Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Monodentate coordination of the normally chelating chiral diamine (*R,R*)-TMCDA

Ana I. Ojeda-Amador, Antonio J. Martínez-Martínez, Alan R. Kennedy David R. Armstrong and Charles T. O'Hara*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL (UK)

E-mail: charlie.ohara@strath.ac.uk

Table of Contents

EXPERIMENTAL SECTION

General Procedures

All reactions and manipulations were performed under a protective atmosphere of dry pure argon gas using standard Schlenk tube or glovebox techniques. *n*-Hexane was dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR solvents were degassed and stored under argon over activated molecular sieves (4 Å) prior to use. Bis(trimethylsilyl)amine [HMDS(H)] was purchased from Aldrich, distilled under nitrogen atmosphere with CaH_2, and stored under argon over activated molecular sieves (4 Å). *n*BuNa was prepared according to literature methods and stored in a glove box.[1] Sodium 1,1,1,3,3,3-hexamethyldisilazide (NaHMDS) was prepared from *n*BuNa and HMDS(H) and stored in a glove box. *N,N,N′,N′*-(1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine (*R*,*R*)-TMCDA was prepared according to literature methods and stored under argon over activated molecular sieves (4 Å) prior to use.[2] NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer, operating at 400.1 and 100.6 MHz for ^{1}H and ^{13}C, respectively. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are expressed in parts per million (δ, ppm) and referenced to the appropriate residual solvent signal. Elemental analyses of compounds **1** and **2** were satisfactorily obtained using a Perkin Elmer 2400 elemental analyser.

Crystal Structure Determinations

Single-crystal data were measured at 123(2) K with an Oxford Diffraction Gemini Diffractometer and monochromated Cu-*Kα* radiation (λ = 1.5418 Å) for **1** and Mo-*Kα* radiation (λ = 0.71073 Å) for **2**. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL programs.[3] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed and allowed to ride on their parent atoms. For **1**, the Flack parameter was refined by inclusion of TWIN and BASF lines to the model file. This gave a refined Flack parameter of 0.013 +/- 0.013. This is essentially zero and indicates that compound **1** is enantiomerically pure. The κ^1-(*R*,*R*)-TMCDA ligand in **2** was modelled as disordered over two sites with the geometry and displacement parameters of this group restrained to approximate typical values. Figures S1-S2 and Table S1 contain selected metrics, crystallographic and refinement data for **1** and **2**. CCDC-1501992 (**1**) and CCDC-1501993 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

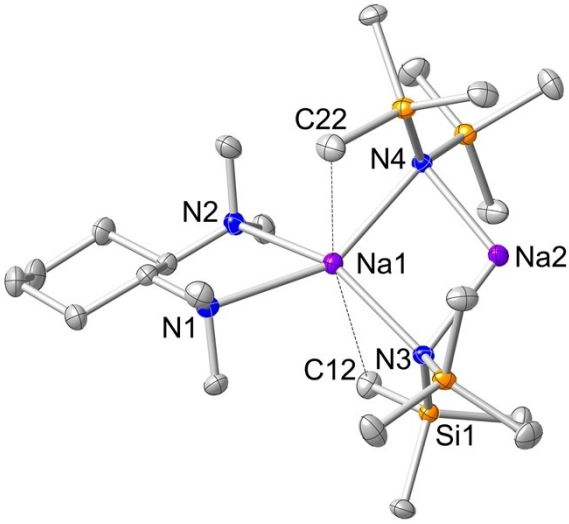


Figure S1. Molecular structure of [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]$_\infty$ **1** showing one unit of the six crystallographically independent units present in the asymmetric unit. Thermal ellipsoids are displayed at 35% probability and hydrogen atoms are omitted for clarity. The dashed lines illustrate Na···Me(SiMe$_2$) interactions. Selected bond lengths (Å) and angles (º): Na(1)-N(1) 2.608(3), Na(1)-N(2) 2.527(3), Na(1)-N(3) 2.536(3), Na(1)-N(4) 2.524(3), Na(2)-N(3) 2.350(3), Na(2)-N(4) 2.367(3), Na(1)-C(22) 2.987(4), Na(1)-C(12) 3.043(4), N(4)-Na(1)-N(2) 100.50(10), N(4)-Na(1)-N(3) 95.74(9), N(2)-Na(1)-N(3) 151.55(10), N(4)-Na(1)-N(1) 149.54(10), N(2)-Na(1)-N(1) 68.70(9), N(3)-Na(1)-N(1) 106.75(10), N(4)-Na(1)-C(22) 63.84(9), N(2)-Na(1)-C(22) 101.96(12), N(3)-Na(1)-C(22) 106.15(11), N(1)-Na(1)-C(22) 89.84(10), N(4)-Na(1)-C(12) 109.06(10), N(2)-Na(1)-C(12) 89.36(10), N(3)-Na(1)-C(12) 63.16(9), N(1)-Na(1)-C(12) 99.46(10), C(22)-Na(1)-C(12) 167.43(11), N(3)-Na(2)-N(4) 105.39(10), N(3)-Na(2)-C(65) 118.32(11), N(4)-Na(2)-C(65) 136.23(11).

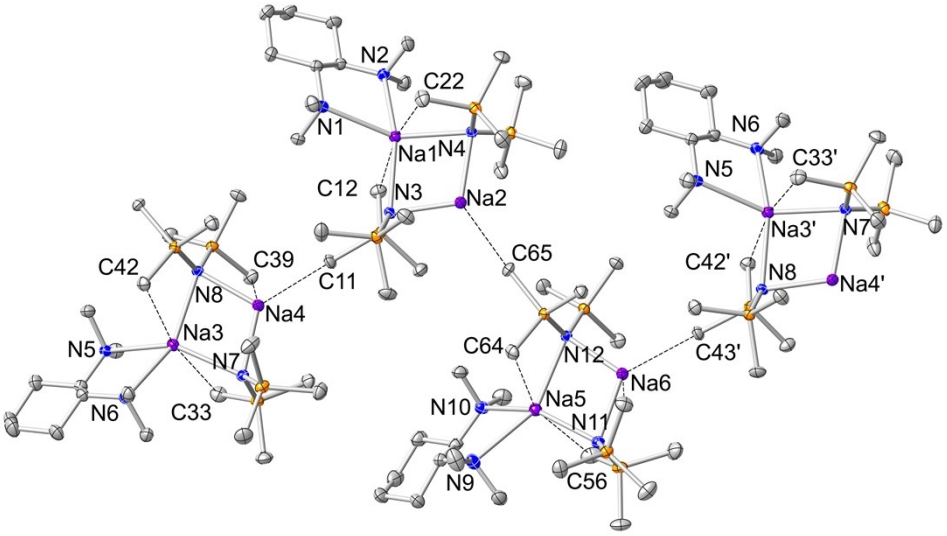


Figure S2. Section of one of the two crystallographically independent zigzag polymeric chains of [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]$_\infty$ **1** comprising the monomeric units [Na(1),Na(2)], [Na(3),Na(4)], [Na(5),Na(6)] and [Na(3'),Na(4')]. Thermal ellipsoids are displayed at 35% probability and hydrogen atoms are omitted for clarity. The dashed lines illustrate Na···Me(SiMe$_2$) interactions. The symmetry operation used to generate equivalent atoms denoted with ´ is 1-x,1/2+y,1-z. Selected bond lengths (Å) and angles (º): Na(1)-N(1) 2.608(3), Na(1)-N(2) 2.527(3), Na(1)-N(3) 2.536(3), Na(1)-N(4) 2.524(3), Na(2)-N(3) 2.350(3), Na(2)-N(4) 2.367(3), Na(1)-C(22) 2.987(4), Na(1)-C(12) 3.043(4), Na(2)-C(65) 2.818(4), Na(3)-N(5) 2.605(3), Na(3)-N(6) 2.522(3), Na(3)-N(7) 2.556(3), Na(3)-N(8) 2.537(3), Na(4)-N(7) 2.351(3), Na(4)-N(8) 2.341(3), Na(3)-C(33) 3.083(4), Na(4) C(11) 2.763(4), Na(5)-N(9) 2.686(3), Na(5)-N(10) 2.528(3), Na(5)-N(11) 2.508(3), Na(5)-N(12) 2.609(3), Na(6)-N(11) 2.378(3), Na(6)-N(12) 2.357(3), Na(5)-C(64) 2.983(4), Na(5)-C(56) 3.047(4), Na(6)-C(43') 2.816(3), Na(6)-C(60) 2.958(4), N(4)-Na(1)-N(2) 100.50(10), N(4)-Na(1)-N(3) 95.74(9), N(2)-Na(1)-N(3) 151.55(10), N(4)-Na(1)-N(1) 149.54(10), N(2)-Na(1)-N(1) 68.70(9), N(3)-Na(1)-N(1) 106.75(10), N(4)-Na(1)-C(22) 63.84(9), N(2)-Na(1)-C(22) 101.96(12), N(3)-Na(1)-C(22) 106.15(11), N(1)-Na(1)-C(22) 89.84(10), N(4)-Na(1)-C(12) 109.06(10), N(2)-Na(1)-C(12) 89.36(10), N(3)-Na(1)-C(12) 63.16(9), N(1)-Na(1)-C(12) 99.46(10), C(22)-Na(1)-C(12) 167.43(11), N(3)-Na(2)-N(4) 105.39(10), N(3)-Na(2)-C(65) 118.32(11), N(4)-Na(2)-C(65) 136.23(11), N(6)-Na(3)-N(8) 149.46(10), N(6)-Na(3)-N(7) 100.99(10), N(8)-Na(3)-N(7) 95.86(9), N(6)-Na(3)-N(5) 68.67(10), N(8)-Na(3)-N(5) 108.12(10), N(7)-Na(3)-N(5) 147.64(10), N(6)-Na(3)-C(33) 102.37(11), N(8)-Na(3)-C(33) 108.01(11), N(7)-Na(3)-C(33) 62.19(9), N(5)-Na(3)-C(33) 89.32(10), N(6)-Na(3)-C(29) 27.59(9), N(8)-Na(3)-C(29) 172.24(11), N(7)-Na(3)-C(29) 80.56(10), N(5)-Na(3)-C(29) 77.87(10), C(33)-Na(3)-C(29) 76.51(11), Na(4)-Na(3)-C(29) 128.13(8), N(8)-Na(4)-N(7) 107.39(10), N(8)-Na(4)-C(39) 63.81(9), N(7)-Na(4)-C(39) 109.68(11), N(8)-Na(4)-C(11) 119.00(11), N(7)-Na(4)-C(11) 133.41(11), C(11)-Na(4)-C(39) 88.14(11), N(11)-Na(5)-N(10) 149.22(10), N(11)-Na(5)-N(12) 94.95(9), N(10)-Na(5)-N(12) 102.64(10), N(11)-Na(5)-N(9) 107.20(10), N(10)-Na(5)-N(9) 66.13(10), N(12)-Na(5)-N(9) 152.13(10), N(11)-Na(5)-C(64) 100.66(10), N(10)-Na(5)-C(64) 109.79(11), N(12)-Na(5)-C(64) 62.93(9), N(9)-Na(5)-C(64) 95.78(10), N(11)-Na(5)-C(56) 62.94(10), N(10)-Na(5)-C(56) 88.70(11), N(12)-Na(5)-C(56) 101.36(11), N(9)-Na(5)-C(56) 103.67(12), C(64)-Na(5)-C(56) 157.47(12), N(11)-Na(5)-C(54) 177.39(11), N(10)-Na(5)-C(54) 28.28(9), N(12)-Na(5)-C(54) 85.90(10), N(9)-Na(5)-C(54) 72.74(11), C(64)-Na(5)-C(54) 81.93(11), C(56)-Na(5)-C(54) 114.48(11), N(11)-Na(5)-C(52) 83.50(10), N(10)-Na(5)-C(52) 79.72(10), N(12)-Na(5)-C(52) 177.28(11), N(9)-Na(5)-C(52) 27.88(10), C(64)-Na(5)-C(52) 115.10(12), C(56)-Na(5)-C(52) 79.95(13), C(54)-Na(5)-C(52) 95.74(11), N(12)-Na(6)-N(11) 105.57(10), N(12)-Na(6)-C(43') 115.92(11), N(11)-Na(6)-C(43') 137.39(11), N(12)-Na(6)-C(60) 121.72(12), N(11)-Na(6)-C(60) 66.28(10), C(43')-Na(6)-C(60) 97.82(11).

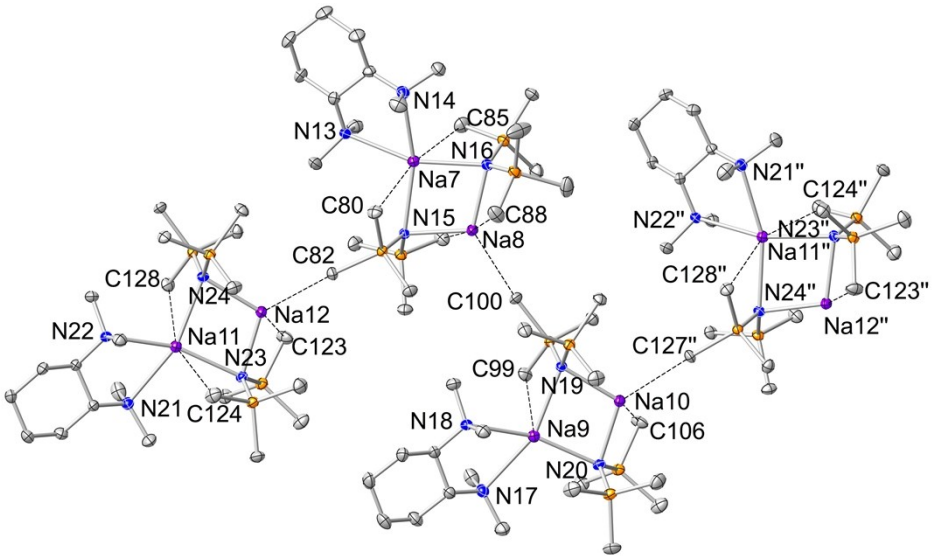


Figure S3. Section of one of the two crystallographically independent zigzag polymeric chains of [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]$_\infty$ **1** comprising the monomeric units [Na(7),Na(8)], [Na(9),Na(10)], [Na(11),Na(12)] and [Na(11"),Na(12")]. Thermal ellipsoids are displayed at 35% probability and hydrogen atoms are omitted for clarity. The dashed lines illustrate Na···Me(SiMe$_2$) interactions. The symmetry operation used to generate equivalent atoms denoted with ´ is -x,y-1/2,1-z. Selected bond lengths (Å) and angles (º): Na(7)-N(13) 2.594(3), Na(7)-N(14) 2.582(3), Na(7)-N(15) 2.560(3), Na(7)-N(16) 2.531(3), Na(8)-N(15) 2.344(3), Na(8)-N(16) 2.352(3), Na(7)-C(80) 3.068(4), Na(7)-C(73) 3.068(4), Na(7)-C(76) 3.088(5), Na(7)-C(85) 3.094(4), Na(8)-C(100) 2.798(3), Na(8)-C(88) 3.038(4), Na(8)-C(77) 3.072(4), Na(9)-N(17) 2.658(3), Na(9)-N(18) 2.565(3), Na(9)-N(19) 2.638(3), Na(9)-N(20) 2.486(3), Na(10)-N(19) 2.364(3), Na(10)-N(20) 2.376(3), Na(9)-C(97) 2.929(4), Na(9)-C(99) 2.969(3), Na(10)-C(127") 2.901(3), Na(10)-C(106) 2.948(4), Na(11)-N(23) 2.517(3), Na(11)-N(22) 2.580(3), Na(11)-N(24) 2.611(3), Na(11)-N(21) 2.628(3), Na(12)-N(24) 2.362(3), Na(12)-N(23) 2.377(3), Na(11)-C(120) 2.980(4), Na(11)-C(128) 3.068(4), Na(12)-C(82) 2.835(4), Na(12)-C(123) 2.922(4), N(16)-Na(7)-N(15) 95.28(9) N(16)-Na(7)-N(14) 99.40(10), N(15)-Na(7)-N(14) 161.84(10), N(16)-Na(7)-N(13) 158.68(10), N(15)-Na(7)-N(13) 101.30(9), N(14)-Na(7)-N(13) 67.40(10), N(16)-Na(7)-C(80) 111.11(10), N(15)-Na(7)-C(80) 62.68(9), N(14)-Na(7)-C(80) 101.74(10), N(13)-Na(7)-C(80) 88.56(10), N(16)-Na(7)-C(73) 135.60(11), N(15)-Na(7)-C(73) 99.14(10), N(14)-Na(7)-C(73) 77.65(10), N(13)-Na(7)-C(73) 28.27(10), C(80)-Na(7)-C(73) 112.85(11), N(16)-Na(7)-C(76) 98.65(12), N(15)-Na(7)-C(76) 138.55(11), N(14)-Na(7)-C(76) 28.08(10), N(13)-Na(7)-C(76) 77.63(12), C(80)-Na(7)-C(76) 75.88(11), C(73)-Na(7)-C(76) 97.64(12), N(16)-Na(7)-C(85) 62.27(9), N(15)-Na(7)-C(85) 107.61(11), N(14)-Na(7)-C(85) 88.76(11), N(13)-Na(7)-C(85) 99.58(10), C(80)-Na(7)-C(85) 168.64(11), C(73)-Na(7)-C(85) 73.35(11), C(76)-Na(7)-C(85) 113.45(12), N(15)-Na(8)-N(16) 106.49(10), N(15)-Na(8)-C(100) 118.73(11), N(16)-Na(8)-C(100) 134.77(11), N(15)-Na(8)-C(88) 111.69(11), N(16)-Na(8)-C(88) 64.86(11), C(100)-Na(8)-C(88) 96.12(12), N(15)-Na(8)-C(77) 64.38(10), N(16)-Na(8)-C(77) 110.54(11), C(100)-Na(8)-C(77) 90.43(11), C(88)-Na(8)-C(77) 173.43(13), N(20)-Na(9)-N(18) 160.94(10), N(20)-Na(9)-N(19) 94.41(9), N(18)-Na(9)-N(19) 95.65(9), N(20)-Na(9)-N(17) 106.14(10), N(18)-Na(9)-N(17) 66.10(9), N(19)-Na(9)-N(17) 158.94(10), N(20)-Na(9)-C(97) 134.35(10), N(18)-Na(9)-C(97) 30.05(9), N(19)-Na(9)-C(97) 89.10(10), N(17)-Na(9)-C(97) 79.94(10), N(20)-Na(9)-C(99) 104.83(10), N(18)-Na(9)-C(99) 94.16(10), N(19)-Na(9)-C(99) 63.04(9), N(17)-Na(9)-C(99) 106.11(10), C(97)-Na(9)-C(99) 117.00(11), N(19)-Na(10)-N(20) 105.00(10), N(19)-Na(10)-C(127") 114.38(10), N(20)-Na(10)-C(127") 140.53(10), N(19)-Na(10)-C(106) 119.49(11), N(20)-Na(10)-C(106) 66.55(9), C(127")-Na(10)-C(106) 95.09(11), N(23)-Na(11)-N(22) 160.52(10), N(23)-Na(11)-N(24) 94.72(9), N(22)-Na(11)-N(24) 98.37(9), N(23)-Na(11)-N(21) 103.15(10), N(22)-Na(11)-N(21) 65.98(9), N(24)-Na(11)-N(21) 161.22(9), N(23)-Na(11)-C(120) 136.49(10), N(22)-Na(11)-C(120) 29.40(9), N(24)-Na(11)-C(120) 91.30(10), N(21)-Na(11)-C(120) 79.76(10), N(23)-Na(11)-C(128) 105.04(10), N(22)-Na(11)-C(128) 93.87(10), N(24)-Na(11)-C(128) 61.79(9), N(21)-Na(11)-C(128) 107.19(10), C(120)-Na(11)-C(128) 115.61(11), N(24)-Na(12)-N(23) 105.54(10), N(24)-Na(12)-C(82) 117.63(11), N(23)-Na(12)-C(82) 136.05(10), N(24)-Na(12)-C(123) 121.80(12), N(23)-Na(12)-C(123) 66.90(10),C(82)-Na(12)-C(123) 95.20(11).

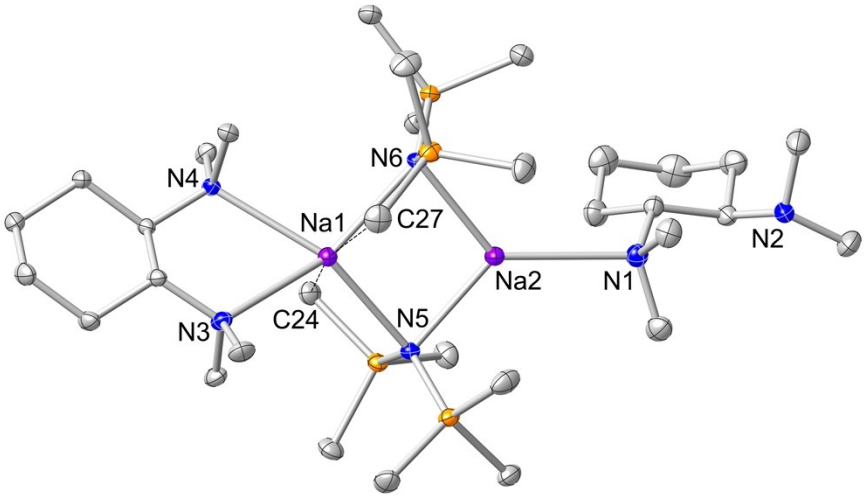


Figure S4. Molecular structure of [{κ^2-(*R*,*R*)-TMCDA}·(NaHMDS)$_2$}{κ^1-(*R*,*R*)-TMCDA}] **2**. Hydrogen atoms and one disordered component of the mono-dentate (*R,R*)-TMCDA ligand are omitted for simplicity. Thermal ellipsoids are displayed at 35% probability. Selected bond lengths (Å) and angles (º): Na(1)-N(6) 2.501(2), Na(1)-N(5) 2.537(2), Na(1)-N(4) 2.578(2), Na(1)-N(3) 2.665(2), Na(1)-C(27) 2.968(3), Na(1)-C(24) 2.976(3), Na(2)-N(5) 2.416(2), Na(2)-N(6) 2.444(2), N(6)-Na(1)-N(5) 95.87(7), N(6)-Na(1)-N(4) 102.03(7), N(5)-Na(1)-N(4) 151.05(8), N(6)-Na(1)-N(3) 146.63(8), N(5)-Na(1)-N(3) 108.27(7), N(4)-Na(1)-N(3) 66.90(6), N(6)-Na(1)-C(27) 65.05(8), N(5)-Na(1)-C(27) 107.18(8), N(4)-Na(1)-C(27) 100.99(8), N(3)-Na(1)-C(27) 85.57(8), N(6)-Na(1)-C(24) 105.87(8), N(5)-Na(1)-C(24) 64.21(7), N(4)-Na(1)-C(24) 88.89(8), N(3)-Na(1)-C(24) 105.28(8), C(27)-Na(1)-C(24) 167.65(9), N(5)-Na(2)-N(6) 100.63(7).

Selected crystallographic and refinement data for **1** and **2**

Table S1. Selected crystallographic and refinement data for **1** and **2**.

	1	**2**
Formula	$C_{22}H_{58}N_4Na_2Si_4$	$C_{32}H_{80}N_6Na_2Si_4$
Fw	537.06	707.36
Cryst. System	Monoclinic	Orthorhombic
Space Group	$P2_1$	$P2_12_12_1$
Wavelength/Å	1.54184	0.71073
a/Å	16.9445(2)	11.6278(4)
b/Å	37.8065(3)	11.8670(5)
c/Å	17.8856(2)	32.841(2)
α/°	90	90
β/°	116.408(2)	90
γ/°	90	90
Volume/Å^3	10262.1(2)	4531.6(4)
Z	12	4
Temp./K	123(2)	123(2)
Refls. Collect.	101381	25854
$2\theta_{max}$	146.36	60.95
Refls. Ind.	39530	11578
Refls. Obs.	37174	9541
R_{int}	0.0439	0.0349
Goodness of fit	1.014	1.025
$R[F^2>2\sigma]$, F	0.0410	0.0431
R_w (all data), F^2	0.1059	0.0927
Flack	0.013(13)	-0.03(4)

Preparation of NaHMDS[4]

*n*BuNa (1.6 g, 20 mmol) was suspended in *n*-hexane (40 mL), stirred for 10 min and HMDS(H) (4.2 mL, 20 mmol) was then added at room temperature. The reaction mixture was stirred for 2 h to give a white suspension. The solvent was partially removed under vacuum (*c.a.* 20 mL) and the suspension was filtered. The solid was washed with *n*-hexane (3 x 5 mL) and dried under vacuum for 20 minutes to give NaHMDS as a white solid. The product was stored under the inert atmosphere of a glove box.

Synthesis of [{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$]∞ **1**

Freshly prepared NaHMDS (440 mg, 2.4 mmol) was suspended in *n*-hexane (10 mL) and stirred for 5 min at room temperature. (*R*,*R*)-TMCDA (22.8 µL, 1.2 mmol) was then added and the reaction mixture was stirred for 15 min to give a slightly cloudy pale orange solution. The reaction mixture was filtered via cannula and the solvent was partially removed under vacuum (*c.a.* 3 mL). Suitable crystals of **1** for an X-ray diffraction study were obtained at -33°C after 24 hours. The colourless crystalline material was filtered, washed with cold *n*-hexane (3 x 5 mL) and dried under vacuum for 15 min. Yield: 230 mg, 0.43 mmol, 36% (based on (*R*,*R*)-TMCDA consumption).
Alternatively, **1** can be prepared by reacting NaHMDS (367 mg, 2 mmol) with (*R*,*R*)-TMCDA (38 µL, 2 mmol) at room temperature in *n*-hexane (10 mL) for 1 h. The reaction mixture was filtered via cannula to give a pale orange solution. The solvent was partially removed under vacuum (*c.a.* 3 mL) and crystals were obtained at -33°C after 48 h. X-ray crystallographic and NMR spectroscopic studies proved that this crystalline material resembles **1**. The colourless crystalline material was filtered, washed with *n*-hexane (3 x 5 mL) and dried under vacuum for 20 min. Yield: 290 mg, 0.54 mmol, 27% (based on (*R*,*R*)-TMCDA consumption). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): *δ* 0.27 (s, 36 H, $SiMe_3$), 0.74 (m, 4 H, β/γ-CH_2, (*R*,*R*)-TMCDA), 1.46 (m, 4 H, β/γ-CH_2, (R,R)-TMCDA), 1.90 (m, 2 H, α-CH, (*R*,*R*)-TMCDA), 2.01 (s, 12 H, Me, (*R*,*R*)-TMCDA). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): *δ* 7.1 (Si*Me*$_3$), 22.1 (β/γ-CH_2, (*R*,*R*)-TMCDA), 25.5 (β/γ-CH_2, (*R*,*R*)-TMCDA), 40.4 (Me, (*R*,*R*)-TMCDA), 63.9 (α-CH, (*R*,*R*)-TMCDA). Anal. Calcd (Found) for $C_{22}H_{58}N_4Na_2Si_4$: C, 49.20 (49.14); H, 10.89 (10.69); N, 10.43% (10.17%).

Synthesis of [κ^2-{(*R*,*R*)-TMCDA}·(NaHMDS)$_2$}{κ^1-(*R*,*R*)-TMCDA}] **2**

Freshly prepared NaHMDS (551 mg, 3 mmol) was suspended in *n*-hexane (10 mL) and stirred for 5 min at room temperature. (*R*,*R*)-TMCDA (1.14 mL, 6 mmol) was then added and the reaction mixture was stirred for 15 min. The resulting pale orange solution was filtered via cannula and the solvent was partially removed under vacuum (*c.a.* 3 mL). Suitable crystals of **2** for an X-ray diffraction study were obtained at -33 °C after 24 hours. The colourless crystalline material was filtered, washed with cool *n*-hexane (3 x 5 mL) and dried under vacuum for 15 min. Yield: 420 mg, 0.59 mmol, 40% (based on (*R*,*R*)-TMCDA consumption). ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): *δ* 0.30 (s, 18 H, $SiMe_3$), 0.80 (m, 4 H, β/γ-CH_2, (*R*,*R*)-TMCDA), 1.51 (m, 4 H, β/γ-CH_2, (*R*,*R*)-TMCDA), 1.99 (m, 2 H, α-CH, (*R*,*R*)-TMCDA), 2.06 (s, 12 H, Me, (*R*,*R*)-TMCDA). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): *δ* 7.2 ($SiMe_3$), 23.2 (β/γ-CH_2, (*R*,*R*)-TMCDA), 25.6 (β/γ-CH_2, (*R*,*R*)-TMCDA), 40.4 (α-CH, (*R*,*R*)-TMCDA), 64.0 (Me, (*R*,*R*)-TMCDA). Anal. Calcd (Found) for $C_{32}H_{80}N_6Na_2Si_4$: C, 54.34 (54.48); H, 11.40 (11.06); N, 11.88% (11.88%).

NMR SPECTRA

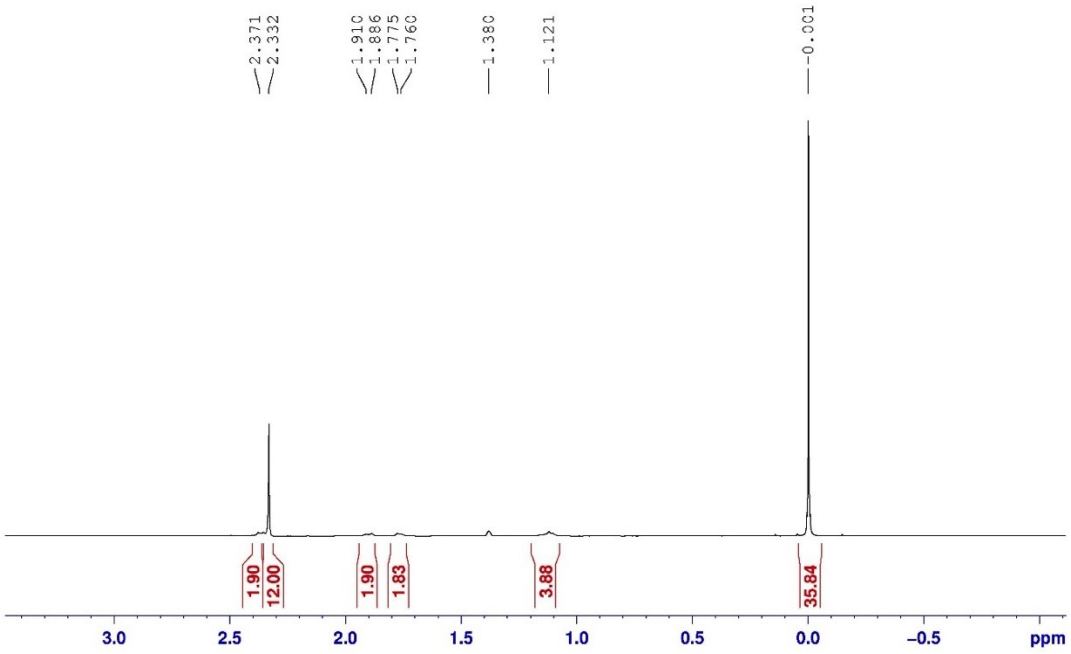


Figure S5. ^{1}H NMR spectrum of isolated crystals of enantiomerically pure **1** (400.1 MHz, $[D_{12}]$-cyclohexane, 300 K).

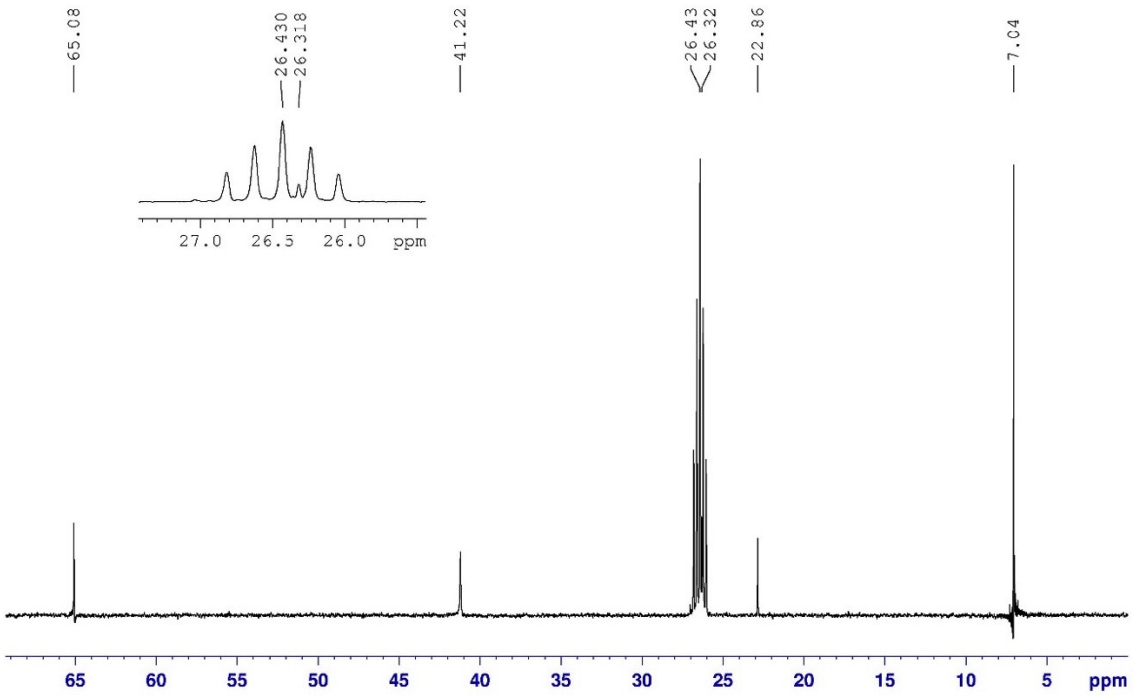


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of isolated crystals of enantiomerically pure **1** (100.6 MHz, $[D_{12}]$-cyclohexane, 300 K).

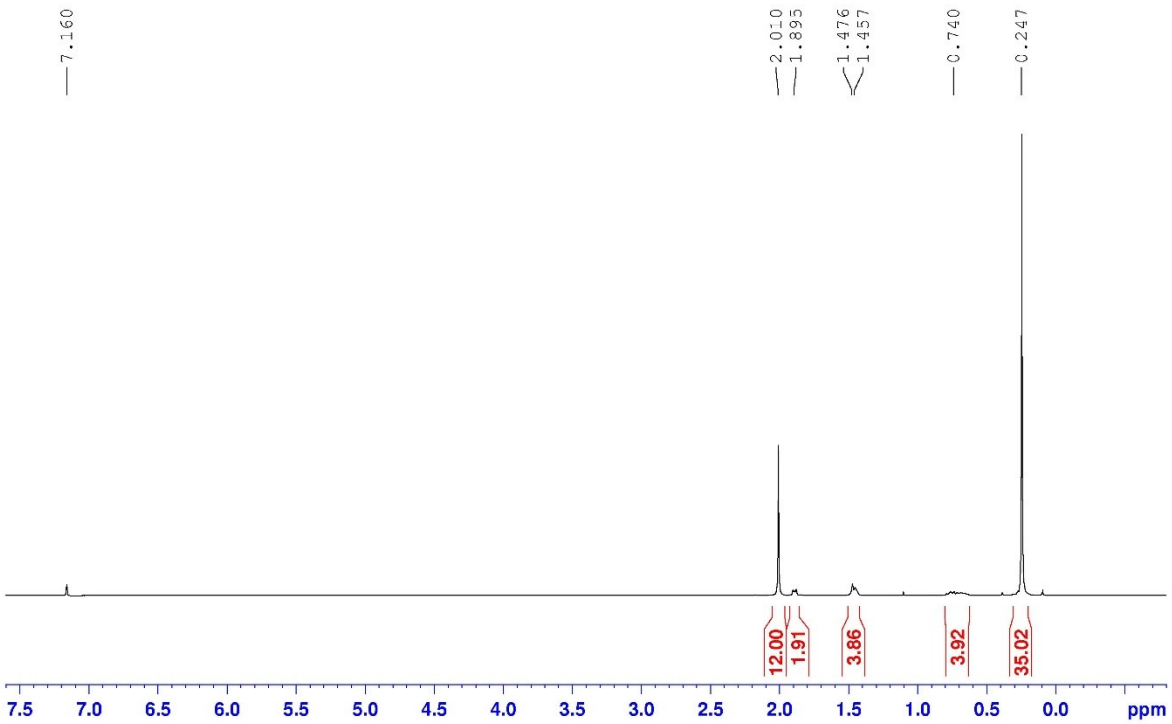


Figure S7. ^{1}H NMR spectrum of isolated crystals of enantiomerically pure **1** (400.1 MHz, C_6D_6, 300 K).

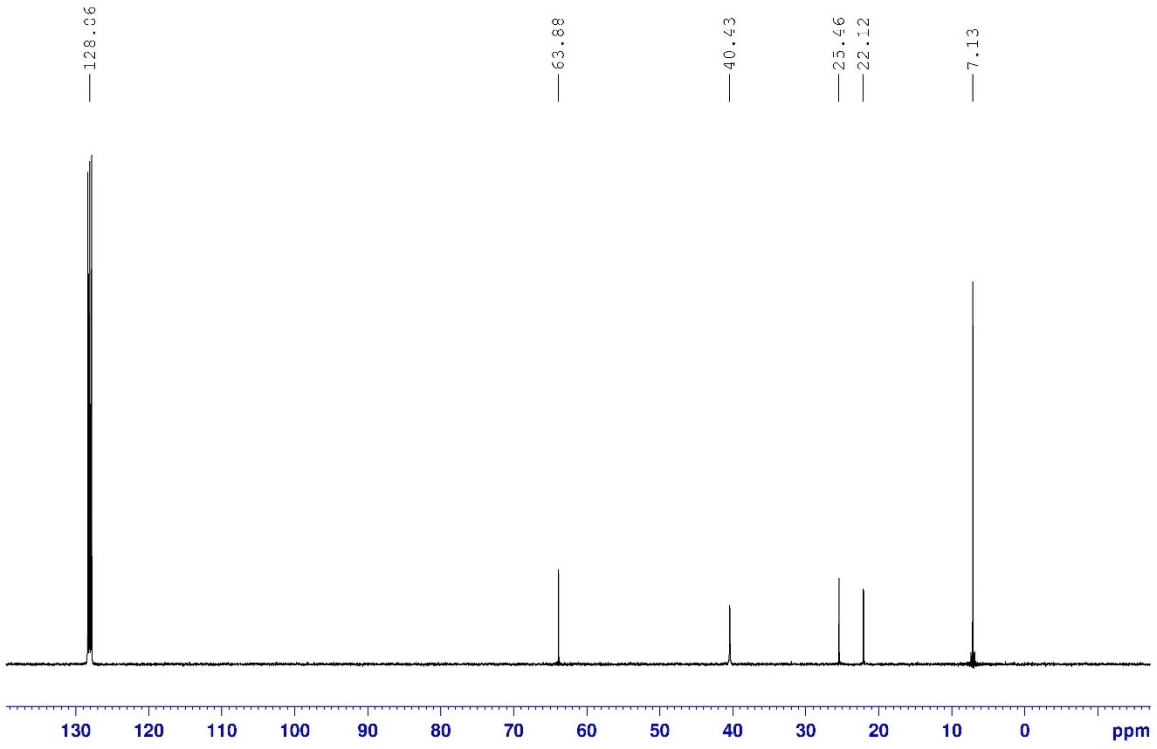


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of isolated crystals of enantiomerically pure **1** (100.6 MHz, C_6D_6, 300 K).

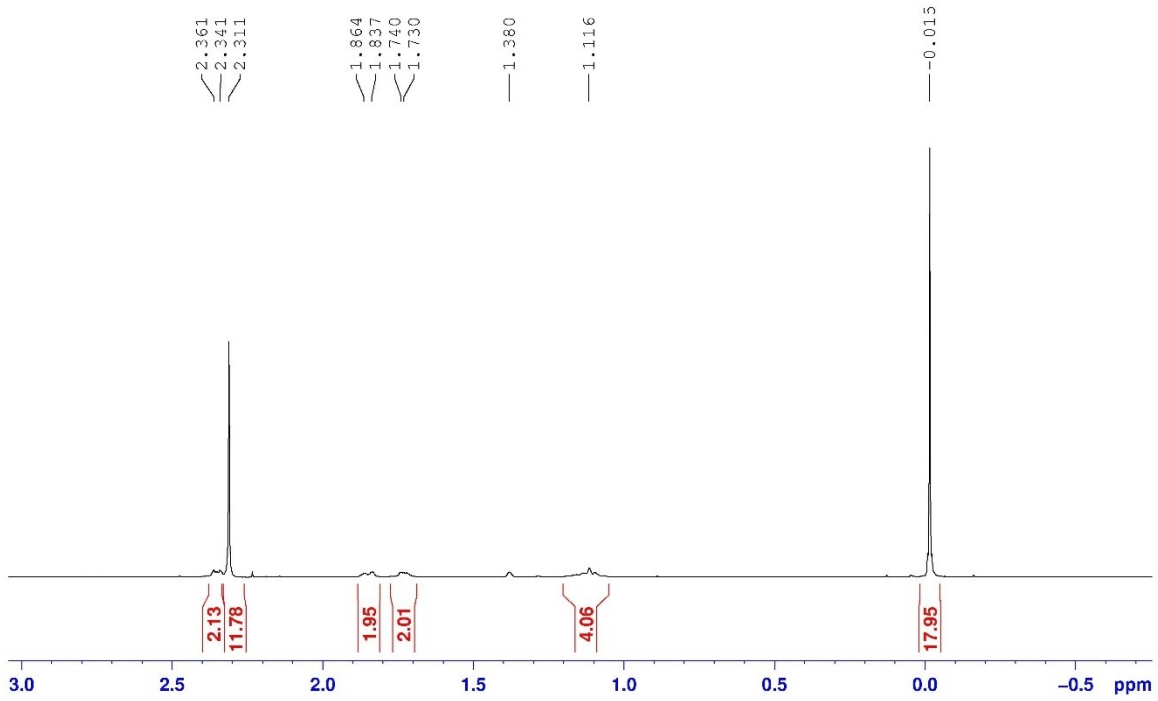


Figure S9. ^{1}H NMR spectrum of isolated crystals of enantiomerically pure **2** (400.1 MHz, $[D_{12}]$-cyclohexane, 300 K).

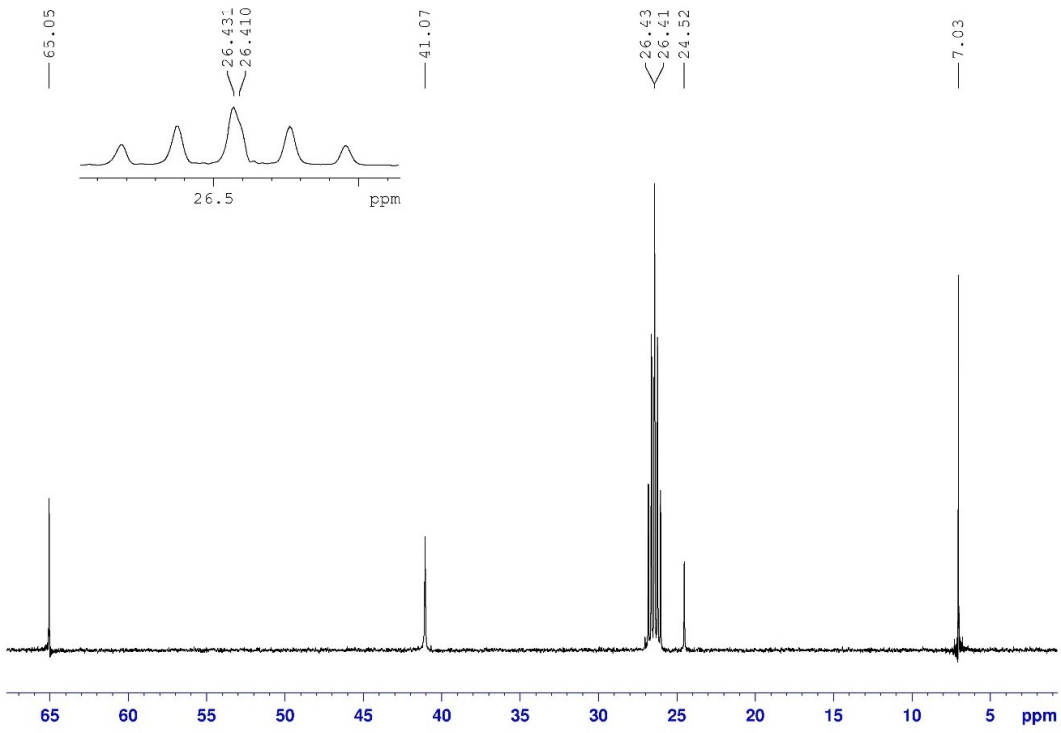


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of isolated crystals of enantiomerically pure **2** (100.6 MHz, $[D_{12}]$-cyclohexane, 300 K).

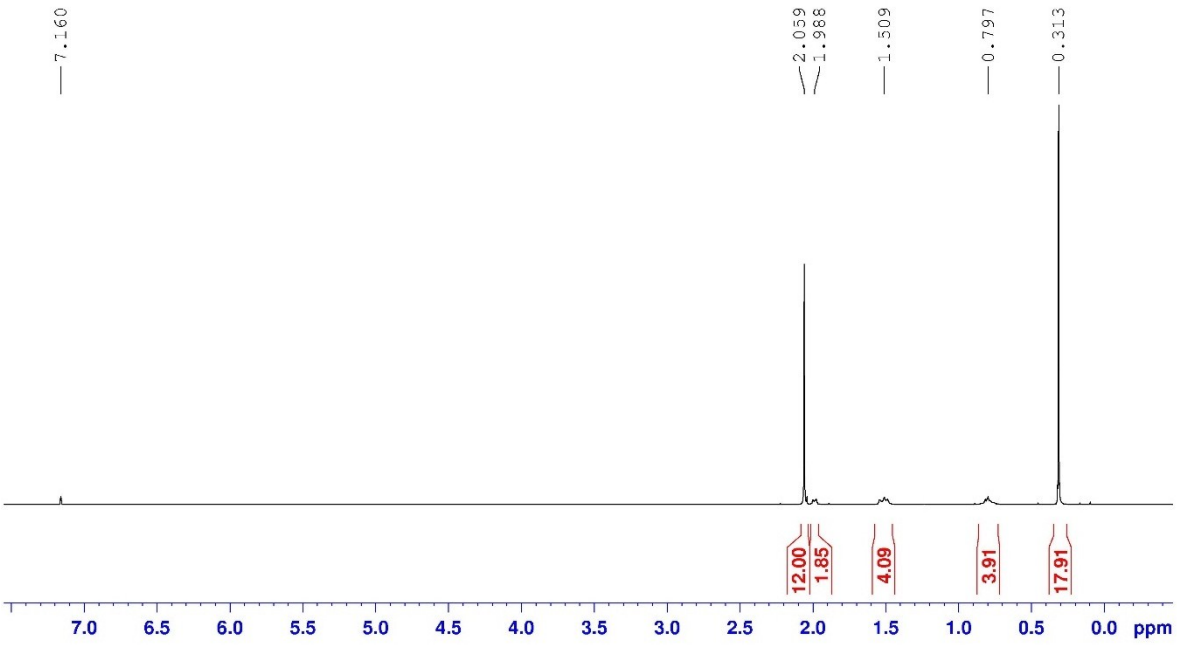


Figure S11. ^{1}H NMR spectrum of isolated crystals of enantiomerically pure **2** (400.1 MHz, C_6D_6, 300 K).

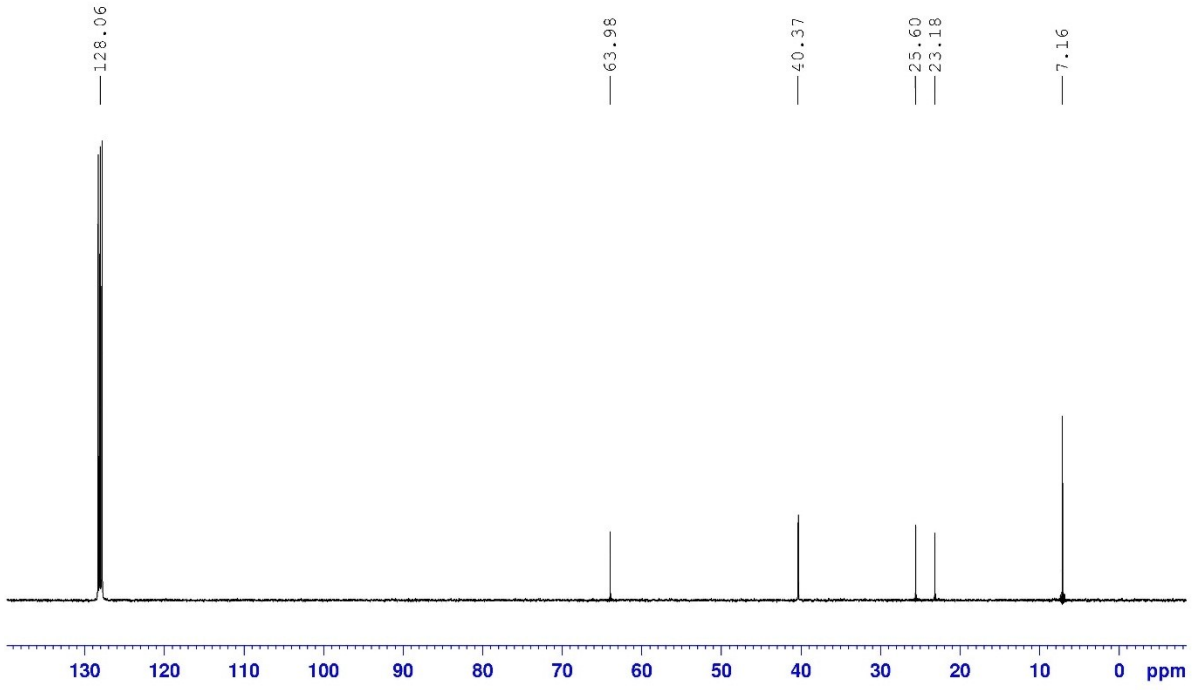


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of isolated crystals of enantiomerically pure **2** (100.6 MHz, C_6D_6, 300 K).

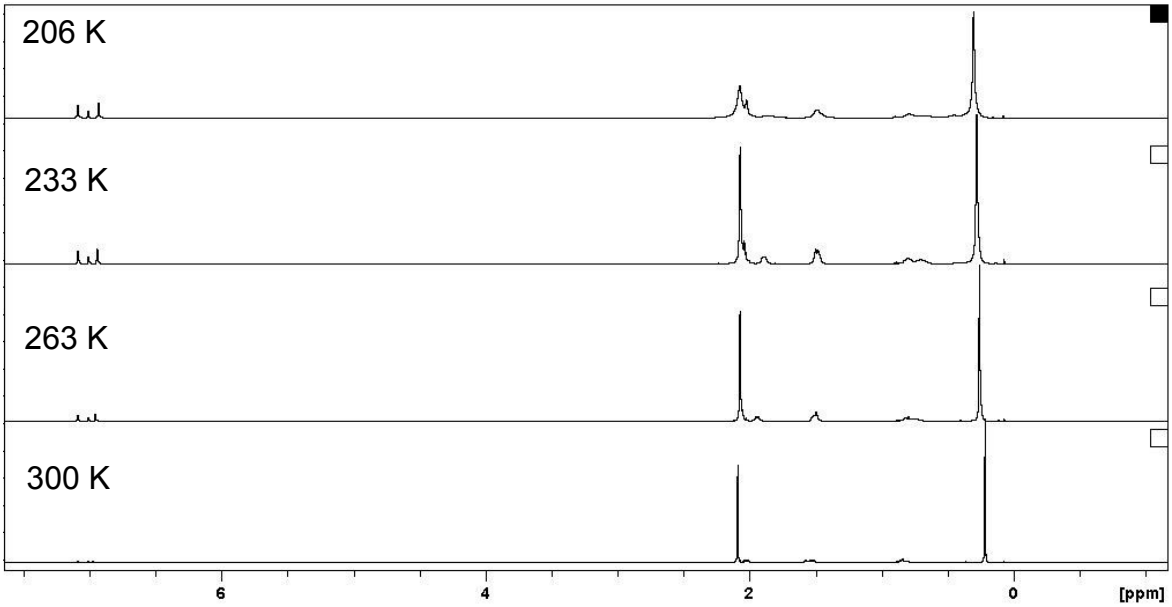


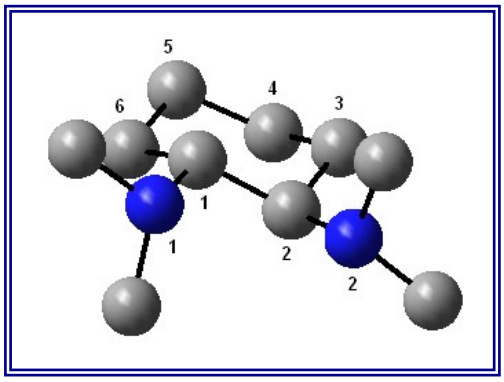
Figure S13. Variable temperature ^{1}H NMR spectra of isolated crystals of enantiomerically pure **2** (100.6 MHz, [D_8]-toluene) from 300 K to 206 K showing only one type of (*R*,*R*)-TMCDA.

DFT Calculations

Theoretical calculations were performed using the Gaussian G03 package[5] at the DFT level of theory[6] employing the B3LYP density functional[7] and the 6-311G** basis set[8].

Optimised geometries and XYZ coordinates [b3lyp/6-311g(d,p)]

Model 1 (NMe_2 groups "poised" for bidentate-coordination)



(hydrogen atoms omitted for clarity)

E = -503.925014 a.u.

Principal bond lengths (Å) and bonds angles (°):

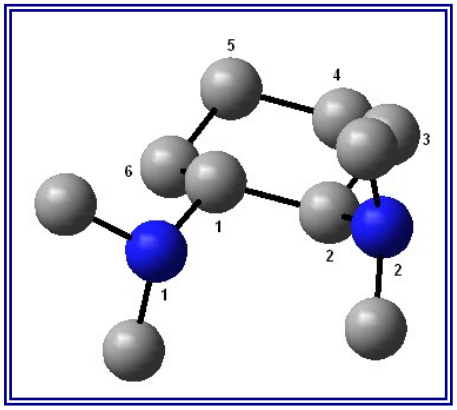
C_1-C_2	1.551	C_1-C_2-C_3	108.9
C_2-C_3	1.550	C_2-C_3-C_4	111.7
C_3-C_4	1.535	C_3-C_4-C_5	111.4
C_4-C_5	1.533	C_4-C_5-C_6	111.4
C_5-C_6	1.535	C_5-C_6-C_1	111.7
C_6-C_1	1.550	C_6-C_1-C_2	108.9
C_1-N_1	1.467	C_2-C_1-N_1	113.0
C_2-N_2	1.467	C_1-C_2-N_2	113.0
N_1-C_{Me}	1.453 1.454	C_1-N_1-C_{Me}	113.8 116.3
N_2-C_{Me}	1.453 1.454	C_2-N_2-C_{Me}	113.8 116.3

XYZ coordinates:

C	-0.72658600	0.11540800	0.27045400
C	0.72667300	0.11517600	-0.27052900
C	1.45125600	1.38678300	0.23910700
C	0.73608500	2.66675900	-0.21459000
C	-0.73516900	2.66698800	0.21462300
C	-1.45074900	1.38726700	-0.23914100
C	2.69366500	-1.26170000	-0.73756400
C	1.51964900	-1.58918800	1.34937500
C	-1.52036400	-1.58869900	-1.34938700
C	-2.69400800	-1.26078900	0.73764900
H	-0.66606300	0.20969800	1.36349300
H	0.66620600	0.20950300	-1.36356700
H	1.50562900	1.36547200	1.33422900
H	2.48258200	1.39275100	-0.12533400

H	1.24998200	3.54876300	0.18160500
H	0.79274700	2.74047200	-1.30845000
H	-1.24878200	3.54917800	-0.18152800
H	-0.79180900	2.74066300	1.30848700
H	-1.50510200	1.36601000	-1.33426500
H	-2.48208100	1.39355200	0.12528000
H	3.50735300	-0.63996900	-0.32089800
H	2.56183500	-0.97929600	-1.78636700
H	3.03250500	-2.30168100	-0.71191700
H	2.14221800	-0.93858500	1.99052300
H	1.96209400	-2.58912800	1.37219500
H	0.52124300	-1.66547400	1.77996400
H	-2.14359600	-0.93841700	-1.99021700
H	-1.96222900	-2.58890100	-1.37207700
H	-0.52211500	-1.66439100	-1.78043300
H	-2.56196100	-0.97856000	1.78647100
H	-3.03328300	-2.30062700	0.71191000
H	-3.50747300	-0.63867400	0.32112100
N	1.42698300	-1.15169100	-0.03441400
N	-1.42735600	-1.15122100	0.03438500

Model 2 (NMe_2 groups "poised" for monodentate co-ordination by rotation of one NMe_2 group)



(hydrogen atoms omitted for clarity)

E = -503.925092 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.556	C_1-C_2-C_3	110.0
C_2-C_3	1.545	C_2-C_3-C_4	113.2
C_3-C_4	1.533	C_3-C_4-C_5	111.1
C_4-C_5	1.532	C_4-C_5-C_6	110.6
C_5-C_6	1.533	C_5-C_6-C_1	112.3
C_6-C_1	1.547	C_6-C_1-C_2	110.8
C_1-N_1	1.475	C_2-C_1-N_1	112.2
C_2-N_2	1.470	C_1-C_2-N_2	116.5
N_1-C_{Me}	1.456 1.457	C_1-N_1-C_{Me}	113.6 115.7
N_2-C_{Me}	1.456 1.454	C_2-N_2-C_{Me}	116.2 116.3

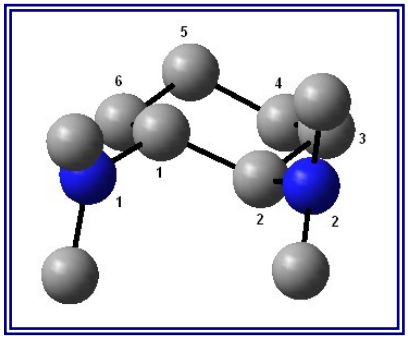
XYZ coordinates:

C	0.23893000	-0.82219900	-0.36318000
C	-1.21782300	-1.90860200	1.33087100

C	1.60244800	-1.46115400	-0.01812500
C	2.79609400	-0.56721000	-0.37293200
C	2.67244100	0.80659900	0.29304700
C	1.33725500	1.46606400	-0.07212400
C	0.12420300	0.58093700	0.30055800
C	-1.39895800	1.73947700	-1.28001700
C	-1.56752800	2.17696000	1.07678800
C	-2.00496300	-1.71930400	-0.93574400
H	-1.81712000	-2.81608800	1.45494100
H	-1.81383700	-1.06020600	1.70806600
H	-0.33411600	-2.01754700	1.96342800
H	1.63431900	-1.68438000	1.05532600
H	1.66223300	-2.42191000	-0.53556000
H	3.73049100	-1.05551900	-0.07772200
H	2.84446800	-0.43623900	-1.46188200
H	3.50535900	1.45369800	-0.00124400
H	2.73862300	0.69042700	1.38268200
H	1.32560100	1.66346700	-1.15090600
H	1.24820200	2.43869200	0.42313900
H	-1.11799400	1.00389800	-2.03527200
H	-0.83879400	2.66859300	-1.48448300
H	-2.46193700	1.95980600	-1.41653800
H	-1.48846900	1.72609500	2.06935800
H	-2.60992500	2.47287600	0.92676800
H	-0.95847200	3.09952800	1.06978700
H	-1.68581300	-1.66617500	-1.98014300
H	-2.66778800	-0.86558600	-0.72864900
H	-2.58528900	-2.64103200	-0.81799900
N	-0.83845100	-1.77746700	-0.06678300
N	-1.18930800	1.20695900	0.05954500

H	0.22365300	-0.68408200	-1.45100500
H	0.16832300	0.41583500	1.38371900

Model 3 (NMe_2 groups "poised" for monodentate co-ordination by rotation of both NMe_2 groups)



(hydrogen atoms omitted for clarity)

E = -503.918172 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.570	C_1-C_2-C_3	110.7
C_2-C_3	1.548	C_2-C_3-C_4	114.1
C_3-C_4	1.531	C_3-C_4-C_5	110.4
C_4-C_5	1.529	C_4-C_5-C_6	110.4
C_5-C_6	1.531	C_5-C_6-C_1	114.1
C_6-C_1	1.548	C_6-C_1-C_2	110.7
C_1-N_1	1.468	C_2-C_1-N_1	117.9
C_2-N_2	1.468	C_1-C_2-N_2	117.9
N_1-C_{Me}	1.448 1.451	C_1-N_1-C_{Me}	118.6 118.6
N_2-C_{Me}	1.448 1.451	C_2-N_2-C_{Me}	118.7 118.6

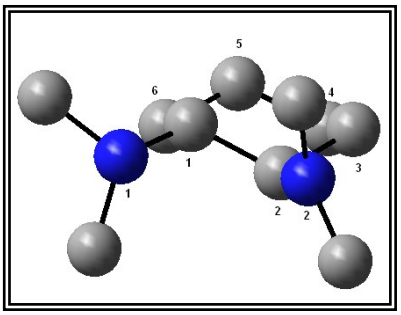
XYZ coordinates:

C	-0.22186600	0.68225800	-0.38864800
C	-0.22122300	-0.68190100	0.38839900
C	-1.53748500	-1.45708100	0.13633800

C	-2.80392600	-0.64363400	0.41413300
C	-2.80452000	0.64182100	-0.41400300
C	-1.53871100	1.45633700	-0.13639900
C	1.25133100	-1.95191500	-1.19925900
C	2.04568700	-1.52508000	1.04957000
C	2.04503500	1.52534400	-1.04907600
C	1.24979600	1.95277200	1.19910700
H	-0.19538400	0.44123100	-1.45809500
H	-0.19481600	-0.44082300	1.45782800
H	-1.56264300	-1.79196300	-0.90792000
H	-1.50803100	-2.36232500	0.74853200
H	-3.69077400	-1.24793300	0.19660700
H	-2.85490200	-0.38893200	1.48096000
H	-3.69183500	1.24538800	-0.19635100
H	-2.85543700	0.38708500	-1.48082600
H	-1.56400800	1.79119900	0.90786000
H	-1.51010100	2.36160000	-0.74860000
H	1.91161000	-1.22534900	-1.70262500
H	0.35374800	-2.06613600	-1.80955600
H	1.76984200	-2.91718900	-1.20357800
H	2.78080000	-0.74123000	0.79592300
H	2.57895100	-2.48267300	1.03474000
H	1.71169900	-1.35158900	2.07549400
H	2.77924300	0.74093400	-0.79464900
H	2.57902600	2.48250800	-1.03394600
H	1.71170000	1.35196800	-2.07523300
H	0.35210200	2.06763900	1.80911800
H	1.76907100	2.91761400	1.20369900
H	1.90934100	1.22557600	1.70250600
N	0.90326300	-1.59890300	0.16384100

N	0.90189200	1.60031400	-0.16424900

Model 4 (transition state between Models 1 and 2 through inversion at N_2)



(hydrogen atoms omitted for clarity)

E = -503.9169816 a.u.

Principal bond lengths (Å) and bonds angles (°):

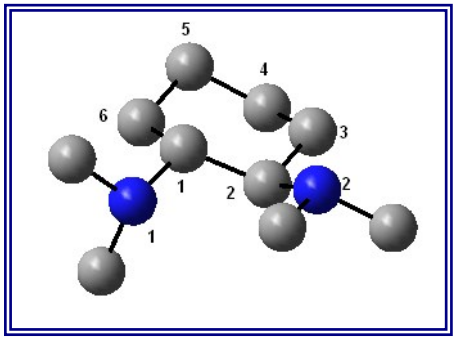
C_1-C_2	1.553	C_1-C_2-C_3	109.6
C_2-C_3	1.550	C_2-C_3-C_4	112.9
C_3-C_4	1.533	C_3-C_4-C_5	111.0
C_4-C_5	1.533	C_4-C_5-C_6	111.1
C_5-C_6	1.534	C_5-C_6-C_1	112.2
C_6-C_1	1.548	C_6-C_1-C_2	109.8
C_1-N_1	1.471	C_2-C_1-N_1	112.4
C_2-N_2	1.448	C_1-C_2-N_2	114.1
N_1-C_{Me}	1.454 1.454	C_1-N_1-C_{Me}	113.7 116.2
N_2-C_{Me}	1.441 1.443	C_2-N_2-C_{Me}	120.7 118.0

XYZ coordinates:

C	-0.01804300	-0.80037600	-0.24471200
C	0.28418100	0.62976500	0.28097500
C	1.67868000	1.08632800	-0.21248000
C	2.79096400	0.12254500	0.22173700

C	2.50223000	-1.30456700	-0.25701400
C	1.11211300	-1.76602500	0.19577900
C	-0.74236000	2.79109000	0.79913100
C	-1.09426700	1.84824400	-1.38759400
C	-1.85803300	-1.10511900	1.43919900
C	-2.08509300	-1.99617400	-0.90048000
H	0.01517700	-0.75627400	-1.34157400
H	0.33735900	0.56006800	1.37552300
H	1.67121100	1.15736700	-1.30694000
H	1.88979900	2.09205300	0.16400300
H	3.75832300	0.46751000	-0.15831900
H	2.86804000	0.12869100	1.31686300
H	3.27039900	-1.99431800	0.10825400
H	2.55549500	-1.33425800	-1.35335600
H	1.09348400	-1.85433900	1.28931000
H	0.89004100	-2.76168300	-0.20048500
H	0.06630500	3.48191600	0.49715800
H	-0.59750200	2.54413100	1.85449600
H	-1.68675000	3.33621000	0.70977800
H	-0.31413800	2.44422300	-1.89538700
H	-2.03102400	2.40873300	-1.45697100
H	-1.22948400	0.91937400	-1.94287900
H	-1.13319300	-1.38975700	2.21591200
H	-2.73025300	-1.74730900	1.57959200
H	-2.16750500	-0.06760400	1.63203200
H	-2.37468800	-1.35501400	-1.75078300
H	-3.00807600	-2.38643300	-0.46714400
H	-1.53912700	-2.85778200	-1.31849000
N	-0.81366300	1.57053700	0.01214600
N	-1.33292500	-1.29479100	0.10816400

Model 5 (transition state between Models 1 and 2 through clockwise rotation about N_2 of Model 1)



(hydrogen atoms omitted for clarity)

E = -503.917383 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.559	C_1-C_2-C_3	110.1
C_2-C_3	1.553	C_2-C_3-C_4	116.0
C_3-C_4	1.530	C_3-C_4-C_5	110.7
C_4-C_5	1.525	C_4-C_5-C_6	108.8
C_5-C_6	1.526	C_5-C_6-C_1	114.2
C_6-C_1	1.548	C_6-C_1-C_2	112.8
C_1-N_1	1.478	C_2-C_1-N_1	113.3
C_2-N_2	1.485	C_1-C_2-N_2	113.6
N_1-C_{Me}	1.453 1.456	C_1-N_1-C_{Me}	114.0 116.8
N_2-C_{Me}	1.464 1.463	C_2-N_2-C_{Me}	117.5 112.0

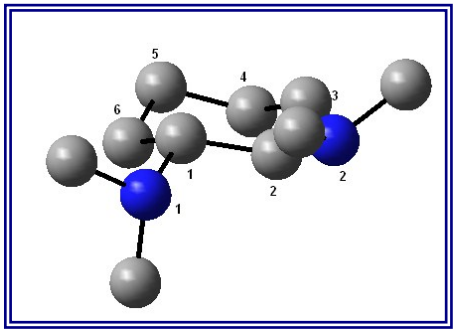
XYZ coordinates:

C	0.62529600	0.22979800	-0.33724000
C	-0.80088000	-0.06798900	0.21889100
C	-1.74831600	1.12898400	-0.06850200

C	-1.20303300	2.51582400	0.27960300
C	0.13004500	2.76145900	-0.41940600
C	1.10866300	1.66376500	-0.01070300
C	-0.63862700	-2.50826000	-0.39562700
C	-2.72578000	-1.57441800	0.23329700
C	2.07186600	-0.74722800	1.45023700
C	2.74921300	-0.89361600	-0.85515600
H	0.53764200	0.14289400	-1.42722300
H	-0.72180200	-0.18403300	1.31799300
H	-1.99153400	1.09173100	-1.13726200
H	-2.68634000	0.98422700	0.46859800
H	-1.94259900	3.27243000	-0.00214400
H	-1.06496000	2.60571600	1.36492600
H	0.53499100	3.74584400	-0.16206800
H	-0.01617100	2.75425500	-1.50715900
H	1.28129500	1.74616900	1.06867300
H	2.08048000	1.81695500	-0.48994400
H	-0.36726600	-2.87449100	0.61115800
H	0.28101500	-2.38045700	-0.95452900
H	-1.23920000	-3.28105000	-0.88384100
H	-2.66105100	-1.73793200	1.32684200
H	-3.12338200	-2.48752700	-0.21397400
H	-3.45387200	-0.78586500	0.04986400
H	2.77401000	0.07296000	1.68356100
H	2.57982800	-1.68832400	1.68327700
H	1.21798800	-0.66194900	2.12401900
H	2.38211000	-1.03029700	-1.87616200
H	3.34385500	-1.77437800	-0.59360600
H	3.43333700	-0.02517200	-0.85339900
N	-1.42904100	-1.27611900	-0.37454400

N	1.63060500	-0.77697000	0.06454800

Model 6 (transition state between Models 1 and 2 through anti-clockwise rotation about N_2 of Model 1)



(hydrogen atoms omitted for clarity)

E = -503.906270 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.566	C_1-C_2-C_3	109.9
C_2-C_3	1.551	C_2-C_3-C_4	115.1
C_3-C_4	1.530	C_3-C_4-C_5	110.5
C_4-C_5	1.526	C_4-C_5-C_6	108.8
C_5-C_6	1.527	C_5-C_6-C_1	114.5
C_6-C_1	1.549	C_6-C_1-C_2	112.3
C_1-N_1	1.480	C_2-C_1-N_1	113.0
C_2-N_2	1.498	C_1-C_2-N_2	116.1
N_1-C_{Me}	1.453 1.455	C_1-N_1-C_{Me}	114.0 116.9
N_2-C_{Me}	1.457 1.456	C_2-N_2-C_{Me}	120,2 119.2

XYZ coordinates:

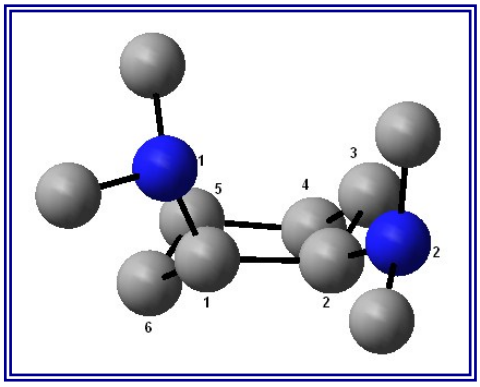
C	0.57658000	0.22568000	-0.31163600
C	-0.74059600	-0.12006600	0.46121900
C	-1.83374700	0.93138400	0.13889300

C	-1.39696700	2.38965500	0.29201200
C	-0.18786100	2.68070700	-0.59188000
C	0.94183000	1.72791300	-0.20922700
C	-2.65356900	-1.69134600	-0.14066900
C	-0.43345600	-2.53388100	-0.33806300
C	2.28405800	-0.38885000	1.40964900
C	2.74955000	-0.74719500	-0.92874500
H	0.39331400	-0.00393900	-1.36813900
H	-0.50606700	-0.00344900	1.53072700
H	-2.17950200	0.78227300	-0.89039200
H	-2.69469000	0.75623300	0.78568700
H	-2.23735300	3.04498800	0.04120300
H	-1.14012800	2.59758700	1.33872300
H	0.14020100	3.71974300	-0.48269400
H	-0.46032800	2.54576400	-1.64666300
H	1.23521300	1.95018900	0.82305500
H	1.82672600	1.91124400	-0.82634100
H	-2.85630200	-1.46016600	-1.20393900
H	-3.34882200	-1.11454100	0.46824200
H	-2.91044300	-2.74417300	0.00708700
H	-0.33851100	-2.44031800	-1.43808500
H	-0.88898800	-3.50967300	-0.14137000
H	0.56654100	-2.51906500	0.08207300
H	2.89318800	0.52890900	1.48747900
H	2.92997700	-1.23195700	1.67346400
H	1.49456100	-0.33602900	2.16114300
H	2.29832900	-1.03881300	-1.88094000
H	3.45376200	-1.53311800	-0.63887700
H	3.33750900	0.17355700	-1.09671800
N	-1.26936500	-1.50834200	0.27179200

N	1.72034800	-0.62297900	0.08905900

The following models examine two other arrangements of the NMe2 groups *i.e*. in place of the previous equatorial positioning of these groups (*R,R*) we looked at: i) both NMe2 groups occupying axial positions (*S,S*) and ii) one NMe2 group placed axially and the other equatorially (*S,R*).

Model 7 (both NMe2 groups occupying axial positions (*S,S*))



(hydrogen atoms omitted for clarity)

E = -503.916110 a.u.

Principal bond lengths (Å) and bonds angles (°):

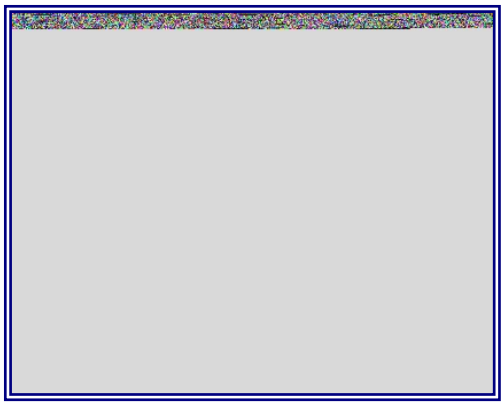
C_1-C_2	1.567	C_1-C_2-C_3	114.3
C_2-C_3	1.538	C_2-C_3-C_4	111.0
C_3-C_4	1.534	C_3-C_4-C_5	111.5
C_4-C_5	1.534	C_4-C_5-C_6	111.7
C_5-C_6	1.538	C_5-C_6-C_1	115.4
C_6-C_1	1.557	C_6-C_1-C_2	110.1
C_1-N_1	1.477	C_2-C_1-N_1	115.3
C_2-N_2	1.466	C_1-C_2-N_2	117.2
N_1-C_{Me}	1.457 1.457	C_1-N_1-C_{Me}	112.6 118.1
N_2-C_{Me}	1.452 1.458	C_2-N_2-C_{Me}	114.2 118.5

XYZ coordinates:

C	-0.61058300	-0.42461700	-0.35672600
C	0.66229200	-0.25229900	0.53678400
C	0.83029200	1.19169800	1.04911500
C	0.74235500	2.25999600	-0.04748100
C	-0.59066500	2.15475500	-0.79555200
C	-0.78520900	0.74251300	-1.36547200
C	1.89177200	-2.19310900	-0.26527100
C	3.13817900	-0.22693800	0.17975500
C	-2.73123200	-1.63700000	-0.35434000
C	-2.52176600	0.19200300	1.16886600
H	0.03800400	1.37781200	1.77947000
H	1.76148300	1.28501400	1.61193300
H	0.85426400	3.25484400	0.39639600
H	1.56533600	2.13835400	-0.76072000
H	-0.62519200	2.88312100	-1.61284800
H	-1.40842200	2.41635200	-0.11637500
H	-0.03598600	0.59157200	-2.15022200
H	-1.76243400	0.65576000	-1.85238200
H	0.94763000	-2.62199500	-0.60126000
H	2.11597000	-2.62134800	0.72985000
H	2.66904700	-2.52175800	-0.95985700
H	3.20639600	0.85407700	0.06298500
H	3.90404400	-0.66999600	-0.46178200
H	3.39486600	-0.48149000	1.22549900
H	-3.26265700	-1.07533700	-1.14568500
H	-3.49029200	-2.05791500	0.31151500
H	-2.20451800	-2.46944700	-0.82735600
H	-1.85090700	0.75040800	1.81995000
H	-3.26209700	-0.29716800	1.80903000

H	-3.06472200	0.91286400	0.53147000
N	1.83601100	-0.73278800	-0.24229600
N	-1.80019300	-0.83080000	0.42345900
H	0.51644000	-0.90050400	1.41746700
H	-0.40958200	-1.30011300	-0.97328600

Model 8 (one NMe2 group placed axially and the other equatorially (*S,R*))



(hydrogen atoms omitted for clarity)

E = -503.916110 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.567		C_1-C_2-C_3	114.3	
C_2-C_3	1.538		C_2-C_3-C_4	111.0	
C_3-C_4	1.534		C_3-C_4-C_5	111.5	
C_4-C_5	1.534		C_4-C_5-C_6	111.7	
C_5-C_6	1.538		C_5-C_6-C_1	115.4	
C_6-C_1	1.557		C_6-C_1-C_2	110.1	
C_1-N_1	1.477		C_2-C_1-N_1	115.3	
C_2-N_2	1.466		C_1-C_2-N_2	117.2	
N_1-C_{Me}	1.457	1.457	C_1-N_1-C_{Me}	112.6	118.1
N_2-C_{Me}	1.452	1.458	C_2-N_2-C_{Me}	114.2	118.5

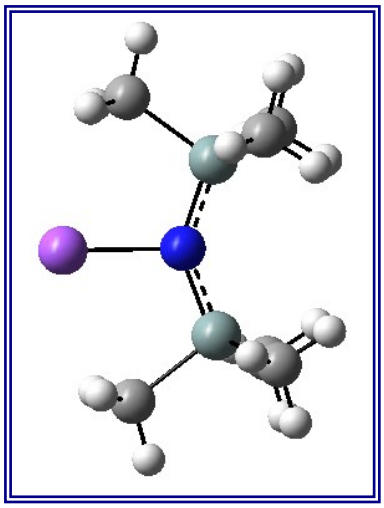
XYZ coordinates:

C	-0.32458700	-0.96348600	-0.38089900
C	0.22875800	0.46601400	-0.70693400
C	1.74529100	0.38743900	-1.04985300

C	2.59550600	-0.45796300	-0.08691600
C	1.99186600	-1.85171000	0.12729000
C	0.53724400	-1.76654600	0.60834300
C	-0.27667800	2.83579200	-0.40730700
C	0.52929000	1.63824700	1.49881300
C	-2.62565700	-0.62069600	-1.14788100
C	-2.22718100	-0.63483700	1.22830500
H	-0.20895300	-1.49539100	-1.33730800
H	-0.27082100	0.74858400	-1.63810100
H	-1.59107300	-1.03617000	2.01855000
H	-3.23267100	-1.03841800	1.38950600
H	-2.26715400	0.45802800	1.33625800
H	1.83576600	-0.04599200	-2.05388500
H	2.15336900	1.40099500	-1.12718800
H	3.61150800	-0.54714900	-0.48662200
H	2.69223400	0.04461500	0.88004200
H	2.02634000	-2.41063300	-0.81709700
H	2.59312300	-2.41930300	0.84478300
H	0.51703500	-1.32983300	1.61082800
H	0.10065600	-2.76599300	0.69641100
H	0.69975300	3.26354700	-0.70249600
H	-0.74749100	3.54359900	0.28106200
H	-0.90231400	2.77279700	-1.30087900
H	0.55020000	0.68205000	2.01848100
H	-0.00022600	2.34867500	2.14106700
H	1.56830700	1.99937800	1.39888100
H	-2.29296300	-1.03803700	-2.10330300
H	-2.67856100	0.47770200	-1.25165500
H	-3.64334300	-0.98060200	-0.96543900
N	-1.75510400	-1.07635300	-0.07907400

N	-0.18144400	1.52978600	0.23197900

Model 9 (donor-free NaHMDS monomer)



(hydrogen atoms omitted for clarity)

E = -1035.803641 a.u.

Principal bond lengths (Å) and bonds angles (°):

Na-N 2.170

N- Si 1.692

Si-C_{Me} 1.924 1.900 1.900

C_{Me}…Na 3.00*

Na-N-Si 109.9

Si-N-Si 140.2

N-Si-C_{Me} 107.0 115.3 115.3

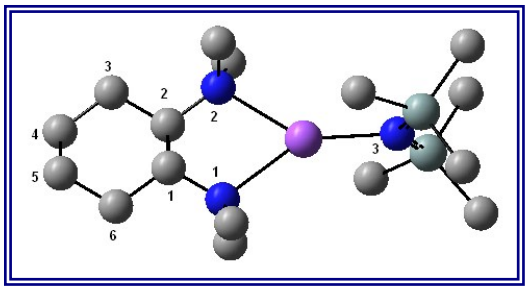
* Agostic bonding

XYZ coordinates:

C	-1.46807400	2.04923200	-1.36125400
C	-0.11407500	2.74451800	1.28983500

C	1.57736300	2.11424800	-1.16712900
C	-1.57736300	-2.11424800	-1.16712900
C	0.11407500	-2.74451800	1.28983500
C	1.46807400	-2.04923200	-1.36125400
H	-1.03873000	2.57077600	1.85821800
H	-0.11687700	3.80478300	1.01730300
H	0.74507200	2.60819300	1.96363200
H	2.46730600	1.95544700	-0.54949900
H	1.55191400	3.17086200	-1.45549500
H	1.70879800	1.52554700	-2.08073000
H	-1.55191400	-3.17086200	-1.45549500
H	-1.70879800	-1.52554700	-2.08073000
H	-2.46730600	-1.95544700	-0.54949900
H	-1.44831300	1.46486800	-2.28705400
H	-1.45738000	3.10849500	-1.64051800
H	-2.42172200	1.83994200	-0.86643600
H	-0.74507200	-2.60819300	1.96363200
H	1.03873000	-2.57077600	1.85821800
H	0.11687700	-3.80478300	1.01730300
H	2.42172200	-1.83994200	-0.86643600
H	1.44831300	-1.46486800	-2.28705400
H	1.45738000	-3.10849500	-1.64051800
N	0.00000000	0.00000000	0.33045400
Na	0.00000000	0.00000000	2.50037700
Si	0.00000000	1.59059200	-0.24548500
Si	0.00000000	-1.59059200	-0.24548500

Model 10 (monomeric (R,R)-TMCDA·NaHMDS complex)



(hydrogen atoms omitted for clarity)

E = -1539.767281 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.553	C_1-C_2-C_3	110.2
C_2-C_3	1.547	C_2-C_3-C_4	112.9
C_3-C_4	1.532	C_3-C_4-C_5	110.4
C_4-C_5	1.530	C_4-C_5-C_6	110.4
C_5-C_6	1.532	C_5-C_6-C_1	112.9
C_6-C_1	1.547	C_6-C_1-C_2	110.2
C_1-N_1	1.488	C_2-C_1-N_1	112.9
C_2-N_2	1.488	C_1-C_2-N_2	112.9
N_1-C_{Me}	1.469 1.470	C_1-N_1-C_{Me}	114.8 112.3
N_2-C_{Me}	1.469 1.470	N_1-Na-N_2	73.4
Na-N_3	2.466	N_1-Na-N_3	143.3
N_3- Si	1.692	Na-N_3-Si	112.8
Si-C_{Me}	1.919 1.906 1.905	Si-N_3-Si	134.5
C_{Me}…Na	3.19	N_3-Si-C_{Me}	109.0 115.3 115.0

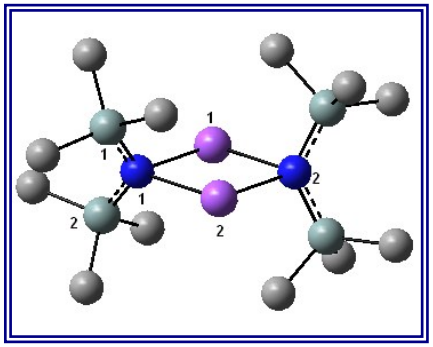
XYZ coordinates:

C	-3.01834600	-0.60859200	-0.48456600
C	-4.31415100	-0.61684600	-1.32911700
C	-5.58507300	-0.60232800	-0.47335500
C	-5.58491900	0.60911200	0.46196600
C	-4.31788300	0.61884800	1.32352900
C	-3.01832600	0.60592500	0.48480400
C	-1.68030400	0.28487900	-2.38643900
C	-1.54578900	-2.05268600	-1.81728900
C	-1.54691500	2.04446800	1.82492400
C	-1.69199800	-0.29285700	2.39225700
C	4.25136400	1.31455700	-2.04743200
C	1.64304000	2.59619800	-1.13674100
C	4.01430500	2.48142000	0.75505500
C	4.04147000	-2.46385700	-0.75264600
C	1.65338600	-2.60564800	1.11670300
C	4.24315700	-1.30843400	2.05710800
H	-3.02327800	-1.51599500	0.13044000
H	-3.01723500	1.51336600	-0.13017000
H	-2.40518400	-0.10692400	3.20802200
H	-0.68755900	-0.26155600	2.82259400
H	-1.85906900	-1.30293800	2.01393300
H	1.08452700	2.14878000	-1.96826700
H	2.01223300	3.56543700	-1.48819100
H	0.93787700	2.80558900	-0.32151700
H	3.37575700	2.69753100	1.61828900
H	4.36801800	3.43740700	0.35239300
H	4.88777500	1.93728400	1.12876400
H	4.39848300	-3.41891800	-0.35066100
H	4.91449100	-1.91158800	-1.11523300
H	3.41311000	-2.68097200	-1.62306200

H	5.15600200	0.75762200	-1.78164500
H	4.56753400	2.29522500	-2.42046000
H	3.77257100	0.77784100	-2.87291200
H	0.95851500	-2.81830000	0.29362000
H	1.08272200	-2.16605800	1.94430500
H	2.02709700	-3.57281400	1.46909200
H	3.75310500	-0.77828200	2.88025000
H	5.14639200	-0.74425900	1.80200600
H	4.56256200	-2.28836700	2.42934100
H	-4.32599600	0.26354800	-1.98125000
H	-4.31336900	-1.49137200	-1.98604200
H	-6.46772100	-0.59242200	-1.11992700
H	-5.64377800	-1.52292200	0.12092300
H	-6.47055900	0.60260300	1.10447500
H	-5.63737300	1.52989500	-0.13259800
H	-4.33599100	-0.26159400	1.97545900
H	-4.31692000	1.49329000	1.98055600
H	-2.39130400	0.10182700	-3.20474200
H	-0.67440500	0.24894300	-2.81285200
H	-1.84413200	1.29585700	-2.00909300
H	-1.56095700	-2.77423400	-0.99762600
H	-0.56015600	-2.09783600	-2.28706300
H	-2.28759100	-2.36455600	-2.56844700
H	-2.29056800	2.35812200	2.57347100
H	-1.55679900	2.76656400	1.00567200
H	-0.56289800	2.08643200	2.29840100
N	-1.77567500	-0.69853200	-1.29791600
N	-1.77903600	0.69134600	1.30377700
N	2.42811000	0.00086200	-0.00003400
Na	0.19886900	-0.00451200	0.00669600

Si	3.07712700	1.46198300	-0.55446100
Si	3.08391800	-1.45786200	0.55251400

Model 11 (dimeric solvent-free NaHMDS complex, input geometry as C_1 symmetry, optimised to ~D_2)



(hydrogen atoms omitted for clarity)

E = -2071.6693032 a.u.

Principal bond lengths (Å) and bonds angles (°):

Na_1-N_1	2.362	Na_1-N_1-Na_2	74.8
Na_1-N_2	2.362	Na_1-N_2-Na_2	74.8
Na_2-N_1	2.361	N_1-Na_1-N_2	105.2
Na_2-N_2	2.362	N_1-Na_2-N_2	105.2
N_1-Si_1	1.716	Na_1-N_1-Si_1	123.4
Si_1-C_{Me}	1.919 1.900 1.901	Si_1-N_1-Si_2	126.5
C_{Me}…Na	2.80*	N_1-Si_1-C_{Me}	108.9 113.9 115.6

* Agostic bonding

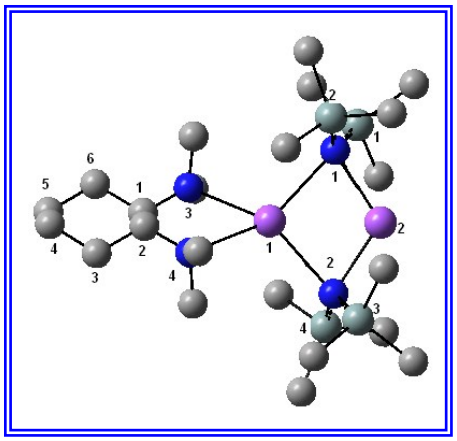
XYZ coordinates:

C	4.24613400	-1.17684400	1.54162800
C	1.47080700	-2.35892600	1.74242400
C	3.05166700	-2.66329200	-0.84598000
C	3.05137500	2.66340200	0.84611100

C	1.47152700	2.35885200	-1.74280200
C	4.24693600	1.17677700	-1.54081400
C	-3.05075800	-2.66351300	0.84610100
C	-4.24665100	-1.17735900	-1.54095600
C	-1.47098200	-2.35857100	-1.74290400
C	-4.24717500	1.17700300	1.54049000
C	-3.05088700	2.66373500	-0.84607400
C	-1.47166300	2.35846300	1.74322800
H	1.31432700	-1.81298000	2.68444800
H	1.90312200	-3.32139000	2.03304800
H	0.49180500	-2.58743200	1.30312700
H	2.15527400	-2.95353300	-1.40476200
H	3.50733500	-3.58062900	-0.45809500
H	3.75456500	-2.22344700	-1.56075000
H	3.50714000	3.58073600	0.45832900
H	3.75397600	2.22369100	1.56124300
H	2.15470500	2.95366800	1.40445200
H	5.04066500	-0.72796600	0.93863700
H	4.62708500	-2.13061700	1.92228100
H	4.07916800	-0.52158700	2.40289100
H	0.49265900	2.58778400	-1.30346400
H	1.31478400	1.81260000	-2.68459600
H	1.90414100	3.32107500	-2.03380900
H	4.08040400	0.52132400	-2.40201500
H	5.04124800	0.72812100	-0.93737500
H	4.62794800	2.13051300	-1.92150400
H	-3.75325600	-2.22377900	1.56132800
H	-2.15398400	-2.95369400	1.40430800
H	-3.50656200	-3.58086900	0.45843100
H	-5.04114200	-0.72888600	-0.93761400

H	-4.62733800	-2.13124900	-1.92157500
H	-4.08028400	-0.52193600	-2.40220900
H	-0.49214300	-2.58761100	-1.30353000
H	-1.31422000	-1.81208300	-2.68456400
H	-1.90353200	-3.32071900	-2.03424500
H	-4.08102700	0.52092000	2.40128800
H	-5.04171300	0.72916400	0.93674300
H	-4.62765900	2.13070500	1.92178300
H	-3.75326000	2.22415900	-1.56152400
H	-2.15398700	2.95396000	-1.40405800
H	-3.50672800	3.58106600	-0.45837100
H	-1.90371900	3.32109700	2.03368600
H	-0.49234100	2.58661500	1.30446600
H	-1.31594300	1.81230900	2.68524600
N	1.87649100	0.00005200	-0.00013300
N	-1.87667600	0.00016000	-0.00013700
Na	-0.00002300	-0.00002200	1.43354700
Na	-0.00007400	0.00003200	-1.43371200
Si	2.64885200	-1.43239400	0.54353600
Si	2.64918000	1.43241300	-0.54352700
Si	-2.64889100	-1.43243200	-0.54353500
Si	-2.64922100	1.43248100	0.54347800

Model 12 (compound **1**, input geometry as C_1 symmetry, optimised to ~C_2)



(hydrogen atoms omitted for clarity)

E = -2575.6086877 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.551	Na_1-N_1	2.626
C_2-C_3	1.548	Na_1-N_2	2.626
C_3-C_4	1.532	N_1-Na_2	2.321
C_4-C_5	1.530	N_2-Na_2	2.321
C_5-C_6	1.532	N_1-Si_1	1.719
C_6-C_1	1.548	N_1-Si_2	1.720
C_1-N_3	1.486	N_2-Si_3	1.719
C_2-N_4	1.487	N_2-Si_4	1.720
N_3-C_{Me}	1.471 1.467	Si_1-C_{Me}	1.913 1.908 1.902
N_4-C_{Me}	1.471 1.467	Si_2-C_{Me}	1.905 1.905 1.906
N_3-Na_1	2.629	Si_3-C_{Me}	1.913 1.908 1.902
N_4-Na_1	2.630	Si_4-C_{Me}	1.905 1.905 1.906
		C_{Me}…Na_1	3.21 3.21
		C_{Me}…Na_2	3.02 3.01
C_1-C_2-C_3	110.2	Na_1-N_1-Na_2	74.7

C_2-C_3-C_4	112.9	N_1-Na_2-N_2	114.5
C_3-C_4-C_5	110.4	Na_2-N_2-Na_1	74.7
C_4-C_5-C_6	110.4	N_2-Na_1-N_1	96.1
C_5-C_6-C_1	112.9	Na_1-N_1-Si_1	126.1
C_6-C_1-C_2	110.2	Na_1-N_1-Si_2	106.1
C_2-C_1-N_1	112.7	Na_1-N_2-Si_3	126.1
C_1-C_2-N_2	112.7	Na_1-N_2-Si_4	106.0
C_1-N_3-C_{Me}	114.3 111.8	N_1-Si_1-C_{Me}	110.1 115.0 115.6
C_2-N_4-C_{Me}	114.3 111.8	N_1-Si_2-C_{Me}	110.6 115.7 113.5
C_1-N_3-Na_1	114.1	N_2-Si_3-C_{Me}	110.1 115.1 115.6
C_2-N_4-Na_1	114.0	N_2-Si_4-C_{Me}	110.6 115.7 113.5
N_3-Na_1-N_1	106.4		
N_4-Na_1-N_2	106.4		

XYZ coordinates:

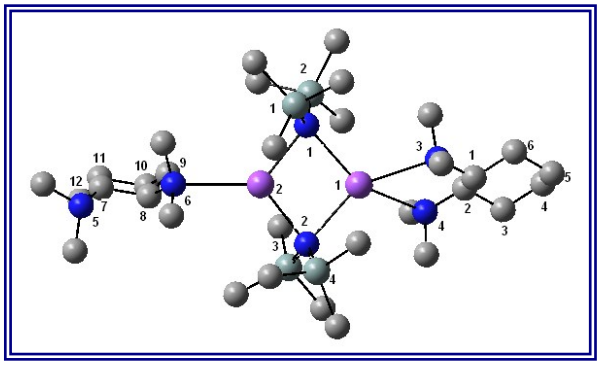
C	3.66902000	0.28726000	0.71955200
C	4.96773300	1.08963000	0.97409800
C	6.23601200	0.27057600	0.71393000
C	6.23560900	-0.27503900	-0.71515300
C	4.96675200	-1.09333500	-0.97492700
C	3.66857300	-0.29022900	-0.71990800
C	2.32515400	2.34591500	0.36427200
C	2.25087400	1.21645300	2.48231200
C	2.24916800	-1.21846900	-2.48217600
C	2.32362800	-2.34817100	-0.36434800
C	-0.70737700	4.41116500	-1.79424700
C	-0.09690000	1.61003800	-2.75141100
C	-2.96321800	2.59929400	-2.72944200
C	-0.92106000	4.00051100	2.05404800
C	-2.78332100	1.64214900	2.52805700

C	-3.66447800	3.91841400	0.76944000
C	-0.92583400	-3.99888600	-2.05546200
C	-3.66754000	-3.91692800	-0.76754400
C	-2.78841000	-1.64000900	-2.52615000
C	-0.71285700	-4.41101400	1.79480400
C	-2.96520100	-2.59465000	2.72968800
C	-0.09667800	-1.61132700	2.75110800
H	3.67249200	-0.56206500	1.41291900
H	3.67231200	0.55911800	-1.41325400
H	3.01531800	-3.10003600	-0.77269800
H	1.30659600	-2.72725800	-0.47651000
H	2.52289000	-2.24647800	0.70308100
H	0.91666800	1.68673900	-2.34551400
H	-0.05794500	1.98303200	-3.78015100
H	-0.35899400	0.54875000	-2.81207700
H	-3.34580100	1.58200700	-2.87001400
H	-2.81712800	3.02671600	-3.72765300
H	-3.74536100	3.18261100	-2.23401000
H	-1.41826200	4.55540300	2.85709300
H	-0.50659400	4.73440400	1.35616700
H	-0.08092300	3.46271300	2.50306800
H	-1.39482600	5.11487200	-1.31541500
H	-0.58663500	4.73393500	-2.83412100
H	0.26469600	4.51695800	-1.30228300
H	-2.02225700	0.93713500	2.87512200
H	-3.66078400	1.05917700	2.21400000
H	-3.11153800	2.21190500	3.40362800
H	-4.47506500	3.32725000	0.32943800
H	-3.42873300	4.71986700	0.06320500
H	-4.05882900	4.38999000	1.67631000

H	-0.51274800	-4.73476300	-1.35886000
H	-0.08473300	-3.46138600	-2.50298600
H	-1.42353300	-4.55143000	-2.85981800
H	-3.43161400	-4.71807600	-0.06106200
H	-4.06190000	-4.38888200	-1.67422100
H	-4.47819100	-3.32571400	-0.32773200
H	-2.02737900	-0.93538200	-2.87408800
H	-3.66528900	-1.05669800	-2.21102300
H	-3.11804400	-2.20941000	-3.40139600
H	0.25821400	-4.51903200	1.30132700
H	-1.40228600	-5.11419300	1.31805900
H	-0.59084800	-4.73266800	2.83488700
H	-3.74836600	-3.17682400	2.23450100
H	-3.34596800	-1.57665500	2.86986400
H	-2.81979000	-3.02199600	3.72803200
H	-0.06212300	-1.98141200	3.78104800
H	-0.35398600	-0.54865100	2.80803700
H	0.91745300	-1.69404300	2.34785500
H	4.98343300	1.97090700	0.32317600
H	4.96924700	1.46209800	2.00203300
H	7.12121900	0.88879200	0.89283300
H	6.29071800	-0.56518400	1.42327600
H	7.12038700	-0.89378500	-0.89434300
H	6.29059100	0.56068800	-1.42451700
H	4.98215800	-1.97467200	-0.32408000
H	4.96770500	-1.46572600	-2.00289000
H	3.01775600	3.09734000	0.77188700
H	1.30853100	2.72583800	0.47719500
H	2.52345200	2.24388300	-0.70330900
H	2.31086900	0.25113800	2.98734700

H	1.26313300	1.63771700	2.67906500
H	2.99291100	1.89404900	2.93285700
H	2.99054300	-1.89659300	-2.93302300
H	2.30969900	-0.25319300	-2.98719700
H	1.26104300	-1.63895800	-2.67856300
N	2.42791100	1.04162500	1.03615600
N	2.42687400	-1.04383800	-1.03608300
N	-1.50854900	1.94768900	-0.14690000
N	-1.50990600	-1.94647800	0.14677300
Na	0.24689600	0.00026800	0.00062500
Na	-2.76431900	0.00102700	-0.00221900
Si	-1.34453900	2.61755700	-1.72249600
Si	-2.14603100	2.83817300	1.17842100
Si	-2.14941700	-2.83672300	-1.17769600
Si	-1.34673400	-2.61623600	1.72249800

Model 13 (compound **2**, input geometry as C_1 symmetry, optimised to ~C_2)



(hydrogen atoms omitted for clarity)

E = -3079.542463 a.u.

Principal bond lengths (Å) and bonds angles (°):

C_1-C_2	1.550	N_2-Si_3	1.717
C_2-C_3	1.549	N_2-Si_4	1.719
C_3-C_4	1.533	Si_1-C_{Me}	1.909 1.910 1.905
C_4-C_5	1.530	Si_2-C_{Me}	1.906 1.908 1.906
C_5-C_6	1.532	Si_3-C_{Me}	1.908 1.910 1.907
C_6-C_1	1.548	Si_4-C_{Me}	1.908 1.906 1.906
C_1-N_3	1.484	C_{Me}…Na_1	3.12 3.04
C_2-N_4	1.485	C_{Me}…Na_2	3.18 3.49
N_3-C_{Me}	1.468 1.466	Na_2-N_6	2.801
N_4-C_{Me}	1.468 1.466	C_7-C_8	1.559
N_3-Na_1	2.805	C_8-C_9	1.542
N_4-Na_1	2.715	C_9-C_{10}	1.533
Na_1-N_1	2.589	C_{10}-C_{11}	1.531
Na_1-N_2	2.537	C_{11}-C_{12}	1.531
N_1-Na_2	2.416	C_{12}-C_7	1.548
N_2-Na_2	2.443	C_7-N_5	1.475
N_1-Si_1	1.718	C_8-N_6	1.493
N_1-Si_2	1.719	N_5-C_{Me}	1.457 1.459
		N_6-C_{Me}	1.469 1.473
C_1-C_2-C_3	109.8	Na_1-N_1-Si_1	124.9
C_2-C_3-C_4	112.9	Na_1-N_1-Si_2	103.9
C_3-C_4-C_5	110.6	Na_1-N_2-Si_3	125.1
C_4-C_5-C_6	110.4	Na_1-N_2-Si_4	103.1
C_5-C_6-C_1	112.7	N_1-Si_1-C_{Me}	110.8 115.4 115.9
C_6-C_1-C_2	110.2	N_1-Si_2-C_{Me}	110.7 116.1 114.0
C_2-C_1-N_1	112.9	N_2-Si_3-C_{Me}	111.0 117.4 113.6
C_1-C_2-N_2	112.7	N_2-Si_4-C_{Me}	110.5 116.4 114.6
C_1-N_3-C_{Me}	114.1 111.7	C_7-C_8-C_9	109.5
C_2-N_4-C_{Me}	114.2 111.9	C_8-C_9-C_{10}	113.5

C_1-N_3-Na_1	115.6	C_9-C_{10}-C_{11}	110.0
C_2-N_4-Na_1	116.2	C_{10}-C_{11}-C_{12}	110.3
N_3-Na_1-N_1	107.9	C_{11}-C_{12}-C_1	112.5
N_4-Na_1-N_2	105.2	C_{12}-C_1-C_2	110.6
Na_1-N_1-Na_2	78.4	C_8-C_7-N_5	113.0
N_1-Na_2-N_2	105.0	C_7-C_8-N_6	116.6
Na_2-N_2-Na_1	79.0	C_7-N_5-C_{Me}	113.5 115.6
N_2-Na_1-N_1	97.5	C_8-N_6-C_{Me}	113.6 113.7
N_1-Na_2-N_6	127.2	Na_2-N_6-C_8	118.0

XYZ coordinates:

C	-4.81110700	-0.23598700	-0.50915200
C	-6.33105300	0.10958100	-0.53676700
C	-7.03459200	-0.62692900	-1.70211600
C	-6.40125500	-0.31333800	-3.06065900
C	-4.91071000	-0.66031600	-3.04317200
C	-4.19305800	0.05286800	-1.89150300
C	-7.25579000	-1.45355200	1.15506500
C	-8.16546000	0.76357200	0.95331200
C	-4.09706900	-0.22349400	1.86746700
C	-4.25930200	1.86518700	0.68645500
C	5.30105600	-0.66015500	-1.07093900
C	5.63758800	0.06890900	0.25477800
C	6.97869700	0.83049400	0.12008500
C	8.13798100	-0.08035300	-0.29647700
C	7.80922300	-0.79379600	-1.60927600
C	6.48862800	-1.56222900	-1.48949100
C	4.64001400	1.17418500	2.18822400
C	4.34026200	2.16595200	0.02025800

C	3.97720100	-2.52978500	-0.12001000
C	3.53800000	-1.76600300	-2.35427800
C	-0.65917600	2.17012400	2.83364000
C	-1.18672500	4.50547200	0.98026000
C	1.58787300	4.01931900	2.03231300
C	1.47088200	1.32460500	-2.65009000
C	-1.15419100	2.82054500	-2.48513000
C	1.44734500	4.23254200	-1.83478000
C	1.86026400	-1.12085300	2.96838100
C	-1.01713700	-1.96095200	3.40271700
C	1.03977300	-3.99521500	2.55056600
C	0.56020600	-4.41837100	-0.96682200
C	-0.68592200	-2.00753600	-2.25555900
C	-2.18987500	-3.54792200	-0.10336400
H	-4.70907500	-1.31123100	-0.32672100
H	-6.40317400	1.18215900	-0.75009100
H	5.18184200	0.10379400	-1.84897700
H	5.78406000	-0.70120800	1.02025200
H	-4.16047900	2.36876000	-0.27615400
H	-3.52428200	2.30455600	1.36335300
H	-5.25638500	2.07288200	1.09824700
H	6.87330600	1.62325500	-0.62869200
H	7.21263000	1.32518400	1.06695000
H	9.05697300	0.50616700	-0.39407800
H	8.32513600	-0.82537600	0.48743100
H	8.61452800	-1.48010600	-1.88952300
H	7.73513700	-0.05420700	-2.41680700
H	6.61520700	-2.35919900	-0.74802000
H	6.25882100	-2.05349600	-2.43858700
H	5.49781100	1.81861300	2.44071100

H	4.73745000	0.23620900	2.73779300
H	3.73887400	1.67639900	2.54314900
H	5.12751000	2.90581900	0.23183700
H	3.38317400	2.60921600	0.29591200
H	4.32506000	1.98479200	-1.05523700
H	4.57063900	-3.37873600	-0.49260900
H	2.94726300	-2.86738300	0.00009600
H	4.35283100	-2.25756500	0.86663000
H	3.53235100	-0.90159000	-3.02066300
H	2.51747000	-2.14594600	-2.28633100
H	4.15311400	-2.55659500	-2.81227800
H	-1.63923200	1.72371100	2.62915600
H	-0.80994600	2.86083400	3.67006900
H	-0.00183600	1.37354300	3.19288700
H	-0.80475400	5.22098500	0.24550700
H	-1.40026800	5.06852900	1.89584400
H	-2.13892600	4.12667500	0.59805800
H	2.08902900	4.61405100	1.26262500
H	2.32642100	3.33229100	2.45457600
H	1.28891300	4.70513700	2.83276500
H	1.49689300	1.64698400	-3.69637400
H	1.00995100	0.33278600	-2.63810500
H	2.51135300	1.22241200	-2.32466600
H	-1.00732400	3.15873700	-3.51694200
H	-1.77305800	3.56701200	-1.97811700
H	-1.72773600	1.88874000	-2.52757900
H	1.53776200	4.46346500	-2.90207000
H	2.45963900	4.19564500	-1.42072200
H	0.93308300	5.07585600	-1.36473300
H	2.82288600	-1.31611000	2.48543400

H	1.99077900	-1.33765600	4.03375300
H	1.65460700	-0.04809000	2.89165200
H	-1.35071300	-0.91953500	3.44315800
H	-0.75759900	-2.25292800	4.42650700
H	-1.87137800	-2.57207100	3.09478900
H	0.26590100	-4.72439600	2.29180400
H	1.27250200	-4.13351800	3.61218400
H	1.93694700	-4.25208000	1.97945500
H	0.27459200	-1.85307500	-2.75624500
H	-1.17548200	-1.02998400	-2.20004500
H	-1.29519500	-2.63043100	-2.91912700
H	-2.57971000	-4.21012300	-0.88422100
H	-2.91941600	-2.74504800	0.04290300
H	-2.15246700	-4.12446700	0.82684800
H	0.06970400	-4.98747500	-1.76486200
H	0.66219000	-5.08507600	-0.10687500
H	1.56850700	-4.17840600	-1.31578300
H	-6.98597600	-1.70877400	-1.53168400
H	-8.09620600	-0.35973600	-1.70749700
H	-6.91578000	-0.86513700	-3.85382900
H	-6.52677700	0.75267100	-3.28980900
H	-4.79274000	-1.74535900	-2.93120100
H	-4.43835600	-0.39223100	-3.99311100
H	-4.20656100	1.13233500	-2.07946500
H	-3.14310600	-0.24639400	-1.87050800
H	-8.08733900	-1.91450000	0.59614500
H	-7.51391600	-1.48728200	2.21762600
H	-6.36971600	-2.07442900	1.01280600
H	-7.91910300	1.80796600	0.74515900
H	-8.49793300	0.69990800	1.99332100

H	-9.02121600	0.47930400	0.31524300
H	-3.88872000	-1.29060100	1.77150100
H	-5.08179500	-0.09065900	2.32672200
H	-3.34537800	0.20130700	2.53835700
N	-3.99383800	0.42665200	0.54978300
N	-6.98616400	-0.07221000	0.77198500
N	4.51829700	0.90577500	0.75260700
N	3.99726700	-1.36931800	-1.01950100
N	0.36715900	2.03391500	0.02964400
N	0.17212000	-1.77294100	0.59823500
Na	1.94341000	-0.01775000	0.13120300
Na	-1.20527000	0.23198500	0.37295600
Si	0.06624800	3.10831000	1.33744000
Si	0.51322300	2.58692500	-1.59106700
Si	0.47057200	-2.20368500	2.23585100
Si	-0.46737600	-2.86294900	-0.56433000

Energetics

(R,R)-TMCDA + NaHMDS → (R,R)-TMCDA·NaHMDS; ΔE = -24.19 kcal mol-1

2 NaHMDS → $[NaHMDS]_2$; ΔE = -38.92 kcal mol-1

(R,R)-TMCDA + $[NaHMDS]_2$ → compound 1; ΔE = -8.97 kcal mol-1

2 TMCDA + $[NaHMDS]_2$ → compound 2; ΔE = -14.41 kcal mol-1

REFERENCES

1 C. Schade, W. Bauer and P. v. R. Schleyer, *J. Organomet. Chem.*, 1985, **295**, c25.

2 (a) G. J. P. Britovsek, J. England and A. J. P. White, *Inorg. Chem.*, 2005, **44**, 8125; (b) J.-C. Kizirian, N. Cabello, L. Pinchard, J.-C. Caille and A. Alexakis, *Tetrahedron*, 2005, **61**, 8939.

3 G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.

4 (a) R. Grüning and J. L. Atwood, *J. Organomet. Chem.*, 1977, **137**, 101-111; (b) M. Driess, H. Pritzkow, M. Skipinski and U. Winkler, *Organometallics*, 1997, **16**, 5108-5112; (c) J. Knizek, I. Krossing, H. Nöth, H. Schwenk and T. Seifert, *Chem. Ber./Recl.*, 1997, **130**, 1053-1062.

5 Gaussian 03, Revision B.0.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al- Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

6 W. Kohn, A. D. Becke and R. G. Parr, J. Phys. Chem., 1996, 100, 12974

7 (a) A. D. Becke, Phys. Rev. A, 1988, 38, 3098; (b) C. T. Lee, W. T. Yang and R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys., 1998, 37, 785

8 (a) A. D. McLean and G. S. Chandler, J. Chem. Phys., 1980, 72, 5639; (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., 1980, 72, 650