A quantitative structure–reactivity relationship in decarboxylative Claisen rearrangement reactions of allylic tosylmalonate esters

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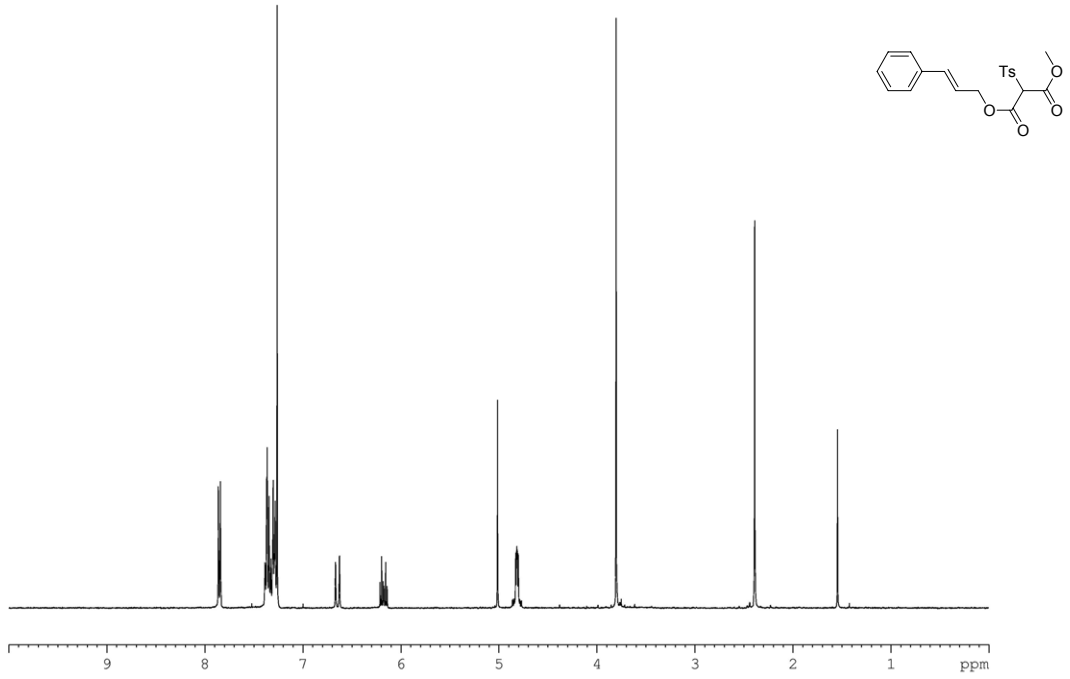
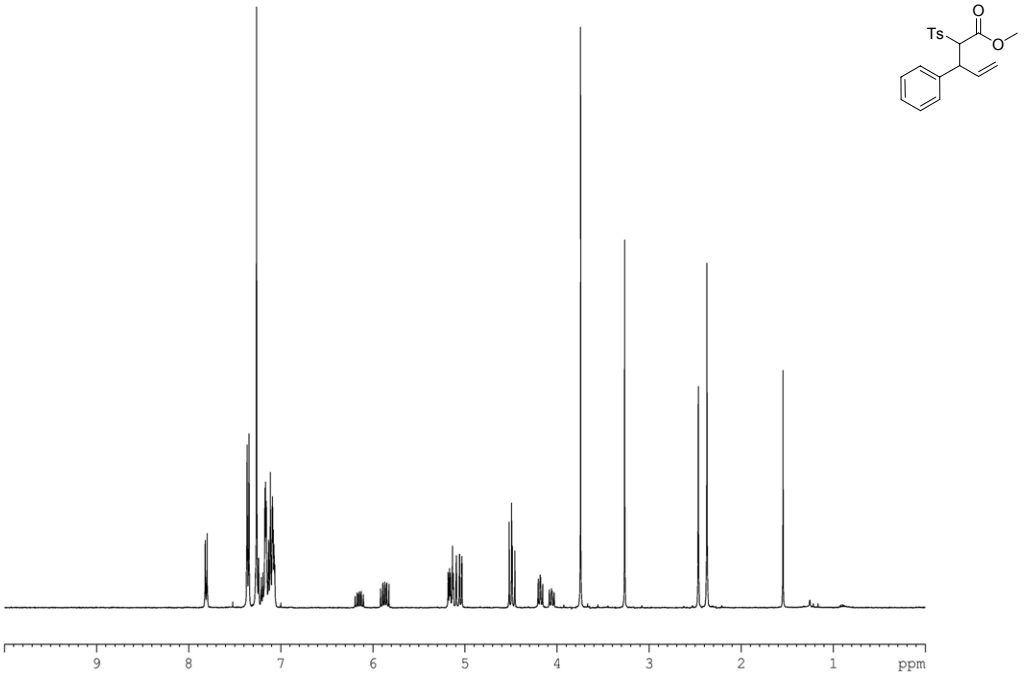
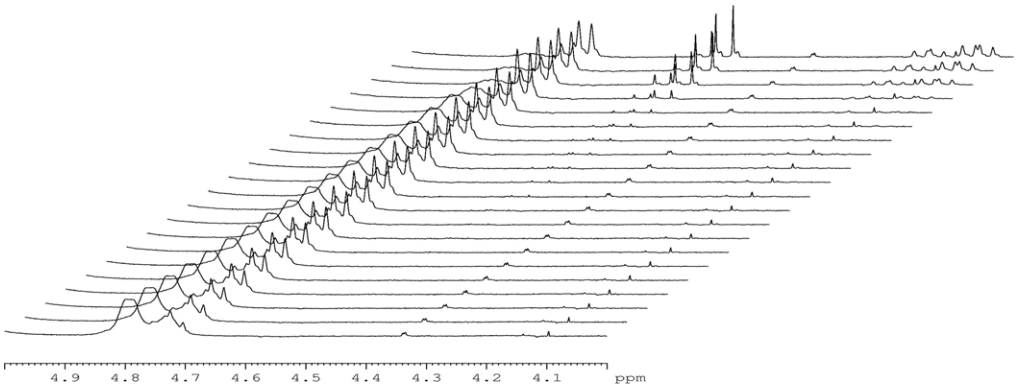
Determination of k_{obs} values: summarised kinetic data

Substrate **1a** (S = H)







Integrated signals in the dCr reaction of substrate 1a

Time intervals

Traces 1–10: 150 s

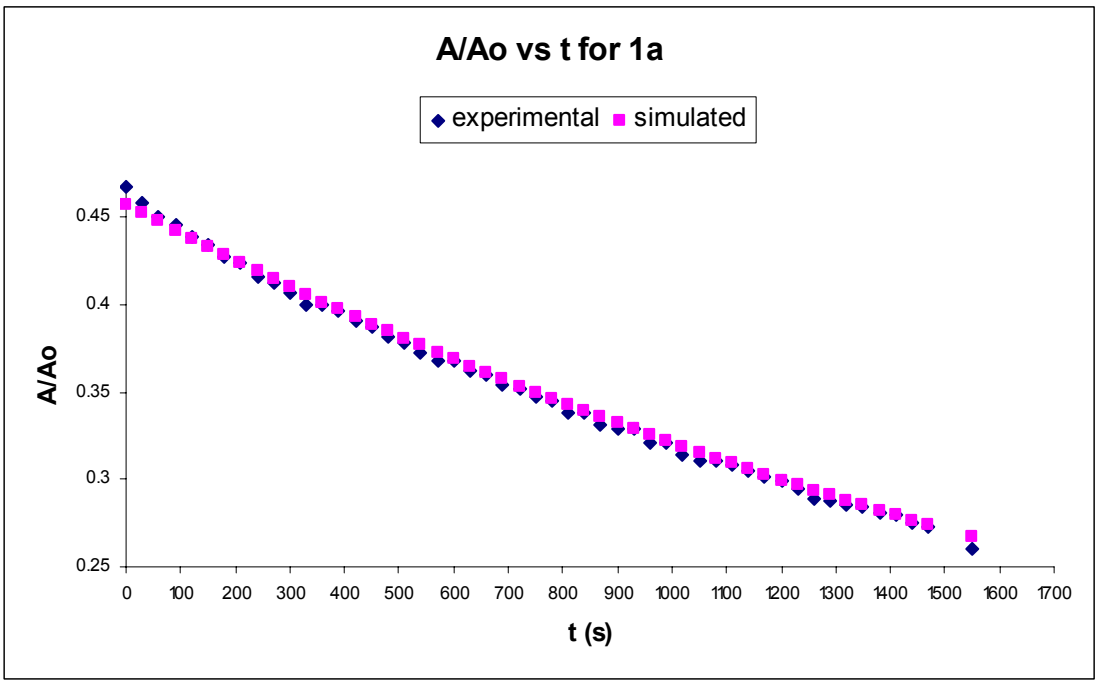
Traces 10–21: 1200 s

Range of integrated signals

5a: [4.877–4.763] ppm

6a: [4.763–4.652] ppm

3a: [4.545–4.452] ppm

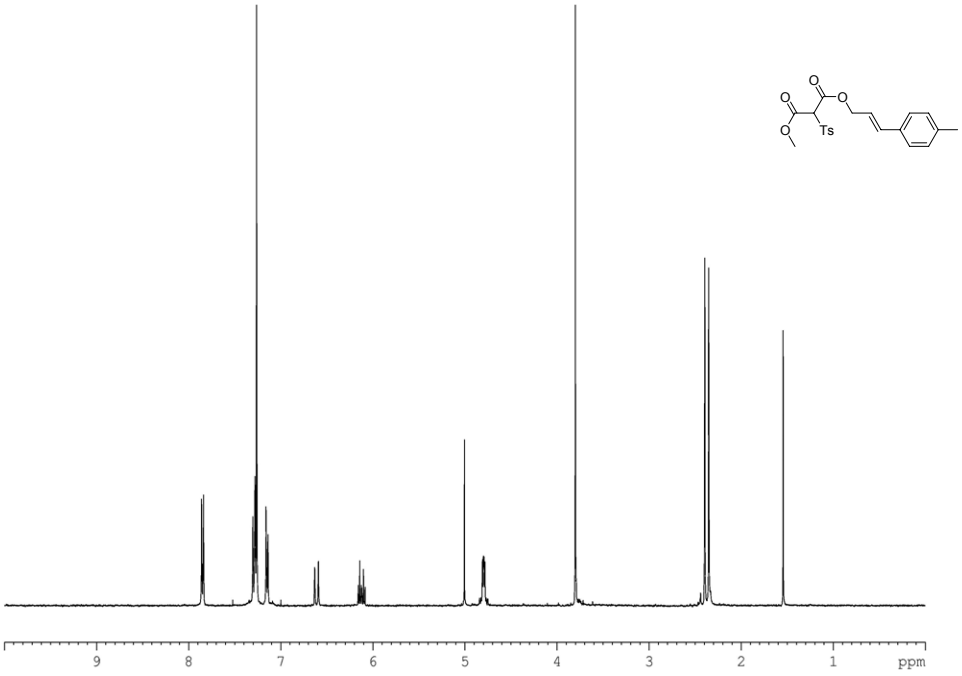


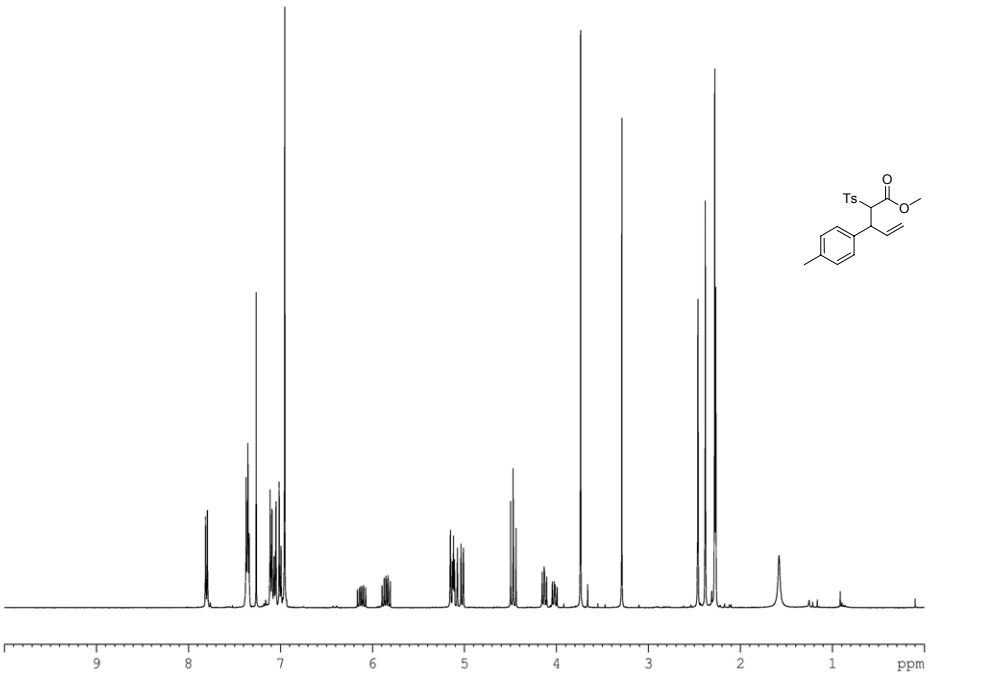
Graph 1: Plot $[A]/[A_0]$) vs. t for reaction of **1a**

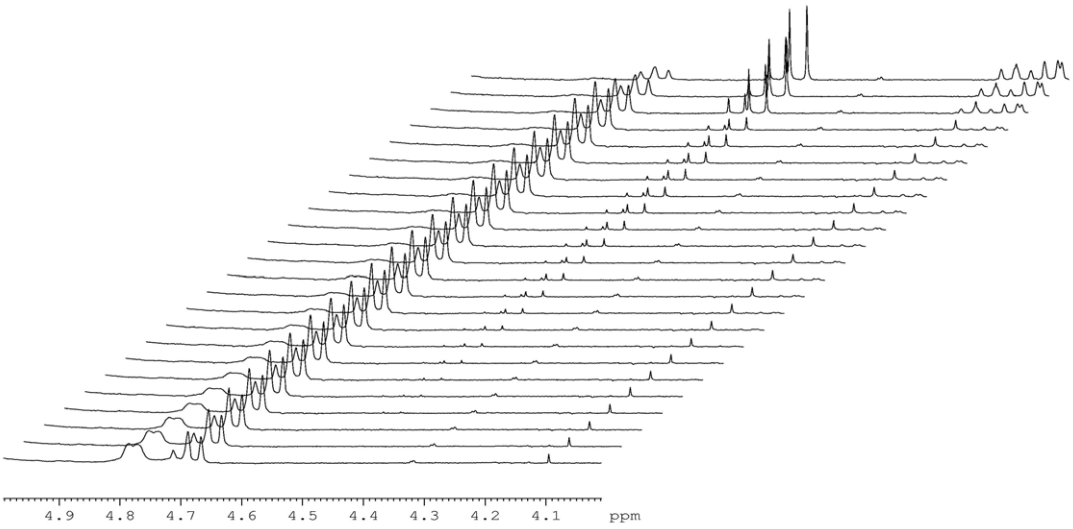
Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_H = 41.4 \times 10^{-5}$ s^{-1}, with $[A]_0 = 0.403$; B = 0.054

Substrate **1b** (S = Me)







Integrated signals in the dCr reaction of substrate 1b

Time intervals

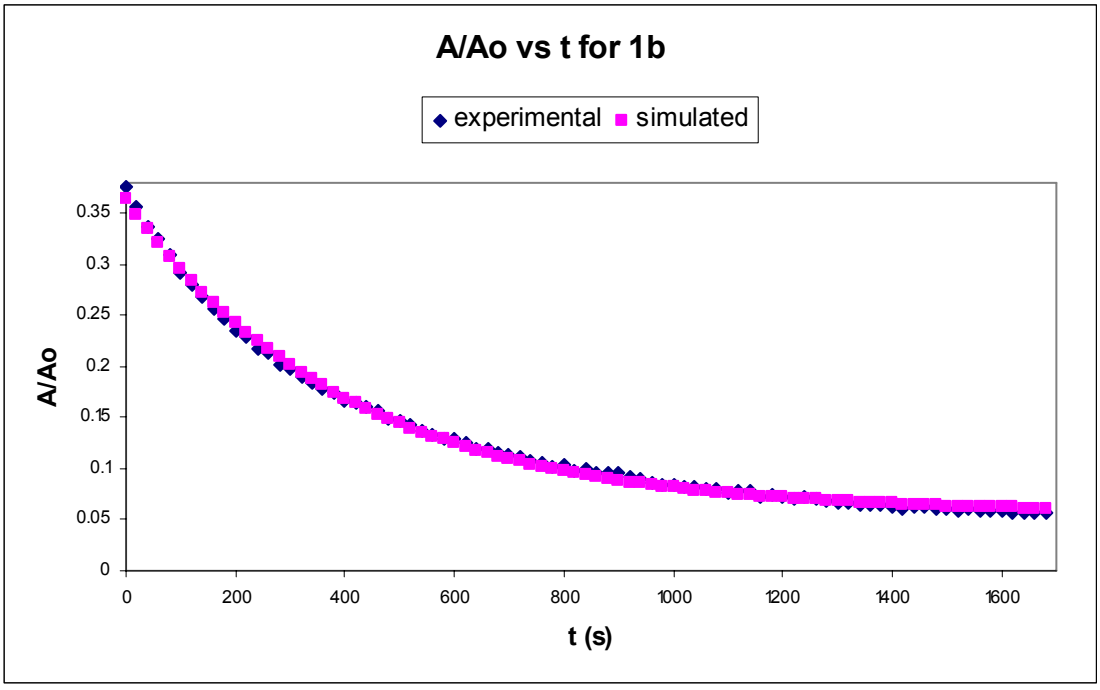
All traces: 60 s

Range of integrated signals

5b: [4.834–4.734] ppm

6b: [4.734–4.638] ppm

3b: [4.507–4.426] ppm

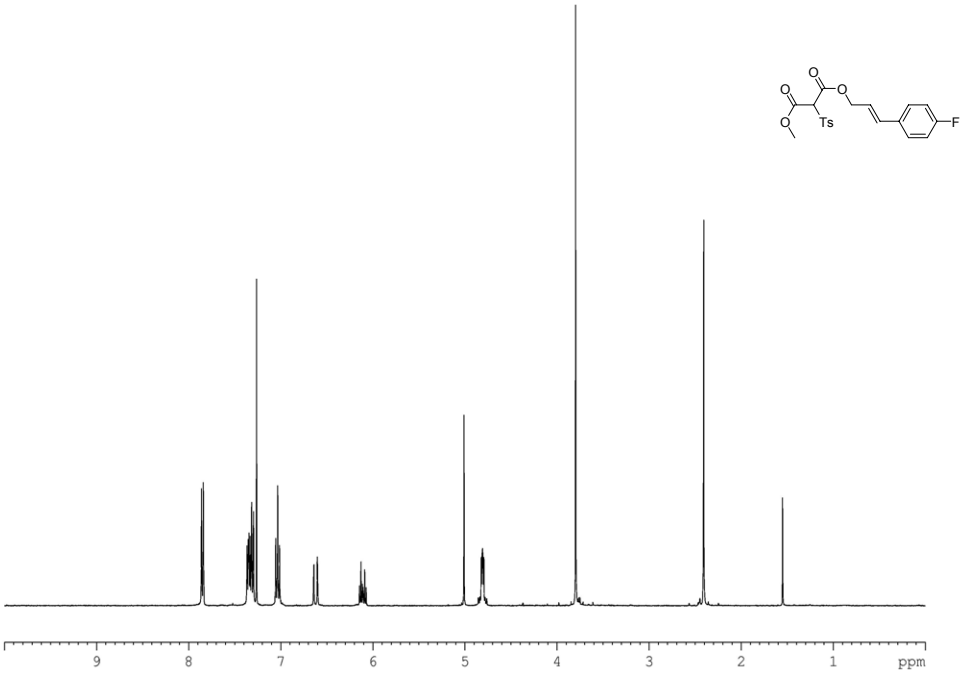


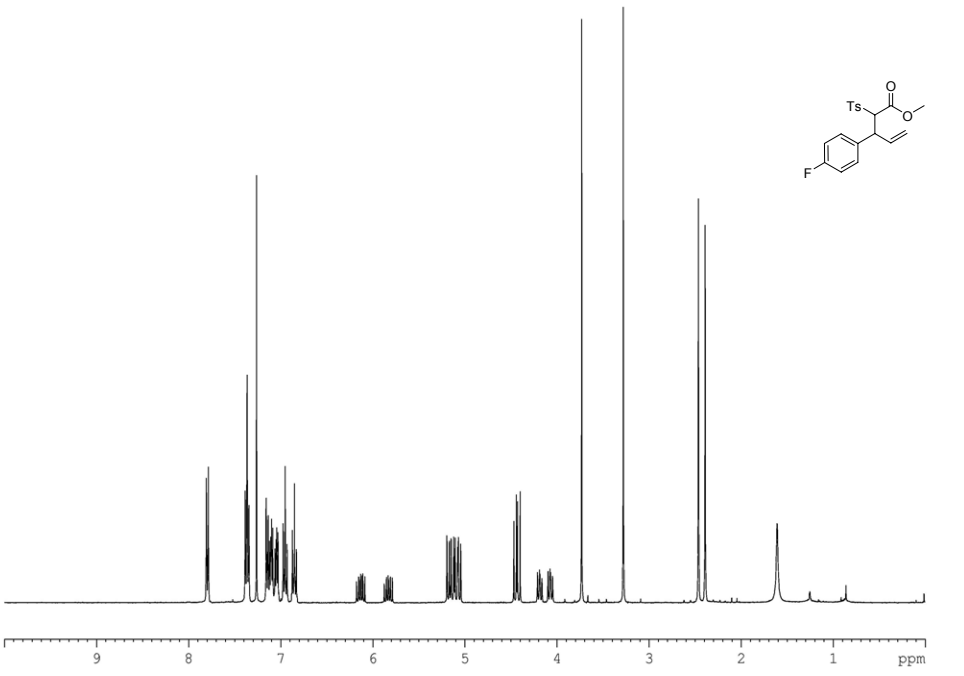
Graph 2: Plot $[A]/[A_0]$) vs. t for reaction of **1b**

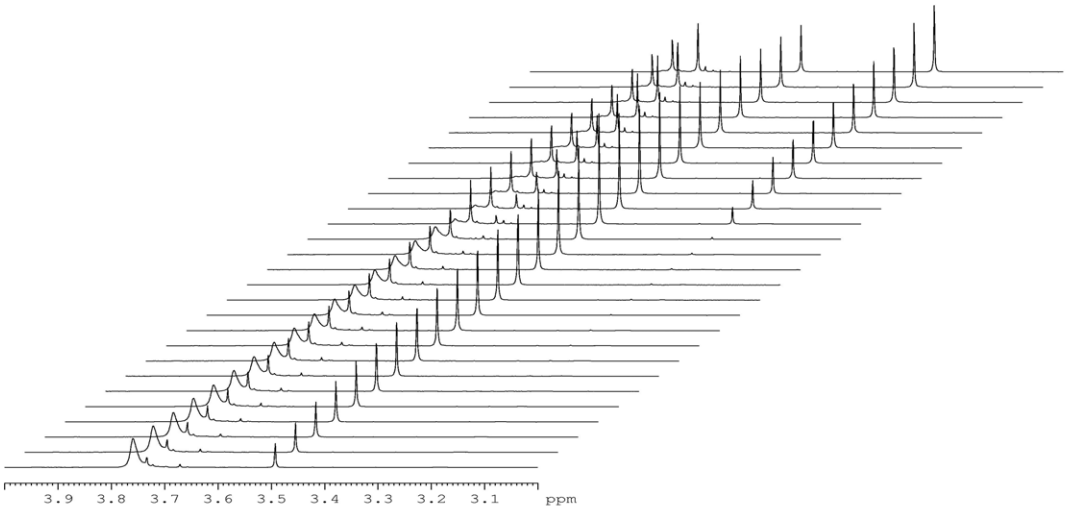
Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_{Me} = 250.8 \times 10^{-5}\ s^{-1}$, with $[A]_0 = 0.308$; $B = 0.056$

Substrate **1c** (S = F)







Integrated signals in the dCr reaction of substrate 1c

Time intervals

Traces 1–20: 60 s

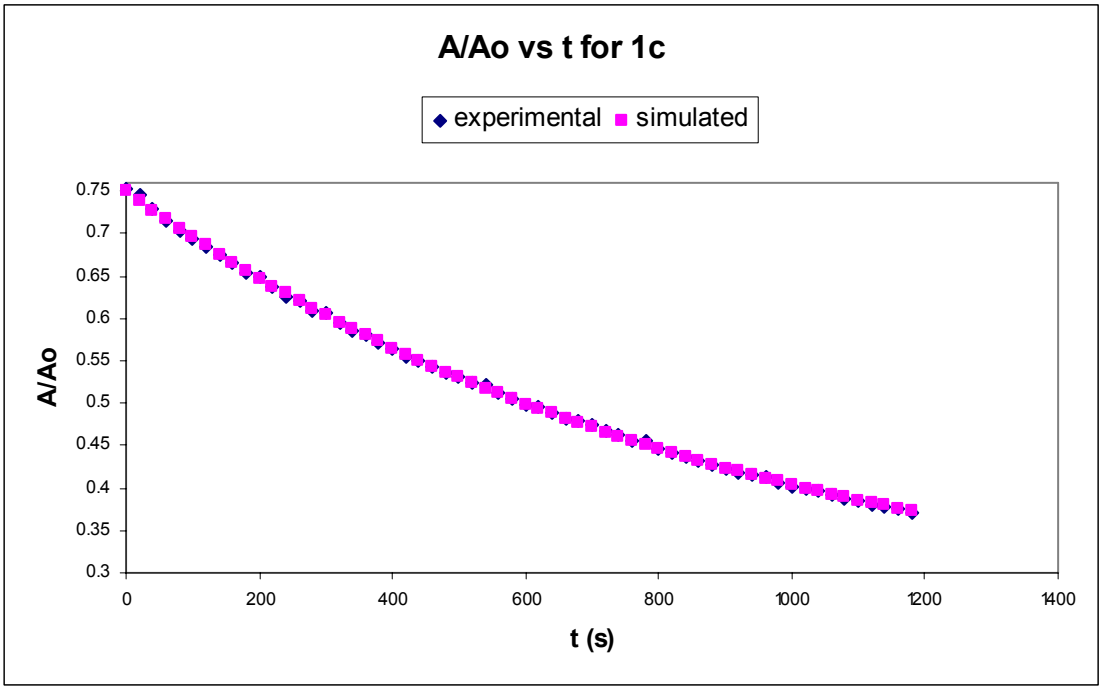
Traces 21–27: 3600 s

Range of integrated signals

5c: [3.783–3.740]

6c: 1st diast. [3.740–3.726] ppm 2nd diast. [3.505–3.478] ppm

3c: 1st diast. [3.695–3.675] ppm 2nd diast. [3.258–3.221] ppm

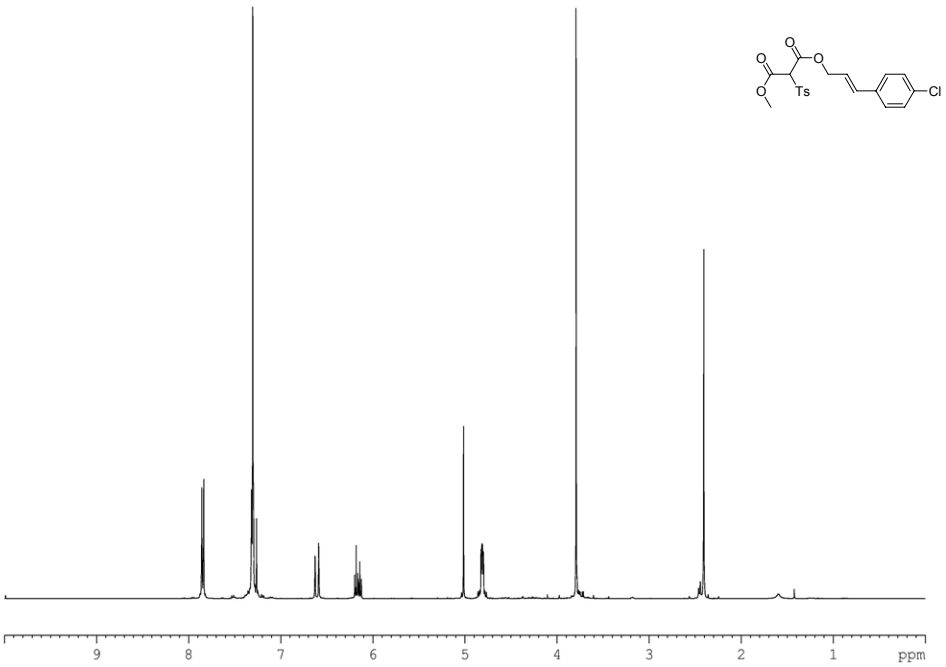


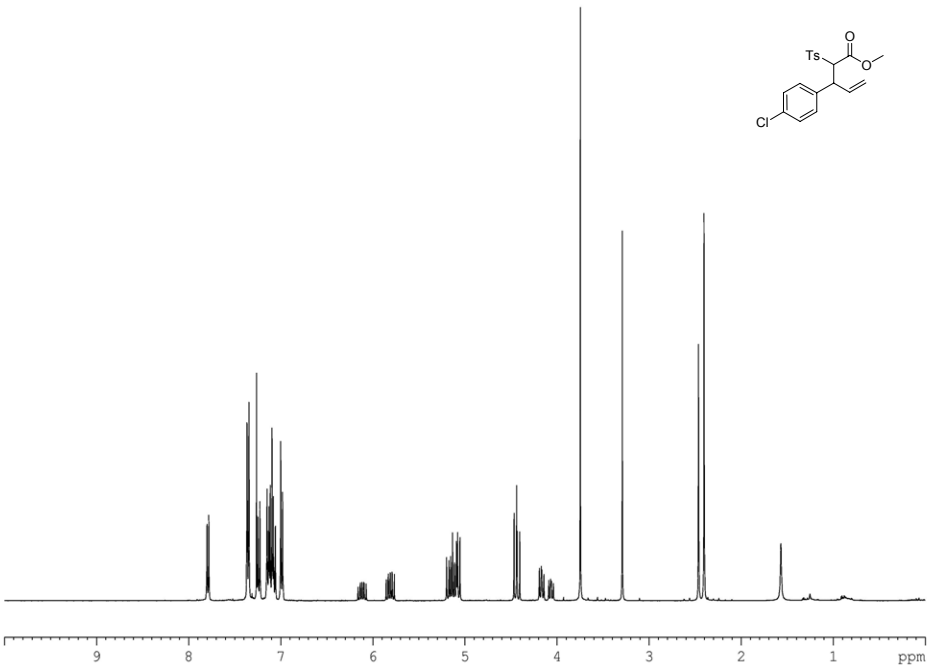
Graph 3: Plot $[A]/[A_0]$) vs. t for reaction of **1c**

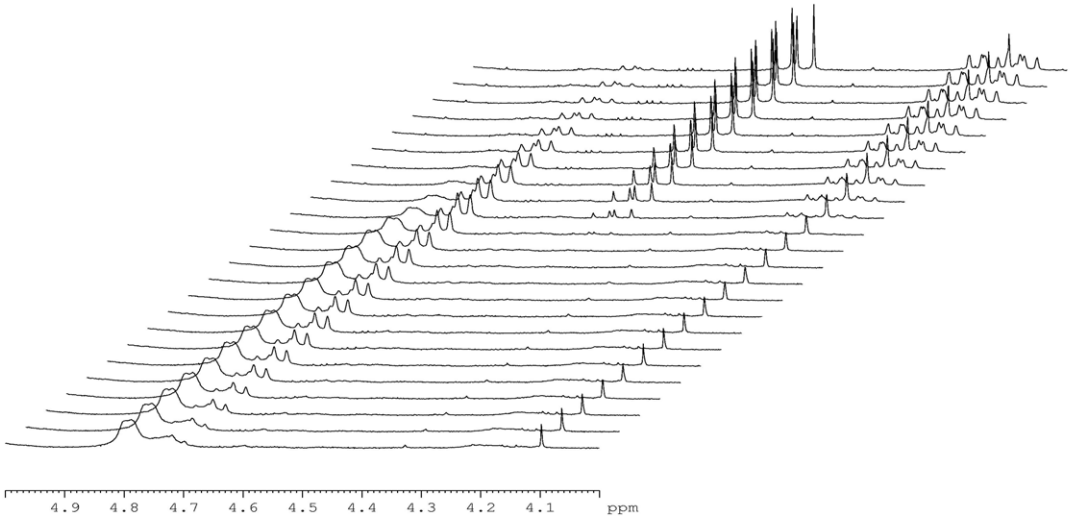
Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_F = 110.6 \times 10^{-5}$ s^{-1}, with $[A]_0 = 0.518$; $B = 0.232$

Substrate **1d** (S = Cl)







Integrated signals in the dCr reaction of substrate 1d

Time intervals

Traces 1–10: 150 s

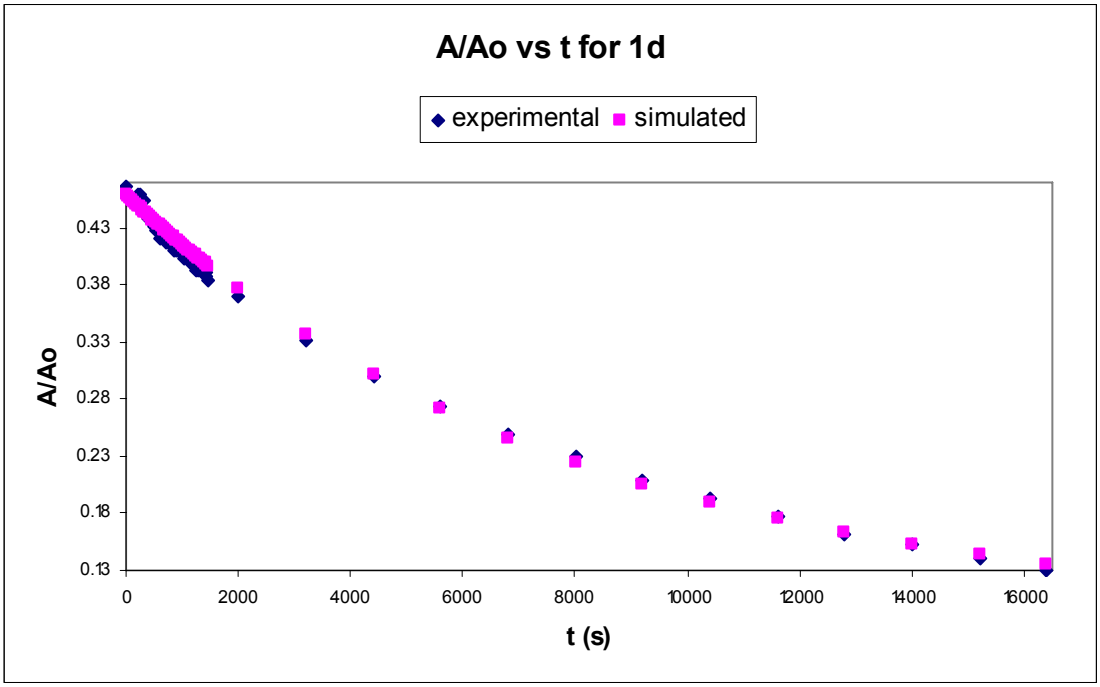
Traces 11–24: 1200 s

Range of integrated signals

5d: [4.871–4.759] ppm

6d: [4.759–4.673] ppm

3d: [4.507–4.410] ppm

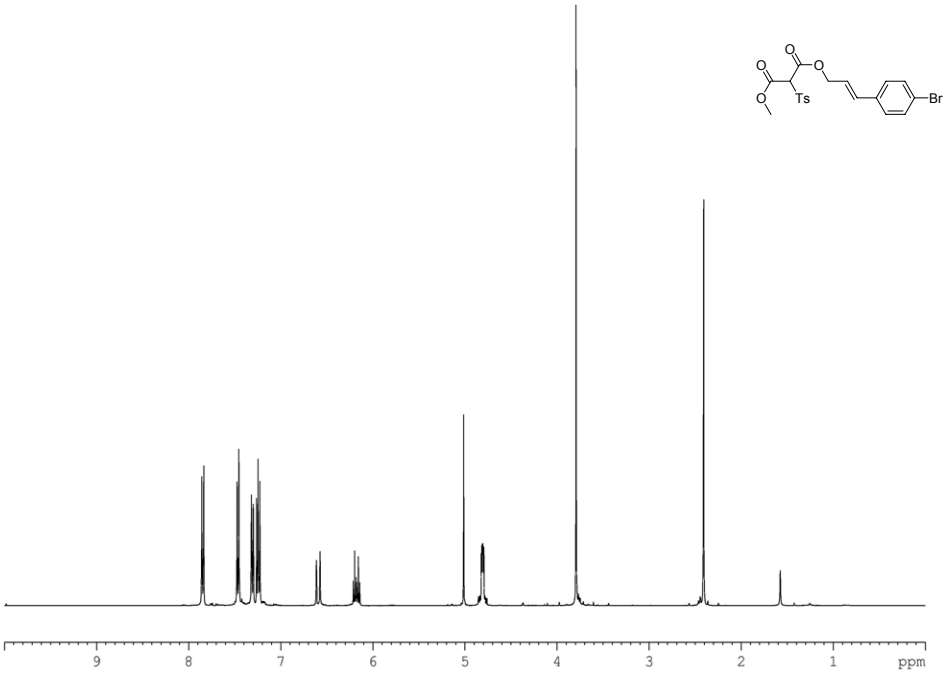


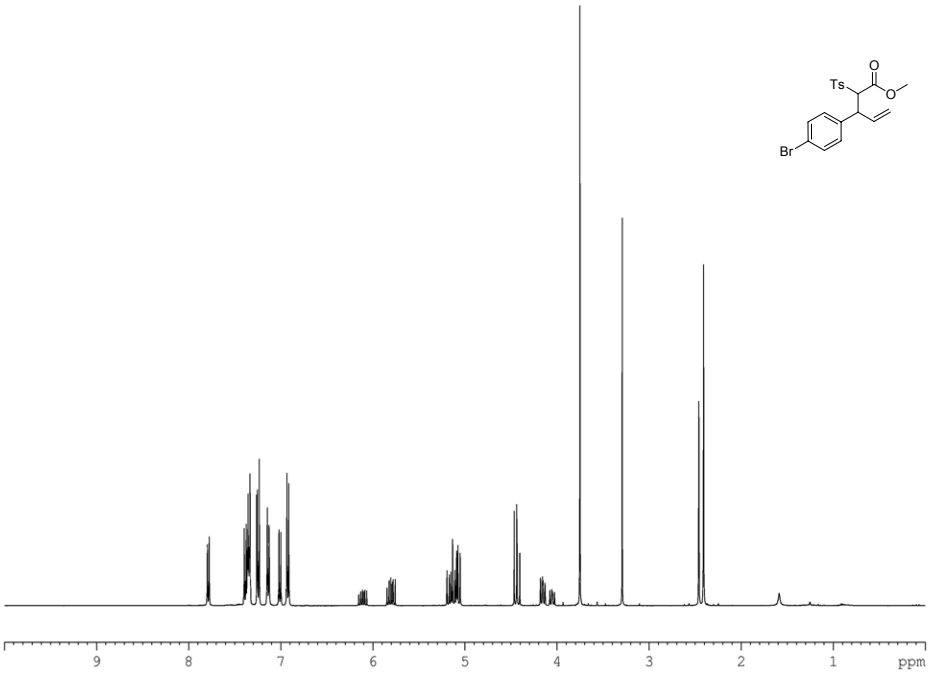
Graph 4: Plot $[A]/[A_0]$) vs. t for reaction of **1d**

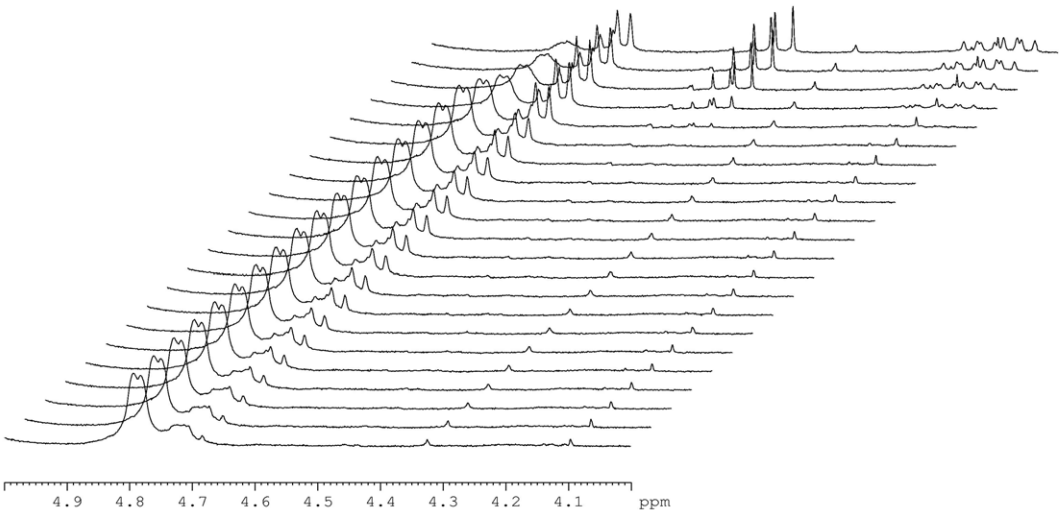
Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_{Cl} = 12.5 \times 10^{-5}$ s^{-1}, with $[A]_0 = 0.371$; B = 0.088

Substrate **1e** (S = Br)







Integrated signals in the dCr reaction of substrate 1e

Time intervals

Traces 1–10: 150 s

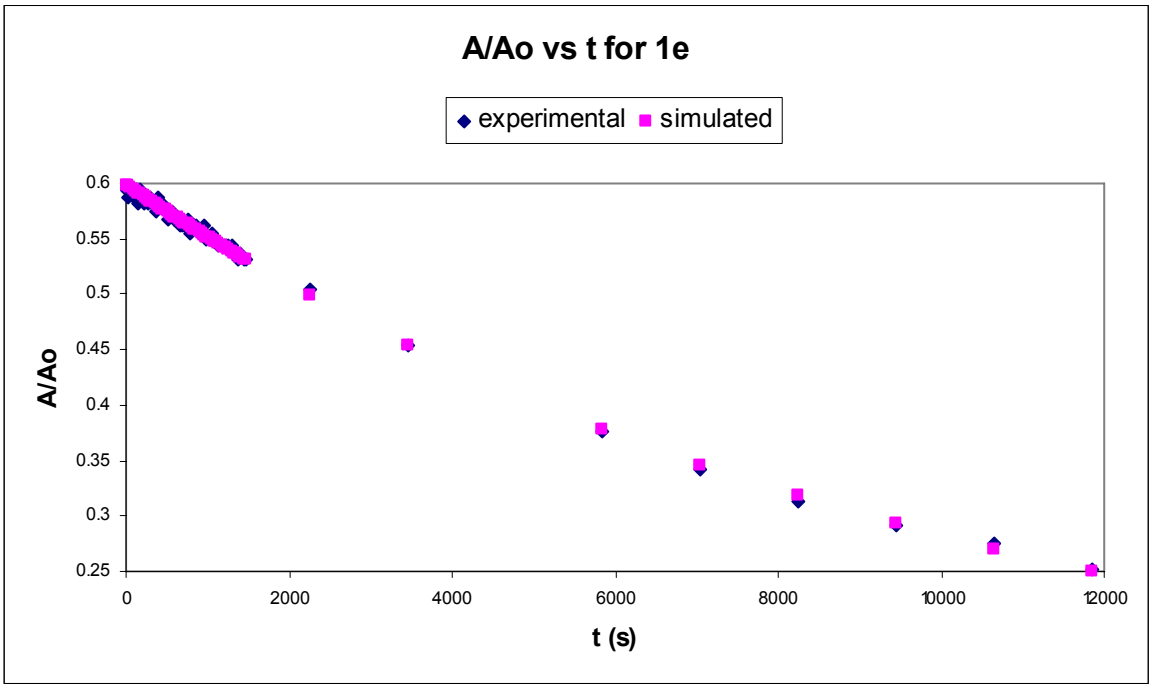
Traces 11–22: 1200 s

Range of integrated signals

5e: [4.862–4.747] ppm

6e: [4.747–4.665] ppm

3e: [4.497–4.408] ppm

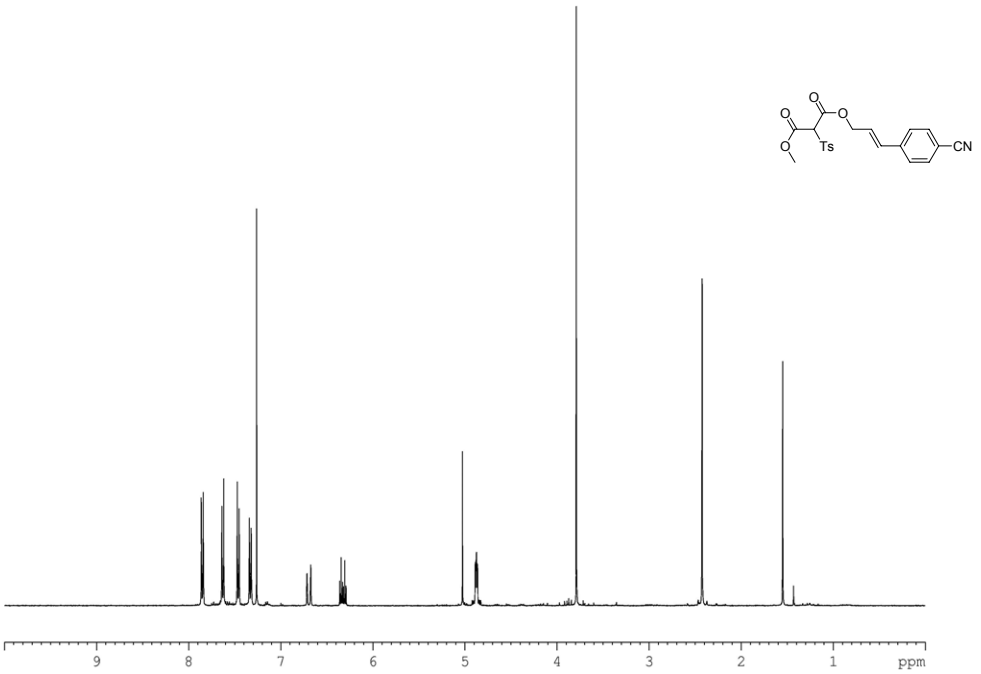


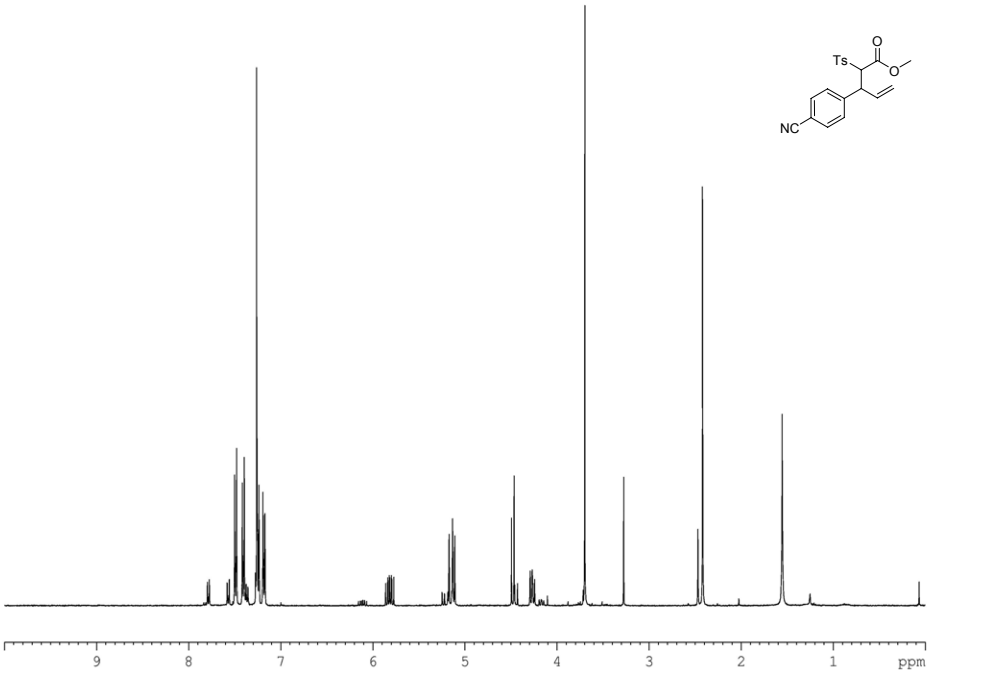
Graph 5: Plot $[A]/[A_0]$) vs. t for reaction of **1e**

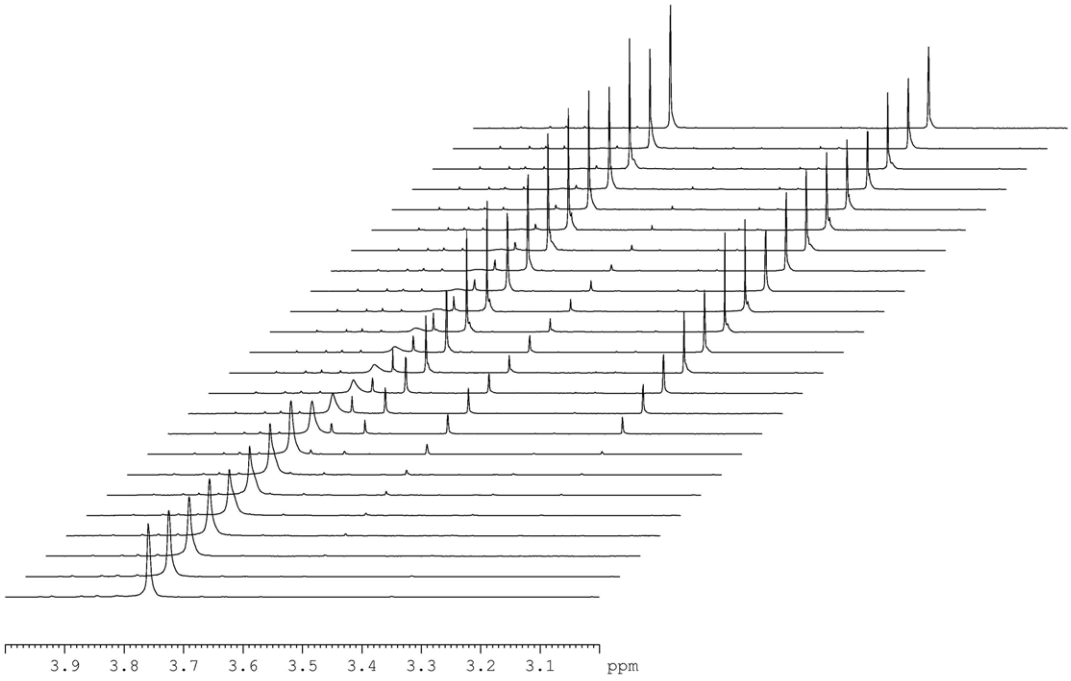
Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_{Br} = 9.8 \times 10^{-5}$ s^{-1}, with $[A]_0 = 0.508$; $B = 0.091$

Substrate **1f** (S = CN)







Integrated signals in the dCr reaction of substrate 1f

Time intervals

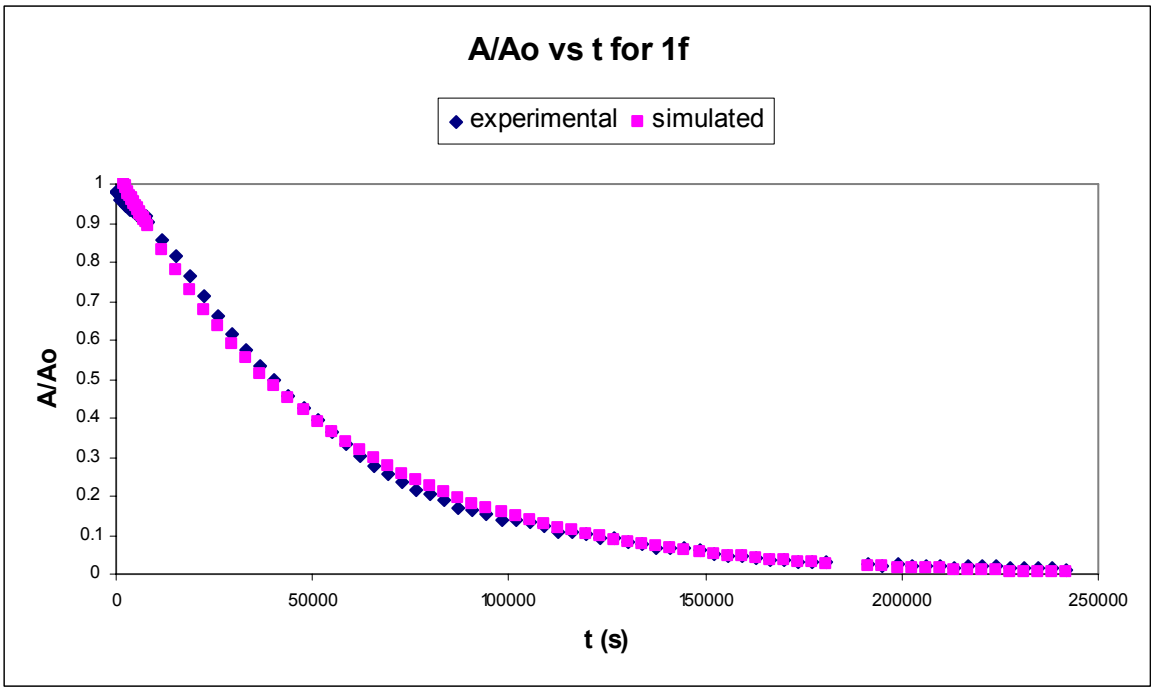
Traces 1–6: 720 s Traces 7–24: 14400 s

Range of integrated signals

5f: [3.801–3.732] ppm

6f: 1st diast. [3.732–3.704] ppm 2nd diast. [3.545–3.511] ppm

3f: 1st diast. [3.695–3.640] ppm 2nd diast. [3.282–3.202] ppm



Graph 6: Plot $[A]/[A_0]$) vs. t for reaction of **1f**

Simulated data: $[A] = [A]_0 e^{-kt} + B$

After non-linear fit $k_{CN} = 1.9 \times 10^{-5}$ s^{-1}, with $[A]_0 = 1.05$; $B = -0.01$