Supporting Information for

Oxidation of *o*-Dioxime by (Diacetoxyiodo)benzene: A Green and Mild Access to Furoxans

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Contents

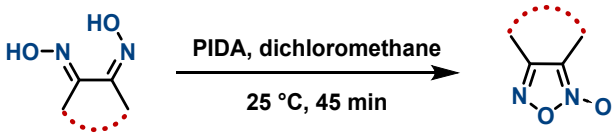
I. General information

All reagents were purchased from commercial sources (Energy Chemical, Adamas-beta®, J&K Scientific, Sigma-Aldrich) and used without purification unless otherwise mentioned. The products were purified by column chromatography over silica gel (200-300 size). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded at 25 °C on a Bruker 400 MHz, 100 MHz, and TMS was used as internal standard. High resolution mass spectra (HRMS) were recorded on Thermo Scientific LTQ Orbitrap XL and Thermo Scientific Q Exactive by using ESI method. Melting point were recorded on TA Discovery DSC 25. All the *o*-dioximes were prepared from 1,2-diones as previous report.[1,2,4,5] All the 1,2-diones were commercially available or prepared from aryl bromide.[3]

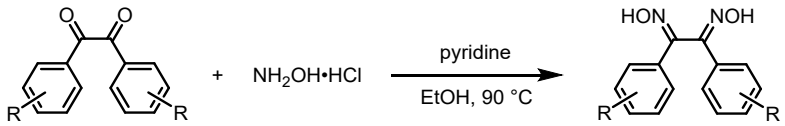
Note of Caution:

Furoxan is an explosive substance and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and handling.

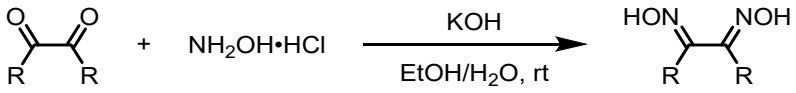
II. Experimental procedure



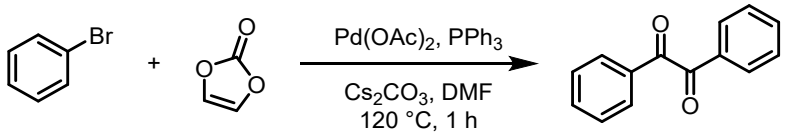
General procedure for the synthesis of furoxans: In a Schlenk tube, a solution of 1,2-dioxime (0.30 mmol, 1.0 equiv), PIDA (0.36 mmol, 1.2 equiv) in anhydrous DCM (0.1 M) was stirred for 45 min at 25 °C. Then saturated aq $NaHCO_3$ solution is added and extracted with DCM (3 × 30 mL). Combined organic layers was dried over Na_2SO_4 and filtered, evacuated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to give furoxans.



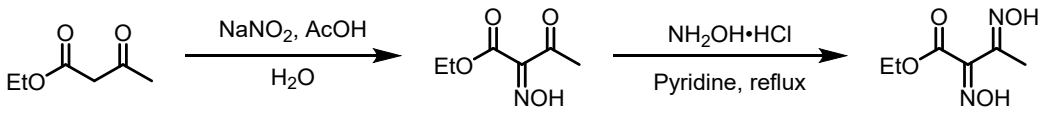
General procedure for the synthesis of aryl dioximes[1]: To a dry round bottom flask containing a magnetic stir bar was added a 1,2-dione (2.0 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (20.0 mmol, 10.0 equiv), pyridine (10 mL) and EtOH (10 mL). The mixture was stirred at 90 °C for 48 h. After cooling down to room temperature 2 N aqueous HCl was add to the round bottom flask, and extracted with ethyl acetate. Then combined organic layers was dried over Na_2SO_4 and filtered, evacuated under vacuum. The residue was purified by a short silica gel column (petroleum ether/ethyl acetate = 2/1) to give dioxime.



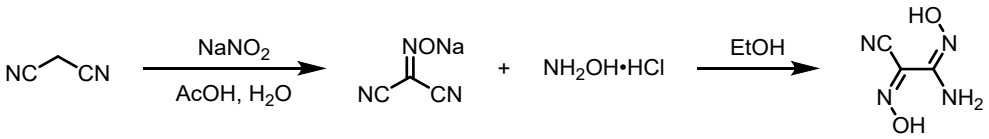
General procedure for the synthesis of alkyl dioximes[2]: hydroxylamine hydrochloride (5.0 mmol, 2.5 equiv) is dissolved in water (2 mL), and potassium hydroxide (5.0 mmol, 2.5 equiv), dissolved in water (2 mL), is added at 0 °C. 1,2-Dione (2.0 mmol, 1.0 equiv) is added dropwise at 0 °C. Subsequently, 15 mL of ethanol are added and the reaction mixture is stirred for 48 h at room temperature. The precipitate is filtered, and the filtrate is extracted with ethyl acetate. The combined organic phases are dried over Na_2SO_4, filtered and the solvent is removed in vacuo. The residue was purified by a short silica gel column (petroleum ether/ethyl acetate = 2/1) to give dioxime.



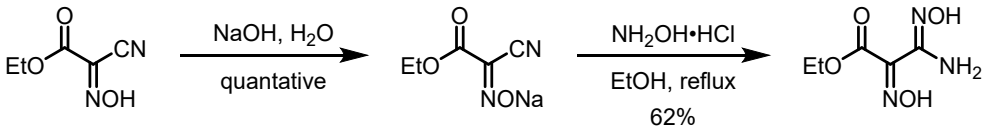
General procedure for the synthesis of 1,2-diones[3]: A stirred mixture of ArBr (6.0 mmol, 3.0 equiv), vinylene carbonate (2.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), and Cs_2CO_3 (4.4 mmol, 2.2 equiv) in DMF (10.0 mL) was heated to 120 °C for 1 h under nitrogen atmosphere. After aqueous extractive workup and silica gel column chromatography purification process (petroleum ether/ethyl acetate = 20/1), 1,2-dione was obtained.



Procedure for the synthesis of 1v (ethyl-2,3-bis(hydroxyimino)butanoate)[4]: To a solution of $NaNO_2$ (5.5 mmol, 1.1 equiv) in H_2O (30 mL) at 0 °C was added ethyl acetoacetate (5.0 mmol, 1.0 equiv). Then the AcOH was added dropwise to the reaction system. The reaction mixture was allowed to warm to room temperature and stirred overnight at room temperature. The reaction mixture was extracted with H_2O (2 × 50 mL), ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure to give the crude product. Then add the product of the previous step (3.0 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (15.0 mmol, 5.0 equiv), pyridine (15 mL) and EtOH (15 mL) to a dry round bottom flask. The mixture was stirred at 90 °C for 18 h. After cooling down to room temperature 2 N aqueous HCl was add to the round bottom flask, and extracted with ethyl acetate. Then combined organic layers was dried over Na_2SO_4 and filtered, evacuated under vacuum. The residue was purified by a short silica gel column (petroleum ether/ethyl acetate = 2/1) to give dioxime.



Procedure for the synthesis of 1y (2-amino-N-hydroxy-2-(hydroxyimino)acetimidoyl cyanide)[5]: 4.0 mL (70.0 mmol) acetic acid was added to the solution of malononitrile (3.00 g, 45.4 mmol) and $NaNO_2$(3.7 g, 53.6 mmol) in 50 mL H_2O at -5 to 0 °C. The mixture was stirred at 20 °C for 4 hours. Then the solution of 3.15 g (45.4 mmol) $NH_2OH{\cdot}HCl$ in 15 mL H_2O was added at 25 °C. The reaction mixture was stirred for another 4 hours at 25 °C. The precipitate was filtered, washed with ice water and air-dried to obtain yellowish solid.



Procedure for the synthesis of 1z ethyl-3-amino-2,3-bis(hydroxyimino)propanoate: To a solution of NaOH (3.0 mmol, 1.0 equiv) and H_2O (10 mL) at 25 ºC, ethyl cyanoglyoxylate-2-oxime (3.0 mmol, 1.0 equiv) was added. The mixture was then stirred for 30 min until substrate disappeared can obtain the quantative crude of product. Then the crude product of previous step (3.0 mmol, 1.0

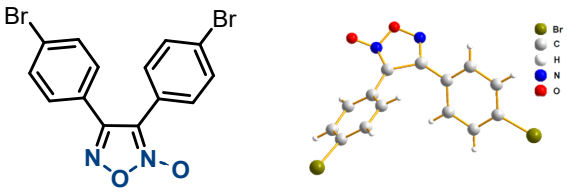
equiv), $NH_2OH·HCl$ (3.0 mmol, 1.0 equiv) and EtOH (15 mL) to a dry round bottom flask. The mixture was stirred at 80 °C for 4 h. After cooling down to room temperature 2 N aqueous HCl was add to the round bottom flask, and extracted with ethyl acetate. Then combined organic layers was dried over Na_2SO_4 and filtered, evacuated under vacuum. The residue was purified by a short silica gel column (petroleum ether/ethyl acetate = 2/1) to give dioxime (62% yield).

III. X-Ray crystallographic data

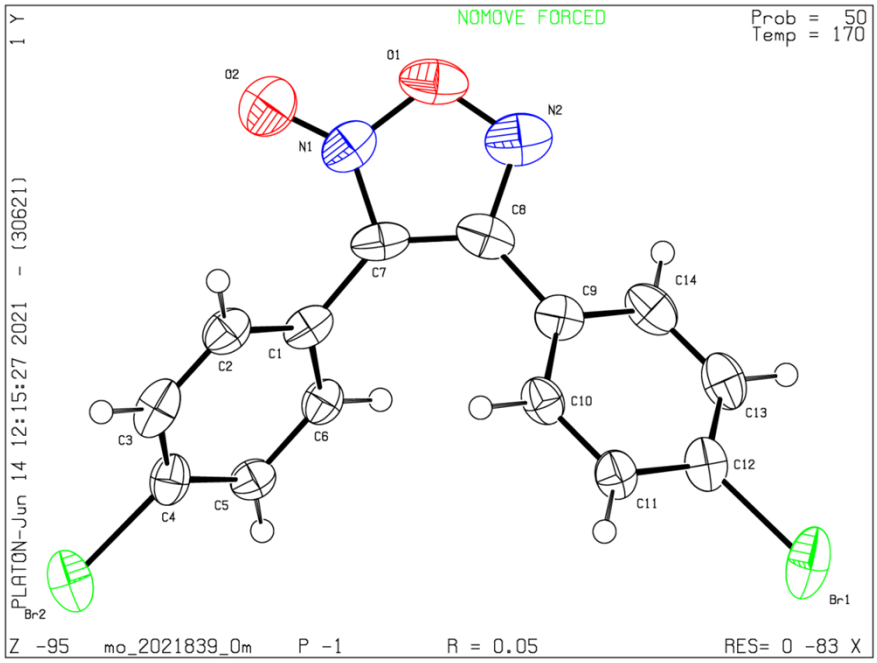
Crystal Structure of

3,4-bis(4-bromophenyl)-1,2,5-oxadiazole-2-oxide (2d)

(CCDC No. **2106116**)



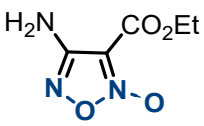
Empirical formula	$Br_2C_{14}N_2O_2$
Temperature	170.0 K
Wavelength	0.71073 Å
Unit cell dimensions	a = 7.9284(18) Å b = 8.2719(15) Å c = 12.334(2) Å alpha = 85.421(7) deg. beta = 71.683(7) deg. gamma = 63.651(9) deg.
Volume	686.4(2) $Å^3$
Z	2
Calculated density	1.877 g/cm^3
Absorption coefficient	5.904 mm^{-1}
F(000)	368.0
Crystal size	0.07 x 0.05 x 0.04 mm
Theta range for data collection	5.51 to 53.084 deg.

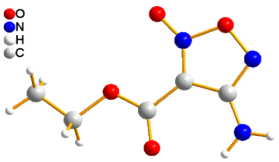
Reflections collected / unique	7147 / 2782 [R(int) = 0.0373]
Data / restraints / parameters	2782 / 0 / 181
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1512
Rindices (all data)	R1 = 0.0916, wR2 = 0.1688

Growth in DCM at room temperature	

Crystal Structure of

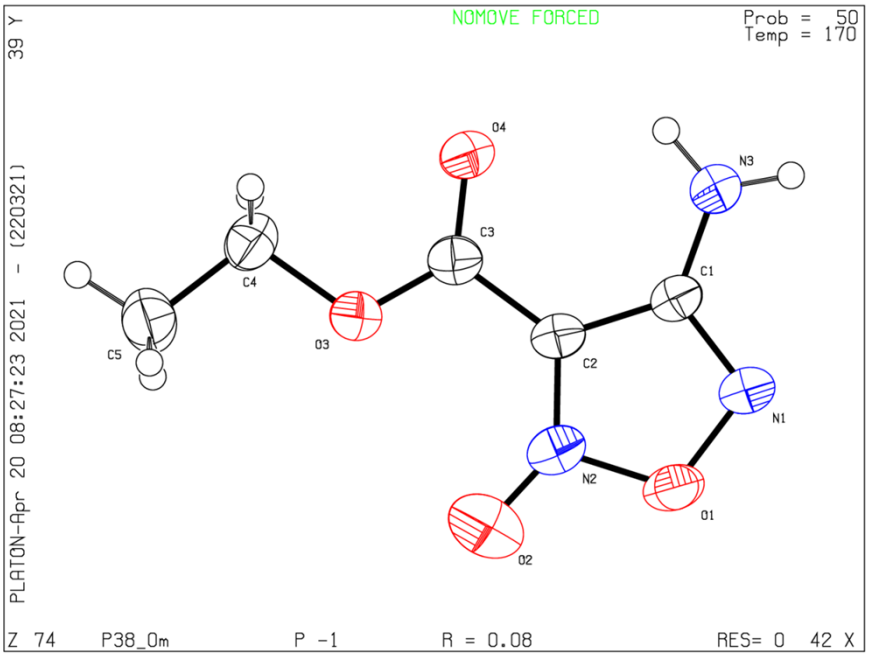
4-amino-3-(ethoxycarbonyl)-1,2,5-oxadiazole 2-oxide (2z)

(CCDC No. **2106118**)

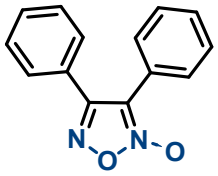




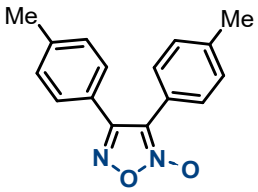
Empirical formula	$C_5H_7N_3O_4$
Temperature	170.0 K
Wavelength	0.71073 Å
Unit cell dimensions	a = 4.8238(6) Å

	b = 7.3029(9) Å c = 11.0533(14) Å alpha = 76.643(4) deg. beta = 78.988(4) deg. gamma = 87.455(4) deg.
Volume	371.87(8) $Å^3$
Z	2
Calculated density	1.546 g/cm^3
Absorption coefficient	0.135 mm^{-1}
F(000)	180.0
Crystal size	0.16 x 0.10 x 0.06 mm
Theta range for data collection	5.734 to 55.14 deg.
Reflections collected / unique	4446 / 1688 [R(int) = 0.0425]
Data / restraints / parameters	1688 / 1 / 110
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0816, wR2 = 0.2498
Rindices (all data)	R1 = 0.1234, wR2 = 0.3011
	
Growth in DCM at room temperature	

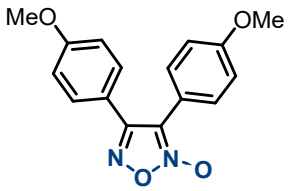
IV. Characterization data for the products



3,4-diphenyl-1,2,5-oxadiazole-2-oxide (2a) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (113.1 mg, 95%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 115-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 5H), 7.48-7.42 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.23, 130.98, 130.55, 129.02, 128.95, 128.69, 128.29, 126.67, 122.89, 114.28. **HRMS** (ESI) m/z calcd for $C_{14}H_{10}N_2O_2Na^+$ $(M+Na)^+$ 261.06345, found 261.06348.[6]



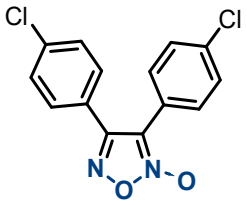
3,4-di-p-tolyl-1,2,5-oxadiazole-2-oxide (2b) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (122.5 mg, 92%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 135-136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 4H), 7.25-7.23 (m, 4H), 2.41 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.25, 141.27, 140.86, 129.65, 129.60, 128.55, 128.14, 123.88, 119.97, 114.36, 21.48, 21.46. **HRMS** (ESI) m/z calcd for $C_{16}H_{14}N_2O_2Na^+$ $(M+Na)^+$ 289.09475, found 289.09488.[6]



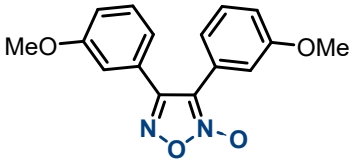
3,4-diphenyl-1,2,5-oxadiazole-2-oxide (2c) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (144.5 mg, 97%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 110-111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 4H), 6.97-6.93 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 161.58, 161.02, 155.91, 130.22, 129.73, 118.97, 114.87, 114.42, 114.20, 55.36. **HRMS** (ESI) m/z calcd for $C_{16}H_{14}N_2O_4Na^+$ $(M+Na)^+$ 321.08458, found 321.08481.[6]

3,4-bis(4-bromophenyl)-1,2,5-oxadiazole-2-oxide (2d) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (168.3mg, 85%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 164-165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 7.48-7.42 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.06, 132.52, 132.45, 130.00, 129.71, 125.92, 125.28, 121.50, 113.30. **HRMS** (ESI) m/z calcd for $C_{14}H_9Br_2N_2O_2^+$ $(M+H)^+$ 396.90048, found 396.90030.[7]

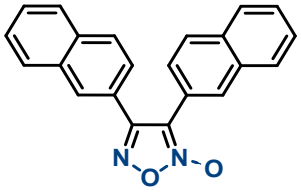


3,4-bis(4-chlorophenyl)-1,2,5-oxadiazole-2-oxide (2e) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (132.0 mg, 86%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 141-142 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.02, 137.56, 136.92, 129.85, 129.54, 129.47, 124.84, 121.03, 113.27. **HRMS** (ESI) m/z calcd for $C_{14}H_{10}Cl_2N_2O_2^+$ $(M+H)^+$ 307.00356, found 307.00357.[8]

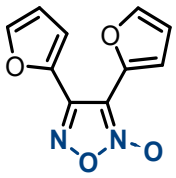


3,4-bis(3-methoxyphenyl)-1,2,5-oxadiazole-2-oxide (2f) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (134.1 mg, 90%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 7.02-6.94 (m, 5H), 6.92-6.89 (m, 1H), 3.68 (s, 3H), 3.65 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.80, 159.68, 156.06, 130.04, 129.93, 127.71, 123.89, 121.01,

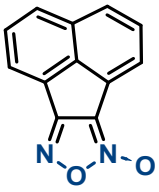
120.64, 117.00, 116.66, 114.15, 113.62, 113.31, 55.30, 55.26. **HRMS** (ESI) m/z calcd for $C_{16}H_{14}N_2O_4Na^+$ $(M+Na)^+$ 321.08458, found 321.08459.



3,4-di(naphthalen-2-yl)-1,2,5-oxadiazole-2-oxide (2g) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (131.8 mg, 78%) (petroleum ether/ethyl acetate = 10/1). Yellow solid; mp: 192-193 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.12 (s, 1H), 7.90-7.79 (m, 6H), 7.60-7.52 (m, 5H), 7.6 (dd, *J* = 8.8, 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.37, 134.17, 133.78, 132.84, 129.31, 128.91, 128.70, 128.68, 128.63, 128.60, 127.89, 127.86, 127.84, 127.80, 127.03, 126.98, 124.78, 124.62, 124.02, 120.12, 114.50. **HRMS** (ESI) m/z calcd for $C_{22}H_{14}N_2O_2Na^+$ $(M+Na)^+$ 361.09475, found 361.09451.

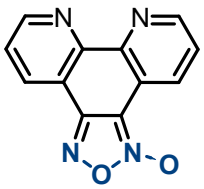


3,4-di(furan-2-yl)-1,2,5-oxadiazole-2-oxide (2h) This compound was prepared according to the general procedure for the synthesis offuroxans. Purified on silica gel chromatography to give the product (63.2 mg, 58%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 110-111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.6 Hz, 1H), 7.65 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 6.67 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.62 (dd, *J* = 3.6, 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.33, 145.36, 144.50, 140.40, 137.79, 115.33, 114.10, 112.30, 111.85, 108.13. **HRMS** (ESI) m/z calcd for $C_{10}H_7N_2O_4^+$ $(M+H)^+$ 219.04003, found 219.04016.[9]

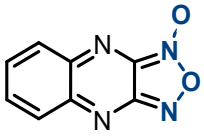


acenaphtho[1,2-c][1,2,5]oxadiazole-7-oxide (2i) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the

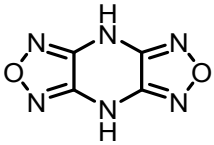
product (80.9 mg, 77%) (petroleum ether/ethyl acetate = 10/1). Yellow solid; mp: 195 °C (dec.); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.75 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.69 (dd, *J* = 8.4, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.27, 138.85, 131.03, 129.71, 128.87, 128.56, 128.51, 123.61, 123.54, 122.92, 120.50, 113.55. **HRMS** (ESI) m/z calcd for $C_{12}H_9N_2O_2^+$ $(M+H)^+$ 213.06585, found 213.06596.



[1,2,5]oxadiazolo[3,4-f][1,10]phenanthroline-1-oxide (2j) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (89.3 mg, 75%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 250 °C (dec.); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (dd, *J* = 4.4, 1.6 Hz, 1H), 9.13 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (ddd, *J* = 10.0, 8.0, 4.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.71, 152.16, 148.87, 148.30, 147.04, 131.90, 130.97, 124.83, 124.73, 119.18, 116.27, 107.49. **HRMS** (ESI) m/z calcd for $C_{12}H_7N_4O_2^+$ $(M+H)^+$ 239.05635, found 239.05656.[10]

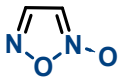


[1,2,5]oxadiazolo[3,4-b]quinoxaline-1-oxide (2k) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (80.8 mg, 86%) (petroleum ether/ethyl acetate = 10/1). Red solid; mp: 161-162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.74-7.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.43, 134.88, 130.39.[11]

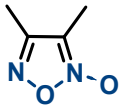


4H,8H-bis([1,2,5]oxadiazolo)[3,4-b:3',4'-e]pyrazine (2l) This compound was prepared according to the general procedure for the synthesis of furoxans (MeCN as solvent). Purified on silica gel

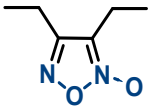
chromatography to give the product (50.6 mg, 61%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 296 °C (dec.); **^{1}H NMR** (400 MHz, DMSO) δ 11.85 (s, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 146.91. **HRMS** (ESI) m/z calcd for $C_4H_3N_6O_2^+$ $(M+Na)^+$ 167.03120, found 167.03166.[12]



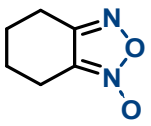
1,2,5-oxadiazole-2-oxide (2m) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (37.0 mg, 86%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 6.98 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.28, 103.17.[13]



3,4-dimethyl-1,2,5-oxadiazole-2-oxide (2n) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (44.5mg, 78%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.33 (s, 3H),. 2.15 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.61, 113.09, 11.13, 7.58. **HRMS** (ESI) m/z calcd for $C_4H_7N_2O_2^+$ $(M+H)^+$ 115.05020, found 115.05054.[6]

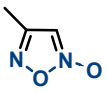


3,4-diethyl-1,2,5-oxadiazole-2-oxide (2o) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (61.8 mg, 87%) (petroleum ether/ethyl acetate = 10/1). Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.67 (q, J = 7.6 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H), 1.20 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.69, 116.73, 19.23, 15.91, 10.91, 9.73. **HRMS** (ESI) m/z calcd for $C_6H_{10}N_2O_2Na^+$ $(M+Na)^+$ 165.06345, found 165.06358.[6]

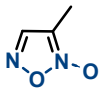


4,5,6,7-tetrahydrobenzo[c][1,2,5]oxadiazole-1-oxide (2p) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (58.2 mg, 83%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.78 (t, J = 6.4 Hz, 2H), 2.58 (t, J = 6.4 Hz, 2H), 1.88-1.79 (m,

4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.04, 112.92, 22.05, 21.21, 20.99, 19.36. **HRMS** (ESI) m/z calcd for $C_6H_9N_2O_2^+$ $(M+H)^+$ 141.06585, found 141.06590.[10]

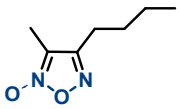


major product

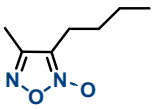


minor product

4-methyl-1,2,5-oxadiazole-2-oxide (2q) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (34.0 mg, 68%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; Major product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.86, 104.71, 11.26. Minor product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.92, 112.21, 7.93.

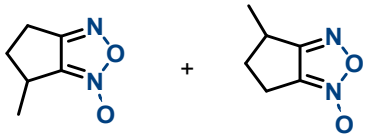


major product



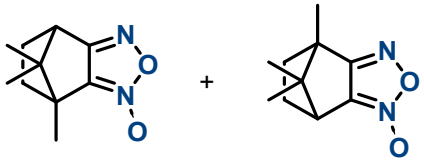
minor product

4-butyl-3-methyl-1,2,5-oxadiazole-2-oxide (2r) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (65.5 mg, 84%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; Major product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.62 (d, J = 7.2 Hz, 2H), 2.12-2.11 (m, 3H), 1.70-1.62 (m, 2H), 1.45-1.36 (m, 2H), 0.96-0.89 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.12, 112.70, 28.47, 25.24, 22.16, 13.49, 7.59. Minor product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.49 (d, J = 7.2 Hz, 2H), 2.31-2.30 (m, 3H), 1.60-1.53 (m, 2H), 1.34-1.29 (m, 2H), 0.96-0.89 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.31, 116.21, 27.40, 22.03, 21.93, 13.49, 11.01. **HRMS** (ESI) m/z calcd for $C_7H_{13}N_2O_2^+$ $(M+H)^+$ 157.09715, found 157.09726.

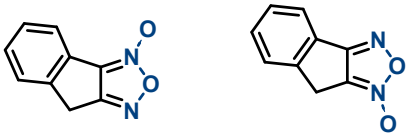


6-methyl-5,6-dihydro-4H-cyclopenta[c][1,2,5]oxadiazole-1-oxide (2s) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (59.5 mg, 85%) (petroleum ether/ethyl acetate = 10/1). Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.26-3.14 (m, 2H), 2.88-2.62 (m, 6H), 2.17-2.06 (m,

2H), 1.33 (d, J = 6.8 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.21, 166.37, 119.91, 117.02, 37.61, 37.44, 31.71, 29.57, 22.41, 20.23, 17.18, 15.57. **HRMS** (ESI) m/z calcd for $C_6H_8N_2O_2Na^+$ $(M+Na)^+$ 163.04780, found 163.04785.

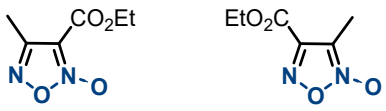


7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanobenzo[c][1,2,5]oxadiazole-1-oxide (2t) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (86.3 mg, 86%) (petroleum ether/ethyl acetate = 10/1). Yellow solid; mp: 135 °C (dec.); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.01 (d, J = 4.4 Hz, 1H), 2.97 (d, J = 4.4 Hz, 1H), 2.26-2.15 (m, 2H), 2.02-1.93 (m, 2H), 1.74-1.64 (m, 2H), 1.61-1.52 (m, 2H), 1.32 (s, 3H), 1.32 (s, 3H), 1.01 (s, 3H), 1.00 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.00, 166.18, 117.32, 116.34, 59.52, 59.36, 51.80, 51.46, 47.73, 46.54, 32.57, 32.54, 25.20, 24.88, 20.37, 20.31, 17.83, 17.75, 9.59, 8.94. **HRMS** (ESI) m/z calcd for $C_{10}H_{14}N_2O_2Na^+$ $(M+Na)^+$ 217.09475, found 217.09496.



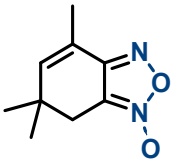
major product ***minor product***

8H-indeno[1,2-c][1,2,5]oxadiazole-3-oxide (2u) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (74.8 mg, 86%) (petroleum ether/ethyl acetate = 10/1).White solid; mp: 114-115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.75-7.73 (m, 1H), 7.54-7.49 (m, 3H), 7.48-7.43 (m, 3H), 4.00 (s, 2H), 3.87 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.54, 163.51, 145.76, 144.01, 131.48, 130.49, 128.74, 128.71, 128.53, 126.75, 126.52, 125.37, 123.09, 122.98, 116.83, 114.41, 29.27, 26.82. **HRMS** (ESI) m/z calcd for $C_9H_7O_2N_2^+$ $(M+H)^+$ 175.05020, found 175.05038.

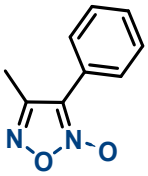


major product ***minor product***

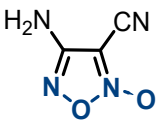
3-(ethoxycarbonyl)-4-methyl-1,2,5-oxadiazole-2-oxide (2v) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (64.5 mg, 75%) (petroleum ether/ethyl acetate = 10/1). Yellow oil; Major product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.94, 149.24, 112.27, 62.93, 13.93, 8.48. Minor product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.41 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.63, 153.85, 108.59, 62.70, 13.95, 12.74. **HRMS** (ESI) m/z calcd for $C_6H_8N_2O_4Na^+$ $(M+Na)^+$ 195.03763, found 195.03778.



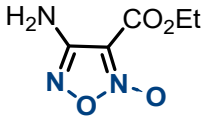
4,6,6-trimethyl-6,7-dihydrobenzo[c][1,2,5]oxadiazole-1-oxide (2w) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (77.4 mg, 86%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 53-54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 (q, *J* = 1.6 Hz, 1H), 2.60 (s, 2H), 2.08 (d, *J* = 1.6 Hz, 3H), 1.16 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.87, 144.44, 122.30, 110.26, 34.54, 31.52, 29.46, 15.84. **HRMS** (ESI) m/z calcd for $C_9H_{13}N_2O_2^+$ $(M+H)^+$ 181.09715, found 181.09721.



4-methyl-3-phenyl-1,2,5-oxadiazole-2-oxide (2x) This compound was prepared according to the general procedure for the synthesis of furoxans. Purified on silica gel chromatography to give the product (64.2 mg, 73%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 62-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.56-7.48 (m, 3H), 2.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.43, 130.48, 129.17, 127.40, 123.05, 115.03, 12.96. **HRMS** (ESI) m/z calcd for $C_9H_9N_2O_2^+$ $(M+H)^+$ 177.06585, found 177.06595.[14]



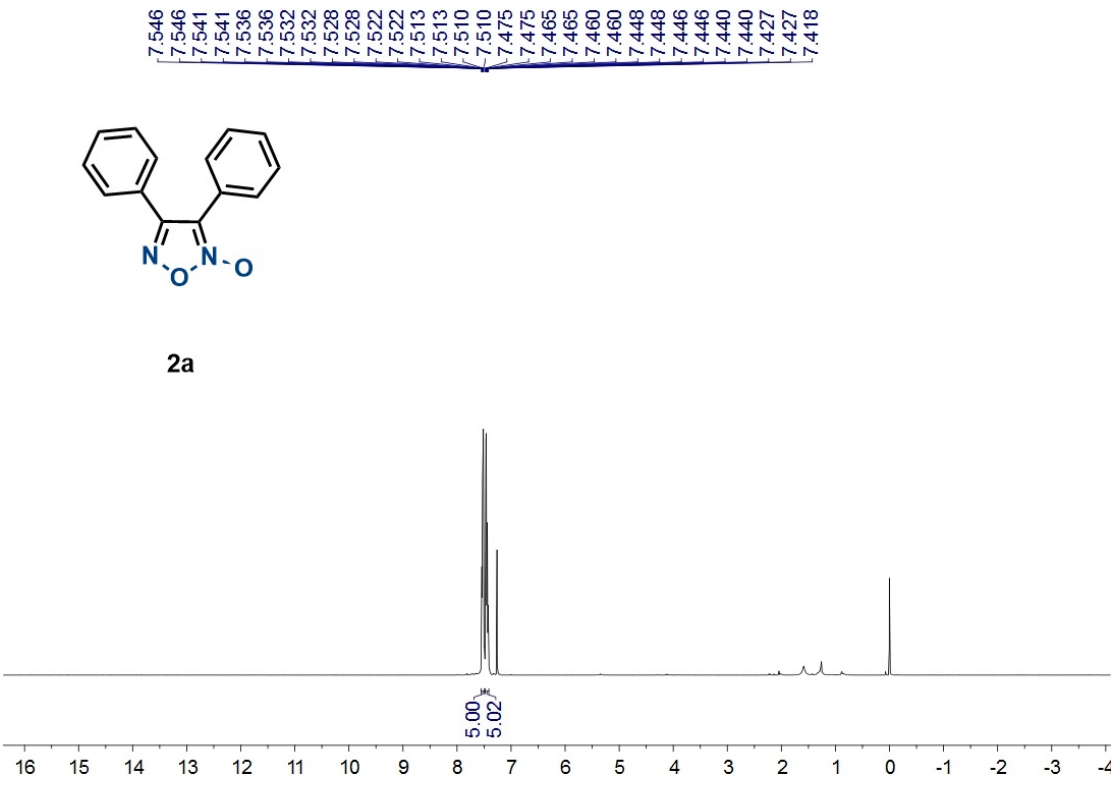
4-amino-3-cyano-1,2,5-oxadiazole-2-oxide (2y) This compound was prepared according to the general procedure for the synthesis of furoxans (MeCN as solvent). Purified on silica gel chromatography to give the product (44.1 mg, 70%) (petroleum ether/ethyl acetate = 10/1). Yellow solid; mp: 117-118 °C; **^{1}H NMR** (400 MHz, DMSO) δ 7.13 (s, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 156.26, 107.25, 93.59. **HRMS** (ESI) m/z calcd for $C_3H_2N_4O_2^+$ $(M)^+$ 126.01723, found 126.01640.[15]



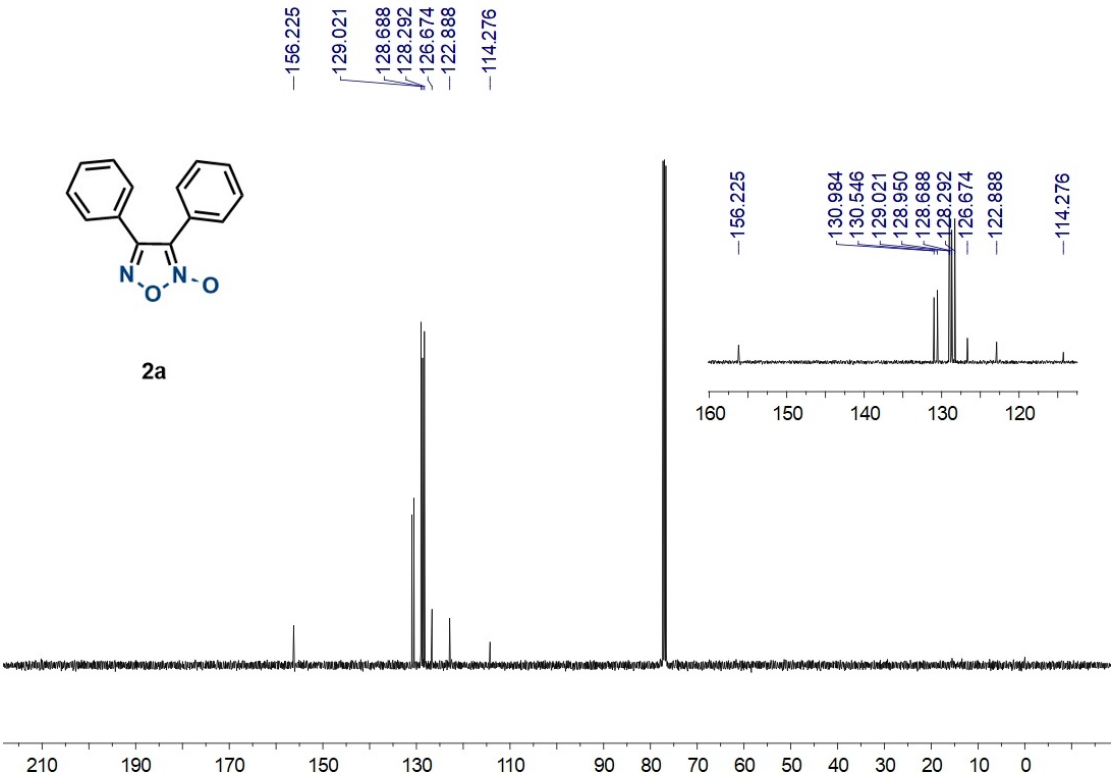
4-amino-3-(ethoxycarbonyl)-1,2,5-oxadiazole-2-oxide (2z) This compound was prepared according to the general procedure for the synthesis of oxetanes (MeCN as solvent). Purified on silica gel chromatography to give the product (58.0 mg, 67%) (petroleum ether/ethyl acetate = 10/1). White solid; mp: 125-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.04 (s, 2H), 4.46 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.73, 155.43, 102.40, 62.97, 14.06. **HRMS** (ESI) m/z calcd for $C_5H_7N_3O_4Na^+$ $(M+Na)^+$ 196.03288, found 196.03300.[16]

VII. Copies of ^{1}H-NMR, ^{13}C-NMR spectra

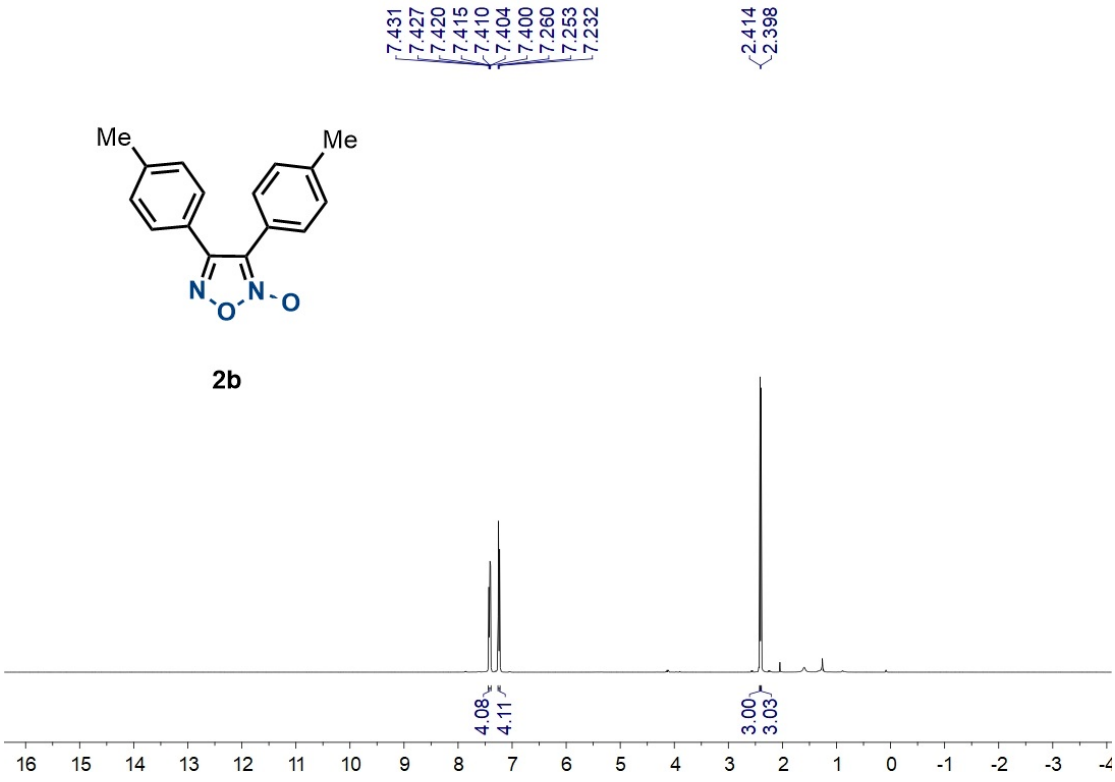
^{1}H NMR Spectrum of **2a** ($CDCl_3$, 400 MHz)



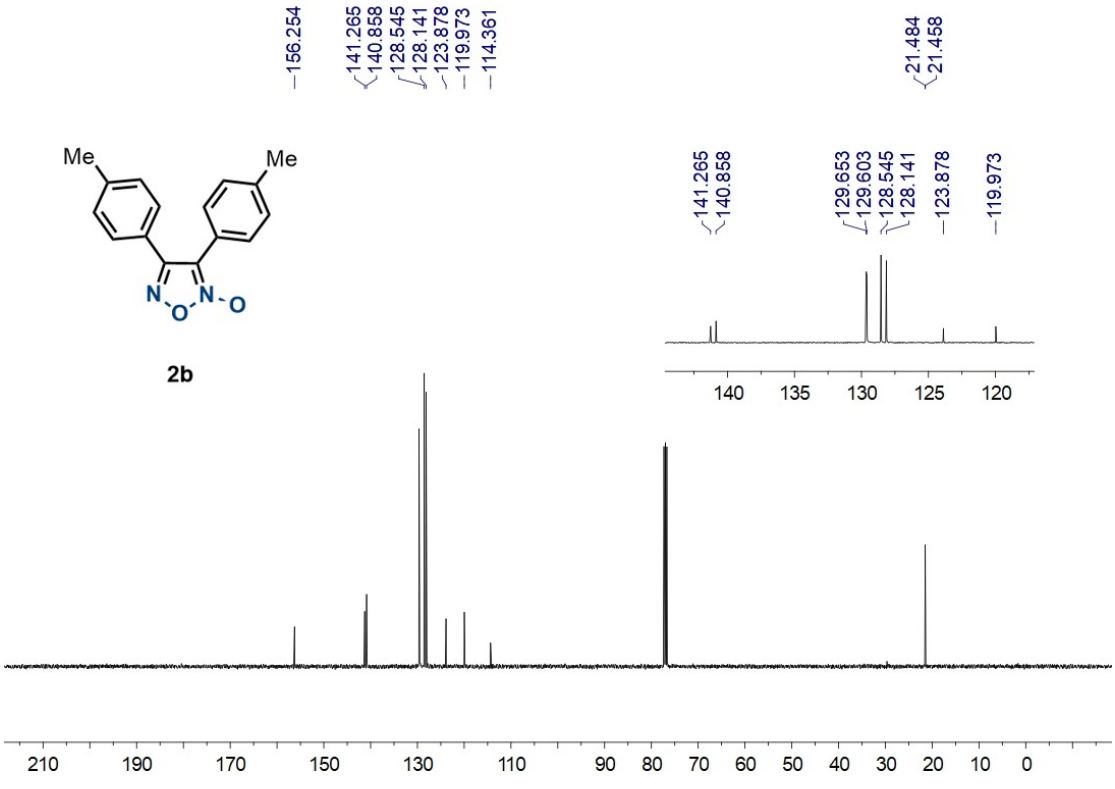
^{13}C NMR Spectrum of **2a** ($CDCl_3$, 100 MHz)



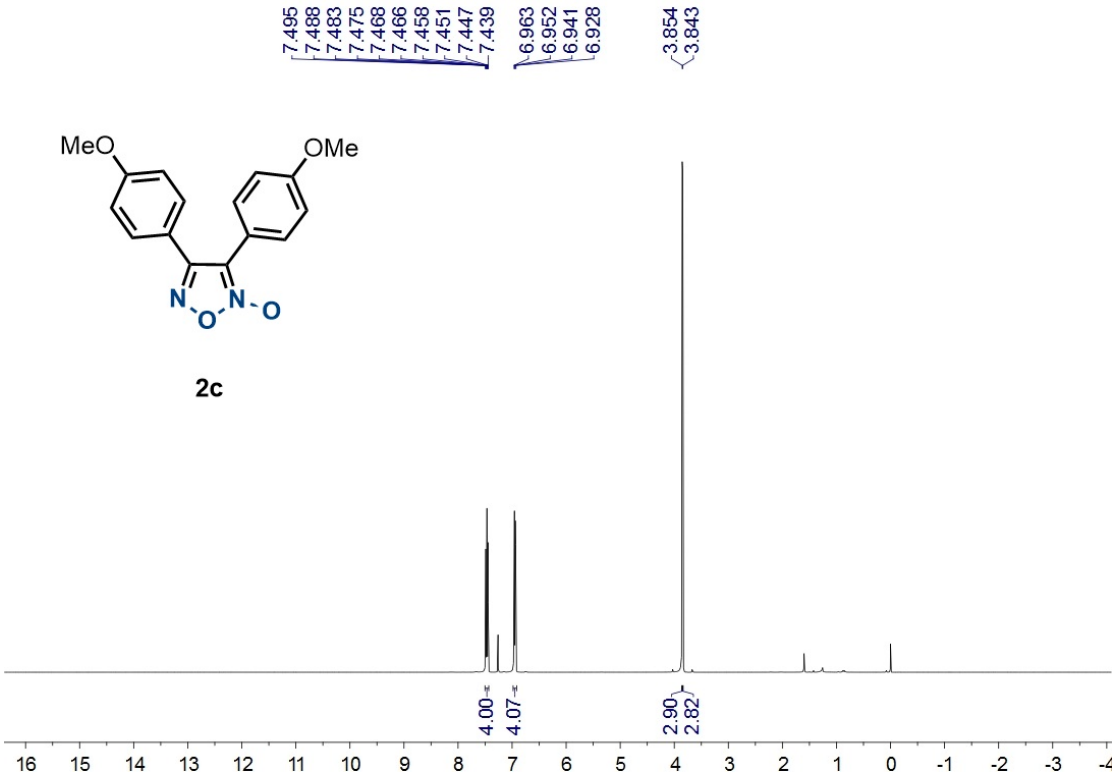
^{1}H NMR Spectrum of **2b** ($CDCl_3$, 400 MHz)



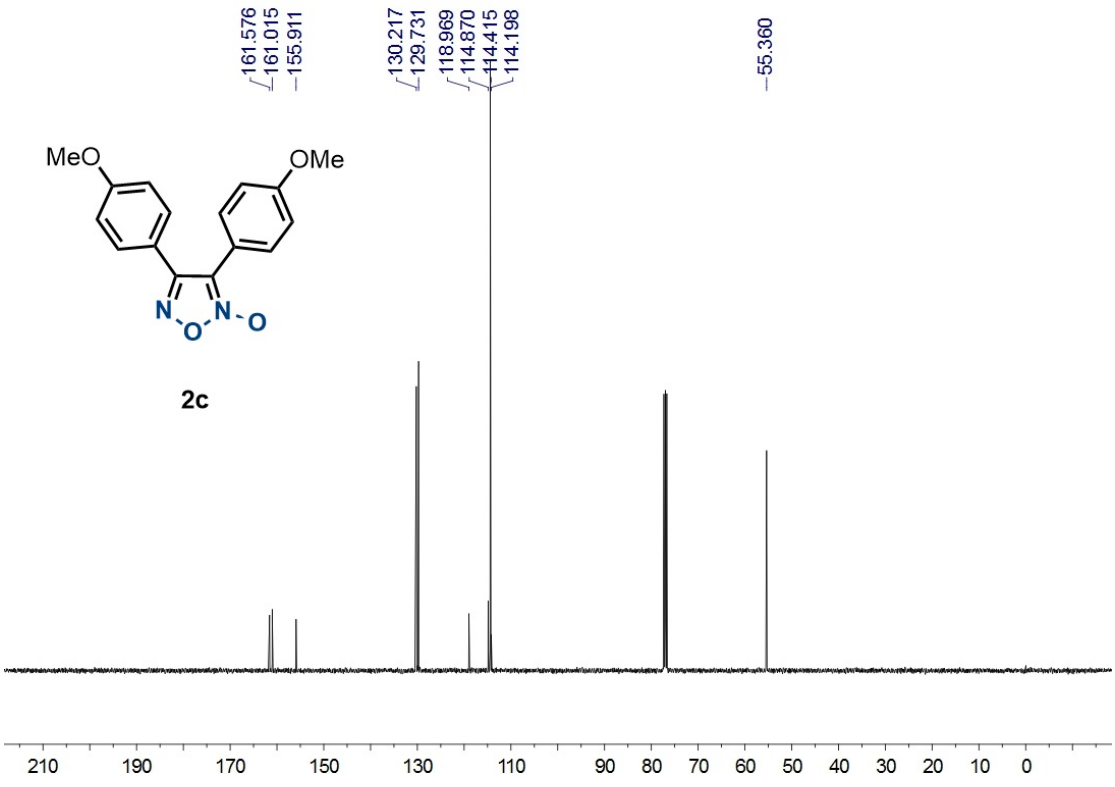
^{13}C NMR Spectrum of **2b** ($CDCl_3$, 100 MHz)



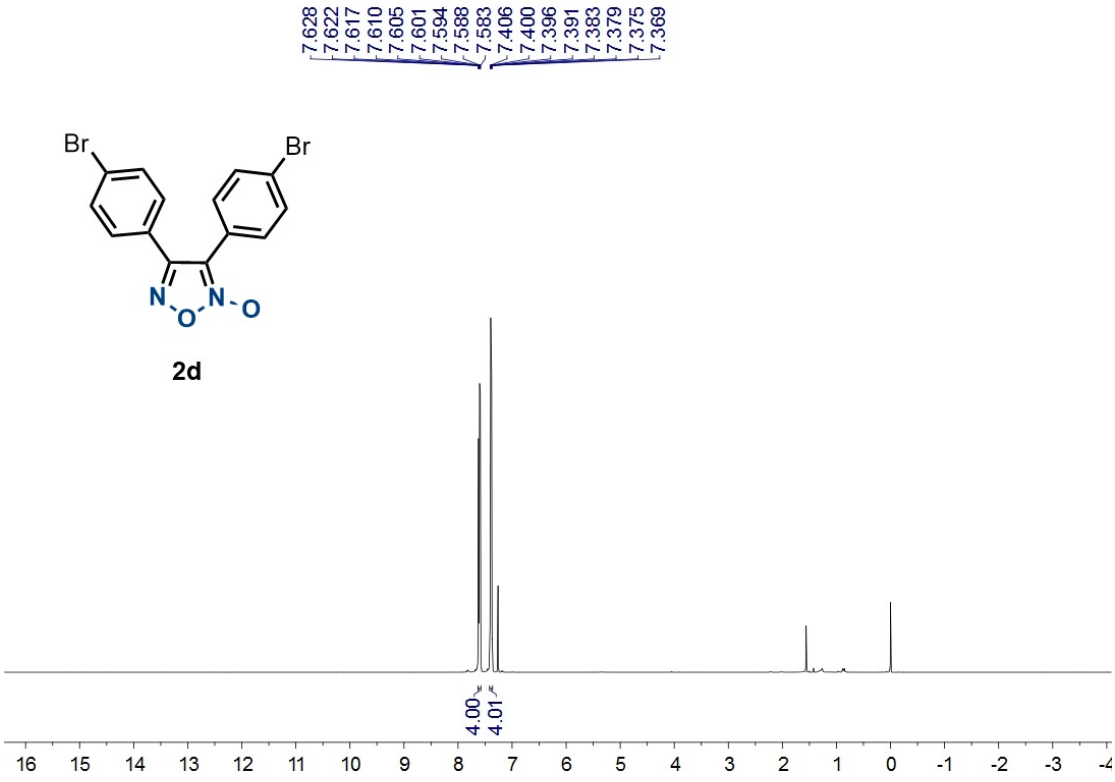
^{1}H NMR Spectrum of **2c** ($CDCl_3$, 400 MHz)



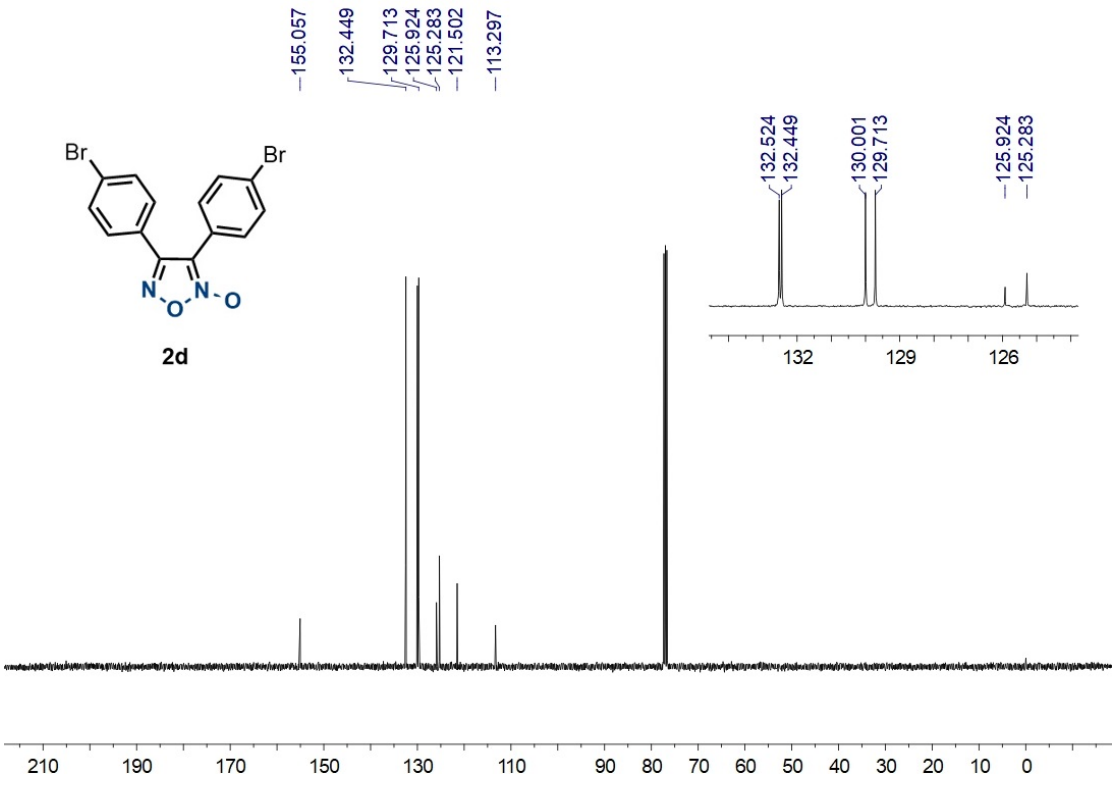
^{13}C NMR Spectrum of **2c** ($CDCl_3$, 100 MHz)



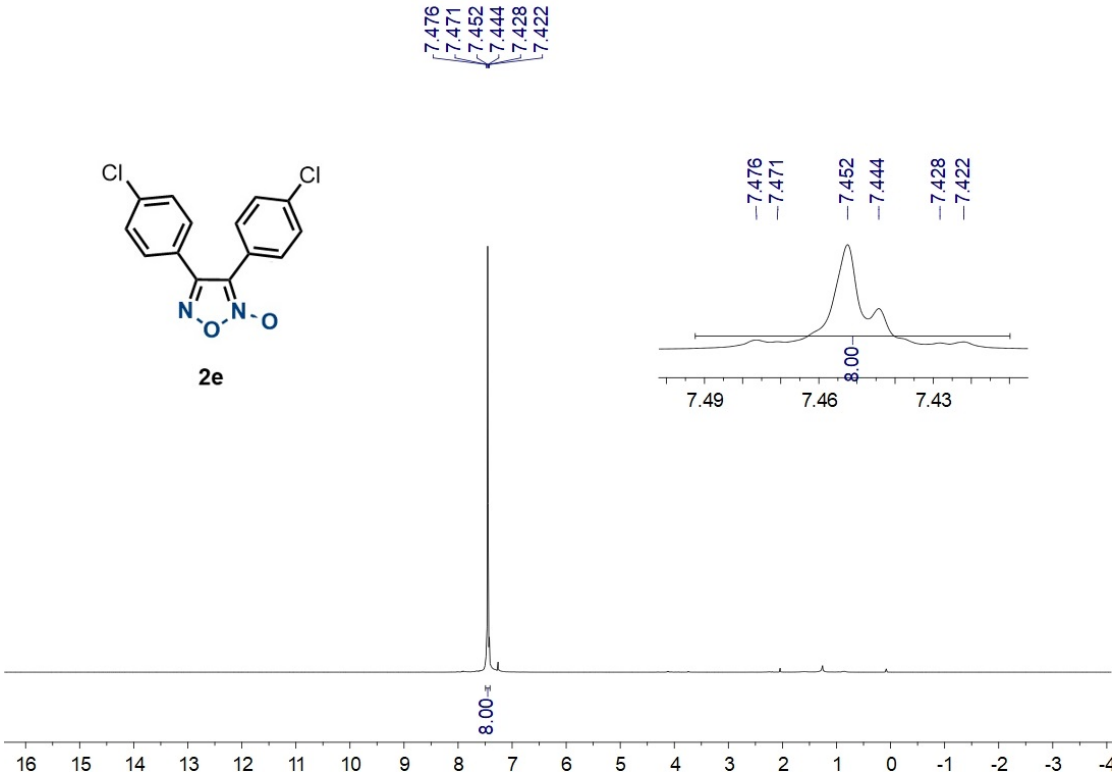
^{1}H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz)



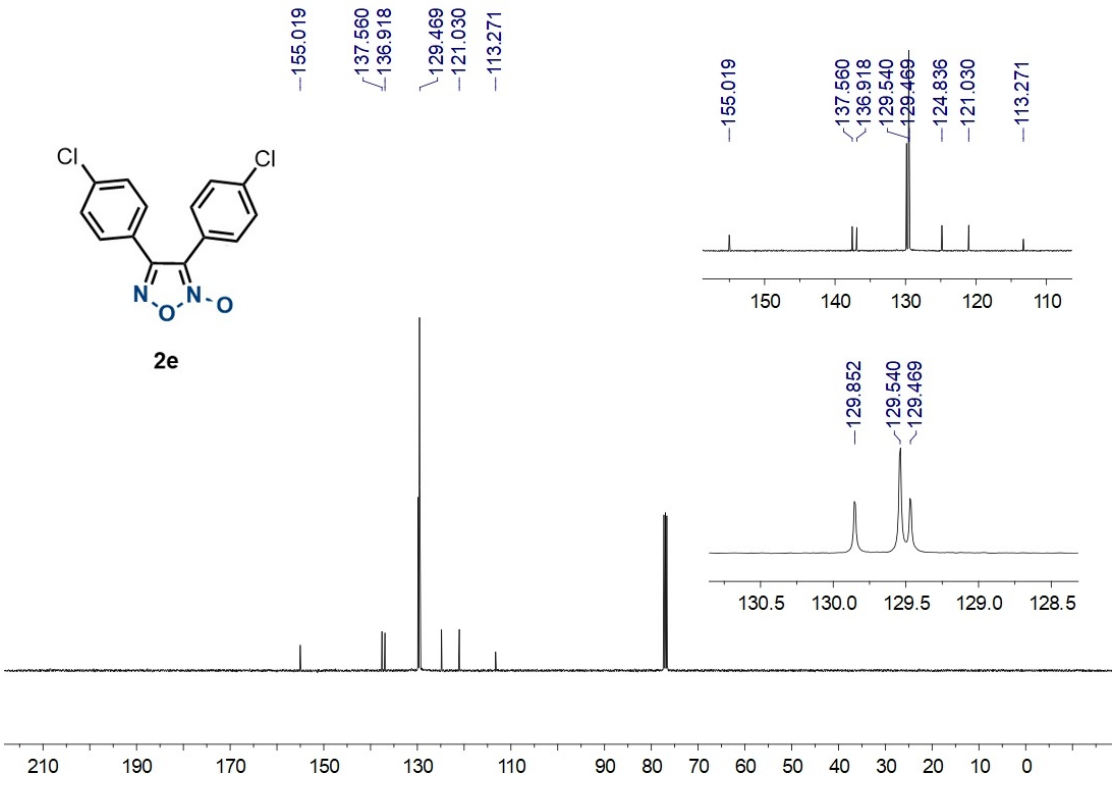
^{13}C NMR Spectrum of **2d** ($CDCl_3$, 100 MHz)



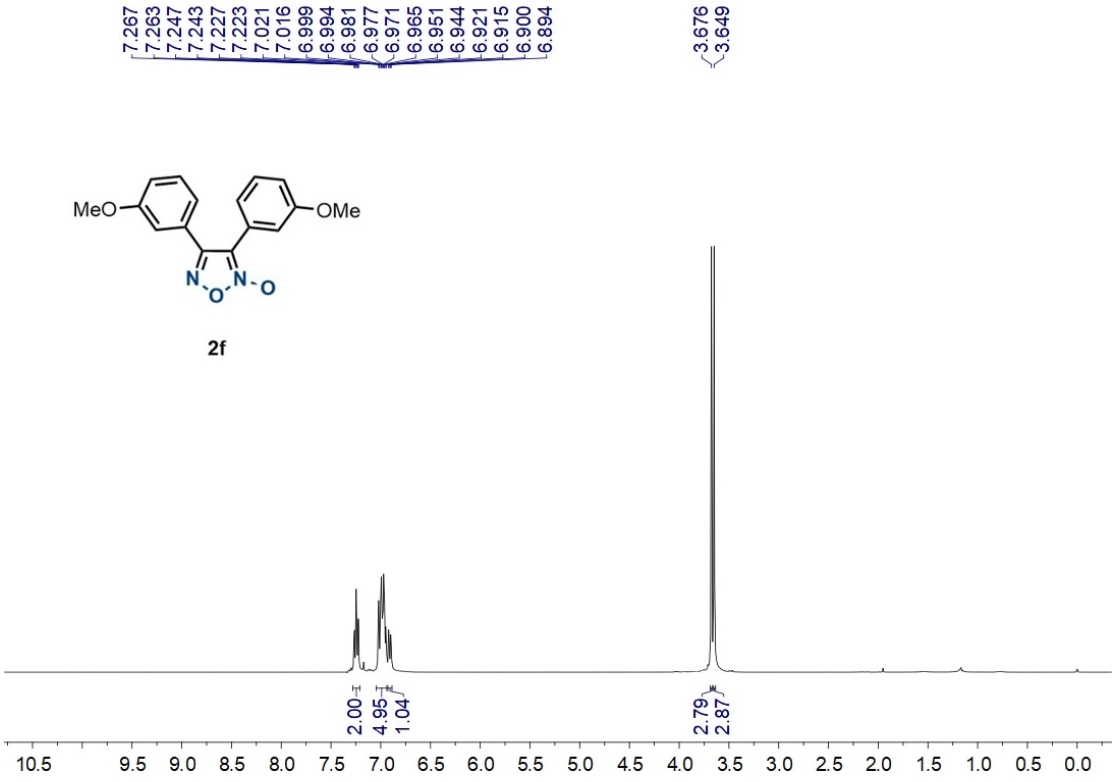
^{1}H NMR Spectrum of **2e** ($CDCl_3$, 400 MHz)



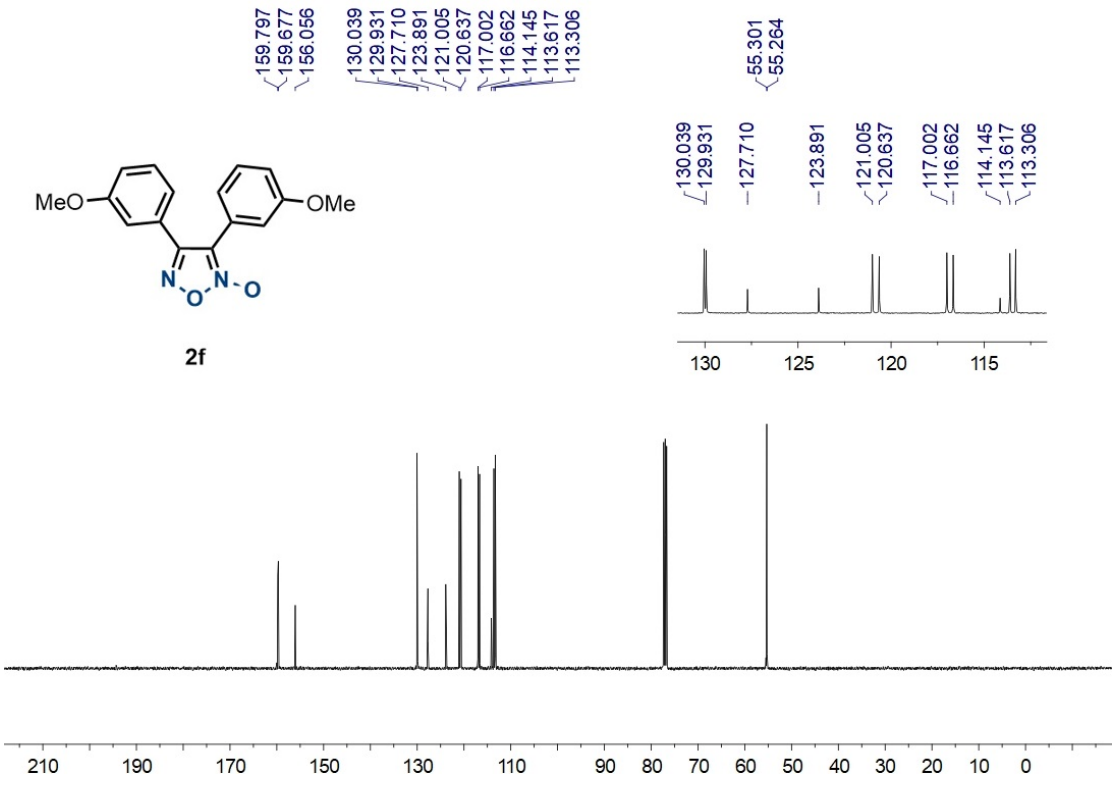
^{13}C NMR Spectrum of **2e** ($CDCl_3$, 100 MHz)



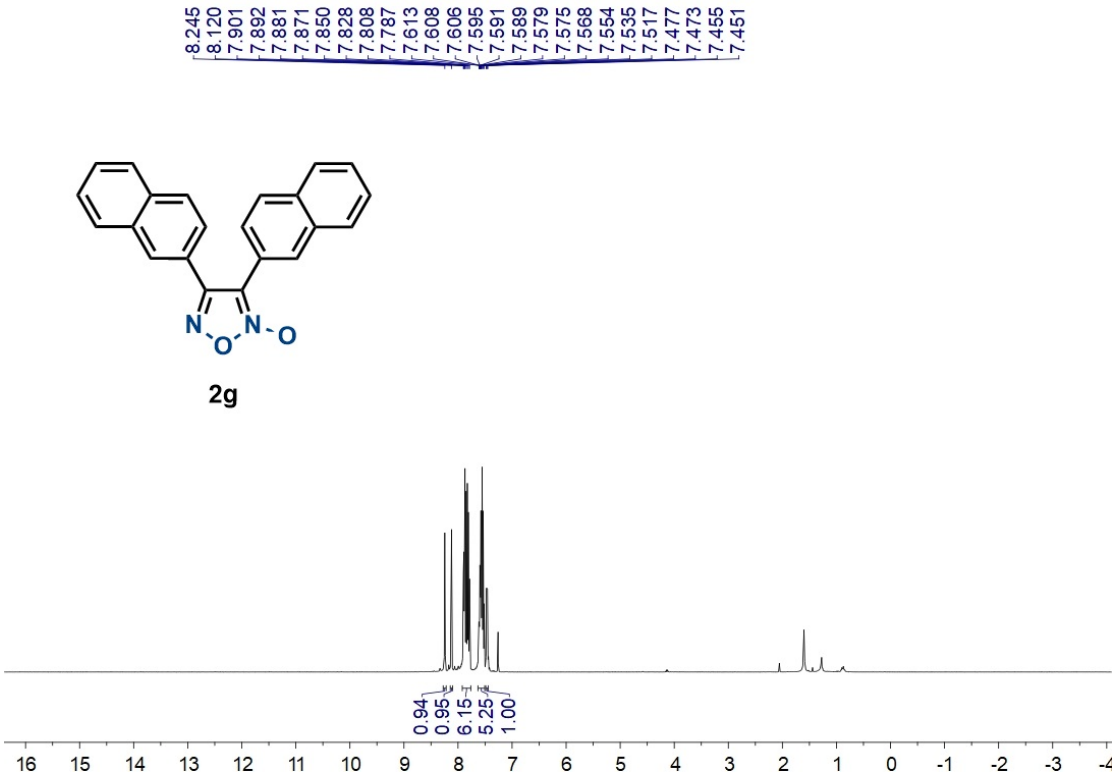
^{1}H NMR Spectrum of **2f** ($CDCl_3$, 400 MHz)



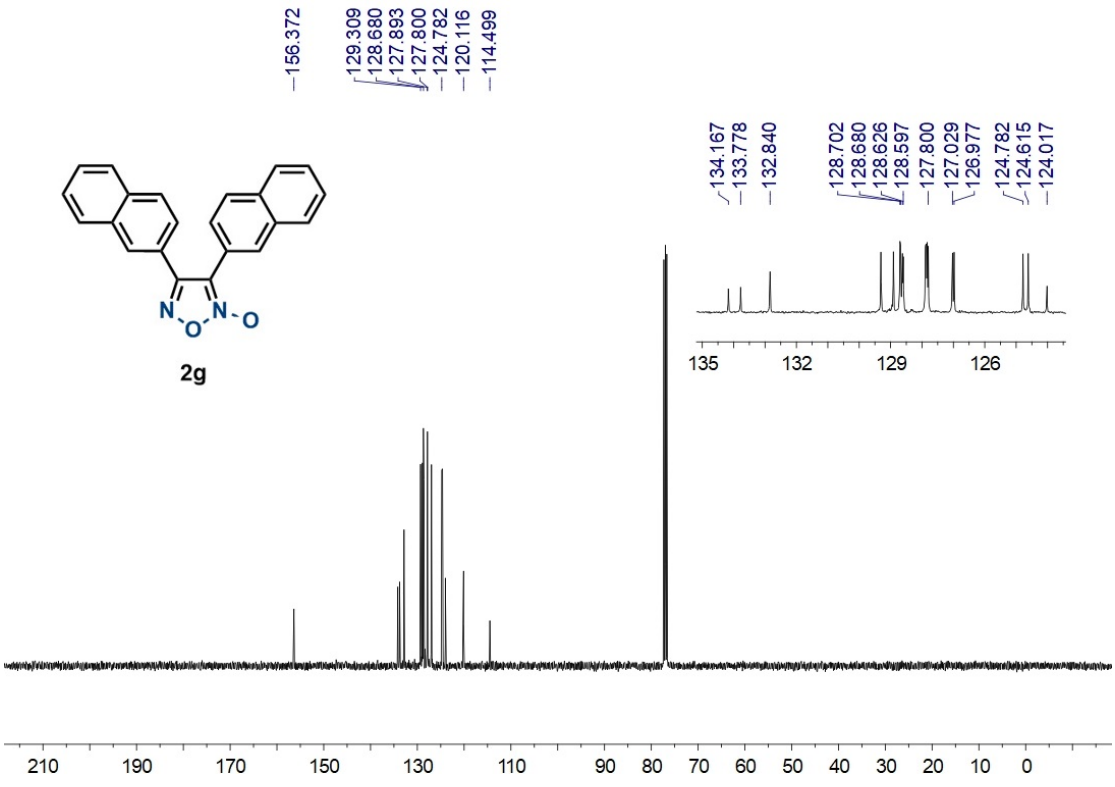
^{13}C NMR Spectrum of **2f** ($CDCl_3$, 100 MHz)



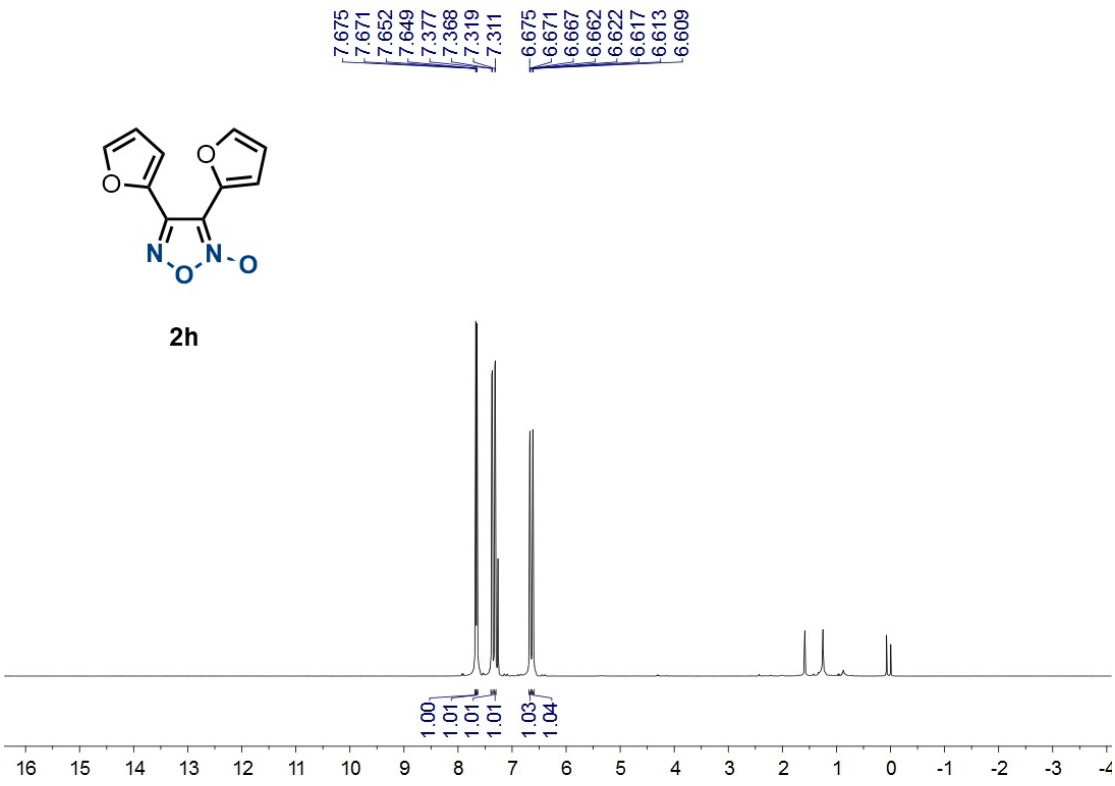
^{1}H NMR Spectrum of **2g** ($CDCl_3$, 400 MHz)



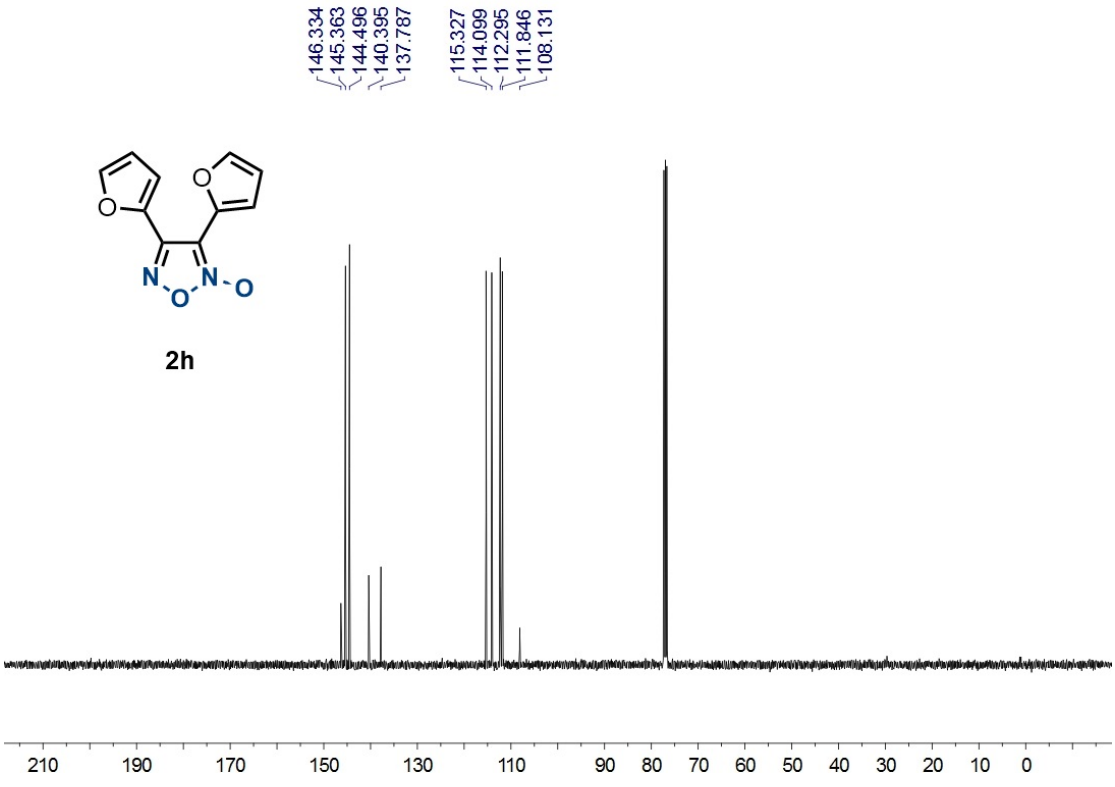
^{13}C NMR Spectrum of **2g** ($CDCl_3$, 100 MHz)



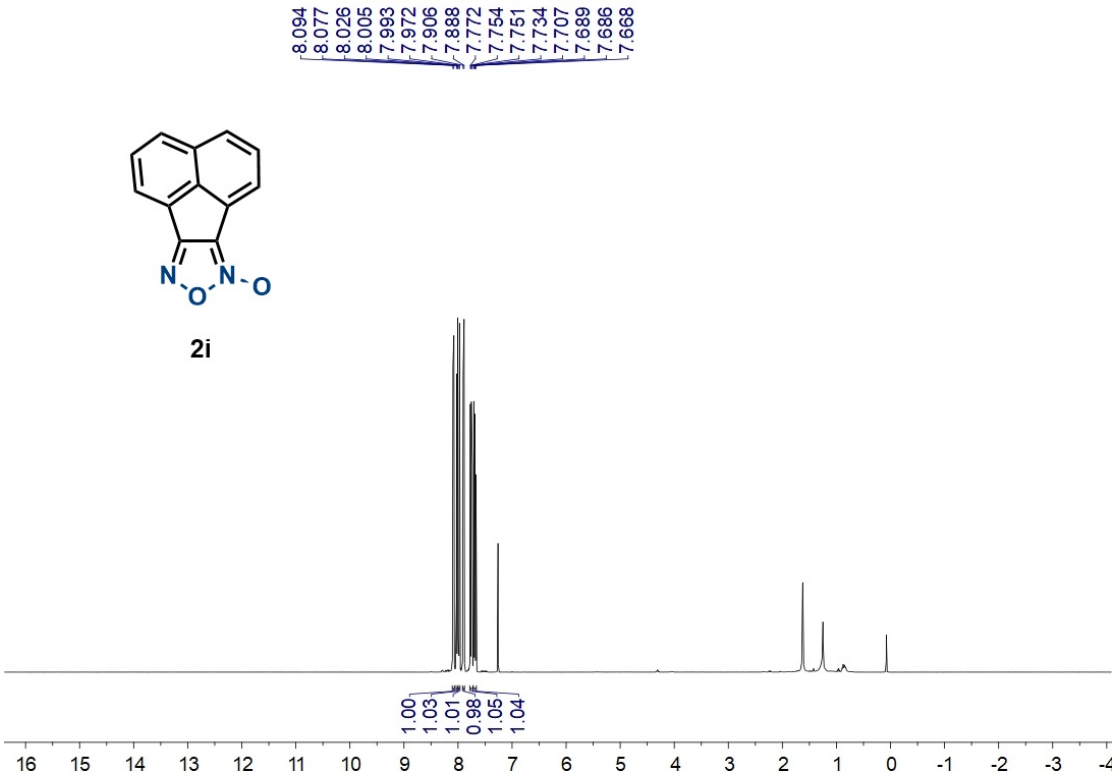
^{1}H NMR Spectrum of **2h** ($CDCl_3$, 400 MHz)



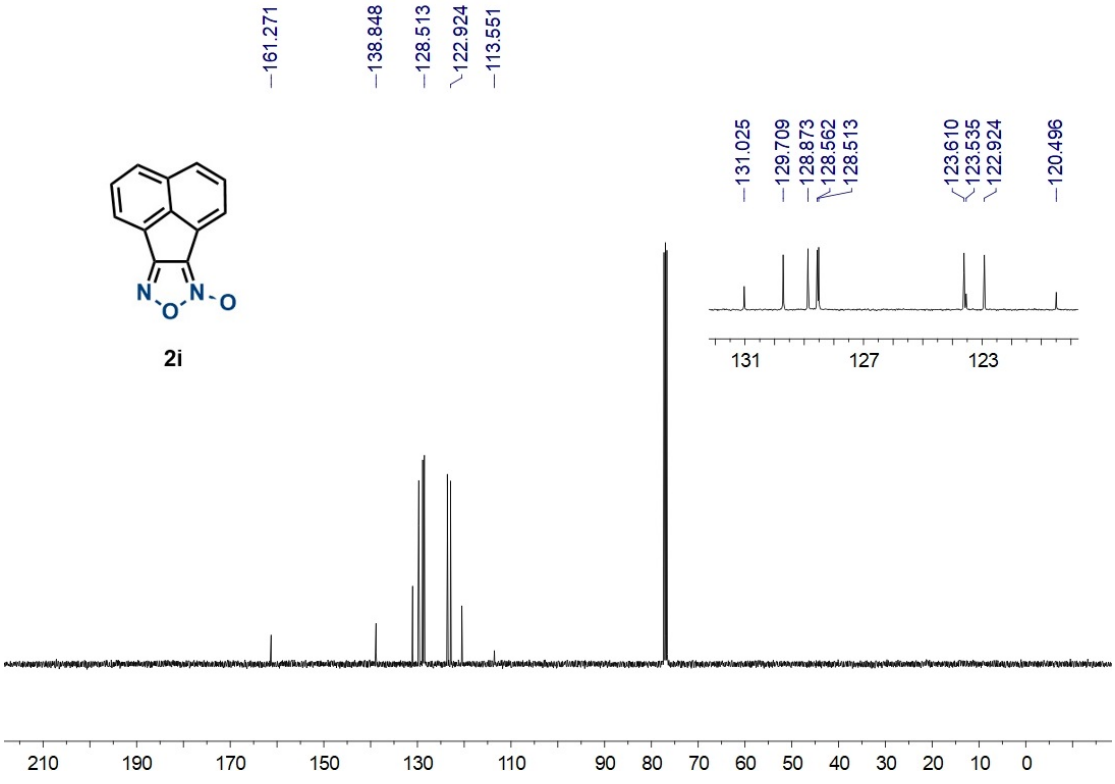
^{13}C NMR Spectrum of **2h** ($CDCl_3$, 100 MHz)



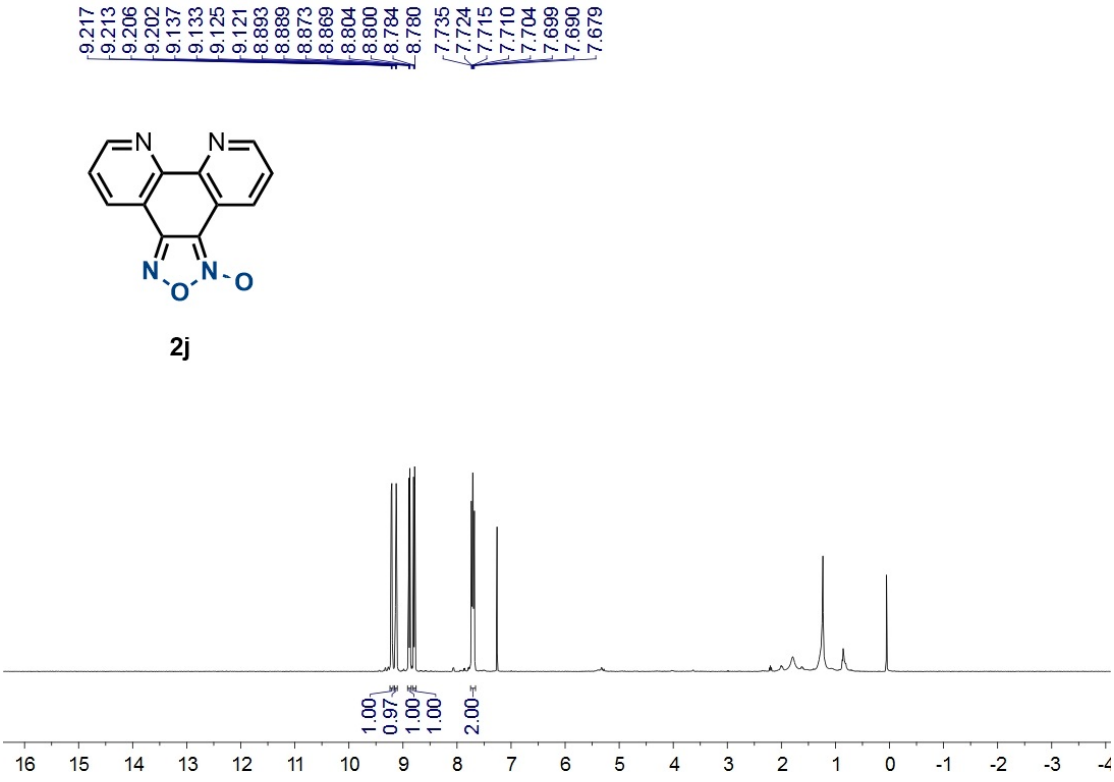
^{1}H NMR Spectrum of **2i** ($CDCl_3$, 400 MHz)



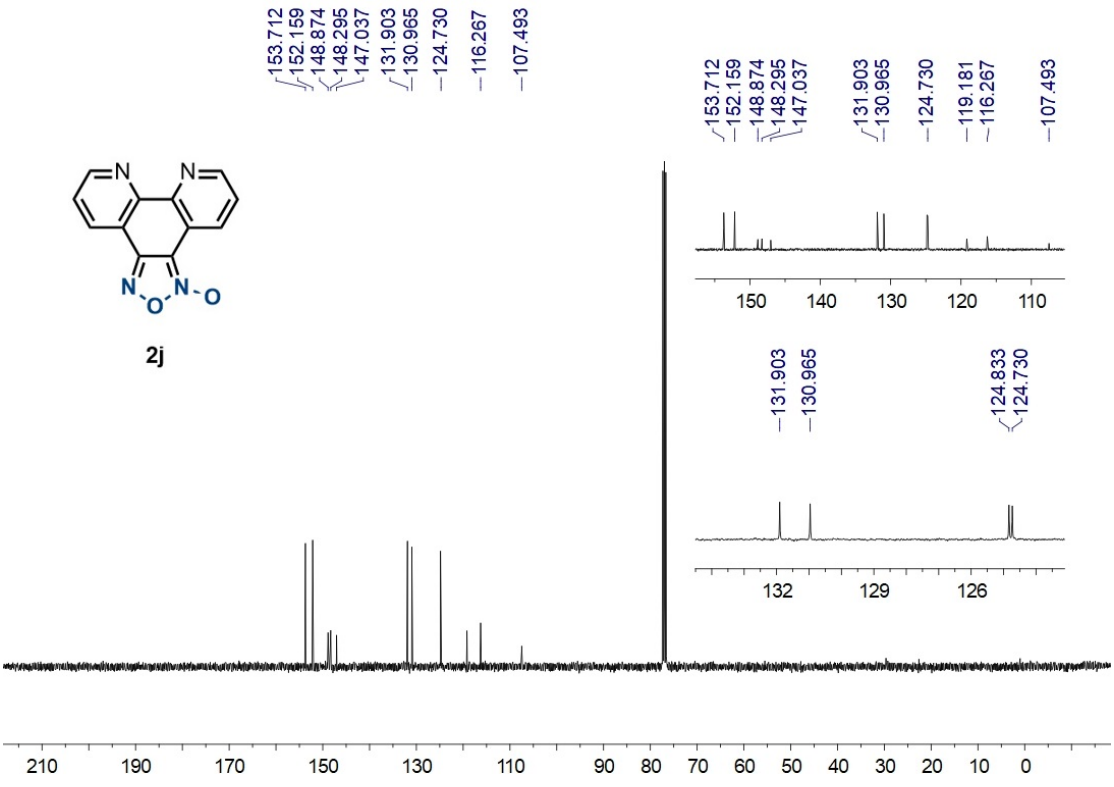
^{13}C NMR Spectrum of **2i** ($CDCl_3$, 100 MHz)



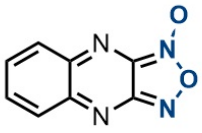
^{1}H NMR Spectrum of **2j** ($CDCl_3$, 400 MHz)



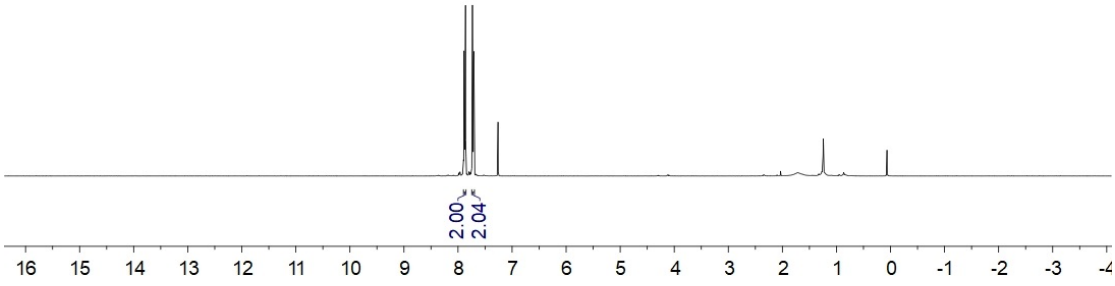
^{13}C NMR Spectrum of **2j** ($CDCl_3$, 100 MHz)



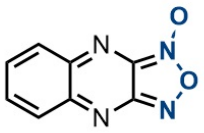
^{1}H NMR Spectrum of **2k** ($CDCl_3$, 400 MHz)



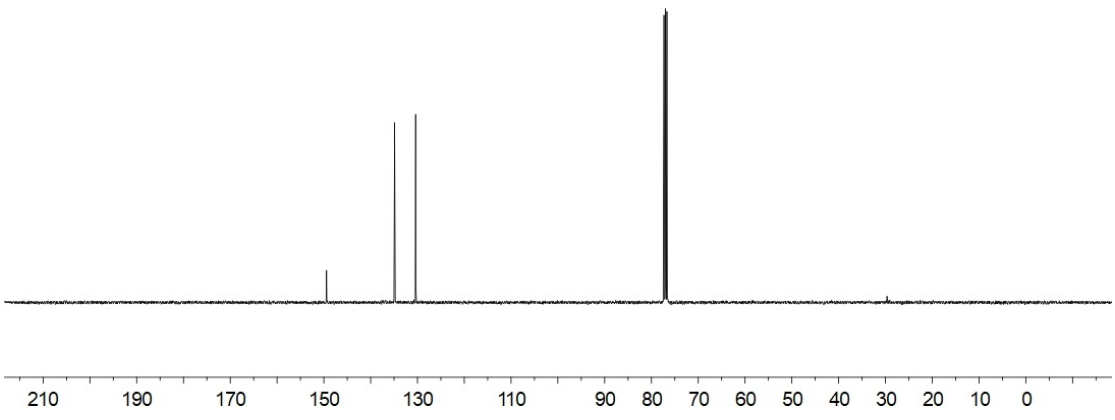
2k



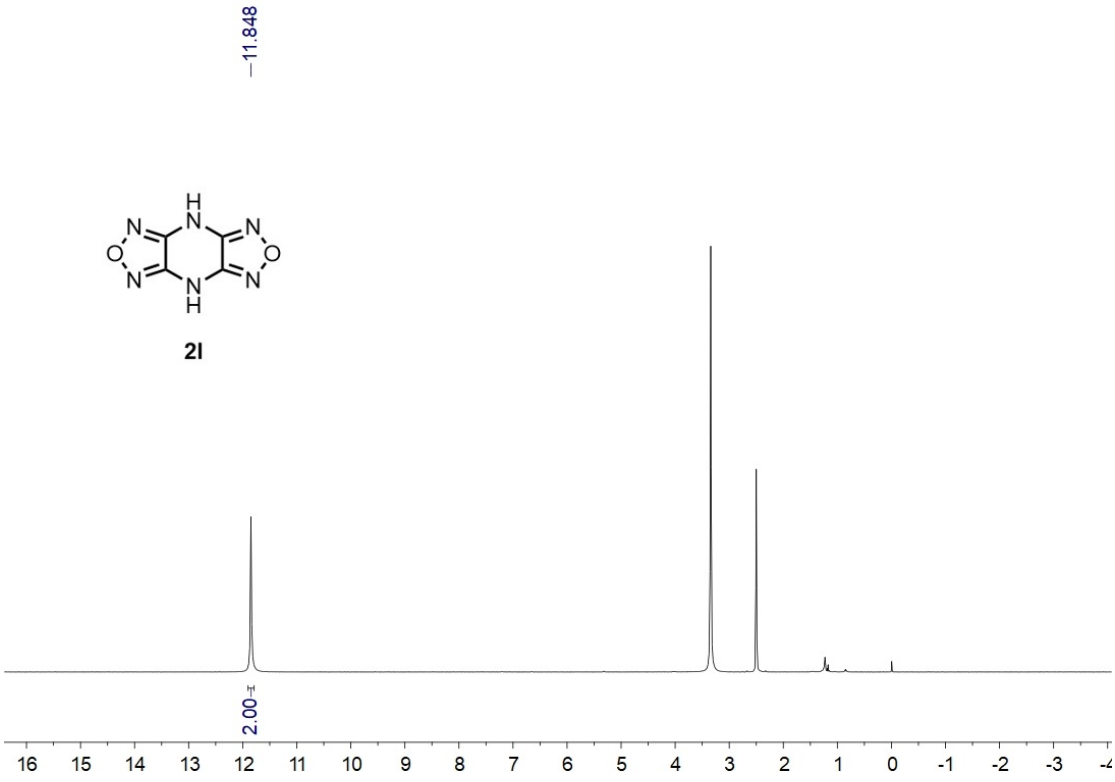
^{13}C NMR Spectrum of **2k** ($CDCl_3$, 100 MHz)



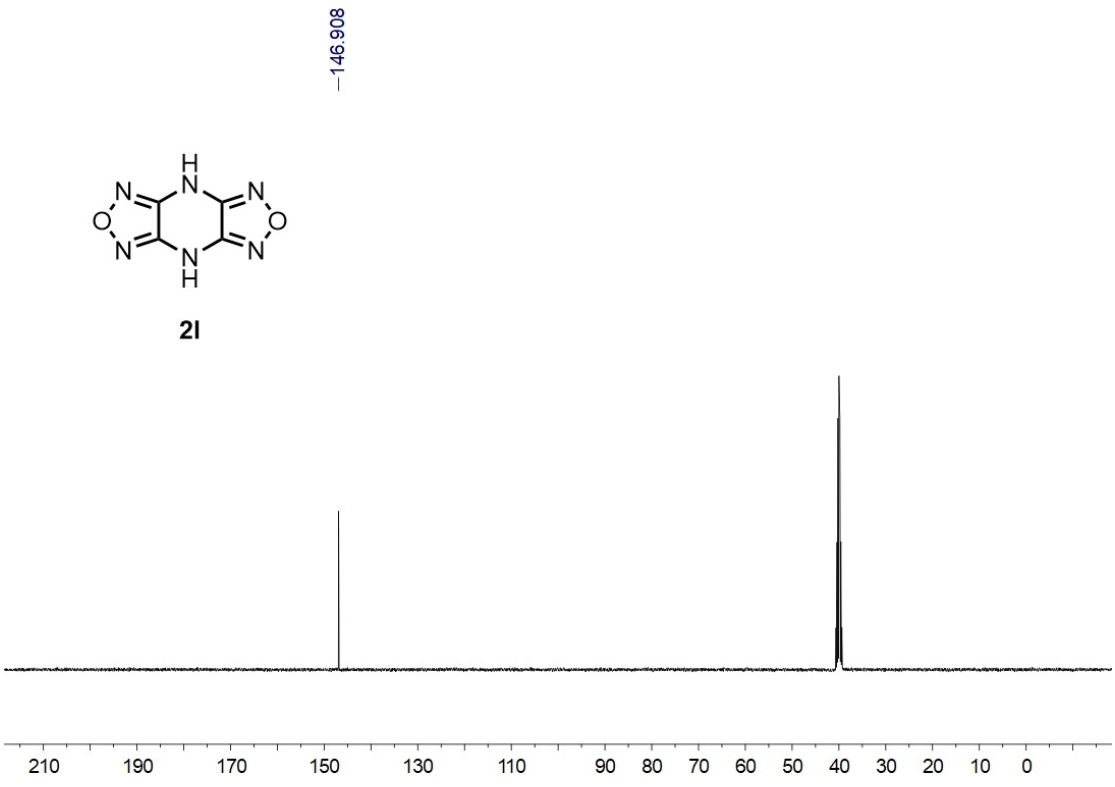
2k



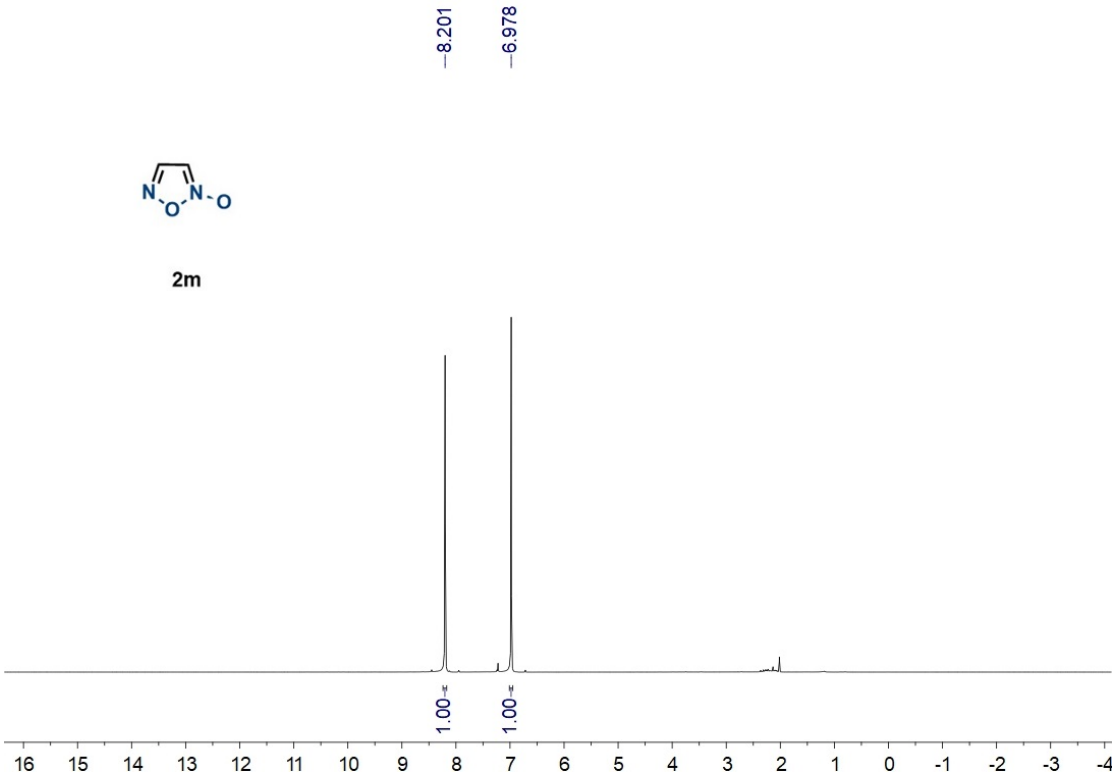
^{1}H NMR Spectrum of **2l** (DMSO, 400 MHz)



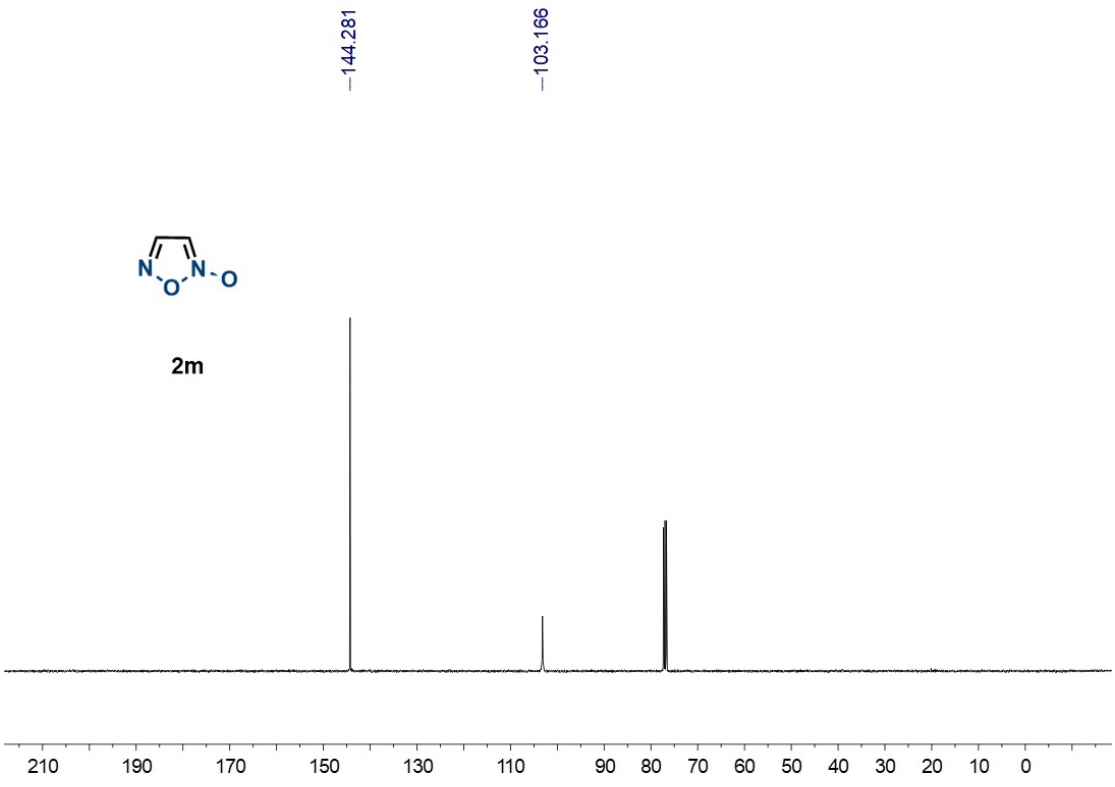
^{13}C NMR Spectrum of **2l** (DMSO, 100 MHz)



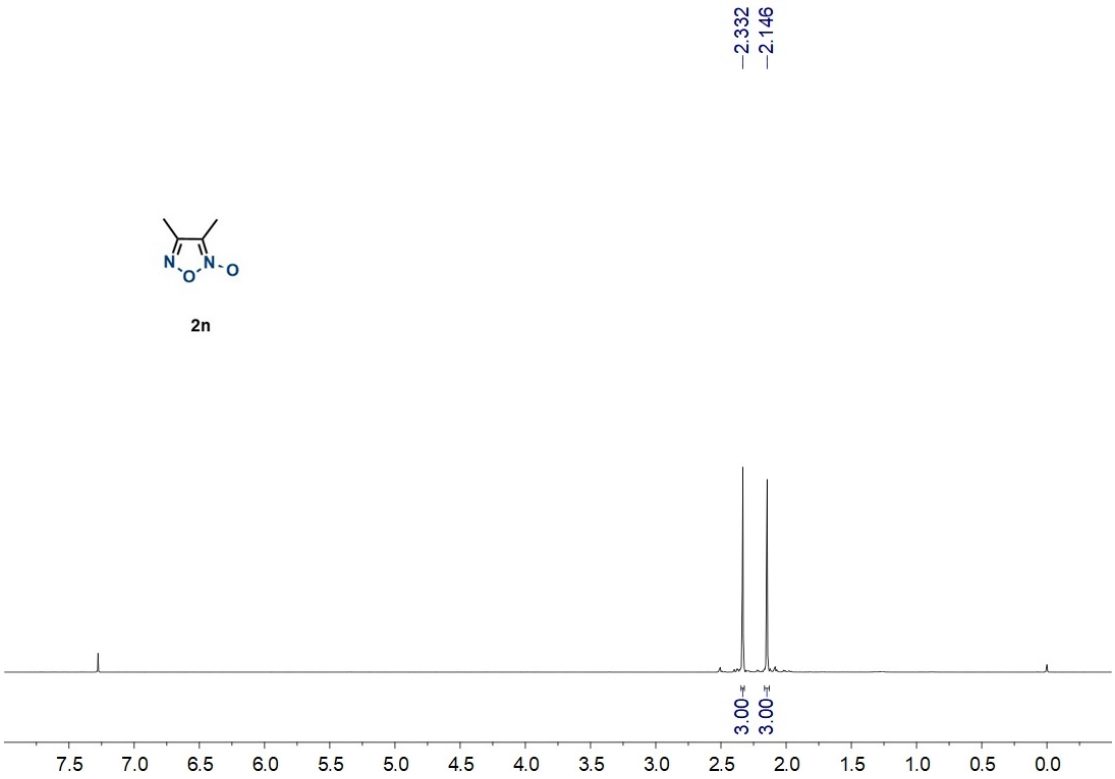
^{1}H NMR Spectrum of **2m** ($CDCl_3$, 400 MHz)



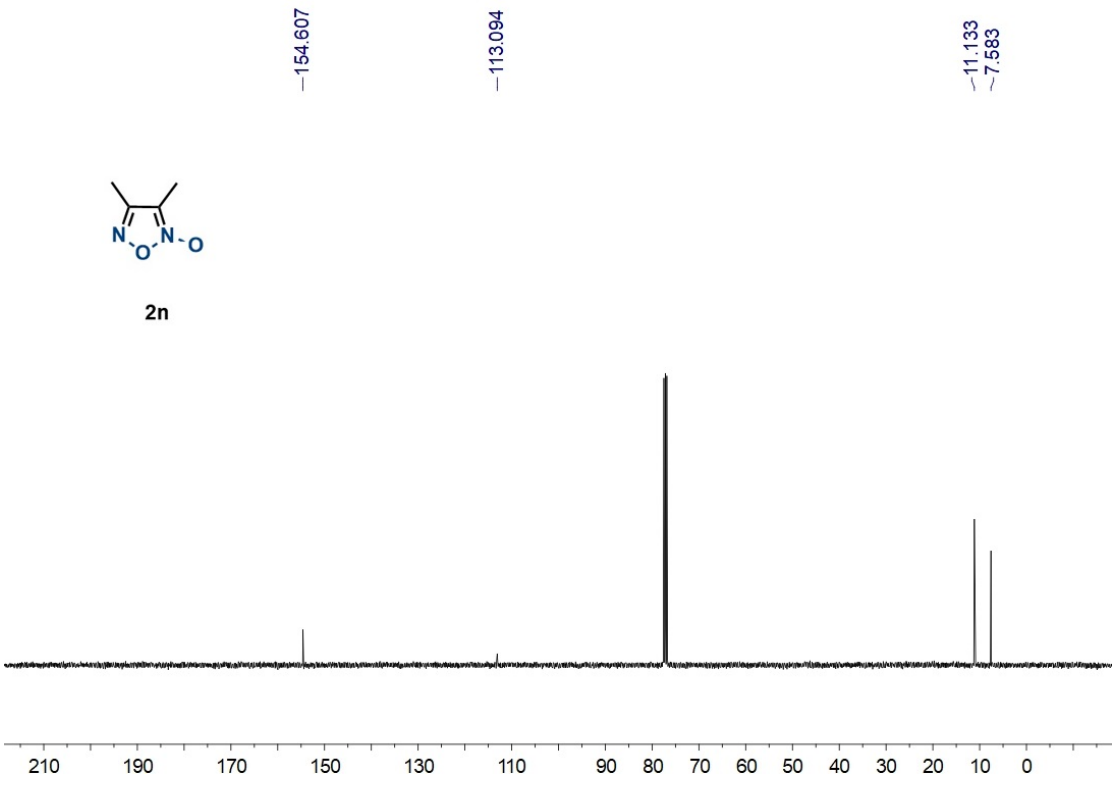
^{13}C NMR Spectrum of **2m** ($CDCl_3$, 100 MHz)



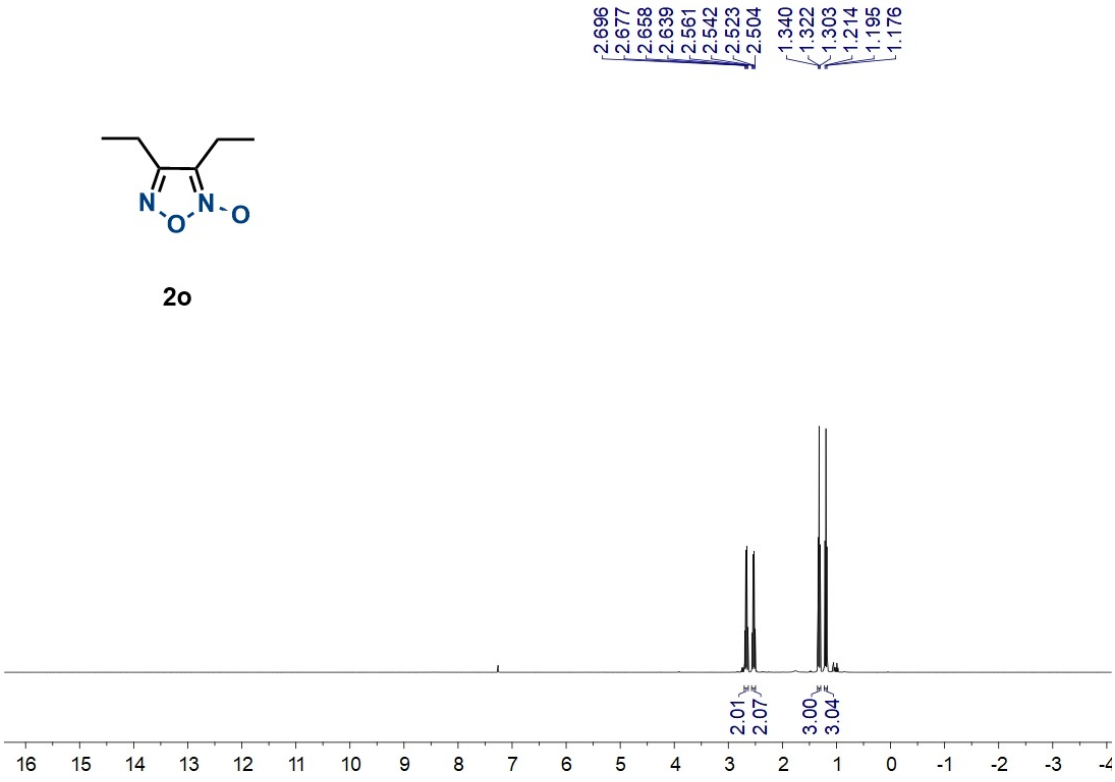
^{1}H NMR Spectrum of **2n** ($CDCl_3$, 400 MHz)



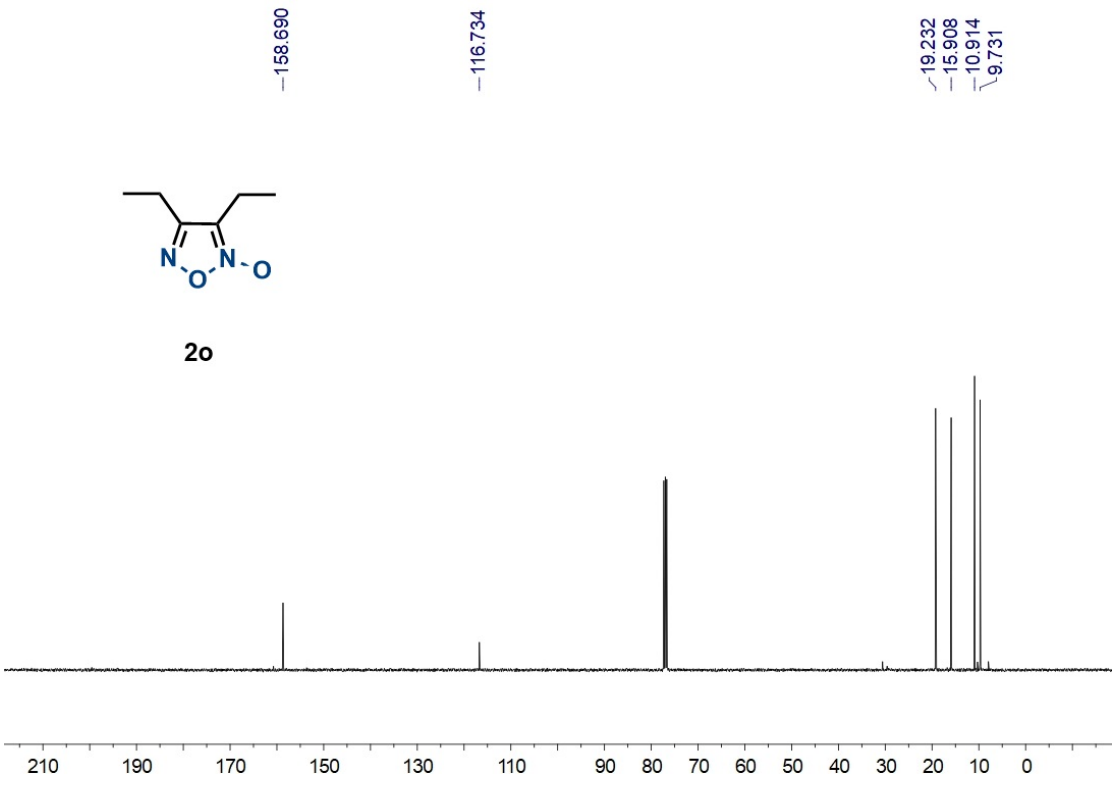
^{13}C NMR Spectrum of **2n** ($CDCl_3$, 100 MHz)



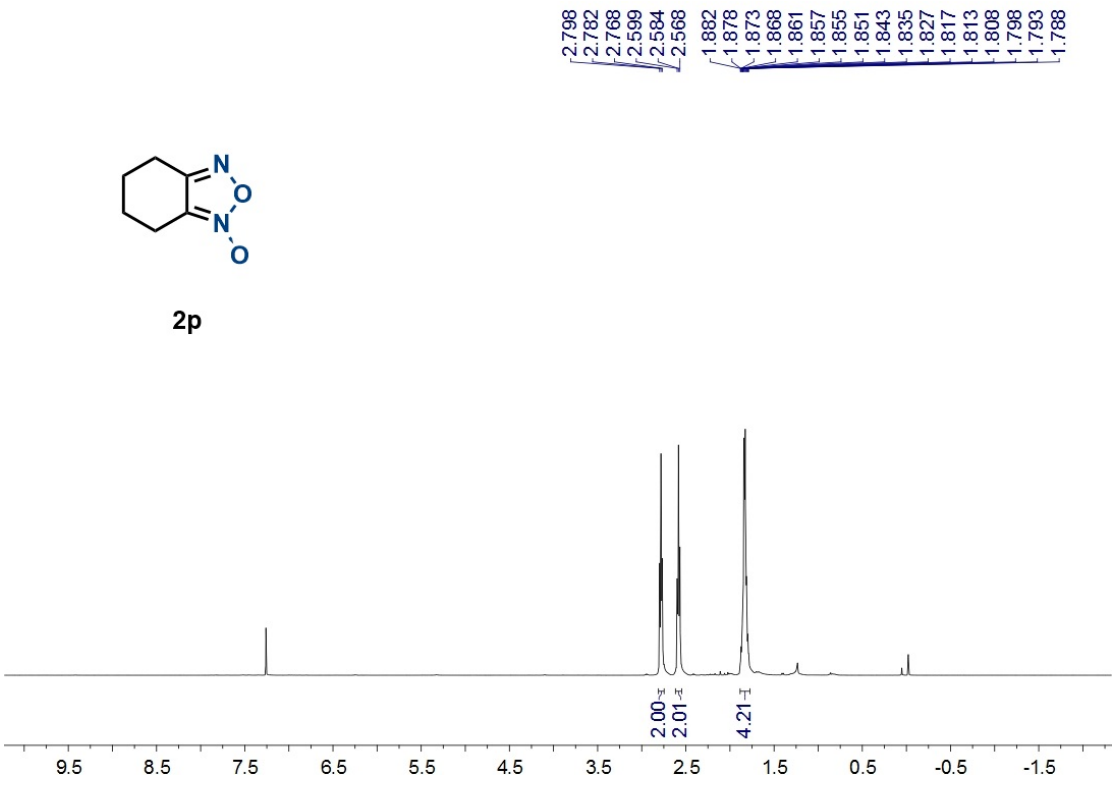
^{1}H NMR Spectrum of **2o** ($CDCl_3$, 400 MHz)



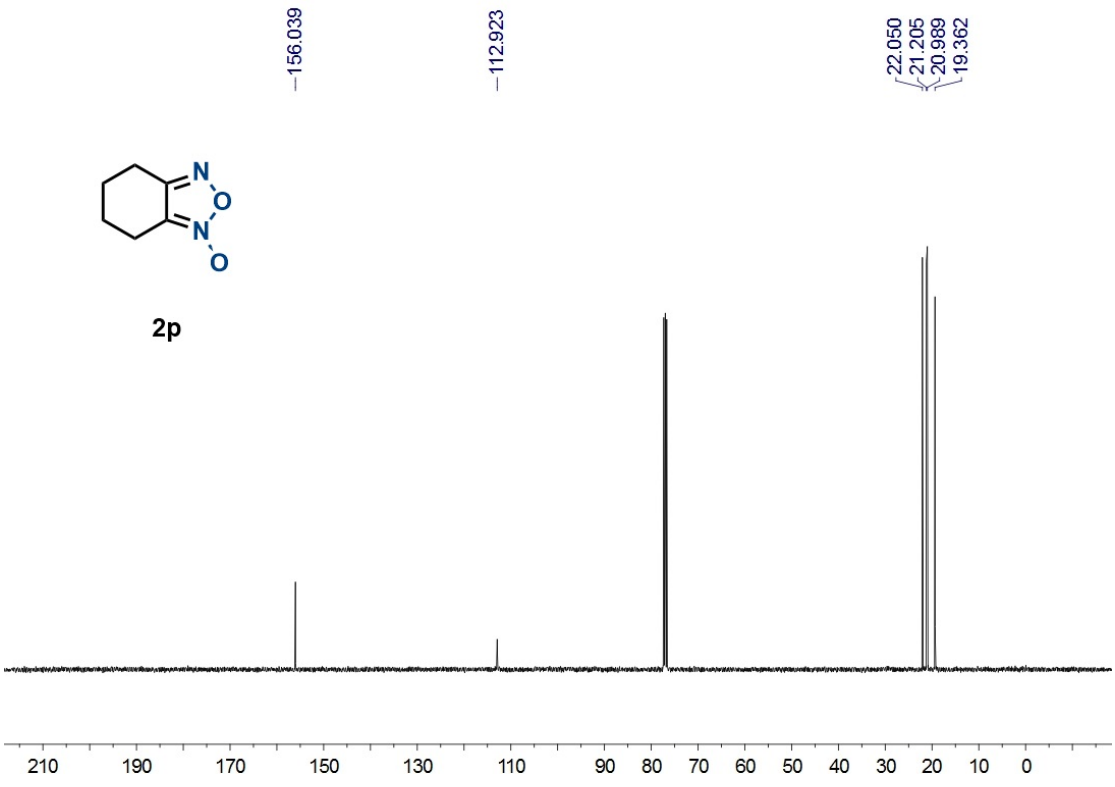
^{13}C NMR Spectrum of **2o** ($CDCl_3$, 100 MHz)



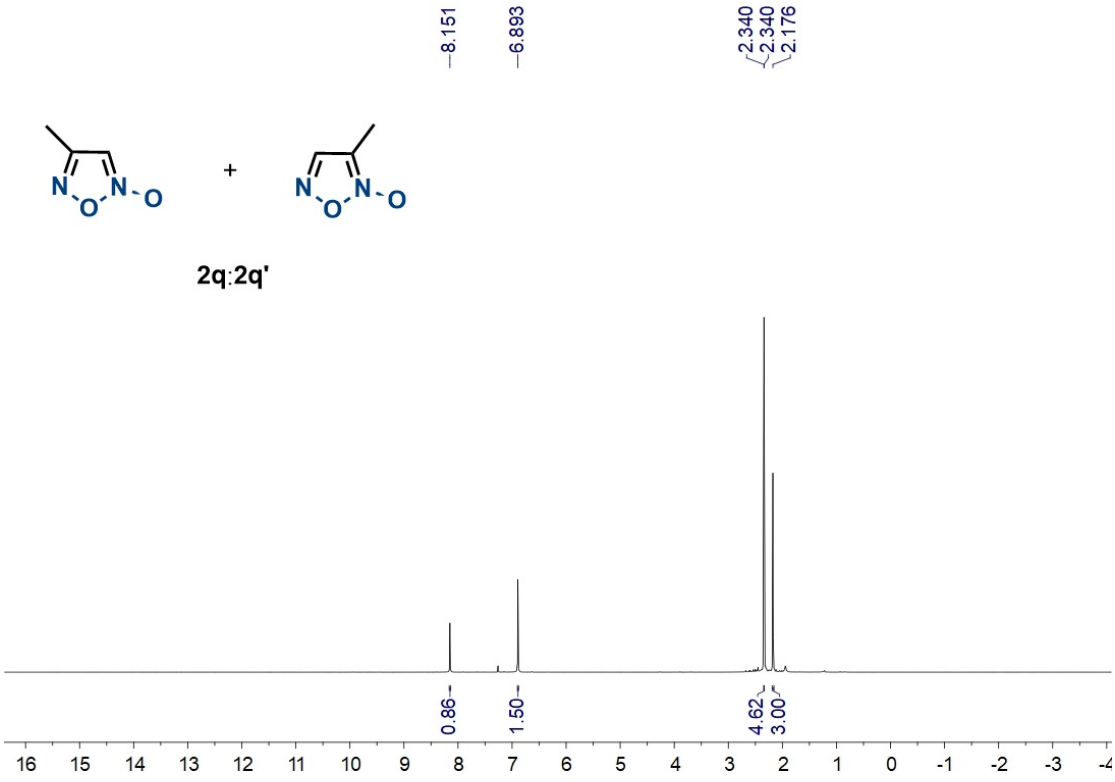
^{1}H NMR Spectrum of **2p** ($CDCl_3$, 400 MHz)



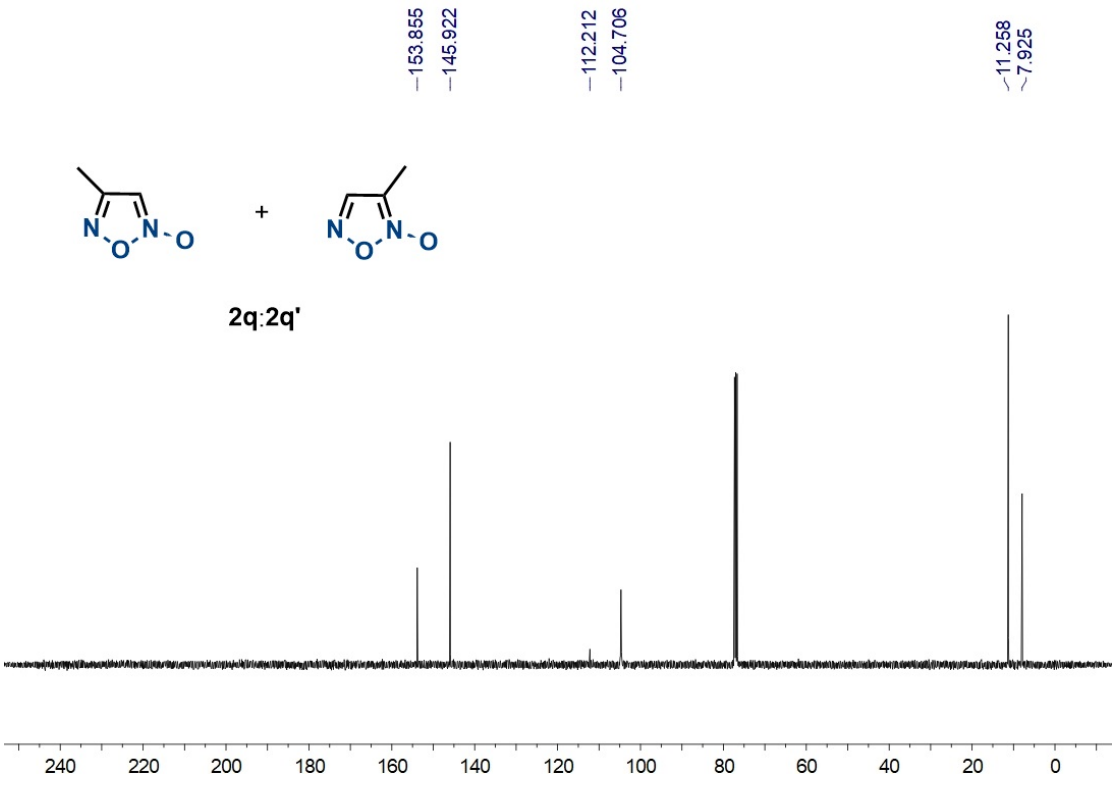
^{13}C NMR Spectrum of **2p** ($CDCl_3$, 100 MHz)



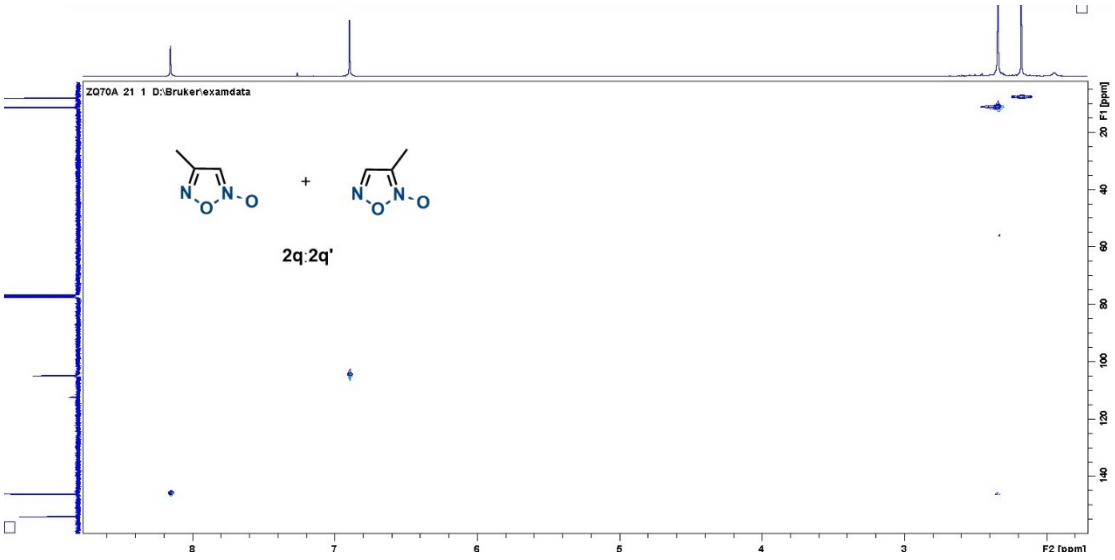
^{1}H NMR Spectrum of **2q** ($CDCl_3$, 400 MHz)



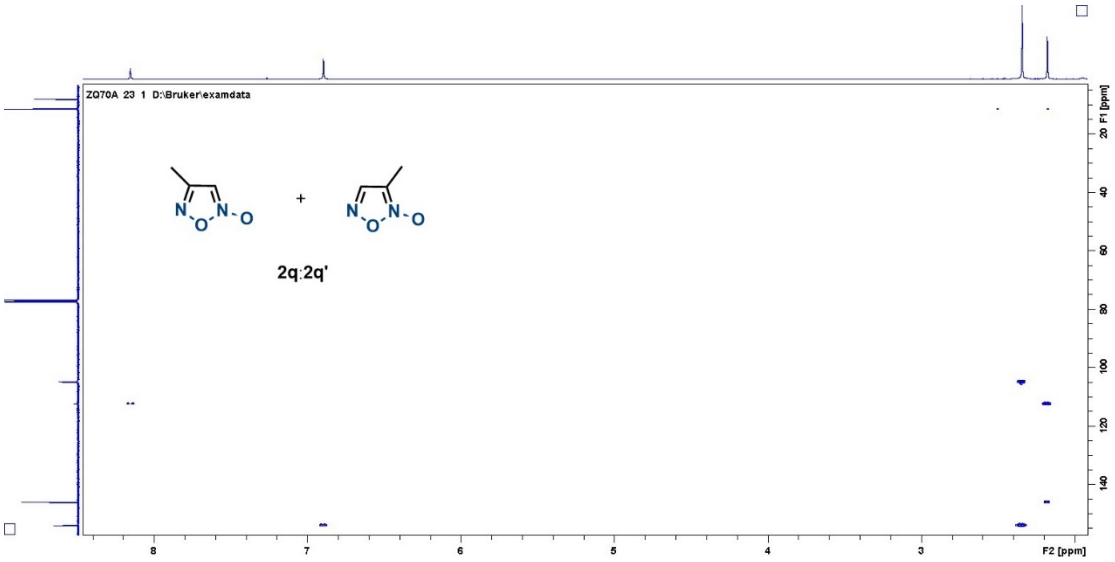
^{13}C NMR Spectrum of **2q** ($CDCl_3$, 100 MHz)



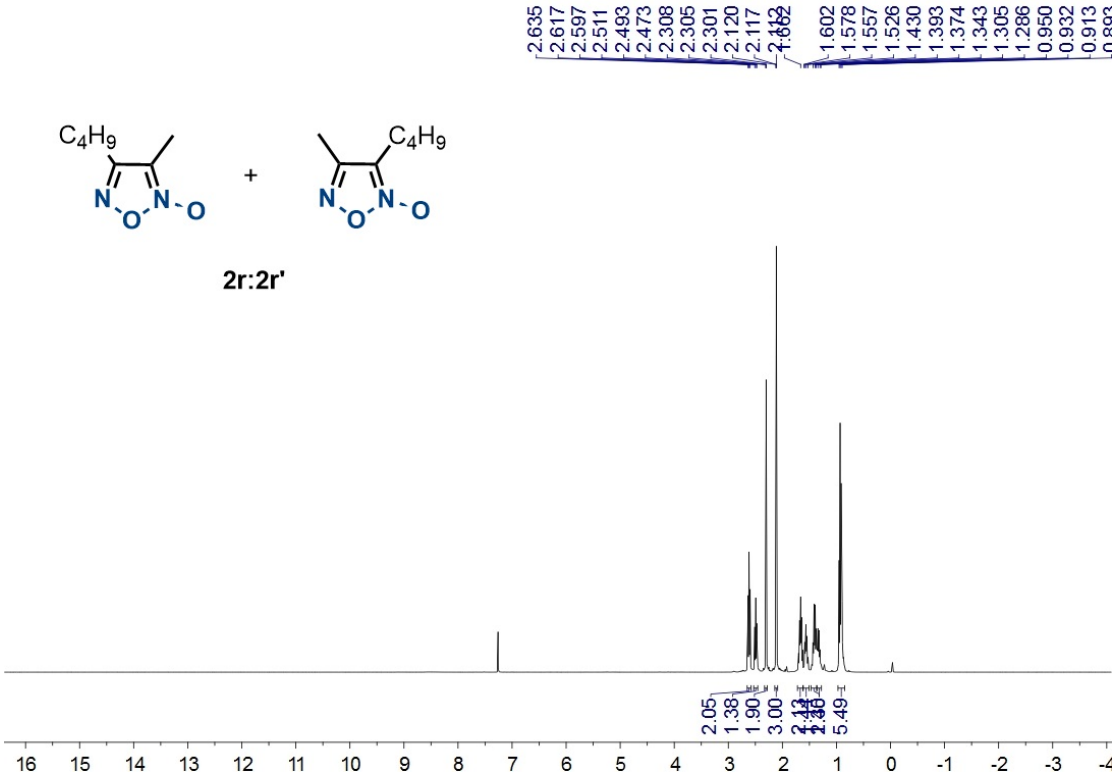
^{1}H-^{13}C HSQC NMR Spectrum of **2q** ($CDCl_3$, 400 MHz)



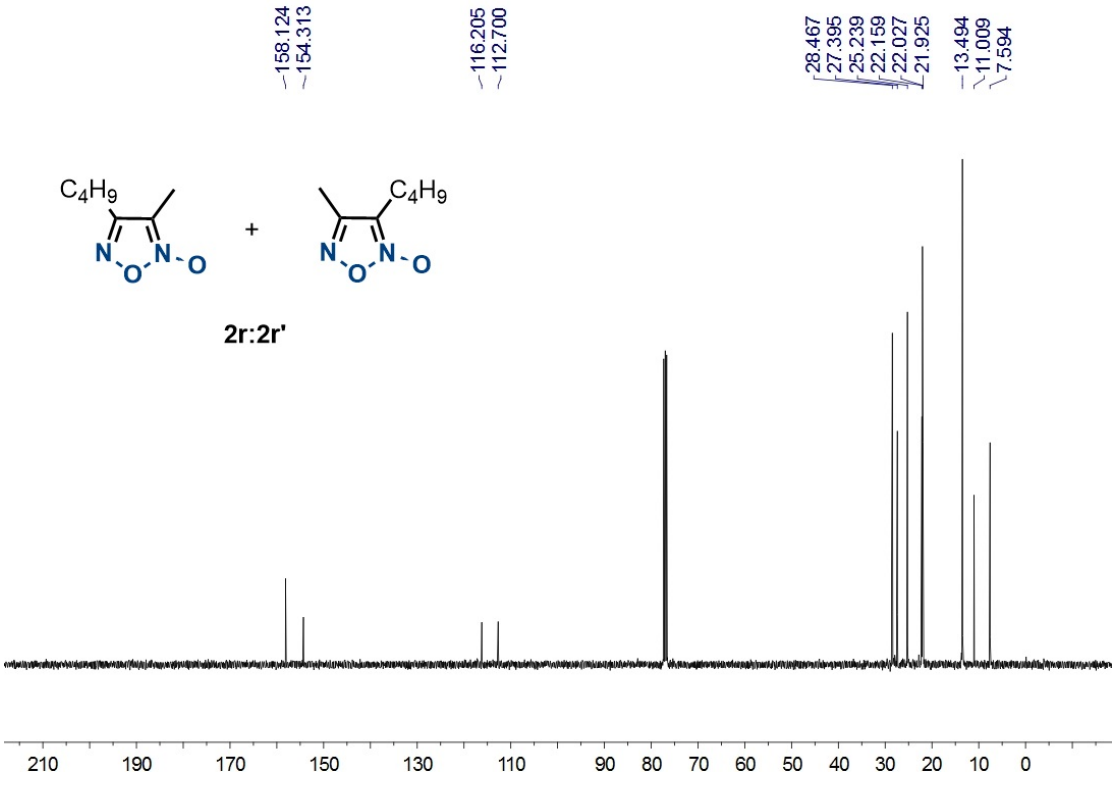
^{1}H-^{13}C HMBC NMR Spectrum of **2q** ($CDCl_3$, 400 MHz)



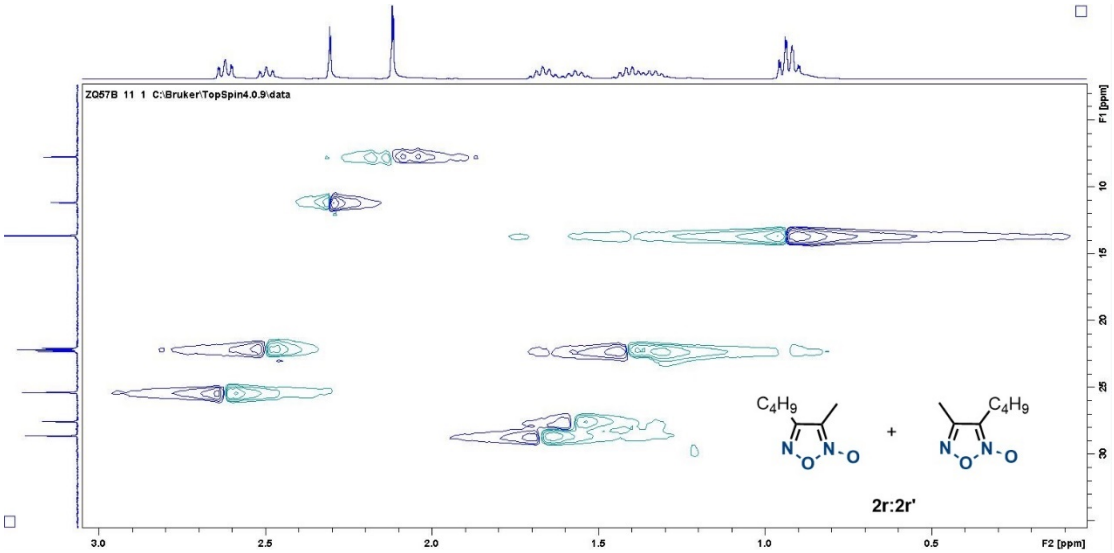
^{1}H NMR Spectrum of **2r** ($CDCl_3$, 400 MHz)



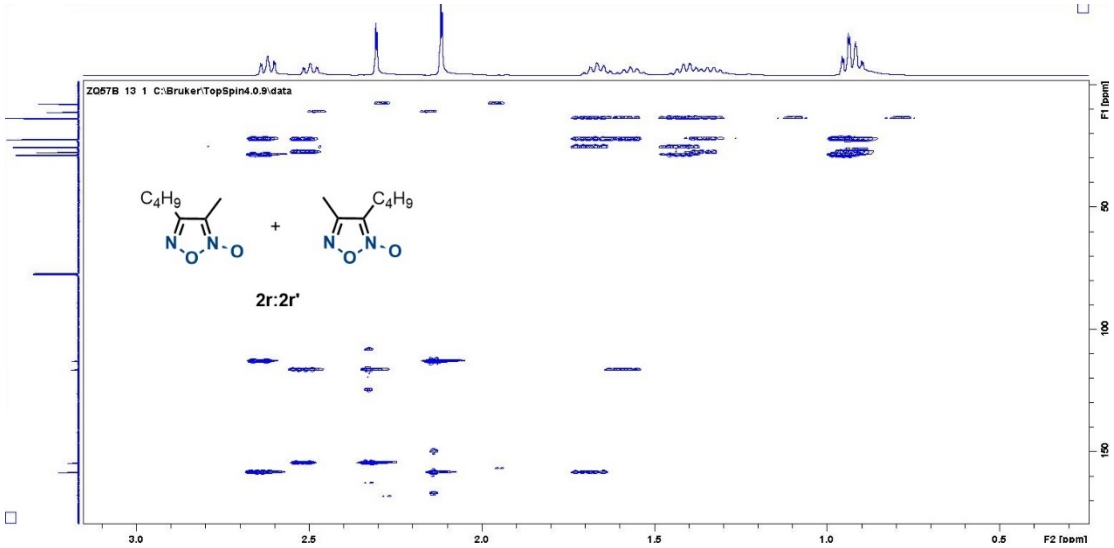
^{13}C NMR Spectrum of **2r** ($CDCl_3$, 100 MHz)



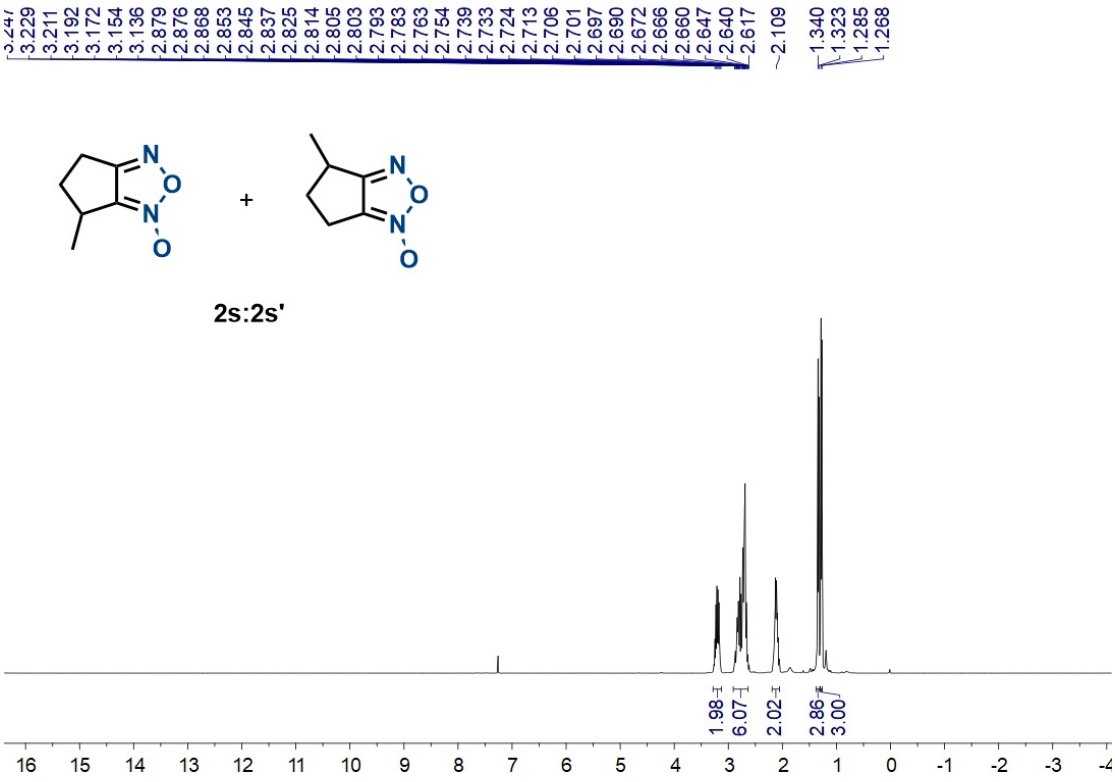
^{1}H-^{13}C HSQC NMR Spectrum of **2r** ($CDCl_3$, 400 MHz)



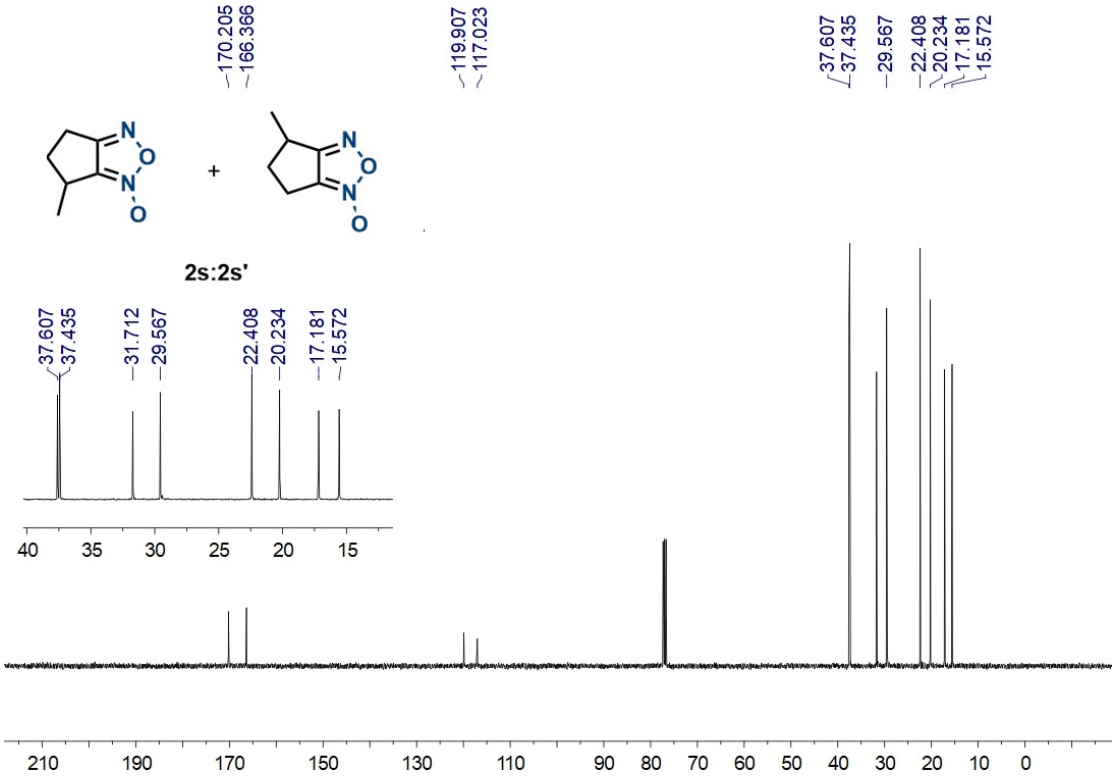
^{1}H-^{13}C HMBC NMR Spectrum of **2r** ($CDCl_3$, 400 MHz)



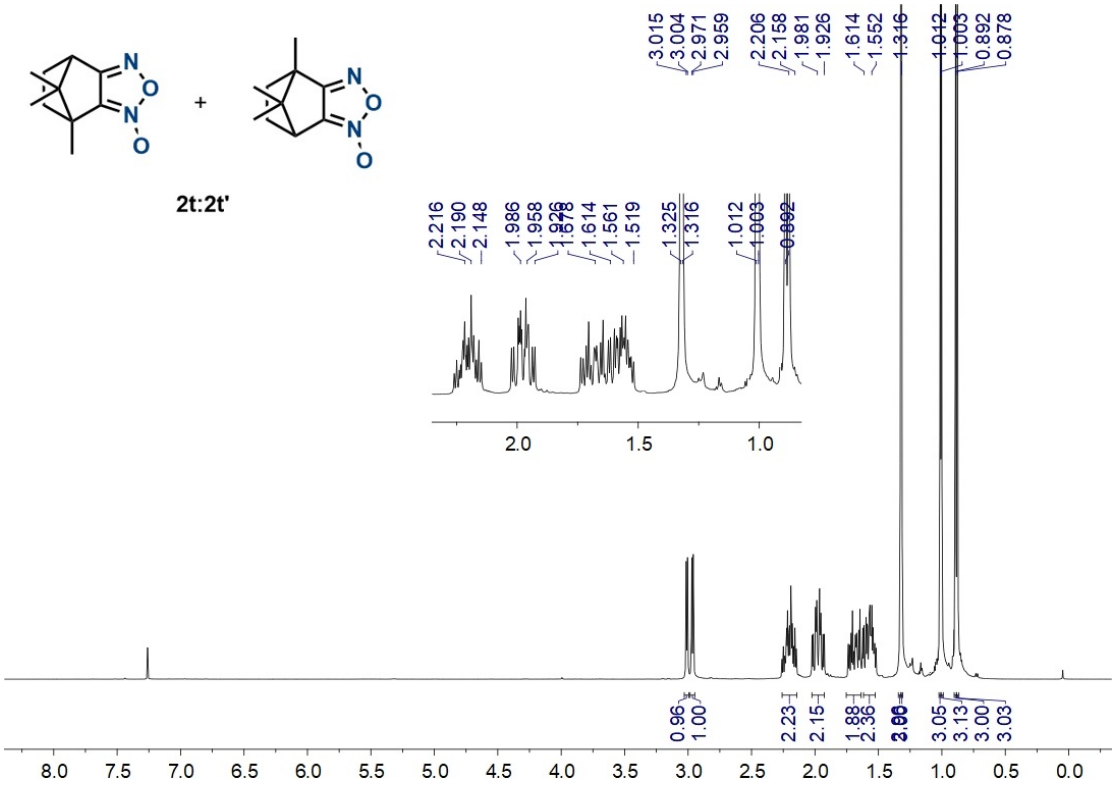
^{1}H NMR Spectrum of **2s** ($CDCl_3$, 400 MHz)



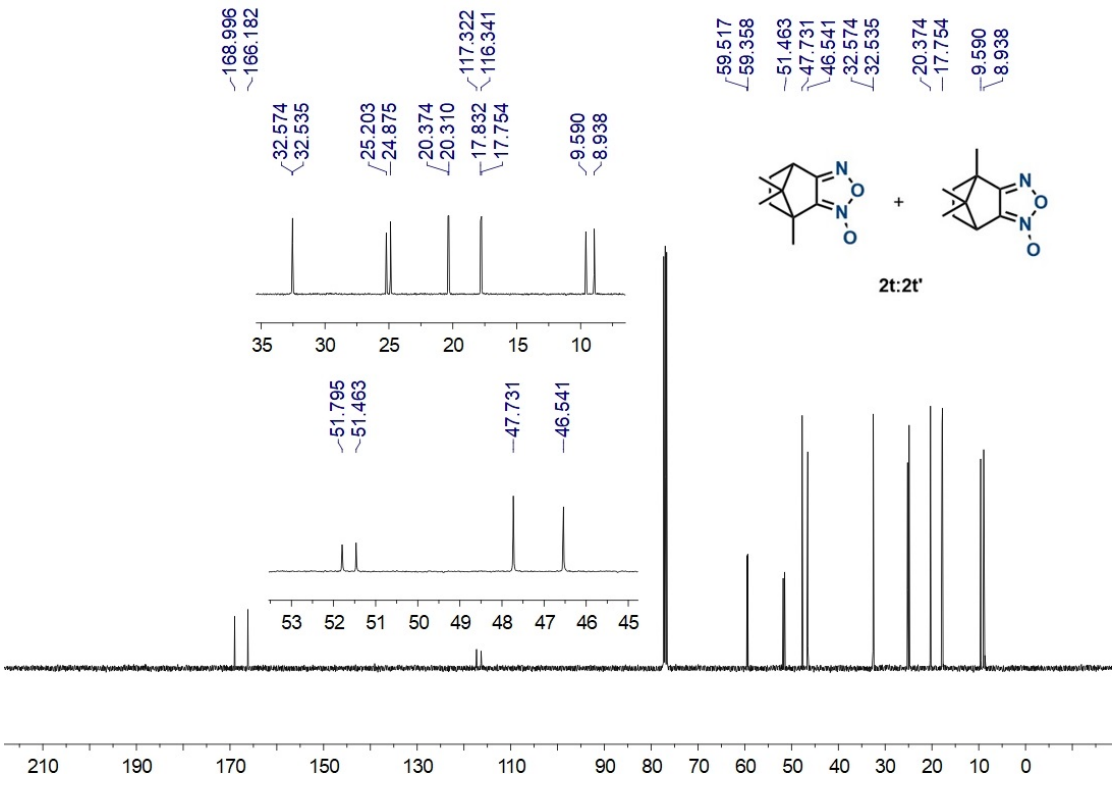
^{13}C NMR Spectrum of **2s** ($CDCl_3$, 100 MHz)



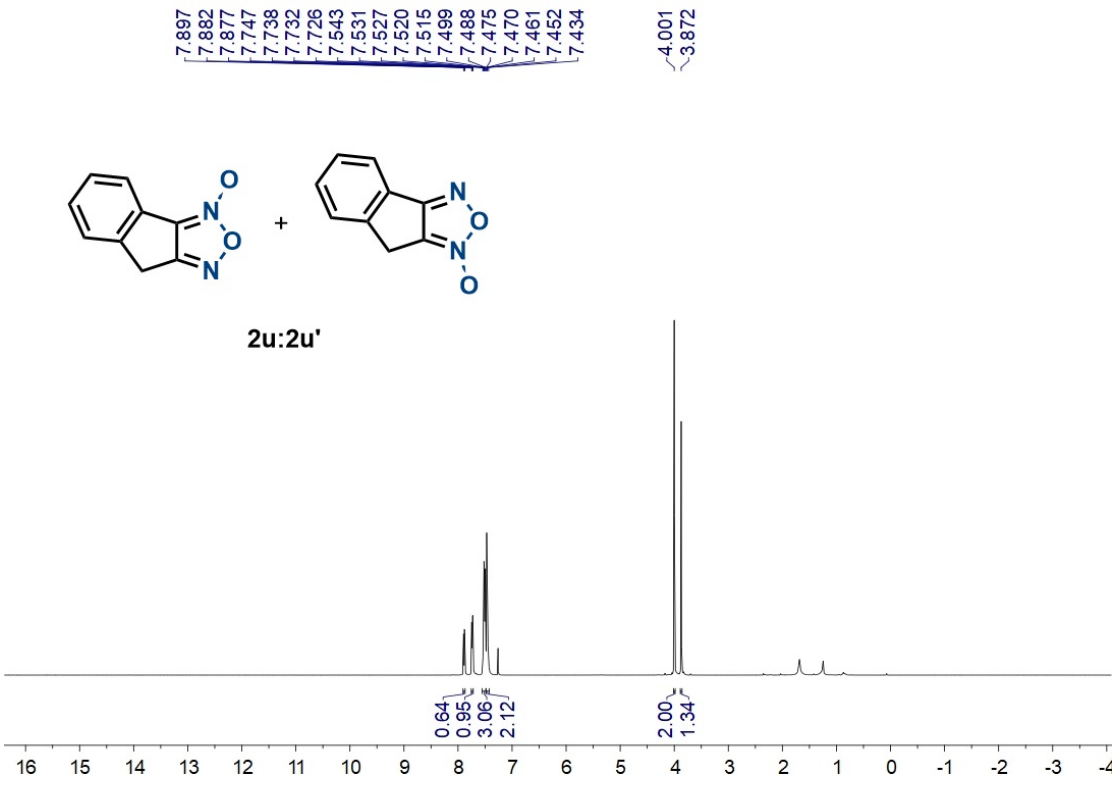
^{1}H NMR Spectrum of **2t**($CDCl_3$, 400 MHz)



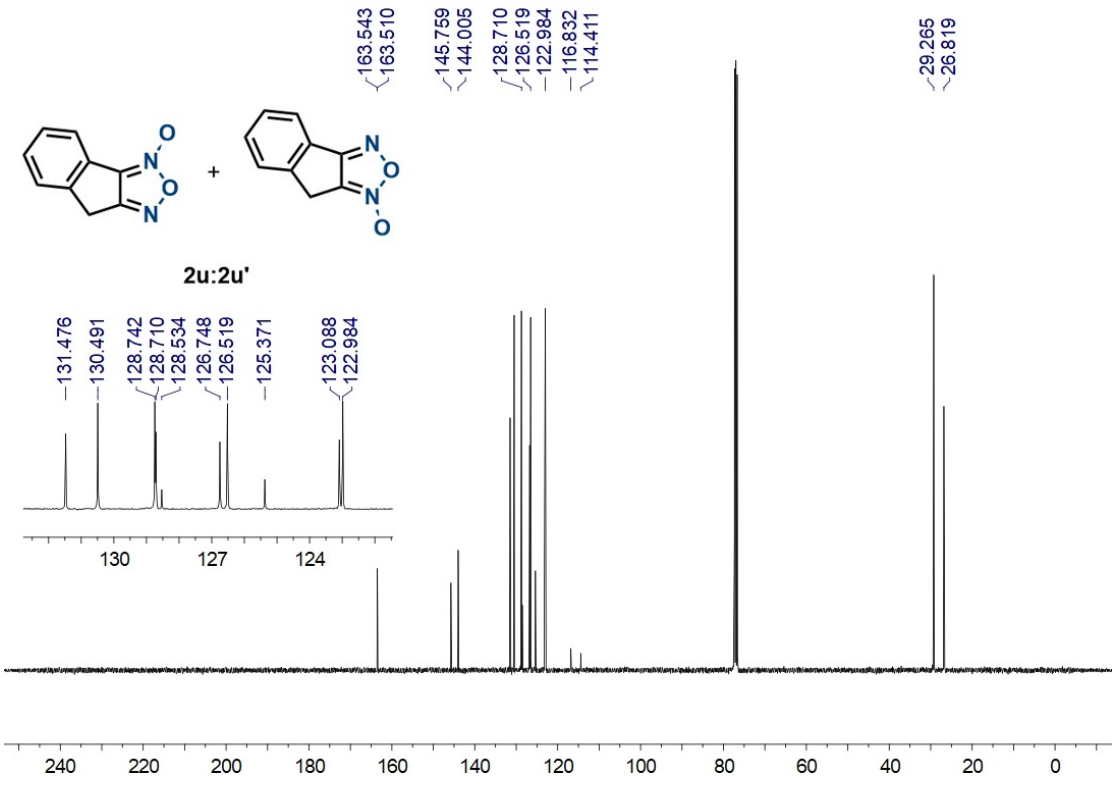
^{13}C NMR Spectrum of **2t** ($CDCl_3$, 100 MHz)



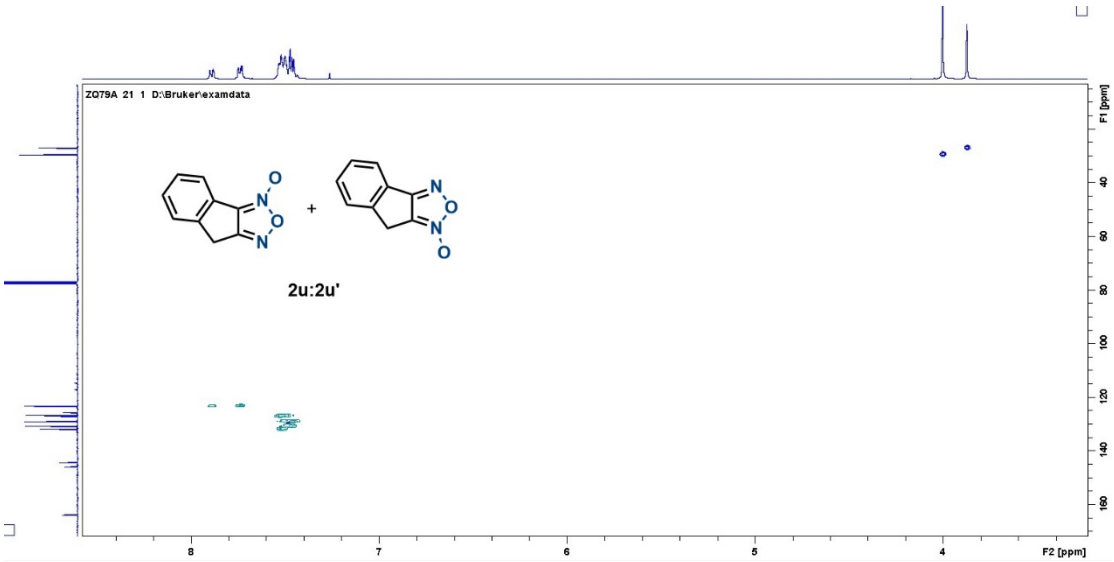
^{1}H NMR Spectrum of **2u** ($CDCl_3$, 400 MHz)



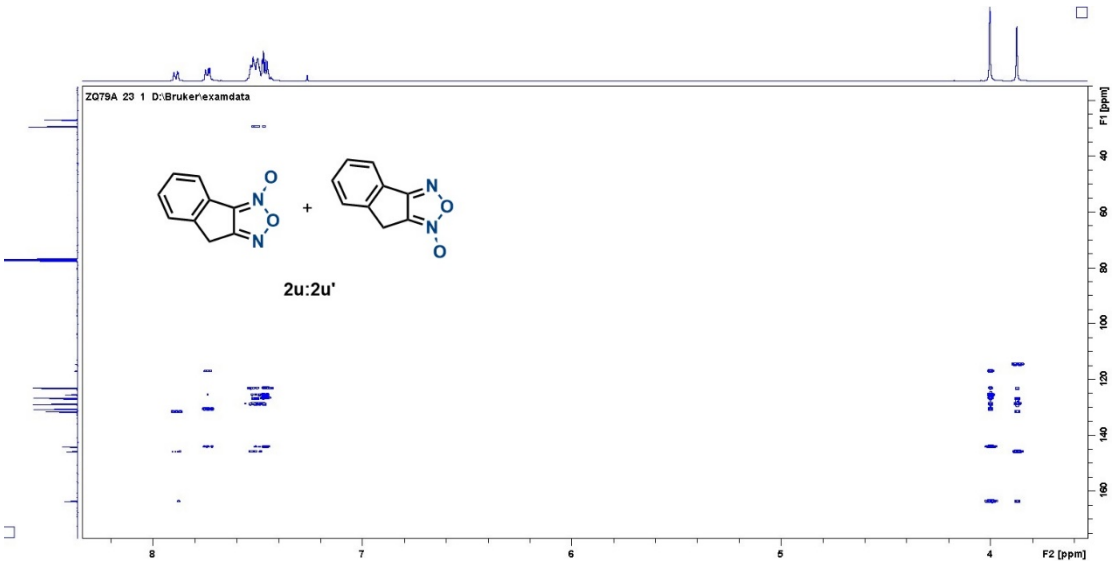
^{13}C NMR Spectrum of **2u** ($CDCl_3$, 100 MHz)



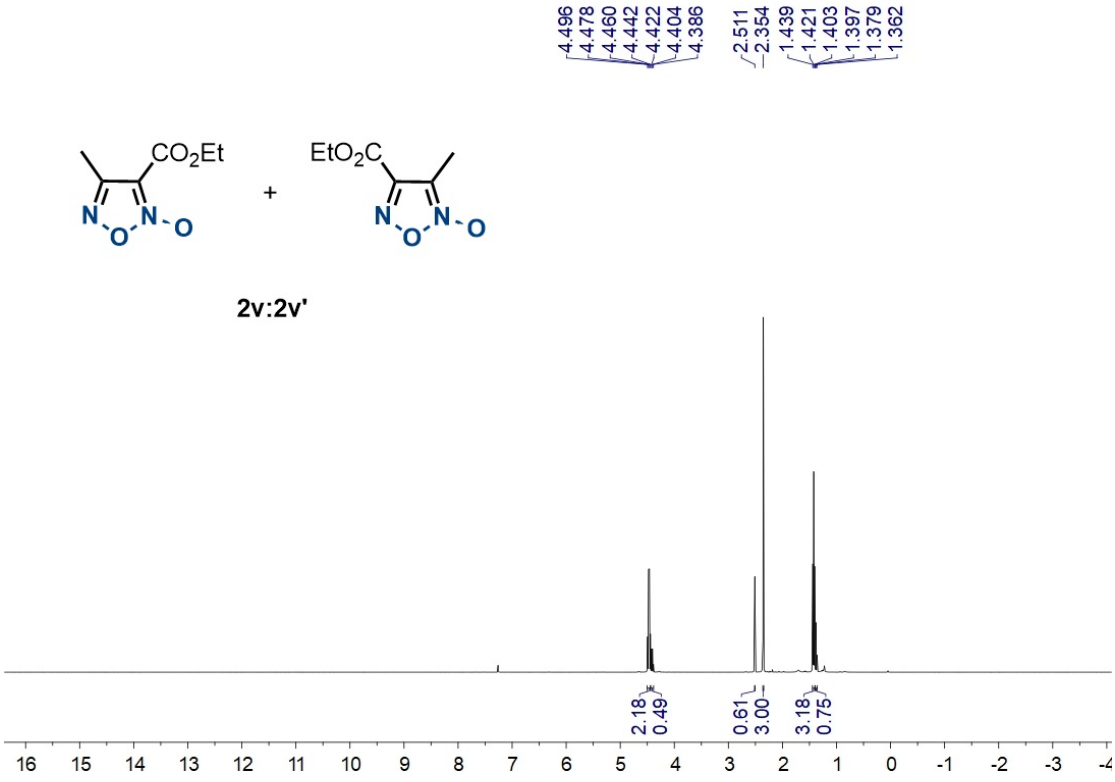
^{1}H-^{13}C HSQC NMR Spectrum of **2u** ($CDCl_3$, 400 MHz)



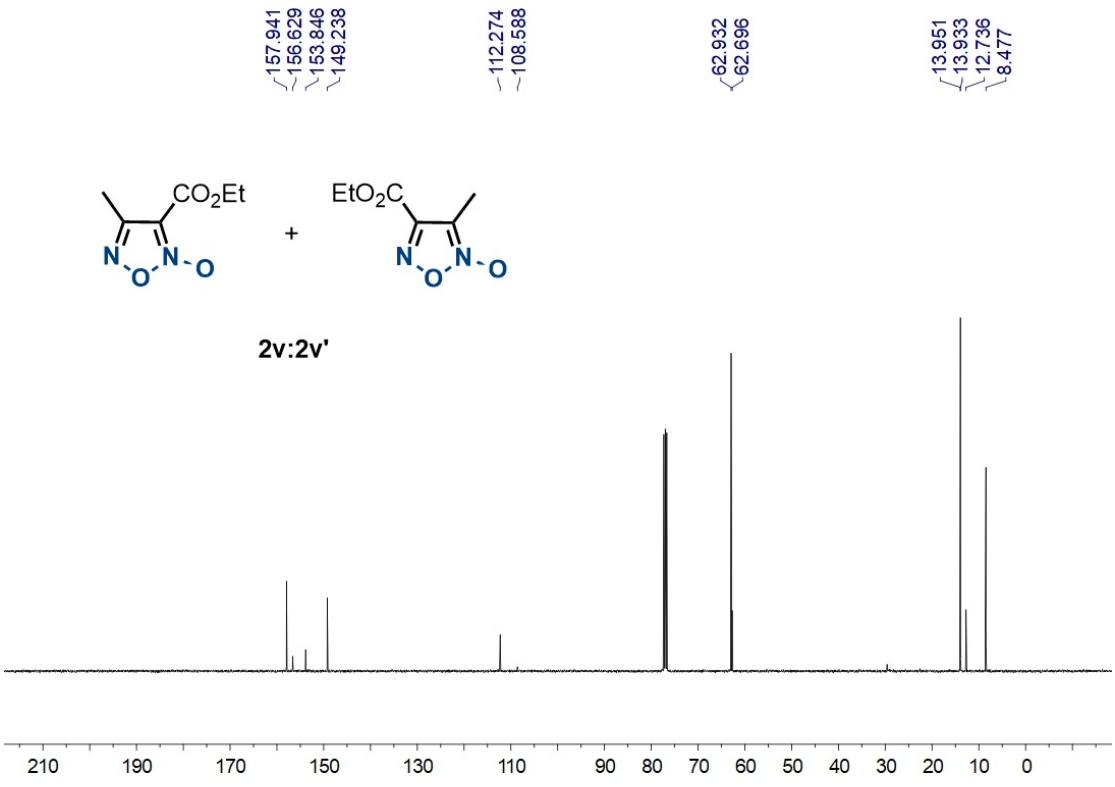
^{1}H-^{13}C HMBC NMR Spectrum of **2u** ($CDCl_3$, 400 MHz)



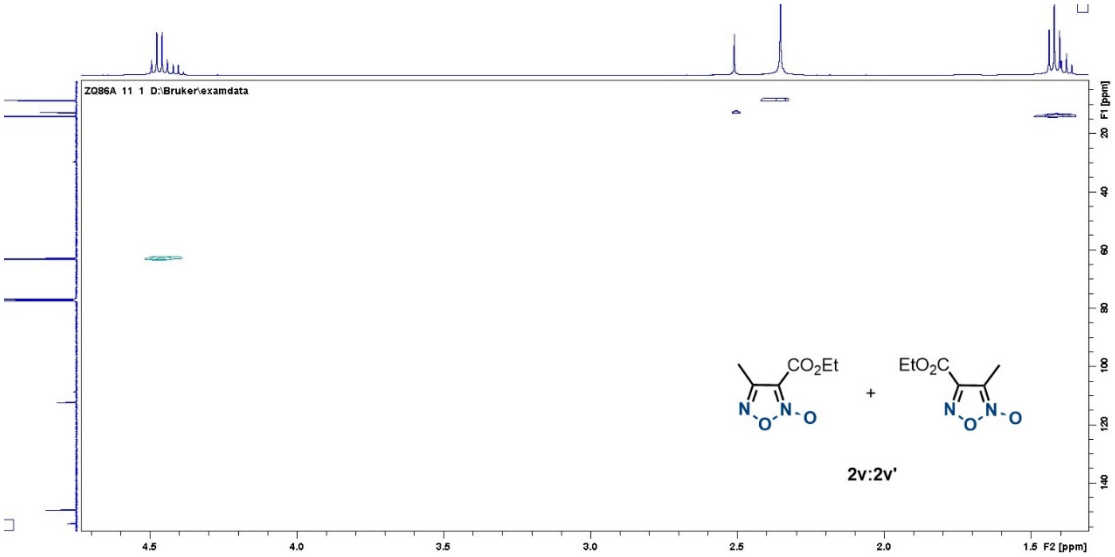
^{1}H NMR Spectrum of **2v** ($CDCl_3$, 400 MHz)



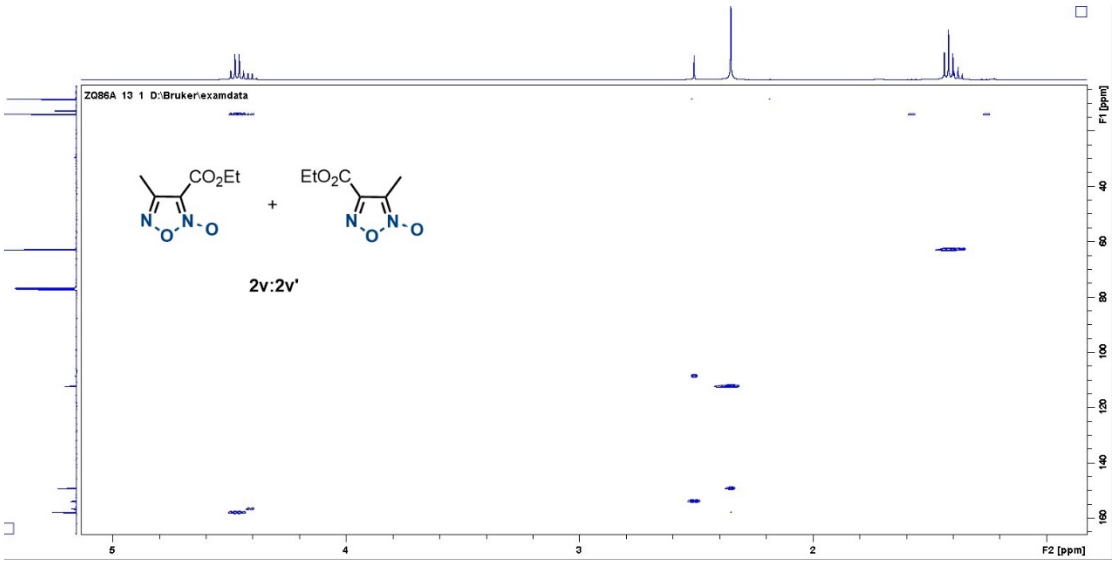
^{13}C NMR Spectrum of **2v** ($CDCl_3$, 100 MHz)



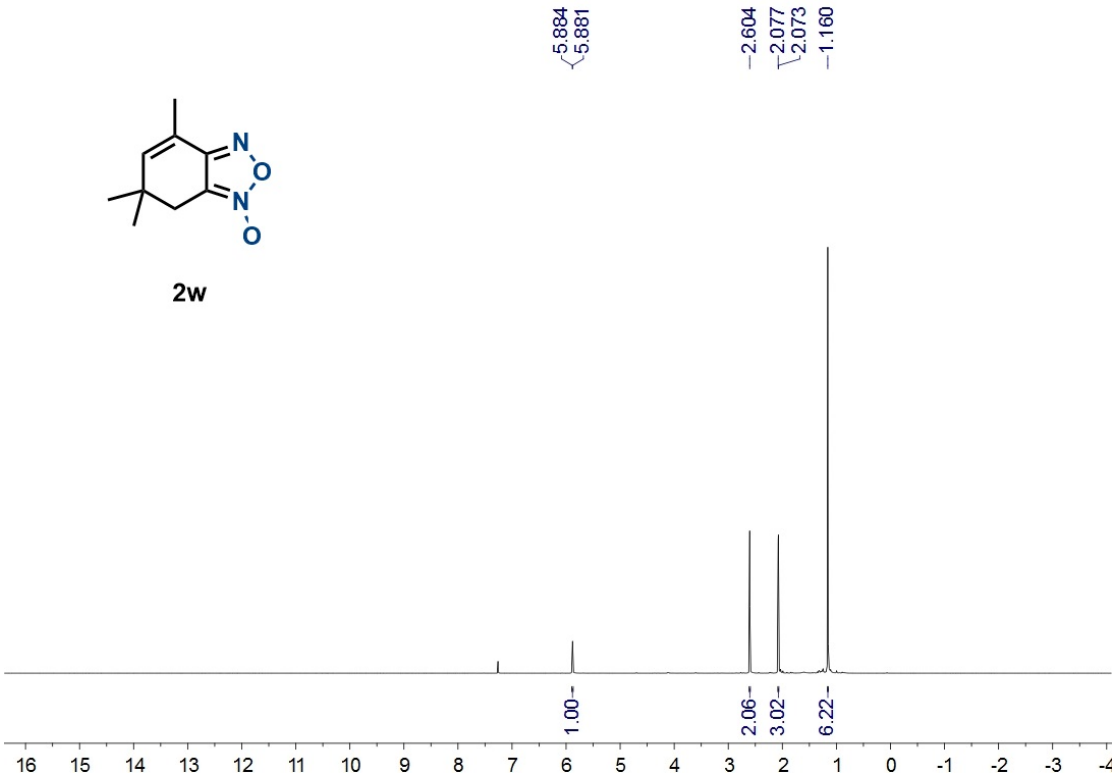
^{1}H-^{13}C HSQC NMR Spectrum of **2v** ($CDCl_3$, 400 MHz)



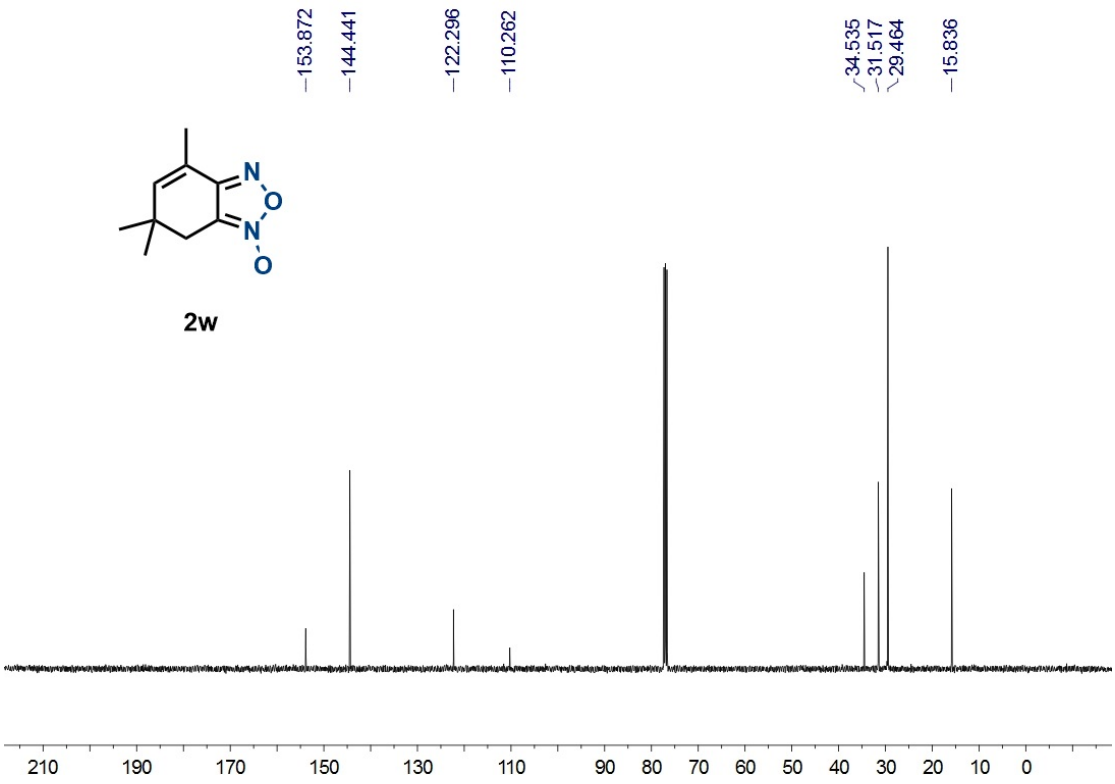
^{1}H-^{13}C HMBC NMR Spectrum of **2v** ($CDCl_3$, 400 MHz)



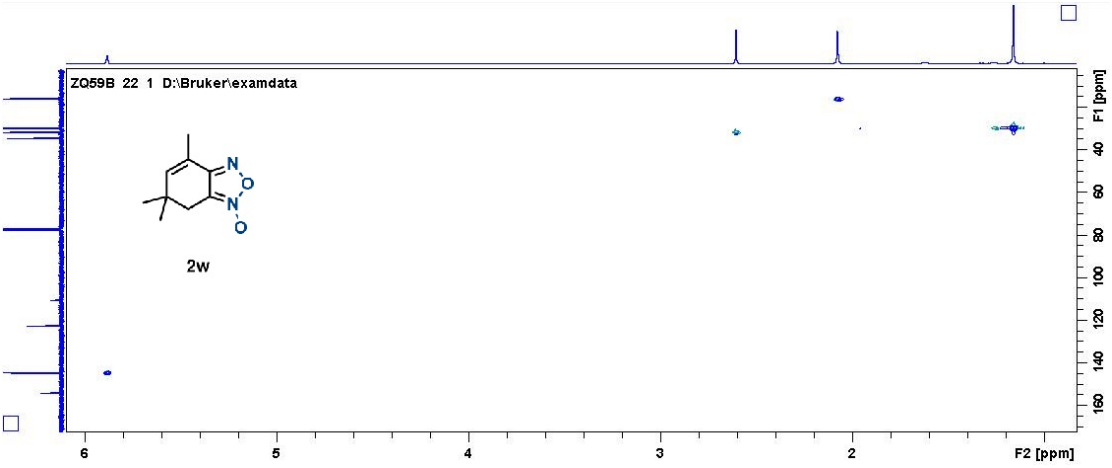
^{1}H NMR Spectrum of **2w** ($CDCl_3$, 400 MHz)



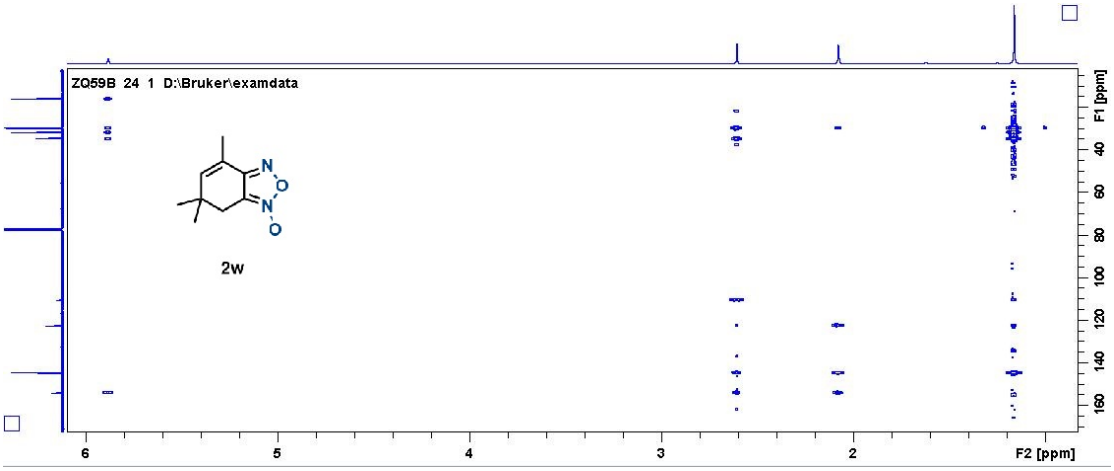
^{13}C NMR Spectrum of **2w** ($CDCl_3$, 100 MHz)



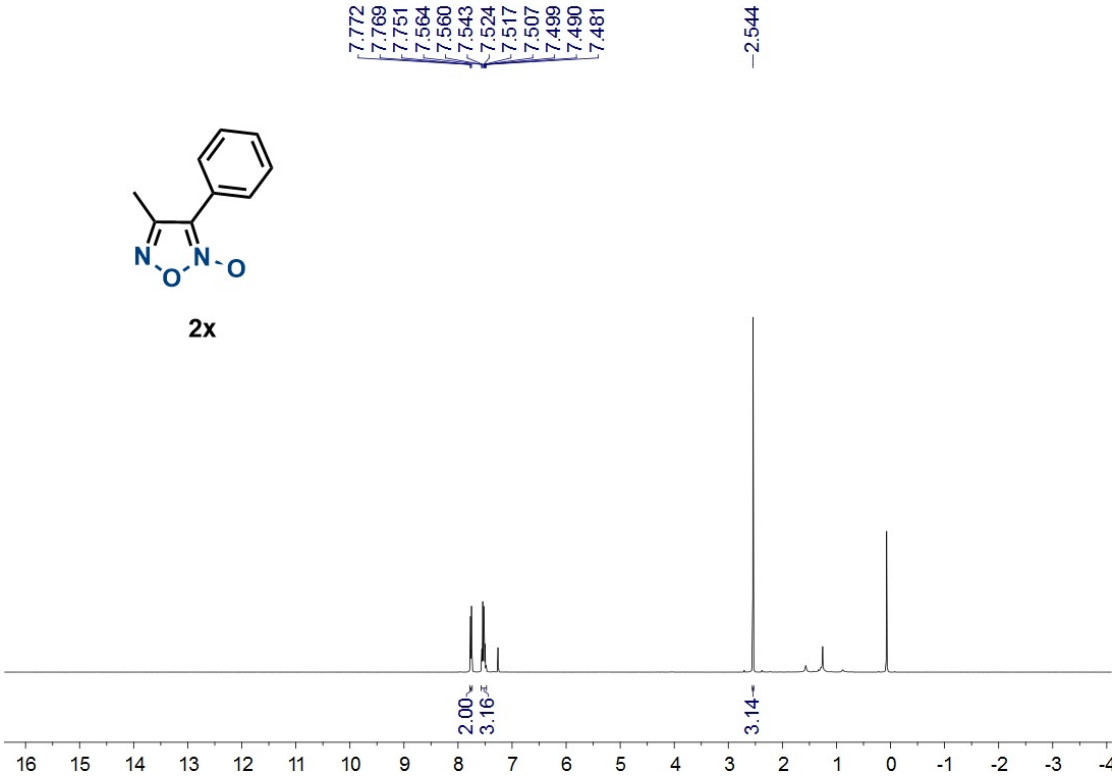
^{1}H-^{13}C HSQC NMR Spectrum of **2w** ($CDCl_3$, 400 MHz)



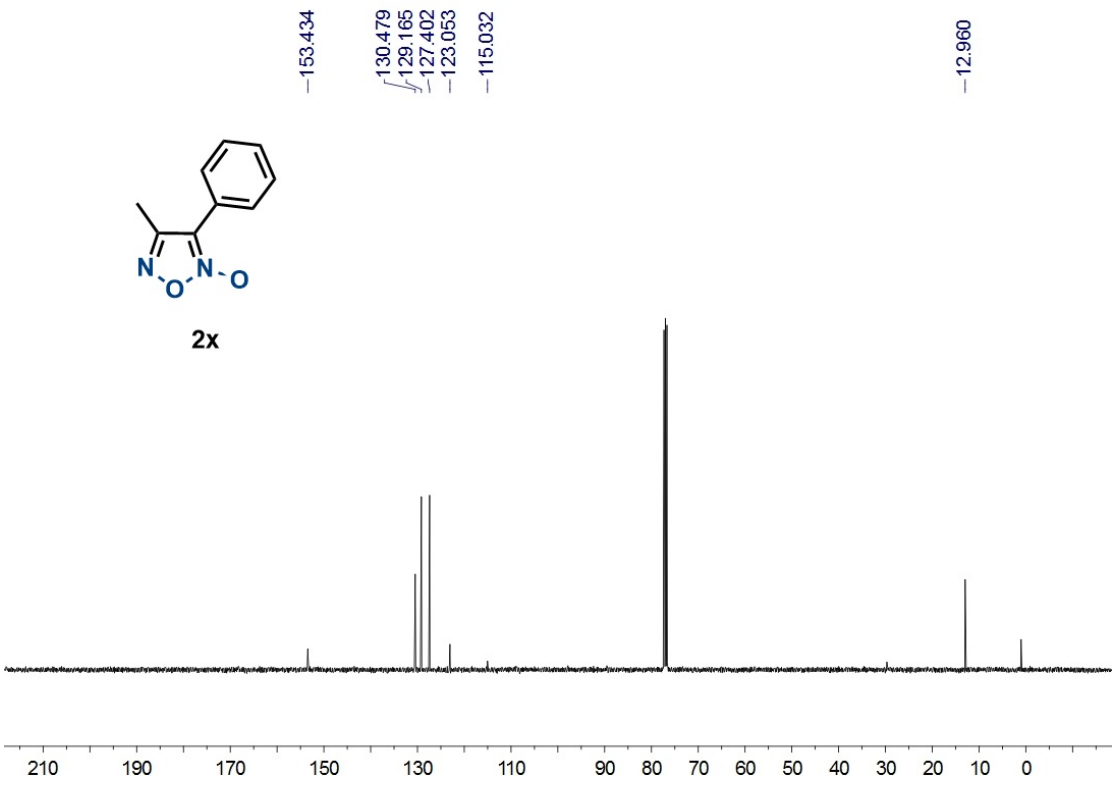
^{1}H-^{13}C HMBC NMR Spectrum of **2w** ($CDCl_3$, 400 MHz)



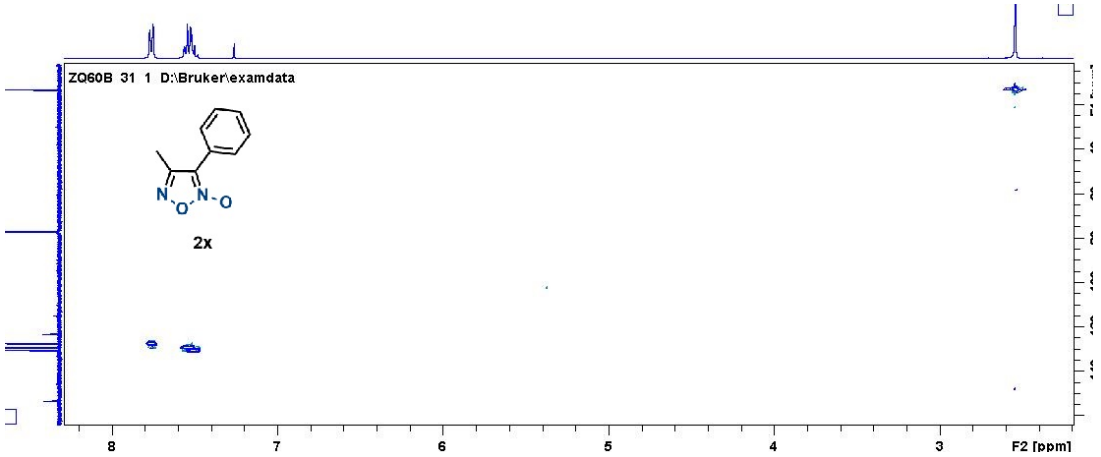
^{1}H NMR Spectrum of **2x** ($CDCl_3$, 400 MHz)



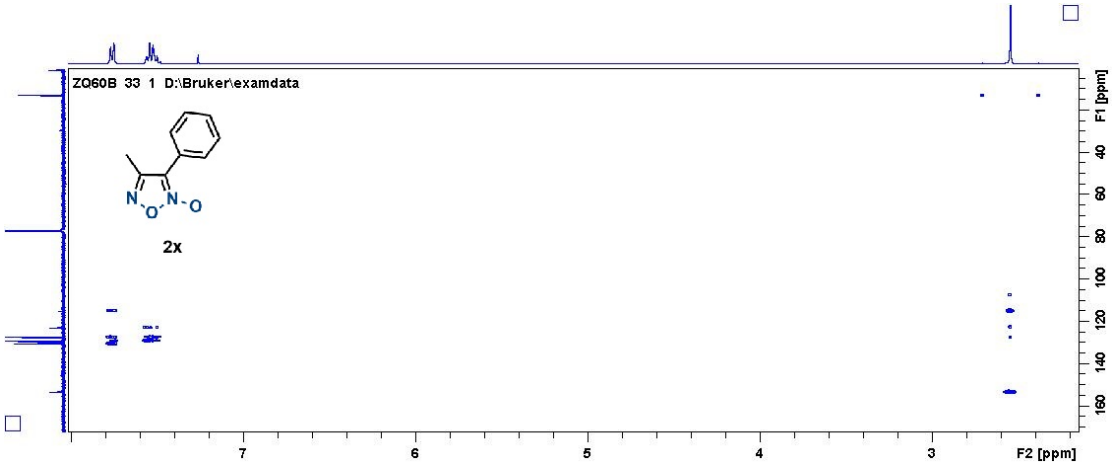
^{13}C NMR Spectrum of **2x** ($CDCl_3$, 100 MHz)



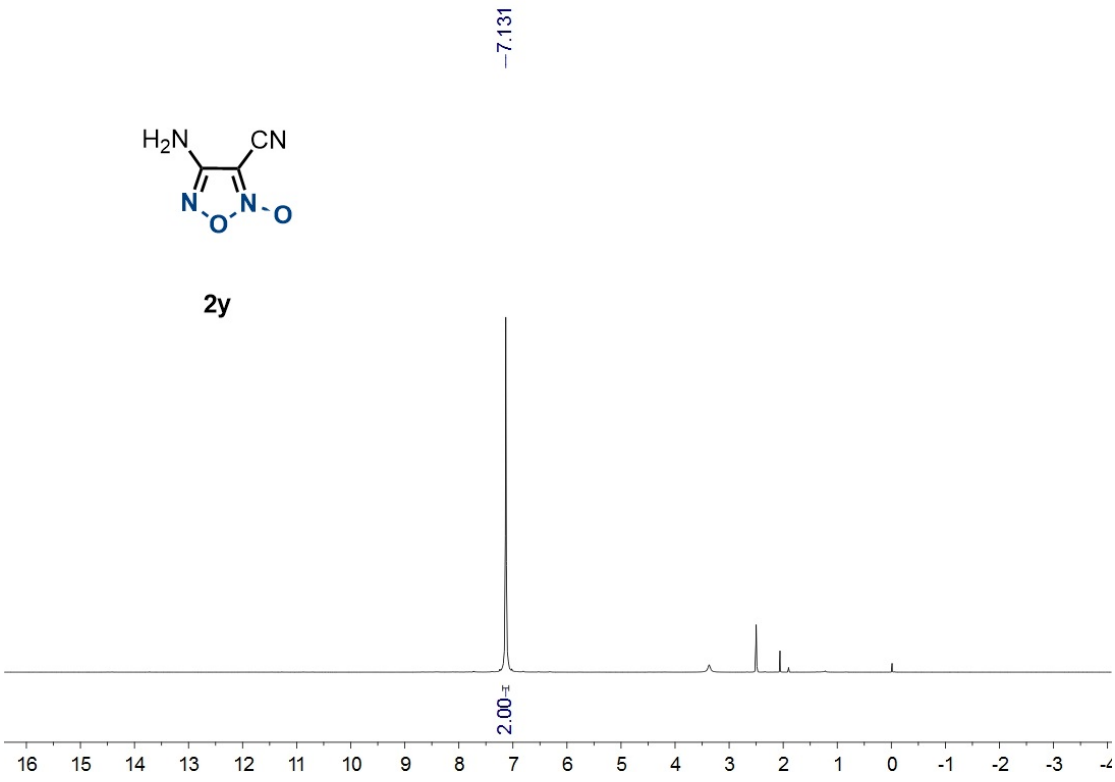
^{1}H-^{13}C HSQC NMR Spectrum of **2x** ($CDCl_3$, 400 MHz)



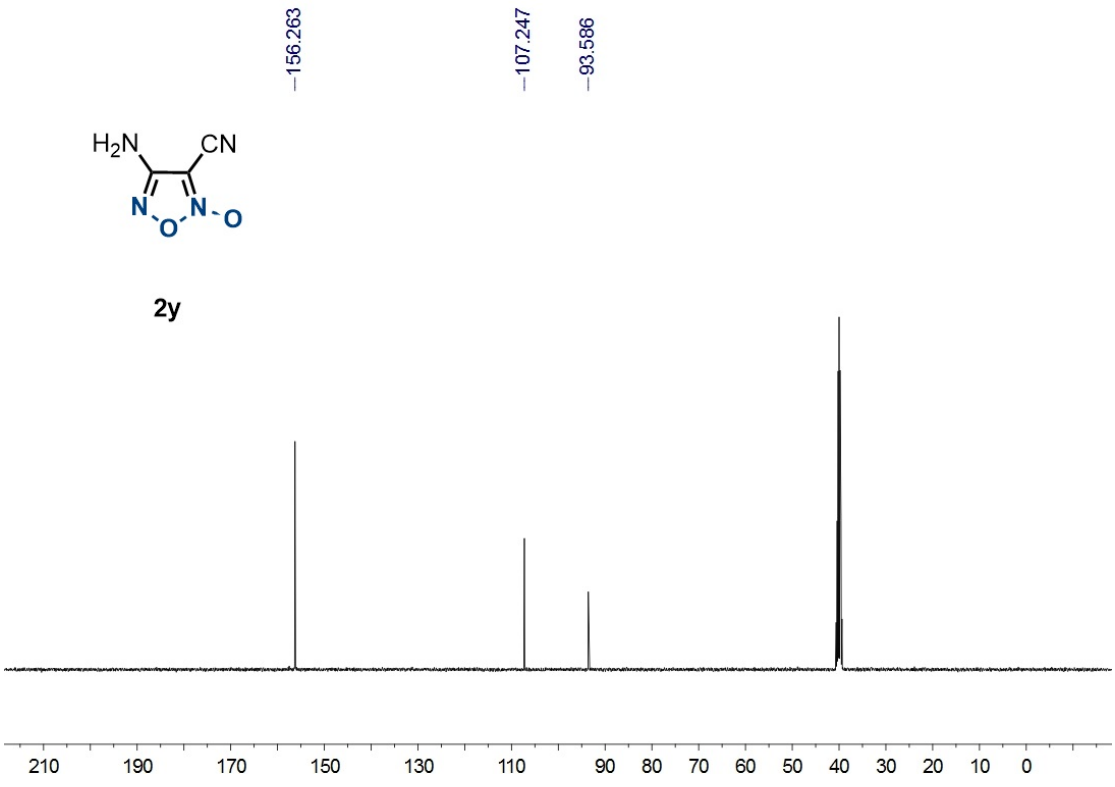
^{1}H-^{13}C HMBC NMR Spectrum of **2x** ($CDCl_3$, 400 MHz)



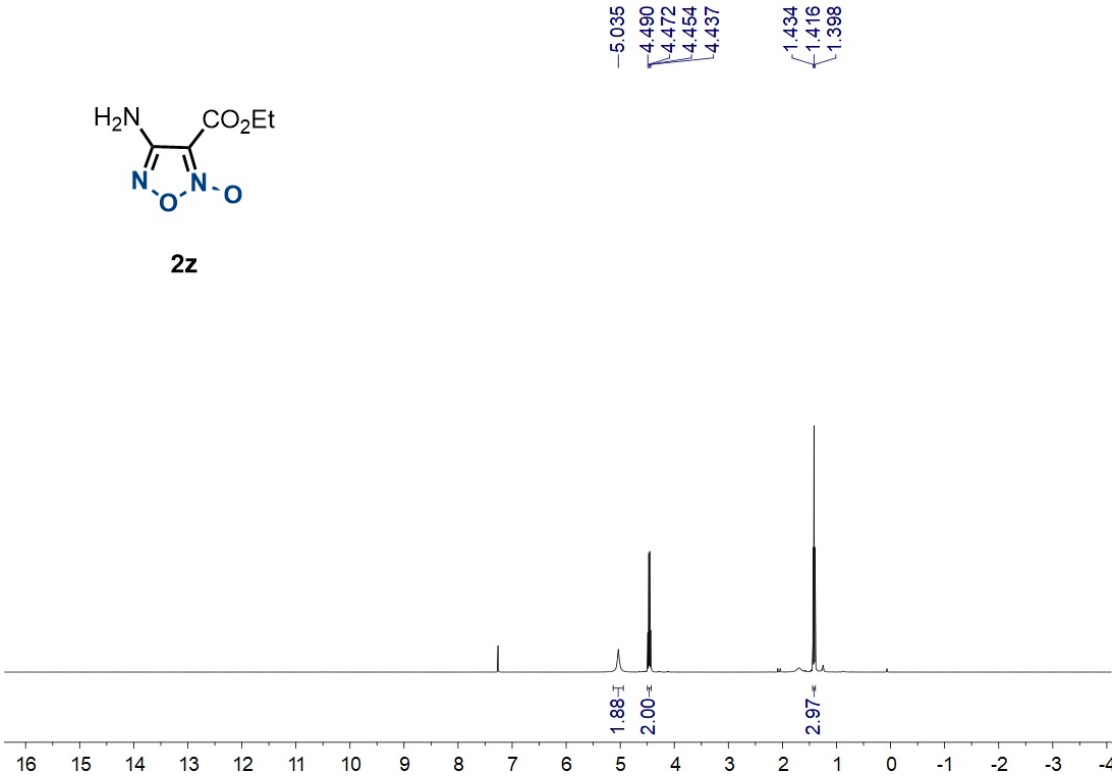
^{1}H NMR Spectrum of **2y** (DMSO, 400 MHz)



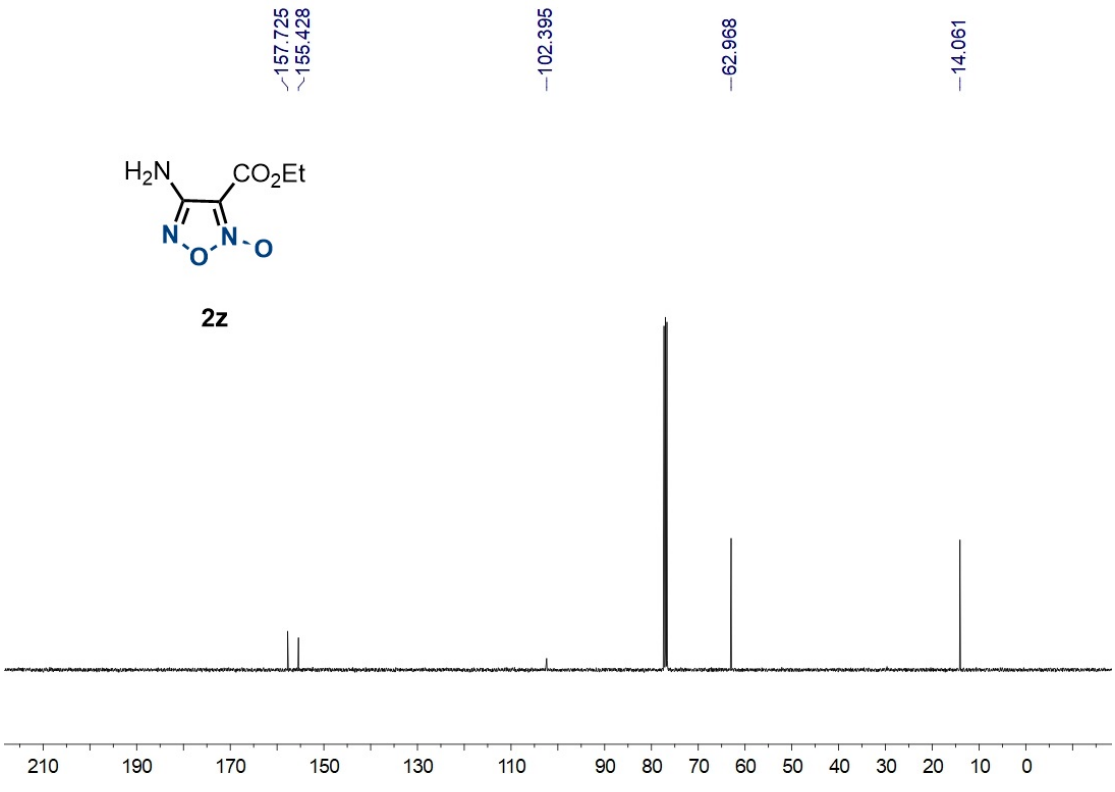
^{13}C NMR Spectrum of **2y** (DMSO, 100 MHz)



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



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



VIII. References

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