SUPPORTING INFORMATION

Preparation of *N*-heterylarenes from the perspective of phenylhydrazine-based green chemistry

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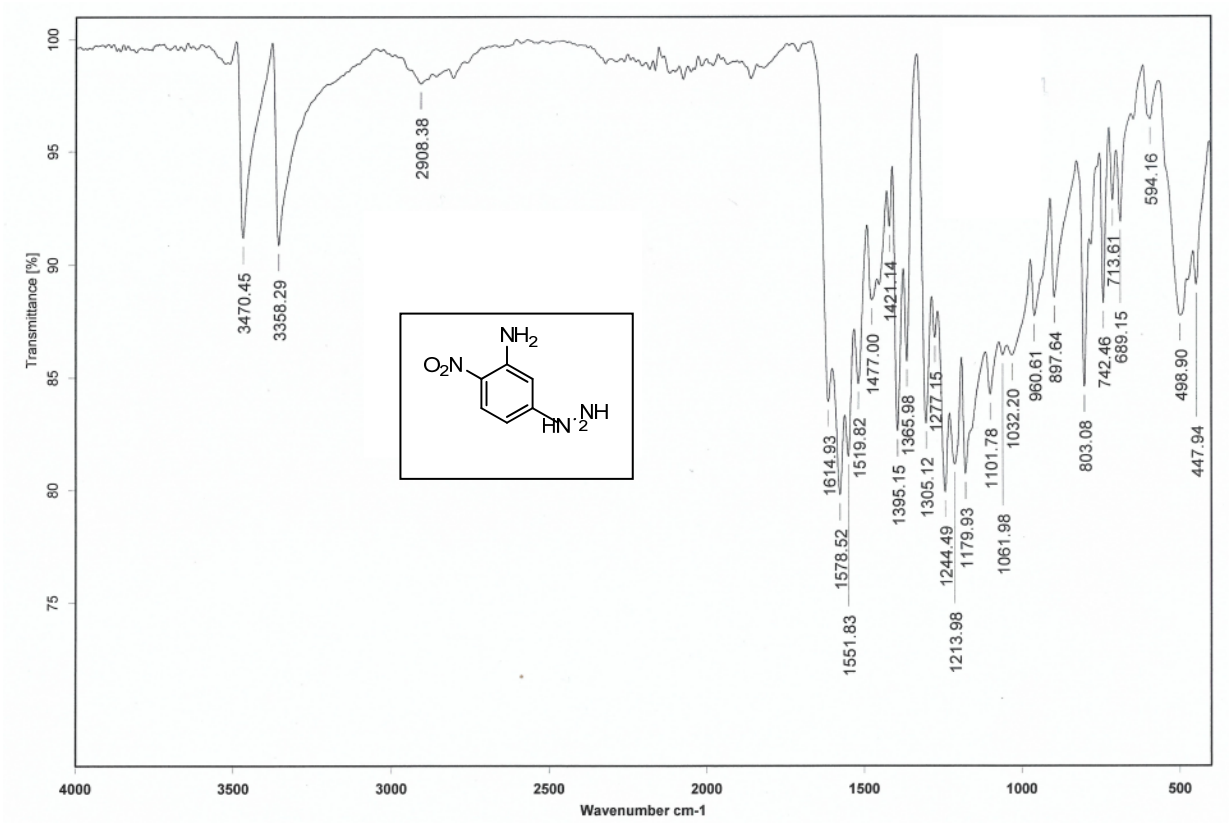
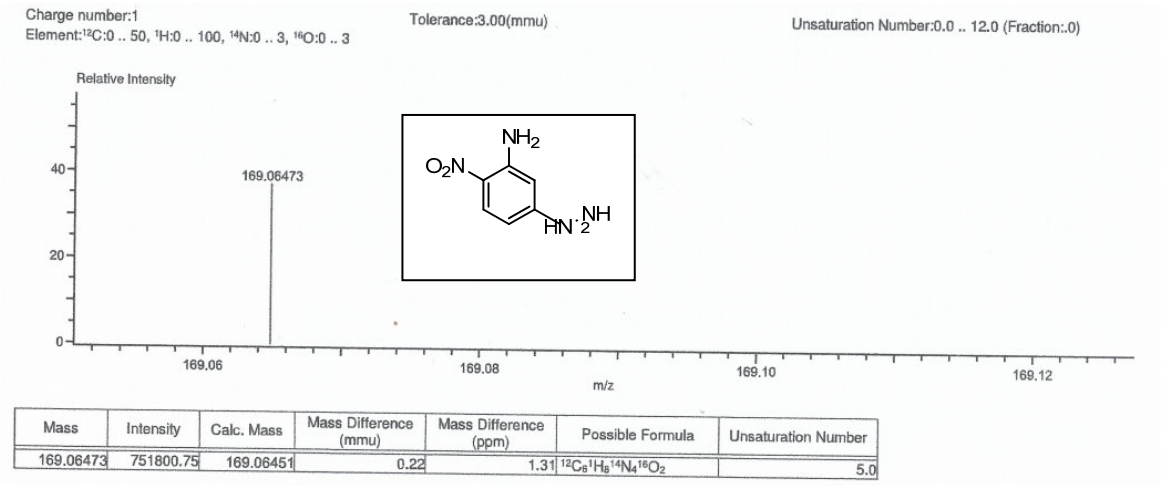
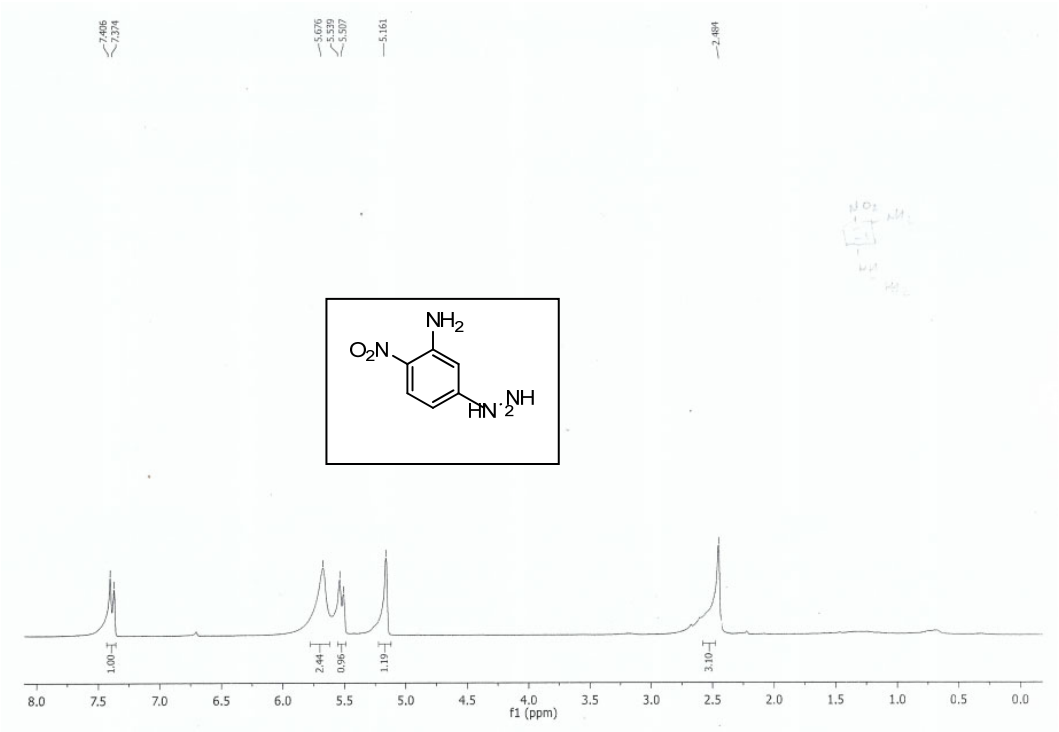


FT-IR 5-hydrazinyl-2-nitroaniline (**3**)

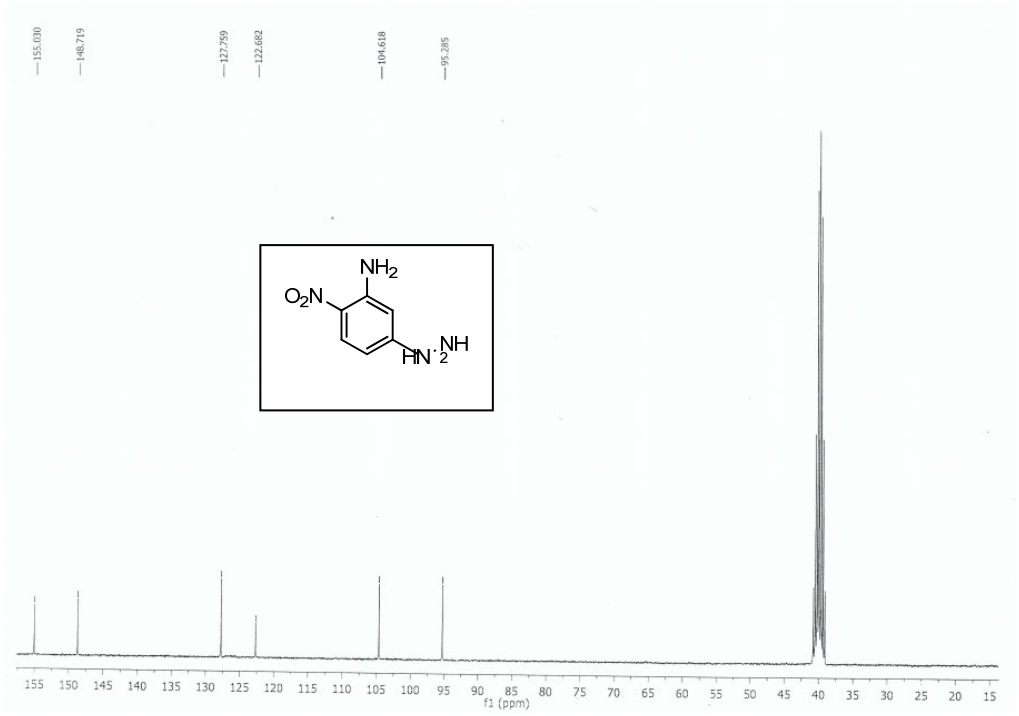


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
169.06473	751800.75	169.06451	0.22	1.31	$^{12}C_6{}^{1}H_8{}^{14}N_4{}^{16}O_2$	5.0

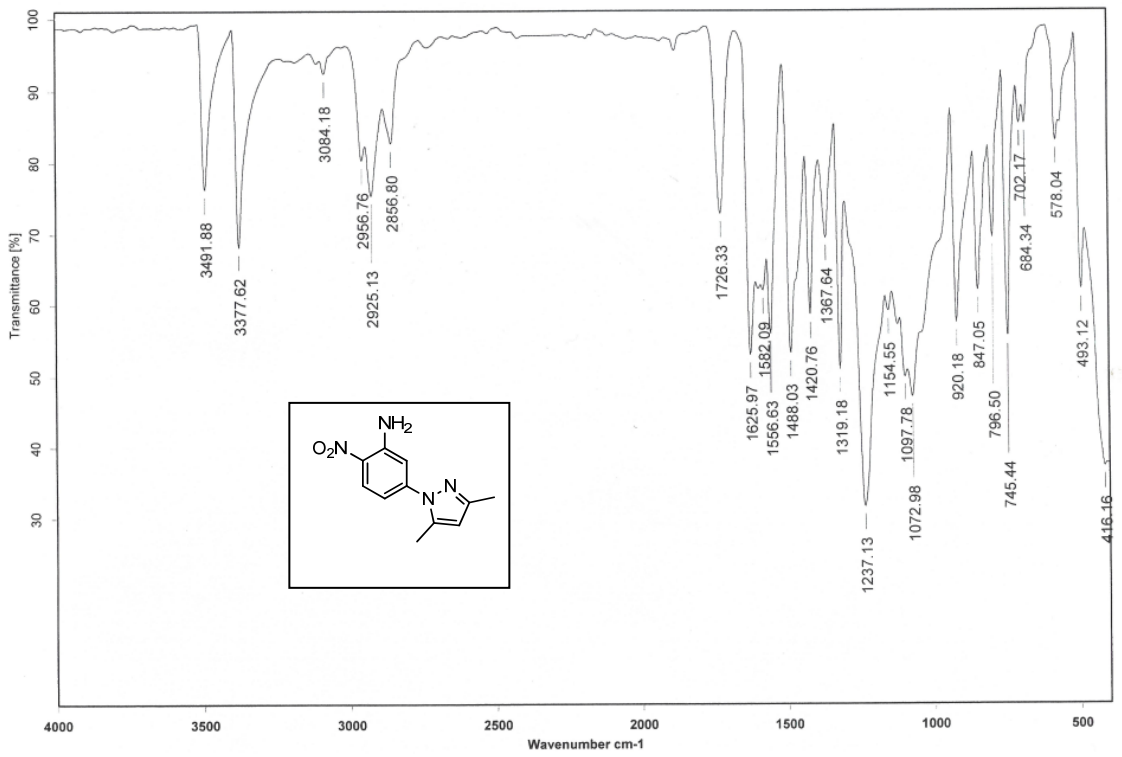
MS-Elemental Analysis 5-hydrazinyl-2-nitroaniline (**3**)



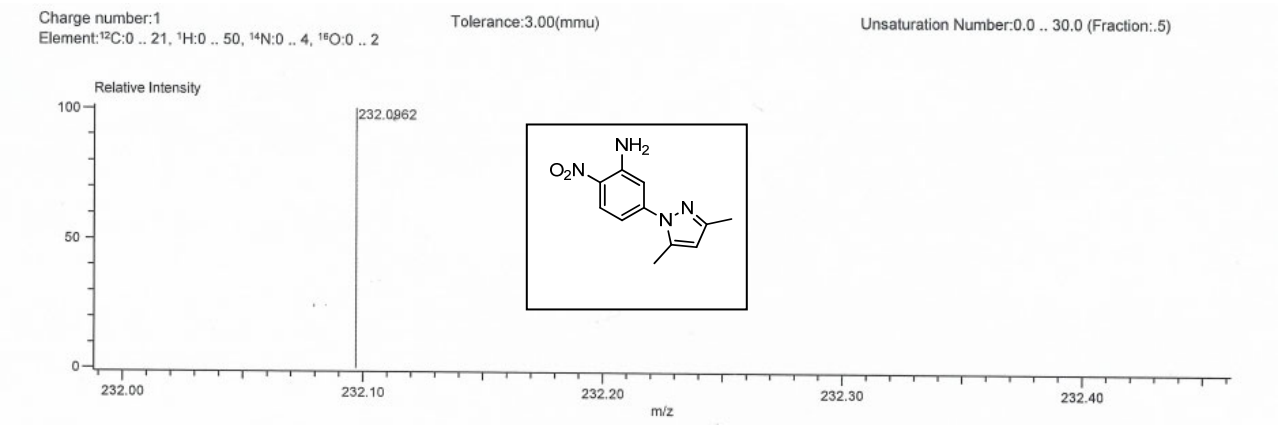
^{1}H NMR (300 MHz, DMSO-d6) 5-hydrazinyl-2-nitroaniline (**3**)



^{13}C NMR (75 MHz, DMSO-d6) 5-hydrazinyl-2-nitroaniline (**3**)

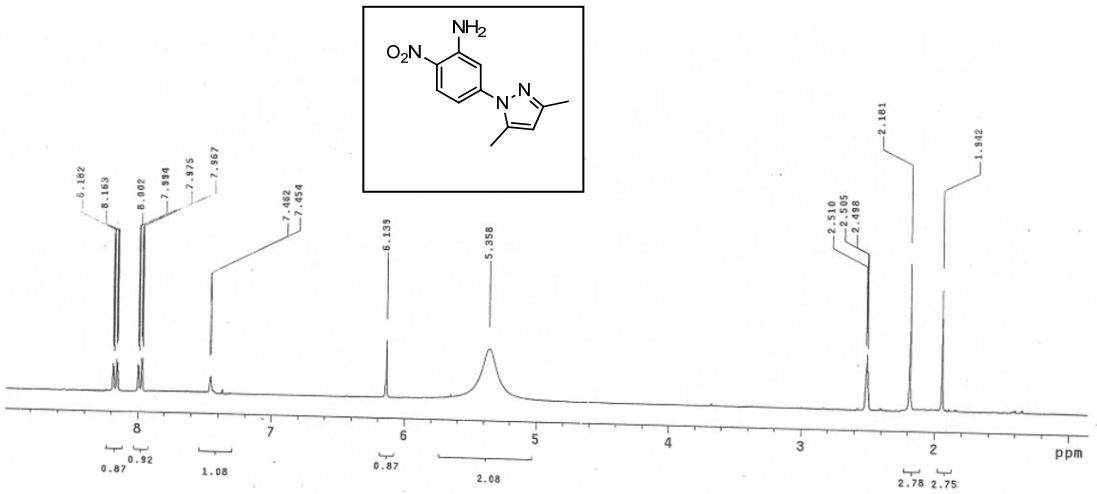


FT-IR 5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-nitroaniline (**6**)

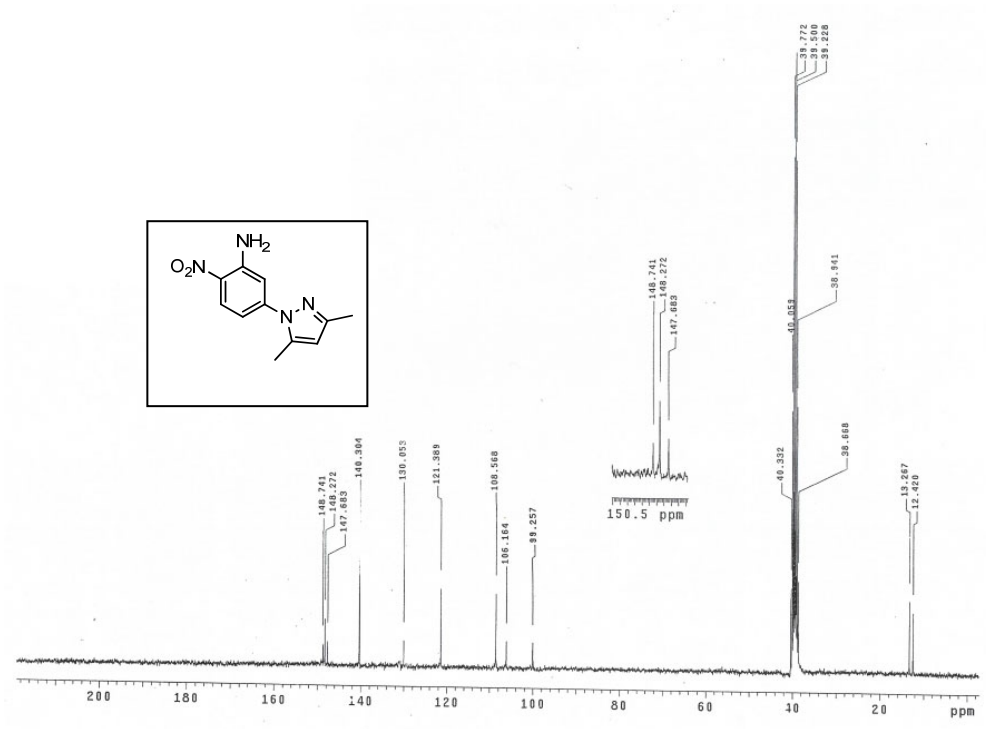


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
232.0962	688369.84	232.0960	-0.20	-0.86	$^{12}C_{11}{}^{1}H_{13}{}^{14}N_4{}^{16}O_2$	6.5

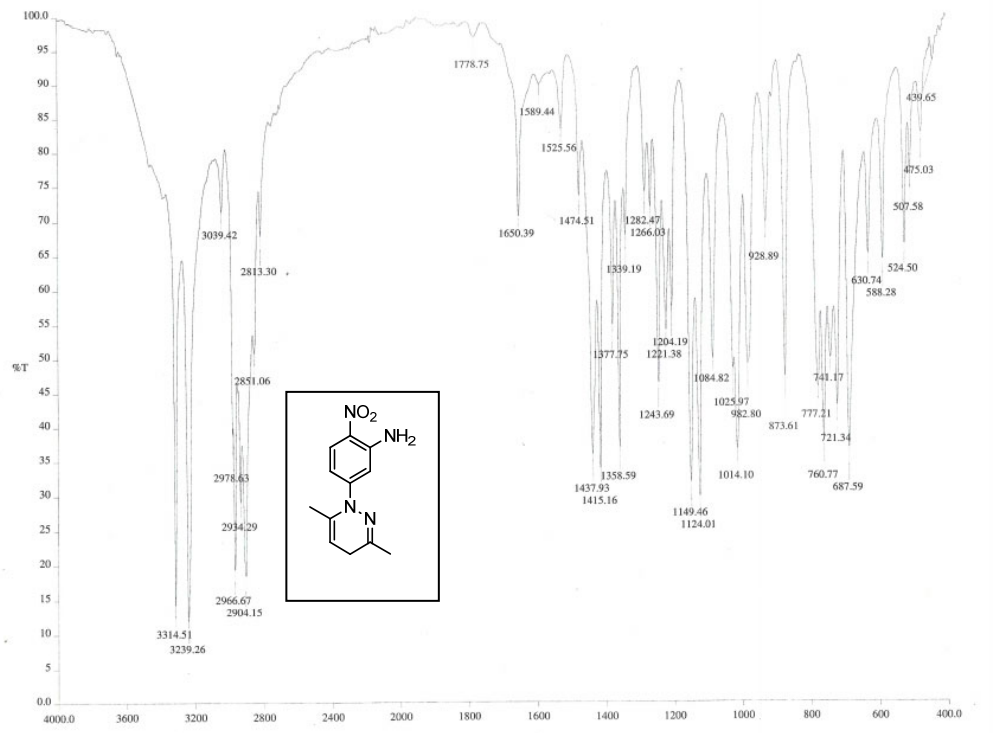
MS-Elemental Analysis 5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-nitroaniline (**6**)



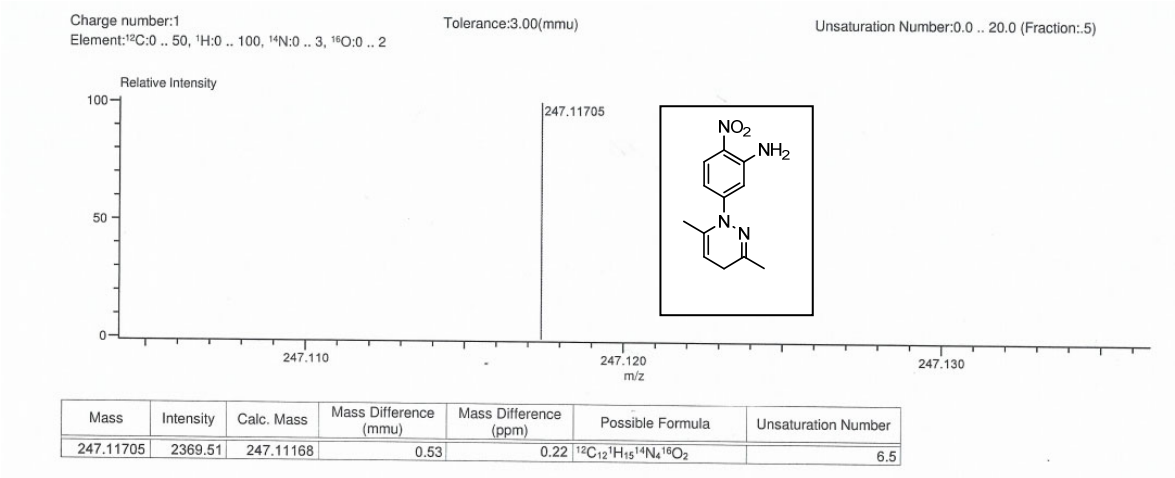
^{1}H NMR (300 MHz, DMSO-d6) 5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-nitroaniline (**6**)



^{13}C NMR (75 MHz, DMSO-d6) 5-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-nitroaniline (**6**)

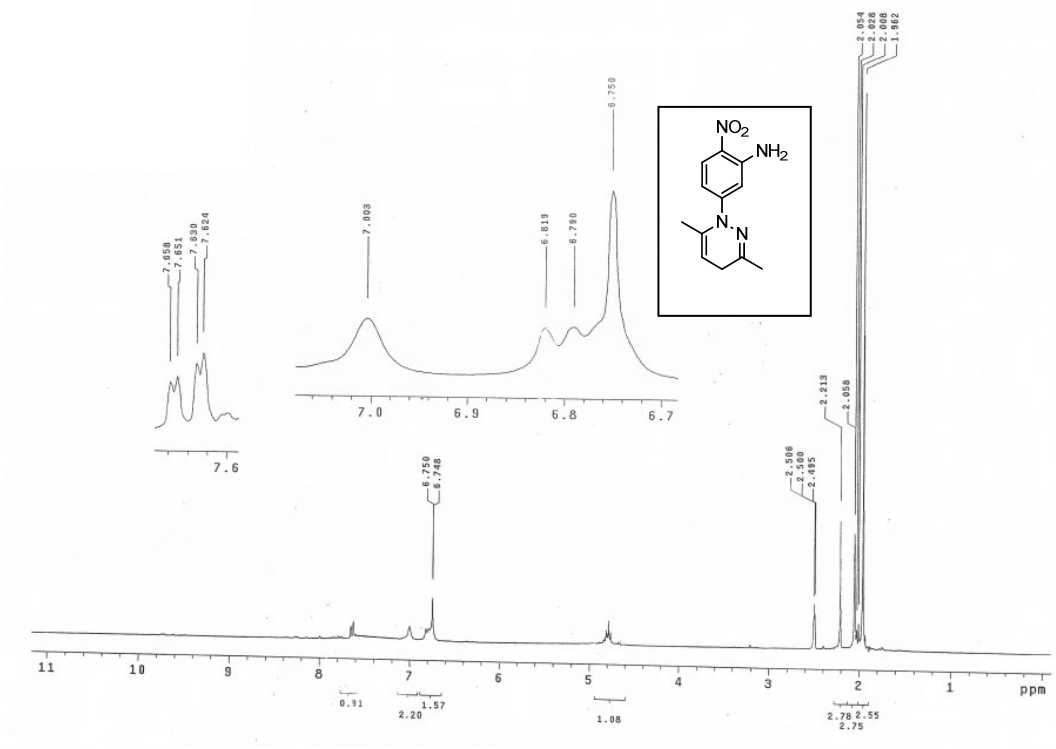


FT-IR 5-(3,6-dimethylpyridazin-1(4*H*)-yl)-2-nitroaniline (**7**)

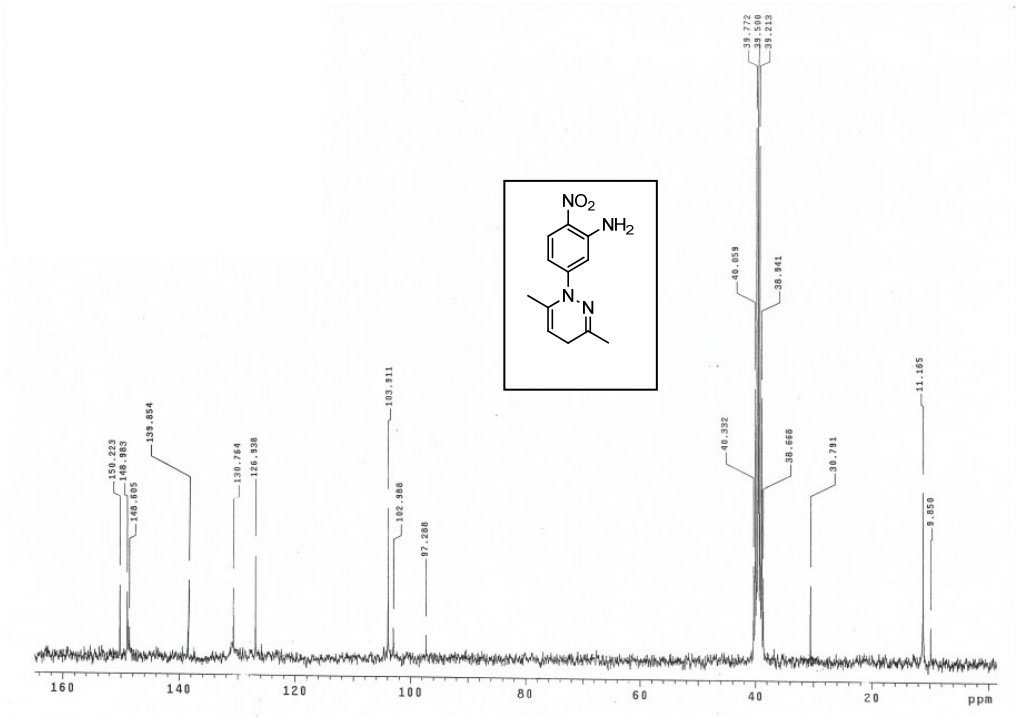


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
247.11705	2369.51	247.11168	0.53	0.22	$^{12}C_{12}{}^{1}H_{15}{}^{14}N_4{}^{16}O_2$	6.5

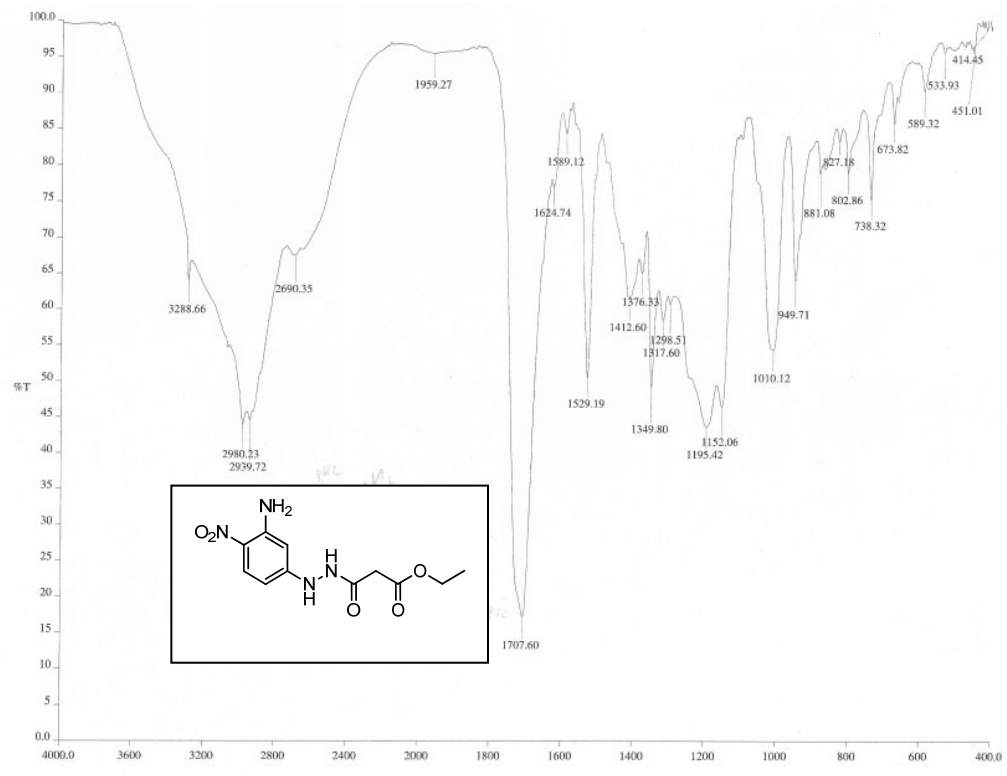
MS-Elemental Analysis 5-(3,6-dimethylpyridazin-1(4*H*)-yl)-2-nitroaniline (**7**)



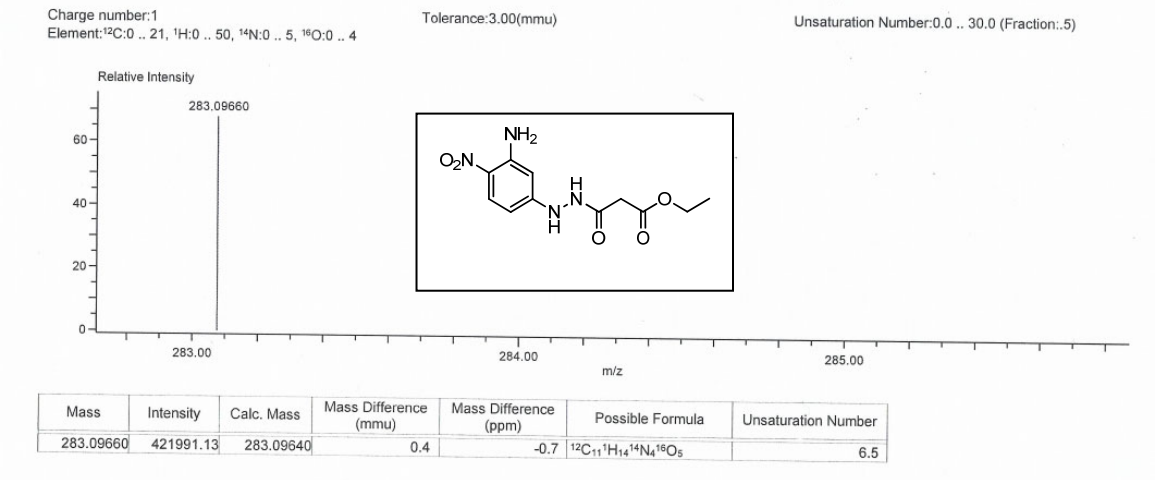
^{1}H NMR (300 MHz, DMSO-d6) 5-(3,6-dimethylpyridazin-1(4*H*)-yl)-2-nitroaniline (**7**)



^{13}C NMR (75 MHz, DMSO-d6) 5-(3,6-dimethylpyridazin-1(4*H*)-yl)-2-nitroaniline (**7**)

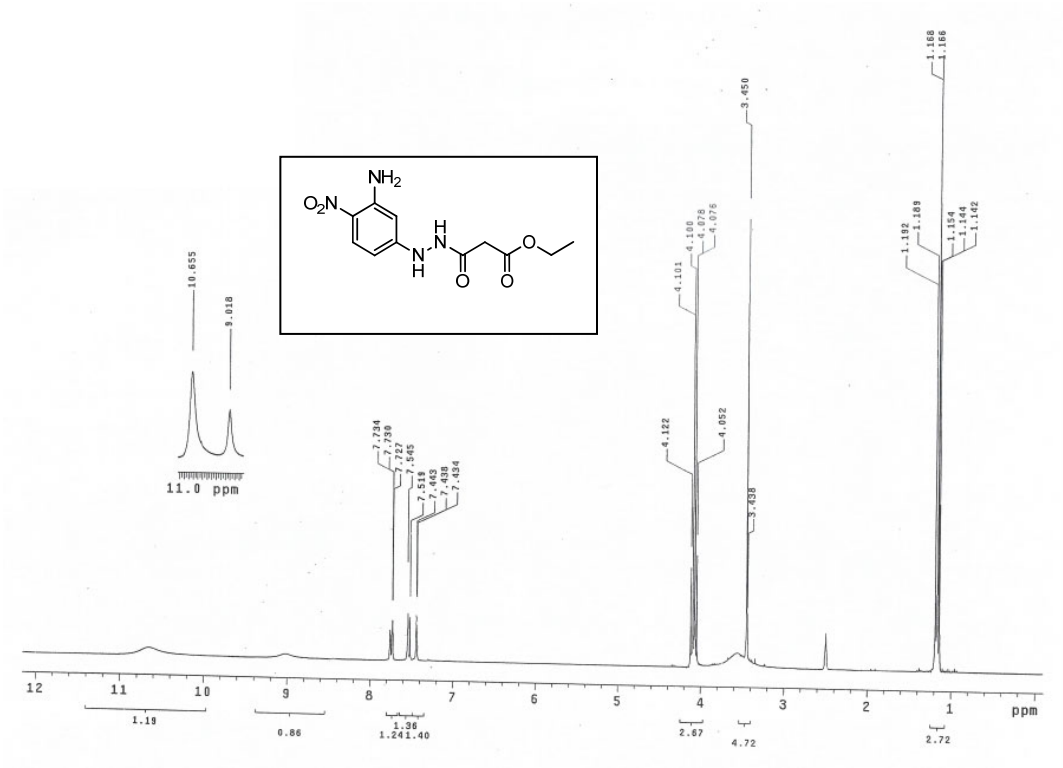


FT-IR Ethyl 3-(2-(3-amino-4-nitrophenyl)hydrazinyl)-3-oxopropanoate (**14**)

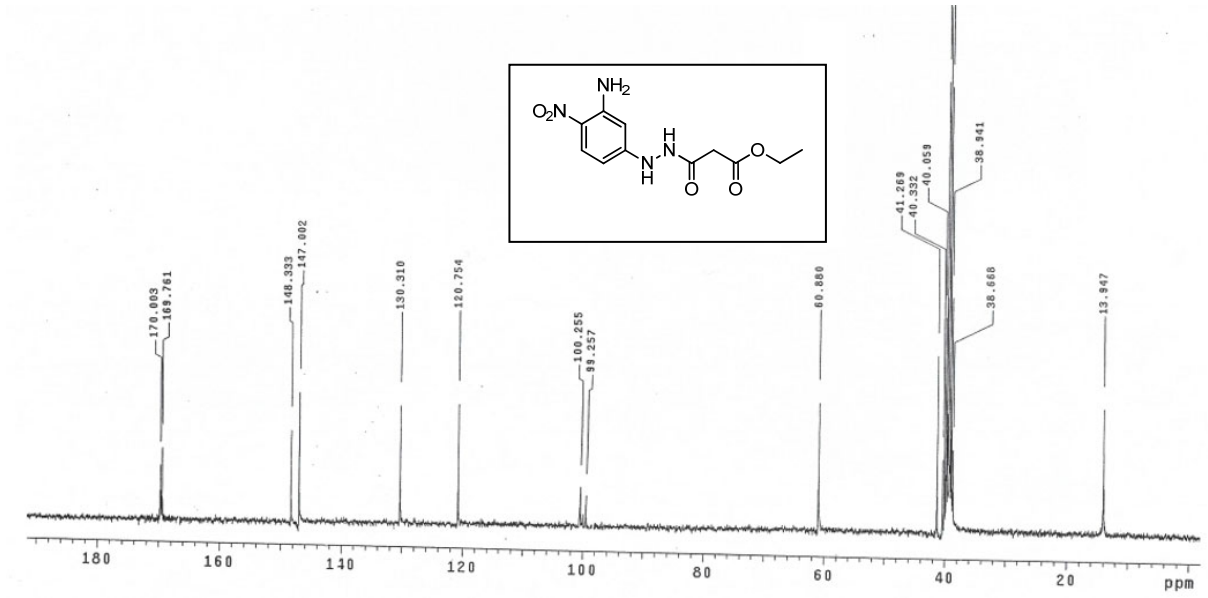


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
283.09660	421991.13	283.09640	0.4	-0.7	$^{12}C_{11}{}^{1}H_{14}{}^{14}N_{4}{}^{16}O_{5}$	6.5

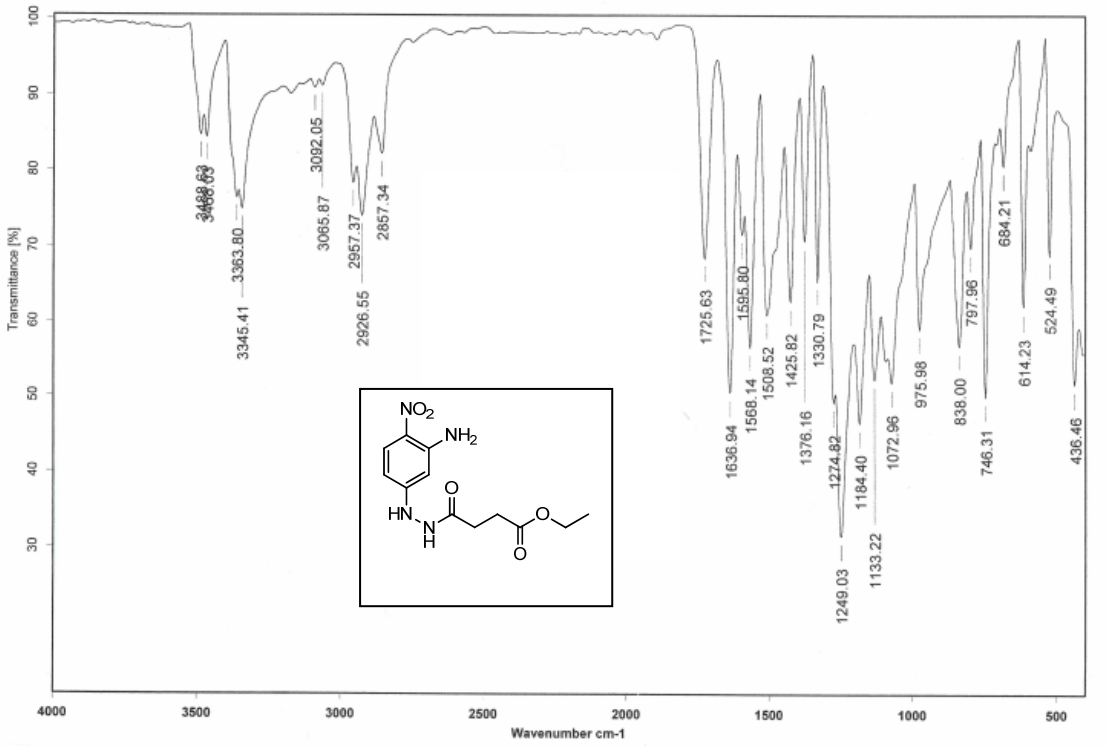
MS-Elemental Analysis Ethyl 3-(2-(3-amino-4-nitrophenyl)hydrazinyl)-3-oxopropanoate (**14**)



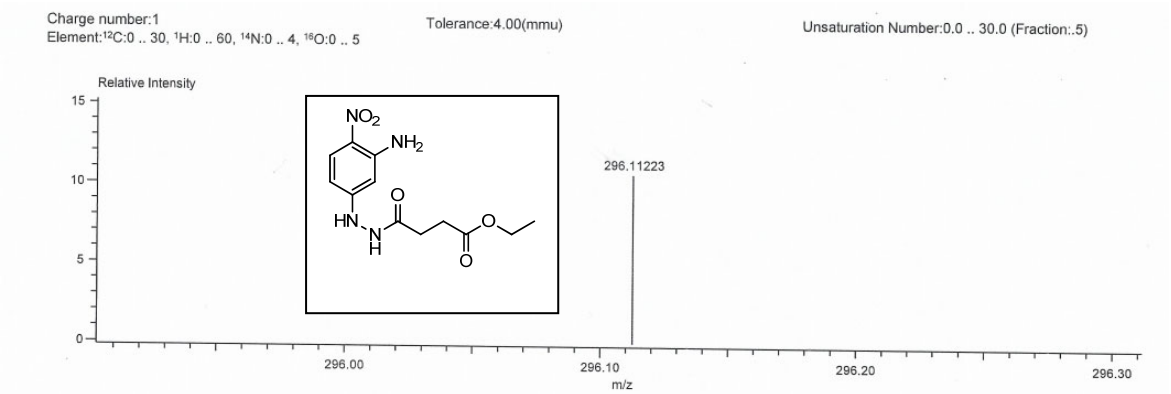
^{1}H NMR (300 MHz, DMSO-d6) Ethyl 3-(2-(3-amino-4-nitrophenyl)hydrazinyl)-3-oxopropanoate (**14**)



^{13}C NMR (75 MHz, DMSO-d6) Ethyl 3-(2-(3-amino-4-nitrophenyl)hydrazinyl)-3-oxopropanoate (**14**)

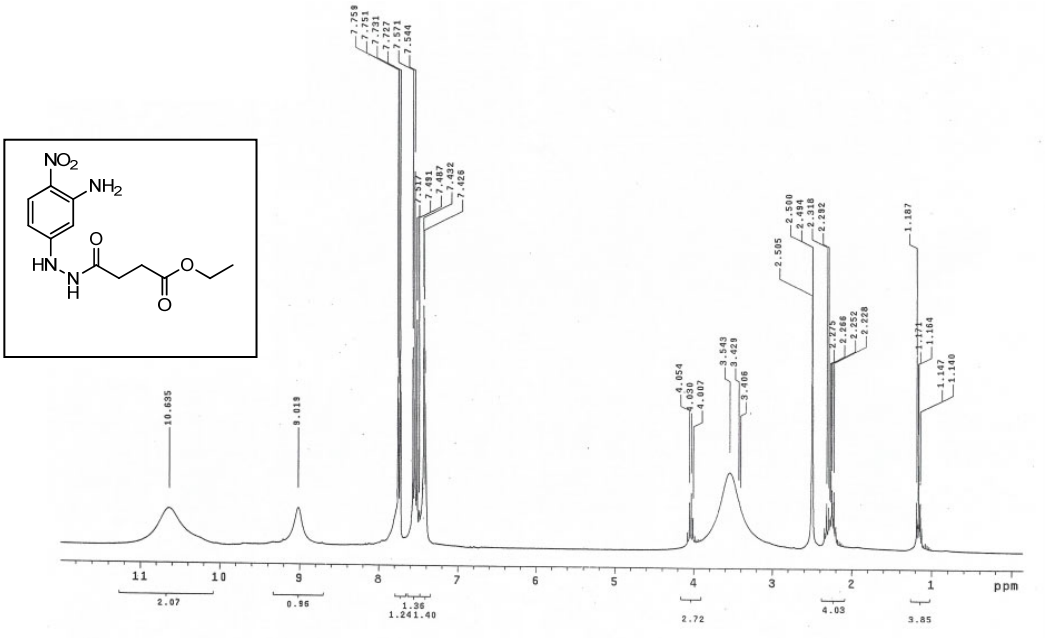


FT-IR Ethyl 4-(2-(3-amino-4-nitrophenyl)hydrazinyl)-4-oxobutanoate (**15**)

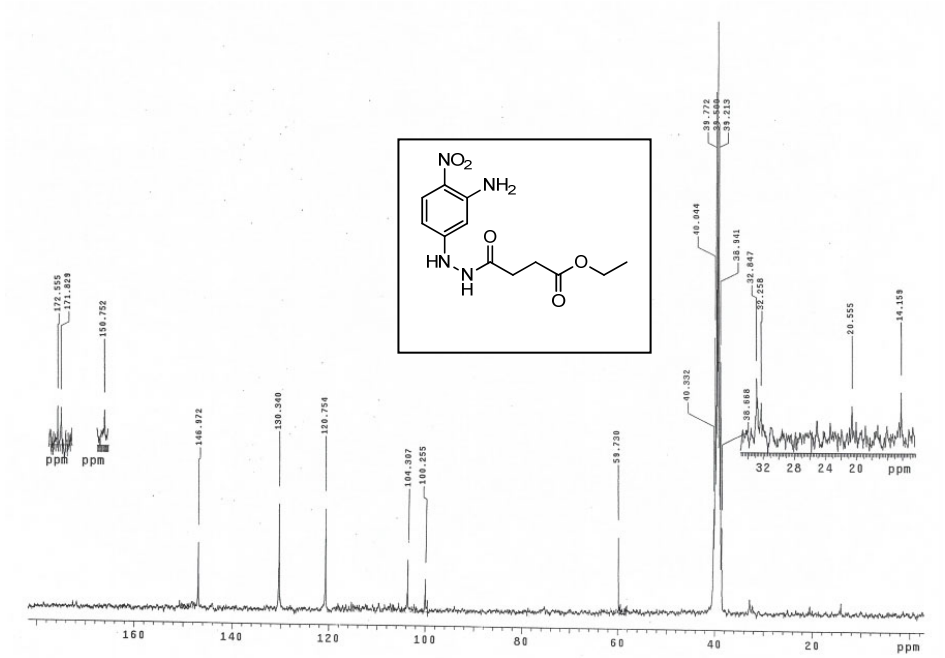


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
296.11223	116450.25	296.11207	-0.16	-0.54	$^{12}C_{12}{}^{1}H_{17}{}^{14}N_{4}{}^{16}O_{5}$	6.5

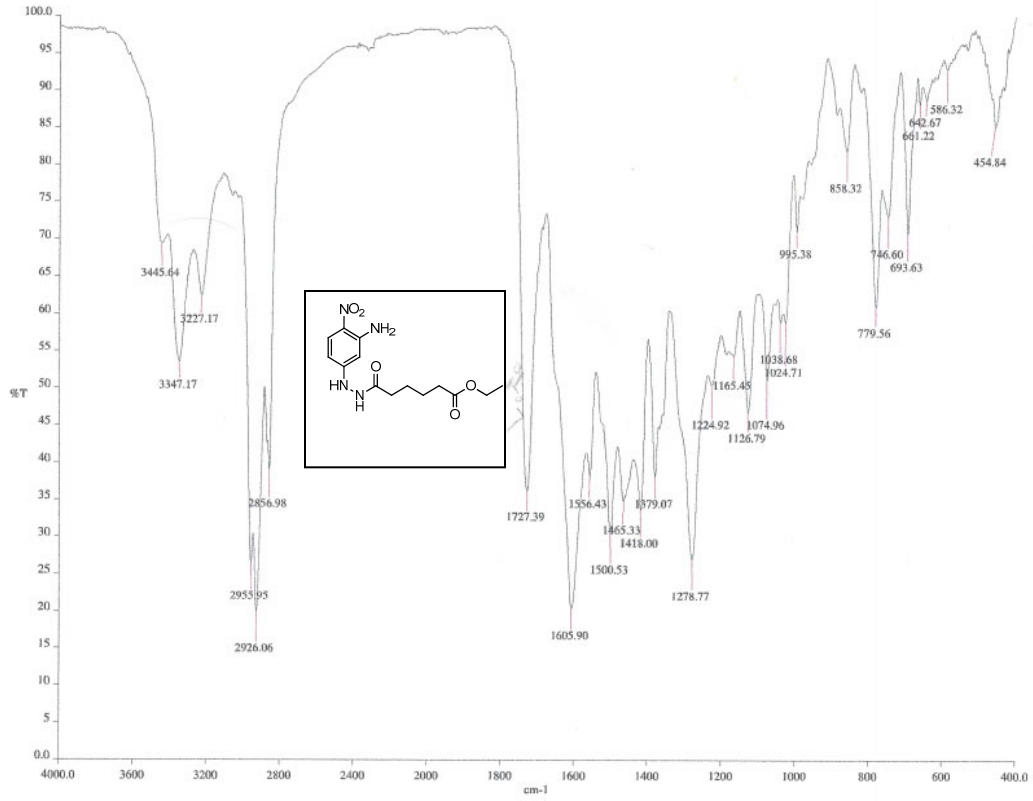
MS-Elemental Analysis Ethyl 4-(2-(3-amino-4-nitrophenyl)hydrazinyl)-4-oxobutanoate (**15**)



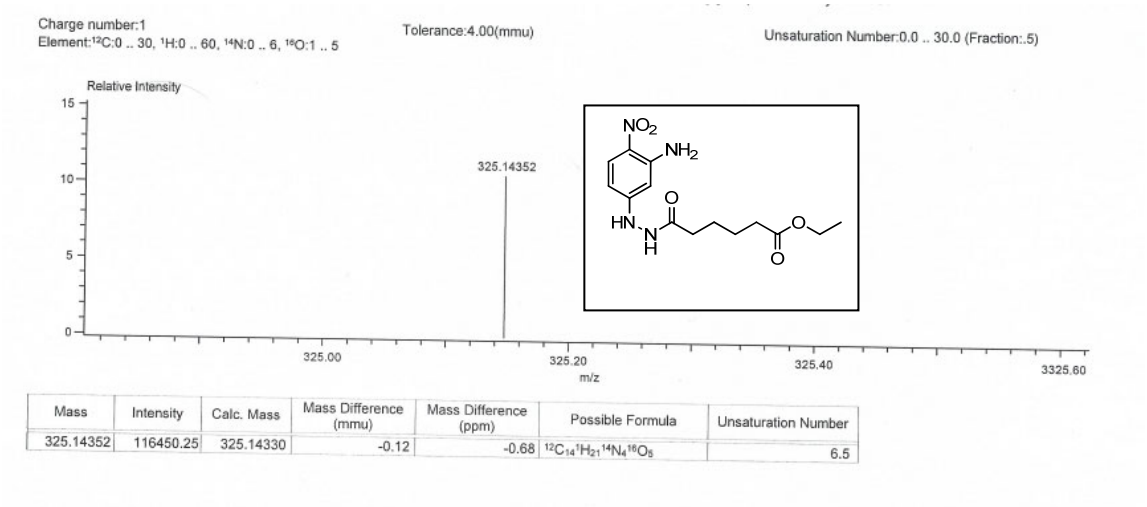
^{1}H NMR (300 MHz, DMSO-d6) Ethyl 4-(2-(3-amino-4-nitrophenyl)hydrazinyl)-4-oxobutanoate (**15**)



^{13}C NMR (75 MHz, DMSO-d6) Ethyl 4-(2-(3-amino-4-nitrophenyl)hydrazinyl)-4-oxobutanoate (**15**)

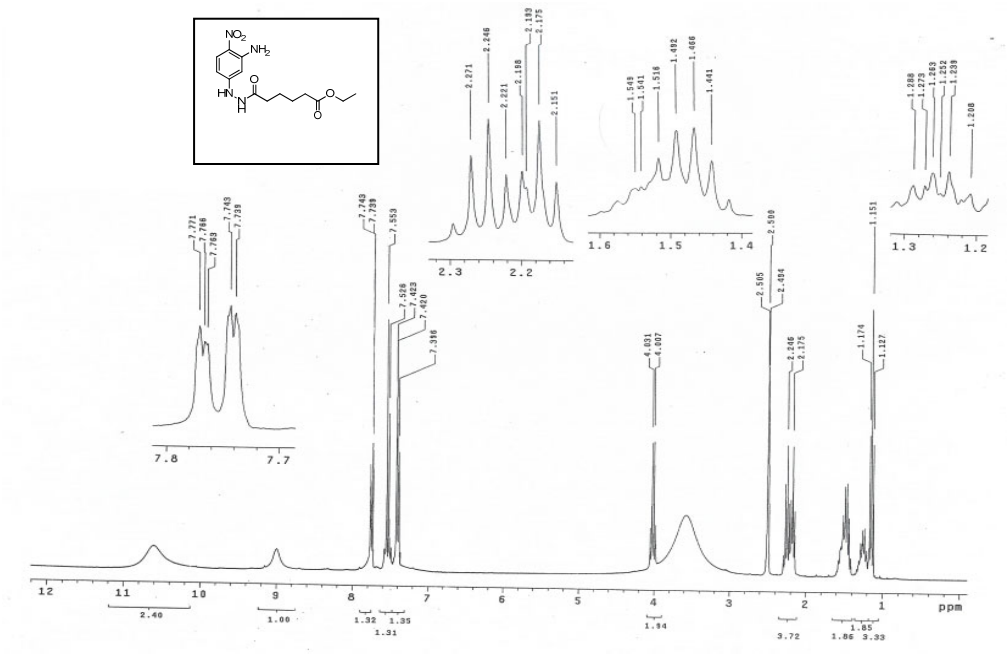


FT-IR Ethyl 6-(2-(3-amino-4-nitrophenyl)hydrazinyl)-6-oxohexanoate (**16**)

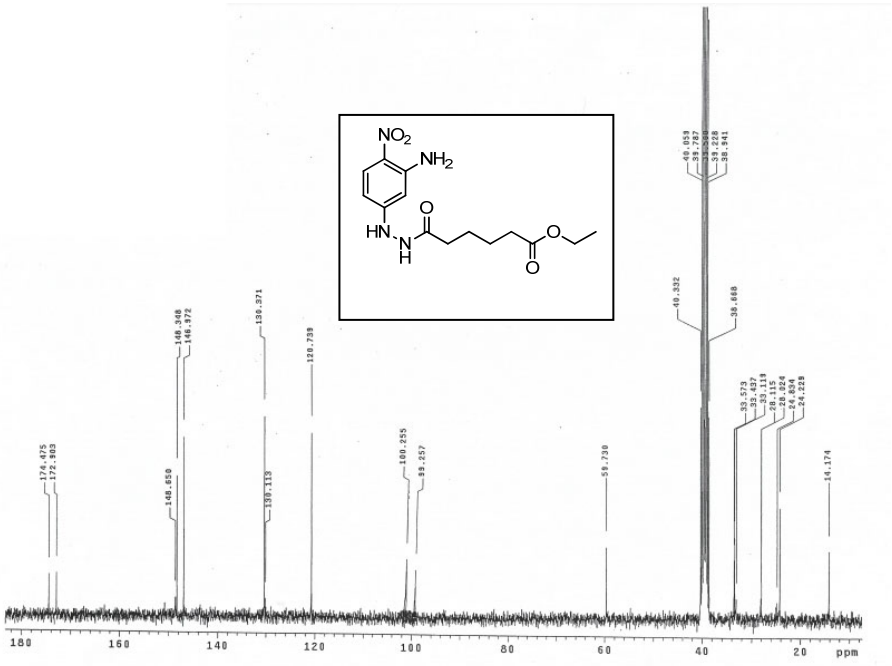


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
325.14352	116450.25	325.14330	-0.12	-0.68	$^{12}C_{14}{}^{1}H_{21}{}^{14}N_{4}{}^{16}O_{5}$	6.5

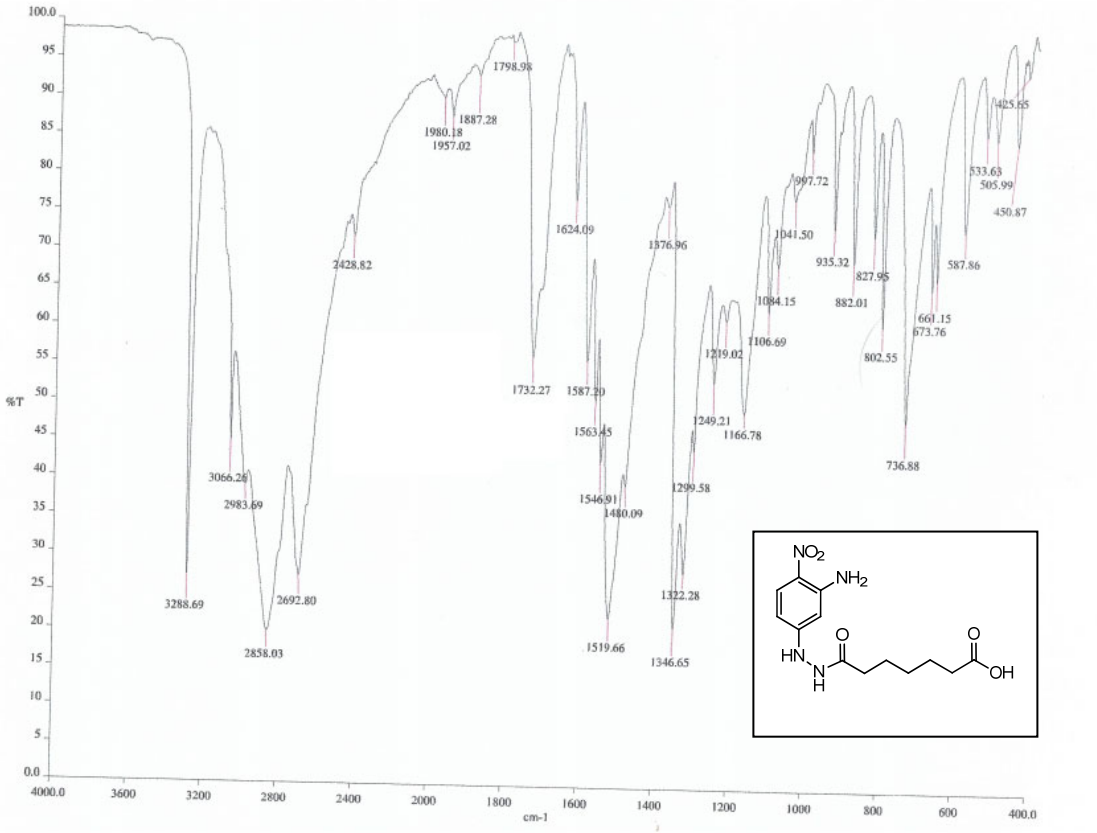
MS-Elemental Analysis Ethyl 6-(2-(3-amino-4-nitrophenyl)hydrazinyl)-6-oxohexanoate (**16**)



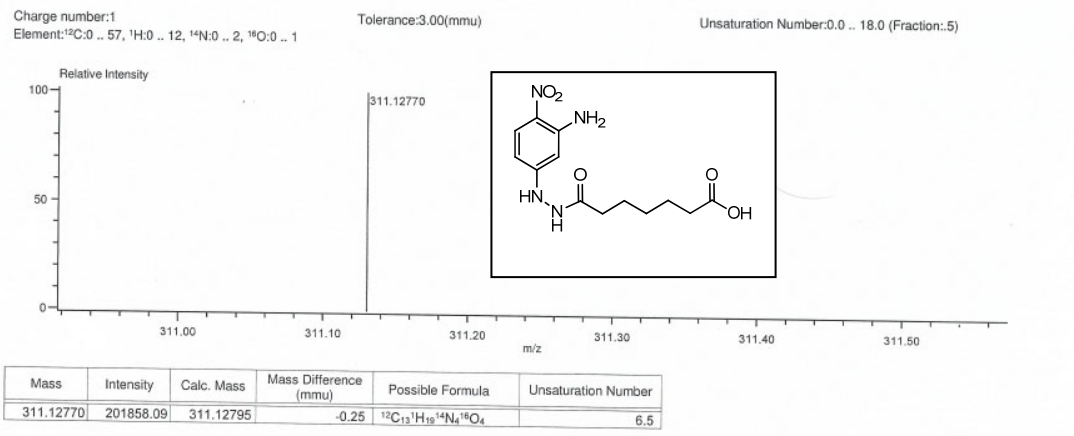
^{1}H NMR (300 MHz, DMSO-d6) Ethyl 6-(2-(3-amino-4-nitrophenyl)hydrazinyl)-6-oxohexanoate (**16**)



^{13}C NMR (75 MHz, DMSO-d6) Ethyl 6-(2-(3-amino-4-nitrophenyl)hydrazinyl)-6-oxohexanoate (**16**).

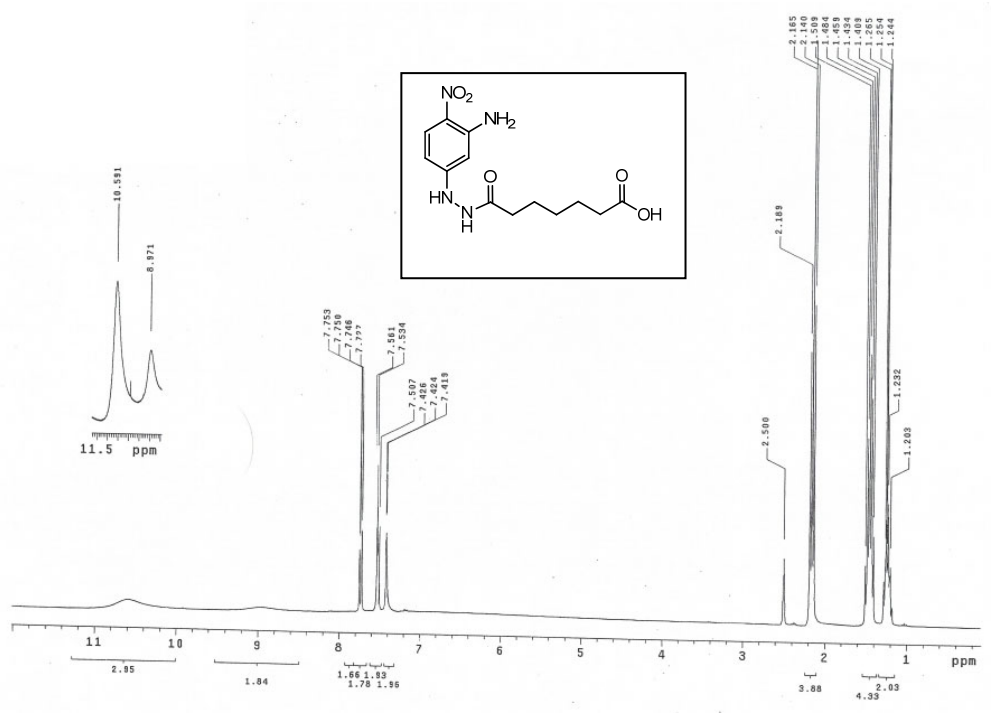


FT-IR 7-(2-(3-amino-4-nitrophenyl)hydrazinyl)-7-oxoheptanoic acid (**18**)

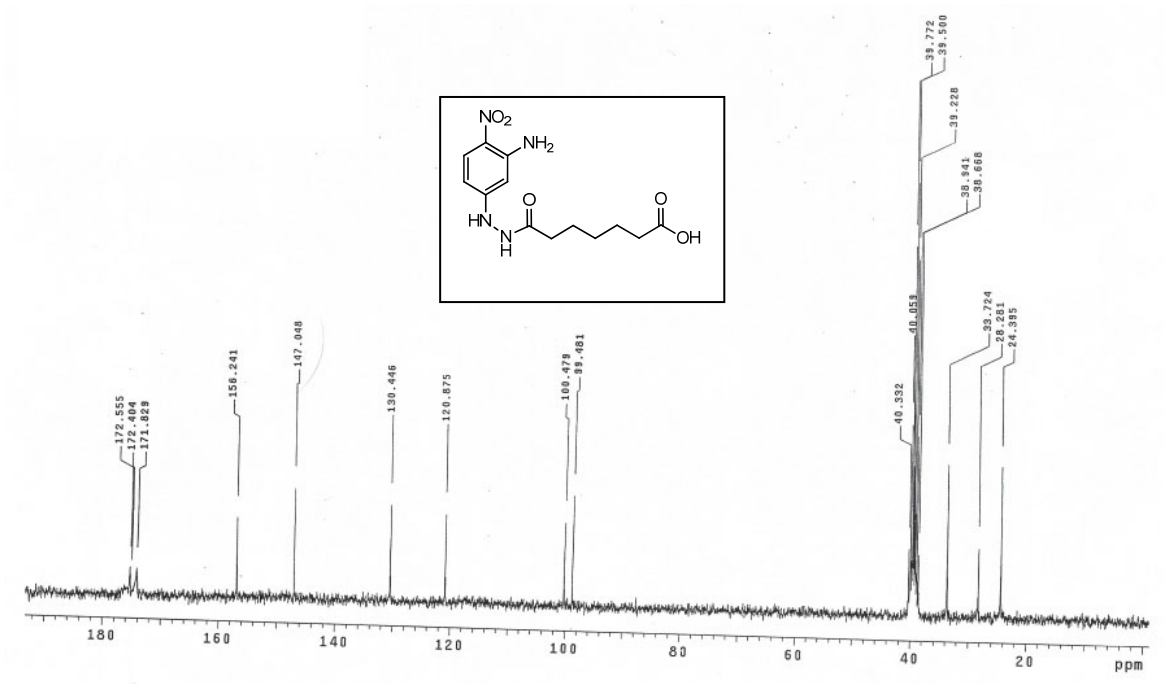


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Possible Formula	Unsaturation Number
311.12770	201858.09	311.12795	-0.25	$^{12}C_{13}{}^{1}H_{19}{}^{14}N_{4}{}^{16}O_{4}$	6.5

MS-Elemental Analysis 7-(2-(3-amino-4-nitrophenyl)hydrazinyl)-7-oxoheptanoic acid (**18**)



^{1}H NMR (300 MHz, DMSO-d6) 7-(2-(3-amino-4-nitrophenyl)hydrazinyl)-7-oxoheptanoic acid (**18**)



^{13}C NMR (75 MHz, DMSO-d6) 7-(2-(3-amino-4-nitrophenyl)hydrazinyl)-7-oxoheptanoic acid (**18**)

Microwave

A standard configuration of the Anton Para monowave synthesis reactor, 300 MW, was used for the experiments. All reactions were performed in sealed microwave vials. The reaction temperature was monitored using an immersing ruby thermometer. Fig. 1.

Fig. 1. Microwave monowave mode.

Ultrasound

A Cole Parmer 500-W 20 kHz ± 50 Hz ultrasonic processor, operating at 120 VAC, was employed in its standard configuration. The reaction temperature was monitored using an InfraPro IR thermometer. Fig. 2.

Fig. 2. Probe ultrasound equipment.

Infrared

An electric homemade metallic cylindrical can measuring 29.5 cm in length and 15.3 cm in width was explicitly designed to hold and position an IR emission bulb securely. The bulb used in this setup was a THERA-TERM OSRAM 250-W Red IR bulb, operating at 125 V and emitting a wavelength of 1100 nm (9.09 cm^{-1}). The device is equipped with a varicap diode for precise regulation of power output. The reaction temperature was continuously monitored using an InfraPro IR thermometer. Please refer to Fig. 3.

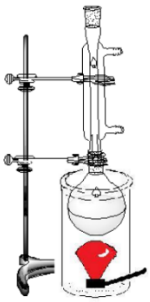


Fig. 3. Heating through an infrared lamp.

US-IR coupling

The US-IR coupling setup consists of two independent devices: a custom-built IR device equipped with a THERA-TERM OSRAM 250-W Red IR bulb (125 V), emitting a wavelength of 1100 nm (9.09 cm^{-1}), and a thermostat for power output regulation. A Cole Parmer 500-W 20 kHz ± 50 Hz ultrasonic processor was also utilized. These devices were assembled as depicted in Fig. 4. The US equipment operated at 80% power and 50% amplitude, with an irradiation frequency of 20 kHz ± 50 Hz. The reaction temperature was monitored using an InfraPro IR thermometer.

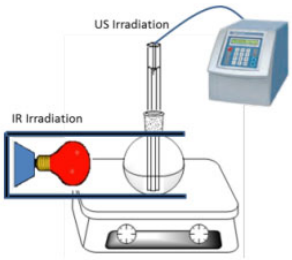


Fig. 4. Mounting for reactions with IR/US equipment.