



Supporting Information

for

Substituent effects in *N*-acetylated phenylazopyrazole photoswitches

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Materials and methods, analytical equipment, experimental procedures, compound characterization, UV–vis spectra at different concentrations, photochemical experiments, thermal isomerization analysis, and NMR spectra

Table of contents

1. Materials and methods	S2
2. Synthesis	S3
2.1 General procedure 1 to synthesize 3-(2-phenylhydrazono)pentane-2,4-diones	S3
2.2 General procedure 2 to synthesize 1,3-dimethyl-arylazopyrazoles	S6
2.3 General procedure 3 to synthesize (<i>E</i>)-1-(4-(diazenyl-3,5-dimethyl-1 <i>H</i> -pyrazol-1-yl)ethan-1-one	S11
2.4 pH-Dependent stability of NAc-PAP-H	S15
3. Photochemical and photophysical studies	S17
3.1 Determination of photostationary state distribution by ¹ H NMR	S17
3.2 Cyclic irradiation to study fatigue resistance	S23
3.3 Determination of molar extinction coefficients	S27
3.3.1 Absorbance vs. concentrations of NAc-PAP derivatives	S27
3.3.2 Absorbance vs. concentrations of NMe-PAP derivatives	S31
3.3.3 Absorbance vs. concentrations of NH-PAP derivatives	S35
3.4 Chemical actinometry	S39
3.5 Determination of quantum yields	S39
3.5.1 Irradiation of NAc-PAP derivatives and evaluation of the kinetic traces	S40
3.5.2 Irradiation of NH-PAP derivatives and evaluation of the kinetic traces	S48
3.5.3 Irradiation of NMe-PAP derivatives and evaluation of the kinetic traces	S52
3.6 Determination of thermal half-lives	S56
3.7 Hammett correlation of thermal half-lives of NAc-PAP derivatives	S60
3.7.1 Thermal relaxation of NAc-PAP-CN at different temperatures	S62
3.7.2 Thermal relaxation of NAc-PAP-OMe at different temperatures	S65
4. NMR Spectra	S68
5. References	S160

1. Materials and methods

Reagents and solvents: Reagents and solvents were purchased in the highest grade of purity available. Dry solvents were purchased from Sigma-Aldrich (Taufkirchen, Germany). Technical solvents were distilled before use. HPLC-grade solvents have been used for photoswitching and kinetics studies. For column chromatography, distilled solvents have been utilized. Solvents for the NMR measurements were supplied by Deuterio (Kastellaun, Germany) or Eurisotop (Saarbrücken, Germany).

Chromatography: TLC was performed on 0.25 mm silica-gel 60 F plates with a 254 nm fluorescence indicator from Merck (Darmstadt, Germany). The substance detection took place by light with wavelengths of 254 nm and 360 nm. Non-UV-active substances have been visualized by the following TLC stains: ninhydrin solution (1.5 g ninhydrin, 3 mL acetic acid in 100 mL *n*-butanol) or potassium permanganate solution (3.0 g KMnO₄, 20 g K₂CO₃ and 2.5 mL NaOH (10%) in 400 mL water) and gentle heating afterwards.

Flash column chromatography was performed using silica-gel of the type Geduran[®] Si 60 (40–63 µm mesh ASTM) purchased from Merck (Darmstadt, Germany). Columns were packed with wet silica gel and the samples were loaded as a concentrated solution or as a silica pad.

NMR spectroscopy: ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on 300 or 400 MHz spectrometers; ¹³C NMR spectra were obtained on 101 or 75 MHz instruments. ¹H chemical shifts (δ) are reported in parts per million (ppm) relative to DMSO-*d*₆ (δ= 2.50 ppm), CD₃OD (δ= 3.31 ppm), CDCl₃ (δ= 7.26 ppm), or CD₃CN (δ= 1.94 ppm) as internal references. ¹³C δ are reported in ppm with DMSO-*d*₆ (δ= 77.67 ppm), CD₃CN (δ= 118.26, 1.32 ppm) as internal references. ¹⁹F NMR spectra were measured without any internal standard to qualitatively confirm the structure and purity of the desired product.

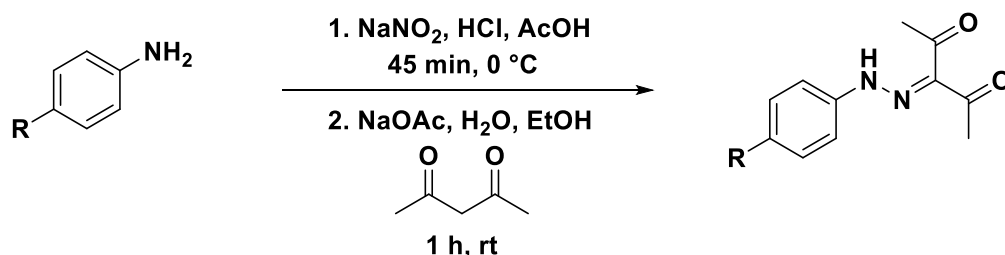
MS/HRMS: Electron spray ionization mass spectrometry (ESI-MS) and high-resolution ESI (HRMS) were performed on a maXis or MicroTOF spectrometer from Bruker (Bremen Germany).

UV–vis spectroscopy: UV–vis absorption spectroscopy was performed on a Specord S600 or Jasco V-670 in quartz cuvettes (path 1.00 cm) at a controlled temperature of 20 °C. Molar extinction coefficients (ε) were determined by fitting the slope of absorbance dependency to the concentration taken from at least three separate dilutions. Photoisomerization was

measured under 365 (at concentration 12.5 μM) or 445 nm (at concentration 50 μM) irradiation at 25% or 10% intensity.

2. Synthesis

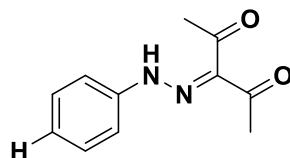
2.1 General procedure 1 to synthesize 3-(2-phenylhydrazono)pentane-2,4-diones



The synthesis was adopted from Weston et al.¹ The starting compound (10.74 mmol, 1.0 equiv) was dissolved in AcOH (16.1 mL) and HCl (12 M, 2.5 mL) and in water dissolved NaNO₂ (0.89 g, 12.9 mmol, 1.3 equiv) was added after cooling to 0 °C. The mixture was stirred for 45 minutes and then added dropwise to a solution of pentane-2,4-dione (1.4 mL, 14.0 mmol, 1.3 equiv) and NaOAc (2.64 g, 32.22 mmol, 3.0 equiv) in water (6.4 mL) and EtOH (10.7 mL). After stirring for 1 hour the solution was vacuum filtrated to collect the yellow solid. It was washed with water, water/EtOH 1:1, and hexane and dried in vacuo.

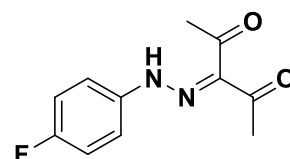
3-(2-Phenylhydrazono)pentane-2,4-dione

Yield: 0.85 g (4.15 mmol, 38 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 14.05 (s, 1H), 7.59 – 7.54 (m, 2H), 7.46 – 7.39 (m, 2H), 7.22 – 7.16 (m, 1H), 2.44 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.5, 141.8, 133.3, 129.6, 125.4, 116.3, 31.2, 26.5. **MS(EI) m/z:** 205.1 [M+H]⁺, 227.1 [M+Na]⁺. The spectral data are in accordance with the literature.^{2,3}



3-(2-(4-Fluorophenyl)hydrazono)pentane-2,4-dione

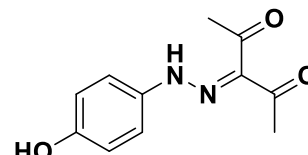
Yield: 2.16 g (9.71 mmol, 90 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 14.03 (s, 1H), 7.65 – 7.59 (m, 2H), 7.30 – 7.23 (m, 2H), 2.43 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.4, 160.9, 158.5, 138.5, 138.4, 133.3, 118.2, 118.1, 116.4, 116.2, 31.0, 26.4. **¹⁹F NMR** (282 MHz, DMSO-d₆): δ



(ppm) = -117.4. **MS(EI) m/z**: 223.1 [M+H]⁺, 245.1 [M+Na]⁺. The spectral data are in accordance with the literature.³

3-(2-(4-Hydroxyphenyl)hydrazono)pentane-2,4-dione

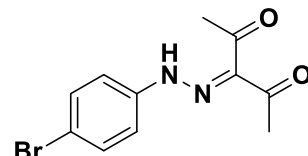
Yield: 0.60 g (2.72 mmol, 25 %). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 14.49 (s, 1H), 9.65 (s, 1H), 7.46 – 7.40 (m, 2H), 6.87 – 6.79 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ



(ppm) = 196.0, 155.9, 133.7, 132.1, 118.1, 116.1, 31.1, 26.4. **MS(EI) m/z**: 243.1 [M+Na]⁺. The spectral data are in accordance with the literature.³

3-(2-(4-Bromophenyl)hydrazono)pentane-2,4-dione

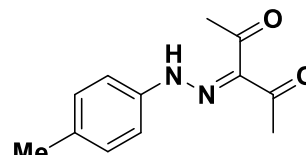
Yield: 2.57 g (9.09 mmol, 85 %) **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 14.65 (s, 1H), 7.52 – 7.48 (m, 2H), 7.27 (d, J = 7.0 Hz, 2H), 2.59 (s, 3H), 2.47 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 198.3, 197.0,



140.8, 133.6, 132.8, 118.7, 117.8, 31.8, 26.7. **MS(EI) m/z**: 283.0, 285.0 [M+Na]⁺. The spectral data are in accordance with the literature.³

3-(2-(p-Tolyl)hydrazono)pentane-2,4-dione

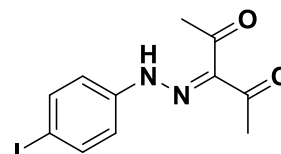
Yield: 1.74 g (7.98 mmol, 74 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 14.17 (s, 1H), 7.48 – 7.44 (m, 2H), 7.26 – 7.21 (m, 2H), 2.43 (s, 6H), 2.30 (s, 3H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.3,



139.4, 134.9, 132.9, 130.0, 116.3, 31.1, 26.3, 20.5. **MS(EI) m/z**: 219.1 [M+H]⁺, 241.1 [M+Na]⁺. The spectral data are in accordance with the literature.^{2,3}

3-(2-(4-Iodophenyl)hydrazono)pentane-2,4-dione

Yield: 3.15 g (9.56 mmol, 89 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 13.81 (s, 1H), 7.76 – 7.71 (m, 2H), 7.41 – 7.37 (m, 2H), 2.43 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.8, 141.8,



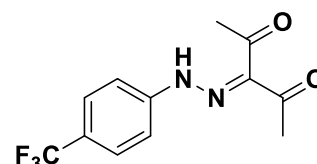
138.1, 133.8, 118.4, 89.3, 31.2, 26.3. **MS(EI) m/z**: 331.0 [M+H]⁺. The spectral data are in accordance with the literature.³

3-(2-(4-(Trifluoromethyl)phenyl)hydrazono)pentane-2,4-dione

Yield: 2.76 g (10,16 mmol, 95 %). **¹H NMR** (300 MHz, CDCl₃): δ (ppm)

= 14.58 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 2.62 (s, 3H), 2.50 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃): δ (ppm) = 198.6, 197.1,

144.4, 134.3, 127.7, 127.1, 127.1, 116.1, 31.9, 26.8. **¹⁹F NMR** (282 MHz, CDCl₃): δ (ppm) = -66.54. The spectral data are in accordance with the literature.^{2,3}

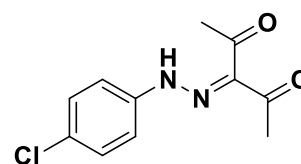


3-(2-(4-Chlorophenyl)hydrazono)pentane-2,4-dione

Yield: 2.17 g (9.10 mmol, 85 %). **¹H NMR** (400 MHz, DMSO-d₆): δ

(ppm) = 13.84 (s, 1H), 7.62 – 7.57 (m, 2H), 7.49 – 7.43 (m, 2H), 2.43 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.5, 140.9,

133.8, 129.4, 129.0, 117.9, 31.2, 26.4. **MS(EI) m/z:** 239.06 [M+H]⁺, 261.04 [M+Na]⁺. The spectral data are in accordance with the literature.³

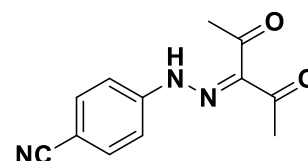


4-(2-(2,4-Dioxopentan-3-ylidene)hydrazineyl)benzonitrile

Yield: 1.24 g (5.39 mmol, 50 %). **¹H NMR** (300 MHz, DMSO-d₆): δ

(ppm) = 13.39 (s, 1H), 7.88 – 7.81 (m, 2H), 7.73 – 7.66 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 197.6,

196.5, 145.9, 135.8, 133.8, 119.0, 116.4, 106.1, 31.3, 26.3. **MS(EI) m/z:** 252.1 [M+Na]⁺. The spectral data are in accordance with the literature.²

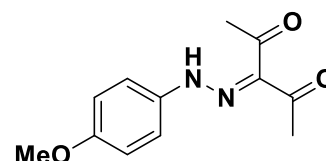


3-(2-(4-Methoxyphenyl)hydrazono)pentane-2,4-dione

Yield: 0.55 g (2.36 mmol, 22 %). **¹H NMR** (300 MHz, DMSO-d₆):

δ (ppm) = 14.36 (s, 1H), 7.58 – 7.51 (m, 2H), 7.05 – 6.97 (m, 2H), 3.77 (s, 3H), 2.48 – 2.35 (m, 6H). **¹³C NMR** (75 MHz, DMSO-d₆):

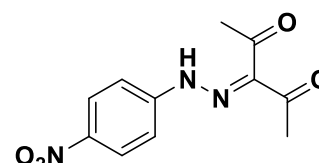
δ (ppm) = 196.1, 157.4, 135.2, 132.5, 117.9, 114.9, 55.4, 31.1, 26.4. **MS(EI) m/z:** 257.1 [M+Na]⁺. The spectral data are in accordance with the literature.^{2,3}



3-(2-(4-Nitrophenyl)hydrazono)pentane-2,4-dione

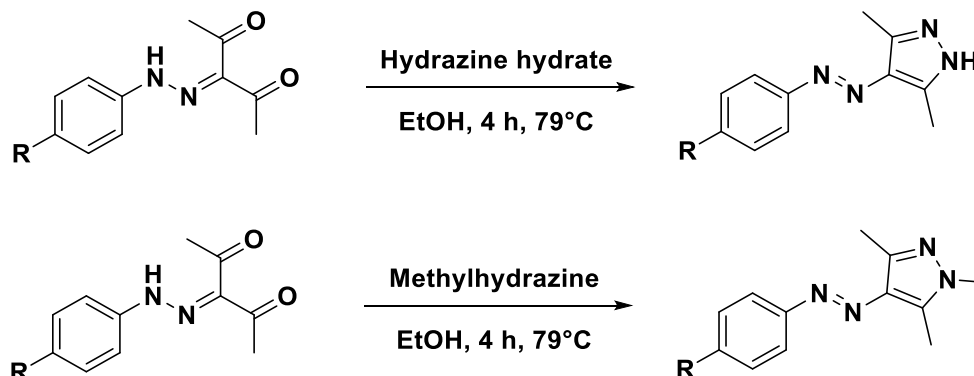
Yield: 1.61 g (6.47 mmol, 60%). **¹H NMR** (400 MHz, CD₂Cl₂): δ

(ppm) = 14.43 (s, 1H), 8.36 – 8.16 (m, 2H), 7.73 – 7.43 (m, 2H), 2.59 (s, 3H), 2.49 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂): (ppm) =



199.0, 197.1, 147.3, 144.8, 135.5, 126.0, 116.2, 31.9, 26.8. **MS(EI) m/z:** 272.1 [M+Na]⁺. The spectral data are in accordance with the literature.^{2,3}

2.2 General procedure 2 to synthesize 1,3-dimethyl-arylazopyrazoles



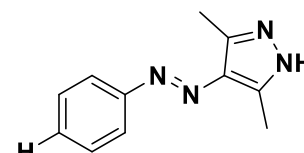
The synthesis was adopted from Patel et al.⁴ The 3-(2-phenylhydrazono)pentane-2,4-dione (0.5 mmol, 1 equiv) was dissolved in EtOH (7 mL) and then the hydrazine hydrate/methylhydrazine (0.5 mmol, 1 equiv) was added. The solution was refluxed for 4 hours, and the solvent was removed in vacuo.

(E)-3,5-Dimethyl-4-(phenyldiazenyl)-1H-pyrazole

Yield: 101,5 mg (quant.) ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.74 – 7.69 (m, 2H), 7.54 – 7.48 (m, 2H), 7.44 – 7.40 (m, 1H), 2.6 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 153.7, 141.7, 134.9, 129.7,

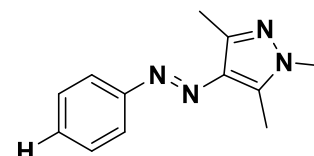
129.1, 122.0, 12.3. **MS(EI) m/z:** 201.1 [M+H]⁺, 223.1 [M+Na]⁺. The spectral data are in accordance with the literature.⁵



(E)-1,3,5-Trimethyl-4-(phenyldiazenyl)-1H-pyrazole

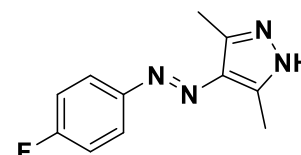
Yield: 88.0mg (0.41 mmol, 82 %). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 7.75 - 7.70 (m, 2H), 7.54 - 7.48 (m, 2H), 7.46 - 7.39 (m, 1H), 3.74 (s, 3H), 2.55 (s, 3H), 2.37 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆):

δ (ppm) = 153.0, 140.3, 139.6, 134.4, 129.5, 129.2, 121.4, 36.0, 13.8, 9.5. **MS(EI) m/z:** 215.13 [M+H]⁺, 237.11 [M+Na]⁺. The spectral data are in accordance with the literature.¹



(E)-4-((4-Fluorophenyl)diazenyl)-3,5-dimethyl-1H-pyrazole

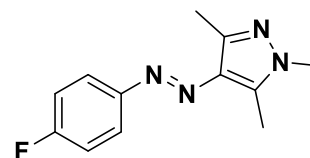
Yield: 111.4mg (quant.). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 12.84 (s, 1H), 7.80 - 7.73 (m, 2H), 7.36 - 7.29 (m, 2H), 2.44 (s, 6H).



¹³C NMR (101 MHz, DMSO-d₆): δ (ppm) = 163.8, 161.3, 149.8, 134.0, 123.4, 123.3, 116.1, 115.9, 13.7, 10.0. **MS(EI) m/z**: 219.10 [M+H]⁺, 241.08 [M+Na]⁺. The spectral data are in accordance with the literature.^{5,6}

(E)-4-((4-Fluorophenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole

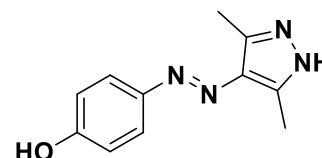
Yield: 157.7mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.78 (dd, J = 9.2, 5.3 Hz, 2H), 7.34 (t, J = 8.9 Hz, 2H), 3.74 (s, 3H), 2.54 (s, 3H), 2.36 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 161.0,



149.7, 140.3, 139.7, 123.3, 116.2, 115.9, 36.0, 13.8, 9.5. **¹⁹F NMR** (282 MHz, DMSO-d₆): δ (ppm) = -112.4. **MS(EI) m/z**: 233.12 [M+H]⁺, 255.10 [M+Na]⁺.

(E)-4-((3,5-Dimethyl-1H-pyrazol-4-yl)diazenyl)phenol

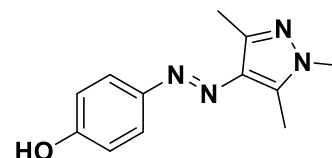
Yield: 105.1mg (0.49 mmol, 98 %). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) 12.67 (s, 1H), 9.91 (s, 1H), 7.65 – 7.56 (m, 2H), 6.92 – 6.83 (m, 2H), 2.48 – 2.34 (m, 6H). **¹³C NMR** (75 MHz, DMSO-d₆):



δ (ppm) = 159.1, 146.1, 133.7, 123.1, 115.6, 31.1, 26.4. **MS(EI) m/z**: 217.1 [M+H]⁺, 215.1 [M-H]⁻. The spectral data are in accordance with the literature.⁶

(E)-4-((1,3,5-Trimethyl-1H-pyrazol-4-yl)diazenyl)phenol

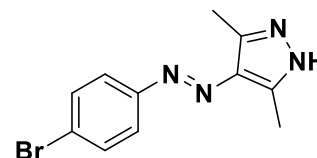
Yield: 75.5mg (0.33 mmol, 66 %). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 9.93 (s, 1H), 7.65 - 7.57 (m, 2H), 6.90 - 6.83 (m, 2H), 3.71 (s, 3H), 2.51 (s, 3H), 2.34 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ



(ppm) = 196.0, 159.1, 155.9, 146.1, 139.9, 138.2, 134.0, 123.2, 118.1, 116.14, 115.6, 35.9, 31.1, 13.7, 9.4. **MS(EI) m/z**: 231.1 [M+H]⁺, 253.1 [M+Na]⁺. The spectral data are in accordance with the literature.⁷

(E)-4-((4-Bromophenyl)diazenyl)-3,5-dimethyl-1H-pyrazole

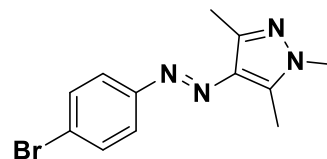
Yield: 144.0mg (0.49 mmol, 98 %). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 12.89 (s, 1H), 7.71 - 7.62 (m, 4H), 2.43 (d, J = 7.3 Hz, 6H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 196.5, 151.9, 141.4,



134.2, 132.3, 123.3, 122.4, 13.6, 10.1. **MS(EI) m/z**: 279.0 [M+H]⁺, 281.0 [M+H]⁺. The spectral data are in accordance with the literature.^{5,6}

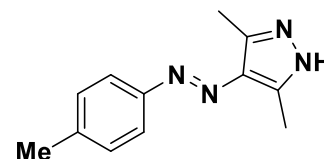
(E)-4-((4-Bromophenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole

Yield: 147.6mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.73 - 7.64 (m, 4H), 3.74 (s, 3H), 2.54 (s, 3H), 2.36 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 151.9, 140.5, 140.1, 134.4, 132.2, 123.3, 122.4, 36.0, 13.8, 9.5. **MS(EI) m/z:** 293.0 [M+H]⁺, 295.0 [M+H]⁺, 315.0 [M+Na]⁺, 317.0 [M+Na]⁺.



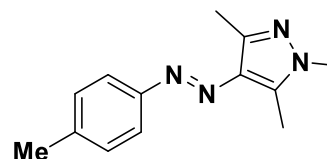
(E)-3,5-Dimethyl-4-(p-tolyldiazenyl)-1H-pyrazole

Yield: 113.9mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 12.79 (s, 1H), 7.65 - 7.60 (m, 2H), 7.33 - .28 (m, 2H), 2.44 (s, 6H), 2.36 (s, 3H), 2.30 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 151.0, 139.2, 134.0, 129.7, 121.3, 20.9, 20.5. **MS(EI) m/z:** 215.13 [M+H]⁺, 237.11 [M+Na]⁺. The spectral data are in accordance with the literature.^{5,6}



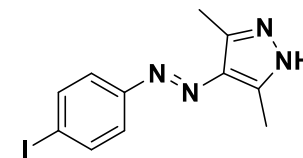
(E)-1,3,5-Trimethyl-4-(p-tolyldiazenyl)-1H-pyrazole

Yield: 126.2mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.63 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.7Hz, 2H), 3.73 (s, 3H), 2.53 (s, 3H), 2.36 (s, 6H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 151.0, 140.2, 139.3, 130.0, 129.7, 121.3, 116.3, 35.9, 20.9, 13.7, 9.4. **MS(EI) m/z:** 229.1 [M+H]⁺, 251.1 [M+Na]⁺. The spectral data are in accordance with the literature.¹



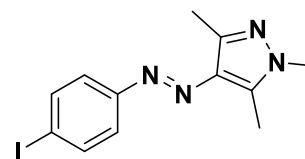
(E)-4-((4-Iodophenyl)diazenyl)-3,5-dimethyl-1H-pyrazole

Yield: 166.5mg (0.35 mmol, 70 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 12.89 (s, 1H), 7.90 - 7.84 (m, 2H), 7.53 - 7.48 (m, 2H), 2.49 (s, 3H), 2.39 (d, J = 5.9 Hz, 3H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 196.3, 152.4, 138.0, 123.4, 95.8, 26.4, 10.1. **MS(EI) m/z:** 327.0 [M+H]⁺. The spectral data are in accordance with the literature.⁸



(E)-4-((4-Iodophenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole

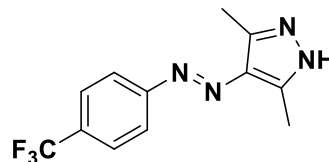
Yield: 168.3mg (0.49 mmol, 98 %). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.91 - 7.82 (m, 2H), 7.56 - 7.47 (m, 2H), 3.73 (s, 3H), 2.53 (s, 3H), 2.35 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 152.3,



140.5, 140.0, 138.0, 134.4, 123.4, 95.9, 36.0, 13.8, 9.5. **MS(EI) m/z:** 341.0 [M+H]⁺, 363.0 [M+Na]⁺. The spectral data are in accordance with the literature.^{9,10}

(E)-3,5-Dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1H-pyrazole

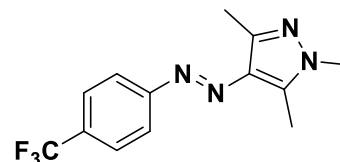
Yield: 125.3mg (0.34 mmol, 68 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 12.99 (s, 1H), 7.89 - 7.82 (m, 4H), 2.45 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆): δ (ppm) = 155.3, 134.6, 126.4, 126.4, 121.9, 116.4.



¹⁹F NMR (282 MHz, DMSO-d₆): δ (ppm) = -60.77. **MS(EI) m/z:** 269.1 [M+H]⁺. The spectral data are in accordance with the literature.⁶

(E)-1,3,5-Trimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1H-pyrazole

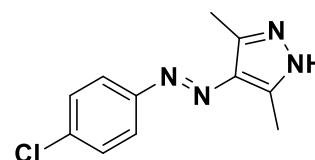
Yield: 130.3mg (0.46 mmol, 92%). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.87 (d, J = 1.8 Hz, 4H), 3.75 (s, 3H), 2.57 (s, 3H), 2.38 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 155.3, 140.8, 134.8,



126.4, 121.9, 36.0, 13.8, 9.5. **¹⁹F NMR** (282 MHz, CDCl₃): δ (ppm) = -62.34. **MS(EI) m/z:** 283.1 [M+H]⁺.

(E)-4-((4-Chlorophenyl)diazenyl)-3,5-dimethyl-1H-pyrazole

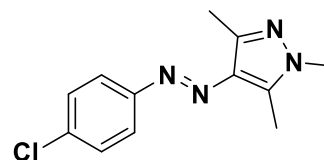
Yield: 118.6mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 12.89 (s, 1H), 7.75 - 7.71 (m, 2H), 7.58 - 7.53 (m, 2H), 2.43 (s, 6H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 151.6, 134.2, 133.7, 129.4,



129.3, 123.0, 117.9. **MS(EI) m/z:** 235.1 [M+H]⁺. The spectral data are in accordance with the literature.⁶

(E)-4-((4-Chlorophenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole

Yield: 123.6mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.76 - 7.70 (m, 2H), 7.59 - 7.52 (m, 2H), 3.73 (s, 3H), 2.54 (s, 3H), 2.36 (s, 3H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) = 151.6, 140.5,



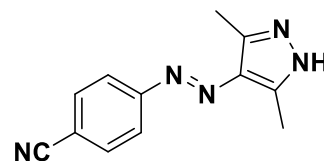
140.0, 134.4, 133.7, 129.2, 123.0, 117.9, 36.0, 13.8, 9.5. **MS(EI) m/z:** 249.1 [M+H]⁺, 271.1 [M+Na]⁺.

(E)-4-((3,5-Dimethyl-1H-pyrazol-4-yl)diazenyl)benzonitrile

Yield: 114.9mg (quant.). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 13.03 (s, 1H), 7.98 - 7.92 (m, 2H), 7.86 - 7.79 (m, 2H), 2.45 (s, 6H).

¹³C NMR (101 MHz, DMSO-d₆): δ (ppm) = 155.3, 134.8, 133.8,

133.6, 122.1, 111.1, 106.0, 30.9, 25.9. **MS(EI) m/z:** 226.1 [M+H]⁺, 248.1 [M+Na]⁺. The spectral data are in accordance with the literature.²

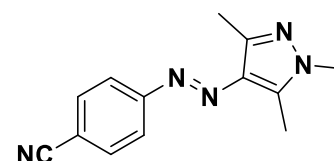


(E)-4-((1,3,5-Trimethyl-1H-pyrazol-4-yl)diazenyl)benzonitrile

Yield: 121.0mg (quant.). **¹H NMR** (300 MHz, CDCl₃): δ (ppm) = 7.86 - 7.80 (m, 2H), 7.76 - 7.71 (m, 2H), 3.79 (s, 3H), 2.59 (s, 3H),

2.48 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃): δ (ppm) = 155.9, 143.0,

140.5, 135.8, 133.2, 122.5, 119.0, 116.4, 112.1, 36.3, 14.1, 10.2. **MS(EI) m/z:** 240.1 [M+H]⁺, 262.1 [M+Na]⁺.



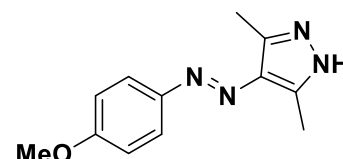
(E)-4-((4-Methoxyphenyl)diazenyl)-3,5-dimethyl-1H-pyrazole

Yield: 115.3mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 12.73 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 7.04 (dd, J = 9.1, 2.3 Hz, 2H),

3.82 (s, 3H), 2.38 (s, 6H). **¹³C NMR** (75 MHz, DMSO-d₆): δ (ppm) =

160.4, 147.2, 133.8, 122.9, 117.9, 114.9, 114.3, 55.4, 13.7, 10.0. **MS(EI) m/z:** 231.1 [M+H]⁺.

The spectral data are in accordance with the literature.⁵



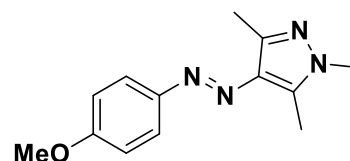
(E)-4-((4-Methoxyphenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole

Yield: 122.2mg (quant.). **¹H NMR** (300 MHz, DMSO-d₆): δ (ppm) = 7.74 - 7.67 (m, 2H), 7.04 (dd, J = 9.1, 2.2 Hz, 2H), 3.82 (s, 3H),

3.72 (s, 3H), 2.52 (s, 3H), 2.35 (s, 3H). **¹³C NMR** (75 MHz,

DMSO-d₆): δ (ppm) = 196.1, 160.4, 147.1, 140.1, 138.6, 123.0, 114.3, 55.5, 35.9, 13.7, 9.4.

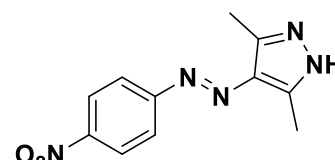
MS(EI) m/z: 245.1 [M+H]⁺, 267.1 [M+Na]⁺. The spectral data are in accordance with the literature.⁴



(E)-3,5-Dimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole

Yield: 116.3mg (0.47 mmol, 94 %). **¹H NMR** (400 MHz, DMSO-d₆): δ (ppm) = 13.07 (s, 1H), 8.38 - 8.32 (m, 2H),

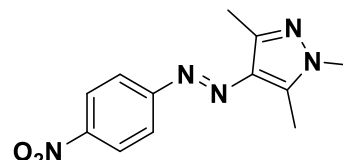
7.91 - 7.86 (m, 2H), 2.47 (s, 6H). **¹³C NMR** (101 MHz, DMSO-d₆):



δ (ppm) = 156.7, 147.0, 135.1, 124.9, 122.2, 30.7. **MS(EI)** m/z : 246.1 $[M+H]^+$. The spectral data are in accordance with the literature.^{5,6}

(E)-1,3,5-Trimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole

Yield: 129.5mg (quant.). **¹H NMR** (400 MHz, DMSO- d_6): δ (ppm) = 8.36 - .31 (m, 2H), 7.91 - 7.86 (m, 2H), 3.75 (s, 3H), 2.57 (s, 3H), 2.38 (s, 3H). **¹³C NMR** (101 MHz, DMSO- d_6): δ (ppm) = 156.6,



147.0, 141.5, 141.0, 135.2, 124.9, 122.2, 36.1, 13.9, 9.6. **MS(EI)** m/z : 260.1 $[M+H]^+$, 282.1 $[M+Na]^+$. The spectral data are in accordance with the literature.⁴

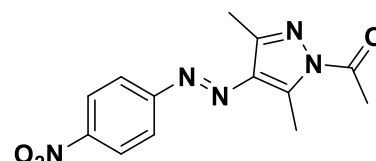
2.3 General procedure 3 to synthesize (E)-1-(4-(diazenyl-3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one

A solution of acetyl chloride (0.5 mol L⁻¹, 2.5 equiv) in DCM was added to the ice-cooled solution of (E)-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole derivative (1.0 equiv), NaHCO₃ (2.5 equiv) in DCM (0.045 mol L⁻¹), and the reaction mixture was stirred for 16 hours under N₂ atmosphere. Then, 5 mL of water was added, and the resulting solution was extracted (3 × 50 mL) with brine and (3 × 50 mL) DCM. The organic layer was separated, dried using Na₂SO₄, and concentrated under reduced pressure. The crude was purified via FCC (silica gel) to yield the desired product.

(E)-1-(4-((4-Nitrophenyl)diazenyl)-3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one

Synthesized according General procedure 3. 0.020 g of (E)-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1H-pyrazole was used.

Mobile phase: 20 % ethyl acetate in pentane. Yellow solid (0.020 g, 85%). **Mp.**: 155.3–157.4 °C **¹H NMR** (400 MHz, CD₂Cl₂) δ 8.39 –

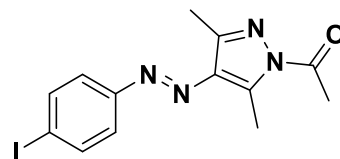


8.26 (m, 2H), 8.00 – 7.86 (m, 2H), 2.94 (s, 3H), 2.69 (s, 3H), 2.49 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.1, 156.9, 148.7, 147.3, 145.0, 138.4, 125.1, 123.1, 23.6, 15.5, 12.5. **HRMS(ESI)** m/z : $[M]^+$ calcd. for C₁₃H₁₄N₅O₃Na⁺ 310.0911; found 310.0911. **IR (ATR)**: $\tilde{\nu}$ (cm⁻¹) 2355, 2335, 1980, 1730, 1574, 1517, 1335, 1289, 872, 772, 593.

(E)-1-(4-((4-Iodophenyl)diazenyl)-3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one

Synthesized according General procedure 3. 0.020 g of (E)-3,5-dimethyl-4-((4-iodophenyl)diazenyl)-1H-pyrazole was used.

Mobile phase: 15 % ethyl acetate in pentane. Yellow solid

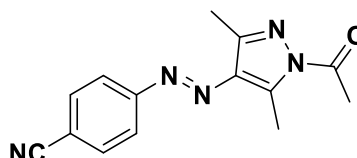


(0.014 g, 61%). **Mp.**: 146.3–148.2 °C. **¹H NMR** (400 MHz, CD₂Cl₂) δ 7.95 – 7.77 (m, 2H), 7.58 (dq, *J* = 9.2, 3.0 Hz, 2H), 2.90 (s, 3H), 2.68 (s, 3H), 2.47 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.1, 153.0, 145.7, 145.2, 138.7, 138.0, 124.2, 97.0, 23.6, 15.4, 12.5. **HRMS(ESI)** *m/z*: [M]⁺ calcd. for C₁₃H₁₃IN₄ONa⁺ 391.0026; found 391.0026. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2914, 2846, 1738, 1577, 1370, 1334, 1031, 1000, 960, 889, 776, 589.

(E)-4-((1-Acetyl-3,5-dimethyl-1H-pyrazol-4-yl)diazenyl)benzonitrile

Synthesized according General procedure 3. 0.020 g of (E)-4-((3,5-dimethyl-1H-pyrazol-4-yl)diazenyl)benzonitrile was used.

Mobile phase: 10 % ethyl acetate in pentane. Yellow solid

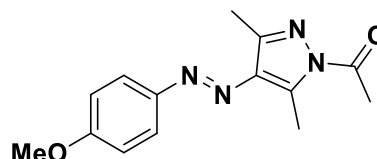


(0.016 g, 67%). **Mp.**: 177.7–180.1 °C. **¹H NMR** (400 MHz, CD₂Cl₂) δ 7.93 – 7.87 (m, 2H), 7.82 – 7.74 (m, 2H), 2.93 (s, 3H), 2.68 (s, 3H), 2.48 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.1, 155.6, 146.9, 145.1, 138.3, 133.6, 123.0, 118.9, 113.7, 23.6, 15.4, 12.5. **HRMS (ESI)** *m/z*: [M]⁺ calcd. for C₁₄H₁₃N₅ONa⁺ 290.1012; found 290.1012. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2227, 1739, 1369, 1340, 1286, 959, 851, 695, 689, 593.

(E)-1-(4-((4-Methoxyphenyl)diazenyl)-3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-one

Synthesized according General procedure 3. 0.020 g of (E)-3,5-dimethyl-4-((4-methoxyphenyl)diazenyl)-1H-pyrazole was

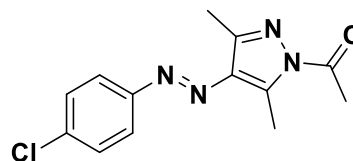
used. Mobile phase: 15 % ethyl acetate in pentane. Yellow solid



(0.020 g, 84%). **Mp.**: 145.3–146.0 °C. **¹H NMR** (400 MHz, CD₂Cl₂) δ 7.87 – 7.76 (m, 2H), 7.06 – 6.94 (m, 2H), 3.87 (s, 3H), 2.89 (s, 3H), 2.67 (s, 3H), 2.48 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.1, 162.1, 148.0, 145.4, 144.0, 137.8, 124.2, 114.5, 56.0, 23.6, 15.3, 12.4. **HR-MS (ESI)** *m/z*: [M]⁺ calcd. for C₁₄H₁₇N₄O₂⁺ 273.1346; found 273.1346. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2960, 2918, 2831, 1736, 1593, 1343, 1244, 1028, 838, 587, 533.

(*E*)-1-(4-((4-Chlorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one

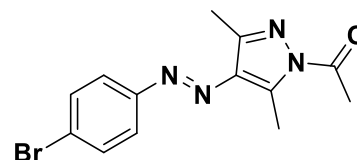
Synthesized according to General procedure 3. 0.010 g of (*E*)-3,5-dimethyl-4-((4-chlorophenyl)diazenyl)-1*H*-pyrazole was used. Mobile phase: 10 % ethyl acetate in pentane. Yellow solid



(0.0067 g, 57%). **Mp.**: 76.8–78.7 °C. **¹H NMR** (400 MHz, CD₂Cl₂) δ 7.91 – 7.77 (m, 2H), 7.63 – 7.46 (m, 2H), 2.95 (s, 3H), 2.72 (s, 3H), 2.52 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.1, 152.1, 145.4 (d, *J* = 3.6 Hz), 137.9, 136.4, 129.6, 123.8, 23.6, 15.4, 12.5. **HR-MS (ESI)**: *m/z*: [M]⁺ calcd. for C₁₃H₁₃ClN₄O⁺ 299.0670; found 299.0670. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 1667, 1506, 1406, 1389, 1085, 1081, 830, 773, 583, 522. The spectral data are in accordance with the literature.¹¹

(*E*)-1-(4-((4-Bromophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one

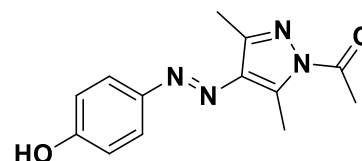
Synthesized according to General procedure 3. 0.010 g of (*E*)-3,5-dimethyl-4-((4-bromophenyl)diazenyl)-1*H*-pyrazole was used. Mobile phase: 10 % ethyl acetate in pentane. Yellow solid



(0.015 g, 65%). **Mp.**: 70.8–73.4 °C. **¹H NMR** (300 MHz, CD₃CN) δ 7.80 – 7.73 (m, 2H), 7.72 – 7.66 (m, 2H), 2.88 (s, 3H), 2.63 (s, 3H), 2.46 (s, 3H). **¹³C NMR** (101 MHz, CD₂Cl₂) δ 172.2, 152.5, 145.6, 145.2, 132.6, 124.8, 124.1, 23.6, 15.4, 12.5. **HR-MS (ESI)**: *m/z*: [M]⁺ calcd. for C₁₃H₁₃BrN₄O⁺ 343.0165; found 343.0171. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2920, 2359, 2340, 1734.66, 1373, 1164, 1062, 1059, 827, 776.

(*E*)-1-(4-((4-Hydroxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one

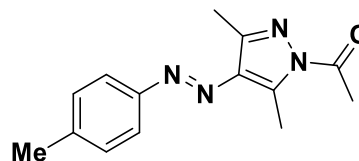
Synthesized according to General procedure 3. 0.021 g of (*E*)-3,5-dimethyl-4-((4-hydroxyphenyl)diazenyl)-1*H*-pyrazole was used. Mobile phase: 10 % ethyl acetate in pentane. Yellow solid



(0.019 g, 92%). **Mp.**: 185.1–187.0 °C. **¹H NMR** (400 MHz, DMSO-*d*₆): δ (ppm) 10.17 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 2.81 (s, 3H), 2.62 (s, 3H), 2.41 (s, 3H). **¹³C NMR** (125 MHz, DMSO-*d*₆): δ (ppm) 171.4, 160.4, 145.9, 144.0, 142.6, 136.7, 124.0, 115.9, 23.2, 14.9, 12.0. **HR-MS (ESI)**: calc. for: C₁₃H₁₄N₄O₂H: 259.1190, found.: 259.1183. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 3210, 2918, 1701, 1588, 1380, 1332, 1199, 1139, 841, 809.

(E)-1-(3,5-Dimethyl-4-(*p*-tolylidiazenyl)-1*H*-pyrazol-1-yl)ethan-1-one

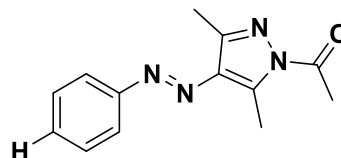
Synthesised according to General procedure **3**. 0.020 g of (*E*)-3,5-dimethyl-4-((4-methylphenyl)diazenyl)-1*H*-pyrazole was used. Mobile phase: 20 % ethyl acetate in pentane. Yellow solid



(0.021 g, 84%). **Mp.**: 119.4 – 120.2 °C. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.75 – 7.71 (m, 2H), 7.31 – 7.26 (m, 2H), 2.93 (s, 3H), 2.71 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ (ppm) 172.0, 151.5, 145.5, 144.4, 141.1, 137.8, 129.8, 122.3, 23.6, 21.6, 15.3, 12.5. **HR-MS (ESI)**: calc. for: C₁₄H₁₆N₄O: 257.1397, found.: 257.1389. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2924, 1733, 1582, 1369, 1335, 1283, 962, 821, 739, 590. The spectral data are in accordance with the literature.¹¹

(E)-1-(3,5-Dimethyl-4-(phenyldiazenyl)-1*H*-pyrazol-1-yl)ethan-1-one

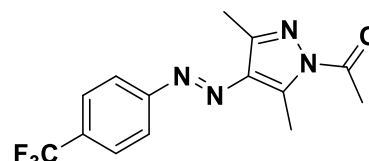
Synthesized according to general procedure **3**. 0.02 g of (*E*)-3,5-dimethyl-4-(phenyldiazenyl)-1*H*-pyrazole was used. Mobile phase: 20 % ethyl acetate in pentane. Yellow solid (16 mg,



66%). **Mp.**: 103.2 – 103.9 °C. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.85 – 7.80 (m, 2H), 7.52 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 2.94 (s, 3H), 2.71 (s, 3H), 2.51 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ (ppm) 172.0, 153.3, 145.4, 144.9, 137.8, 130.6, 129.2, 122.3, 23.6, 15.3, 12.5. **HR-MS (ESI)**: calc. for: C₁₃H₁₄N₄O: 243.1240, found.: 243.1240. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 2924, 1733, 1571, 1394, 1372, 1346, 1289, 769, 694, 673.

(E)-1-(3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethan-1-one

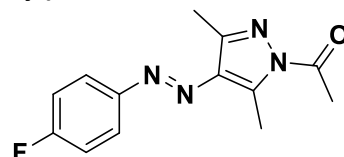
Synthesized according to general procedure **3**. 0.021 g of (*E*)-3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-



pyrazole was used. Mobile phase: 20 % ethyl acetate in pentane. Orange solid (19.7 mg, 95%). **Mp.**: 112.8 – 113.4 °C. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.90 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 2.95 (s, 3H), 2.72 (s, 3H), 2.51 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ (ppm) 172.0, 155.2, 146.1, 145.1, 137.9, 131.8 (q, *J* = 32.4 Hz), 126.4 (q, *J* = 3.8 Hz), 125.5, 122.5, 23.6, 12.4, 12.5. **¹⁹F NMR** (377 MHz, CDCl₃): δ (ppm) -62.5. **HR-MS (ESI)**: calc. for: C₁₄H₁₃F₃N₄O: 311.1114, found.: 311.1115. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 1747, 1372, 1337, 1321, 1278, 1167, 1116, 1113, 1065, 596.

(E)-1-(3,5-Dimethyl-4-((4-(fluoro)phenyl)diazenyl)-1H-pyrazol-1-yl)ethan-1-one

Synthesized according to general procedure **3**. 0.020 g of (E)-4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1H-pyrazole was used. Mobile phase: 20 % ethyl acetate in pentane. Orange



solid (18.0 mg, 75%). **Mp.**: 114.7 – 115.3 °C. **¹H NMR** (400 MHz, CDCl₃): δ (ppm) 7.83 (ddt, J = 7.1, 5.3, 2.5 Hz, 2H), 7.20 – 7.06 (m, 2H), 2.92 (s, 3H), 2.71 (s, 3H), 2.49 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ (ppm) 172.0, 165.4, 162.9, 149.9, 145.3, 137.6, 124.2, 116.2, 116.2, 116.0, 23.5, 15.3, 12.4. **¹⁹F NMR** (377 MHz, CDCl₃): δ (ppm) -110.2 (tt, J = 8.2, 5.3 Hz). HR-MS (ESI): calc. for: C₁₃H₁₃FN₄OH: 261.1146, found.: 261.1149. **IR** (ATR): $\tilde{\nu}$ (cm⁻¹) 1733, 1380, 1366, 1346, 1286, 1227, 846, 664, 590, 514.

2.4 pH-Dependent stability of NAc-PAP-H

A stock solution of **NAc-PAP-H** (1 mM) in MeOH was prepared in dark at room temperature at pH 2 and 12 (HCl as acid and NaOCH₃ as a base). Both samples were stirred for 2 h and we observed full conversion to **NH-PAP-H** (detected on LC–MS; 95–5% water in CH₃CN, 0.1% formic acid) in both cases as shown in Figure S1.

We reperformed the experiment in MeCN with DBU (10⁻² M), and we observed after 2 h full conversion to various products and **NH-PAP-H**.

Already on the standard LC–MS trace, one can already observe a small appearance of the decomposition (NMR showed no impurities), since the mobile phase contained 0.1% of formic acid.

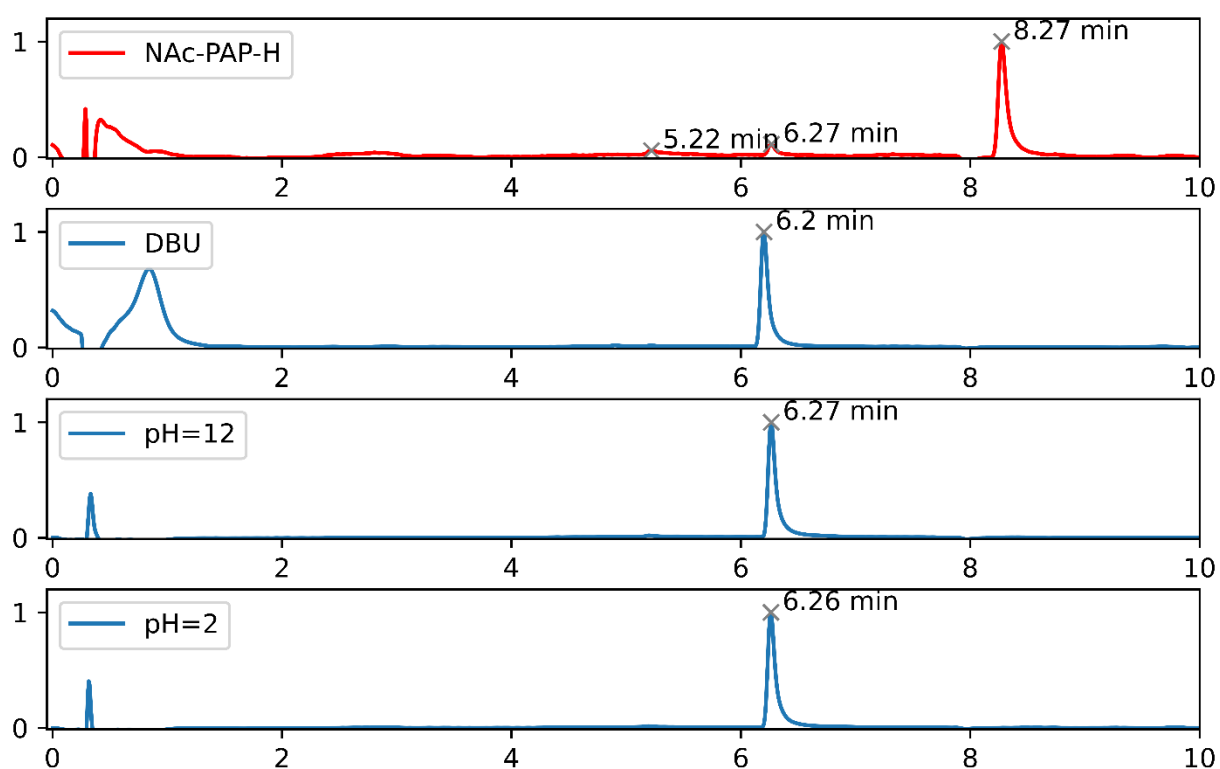


Figure S1: Chromatograph at 365 nm (maximum set to 1) of the pH stability experiments after 2 hours with the comparison of the starting material (**NAc PAP-H**).

3. Photochemical and photophysical studies

Upon 365 nm irradiation, the solution undergoes a color change from pale yellow to dark yellow, corresponding to an increased absorption of the $n\rightarrow\pi^*$ transition associated with the Z-isomer, which can be observed by naked eye. The solution changes from pale to dark yellow.

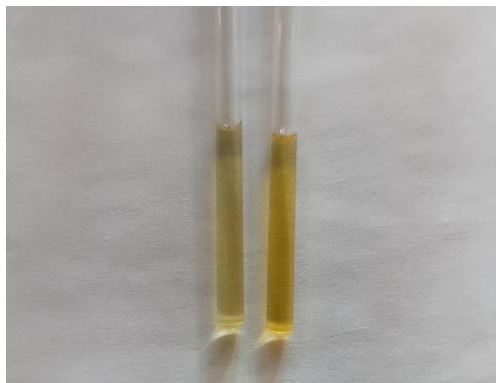


Figure S2: 0.5mm **NAc-PAP-H** on the right kept in the dark and on the left after 365 nm irradiation.

3.1 Determination of photostationary state distribution by ^1H NMR

The NMR samples of **NAc-PAPs** were irradiated with 365 or 445 nm LED for 10 min, and then immediately ^1H NMR spectra were recorded using a Bruker Advance III HD 300 at 25 °C. The PSS was determined by the integration of the *E* isomer and Z isomer signals.

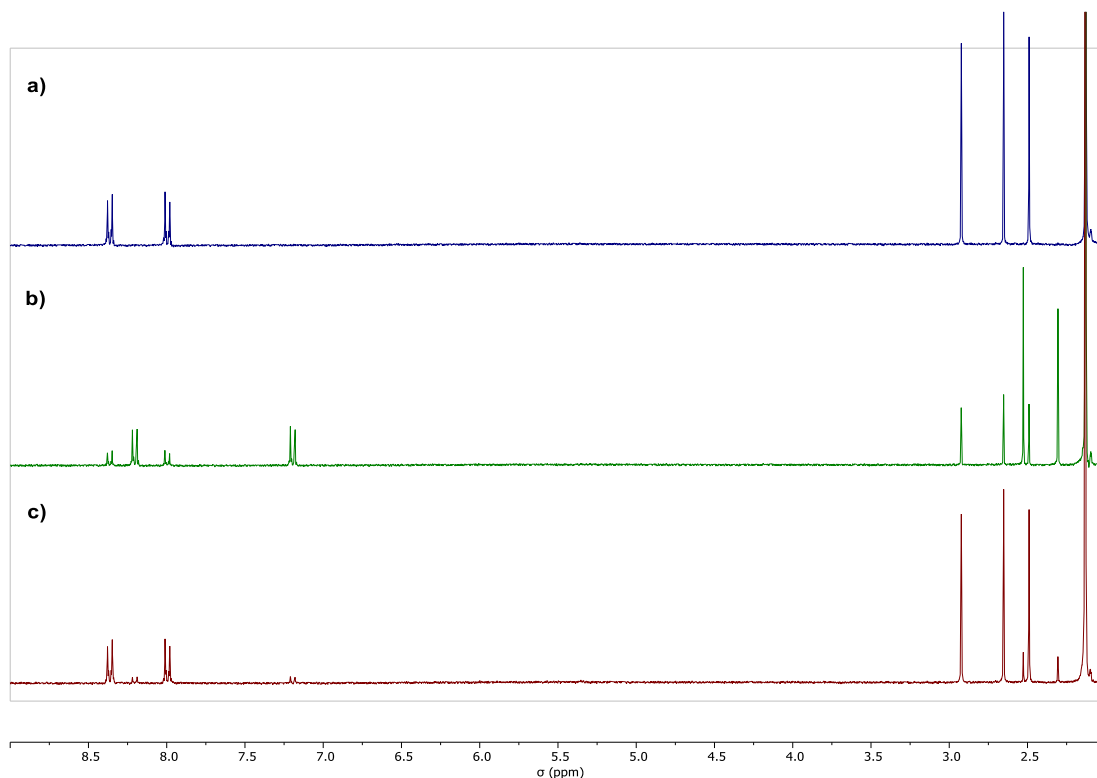


Figure S3: ^1H NMR spectra of **NAc-PAP-NO₂** a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CD_3CN .

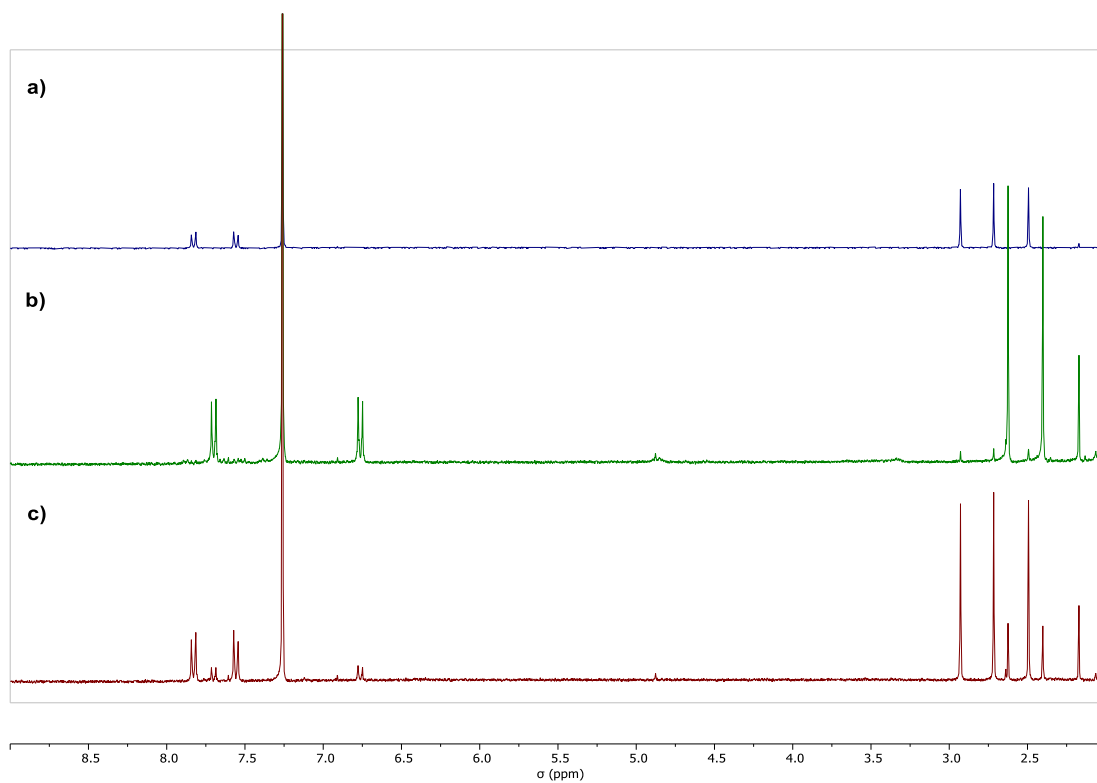


Figure S4: ^1H NMR spectra of **NAc-PAP-I**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CDCl_3 .

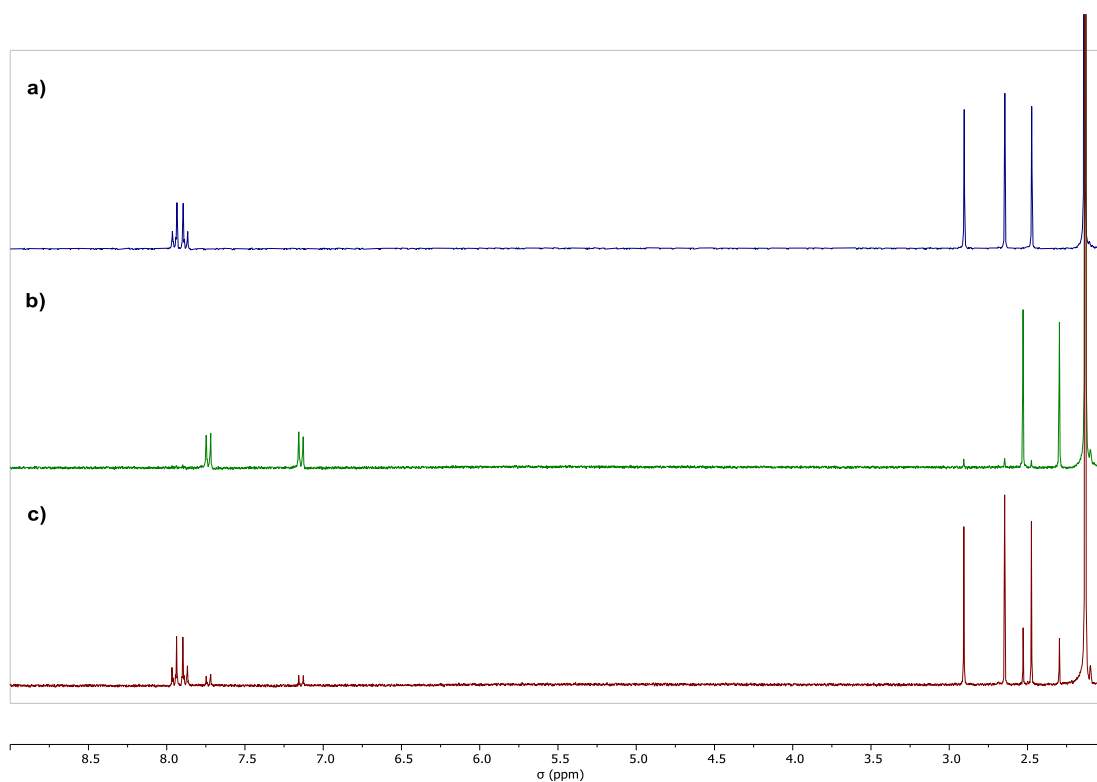


Figure S5: ^1H NMR spectra of **NAc-PAP-CN**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CD_3CN .

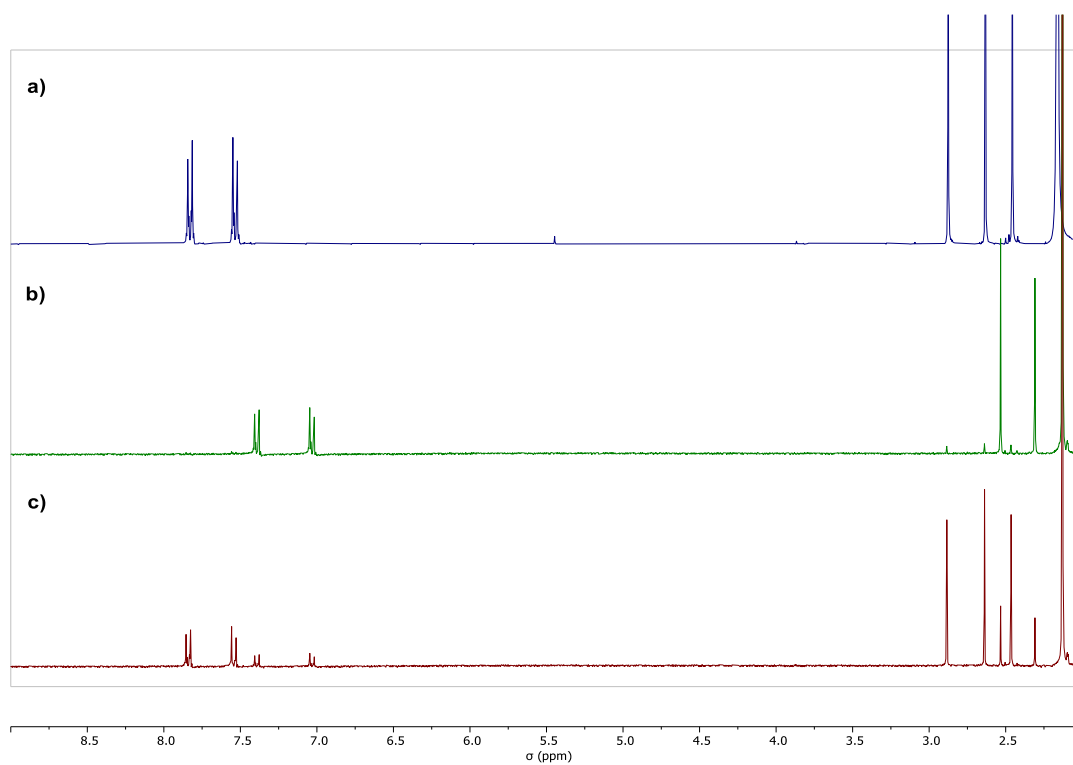


Figure S6: ^1H NMR spectra of **NAc-PAP-Cl**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CD_3CN .

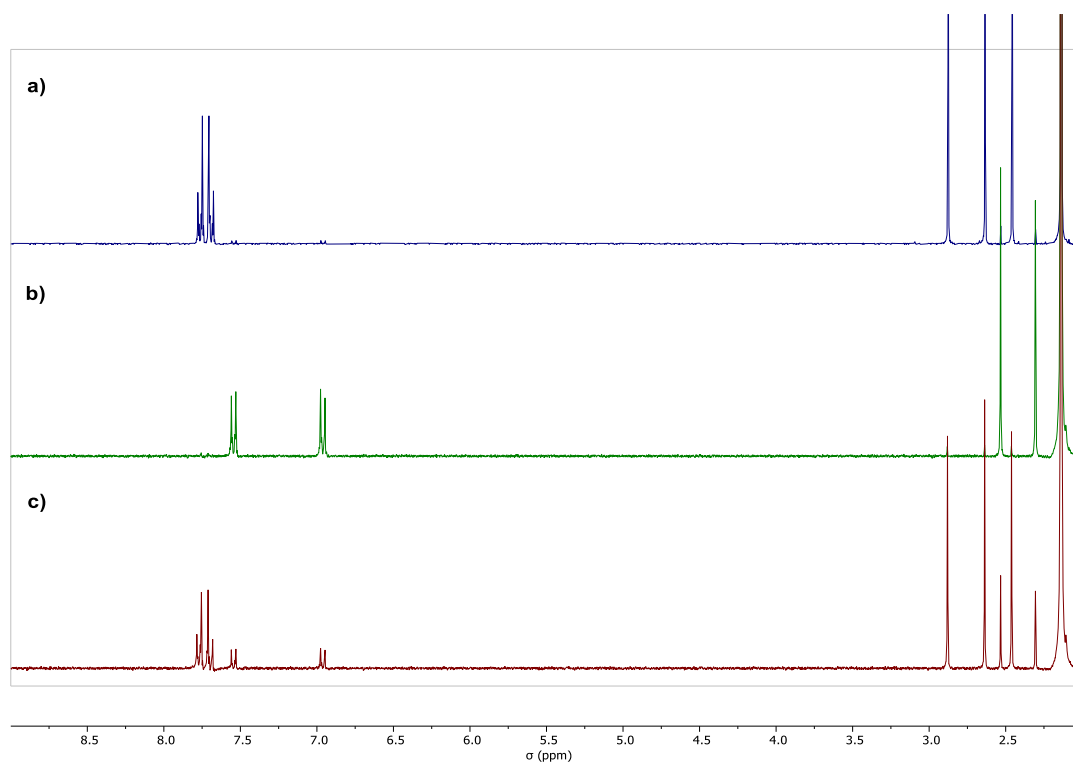


Figure S7: ^1H NMR spectra of **NAc-PAP-Br**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CD_3CN .

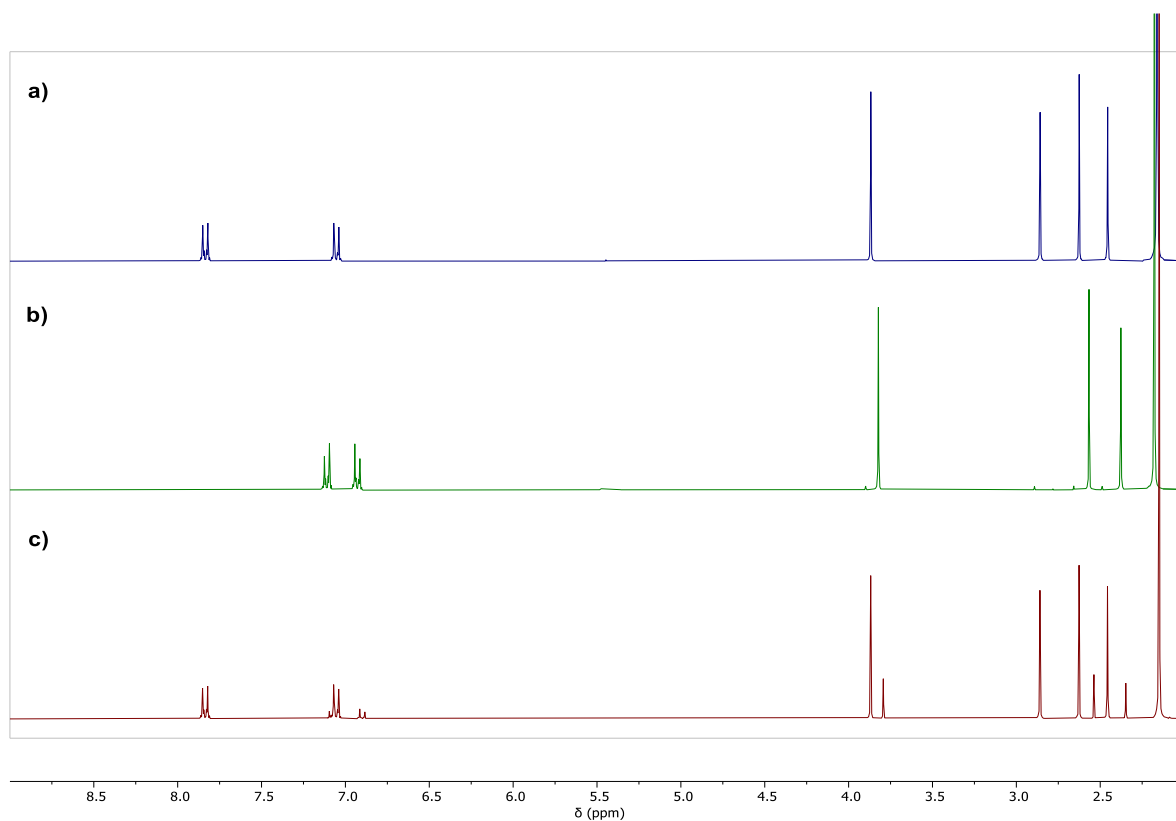


Figure S8: ^1H NMR spectra of **NAc-PAP-OMe**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CD_3CN .

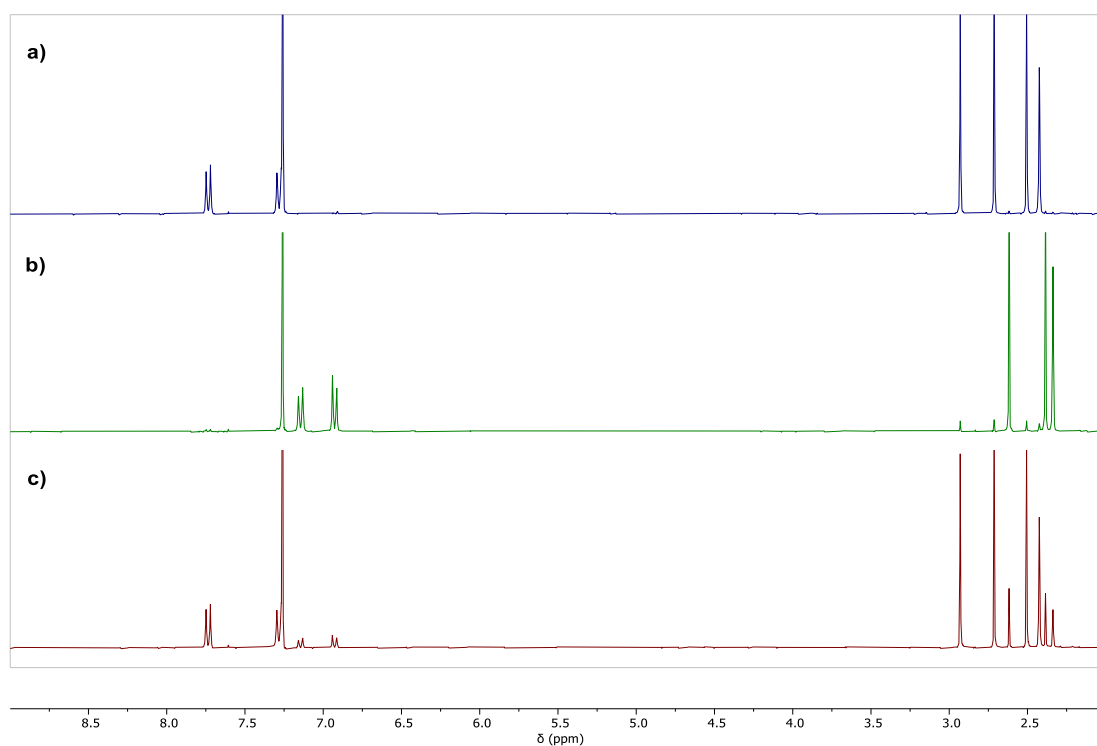


Figure S9: ^1H NMR spectra of **NAc-PAP-Me**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CDCl_3 .

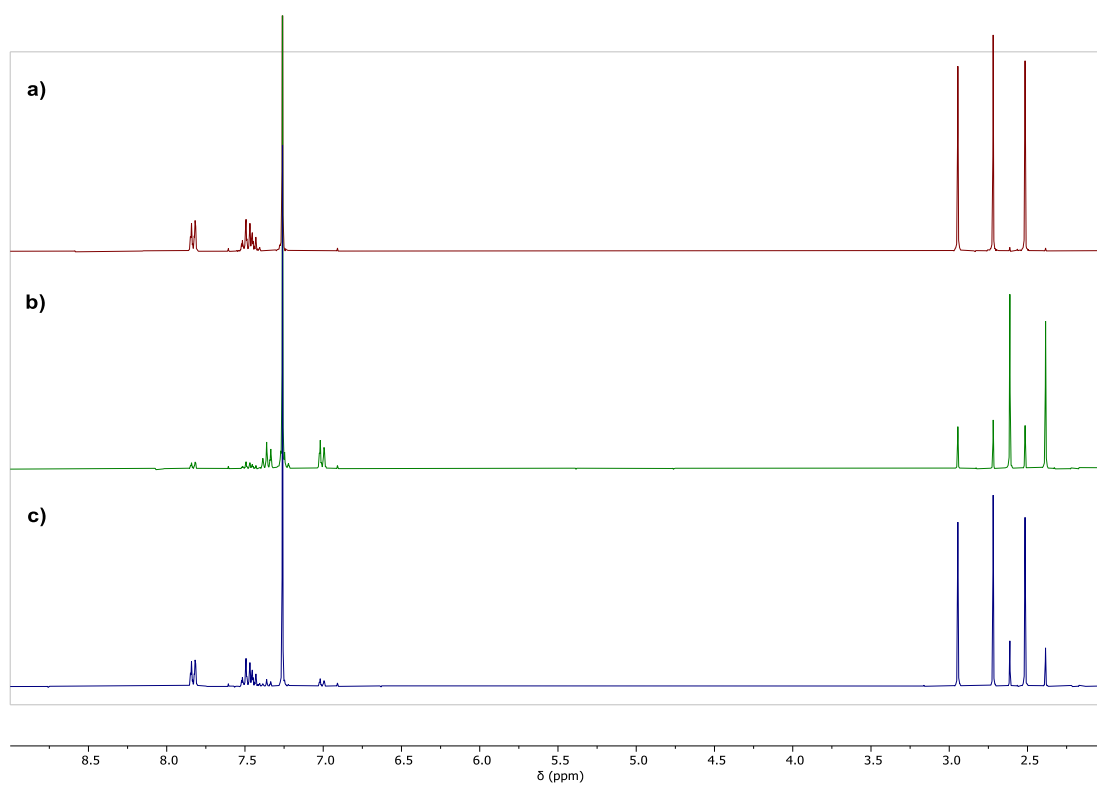


Figure S10: ^1H NMR spectra of **NAc-PAP-H**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CDCl_3 .

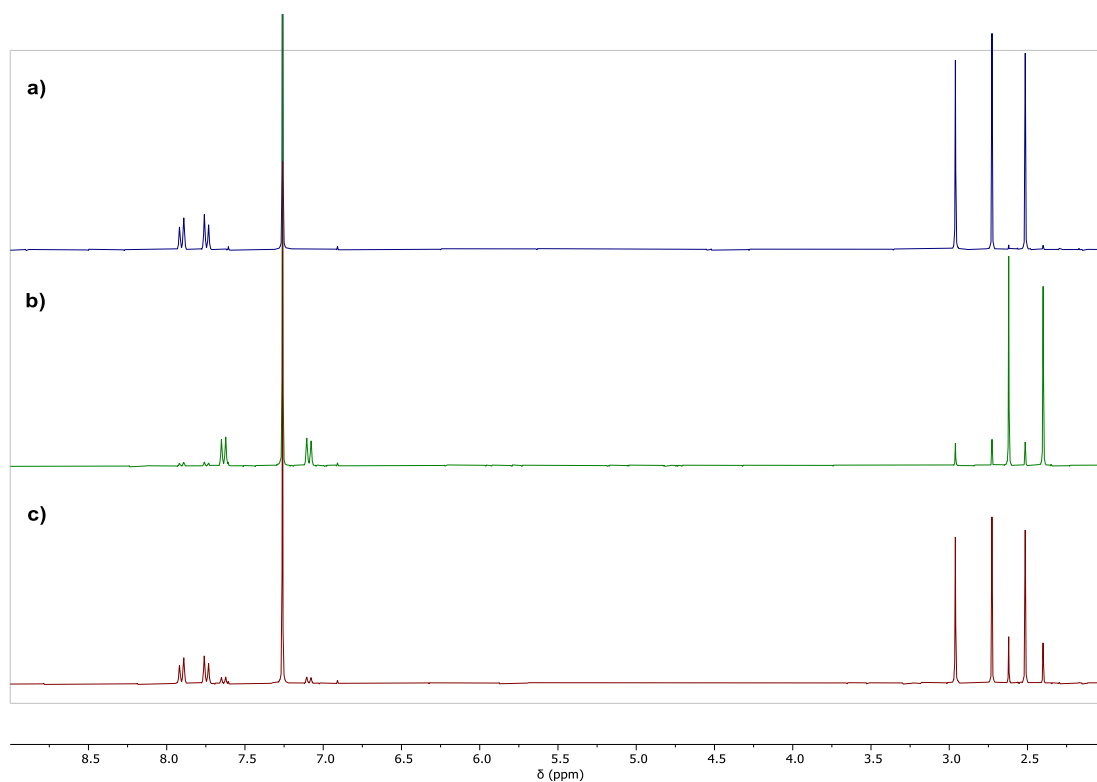


Figure S11: ^1H NMR spectra of **NAc-PAP- CF_3** . a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CDCl_3 .

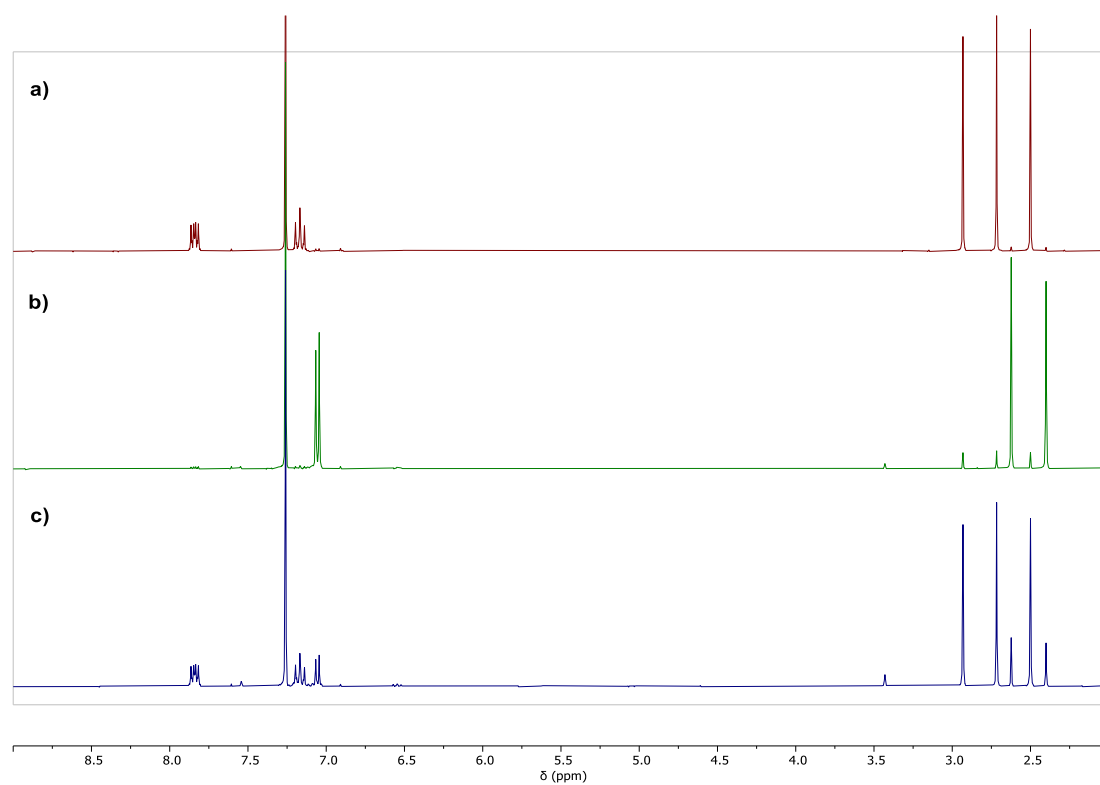


Figure S12: ^1H NMR spectra of **NAc-PAP-F**. a) in dark b) irradiated by 365 nm c) irradiated with 445 nm in CDCl_3 .

3.2 Cyclic irradiation to study fatigue resistance

Photoswitching stability of **NAc-PAP** derivatives was investigated in CH₃CN. For the forward *E*→*Z*-isomerization step, 365 nm light was used until the PSS was reached, whereas for the *Z*→*E*-isomerization, 445 nm light was used until reaching PSS. Both the irradiation steps were repeated 10 to 20 times.

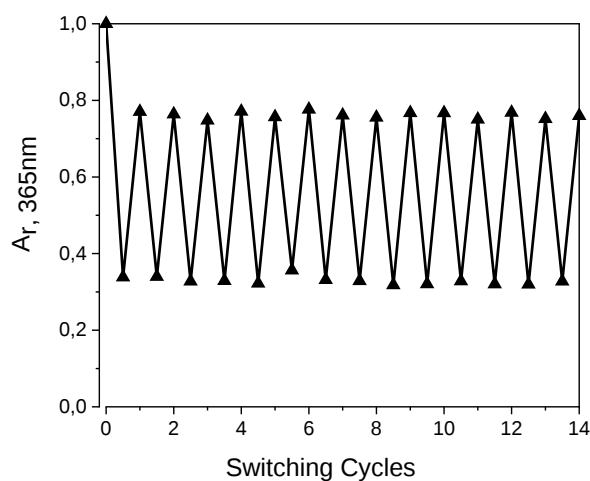


Figure S13: Photoswitching cycles of **NAc-PAP-NO₂** in CH₃CN at 25 °C.

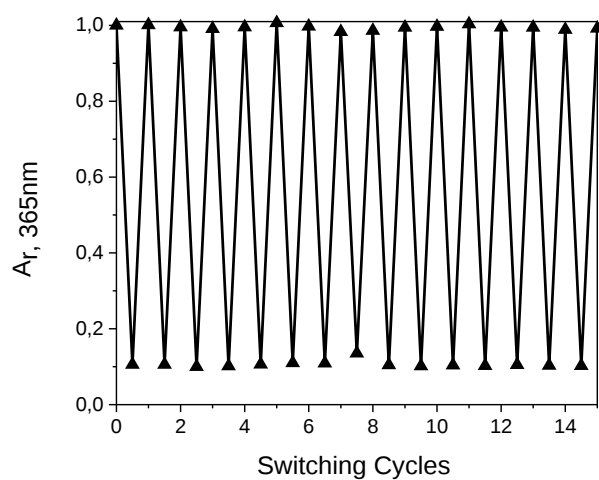


Figure S14: Photoswitching cycles of **NAc-PAP-I** in CH₃CN at 25 °C.

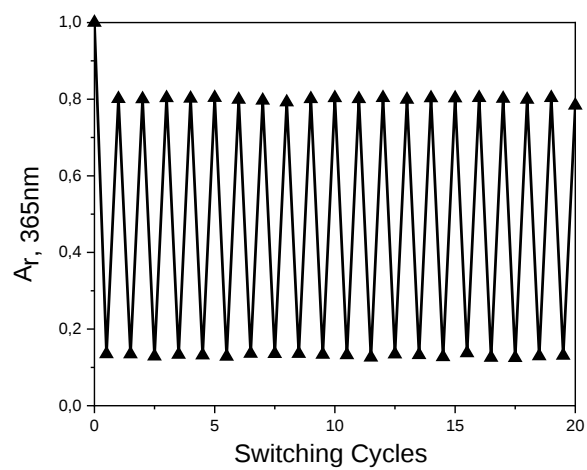


Figure S15: Photoswitching cycles of **NAc-PAP-CN** in CH_3CN at 25°C .

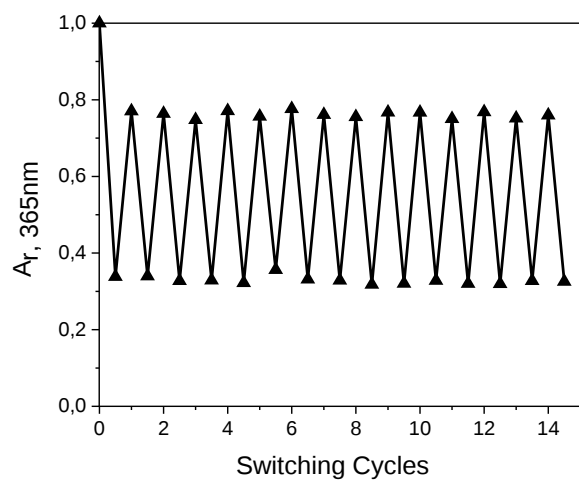


Figure S16: Photoswitching cycles of **NAc-PAP-OMe** in CH_3CN at 25°C .

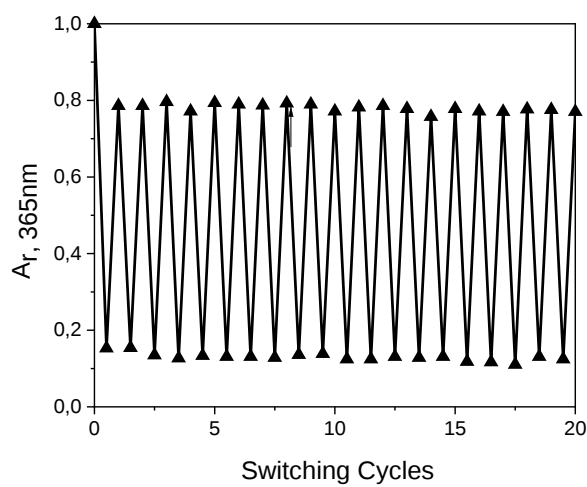


Figure S17: Photoswitching cycles of **NAc-PAP-Cl** in CH_3CN at 25°C .

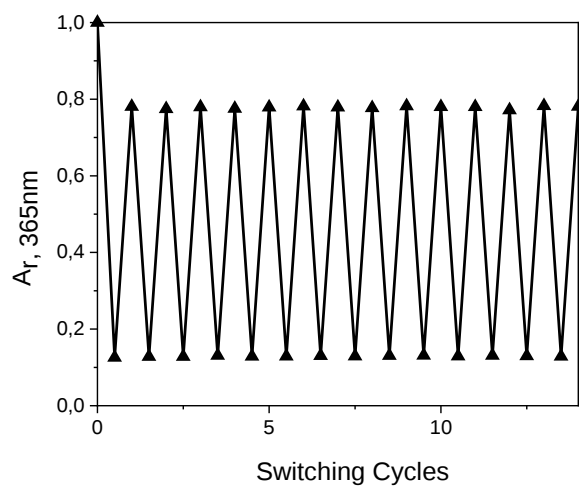


Figure S18: Photoswitching cycles of **NAc-PAP-Br** in CH_3CN at 25°C .

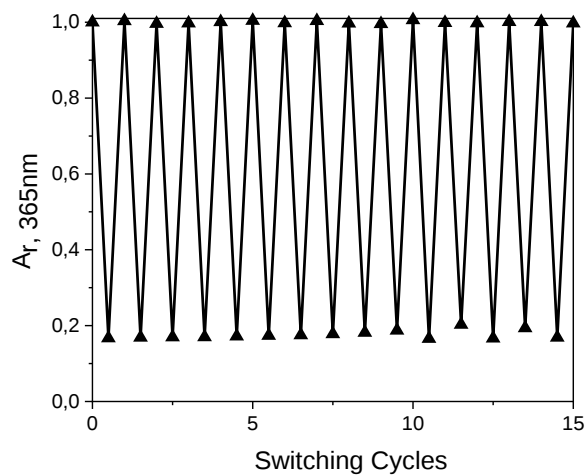


Figure S19: Photoswitching cycles of **NAc-PAP- CF_3** in CH_3CN at 25°C .

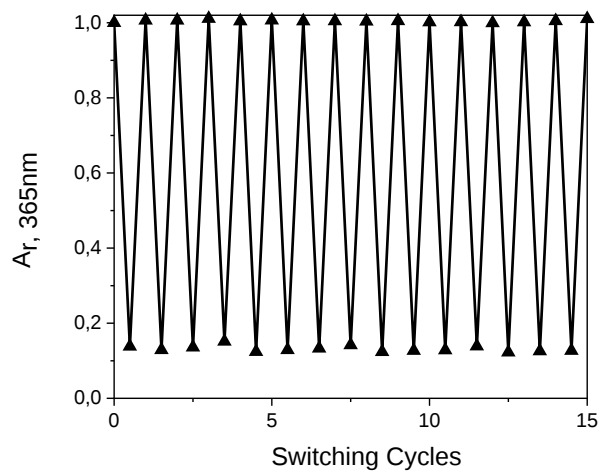


Figure S20: Photoswitching cycles of **NAc-PAP-F** in CH_3CN at 25°C .

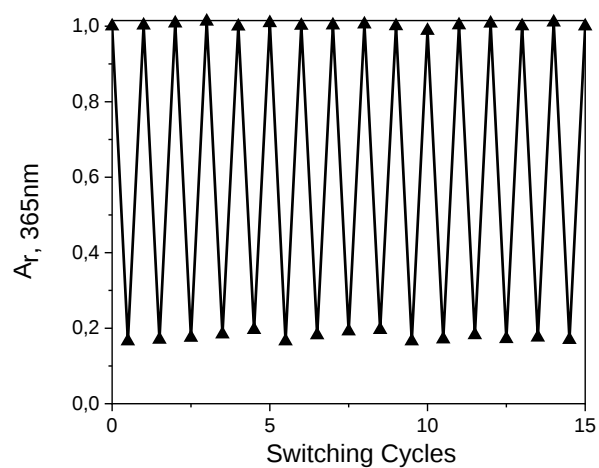


Figure S21: Photoswitching cycles of **NAc-PAP-H** in CH₃CN at 25 °C.

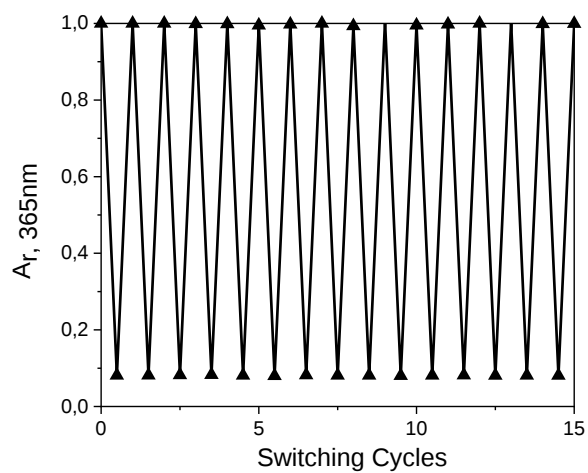


Figure S22: Photoswitching cycles of **NAc-PAP-Me** in CH₃CN at 25 °C.

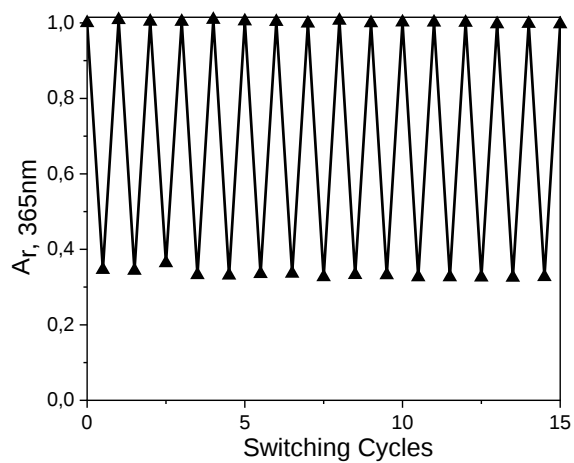


Figure S23: Photoswitching cycles of **NAc-PAP-OH** in CH₃CN at 25 °C.

3.3 Determination of molar extinction coefficients

Molar extinction coefficients (ϵ) were determined by fitting the slope of absorbance dependency to the concentration taken from at least two separate dilutions at 12.5 μM , 25 μM , 50 μM or 100 μM in CH_3CN . The values were fitted linearly and the y-intercept was set to zero.

3.3.1 Absorbance vs. concentrations of NAc-PAP derivatives

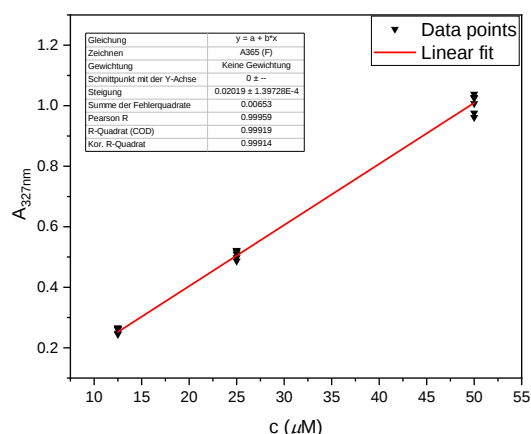


Figure S24: Absorbance at 327 nm dependency on concentration and the slopes of **NAc-PAP-F** in CH_3CN at 12.5, 25 and 50 μM .

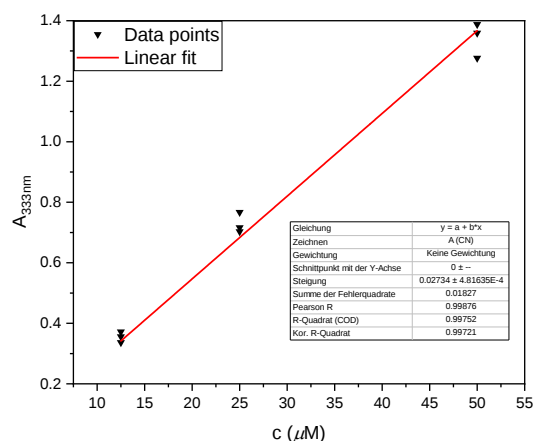


Figure S25: Absorbance at 333 nm dependency on concentration and the slopes of **NAc-PAP-CN** in CH_3CN at 12.5, 25 and 50 μM .

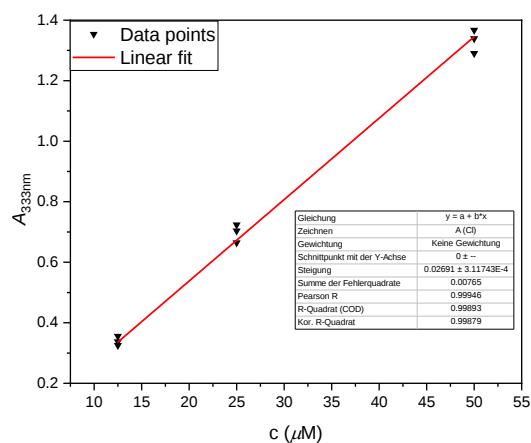


Figure S26: Absorbance at 333 nm dependency on concentration and the slopes of **NAc-PAP-Cl** in CH₃CN at 12.5, 25 and 50 μM.

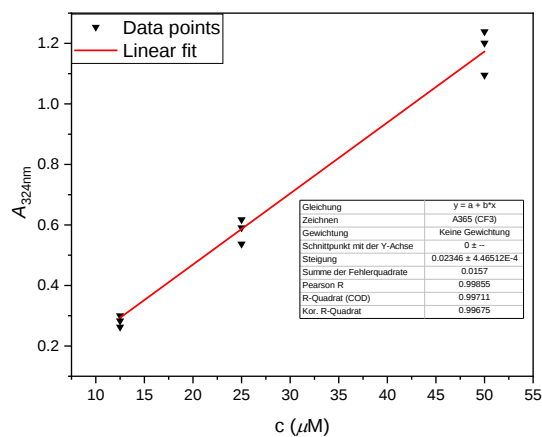


Figure S27: Absorbance at 324 nm dependency on concentration and the slopes of **NAc-PAP-CF₃** in CH₃CN at 12.5, 25 and 50 μM.

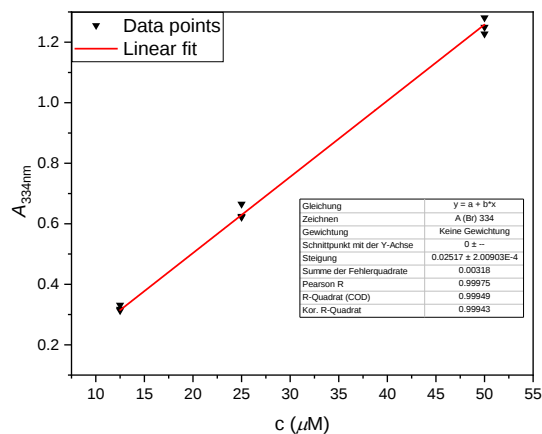


Figure S28: Absorbance at 344 nm dependency on concentration and the slopes of **NAc-PAP-Br** in CH₃CN at 12.5, 25 and 50 μM.

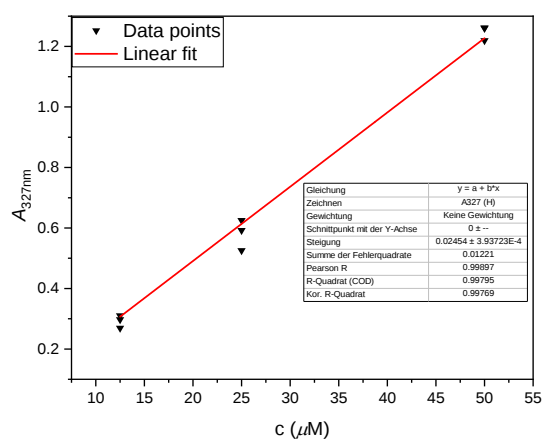


Figure S29: Absorbance at 327 nm dependency on concentration and the slopes of **NAc-PAP-H** in CH₃CN at 12.5, 25 and 50 μM.

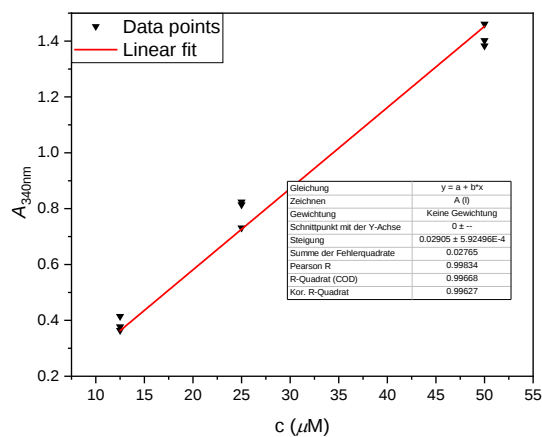


Figure S30: Absorbance at 340 nm dependency on concentration and the slopes of **NAc-PAP-I** in CH₃CN at 12.5, 25 and 50 μM.

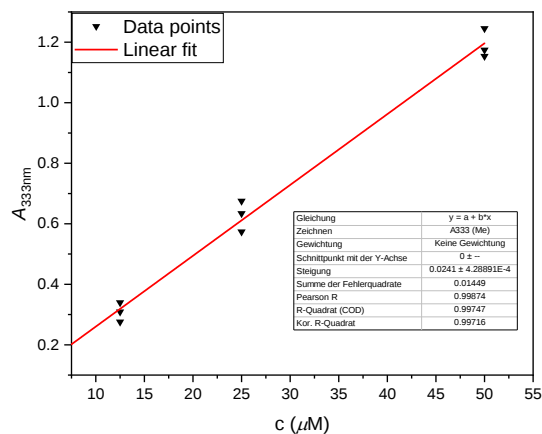


Figure S31: Absorbance at 333 nm dependency on concentration and the slopes of **NAc-PAP-Me** in CH₃CN at 12.5, 25 and 50 μM.

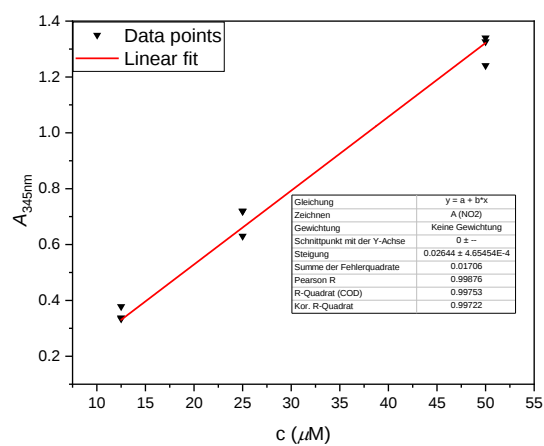


Figure S32: Absorbance at 345 nm dependency on concentration and the slopes of **NAc-PAP-NO₂** in CH₃CN at 12.5, 25 and 50 μM.

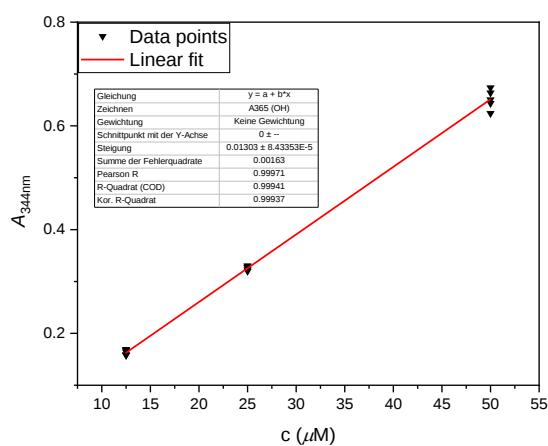


Figure S33: Absorbance at 344 nm dependency on concentration and the slopes of **NAc-PAP-OH** in CH₃CN at 12.5, 25 and 50 μM.

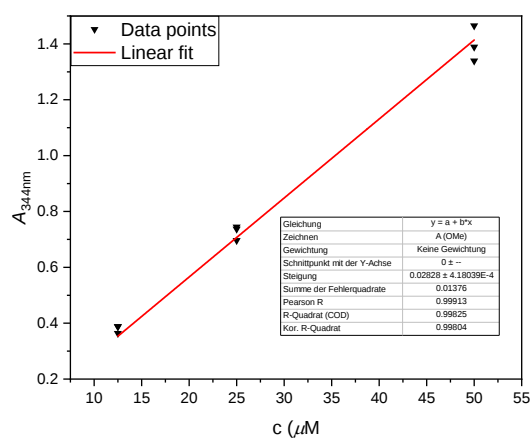


Figure S34: Absorbance at 344 nm dependency on concentration and the slopes of **NAc-PAP-OMe** in CH₃CN at 12.5, 25 and 50 μM.

3.3.2 Absorbance vs. concentrations of NMe-PAP derivatives

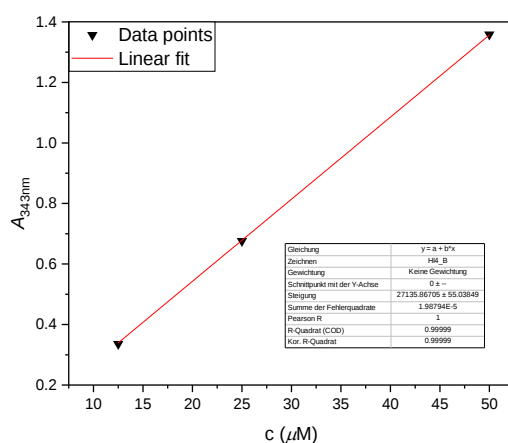


Figure S35: Absorbance at 343 nm dependency on concentration and the slopes of **NMe-PAP-Br** in CH_3CN at 12.5, 25 and 50 μM .

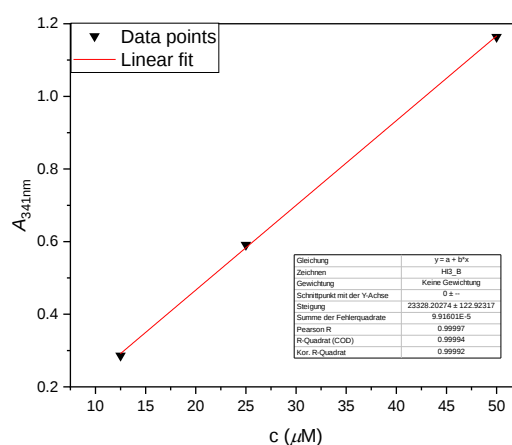


Figure S36: Absorbance at 341 nm dependency on concentration and the slopes of **NMe-PAP- CF_3** in CH_3CN at 12.5, 25 and 50 μM .

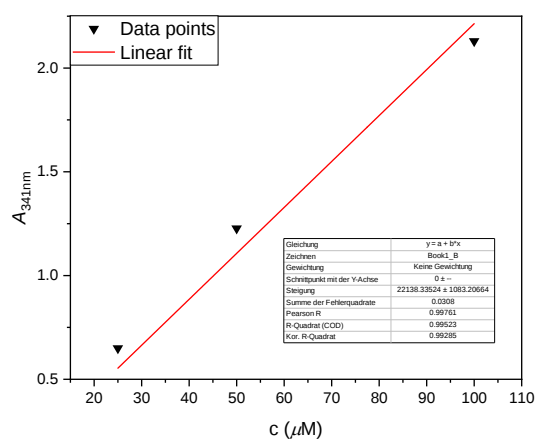


Figure S37: Absorbance at 341 nm dependency on concentration and the slopes of **NMe-PAP-Cl** in CH_3CN at 25, 50 and 100 μM .

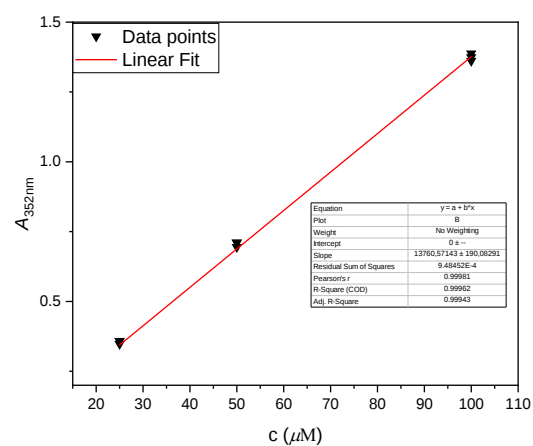


Figure S38: Absorbance at 352 nm dependency on concentration and the slopes of **NMe-PAP-CN** in CH_3CN at 25, 50 and 100 μM .

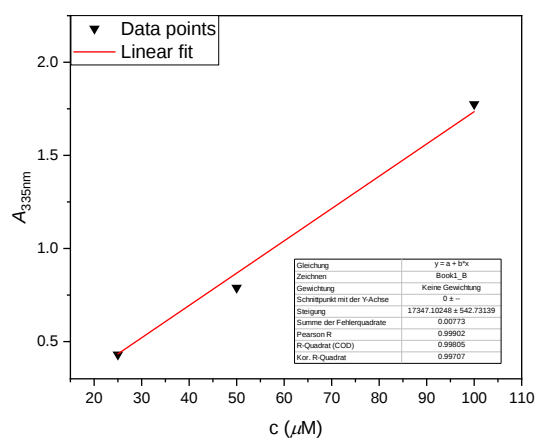


Figure S39: Absorbance at 335 nm dependency on concentration and the slopes of **NMe-PAP-F** in CH_3CN at 25, 50 and 100 μM .

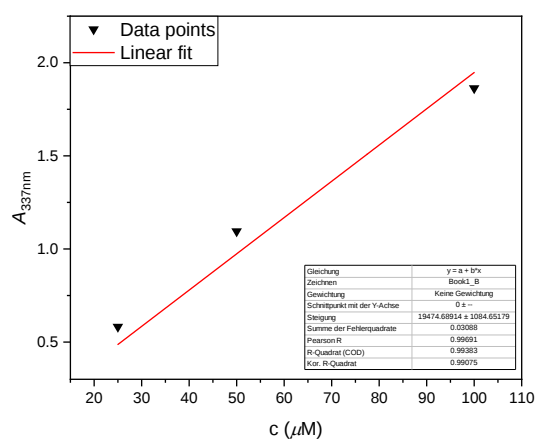


Figure S40: Absorbance at 337 nm dependency on concentration and the slopes of **NMe-PAP-H** in CH_3CN at 25, 50 and 100 μM .

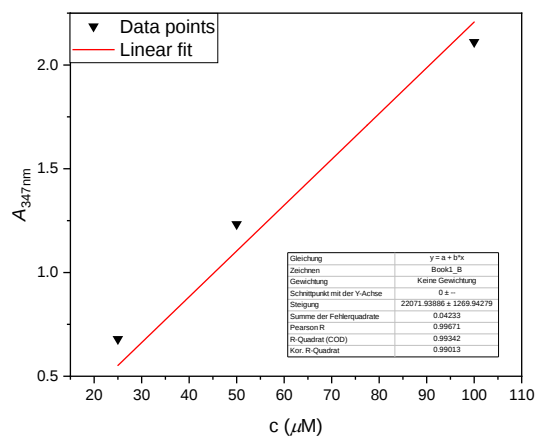


Figure S41: Absorbance at 347 nm dependency on concentration and the slopes of **NMe-PAP-I** in CH_3CN at 25, 50 and 100 μM .

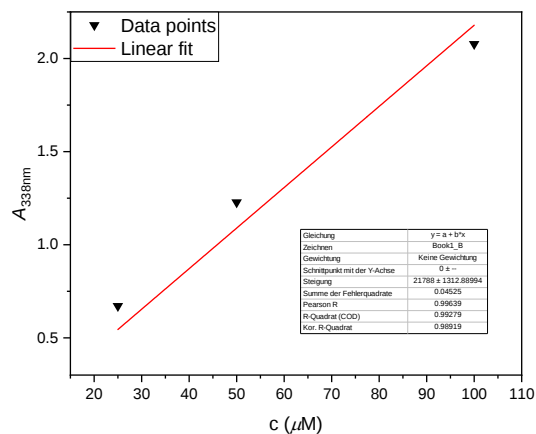


Figure S42: Absorbance at 338 nm dependency on concentration and the slopes of **NMe-PAP-Me** in CH_3CN at 12.5, 25 and 50 μM .

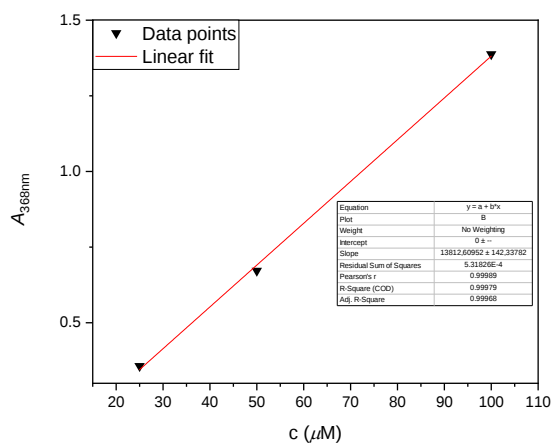


Figure S43: Absorbance at 368 nm dependency on concentration and the slopes of **NMe-PAP-NO₂** in CH₃CN at 25, 50 and 100 μM.

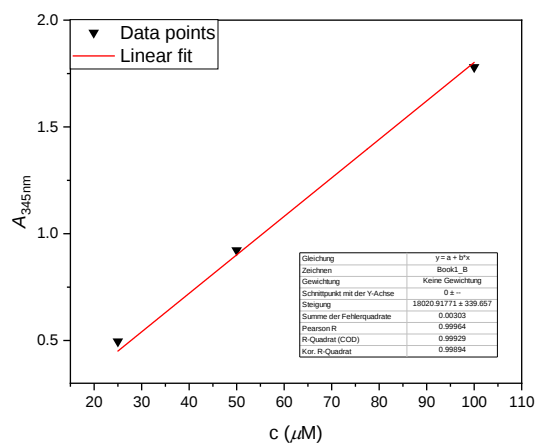


Figure S44: Absorbance at 345 nm dependency on concentration and the slopes of **NMe-PAP-OH** in CH₃CN at 12.5, 25 and 50 μM.

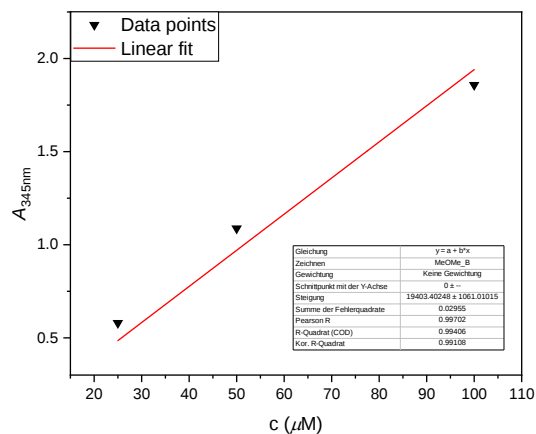


Figure S45: Absorbance at 345 nm dependency on concentration and the slopes of **NMe-PAP-OMe** in CH₃CN at 25, 50 and 100 μM.

3.3.3 Absorbance vs. concentrations of NH-PAP derivatives

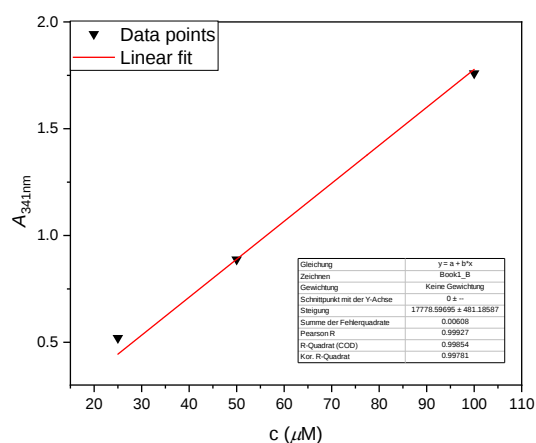


Figure S46: Absorbance at 341 nm dependency on concentration and the slopes of **NH-PAP-Br** in CH_3CN at 25, 50 and 100 μM .

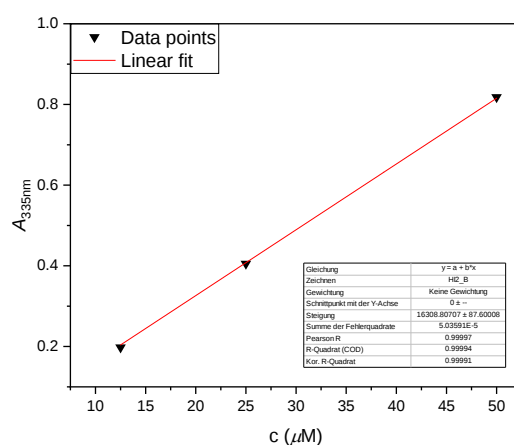


Figure S47: Absorbance at 335 nm dependency on concentration and the slopes of **NH-PAP-CF₃** in CH_3CN at 12.5, 25 and 50 μM .

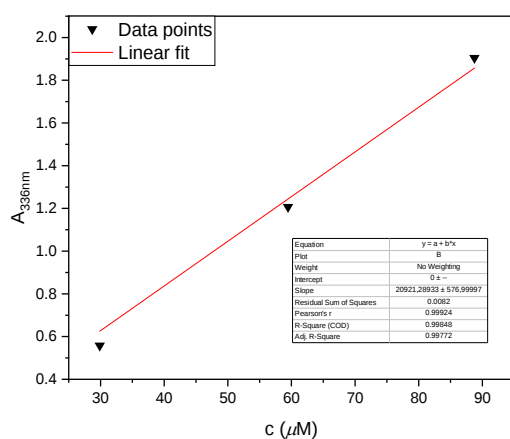


Figure S48: Absorbance at 336 nm dependency on concentration and the slopes of **NH-PAP-Cl** in CH_3CN at 30, 60 and 90 μM .

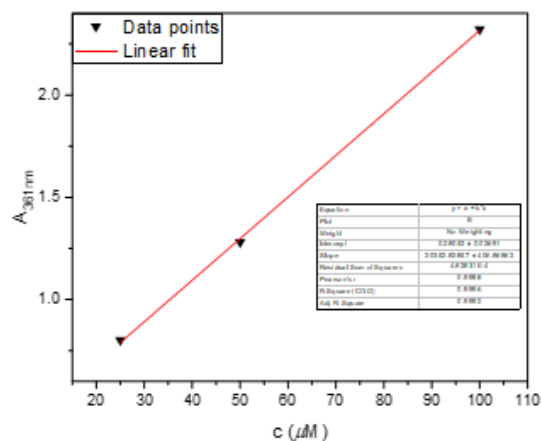


Figure S49: Absorbance at 361 nm dependency on concentration and the slopes of **NH-PAP-CN** in CH_3CN at 25, 50 and 100 μM .

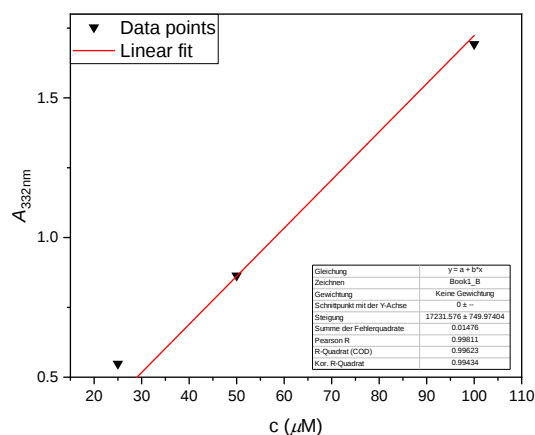


Figure S50: Absorbance at 332 nm dependency on concentration and the slopes of **NH-PAP-F** in CH_3CN at 25, 50 and 100 μM .

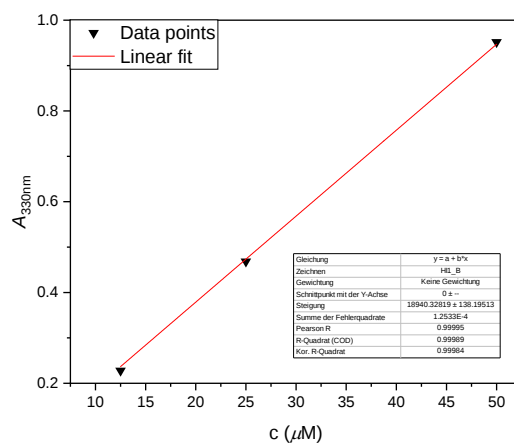


Figure S51: Absorbance at 330 nm dependency on concentration and the slopes of **NH-PAP-H** in CH₃CN at 12.5, 25 and 50 μM.

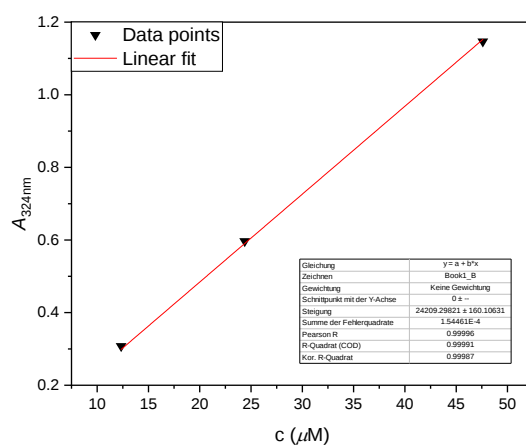


Figure S52: Absorbance at 324 nm dependency on concentration and the slopes of **NH-PAP-I** in CH₃CN at 12.5, 25 and 50 μM.

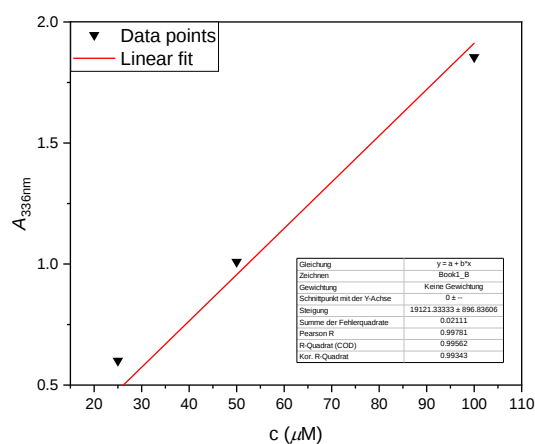


Figure S53: Absorbance at 336 nm dependency on concentration and the slopes of **NH-PAP-Me** in CH₃CN at 25, 50 and 100 μM.

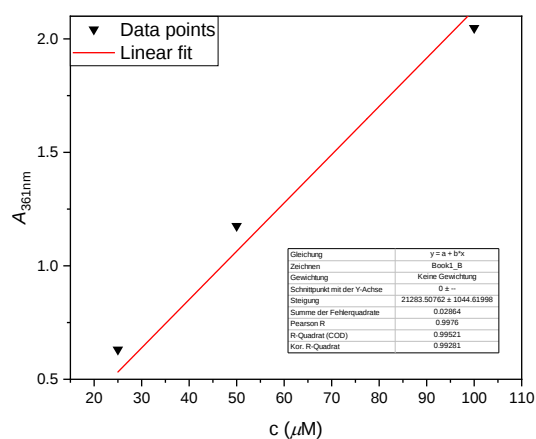


Figure S54: Absorbance at 361 nm dependency on concentration and the slopes of **NH-PAP-NO₂** in CH₃CN at 25, 50 and 100 μM.

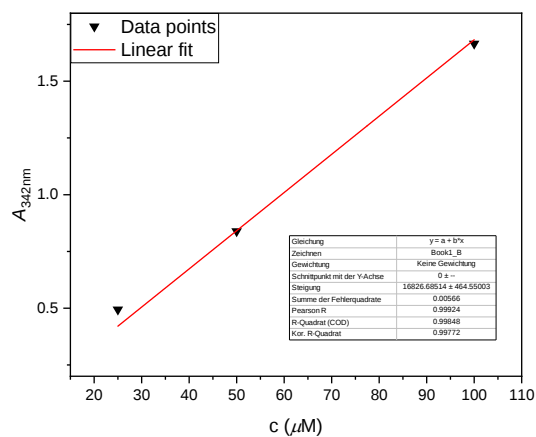


Figure S55: Absorbance at 342 nm dependency on concentration and the slopes of **NH-PAP-OH** in CH₃CN at 25, 50 and 100 μM.

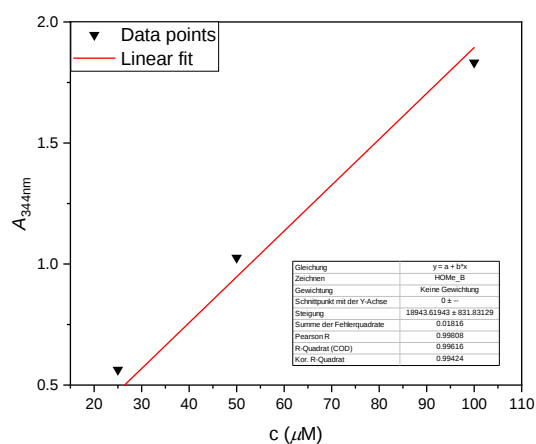


Figure S56: Absorbance at 344 nm dependency on concentration and the slopes of **NH-PAP-OMe** in CH₃CN at 25, 50 and 100 μM.

3.4 Chemical actinometry

A modification of a standard protocol was applied for the determination of the photon flux.¹² An aqueous H₂SO₄ solution (50 mM) containing freshly recrystallized K₃[Fe(C₂O₄)₃] (41 mM, 2 mL, 1 cm quartz cuvette) was irradiated at 20 °C for a given period in the dark with a 365 nm then 445 nm LED. The solution was then diluted with 1.0 mL of an aqueous H₂SO₄ solution (0.5 M) containing phenanthroline (1 g/L) and NaOAc (122.5 g/L) and left to react for 10 min. The absorption at $\lambda = 510$ nm was measured and compared to an identically prepared non-irradiated sample. The concentration of [Fe(phenanthroline)₃]²⁺ complex was calculated using its molar absorptivity ($\epsilon = 11\,100\text{ M}^{-1}\text{ cm}^{-1}$) and considering the dilution. The quantity of Fe²⁺ ions expressed in mol was plotted versus time (expressed in seconds) and the slope, obtained by linear fitting the data points to the equation $y = ax + b$, equals the rate of formation of the Fe²⁺ ion at the given wavelength. This rate can be converted into the photon flux (I) by dividing it by the quantum yield of [Fe(phenanthroline)₃]²⁺ complex ($\Phi^{365\text{nm}} = 1.29$, $\Phi^{445\text{nm}} = 1.06$) at 365 or 445 nm and by the probability of photon absorption at 365 nm of the Fe³⁺ complex (approximated to 1 as we were working in the total absorption regime). The obtained photon flux values for 365 nm and 445 nm are listed in Table S1.

Table S1: Determined photon flux values for 365 nm and 445 nm.

λ / nm	$I / 10^{-5} \text{ mE s}^{-1}$
365	2.38
445	6.43

3.5 Determination of quantum yields

The quantum yield of the photochemical isomerization of **PAP** compounds is determined using the initial slope method. Photoisomerization was measured under 365 (at concentration 12.5 μM) or 445 nm (at concentration 50 μM) irradiation at 25% or 10% intensity, the natural logarithm of the absorbance was plotted as a function of time. By applying equation 1,¹² the quantum yield of the light-induced isomerization of **PAP** compounds can be calculated.

$$\Phi = \frac{-k[X]_{t_0} V}{I (1 - 10^{A(t_0, \lambda)})} \quad (1)$$

Where Φ is the quantum yield; $-k$ is the reaction rate; $[X]_{t_0}$ is the concentration of the **PAP** compounds in the dark state (e.g. >>99% trans-isomer), V is the volume, I is the photon flux and $A(t_0, \lambda)$ is the absorption value before irradiation at 365 nm or 445 nm respectively. By applying first-order kinetics, $-k$ can be derived from the slope of the linear fit to the plot of the natural logarithm of absorbance as a function of time.

3.5.1 Irradiation of NAc-PAP derivatives and evaluation of the kinetic traces

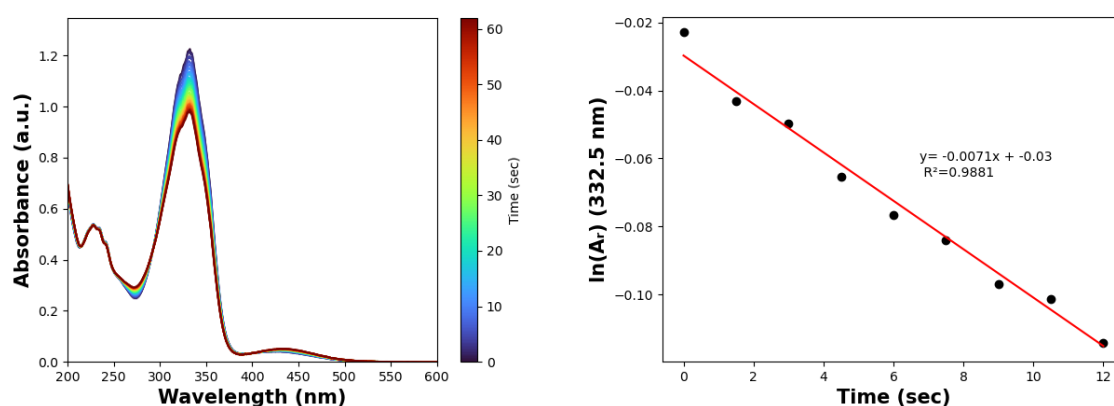


Figure S57: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Me** (50 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Me**.

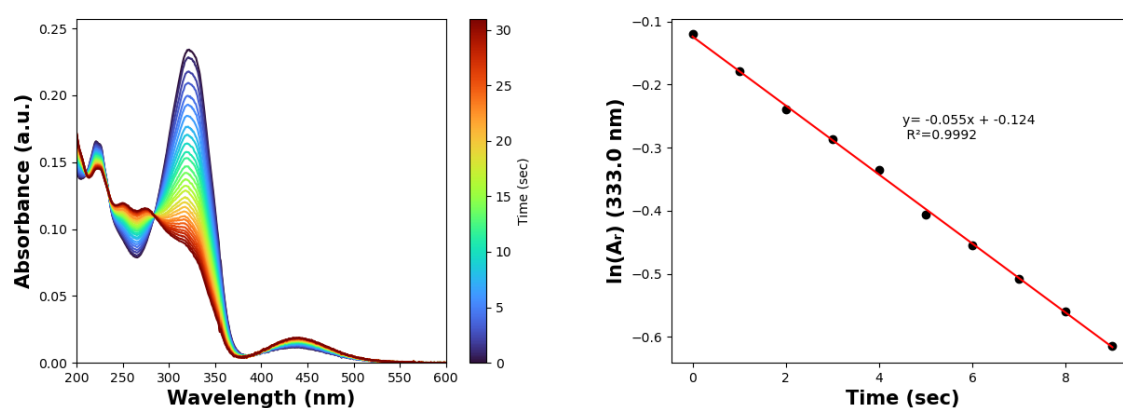


Figure S58: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Me** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Me**.

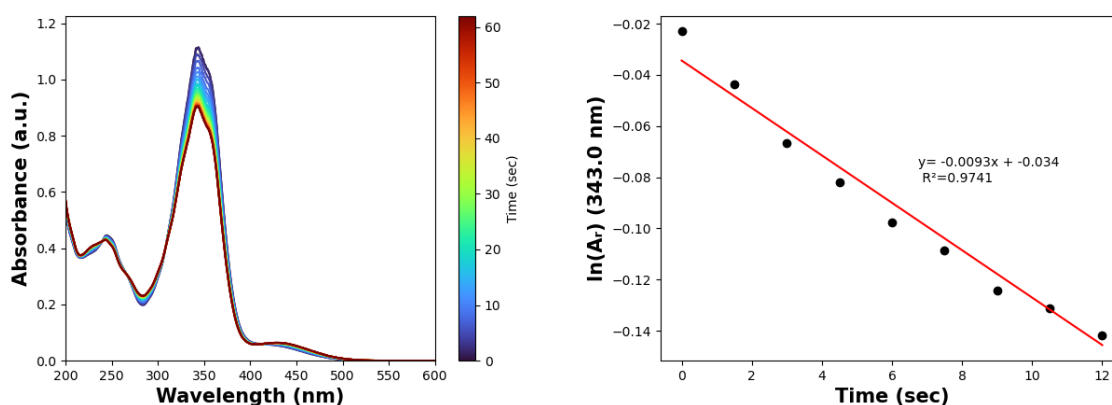


Figure S59: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-OMe** (37.5 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-OMe**.

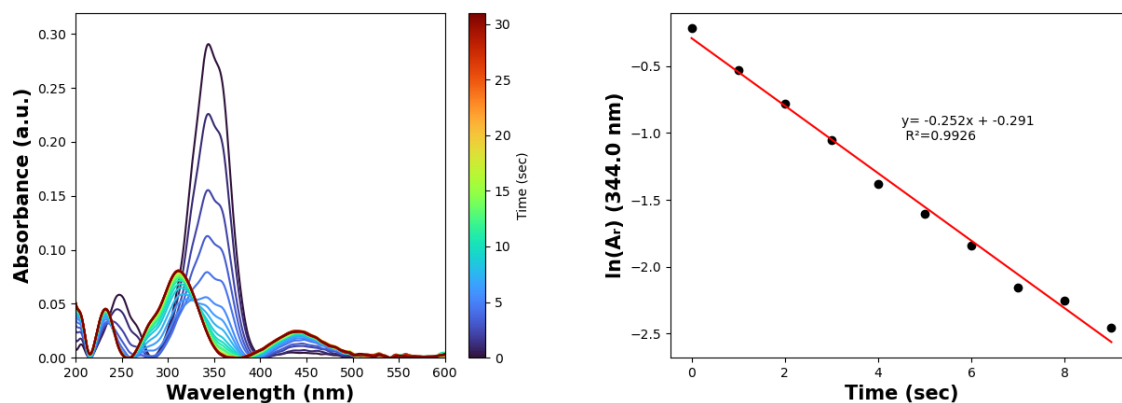


Figure S60: Time-resolved UV-vis absorption spectra of **NAc-PAP-OMe** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-OMe**.

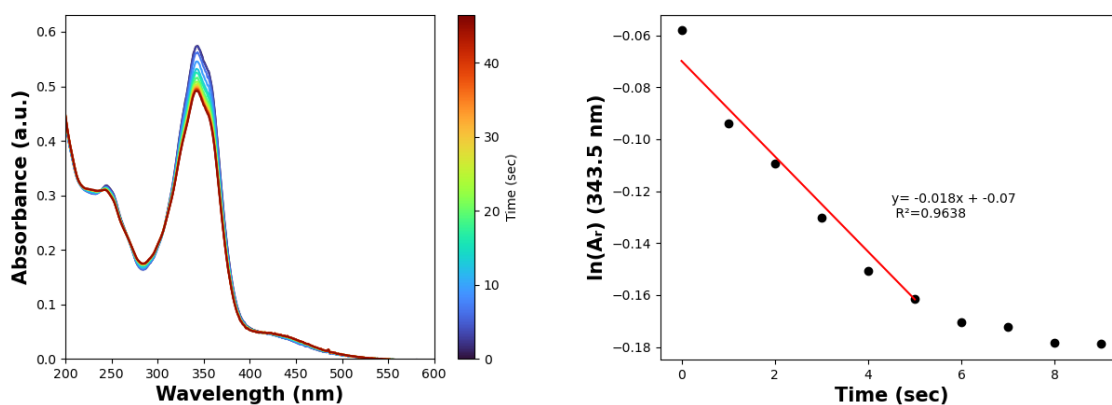


Figure S61: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-OH** (50 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-OH**.

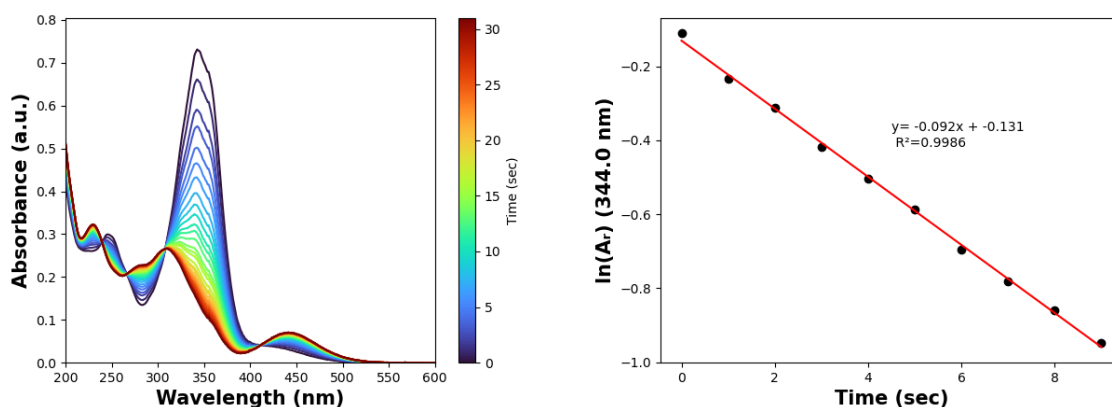


Figure S62: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-OH** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-OH**.

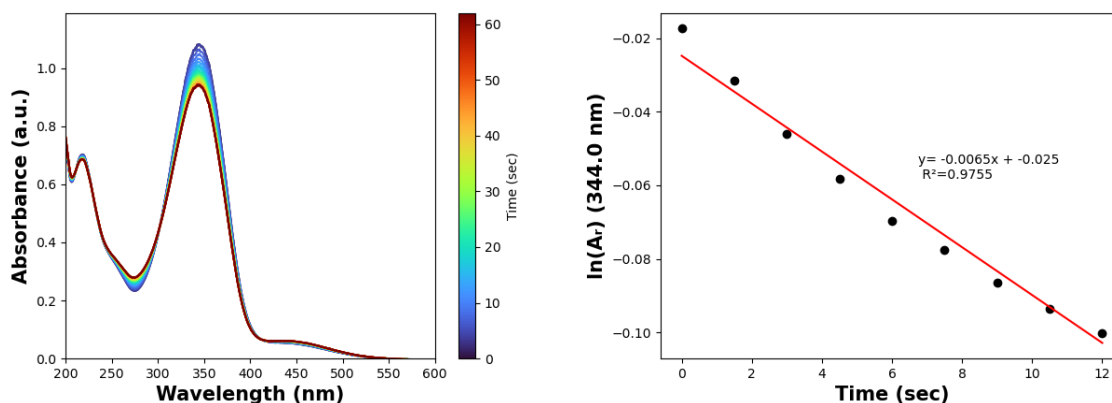


Figure S63: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-NO₂** (37.5 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-NO₂**.

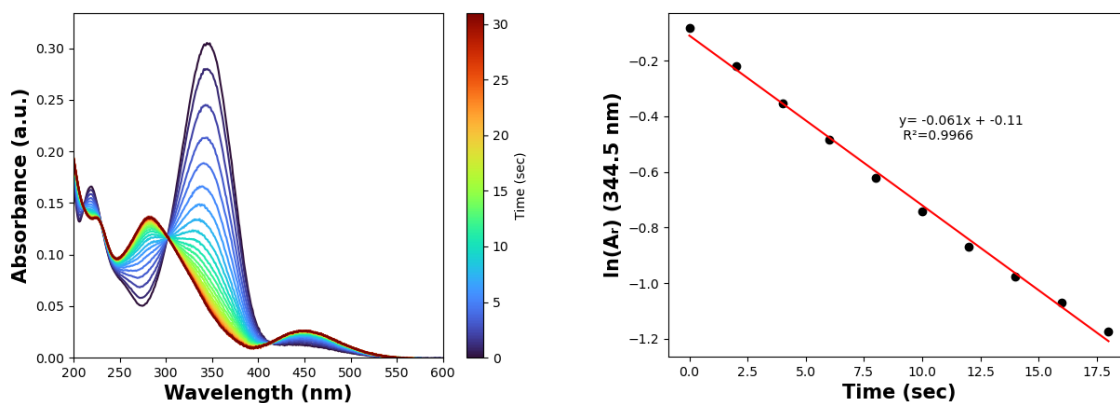


Figure S64: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-NO₂** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-NO₂**.

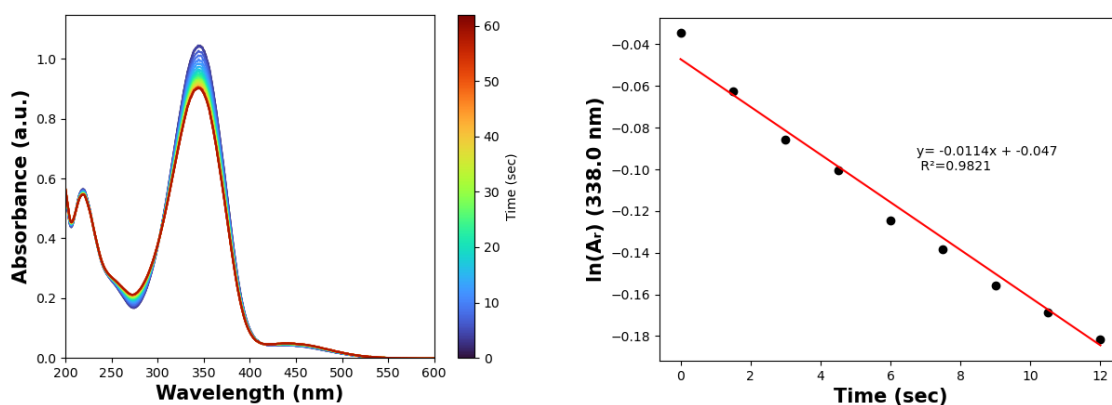


Figure S65: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-I** (37.5 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-I**.

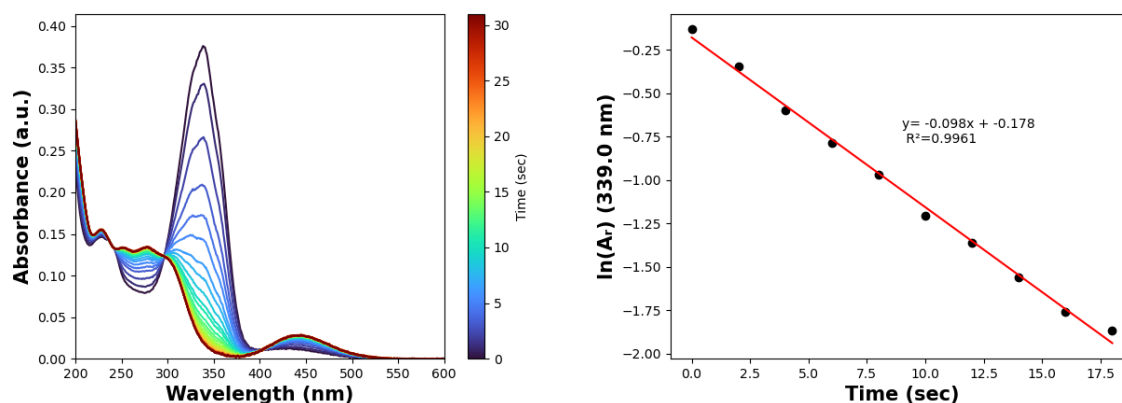


Figure S66: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-I** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-I**.

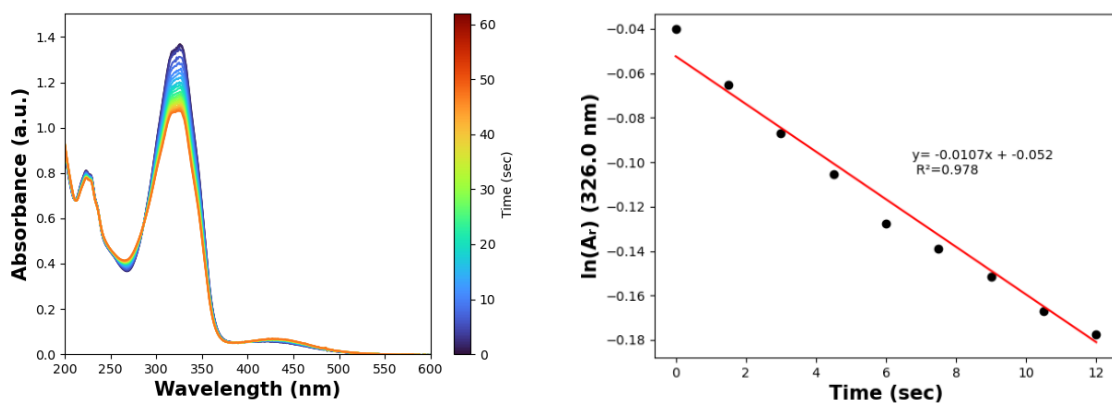


Figure S67: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-H** (50 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-H**.

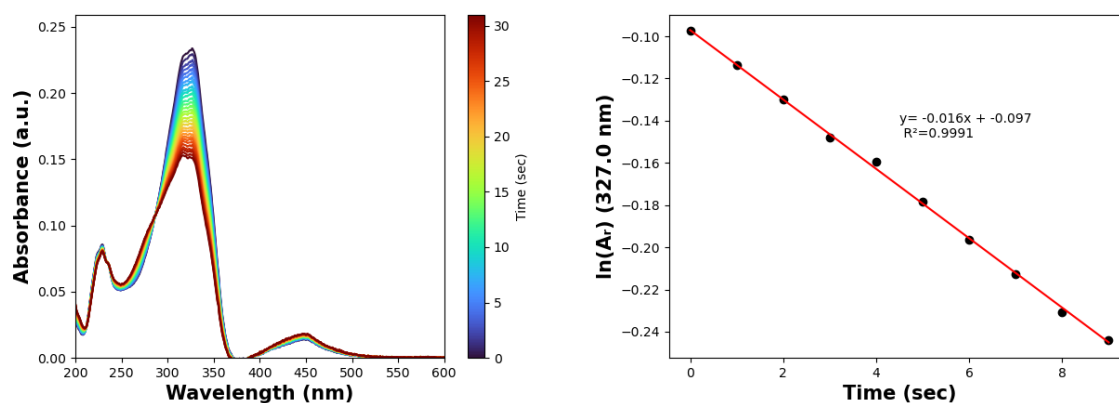


Figure S68: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-H** (12.5 μM in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-H**.

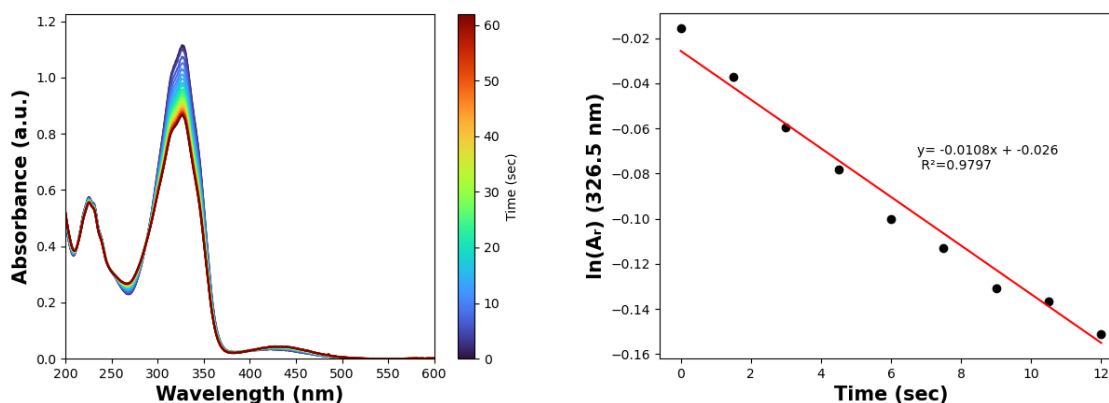


Figure S69: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-F** (50 μM in CH₃CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-F**.

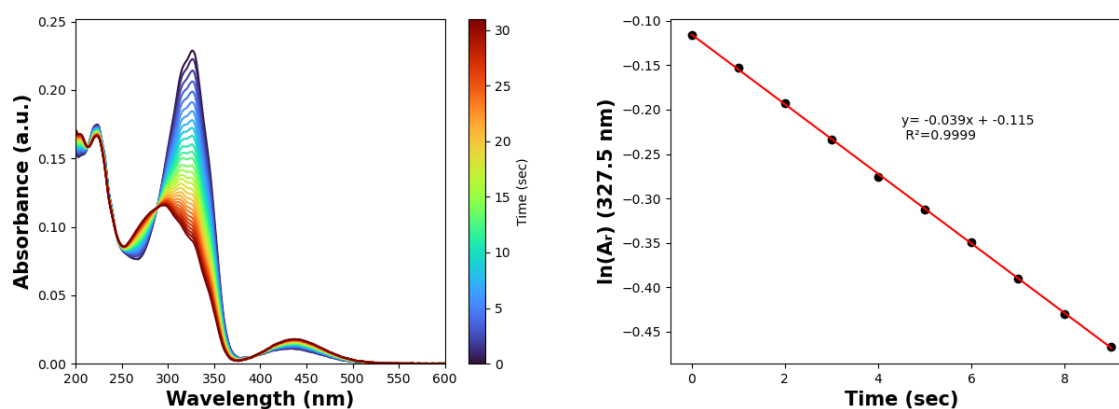


Figure S70: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-F** (12.5 μM in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-F**.

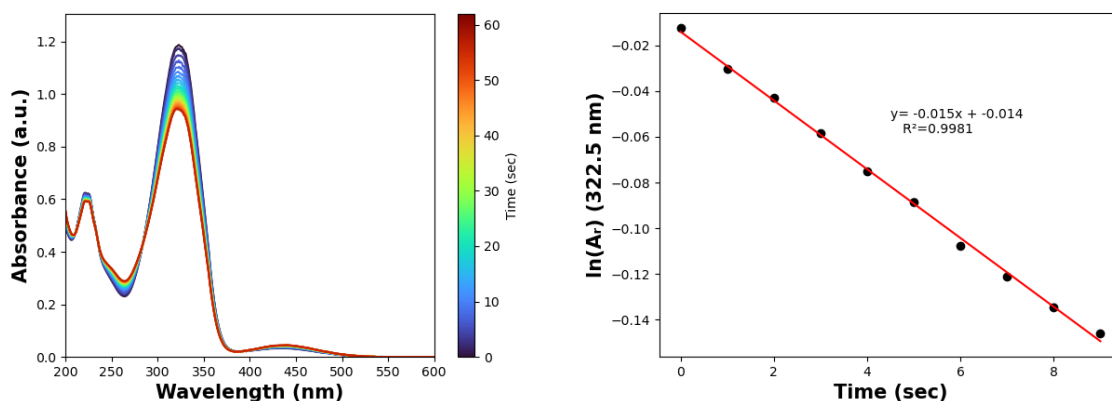


Figure S71: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-CF₃** (50 μ M in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-CF₃**.

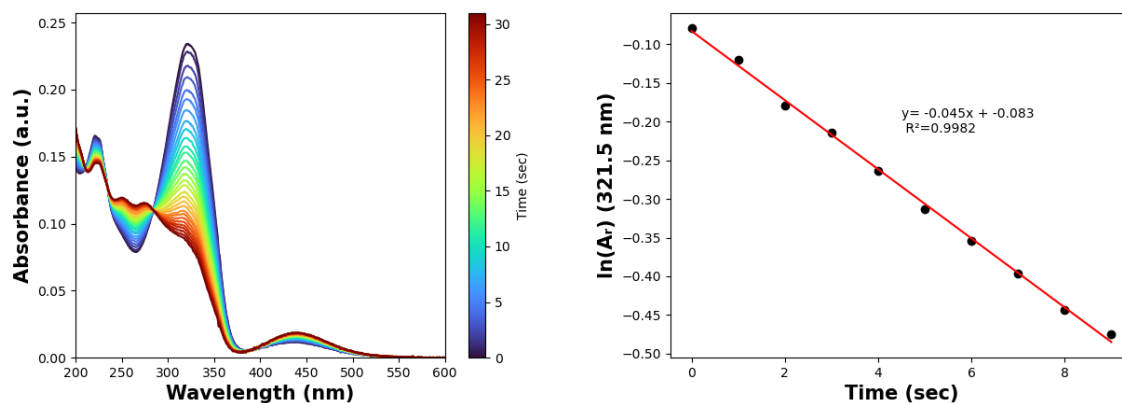


Figure S72: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-CF₃** (50 μ M in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-CF₃**.

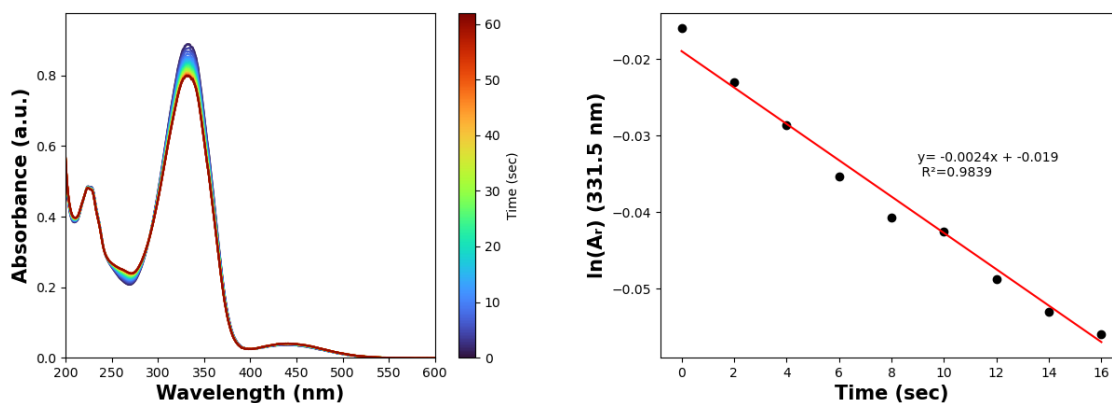


Figure S73: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-CN** (50 μ M in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-CN**.

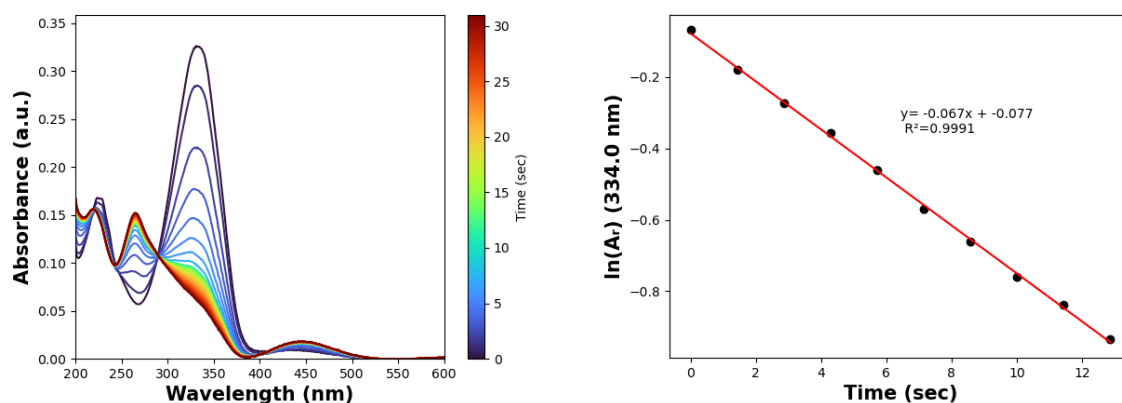


Figure S74: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-CN** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-CN**.

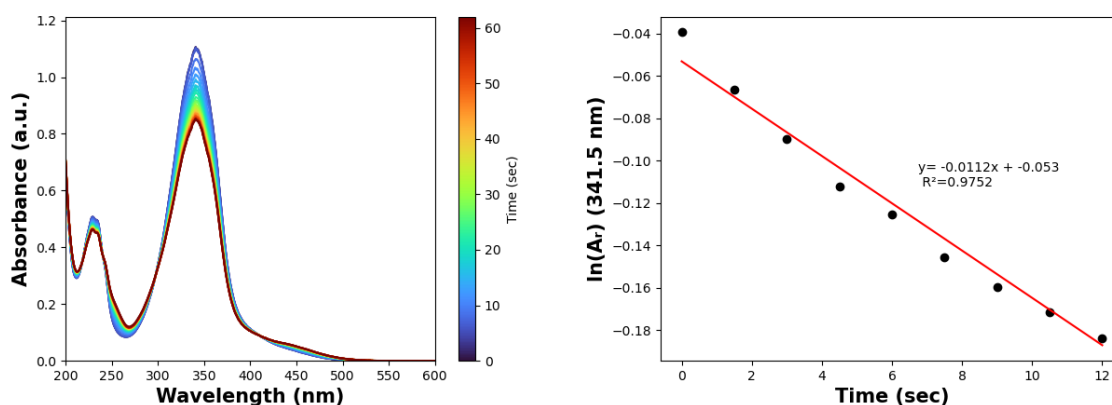


Figure S75: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Cl** (50 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Cl**.

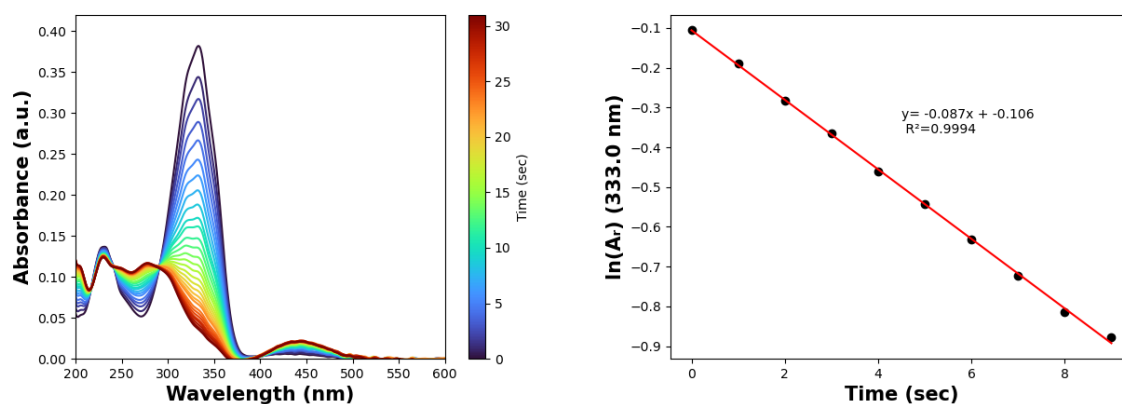


Figure S76: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Cl** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Cl**.

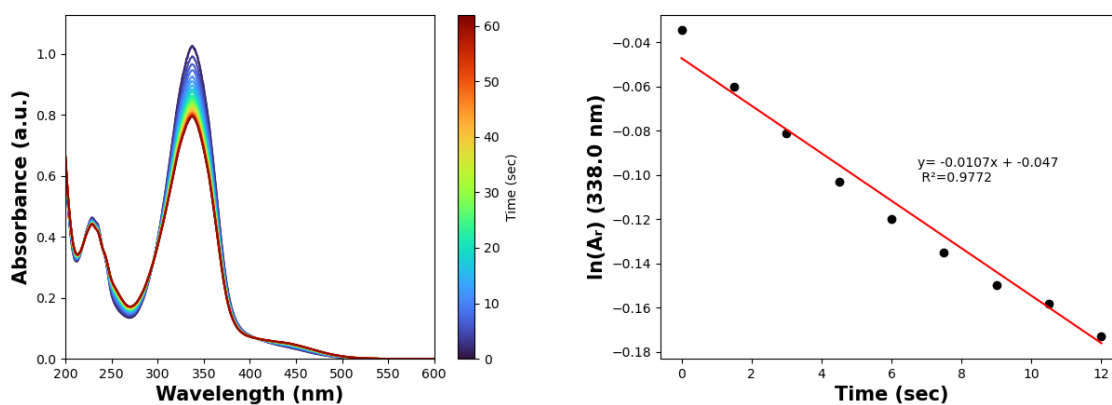


Figure S77: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Br** (50 μM in CH_3CN) upon 445 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Br**.

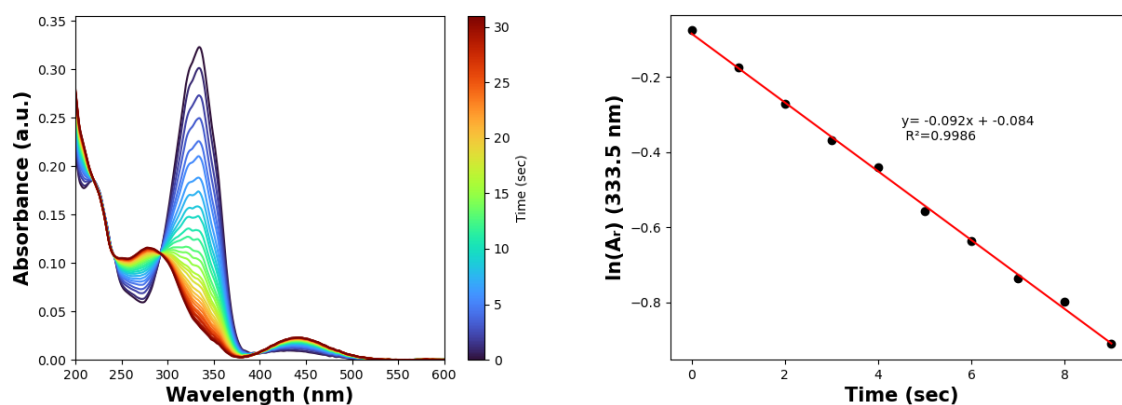


Figure S78: Left: Time-resolved UV-vis absorption spectra of **NAc-PAP-Br** (12.5 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NAc-PAP-Br**.

3.5.2 Irradiation of NH-PAP derivatives and evaluation of the kinetic traces

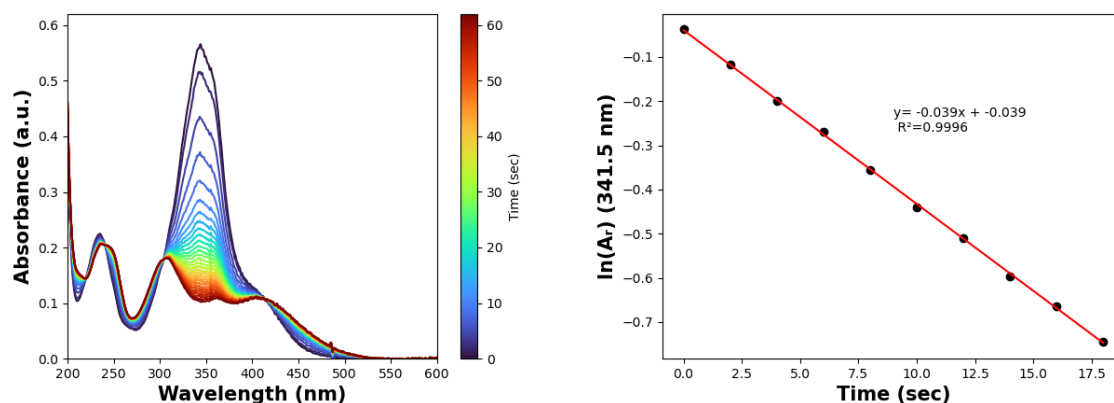


Figure S79: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-OMe** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-OMe**.

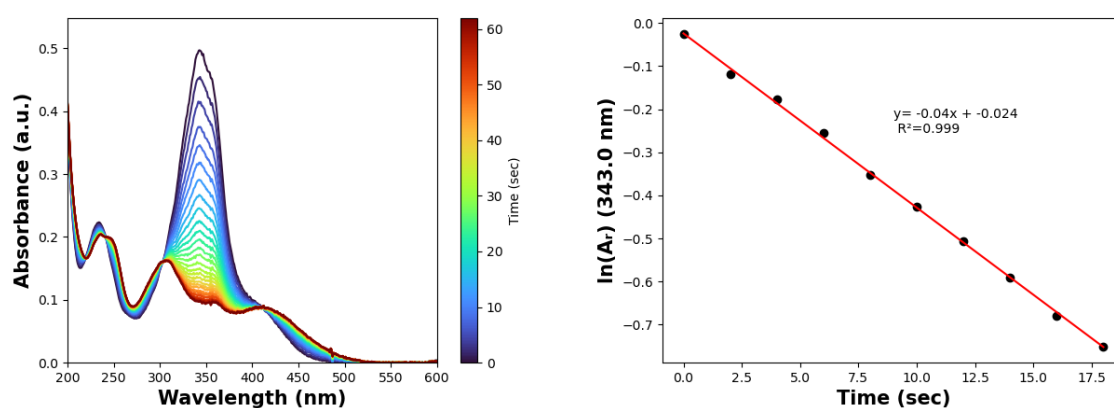


Figure S80: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-OH** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-OH**.

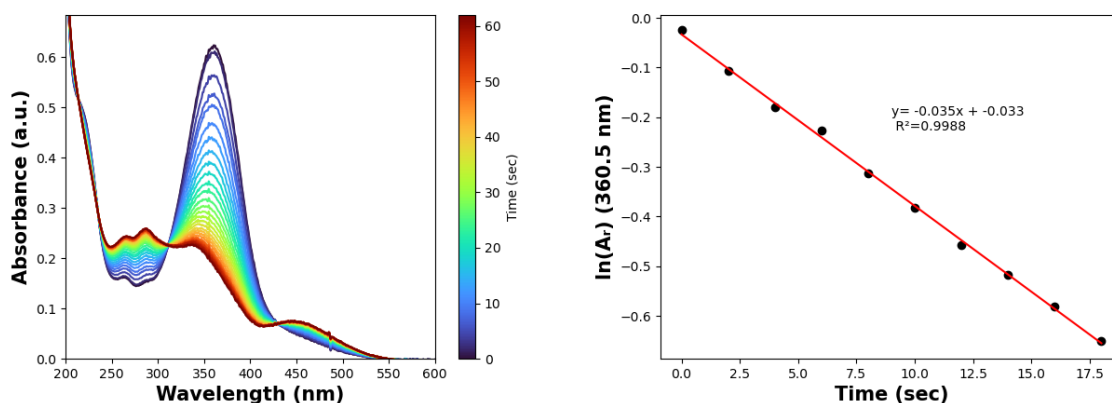


Figure S81: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-NO₂** (25 μ M in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-NO₂**.

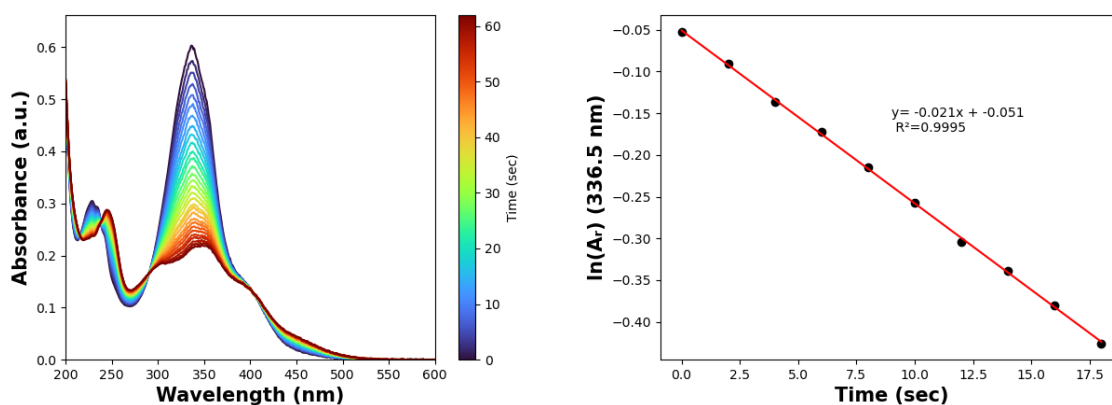


Figure S82: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-Me** (25 μ M in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-Me**.

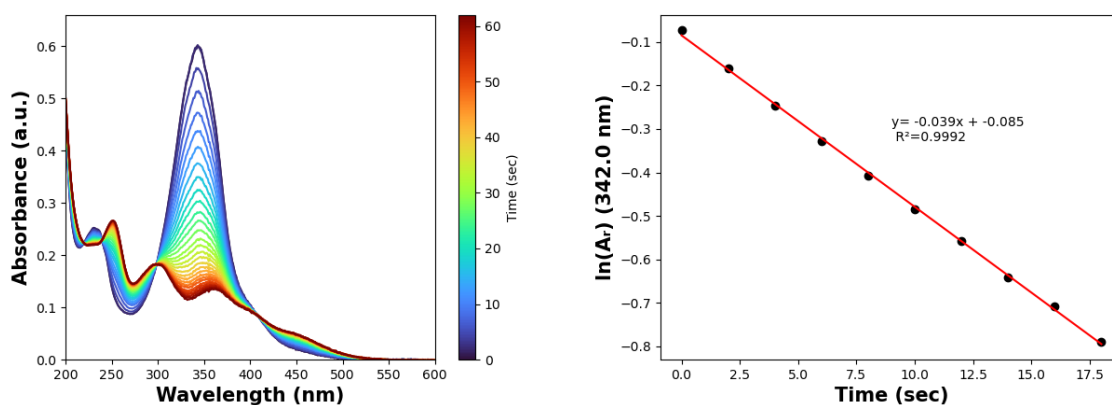


Figure S83: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-I** (25 μ M in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-I**.

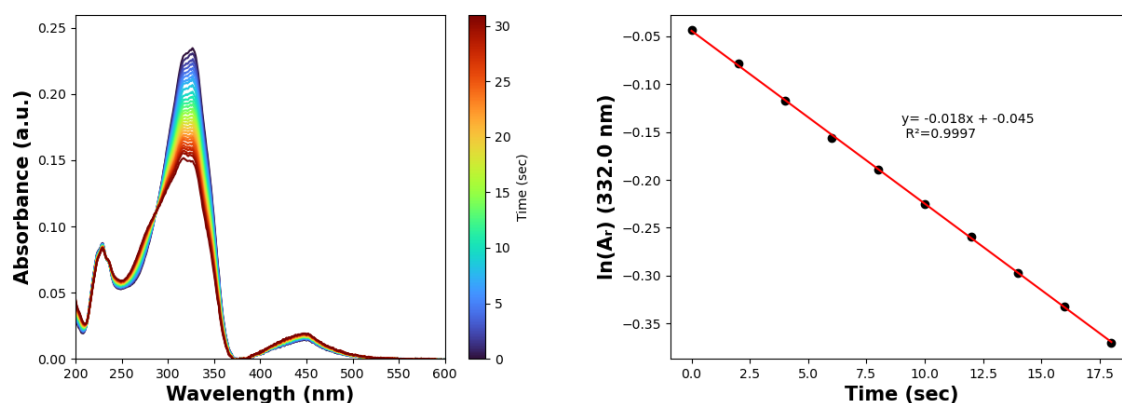


Figure S84: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-H** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-H**.

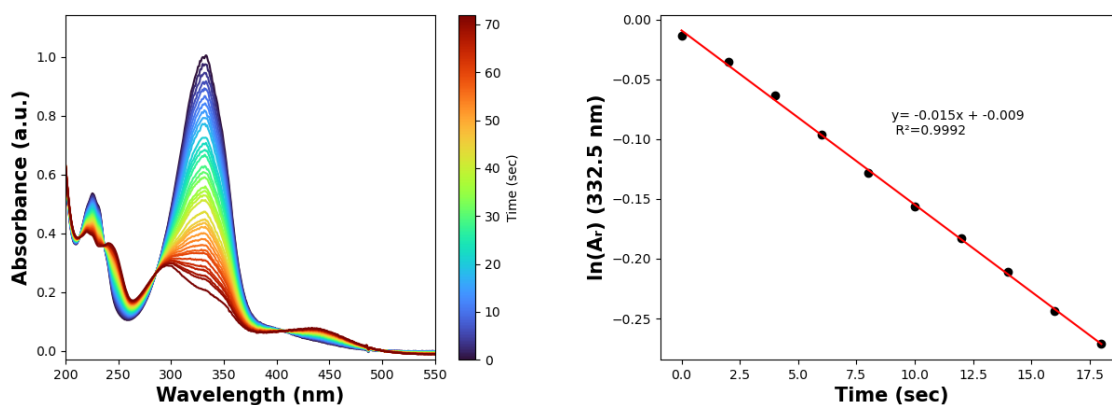


Figure S85: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-F** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-F**.

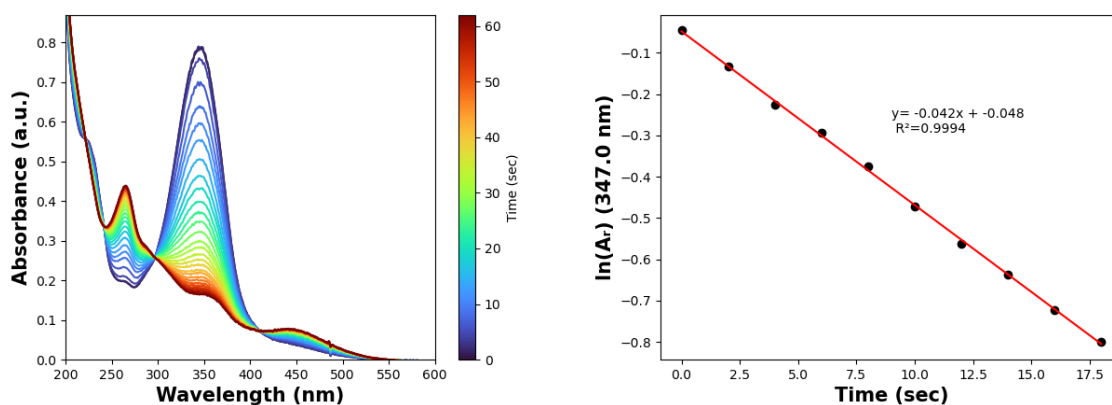


Figure S86: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-CN** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-CN**.

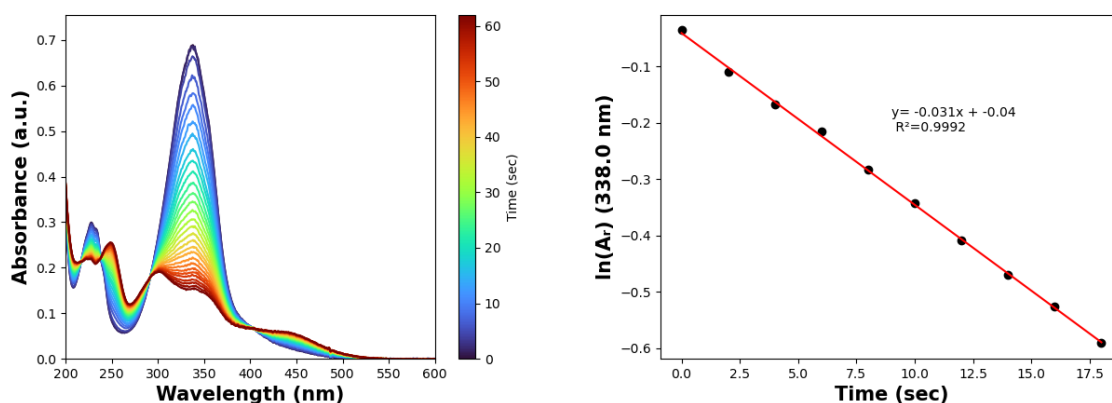


Figure S87: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-Cl** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-Cl**.

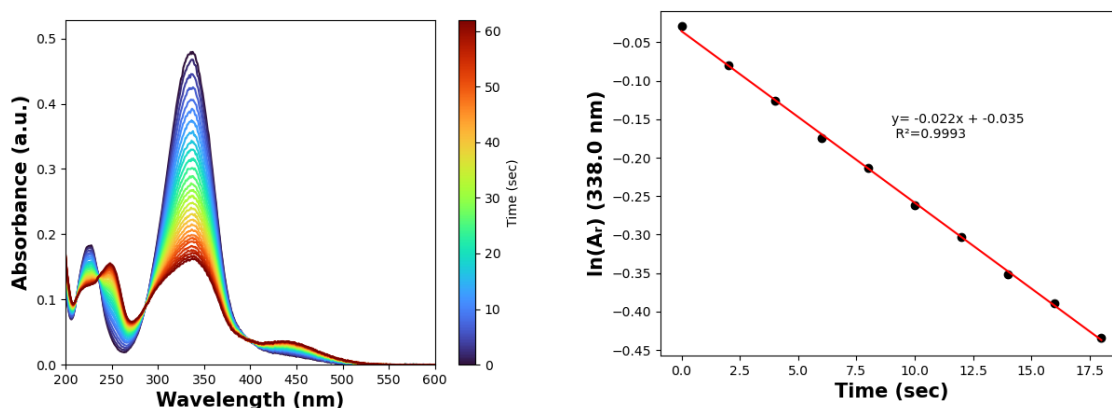


Figure S88: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-CF₃** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-CF₃**.

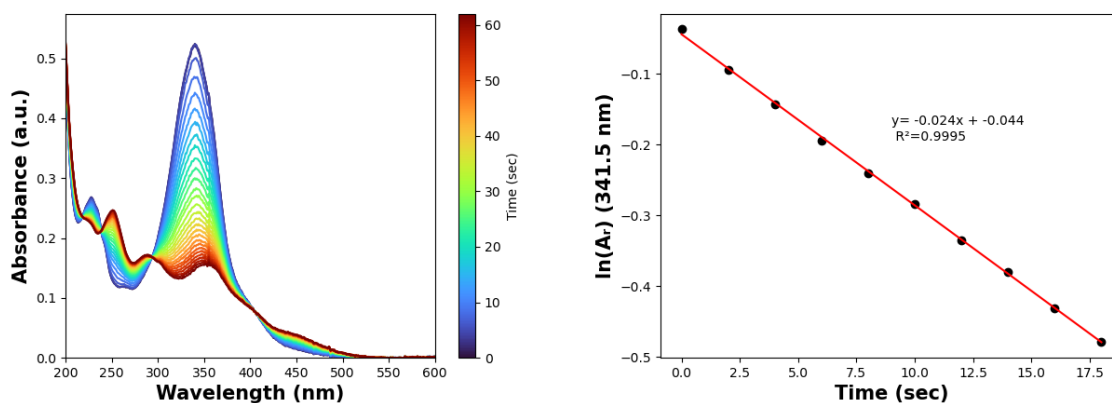


Figure S89: Left: Time-resolved UV-vis absorption spectra of **NH-PAP-Br** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NH-PAP-Br**.

3.5.3 Irradiation of NMe-PAP derivatives and evaluation of the kinetic traces

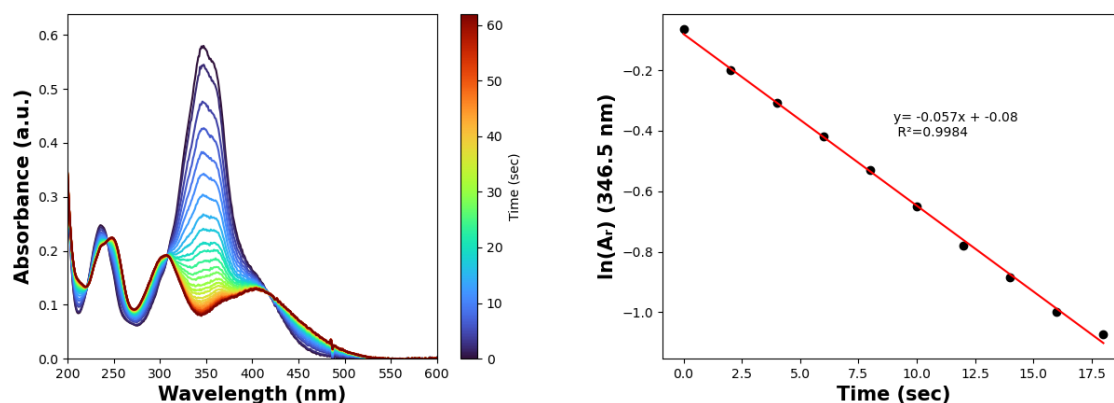


Figure S90: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-OMe** (25 μ M in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-OMe**.

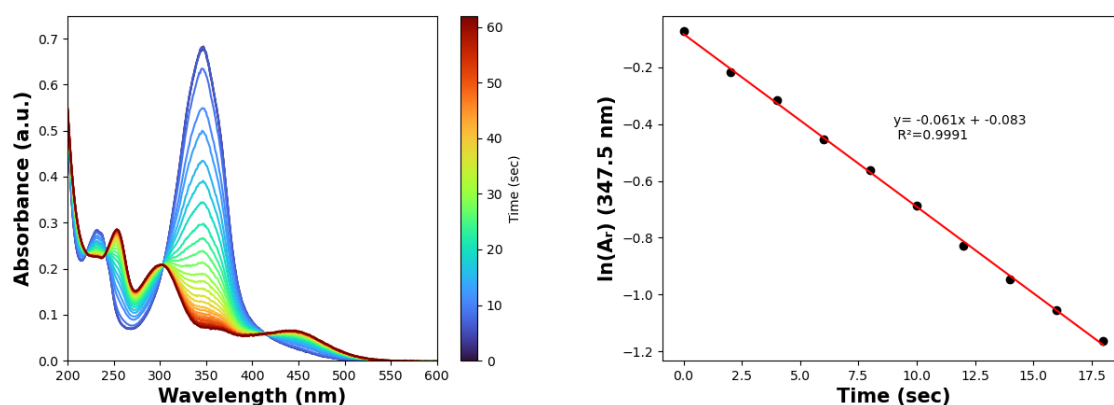


Figure S91: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-I** (25 μ M in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-I**.

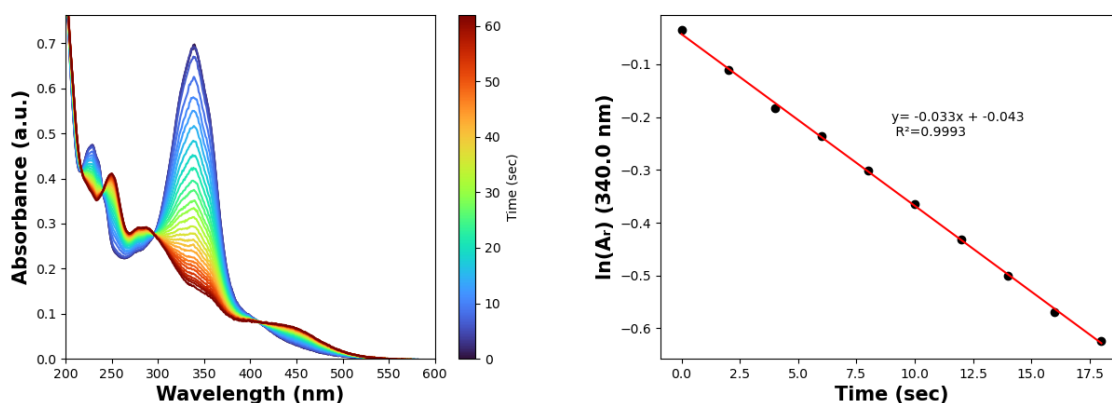


Figure S92: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-Me** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-Me**.

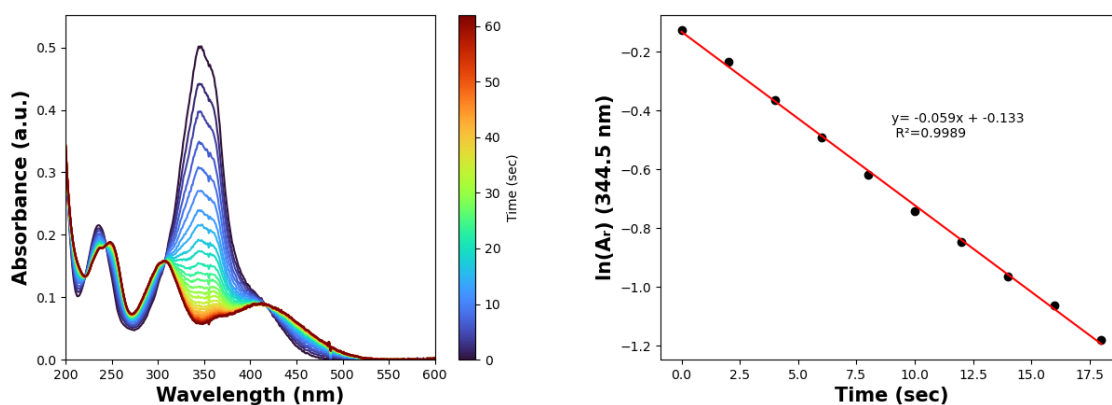


Figure S93: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-OH** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-OH**.

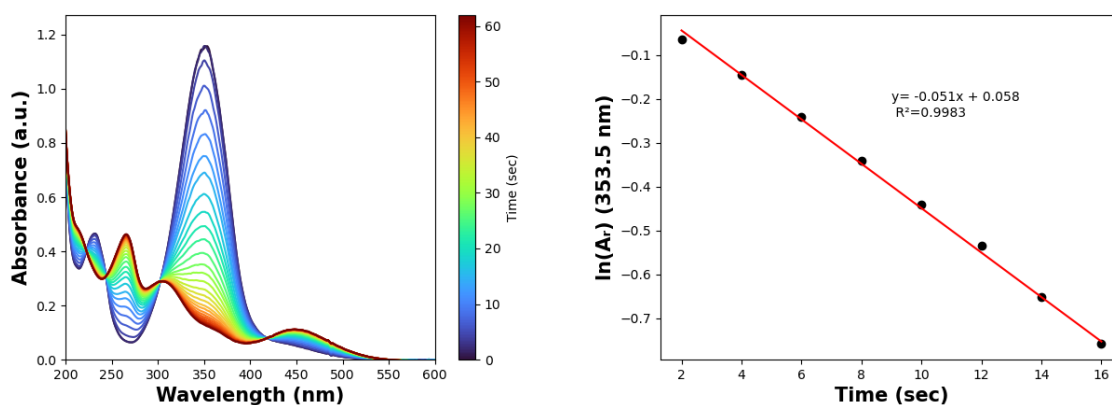


Figure S94: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-CN** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-CN**.

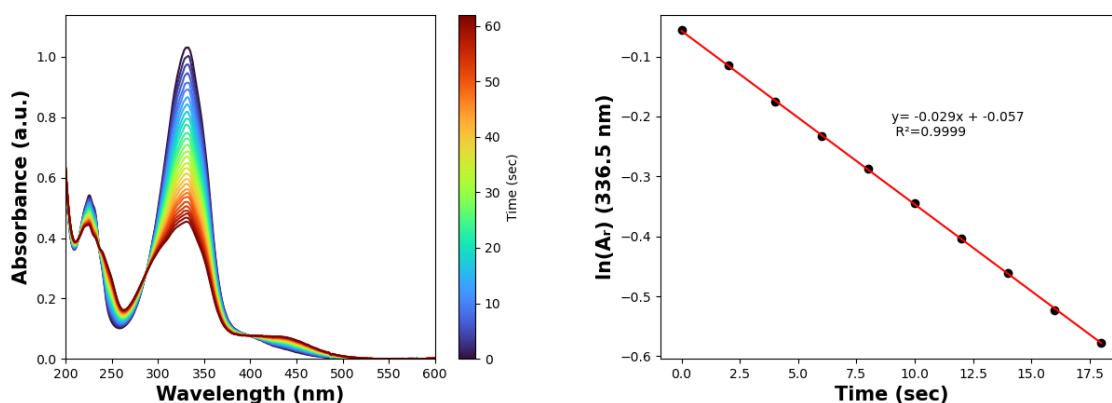


Figure S95: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-F** (50 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-F**.

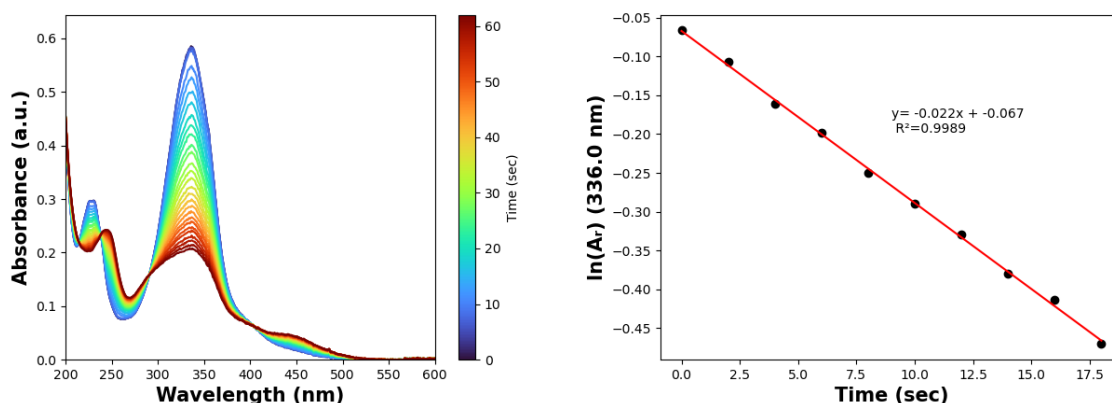


Figure S96: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-H** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-H**.

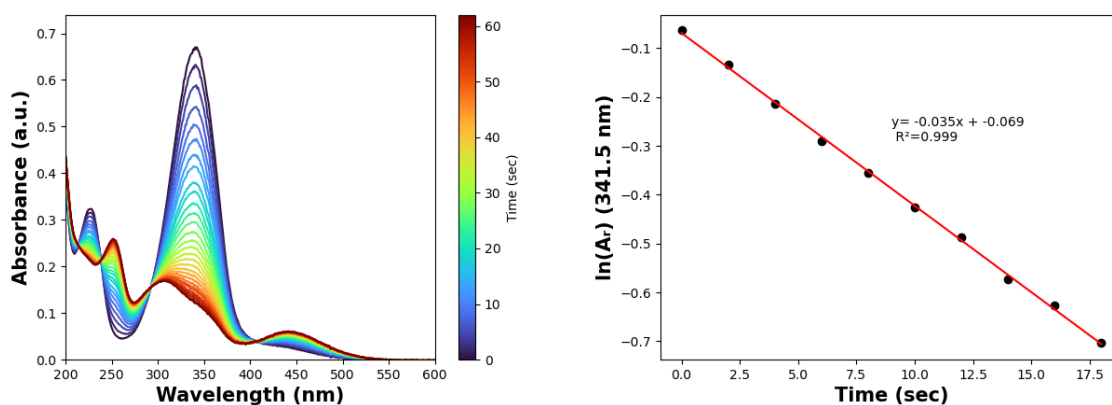


Figure S97: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-CF₃** (25 μM in CH_3CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-CF₃**.

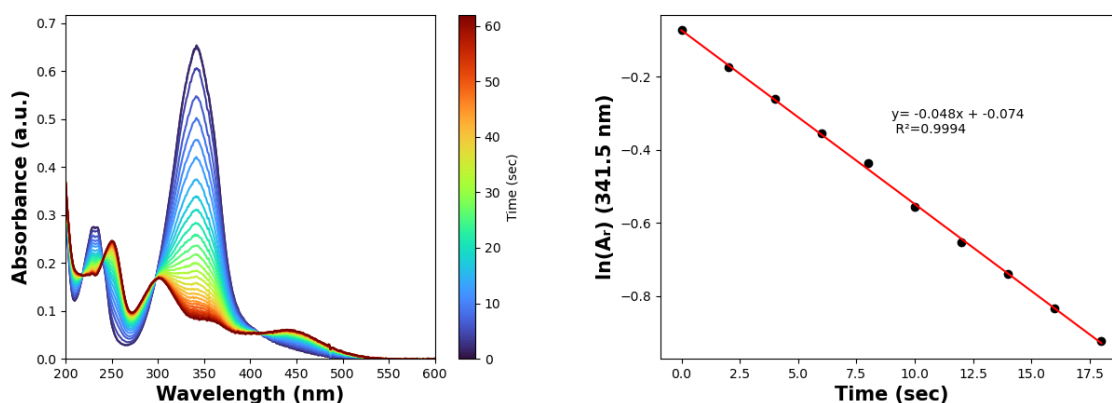


Figure S98: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-Cl** (25 μM in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-Cl**.

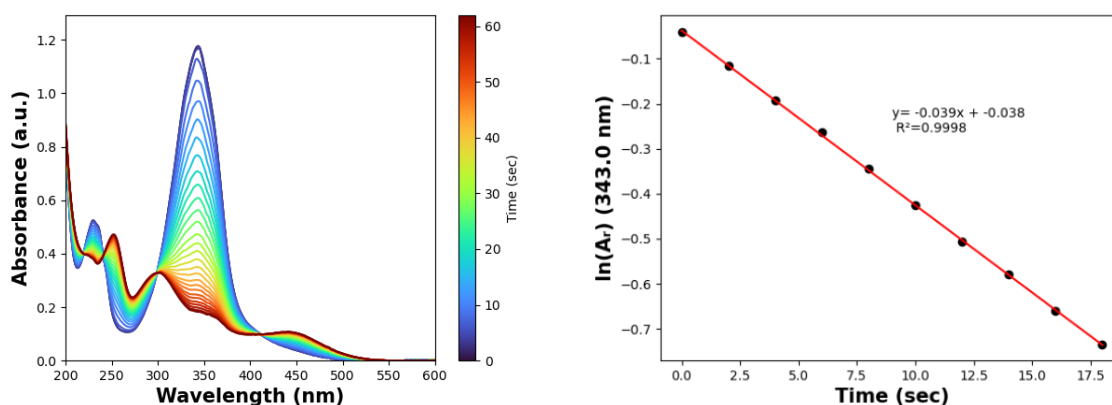


Figure S99: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-Br** (25 μM in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-Br**.

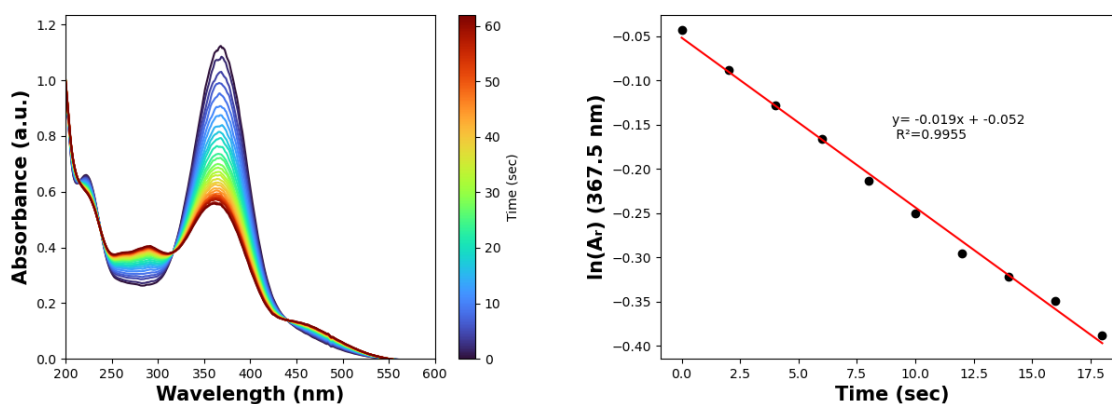


Figure S100: Left: Time-resolved UV-vis absorption spectra of **NMe-PAP-NO₂** (50 μM in CH₃CN) upon 365 nm irradiation. Right: Linear fit of the logarithmic kinetic trace of the change of absorbance at the absorption maximum of **NMe-PAP-NO₂**.

3.6 Determination of thermal half-lives

Determination of the thermal half-lives $\tau_{1/2}$ of the metastable Z isomers were recorded as follows. A freshly prepared solution of the **NAc-PAPs** of interest in CH_3CN was irradiated at 365 nm until reaching the $\text{PSS}_{365\text{nm}}$ and immediately moved to a Jasco V-670 spectrometer for thermal back Z→E isomerization in the dark at 30 °C. Then, a first-order rate constant $-k$ for the thermal back Z→E isomerization reaction was obtained using equation 2.

$$\ln\left(\frac{A_t}{A_0}\right) = \ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = -kt \quad (2)$$

Where A_∞ is the absorbance at λ_{max} before irradiation (e.g. >>99 % trans-Isomer); A_0 is the absorbance at λ_{max} at $\text{PSS}_{365\text{nm}}$ and A_t is the absorbance at λ_{max} at a certain time.

The linearized data is shown in black, the fit is shown in red.

From $-k$ the half-life $\tau_{1/2}$ can be calculated as shown in equation 3.

$$\tau_{1/2} = \frac{\ln(2)}{k} \quad (3)$$

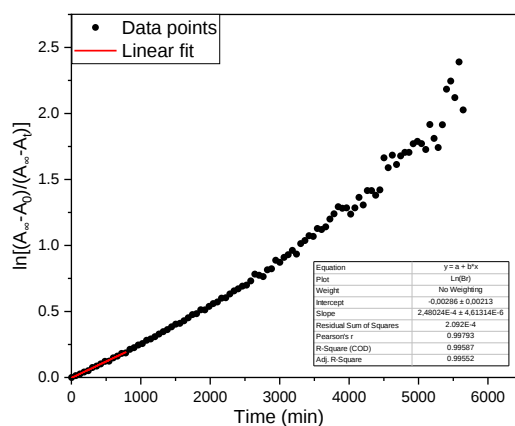


Figure S101: Thermal Z-E isomerization of **NAc-PAP-Br** in CH_3CN at 30 °C.

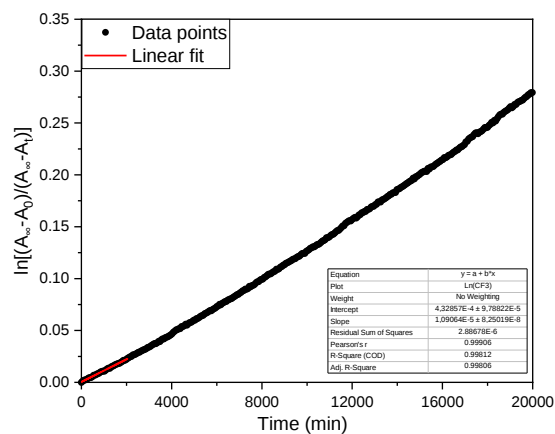


Figure S102: Thermal Z-E isomerization of **NAc-PAP-CF₃** in CH₃CN at 30 °C.

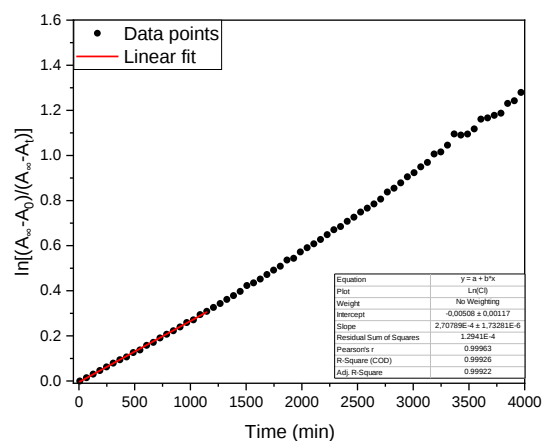


Figure S103: Thermal Z-E isomerization of **NAc-PAP-Cl** in CH₃CN at 30 °C.

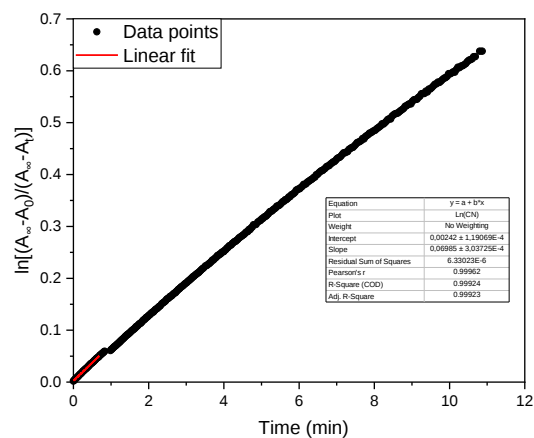


Figure S104: Thermal Z-E isomerization of **NAc-PAP-CN** in CH₃CN at 30 °C.

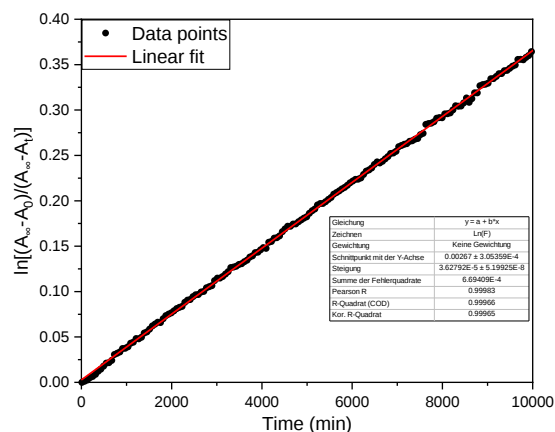


Figure S105: Thermal Z-E isomerization of **NAc-PAP-F** in CH₃CN at 30 °C.

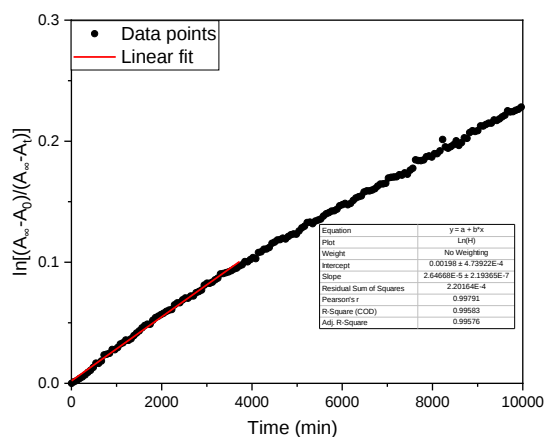


Figure S106: Thermal Z-E isomerization of **NAc-PAP-H** in CH₃CN at 30 °C.

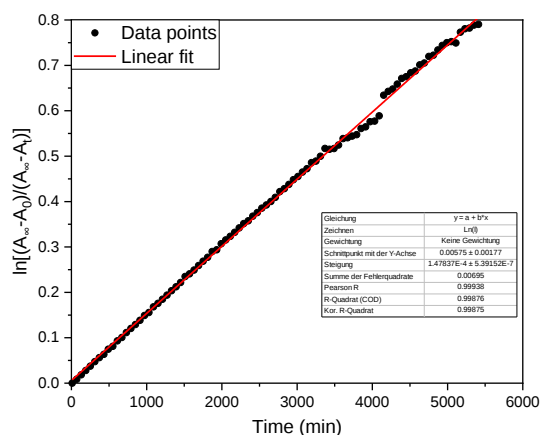


Figure S107: Thermal Z-E isomerization of **NAc-PAP-I** in CH₃CN at 30 °C.

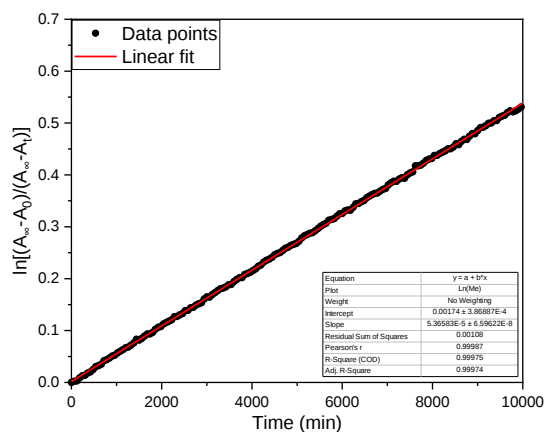


Figure S108: Thermal Z-E isomerization of **NAc-PAP-Me** in CH_3CN at 30 °C.

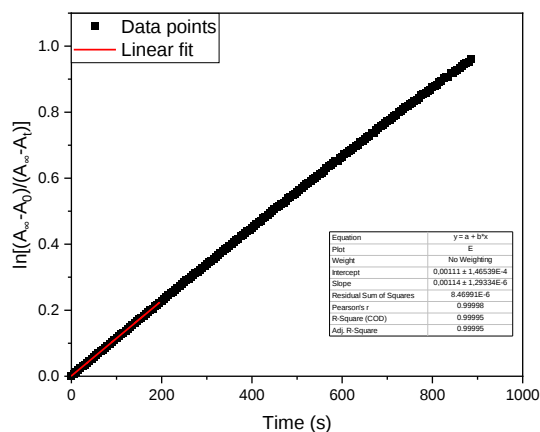


Figure S109: Thermal Z-E isomerization of **NAc-PAP-NO₂** in CH_3CN at 30 °C.

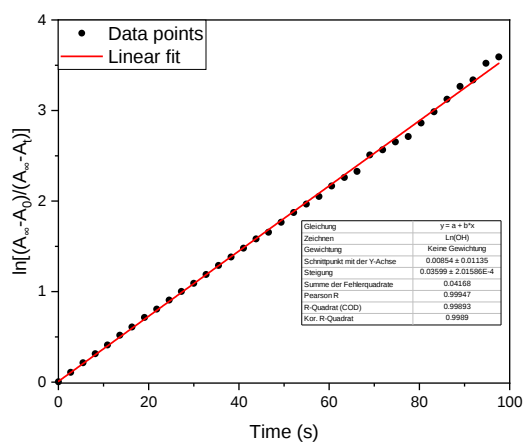


Figure S110: Thermal Z-E isomerization of **NAc-PAP-OH** in CH_3CN at 30 °C.

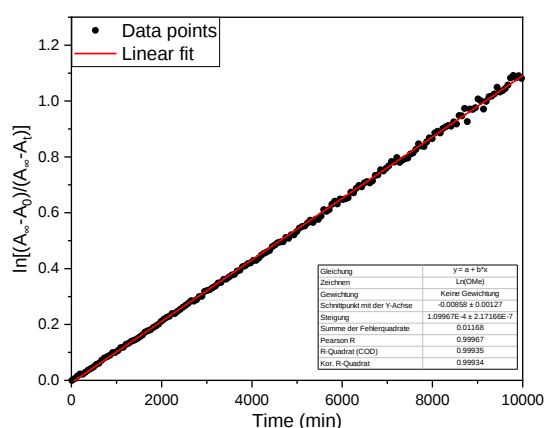


Figure S111: Thermal Z-E isomerization of **NAc-PAP-OMe** in CH₃CN at 30 °C.

3.7 Hammett correlation of thermal half-lives of NAc-PAP derivatives

The correlation of thermal relaxation with the R-substituent parameters resulted in the Hammett plot, depicted in Figure S112. We found the best correlation using the Hammett substitution constant σ resulting in two linear fits (OH was treated as exception due to the possible presence of a tautomerism mechanism).

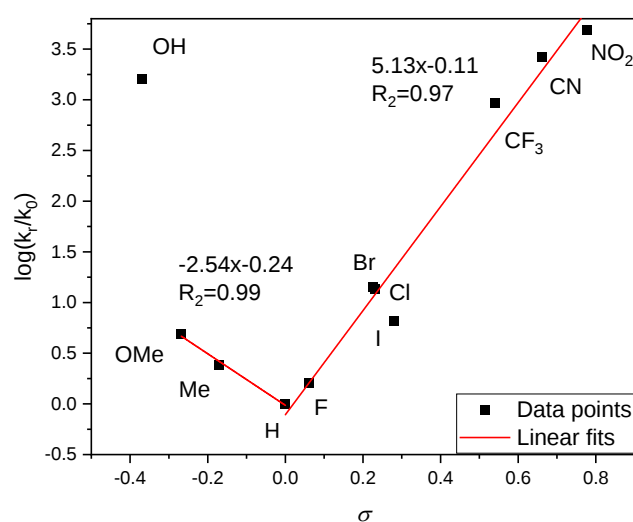


Figure S112: Hammett plot of thermal relaxation for **NAc-PAP** derivatives.

To get a deeper insight into the nature of those, two representative compounds were chosen (**NAc-PAP-CN** and **NAc-PAP-OMe**) and their $Z \rightarrow E$ thermal relaxation was measured at different temperatures in toluene. Three measurements were conducted at every temperature and were then fitted to the linearized form of the Eyring equation:

$$\ln \frac{k}{T} = \frac{-\Delta H^\ddagger}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (4)$$

where $\Delta H^\ddagger$ is activation enthalpy, $\Delta S^\ddagger$ is activation entropy, R is the universal gas constant, T is the temperature, k the kinetic constant, h is the Planck constant, and k_B is the Boltzmann constant. By numerically fitting the data using the package *lift* as implemented in Python3, it is possible to obtain the standard errors on the slope and intercept and directly the standard errors on $\Delta H^\ddagger$ ($\sigma_{\Delta H}$) and $\Delta S^\ddagger$ ($\sigma_{\Delta S}$) by multiplying these values with R . Using the covariance matrix obtained from the fit, it is possible to numerically obtain the correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ ($\rho_{\Delta H \Delta S}$) which resulted to be close to 1 for both CN- (0.9979) and MeO- (0.9995) derivatives. This correlation can be used to obtain the error on the Gibbs free energy of activation, $\Delta G^\ddagger$, by exploiting the formula

$$\sigma_{\Delta G} = \sqrt{\sigma_{\Delta H}^2 + T^2 + \sigma_{\Delta S}^2 - 2T\rho_{\Delta H \Delta S}\sigma_{\Delta H}\sigma_{\Delta S}} \quad (5)$$

associated with the canonical form of the Eyring equation

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6)$$

Table S2 provides an overview of the measured rates and the resulting thermodynamic parameters and Table S3 of the results of the Eyring analysis of the data set.

Table S2: Thermal relaxation rates (recorded in min^{-1}) of **NAc-PAP-CN** and **NAc-PAP-OMe** in toluene at different temperatures.

Temperatures / °C	CN			OMe		
20	0.0008	0.0008	0.0008	0.0001	0.0001	0.0001
35	0.0057	0.0054	0.0056	0.0008	0.0007	0.0008
50	0.0251	0.0240	0.0266	0.0040	0.0037	0.0040
65	0.1248	0.1312	0.1280	0.0188	0.0190	0.0179
80	0.5870	0.5390	0.5330	0.0677	0.0705	0.0715

Table S3: Eyring analysis of the measurements in Table S2.

	NAC-PAP-CN	NAC-PAP-OMe
$\Delta G^\ddagger$ / kJ/mol	99.1 ± 0.07^a	104.3 ± 0.1^a
$\Delta H^\ddagger$ / kJ/mol	90.0 ± 0.7	93.0 ± 1.0
$\Delta S^\ddagger$ / J/(mol K)	-30.0 ± 2.0	-39.0 ± 4.0

3.7.1 Thermal relaxation of NAc-PAP-CN at different temperatures

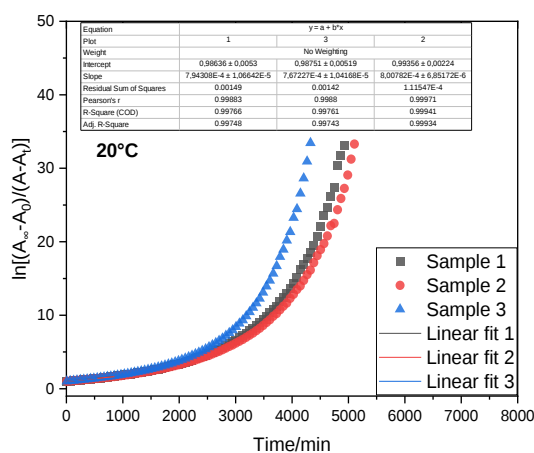


Figure S113: Thermal relaxation absorbance trace of the **NAc-PAP-CN** at 20 °C in toluene.

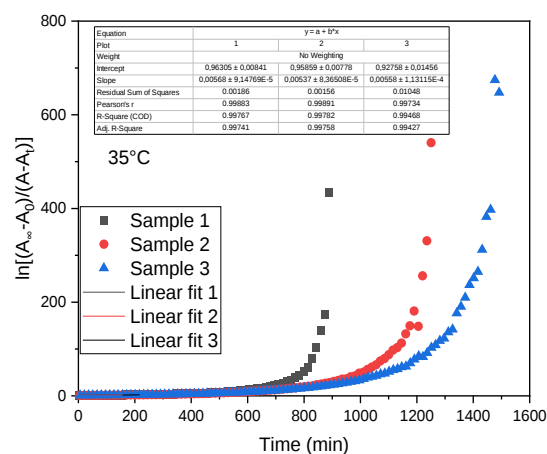


Figure S114: Thermal relaxation absorbance trace of the **NAc-PAP-CN** at 35 °C in toluene.

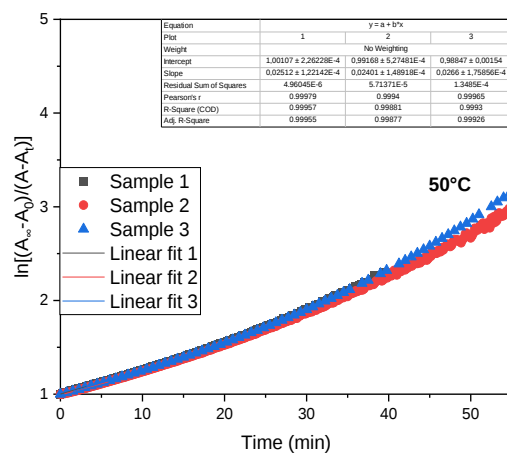


Figure S115: Thermal relaxation absorbance trace of the **NAc-PAP-CN** at 50 °C in toluene.

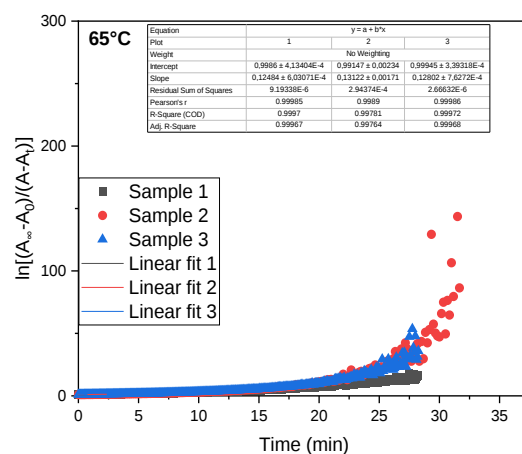


Figure S116: Thermal relaxation absorbance trace of the **NAc-PAP-CN** at 65 °C in toluene.

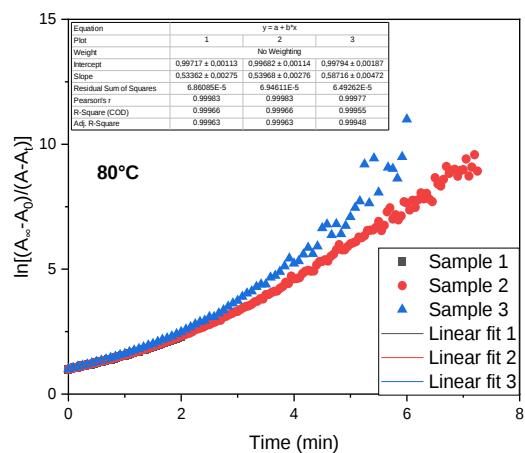


Figure S117: Thermal relaxation absorbance trace of the **NAc-PAP-CN** at 80 °C in toluene.

3.7.2 Thermal relaxation of NAc-PAP-OMe at different temperatures

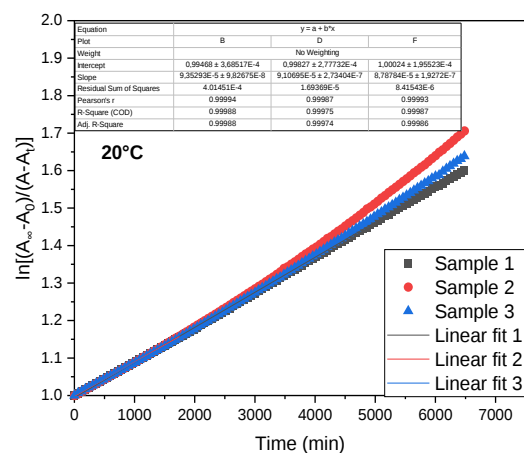


Figure S118: Thermal relaxation absorbance trace of the **NAc-PAP-OMe** at 20 °C in toluene.

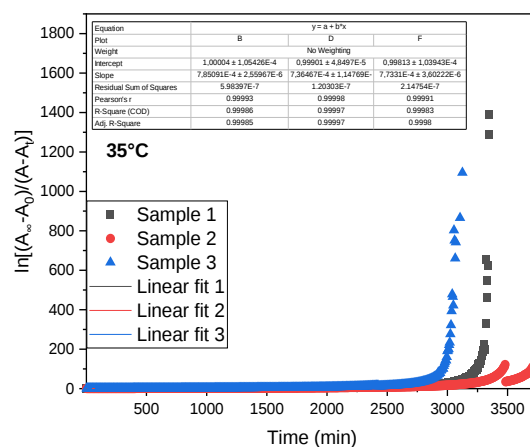


Figure S119: Thermal relaxation absorbance trace of the **NAc-PAP-OMe** at 35 °C in toluene.

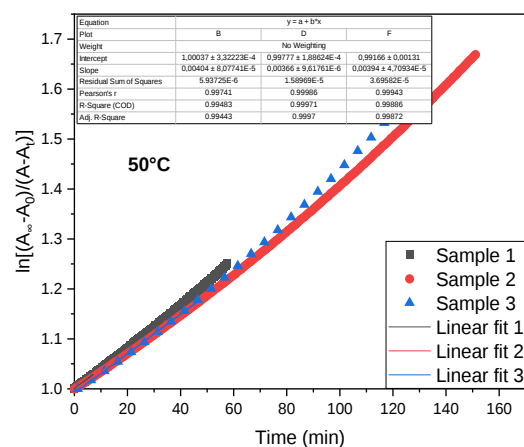


Figure S120: Thermal relaxation absorbance trace of the **NAc-PAP-OMe** at 50 °C in toluene.

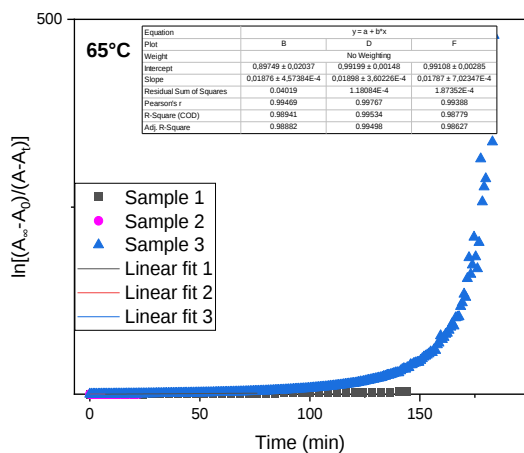


Figure S121: Thermal relaxation absorbance trace of the **NAc-PAP-OMe** at 65 °C in toluene.

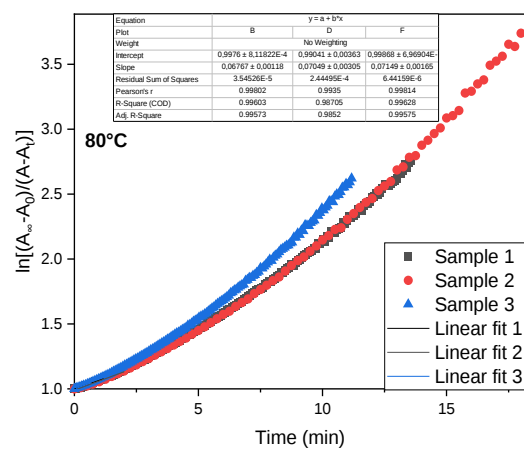


Figure S122: Thermal relaxation absorbance trace of the **NAc-PAP-OMe** at 80 °C in toluene.

4. NMR Spectra

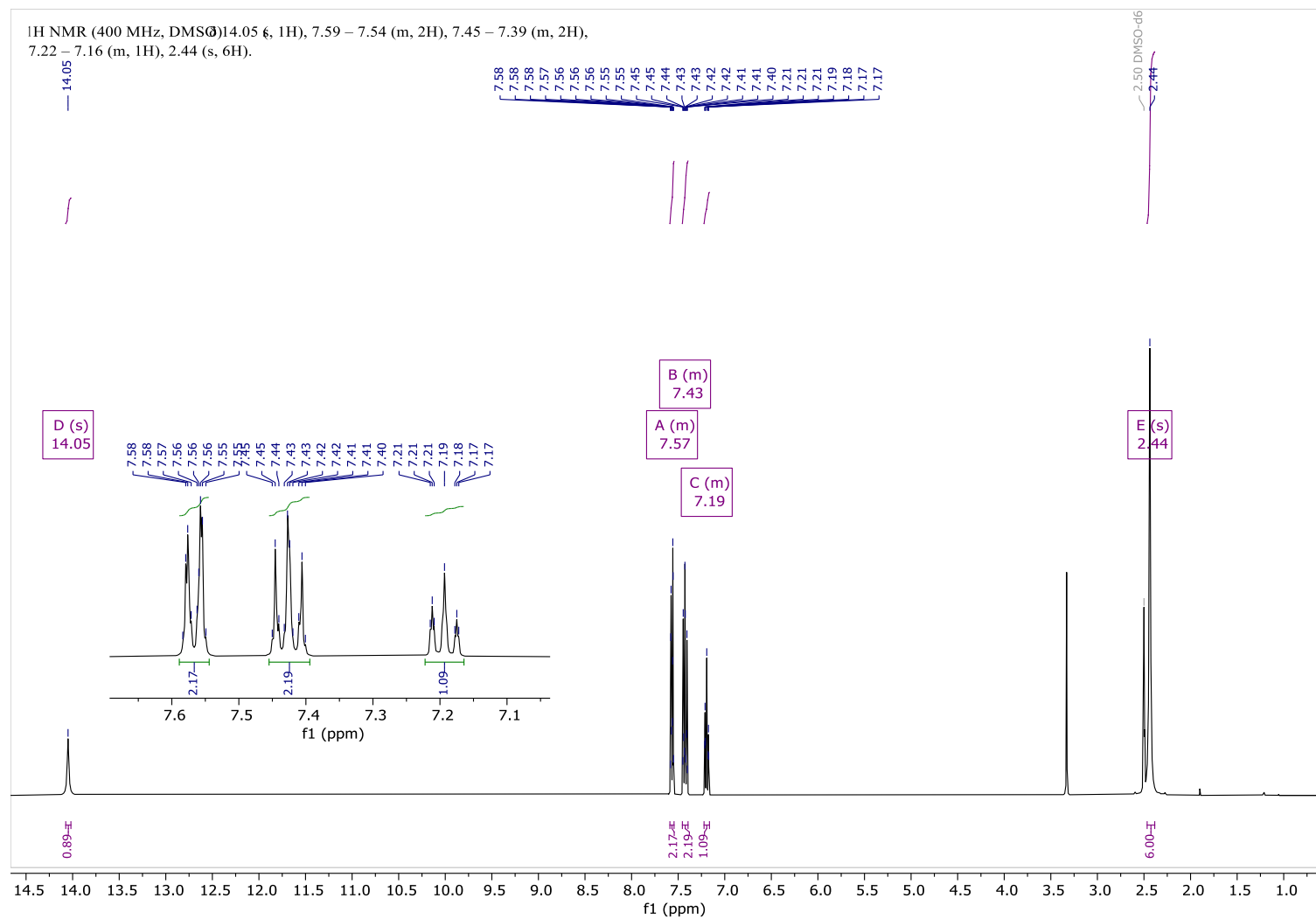


Figure S123: ¹H NMR spectrum of 3-(2-phenylhydrazono)pentane-2,4-dione in DMSO-d₆.

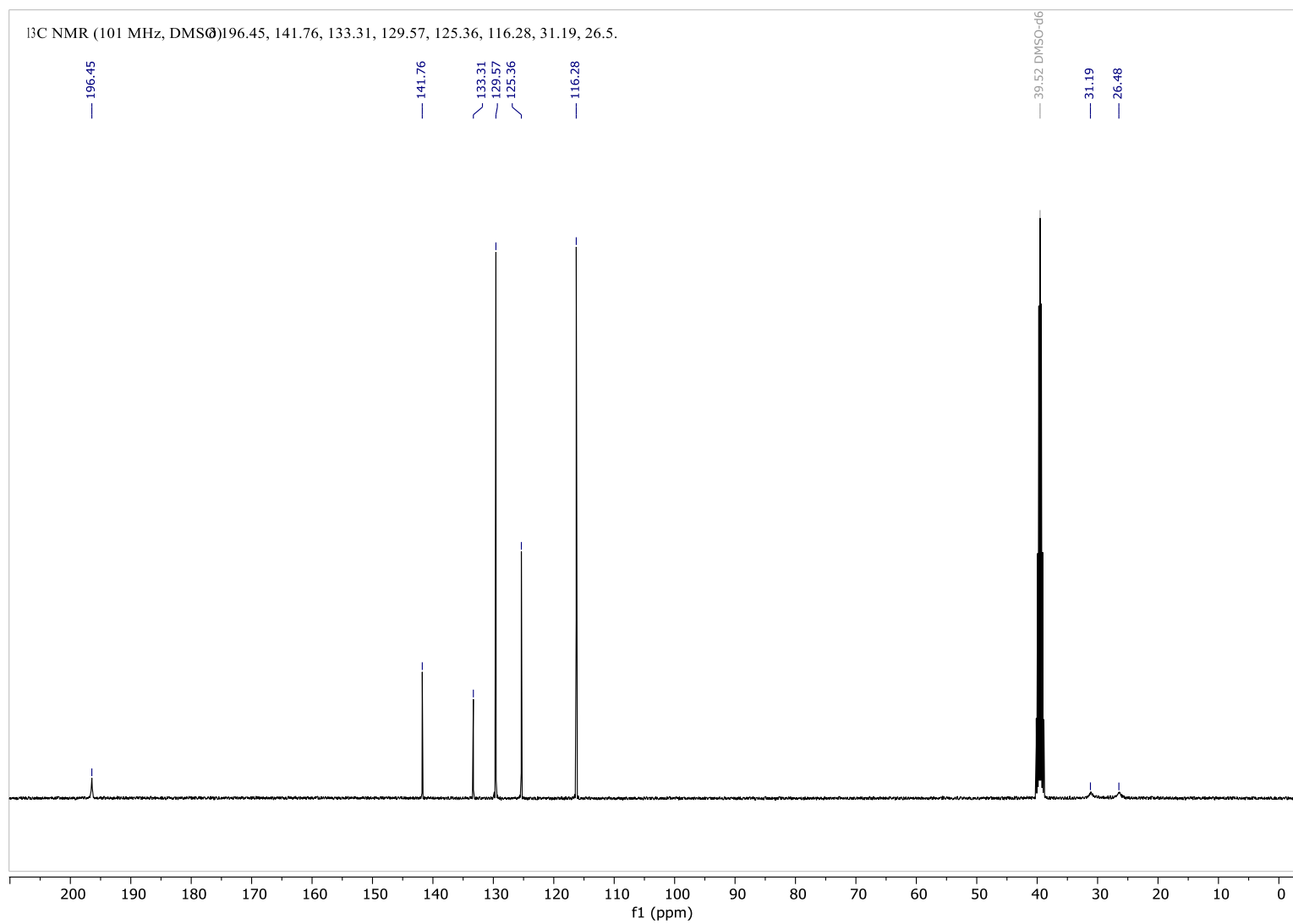


Figure S124: ¹³C NMR spectrum of 3-(2-phenylhydrazono)pentane-2,4-dione in DMSO-*d*₆.

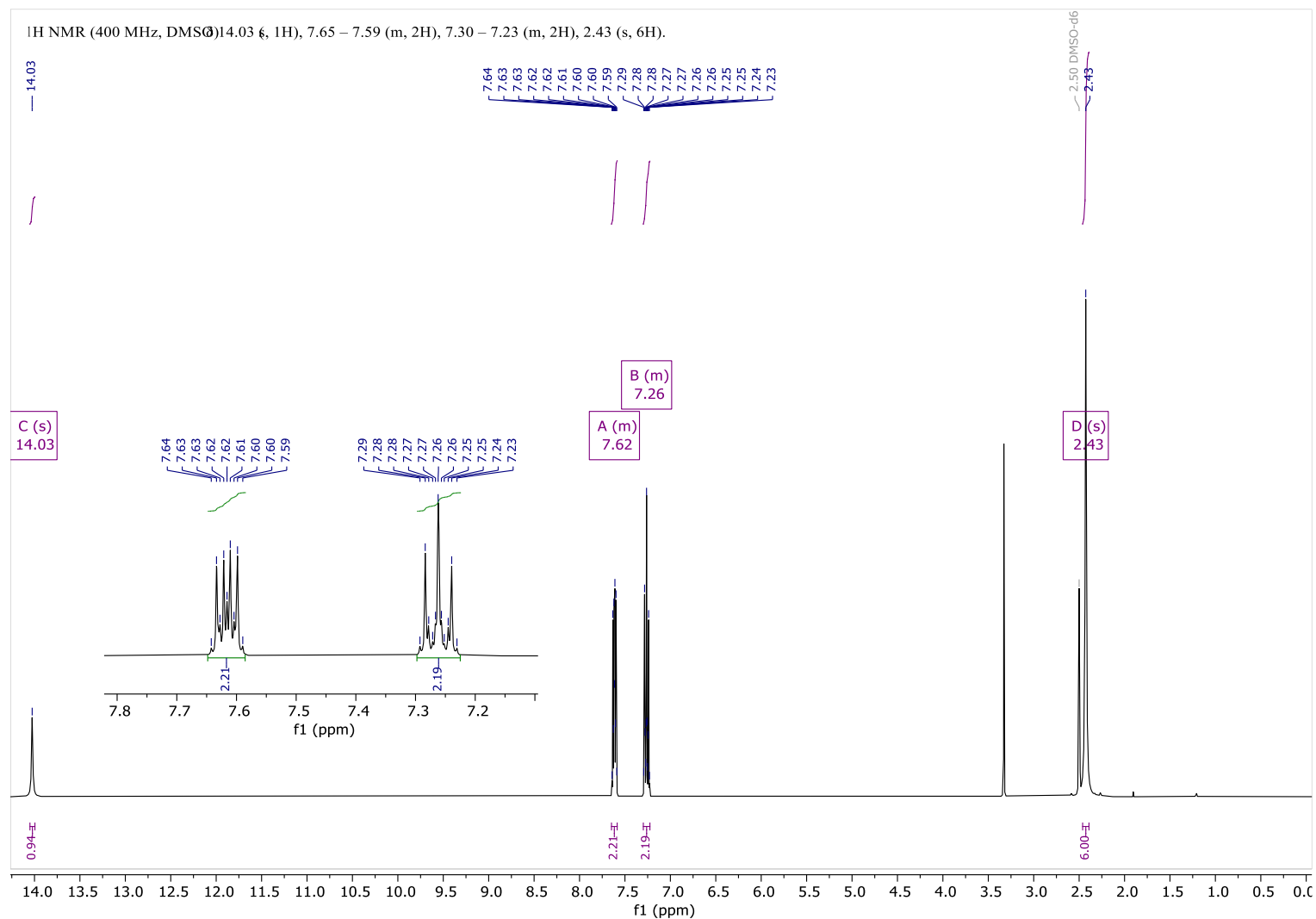


Figure S125: ¹H NMR spectrum of 3-(2-(4-fluorophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

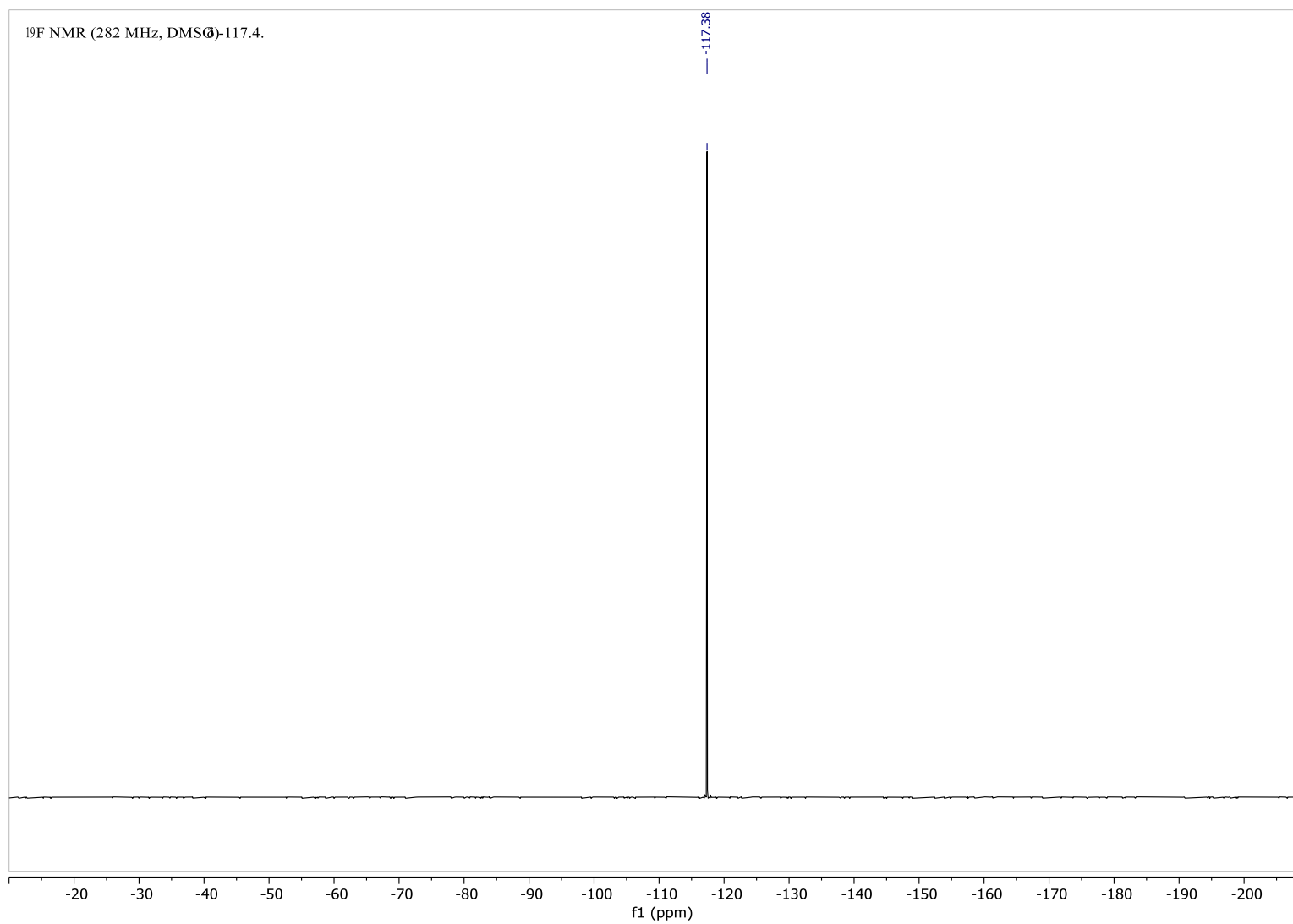


Figure S126: ¹⁹F NMR spectrum of 3-(2-(4-fluorophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

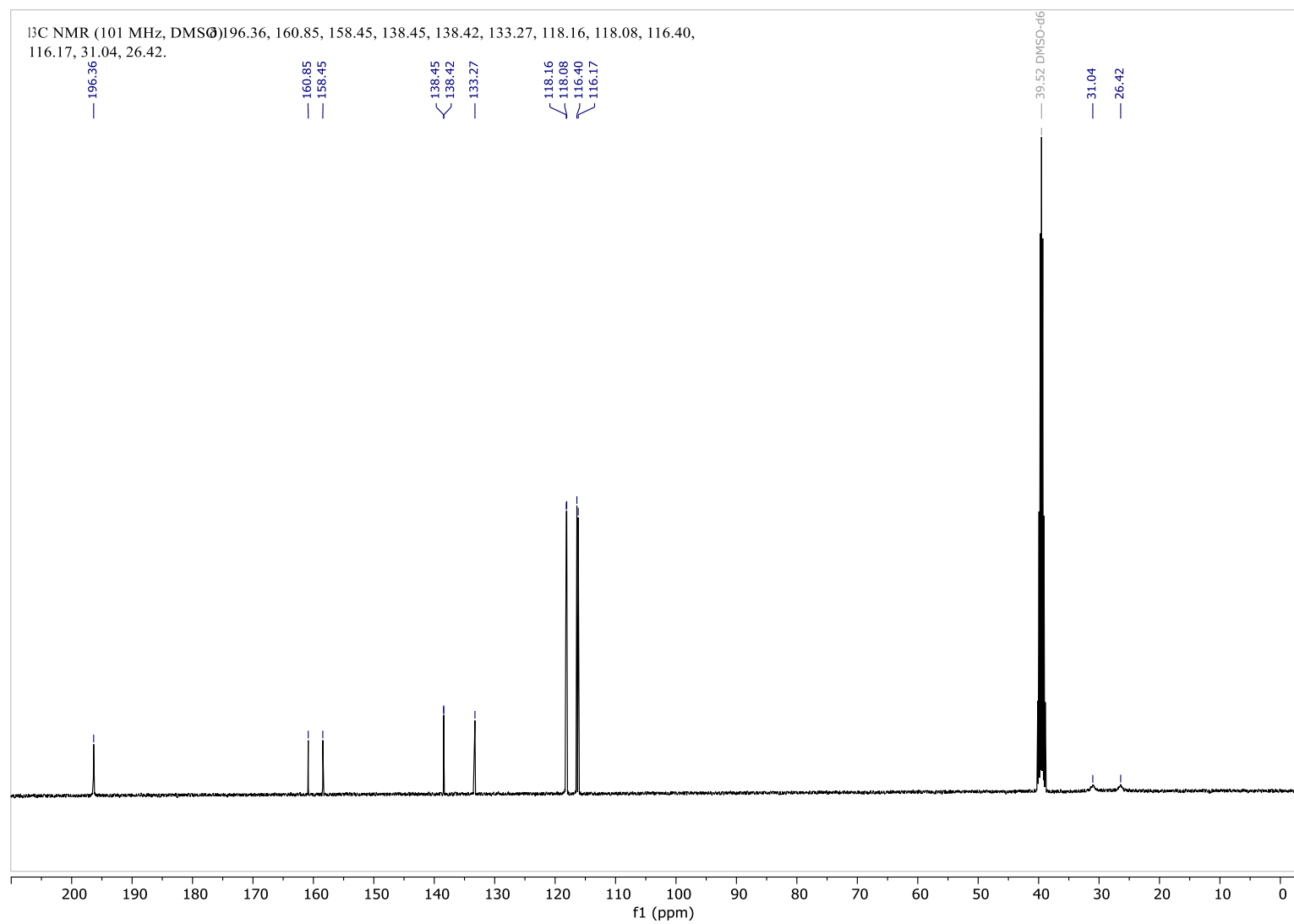


Figure S127: ¹³C NMR spectrum of 3-(2-(4-fluorophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

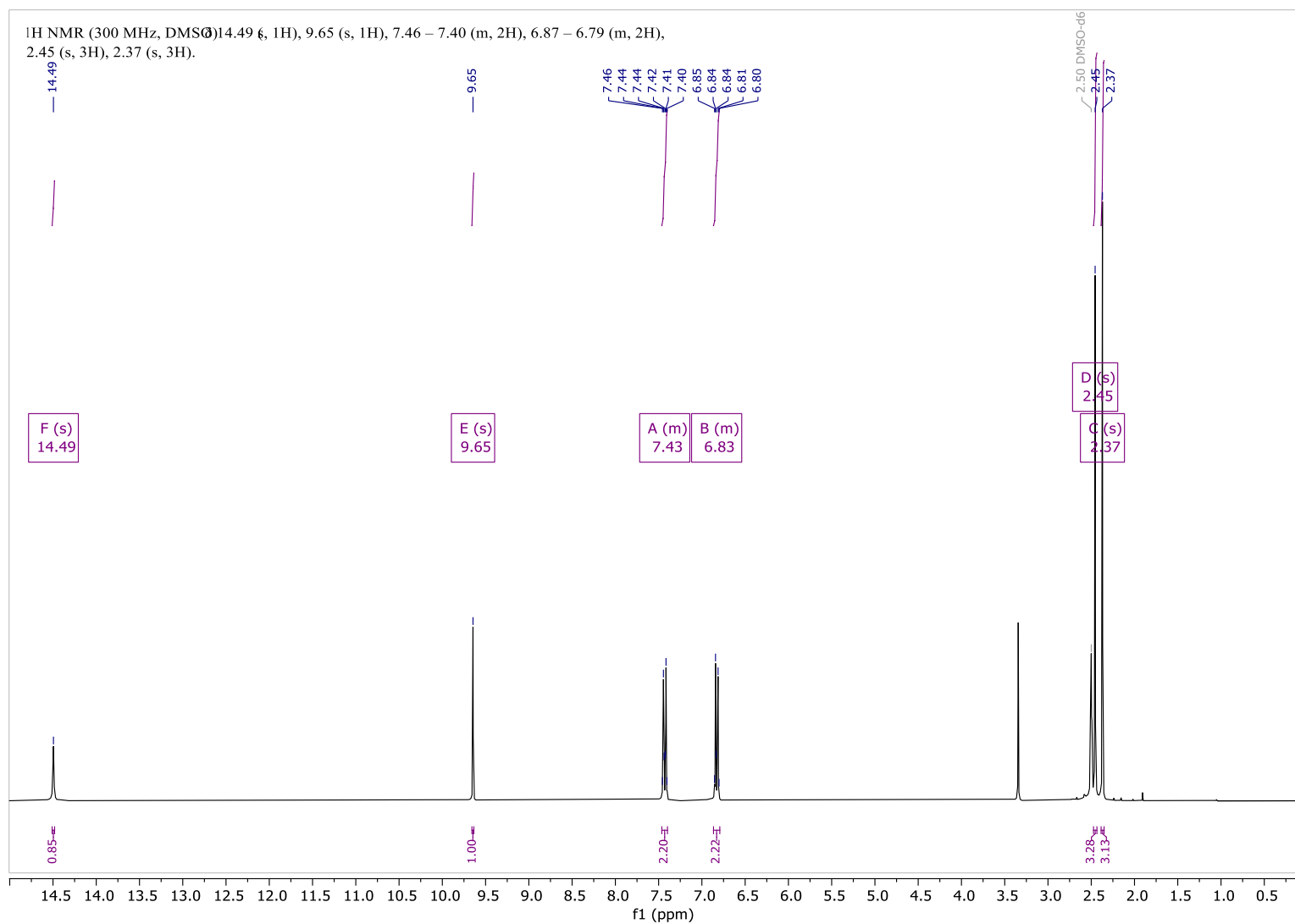


Figure S128: ¹H NMR spectrum of 3-(2-(4-hydroxyphenyl)hydrazono)pentane-2,4-dione in DMSO-d₆.

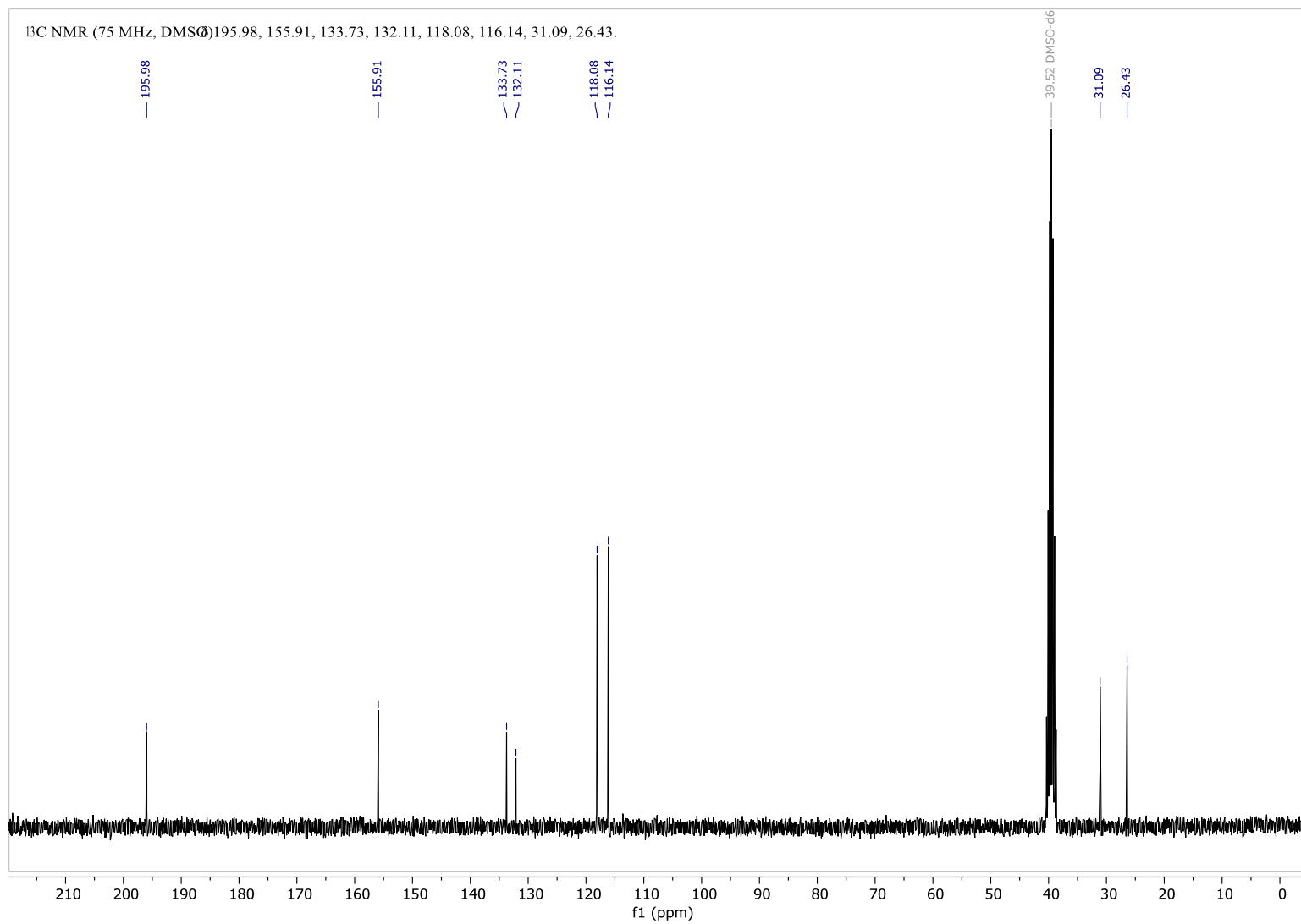


Figure S129: ¹³C NMR spectrum of 3-(2-(4-hydroxyphenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

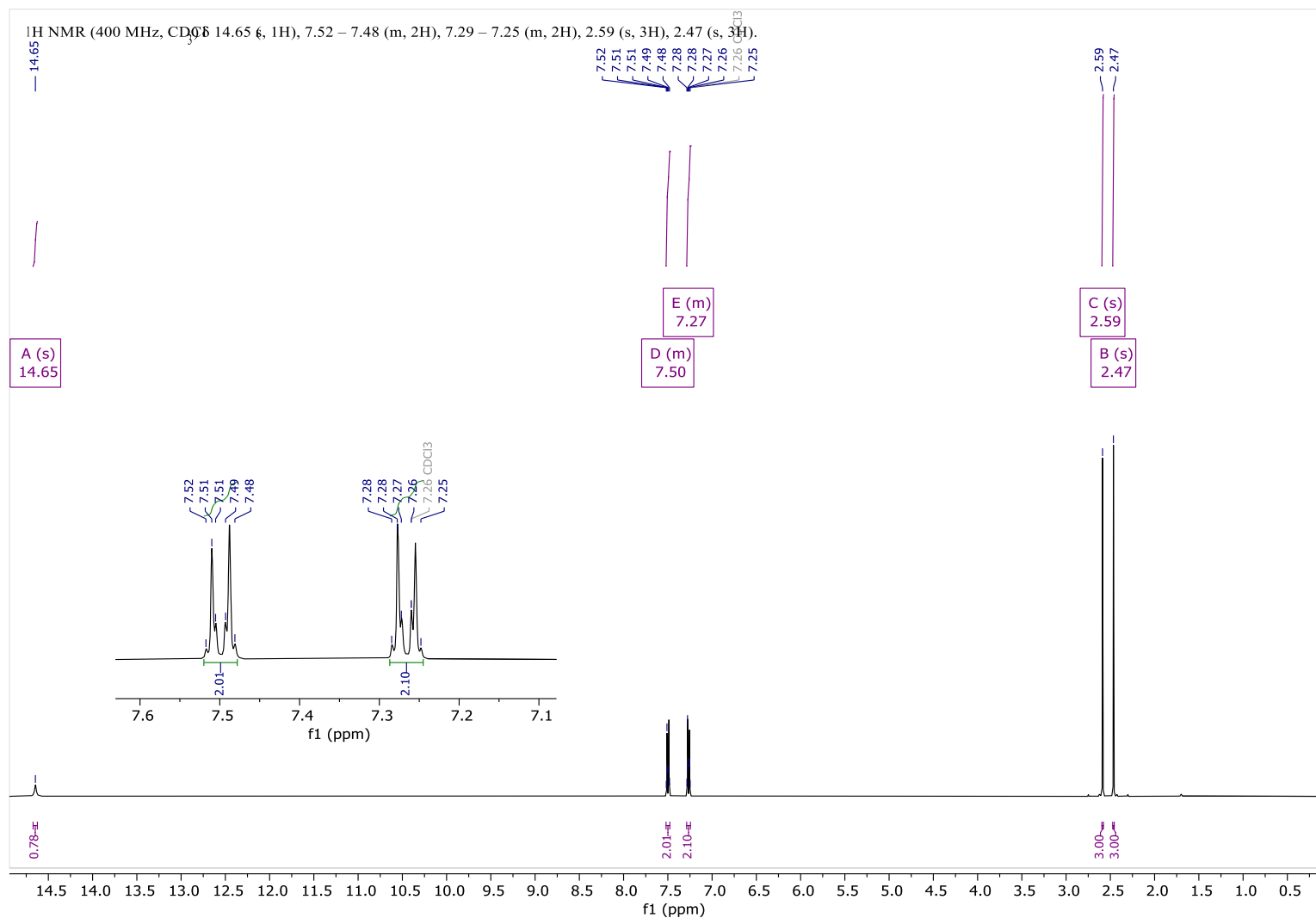


Figure S130: ¹H NMR spectrum of 3-(2-(4-bromophenyl)hydrazono)pentane-2,4-dione in CDCl₃.

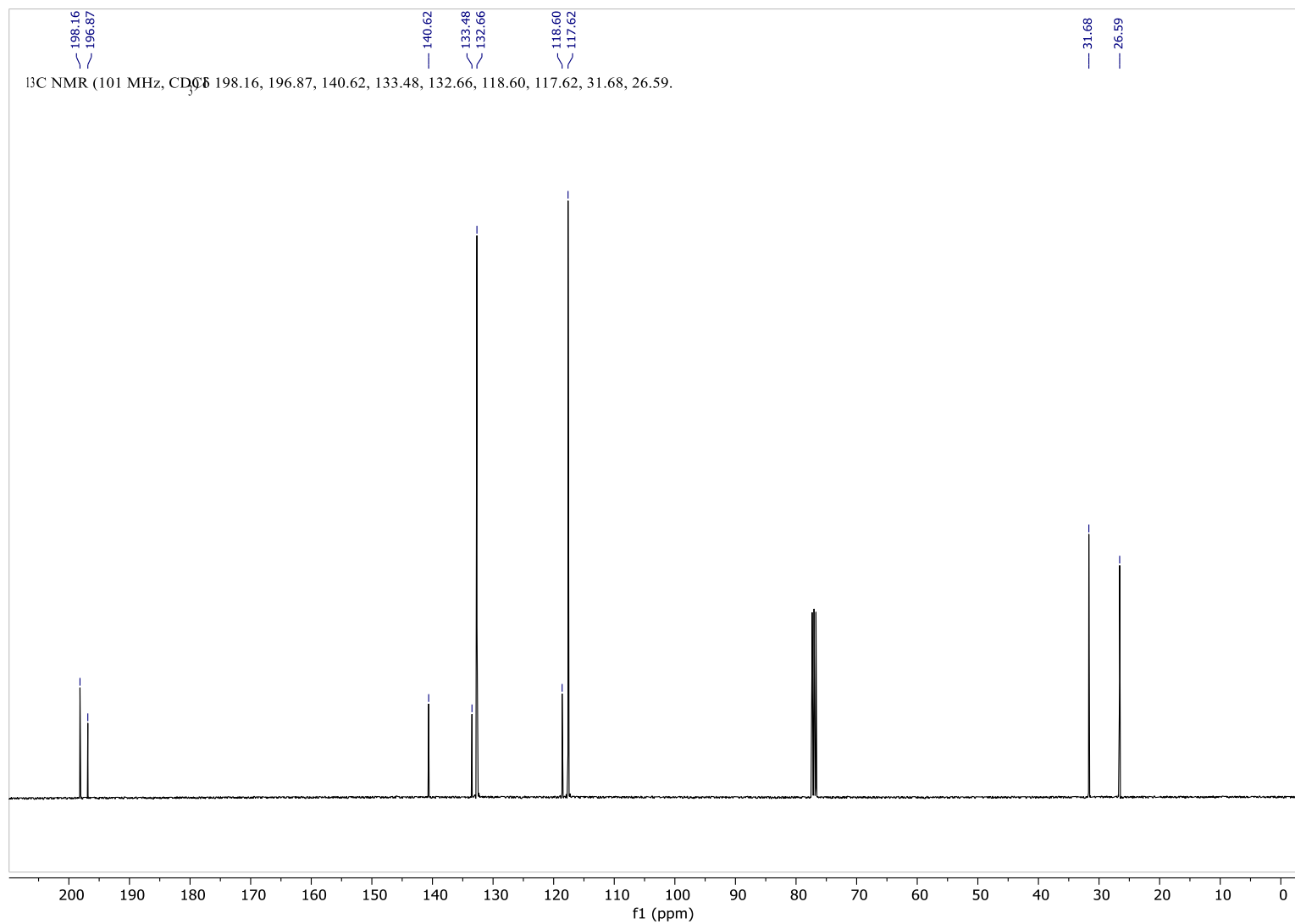


Figure S131: ¹³C NMR spectrum of 3-(2-(4-bromophenyl)hydrazono)pentane-2,4-dione in CDCl₃.

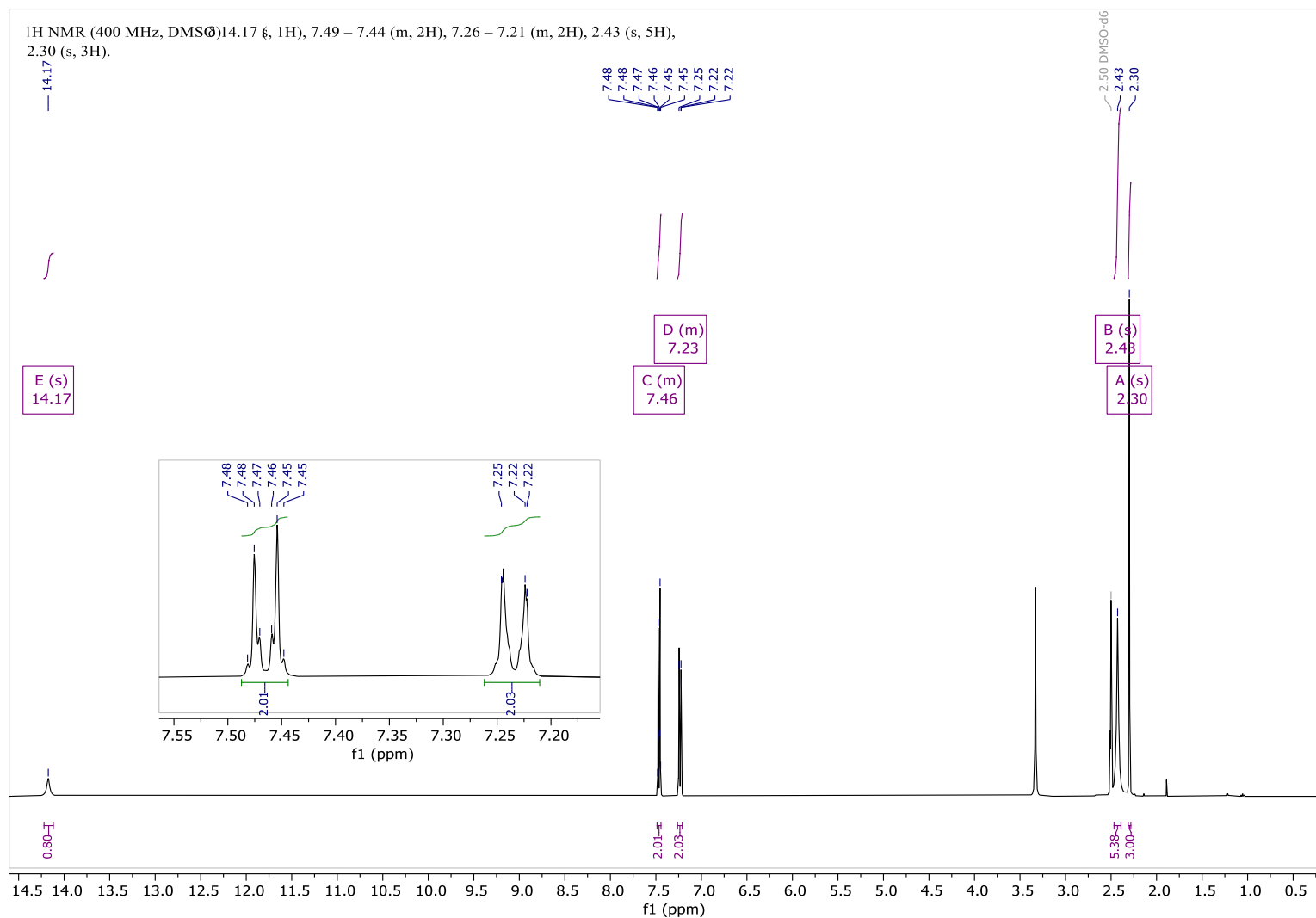


Figure S132: ¹H NMR spectrum of 3-(2-(*p*-tolyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

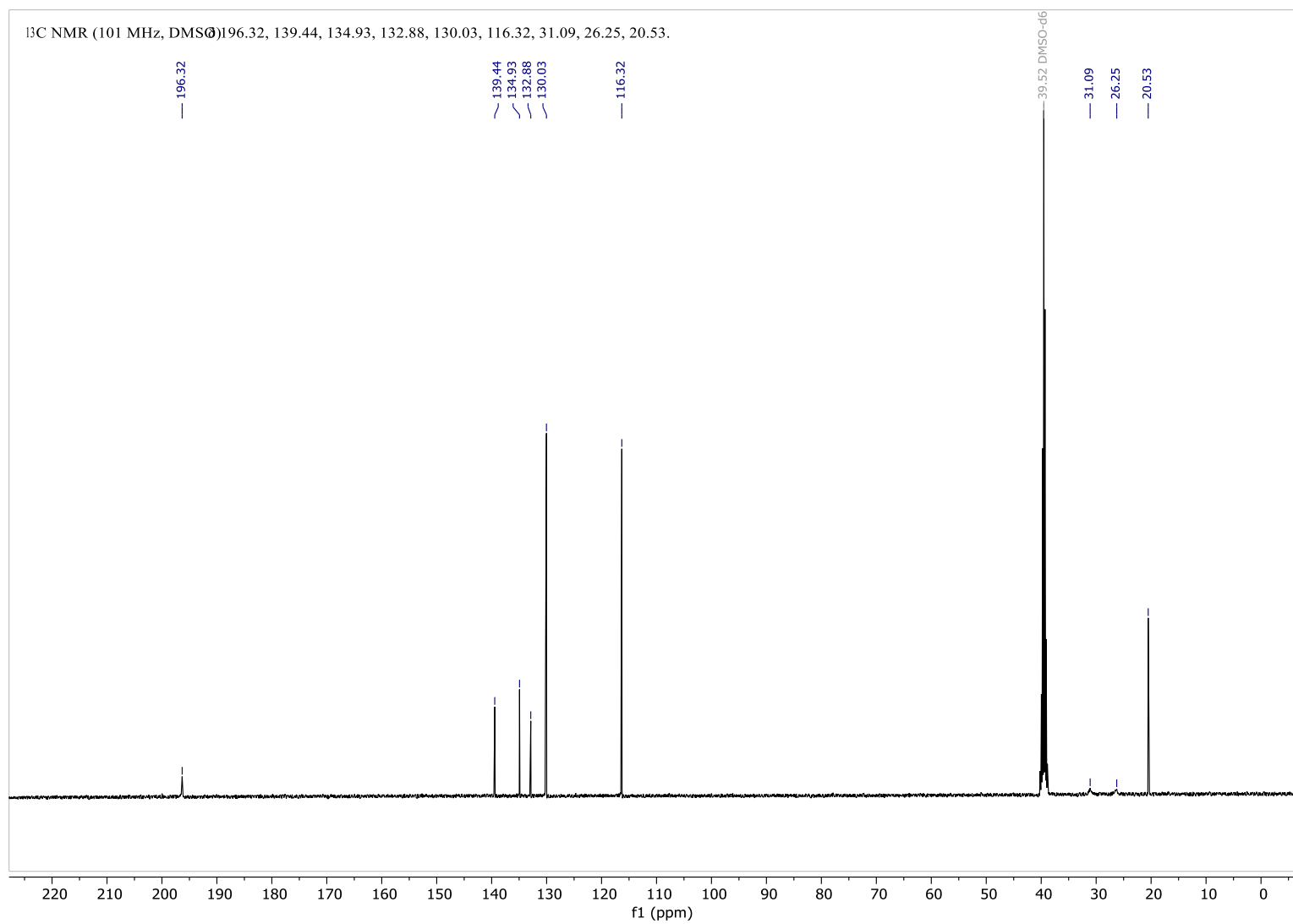


Figure S133: ¹³C NMR spectrum of 3-(2-(*p*-tolyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

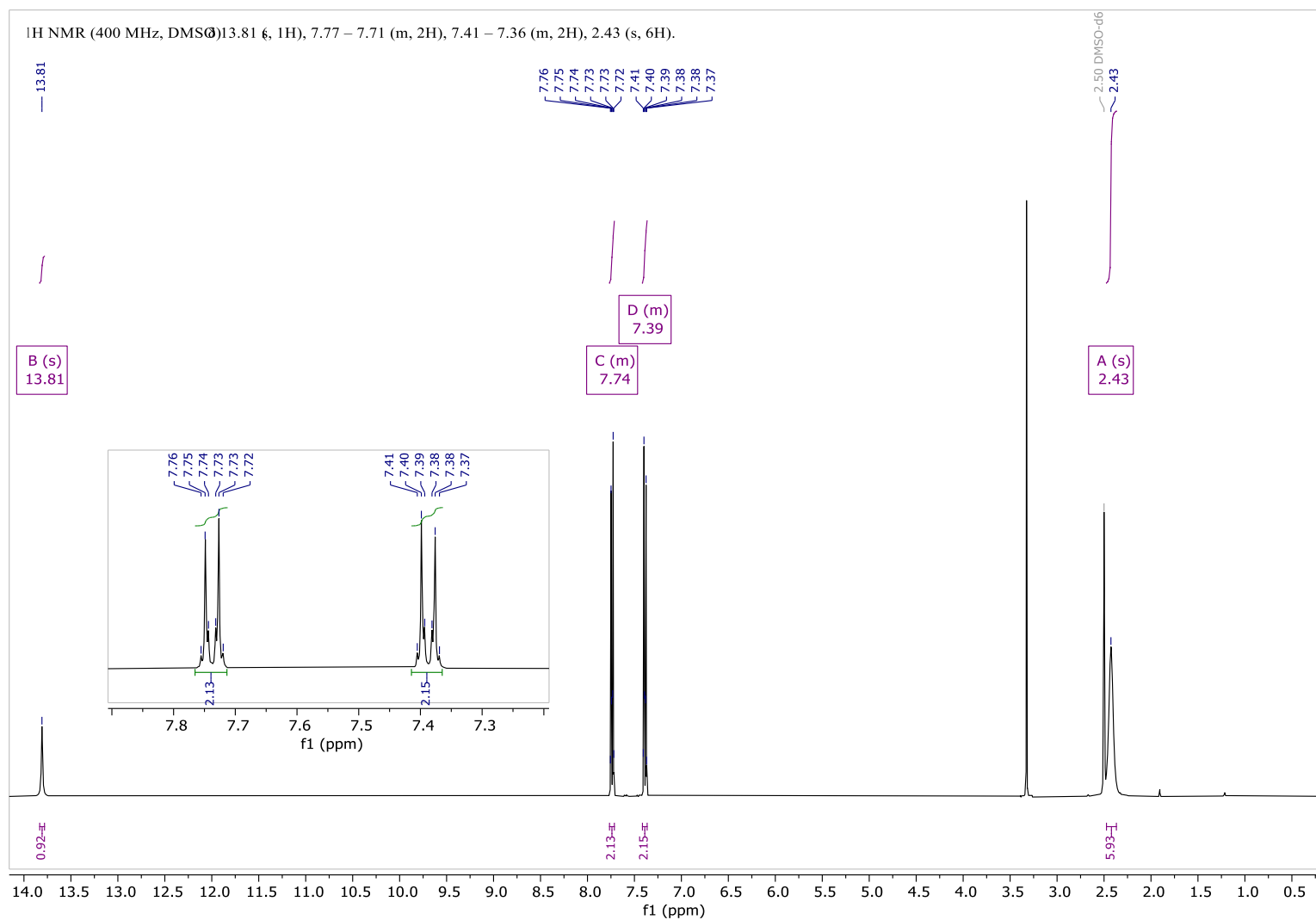


Figure S134: ¹H NMR spectrum of 3-(2-(4-iodophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

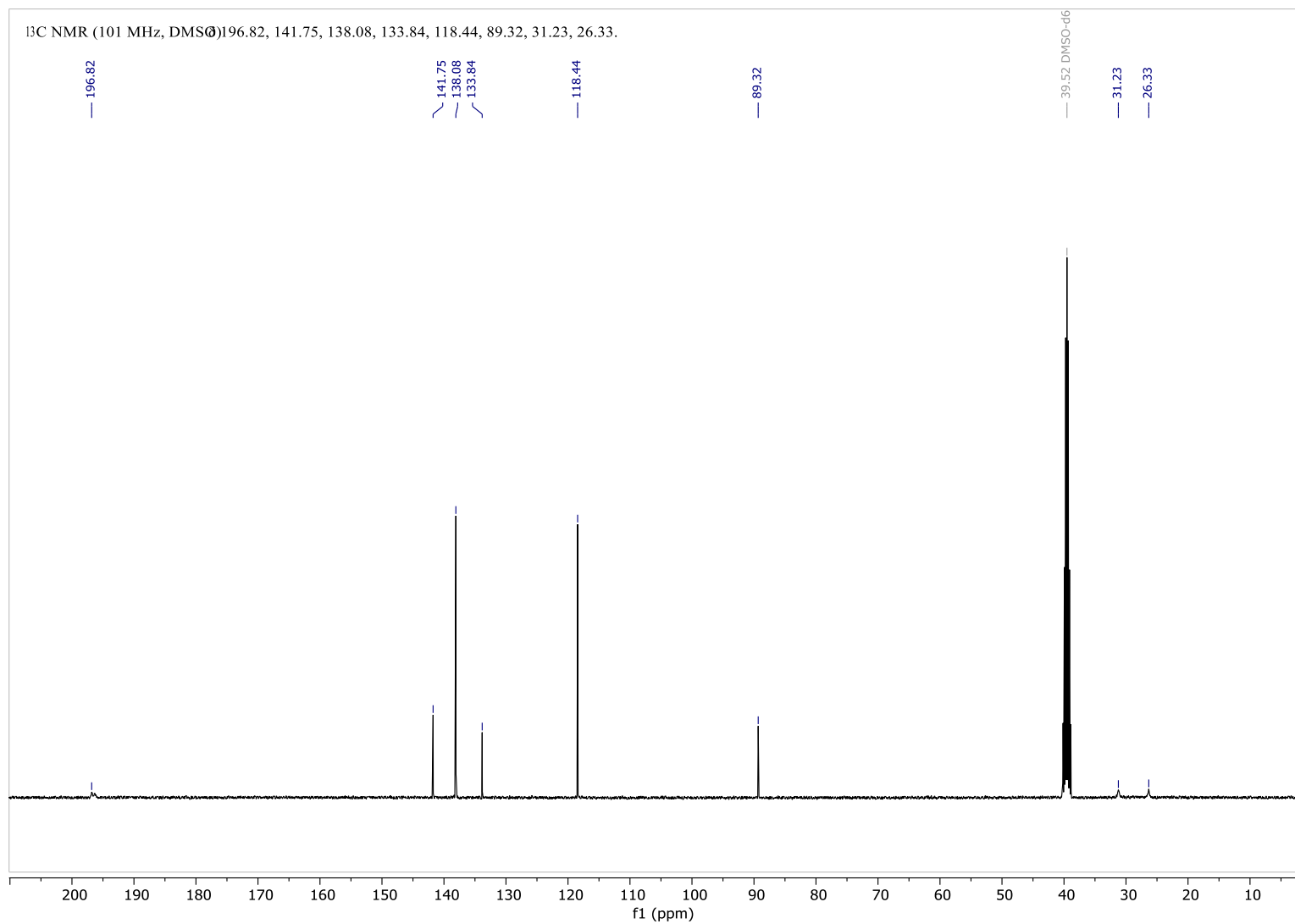


Figure S135: ¹³C NMR spectrum of 3-(2-(4-iodophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

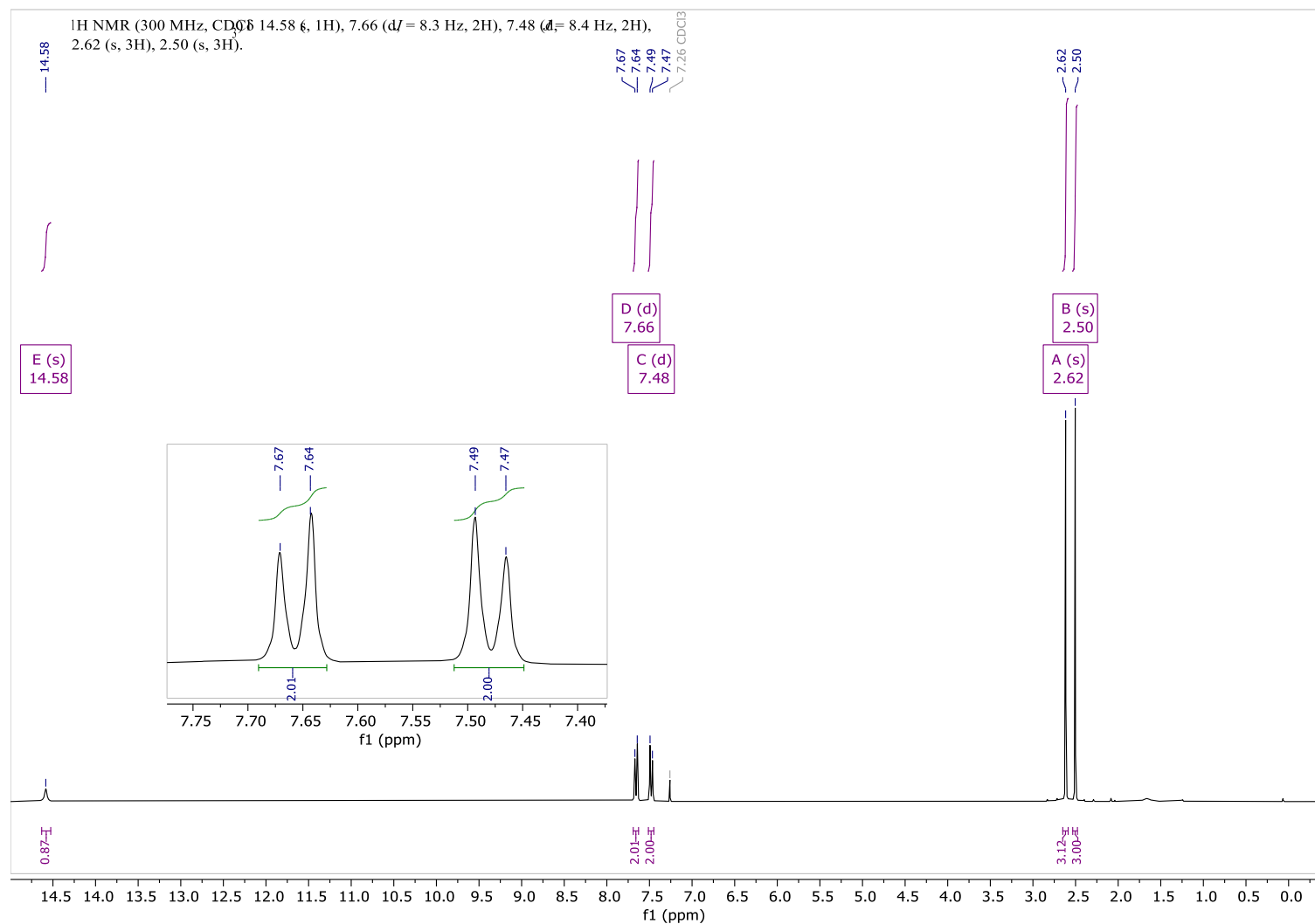


Figure S136: ¹H NMR spectrum of 3-(2-(4-(trifluoromethyl)phenyl)hydrazono)pentane-2,4-dione in CDCl₃.

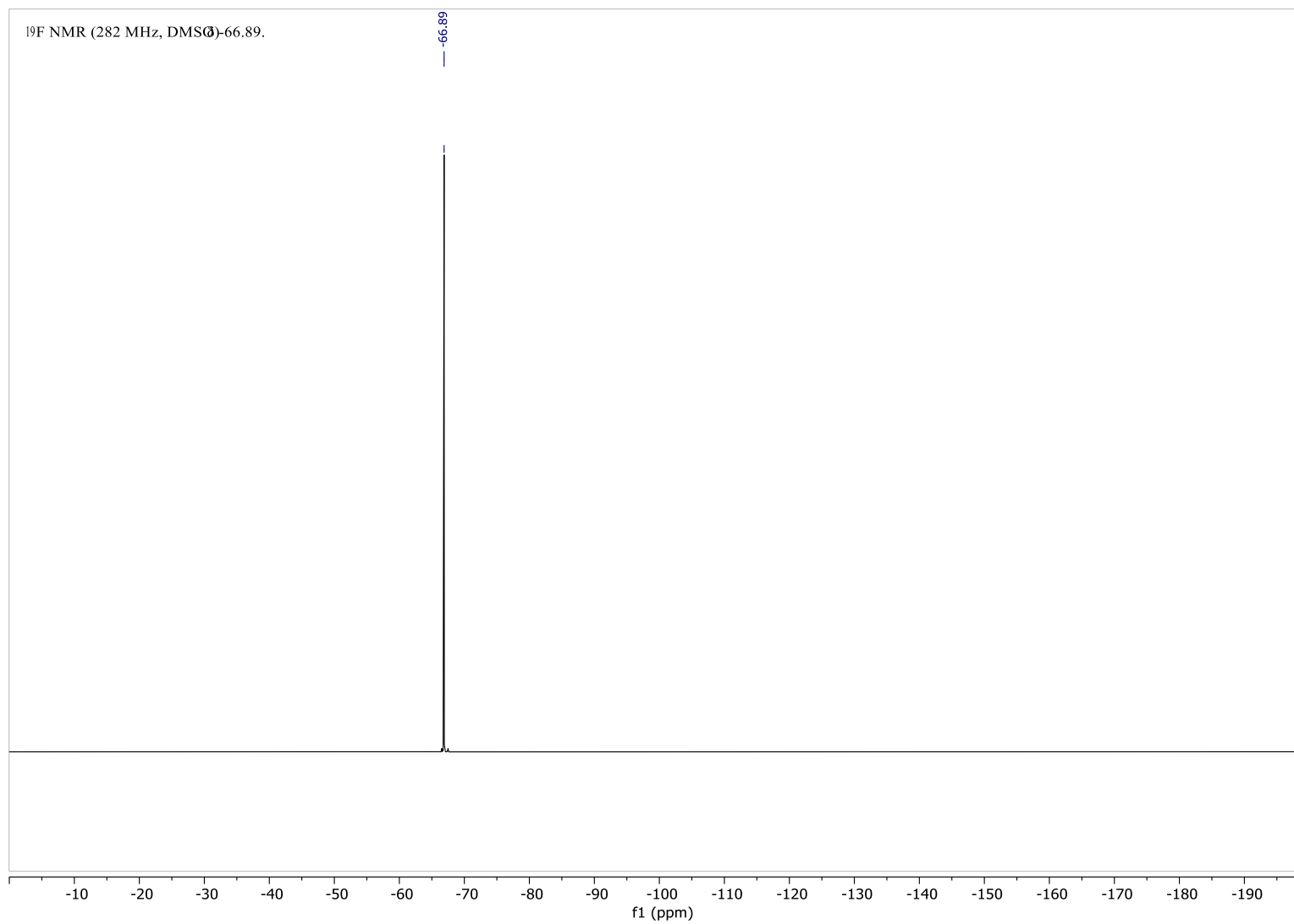


Figure S137: ¹⁹F NMR spectrum of 3-(2-(4-(trifluoromethyl)phenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

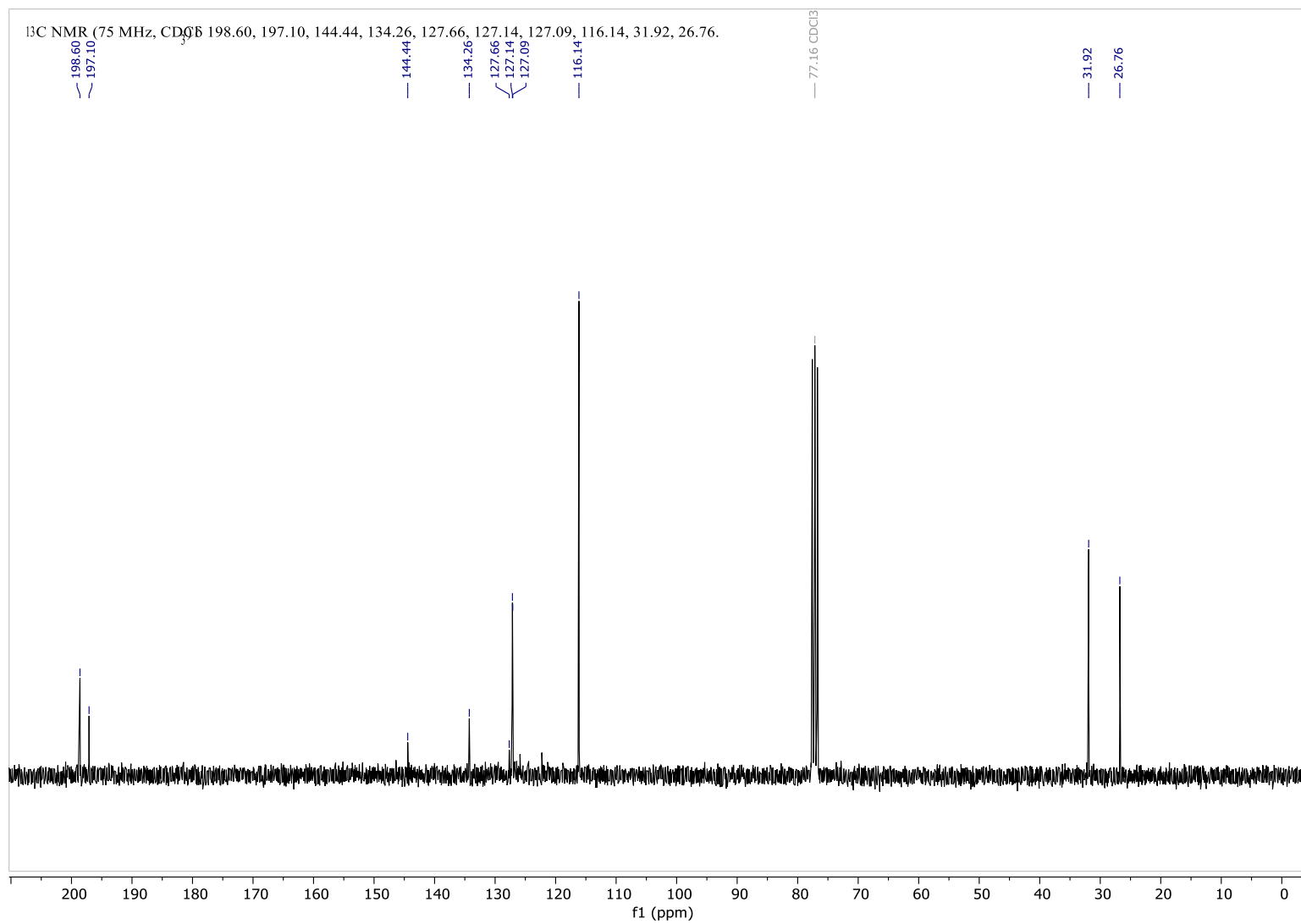


Figure S138: ¹³C NMR spectrum of 3-(2-(4-(trifluoromethyl)phenyl)hydrazono)pentane-2,4-dione in CDCl₃.

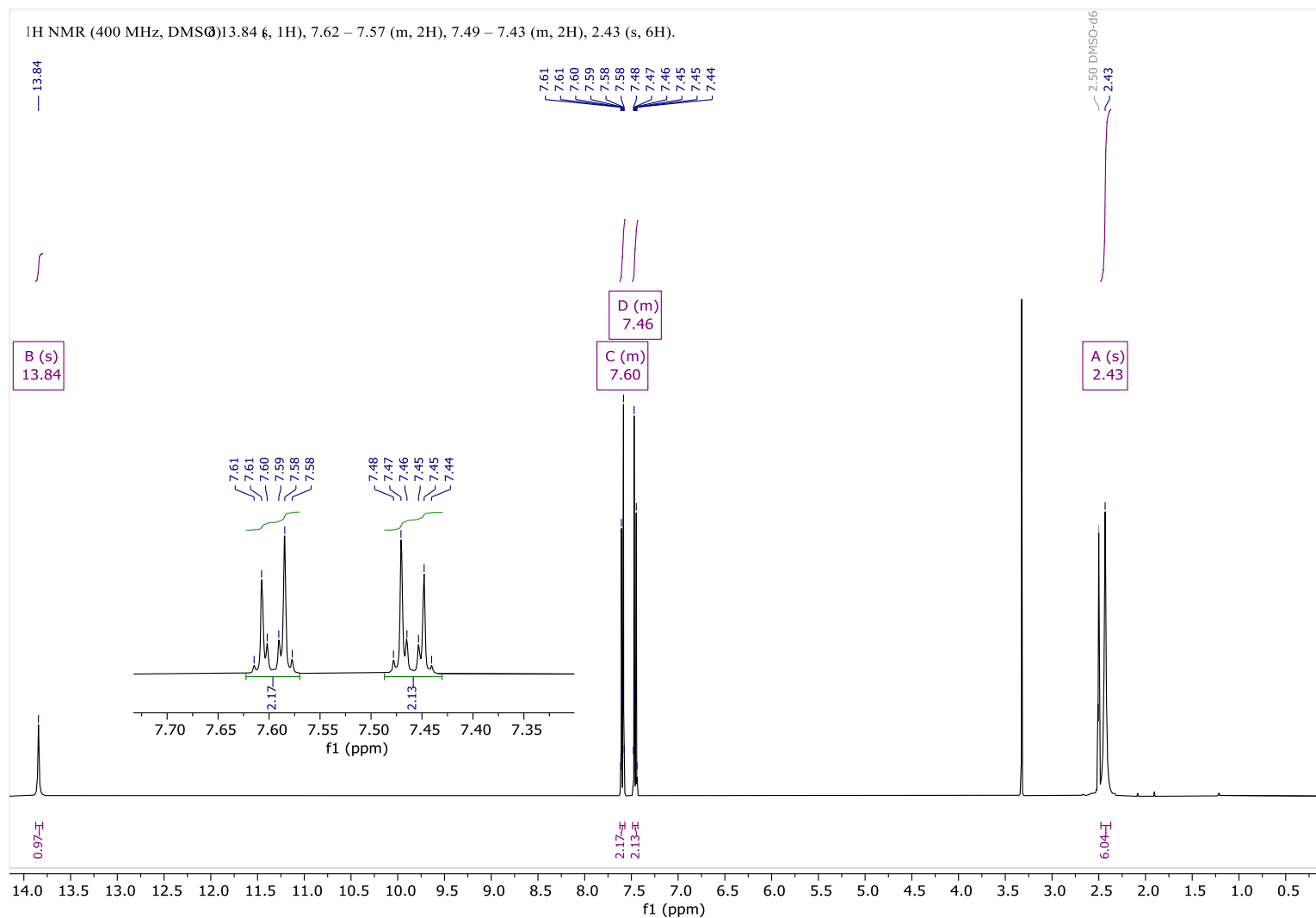


Figure S139: ¹H NMR spectrum of 3-(2-(4-chlorophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

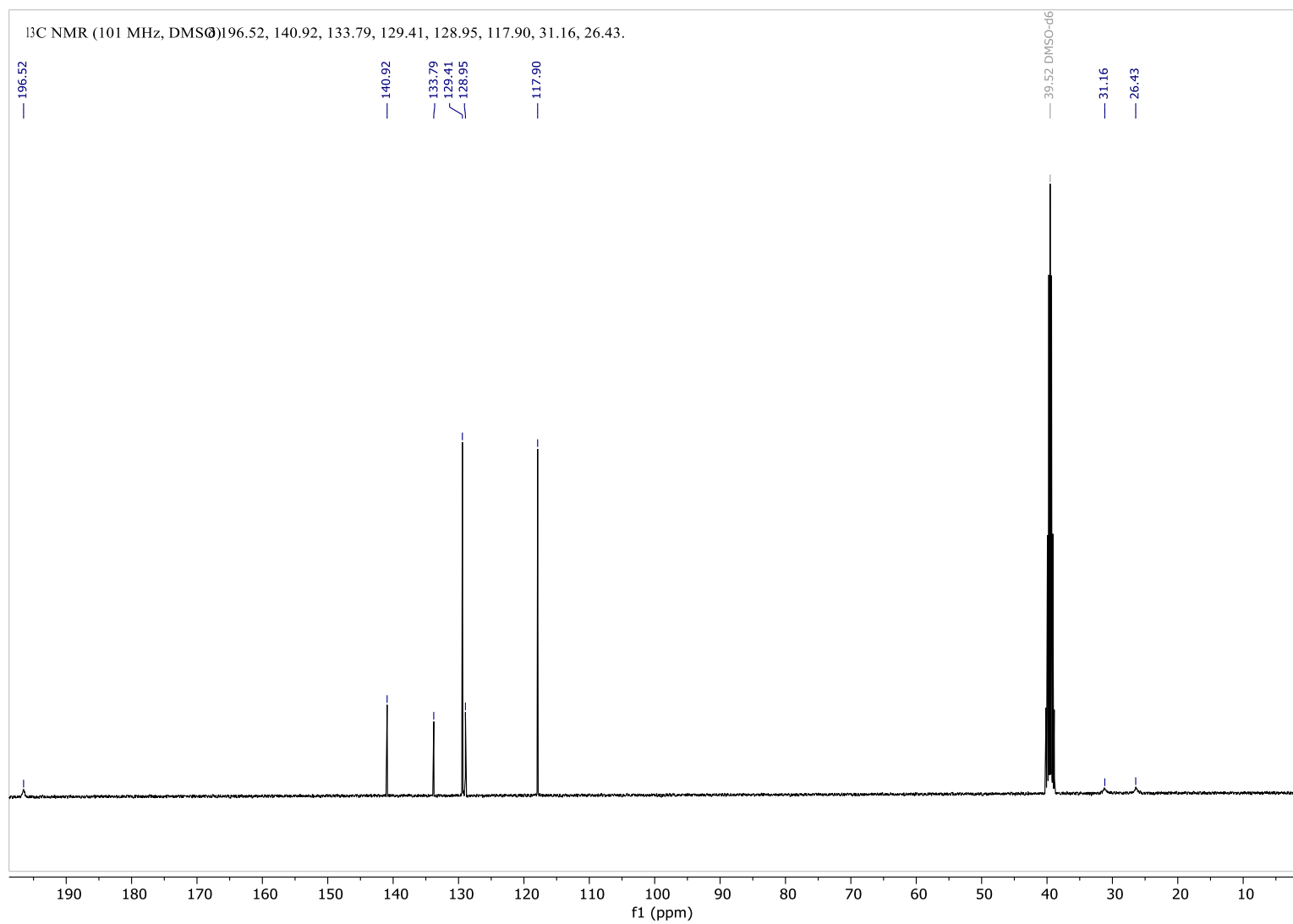


Figure S140: ¹³C NMR spectrum of 3-(2-(4-chlorophenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

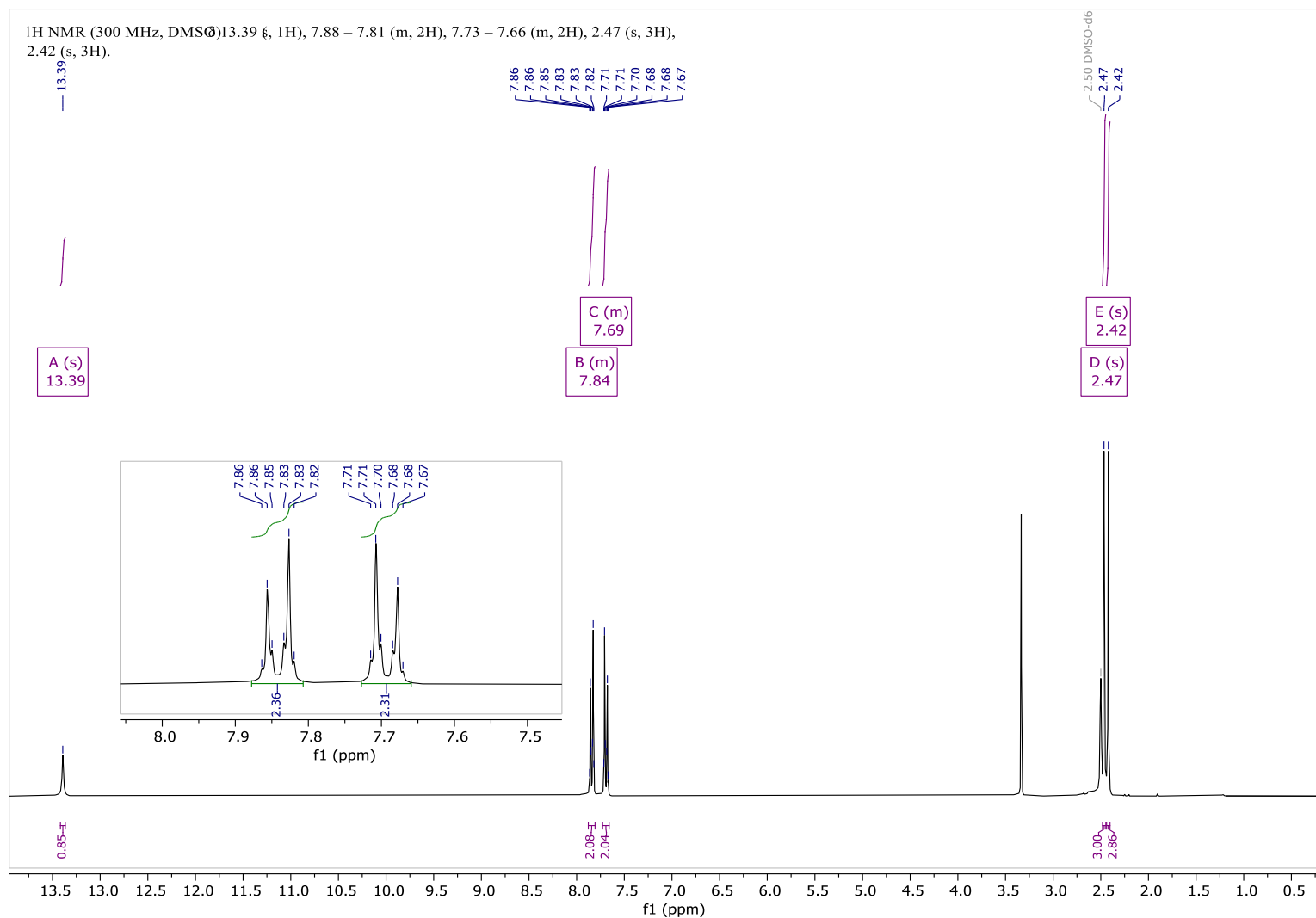


Figure S141: ¹H NMR spectrum of 4-(2-(2,4-dioxopent-3-ylidene)hydrazineyl)benzonitrile in DMSO-*d*₆.

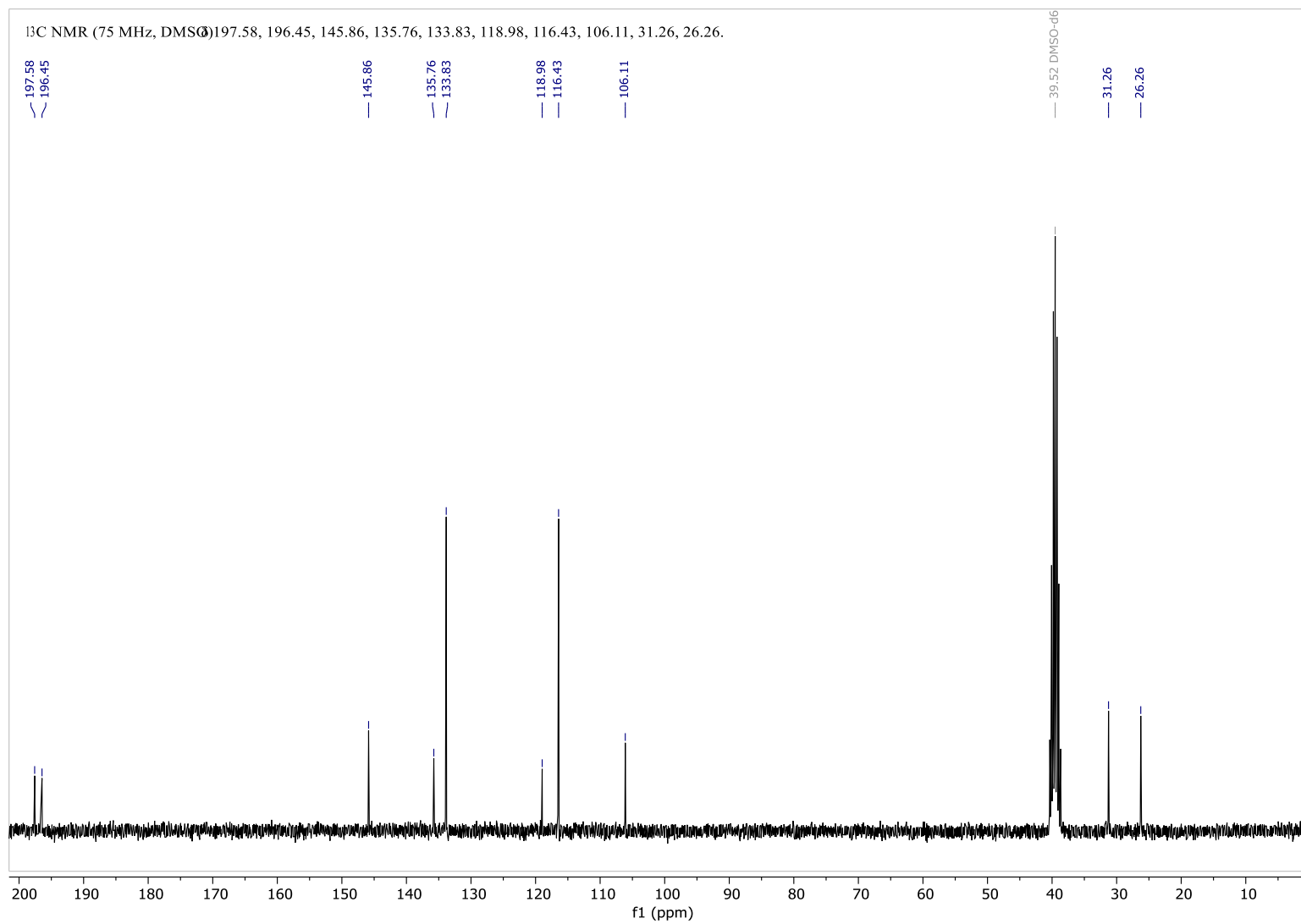


Figure S142: ¹³C NMR spectrum of 4-(2-(2,4-dioxopent-3-ylidene)hydrazineyl)benzonitrile in DMSO-*d*₆.

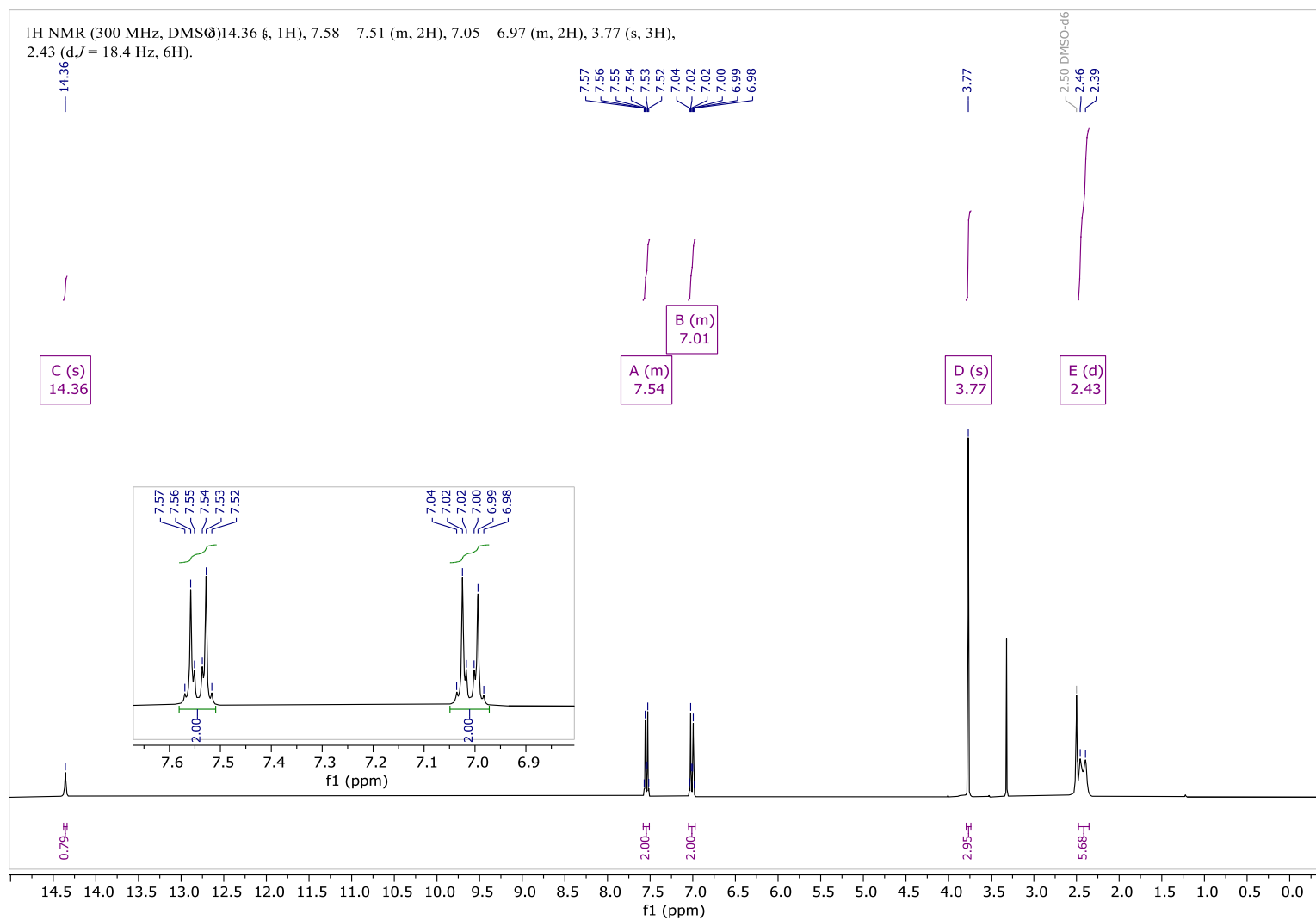


Figure S143: ¹H NMR spectrum of 3-(2-(4-methoxyphenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

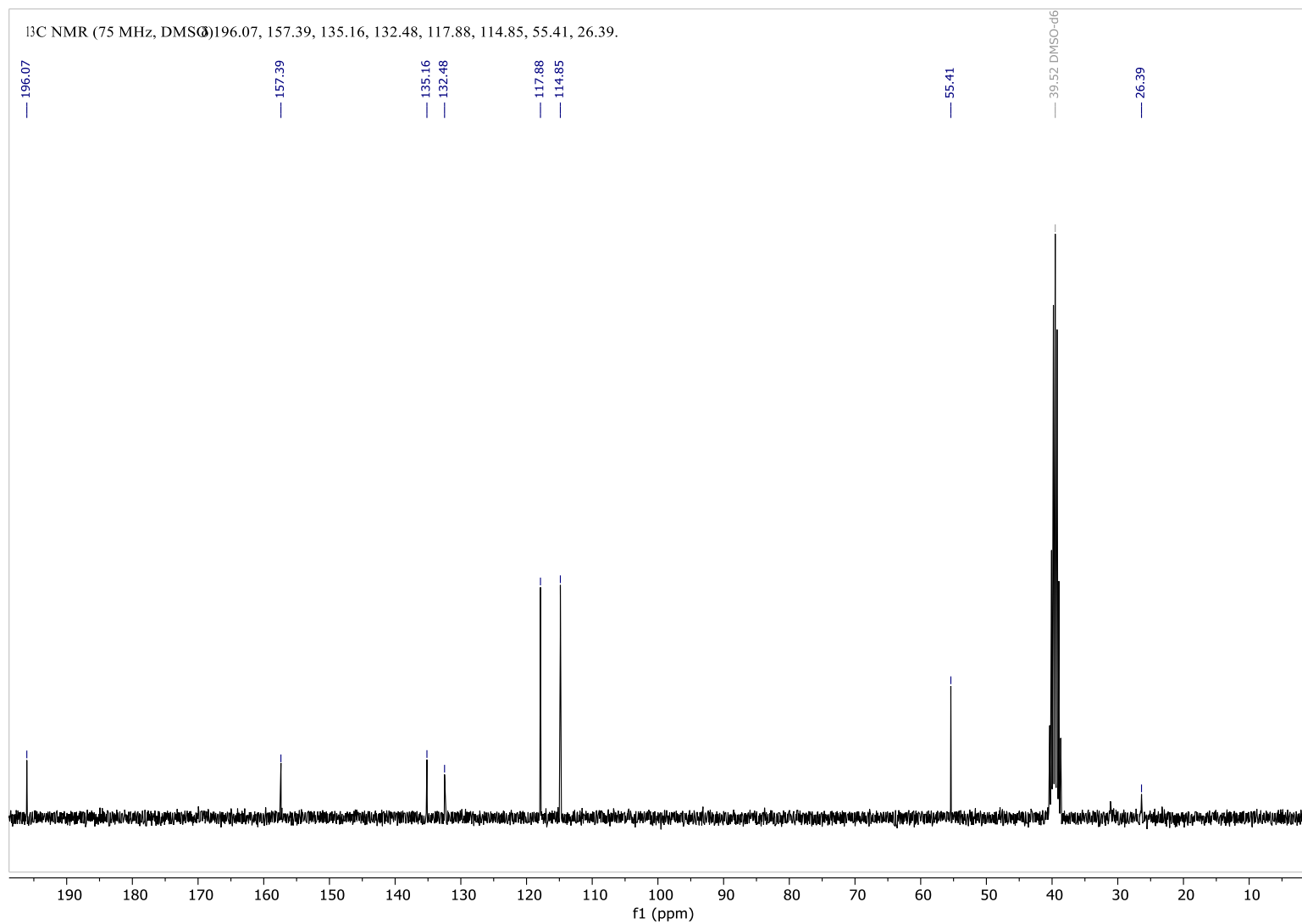


Figure S144: ¹³C NMR spectrum of 3-(2-(4-methoxyphenyl)hydrazono)pentane-2,4-dione in DMSO-*d*₆.

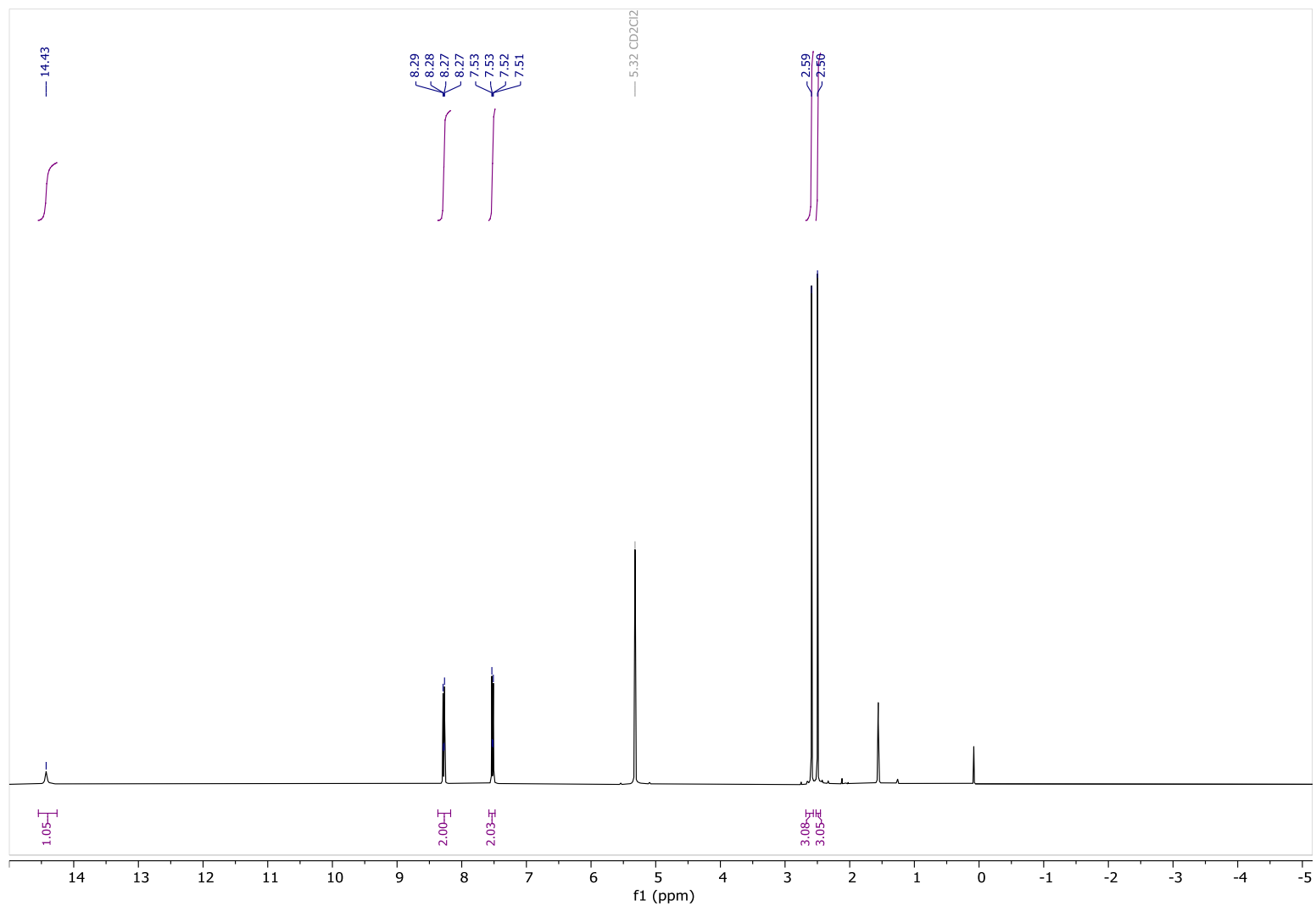


Figure S145: ^1H NMR spectrum of 3-(2-(4-nitrophenyl)hydrazono)pentane-2,4-dione in CD_2Cl_2 .

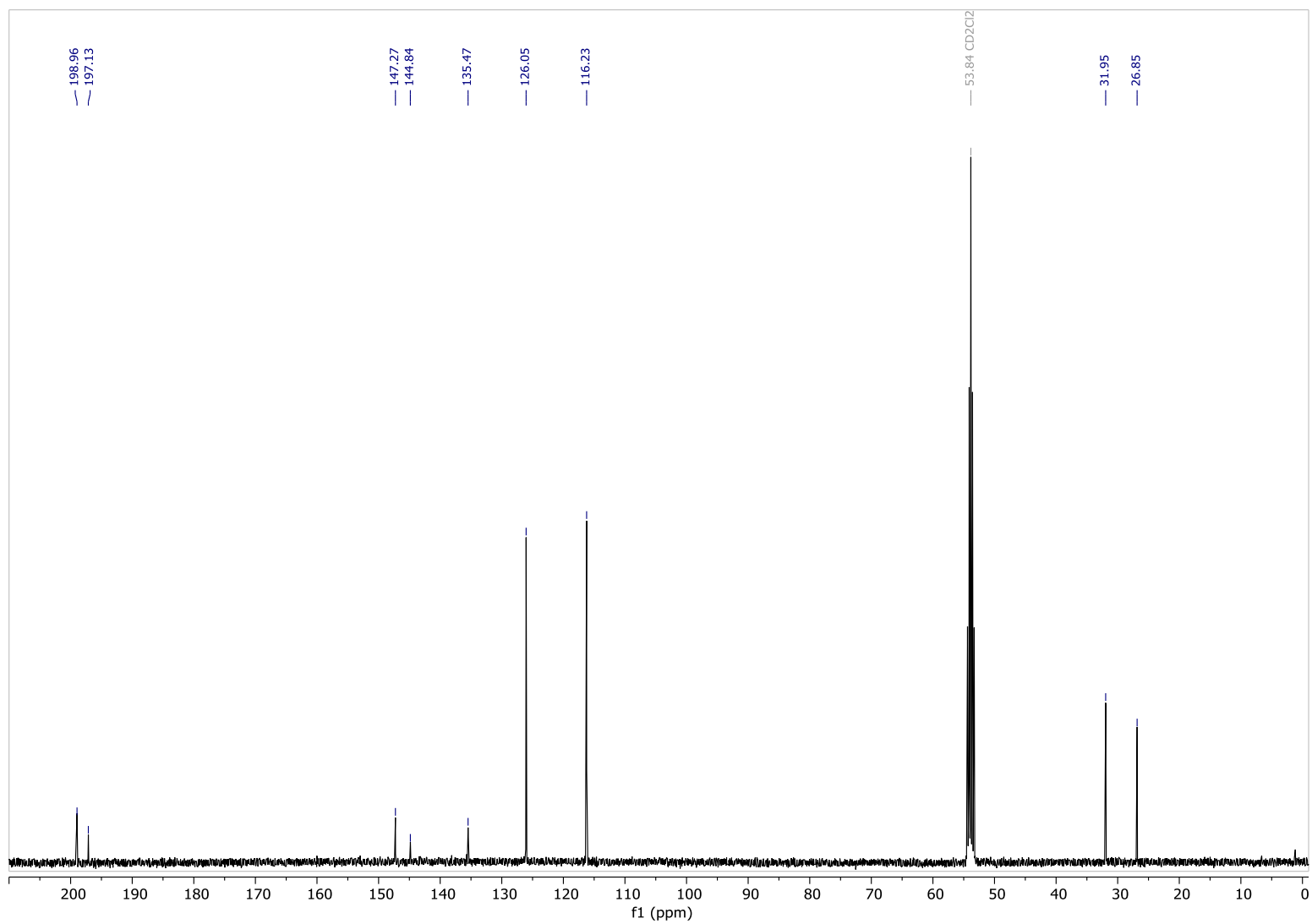


Figure S146: ¹³C NMR spectrum of 3-(2-(4-nitrophenyl)hydrazono)pentane-2,4-dione in CD₂Cl₂.

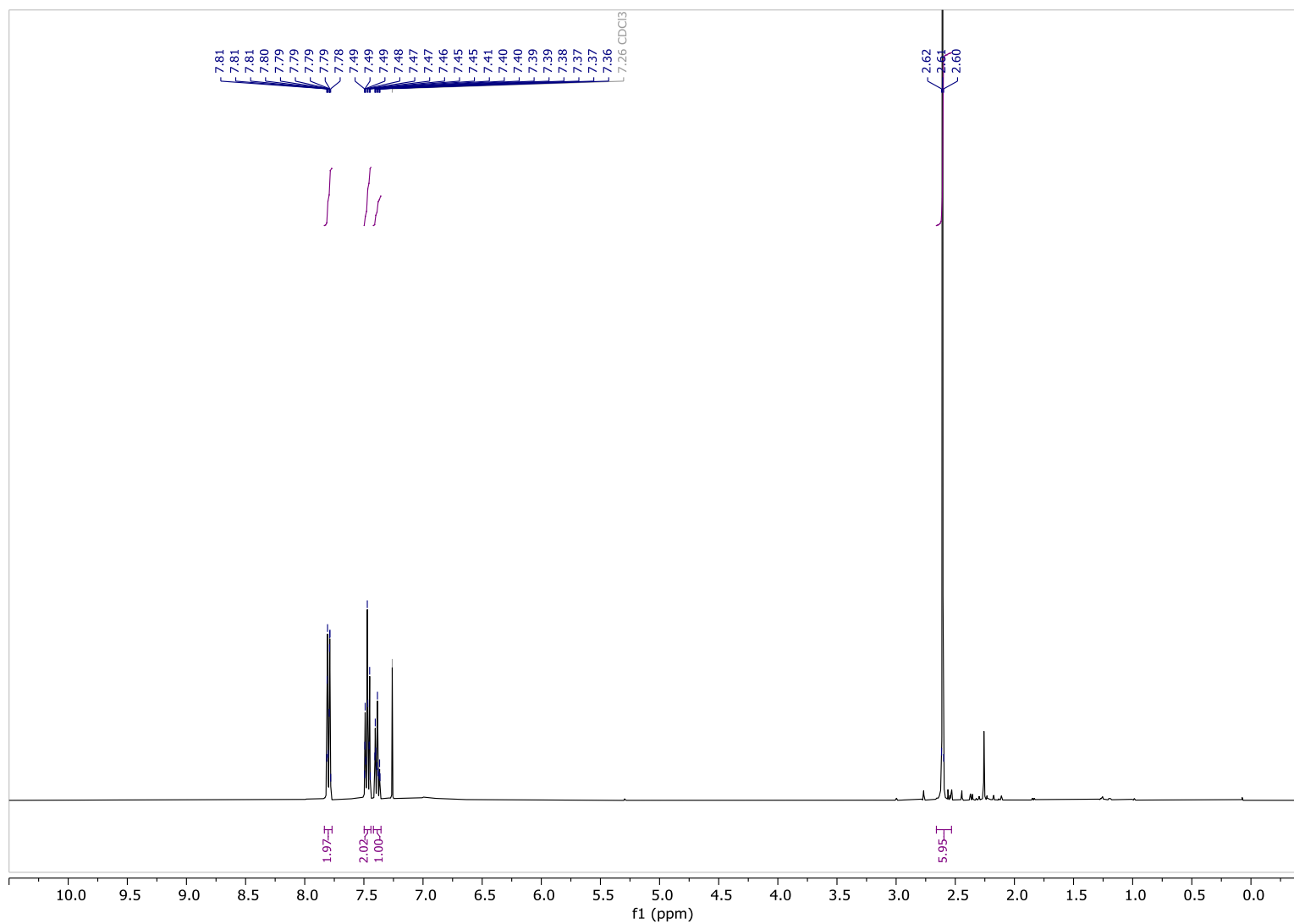


Figure S147: ¹H NMR spectrum of (E)-3,5-dimethyl-4-(phenyldiazenyl)-1H-pyrazole in CDCl₃.

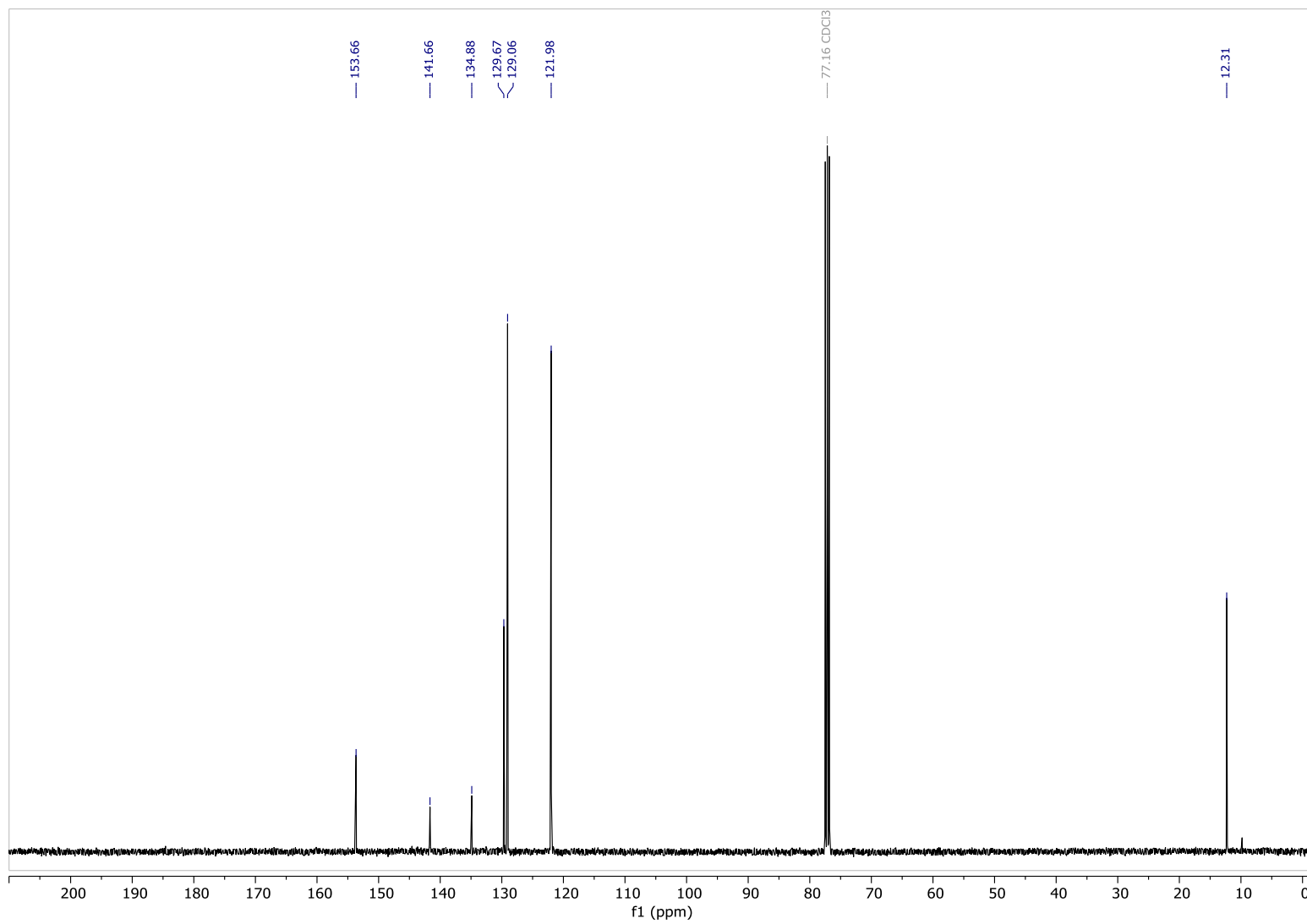


Figure S148: ^{13}C NMR spectrum of *(E)*-3,5-dimethyl-4-(phenyldiazenyl)-1*H*-pyrazole in CDCl_3 .

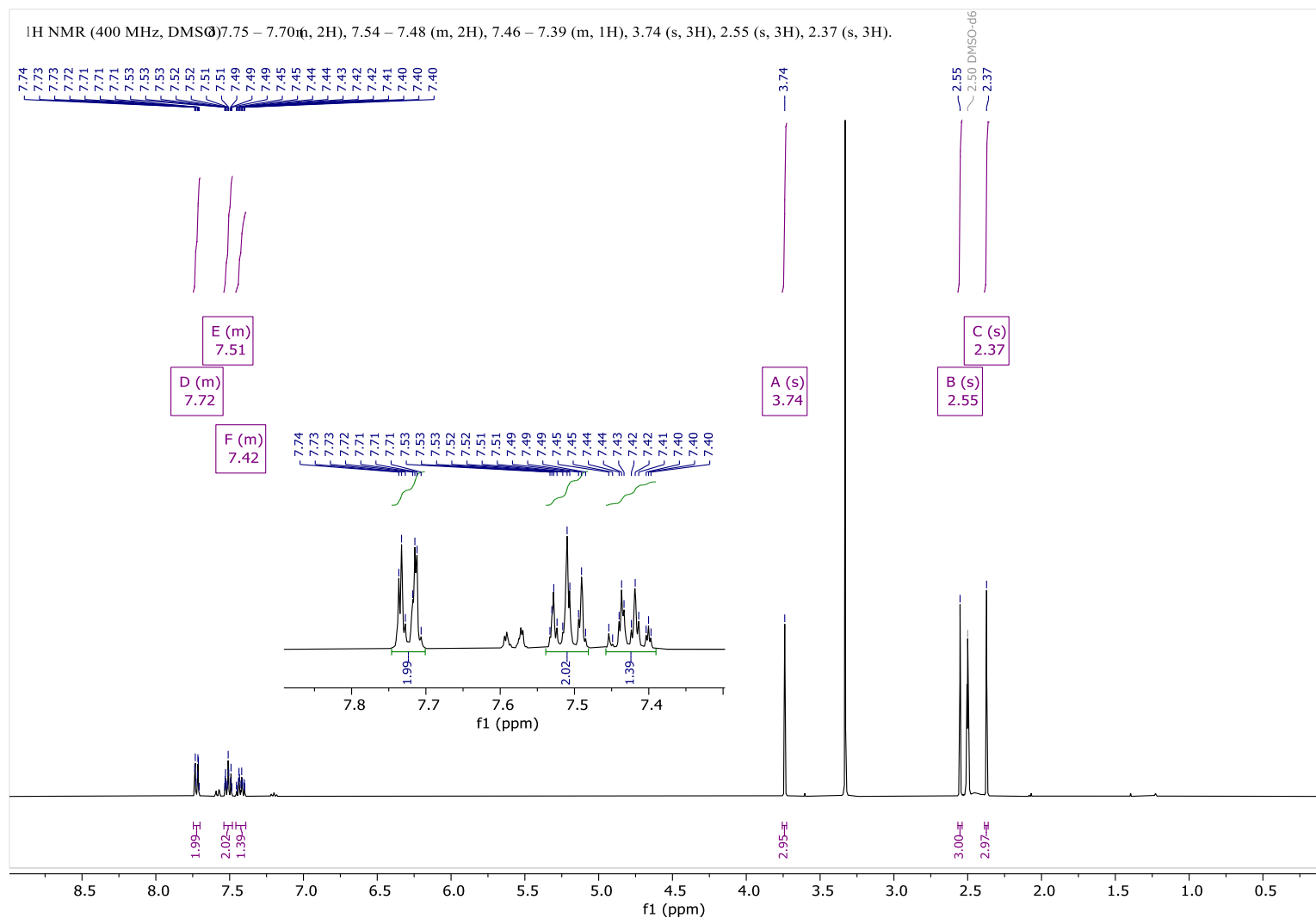


Figure S149: ¹H NMR spectrum of (*E*)-1,3,5-trimethyl-4-(phenyldiazenyl)-1*H*-pyrazole in DMSO-*d*₆.

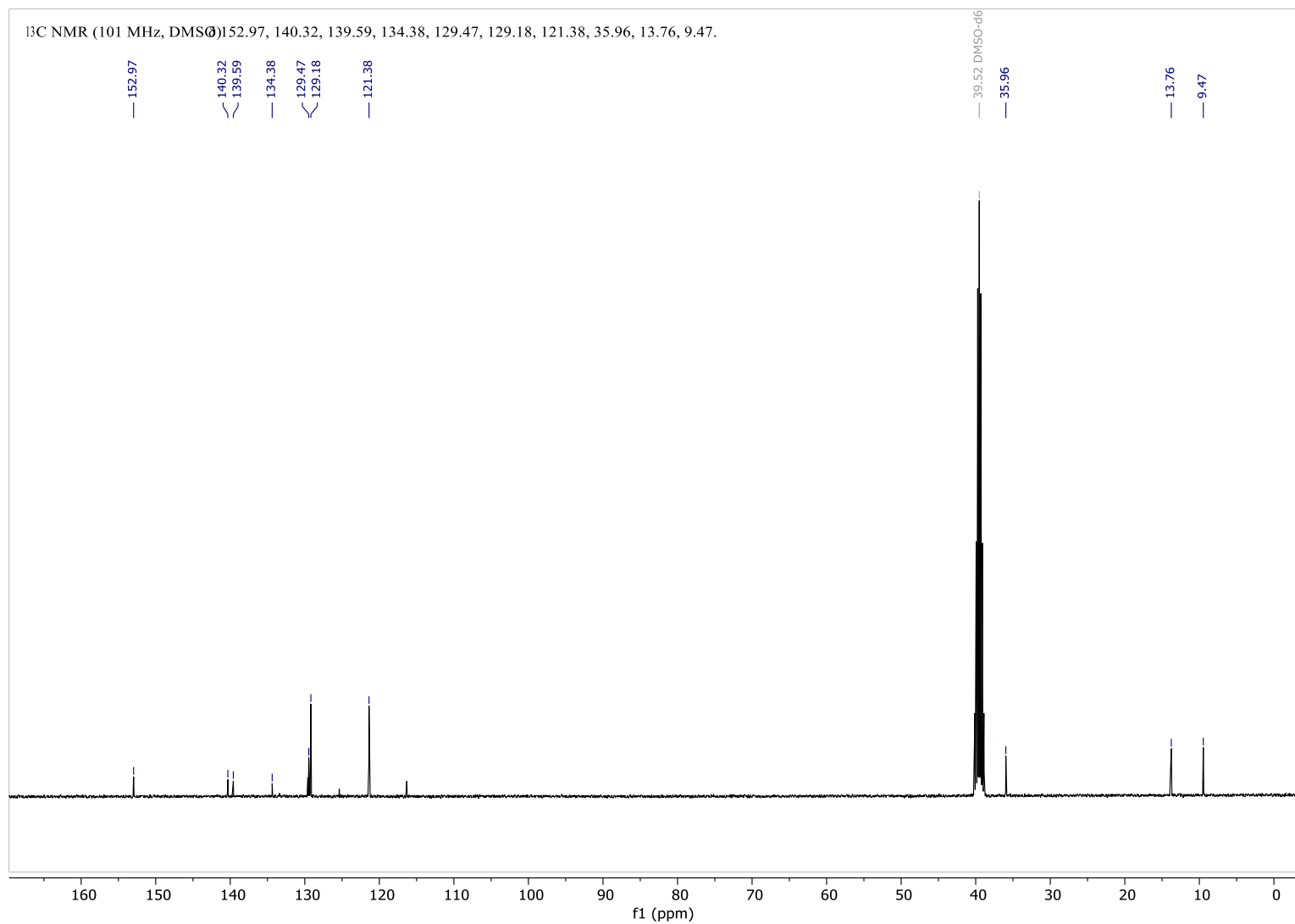


Figure S150: ¹³C NMR spectrum of (*E*)-1,3,5-trimethyl-4-(phenyldiazenyl)-1*H*-pyrazole in DMSO-*d*₆.

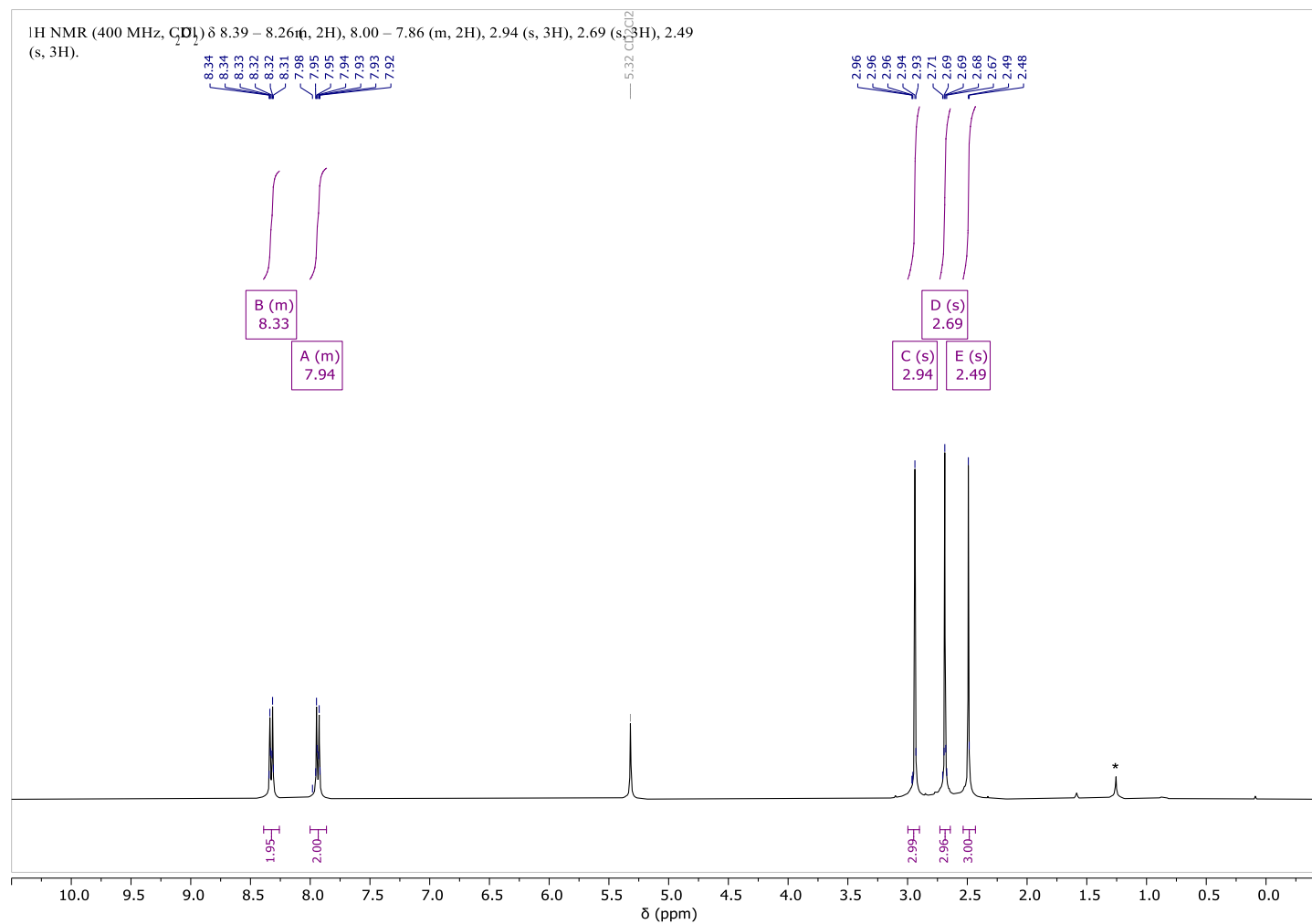


Figure S151: ¹H NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in CD₂Cl₂.

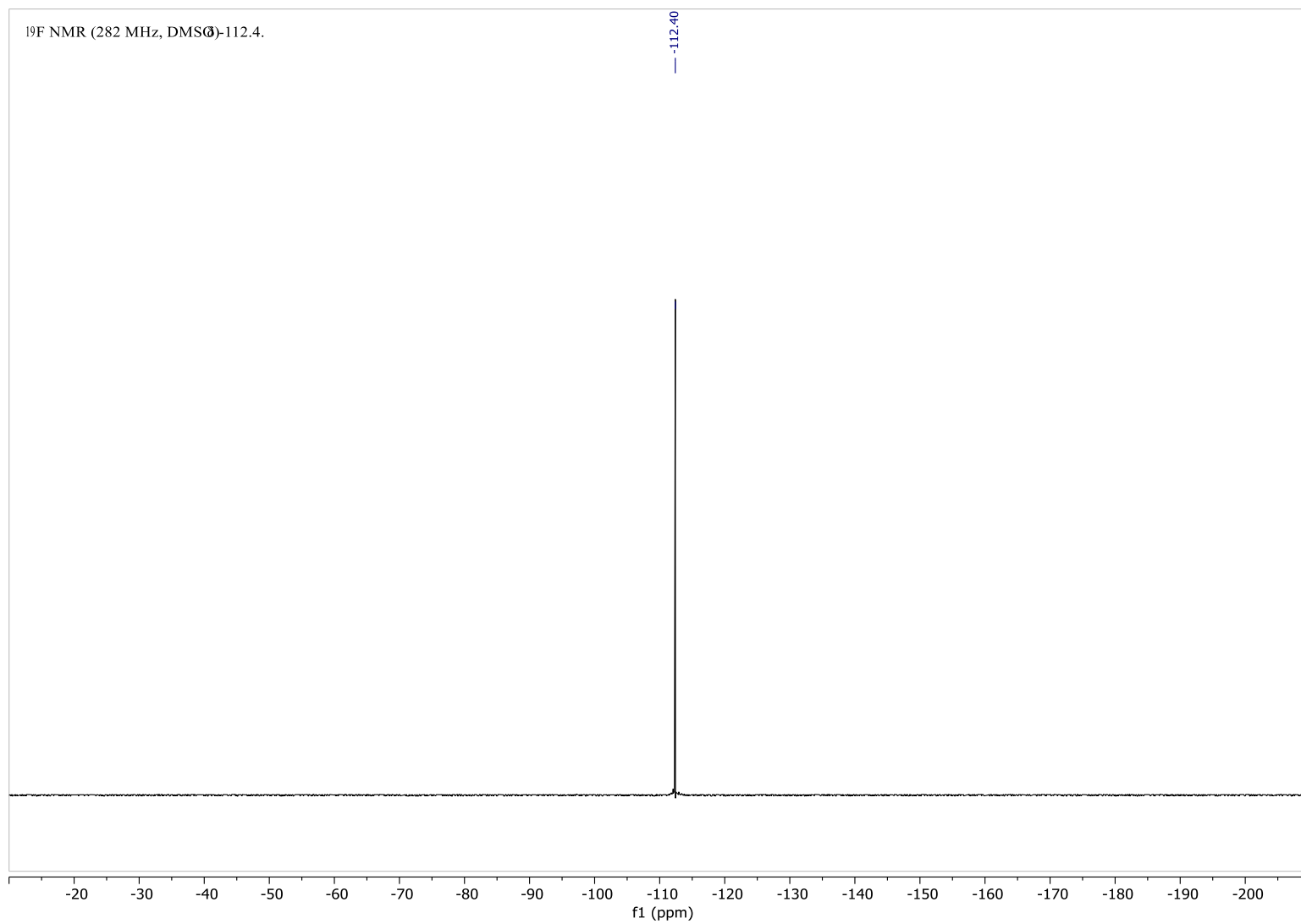


Figure S152: ¹⁹F NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

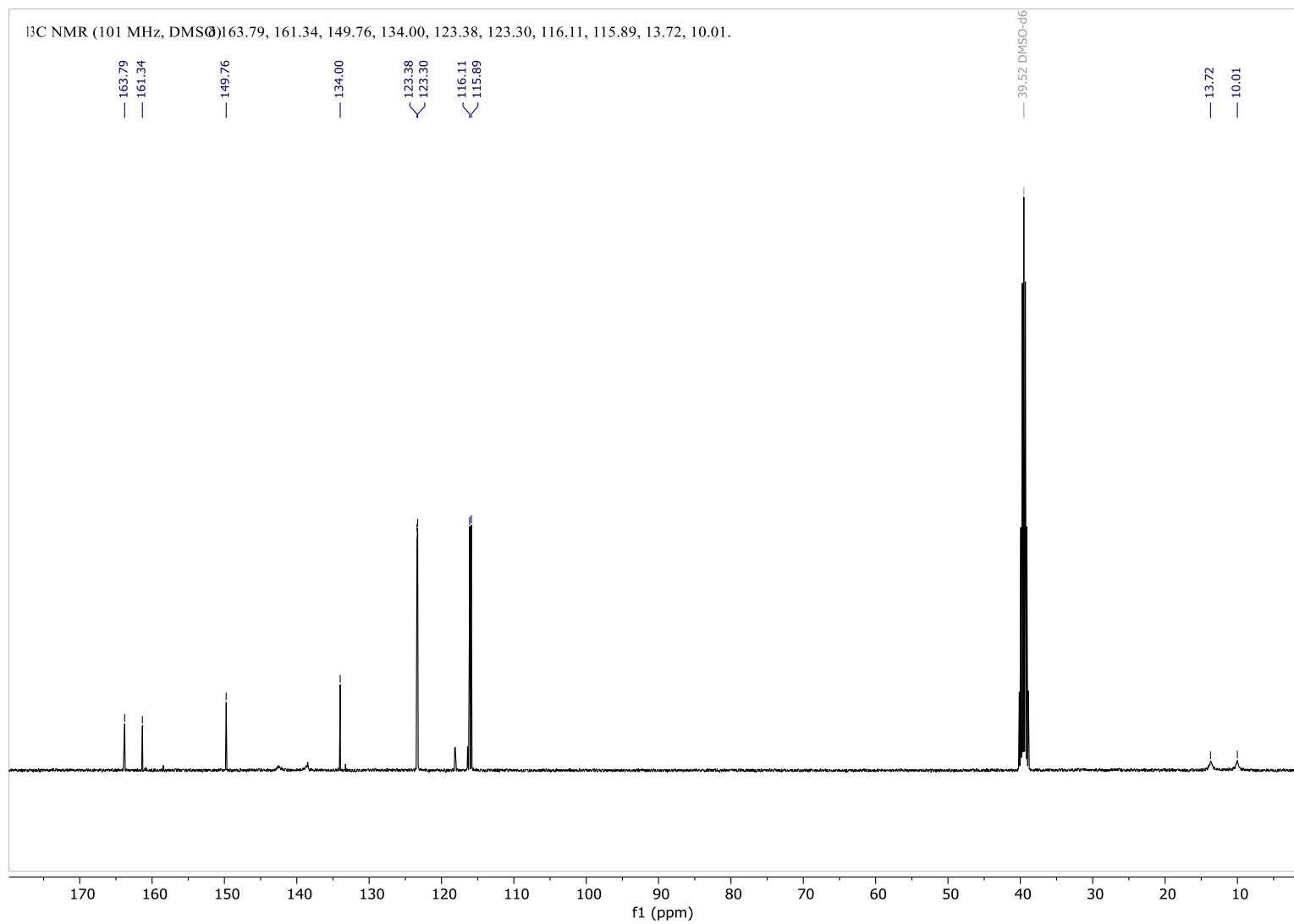


Figure S153: ¹³C NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

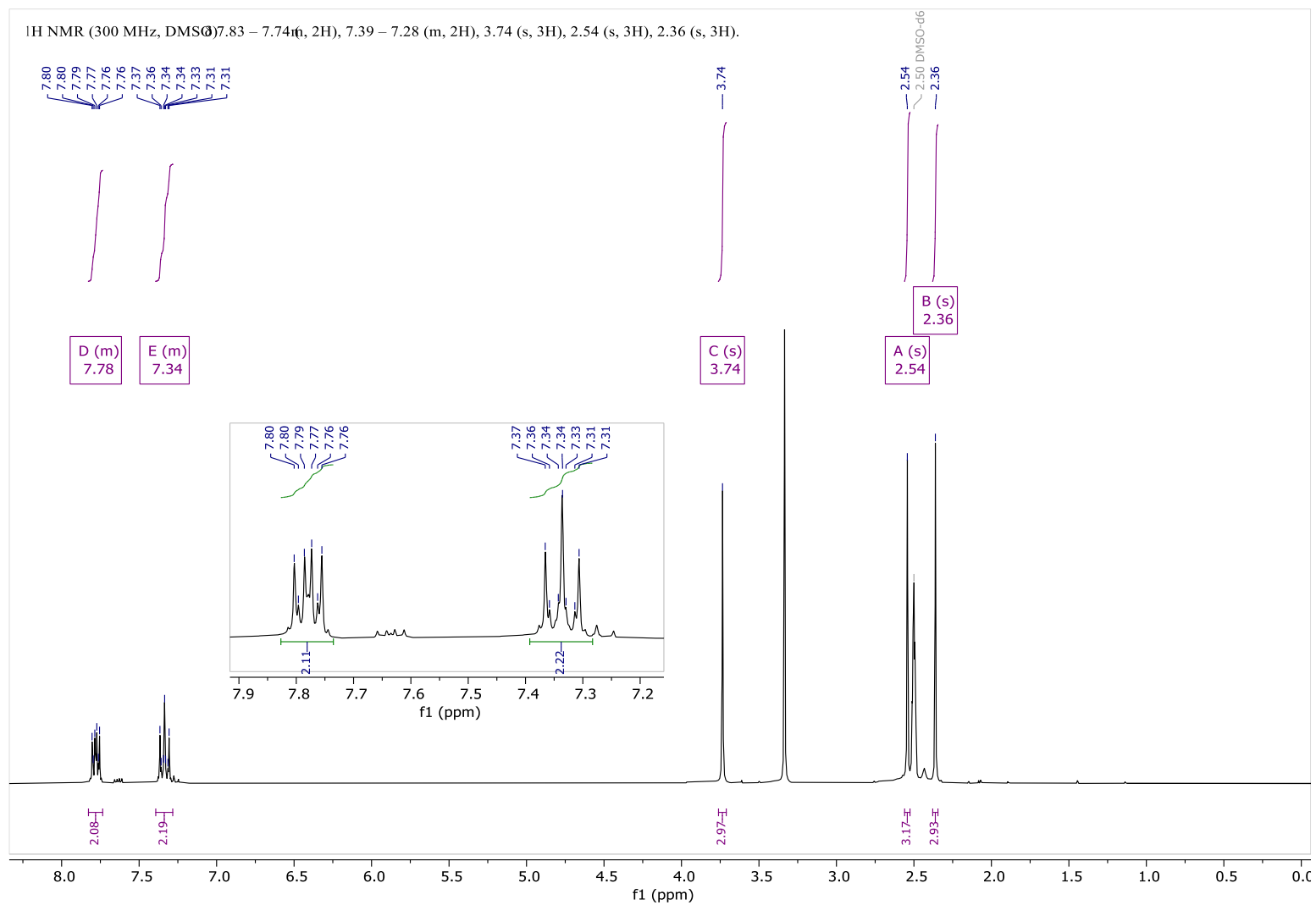


Figure S154: ¹H NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

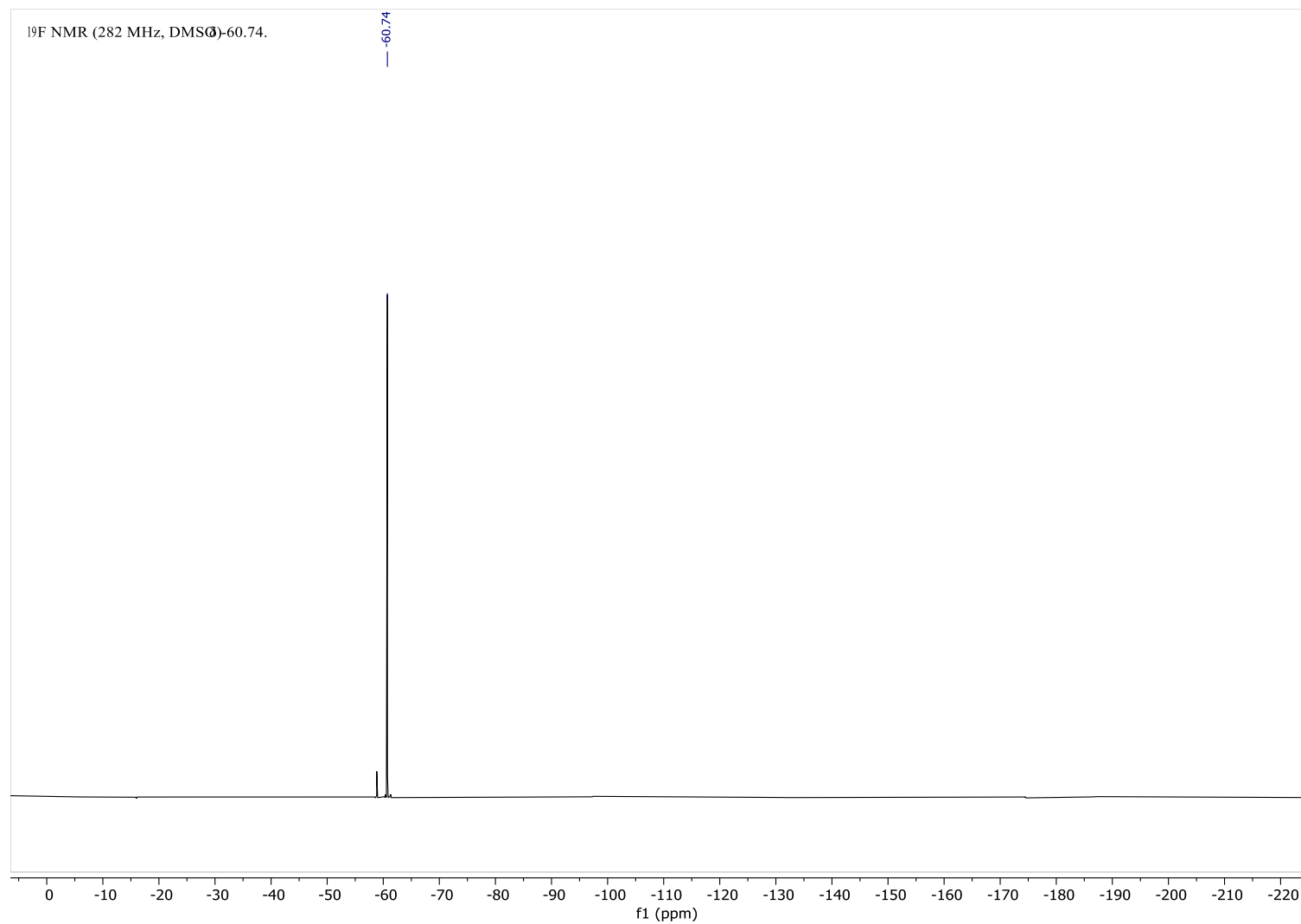


Figure S155: ¹⁹F NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

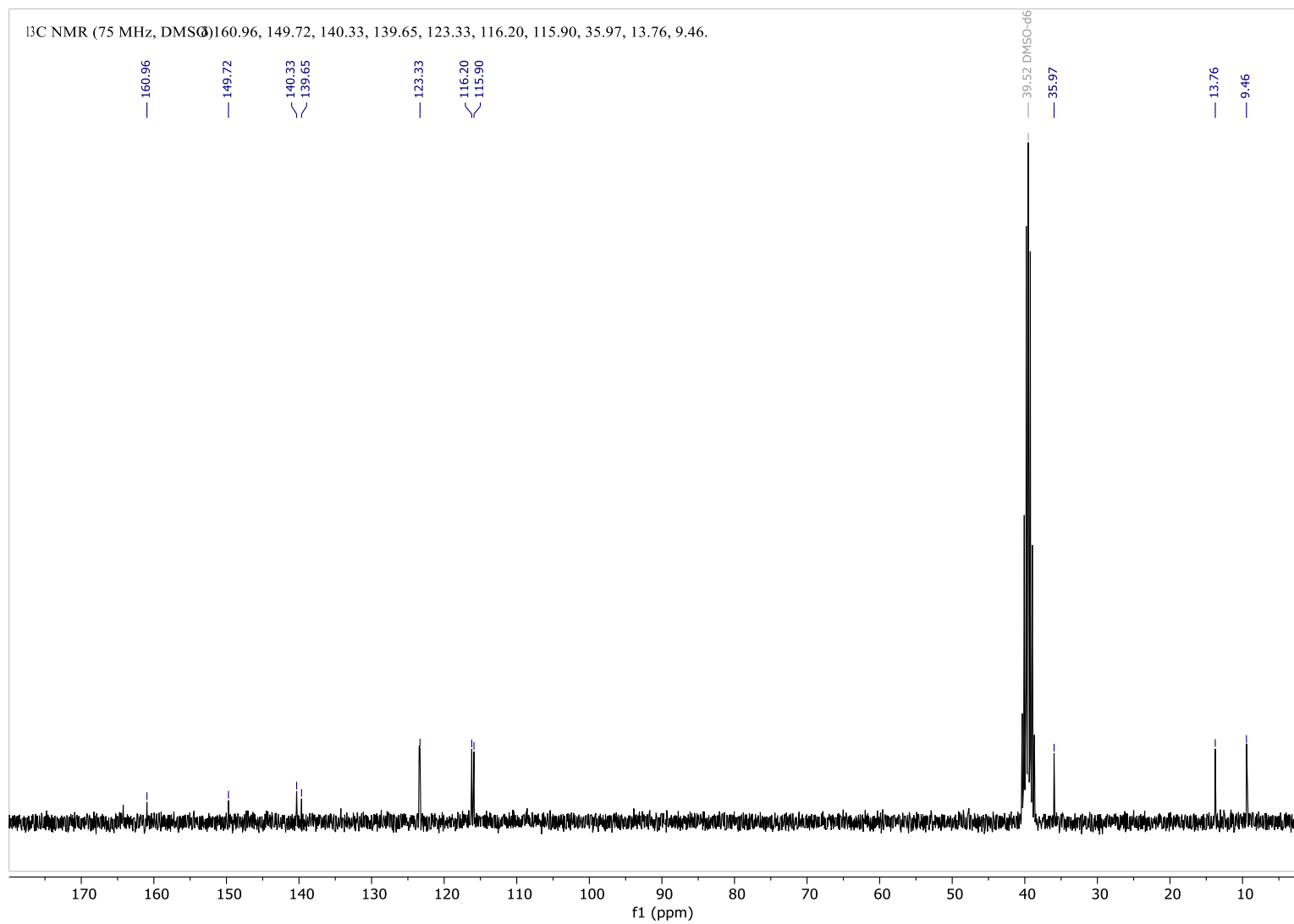


Figure S156: ¹³C NMR spectrum of (*E*)-4-((4-fluorophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

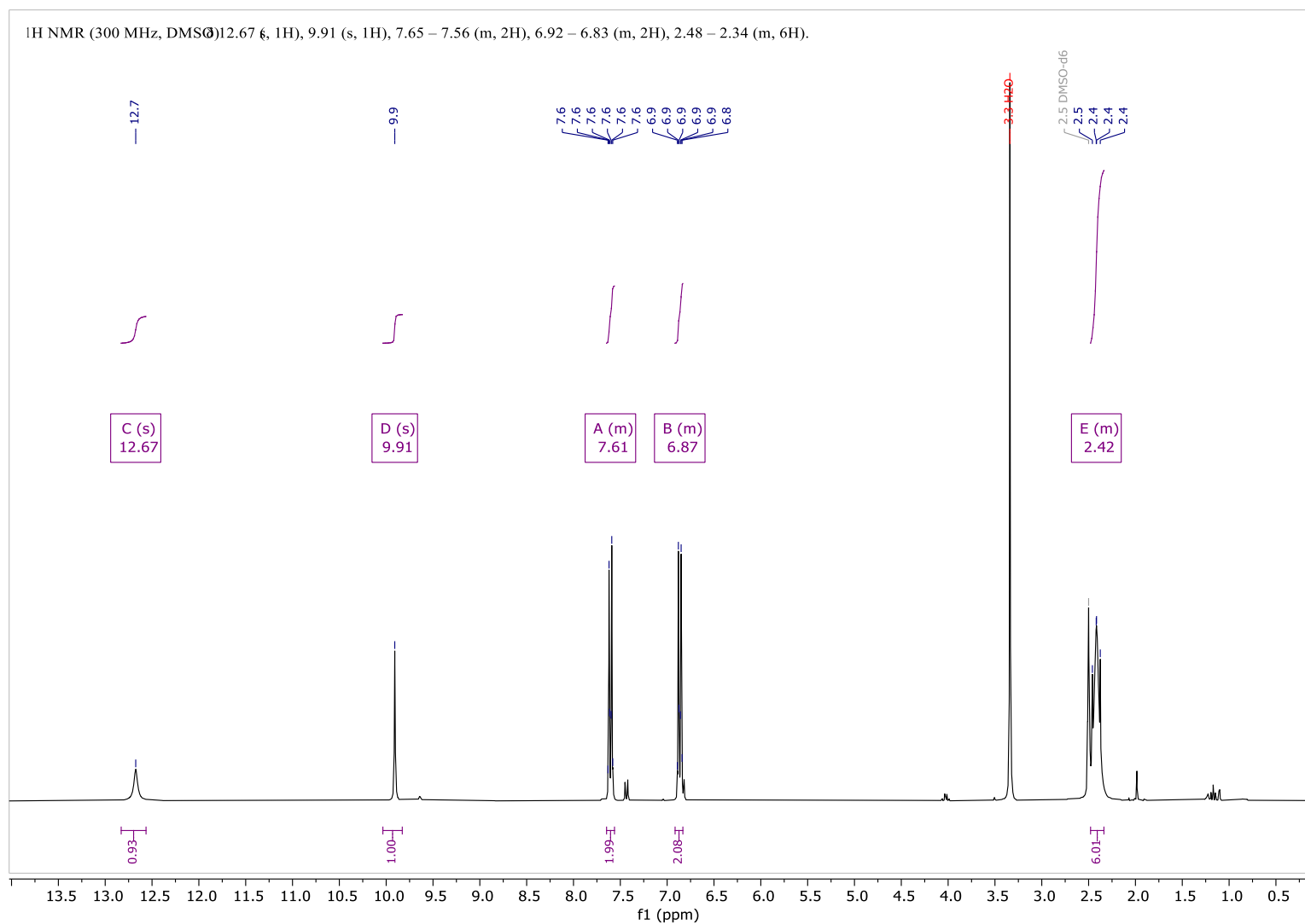


Figure S157: ¹H NMR spectrum of (*E*)-4-((3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl)phenol in DMSO-*d*₆.

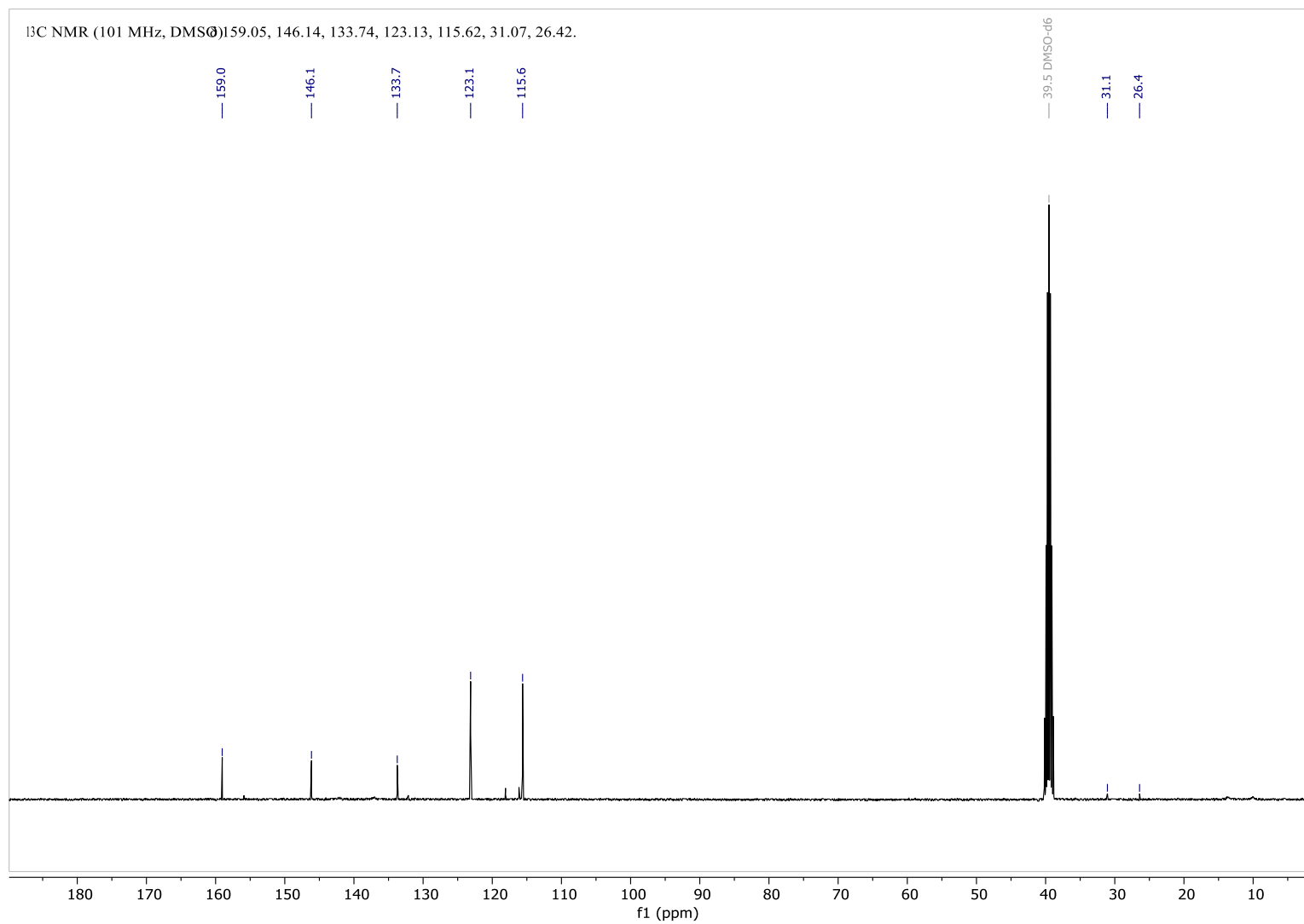


Figure S158: ¹³C NMR spectrum of (*E*)-4-((3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl)phenol in DMSO-*d*₆.

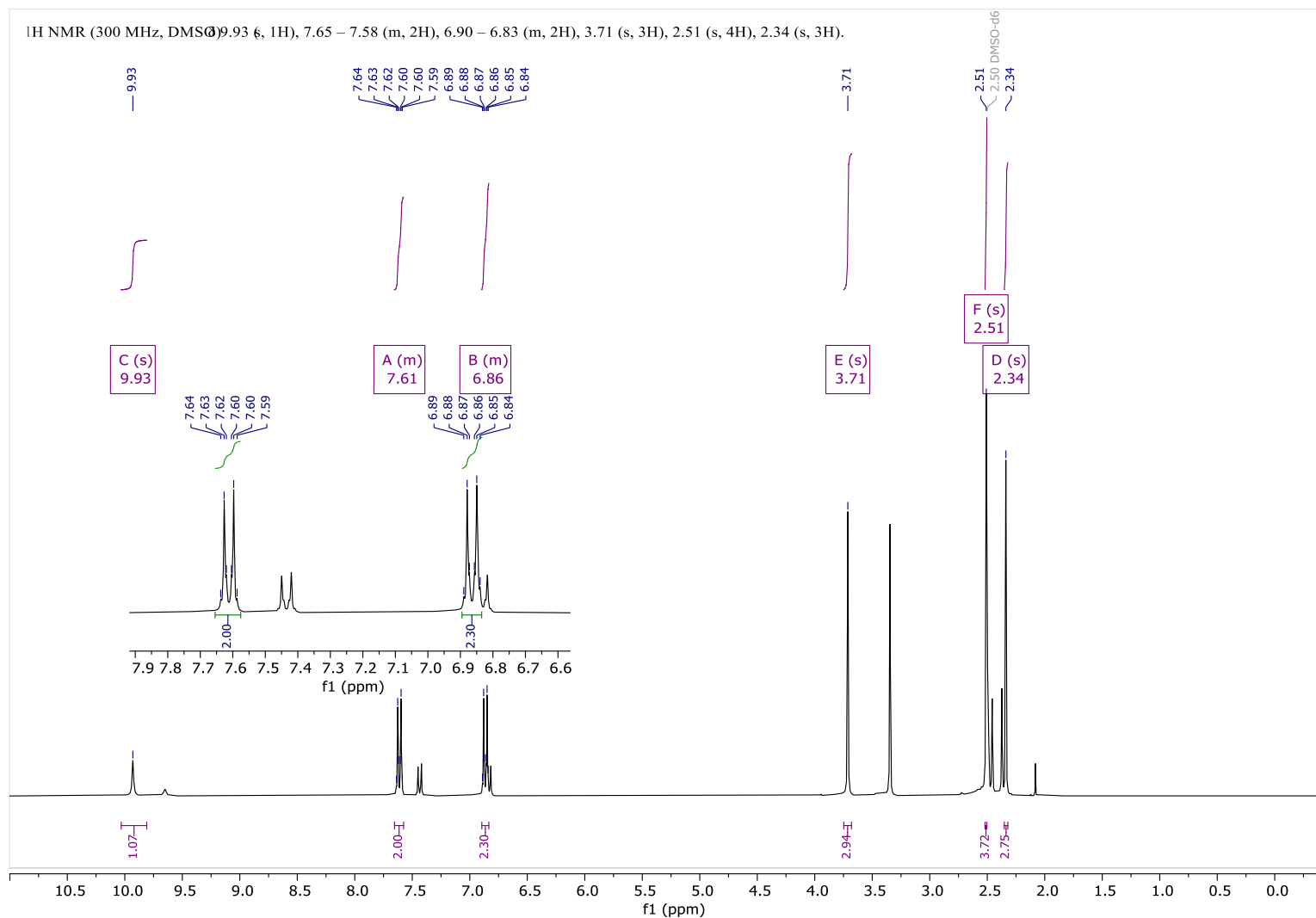


Figure S159: ¹H NMR spectrum of (*E*)-4-((1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazenyl)phenol in DMSO-*d*₆.

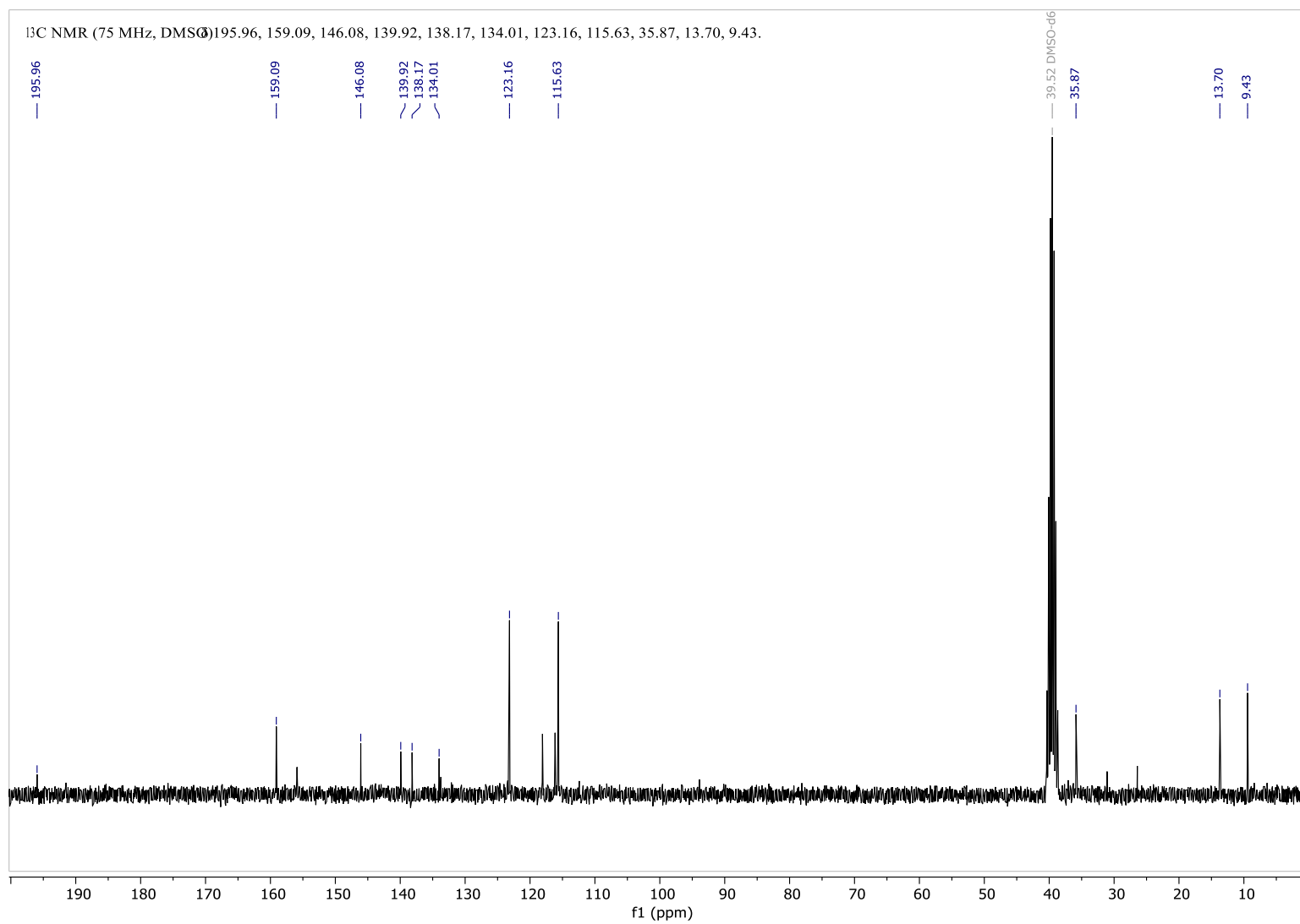


Figure S160: ¹³C NMR spectrum of (*E*)-4-((1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazenyl)phenol in DMSO-*d*₆.

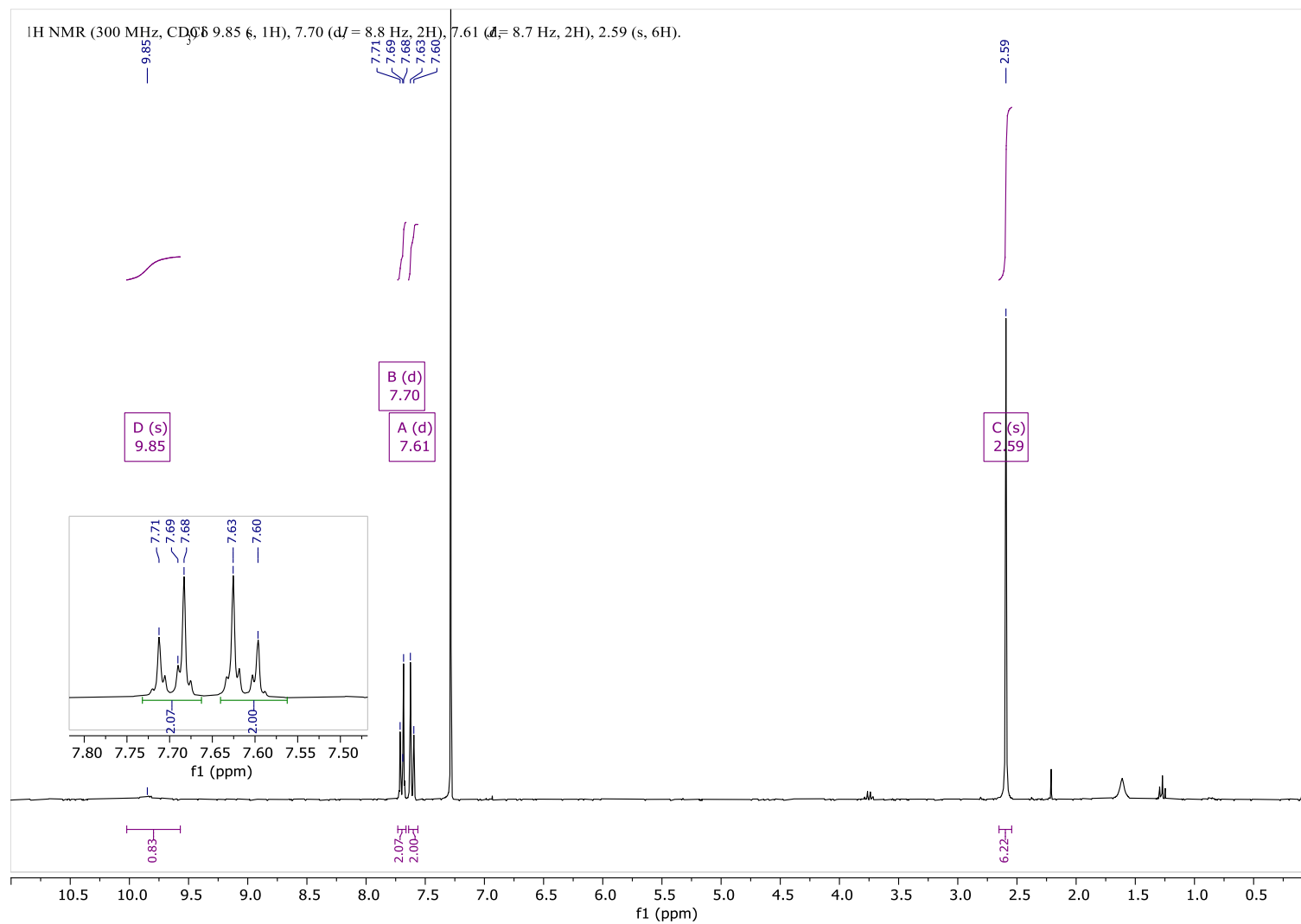


Figure S161: ¹H NMR spectrum of (*E*)-4-((4-bromophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

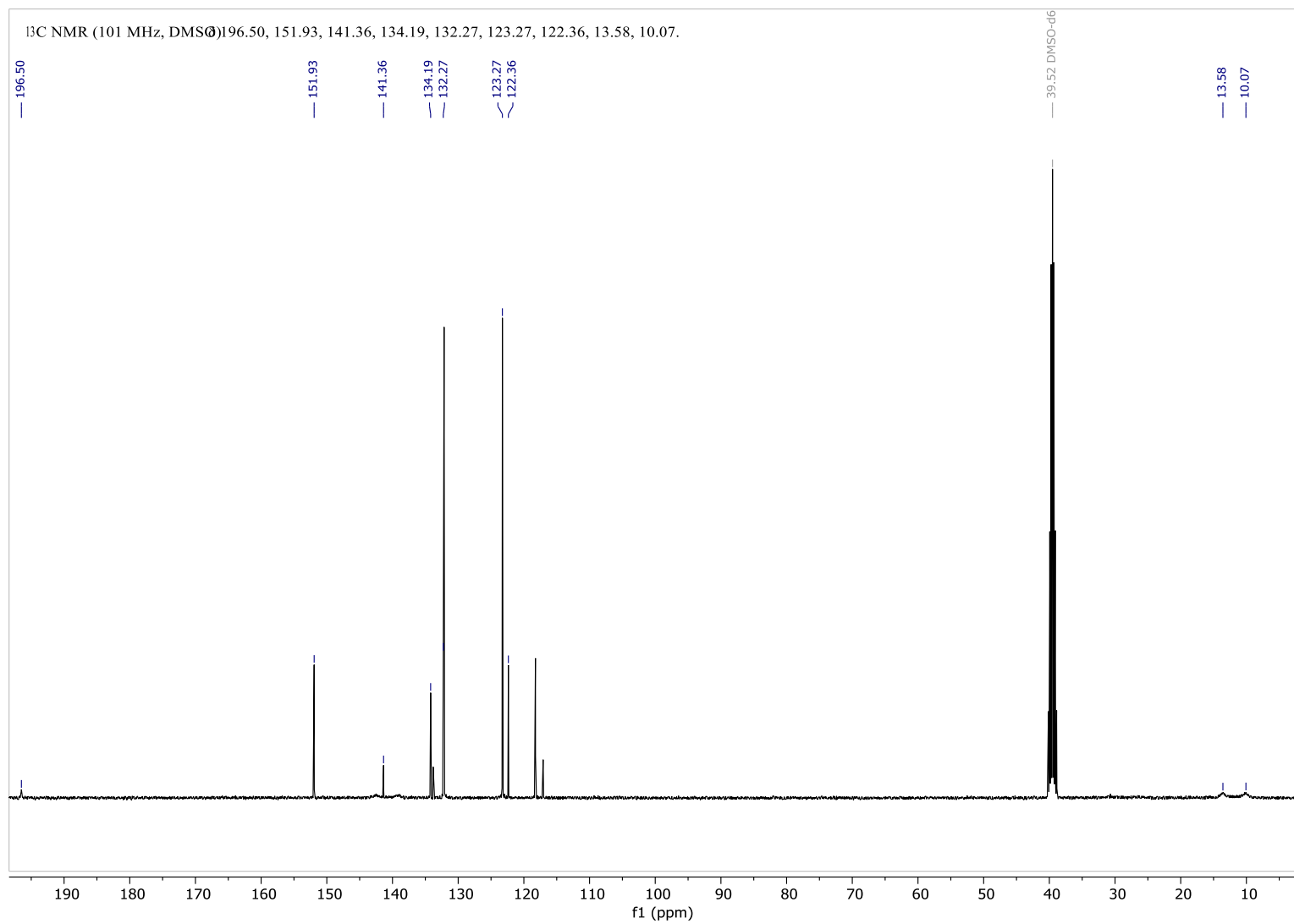


Figure S162: ¹³C NMR spectrum of (*E*)-4-((4-bromophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

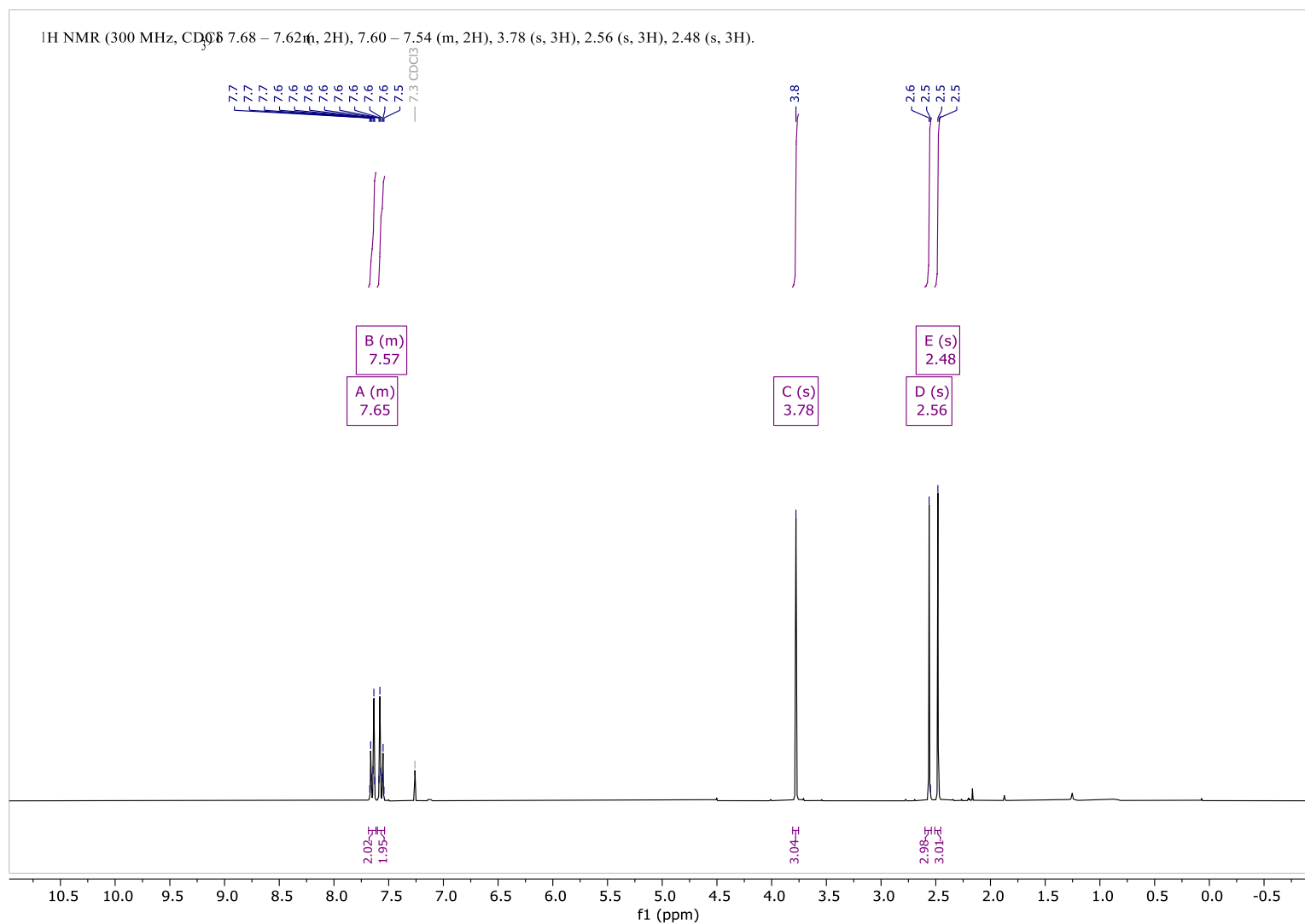


Figure S163: ¹H NMR spectrum of (*E*)-4-((4-bromophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

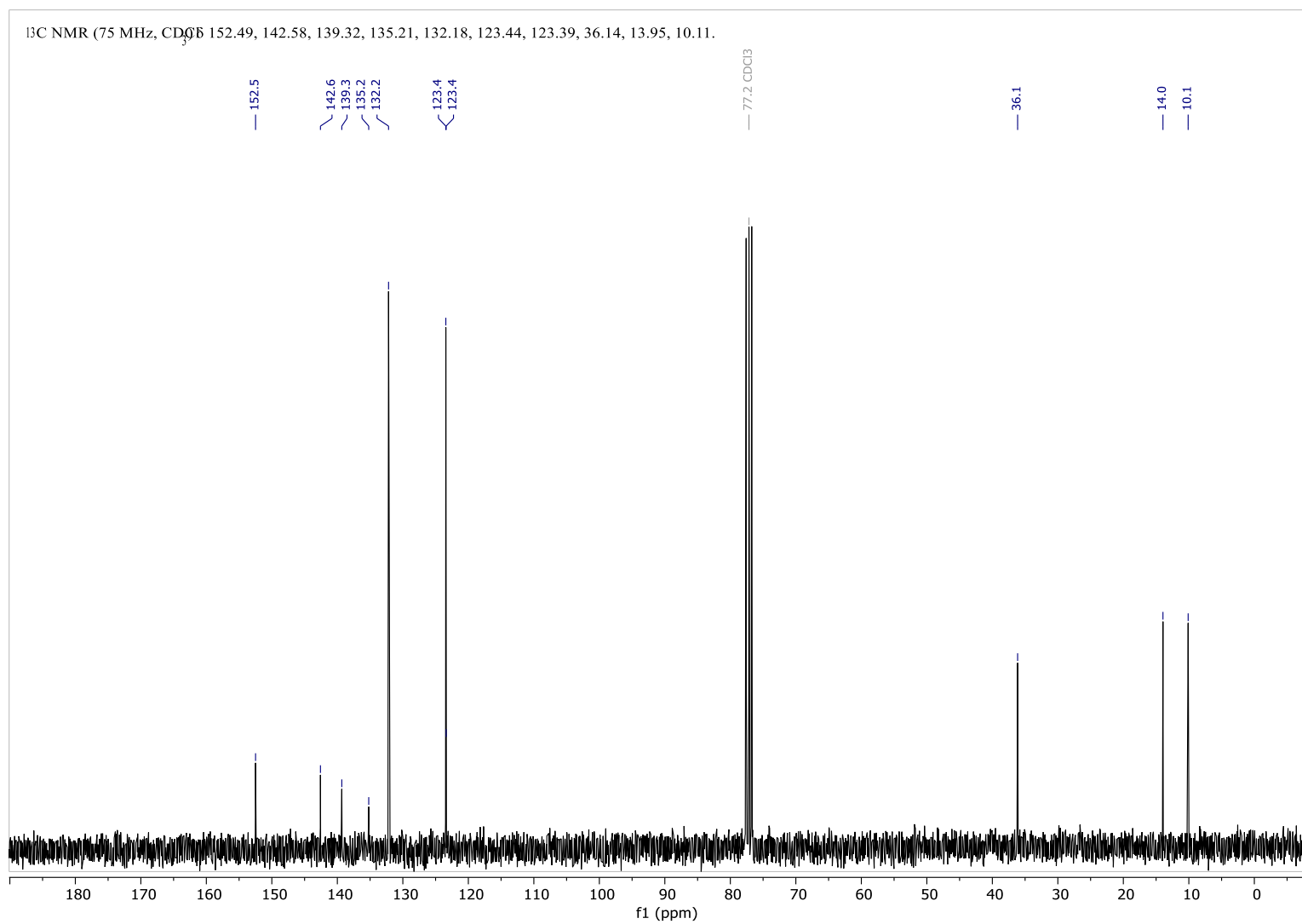


Figure S164: ¹³C NMR spectrum of (*E*)-4-((4-bromophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

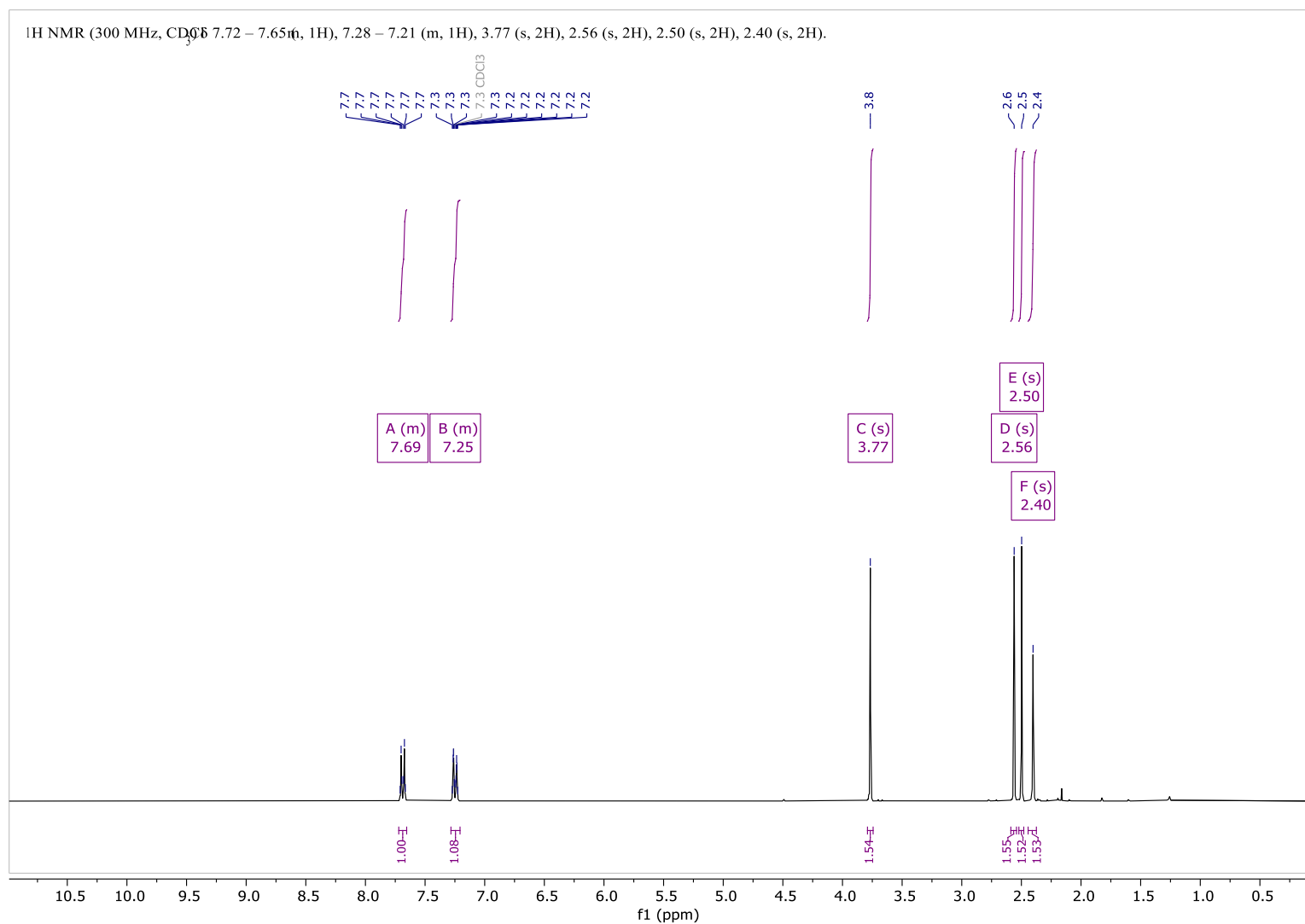


Figure S165: ¹H NMR spectrum (*E*)-3,5-dimethyl-4-(*p*-tolyl-diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

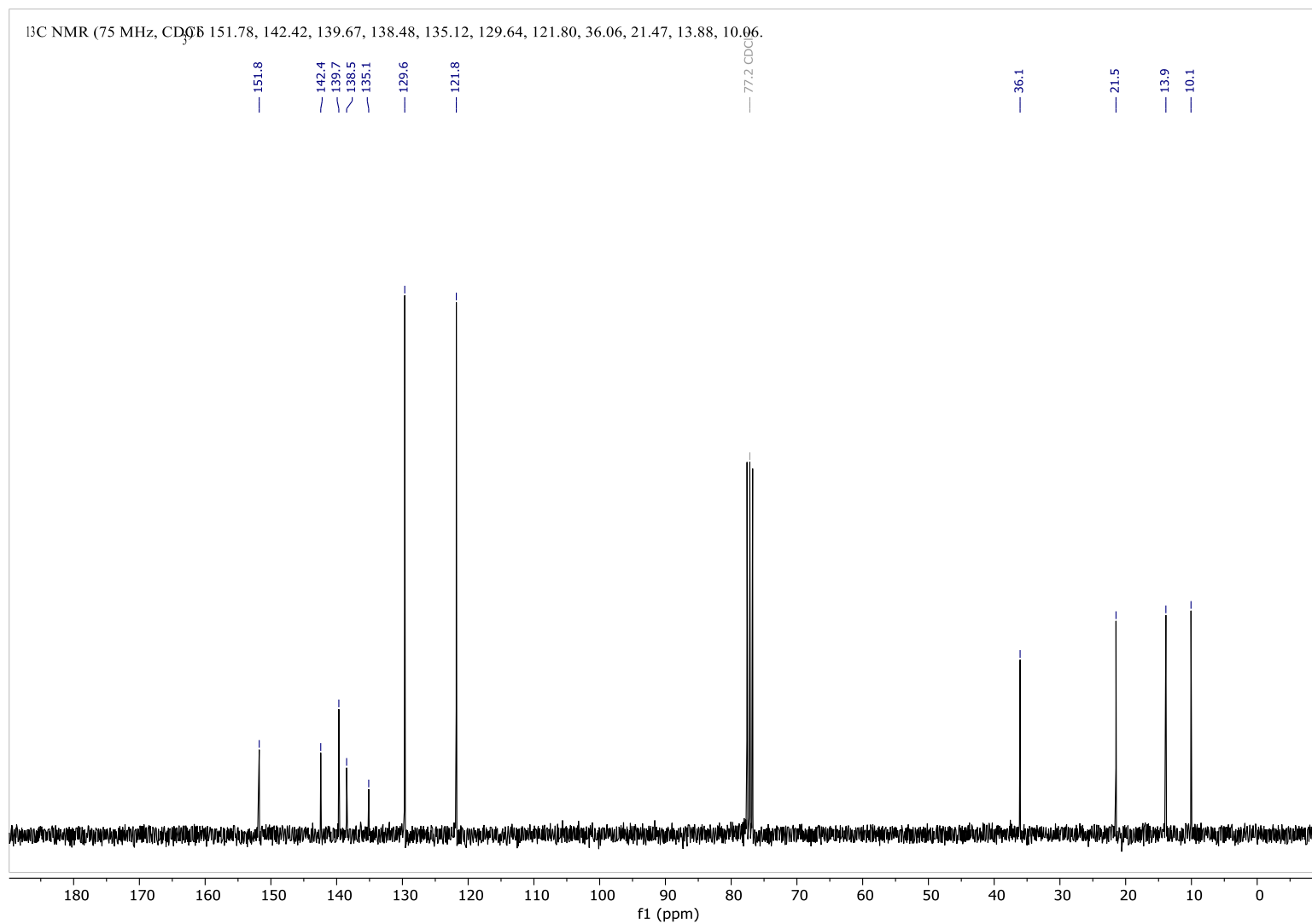


Figure S166: ¹³C NMR spectrum of (*E*)-3,5-dimethyl-4-(*p*-tolyldiazenyl)-1*H*-pyrazole in DMSO-*d*₆.

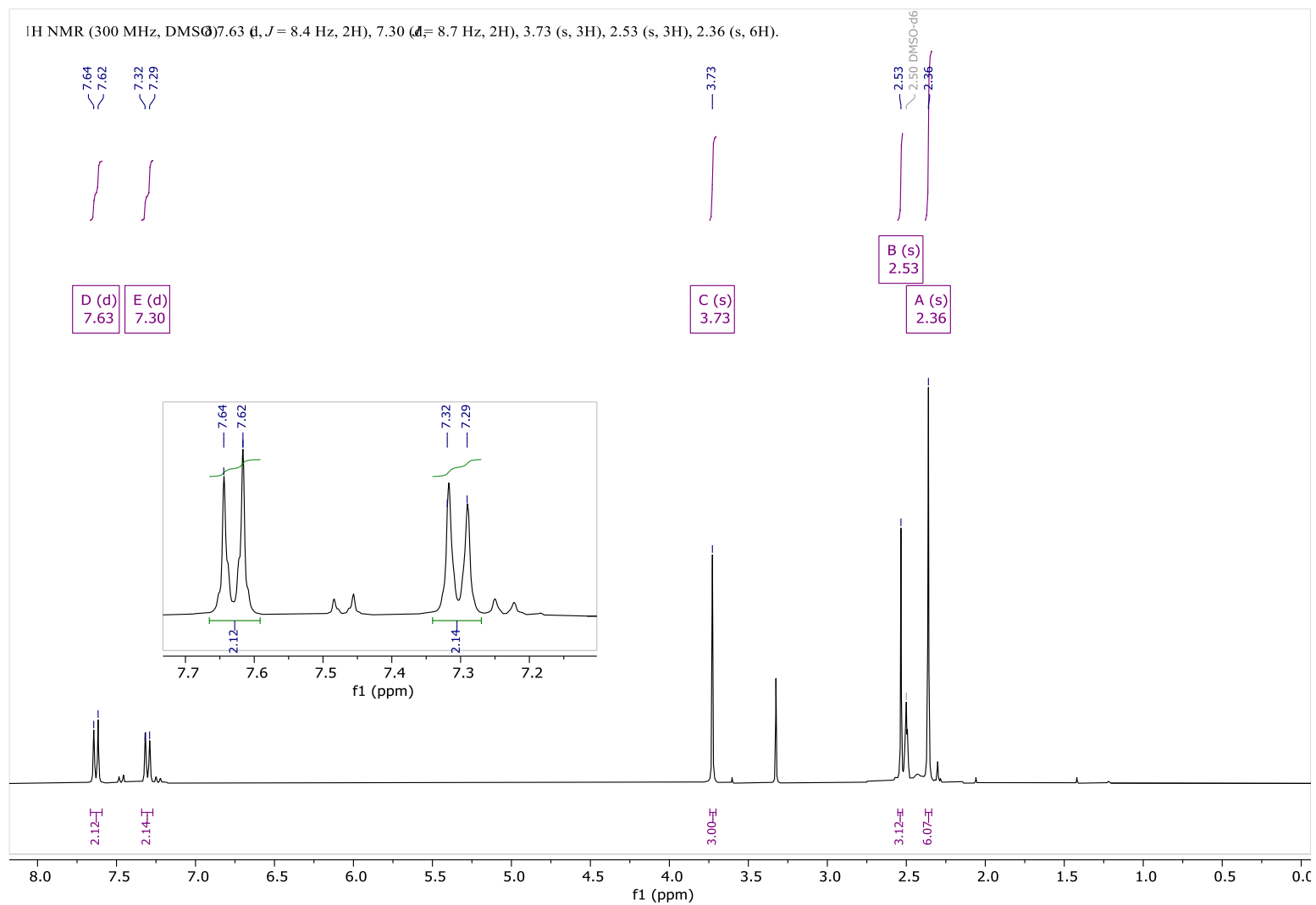


Figure S167: ¹H NMR spectrum of (*E*)-1,3,5-trimethyl-4-(*p*-toluidiazenyl)-1*H*-pyrazole in DMSO-*d*₆.

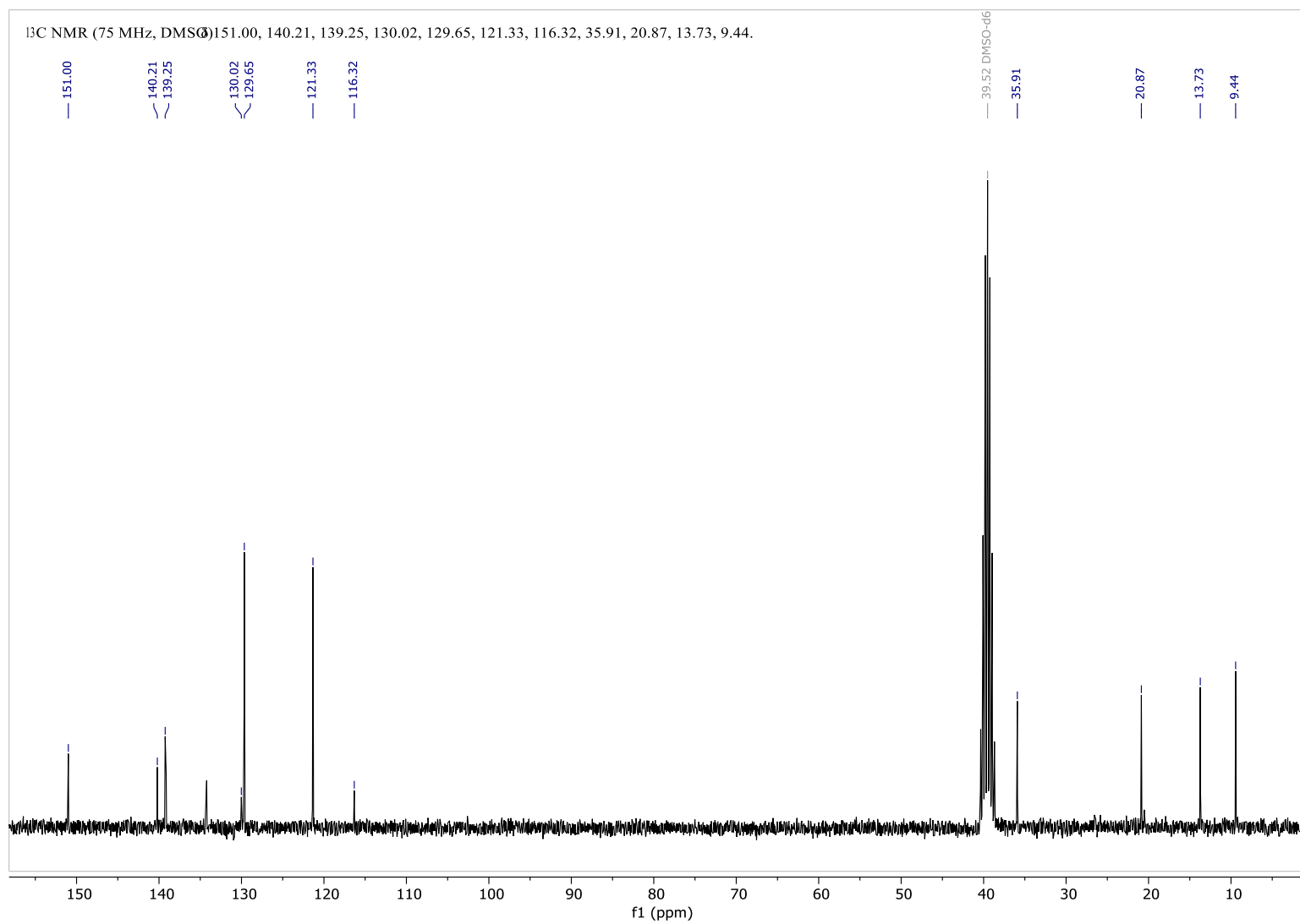


Figure S168: ¹³C NMR spectrum of (*E*)-1,3,5-trimethyl-4-(*p*-tolyl diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

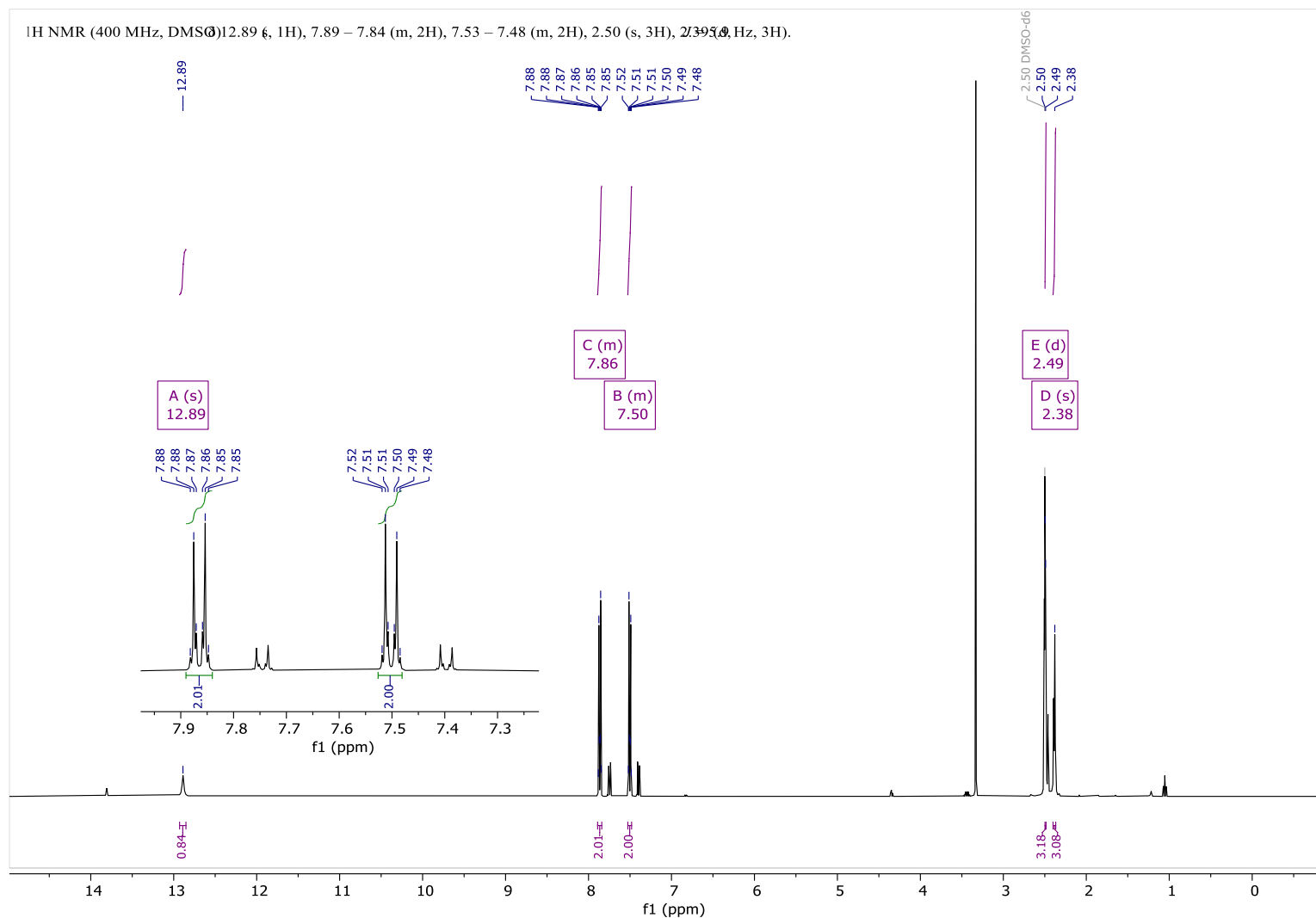


Figure S169: ¹H NMR spectrum of (*E*)-4-((4-iodophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

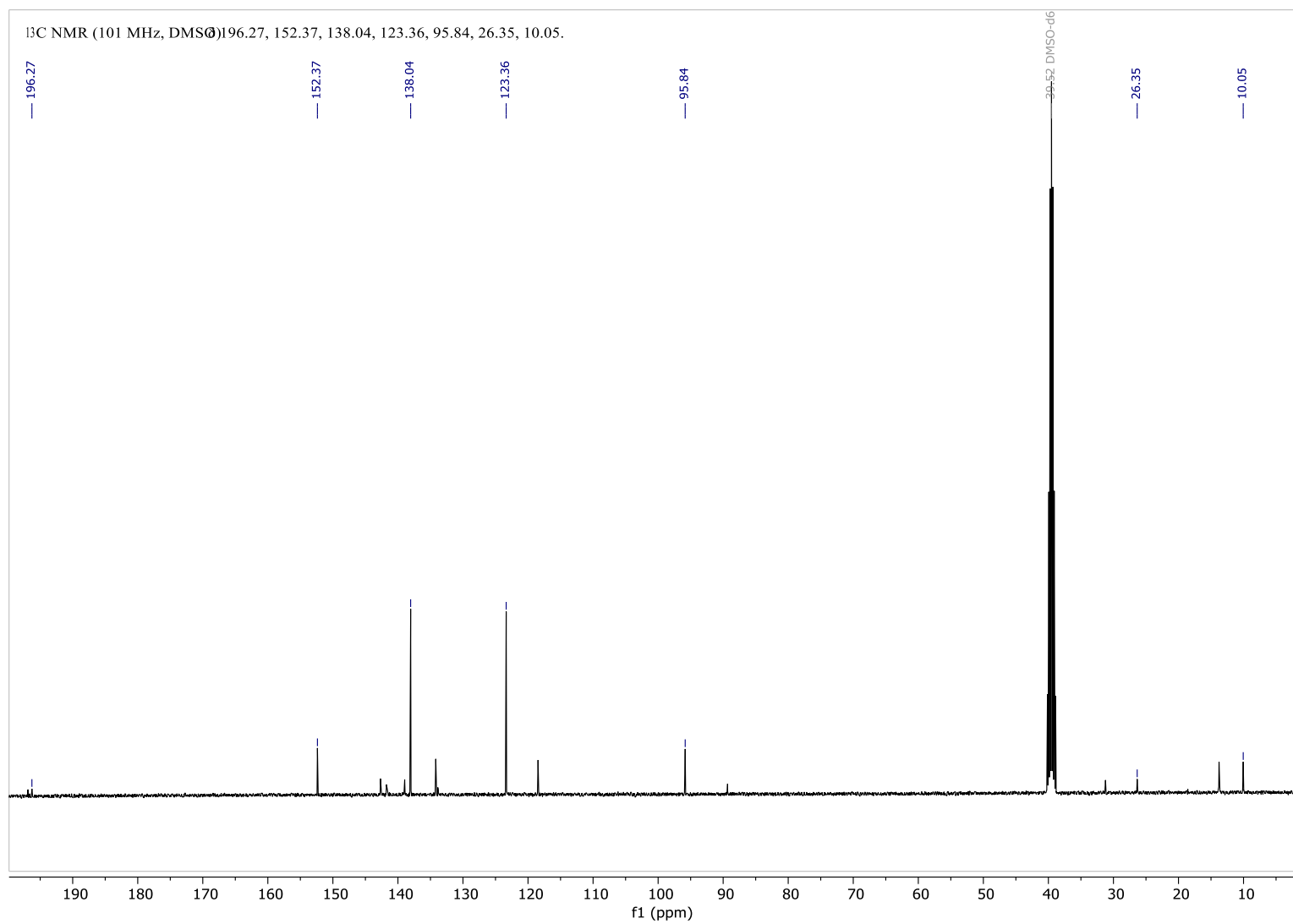


Figure S170: ¹³C NMR spectrum of (*E*)-4-((4-iodophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

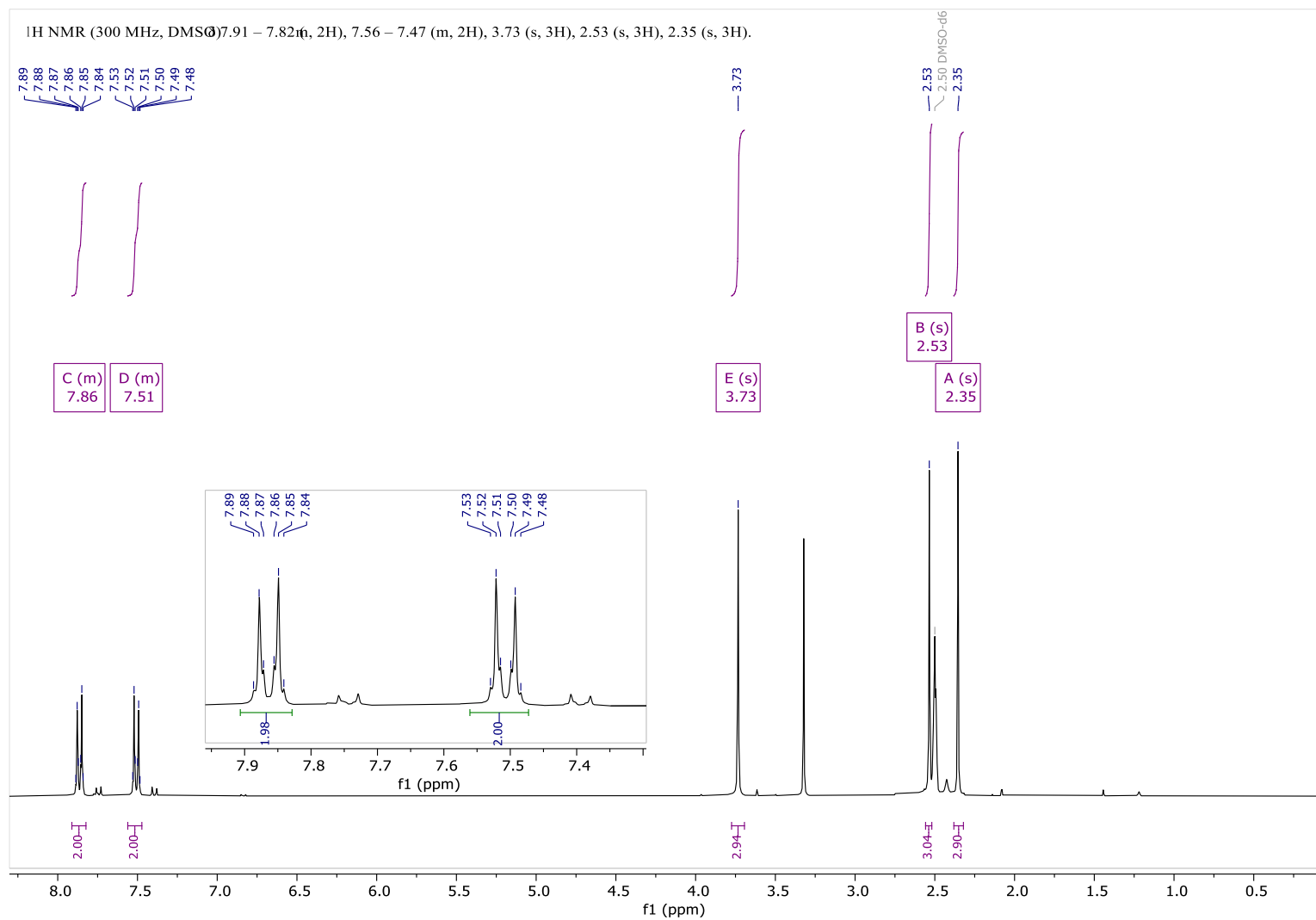


Figure S171: ¹H NMR spectrum of (*E*)-4-((4-iodophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

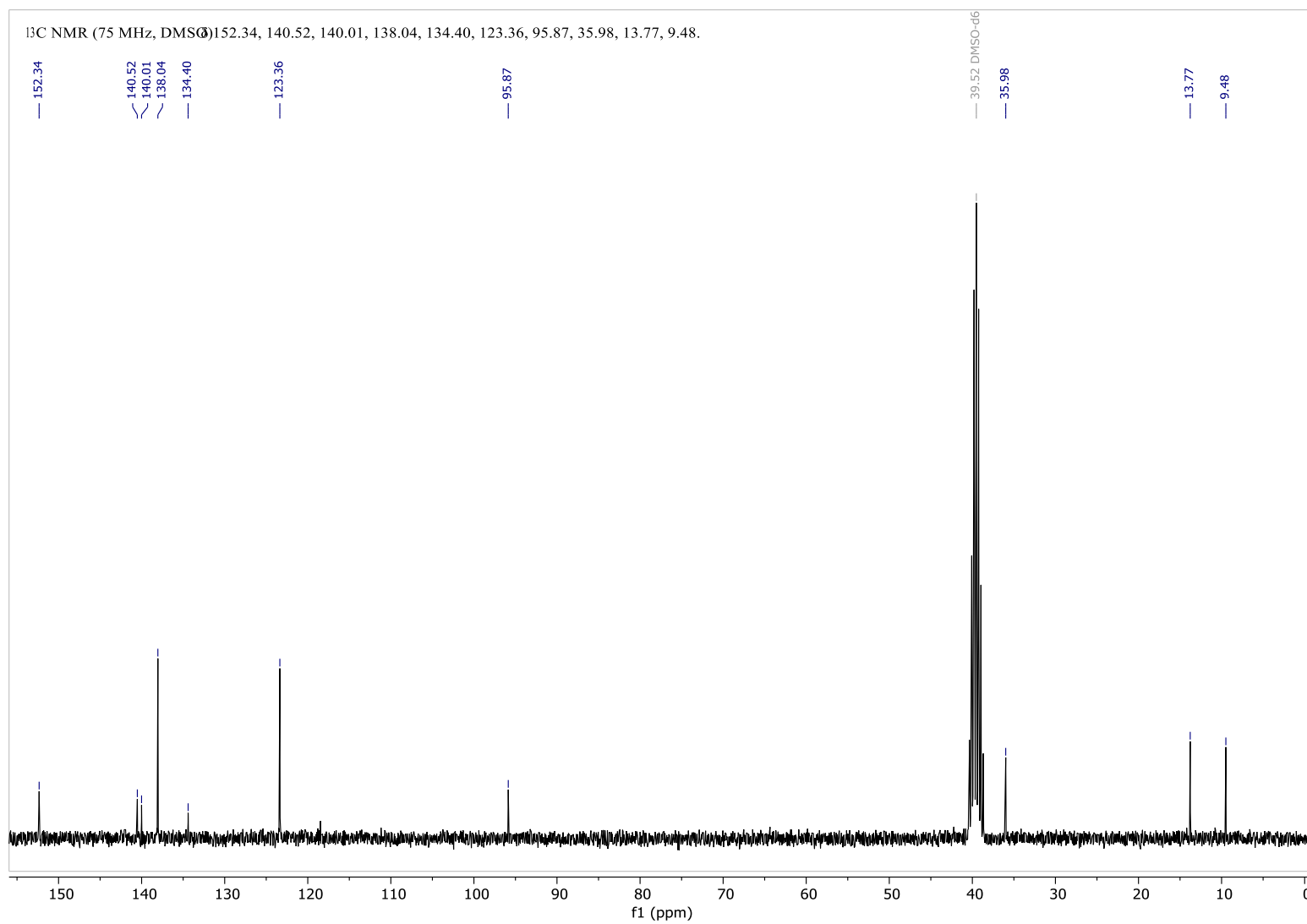


Figure 172: ¹³C NMR spectrum of (*E*)-4-((4-iodophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-d₆.

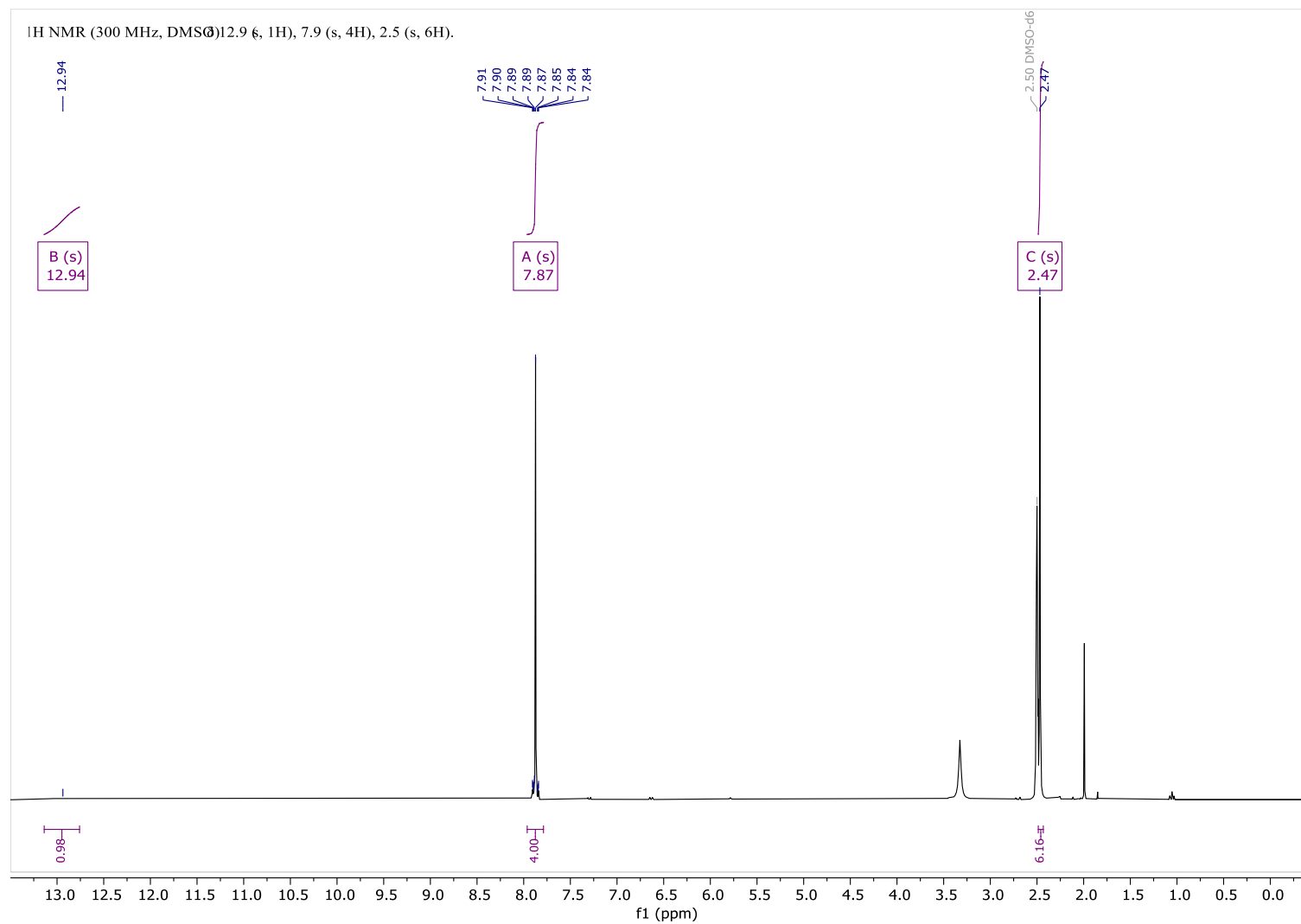


Figure S173: ¹H NMR spectrum of (*E*)-3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

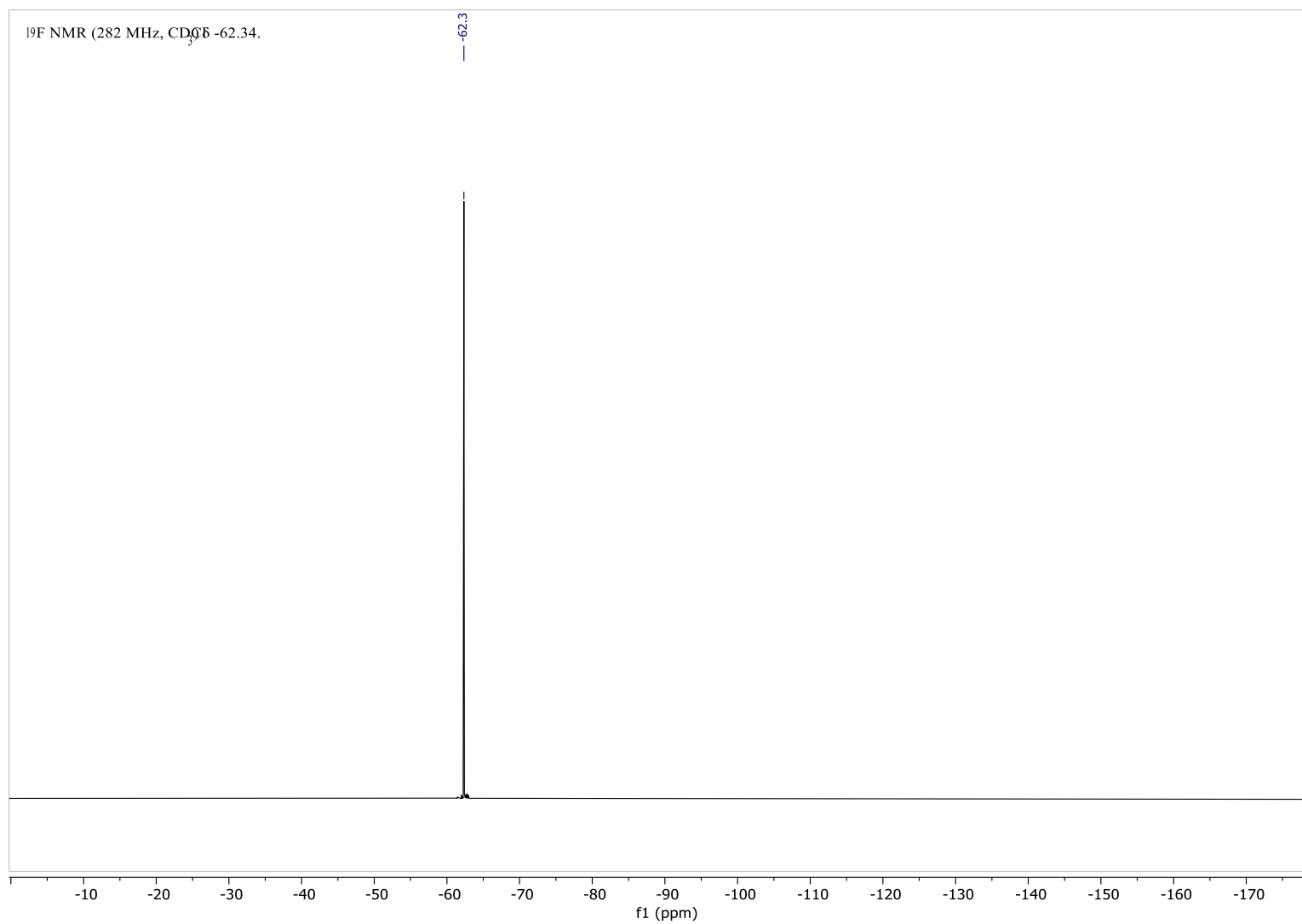


Figure S174: ¹⁹F NMR spectrum of (*E*)-3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

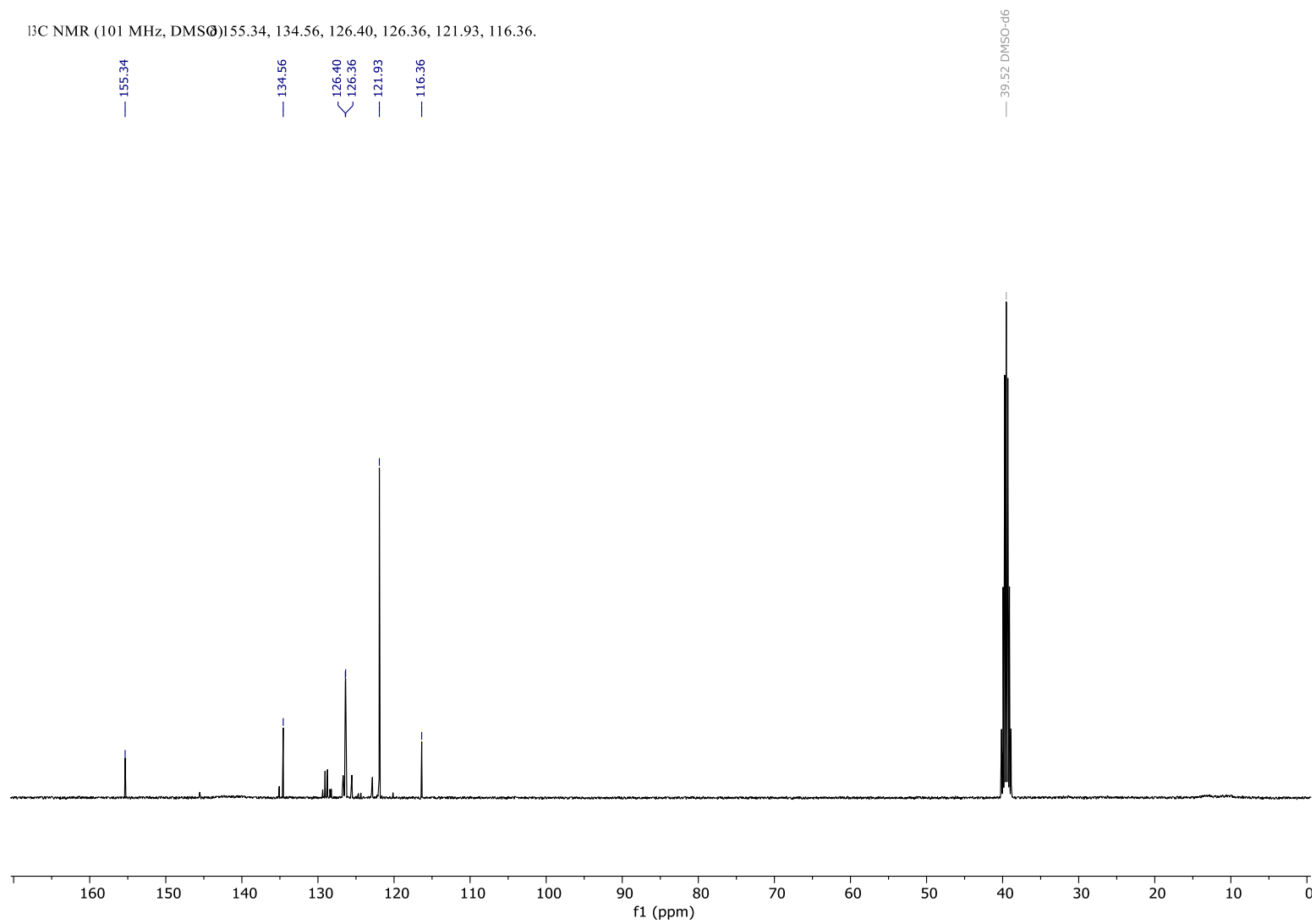


Figure S175: ¹³C NMR spectrum of (*E*)-3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

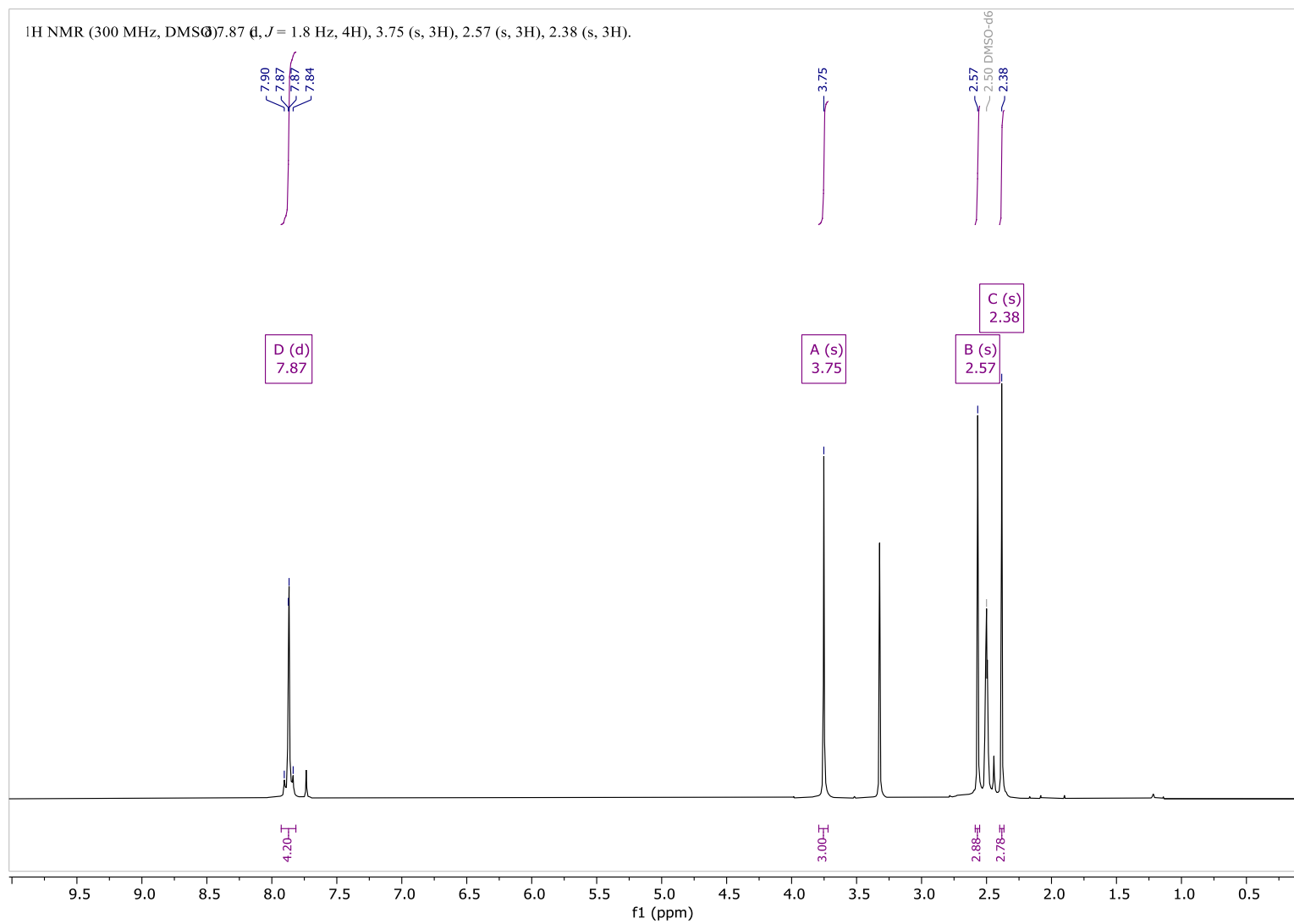


Figure S176: ¹H NMR spectrum of (*E*)-1,3,5-trimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

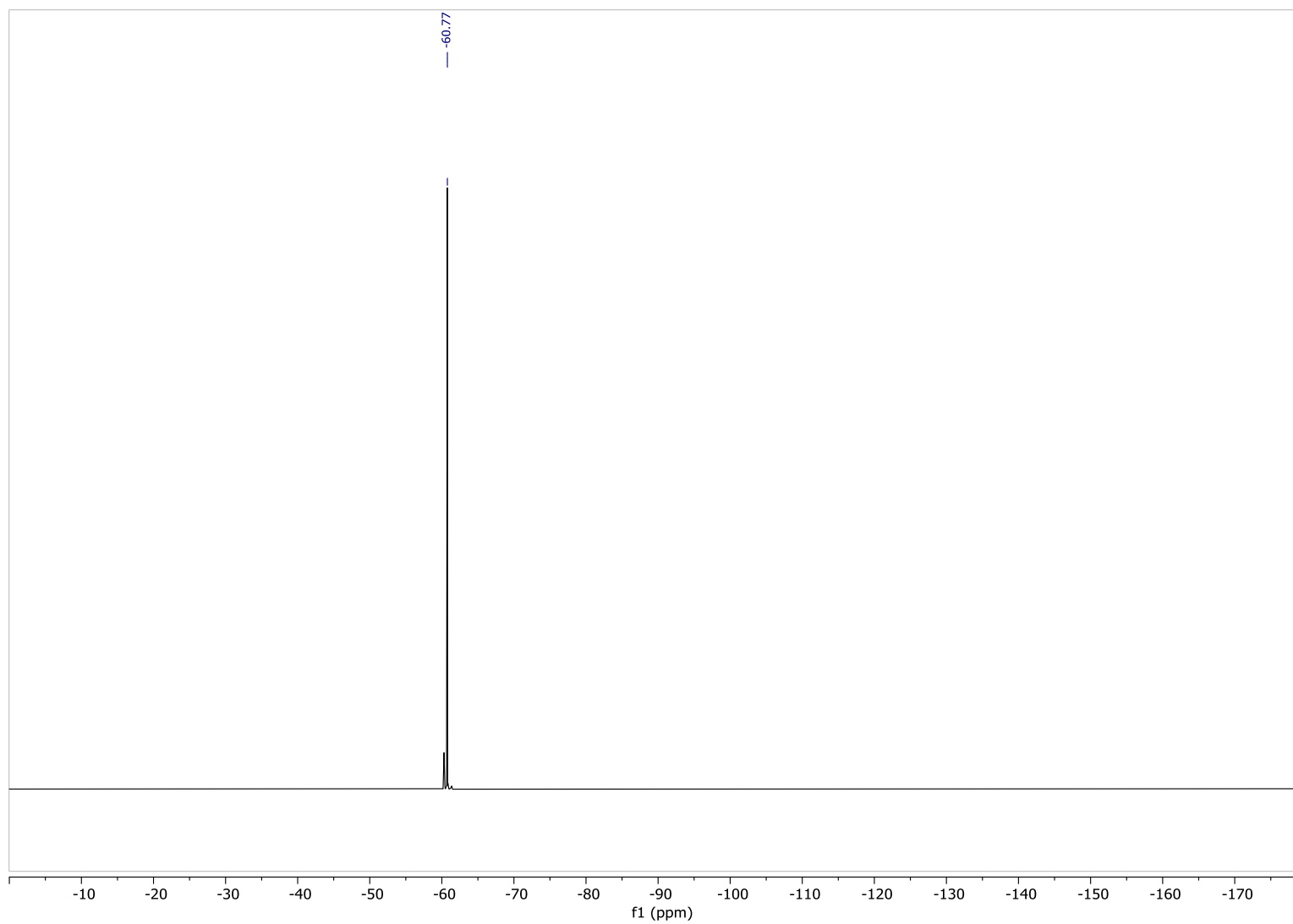


Figure S177: ^{19}F NMR spectrum of (*E*)-1,3,5-trimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in $\text{DMSO}-d_6$.

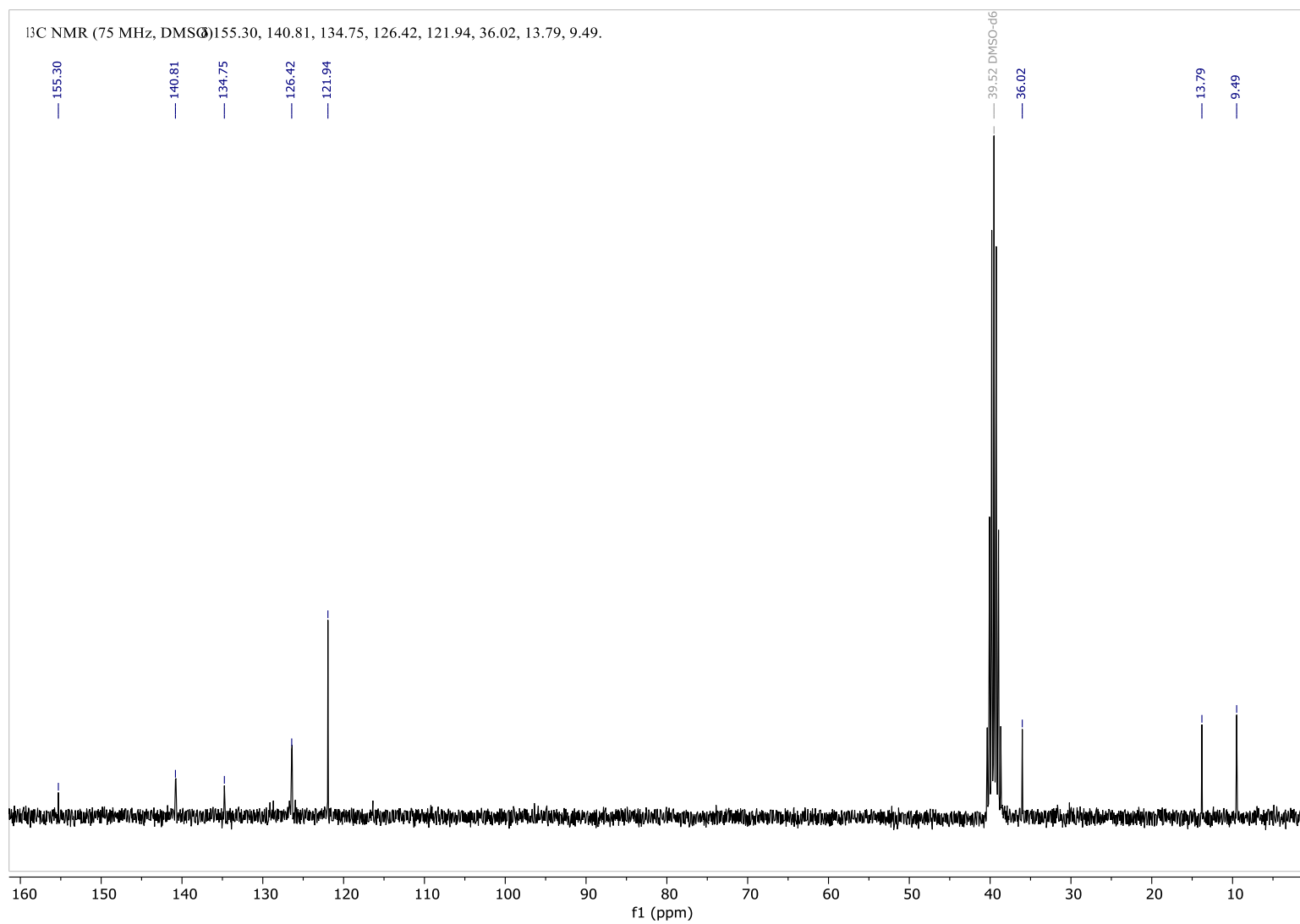


Figure S178: ¹³C NMR spectrum of (*E*)-1,3,5-trimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

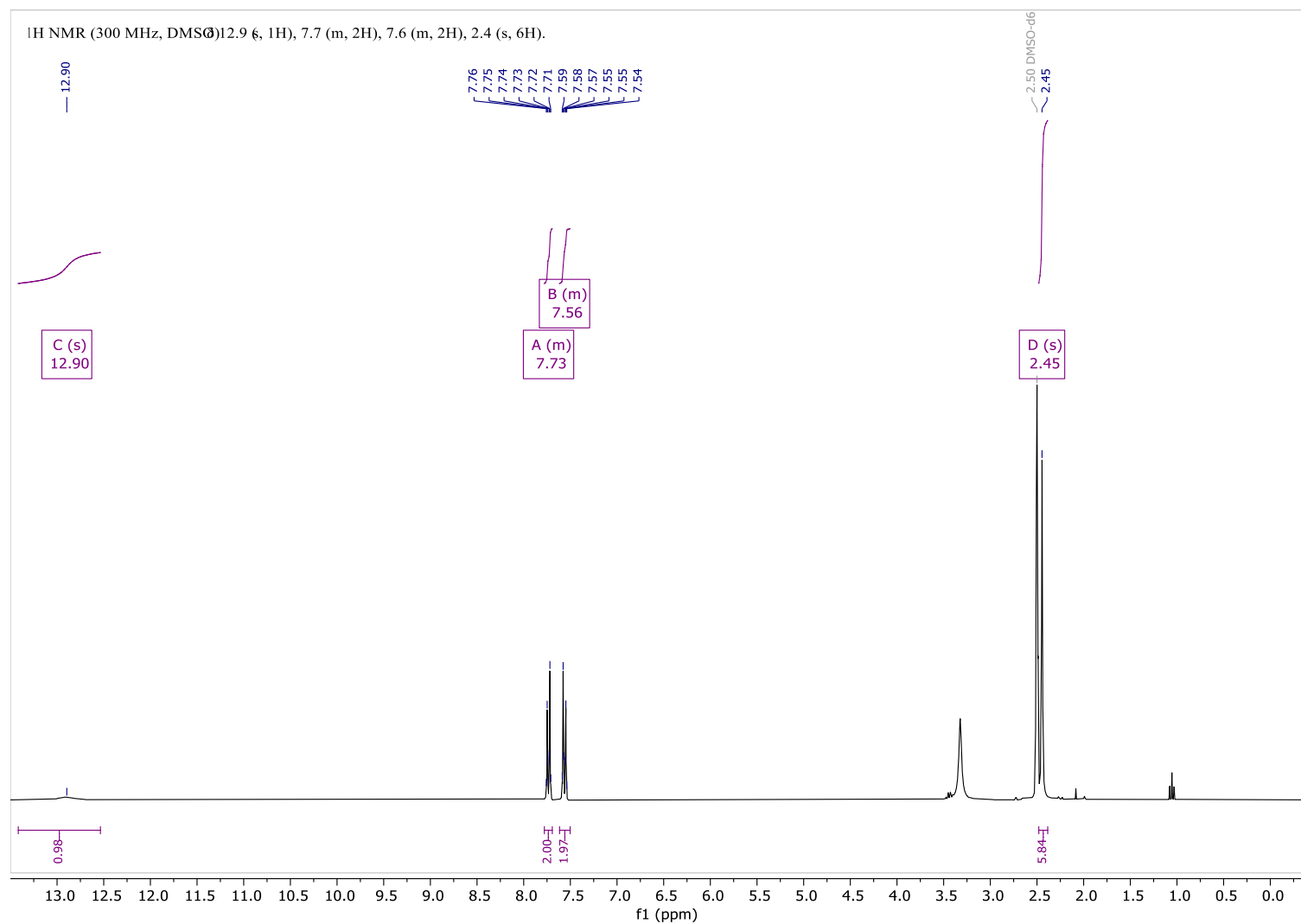


Figure S179: ¹H NMR spectrum of (*E*)-4-((4-chlorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

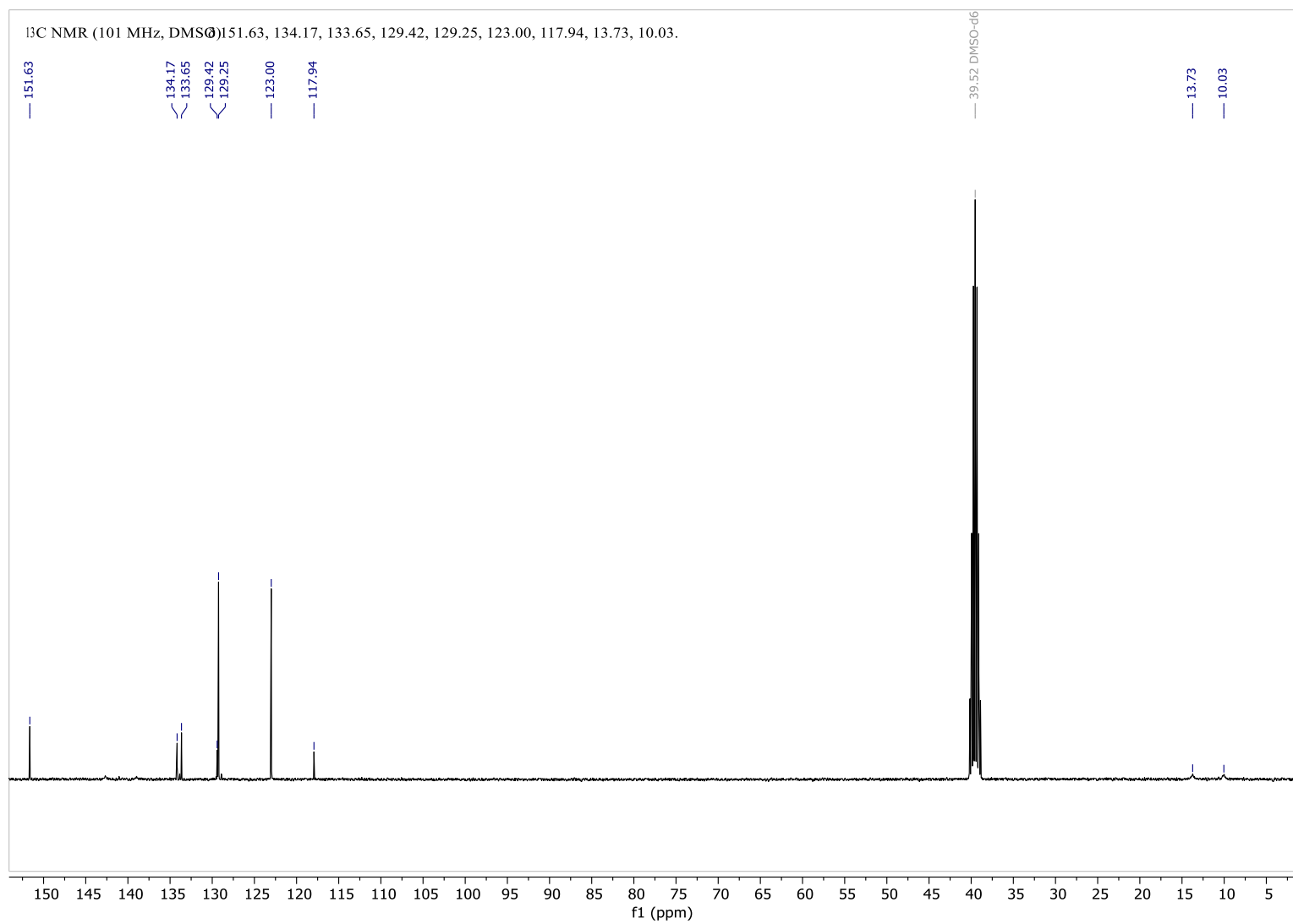


Figure S180: ¹³C NMR spectrum of (*E*)-4-((4-chlorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

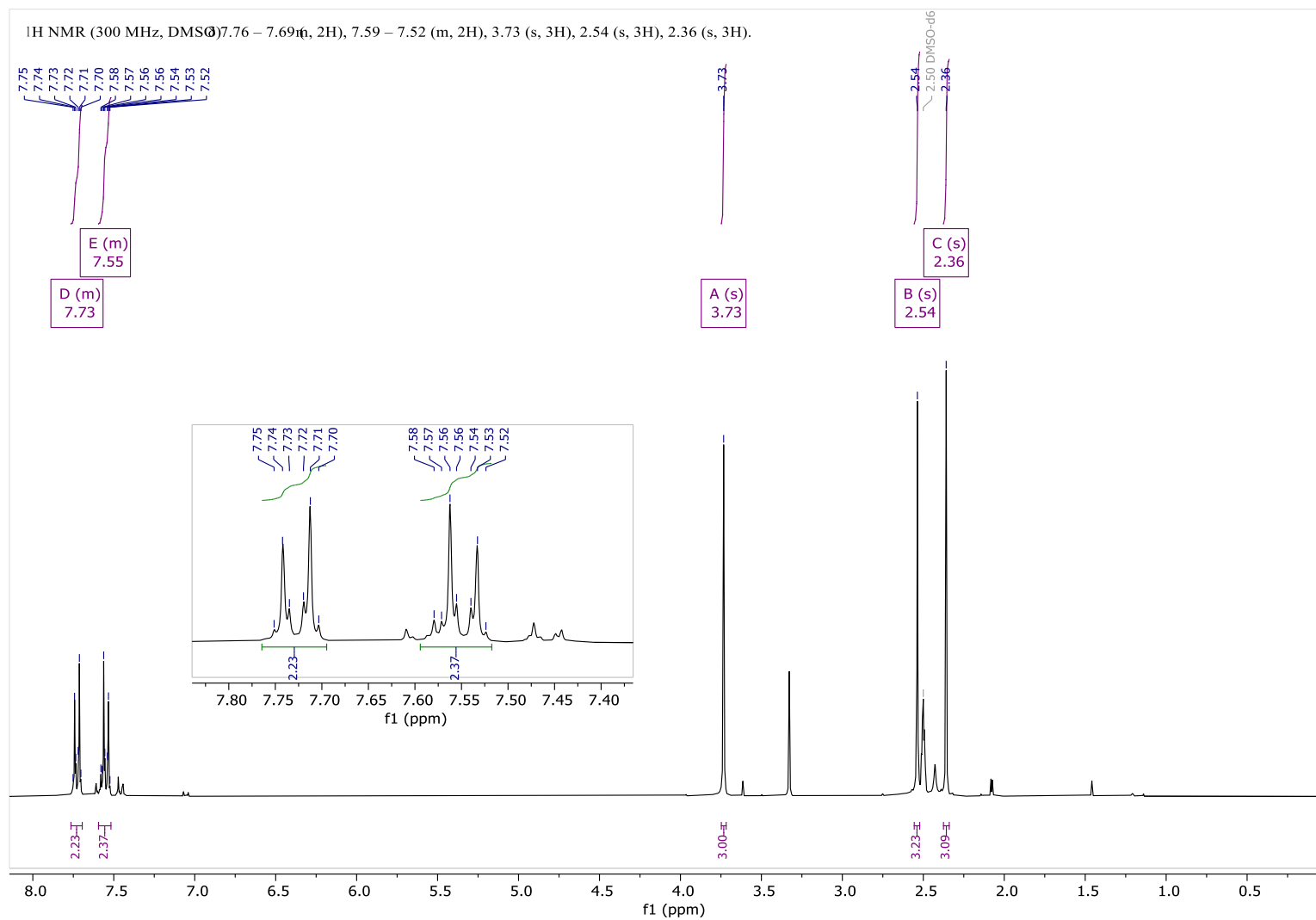


Figure S181: ¹H NMR spectrum of (*E*)-4-((4-chlorophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

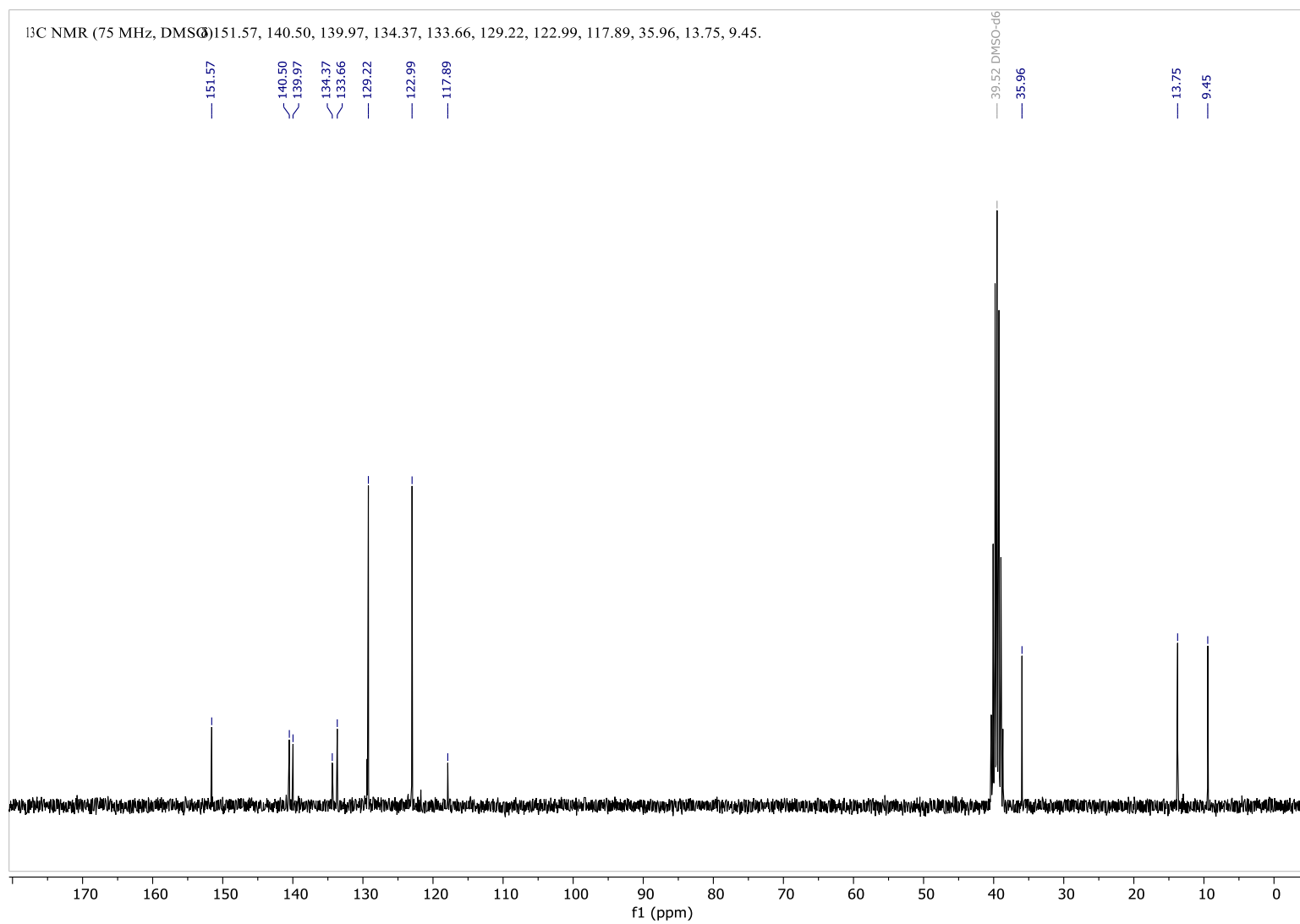


Figure S182: ¹³C NMR spectrum of (*E*)-4-((4-chlorophenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

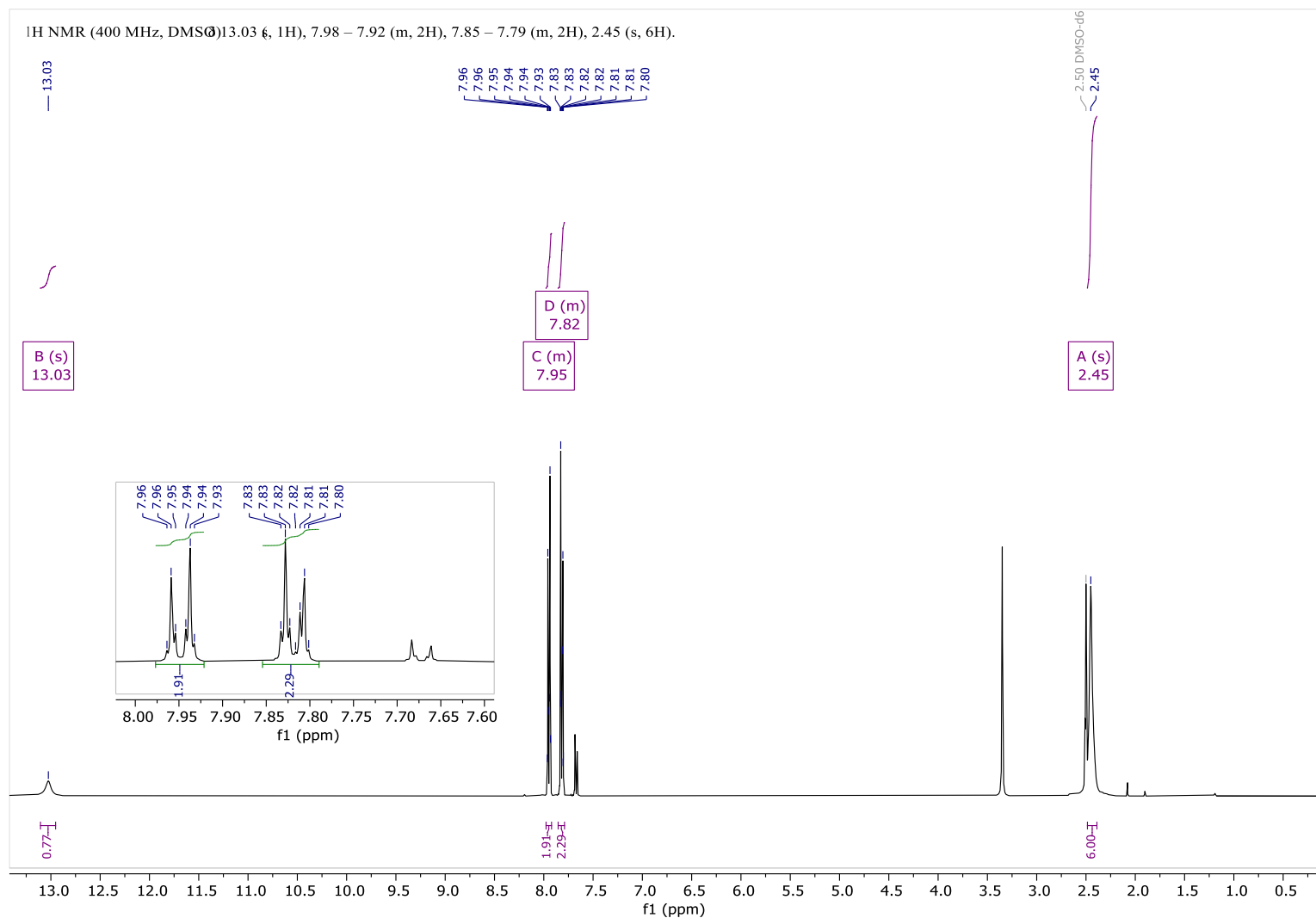


Figure S183: ¹H NMR spectrum of (*E*)-4-((3,5-dimethyl-1*H*-pyrazol-4-yl)diazanyl)benzonitrile in DMSO-*d*₆.

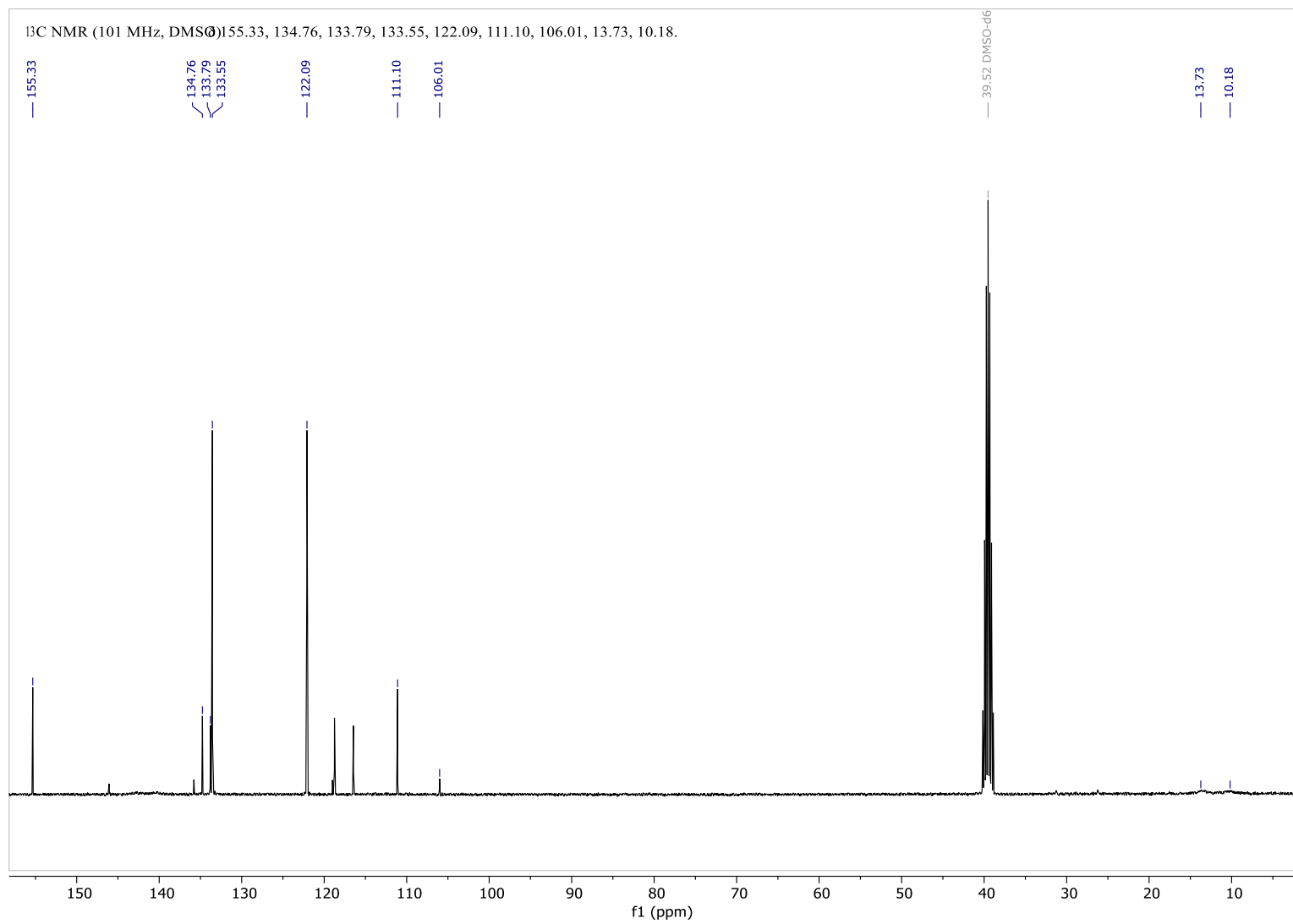


Figure S184: ¹³C NMR spectrum of (*E*)-4-((3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl)benzonitrile in DMSO-*d*₆.

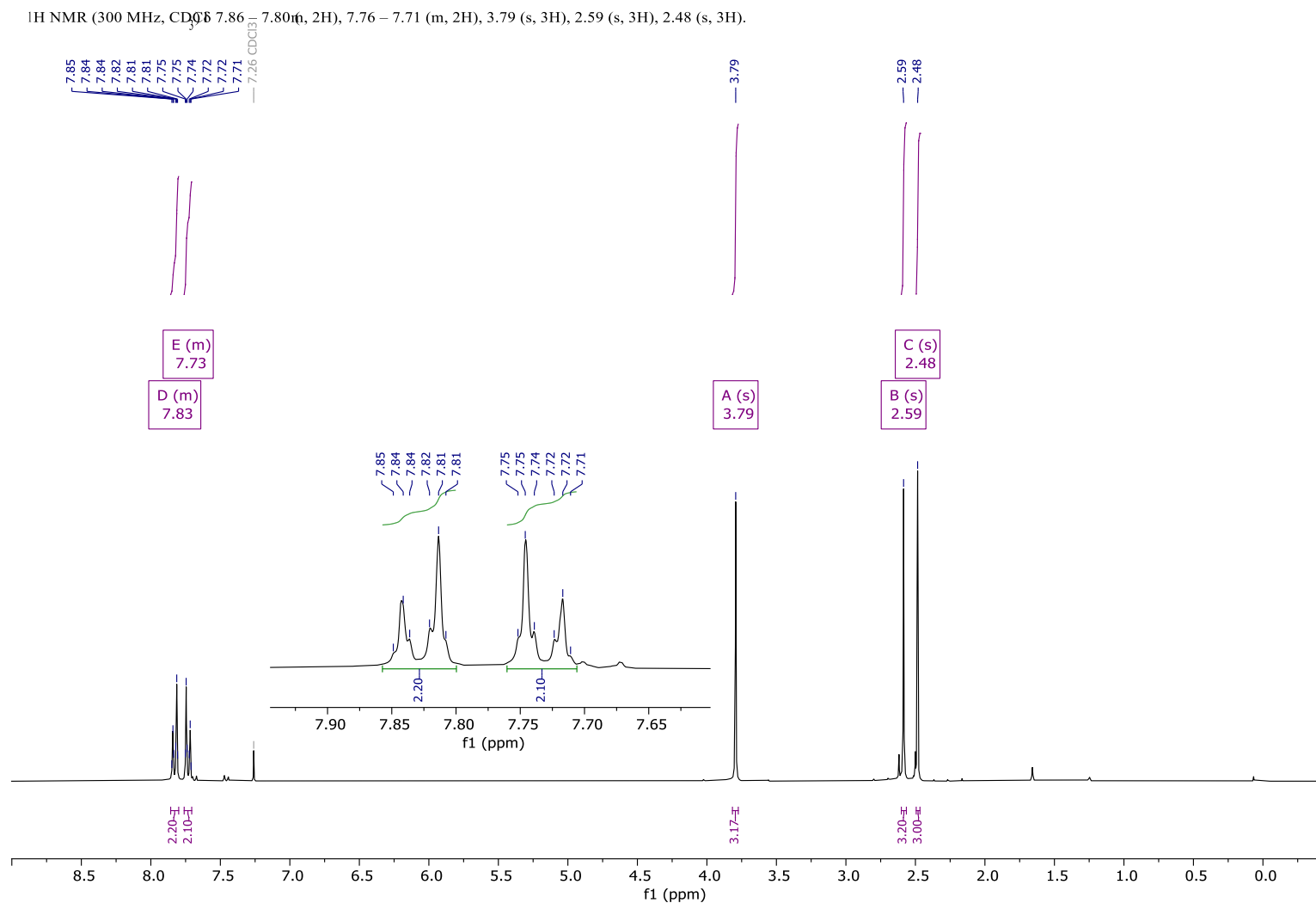


Figure S185: ^1H NMR spectrum of (*E*)-4-((1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazenyl)benzonitrile in CDCl_3 .

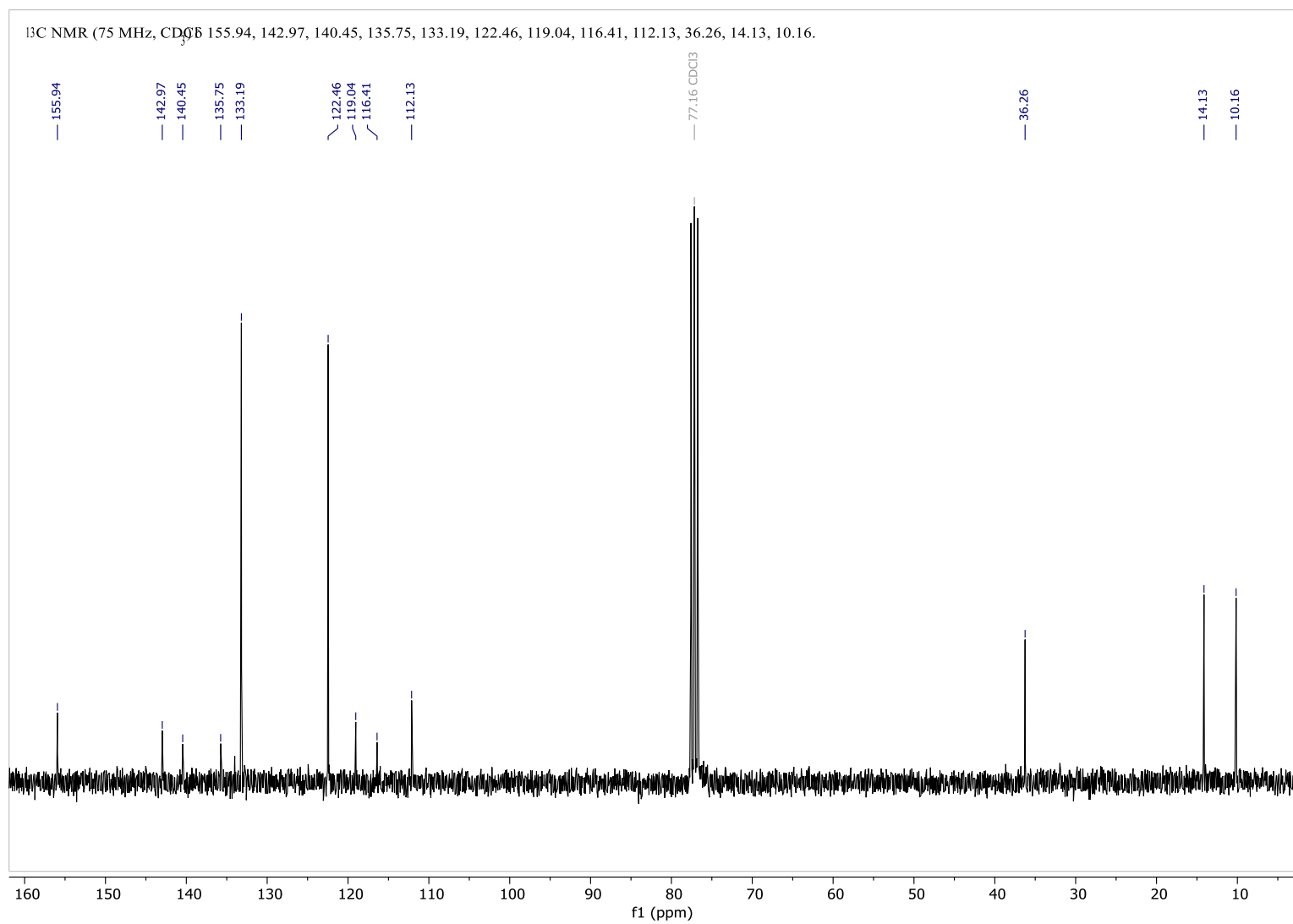


Figure S186: ¹³C NMR spectrum of (*E*)-4-((1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazenyl)benzonitrile in CDCl₃.

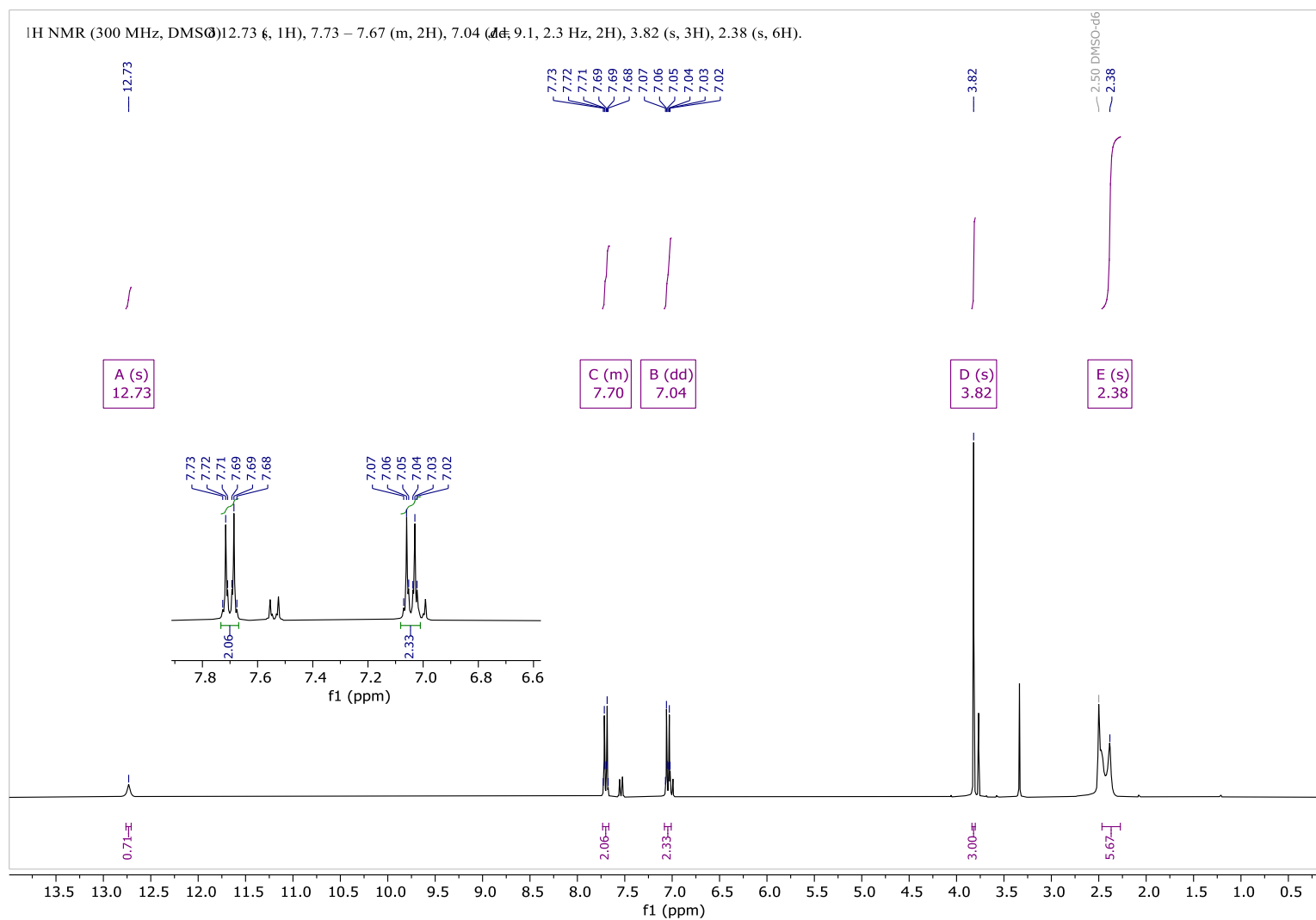


Figure S187: ¹H NMR spectrum of (*E*)-4-((4-methoxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

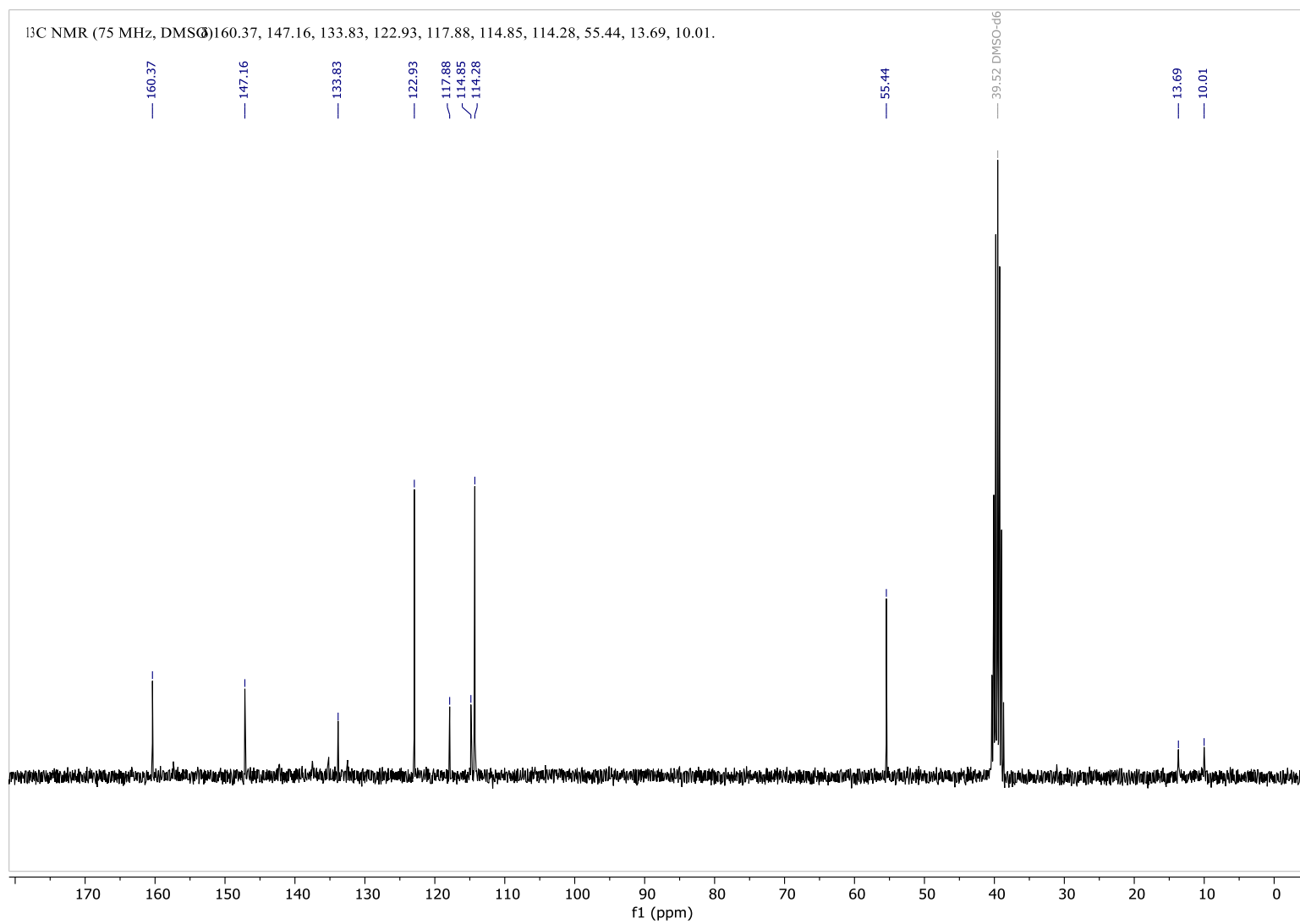


Figure S188: ¹³C NMR spectrum of (*E*)-4-((4-methoxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazole in DMSO-*d*₆.

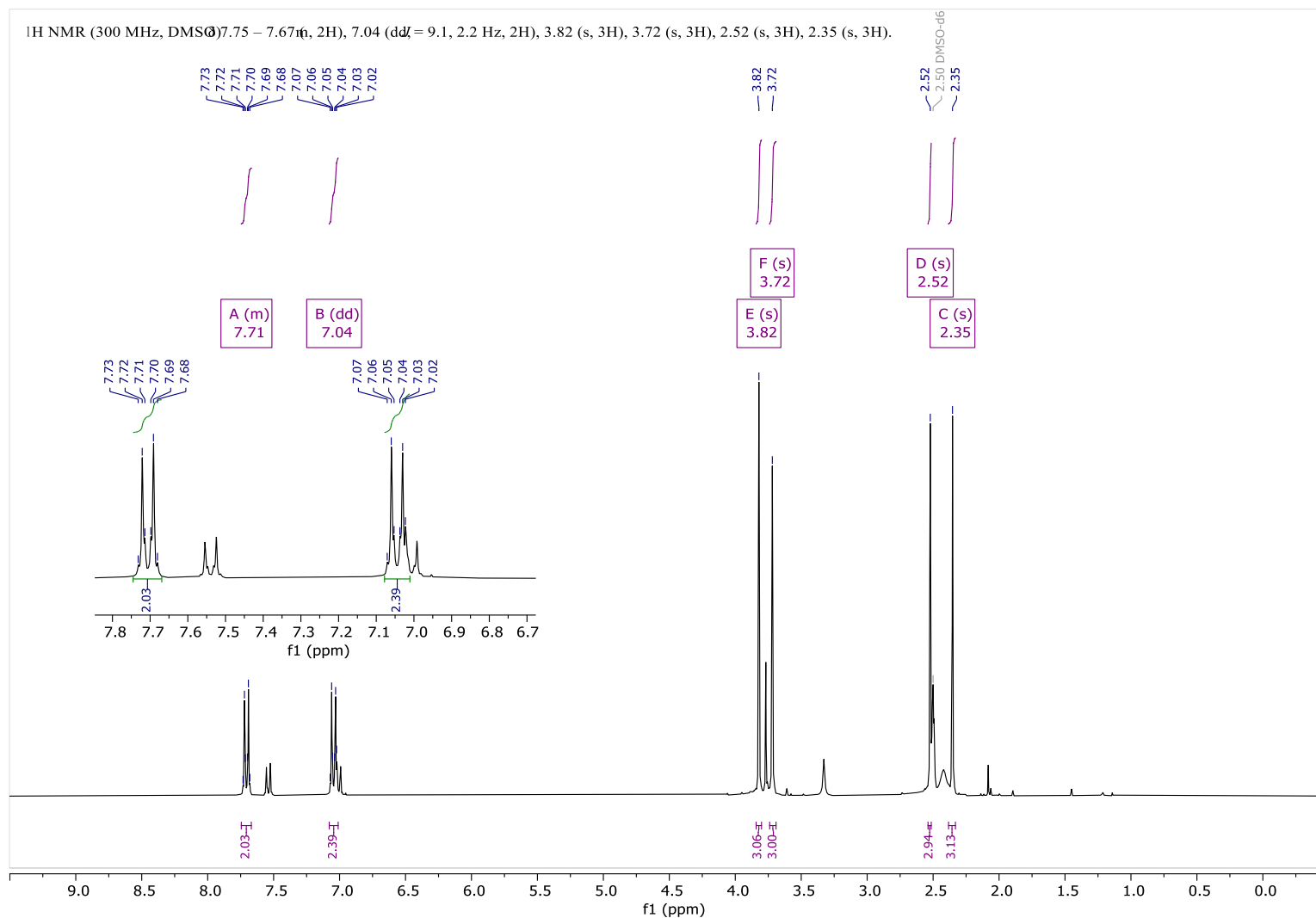


Figure S189: ¹H NMR spectrum of (*E*)-4-((4-methoxyphenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

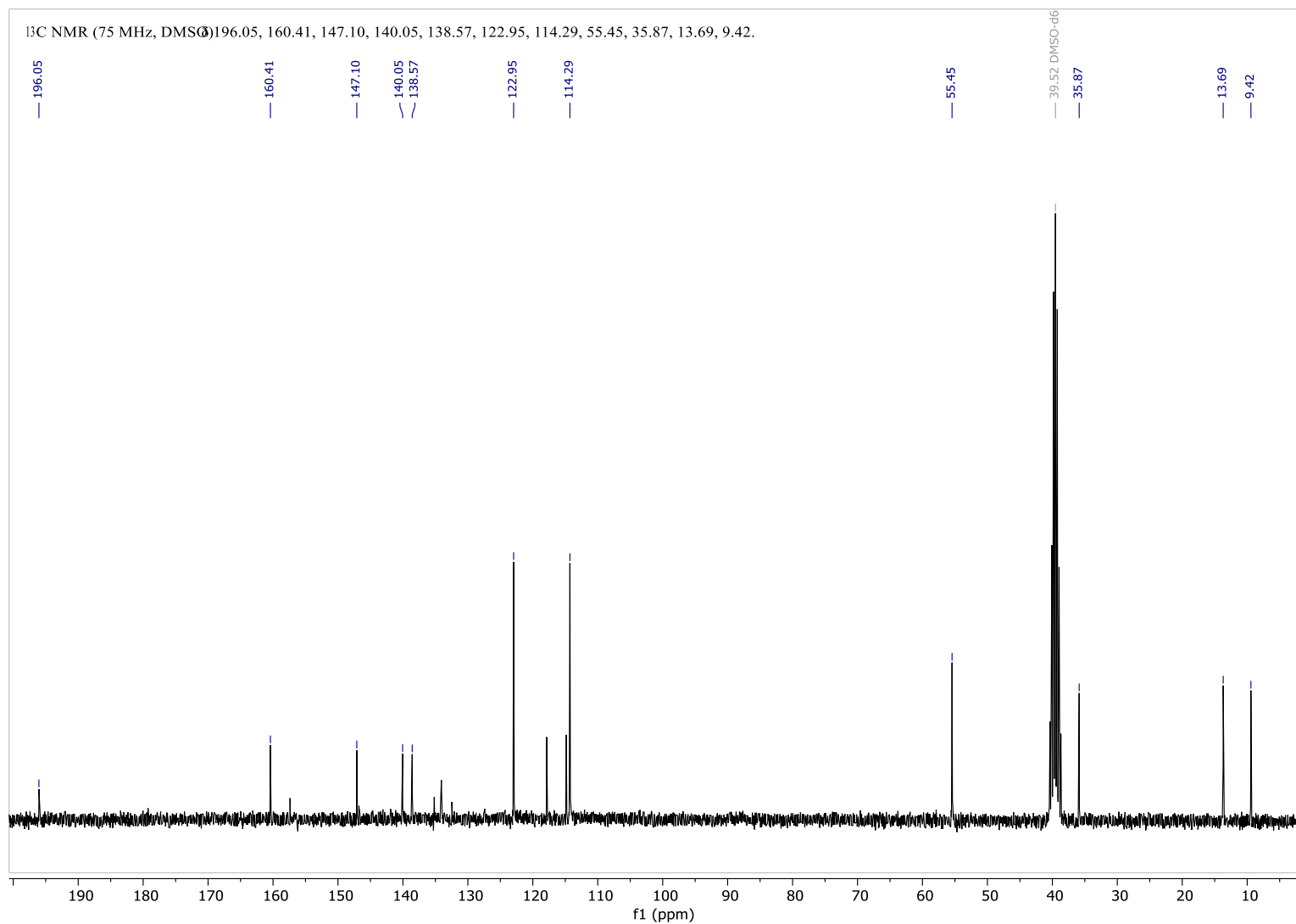


Figure S190: ¹³C NMR spectrum of (*E*)-4-((4-methoxyphenyl)diazenyl)-1,3,5-trimethyl-1*H*-pyrazole in DMSO-*d*₆.

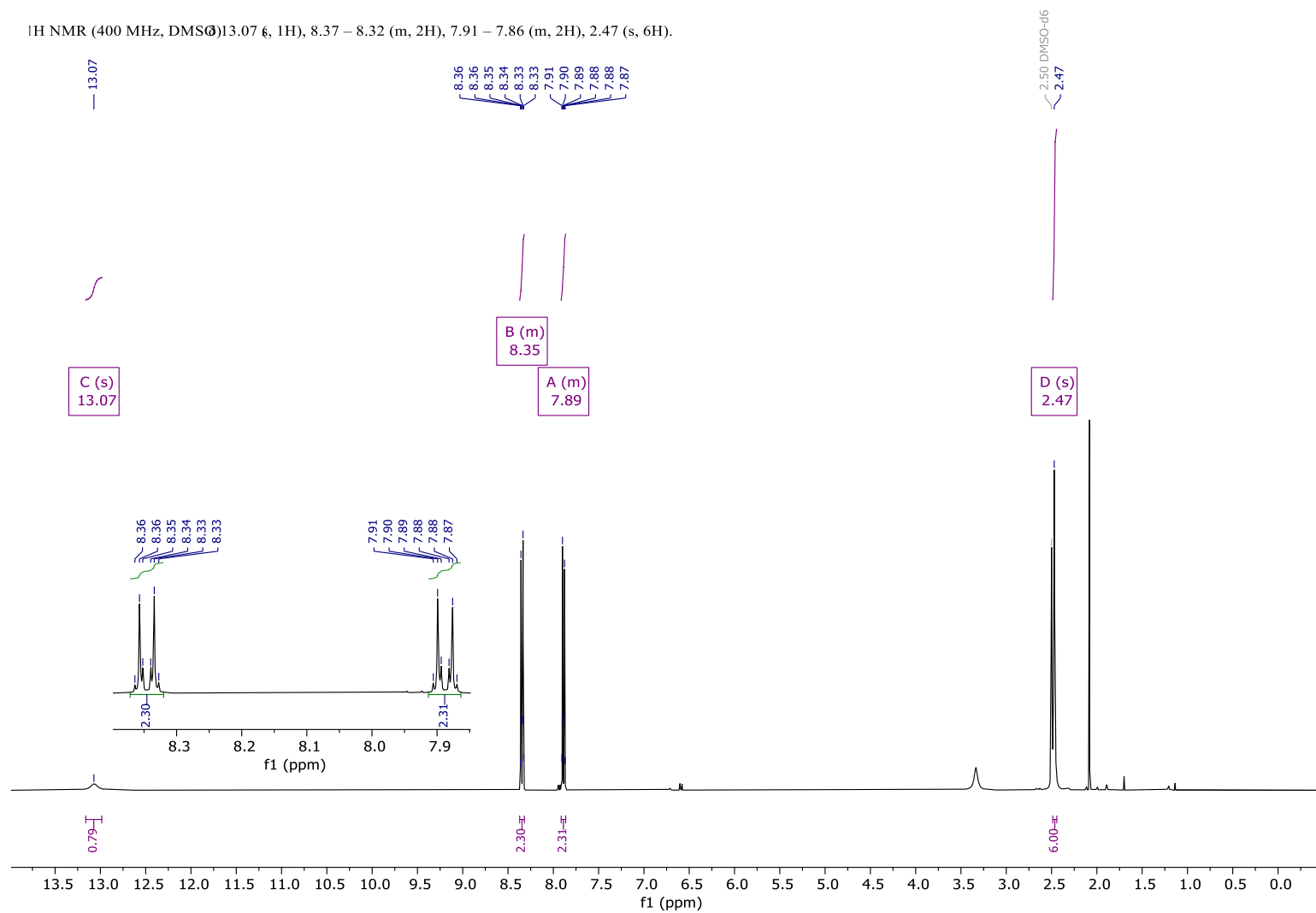


Figure S191: ¹H NMR spectrum of (*E*)-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

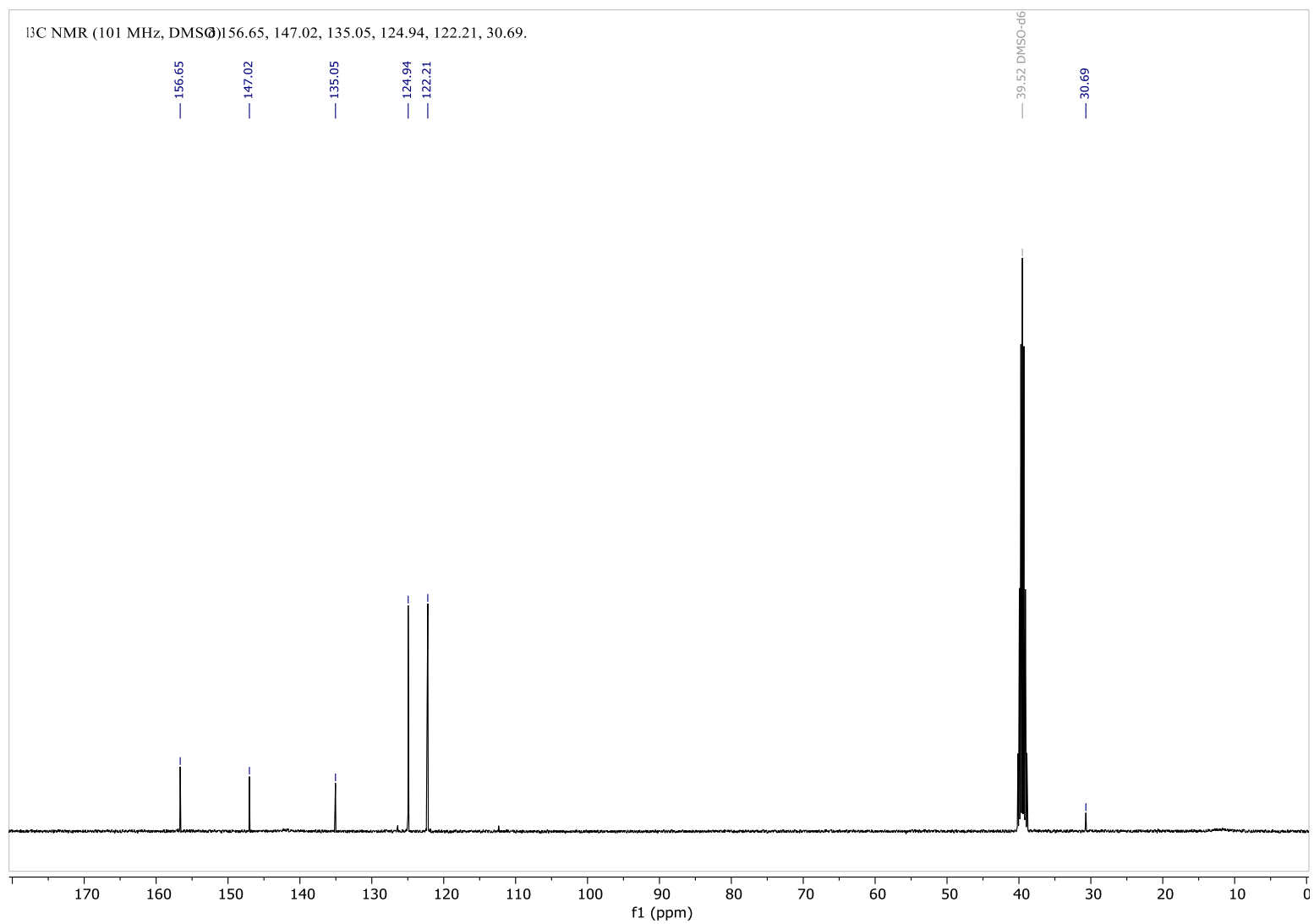


Figure S192: ¹³C NMR spectrum of (*E*)-3,5-dimethyl-4-((4-nitrophenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

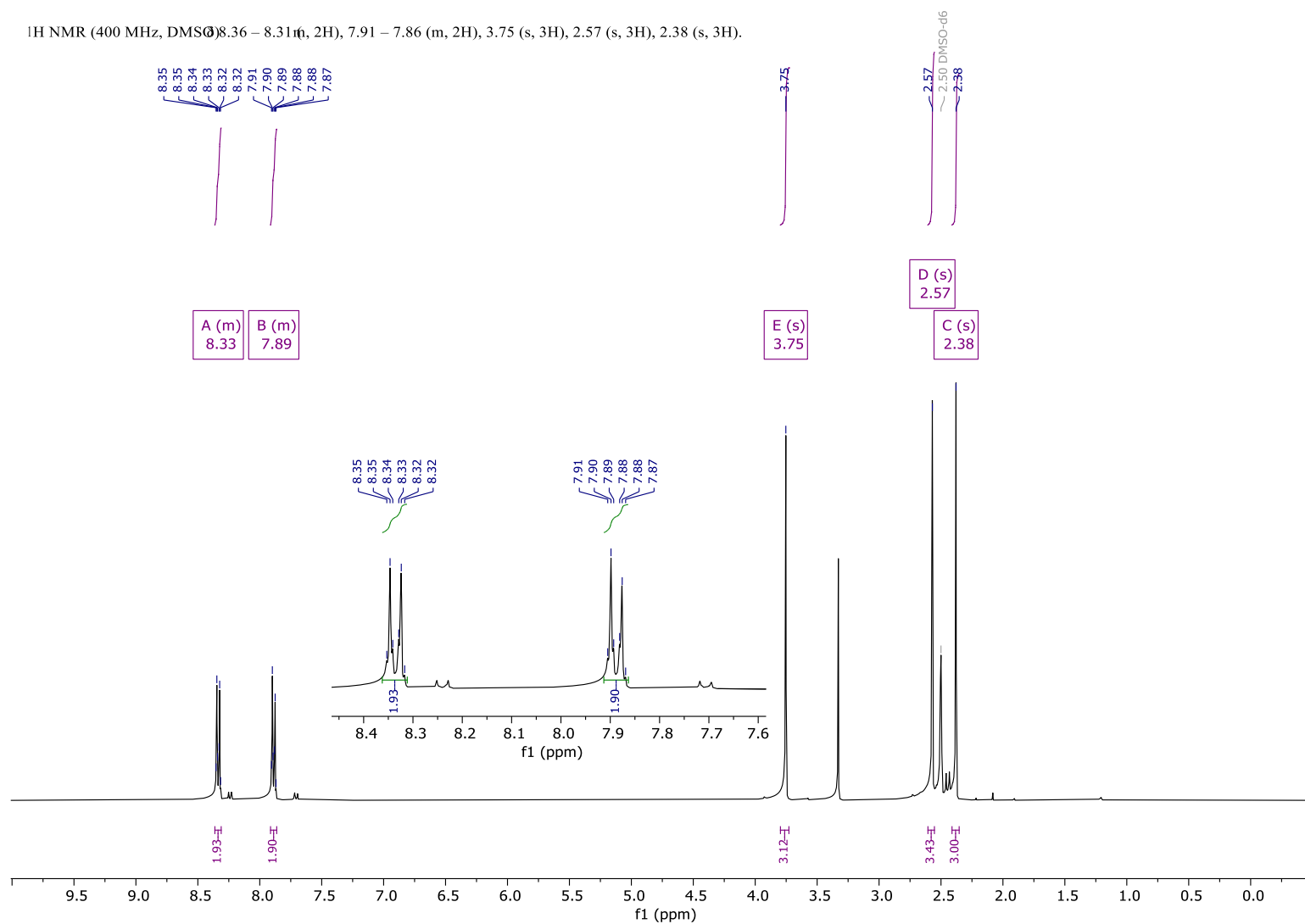


Figure S193: ¹H NMR spectrum of (*E*)-1,3,5-trimethyl-4-((4-nitrophenyl)diazonyl)-1*H*-pyrazole in DMSO-*d*₆.

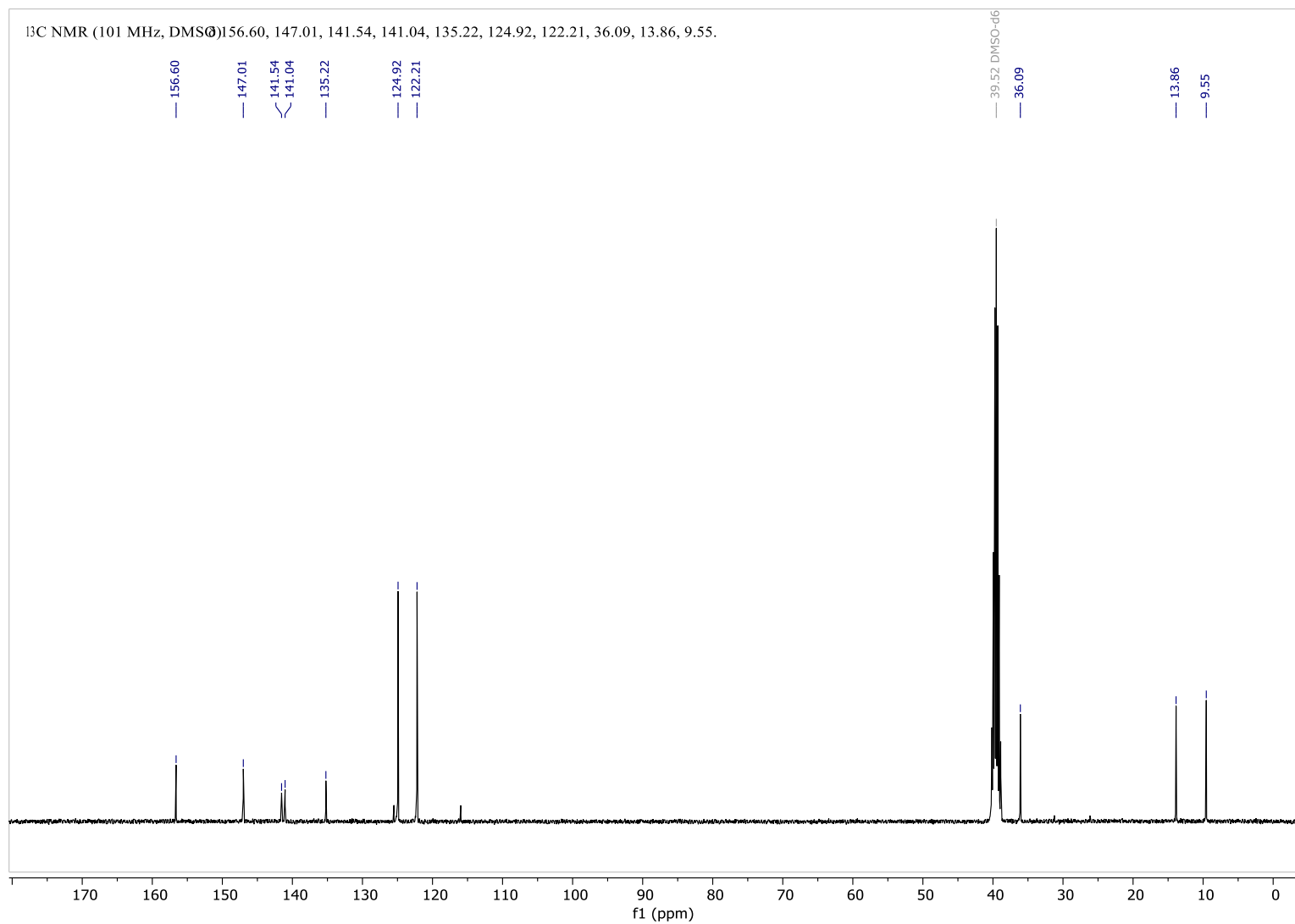


Figure S194: ¹³C NMR spectrum of (*E*)-1,3,5-trimethyl-4-((4-nitrophenyl)diazenyl)-1*H*-pyrazole in DMSO-*d*₆.

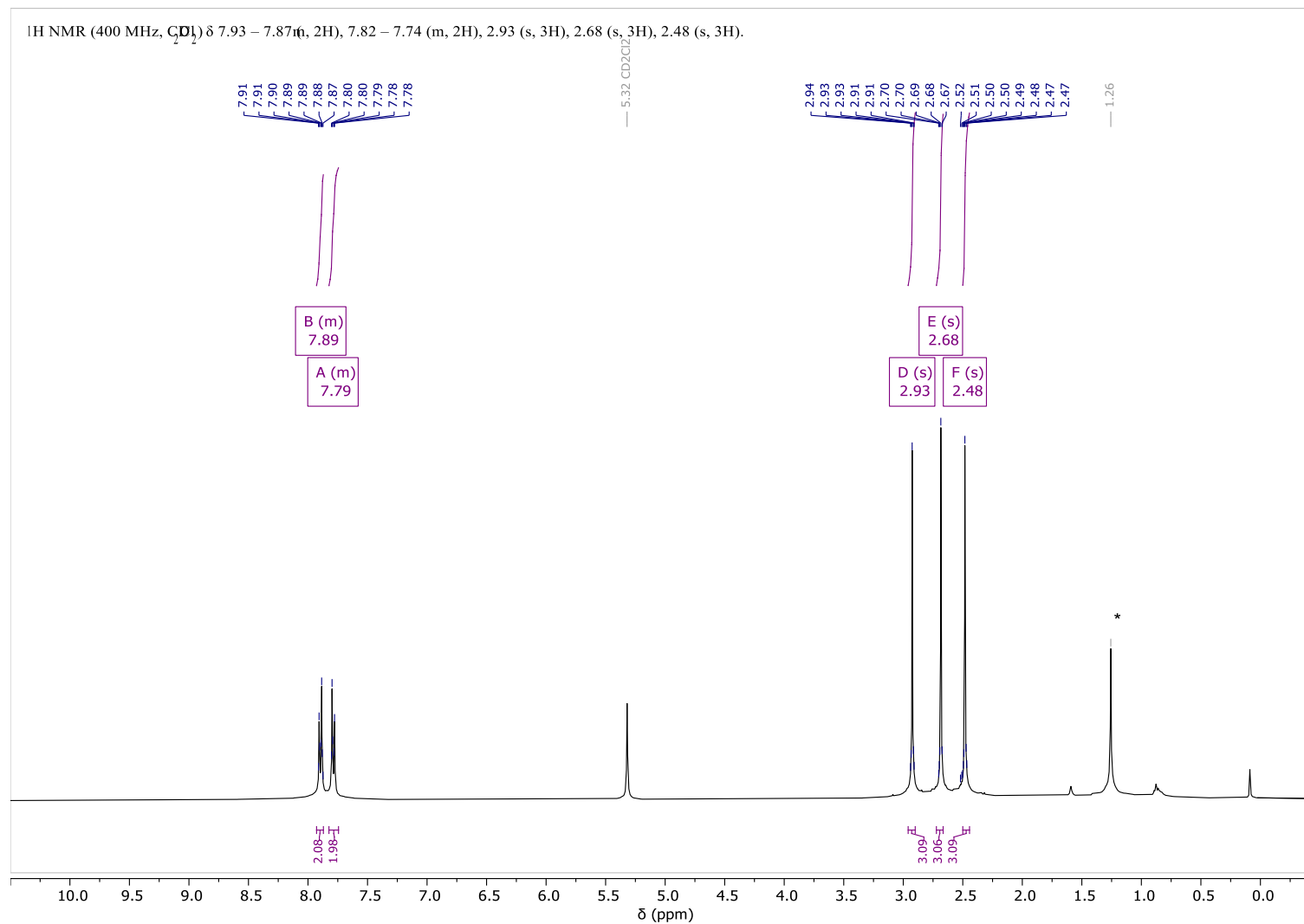


Figure S195: ¹H NMR spectrum of (*E*)-4-((1-acetyl-3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl)benzonitrile in CD₂Cl₂. Asterisk denotes grease.

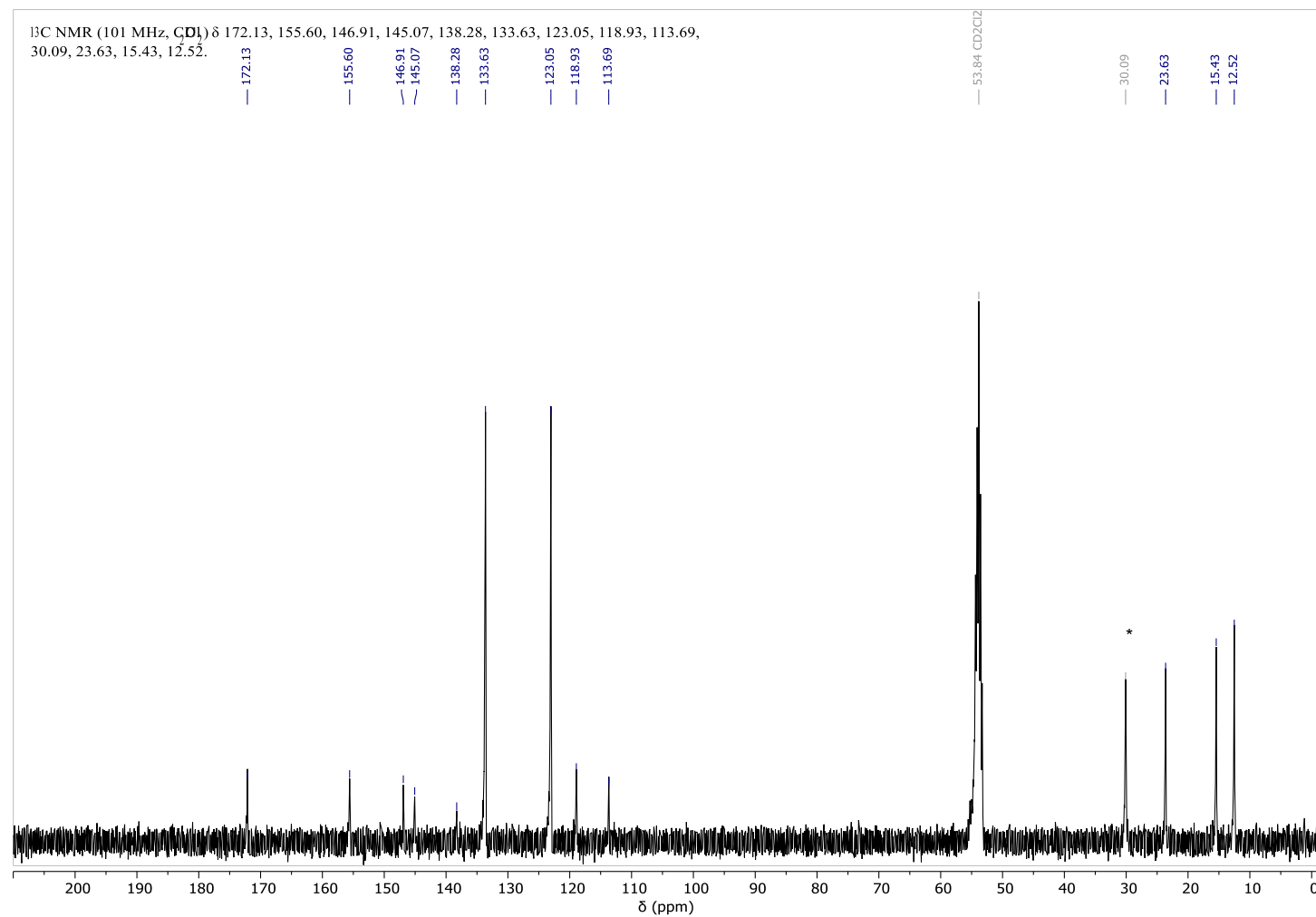


Figure S196: ¹³C NMR spectrum of (*E*)-4-((1-acetyl-3,5-dimethyl-1*H*-pyrazol-4-yl)diazenyl)benzonitrile in CD₂Cl₂. Asterisk denotes grease.

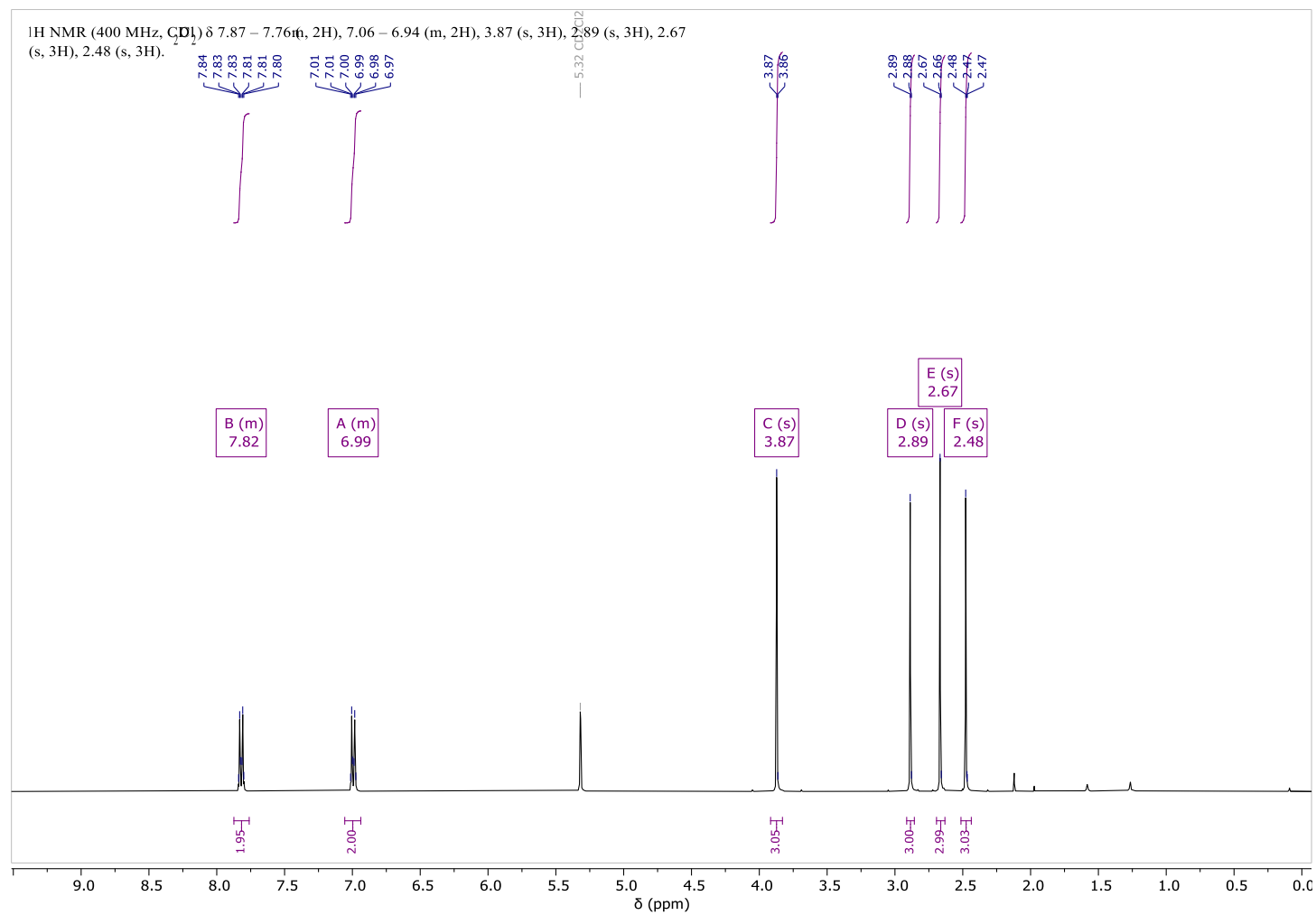


Figure S197: ¹H NMR spectrum of (*E*)-1-(4-((4-methoxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD₂Cl₂.

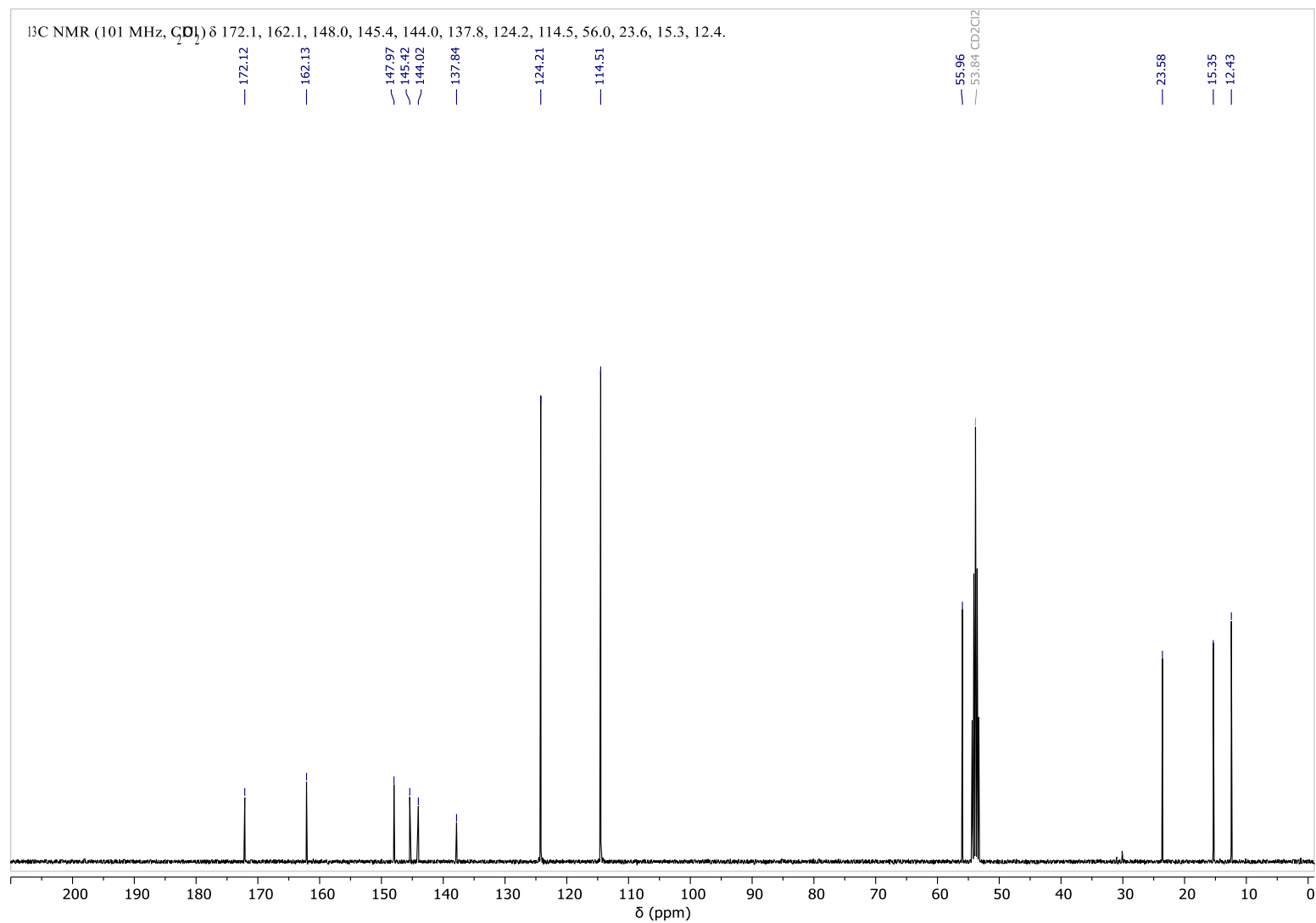


Figure S198: ^{13}C NMR spectrum of (*E*)-1-(4-((4-methoxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD_2Cl_2 .

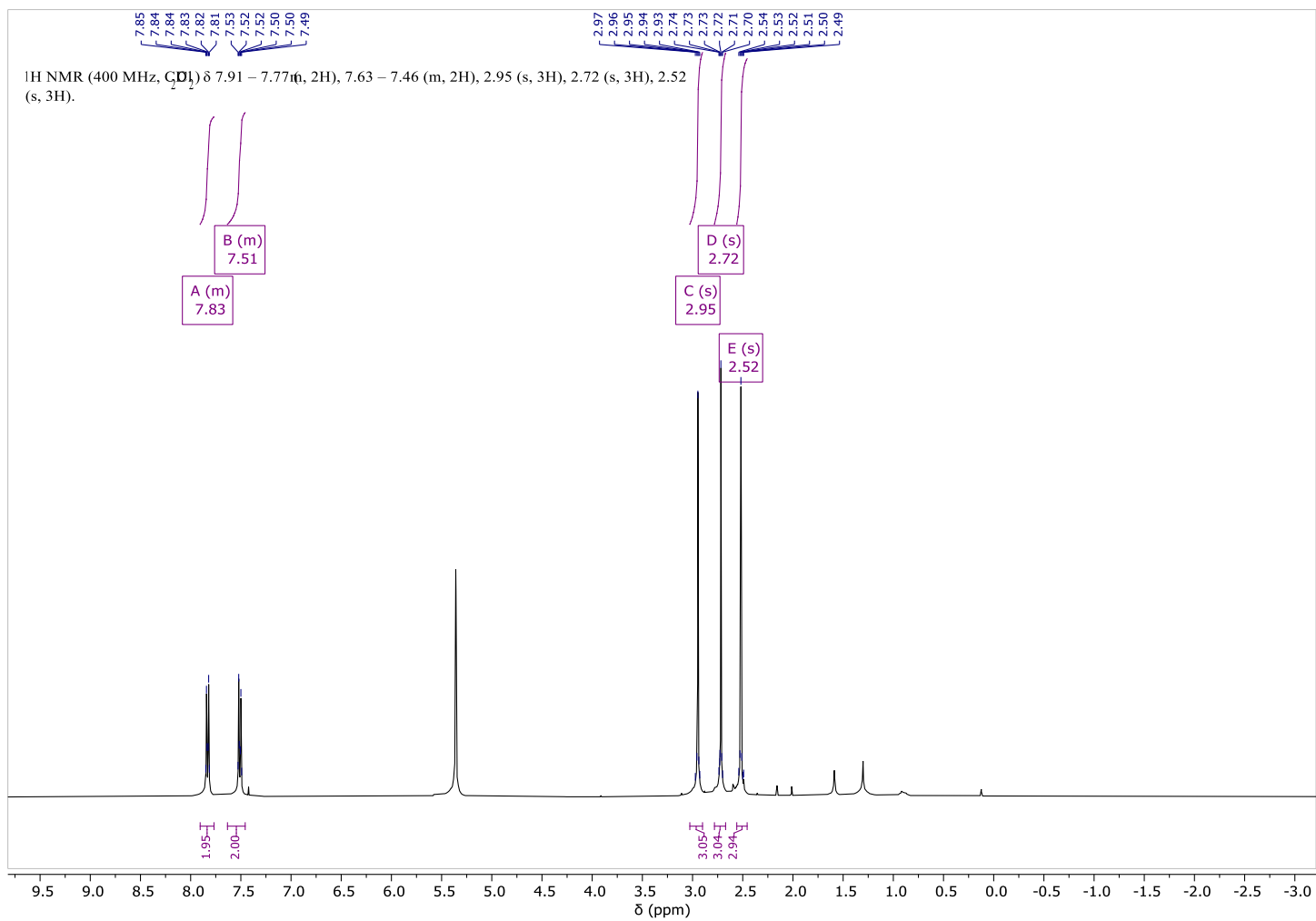


Figure S199: ¹H NMR spectrum of (*E*)-1-(4-((4-chlorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD₂Cl₂.

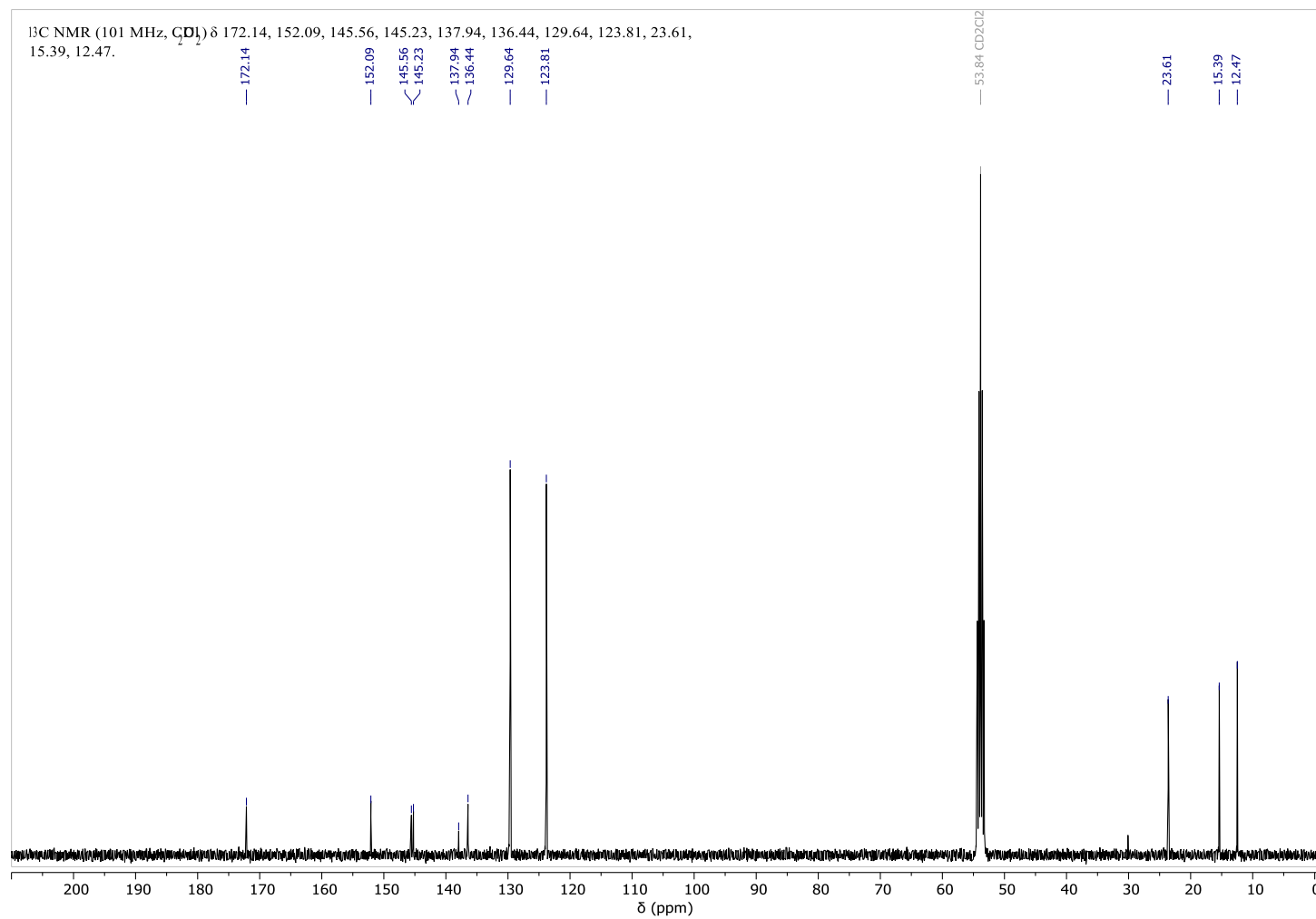


Figure S200: ^{13}C NMR spectrum of (*E*)-1-(4-((4-chlorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD_2Cl_2 .

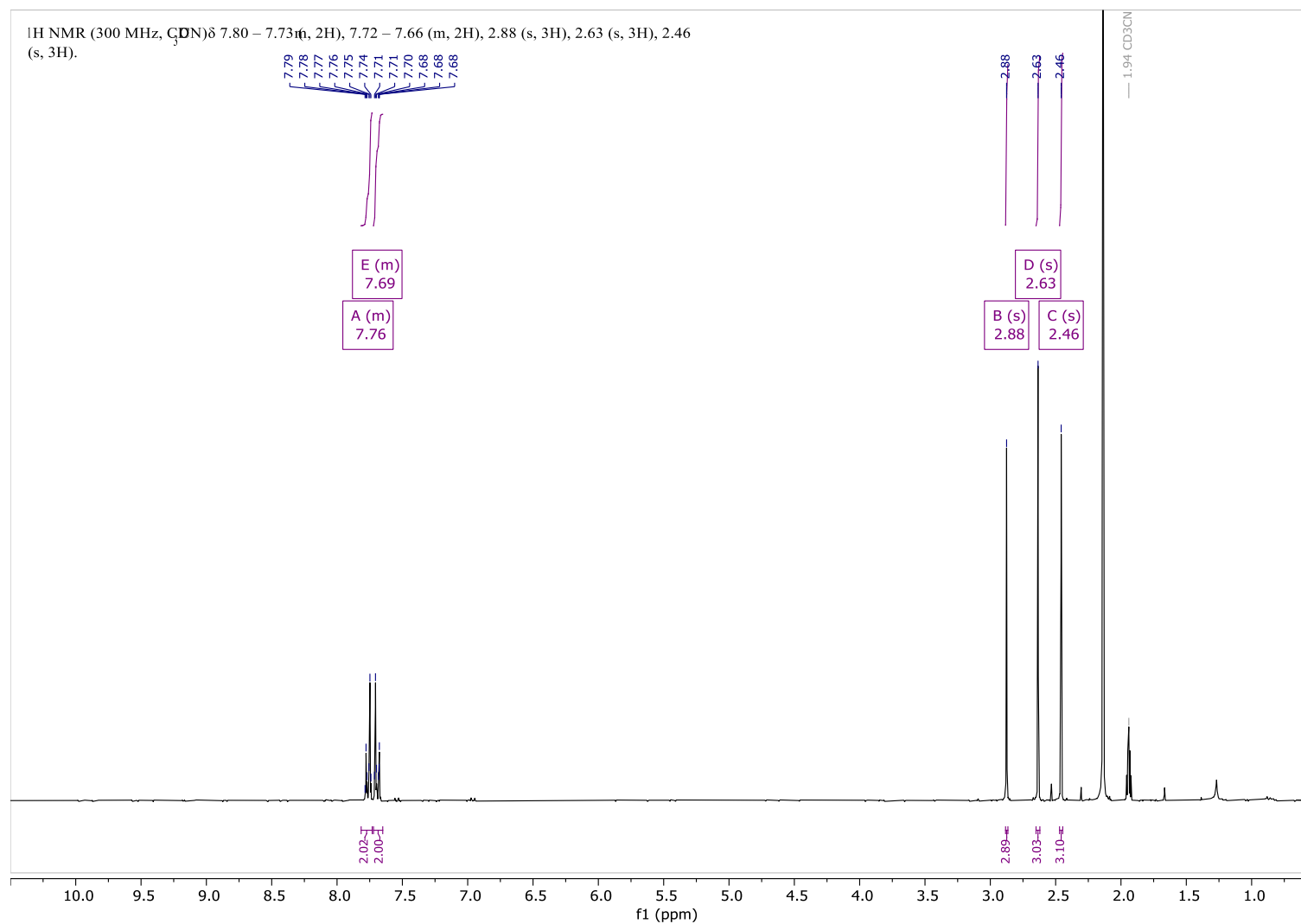


Figure S201: ¹H NMR spectrum of (*E*)-1-((4-bromophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD₂Cl₂.

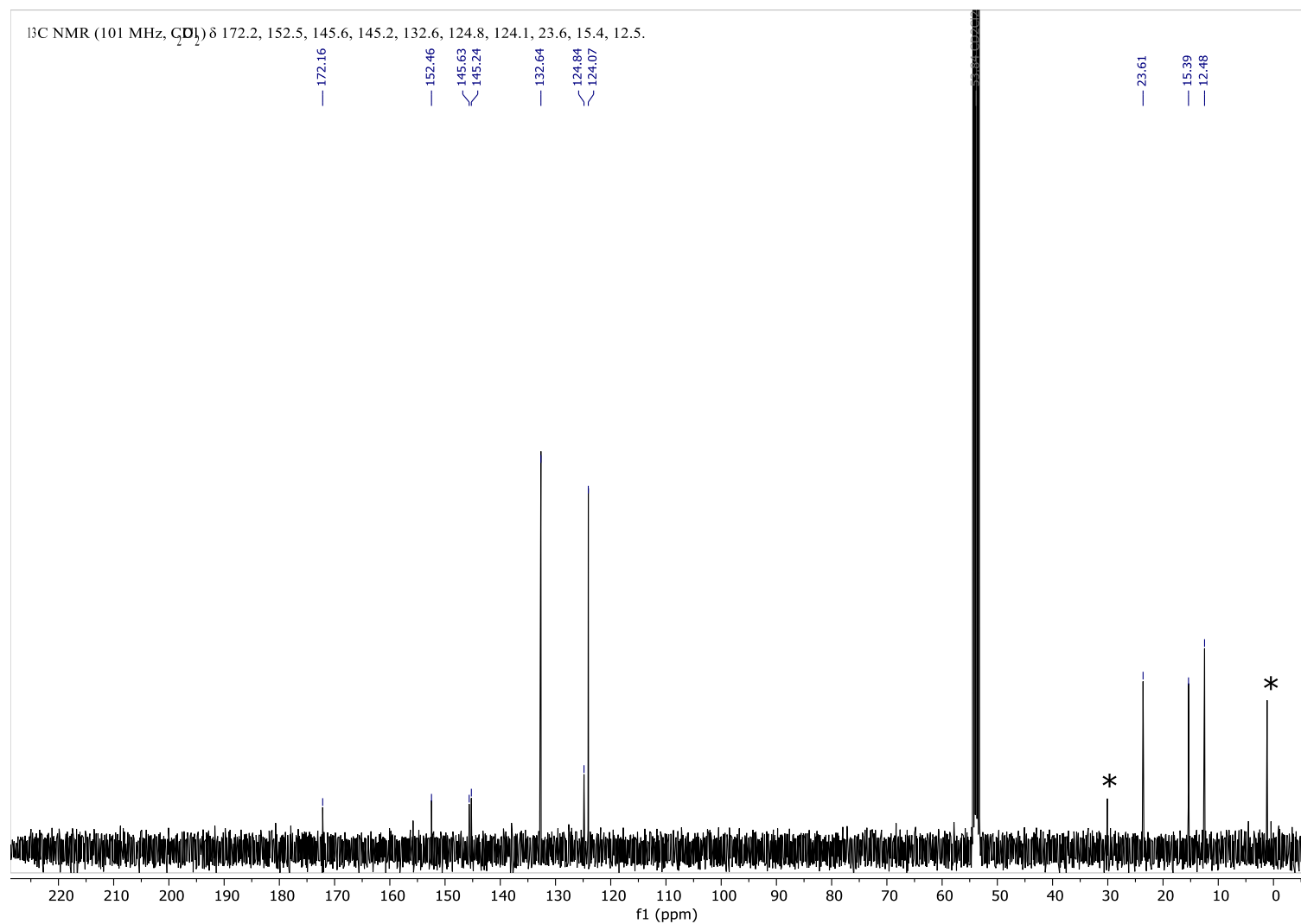


Figure S202: ^{13}C NMR spectrum of (*E*)-1-(4-((4-bromophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CD_2Cl_2 . Asterisks denote grease.

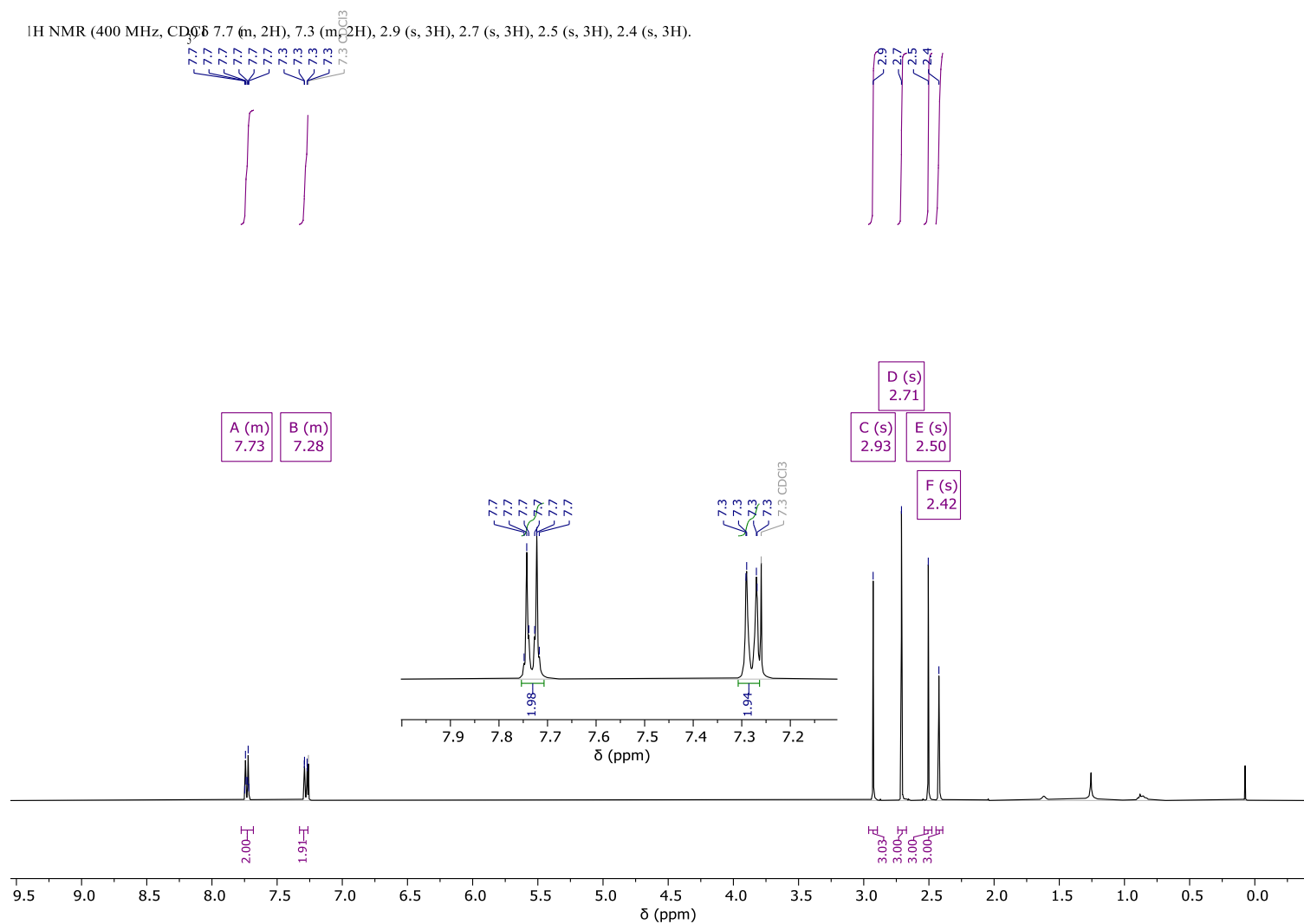


Figure S203: ¹H NMR spectrum of (*E*)-1-(3,5-dimethyl-4-(*p*-tolyldiazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

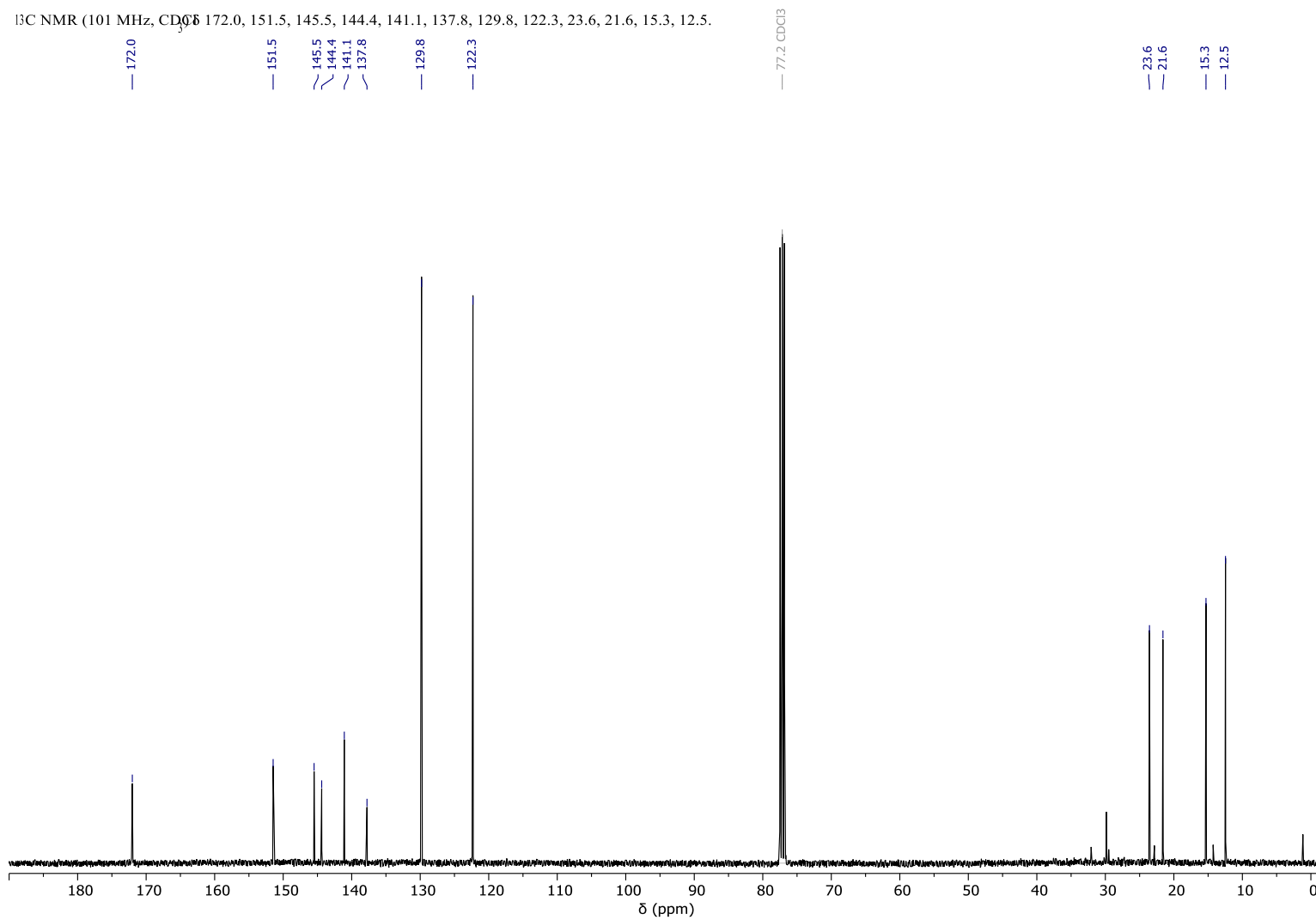


Figure S204: ¹³C NMR spectrum of (*E*)-1-(3,5-dimethyl-4-(*p*-tolyl diazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

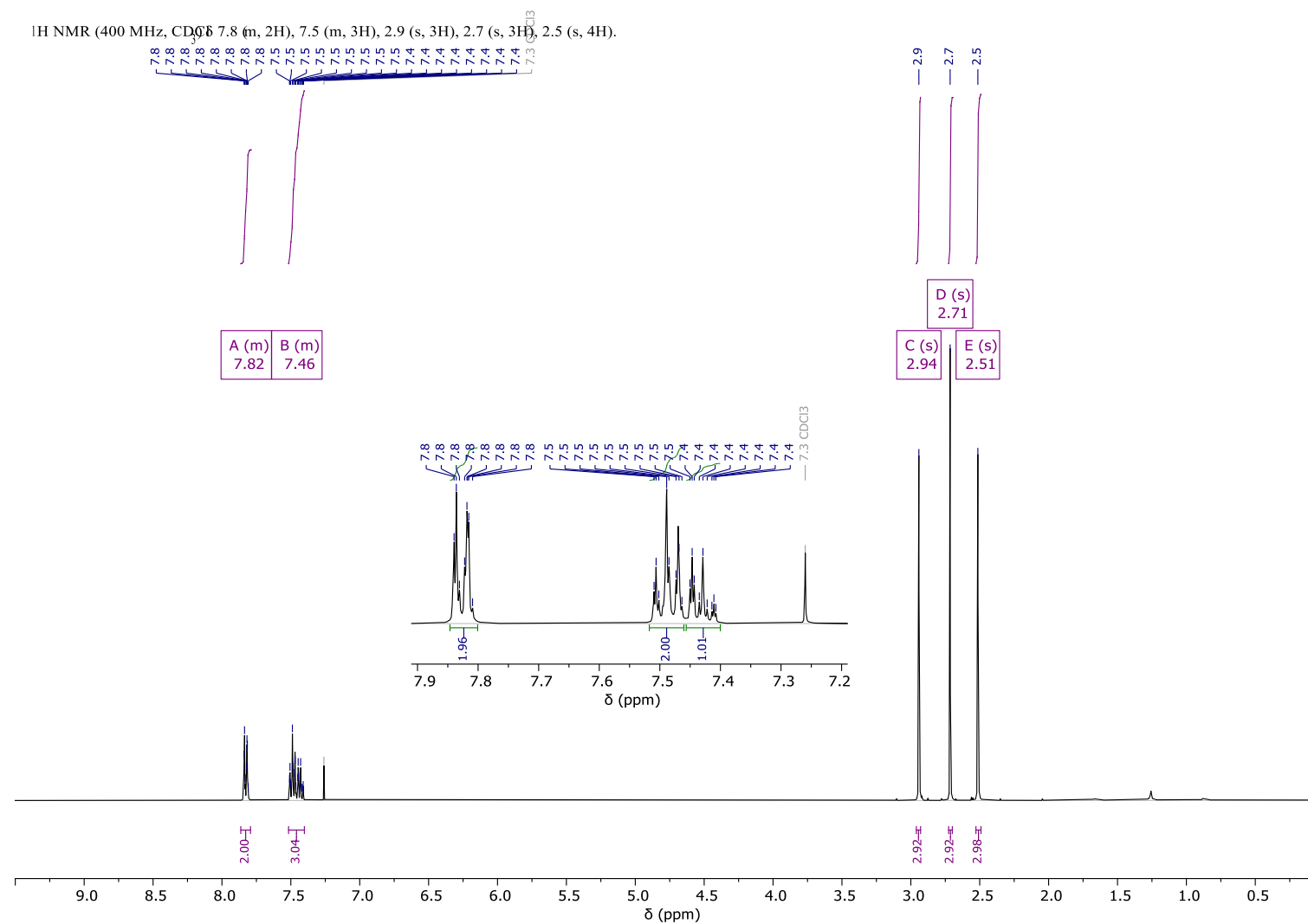


Figure S205: ¹H NMR spectrum of (*E*)-1-(3,5-dimethyl-4-(phenyldiazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

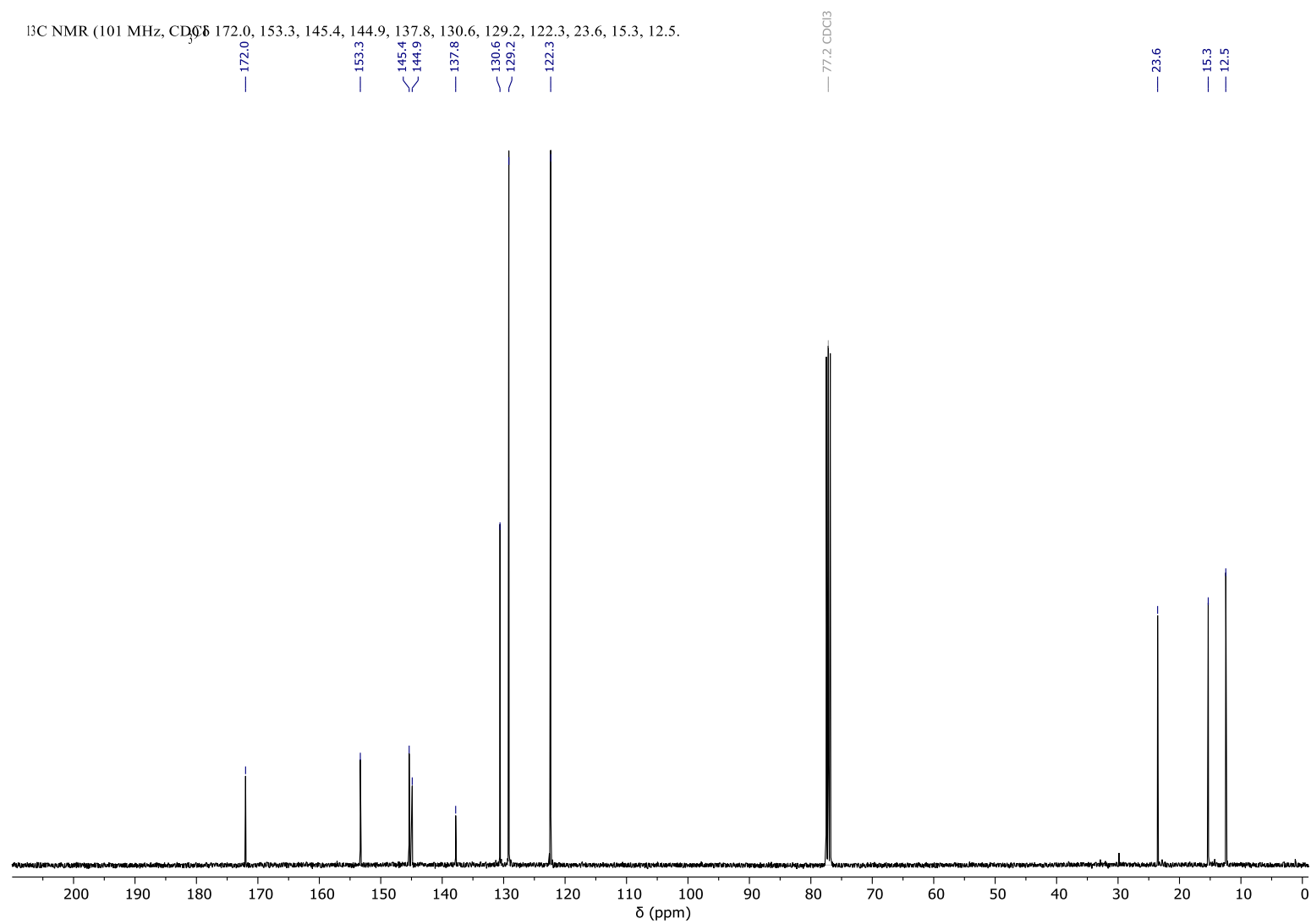


Figure S206: ¹³C NMR spectrum of (*E*)-1-(3,5-dimethyl-4-(phenyldiazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

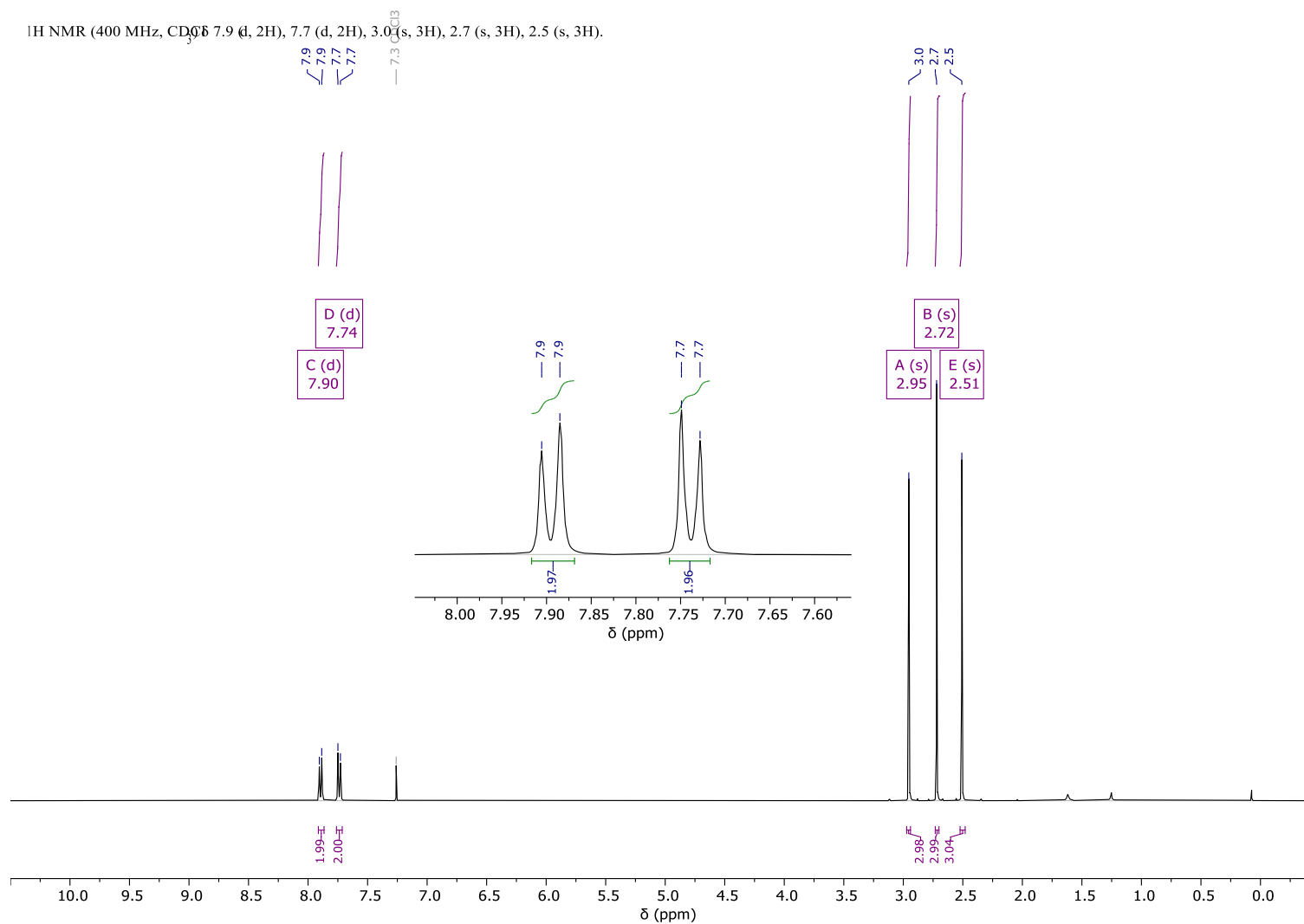


Figure S207: ¹H NMR spectrum of (*E*)-1-(3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

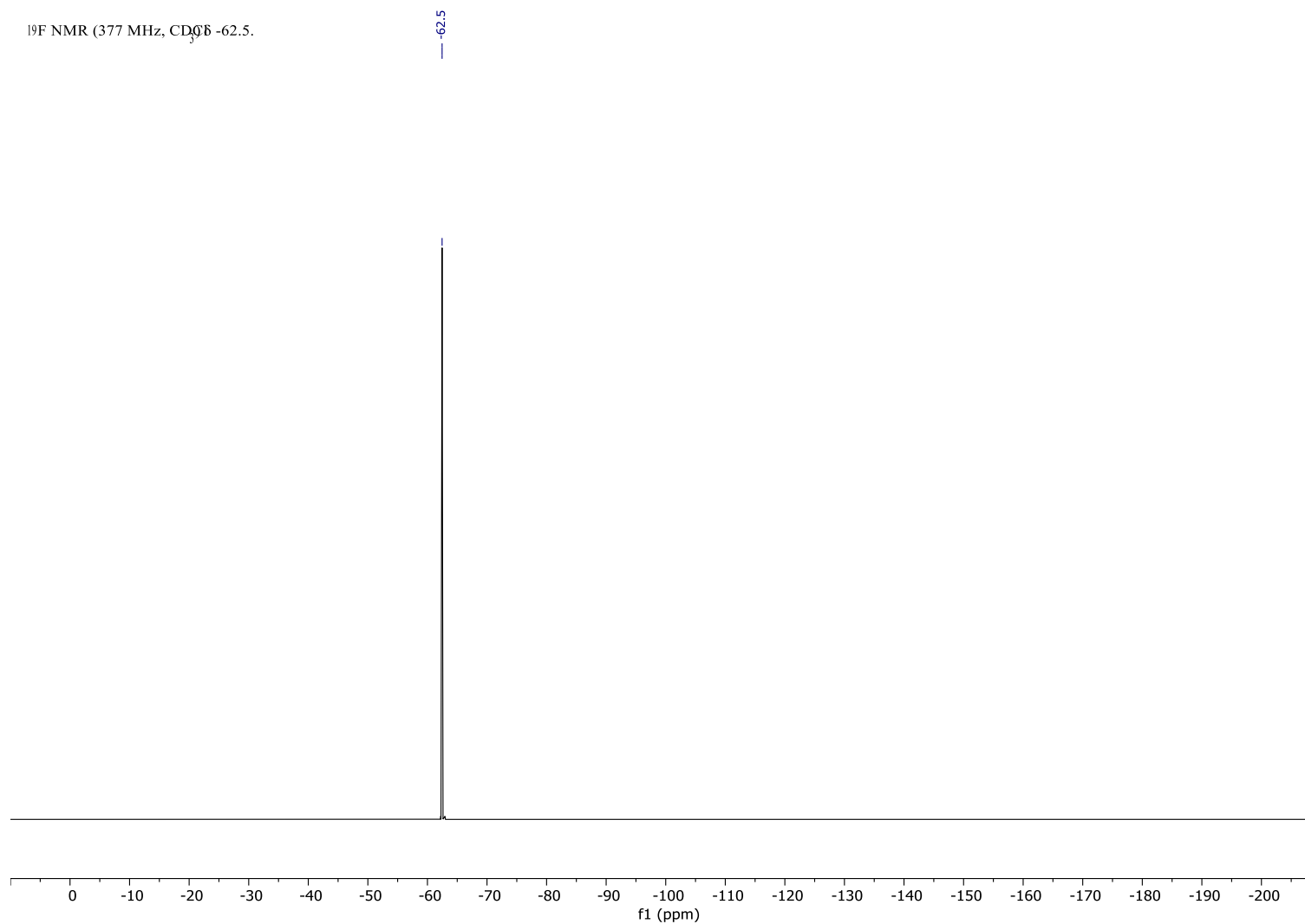


Figure S208: ¹⁹F NMR spectrum of (*E*)-1-(3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

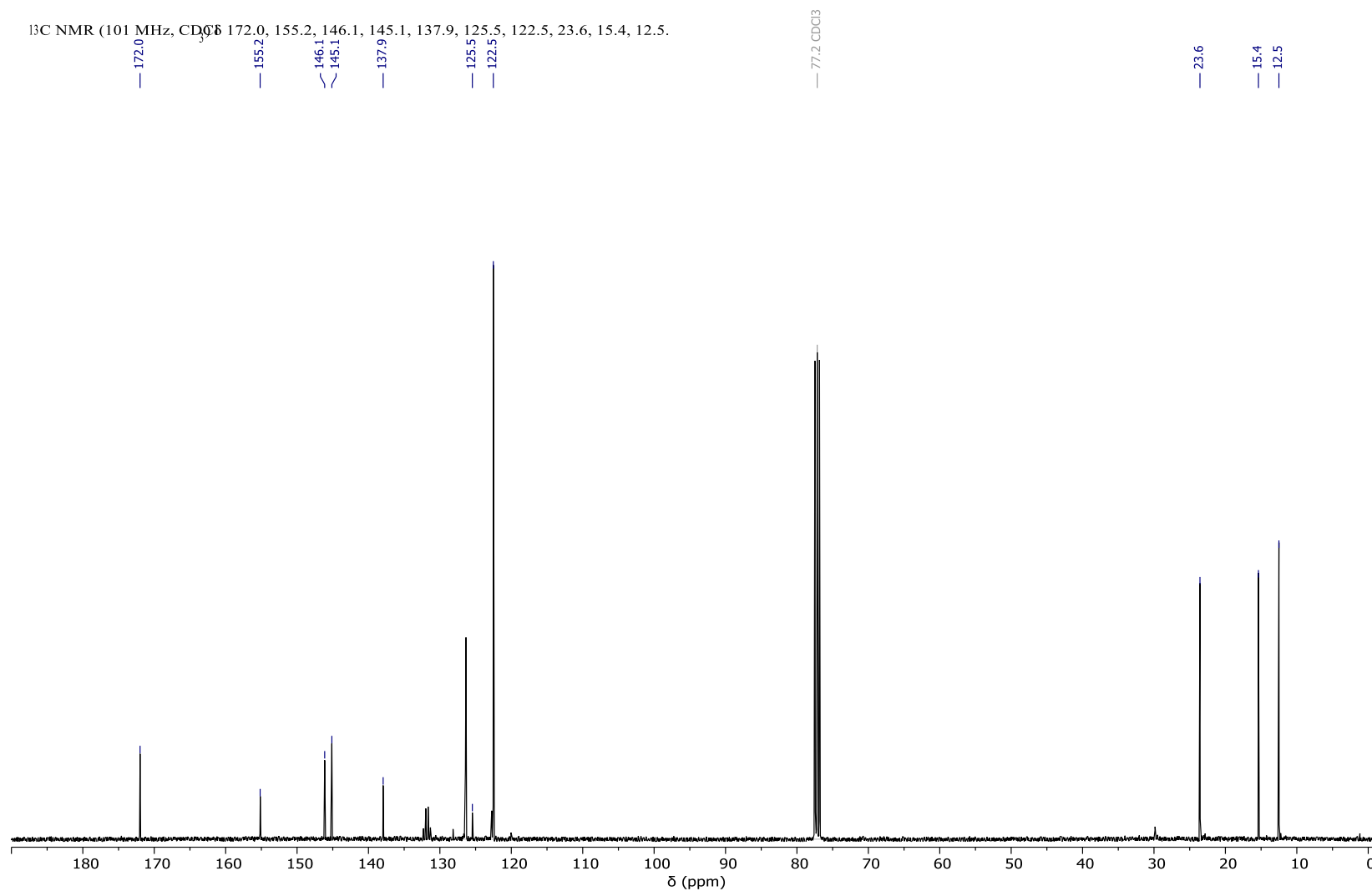


Figure S209: ¹³C NMR spectrum of (*E*)-1-(3,5-dimethyl-4-((4-(trifluoromethyl)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

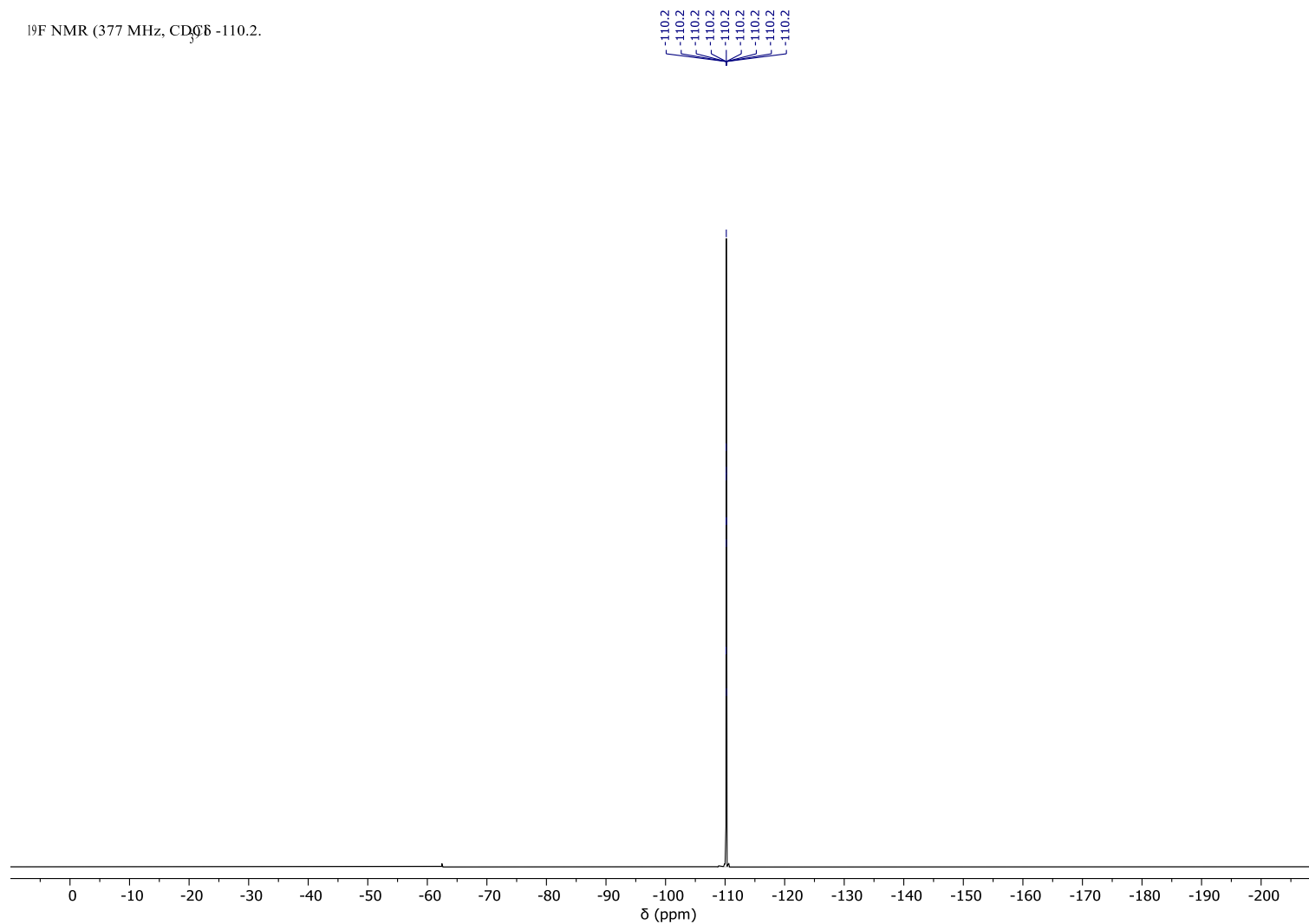


Figure S211: ^{19}F NMR spectrum of (*E*)-1-(4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CDCl_3 .

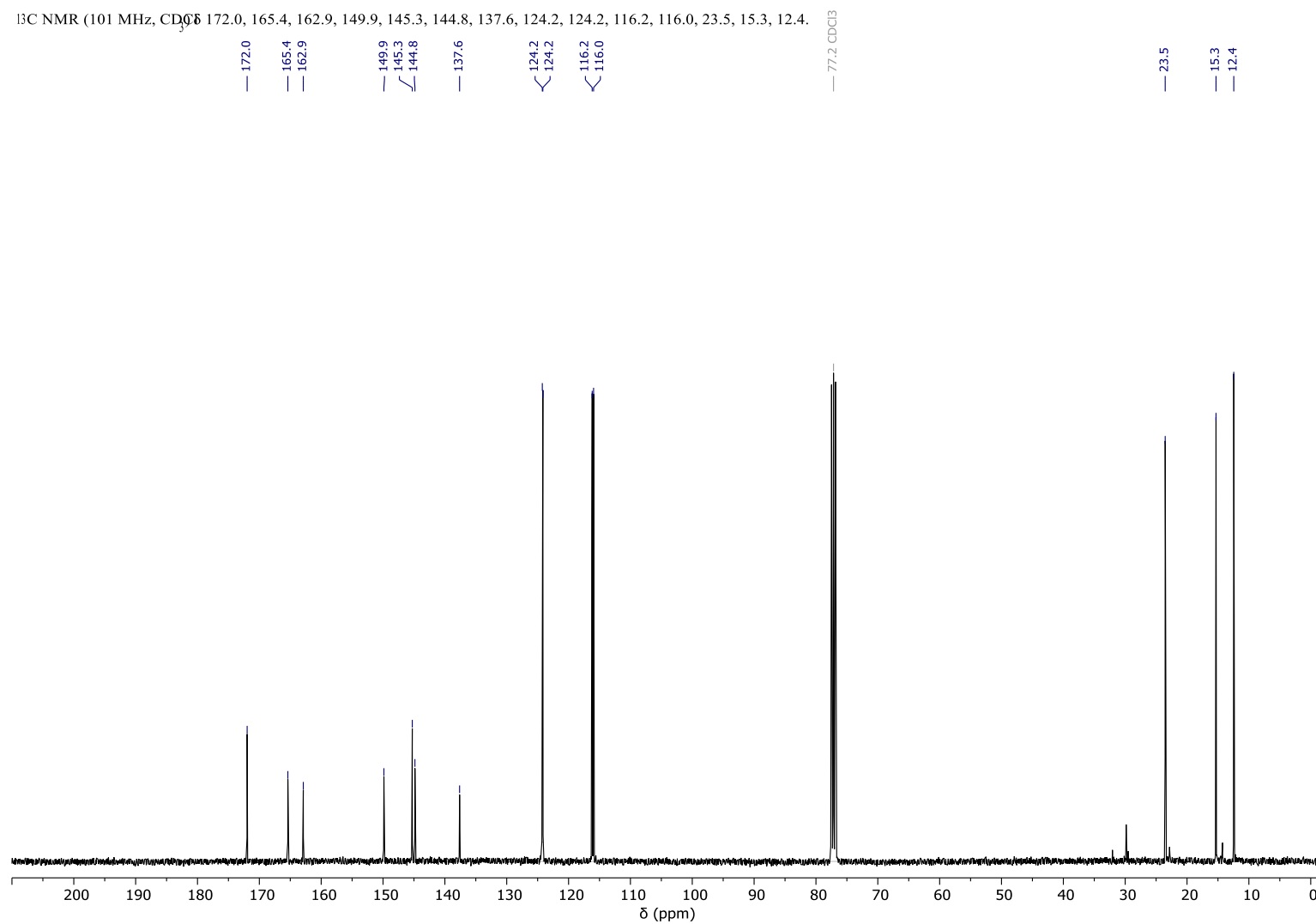


Figure S212: ¹³C NMR spectrum of (*E*)-1-(4-((4-fluorophenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in CDCl₃.

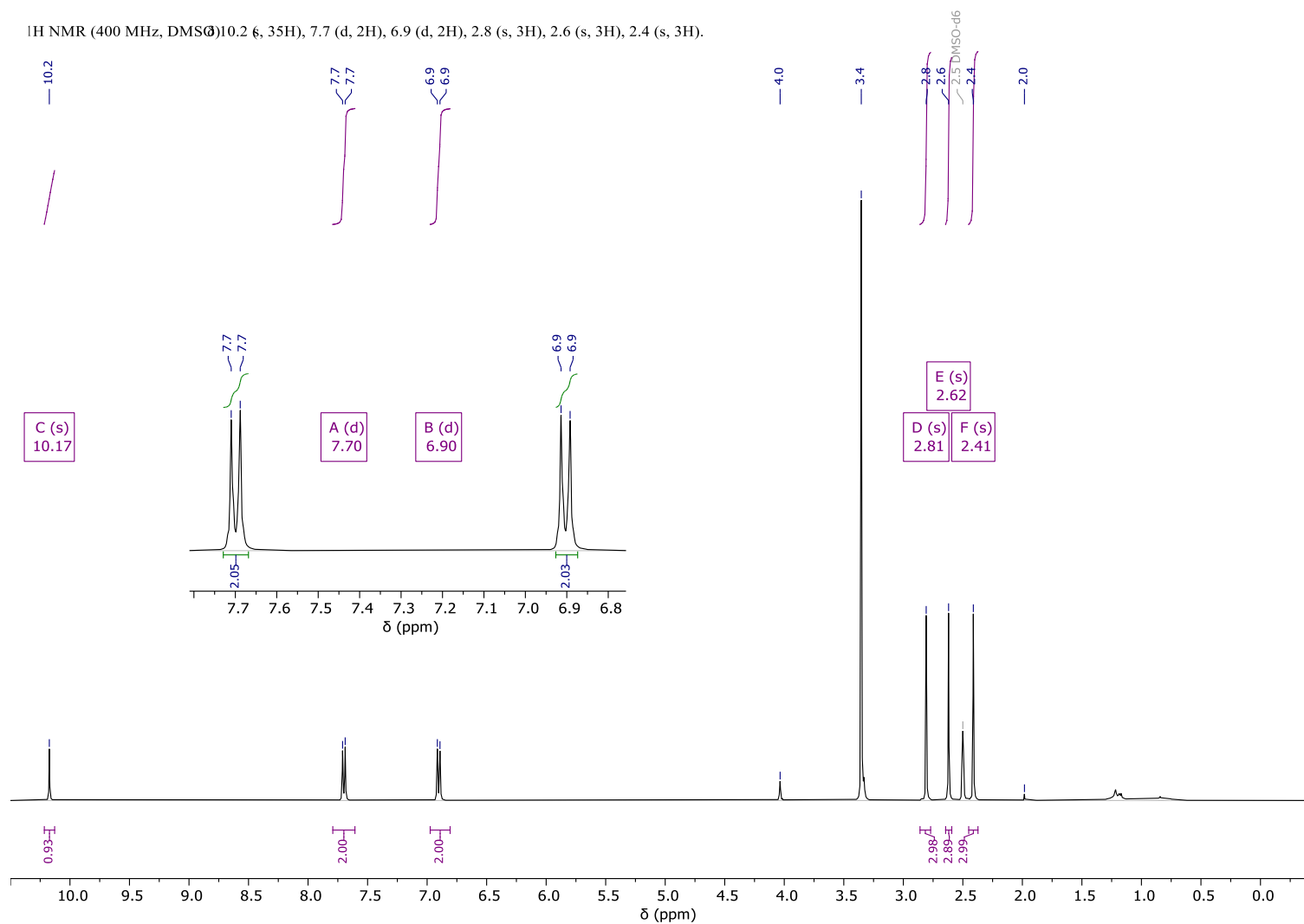


Figure S213: ¹H NMR spectrum of (*E*)-1-(4-((4-hydroxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in DMSO-*d*₆.

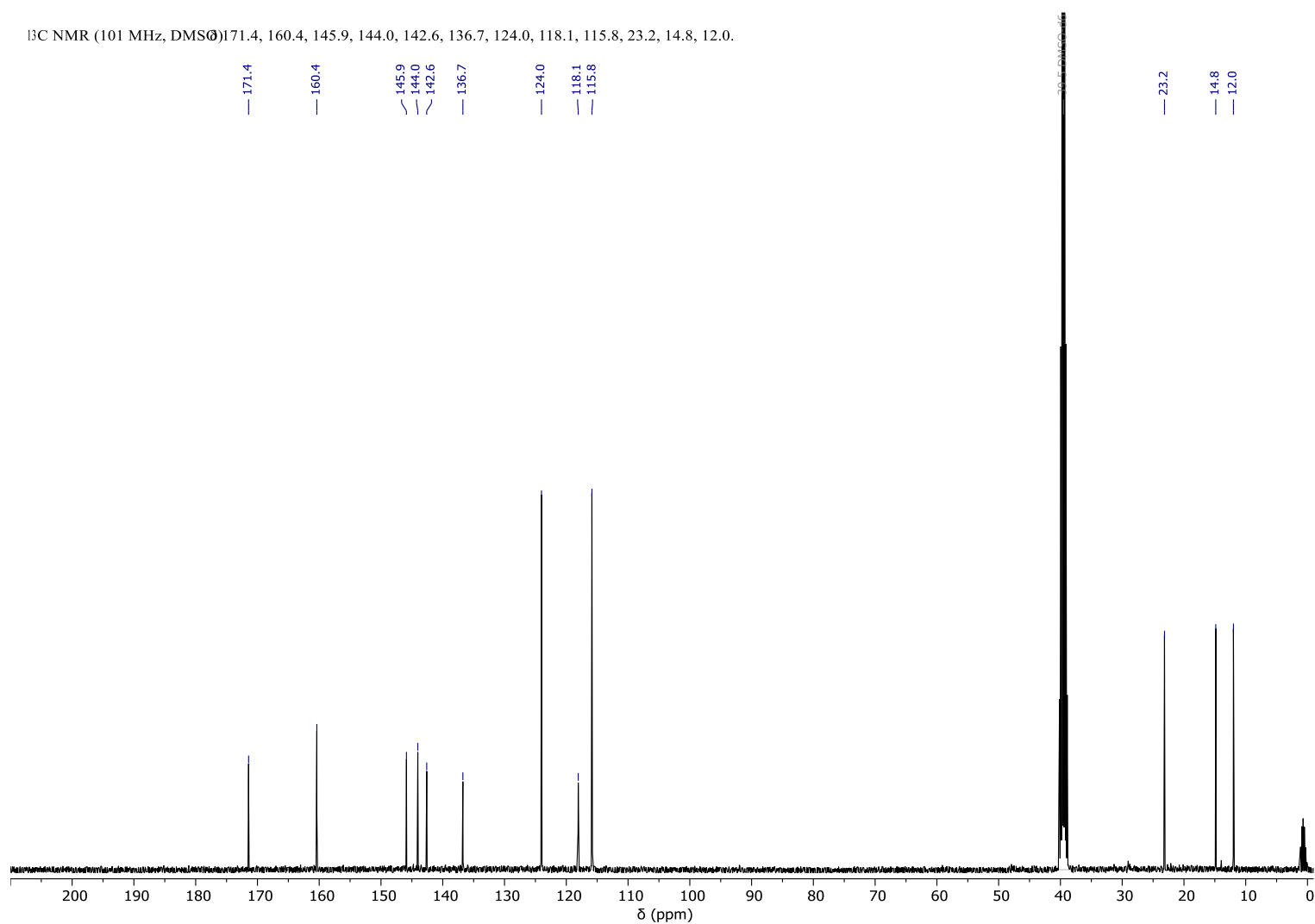


Figure S214: ¹³C NMR spectrum of (*E*)-1-(4-((4-hydroxyphenyl)diazenyl)-3,5-dimethyl-1*H*-pyrazol-1-yl)ethan-1-one in DMSO-*d*₆.

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