Supporting Information

The design, synthesis, and evaluation of azo D-π-A dyes as photothermal agents

Shinichiro Fuse,* Tsukasa Oishi, Keisuke Matsumura, Yoshihiro Hayashi, Susumu Kawauchi, and Hiroyuki Nakamura*

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Evaluation of photothermal conversion efficiency

Photothermal conversion efficiency of synthesized dyes was evaluated in an air-conditioned room. In order to completely dissolve the synthesized dyes, DMSO solution (20 mM) was used for the measurement. A 2 mL DMSO solution containing dye in a quartz derived cell (1cm × 1 cm × 5 cm) was stirred using a magnetic stirrer bar (Figure S1). The thermocouple (Yokogawa Electric Corporatio, DX112-1-1) was introduced in the solution. The prepared sample was irradiated by CCS Inc. PJ2-3005-4CA-PE with HLV3-22RD-4S (465 nm, 316 mW/cm^2) or HLV3-22GR-4S (640 nm, 193 mW/cm^2) light source that was 2 mm away from the sample. Irradiation area (*ca.* 0.8 cm^2) was above the stirrer bar and apart from the thermocouple in an identical manner in every experiment. The cell and light source were continuously cooled by fan during the experiment to avoid undesired influence of heat generated from the light source.

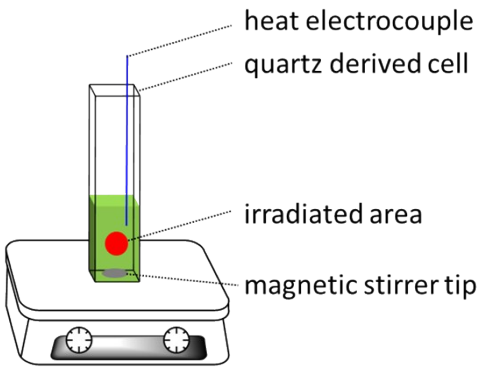


Fig. S1 Set-up for evaluation of photothermal conversion efficiency of dyes.

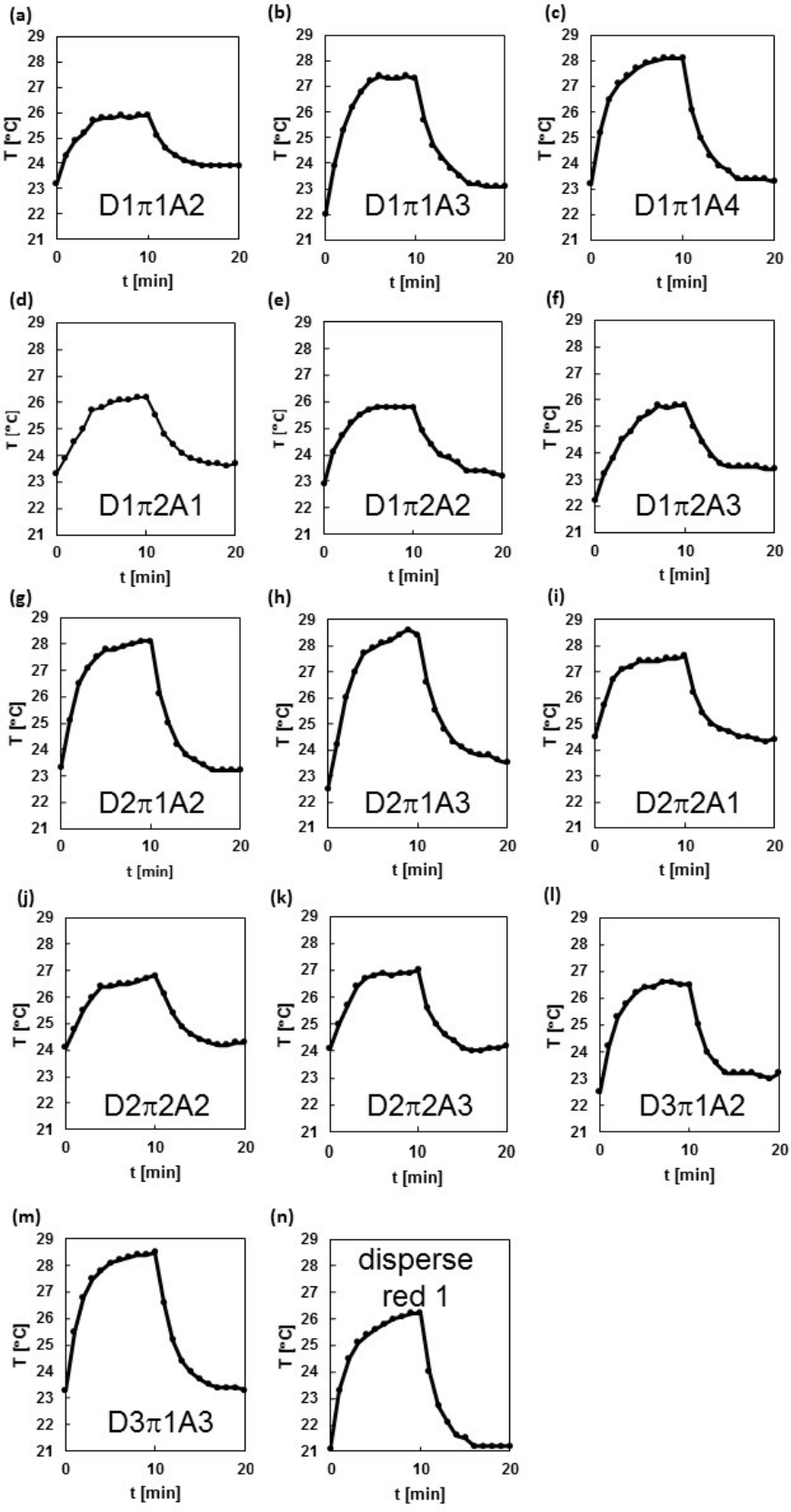


Fig. S2 Photothermal curves of the synthesized dyes.

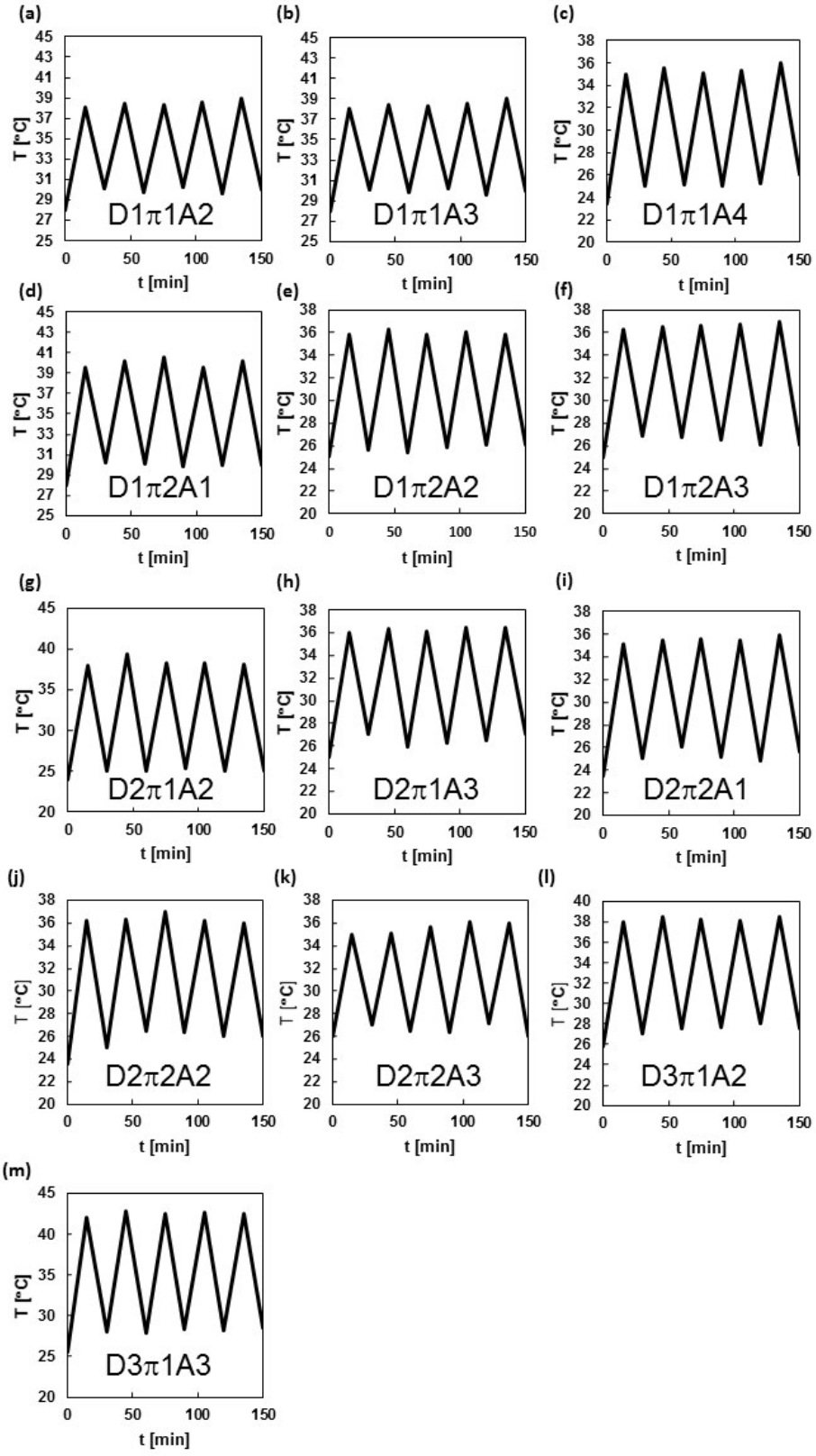


Fig. S2 Iterative photoiiradiation and cooling curves of the synthesized dyes.

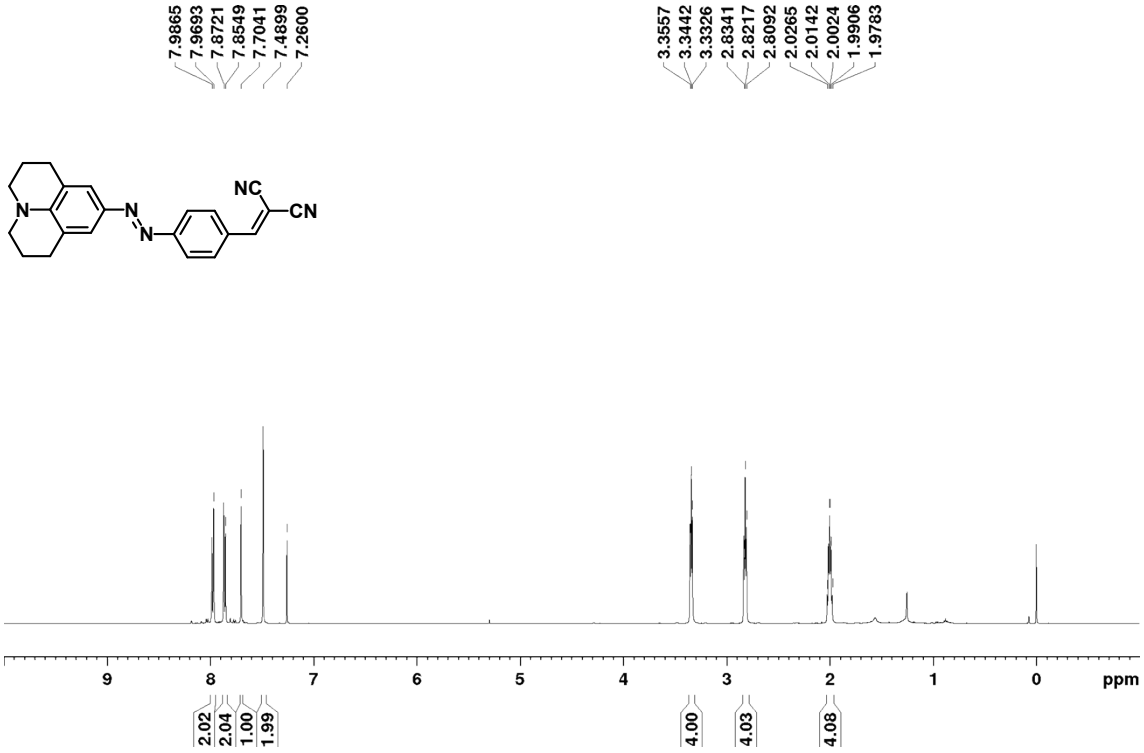
Computational method

All calculations were carried out using the Gaussian 16 program.[1] The DFT calculations were carried out using the long-range and dispersion-corrected ωB97X-D functional.[2] The 6-311G(d,p) basis set was used for all atoms.[3] The torsional potential energy surfaces were performed with a relaxed scan.

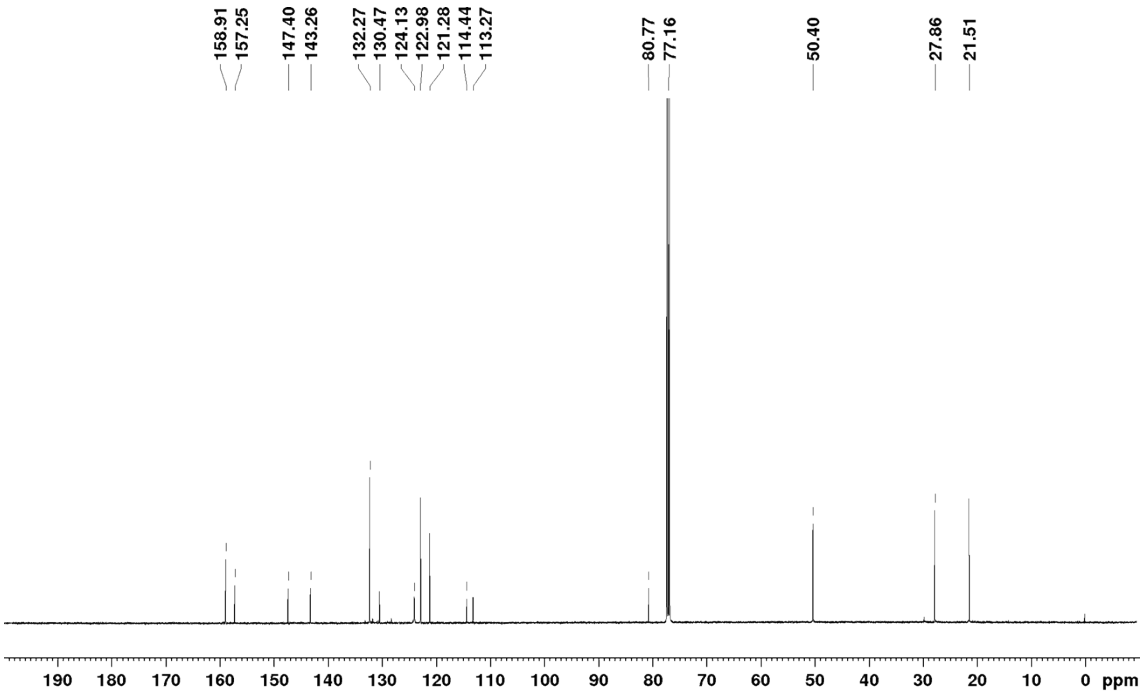
NMR spectra

(*E*)-2-(4-((2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)diazenyl)benzylidene)malononitrile **D1π1A2**

^{1}H NMR

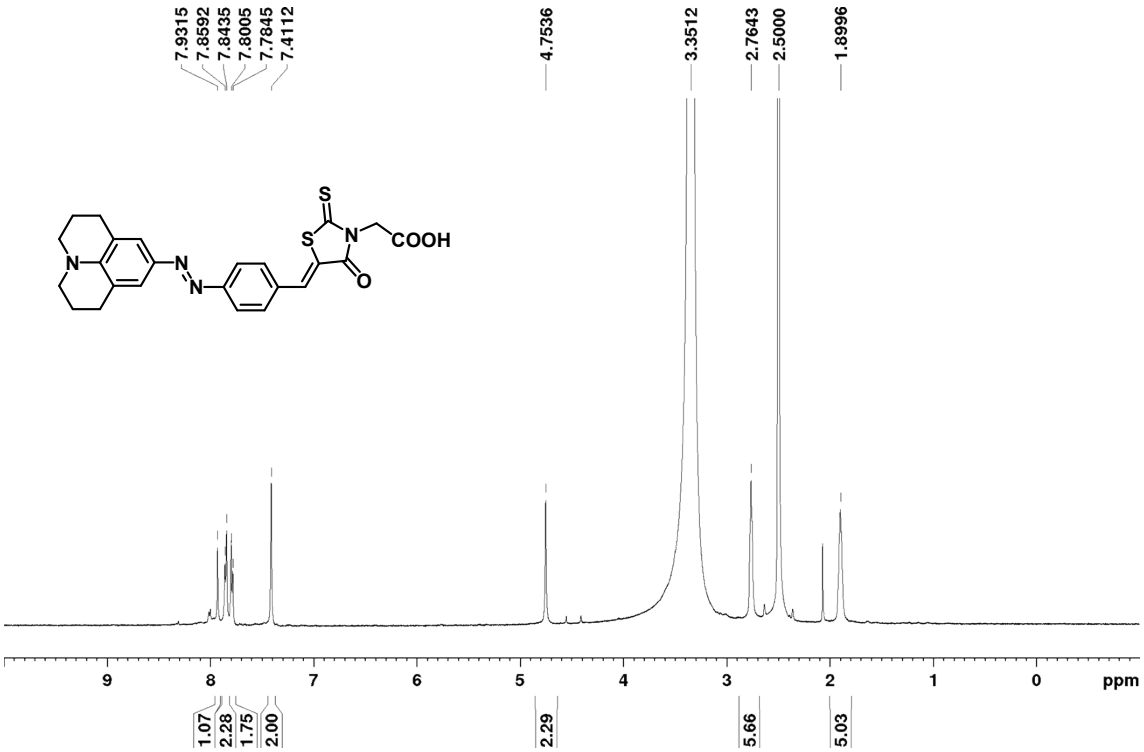


^{13}C NMR

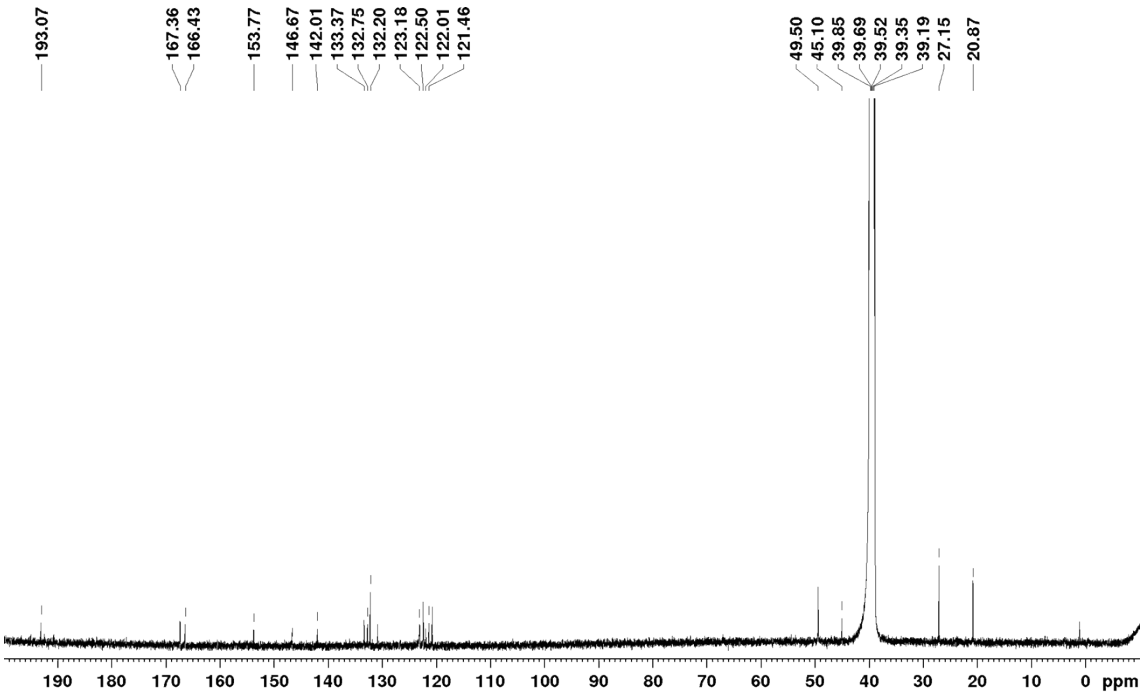


2-(4-Oxo-5-((*Z*)-4-((*E*)-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)diazenyl)benzylidene)-2-thioxothiazolidin-3-yl)acetic acid **D1π1A3**

^{1}H NMR

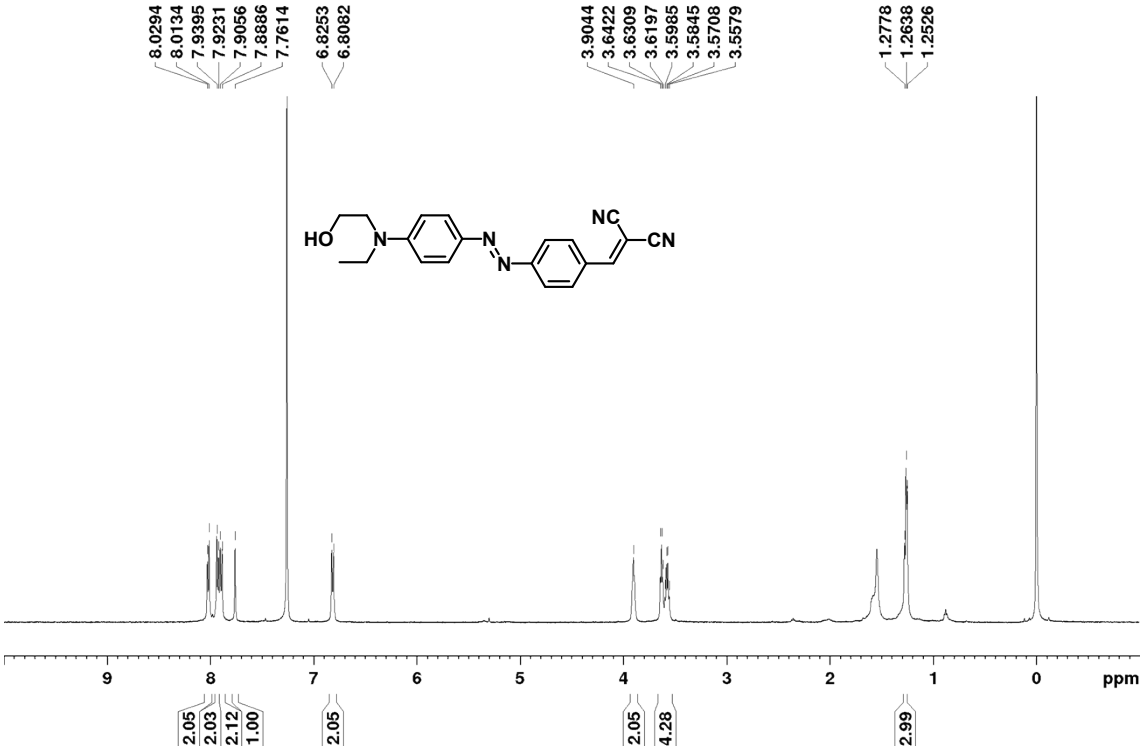


^{13}C NMR



(*E*)-2-(4-((4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)benzylidene)malononitrile **D2π1A2**

^{1}H NMR



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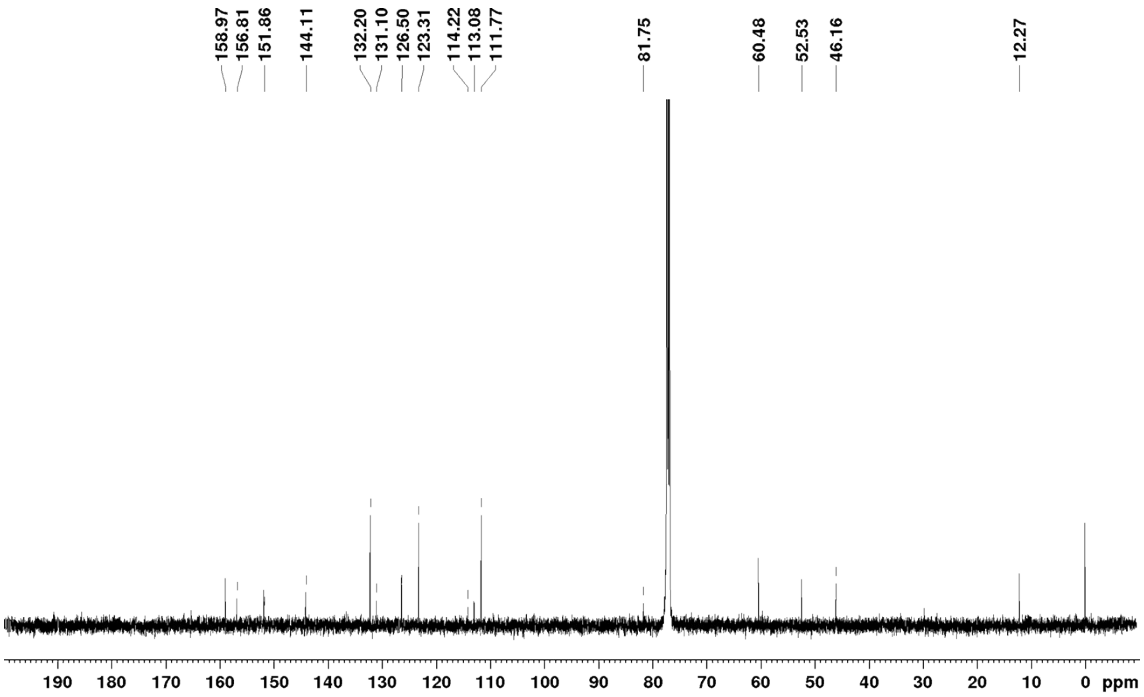
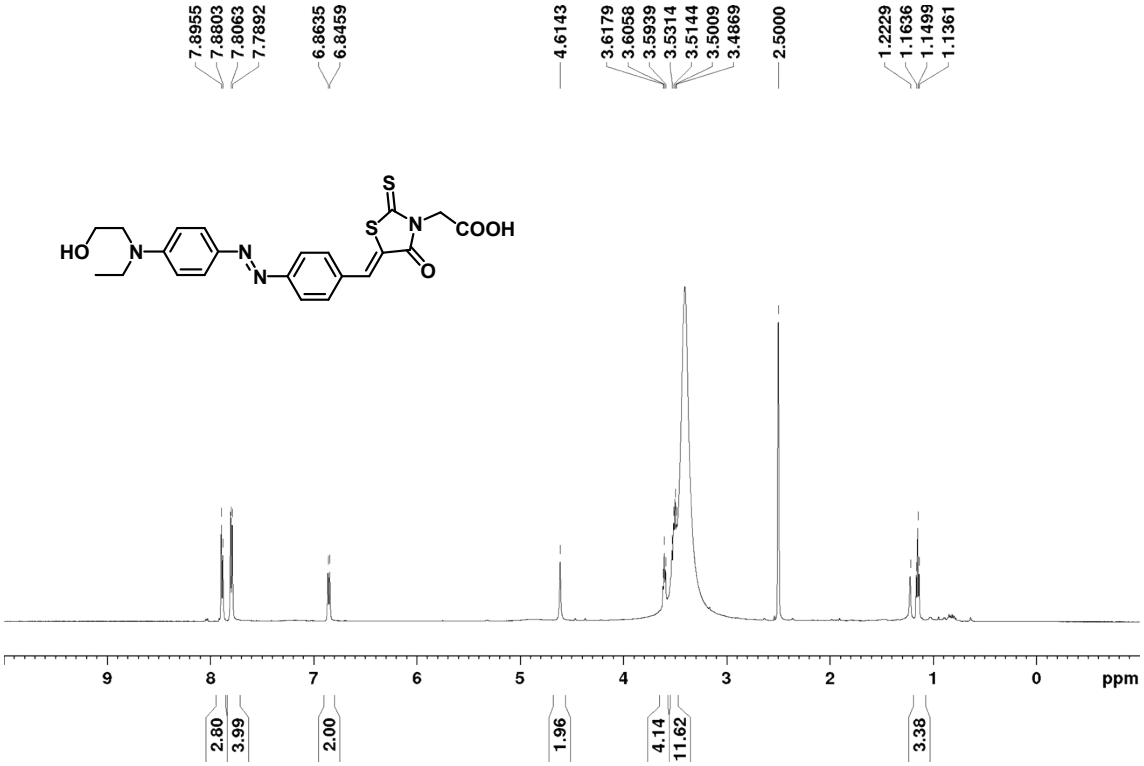


2-(5-((*Z*)-4-((*E*)-(4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid **D2π1A3**

^{1}H NMR



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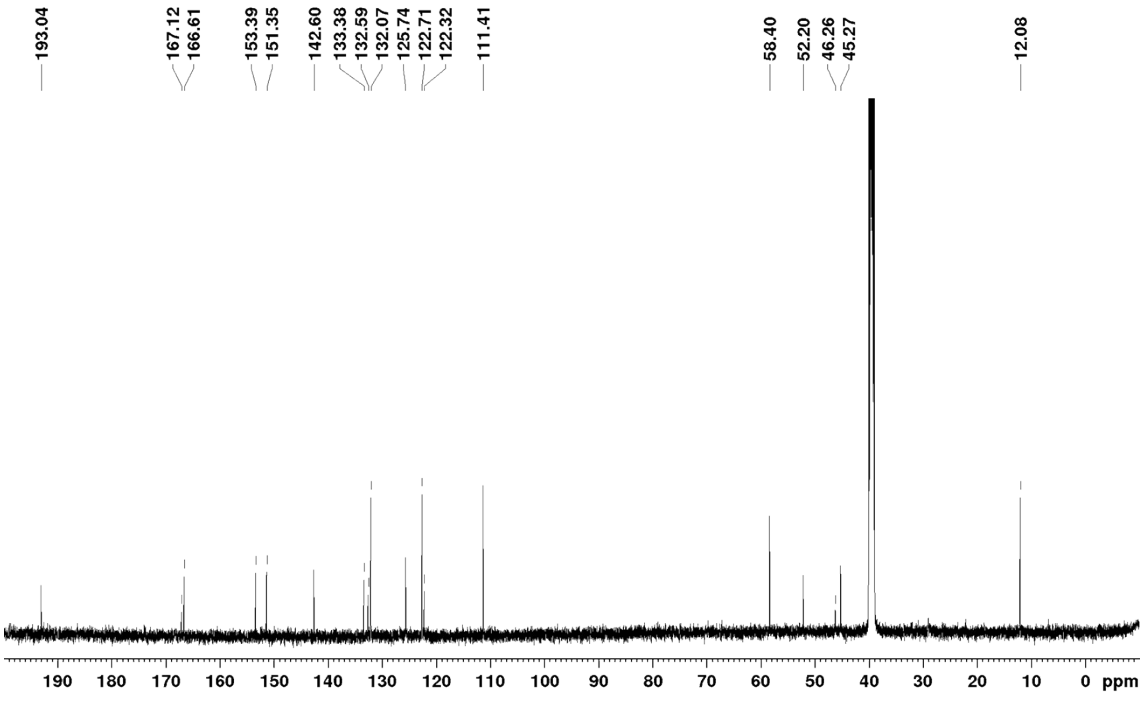
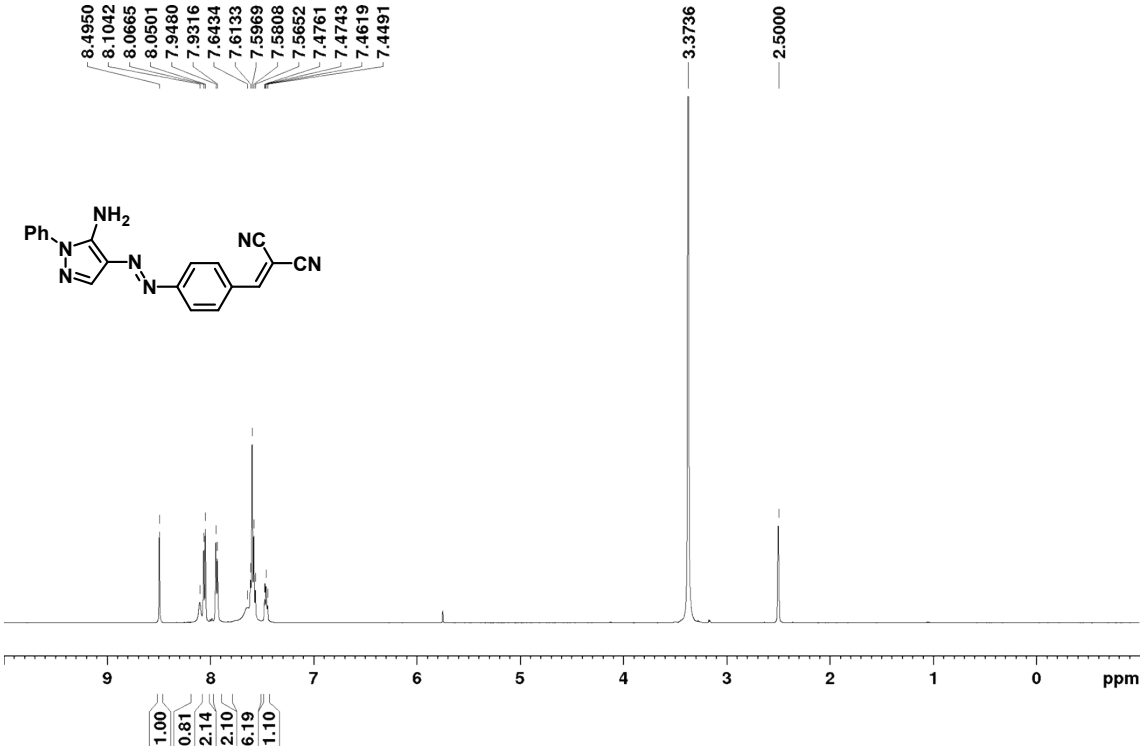


(*E*)-2-(4-((5-Amino-1-phenyl-1*H*-pyrazol-4-yl)diazenyl)benzylidene)malononitrile **D3π1A2**

^{1}H NMR



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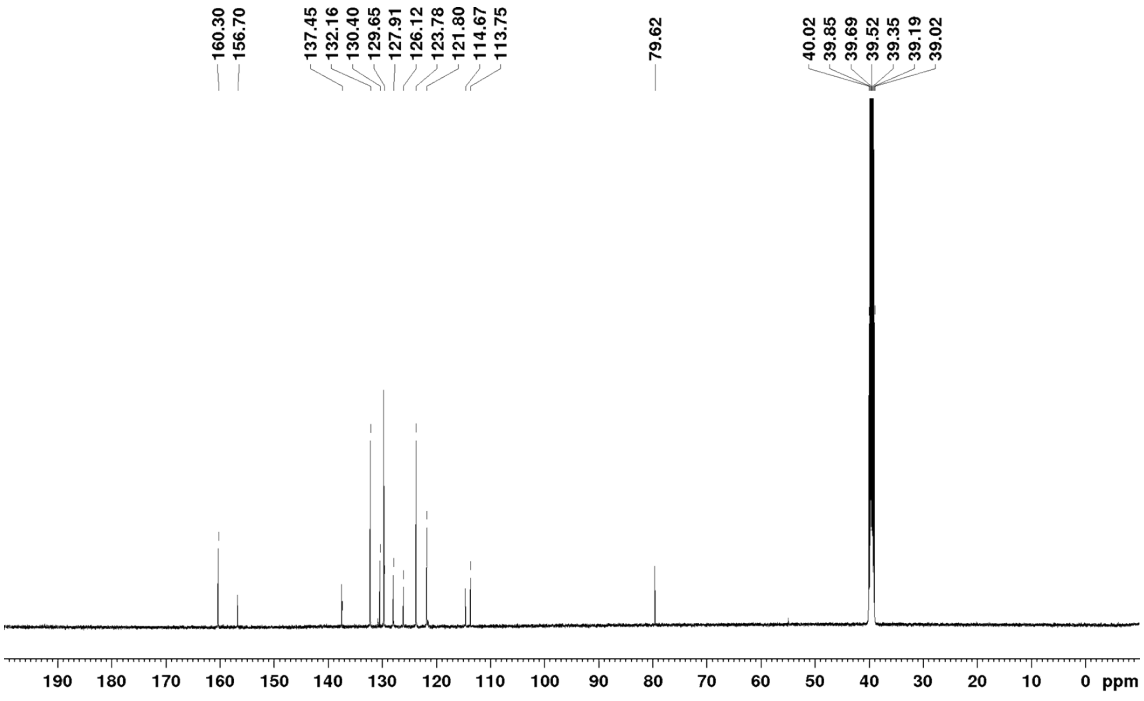

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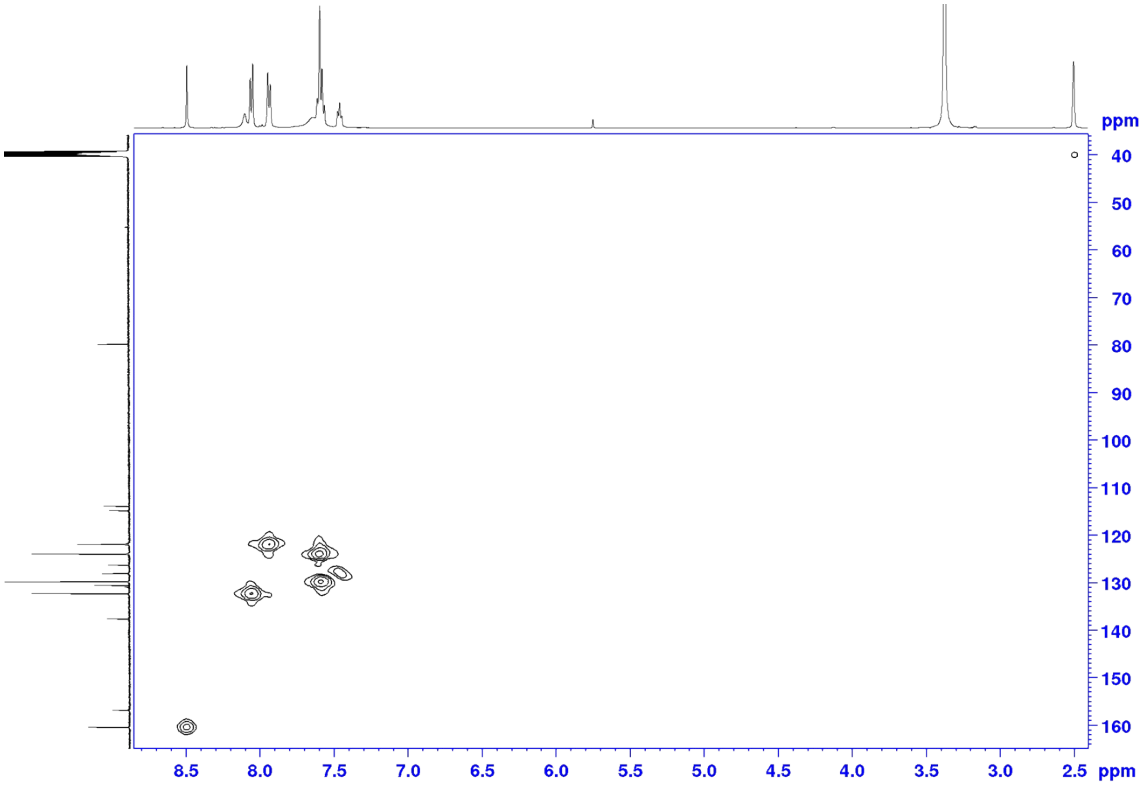
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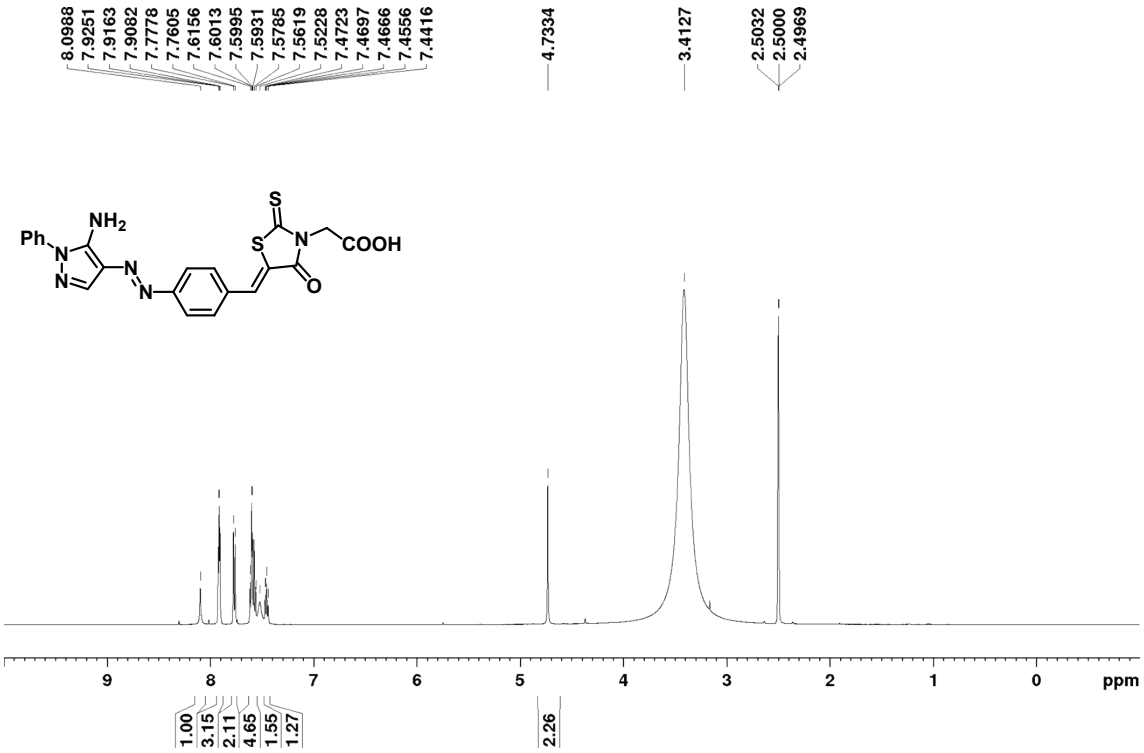
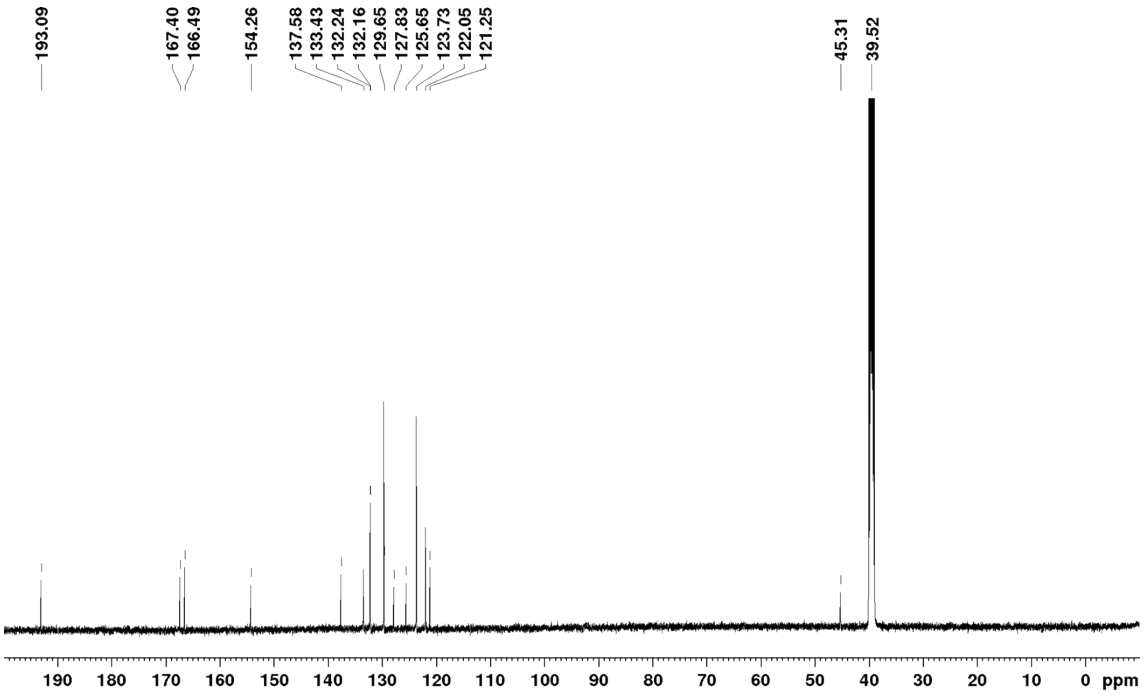
ppm

2-(5-((*Z*)-4-((*E*)-(5-Amino-1-phenyl-1*H*-pyrazol-4-yl)diazenyl)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid **D3π1A3**

^{1}H NMR



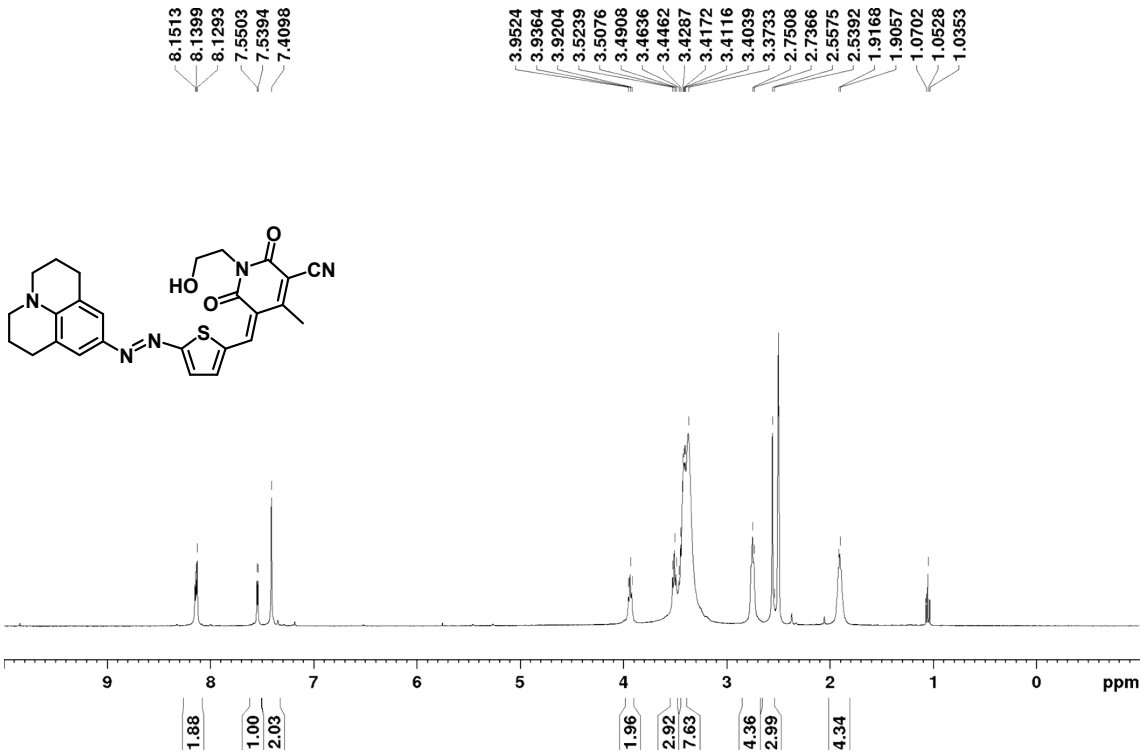
^{13}C NMR



(*Z*)-1-(2-Hydroxyethyl)-4-methyl-2,6-dioxo-5-((5-((*E*)-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)diazenyl)thiophen-2-yl)methylene)-1,2,5,6-tetrahydropyridine-3-carbonitrile

D1π2A1

^{1}H NMR



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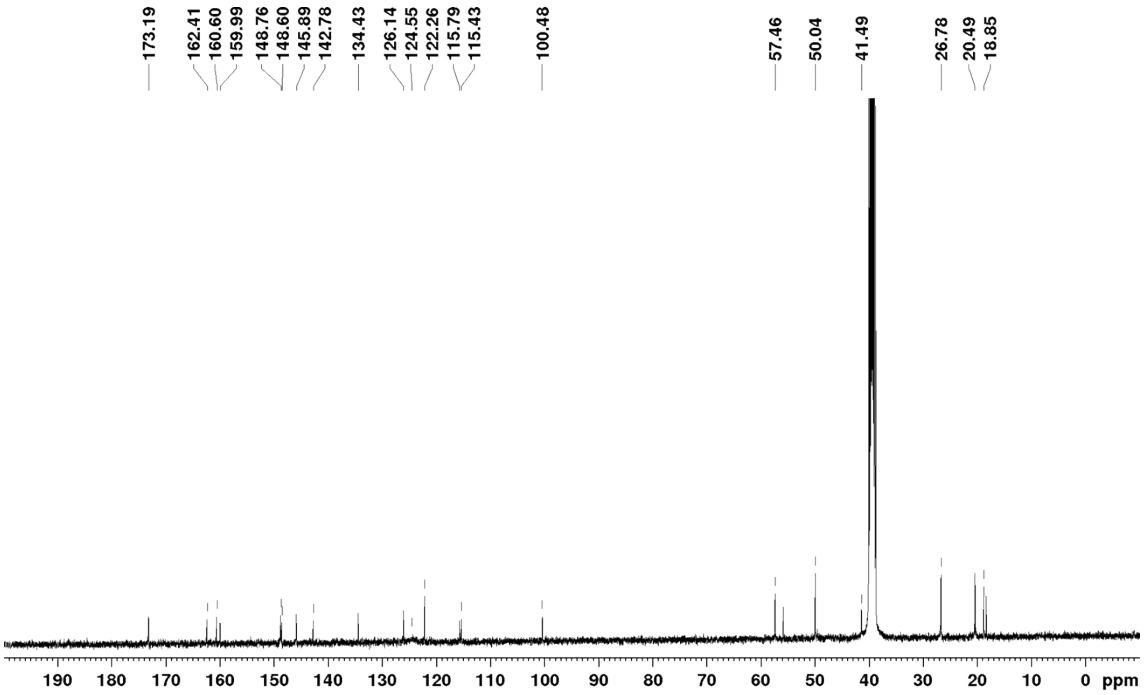
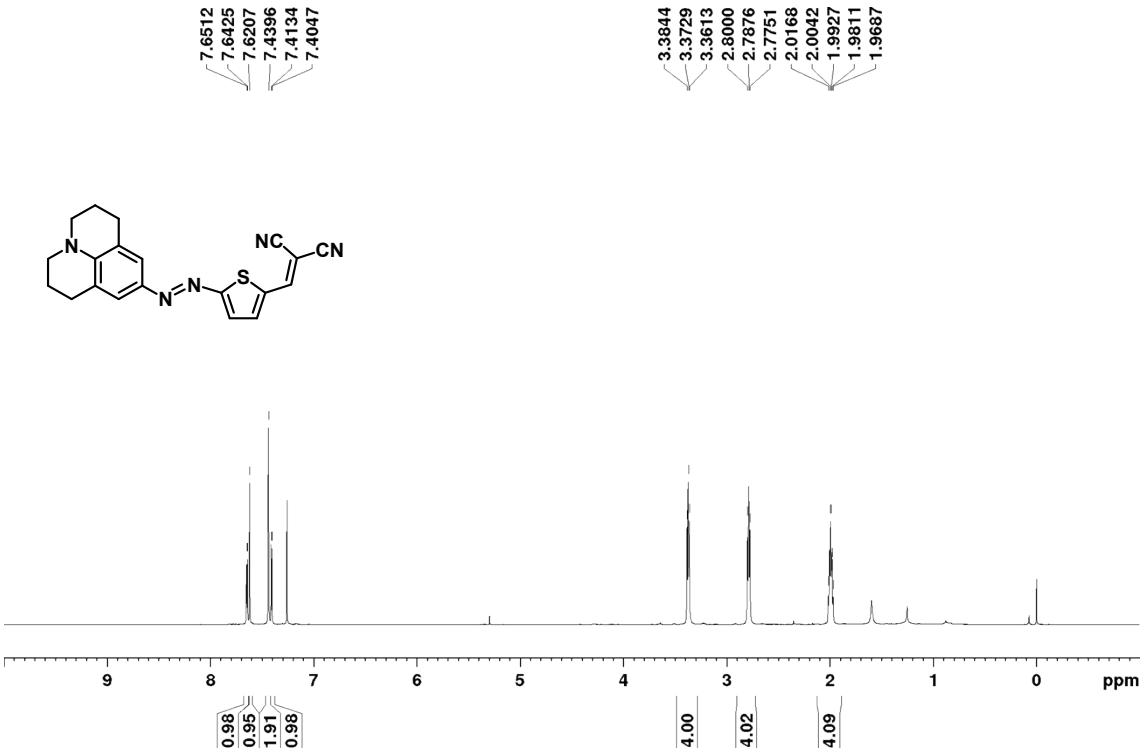


(*E*)-2-((5-((2,3,6,7-Tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)diazenyl)thiophen-2-yl)methylene)malononitrile **D1π2A2**

^{1}H NMR



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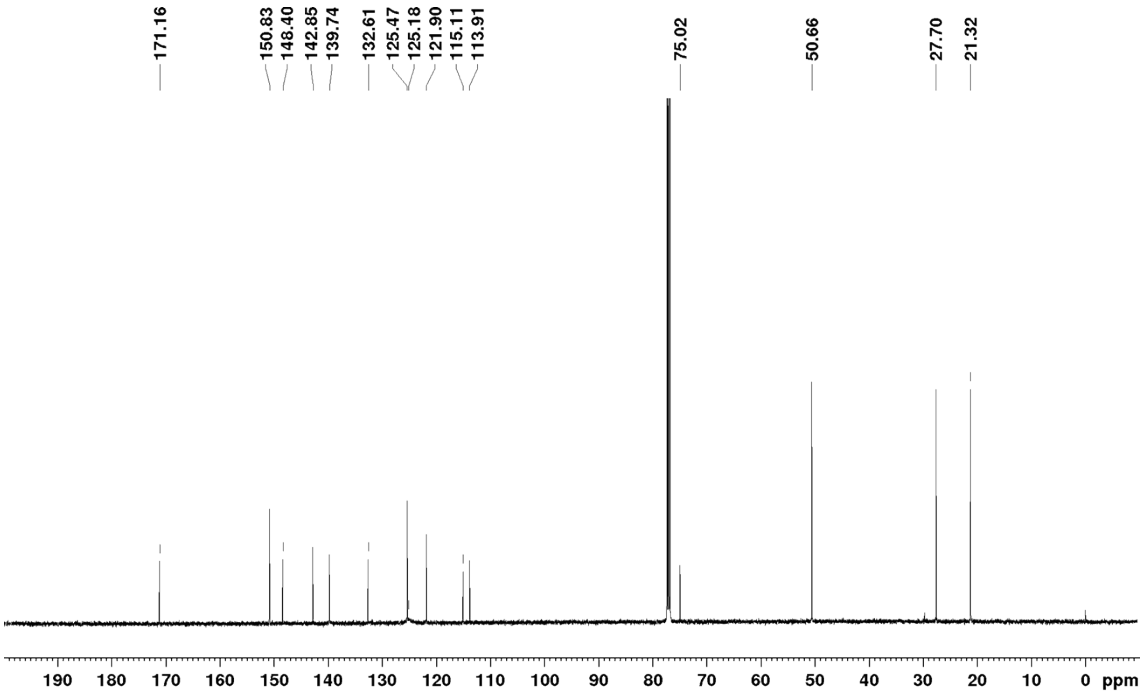

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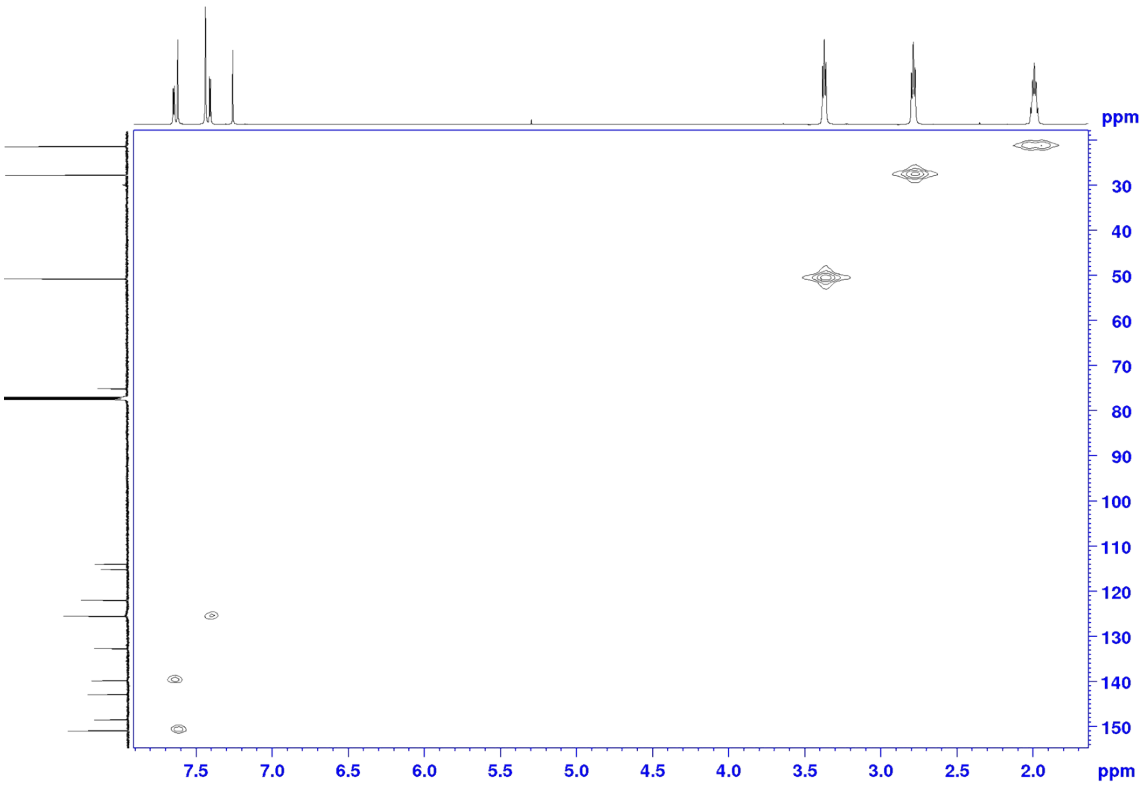
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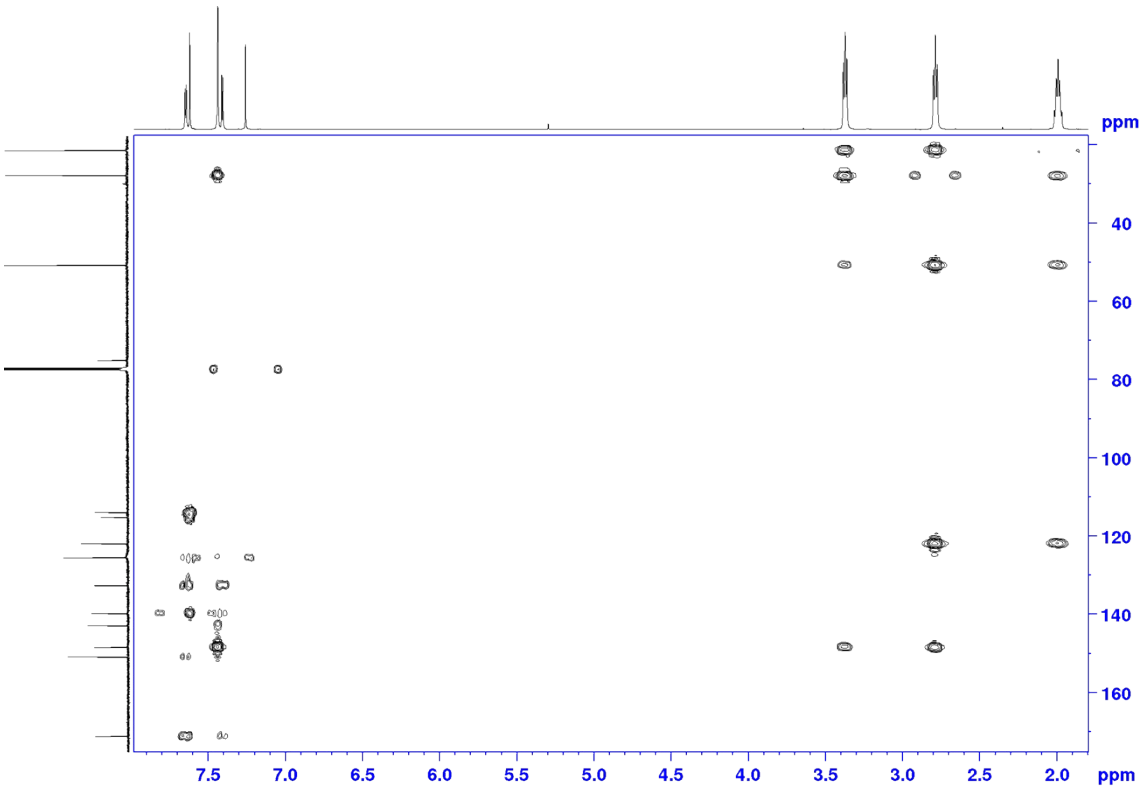
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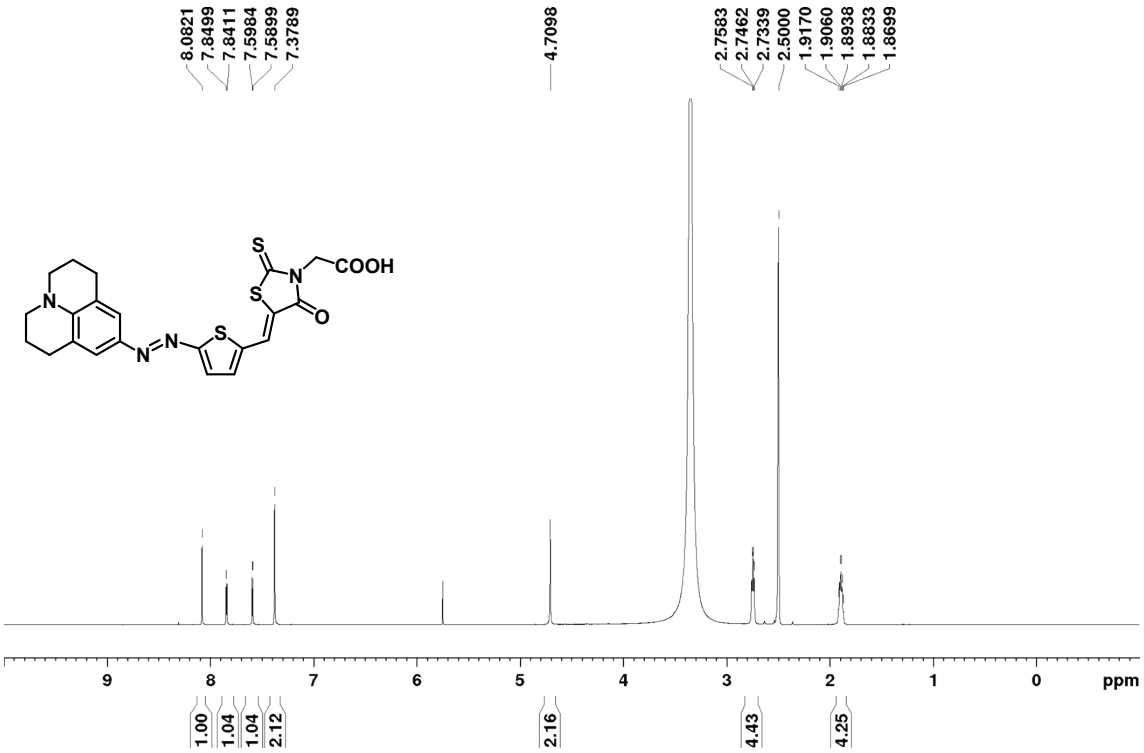
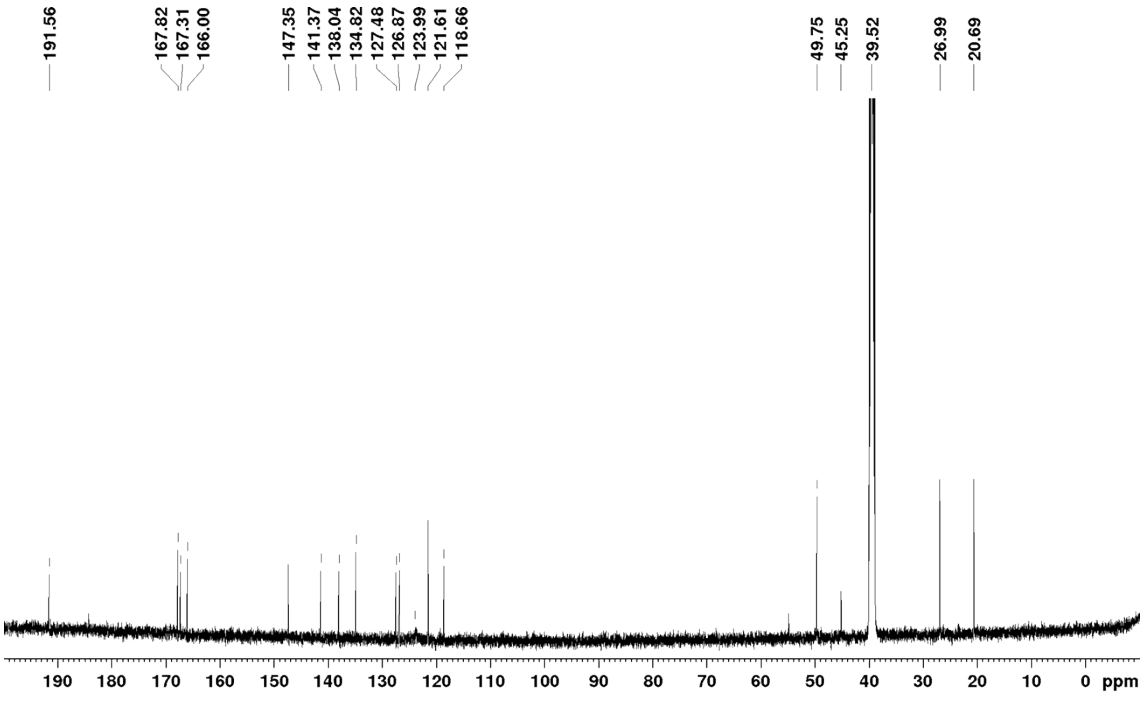
2-((*Z*)-4-Oxo-5-((5-((*E*)-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)diazenyl)thiophen-2-yl)methylene)-2-thioxothiazolidin-3-yl)acetic acid **D1π2A3**

^{1}H NMR

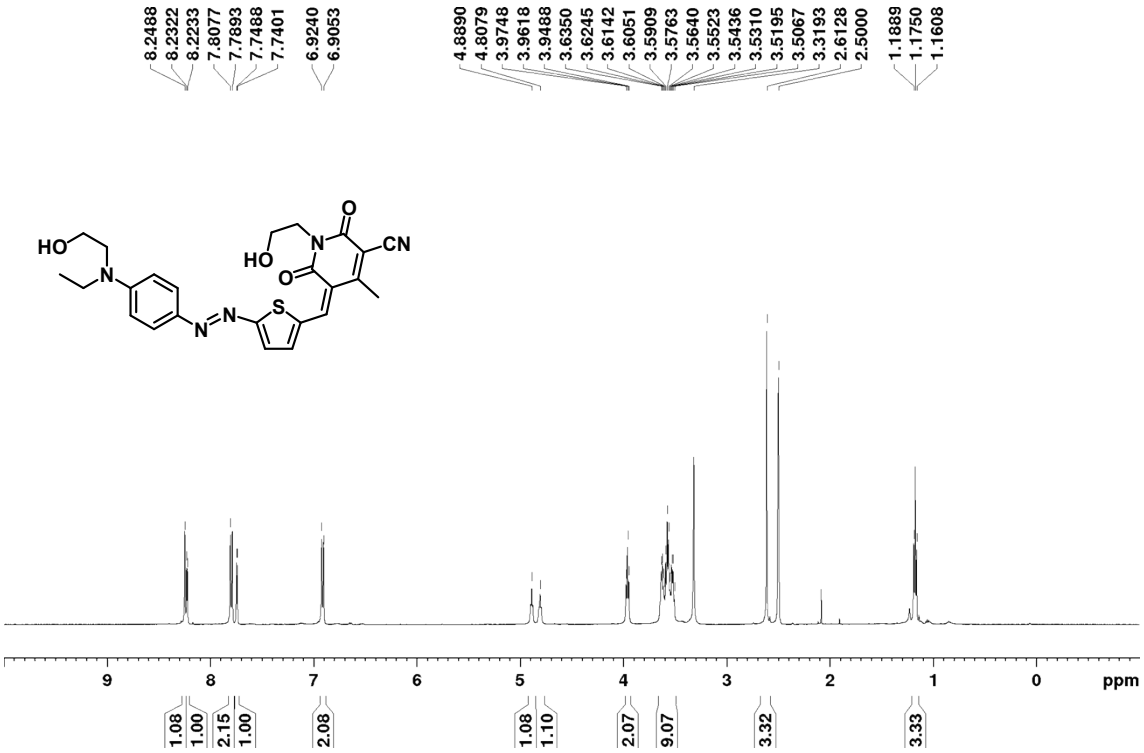


^{13}C NMR



(*Z*)-5-((5-((*E*)-(4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)thiophen-2-yl)methylene)-1-(2-hydroxyethyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile **D2π2A1**

^{1}H NMR



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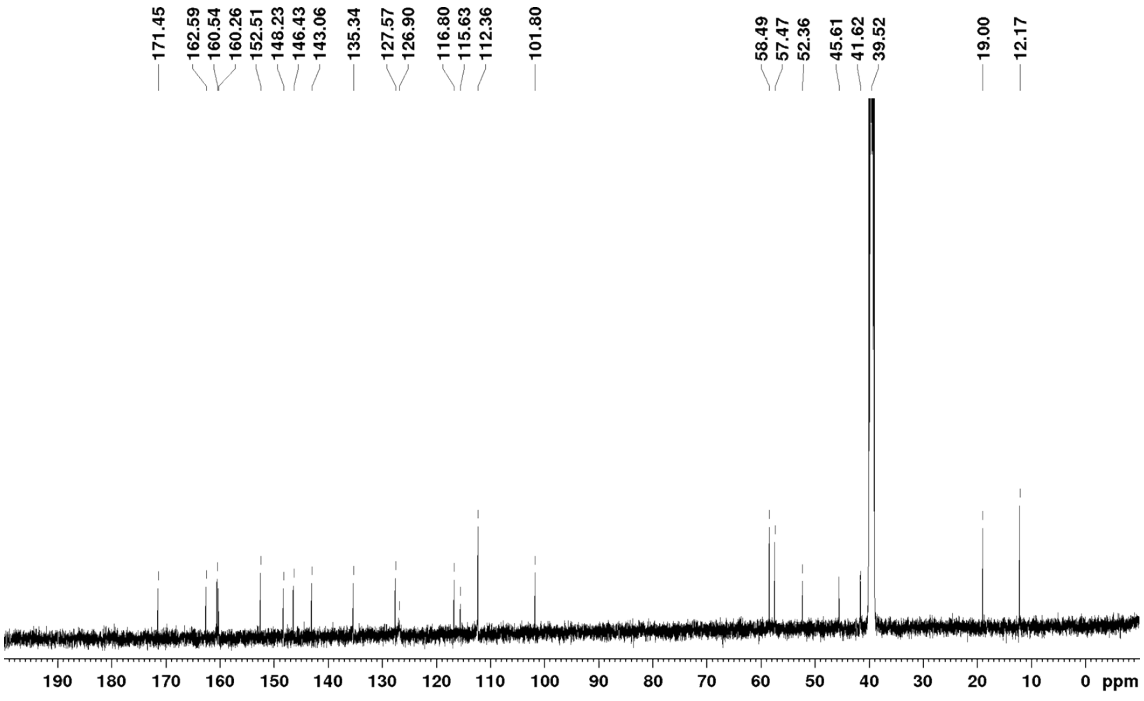

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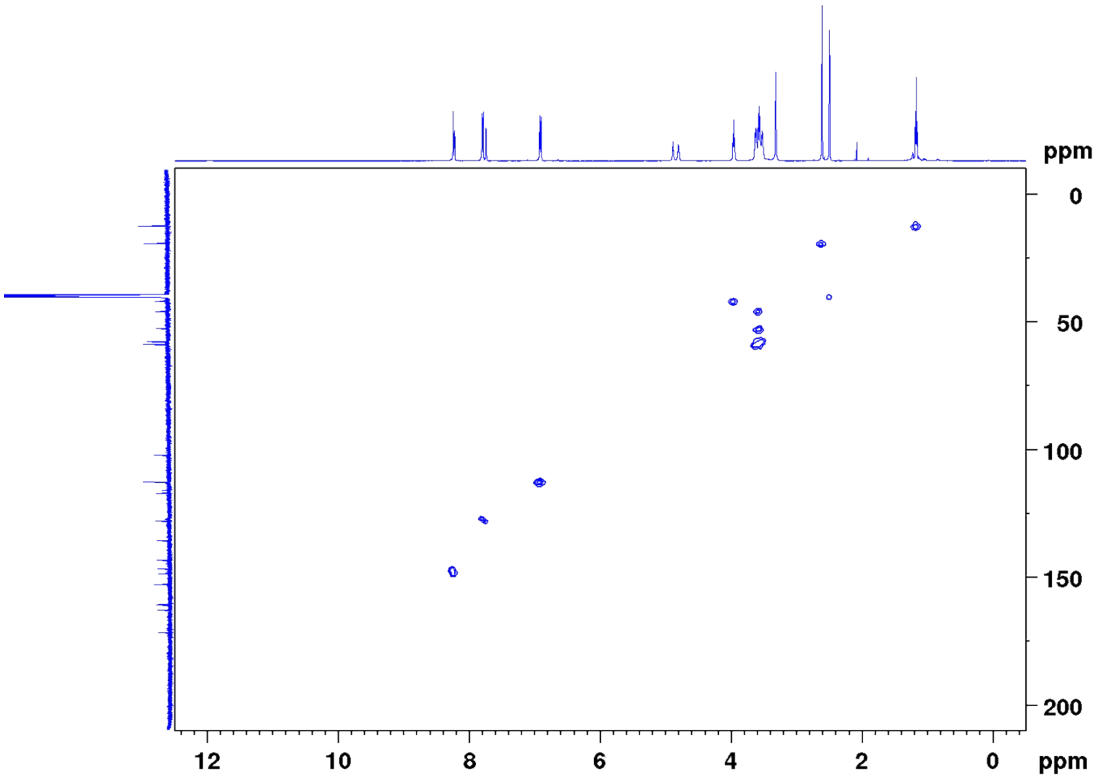

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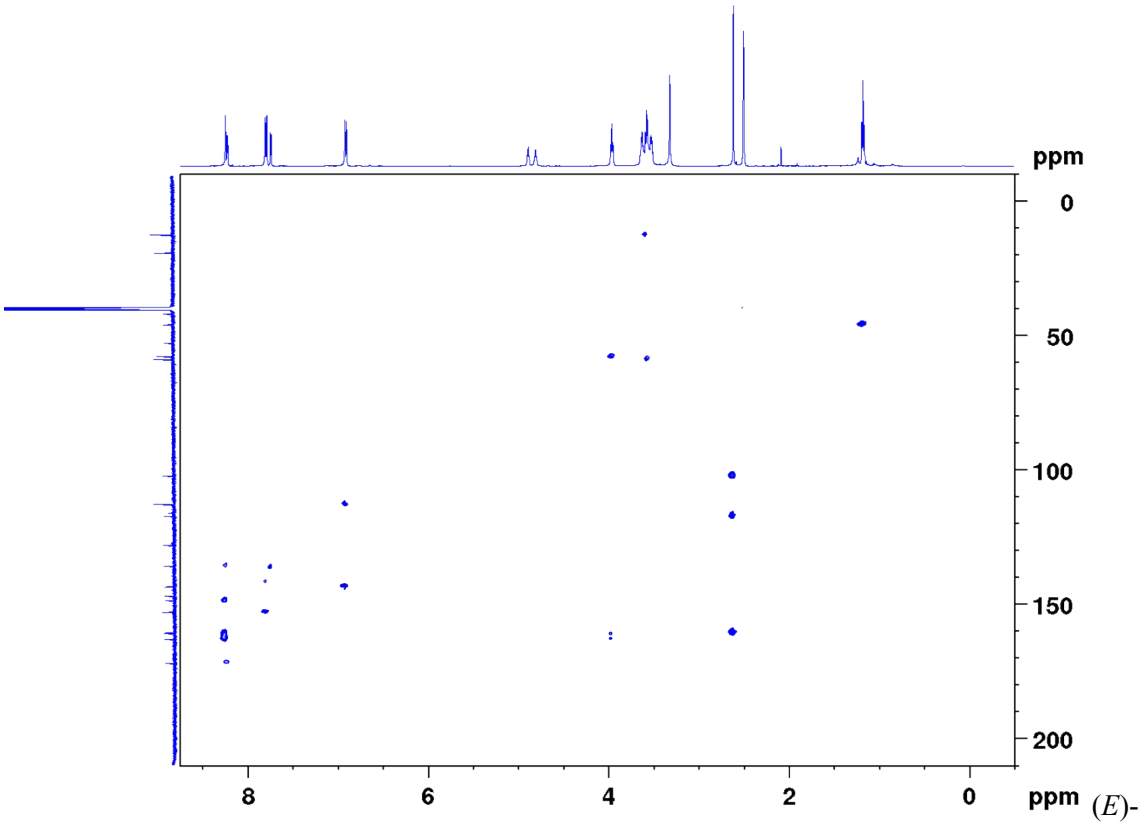
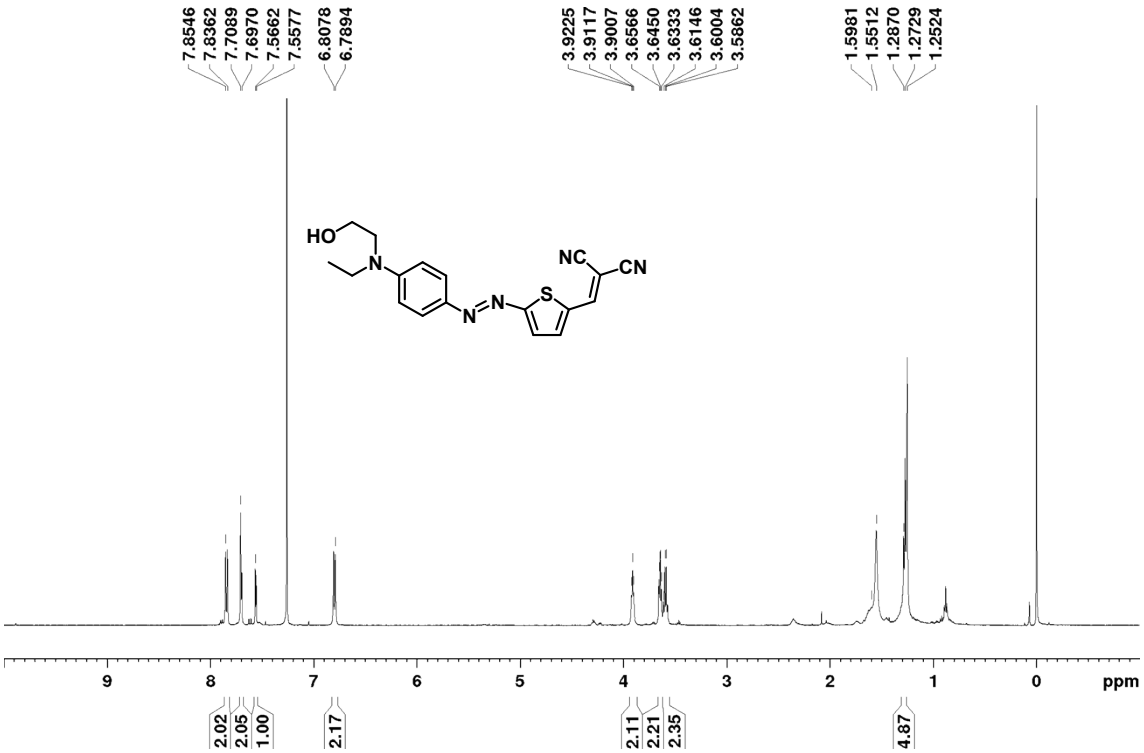


(*E*)-2-((5-((4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)thiophen-2-yl)methylene)malononitrile

D2π2A2

^{1}H NMR



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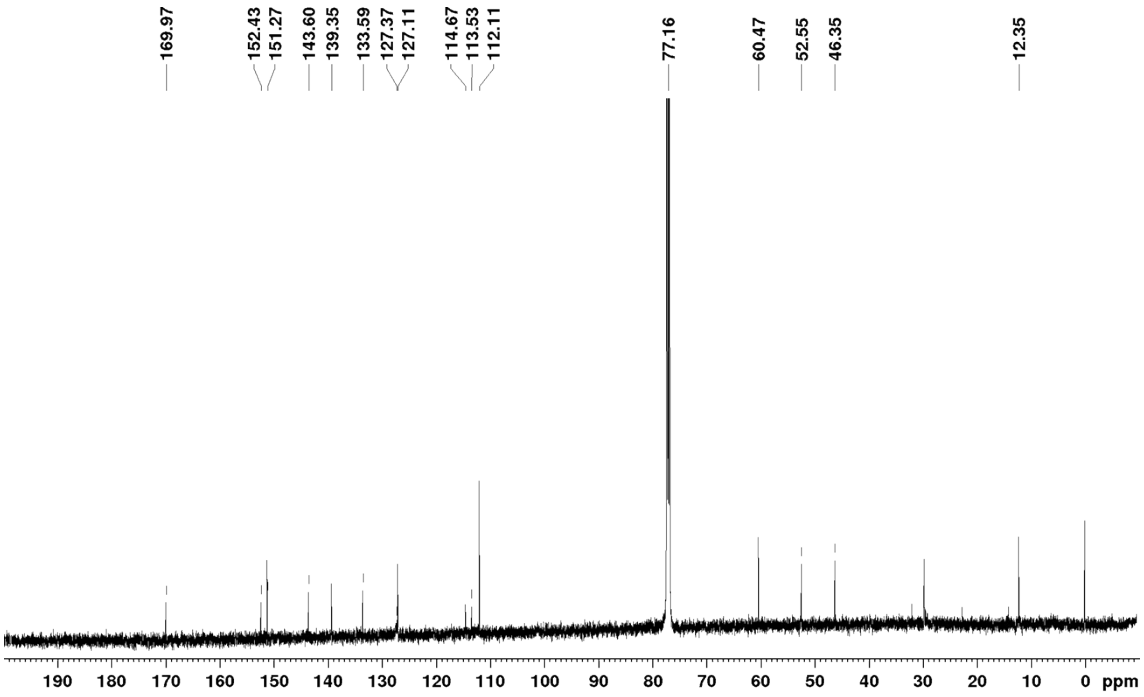
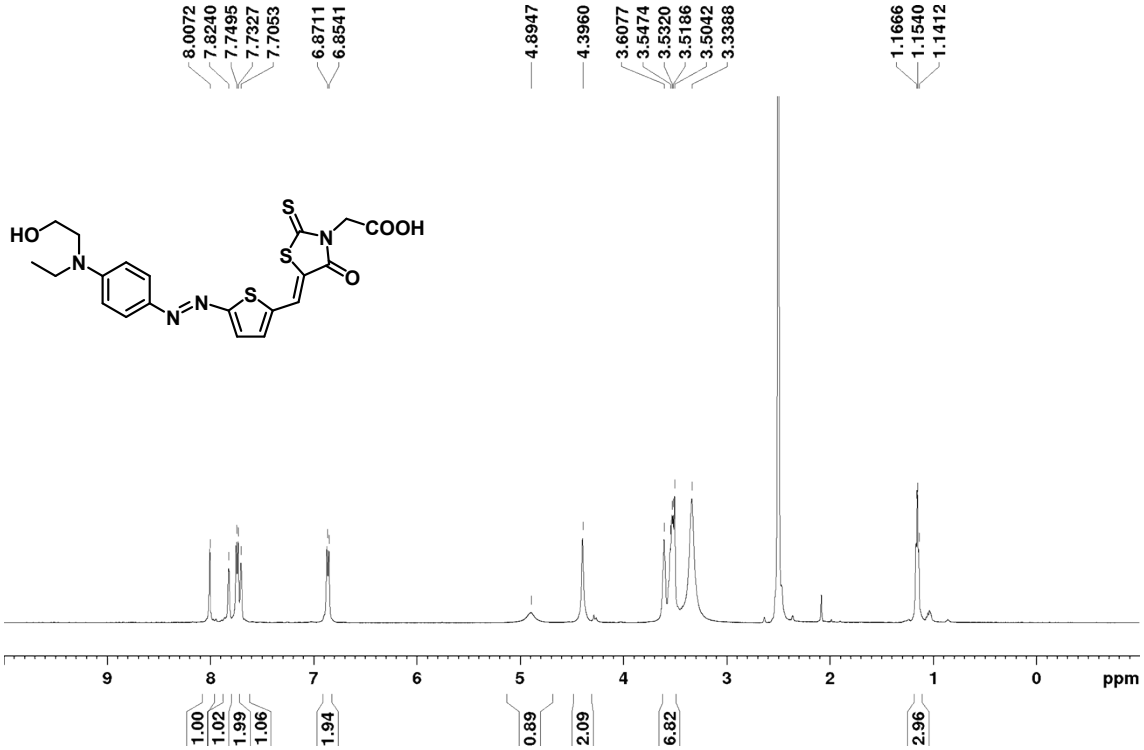


(*E*)-5-((4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)thiophene-2-carbaldehyde

2-((*Z*)-5-((5-((*E*)-(4-(Ethyl(2-hydroxyethyl)amino)phenyl)diazenyl)thiophen-2-yl)methylene)-4-

oxo-2-thioxothiazolidin-3-yl)acetic acid **D2π2A3**

^{1}H NMR



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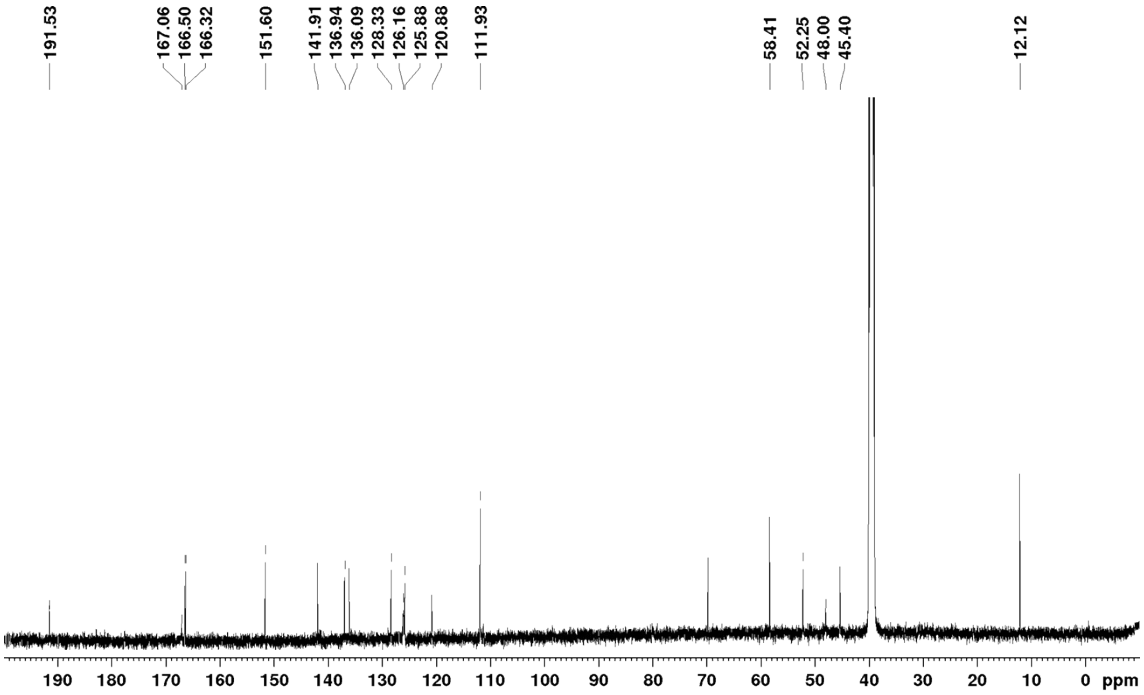
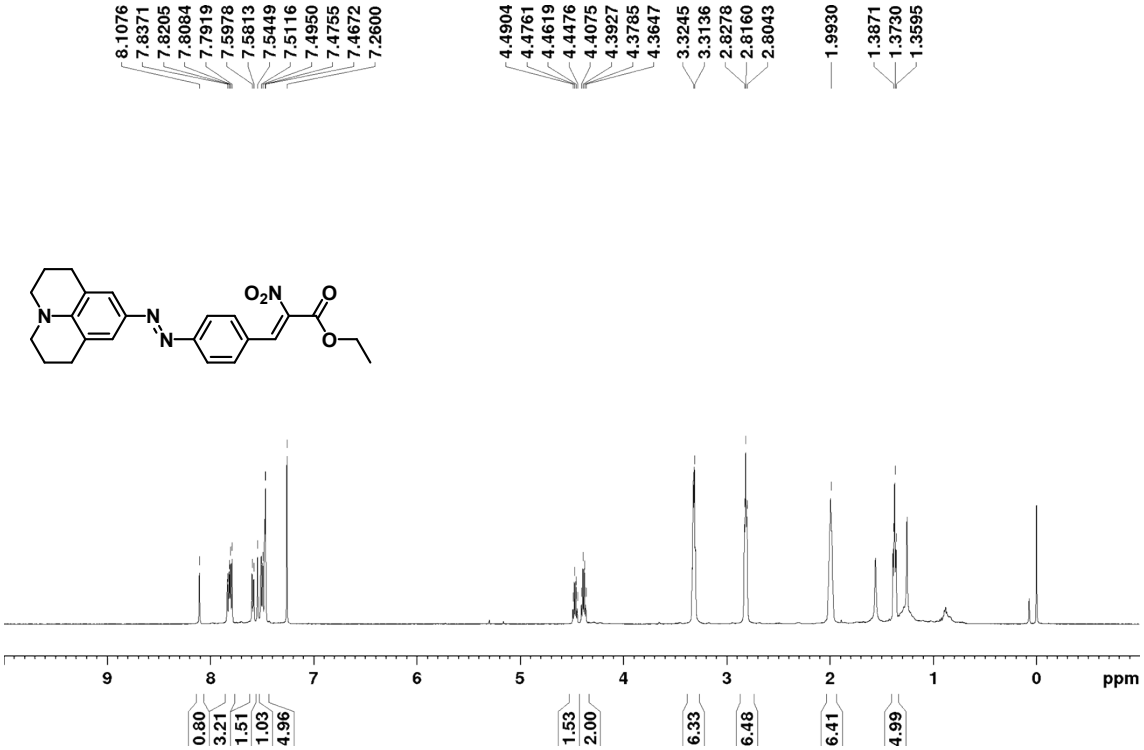


Ethyl(*Z*)-2-nitro-3-(4-((*E*)-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-

yl)diazenyl)phenyl)acrylate **D1π1A4**

^{1}H NMR



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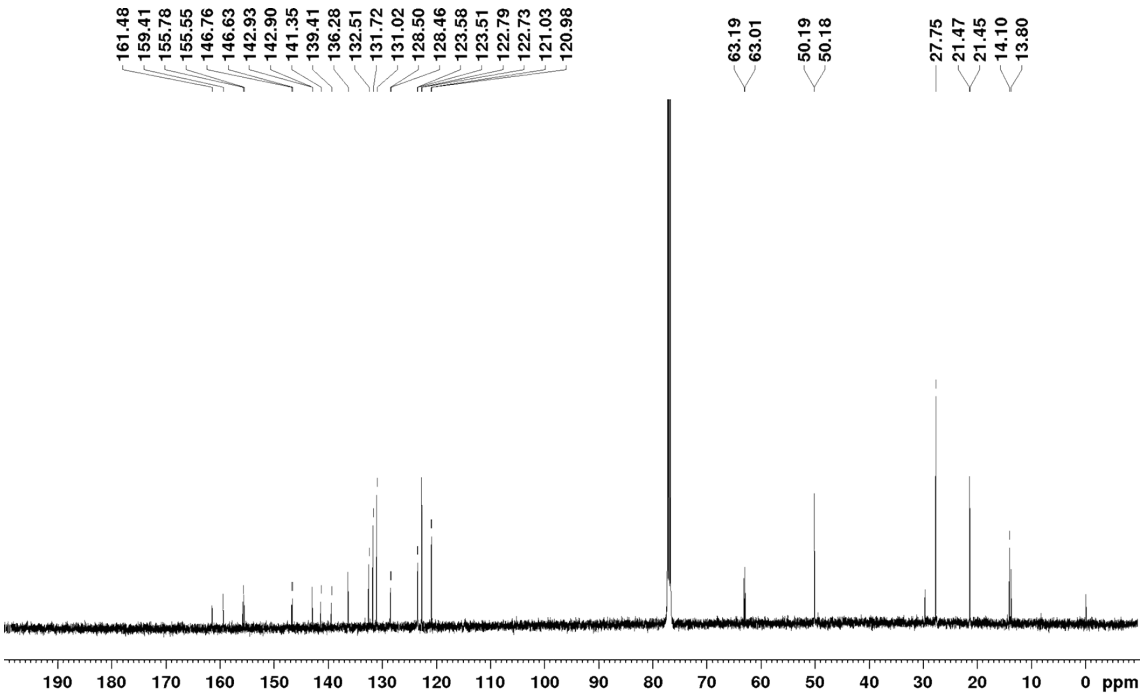

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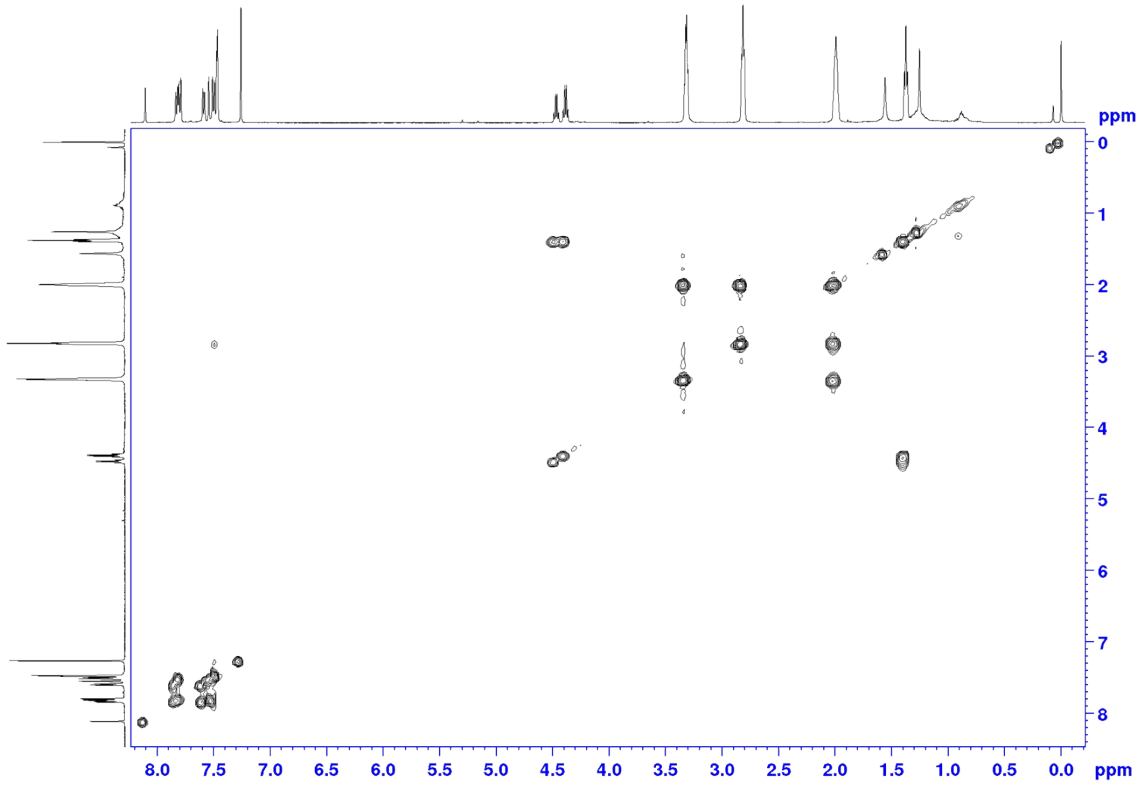

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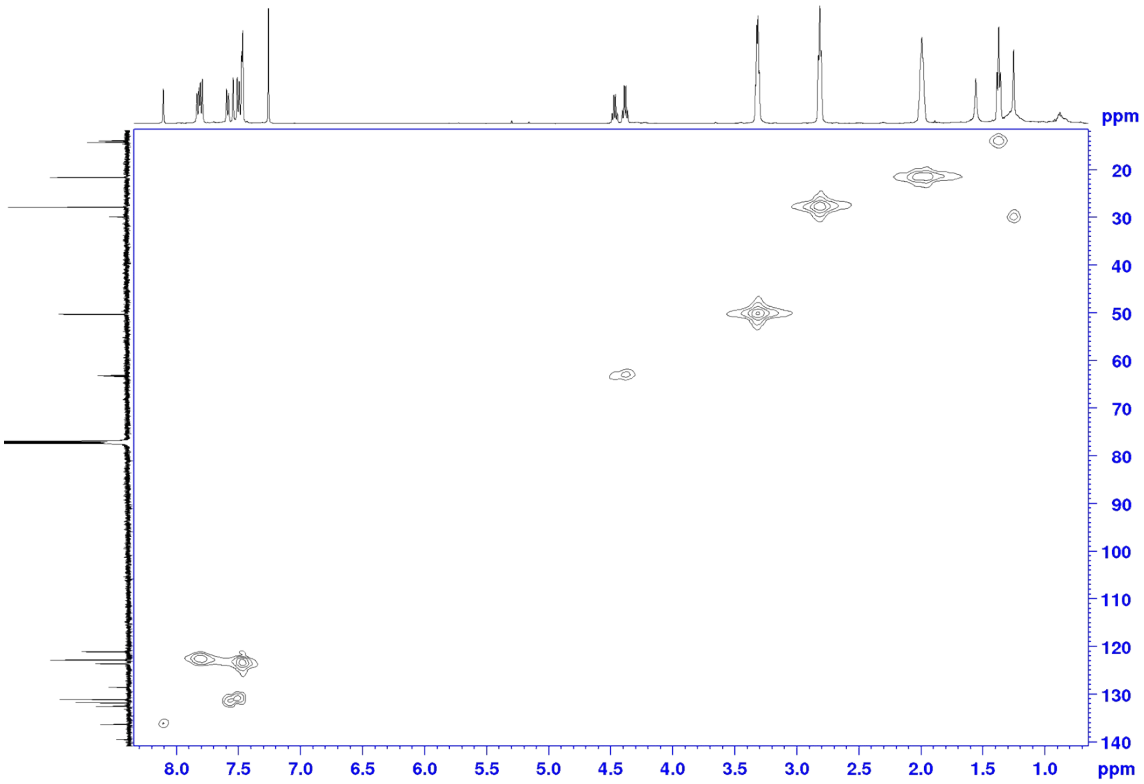

References

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2. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.
3. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.