Supporting Information

New Aminotetrazole Derivatives as Hydrogen Bonding Catalysts. A Green and Selective Oxidation of Organosulphides with H₂O₂ in H₂O

Francesco Secci*, Massimiliano Arca, Angelo Frongia, Pier Paolo Piras

Dipartimento di Scienze Chimiche e Geologiche, Università degli studi di Cagliari, Complesso Universitario di Monserrato, S.S. 554, Bivio per Sestu, I-09042, Monserrato, Cagliari, ITALY e-mail: fsecci@unica.it, phone number (+39) 0706754384

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1.1 General methods

$^1$H NMR spectra were recorded on 400 and 500 MHz Varian spectrometers at 27°C using CDCl$_3$, DMF-$d_7$ or DMSO-$d_6$ as solvent. $^{13}$C NMR were recorded at 100 and 125 MHz at 27°C using CDCl$_3$, DMF-$d_7$ or DMSO-$d_6$ as solvent. Chemical shifts (δ) are given in ppm. Coupling constants (J) are reported in Hz. Infrared spectra were recorded on a FT-IR Bruker spectrophotometer and are reported in wavenumbers. Low Mass spectra analysis were recorded on an Agilent-HP GC-MS (E.I. 70eV).

Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 70-200 mesh silica gel. Yields refer to chromatography and spectroscopically pure materials.

1.2 General procedure for the oxidation of sulphides 5a-p to sulfoxides 6a-6p using cat. 1a-H$_2$O$_2$

\[
\begin{array}{c}
\text{R}^1\text{S}^{-}\text{R}^2 \rightarrow \\
\text{cat. 1a, 5 mol %} \\
\text{H}_2\text{O}_2 \text{ 1.1 equiv.} \\
\text{H}_2\text{O, r.t.} \\
\text{5a-p} \rightarrow \\
\text{6a-p} + \\
\text{7a-p}
\end{array}
\]

To a 3 M solution of sulphide 5a (100 mg, 0.8 mmol) and tetrazole 1a (5 mol. %) in water (2.7 mL), H$_2$O$_2$ (30% v/v in water, 1.1 equiv.) was added in one injection and the resulting mixture was stirred at room temperature and followed by Gc-Ms until completion (6a/7a ratio 98:2). The reaction mixture was filtered and the water solution was extracted with. The organic phase was dried on Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The catalyst was recovered by washing up the filtered solid with Ethyl acetate and dried. Pure sulfoxide 6a was obtained after flash column chromatography (silica gel, 80:20 hexane/ether) in 92% yield. Colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ: 7.62-7.60 (m, 2 H), 7.48-7.46 (m, 3 H), 2.68 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ: 145.6, 130.8, 129.2, 123.3, 43.8. Ms m/z: (M+140, (100%), 125 (98%), 97 (60%), 77 (50%), 51 (35%).
1.3 Synthesis of aminotetrazole-thiourea ligands 9a-c

**Synthesis of catalyst 9a.** To a stirred solution of CS₂ (2.22 mL) and DCC (1.20 g, 5.84 mmol) at -10°C, in dry Et₂O (5 mL), (S)-1-Naphthalen-2-yl-ethylamine (1.0 g, 5.84 mmol), in Et₂O (3 mL), was added dropwise. After 1 hour the reaction mixture was warmed to room temperature and stirred for additional 12 hours. The reaction mixture was filtered and the resulting solid was washed with Et₂O. The organic phase was passed through a pad of silica, washed with hexane and concentrated under reduced pressure to afford the isothiocyanate intermediate as a colorless liquid which was used in the next step without further manipulations. Isothiocyanate was diluted in DCM (20 mL) and aminotetrazole-1H₂O 0.381 g, 3.70 mmol) was added at room temperature. The resulting suspension was stirred for 48 h and concentrated under reduced pressure. The crude solid was chromatographed using EtOAc/EtOH 3:1 to afford compound 9a as a white solid in 87% yield (1.51 g). Mp = 108-112°C, [a]D²¹ = -107.46 (c. 1.488 in MeOH). ¹H NMR (500 MHz, DMSO-d₆) δ: 8.12 (d, 1 H, J = 8.5 Hz), 7.99 (d, 1 H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.5 Hz), 6.45 (br.s, 2H), 6.05 (q, 1H, J = 6.5 Hz), 1.77 (d, 3 H, J = 6.5 Hz); ¹³C NMR (125 MHz, DMSO-d₆) δ: 156.3, 135.3, 133.3, 130.1, 129.1, 128.7, 128.6, 126.6, 125.9, 125.4, 122.9, 122.6, 110.5, 53.3, 22.9.
Synthesis of catalyst 9b. To a stirred solution of CS$_2$ (3.13 mL) and DCC (1.69g, 8.26 mmol) at -10°C, in dry Et$_2$O, (5 mL), (S)-1-1-Phenyl-ethylamine (1.0g, 8.26 mmol), in Et$_2$O (5 mL), was added dropwise. After 1 hour the reaction mixture was warmed to room temperature and stirred for additional 12 hours. The reaction mixture was filtered and the resulting solid was washed with Et$_2$O. The organic phase was passed through a pad of silica, washed with hexane and concentrated under reduced pressure to afford the isothiocyanate intermediate as a colorless liquid which was used in the next step without further manipulations. Isothiocyanate was diluted in DCM (35 mL) and aminotetrazole-1H$_2$O (0.851g, 8.25 mmol) was added at room temperature. The resulting suspension was stirred for 48 h and concentrated under reduced pressure. The crude solid was chromatographed using EtOAc/EtOH 3:1 to afford compound 9b as a white solid in 91% yield (1.85g). Mp = 53-55°C, $[a]^{21}_{D} = -7.03$ (c. 2.274 in MeOH). $^1$H NMR (500 MHz, DMF-d$_7$) δ: 7.62-7.60 (m, 2 H), 7.62-7.59 (m, 4 H), 7.55-7.52 (m, 1 H), 6.67 (br.s, 2H), 5.42 (q, 1H, $J = 6.5$Hz), 3.65 (br.s, 1H), 1.83 (d, 3H, $J = 6.5$Hz); $^{13}$C NMR (125 MHz, DMF-d$_7$) δ: 158.7, 142.0, 132.4, 130.3, 129.8, 129.6, 127.7, 127.1, 58.3, 25.3

Synthesis of catalyst 9c. To a stirred solution of CS$_2$ (3.13 mL) and DCC (1.69g, 8.26 mmol) at -10°C, in dry Et$_2$O, (5 mL), (S)-1-1-cyclohexyl-ethylamine (1.05g, 8.26 mmol), in Et$_2$O (5 mL), was added dropwise. After 1 hour the reaction mixture was warmed to room temperature and stirred for additional 12 hours. The reaction mixture was filtered and the resulting solid was washed with Et$_2$O. The organic phase was passed through a pad of silica, washed with hexane and concentrated under reduced pressure to afford the isothiocyanate intermediate as a colorless liquid which was used in the next step without further manipulations. Isothiocyanate was diluted in DCM (35 mL) and aminotetrazole-1H$_2$O (0.851g, 8.25 mmol) was added at room temperature. The resulting
suspension was stirred for 48 h and concentrated under reduced pressure. The crude solid was chromatographed using EtOAc/EtOH 3:1 to afford compound 9c as a white solid in 90% yield (1.88 g). Mp = 68-70°C, [α]$_{22}^{22}$C$_{D}$ = +31.83 (c. 2.764 in DMSO). $^{1}$H NMR (500 MHz, DMSO-d$_{6}$) δ: 6.40 (br.s., 2 H), 3.75 (quint, 1 H, $J = 6.5$Hz), 1.76-1.67 (m, 3 H), 1.63-1.58 (m, 2H), 1.45-1.38 (m, 1H), 1.24 (d, 3H, $J = 6.5$Hz), 1.22-1.14 (m, 2H), 1.11-1.03 (m, 1H), 1.00 (dd, 1H, $J = 3.0$Hz, $J = 14.0$Hz), 0.95 (dd, 1H, $J = 2.5$Hz, $J = 12.0$Hz); $^{13}$C NMR (125 MHz, DMSO-d$_{6}$) δ: 156.6, 128.2, 58.5, 42.9, 29.0, 27.5, 25.7, 25.4, 25.3, 18.5.

1.4 General procedure for the oxidation of sulphide 5a using catalysts 9a-c/H$_{2}$O$_{2}$.

![chemical structure](image)

**Method A (room temperature oxidation)** To a 3 M solution of sulphide 5a (100 mg, 0.8 mmol) and tetrazole thiourea 9a (5 mol. %) in water (2.7 mL), H$_{2}$O$_{2}$ (30% v/v in water, 1.1 equiv.) was added in one injection and the resulting mixture was stirred at room temperature and followed by Gc-Ms until completion (6a/7a ratio >99<1). The reaction mixture was filtered and the water solution was extracted with. The organic phase was dried on Na$_{2}$SO$_{4}$, filtered and concentrated under reduced pressure. The catalyst was recovered by washing up the filtered solid with Ethyl acetate and dried. Pure sulfoxide 6a was obtained after flash column chromatography (silica gel, 80:20 hexane/ether) in 92% yield. Colorless oil. HPLC chiral column: Phenomenex IPA/Hex 90:10, 1.0 mL/min, $\lambda = 254$ nm, Rt = 14.10, Rt = 18.33 (e.r. 49:51).

**Method B (0°C oxidation)** To a 3 M solution of sulphide 5a (100 mg, 0.8 mmol) and tetrazole thiourea 9a (5 mol. %) in water (2.7 mL), H$_{2}$O$_{2}$ (30% v/v in water, 1.1 equiv.) was added in one injection and the resulting mixture was stirred at room temperature and followed by Gc-Ms until completion (6a/7a ratio >99<1). The reaction mixture was filtered and the water
solution was extracted with. The organic phase was dried on Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The catalyst was recovered by washing up the filtered solid with Ethyl acetate and dried. Pure sulphoxide 6a was obtained after flash column chromatography (silica gel, 80:20 hexane/ether) in 90% yield. Colorless oil. Colorless oil. HPLC chiral column: Phenomenex IPA/Hex 90:10, 1.0 mL/min, $\lambda = 254$ nm, Rt = 14.10, Rt = 18.33 (e.r. 48:52).

### 1.5 Catalyst recovery procedure

To value the catalyst recovery, we carried out a set of experiments as reported:

1) 150 mg of cat. 2a were loaded for the oxidation of 2 g of sulphide 5a. At completion, the reaction mixture was filtered and washed with EtOAc (2 x 30 mL). Cat. 2a was collected and dried under reduced pressure for 12h at room temperature. The catalyst recovery % was determined by weighting of the dried white solid. (132 mg of catalyst, 88% recovered).

2) 130 mg of cat. 2a were loaded for the oxidation of 1.73 g of sulphide 5a. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (113 mg of catalyst, 87% recovered).

3) 100 mg of cat. 2a were loaded for the oxidation of 1.33 g of sulphide 5a. After filtration and drying, the catalyst recovery % was determined by weighting of the dried white solid. (76 mg of catalyst, 76% recovered).
$^1$H and $^{13}$C NMR spectra of compound 6a-p
4-Methanesulfonylphenol 6c

S9
Cyclopropanesulfinyl-benzene 6d

S10
Methoxymethanesulfinyl-benzene 6e
(Prop-2-ene-1-sulfinyl)-benzene 6f
Methanesulfinylmethyl-benzene $6i$
1-Oxo-tetrahydro-1H-thiopyran-4-one 6k
2-Methyl-2-phenylmethanesulfinyl-propionic acid ethyl ester 6j
[1,3]Dithiane 1-oxide 6l
S21

(2-Methyl-propane-2-sulfinyl)-benzene 60
$^1$H and $^{13}$C NMR spectra of catalysts 9a-c