Enantioselective Alkylation of Aldehydes with Chiral Organomagnesium Amides (COMAs)

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Supporting Information

General Experimental

All reactions were performed using flame-dried glassware under an argon atmosphere. Diethyl ether and THF were freshly distilled from Na/benzophenone. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 and 75 MHz, respectively. Optical rotations were recorded in cells with 10 cm path length on a Perkin-Elmer 241 digital polarimeter. The known diamines **1a**,¹ **1b**,² **1c**,² and **1d**² were prepared from (*R*)-phenylglycine as previously described; analogously, **1h**, **1i**, and **1j** were prepared from (*S*)-valine, (*S*)-phenylalanine, and (*S*)-*tert*-leucine, respectively.² Diamines **1e**,² **1f**, and **1g**³ were prepared from (*R*)-2-phenyl-2-(1-piperidiny)ethanol and the appropriate amine.⁴ Enantiomer ratios were determined by HPLC using a 4.6 mm x 150 mm Chiralcel OD column, eluting with 1-2% isopropanol in hexanes.

Preparation of dibutylmagnesium solution.⁵ 1,4-Dioxane (18 mL, 0.22 mole) was added slowly to a mechanically stirred 1 M solution of *n*-butylmagnesium bromide (200 mL, 0.2 mole). The resultant heterogeneous solution was stirred at ambient temperature overnight (8-12 h). The

¹ Rossiter, B. E.; Eguchi, M.; Hernandez, A. E.; Vickers, D.; Medich, J.; Marr, J.; Heinis, D. *Tetrahedron Lett.* **1991**, 32, 3973-3976.

² Rossiter, B. E.; Eguchi, M.; Miao, G.; Swingle, N. M.; Hernandez, A. E.; Vickers, D.; Medich, J.; Marr, J.; Heinis, D. *Tetrahedron* **1993**, 49, 965-986.

³ Saraavanan, P.; Singh, V. K. *Tetrahedron Lett.* **1998**, 39, 167-170.

⁴ Sousa, S. E.; O'Brien, P.; Poumellec, P. *J. Chem. Soc., Perkin Trans. I* **1998**, 1483-1492.

⁵ Wakefield, B. J. "Organomagnesium Methods in Organic Synthesis" Academic Press, **1995**, 65-67.

suspension was then transferred *via* cannula to centrifuge tubes and centrifuged (2500 rpm, 30 min) to give a clear and colorless dibutylmagnesium solution. A few drops of 1,4-dioxane were added to the solution to confirm the complete precipitation of magnesium dibromide, and the clear supernatant was then transferred *via* cannula into a Schlenk tube and the concentration was determined by titration before use.

Titration of dialkylmagnesium solution. The following procedure was an extension of the titration procedure for Grignard reagents.⁶ The dialkylmagnesium solution (~0.5 M) was added dropwise to a stirred solution of accurately weigh salicylaldehyde phenylhydrazone (~ 1 mmol) in THF (15 mL) under argon at room temperature. The solution turned yellow initially and the end point is indicated by the bright golden orange color. The exact amount of dialkylmagnesium solution needed to reach the end point was recorded. Each mole of dialkylmagnesium will react with two moles of indicator and the concentration was calculated by:

$$M = \text{mmol of indicator} / (2 \times \text{volume of R}_2\text{Mg in mL})$$

Preparation of *n*-Bu-COMA (2) solution using ligand 1a. *n*-Bu₂Mg (0.50 M, 2.0 mL, 1.0 mmol) was added to a solution of diamine **1a** (225 mg, 1.03 mmol) in ether (15 mL) at –78 °C under argon. The cooling bath was then removed and the reaction allowed to warm to room temperature. THF (3 mL) was then added to the cloudy mixture and the resultant clear COMA solution was stirred for a further 15 min. The resultant COMA solution was used directly in the next reaction.

Bu-COMA addition to benzaldehyde – Preparation of 1-Phenyl-1-pentanol (3a). Benzaldehyde (45 mg, 0.42 mmol) in ether (2 mL) was added slowly to the Bu-COMA solution (1 mmol) at –78°C under argon. The reaction was stirred at –78 °C for 30 min then allowed to warm up to room

⁶ Love, B. E.; Jones, E. G. *J. Org. Chem.* **1999**, *64*, 3755-3756.

temperature slowly. The reaction was quenched with saturated aqueous NH_4Cl (5 mL), the layers were separated and the aqueous phase was extracted with ether (3 x 7 mL). The combined organic phase was washed with dilute HCl (1 M, 2 x 2 mL) to remove the diamine (see recovery procedure below). The organic phase was washed with water, saturated aqueous NaHCO_3 and brine (3 mL each), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (10-20% ether in hexanes) to afford 1-phenyl-1-pentanol (52 mg, 76%, er = 89:11). The enantiomeric excess of the product was determined by chiral phase HPLC (Chiralcel-OD, 1% isopropanol in hexanes, 1.0 mL/min *R*: 22.26 min, *S*: 24.25 min). $[\alpha]_{\text{D}}^{25} = 31.6$ ($c = 1.02$, C_6H_6); lit.⁷ (*R*)-isomer $[\alpha]_{\text{D}}^{25} = 45.9$ ($c = 6$, C_6H_6). ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.22 (5H, m), 4.64 (1H, dt, $J = 2.1, 6.5$ Hz), 1.91 (1H, d, $J = 2.1$ Hz), 1.90-1.65 (2H, m), 1.44-1.18 (4H, m) 0.87 (3H, t, $J = 6.1$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 144.9, 128.4 (2C), 127.4, 125.9 (2C), 74.6, 38.8, 27.9, 22.6, 14.0.

Recovery of diamine ligand. The acidic aqueous phase was washed once with ether (1 mL), before basify with 5 M KOH . The diamine **1a** was then extracted into ether (3 x 5 mL). The organic layer was dried (Na_2SO_4), filtered and evaporated under reduced pressure to give a light yellow oil. Kugelrohr distillation (0.5 mm Hg) gave the recovered amine as colorless oil (~80% recovery).

1-(4-methylphenyl)-1-pentanol (3b). This product was obtained using Bu-COMA **2** and tolualdehyde following the procedure described for **3a**. Yield (39 mg, 57 %, er = 88:12.) The er was determined by chiral phase HPLC using a Chiralcel-OD column (1 % isopropanol in hexanes, flow 1.0 mL/min). *S*-isomer : 16.67 min, *R*-isomer: 17.25 min. $[\alpha]_{\text{D}}^{25} = 28.5$ ($c = 1.1$, C_6H_6); lit.⁸ (*S*-isomer, 91% e.e.) $[\alpha]_{\text{D}}^{24} = -34.8$ [$c = 2.3$, C_6H_6], ^1H NMR (300 MHz, CDCl_3) δ 7.22 (2H, d, $J =$

⁷ Mukaiyama T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455-1460.

⁸ Soai, K.; Konishi, T.; Shibata, T. *Heterocycles* **1999**, *51*, 1421-1426.

8.0 Hz), 7.14 (2H, d, $J = 8.0$ Hz), 4.60 (1H, t, $J = 7.0$ Hz), 2.32 (3H, s), 1.6-1.8 (3H, m), 1.2-1.4 (4H, m), 0.86 (3H, t, $J = 7.0$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 141.9, 137.1, 129.1 (2C), 125.8 (2C), 74.5, 38.7, 28.0, 22.6, 21.1, 14.0.

1-(4-chlorophenyl)-1-pentanol (3c). This product was obtained using Bu-COMA **2** and 4-chlorobenzaldehyde following the procedure described for **3a**. Yield 50 % (42 mg, er = 83:17.). The er was determined by chiral phase HPLC using a Chiralcel-OD column (2 % isopropanol in hexanes, flow 0.8 mL/min). *S*-isomer : 16.93 min, *R*-isomer: 18.28 min. $[\alpha]_{\text{D}}^{25} = 14.8$ ($c = 0.87$, C_6H_6); for (*S*)-1-(4-chlorophenyl)-1-propanol, lit⁹ $[\alpha]_{\text{D}}^{25} = -28.3$ ($c = 0.52$, C_6H_6) which suggests that the major isomer of **3c** formed has *R* configuration. ^1H NMR (300 MHz, CDCl_3) δ 7.2-7.3 (4H, m), 4.63 (1H, t, $J = 6.6$ Hz), 1.6-1.8 (3H, m), 1.2-1.4 (4H, m), 0.86 (3H, t, $J = 6.8$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 143.3, 133.0, 128.5 (2C), 127.2 (2C), 73.9, 38.8, 27.8, 22.5, 14.0

1-(1-naphthyl)-1-pentanol (3d). This product was obtained using Bu-COMA **2** and 1-naphthaldehyde following the procedure described for **3a**. Yield 71 % (60 mg, er = 77:23.) of white solid m.p. 66 °C (Lit¹⁰ m.p. 67 °C). The er was determined by chiral phase HPLC using a Chiralcel-OD column (1% isopropanol in hexanes, flow 1.0 mL/min). *S*-isomer : 39.11 min, *R*-isomer: 93.86 min. $[\alpha]_{\text{D}}^{25} = 36.3$ ($c = 1.25$, CHCl_3); for (*S*)-1-(1-naphthyl)-1-propanol, lit⁹ $[\alpha]_{\text{D}}^{25} = -50.53$ ($c = 2.5$, CHCl_3) which suggests that the major isomer of **3d** formed has *R* configuration. ^1H NMR (300 MHz, CDCl_3) δ 8.10 (1H, d, $J = 8.1$ Hz), 7.86 (1H, d, $J = 8.0$ Hz), 7.76 (1H, d, $J = 8.1$ Hz), 7.63 (1H, d, $J = 7.1$ Hz), 7.4-7.5 (3H, m), 5.46 (1H, dd, $J = 5.4, 7.1$ Hz), 2.0-1.9 (2H, m), 1.73

⁹ Prasad, K. R. K.; Joshi, N. N. *J. Org. Chem.* **1997**, 62, 3770-3771.

¹⁰ Badr, M. Z. A.; Hickinbottom, W. J. *J. Chem. Soc.* **1965**, 4101-4107.

(1H, br), 1.3-1.6 (4H, m), 0.89 (3H, t, $J = 6.9$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 140.6, 133.8, 130.4, 128.9, 127.8, 125.9, 125.4(2C), 123.1, 122.7, 71.2, 38.0, 28.4, 22.6, 14.0.

13-(methoxymethoxy)-5-tridecanol (3e). This product was obtained using Bu-COMA **2** and 9-methoxymethoxynonanal¹¹ following the procedure described for **3a**. Yield (37 mg, 34 %, er = 82:18). The er was determined by derivatizing **3e** to the corresponding benzoate which can then be analyzed by chiral phase HPLC using a Chiralcel-OD column (0.2 % isopropanol in hexanes, 1.0 mL/min). *R*-isomer : 12.8 min, *S*-isomer: 15.9 min. $[\alpha]_{\text{D}}^{25} = -0.81$ ($c = 1.6$, CHCl_3); lit.¹¹ (*R*)-isomer $[\alpha]_{\text{D}}^{25} = -1.4$ ($c = 1.0$, CHCl_3), ^1H NMR (250 MHz, CDCl_3) δ 4.58 (2H, s), 3.6-3.5 (1H, m), 3.48 (2H, t, $J = 6.6$ Hz), 3.33 (3H, s), 1.6-1.5 (2H, m), 1.5-1.2 (19H, m), 0.87 (3H, t, $J = 7.0$ Hz). ^{13}C NMR (63 MHz, CDCl_3) δ 96.3, 71.8, 67.8, 55.0, 37.4, 37.1, 29.6 (2C), 29.5, 29.3, 27.8, 26.1, 25.6, 22.7, 14.0.

12-(benzyloxy)-5-dodecanol (3f). This product was obtained using Bu-COMA **2** and 8-(benzyloxy)octanal¹² following the procedure described for **3a**. Yield (63 mg, 51 %, er = 84:16). The er was determined by chiral phase HPLC using a Chiralcel-OD column (1% isopropanol in hexanes, 1.0 mL/min). *S*-isomer : 26.82 min, *R*-isomer: 27.81 min. $[\alpha]_{\text{D}}^{25} = -0.2$ ($c = 2.0$, EtOH); lit.¹³ (*S*)-isomer $[\alpha]_{\text{D}}^{25} = 1$ ($c = 2.59$, EtOH), ^1H NMR (300 MHz, CDCl_3) δ 7.3-7.2 (5H, m), 4.48 (2H, s), 3.6-3.5 (1H, m), 3.44 (2H, t, $J = 6.6$ Hz), 1.6-1.5 (4H, m), 1.5-1.2 (14H, m), 0.89 (3H, br t, $J = 6.7$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 138.6, 128.3, 127.6, 127.4, 72.8, 72.0, 70.4, 37.4, 37.1, 29.7, 29.6, 29.4, 27.8, 26.1, 25.5, 22.7, 14.1.

¹¹ Abad, J.-L.; Fabrias, G.; Camps, F. *J. Org. Chem.* **2000**, *65*, 8582-8588.

¹² Fujita, T.; Hamamichi, N.; Matsuzaki, T.; Kitao, Y.; Kiuchi, M.; Node, M.; Hirose, R. *Tetrahedron Lett.* **1995**, *36*, 8599-8602.

¹³ Jakob, B.; Gerlach, H. *Liebigs Ann.* **1996**, *12*, 2123-2130.

1-Phenylethanol (4a). This compound was prepared in THF as the Me-COMA (prepared from Me₂Mg and **1a**) is not soluble in ether. A better er was also obtained using THF. Yield: (18 mg, 34%, er = 86:14). The er was determined by chiral phase HPLC using a Chiralcel-OD column (2 % isopropanol in hexanes, flow 1.0 mL/min). *R*-isomer : 13.90 min, *S*-isomer: 18.25 min. $[\alpha]_D^{25} = 35.0$ (c = 1.0, CHCl₃); lit.¹⁴ $[\alpha]_D^{25} = 41.9$ (c = 2.8, CHCl₃), ¹H NMR (300 MHz, CDCl₃) δ 7.4-7.2 (5H, m), 4.87 (1H, dq, *J* = 3.0, 6.5 Hz), 1.95 (1H, d, *J* = 3.0 Hz), 1.48 (1H, d, *J* = 6.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 145.8, 128.5 (2C), 127.4, 125.3 (2C), 70.4, 25.1.

1-phenyl-1-propanol (4b). This product was obtained using Et-COMA (prepared from Et₂Mg and **1a**) and benzaldehyde following the procedure described for **3a**. Yield (40 mg, 70 %, er = 84:16) The er was determined by chiral phase HPLC using a Chiralcel-OD column (2% isopropanol in hexanes, flow 1.0 mL/min). *R*-isomer : 12.57 min, *S*-isomer: 15.62 min. $[\alpha]_D^{25} = 34.5$ (c = 0.76, CHCl₃); lit.¹⁵ 98%e.e. $[\alpha]_D^{25} = 43.9$ (c = 5.62, CHCl₃), ¹H NMR (300 MHz, CDCl₃) δ 7.4-7.2 (5H, m), 4.58 (1H, br t, *J* = 6.5 Hz), 1.88 (1H, br s), 1.8-1.7(2H, m), 0.90 (3H, t, *J* = 7.4 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 144.5, 128.4 (2C), 127.5, 125.9 (2C), 76.0, 31.9, 10.1.

1-phenyl-1-octanol (4c). This product was obtained using *n*-C₇H₁₅-COMA (prepared from (*n*-C₇H₁₅)₂Mg and **1a**) and benzaldehyde following the procedure described for **3a**. Yield (61 mg, 70 %, er = 89:11). The er was determined by chiral phase HPLC using a Chiralcel-OD column (1 % isopropanol in hexanes, flow 1.0 mL/min). *R*-isomer : 20.53 min, *S*-isomer: 24.17 min. $[\alpha]_D^{25} =$

¹⁴ Jesus, P. C.; Rezende, M. C.; Nascimento, M. G. *Tetrahedron: Asymmetry* **1995**, 6 , 63-66.

¹⁵ Paquette, L. A.; Zhou, R. *J.Org.Chem.* **1999**, 64, 7929–7934.

13.0 (c = 0.91, EtOH); lit.¹⁶ 97.8% e.e. $[\alpha]_D^{25} = 17.3$ (c = 0.855, EtOH). ¹H NMR (300 MHz, CDCl₃) δ 7.4-7.2 (5H, m), 4.62 (1H, br t, $J = 6.2$ Hz), 2.09 (1H, br s), 1.8-1.7 (2H, m), 1.42-1.2 (10H, m), 0.87 (3H, br t, $J = 7.0$ Hz), ¹³C NMR (75 MHz, CDCl₃) δ 144.9, 128.3 (2C), 127.4, 125.9 (2C), 74.6, 39.1, 31.8, 29.5, 29.2, 25.8, 22.6, 14.0.

1-phenyl-1-undecanol (4d). This compound was obtained using *n*-C₁₀H₂₁-COMA (prepared from (*n*-C₇H₁₅)₂Mg and **1a**) and benzaldehyde following the procedure described for **3a**. Yield (68 mg, 69 %, er = 88:12). The er was determined by chiral phase HPLC using a Chiralcel-OD column (1 % isopropanol in hexanes, flow 1.0 mL/min). *R*-isomer : 19.04 min, *S*-isomer: 22.33 min. $[\alpha]_D^{25} = +16.3^\circ$ [c = 2.2, CHCl₃] (lit.¹⁷ (*S*-isomer) $[\alpha]_D^{25} = -20.1^\circ$ [c = 6.71, CHCl₃]), ¹H NMR (300 MHz, CDCl₃) δ 7.4-7.2 (5H, m), 4.67-4.62 (1H, m), 1.8-1.7 (3H, m), 1.4-1.2 (16H, m), 0.86 (3H, br t, $J = 6.5$ Hz), ¹³C NMR (75 MHz, CDCl₃) δ 144.9, 128.4 (2C), 127.4, 125.9 (2C), 74.7, 39.1, 31.9, 29.6 (2C), 29.5 (2C), 29.3, 25.3, 22.7, 14.1.

1-phenyl-2-methyl-1-propanol (4e). This compound was obtained using *i*-Pr-COMA (prepared from *i*-Pr₂Mg and **1a**) and benzaldehyde following the procedure described for **3a**. **4e** (33 mg, 44% yield, er = 72:28) was isolated along with 22 mg (41 %) of benzyl alcohol. The er of **3a** was determined by chiral phase HPLC using a Chiralcel-OD column (1% isopropanol in hexanes, flow 1.0 mL/min). *S*-isomer : 20.33 min, *R*-isomer: 18.25 min. $[\alpha]_D^{25} = +19.1$ [c = 0.91, Et₂O] (lit.¹⁸ $[\alpha]_D^{21} = 52.1$ (c = 1.6, Et₂O)), ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.2 (5H, m), 4.34 (1H, dd, $J = 3.2, 6.9$ Hz), 1.94 (1H, oct, $J = 6.8$ Hz), 1.86 (2H, d, $J = 3.2$ Hz), 0.98 (3H, d, $J = 6.8$ Hz), 0.78 (3H,

¹⁶ Mori, K.; Bernotas, R. *Tetrahedron: Asymmetry* **1990**, 2, 87-96.

¹⁷ Langer, F.; Schwink, L.; Devasagayaram, A.; Chavant, P.Y.; Knochel, P. *J. Org. Chem.* **1996**, 61, 8229-8243.

¹⁸ Yang, W.K.; Cho, B.T. *Tetrahedron: Asymmetry* **2000**, 11, 2947-2953.

d, $J = 6.8$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ 143.6, 128.2 (2C), 127.4, 126.5 (2C), 80.0, 35.2, 19.0, 18.2.

Phenyl pentafluorophenyl carbinol (5). This compound was obtained using Ph-COMA (prepared from Ph_2Mg and **1a**) and pentafluorobenzaldehyde following the procedure described for **3a**. Yield: 97 mg, 71% yield, er = 85:15. The er was determined by chiral phase HPLC using a Chiralcel-OD column (2% isopropanol in hexanes, flow 1.0 mL/min). *R*-isomer : 15.32 min, *S*-isomer: 18.46 min. $[\alpha]_{\text{D}}^{25} = +31.0^\circ$ [$c = 1.0$, CHCl_3], ^1H NMR (300 MHz, CDCl_3) δ 7.3-7.4 (5H, m), 5.97 (1H, s), 2.69 (1H, br s); ^{13}C NMR (75 MHz, CDCl_3) δ 144.7 (dm, $J = 241$ Hz), 140.9 (dm, $J = 239$ Hz), 140.5, 137.6 (dm, $J = 238$ Hz), 128.8(2C), 128.3, 125.3 (2C), 116.9 (m), 67.6. The configuration was tentatively assigned to be *R*- based on the fact that ligands with *R* configuration consistently favor products resulted from *Re*- face attack.

X-ray Crystallographic Data for COMA 2

ORTEP drawing of COMA 2

Table 1. Crystal data and structure refinement for COMA 2.

Identification code	mc1040m
Empirical formula	C ₃₆ H ₆₀ Mg ₂ N ₄
Formula weight	597.50
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.4984(4) Å α = 90 °. b = 16.0509(6) Å β = 109.201(1) ° c = 12.3963(5) Å γ = 90 °
Volume	1784.78(12) Å ³
Z, Calculated density	2, 1.112 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
F(000)	656
Crystal size	0.38 x 0.32 x 0.24 mm
Theta range for data collection	1.74 to 30.03°
Limiting indices	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected / unique	22328 / 10342 [R(int) = 0.0263]
Completeness to theta = 30.03	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.9797 and 0.9636
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10342 / 1 / 620
Goodness-of-fit on F ²	1.308
Final R indices [I > 2sigma(I)]	R1 = 0.0347, wR2 = 0.0784
R indices (all data)	R1 = 0.0372, wR2 = 0.0790
Absolute structure parameter	0.02(9)
Extinction coefficient	0.0071(9)
Largest diff. peak and hole	0.281 and -0.210 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mc1040m. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mg(1)	-68(1)	389(1)	3578(1)	20(1)
Mg(2)	61(1)	43(1)	1296(1)	19(1)
N(1)	1421(1)	728(1)	2680(1)	20(1)
N(2)	-336(1)	1764(1)	3710(1)	22(1)
N(3)	-1582(1)	-204(1)	2087(1)	19(1)
N(4)	619(1)	-1284(1)	1593(1)	20(1)
C(1)	2967(2)	582(1)	3414(1)	28(1)
C(2)	1153(1)	1623(1)	2389(1)	21(1)
C(3)	912(2)	2120(1)	3374(1)	25(1)
C(4)	-1794(2)	2081(1)	2944(1)	30(1)
C(5)	-3070(2)	1733(1)	3293(1)	35(1)
C(6)	-2903(2)	1997(1)	4503(2)	45(1)
C(7)	-1389(2)	1736(1)	5297(1)	38(1)
C(8)	-147(2)	2058(1)	4894(1)	32(1)
C(9)	2311(1)	2029(1)	1937(1)	24(1)
C(10)	2939(2)	2806(1)	2284(1)	31(1)
C(11)	3890(2)	3170(1)	1768(2)	38(1)
C(12)	4240(2)	2765(1)	915(1)	40(1)
C(13)	3669(2)	1977(1)	583(1)	37(1)
C(14)	2710(2)	1617(1)	1092(1)	30(1)
C(15)	780(2)	-277(1)	5178(1)	30(1)
C(16)	1708(2)	176(1)	6260(1)	30(1)
C(17)	2321(2)	-357(1)	7332(1)	39(1)
C(18)	3188(2)	147(1)	8383(1)	51(1)
C(19)	-3035(1)	155(1)	1415(1)	25(1)
C(20)	-1738(1)	-1113(1)	2058(1)	18(1)
C(21)	-198(1)	-1520(1)	2384(1)	21(1)
C(22)	2219(1)	-1502(1)	2120(1)	28(1)
C(23)	3094(2)	-1266(1)	1339(1)	34(1)
C(24)	2501(2)	-1715(1)	208(1)	38(1)
C(25)	839(2)	-1545(1)	-324(1)	31(1)
C(26)	5(2)	-1757(1)	498(1)	27(1)
C(27)	-2622(1)	-1496(1)	2769(1)	21(1)
C(28)	-3114(2)	-2315(1)	2555(1)	27(1)
C(29)	-3936(2)	-2692(1)	3162(1)	35(1)
C(30)	-4288(2)	-2244(1)	3992(1)	37(1)
C(31)	-3820(2)	-1430(1)	4210(1)	35(1)
C(32)	-2989(1)	-1054(1)	3604(1)	27(1)
C(33)	-673(2)	602(1)	-373(1)	30(1)
C(34)	-1944(2)	216(1)	-1331(1)	30(1)
C(35)	-2420(2)	675(1)	-2455(1)	53(1)
C(36)	-3609(3)	250(1)	-3416(1)	55(1)

Table 3. Bond lengths [Å] and angles [deg] for mc1040m.

Mg(1)-N(1)	2.1374(10)
Mg(1)-N(3)	2.1537(10)
Mg(1)-C(15)	2.1622(13)
Mg(1)-N(2)	2.2339(11)
Mg(1)-Mg(2)	2.9242(5)
Mg(2)-N(1)	2.0889(10)
Mg(2)-N(3)	2.1363(10)
Mg(2)-C(33)	2.1497(13)
Mg(2)-N(4)	2.1964(11)
N(1)-C(1)	1.4695(16)
N(1)-C(2)	1.4828(15)
N(2)-C(4)	1.4880(17)
N(2)-C(3)	1.4933(16)
N(2)-C(8)	1.4960(16)
N(3)-C(20)	1.4658(15)
N(3)-C(19)	1.4744(15)
N(4)-C(21)	1.4852(14)
N(4)-C(22)	1.4853(15)
N(4)-C(26)	1.4966(15)
C(2)-C(9)	1.5338(17)
C(2)-C(3)	1.5370(16)
C(4)-C(5)	1.520(2)
C(5)-C(6)	1.517(2)
C(6)-C(7)	1.510(3)
C(7)-C(8)	1.516(2)
C(9)-C(10)	1.3886(19)
C(9)-C(14)	1.3931(19)
C(10)-C(11)	1.395(2)
C(11)-C(12)	1.372(2)
C(12)-C(13)	1.383(2)
C(13)-C(14)	1.3919(19)
C(15)-C(16)	1.5255(18)
C(16)-C(17)	1.5258(19)
C(17)-C(18)	1.525(2)
C(20)-C(21)	1.5304(15)
C(20)-C(27)	1.5316(16)
C(22)-C(23)	1.517(2)
C(23)-C(24)	1.511(2)
C(24)-C(25)	1.521(2)
C(25)-C(26)	1.5206(18)
C(27)-C(32)	1.3896(17)
C(27)-C(28)	1.3912(18)
C(28)-C(29)	1.3891(19)
C(29)-C(30)	1.383(2)
C(30)-C(31)	1.379(2)
C(31)-C(32)	1.3934(18)
C(33)-C(34)	1.5191(19)
C(34)-C(35)	1.507(2)
C(35)-C(36)	1.509(3)

N(1)-Mg(1)-N(3)	92.04(4)
N(1)-Mg(1)-C(15)	119.54(5)
N(3)-Mg(1)-C(15)	120.74(5)
N(1)-Mg(1)-N(2)	84.09(4)
N(3)-Mg(1)-N(2)	116.06(4)
C(15)-Mg(1)-N(2)	115.96(5)
N(1)-Mg(1)-Mg(2)	45.54(3)
N(3)-Mg(1)-Mg(2)	46.78(3)
C(15)-Mg(1)-Mg(2)	132.27(4)
N(2)-Mg(1)-Mg(2)	107.47(3)
N(1)-Mg(2)-N(3)	93.91(4)
N(1)-Mg(2)-C(33)	119.26(5)
N(3)-Mg(2)-C(33)	117.71(5)
N(1)-Mg(2)-N(4)	108.82(4)
N(3)-Mg(2)-N(4)	85.12(4)
C(33)-Mg(2)-N(4)	123.33(5)
N(1)-Mg(2)-Mg(1)	46.91(3)
N(3)-Mg(2)-Mg(1)	47.28(3)
C(33)-Mg(2)-Mg(1)	138.47(5)
N(4)-Mg(2)-Mg(1)	96.09(3)
C(1)-N(1)-C(2)	111.23(9)
C(1)-N(1)-Mg(2)	130.29(8)
C(2)-N(1)-Mg(2)	107.42(7)
C(1)-N(1)-Mg(1)	109.53(8)
C(2)-N(1)-Mg(1)	106.47(7)
Mg(2)-N(1)-Mg(1)	87.55(4)
C(4)-N(2)-C(3)	110.42(10)
C(4)-N(2)-C(8)	107.71(11)
C(3)-N(2)-C(8)	107.61(10)
C(4)-N(2)-Mg(1)	113.29(8)
C(3)-N(2)-Mg(1)	103.77(7)
C(8)-N(2)-Mg(1)	113.87(8)
C(20)-N(3)-C(19)	107.84(9)
C(20)-N(3)-Mg(2)	104.88(7)
C(19)-N(3)-Mg(2)	110.91(7)
C(20)-N(3)-Mg(1)	119.63(7)
C(19)-N(3)-Mg(1)	123.33(8)
Mg(2)-N(3)-Mg(1)	85.94(4)
C(21)-N(4)-C(22)	109.27(9)
C(21)-N(4)-C(26)	109.71(9)
C(22)-N(4)-C(26)	108.44(10)
C(21)-N(4)-Mg(2)	102.08(7)
C(22)-N(4)-Mg(2)	117.22(8)
C(26)-N(4)-Mg(2)	109.85(8)
N(1)-C(2)-C(9)	114.44(10)
N(1)-C(2)-C(3)	111.59(9)
C(9)-C(2)-C(3)	112.43(10)
N(2)-C(3)-C(2)	111.20(9)
N(2)-C(4)-C(5)	110.79(11)
C(6)-C(5)-C(4)	110.17(14)
C(7)-C(6)-C(5)	109.53(12)
C(6)-C(7)-C(8)	111.60(13)
N(2)-C(8)-C(7)	111.11(11)
C(10)-C(9)-C(14)	117.59(12)
C(10)-C(9)-C(2)	123.72(12)
C(14)-C(9)-C(2)	118.62(11)
C(9)-C(10)-C(11)	120.73(15)

C(12)-C(11)-C(10)	120.83 (15)
C(11)-C(12)-C(13)	119.44 (14)
C(12)-C(13)-C(14)	119.71 (15)
C(13)-C(14)-C(9)	121.63 (14)
C(16)-C(15)-Mg(1)	120.31 (9)
C(15)-C(16)-C(17)	116.28 (12)
C(18)-C(17)-C(16)	112.96 (13)
N(3)-C(20)-C(21)	109.78 (9)
N(3)-C(20)-C(27)	117.06 (9)
C(21)-C(20)-C(27)	109.54 (9)
N(4)-C(21)-C(20)	112.21 (9)
N(4)-C(22)-C(23)	110.92 (11)
C(24)-C(23)-C(22)	110.97 (12)
C(23)-C(24)-C(25)	109.52 (11)
C(26)-C(25)-C(24)	111.36 (12)
N(4)-C(26)-C(25)	111.18 (10)
C(32)-C(27)-C(28)	118.20 (11)
C(32)-C(27)-C(20)	122.92 (11)
C(28)-C(27)-C(20)	118.86 (11)
C(29)-C(28)-C(27)	121.51 (14)
C(30)-C(29)-C(28)	119.51 (15)
C(31)-C(30)-C(29)	119.80 (13)
C(30)-C(31)-C(32)	120.55 (14)
C(27)-C(32)-C(31)	120.42 (13)
C(34)-C(33)-Mg(2)	120.37 (9)
C(35)-C(34)-C(33)	116.33 (13)
C(34)-C(35)-C(36)	115.35 (16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mc1040m.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mg(1)	23(1)	18(1)	17(1)	0(1)	6(1)	-2(1)
Mg(2)	19(1)	20(1)	18(1)	0(1)	7(1)	-2(1)
N(1)	19(1)	18(1)	23(1)	2(1)	6(1)	-1(1)
N(2)	28(1)	20(1)	20(1)	0(1)	11(1)	-1(1)
N(3)	19(1)	17(1)	21(1)	0(1)	7(1)	0(1)
N(4)	15(1)	23(1)	23(1)	-2(1)	8(1)	0(1)
C(1)	23(1)	27(1)	30(1)	2(1)	2(1)	-2(1)
C(2)	22(1)	20(1)	21(1)	0(1)	7(1)	-3(1)
C(3)	31(1)	20(1)	24(1)	-1(1)	11(1)	-5(1)
C(4)	33(1)	26(1)	31(1)	6(1)	13(1)	8(1)
C(5)	29(1)	37(1)	43(1)	7(1)	16(1)	11(1)
C(6)	55(1)	33(1)	61(1)	-5(1)	40(1)	5(1)
C(7)	61(1)	34(1)	30(1)	-10(1)	29(1)	-9(1)
C(8)	46(1)	25(1)	25(1)	-7(1)	14(1)	-7(1)
C(9)	21(1)	25(1)	25(1)	5(1)	7(1)	-3(1)
C(10)	26(1)	23(1)	44(1)	3(1)	12(1)	-1(1)
C(11)	26(1)	26(1)	62(1)	11(1)	15(1)	-3(1)
C(12)	26(1)	44(1)	52(1)	19(1)	17(1)	-3(1)
C(13)	29(1)	54(1)	32(1)	4(1)	16(1)	-6(1)
C(14)	28(1)	36(1)	29(1)	-1(1)	11(1)	-9(1)
C(15)	41(1)	24(1)	21(1)	1(1)	5(1)	-9(1)
C(16)	38(1)	27(1)	22(1)	2(1)	4(1)	-5(1)
C(17)	49(1)	35(1)	23(1)	5(1)	0(1)	-7(1)
C(18)	64(1)	53(1)	24(1)	3(1)	0(1)	-16(1)
C(19)	21(1)	26(1)	26(1)	2(1)	7(1)	4(1)
C(20)	18(1)	19(1)	19(1)	-1(1)	7(1)	-2(1)
C(21)	20(1)	20(1)	23(1)	2(1)	9(1)	0(1)
C(22)	19(1)	27(1)	36(1)	5(1)	8(1)	5(1)
C(23)	18(1)	36(1)	51(1)	8(1)	15(1)	3(1)
C(24)	35(1)	38(1)	52(1)	1(1)	30(1)	8(1)
C(25)	31(1)	37(1)	33(1)	-8(1)	19(1)	-2(1)
C(26)	25(1)	29(1)	30(1)	-10(1)	13(1)	-4(1)
C(27)	17(1)	25(1)	20(1)	3(1)	6(1)	-2(1)
C(28)	24(1)	24(1)	35(1)	1(1)	12(1)	-1(1)
C(29)	27(1)	27(1)	53(1)	12(1)	14(1)	-2(1)
C(30)	27(1)	48(1)	40(1)	19(1)	17(1)	-1(1)
C(31)	32(1)	50(1)	27(1)	0(1)	16(1)	-4(1)
C(32)	25(1)	33(1)	24(1)	-3(1)	10(1)	-5(1)
C(33)	35(1)	28(1)	24(1)	2(1)	7(1)	-6(1)
C(34)	35(1)	31(1)	22(1)	3(1)	5(1)	-4(1)
C(35)	65(1)	51(1)	28(1)	13(1)	-3(1)	-16(1)
C(36)	70(1)	55(1)	26(1)	5(1)	-5(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mc1040m.

	x	y	z	U(eq)
H(1X)	3070(17)	36(11)	3771(13)	34(4)
H(1Y)	3718(19)	581(11)	3028(14)	44(5)
H(1Z)	3331(16)	1001(10)	4036(13)	28(4)
H(2)	221(16)	1676(9)	1789(12)	25(4)
H(3X)	641(15)	2691(9)	3149(11)	22(3)
H(3Y)	1828(17)	2105(9)	4033(13)	29(4)
H(4X)	-1760(16)	2709(10)	2971(12)	29(4)
H(4Y)	-1874(17)	1946(10)	2221(14)	34(4)
H(5X)	-3030(17)	1102(11)	3261(13)	33(4)
H(5Y)	-3976(17)	1934(9)	2788(13)	27(4)
H(6X)	-3010(20)	2543(15)	4576(18)	68(7)
H(6Y)	-3732(19)	1726(11)	4731(14)	40(4)
H(7X)	-1315(19)	1132(12)	5351(14)	45(5)
H(7Y)	-1180(20)	1908(13)	6063(18)	63(6)
H(8X)	-70(20)	2685(12)	4882(16)	47(5)
H(8Y)	804(18)	1846(10)	5408(15)	42(5)
H(10)	2693(19)	3119(12)	2875(14)	38(4)
H(11)	4290(20)	3706(13)	2056(16)	51(5)
H(12)	4890(20)	3033(12)	500(15)	51(5)
H(13)	3848(19)	1694(12)	14(15)	45(5)
H(14)	2231(15)	1080(9)	809(12)	24(3)
H(15X)	-10(20)	-559(11)	5323(14)	45(5)
H(15Y)	1375(19)	-687(12)	5073(14)	44(5)
H(16X)	2567(17)	441(10)	6107(13)	30(4)
H(16Y)	1044(19)	634(12)	6447(15)	45(5)
H(17X)	1491(19)	-679(11)	7466(14)	46(5)
H(17Y)	3070(20)	-815(13)	7246(16)	55(5)
H(18X)	2590(20)	586(15)	8545(18)	64(7)
H(18Y)	4040(20)	358(13)	8254(16)	57(6)
H(18Z)	3560(30)	-184(16)	9100(20)	89(8)
H(19X)	-2987(18)	765(12)	1317(14)	41(5)
H(19Y)	-3857(18)	105(11)	1737(14)	38(4)
H(19Z)	-3432(15)	-120(9)	635(12)	24(4)
H(20)	-2270(14)	-1295(8)	1262(11)	14(3)
H(21X)	-304(16)	-2134(10)	2399(11)	26(4)
H(21Y)	428(15)	-1331(9)	3146(12)	20(3)
H(22X)	2607(16)	-1215(10)	2851(13)	31(4)
H(22Y)	2324(17)	-2142(10)	2294(13)	34(4)
H(23X)	3042(17)	-647(11)	1192(13)	35(4)
H(23Y)	4075(18)	-1356(10)	1746(13)	32(4)
H(24X)	2672(17)	-2309(11)	332(13)	30(4)
H(24Y)	2993(19)	-1564(11)	-312(14)	42(4)
H(25X)	665(17)	-986(11)	-515(13)	31(4)
H(25Y)	400(20)	-1853(12)	-1008(16)	51(5)
H(26X)	-1104(17)	-1610(9)	148(12)	29(4)
H(26Y)	81(17)	-2368(11)	667(14)	37(4)
H(28)	-2873(18)	-2584(11)	2075(14)	33(4)
H(29)	-4280(20)	-3257(14)	3026(16)	56(5)

H(30)	-4880(19)	-2506(11)	4357(14)	43(5)
H(31)	-4089(18)	-1092(12)	4806(15)	47(5)
H(32)	-2716(16)	-474(10)	3743(12)	27(4)
H(33X)	-970(30)	1130(16)	-240(20)	83(7)
H(33Y)	220(20)	737(11)	-601(15)	48(5)
H(34X)	-1673(19)	-337(12)	-1433(15)	48(5)
H(34Y)	-2870(30)	198(14)	-1080(20)	85(7)
H(35X)	-2630(30)	1167(19)	-2420(30)	104(10)
H(35Y)	-1360(30)	815(14)	-2658(18)	73(7)
H(36X)	-3270(30)	-284(17)	-3500(20)	84(8)
H(36Y)	-4580(30)	120(16)	-3230(19)	81(7)
H(36Z)	-3890(20)	567(13)	-4115(18)	60(6)