Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of Dihydroquinoline Based Merocyanines as 'Naked Eye' and 'Fluorogenic' sensors for Hydrazine Hydrate in Aqueous Medium

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Section	Contents

1 Synthetic Procedures:

General Information

All chemicals are commercially available. All chemicals were obtained from S.D.Fine. All solvents were directly used from commercial sources. ^{1}HNMR and ^{13}C-NMR spectra were recorded on Bruker 400 MHz or Varian 300 MHz spectrometer. UV-vis absorption spectra were recorded with a Shimadzu UV-Vis spectrophotometer - 1650. Fluorescence was measured in Shimadzu spectrofluorimeter.

i. 1,2,2,4-Tetramethyl-1,2-dihydroquinoline

A mixture of TDQ (10.0 g), iodomethane (5.5 ml) and potassium carbonate (10.0 g) in 80 ml of DMF was maintained at 110 °C under nitrogen atmosphere for 24 hours. After completion of reaction as monitored by TLC, it was cooled to room temperature and poured into water. The product was then extracted with ethyl acetate. After removal of solvent, the product was purified by flash chromatography using pet ether/ethyl acetate (100/1, v/v) as mobile phase and silica gel (230-400 mesh) as stationary phase to give a yield of 82%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.2 (t, J=7.2 Hz, 1H), 7.05 (d, J=7.6 Hz, 1H), 6.65 (t, J=7.2 Hz, 1H), 6.53 (d, J=8.0 Hz, 1H), 5.29 (s, 1H), 2.79 (s, 3H), 1.98 (s, 3H), 1.29 (s, 6H).

ii. 1,2,2,4-Tetramethyl-1,2-dihydro-6-quinolinecarbaldehyde

Phosphorus oxychloride (8.1 ml) was added slowly in to dry DMF (100 ml) at 5-10 °C under nitrogen atmosphere and maintained at 50-60 °C for 30 min. 1,2,2,4-tetramethyl-1,2-dihydroquinoline (10 g) in dry DMF (50 ml) was slowly added into it over 10 min and the temperature was raised to 90 °C and maintained overnight under nitrogen. TLC showed absence of starting material and formation of spot that is DNP active. Reaction mass was then cooled to room temperature and poured into ice water (400 ml) and basified with aqueous solution of sodium hydroxide. Then extracted with ethyl acetate and the combined organic layer was washed with water and dried over sodium sulphate. After removal of solvent, the product was purified by flash column chromatography using pet ether/ethyl acetate (100/10, v/v) as mobile phase and silica gel (230-400 mesh) as stationary phase to give a yield of 60%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.8 (s, 1H), 7.57 (d, J=8.7 Hz, 1H), 7.55 (s, 1H), 6.50 (d, J=8.4Hz, 1H), 5.31 (s, 1H), 2.90 (s, 3H), 2.01 (s, 1H), 1.37 (s, 6H).

iii. Protocol for the synthesis of 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one

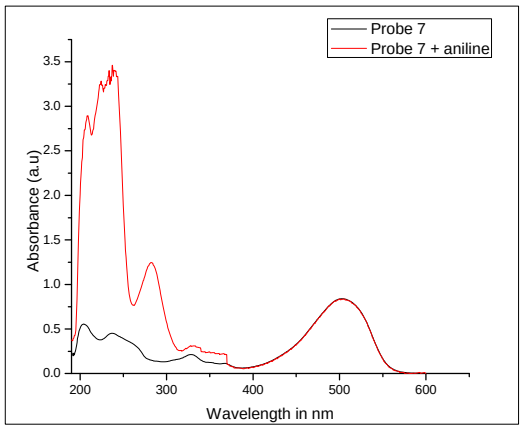
Methyl acetoacetate (11 mL, 101.4 mmol), Phenyl hydrazine (10 mL, 101.4 mmol) and 50 mL of glacial acetic acid were mixed and refluxed for 3 h. The reaction mixture was distilled to dryness and water (50 mL) was added. It was then extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulphate. After removal of solvent, the product was purified by flash column chromatography using pet ether/ethyl acetate (100/10, v/v) as mobile phase and silica gel (230-400 mesh) as stationary phase to give a yield of (14.68 g, 98%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, J=7.6 Hz, 2H), 7.39 (t, J=8 Hz, 2H), 7.17 (7, J=7.6 Hz, 1H), 3.41 (s, 2H), 2.18 (s, 3H).

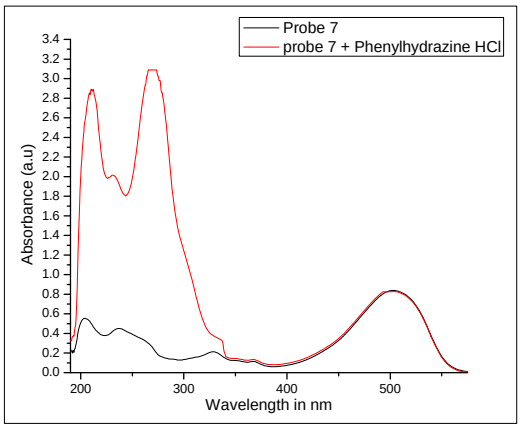
iv. Protocol for the synthesis of (E)-3-methyl-1-phenyl-4-((1,2,2,4-tetramethyl-1,2-dihydroquinolin-6-yl)methylene)-1H-pyrazol-5(4H)-one

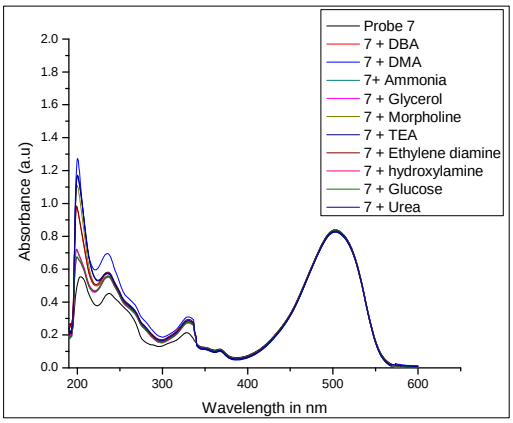
5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (1.74 g, 10 mmol), and 1,2,2,4-Tetramethyl-1,2-dihydro-6-quinolinecarbaldehyde.(2.37 g, 10.5 mmol) were mixed in absolute alcohol (20 ml). Triethylamine (2.53 g, 25 mmol) was added to it and stirred at room temperature for 30 min. The reaction mixture turned orange red coloured solution. Then it was refluxed for 20 h after which reaction mixture turned dark red coloured mass. It was then allowed to cool to room temperature and stirred for 5 h at room temperature. Formed orange coloured solids were filtered and washed with ethanol. Then vacuum dried at 60 °C for 2 h to get a yield of (g, 84%). MS (ESI MS): (m/z, %): 372 [M^++1].^{1}HNMR (400 MHz, $CDCl_3$): δ_H 8.46 (d, J=8.8 Hz, 1H), 8.42 (s, 1H), 8.00 (d, J=7.6 Hz 2H), 7.40 (t, J=8.4 Hz, 2H), 7.22 (s, 1H), 7.14 (t, J=7.2 Hz, 1H), 6.55 (d, J=9.2 Hz, 1H), 5.31 (s, 1H), 2.96 (s, 3H), 2.33 (s, 3H), 2.10 (s, 3H), 1.41 (s, 6H).

2 UV data

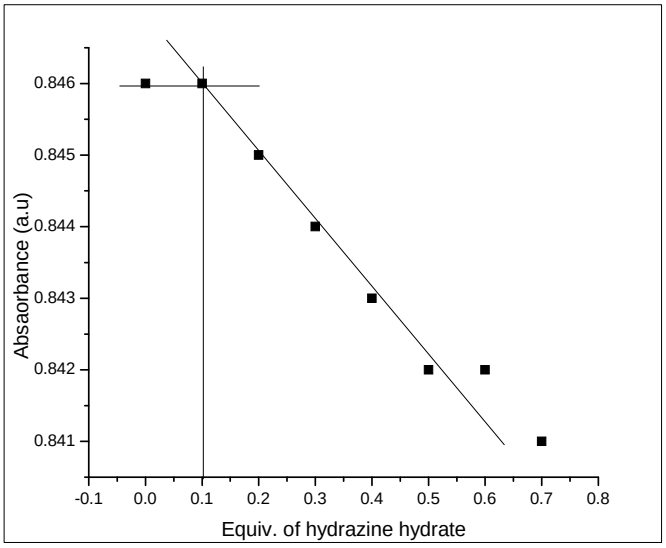
For 1 equivalent of probe 7, 50 equivalents of hydrazine hydrate and other common interfering neutral molecules were added and the spectra were noted. The spectra were recorded after 90 minutes of addition of hydrazine hydrate. This showed selectivity towards hydrazine hydrate. The tested molecules are ethylene diamine, dibutylamine, aniline, ammonia, glycerol, morpholine, hydroxylamine, phenyl hydrazine hydrochloride, triethylamine, glucose, urea, thiourea.







3 Detection Limit Calculation

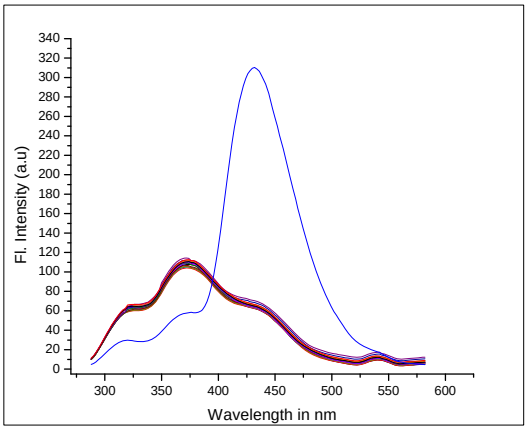


The detection limit of probe 7 for hydrazine hydrate was estimated to be of 16×10^{-7} M. To establish the detection limit, a graph of minimum equivalents of hydrazine hydrate versus absorbance was plotted. The point where a good sensitivity was observed was obtained by extrapolating the lines.
Equation used for calculating detection limit (DL)
Detection Limit = Conc. of Ligand x Equiv. of titrant at which change observed.

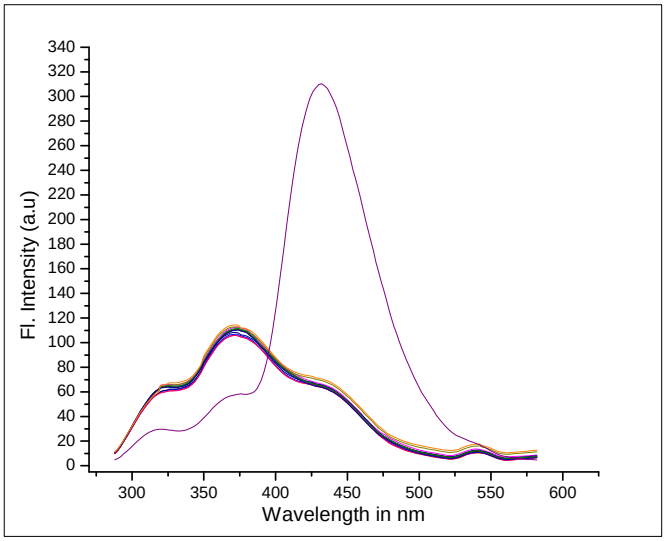
Therefore;
DL = $16.16 \times 10^{-6} \times 0.1 = 1.6 \times 10^{-6}$ M = 16×10^{-7} M.

4 Fluorescence Study

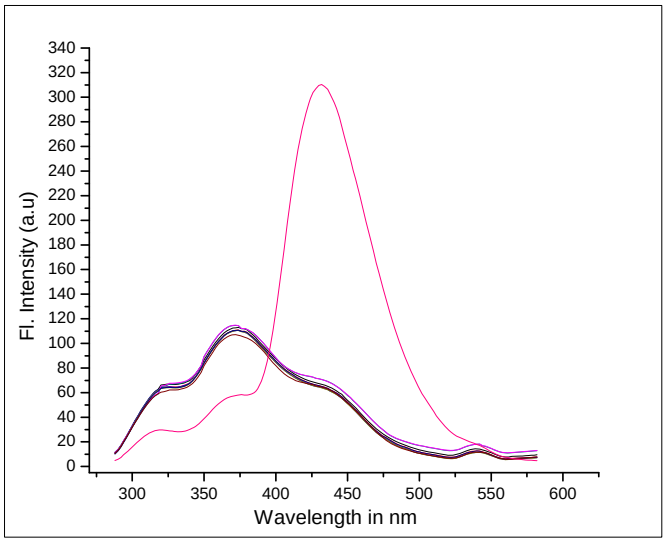
All the spectra were recorded 90 minutes after the addition of the respective analytes.



Fluorescence response of probe 7 (16.16 μM) to 120×10^{-5} M of various metals and hydrazine. The metals tested are Ag^{+}, $Al3^{+}$, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+}, and Zn^{2+}.



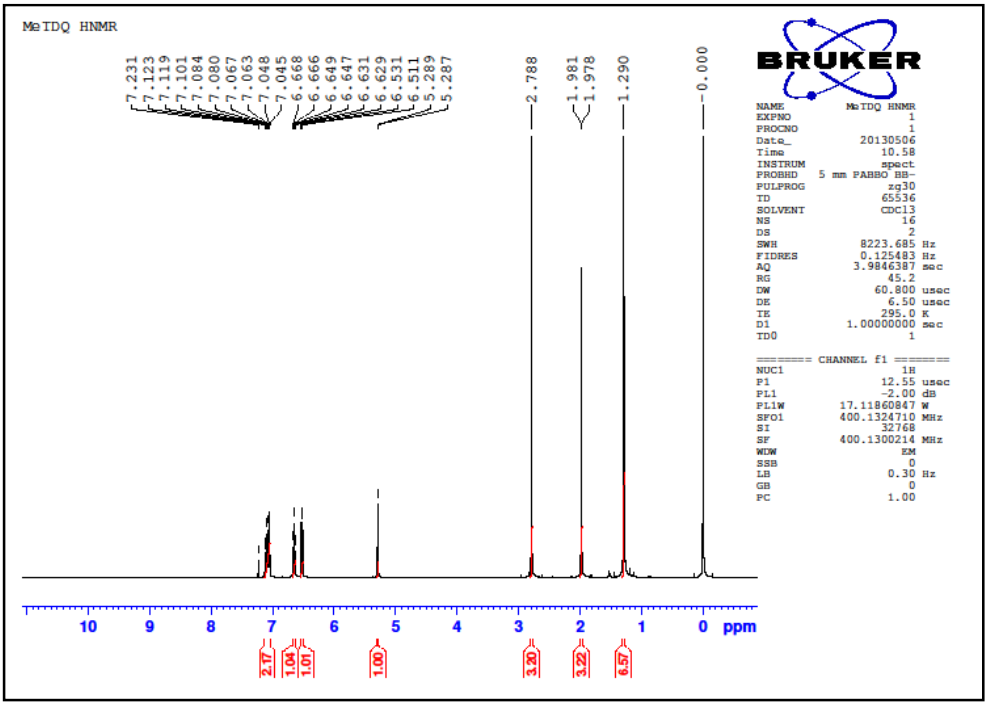
Fluorescence response of probe 7 (16.16 µM) to 120 x 10^{-5} M of various anions and hydrazine. The anions tested are AcO^-, Br^-, Cl^-, CN^-, CO^{3-}, F^-, HCO^{3-}, HPO^{4-}, NO^{2-}, NO^{3-}, SO^{3-}, and SO^{4-}



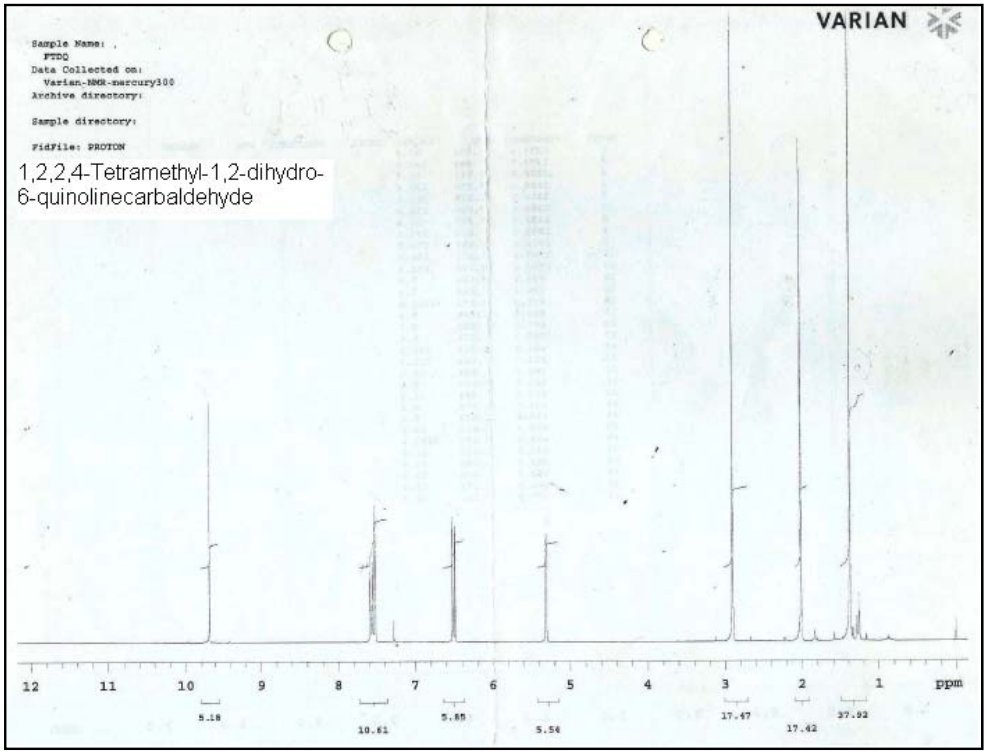
Fluorescence response of probe 7 (16.16 µM) to 120 x 10^{-5} M of commonly encountered neutral molecules and hydrazine. The tested molecules are ethylene diamine, dibutylamine, dimethylamine, ammonia, glycerol, morpholine, hydroxylamine, triethylamine, glucose, urea, and thiourea.

5 NMR Spectra

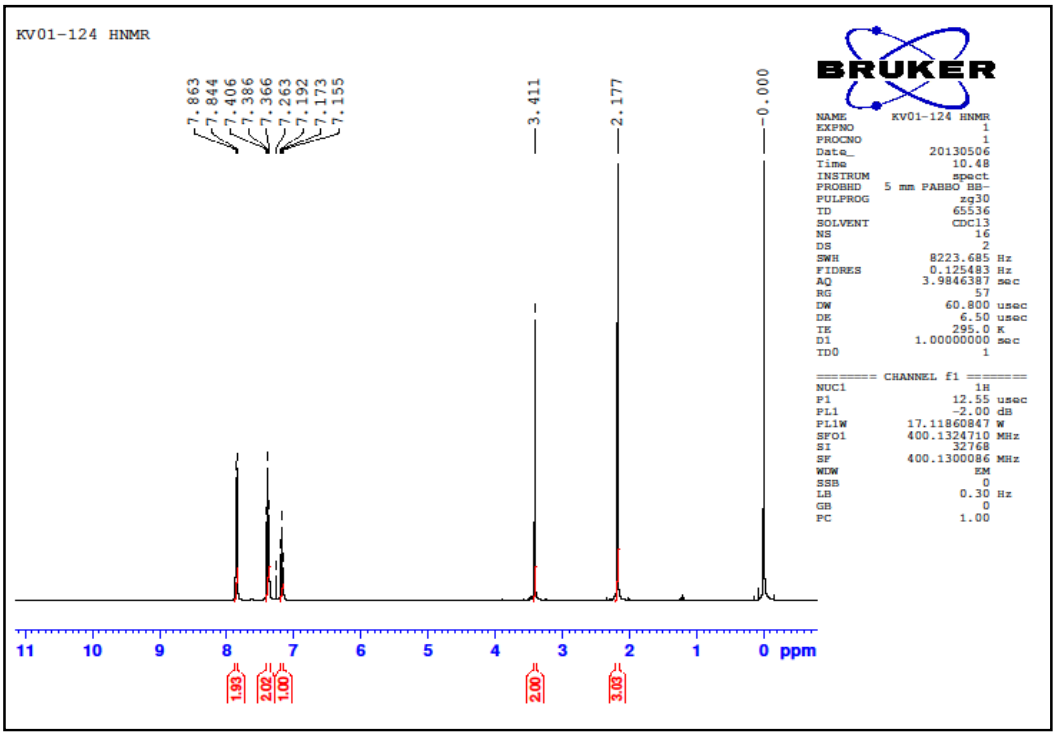
i. 1,2,2,4-Tetramethyl-1,2-dihydroquinoline



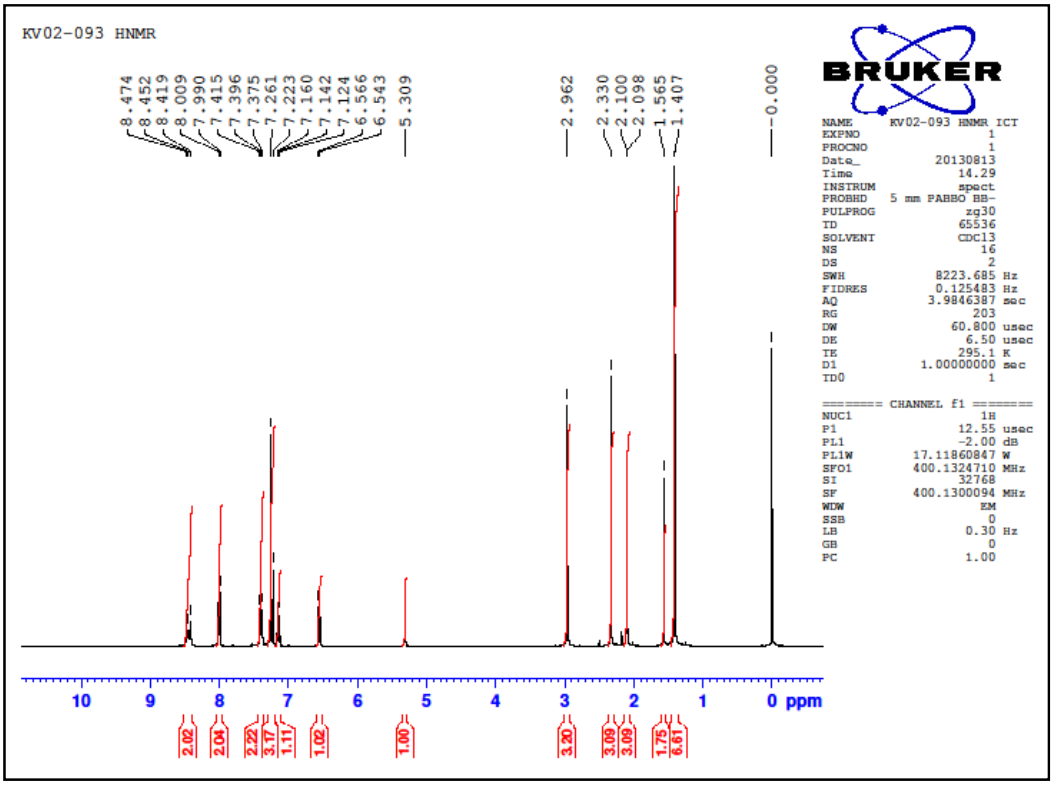
ii. 1,2,2,4-Tetramethyl-1,2-dihydro-6-quinolinecarbaldehyde

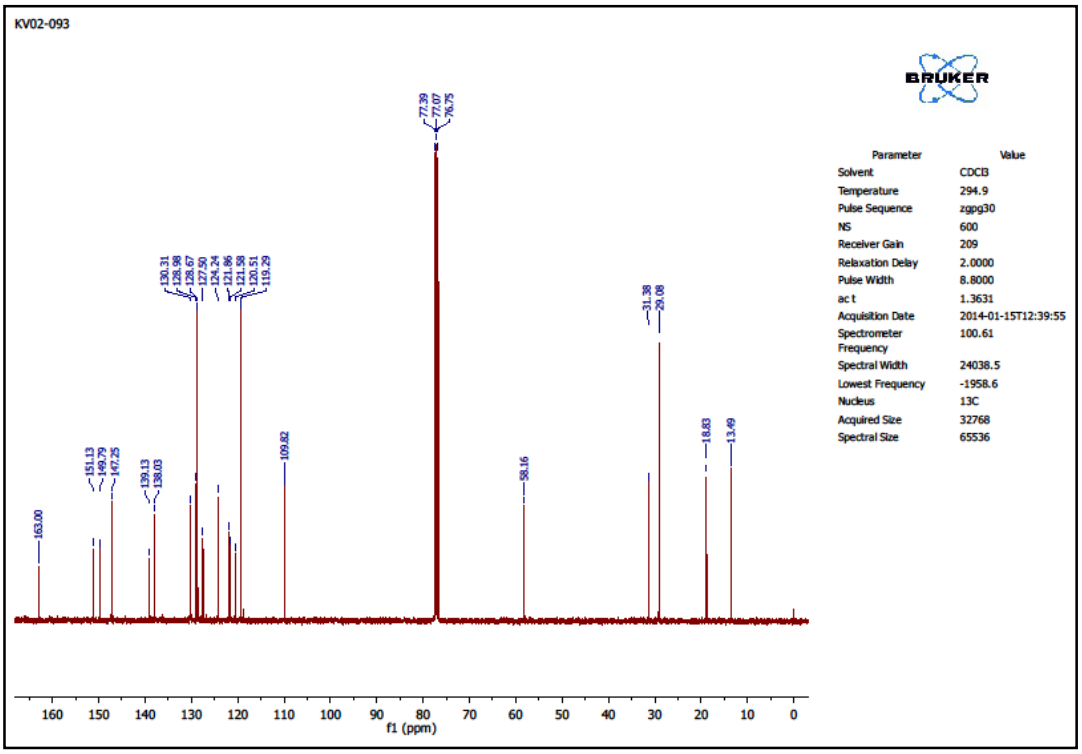


iii. 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one

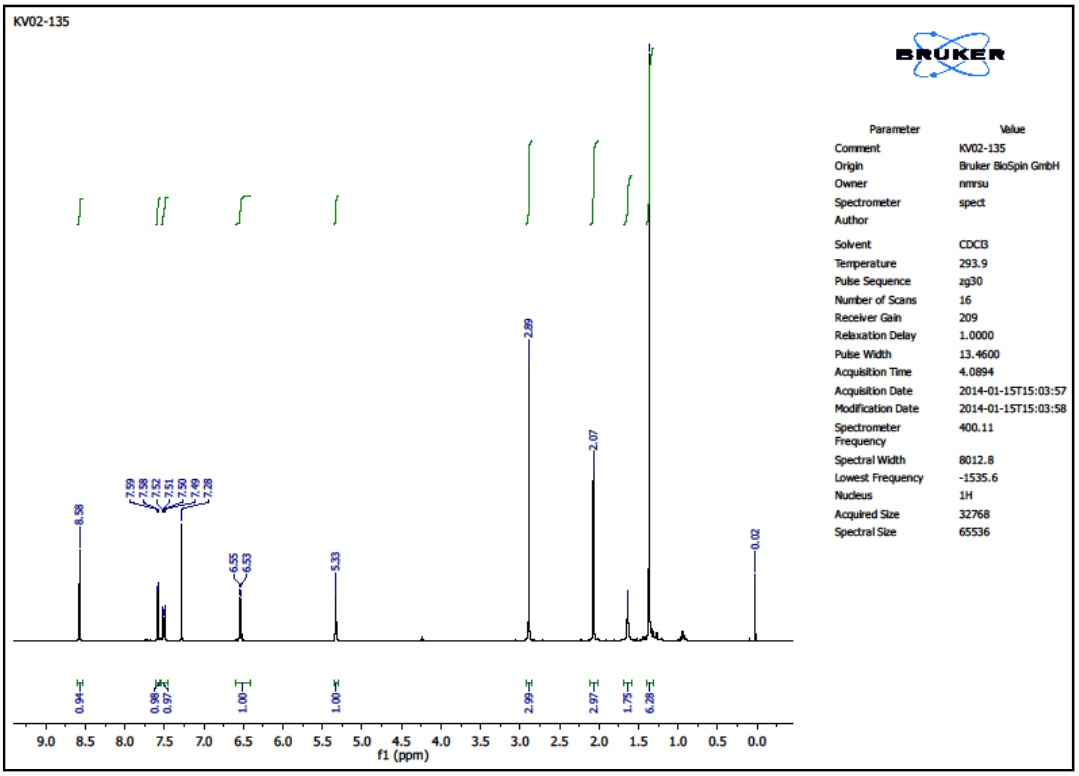


iv. (E)-3-methyl-1-phenyl-4-((1,2,2,4-tetramethyl-1,2-dihydroquinolin-6-yl)methylene)-1H-pyrazol-5(4H)-one

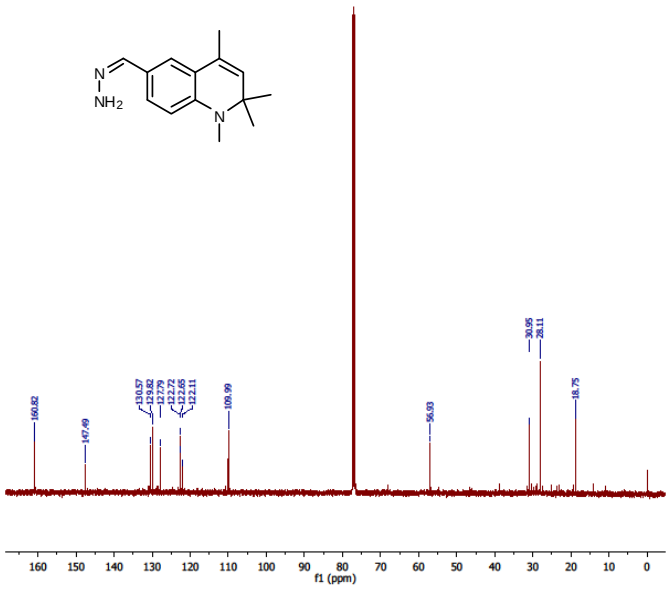




v. 6-(Hydrazonomethyl)-1,2,2,4-tetramethyl-1,2-dihydroquinoline



KVIJAY 08APRIL
KVO2-135



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Spectrometer	spect
Author	
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