Sustainable Two-phase Procedure for V-catalyzed Toluene Oxidative Bromination with H_2O_2/KBr

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ELECTRONIC SUPPORTING INFORMATION

Results and Discussion

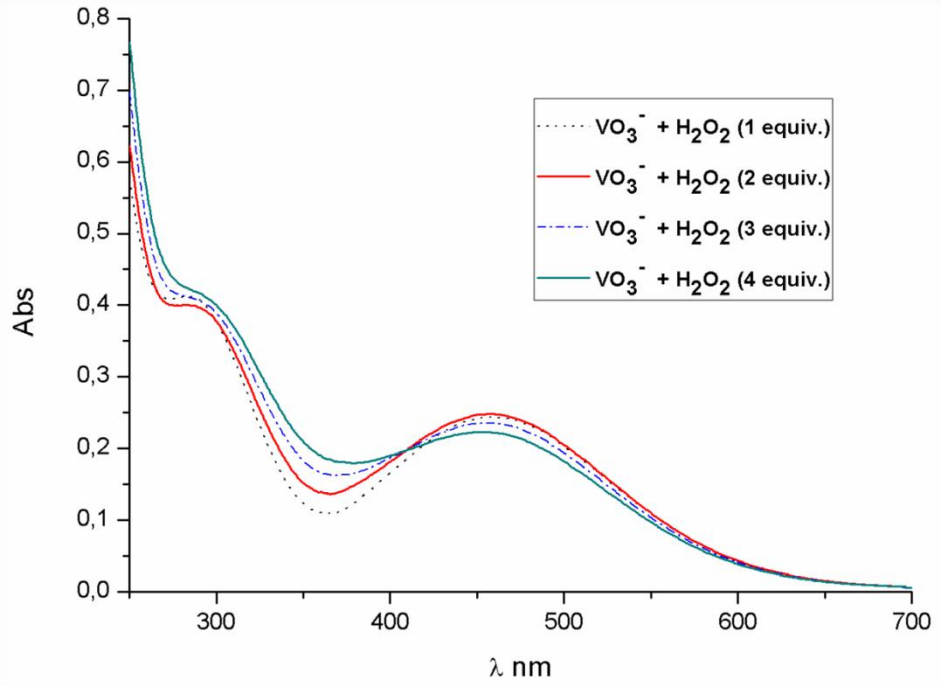


Figure ESI 1 Absorption spectra of VO_3^- + increasing amounts of H_2O_2 at pH=1.

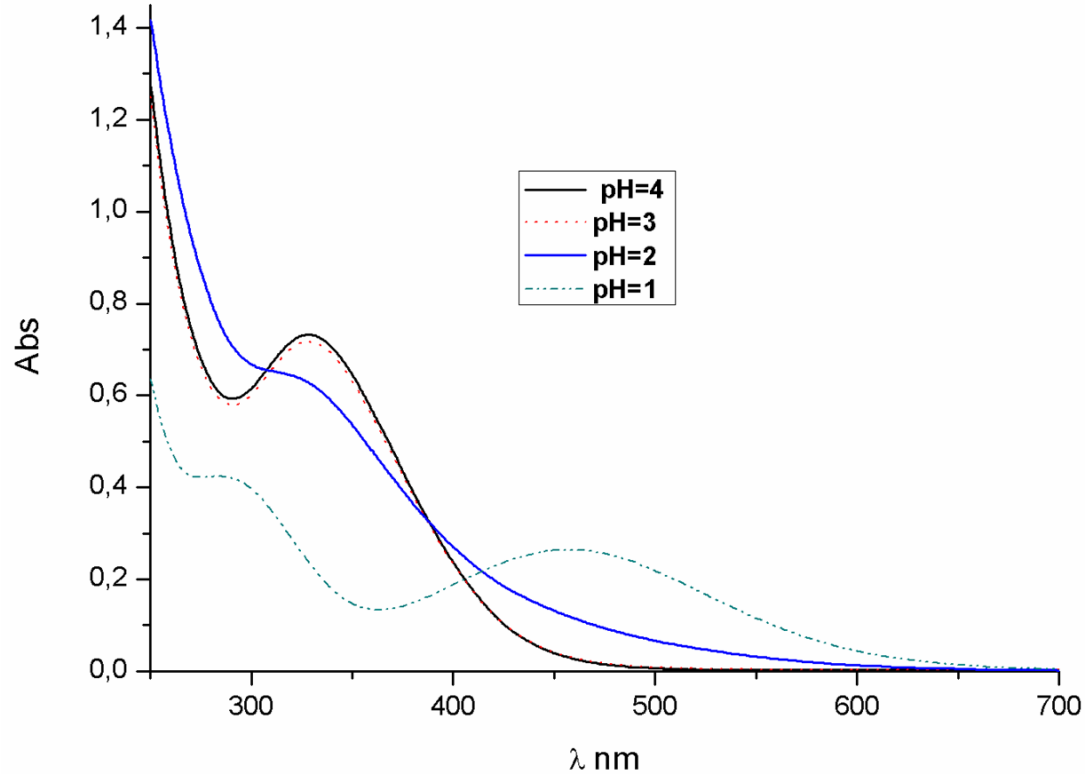


Figure ESI 2 Absorption spectra of VO_3^- + 2 equivalents H_2O_2 at increasing pH values.

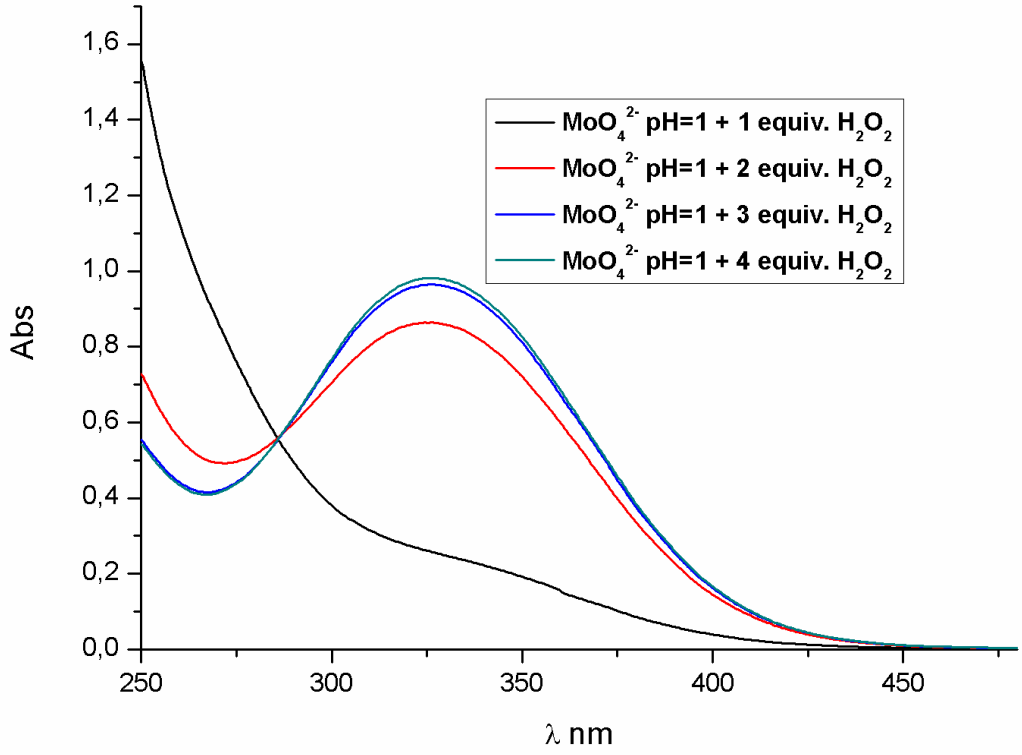


Figure ESI 3 Absorption spectra of MoO_4^{2-} + increasing amounts of H_2O_2 at pH=1.

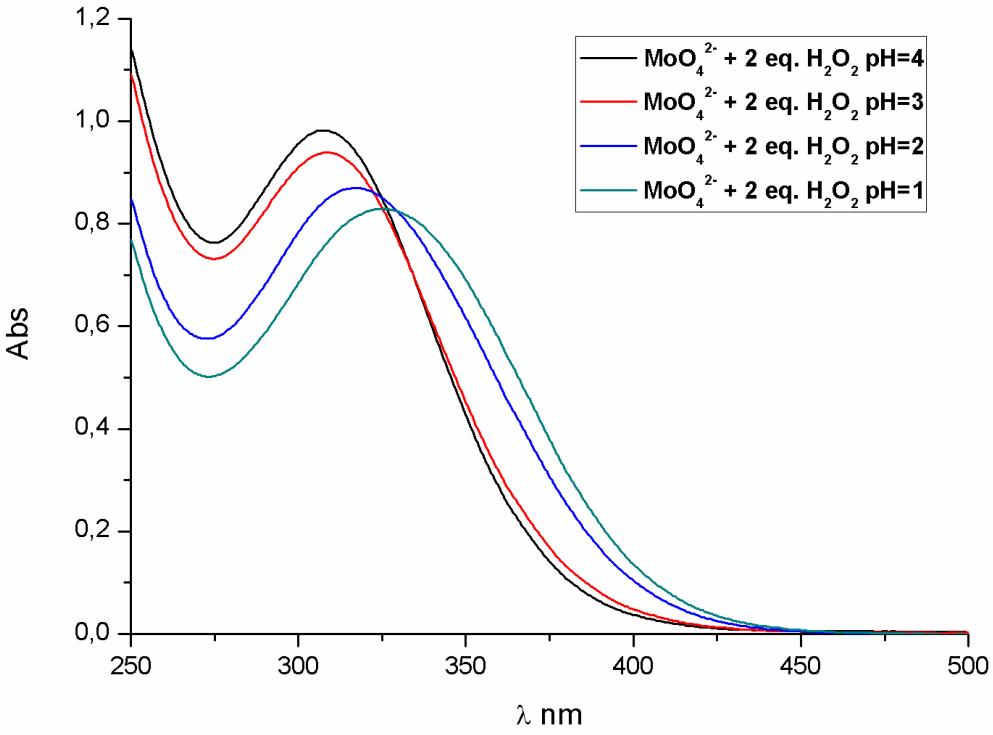


Figure ESI 4 Absorption spectra of MoO_4^{2-} + 2 equivalents H_2O_2 at increasing pH values.

Table ESI 1. Benzylic Bromination of Toluene in H_2O/DCM with KBr+H_2O_2 and V(V) or Mo(VI).

PhMe, 10^3 x mmol	$PhCH_2Br$ 10^3 x mmol	PhCHO 10^3 x mmol	$PhCHBr_2$ 10^3 x mmol	time, h	conversion PhMe, %
Run 1					
VO_3^- 0.01 M, KBr 0.025 M, H_2O_2 0.02 M					
199	0	0	0	0	0
145	56.7	2.8	0.6	2	27
119	79.6	5.0	0.8	4	40
112	81.8	5.5	0.9	6	44
92.5	92.5	7.3	1.1	24	53.5
MoO_4^{2-} 0.01 M, KBr 0.025 M, H_2O_2 0.02 M					
197	0	0	0	0	0
157	41.0	3.8	0	2	20.3
132	59.4	6.3	0.4	4	30
127	65.7	7.5	0.5	6	35.5
115	74.4	9.6	0.7	24	41.6
Run 2					
VO_3^- 0.01 M, KBr 0.05 M, H_2O_2 0.02 M					
197	0	0	0	0	0
141	62.9	2.5	0.5	2	28.9
110	87.9	4.0	1.1	4	44.6
102	96.8	4.7	1.3	6	48.2
91.3	107	6.4	1.7	24	53.7
MoO_4^{2-} 0.01 M, KBr 0.05 M, H_2O_2 0.02 M					
195	0	0	0	0	0
108	92.6	4.0	1.1	2	44.5
80.6	115	7.7	2.2	4	58.8
71.1	122	9.6	2.6	6	63.6
57.3	135	11	3.2	24	70.6
Run 3					
VO_3^- 0.01 M, KBr 0.025 M, H_2O_2 0.04 M					
198	0	0	0	0	0
147	54.2	1.46	0.47	2	25.8
122	77.7	1.62	0.82	4	38.4
112	87.9	1.90	0.98	6	43.4
104	93.2	2.36	1.17	24	47.5
MoO_4^{2-} 0.01 M, KBr 0.025 M, H_2O_2 0.04 M					
198	0	0	0	0	0
130	66.9	3.7	0.6	2	34
93.2	103	6.9	1.5	4	63
82.8	110	9.0	1.9	6	58
66.9	115	10.1	2.3	24	66

Run 4					
VO_3^- 0.01 M, KBr 0.025 M, H_2O_2 0.04 M, in two portions, the second one added after 6h					
200	0	0	0	0	0
145	59.1	2.9	0.4	2	27.5
125	75.4	4.8	0.8	4	37.5
82.9	117	5.9	2.3	6	58.6
58.8	138	6.4	3.4	24	70.7
MoO_4^{2-} 0.01 M, KBr 0.025 M, H_2O_2 0.04 M, in two portions, the second one added after 6h					
206	0	0	0	0	0
136	63.6	6.2	0.5	2	34
111	87	7.6	1.0	4	46.1
65.4	131	8.5	3.4	6	68.3
33.6	158	8.6	6.8	24	83.7
Run 5					
VO_3^- 0.01 M, KBr 0.05 M, H_2O_2 0.04 M					
195	0	0	0	0	0
50.3	151	2.7	5.3	2	74.2
31.0	165	3.5	8.2	4	84.1
26.5	168	3.9	8.8	6	90
MoO_4^{2-} 0.01 M, KBr 0.05 M, H_2O_2 0.04 M					
199	0	0	0	0	0
9.2	177	2.3	18.1	2	95.4
0.4	148	1.1	55.2	4	99.8
0.4	137	1.57	66.8	6	99.8

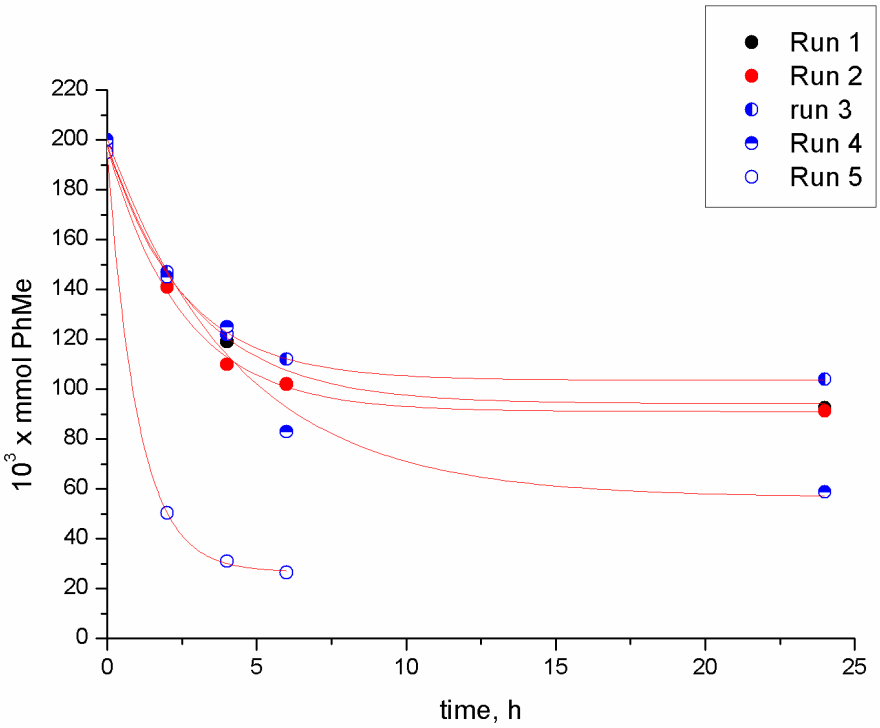


Figure ESI 5 Disappearamce of PhMe with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, VO_3^-.

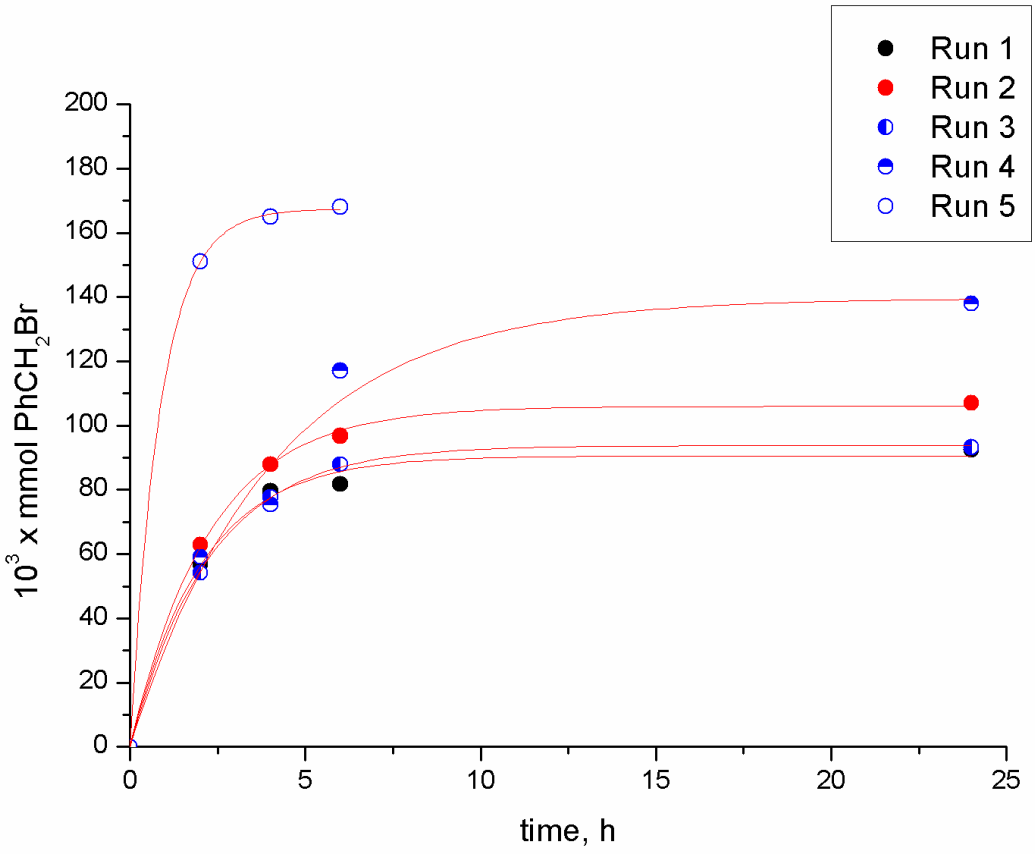


Figure ESI 6 Formation of benzyl bromide with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, VO_3^-.

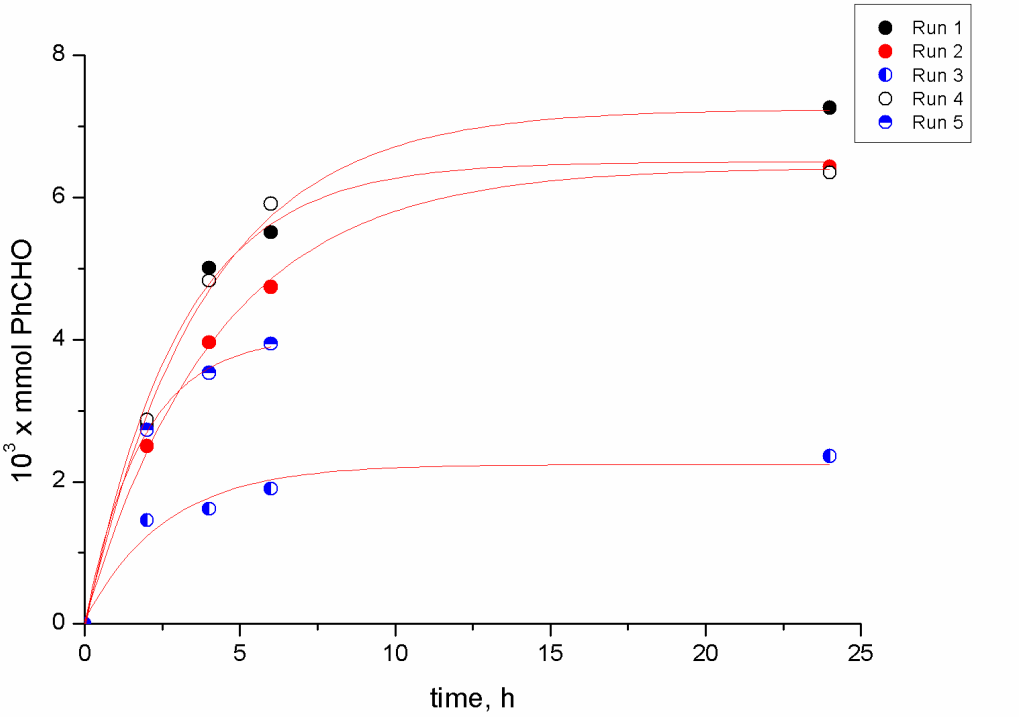


Figure ESI 7 Formation of PhCHO with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, VO_3^-.

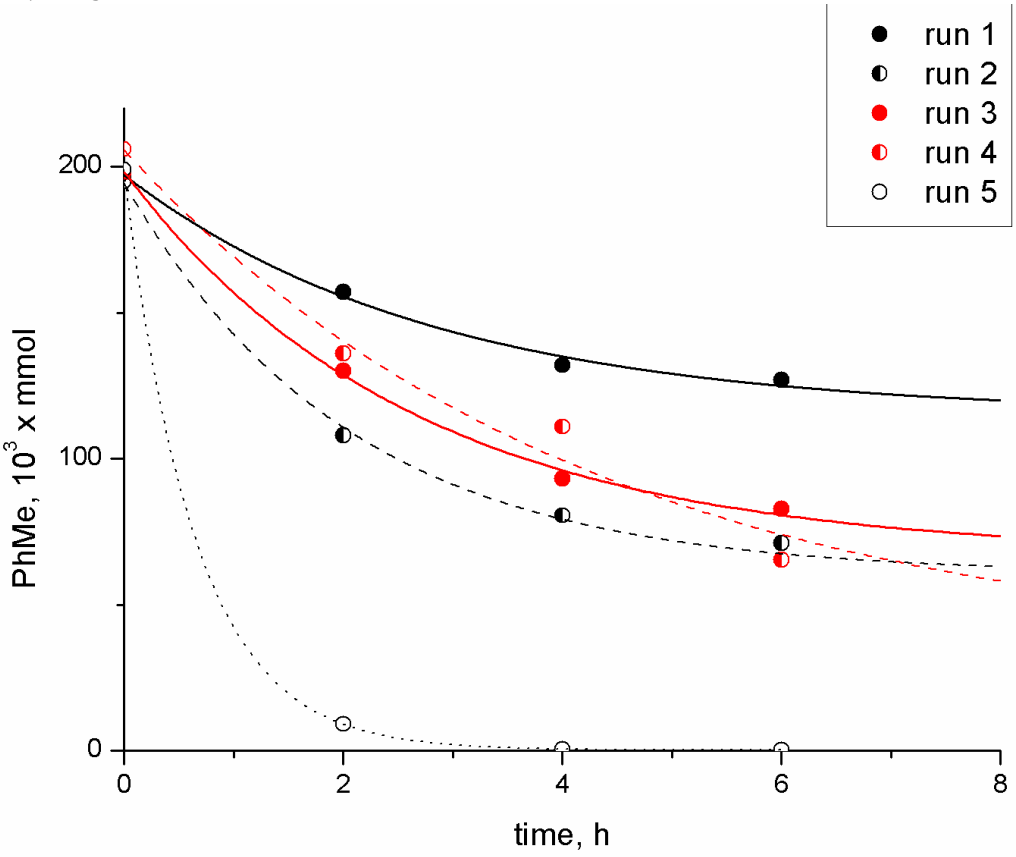


Figure ESI 8 Disappearamce of PhMe with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, MoO_4^{2-}.

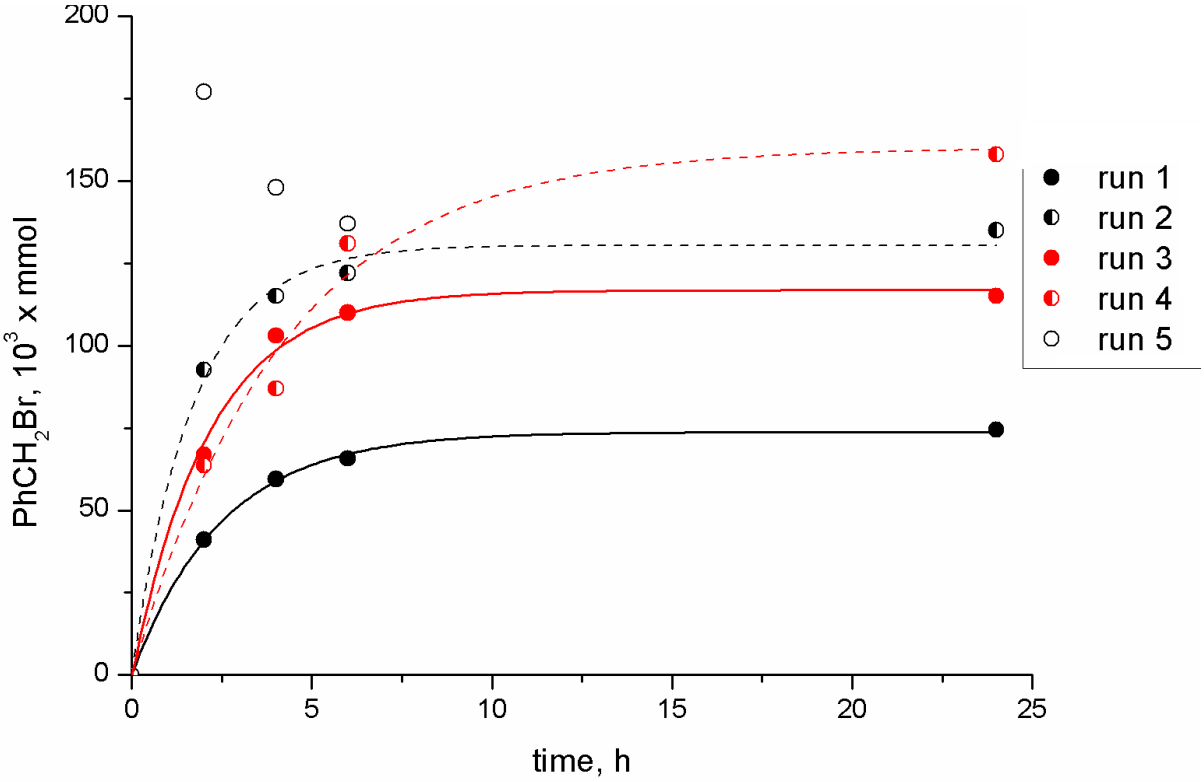


Figure ESI 9 Formation of bromomethylbenzene with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, MoO_4^{2-}.

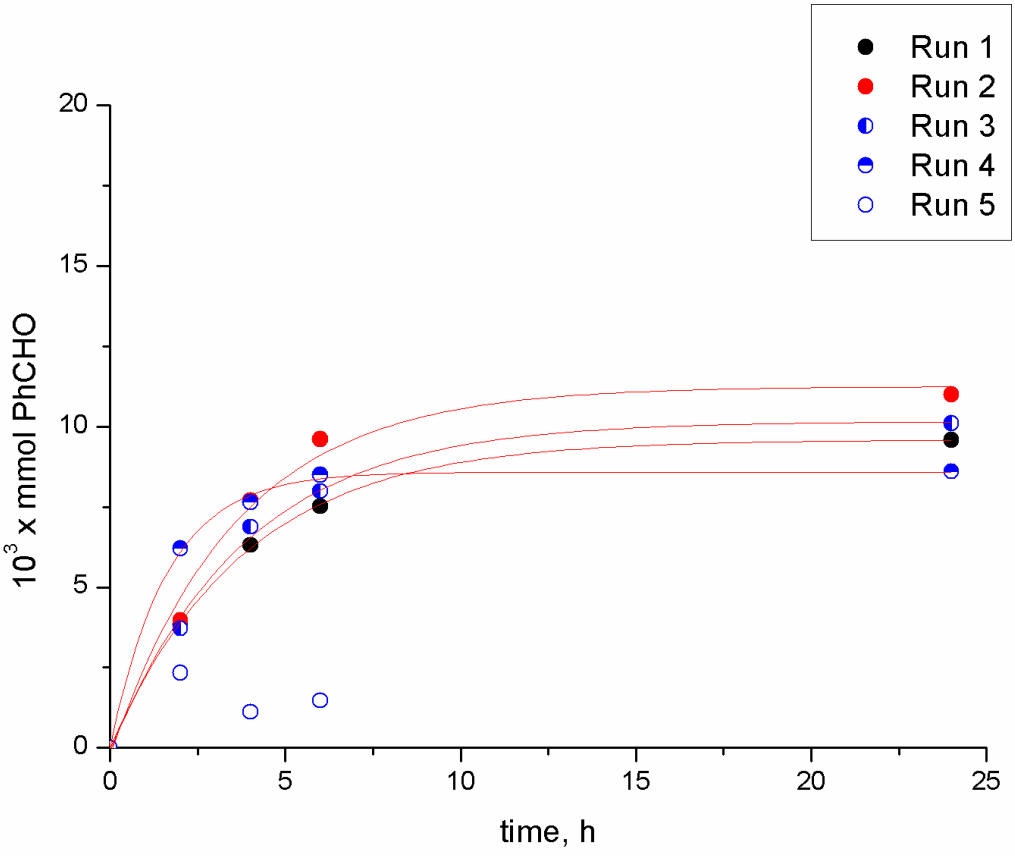


Figure ESI 10 Formation of dibromomethylbenzene with time, in the different runs of Table 1. Reaction conditions, H_2O/DCM, MoO_4^{2-}.

Table ESI 2. Benzylic Bromination of Toluene in PhMe/H_2O with KBr+H_2O_2 and V(V) or Mo(VI).

$PhCH_2Br$ 10^3 x mmol	*o*- + *p*- C_6H_4MeBr 10^3 x mmol	PhCHO 10^3 x mmol	time, h	overall yield, %	
Run 1					
VO_3^- 0.01 M, H_2O_2 0.02 M, T = 25 °C					
55.7	2.6	7.8	2	33.1	
70.6	4.5	11.0	4	43.1	
75.1	6.0	13.9	6	47.5	
84.2	13.9	20.2	24	58.2	
MoO_4^{2-} 0.01 M, KBr 0.025 M, H_2O_2 0.02 M, T = 25 °C					
73.1	4.7	8.6	2	43.2	
109	8.8	15.2	4	66.5	
124	9.9	19.6	6	76.7	
144	26.2	27.8	24	99.0	
Run 2					
VO_3^- 0.01 M, KBr 0.025 M, H_2O_2 0.02 M, T = 40 °C					
55.5	14.1	11.5	2	40.5	
57.6	17.0	15.9	4	45.2	
57,3	18.7	18.0	6	47.0	
55.8	19.0	20.2	24	47.5	
MoO_4^{2-} 0.01 M, KBr 0.025 M, H_2O_2 0.02 M, T = 40 °C					
121.7	19.9	15.1	2	78.3	
140	26.3	23.9	4	95.1	
143.7	28.7	27.8	6	99.6	
Run 3					
VO_3^- 0.002 M, KBr 0.025 M, H_2O_2 0.02 M,					
10.4	1.2	4.6	2	8.1	
33.1	3.2	10.4	4	23.4	
48.4	8.5	15.8	6	36.3	
54.6	9.8	22.2	24	43.3	
MoO_4^{2-} 0.002 M, KBr 0.025 M, H_2O_2 0.02 M, T = 25 °C					
33	2.5	7.14	2	21.3	
81.5	6.4	16.7	4	52.3	
115	9.8	24.1	6	745	
138	22.2	37.0	24	98.6	
Run 4					
VO_3^- 0.002 M, KBr 0.025 M, H_2O_2 0.02 M, T = 40 °C					
40.5	9.8	9.1	2	29.7	
45.1	14.8	14.7	4	37.3	
44.2	15.7	17.0	6	38.5	
43.8	16.9	20.4	24	40.5	
MoO_4^{2-} 0.002 M, KBr 0.025 M, H_2O_2 0.02 M, T = 40 °C					
61.0	10.1	8.4	2	39.7	
77.6	15.9	14.0	4	53.8	
79.7	17.2	16.5	6	56.7	
78.2	18.3	18.0	24	57.3	

Run 5					
VO_3^- 0.01 M, KBr 0.025 M, H_2O_2 0.02 M, in two portions (the second one added after 4h), **T = 25 °C**					
14.8	1.6	4.8	2	10.6	
23.2	5.4	11.0	4*	19.8	
74.1	9.7	19.2	6		
84.2	20.9	26.3	24		
Run 6					
VO_3^- 0.002 M, KBr 0.05 M, H_2O_2 0.04 M, T = 40 °C					
72.1	10.7	10.6	2	23.3	
88.1	16.7	16.5	4	30.3	
88.7	17.6	18.9	6	31.3	
87.4	18.3	21.3	24	31.8	
MoO_4^{2-} 0.002 M, KBr 0.05 M, H_2O_2 0.04 M, T = 40 °C					
172	22.6	14.4	2	52.3	
185	28.5	20.2	4	58.4	
186	29.7	23.1	6	59.5	
185	30.9	24.4	24	60.1	
Run 7					
VO_3^- 0.01 M, H_2O_2 0.04 M, in two portions (the second one after 4 h), **T = 40 °C**					
40.6	9.7	8.5	2	29.4	
40.9	11.0	11.5	4*	31.7	
69.3	19.7	17.8	6	26.7	
66.5	22.6	21.4	24	27.6	
MoO_4^{2-} 0.01 M, H_2O_2 0.04 M, in two portions (the second one after 4 h), **T = 40 °C**					
118	18.8	14,6	2	75.7	
134	24.5	20,9	4*	89.7	
174	35.5	30,0	6	59.88	
187	58.3	39,1	24	71.25	

* Second portion of H_2O_2; subsequent yields were calculated on the total amount of hydrogen peroxide.

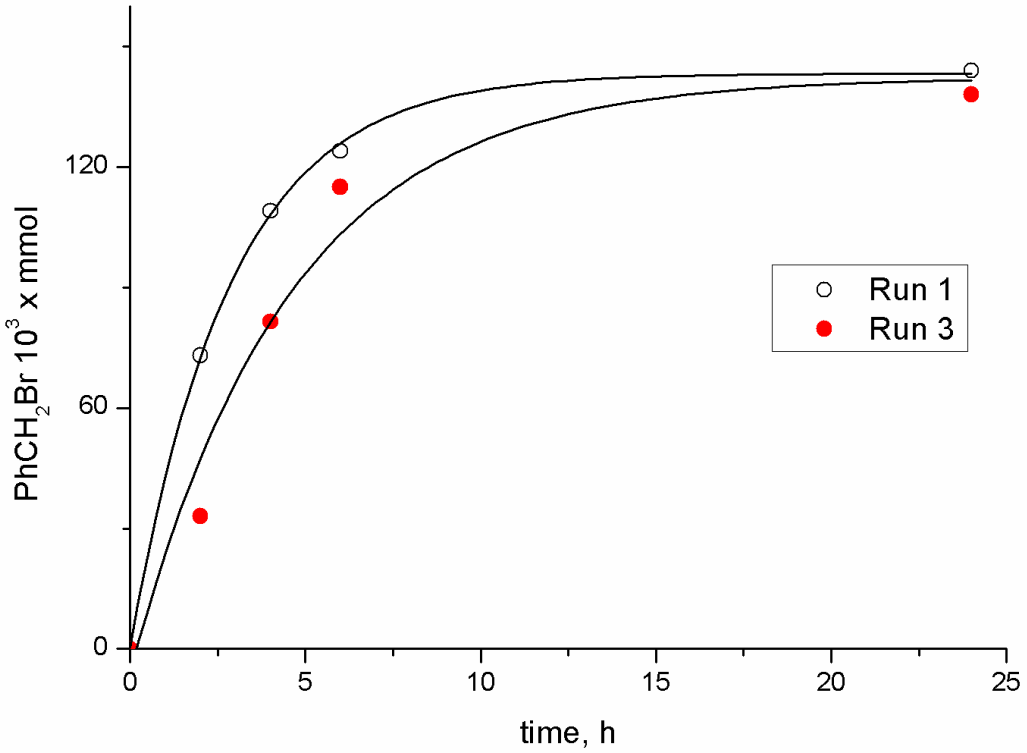


Figure ESI 11 Formation of benzyl bromide with time, in the different runs of Table 2. Reaction conditions, PhMe/H_2O, MoO_4^{2-} 25 °C.

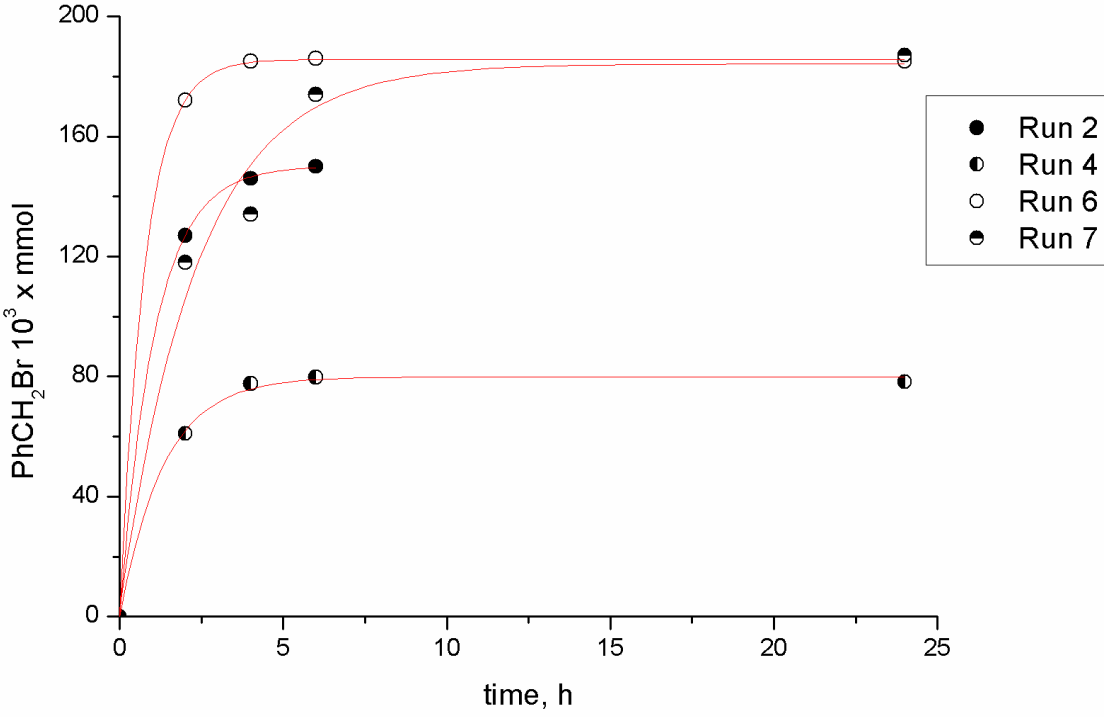


Figure ESI 12 Formation of benzyl bromide with time, in the different runs of Table 2. Reaction conditions, PhMe/H_2O, MoO_4^{2-} 40 °C.

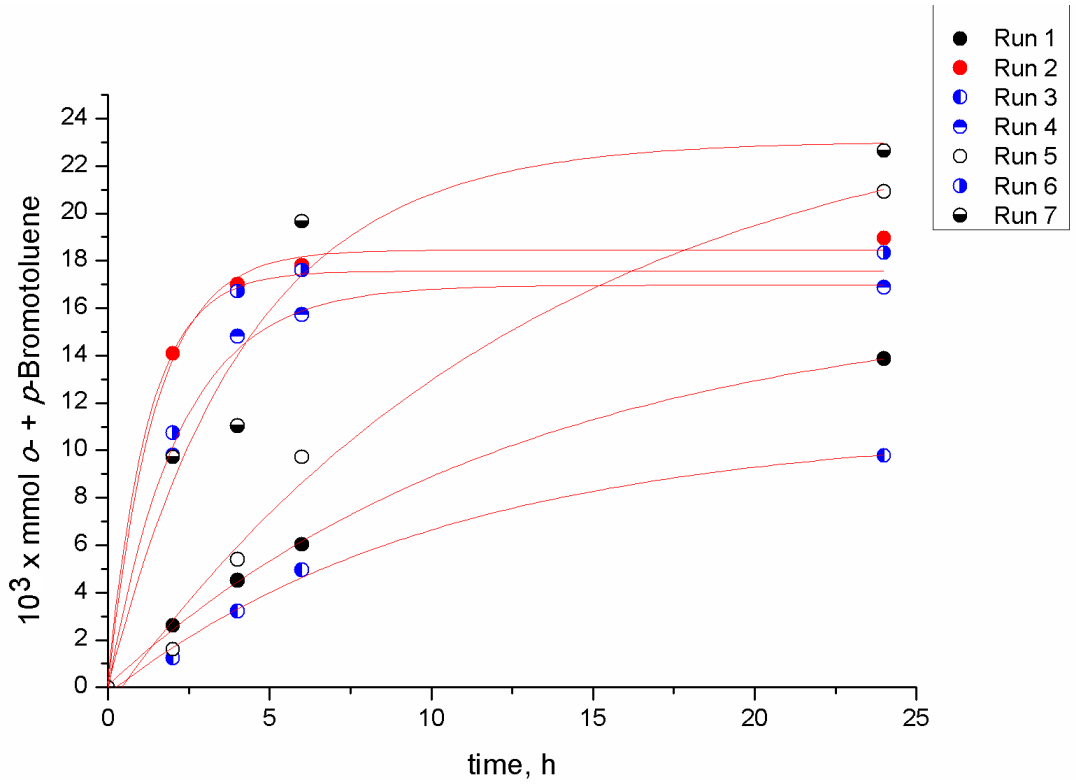


Figure ESI 13 Formation of *o*- + *p*-bromotoluene with time, in the different runs of Table 2. Reaction conditions, PhMe/H_2O, VO_3.

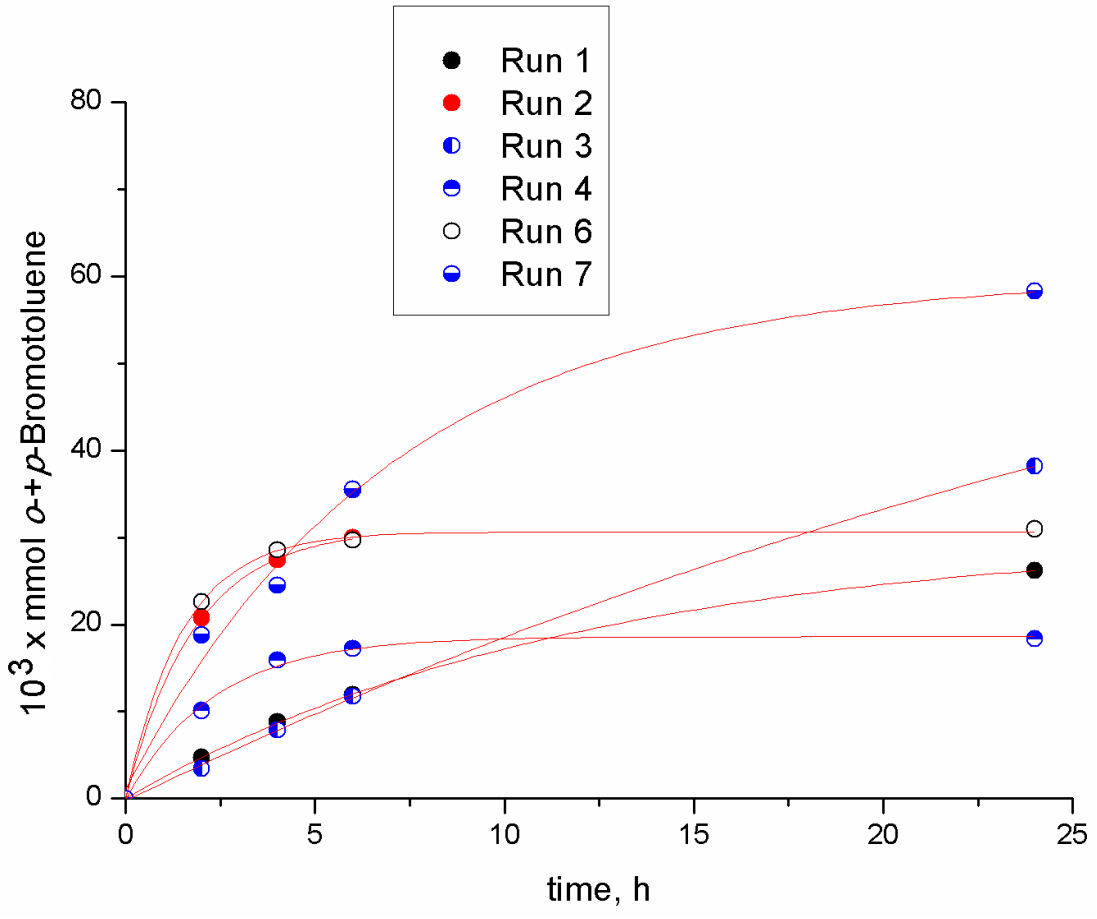
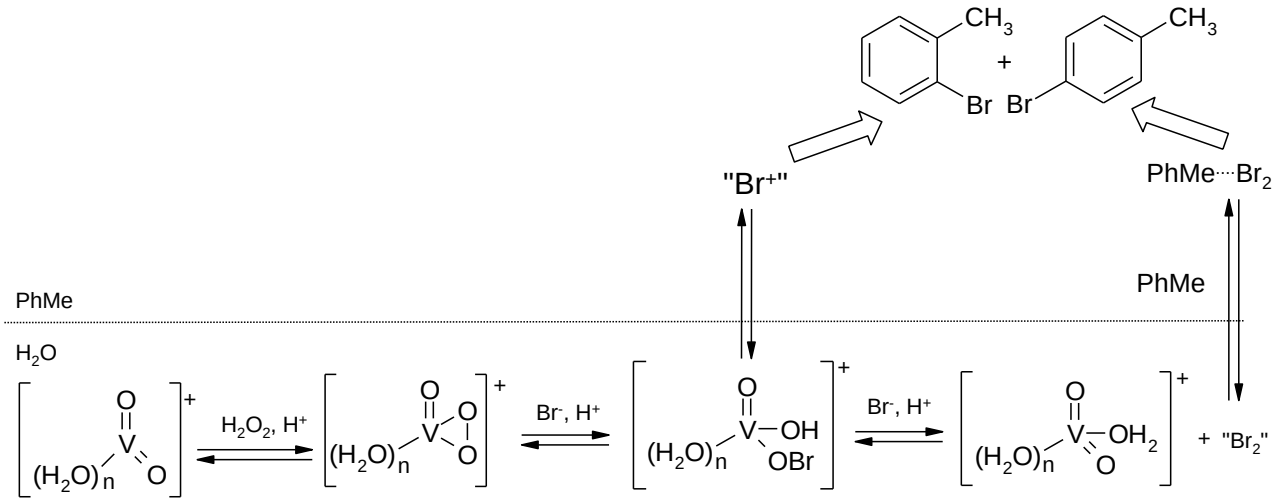


Figure ESI 14 Formation of *o*- + *p*-bromotoluene with time, in the different runs of Table 2. Reaction conditions, PhMe/H_2O, MoO_4^{2-}.



Scheme ESI 1 Possible mechanism for electrophilic aromatic bromination of toluene.

Experimental Section

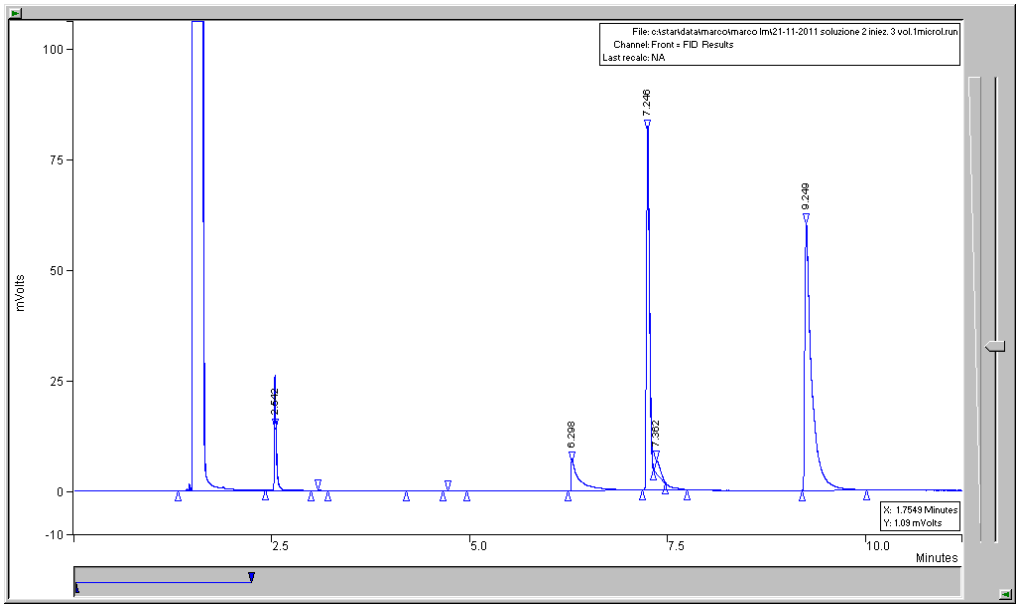


Figure ESI 15. Typical gas-chromatogram of a mixture containing (with increasing retention times): toluene, benzaldehyde, decane (internal standard), and benzyl bromide.

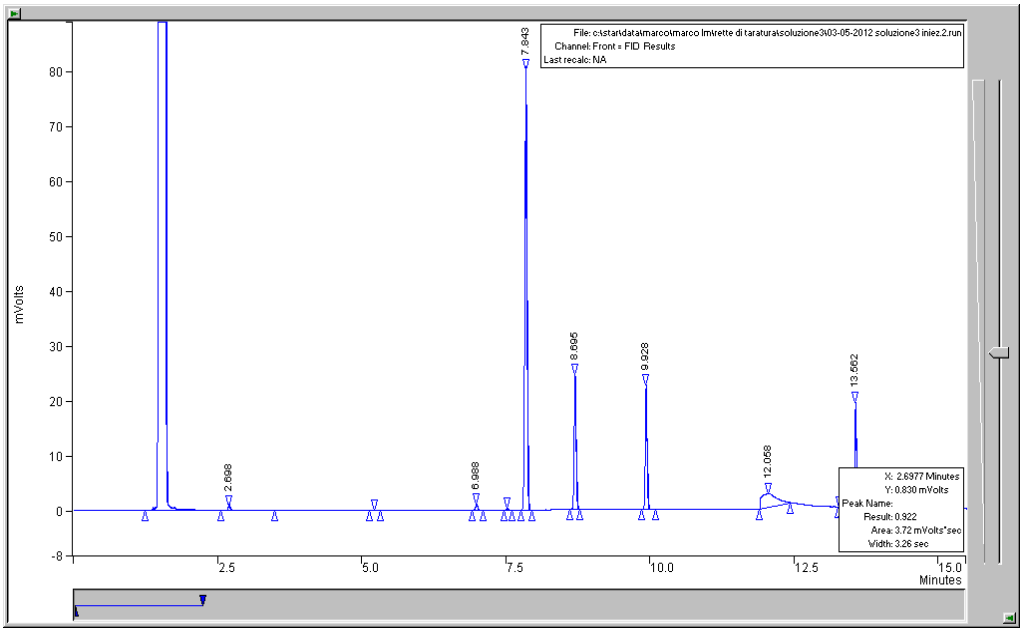


Figure ESI 16. Typical gas-chromatogram of a mixture containing (with increasing retention times): decane (internal standard), *o*-bromotoluene, *p*-bromotoluene, dibromomethylbenzene

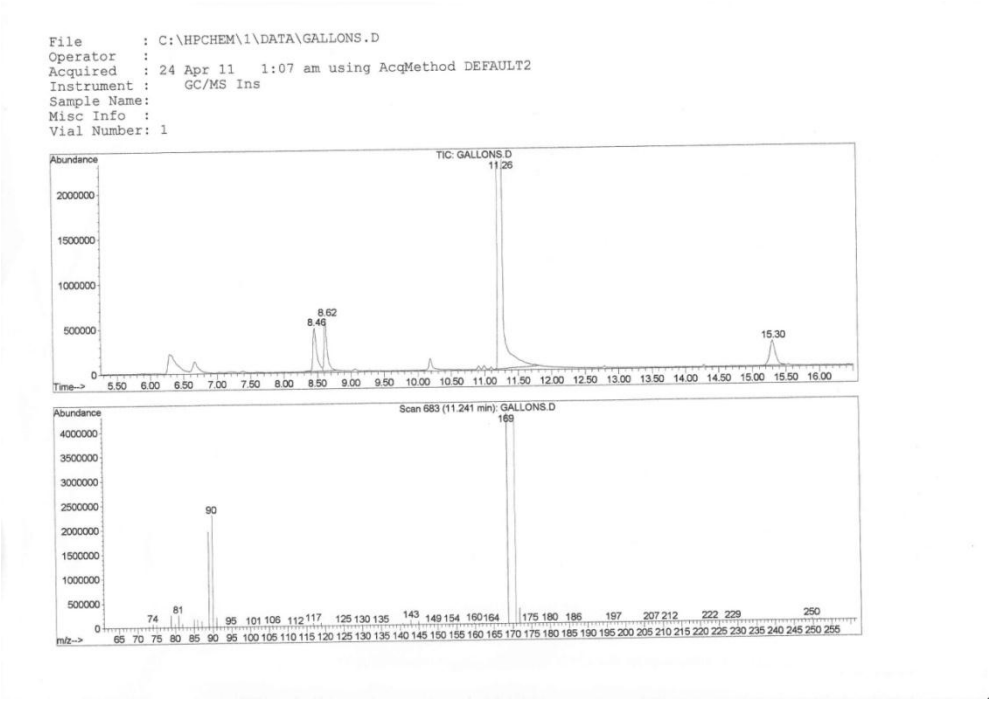


Figure ESI 19. Gas-chromatogram (TIC) and mass spectrum of dibromomethylnenzene.

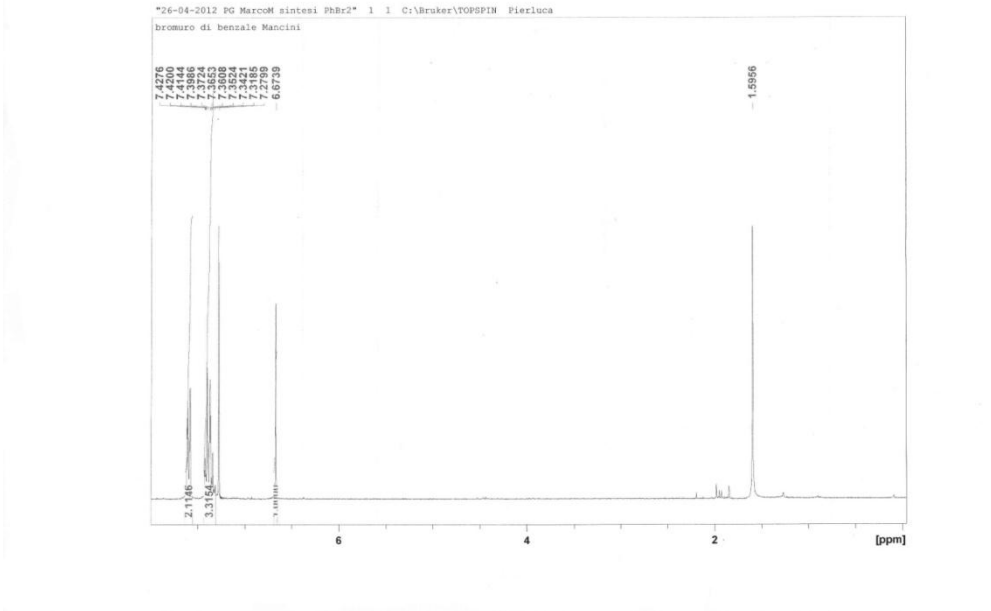
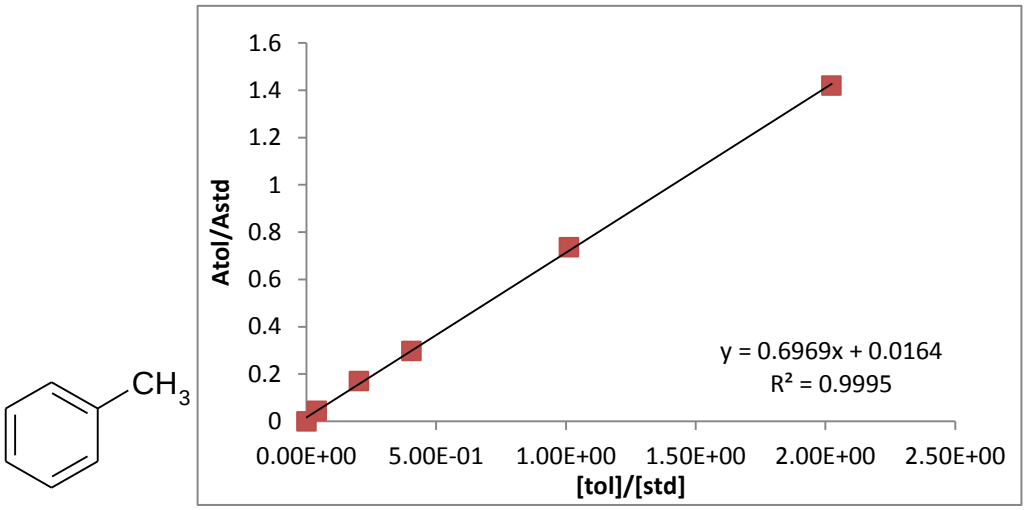
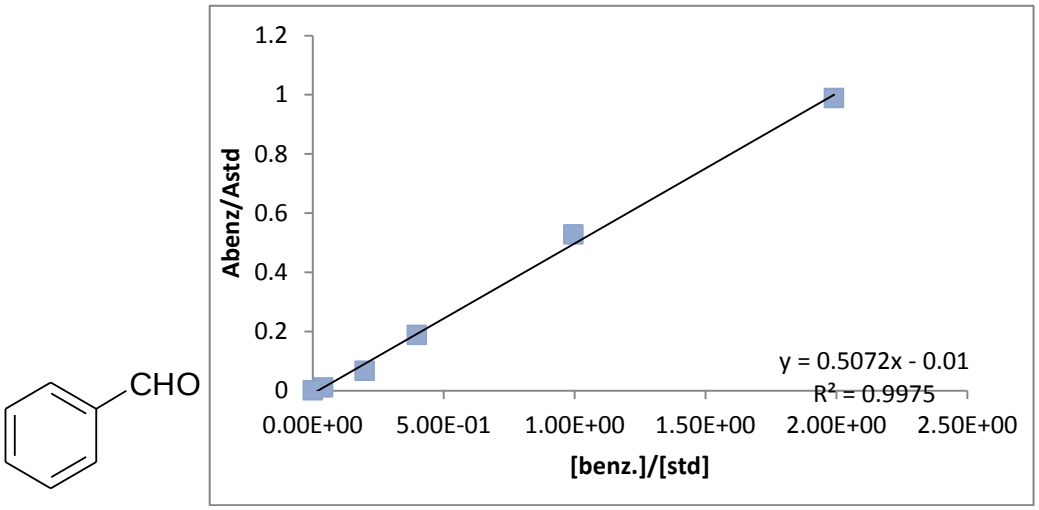
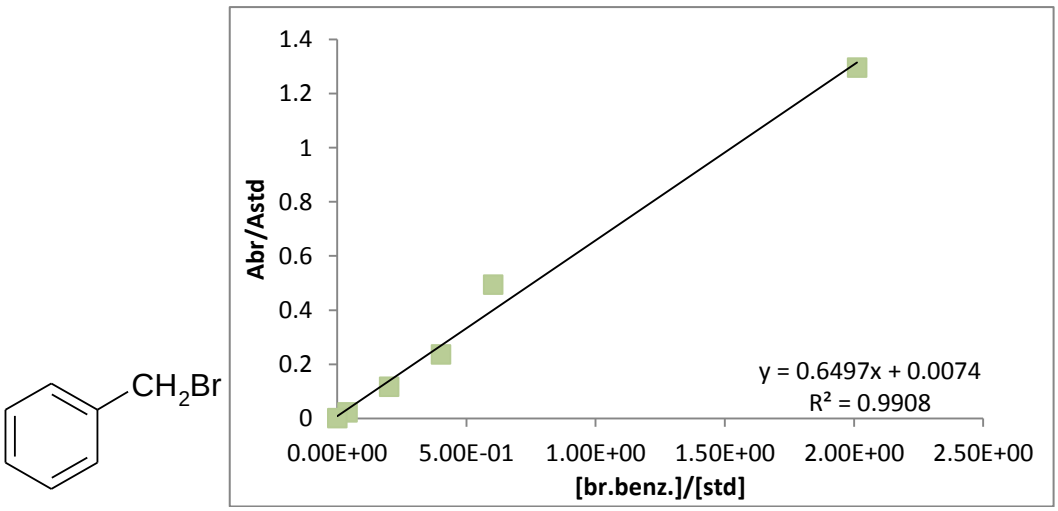


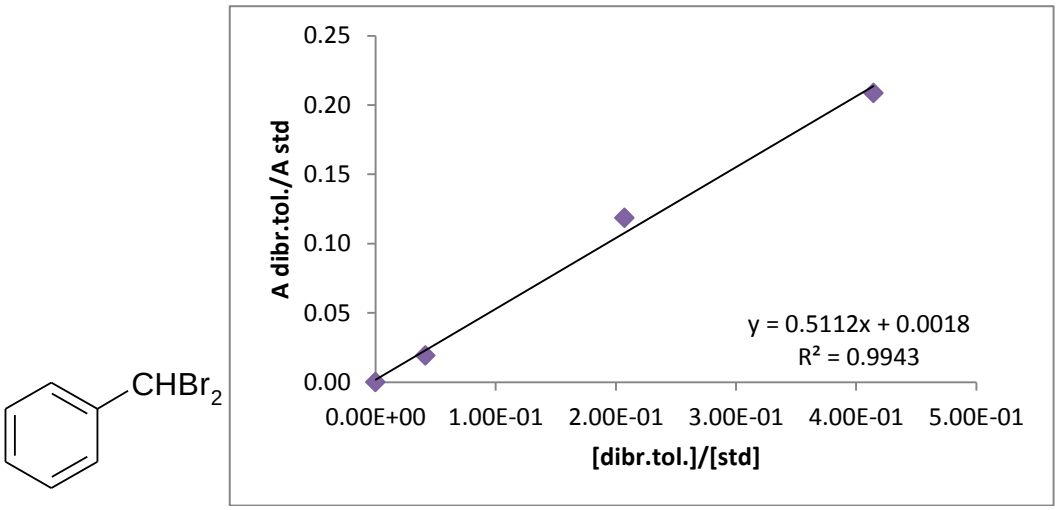
Figure ESI 20. ^{1}H-NMR spectrum of dibromomethylnenzene.

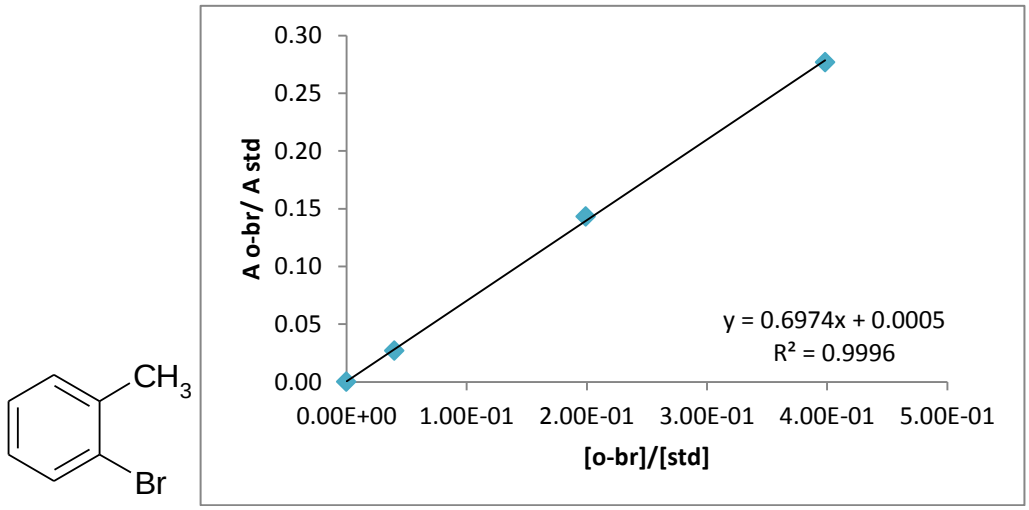
Calibration curves for quantitative gas-chromatographic analyses.











p-bromotoluene has the same response factor.