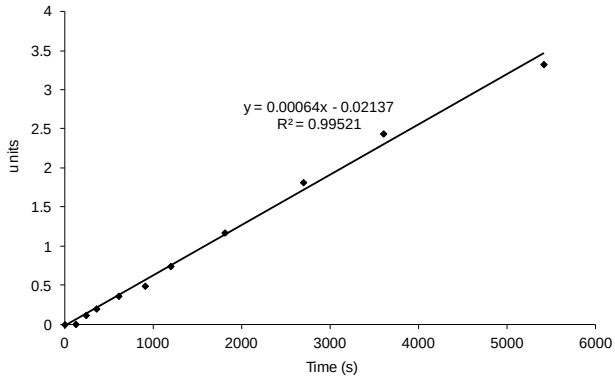
3-Methylbenzaldehyde run 1



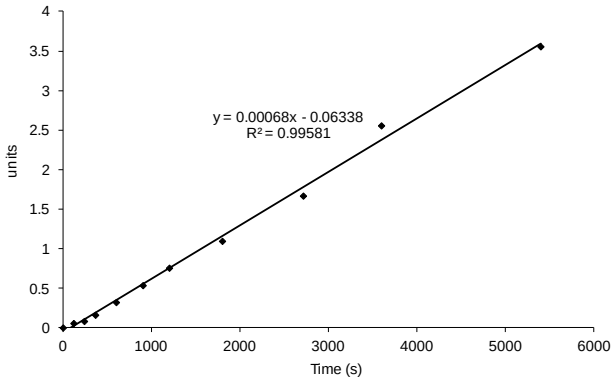
3-Methylbenzaldehyde run-2



4-Methylbenzaldehyde run 1

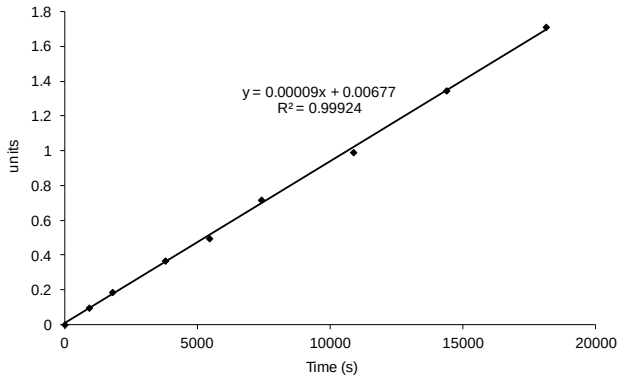


4-Methylbenzaldehyde run 2

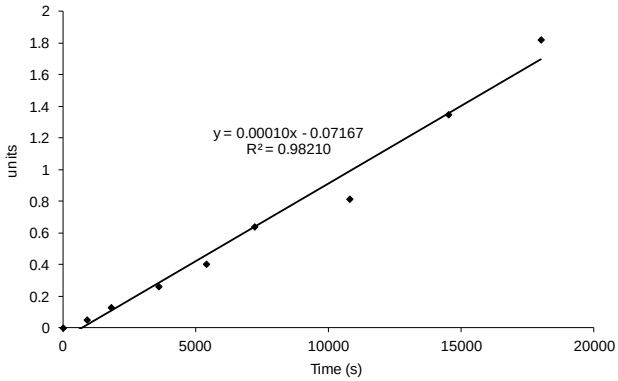


The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

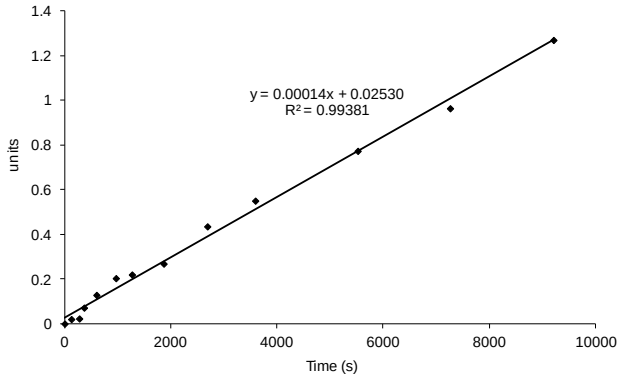
3,4-Dimethylbenzaldehyde run 1



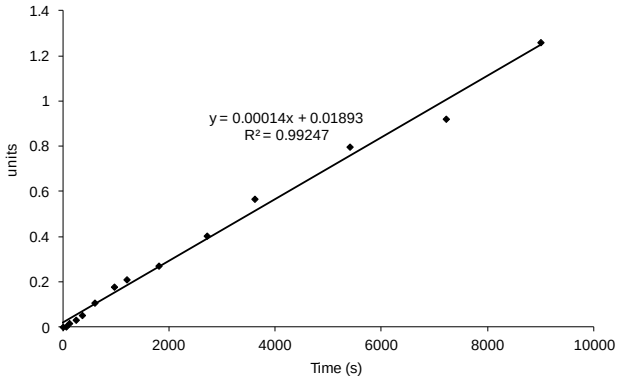
3,4-Dimethylbenzaldehyde run 2



4-Methoxybenzaldehyde run 1

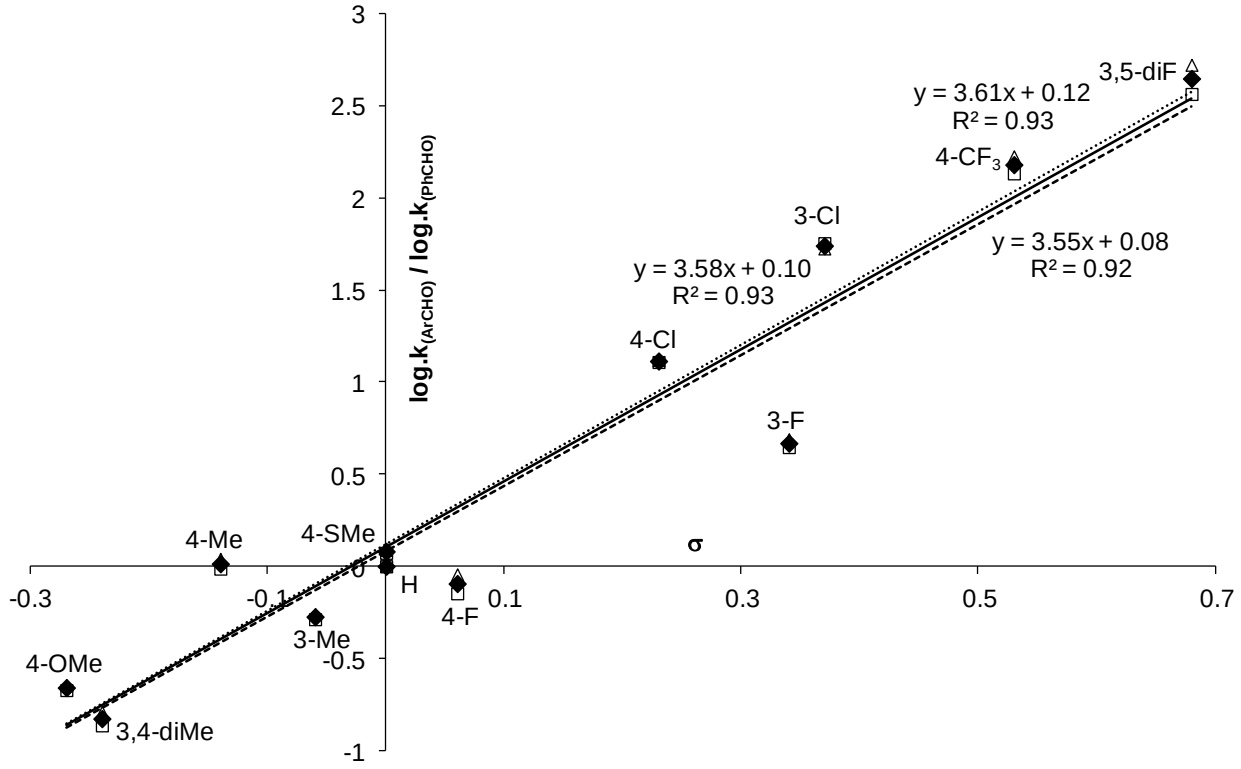


4-Methoxybenzaldehyde run 2



The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

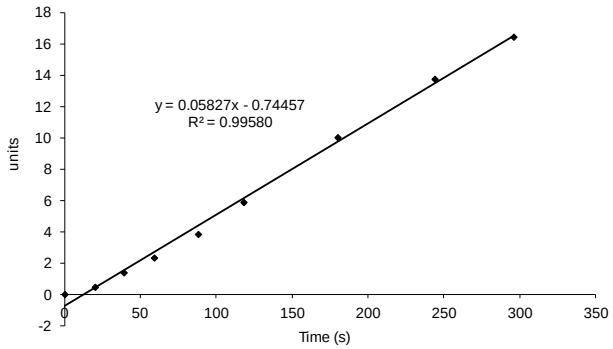
Hammett plot for the reaction catalysed by Bu_4NNCS 2



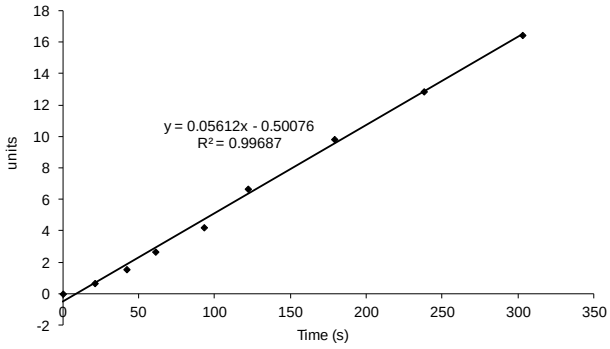
The filled diamonds and solid line correspond to the average rate data for each aldehyde whilst the unfilled squares and triangles and the broken lines correspond to each individual set of rate data.

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Bu_4NN_3 3

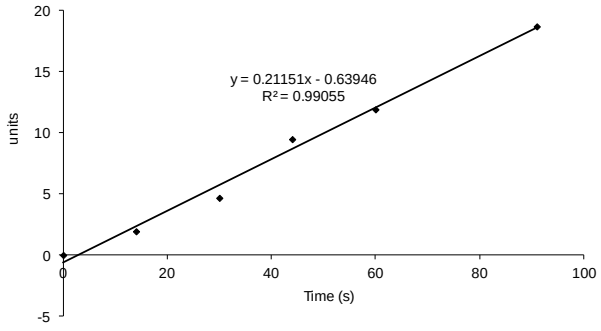
Benzaldehyde run 1



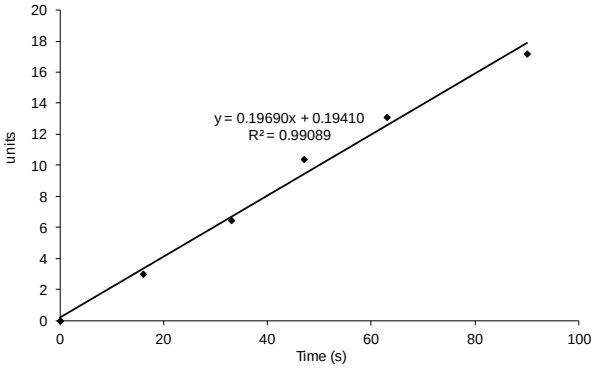
Benzaldehyde run 2



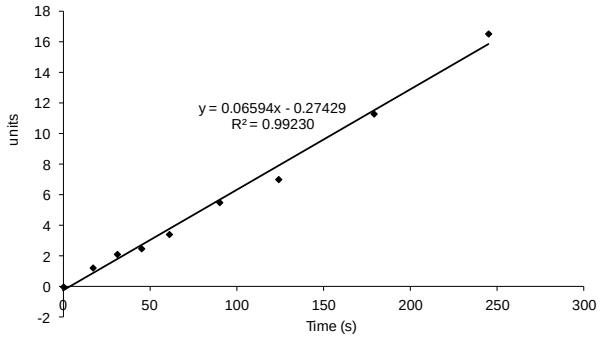
4-Chlorobenzaldehyde run 1



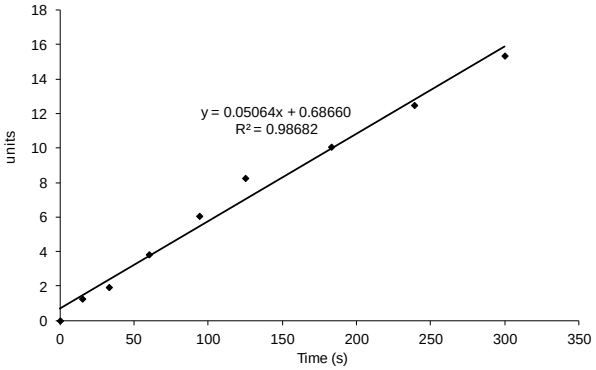
4-Chlorobenzaldehyde run 2



4-Fluorobenzaldehyde run 1

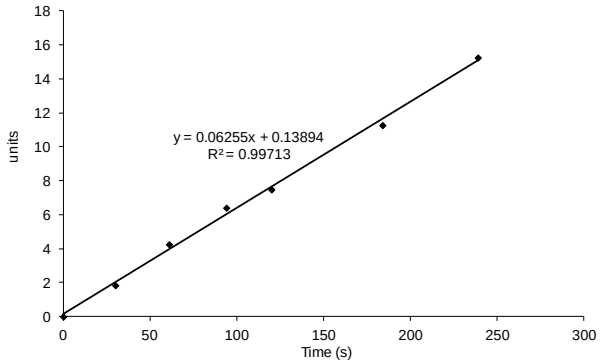


4-Fluorobenzaldehyde run 2

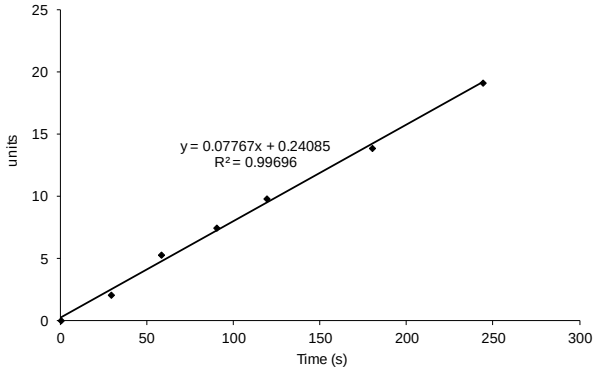


The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

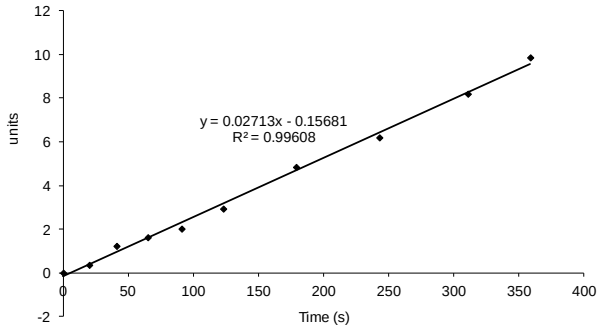
4-Thiomethylbenzaldehyde run 1



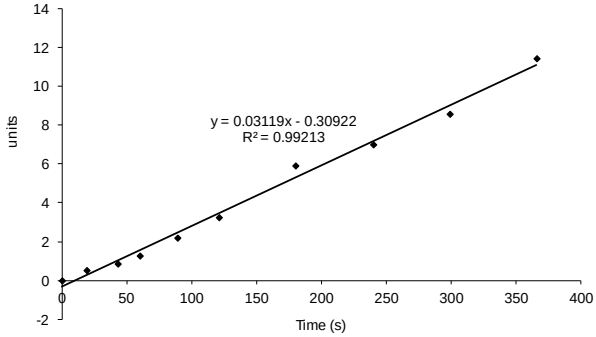
4-Thiomethylbenzaldehyde run 2



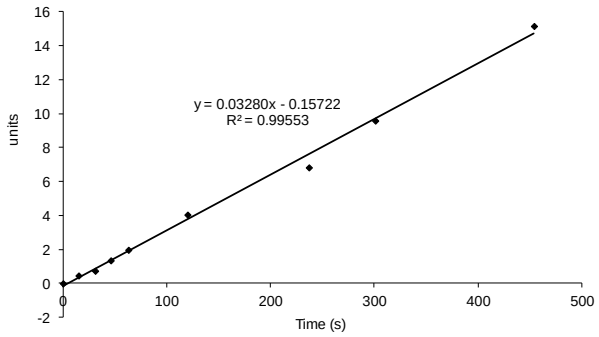
3-Methylbenzaldehyde run 1



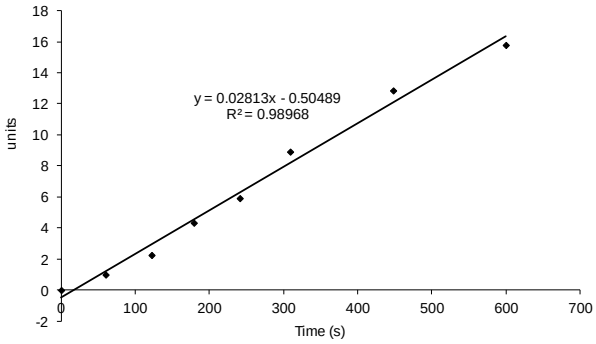
3-Methylbenzaldehyde run 2



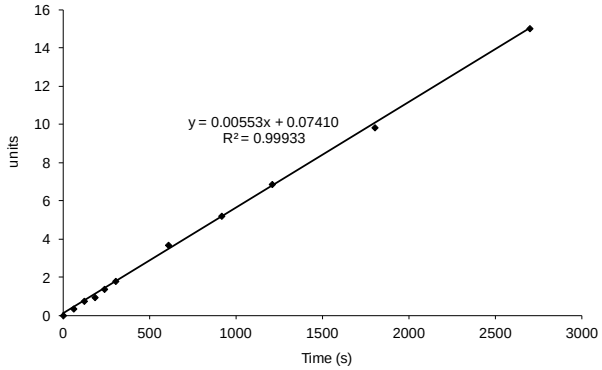
4-Methylbenzaldehyde run 1



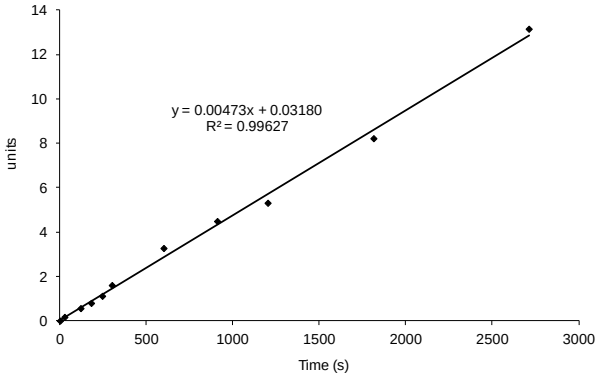
4-Methylbenzaldehyde run 2



3,4-Dimethylbenzaldehyde run 1

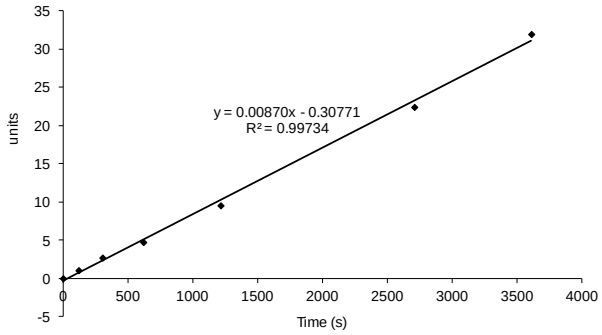


3,4-Dimethylbenzaldehyde run 2

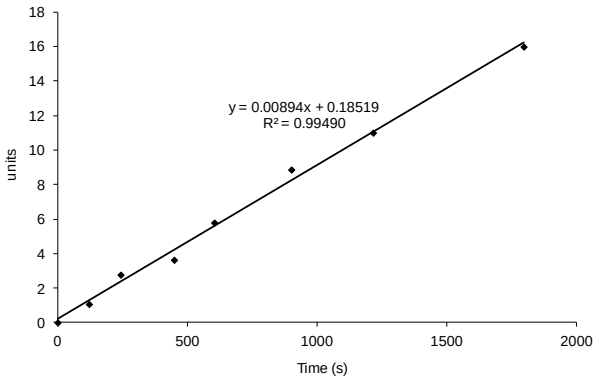


The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

4-Methoxybenzaldehyde run 1

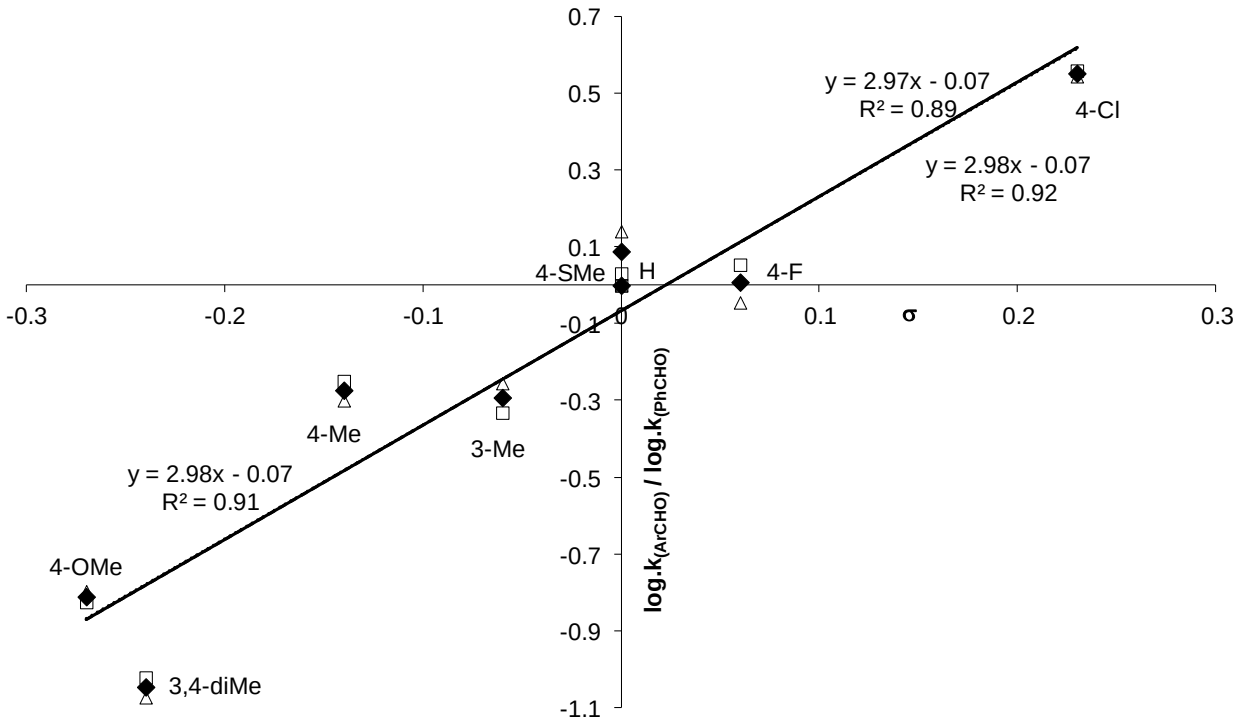


4-Methoxybenzaldehyde run 2



The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

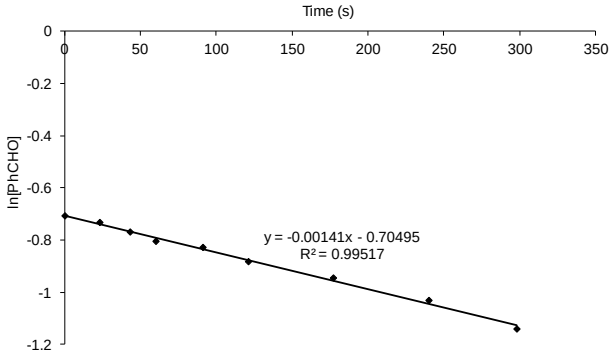
Hammett plot for the reaction catalysed by Bu_4NN_3 3



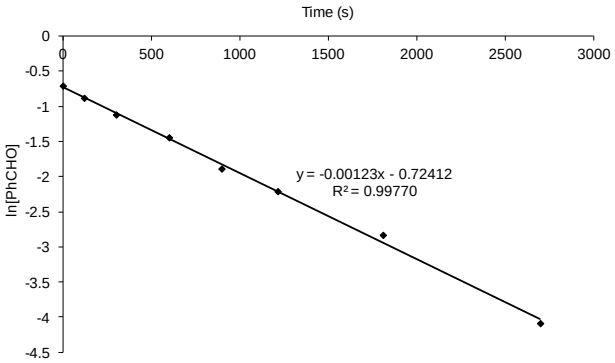
The filled diamonds and solid line correspond to the average rate data for each aldehyde whilst the unfilled squares and triangles and the broken lines correspond to each individual set of rate data.

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Bu_4NCN 4

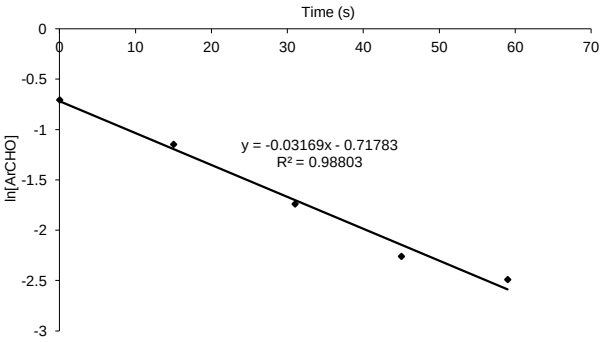
Benzaldehyde run 1



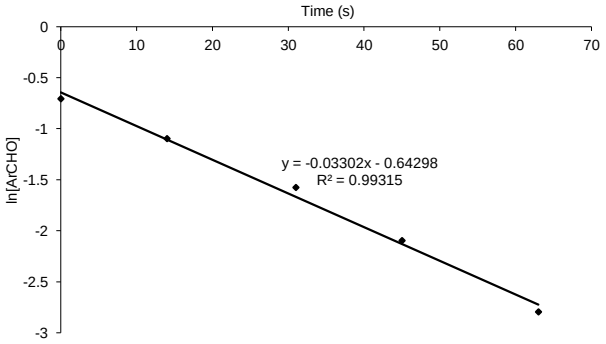
Benzaldehyde run 2



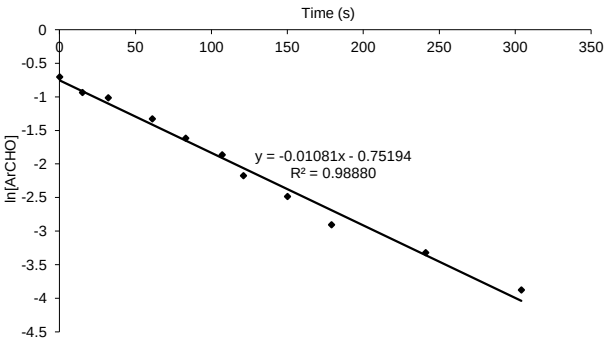
3-Chlorobenzaldehyde run 1



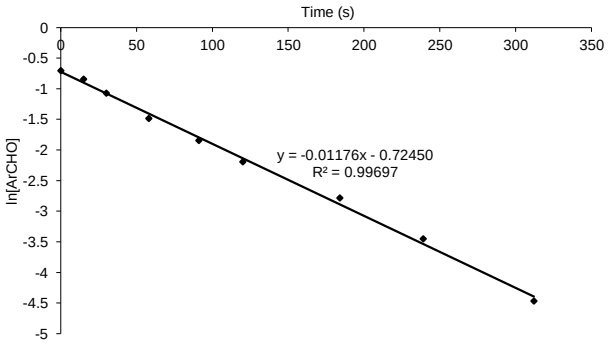
3-Chlorobenzaldehyde run 2



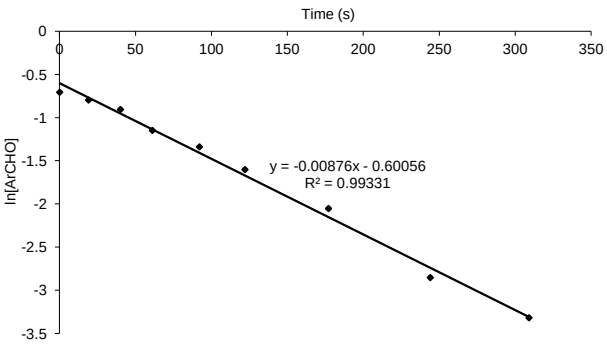
3-Fluorobenzaldehyde run 1



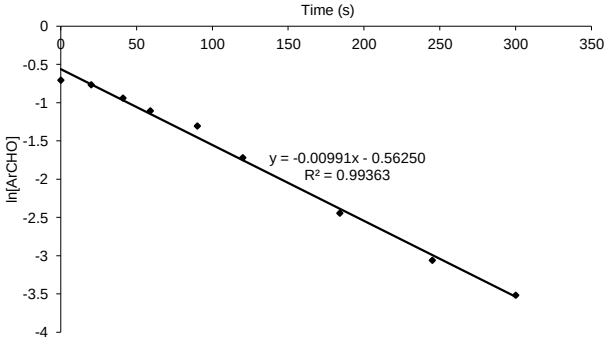
3-Fluorobenzaldehyde run 2



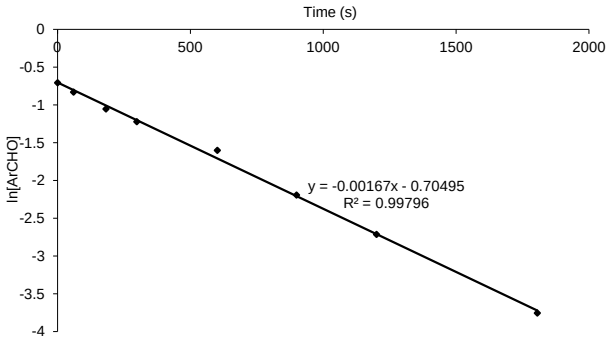
4-Chlorobenzaldehyde run 1



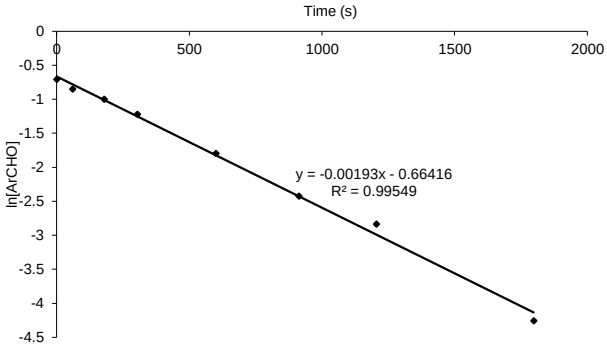
4-Chlorobenzaldehyde run 2



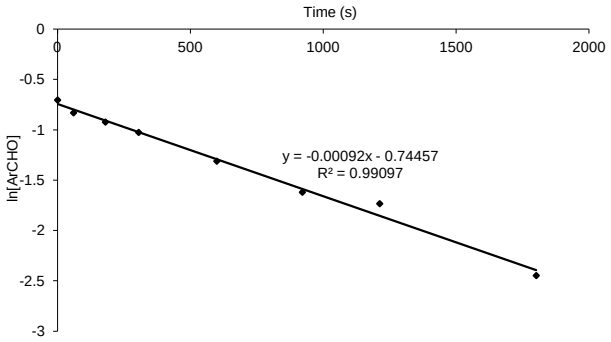
4-Fluorobenzaldehyde run 1



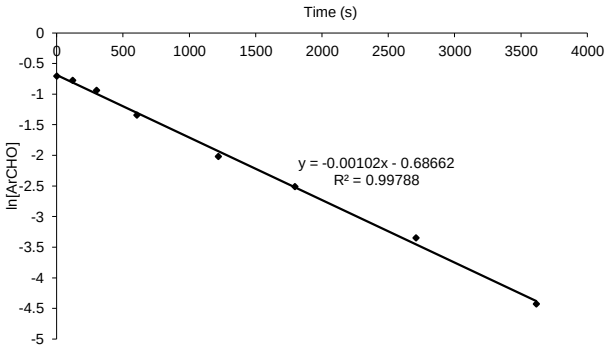
4-Fluorobenzaldehyde run 2



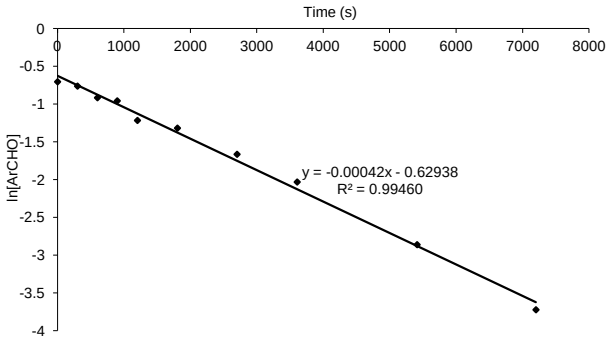
4-Thiomethylbenzaldehyde run 1



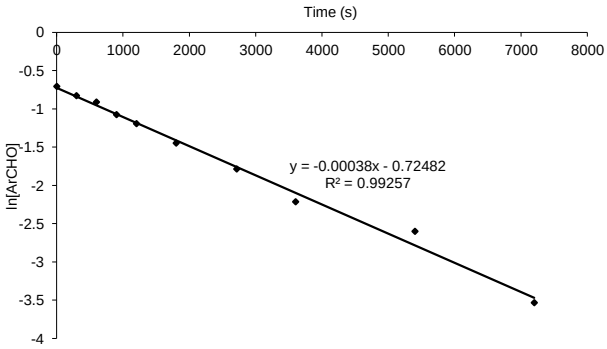
4-Thiomethylbenzaldehyde run 2



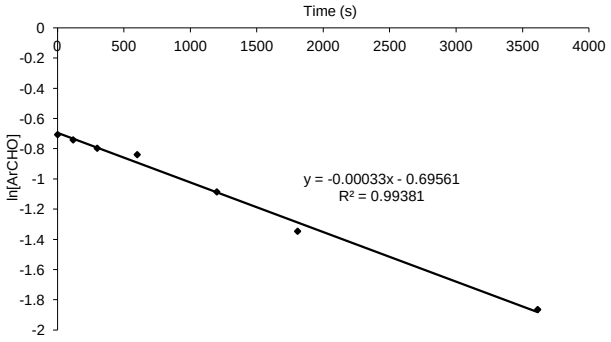
3-Methylbenzaldehyde run 1



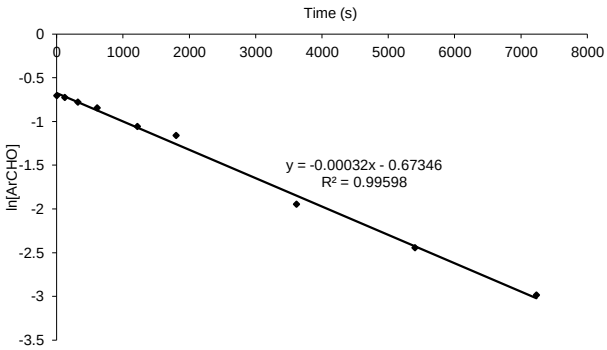
3-Methylbenzaldehyde run 2



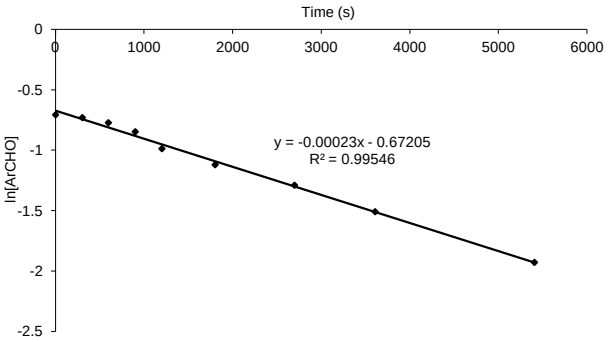
4-Methylbenzaldehyde run 1



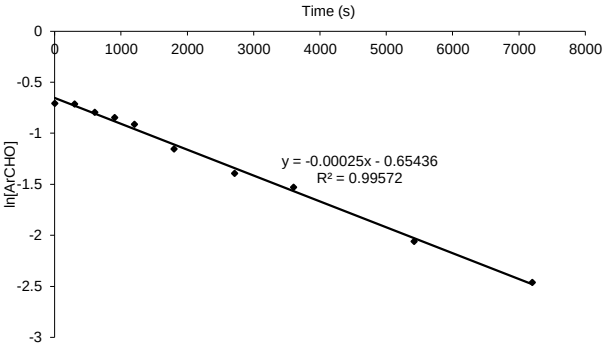
4-Methylbenzaldehyde run 2



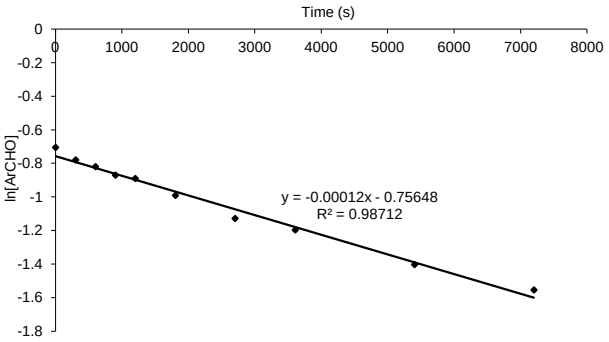
3,4-Dimethylbenzaldehyde run 1



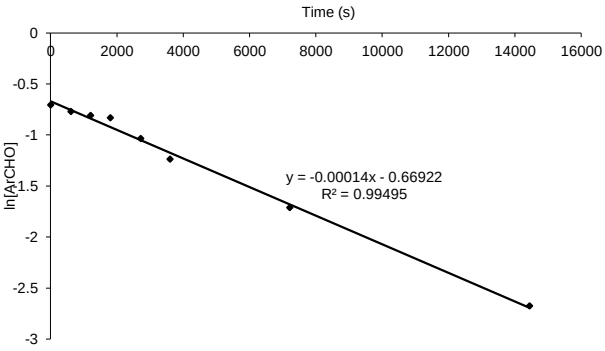
3,4-Dimethylbenzaldehyde run 2



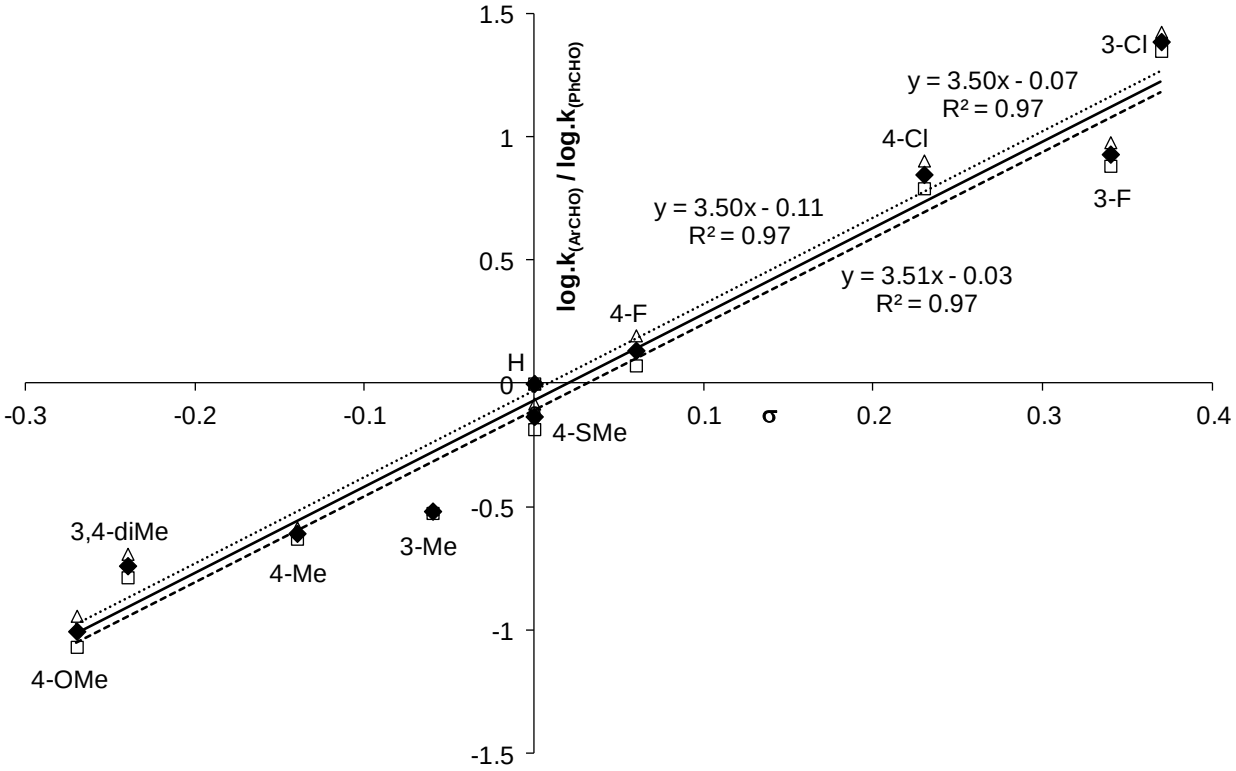
4-Methoxybenzaldehyde run 1



4-Methoxybenzaldehyde run 2



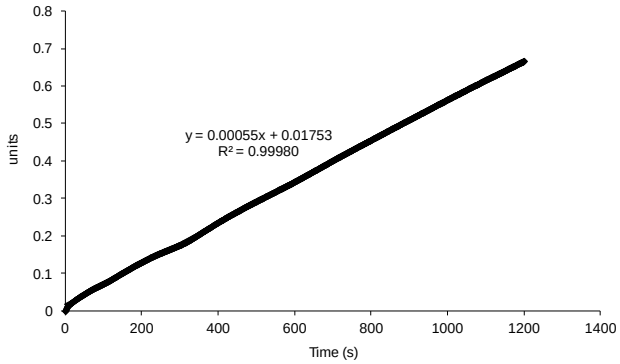
Hammett plot for the reaction catalysed by Bu_4NCN



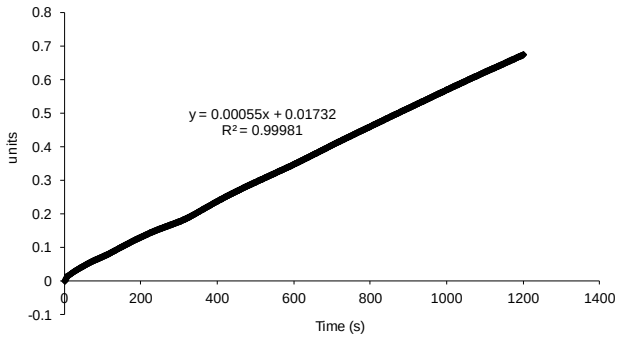
The filled diamonds and solid line correspond to the average rate data for each aldehyde whilst the unfilled squares and triangles and the broken lines correspond to each individual set of rate data.

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Bu_4NNCS 2 in a stopped flow kinetics system

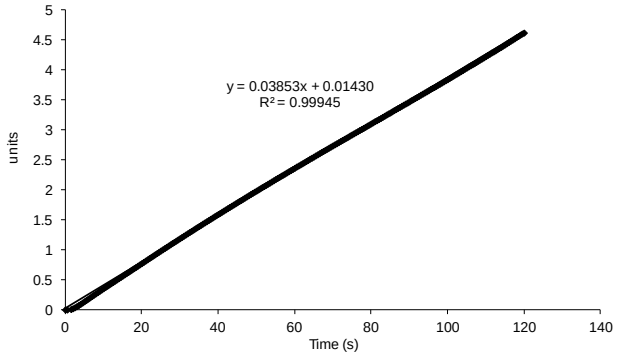
Benzaldehyde run 1



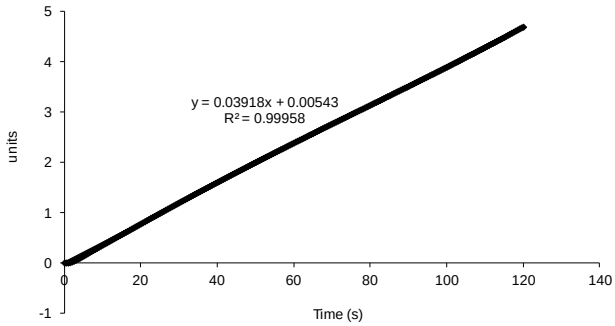
Benzaldehyde run 2



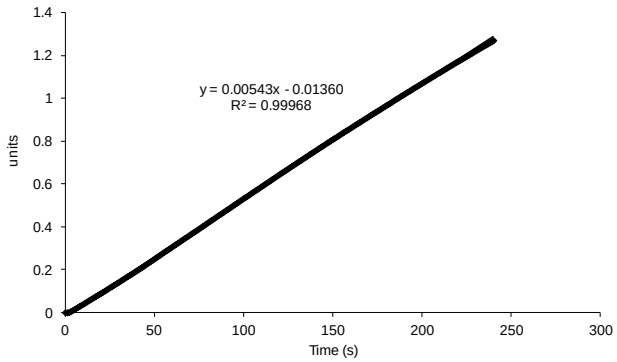
3,5-Difluororobenzaldehyde run 1



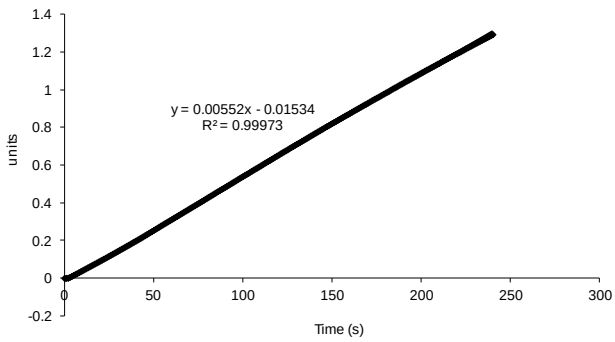
3,5-Difluororobenzaldehyde run 2



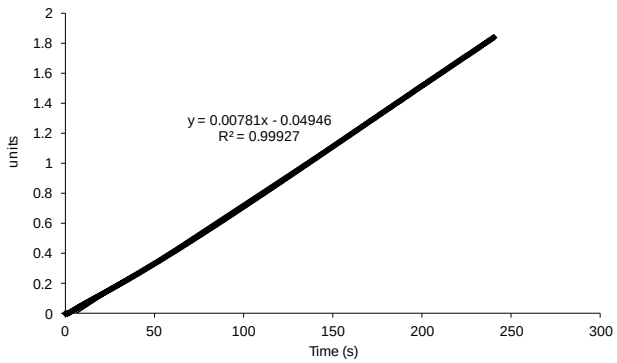
3-Chlorobenzaldehyde run 1



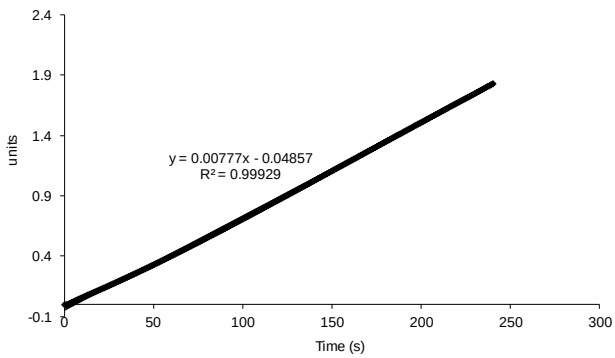
3-Chlorobenzaldehyde run 2



3-Fluorobenzaldehyde run 1

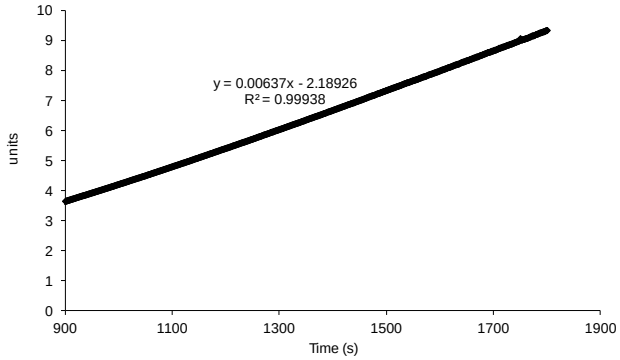


3-Fluorobenzaldehyde run 2

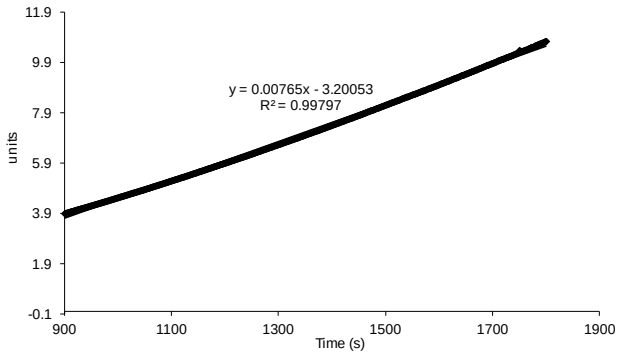


The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

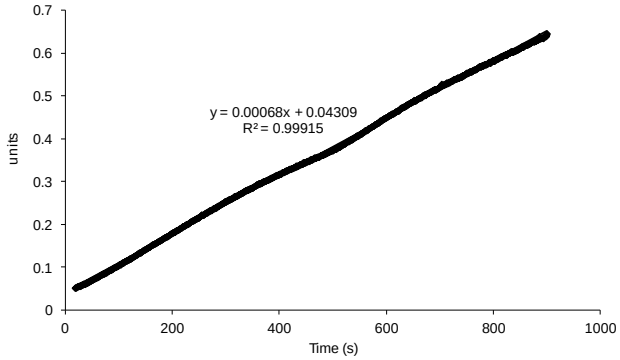
4-Chlorobenzaldehyde run 1



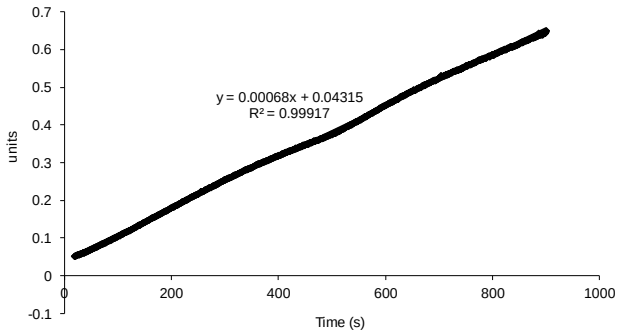
4-Chlorobenzaldehyde run 2



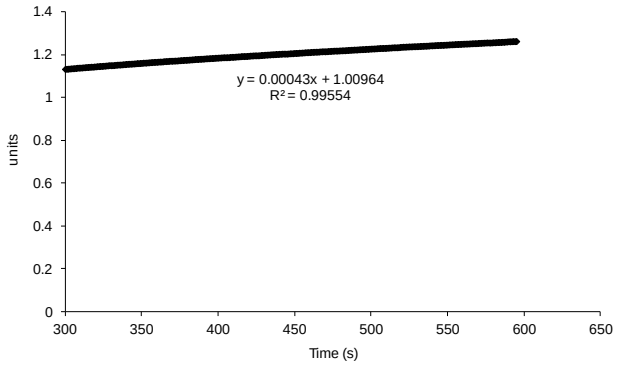
4-Fluorobenzaldehyde run 1



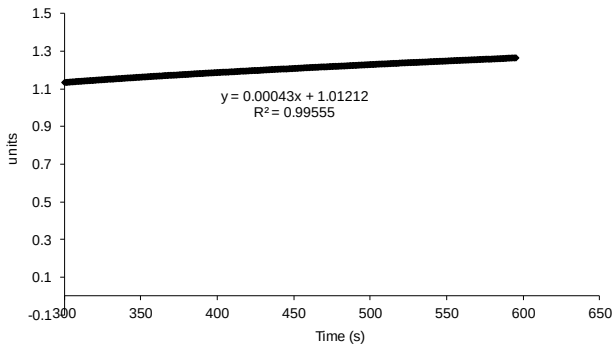
4-Fluorobenzaldehyde run 2



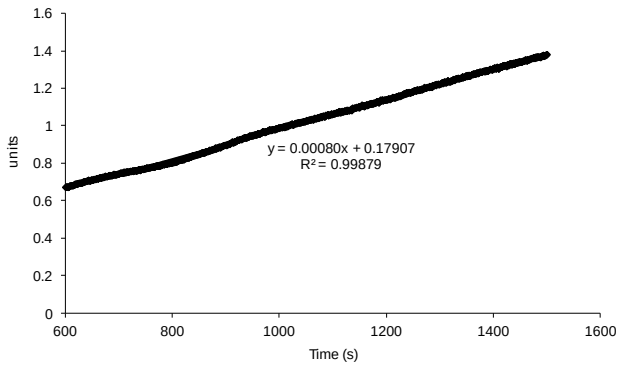
4-Thiomethylbenzaldehyde run 1



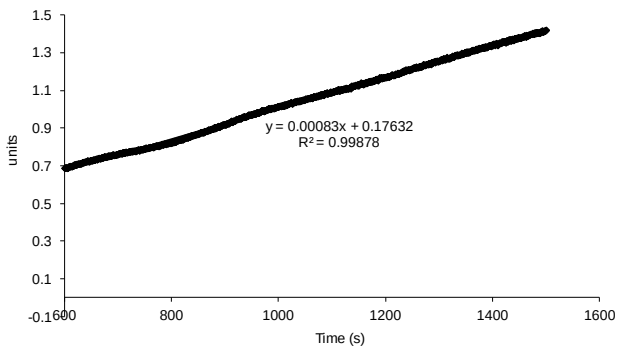
4-Thiomethylbenzaldehyde run 2



3-Methylbenzaldehyde run 1



3-Methylbenzaldehyde run 2



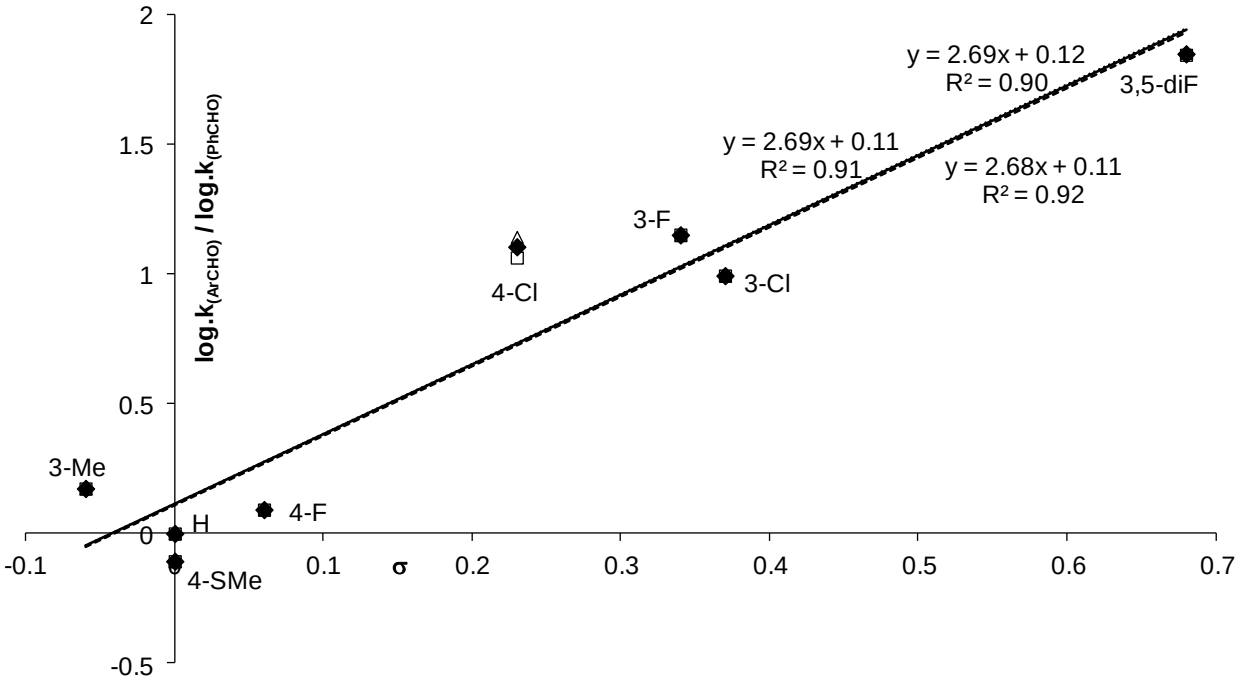
The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Tabulated rate data for the Hammett plot in a stopped flow kinetics system

aldehyde	σ	k ($M^{-1}s^{-1}$)[a]
3,5-$F_2C_6H_3CHO$	0.68	0.0388 ± 0.0003
3-ClC_6H_4CHO	0.37	0.00543 ± 0.00001
3-FC_6H_4CHO	0.34	0.00779 ± 0.00002
4-ClC_6H_4CHO	0.23	0.0070 ± 0.0006
4-FC_6H_4CHO	0.06	0.00068 ± 0.00001
PhCHO	0	0.00055 ± 0.00001
4-$MeSC_6H_4CHO$	0	0.00043 ± 0.00001
3-MeC_6H_4CHO	-0.06	0.00082 ± 0.00001

[a] Average of two experiments

Hammett plot obtained using the stopped flow kinetics system



The filled diamonds and solid line correspond to the average rate data for each aldehyde whilst the unfilled squares and triangles and the broken lines correspond to each individual set of rate data.

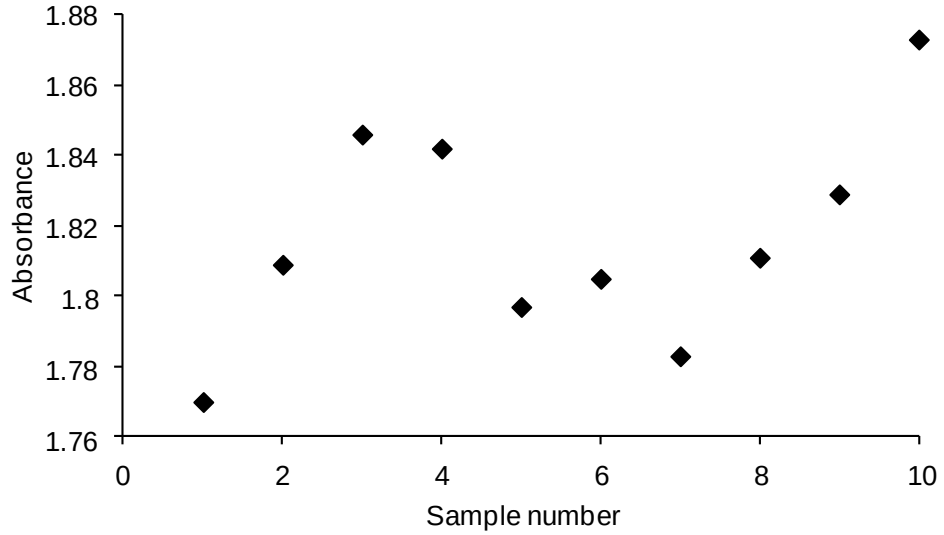
Kinetic plots used to construct the Eyring plots

Error analysis

To provide errors in the enthalpy and entropy of activation, the following approach was adopted.

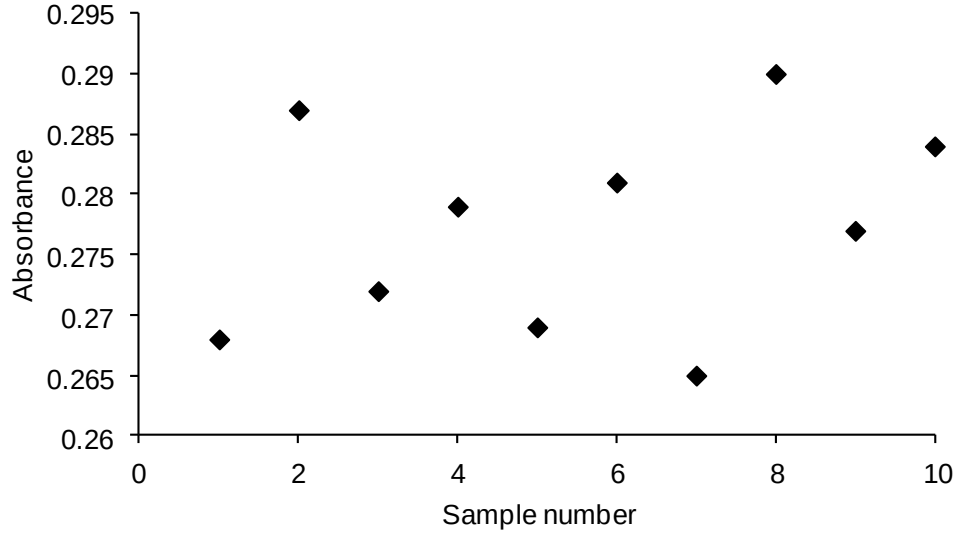
1. Two solution of benzaldehyde in dichloromethane were prepared, one corresponding to the concentration of benzaldehyde at the start of the kinetics experiments and the other to 80% conversion (i.e. a concentration 20% of the first solution). Ten samples were removed from each of these solutions using the same microlitre syringe used for the kinetics study and each sample was analysed at the same wavelength, using the same UV spectrophotometer used for the kinetics work. The resulting data is presented graphically below and allowed the error in the measurement of the concentrations at the start and end of the kinetics experiments to be determined. On the basis of these data, an error of +/- 5% was assumed in all data points in all variable temperature kinetics plots.

Benzaldehyde concentration corresponding to 0% conversion



All of the data points lie within +/- 3.1% of the mean value of 1.817

Benzaldehyde concentration corresponding to 80% conversion



All of the data points lie within +/- 4.6% of the mean value of 0.2772

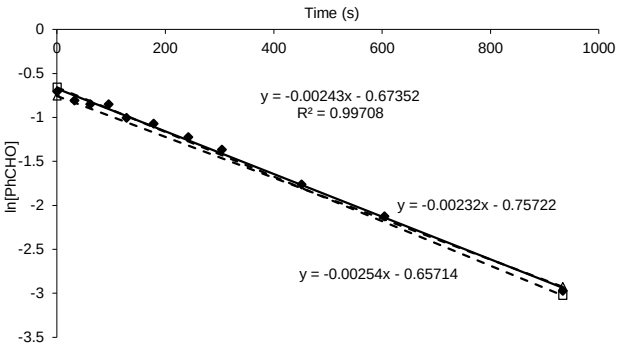
2. For each variable temperature kinetics plot, in addition to determining the best fit line through the data, the lines corresponding to an error of +/- 5% in the absorbance reading used to calculate the first and last data point were determined (these are shown on all the graphs in the following pages). These lines gave an indication of the error in the best fit line gradient.

3. Each variable temperature kinetics plot was conducted in duplicate, and the average of the two gradients was used to determine the data point for the Eyring plot. However, the error bars for this data point were determined from the maximum and minumim gradients of either individual kinetics plot.

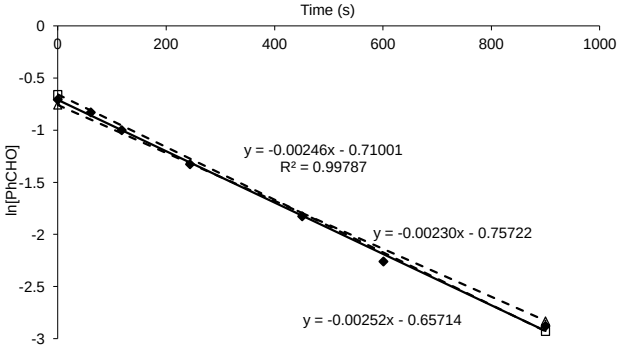
4. The maximum and minimum slope passing through the highest and lowest temperature points were used to determine the errors in the gradient and intercept of the Eyring plot and hence the error limits in the enthalpy and entropy of activation.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Et_3N 1 (2 mol%)

Reaction at +10 ^oC run 1

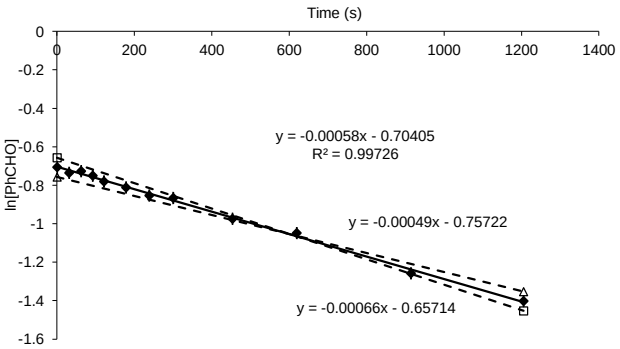


Reaction at +10 ^oC run 2

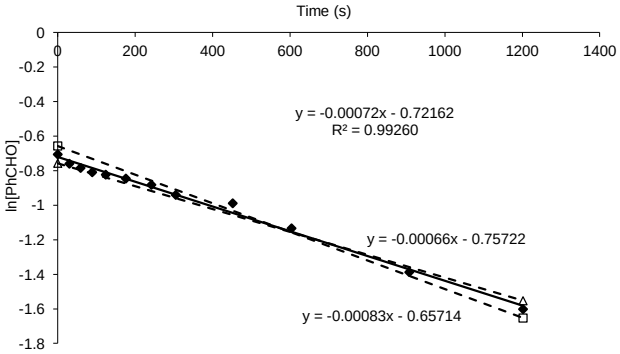


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at 0 ^oC run 1

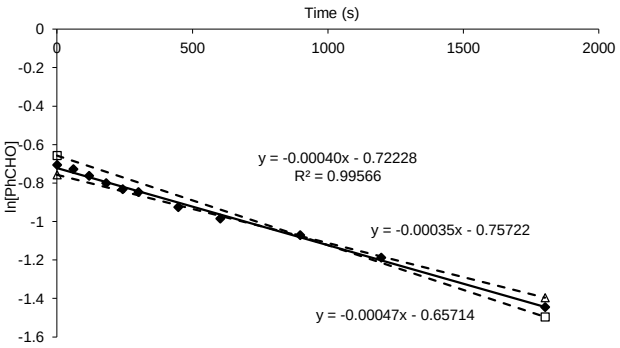


Reaction at 0 ^oC run 2

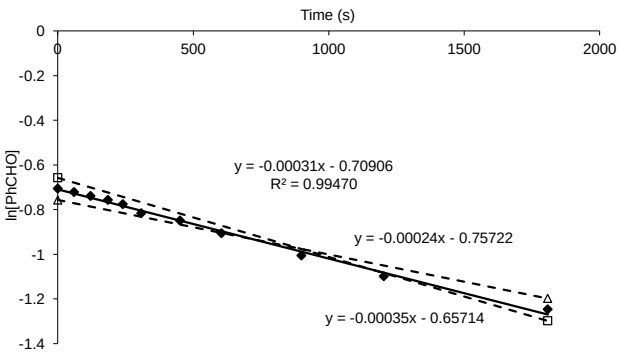


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -10 ^oC run 1

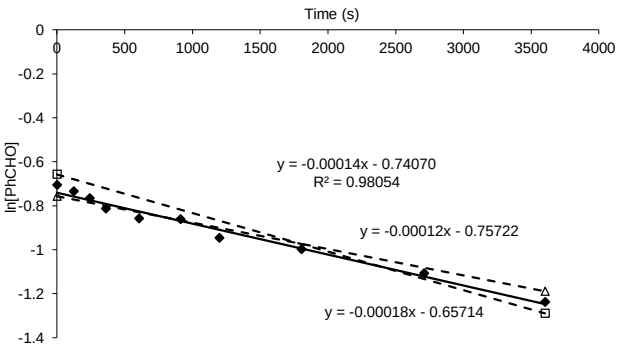


Reaction at -10 ^oC run 2

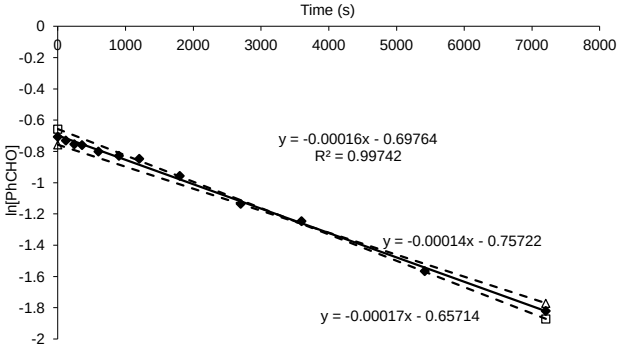


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -20 °C run 1

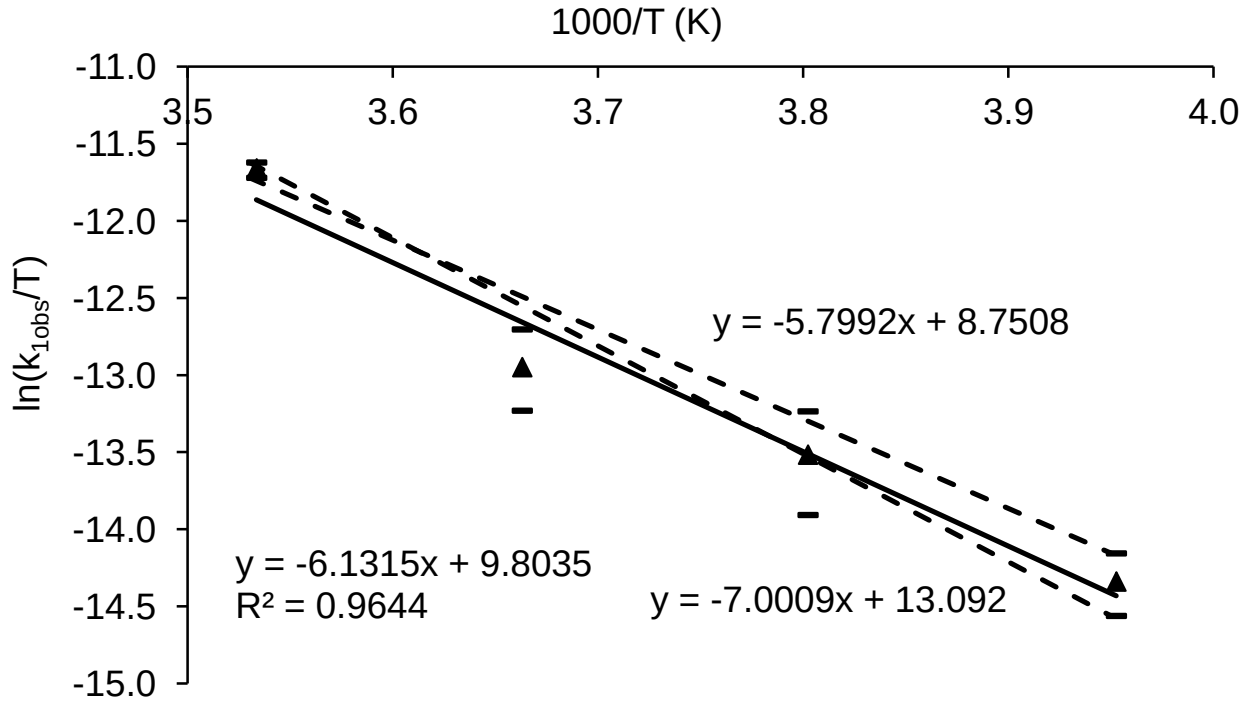


Reaction at -20 °C run 2



The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

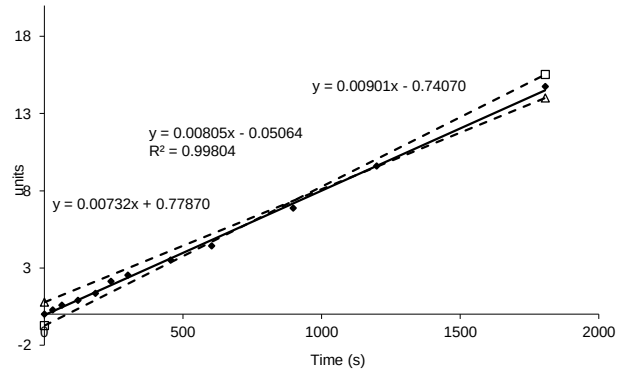
Eyring plot



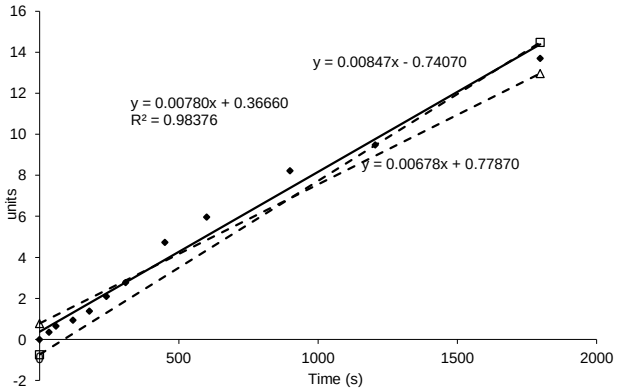
The filled triangles correspond to the average of the two individual rate measurements at each temperature and the solid line (and equation with R^2 value) is the best fit line through these data points. This corresponds to the data given in Figure 4 of the manuscript. The horizontal lines above and below each diamond correspond to the maximum and minimum value for that data point from either of the individual rate measurements. The broken lines (and equations without R^2 values) correspond to the limiting values for the best fit line based on the error limits for the highest and lowest temperature points. The data in Table 5 of the manuscript were obtained by averaging the maximum and minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the broken lines rather than from the solid line so as to ensure that the quoted values were at the midpoint of the maximum and minimum values.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NNCS 2 (1 mol%)

Reaction at +20 ^oC run 1

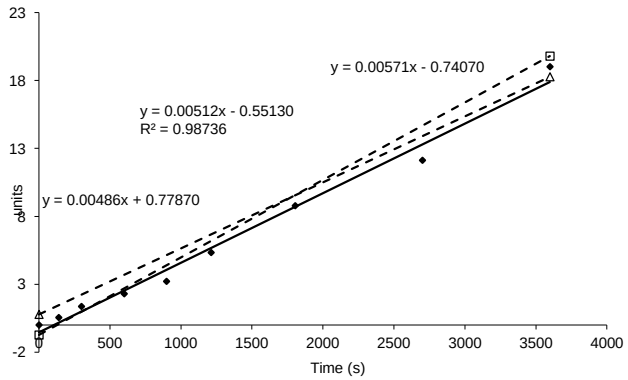


Reaction at +20 ^oC run 2

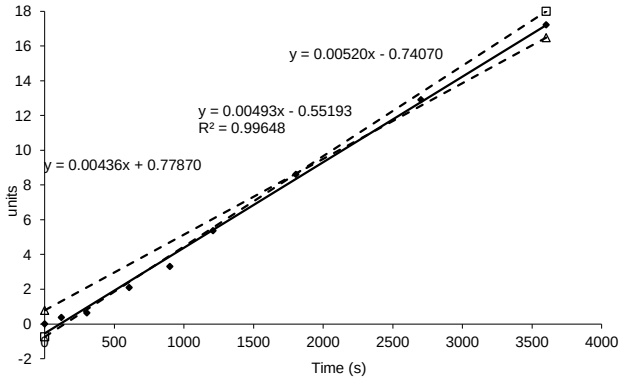


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively.

Reaction at +10 ^oC run 1

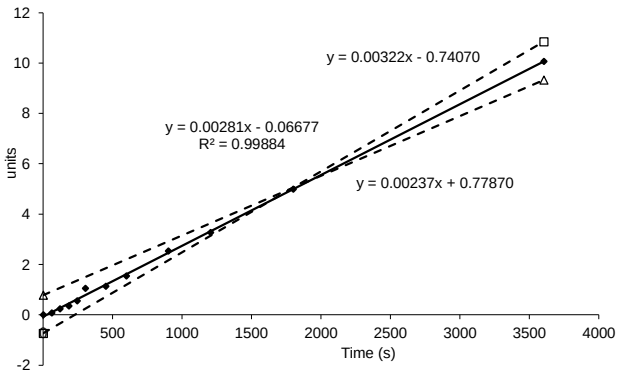


Reaction at +10 ^oC run 2

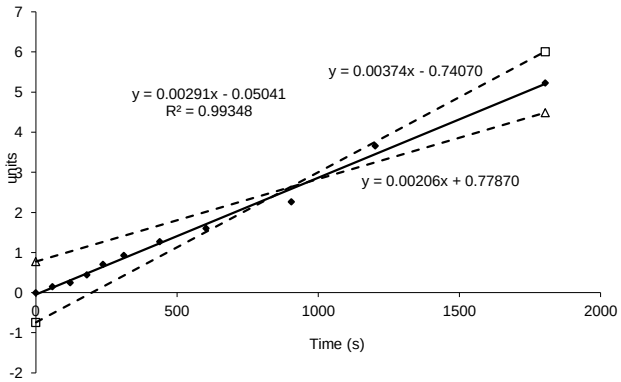


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively.

Reaction at 0 ^{o}C run 1

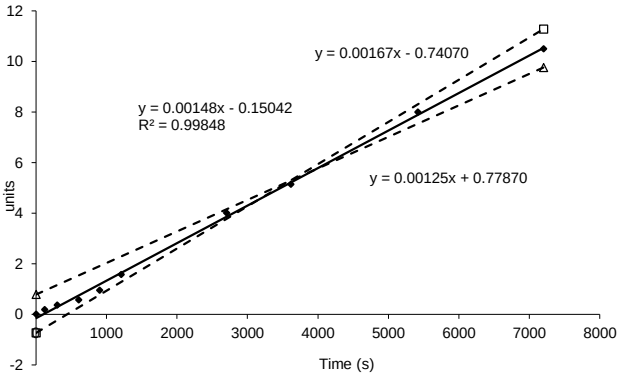


Reaction at 0 ^{o}C run 2

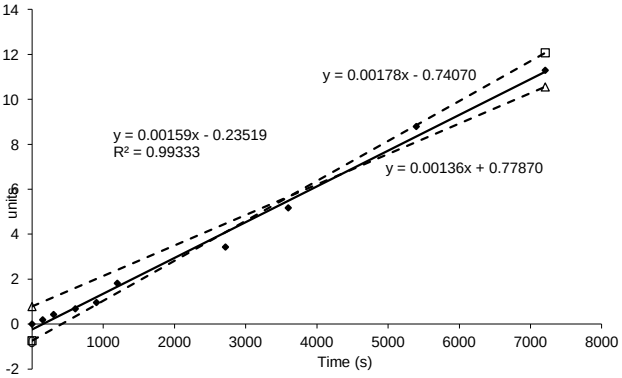


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively.

Reaction at -10 ^{o}C run 1

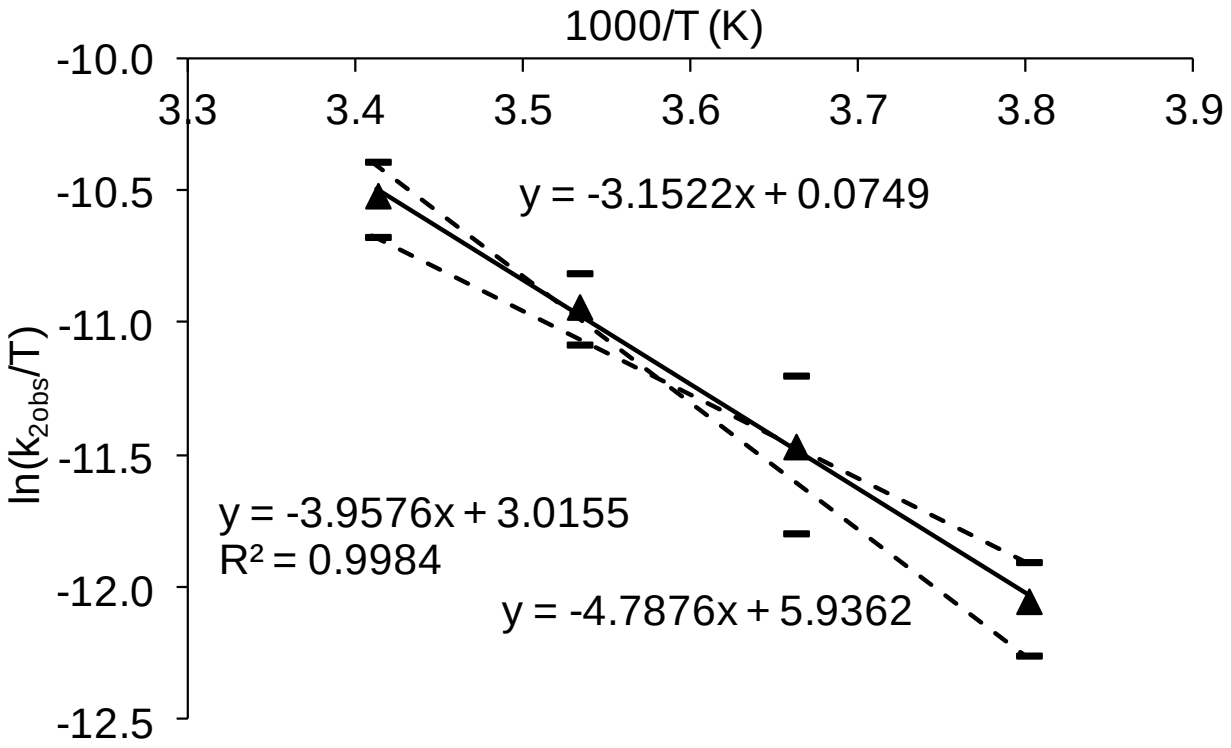


Reaction at -10 ^{o}C run 2



The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively.

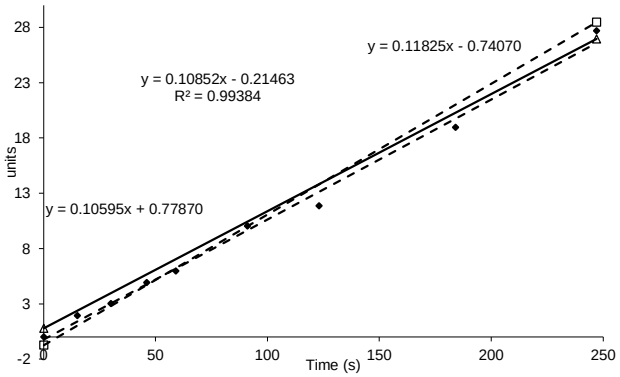
Eyring plot



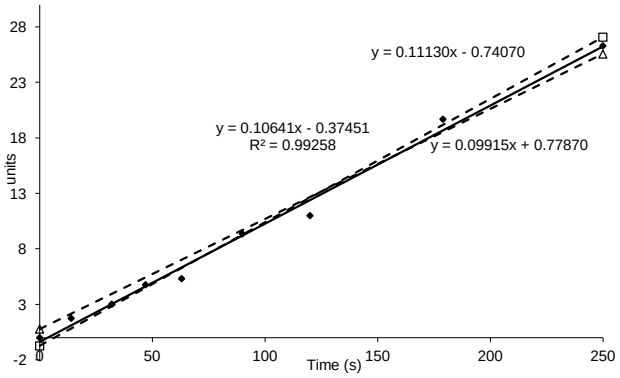
The filled triangles correspond to the average of the two individual rate measurements at each temperature and the solid line (and equation with R^2 value) is the best fit line through these data points. This corresponds to the data given in Figure 4 of the manuscript. The horizontal lines above and below each diamond correspond to the maximum and minimum value for that data point from either of the individual rate measurements. The broken lines (and equations without R^2 values) correspond to the limiting values for the best fit line based on the error limits for the highest and lowest temperature points. The data in Table 5 of the manuscript were obtained by averaging the maximum and minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the broken lines rather than from the solid line so as to ensure that the quoted values were at the midpoint of the maximum and minimum values.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NN_3 3 (0.05 mol%)

Reaction at +10 ^oC run 1

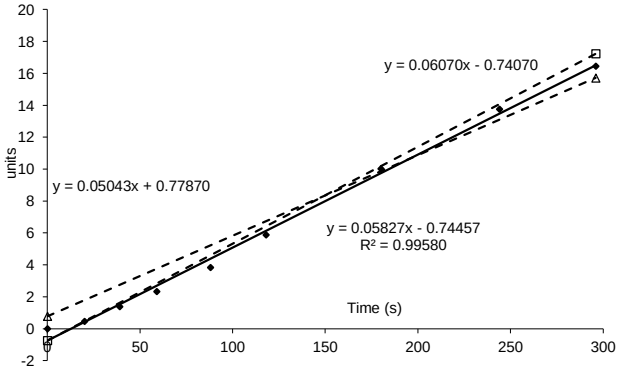


Reaction at +10 ^oC run 2

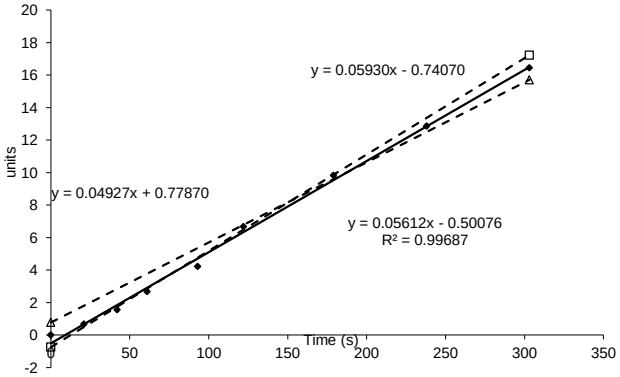


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Reaction at 0 ^oC run 1

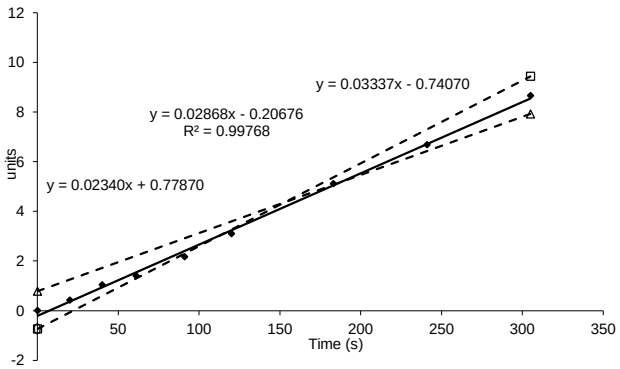


Reaction at 0 ^oC run 2

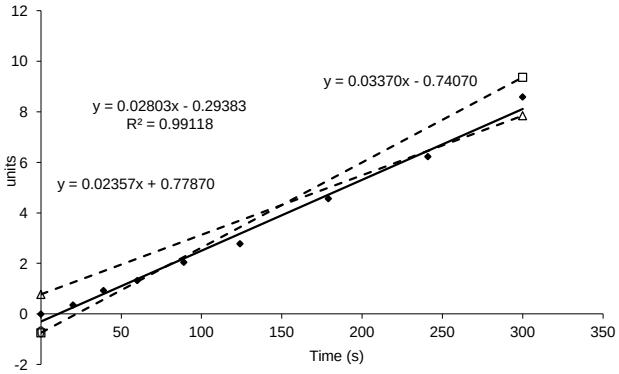


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Reaction at -10 ^{o}C run 1

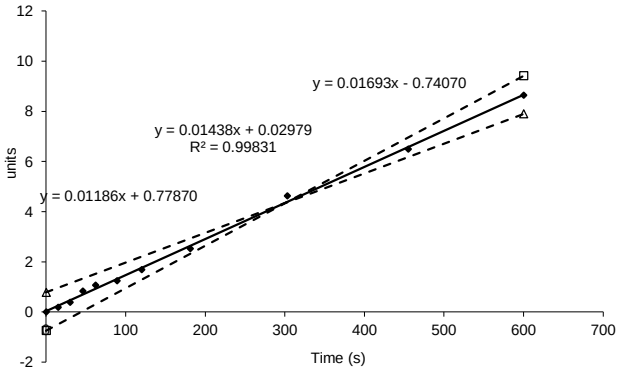


Reaction at -10 ^{o}C run 2

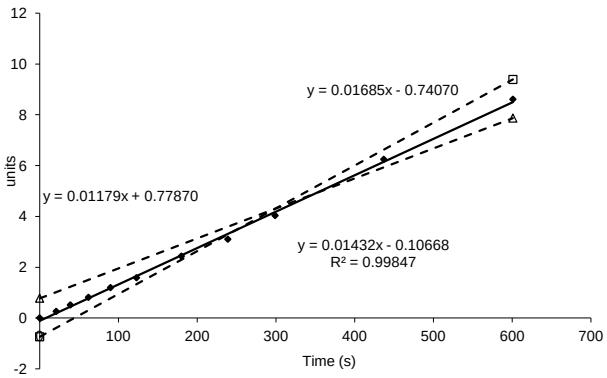


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Reaction at -20 ^{o}C run 1

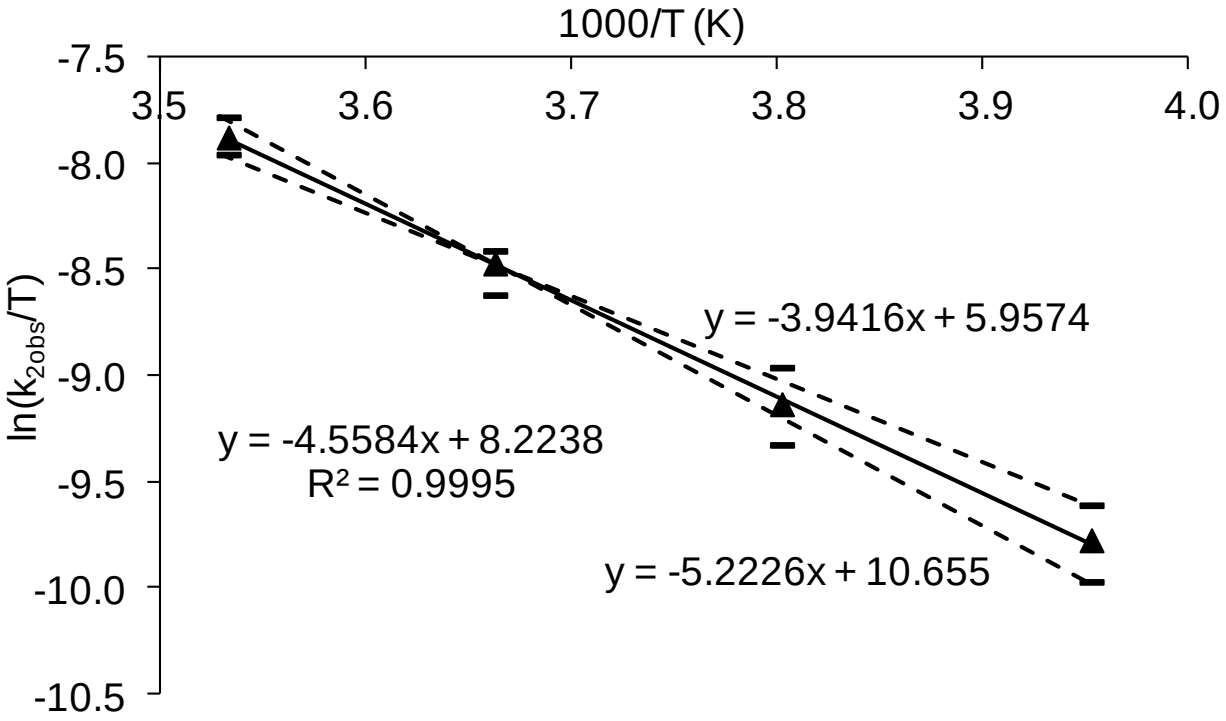


Reaction at -20 ^{o}C run 2



The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points. The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

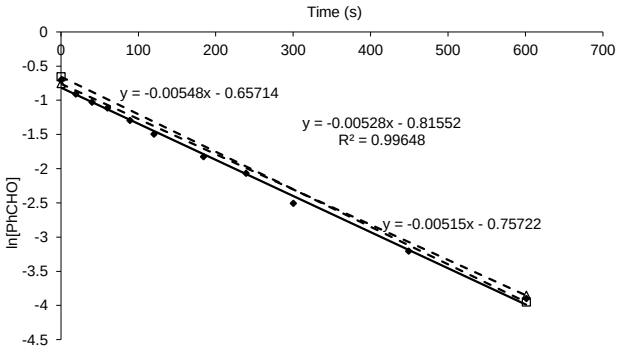
Eyring plot



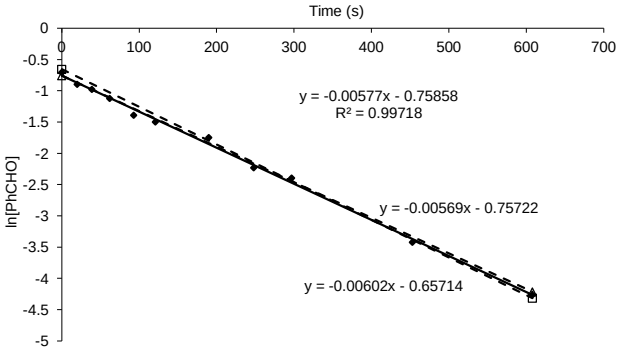
The filled triangles correspond to the average of the two individual rate measurements at each temperature and the solid line (and equation with R^2 value) is the best fit line through these data points. This corresponds to the data given in Figure 4 of the manuscript. The horizontal lines above and below each diamond correspond to the maximum and minimum value for that data point from either of the individual rate measurements. The broken lines (and equations without R^2 values) correspond to the limiting values for the best fit line based on the error limits for the highest and lowest temperature points. The data in Table 5 of the manuscript were obtained by averaging the maximum and minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the broken lines rather than from the solid line so as to ensure that the quoted values were at the midpoint of the maximum and minimum values.

Addition of trimethylsilyl cyanide to benzaldehyde catalysed by Bu_4NCN 4 (0.005 mol%)

Reaction at +20 ^oC run 1

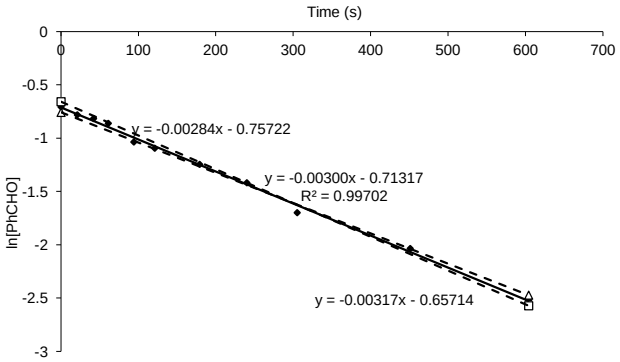


Reaction at +20 ^oC run 2

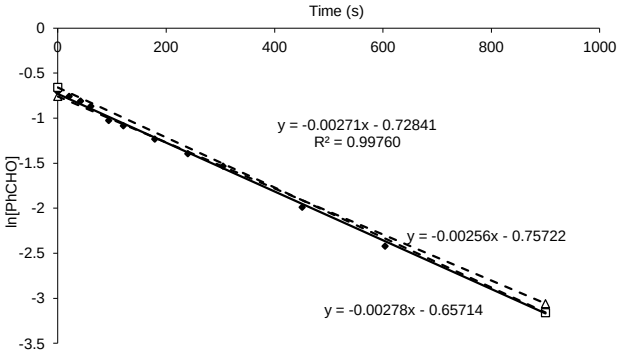


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at +10 ^oC run 1

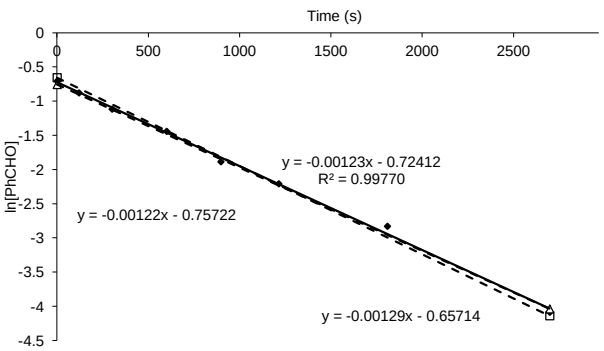


Reaction at +10 ^oC run 2

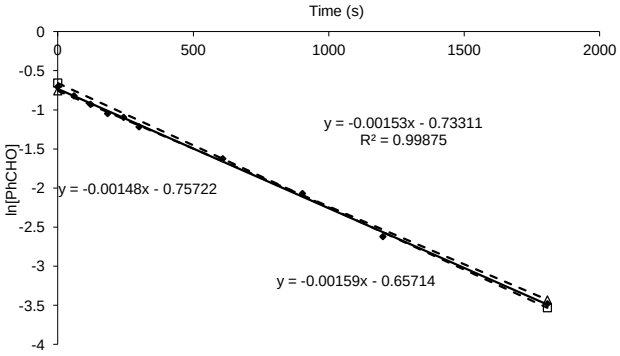


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at 0 ^oC run 1

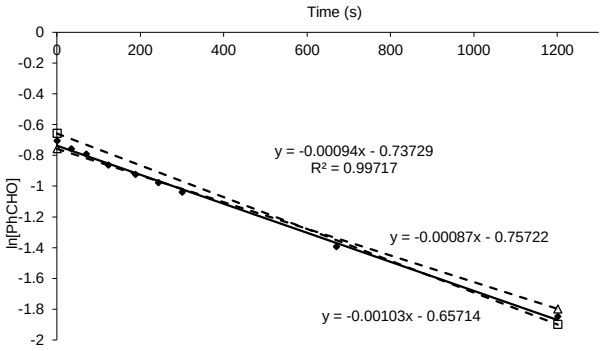


Reaction at 0 ^oC run 2

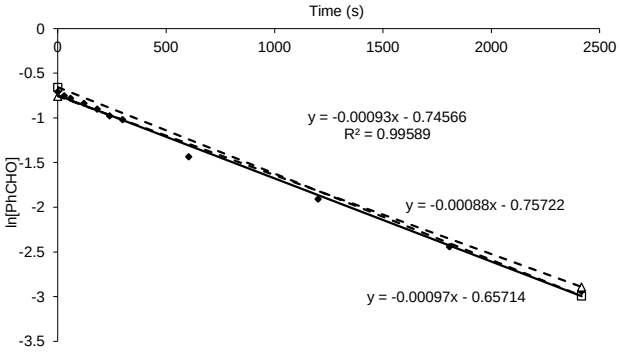


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -10 ^{o}C run 1

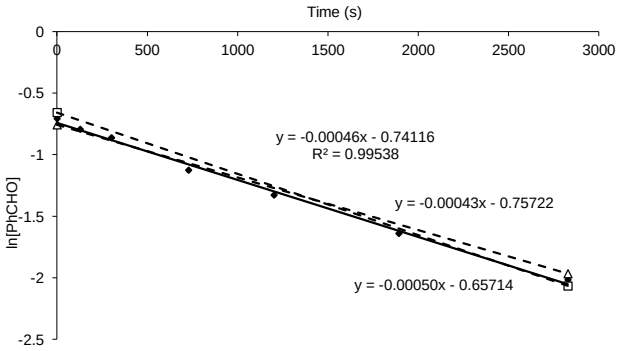


Reaction at -10 ^{o}C run 2

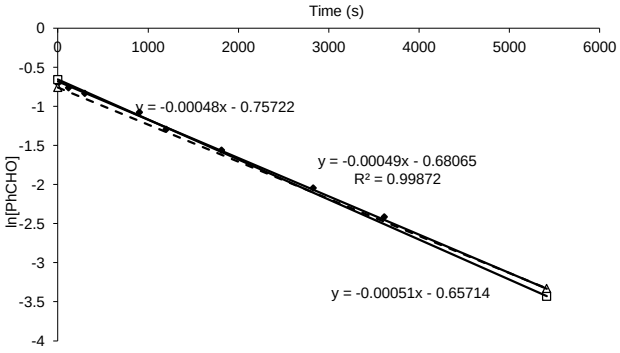


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -20 ^{o}C run 1

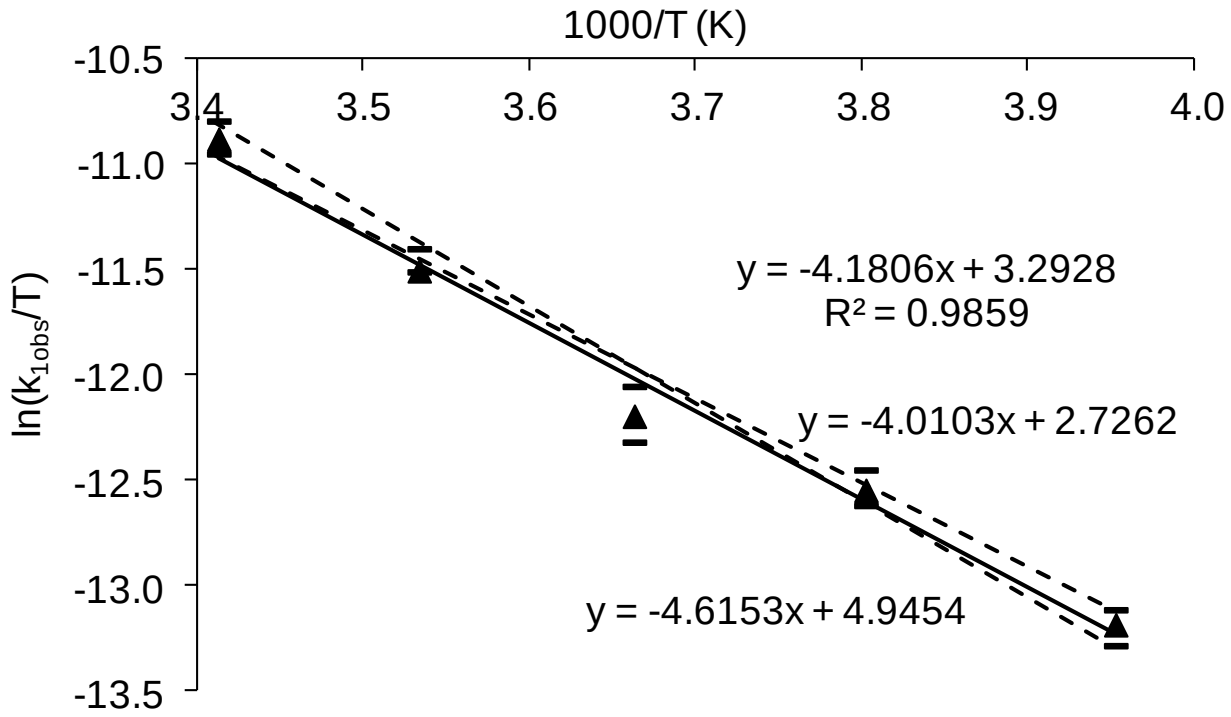


Reaction at -20 ^{o}C run 2



The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Eyring plot

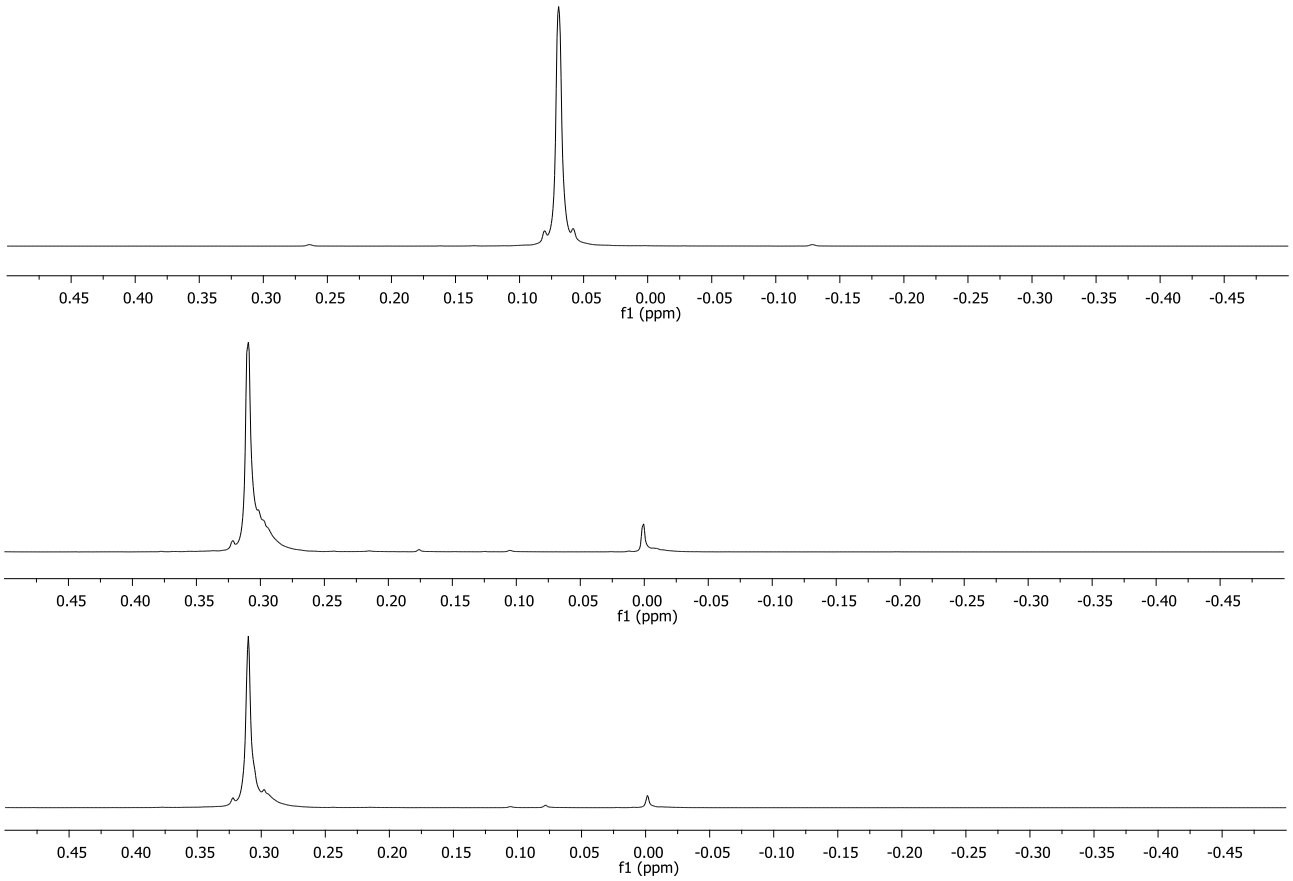


The filled triangles correspond to the average of the two individual rate measurements at each temperature and the solid line (and equation with R^2 value) is the best fit line through these data points. This corresponds to the data given in Figure 4 of the manuscript. The horizontal lines above and below each diamond correspond to the maximum and minimum value for that data point from either of the individual rate measurements. The broken lines (and equations without R^2 values) correspond to the limiting values for the best fit line based on the error limits for the highest and lowest temperature points. The data in Table 5 of the manuscript were obtained by averaging the maximum and minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the broken lines rather than from the solid line so as to ensure that the quoted values were at the midpoint of the maximum and minimum values.

NMR stacked plots to investigate the formation of hypervalent silicon species

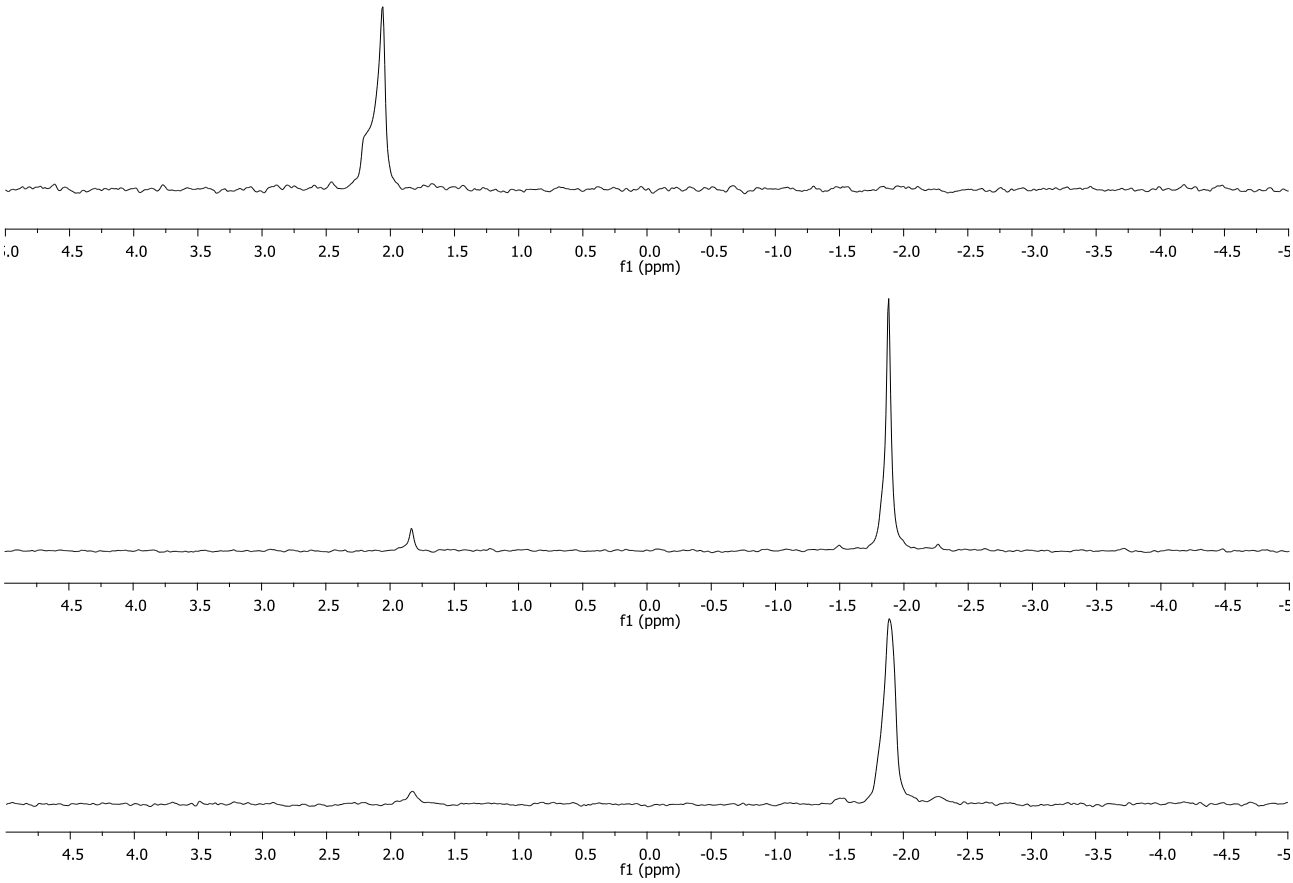
Addition of Et_3N 1 to trimethylsilyl cyanide

^{1}H NMR spectra



Bottom: ^{1}H NMR spectrum of Me_3SiCN.
Middle: ^{1}H NMR spectrum of a 1:1 mixture of Me_3SiCN and Et_3N showing no change in the position of the Me_3SiCN signal and no new signals corresponding to the Me_3Si groups of other silicon containing species.
Top: ^{1}H NMR spectrum of $(Me_3Si)_2O$

^{13}C NMR spectra

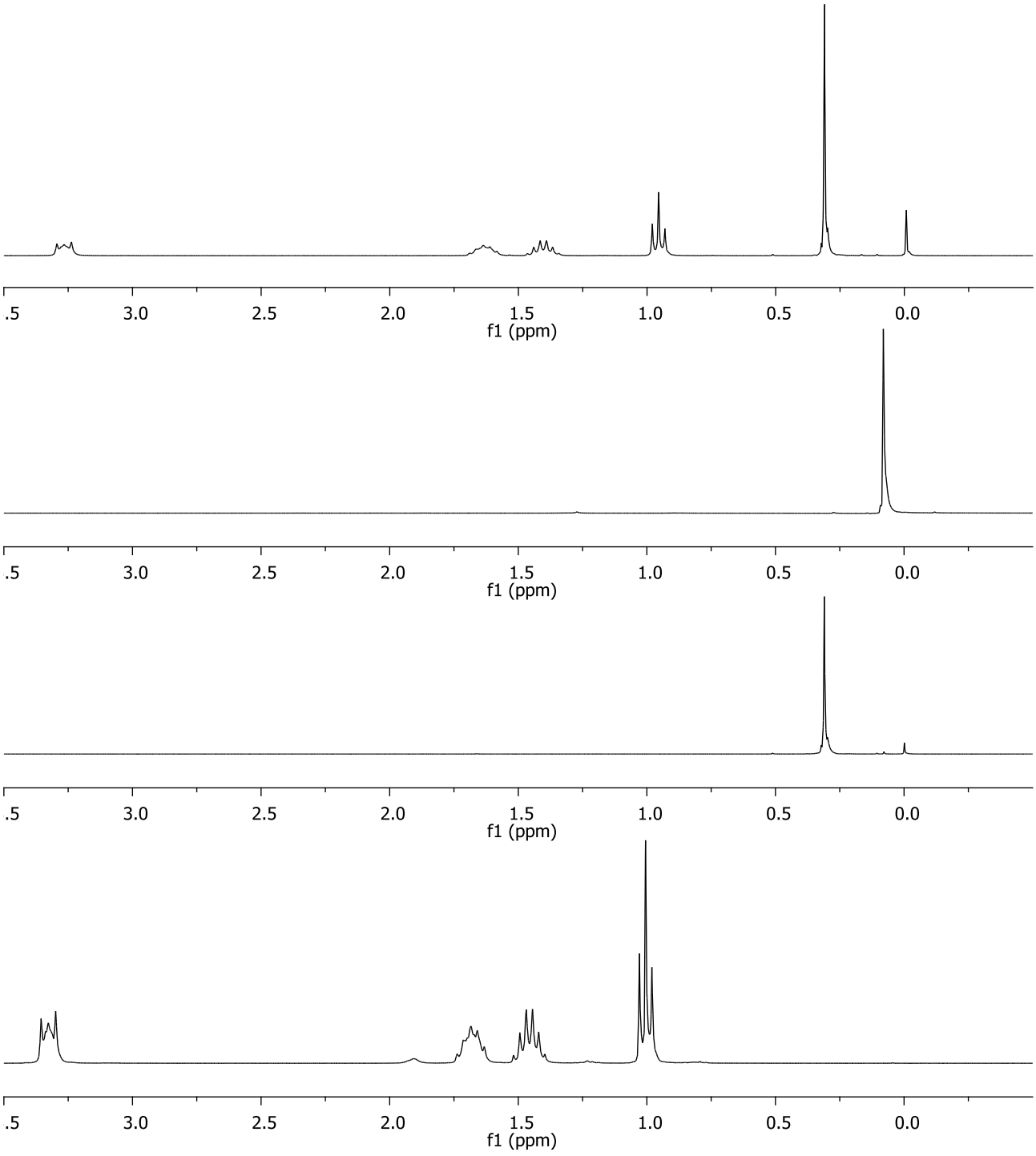


Bottom: ^{13}C NMR spectrum of Me_3SiCN.
Middle: ^{13}C NMR spectrum of a 1:1 mixture of Me_3SiCN and Et_3N showing no change in the position of the Me_3SiCN signal.
Top: ^{13}C NMR spectrum of $(Me_3Si)_2O$

The small signal at 1.8 ppm in both spectra is consistent with the presence of a hypervalent silicon species H^+ $[Me_3Si(CN)(X)]^-$ where X = OH or CN due to partial hydrolysis of Me_3SiCN by adventitious moisture.

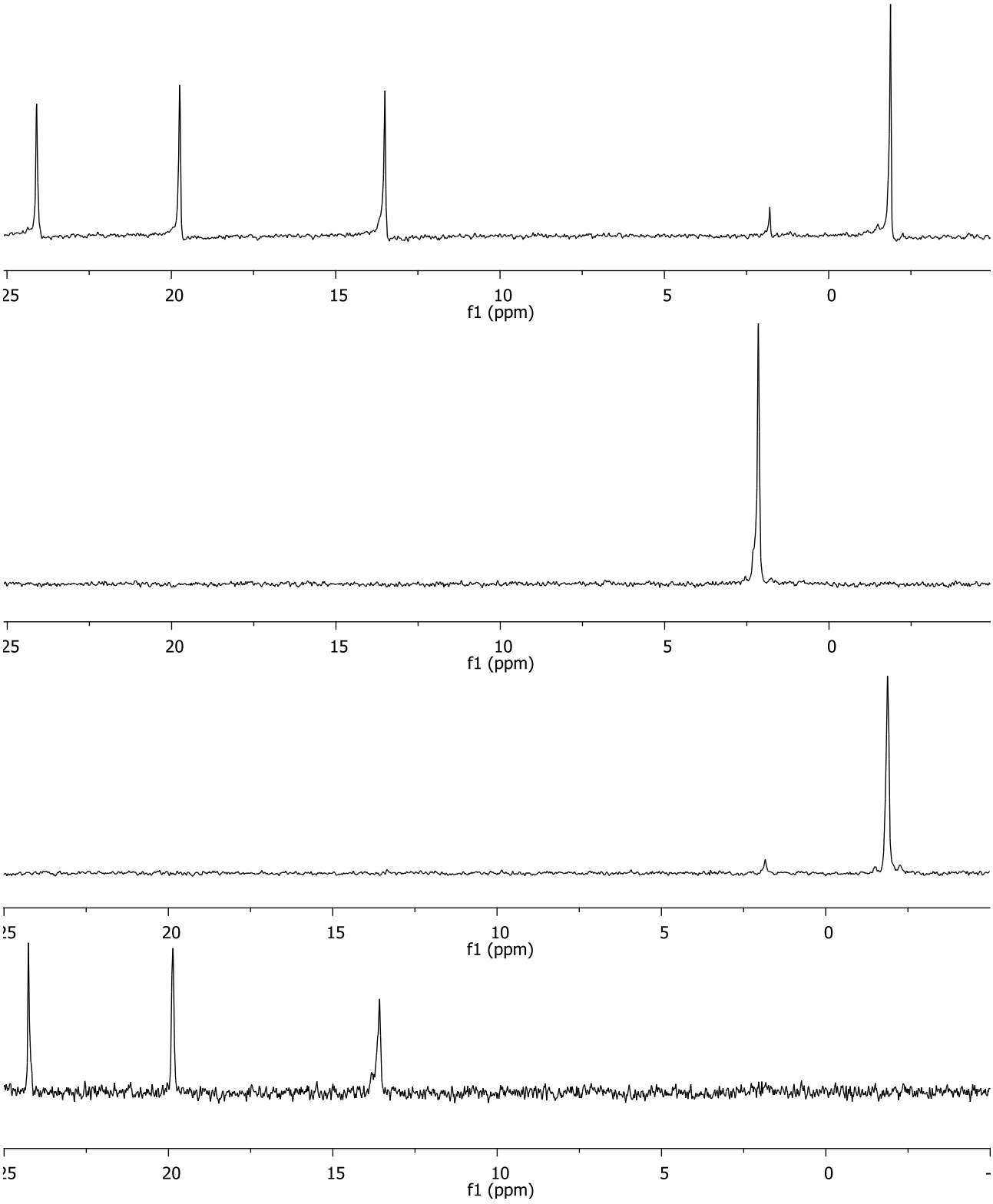
Addition of Bu_4NNCS 2 to trimethylsilyl cyanide

^{1}H NMR spectra



Bottom: ^{1}H NMR spectrum of Bu_4NNCS.
Next to bottom: ^{1}H NMR spectrum of Me_3SiCN.
Next to top: ^{1}H NMR spectrum of Me_3SiNCS.
Top: ^{1}H NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NNCS showing the presence of a new signal at -0.01 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)(NCS)]^-$.

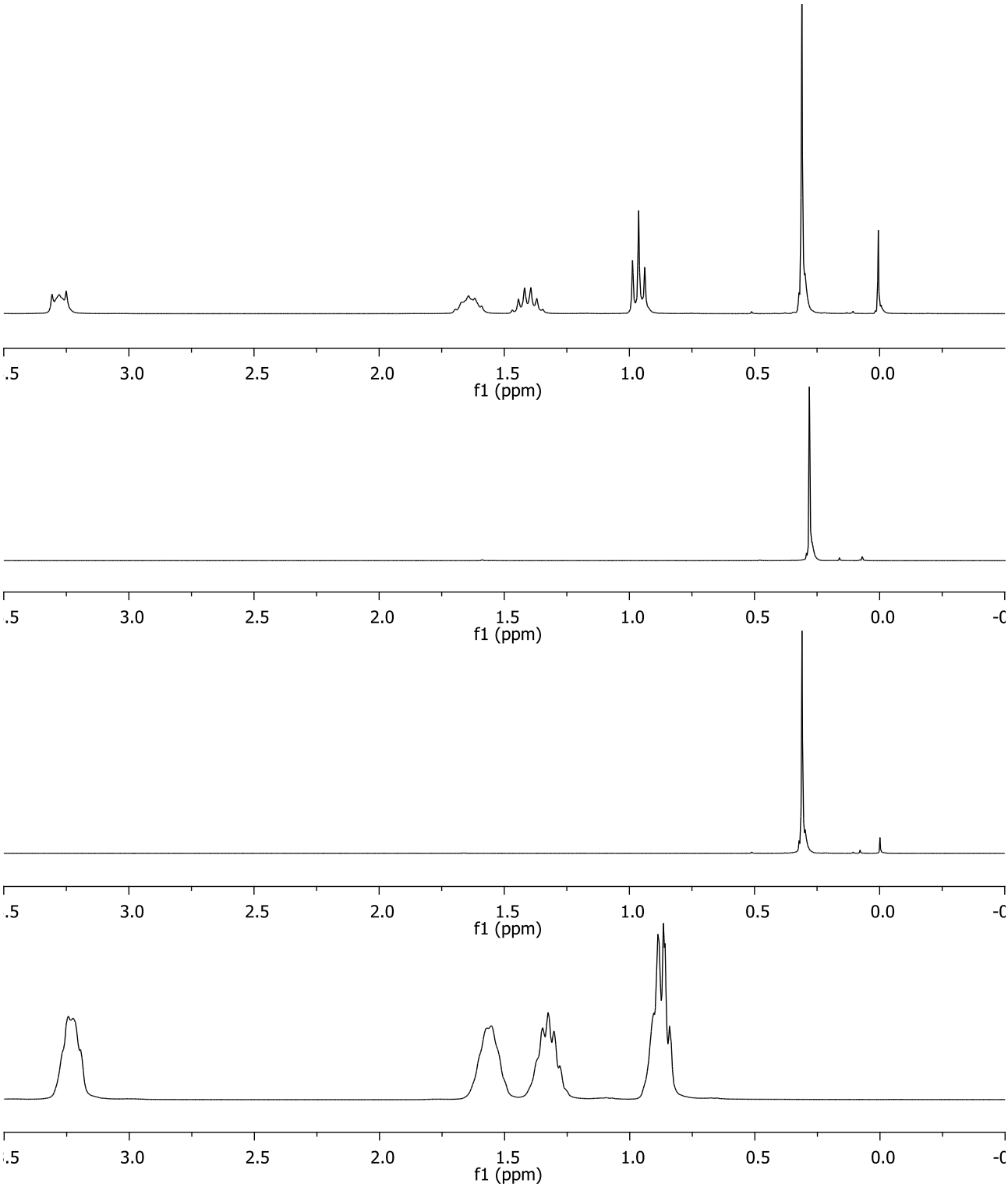
^{13}C NMR spectra



Bottom: ^{13}C NMR spectrum of Bu_4NNCS.
Next to bottom: ^{13}C NMR spectrum of Me_3SiCN.
Next to top: ^{13}C NMR spectrum of Me_3SiNCS.
Top: ^{13}C NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NNCS showing the presence of a new signal at +1.80 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)(NCS)]^-$.

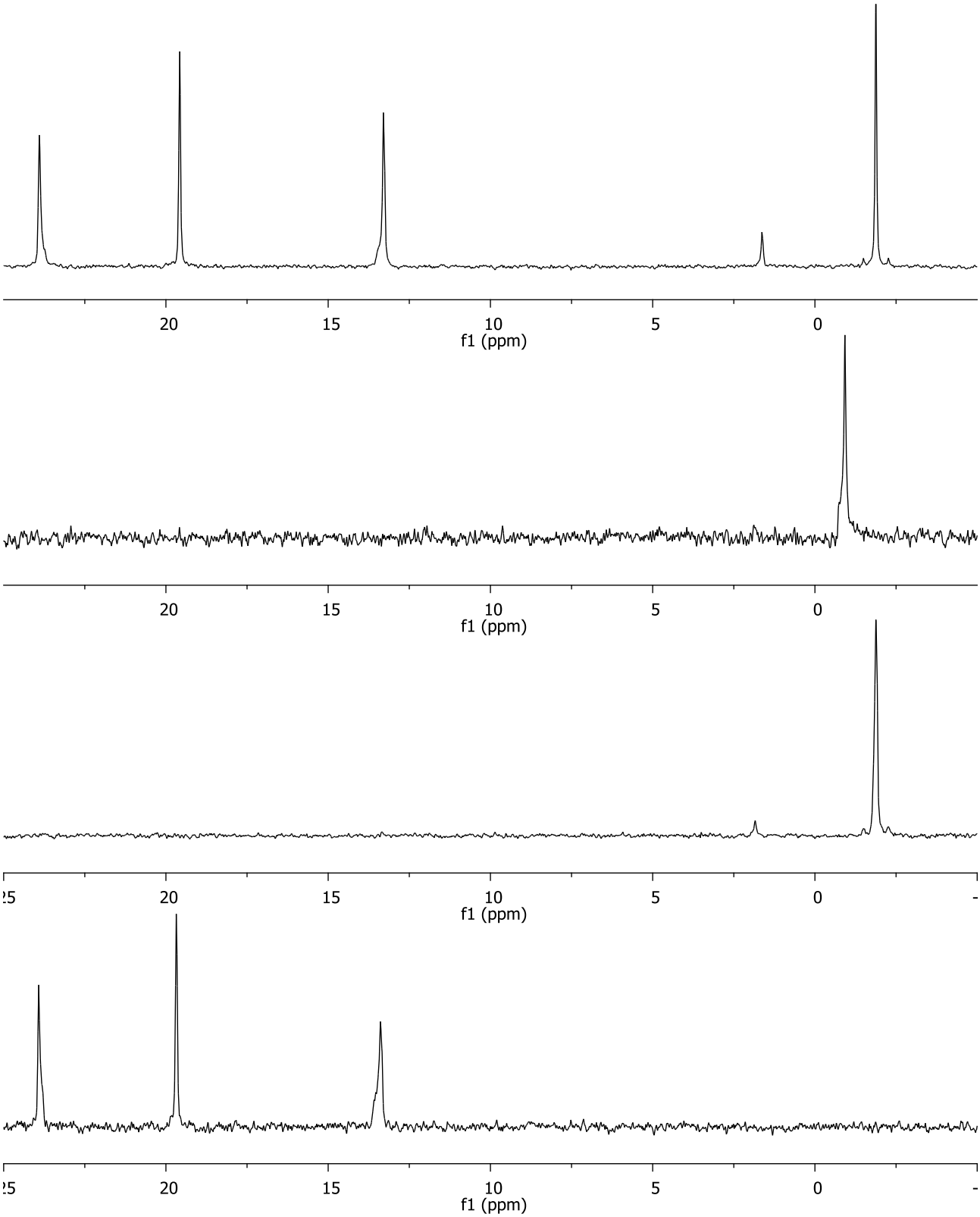
Addition of Bu_4NN_3 3 to trimethylsilyl cyanide

^{1}H NMR spectra



Bottom: ^{1}H NMR spectrum of Bu_4NN_3.
Next to bottom: ^{1}H NMR spectrum of Me_3SiCN.
Next to top: ^{1}H NMR spectrum of Me_3SiN_3.
Top: ^{1}H NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NN_3 showing the presence of a new signal at +0.01 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)(N_3)]^-$.

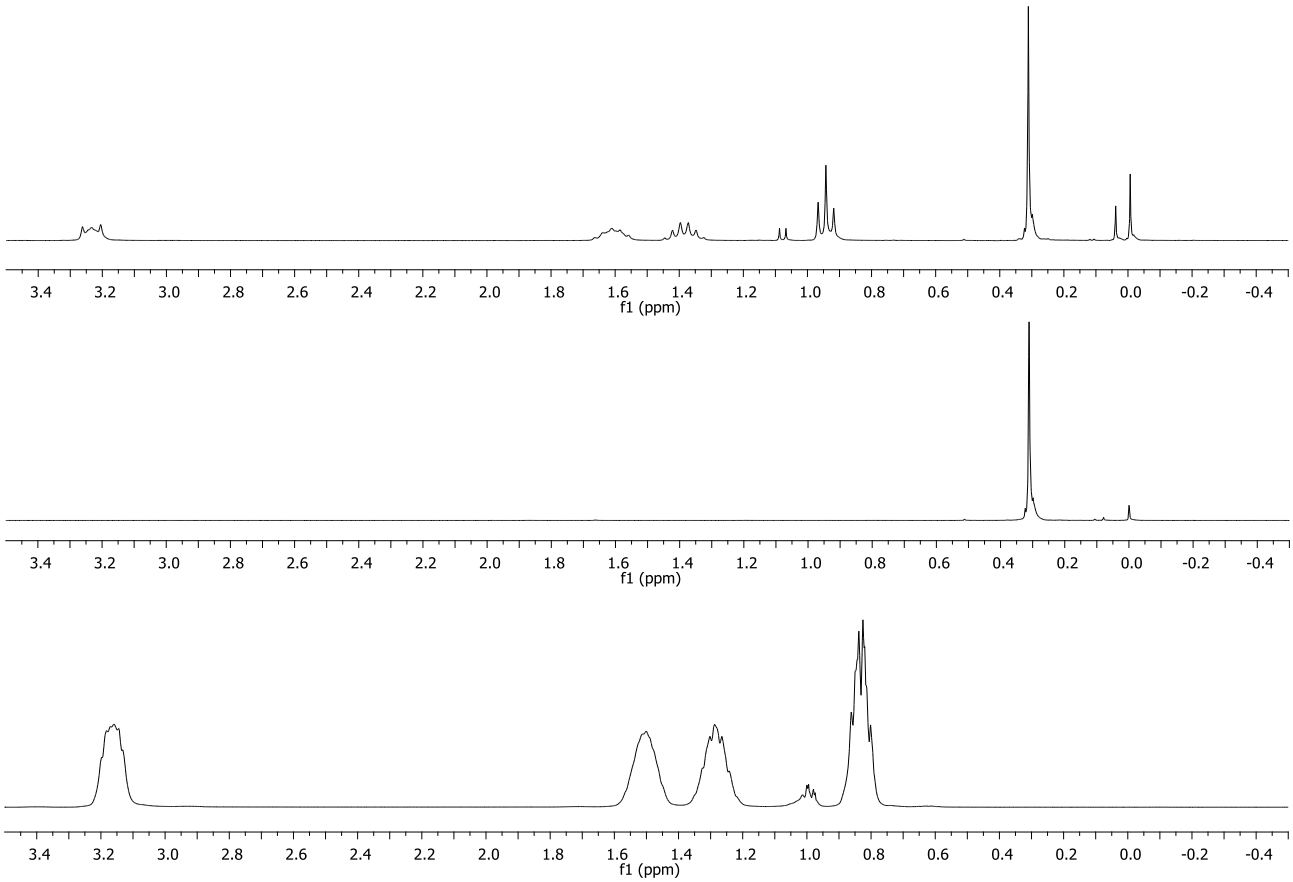
^{13}C NMR spectra



Bottom: ^{13}C NMR spectrum of Bu_4NN_3.
Next to bottom: ^{13}C NMR spectrum of Me_3SiCN.
Next to top: ^{13}C NMR spectrum of Me_3SiN_3.
Top: ^{13}C NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NN_3 showing the presence of a new signal at +1.64 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)(N_3)]^-$.

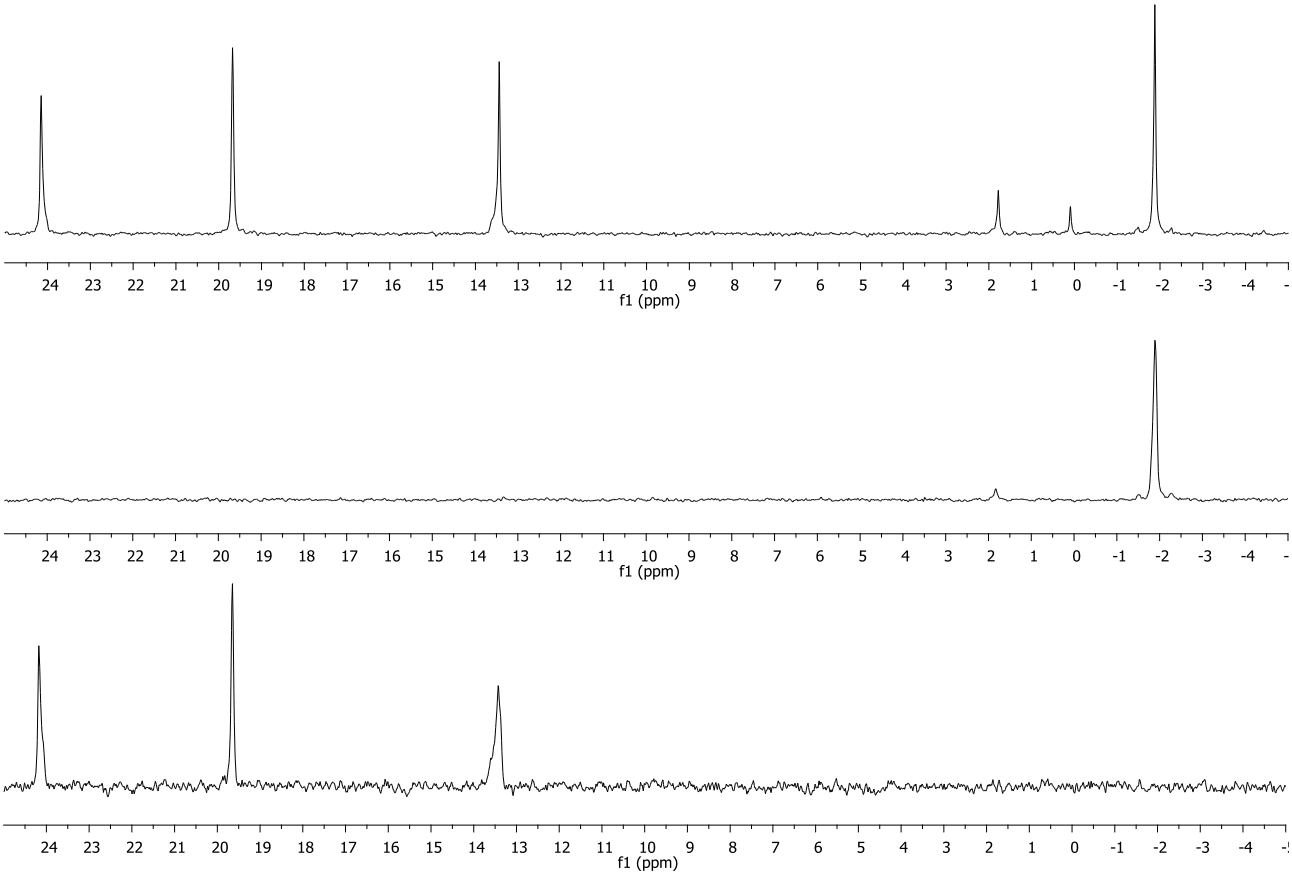
Addition of Bu_4NCN 4 to trimethylsilyl cyanide

^{1}H NMR spectra



Bottom: ^{1}H NMR spectrum of Bu_4NCN.
Middle: ^{1}H NMR spectrum of Me_3SiCN.
Top: ^{1}H NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NCN showing changes in the chemical shift of the butyl groups and the presence of a new signal at +0.04 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)_2]^-$.

^{13}C NMR spectra



Bottom: ^{13}C NMR spectrum of Bu_4NCN.
Middle: ^{13}C NMR spectrum of Me_3SiCN.
Top: ^{13}C NMR spectrum of a 1:1 mixture of Me_3SiCN and Bu_4NCN showing the presence of a new signal at +1.79 ppm consistent with the hypervalent silicon species Bu_4N^+ $[Me_3Si(CN)_2]^-$.

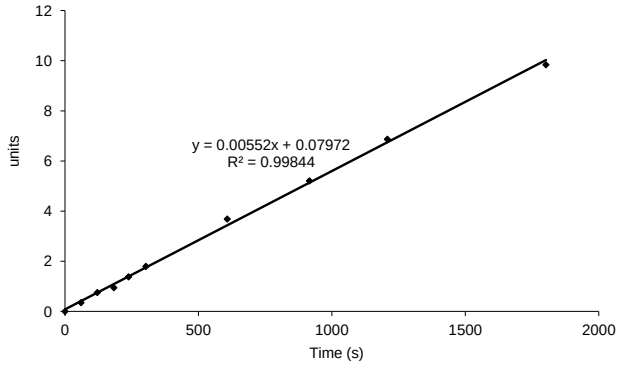
Kinetic plots used to determine the influence of water

Addition of trimethylsilyl cyanide to 3,4-dimethylbenzaldehyde catalysed by Bu_4NN_3 3

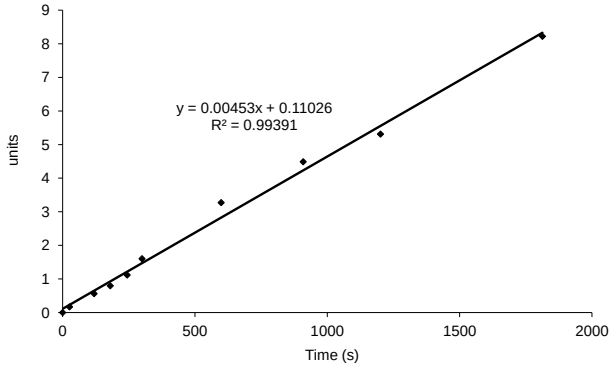
All of the following plots correspond to 86-89% conversion and show both the greatly reduced reaction time and the change in reaction order in the presence of water.

Reaction under anhydrous conditions (second order kinetics plot)

Run 1



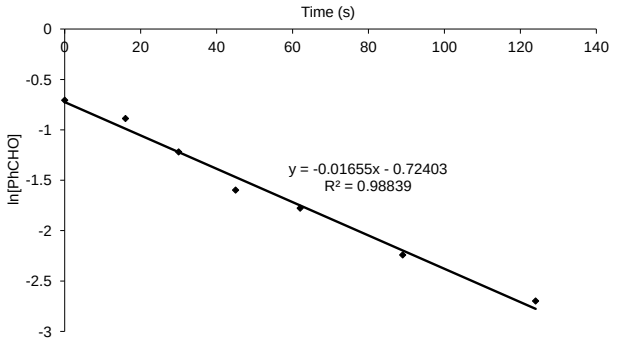
Run 2



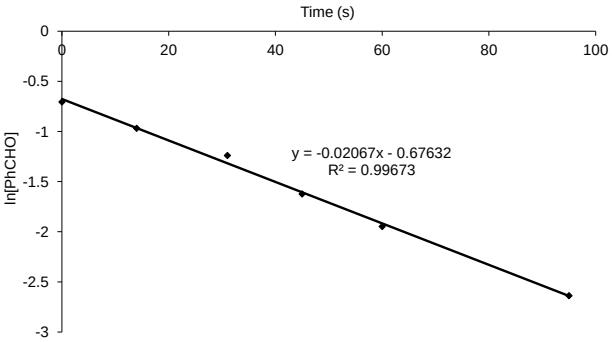
The units for the vertical scale are: $\ln[(B_0A_t)/(B_tA_0)]/(A_0-B_0)$ where: A = [PhCHO], B = [Me_3SiCN] and the subscripts 0 and t refer to initial concentrations and concentrations at time t, respectively. The concentration of benzaldehyde was monitored.

Reaction in the presence of water

Run 1



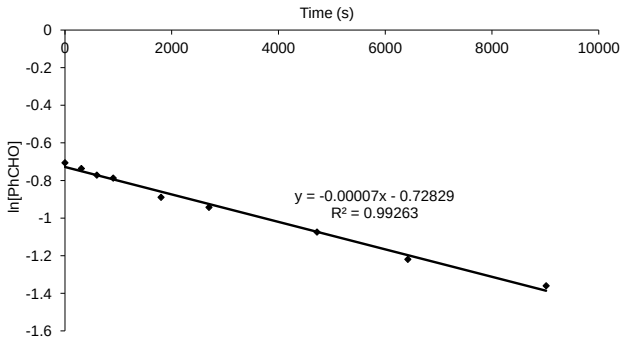
Run 2



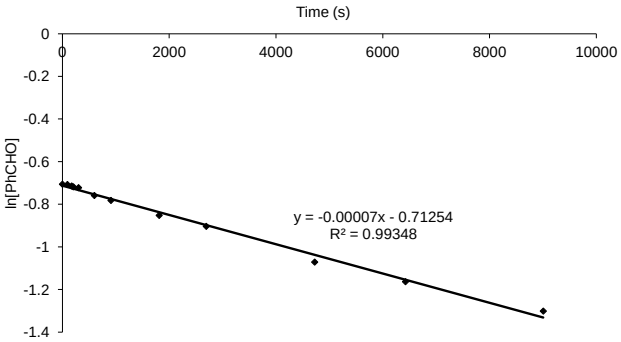
Plots showing that in the presence of water, the reaction is still first order in Et_3N concentration

[Et_3N] = 0.001 M (corresponds to 0.2 mol%)

Run 1

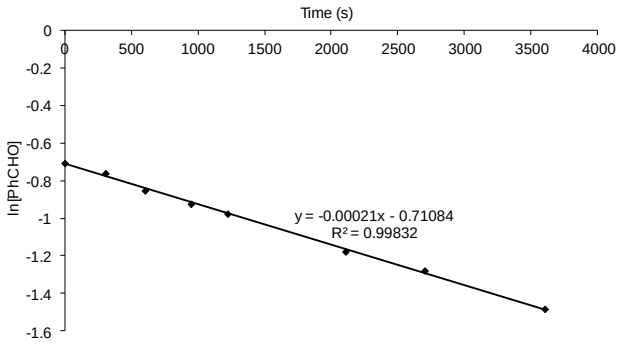


Run 2

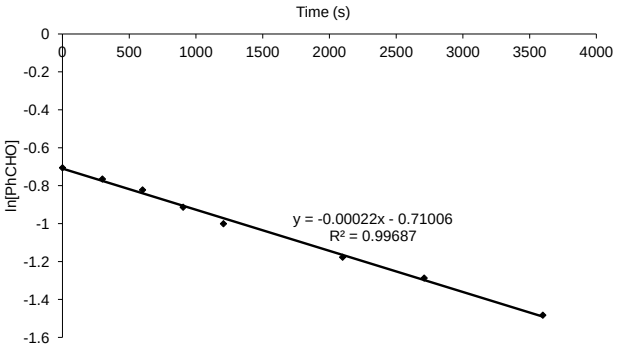


[Et_3N] = 0.002 M (corresponds to 0.4 mol%)

Run 1

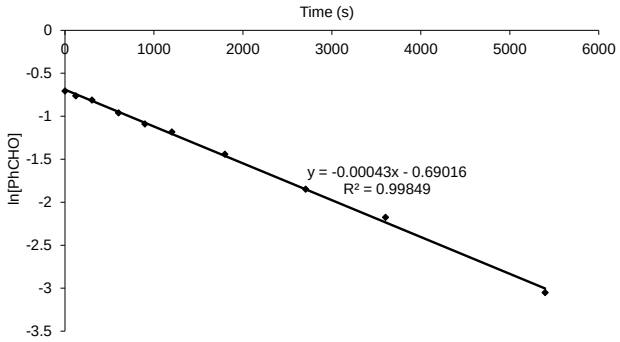


Run 2

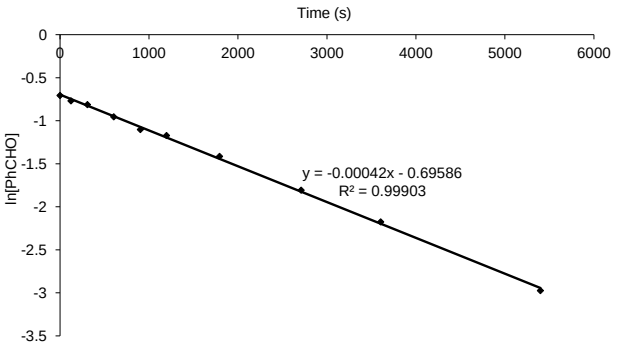


[Et_3N] = 0.004 M (corresponds to 0.8 mol%)

Run 1

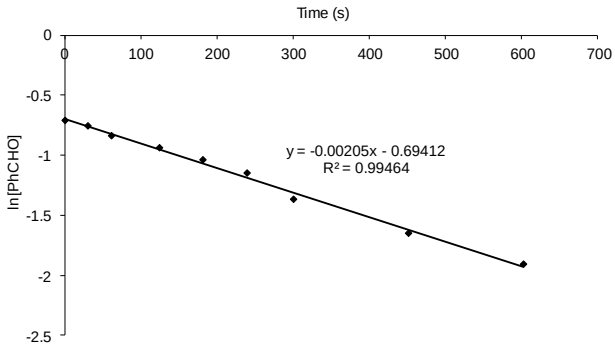


Run 2

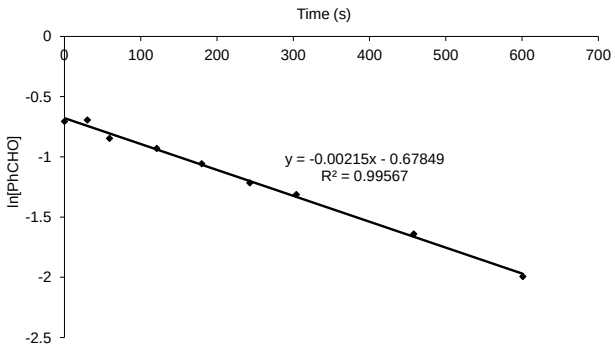


[Et_3N] = 0.02 M (corresponds to 4 mol%)

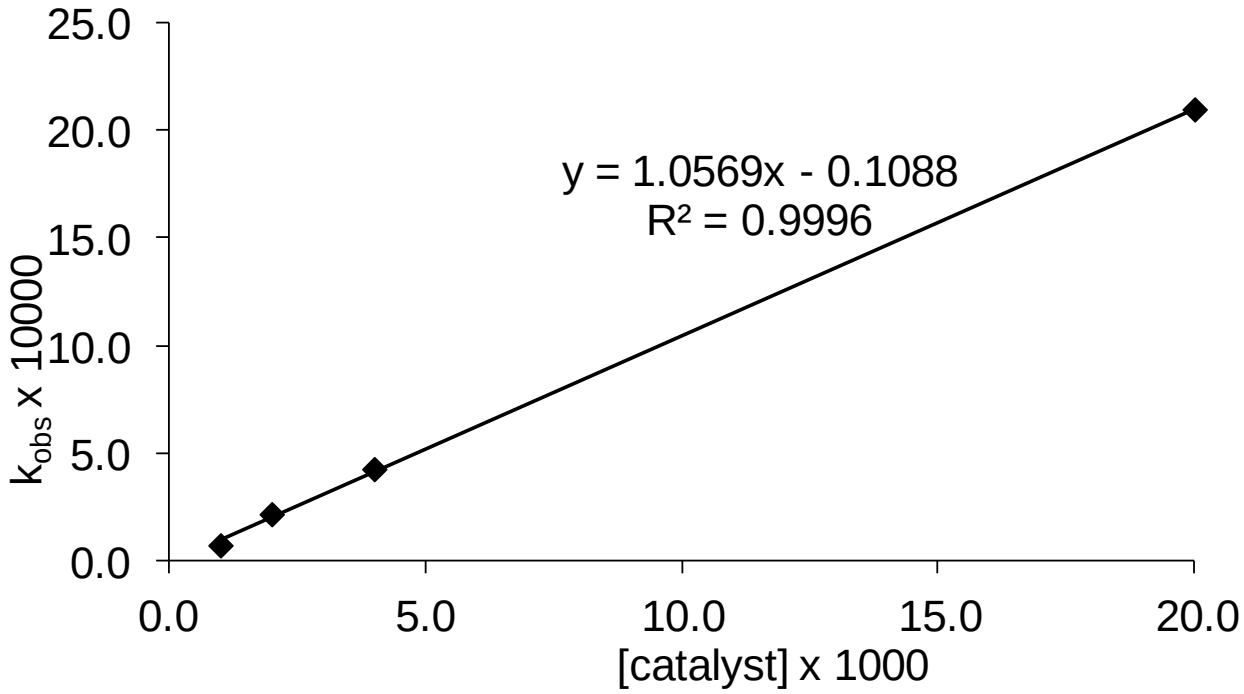
Run 1



Run 2



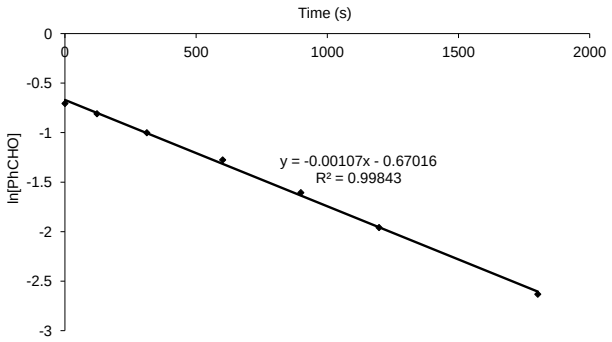
Plot of k_{obs} against [**1**] in the presence of water



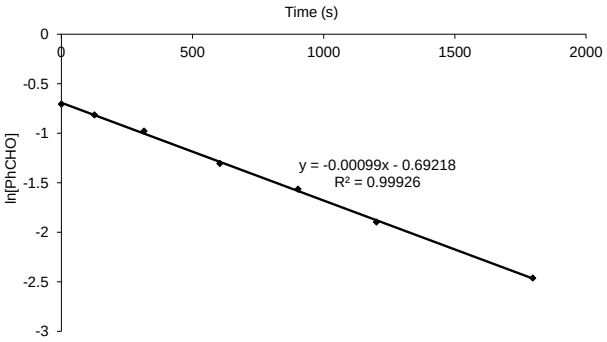
The solid line and filled data points show the average of two data sets.

Addition of trimethylsilyl cyanide to benzaldehydes catalysed by Et_3N 1 in the presence of water

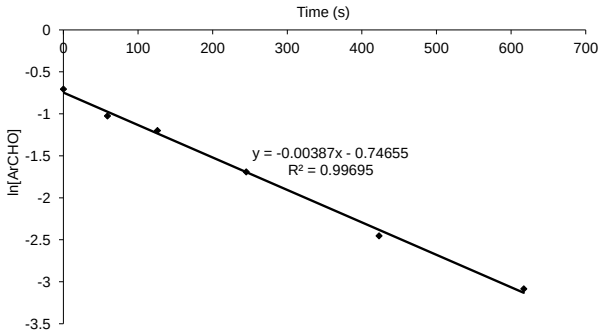
Benzaldehyde run 1



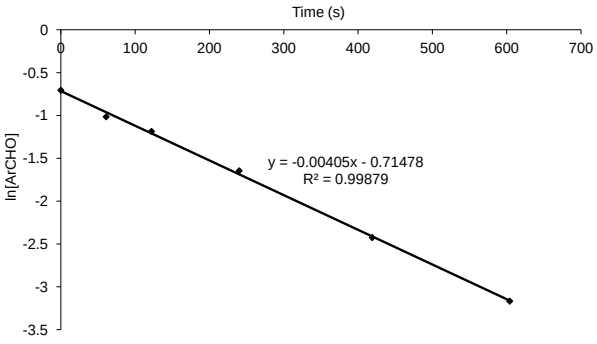
Benzaldehyde run 2



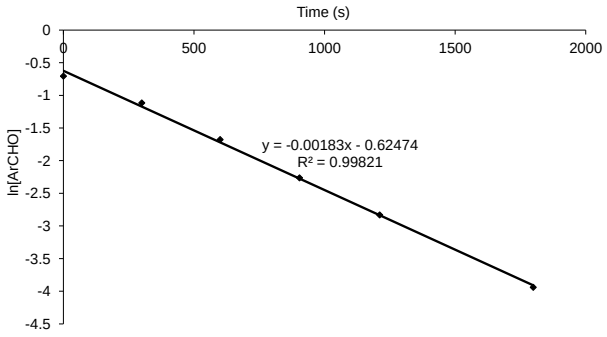
3-Chlorobenzaldehyde run 1



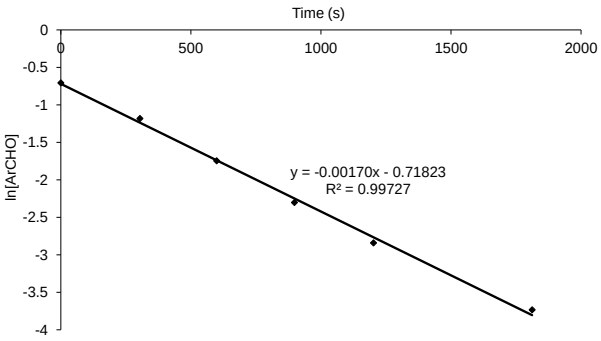
3-Chlorobenzaldehyde run 2



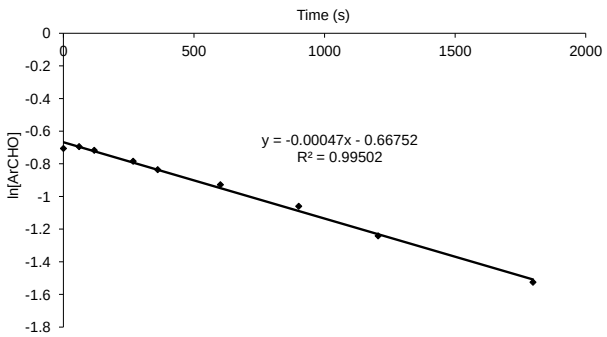
3-Fluorobenzaldehyde run 1



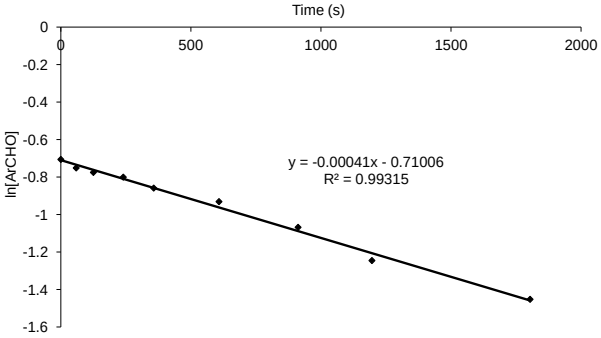
3-Fluorobenzaldehyde run 2



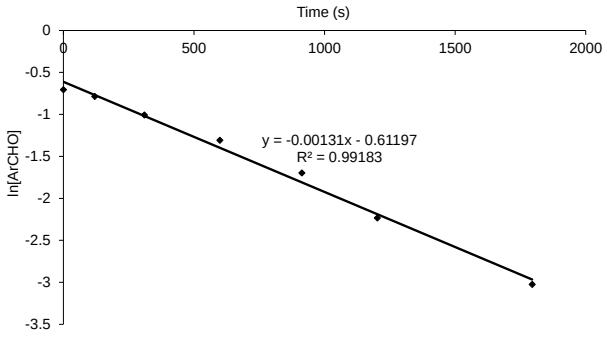
4-Chlorobenzaldehyde run 1



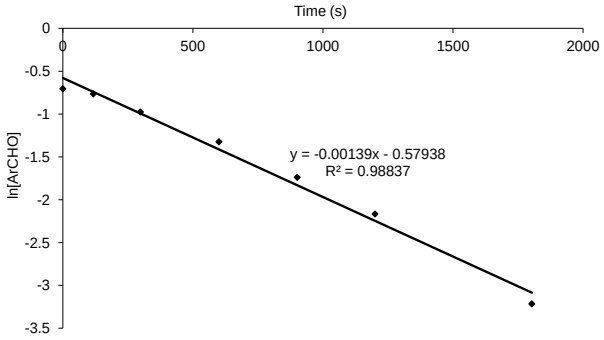
4-Chlorobenzaldehyde run 2



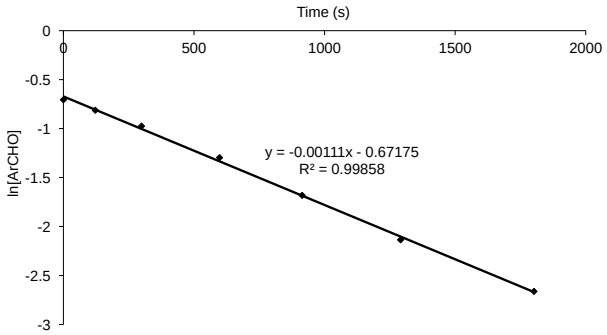
4-Fluorobenzaldehyde run 1



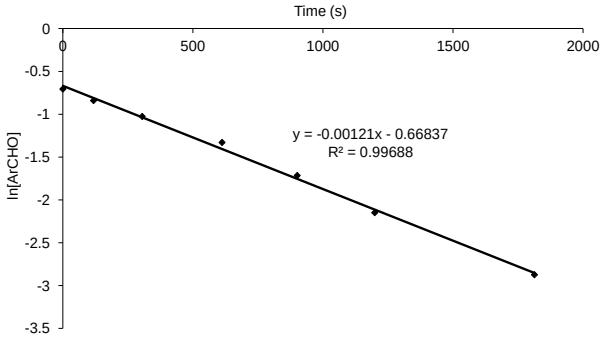
4-Fluorobenzaldehyde run 2



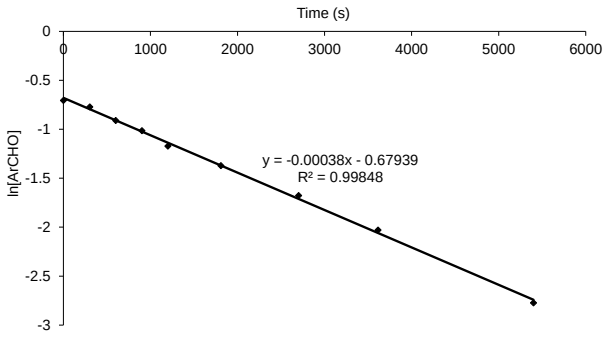
4-Thiomethylbenzaldehyde run 1



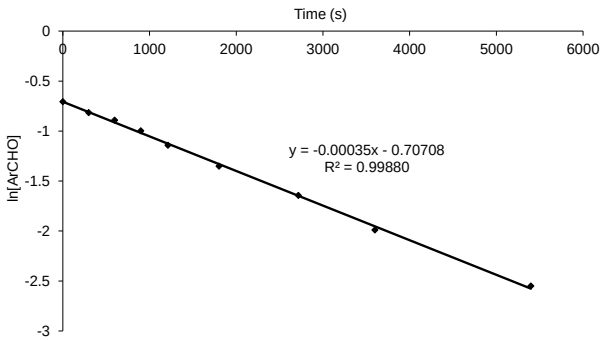
4-Thiomethylbenzaldehyde run 2



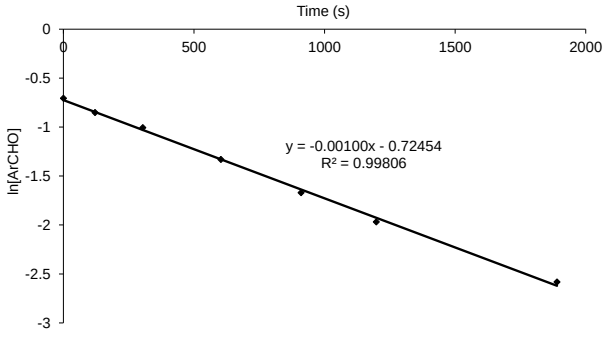
3-Methylbenzaldehyde run 1



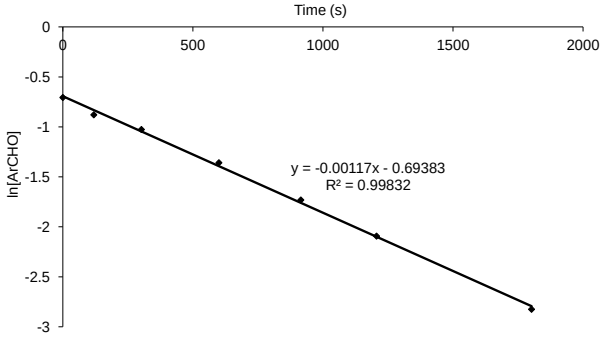
3-Methylbenzaldehyde run 2



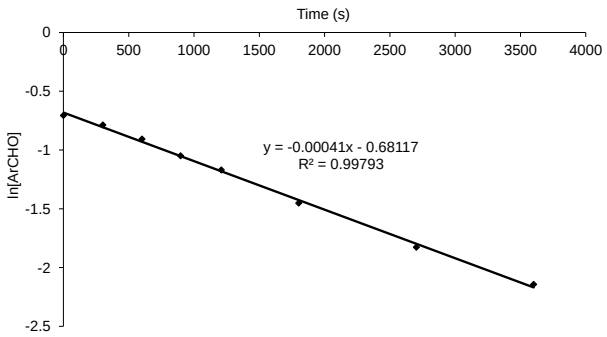
4-Methylbenzaldehyde run 1



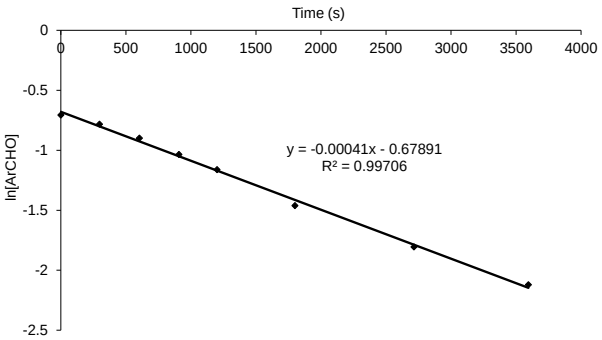
4-Methylbenzaldehyde run 2



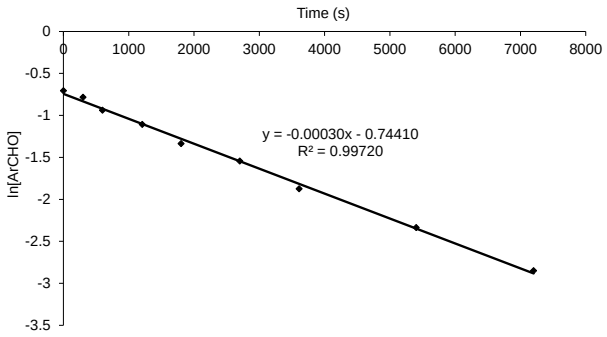
3,4-Dimethylbenzaldehyde run 1



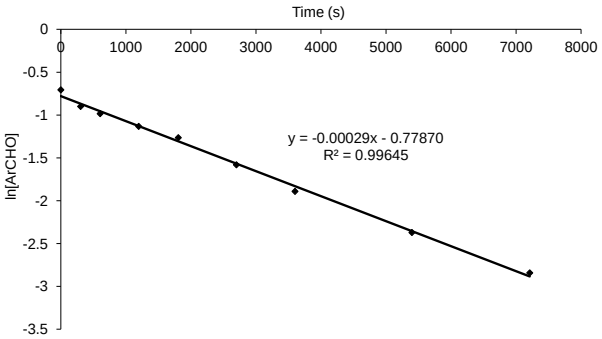
3,4-Dimethylbenzaldehyde run 2



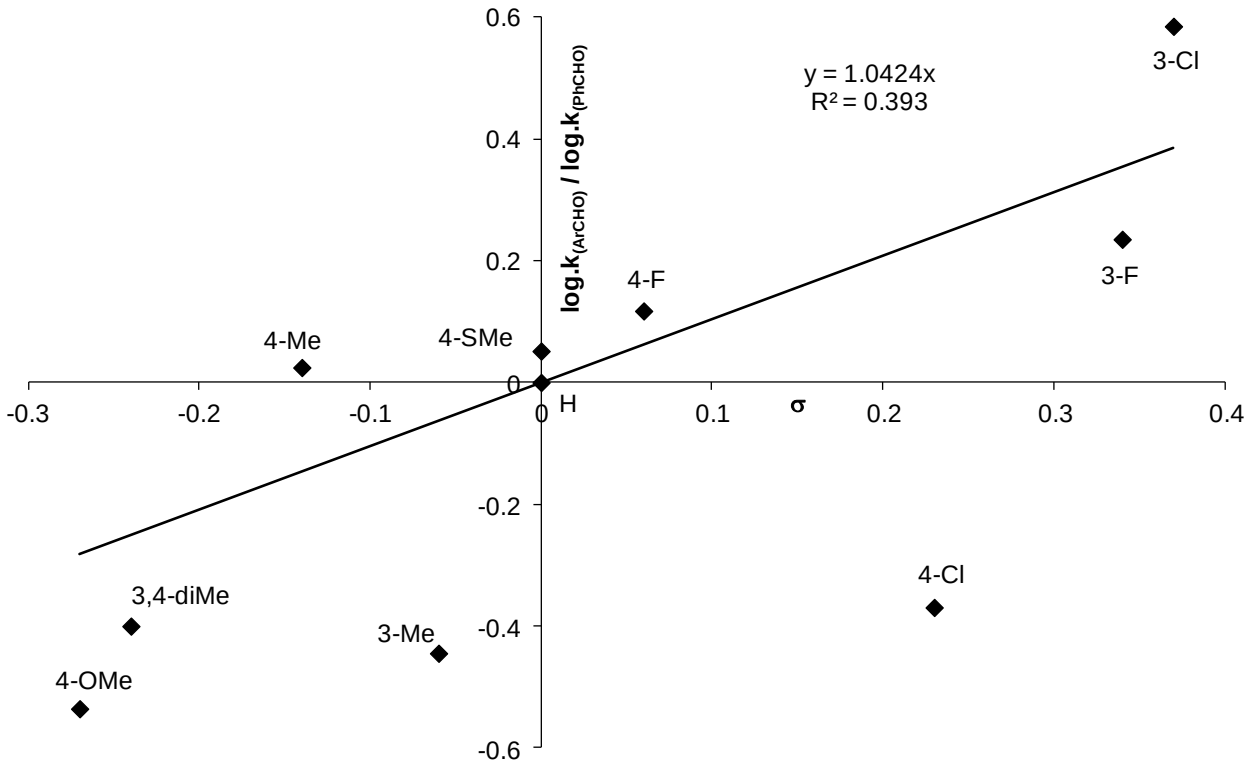
4-Methoxybenzaldehyde run 1



4-Methoxybenzaldehyde run 2

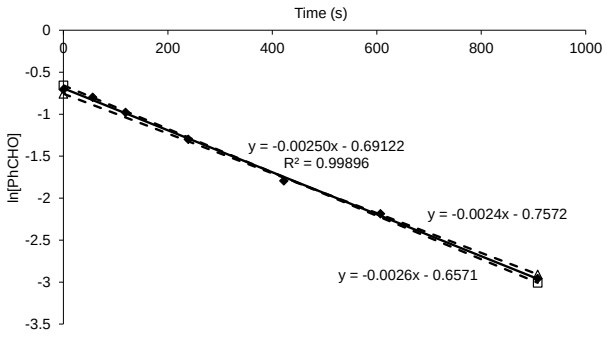


Hammett plot for the Et_3N catalysed reaction in the presence of water

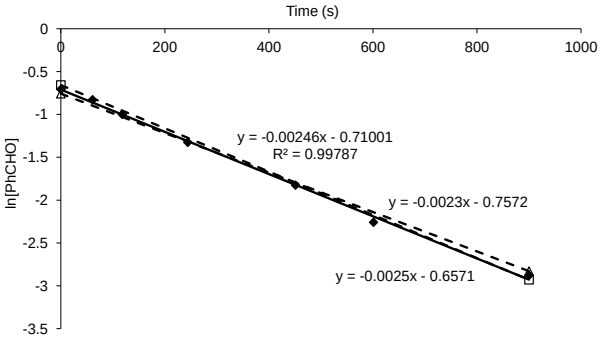


Variable temperature kinetic study of the addition of trimethylsilyl cyanide to benzaldehyde catalysed by Et_3N in the presence of water

Reaction at +10 ^{o}C run 1

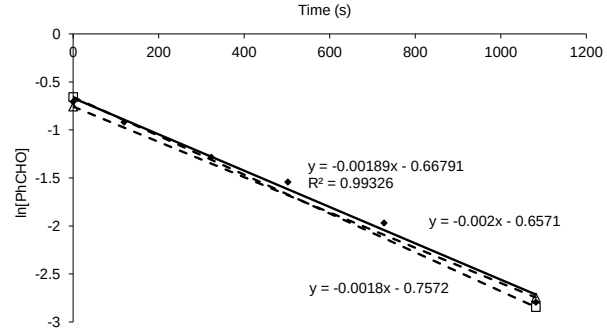


Reaction at +10 ^{o}C run 2

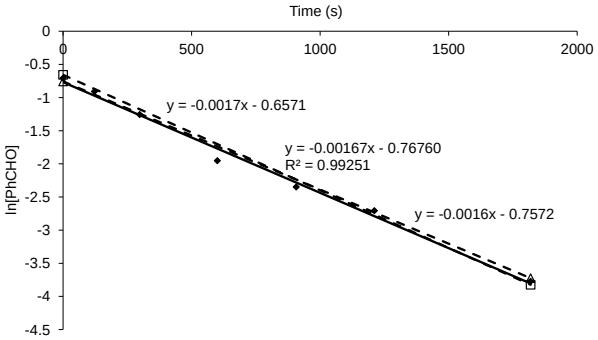


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at 0 ^{o}C run 1

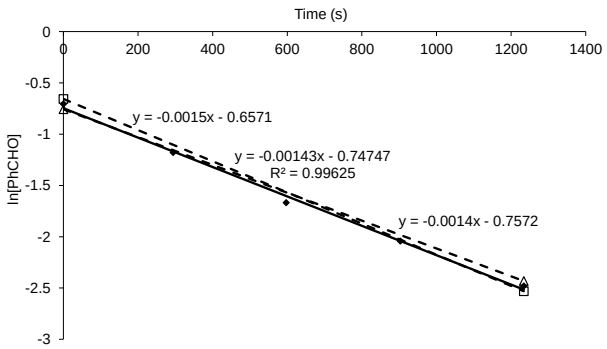


Reaction at 0 ^{o}C run 2

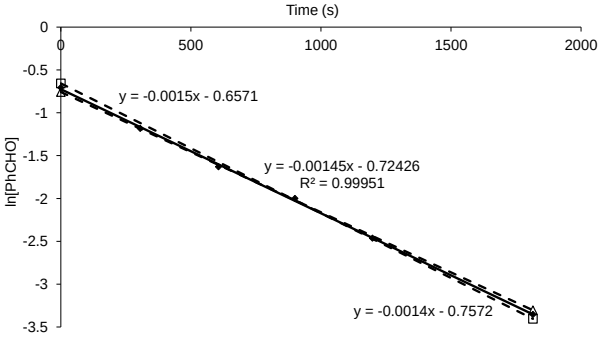


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -10 ^{o}C run 1

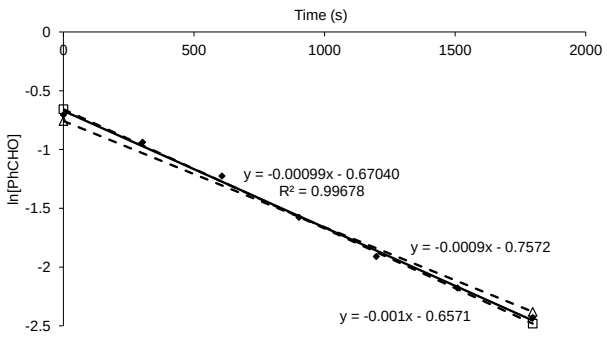


Reaction at -10 ^{o}C run 2

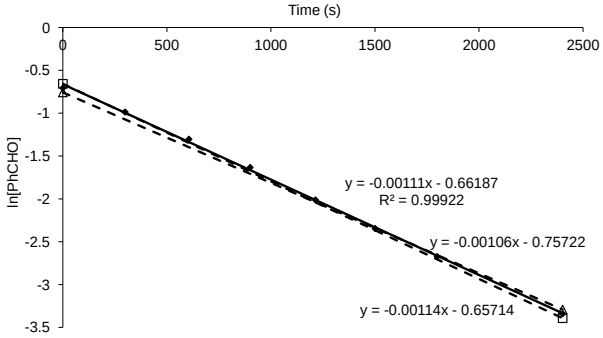


The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

Reaction at -20 ^{o}C run 1

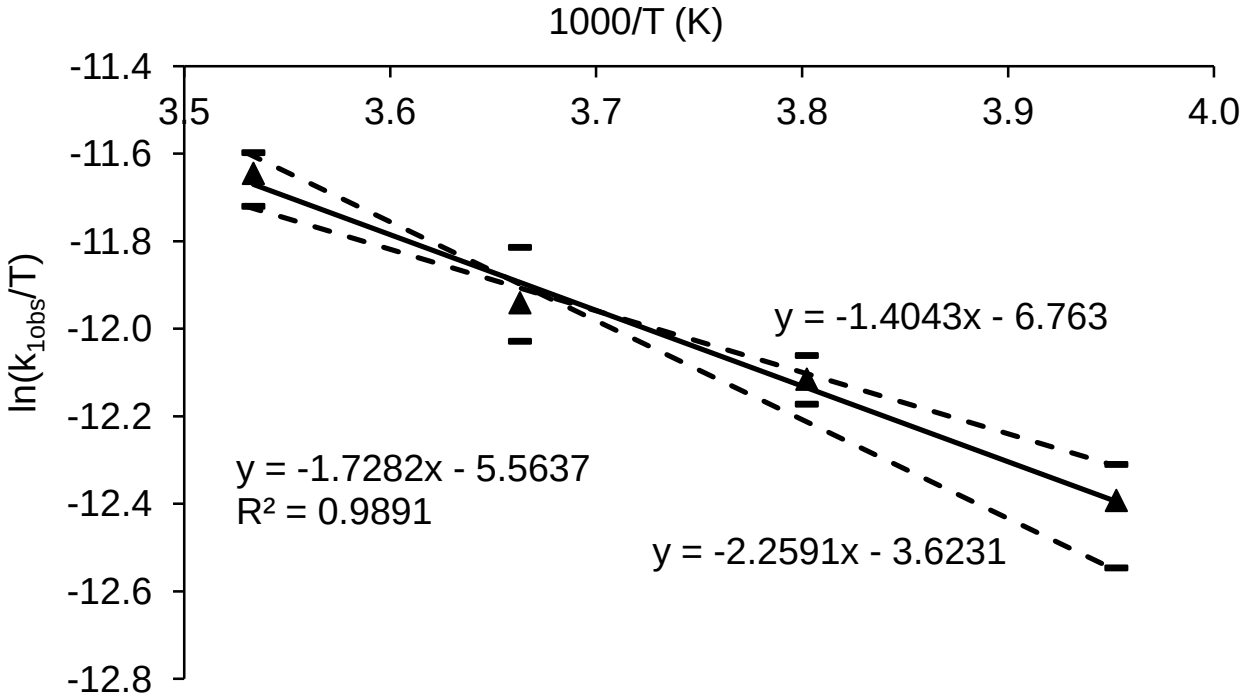


Reaction at -20 ^{o}C run 2



The solid line, filled diamonds and equation with R^2 value correspond to the actual data and best fit line whilst the empty squares and diamonds, broken line and equations without R^2 values correspond to a +/- 5% error applied to the absorbance of the first and last data points.

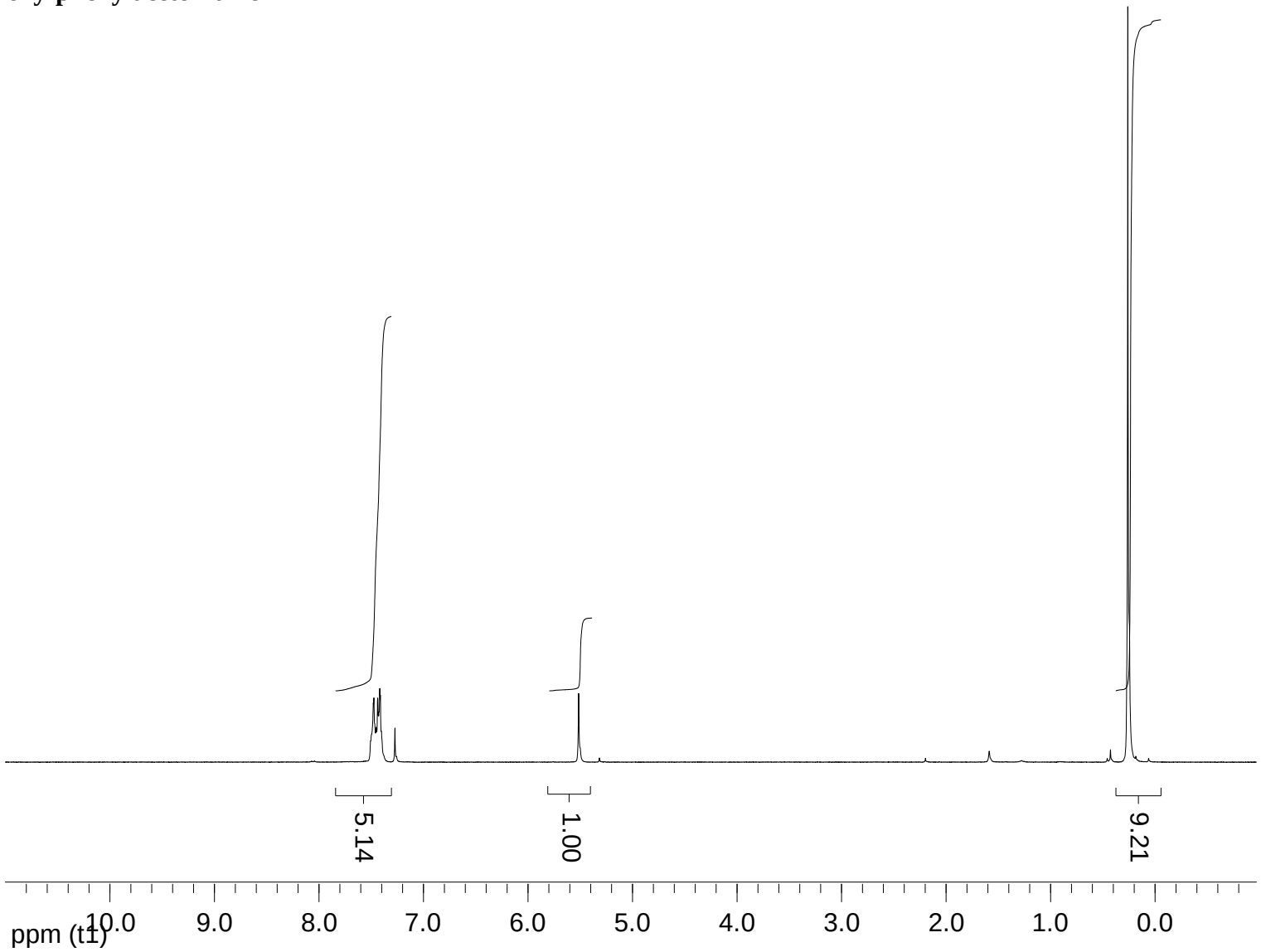
Eyring plot



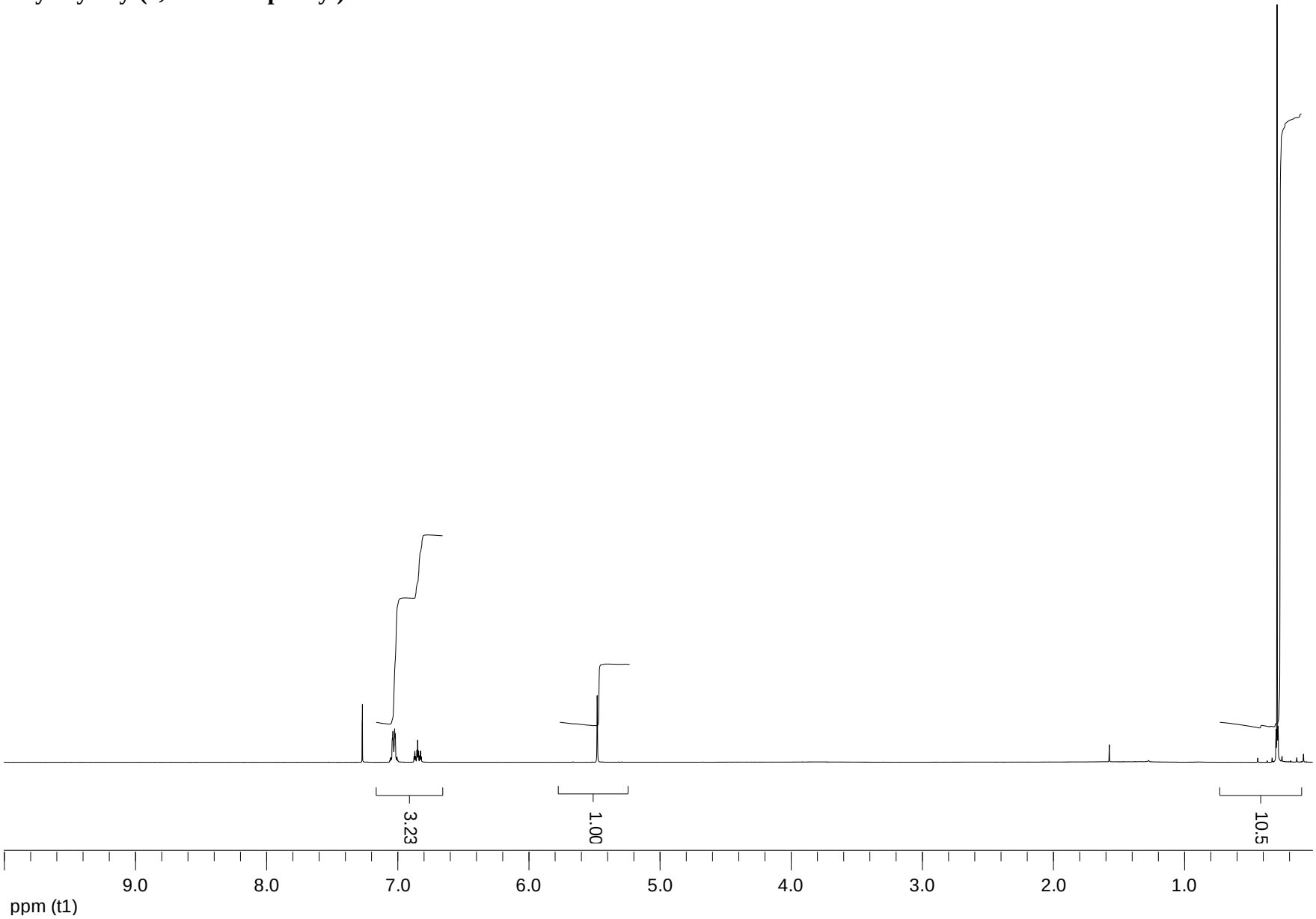
The filled triangles correspond to the average of the two individual rate measurements at each temperature and the solid line (and equation with R^2 value) is the best fit line through these data points. The horizontal lines above and below each diamond correspond to the maximum and minimum value for that data point from either of the individual rate measurements. The broken lines (and equations without R^2 values) correspond to the limiting values for the best fit line based on the error limits for the highest and lowest temperature points. The data in Table 5 of the manuscript were obtained by averaging the maximum and minimum values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the broken lines rather than from the solid line so as to ensure that the quoted values were at the midpoint of the maximum and minimum values.

^{1}H NMR spectra of cyanohydrin trimethylsilyl ethers

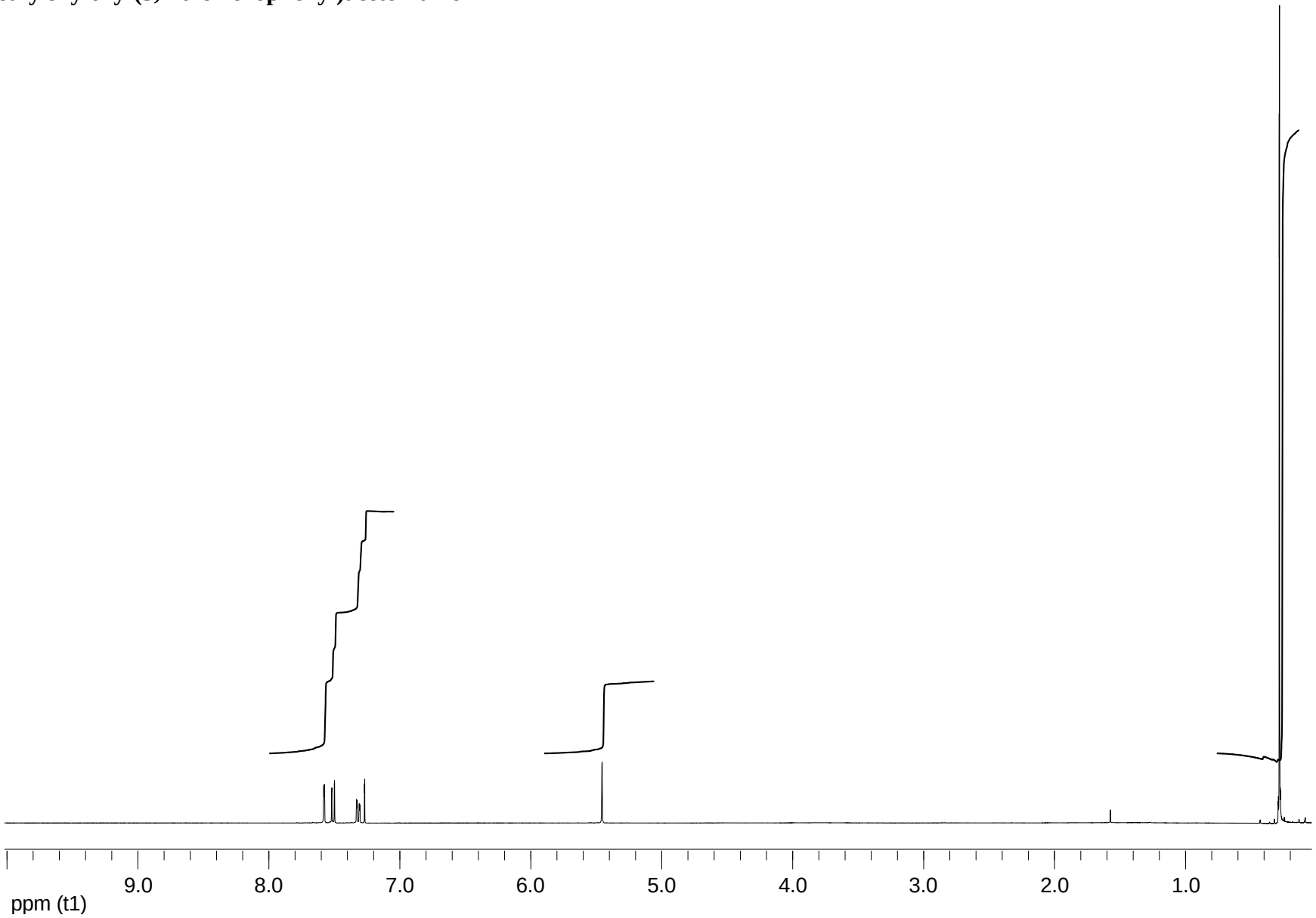
2-Trimethylsilyloxy-phenylacetonitrile



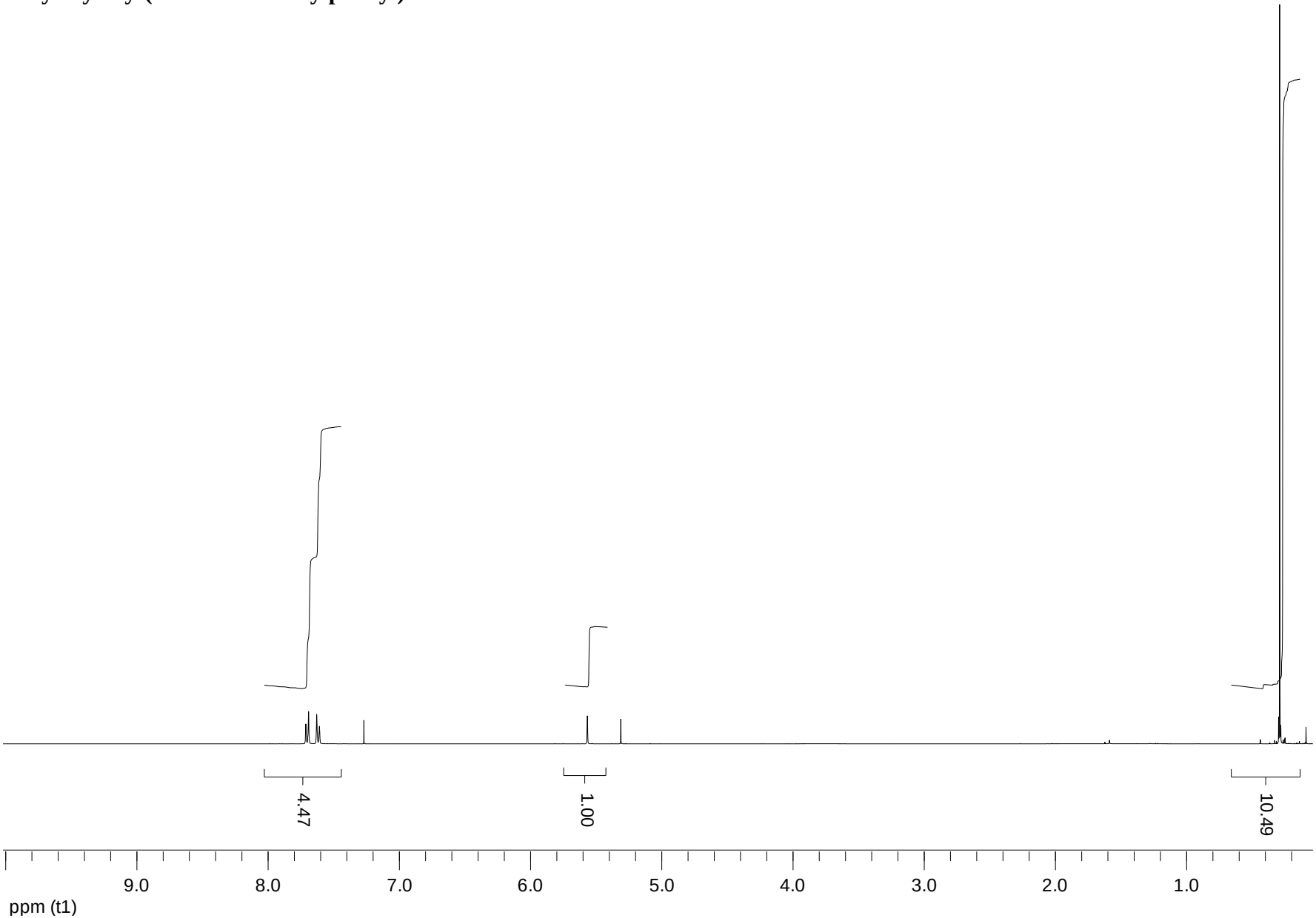
2-Trimethylsilyloxy-(3,5-difluorophenyl)acetonitrile



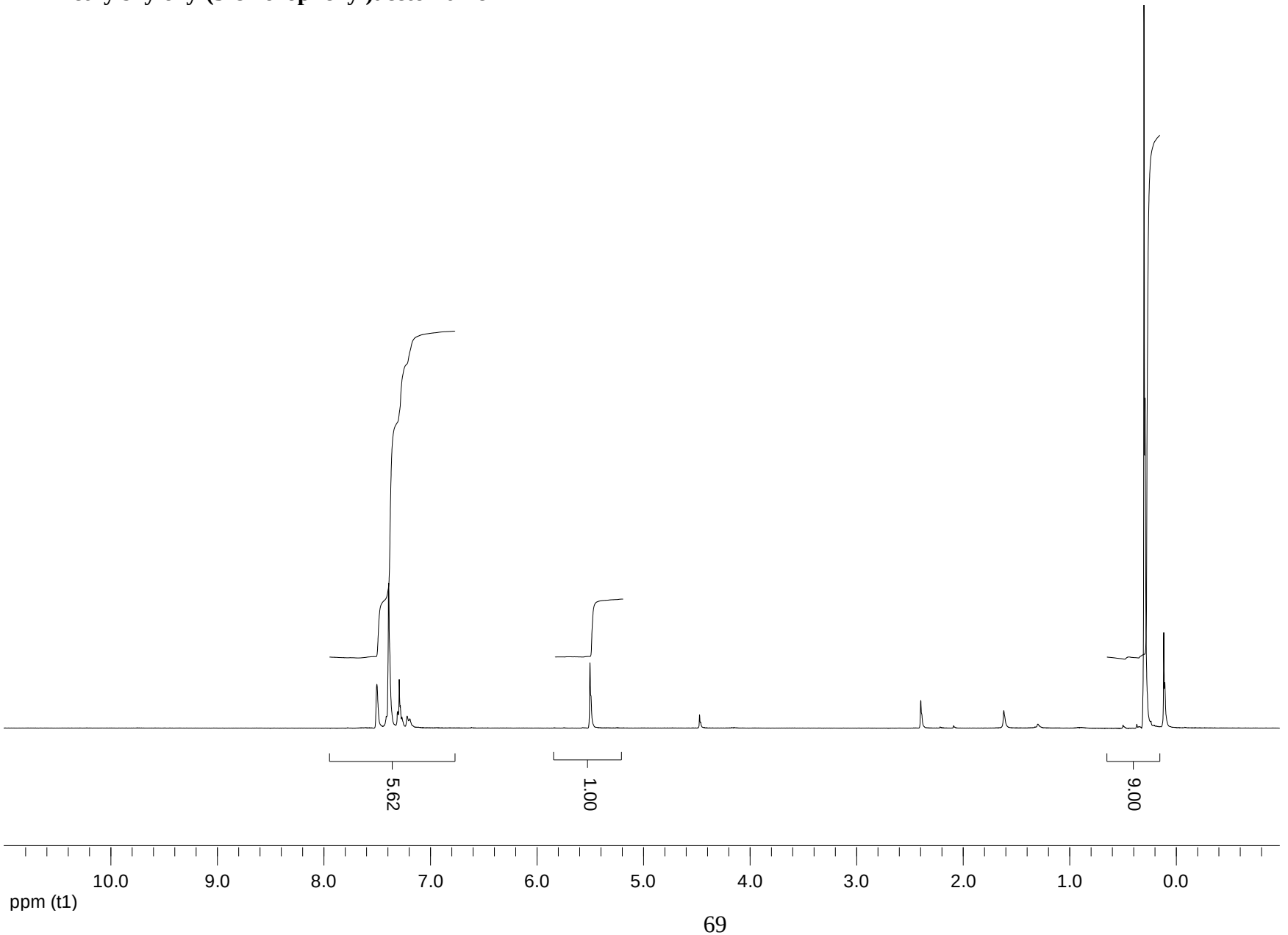
2-Trimethylsilyloxy-(3,4-dichlorophenyl)acetonitrile



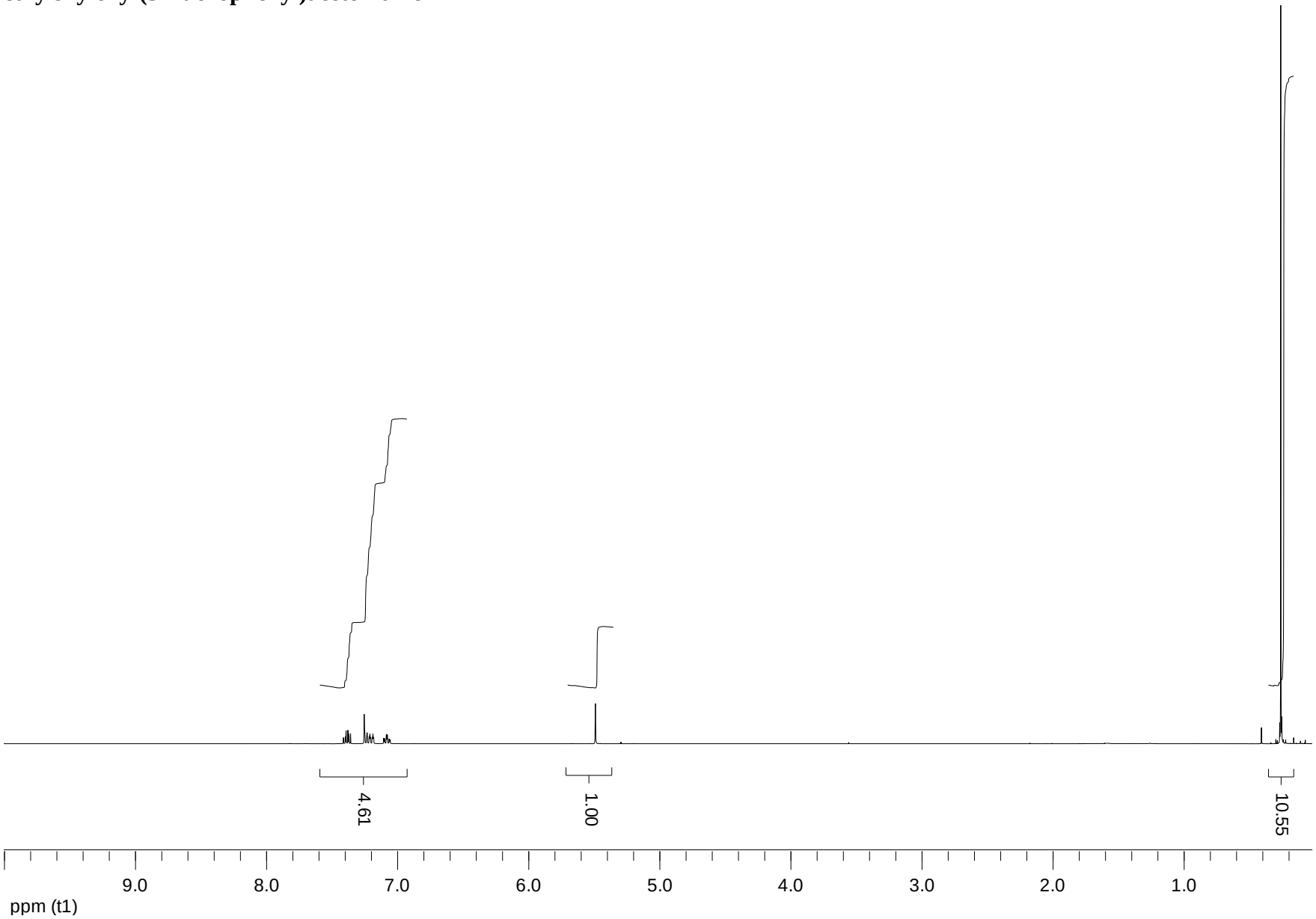
2-Trimethylsilyloxy-(4-trifluoromethylphenyl)acetonitrile



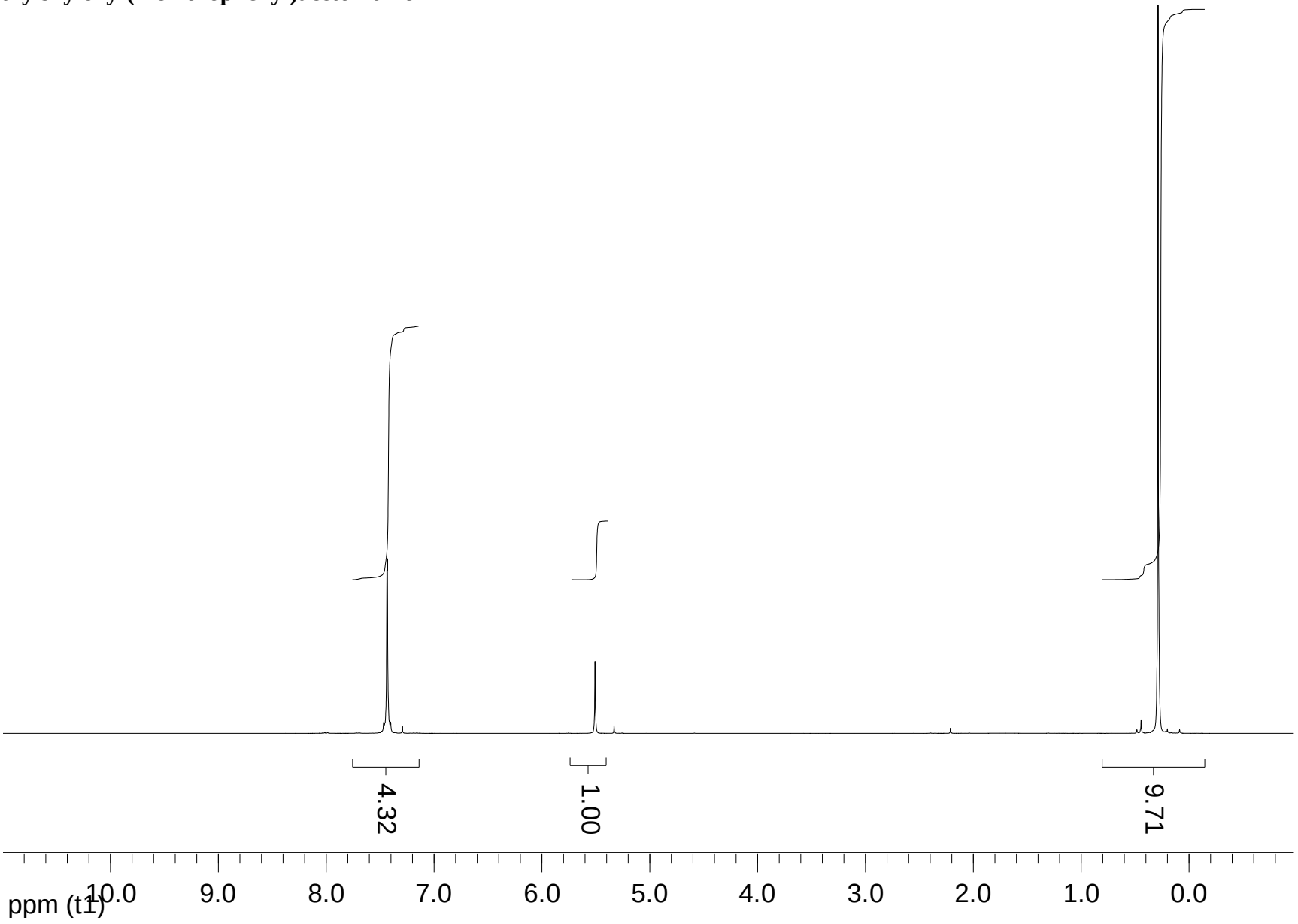
2-Trimethylsilyloxy-(3-chlorophenyl)acetonitrile



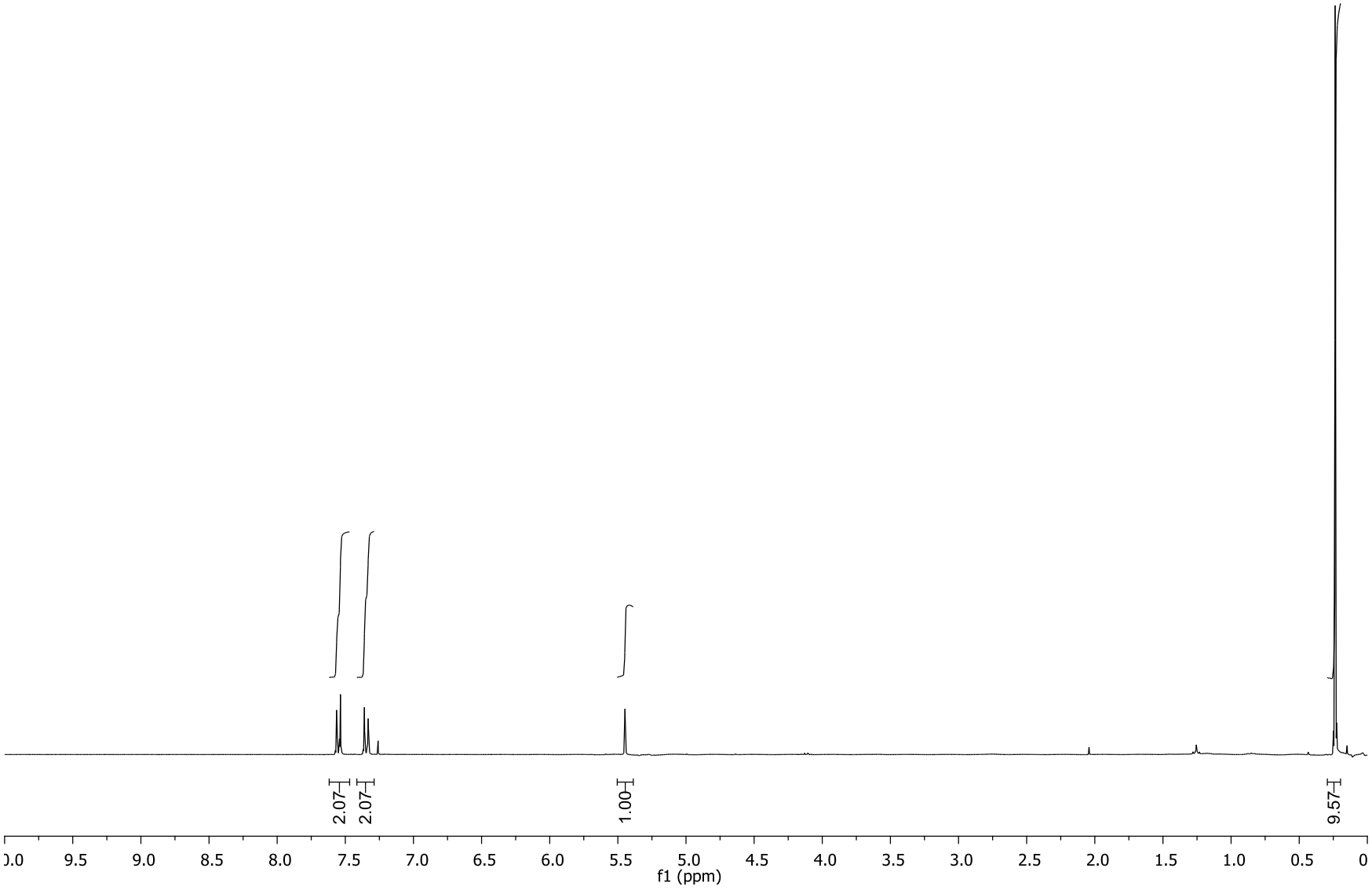
2-Trimethylsilyloxy-(3-fluorophenyl)acetonitrile



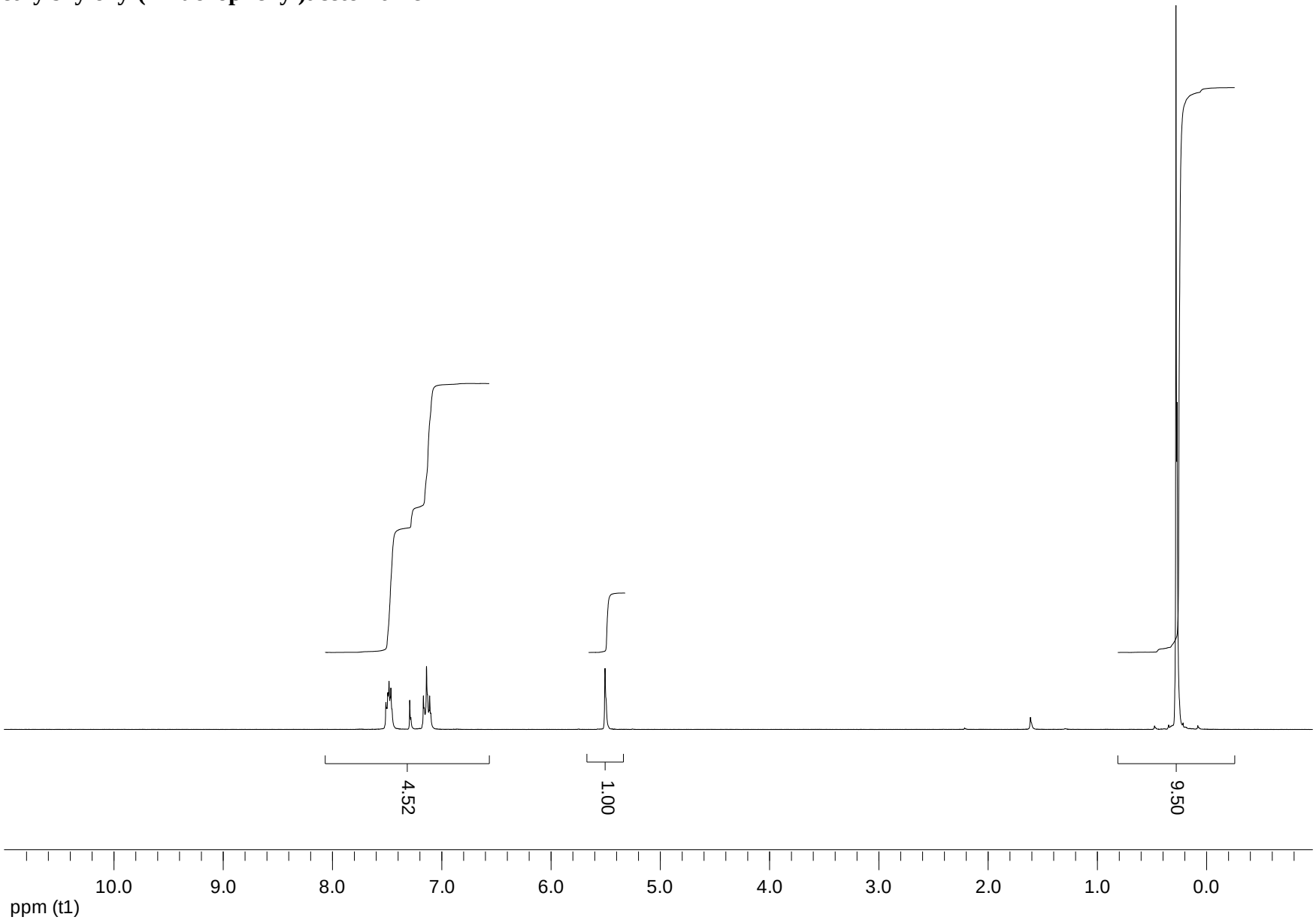
2-Trimethylsilyloxy-(4-chlorophenyl)acetonitrile



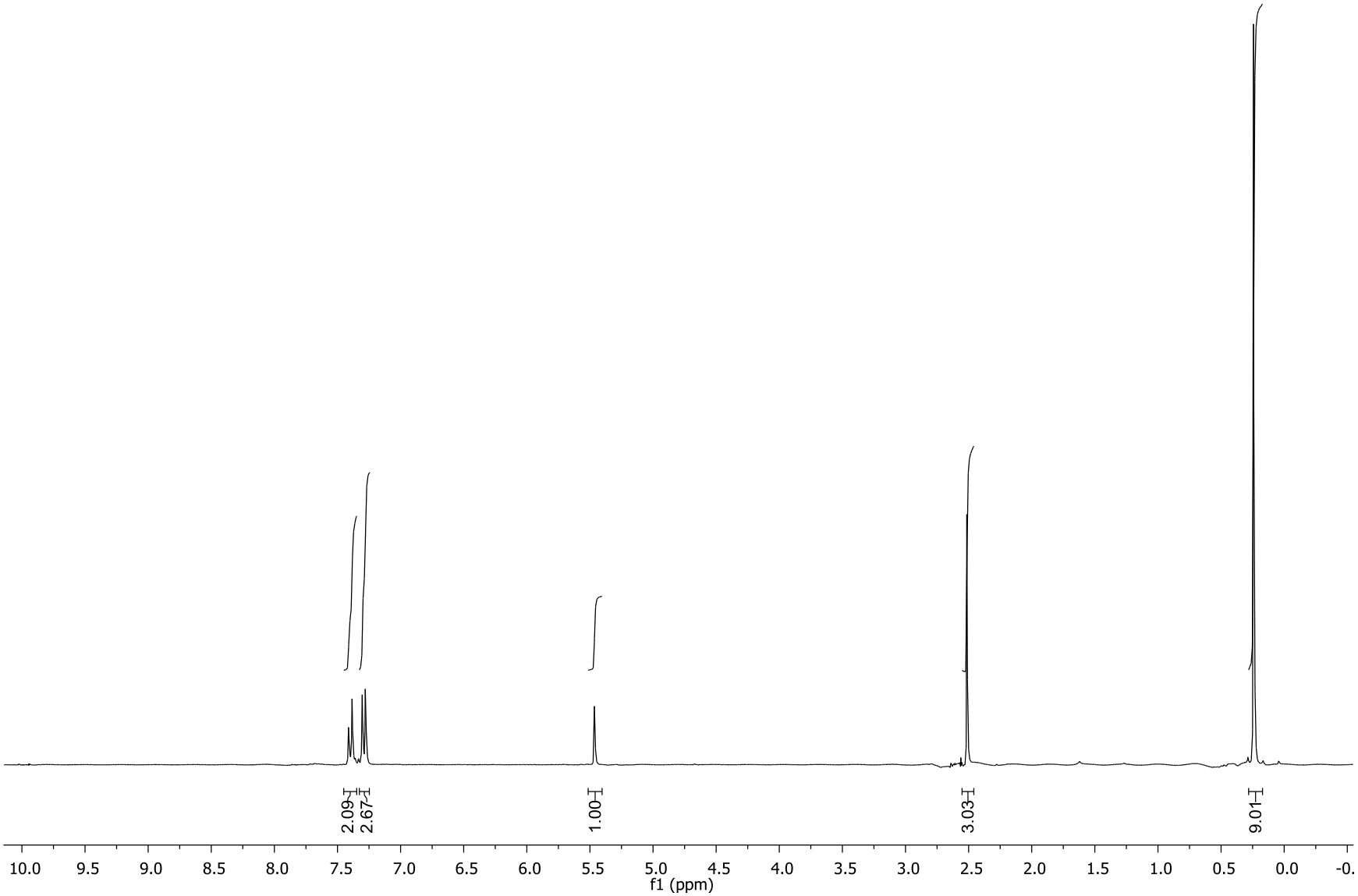
2-Trimethylsilyloxy-(4-bromophenyl)acetonitrile



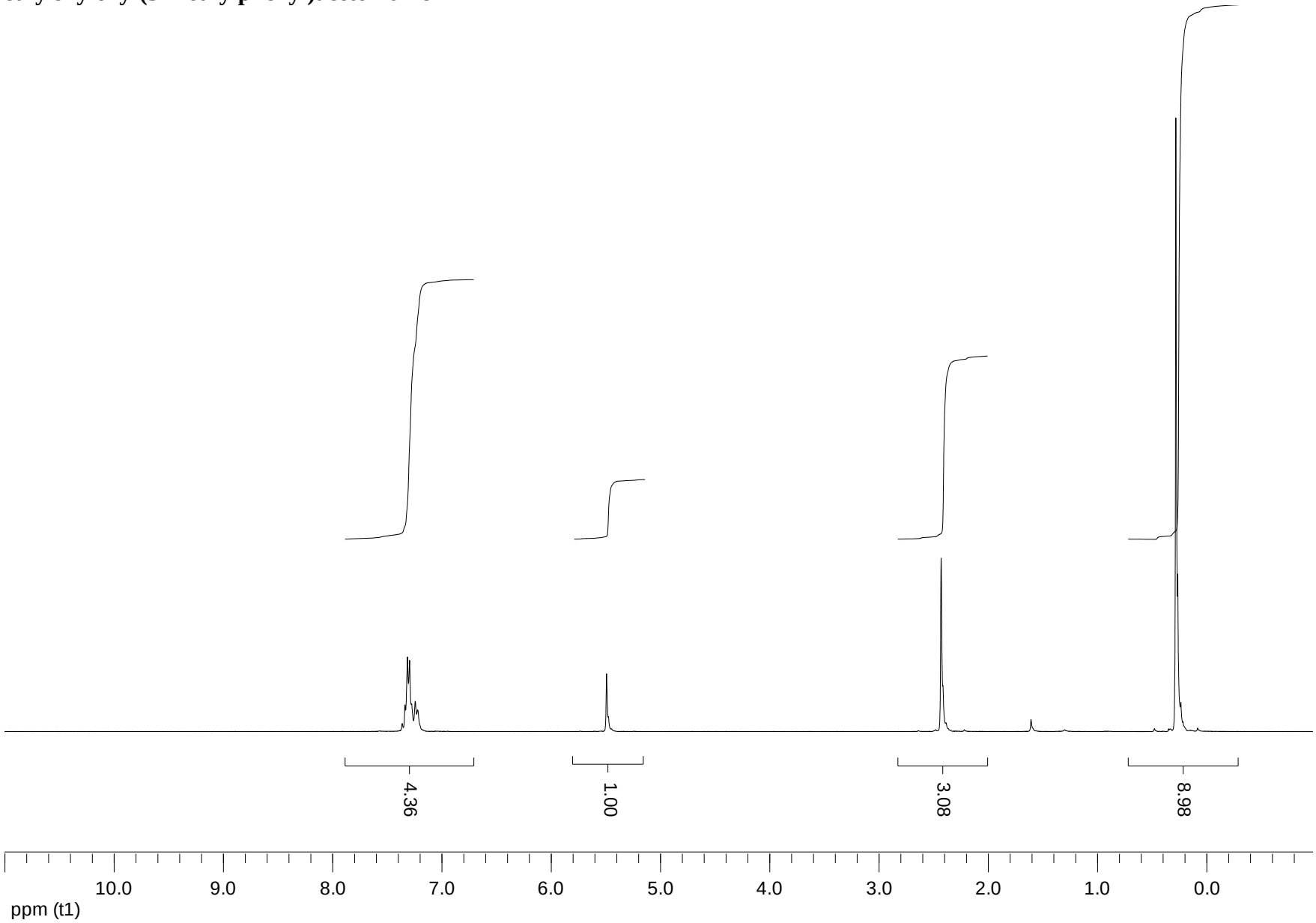
2-Trimethylsilyloxy-(4-fluorophenyl)acetonitrile



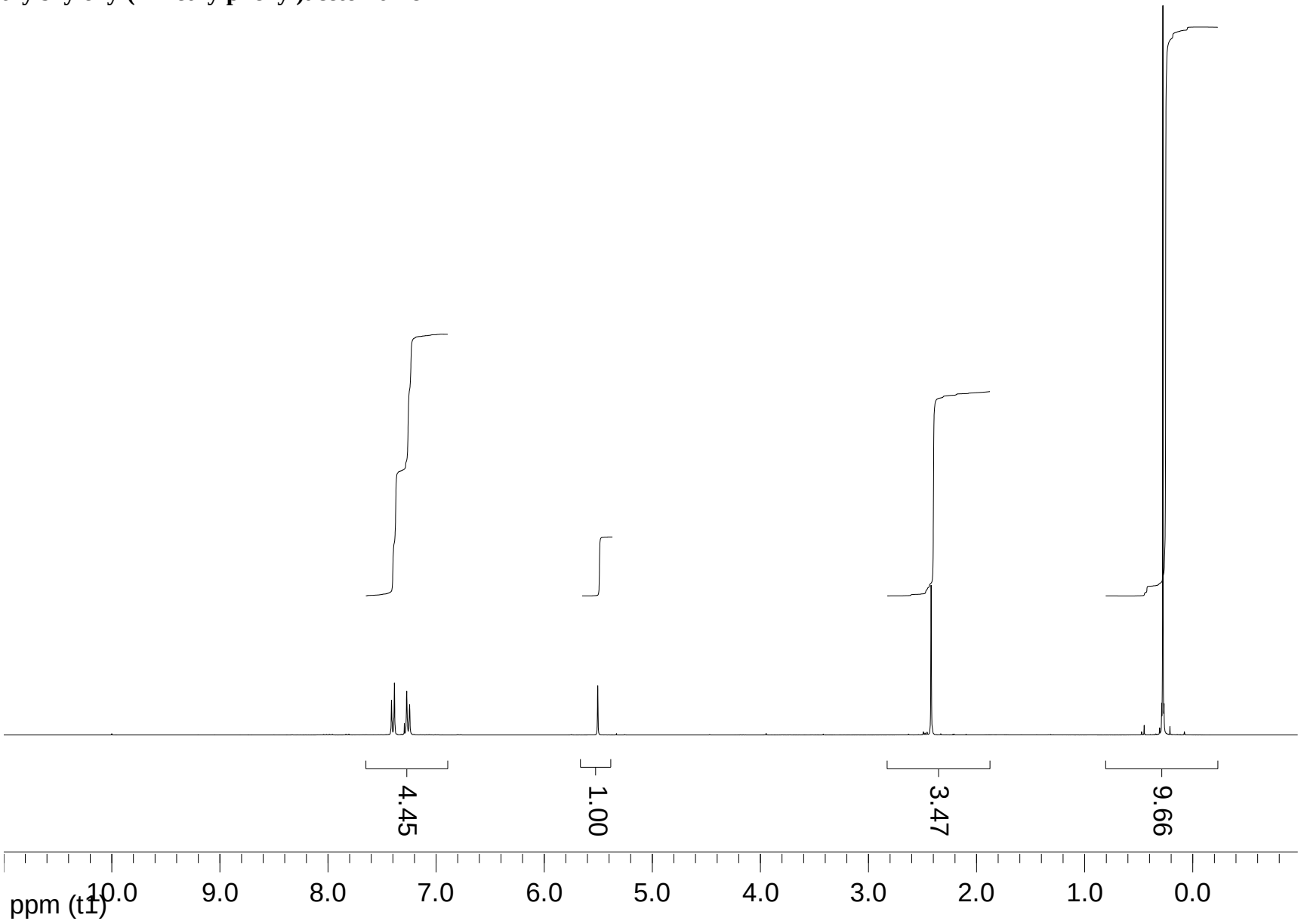
2-Trimethylsilyloxy-(4-thiomethylphenyl)acetonitrile



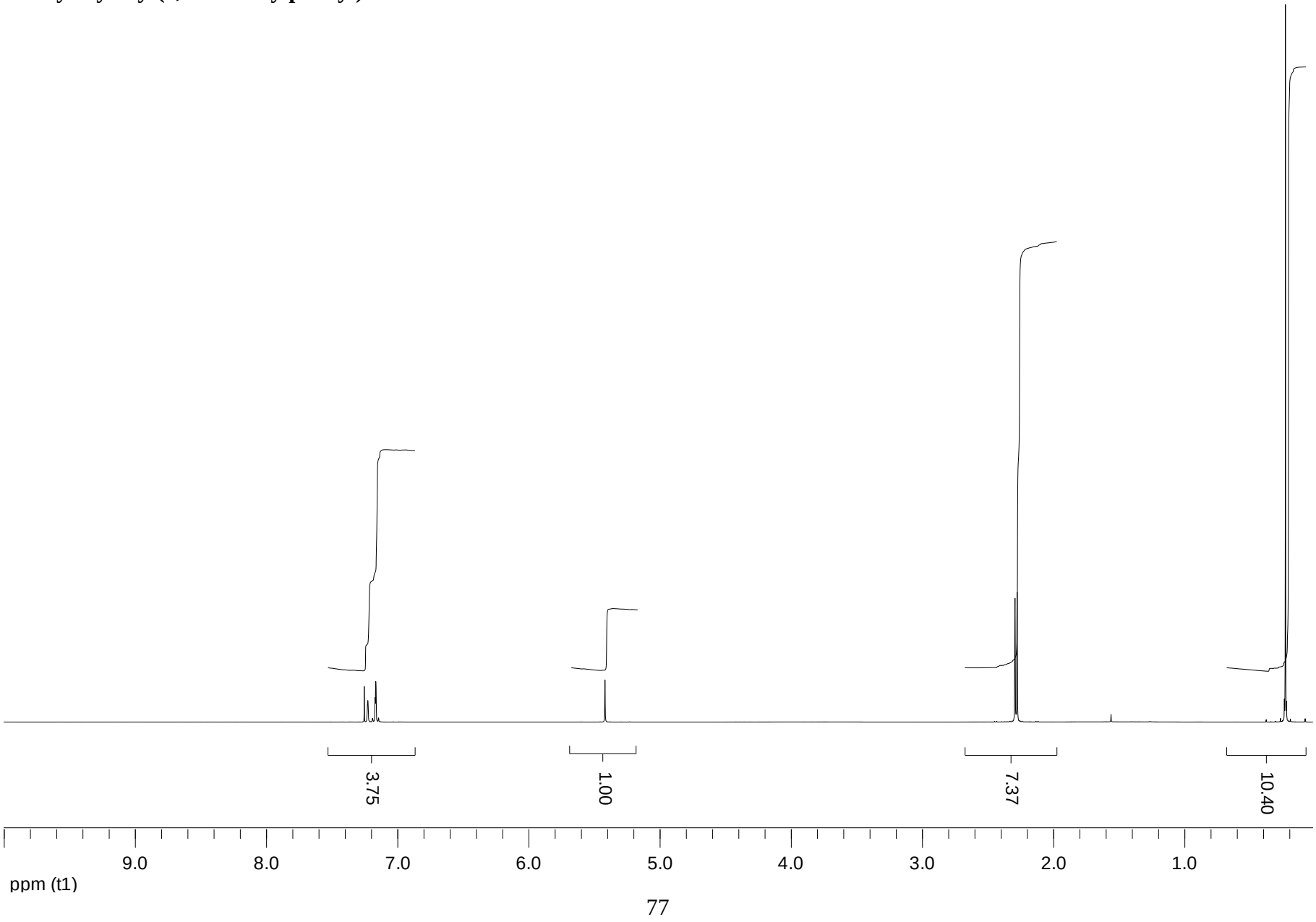
2-Trimethylsilyloxy-(3-methylphenyl)acetonitrile



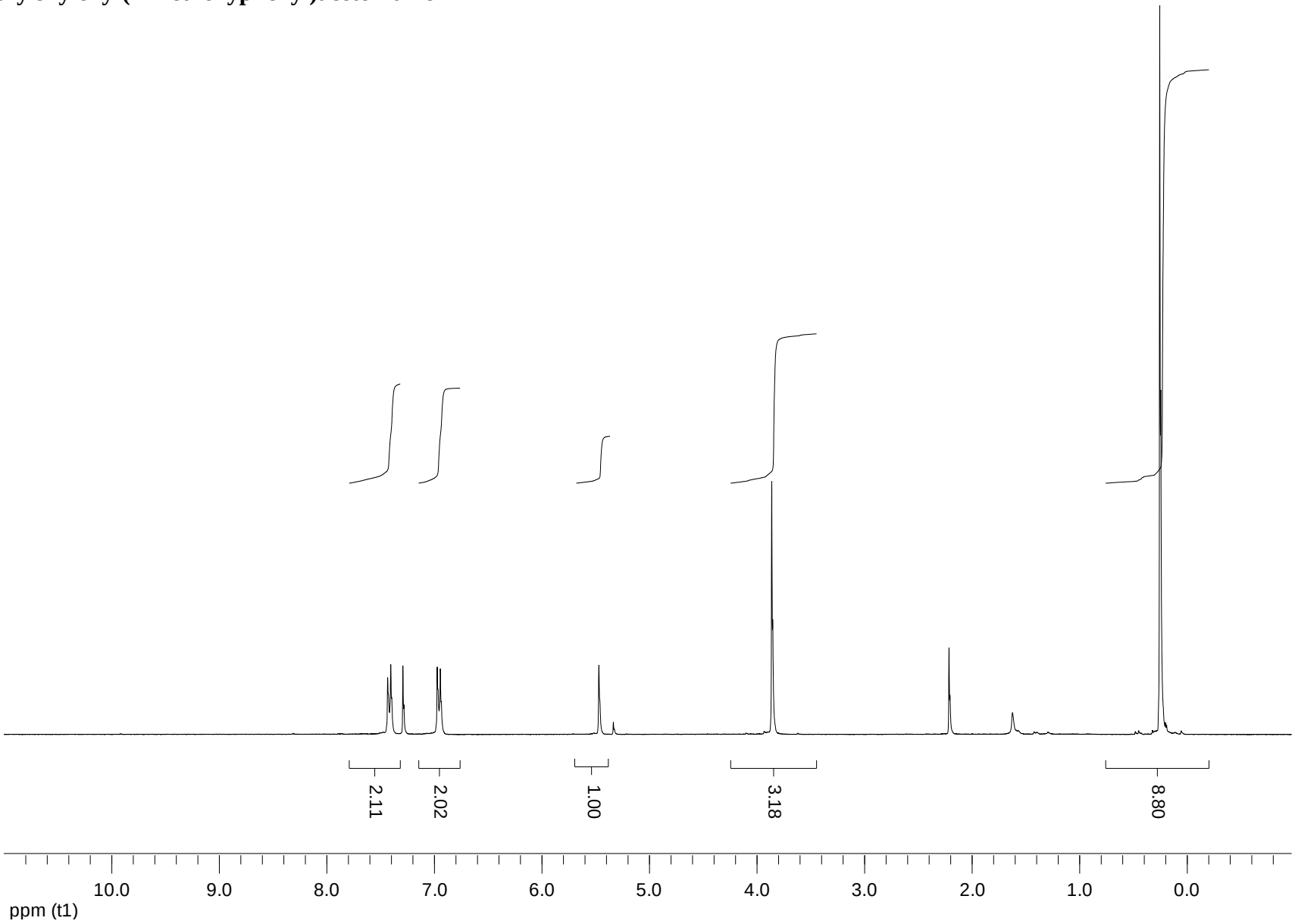
2-Trimethylsilyloxy-(4-methylphenyl)acetonitrile



2-Trimethylsilyloxy-(3,4-dimethylphenyl)acetonitrile



2-Trimethylsilyloxy-(4-methoxyphenyl)acetonitrile



2-Trimethylsilyloxy-(4-*tert*-butoxyphenyl)acetonitrile