SUPPLEMENTARY INFORMATION

Direct Synthesis of Dicarbollides

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Table S1. Assignments in the ^{11}B NMR spectra of the isolated dicarbollide anions (Et_3NH^+ salts in CD_3CN).

compound	B(9,11)	B(5,6)	B(3)	B(2,4)	B(10)	B(1)
2a$^-$	-12.1/136/1.85	-18.0/124/1.13	-18.7/142/1.67	-23.3/147/1.13	-34.4/132/32/0.02	-39.0/140/0.44
2b$^-$	-9.4/131/1.80	-18.6/142/1.25	-9.8/170/ 1.44	-18.6/142/1.01	-35.1/141/53/-0.14	-37.1/146/0.35
2c$^-$	-9.0/147/ 2.00 -10.6/140/2.06	-17.0/146/1.24 -18.2/150/1.19	-13.9/171/1.76	-19.9/150/1.71 -22.8/153/1.22	-33.0/128/25/0.15	-36.1/134/0.62
2d$^-$	-8.8/136/ 2.01 -11.4/137/2.01	-16.4/137/1.41 -18.4/132/1.41	-13.9/159/2.23	-20.4/143/1.53 -22.4/140/1.53	-33.2/129/52/0.43	-36.8/140/0.84
2e$^-$	-10.1/135/ 1.94 -11.1/135/1.87	-13.7/134/1.36 -18.7/138/1.06	-17.5/156/1.63	-20.1/148/1.20 22.7/148/1.09	-33.5/126/43/0.48	-37.5/137/0.00

Ordered as $\delta(^{11}B)/^1J_{BH}/\delta(^1H)_{BH}$, assigned by [^{11}B-^{11}B]-COSY and [^{11}B-^{1}H]-correlation spectroscopy.

EXAMPLES OF NMR MEASUREMENTS

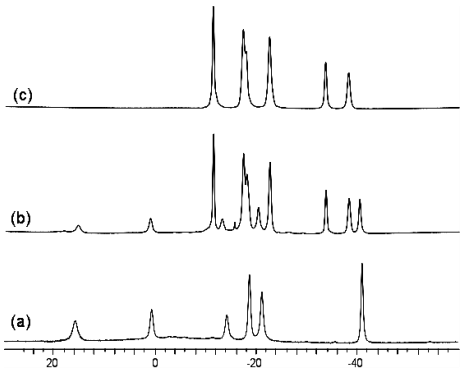

Fig. S1. $^{11}B\{^1H\}$ NMR spectra (128.3 MHz) of (a) 4-Et_3N-*arachno*-B_9H_{13} (**1**) in CD_3CN, (c) 7,8-*nido*-$C_2B_9H_{12}^-$ $NHEt_3^+$ (**2a**) (in CD_3CN), synthesized by Hawthorne's method and (b) reaction mixture, obtained after heating of 1 with an excess of C_2H_2 in toluene (125°C, 4 h) and containing starting **1** and product **2a** in ca. 1:3 ratio.

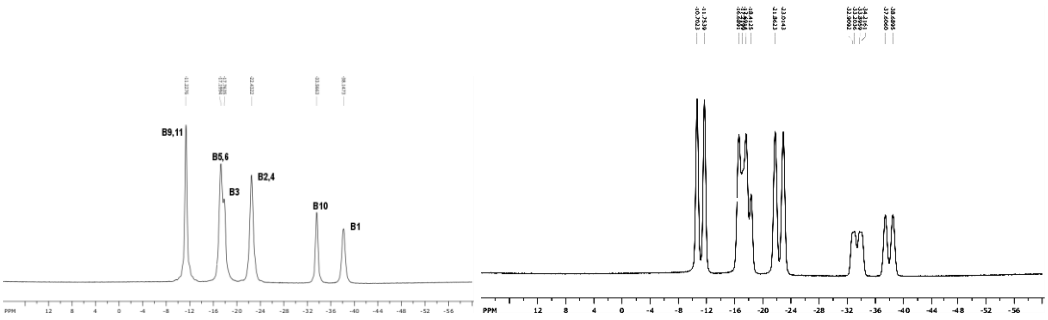

Fig. S2. $^{11}B\{^{1}H\}$ and ^{11}B NMR spectra of *nido*-7,8-$C_2B_9H_{12}^-$ $NHEt_3^+$ (**2a**$^-$) (128.3 MHz, CD_3CN).

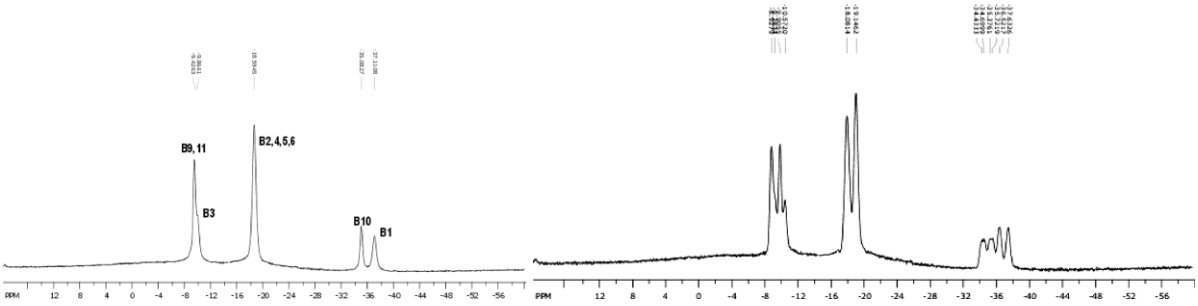

Fig. S3. $^{11}B\{^{1}H\}$ and^{11}B NMR spectra of 7,8-Me_2-*nido*-7,8-$C_2B_9H_{10}^-$ $NHEt_3^+$ (**2b**$^-$) (128.3 MHz, CD_3CN).

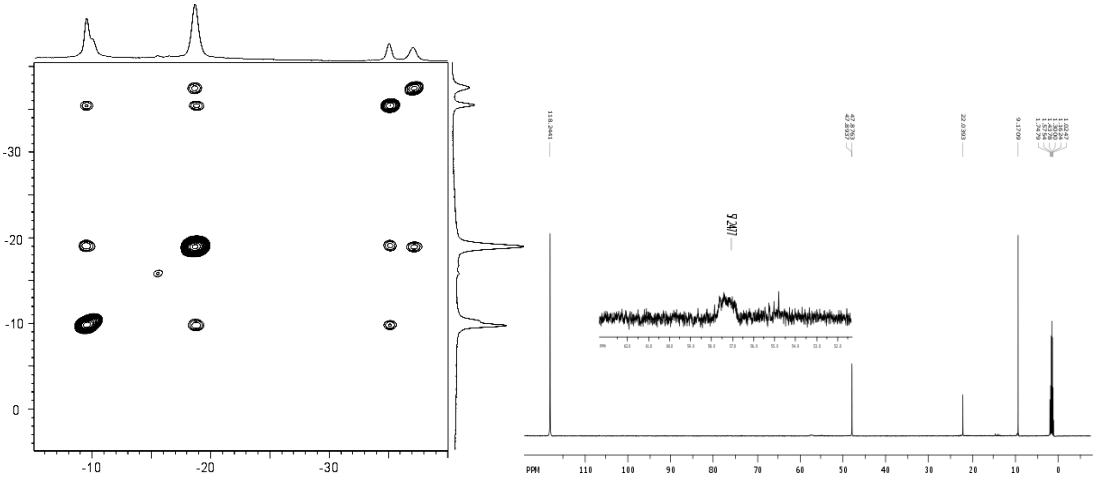

Fig. S4. ^{11}B-^{11}B COSY and ^{13}C NMR NMR spectra of 7,8-Me_2-*nido*-7,8-$C_2B_9H_{10}^-$)$NHEt_3^+$ (**2b**$^-$) (128.3 and 150.9 MHz MHz, CD_3CN).

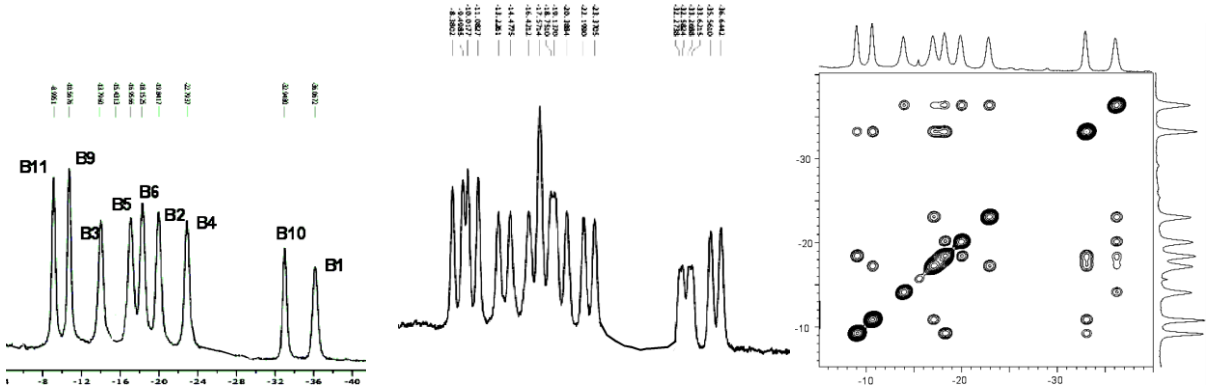

Fig. S5. $^{11}B\{^{1}H\}$, ^{11}B, and [^{11}B-^{11}B]-COSY NMR spectra of 7-Ph-*nido*-7,8-$C_2B_9H_{11}^-$ $NHEt_3^+$ (**2c**$^-$) (128.3 MHz, CD_3CN).

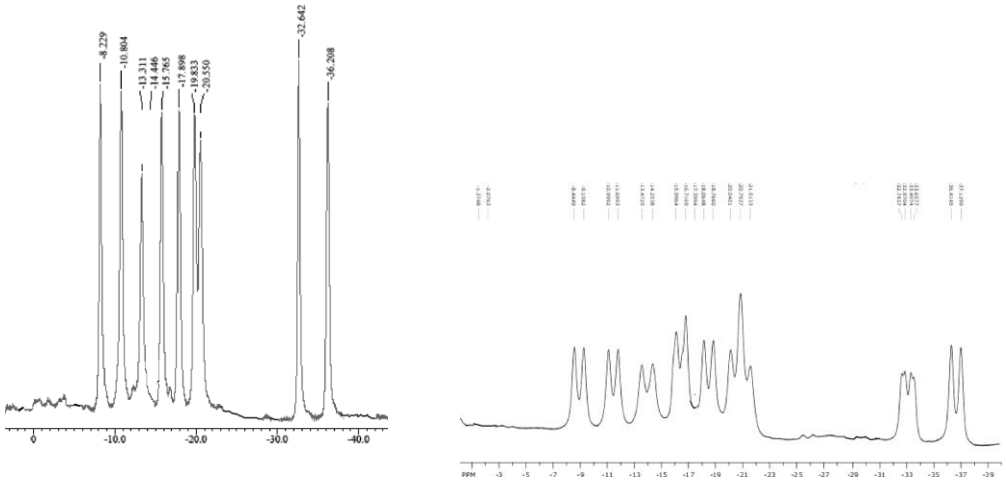

Fig. S6. 190 MHz$^{11}B\{^{1}H\}$ and ^{11}B NMR spectra of 7-naphtyl-*nido*-7,8-$C_2B_9H_{11}^-$ $NHEt_3^+$ (**2d**$^-$)(192.6 MHz, CD_3CN). .

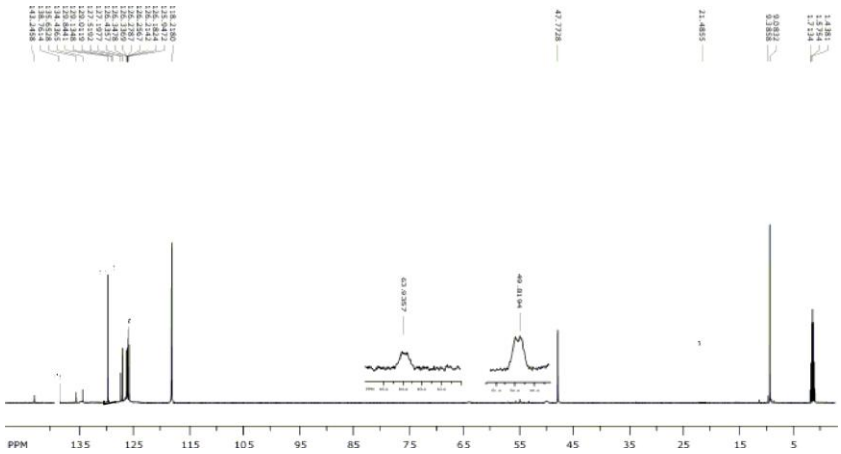

Fig. S7. ^{13}C NMR spectrum (150.9 MHz, CD_3CN) of 7-naph-*nido*-7,8-$C_2B_9H_{11}^-$ $NHEt_3^+$ (**2d**$^-$).

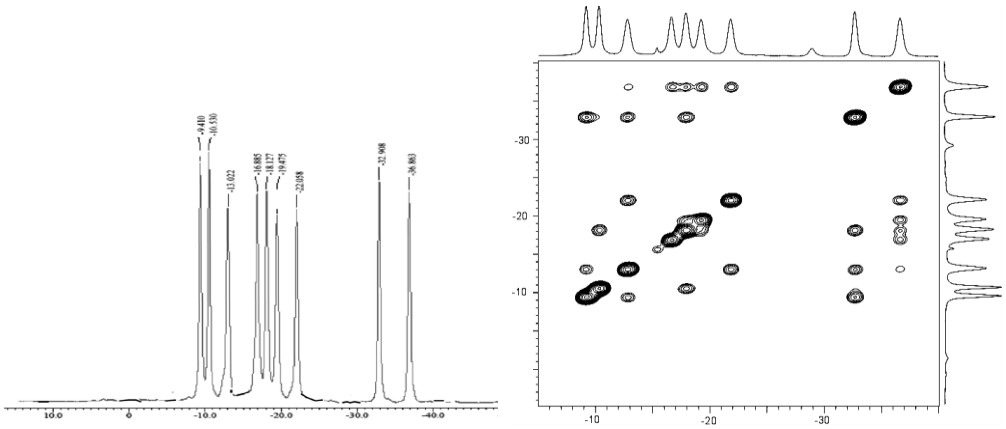

Fig. S8. 190 MHz $^{11}B\{^{1}H\}$ and [^{11}B-^{11}B]-COSY NMR spectra of 7-Me_3Si-*nido*-7,8-$C_2B_9H_{11}^-$ $NHEt_3^+$ (**2e$^-$**) (192.6 MHz, CD_3CN).

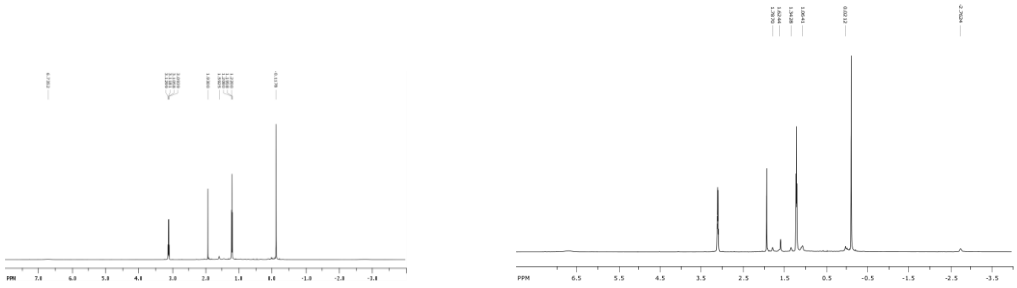

Fig. S9. ^{1}H NMR and ^{1}H $\{^{11}B\}$ spectra of 7-Me_3Si-*nido*-7,8-$C_2B_9H_{11}^-$ $NHEt_3^+$ (**2e$^-$**) (600 MHz, CD_3CN) .