Supplementary Material (ESI) for Chemical Communications

The first asymmetric organolithium tetramers with simple ether donor bases

Tanja Tatic[a], Kathrin Meindl[a], Julian Henn[a], Sushil Kumar Pandey[b], and Dietmar Stalke*[a]

Experimental Section:

General procedure:

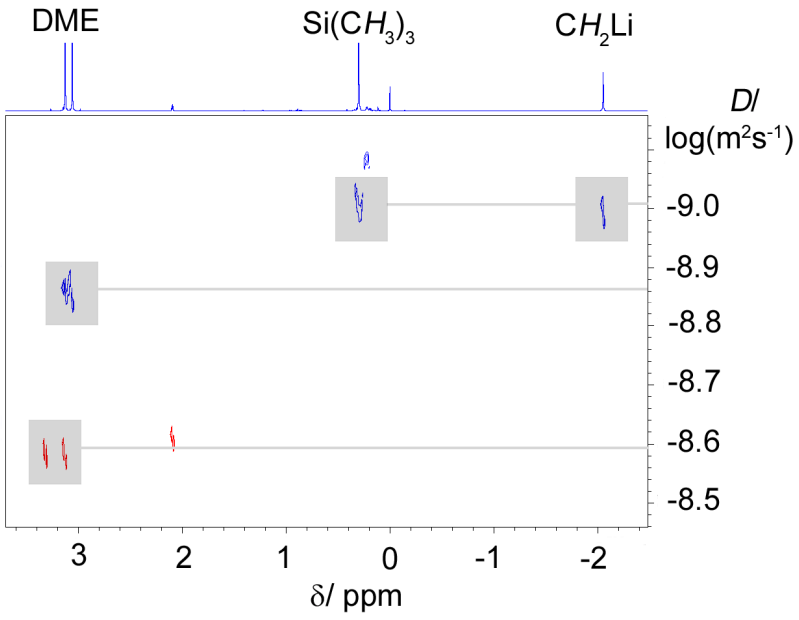
The oxygen donor bases Et_2O (for **1**), *t*BuOMe (for **2**), and DME (for **3**) (1.5 equival.) were added to trimethylsilylmethyllithium in hexane at 0 °C under a protective atmosphere. Crystallization was carried out in a freezer (–45 °C).

$[(Et_2O)_2{\cdot}(LiCH_2SiMe_3)_4]$ (1):
Yield: 0.98 g (1.87 mmol, 58 %) Found: C, 52.74; H, 12.41. $Li_4C_{24}H_{64}O_2Si_4$ requires C, 54.92; H, 12.29 %; δ^1_H (500 MHz, Tol-D_8) –1.96 (s, 8 H, CH_2Li), 0.24 (s, 36 H, $Si(CH_3)_3$), 1.09 (t, 12 H, *J* 7.01 Hz, CH_2CH_3), 3.28 (q, 8 H, *J* 7.01 Hz, OCH_2); δ^{13}_C (75 MHz, Tol-D_8) –5.31 (CH_2Li), 4.25 ($Si(CH_3)_3$), 15.27 (CH_2CH_3), 65.66 (OCH_2); δ^{29}_{Si} (99 MHz, Tol-D_8) –1.13 (s); δ^7_{Li} (194 MHz, Tol-D_8) –1.99 (s), 1.24 (s), 0.95 (s), 0.70 (s).

$[(^tBuOMe)_2{\cdot}(LiCH_2SiMe_3)_4]$ (2):
Yield: 1.12 g, (2.02 mmol, 63 %) Found: C, 56.51; H, 12.62. $Li_4C_{26}H_{68}O_2Si_4$ requires C, 56.48; H, 12.40 %; δ^1_H (500 MHz, Tol-D_8) –1.72 (s, 8 H, CH_2Li), 0.38 (s, 36 H, $Si(CH_3)_3$), 0.96 (s, 18 H, $C(CH_3)_3$), 2.92 (s, 6 H, OCH_3); δ^{13}_C (126 MHz, Tol-D_8) –3.88 (CH_2Li), 5.55 ($Si(CH_3)_3$), 27.47 ($C(CH_3)_3$), 50.27 (CH_3O), 75.07 ($C(CH_3)_3$); δ^7_{Li} (194 MHz, Tol-D_8) 2.75 (s). All the spectra had to be measured at –50 °C because of the low stability of the compound in solution.
At room temperature: δ^7_{Li} (194 MHz, Tol-D_8) 2.41 (s), 1.61 (s), 1.33 (s), 1.07 (s)

$[(DME){\cdot}(LiCH_2SiMe_3)]_2$ (3):
Yield: 0.64 g (1.94 mmol, 61 %); Found: C, 50.37; H, 10.98. $Li_4C_{16}H_{42}O_4Si_2$ requires C, 52.14; H, 11.49 %; δ^1_H (300 MHz, C_6D_6) –1.95 (s, 4 H, CH_2Li), 0.39 (s,18 H, $Si(CH_3)_3$), 2.95 (s, 8 H, CH_2O), 3.09 (s, 12 H, OCH_3); δ^{13}_C (75 MHz, C_6D_6) –6.55 (CH_2Li), 5.76 ($Si(CH_3)_3$), 58.80 (OCH_3), 70.18 (CH_2O); δ^{29}_{Si} (60 MHz, C_6D_6) –0.68 (s); δ^7_{Li} (117 MHz, C_6D_6) –1.92 (s).

Fig. 1 ^{1}H-DOSY-NMR-spectra of $[(DME){\cdot}(LiCH_2SiMe_3)]_2$ (**3**)
$LiCH_2SiMe_3$ $D = -9.024$ log(m^2s^{-1})
1,2-dimethoxyethane $D = -8.868$ log(m^2s^{-1})



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Single-crystal structural analysis:

The single crystals were mounted in inert oil under protective atmosphere by applying special cryo application techniques.[1] The X-ray data sets were collected at 100(2)K on an INCOATEC Microsource device[2] (**1**, **2**) or on a sealed tube (**3**) with mirror-monochromated Mo-K_α radiation (λ = 0.71073 Å). Both instruments were equipped with a Bruker Smart Apex II detector. Structures were solved by direct methods with SHELXS and refined by full-matrix least squares on F^2 for all data with SHELXL.[3] Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms in non-disordered C_α-positions were located in the difference Fourier map and refined isotropically, all other H atoms were placed in calculated positions and refined using a "riding-model".

$[(Et_2O)_2{\cdot}(LiCH_2SiMe_3)_4]$ (1):
$Li_4C_{24}H_{64}O_2Si_4$, M = 524.87, monoclinic, space group $P2_1$, a = 10.882(7), b = 19.081(13), c = 18.544(12) Å, V = 3719(4) Å^3, Z = 4, μ(Mo-K_α) = 0.175 mm^{-1}, T = 100(2) K, 146011 reflections measured, 24606 unique reflections, R_{int} = 0.0386, 767 parameters refined, R_1 (all data) = 0.0433, R_1 [I>2σ(I)] = 0.0336, wR_2 (all data) = 0.0832, wR_2[I>2σ(I)] = 0.0782, GOF = 1.045, largest diff. peak and hole 0.449 and –0.213 eÅ^{-3}.

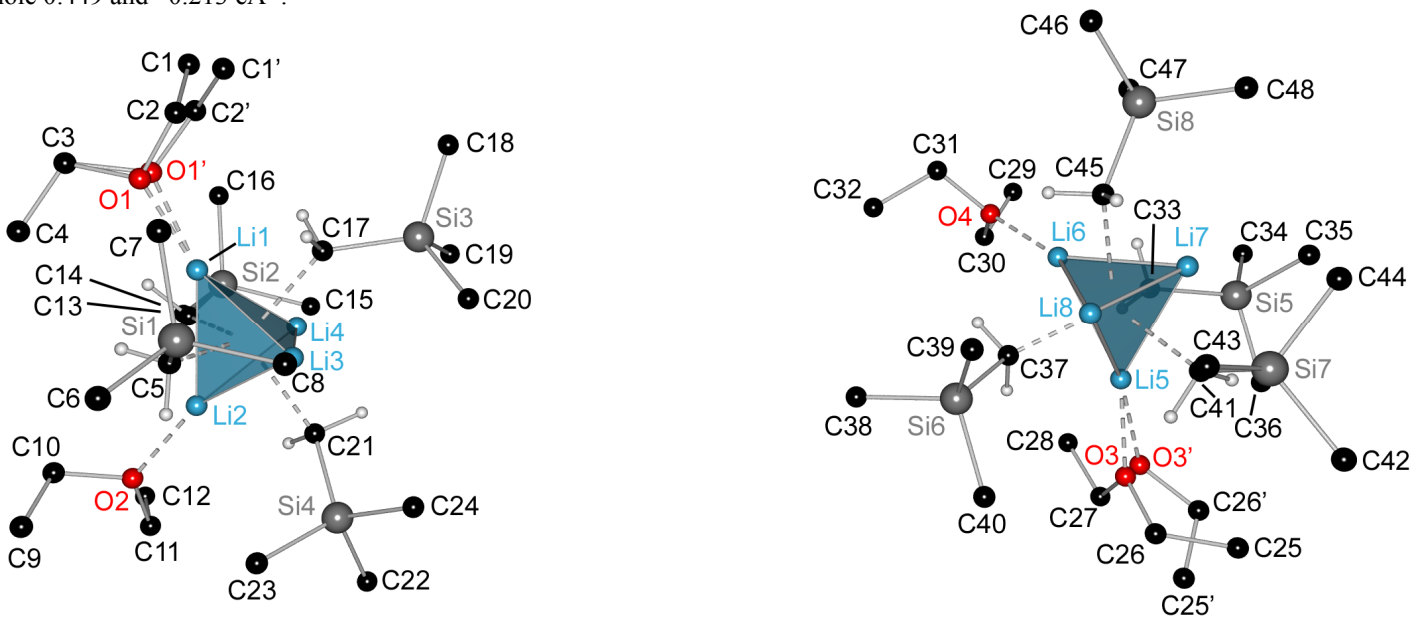

Figure 2 Molecular structure of $[(Et_2O)_2{\cdot}(LiCH_2SiMe_3)_4]$ (**1**) in the crystal (asymmetric unit) including disordered sites.

Table 1. Bond lengths [Å] and angles [°] for **1**.

Li(1)-O(1)	1.978(3)	Li(1)-Li(2)	2.672(3)
Li(1)-O(1')	2.005(8)	Li(2)-O(2)	1.953(2)
Li(1)-C(13)	2.287(3)	Li(2)-C(5)	2.266(3)
Li(1)-C(5)	2.292(3)	Li(2)-C(21)	2.291(3)
Li(1)-C(17)	2.340(3)	Li(2)-C(13)	2.298(3)
Li(1)-Li(3)	2.569(3)	Li(2)-Li(3)	2.523(3)
Li(1)-Li(4)	2.580(3)	Li(2)-Li(4)	2.559(3)

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Li(3)-C(5)	2.222(3)	Si(2)-C(15)	1.8884(18)
Li(3)-C(21)	2.244(3)	Si(3)-C(17)	1.8414(14)
Li(3)-C(17)	2.247(3)	Si(3)-C(18)	1.8831(15)
Li(3)-Li(4)	2.420(3)	Si(3)-C(20)	1.8834(16)
Li(4)-C(17)	2.203(3)	Si(3)-C(19)	1.8839(18)
Li(4)-C(13)	2.214(3)	Si(4)-C(21)	1.8493(15)
Li(4)-C(21)	2.255(3)	Si(4)-C(23)	1.8820(16)
Li(5)-O(3)	1.996(3)	Si(4)-C(24)	1.8832(18)
Li(5)-O(3')	2.019(6)	Si(4)-C(22)	1.8834(17)
Li(5)-C(37)	2.291(3)	Si(5)-C(33)	1.8407(15)
Li(5)-C(33)	2.309(3)	Si(5)-C(36)	1.8808(16)
Li(5)-C(41)	2.313(3)	Si(5)-C(34)	1.8814(18)
Li(5)-Li(8)	2.575(3)	Si(5)-C(35)	1.8952(18)
Li(5)-Li(7)	2.580(3)	Si(6)-C(37)	1.8383(15)
Li(5)-Li(6)	2.672(3)	Si(6)-C(40)	1.8635(18)
Li(6)-O(4)	1.956(2)	Si(6)-C(38)	1.8817(18)
Li(6)-C(33)	2.259(3)	Si(6)-C(39)	1.8927(18)
Li(6)-C(45)	2.296(3)	Si(7)-C(41)	1.8395(15)
Li(6)-C(37)	2.303(3)	Si(7)-C(43)	1.8793(18)
Li(6)-Li(7)	2.527(3)	Si(7)-C(44)	1.8818(16)
Li(6)-Li(8)	2.569(3)	Si(7)-C(42)	1.8880(15)
Li(7)-C(33)	2.219(3)	Si(8)-C(45)	1.8480(15)
Li(7)-C(41)	2.230(3)	Si(8)-C(47)	1.8759(16)
Li(7)-C(45)	2.254(3)	Si(8)-C(48)	1.8805(18)
Li(7)-Li(8)	2.416(3)	Si(8)-C(46)	1.8828(17)
Li(8)-C(37)	2.204(3)	C(4)-C(3)	1.502(3)
Li(8)-C(41)	2.211(3)	C(3)-O(1)	1.418(3)
Li(8)-C(45)	2.227(3)	C(3)-O(1')	1.516(8)
Si(1)-C(5)	1.8422(14)	O(1)-C(2)	1.430(2)
Si(1)-C(7)	1.8761(16)	C(2)-C(1)	1.499(3)
Si(1)-C(6)	1.8810(18)	O(1')-C(2')	1.456(9)
Si(1)-C(8)	1.8911(17)	C(2')-C(1')	1.509(10)
Si(2)-C(13)	1.8387(15)	O(4)-C(30)	1.4385(17)
Si(2)-C(16)	1.8702(17)	O(4)-C(31)	1.4401(16)
Si(2)-C(14)	1.8798(17)	C(31)-C(32)	1.507(2)

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C(30)-C(29)	1.506(2)	C(5)-Li(1)-Li(2)	53.64(7)
C(28)-C(27)	1.486(3)	C(17)-Li(1)-Li(2)	100.71(9)
C(27)-O(3)	1.470(3)	Li(3)-Li(1)-Li(2)	57.50(8)
O(3)-C(26)	1.441(3)	Li(4)-Li(1)-Li(2)	58.27(8)
C(26)-C(25)	1.529(4)	O(2)-Li(2)-C(5)	116.03(11)
O(3')-C(26')	1.417(8)	O(2)-Li(2)-C(21)	114.20(10)
C(26')-C(25')	1.439(9)	C(5)-Li(2)-C(21)	106.58(10)
C(9)-C(10)	1.502(2)	O(2)-Li(2)-C(13)	107.63(11)
C(10)-O(2)	1.4439(17)	C(5)-Li(2)-C(13)	106.41(9)
O(2)-C(11)	1.4382(16)	C(21)-Li(2)-C(13)	105.20(9)
C(11)-C(12)	1.514(2)	O(2)-Li(2)-Li(3)	152.29(11)
O(1)-Li(1)-O(1')	14.96(17)	C(5)-Li(2)-Li(3)	54.98(7)
O(1)-Li(1)-C(13)	116.36(12)	C(21)-Li(2)-Li(3)	55.32(8)
O(1')-Li(1)-C(13)	105.3(2)	C(13)-Li(2)-Li(3)	100.05(9)
O(1)-Li(1)-C(5)	114.69(12)	O(2)-Li(2)-Li(4)	142.82(11)
O(1')-Li(1)-C(5)	129.3(2)	C(5)-Li(2)-Li(4)	100.83(9)
C(13)-Li(1)-C(5)	105.90(9)	C(21)-Li(2)-Li(4)	55.08(7)
O(1)-Li(1)-C(17)	110.40(11)	C(13)-Li(2)-Li(4)	53.93(8)
O(1')-Li(1)-C(17)	105.3(2)	Li(3)-Li(2)-Li(4)	56.87(8)
C(13)-Li(1)-C(17)	103.16(10)	O(2)-Li(2)-Li(1)	141.52(11)
C(5)-Li(1)-C(17)	105.17(9)	C(5)-Li(2)-Li(1)	54.56(7)
O(1)-Li(1)-Li(3)	144.46(12)	C(21)-Li(2)-Li(1)	103.82(9)
O(1')-Li(1)-Li(3)	151.7(2)	C(13)-Li(2)-Li(1)	54.17(8)
C(13)-Li(1)-Li(3)	98.99(10)	Li(3)-Li(2)-Li(1)	59.19(7)
C(5)-Li(1)-Li(3)	54.04(7)	Li(4)-Li(2)-Li(1)	59.05(9)
C(17)-Li(1)-Li(3)	54.25(8)	C(5)-Li(3)-C(21)	109.78(10)
O(1)-Li(1)-Li(4)	145.54(13)	C(5)-Li(3)-C(17)	110.81(10)
O(1')-Li(1)-Li(4)	131.2(2)	C(21)-Li(3)-C(17)	108.97(10)
C(13)-Li(1)-Li(4)	53.72(8)	C(5)-Li(3)-Li(4)	106.57(10)
C(5)-Li(1)-Li(4)	99.49(9)	C(21)-Li(3)-Li(4)	57.68(8)
C(17)-Li(1)-Li(4)	52.94(7)	C(17)-Li(3)-Li(4)	56.19(8)
Li(3)-Li(1)-Li(4)	56.06(8)	C(5)-Li(3)-Li(2)	56.62(8)
O(1)-Li(1)-Li(2)	148.88(12)	C(21)-Li(3)-Li(2)	57.11(7)
O(1')-Li(1)-Li(2)	150.5(2)	C(17)-Li(3)-Li(2)	108.14(9)
C(13)-Li(1)-Li(2)	54.54(7)	Li(4)-Li(3)-Li(2)	62.32(9)

C(5)-Li(3)-Li(1)	56.61(8)	O(3)-Li(5)-Li(7)	149.39(13)
C(21)-Li(3)-Li(1)	108.63(10)	O(3')-Li(5)-Li(7)	140.7(2)
C(17)-Li(3)-Li(1)	57.67(7)	C(37)-Li(5)-Li(7)	98.62(10)
Li(4)-Li(3)-Li(1)	62.20(9)	C(33)-Li(5)-Li(7)	53.62(8)
Li(2)-Li(3)-Li(1)	63.32(9)	C(41)-Li(5)-Li(7)	53.88(8)
C(17)-Li(4)-C(13)	110.31(11)	Li(8)-Li(5)-Li(7)	55.89(8)
C(17)-Li(4)-C(21)	110.17(10)	O(3)-Li(5)-Li(6)	151.90(13)
C(13)-Li(4)-C(21)	109.34(9)	O(3')-Li(5)-Li(6)	147.5(2)
C(17)-Li(4)-Li(3)	57.94(8)	C(37)-Li(5)-Li(6)	54.64(7)
C(13)-Li(4)-Li(3)	105.77(11)	C(33)-Li(5)-Li(6)	53.35(8)
C(21)-Li(4)-Li(3)	57.25(8)	C(41)-Li(5)-Li(6)	101.07(10)
C(17)-Li(4)-Li(2)	108.31(10)	Li(8)-Li(5)-Li(6)	58.60(8)
C(13)-Li(4)-Li(2)	57.02(7)	Li(7)-Li(5)-Li(6)	57.47(8)
C(21)-Li(4)-Li(2)	56.43(8)	O(4)-Li(6)-C(33)	112.04(11)
Li(3)-Li(4)-Li(2)	60.82(9)	O(4)-Li(6)-C(45)	117.69(10)
C(17)-Li(4)-Li(1)	57.93(8)	C(33)-Li(6)-C(45)	106.91(11)
C(13)-Li(4)-Li(1)	56.38(8)	O(4)-Li(6)-C(37)	108.80(11)
C(21)-Li(4)-Li(1)	107.92(10)	C(33)-Li(6)-C(37)	107.24(9)
Li(3)-Li(4)-Li(1)	61.74(9)	C(45)-Li(6)-C(37)	103.40(9)
Li(2)-Li(4)-Li(1)	62.68(8)	O(4)-Li(6)-Li(7)	151.24(12)
O(3)-Li(5)-O(3')	16.37(18)	C(33)-Li(6)-Li(7)	54.89(8)
O(3)-Li(5)-C(37)	109.01(12)	C(45)-Li(6)-Li(7)	55.48(8)
O(3')-Li(5)-C(37)	120.7(2)	C(37)-Li(6)-Li(7)	99.86(9)
O(3)-Li(5)-C(33)	126.48(13)	O(4)-Li(6)-Li(8)	146.83(12)
O(3')-Li(5)-C(33)	110.3(2)	C(33)-Li(6)-Li(8)	100.64(10)
C(37)-Li(5)-C(33)	105.99(9)	C(45)-Li(6)-Li(8)	54.15(7)
O(3)-Li(5)-C(41)	105.40(12)	C(37)-Li(6)-Li(8)	53.45(8)
O(3')-Li(5)-C(41)	110.8(2)	Li(7)-Li(6)-Li(8)	56.60(8)
C(37)-Li(5)-C(41)	103.62(11)	O(4)-Li(6)-Li(5)	138.66(11)
C(33)-Li(5)-C(41)	104.11(10)	C(33)-Li(6)-Li(5)	55.06(8)
O(3)-Li(5)-Li(8)	134.24(13)	C(45)-Li(6)-Li(5)	103.44(10)
O(3')-Li(5)-Li(8)	149.8(2)	C(37)-Li(6)-Li(5)	54.23(8)
C(37)-Li(5)-Li(8)	53.48(8)	Li(7)-Li(6)-Li(5)	59.44(8)
C(33)-Li(5)-Li(8)	99.14(9)	Li(8)-Li(6)-Li(5)	58.80(9)
C(41)-Li(5)-Li(8)	53.46(7)	C(33)-Li(7)-C(41)	110.03(9)

C(33)-Li(7)-C(45)	109.82(10)	C(13)-Si(2)-C(16)	111.30(8)
C(41)-Li(7)-C(45)	109.03(10)	C(13)-Si(2)-C(14)	115.67(6)
C(33)-Li(7)-Li(8)	106.75(11)	C(16)-Si(2)-C(14)	107.52(8)
C(41)-Li(7)-Li(8)	56.66(8)	C(13)-Si(2)-C(15)	109.65(7)
C(45)-Li(7)-Li(8)	56.85(8)	C(16)-Si(2)-C(15)	106.61(9)
C(33)-Li(7)-Li(6)	56.42(8)	C(14)-Si(2)-C(15)	105.57(8)
C(41)-Li(7)-Li(6)	108.13(10)	C(17)-Si(3)-C(18)	114.83(7)
C(45)-Li(7)-Li(6)	57.06(7)	C(17)-Si(3)-C(20)	109.95(7)
Li(8)-Li(7)-Li(6)	62.59(9)	C(18)-Si(3)-C(20)	107.56(8)
C(33)-Li(7)-Li(5)	56.91(8)	C(17)-Si(3)-C(19)	112.09(7)
C(41)-Li(7)-Li(5)	56.92(8)	C(18)-Si(3)-C(19)	104.56(8)
C(45)-Li(7)-Li(5)	107.64(10)	C(20)-Si(3)-C(19)	107.44(8)
Li(8)-Li(7)-Li(5)	61.93(10)	C(21)-Si(4)-C(23)	112.35(7)
Li(6)-Li(7)-Li(5)	63.09(9)	C(21)-Si(4)-C(24)	111.22(6)
C(37)-Li(8)-C(41)	110.11(11)	C(23)-Si(4)-C(24)	105.58(6)
C(37)-Li(8)-C(45)	109.06(10)	C(21)-Si(4)-C(22)	114.30(6)
C(41)-Li(8)-C(45)	110.69(10)	C(23)-Si(4)-C(22)	106.03(8)
C(37)-Li(8)-Li(7)	106.29(11)	C(24)-Si(4)-C(22)	106.78(7)
C(41)-Li(8)-Li(7)	57.43(9)	C(33)-Si(5)-C(36)	112.26(7)
C(45)-Li(8)-Li(7)	57.90(8)	C(33)-Si(5)-C(34)	115.23(7)
C(37)-Li(8)-Li(6)	57.09(8)	C(36)-Si(5)-C(34)	106.42(9)
C(41)-Li(8)-Li(6)	107.29(11)	C(33)-Si(5)-C(35)	109.07(8)
C(45)-Li(8)-Li(6)	56.65(8)	C(36)-Si(5)-C(35)	107.45(7)
Li(7)-Li(8)-Li(6)	60.82(9)	C(34)-Si(5)-C(35)	105.97(9)
C(37)-Li(8)-Li(5)	56.67(8)	C(37)-Si(6)-C(40)	111.78(8)
C(41)-Li(8)-Li(5)	57.21(8)	C(37)-Si(6)-C(38)	114.80(7)
C(45)-Li(8)-Li(5)	108.67(10)	C(40)-Si(6)-C(38)	107.02(8)
Li(7)-Li(8)-Li(5)	62.18(9)	C(37)-Si(6)-C(39)	109.87(7)
Li(6)-Li(8)-Li(5)	62.60(8)	C(40)-Si(6)-C(39)	107.46(9)
C(5)-Si(1)-C(7)	112.51(7)	C(38)-Si(6)-C(39)	105.47(8)
C(5)-Si(1)-C(6)	115.14(7)	C(41)-Si(7)-C(43)	109.81(8)
C(7)-Si(1)-C(6)	106.13(9)	C(41)-Si(7)-C(44)	111.14(7)
C(5)-Si(1)-C(8)	109.07(8)	C(43)-Si(7)-C(44)	108.43(8)
C(7)-Si(1)-C(8)	106.84(7)	C(41)-Si(7)-C(42)	114.62(7)
C(6)-Si(1)-C(8)	106.69(9)	C(43)-Si(7)-C(42)	105.51(8)

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C(44)-Si(7)-C(42)	107.03(8)	Li(2)-C(5)-Li(1)	71.80(8)
C(45)-Si(8)-C(47)	111.85(7)	Si(5)-C(33)-Li(7)	96.81(9)
C(45)-Si(8)-C(48)	111.63(6)	Si(5)-C(33)-Li(6)	162.63(9)
C(47)-Si(8)-C(48)	105.99(7)	Li(7)-C(33)-Li(6)	68.69(9)
C(45)-Si(8)-C(46)	114.84(6)	Si(5)-C(33)-Li(5)	113.29(8)
C(47)-Si(8)-C(46)	106.18(8)	Li(7)-C(33)-Li(5)	69.46(8)
C(48)-Si(8)-C(46)	105.75(7)	Li(6)-C(33)-Li(5)	71.59(8)
O(1)-C(3)-C(4)	107.74(15)	Si(3)-C(17)-Li(4)	108.76(9)
O(1)-C(3)-O(1')	20.0(2)	Si(3)-C(17)-Li(3)	112.55(8)
C(4)-C(3)-O(1')	117.1(3)	Li(4)-C(17)-Li(3)	65.87(8)
C(3)-O(1)-C(2)	110.98(17)	Si(3)-C(17)-Li(1)	177.47(9)
C(3)-O(1)-Li(1)	126.68(15)	Li(4)-C(17)-Li(1)	69.13(9)
C(2)-O(1)-Li(1)	121.47(15)	Li(3)-C(17)-Li(1)	68.09(8)
O(1)-C(2)-C(1)	113.14(18)	Si(7)-C(41)-Li(8)	110.31(10)
C(2')-O(1')-C(3)	118.6(6)	Si(7)-C(41)-Li(7)	113.93(8)
C(2')-O(1')-Li(1)	122.3(5)	Li(8)-C(41)-Li(7)	65.92(8)
C(3)-O(1')-Li(1)	119.1(4)	Si(7)-C(41)-Li(5)	176.56(9)
O(1')-C(2')-C(1')	115.0(6)	Li(8)-C(41)-Li(5)	69.34(10)
Si(2)-C(13)-Li(4)	88.69(8)	Li(7)-C(41)-Li(5)	69.19(8)
Si(2)-C(13)-Li(1)	128.23(8)	Si(6)-C(37)-Li(8)	90.24(8)
Li(4)-C(13)-Li(1)	69.90(10)	Si(6)-C(37)-Li(5)	128.14(9)
Si(2)-C(13)-Li(2)	144.07(9)	Li(8)-C(37)-Li(5)	69.85(10)
Li(4)-C(13)-Li(2)	69.05(8)	Si(6)-C(37)-Li(6)	146.16(9)
Li(1)-C(13)-Li(2)	71.29(8)	Li(8)-C(37)-Li(6)	69.46(8)
Si(4)-C(21)-Li(3)	104.71(8)	Li(5)-C(37)-Li(6)	71.13(8)
Si(4)-C(21)-Li(4)	168.33(8)	C(30)-O(4)-C(31)	114.17(10)
Li(3)-C(21)-Li(4)	65.07(8)	C(30)-O(4)-Li(6)	118.40(10)
Si(4)-C(21)-Li(2)	113.94(8)	C(31)-O(4)-Li(6)	126.12(10)
Li(3)-C(21)-Li(2)	67.58(9)	O(4)-C(31)-C(32)	112.83(11)
Li(4)-C(21)-Li(2)	68.49(8)	O(4)-C(30)-C(29)	112.11(11)
Si(1)-C(5)-Li(3)	96.37(9)	Si(8)-C(45)-Li(8)	165.43(9)
Si(1)-C(5)-Li(2)	161.24(9)	Si(8)-C(45)-Li(7)	102.84(8)
Li(3)-C(5)-Li(2)	68.40(9)	Li(8)-C(45)-Li(7)	65.24(8)
Si(1)-C(5)-Li(1)	114.15(7)	Si(8)-C(45)-Li(6)	115.26(8)
Li(3)-C(5)-Li(1)	69.36(8)	Li(8)-C(45)-Li(6)	69.20(8)

The first asymmetric organolithium tetramers with simple ether donor bases

Tanja Tatic[a], Kathrin Meindl[a], Julian Henn[a], Sushil Kumar Pandey[b], and Dietmar Stalke[*a]

Li(7)-C(45)-Li(6)	67.47(9)	O(3')-C(26')-C(25')	116.8(7)
O(3)-C(27)-C(28)	112.47(15)	O(2)-C(10)-C(9)	112.07(11)
C(26)-O(3)-C(27)	114.16(17)	C(11)-O(2)-C(10)	114.84(10)
C(26)-O(3)-Li(5)	121.79(16)	C(11)-O(2)-Li(2)	127.25(10)
C(27)-O(3)-Li(5)	124.05(16)	C(10)-O(2)-Li(2)	116.51(10)
O(3)-C(26)-C(25)	112.92(18)	O(2)-C(11)-C(12)	112.66(11)
C(26')-O(3')-Li(5)	122.3(5)		

The first asymmetric organolithium tetramers with simple ether donor bases

Tanja Tatic[a], Kathrin Meindl[a], Julian Henn[a], Sushil Kumar Pandey[b], and Dietmar Stalke[*a]

Supplementary Material

[(^{t}BuOMe)$_2$·(LiCH$_2$SiMe$_3$)$_4$] (2):
$Li_4C_{26}H_{68}O_2Si_4$, M = 552.92, orthorhombic, space group $Pna2_1$, a = 21.569(3), b = 10.6442(14), c = 17.116(2) Å, V = 3929.6(9) Å^3, Z = 4, μ(Mo-K$_\alpha$) = 0.169 mm^{-1}, T = 100(2) K, 38585 reflections measured, 7279 unique reflections, R_{int} = 0.0549, 566 parameters refined, R_1 (all data) = 0.0725, R_1 [I>2σ(I)] = 0.0588, wR_2 (all data) = 0.1619, wR_2[I>2σ(I)] = 0.1520, GOF = 1.079, largest diff. peak and hole 0.594 and –0.225 eÅ^{-3}.

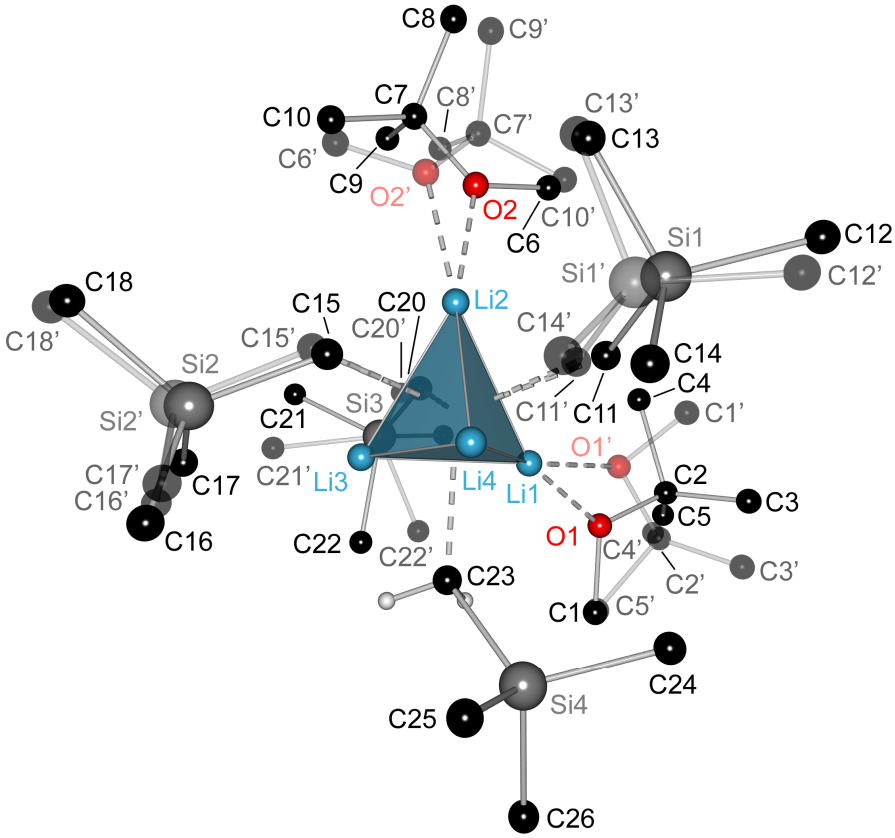

Figure 3 Molecular structure of [(^{t}BuOMe)$_2$·(LiCH$_2$SiMe$_3$)$_4$] (**2**) in the crystal (asymmetric unit) including disordered sites.

Table 2. Bond lengths [Å] and angles [°] for **2**.

Li(1)-O(1)	200.1(8)	Li(2)-C(11')	207.2(16)
Li(1)-O(1')	221.0(18)	Li(2)-C(19)	229.3(8)
Li(1)-C(11')	226.8(14)	Li(2)-C(15')	231.8(15)
Li(1)-C(19)	234.2(9)	Li(2)-C(11)	234.5(12)
Li(1)-C(23)	238.1(9)	Li(2)-C(15)	245.5(8)
Li(1)-C(11)	239.3(11)	Li(2)-Li(4)	254.9(9)
Li(1)-Li(3)	255.8(10)	Li(2)-Li(3)	262.3(9)
Li(1)-Li(4)	257.1(10)	Li(3)-C(15')	203.2(18)
Li(1)-Li(2)	271.3(9)	Li(3)-C(19)	215.8(8)
Li(2)-O(2)	202.7(7)	Li(3)-C(23)	220.4(7)
Li(2)-O(2')	205.2(15)	Li(3)-C(15)	227.4(8)

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Supplementary Material

Li(3)-Li(4)	237.6(9)	Si(1')-C(12')	185.3(11)
Li(3)-Si(2')	296.8(15)	Si(1')-C(13')	186.0(11)
Li(4)-C(11')	190.9(16)	Si(1')-C(14')	190.1(11)
Li(4)-C(15)	213.3(8)	C(15)-Si(2)	181.30
Li(4)-C(23)	218.7(8)	Si(2)-C(16)	182.8(8)
Li(4)-C(11)	230.7(11)	Si(2)-C(18)	188.59
Li(4)-C(15')	246.5(19)	Si(2)-C(17)	191.2(7)
Li(4)-C(14')	268.4(15)	C(15')-Si(2')	188.0(11)
O(1)-C(1)	142.5(9)	Si(2')-C(16')	186.8(12)
O(1)-C(2)	146.3(7)	Si(2')-C(18')	187.3(12)
C(2)-C(4)	145.1(8)	Si(2')-C(17')	190.5(12)
C(2)-C(3)	146.1(9)	C(19)-Si(3)	185.7(4)
C(2)-C(5)	166.3(10)	Si(3)-C(21)	183.8(7)
O(1')-C(1')	145.2(13)	Si(3)-C(22')	186.4(12)
O(1')-C(2')	147.8(11)	Si(3)-C(20)	186.9(7)
C(2')-C(4')	146.0(13)	Si(3)-C(21')	188.2(12)
C(2')-C(3')	146.4(13)	Si(3)-C(22)	188.7(6)
C(2')-C(5')	166.0(14)	Si(3)-C(20')	189.0(12)
O(2)-C(6)	140.8(12)	O(1)-Li(1)-O(1')	29.1(4)
O(2)-C(7)	145.7(6)	O(1)-Li(1)-C(11')	128.6(5)
C(7)-C(9)	152.2(8)	O(1')-Li(1)-C(11')	111.9(6)
C(7)-C(8)	152.7(9)	O(1)-Li(1)-C(19)	116.6(4)
C(7)-C(10)	153.4(11)	O(1')-Li(1)-C(19)	103.8(6)
O(2')-C(6')	141(2)	C(11')-Li(1)-C(19)	101.3(5)
O(2')-C(7')	146.5(16)	O(1)-Li(1)-C(23)	107.5(4)
C(7')-C(9')	152.7(19)	O(1')-Li(1)-C(23)	136.5(6)
C(7')-C(8')	154.0(18)	C(11')-Li(1)-C(23)	96.0(5)
C(7')-C(10')	154(2)	C(19)-Li(1)-C(23)	102.5(3)
C(23)-Si(4)	187.3(4)	O(1)-Li(1)-C(11)	118.9(4)
Si(4)-C(25)	186.7(5)	O(1')-Li(1)-C(11)	101.9(5)
Si(4)-C(24)	188.1(4)	C(11')-Li(1)-C(11)	10.2(4)
Si(4)-C(26)	188.1(4)	C(19)-Li(1)-C(11)	105.9(4)
C(11)-Si(1)	188.5(8)	C(23)-Li(1)-C(11)	103.5(4)
Si(1)-C(13)	186.0(9)	O(1)-Li(1)-Li(3)	139.7(4)
Si(1)-C(12)	187.1(8)	O(1')-Li(1)-Li(3)	150.9(6)
Si(1)-C(14)	188.3(8)	C(11')-Li(1)-Li(3)	90.8(5)
C(11')-Si(1')	196.2(11)	C(19)-Li(1)-Li(3)	52.0(2)

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C(23)-Li(1)-Li(3)	52.8(2)	C(11)-Li(2)-C(15)	102.6(3)
C(11)-Li(1)-Li(3)	100.8(4)	O(2)-Li(2)-Li(4)	157.6(4)
O(1)-Li(1)-Li(4)	145.9(4)	O(2')-Li(2)-Li(4)	150.3(5)
O(1')-Li(1)-Li(4)	153.6(6)	C(11')-Li(2)-Li(4)	47.4(5)
C(11')-Li(1)-Li(4)	46.0(4)	C(19)-Li(2)-Li(4)	97.9(3)
C(19)-Li(1)-Li(4)	96.0(3)	C(15')-Li(2)-Li(4)	60.6(5)
C(23)-Li(1)-Li(4)	52.2(2)	C(11)-Li(2)-Li(4)	56.1(3)
C(11)-Li(1)-Li(4)	55.3(3)	C(15)-Li(2)-Li(4)	50.4(2)
Li(3)-Li(1)-Li(4)	55.2(2)	O(2)-Li(2)-Li(3)	147.3(4)
O(1)-Li(1)-Li(2)	151.8(4)	O(2')-Li(2)-Li(3)	133.9(5)
O(1')-Li(1)-Li(2)	122.9(5)	C(11')-Li(2)-Li(3)	93.6(5)
C(11')-Li(1)-Li(2)	48.1(4)	C(19)-Li(2)-Li(3)	51.5(2)
C(19)-Li(1)-Li(2)	53.3(2)	C(15')-Li(2)-Li(3)	48.1(5)
C(23)-Li(1)-Li(2)	100.6(3)	C(11)-Li(2)-Li(3)	100.3(4)
C(11)-Li(1)-Li(2)	54.2(3)	C(15)-Li(2)-Li(3)	53.1(2)
Li(3)-Li(1)-Li(2)	59.6(2)	Li(4)-Li(2)-Li(3)	54.7(2)
Li(4)-Li(1)-Li(2)	57.6(2)	O(2)-Li(2)-Li(1)	129.8(4)
O(2)-Li(2)-O(2')	23.6(4)	O(2')-Li(2)-Li(1)	150.8(6)
O(2)-Li(2)-C(11')	116.3(5)	C(11')-Li(2)-Li(1)	54.6(4)
O(2')-Li(2)-C(11')	132.0(6)	C(19)-Li(2)-Li(1)	55.0(2)
O(2)-Li(2)-C(19)	103.0(3)	C(15')-Li(2)-Li(1)	101.1(5)
O(2')-Li(2)-C(19)	107.3(5)	C(11)-Li(2)-Li(1)	55.9(3)
C(11')-Li(2)-C(19)	109.4(5)	C(15)-Li(2)-Li(1)	99.0(3)
O(2)-Li(2)-C(15')	126.1(6)	Li(4)-Li(2)-Li(1)	58.4(3)
O(2')-Li(2)-C(15')	102.5(7)	Li(3)-Li(2)-Li(1)	57.3(3)
C(11')-Li(2)-C(15')	106.5(7)	C(15')-Li(3)-C(19)	103.8(6)
C(19)-Li(2)-C(15')	91.3(5)	C(15')-Li(3)-C(23)	118.5(7)
O(2)-Li(2)-C(11)	108.5(4)	C(19)-Li(3)-C(23)	115.3(4)
O(2')-Li(2)-C(11)	125.8(6)	C(15')-Li(3)-C(15)	14.2(6)
C(11')-Li(2)-C(11)	8.7(5)	C(19)-Li(3)-C(15)	111.9(3)
C(19)-Li(2)-C(11)	109.2(4)	C(23)-Li(3)-C(15)	104.3(3)
C(15')-Li(2)-C(11)	115.2(6)	C(15')-Li(3)-Li(4)	67.5(6)
O(2)-Li(2)-C(15)	130.9(4)	C(19)-Li(3)-Li(4)	107.3(3)
O(2')-Li(2)-C(15)	107.9(5)	C(23)-Li(3)-Li(4)	56.9(3)
C(11')-Li(2)-C(15)	94.2(5)	C(15)-Li(3)-Li(4)	54.5(3)
C(19)-Li(2)-C(15)	101.3(3)	C(15')-Li(3)-Li(1)	115.5(5)
C(15')-Li(2)-C(15)	13.7(5)	C(19)-Li(3)-Li(1)	58.8(3)

C(23)-Li(3)-Li(1)	59.5(3)	C(11')-Li(4)-Li(1)	58.6(4)
C(15)-Li(3)-Li(1)	108.8(3)	C(15)-Li(4)-Li(1)	113.1(4)
Li(4)-Li(3)-Li(1)	62.7(3)	C(23)-Li(4)-Li(1)	59.4(3)
C(15')-Li(3)-Li(2)	58.1(4)	C(11)-Li(4)-Li(1)	58.5(3)
C(19)-Li(3)-Li(2)	56.3(2)	Li(3)-Li(4)-Li(1)	62.1(3)
C(23)-Li(3)-Li(2)	108.5(3)	C(15')-Li(4)-Li(1)	101.2(5)
C(15)-Li(3)-Li(2)	59.7(2)	Li(2)-Li(4)-Li(1)	64.0(3)
Li(4)-Li(3)-Li(2)	61.1(3)	C(11')-Li(4)-C(14')	82.4(5)
Li(1)-Li(3)-Li(2)	63.1(3)	C(15)-Li(4)-C(14')	95.4(5)
C(15')-Li(3)-Si(2')	38.8(4)	C(23)-Li(4)-C(14')	139.8(4)
C(19)-Li(3)-Si(2')	131.1(4)	C(11)-Li(4)-C(14')	81.3(5)
C(23)-Li(3)-Si(2')	111.8(4)	Li(3)-Li(4)-C(14')	155.6(6)
C(15)-Li(3)-Si(2')	41.6(4)	C(15')-Li(4)-C(14')	106.4(7)
Li(4)-Li(3)-Si(2')	87.4(4)	Li(2)-Li(4)-C(14')	107.5(4)
Li(1)-Li(3)-Si(2')	149.1(4)	Li(1)-Li(4)-C(14')	137.3(5)
Li(2)-Li(3)-Si(2')	96.8(3)	C(1)-O(1)-C(2)	111.1(6)
C(11')-Li(4)-C(15)	110.6(6)	C(1)-O(1)-Li(1)	121.4(5)
C(11')-Li(4)-C(23)	114.9(5)	C(2)-O(1)-Li(1)	126.2(4)
C(15)-Li(4)-C(23)	109.9(3)	C(4)-C(2)-C(3)	114.4(6)
C(11')-Li(4)-C(11)	4.6(6)	C(4)-C(2)-O(1)	112.8(6)
C(15)-Li(4)-C(11)	115.1(4)	C(3)-C(2)-O(1)	114.9(5)
C(23)-Li(4)-C(11)	113.0(4)	C(4)-C(2)-C(5)	109.3(5)
C(11')-Li(4)-Li(3)	106.4(5)	C(3)-C(2)-C(5)	103.5(6)
C(15)-Li(4)-Li(3)	60.3(3)	O(1)-C(2)-C(5)	100.4(4)
C(23)-Li(4)-Li(3)	57.6(2)	C(1')-O(1')-C(2')	103.4(12)
C(11)-Li(4)-Li(3)	109.2(4)	C(1')-O(1')-Li(1)	105.7(15)
C(11')-Li(4)-C(15')	106.5(6)	C(2')-O(1')-Li(1)	124.1(12)
C(15)-Li(4)-C(15')	12.0(4)	C(4')-C(2')-C(3')	112.8(13)
C(23)-Li(4)-C(15')	102.9(5)	C(4')-C(2')-O(1')	109.1(13)
C(11)-Li(4)-C(15')	111.1(5)	C(3')-C(2')-O(1')	120.7(13)
Li(3)-Li(4)-C(15')	49.6(5)	C(4')-C(2')-C(5')	108.9(14)
C(11')-Li(4)-Li(2)	53.0(5)	C(3')-C(2')-C(5')	104.1(14)
C(15)-Li(4)-Li(2)	62.5(3)	O(1')-C(2')-C(5')	99.7(12)
C(23)-Li(4)-Li(2)	111.7(3)	C(6)-O(2)-C(7)	114.0(6)
C(11)-Li(4)-Li(2)	57.5(3)	C(6)-O(2)-Li(2)	114.2(5)
Li(3)-Li(4)-Li(2)	64.2(3)	C(7)-O(2)-Li(2)	129.7(4)
C(15')-Li(4)-Li(2)	55.1(4)	O(2)-C(7)-C(9)	111.1(5)

O(2)-C(7)-C(8)	111.8(5)	C(14)-Si(1)-C(11)	109.2(4)
C(9)-C(7)-C(8)	111.0(6)	Li(4)-C(11')-Si(1')	95.5(6)
O(2)-C(7)-C(10)	104.1(5)	Li(4)-C(11')-Li(2)	79.5(6)
C(9)-C(7)-C(10)	109.7(6)	Si(1')-C(11')-Li(2)	112.7(7)
C(8)-C(7)-C(10)	109.0(6)	Li(4)-C(11')-Li(1)	75.4(5)
C(6')-O(2')-C(7')	108.6(17)	Si(1')-C(11')-Li(1)	165.5(9)
C(6')-O(2')-Li(2)	120.9(18)	Li(2)-C(11')-Li(1)	77.2(5)
C(7')-O(2')-Li(2)	123.0(13)	C(12')-Si(1')-C(13')	108.8(10)
O(2')-C(7')-C(9')	109.8(17)	C(12')-Si(1')-C(14')	108.0(9)
O(2')-C(7')-C(8')	112.5(14)	C(13')-Si(1')-C(14')	104.4(10)
C(9')-C(7')-C(8')	109.3(17)	C(12')-Si(1')-C(11')	119.3(8)
O(2')-C(7')-C(10')	103(2)	C(13')-Si(1')-C(11')	109.4(10)
C(9')-C(7')-C(10')	109(2)	C(14')-Si(1')-C(11')	105.8(6)
C(8')-C(7')-C(10')	113(2)	Si(1')-C(14')-Li(4)	75.2(5)
Si(4)-C(23)-Li(4)	99.4(3)	Si(2)-C(15)-Li(4)	127.1(2)
Si(4)-C(23)-Li(3)	161.5(3)	Si(2)-C(15)-Li(3)	87.9(2)
Li(4)-C(23)-Li(3)	65.5(3)	Li(4)-C(15)-Li(3)	65.2(3)
Si(4)-C(23)-Li(1)	118.2(3)	Si(2)-C(15)-Li(2)	143.7(2)
Li(4)-C(23)-Li(1)	68.3(3)	Li(4)-C(15)-Li(2)	67.1(3)
Li(3)-C(23)-Li(1)	67.7(3)	Li(3)-C(15)-Li(2)	67.3(3)
C(25)-Si(4)-C(23)	108.6(2)	C(15)-Si(2)-C(16)	112.6(4)
C(25)-Si(4)-C(24)	107.5(2)	C(15)-Si(2)-C(18)	116.4
C(23)-Si(4)-C(24)	112.1(2)	C(16)-Si(2)-C(18)	106.6(4)
C(25)-Si(4)-C(26)	108.1(2)	C(15)-Si(2)-C(17)	108.7(3)
C(23)-Si(4)-C(26)	115.7(2)	C(16)-Si(2)-C(17)	107.4(5)
C(24)-Si(4)-C(26)	104.5(2)	C(18)-Si(2)-C(17)	104.6(3)
Si(1)-C(11)-Li(4)	97.3(4)	Si(2')-C(15')-Li(3)	98.6(8)
Si(1)-C(11)-Li(2)	111.2(4)	Si(2')-C(15')-Li(2)	171.1(12)
Li(4)-C(11)-Li(2)	66.4(3)	Li(3)-C(15')-Li(2)	73.8(5)
Si(1)-C(11)-Li(1)	162.1(5)	Si(2')-C(15')-Li(4)	117.0(10)
Li(4)-C(11)-Li(1)	66.3(3)	Li(3)-C(15')-Li(4)	62.9(5)
Li(2)-C(11)-Li(1)	69.8(3)	Li(2)-C(15')-Li(4)	64.3(4)
C(13)-Si(1)-C(12)	106.3(7)	C(16')-Si(2')-C(18')	107.5(10)
C(13)-Si(1)-C(14)	107.0(7)	C(16')-Si(2')-C(15')	109.3(10)
C(12)-Si(1)-C(14)	108.5(6)	C(18')-Si(2')-C(15')	117.2(8)
C(13)-Si(1)-C(11)	110.3(6)	C(16')-Si(2')-C(17')	106.3(9)
C(12)-Si(1)-C(11)	115.2(6)	C(18')-Si(2')-C(17')	107.2(10)

C(15')-Si(2')-C(17')	108.8(9)	C(21)-Si(3)-C(21')	37.3(10)
C(16')-Si(2')-Li(3)	108.6(9)	C(19)-Si(3)-C(21')	114.0(9)
C(18')-Si(2')-Li(3)	143.4(7)	C(22')-Si(3)-C(21')	105.9(10)
C(15')-Si(2')-Li(3)	42.6(6)	C(20)-Si(3)-C(21')	130.5(9)
C(17')-Si(2')-Li(3)	68.3(7)	C(21)-Si(3)-C(22)	108.0(5)
Si(3)-C(19)-Li(3)	105.4(3)	C(19)-Si(3)-C(22)	112.0(3)
Si(3)-C(19)-Li(2)	169.5(3)	C(22')-Si(3)-C(22)	35.0(10)
Li(3)-C(19)-Li(2)	72.2(3)	C(20)-Si(3)-C(22)	102.1(4)
Si(3)-C(19)-Li(1)	117.5(3)	C(21')-Si(3)-C(22)	74.2(11)
Li(3)-C(19)-Li(1)	69.2(3)	C(21)-Si(3)-C(20')	72.7(11)
Li(2)-C(19)-Li(1)	71.6(3)	C(19)-Si(3)-C(20')	117.0(8)
C(21)-Si(3)-C(19)	113.7(4)	C(22')-Si(3)-C(20')	102.8(9)
C(21)-Si(3)-C(22')	131.3(9)	C(20)-Si(3)-C(20')	37.0(10)
C(19)-Si(3)-C(22')	111.1(8)	C(21')-Si(3)-C(20')	104.9(9)
C(21)-Si(3)-C(20)	107.4(5)	C(22)-Si(3)-C(20')	125.5(10)
C(19)-Si(3)-C(20)	112.9(3)		
C(22')-Si(3)-C(20)	70.4(11)		

The first asymmetric organolithium tetramers with simple ether donor bases

Tanja Tatic[a], Kathrin Meindl[a], Julian Henn[a], Sushil Kumar Pandey[b], and Dietmar Stalke[*a]

Supplementary Material

[(DME)·(LiCH$_2$SiMe$_3$)]$_2$ (3):
$Li_4C_{16}H_{42}O_4Si_2$, M = 368.56, monoclinic, space group $P2_1/c$, a = 10.4667(8), b = 18.33838(13), c = 19.22670(14) Å, β = 92.8900°(10), V = 3702.6(5) Å^3, Z = 6, μ(Mo-K$_\alpha$) = 0.156 mm^{-1}, T = 100(2) K, 65904 reflections measured, 7276 unique reflections, R_{int} = 0.0239, 358 parameters refined, R_1 (all data) = 0.0324, R_1 [I>2σ(I)] = 0.0287, wR_2 (all data) = 0.0778, wR_2[I>2σ(I)] = 0.0755, GOF = 1.029, largest diff. peak and hole 0.344 and –0.169 eÅ^{-3}.

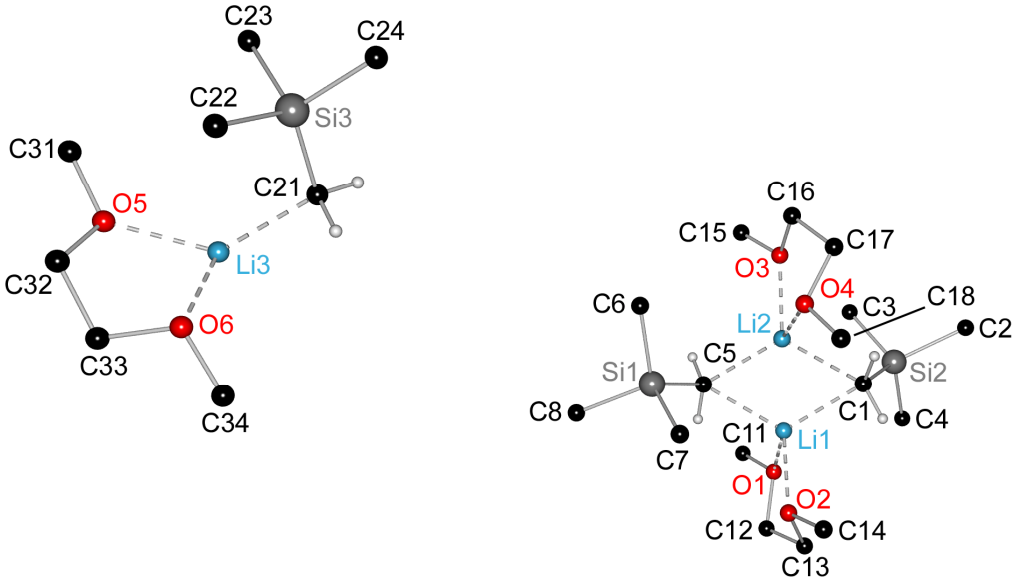

Figure 4 Molecular structure of [(DME)·(LiCH$_2$SiMe$_3$)]$_2$ (**3**) in the crystal (asymmetric unit).

Table 3. Bond lengths [Å] and angles [°] for **3**.

Si(1)-C(1)	1.8268(11)	O(2)-Li(1)	2.041(2)
Si(1)-C(3)	1.8825(12)	O(3)-C(16)	1.4255(14)
Si(1)-C(4)	1.8856(12)	O(3)-C(15)	1.4258(14)
Si(1)-C(2)	1.8908(12)	O(3)-Li(2)	1.9944(19)
Si(2)-C(5)	1.8215(11)	O(4)-C(18)	1.4264(14)
Si(2)-C(6)	1.8819(12)	O(4)-C(17)	1.4265(13)
Si(2)-C(7)	1.8844(12)	O(4)-Li(2)	2.128(2)
Si(2)-C(8)	1.8941(12)	O(5)-C(31)	1.4236(14)
Si(3)-C(21)	1.8202(11)	O(5)-C(32)	1.4293(14)
Si(3)-C(22)	1.8837(11)	O(5)-Li(3)	2.0726(19)
Si(3)-C(23)	1.8870(12)	O(6)-C(34)	1.4275(15)
Si(3)-C(24)	1.8960(11)	O(6)-C(33)	1.4279(14)
O(1)-C(11)	1.4175(15)	O(6)-Li(3)	2.034(2)
O(1)-C(12)	1.4261(14)	Li(1)-C(1)	2.196(2)
O(1)-Li(1)	2.0374(19)	Li(1)-C(5)	2.226(2)
O(2)-C(13)	1.4209(13)	Li(1)-C(13)	2.781(2)
O(2)-C(14)	1.4296(14)	Li(2)-C(5)	2.213(2)

Li(2)-C(1)	2.261(2)	C(17)-O(4)-Li(2)	103.38(8)
Li(3)-C(21)	2.180(2)	C(31)-O(5)-C(32)	112.45(9)
Li(3)-C(21)#1	2.256(2)	C(31)-O(5)-Li(3)	128.23(9)
Li(3)-Li(3)#1	2.461(3)	C(32)-O(5)-Li(3)	110.80(8)
C(12)-C(13)	1.4927(17)	C(34)-O(6)-C(33)	112.16(9)
C(16)-C(17)	1.4932(17)	C(34)-O(6)-Li(3)	121.31(9)
C(21)-Li(3)#1	2.256(2)	C(33)-O(6)-Li(3)	108.02(8)
C(32)-C(33)	1.4940(17)	O(1)-Li(1)-O(2)	82.37(7)
C(1)-Si(1)-C(3)	111.56(5)	O(1)-Li(1)-C(1)	120.54(9)
C(1)-Si(1)-C(4)	111.69(5)	O(2)-Li(1)-C(1)	110.87(9)
C(3)-Si(1)-C(4)	106.81(6)	O(1)-Li(1)-C(5)	109.18(9)
C(1)-Si(1)-C(2)	116.25(5)	O(2)-Li(1)-C(5)	114.30(9)
C(3)-Si(1)-C(2)	104.41(6)	C(1)-Li(1)-C(5)	115.40(9)
C(4)-Si(1)-C(2)	105.41(6)	O(1)-Li(1)-C(13)	55.55(5)
C(5)-Si(2)-C(6)	111.11(5)	O(2)-Li(1)-C(13)	29.50(4)
C(5)-Si(2)-C(7)	110.08(5)	C(1)-Li(1)-C(13)	111.52(8)
C(6)-Si(2)-C(7)	108.22(6)	C(5)-Li(1)-C(13)	130.47(9)
C(5)-Si(2)-C(8)	117.89(5)	O(3)-Li(2)-O(4)	80.82(7)
C(6)-Si(2)-C(8)	105.46(6)	O(3)-Li(2)-C(5)	114.37(9)
C(7)-Si(2)-C(8)	103.47(6)	O(4)-Li(2)-C(5)	125.98(9)
C(21)-Si(3)-C(22)	111.51(5)	O(3)-Li(2)-C(1)	115.19(9)
C(21)-Si(3)-C(23)	110.90(5)	O(4)-Li(2)-C(1)	103.45(8)
C(22)-Si(3)-C(23)	107.94(5)	C(5)-Li(2)-C(1)	113.33(9)
C(21)-Si(3)-C(24)	116.20(5)	O(6)-Li(3)-O(5)	80.78(7)
C(22)-Si(3)-C(24)	105.18(5)	O(6)-Li(3)-C(21)	113.13(9)
C(23)-Si(3)-C(24)	104.52(5)	O(5)-Li(3)-C(21)	130.23(9)
C(11)-O(1)-C(12)	112.60(10)	O(6)-Li(3)-C(21)#1	111.83(9)
C(11)-O(1)-Li(1)	124.64(9)	O(5)-Li(3)-C(21)#1	104.13(8)
C(12)-O(1)-Li(1)	108.93(8)	C(21)-Li(3)-C(21)#1	112.61(8)
C(13)-O(2)-C(14)	111.90(9)	O(6)-Li(3)-Li(3)#1	133.52(13)
C(13)-O(2)-Li(1)	105.49(8)	O(5)-Li(3)-Li(3)#1	142.72(13)
C(14)-O(2)-Li(1)	121.24(9)	C(21)-Li(3)-Li(3)#1	57.78(8)
C(16)-O(3)-C(15)	112.32(9)	C(21)#1-Li(3)-Li(3)#1	54.83(7)
C(16)-O(3)-Li(2)	113.32(8)	Si(1)-C(1)-Li(1)	114.29(7)
C(15)-O(3)-Li(2)	124.20(9)	Si(1)-C(1)-Li(2)	119.74(7)
C(18)-O(4)-C(17)	111.23(9)	Li(1)-C(1)-Li(2)	65.13(7)
C(18)-O(4)-Li(2)	123.55(8)	Si(2)-C(5)-Li(2)	106.29(7)

Si(2)-C(5)-Li(1)	131.61(8)
Li(2)-C(5)-Li(1)	65.43(7)
O(1)-C(12)-C(13)	106.55(9)
O(2)-C(13)-C(12)	107.09(9)
O(2)-C(13)-Li(1)	45.01(6)
C(12)-C(13)-Li(1)	76.83(7)
O(3)-C(16)-C(17)	107.87(9)
O(4)-C(17)-C(16)	107.59(9)
Si(3)-C(21)-Li(3)	109.16(7)
Si(3)-C(21)-Li(3)#1	148.04(8)
Li(3)-C(21)-Li(3)#1	67.39(8)
O(5)-C(32)-C(33)	107.54(9)
O(6)-C(33)-C(32)	107.51(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

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Supplementary Material

Final Energy: **1**: -2292.2441095 a.u.
2: -2370.880678 a.u.
3: -1530.29689 a.u.

Final Geometry **1**:

Li1	1.209606	0.287585	0.984151
Li2	-1.299998	0.760385	0.192880
Li3	-0.270047	-1.496710	-0.070253
Li4	0.534726	0.226287	-1.458171
Si5	-0.482805	-2.238699	2.823078
Si6	1.271452	3.117808	-1.718630
Si7	2.481801	-2.231287	-2.116214
Si8	-3.053392	-1.625338	-1.826470
C9	1.439262	2.312818	3.631351
H10	0.811101	2.620754	2.793181
H11	1.534159	3.167688	4.306909
H12	0.936346	1.507454	4.170336
C13	2.817698	1.884270	3.167399
H14	3.431797	1.595421	4.029427
H15	3.325600	2.710158	2.657631
O16	2.728338	0.757208	2.280012
C17	3.958041	0.012274	2.175981
H18	3.701353	-0.884992	1.614265
H19	4.256764	-0.297883	3.184815
C20	5.081560	0.767577	1.480721
H21	4.774264	1.103352	0.487793
H22	5.942761	0.104419	1.359330
H23	5.415748	1.637407	2.051133
C24	0.566476	2.098681	-0.316640
C25	1.060149	4.997197	-1.502414
H26	0.003520	5.281465	-1.449848
H27	1.506432	5.561695	-2.328743
H28	1.530956	5.345816	-0.576951
C29	0.443783	2.683130	-3.379817
H30	0.633203	1.655055	-3.711207
H31	0.808087	3.333899	-4.181899
H32	-0.643787	2.806411	-3.337031
C33	3.135100	2.795235	-1.909790
H34	3.687980	3.120196	-1.021740
H35	3.550945	3.339665	-2.763893
H36	3.363566	1.735213	-2.062074
C37	-1.553509	-0.517131	-1.652836
C38	-2.549479	-3.428345	-2.147266
H39	-1.963831	-3.521086	-3.067747
H40	-3.433423	-4.064063	-2.265723
H41	-1.953321	-3.863646	-1.339220
C42	-4.138377	-1.602429	-0.263624
H43	-3.603609	-1.970722	0.617488
H44	-5.025186	-2.232517	-0.390286
H45	-4.492279	-0.594532	-0.024004
C46	-4.192801	-1.126731	-3.268969
H47	-4.580990	-0.109064	-3.147355
H48	-5.057969	-1.792815	-3.362392
H49	-3.658439	-1.150778	-4.224547
C50	-0.664910	-0.613464	1.918220
C51	1.245023	-2.430681	3.587192
H52	2.035764	-2.427384	2.831078
H53	1.327651	-3.374700	4.135924
H54	1.466514	-1.624966	4.294734
C55	-0.722569	-3.705443	1.624847
H56	-1.712562	-3.704122	1.156476
H57	-0.636531	-4.657349	2.159113
H58	0.027678	-3.748833	0.824369
C59	1.895036	-1.274011	-0.622634
C60	4.343718	-2.627332	-2.092808
H61	4.948079	-1.714365	-2.053191
H62	4.660152	-3.187238	-2.980006
H63	4.610847	-3.228597	-1.216961
C64	1.569913	-3.888209	-2.267802
H65	1.731761	-4.519301	-1.387009
H66	1.924458	-4.455614	-3.134715
H67	0.489459	-3.765216	-2.386567
C68	2.171875	-1.250939	-3.720649

H69	1.105463	-1.099915	-3.923370
H70	2.579001	-1.780566	-4.588414
H71	2.650854	-0.265155	-3.706152
C72	-1.740493	-2.503041	4.225944
H73	-1.644398	-1.730884	4.996955
H74	-1.613764	-3.473299	4.719252
H75	-2.770403	-2.460112	3.855452
C76	-4.151285	1.602168	2.772349
H77	-5.131359	1.765271	2.317840
H78	-4.210184	1.944162	3.810015
H79	-3.950618	0.529429	2.780030
C80	-3.044198	2.354897	2.048734
H81	-3.221339	3.435284	2.065015
H82	-2.084433	2.174378	2.535229
O83	-2.865365	1.921455	0.686434
C84	-3.806935	2.465684	-0.257802
H85	-4.811165	2.439431	0.176605
H86	-3.802961	1.773748	-1.100837
C87	-3.444972	3.870514	-0.718670
H88	-3.447451	4.590122	0.103517
H89	-4.174391	4.214201	-1.458099
H90	-2.457488	3.888647	-1.183858
H91	-0.365976	2.625202	-0.040626
H92	1.240269	2.344500	0.525403
H93	-1.758710	-0.460037	1.861163
H94	-0.342222	0.149227	2.648364
H95	2.038548	-1.967324	0.226618
H96	2.679872	-0.509177	-0.466485
H97	-1.955932	0.501774	-1.826794
H98	-1.000321	-0.702021	-2.595907

Final Geometry **2**:

Li	-1.379704	-0.648656	-0.122104
Li	1.299330	-0.499195	0.381168
Li	0.211613	0.765912	-1.530203
Li	-0.268280	1.503464	0.638418
O	-2.993928	-2.011971	-0.333580
C	-3.949066	-1.654904	-1.334356
H	-3.673710	-0.669220	-1.700251
H	-4.962444	-1.600462	-0.927824
H	-3.930517	-2.356119	-2.172044
C	-3.291142	-3.233066	0.430004
C	-3.694464	-4.378899	-0.505340
H	-2.946568	-4.526578	-1.288512
H	-4.665025	-4.215392	-0.977698
H	-3.767372	-5.306693	0.066773
C	-4.393194	-2.931066	1.451022
H	-5.337772	-2.664539	0.971396
H	-4.097179	-2.107160	2.103420
H	-4.584146	-3.808232	2.074919
C	-1.985637	-3.583100	1.139229
H	-1.195426	-3.781548	0.411515
H	-2.117404	-4.478277	1.751676
H	-1.665238	-2.773402	1.796193
O	2.738383	-1.907710	1.025553
C	2.090459	-3.086423	1.503461
H	1.051699	-3.028543	1.185528
H	2.121473	-3.146646	2.594584
H	2.526986	-3.991817	1.075625
C	4.207015	-1.904051	1.103677
C	4.781009	-2.934161	0.122863
H	4.545747	-3.962469	0.405777
H	5.870374	-2.852489	0.092172
H	4.400137	-2.757852	-0.885323
C	4.665285	-2.184895	2.538949
H	4.437744	-3.204541	2.858080
H	4.197010	-1.489248	3.238665
H	5.748095	-2.059157	2.612863

Tanja Tatic[a], Kathrin Meindl[a], Julian Henn[a], Sushil Kumar Pandey[b], and Dietmar Stalke[*a]

Supplementary Material

C	4.620734	-0.497692	0.683528
H	4.183966	0.255523	1.341160
H	4.306856	-0.284276	-0.339285
H	5.707453	-0.396005	0.727735
C	-1.818702	1.459905	-0.980629
Si	-3.330693	2.360552	-0.338028
C	-4.694789	2.579842	-1.649752
H	-5.559515	3.126172	-1.256446
H	-5.064155	1.617333	-2.021366
H	-4.324698	3.135798	-2.517470
C	-2.884105	4.107090	0.258043
H	-2.144420	4.115603	1.064186
H	-3.770961	4.626421	0.636578
H	-2.481056	4.715607	-0.558069
C	-4.147929	1.454430	1.122857
H	-3.473921	1.361013	1.980225
H	-4.467909	0.442184	0.855253
H	-5.038523	1.989816	1.469174
C	-0.388987	-0.251623	1.956713
H	-1.481153	-0.427051	2.002048
H	0.032334	-1.245867	2.180714
Si	-0.023655	0.739739	3.500205
C	-1.038214	0.220449	5.022599
H	-0.851178	-0.826133	5.286162
H	-2.113607	0.317580	4.839154
H	-0.803043	0.826483	5.904693
C	1.808319	0.607917	3.982365
H	2.091876	-0.428221	4.194210
H	2.023019	1.192133	4.883089
H	2.471455	0.975166	3.193059
C	-0.392836	2.592592	3.233811
H	-1.444414	2.778723	2.991860
H	0.218673	3.060412	2.451336
H	-0.182631	3.158810	4.147262
C	1.755130	1.688423	-0.298186
H	2.504256	1.022324	-0.766116
H	2.129211	1.792342	0.737323
Si	2.091876	3.351791	-1.080404
C	3.936067	3.820492	-1.134899
H	4.099869	4.800507	-1.597035
H	4.519506	3.090564	-1.706588
H	4.367056	3.858821	-0.128705
C	1.205772	4.743974	-0.142272
H	1.403030	5.717900	-0.602590
H	1.545976	4.809949	0.897017
H	0.119516	4.615019	-0.123191
C	1.488577	3.393301	-2.887419
H	1.737127	4.349358	-3.360139
H	0.402778	3.275342	-2.977333
H	1.958513	2.613058	-3.497096
C	0.321727	-1.419667	-1.542117
H	-0.614038	-2.007819	-1.503628
H	1.049571	-2.084944	-1.042514
Si	0.826789	-1.506585	-3.341016
C	0.565116	-3.211088	-4.145833
H	-0.489549	-3.506451	-4.120242
H	1.129138	-3.989152	-3.620377
H	0.882488	-3.228450	-5.194476
C	2.665368	-1.070650	-3.550573
H	2.964060	-1.087913	-4.603846
H	3.307725	-1.784253	-3.023349
H	2.906063	-0.074320	-3.164894
C	-0.169680	-0.267841	-4.394226
H	-1.248837	-0.429248	-4.298766
H	0.075843	-0.370517	-5.456619
H	0.019554	0.782266	-4.139895
H	-2.214192	0.719742	-1.701526
H	-1.361512	2.209231	-1.657519

The first asymmetric organolithium tetramers with simple ether donor bases

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Supplementary Material

Final Geometry **3**:

Si	-3.050408	-1.384928	0.185864
Si	3.050385	1.384915	-0.185828
O	-1.782340	2.229573	-1.281259
O	-0.964281	2.635038	1.258088
O	0.964243	-2.635011	-1.258093
O	1.782362	-2.229583	1.281233
Li	-0.649345	0.994720	0.020486
Li	0.649308	-0.994723	-0.020451
C	-1.400099	-0.890301	0.864476
H	-1.571882	-0.427259	1.853952
H	-0.892565	-1.840902	1.116445
C	-3.940038	-2.788208	1.130832
H	-3.338172	-3.704359	1.141742
H	-4.910868	-3.043615	0.689574
H	-4.118320	-2.512024	2.176020
C	-2.902864	-2.010590	-1.610222
H	-2.547522	-1.221354	-2.282241
H	-3.860271	-2.368788	-2.004085
H	-2.190180	-2.839803	-1.680777
C	-4.271674	0.077938	0.165575
H	-4.448218	0.462886	1.176915
H	-5.246229	-0.215145	-0.239877
H	-3.894380	0.904846	-0.442718
C	1.400065	0.890314	-0.864431
H	1.571818	0.427293	-1.853921
H	0.892530	1.840924	-1.116360
C	4.271673	-0.077935	-0.165654
H	3.894432	-0.904875	0.442629
H	5.246245	0.215152	0.239756
H	4.448168	-0.462841	-1.177019
C	2.902857	2.010471	1.610296
H	2.190173	2.839680	1.680900
H	3.860262	2.368643	2.004185
H	2.547507	1.221195	2.282263
C	3.939983	2.788257	-1.130733
H	4.118260	2.512126	-2.175936
H	4.910814	3.043657	-0.689471
H	3.338104	3.704400	-1.141595
C	-1.649004	2.169867	-2.696206
H	-2.474662	2.702032	-3.182466
H	-1.684434	1.118407	-2.974399
H	-0.693995	2.598048	-3.019123
C	-1.776126	3.555379	-0.769552
H	-2.584540	4.145302	-1.222246
H	-0.818834	4.041493	-1.000632
C	-1.981518	3.473965	0.726274
H	-1.916434	4.479739	1.163049
H	-2.969726	3.055551	0.956184
C	-1.010885	2.517273	2.674639
H	-0.880321	3.498102	3.146214
H	-0.190360	1.865490	2.965996
H	-1.960217	2.078497	3.001282
C	1.010763	-2.517202	-2.674643
H	1.960051	-2.078360	-3.001324
H	0.190184	-1.865459	-2.965937
H	0.880231	-3.498024	-3.146239
C	1.981565	-3.473884	-0.726362
H	2.969733	-3.055396	-0.956309
H	1.916528	-4.479649	-1.163167
C	1.776255	-3.555369	0.769472
H	0.819022	-4.041586	1.000581
H	2.584749	-4.145230	1.222105
C	1.649114	-2.169960	2.696191
H	0.694172	-2.598258	3.019151
H	1.684452	-1.118510	2.974434
H	2.474860	-2.702063	3.182371

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Supplementary Material

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