Supplementary Information

Mechanosynthesis of Sydnone-containing Coordination Complexes

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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$_3$CN 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$_3$CN 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 MgSO₄, filtered and evaporated under vacuum to furnish the expected *N*-aryl-glycine.

*N*-Phenyl-glycine 1a

**CAS:** 103-01-5

![Chemical Structure](image)

*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-*d₆*) δ (ppm):** 3.78 (s, 2H), 6.55 (m, 3H), 7.07 (m, 2H).

**¹³C NMR (100 MHz, DMSO-*d₆*) 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 Structure](Image)

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-$d_6$) $\delta$ (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-$d_6$) $\delta$ (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 Structure](Image)

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-$d_6$) $\delta$ (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-$d_6$) $\delta$ (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

\[ N-(4\text{-}Bromophenyl)-\text{glycine} \, 1\text{d} \]

**CAS:** 13370-62-2

![Chemical Structure](image)

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 \( 1\text{d} \) as a brown solid (164 mg, 0.71 mmol, 76%).

\(^1\text{H NMR} \,(300 \text{ MHz, DMSO-}d_6) \delta \,(ppm): \) 3.77 (s, 2H), 6.51 (d, \( J = 8.9 \text{ Hz, 2H} \)), 7.20 (d, \( J = 8.9 \text{ Hz, 2H} \)).

\(^1\text{H NMR} \,(300 \text{ MHz, DMSO-}d_6) \delta \,(ppm): \) 4.4, 106.8, 114.2 (2C), 131.4 (2C), 147.6, 172.4.

**HRMS** ESI-(+) calcd. for C₈H₈BrNO₂ [M+H]\(^+\) 229.9817, found 229.9818.

\[ N-(4\text{-}Nitrophenyl)-\text{glycine} \, 1\text{e} \]

**CAS:** 619-91-0

![Chemical Structure](image)

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 \( 1\text{e} \) as a yellow powder (73 mg, 0.37 mmol, 53%).

\(^1\text{H NMR} \,(400 \text{ MHz, DMSO-}d_6) \delta \,(ppm): \) 3.98 (d, \( J = 6.2 \text{ Hz, 2H} \)), 6.66 (d, \( J = 9.2 \text{ Hz, 2H} \)), 7.45 (t, \( J = 6.2 \text{ Hz, 1H} \)), 8.00 (d, \( J = 9.2 \text{ Hz, 2H} \)), 12.80 (br. s, 1H).

\(^1\text{H NMR} \,(400 \text{ MHz, DMSO-}d_6) \delta \,(ppm): \) 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 Structure 1f](image)

**Chemical Formula:** C\(_9\)H\(_8\)N\(_2\)O\(_2\)

**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\(_2\)O\(_5\) 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\(_6\)) \(\delta\) (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\(_6\)) \(\delta\) (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 Structure 1g](image)

**Chemical Formula:** C\(_9\)H\(_8\)F\(_3\)NO\(_2\)

**Molecular Weight:** 219.16

**Procedure (Method B):** 4-Trifluoromethylaniline (255 \(\mu\)L, 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-d₆) 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-d₆) 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-d₆) 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 Structure](image)

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 Structure](image)

**Chemical Formula:** C\textsubscript{11}H\textsubscript{15}NO\textsubscript{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\textsubscript{4}, filtered and evaporated under vacuum. The crude product was triturated with Et\textsubscript{2}O 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-\textit{d\textsubscript{6}}) \(\delta \) (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-\textit{d\textsubscript{6}}) \(\delta \) (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-sydrones 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

Chemical Formula: C$_8$H$_6$N$_2$O$_2$

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$_3$) $\delta$ (ppm): 6.73 (s, 1H), 7.60-7.74 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (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: C$_9$H$_8$N$_2$O$_2$

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%).

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (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\(_3\)) \( \delta \) (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

\[
\begin{align*}
\text{Chemical Formula: } & C_9H_8N_2O_3 \\
\text{Molecular Weight: } & 192.17
\end{align*}
\]

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\(_2\)O and recrystallization from EtOAc/heptane as brown solid (55 mg, 0.28 mmol, 54%).

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (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\(_3\)) \( \delta \) (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

\[
\begin{align*}
\text{Chemical Formula: } & C_8H_5BrN_2O_2 \\
\text{Molecular Weight: } & 241.04
\end{align*}
\]

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.
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 6.73 (s, 1H), 7.62 (d, \(J = 8.5\) Hz, 2H), 7.77 (d, \(J = 8.5\) Hz, 2H).
\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 93.7, 122.8, 127.0, 133.7, 168.9.

LCMS (ESI) \(m/z\): 241, 243 [M+H]\textsuperscript{+}.

HRMS ESI-(+) calcd. for C\textsubscript{8}H\textsubscript{6}N\textsubscript{2}O\textsubscript{2}Br [M+H]\textsuperscript{+} 240.9613, found 240.9613.

The analytical data obtained is in agreement with those reported in the literature.\textsuperscript{6}

\textbf{3-(4-Nitrophenyl)-sydnone 2e}

\textbf{CAS: 6299-51-0}

\[
\begin{array}{c}
\text{O}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{N} \\
\end{array}
\]

Chemical Formula: C\textsubscript{8}H\textsubscript{5}N\textsubscript{3}O\textsubscript{4}
Molecular Weight: 207.15

\textbf{Procedure:} according to the general procedure GP1 starting from \(N\)-4-nitrophenyl-glycine \textbf{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 \textbf{2e} as a orange powder (52 mg, 0.25 mmol, 42%).

\textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN) \(\delta\) (ppm): 7.14 (s, 1H), 8.03 (d, \(J = 8.7\) Hz, 2H), 8.46 (d, \(J = 8.7\) Hz, 2H).
\textsuperscript{13}C NMR (100 MHz, CD\textsubscript{3}CN) \(\delta\) (ppm): 96.2, 124.2, 126.5, 139.9, 150.9, 169.6.

LCMS (ESI) \(m/z\): 208 [M+H]\textsuperscript{+}.

The analytical data obtained is in agreement with those reported in the literature.\textsuperscript{7}

\textbf{3-(4-Cyanophenyl)-sydnone 2f}

\textbf{CAS: 68657-48-7}

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{O} \\
\end{array}
\]

Chemical Formula: C\textsubscript{9}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}
Molecular Weight: 187.16

\textbf{Procedure:} according to the general procedure GP1, starting from \(N\)-4-cyanophenyl-glycine \textbf{1f}, with addition of 1 eq of KHSO\textsubscript{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 \textbf{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$_3$CN) $\delta$ (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$_3$CN) $\delta$ (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$_9$H$_6$N$_3$O$_2$ [M+H]$^+$ 188.0460, found 188.0461.

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

CAS: 1620220-61-2

Chemical Formula: C$_9$H$_5$F$_3$N$_2$O$_2$
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$_3$) $\delta$ (ppm): 6.82 (s, 1H), 7.89-7.94 (m, 4H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (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$_6$) $\delta$ (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: C$_9$H$_5$BrN$_2$O$_2$
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$_8$H$_6$N$_2$O$_2$Br [M+H]$^+$ 240.9613, found 240.9615.

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

**CAS:** 104411-99-6

![Chemical Structure of 3-(2,4,6-Trimethylphenyl)-sydnone 2i]

**Chemical Formula:** C$_{11}$H$_{12}$N$_2$O$_2$  
**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$_2$O 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$_2$O$_2$ [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

![Chemical Structure of 3-Phenyl-4-(2-pyridinyl)-sydnone 3a]

**Chemical Formula:** C$_{13}$H$_9$N$_3$O$_2$  
**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.

**¹H NMR (400 MHz, CDCl₃) 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).

**¹³C 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.
<table>
<thead>
<tr>
<th>CCDC 1913664</th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
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<td><strong>Space group</strong></td>
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<td><strong>$b$ / Å</strong></td>
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<td><strong>$c$ / Å</strong></td>
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<tr>
<td><strong>$\beta$ / Å</strong></td>
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<td><strong>$\gamma$ / Å</strong></td>
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<td><strong>$\mu$ (Mo Kα) / mm$^{-1}$</strong></td>
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<td><strong>Number of unique reflections</strong></td>
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<tr>
<td><strong>$R1$, $wR2$ (all data)</strong></td>
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<td><strong>GOF</strong></td>
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### IV. Comparison of N-aryl glycines synthesis with literature procedures

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>Yield</th>
<th>Yield in lit.</th>
<th>Conditions from literature</th>
</tr>
</thead>
</table>
| ![1a](image) | 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](image) | 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. |
| ![1c](image) | 22094-69-5 | 80%   | 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\(_2\)O, 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. |
| ![1d](image) | 13370-62-2 | 76%   | 48%\(^{7}\) | 1) 4-Methoxyaniline, ethyl bromoacetate (1.0 eq.), SiO\(_2\), MW (300 W), 4 h.  
2) NaOH (excess) in EtOH, reflux, 10 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. |
| ![1e](image) | 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. |
| ![1f](image) | 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 |
<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>Yield</th>
<th>Yield in lit.</th>
<th>Conditions from literature</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="1f" /></td>
<td>42288-26-6</td>
<td>56%</td>
<td>47%&lt;sup&gt;11&lt;/sup&gt;</td>
<td>4-aminobenzonitrile, chloroacetic acid (2 eq.), H₂O, reflux, 10h</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80-87%&lt;sup&gt;12&lt;/sup&gt;</td>
<td>4-aminobenzonitrile, chloroacetic acid (1.5 eq.), H₂O, reflux, 5h</td>
</tr>
<tr>
<td><img src="image2" alt="1g" /></td>
<td>77311-21-8</td>
<td>74%</td>
<td>30%&lt;sup&gt;11&lt;/sup&gt;</td>
<td>4-Trifluoromethylaniline, NaOAc (2.0 eq.), AcOH (4.0 eq.), glyoxylic acid (1.5 eq.), NaBH₃CN (1.0 eq.), 0°C to rt in 2 h.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>88%&lt;sup&gt;13&lt;/sup&gt;</td>
<td>4-Trifluoromethylaniline, NaOAc (2.0 eq.), AcOH (4.0 eq.), glyoxylic acid (1.5 eq.), NaBH₃CN (1.0 eq.), MeOH, 0°C to rt, 2 h, N₂.</td>
</tr>
<tr>
<td><img src="image3" alt="1h" /></td>
<td>42288-20-0</td>
<td>85%</td>
<td>n.a.</td>
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<tr>
<td><img src="image4" alt="1i" /></td>
<td>104412-17-1</td>
<td>37%</td>
<td>n.a.&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1) 2,4,6-Trimethylaniline, NaOAc.3H₂O (1.5 eq.), ethyl bromoacetate (1.0 eq.), EtOH, reflux, overnight, 2) 10% NaOH&lt;sub&gt;aq&lt;/sub&gt; (1.0 eq.), 40 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%&lt;sup&gt;14&lt;/sup&gt;</td>
<td>1) 2,4,6-Trimethylaniline, NaOAc.3H₂O (1.5 eq.), ethyl bromoacetate (1.0 eq.), EtOH, reflux, overnight, 2) 20% HCl (excess), 100°C, 4h.</td>
</tr>
</tbody>
</table>
V. Comparison of sydnones synthesis with literature procedures

<table>
<thead>
<tr>
<th>Formule</th>
<th>CAS</th>
<th>Yield</th>
<th>Yield in lit.</th>
<th>Conditions from literature</th>
</tr>
</thead>
</table>
| ![2a](image) | 120-06-9 | 95%   | 78%<sup>10</sup> | 1) Glycine 1a, silica chloride, wet SiO₂, NaNO₂ (1.5 eq.), CH₂Cl₂, 0°C, 2.5 h.  
2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH₂Cl₂, 0°C, 4 h. |
| ![2b](image) | 3483-19-0 | 91%   | 63%<sup>8</sup>  | 1) Glycine 1a, NaNO₂ (1.5 eq., dropwise addition), H₂O at 0°C, HCl cc. Drying overnight.  
2) Ac₂O (large excess), 100°C, 1.5 h. |
| ![2c](image) | 3815-80-3 | 54%   | 49%<sup>8</sup>  | 1) Glycine 1a in HCl cc., NaNO₂ (1.0 eq., dropwise addition), 14h under Ar.  
2) Ac₂O (large excess), 100°C, 3 h. |
| ![2d](image) | 26537-61-1 | 91%   | 89%<sup>5</sup>  | 1) Glycine 1a, t-BuONO (1.1 eq.), anh. THF, Ar, 30 min.  
2) TFAA (1.1 eq.), 1h. |
| ![2](image) |          |       | 73%<sup>10</sup> | 1) Glycine 1b, silica chloride, wet SiO₂, NaNO₂ (1.5 eq.), CH₂Cl₂, 0°C, 2.2 h.  
2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH₂Cl₂, 0°C, 4 h. |
| ![2c](image) |          |       | 60%<sup>8</sup>  | 1) Glycine 1b, NaNO₂ (1.5 eq., dropwise addition), H₂O at 0°C, HCl cc., Drying overnight.  
2) Ac₂O (large excess), 100°C, 1.5 h. |
| ![2c](image) |          |       | 82%<sup>8</sup>  | 1) Glycine 1b, t-BuONO, anh. THF, Ar, 30 min.  
2) TFAA, 1h. |
| ![2](image) |          |       | 69%<sup>8</sup>  | 1) Glycine 1b, t-BuONO (1.5 eq.), anh. THF, Ar, 30 min.  
2) CDI (1.1 eq.), 1h. |
| ![2c](image) |          |       | 81%<sup>10</sup> | 1) Glycine 1c, silica chloride, wet SiO₂, NaNO₂ (1.5 eq.), CH₂Cl₂, 0°C, 1.7 h.  
2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH₂Cl₂, 0°C, 4 h. |
| ![2c](image) |          |       | 59%<sup>5</sup>  | 1) Glycine 1c, t-BuONO (1.1 eq.), anh. THF, Ar, 30 min.  
2) TFAA (1.1 eq.), 1h. |
| ![2c](image) |          |       | 50%<sup>8</sup>  | 1) Glycine 1c, t-BuONO (1.5 eq.), anh. THF, Ar, 30 min.  
2) CDI (1.1 eq.), 1h. |
| ![2](image) |          |       | 78%<sup>8</sup>  | 1) Glycine 1c, NaNO₂ (1.5 eq., dropwise addition), H₂O at 0°C, HCl cc., Drying overnight.  
2) Ac₂O (large excess), 100°C, 1.5 h. |
| ![2c](image) |          |       | 73%<sup>7</sup>  | 1) Glycine 1c, t-BuONO (1.5 eq.), anh. THF, Ar, 0°C to rt.  
2) TFAA (1.1 eq.), 1h. |
| ![2](image) |          |       | 78%<sup>15</sup> | 1) Glycine 1c, t-BuONO, anh. THF, Ar, 30 min.  
2) TFAA, 1h. |
| ![2c](image) |          |       | 79%<sup>10</sup> | 1) Glycine 1d, silica chloride, wet SiO₂, NaNO₂ (1.5 eq.), CH₂Cl₂, 0°C, 2.4 h.  
2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH₂Cl₂, 0°C, 4 h. |
| ![2c](image) |          |       | 50%<sup>8</sup>  | 1) Glycine 1d, NaNO₂ (1.5 eq., dropwise addition), H₂O at 0°C, HCl cc., Drying overnight.  
2) Ac₂O (large excess), 100°C, 1.5 h. |
<table>
<thead>
<tr>
<th>Formule</th>
<th>CAS</th>
<th>Yield</th>
<th>Yield in lit</th>
<th>Conditions from literature</th>
</tr>
</thead>
</table>
| ![2e](image) | 6299-51-0 | 42%   | 80%<sup>10</sup> | 1) Glycine 1e, silica chloride, wet SiO<sub>2</sub>, NaNO<sub>2</sub> (1.5 eq.), CH<sub>2</sub>Cl<sub>2</sub>, 0°C, 2.0 h.  
2) 1,3-dibromo-5,5-dimethylhydantoin (DBH, 1.0 eq.), CH<sub>2</sub>Cl<sub>2</sub>, 0°C, 4 h. |
| ![2f](image) | 68657-48-7 | 34%   | n.a.<sup>16</sup> | 1) Glycine 1f, t-BuONO (1.1 eq.), anh. THF, Ar, 30 min.  
2) TFAA (1.15 eq.), 0°C to rt, 1h. |
| ![2g](image) | 1620220-61-2 | 46%   | 70%<sup>8</sup> | 1) Glycine 1g, t-BuONO (1.5 eq.), anh. THF, Ar, 30 min.  
2) TFAA (1.1 eq.), 1h. |
| ![2h](image) | 60816-43-5 | 81%   | n.a.<sup>17</sup> | no detailed experimental procedure given |
| ![2i](image) | 104411-99-6 | 53%   | n.a.<sup>9</sup> | 1) Glycine 1i in 12% HCl, NaNO<sub>3</sub> in H<sub>2</sub>O (1.2 eq., dropwise addition at 0°C), 4 h.  
2) TFAA, CH<sub>2</sub>Cl<sub>2</sub>, 0°C, 1 h.  
| ![2j](image) | 104411-99-6 | 53%   | n.a.<sup>18</sup> | Procedure according to ref<sup>19</sup> (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 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. 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(µ-Cl)(3a)_2]_2·CoCl₄**

**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 C₅₂H₃₆Cl₆Co₃N₁₂O₈ [M-CoCl₄]⁺/2 572.0405, found 572.0421.
ORTEPs (probability at 50% level) of complex [Co(µ-Cl)(3a)₂]₂.CoCl₄. H atoms and CoCl₄ are omitted for clarity.

Of note, the [Co(µ-Cl)(3a)₂]₂.CoCl₄ 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 CoCl₄ component on a twofold axis.
**[CuCl₂(3a)₂]**

Chemical Formula: C₂₆H₁₈Cl₂CuN₆O₄
Molecular Weight: 612.91

**Procedure:** according to the general procedure GP2, using 1.0 eq of copper chloride dihydrate CuCl₂·2H₂O and 2.0 eq of sydnone 3a in a 10 mL ZrO₂ jar with one ZrO₂ 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, 1288, 1008, 783, 769, 752, 730.
**HRMS ESI-(+) calcd. for C₂₆H₁₈N₆O₄ClCu [M-Cl]⁺ 576.0376, found 576.0374.

ORTEPs (probability at 50% level) of complex [CuCl₂(3a)₂]. H atoms are omitted for clarity.
Of note, the complex lies about an inversion centre with the Cu atom on the inversion centre.

**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$_6$N$_6$O$_{10}$S$_2$ [M-TfO]$^+$ 690.0206, found 690.0209.
ORTEPs (probability at 50% level) of complex [Cu(OTf)$_2$(3a)$_2$]. H atoms are omitted for clarity.

<table>
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<tr>
<th>CCDC 1913662</th>
<th>[Cu(OTf)$_2$(3a)$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
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<td><strong>M / g.mol$^{-1}$</strong></td>
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<td><strong>μ (Mo Kα) / mm$^{-1}$</strong></td>
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<td><strong>Number of reflections</strong></td>
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<tr>
<td><strong>Number of unique reflections</strong></td>
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<td><strong>R1, wR2 (I &gt; 2σ(I))</strong></td>
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<td><strong>R1, wR2 (all data)</strong></td>
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<tr>
<td><strong>GOF</strong></td>
<td>1.037</td>
</tr>
</tbody>
</table>

Of note, the complex lies about an inversion centre with the Cu atom on the inversion centre.
**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$_3$CN) $\delta$ (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$_3$CN) $\delta$ (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$-$Cl]$^+$ 337.9676, found 337.9669.

ORTEPs (probability at 50% level) of complex $[\text{ZnCl}_2(3\text{a})]$. H atoms are omitted for clarity.
<table>
<thead>
<tr>
<th>CCDC 1913665</th>
<th>[ZnCl$_2$(3a)]</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$_{13}$H$_9$Cl$_2$N$_3$O$_2$Zn</td>
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<tr>
<td><strong>$M$ / g.mol$^{-1}$</strong></td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>P -1</td>
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<td><strong>$a$ / Å</strong></td>
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<tr>
<td><strong>$b$ / Å</strong></td>
<td>8.9361 (3)</td>
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<tr>
<td><strong>$c$ / Å</strong></td>
<td>9.9810 (3)</td>
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<tr>
<td><strong>$\alpha$ / Å</strong></td>
<td>94.269 (3)</td>
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<tr>
<td><strong>$\beta$ / Å</strong></td>
<td>99.231 (3)</td>
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<td><strong>$\gamma$ / Å</strong></td>
<td>94.285 (3)</td>
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<tr>
<td><strong>$V$ (Å$^3$)</strong></td>
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<td><strong>$Z$</strong></td>
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<tr>
<td><strong>$\mu$ (Mo Kα) / mm$^{-1}$</strong></td>
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<td><strong>$T$ / K</strong></td>
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<td><strong>Number of unique reflections</strong></td>
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<tr>
<td><strong>$R_{int}$</strong></td>
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</tr>
<tr>
<td><strong>$R1$, wR2 ($I &gt; 2\sigma(I)$)</strong></td>
<td>0.0305, 0.0742</td>
</tr>
<tr>
<td><strong>$R1$, wR2 (all data)</strong></td>
<td>0.0431, 0.0773</td>
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<tr>
<td><strong>GOF</strong></td>
<td>1.065</td>
</tr>
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</table>
VII. References

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-$d_6$):

![1H NMR spectrum](image)

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

![13C NMR spectrum](image)
$^1$H NMR spectrum of $N$-(4-trifluoromethylphenyl)-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$_3$):

![NMR Spectrum](image1)

$^{13}$C NMR spectrum of 3-(4-methylphenylsydnone) 2b (100 MHz, CDCl$_3$):

![NMR Spectrum](image2)
$^1$H NMR spectrum of 3-(4-methoxyphenylsydnone) 2c (400 MHz, CDCl$_3$):

\[N\]

$^{13}$C NMR spectrum of 3-(4-methoxyphenylsydnone) 2c (100 MHz, CDCl$_3$):
$^1$H NMR spectrum of 3-{(4-bromophenyl)sydnone} 2d (400 MHz, CDCl$_3$):

\begin{center}
\includegraphics[width=\textwidth]{hnmr_spectrum}
\end{center}

$^{13}$C NMR spectrum of 3-{(4-bromophenyl)sydnone} 2d (100 MHz, CDCl$_3$):

\begin{center}
\includegraphics[width=\textwidth]{cnmr_spectrum}
\end{center}
$^1$H NMR spectrum of 3-(4-nitrophenylsydnone) 2e (400 MHz, CD$_3$CN):

$^{13}$C NMR spectrum of 3-(4-nitrophenylsydnone) 2e (100 MHz, CD$_3$CN):
$^1$H NMR spectrum of 3-(4-cyanophenylsydnone) 2f (400 MHz, CD$_3$CN):

$^{13}$C NMR spectrum of 3-(4-cyanophenylsydnone) 2f (100 MHz, CD$_3$CN):
$^1$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 $[\text{ZnCl}_2(3a)]$ (500 MHz, CD$_3$CN):

$^{13}$C NMR spectrum of complex $[\text{ZnCl}_2(3a)]$ (125 MHz, CD$_3$CN):
IX. FT-IR spectra

FT-IR spectrum of complex 3-phenyl-4-(2-pyridinyl)-sydnone 3a:
FT-IR spectrum of complex $[\text{Co(μ-Cl)}(3a)_2]_2\cdot\text{CoCl}_4$:

$\begin{align*}
\text{FT-IR spectrum of complex } [\text{Co(μ-Cl)}(3a)_2]_2\cdot\text{CoCl}_4 & : \\
\end{align*}$

$\begin{align*}
\text{FT-IR spectrum of complex } [\text{CuCl}_2(3a)_2] & : \\
\end{align*}$
FT-IR spectrum of complex \([\text{Cu(OTf)}_2(3a)_2]\):

![FT-IR spectrum of Cu(OTf)2(3a)2 complex](image)

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

![FT-IR spectrum of ZnCl2(3a) complex](image)