Supporting Information

for

Kinetics and mechanism of vanadium catalysed asymmetric cyanohydrin synthesis in propylene carbonate

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Contents

Kinetic plots used to construct the Hammett plot

Chiral GC conditions

Chiral gas chromatography was performed on a Varian450-GC instrument with a TCD detector using Supelco Gamma DEX 120 fused silica capillary columns (26–30 m × 0.25 mm × 0.25 μm film thickness) with hydrogen as a carrier gas. Analyses were performed using one of the following methods:

Method 1: initial temperature 95 °C, hold for 2 minutes then ramp rate of 3 °C/minute to 180 °C, then hold for another 5 minutes. Flow rate: 2 mL/min.

Method 2: initial temperature 95 °C, hold for 2 minutes then ramp rate of 5 °C/minute to 180 °C, then hold for another 5 minutes. Flow rate: 1 mL/min.

Method 3: initial temperature 95 °C, hold for 2 minutes then ramp rate of 2 °C/minute to 180 °C, then hold for another 5 minutes. Flow rate: 2 mL/min.

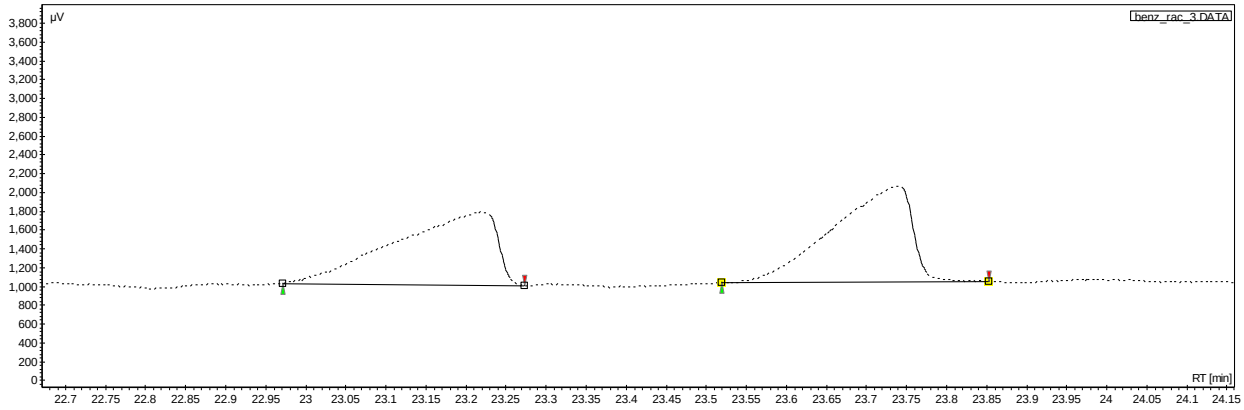
Method 4: initial temperature 95 °C, hold for 5 minutes then ramp rate of 0.5 °C/minute to 180 °C, then hold for another 5 minutes. Flow rate: 2 mL/min.

Method 5: initial temperature 95 °C, hold for 2 minutes then ramp rate of 5 °C/minute to 180 °C, then hold for another 5 minutes. Flow rate: 2 mL/min.

Retention times were found to vary as the chiral GC column aged and were also different from column to column. In many cases it was necessary to change the method used to analyse a particular cyanohydrin acetate when the chiral GC column was replaced. The GC traces presented in the following pages were recorded over a period of three years on three different chiral columns, which accounts for the variation in retention times.

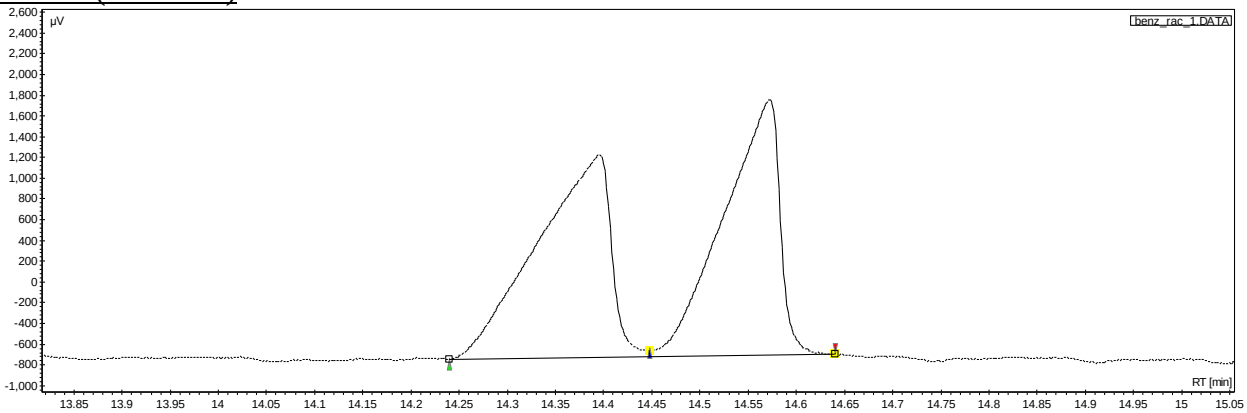
Cyanohydrin acetate derived from benzaldehyde (Analysed using GC methods 1 or 5).

Racemate (method 1)



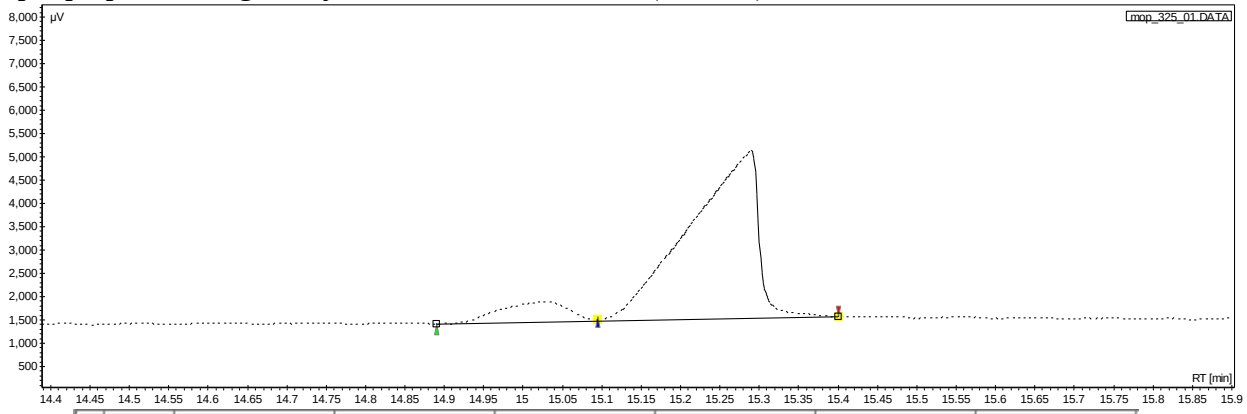
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	23.22	49.25	779.2	113.7	49.252
	1	UNKNOWN	23.74	50.75	1021.3	117.1	50.748
▶							
	Total			100.00	1800.5	230.8	100.000

Racemate (method 5)



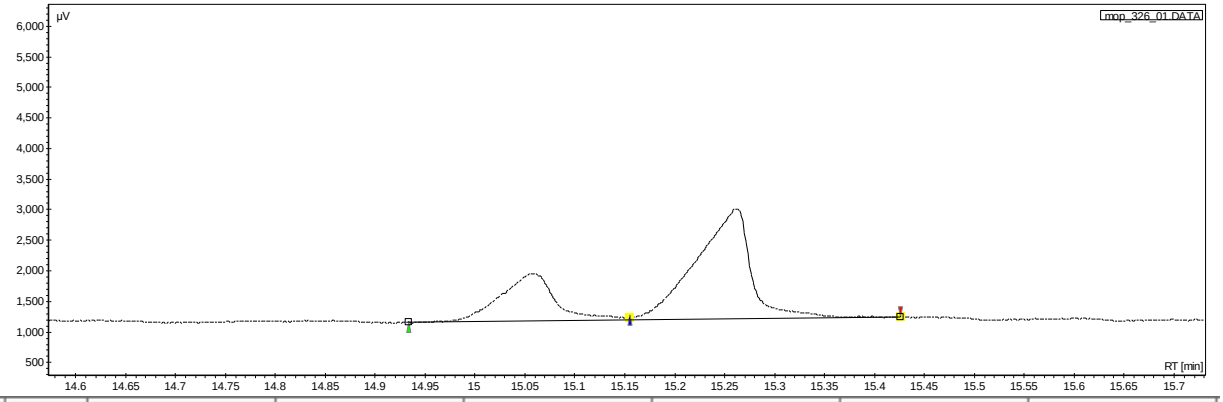
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.40	50.99	1949.6	173.4	50.985
	2	UNKNOWN	14.57	49.01	2461.5	166.7	49.015
▶							
	Total			100.00	4411.1	340.1	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



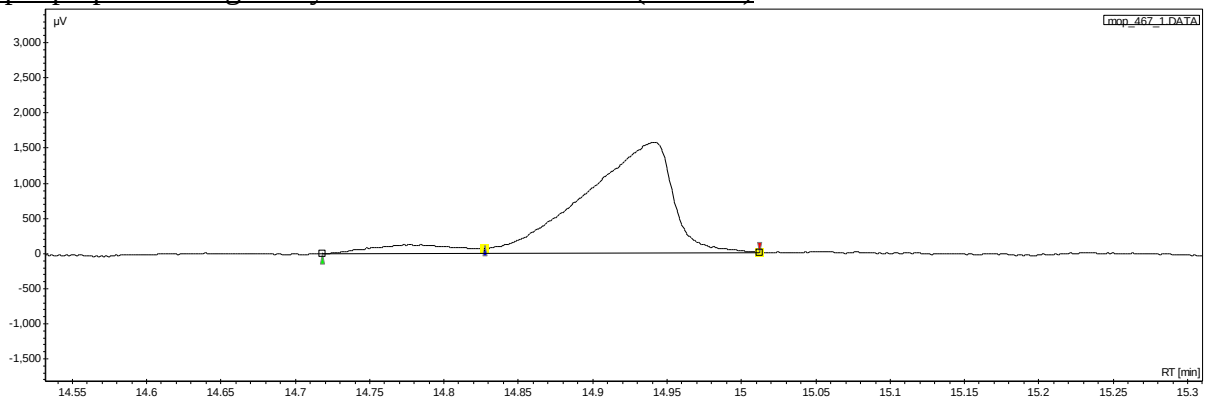
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.03	10.95	437.2	45.3	10.951
	2	UNKNOWN	15.29	89.05	3599.5	368.5	89.049
▶							
	Total			100.00	4036.6	413.9	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



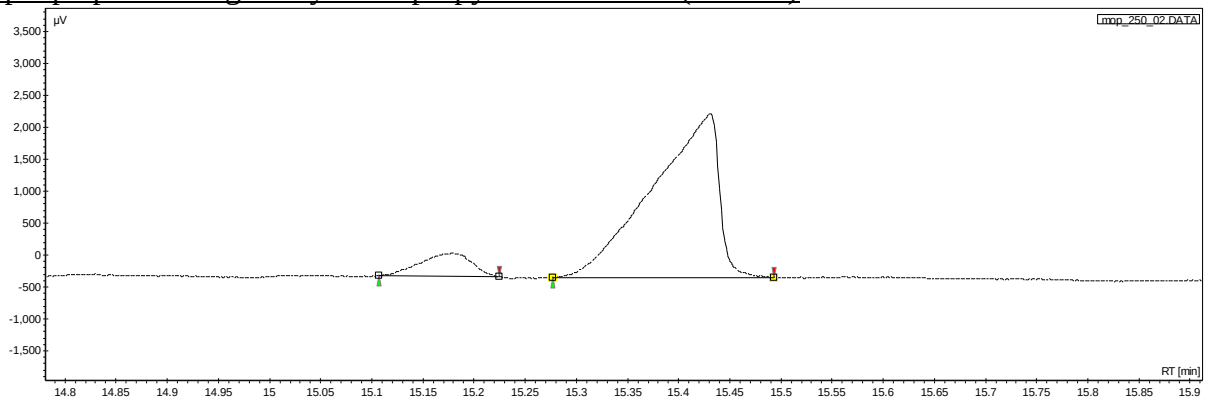
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.06	30.17	772.9	50.4	30.168
	2	UNKNOWN	15.26	69.83	1803.0	116.6	69.832
▶							
	Total			100.00	2575.9	167.0	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



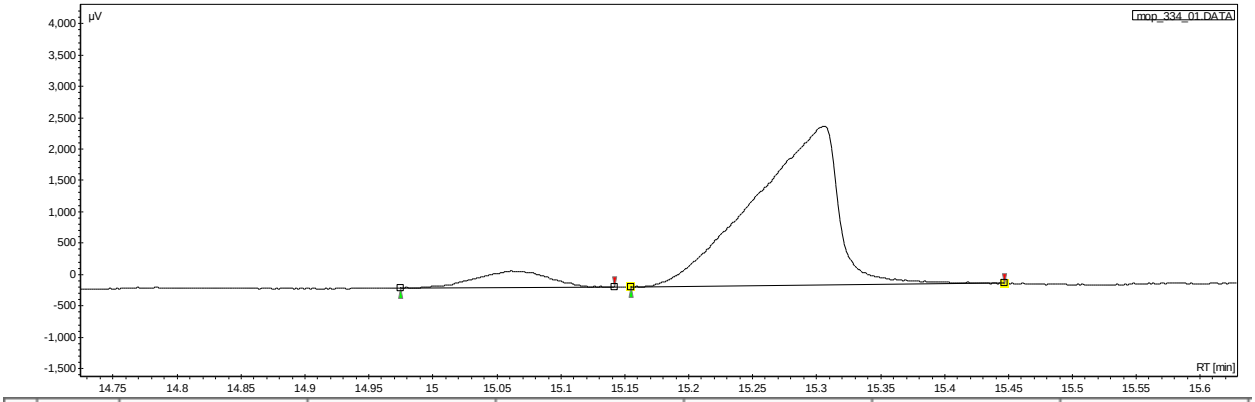
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.78	7.23	115.5	8.3	7.233
	2	UNKNOWN	14.94	92.77	1576.7	106.9	92.767
▶							
	Total			100.00	1692.2	115.3	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



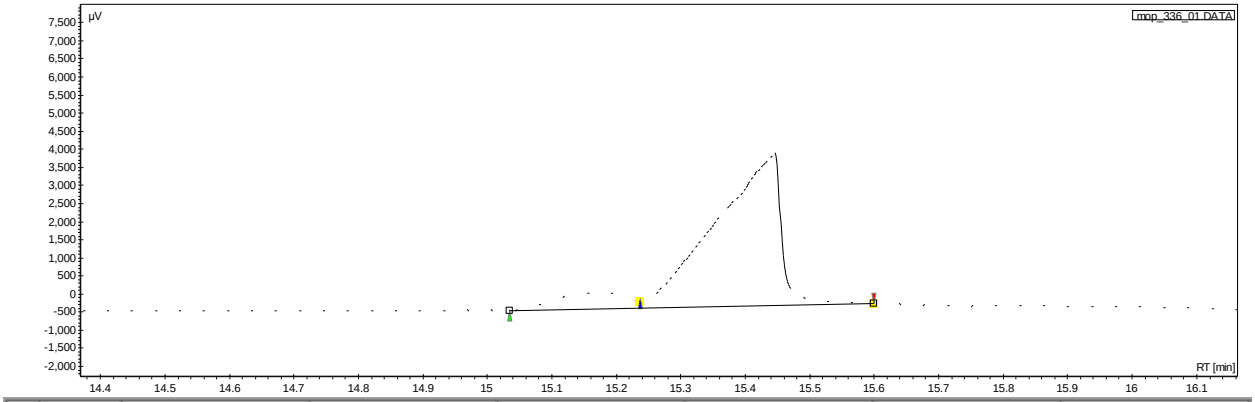
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	15.18	9.93	360.4	21.2	9.931
	1	UNKNOWN	15.43	90.07	2562.2	192.7	90.069
▶							
	Total			100.00	2922.6	213.9	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 1)



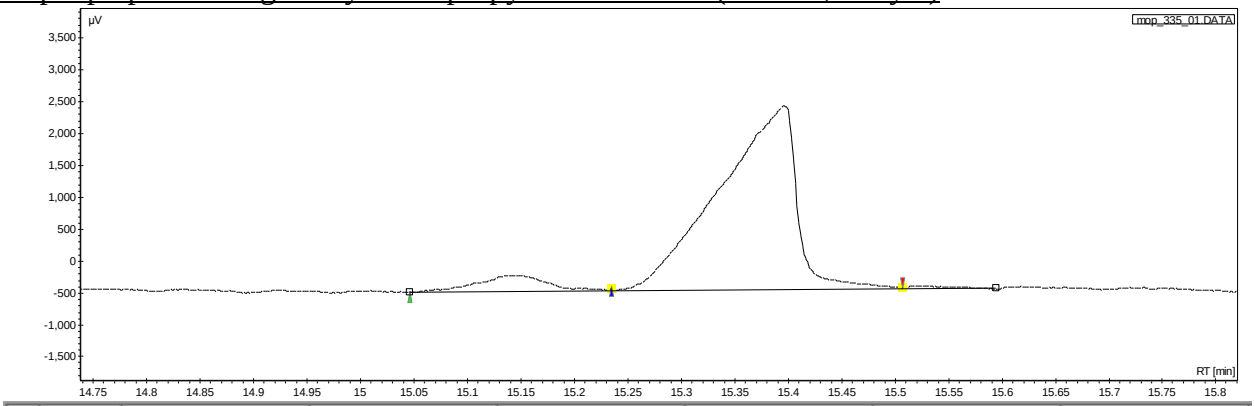
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.07	8.34	262.9	17.7	8.341
	2	UNKNOWN	15.31	91.66	2537.0	194.0	91.659
▶							
	Total			100.00	2799.9	211.7	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 2)



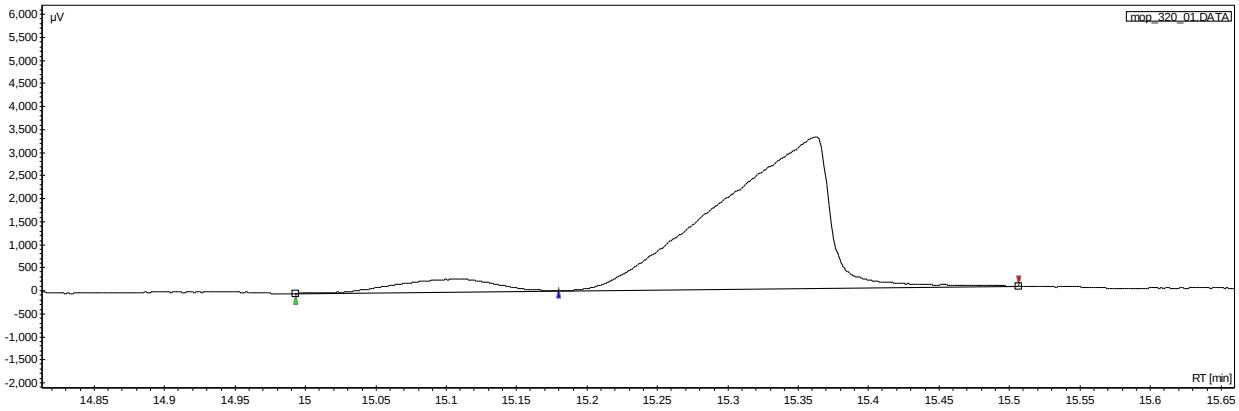
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.18	10.14	438.9	55.3	10.144
	2	UNKNOWN	15.45	89.86	4189.4	490.2	89.856
▶							
	Total			100.00	4628.3	545.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 3)



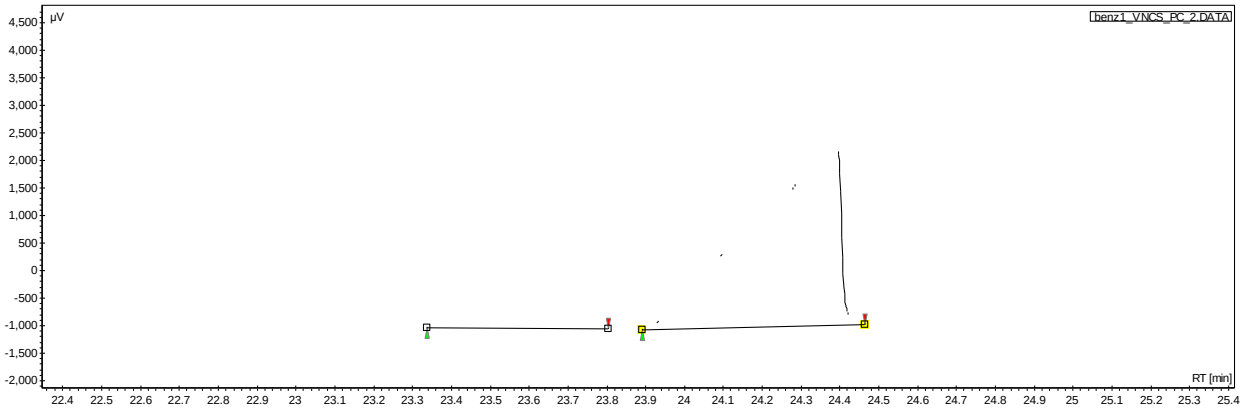
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.15	7.54	249.8	20.0	7.544
	2	UNKNOWN	15.40	92.46	2899.2	245.0	92.456
▶							
	Total			100.00	3149.0	265.0	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 4)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.11	6.98	279.3	22.7	6.981
	2	UNKNOWN	15.36	93.02	3292.9	302.0	93.019
▶							
	Total			100.00	3572.2	324.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 1)

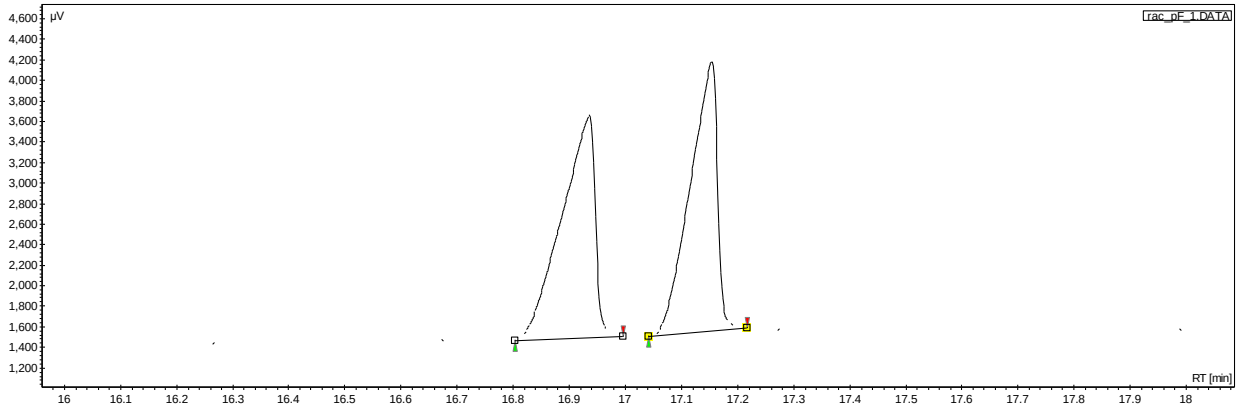


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	23.58	7.41	240.0	67.6	7.409
	1	UNKNOWN	24.39	92.59	3147.5	845.1	92.591
▶							
	Total			100.00	3387.6	912.7	100.000

Cyanohydrin acetate derived from 4-fluorobenzaldehyde

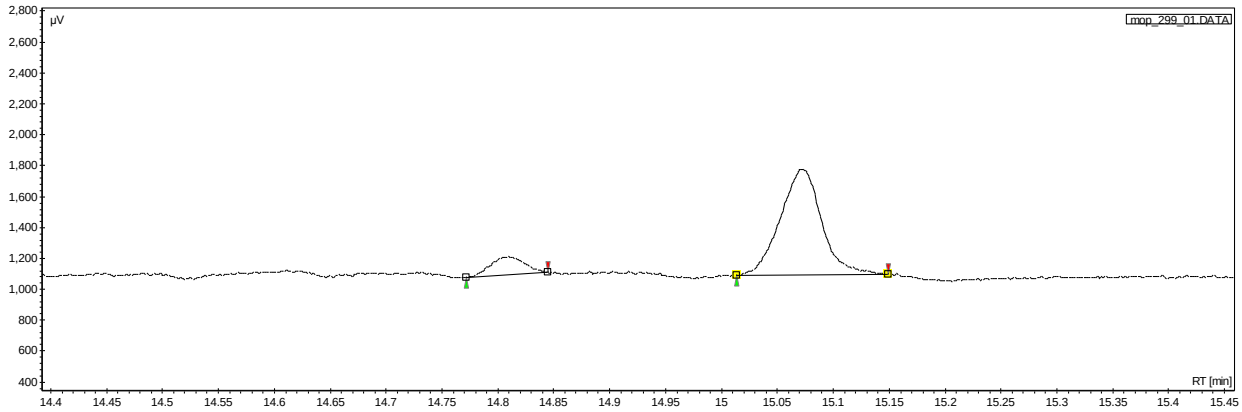
Analysed using GC method 2.

Racemate



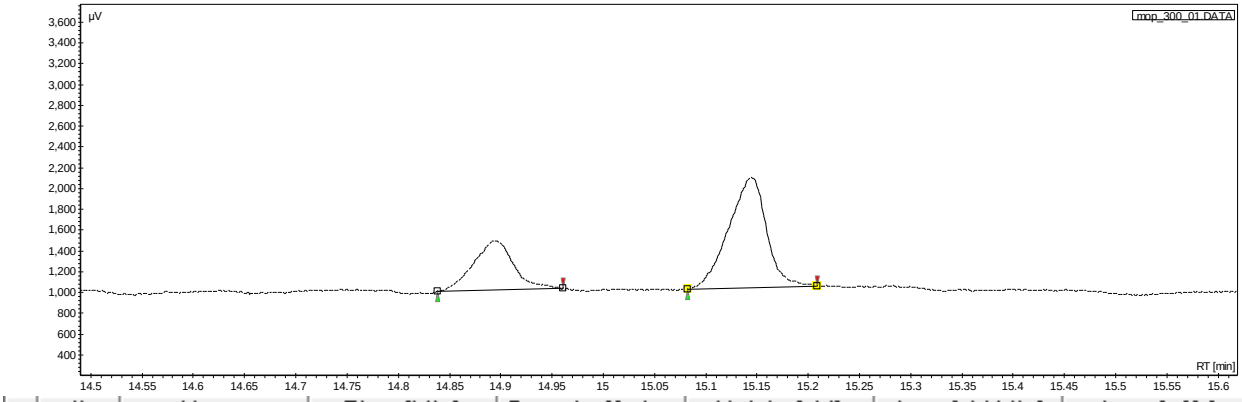
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.94	50.34	2170.6	149.8	50.339
▶	2	UNKNOWN	17.15	49.66	2628.3	147.8	49.661
	Total			100.00	4798.9	297.6	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



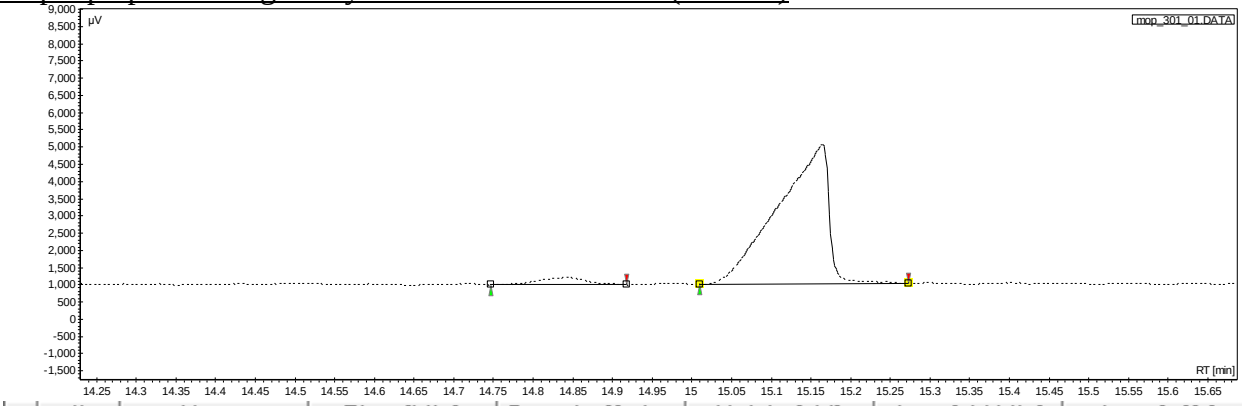
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.81	12.19	119.6	4.1	12.193
	2	UNKNOWN	15.07	87.81	684.5	29.4	87.807
▶							
	Total			100.00	804.2	33.5	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



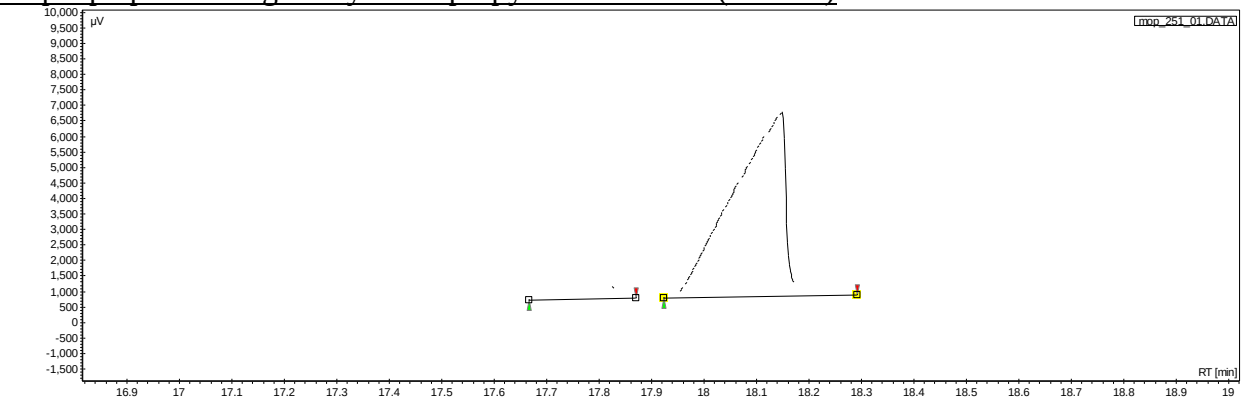
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	14.90	32.50	477.1	21.8	32.496
2	UNKNOWN	15.15	67.50	1056.5	45.3	67.504
Total			100.00	1533.6	67.2	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



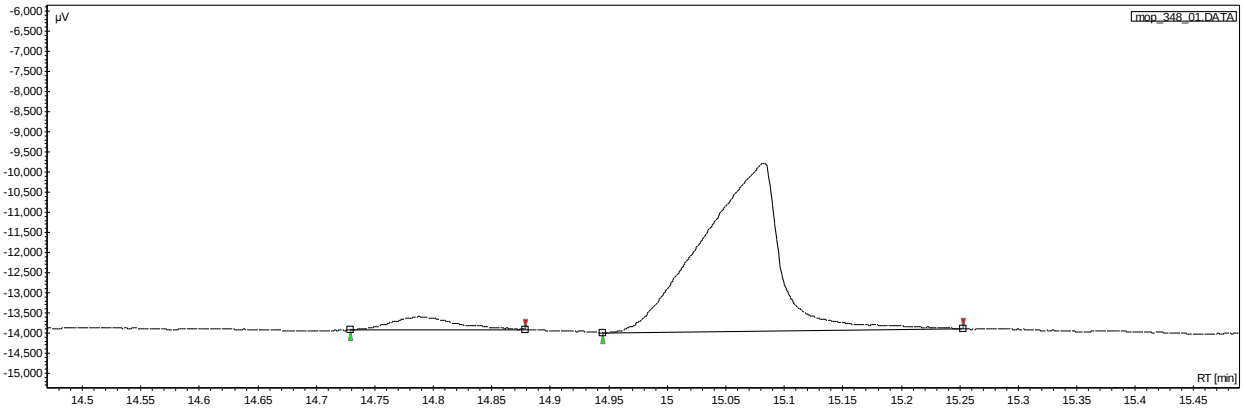
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	14.85	4.65	212.0	14.8	4.653
2	UNKNOWN	15.17	95.35	4038.3	304.0	95.347
Total			100.00	4250.3	318.9	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



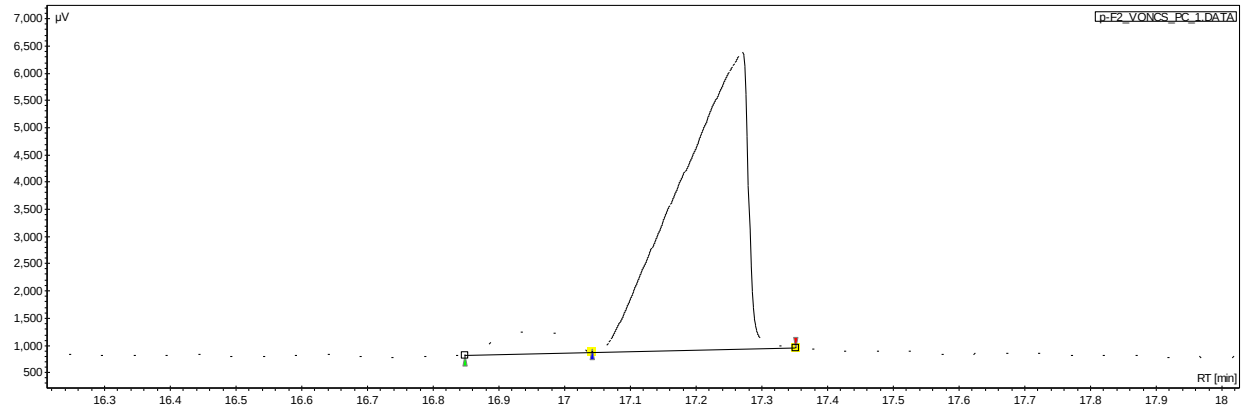
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	17.77	12.01	902.0	93.9	12.011
2	UNKNOWN	18.15	87.99	5918.9	688.1	87.989
Total			100.00	6820.9	782.1	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 5)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.79	5.97	325.9	20.5	5.966
	2	UNKNOWN	15.08	94.03	4179.9	323.0	94.034
▶							
	Total			100.00	4505.8	343.5	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 5)

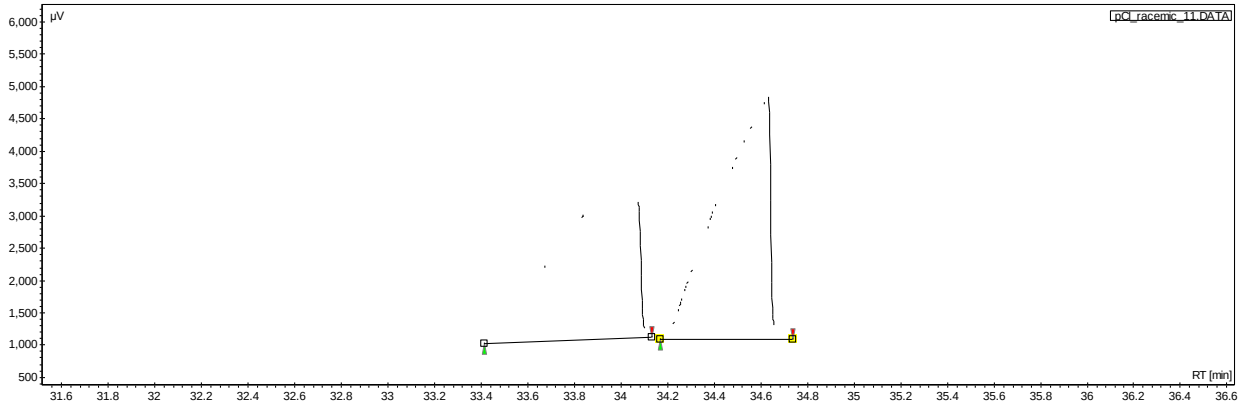


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.97	7.87	471.9	68.4	7.873
	2	UNKNOWN	17.31	92.13	6087.2	800.6	92.127
▶							
	Total			100.00	6559.1	869.0	100.000

Cyanohydrin acetate derived from 4-chlorobenzaldehyde

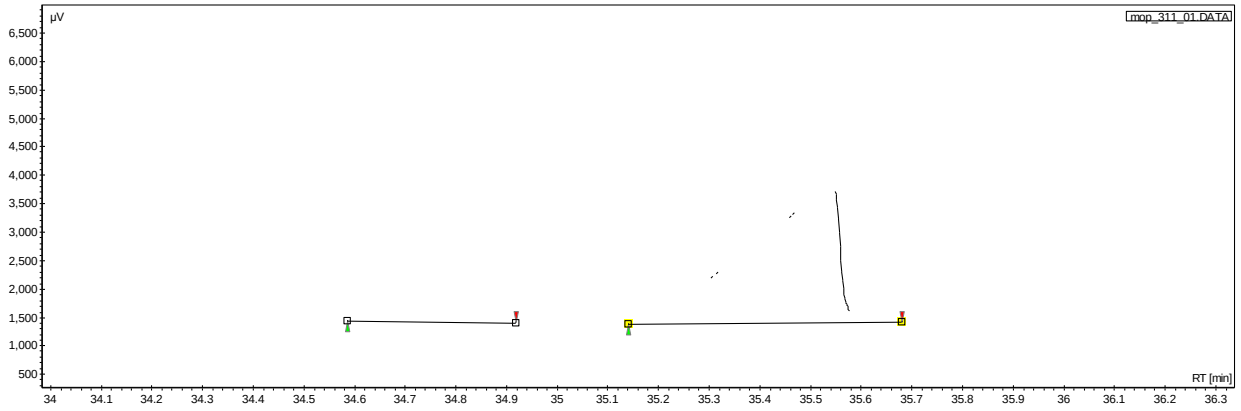
Analysed using GC method 3.

Racemate



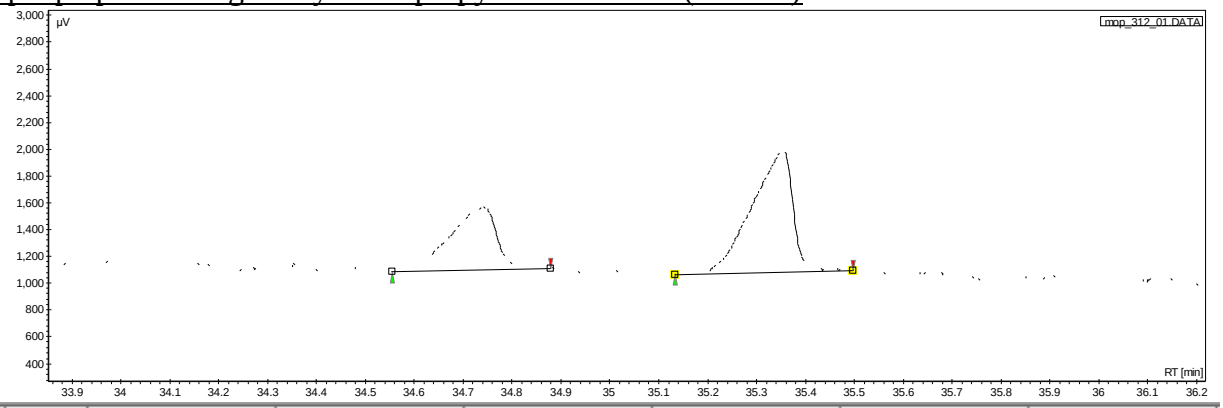
	#	Name	Time [Min]	Quantity [% Area	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	33.96	50.12	2398.3	940.1	50.122
	2	UNKNOWN	34.63	49.88	3767.0	935.6	49.878
▶							
	Total			100.00	6165.3	1875.7	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



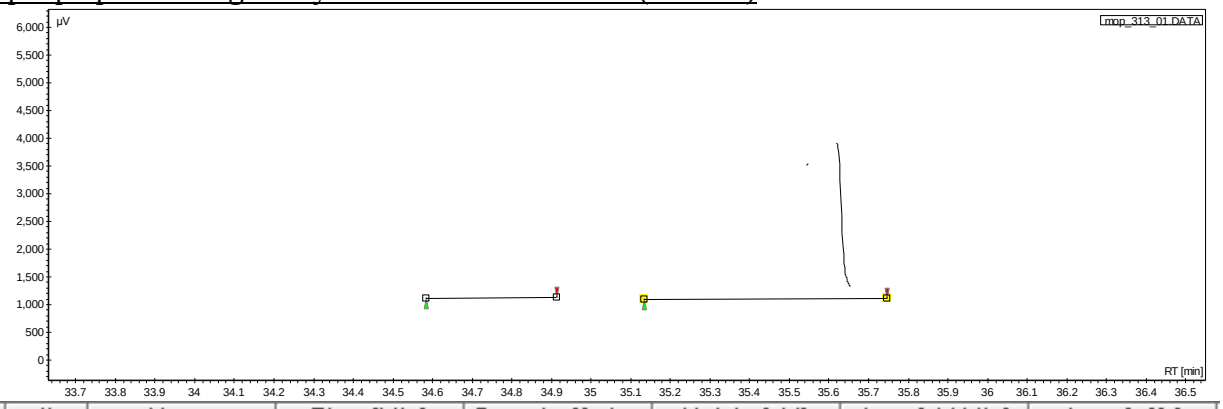
	#	Name	Time [Min]	Quantity [% Area	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	34.76	8.32	267.9	43.8	8.320
	2	UNKNOWN	35.55	91.68	2310.5	483.0	91.680
▶							
	Total			100.00	2578.3	526.8	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



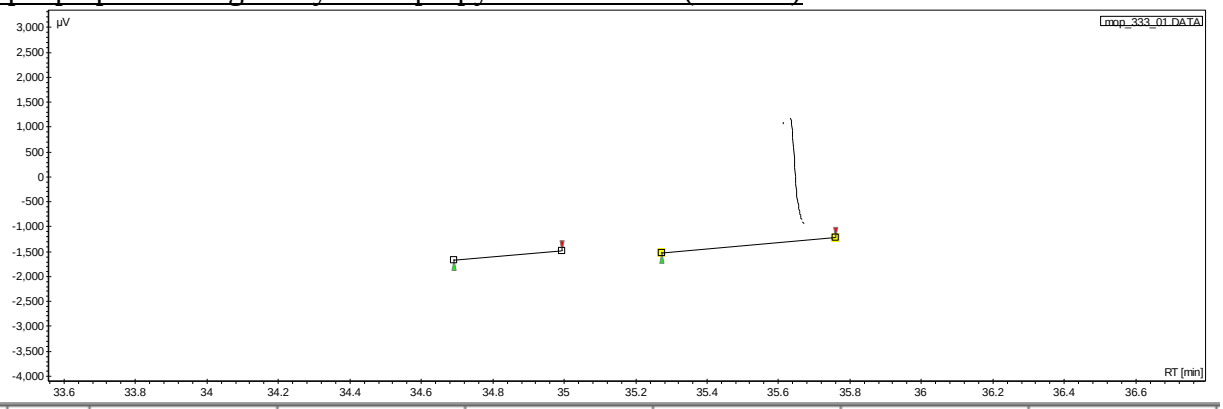
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	34.74	37.48	469.6	52.9	37.479
	2	UNKNOWN	35.35	62.52	900.4	88.3	62.521
▶							
	Total			100.00	1370.0	141.2	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



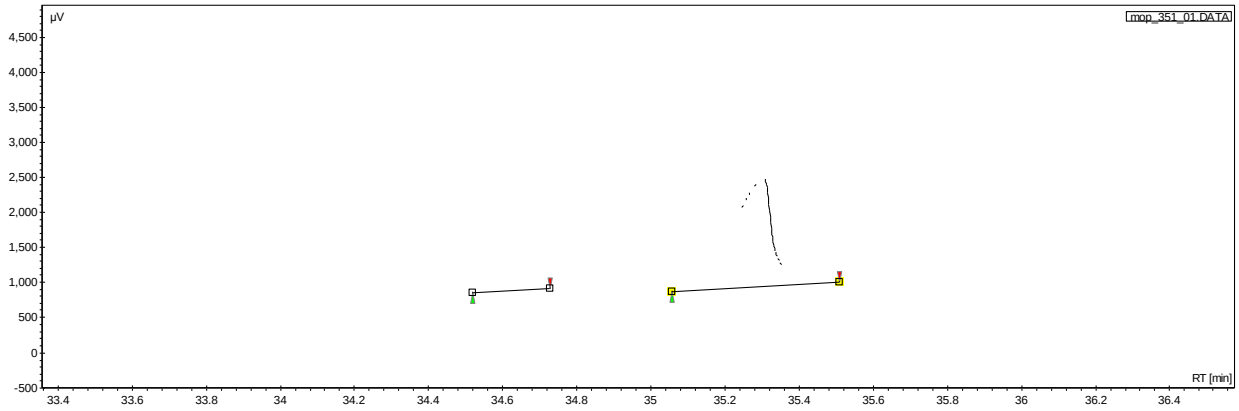
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	34.79	3.47	114.9	24.9	3.471
	1	UNKNOWN	35.62	96.53	2789.3	692.9	96.529
▶							
	Total			100.00	2904.2	717.8	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



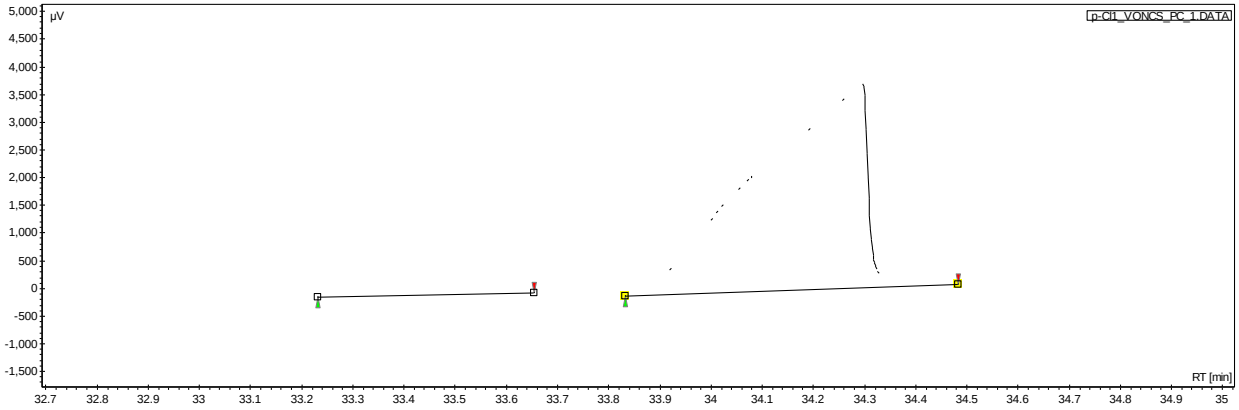
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	34.88	12.15	446.4	69.2	12.153
	2	UNKNOWN	35.63	87.85	2487.2	500.1	87.847
▶							
	Total			100.00	2933.6	569.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 7)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	34.62	10.05	258.1	24.7	10.051
	2	UNKNOWN	35.30	89.95	1554.5	221.5	89.949
▶							
	Total			100.00	1812.6	246.2	100.000

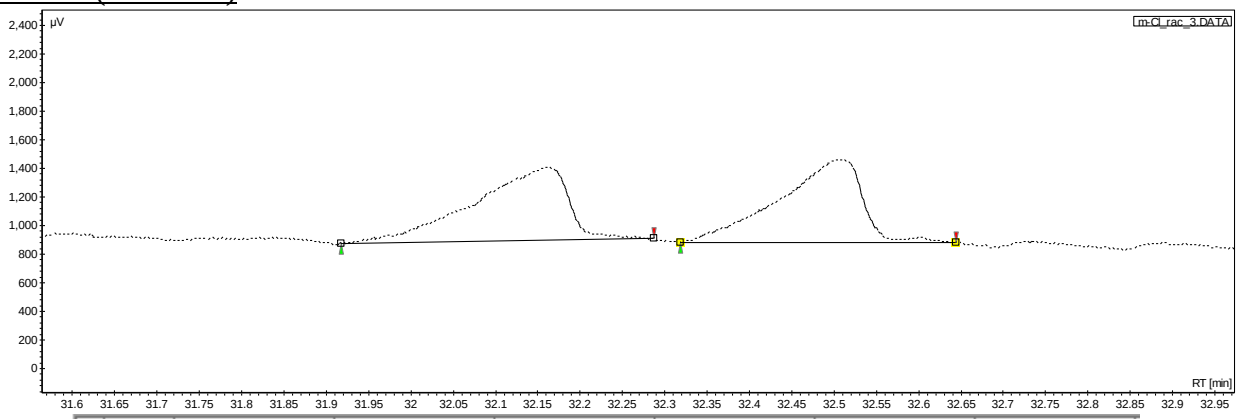
Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 3)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	33.49	13.02	577.3	135.7	13.019
	2	UNKNOWN	34.30	86.98	3689.2	906.7	86.981
▶							
	Total			100.00	4266.5	1042.4	100.000

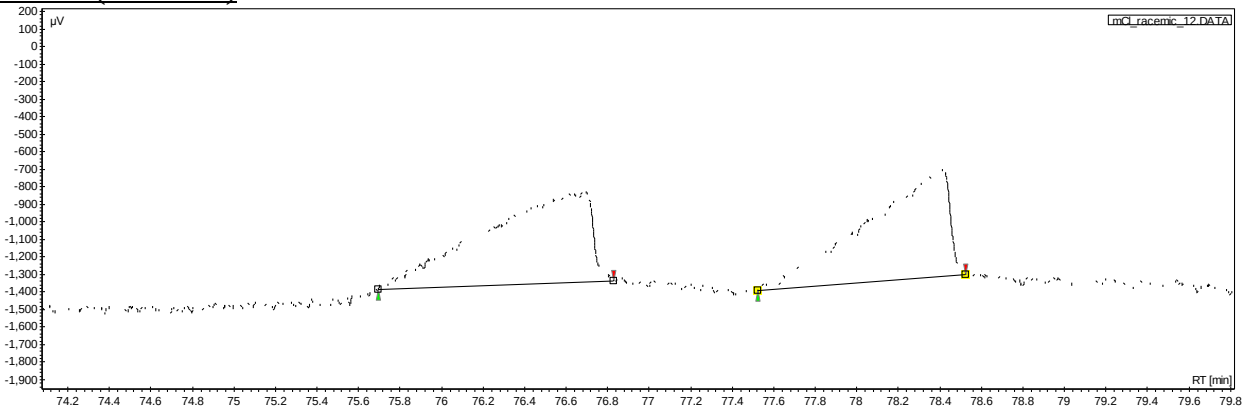
Cyanohydrin acetate derived from 3-chlorobenzaldehyde (Analysed using GC methods 3 or 4).

Racemate (method 3)



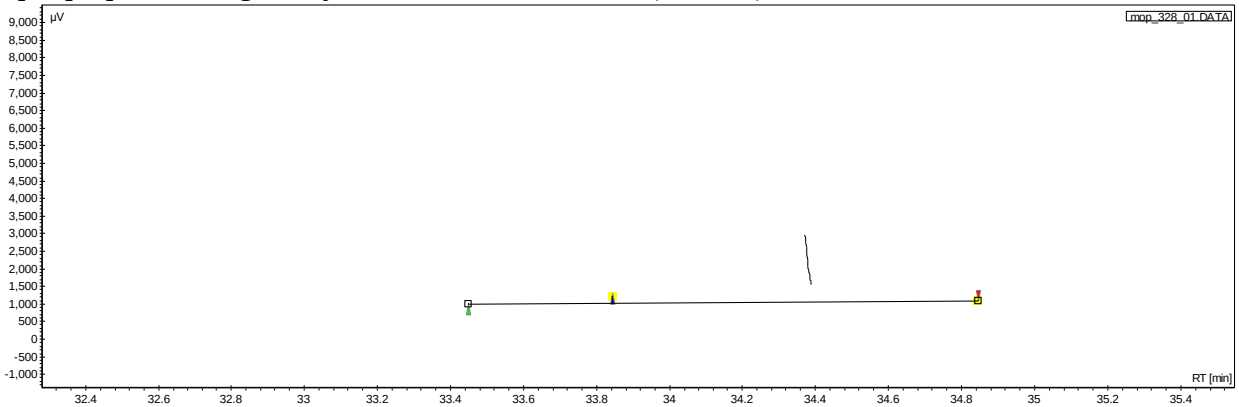
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	32.16	49.65	513.7	66.1	49.646
2	UNKNOWN	32.51	50.35	583.5	67.0	50.354
Total			100.00	1097.1	133.1	100.000

Racemate (method 4)



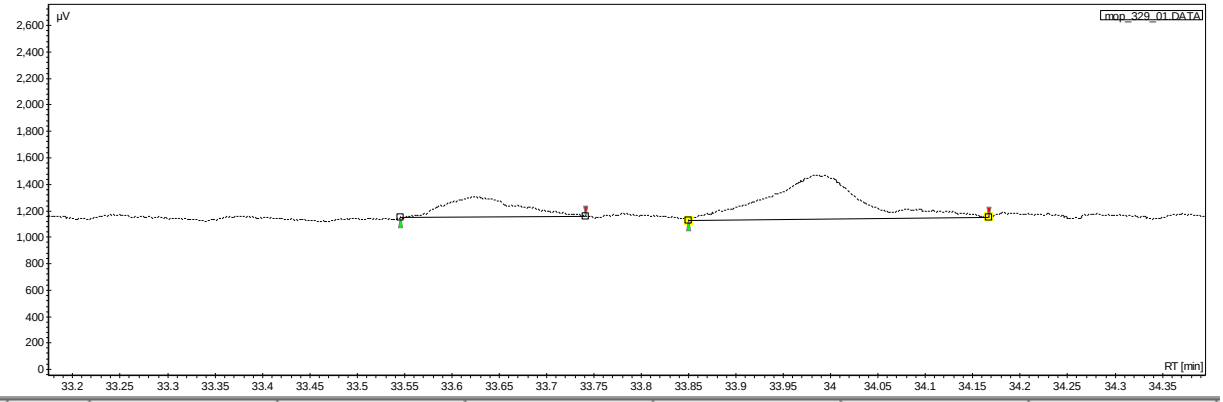
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
2	UNKNOWN	76.68	52.60	528.2	311.1	52.598
1	UNKNOWN	78.41	47.40	607.6	280.4	47.402
Total			100.00	1135.8	591.5	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



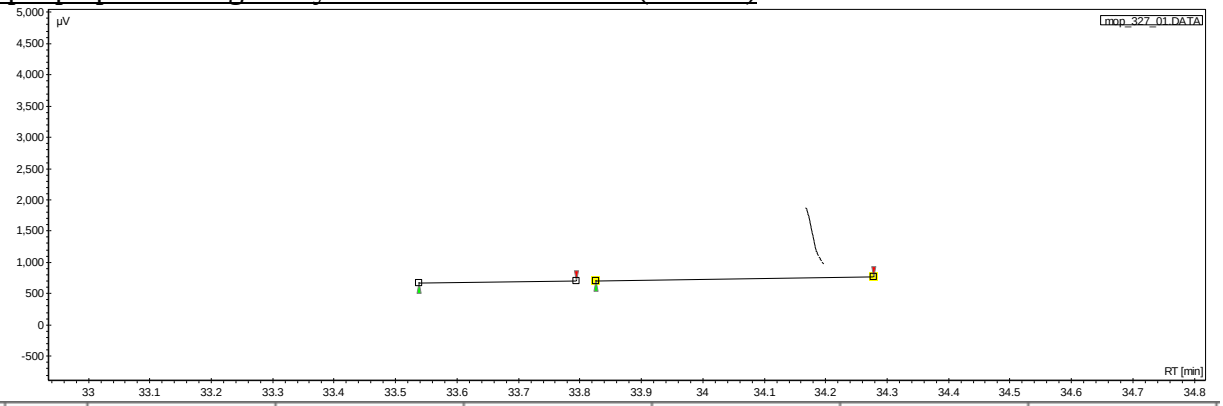
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	33.84	7.76	192.7	48.7	7.761
2	UNKNOWN	34.36	92.24	1973.8	579.0	92.239
Total			100.00	2166.5	627.7	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



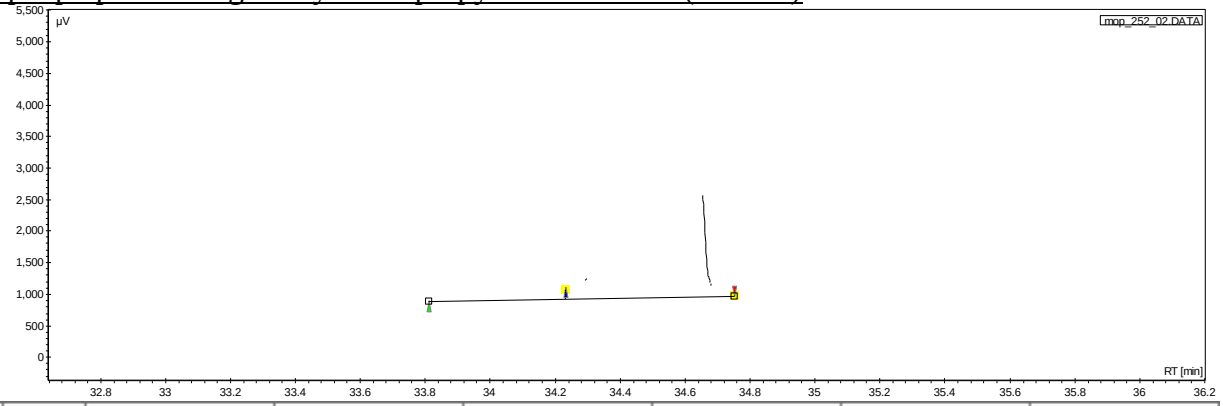
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	33.62	26.76	150.2	13.9	26.759
	2	UNKNOWN	33.99	73.24	327.5	38.0	73.241
▶							
	Total			100.00	477.7	51.8	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



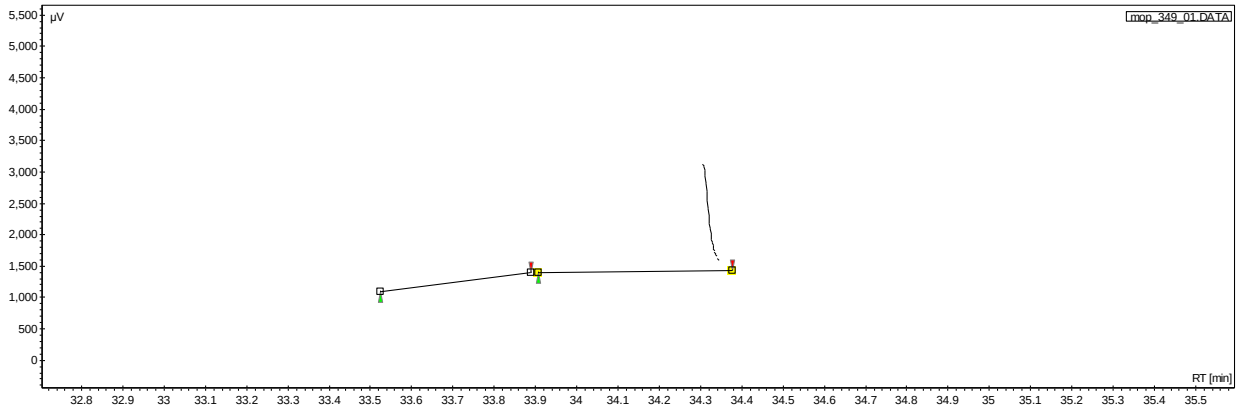
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	33.63	5.64	95.1	12.0	5.637
	1	UNKNOWN	34.16	94.36	1154.1	200.2	94.363
▶							
	Total			100.00	1249.1	212.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



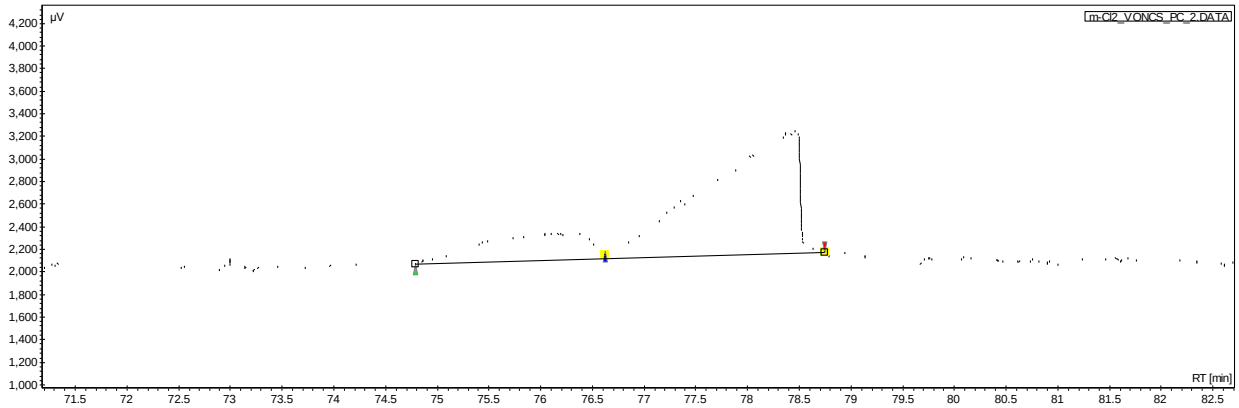
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	34.14	18.81	320.1	91.6	18.814
	2	UNKNOWN	34.65	81.19	1634.3	395.1	81.186
▶							
	Total			100.00	1954.4	486.7	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 6)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	33.74	9.14	161.6	36.5	9.142
	2	UNKNOWN	34.30	90.86	1706.8	362.6	90.858
▶							
	Total			100.00	1868.4	399.0	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 12)

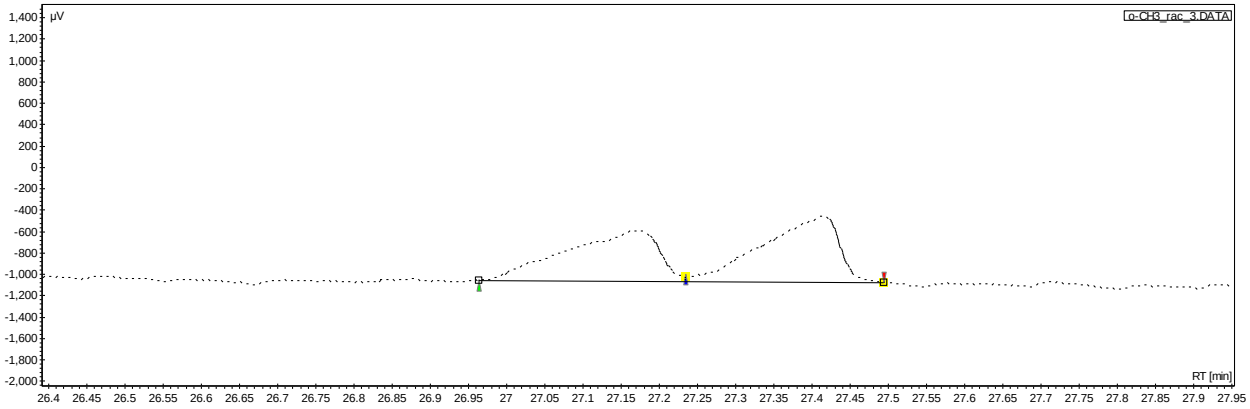


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	76.25	21.28	245.5	298.3	21.282
	2	UNKNOWN	78.47	78.72	1108.7	1103.4	78.718
▶							
	Total			100.00	1354.2	1401.8	100.000

Cyanohydrin acetate derived from 2-methylbenzaldehyde

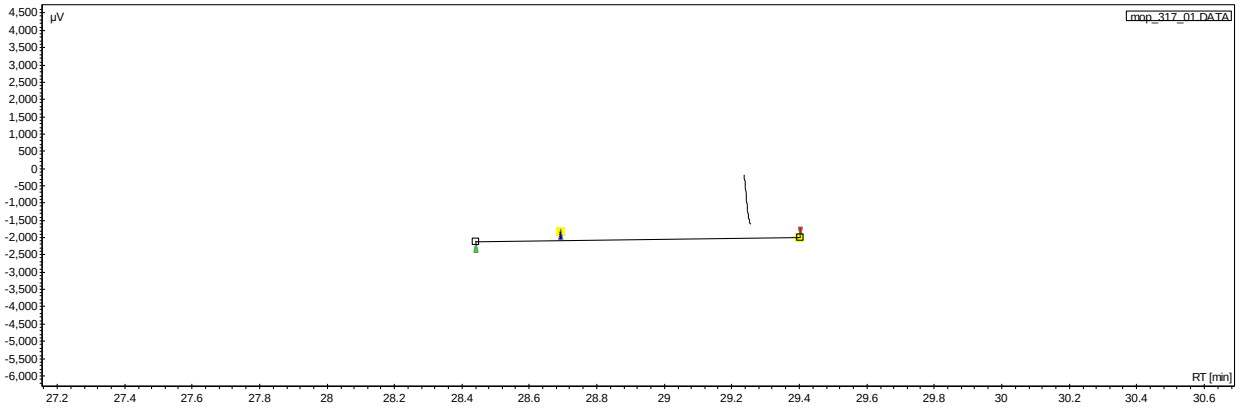
Analysed using GC method 3.

Racemate



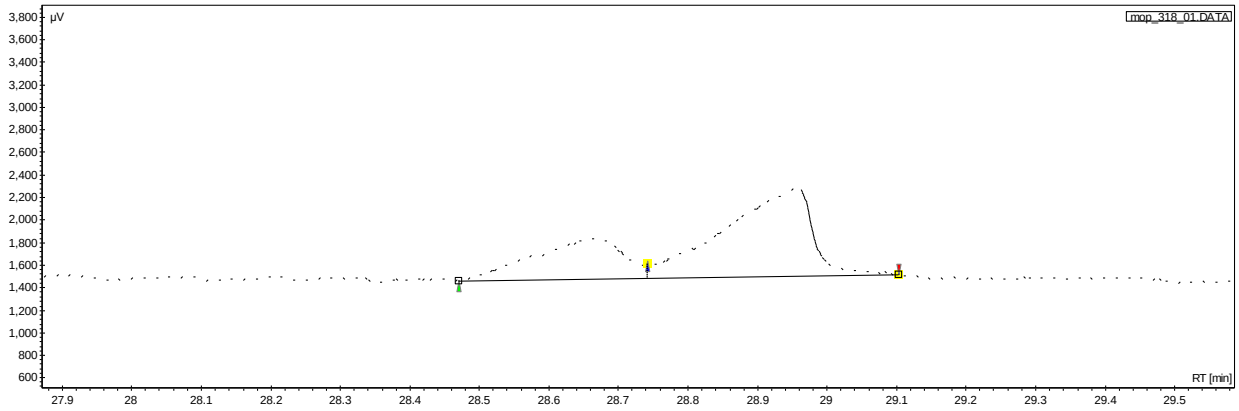
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	27.17	48.38	473.3	67.3	48.382
	2	UNKNOWN	27.42	51.62	619.3	71.8	51.618
▶							
	Total			100.00	1092.6	139.1	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



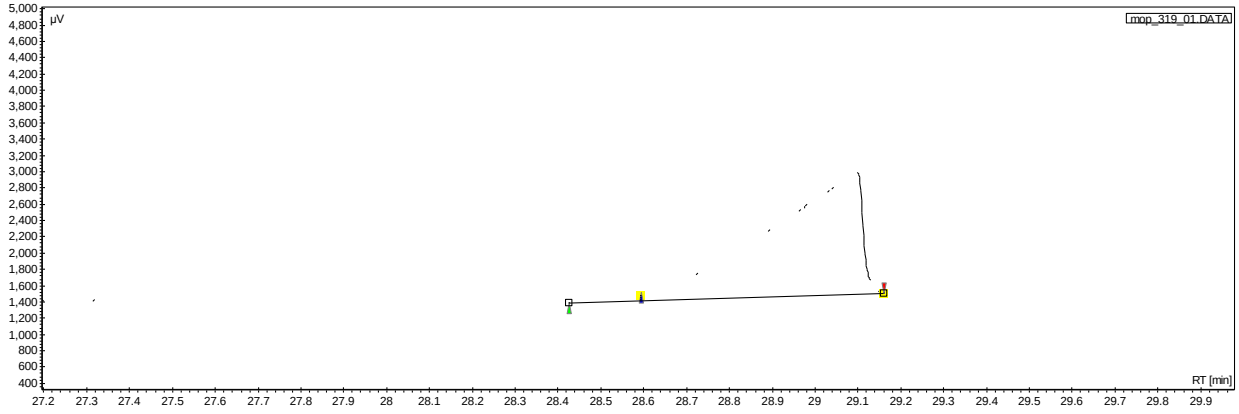
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	28.69	5.72	256.1	36.5	5.724
	2	UNKNOWN	29.23	94.28	1891.2	601.3	94.276
▶							
	Total			100.00	2147.3	637.8	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



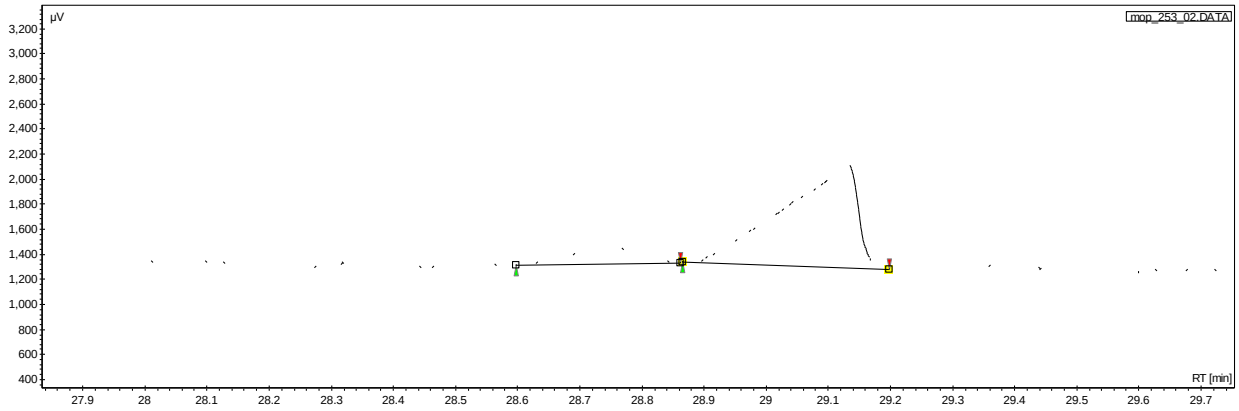
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	28.67	31.94	361.8	54.0	31.943
	2	UNKNOWN	28.96	68.06	782.9	115.0	68.057
▶							
	Total			100.00	1144.7	168.9	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



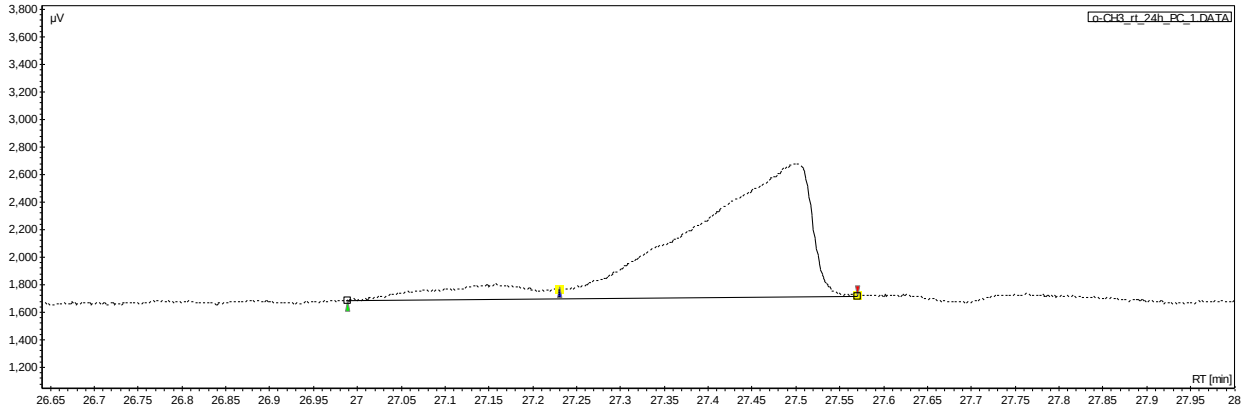
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	28.56	2.20	77.4	8.6	2.195
	2	UNKNOWN	29.10	97.80	1490.6	384.3	97.805
▶							
	Total			100.00	1568.1	392.9	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	28.74	13.68	127.2	18.0	13.675
2	UNKNOWN	29.13	86.32	825.4	113.5	86.325
Total			100.00	952.6	131.5	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 9)

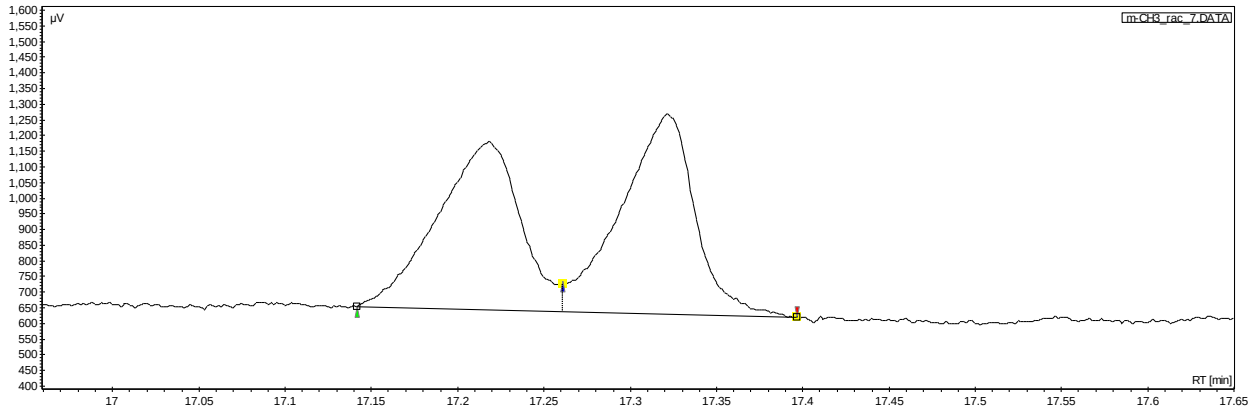


#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	27.16	9.56	100.3	15.4	9.558
2	UNKNOWN	27.50	90.44	961.7	145.3	90.442
Total			100.00	1062.0	160.6	100.000

Cyanohydrin acetate derived from 3-methylbenzaldehyde

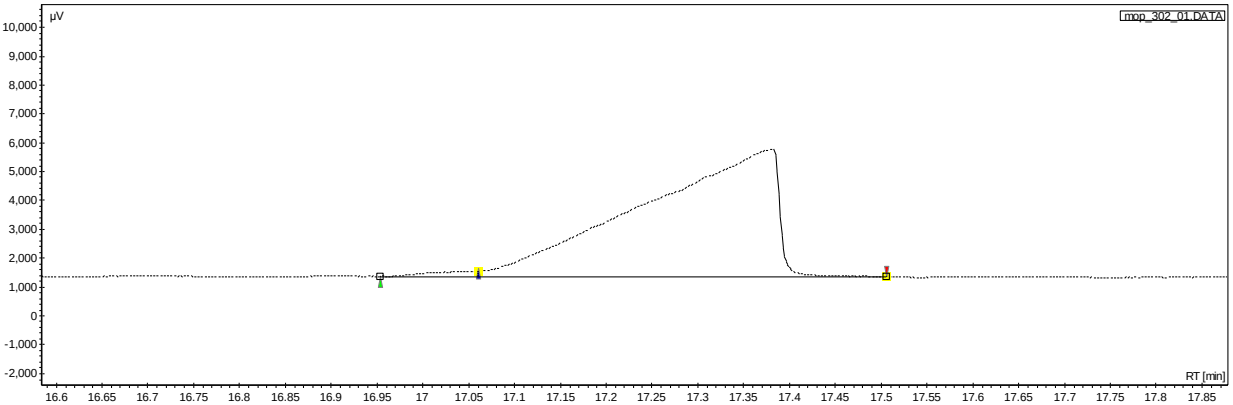
Analysed using GC method 5.

Racemate



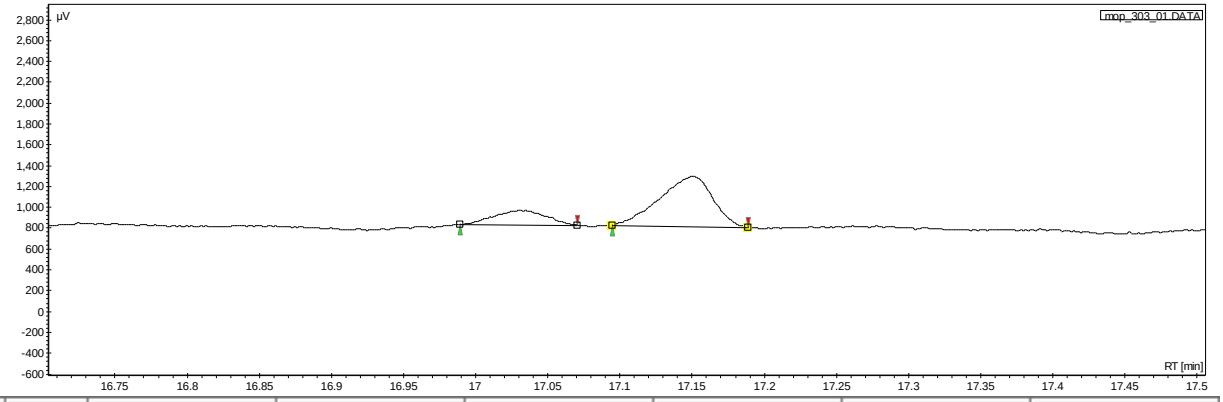
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	17.22	48.45	535.5	29.8	48.450
	2	UNKNOWN	17.32	51.55	638.7	31.7	51.550
▶							
	Total			100.00	1174.2	61.6	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



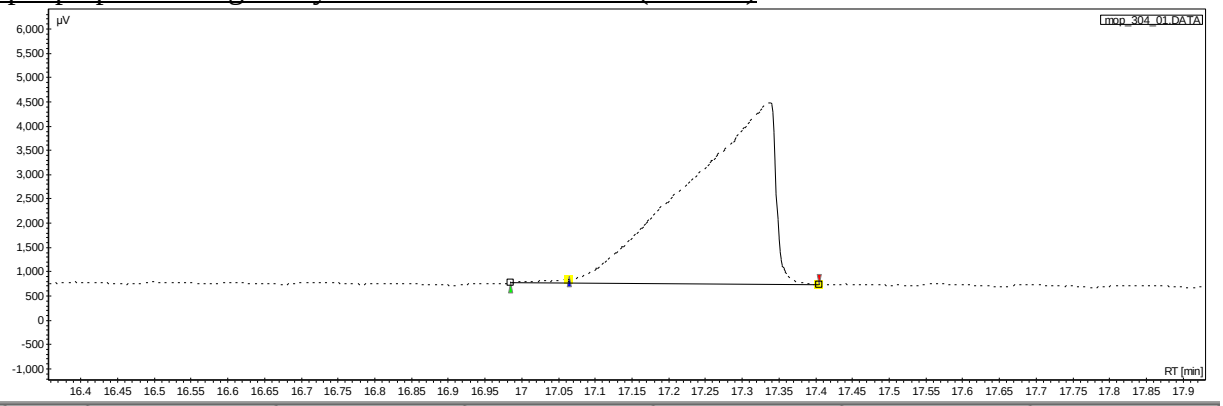
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	17.06	1.45	180.4	11.1	1.450
	2	UNKNOWN	17.38	98.55	4434.4	751.2	98.550
▶							
	Total			100.00	4614.9	762.3	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



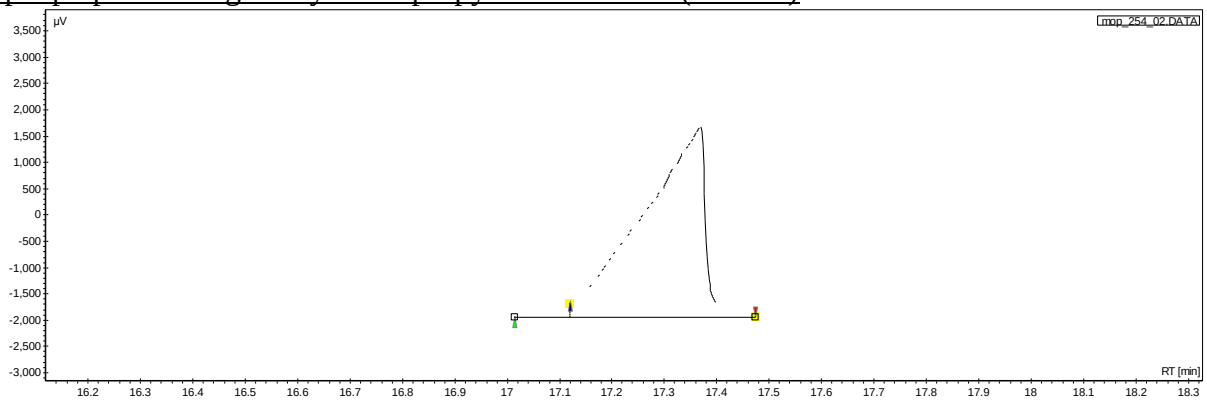
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	17.03	21.68	136.6	5.7	21.679
	2	UNKNOWN	17.15	78.32	486.1	20.5	78.321
▶							
	Total			100.00	622.6	26.2	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



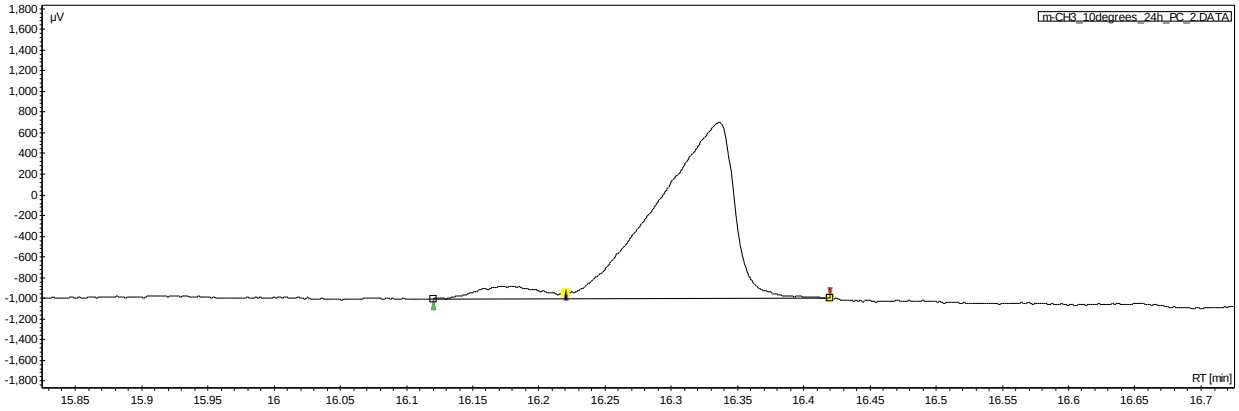
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	17.06	0.59	77.2	3.1	0.590
	2	UNKNOWN	17.34	99.41	3749.6	515.8	99.410
▶							
	Total			100.00	3826.8	518.9	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



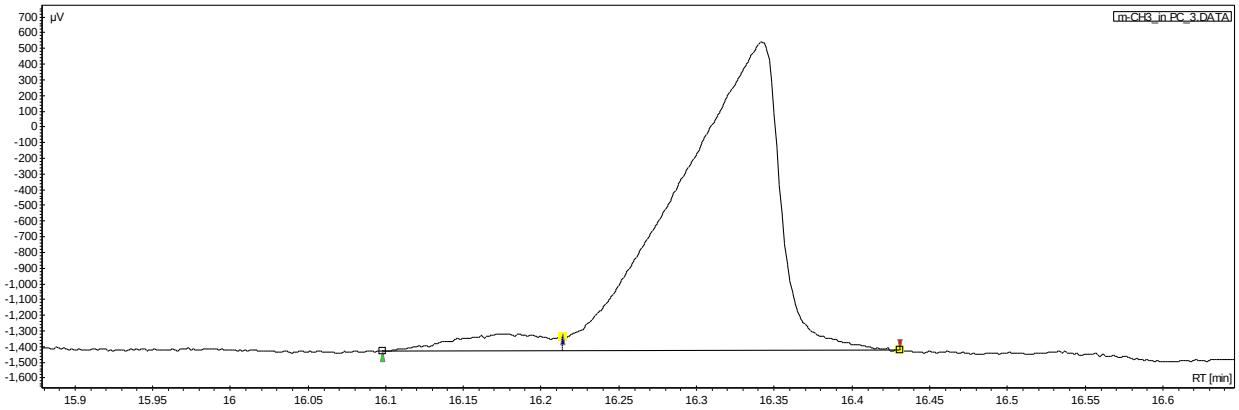
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	17.12	3.49	248.9	17.9	3.488
	2	UNKNOWN	17.37	96.51	3623.0	494.3	96.512
▶							
	Total			100.00	3871.9	512.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 10)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.18	5.57	110.9	6.8	5.574
	2	UNKNOWN	16.34	94.43	1701.4	114.6	94.426
▶							
	Total			100.00	1812.3	121.4	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 7)

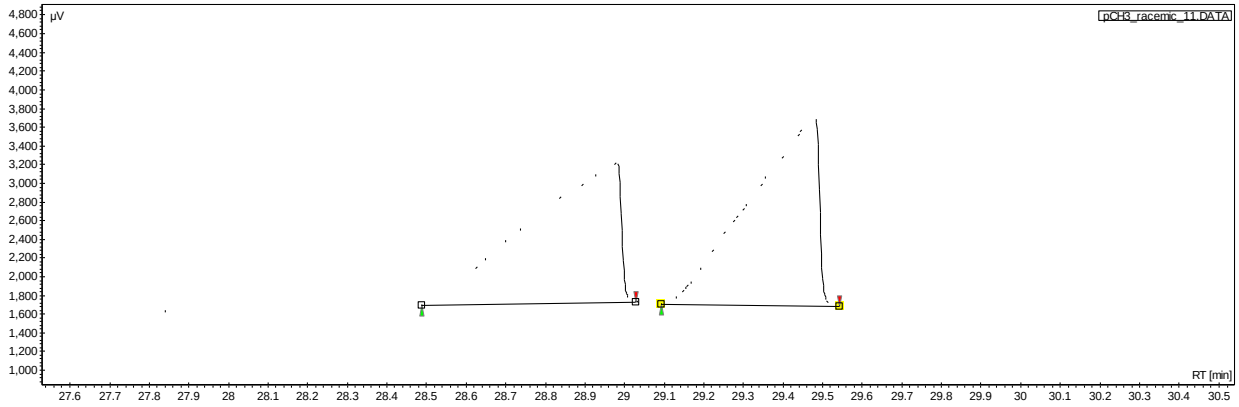


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.18	4.85	102.6	7.5	4.850
▶	2	UNKNOWN	16.34	95.15	1964.7	146.7	95.150
	Total			100.00	2067.3	154.2	100.000

Cyanohydrin acetate derived from 4-methylbenzaldehyde

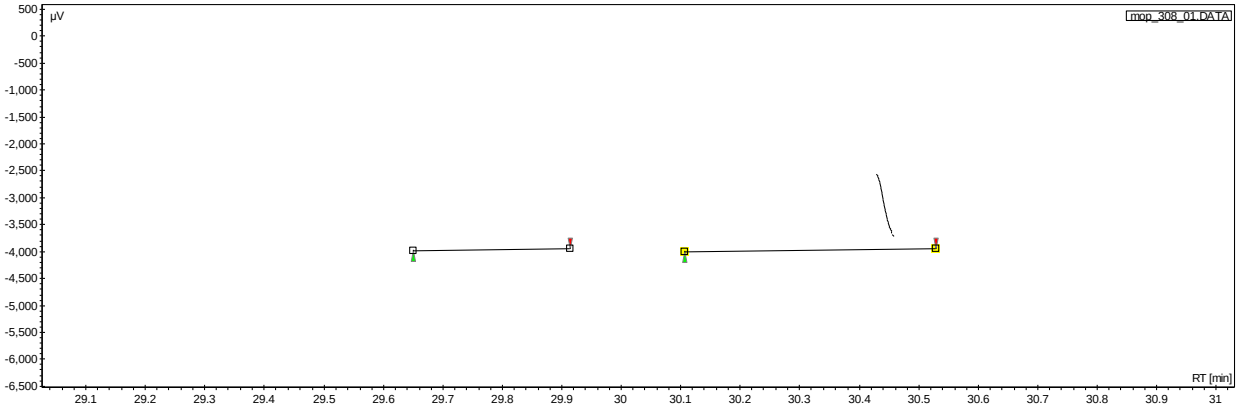
Analysed using GC method 3.

Racemate



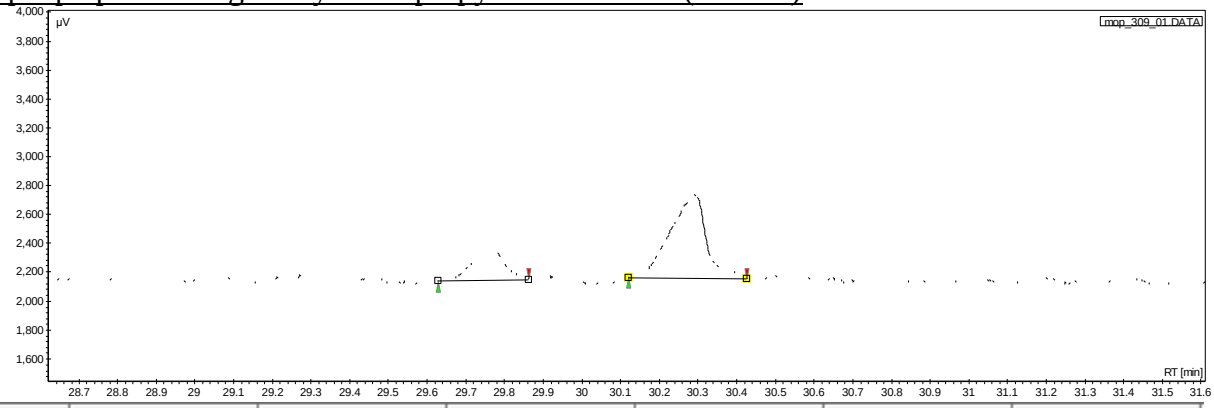
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	28.98	49.68	1492.5	396.4	49.683
	2	UNKNOWN	29.48	50.32	2011.9	401.5	50.317
▶							
	Total			100.00	3504.4	797.9	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



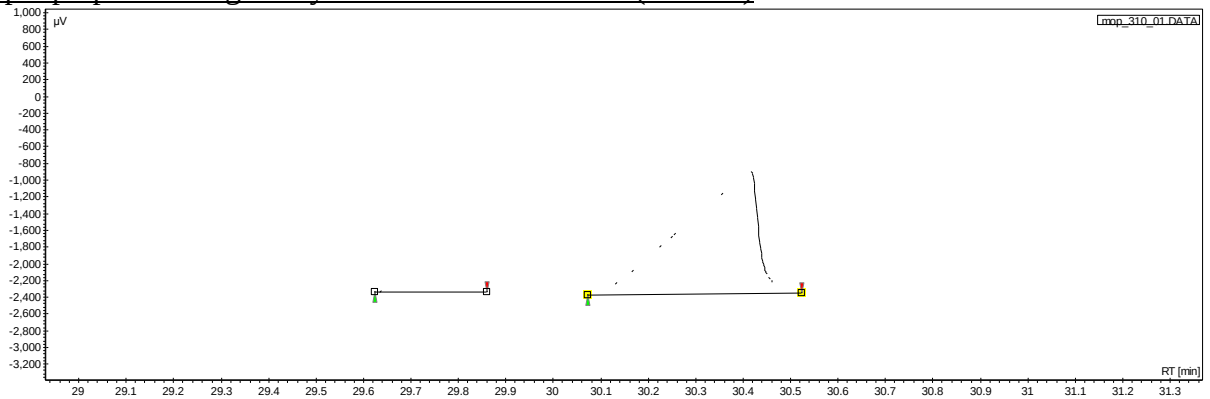
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	29.82	15.79	329.8	47.5	15.790
	2	UNKNOWN	30.43	84.21	1406.5	253.5	84.210
▶							
	Total			100.00	1736.2	301.1	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



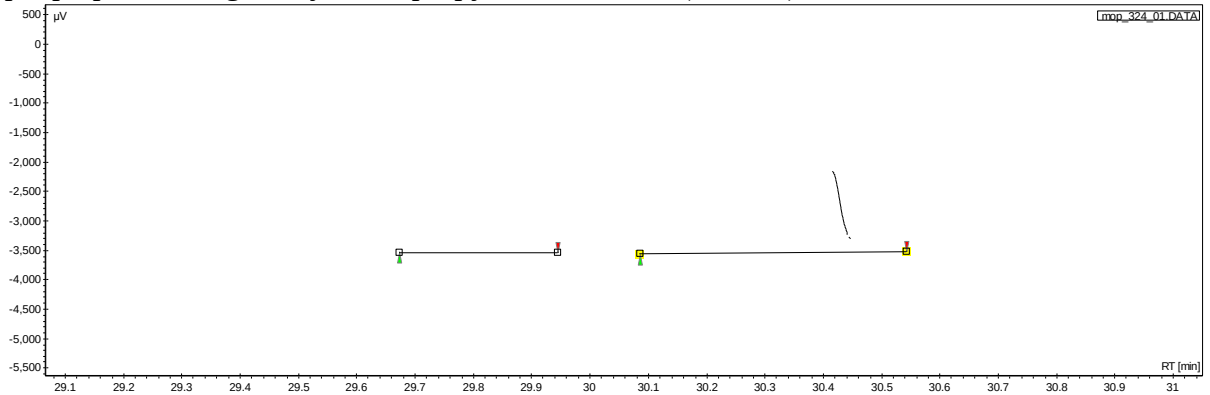
	#	Name	Time [Min]	Quantity [% Area	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	29.76	25.28	224.1	21.4	25.283
	2	UNKNOWN	30.29	74.72	579.2	63.3	74.717
▶							
	Total			100.00	803.3	84.8	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



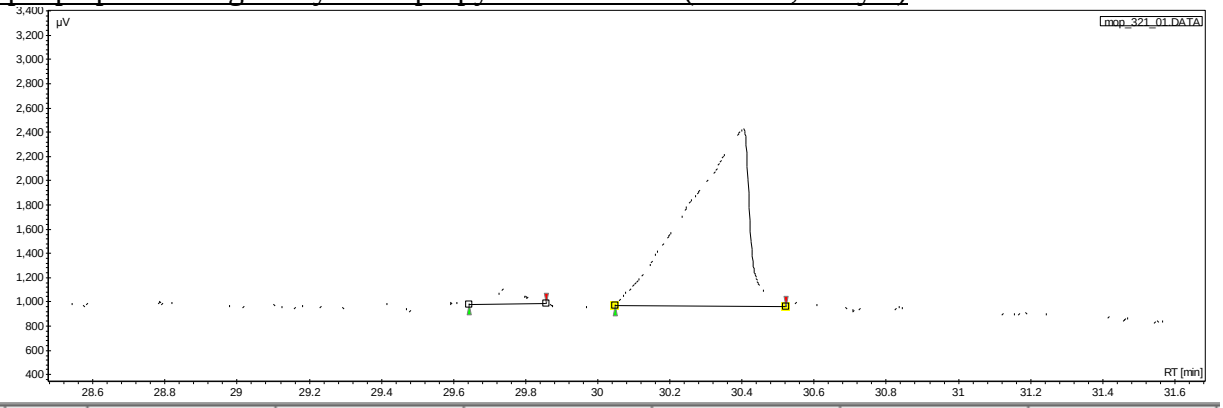
	#	Name	Time [Min]	Quantity [% Area	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	29.77	6.39	140.4	18.1	6.389
	2	UNKNOWN	30.42	93.61	1465.6	265.1	93.611
▶							
	Total			100.00	1606.0	283.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



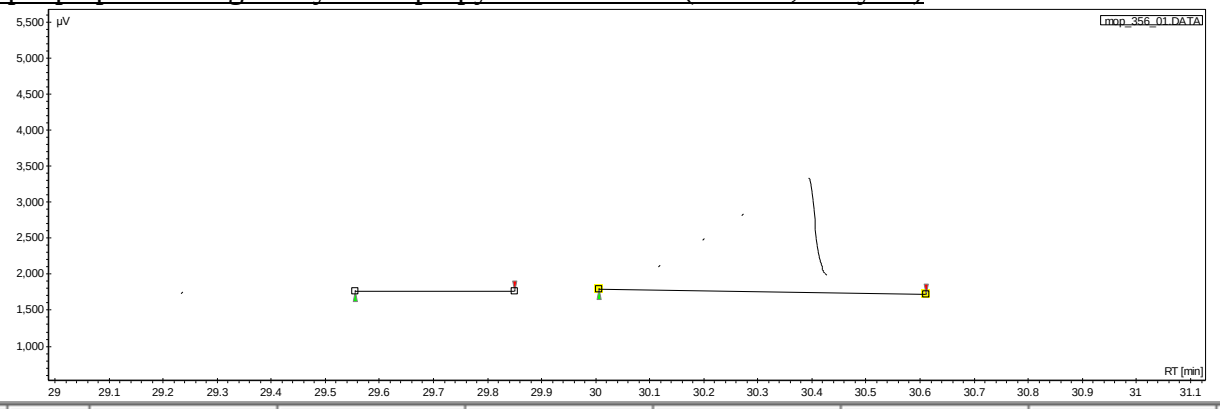
	#	Name	Time [Min]	Quantity [% Area	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	29.78	6.87	140.1	18.2	6.874
	1	UNKNOWN	30.41	93.13	1396.2	246.3	93.126
▶							
	Total			100.00	1536.4	264.5	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 8)



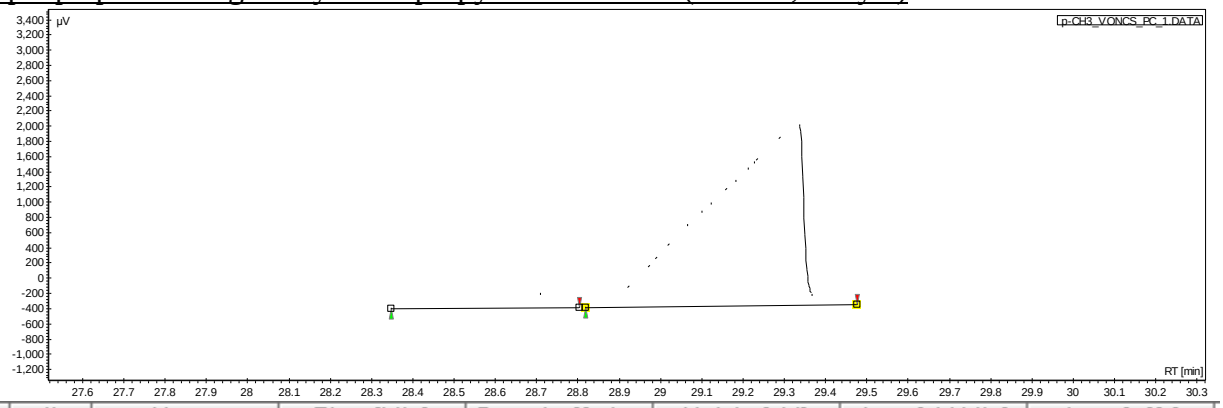
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	29.74	4.89	133.2	14.8	4.891
	1	UNKNOWN	30.40	95.11	1462.1	288.4	95.109
▶							
	Total			100.00	1595.3	303.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 11)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	29.74	8.41	183.0	29.6	8.413
	2	UNKNOWN	30.39	91.59	1608.6	322.1	91.587
▶							
	Total			100.00	1791.6	351.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 4)

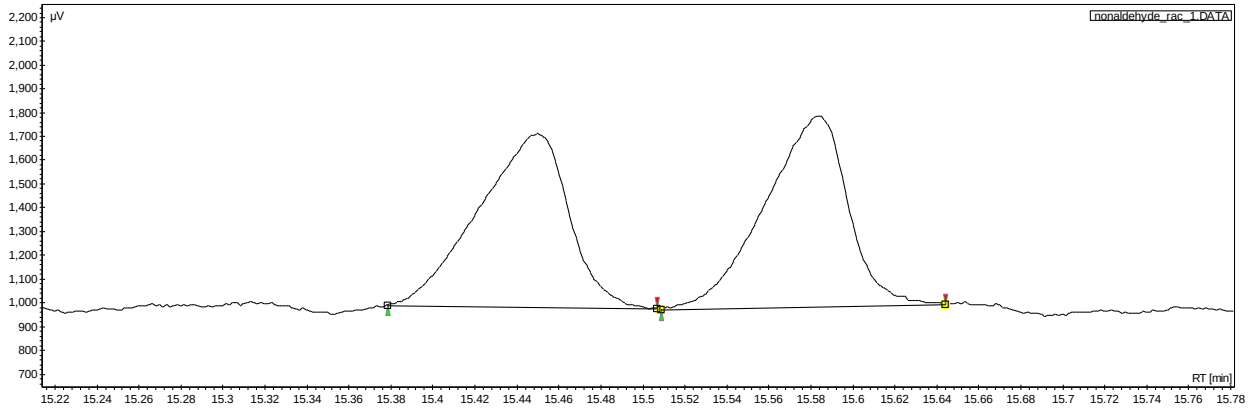


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	28.59	11.45	291.5	79.7	11.453
	2	UNKNOWN	29.34	88.55	2378.0	616.0	88.547
▶							
	Total			100.00	2669.5	695.7	100.000

Cyanohydrin acetate derived from nonanal

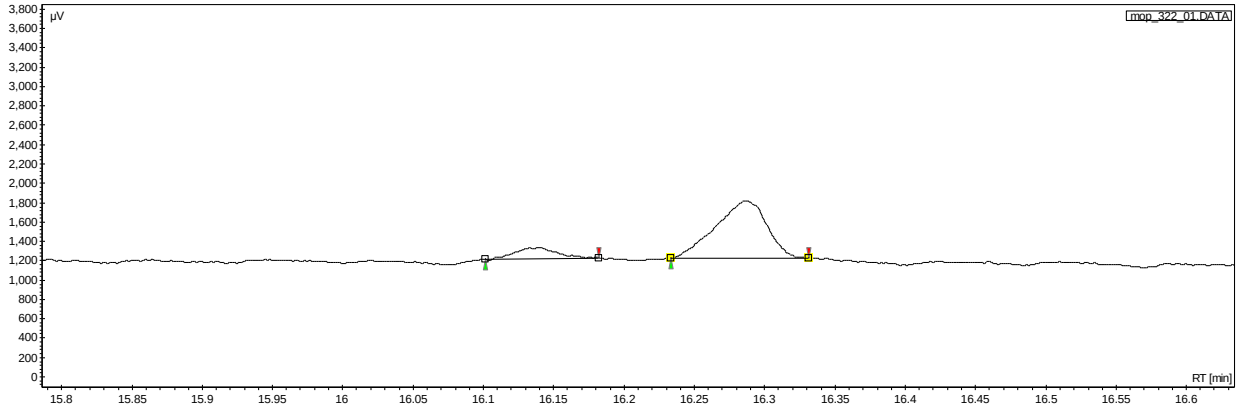
Analysed using GC method 5.

Racemate



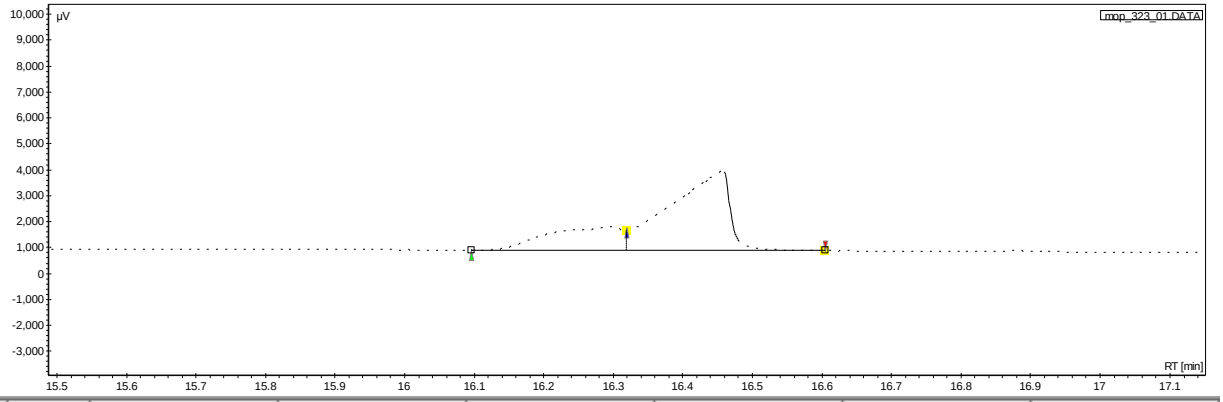
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.45	49.55	731.8	36.4	49.551
	2	UNKNOWN	15.58	50.45	803.7	37.1	50.449
▶							
	Total			100.00	1535.5	73.5	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



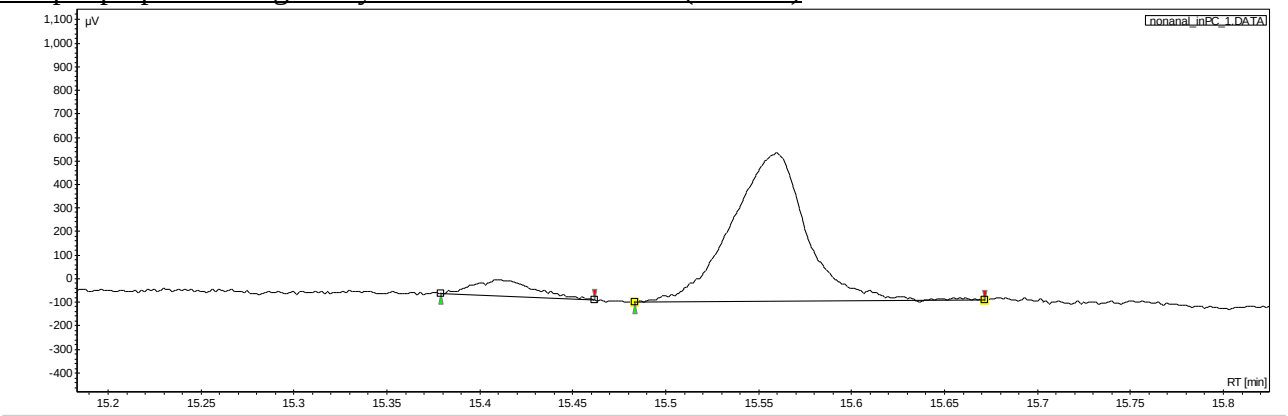
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.14	13.50	106.5	3.9	13.505
	2	UNKNOWN	16.29	86.50	586.6	25.1	86.495
▶							
	Total			100.00	693.1	29.0	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



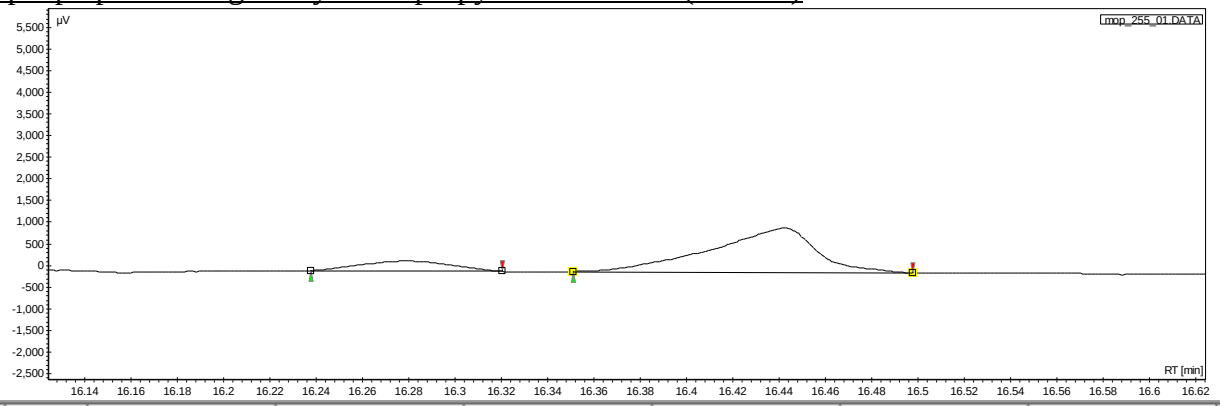
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.30	27.52	920.2	115.2	27.516
	2	UNKNOWN	16.46	72.48	3072.9	303.4	72.484
▶							
	Total			100.00	3993.1	418.6	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



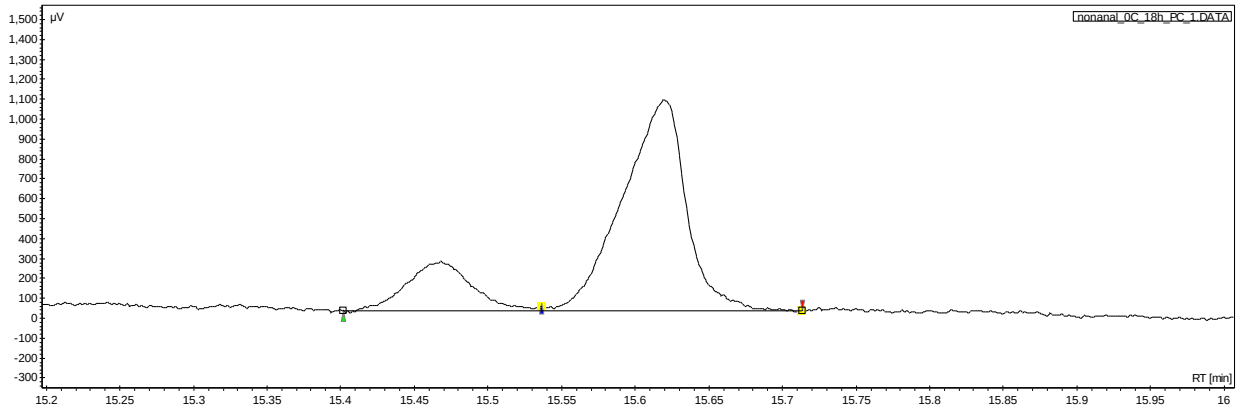
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	15.41	8.43	67.9	2.7	8.429
	1	UNKNOWN	15.56	91.57	618.6	29.0	91.571
▶							
	Total			100.00	686.5	31.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



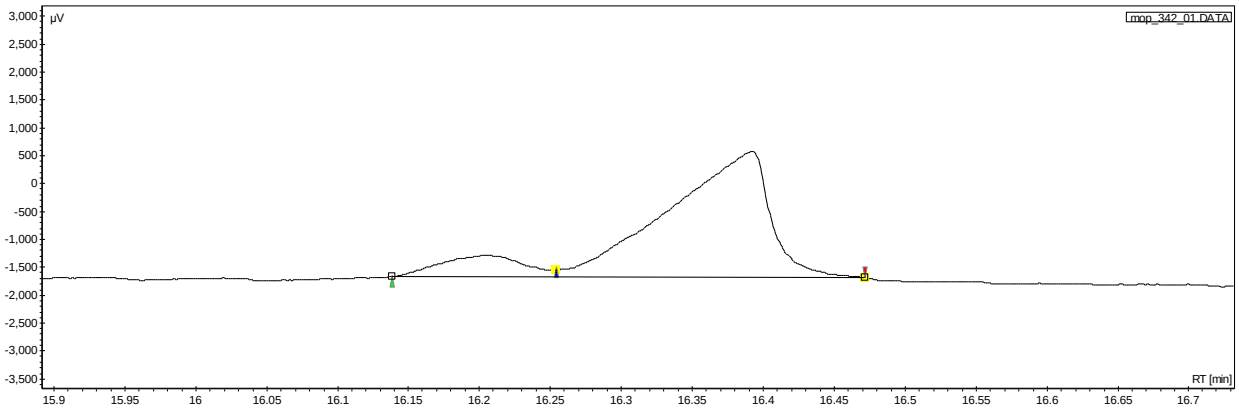
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.28	16.43	230.3	10.5	16.434
	2	UNKNOWN	16.44	83.57	1019.8	53.6	83.566
▶							
	Total			100.00	1250.2	64.2	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 12)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	15.47	19.46	244.2	13.0	19.460
	2	UNKNOWN	15.62	80.54	1059.8	53.6	80.540
▶							
	Total			100.00	1304.0	66.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 15)

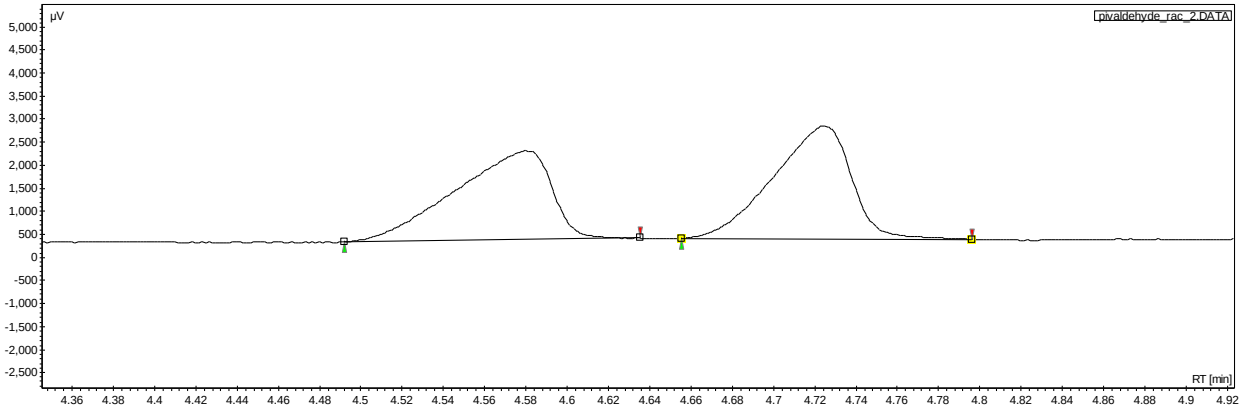


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.21	12.39	378.5	26.2	12.391
	2	UNKNOWN	16.39	87.61	2259.4	185.4	87.609
▶							
	Total			100.00	2637.9	211.7	100.000

Cyanohydrin acetate derived from pivaldehyde

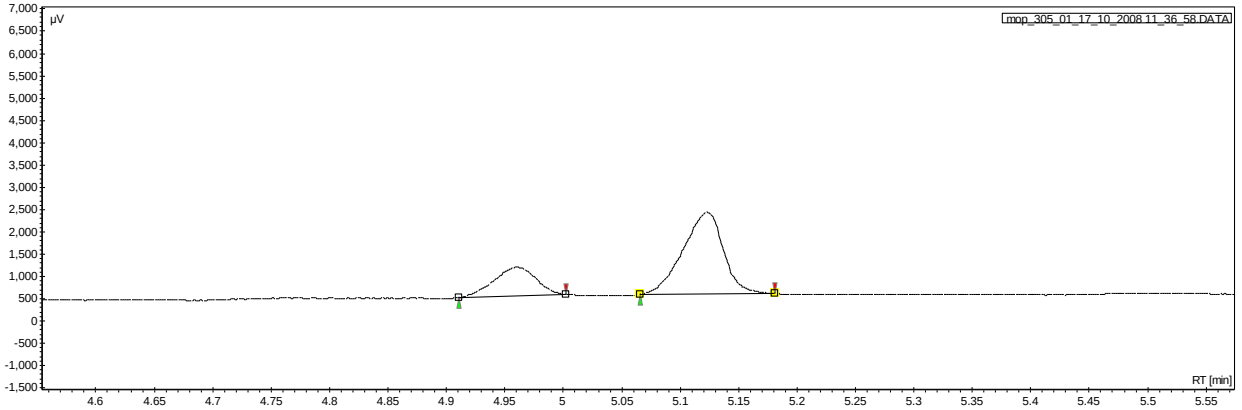
Analysed using GC method 5.

Racemate



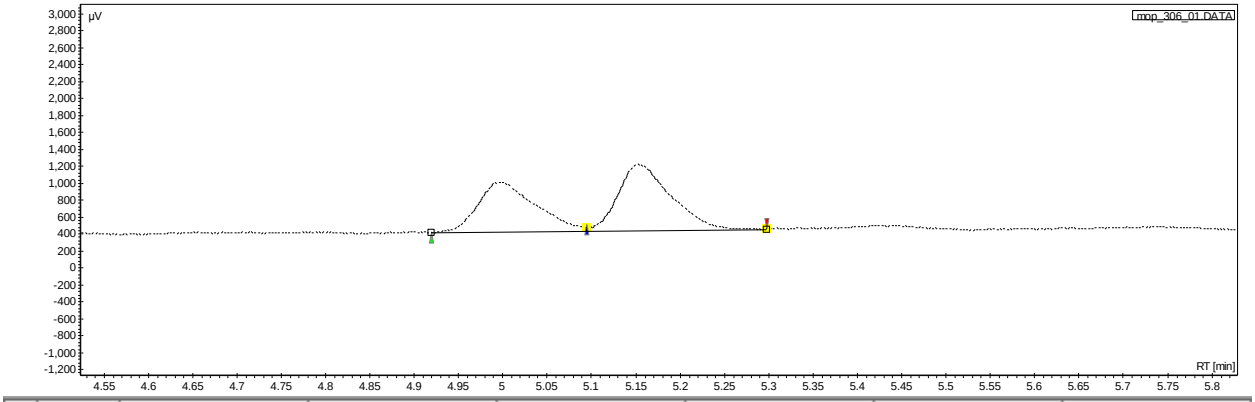
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	4.58	49.16	1917.7	103.2	49.157
	1	UNKNOWN	4.73	50.84	2449.9	106.7	50.843
▶							
	Total			100.00	4367.6	209.9	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



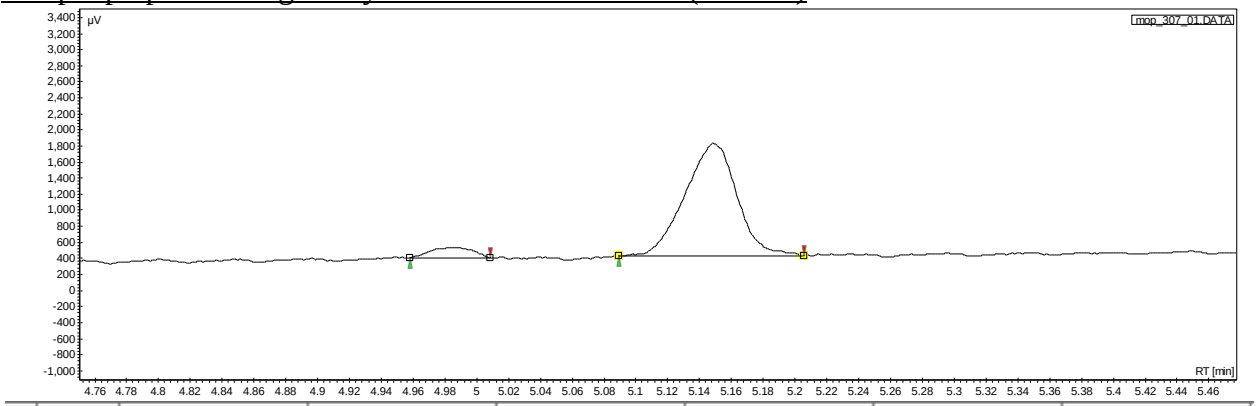
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	4.96	26.57	647.0	26.8	26.570
	2	UNKNOWN	5.12	73.43	1843.8	74.0	73.430
▶							
	Total			100.00	2490.8	100.7	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



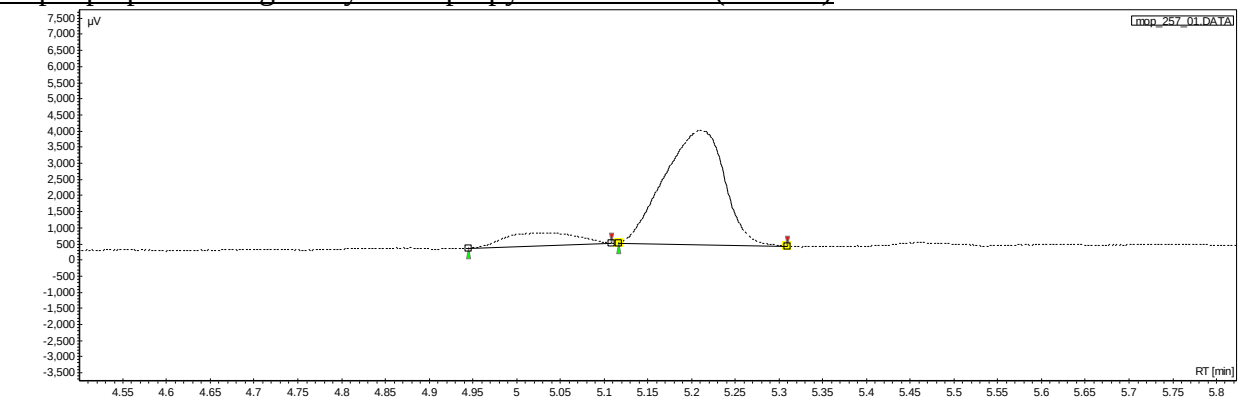
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	5.00	44.94	584.9	44.0	44.941
2	UNKNOWN	5.15	55.06	784.5	53.9	55.059
Total			100.00	1369.3	98.0	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



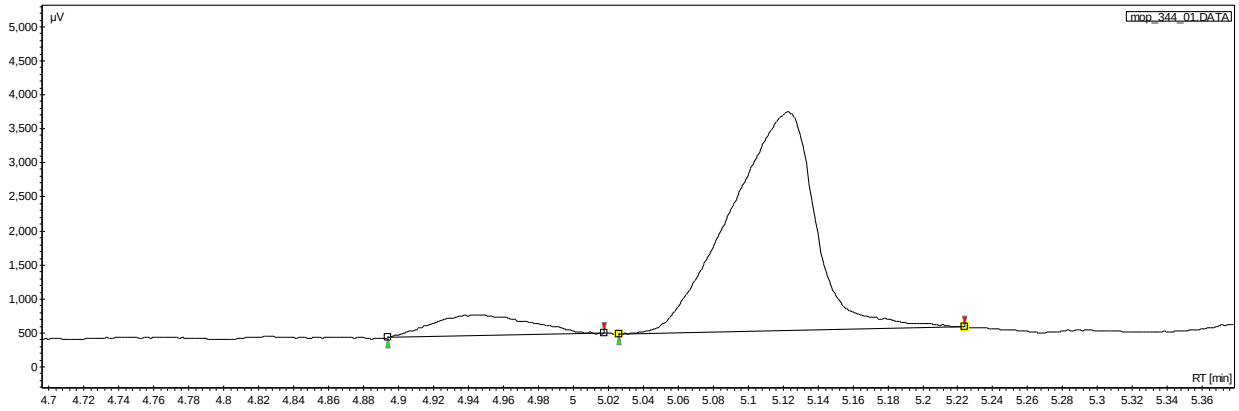
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	4.99	6.99	123.9	4.0	6.992
2	UNKNOWN	5.15	93.01	1401.9	53.0	93.008
Total			100.00	1525.8	57.0	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



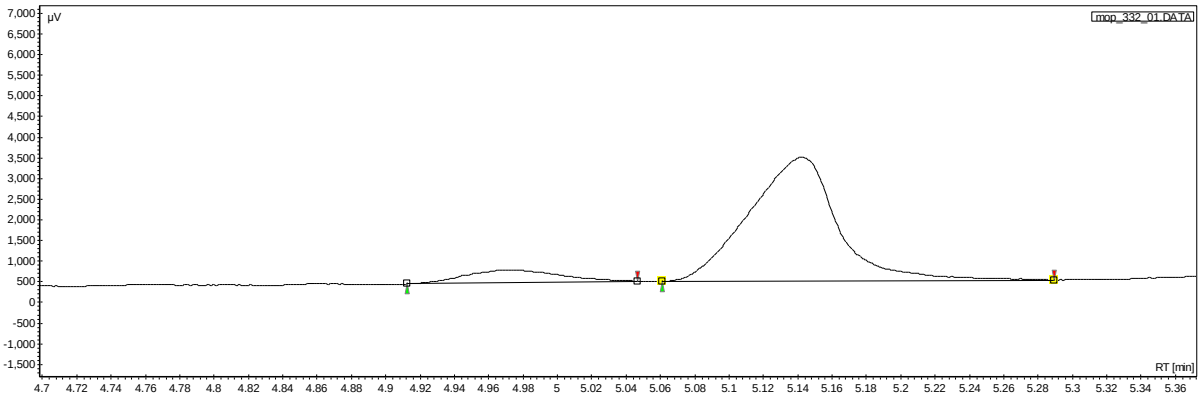
#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	5.03	12.12	408.2	38.9	12.115
2	UNKNOWN	5.21	87.88	3544.5	281.9	87.885
Total			100.00	3952.7	320.8	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 14)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	4.95	10.07	300.6	20.3	10.065
	2	UNKNOWN	5.12	89.93	3217.5	181.3	89.935
▶							
	Total			100.00	3518.2	201.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 17)

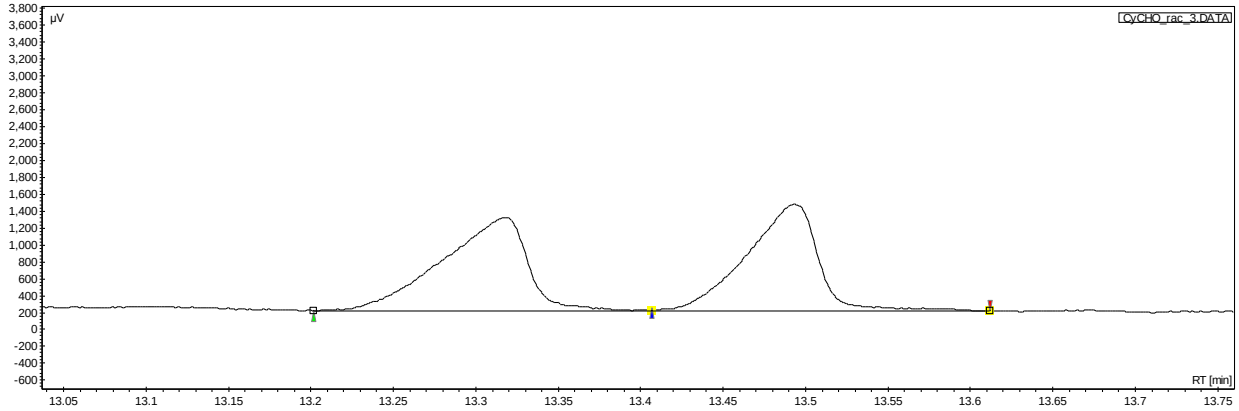


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	4.97	9.95	305.6	19.9	9.952
	2	UNKNOWN	5.14	90.05	2994.2	180.4	90.048
▶							
	Total			100.00	3299.8	200.4	100.000

Cyanohydrin acetate derived from cyclohexane carboxaldehyde

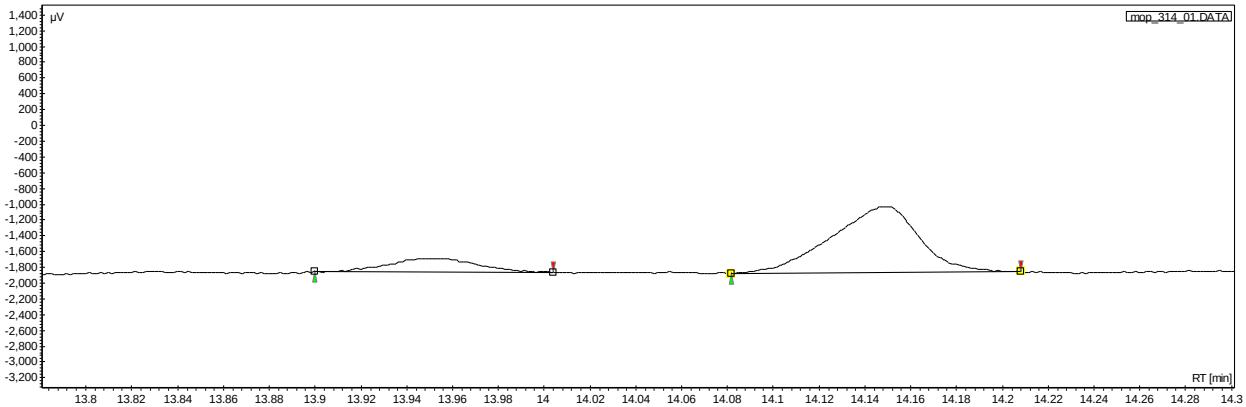
Analysed using GC method 5.

Racemate



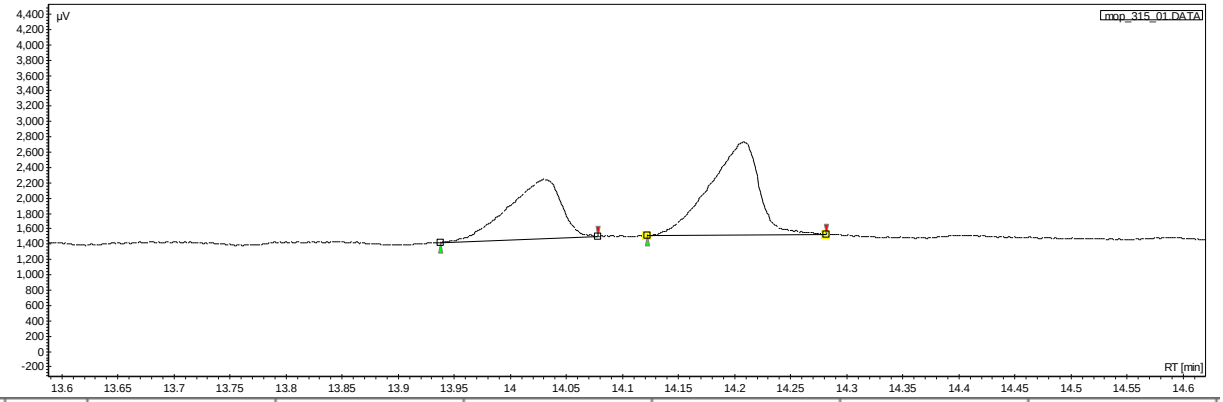
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	13.32	50.93	1104.2	65.8	50.929
	2	UNKNOWN	13.49	49.07	1263.5	63.4	49.071
▶							
	Total			100.00	2367.7	129.2	100.000

Sample prepared using catalyst **1** in dichloromethane (Table 1)



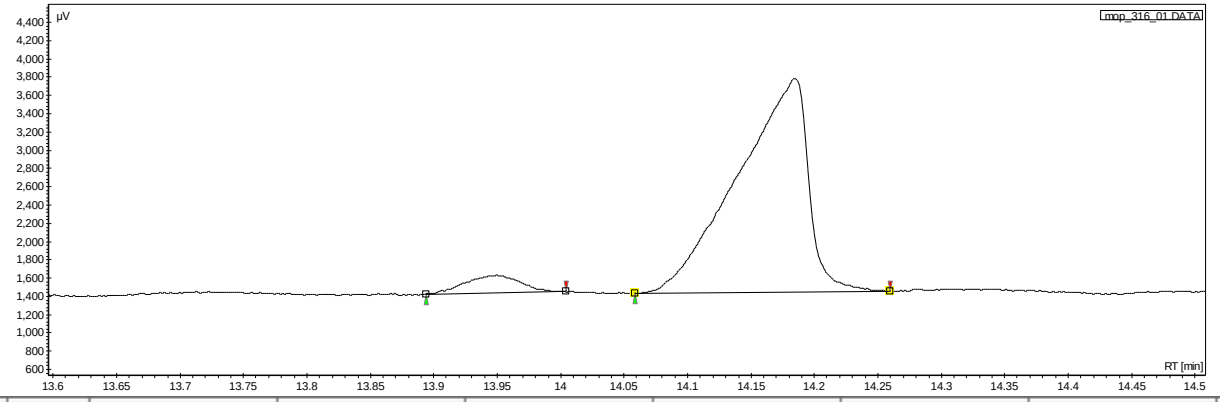
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	13.95	17.04	174.2	7.6	17.035
	2	UNKNOWN	14.15	82.96	831.7	36.9	82.965
▶							
	Total			100.00	1005.9	44.5	100.000

Sample prepared using catalyst **1** in propylene carbonate (Table 1)



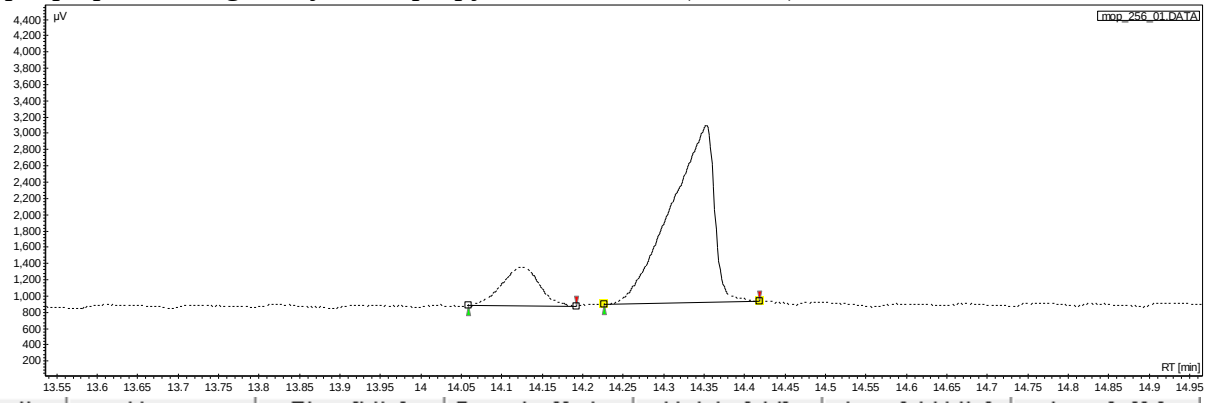
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.03	40.57	772.1	42.4	40.569
	2	UNKNOWN	14.21	59.43	1210.0	62.2	59.431
▶							
	Total			100.00	1982.1	104.6	100.000

Sample prepared using catalyst **2** in dichloromethane (Table 1)



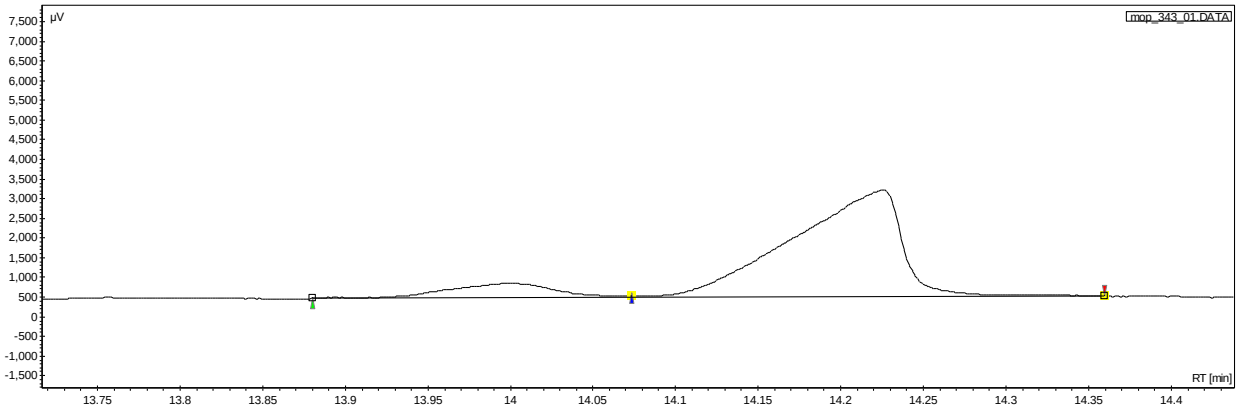
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	2	UNKNOWN	13.95	6.11	184.4	9.9	6.114
	1	UNKNOWN	14.19	93.89	2337.8	151.8	93.886
▶							
	Total			100.00	2522.2	161.7	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 1)



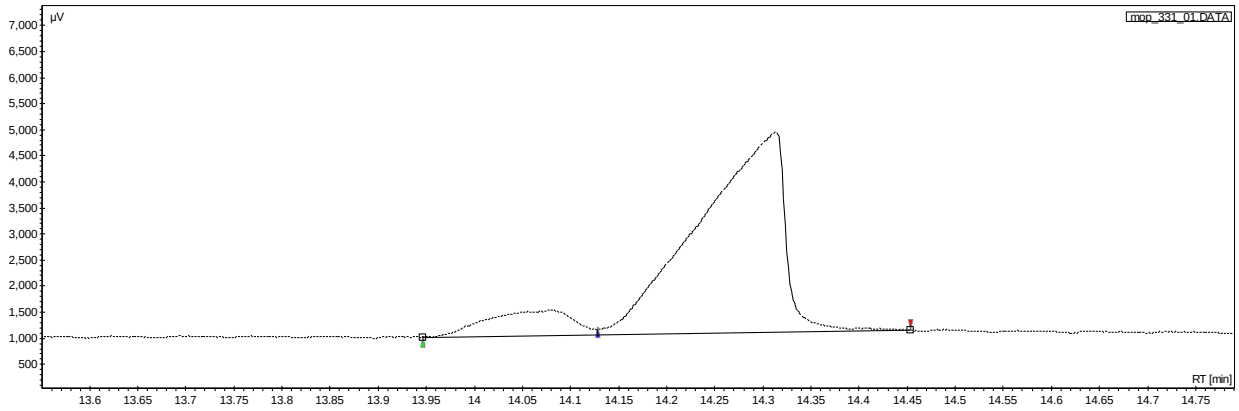
	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.13	16.43	481.9	26.4	16.427
	2	UNKNOWN	14.35	83.57	2169.3	134.4	83.573
▶							
	Total			100.00	2651.1	160.8	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 13)



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.00	11.98	367.8	28.6	11.983
	2	UNKNOWN	14.23	88.02	2718.8	210.0	88.017
▶							
	Total			100.00	3086.6	238.6	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 2, entry 16)

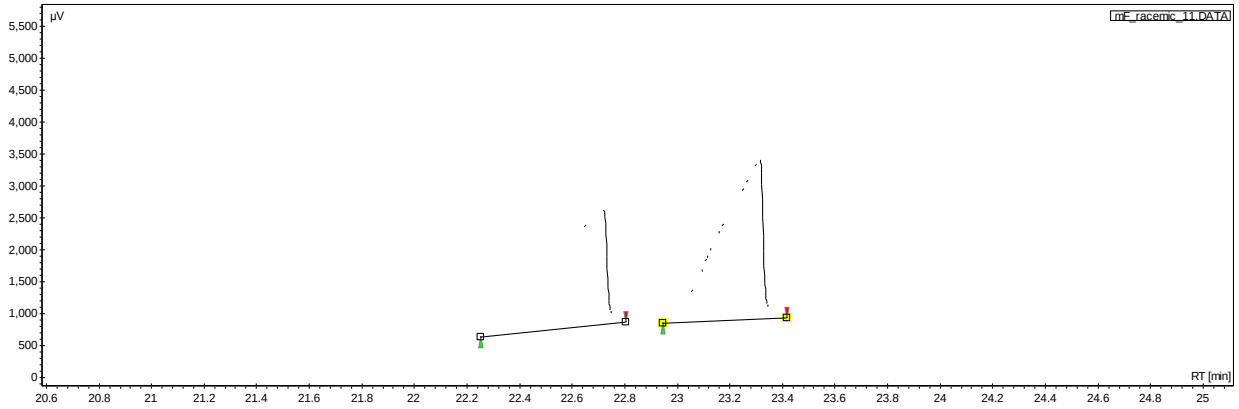


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.08	11.27	480.2	50.6	11.274
	2	UNKNOWN	14.31	88.73	3842.0	398.1	88.726
▶							
	Total			100.00	4322.2	448.7	100.000

Cyanohydrin acetate derived from 3-fluorobenzaldehyde

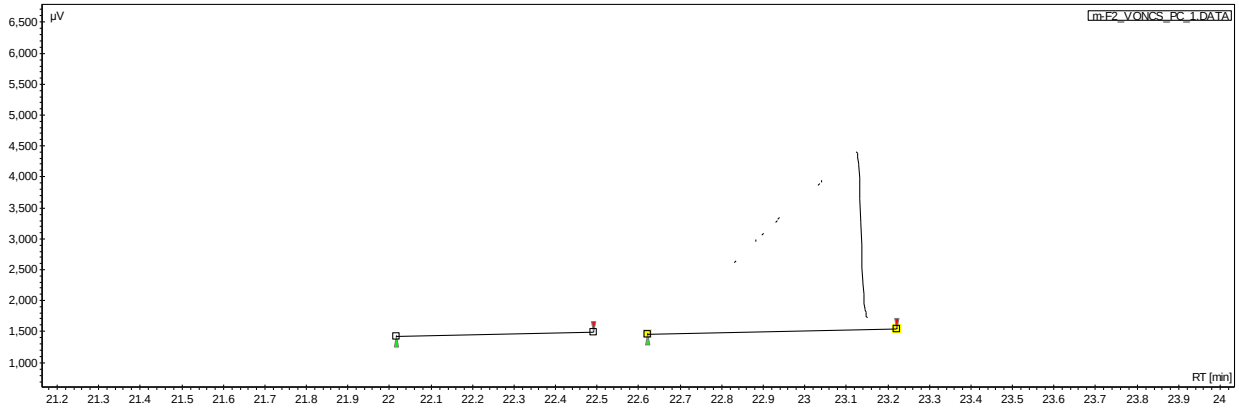
Analysed using GC method 3.

Racemate



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	22.71	50.14	1828.7	462.9	50.142
	2	UNKNOWN	23.31	49.86	2496.6	460.3	49.858
▶							
	Total			100.00	4325.3	923.1	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 6)

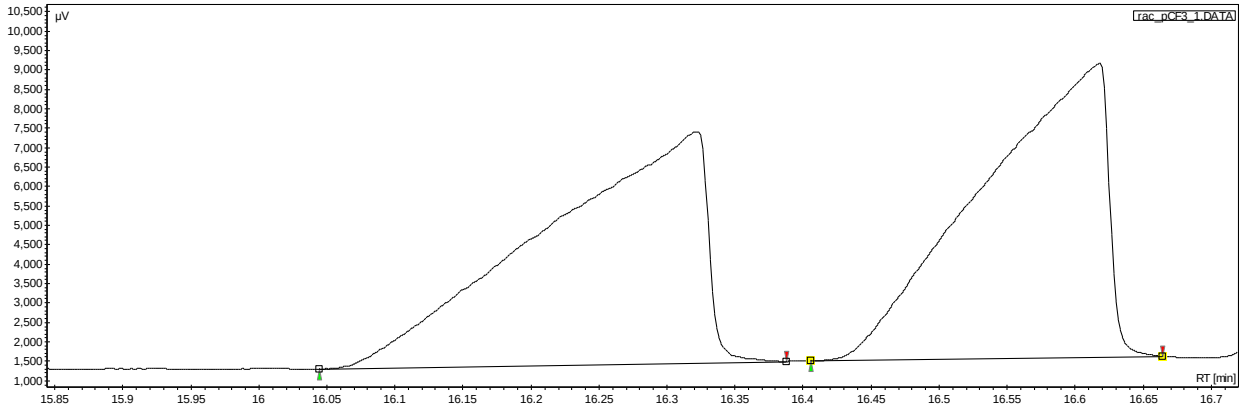


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	22.30	14.06	413.6	121.0	14.060
	2	UNKNOWN	23.12	85.94	2860.7	739.5	85.940
▶							
	Total			100.00	3274.2	860.5	100.000

Cyanohydrin acetate derived from 4-trifluoromethylbenzaldehyde

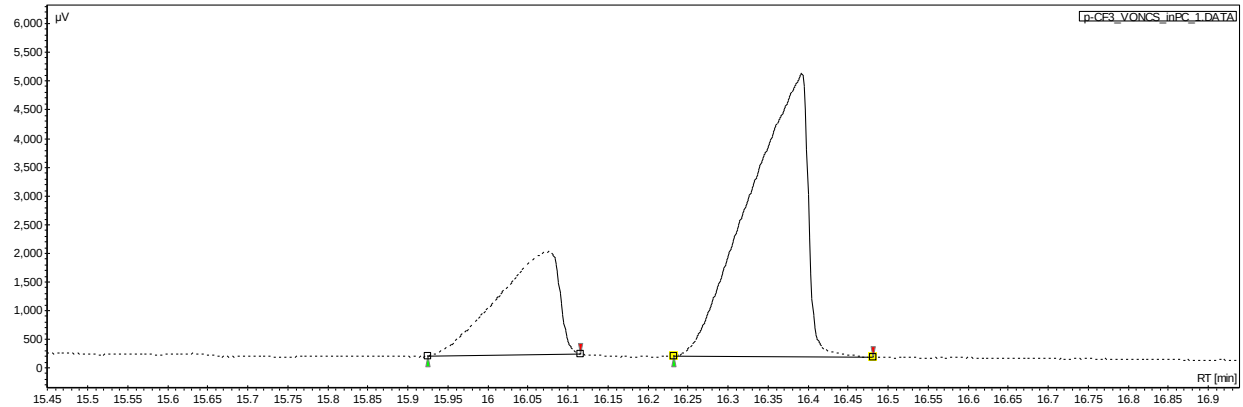
Analysed using GC method 2.

Racemate



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.32	50.65	5947.7	834.4	50.650
	2	UNKNOWN	16.62	49.35	7563.4	813.0	49.350
▶							
	Total			100.00	13511.1	1647.4	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 8)

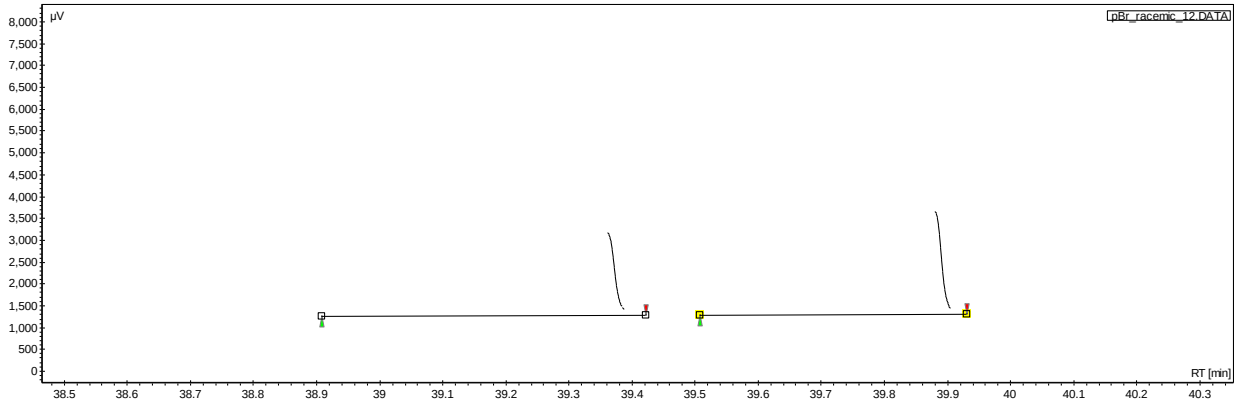


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	16.08	27.83	1795.2	158.9	27.830
	2	UNKNOWN	16.39	72.17	4931.2	412.1	72.170
▶							
	Total			100.00	6726.4	571.0	100.000

Cyanohydrin acetate derived from 4-bromobenzaldehyde

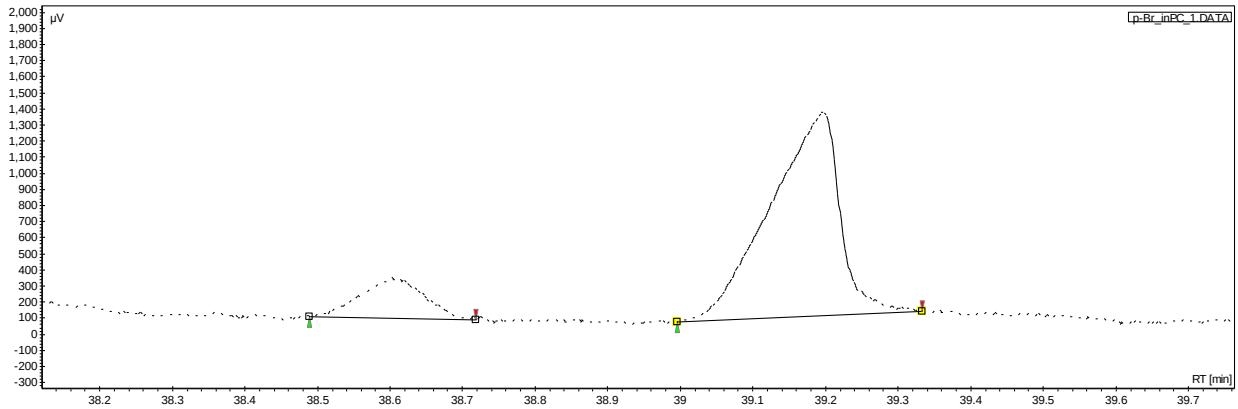
Analysed using GC method 3.

Racemate



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	39.36	50.34	1901.8	444.3	50.336
	2	UNKNOWN	39.88	49.66	2365.6	438.4	49.664
▶							
	Total			100.00	4267.4	882.7	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 9)

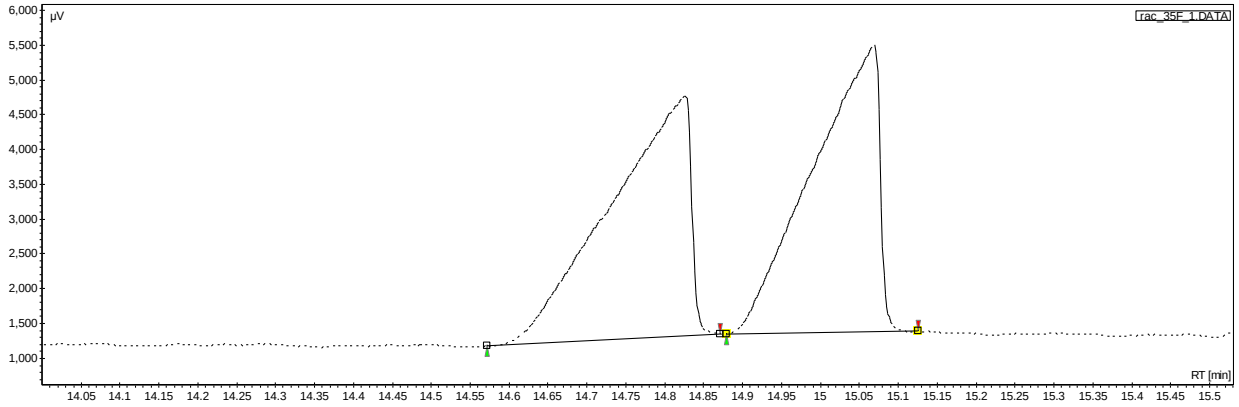


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	38.61	14.93	239.3	24.8	14.934
	2	UNKNOWN	39.20	85.07	1265.6	141.5	85.066
▶							
	Total			100.00	1504.9	166.3	100.000

Cyanohydrin acetate derived from 3,5-difluorobenzaldehyde

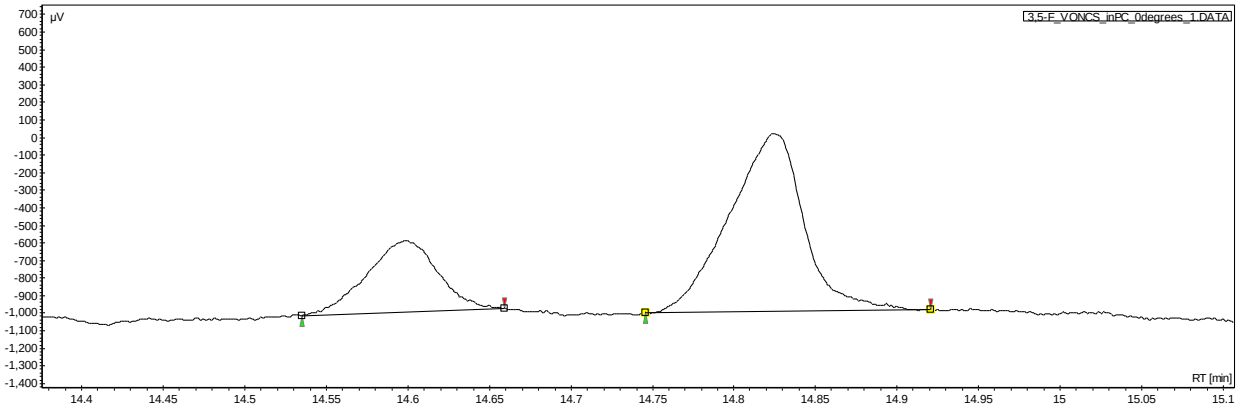
Analysed using GC method 2.

Racemate



	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.83	50.11	3452.5	412.8	50.112
	2	UNKNOWN	15.07	49.89	4128.0	410.9	49.888
▶							
	Total			100.00	7580.5	823.7	100.000

Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 10)

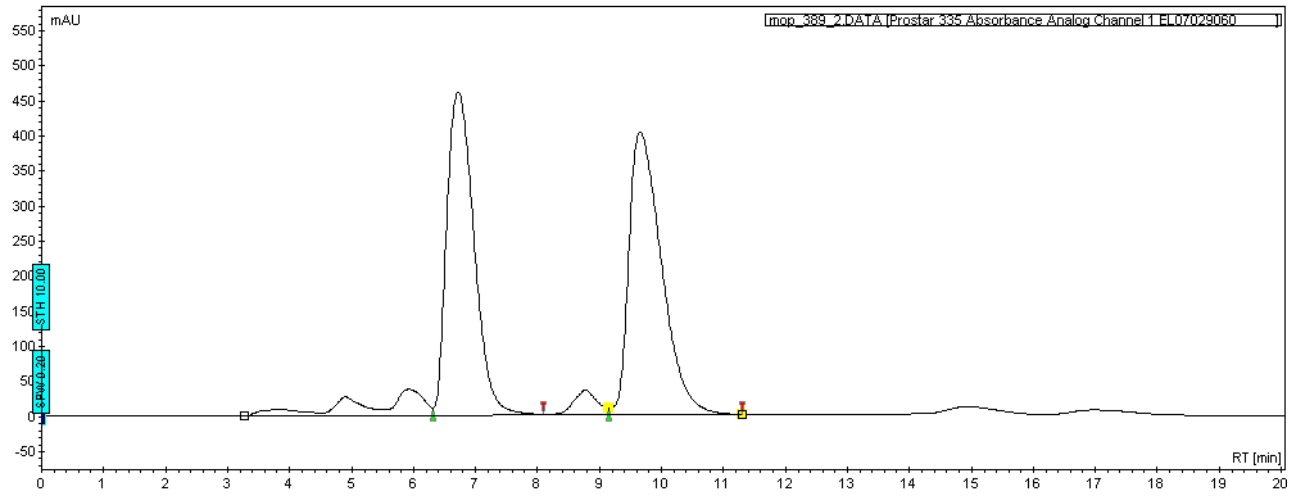


	#	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
	1	UNKNOWN	14.60	27.55	403.6	20.4	27.549
	2	UNKNOWN	14.83	72.45	1014.1	53.7	72.451
▶							
	Total			100.00	1417.7	74.2	100.000

HPLC of methyl mandelate

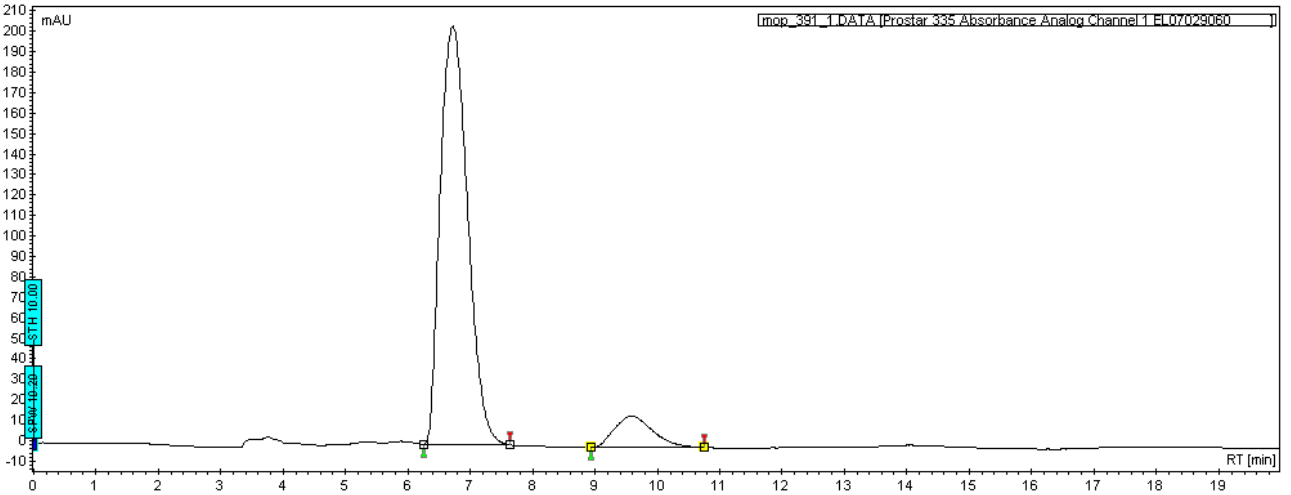
The analysis was performed on a Chirasil OD column using 80% hexane, 20% propan-2-ol as eluent with a flow rate of 1 mL per minute.

Racemate



	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
	1	UNKNOWN	6.72	48.90	460.4	235.4	48.899
	2	UNKNOWN	9.65	51.10	402.7	246.0	51.101
▶							
	Total			100.00	863.1	481.4	100.000

Sample with 81% ee

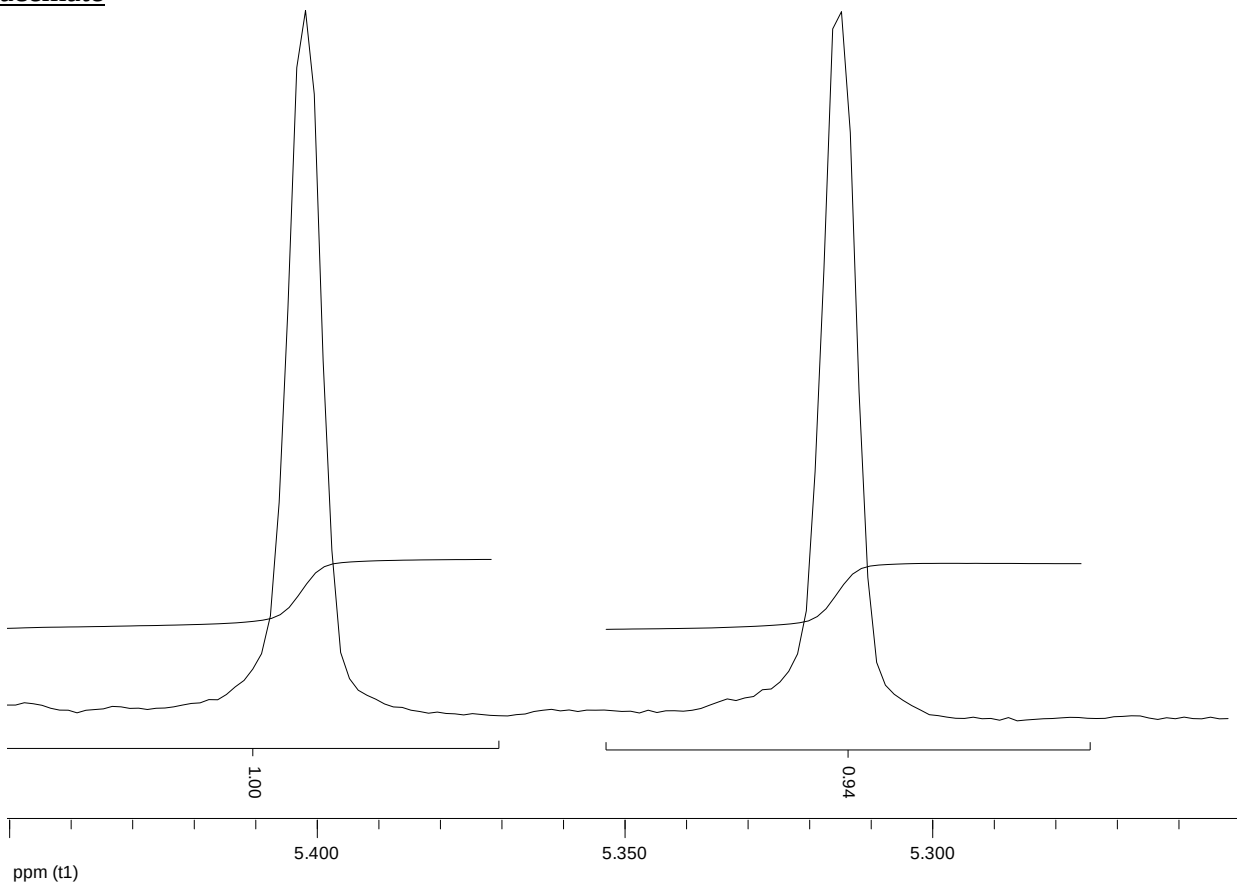


	#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
	2	UNKNOWN	6.72	90.52	204.2	103.8	90.521
	1	UNKNOWN	9.59	9.48	15.4	10.9	9.479
▶							
	Total			100.00	219.6	114.7	100.000

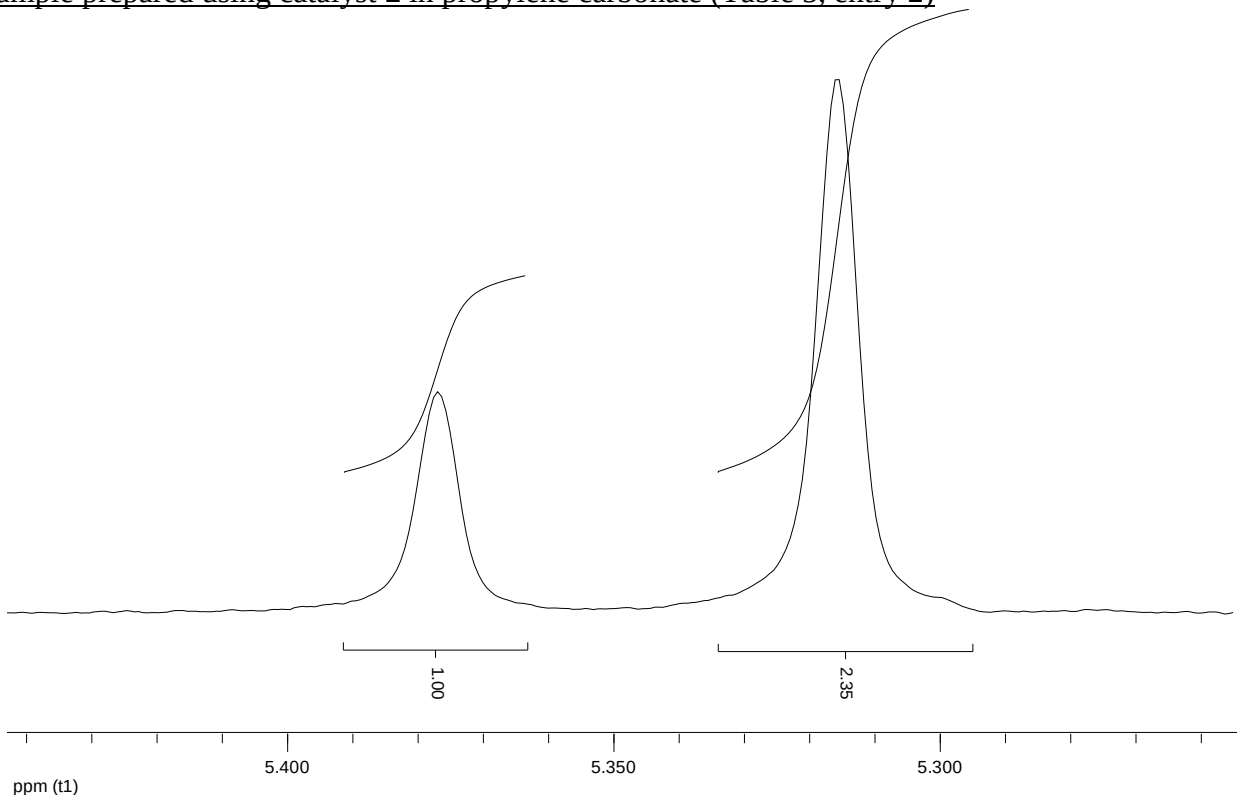
NMR spectra of (*R*)-mandelic acid complexes used to determine enantiomeric excesses

(3,4-Dichlorophenyl)hydroxyacetonitrile

Racemate

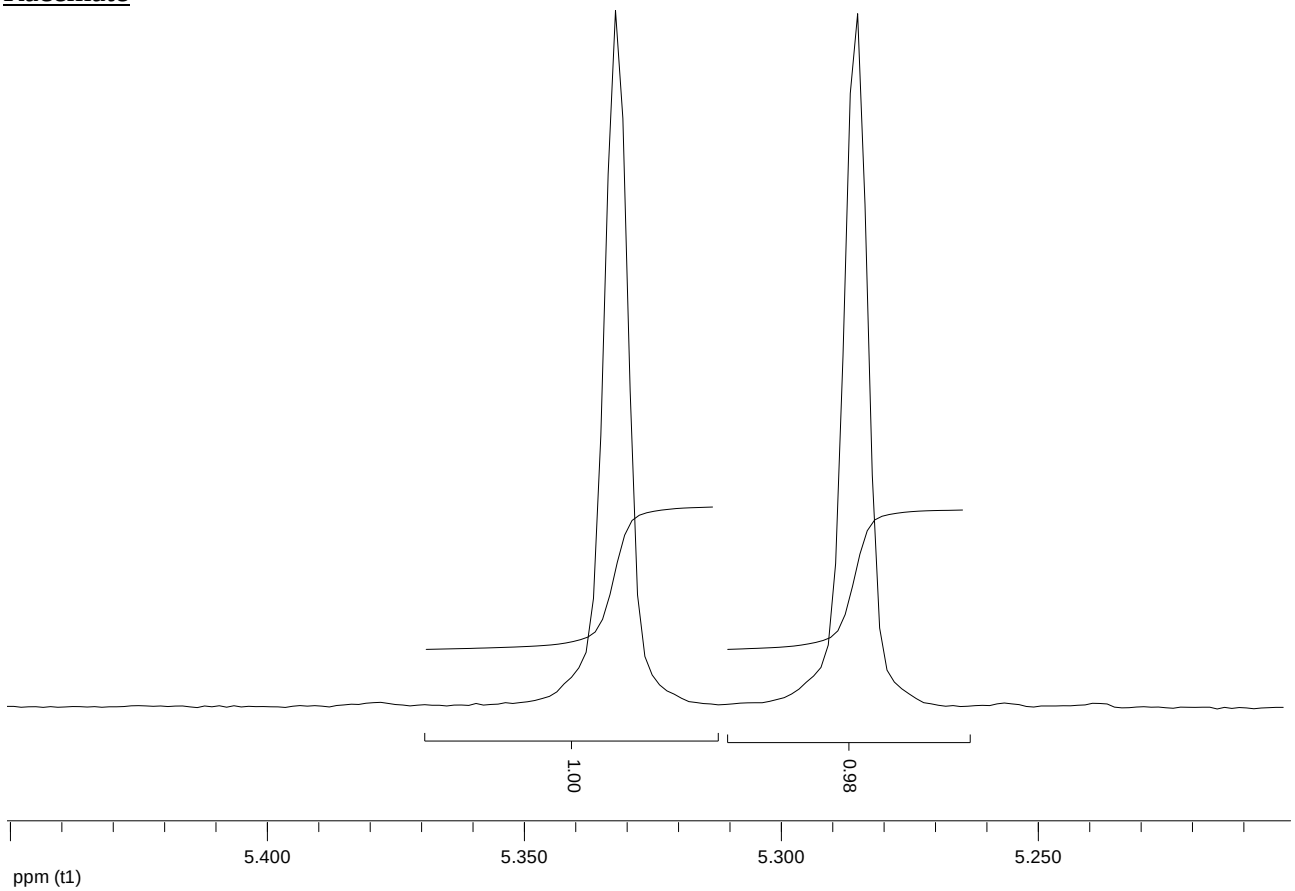


Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 2)

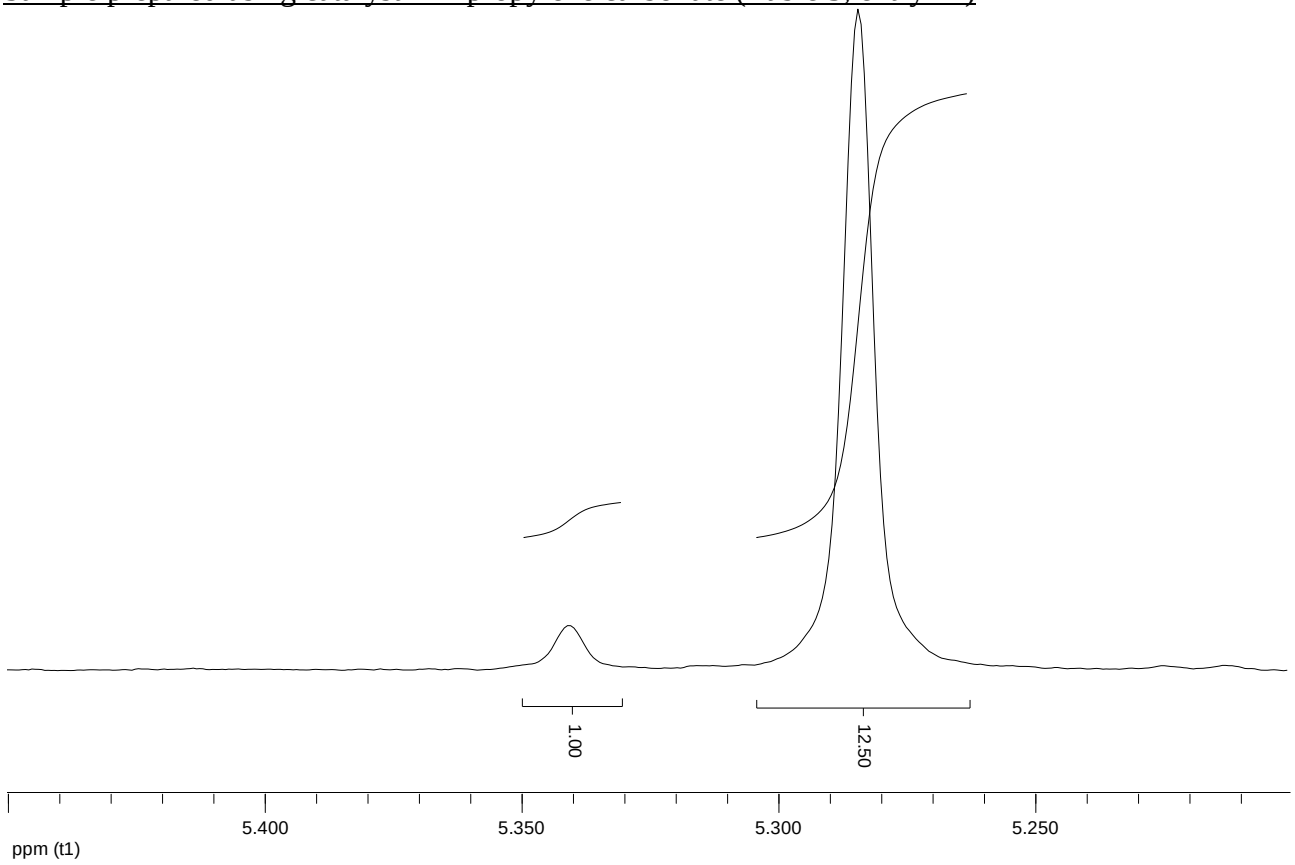


(3,4-Dimethylphenyl)hydroxyacetonitrile

Racemate



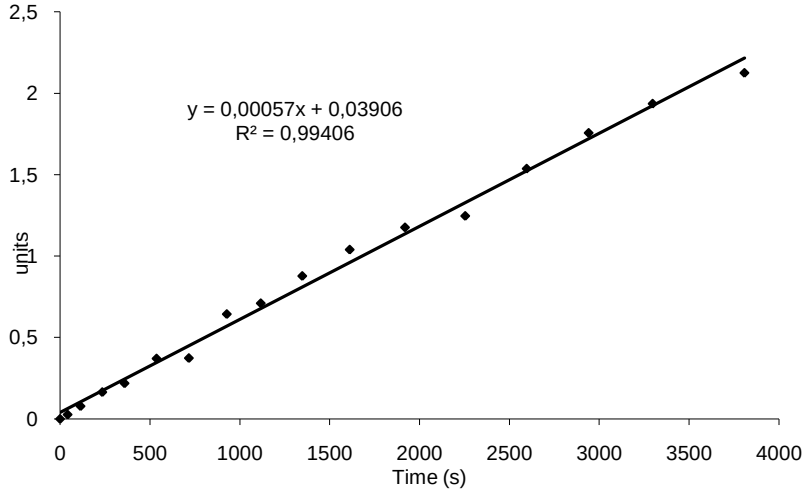
Sample prepared using catalyst **2** in propylene carbonate (Table 5, entry 11)



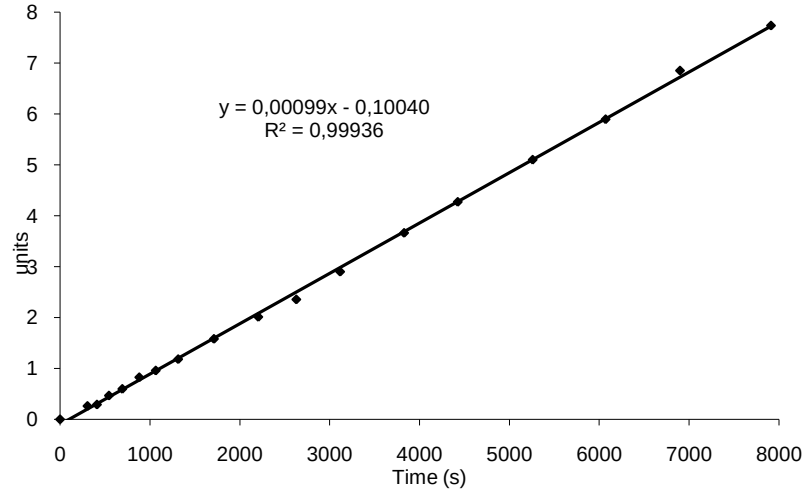
Kinetic plots used to determine the order with respect to catalyst concentration

The units for the vertical scales 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.

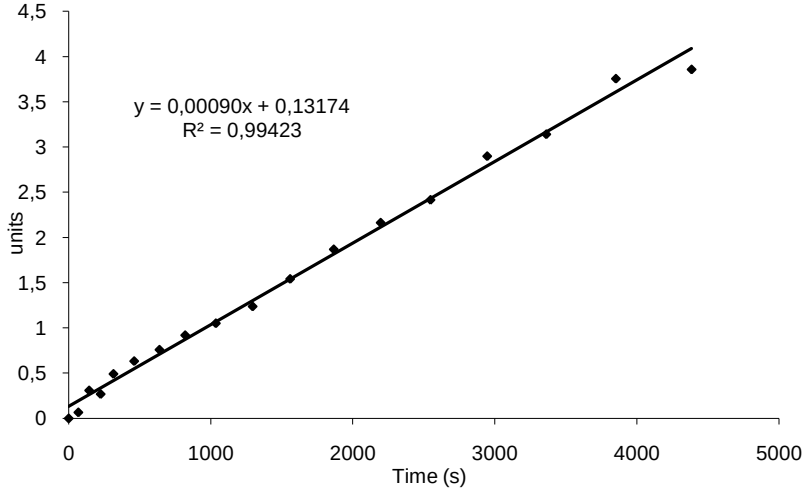
0.2 mol % catalyst run 1



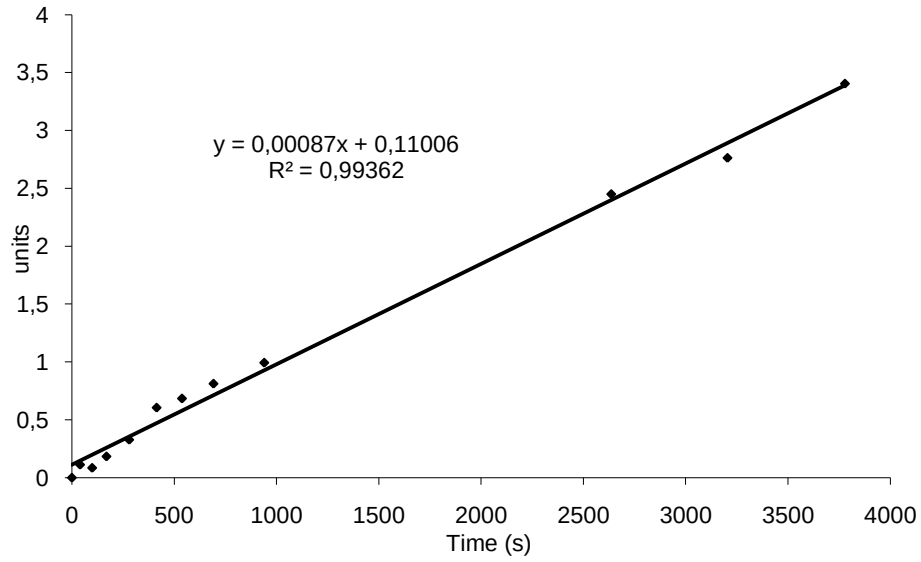
0.2 mol % catalyst run 2



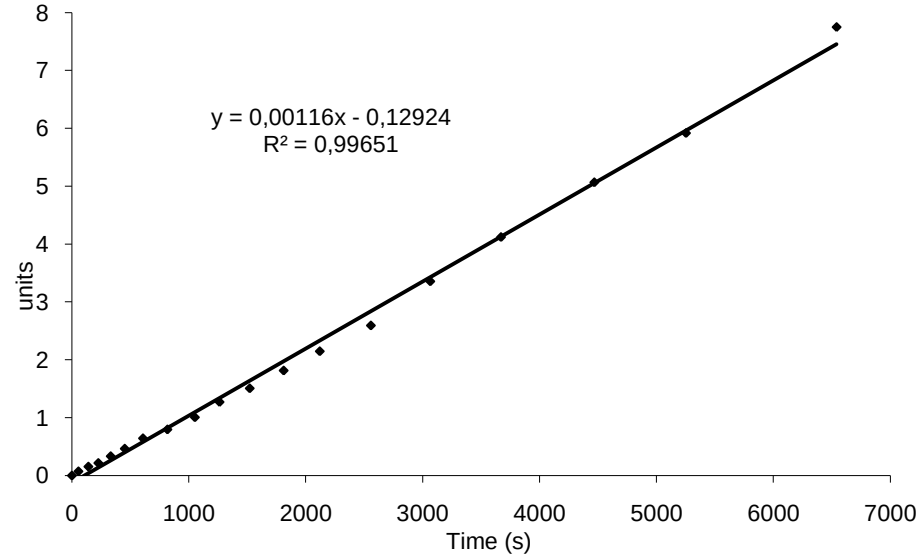
0.2 mol % catalyst run 3



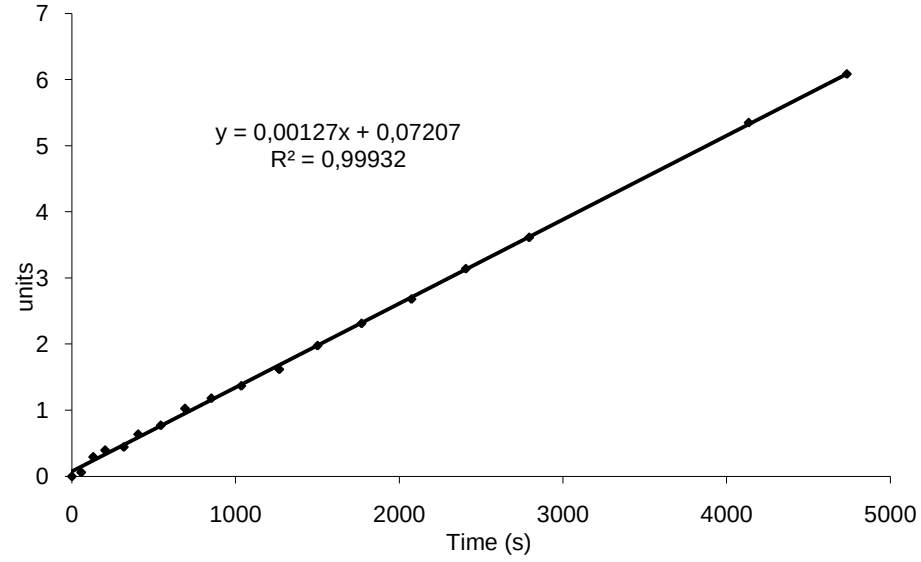
0.3 mol % catalyst run 1



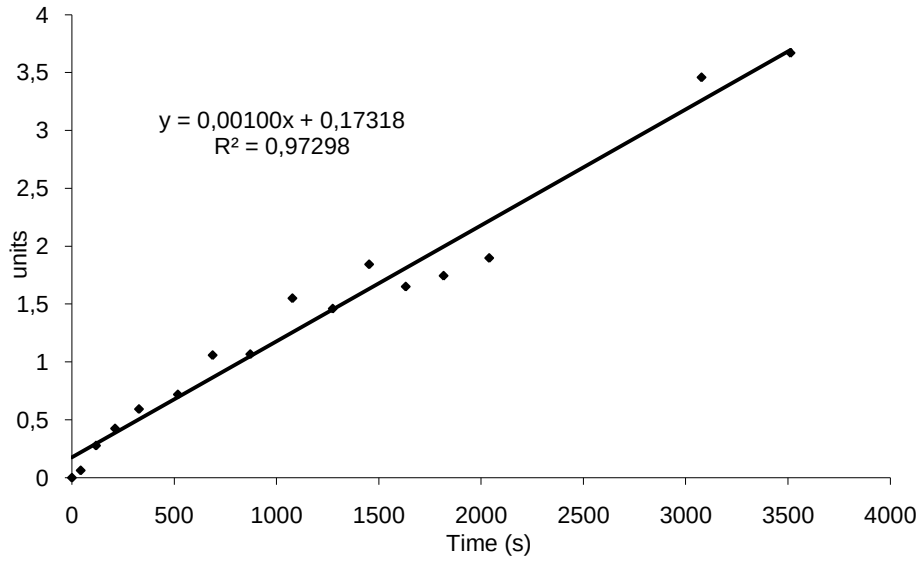
0.3 mol % catalyst run 2



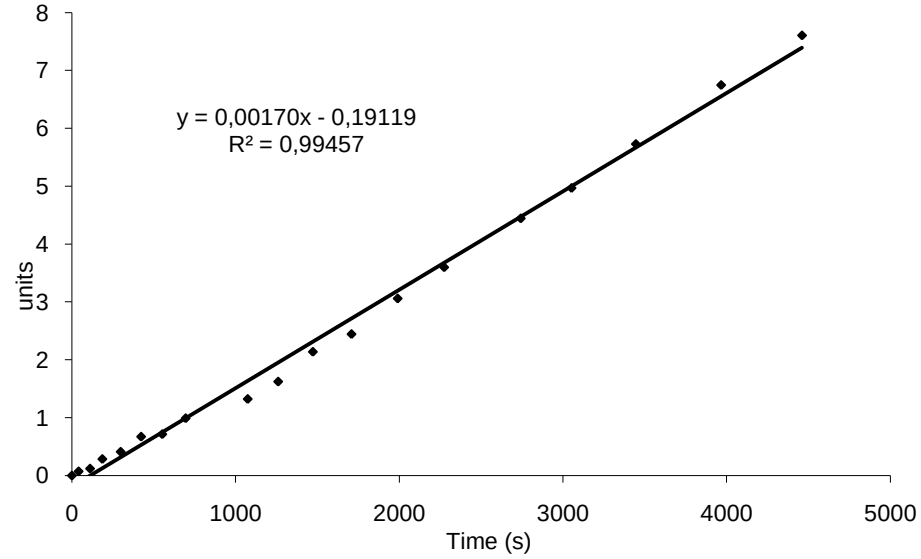
0.3 mol % catalyst run 3



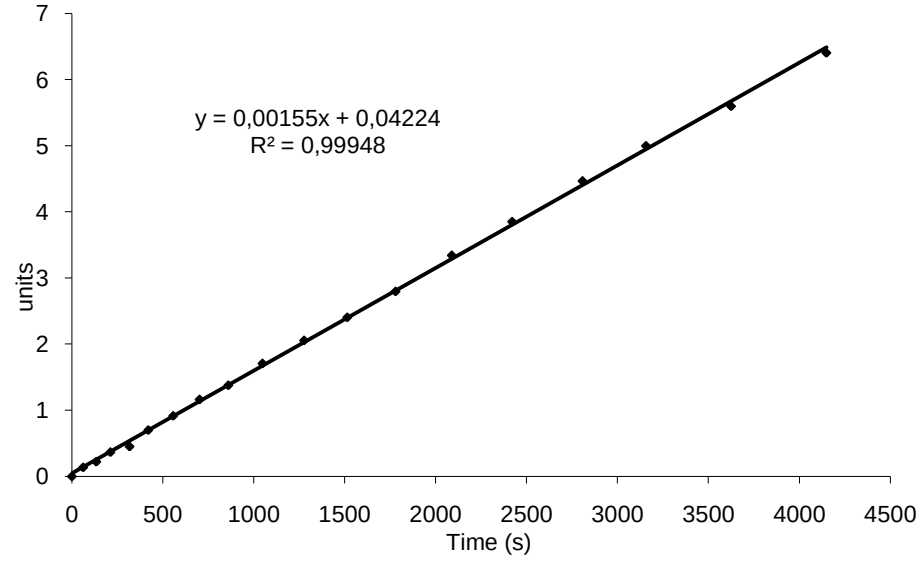
0.4 mol % catalyst run 1



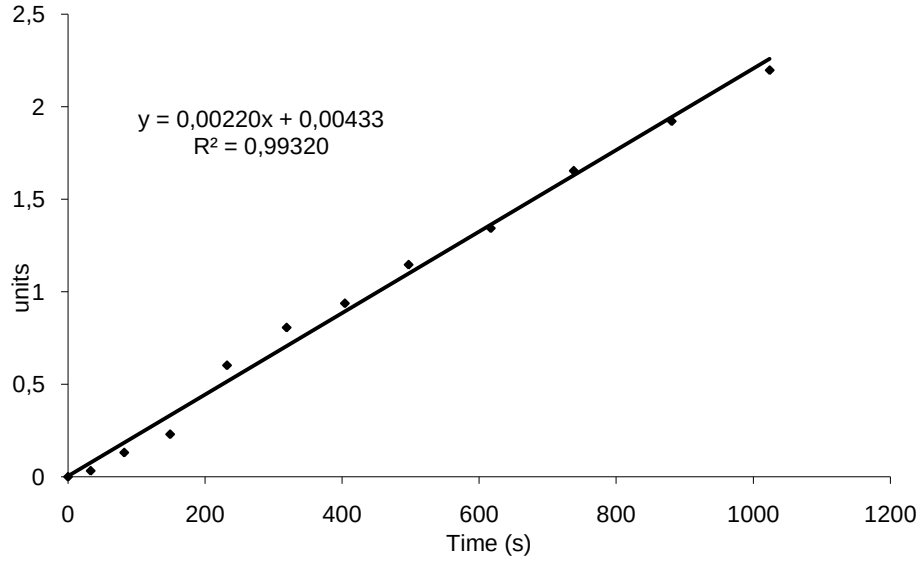
0.4 mol % catalyst run 2



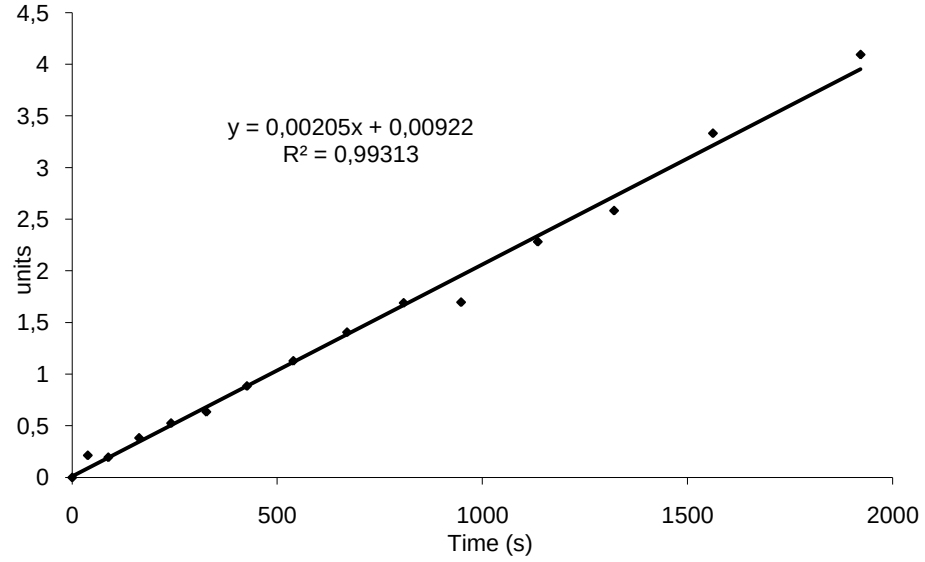
0.4 mol % catalyst run 3



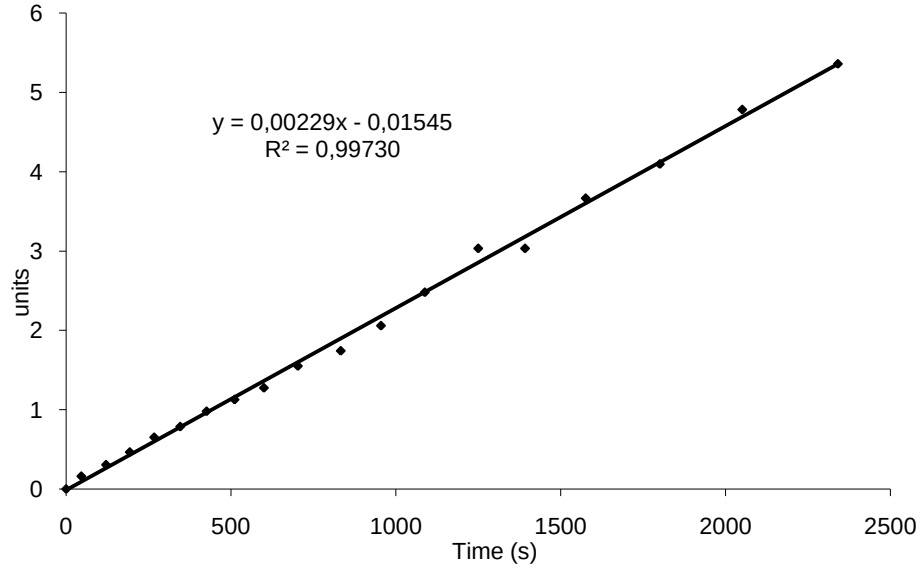
0.6 mol % catalyst run 1



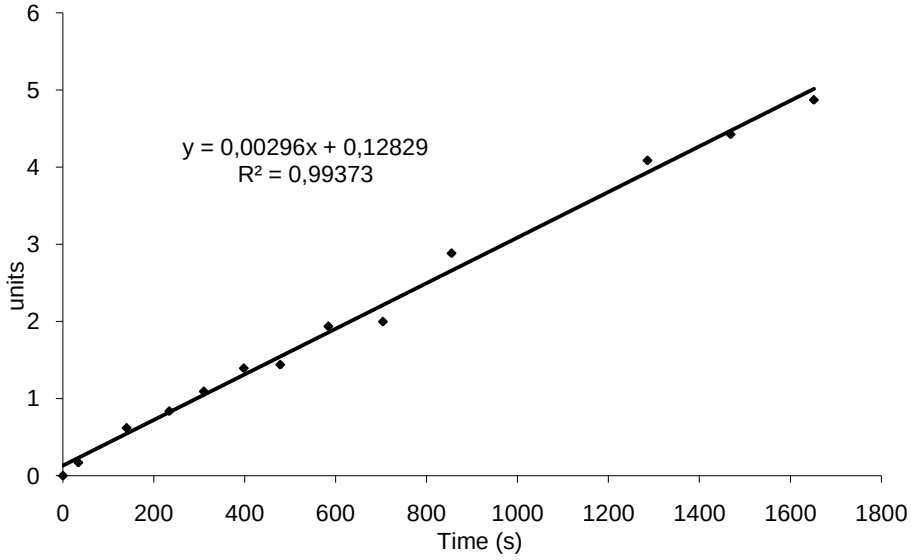
0.6 mol % catalyst run 2



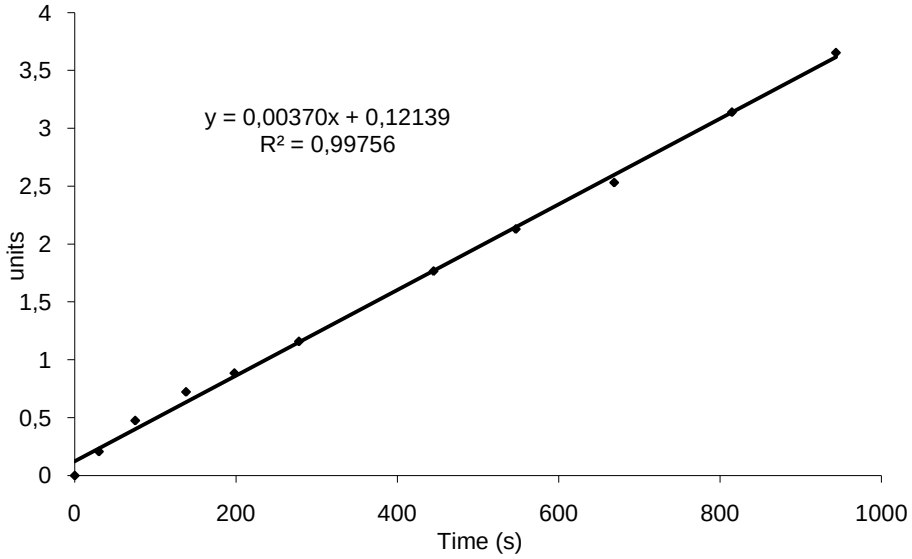
0.6 mol % catalyst run 3



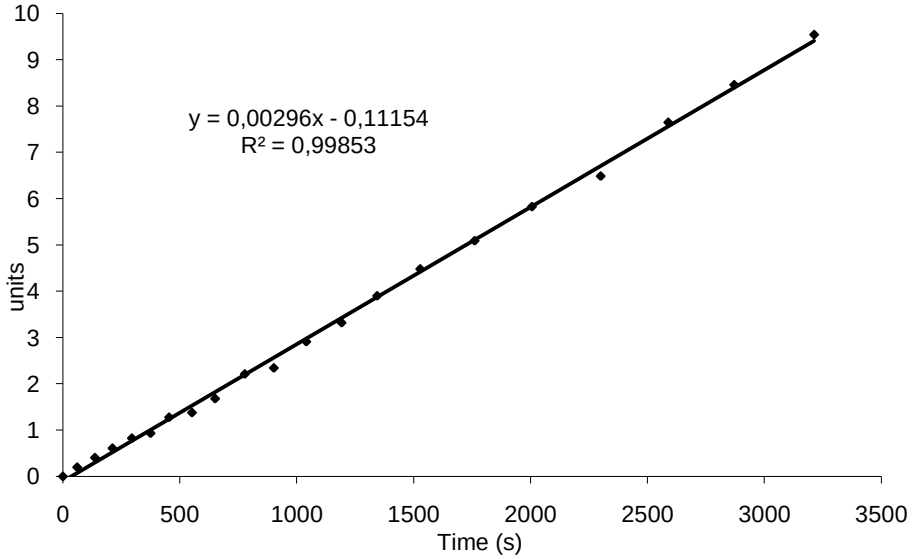
0.8 mol % catalyst run 1



0.8 mol % catalyst run 2

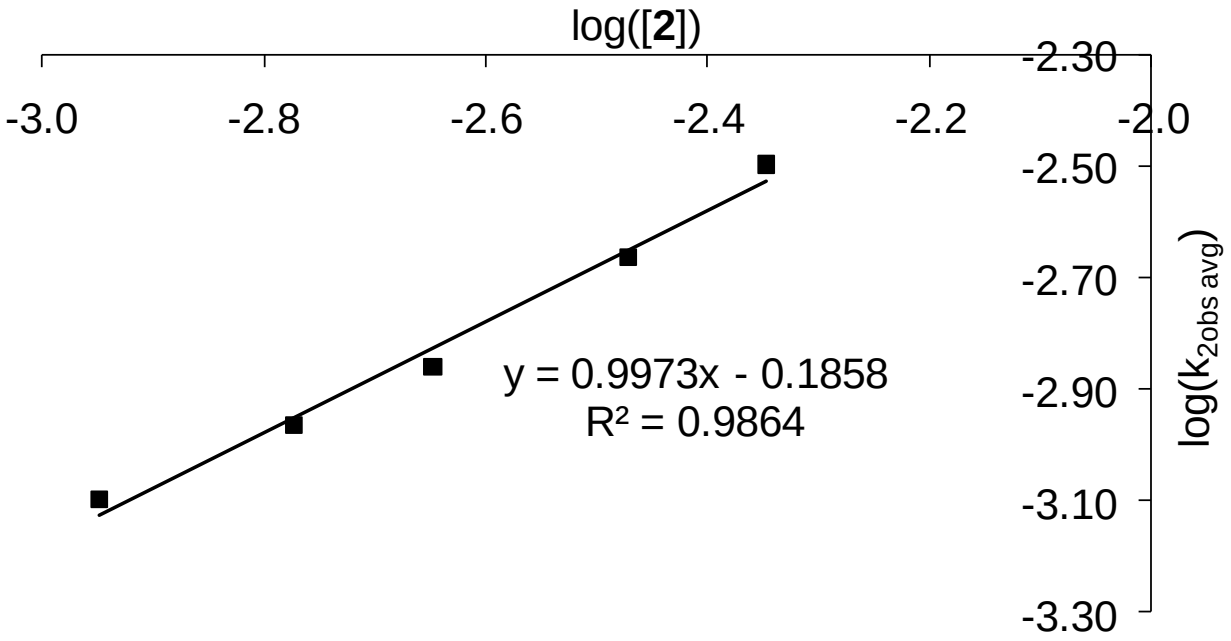


0.8 mol % catalyst run 3



Plot of log([2]) against log($k_{2obs\ avg}$)

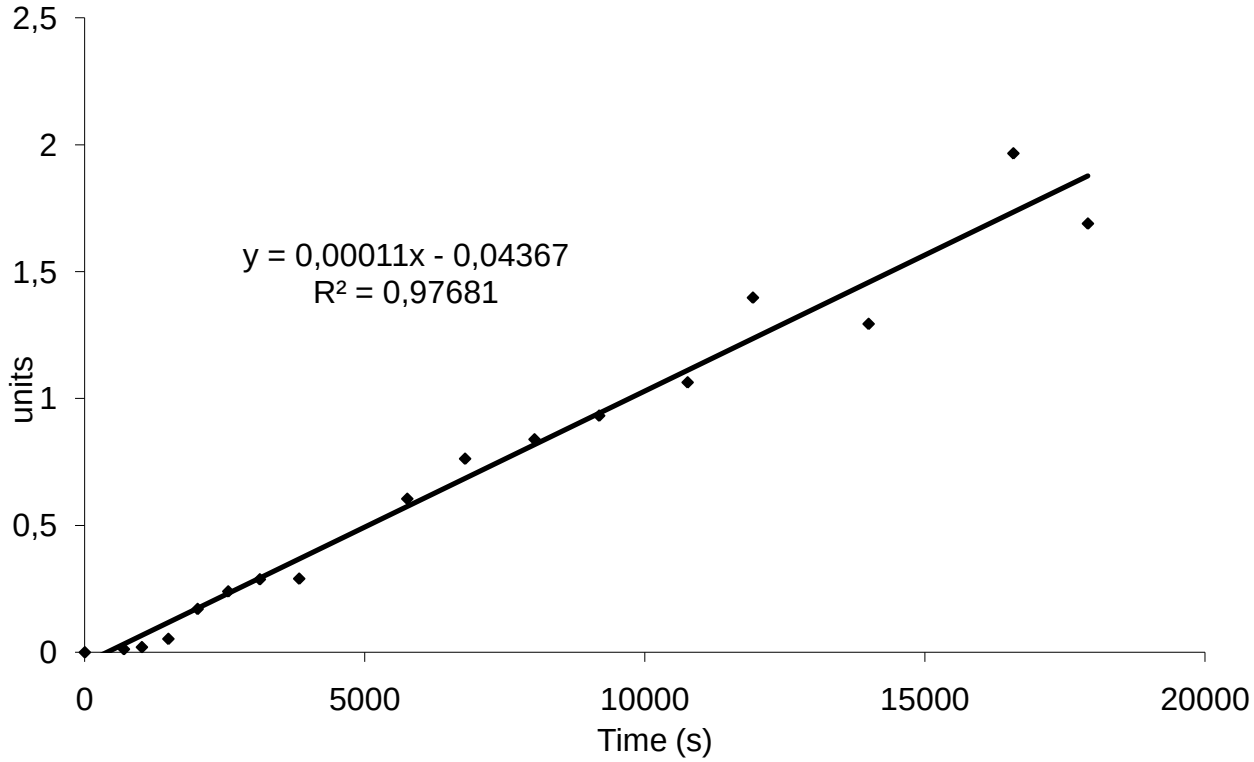
Since $k_{2obs} = k_2[\mathbf{2}]^x$, $\log(k_{2obs}) = \log(k_2) + x\log([\mathbf{2}])$, therefore a plot of log([2]) against $\log(k_{2obs})$ provides an alternative way of determining the order with respect to catalyst **2**. The plot is shown below and its slope is consistent with an order of 1.0 with respect to catalyst.



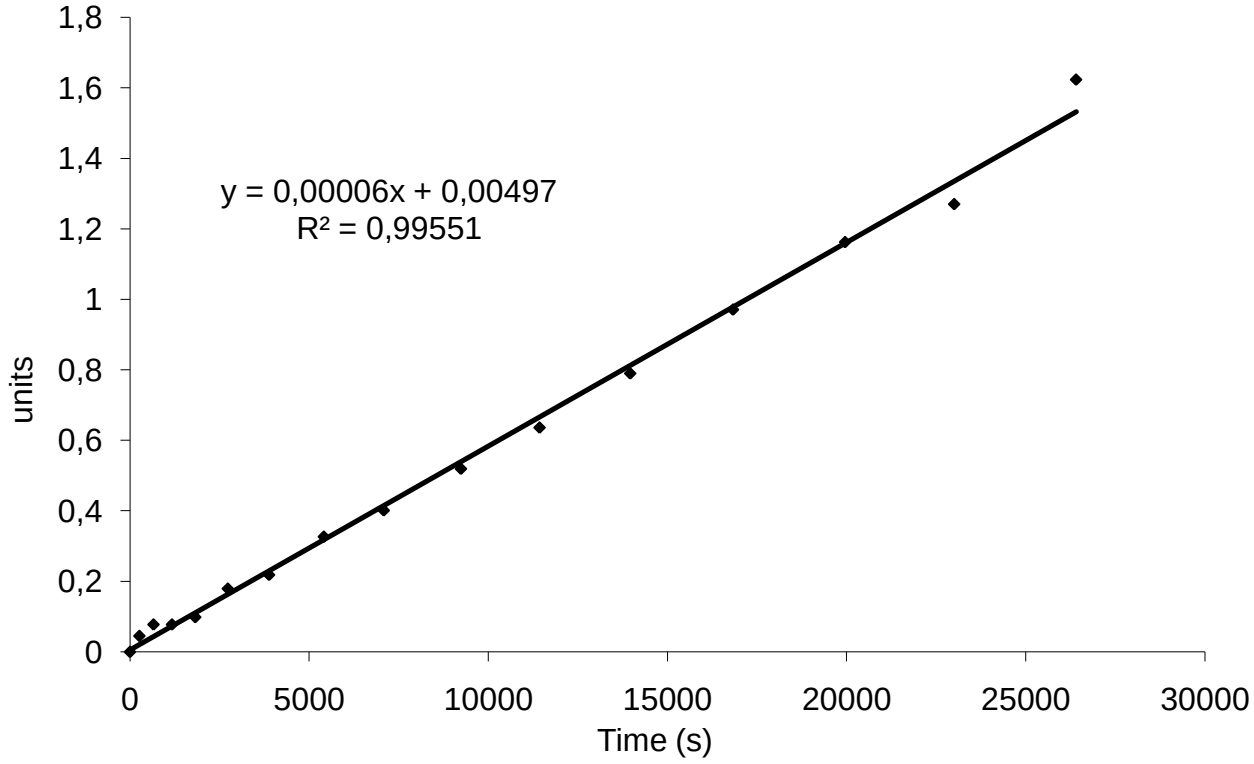
Kinetic plots used to determine the activation parameters in propylene carbonate

The units for the vertical scales 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.

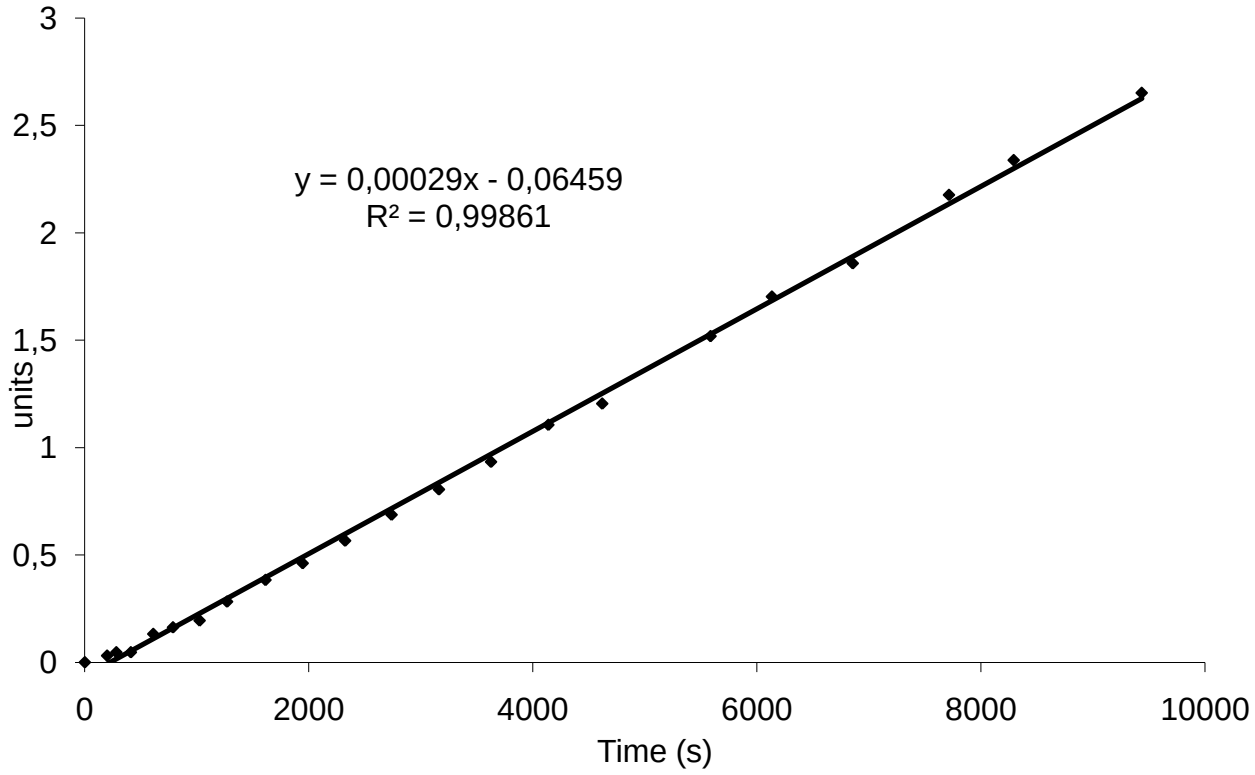
Kinetics at 253 K (run 1)



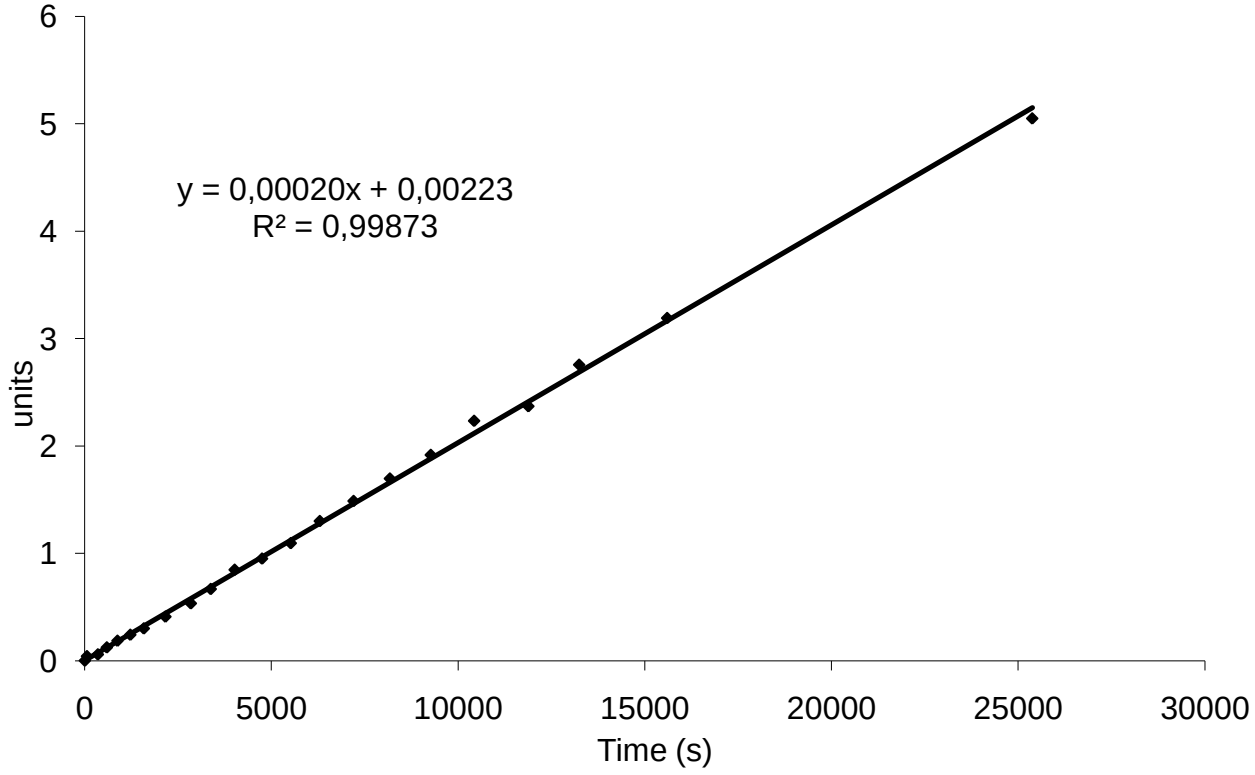
Kinetics at 253 K (run 2)



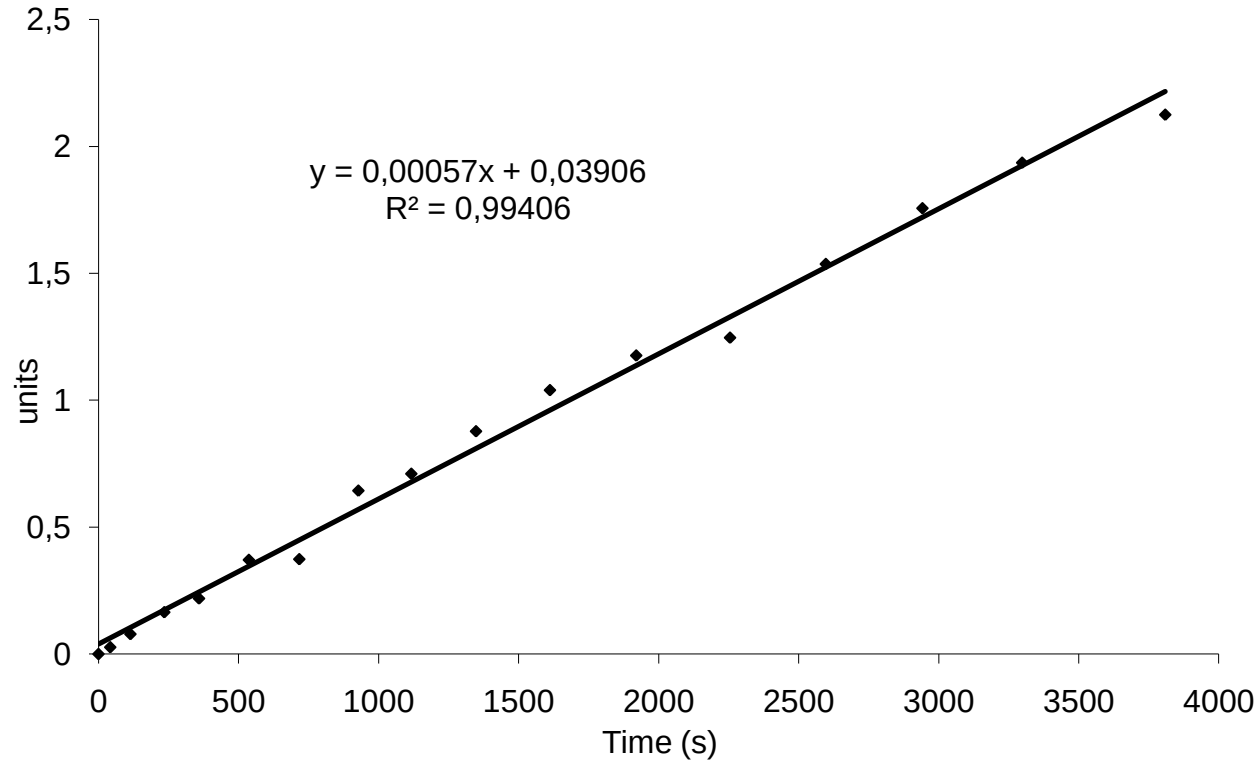
Kinetics at 263 K (run 1)



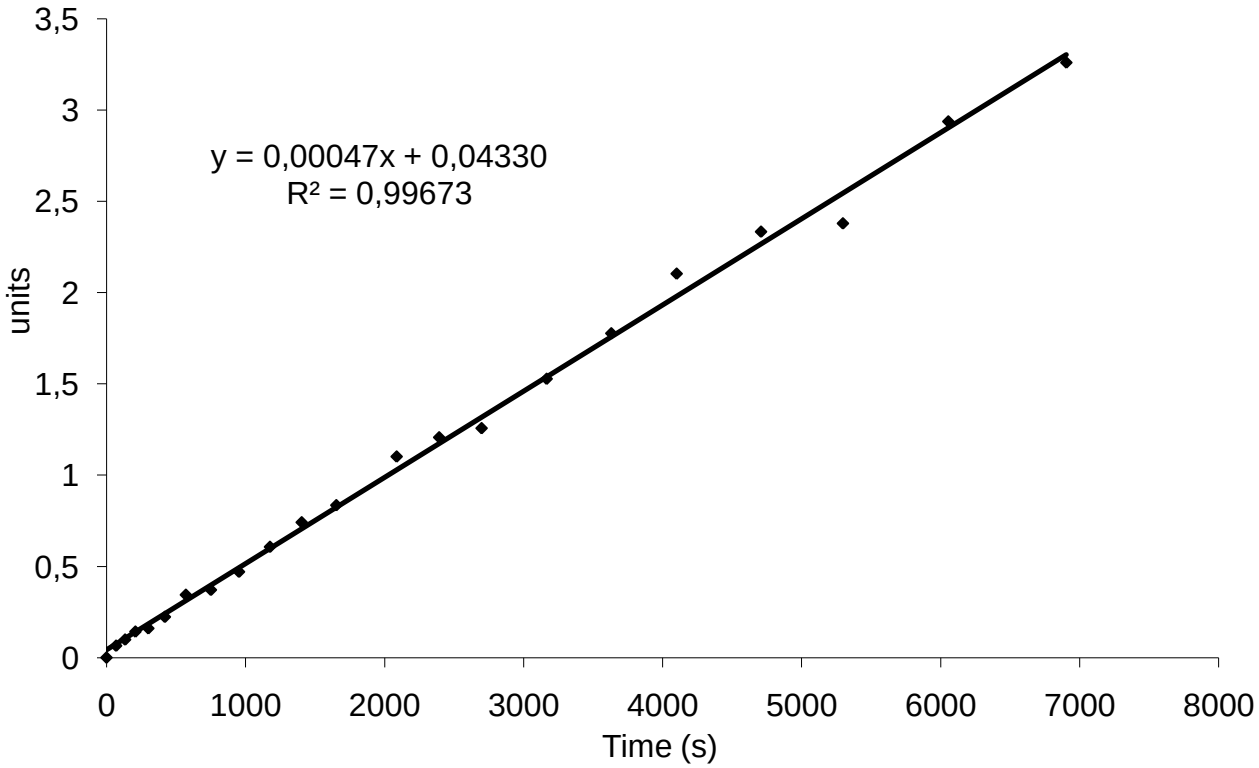
Kinetics at 263 K (run 2)



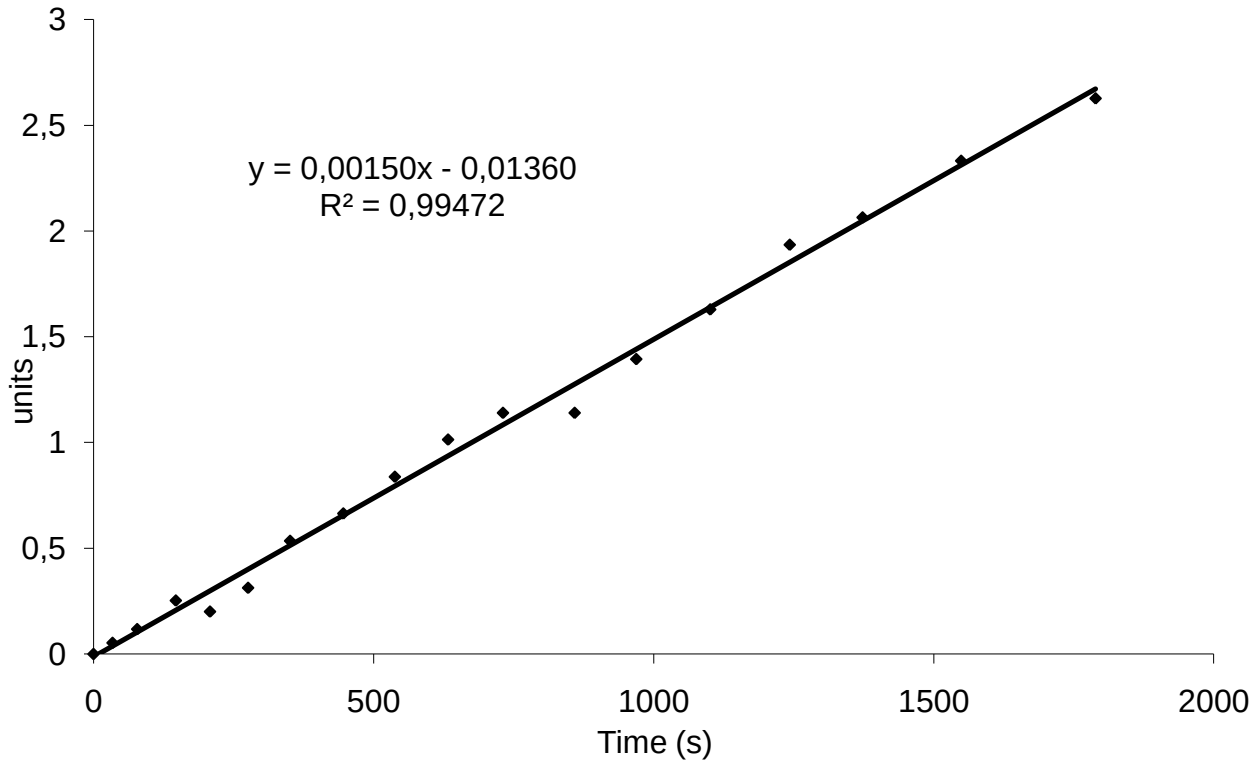
Kinetics at 273 K (run 1)



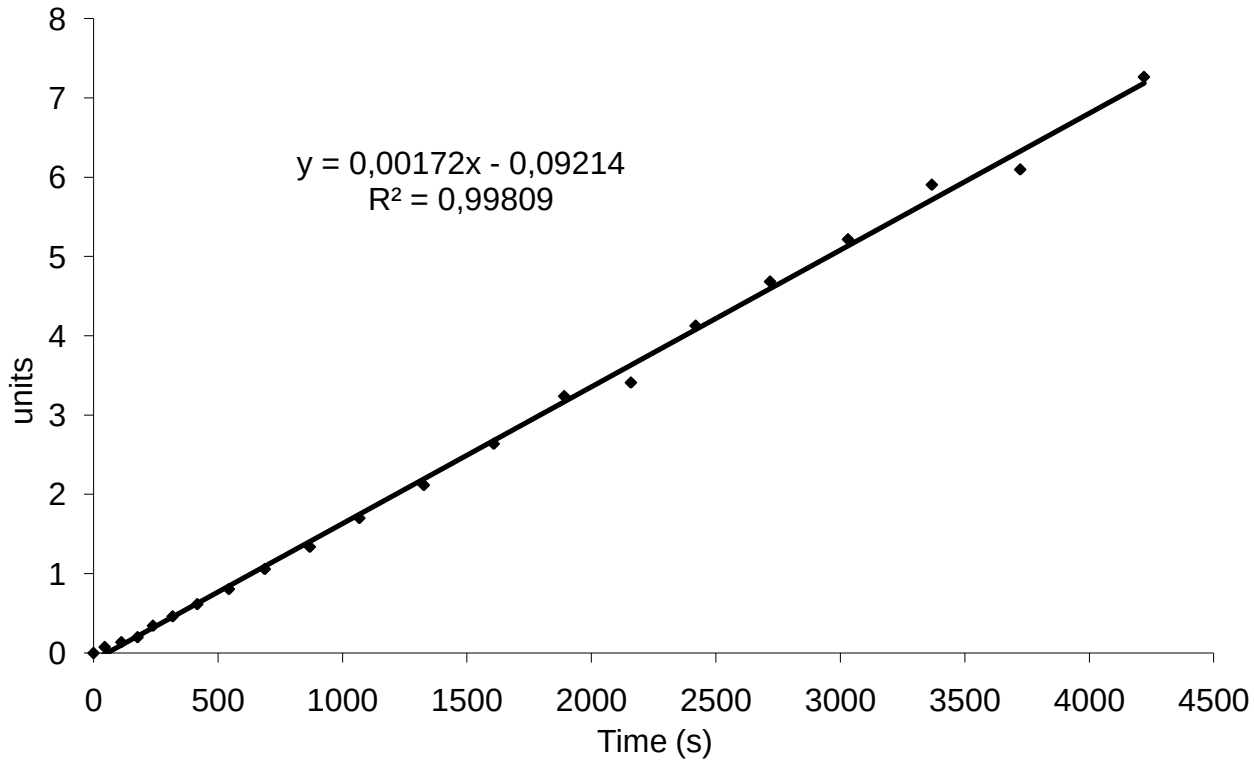
Kinetics at 273 K (run 2)



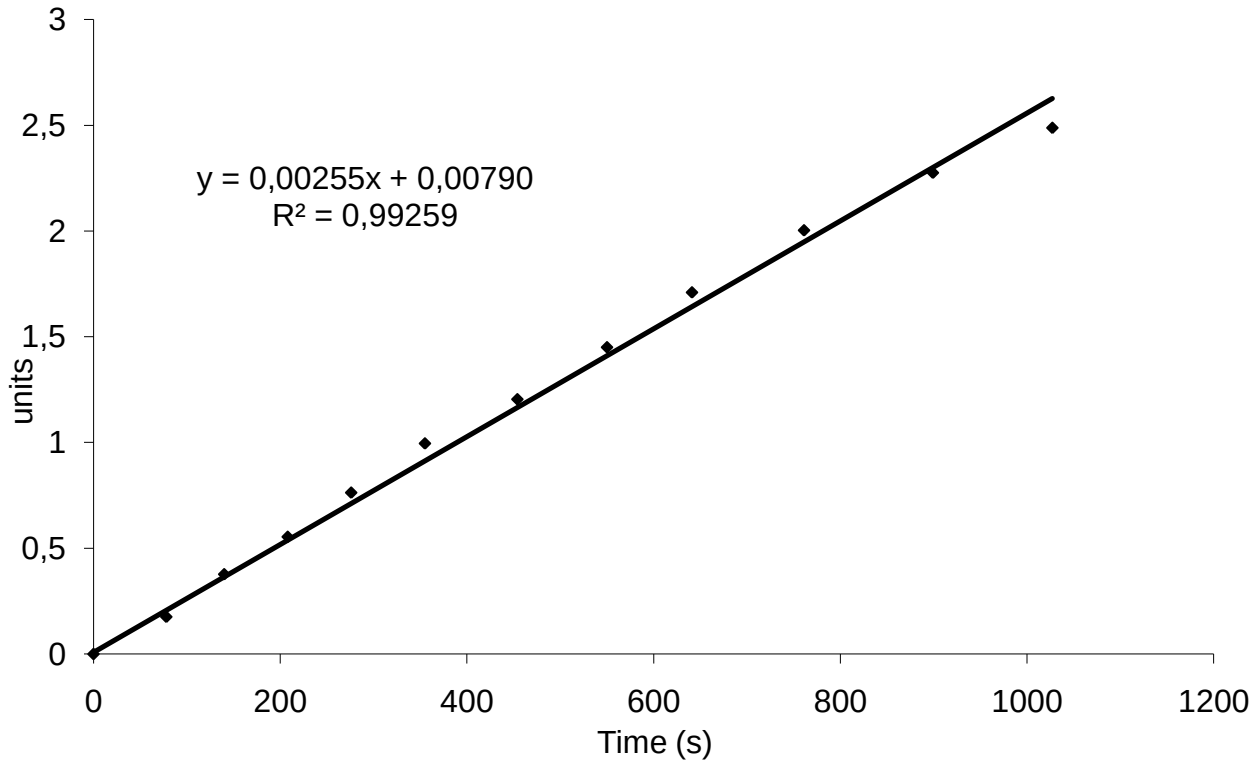
Kinetics at 283 K (run 1)



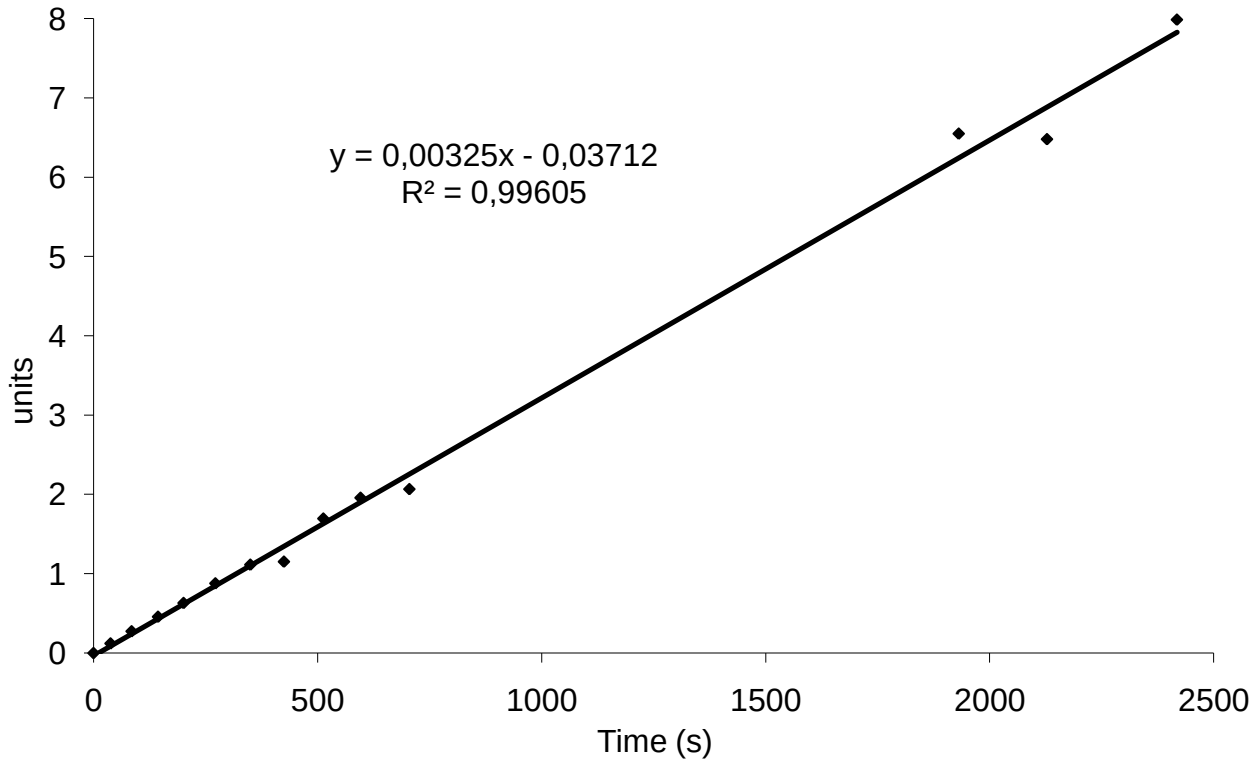
Kinetics at 283 K (run 2)



Kinetics at 293 K (run 1)



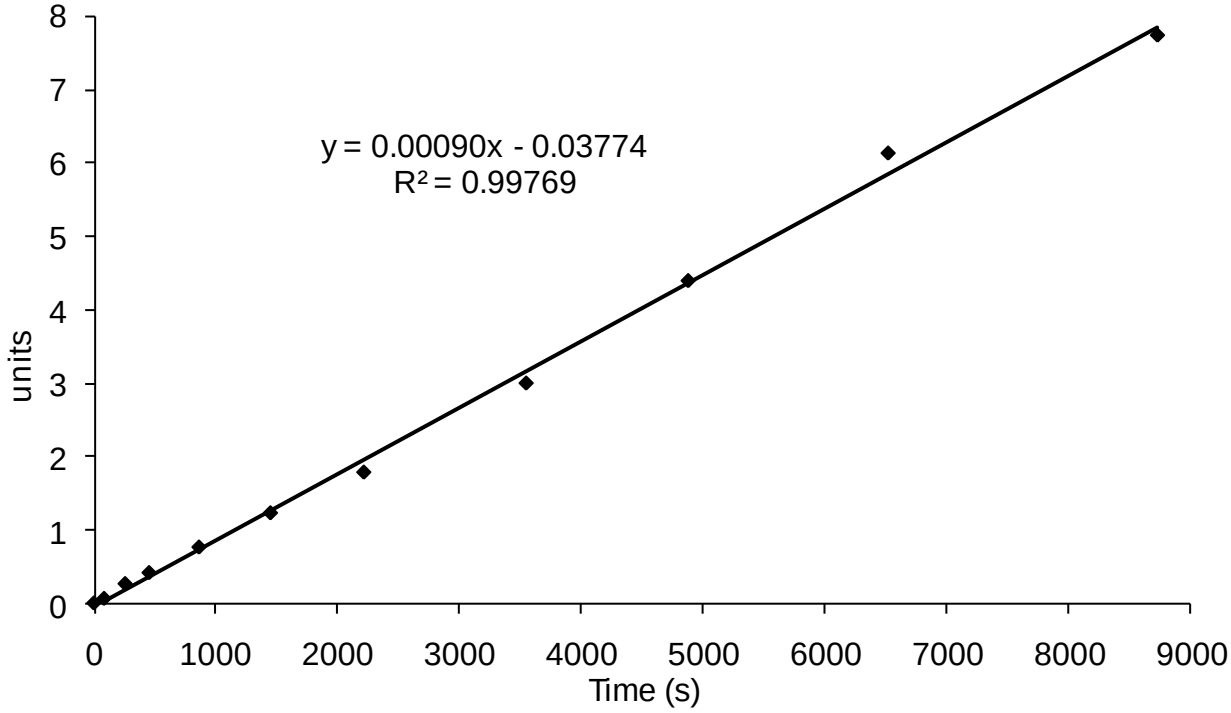
Kinetics at 293 K (run 1)



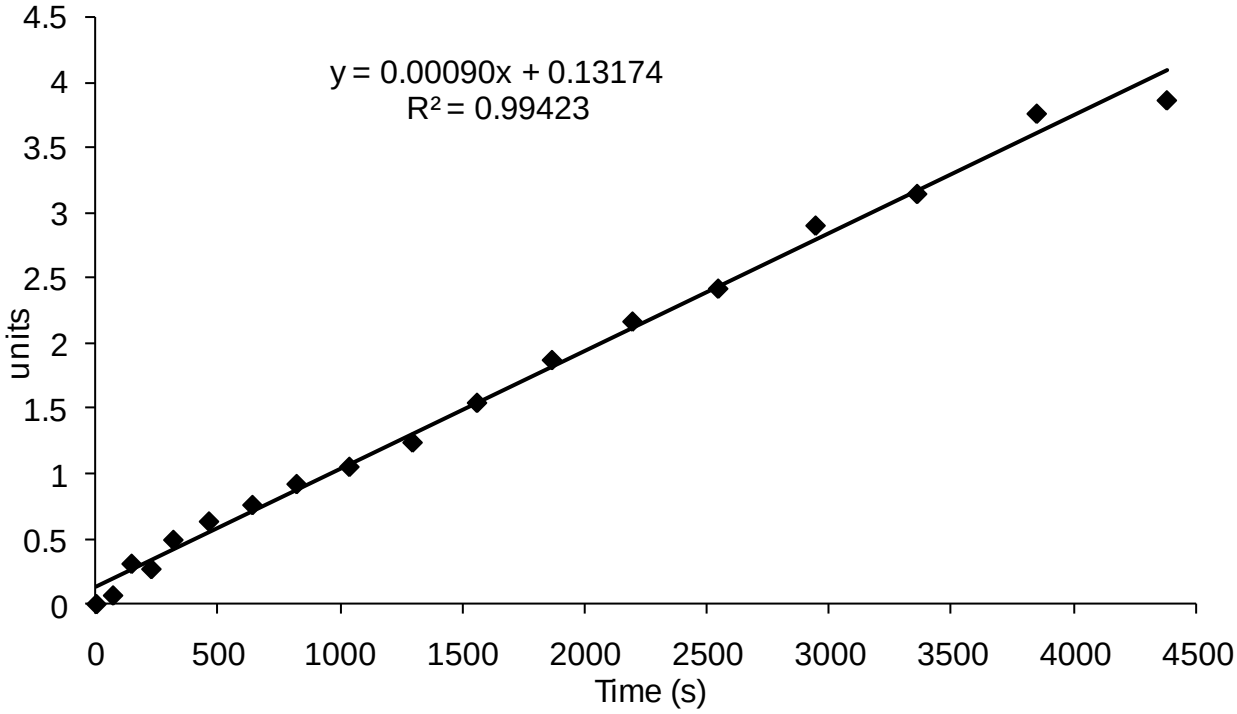
Kinetic plots used to construct the Hammett plot

The units for the vertical scales 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.

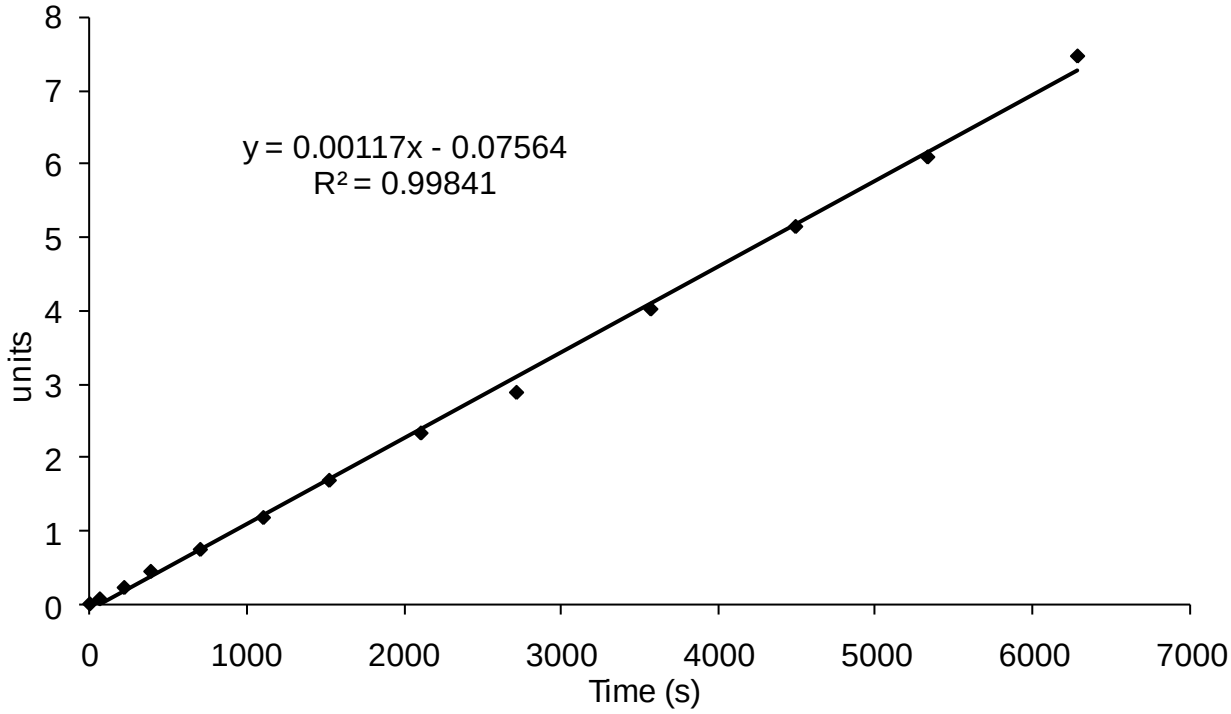
Benzaldehyde run 1



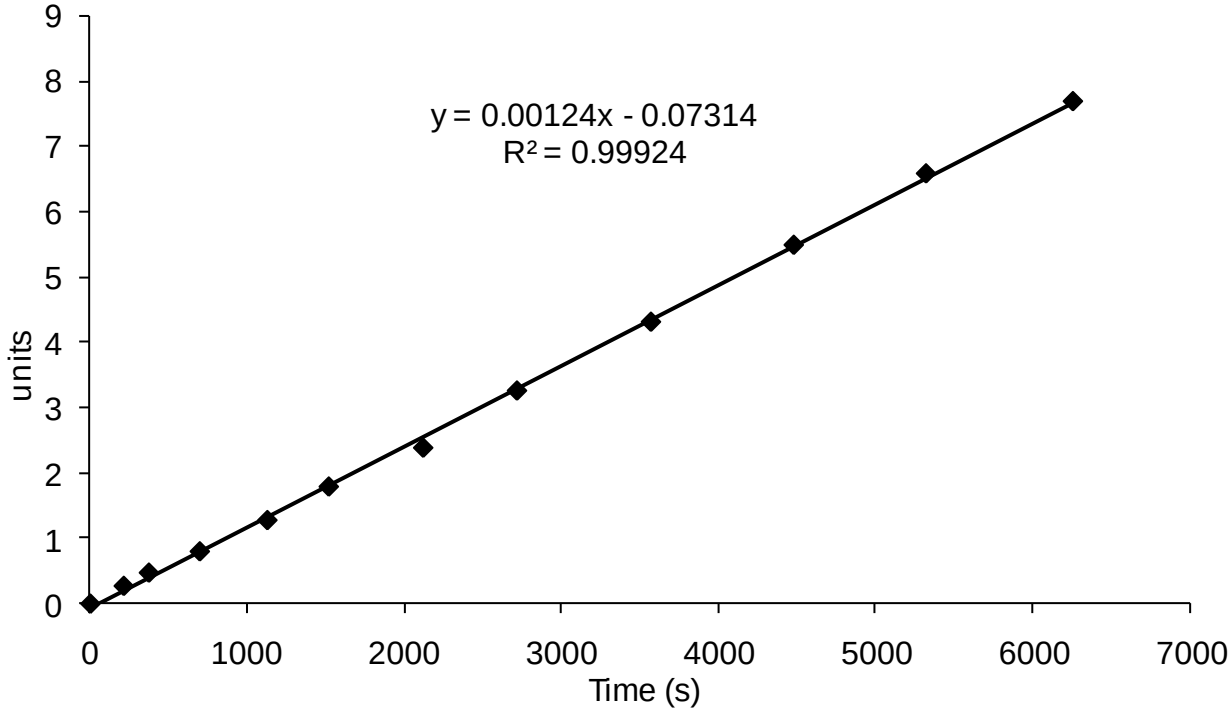
Benzaldehyde run 2



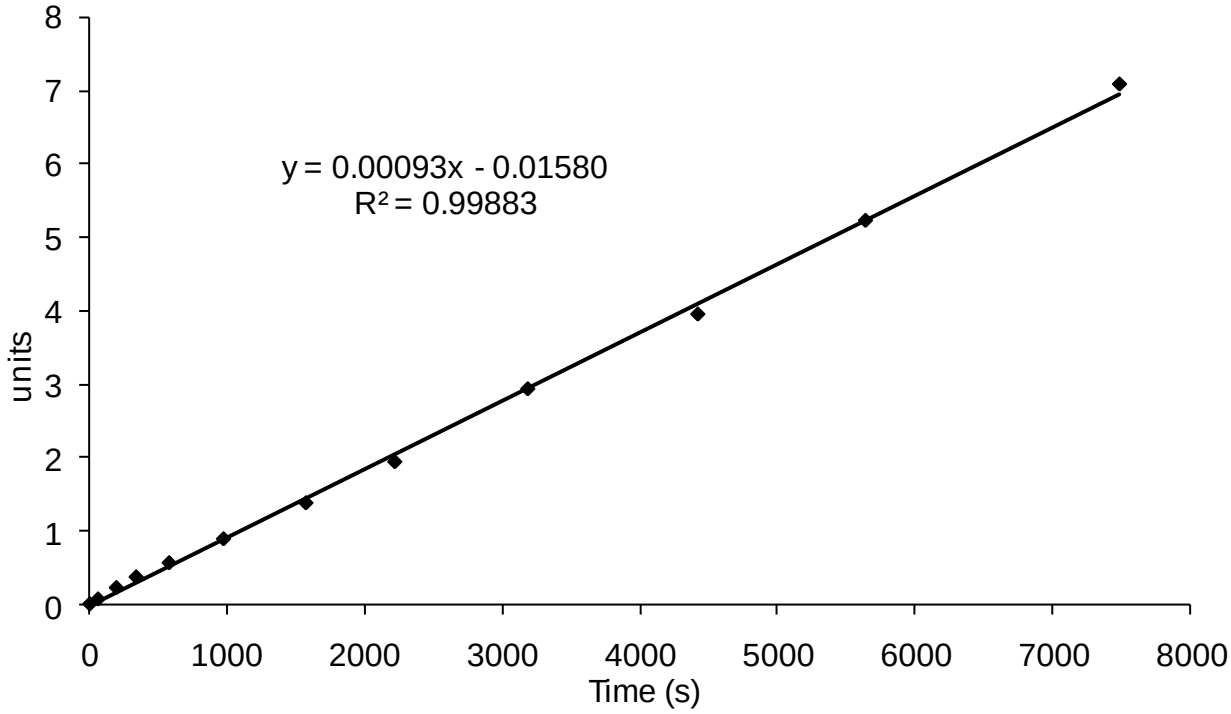
3,4-Dichlorobenzaldehyde run 1



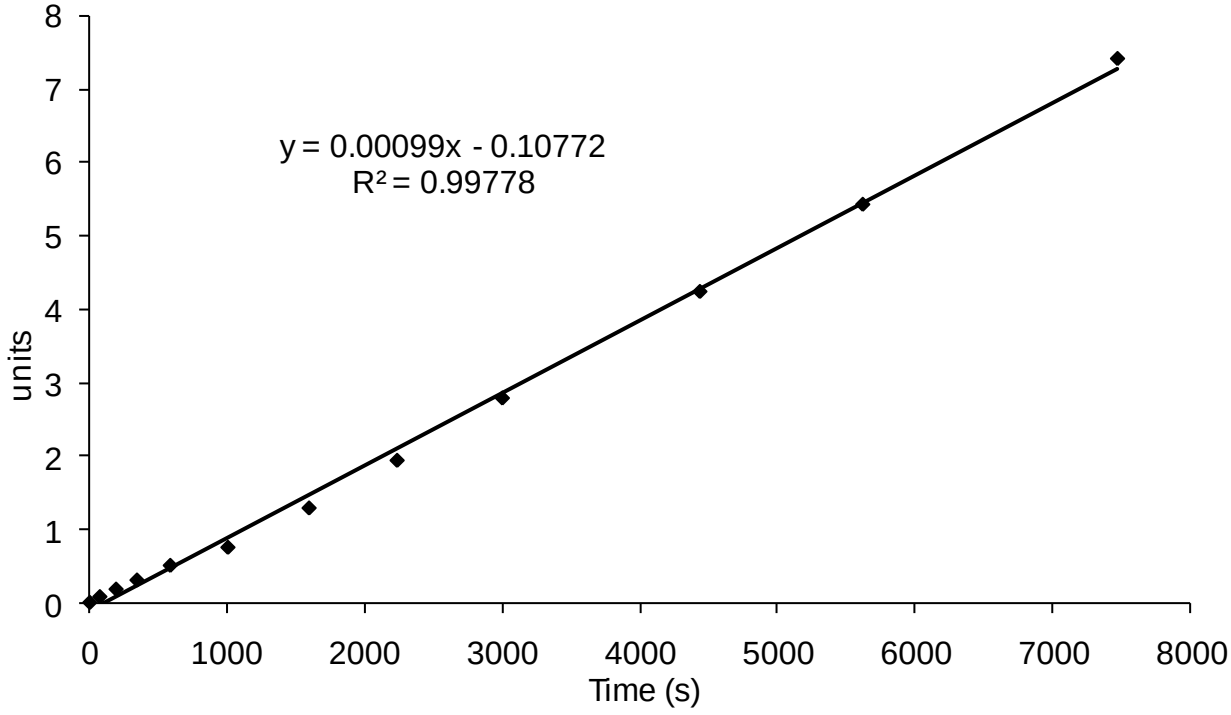
3,4-Dichlorobenzaldehyde run 2



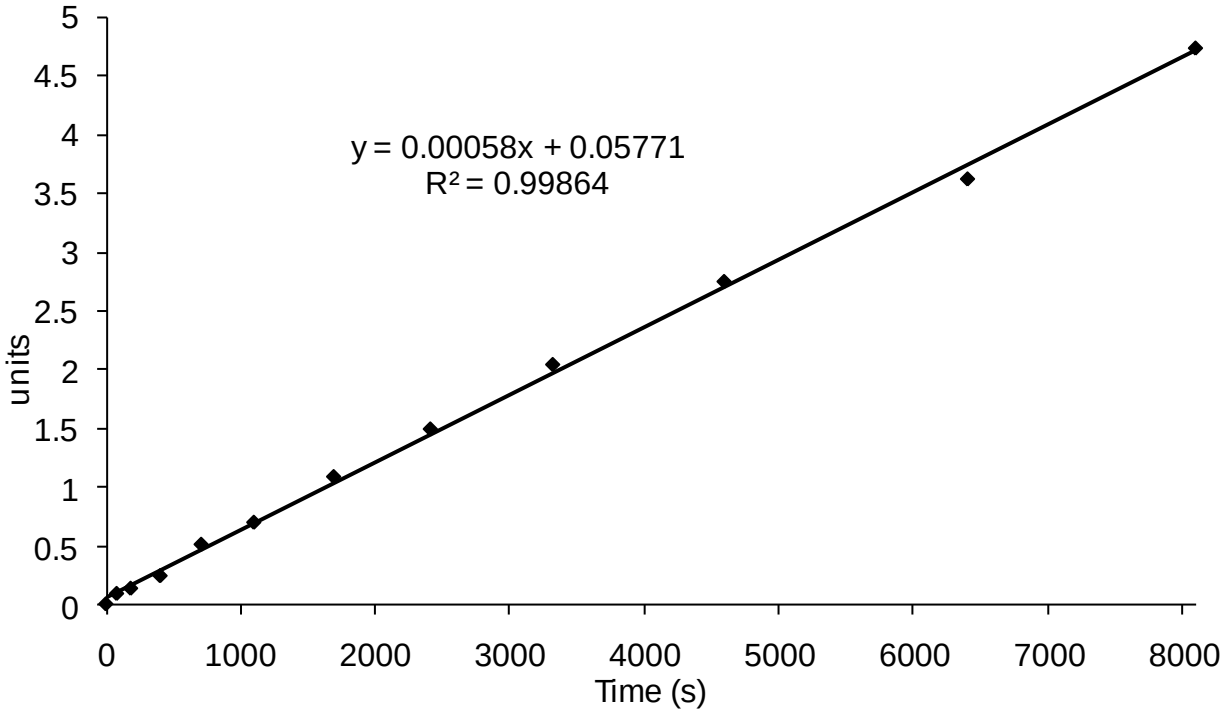
4-Chlorobenzaldehyde run 1



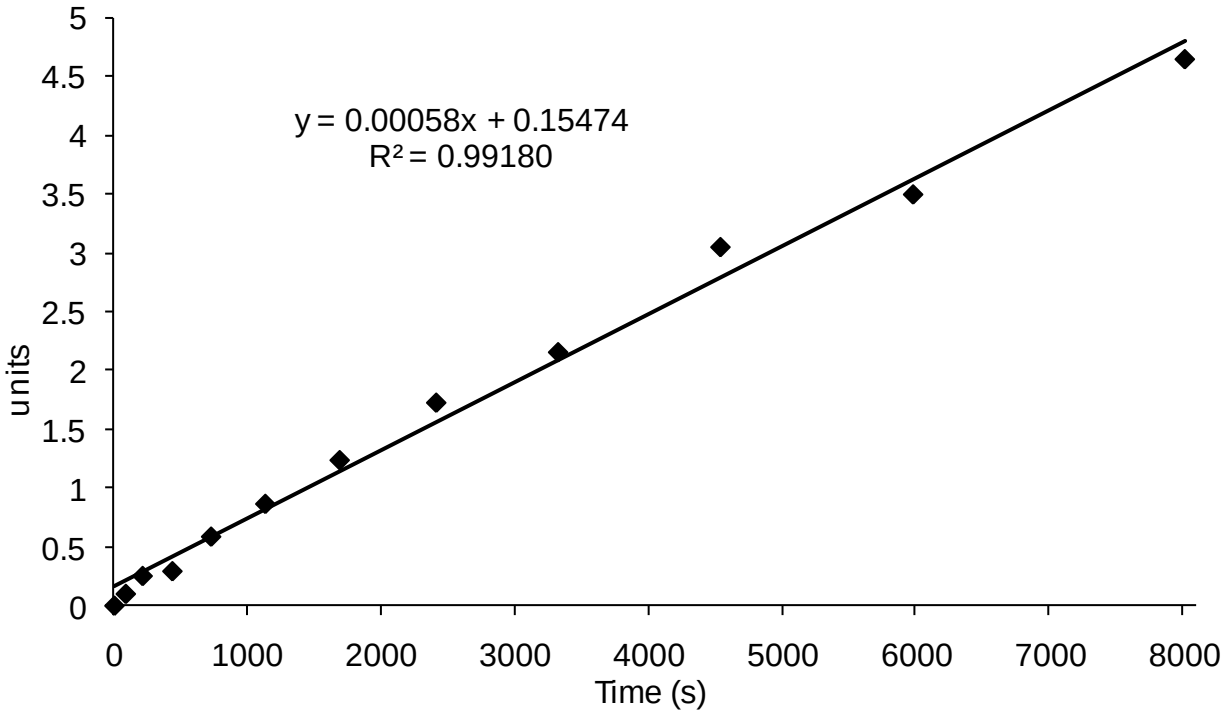
4-Chlorobenzaldehyde run 2



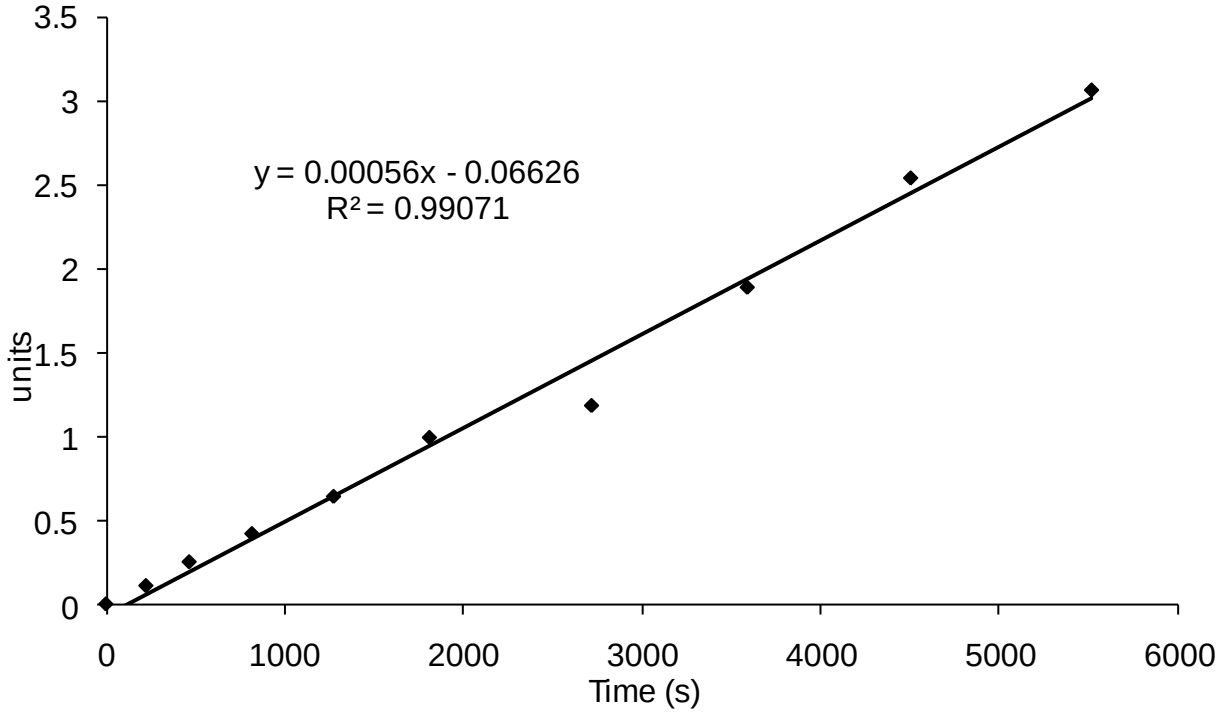
4-Methylbenzaldehyde run 1



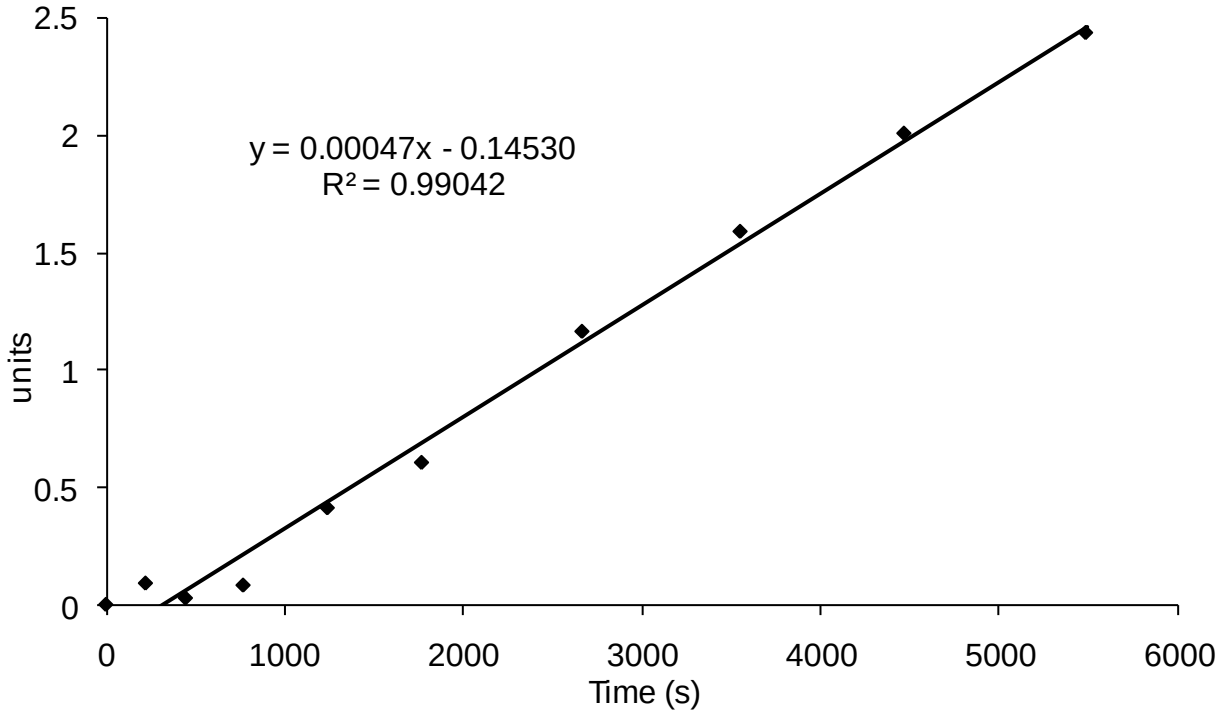
4-Methylbenzaldehyde run 2



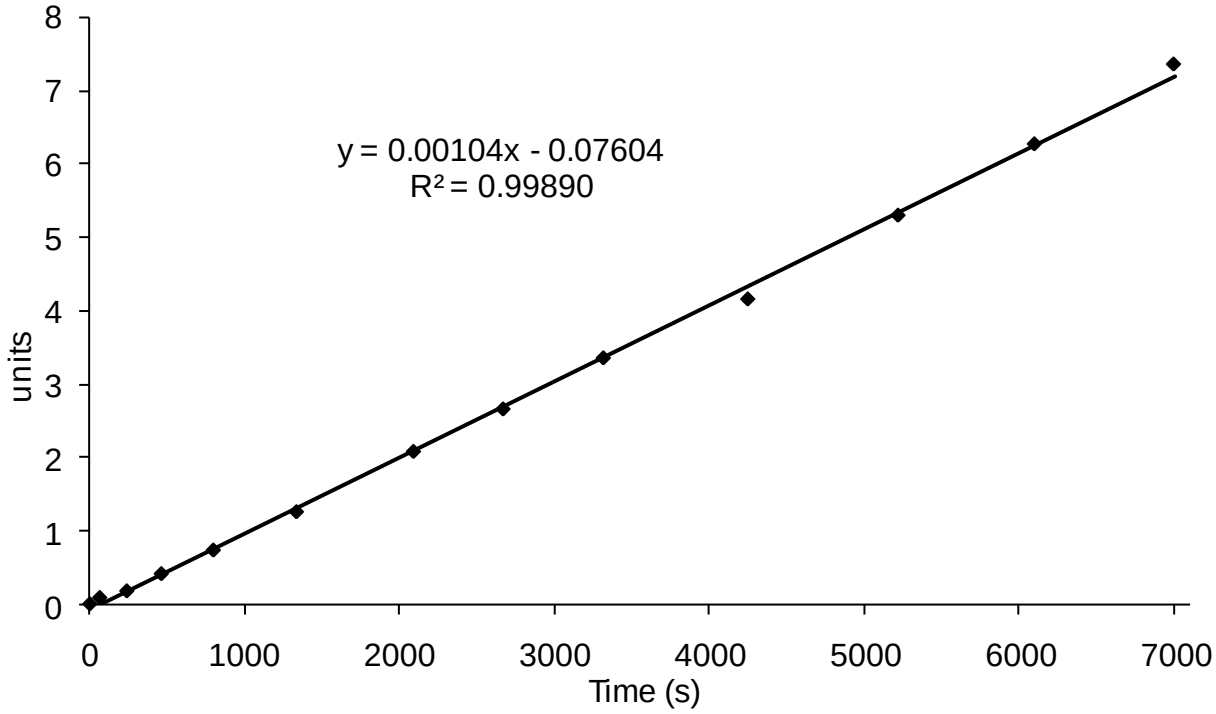
4-Fluorobenzaldehyde run 1



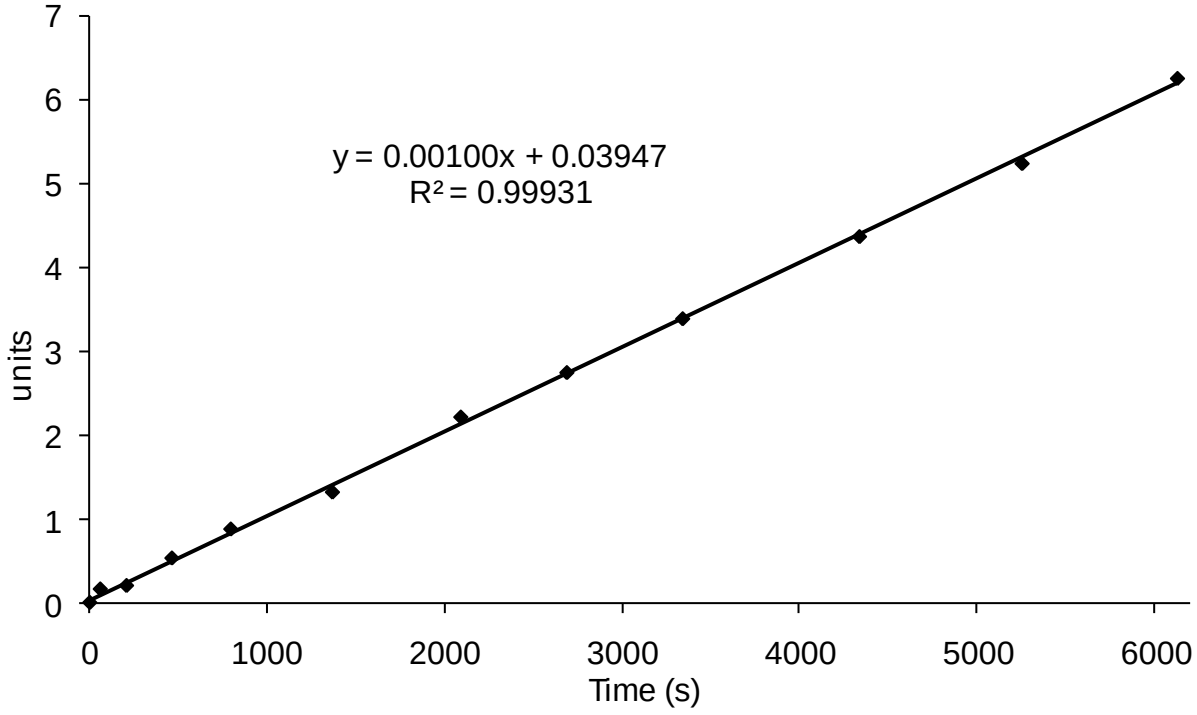
4-Fluorobenzaldehyde run 2



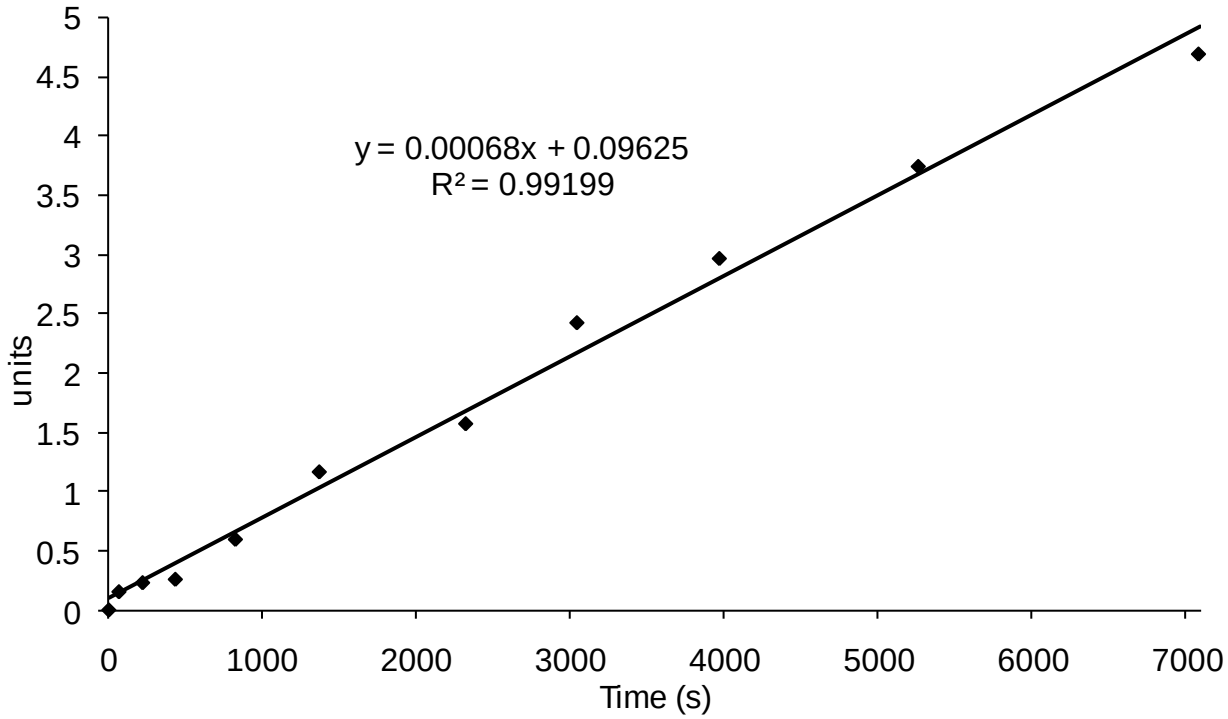
3-Fluorobenzaldehyde run 1



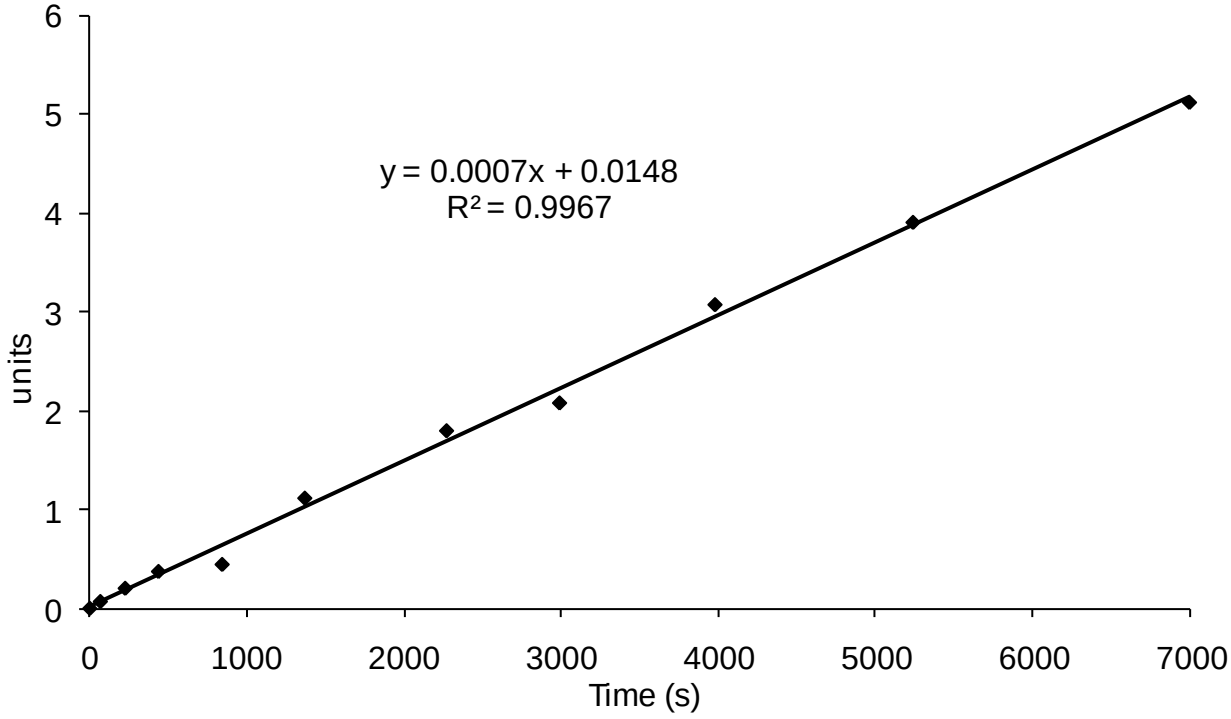
3-Fluorobenzaldehyde run 2



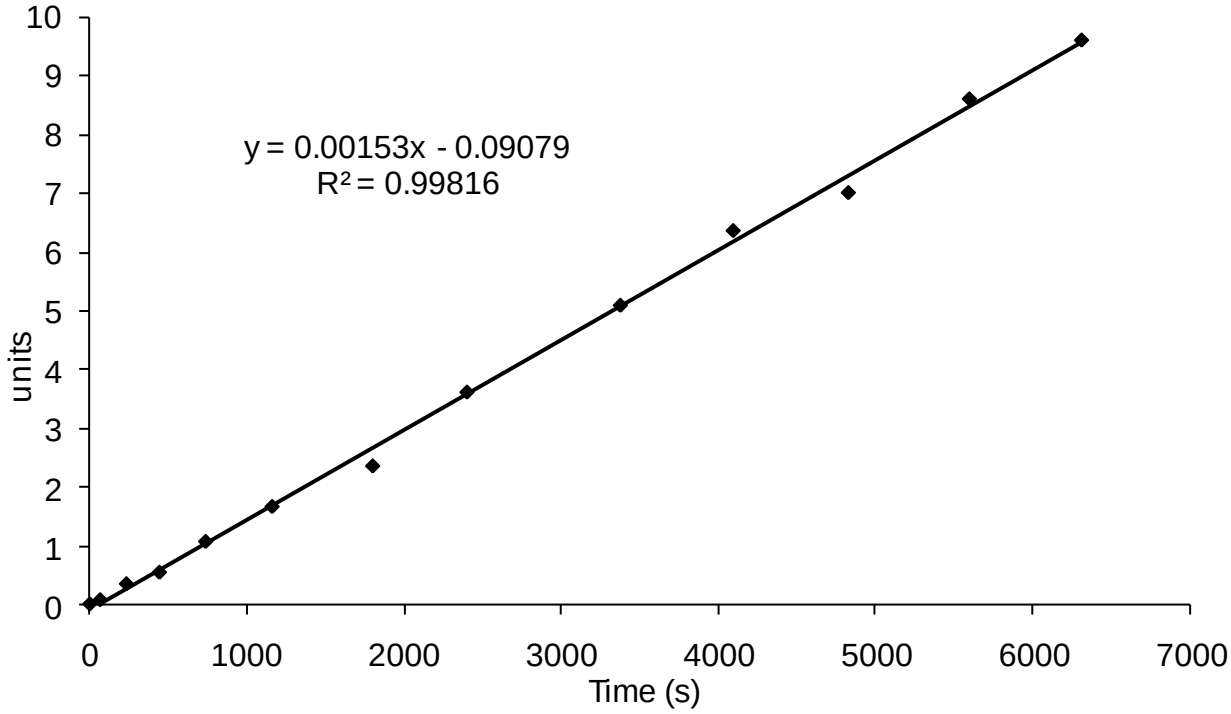
3-Methylbenzaldehyde run 1



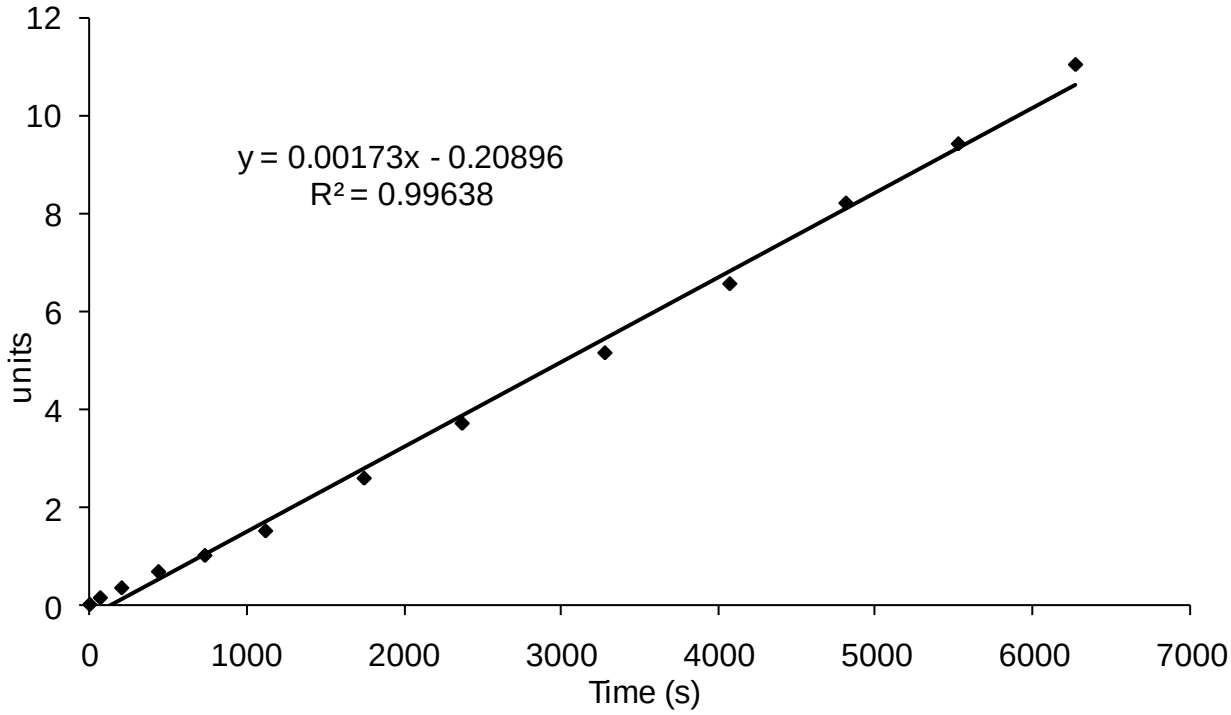
3-Methylbenzaldehyde run 2



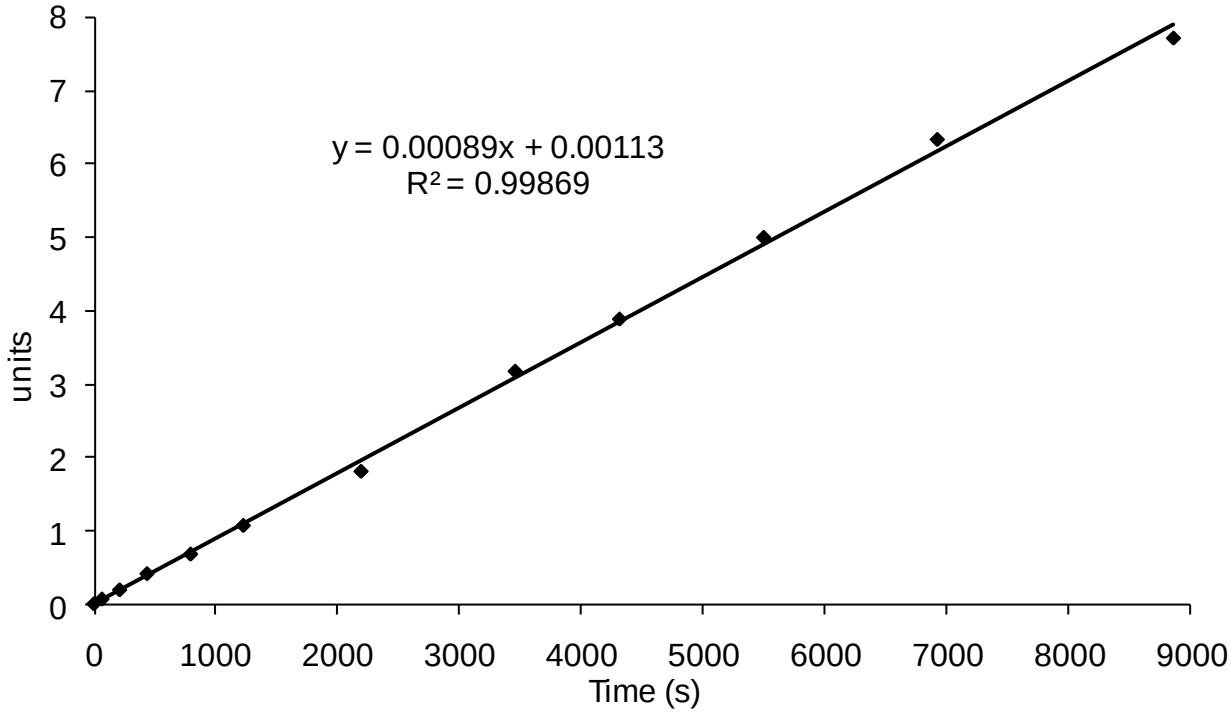
4-Trifluoromethylbenzaldehyde run 1



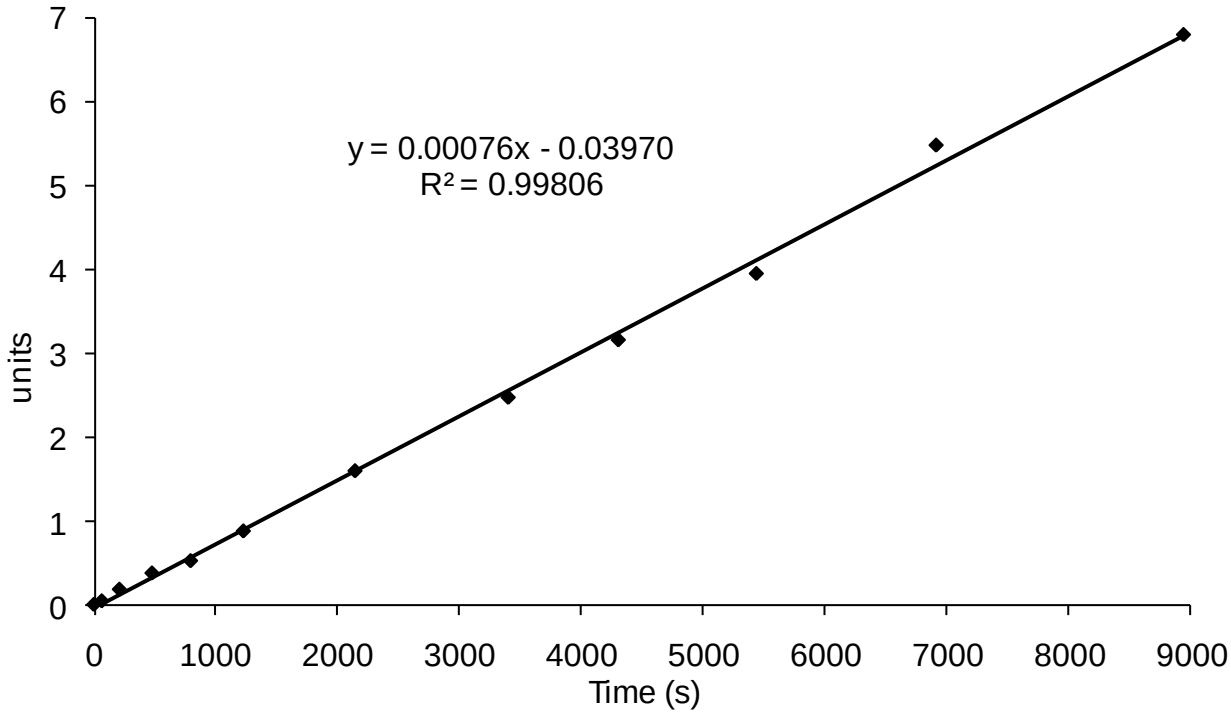
4-Trifluoromethylbenzaldehyde run 2



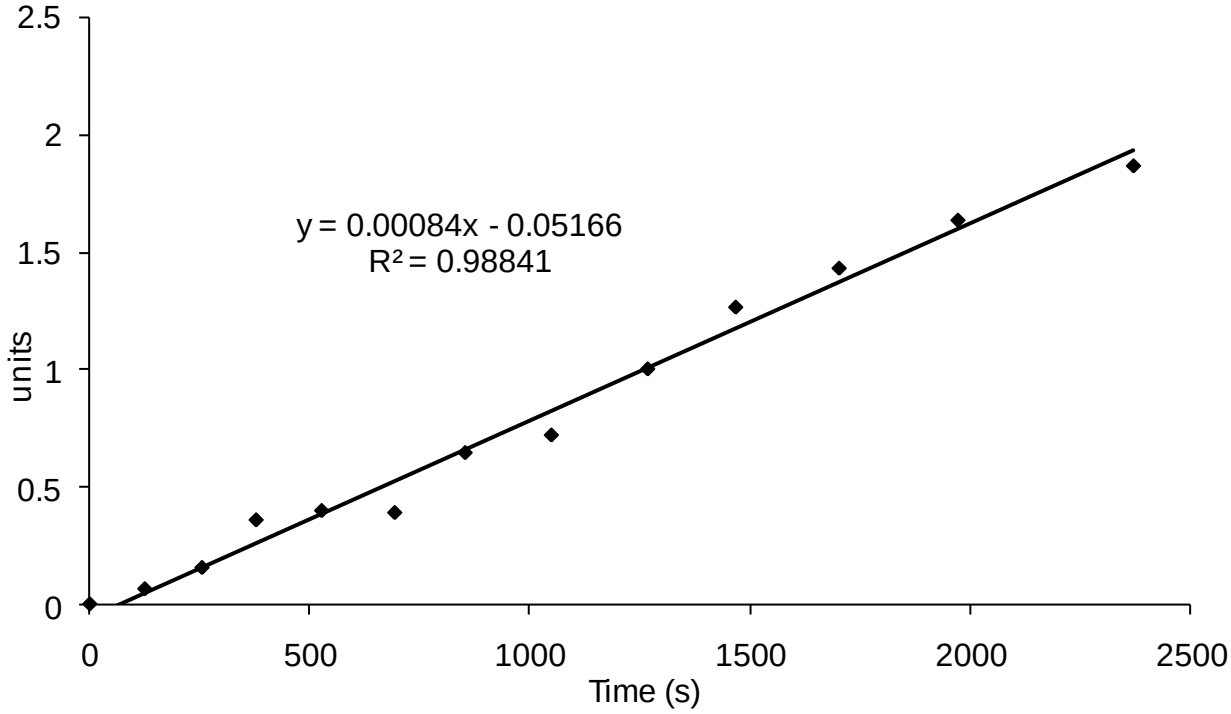
4-Bromobenzaldehyde run 1



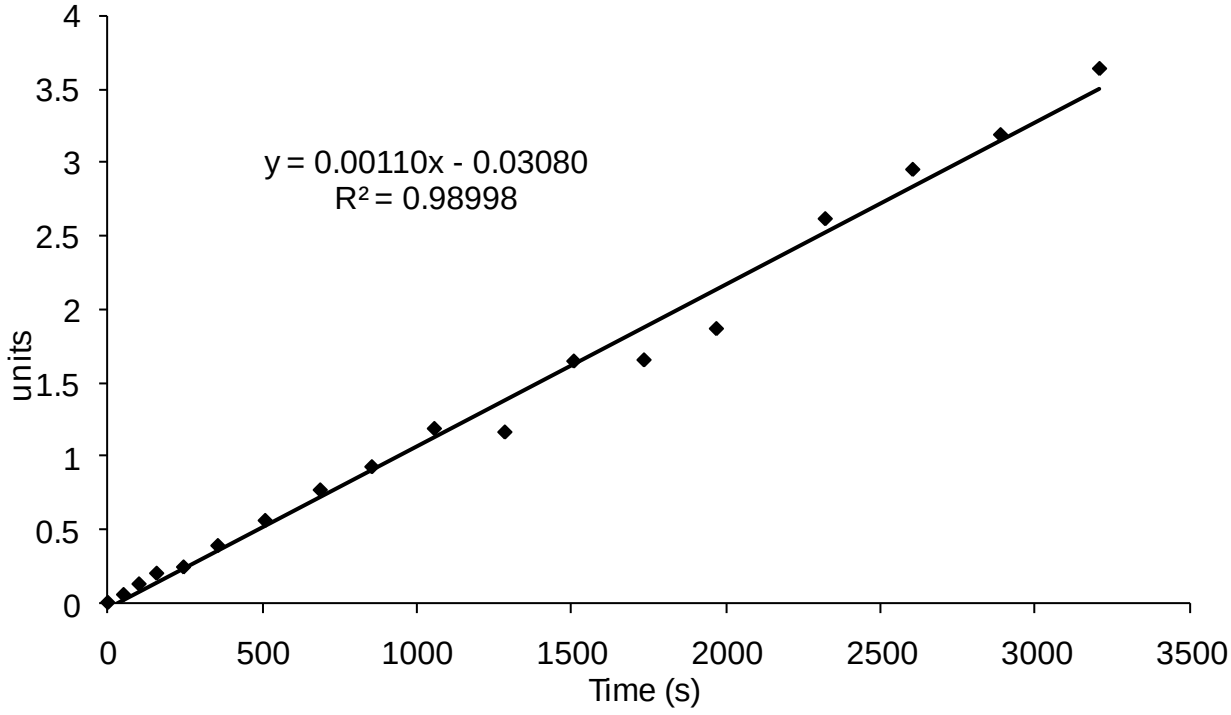
4-Bromobenzaldehyde run 2



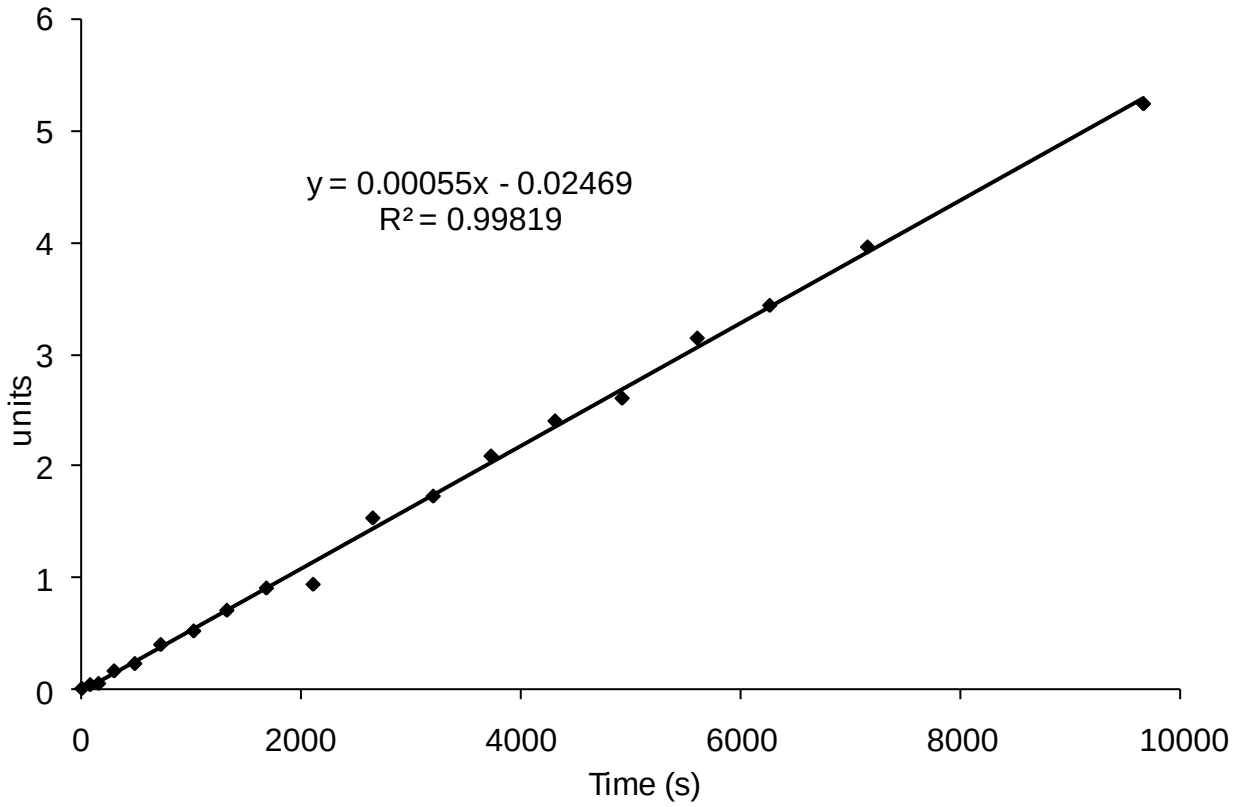
3,5-Difluorobenzaldehyde run 1



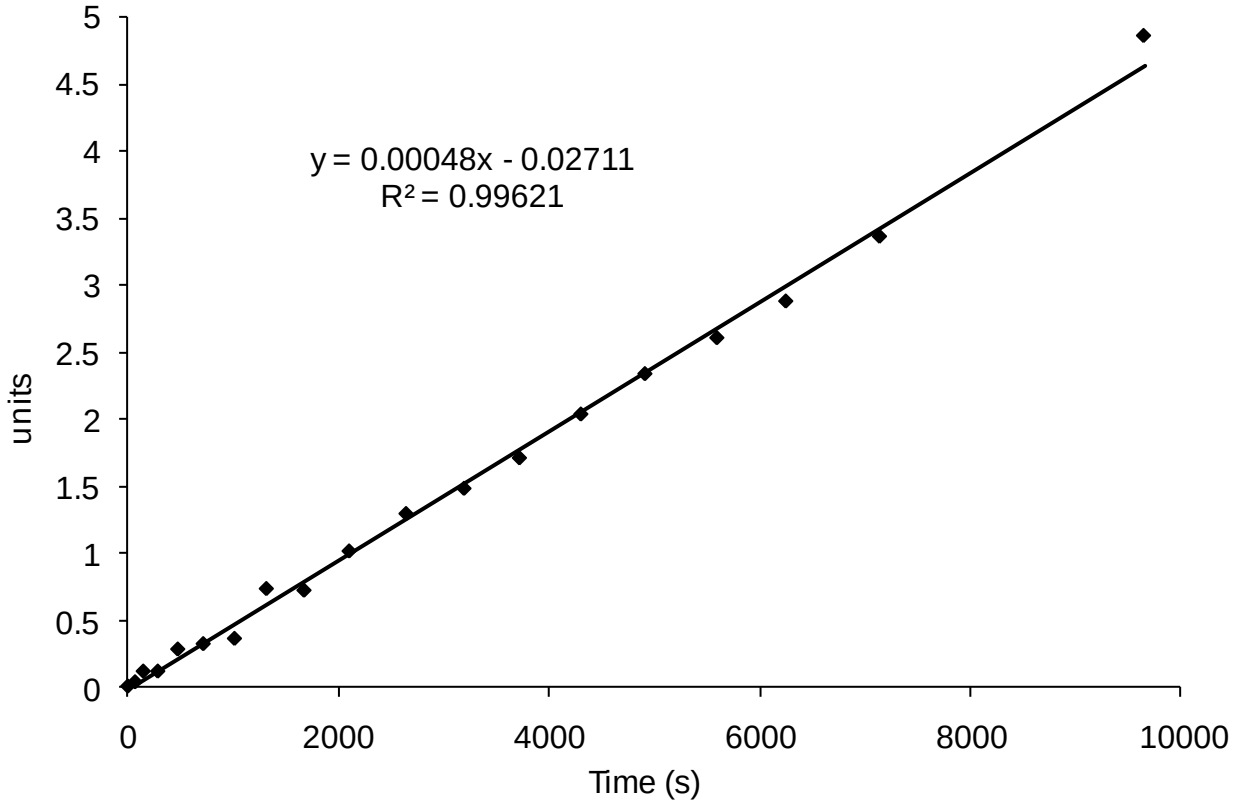
3,5-Difluorobenzaldehyde run 2



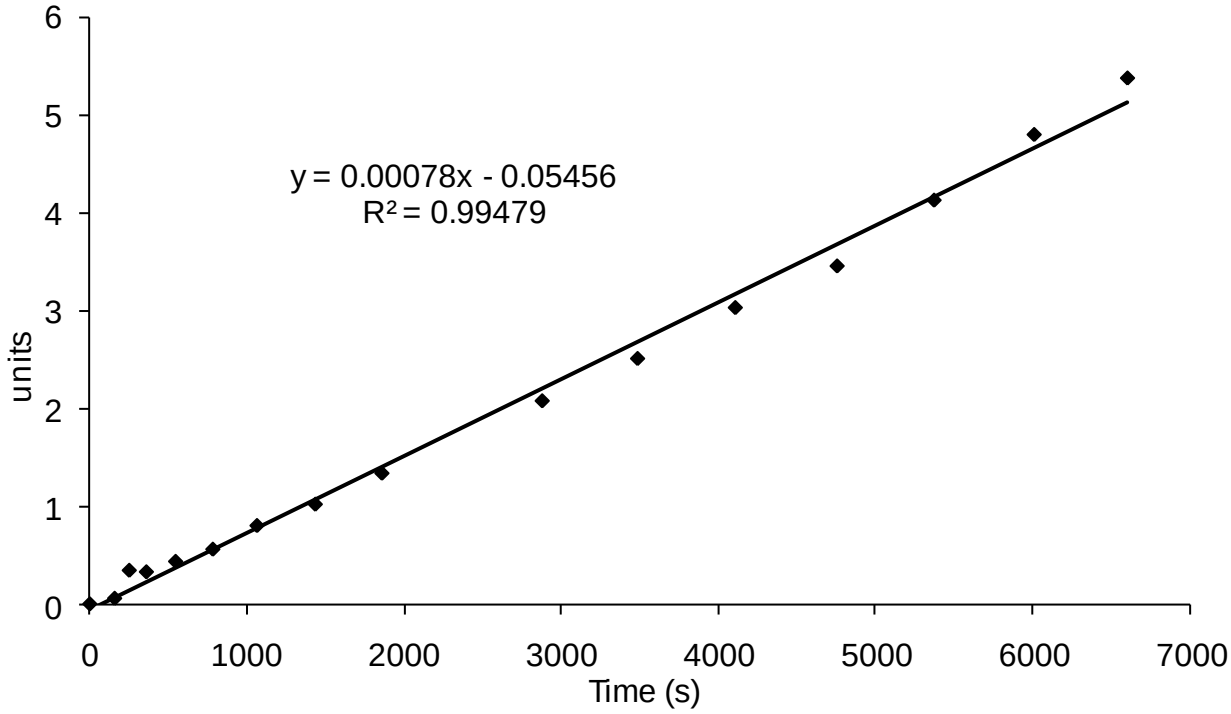
3,4-Dimethylbenzaldehyde run 1



3,4-Dimethylbenzaldehyde run 2



3-Chlorobenzaldehyde run 1



3-Chlorobenzaldehyde run 2