Spectroscopic data

**Compound 2:** 1-C$_6$H$_{13}$-1,2-C$_2$B$_{10}$H$_{11}$

\[\text{[Diagram]}\]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.58 (1H, s, C$_{-}$H), 2.98-1.62 (m, 10H, B$_{10}$H$_{10}$), 2.25 – 2.18 (2H, m, CH$_{2}$_-C$_{5}$), 1.53 – 1.39 (2H, m, CH$_{2}$-CH$_{2}$-C$_{5}$), 1.29 (6H, m, (CH$_{2}$)-(CH$_{2}$)-(CH$_{2}$)-CH$_{3}$), 0.91 (3H, t, CH$_{3}$).

$^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ -2.37 (d, 1B), -5.87 (d, 1B), -9.24 (d, 2B), -12.24 (q, 6B).

Reported in Ref [11] in the manuscript.

**Compound 3:** 1-C$_6$H$_5$-1,2-C$_2$B$_{10}$H$_{11}$

\[\text{[Diagram]}\]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.55-7.49 (m, 2H, C$_{ar}$H-C$_{ar}$), 7.45-7.40 (m, 1H, C$_{ar}$H-C$_{ar}$H-C$_{ar}$-C$_{5}$), 7.40-7.34 (m, 2H, C$_{ar}$H-C$_{ar}$H-C$_{ar}$-C$_{5}$), 4.00 (s, 1H, C$_{-}$H), 3.30-1.70 (m, 10H, B$_{10}$H$_{10}$).

$^{11}$B NMR (160 MHz, CDCl$_3$): $\delta$ -2.01 (d, 1B), -4.32 (d, 1B), -8.91 (d, 2B), -9.92-14.44 (m, 6B).

Reported in Ref [11] in the manuscript.

**Compound 4:** 1-C$_4$H$_9$-1,2-C$_2$B$_{10}$H$_{11}$

\[\text{[Diagram]}\]

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.58 (s, 1H, C$_{-}$H), 2.98-1.62 (m, 10H, B$_{10}$H$_{10}$), 2.28 – 2.17 (m, 2H, CH$_{2}$-C$_{5}$), 1.54 – 1.40 (m, 2H, CH$_{2}$-CH$_{2}$-C$_{5}$), 1.32 (m, 2H, CH$_{2}$-CH$_{3}$), 0.93 (t, 3H, CH$_{3}$).

$^{11}$B NMR (160 MHz, CDCl$_3$): -2.39 (d, 1B), -5.86 (d, 1B), -9.34 (d, 2B), -12.24 (q, 6B).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$C 75.44 (C$_{-}$CH$_{2}$), 60.91 (C$_{-}$H), 37.87 (CH$_{2}$-C$_{5}$), 31.23 (CH$_{2}$-CH$_{2}$-CH$_{2}$), 22.13 (CH$_{2}$-CH$_{3}$), 13.62 (CH$_{3}$).

Elemental analysis: Theoretical: 35.97% C; 10.06% H. Experimental: 36.01% C; 10.15% H.
**Compound 5:** 1-C₇H₁₁-1,2-C₂B₁₀H₁₁

![Structure of Compound 5](image)

^1H NMR (500 MHz, CDCl₃): δ 3.58 (s, 1H, cage C-H), 2.29 – 2.16 (m, 4H, CH₂⁻ Cₛ & CH₂-C), 1.97 (t, 1H, CH), 1.62 – 1.45 (m, 4H, CH₂⁻ CH₂⁻ Cₛ & CH₂-CH₂⁻Cₛ), 1.45 – 1.32 (m, 2H, CH₂⁻ CH₂-CH₂⁻Cₛ).

^11B NMR (160 MHz, CDCl₃): -2.33 (d, 1B), -5.82 (d, 1B), -9.31 (d, 2B), -12.26 (q, 6B).

Reported in Ref [11] in the manuscript.

**Compound 6:** 1-C₆H₄CH₃-1,2-C₂B₁₀H₁₁

![Structure of Compound 6](image)

^1H NMR (500 MHz, CDCl₃): δ 7.46 – 7.33 (d, 2H, Cₛ-Cₛ-Cₛ-Cₛ), 7.16 (d, 2H, Cₛ-Cₛ-Cₛ-Cₛ), 3.96 (s, 1H, cage C-H), 2.37 (s, 3H, C₃H₃)

^11B NMR (160 MHz, CDCl₃, decoupled): -2.02 (d, 1B), -4.52 (d, 1B), -10.94 (m, 8B).

^13C NMR (126 MHz, CDCl₃): δ C 140.22 (Cₛ-Cₛ), 130.67 (Cₛ-Cₛ), 129.48 (Cₛ-Cₛ-Cₛ), 127.49 (Cₛ-Cₛ-Cₛ), 76.70 (Cₛ-Cₛ), 60.37 (Cₛ-Cₛ), 20.9 (C₃H₃).

Elemental analysis: Theoretical: 46.13% C; 7.74% H. Experimental: 45.90% C; 7.55% H.
**Figure S1:** $^1$H-NMR spectrum of compound 6. Protons attached to boron atoms appear as broad signals in the range 1.5-3.3 ppm, due to coupling with protons.

**Figure S2:** $^{13}$C-NMR spectrum of compound 6. The signal corresponding to the cluster carbon atom attached to the phenyl ring (f) is very small and appears very close to the signal of CDCl$_3$. 
**Figure S3:** $^{11}$B-NMR spectrum of compound 6. All signals appear as singlets in the $^{11}$B-$^1$H spectrum (results not shown). They become doublets in the $^{11}$B-NMR spectrum.

**Compound 7:** 1-C$_2$H$_3$OCO-1,2-C$_{10}$B$_{10}$H$_{11}$

![Compound 7](image)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 4.29 – 4.25 (q, 2H, CH$_2$-O), 4.06 (s, 1H, cage C-H), 3.13 – 1.58 (m, 10B, B$_{10}$H$_{10}$), 1.31 – 1.28 (t, 3H, CH$_3$)

$^{11}$B NMR (160 MHz, CDCl$_3$, decoupled): -2.62 (d, 2B), -8.90 (d, 2B), -12.82 (dd, 6B).

Reported in Ref [12] in the manuscript.

**Compound 8:** 1-C$_6$H$_5$-9-I-closo-1,2-C$_{10}$B$_{10}$H$_{11}$

![Compound 8](image)

$^1$H NMR (500 MHz, CDCl$_3$): 7.51 (dd, 1H, C$_{ar}$H-C$_{ar}$H-C$_{ar}$H-C$_{ar}$C), 7.49–7.43 (m, 2H, C$_{ar}$H-C$_{ar}$C), 7.43–7.34 (m, 2H, C$_{ar}$H-C$_{ar}$H-C$_{ar}$C), 4.29 (s, 0.3H, cage C-H, isomer 1), 4.10 (s, 0.7H, cage C-H,
isomer 2), 3.39 – 2.02 (m, 9 H, B-H). Two different positional isomers (named as 1 and 2) are formed, in 0.3:0.7 ratio.

$^{11}$B NMR (160 MHz, CDCl$_3$): -0.02 – -0.95 (d, 1 B), -6.73 – -7.72 (d, 2B), -9.90 – -14.47 (m, 6B), -16.15 – -17.05 (s, 1B).

$^{13}$C NMR (126 MHz, CDCl$_3$): δC 130.36, 129.12, 127.49, 73.43, 61.06, 56.67.

LCMS (ESI) Experimental [M] $\cdot$ m/z = 344.44; theoretical [M] $\cdot$ m/z = 345.

FTIR (KBr, cm$^{-1}$): ν 3083, 2642, 2606, 2572, 1495, 1446. The typical strong bands corresponding to B-H stretching are seen in the range 2573-2642.

Elemental analysis: Theoretical: 27.75% C; 4.37% H. Experimental: 27.95% C; 4.31% H

**Compound 9:** 1-C$_{6}$H$_{5}$CH$_{3}$-9-I-closo-1,2-C$_{2}$B$_{10}$H$_{10}$

$^{1}$H NMR (500 MHz, CDCl$_3$): 7.36 – 7.32 (m, 2H, $C_{ar}$H-$C_{ar}$-C$_{C}$), 7.17 – 7.14 (m, 2H, $C_{ar}$H-$C_{ar}$-CH$_{3}$), 4.04 (s, 1H, cage C-H), 2.37 (s, 3H, CH$_{3}$-$C_{ar}$), 3.52 – 1.91 (m, 9H, B-H). Only one positional isomer is detected in this case.

$^{11}$B NMR (160 MHz, CDCl$_3$): -0.07 – -0.91 (d, 1B), -6.73 – -7.71 (d, 2B), -9.37 – -12.22 (m, 6B), -16.12 – -17.11 (s, 1B).

$^{13}$C NMR (126 MHz, CDCl$_3$): δC 140.67 ($C_{ar}$-C$_{C}$), 129.9 ($C_{ar}$-CH$_{3}$), 129.64 ($C_{ar}$H-$C_{ar}$-C$_{C}$), 127.39 ($C_{ar}$H-$C_{ar}$-CH$_{3}$), 73.48 ($C_{C}$-$C_{ar}$), 61.26 ($C_{ar}$-H), 21.00 (CH$_{3}$).

LCMS (ESI) Experimental [M] $\cdot$ m/z = 358.18; theoretical [M] $\cdot$ m/z = 359

FTIR (KBr, cm$^{-1}$): ν 3078, 2647, 2602, 1506. The typical strong bands corresponding to B-H stretching are seen in the range 2602-2647.

Elemental analysis: Theoretical: 30.01% C; 4.76% H. Experimental: 29.89% C; 4.79% H
Figure S4: $^1$H-NMR spectrum of compound 9. Protons attached to boron atoms appear as broad signals in the range 1.5-3.3 ppm due to coupling with protons.

Figure S5: $^{13}$C-NMR spectrum of compound 9.
Figure S6: $^{11}$B-NMR spectrum of compound 9. All signals appear as singlets in the $^{11}$B-$^1$H$\{}$ spectrum (results not shown). All signals become doublets in the $^{11}$B-NMR spectrum except the one corresponding to B-I, which appears upfield as a singlet, confirming the presence of the iodine atom.

Compound 10: 1-C$_2$H$_5$COO-9-I-closo-1,2-C$_2$B$_{10}$H$_{10}$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ H 4.40 (s, 0.4H, cage C-H), 4.36-4.29 (dq, 2H, CH$_2$-O), 4.19 (s, 0.6H, cage C-H), 3.40-1.60 (bm, 9H, B-H), 1.37 – 1.33 (m, 3H, CH$_3$). The presence of two positional isomers in 0.6:0.4 ratio can be found.

$^{11}$B NMR (160 MHz, CDCl$_3$, decoupled): -0.70 – -1.69 (d, 1B), -6.70 – -7.69 (d, 2B), -11.19 – -14.05 (m, 6B), -15.85(s, 0.4B), -16.79 (s, 0.6B).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ C 160.4 (CO), 64.35 (C-CO), 56.81 (C-C-H), 52.14 (CH$_2$-O), 12.75 (CH$_3$).

FTIR (KBr, cm$^{-1}$): $\nu$ 3079, 3002, 2987, 2581, 1740. The typical strong band corresponding to B-H stretching is seen at 2581.

Elemental analysis: Theoretical: 17.55% C; 4.42% H. Experimental: 17.62% C; 4.51% H
Compound 11: \( \text{1-(CH}_2\text{)}_5\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-9-I-} \text{closo-1,2-C}_2\text{B}_{10}\text{H}_{10} \)

\[ + \]

\[ \text{1B NMR (160 MHz, CDCl}_3, \text{decoupled): } \delta\text{ }-0.72 \text{ (d, 1B), -7.56 (d, 2B), -12.39 \text{-- }-13.67 \text{ (hep, 6B), -16.48 (s, 0.3B), -18.45 (s, 0.7B). The presence of two peaks that remain as singlets in the } \text{1B NMR spectrum (} -16.48 \text{ and } -18.45 \text{ ppm, respectively) confirms the presence of two positional isomers in 0.3:0.7 ratio (as observed in the } \text{1H NMR spectrum.} \]

\[ \text{LCMS (ESI) Experimental [M] } - m/z + \text{HCOO}^- = 554.15; \text{theoretical [M] } m/z = 554.\]

Reported in Ref [13c] in the manuscript

Figure S7: Chromatographic profiles (radiometric detection) for: (A) reaction crude and (B) pure 1-[\(^{125}\text{I}\)]decaborane.
Figure S8: Chromatographic profiles (UV and radiometric detection) for reference compound 8 (top) and purified [¹²⁵I]8 (bottom).

Figure S9: Chromatographic profiles (UV and radiometric detection) for reference compound 9 (top) and purified [¹²⁵I]9 (bottom).
Figure S10: Chromatographic profiles (UV and radiometric detection) for reference compound 10 (top) and purified [\(^{125}\)I]10 (bottom).

Figure S11: Chromatographic profiles (UV and radiometric detection) for reference compound 11 (top) and purified [\(^{125}\)I]11 (bottom).