

Mechanosynthesis of Sydnone--Containing Coordination Complexes

Nicolas Petry, Thibaut Vanderbeeken, Astrid Malher, Yoan Bringer, Pascal Retailleau, Xavier Bantreil, **Frédéric Lamaty**

Submitted date: 03/05/2019 • Posted date: 06/05/2019

Licence: CC BY-NC-ND 4.0

Citation information: Petry, Nicolas; Vanderbeeken, Thibaut; Malher, Astrid; Bringer, Yoan; Retailleau, Pascal; Bantreil, Xavier; et al. (2019): Mechanosynthesis of Sydnone--Containing Coordination Complexes.

ChemRxiv. Preprint.

N-Phenyl-4-(2-pyridinyl) sydnone was shown to act as a four-electron donor N,O-ligand in unprecedented coordination complexes featuring four different metallic centers (Co, Cu, Ni, Zn). Starting from various anilines, the use of ball-mill enabled efficiently the synthesis of N-arylglycines, subsequent nitrosylation and cyclization into sydnone, and further metalation.

File list (3)

ChemArxiv_Manuscript.pdf (830.13 KiB)

[view on ChemRxiv](#) • [download file](#)

ChemRxi_GA.png (1.33 MiB)

[view on ChemRxiv](#) • [download file](#)

ChemArxiv_ESI.pdf (2.68 MiB)

[view on ChemRxiv](#) • [download file](#)

Mechanosynthesis of Sydnone-containing Coordination Complexes

Nicolas Pétry,^a Thibaut Vanderbeeken,^a Astrid Malher,^a Yoan Bringer,^a Pascal Retailleau,^b Xavier Bantreil^a and Frédéric Lamaty^{a,*}

N-Phenyl-4-(2-pyridinyl) sydnone was shown to act as a four-electron donor *N,O*-ligand in unprecedented coordination complexes featuring four different metallic centers (Co, Cu, Ni, Zn). Starting from various anilines, the use of ball-mill enabled efficiently the synthesis of *N*-arylglycines, subsequent nitrosylation and cyclization into sydnone, and further metalation.

Sydnes, mesoionic heterocyclic compounds, are versatile building blocks for heterocyclic chemistry, for example in the formation of pyrazoles through copper-catalyzed 1,3-dipolar cycloaddition.¹ They also display interesting biological activities, e.g., as antibacterial, antineoplastic and anti-inflammatory agents.² Sydnone synthesis from α -amino acids involves a nitrosylation step, using sodium nitrite in highly acidic media or isoamyl nitrite,³ and subsequent cyclization using acetic or trifluoroacetic anhydride (TFAA).⁴ In 2014, Shih *et al.* showed that palladium complexes featuring a sydnone-4-carbaldehyde *N*(4)-phenylthiosemicarbazone ligand exhibited higher anticancer activities than 5-fluorouracil (Figure 1).⁵ To date, this is the only reported example in which the exocyclic oxygen of the sydnone is shown to coordinate a metal. Indeed, in the literature, sydnones have been modified as phosphine ligands for palladium complexation (Figure 1),⁶ directly metalated at C₄,⁷ through deprotonation or carbon-halogen insertion, or modified at N₃ with a 3-pyridine for iron coordination.⁸ In this context, we wondered if the presence of a 2-pyridine at C₄ would enable the access to unprecedented coordination structures featuring sydnones as *N,O*-ligands.⁹ Given our expertise in mechanochemistry for organic and organometallic synthesis,¹⁰ we envisioned a solvent-free mechanochemical approach¹¹ for an efficient access to sydnones and to unprecedented coordination complexes.

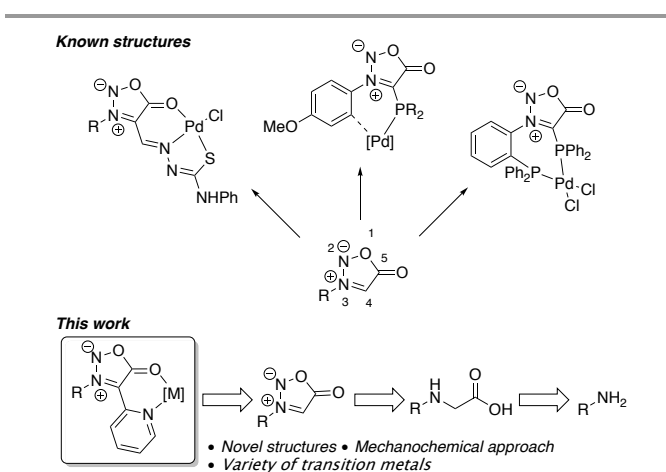


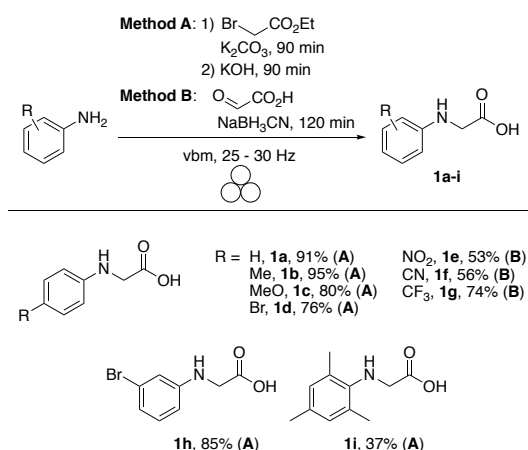
Figure 1. Coordination complexes featuring sydnone-based polydentate ligands

During our study, we realized that accessing sydnone precursors could also benefit from mechanochemistry in terms of reaction time and yield. *N*-arylglycines were thus prepared *via* solvent-free mechanochemistry, using a 15 mL Teflon jar (filled with one 1mm diameter stainless steel ball) agitated at 25 – 30 Hz in a vibratory ball-mill (Scheme 1), through either alkylation of substituted anilines with ethylbromoacetate and subsequent saponification (one-pot two-step, Method A) or reductive amination involving glyoxylic acid and sodium cyanoborohydride (Method B). *N*-arylglycines featuring in para position electron-donating groups such as methyl (**1b**) or methoxy (**1c**) could be isolated in 95% and 80% yield over the two steps, respectively, using method A. When a bromine atom was either in meta or para position, method A was also found efficient, giving corresponding glycines in 85% (**1h**) and 76% (**1d**) yield, respectively. Mesitylamine, even though extremely sterically hindered reacted using method A to furnish the expected glycine **1i** in 37% yield. Even if modest, this yield is four-fold higher than the 10% yield reported in literature.¹² When using anilines bearing electron-withdrawing groups such as NO₂, CF₃ or CN, method B was found more

^a Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, CNRS, Université de Montpellier, ENSCM, Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France. E-Mail: frederic.lamaty@umontpellier.fr

^b Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Saclay, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette, France

Electronic Supplementary Information (ESI) available: Synthetic procedures, characterization of compounds, crystallographic data and copies of ¹H and ¹³C NMR and IR spectra. See DOI:



Scheme 1. Mechanosynthesis of *N*-arylglycines **1a-i**

efficient, giving corresponding products in 53–74% yield (**1e-g**). In all the cases, yields obtained using the mechanochemical approaches were similar if not better compared to literature conditions in solution.¹³ In addition, reaction time was limited to 2–3 h, and a simple extraction/precipitation procedure was required to isolate pure compounds.

Using *N*-phenylglycine **1a** as model substrate, the synthesis of corresponding sydnone in a mechanochemical one-pot two-step approach was next investigated. Recently, the Taran group developed a one-pot procedure using *tert*-butyl nitrite and TFAA under solvent-free conditions and magnetic stirring, but sydnones were not isolated and directly engaged in a cycloaddition step.¹⁴ Under mechanochemical activation, *t*BuONO was found to be efficient and nitrosylation was complete within 5 min, as confirmed by HPLC analysis (Table 1, entry 1). Addition of trifluoroacetic anhydride (2.5 equiv.) to the reaction mixture in the same jar furnished sydnone **2a** in 51% yield. Even though this method is sodium nitrite and acid free, *t*BuONO has to be prepared from *tert*-butanol using these reagents. We reasoned that sodium nitrite, without the addition of concentrated HCl, could furnish the nitrosylated intermediate. Indeed, the two hydrogen atoms necessary for water release in the nitrosylation mechanism would in this

Table 1. Optimization of the reaction conditions of sydnone mechanosynthesis^a

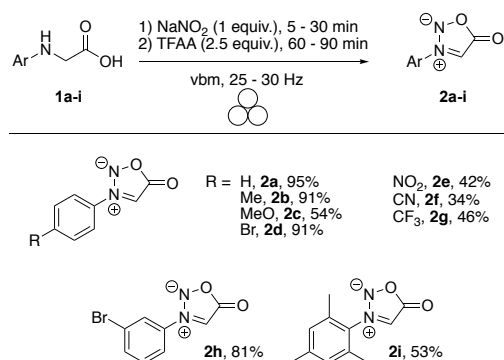
Entry	NO source (equiv.)	TFAA (equiv.)	t ₂ (min)	Yield 2a (%)
1	<i>t</i> BuONO (1.2)	2.5	30	51
2	NaNO ₂ (1.0)	2.5	30	54
3	NaNO ₂ (1.0)	2.5	60	95
4	NaNO ₂ (1.0)	2	60	77
5	NaNO ₂ (1.0)	3	60	92

^a Total mass of the reagents was calculated to obtain a milling load (ML) of 20 mg.mL⁻¹. Reactions were performed in a vbm at 25 Hz.

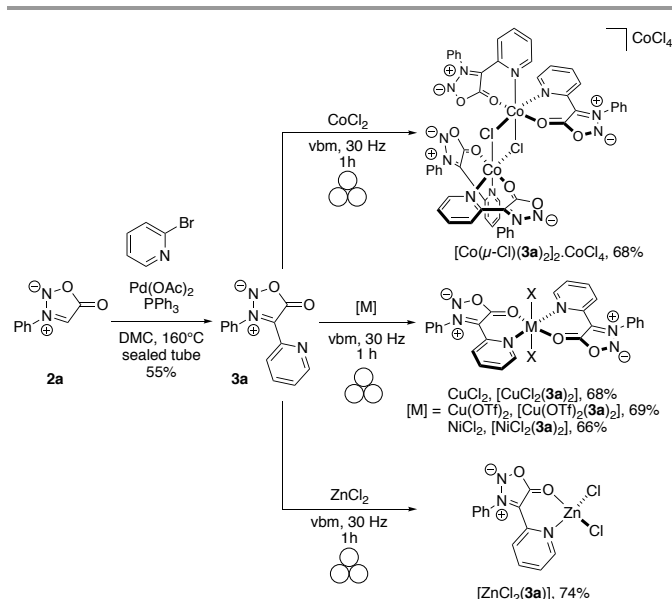
case come from the amine and acid functions of **1a**. Gratifyingly, milling **1a** and NaNO₂ in stoichiometric quantity for 5 min resulted in full conversion of **1a** into *N*-nitroso-*N*-phenylglycinate. Subsequent addition of TFAA to the crude mixture and milling for 30 min yielded sydnone **2a** in 54% yield (Table 1, entry 2). Increasing the milling time of the second step to 1 h enabled an excellent 95% yield (Table 1, entry 3). Notably, changing the stoichiometry of TFAA did not improve the final yield (Table 1, entries 4 and 5).

Milling conditions were then applied to *N*-arylglycines **1a-i** (Scheme 2). Reaction time and milling frequency were modulated to obtain in each case fast and full conversion, which enabled the avoidance of chromatography on silica gel. In all cases, total reaction time did not exceed 120 min with yields comparable to those obtained in solution.¹³ Sydnones featuring methyl (**2b**) and methoxy (**2c**) groups in para position of the phenyl moiety were produced in 91% and 54% yield, respectively. With a bromine atom either in para or meta position, corresponding sydnones **2d** and **2h** could be obtained in 91% and 81% yield, respectively. Sydnones **2e-g**, featuring NO₂, CN and CF₃ electron-withdrawing groups were isolated in lower yields of 34–46%. Even though full conversion was reached, a recrystallization step that reduced the final yield was required to obtain pure compounds. The same remark applies to sydnone **2i**, featuring sterically hindered mesityl group, which was yielded in 53%. To the best of our knowledge, it is the first time that sydnone **2i** is synthesized and fully characterized.^{15, 7f}

The introduction of a pyridine at C₄ of the sydnone was next performed to obtain a putative bidentate ligand. *N*-Phenylsydnone **2a** was reacted with 2-bromopyridine in the presence of Pd(PPh₃)₄ or Pd(OAc)₂/XPhos as catalytic systems according to literature methods.¹⁶ However, yields obtained were not reproducible and separation of XPhos ligand revealed complicated. Although other palladium-catalysed cross-couplings were successful in the ball-mill,¹⁷ attempts to perform the coupling reaction with **2a** under mechanochemical conditions failed. A quick study showed that this coupling could be performed using Pd(OAc)₂/PPh₃ (1:2) in DMC (dimethylcarbonate), an environmentally friendly solvent, giving corresponding 3-phenyl-4-(2-pyridine)sydnone **3a** in 55% yield, with a facilitated purification (Scheme 3).



Scheme 2. Mechanochemical synthesis of *N*-arylsydnones **2a-i**



Scheme 3. Synthesis of coordination complexes with sydnone **3a** as *N,O*-ligand

Bidentate compound **3a** was then reacted, using a vibratory ball-mill, with various metallic salts (CoCl_2 , CuCl_2 , $\text{Cu}(\text{OTf})_2$, NiCl_2 and ZnCl_2) under solvent-free conditions. We were pleased to observe that after 1 h of milling corresponding complexes were obtained in yields of 66–74%. Conversion was followed in the solid state using IR spectroscopy, as the $\text{C}=\text{O}$ stretching band in **3a** ($\nu = 1757 \text{ cm}^{-1}$) shifts to lower wave numbers upon coordination ($\nu = 1660 - 1726 \text{ cm}^{-1}$). The structure of the complexes $[\text{Co}(\mu\text{-Cl})(\mathbf{3a})_2]_2 \cdot \text{CoCl}_4$, $[\text{CuCl}_2(\mathbf{3a})_2]$, $[\text{Cu}(\text{OTf})_2(\mathbf{3a})_2]$, $[\text{NiCl}_2(\mathbf{3a})_2]$ and $[\text{ZnCl}_2(\mathbf{3a})]$ were confirmed by single crystal X-ray diffraction after crystallisation (Figure 2).¹³ Interestingly, cobalt complex possesses a dimeric structure with two sydnone ligands on each metallic center, and bridging chloride atoms. This kind of arrangement was rarely observed in literature with bidentate *N,O* ligands.¹⁸ For copper and nickel containing species, an octahedral geometry with two sydnone ligands and with a *trans*-arrangement between the two chloride (or triflate) ligands was observed. On the other hand, reaction with zinc(II) chloride provided the complex with only one sydnone ligand and a tetrahedral geometry. In all the

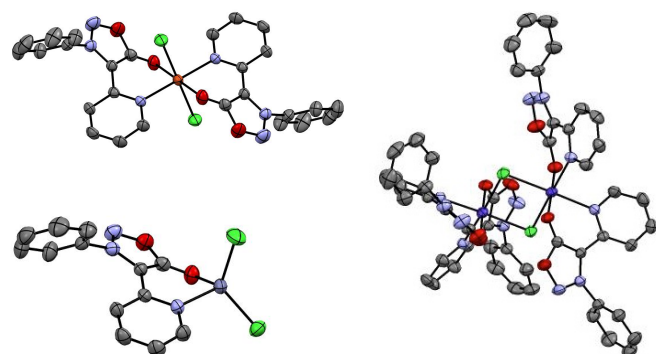


Figure 2. X-ray diffraction of complexes $[\text{CuCl}_2(\mathbf{3a})_2]$, $[\text{Co}(\mu\text{-Cl})(\mathbf{3a})_2]_2 \cdot \text{CoCl}_4$ and $[\text{ZnCl}_2(\mathbf{3a})]$. H atoms and CoCl_4^{2-} are omitted for clarity.

X-ray structures, the pyridine and sydnone rings were not found in the same plane and a twist of $22 - 35^\circ$ was observed in the complexes. This non-planarity was also witnessed in the X-ray structure of **3a**.¹³ Such observation tends to indicate that pyridine and sydnone rings may not be conjugated. Additionally, the exocyclic $\text{C}-\text{O}$ bond was measured at $1.21 - 1.24 \text{ \AA}$, which is consistent with a double bond character. Bidentate sydnone **3a** may thus act as a four-electron rather than a three-electron donor ligand.

In conclusion, the use of ball mills enabled the efficient preparation of a series of *N*-aryl glycines and of corresponding sydnones. *N*-Phenyl-4-(2-pyridinyl) sydnone **3a** was used for the first time as ligand to coordinate metals, leading to unprecedented compounds via a mechanochemical solvent-free approach. Such results pave the way for the development of novel families of coordination complexes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded by the University of Montpellier, CNRS and the French Government through the program “Investissements d’Avenir” ANR-10-LABX-05-01 managed by Agence Nationale pour la Recherche (TV).

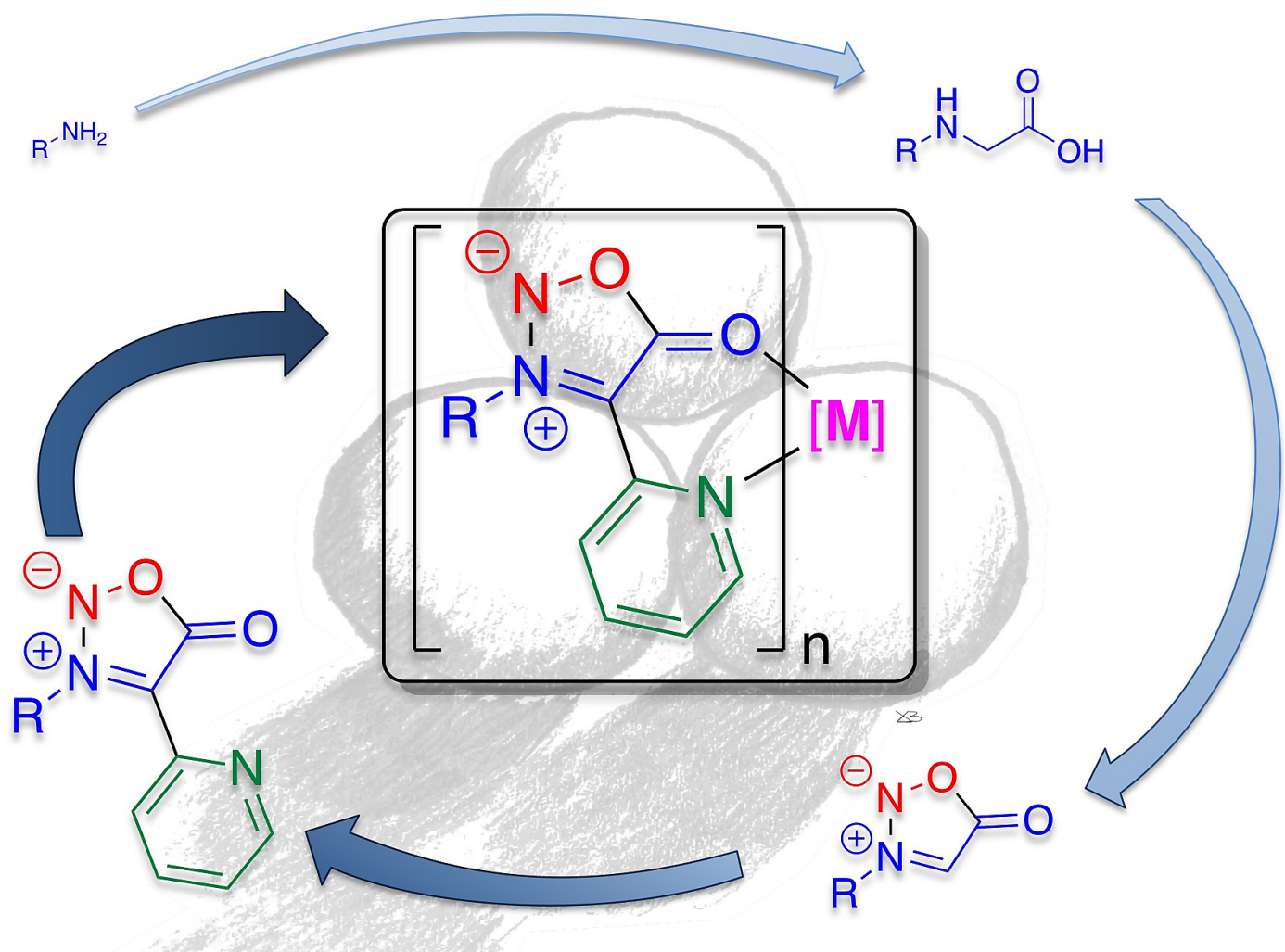
Notes and references

1. E. Decuypère, L. Plougastel, D. Audisio and F. Taran, *Chem. Commun.*, **2017**, 53, 11515.
2. D. L. Browne and J. P. A. Harrity, *Tetrahedron*, **2010**, 66, 553.
3. J. Applegate and K. Turnbull, *Synthesis*, **1988**, 1011.
4. W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.*, **1950**, 1542.
5. M.-H. Shih, J.-C. Chen, G.-L. Lin, T.-T. Lin and M.-H. Sun, *J. Pharm. Pharmacol.*, **2014**, 66, 73.
6. (a) S.-T. Lin, H.-S. Cheo, L.-S. Liu and J.-C. Wang, *Organometallics*, **1997**, 16, 1803; (b) S.-T. Lin, H.-S. Choe, L.-S. Liu and J.-C. Wang, *J. Organomet. Chem.*, **2000**, 610, 1; (c) S. T. Lin, K. J. Peng, T. M. Barclay and A. W. Cordes, *Inorg. Chim. Acta*, **2001**, 321, 89; (d) S. T. Lin, K. J. Peng, T. F. Hung and H. J. Tien, *J. Chin. Chem. Soc.*, **2002**, 49, 19.
7. (a) V. N. Kalinin and P. M. Se, *J. Organomet. Chem.*, **1988**, 352, C34; (b) V. N. Kalinin, P. M. Se and P. V. Petrovskii, *J. Organomet. Chem.*, **1989**, 379, 195; (c) L. N. Morozova, L. S. Isaeva, P. V. Petrovskii, D. N. Kravtsov, S. P. Minh and V. N. Kalinin, *J. Organomet. Chem.*, **1990**, 381, 281; (d) V. N. Kalinin, D. N. Pashchenko and M. S. Phan, *Mendeleev Commun.*, **1992**, 60; (e) V. N. Kalinin, F. M. She, V. N. Khandozhko and P. V. Petrovskii, *Russ. Chem. Bull.*, **2001**, 50, 525; (f) S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger and A. Schmidt, *Chem. Commun.*, **2014**, 50, 11822; (g) H. Liu, D. Audisio, L. Plougastel, E. Decuypère, D.-A. Buisson, O. Koniev, S. Kolodych, A. Wagner, M. Elhabiri, A. Krzyczmonik, S. Forsback, O. Solin, V. Gouverneur and F. Taran, *Angew. Chem., Int. Ed.*, **2016**, 55, 12073.

8. (a) S. M. Lee, US3549639A, 1970; (b) C. S. Lin, A. Yeh, T. Y. Liu, K. S. Kwan, D. J. Hodgson and H. J. Tien, *Inorg. Chim. Acta*, **1992**, *192*, 81.
9. Contrary to the historical representation of sydnones with a negatively charged exocyclic oxygen, the mesomeric form having a negative charge on N₂ and an exocyclic carbon oxygen double bond was chosen in agreement with the X-Ray structures obtained herein and in literature.
10. (a) A. Beillard, E. Golliard, V. Gillet, X. Bantreil, T.-X. Métro, J. Martinez and F. Lamaty, *Chem. Eur. J.*, **2015**, *21*, 17614; (b) A. Beillard, T.-X. Métro, X. Bantreil, J. Martinez and F. Lamaty, *Chem. Sci.*, **2017**, *8*, 1086; (c) N. Pétry, H. Benakki, E. Clot, P. Retailleau, F. Guenoun, F. Asserar, C. Sekkat, T.-X. Métro, J. Martinez and F. Lamaty, *Beilstein J. Org. Chem.*, **2017**, *13*, 2169; (d) A. Beillard, X. Bantreil, T.-X. Métro, J. Martinez and F. Lamaty, *Green Chem.*, **2018**, *20*, 964.
11. (a) N. R. Rightmire and T. P. Hanusa, *Dalton Trans.*, **2016**, *45*, 2352; (b) J. Andersen and J. Mack, *Green Chem.*, **2018**, *20*, 1435; (c) J. Howard, Q. Cao and D. L. Browne, *Chem. Sci.*, **2018**, *9*, 3080; (d) D. Tan and T. Friščić, *Eur. J. Org. Chem.*, **2018**, 18.
12. S. Ikeda and S. Murata, *J. Photochem. Photobiol., A*, **2002**, *149*, 121.
13. See Supporting Information for details.
14. S. Specklin, E. Decuypere, L. Plougastel, S. Aliani and F. Taran, *J. Org. Chem.*, **2014**, *79*, 7772.
15. K. Turnbull, *J. Heterocycl. Chem.*, **1985**, *22*, 965.
16. (a) A. Rodriguez and W. J. Moran, *Synthesis*, **2009**, 650; (b) A. W. Brown, J. Comas-Barceló and J. P. A. Harrity, *Chem. Eur. J.*, **2017**, *23*, 5228.
17. J. G. Hernández and T. Friščić, *Tetrahedron Lett.*, **2015**, *56*, 4253.
18. V. T. Yilmaz, S. Hamamci and C. Thöne, *Polyhedron*, **2004**, *23*, 841.

ChemArxiv_Manuscript.pdf (830.13 KiB)

[view on ChemRxiv](#) • [download file](#)



Supplementary Information

Mechanosynthesis of Sydnone-containing Coordination Complexes

Nicolas Pétry,^a Thibaut Vanderbeeken,^a Astrid Malher,^a Yoan Bringer,^a Pascal Retailleau,^b
Xavier Bantreil^a and Frédéric Lamaty^{a,*}

a. Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, CNRS, Université de Montpellier, ENSCM, Campus Triolet, Place Eugène Bataillon, 34095 Montpellier cedex 5, France. E-Mail: frederic.lamaty@umontpellier.fr

b. Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Saclay, 1 Avenue de la Terrasse, 91198 Gif-sur-Yvette, France

Table of Content

I. General Information	2
II. Preparation of <i>N</i> -aryl glycines in ball-mill.....	3
A. General procedure for alkylation-saponification (Method A)	3
III. Preparation of <i>N</i> -aryl-sydnone in ball-mill	9
A. General procedure for nitrosation-cyclization (GP1).....	9
IV. Comparison of <i>N</i> -aryl glycines synthesis with literature procedures.....	16
V. Comparison of sydnones synthesis with literature procedures	18
VI. Preparation of organometallic complexes with sydnone 3a as ligand in ball-mill	20
A. General procedure for preparation of complexes (GP2)	20
VII. References	28
VIII. ¹ H and ¹³ C NMR spectra.....	29
IX. FT-IR spectra	51

I. General Information

All reagents were purchased from Sigma Aldrich, Fluka, Acros or Alfa Aesar and used without further purification. The milling treatments were carried out either in a vibrating Retsch Mixer Mill 400 (vbm) or in a Fritsch Pulverisette 7 Planetary Mill (pbm).

NMR spectra were recorded on a Bruker AVANCE 400 MHz or a Bruker AVANCE III 500 MHz spectrometer, operating at 400.17 MHz (^1H), at 376.5 MHz (^{19}F) and 100.62 MHz (^{13}C) or at 500.17 MHz (^1H) and 125.77 MHz (^{13}C). ^1H NMR spectra are reported in ppm using solvents as internal standards (CDCl_3 at 7.26 ppm, CD_3CN at 1.94 ppm, $\text{DMSO-}d_6$ at 2.50 ppm). Data are reported as s = singlet, d = doublet, t = triplet, m = multiplet or overlap of non-equivalent resonances; coupling constant in Hz; integration. ^{13}C NMR spectra are reported in ppm using solvents as internal standards (CDCl_3 at 77.16 ppm, CD_3CN at 1.32 and 118.26 ppm, $\text{DMSO-}d_6$ at 39.52 ppm).

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer and wavelength numbers of the most relevant bands are reported in cm^{-1} .

Mass spectra were obtained by LC-MS with ESI using a Water Alliance 2695 as LC, coupled to a Waters ZQ spectrometer with electrospray source, a simple quadrupole analyzer and a UV Waters 2489 detector. HRMS analyses were performed on UPLC Acquity H-Class from Waters hyphenated to a Synapt G2-S mass spectrometer with a dual ESI source from Waters. High resolution MS analyses were performed on UPLC Acquity H-Class from Waters hyphenated to a Synapt G2-S mass spectrometer with a dual ESI source from Waters.

HPLC conversion was measured on an Agilent technologies 1220 Infinity LC using a Chromolith® high resolution RP-18e 50-4.6 mm column and a linear gradient of 0 to 100% $\text{CH}_3\text{CN}/0.1\% \text{ TFA}$ in $\text{H}_2\text{O}/0.1\% \text{ TFA}$ over 10 min, detection at 214 nm. Flow rate: 3 mL/min.

Flash chromatography was performed by using prepacked silica columns on a Biotage® Isolera™ Four system.

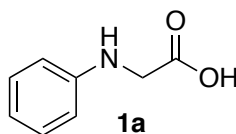
II. Preparation of *N*-aryl glycines in ball-mill

A. General procedure for alkylation-saponification (Method A)

Ethyl bromoacetate (1 eq), the corresponding aniline (2.0 eq) and potassium carbonate (1.5 eq) were introduced in a grinding jar (10 mL stainless steel or 15 mL PTFE) with one stainless steel ball (10 mm diameter). The jar was closed and subjected to grinding in a vibratory ball-mill at 30 Hz for 90 min. Potassium hydroxide 90% KOH (3 eq) was then added to the reaction mixture which was again subjected to vibratory milling at 30 Hz for 90 min. Reaction mixture was taken up with water. The aqueous solution was washed with EtOAc to remove residual aniline in excess and then acidified to pH 1 with aqueous hydrochloric acid. The acidic phase was extracted with EtOAc, the combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated under vacuum to furnish the expected *N*-aryl-glycine.

N-Phenyl-glycine **1a**

CAS: 103-01-5



Chemical Formula: C₈H₉NO₂

Molecular Weight: 151.17

Procedure: according to the general procedure GP1 starting from aniline, 2 step-one pot alkylation-saponification allowed to obtain *N*-pheny-glycine **1a** as a beige solid (110 mg, 0.73 mmol, 91%).

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.78 (s, 2H), 6.55 (m, 3H), 7.07 (m, 2H).

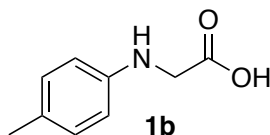
¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 44.6, 112.1 (2C), 116.1, 128.8 (2C), 148.2, 172.7.

LCMS (ESI) *m/z*: 152 [M+H]⁺, 150 [M-H]⁻.

The analytical data obtained is in agreement with those reported in the literature.¹

N-(4-Methylphenyl)-glycine **1b**

CAS: 21911-69-3



Chemical Formula: C₉H₁₁NO₂

Molecular Weight: 165.19

Procedure: according to the general procedure GP1 starting from *p*-toluidine, 2 step-one pot alkylation-saponification allowed to obtain glycine **1b** as a cream solid (220 mg, 1.33 mmol, 95%).

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.14 (s, 3H), 3.74 (s, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H).

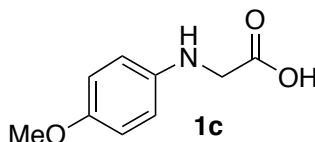
¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 20.1, 45.0, 112.2 (2C), 124.6, 129.3 (2C), 145.9, 172.8.

LCMS (ESI) *m/z*: 166 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.²

N-(4-Methoxyphenyl)-glycine **1c**

CAS: 22094-69-5



Chemical Formula: C₉H₁₁NO₃

Molecular Weight: 181.19

Procedure: according to the general procedure (GP1), the alkylation-saponification sequence performed in a stainless steel jar starting from *p*-anisidine yielded the *N*-arylglycine **1c** as a brown powder (175 mg, 0.96 mmol, 80%).

Appearance: beige solid

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.63 (s, 3H), 3.72 (s, 2H), 6.51 (m, 2H), 6.71 (m, 2H), 8.90 (br. s, 1H).

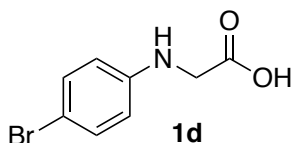
¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 45.6, 55.4, 113.3 (2C), 114.7 (2C), 142.5, 151.1, 173.0.

LCMS (ESI) *m/z*: 182 [M+H]⁺, 180 [M-H]⁻.

The analytical data obtained is in agreement with those reported in the literature.²

N-(4-Bromophenyl)-glycine **1d**

CAS: 13370-62-2



Chemical Formula: C₈H₈BrNO₂

Molecular Weight: 230.06

Procedure: according to the general procedure (GP1), the alkylation-saponification sequence performed in a PTFE jar starting from 4-bromoaniline yielded the *N*-arylglycine **1d** as a brown solid (164 mg, 0.71 mmol, 76%).

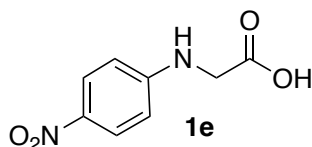
¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 3.77 (s, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 44.6, 106.8, 114.2 (2C), 131.4 (2C), 147.6, 172.4.

HRMS ESI-(+) calcd. for C₈H₉NO₂Br [M+H]⁺ 229.9817, found 229.9818.

N-(4-Nitrophenyl)-glycine **1e**

CAS: 619-91-0



Chemical Formula: C₈H₈N₂O₄

Molecular Weight: 196.16

Procedure (Method B): 4-Nitroaniline (98 mg, 0.70 mmol, 1 eq), glyoxylic acid monohydrate (160 mg, 1.68 mmol, 2.4 eq) and sodium cyanoborohydride (47 mg, 0.70 mmol, 1 eq) were introduced in a 10 mL stainless steel milling jar with one stainless steel ball (10 mm diameter). The jar was closed and submitted to grinding for 2 h in a vibratory ball-mill operated at 30 Hz. The reaction mixture was taken up with EtOAc and water. The aqueous phase was acidified with 1N HCl and extracted with EtOAc. The combined organic extracts were washed with 1N HCl and brine, dried over MgSO₄ and evaporated under vacuum. The crude product was taken up with 1N NaOH; the basic aqueous solution was washed with EtOAc (3x) and then acidified to pH 1-2 with a HCl solution. The resulting precipitate was filtered, rinsed with cold water and dried over P₂O₅ under vacuum to yield the expected *N*-aryl-glycine **1e** as a yellow powder (73 mg, 0.37 mmol, 53%).

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.98 (d, *J* = 6.2 Hz, 2H), 6.66 (d, *J* = 9.2 Hz, 2H), 7.45 (t, *J* = 6.2 Hz, 1H), 8.00 (d, *J* = 9.2 Hz, 2H), 12.80 (br. s, 1H).

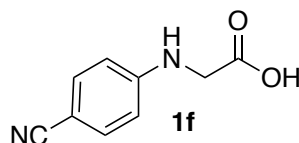
¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 44.0, 111.2 (2C), 126.0 (2C), 136.3, 154.3, 171.4.

LCMS (ESI) *m/z*: 197 [M+H]⁺, 195 [M-H]⁻.

The analytical data obtained is in agreement with those reported in the literature.²

N-(4-Cyanophenyl)-glycine **1f**

CAS: 42288-26-6



Chemical Formula: C₉H₈N₂O₂

Molecular Weight: 176.18

Procedure (Method B): 4-Aminobenzonitrile (181 mg, 1.50 mmol, 1 eq), glyoxylic acid monohydrate (342 mg, 3.60 mmol, 2.4 eq) and sodium cyanoborohydride (100 mg, 1.50 mmol, 1 eq) were introduced in a 15 mL stainless steel milling jar with one stainless steel ball (10 mm diameter). The jar was closed and submitted to grinding for 2 h in a vibratory ball-mill operated at 30 Hz. The reaction mixture was taken up with EtOAc and water. The aqueous phase was acidified with 1N HCl and extracted with EtOAc. The combined organic extracts were washed with 1N HCl and brine, dried over MgSO₄ and evaporated under vacuum. The crude product was taken up with 1N NaOH; the basic aqueous solution was washed with EtOAc (3x) and then acidified to pH 1-2 with a HCl solution. The resulting precipitate was filtered, rinsed with cold water and dried over P₂O₅ under vacuum to yield the expected *N*-aryl-glycine **1f** as a beige powder (148 mg, 0.84 mmol, 56%).

Appearance: beige solid

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.90 (d, *J* = 5.9 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.90 (t, *J* = 5.9 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 12.72 (br. s, 1H).

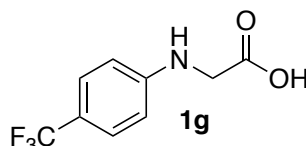
¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 43.9, 96.4, 112.1 (2C), 120.5, 133.3 (2C), 151.9, 171.8.

LCMS (ESI) *m/z*: 177 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.²

N-(4-Trifluoromethylphenyl)-glycine **1g**

CAS: 77311-21-8



Chemical Formula: C₉H₈F₃NO₂

Molecular Weight: 219.16

Procedure (Method B): 4-Trifluoromethylaniline (255 μL, 2.0 mmol, 1 eq), glyoxylic acid monohydrate (475 mg, 5.0 mmol, 2.5 eq) and sodium cyanoborohydride (140 mg, 2.1 mmol, 1.05 eq) were introduced in a 20 mL stainless steel milling jar with 80 stainless steel balls (5

mm diameter). The jar was closed and submitted to grinding for 2 h in a planetary ball-mill operated at 400 rpm. The reaction mixture was taken up with EtOAc and water. The organic layer was washed with 1N HCl and brine, dried over MgSO₄ and evaporated under vacuum. The crude product was taken up with 1N NaOH; the basic aqueous solution was washed with EtOAc (3x) and then acidified to pH 1-2 with a HCl solution. The resulting precipitate was filtered, rinsed with cold water and dried over P₂O₅ under vacuum to yield the expected *N*-aryl-glycine **1g** as an offwhite powder (325 mg, 1.48 mmol, 74%).

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 3.87 (s, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 44.1, 111.6 (2C), 115.8 (q, *J* = 32 Hz), 125.3 (q, *J* = 270 Hz), 126.1 (q, *J* = 3.7 Hz, 2C), 151.3, 172.1.

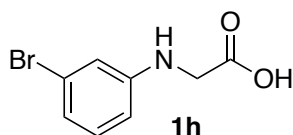
¹⁹F NMR (376 MHz, DMSO-*d*₆) δ (ppm): -59.9.

LCMS (ESI) *m/z*: 220 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.²

N-(3-Bromophenyl)-glycine **1h**

CAS: 42288-20-0



Chemical Formula: C₈H₈BrNO₂

Molecular Weight: 230.06

Procedure: according to the general procedure (GP1), the alkylation-saponification sequence performed in a PTFE jar starting from 3-bromoaniline yielded the *N*-arylglycine **1c** as a brown solid (166 mg, 0.72 mmol, 85%).

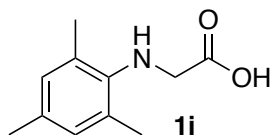
¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.97 (s, 2H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 45.4, 111.9, 115.9, 121.6, 123.5, 130.8, 148.0, 175.8.

HRMS ESI-(+) calcd. for C₈H₉NO₂Br [M+H]⁺ 229.9817, found 229.9818.

N-(2,4,6-Trimethylphenyl)-glycine **1i**

CAS: 104412-17-1



Chemical Formula: C₁₁H₁₅NO₂

Molecular Weight: 193.25

Procedure: Ethyl bromoacetate (340 μ L, 3.0 mmol), 2,4,6-trimethylaniline (1.07 mL, 7.5 mmol, 2.5 eq) and potassium carbonate (1.24 g, 9 mmol, 3 eq) were introduced in a 20 mL stainless steel jar with 80 stainless steel balls (5 mm diameter). The jar was closed and subjected to grinding in a planetary ball-mill operated at 500 rpm for 160 min. Potassium hydroxide 90% KOH (560 mg, 9.0 mmol, 3 eq) was then added to the reaction mixture then subjected to planetary milling at 500 Hz for 60 min. Reaction mixture was taken up with water. The aqueous solution was washed with EtOAc (3 times) and then acidified to pH 1 with aqueous hydrochloric acid. The acidic phase was extracted with EtOAc, the combined organic extracts were washed with brine, dried over MgSO₄, filtered and evaporated under vacuum. The crude product was triturated with Et₂O to yield the expected *N*-aryl-glycine **1i** as a clear yellow solid (214 mg, 1.11 mmol, 37%).

Appearance: clear yellow solid

¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 2.13 (s, 3H), 2.18 (s, 6H), 3.65 (s, 2H), 6.72 (s, 2H), 8.34 (br. s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 18.3 (2C), 20.1, 49.3, 127.9 (2C), 129.1 (2C), 129.3, 143.3, 173.4.

LCMS (ESI) *m/z*: 194 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.³

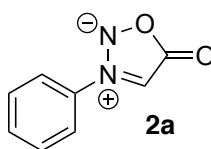
III. Preparation of N-aryl-sydnones in ball-mill

A. General procedure for nitrosation-cyclization (GP1)

N-aryl-glycine and sodium nitrite (1 eq) were introduced in a 10 mL ZrO₂ jar with one ZrO₂ ball (10 mm diameter). The jar was closed and subjected to grinding in a vibratory ball-mill at 30 Hz for 30 to 90 min. Trifluoroacetic anhydride was then added to the reaction mixture then subjected to vibratory milling at 25 Hz for 30 to 90 min. Reaction mixture was taken up with EtOAc. The organic solution was washed with water, a saturated aqueous NaCHO₃ solution, water and brine. After drying over MgSO₄, filtration and evaporation of the solvent under vacuum the crude sydnone was obtained and if necessary purified by recrystallization or flash chromatography on silica.

N-Phenylsydnone **2a**

CAS: 120-06-9



Chemical Formula: C₈H₆N₂O₂
Molecular Weight: 162.15

Procedure: according to the general procedure GP1 starting from *N*-phenyl-glycine **1a** and with milling times of 30 and 60 min, the expected sydnone **2a** was obtained as a brown solid (186 mg, 1.15 mmol, 95%) without needing further purification.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.73 (s, 1H), 7.60-7.74 (m, 5H).

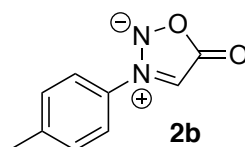
¹³C NMR (100 MHz, CDCl₃) δ (ppm): 93.7, 121.4, 130.3, 132.5, 134.9, 169.0.

LCMS (ESI) *m/z*: 163 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.⁴

3-(4-Methylphenyl)-sydnone **2b**

CAS: 3483-19-0



Chemical Formula: C₉H₈N₂O₂
Molecular Weight: 176.18

Procedure: according to the general procedure GP1, starting from *N*-(4-methylphenyl)-glycine **1b** with milling times of 45 and 45 min, the expected *N*-aryl-sydnone **2b** was obtained as a beige solid (53 mg, 0.30 mmol, 91%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.47 (s, 3H), 6.68 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H).

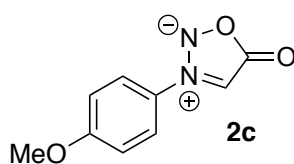
¹³C NMR (100 MHz, CDCl₃) δ (ppm): 21.5, 93.6, 121.2, 130.9, 132.6, 143.4, 169.2.

LCMS (ESI) *m/z*: 177 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.⁴

3-(4-Methoxyphenyl)-sydnone **2c**

CAS: 3815-80-3



Chemical Formula: C₉H₈N₂O₃

Molecular Weight: 192.17

Procedure: according to the general procedure GP1, starting from *N*-(4-methoxyphenyl)-glycine **1c** with milling times of 30 and 45 min, the expected *N*-aryl-sydnone **2c** was obtained after trituration of the crude with Et₂O and recrystallization from EtOAc/heptane as brown solid (55 mg, 0.28 mmol, 54%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.90 (s, 3H), 6.65 (s, 1H), 7.07 (d, *J* = 9.1 Hz, 2H), 7.64 (d, *J* = 9.1 Hz, 2H).

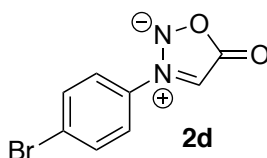
¹³C NMR (100 MHz, CDCl₃) δ (ppm): 56.0, 93.5, 115.4, 122.8, 127.9, 162.6, 169.2.

LCMS (ESI) *m/z*: 193 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.⁵

3-(4-Bromophenyl)-sydnone **2d**

CAS: 26537-61-1



Chemical Formula: C₈H₅BrN₂O₂

Molecular Weight: 241.04

Procedure: according to the general procedure GP1 starting from *N*-4-bromophenyl-glycine **1d** and with milling times of 30 and 90 min, the expected sydnone **2d** was obtained as a brown powder (152 mg, 0.63 mmol, 91%) without needing further purification.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.73 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 93.7, 122.8, 127.0, 133.7, 168.9.

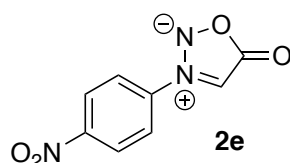
LCMS (ESI) *m/z*: 241, 243 [M+H]⁺.

HRMS ESI-(+) calcd. for C₈H₆N₂O₂Br [M+H]⁺ 240.9613, found 240.9613.

The analytical data obtained is in agreement with those reported in the literature.⁶

3-(4-Nitrophenyl)-sydnone 2e

CAS: 6299-51-0



Chemical Formula: C₈H₅N₃O₄

Molecular Weight: 207.15

Procedure: according to the general procedure GP1 starting from *N*-4-nitrophenyl-glycine **1e**, complete conversion was obtained with milling times of 30 and 45 min. The crude product was purified by recrystallization from EtOAc/heptane to afford the expected sydnone **2e** as a orange powder (52 mg, 0.25 mmol, 42%).

¹H NMR (400 MHz, CD₃CN) δ (ppm): 7.14 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 8.46 (d, *J* = 8.7 Hz, 2H).

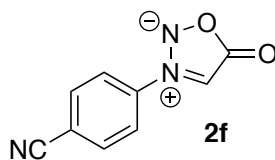
¹³C NMR (100 MHz, CD₃CN) δ (ppm): 96.2, 124.2, 126.5, 139.9, 150.9, 169.6.

LCMS (ESI) *m/z*: 208 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.⁷

3-(4-Cyanophenyl)-sydnone 2f

CAS: 68657-48-7



Chemical Formula: C₉H₅N₃O₂

Molecular Weight: 187.16

Procedure: according to the general procedure GP1, starting from *N*-4-cyanophenyl-glycine **1f**, with addition of 1 eq of KHSO₄ (to obtain full conversion of the nitrosation step) and with a milling time of 90 min for the cyclization step, the expected *N*-aryl-sydnone **2f** was obtained after purification of the crude by recrystallization from ethanol/heptane 8/2 as a beige powder (62 mg, 0.33 mmol, 34%).

¹H NMR (400 MHz, CD₃CN) δ (ppm): 7.09 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H).

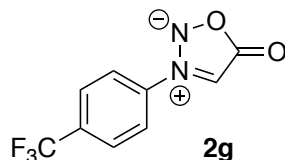
¹³C NMR (100 MHz, CD₃CN) δ (ppm): 95.9, 116.8, 118.2, 123.6, 135.4, 138.8, 169.6.

LCMS (ESI) *m/z*: 188 [M+H]⁺.

HRMS ESI-(+) calcd. for C₉H₆N₃O₂ [M+H]⁺ 188.0460, found 188.0461.

3-[4-(Trifluoromethyl)phenyl]-sydnone **2g**

CAS: 1620220-61-2



Chemical Formula: C₉H₅F₃N₂O₂

Molecular Weight: 230.15

Procedure: according to the general procedure GP1, starting from *N*-(4-trifluoromethylphenyl)-glycine **1g**, the nitrosation step was achieved after 30 min of milling. Then MgSO₄ (4.4 eq) was added as a grinding auxiliary and the mixture milled for 5 min at 30 Hz. The cyclization step was then performed at 30 Hz for 30 min. The crude product was purified by flash chromatography on silica (cyclohexane/EtOAc 100/0 to 50/50) to furnish the expected *N*-aryl-sydnone **2g** as an offwhite powder (41 mg, 0.18 mmol, 46%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.82 (s, 1H), 7.89-7.94 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 94.0, 122.1 (2C), 123.0 (q, *J* = 273 Hz), 127.8 (2C), 134.7 (q, *J* = 33.5 Hz), 137.3, 168.8.

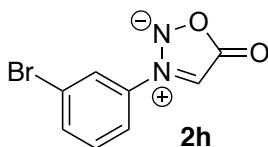
¹⁹F NMR (376 MHz, DMSO-*d*₆) δ (ppm): -64.1.

LCMS (ESI) *m/z*: 231 [M+H]⁺.

The analytical data obtained is in agreement with those reported in the literature.^{5, 8}

3-(3-Bromophenyl)-sydnone **2h**

CAS: 60816-43-5



Chemical Formula: C₈H₅BrN₂O₂

Molecular Weight: 241.04

Procedure: according to the general procedure GP1 starting from *N*-3-bromophenyl-glycine **1h** and with milling times of 30 and 90 min, the expected sydnone **2h** was obtained as a brown powder (136 mg, 0.56 mmol, 81%) without needing further purification.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.75 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H).

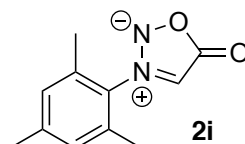
¹³C NMR (100 MHz, CDCl₃) δ (ppm): 94.0, 120.1, 124.0, 124.7, 131.7, 135.8, 168.9.

LCMS (ESI) *m/z*: 241, 243 [M+H]⁺.

HRMS ESI-(+) calcd. for C₈H₆N₂O₂Br [M+H]⁺ 240.9613, found 240.9615.

3-(2,4,6-Trimethylphenyl)-sydnone 2i

CAS: 104411-99-6



Chemical Formula: C₁₁H₁₂N₂O₂

Molecular Weight: 204.23

Procedure: according to the general procedure GP1, starting from *N*-(2,4,6-trimethylphenyl)-glycine **1i** with addition of 2 eq of KHSO₄ and milling times of 90 and 45 min, the expected *N*-aryl-sydnone **2i** was obtained after trituration of the crude with Et₂O and recrystallization from EtOAc/heptane as an offwhite powder (56 mg, 0.27 mmol, 53%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.16 (s, 6H), 2.37 (s, 3H), 6.34 (s, 1H), 7.04 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 16.8, 21.3, 97.3, 129.7, 131.4, 133.8, 142.3, 169.4.

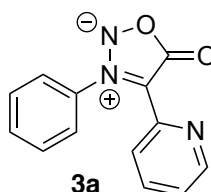
LCMS (ESI) *m/z*: 205 [M+H]⁺.

HRMS ESI-(+) calcd. for C₁₁H₁₃N₂O₂ [M+H]⁺ 205.0977, found 205.0979.

The analytical data obtained is in agreement with those reported in the literature.³

3-Phenyl-4-(2-pyridinyl)-sydnone 3a

CAS: 142335-48-6



Chemical Formula: C₁₃H₉N₃O₂

Molecular Weight: 239.23

Procedure: *N*-phenylsydnone (179 mg, 1.10 mmol), palladium acetate (15 mg, 0.066 mmol, 0.06 eq), triphenylphosphine (35 mg, 0.13 mmol, 0.12 eq) and potassium carbonate (304 mg, 2.20 mmol, 2 eq) were suspended in dimethylcarbonate (4.20 mL) in a vial. 2-bromopyridine was added (155 μL, 1.65 mmol, 1.5 eq), the vial sealed and heated to 150-160 °C in a silicon oil bath for 20 h. The reaction mixture was diluted with EtOAc, filtered on a pad of Celite and

evaporated under vacuum. The crude product was purified by flash chromatography on silica (cyclohexane/EtOAc 100/0 to 70/30) to afford the C4-arylated sydnone **3a** as a beige solid (145 mg, 0.60 mmol, 55%).

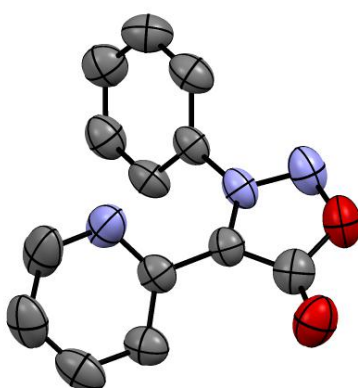
IR (neat, cm^{-1}): 3050, 1757, 1739, 1582, 1566, 1510, 1277, 1240, 1017, 789, 764, 748, 730.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.11 (ddd, $J = 7.8, 4.8, 1.1$ Hz, 1H), 7.47-7.56 (m, 4H), 7.62 (m, 1H), 7.73 (td, $J = 7.8, 1.8$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 8.23 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 107.0, 121.9, 122.7, 125.2 (2C), 129.4 (2C), 131.6, 136.1, 136.9, 144.9, 149.1, 167.1.

LCMS (ESI) m/z : 240 $[\text{M}+\text{H}]^+$.

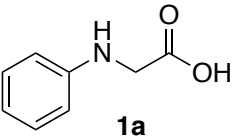
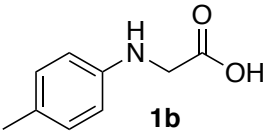
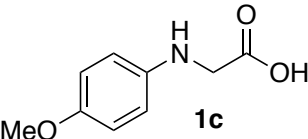
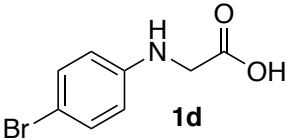
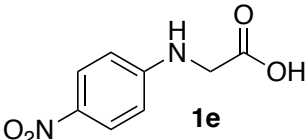
The analytical data obtained is in agreement with those reported in the literature.⁹

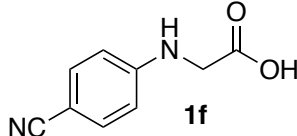
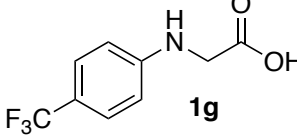
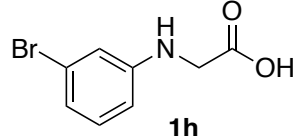
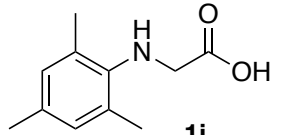


X-ray diffraction of complexes **3a**. H atoms are omitted for clarity.

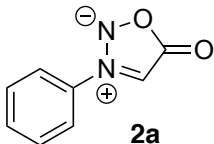
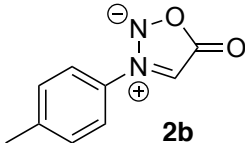
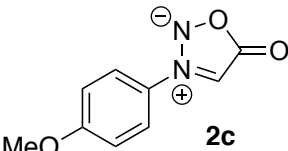
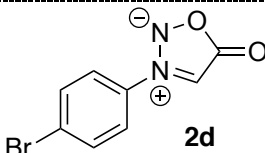
CCDC 1913664	3a
Formula	C ₁₃ H ₉ N ₃ O ₂
<i>M</i> / g.mol ⁻¹	239.23
Crystal system	Monoclinic
Space group	P2 1/n
<i>a</i> / Å	8.7441 (8)
<i>b</i> / Å	13.0971 (15)
<i>c</i> / Å	10.0411 (10)
α / °	90
β / °	100.651 (10)
γ / °	90
<i>V</i> (Å ³)	1130.1 (2)
<i>Z</i>	4
ρ_{calcd} / g.cm ⁻³	1.406
μ (Mo K α) / mm ⁻¹	0.71073
<i>T</i> / K	293 (2)
Number of reflections	2212
Number of unique reflections	1337
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0513, 0.1181
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0960, 0.1412
GOF	1.018

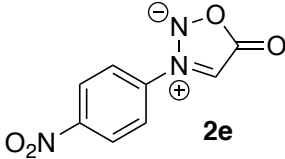
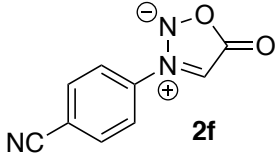
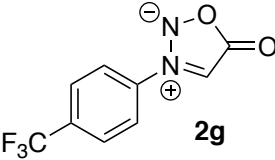
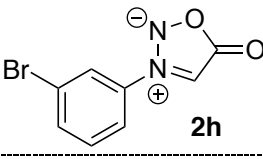
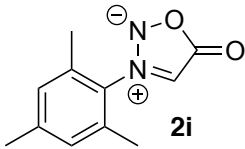
IV. Comparison of *N*-aryl glycines synthesis with literature procedures

Compound	CAS	Yield	Yield in lit.	Conditions from literature
 1a	103-01-5	91%	93% ¹⁰	1) Aniline, ethyl bromoacetate (1.0 eq.), SiO ₂ , MW (300 W), 7 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
 1b	21911-69-3	95%	90% ¹⁰	1) <i>p</i> -Toluidine, ethyl bromoacetate (1.0 eq.), SiO ₂ , MW (300 W), 5 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
			42% ¹¹	1) <i>p</i> -Toluidine, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, 7h, overnight at rt, 2) NaOH (1.1 eq.), H ₂ O, reflux, 30 min.
			53% ⁶	1) <i>p</i> -Toluidine, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, overnight, 2) LiOH (3 eq.), THF/water, 2 h at 0°C then rt.
 1c	22094-69-5	80%	89% ¹⁰	1) 4-Methoxyaniline, ethyl bromoacetate (1.0 eq.), SiO ₂ , MW (300 W), 4 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
			57% ¹¹	1) 4-Methoxyaniline, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, 7h, overnight at rt, 2) NaOH (1.1 eq.), reflux, 30 min.
			50% ⁶	1) 4-Methoxyaniline, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, overnight, 2) LiOH (3 eq.), THF/water, 2 h at 0°C then rt.
			48% ⁷	1) 4-Methoxyaniline, NEt ₃ (large excess), ethyl bromoacetate (1.0 eq.), 0°C to rt. 2) LiOH (5.8 eq.), THF/H ₂ O/EtOH 1:1:1, rt.
 1d	13370-62-2	76%	88% ¹⁰	1) 4-Bromoaniline, ethyl bromoacetate (1.0 eq.), SiO ₂ , MW (300 W), 6.3 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
			65% ⁶	1) 4-Bromoaniline, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, overnight, 2) LiOH (3 eq.), THF/water, 2 h at 0°C then rt.
 1e	619-91-0	53%	90% ¹⁰	1) 4-Nitroaniline, ethyl bromoacetate (1.0 eq.), SiO ₂ , MW (300 W), 5 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
			61% ¹¹	4-Nitroaniline, chloroacetic acid (2 eq.), H ₂ O, reflux, overnight
			65% ⁶	1) Glycine, N(<i>n</i> -Bu) ₄ OH (1.0 eq.), DMSO 2) <i>p</i> -Fluoro-nitrobenzene (1.1 eq.), K ₂ CO ₃ (1.1 eq.), 45°C.
			53% ⁷	4-Nitroaniline, bromoacetic acid (2 eq.), H ₂ O, reflux, overnight

Compound	CAS	Yield	Yield in lit.	Conditions from literature
 1f	42288-26-6	56%	47% ¹¹	4-aminobenzonitrile, chloroacetic acid (2 eq.), H ₂ O, reflux, 10h
			80-87% ¹²	4-aminobenzonitrile, chloroacetic acid (1.5 eq.), H ₂ O, reflux, 5h
 1g	77311-21-8	74%	30% ¹¹	4-Trifluoromethylaniline, NaOAc (2.0 eq.), AcOH (4.0 eq.), glyoxylic acid (1.5 eq.), NaBH ₃ CN (1.0 eq.), 0°C to rt in 2 h.
			88% ¹³	4-Trifluoromethylaniline, NaOAc (2.0 eq.), AcOH (4.0 eq.), glyoxylic acid (1.5 eq.), NaBH ₃ CN (1.0 eq.), MeOH, 0°C to rt, 2 h, N ₂ .
 1h	42288-20-0	85%	n.a.	
 1i	104412-17-1	37%	n.a. ³	1) 2,4,6-Trimethylaniline, NaOAc.3H ₂ O (1.5 eq.), ethyl bromoacetate (1.0 eq.), EtOH, reflux, overnight, 2) 10% NaOH _{aq} . (1.0 eq.), 40 min.
			10% ¹⁴	1) 2,4,6-Trimethylaniline, NaOAc.3H ₂ O (1.5 eq.), ethyl bromoacetate (1.0 eq.), EtOH, reflux, overnight, 2) 20% HCl (excess), 100°C, 4h.

V. Comparison of sydnone synthesis with literature procedures

Formule	CAS	Yield	Yield in lit.	Conditions from literature
 2a	120-06-9	95%	78% ¹⁰	1) Glycine 1a , silica chloride, wet SiO ₂ , NaNO ₂ (1.5 eq.), CH ₂ Cl ₂ , 0°C, 2.5 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH ₂ Cl ₂ , 0°C, 4 h.
			63% ⁶	1) Glycine 1a , NaNO ₂ (1.5 eq., dropwise addition), H ₂ O at 0°C, HCl cc. Drying overnight. 2) Ac ₂ O (large excess), 100°C, 1.5 h.
			49% ⁸	1) Glycine 1a in HCl cc., NaNO ₂ (1.0 eq., dropwise addition), 14h under Ar. 2) Ac ₂ O (large excess), 100°C, 3 h.
			89% ⁵	1) Glycine 1a , <i>t</i> -BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
			73% ¹⁰	1) Glycine 1b , silica chloride, wet SiO ₂ , NaNO ₂ (1.5 eq.), CH ₂ Cl ₂ , 0°C, 2.2 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH ₂ Cl ₂ , 0°C, 4 h.
 2b	3483-19-0	91%	60% ⁶	1) Glycine 1b , NaNO ₂ (1.5 eq., dropwise addition), H ₂ O at 0°C, HCl cc., Drying overnight. 2) Ac ₂ O (large excess), 100°C, 1.5 h.
			82% ¹⁵	1) Glycine 1b , <i>t</i> -BuONO, anh. THF, Ar, 30 min. 2) TFAA, 1h.
			69% ⁸	1) Glycine 1b , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 30 min. 2) CDI (1.1 eq.), 1h.
			81% ¹⁰	1) Glycine 1c , silica chloride, wet SiO ₂ , NaNO ₂ (1.5 eq.), CH ₂ Cl ₂ , 0°C, 1.7 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH ₂ Cl ₂ , 0°C, 4 h.
 2c	3815-80-3	54%	59% ⁵	1) Glycine 1c , <i>t</i> -BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
			50% ⁸	1) Glycine 1c , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 30 min. 2) CDI (1.1 eq.), 1h.
			78% ⁶	1) Glycine 1c , NaNO ₂ (1.5 eq., dropwise addition), H ₂ O at 0°C, HCl cc., Drying overnight. 2) Ac ₂ O (large excess), 100°C, 1.5 h.
			73% ⁷	1) Glycine 1c , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 0°C to rt. 2) TFAA (1.1 eq.), 1h.
			78% ¹⁵	1) Glycine 1c , <i>t</i> -BuONO, anh. THF, Ar, 30 min. 2) TFAA, 1h.
			79% ¹⁰	1) Glycine 1d , silica chloride, wet SiO ₂ , NaNO ₂ (1.5 eq.), CH ₂ Cl ₂ , 0°C, 2.4 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH ₂ Cl ₂ , 0°C, 4 h.
 2d	26537-61-1	91%	50% ⁶	1) Glycine 1d , NaNO ₂ (1.5 eq., dropwise addition), H ₂ O at 0°C, HCl cc., Drying overnight. 2) Ac ₂ O (large excess), 100°C, 1.5 h.

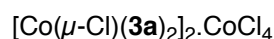
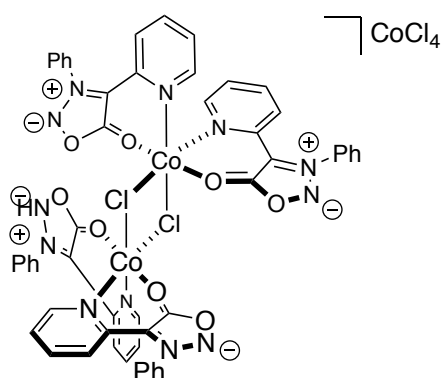
Formule	CAS	Yield	Yield in lit.	Conditions from literature
 2e	6299-51-0	42%	80% ¹⁰	1) Glycine 1e , silica chloride, wet SiO ₂ , NaNO ₂ (1.5 eq.), CH ₂ Cl ₂ , 0°C, 2.0 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH ₂ Cl ₂ , 0°C, 4 h.
			36% ⁶	1) Glycine 1e , NaNO ₂ (1.5 eq., dropwise addition), H ₂ O at 0°C, HCl cc., Drying overnight. 2) Ac ₂ O (large excess), 100°C, 1.5 h.
			77% ⁷	1) Glycine 1e , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 0°C to rt. 2) TFAA (2.5 eq.), 1h.
			57% ⁸	1) Glycine 1e , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
 2f	68657-48-7	34%	n.a. ¹⁶	1) Glycine 1f , <i>t</i> -BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.15 eq.), 0°C to rt, 1h.
 2g	1620220-61-2	46%	70% ⁸	1) Glycine 1g , <i>t</i> -BuONO (1.5 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
			35% ¹³	1) Glycine 1g , isoamyl nitrite (1.1 eq.), dimethoxyethane, 5 h. 2) TFAA (1.5 eq., dropwise addition), CH ₂ Cl ₂ , 0°C, 1.5 h.
			65% ⁵	1) Glycine 1g , <i>t</i> -BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
 2h	60816-43-5	81%	n.a. ¹⁷	no detailed experimental procedure given
 2i	104411-99-6	53%	n.a. ³	1) Glycine 1i in 12% HCl, NaNO ₂ in H ₂ O (1.2 eq., dropwise addition at 0°C), 4 h. 2) TFAA, CH ₂ Cl ₂ , 0°C, 1 h.
			n.a. ¹⁸	Procedure according to ref ^{3, 19} (no characterization given).

VI. Preparation of organometallic complexes with sydnone **3a** as ligand in ball-mill

A. General procedure for preparation of complexes (GP2)

4-(2-Pyridyl)-*N*-phenylsydnone **3a** and the corresponding metallic salt were introduced in a grinding jar (10 mL zirconium oxide ZrO₂ or 15 mL PTFE) with one ball (ZrO₂ or stainless steel, 10 mm diameter). The jar was closed and subjected to grinding in a vibratory ball-mill at 30 Hz for 1h. The obtained powder was taken up with MeCN and evaporated under vacuum. The resulting solid was suspended in DCM, filtered on sintered glass and dried under vacuum to furnish the expected sydnone-metal complex. X-ray quality crystals were grown by slow evaporation of an acetonitrile solution of the complex.

Of note, cobalt, copper and nickel complexes were found to be paramagnetic. Hence, no NMR data could be acquired.



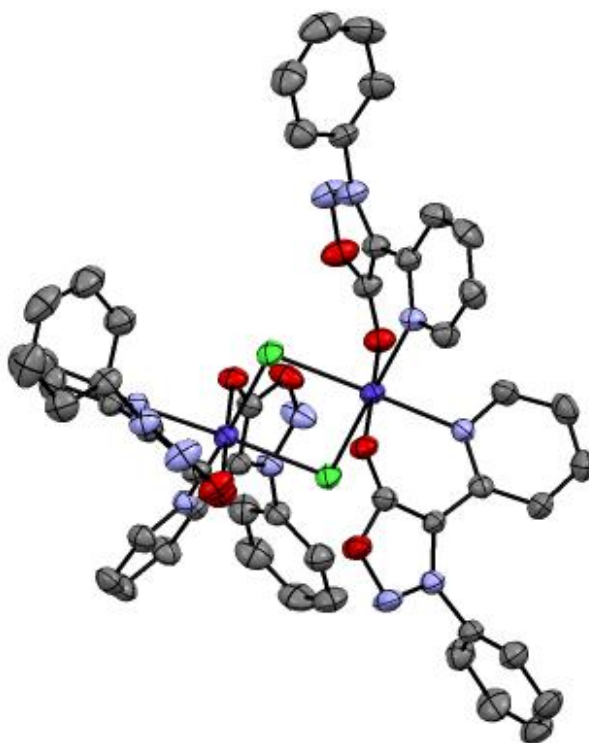
Chemical Formula: C₅₂H₃₆Cl₆Co₃N₁₂O₈

Molecular Weight: 1346.44

Procedure: according to the general procedure GP2, using 3.0 eq of cobalt chloride CoCl₂ and 4.0 eq of sydnone **3a** in a 10 mL ZrO₂ jar with one ZrO₂ ball (10 mm diameter), the dimeric complex was obtained as a blue-green powder (64 mg, 0.047 mmol, 68%).

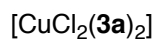
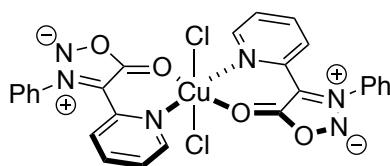
IR (neat, cm⁻¹): 3345, 1675, 1600, 1507, 1276, 1022, 918, 765.

HRMS ESI-(+) calcd. for C₅₂H₃₆N₁₂O₈Cl₂Co₂ [M-CoCl₄]²⁺/2 572.0405, found 572.0421.



X-ray diffraction of complexes $[\text{Co}(\mu\text{-Cl})(\mathbf{3a})_2]_2 \cdot \text{CoCl}_4$. H atoms and CoCl_4 are omitted for clarity.

CCDC 1913663	$[\text{Co}(\mu\text{-Cl})(\mathbf{3a})_2]_2 \cdot \text{CoCl}_4$
Formula	$\text{C}_{52}\text{H}_{36}\text{Cl}_6\text{Co}_3\text{N}_{12}\text{O}_8$
$M / \text{g.mol}^{-1}$	1346.42
Crystal system	Orthorhombic
Space group	P 2 2ab
$a / \text{\AA}$	17.0950 (4)
$b / \text{\AA}$	16.1670 (3)
$c / \text{\AA}$	10.0791 (2)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
$V (\text{\AA}^3)$	2785.61 (10)
Z	2
$\rho_{\text{calcd}} / \text{g.cm}^{-3}$	1.605
$\mu (\text{Mo K}\alpha) / \text{mm}^{-1}$	0.71073
T / K	293 (2)
Number of reflections	6983
Number of unique reflections	5417
$R1, wR2 (I > 2\sigma(I))$	0.0332, 0.0630
$R1, wR2 (\text{all data})$	0.0563, 0.0689
GOF	1.033



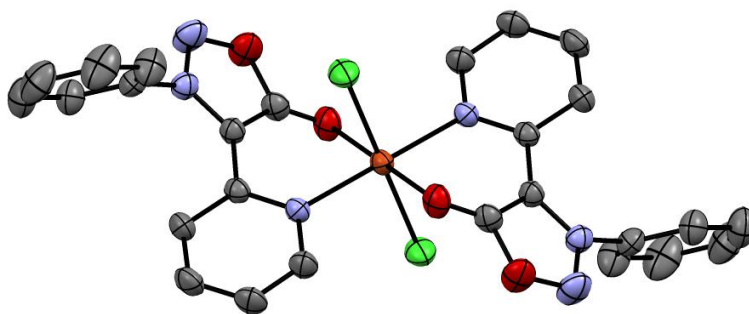
Chemical Formula: $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{CuN}_6\text{O}_4$

Molecular Weight: 612.91

Procedure: according to the general procedure GP2, using 1.0 eq of copper chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.0 eq of sydnone **3a** in a 10 mL ZrO_2 jar with one ZrO_2 ball (10 mm diameter), the bidentate complex was obtained as a green powder (42 mg, 0.068 mmol, 68%).

IR (neat, cm^{-1}): 3057, 1726, 1717, 1601, 1509, 1288, 1008, 783, 769, 752, 730.

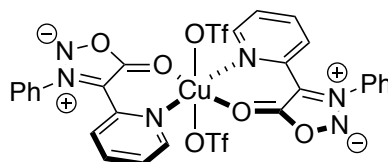
HRMS ESI-(+) calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_6\text{O}_4\text{ClCu} [\text{M}-\text{Cl}]^+$ 576.0376, found 576.0374.



X-ray diffraction of complexes $[\text{CuCl}_2(\mathbf{3a})_2]$. H atoms are omitted for clarity.

CCDC 1913667	[CuCl ₂ (3a) ₂]
Formula	C ₂₆ H ₁₈ Cl ₂ CuN ₆ O ₄
<i>M</i> / g.mol ⁻¹	612.90
Crystal system	Triclinic
Space group	P -1
<i>a</i> / Å	8.0661 (3)
<i>b</i> / Å	8.8517 (4)
<i>c</i> / Å	10.0437 (4)
α / °	108.745 (4)
β / °	104.613 (3)
γ / °	96.672 (4)
<i>V</i> (Å ³)	641.70 (5)
<i>Z</i>	1
ρ_{calcd} / g.cm ⁻³	1.586
μ (Mo K α) / mm ⁻¹	0.71073
<i>T</i> / K	293 (2)
Number of reflections	3708
Number of unique reflections	3195
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0301, 0.0789
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0371, 0.0822
GOF	1.050

[Cu(OTf)₂(**3a**)₂]



[Cu(OTf)₂(**3a**)₂]

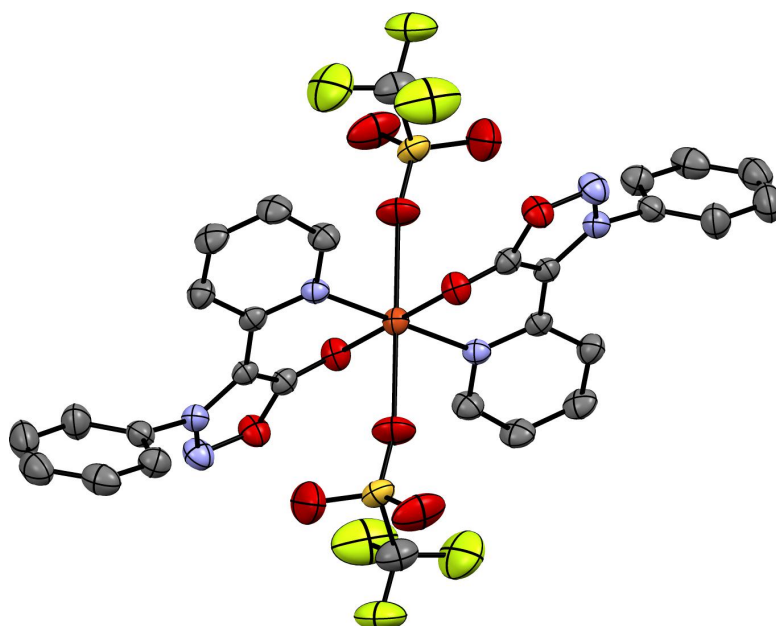
Chemical Formula: C₂₈H₁₈CuF₆N₆O₁₀S₂

Molecular Weight: 840.14

Procedure: according to the general procedure GP2, using 1.0 eq of copper triflate Cu(OTf)₂ and 2.0 eq of sydnone **3a** in a 15 mL PTFE jar with one stainless steel ball (10 mm diameter), the bidentate complex was obtained as a yellow powder (27 mg, 0.032 mmol, 69%).

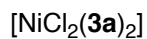
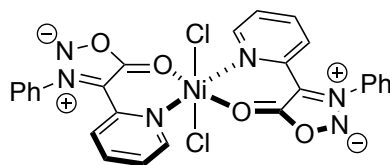
IR (neat, cm⁻¹): 3070, 1663, 1606, 1529, 1283, 1254, 1225, 1152, 1036, 775, 765.

HRMS ESI-(+) calcd. for C₂₇H₁₈CuF₃N₆O₇S [M-TfO]⁺ 690.0206, found 690.0209.



X-ray diffraction of complexes $[\text{CuCl}_2(\mathbf{3a})_2]$. H atoms are omitted for clarity.

CCDC 1913662	$[\text{Cu}(\text{OTf})_2(\mathbf{3a})_2]$
Formula	$\text{C}_{28}\text{H}_{18}\text{CuF}_6\text{N}_6\text{O}_{10}\text{S}_2$
$M / \text{g.mol}^{-1}$	840.14
Crystal system	Triclinic
Space group	P -1
$a / \text{\AA}$	7.9107 (4)
$b / \text{\AA}$	7.9633 (4)
$c / \text{\AA}$	13.4394 (8)
$\alpha / ^\circ$	81.297 (4)
$\beta / ^\circ$	82.418 (5)
$\gamma / ^\circ$	84.920 (4)
$V (\text{\AA}^3)$	827.53 (8)
Z	1
$\rho_{\text{calcd}} / \text{g.cm}^{-3}$	1.686
$\mu (\text{Mo K}\alpha) / \text{mm}^{-1}$	0.71073
T / K	293 (10)
Number of reflections	4448
Number of unique reflections	3655
$R1, wR2 (I > 2\sigma(I))$	0.0542, 0.1401
$R1, wR2 (\text{all data})$	0.0671, 0.1480
GOF	1.037



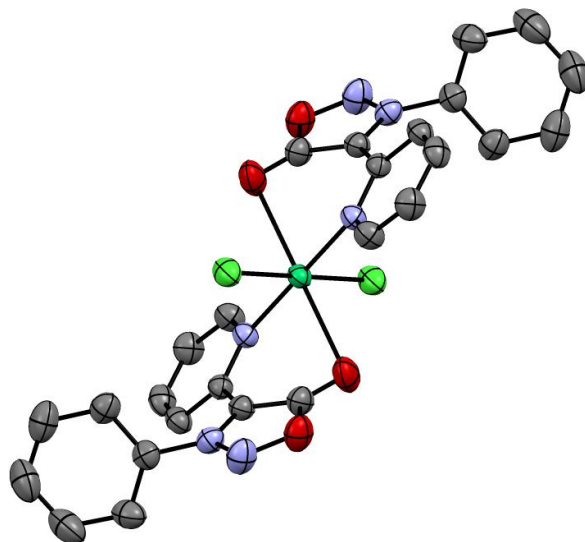
Chemical Formula: $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}_6\text{NiO}_4$

Molecular Weight: 608.06

Procedure: according to the general procedure GP2, using 1.0 eq of nickel chloride NiCl_2 and 2.0 eq of sydnone **3a** in a 10 mL ZrO_2 jar with one ZrO_2 ball (10 mm diameter), the bidentate complex was obtained as a pale green powder (40 mg, 0.066 mmol, 66%).

IR (neat, cm^{-1}): 3071, 1706, 1700, 1605, 1529, 1274, 1023, 1009, 906, 793, 775, 759, 732.

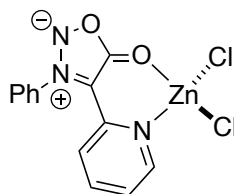
HRMS ESI-(+) calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_6\text{O}_4\text{ClNi} [\text{M}-\text{Cl}]^+$ 571.0432, found 571.0437.



X-ray diffraction of complexes $[\text{NiCl}_2(\mathbf{3a})_2]$. H atoms are omitted for clarity.

CCDC 1913666	[NiCl ₂ (3a) ₂]
Formula	C _{9.33} H _{0.33} Cl _{0.33} N _{0.67} Ni _{0.33} O _{2.67}
<i>M</i> / g.mol ⁻¹	195.82
Crystal system	Triclinic
Space group	P -1
<i>a</i> / Å	8.2233 (5)
<i>b</i> / Å	8.4289 (4)
<i>c</i> / Å	11.1858 (9)
α / °	72.182 (5)
β / °	69.495 (6)
γ / °	79.039 (4)
<i>V</i> (Å ³)	688.37 (8)
<i>Z</i>	3
ρ_{calcd} / g.cm ⁻³	1.417
μ (Mo K α) / mm ⁻¹	0.71073
<i>T</i> / K	293 (2)
Number of reflections	3435
Number of unique reflections	3071
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0319, 0.0884
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0411, 0.0908
GOF	1.331

[ZnCl₂(**3a**)]



[ZnCl₂(**3a**)]

Chemical Formula: C₁₃H₉Cl₂N₃O₂Zn

Molecular Weight: 375.51

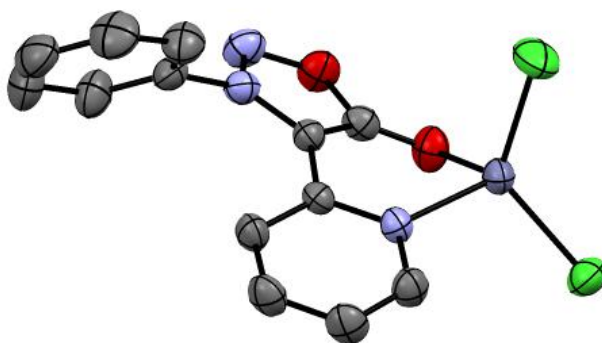
Procedure: according to the general procedure GP2, using 1.0 eq of zinc chloride ZnCl₂ and 2.0 eq of sydnone **3a** in a 10 mL ZrO₂ jar with one ZrO₂ ball (10 mm diameter), the monodentate complex was obtained as a beige solid (58 mg, 0.155 mmol, 74%).

¹H NMR (500 MHz, CD₃CN) δ (ppm): 7.37 (m, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.61-7.68 (m, 4H), 7.76 (m, 1H), 7.85 (td, *J* = 7.9, 1.7 Hz, 1H), 8.43 (d, *J* = 4.7 Hz, 1H).

¹³C NMR (125 MHz, CD₃CN) δ (ppm): 108.7, 123.0, 125.0, 126.0, 131.0, 133.4, 136.0, 139.7, 145.0, 150.4, 169.4.

IR (neat, cm⁻¹): 3080, 1660, 1604, 1509, 1288, 1038, 1017, 925, 920, 795, 781, 762, 735.

HRMS ESI-(+) calcd. for C₁₃H₉N₃O₂ClZn [M-Cl]⁺ 337.9676, found 337.9669.



X-ray diffraction of complexes [ZnCl₂(**3a**)]. H atoms are omitted for clarity.

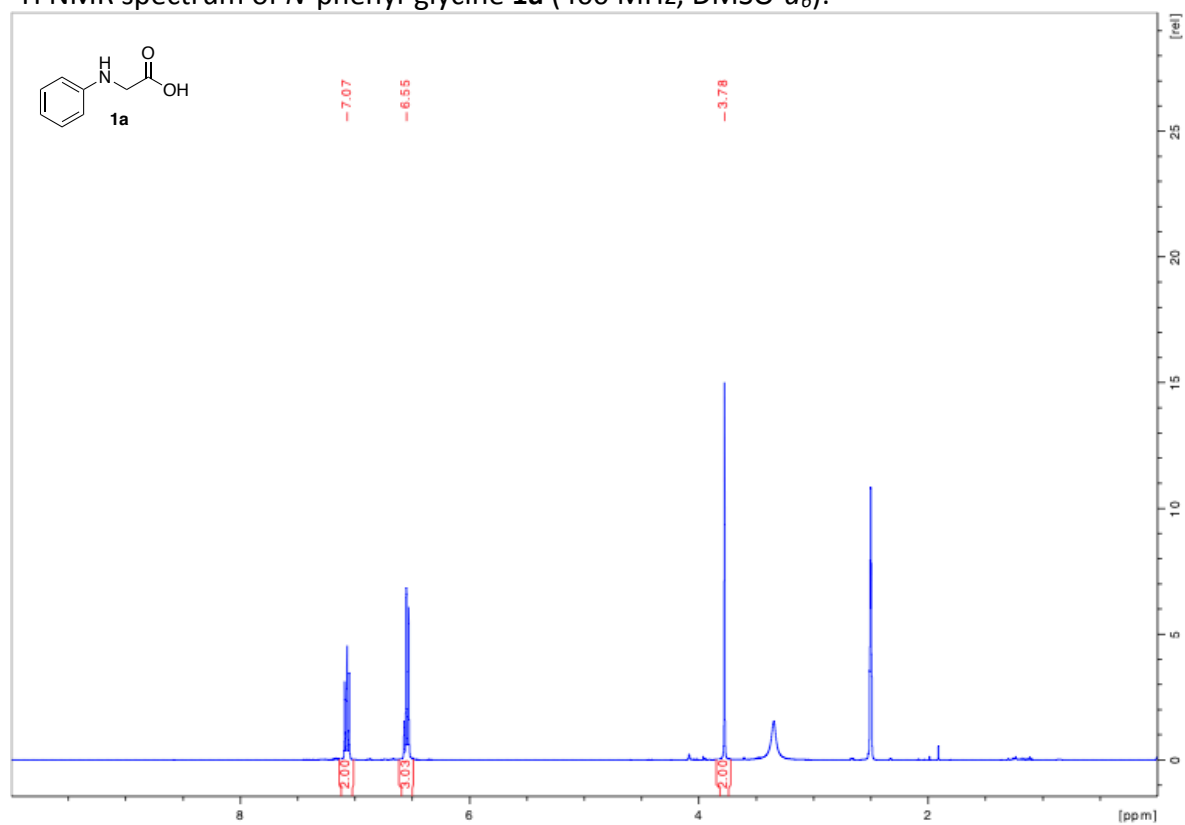
CCDC 1913665	[ZnCl ₂ (3a)]
Formula	C ₁₃ H ₉ Cl ₂ N ₃ O ₂ Zn
<i>M</i> / g.mol ⁻¹	375.50
Crystal system	Triclinic
Space group	P -1
<i>a</i> / Å	8.5206 (4)
<i>b</i> / Å	8.9361 (3)
<i>c</i> / Å	9.9810 (3)
<i>α</i> / Å	94.269 (3)
<i>β</i> / Å	99.231 (3)
<i>γ</i> / Å	94.285 (3)
<i>V</i> (Å ³)	745.15 (5)
<i>Z</i>	2
<i>ρ</i> _{calcd} / g.cm ⁻³	1.674
<i>μ</i> (Mo Kα) / mm ⁻¹	0.71073
<i>T</i> / K	293 (2)
Number of reflections	4322
Number of unique reflections	3627
<i>R</i> _{int}	0.024 (3)
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0305, 0.0742
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0431, 0.0773
GOF	1.065

VII. References

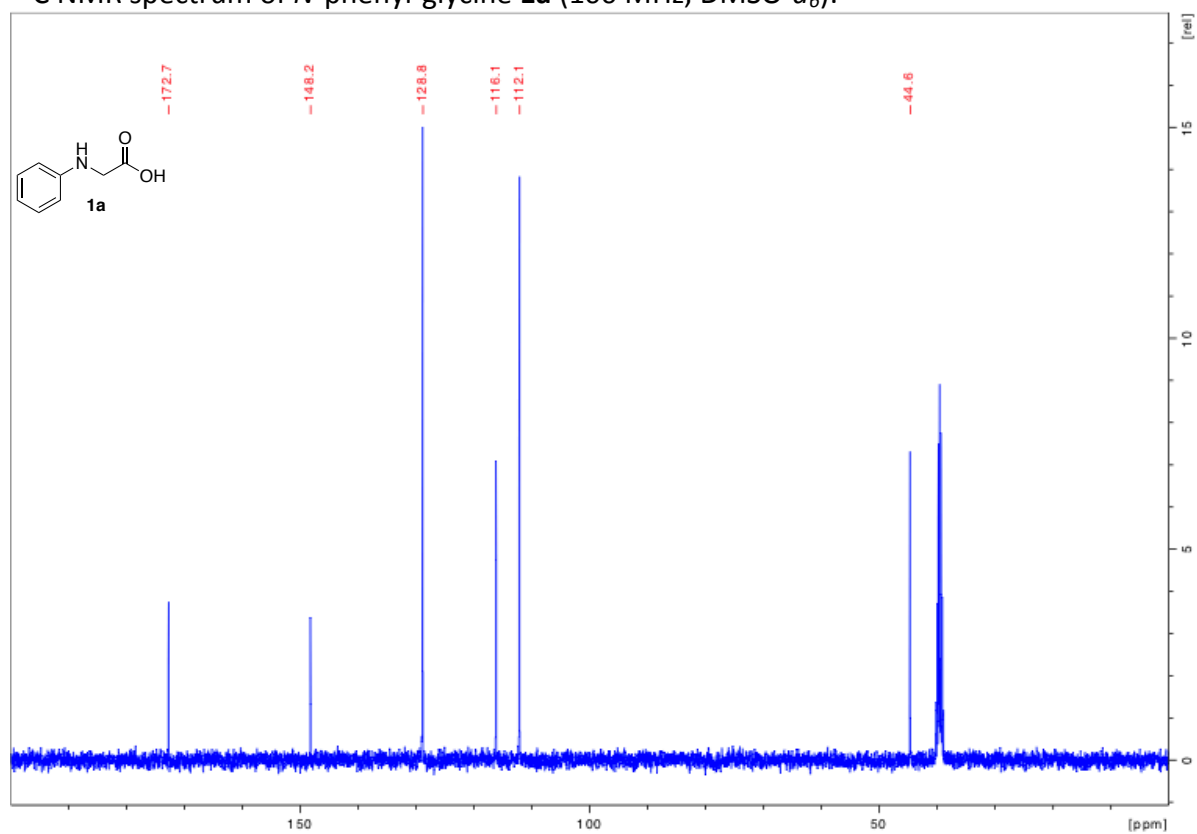
1. Z. Lu and R. J. Twieg, *Tetrahedron Lett.*, **2005**, 46, 2997.
2. S. Specklin, E. Decuypere, L. Plougastel, S. Aliani and F. Taran, *J. Org. Chem.*, **2014**, 79, 7772.
3. K. Turnbull, *J. Heterocycl. Chem.*, **1985**, 22, 965.
4. C. Wu, Y. Fang, R. C. Larock and F. Shi, *Organic Letters*, **2010**, 12, 2234.
5. C. Favre, L. de Cremoux, J. Badaut and F. Friscourt, *J. Org. Chem.*, **2018**, 83, 2058.
6. Y. Fang, C. Wu, R. C. Larock and F. Shi, *J. Org. Chem.*, **2011**, 76, 8840.
7. L. Zhang, X. Zhang, Z. Yao, S. Jiang, J. Deng, B. Li and Z. Yu, *J. Am. Chem. Soc.*, **2018**, 140, 7390.
8. L. Plougastel, O. Koniev, S. Specklin, E. Decuypere, C. Créminon, D.-A. Buisson, A. Wagner, S. Kolodych and F. Taran, *Chem. Commun.*, **2014**, 50, 9376.
9. A. Rodriguez and W. J. Moran, *Synthesis*, **2009**, 650.
10. D. Azarifar, H. G. Bosra, M.-A. Zolfigol and M. Tajbaksh, *Heterocycles*, **2006**, 68, 175.
11. S. Specklin, E. Decuypere, L. Plougastel, S. Aliani and F. Taran, *J. Org. Chem.*, **2014**, 79, 7772.
12. W. Ren, Y. Ren and S. Wang, *Eur. J. Med. Chem.*, **2016**, 120, 148.
13. T. Wezeman, J. Comas-Barceló, M. Nieger, J. P. A. Harrity and S. Bräse, *Org. Biomol. Chem.*, **2017**, 15, 1575.
14. S. Ikeda and S. Murata, *J. Photochem. Photobiol., A*, **2002**, 149, 121.
15. H. Liu, D. Audisio, L. Plougastel, E. Decuypere, D.-A. Buisson, O. Koniev, S. Kolodych, A. Wagner, M. Elhabiri, A. Krzyczmonik, S. Forsback, O. Solin, V. Gouverneur and F. Taran, *Angew. Chem., Int. Ed.*, **2016**, 55, 12073.
16. M. K. Narayanam, G. Ma, P. A. Champagne, K. N. Houk and J. M. Murphy, *Angew. Chem. Int. Ed.*, **2017**, 56, 13006.
17. J. Jaźwiński and O. Staszewska-Krajewska, *J. Mol. Struct.*, **2002**, 602-603, 269.
18. S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger and A. Schmidt, *Chem. Commun.*, **2014**, 50, 11822.
19. (a) K. L. McChord, S. A. Tullis and K. Turnbull, *Synth. Commun.*, **1989**, 19, 2249; (b) K. Turnbull, T. L. Blackburn and J. J. Miller, *J. Heterocycl. Chem.*, **1996**, 33, 485.

VIII. ^1H and ^{13}C NMR spectra

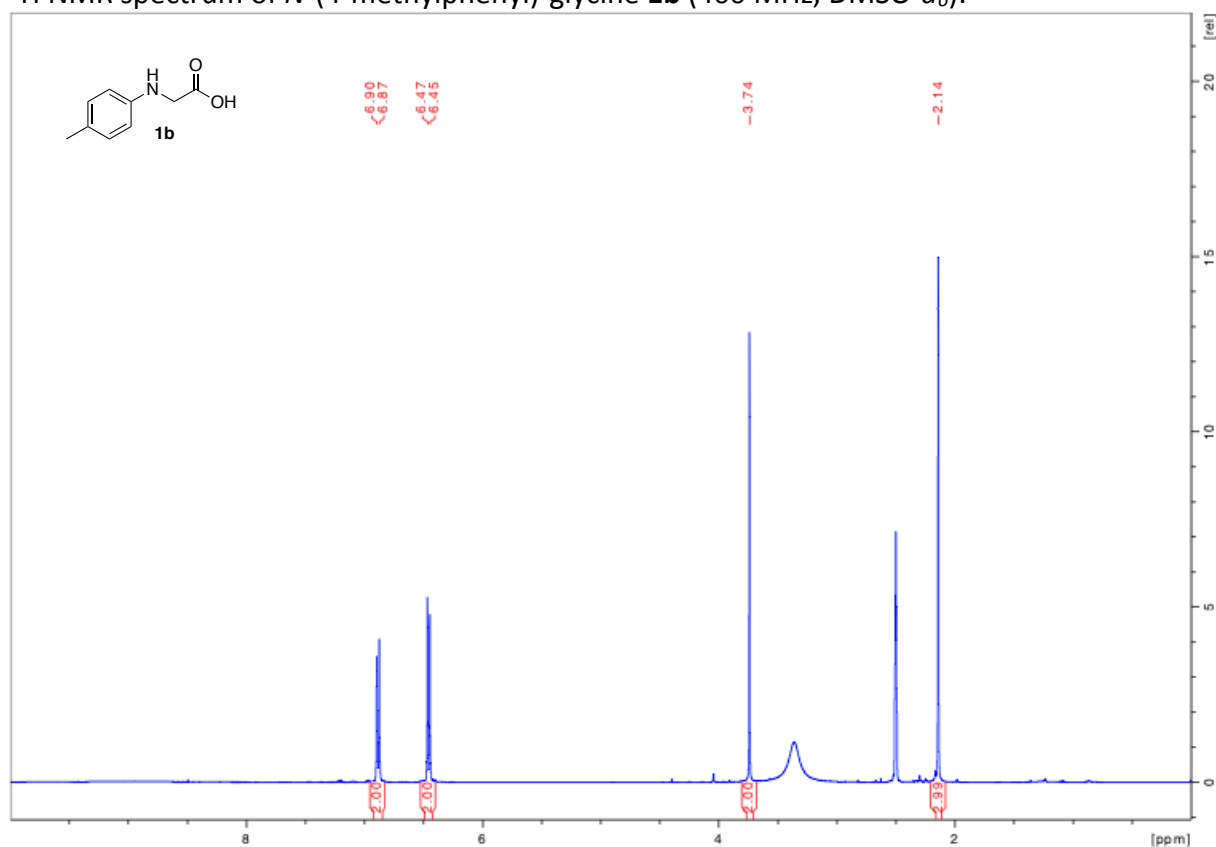
^1H NMR spectrum of *N*-phenyl-glycine **1a** (400 MHz, $\text{DMSO}-d_6$):



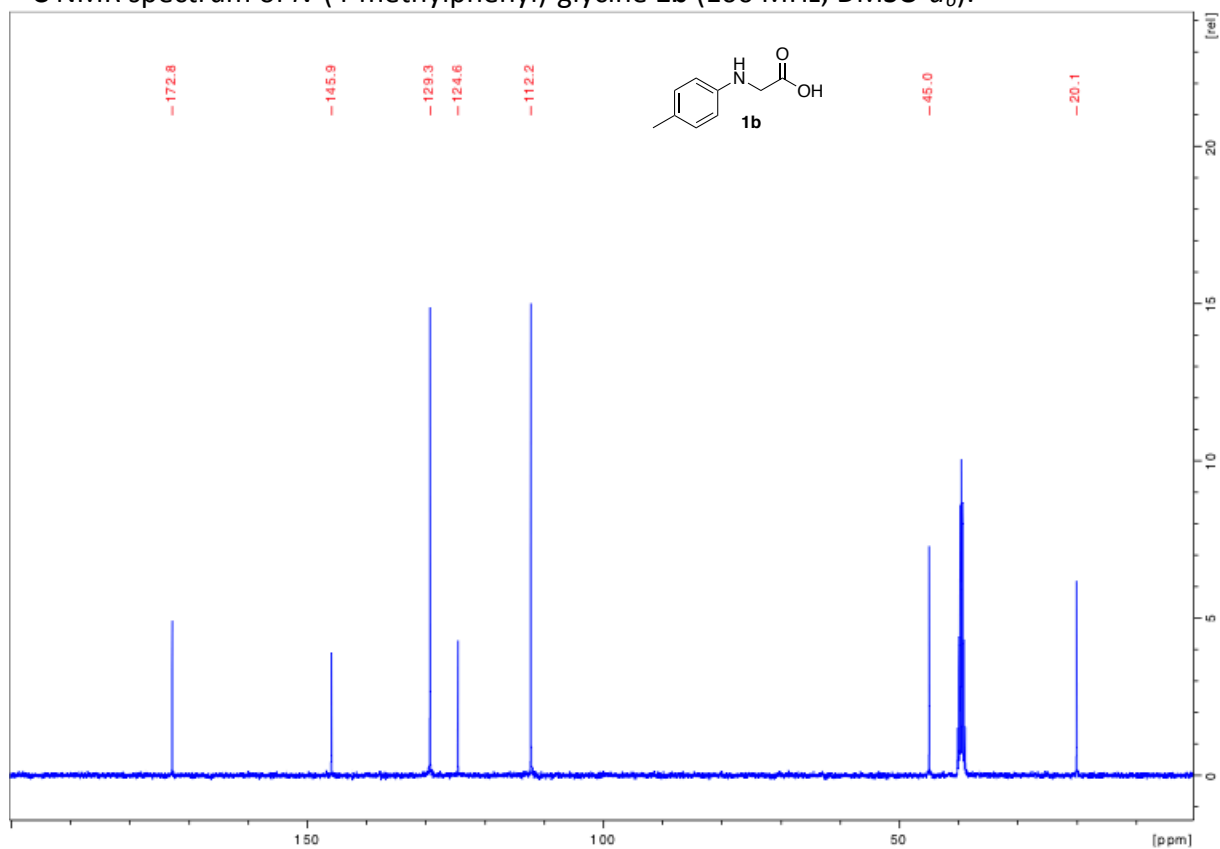
^{13}C NMR spectrum of *N*-phenyl-glycine **1a** (100 MHz, $\text{DMSO}-d_6$):



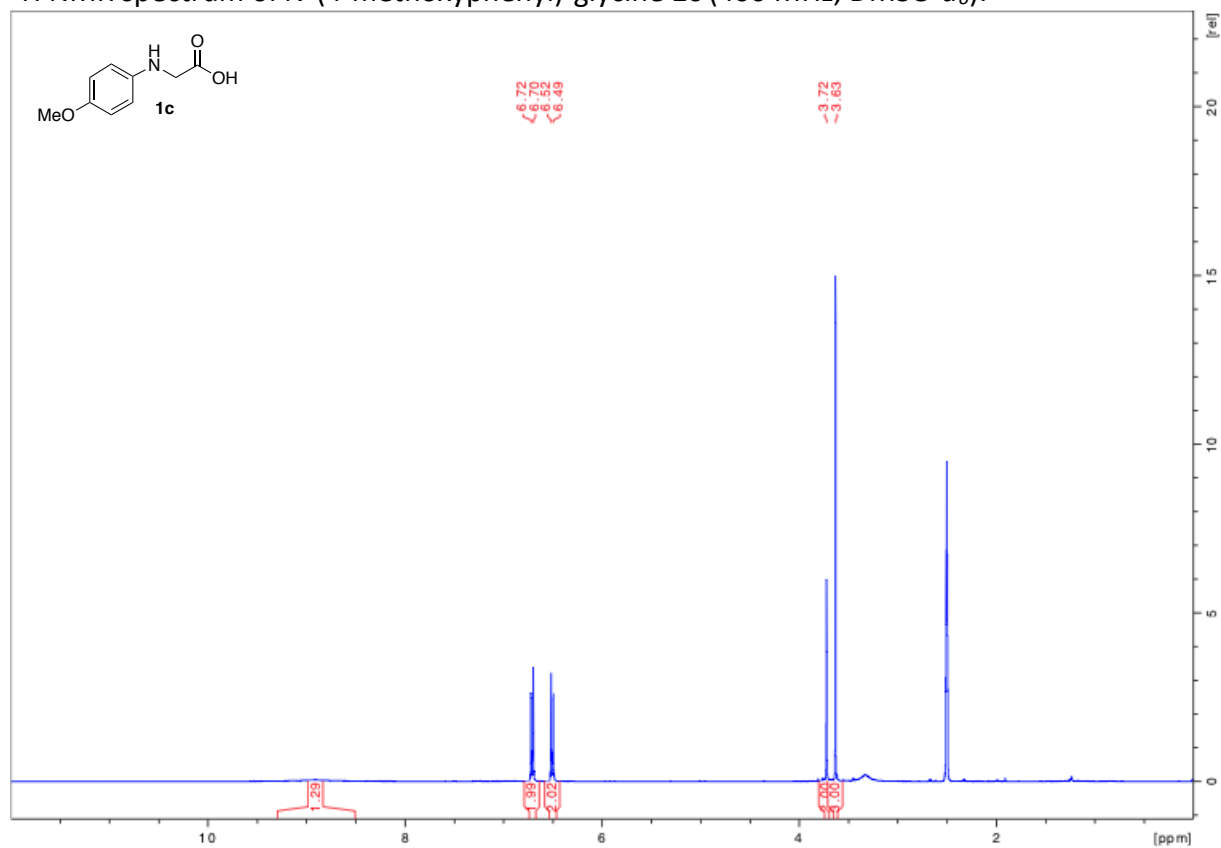
^1H NMR spectrum of *N*-(4-methylphenyl)-glycine **1b** (400 MHz, $\text{DMSO}-d_6$):



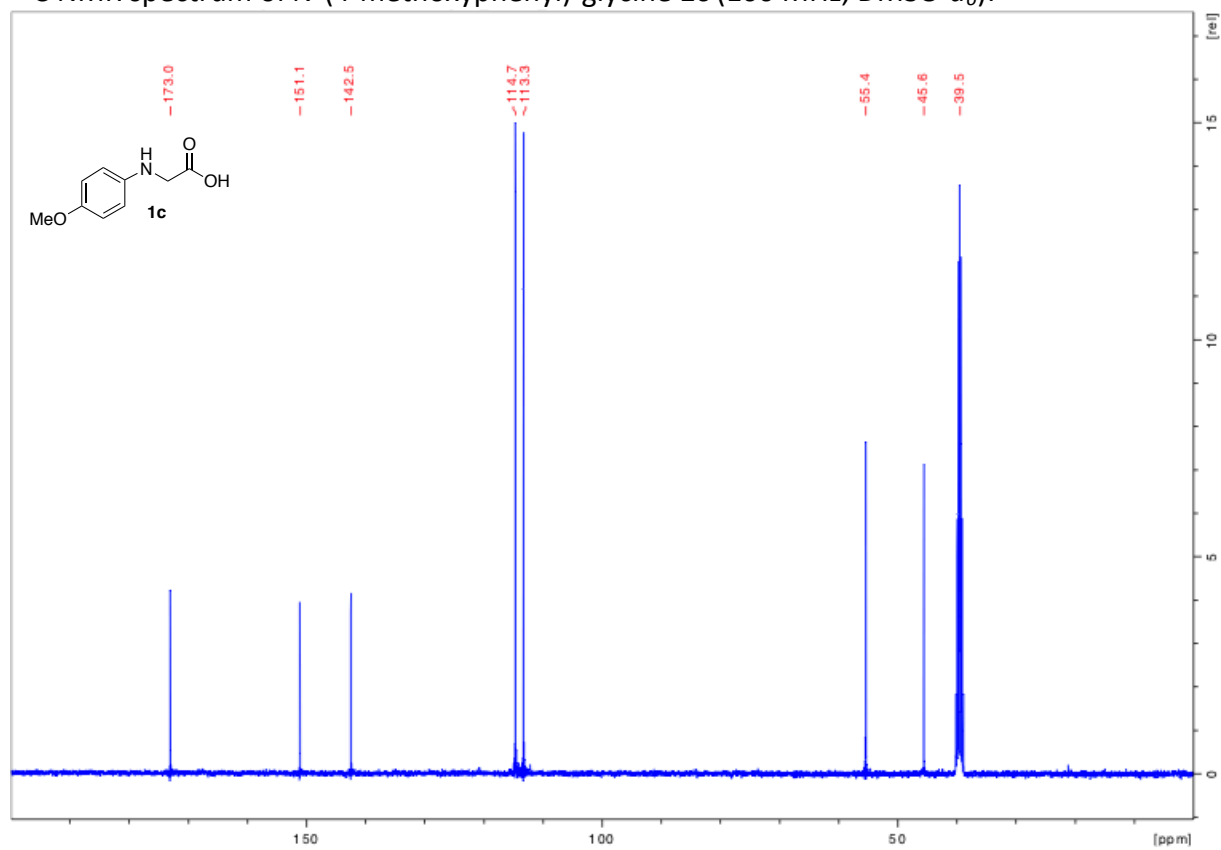
^{13}C NMR spectrum of *N*-(4-methylphenyl)-glycine **1b** (100 MHz, $\text{DMSO}-d_6$):



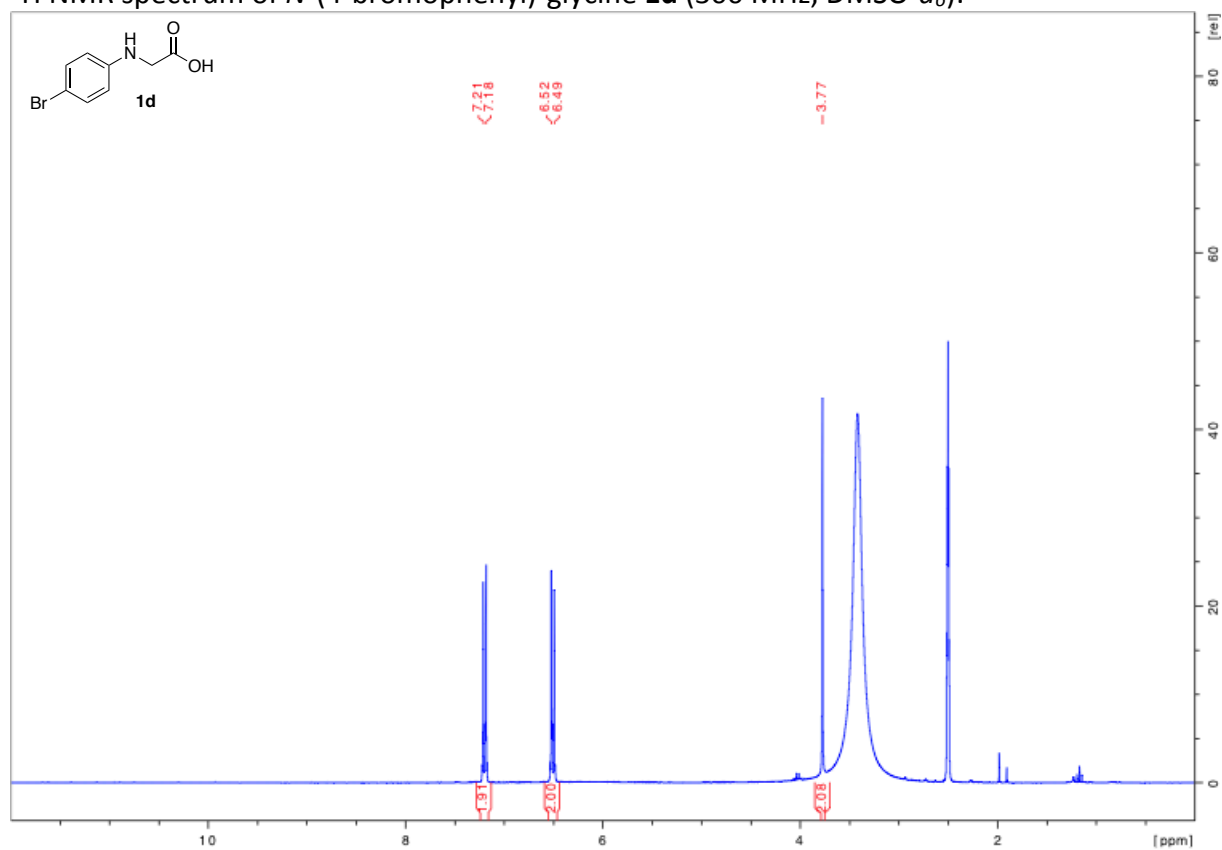
^1H NMR spectrum of *N*-(4-methoxyphenyl)-glycine **1c** (400 MHz, $\text{DMSO}-d_6$):



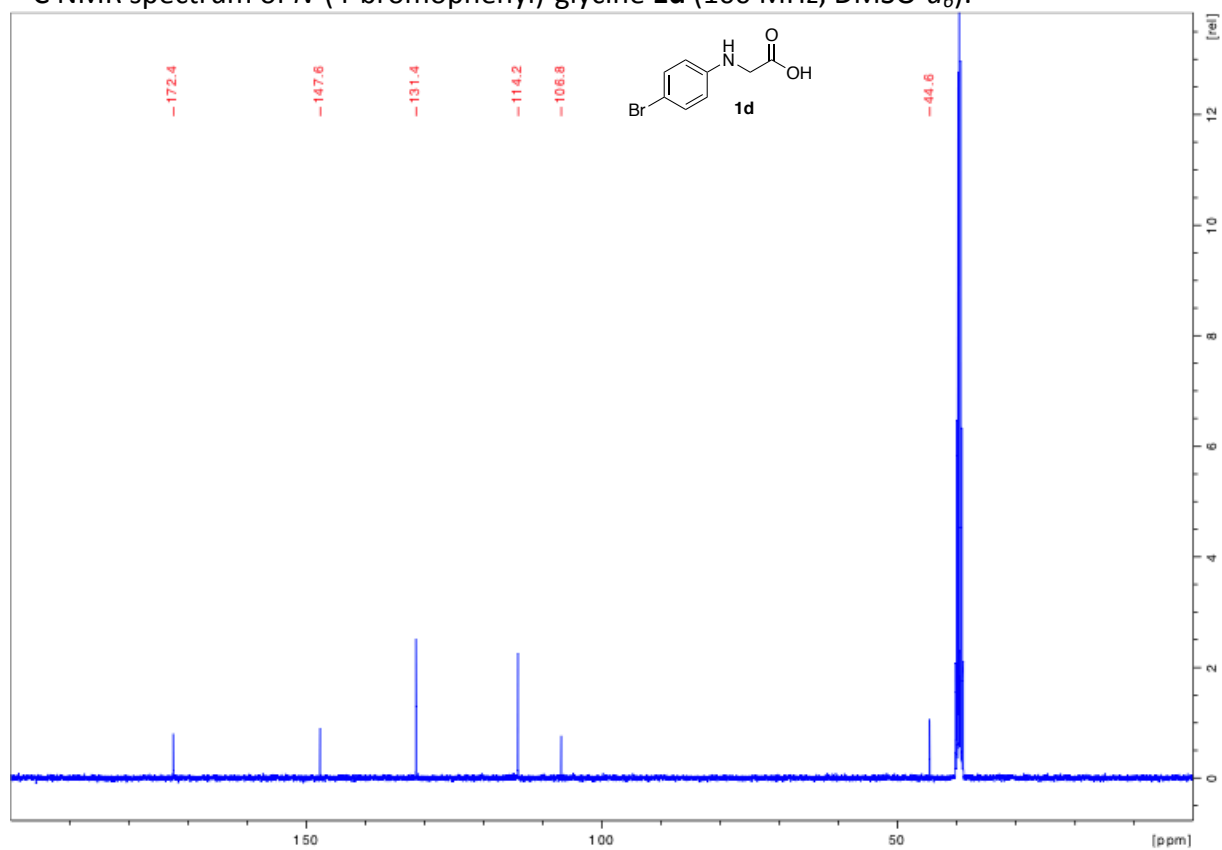
^{13}C NMR spectrum of *N*-(4-methoxyphenyl)-glycine **1c** (100 MHz, $\text{DMSO}-d_6$):



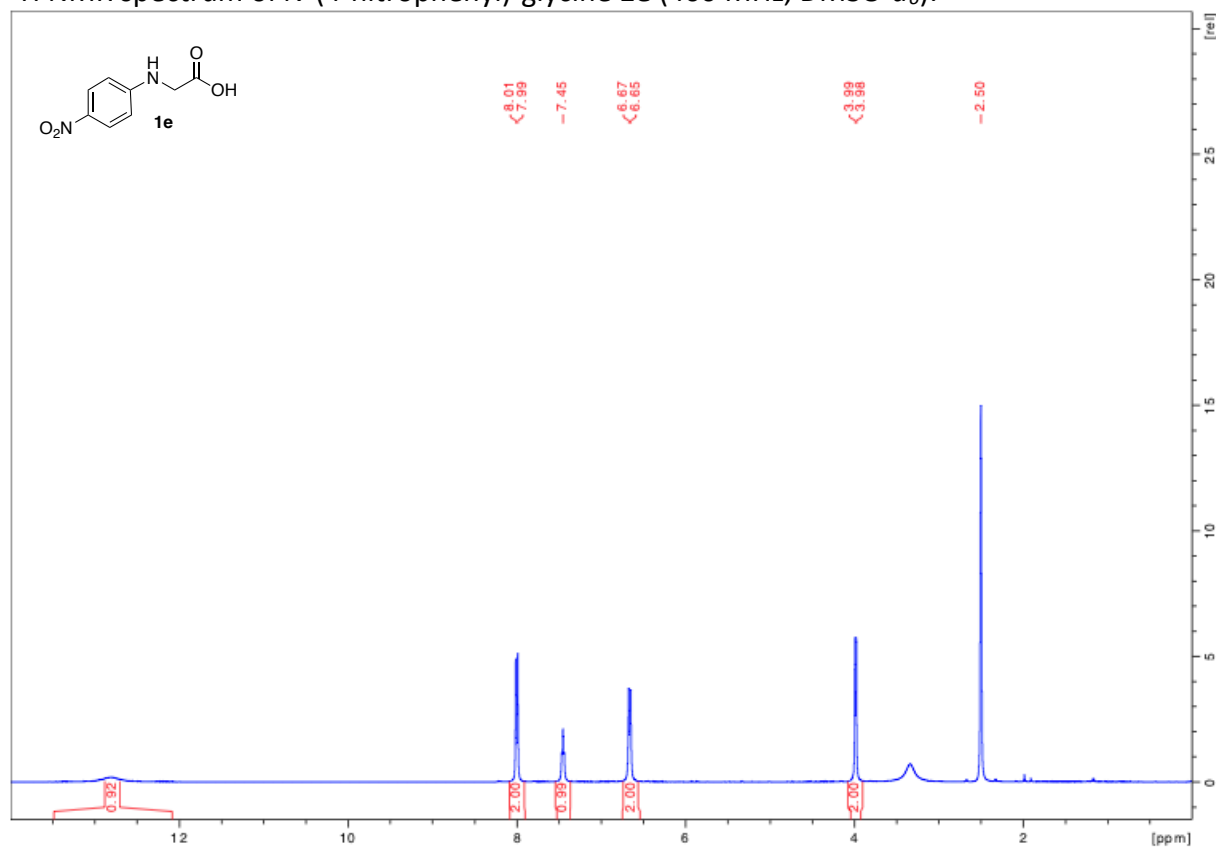
^1H NMR spectrum of *N*-(4-bromophenyl)-glycine **1d** (300 MHz, DMSO- d_6):



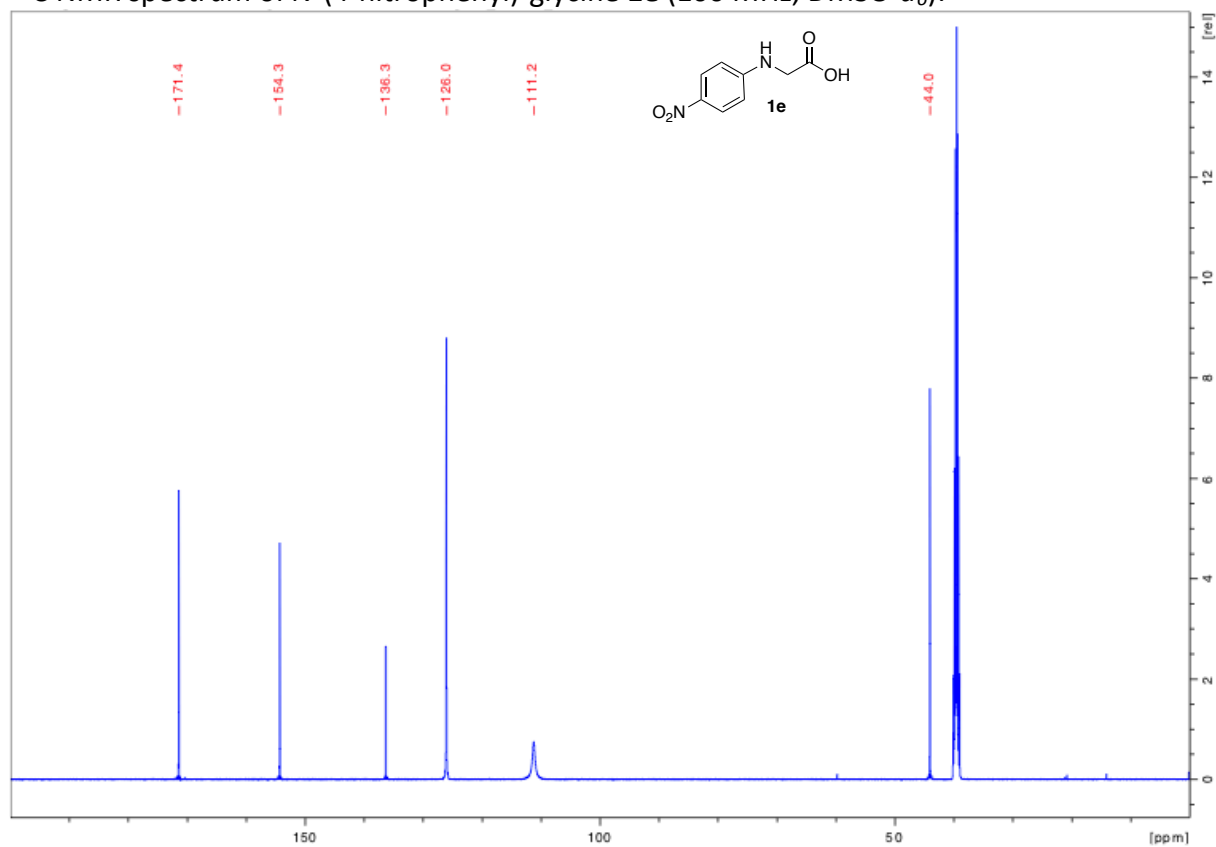
^{13}C NMR spectrum of *N*-(4-bromophenyl)-glycine **1d** (100 MHz, DMSO- d_6):



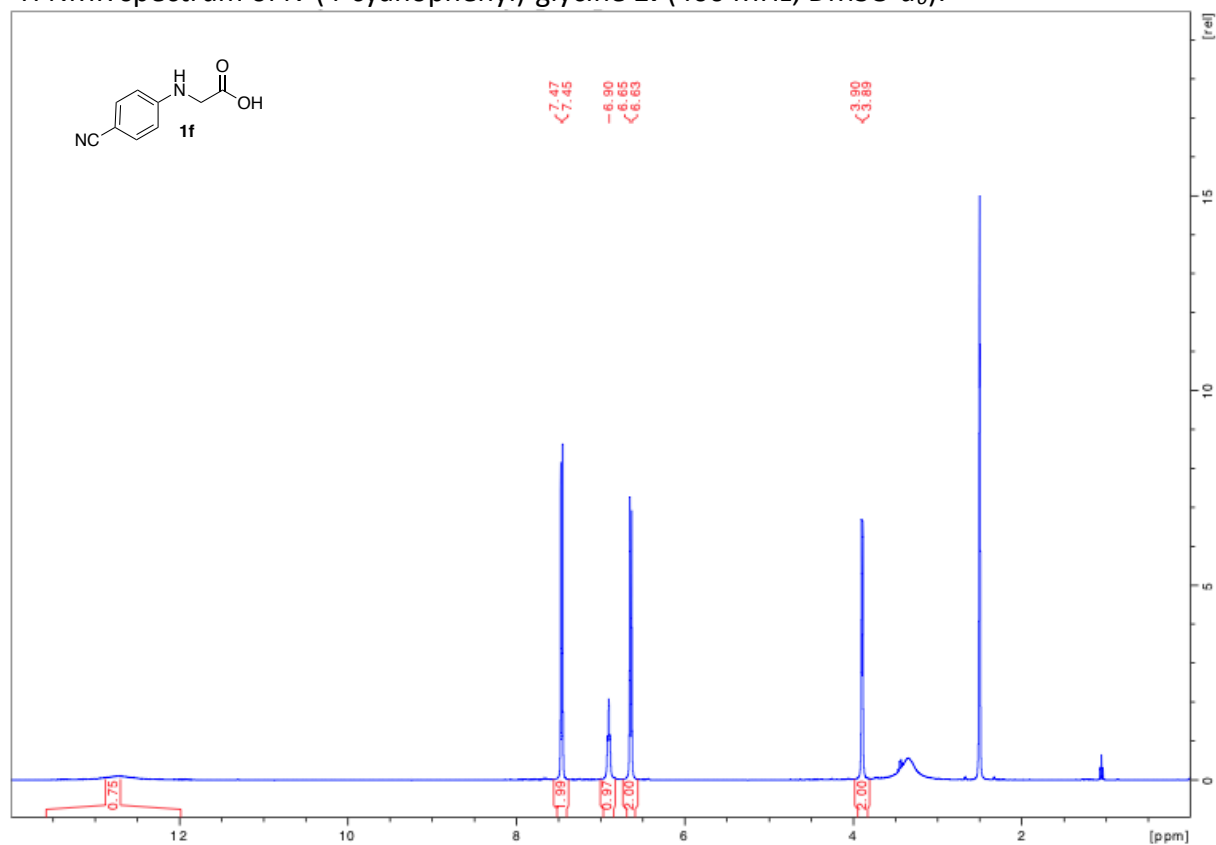
^1H NMR spectrum of *N*-(4-nitrophenyl)-glycine **1e** (400 MHz, DMSO- d_6):



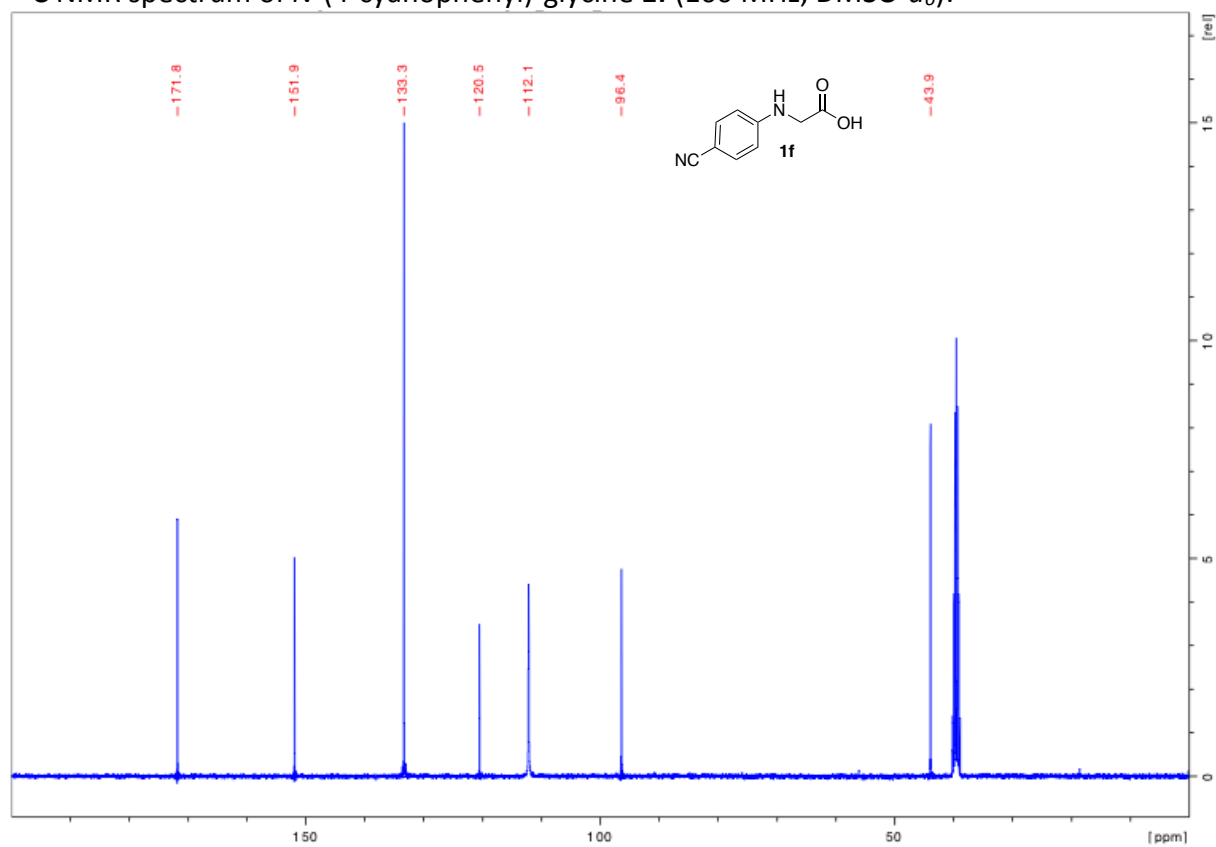
^{13}C NMR spectrum of *N*-(4-nitrophenyl)-glycine **1e** (100 MHz, DMSO- d_6):



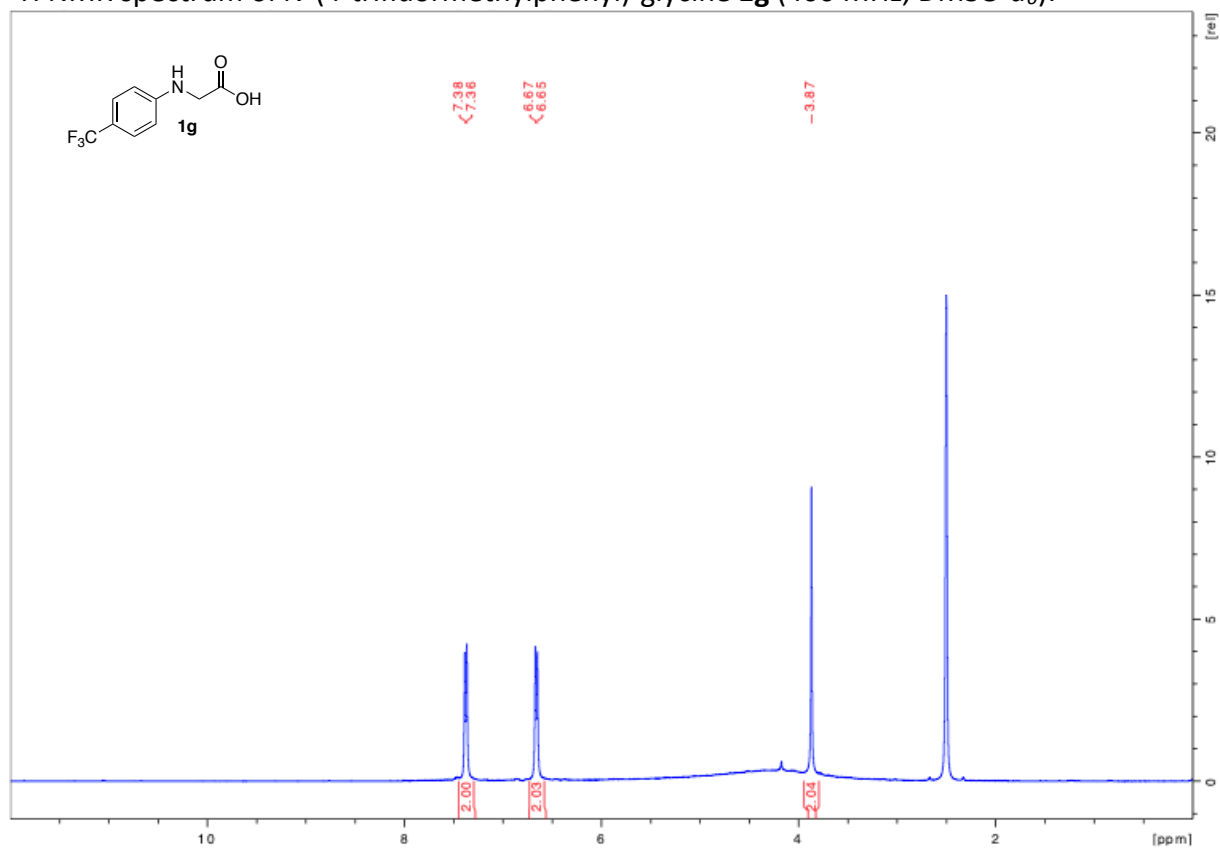
^1H NMR spectrum of *N*-(4-cyanophenyl)-glycine **1f** (400 MHz, DMSO- d_6):



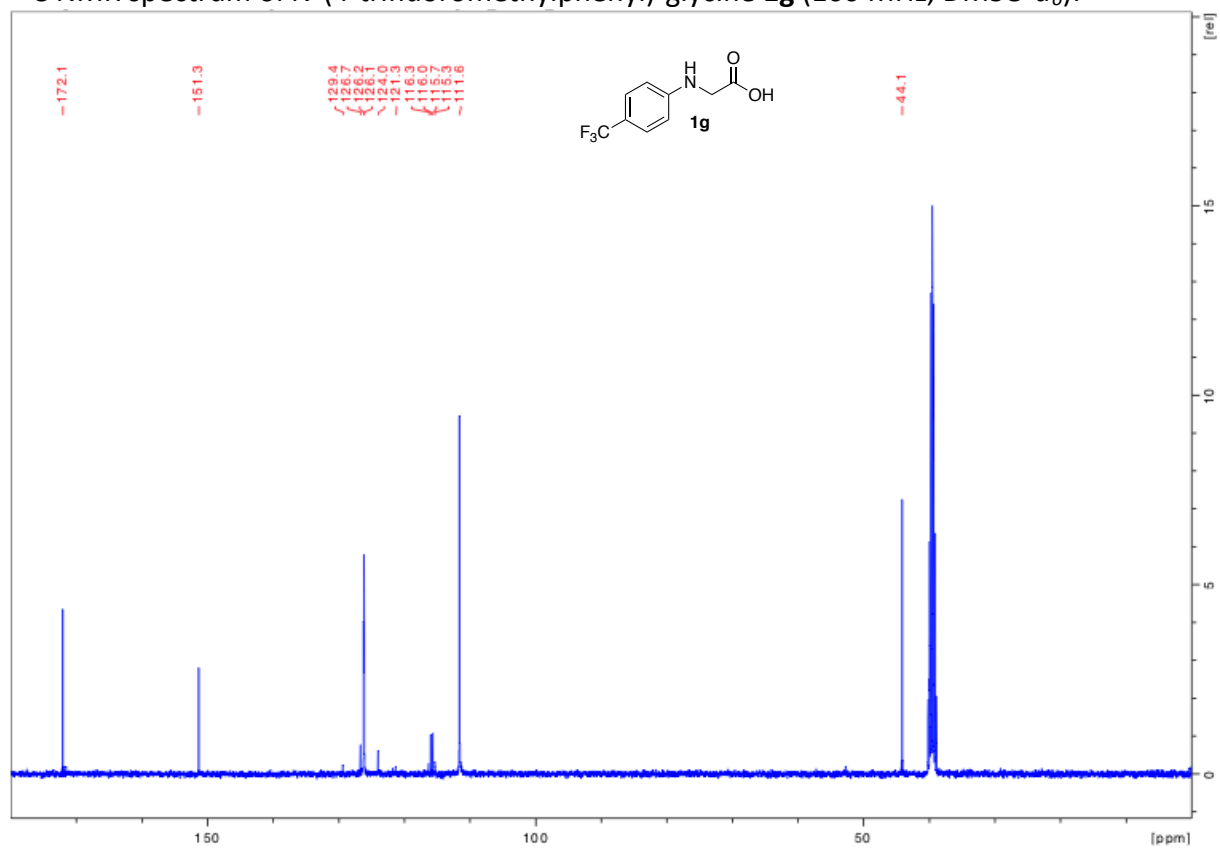
^{13}C NMR spectrum of *N*-(4-cyanophenyl)-glycine **1f** (100 MHz, DMSO- d_6):



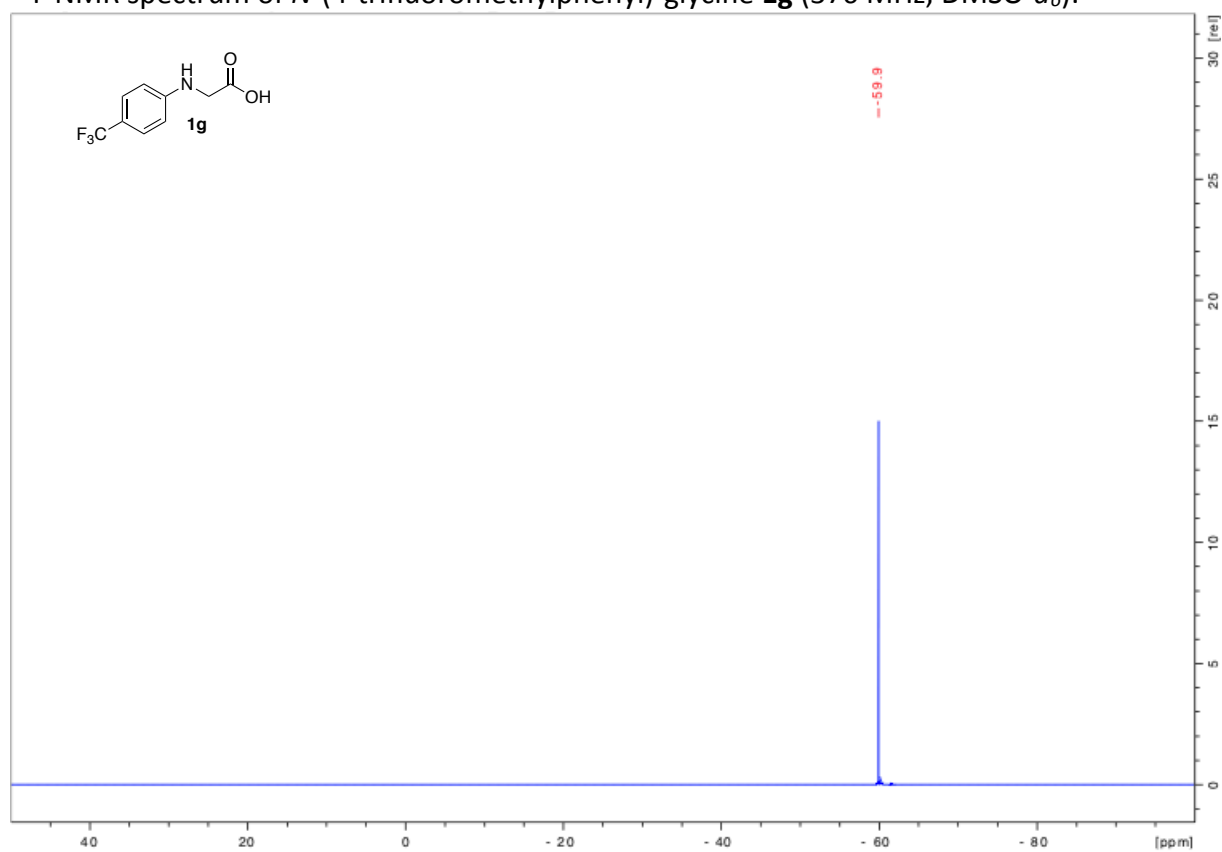
^1H NMR spectrum of *N*-(4-trifluoromethylphenyl)-glycine **1g** (400 MHz, $\text{DMSO}-d_6$):



^{13}C NMR spectrum of *N*-(4-trifluoromethylphenyl)-glycine **1g** (100 MHz, $\text{DMSO}-d_6$):



^{19}F NMR spectrum of *N*-(4-trifluoromethylphenyl)-glycine **1g** (376 MHz, $\text{DMSO}-d_6$):



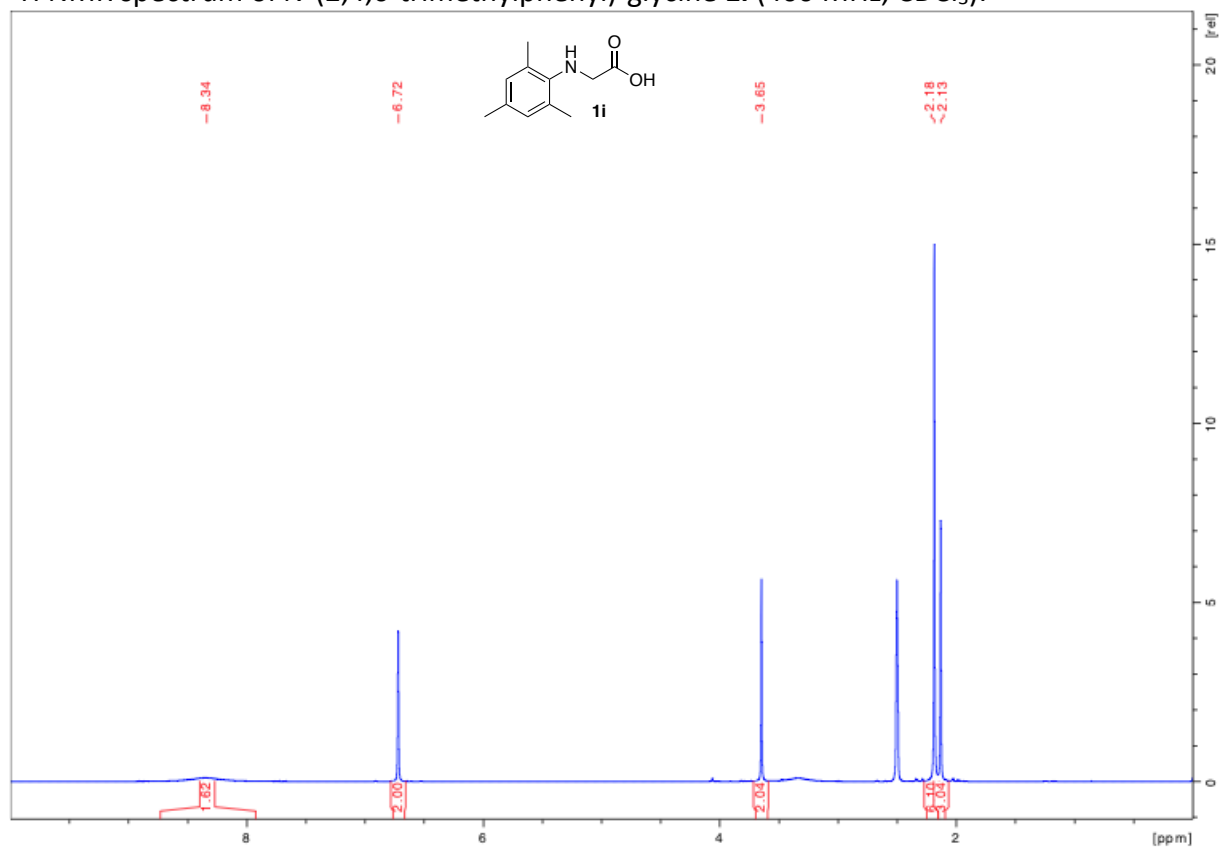
BrC1=CC=C(NCC(=O)O)C=C1 **1h**

11.50 (broad s, 1H, COOH)
 7.05 (d, 1H, ArH)
 6.91 (d, 1H, ArH)
 6.89 (d, 1H, ArH)
 6.86 (d, 1H, ArH)
 6.66 (d, 1H, ArH)
 6.56 (d, 1H, ArH)
 0.00 (s, 3H, TMS)

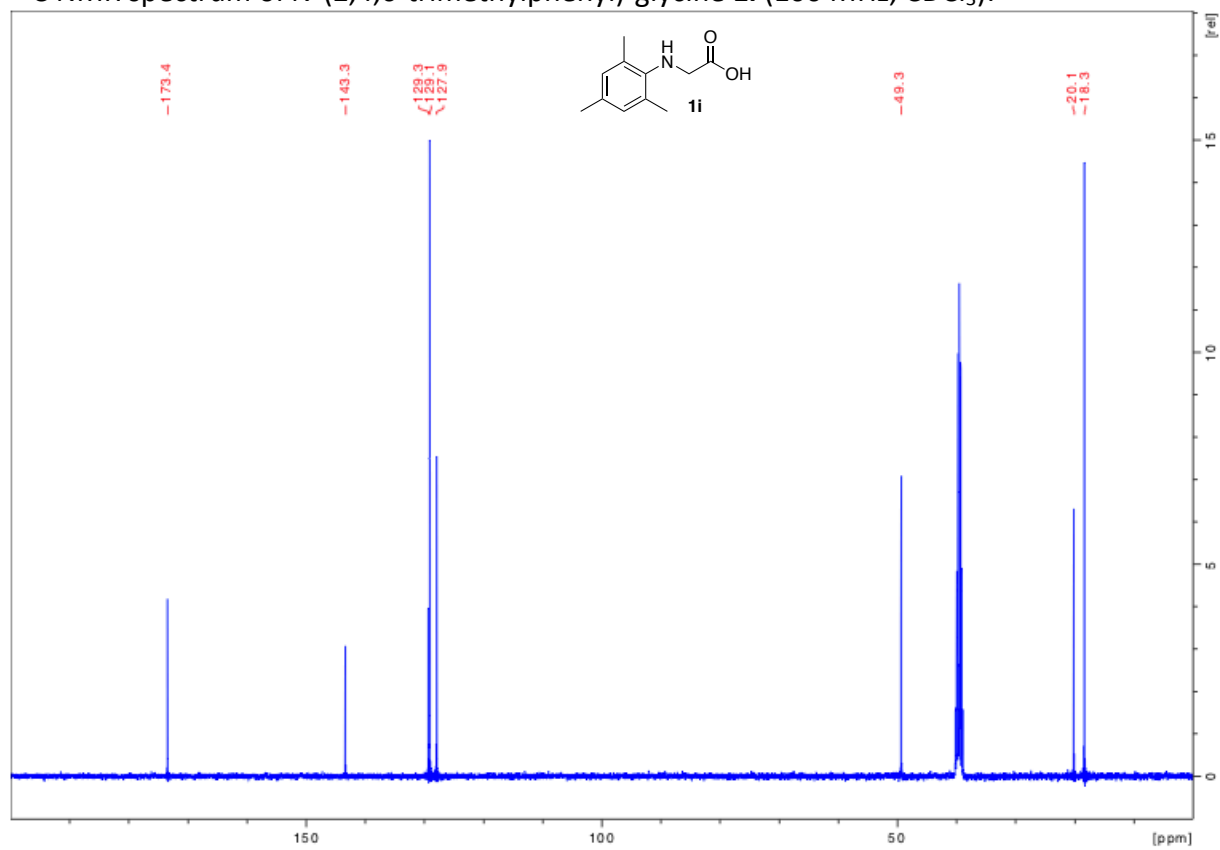
Chemical structure of **1h**: NC(=O)Cc1ccc(Br)cc1

¹³C NMR spectrum (DMSO-d₆) of **1h**. The spectrum shows peaks at the following chemical shifts (ppm): 175.8, 148.0, 130.8, 123.5, 121.6, 115.9, 111.9, 45.4, and -45.4.

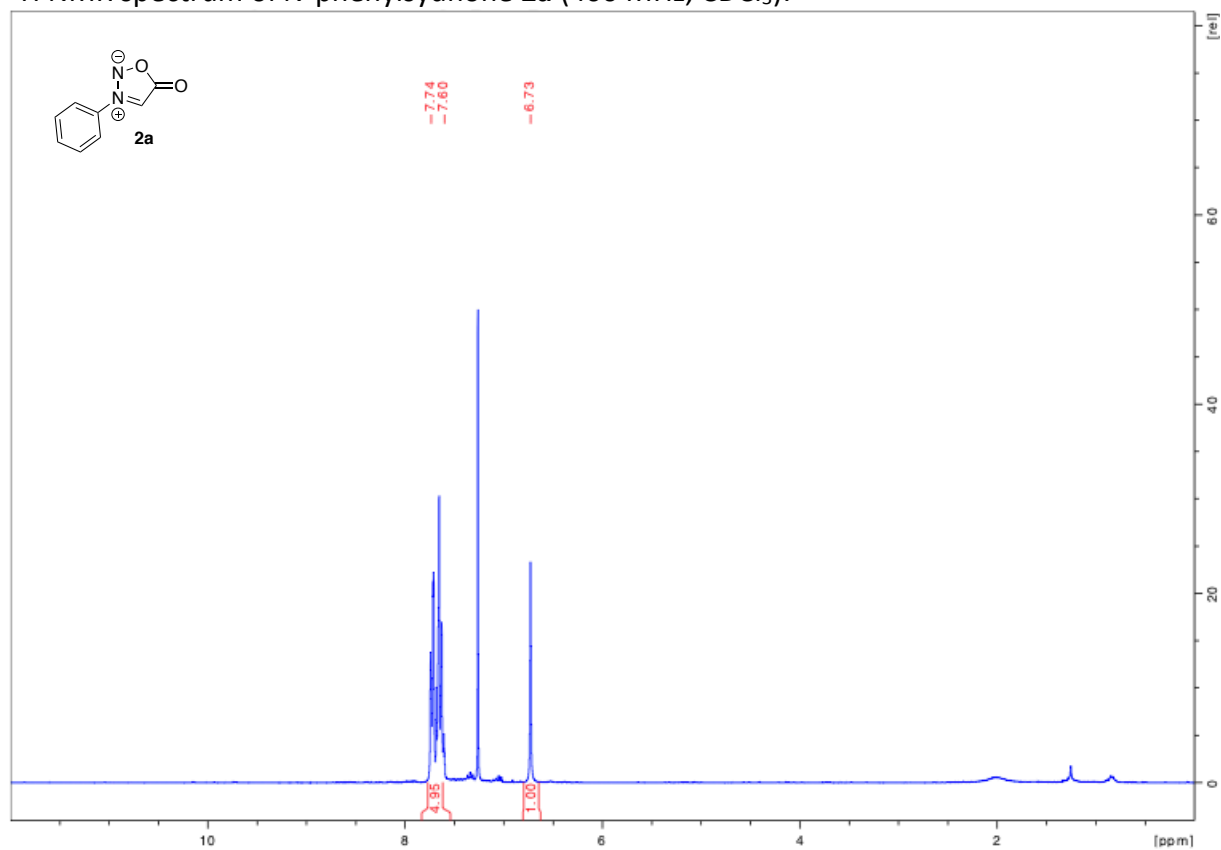
^1H NMR spectrum of *N*-(2,4,6-trimethylphenyl)-glycine **1i** (400 MHz, CDCl_3):



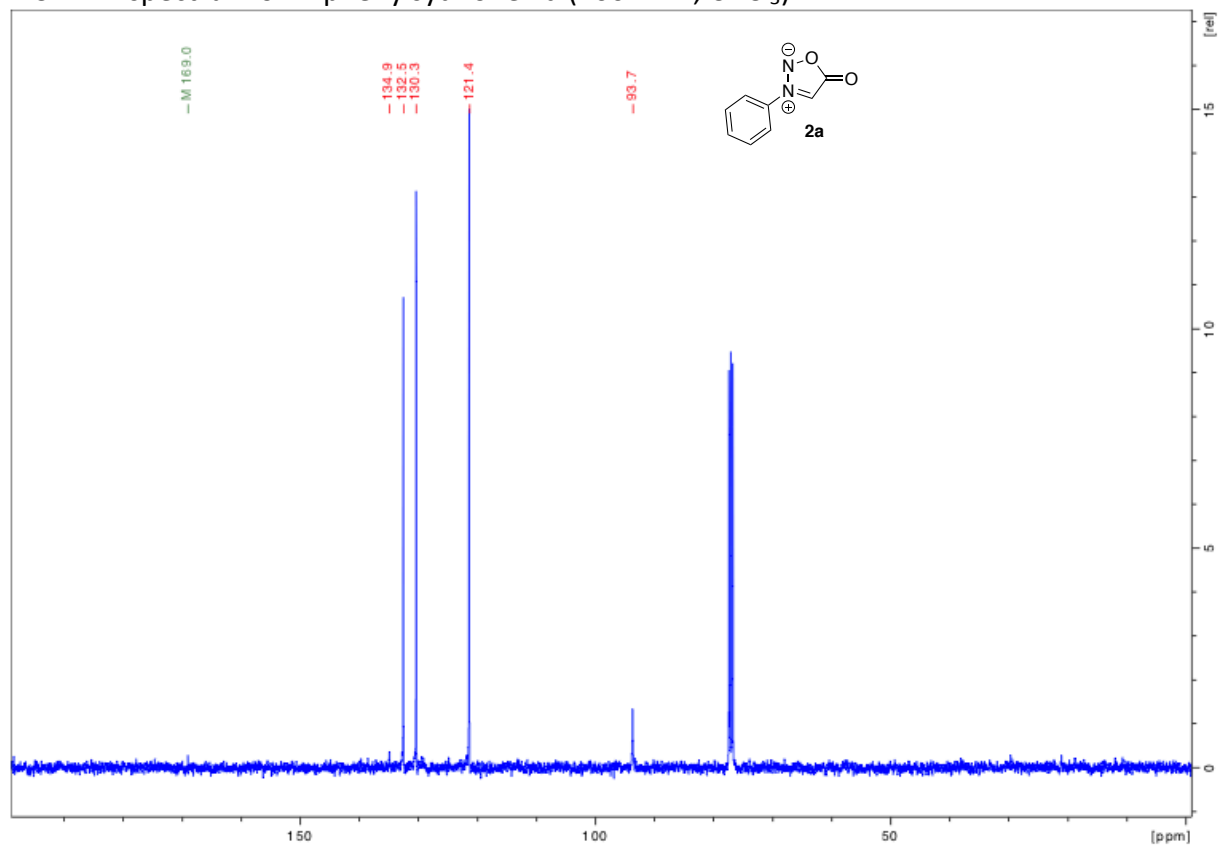
^{13}C NMR spectrum of *N*-(2,4,6-trimethylphenyl)-glycine **1i** (100 MHz, CDCl_3):



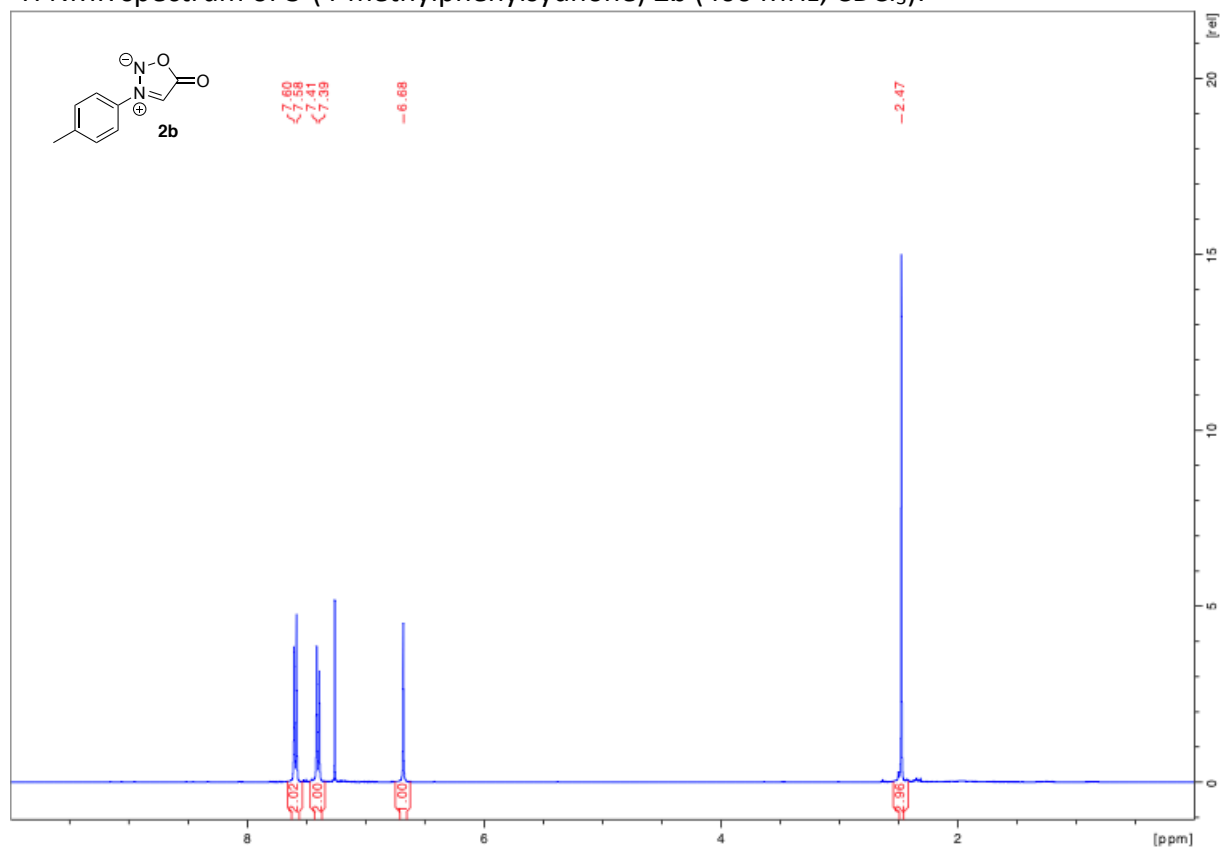
^1H NMR spectrum of *N*-phenylsydnone **2a** (400 MHz, CDCl_3):



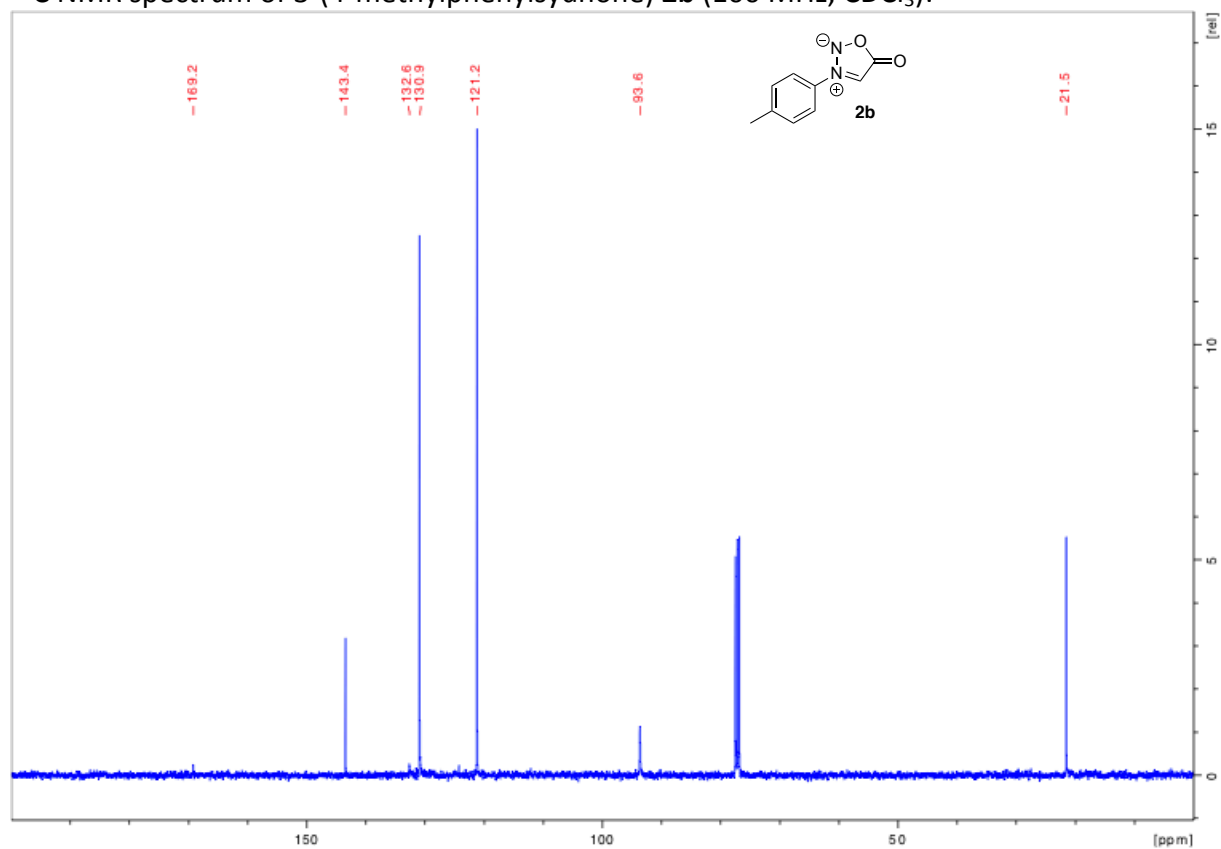
^{13}C NMR spectrum of *N*-phenylsydnone **2a** (100 MHz, CDCl_3):



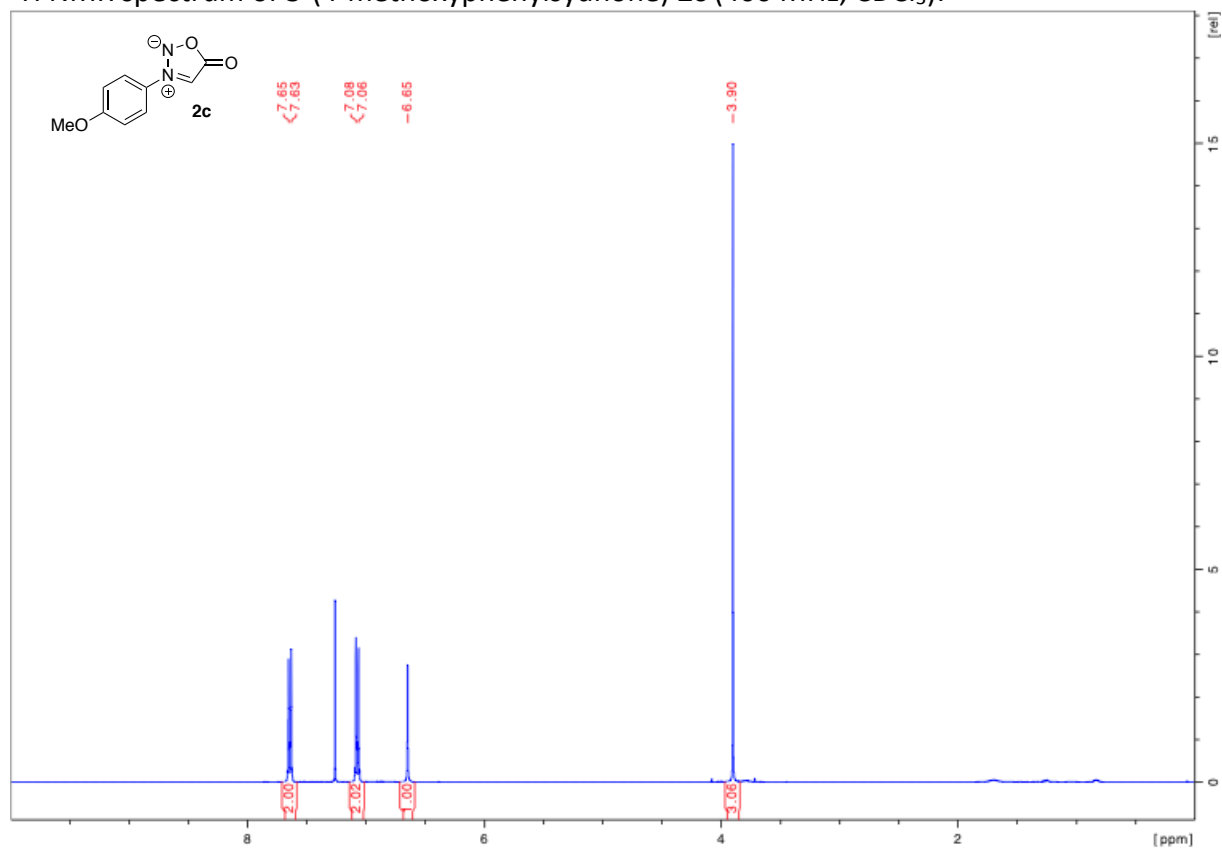
^1H NMR spectrum of 3-(4-methylphenylsydnone) **2b** (400 MHz, CDCl_3):



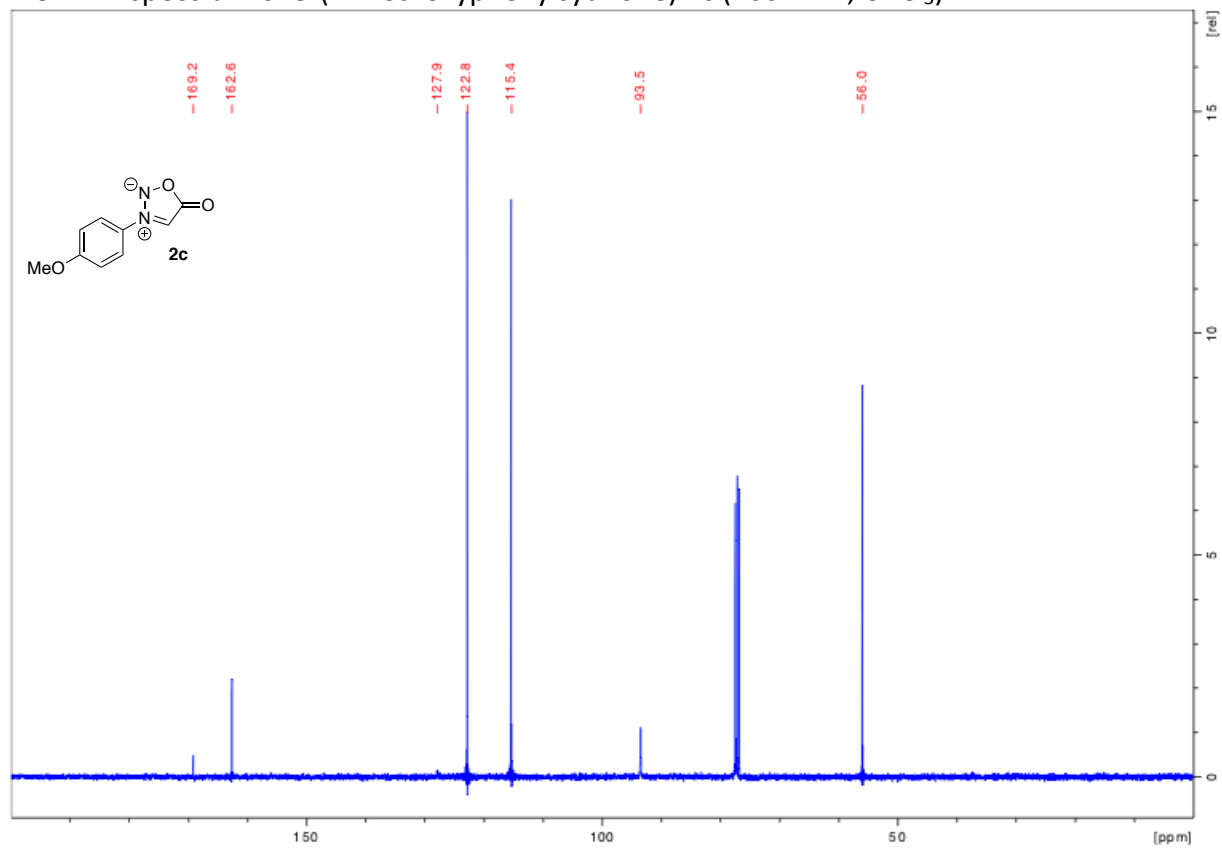
^{13}C NMR spectrum of 3-(4-methylphenylsydnone) **2b** (100 MHz, CDCl_3):



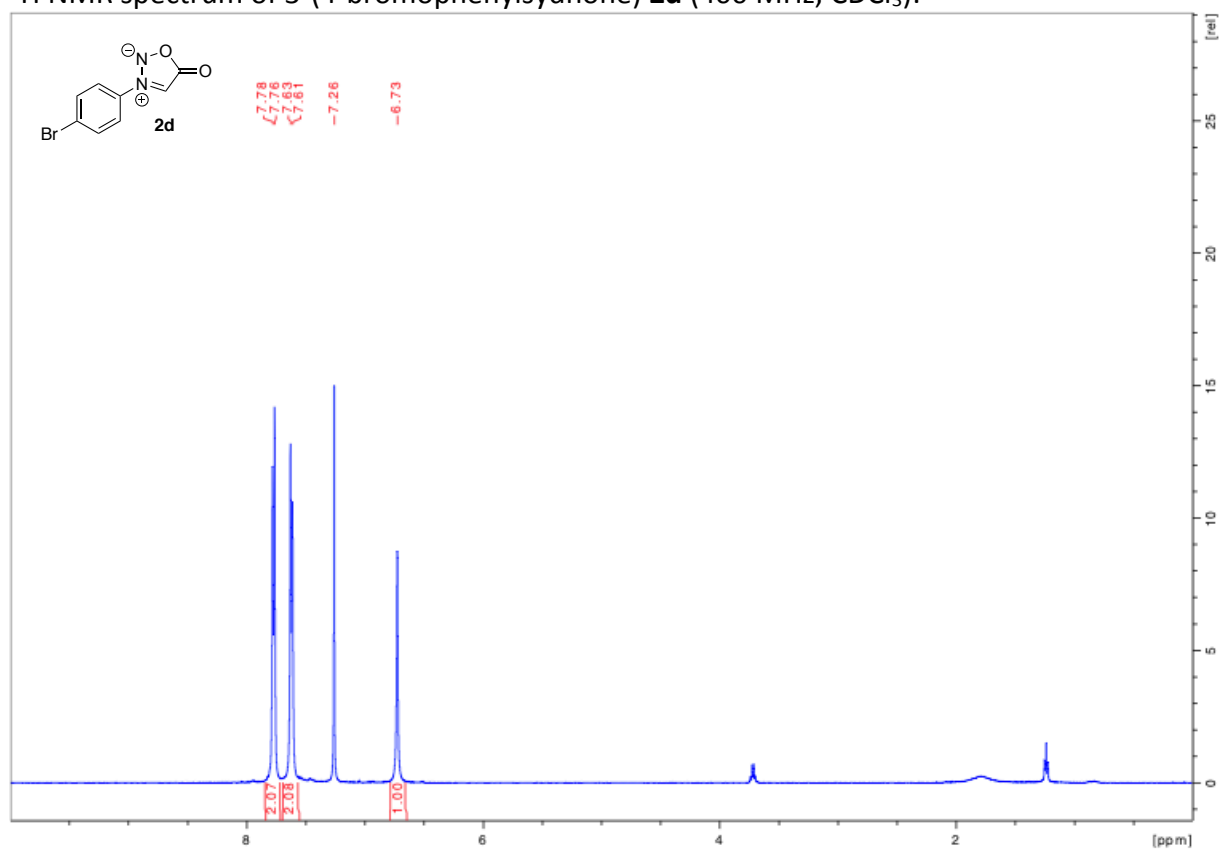
^1H NMR spectrum of 3-(4-methoxyphenylsydnone) **2c** (400 MHz, CDCl_3):



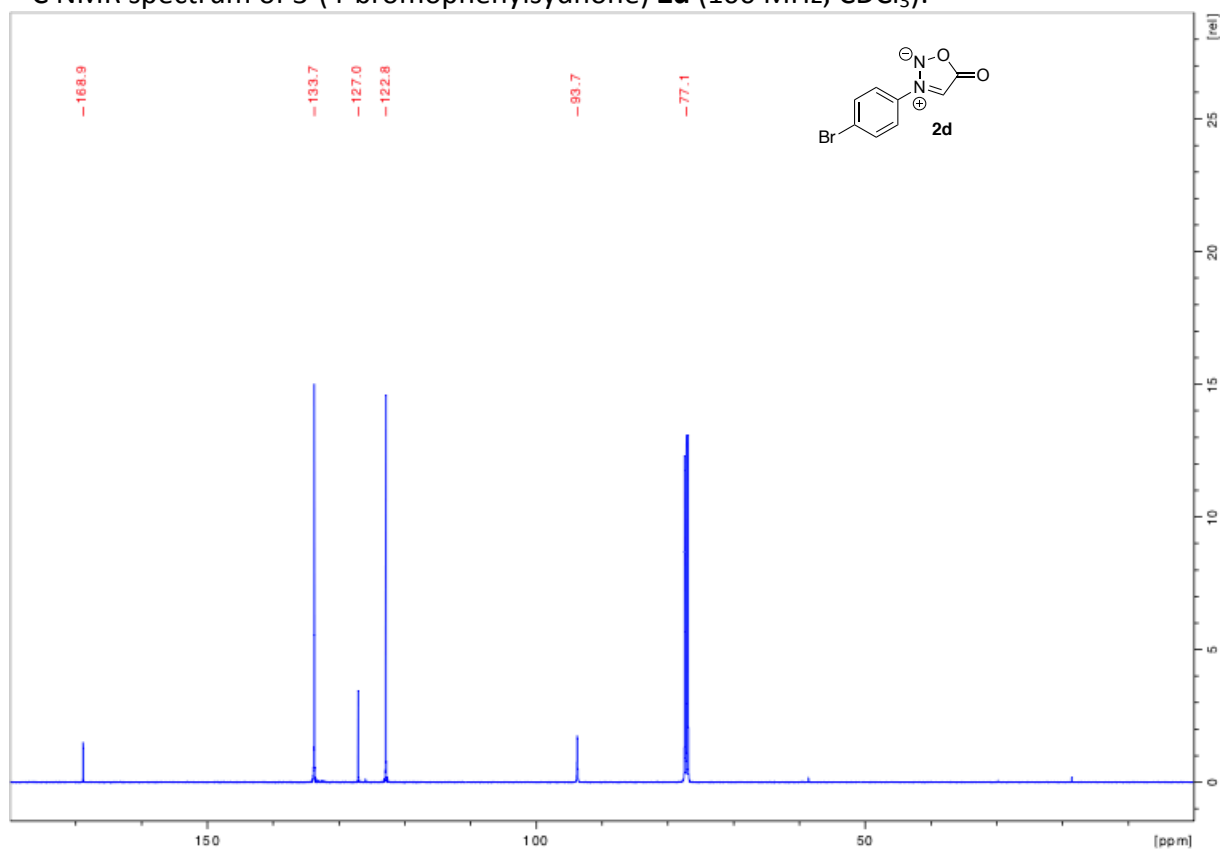
^{13}C NMR spectrum of 3-(4-methoxyphenylsydnone) **2c** (100 MHz, CDCl_3):



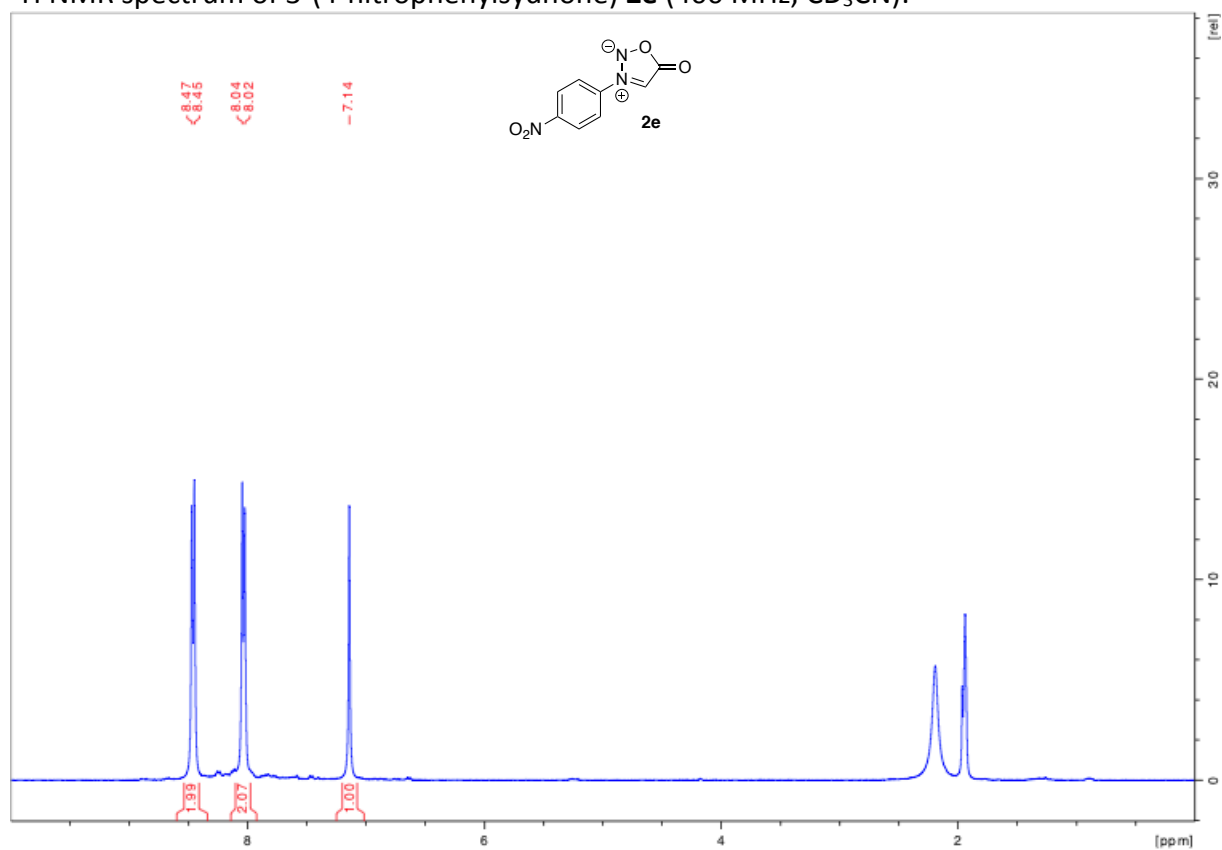
^1H NMR spectrum of 3-(4-bromophenylsydnone) **2d** (400 MHz, CDCl_3):



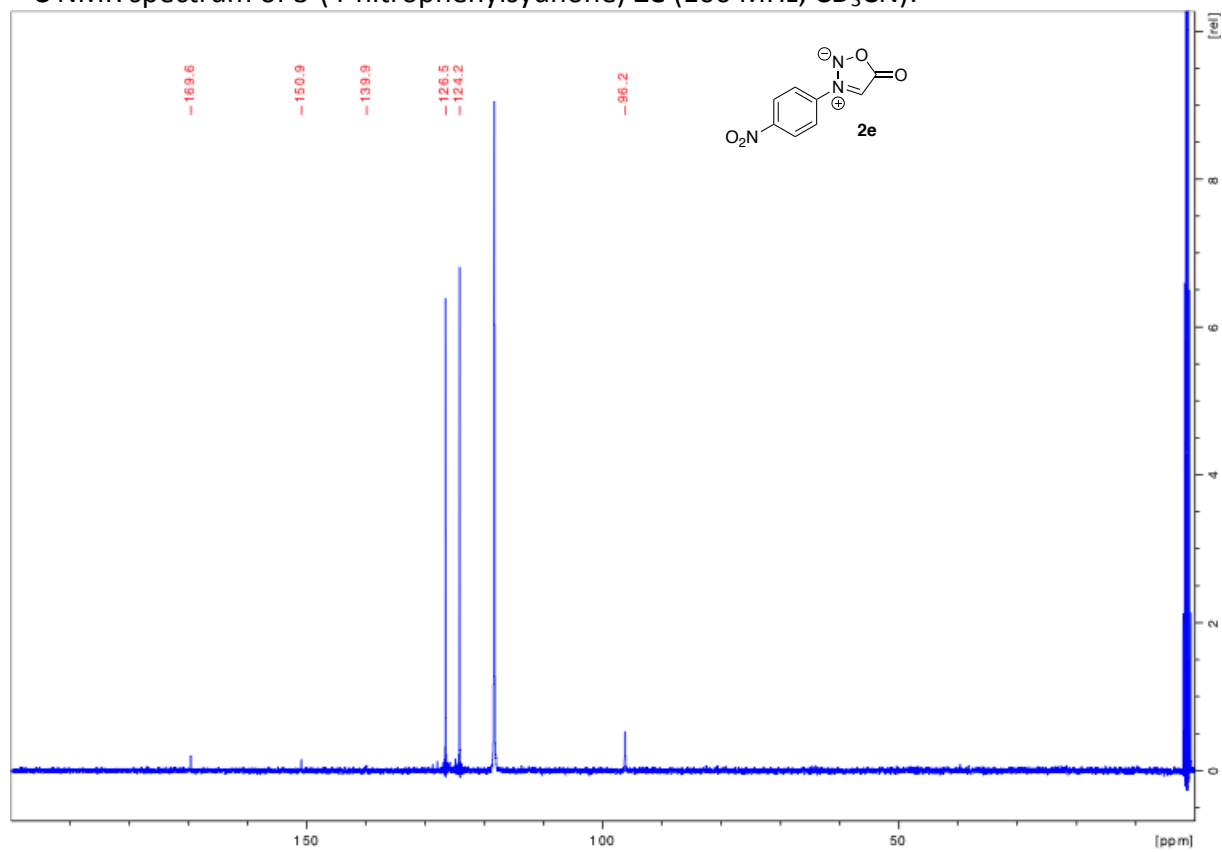
^{13}C NMR spectrum of 3-(4-bromophenylsydnone) **2d** (100 MHz, CDCl_3):



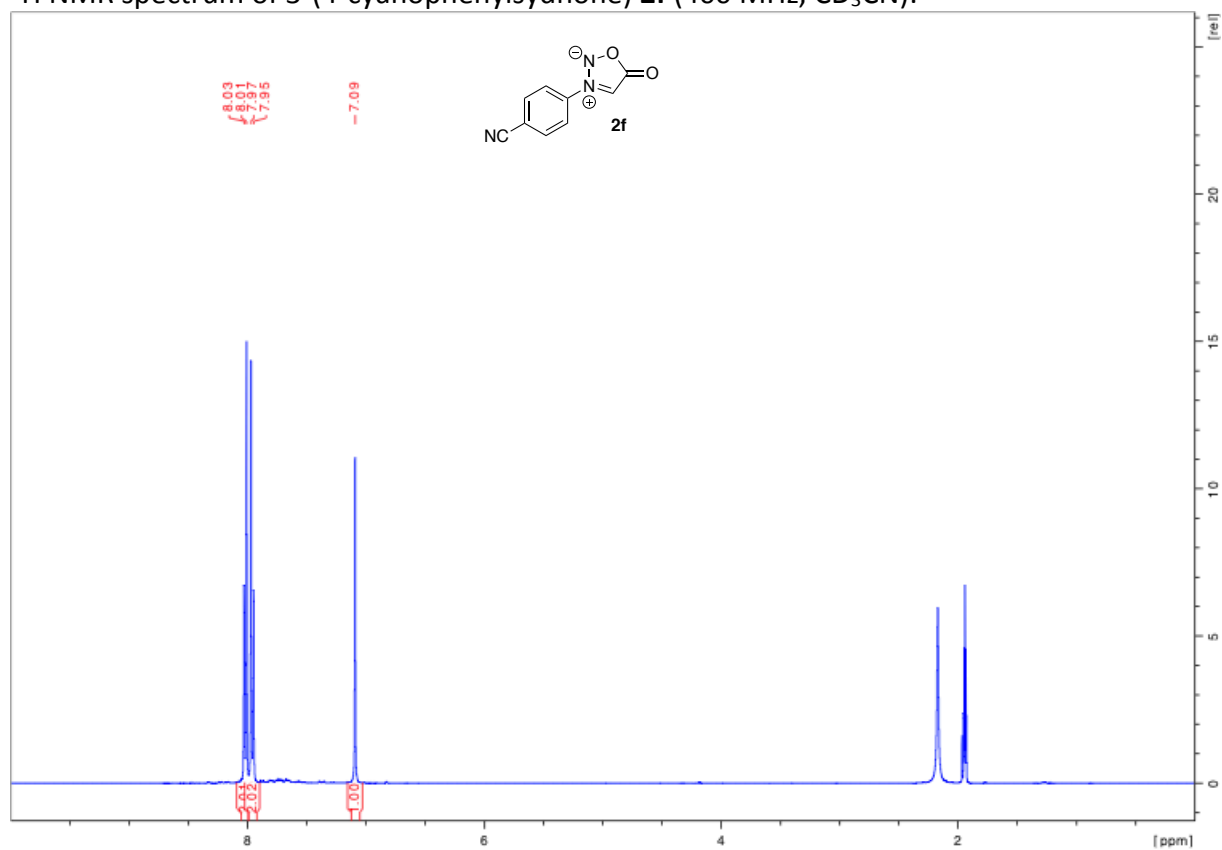
^1H NMR spectrum of 3-(4-nitrophenylsydnone) **2e** (400 MHz, CD_3CN):



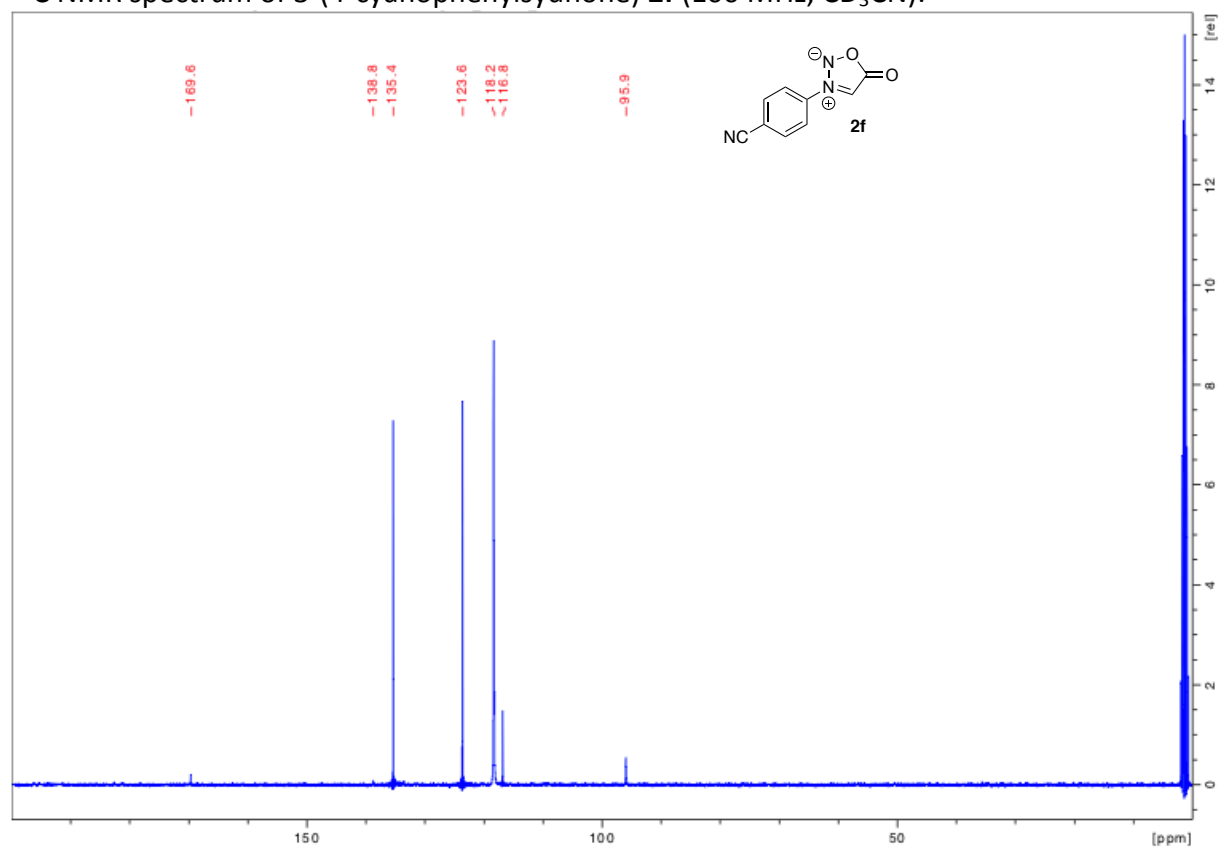
^{13}C NMR spectrum of 3-(4-nitrophenylsydnone) **2e** (100 MHz, CD_3CN):



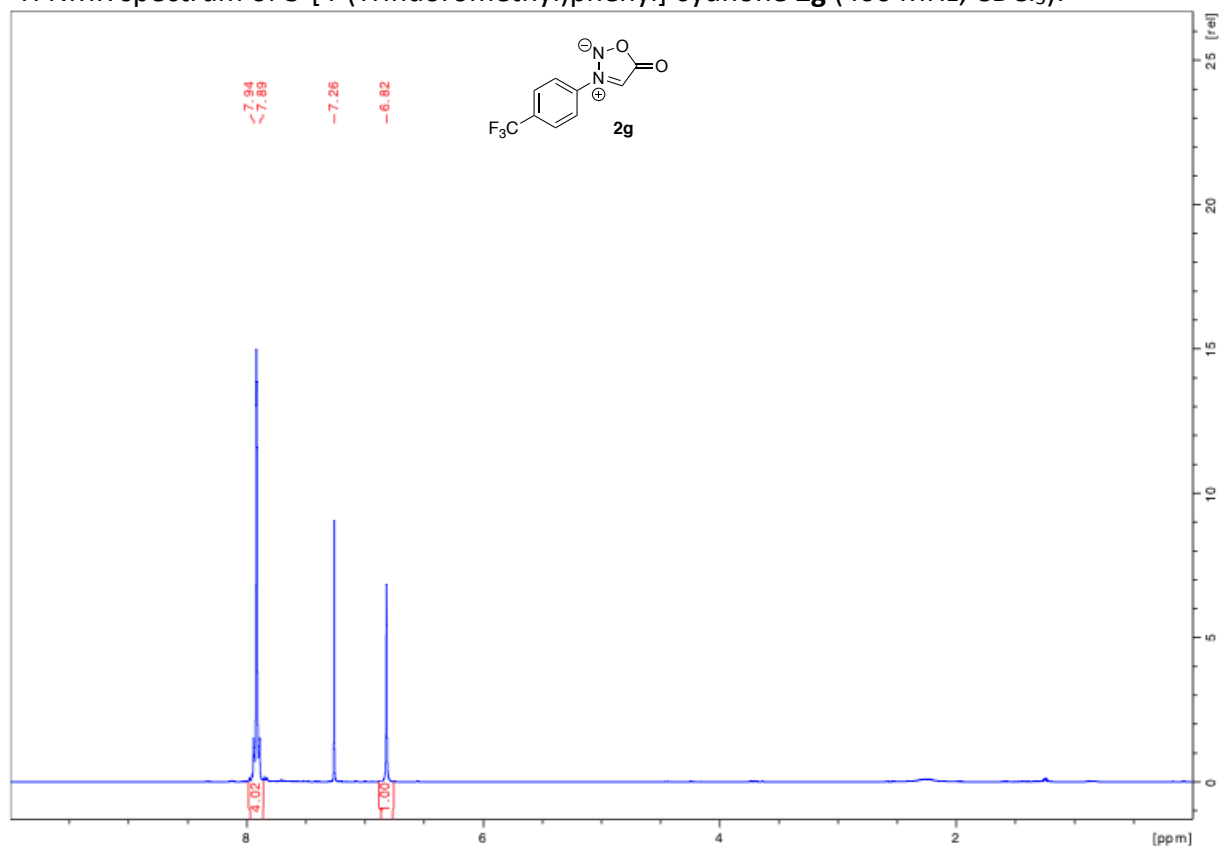
^1H NMR spectrum of 3-(4-cyanophenylsydnone) **2f** (400 MHz, CD_3CN):



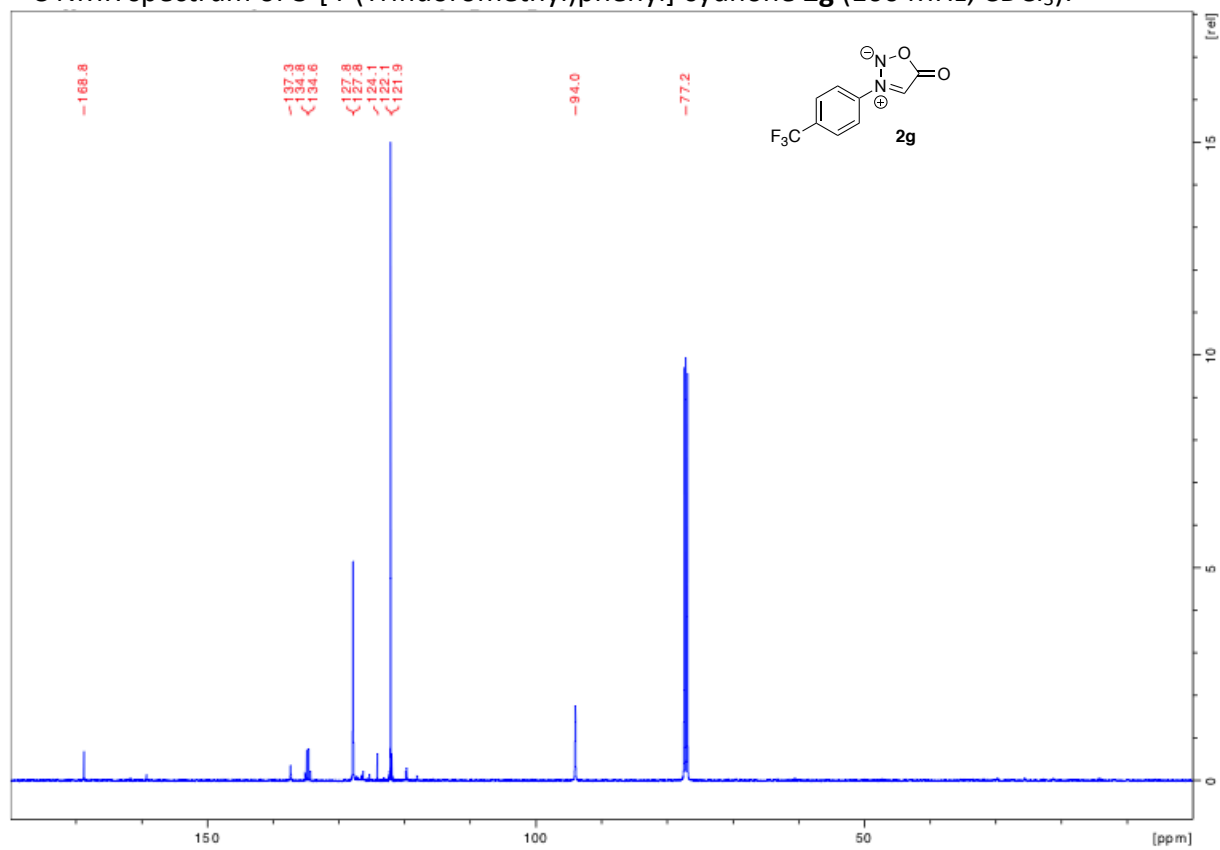
^{13}C NMR spectrum of 3-(4-cyanophenylsydnone) **2f** (100 MHz, CD_3CN):



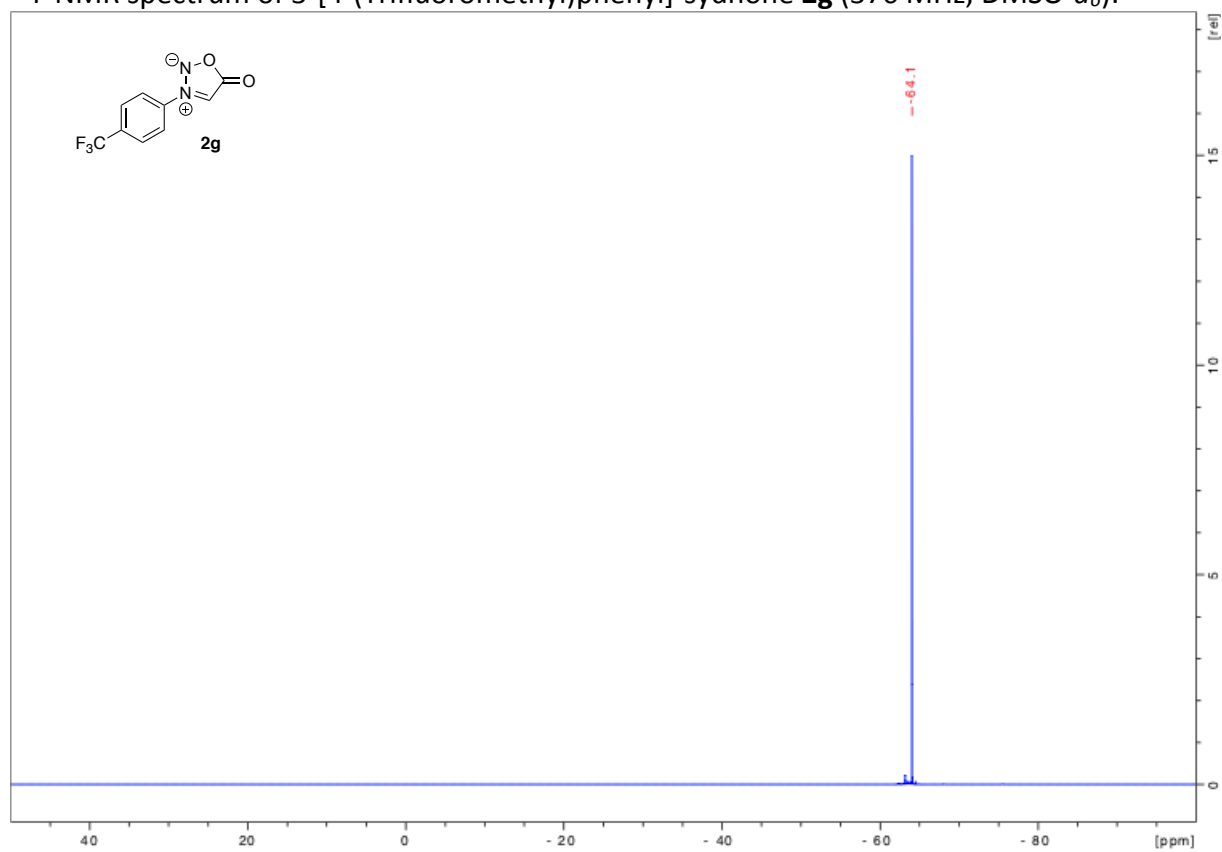
^1H NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (400 MHz, CDCl_3):



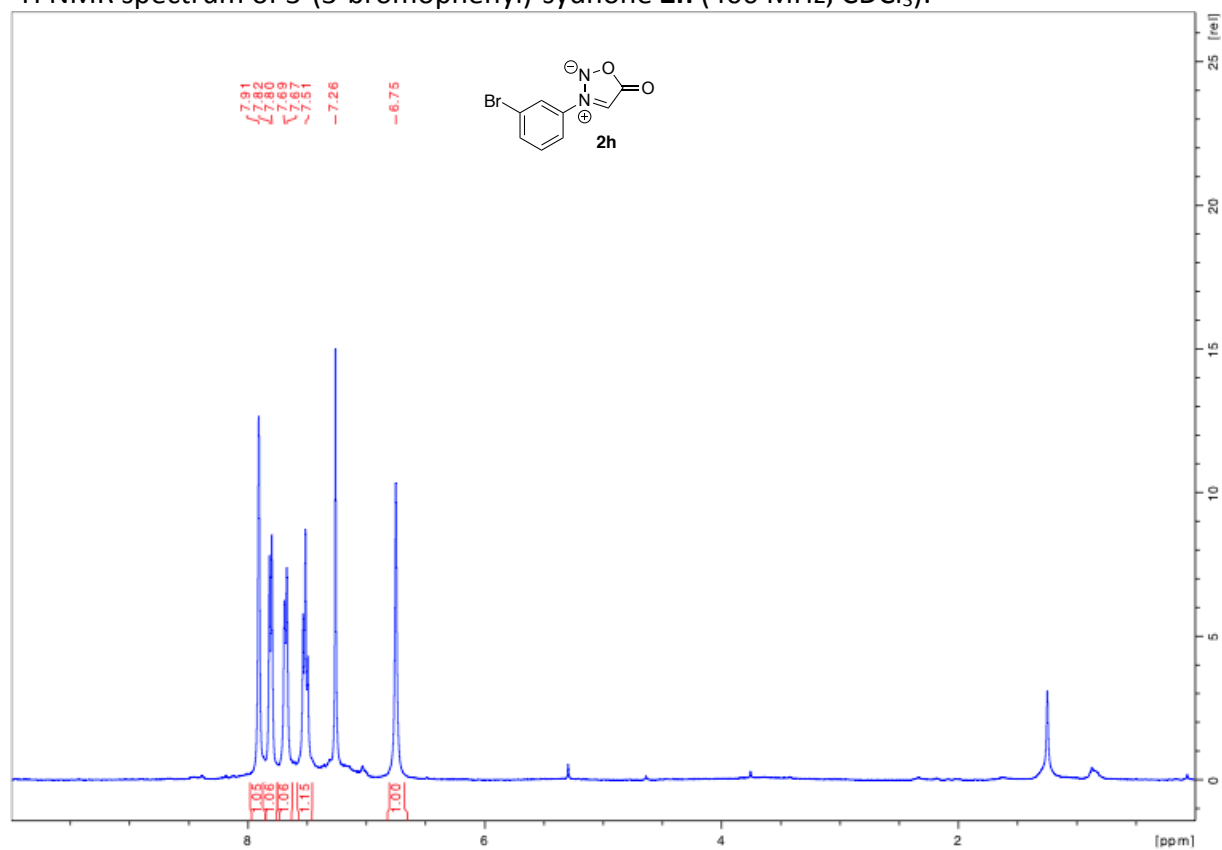
^{13}C NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (100 MHz, CDCl_3):



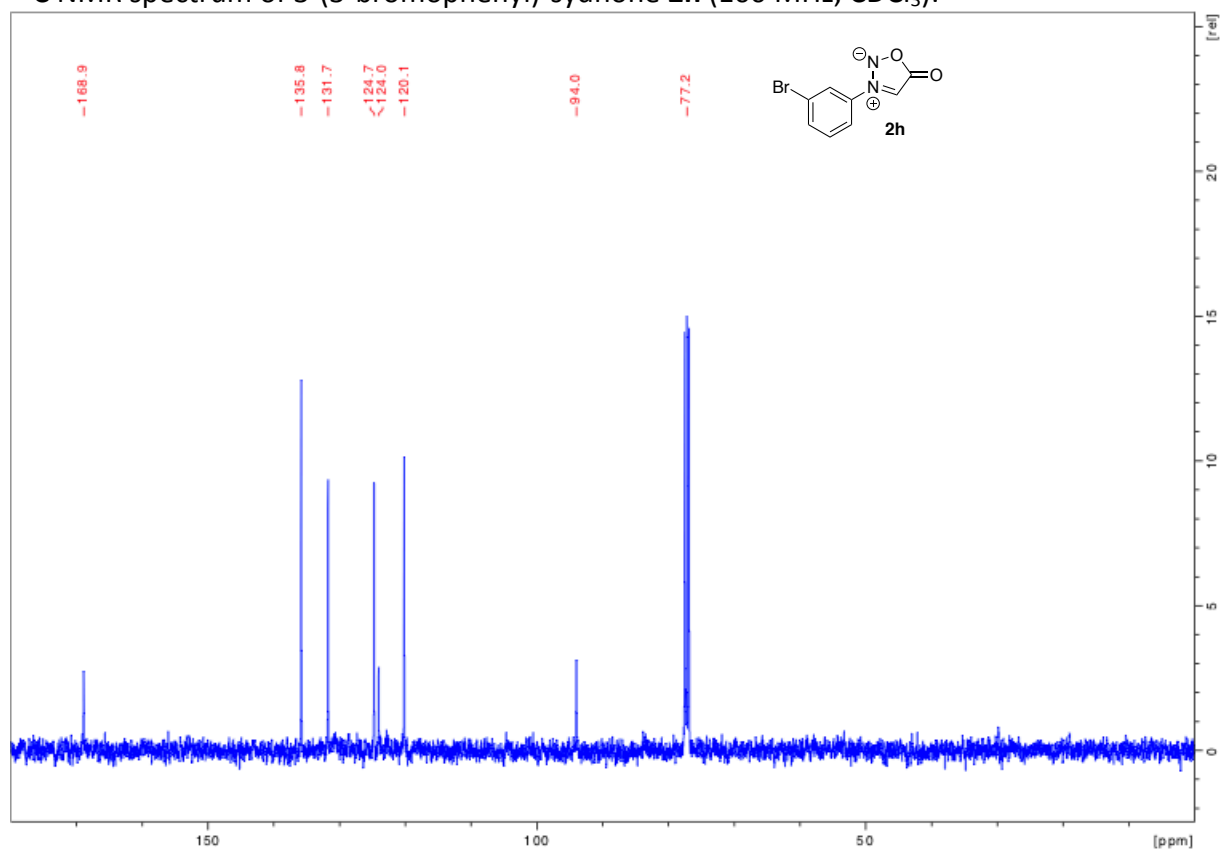
^{19}F NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (376 MHz, $\text{DMSO-}d_6$):



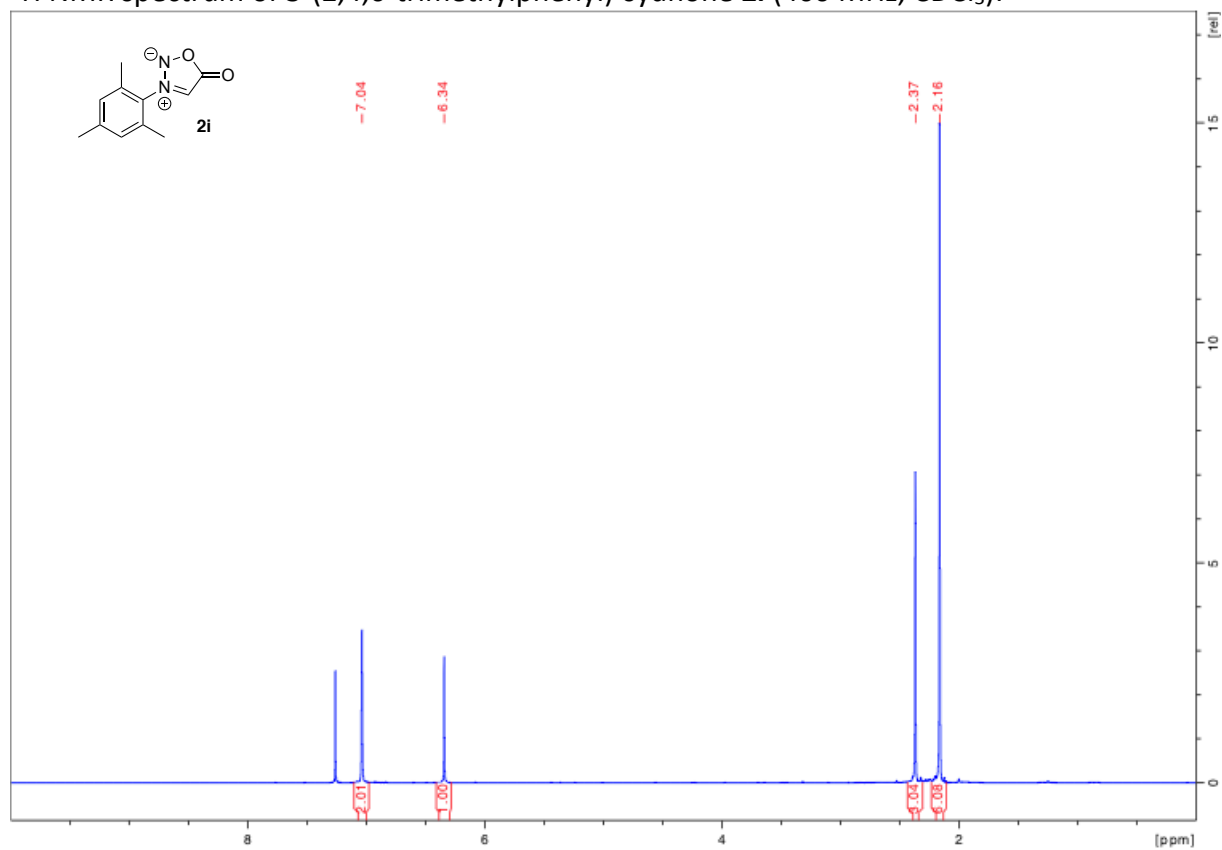
^1H NMR spectrum of 3-(3-bromophenyl)-sydnone **2h** (400 MHz, CDCl_3):



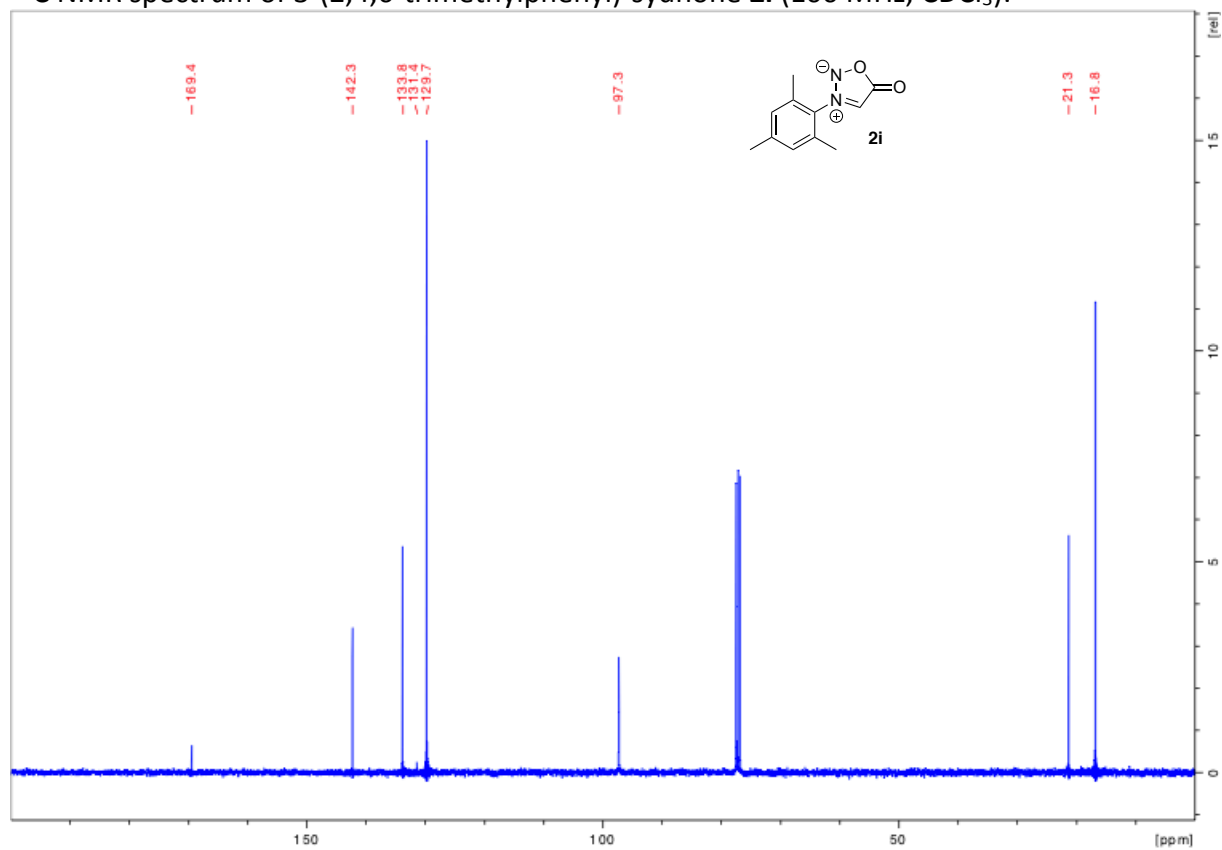
^{13}C NMR spectrum of 3-(3-bromophenyl)-sydnone **2h** (100 MHz, CDCl_3):



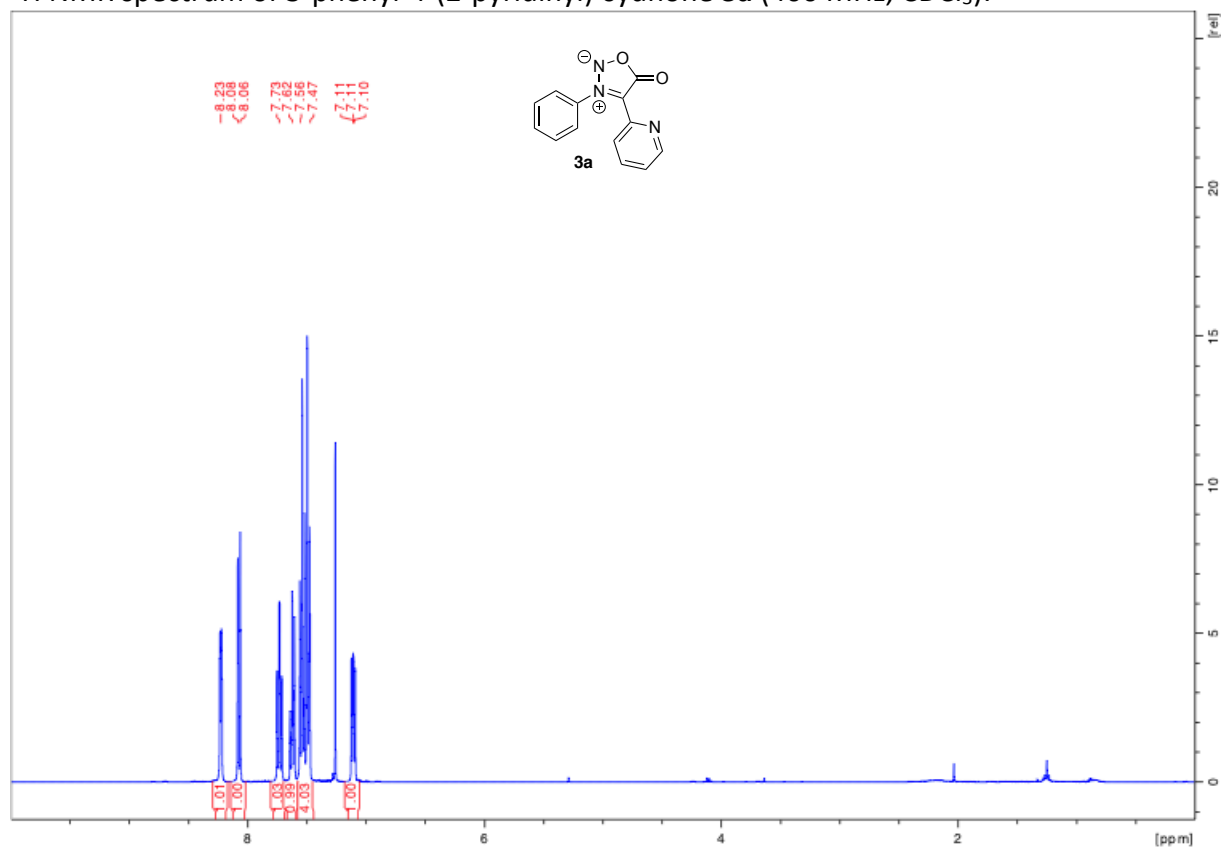
^1H NMR spectrum of 3-(2,4,6-trimethylphenyl)-sydnone **2i** (400 MHz, CDCl_3):



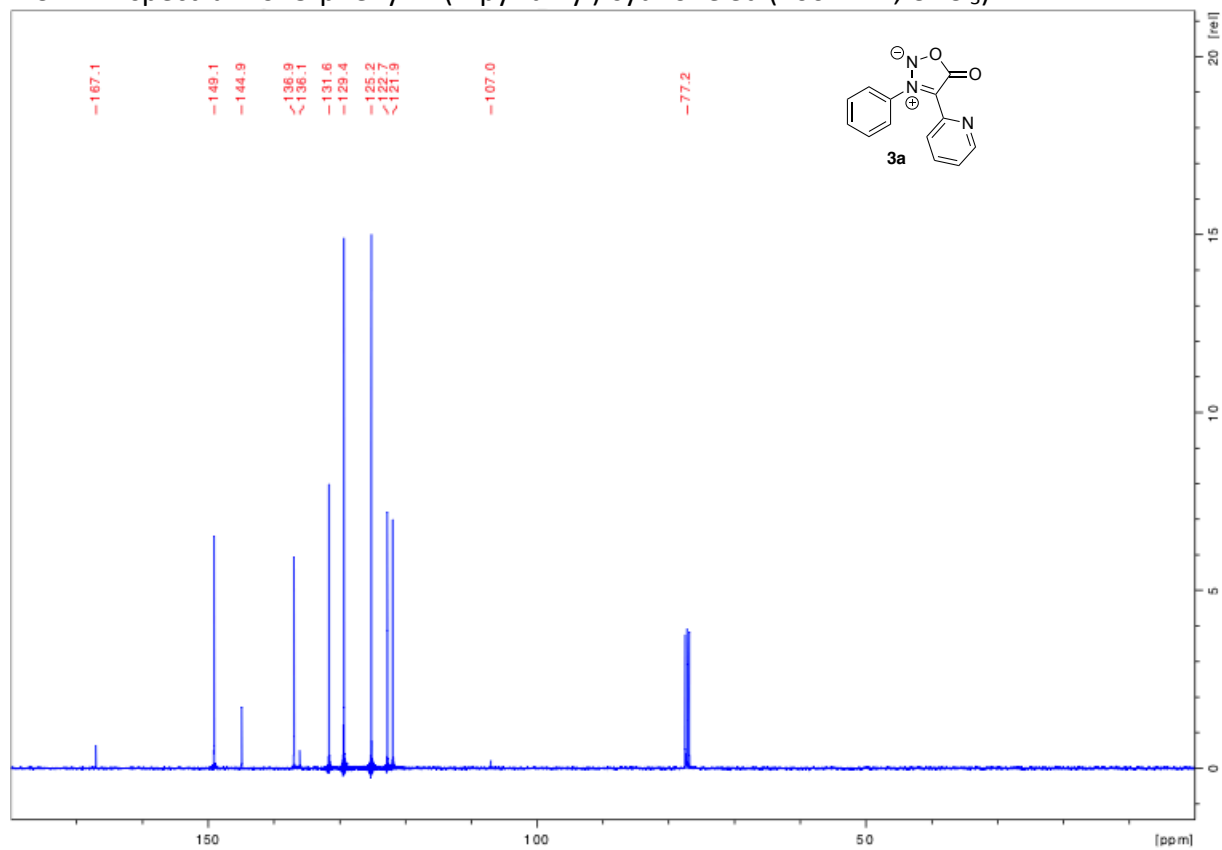
^{13}C NMR spectrum of 3-(2,4,6-trimethylphenyl)-sydnone **2i** (100 MHz, CDCl_3):



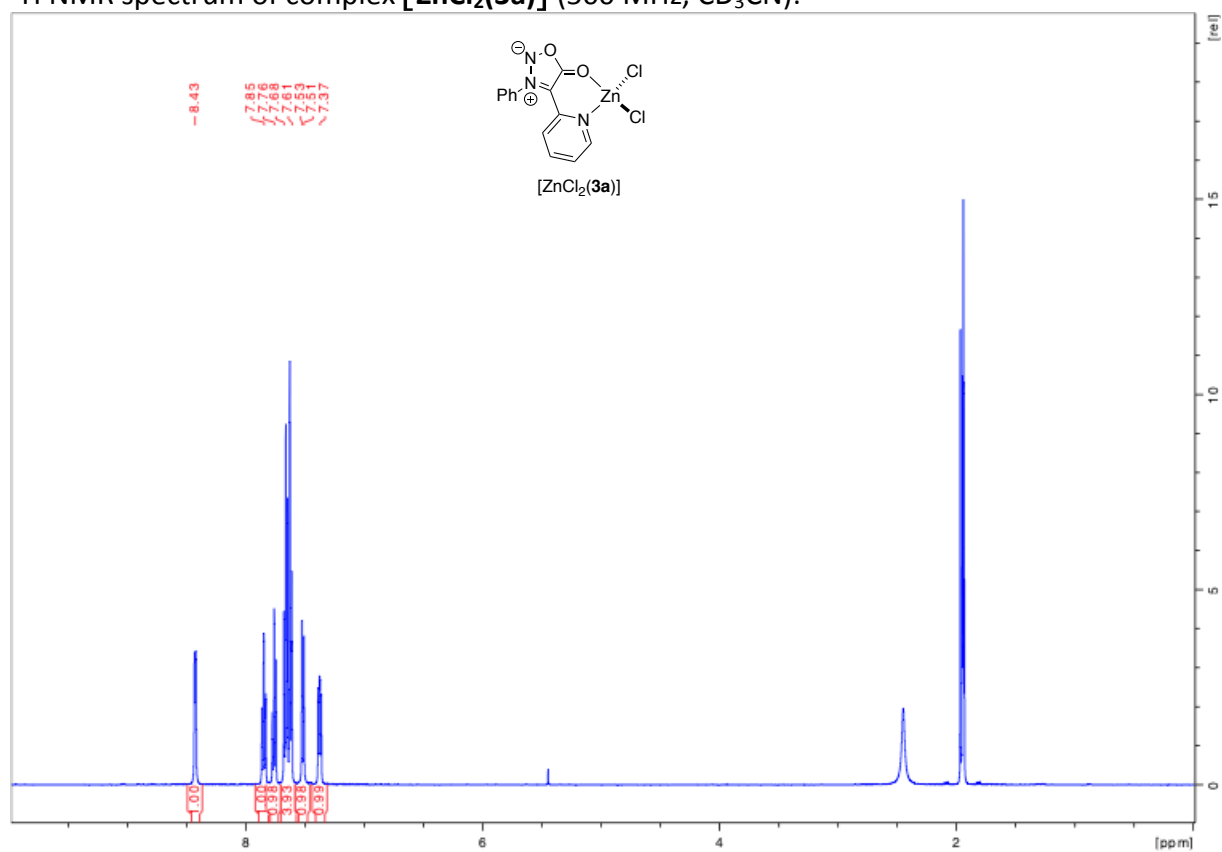
^1H NMR spectrum of 3-phenyl-4-(2-pyridinyl)-sydnone **3a** (400 MHz, CDCl_3):



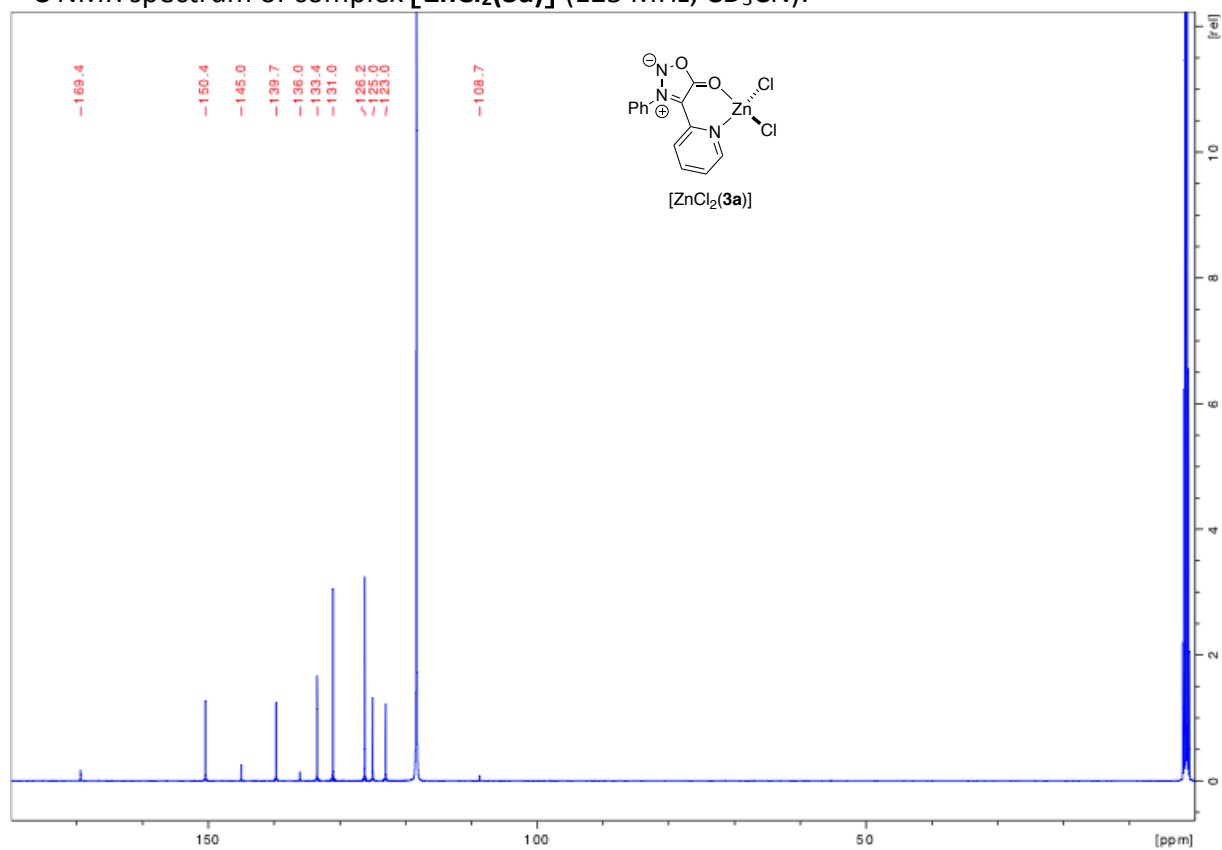
^{13}C NMR spectrum of 3-phenyl-4-(2-pyridinyl)-sydnone **3a** (100 MHz, CDCl_3):



^1H NMR spectrum of complex $[\text{ZnCl}_2(\mathbf{3a})]$ (500 MHz, CD_3CN):

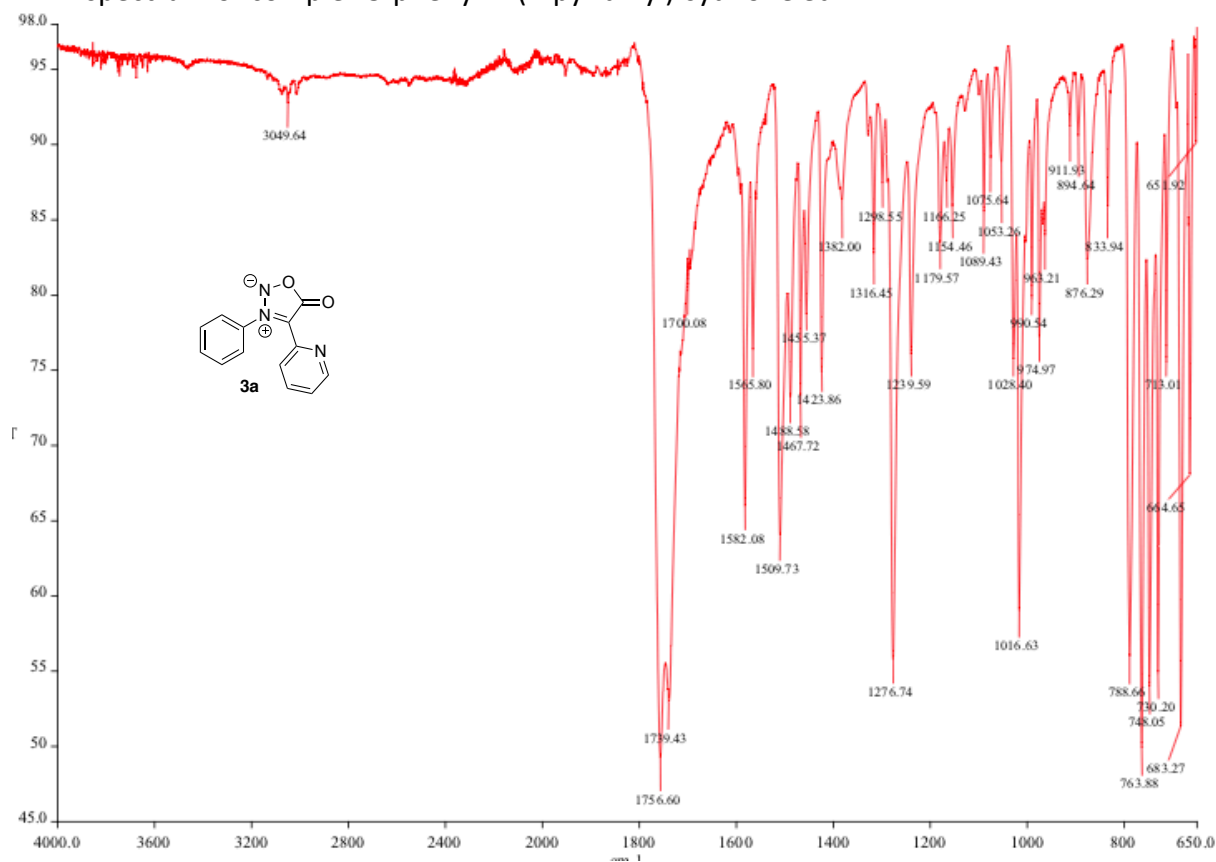


^{13}C NMR spectrum of complex $[\text{ZnCl}_2(\mathbf{3a})]$ (125 MHz, CD_3CN):

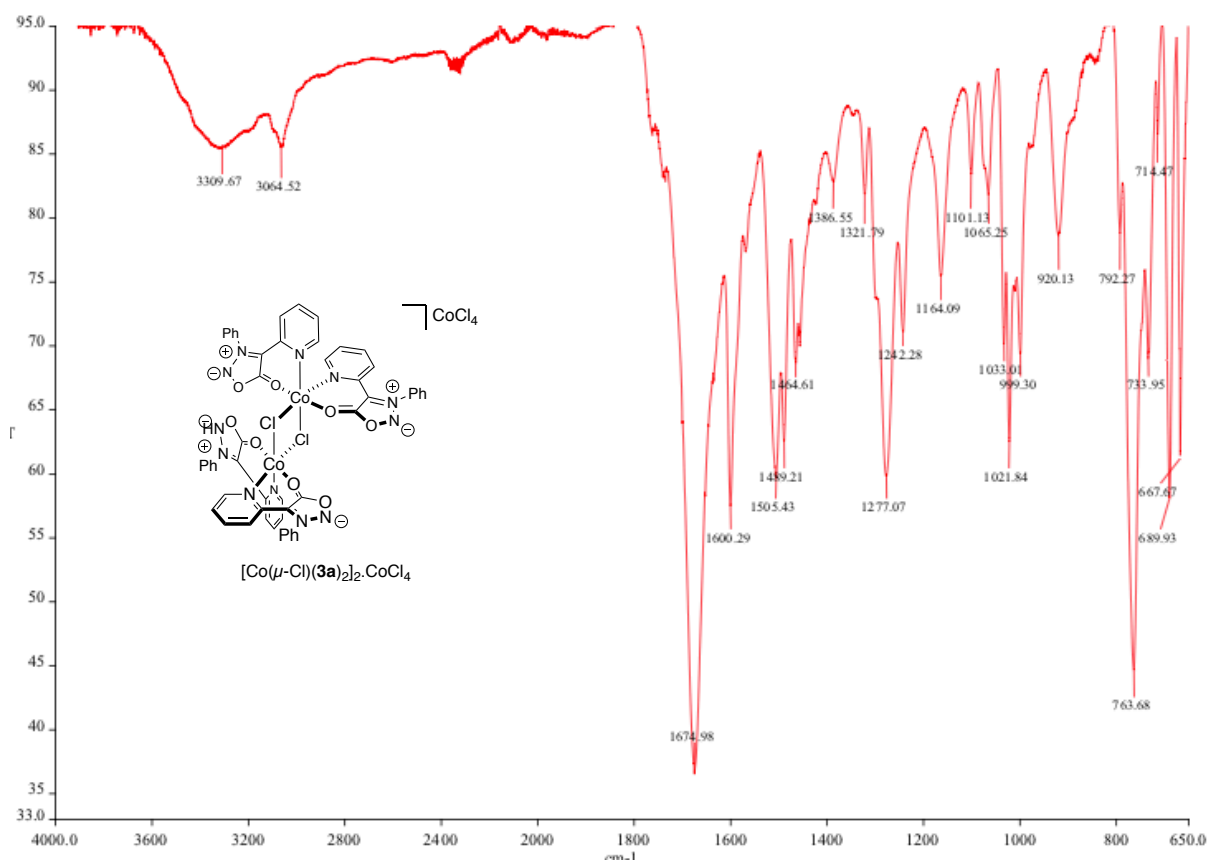


IX. FT-IR spectra

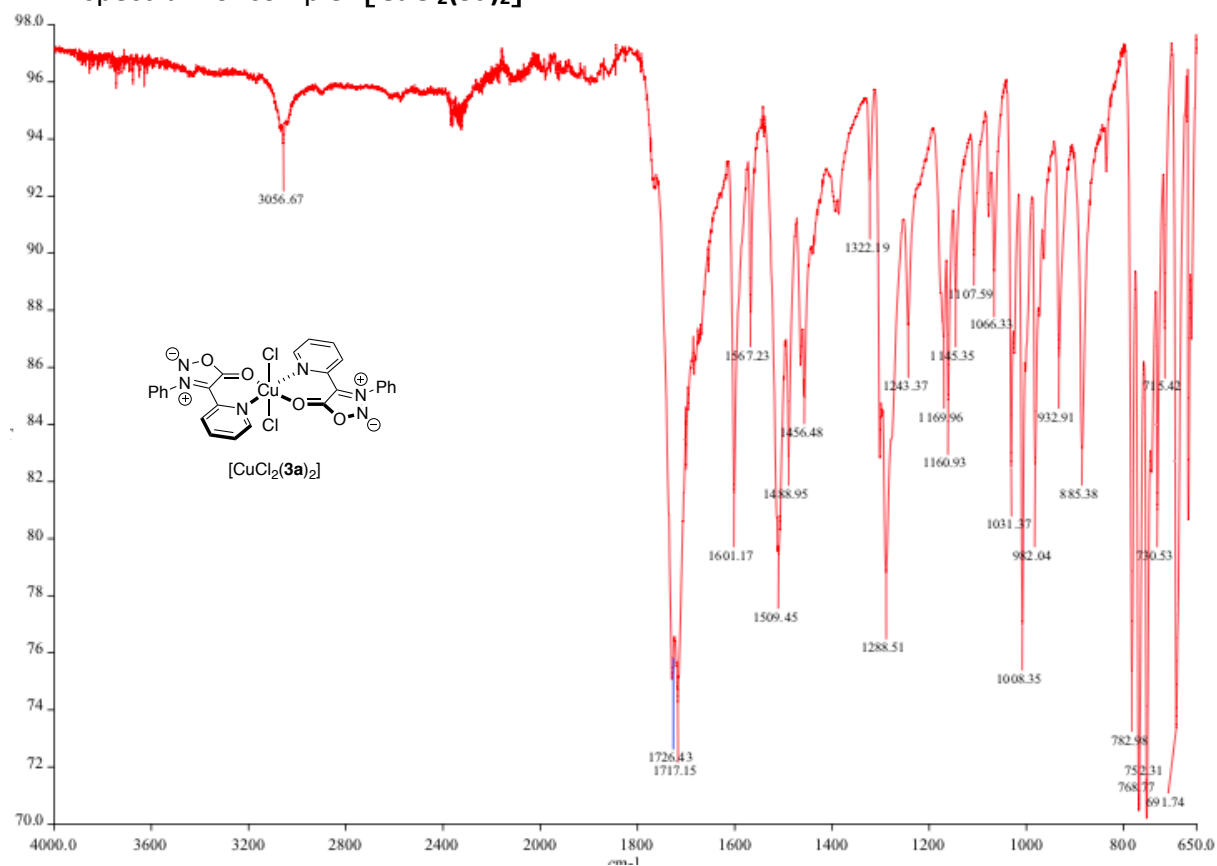
FT-IR spectrum of complex 3-phenyl-4-(2-pyridinyl)-sydnone **3a** :



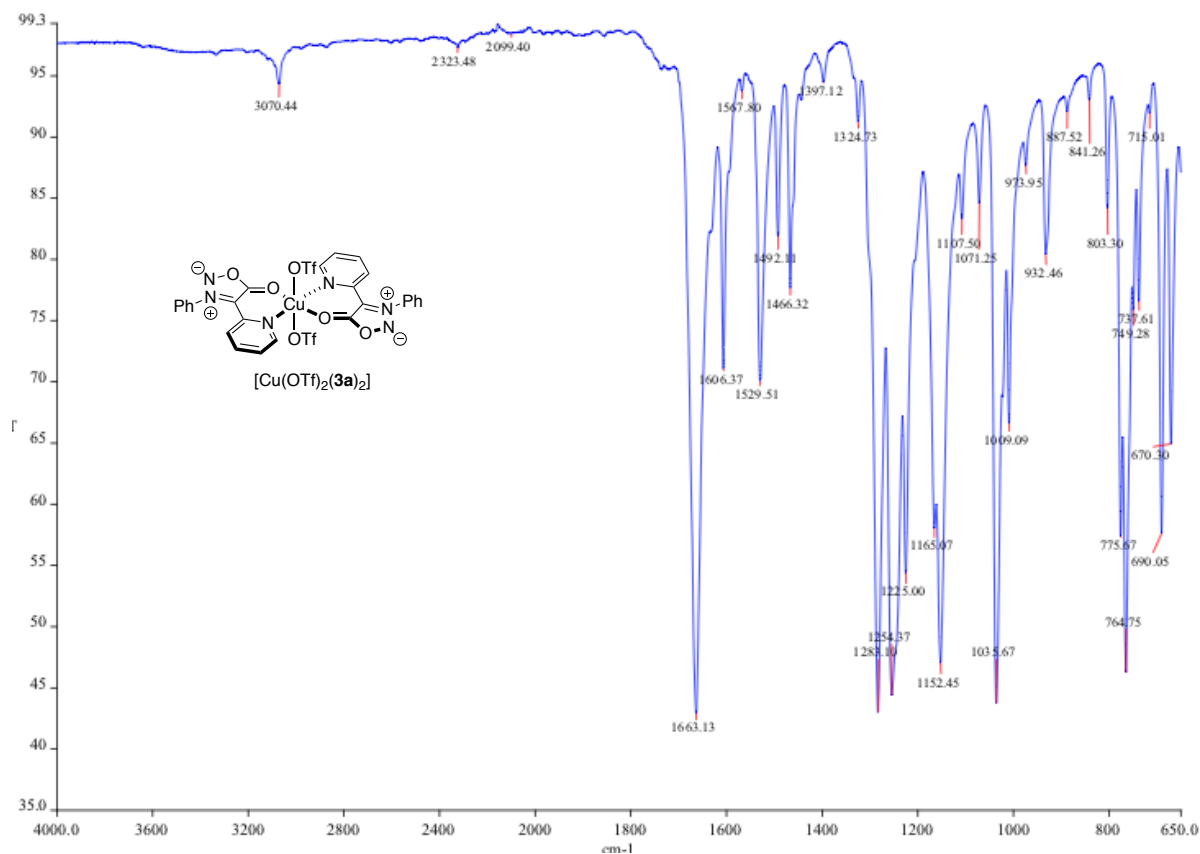
FT-IR spectrum of complex $[\text{Co}(\mu\text{-Cl})(\mathbf{3a})_2]_2 \cdot \text{CoCl}_4$:



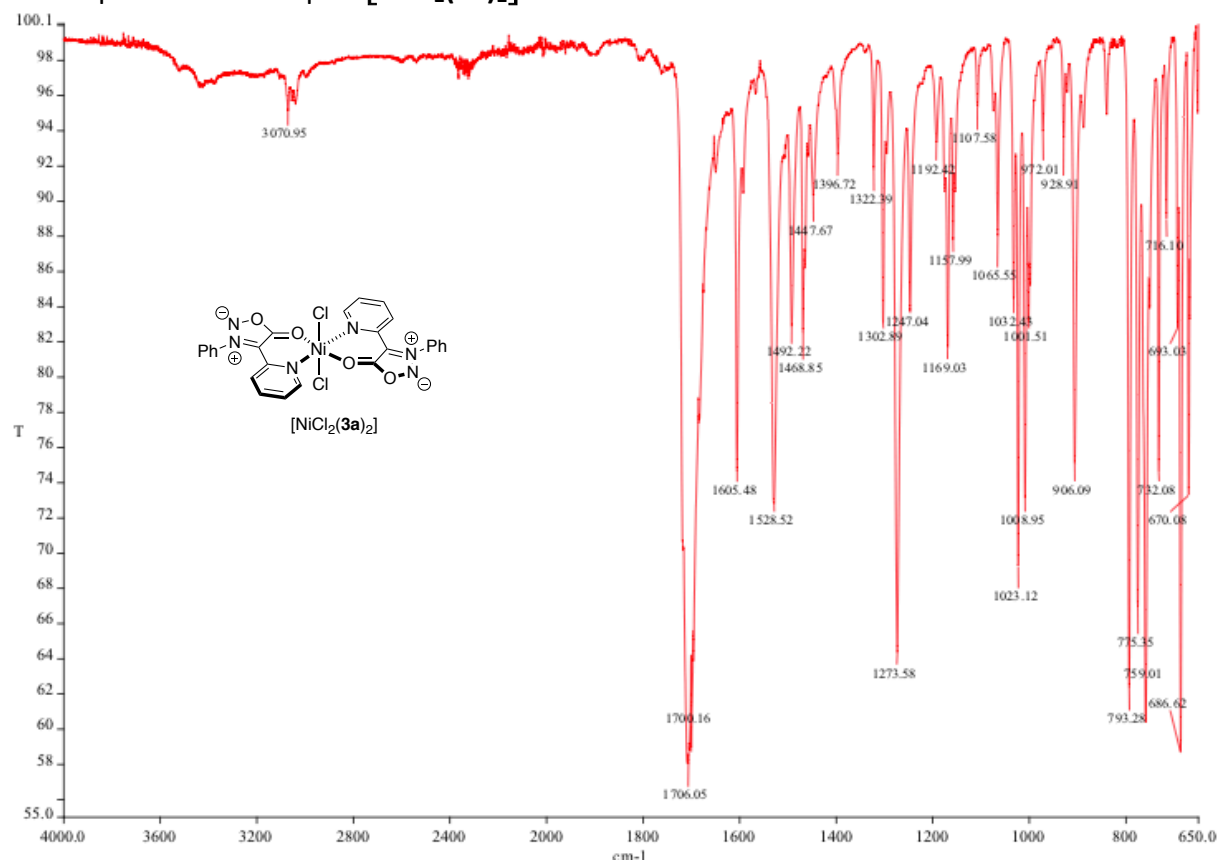
FT-IR spectrum of complex $[\text{CuCl}_2(\mathbf{3a})_2]$:



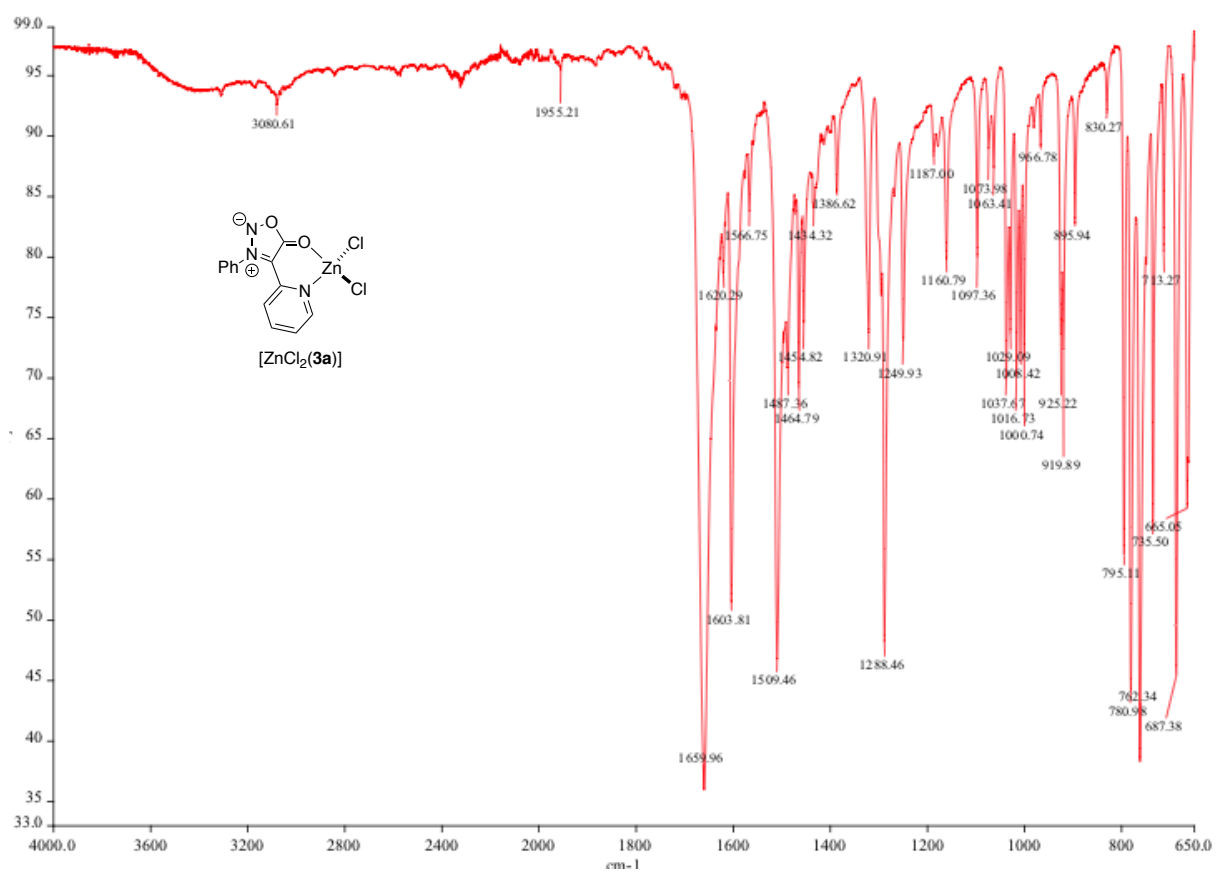
FT-IR spectrum of complex $[\text{Cu}(\text{OTf})_2(\mathbf{3a})_2]$:



FT-IR spectrum of complex $[\text{NiCl}_2(\mathbf{3a})_2]$:



FT-IR spectrum of complex $[\text{ZnCl}_2(\mathbf{3a})]$:



ChemArxiv_ESI.pdf (2.68 MiB)

[view on ChemRxiv](#) • [download file](#)
