Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Olefin Epoxidation by a (salen)Mn(III) Catalyst Covalently Grafted on Glass Beads

Giuseppe Trusso Sfrazzetto,[a] Salvatrice Millesi,[a] Andrea Pappalardo,[a] Rosa Maria Toscano,[a] Francesco P. Ballistreri,[a] Gaetano A. Tomaselli,[a] and Antonino Gulino [*a,b]

[a] *Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy Fax: +39-095-580138; Tel: +39-095-7385067; E-mail: agulino@unict.it*

[b] I.N.S.T.M. UdR of Catania, Viale A. Doria 6, 95125 Catania, Italy

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General experimental methods. The NMR experiments were carried out at 27° C on a Varian UNITY Inova 500 MHz spectrometer (^{1}H at 499.88 MHz, ^{13}C-NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tuneable5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on a ES-MS Thermo-Finnigan LCQ-DECA using MeOH (positive ion mode). All chemicals were reagent grade and were used without further purification.*N*-hexanol-phtalimide[1] and (*1R,2R*)-diphenylethylenediamine, 3,5-di-*tert*-butylsalicylaldehyde hydrochloride[2] were synthesized in according to the literature methods.

Synthesis of 5-chloromethyl-3-*t*Butyl-salicylaldehyde (2)

729µL (8.8mmol) of aqueous formaldehyde, 95 mg (0.28 mmol) and 9 mL of HClconc. were added to 1 g (5.6mmol) of the 3-tButyl-salicylaldehyde. The mixture was stirred at 90°C overnight. The organic phase was extracted with diethyl ether (3 times), dried over $MgSO_4$ and concentrated in vacuo, thus giving the pure compound 2 as a yellow solid (yield = 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.8 (s, 1H), 9.9 (s, 1H), 7.5 ppm (d, *J* = 8 Hz, 1H), 7.4 (d, *J* = 8 Hz, 1H), 4.5 (s, 2H), 1.5 (s, 9H). ESI/MS m/z = 226.1 $[M+H]^+$. Anal. Calcd. for C, 63.58; H, 6.67; Cl, 15.64. Found: C, 63.53; H, 6.61; Cl, 15.62.

Synthesis of aldehyde 3

N-hexanol-phtalimide (916 mg, 3.71 mmol) and K_2CO_3 (1.5 g, 11.13 mmol) were stirred in dry CH_3CN at 70°C for two hours under nitrogen atmosphere. Then a solution of **2** in dry acetonitrile was added dropwise in 1 hour. The mixture was stirred overnight at 70°C. The solvent was removed under reduced pressure and aldehyde **3** was purified by flash chromatography (hexane: EtOAc 98:2) (yield = 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ11.76 (s, 1H), 9.87 (s, 1H), 7.84 (m, 2H), 7.71 (m, 2H), 7.47 (d, *J* = 2 Hz, 1H), 7.38 (d, *J* = 2 Hz, 1H), 4.42 (s, 2H), 3.68 (t, *J* = 7 Hz, 2H), 3.48 (t, *J* = 7.5 Hz, 2H), 1.69 (m, 2H), 1.61 (m, 2H), 1.41 (s, 9H), 1.35-1.40 (m, 4H). ESI-MS *m/z* 438.2 $[M+H]^+$. Anal. Calcd. for C, 71.37; H, 7.14; N, 3.20. Found: C, 71.32; H, 7.10; N, 3.18.

Synthesis of the salen ligand 4

250 µL of triethylamine (1.80 mmol) were added to an ethanol solution (20 mL) containing 200 mg (0.46 mmol) of aldehyde **3** and 212 mg (0.46 mmol) of (*1R,2R*)-diphenylethylenediamine, 3,5-di-*tert*-butylsalicylaldehyde hydrochloride. The reaction was followed by TLC (hexane:EtOAc 90:10) to monitor the disappearing of compound **3** and, then quenched by evaporation of solvent under vacuum. The compound **4** was isolated by flash chromatography (hexane:EtOAc 95:5) (yield = 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.79 (s, 1H), 13.54 (s, 1H), 8.4 (s, 2H), 7.8 (m, 2H), 7.7 (m, 2H), 7.31 (d, *J* = 2 Hz, 2H), 7.15-7.23 (m, 11H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.96 (d, *J* = 2 Hz, 1H), 4.73 (d, *J* = 4.5 Hz, 2H), 4.31 (s, 2H), 3.7 (t, *J* = 7 Hz, 2H), 3.4 (t, J = 7 Hz, 2H), 1.7 (m, 2H), 1.6 (m, 2H), 1.42 (s, 9H), 1.4 (s, 9H), 1.3 (m, 4H), 1.2 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 168.4, 166.8, 159.8, 157.9, 140.0, 139.6, 137.2, 136.4, 133.8, 132.2, 129.6, 128.4, 128.4, 128.2, 127.4, 127.6, 127.2, 126.2, 123.1, 118.2, 117.8, 80.1, 77.6, 77.0, 76.8, 72.7, 70.1, 38.0, 35.0, 34.8, 34.1, 31.4, 29.6, 28.5, 26.9, 25.8, 22.7, 14.1. ESI-MS *m/z* 848 $[M+H]^+$. Anal. Calcd. for C, 77.89; H, 7.72; N, 4.95. Found: C, 77.83; H, 7.70; N, 4.63.

Synthesis of catalyst 5

The absolute ethanol solution of the salen ligand **4** was stirred overnight at room temperature with 1.5 equivalents of manganese(III) acetate. When the starting ligand was completely converted (checked by TLC analysis), the solvent was removed under reduced pressure. Then, 5 mL of CH_2Cl_2 were added to the remaining crude solid to dissolve the Mn

complex. The residual precipitate (not reacted manganese(III) acetate) was removed and the CH_2Cl_2 solution was concentrated in vacuo thus giving the corresponding catalyst with nearly quantitative yield. Catalyst 5 was characterized by ESI-MS measurement: *m/z* 899 $[M]^+$.

Synthesis of catalysts 1 (de-protection)

40 equivalents of hydrazine monohydrate were added to the solution containing catalyst **5** in ethanol. The mixture was stirred at 60°C for 10 minutes. Then, the solvent was removed under reduced pressure and the given compound extracted by addition of chloroform (yield 80%). Catalyst 1 was characterized by ESI-MS measurement: *m/z* 771 $[M]^+$.

General Procedure for Epoxidation Reactions

To a stirred solution of alkene (0.081mmol), catalyst (10, 30 or 60 spheres) in CH_2Cl_2 (1 mL), kept in a round-bottomed flask and maintained at 25 °C in a thermostatic bath, buffered bleach (0.35 mmol, buffered to pH = 11.2 with 0.05 M Na_2HPO_4 and 1 M NaOH) and NaClO (1.6 mmol) was added. The course of the reaction was monitored by GC against an internal quantitative standard (*n*-dodecane). In order to determine the absolute configuration of the major enantiomer, after complete consumption of the starting olefin, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by PLC (SiO_2).1,2-epoxy-1,2,3,4-tetrahydronaphthalene and 1,2-epoxy-1-phenylbutane were isolated from the reaction mixture by preparative PLC (SiO_2) using cyclohexane/EtOAc (15:1, v/v) and cyclohexane, respectively. Measurements of optical rotation gave $[\alpha]_D^{20}$ = +17.5 (*c* = 0.20, $CHCl_3$) for 1,2-epoxy-1,2,3,4-tetrahydronaphthalene and $[\alpha]_D^{20}$= –6.0 (*c* = 0.125, $CHCl_3$) for 1,2-epoxy-1-phenylbutane. Absolute configurations were assigned by comparison of the signs of measured $[\alpha]_D^{20}$ to the literature values[3]

Table S1. Results obtained for the epoxidation of selected alkenes using catalyst **5** in solution at 25°C[a]

Alkene	Time (h)	Conv (%)[b]	*e.e.*(%)[b]	TON[c]	TOF[d]
6-cyano-2,2-dimethylchromene	2	100	80	20	10
Cis-β-ethylstyrene	7	100	70 (cis) 80 (trans)[e]	18	3
1,2-dihydronapthalene	2	100	78	20	10
Indene	2	100	95	20	10

[a]In all these experiments 0.081 mmol of alkene and 5% of catalyst **5** were dissolved in 1 mL of CH_2Cl_2; NaClO was 0.81 mmol and the total volume of the reacting solutions, buffered with 1 mL 0.05 M Na_2HPO_4 at pH = 11.2, was 3 mL. [b]determined by GC on a specific chiral column. [c]TON= mmol of the overall products/mmol of the catalyst. [d] TOF = TON/reaction time (h).[e]*cis/trans* = 5

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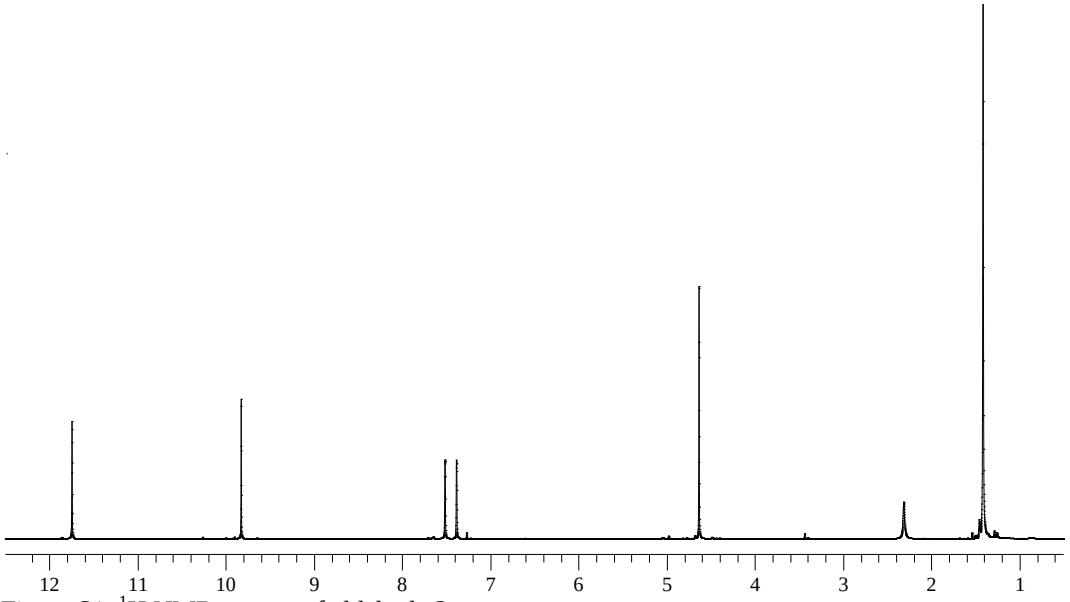

Figure S1. ^{1}H NMR spectra of aldehyde **2**

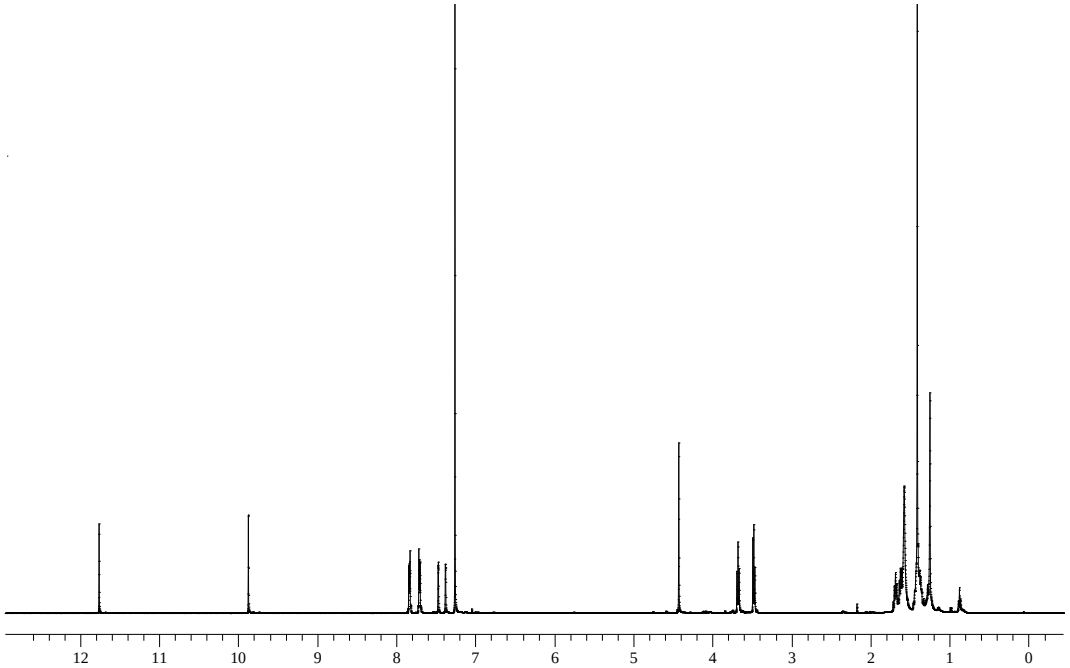

Figure S2. ^{1}H NMR of aldehyde **3** in $CDCl_3$

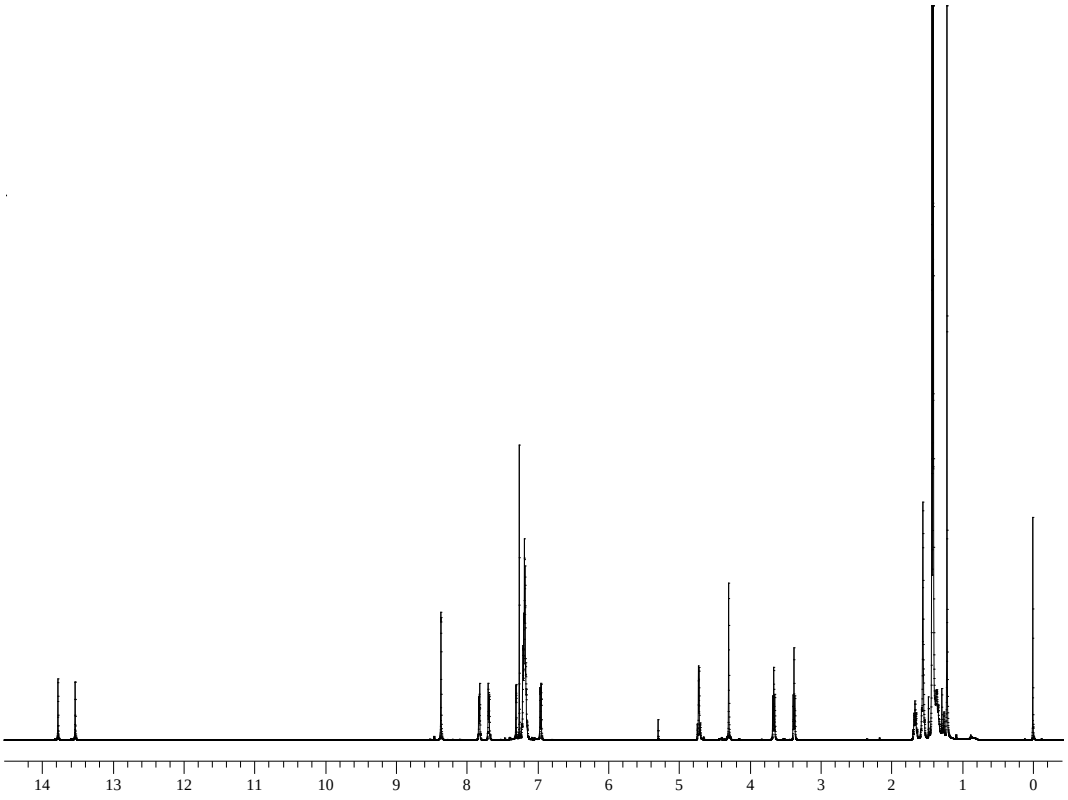

Figure S3. ^{1}H NMR of salen ligand **4** in $CDCl_3$

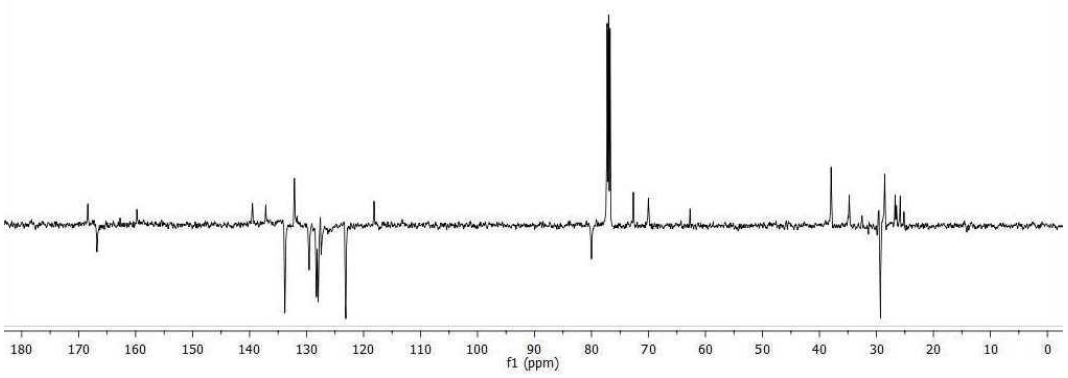

Figure S4. APT of salen ligand **4** in $CDCl_3$

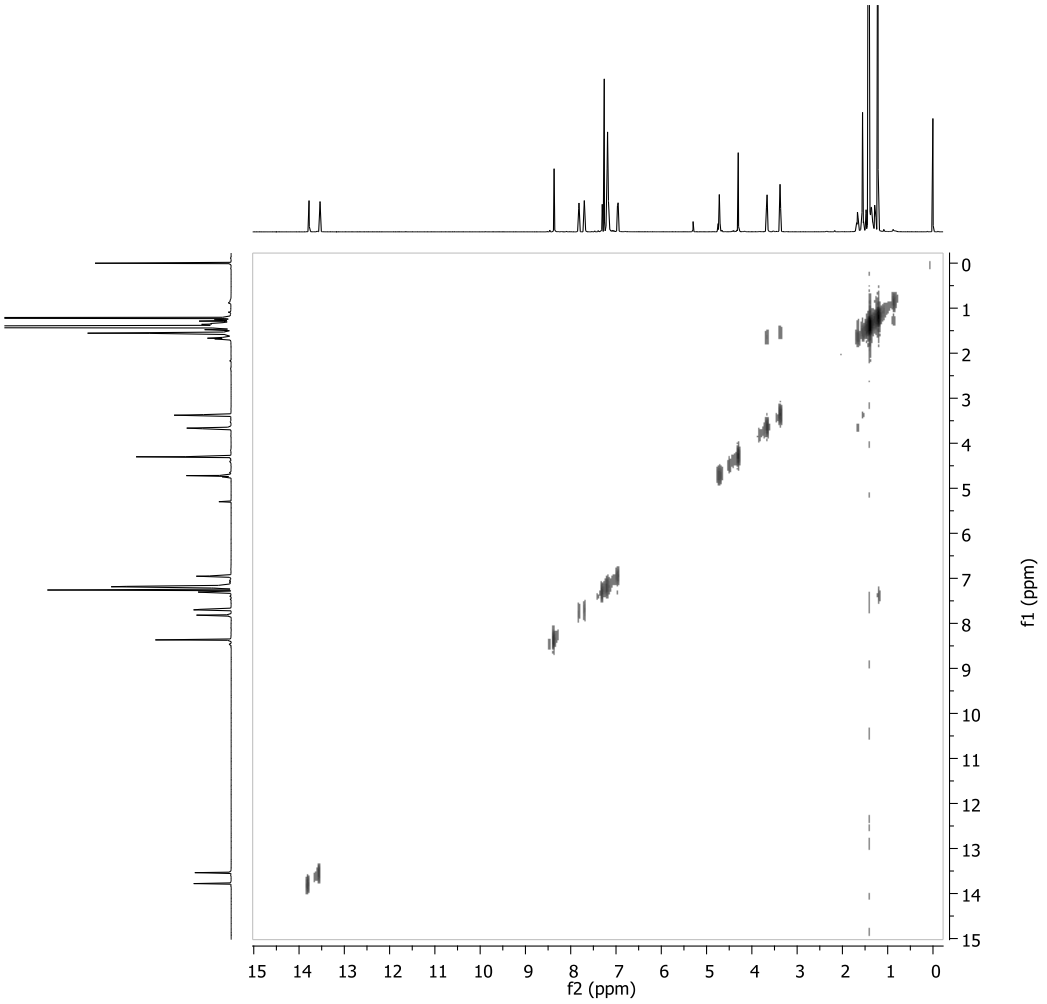

Figure S5. gCOSY of salen ligand **4** in $CDCl_3$

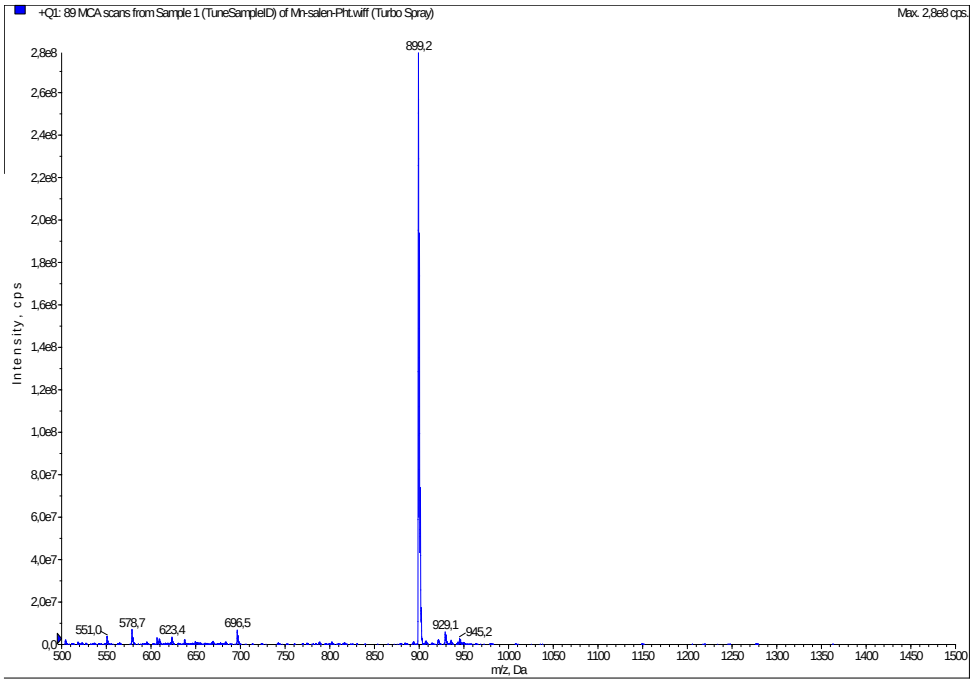

Figure S6. ESI MS of catalyst **5**

The surface morphology of the **Mn_1_MGB** was investigated by AFM. The system showed surfaces mainly consisting of grains with lateral dimensions of order 300-700 nm. The root mean square roughness of the films was typically around 13.9 nm and with a total range of 97.0 nm in the images.

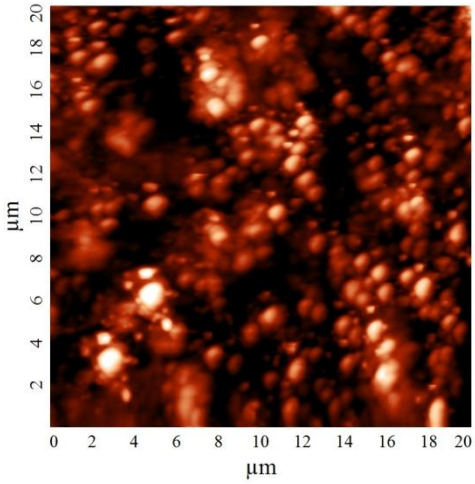

Figure S7. AFM micrograph of a representative **Mn_1_MGB**.