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Synthesis of *B*-silylmethyl substituted *o*- and *m*-carboranes

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^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 spectrometer. The composition and properties of chloro(organyl)silylmethyl-*o*(*m*)-carboranes prepared at 250°C and 25 atm are presented in Table S1.

Table S1. The yield and characteristics of substances **(1**+**1')a-c** and **2**+**2'.**

Compound (Empirical formula)	Yield (%)	bp °C/1 Torr	n_D^{20}	M_n * found calcd.	Elemental analysis (%) found/calcd C	H	B	Cl	Si
1a+**1'a** ($C_3H_{13}B_{10}Cl_3Si$)	43	136-138	1.5512	295 291	12.68 12.34	4.47 4.49	36.53 37.23	38.30 36.49	9.29 9.62
1b+**1'b** ($C_4H_{16}B_{10}Cl_2Si$)	17	122-124	1.5290	267 271	18.10 17.70	5.98 5.94	39.20 39.84	26.30 26.16	10.40 10.35
1c+**1'c** ($C_5H_{19}B_{10}ClSi$)	3	117-119	1.5635	254 250	24.10 23.93	7.70 7.63	42.60 43.09	14.30 14.15	10.95 11.19
2+**2'** ($C_3H_{13}B_{10}Cl_3Si$)	42	126-128	1.5450	286 291	13.48 12.34	4.59 4.49	36.32 37.04	37.00 36.49	9.72 9.62

*Number-average molecular weight M_n was determined by cryoscopy in benzene.

Synthesis of B-trichlorosilylmethyl-o-carboranes **1a**+**1'a.** A stainless steel autoclave was charged with *o*-carborane (25.0 g, 0.173 mol), trichloro(chloromethyl)silane (105.0 g, 0.570 mol) and $AlCl_3$ (2.6 g, 0.0187 mol). The mixture was heated up to 250 °C and kept under stirring for 12 hours, the pressure having been 25 atm. The autoclave was then cooled, the resulting mixture was dissolved in heptane (300 ml) and treated with $POCl_3$ (3.4 g) to quench aluminum chloride. The solid product was filtered off on a glass filter, the volatiles were distilled off from the filtrate, and the residue was distilled *in vacuo* to collect fraction with 136-138 °C (1 Torr); yield: 21.7 g (43%). ^{1}H NMR ($CDCl_3$) ppm: 0.23 and 1.06 (each s, Σ 2H, CH_2); 1.6-3.2 (m, 9H, B-H); 3.56 (s, 2H, $C_{cb}H$). ^{13}C NMR ($CDCl_3$) ppm: 1.27 and 12.67 (Σ 2C, CH_2); 54.48 (2C, $C_{cb}H$). Found (%): C, 12.68; H,4.47; B, 36.53 Cl, 38.30; Si, 9.29 . Calc. for $C_3H_{13}B_{10}Cl_3Si$ (%): C, 12.34; H, 4.49; B, 35.23;Cl 36.49 Si, 9.62. M_n 295 (found), 291 (calc.).

Synthesis of B-[dichloro(methyl)silylmethyl]-o-carboranes **1b**+**1'b.** A stainless steel autoclave was charged with *o*-carborane (25.0 g, 0.173 mol), dichloro(chloromethyl)methylsilane

(38.6 g, 0.240 mol) and $AlCl_3$ (1.0 g, 0.0075 mol). The mixture was heated up to 250 °C and kept under stirring for 12 hours, the pressure having been 25 atm. The autoclave was then cooled, the resulting mixture was dissolved in heptane (120 ml) and treated with $POCl_3$ (3.4 g) to quench aluminum chloride. The solid product was filtered off on a glass filter, the volatiles were distilled off from the filtrate, and the residue was distilled *in vacuo* to collect fraction with 122-124 °C (1 Torr); yield: 3.4 g (17%). ^{1}H NMR ($CDCl_3$) ppm: 0.23 and 1.06 (each s, Σ 2H, CH_2); 0.71 (s, 3H, CH_3); 1.6-3.2 (m, 9H, B-H); 3.56 (s, 2H, $C_{cb}H$). Found (%): C, 18.10; H, 5.98; B, 39.20; Cl, 26.30; Si, 10.40. Calc. for $C_4H_{16}B_{10}Cl_2Si$ (%): C, 17.10; H, 5.94; B, 39.84; Cl 26.16; Si, 10.35. M_n 295 (found), 291 (calc.).

Synthesis of B-[chloro(dimethyl)silylmethyl]-o-carboranes **1c**+**1'c.** A stainless steel autoclave was charged with *o*-carborane (25.0 g, 0.173 mol), chloro(chloromethyl)dimethylsilane (32.5 g, 0.227 mol) and $AlCl_3$ (1.0 g, 0.0075 mol). The mixture was heated up to 250 °C and kept under stirring for 12 hours, the pressure having been 25 atm. The autoclave was then cooled, the resulting mixture was dissolved in heptane (120 ml) and treated with $POCl_3$ (3.4 g) to quench aluminum chloride. The solid product was filtered off on a glass filter, the volatiles were distilled off from the filtrate, and the residue was distilled *in vacuo* to collect fraction with 117-119 °C (1 Torr); yield: 0.52 g (3%). ^{1}H NMR ($CDCl_3$) ppm: 0.23 and 1.06 (each s, Σ 2H, CH_2), 1.22 (s, 6H, $2CH_3$), 1.6-3.2 (m, 9H, B-H); 3.56 (s, 2H, $C_{cb}H$). Found (%): C, 24.10; H,7.70; B, 42.60; Cl, 14.30; Si,10.95. Calc. for (%): C, 23.93; H, 7.63; B, 43.09; Cl 14.15; Si, 11.19. M_n 254 (found), 250 (calc.).

Synthesis of B-thrichlorosilylmethyl-m-carboranes **2**+**2'.** A stainless steel autoclave was charged with *m*-carborane (25.0 g, 0.173 mol), trichloro(chloromethyl)silane (105.0 g, 0.570 mol) and $AlCl_3$ (2.5 g, 0.0187 mol). The mixture was heated up to 250 °C and kept under stirring for 12 hours, the pressure having been 25 atm. The autoclave was then cooled, the resulting mixture was dissolved in heptane (300 ml) and treated with $POCl_3$ (3.4 g) to quench aluminum chloride. The solid product was filtered off on a glass filter, the volatiles were distilled off from the filtrate, and the residue was distilled *in vacuo* to collect fraction with 126-128 °C (1 Torr); yield: 21.2 g (42%). ^{1}H NMR ($CDCl_3$) ppm: 0.39 and 1.19 (each s, Σ 2H, CH_2); 1.55-3.50 (m, 9H, B-H; 2.90 (s, 2H, $C_{cb}H$). ^{13}C NMR ($CDCI_3$) ppm: 1.3 and 12.45 (Σ 2C, CH_2); 55.17 (2C, $C_{cb}H$). Found (%): C, 13.48; H, 4.59; B, 36.32; Cl, 37.00; Si, 9.72. Calc. for $C_3H_{13}B_{10}Cl_3Si$ (%): C, 12.34; H, 4.49; B, 37.23; Cl 36.49, Si, 9.62. M_n 286 (found), 291 (calc.).

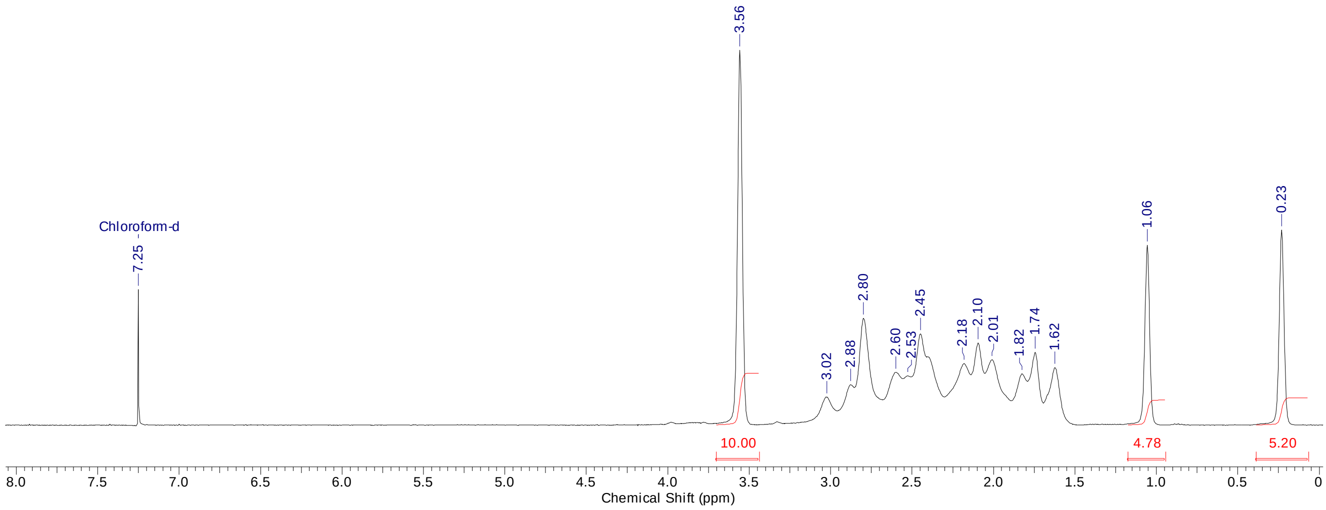

Figure S1 ^{1}H NMR spectrum of substance **1a+1'a**

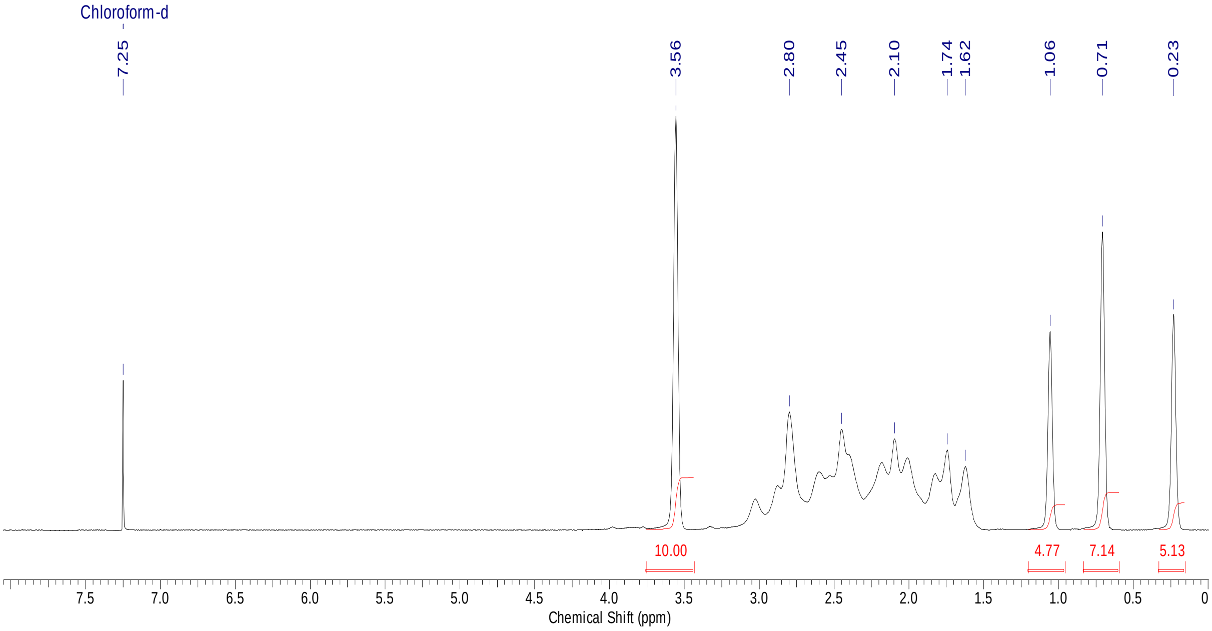

Figure S2 ^{1}H NMR spectrum of substance **1b+1'b**

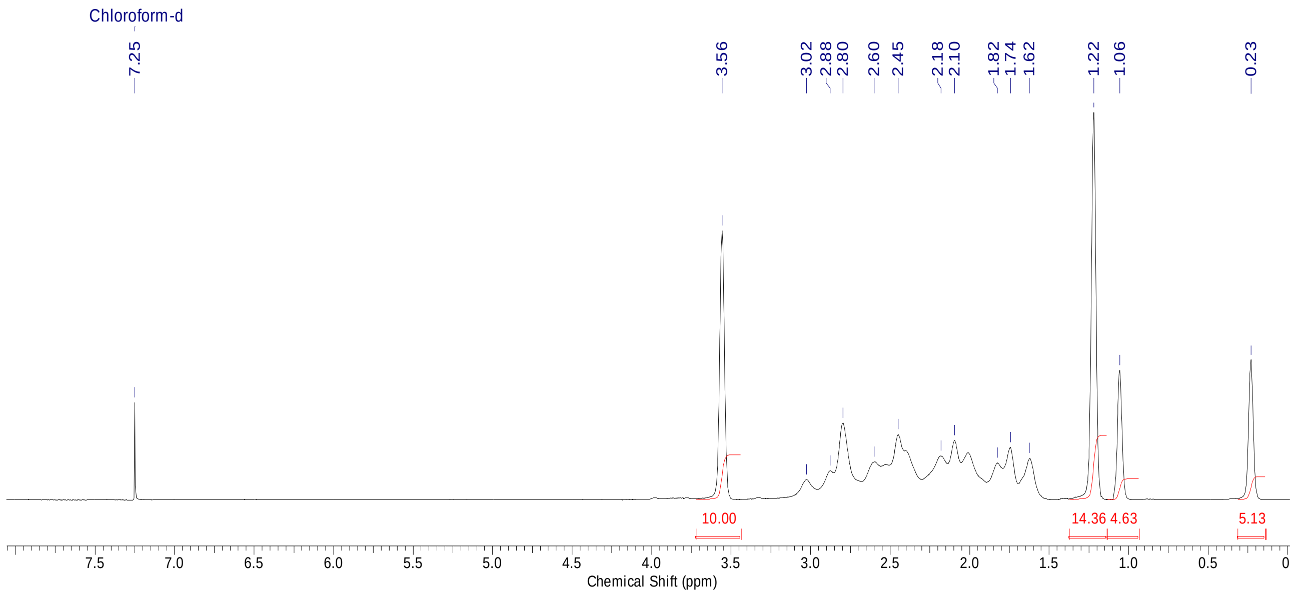

Figure S3 ^{1}H NMR spectrum of substance **1c**+**1'c**

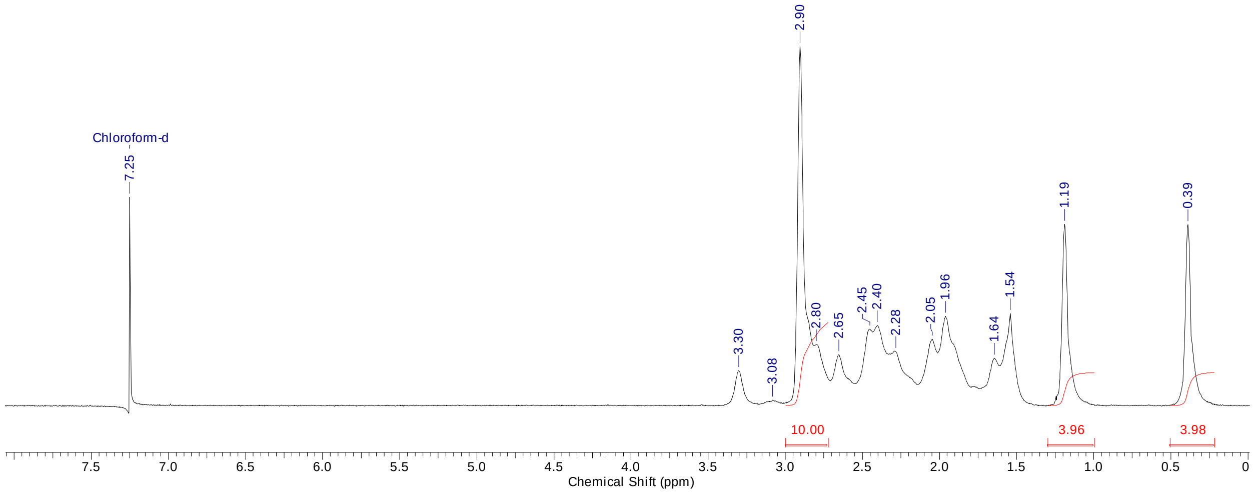

Figure S4 ^{1}H NMR spectrum of substance **2**+**2'**

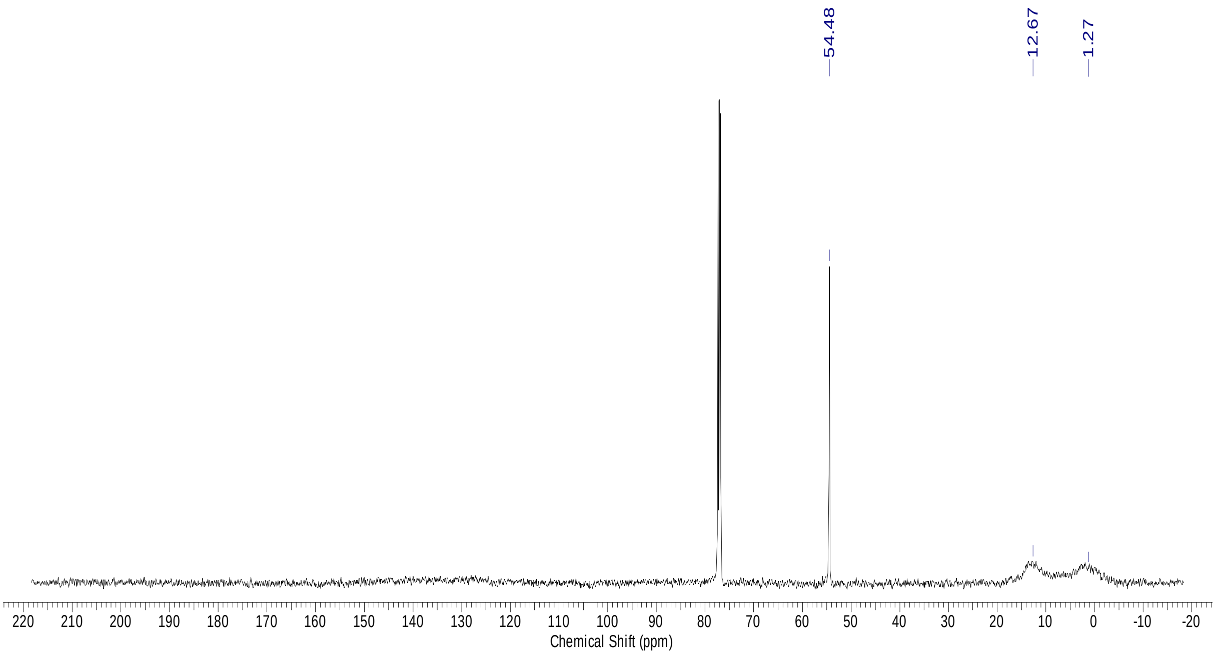

Figure S5 ^{13}C NMR spectrum of substance **1a**+**1'a**

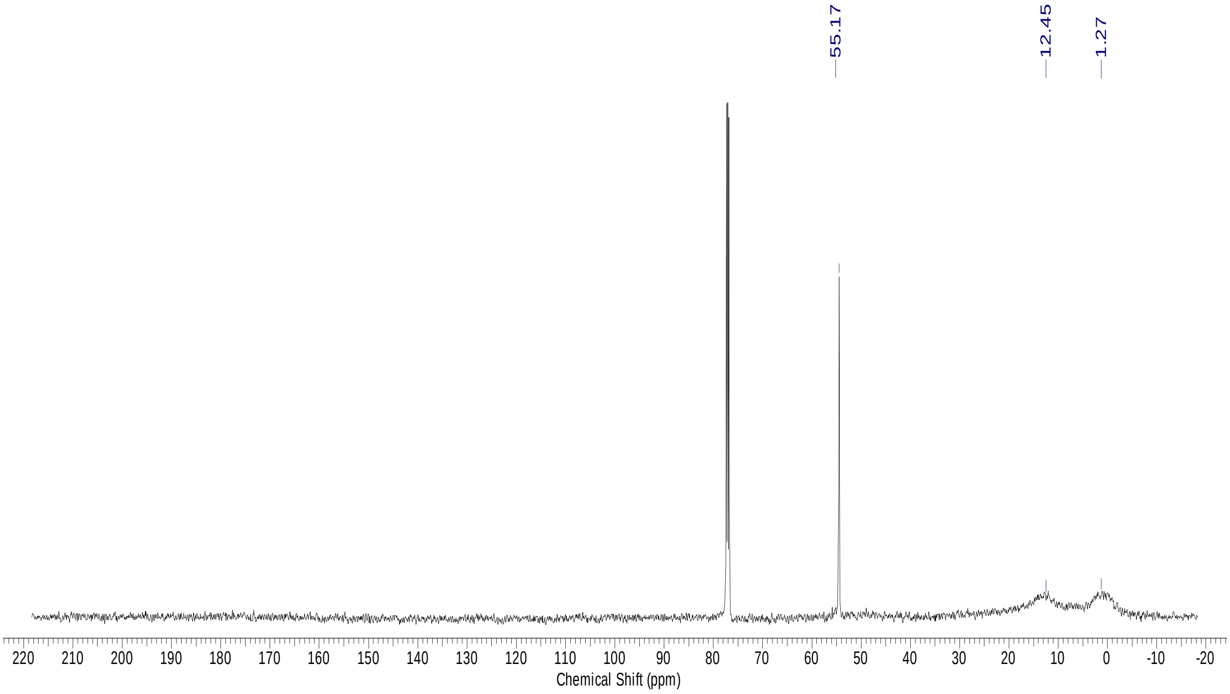

Figure S6 ^{13}C NMR spectrum of substance **2**+**2'**