Supporting Information for

Synthesis of 4-Substituted 3,5-Dinitro-1,4-dihydropyridines by the Self-condensation of β-Formyl-β-nitroenamine

Yumi Nakaike,[†] *Nagatoshi Nishiwaki,*[‡,*] *Masahiro Ariga*[§] *and Yoshito Tobe*[†,*]

[†] Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan.

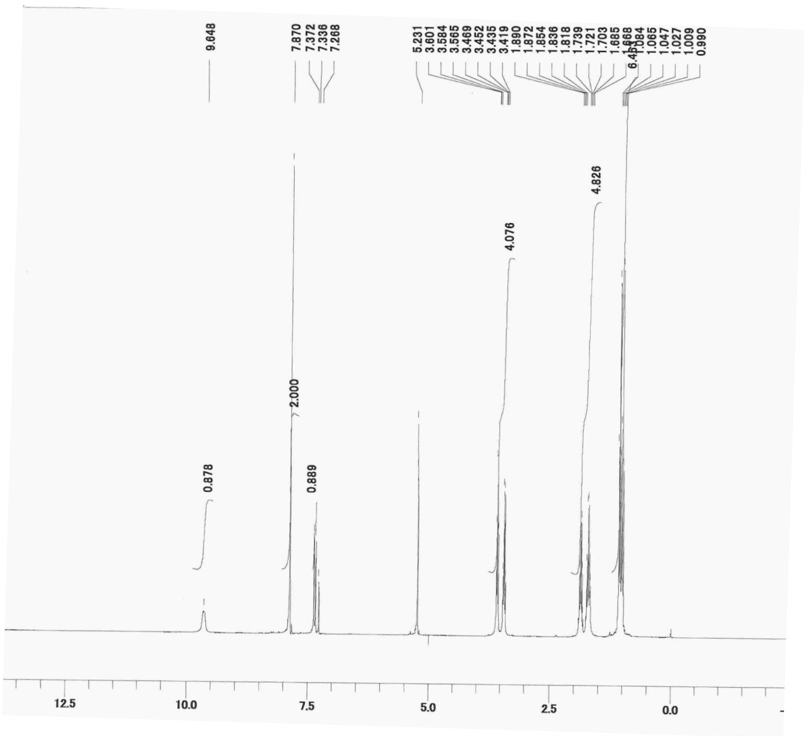
[‡] School of Environmental Science and Engineering, Kochi University of Technology, Tosayamada, Kami, Kochi 782-8502, Japan.

[§] Department of Chemistry, Osaka Kyoiku University, 4-698-1 Asahigaoka, Kashiwara, Osaka, 582-8582, Japan.

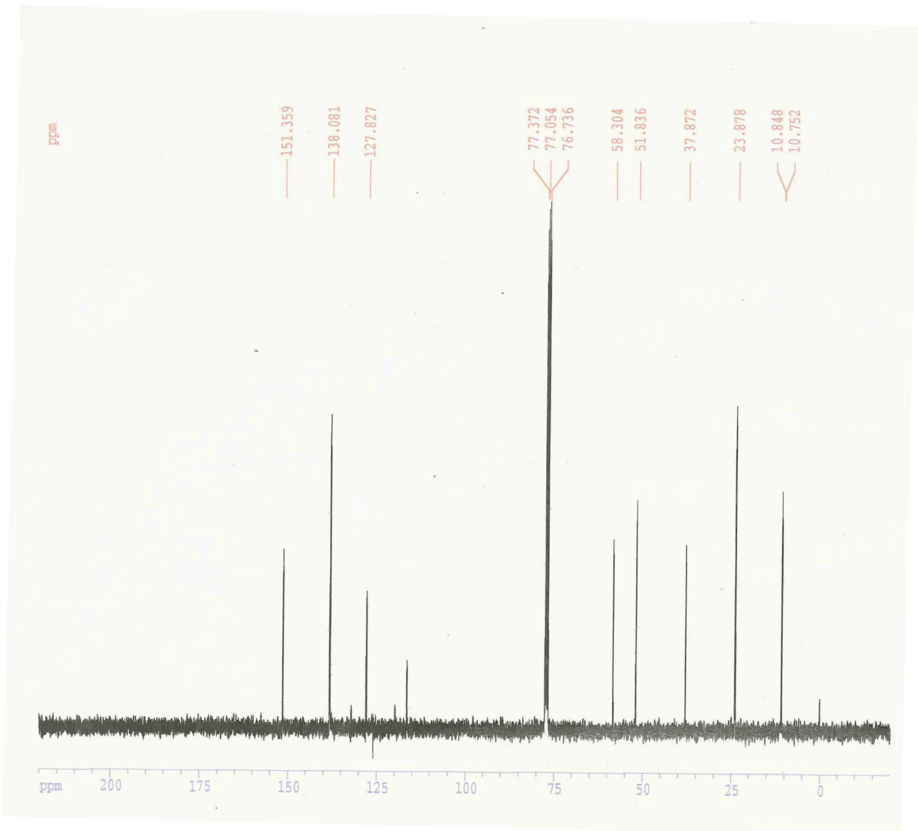
nishiwaki.nagatoshi@kochi-tech.ac.jp, tobe@chem.es.osaka-u.ac.jp

Contents

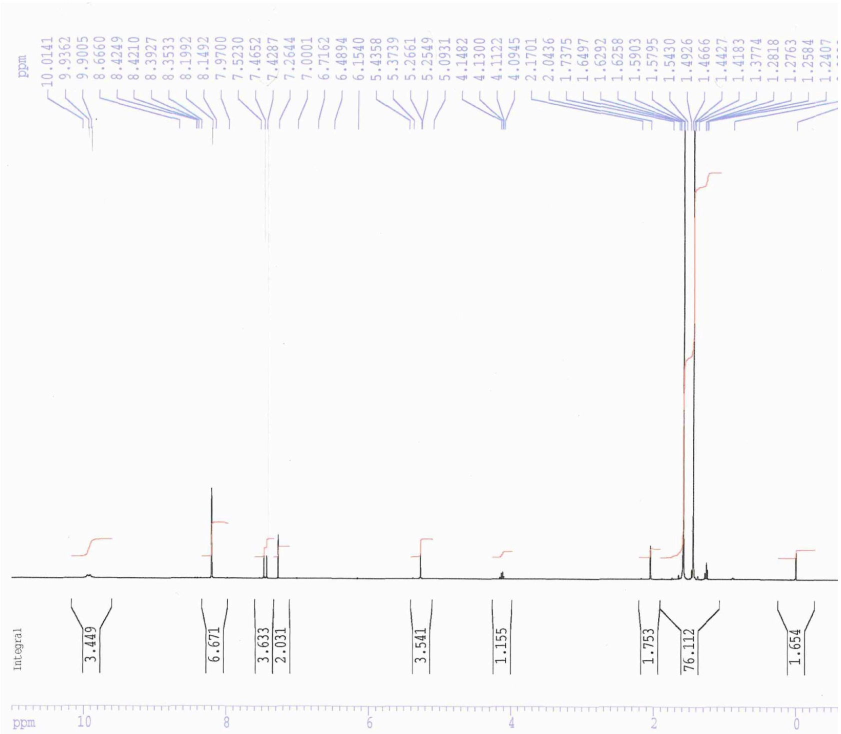
^{1}H NMR Spectrum of **2a** (400 MHz, $CDCl_3$) δ (ppm)



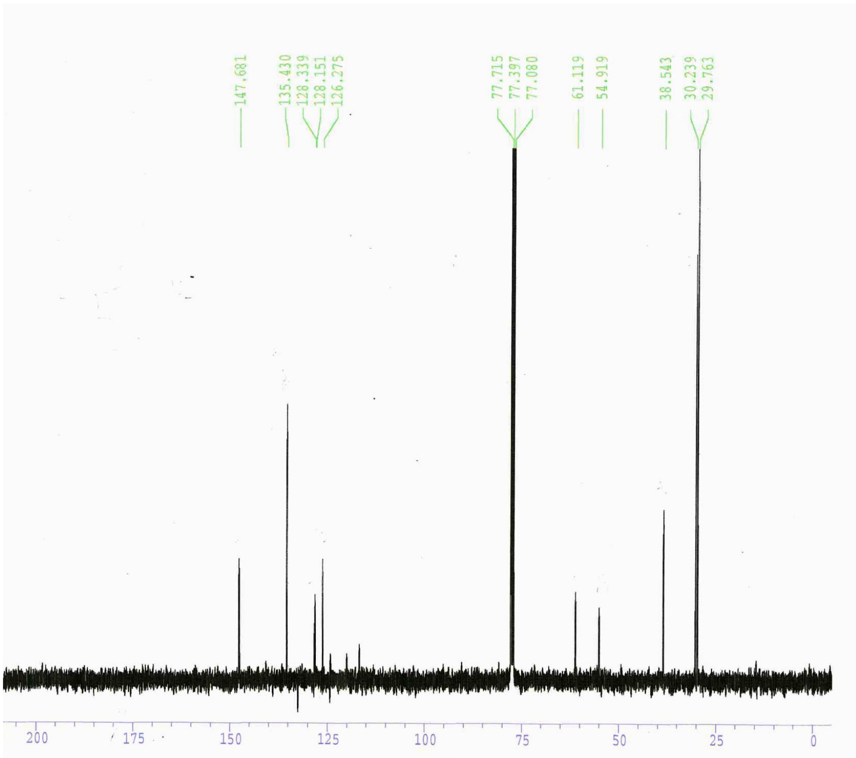
^{13}C NMR Spectrum of **2a** (100 MHz, $CDCl_3$) δ (ppm)



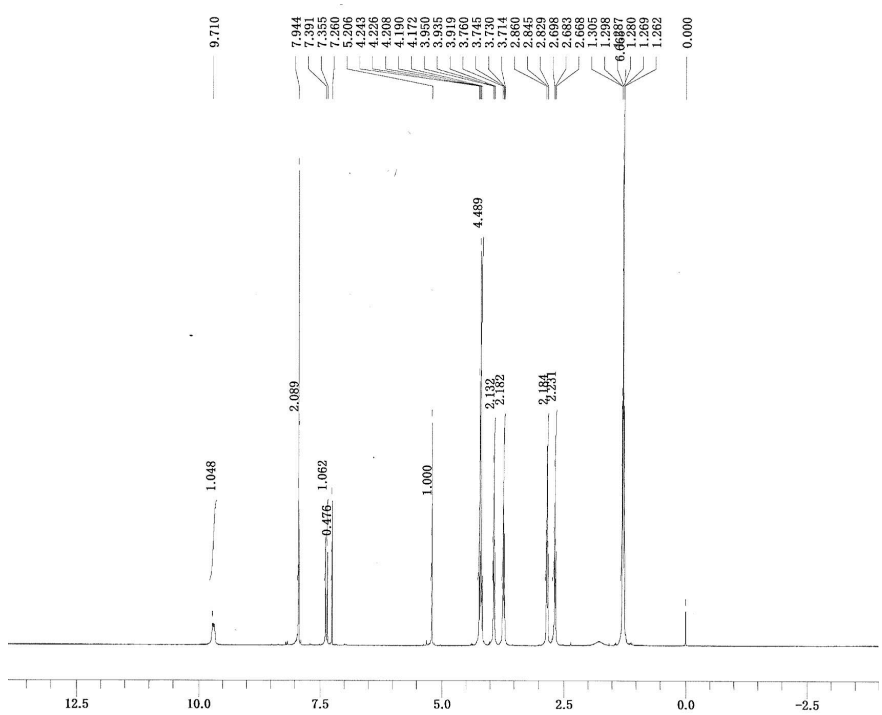
[1]H NMR Spectrum of **2b** (400 MHz, $CDCl_3$) δ (ppm)



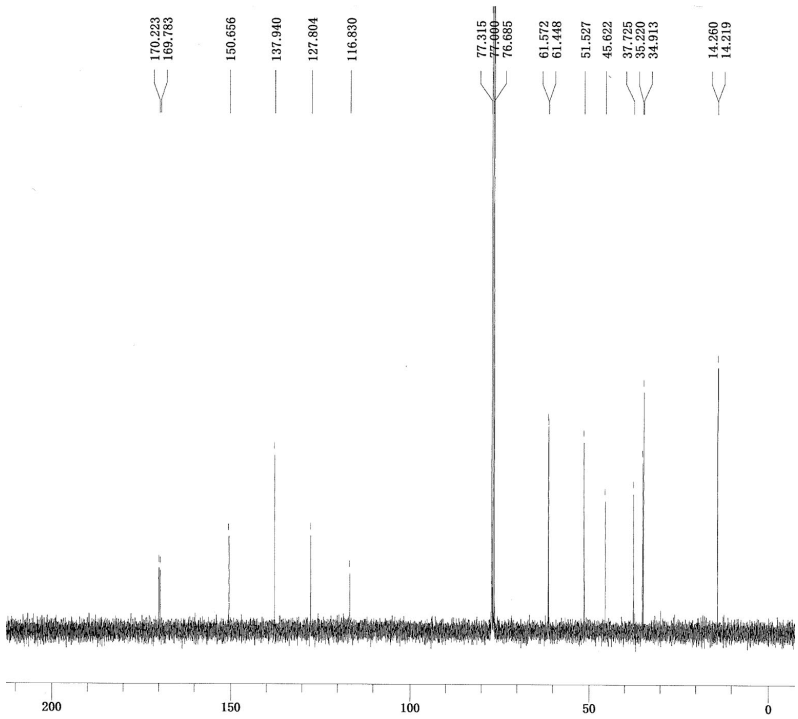
[13]C NMR Spectrum of **2b** (100 MHz, $CDCl_3$) δ (ppm)



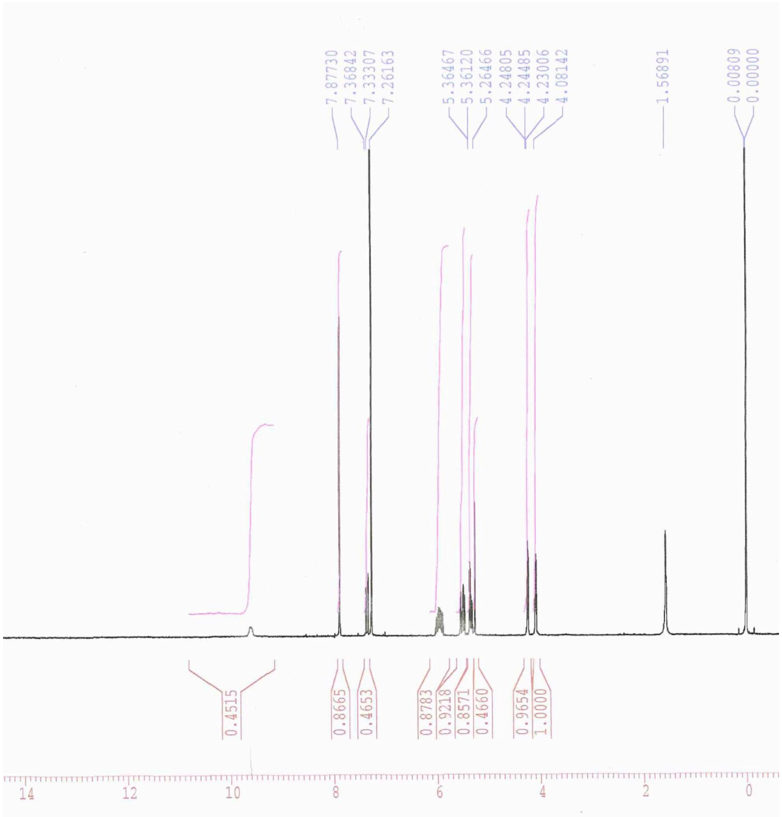
^{1}H NMR Spectrum of **2c** (400 MHz, $CDCl_3$) δ (ppm)



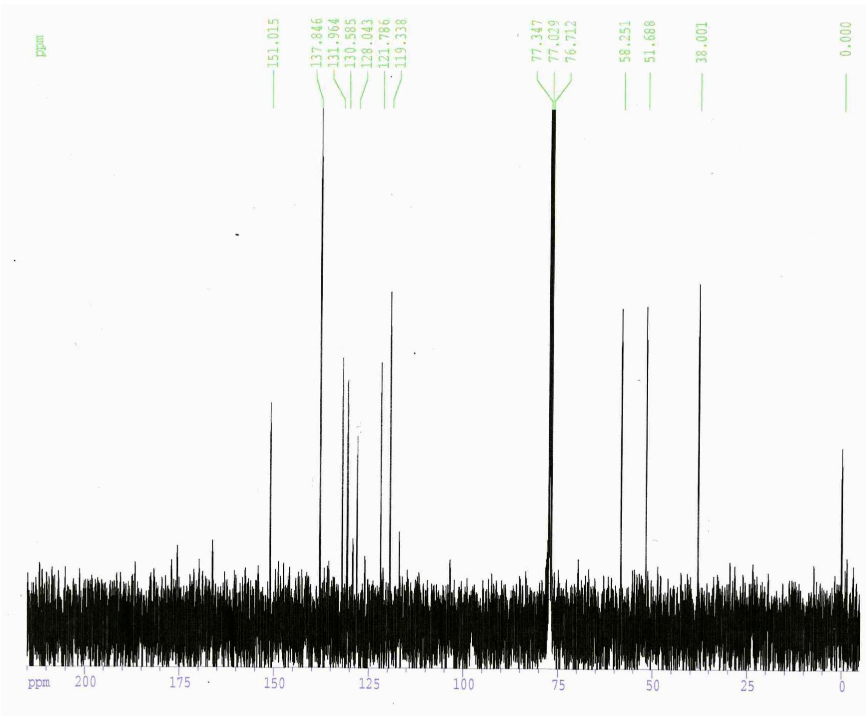
^{13}C NMR Spectrum of **2c** (100 MHz, $CDCl_3$) δ (ppm)



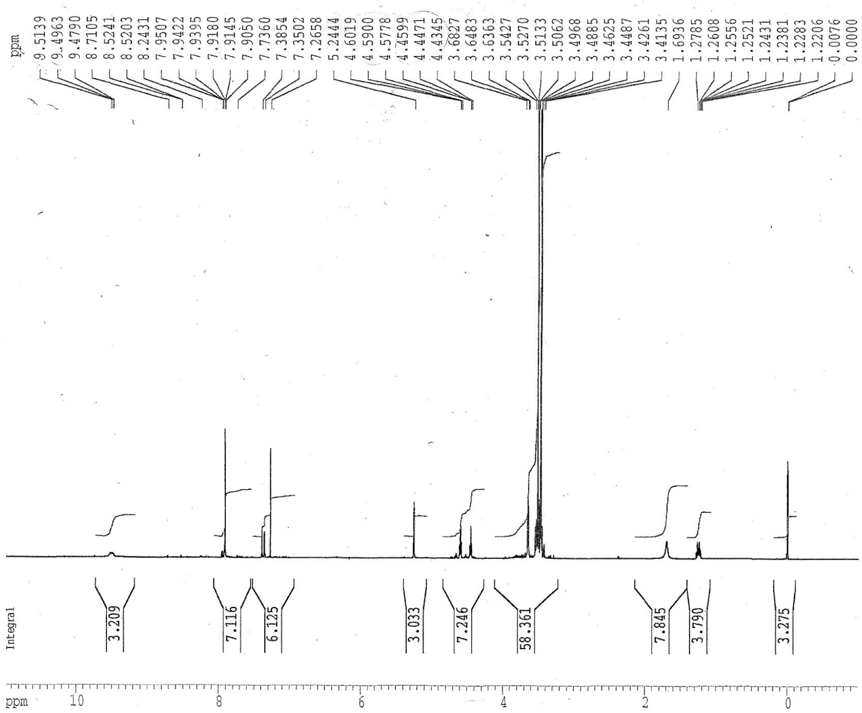
^{1}H NMR Spectrum of **2d** (400 MHz, $CDCl_3$) δ (ppm)



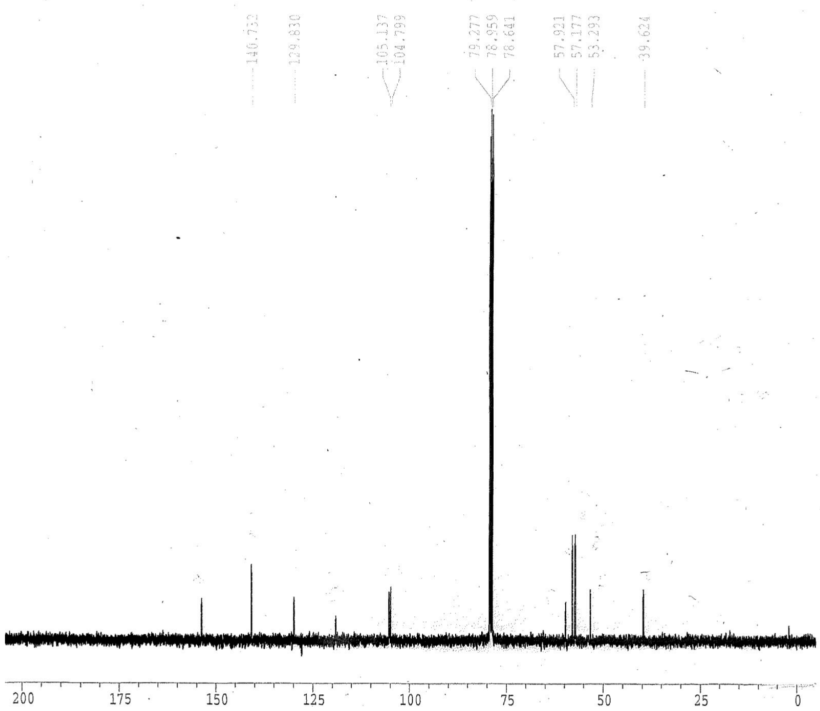
^{13}C NMR Spectrum of **2d** (100 MHz, $CDCl_3$) δ (ppm)



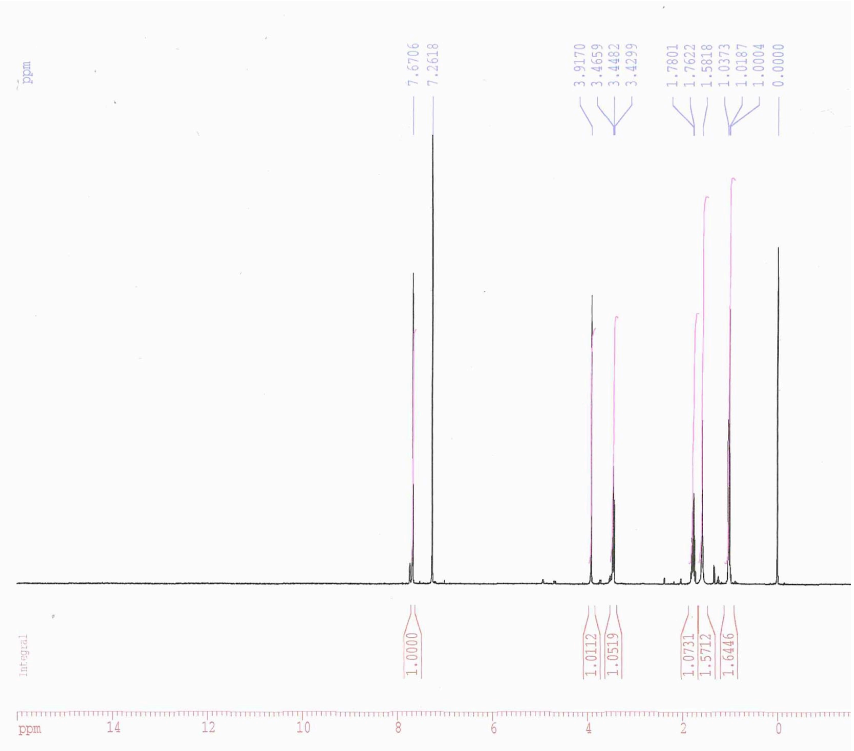
[1]H NMR Spectrum of **2e** (400 MHz, $CDCl_3$) δ (ppm)



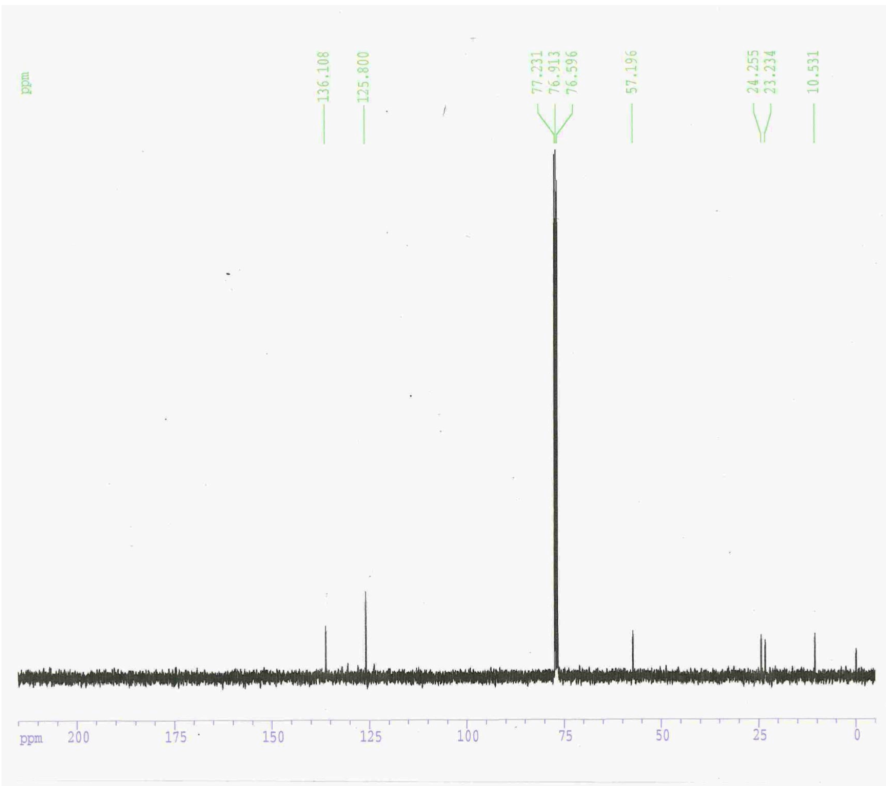
[13]C NMR Spectrum of **2e** (100 MHz, $CDCl_3$) δ (ppm)



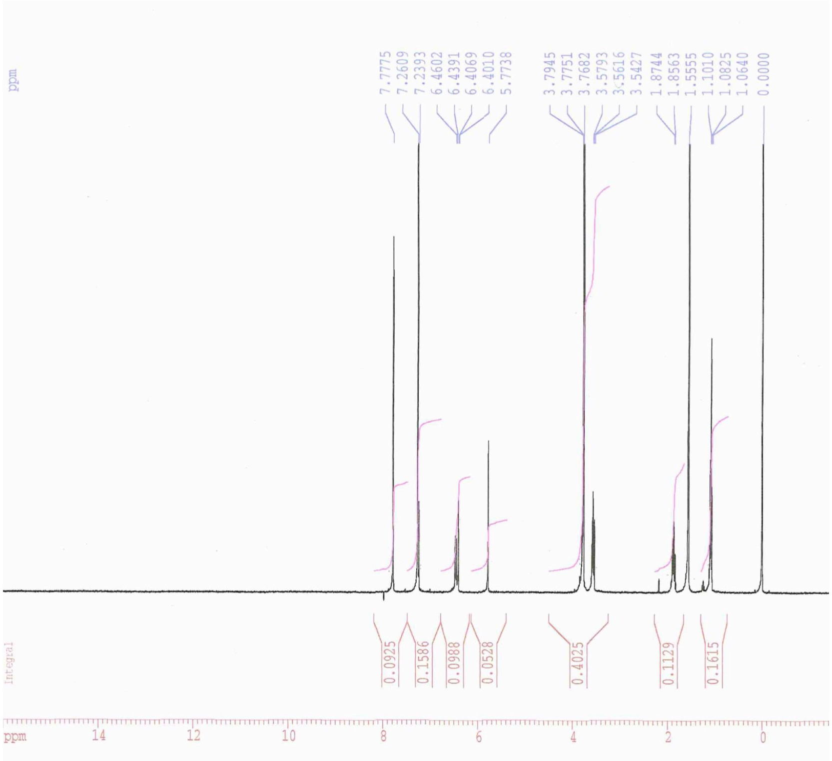
[1]H NMR Spectrum of **3** (400 MHz, $CDCl_3$) δ (ppm)



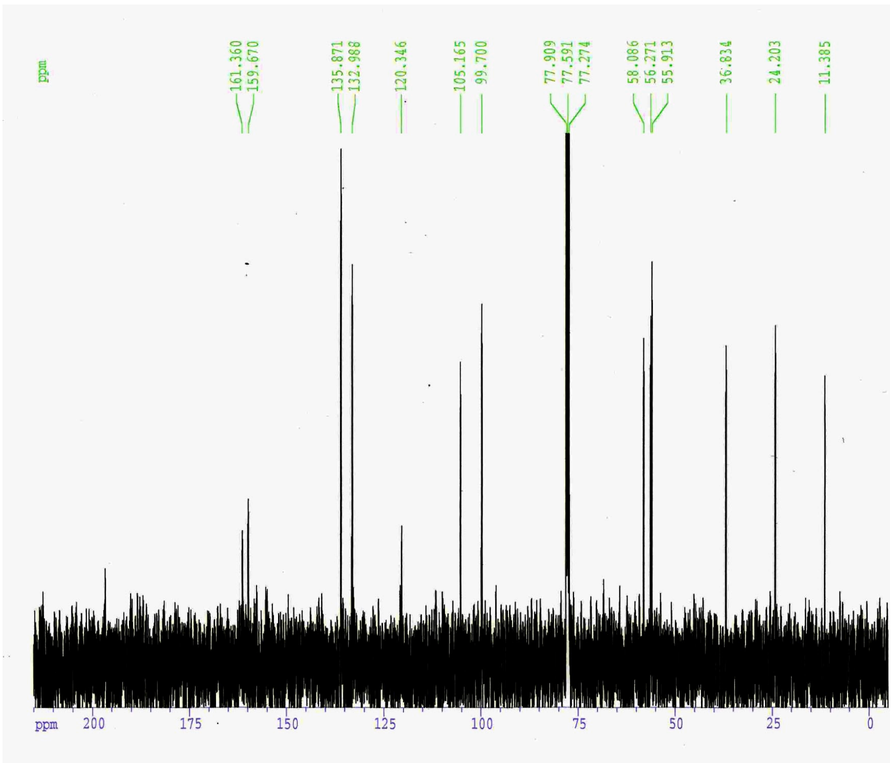
[13]C NMR Spectrum of **3** (100 MHz, $CDCl_3$) δ (ppm)



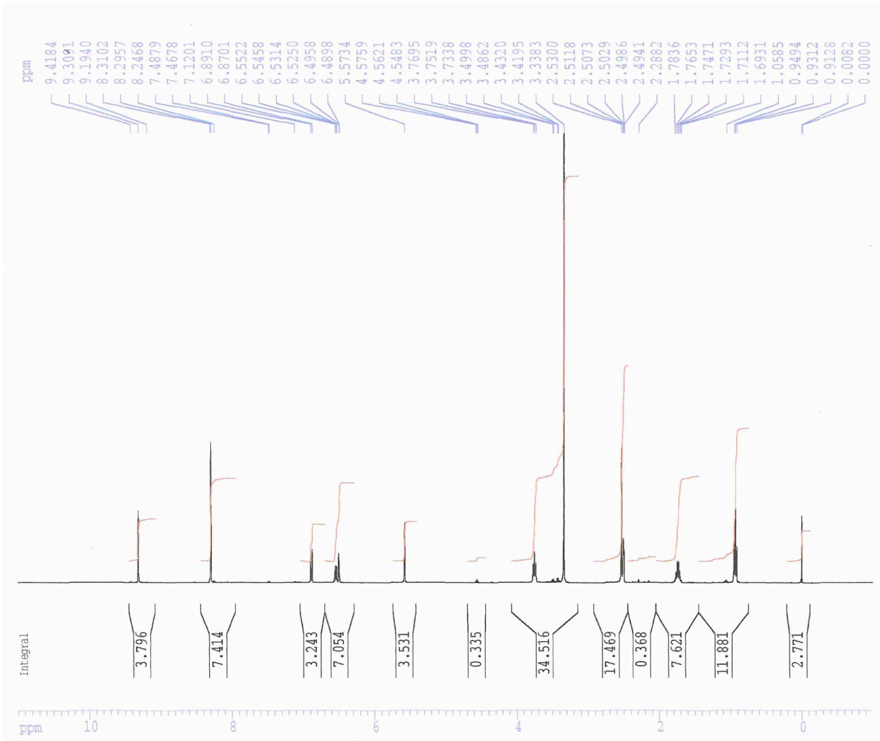
[1]H NMR Spectrum of **6a** (400 MHz, $CDCl_3$) δ (ppm)



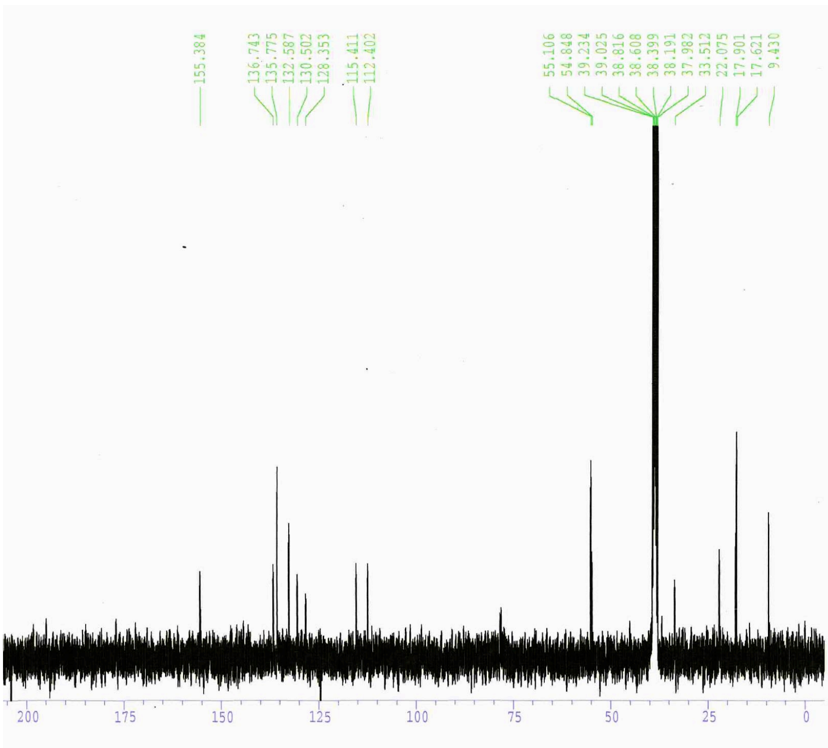
[13]C NMR Spectrum of **6a** (100 MHz, $CDCl_3$) δ (ppm)



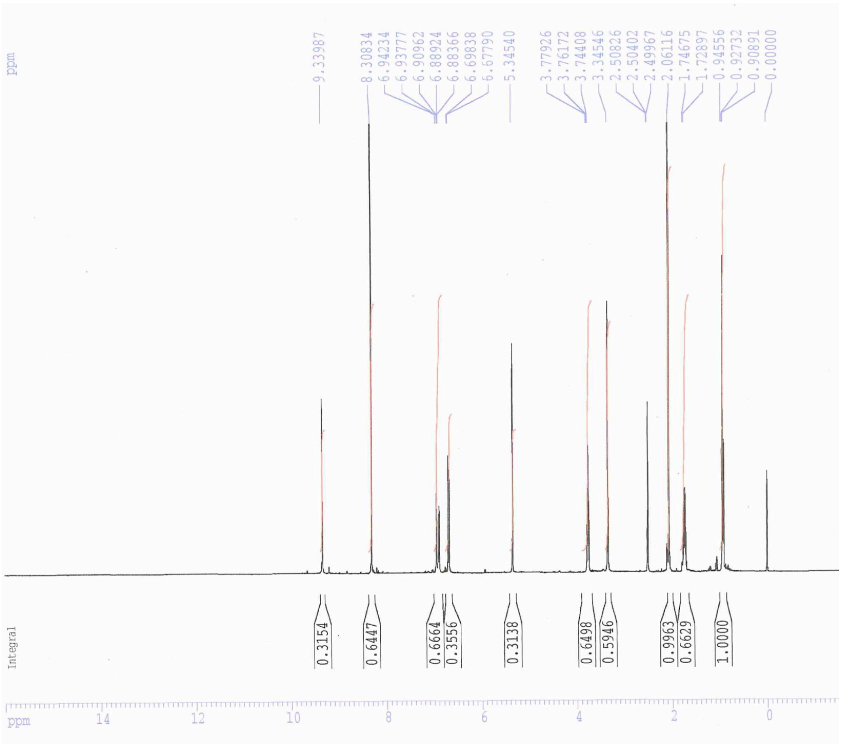
[1]H NMR Spectrum of **6b** (400 MHz, DMSO-d_6) δ (ppm)



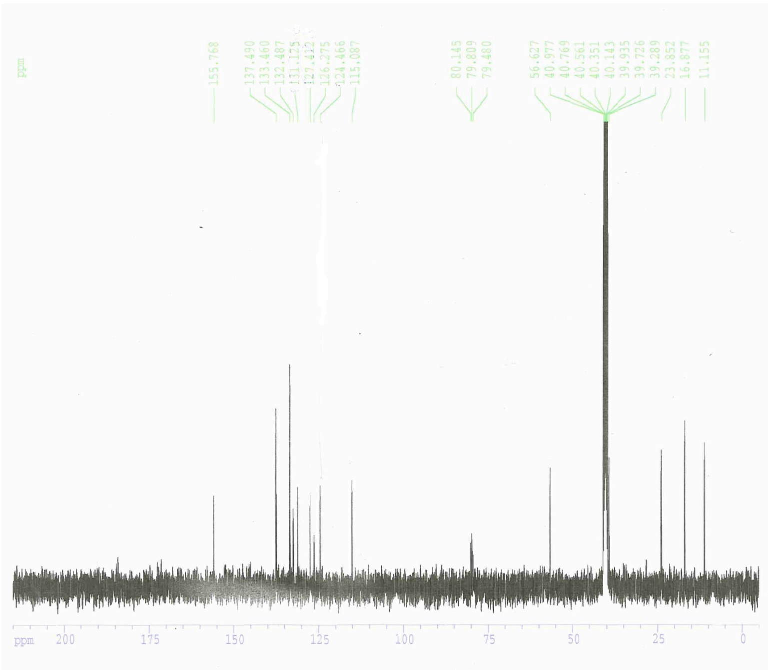
[13]C NMR Spectrum of **6b** (100 MHz, DMSO-d_6) δ (ppm)



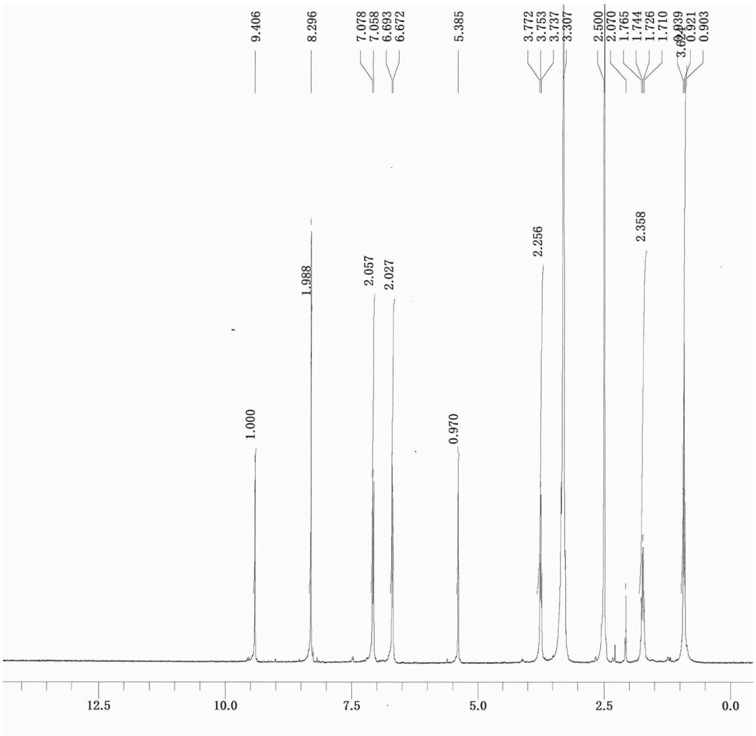
[1]H NMR Spectrum of **6c** (400 MHz, DMSO-d_6) δ (ppm)



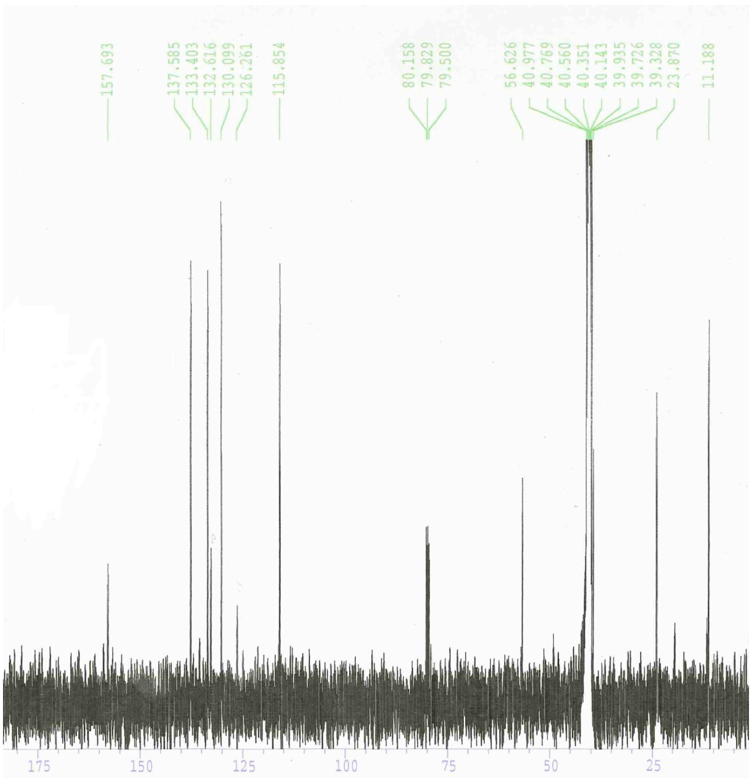
[13]C NMR Spectrum of **6c** (100 MHz, DMSO-d_6) δ (ppm)



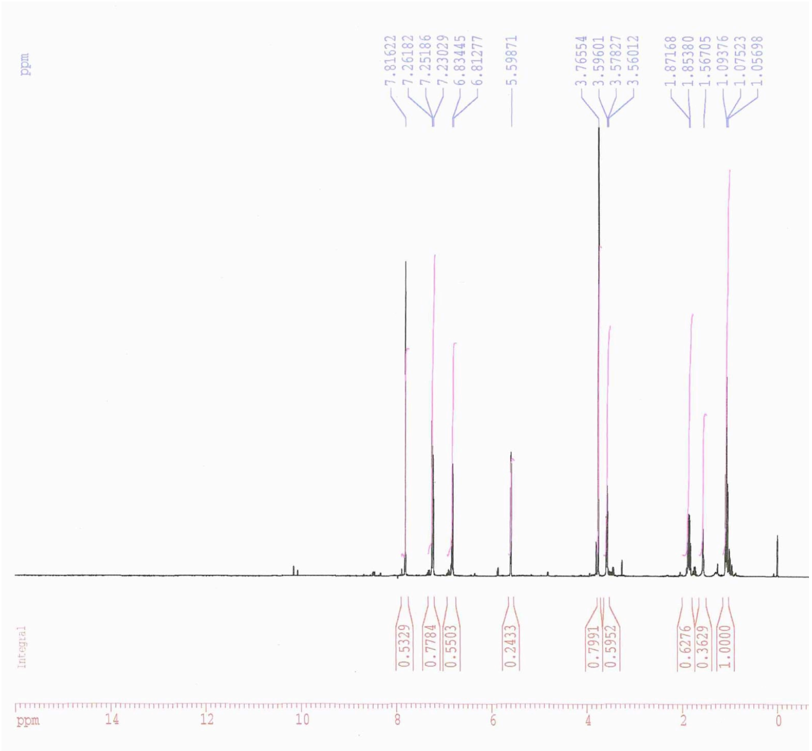
[1]H NMR Spectrum of **6d** (400 MHz, DMSO-d_6) δ (ppm)



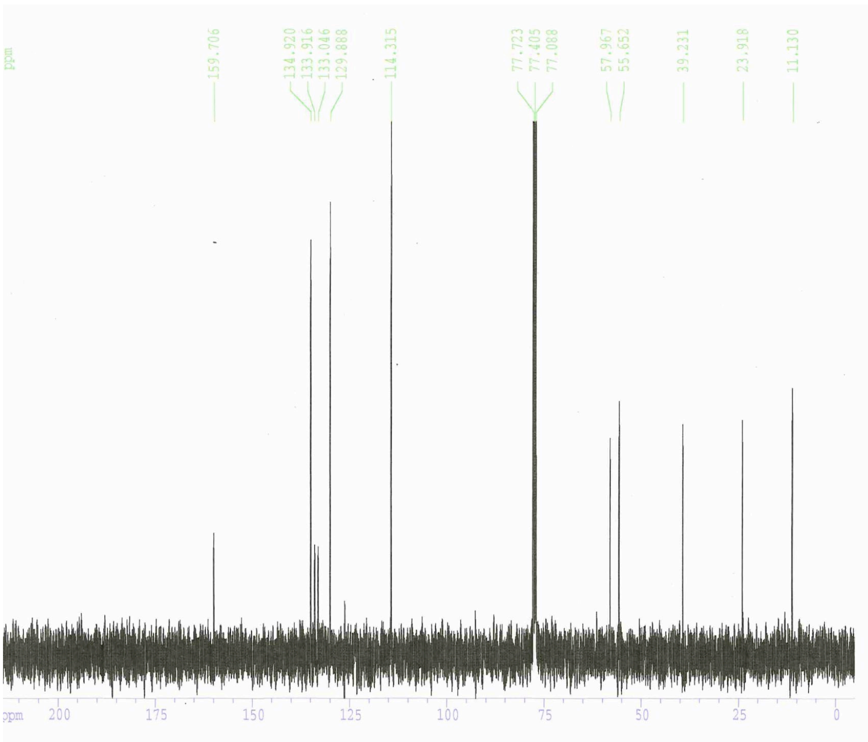
[13]C NMR Spectrum of **6d** (100 MHz, DMSO-d_6) δ (ppm)



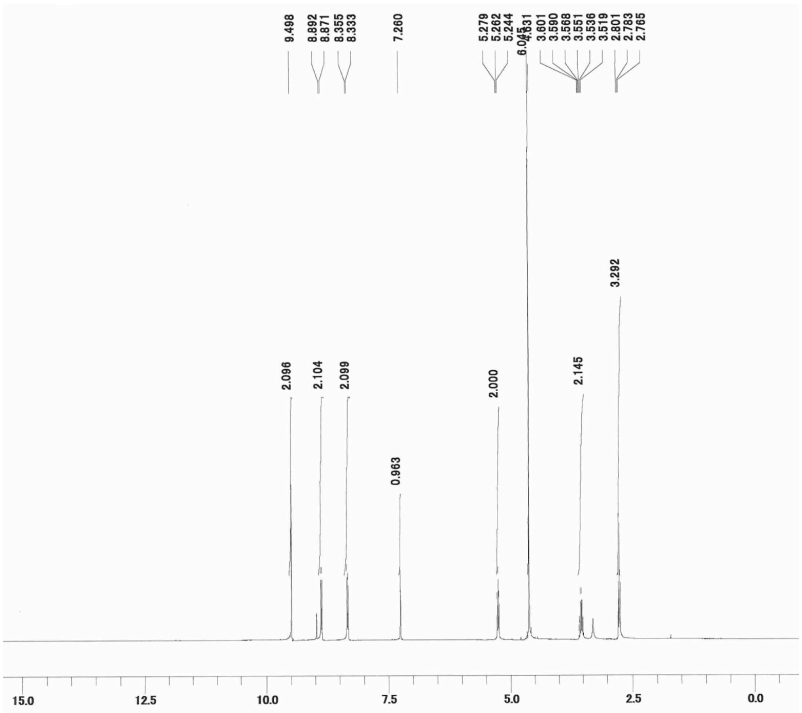
^{1}H NMR Spectrum of **6e** (400 MHz, $CDCl_3$) δ (ppm)



^{13}C NMR Spectrum of **6e** (100 MHz, $CDCl_3$) δ (ppm)



[1]H NMR Spectrum of **6f** (400 MHz, $CDCl_3$) δ (ppm)



[13]C NMR Spectrum of **6f** (100 MHz, $CDCl_3$) δ (ppm)

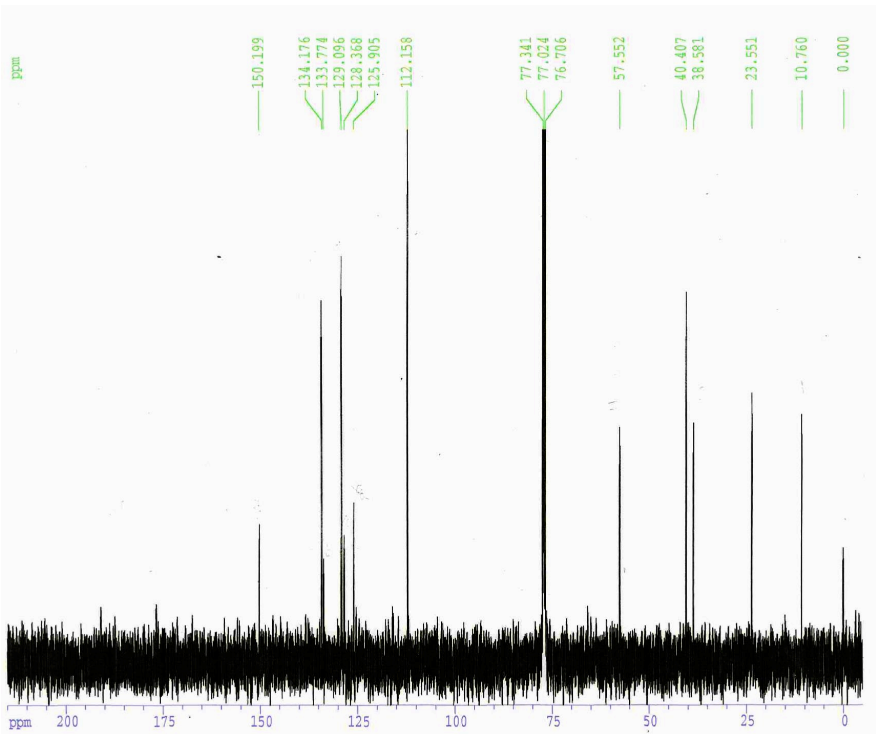


Table 1. Summary of crystallographic data of DNDHP **2a**.

Empirical Formula	$C_{13}H_{19}N_5O_6$
Formula Weight	341.32
Crystal Color, Habit	Orange, block
Crystal Dimensions	0.70 × 0.50 × 0.40 mm
Crystal System	Triclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.125(3) Å
	b = 10.053(4) Å
	c = 10.461(4) Å
	α = 87.508(8) Å
	β = 74.901(8) Å
	γ = 69.29(1) Å
	V = 770.6(5) $Å^3$
Space Group	$P\bar{1}$(#2)
Z Value	2
D_{calcd}	1.471 g/cm^3
F_{000}	360.00
Diffractometer	Rigaku RAXIS-RAPID Imaging Plate
Radiation (MoKα)	λ = 0.71075 Å
	Graphite monochromated
μ(MoKa)	1.08 cm^{-1}
Temperature, ºC	–160
$2\theta_{max}$	55.0º
No. of Reflections Measured	12542
Structure Solution Method	Direct Methods (SHELEXS-97)
No. of Reflections (I>2.00σ(I), 2θ<55.0º)	3533
No. Variables	217
Reflection/Parameter Ration	16.28
Refinement Method	Full-matrix least-squares
Goodness of Fit Indicator	1.05
Residual	R_1 = 0.041, wR_2 = 0.108
R Indices (all data)	R_1 = 0.037
No. of Reflection.to Calc R_1	3189
Max Shift/Error in Final Cycle	0.000
Maximum Peak in Final Diff. Map	0.34 e^-/$Å^3$
Minimum Peak in Final Diff. Map	–0.29 e^-/$Å^3$

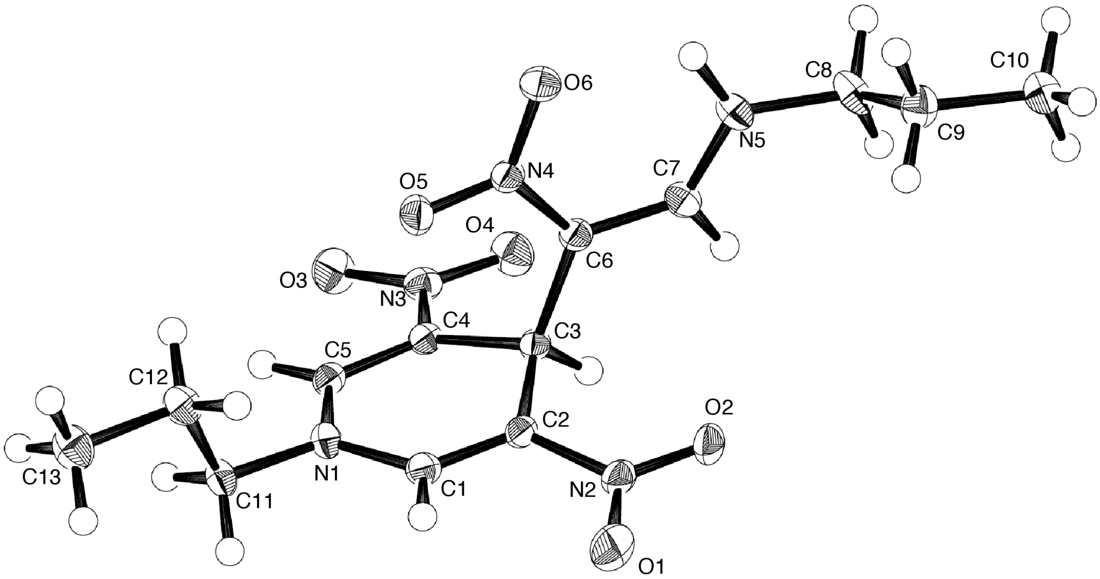


Figure 1. ORTEP diagram of **2a** with full numbering of unhydrogen atoms. Thermal ellipsoids are drawn at 50% probability level.

The DFT calculations were performed with the Gaussian 03 program package.[1] The geometries of N-methyl-3.5-dinitropyridinium ion **4g** was optimized by using the B3LYP method with the 6-31G** basis set.

SCF Done: E(RB+HF-LYP) = -696.930519422 A.U. after 4 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.156352	-0.008692	1.177243
2	6	0	0.2267	-0.000891	1.180215
3	6	0	0.960515	0.00243	0
4	6	0	0.2267	-0.000891	-1.180215
5	6	0	-1.156352	-0.008692	-1.177243
6	1	0	2.046201	0.005476	0
7	1	0	-1.72585	-0.011923	2.099054
8	1	0	-1.72585	-0.011923	-2.099054
9	7	0	0.923965	0	2.495548
10	8	0	2.142643	0.008308	2.455072
11	8	0	0.20268	-0.006946	3.483875
12	7	0	0.923965	0	-2.495548
13	8	0	2.142643	0.008308	-2.455072
14	8	0	0.20268	-0.006946	-3.483875
15	6	0	-3.31557	0.018682	0
16	1	0	-3.677494	-0.493341	0.890458
17	1	0	-3.677494	-0.493341	-0.890458
18	1	0	-3.646215	1.059364	0
19	7	0	-1.823976	-0.01248	0
Rotational	constants	(GHZ):	1.1314108	0.6057465	0.3955317

References

1 Gaussian 03, Revision D.01, Frisch, M. J. G.; Trucks, W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian, Inc., Wallingford CT, (**2004**).