Electronic supplementary information

Hydrolysis of 1-(X-substituted-benzoyl)-4-aminopyridinium ions: Effect of substituent X on reactivity and reaction mechanism

Ik-Hwan Um,[*] Eun-Hee Kim, and Ji-Sun Kang

Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea.

e-mail: ihum@ewha.ac.kr   Tel: 82-2-3277-2349.   Fax: 82-2-3277-2844.

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Table S1 Kinetic data for the hydrolysis of 1-(4-dimethylaminobenzoyl)-4-aminopyridinium ion **2a** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^4 k_{obsd}$ / s^{-1}
24.2	3.21
43.4	4.38
58.9	5.12
71.7	5.73
82.4	6.34
103	7.33

$k_{cat} = 0.00518 \pm 0.0001$ $M^{-1}s^{-1}$
$k_o = 0.000204 \pm 0.000008$ s^{-1}
$R^2 = 0.9990$

Table S2 Kinetic data for the hydrolysis of 1-(4-methoxybenzoyl)-4-aminopyridinium ion **2b** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
9.81	5.23
18.7	6.22
26.9	7.20
34.3	8.03
41.2	8.87

$k_{cat} = 0.116 \pm 0.001$ $M^{-1}s^{-1}$
$k_o = 0.000408 \pm 0.000020$ s^{-1}
$R^2 = 0.9999$

Table S3 Kinetic data for the hydrolysis of 1-(4-methylbenzoyl)-4-aminopyridinium ion **2c** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
9.81	11.5
18.7	13.9
26.9	16.3
34.3	18.3
41.2	20.0

$k_{cat} = 0.273 \pm 0.004$ $M^{-1}s^{-1}$
$k_o = 0.00884 \pm 0.00010$ s^{-1}
$R^2 = 0.9996$

Table S4 Kinetic data for the hydrolysis of 1-(3-methylbenzoyl)-4-aminopyridinium ion **2d** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
9.81	17.8
18.7	22.0
26.9	25.9
34.3	29.1
41.2	32.3

$k_{cat} = 0.461 \pm 0.005 \text{ M}^{-1}\text{s}^{-1}$
$k_o = 0.0134 \pm 0.0001 \text{ s}^{-1}$
$R^2 = 0.9998$

Table S5 Kinetic data for the hydrolysis of 1-benzoyl-4-aminopyridinium ion **2e** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
4.08	19.8
8.00	22.1
15.4	26.1
22.3	30.5
28.7	33.8
34.7	37.7

$k_{cat} = 0.581 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$
$k_o = 0.0174 \pm 0.0002 \text{ s}^{-1}$
$R^2 = 0.9996$

Table S6 Kinetic data for the hydrolysis of 1-(4-chlorobenzoyl)-4-aminopyridinium ion **2f** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
4.04	42.1
7.92	46.4
11.7	50.4
15.3	54.0
18.7	58.0

$k_{cat} = 1.07 \pm 0.01 \text{M}^{-1}\text{s}^{-1}$
$k_o = 0.0378 \pm 0.0002 \text{ s}^{-1}$
$R^2 = 0.9997$

Table S7 Kinetic data for the hydrolysis of 1-(3-chlorobenzoyl)-4-aminopyridinium ion **2g** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	$10^3 k_{obsd}$ / s^{-1}
2.29	69.3
4.06	72.6
7.96	82.3
11.7	91.3
15.3	98.9
18.8	106

$k_{cat} = 2.26 \pm 0.04$ $M^{-1}s^{-1}$
$k_o = 0.0640 \pm 0.0008$ s^{-1}
$R^2 = 0.9993$

Table S8 Kinetic data for the hydrolysis of 1-(4-cyanobenzoyl)-4-aminopyridinium ion **2h** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	k_{obsd} / s^{-1}
1.03	0.143
1.63	0.148
2.44	0.154
2.84	0.157
3.24	0.160
4.04	0.166

$k_{cat} = 7.60 \pm 0.07$ $M^{-1}s^{-1}$
$k_o = 0.135 \pm 0.0002$ s^{-1}
$R^2 = 0.9998$

Table S9 Kinetic data for the hydrolysis of 1-(4-chloro-3-nitrobenzoyl)-4-aminopyridinium ion **2i** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C

[4-aminopyridine] / mM	k_{obsd} / s^{-1}
10.2	0.406
20.4	0.505
30.6	0.614
40.8	0.705
51.0	0.798

$k_{cat} = 9.65 \pm 0.18$ $M^{-1}s^{-1}$
$k_o = 0.310 \pm 0.006$ s^{-1}
$R^2 = 0.9994$

Fig. S1 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-dimethylaminobenzoyl)-4-aminopyridinium ion **2a** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

Fig. S2 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-methoxybenzoyl)-4-aminopyridinium ion **2b** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.
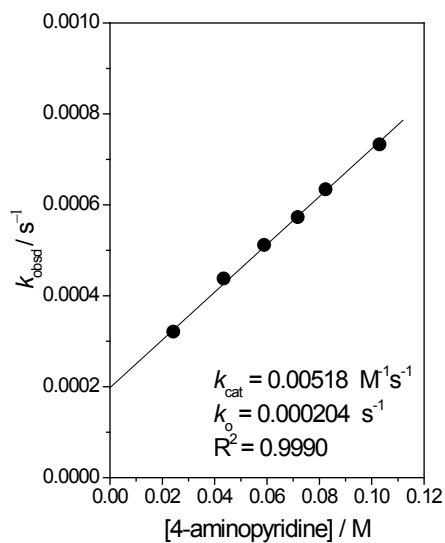
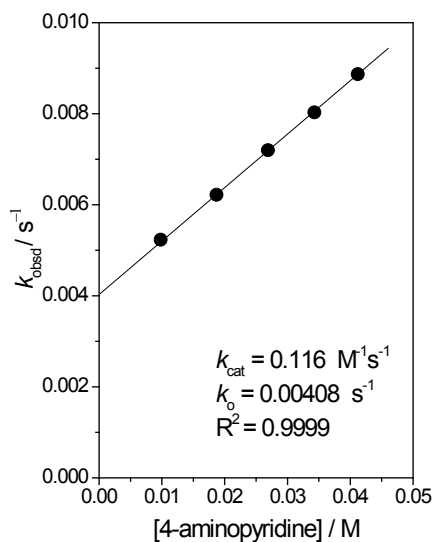**Fig. S3** Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-methylbenzoyl)-4-aminopyridinium ion **2c** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

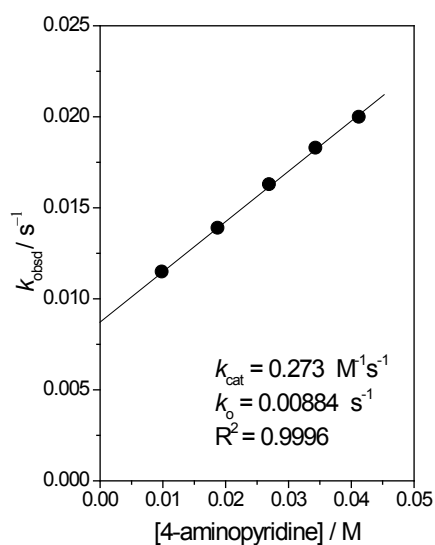**Fig. S4** Plot of k_{obsd} vs. [4-aminopyridine]] for the hydrolysis of 1-(3-methylbenzoyl)-4-aminopyridinium ion **2d** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

Fig. S5 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-chlorobenzoyl)-4-aminopyridinium ion **2f** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

Fig. S6 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(3-chlorobenzoyl)-4-aminopyridinium ion **2g** in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C.

$k_{cat} = 7.60$ M^{-1}s^{-1}
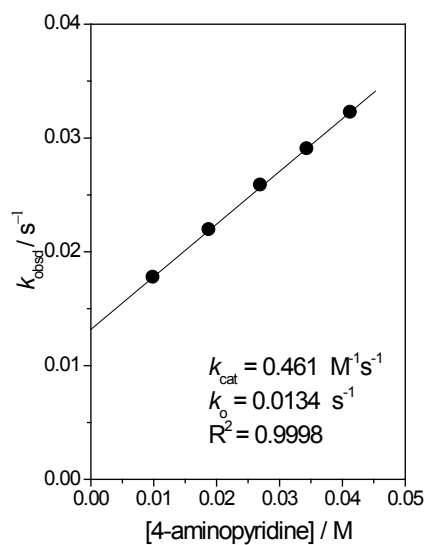$k_o = 0.135$ s^{-1}
$R^2 = 0.9998$

Fig. S7 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-cyanobenzoyl)-4-aminopyridinium ion **2h** in 80 mol % H$_2$O/20 mol % DMSO at 25.0 ± 0.1 °C.

$k_{cat} = 9.65$ M^{-1}s^{-1}
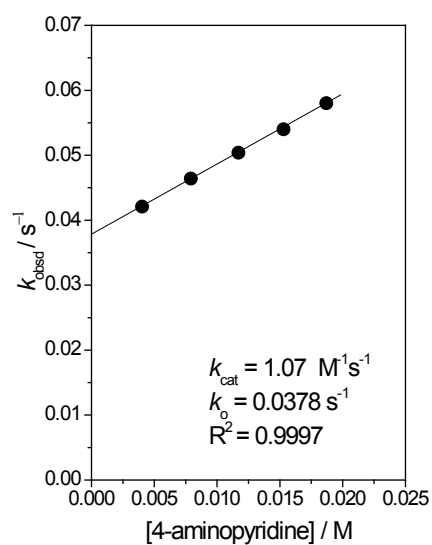$k_o = 0.310$ s^{-1}
$R^2 = 0.9994$

Fig. S8 Plot of k_{obsd} vs. [4-aminopyridine] for the hydrolysis of 1-(4-chloro-3-nitrobenzoyl)-4-aminopyridinium ion **2i** in 80 mol % H$_2$O/20 mol % DMSO at 25.0 ± 0.1.
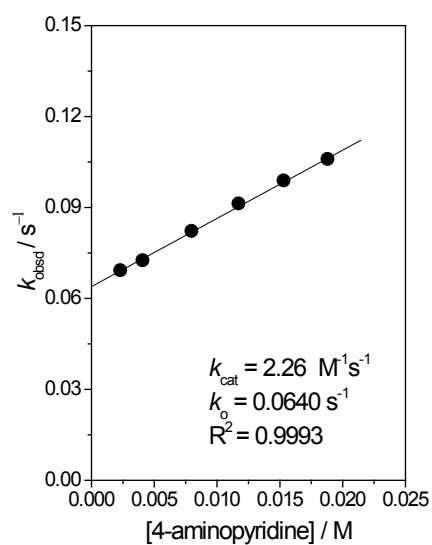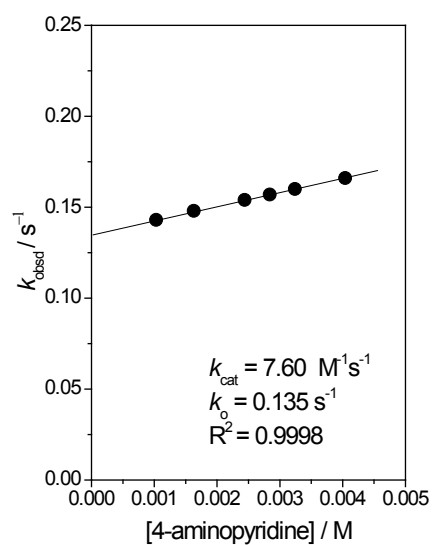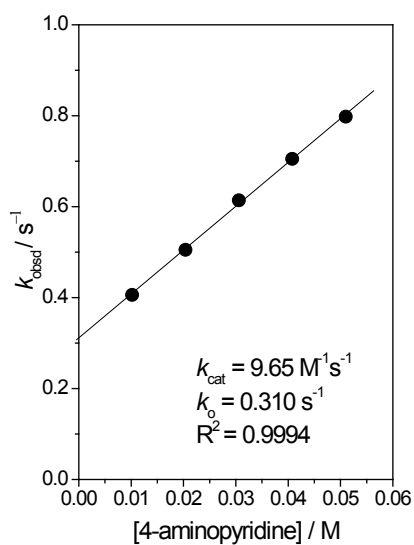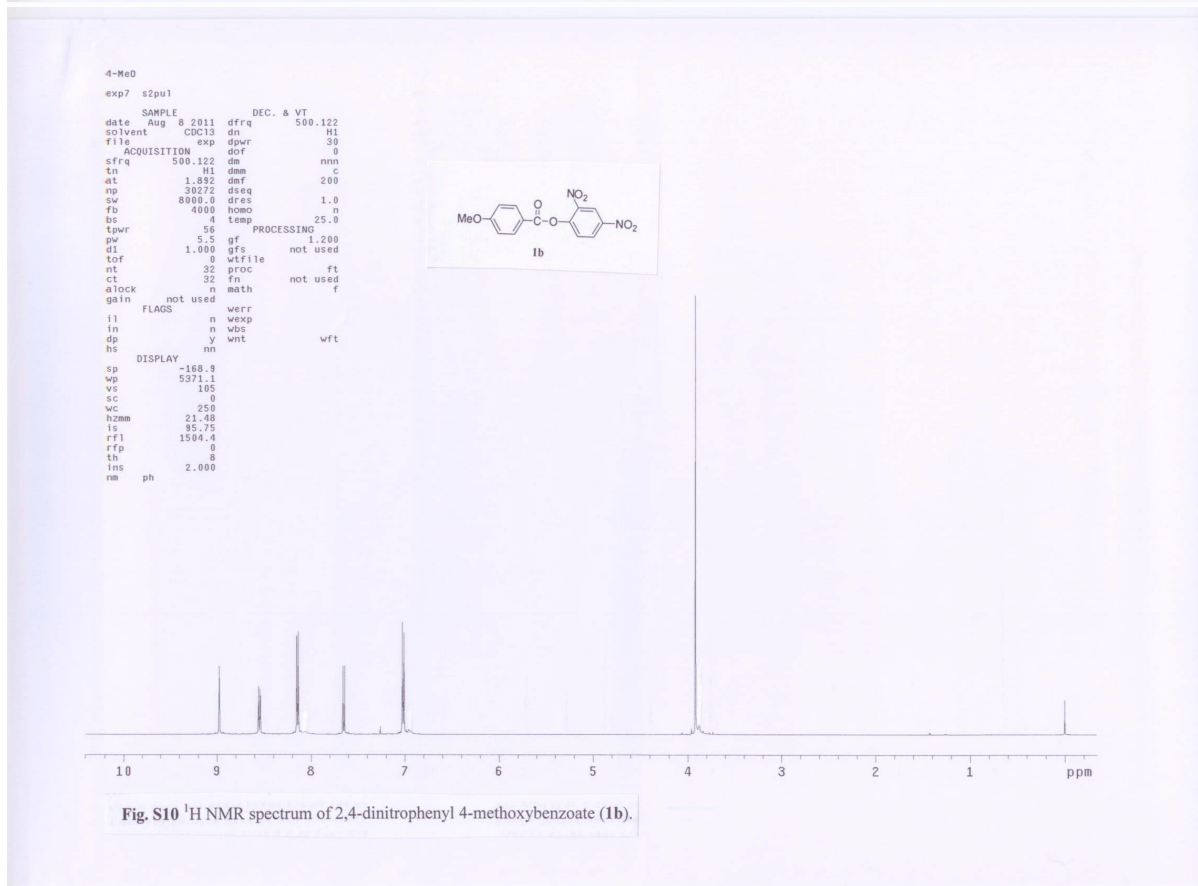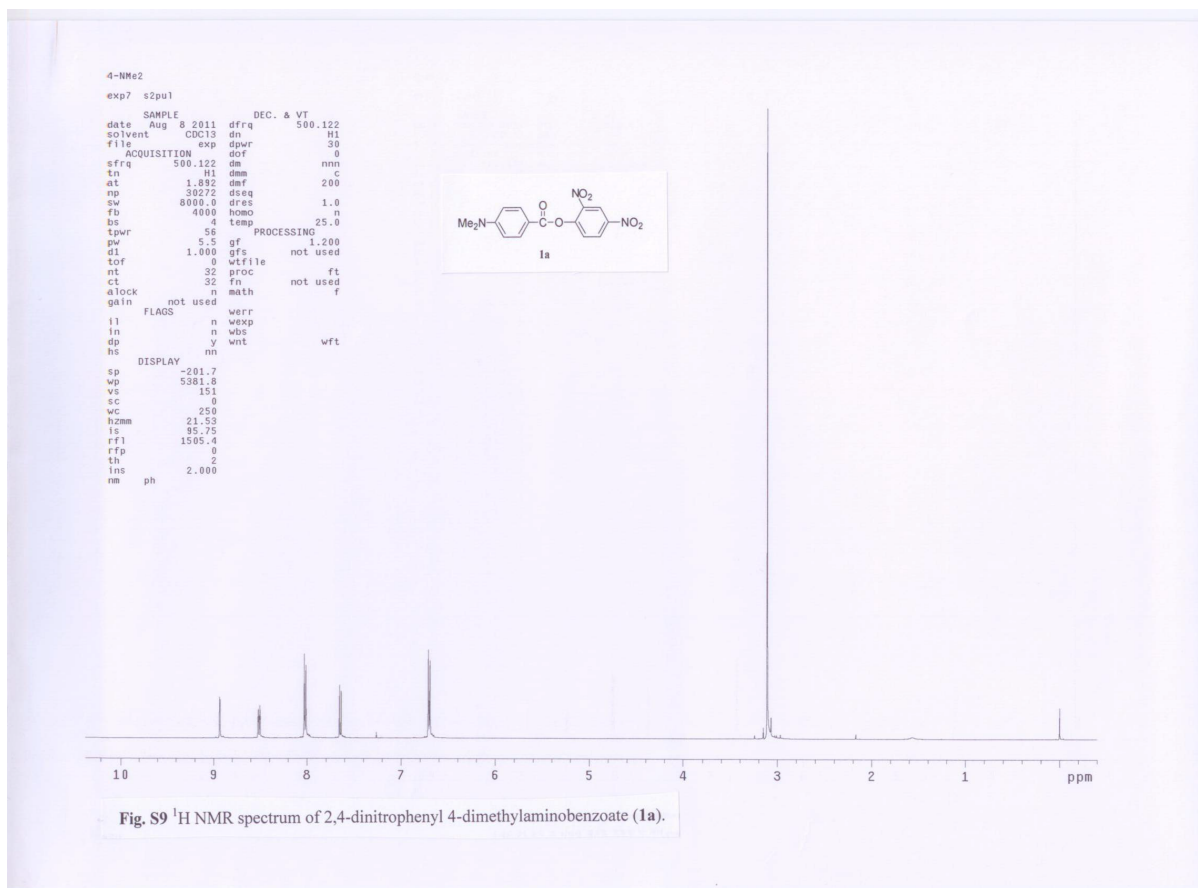
4-NMe2

exp7 s2pul

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tof	0	wtfile	
nt	32	proc	ft
ct	32	fn	not used
alock	n	math	f
gain	not used		
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il	n	wexp	
in	n	wbs	
dp	y	wnt	wft
hs	nn		
DISPLAY			
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rfl	1505.4		
rfp	0		
th	2		
ins	2.000		
nm	ph		

Fig. S9 ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-dimethylaminobenzoate (1a).

4-MeO

exp7 s2pul

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date	Aug 8 2011	dfrq	500.122
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tn	H1	dmm	c
at	1.892	dmf	200
np	30272	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
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d1	1.000	gfs	not used
tof	0	wtfile	
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ct	32	fn	not used
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gain	not used		
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ins	2.000		
nm	ph		

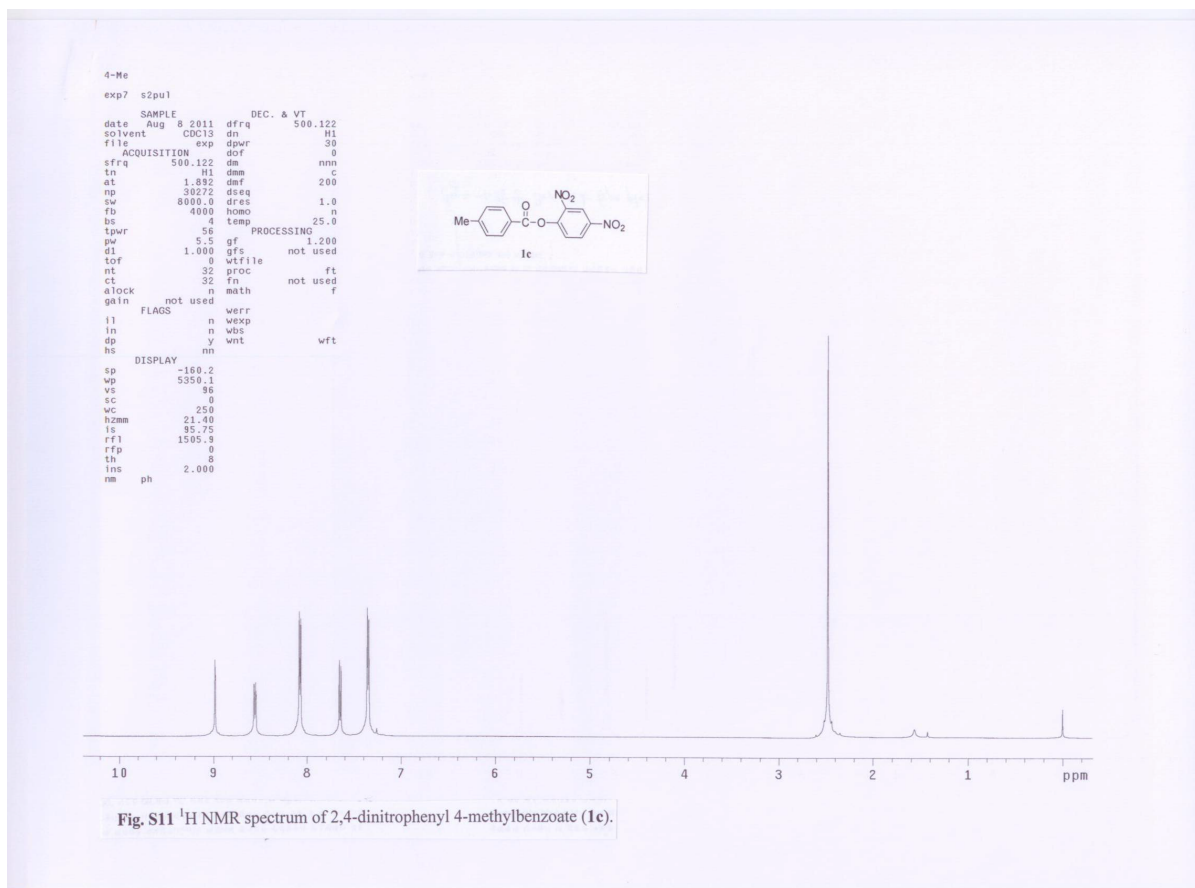Fig. S10 ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-methoxybenzoate (1b).

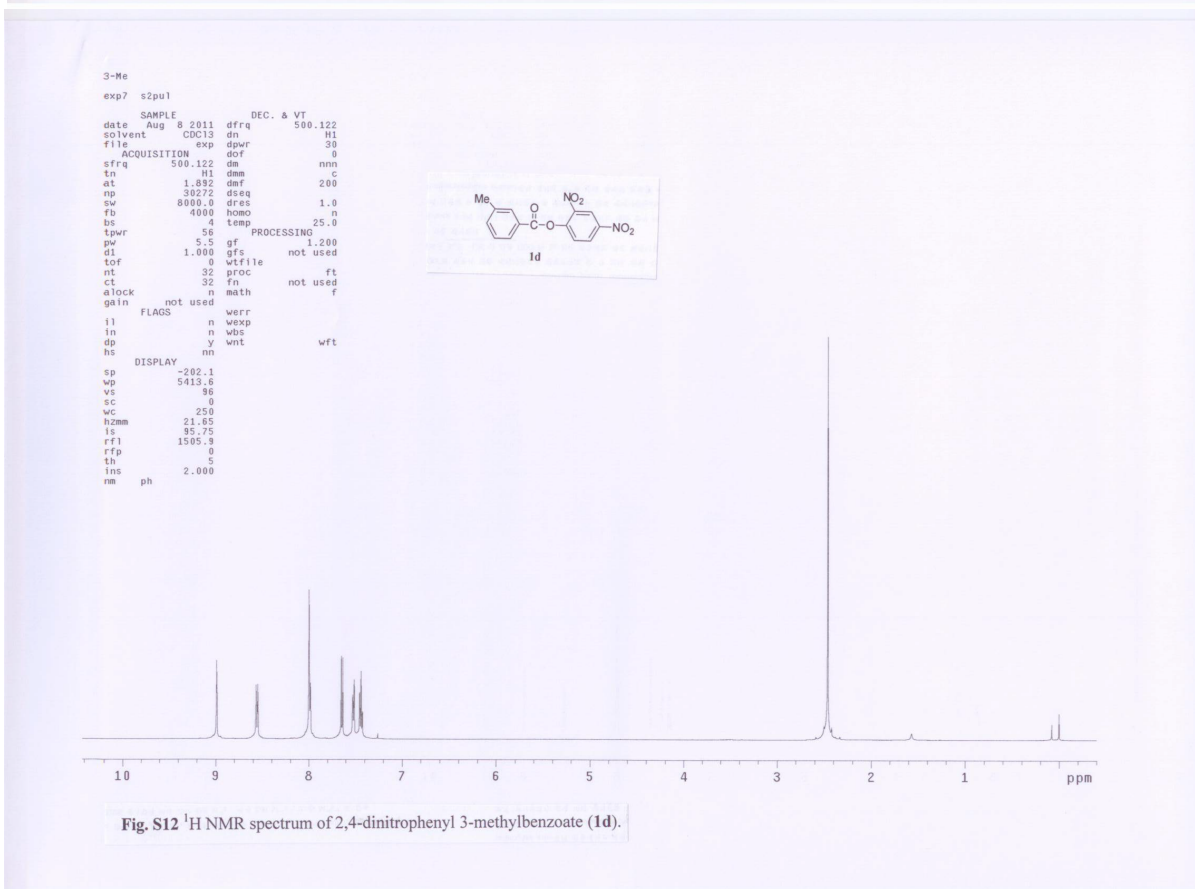**Fig. S11** ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-methylbenzoate (**1c**).

Fig. S12 ^{1}H NMR spectrum of 2,4-dinitrophenyl 3-methylbenzoate (**1d**).

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Fig. S13 ^{1}H NMR spectrum of 2,4-dinitrophenyl benzoate (1e).

Fig. S14 ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-chlorobenzoate (1f).

Fig. S15 ^{1}H NMR spectrum of 2,4-dinitrophenyl 3-chlorobenzoate (**1g**).

Fig. S16 ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-cyanobenzoate (**1h**).

Fig. S17 ^{1}H NMR spectrum of 2,4-dinitrophenyl 4-chloro-3-nitrobenzoate (1i).