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

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 (^{1}H), at 376.5 MHz (^{19}F) and 100.62 MHz (^{13}C) or at 500.17 MHz (^{1}H) and 125.77 MHz (^{13}C). ^{1}H NMR spectra are reported in ppm using solvents as internal standards ($CDCl_3$ at 7.26 ppm, CD_3CN at 1.94 ppm, 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, 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% CH3CN/0.1% TFA in H2O/0.1%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.

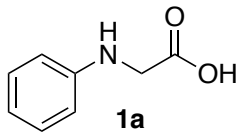
II. Preparation of *N*-aryl glycines in ball-mill

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 $MgSO_4$, filtered and evaporated under vacuum to furnish the expected *N*-aryl-glycine.

N-Phenyl-glycine 1a

CAS: 103-01-5



1a

Chemical Formula: $C_8H_9NO_2$
Molecular Weight: 151.17

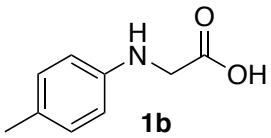
Procedure: according to the general procedure GP1 starting from aniline, 2 step-one pot alkylation-saponification allowed to obtain *N*-pheny-glycine **1a** as a beige solid (110 mg, 0.73 mmol, 91%).

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.78 (s, 2H), 6.55 (m, 3H), 7.07 (m, 2H).
^{13}C 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



1b

Chemical Formula: $C_9H_{11}NO_2$
Molecular Weight: 165.19

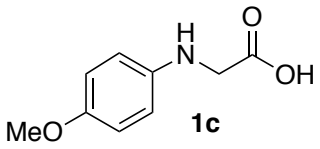
Procedure: according to the general procedure GP1 starting from p-toluidine, 2 step-one pot alkylation-saponification allowed to obtain glycine **1b** as a cream solid (220 mg, 1.33 mmol, 95%).

^{1}H 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).
^{13}C 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



1c

Chemical Formula: $C_9H_{11}NO_3$
Molecular Weight: 181.19

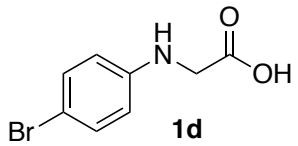
Procedure: according to the general procedure (GP1), the alkylation-saponification sequence performed in a stainless steel jar starting from *p*-anisidine yielded the *N*-arylglycine **1c** as a brown powder (175 mg, 0.96 mmol, 80%).

Appearance: beige solid
^{1}H 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).
^{13}C 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



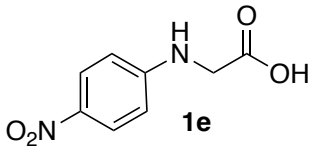
1d

Chemical Formula: $C_8H_8BrNO_2$
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%).
^{1}H 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).
^{13}C 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 $C_8H_9NO_2Br$ $[M+H]^+$ 229.9817, found 229.9818.

N-(4-Nitrophenyl)-glycine 1e

CAS: 619-91-0



1e

Chemical Formula: $C_8H_8N_2O_4$
Molecular Weight: 196.16

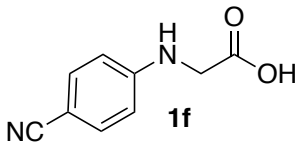
Procedure (Method B): 4-Nitroaniline (98 mg, 0.70 mmol, 1 eq), glyoxylic acid monohydrate (160 mg, 1.68 mmol, 2.4 eq) and sodium cyanoborohydride (47 mg, 0.70 mmol, 1 eq) were introduced in a 10 mL stainless steel milling jar with one stainless steel ball (10 mm diameter). The jar was closed and submitted 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 $MgSO_4$ 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 P_2O_5 under vacuum to yield the expected *N*-aryl-glycine **1e** as a yellow powder (73 mg, 0.37 mmol, 53%).

^{1}H 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).
^{13}C 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



1f

Chemical Formula: $C_9H_8N_2O_2$
Molecular Weight: 176.18

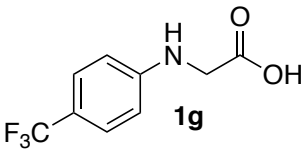
Procedure (Method B): 4-Aminobenzonitrile (181 mg, 1.50 mmol, 1 eq), glyoxylic acid monohydrate (342 mg, 3.60 mmol, 2.4 eq) and sodium cyanoborohydride (100 mg, 1.50 mmol, 1 eq) were introduced in a 15 mL stainless steel milling jar with one stainless steel ball (10 mm diameter). The jar was closed and 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 $MgSO_4$ 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 P_2O_5 under vacuum to yield the expected *N*-aryl-glycine **1f** as a beige powder (148 mg, 0.84 mmol, 56%).

Appearance: beige solid
^{1}H 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).
^{13}C 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



1g

Chemical Formula: $C_9H_8F_3NO_2$
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

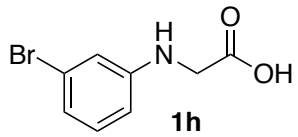
mm diameter). The jar was closed and submitted to grinding for 2 h in a planetary ball-mill operated at 400 rpm. The reaction mixture was taken up with EtOAc and water. The organic layer was washed with 1N HCl and brine, dried over $MgSO_4$ and evaporated under vacuum. The crude product was taken up 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 P_2O_5 under vacuum to yield the expected *N*-aryl-glycine **1g** as an offwhite powder (325 mg, 1.48 mmol, 74%).

^{1}H 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).
^{13}C 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.
^{19}F 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



1h

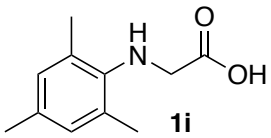
Chemical Formula: $C_8H_8BrNO_2$
Molecular Weight: 230.06

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%).

^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 45.4, 111.9, 115.9, 121.6, 123.5, 130.8, 148.0, 175.8.
HRMS ESI-(+) calcd. for $C_8H_9NO_2Br$ $[M+H]^+$ 229.9817, found 229.9818.

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

CAS: 104412-17-1



1i

Chemical Formula: $C_{11}H_{15}NO_2$
Molecular Weight: 193.25

Procedure: Ethyl bromoacetate (340 μL, 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 $MgSO_4$, filtered and evaporated under vacuum. The crude product was triturated with Et_2O to yield the expected *N*-aryl-glycine **1i** as a clear yellow solid (214 mg, 1.11 mmol, 37%).

Appearance: clear yellow solid
^{1}H 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).
^{13}C 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]

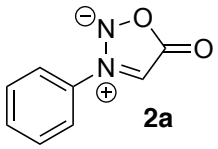
III. Preparation of N-aryl-sydnones in ball-mill

A. General procedure for nitrosation-cyclization (GP1)

N-aryl-glycine and sodium nitrite (1 eq) were introduced in a 10 mL ZrO_2 jar with one ZrO_2 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 with water, a saturated aqueous $NaCHO_3$ solution, water and brine. After drying over $MgSO_4$, filtration and evaporation of the solvent under vacuum the crude sydnone was obtained and if necessary purified by recrystallization or flash chromatography on silica.
Warning: intermediate nitroso-amines generated after the first milling step are highly toxic. Hence, caution should be taken when opening the milling jar.

N-Phenylsydnone 2a

CAS: 120-06-9



2a

Chemical Formula: $C_8H_6N_2O_2$
Molecular Weight: 162.15

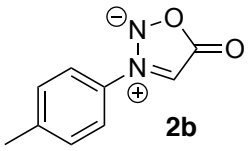
Procedure: according to the general procedure GP1 starting from *N*-phenyl-glycine **1a** and with milling times of 30 and 60 min, the expected sydnone **2a** was obtained as a brown solid (186 mg, 1.15 mmol, 95%) without needing further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.73 (s, 1H), 7.60-7.74 (m, 5H).
^{13}C 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



2b

Chemical Formula: $C_9H_8N_2O_2$
Molecular Weight: 176.18

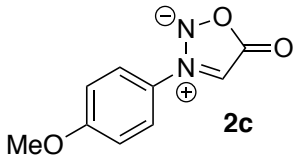
Procedure: according to the general procedure GP1, starting from *N*-(4-methylphenyl-glycine **1b** with milling times of 45 and 45 min, the expected *N*-aryl-sydnone **2b** was obtained as a beige solid (53 mg, 0.30 mmol, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (100 MHz, $CDCl_3$) 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



2c

Chemical Formula: $C_9H_8N_2O_3$
Molecular Weight: 192.17

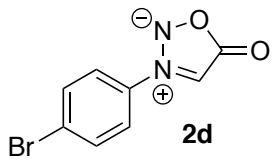
Procedure: according to the general procedure GP1, starting from *N*-(4-methoxyphenyl-glycine **1c** with milling times of 30 and 45 min, the expected *N*-aryl-sydnone **2c** was obtained after trituration of the crude with Et_2O and recrystallization from EtOAc/heptane as brown solid (55 mg, 0.28 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (100 MHz, $CDCl_3$) 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



2d

Chemical Formula: $C_8H_5BrN_2O_2$
Molecular Weight: 241.04

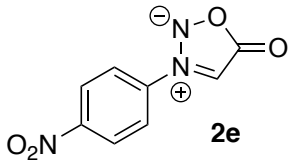
Procedure: according to the general procedure GP1 starting from *N*-4-bromophenyl-glycine **1d** and with milling times of 30 and 90 min, the expected sydnone **2d** was obtained as a brown powder (152 mg, 0.63 mmol, 91%) without needing further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.73 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 93.7, 122.8, 127.0, 133.7, 168.9.
LCMS (ESI) *m/z*: 241, 243 $[M+H]^+$.
HRMS ESI-(+) calcd. for $C_8H_6N_2O_2Br$ $[M+H]^+$ 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



2e

Chemical Formula: $C_8H_5N_3O_4$
Molecular Weight: 207.15

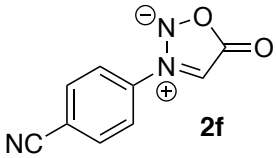
Procedure: according to the general procedure GP1 starting from *N*-4-nitrophenyl-glycine **1e**, complete conversion was obtained with milling times of 30 and 45 min. The crude product was purified by recrystallization from EtOAc/heptane to afford the expected sydnone **2e** as a orange powder (52 mg,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

^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 7.14 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 8.46 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (100 MHz, CD_3CN) 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



2f

Chemical Formula: $C_9H_5N_3O_2$
Molecular Weight: 187.16

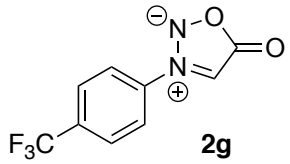
Procedure: according to the general procedure GP1, starting from *N*-4-cyanophenyl-glycine **1f**, with addition of 1 eq of $KHSO_4$ (to obtain full conversion of the nitrosation step) and with a milling time of 90 min for the cyclization step, the expected *N*-aryl-sydnone **2f** was

obtained after purification of the crude by recrystallization from ethanol/heptane 8/2 as a beige powder (62 mg, 0.33 mmol, 34%).

^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 7.09 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H).
^{13}C NMR (100 MHz, CD_3CN) 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 $C_9H_6N_3O_2$ $[M+H]^+$ 188.0460, found 188.0461.

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

CAS: 1620220-61-2



2g

Chemical Formula: $C_9H_5F_3N_2O_2$
Molecular Weight: 230.15

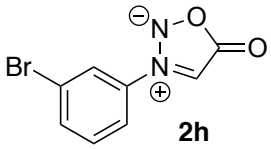
Procedure: according to the general procedure GP1, starting from *N*-(4-trifluoromethylphenyl)-glycine **1g**, the nitrosation step was achieved after 30 min of milling. Then $MgSO_4$ (4.4 eq) was added as a grinding auxiliary and the mixture milled for 5 min at 30 Hz. The cyclization step was then performed 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%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.82 (s, 1H), 7.89-7,.94 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) 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.
^{19}F 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



2h

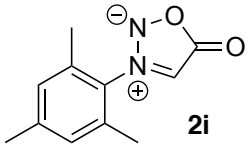
Chemical Formula: $C_8H_5BrN_2O_2$
Molecular Weight: 241.04

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.

^{1}H NMR (400 MHz, $CDCl_3$) 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).
^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_8H_6N_2O_2Br$ $[M+H]^+$ 240.9613, found 240.9615.

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

CAS: 104411-99-6



2i

Chemical Formula: $C_{11}H_{12}N_2O_2$
Molecular Weight: 204.23

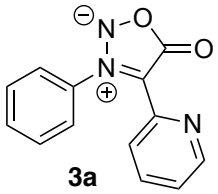
Procedure: according to the general procedure GP1, starting from *N*-(2,4,6-trimethylphenyl-glycine **1i** with addition of 2 eq of $KHSO_4$ and milling times of 90 and 45 min, the expected *N*-aryl-sydnone **2i** was obtained after trituration of the crude with Et_2O and recrystallization from EtOAc/heptane as an offwhite powder (56 mg, 0.27 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.16 (s, 6H), 2.37 (s, 3H), 6.34 (s, 1H), 7.04 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{11}H_{13}N_2O_2$ $[M+H]^+$ 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



3a

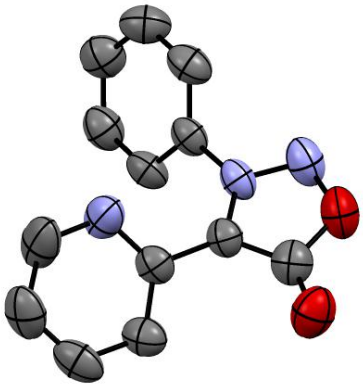
Chemical Formula: $C_{13}H_9N_3O_2$
Molecular Weight: 239.23

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.
^{1}H 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, CDCl3) 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 $[M+H]^+$.

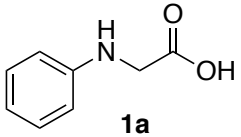
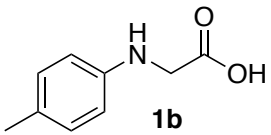
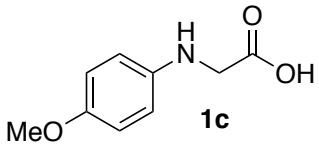
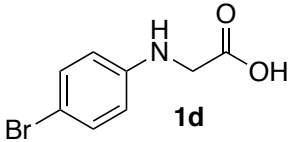
The analytical data obtained is in agreement with those reported in the literature.[9]

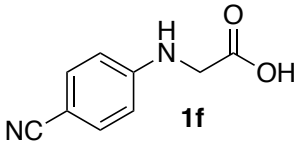
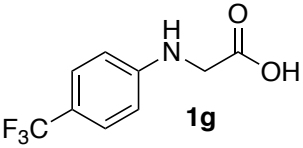
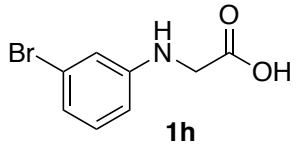
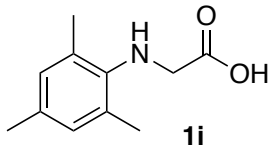


ORTEPs (probability at 50% level) of compound **3a**. H atoms are omitted for clarity.

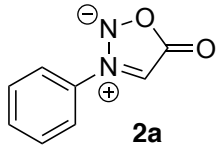
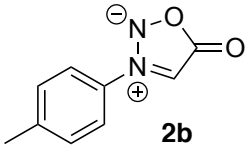
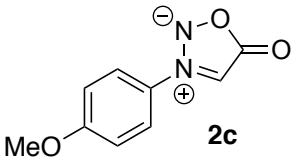
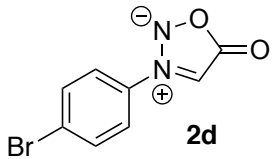
CCDC 1913664	**3a**
Formula	$C_{13}H_9N_3O_2$
M / g.mol^{-1}	239.23
Crystal system	Monoclinic
Space group	P2 1/n
a / Å	8.7441 (8)
b / Å	13.0971 (15)
c / Å	10.0411 (10)
α / Å	90
β / Å	100.651 (10)
γ / Å	90
V (Å^3)	1130.1 (2)
Z	4
ρ_{calcd} / g.cm^{-3}	1.406
μ (Mo Kα) / mm^{-1}	0.71073
T / K	293 (2)
Number of reflections	12373
Number of unique reflections	2212
$R1$, w$R2$ ($I > 2\sigma(I)$)	0.0513, 0.1181
$R1$, w$R2$ (all data)	0.0960, 0.1412
GOF	1.018

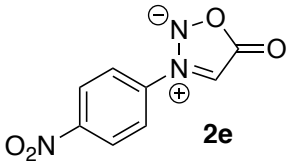
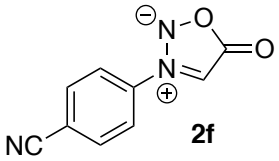
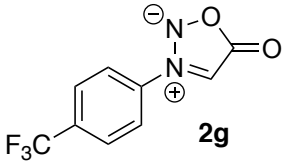
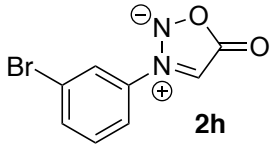
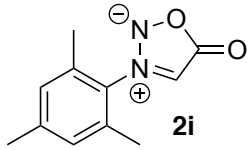
IV. Comparison of *N*-aryl glycines synthesis with literature procedures

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) *p*-Toluidine, ethyl bromoacetate (1.0 eq.), SiO_2, MW (300 W), 5 min. 2) NaOH (excess) in EtOH, reflux, 10 min.
			42%[11]	1) *p*-Toluidine, NaOAc (1.2 eq.), ethyl chloroacetate (1.2 eq.), EtOH, reflux, 7h, overnight at rt, 2) NaOH (1.1 eq.), H_2O, reflux, 30 min.
			53%[6]	1) *p*-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_2O/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.
			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_2O, 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_2O, reflux, 10h
			80-87%[12]	4-aminobenzonitrile, chloroacetic acid (1.5 eq.), H_2O, reflux, 5h
 **1g**	77311-21-8	74%	30%[11]	4-Trifluoromethylaniline, NaOAc (2.0 eq.), AcOH (4.0 eq.), glyoxylic acid (1.5 eq.), $NaBH_3CN$ (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.), $NaBH_3CN$ (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, $NaOAc.3H_2O$ (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, $NaOAc.3H_2O$ (1.5 eq.), ethyl bromoacetate (1.0 eq.), EtOH, reflux, overnight, 2) 20% HCl (excess), 100°C, 4h.

V. Comparison of sydnones 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_2Cl_2, 0°C, 2.5 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH_2Cl_2, 0°C, 4 h.
			63%[6]	1) Glycine **1a**, $NaNO_2$ (1.5 eq., dropwise addition), H_2O at 0°C, HCl cc. Drying overnight. 2) Ac_2O (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_2O (large excess), 100°C, 3 h.
			89%[5]	1) Glycine **1a**, *t*-BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
 **2b**	3483-19-0	91%	73%[10]	1) Glycine **1b**, silica chloride, wet SiO_2, $NaNO_2$ (1.5 eq.), CH_2Cl_2, 0°C, 2.2 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH_2Cl_2, 0°C, 4 h.
			60%[6]	1) Glycine **1b**, $NaNO_2$ (1.5 eq., dropwise addition), H_2O at 0°C, HCl cc., Drying overnight. 2) Ac_2O (large excess), 100°C, 1.5 h.
			82%[15]	1) Glycine **1b**, *t*-BuONO, anh. THF, Ar, 30 min. 2) TFAA, 1h.
			69%[8]	1) Glycine **1b**, *t*-BuONO (1.5 eq.), anh. THF, Ar, 30 min. 2) CDI (1.1 eq.), 1h.
 **2c**	3815-80-3	54%	81%[10]	1) Glycine **1c**, silica chloride, wet SiO_2, $NaNO_2$ (1.5 eq.), CH_2Cl_2, 0°C, 1.7 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH_2Cl_2, 0°C, 4 h.
			59%[5]	1) Glycine **1c**, *t*-BuONO (1.1 eq.), anh. THF, Ar, 30 min. 2) TFAA (1.1 eq.), 1h.
			50%[8]	1) Glycine **1c**, *t*-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_2O at 0°C, HCl cc., Drying overnight. 2) Ac_2O (large excess), 100°C, 1.5 h.
			73%[7]	1) Glycine **1c**, *t*-BuONO (1.5 eq.), anh. THF, Ar, 0°C to rt. 2) TFAA (1.1 eq.), 1h.
			78%[15]	1) Glycine **1c**, *t*-BuONO, anh. THF, Ar, 30 min. 2) TFAA, 1h.
 **2d**	26537-61-1	91%	79%[10]	1) Glycine **1d**, silica chloride, wet SiO_2, $NaNO_2$ (1.5 eq.), CH_2Cl_2, 0°C, 2.4 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH_2Cl_2, 0°C, 4 h.
			50%[6]	1) Glycine **1d**, $NaNO_2$ (1.5 eq., dropwise addition), H_2O at 0°C, HCl cc., Drying overnight. 2) Ac_2O (large excess), 100°C, 1.5 h.

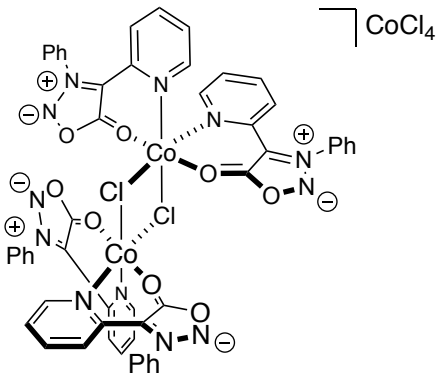
Formule	CAS	Yield	Yield in lit.	Conditions from literature
 **2e**	6299-51-0	42%	80%[10]	1) Glycine **1e**, silica chloride, wet SiO_2, $NaNO_2$ (1.5 eq.), CH_2Cl_2, 0°C, 2.0 h. 2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH_2Cl_2, 0°C, 4 h.
			36%[6]	1) Glycine **1e**, $NaNO_2$ (1.5 eq., dropwise addition), H_2O at 0°C, HCl cc., Drying overnight. 2) Ac_2O (large excess), 100°C, 1.5 h.
			77%[7]	1) Glycine **1e**, *t*-BuONO (1.5 eq.), anh. THF, Ar, 0°C to rt. 2) TFAA (2.5 eq.), 1h.
			57%[8]	1) Glycine **1e**, *t*-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**, *t*-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**, *t*-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_2Cl_2, 0°C, 1.5 h.
			65%[5]	1) Glycine **1g**, *t*-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_2O (1.2 eq., dropwise addition at 0°C), 4 h. 2) TFAA, CH_2Cl_2, 0°C, 1 h.
			n.a.[18]	Procedure according to ref[3, 19] (no characterization given).

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

A. General procedure for preparation of complexes (GP2)

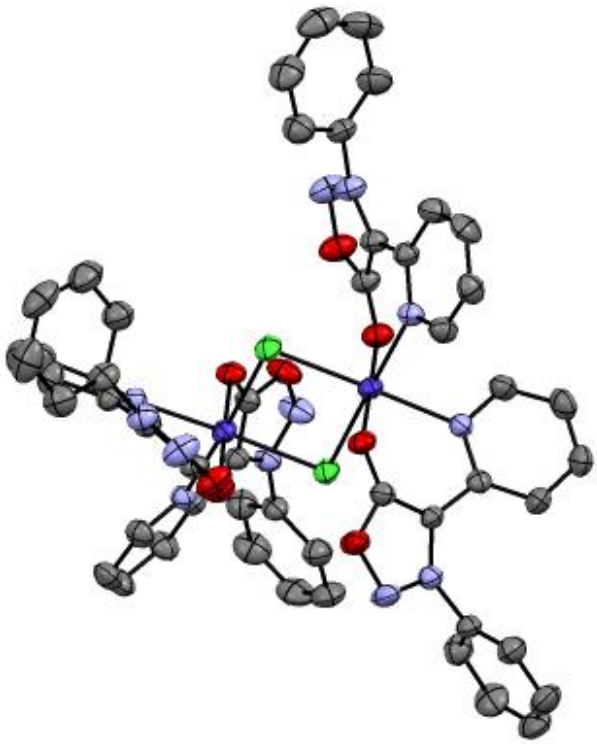
4-(2-Pyridyl)-*N*-phenylsydnone **3a** and the corresponding metallic salt were introduced in a grinding jar (10 mL zirconium oxide ZrO_2 or 15 mL PTFE) with one ball (ZrO_2 or stainless steel, 10 mm diameter). The jar was closed and subjected to grinding in a vibratory ball-mill at 30 Hz for 1h. The 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. In all cases, X-ray quality crystals were grown by slow evaporation of an acetonitrile solution of the complex isolated after milling.
Of note, cobalt and copper complexes were found to be paramagnetic. Hence, no NMR data could be acquired.

$[Co(\mu\text{-}Cl)(3a)_2]_2.CoCl_4$



$[Co(\mu\text{-}Cl)(\mathbf{3a})_2]_2.CoCl_4$
Chemical Formula: $C_{52}H_{36}Cl_6Co_3N_{12}O_8$
Molecular Weight: 1346.44

Procedure: according to the general procedure GP2, using 3.0 eq of cobalt chloride $CoCl_2$ and 4.0 eq of sydnone **3a** in a 10 mL ZrO_2 jar with one ZrO_2 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 $C_{52}H_{36}N_{12}O_8Cl_2Co_2$ $[M\text{-}CoCl_4]^{2+}/2$ 572.0405, found 572.0421.

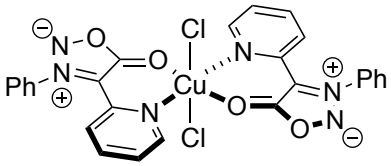


ORTEPs (probability at 50% level) of complex [Co(μ-Cl)(**3a**)$_2$]$_2$.CoCl$_4$. H atoms and CoCl$_4$ are omitted for clarity.

CCDC 1913663	[Co(μ-Cl)(**3a**)$_2$]$_2$.CoCl$_4$
Formula	$C_{52}H_{36}Cl_6Co_3N_{12}O_8$
M / g.mol^{-1}	1346.42
Crystal system	Orthorhombic
Space group	P 2_12_12
a / Å	17.0950 (4)
b / Å	16.1670 (3)
c / Å	10.0791 (2)
α / Å	90
β / Å	90
γ / Å	90
V (Å^3)	2785.61 (10)
Z	2
ρ_{calcd} / g.cm^{-3}	1.605
μ (Mo Kα) / mm^{-1}	0.71073
T / K	293 (2)
Number of reflections	60346
Number of unique reflections	6983
*R*1, w*R*2 (I > 2σ(I))	0.0332, 0.0630
*R*1, w*R*2 (all data)	0.0563, 0.0689
GOF	1.033

Of note, the [Co(μ-Cl)(**3a**)$_2$]$_2$.CoCl$_4$ components of this structure both have crystallographically-imposed two-fold symmetry with the [Co(μ-Cl)(**3a**)$_2$]$_2$ dimer lying about a twofold axis and with the Co2 cobalt atom of the CoCl$_4$ component on a twofold axis.

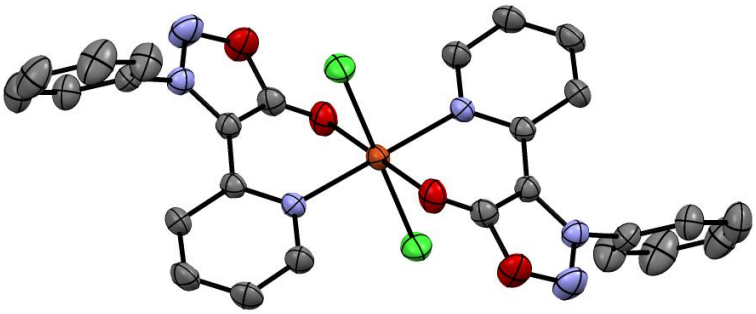
[$CuCl_2$(3a)$_2$]



[$CuCl_2$(**3a**)$_2$]
Chemical Formula: $C_{26}H_{18}Cl_2CuN_6O_4$
Molecular Weight: 612.91

Procedure: according to the general procedure GP2, using 1.0 eq of copper chloride dihydrate $CuCl_2.2H_2O$ 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 $C_{26}H_{18}N_6O_4ClCu$ [M-Cl$^-$]$^+$ 576.0376, found 576.0374.

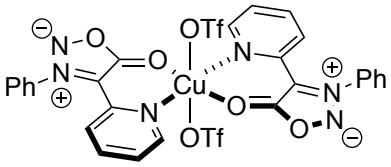


ORTEPs (probability at 50% level) of complex [$CuCl_2$(**3a**)$_2$]. H atoms are omitted for clarity.

CCDC 1913667	$[CuCl_2(\mathbf{3a})_2]$
Formula	$C_{26}H_{18}Cl_2CuN_6O_4$
M / g.mol^{-1}	612.90
Crystal system	Triclinic
Space group	P -1
a / Å	8.0661 (3)
b / Å	8.8517 (4)
c / Å	10.0437 (4)
α / Å	108.745 (4)
β / Å	104.613 (3)
γ / Å	96.672 (4)
V (Å^3)	641.70 (5)
Z	1
ρ_{calcd} / g.cm^{-3}	1.586
μ (Mo Kα) / mm^{-1}	0.71073
T / K	293 (2)
Number of reflections	17478
Number of unique reflections	3711
$R1$, w$R2$ ($I > 2\sigma(I)$)	0.0301, 0.0789
$R1$, w$R2$ (all data)	0.0371, 0.0822
GOF	1.050

Of note, the complex lies about an inversion centre with the Cu atom on the inversion centre.

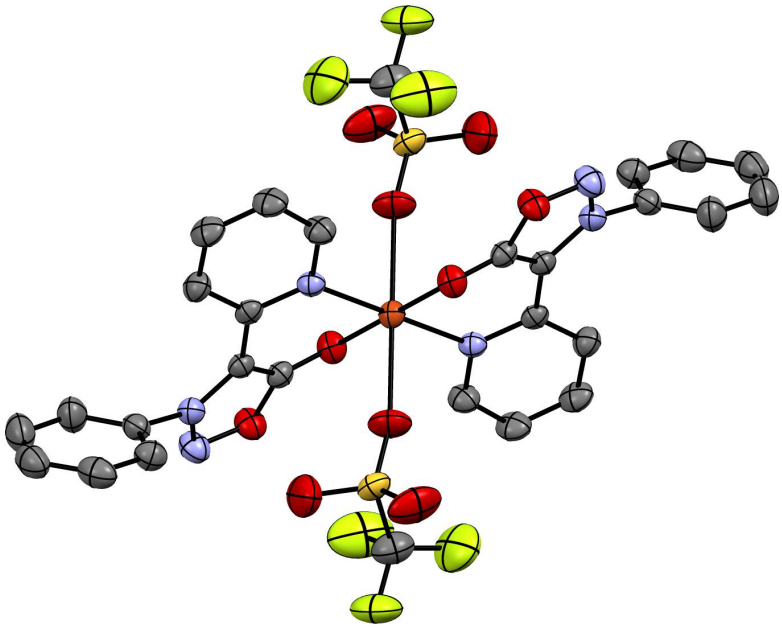
$[Cu(OTf)_2(3a)_2]$



$[Cu(OTf)_2(\mathbf{3a})_2]$
Chemical Formula: $C_{28}H_{18}CuF_6N_6O_{10}S_2$
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 $C_{27}H_{18}CuF_3N_6O_7S$ $[M\text{-}TfO^-]^+$ 690.0206, found 690.0209.

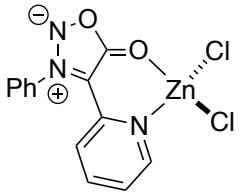


ORTEPs (probability at 50% level) of complex $[Cu(OTf)_2(\mathbf{3a})_2]$. H atoms are omitted for clarity.

CCDC 1913662	$[Cu(OTf)_2(\mathbf{3a})_2]$
Formula	$C_{28}H_{18}CuF_6N_6O_{10}S_2$
M / g.mol^{-1}	840.14
Crystal system	Triclinic
Space group	P -1
a / Å	7.9107 (4)
b / Å	7.9633 (4)
c / Å	13.4394 (8)
α / Å	81.297 (4)
β / Å	82.418 (5)
γ / Å	84.920 (4)
V (Å^3)	827.53 (8)
Z	1
ρ_{calcd} / g.cm^{-3}	1.686
μ (Mo Kα) / mm^{-1}	0.71073
T / K	293 (2)
Number of reflections	11808
Number of unique reflections	4461
$R1$, w$R2$ ($I > 2\sigma(I)$)	0.0542, 0.1401
$R1$, w$R2$ (all data)	0.0671, 0.1480
GOF	1.037

Of note, the complex lies about an inversion centre with the Cu atom on the inversion centre.

[$ZnCl_2$(3a)]



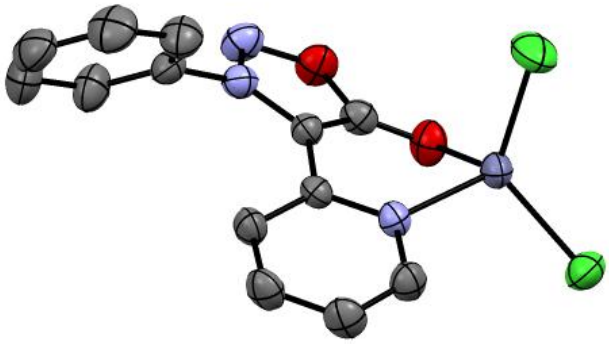
[$ZnCl_2$(**3a**)]

Chemical Formula: $C_{13}H_9Cl_2N_3O_2Zn$

Molecular Weight: 375.51

Procedure: according to the general procedure GP2, using 1.0 eq of zinc chloride $ZnCl_2$ and 2.0 eq of sydnone **3a** in a 10 mL ZrO_2 jar with one ZrO_2 ball (10 mm diameter), the monodentate complex was obtained as a beige solid (58 mg, 0.155 mmol, 74%).

^{1}H NMR (500 MHz, CD_3CN) 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).
^{13}C NMR (125 MHz, CD_3CN) 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 $C_{13}H_9N_3O_2ClZn$ $[M\text{-}Cl^-]^+$ 337.9676, found 337.9669.



ORTEPs (probability at 50% level) of complex [$ZnCl_2$(**3a**)]. H atoms are omitted for clarity.

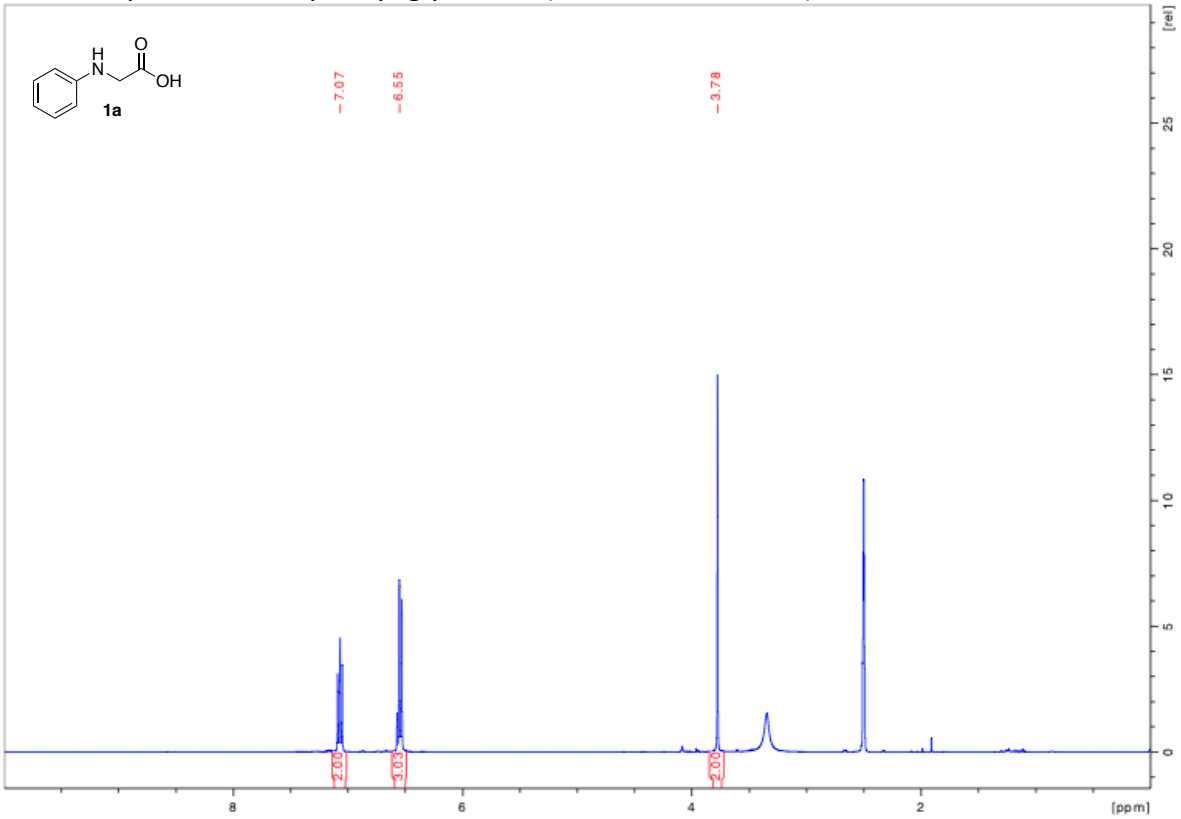
CCDC 1913665	[$ZnCl_2$(**3a**)]
Formula	$C_{13}H_9Cl_2N_3O_2Zn$
M / g.mol^{-1}	375.50
Crystal system	Triclinic
Space group	P -1
a / Å	8.5206 (4)
b / Å	8.9361 (3)
c / Å	9.9810 (3)
α / Å	94.269 (3)
β / Å	99.231 (3)
γ / Å	94.285 (3)
V (Å^3)	745.15 (5)
Z	2
ρ_{calcd} / g.cm^{-3}	1.674
μ (Mo Kα) / mm^{-1}	0.71073
T / K	293 (2)
Number of reflections	19751
Number of unique reflections	4322
R_{int}	0.024 (3)
R1, wR2 ($I > 2\sigma(I)$)	0.0305, 0.0742
R1, wR2 (all data)	0.0431, 0.0773
GOF	1.065

VII. References

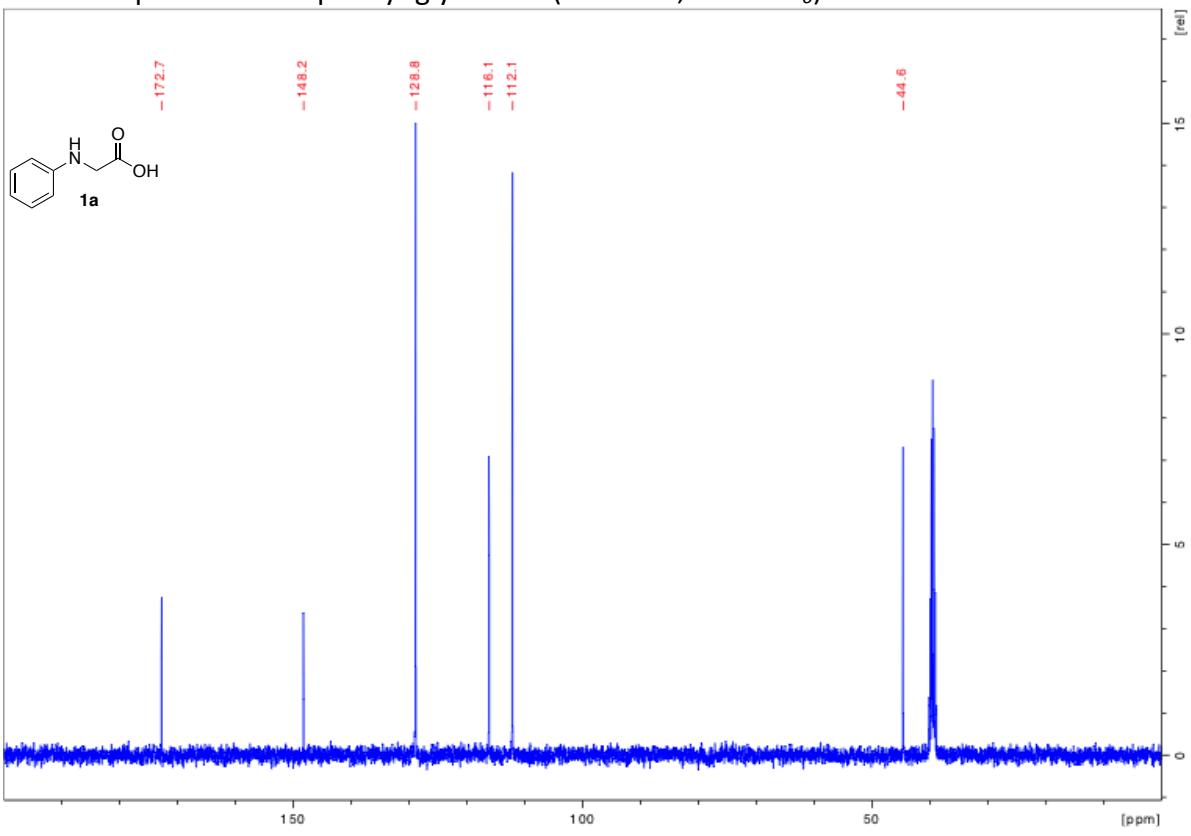
1. Z. Lu and R. J. Twieg, *Tetrahedron Lett.*, **2005**, *46*, 2997.
2. S. Specklin, E. Decuypere, L. Plougastel, S. Aliani and F. Taran, *J. Org. Chem.*, **2014**, *79*, 7772.
3. K. Turnbull, *J. Heterocycl. Chem.*, **1985**, *22*, 965.
4. C. Wu, Y. Fang, R. C. Larock and F. Shi, *Organic Letters*, **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. ^{1}H and ^{13}C NMR spectra

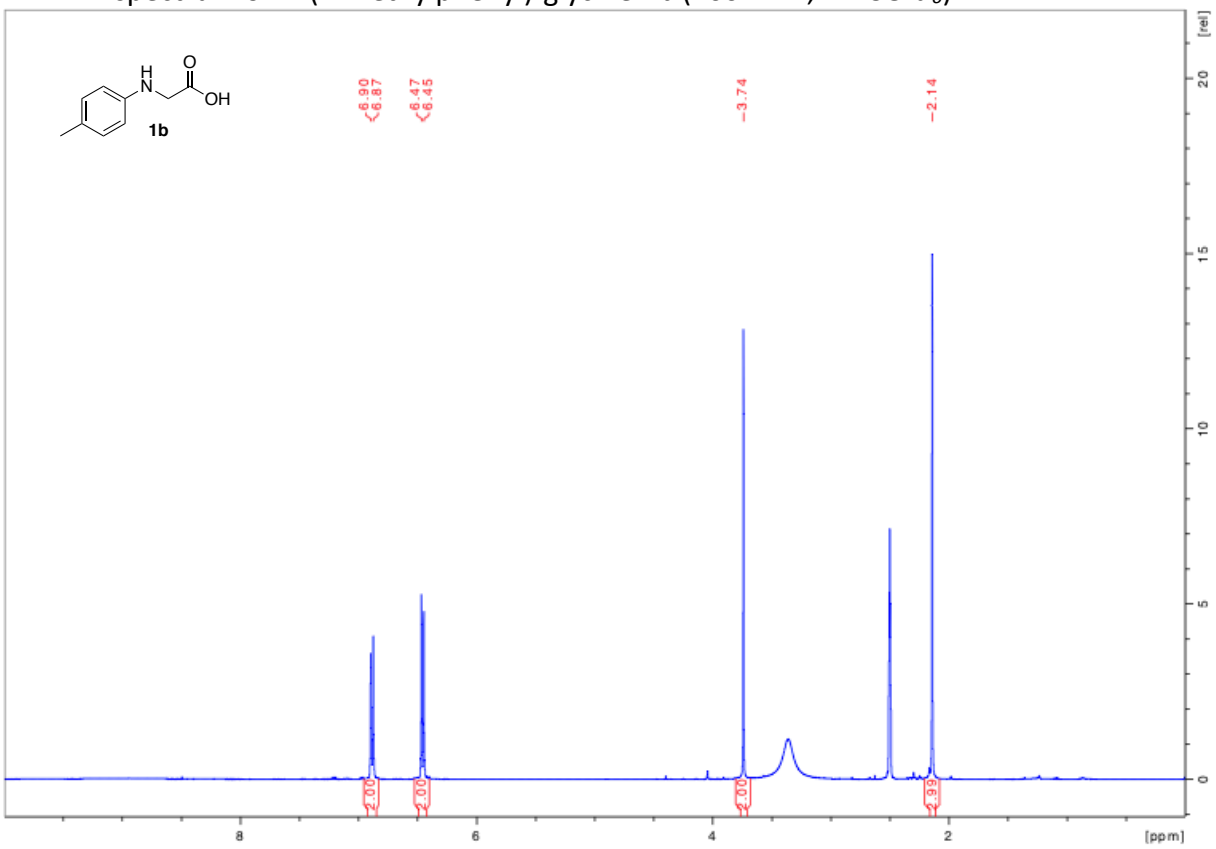
^{1}H NMR spectrum of *N*-phenyl-glycine **1a** (400 MHz, DMSO-d_6):



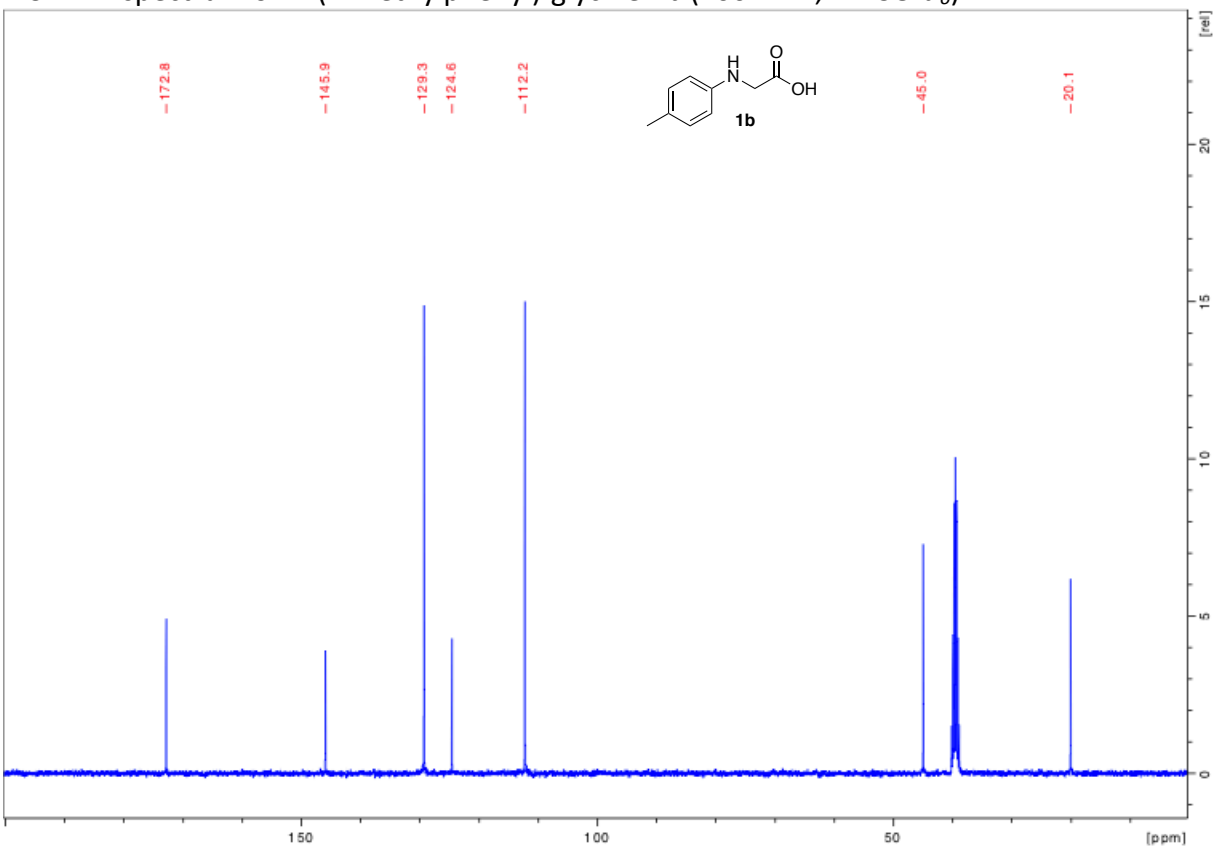
^{13}C NMR spectrum of *N*-phenyl-glycine **1a** (100 MHz, DMSO-d_6):



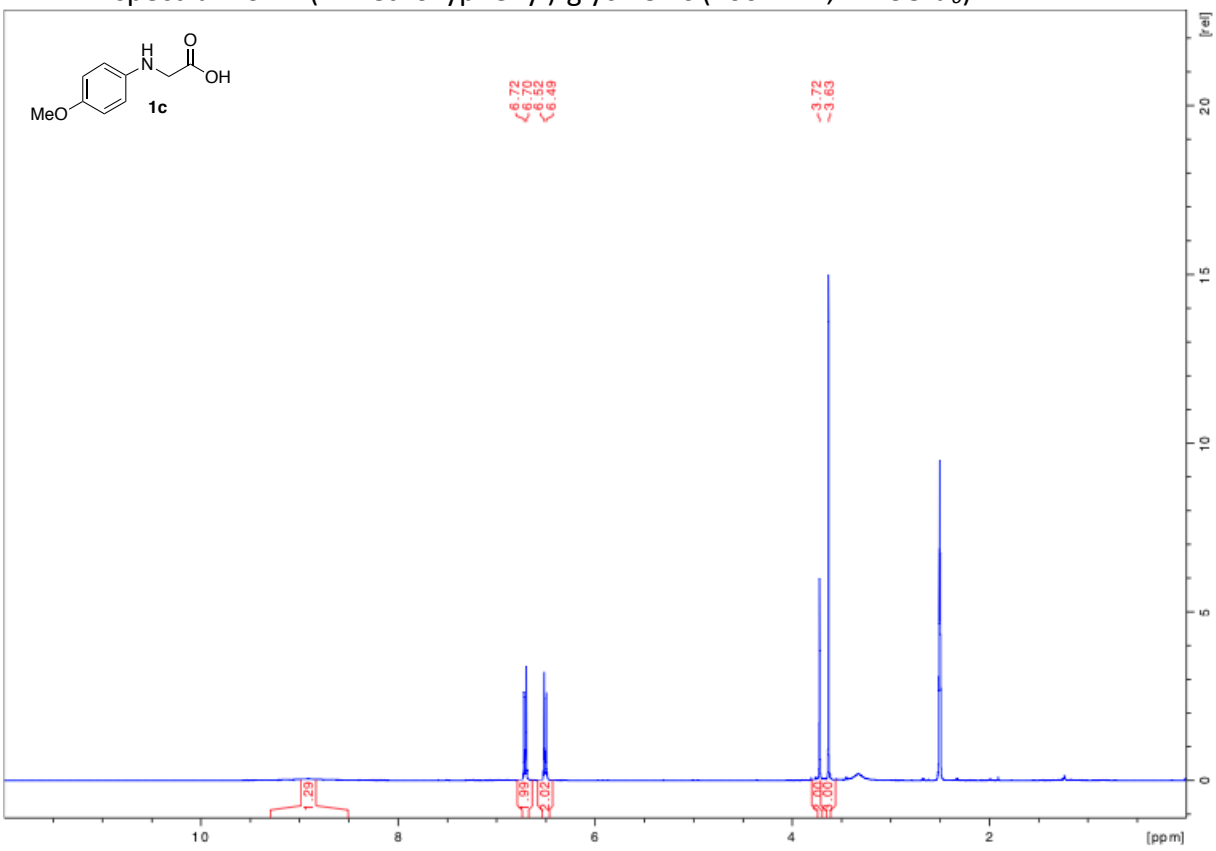
^{1}H NMR spectrum of *N*-(4-methylphenyl)-glycine **1b** (400 MHz, DMSO-d_6):



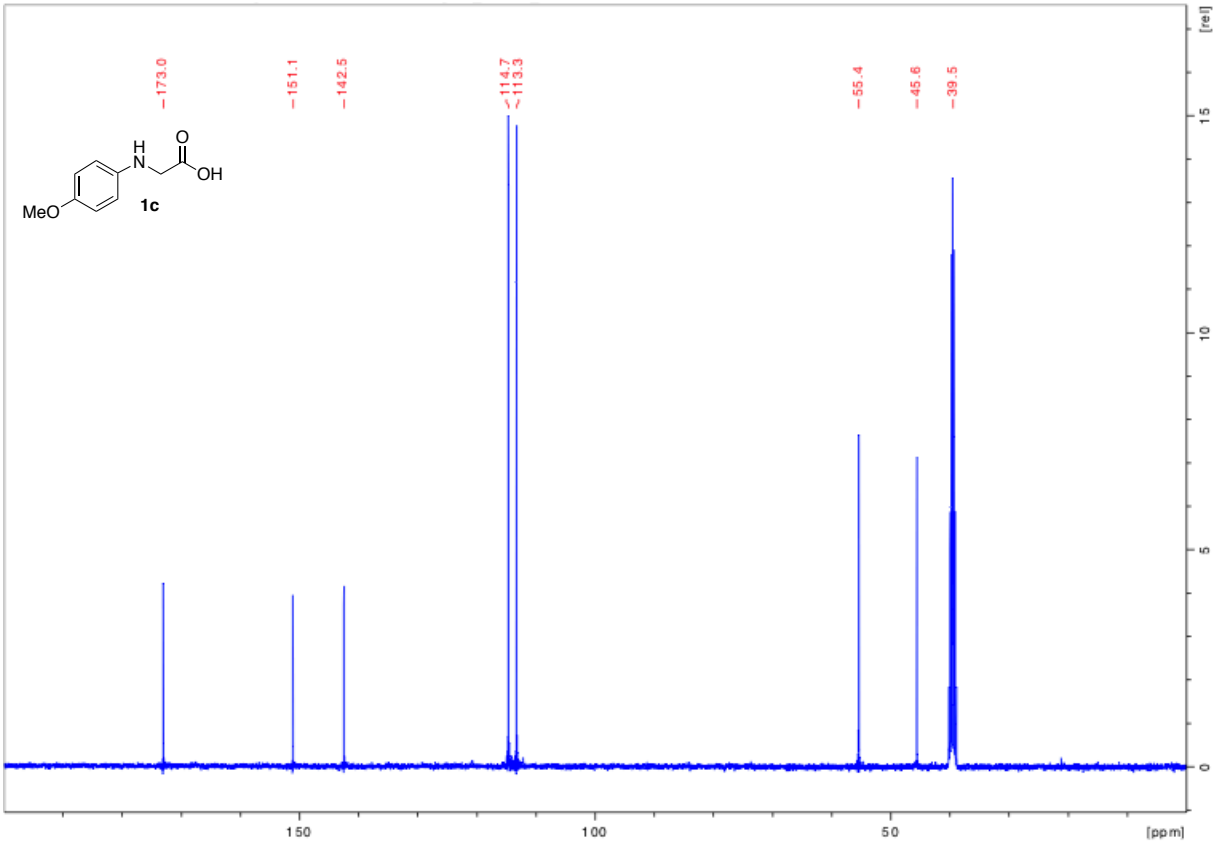
^{13}C NMR spectrum of *N*-(4-methylphenyl)-glycine **1b** (100 MHz, DMSO-d_6):



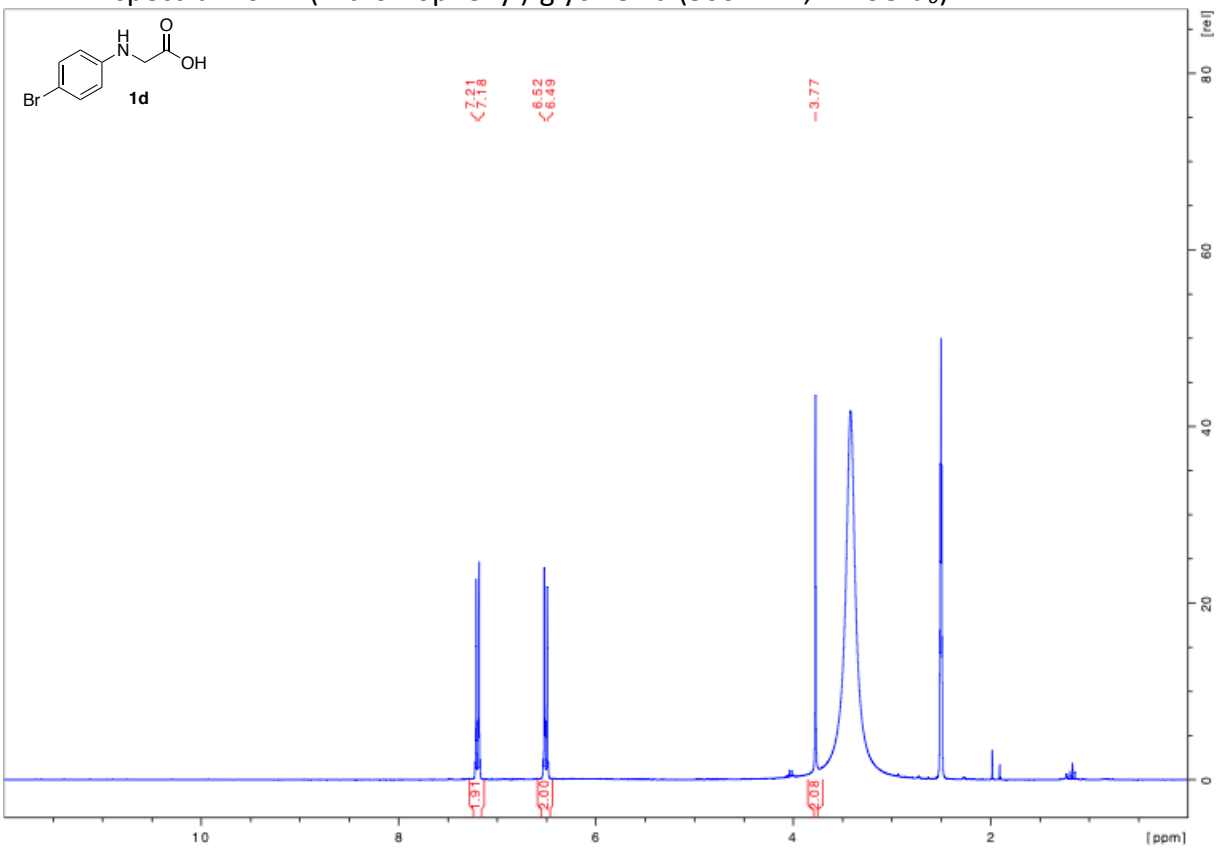
^{1}H NMR spectrum of *N*-(4-methoxyphenyl)-glycine **1c** (400 MHz, DMSO-d_6):



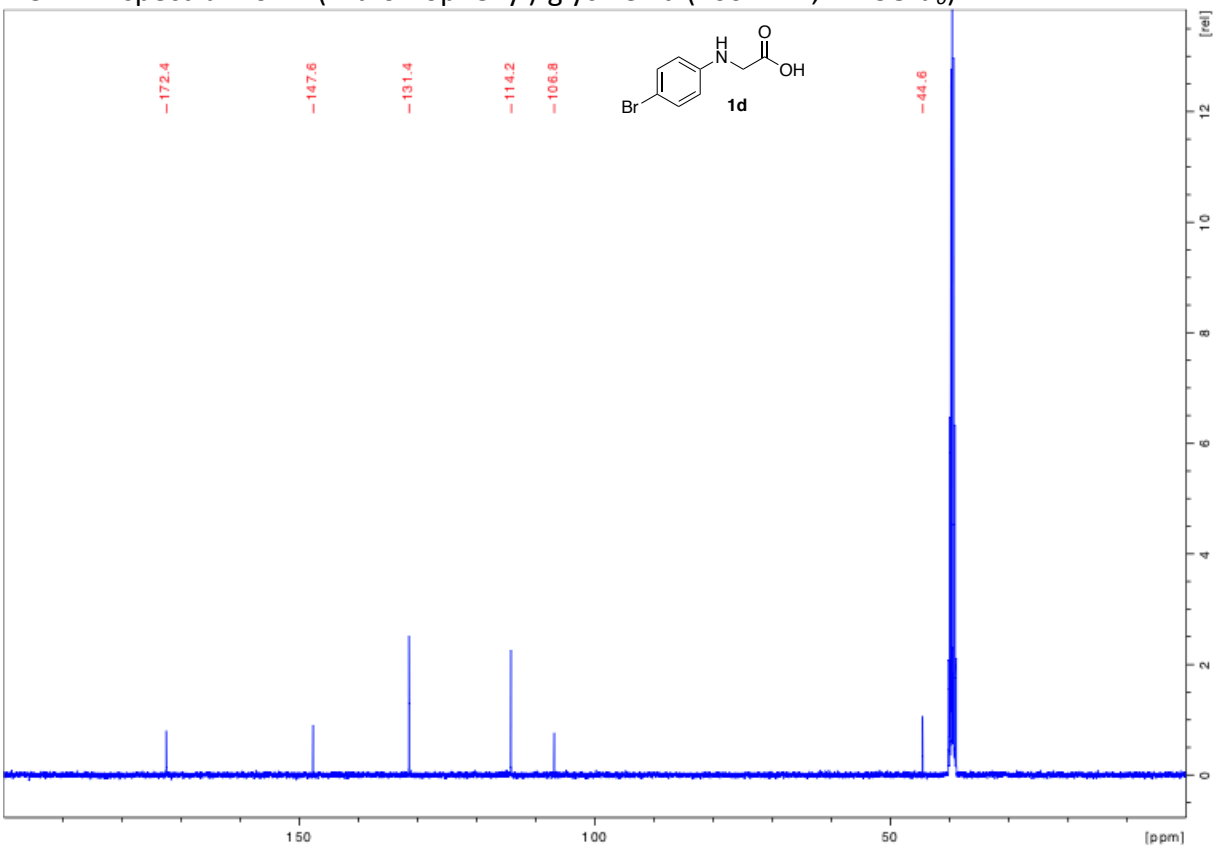
^{13}C NMR spectrum of *N*-(4-methoxyphenyl)-glycine **1c** (100 MHz, DMSO-d_6):



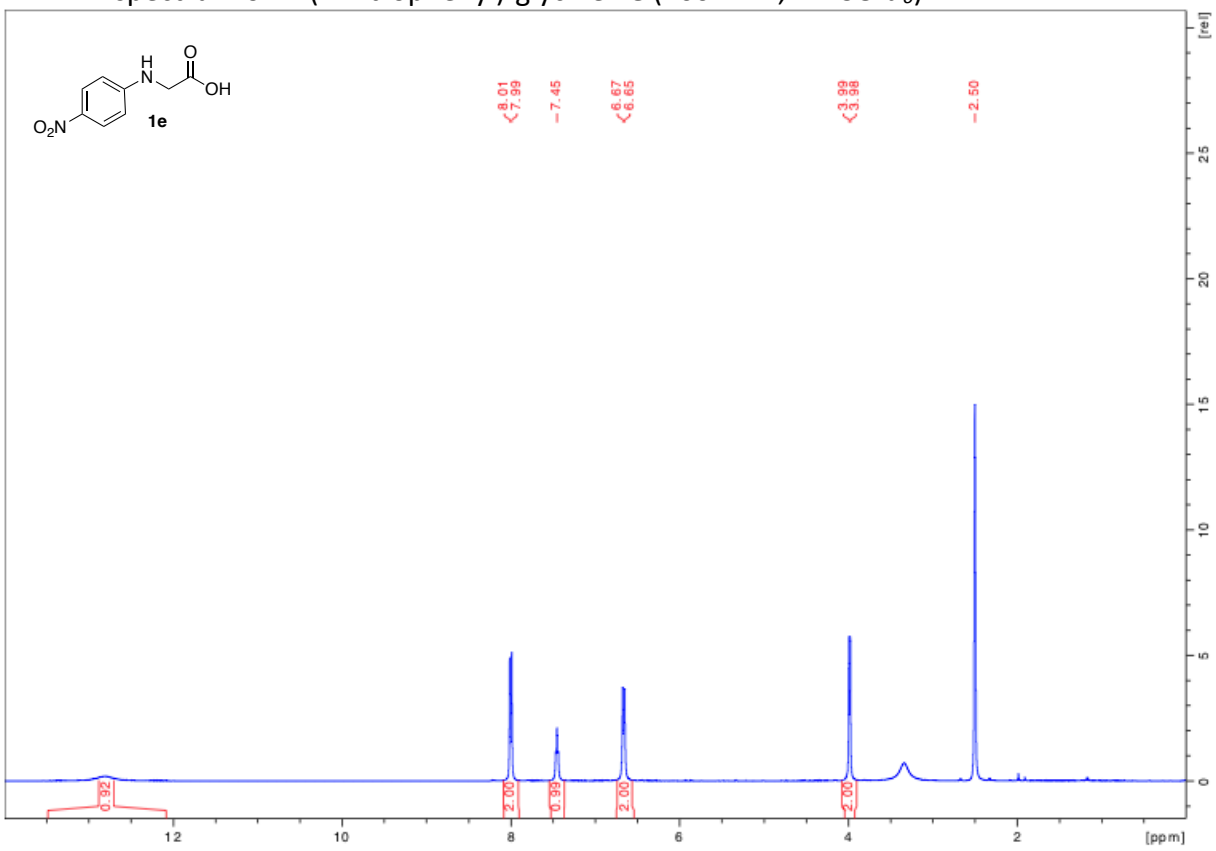
^{1}H NMR spectrum of *N*-(4-bromophenyl)-glycine **1d** (300 MHz, DMSO-d_6):



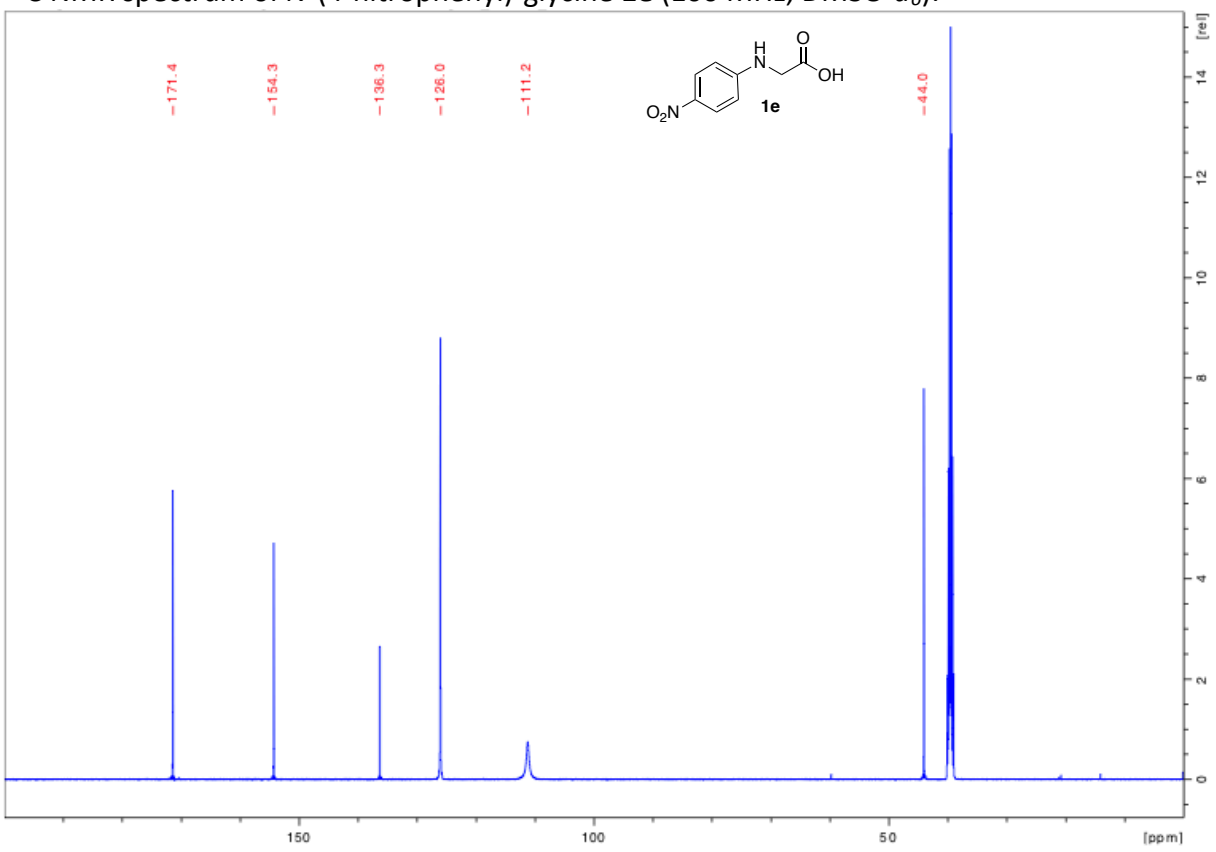
^{13}C NMR spectrum of *N*-(4-bromophenyl)-glycine **1d** (100 MHz, DMSO-d_6):



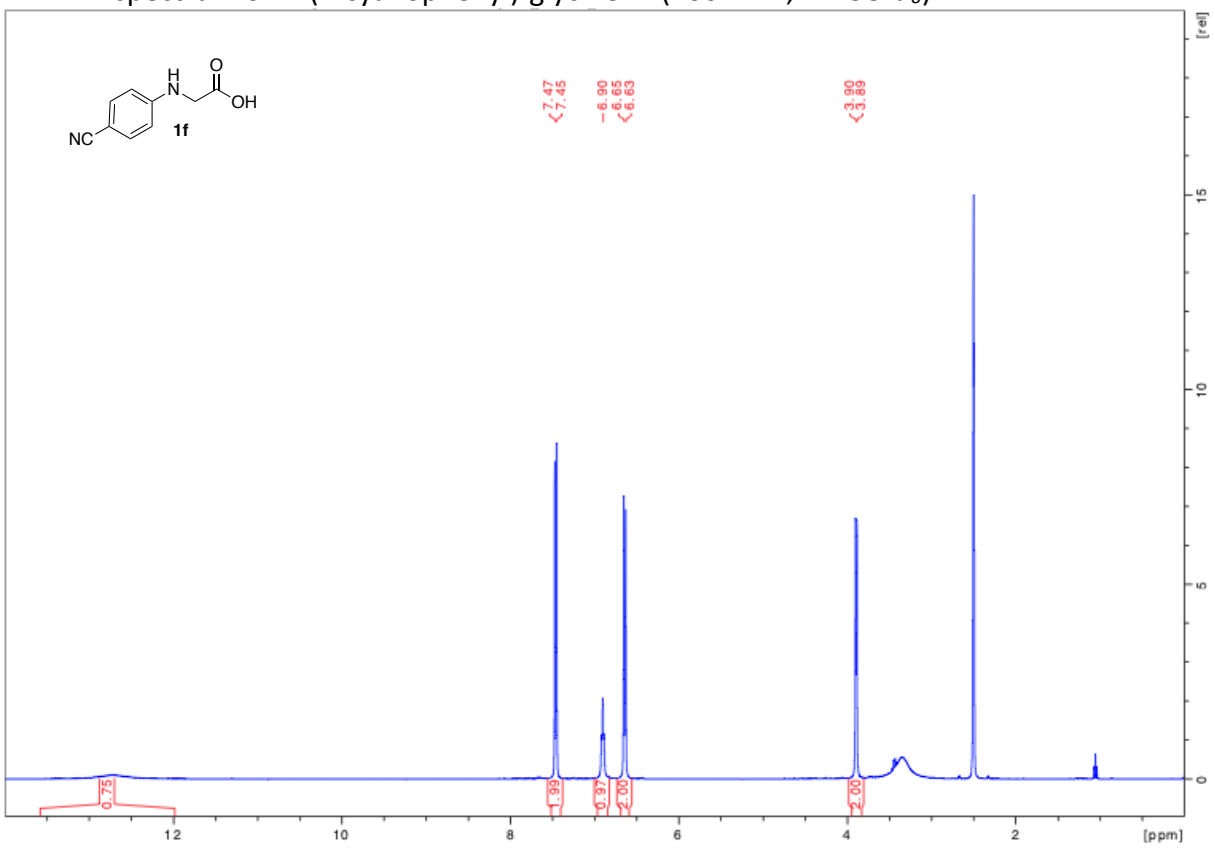
^{1}H NMR spectrum of *N*-(4-nitrophenyl)-glycine **1e** (400 MHz, DMSO-d_6):



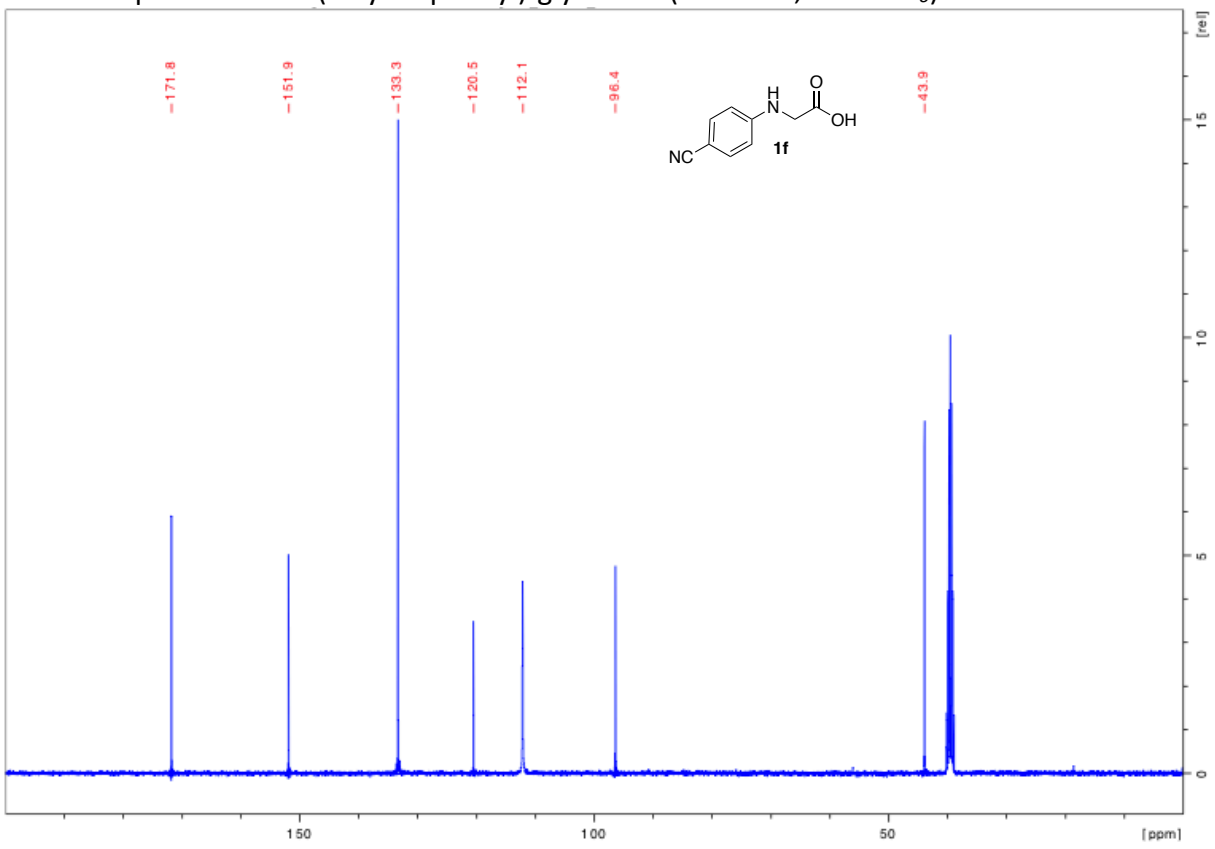
^{13}C NMR spectrum of *N*-(4-nitrophenyl)-glycine **1e** (100 MHz, DMSO-d_6):



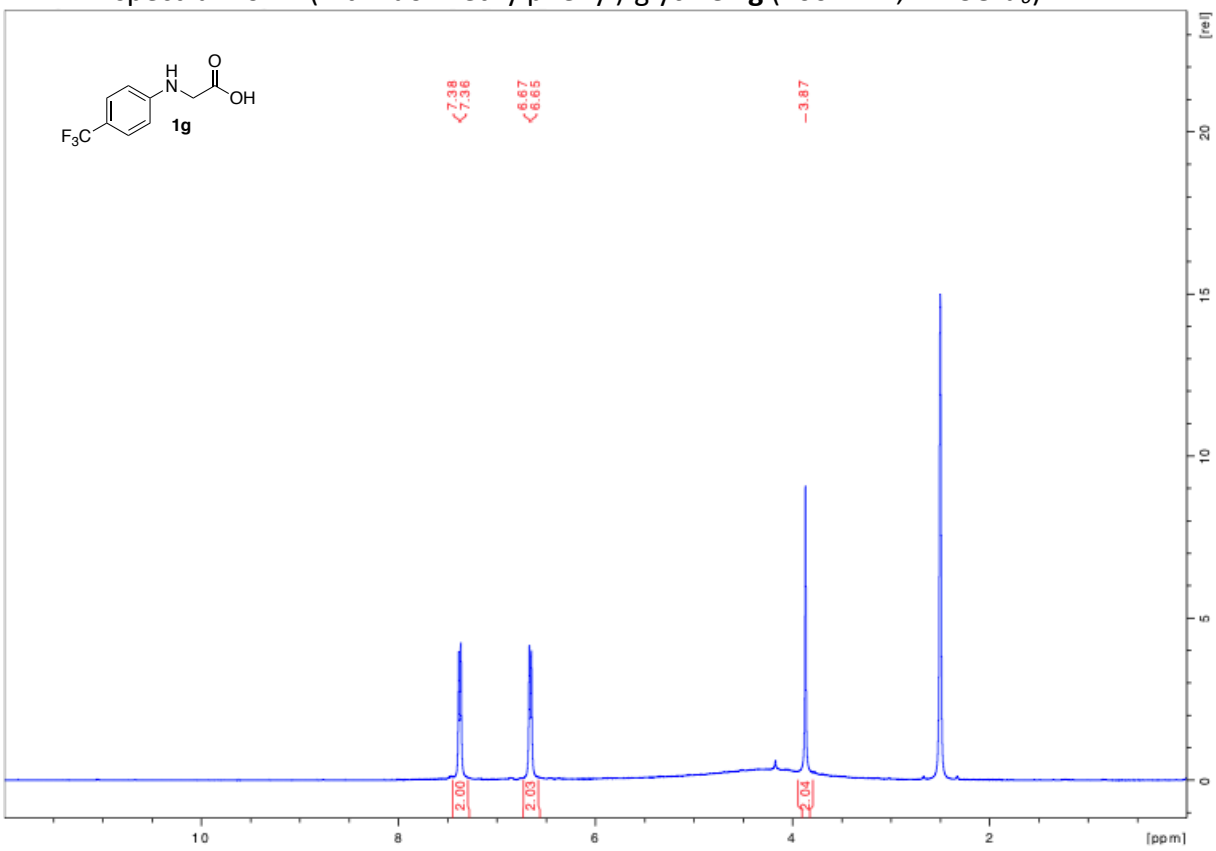
^{1}H NMR spectrum of *N*-(4-cyanophenyl)-glycine **1f** (400 MHz, DMSO-d_6):



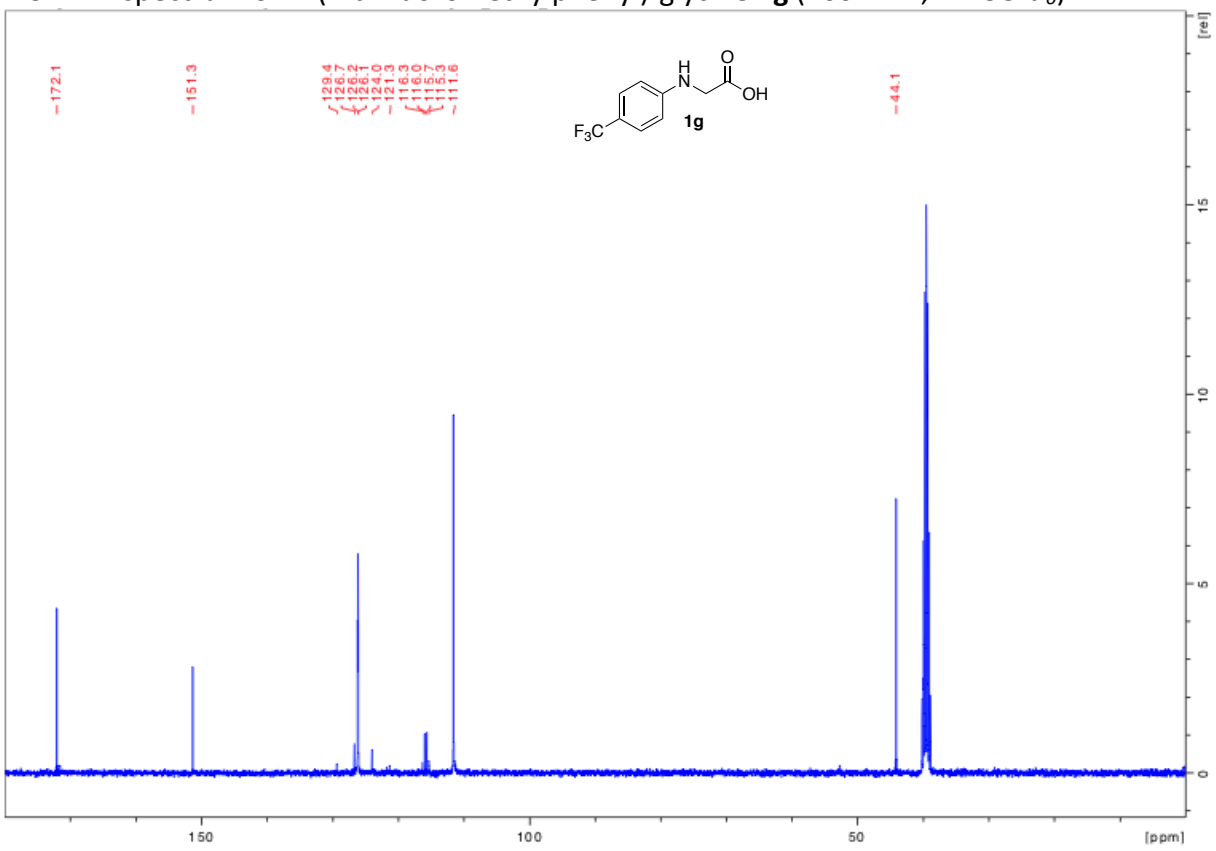
^{13}C NMR spectrum of *N*-(4-cyanophenyl)-glycine **1f** (100 MHz, DMSO-d_6):



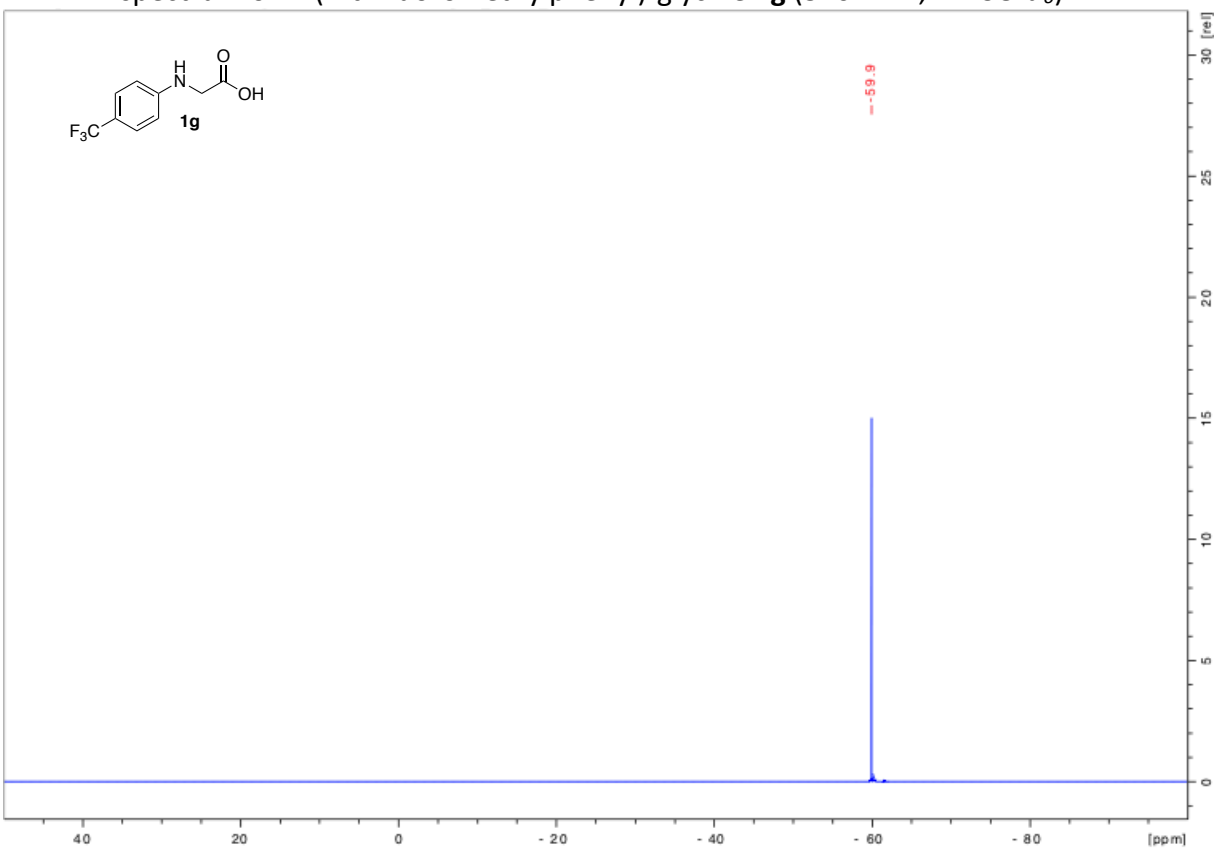
^{1}H NMR spectrum of *N*-(4-trifluormethylphenyl)-glycine **1g** (400 MHz, DMSO-d_6):



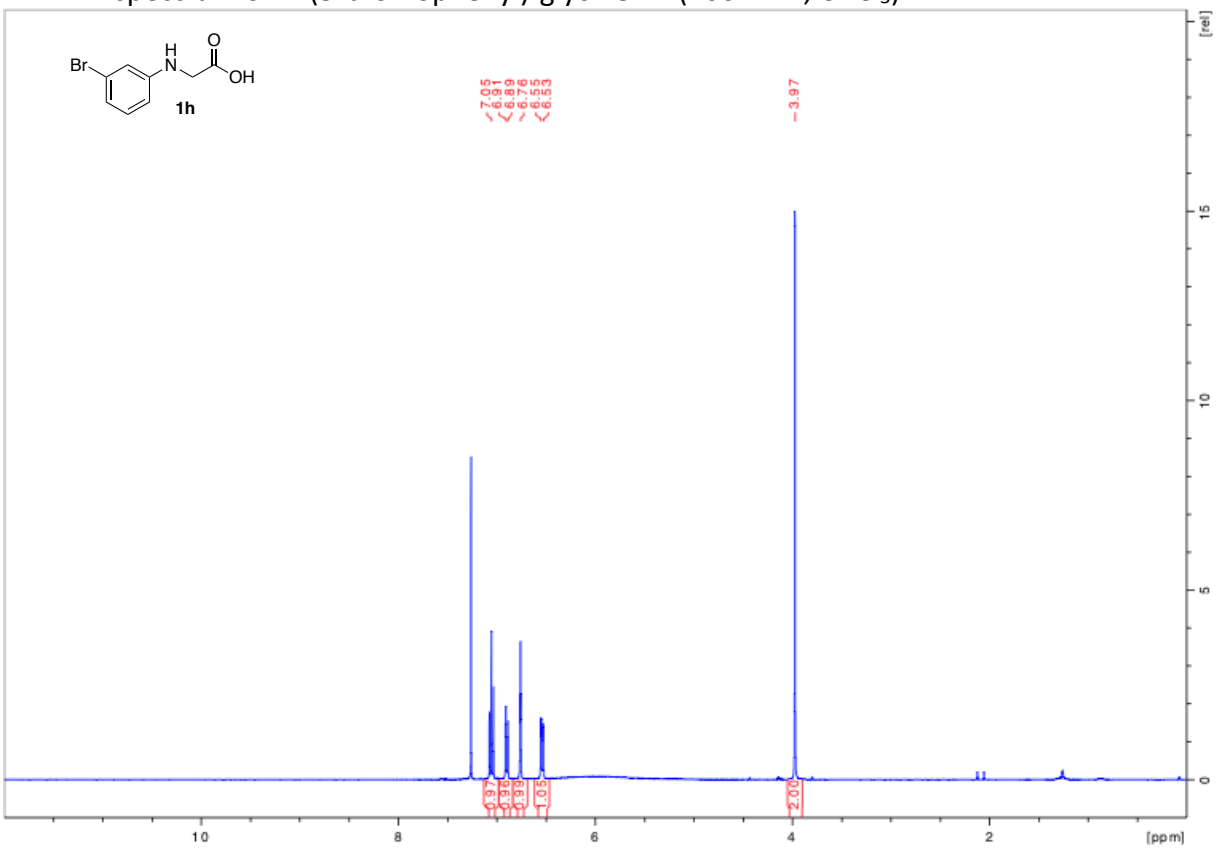
^{13}C NMR spectrum of *N*-(4-trifluoromethylphenyl)-glycine **1g** (100 MHz, DMSO-d_6):



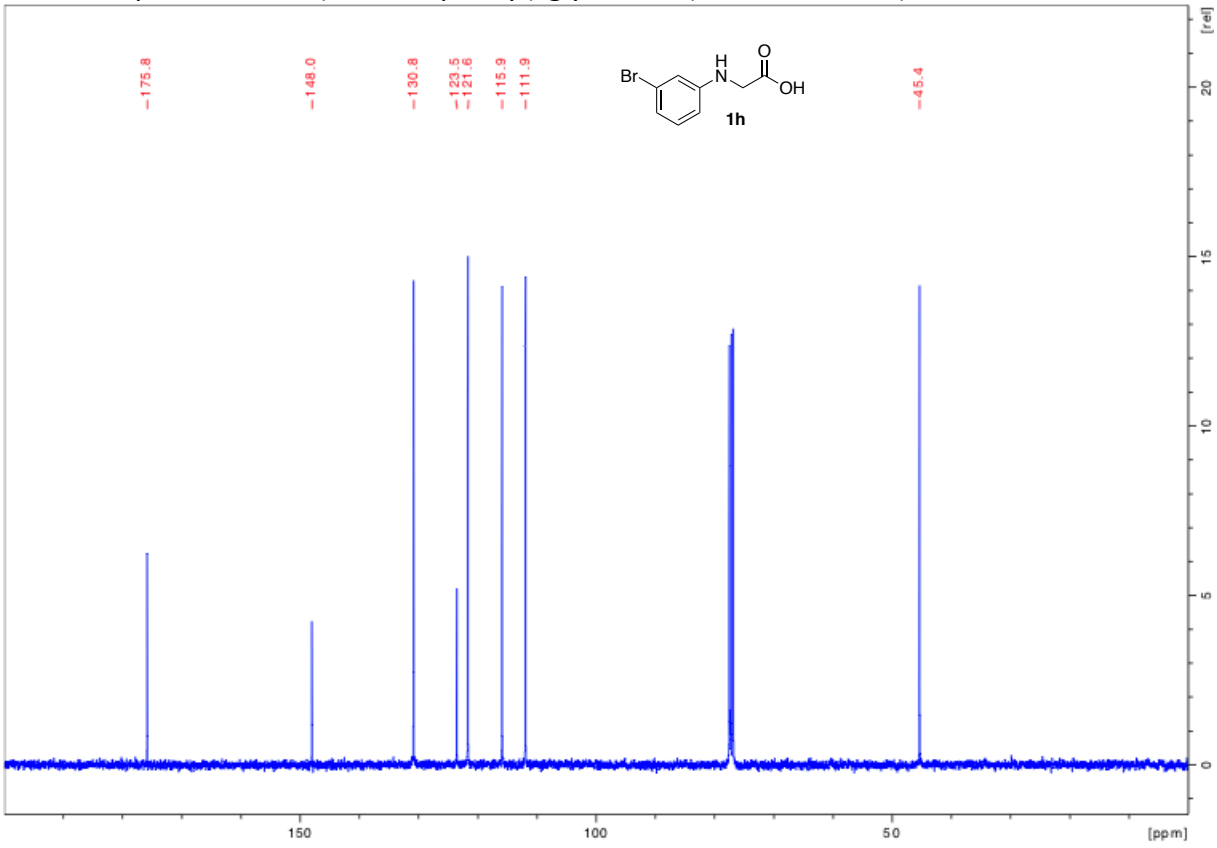
^{19}F NMR spectrum of *N*-(4-trifluoromethylphenyl)-glycine **1g** (376 MHz, DMSO-d_6):



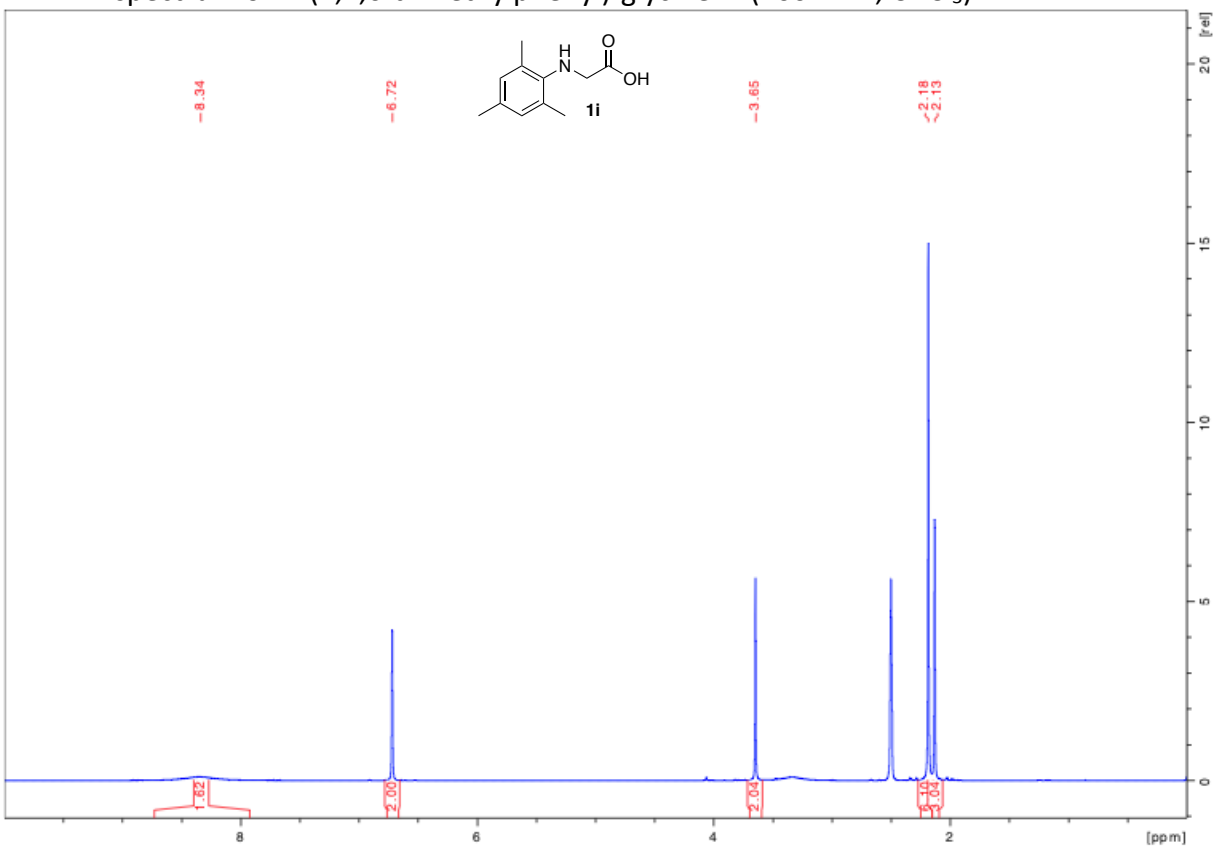
^{1}H NMR spectrum of *N*-(3-bromophenyl)-glycine **1h** (400 MHz, $CDCl_3$):



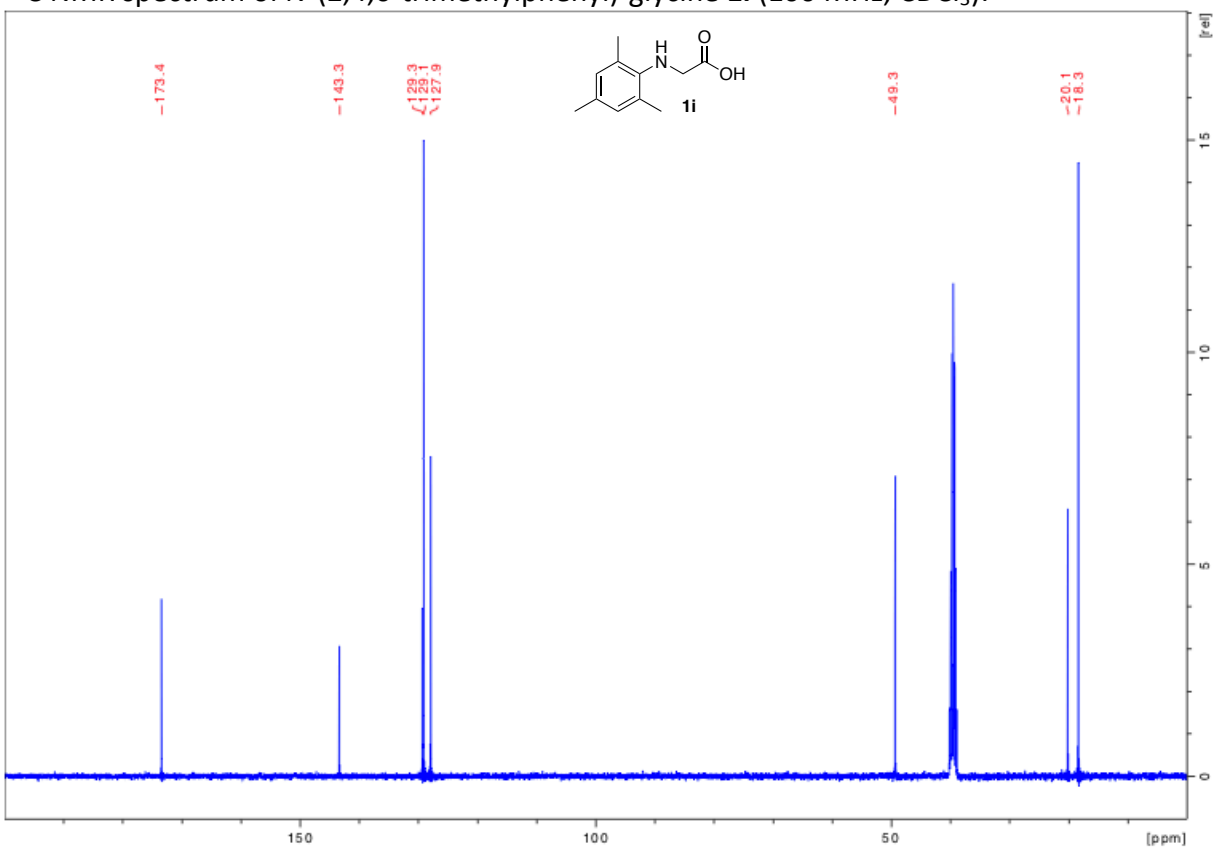
^{13}C NMR spectrum of *N*-(3-bromophenyl)-glycine **1h** (100 MHz, $CDCl_3$):



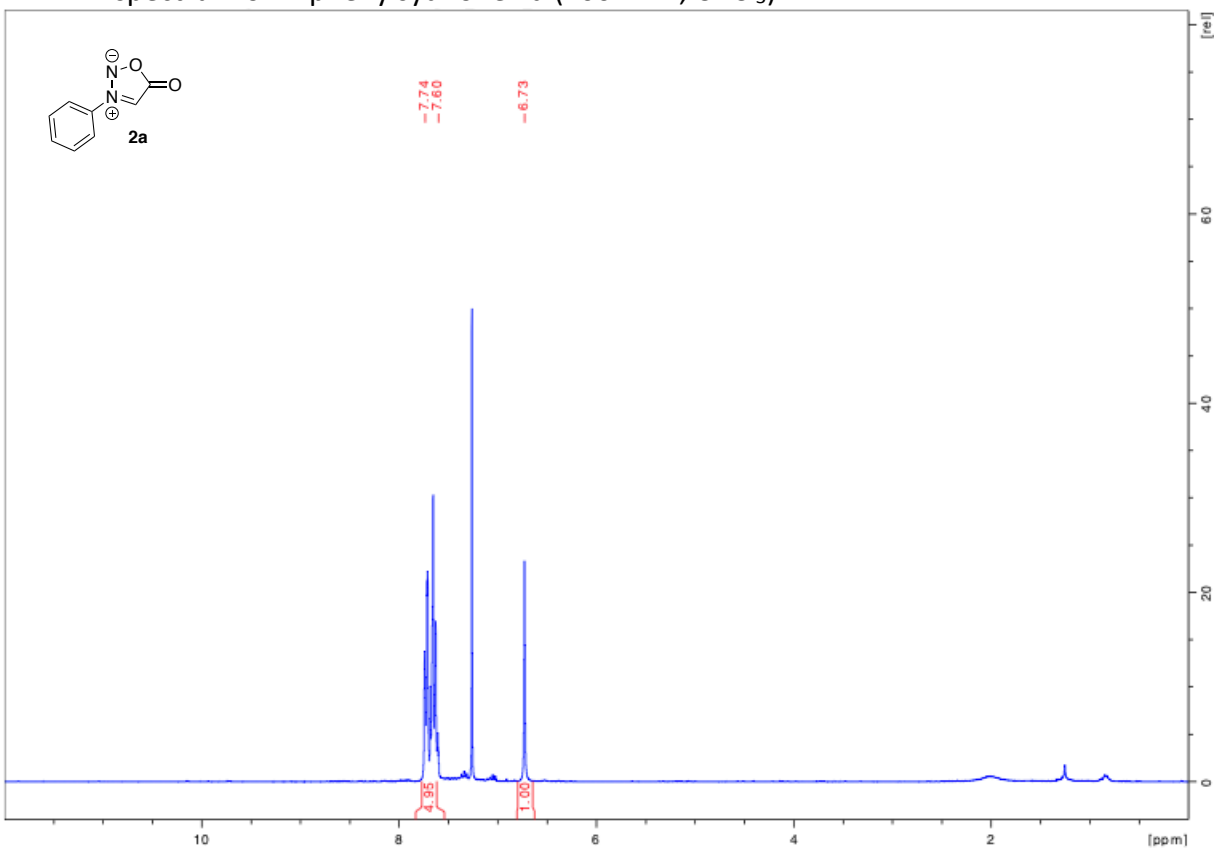
^{1}H NMR spectrum of *N*-(2,4,6-trimethylphenyl)-glycine **1i** (400 MHz, $CDCl_3$):



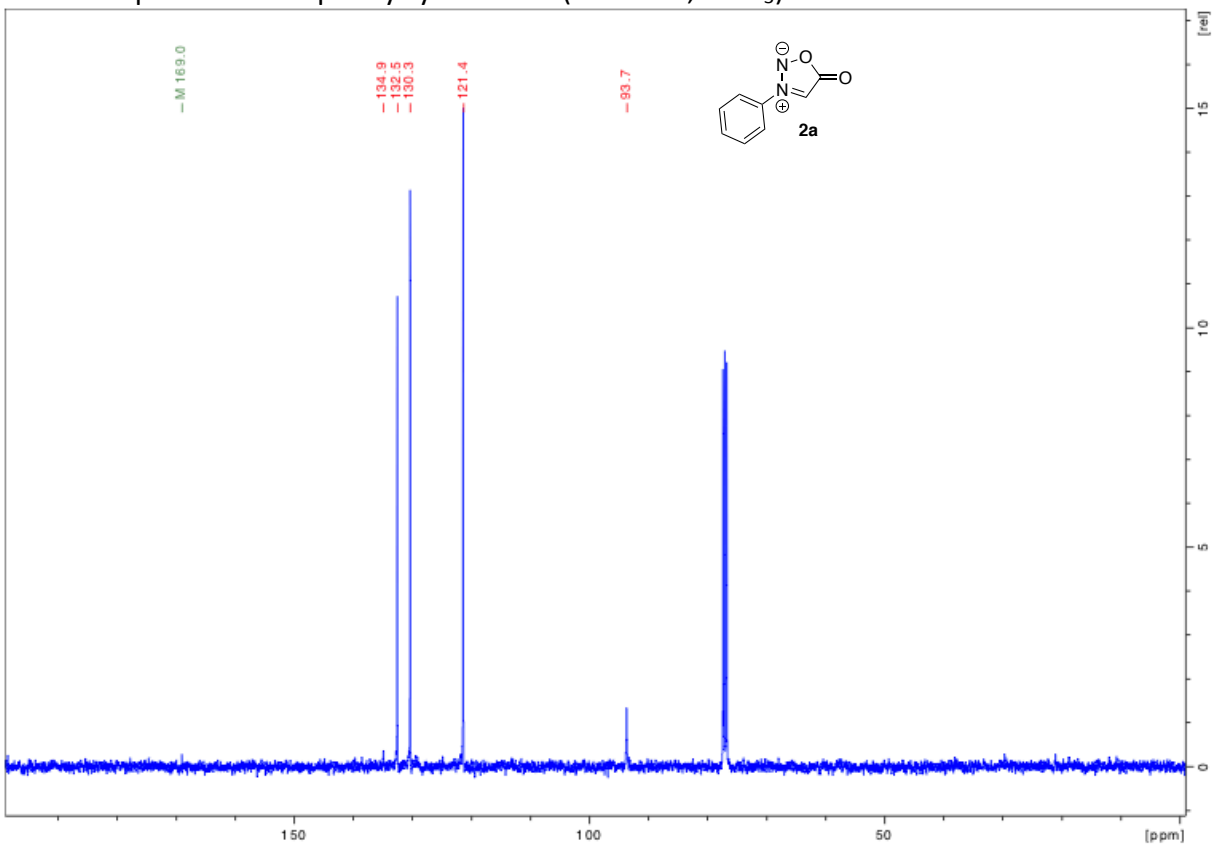
^{13}C NMR spectrum of *N*-(2,4,6-trimethylphenyl)-glycine **1i** (100 MHz, $CDCl_3$):



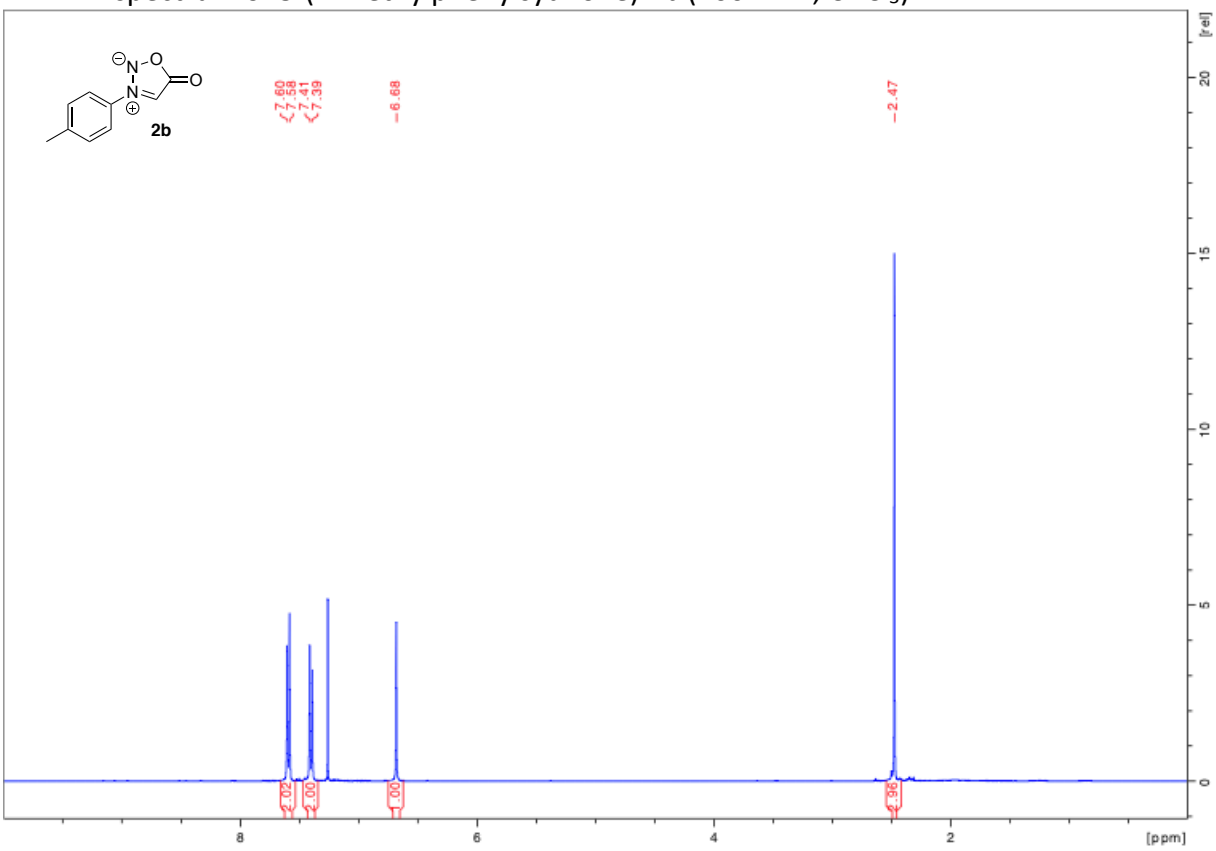
^{1}H NMR spectrum of *N*-phenylsydnone **2a** (400 MHz, $CDCl_3$):



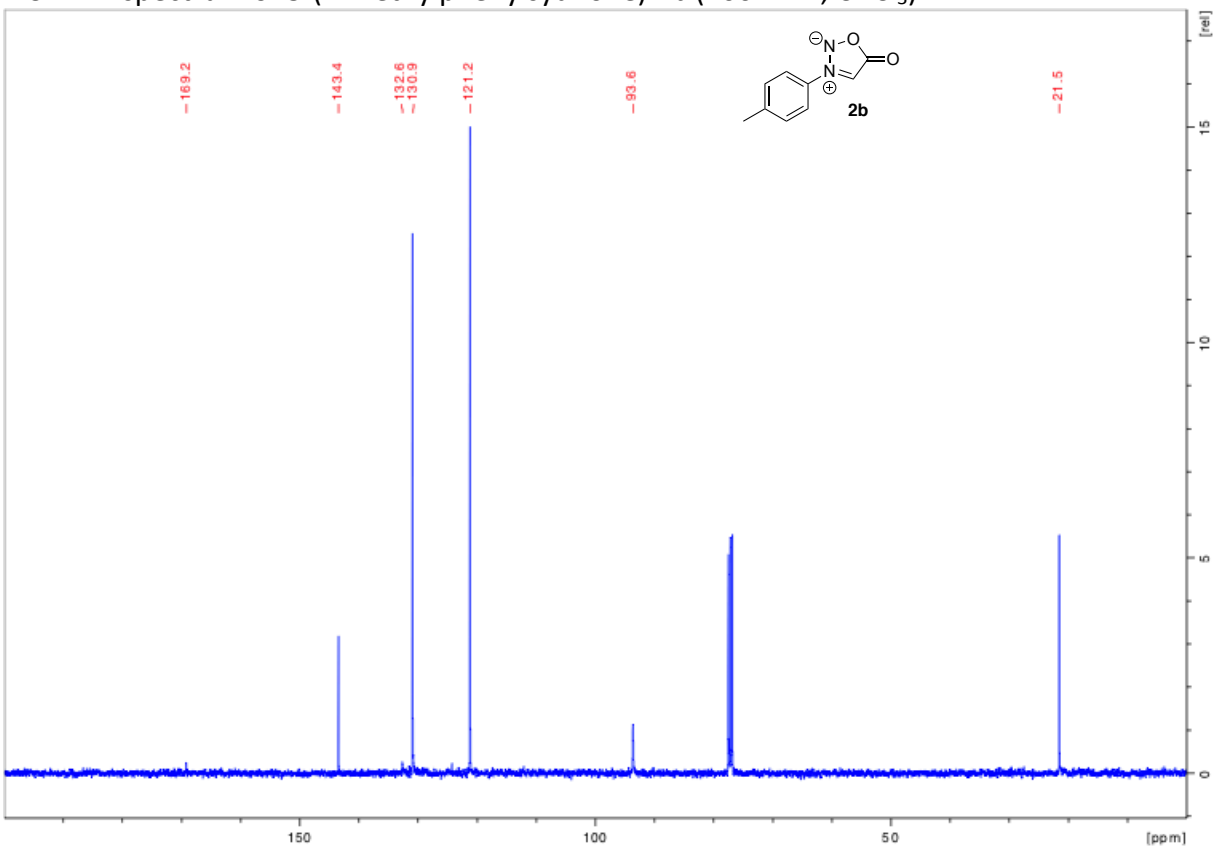
^{13}C NMR spectrum of *N*-phenylsydnone **2a** (100 MHz, $CDCl_3$):



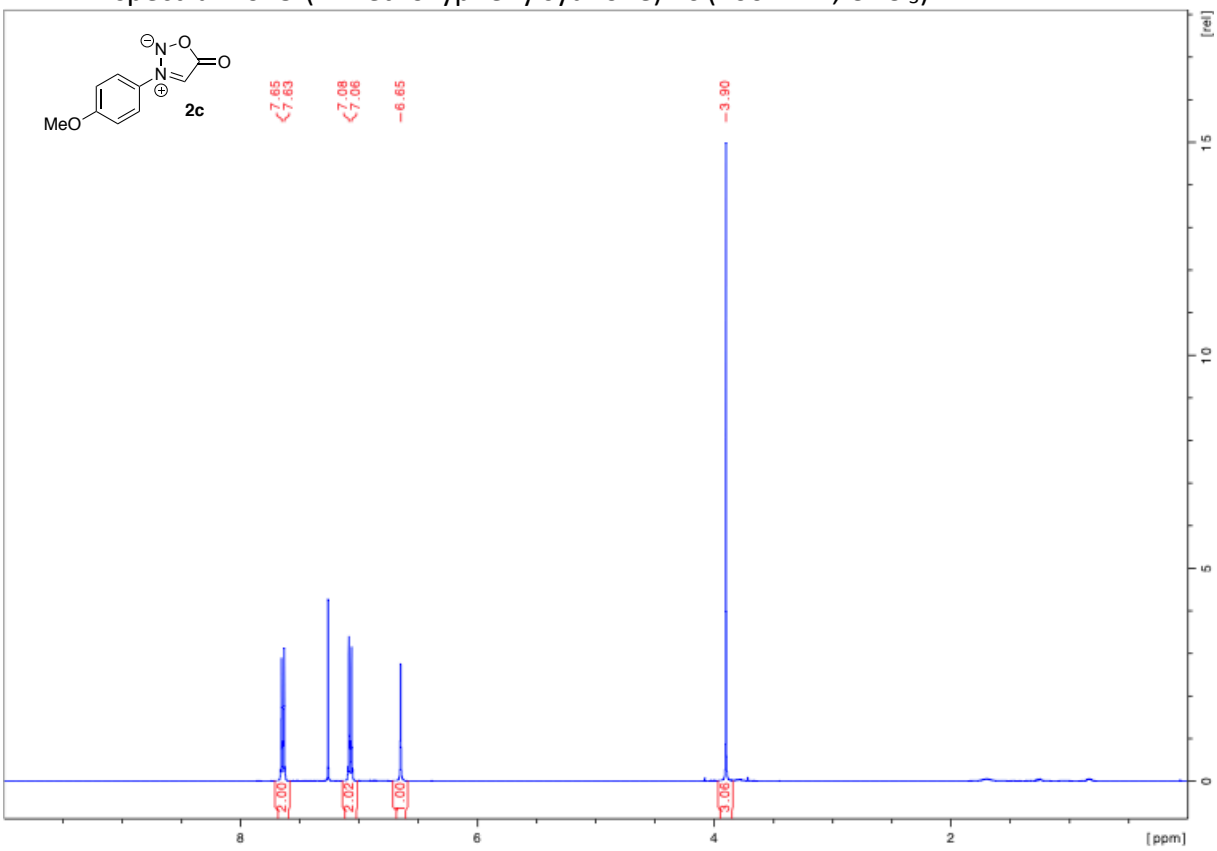
^{1}H NMR spectrum of 3-(4-methylphenylsydnone) **2b** (400 MHz, $CDCl_3$):



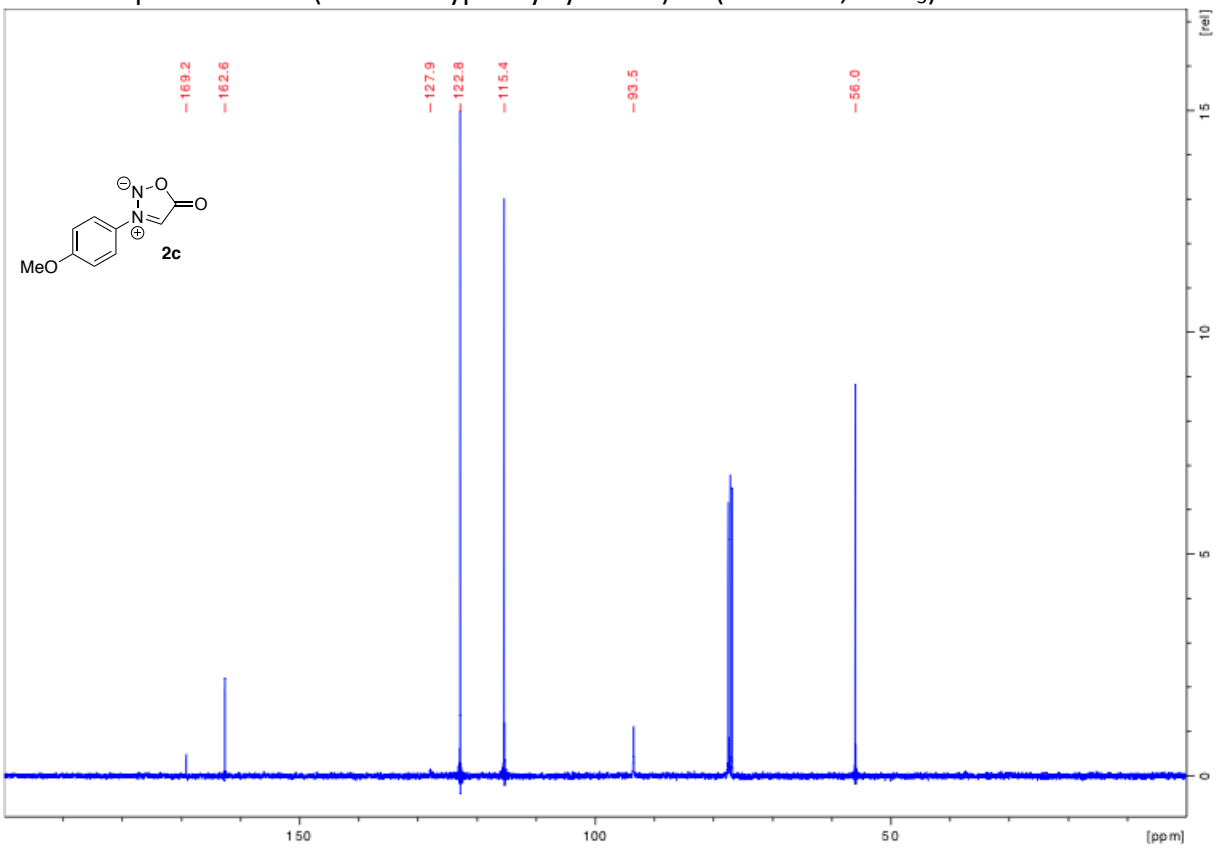
^{13}C NMR spectrum of 3-(4-methylphenylsydnone) **2b** (100 MHz, $CDCl_3$):



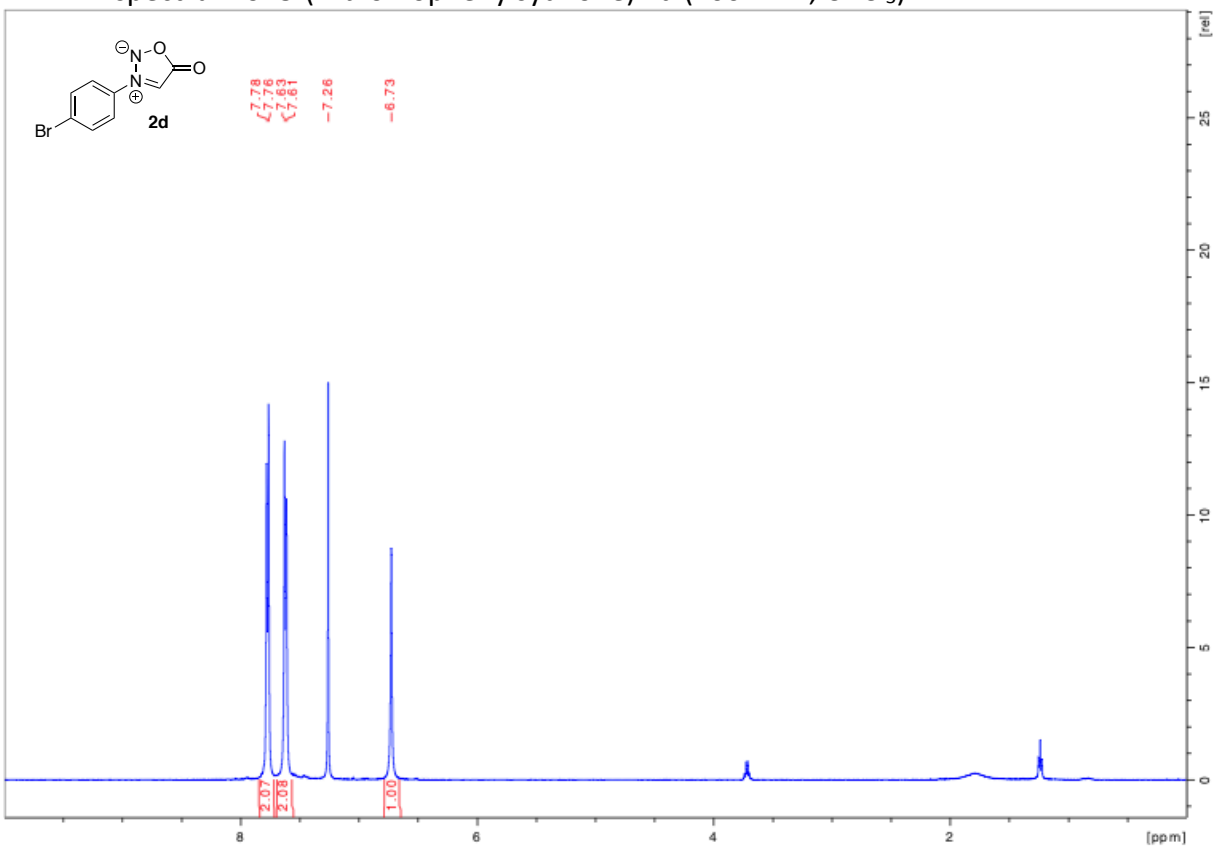
^{1}H NMR spectrum of 3-(4-methoxyphenylsydnone) **2c** (400 MHz, $CDCl_3$):



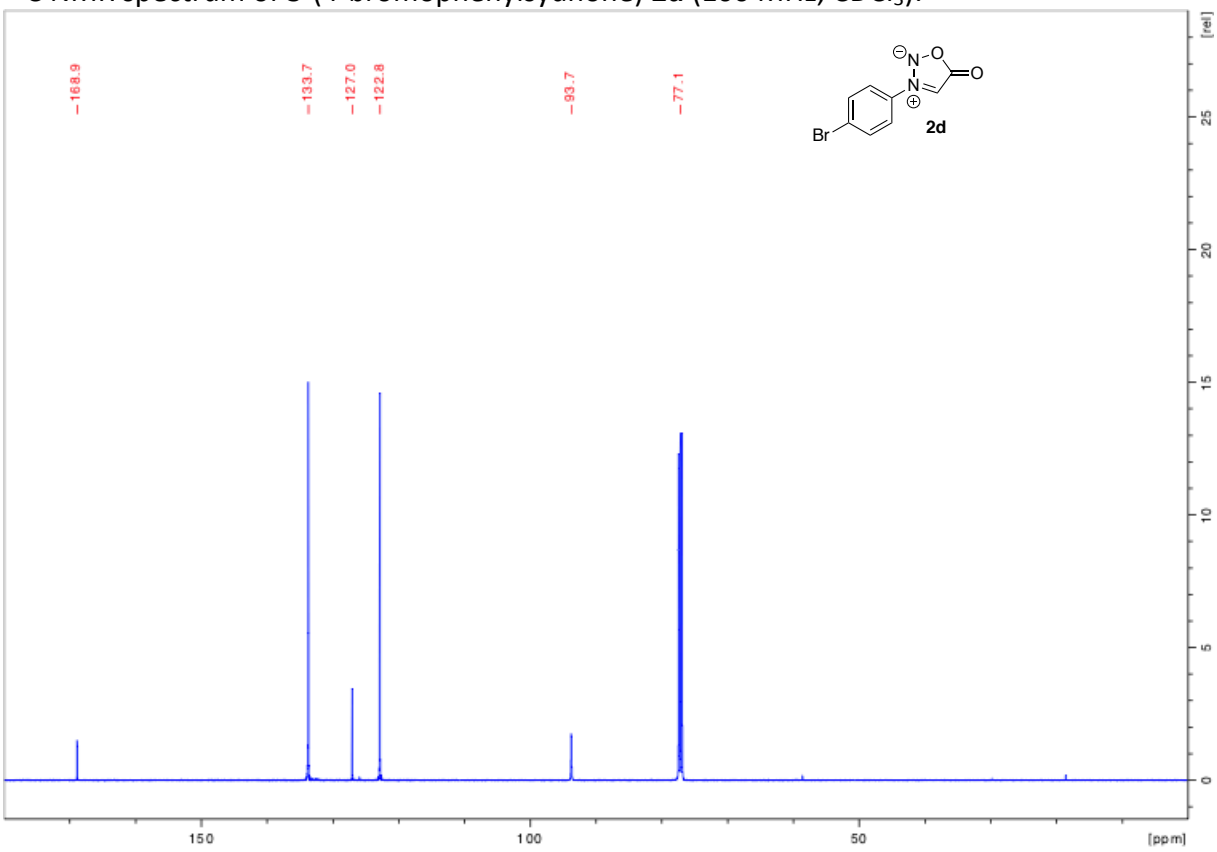
^{13}C NMR spectrum of 3-(4-methoxyphenylsydnone) **2c** (100 MHz, $CDCl_3$):



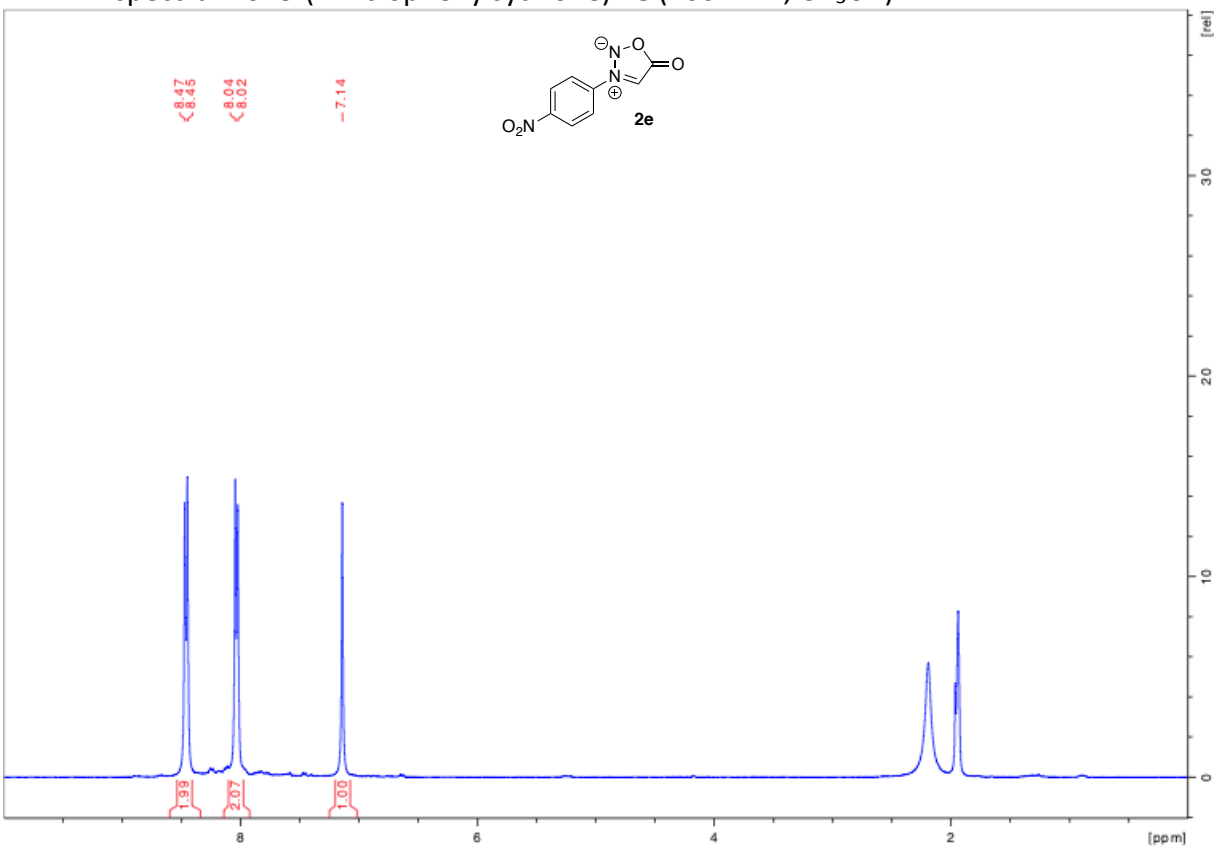
^{1}H NMR spectrum of 3-(4-bromophenylsydnone) **2d** (400 MHz, $CDCl_3$):



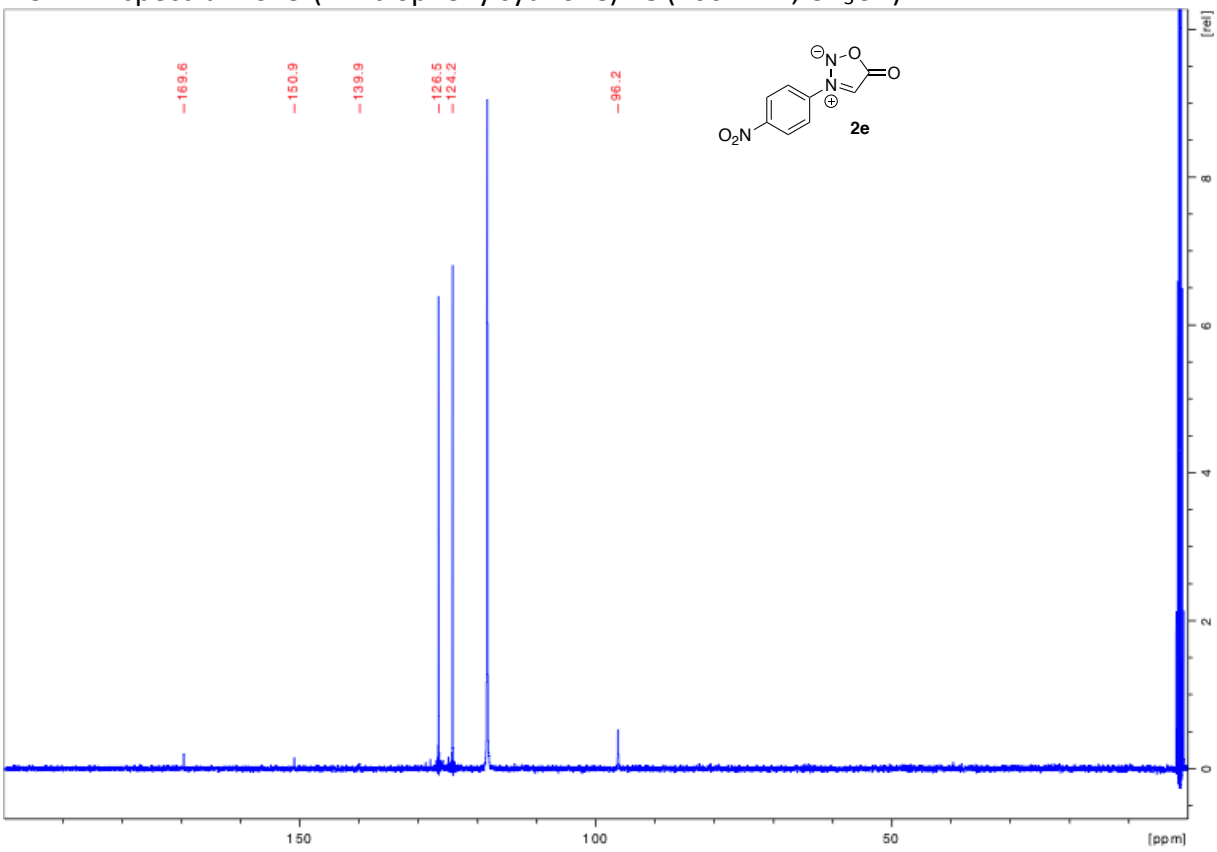
^{13}C NMR spectrum of 3-(4-bromophenylsydnone) **2d** (100 MHz, $CDCl_3$):



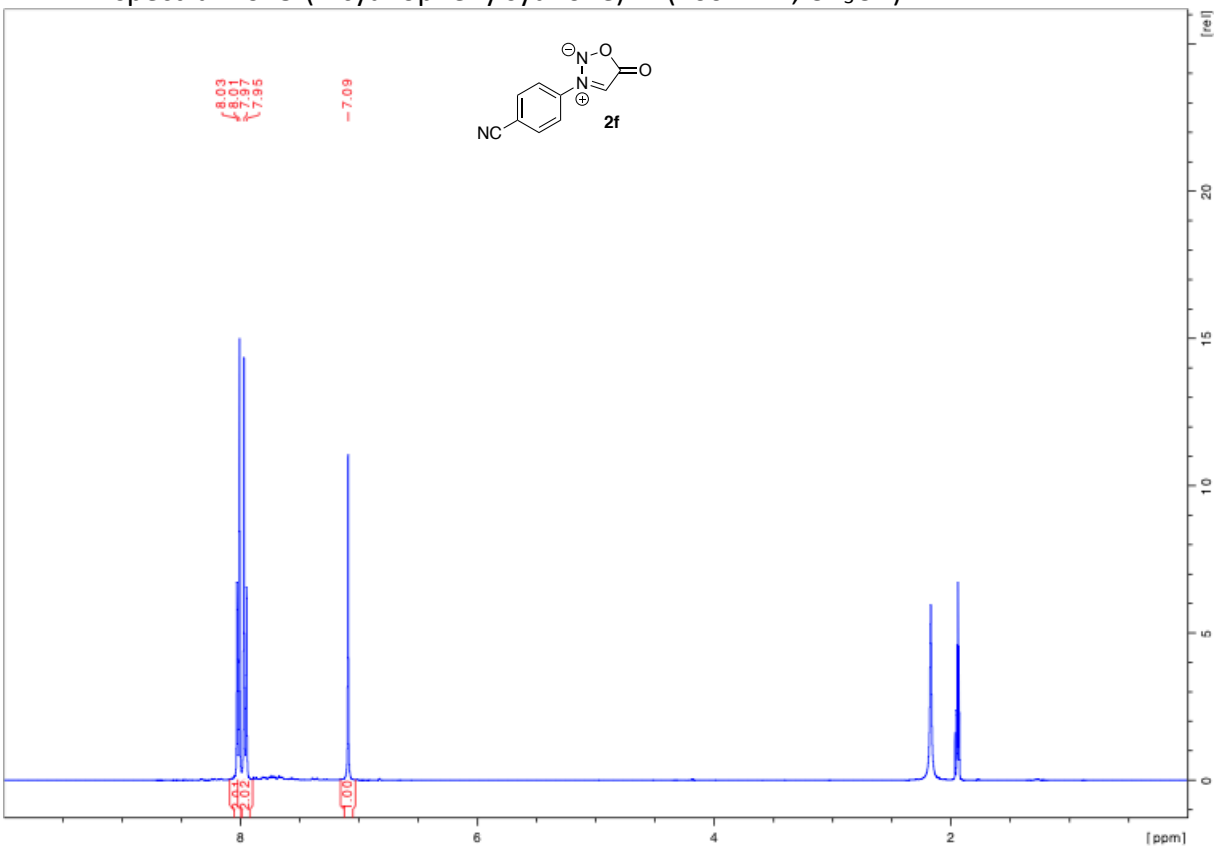
^{1}H NMR spectrum of 3-(4-nitrophenylsydnone) **2e** (400 MHz, CD_3CN):



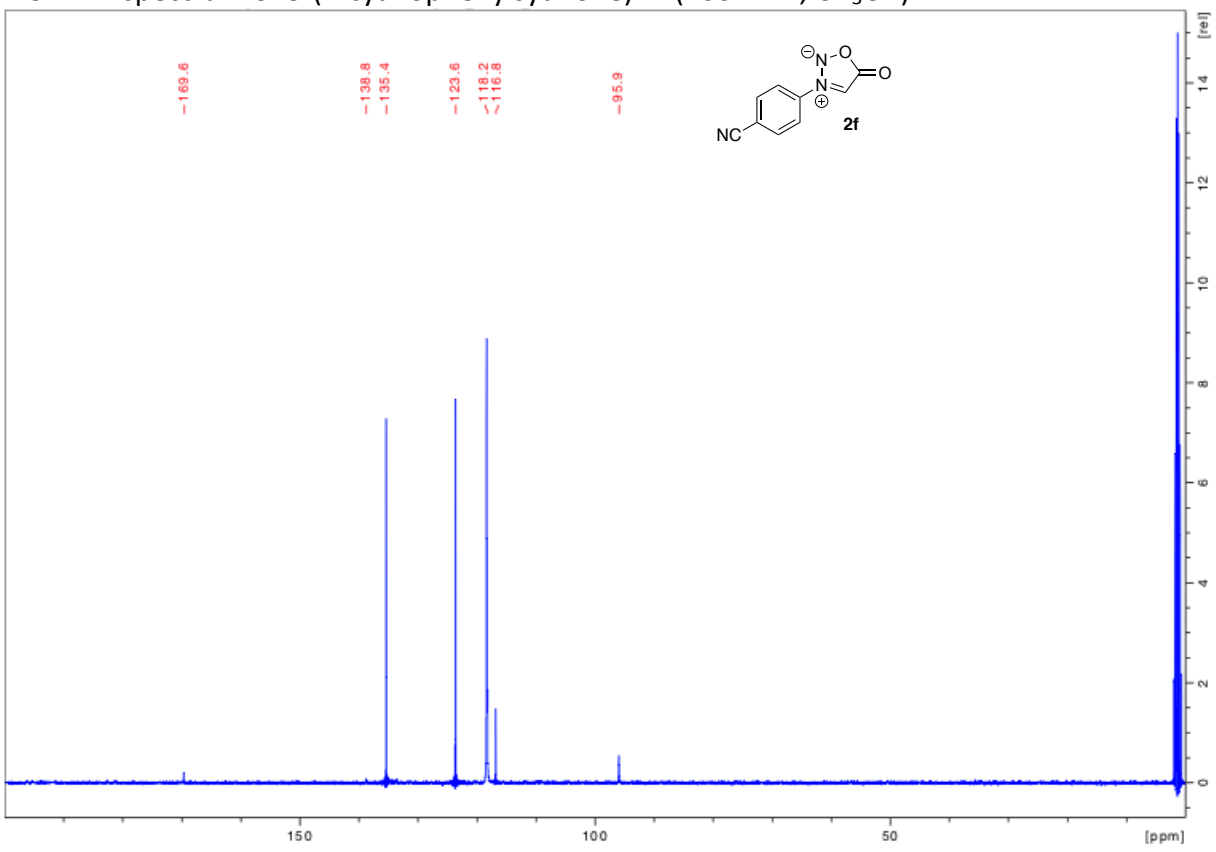
^{13}C NMR spectrum of 3-(4-nitrophenylsydnone) **2e** (100 MHz, CD_3CN):



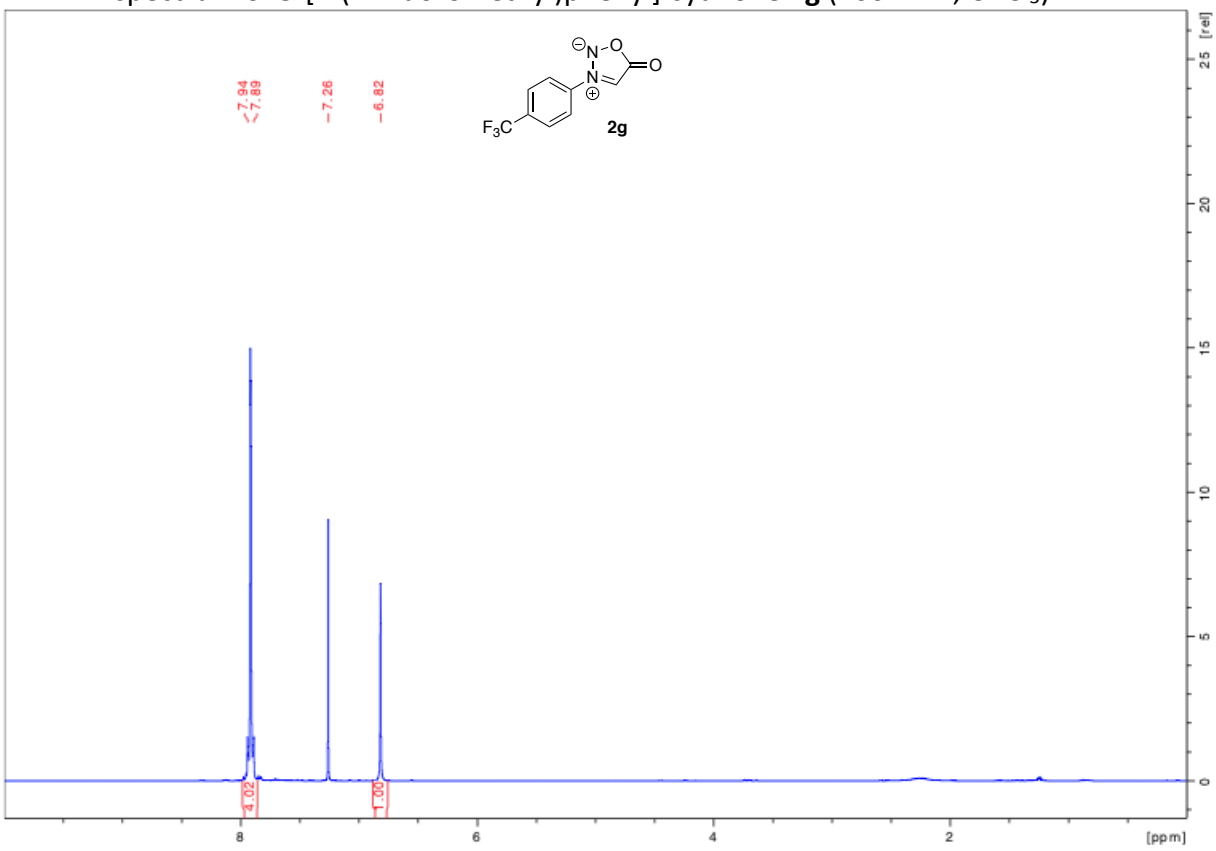
^{1}H NMR spectrum of 3-(4-cyanophenylsydnone) **2f** (400 MHz, CD_3CN):



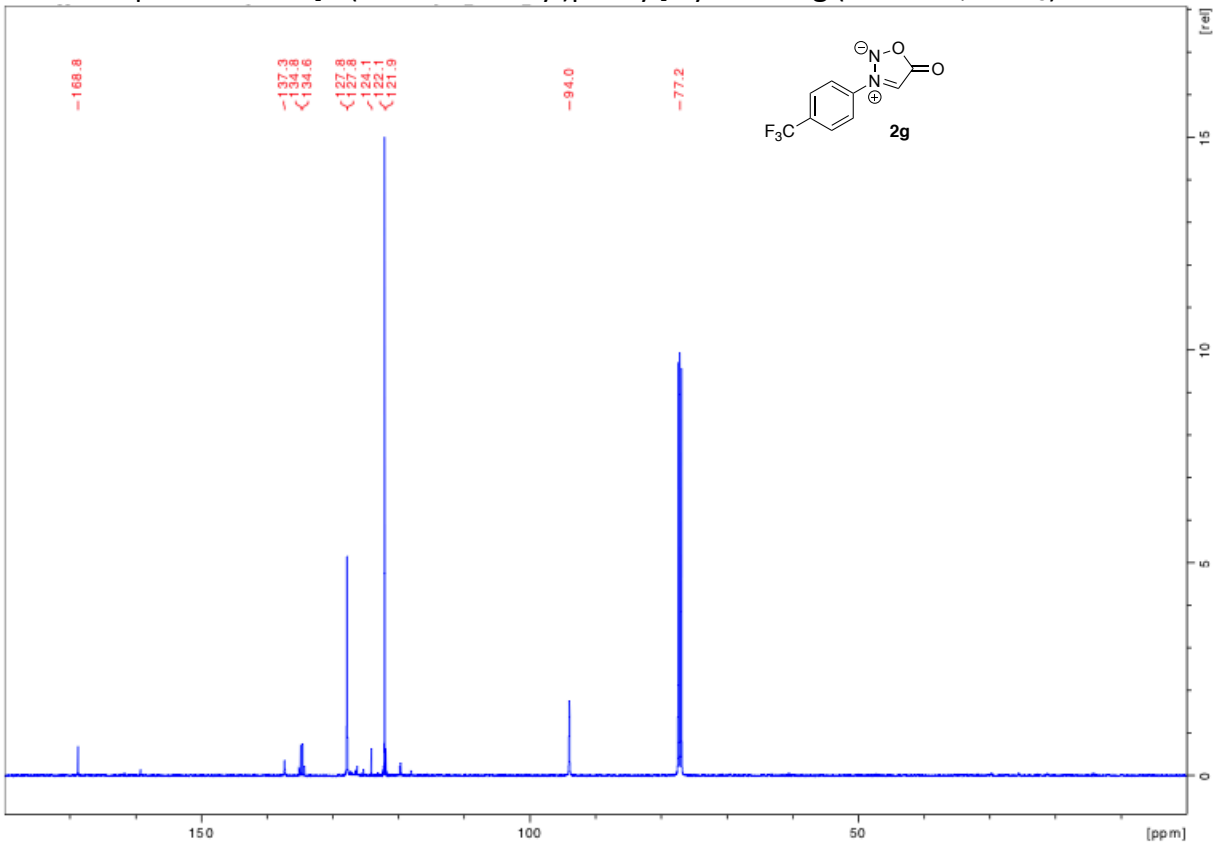
^{13}C NMR spectrum of 3-(4-cyanophenylsydnone) **2f** (100 MHz, CD_3CN):



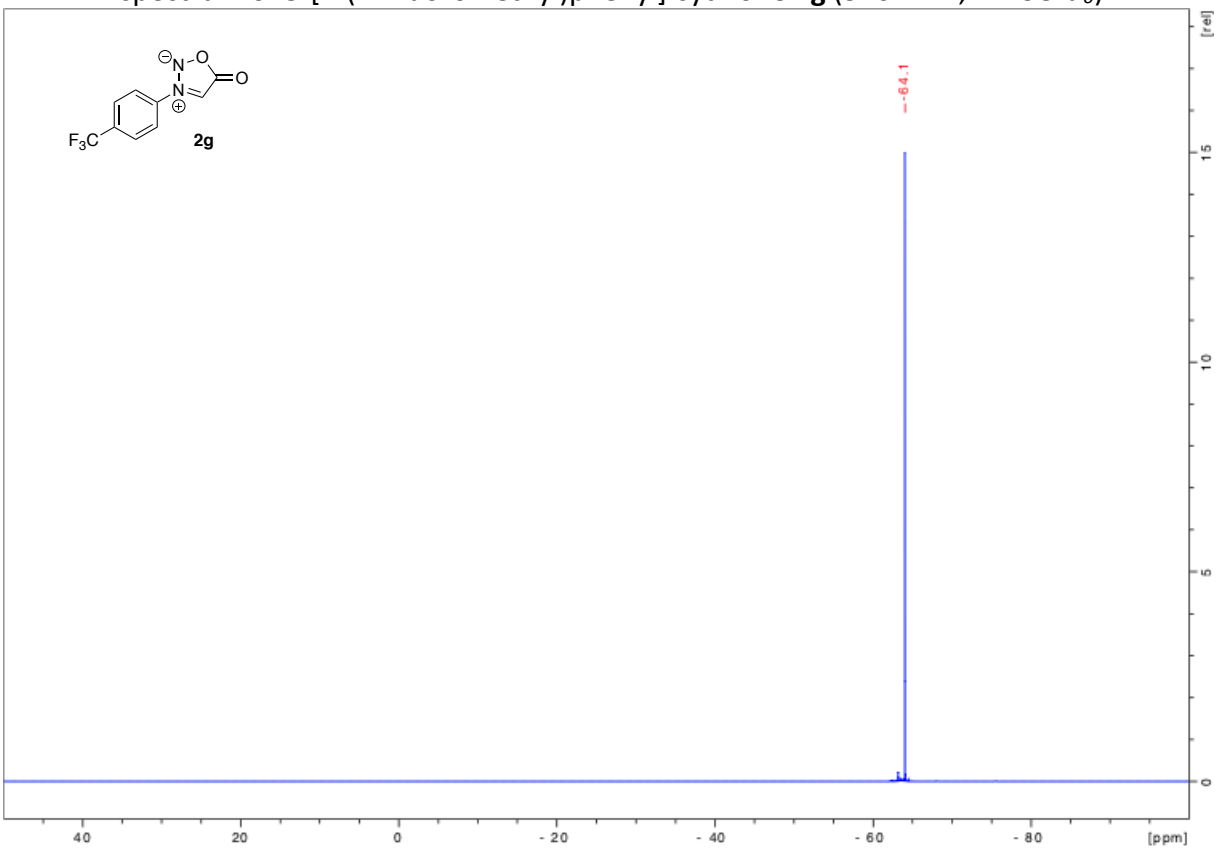
^{1}H NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (400 MHz, $CDCl_3$):



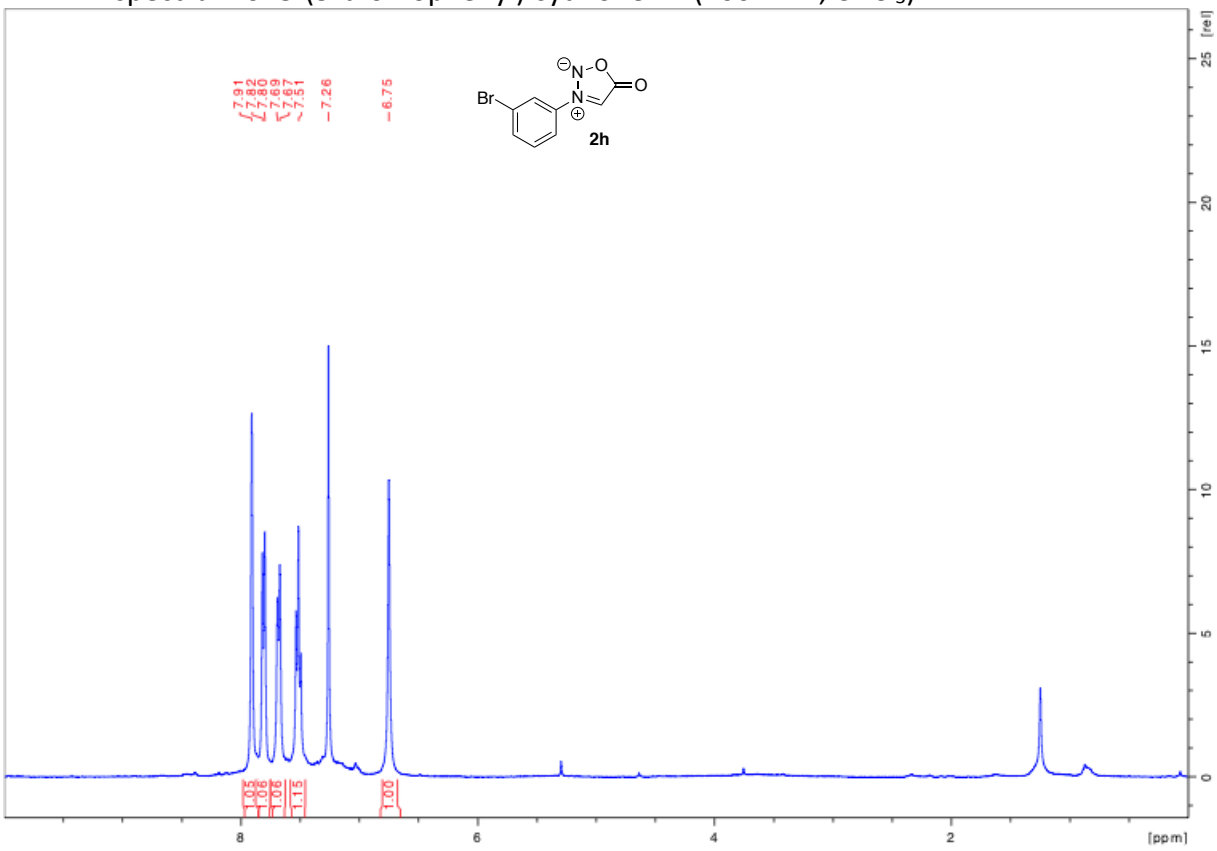
^{13}C NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (100 MHz, $CDCl_3$):



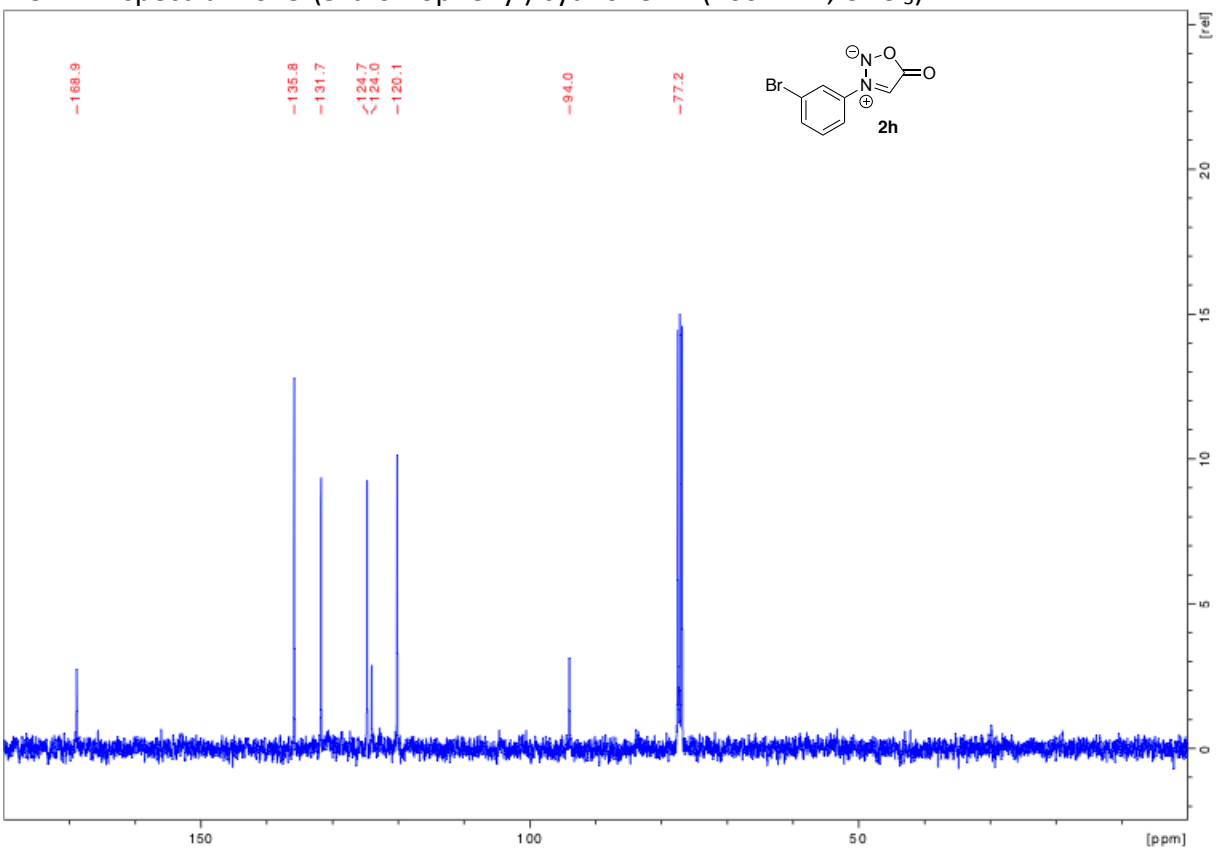
^{19}F NMR spectrum of 3-[4-(Trifluoromethyl)phenyl]-sydnone **2g** (376 MHz, DMSO-d_6):



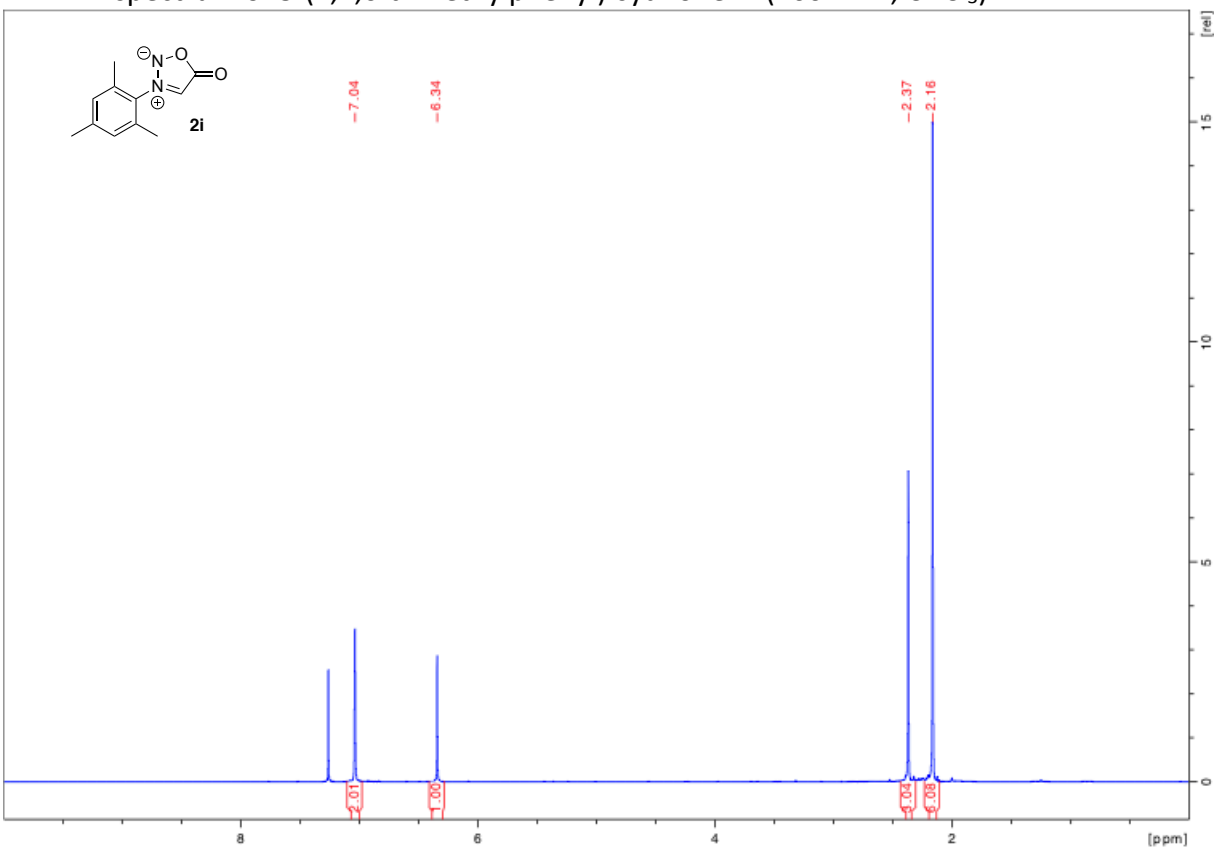
^{1}H NMR spectrum of 3-(3-bromophenyl)-sydnone **2h** (400 MHz, $CDCl_3$):



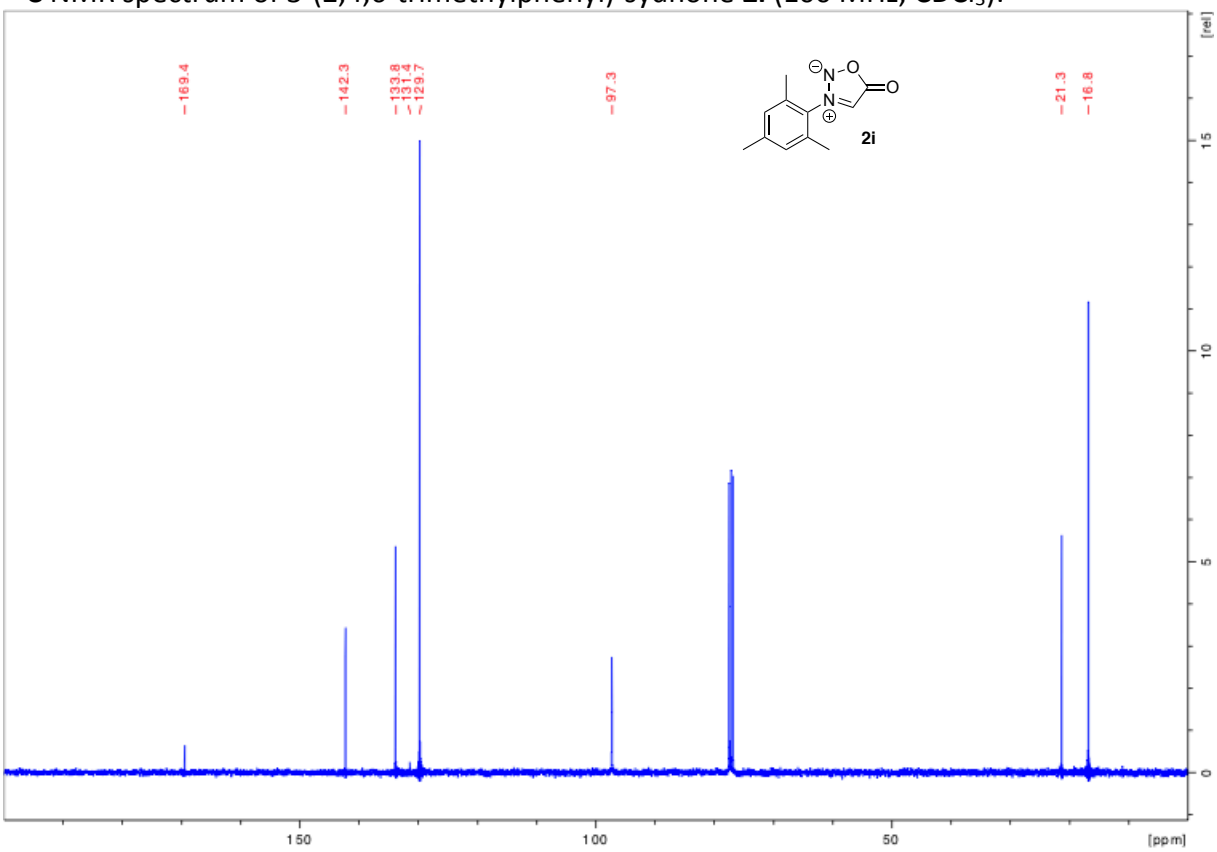
^{13}C NMR spectrum of 3-(3-bromophenyl)-sydnone **2h** (100 MHz, $CDCl_3$):



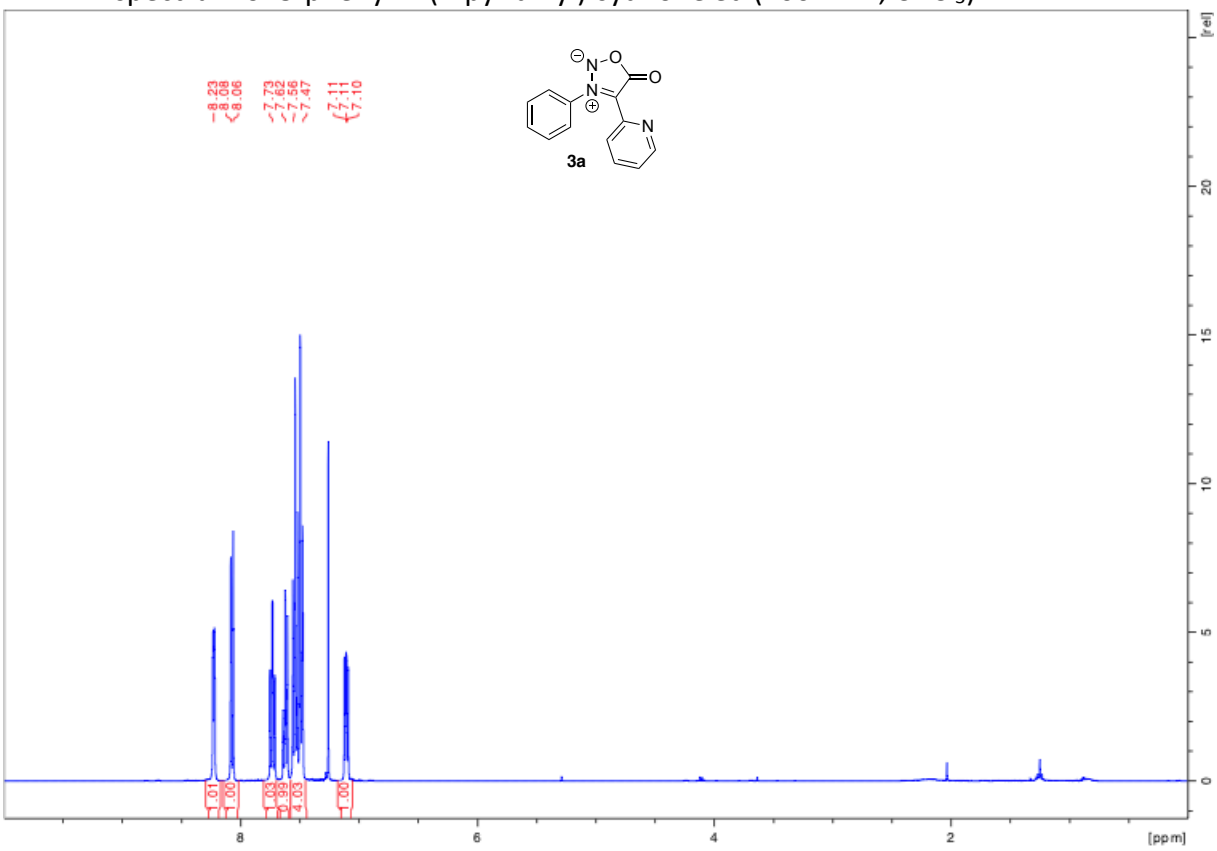
^{1}H NMR spectrum of 3-(2,4,6-trimethylphenyl)-sydnone **2i** (400 MHz, $CDCl_3$):



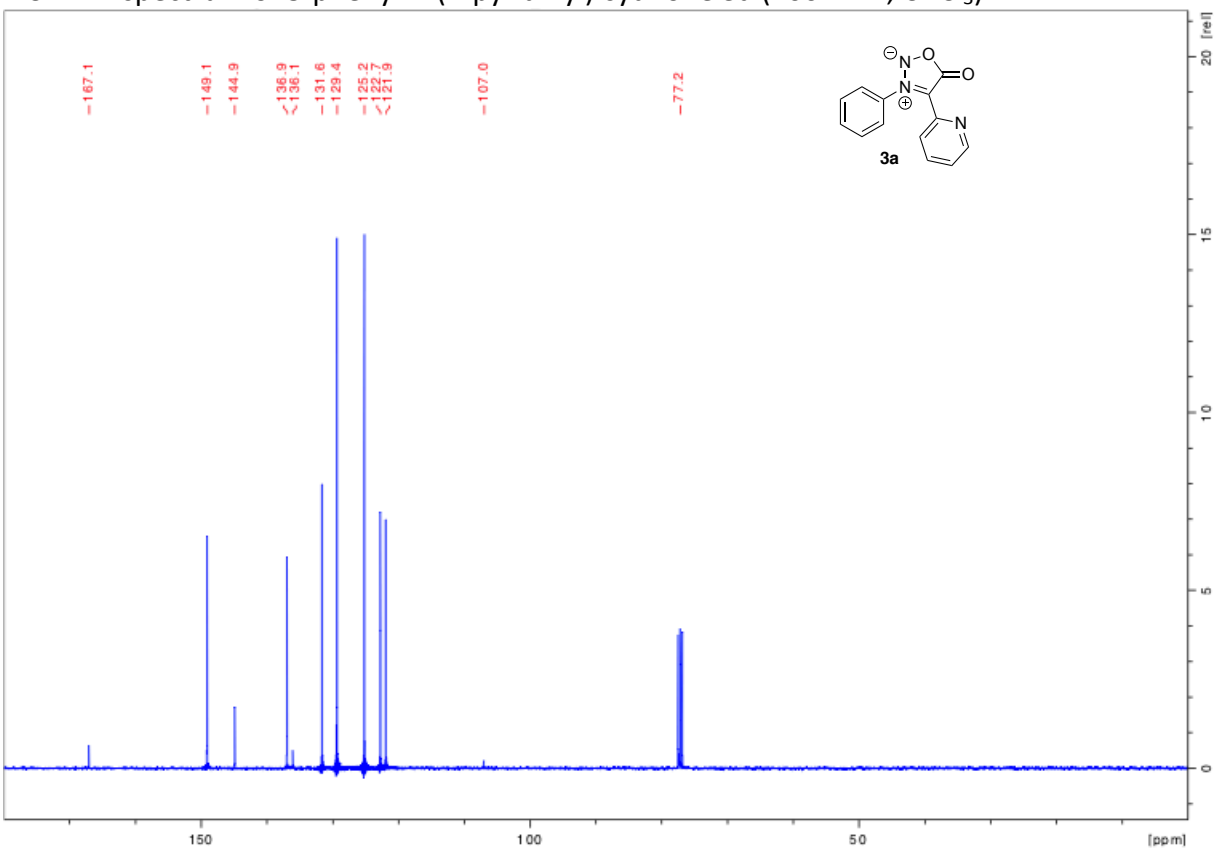
^{13}C NMR spectrum of 3-(2,4,6-trimethylphenyl)-sydnone **2i** (100 MHz, $CDCl_3$):



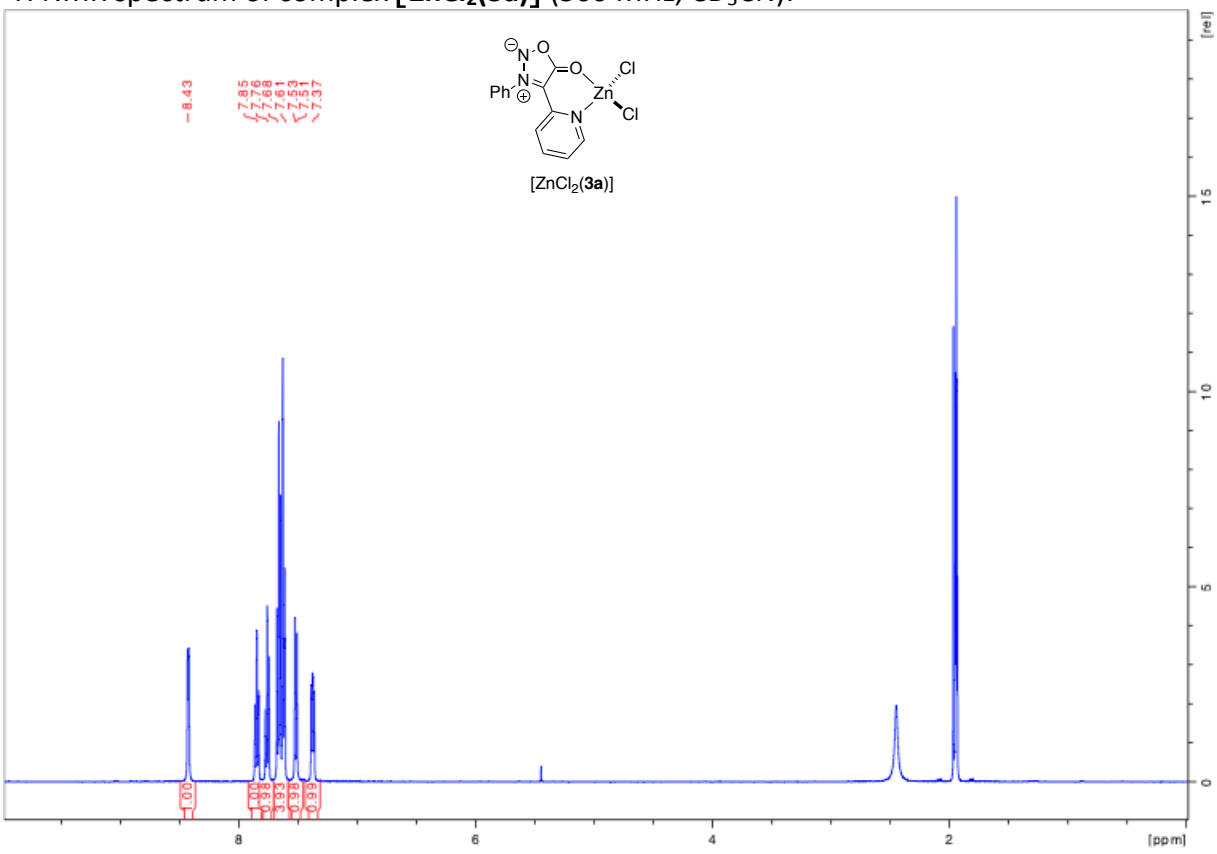
^{1}H NMR spectrum of 3-phenyl-4-(2-pyridinyl)-sydnone **3a** (400 MHz, $CDCl_3$):



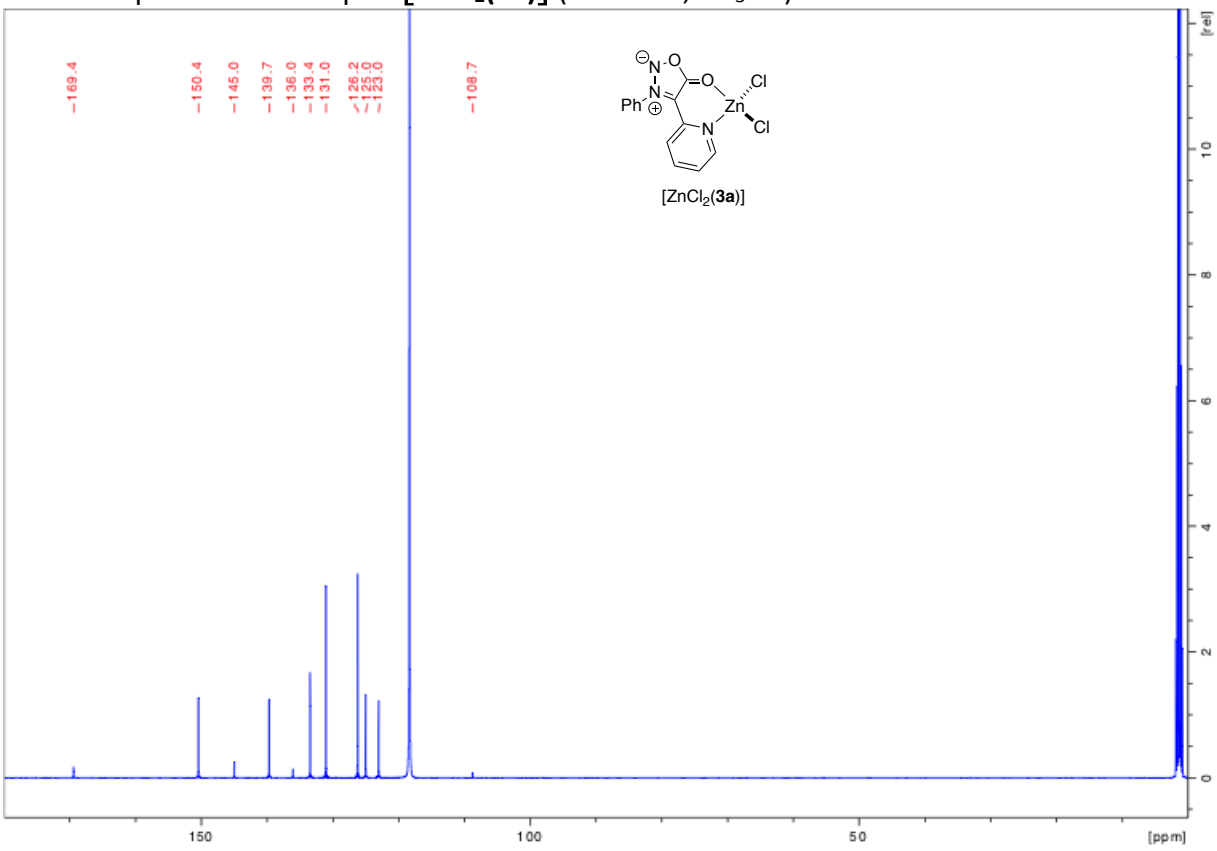
^{13}C NMR spectrum of 3-phenyl-4-(2-pyridinyl)-sydnone **3a** (100 MHz, $CDCl_3$):



^{1}H NMR spectrum of complex **[$ZnCl_2$(3a)]** (500 MHz, CD_3CN):

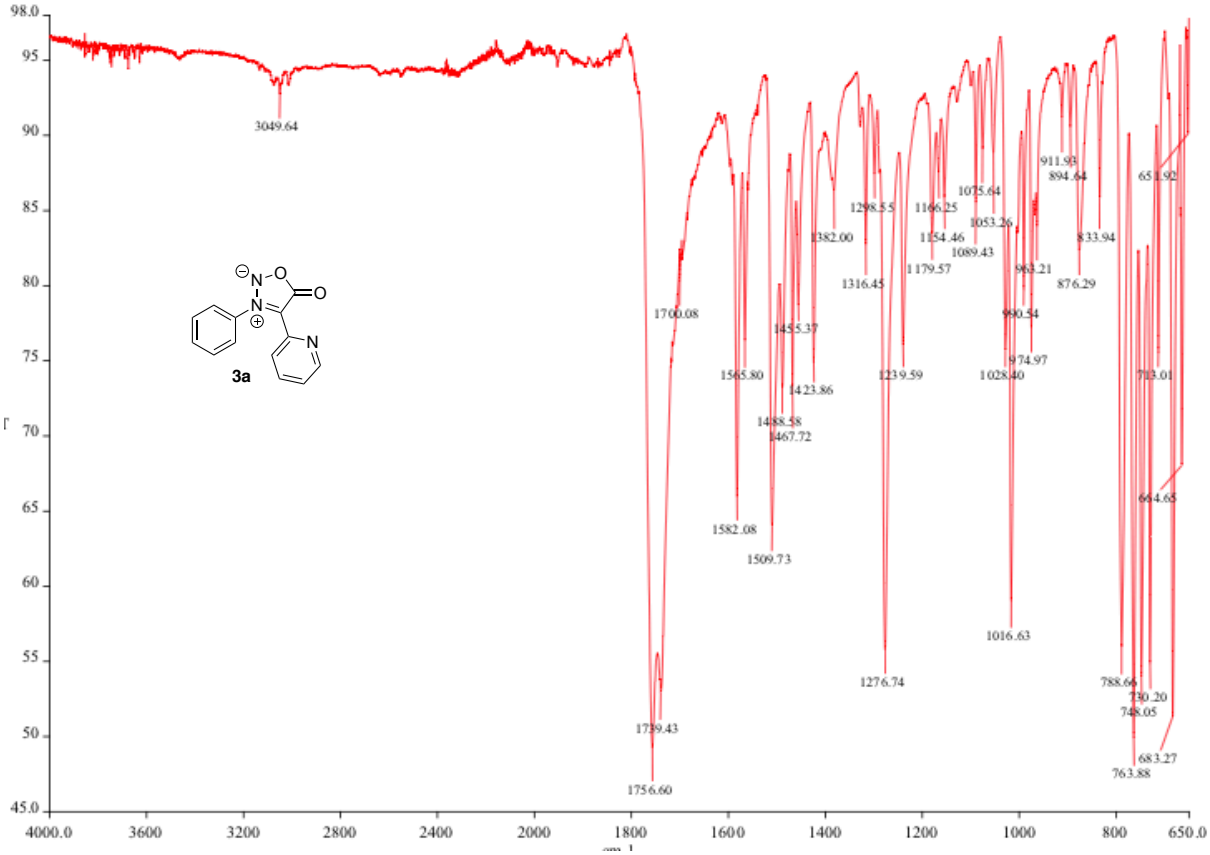


^{13}C NMR spectrum of complex **[$ZnCl_2$(3a)]** (125 MHz, CD_3CN):

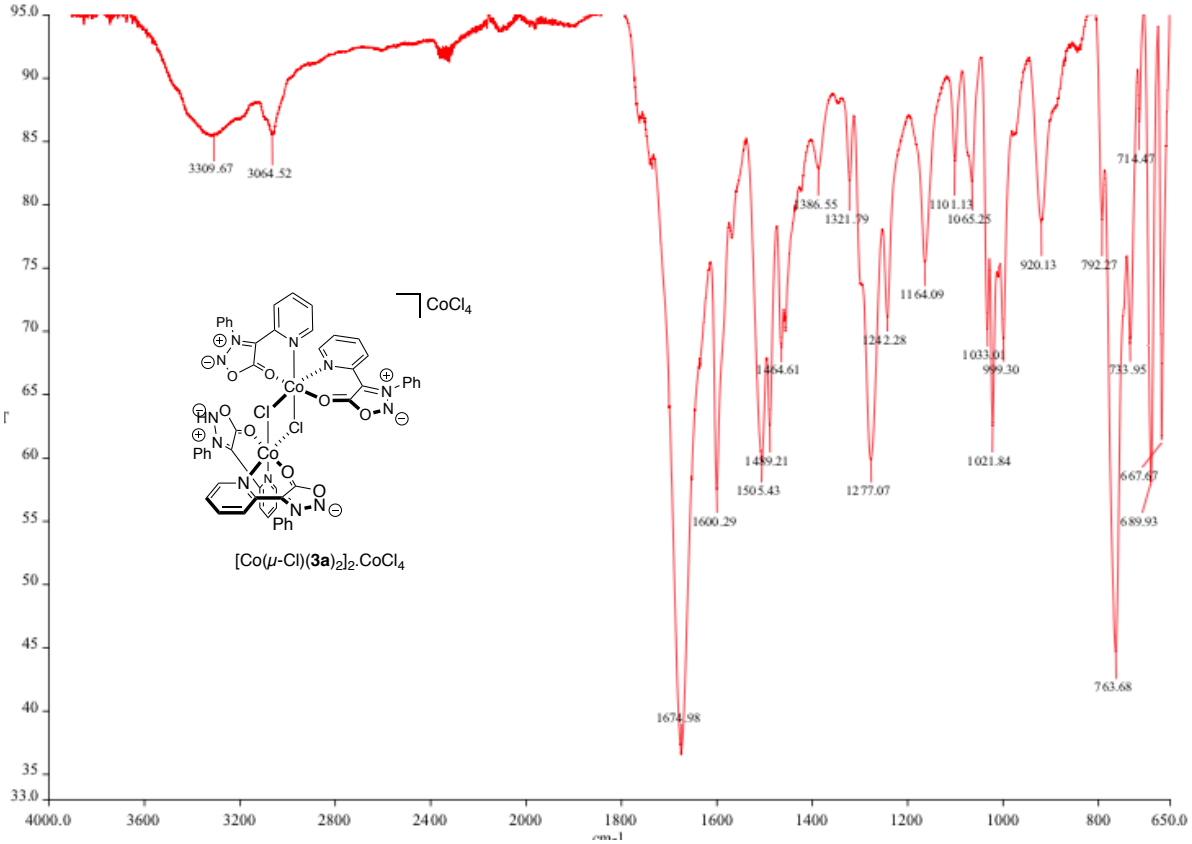


IX. FT-IR spectra

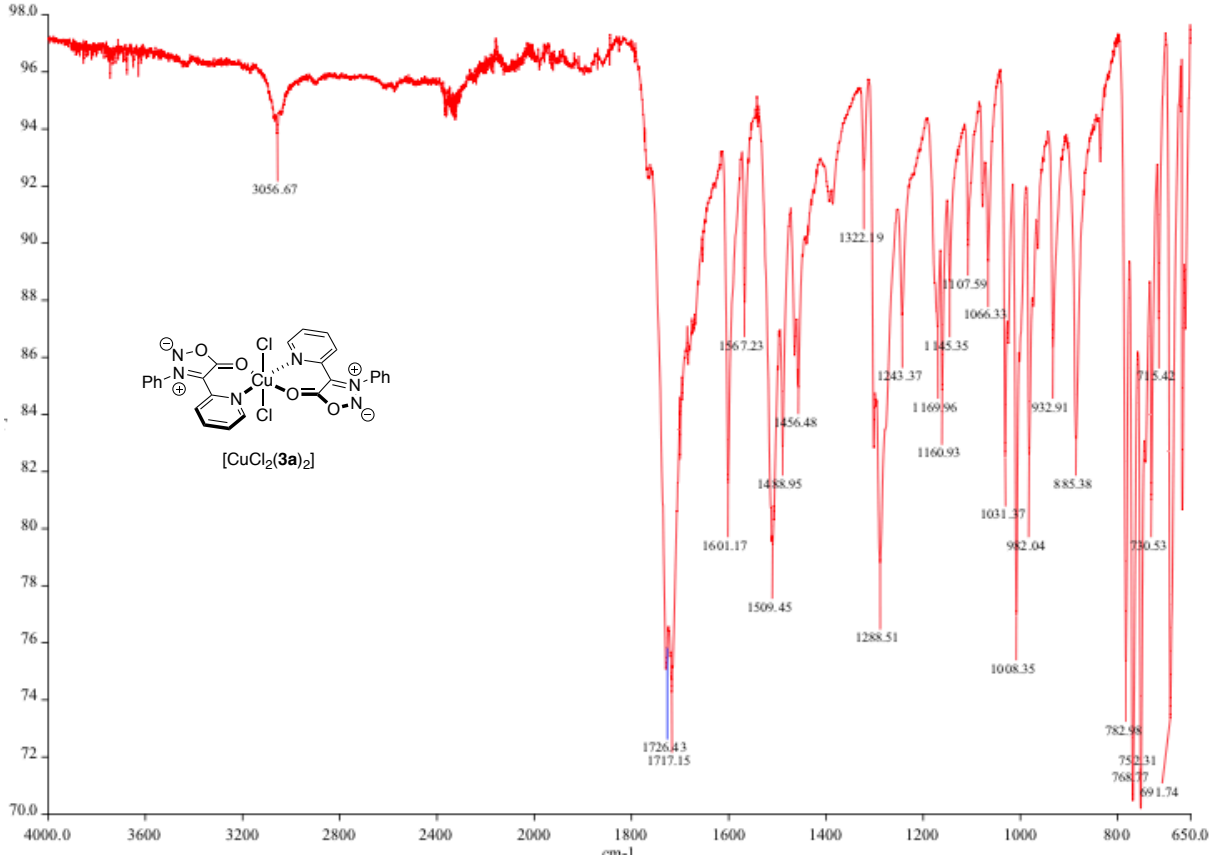
FT-IR spectrum of complex 3-phenyl-4-(2-pyridinyl)-sydnone **3a** :



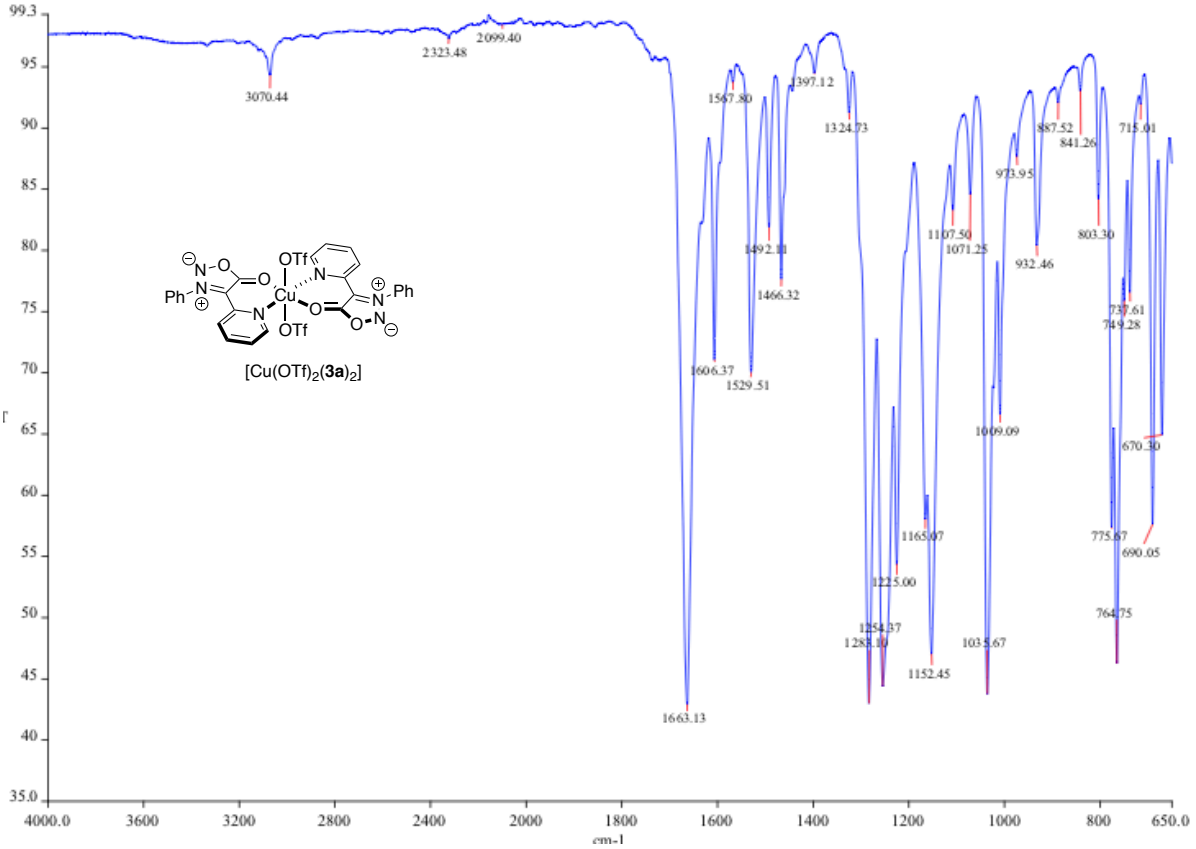
FT-IR spectrum of complex $[Co(\mu\text{-}Cl)(3a)_2]_2.CoCl_4$:



FT-IR spectrum of complex $[CuCl_2(3a)_2]$:



FT-IR spectrum of complex **[Cu(OTf)$_2$(3a)$_2$]** :



FT-IR spectrum of complex **[ZnCl$_2$(3a)]** :