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Supporting Information (ESI-1)

Electrophilicity and Nucleophilicity of Commonly Used Aldehydes

Sanjay Pratihar *

Department of Chemical Sciences, Tezpur University, Napaam,784028, Asam, India

spratihar29@gmail.com, spratihar@tezu.ernet.in

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Experimental Section:

Materials and Instruments: Double distilled water was used throughout the experiments. Degassing of oxygen in water and acetonitrile has been done with bubbling of argon for 30 minute. Acetonitrile, aldehydes, and $KMnO_4$ were of AR grade. All the reagents were used without further purification. All UV-visible absorption spectra were recorded in a double beam digital spectrophotometer attached with a chiller.

UV-vis study for $KMnO_4$ Oxidation of aldehydes: At first an aqueous homogeneous solution of $KMnO_4$ (2×10^{-4} M) in double distilled oxygen free water has been prepared for the study. In another set, 5 ml aldehyde stock solution (2×10^{-1} M) has been prepared in pre-distilled oxygen free acetonitrile. Then 200 μL of aldehyde solution has been mixed with $KMnO_4$ solution (4×10^{-4} M) in a UV-cuvette to record the progress of the reaction. The progress of the reaction has been accounted from a steady decrease of all the four absorbance maxima at specified band (506, 525, 545, and 566 nm) positions (Figure 1). All the rate measurement for $KMnO_4$ oxidation of aldehyde has been done with time scan option at fixed absorbance (545 nm band of $KMnO_4$).

UV-vis study for $NaBH_4$ reduction of aldehydes: For monitoring the reduction kinetics of aldehydes, $NaBH_4$ solution (20 M) in double distilled oxygen free water has been prepared. The aqueous $NaBH_4$ solution is admixed with 100 μL distilled oxygen free acetonitrile stock solution (2×10^{-1} M) of corresponding aldehyde. All the rate measurement for $NaBH_4$ reduction of aldehyde has been done with time scan option at fixed absorbance band of a particular aldehyde.

Theoretical Background:

Global reactivity descriptors are defined for the system as a whole. Recently electrophilicity has been defined by Parr et al.[7a] as the energy of stabilization of a chemical species when it attains an additional fraction of electronic charge from the environment. The global electrophilicity index

ω is defined as $\omega = \mu^2/2\eta$ where μ is the electronic chemical potential[1] and η is the chemical hardness.[2]

In an important contribution, Gazquez et al.[9] have defined *electrodonating power* (ω^-) as

$$\omega^- = \frac{I^2}{2(I-A)} \text{ and } \omega^- = \frac{(3I+A)^2}{16(I-A)} \quad (1)$$

Note that according to this definition, a low value of ω^- signifies a better electron donor. In the present work nucleophilicity has been defined as the inverse of electrodonating power ($10/\omega^-$) in order to equate with the general notion that "*more is better*". They also described *electroaccepting power* (ω^+) as

$$\omega^+ = \frac{A^2}{2(I-A)} \text{ and } \omega^+ = \frac{(I+3A)^2}{16(I-A)} \quad (2)$$

Later on, Ayers *et. al.* introduced two sets of different equation from the IP and EA for both the electrophilicity and nucleophilicity as[8]

$$N = \frac{(3I-A)^2}{8(I-A)} \text{ and } E = \frac{(I+A)^2}{8(I-A)} \quad (3)$$

The electronic chemical potential and the chemical hardness have to be known for the calculation of electrophilicity (E) and nucleophilicity (N) index. The electronic chemical potential is the negative of electronegativity χ, is defined for an N-electron system with external potential v(r) and total energy E as the partial derivative of the energy to the number of electrons at constant external potential and in absence of a magnetic field:[3]

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{V(r)} \approx -\frac{I+A}{2} \quad (4)$$

where I and A are the vertical ionization energy and electron affinity, respectively. These two quantities were calculated in Gaussian 03 program[4] by using the B3LYP methods and 6-311+G** as basis set. Hardness is defined as the corresponding second derivative as proposed by Parr and Pearson.[21]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \approx (I - A) \qquad (5)$$

It is now common to exclude the factor ½ in the above definition. In this paper we calculated the chemical hardness as the difference between the vertical ionization energy I and electron affinity A. Where I = E_{HOMO} = Ionization potential (IP) and A = E_{LUMO} = Electron affinity (EA)

The following absorbance band of aldehydes have been chosen for rate measurement of NaBH4 reduction of aldehyde (Table S1).

Table S1. Absorbane band (Λ_{max}) of six different para substituted benzaldehydes.

Aldehyde	**Λ_{max} (nm)**
4- (dimethyl amino) benzaldehyde	342
4-Methoxy Benzaldehyde	283
4-Methyl Benzaldehyde	263
Benzaldehyde	248
4-Bromo Benzaldehyde	263
4-Chloro Benzaldehyde	258

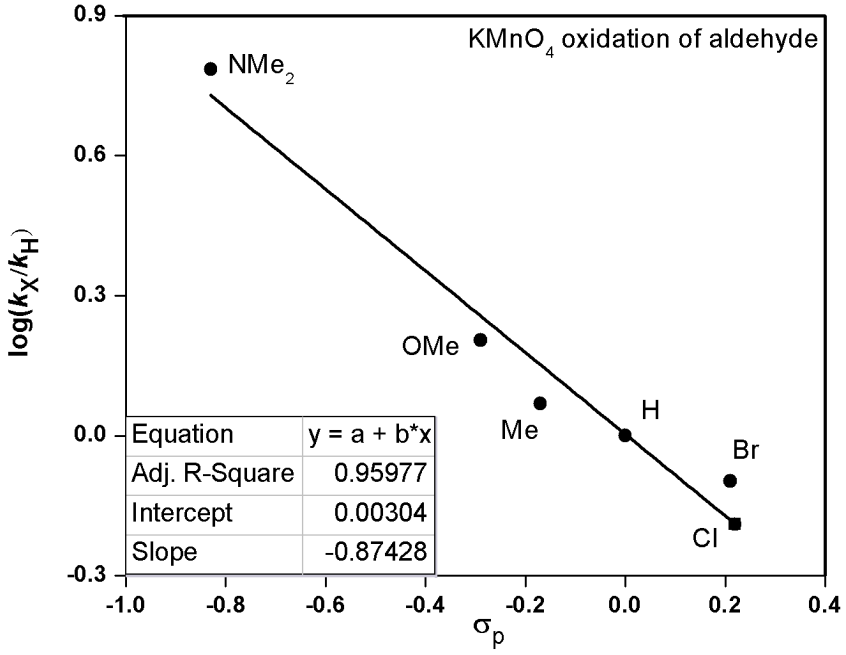


Figure S1: *Hammett plot of $log(k_Y/k_H)$ versus σ_p for $KMnO_4$ oxidation of six different para substituted aldehyde.*

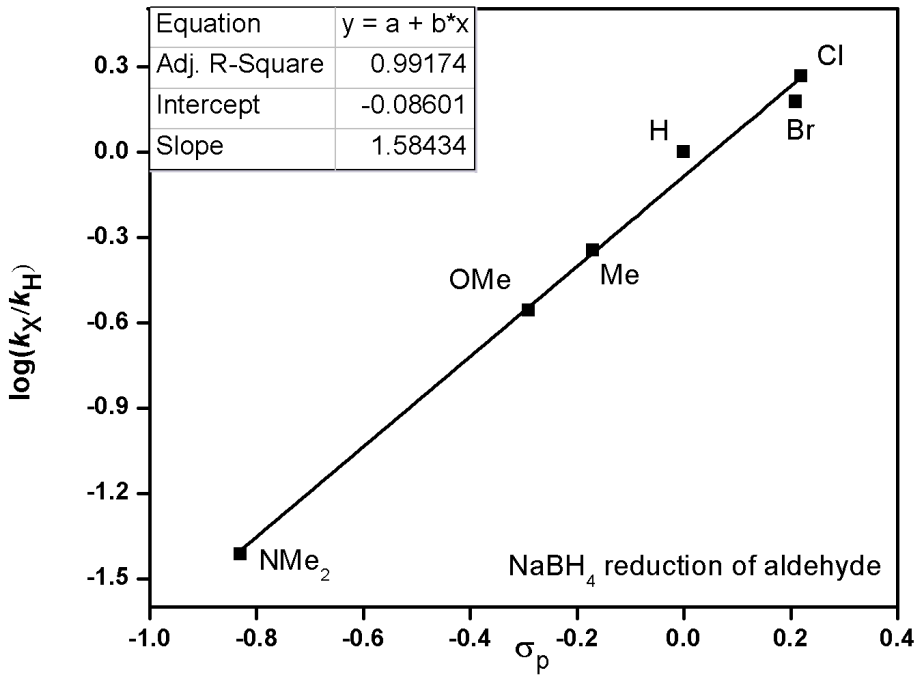


Figure S2: *Hammett plot of $log(k_Y/k_H)$ versus σ_p for $NABH_4$ reduction of six different para substituted aldehyde.*

Table S2. *Pseudo first order rate constant values of $KMnO_4$ Oxidation of five different para substituted benzaldehydes.*

Temperature	Cl (sec^{-1})	Br (sec^{-1})	H (sec^{-1})	OMe (sec^{-1})	NMe_2 (sec^{-1})
275 K	4.08×10^{-4}	4.9×10^{-4}	5.38×10^{-4}	8.11×10^{-4}	26.33×10^{-4}
285 K	5.06×10^{-4}	6.42×10^{-4}	6.65×10^{-4}	9.85×10^{-4}	31.93×10^{-4}
298 K	5.46×10^{-4}	6.6×10^{-4}	8.33×10^{-4}	13.35×10^{-4}	50.73×10^{-4}
309 K	6.64×10^{-4}	8.07×10^{-4}	9.98×10^{-4}	17.4×10^{-4}	72.82×10^{-4}
321 K	8.75×10^{-4}	8.92×10^{-4}	13.55×10^{-4}	19.57×10^{-4}	88.56×10^{-4}
333 K	9.86×10^{-4}	10.53×10^{-4}	16.06×10^{-4}	28.83×10^{-4}	163.04×10^{-4}

Table S3. *Pseudo first order rate constant values of $NaBH_4$ reduction of five different para substituted benzaldehydes.*

Temperature	Cl (sec^{-1})	Br (sec^{-1})	H (sec^{-1})	OMe (sec^{-1})	NMe_2 (sec^{-1})
275 K	21.03×10^{-3}	19.23×10^{-3}	12.5×10^{-3}	3.08×10^{-3}	0.631×10^{-3}
283 K	30.1×10^{-3}	24.47×10^{-3}	16.53×10^{-3}	4.22×10^{-3}	0.776×10^{-3}
291 K	37.01×10^{-3}	32.47×10^{-3}	19.67×10^{-3}	5.09×10^{-3}	0.849×10^{-3}
298 K	44.85×10^{-3}	36.42×10^{-3}	24.3×10^{-3}	6.72×10^{-3}	0.934×10^{-3}

Theoretical Section: The ground state geometry optimizations of all the aldehydes were performed using GAUSSIAN 03.[4] at B3LYP level of theory. All the atoms are treated with 6-311+G(d,p) basis set. Geometries of all species studied were fully optimized, and they were characterized as true intermediates on the potential energy surface by the absence of imaginary frequencies, after frequency calculation on the optimized geometries. During the reaction path analysis The transition state (TS) model of KMnO4 oxidation reaction has been analyzed at B3LYP level of theory. For Manganese Effective core potential (ECP) along with valence basis sets (LANL2DZ) was used, while for other atoms 6-311+G** basic set was used.

Table S4. Optimized structure along with some important bond distance of aldehyde MnO4- intermediates.

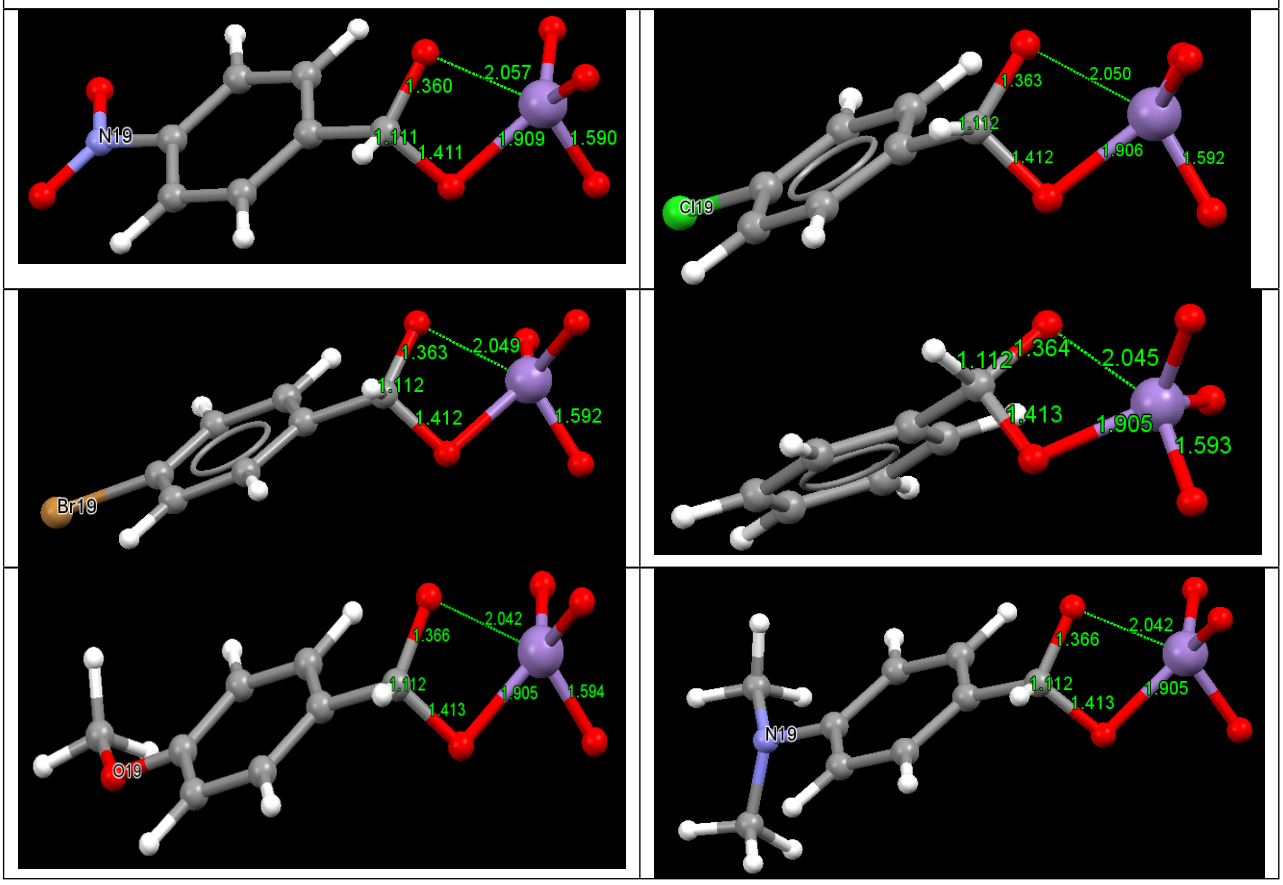


Table S5. Optimized Tranisition state (TS) structure along with some important bond distance of $KMnO_4$ oxidation reaction.

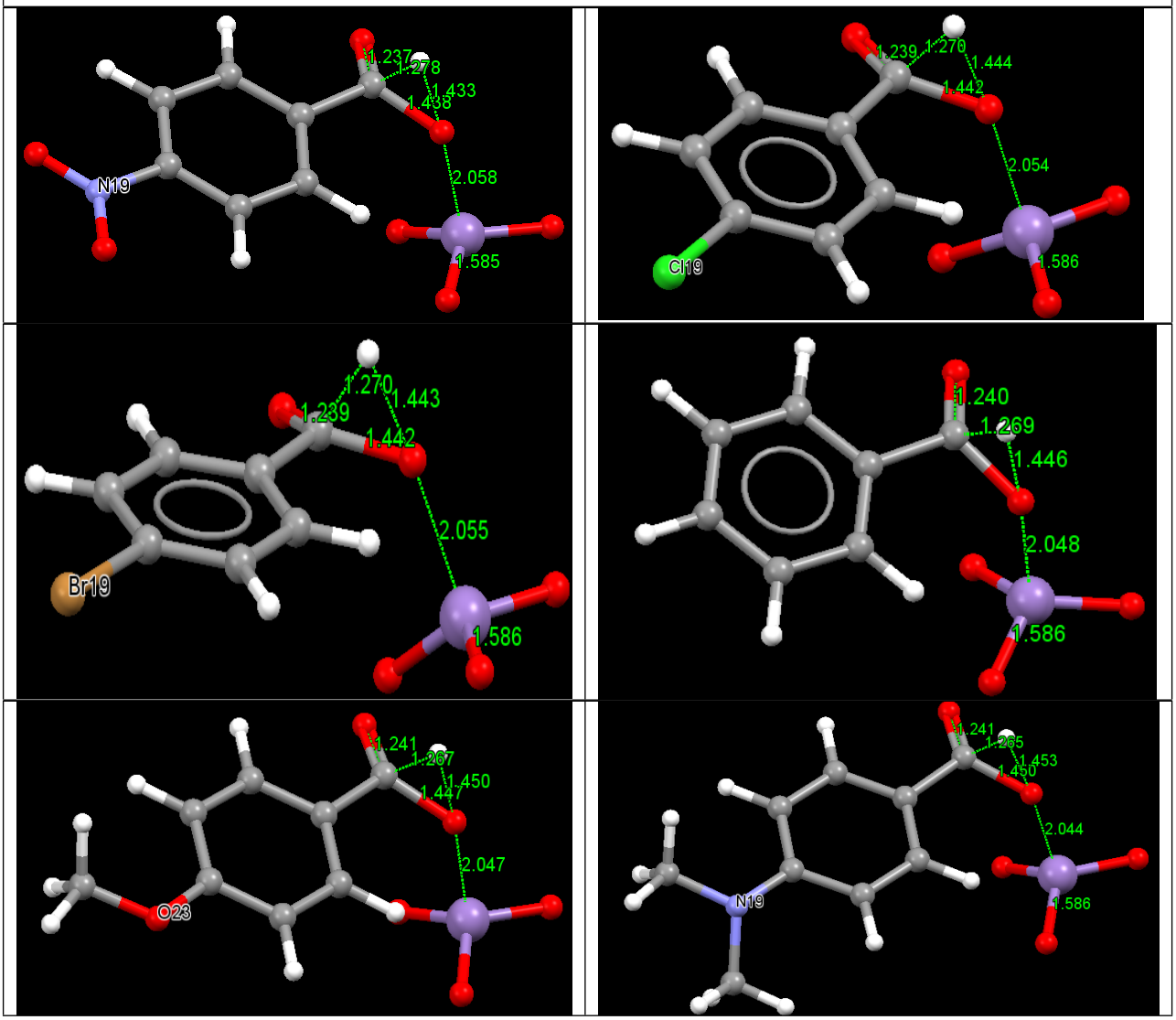


Table S6. *HOMO, LUMO,Hardness (η),Chemical Potential (μ) elecytrophilicity (E), Nucleophilicity (N) values of various mono, di, and tri-substituted aldehydes calculated at B3LYP/6-311+G** level of theory.*

Compound	HOMO (eV)	LUMO (eV)	η	μ	E	N
2-Nitro benzaldehyde	-7.665601	-3.510362	4.155239	-5.58798	3.76	11.42
3-Nitro benzaldehyde	-7.907498	-3.323157	4.584341	-5.61533	3.44	11.35
4-Cyano benzaldehyde	-7.863962	-3.050513	4.813449	-5.45724	3.09	10.96
4-chloroisophthalaldehyde	-7.690634	-2.952013	4.738622	-5.32132	2.99	10.68
5-nitro-1H-indole-3-carbaldehyde	-7.012833	-2.880451	4.132383	-4.94664	2.96	9.97
phthalaldehyde	-7.459622	-2.909837	4.549784	-5.18473	2.95	10.41
4-Acetyl benzaldehyde	-7.480845	-2.889974	4.590871	-5.18541	2.93	10.41
2-formyl benzonitrile	-7.760836	-2.889158	4.871678	-5.325	2.91	10.67
4-formyl benzoic acid	-7.631045	-2.870383	4.760662	-5.25071	2.90	10.53
3,4-dichloropicolinaldehyde	-7.750769	-2.85188	4.898888	-5.30132	2.87	10.62
Ethylglyoxalate	-7.730905	-2.833649	4.897256	-5.28228	2.85	10.58
3-formyl benzonitrile	-7.848725	-2.766713	5.082012	-5.30772	2.77	10.62
4-chloronicotinaldehyde	-7.534449	-2.755829	4.77862	-5.14514	2.77	10.30
4-Trifluromethyl benzaldehyde	-7.751585	-2.759094	4.992491	-5.25534	2.77	10.52
Methyl-4-formylbenzoate	-7.541524	-2.730796	4.810728	-5.13616	2.74	10.28
2,4,5-trifluorobenzaldehyde	-7.769816	-2.734061	5.035755	-5.25194	2.74	10.51
4-Nitro benzaldehyde	-7.878656	-2.730524	5.148132	-5.30459	2.73	10.61
4-chloropicolinaldehyde	-7.632405	-2.711749	4.920656	-5.17208	2.72	10.35
isophthalaldehyde	-7.571455	-2.708483	4.862971	-5.13997	2.72	10.29
2,3-dichlorobenzaldehyde	-7.479757	-2.655424	4.824333	-5.06759	2.66	10.14
4-chlorofuran-2-carbaldehyde	-7.263437	-2.621956	4.641482	-4.9427	2.63	9.90
3-Acetyl benzaldehyde	-7.41799	-2.602364	4.815626	-5.01018	2.61	10.02
2,6-dichlorobenzaldehyde	-7.283301	-2.597195	4.686106	-4.94025	2.60	9.89
2-formyl benzoic acid	-7.277315	-2.590664	4.68665	-4.93399	2.60	9.87
3-phenyl propynal	-7.181535	-2.587399	4.594136	-4.88447	2.60	9.78
3-formyl benzoic acid	-7.578257	-2.575971	5.002286	-5.07711	2.58	10.15
Cinamaldehyde	-6.958141	-2.516925	4.441216	-4.73753	2.53	9.48
2-Acetyl benzaldehyde	-7.11732	-2.514748	4.602572	-4.81603	2.52	9.64
3-Bromo benzaldehyde	-7.317041	-2.463593	4.853448	-4.89032	2.46	9.78
3-Chloro benzaldehyde	-7.430235	-2.458151	4.972083	-4.94419	2.46	9.89
Methyl-3-formylbenzoate	-7.495539	-2.457063	5.038476	-4.9763	2.46	9.95
2-Bromo benzaldehyde	-7.358945	-2.456247	4.902698	-4.9076	2.46	9.82
2-Chloro aldehyde	-7.462887	-2.449988	5.012898	-4.95644	2.45	9.91
picolinaldehyde	-7.380713	-2.448628	4.932085	-4.91467	2.45	9.83
3-Fluro benzaldehyde	-7.54234	-2.431758	5.110582	-4.98705	2.43	9.98
Methyl-2-formylbenzoate	-7.178814	-2.427676	4.751138	-4.80325	2.43	9.61
4-Bromo benzaldehyde	-7.353503	-2.421962	4.93154	-4.88773	2.42	9.78
2-(thiophen-3-yl) benzaldehyde	-6.557338	-2.402915	4.154423	-4.48013	2.42	8.97

biphenyl-4-carbaldehyde	-6.662913	-2.396657	4.266256	-4.52978	2.40	9.07
2-Fluro benzaldehyde	-7.471594	-2.398834	5.07276	-4.93521	2.40	9.87
4-Chloro benzaldehyde	-7.462343	-2.398289	5.064053	-4.93032	2.40	9.86
Biphenyl-2-carbaldehyde	-6.664545	-2.391487	4.273058	-4.52802	2.40	9.06
thiophene-2-carbaldehyde	-7.240581	-2.329992	4.910589	-4.78529	2.33	9.57
2-naphthaldehyde	-6.613391	-2.287817	4.325574	-4.4506	2.29	8.90
4-Fluro benzaldehyde	-7.488464	-2.259518	5.228946	-4.87399	2.27	9.76
2-chloro-3,4-dihydroxybenzaldehyde	-6.735291	-2.230404	4.504888	-4.48285	2.23	8.97
Benzaldehyde	-7.339625	-2.176256	5.16337	-4.75794	2.19	9.53
2-Methyl benzaldehyde	-7.20929	-2.16646	5.042829	-4.68787	2.18	9.39
4-tert-butyl-2-hydroxybenzaldehyde	-6.798146	-2.172174	4.625972	-4.48516	2.17	8.97
3-hydroxy benzaldehyde	-6.857192	-2.169181	4.688011	-4.51319	2.17	9.03
furan-2-carbaldehyde	-7.206024	-2.15612	5.049904	-4.68107	2.17	9.38
2-(naphthalen-2-yl)benzaldehyde	-5.97586	-2.122652	3.853208	-4.04926	2.13	8.10
3-methyl benzaldehyde	-7.218813	-2.094626	5.124187	-4.65672	2.12	9.33
3-chloro-4-hydroxy-5-methoxybenzaldehyde	-6.576929	-2.081565	4.495364	-4.32925	2.08	8.66
4-Methyl benzaldehyde	-7.222895	-2.044015	5.178879	-4.63345	2.07	9.30
3-Methoxy benzaldehyde	-6.678967	-2.058981	4.619986	-4.36897	2.07	8.74
4-Ethyl Benzaldehyde	-7.219357	-2.035308	5.184049	-4.62733	2.07	9.28
4-Mercapto Benzaldehyde	-6.375847	-2.054083	4.321764	-4.21497	2.06	8.43
4-Propyl benzaldehyde	-7.208201	-2.022791	5.18541	-4.6155	2.05	9.26
4-formylphenylboronic acid	-7.179359	-2.02007	5.159288	-4.59971	2.05	9.23
2-Methoxy benzaldehyde	-6.681688	-2.027417	4.654271	-4.35455	2.04	8.72
thiophene-3-carbaldehyde	-7.317041	-1.968644	5.348398	-4.64284	2.02	9.33
3-amino benzaldehyde	-6.22973	-1.995854	4.233876	-4.11279	2.00	8.23
3,4,5-trimethoxybenzaldehyde	-6.277891	-1.971092	4.306799	-4.12449	1.97	8.25
3,4-dihydroxybenzaldehyde	-6.526319	-1.961841	4.564478	-4.24408	1.97	8.50
4-Hydroxy benzaldehyde	-6.932836	-1.932998	4.999838	-4.43292	1.97	8.90
furan-3-carbaldehyde	-7.238948	-1.831233	5.407715	-4.53509	1.90	9.14
4-Methoxy benzaldehyde	-6.755427	-1.83994	4.915487	-4.29768	1.88	8.63
5-chloro-1H-indole-3-carbaldehyde	-6.588085	-1.841845	4.74624	-4.21497	1.87	8.46
Formaldehyde	-7.666962	-1.746882	5.92008	-4.70692	1.87	9.54
3-(dimethylamino) benzaldehyde	-5.773962	-1.859804	3.914159	-3.81688	1.86	7.63
4-hydroxy-3-methoxybenzaldehyde	-6.336393	-1.842661	4.493732	-4.08953	1.86	8.20
2-(dimethylamino) benzaldehyde	-5.83464	-1.716407	4.118234	-3.77552	1.73	7.57
4-Amino benzaldehyde	-6.280612	-1.66634	4.614272	-3.97348	1.71	7.99
Phenyl acetaldehyde	-7.131469	-1.47968	5.651789	-4.30557	1.64	8.77
4-(dimethylamino) benzaldehyde	-5.841715	-1.503897	4.337818	-3.67281	1.55	7.40
3-Phenyl propanal	-7.00467	-1.366758	5.637912	-4.18571	1.55	8.56
Acetaldehyde	-7.342891	-1.28921	6.053681	-4.31605	1.54	8.88
Heptanal	-7.181263	-1.193703	5.987561	-4.18748	1.46	8.65

Table S7. Experimental and theoretical *Nucleophilicity(N), Electrophilicity (E),and Net E of various aldehyde from kinetics and theoretical (gas phase calculation in MI) analysis*

Compound	E (theo)	N (theo)	N (exp)	E (exp)	Net E (exp)
2-Nitro benzaldehyde	3.76	11.42	-3.80	1.28	5.09
3-Nitro benzaldehyde	3.44	11.35	-3.78	0.67	4.45
4-Cyano benzaldehyde	3.09	10.96	-3.63	0.01	3.64
4-chloroisophthalaldehyde	2.99	10.68	-3.53	-0.20	3.33
2-formyl benzonitrile	2.91	10.67	-3.53	-0.35	3.18
phthalaldehyde	2.95	10.41	-3.43	-0.26	3.17
4-Acetyl benzaldehyde	2.93	10.41	-3.43	-0.31	3.12
4-formyl benzoic acid	2.90	10.53	-3.47	-0.37	3.10
3,4-dichloropicolinaldehyde	2.87	10.62	-3.51	-0.43	3.08
Ethylglyoxalate	2.85	10.58	-3.49	-0.46	3.03
5-nitro-1H-indole-3-carbaldehyde	2.96	9.97	-3.27	-0.25	3.02
3-formyl benzonitrile	2.77	10.62	-3.51	-0.61	2.90
4-Trifluromethyl benzaldehyde	2.77	10.52	-3.47	-0.62	2.85
4-Nitro benzaldehyde	2.73	10.61	-3.51	-0.69	2.82
2,4,5-trifluorobenzaldehyde	2.74	10.51	-3.47	-0.68	2.79
4-chloronicotinaldehyde	2.77	10.30	-3.39	-0.62	2.78
Methyl-4-formylbenzoate	2.74	10.28	-3.39	-0.67	2.72
4-chloropicolinaldehyde	2.72	10.35	-3.41	-0.72	2.70
isophthalaldehyde	2.72	10.29	-3.39	-0.72	2.67
2,3-dichlorobenzaldehyde	2.66	10.14	-3.33	-0.82	2.51
4-chlorofuran-2-carbaldehyde	2.63	9.90	-3.24	-0.88	2.36
3-Acetyl benzaldehyde	2.61	10.02	-3.29	-0.93	2.36
3-formyl benzoic acid	2.58	10.15	-3.34	-0.99	2.35
2,6-dichlorobenzaldehyde	2.60	9.89	-3.24	-0.93	2.31
2-formyl benzoic acid	2.60	9.87	-3.24	-0.95	2.29
3-Phenyl propynal	2.60	9.78	-3.20	-0.95	2.25
2-Acetyl benzaldehyde	2.52	9.64	-3.15	-1.10	2.05
Methyl-3-formylbenzoate	2.46	9.95	-3.26	-1.22	2.05
3-Chloro benzaldehyde	2.46	9.89	-3.24	-1.21	2.03
2-Chloro aldehyde	2.45	9.91	-3.25	-1.23	2.02
Cinamaldehyde	2.53	9.48	-3.09	-1.08	2.01
3-Fluro benzaldehyde	2.43	9.98	-3.27	-1.26	2.01
3-Bromo benzaldehyde	2.46	9.78	-3.20	-1.20	2.00
2-Bromo benzaldehyde	2.46	9.82	-3.21	-1.22	2.00
picolinaldehyde	2.45	9.83	-3.22	-1.23	1.99
4-Bromo benzaldehyde	2.42	9.78	-3.20	-1.28	1.92
2-Fluro benzaldehyde	2.40	9.87	-3.24	-1.33	1.91
4-Chloro benzaldehyde	2.40	9.86	-3.23	-1.33	1.90

Methyl-2-formylbenzoate	2.43	9.61	-3.14	-1.27	1.86
thiophene-2-carbaldehyde	2.33	9.57	-3.13	-1.46	1.67
biphenyl-4-carbaldehyde	2.40	9.07	-2.94	-1.32	1.62
4-Fluro benzaldehyde	2.27	9.76	-3.19	-1.57	1.62
Biphenyl-2-carbaldehyde	2.40	9.06	-2.94	-1.33	1.61
2-(thiophen-3-yl) benzaldehyde	2.42	8.97	-2.91	-1.30	1.61
Benzaldehyde	2.19	9.53	-3.11	-1.73	1.38
2-naphthaldehyde	2.29	8.90	-2.88	-1.54	1.34
2-Methyl benzaldehyde	2.18	9.39	-3.06	-1.75	1.31
furan-2-carbaldehyde	2.17	9.38	-3.05	-1.77	1.28
2-chloro-3,4-dihydroxybenzaldehyde	2.23	8.97	-2.90	-1.65	1.25
3-methyl benzaldehyde	2.12	9.33	-3.04	-1.87	1.17
3-hydroxy benzaldehyde	2.17	9.03	-2.93	-1.76	1.16
4-tert-butyl-2-hydroxybenzaldehyde	2.17	8.97	-2.91	-1.76	1.14
4-Methyl benzaldehyde	2.07	9.30	-3.02	-1.96	1.07
4-Ethyl Benzaldehyde	2.07	9.28	-3.02	-1.97	1.05
4-Propyl benzaldehyde	2.05	9.26	-3.01	-1.99	1.02
4-formylphenylboronic acid	2.05	9.23	-3.00	-2.00	1.00
thiophene-3-carbaldehyde	2.02	9.33	-3.04	-2.07	0.97
3-chloro-4-hydroxy-5-methoxybenzaldehyde	2.08	8.66	-2.79	-1.93	0.86
3-Methoxy benzaldehyde	2.07	8.74	-2.82	-1.97	0.85
2-Methoxy benzaldehyde	2.04	8.72	-2.81	-2.02	0.79
Formaldehyde	1.87	9.54	-3.11	-2.34	0.77
2-(naphthalen-2-yl)benzaldehyde	2.13	8.10	-2.59	-1.85	0.74
4-Mercapto Benzaldehyde	2.06	8.43	-2.71	-1.99	0.72
4-Hydroxy benzaldehyde	1.97	8.90	-2.88	-2.16	0.72
furan-3-carbaldehyde	1.90	9.14	-2.97	-2.29	0.68
3,4-dihydroxybenzaldehyde	1.97	8.50	-2.73	-2.15	0.58
3-amino benzaldehyde	2.00	8.23	-2.63	-2.10	0.53
3,4,5-trimethoxybenzaldehyde	1.97	8.25	-2.64	-2.14	0.50
4-Methoxy benzaldehyde	1.88	8.63	-2.78	-2.33	0.45
5-chloro-1H-indole-3-carbaldehyde	1.87	8.46	-2.72	-2.34	0.37
4-hydroxy-3-methoxybenzaldehyde	1.86	8.20	-2.62	-2.36	0.26
3-(dimethylamino) benzaldehyde	1.86	7.63	-2.42	-2.36	0.05
Phenyl acetaldehyde	1.64	8.77	-2.83	-2.79	0.04
4-Amino benzaldehyde	1.71	7.99	-2.55	-2.65	-0.11
Acetaldehyde	1.54	8.88	-2.87	-2.98	-0.11
3-Phenyl propanal	1.55	8.56	-2.75	-2.95	-0.20
2-(dimethylamino) benzaldehyde	1.73	7.57	-2.39	-2.61	-0.22
Heptanal	1.46	8.65	-2.79	-3.13	-0.34
4-(dimethylamino) benzaldehyde	1.55	7.40	-2.33	-2.95	-0.62

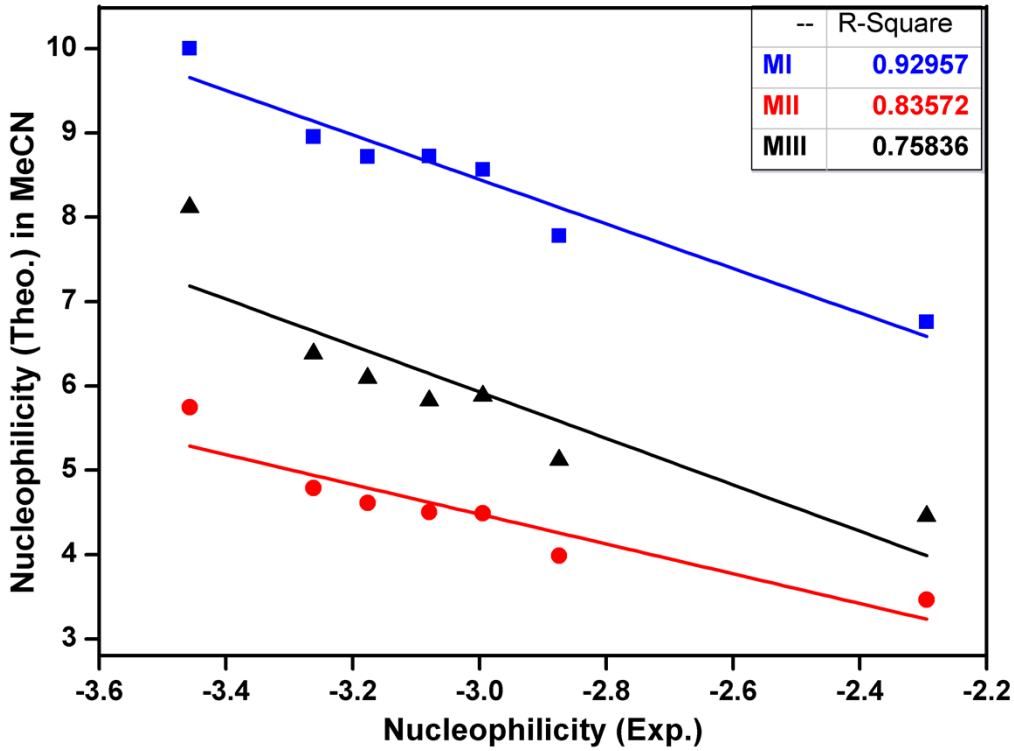


Fig. S3. Theoretical nucleophilicity in acetonitrile *versus* Experimental nucleophilicity plot of various *para* substituted benzaldehydes in three different methods

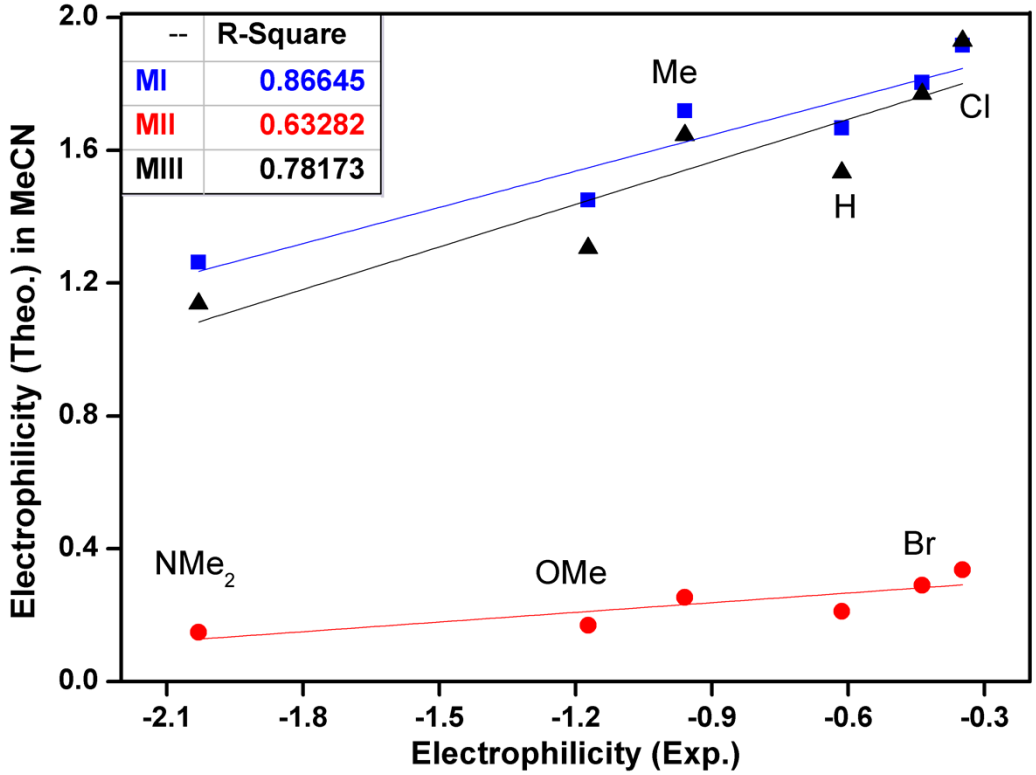


Fig. S4. Theoretical electrophilicity in acetonitrile *versus* Experimental electrophilicity plot of various *para* substituted benzaldehydes in three different methods

Table S8. *HOMO, LUMO, Hardness (η),Chemical Potential (μ), elecytrophilicity (E),and Nucleophilicity (N) values of various mono, di, and tri-substituted aldehydes calculated at B3LYP/6-311+G** level of theory in acetonitrile in method I.*

Compound	HOMO	LUMO	η	μ	E	N
2,4,5-trifluorobenzaldehyde	-6.76658	-3.31472	3.451861	-5.04065	3.68	10.45
2-Nitro benzaldehyde	-7.70968	-3.42519	4.284487	-5.56744	3.62	11.33
3-Nitro benzaldehyde	-7.75458	-3.20479	4.549784	-5.47969	3.30	11.05
picolinaldehyde	-6.63706	-2.94058	3.696479	-4.78882	3.10	9.74
phthalaldehyde	-7.46942	-2.8059	4.663522	-5.13766	2.83	10.30
Ethylglyoxalate	-7.77961	-2.78141	4.998205	-5.28051	2.79	10.57
4-chloroisophthalaldehyde	-7.57989	-2.71964	4.86025	-5.14976	2.73	10.31
3,4-dichloropicolinaldehyde	-7.71186	-2.72018	4.991675	-5.21602	2.73	10.44
2-formyl benzonitrile	-7.77825	-2.71393	5.064325	-5.24609	2.72	10.50
3-Phenyl propynal	-7.15841	-2.67447	4.483936	-4.91644	2.70	9.85
4-Nitro benzaldehyde	-7.33908	-2.65298	4.686106	-4.99603	2.66	10.00
4-chloronicotinaldehyde	-7.55812	-2.63338	4.924738	-5.09575	2.64	10.19
4-chloropicolinaldehyde	-7.70397	-2.61951	5.084461	-5.16174	2.62	10.32
2,3-dichlorobenzaldehyde	-7.29038	-2.54169	4.748689	-4.91603	2.54	9.84
2-formyl benzoic acid	-7.48465	-2.53624	4.948411	-5.01045	2.54	10.02
2,6-dichlorobenzaldehyde	-7.24766	-2.52237	4.725289	-4.88501	2.53	9.77
2-Acetyl benzaldehyde	-7.31922	-2.52291	4.796307	-4.92106	2.52	9.84
3,4,5-trimethoxybenzaldehyde	-7.48874	-2.52155	4.967186	-5.00514	2.52	10.01
Cinamaldehyde	-6.88086	-2.50795	4.372919	-4.69441	2.52	9.40
isophthalaldehyde	-7.54642	-2.49298	5.053441	-5.0197	2.49	10.04
Methyl-2-formylbenzoate	-7.47785	-2.49053	4.987321	-4.98419	2.49	9.97
3-Acetyl benzaldehyde	-7.47758	-2.48672	4.990858	-4.98215	2.49	9.96
Biphenyl-2-carbaldehyde	-6.64223	-2.4674	4.17483	-4.55482	2.48	9.13
biphenyl-4-carbaldehyde	-6.63325	-2.44808	4.18517	-4.54067	2.46	9.10
4-chlorofuran-2-carbaldehyde	-7.0727	-2.45978	4.612911	-4.76624	2.46	9.54
3-formyl benzonitrile	-7.72193	-2.45679	5.265135	-5.08936	2.46	10.18
thiophene-3-carbaldehyde	-7.53282	-2.44455	5.08827	-4.98868	2.45	9.98
2-(thiophen-3-yl) benzaldehyde	-6.42292	-2.42169	4.001231	-4.42231	2.44	8.87
3-formyl benzoic acid	-7.6188	-2.42577	5.193029	-5.02229	2.43	10.05
2-Bromo benzaldehyde	-7.1946	-2.41217	4.78243	-4.80338	2.41	9.61
Methyl-3-formylbenzoate	-7.60819	-2.40319	5.205001	-5.00569	2.41	10.02
2-Chloro aldehyde	-7.28493	-2.404	4.88093	-4.84447	2.40	9.69
4-Cyano benzaldehyde	-7.33554	-2.38931	4.946234	-4.86243	2.39	9.73
4-Acetyl benzaldehyde	-7.13909	-2.36591	4.773178	-4.7525	2.37	9.51
2-Fluro benzaldehyde	-7.37581	-2.34305	5.032762	-4.85943	2.35	9.72
3-Chloro benzaldehyde	-7.25228	-2.33435	4.917935	-4.79331	2.34	9.59
2-naphthaldehyde	-6.54264	-2.32319	4.219455	-4.43292	2.33	8.87

3-Fluro benzaldehyde	-7.34398	-2.31285	5.031129	-4.82841	2.32	9.66
4-formyl benzoic acid	-7.24602	-2.26959	4.976437	-4.7578	2.27	9.52
thiophene-2-carbaldehyde	-7.11596	-2.26578	4.850183	-4.69087	2.27	9.38
Methyl-4-formylbenzoate	-7.23786	-2.25571	4.982151	-4.74678	2.26	9.50
2-Methyl benzaldehyde	-7.16194	-2.22415	4.937799	-4.69304	2.23	9.39
2-chloro-3,4-dihydroxybenzaldehyde	-6.54673	-2.18796	4.35877	-4.36734	2.19	8.73
3-Methoxy benzaldehyde	-6.64849	-2.1817	4.466794	-4.41509	2.18	8.83
3-methyl benzaldehyde	-7.15977	-2.17136	4.988409	-4.66556	2.18	9.34
4-tert-butyl-2-hydroxybenzaldehyde	-6.71026	-2.17109	4.539172	-4.44067	2.17	8.88
4-formylphenylboronic acid	-7.33228	-2.13517	5.19711	-4.73372	2.16	9.49
furan-2-carbaldehyde	-7.06508	-2.13789	4.927187	-4.60148	2.15	9.21
3-hydroxy benzaldehyde	-6.63516	-2.14279	4.492371	-4.38897	2.14	8.78
2-Methoxy benzaldehyde	-6.6572	-2.13082	4.526384	-4.39401	2.13	8.79
2-(naphthalen-2-yl)benzaldehyde	-6.05939	-2.10279	3.956606	-4.08109	2.10	8.16
3-chloro-4-hydroxy-5-methoxybenzaldehyde	-6.44632	-2.09735	4.348974	-4.27183	2.10	8.54
5-chloro-1H-indole-3-carbaldehyde	-6.28333	-2.08782	4.19551	-4.18558	2.09	8.37
4-Trifluromethyl benzaldehyde	-7.26126	-2.05272	5.208538	-4.65699	2.08	9.34
3-amino benzaldehyde	-5.99708	-2.04755	3.949532	-4.02232	2.05	8.05
3-(dimethylamino) benzaldehyde	-5.67138	-2.03585	3.635528	-3.85362	2.04	7.71
3,4-dihydroxybenzaldehyde	-6.32687	-1.92674	4.400129	-4.1268	1.94	8.26
4-hydroxy-3-methoxybenzaldehyde	-6.22782	-1.92103	4.306799	-4.07443	1.93	8.16
2-(dimethylamino) benzaldehyde	-5.81559	-1.92184	3.893751	-3.86872	1.92	7.74
4-Chloro benzaldehyde	-7.03732	-1.86579	5.171533	-4.45156	1.92	8.95
furan-3-carbaldehyde	-7.02698	-1.81491	5.212076	-4.42094	1.87	8.90
4-Bromo benzaldehyde	-6.91433	-1.733	5.181328	-4.32367	1.80	8.72
Formaldehyde	-7.66995	-1.62743	6.042525	-4.64869	1.79	9.46
5-nitro-1H-indole-3-carbaldehyde	-6.39571	-1.74661	4.649101	-4.07116	1.78	8.18
4-Fluro benzaldehyde	-7.00494	-1.67015	5.334793	-4.33755	1.76	8.77
4-Methyl benzaldehyde	-6.84549	-1.62634	5.21915	-4.23592	1.72	8.56
4-Ethyl Benzaldehyde	-6.84277	-1.62008	5.222687	-4.23143	1.71	8.56
4-Propyl benzaldehyde	-6.821	-1.61763	5.203368	-4.21932	1.71	8.53
4-Mercapto Benzaldehyde	-6.09177	-1.67858	4.41319	-3.88518	1.71	7.80
Benzaldehyde	-7.0561	-1.52947	5.526623	-4.29279	1.67	8.72
Phenyl acetaldehyde	-7.03297	-1.47995	5.553017	-4.25646	1.63	8.66
Acetaldehyde	-7.45173	-1.27424	6.177486	-4.36299	1.54	8.99
3-Phenyl propanal	-6.92059	-1.35424	5.56635	-4.13742	1.54	8.46
4-Hydroxy benzaldehyde	-6.34374	-1.4171	4.926643	-3.88042	1.53	7.87
Heptanal	-7.34071	-1.24703	6.09368	-4.29387	1.51	8.85
4-Methoxy benzaldehyde	-6.33013	-1.30526	5.024871	-3.8177	1.45	7.78
4-Amino benzaldehyde	-5.69396	-1.22146	4.472508	-3.45771	1.34	7.03
4-(dimethylamino) benzaldehyde	-5.49778	-1.13819	4.359586	-3.31799	1.26	6.76
3-Bromo benzaldehyde	-7.15296	0.603246	7.756211	-3.27486	0.69	7.84

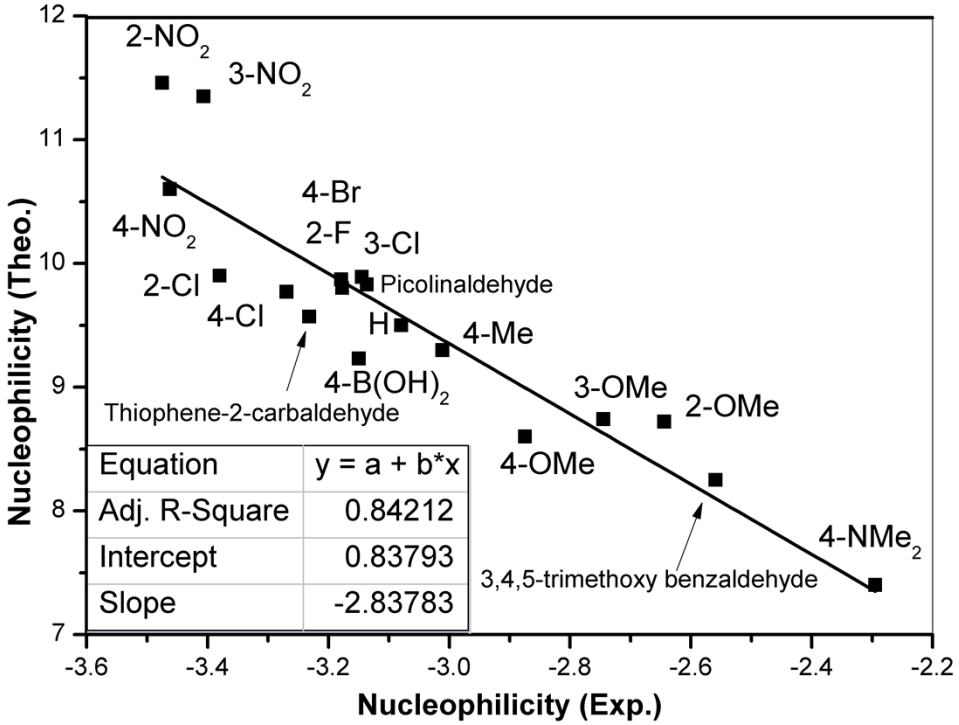


Fig. S5. Theoretical nucleophilicity in method I *versus* Experimental nucleophilicity plot of various aldehyde.

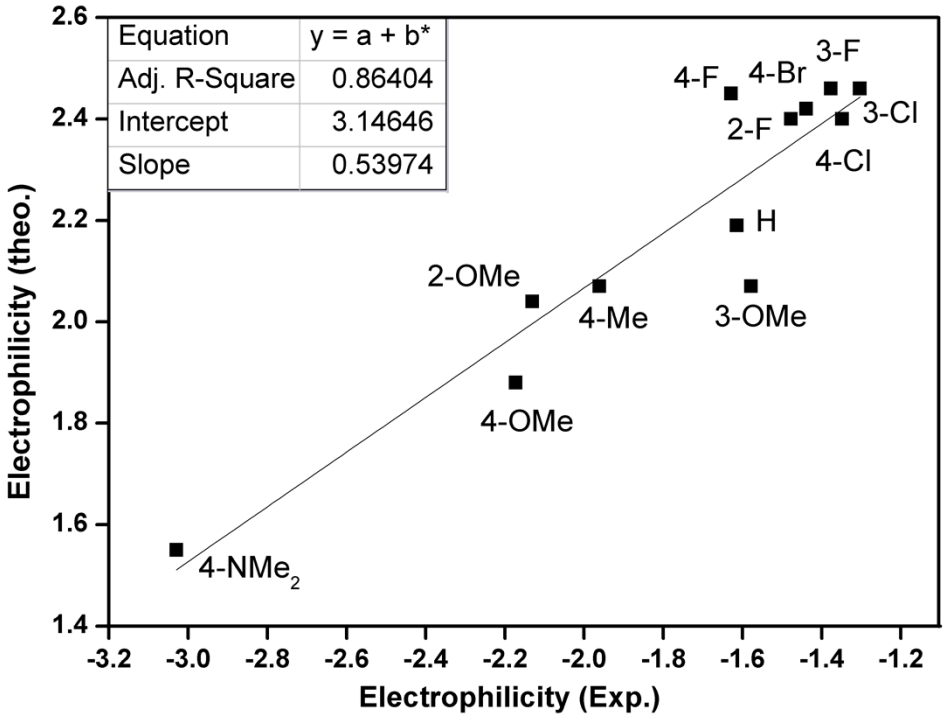


Fig. S6. Theoretical electrophilicity in method I *versus* experimental electrophilicity plot of various *para* substituted benzaldehydes in three different methods

Table S9. Electrophilicity of five different aldehyde in this method and by mayr et al.		
Aldehyde	Electrophilicity (in this method)	Electrophilicity (Mayr *et al.*)[5]
3-chloro benzaldehyde	-18.03	-1.3
3-fluro benzaldehyde	-18.27	-1.37
3-methoxy benzaldehyde	-19.32	-1.57
4-fluro benzaldehyde	-19.42	-1.62
Benzaldehyde	-19.52	-1.61

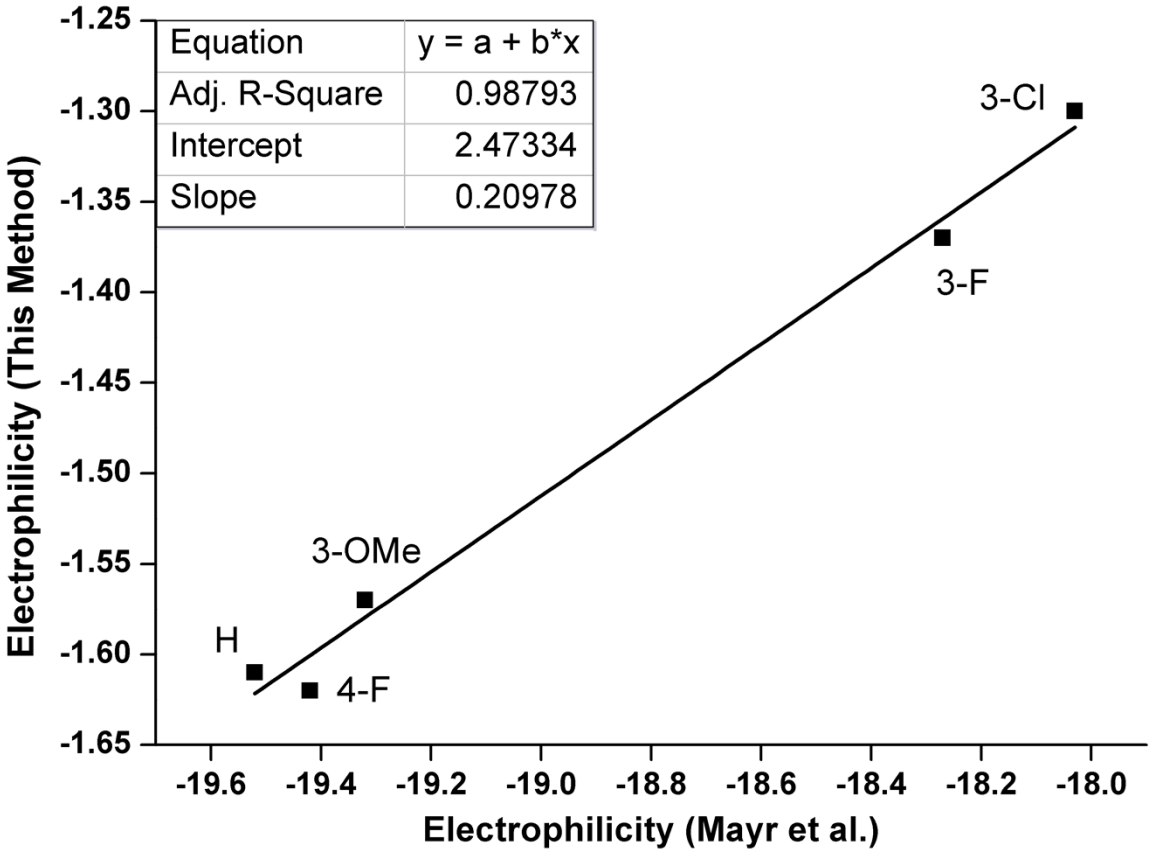


Fig. S7. Experimental electrophilicity in method *versus* experimental electrophilicity by Mayr *et al*.

Table S10. *Ln(K/T) versus (1/T) plot for the determination of activation parameter for* ***$KMnO_4$ oxidation*** *reaction of five different para-substituted benzaldehyde.*

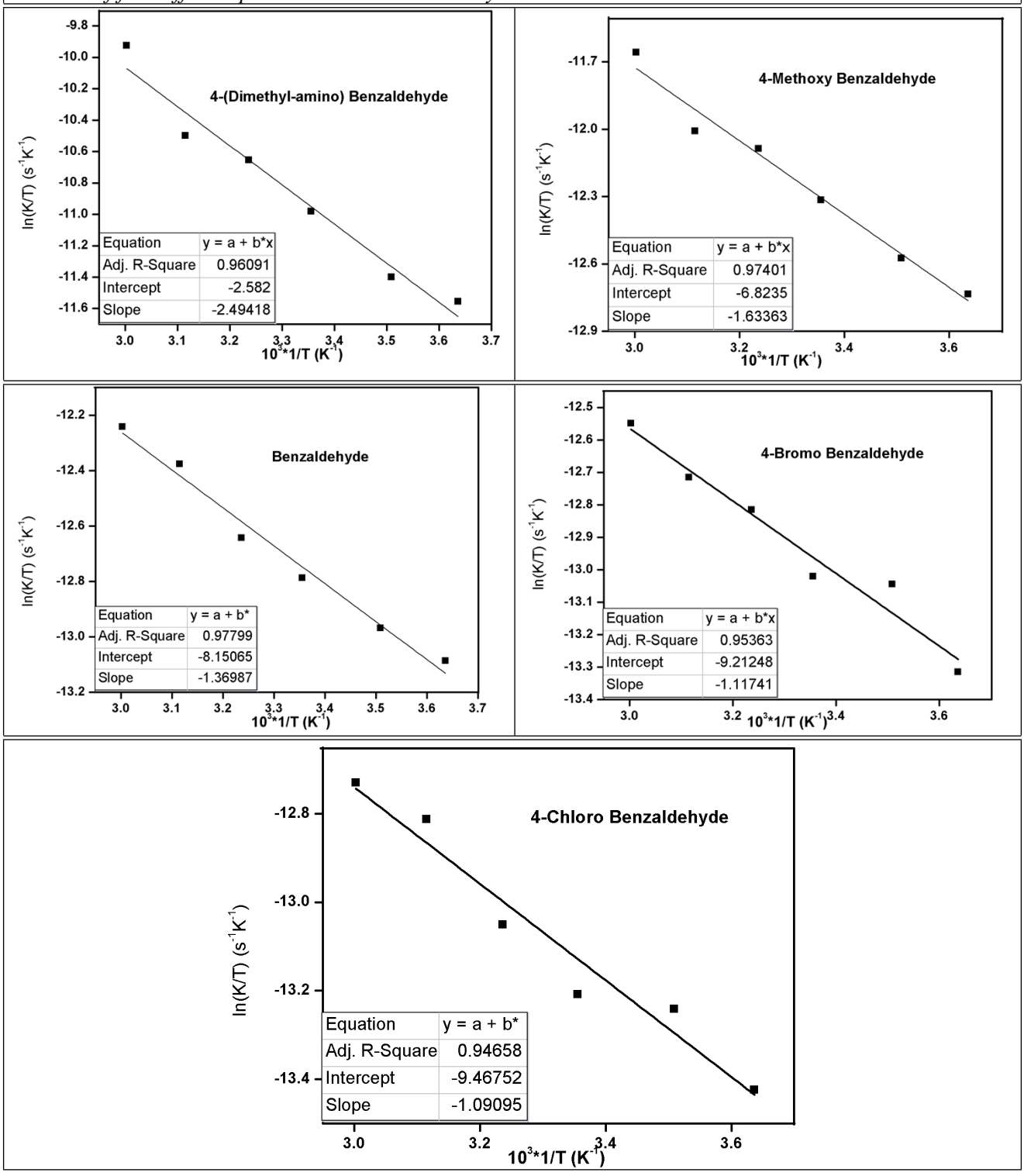


Table S11. *Ln(K/T) versus (1/T) plot for the determination of activation parameter for* ***$NaBH_4$ reduction*** *of five different para-substituted benzaldehyde.*

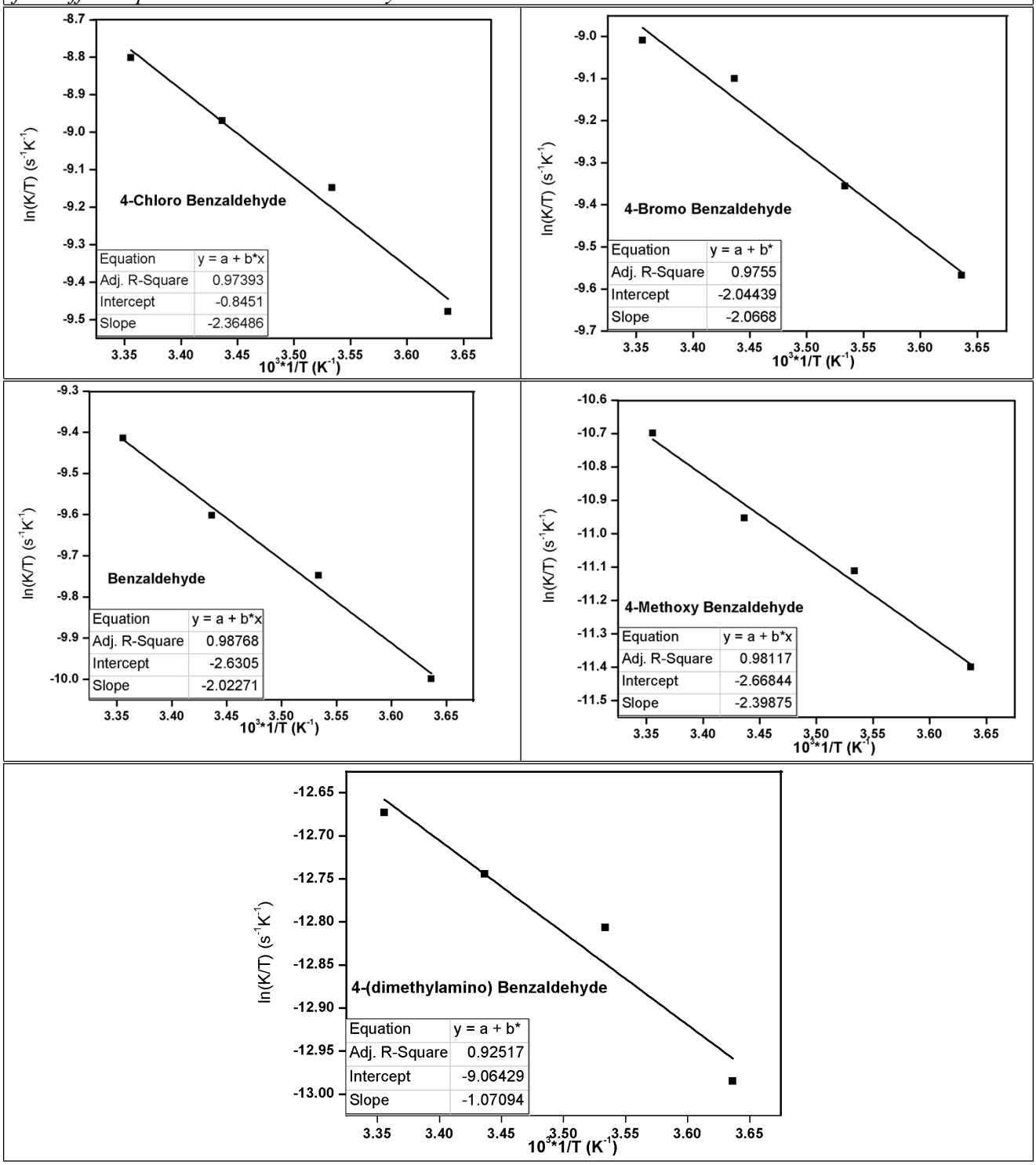


Table S12. Ln(A) versus time plot for the determination of rate constant (k) for **$NaBH_4$ reduction** of six different *para*-substituted benzaldehyde at 298 K.

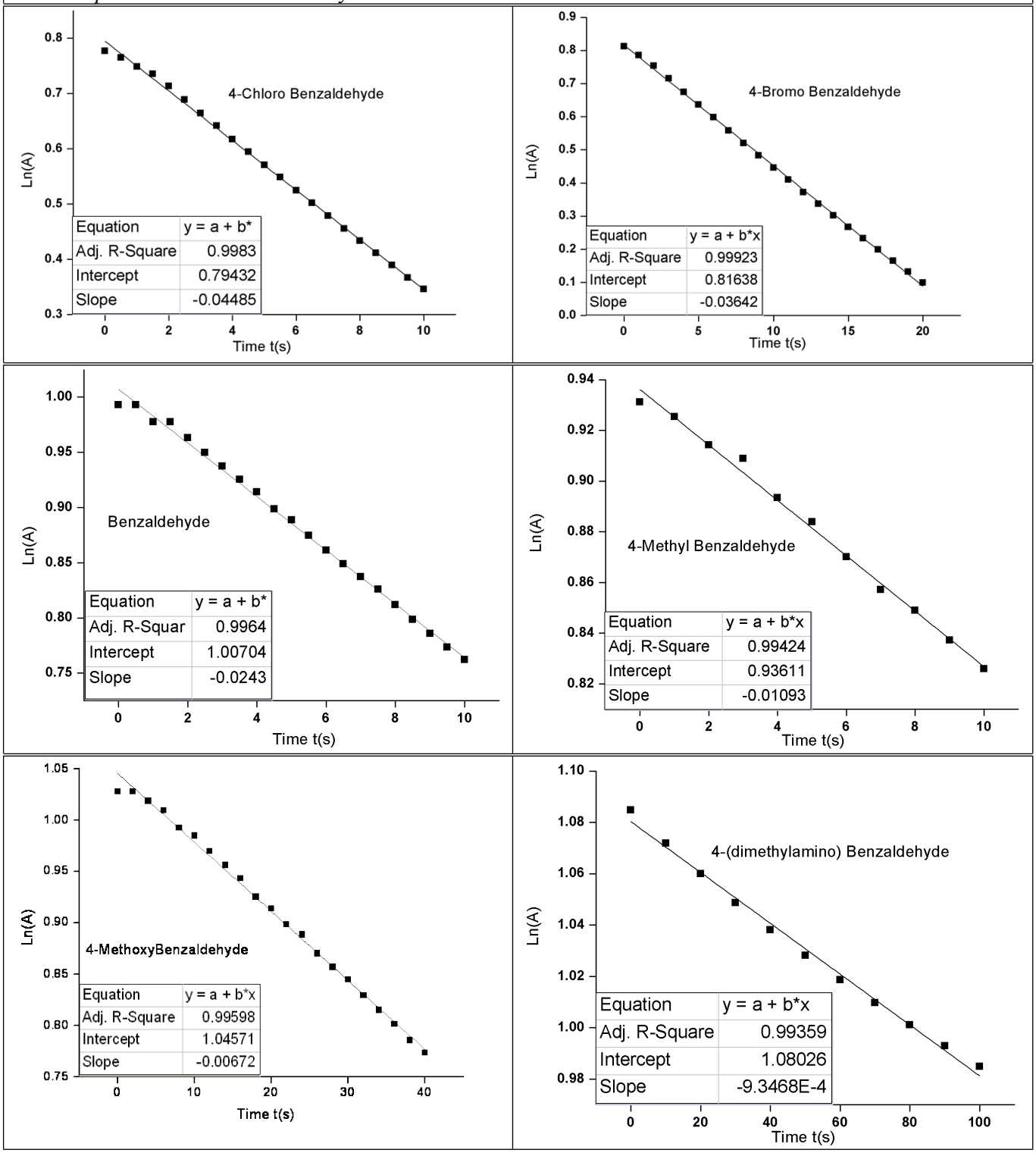


Table S13. Ln(A) versus time plot for the determination of rate constant (k) for $NaBH_4$ reduction of Five different *para*-substituted benzaldehyde at 291 K.

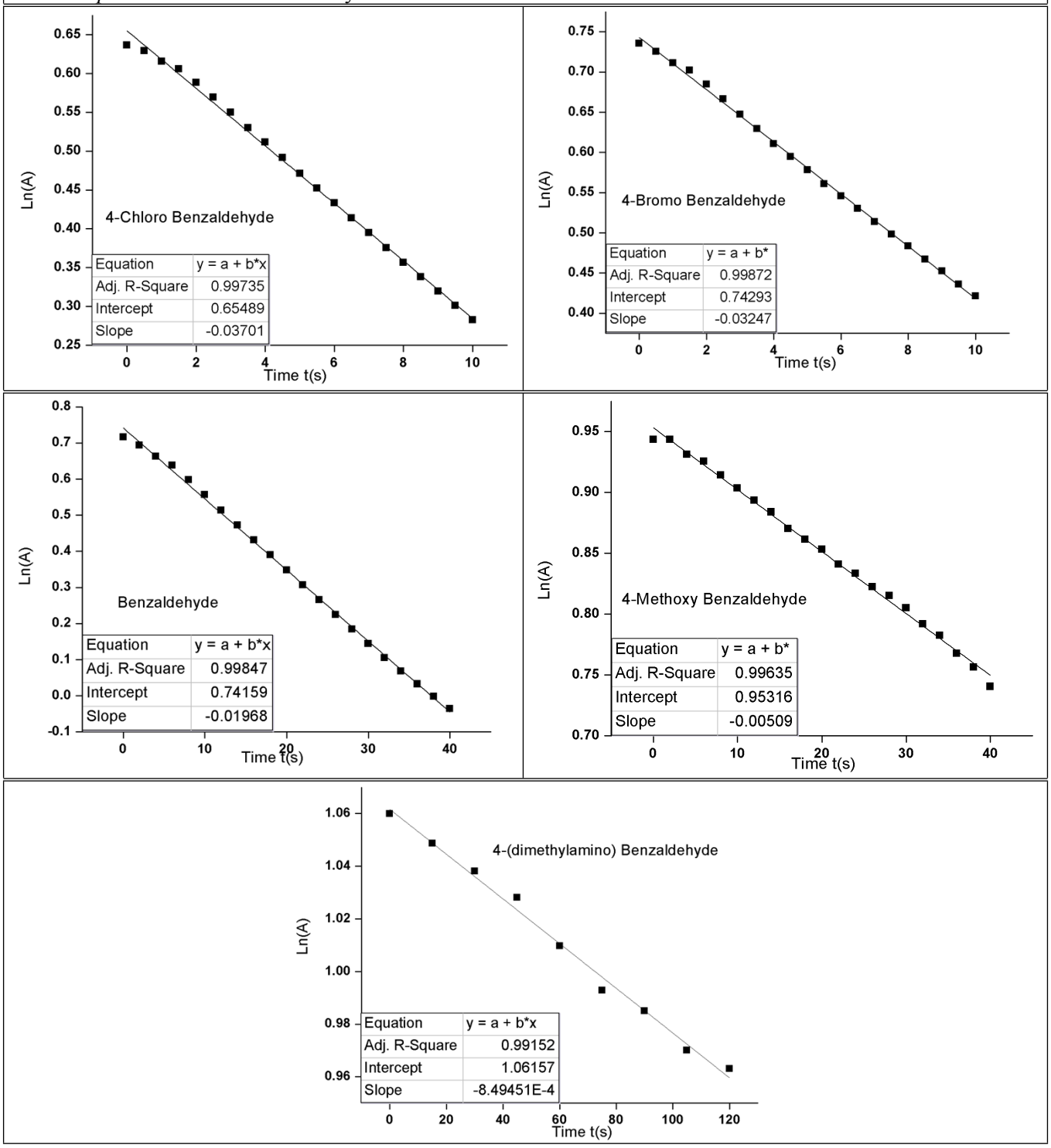


Table S14. Ln(A) versus time plot for the determination of rate constant (k) for $NaBH_4$ reduction of Five different *para*-substituted benzaldehyde at 283 K.

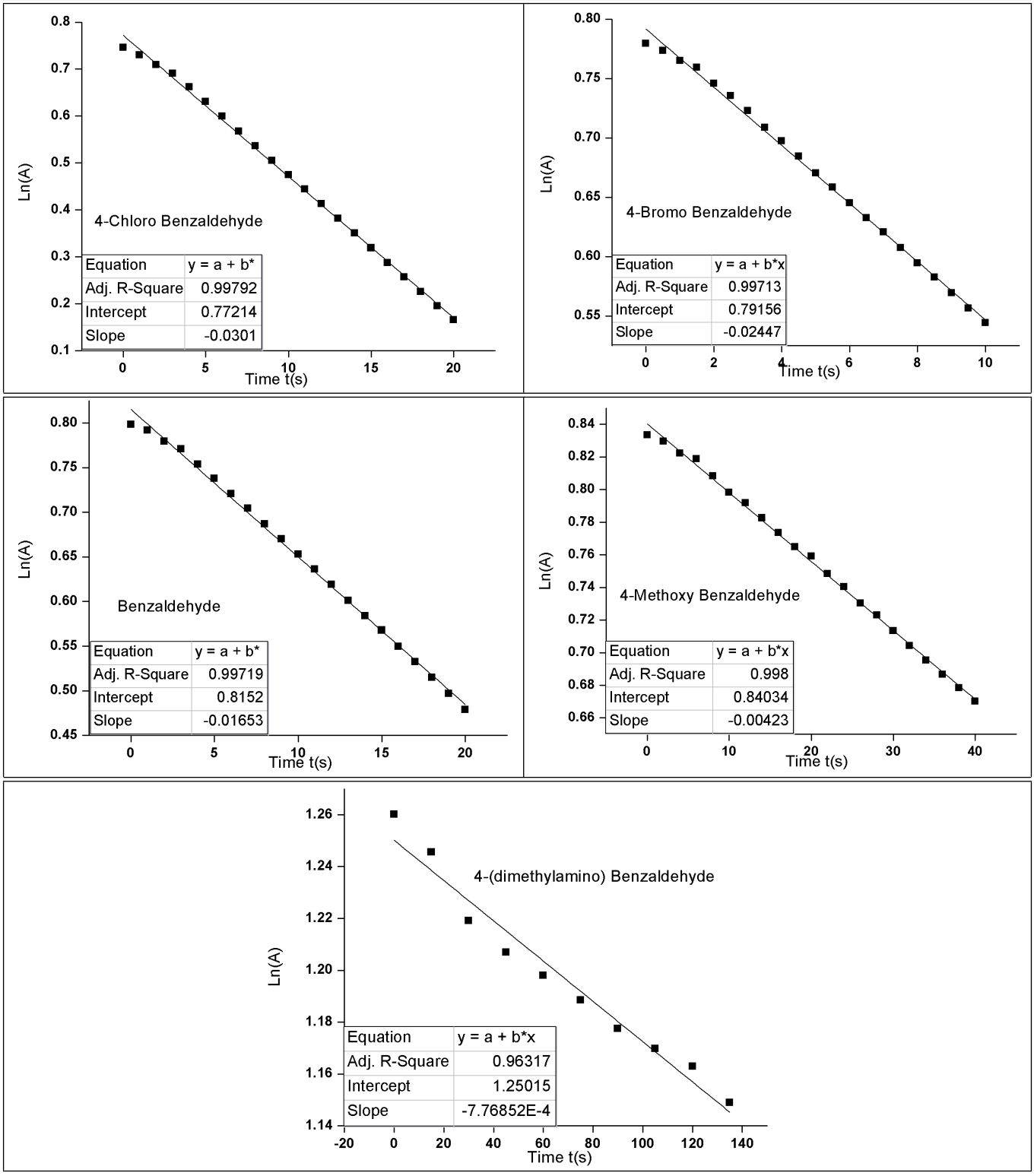


Table S15. Ln(A) versus time plot for the determination of rate constant (k) for $NaBH_4$ reduction of Five different *para*-substituted benzaldehyde at 275 K.

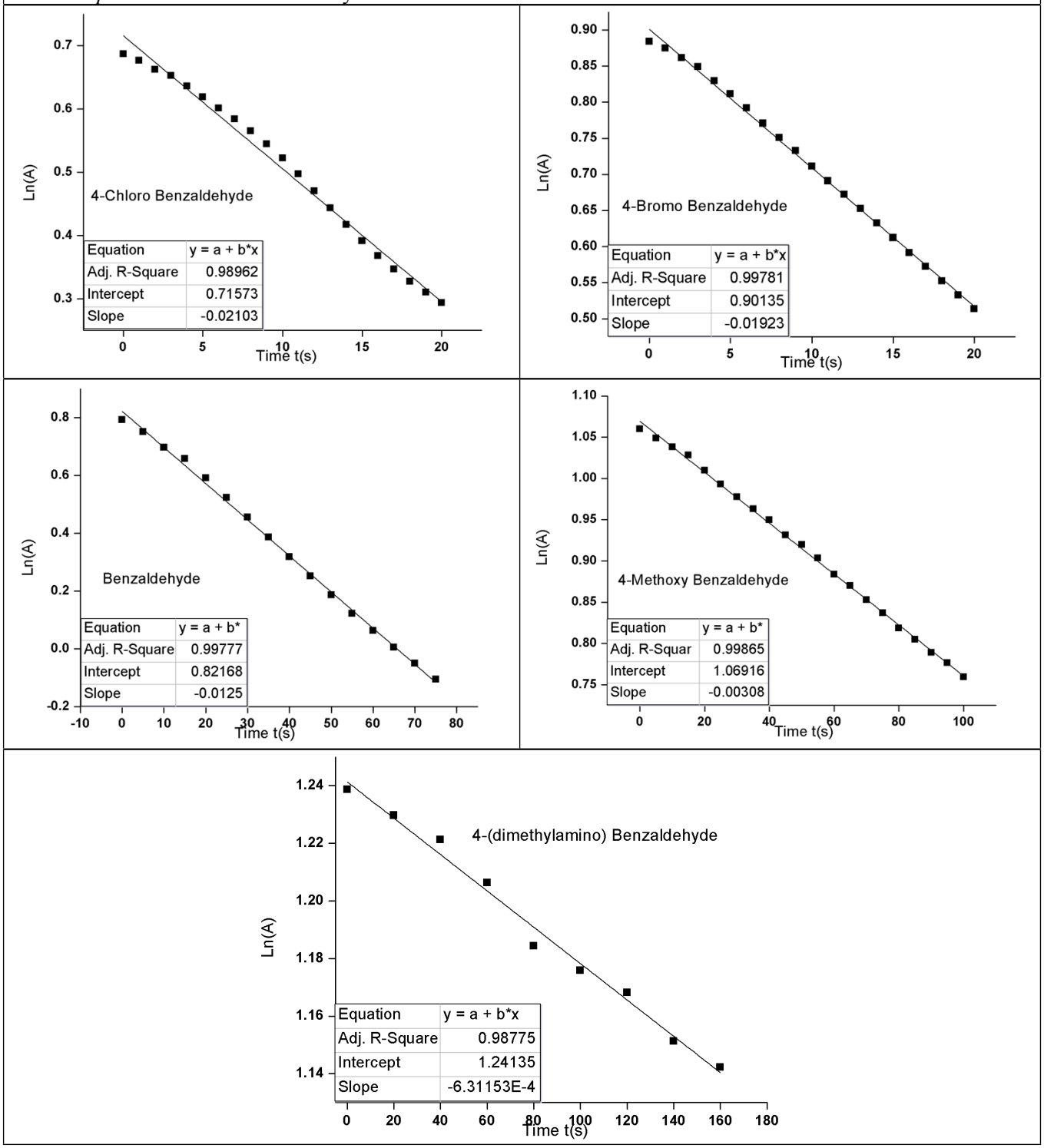


Table S16. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 275 K.

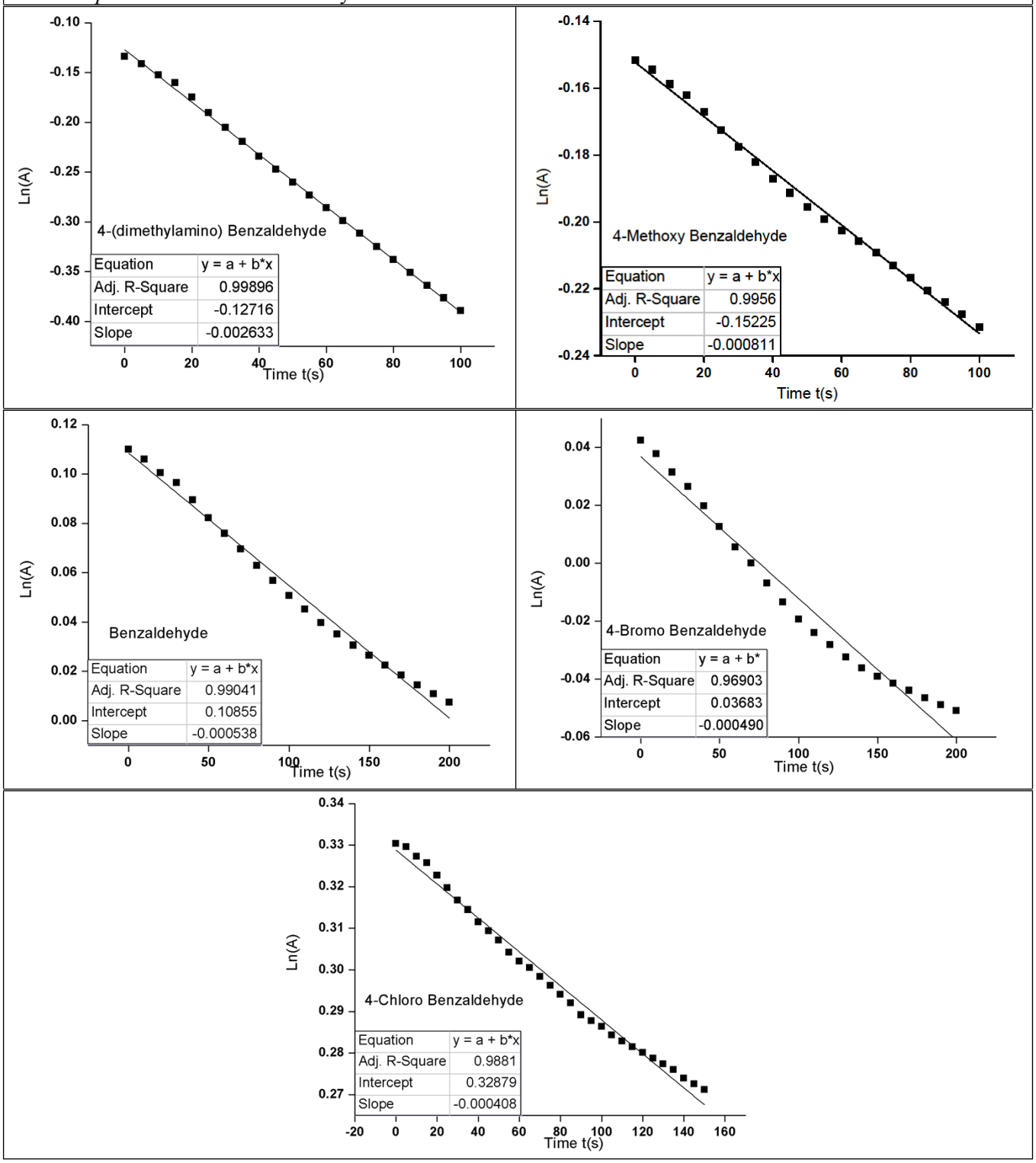


Table S17. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 285 K.

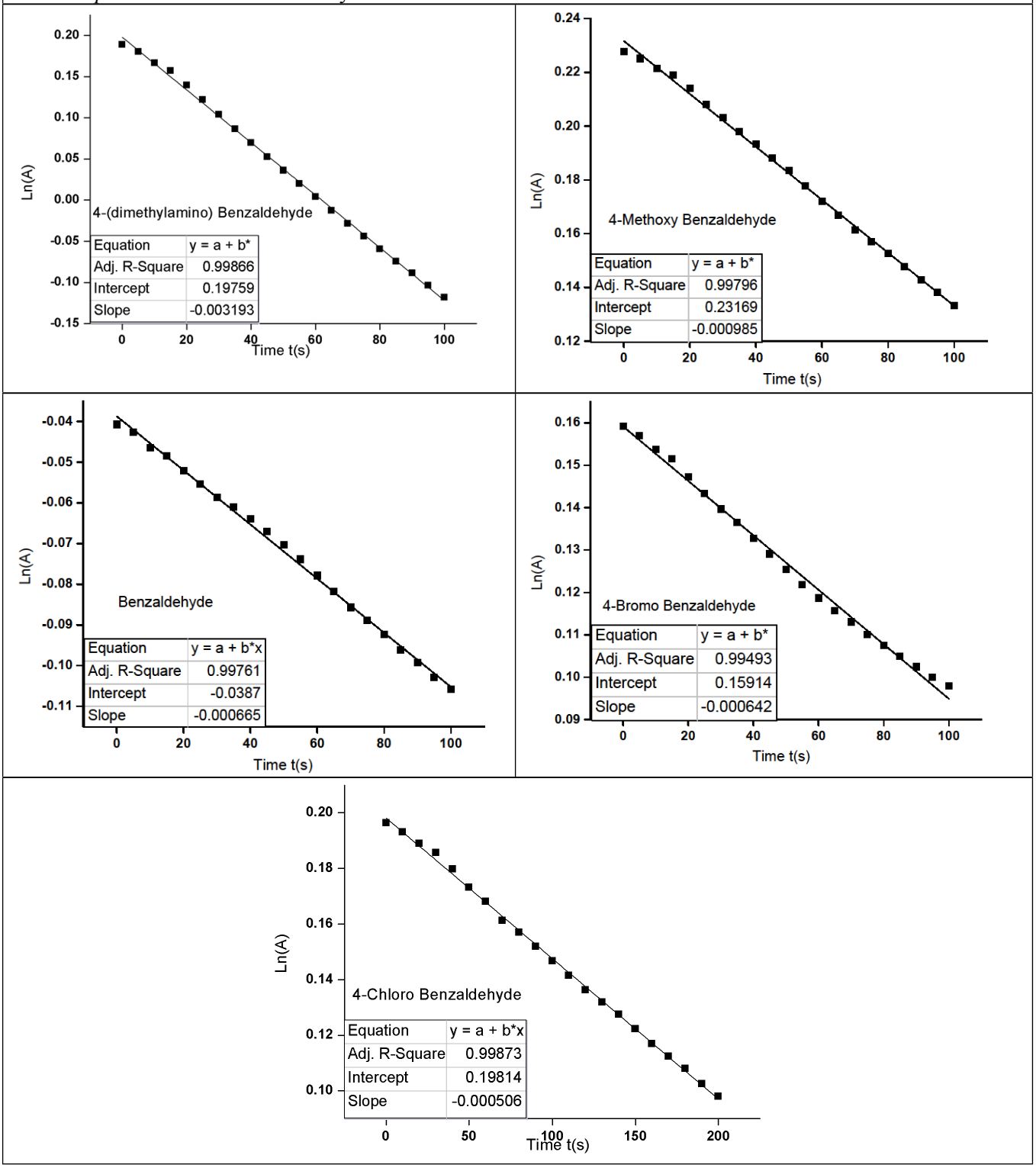
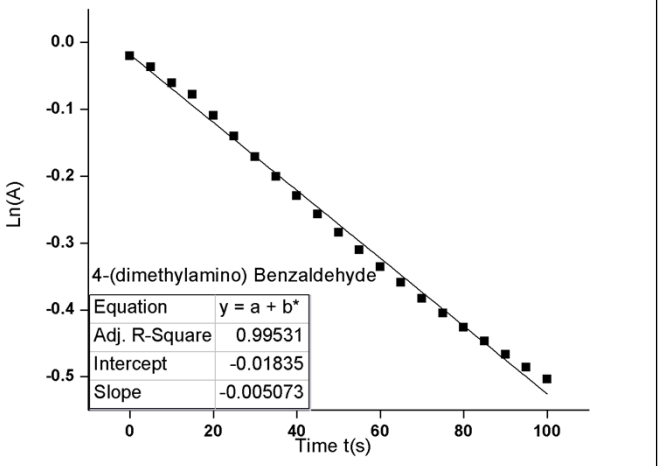
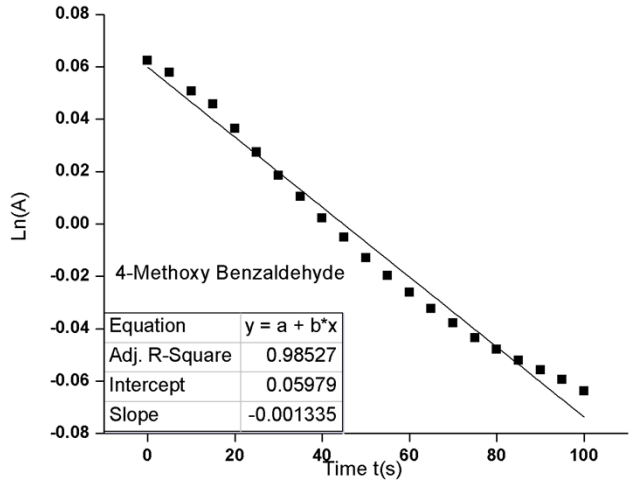
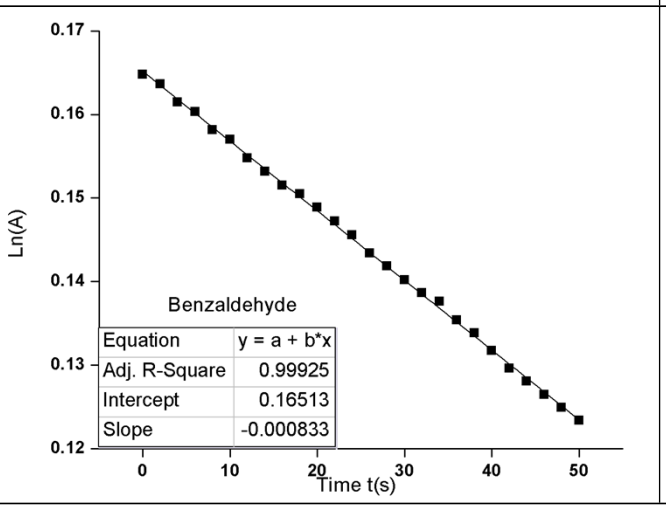
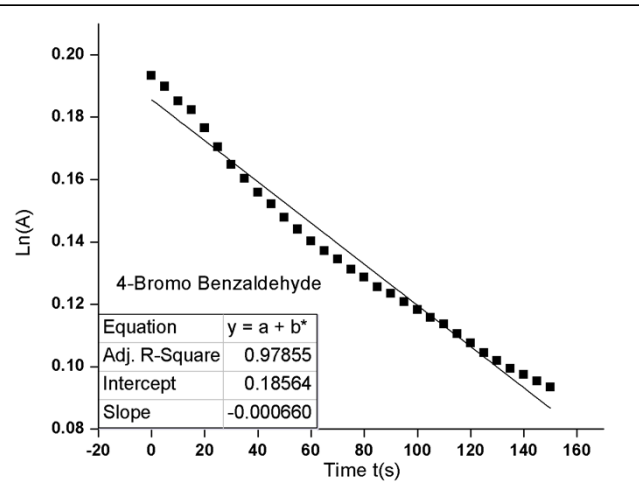


Table S18. Ln(A) versus time plot for the determination of rate constant (k) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 298 K.









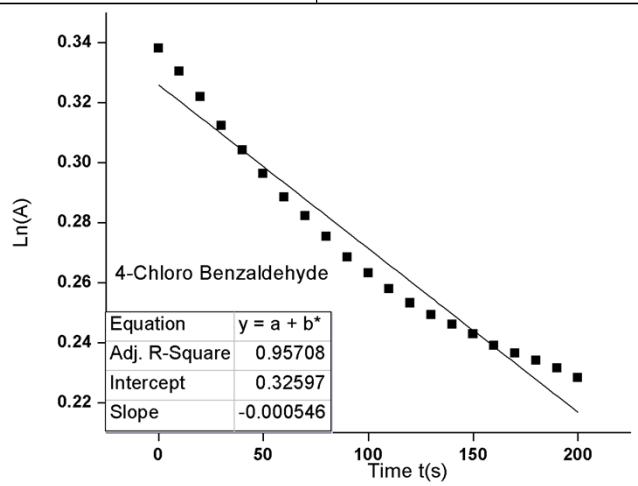


Table S19. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 309 K.

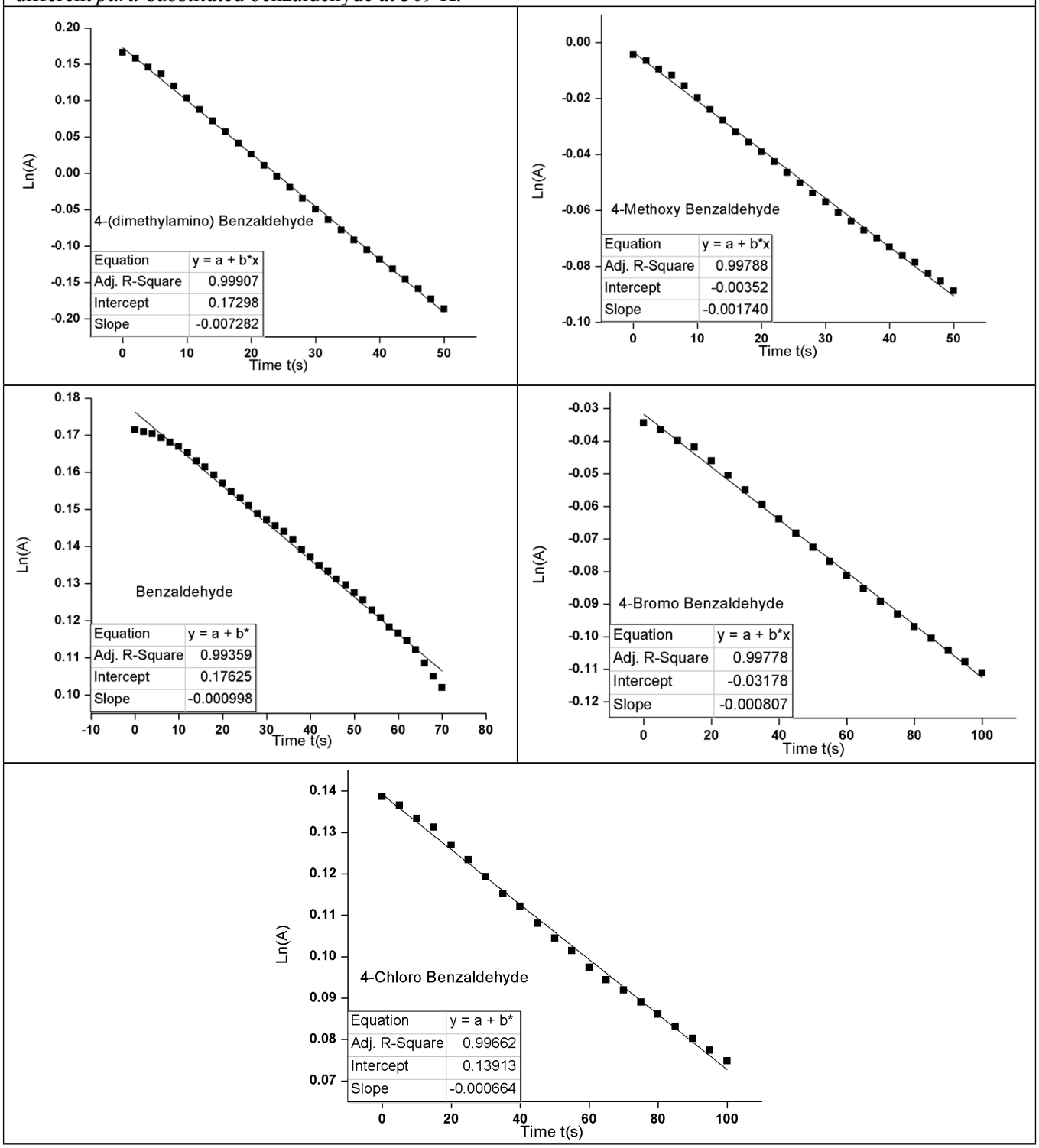


Table S20. Ln(A) versus time plot for the determination of rate constant (k) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 321 K.

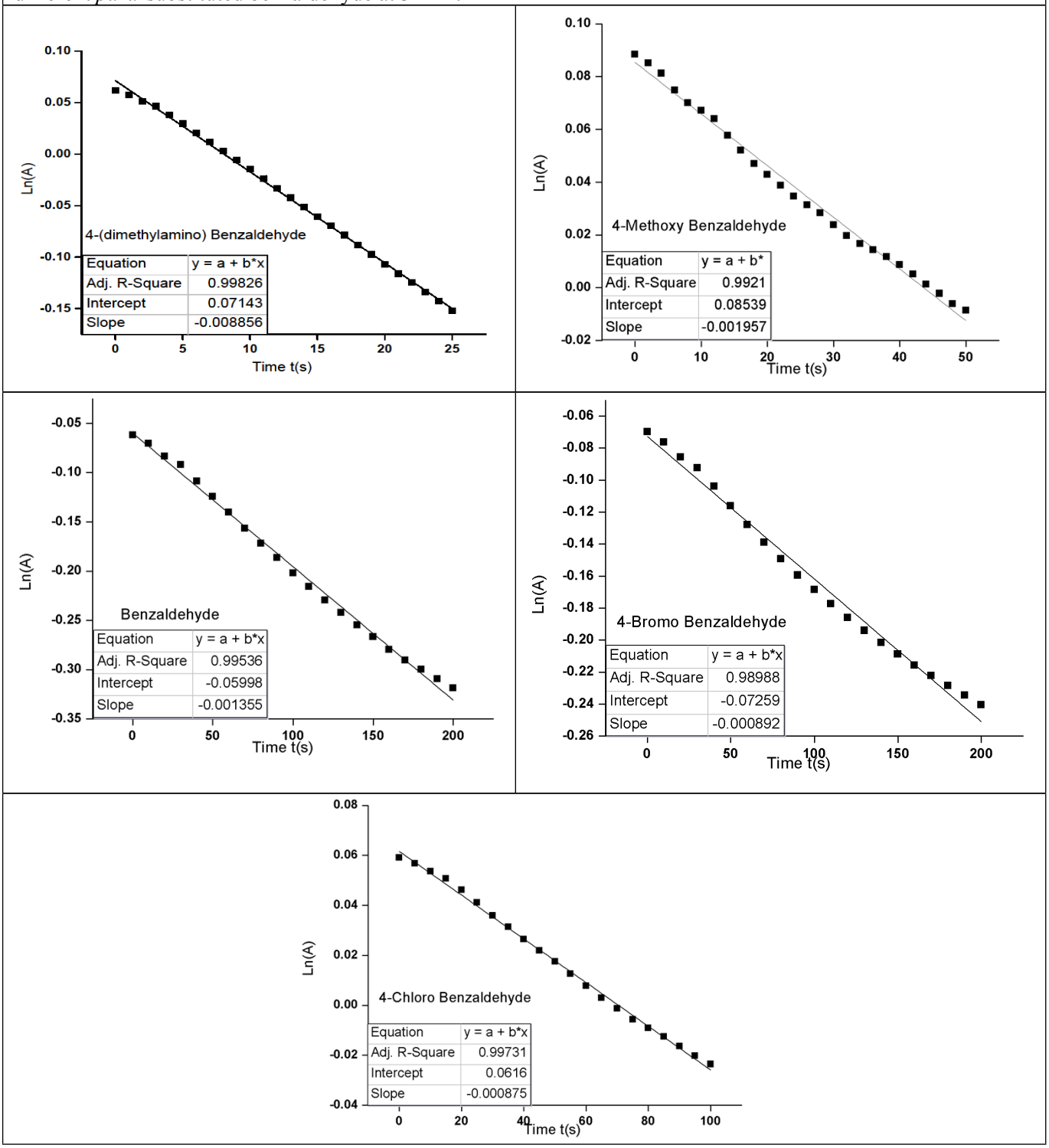


Table S21. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of Five different *para*-substituted benzaldehyde at 333 K.

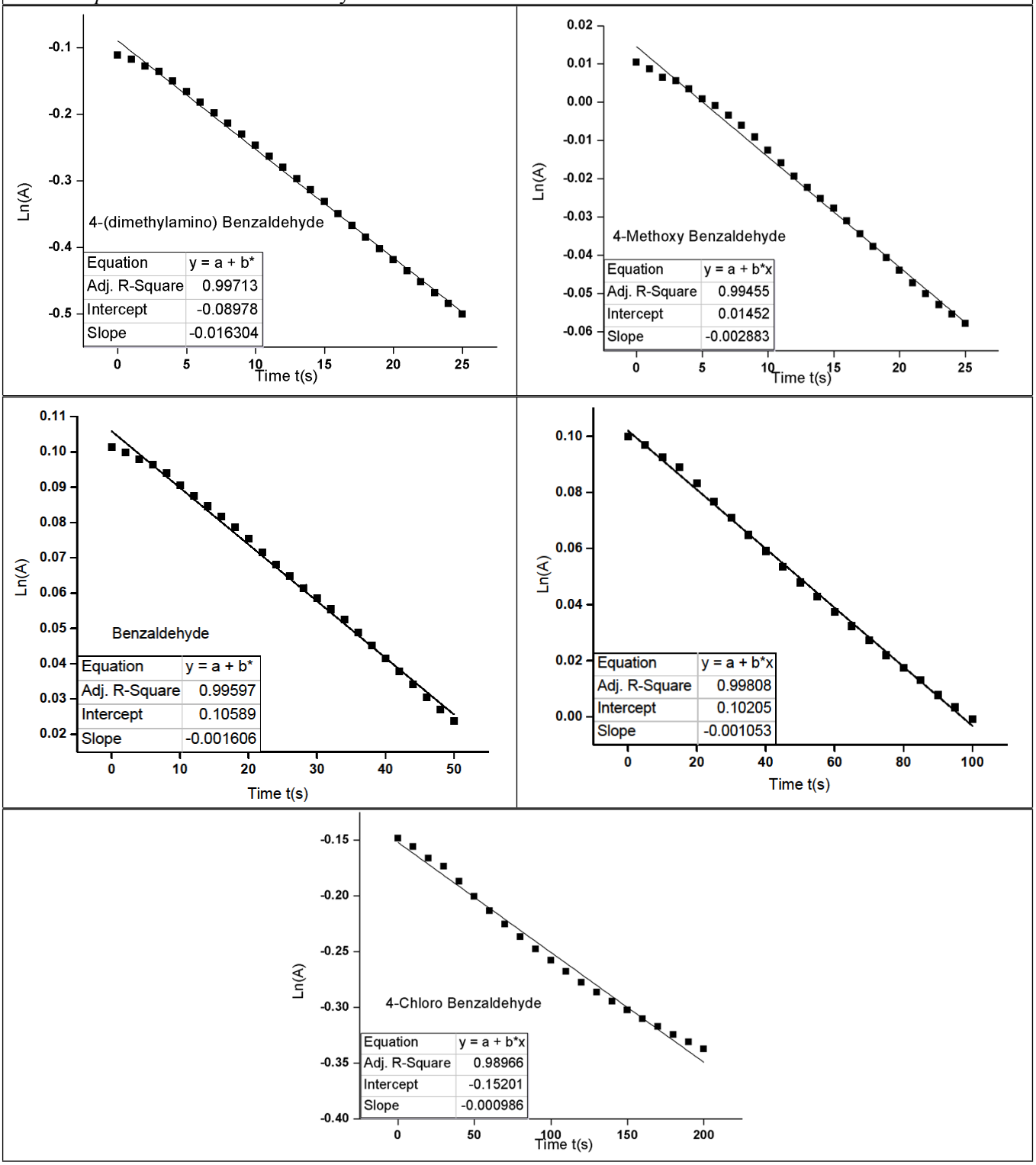


Table S22. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of six different aldehyde at 298 K.

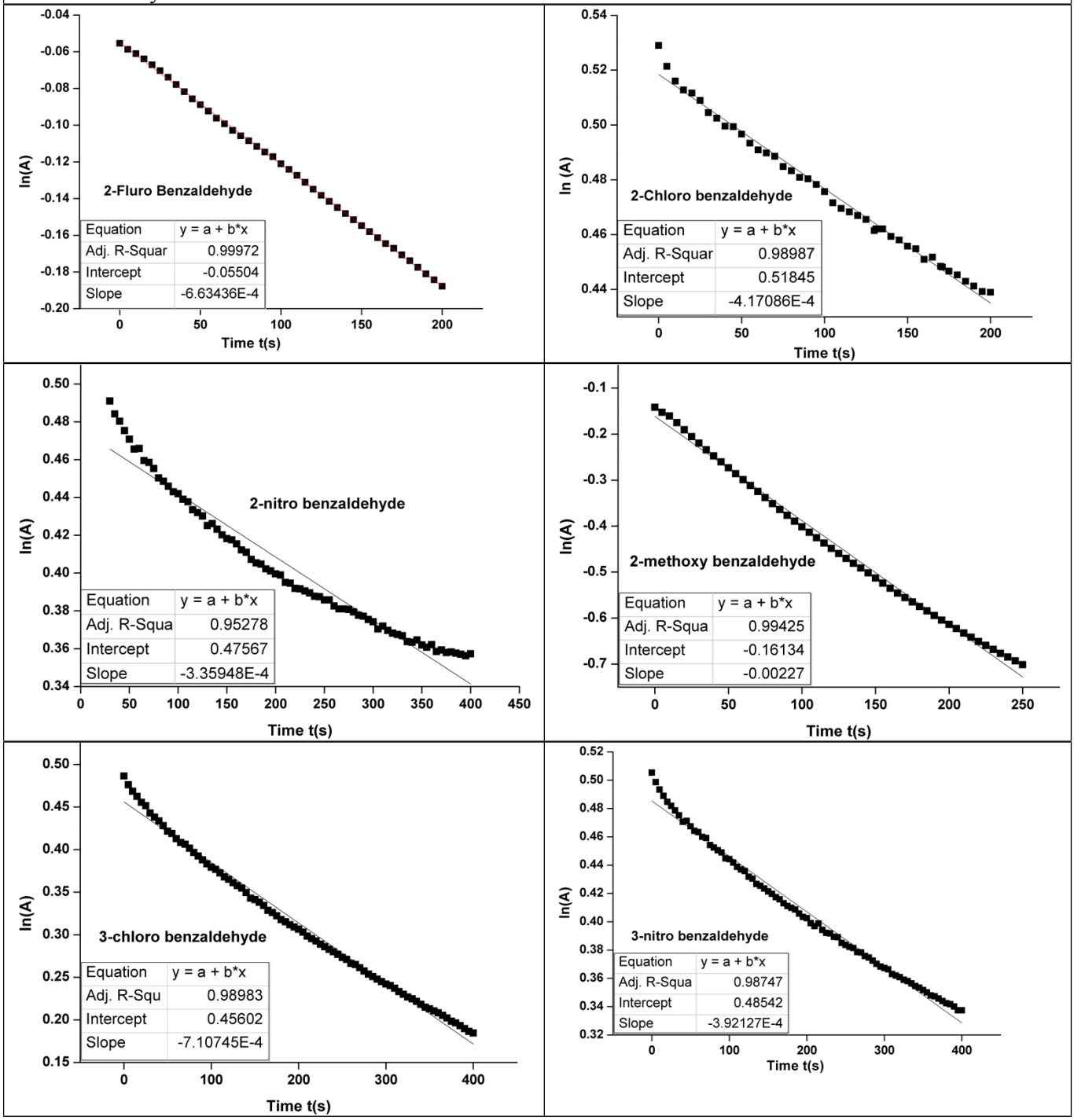


Table S23. Ln(A) versus time plot for the determination of rate constant (*k*) for $KMnO_4$ oxidation of Five different aldehyde at 298 K.

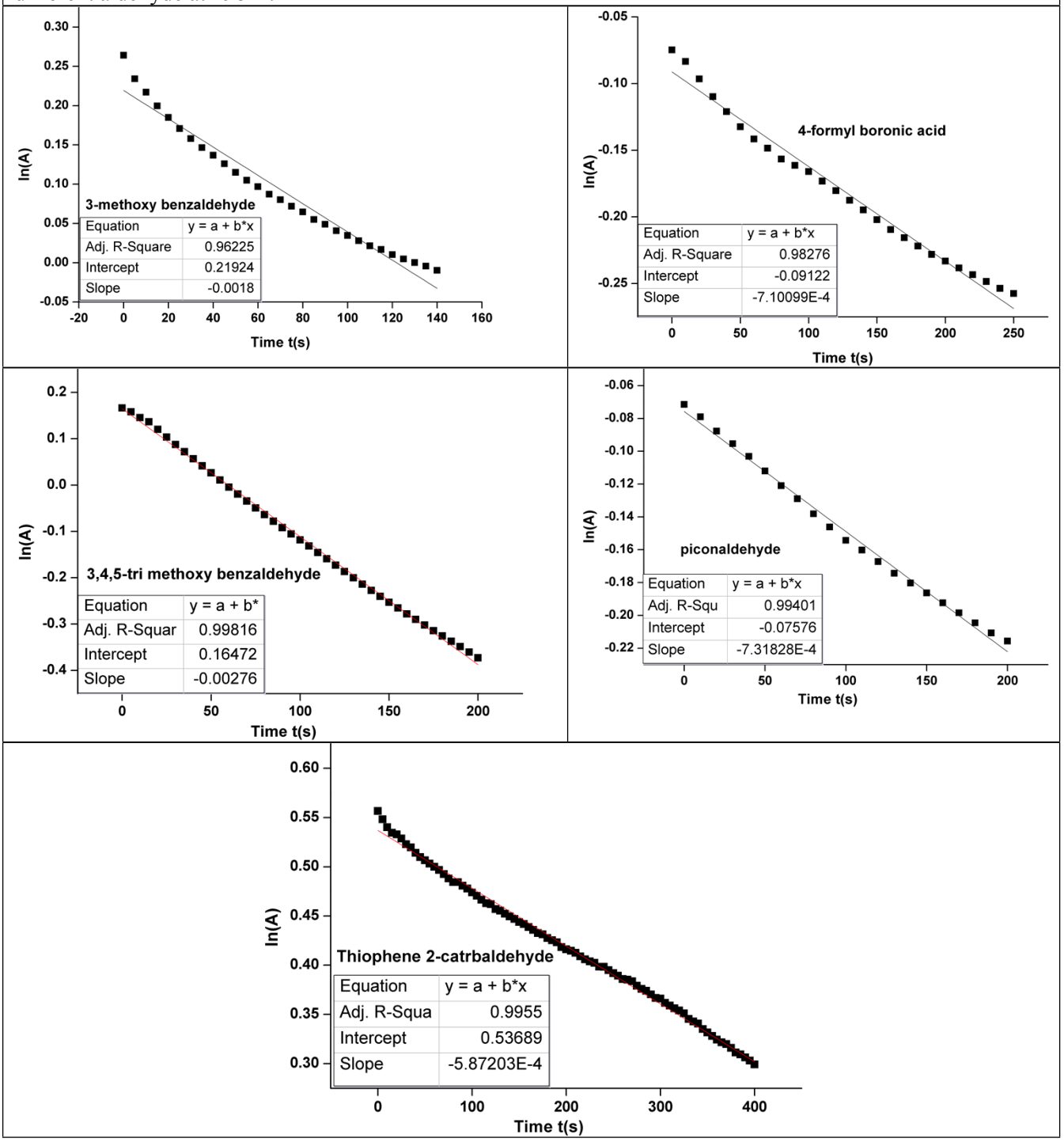
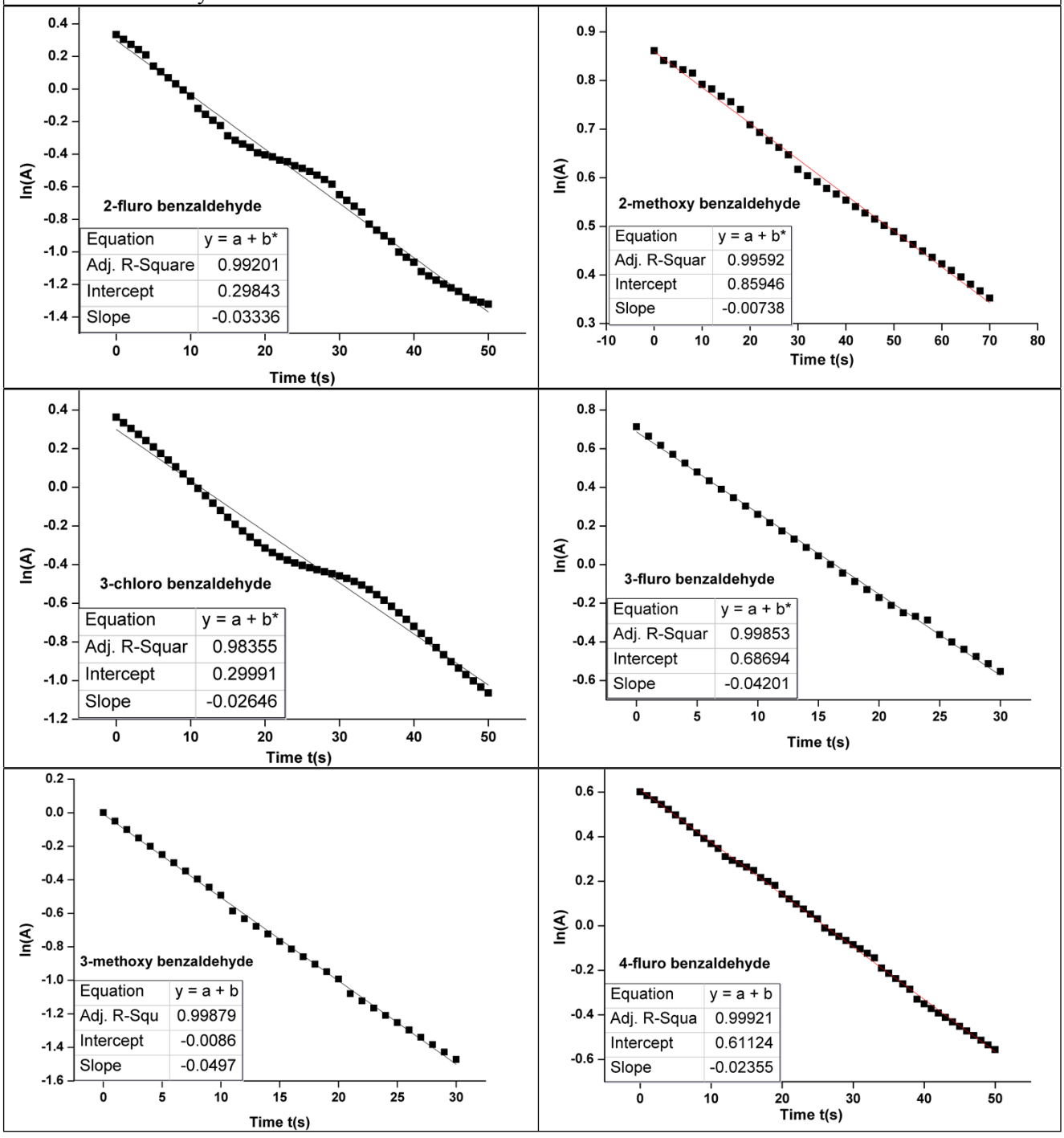


Table S24. Ln(A) versus time plot for the determination of rate constant (k) for $NaBH_4$ reduction of six different benzaldehyde at 298 K.



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