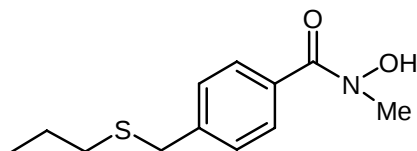


Synthesis of L³



1) Synthesis of 4-(propylthiomethyl)benzoic acid

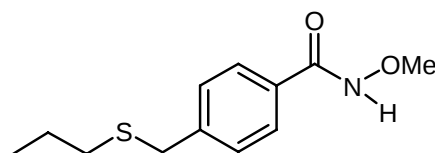
To a suspension of 60% sodium hydride in paraffin oil (1.86 g, 46.6 mmol) in tetrahydrofuran (100 ml) was added propanethiol (5.31 g, 69.8 mmol) and the mixture was stirred until the evolution of hydrogen had ceased. To the resulting white suspension was added a solution of 4-(bromomethyl)benzoic acid (5.0 g, 23.3 mmol) in tetrahydrofuran (50 ml) and the reaction mixture was refluxed for 1 hour. Methanol (100 ml) was added to dissolve the solid and the solution was refluxed for a further 16 hours. The reaction mixture was cooled and concentrated hydrochloric acid (5 ml) was added before being adsorbed onto silica gel and the solvent evaporated. The resulting solids were loaded onto a silica gel column which was eluted with 0% to 5% methanol/dichloromethane to give 4-(propylthiomethyl)benzoic acid as a white solid (4.5 g, 92%). ¹H NMR (250.1 MHz, CDCl₃) δ 11.71 (br s, 1H, OH), 8.07 (AA'XX', 2H, ArH *ortho* to the carboxylic acid), 7.42 (AA'XX', 2H, ArH *ortho* to the propylthiomethyl group), 3.75 (s, 2H, CH₂Ar), 2.40 (t, *J* = 7 Hz, 2H, SCH₂CH₂), 1.58 (m, 2H, SCH₂CH₂), 0.96 (t, *J* = 7 Hz, 3H, CH₃). ¹³C NMR (62.9 MHz, CDCl₃) δ 172.1, 145.2, 130.4, 128.9, 127.9, 36.0, 33.5, 22.5, 13.4. MS (FAB, +ve) *m/z* 211.1 [M+H]⁺.

2) Synthesis of **8**: N-hydroxy-N-methyl-4-propylthiomethyl-benzamide

To a solution of 4-(propylthiomethyl)benzoic acid (4.21 g, 20.0 mmol) (see Section 5.7.3, 1) in chloroform (100 ml) was added oxalyl chloride (3.0 ml, 36.0 mmol) plus a drop of DMF and the mixture was heated at 60°C for 2 hours. The solvent was removed under reduced pressure and chloroform (50 ml) was added and again removed. This process was repeated and the resulting residue was placed under high vacuum.

The preparation follows the method of Coates *et al.*¹ A solution of *N*-methylhydroxylamine (0.146 g, 1.75 mmol) in water was added to a solution of Na₂CO₃ (0.214 g, 2.02 mmol) in 10 ml of water. The resultant solution was covered with 5 ml of ether. The mixture was stirred and cooled in an ice-bath, as 4-(propylthiomethyl)benzoyl chloride earlier prepared (0.40 g, 1.75 mmol) and previously dissolved in 5 ml of ether, was added dropwise. After stirring and cooling for additional 45 minutes, 4.5 ml of 20% NaOH were added. The aqueous layer was neutralized to pH 7 with 6M HCl and extracted five times with chloroform. The organic layer was dried with MgSO₄, filtered and evaporated under reduced pressure leaving a pale yellow viscous solid in 86 % yield. ¹H-NMR (250.1 MHz, CDCl₃) δ 7.40 (d, 2H, ArH *ortho* to the amide group), 7.30 (d, 2H, ArH *ortho* to the propylthiomethyl group), 3.65 (s, 2H, CH₂Ar), 3.35 (s, 3H, NCH₃), 2.30 (t, *J* = 7 Hz, 2H, SCH₂CH₂), 1.50 (m, 2H, SCH₂CH₂), 0.90 (t, *J* = 7 Hz, 3H, CH₃). ¹³C-NMR (62.9 MHz, CDCl₃) δ 166.3, 141.1, 130.0, 128.1, 127.8, 37.4, 34.9, 32.5, 21.5, 12.4. MS (FAB, +ve) *m/z* 240.0 [M+H]⁺. Elemental analysis for C₁₂H₁₇NO₂S: Calc.: C, 60.22 %; H, 7.16 %; N, 5.85 %. Found: C, 60.25 %; H, 7.27 %; N, 5.53 %.

Synthesis of L⁴



To a solution of 4-(propylthiomethyl)benzoic acid (4.21 g, 20.0 mmol) (see Section 5.7.3, 1) in chloroform (100 ml) was added oxalyl chloride (3.0 ml, 36.0 mmol) plus a drop of DMF and the mixture was heated at 60°C for 2 hours. The solvent was removed under reduced pressure and chloroform (50 ml) was added and again removed. This process was repeated and the resulting residue was placed under high vacuum. The residue was dissolved in ethyl acetate (150 ml) and a mixture of *O*-methylhydroxylamine hydrochloride (2.01 g, 24.0 mmol) and potassium carbonate (6.91 g, 50.0 mmol) in water (100 ml) was added and the two phases were intimately stirred for 16 hours. The organic

layer was separated and the aqueous phase was extracted with ethyl acetate (2 x 50 ml). The combined organic layers were evaporated and the residue was chromatographed eluting with 0% to 3% methanol/dichloromethane. The resulting white solid (3.4 g) was recrystallised from diethyl ether to give *N*-methoxy-4-propylthiomethyl-benzamide as colourless crystals. Yield (2.2 g, 46 %). ¹H NMR (250.1 MHz, CDCl₃) δ 9.11 (br s, 1H, NH), 7.69 (d, *J* = 8 Hz, 2H, ArH *ortho* to the amide group), 7.36 (d, *J* = 8 Hz, 2H, ArH *ortho* to the propylthiomethyl group), 3.85 (s, 3H, CH₃O), 3.70 (s, 2H, CH₂Ar), 2.36 (t, *J* = 7 Hz, 2H, SCH₂CH₂), 1.56 (m, 2H, SCH₂CH₂), 0.93 (t, *J* = 7 Hz, 3H, CH₃). ¹³C NMR (62.9 MHz, CDCl₃) δ 166.3, 143.3, 130.3, 129.1, 127.3, 64.5, 35.9, 33.5, 22.4, 13.4. MS (ES, +ve) *m/z* 240.0 [M+H]⁺. Elemental analysis for C₁₂H₁₇NO₂S: Calc.: C, 60.22 %; H, 7.16 %; N, 5.85 %. Found: C, 60.40 %; H, 6.99 %; N, 5.79 %.

Supplementary Crystallography information

[Fe(bha)₃]·1.5MeOH

A crystalline sample was obtained which was suitable for X-ray diffraction. The crystals produced were orange blocks and one measuring 0.53 x 0.34 x 0.14 mm was selected and diffraction data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073 \text{ \AA}$) equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software¹ and found to be monoclinic with $a = 20.2477(8)$, $b = 11.3483(4)$, $c = 22.4035(9) \text{ \AA}$ and $\beta = 115.874(2)^\circ$. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 62259 reflections were collected and from these the space group was determined to be $P2_1/c$. Absorption correction was performed using a multi-scan method by applying the SADABS² program to the data. The data were merged according to the crystal system in SHELX³ which gave 10126 unique reflections with a merging R-factor of 0.0442. The initial solution was determined by direct methods with the SHELXS³ program. All heavy atoms were refined

anisotropically and most hydrogen atoms were placed geometrically and allowed to ride on their host atom. Hydrogen atoms on oxygen and nitrogen atoms were found in a Fourier difference map and their positions refined with a restraint on their distance from their host. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0371 based on 8192 reflections.

X-Ray Crystal Structure of $[\text{Fe}_2(\mu_2\text{-bha})_2(\text{bha})_2\text{Br}_2]$

A crystalline sample was obtained which was suitable for X-ray diffraction. The crystals produced were black blocks and one measuring 0.37 x 0.18 x 0.14 mm was selected and diffraction data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software¹ and found to be C-centred monoclinic with $a = 14.5538(9)$, $b = 16.2543(10)$, $c = 12.9684(8) \text{ \AA}$ and $\beta = 91.814(4)^\circ$. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 43236 reflections were collected and from these the space group was determined to be $C2/c$. Absorption correction was performed using a multi-scan method by applying the SADABS² program to the data. The data were merged according to the crystal system in SHELX³ which gave 4680 unique reflections with a merging R-factor of 0.0422. The initial solution was determined by direct methods with the SHELXS³ program. All heavy atoms were refined anisotropically and most hydrogen atoms were placed geometrically and allowed to ride on their host atom. Hydrogen atoms on oxygen and nitrogen atoms were found in a Fourier difference map and their positions refined with a restraint on their distance from their host. Some static rotational disorder about the C3-C6 axis was encountered in one of the benzene rings which was refined as two components with the main component assigned a 0.7 site occupancy factor occupancy and the secondary component, 0.3. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0338 based on 3511 reflections.

- 1 Bruker-Nonius, Bruker-AXS, Madison, Wisconsin, USA, Edition edn., 2002.
- 2 G. M. Sheldrick, Bruker-AXS, Madison, Wisconsin, USA, Edition edn., 2004.
- 3 G. M. Sheldrick, University of Gottingen, Germany and Bruker-AXS, Gottingen,