

Supporting Information

Eliminations from (*E*)-2,4-Dinitrobenzaldehyde *O*-Aryloximes Promoted by R₃N in MeCN. Effects of β -Aryl Group and Base-Solvent on the Nitrile-Forming Transition-State

Bong Rae Cho, Eun Mi Ryu,[†] and Sang Yong Pyun^{†,*}

Department of Chemistry, Korea University, Seoul 136-713, Korea

[†]Department of Chemistry, Pukyong National University, Pusan 608-737, Korea

**E-mail: syppyun@pknu.ac.kr*

Received May 16, 2012, Accepted June 12, 2012

Table S1. Observed Rate Constants for Eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-2-X-4-NO₂ (**1a-e**) ^aPromoted by Et₃N^b in MeCN at 25.0 °C

Entry	10 ² [buffer], M	10 ² k _{obs} , s ^{-1c,d}				
		1a	1b	1c	1d	1e
1	0.06				0.604	
2	0.08		0.109	0.120		
3	0.1		0.120	0.124	0.960	
4	0.2	0.0355				
5	0.4	0.0340		0.536	0.585	4.70
6	0.6	0.0557	0.0266			
7	0.8	0.0701			9.80	
8	1.0	0.0890				
9	1.2	0.105				
10	1.4	0.123				
11	1.6	0.136	0.0722			
12	1.8	0.153				
13	2.0	0.168		2.87	3.30	
14	3.0	0.214				
15	5.0	0.374				
16	6.0	0.470	0.240			
17	7.0	0.542				
18	8.0	0.619				
19	9.0	0.672				
20	10.0	0.741				
21	18.0		0.647			

^a[Substrate] = 5.0 × 10⁻⁵ M. ^b[R₃N] = 8.0 × 10⁻⁴ – 0.18 M. ^cAverage of three or more rate constants. ^dEstimated uncertainty, ± 3%.

Table S2. Observed Rate Constants for Eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-2-X-4-NO₂ (**1a-e**) ^aPromoted by Et₂N(CH₂CH₂OH) ^bin MeCN at 25.0 °C

Entry	10 ² [buffer], M	10 ² k _{obs} , s ^{-1c,d}				
		1a	1b	1c	1d	1e
1	0.08			0.0177	0.0176	0.101
2	0.6			0.0797	0.0796	0.669
3	0.8			0.102	0.110	1.09
4	1.2			0.155	0.167	1.50
5	1.6	0.0147	0.00981			
6	5.0	0.0395	0.0210			
7	8.0	0.0651	0.0403			
8	10.0	0.0951	0.0501			

^{a-d}See footnotes under Table S1

Table S3. Observed Rate Constants for Eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-2-X-4-NO₂ (**1a-e**) ^aPromoted by EtN(CH₂CH₂OH)₂ ^bin MeCN at 25.0 °C

Entry	10 ² [buffer], M	10 ² k _{obs} , s ^{-1c,d}				
		1a	1b	1c	1d	1e
1	3.0	-	-	0.0229	0.0333	0.257
2	5.0	-	-	0.0698	0.0543	0.517
3	8.0	-	-	0.0826	0.0855	0.838
4	10.0	-	-	0.103	0.109	1.04
5	20.0	0.0174	0.00969			

^{a-d}See footnotes under Table S1

Table S4. Observed Rate Constants for Eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-2-X-4-NO₂ (**1a-e**) ^aPromoted by N(CH₂CH₂OH)₃ ^bin MeCN at 25.0 °C

Entry	10 ² [buffer], M	10 ² k _{obs} , s ^{-1c,d}				
		1a	1b	1c	1d	1e
1	8.0	-	-	0.0185	0.0165	0.108

^{a-d}See footnotes under Table S1

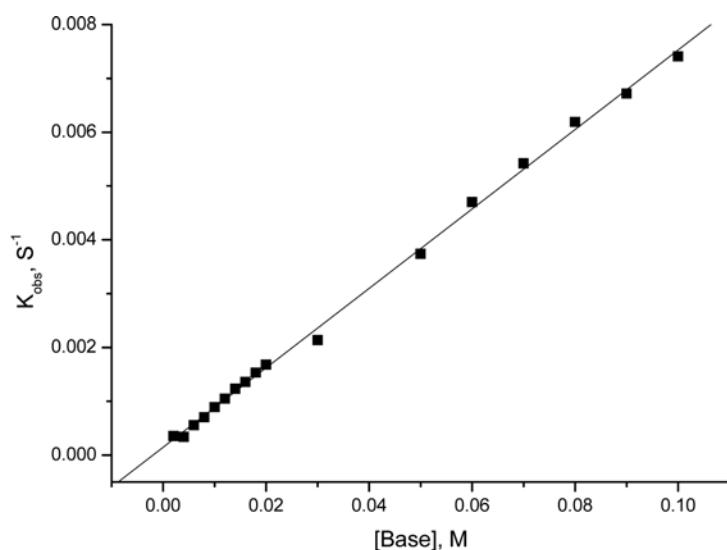


Figure S1. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-
(NO₂)₂C₆H₃CH=NOC₆H₄--4-NO₂ (**1a**) Promoted by Et₃N in MeCN 25 °C.

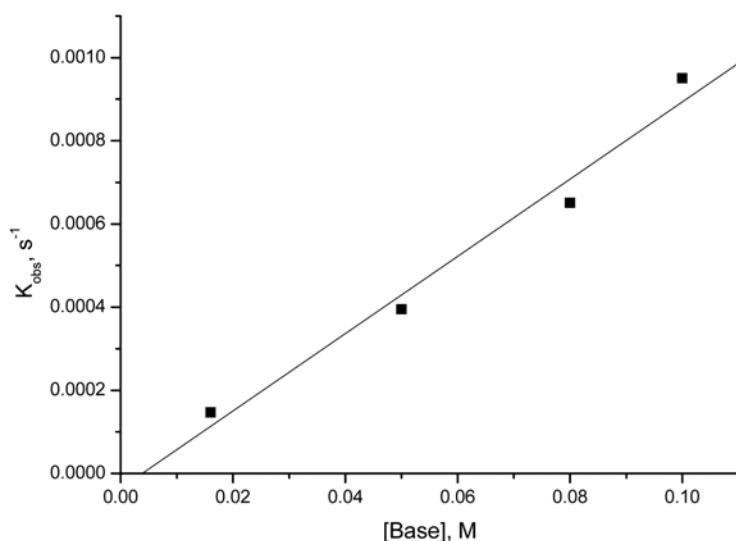


Figure S2. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-
(NO₂)₂C₆H₃CH=NOC₆H₄--4-NO₂ (**1a**) Promoted by Et₂N(CH₂CH₂OH) in MeCN 25 °C.

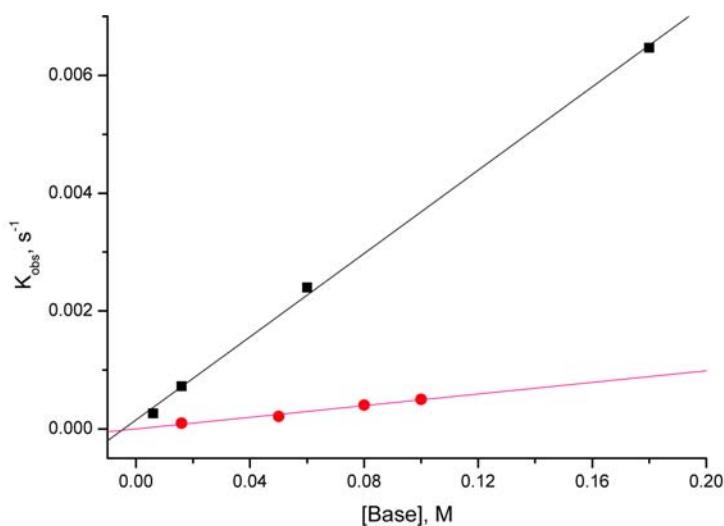


Figure S3. Plots of k_{obs} vs base concentration for eliminations from (E)-2,4- $(NO_2)_2C_6H_3CH=NOC_6H_3-2-CH_3-4-NO_2$ (**1b**) Promoted by R_3N in MeCN 25 °C. [$R_3N = Et_3N$ (■), $Et_2N(CH_2CH_2OH)$ (●)].

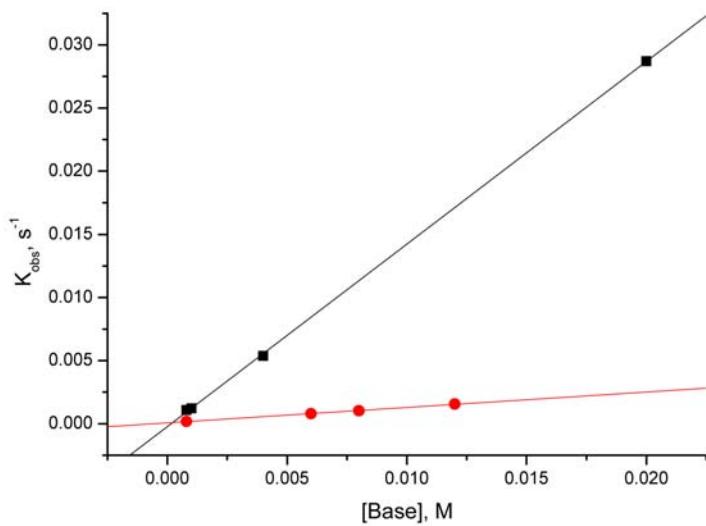


Figure S4. Plots of k_{obs} vs base concentration for eliminations from (E)-2,4- $(NO_2)_2C_6H_3CH=NOC_6H_3-2-Cl-4-NO_2$ (**1c**) Promoted by R_3N in MeCN 25 °C. [$R_3N = Et_3N$ (■), $Et_2N(CH_2CH_2OH)$ (●)].

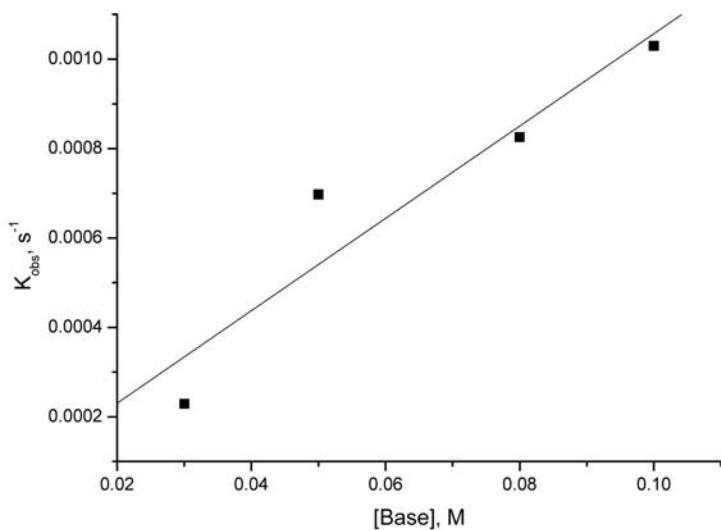


Figure S5. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-2-X-4-NO₂ (**1c**) Promoted by EtN(CH₂CH₂OH)₂ in MeCN 25 °C.

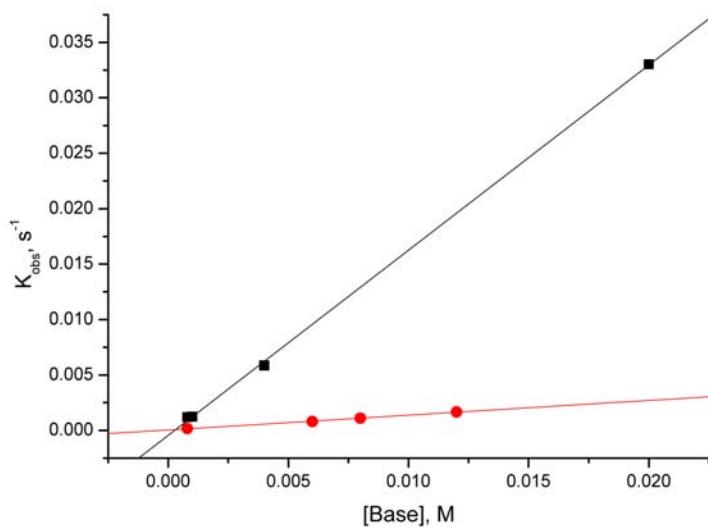


Figure S6. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CF₃-4-NO₂ (**1d**) Promoted by R₃N in MeCN 25 °C. [R₃N = Et₃N (■), Et₂N(CH₂CH₂OH) (●)].

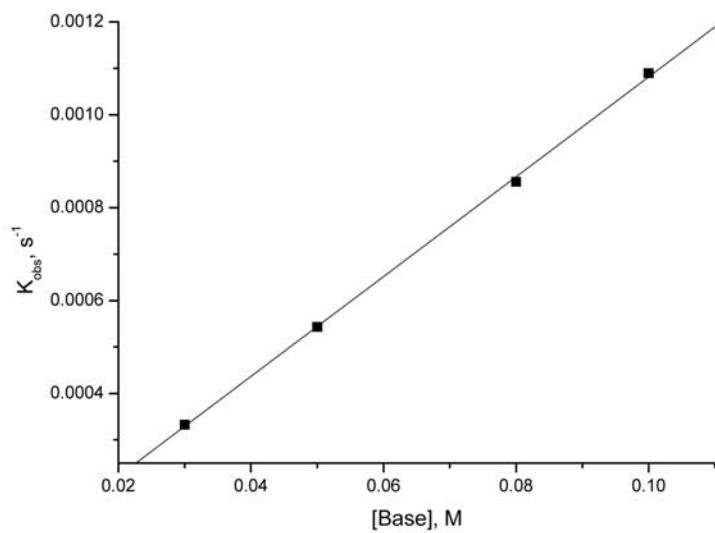


Figure S7. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CF₃-4-NO₂ (**1d**) Promoted by EtN(CH₂CH₂OH)₂ in MeCN 25 °C.

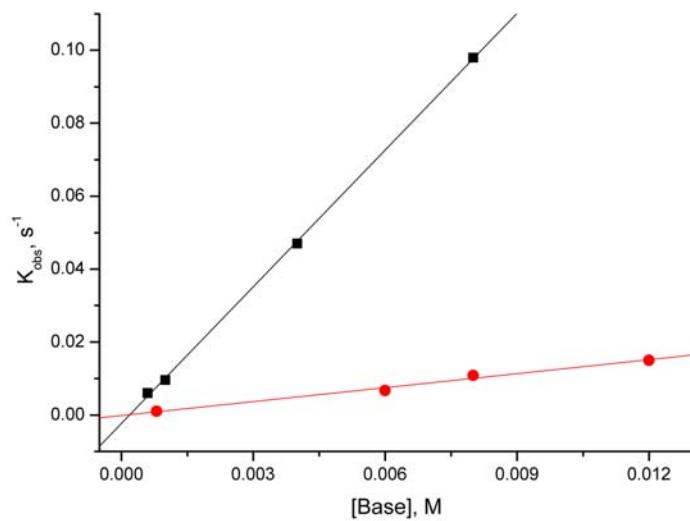


Figure S8. Plots of k_{obs} vs base concentration for eliminations from (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂ (**1e**) Promoted by R₃N in MeCN 25 °C. [R₃N = Et₃N (■), Et₂N(CH₂CH₂OH) (●)].

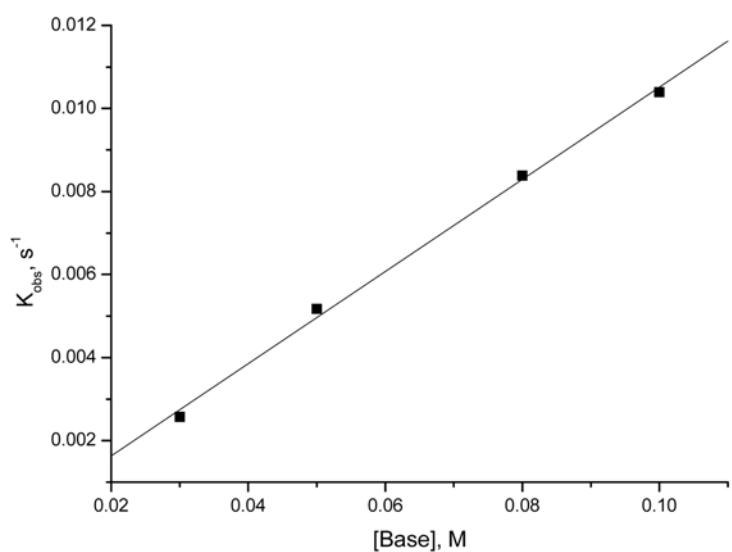


Figure S9. Plots of k_{obs} vs base concentration for eliminations from (E)-2,4-
(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂**(1e)** Promoted by EtN(CH₂CH₂OH)₂ in MeCN 25 °C.

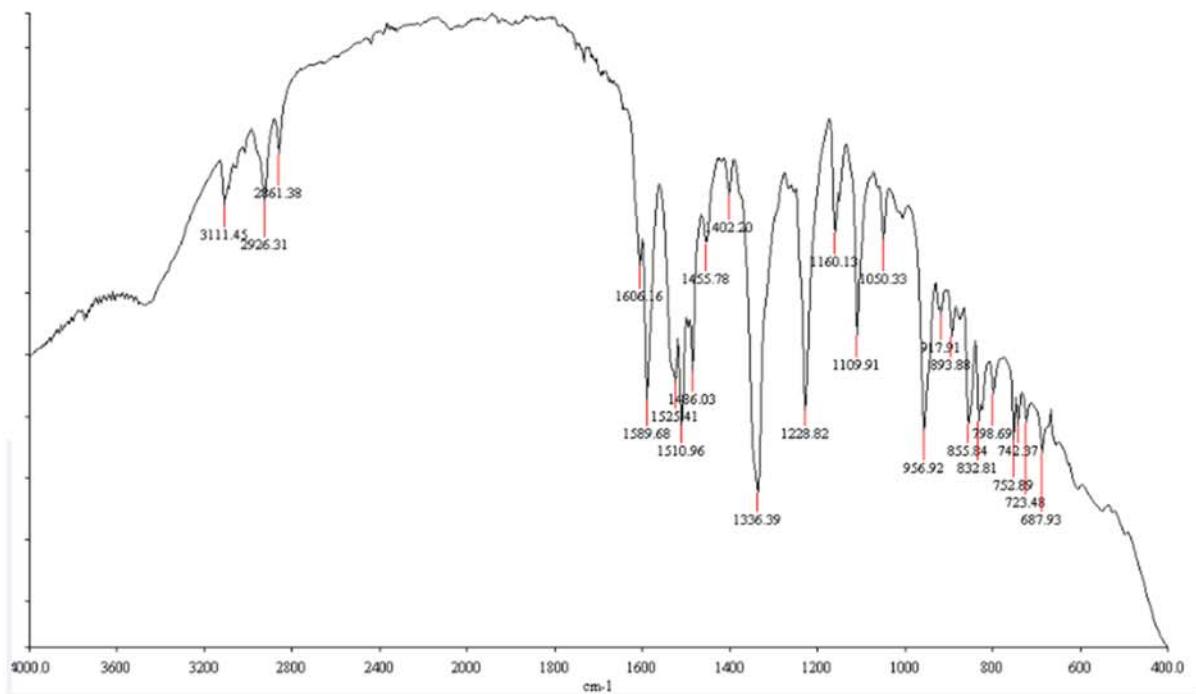


Figure S10. IR spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-4-NO₂ (**1a**).

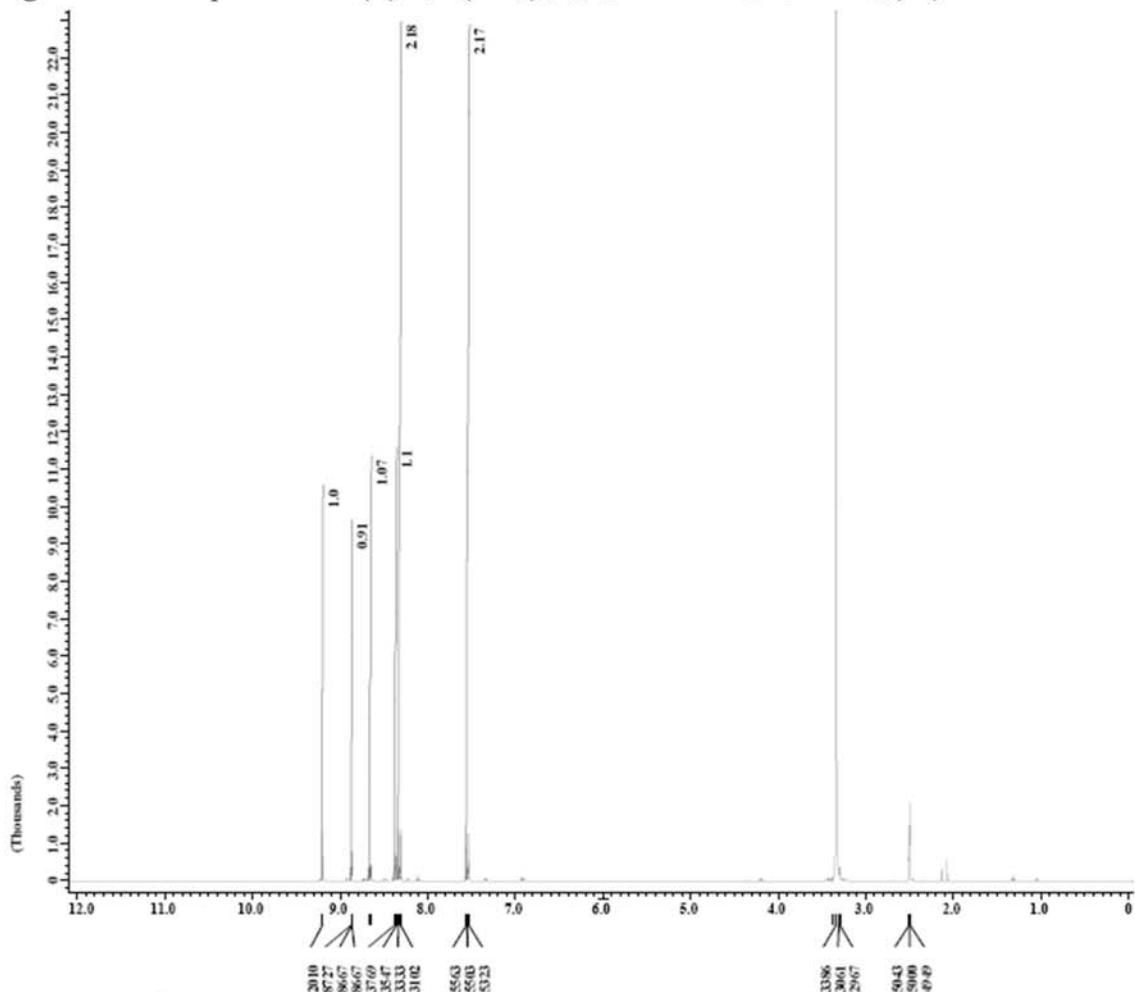
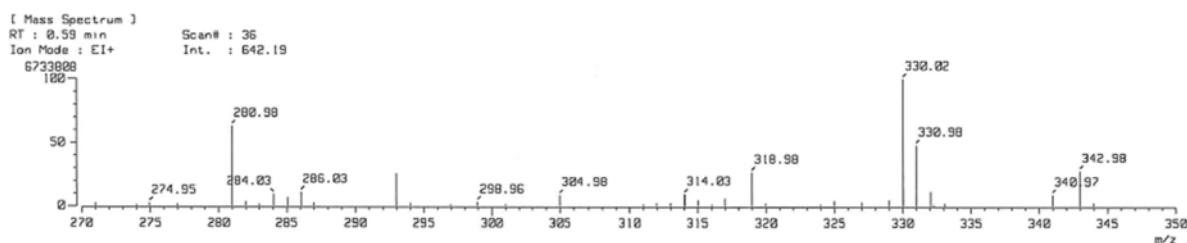


Figure S11. ^1H -NMR spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-4-NO₂ (**1a**).



[Mass Spectrum]
 Data : H-form-002 Date : 30-Jan-2001 20:26
 Sample: -
 Note : -
 Inlet : Direct Ion Mode : EI+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 0.59 min Scan# : 36
 BP : m/z 330.0233 Int. : 642.19
 Output m/z range : 270.0000 to 350.0000 Cut Level : 0.00 %

m/z	Int.	Norm.
271.0015	13.86	2.16
273.9872	6.76	1.05
274.9451	14.42	2.25
276.9416	10.33	1.61
280.9824*	403.71	62.86
281.9830	20.63	3.21
282.9898	8.64	1.35
284.0290	58.57	9.12
285.0328	42.74	6.65
286.0296	69.58	10.83
286.9665	15.34	2.39
292.9824*	164.92	25.68
293.9897	12.41	1.93
296.9661	7.83	1.22
298.9647	19.51	3.04
300.9947	9.08	1.41
304.9824*	54.07	8.42
310.9948	7.69	1.20
311.9736	12.94	2.02
312.9746	12.45	1.94
314.0254	58.73	9.15
315.0342	27.71	4.32
316.0400	6.88	1.07
316.9875	36.95	5.75
318.9792*	169.63	26.41
319.9770	11.94	1.86
323.9624	8.40	1.31
324.9655	24.60	3.83
326.9624	18.09	2.82
328.9748	30.00	4.67
330.0233	642.19	100.00
330.9792*	308.64	48.06
332.0392	74.12	11.54
332.2868	6.66	1.04
333.0348	12.66	1.97
340.9672	57.70	8.98
342.9792*	179.54	27.96
343.9815	15.77	2.46

Figure S12. EIMS spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-4-NO₂ (**1a**).

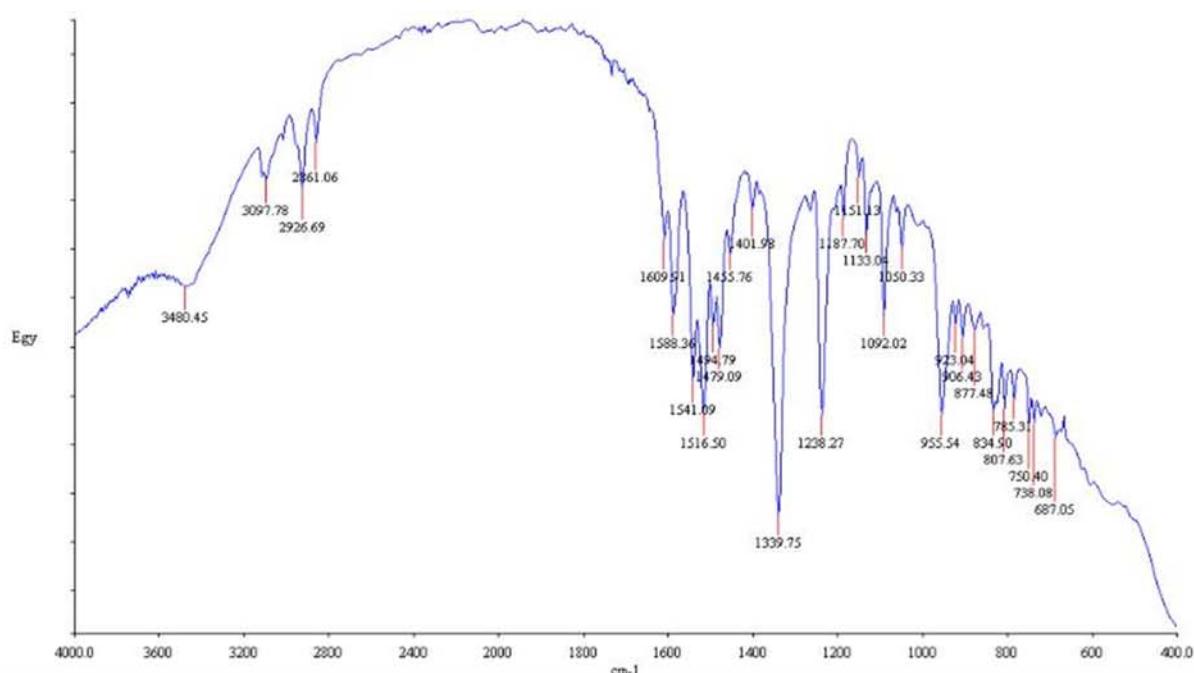


Figure S13. IR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CH₃-4-NO₂ (**1b**).

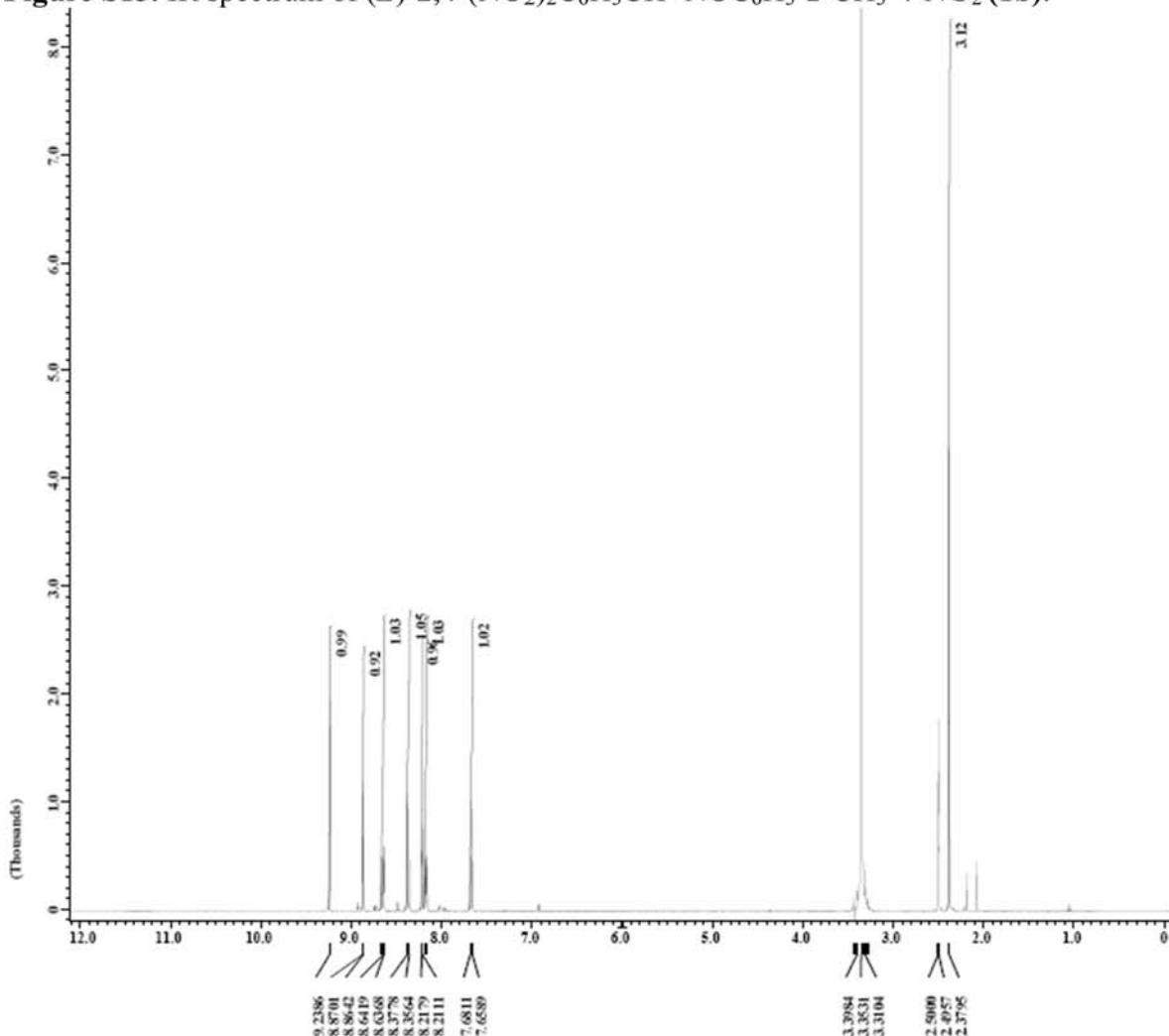
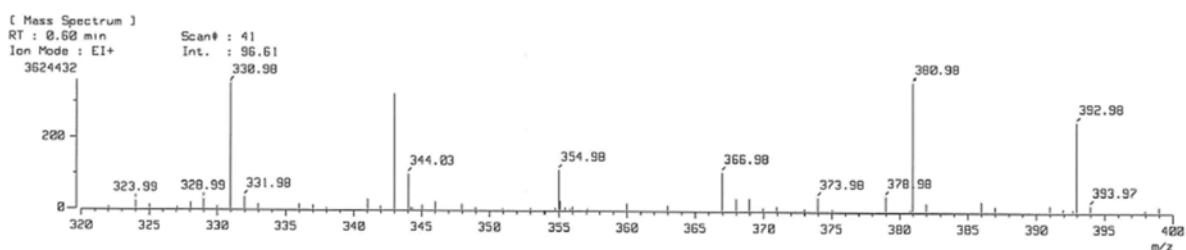


Figure S14. ¹H-NMR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CH₃-4-NO₂ (**1b**).



[Mass Spectrum]
 Data : CH3-form-001 Date : 05-Feb-2001 20:17
 Sample: -
 Note : -

Inlet : Direct Ion Mode : EI+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 0.60 min Scan# : 41
 BP : m/z 344.0333 Int. : 96.61
 Output m/z range : 320.0000 to 400.0000 Cut Level : 0.00 %

m/z	Int.	Norm.	m/z	Int.	Norm.
322.0092	5.41	5.60	392.6923	5.02	5.20
323.9922	21.71	22.47	392.9760*	239.72	248.14
325.0057	11.49	11.89	393.9738	17.16	17.77
327.0435	5.35	5.54	397.9774	5.12	5.30
328.0466	17.34	17.94	398.9866	13.30	13.77
328.9867	26.41	27.34			
330.0081	7.49	7.76			
330.9792*	339.60	351.53			
331.9825	32.88	34.04			
332.9801	13.90	14.39			
335.9726	14.06	14.55			
336.9739	11.40	11.80			
337.9826	4.25	4.40			
341.0178	28.16	29.15			
341.9763	9.61	9.95			
342.9792*	311.50	322.44			
344.0333	96.61	100.00			
344.1963	6.63	6.86			
344.3330	5.39	5.58			
345.0409	12.70	13.14			
346.0549	21.97	22.74			
347.9738	15.82	16.38			
348.9728	6.11	6.32			
350.9676	3.93	4.07			
352.9706	4.00	4.14			
354.7041	5.01	5.18			
354.9792*	107.59	111.37			
355.0717	25.57	26.47			
355.4586	7.18	7.43			
355.7703	3.67	3.80			
355.9822	9.13	9.45			
357.0646	3.70	3.83			
359.9787	18.31	18.95			
362.9858	13.34	13.81			
366.9792*	103.39	107.03			
367.9878	33.10	34.27			
368.9780	33.29	34.46			
369.9669	7.39	7.65			
370.9672	12.39	12.82			
372.9817	5.20	5.38			
373.9810	36.72	38.01			
375.0417	5.31	5.50			
378.9777	39.67	41.06			
380.7974	4.10	4.24			
380.9760*	345.65	357.80			
381.9786	21.60	22.36			
385.9792	26.84	27.78			
386.9731	13.50	13.97			
390.9844	16.17	16.74			
391.9694	7.41	7.67			

Figure S15. EIMS spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CH₃-4-NO₂ (**1b**).

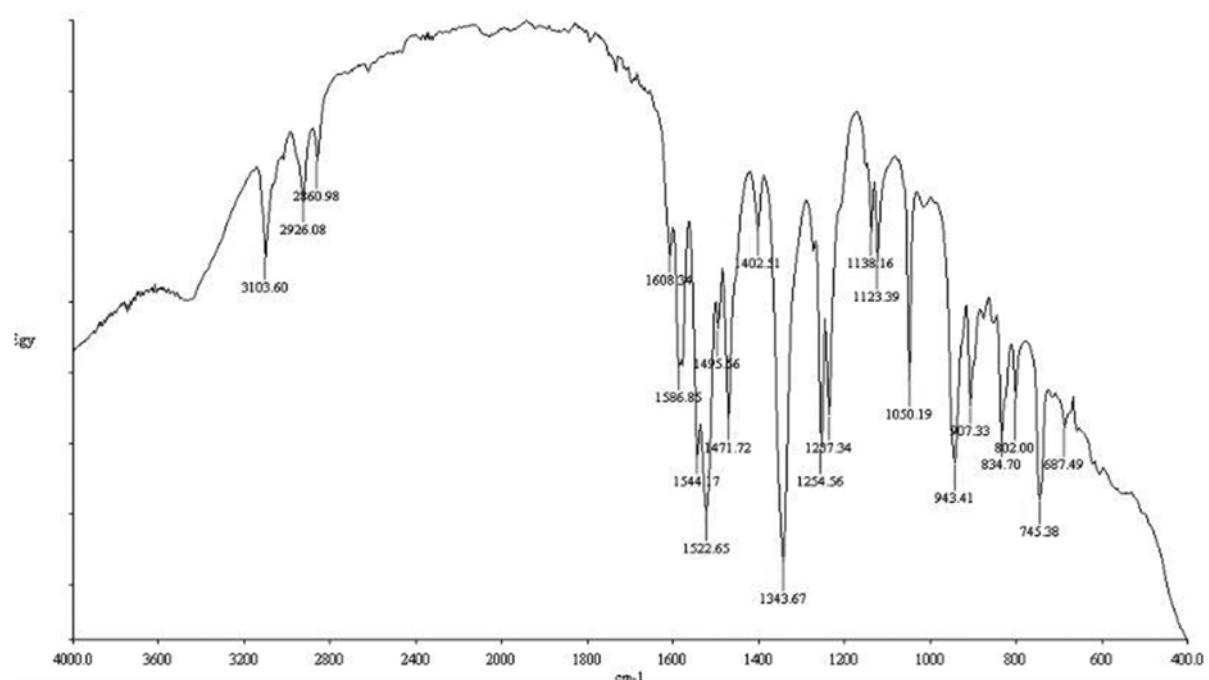


Figure S16. IR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-Cl-4-NO₂ (**1c**).

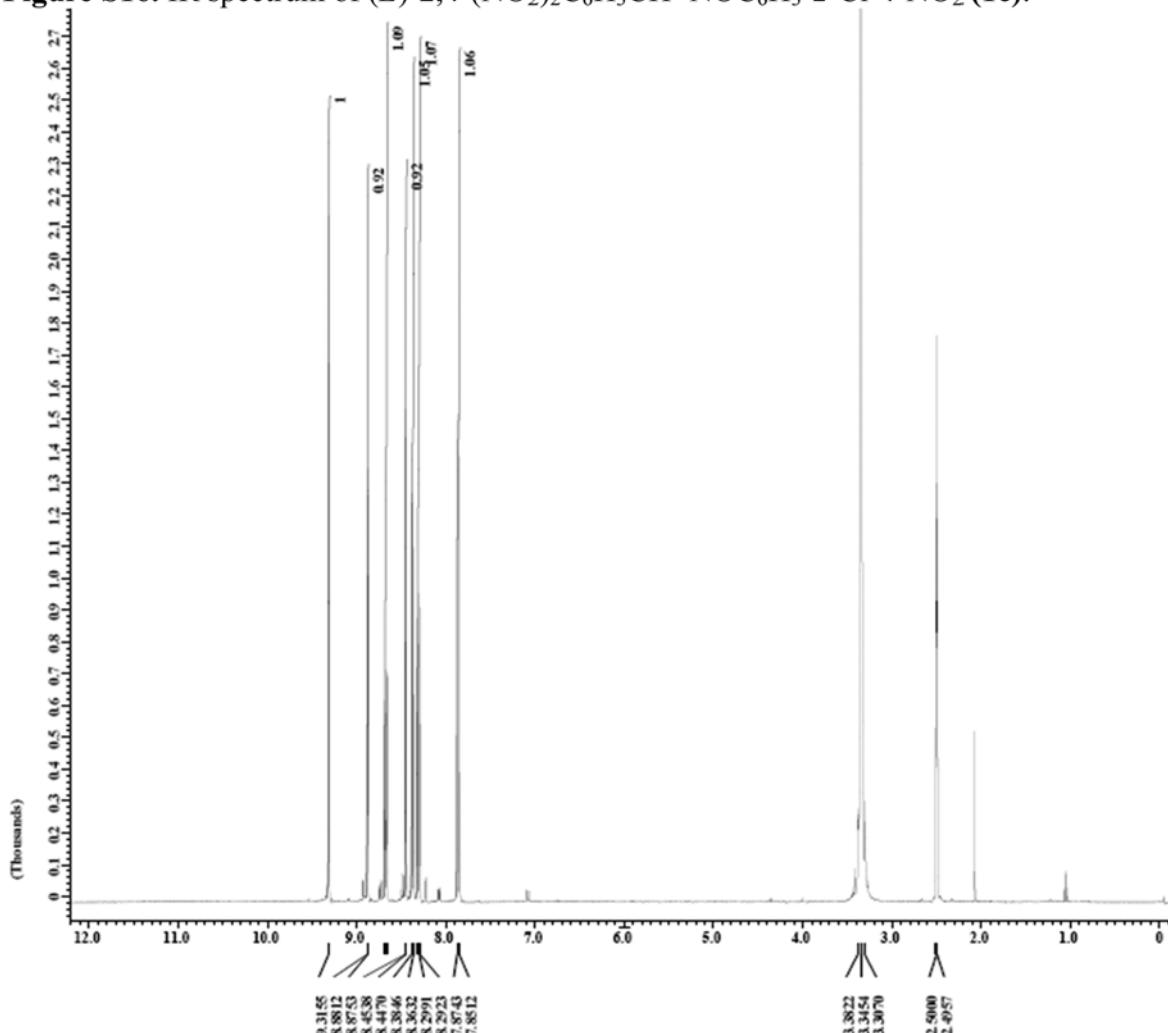
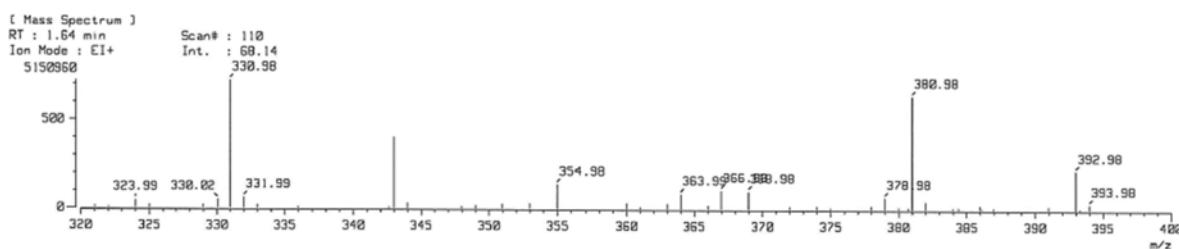


Figure S17. ¹H-NMR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-Cl-4-NO₂ (**1c**).



[Mass Spectrum]
 Data : Cl-form-004 Page: 1
 Sample: - Date : 11-Feb-2001 19:33
 Note : -
 Inlet : Direct Ion Mode : EI+
 Spectrum Type : Normal Ion [MF-Linear]
 RT : 1.64 min Scan# : 110
 BP : m/z 368.9758 Int. : 68.14
 Output m/z range : 320.0000 to 400.0000 Cut Level : 0.00 %

m/z	Int.	Norm.
321.0215	10.24	15.04
322.0028	5.67	8.33
323.9908	31.61	46.39
324.9952	14.02	20.57
328.9863	13.78	20.22
330.0243	34.17	50.15
330.9792*	491.23	720.94
331.9850	42.71	62.68
332.9900	13.67	20.06
335.9807	6.03	8.84
342.6128	5.27	7.73
342.9792*	273.66	401.62
343.9784	21.30	31.26
347.9700	7.88	11.56
348.9885	11.72	17.21
350.9886	18.36	26.95
352.9702	20.32	29.82
354.9792*	94.29	138.37
359.9787	22.64	33.22
360.9789	7.08	10.40
362.9907	19.82	29.08
363.9876	58.16	85.35
366.0004	13.98	20.51
366.9792*	71.80	105.37
368.9758	68.14	100.00
371.9921	9.70	14.24
373.9798	11.49	16.86
374.9857	6.48	9.51
377.9712	12.92	18.96
378.9798	45.62	66.95
379.9848	7.74	11.36
380.7093	7.45	10.94
380.9760*	434.76	638.06
381.9809	29.87	43.83
383.9845	6.92	10.15
384.3813	7.38	10.83
385.9781	14.78	21.70
386.1149	5.51	8.09
386.9794	7.02	10.30
390.9822	13.64	20.02
392.9760*	150.46	220.82
393.2650	5.31	7.79
393.9838	21.04	30.88

Figure S18. EIMS spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-Cl-4-NO₂ (**1c**).

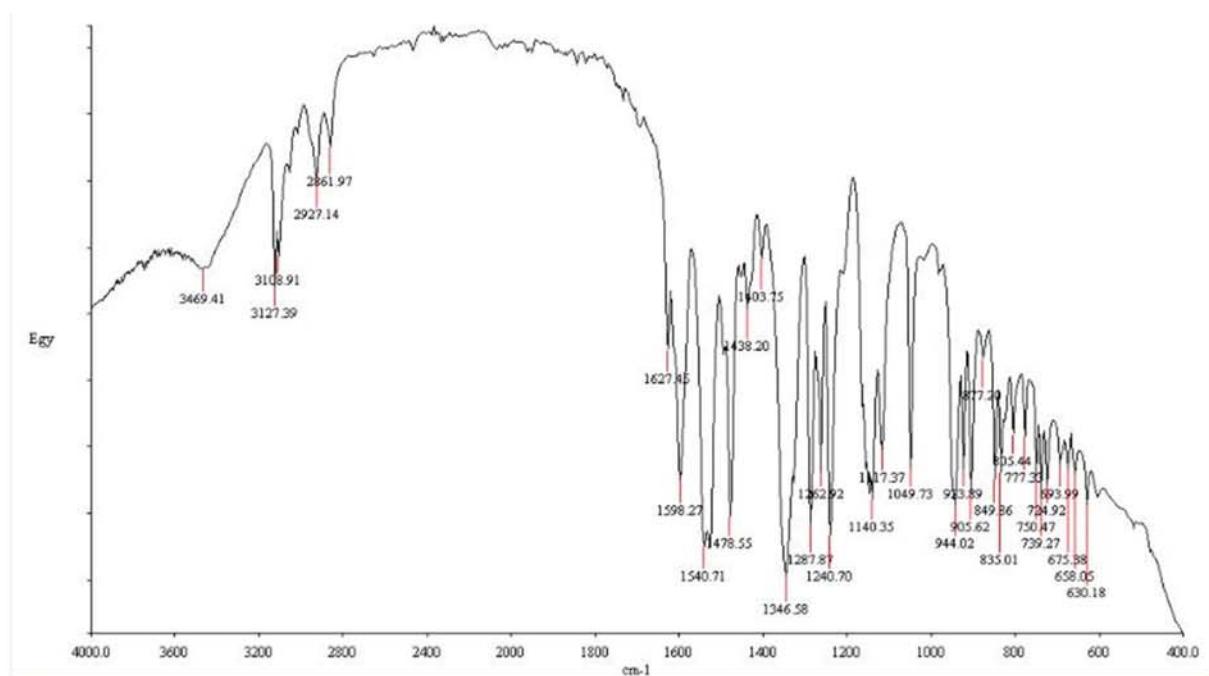


Figure S19. IR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CF₃-4-NO₂ (**1d**).

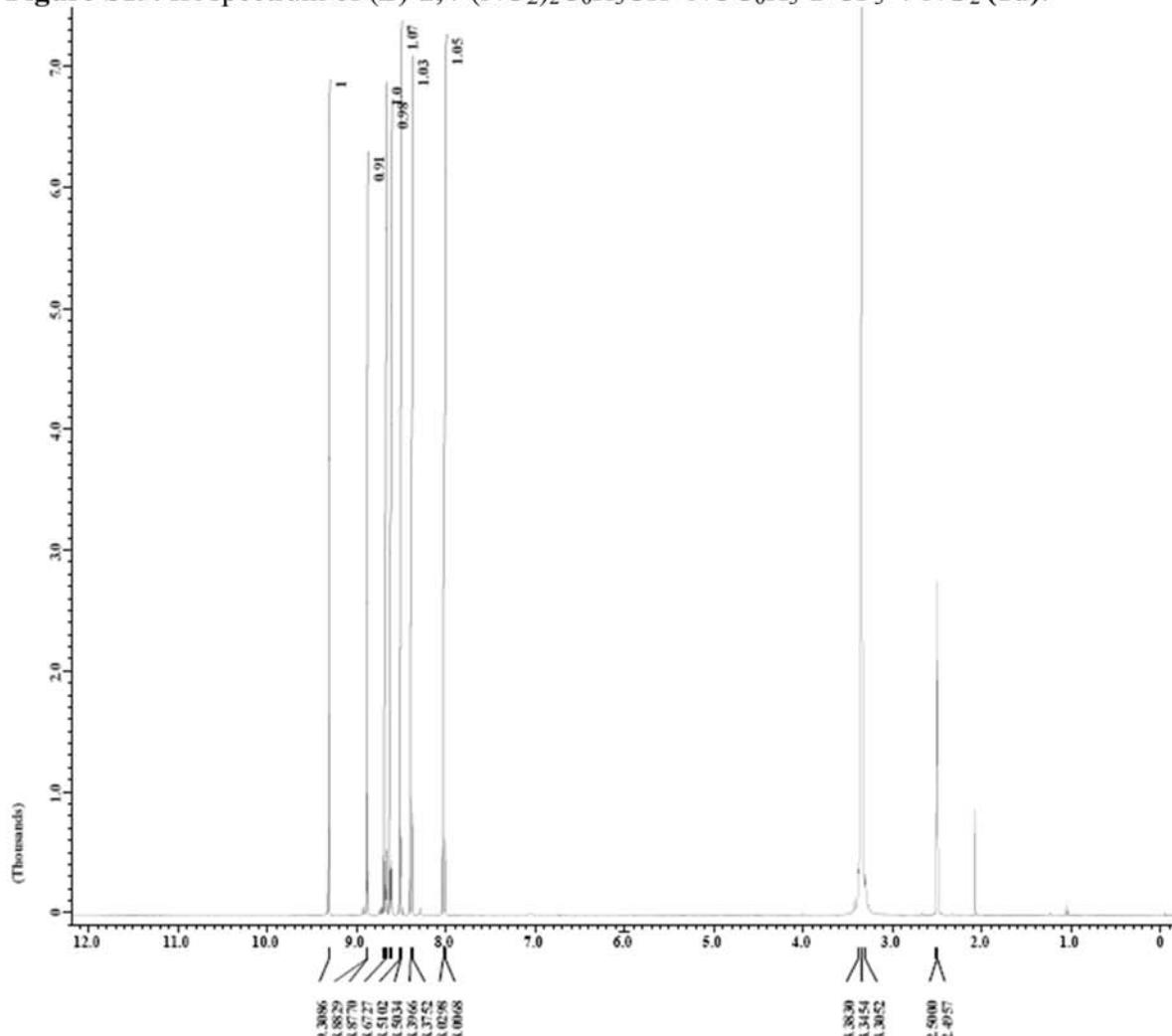
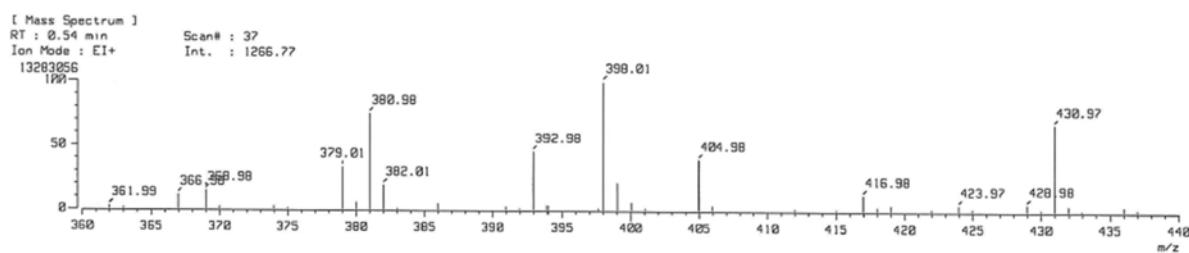


Figure S20. ¹H-NMR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CF₃-4-NO₂ (**1d**).



[Mass Spectrum]
 Data : CF3-form-001 Date : 09-Feb-2001 20:08
 Sample : -
 Note : -
 Inlet : Direct Ion Mode : EI+
 Spectrum Type : Normal Icn [MF-Linear]
 RT : 0.54 min Scan# : 37
 BP : m/z 398.0123 Int. : 1266.77
 Output m/z range : 360.0000 to 440.0000 Cut Level : 0.00 %

m/z	Int.	Norm.
361.9879	33.19	2.62
363.0051	18.26	1.44
366.9792*	144.19	11.38
368.9771	185.18	14.62
369.9827	28.79	2.27
373.9762	33.50	2.64
374.9873	16.44	1.30
379.0112	419.73	33.13
380.0157	74.22	5.86
380.9760*	947.24	74.78
382.0131	244.75	19.32
383.0136	13.79	1.09
385.9767	64.92	5.12
390.9773	33.34	2.63
391.9633	15.15	1.20
392.9760*	578.10	45.64
393.9803	47.41	3.74
397.6295	17.80	1.41
398.0123	1266.77	100.00
399.0150	270.97	21.39
400.0267	78.37	6.19
401.0240	19.89	1.57
404.9760*	500.90	39.54
405.9787	50.10	3.95
411.9854	23.12	1.82
414.9877	13.58	1.07
416.9760*	157.08	12.40
417.9825	39.25	3.10
418.9692	58.12	4.59
421.9735	22.83	1.80
423.9659	61.67	4.87
424.9785	24.75	1.95
428.9758	69.46	5.48
429.9817	19.81	1.56
430.9729*	855.27	67.52
431.9752	54.44	4.30
432.9358	12.90	1.02
435.9692	49.91	3.94
436.9800	20.79	1.64

Figure S21. EIMS spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-CF₃-4-NO₂ (**1d**).

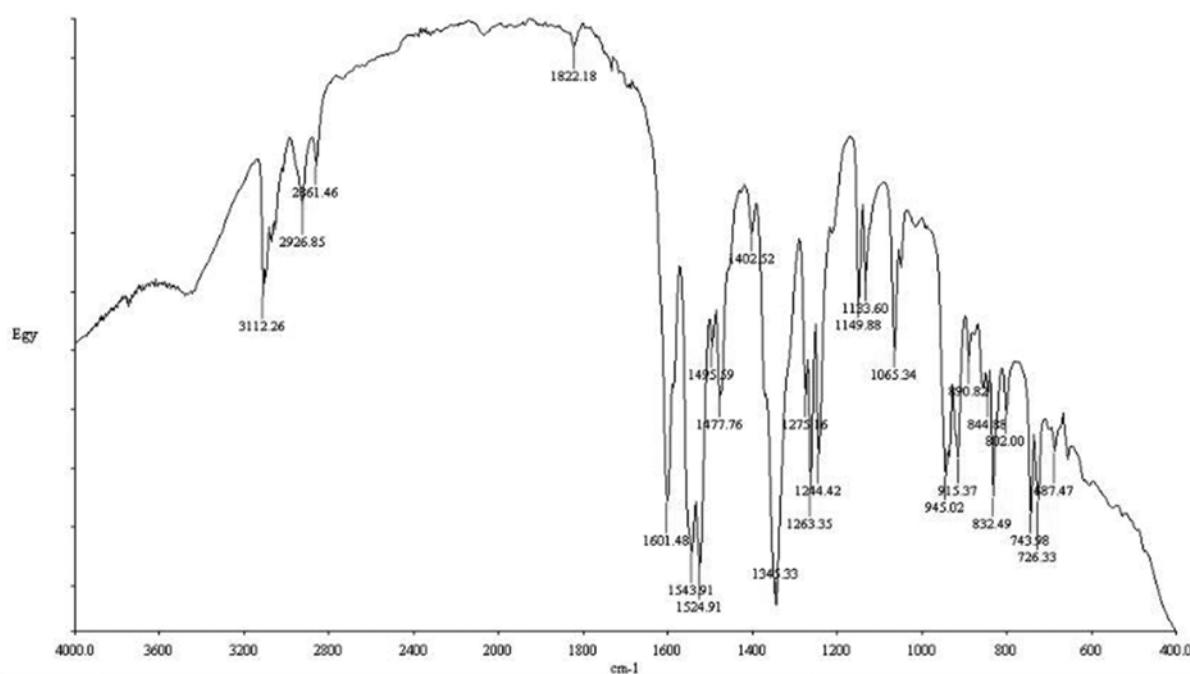


Figure S22. IR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂(1e).

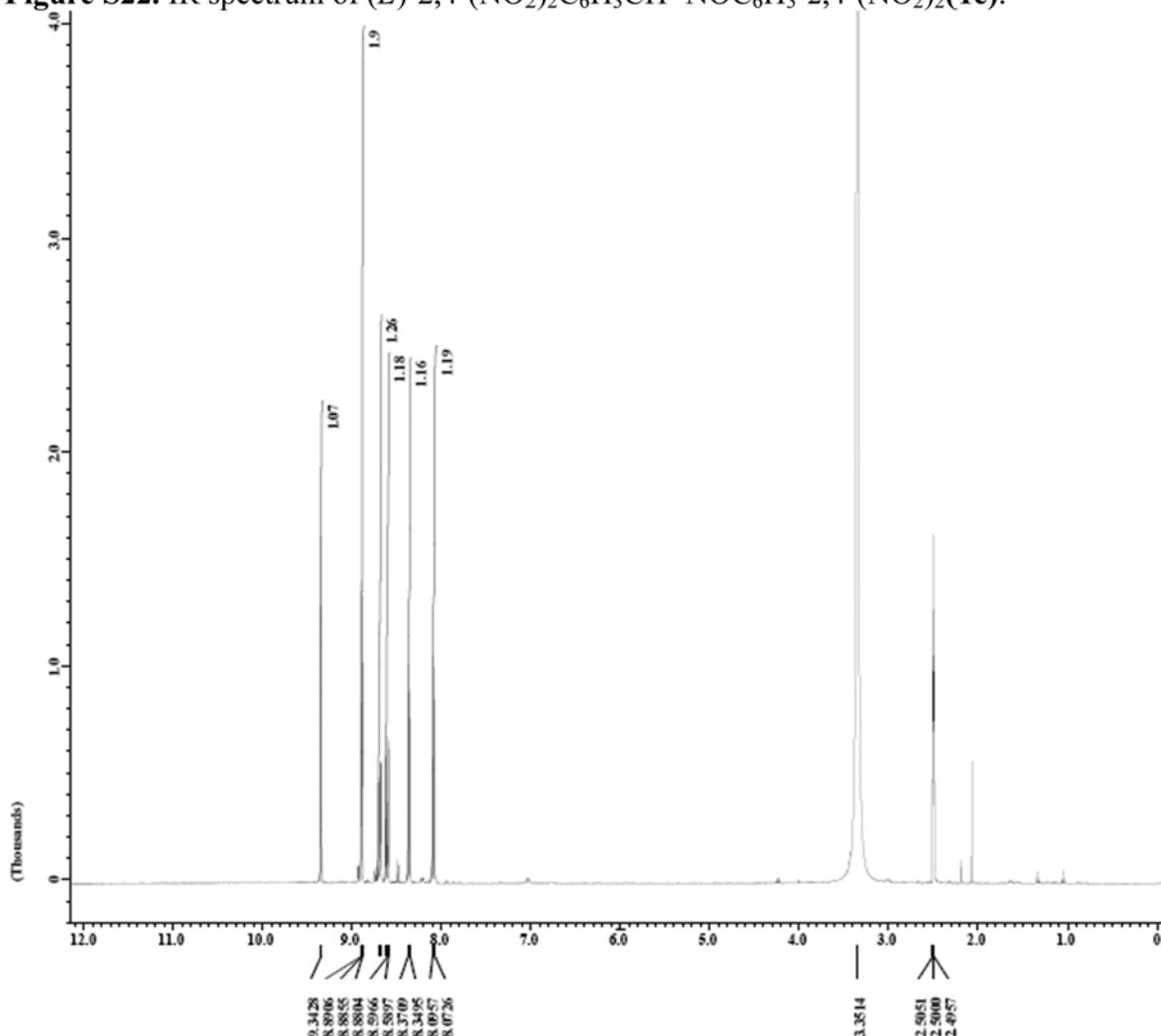
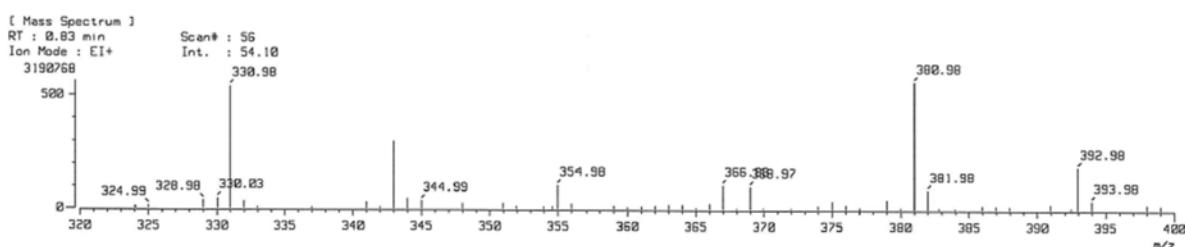


Figure S23. ¹H-NMR spectrum of (E)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂(1e).



[Mass Spectrum]

Data : NO₂-form-001 Date : 12-Feb-2001 16:18 Page: 1
Sample: -
Note: -
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.83 min Scan# : 56
BP : m/z 368.9716 Int. : 54.10
Output m/z range : 320.0000 to 400.0000 Cut Level : 0.00 %

m/z	Int.	Norm.	m/z	Int.	Norm.
324.0010	6.06	11.20	393.9761	20.90	38.63
324.0942	5.40	9.97	397.9737	11.99	22.17
324.9917	8.18	15.13	398.9801	9.76	18.04
328.9836	20.94	38.71			
330.0265	25.87	47.82			
330.9792*	292.38	540.49			
331.9833	18.32	33.86			
332.9817	4.41	8.16			
336.9789	3.48	6.43			
340.9820	16.42	30.36			
341.9763	4.10	7.58			
342.9792*	161.74	298.99			
343.9811	24.89	46.02			
344.9940	19.60	36.23			
347.9830	12.84	23.73			
350.9864	13.41	24.80			
351.9529	6.00	11.10			
353.9870	5.43	10.03			
354.6094	6.31	11.67			
354.9792*	57.21	105.76			
355.9920	12.84	23.74			
359.0017	7.81	14.44			
359.9732	4.49	8.30			
361.0024	5.90	10.91			
362.0059	7.80	14.42			
362.9862	10.60	19.60			
363.9825	10.31	19.07			
364.9752	3.65	6.75			
366.0086	13.42	24.81			
366.9792*	58.04	107.29			
367.9736	3.30	6.10			
368.9716	54.10	100.00			
369.9785	3.74	6.92			
371.9813	3.32	6.14			
373.9744	8.08	14.93			
375.0079	19.42	35.89			
376.0052	10.28	19.01			
377.0239	4.31	7.97			
378.9774	23.12	42.74			
379.9924	4.57	8.44			
380.9760*	304.30	562.52			
381.9786	46.78	86.48			
382.7881	4.79	8.86			
383.9698	3.14	5.81			
385.9685	9.45	17.46			
386.9749	9.10	16.83			
387.9673	7.84	14.50			
390.9749	12.40	22.92			
392.4651	5.44	10.05			
392.9760*	102.02	188.60			

Figure S24. EIMS spectrum of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂(1e).