ORGANIC LETTERS

DYNAMIC HEMICARCERANDS AND HEMICARCEPLEXES

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SUPPORTING INFORMATION

(11 Pages)

Experimental Procedures,

^{1}H NMR and ^{13}C NMR spectroscopic and FAB mass spectrometric data for 5-substituted-MPD and hemicarcerand C_2A_4,output from kinetic analysis of liberation of ferrocene from C_2B_4•Fc

Experimental Section

General

All reagents and solvents were used as received unless otherwise stated. Reactions were carried out under an atmosphere of anhydrous argon. Reactions were monitored by TLC on silica plates (Merck, 0.25 mm) and visualized with UV light (254 nm). Melting points given are uncorrected. NMR spectra were recorded on either a Bruker AMX 400 or AMX 500 spectrometer. Chemical shifts reported are referenced to the residual solvent peak.

Synthesis

Methoxy Ethoxy Ethyl 3,5-Dinitrobenzoate: To a 500 mL round-bottom flask fitted with a condenser and a Dean-Stark water trap, a mixture of 3,5-dinitrobenzoic acid (1.01 g, 4.8 mmol), di(ethylene glycol) methyl ether (1.01 g, 1.0 mL, 8.4 mmol) and one crystal of *p*-TsOH in toluene (130 mL) were heated to reflux. After 24 h, the solution was cooled to room temperature, and evaporated to dryness. The residue was dissolved in ethyl acetate (100 mL) and washed with saturated sodium bicarbonate (3 x 100 mL), dried over sodium sulfate and evaported to give a yellow coloured oil. Purification by column chromatography (SiO_2: EtOAc / hexanes, 2:3) gave methoxy ethoxy ethyl 3,5-dinitrobenzoate (1.27 g, 85%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): d = 9.24 (t, J = 2.2 Hz, 1H), 9.18 (d, J = 2.2 Hz, 2H), 4.62 (m, 2H), 3.90 (m, 2H), 3.71 (m, 2H), 3.58 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 162.6, 148.6, 133.8, 129.6, 122.4, 71.9, 70.6, 68.8, 65.8, 59.1; HRMS (FAB): $C_{12}H_{15}N_2O_8$ $[M + H]^+$; calcd m / z = 315.0828; found m / z = 315.0831.

5-Substituted-MPD: To a flask containing methoxy ethoxy ethyl 3,5-dinitrobenzoate (25 mg, 0.08 mmol) and Pd / C (10%, 5 mg), in 95% EtOH (2 mL), was flushed thrice with argon then thrice with hydrogen. The flask was charged with hydrogen gas, and reaction mixture was left to stir for 24 h. The suspension was filtered through Celite, and

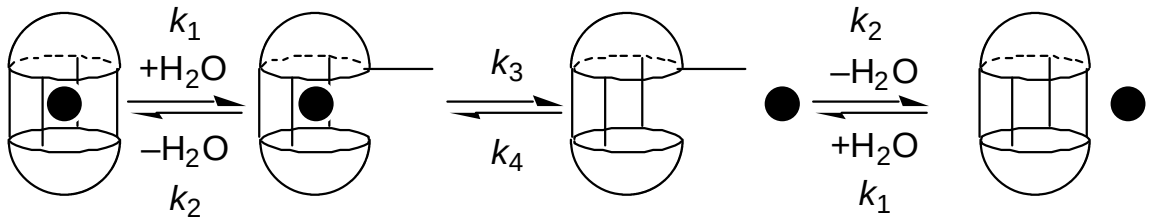
rinsed with EtOAc (15 mL). The filtrate was evaporated and purified by column chromatography (SiO_2: EtOAc) to give the **5-substituted-MPD** (16.5 mg, 82%) as a pale yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): *d* = 6.80 (d, *J* = 2.1 Hz, 2H), 6.19 (t, *J* = 2.1 Hz, 1H), 4.43 (m, 2H), 3.80 (m, 2H), 3.68 (m, 2H), 3.56 (m, 2H), 3.39 (s, 3H), 233 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 166.9, 147.5, 132.0, 107.0, 105.7, 71.9, 70.5, 69.3, 64.0, 59.1; HRMS (FAB): $\mathbf{C_{12}H_{18}N_2O_4}$ $[M + H]^+$; calcd m / z = 254.1267; found m / z = 254.1265.

Hemicarcerand C_2A_4: To a solution of cavitand tetraaldehyde (R = CH_2CH_2Ph) (50 mg, 0.047 mmol) and **5-substituted-MPD** (26 mg, 0.10 mmol), in $CHCl_3$ (6 mL), TFA (1% v/v, $CDCl_3$, 0.0015 mg, 1 uL, 0.000013 mmol) was added and stirred for 24 h at room temperature. Purification by column chromatography (SiO_2: EtOAc / CH_2Cl_2, 1:9) gave pure hemicarcerand C_2A_4 as a white solid (32 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): *d* = 8.54 (s, 8H), 7.51 (d, *J* = 2.0 Hz, 3H), 7.32-7.19 (m, 48H), 6.76 (t, *J* = 2.0 Hz, 4H), 5.71 (d, *J* = 7.7 Hz, 8H), 5.08 (br t, 8H), 4.67 (d, *J* = 7.7 Hz, 8H), 4.50 (br t, 8H), 3.81 (br t, 8H), 3.66 (m, 8H), 3.53 (m, 8H), 3.36 (s, 12H), 2.83-2.68 (m, 16H), 2.75-2.49 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): 165.8, 157.6, 154.0, 153.4, 141.4, 138.7, 132.7, 128.7, 128.5, 126.3, 124.2, 122.8, 122.3, 116.5, 100.7, 71.9, 70.6, 69.2, 64.5, 59.1, 36.6, 34.3, 32.3; MS (FAB): m / z = 3003.3 $[M]^+$; $\mathbf{C_{184}H_{168}N_8O_{32}}$ (3003.4): calcd for $\mathbf{C_{184}H_{168}N_8O_{32}\bullet H_2O}$: C 73.10, H 5.68, N 3.51; found C 73.15, H 5.67, N 3.71.

Dynafit Output for the
Kinetic Monitoring of Decomplexation

It should be noted that in the absence of an excess of MPD, the decomplexation of ferrocene from the hemicarceplex occurs after an initial hydrolysis of one imine bond, as depicted below.

Mechanism 1 — No excess MPD



The following is the series of outputs from Dynafit showing the calculated and observed reaction profiles.

In all cases, $k_1 << k_3$.

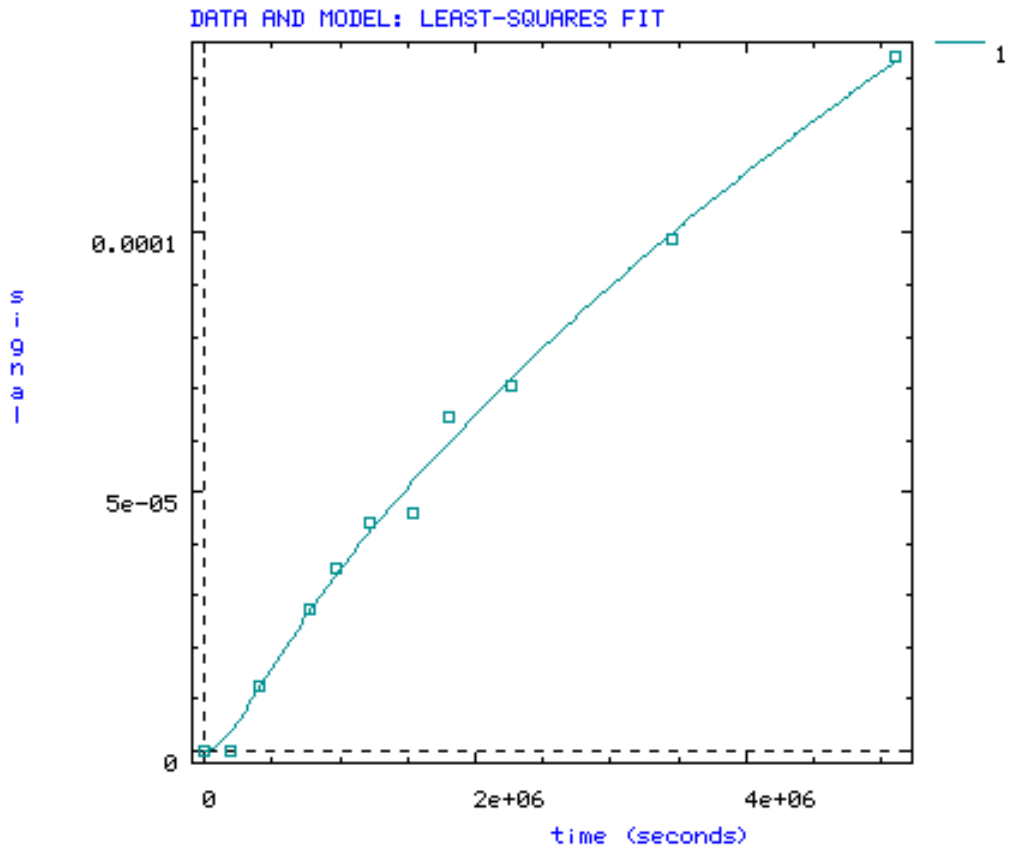
x-axis — time (seconds)

y-axis — $[Cp_2Fe]$ / $mol.dm^{-3}$

Squares — Observed Data

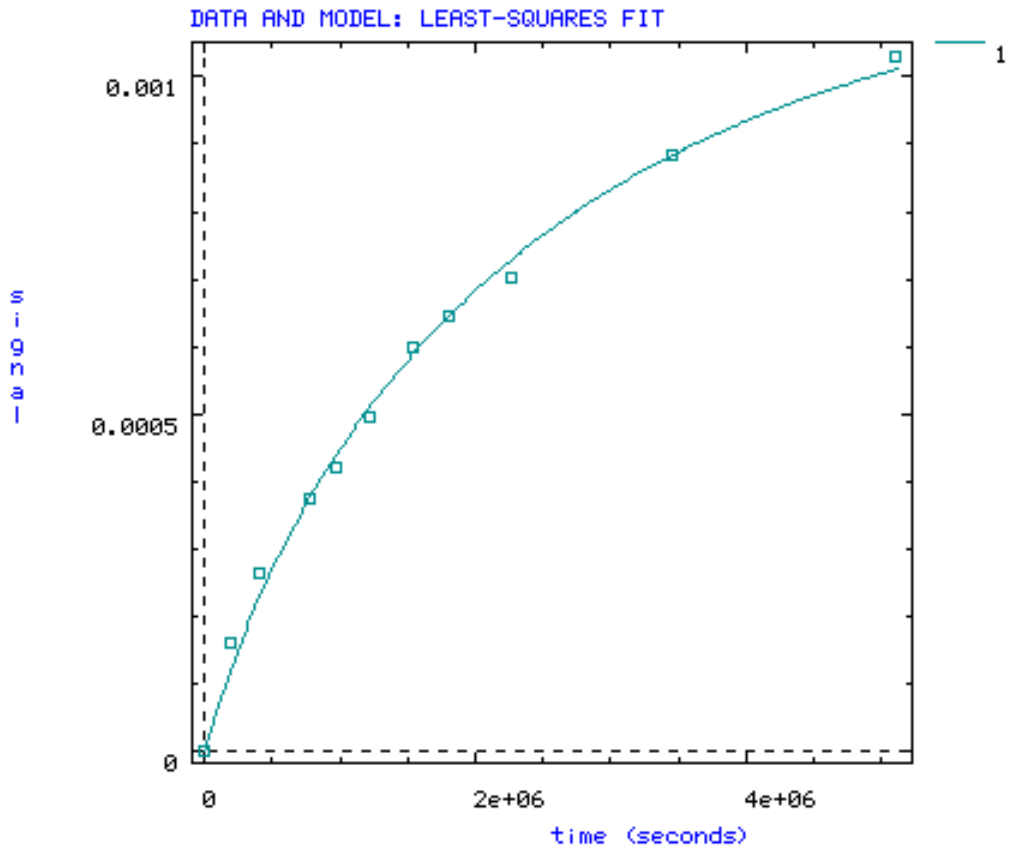
Lines — Fitted Data

1 Equiv C_2B_4, 0 Equiv *m*-phenylene diamine, 0 μL TFA



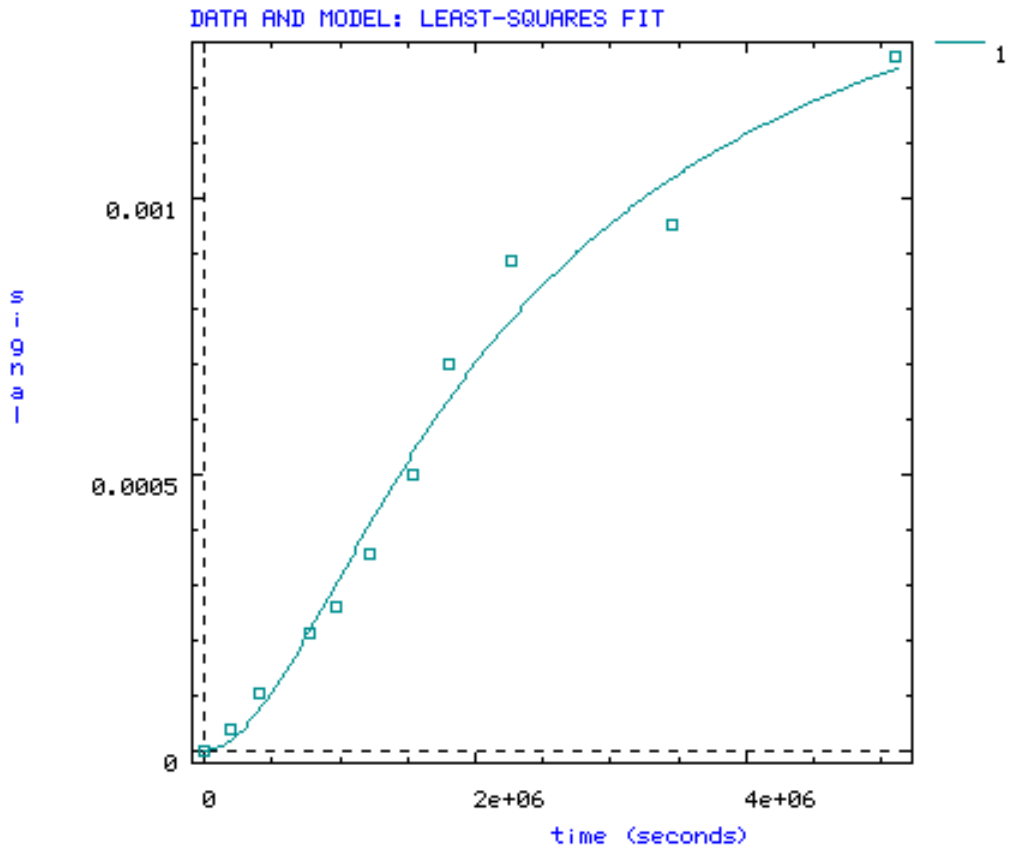
Entry 1 in Table 1. $t_{1/2}$ >4000 h

1 Equiv C_2B_4, 0 Equiv *m*-phenylene diamine, 4 μL TFA



Entry 2 in Table 1. $t_{1/2}$ = 1500 h

1 Equiv C_2B_4, 0 Equiv *m*-phenylene diamine, 8 µL TFA

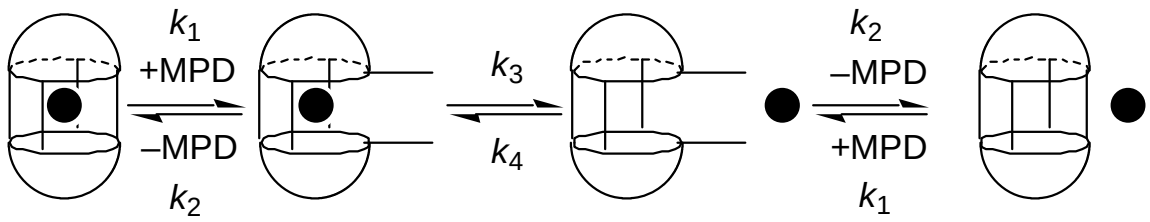


Entry 3 in Table 1. $t_{1/2}$ = 1400 h

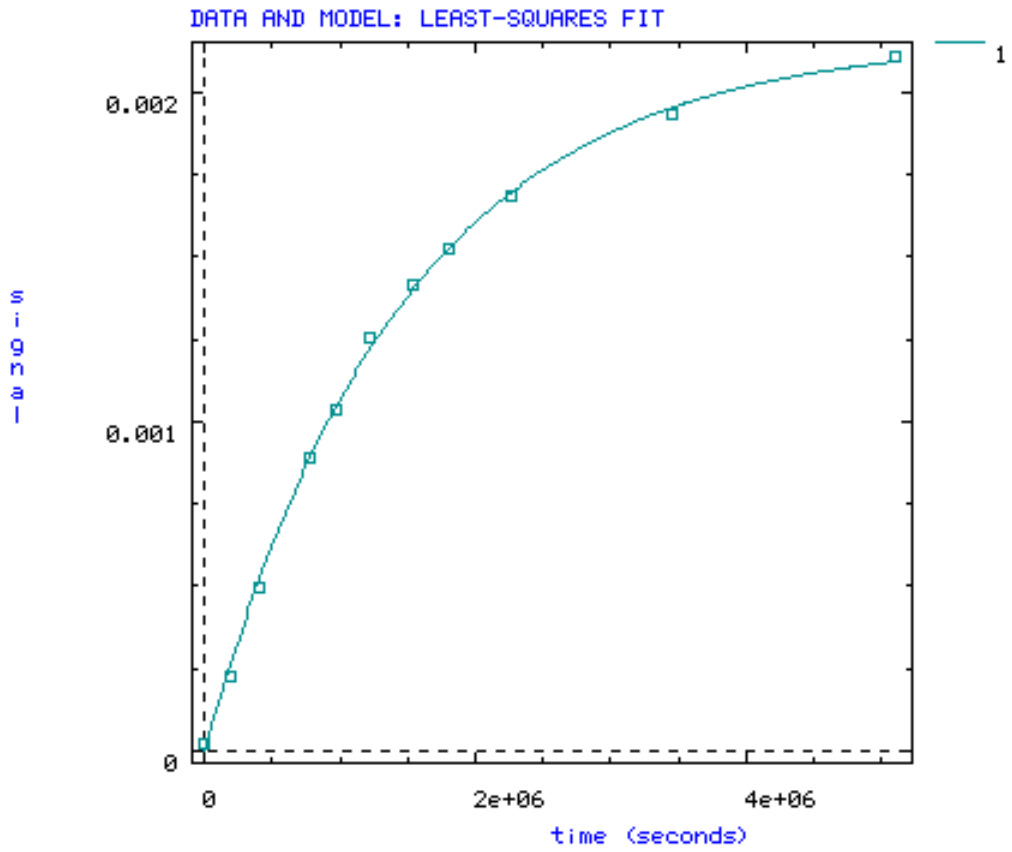
In the presence of an excess of MPD and TFA catalyst, the reaction occurs *via* a second mechanism whereby the initial step is the nucleophilic attack of a molecule of MPD on C_2B_4•Fc, as illustrated below.

In all cases, $k_1 << k_3$.

Mechanism 2 — Excess MPD

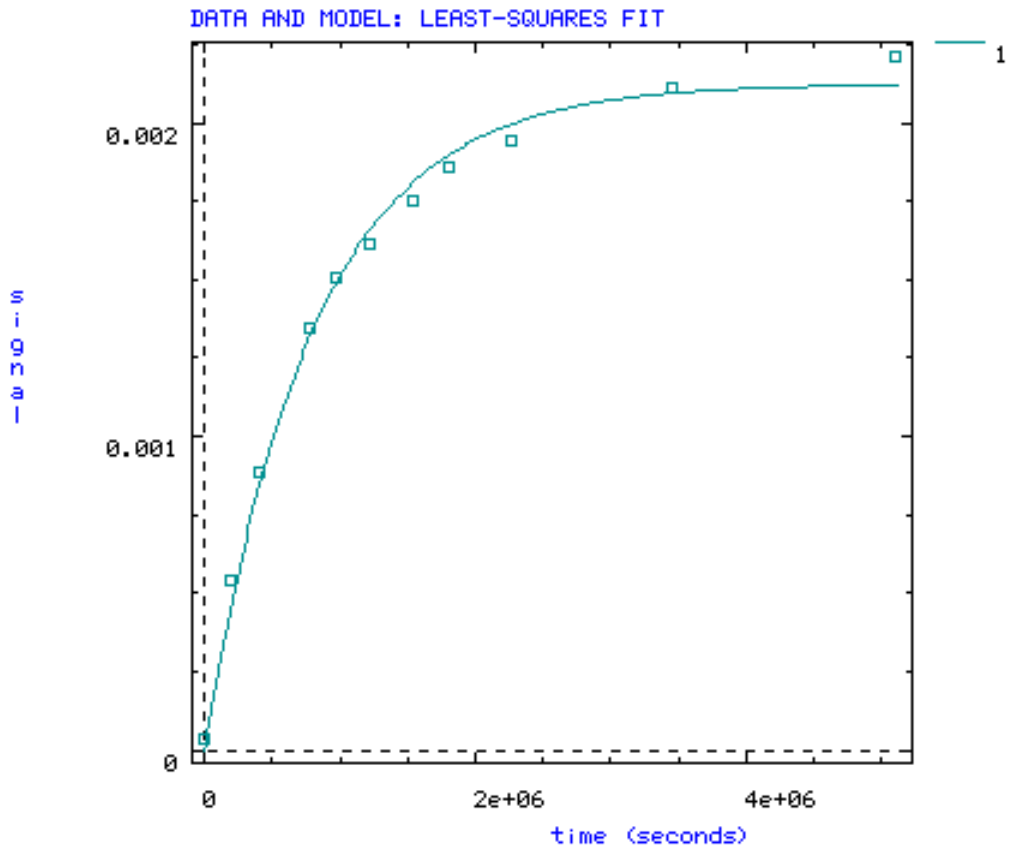


1 Equiv C_2B_4, 4 Equiv *m*-phenylene diamine, 4 μL TFA



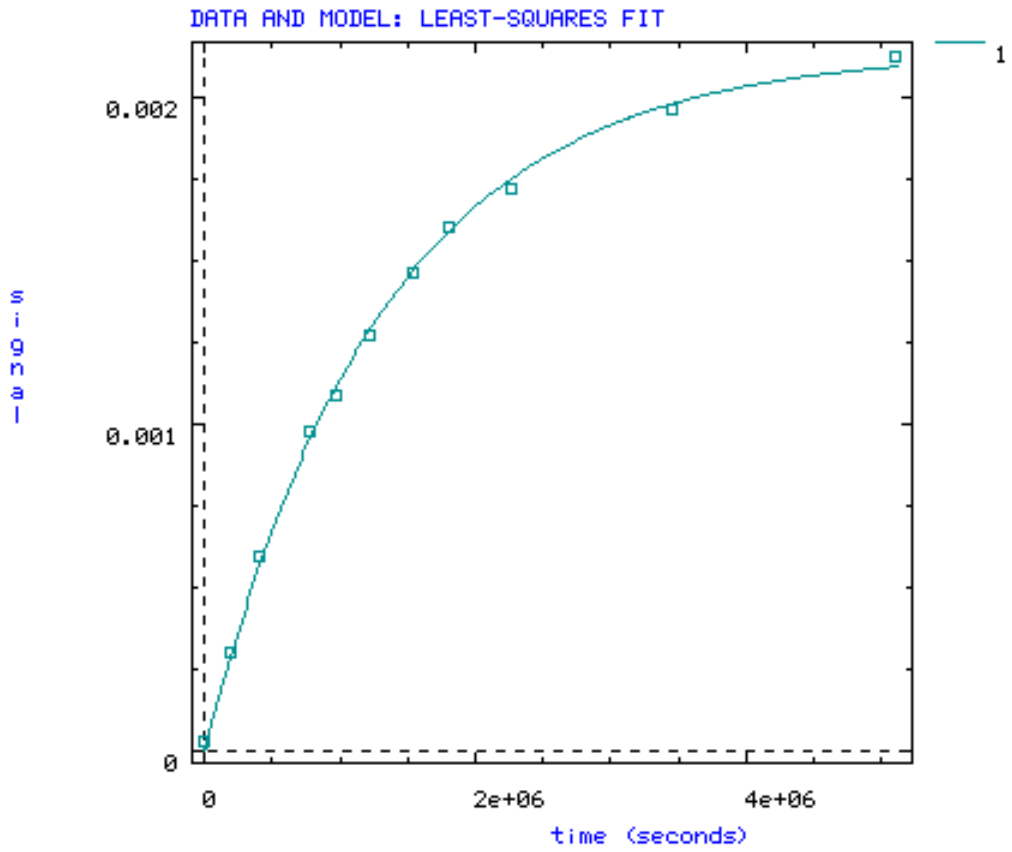
Entry 4 in Table 1. $t_{1/2}$ = 380 h

1 Equiv C_2B_4, 4 Equiv *m*-phenylene diamine, 8 μL TFA



Entry 5 in Table 1. $t_{1/2}$ = 330 h

1 Equiv C_2B_4, 8 Equiv *m*-phenylene diamine, 4 μL TFA



Entry 6 in Table 1. $t_{1/2}$ = 180 h