

**Sequential three-component reaction of homophthalonitrile, salicylaldehydes and nitromethane**

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*General:* Starting reagents [aldehydes, homophthalonitrile (90%, tech.), bases] and solvents were purchased from commercial sources and used without further purification. MW-assisted reactions were carried out in a Monowave 300 MW reactor from Anton Paar GmbH; the reaction temperature was monitored by an IR sensor. Standard 10 mL G10 reaction vials, sealed with silicone septa, were used for the MW irradiation experiments. <sup>1</sup>H NMR spectra were recorded on JEOL-600 (operating frequency 600 MHz) and Bruker-400 (operating frequency 400 MHz) instruments. <sup>13</sup>C NMR spectra were taken on JEOL-600 (operating frequency 150 MHz) and Bruker-WP400 (operating frequency 100 MHz) instruments. Spectra were referenced to the residual signals of the solvent. Infrared spectra were measured on a Infracum FT-801 FT/IR instrument. The wavelengths are reported in reciprocal centimeters ( $\lambda_{\max}$  /cm<sup>-1</sup>). Mass spectra were recorded with LCMS-8040 Triple quadrupole liquid chromatograph mass-spectrometer from Shimadzu. Elemental analyses were determined on a EuroVector EA-3000 elemental analyzer. Melting points of synthesized compounds were determined in capillary tubes on an SMP 10 apparatus. For TLC were used Sorbfil plates (detection in UV light, eluent EtOAc — hexane in proportions 1:1). For column chromatography was used silica gel (0.04-0.06 mm/230-400 mesh, Macherey Nagel GmbH&Co) eluent EtOAc — hexane in different proportions 1:5 - 1:1.

**Mixture of diastereomers of 2-{2-amino-4-[cyano(2-cyanophenyl)methyl]-4H-1-benzopyran-3-yl}benzotrile (3).** Homophthalonitrile **2** (500 mg, 3.5 mmol), salicylaldehyde **1** (215 mg, 1.76 mmol), and Na<sub>2</sub>CO<sub>3</sub> (187 mg, 1.76 mmol) were dissolved in EtOH (8.5 mL), stirred, and refluxed for 2.5 h. The course of the reaction was monitored by TLC. When the reaction was finished, the solvent was evaporated in a rotary evaporator. The solid was triturated with H<sub>2</sub>O (50 mL). The resulting solid was filtered off, washed with H<sub>2</sub>O (5×), and dried in air to

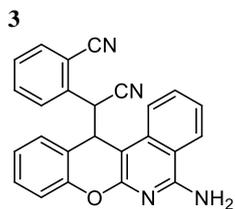
afford a yellow powder (540 mg, 96%), d.r. 61:39, mp 239-242°C.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ ppm, *J*/Hz, 400 MHz) 4.61 (1H, d, *J* = 4.1), 4.83 (1.6H, d, *J* = 5.8), 5.23 (1.6H, d, *J* = 5.8), 5.46 (1H, d, *J* = 4.1), 6.60 (1.6H, d, *J* = 7.5), 6.64 (1H, d, *J* = 8.1), 6.93 (1.6H, t, *J* = 7.5), 6.98 (1H, d, *J* = 8.1), 7.08 (1.6H, d, *J* = 7.7), 7.17 (2H, br.s), 7.19 (1.6H, d, *J* = 8.3), 7.23 (1H, td, *J* = 7.5, 1.6), 7.27 (3.2H, br.s), 7.31-7.39 (6.2H, m), 7.45 (1H, t, *J* = 7.1); 7.51-7.55 (2.6H, m); 7.56-7.62 (4.2H, m); 7.65 (1H, dd, *J* = 7.7, 1.6); 7.82 (1.6H, dd, *J* = 7.7, 1.6); 7.89 (1H, d, *J* = 8.3); 8.10 (1.6H, d, *J* = 8.3); 8.20 (1H, d, *J* = 8.4); 8.23 (1.6H, d, *J* = 8.4). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>), δ, ppm: 39.2, 39.3, 42.0, 43.6, 90.6, 91.8, 111.5, 112.1, 115.7, 115.4, 116.06, 116.14, 116.3, 117.2, 118.3, 119.1 (2C), 119.8, 121.3, 121.4, 122.6, 123.4 (3C), 123.5, 124.7, 128.9, 129.0, 129.1, 129.15, 129.2, 129.4, 130.0, 130.3, 130.5 (2C), 132.4, 132.9, 133.1, 133.4, 135.3, 136.3, 136.5, 137.1, 152.5, 152.7, 154.9, 155.2, 157.3, 157.4. Mass spectrum ESI-MS, *m/z*: 389 [M+H]<sup>+</sup>, 430[M+H+CH<sub>3</sub>CN]<sup>+</sup>. Found, %: C, 77.19; H, 4.19; N, 14.34. C<sub>25</sub>H<sub>16</sub>N<sub>4</sub>O. Calc., %: C, 77.30; H, 4.15; N, 14.42.

**(*E*)-2-(2-Nitrovinyl)phenol (5).** Compound **5** was synthesized by the literature method. The physicochemical data for this compound agreed with those in the literature.<sup>1</sup> mp 133°C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 6.24 (s, 1H), 6.89 (d, *J* = 8.1, 1H), 7.01 (t, *J* = 7.6, 1H), 7.36 (m, 1H), 7.43 (dd, *J* = 7.7, 1.1, 1H), 8.00 (d, *J* = 13.6, 1H), 8.15 (d, *J* = 13.6, 1H). ESI-MS, *m/z*: 164[M-H]<sup>-</sup>.

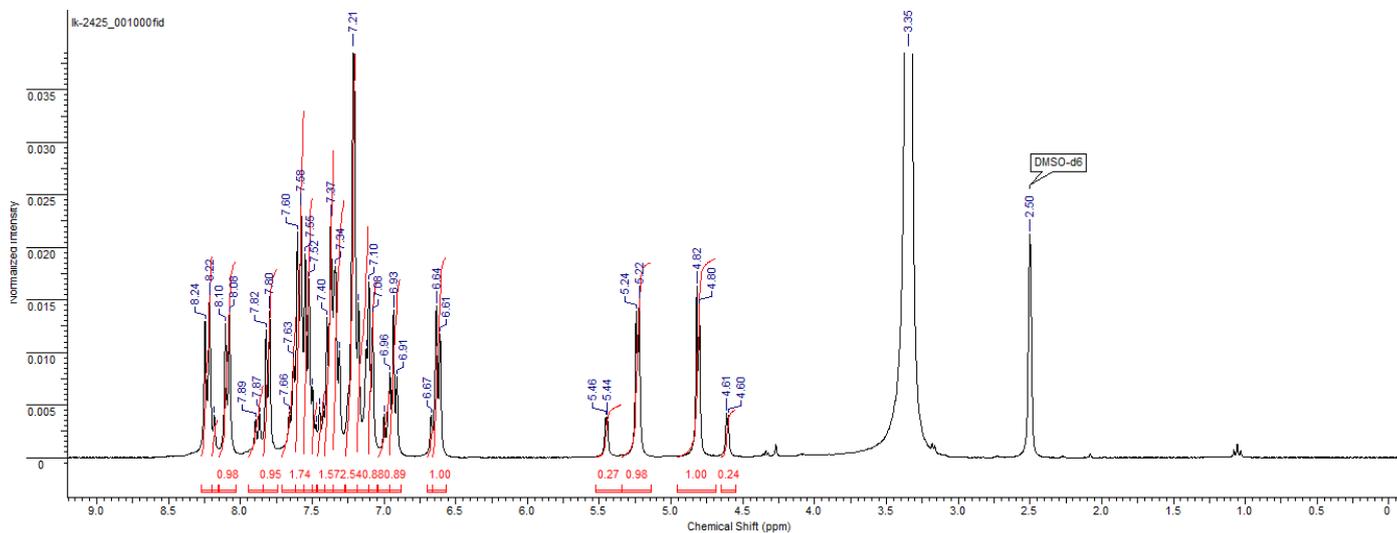
## References

1. X.-F. Xia, X.-Z. Shu, K.-G. Ji, Y.-F. Yang, A. Shaukat, X.-Y. Liu and Y.-M. Liang, *J. Org. Chem.*, 2010, **75**, 2893.

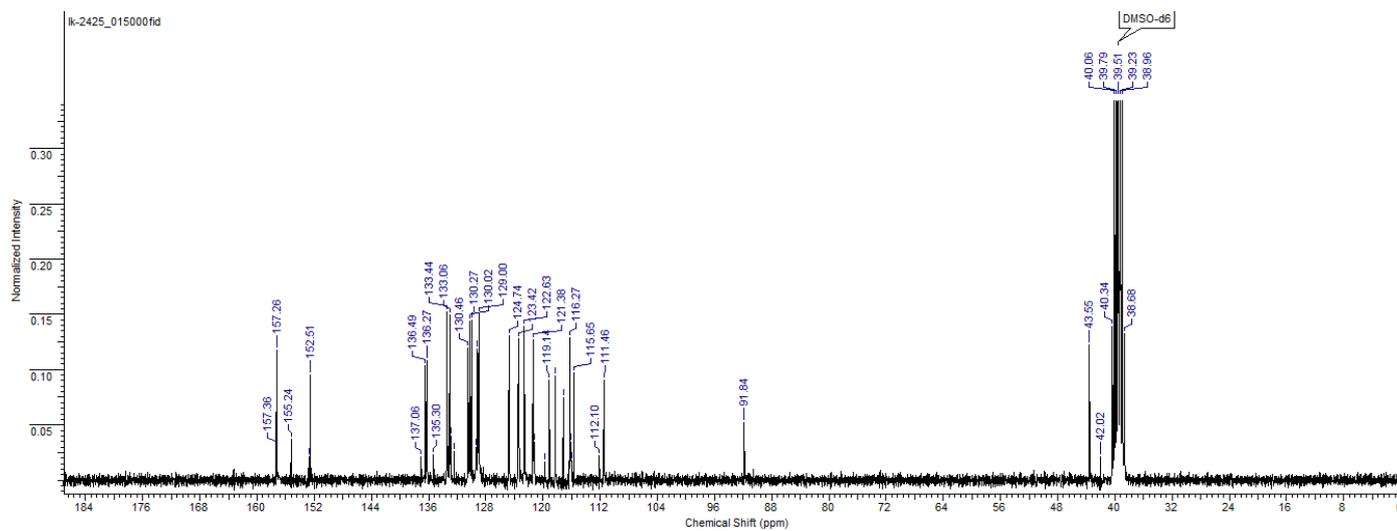


$^1\text{H}$ , DMSO- $d_6$

The analytical sample was recrystallized from EtOAc, giving d.r. 79:21. The d.r. could not be improved through recrystallization, as far as epimerization took place.

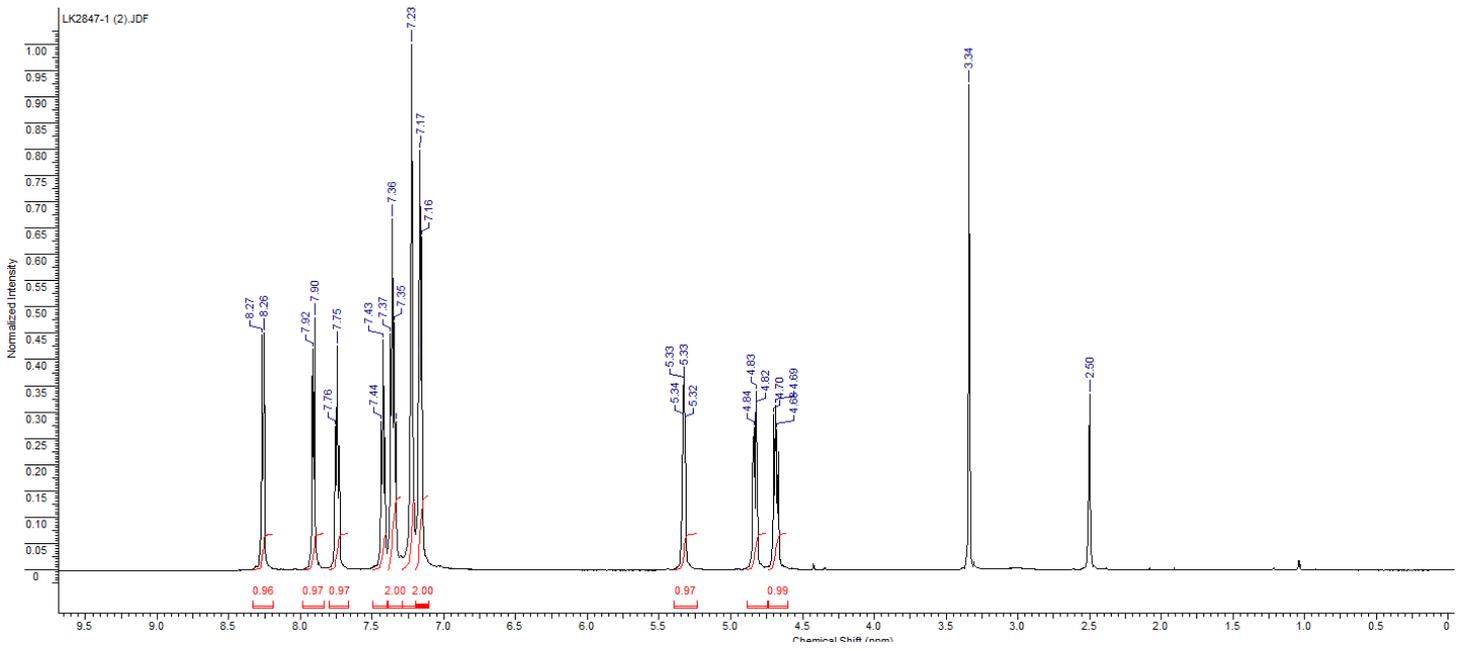
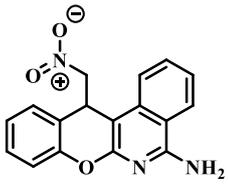


$^{13}\text{C}$ , DMSO- $d_6$

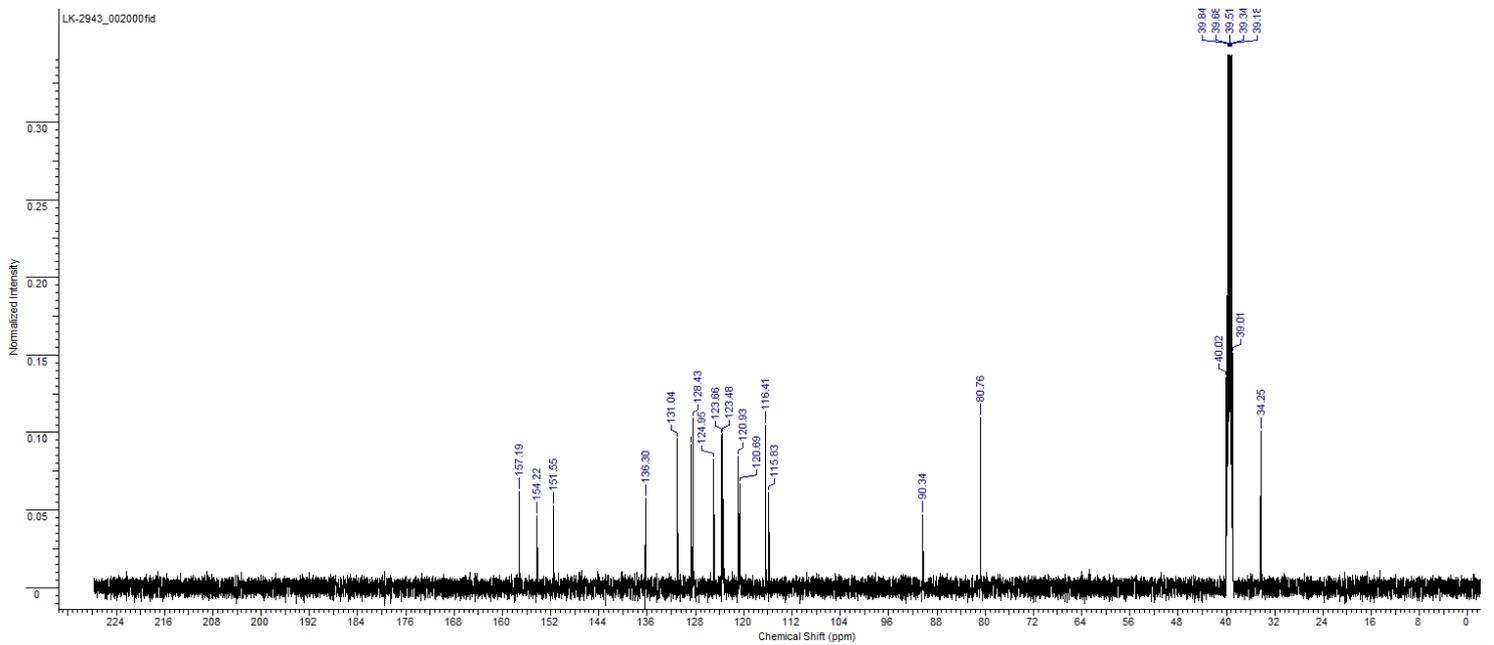


4a

$^1\text{H}$ , DMSO- $d_6$

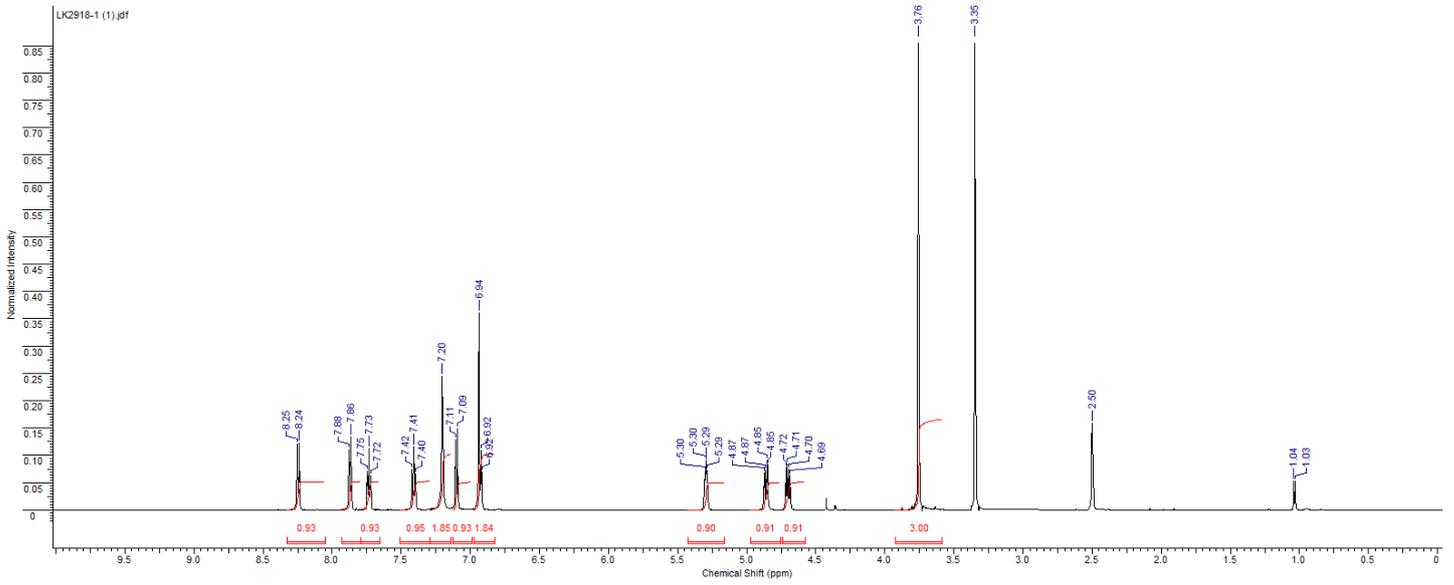
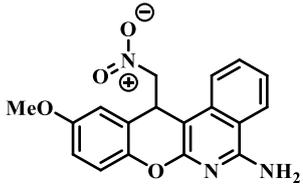


$^{13}\text{C}$ , DMSO- $d_6$

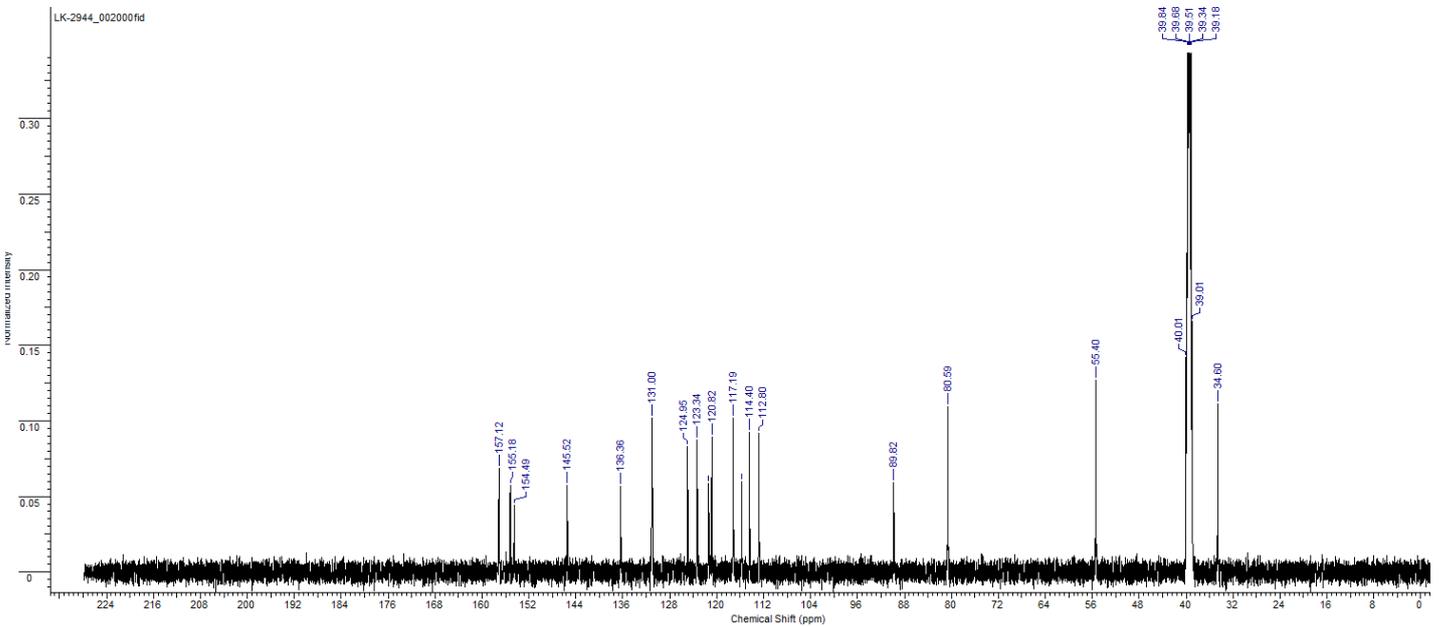


4b

$^1\text{H}$ , DMSO- $d_6$

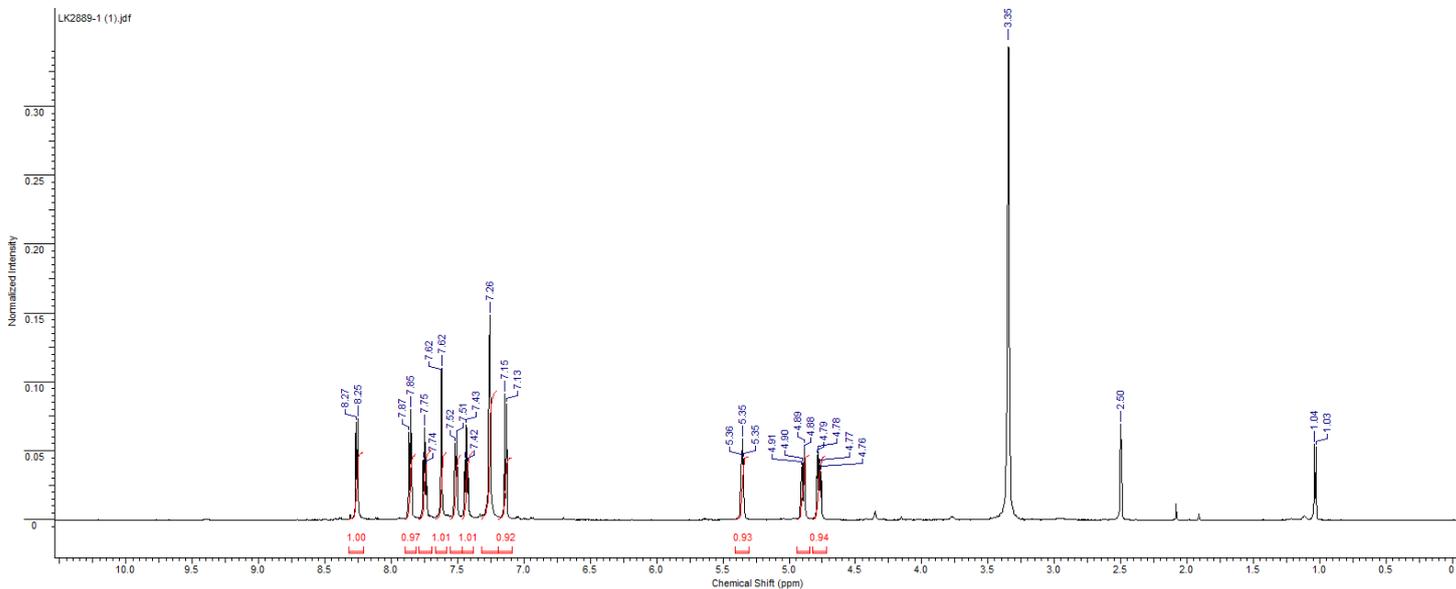
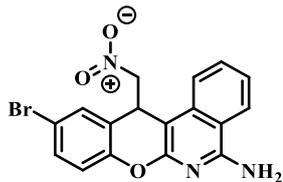


$^{13}\text{C}$ , DMSO- $d_6$

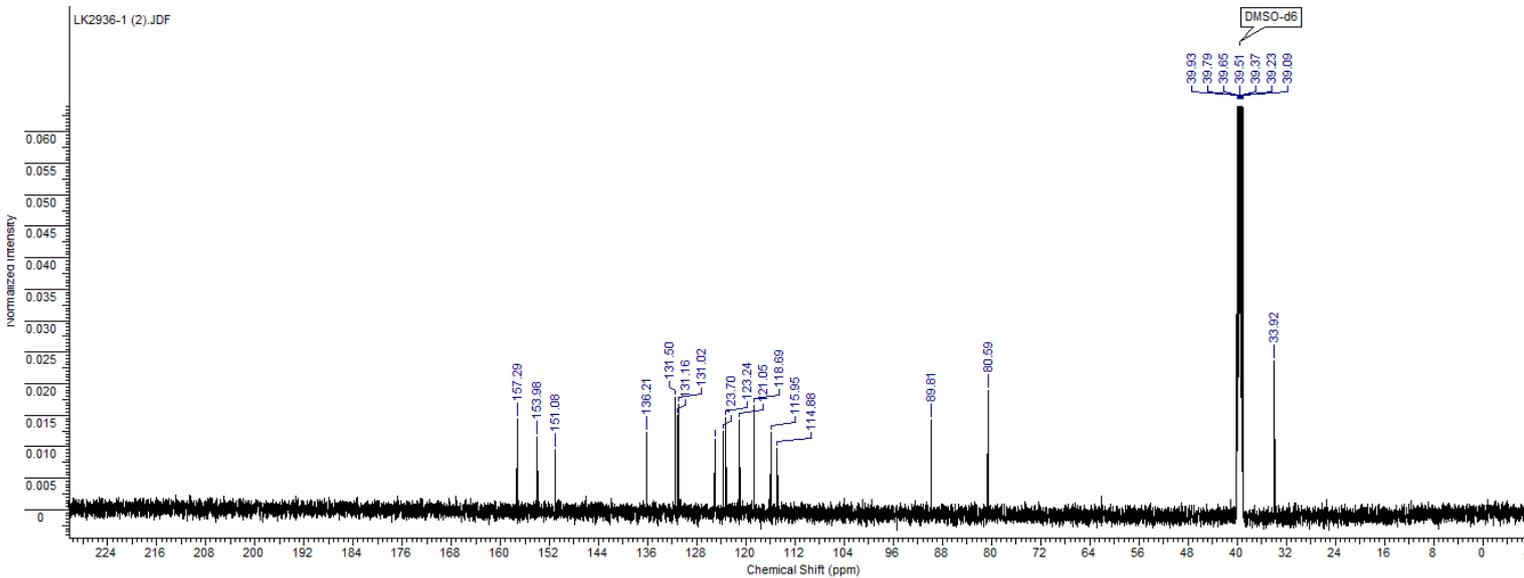


# 4c

<sup>1</sup>H, DMSO-d<sub>6</sub>

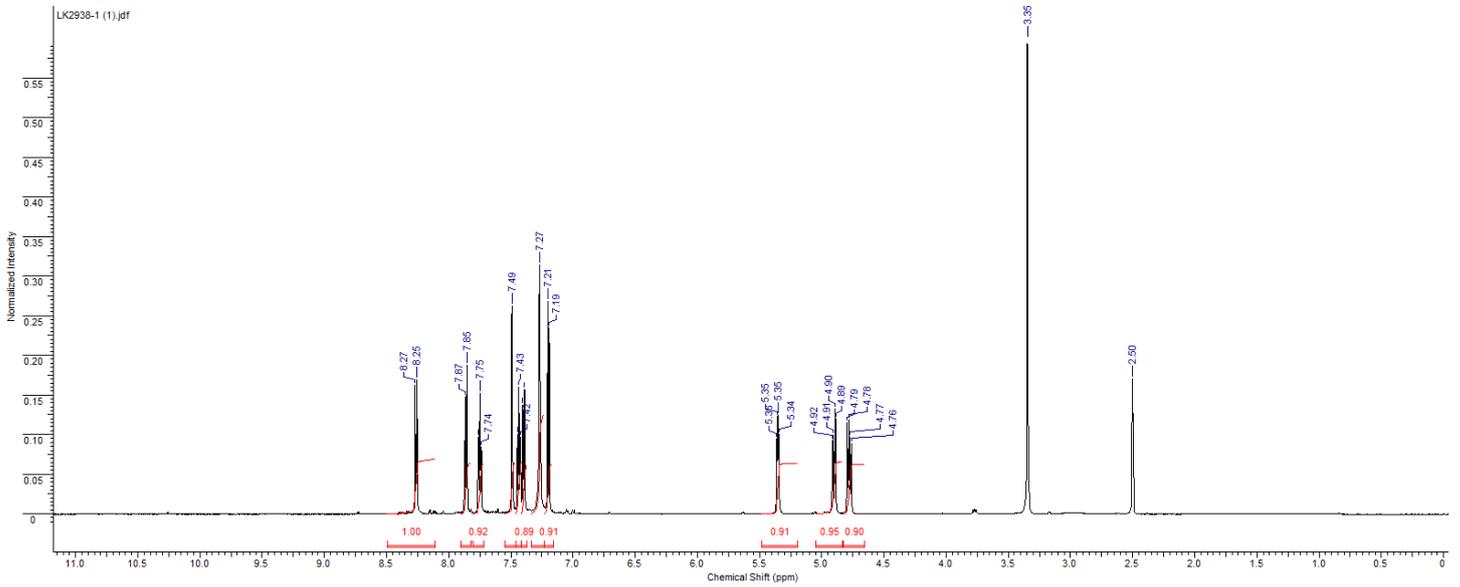
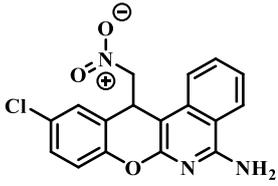


<sup>13</sup>C, DMSO-d<sub>6</sub>

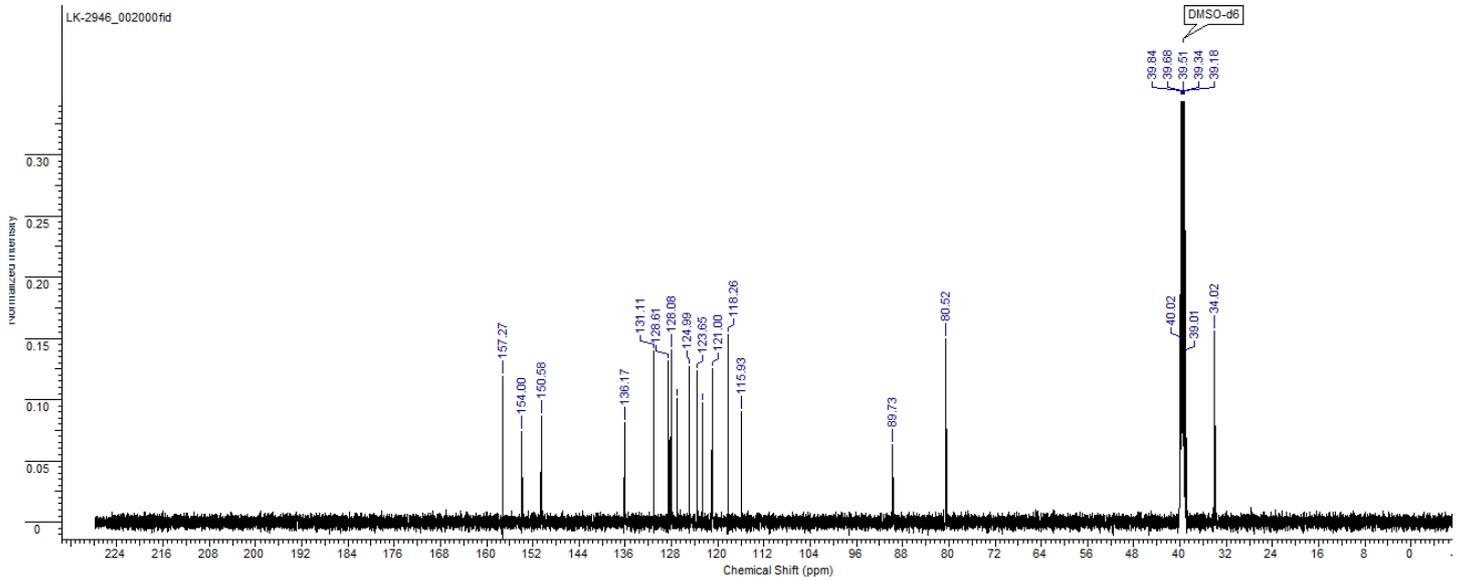


4d

$^1\text{H}$ , DMSO- $d_6$

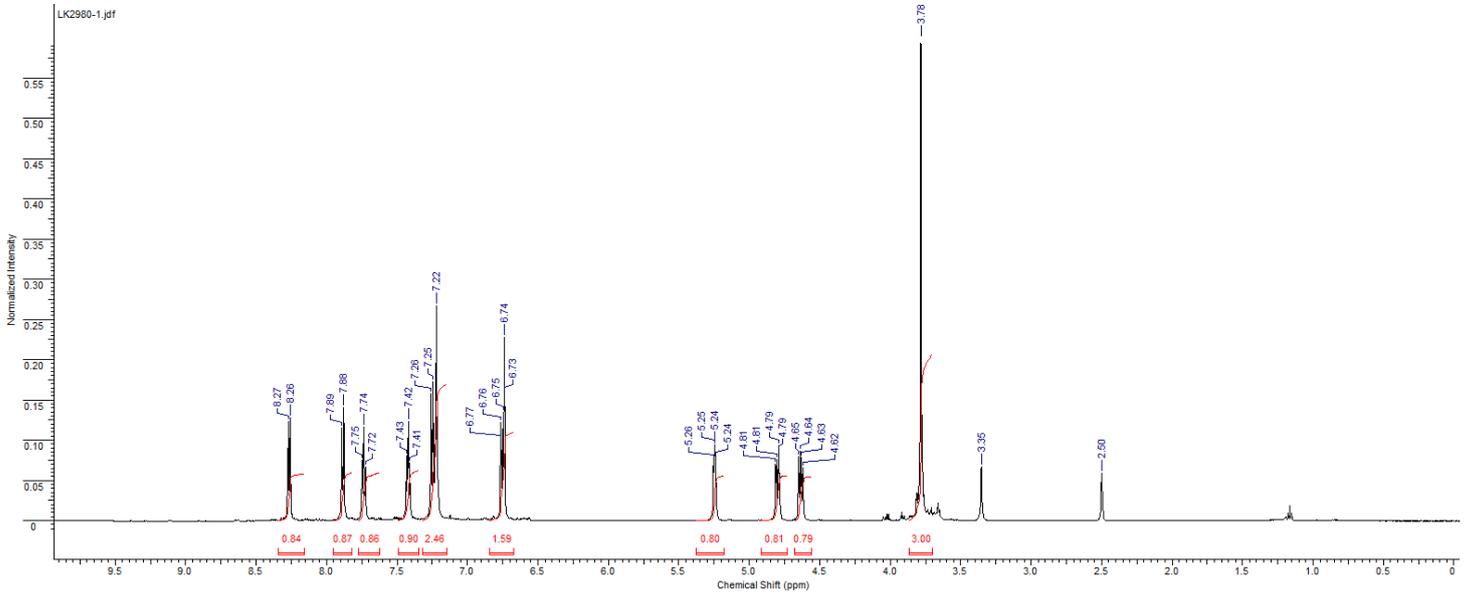
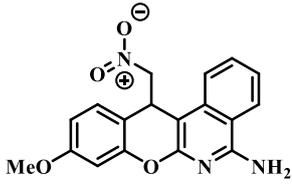


$^{13}\text{C}$ , DMSO- $d_6$

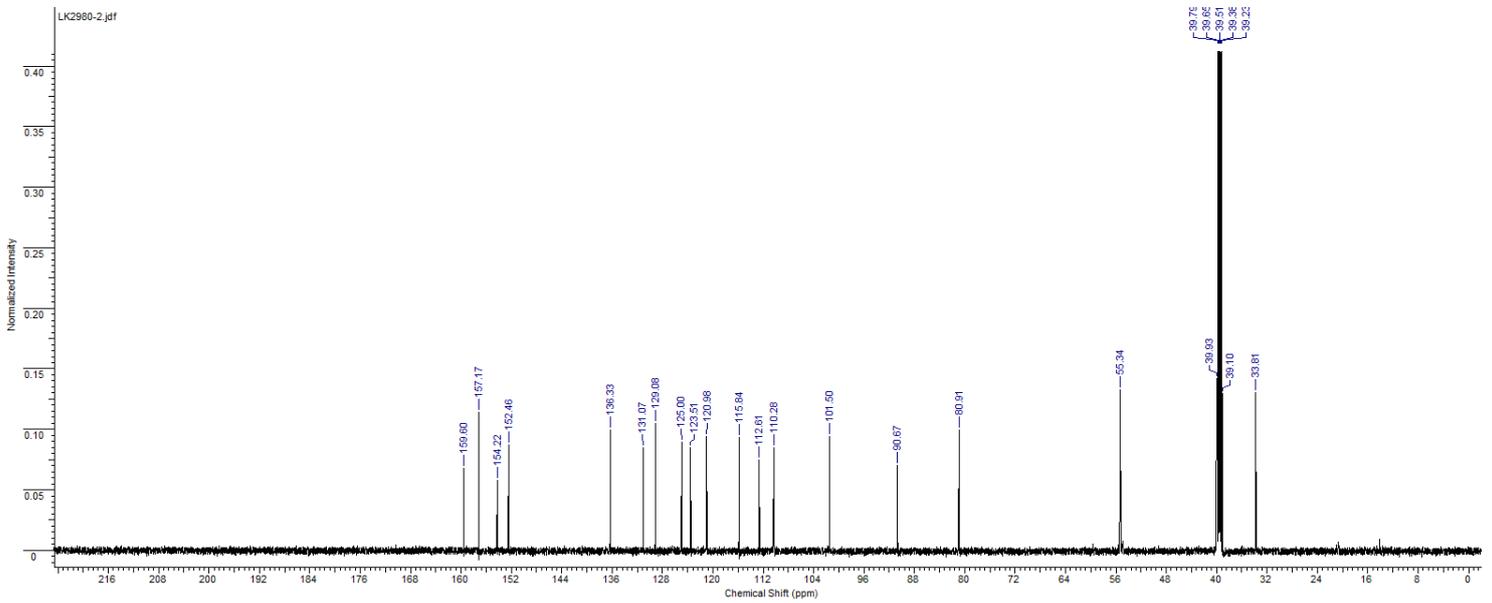


4e

$^1\text{H}$ , DMSO- $d_6$

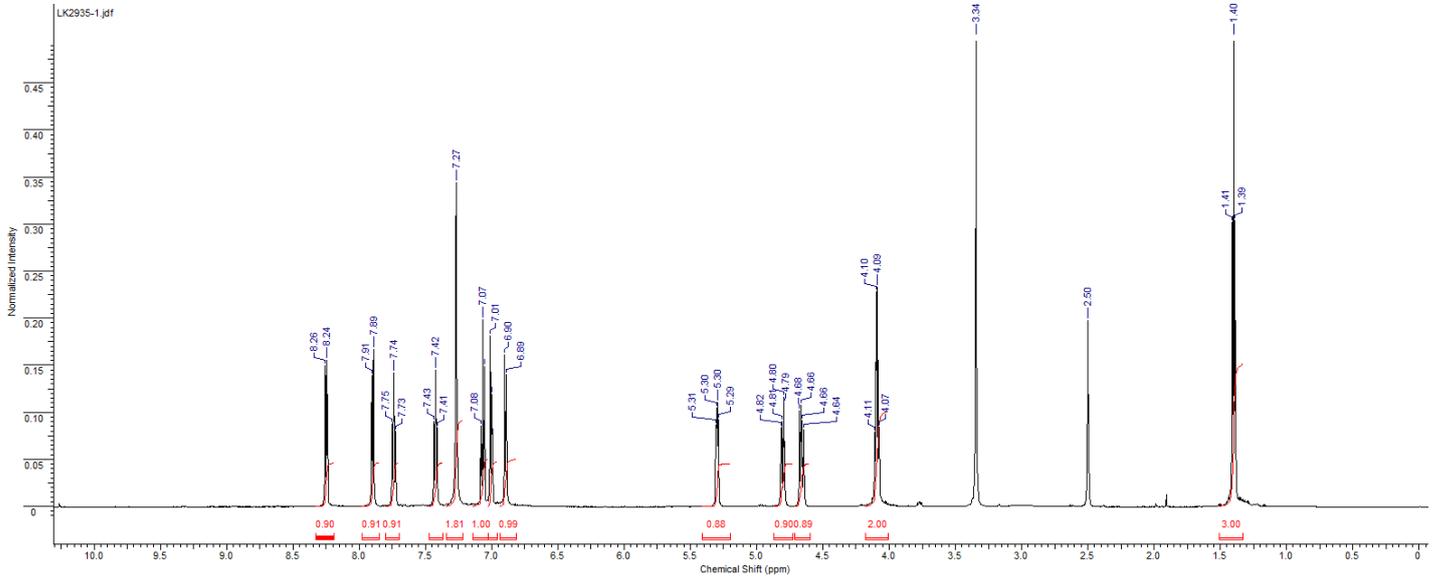
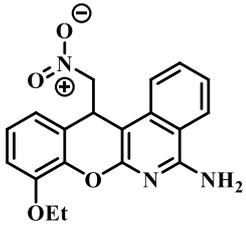


$^{13}\text{C}$ , DMSO- $d_6$

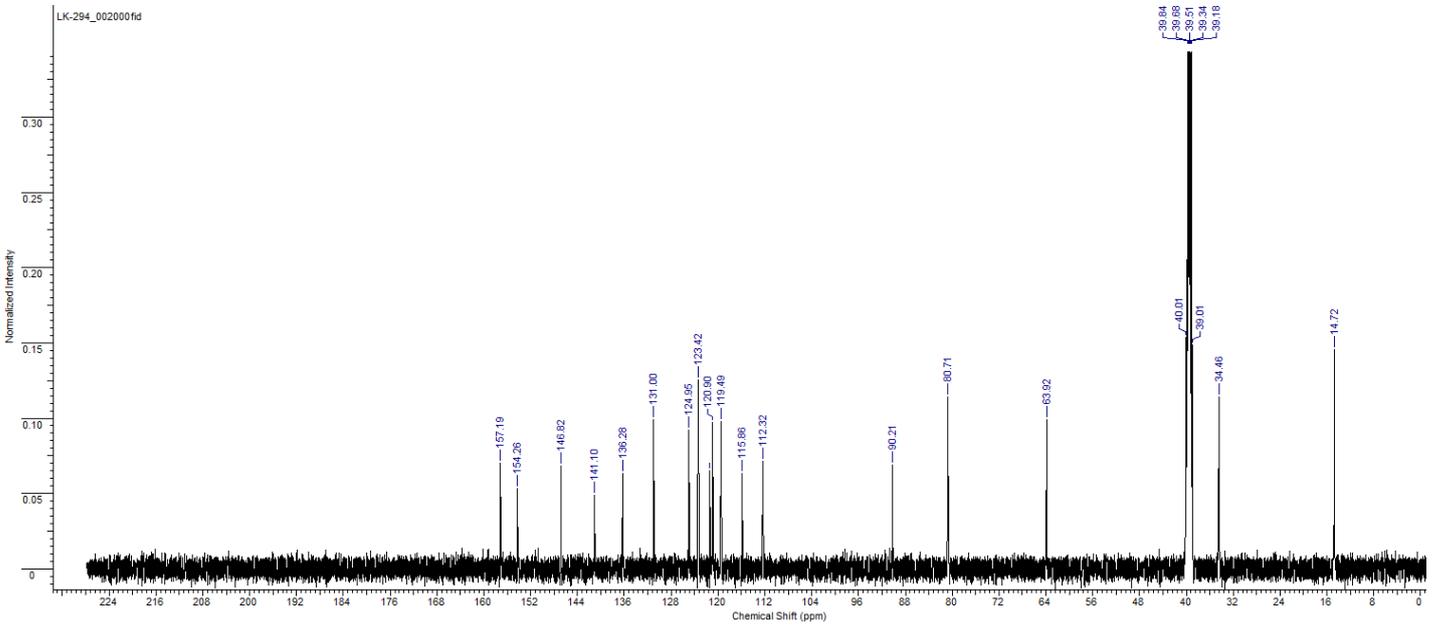


4f

$^1\text{H}$ , DMSO- $d_6$

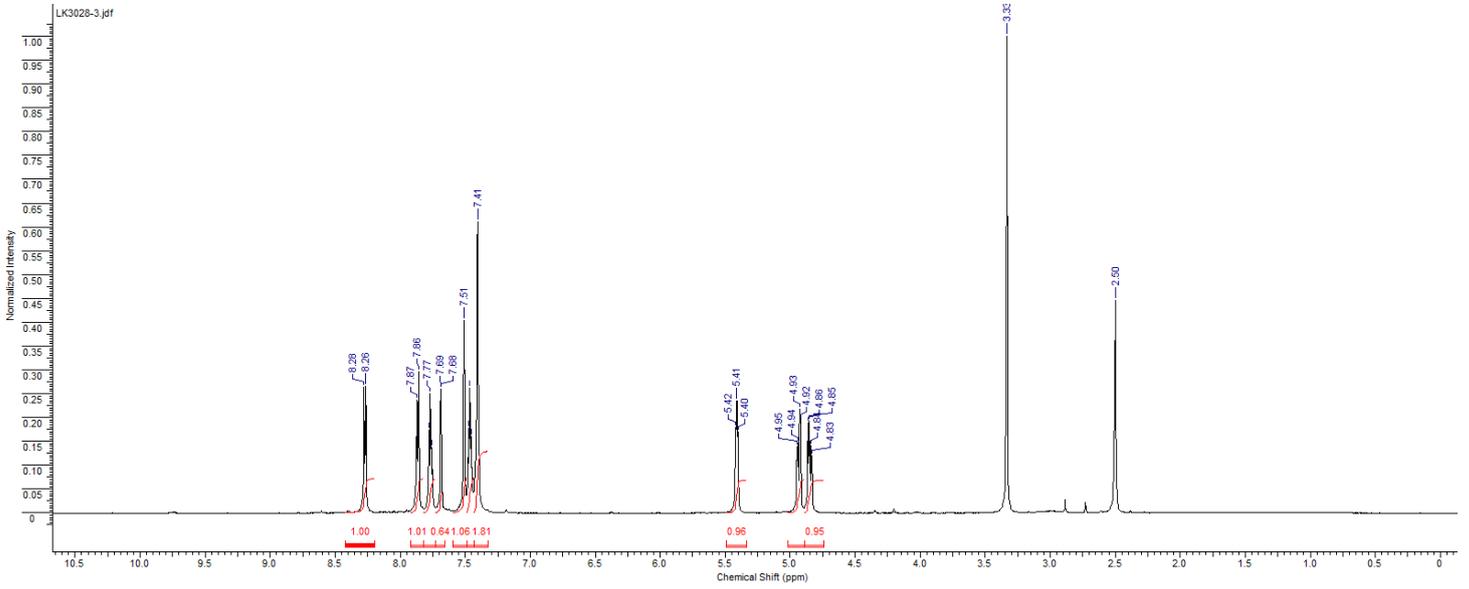
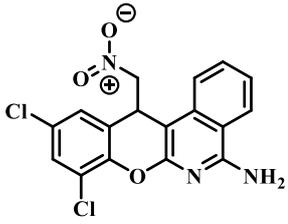


$^{13}\text{C}$ , DMSO- $d_6$

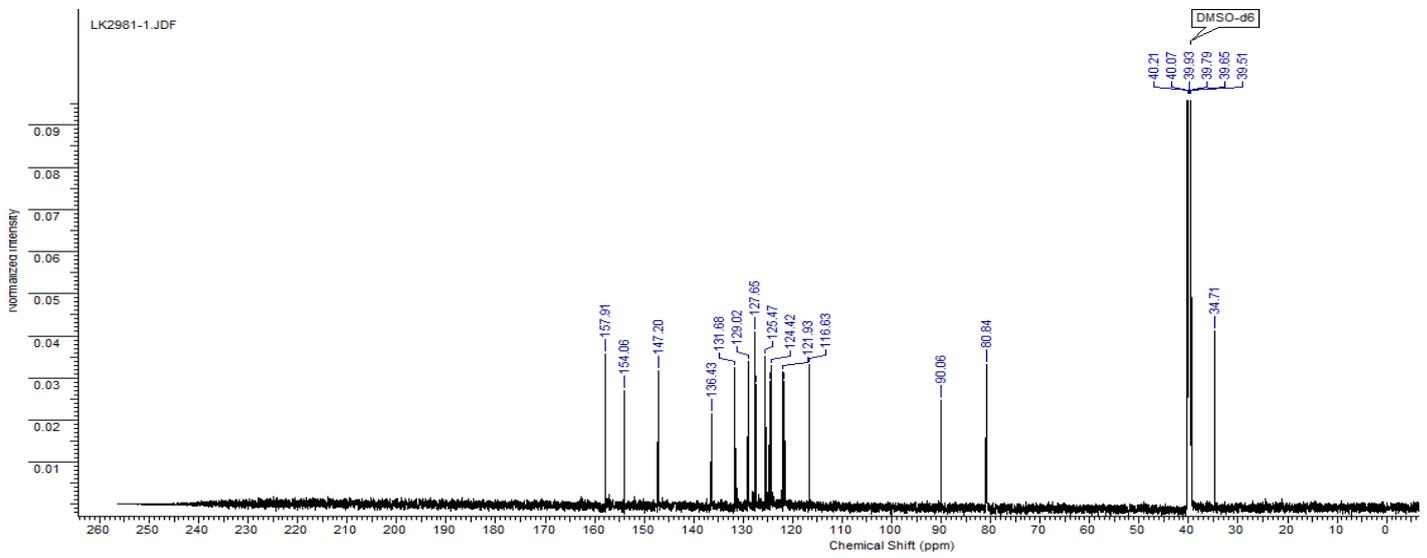


4g

$^1\text{H}$ , DMSO- $d_6$

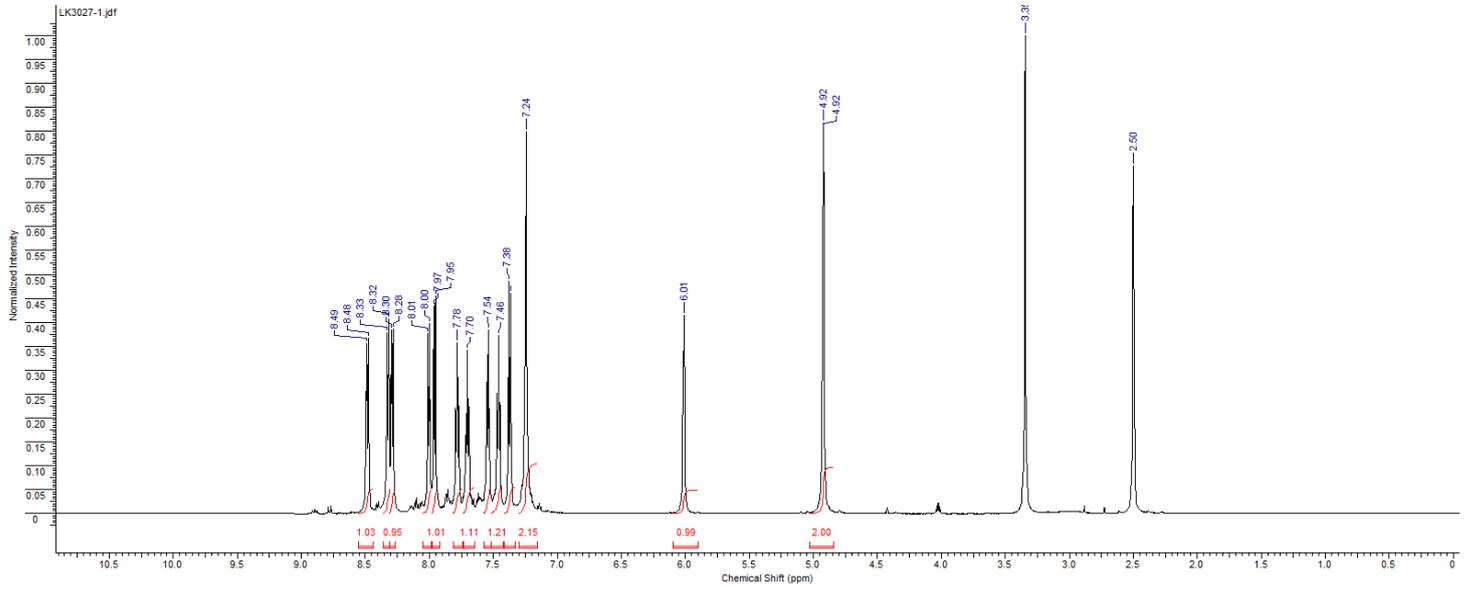
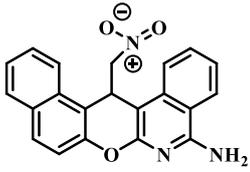


$^{13}\text{C}$ , DMSO- $d_6$



4h

$^1\text{H}$ , DMSO- $d_6$



$^{13}\text{C}$ , DMSO- $d_6$

