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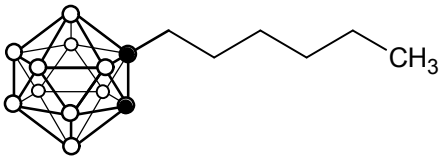
Spectroscopic data

Compound 2: 1-C_6H_{13}-1,2-$C_2B_{10}H_{11}$

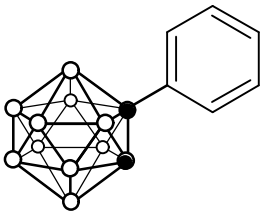


^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.58 (1H, s, C_C-*H*), 2.98-1.62 (m, 10H, $B_{10}H_{10}$), 2.25 – 2.18 (2H, m, CH_2- C_C), 1.53 – 1.39 (2H, m, CH_2-CH_2- C_C), 1.29 (6H, m, (CH_2)-(CH_2)-(CH_2)-CH_3), 0.91 (3H, t, CH_3).

^{11}B NMR (160 MHz, $CDCl_3$): δ_B -2.37 (d, 1*B*), -5.87 (d, 1*B*), -9.24 (d, 2*B*), -12.24 (q, 6*B*).

Reported in Ref [11] in the manuscript.

Compound 3: 1-C_6H_5-1,2-$C_2B_{10}H_{11}$

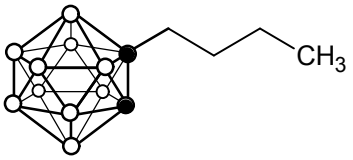


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H, C_{ar}*H*-C_{ar}-C_C), 7.45-7.40 (m, 1H, C_{ar}*H*-C_{ar}H-C_{ar}H-C_{ar}-C_C), 7.40-7.34 (m, 2H, C_{ar}*H*-C_{ar}H-C_{ar}-C_C), 4.00 (s, 1H, C_C-*H*), 3.30-1.70 (m, 10H, $B_{10}H_{10}$).

^{11}B NMR (160 MHz, $CDCl_3$): δ -2.01 (d, 1*B*), -4.32 (d, 1*B*), -8.91 (d, 2*B*), -9.92-14.44 (m, 6*B*).

Reported in Ref [11] in the manuscript.

Compound 4: 1-C_4H_9-1,2-$C_2B_{10}H_{11}$



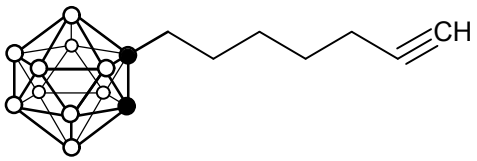
^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.58 (s, 1H, C_C-*H*), 2.98-1.62 (m, 10H, $B_{10}H_{10}$), 2.28 – 2.17 (m, 2H, CH_2-C_C), 1.54 – 1.40 (m, 2H, CH_2-CH_2-C_C), 1.32 (m, 2H, CH_2-CH_3), 0.93 (t, 3H, CH_3).

^{11}B NMR (160 MHz, $CDCl_3$): -2.39 (d, 1*B*), -5.86 (d, 1*B*), -9.34 (d, 2*B*), -12.24 (q, 6*B*).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C 75.44 (C_C-CH_2), 60.91 (C_C-H), 37.87 (CH_2-C_C), 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-C_7H_{11}-1,2-$C_2B_{10}H_{11}$

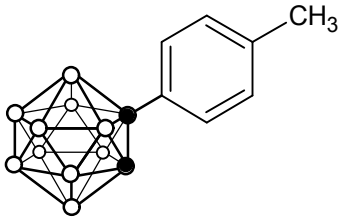


^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.58 (s, 1H, cage C-*H*), 2.29 – 2.16 (m, 4H, C*H*$_2$- C_C & C*H*$_2$-C), 1.97 (t, 1H, C*H*), 1.62 – 1.45 (m, 4H, C*H*$_2$- CH_2- C_C & C*H*$_2$-CH_2-C), 1.45 – 1.32 (m, 2H, C*H*$_2$- CH_2-CH_2-C_C).

^{11}B NMR (160 MHz, $CDCl_3$): -2.33 (d, 1*B*), -5.82 (d, 1*B*), -9.31 (d, 2*B*), -12.26 (q, 6*B*).

Reported in Ref [11] in the manuscript.

Compound 6: 1-$C_6H_4CH_3$-1,2-$C_2B_{10}H_{11}$



^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.46 – 7.33 (d, 2H, C_{ar}*H*-C_{ar}-C_C), 7.16 (d, 2H, C_{ar}*H*-C_{ar}-CH_3), 3.96 (s, 1H, cage C-*H*), 2.37 (s, 3H, C*H*$_3$)

^{11}B NMR (160 MHz, $CDCl_3$, decoupled):-2.02 (d, 1B), -4.52 (d, 1B), -10.94 (m, 8B).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C 140.22 (*C*$_{ar}$-C_C), 130.67 (*C*$_{ar}$-CH_3), 129.48 (*C*$_{ar}$-C_{ar}-C_C), 127.49 (*C*$_{ar}$-C_{ar}-CH_3), 76.70 (*C*$_C$-C_{ar}), 60.37 (*C*$_C$-H), 20.9 (*C*H_3).

Elemental analysis: Theoretical: 46.13% C; 7.74% H. Experimental: 45.90% C; 7.55% H.

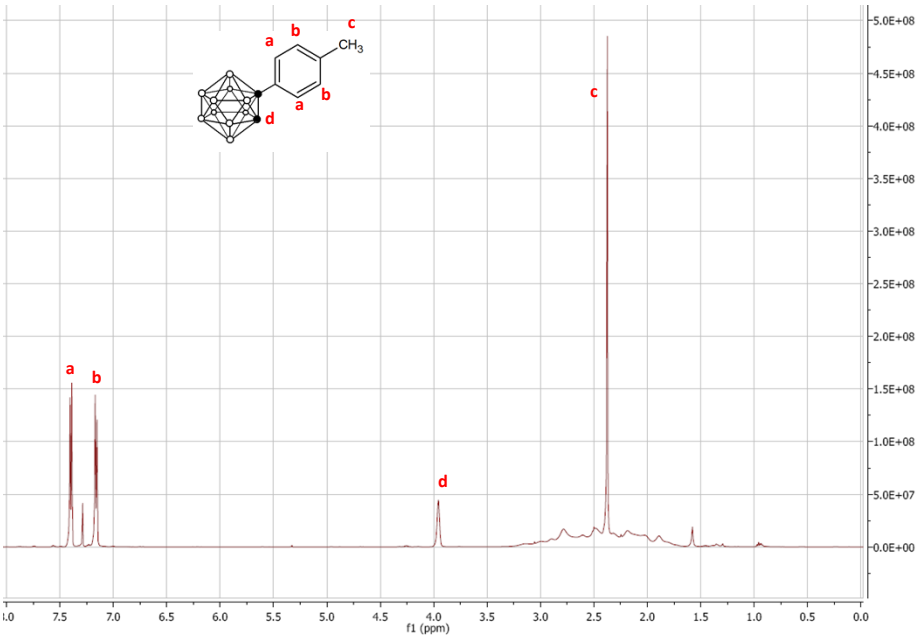


Figure S1: ^{1}H-NMR spectrum of compound **6**. Protons attached to boron atoms appear as broad signals in the range 1.5-3.3 ppm, due to coupling with protons.

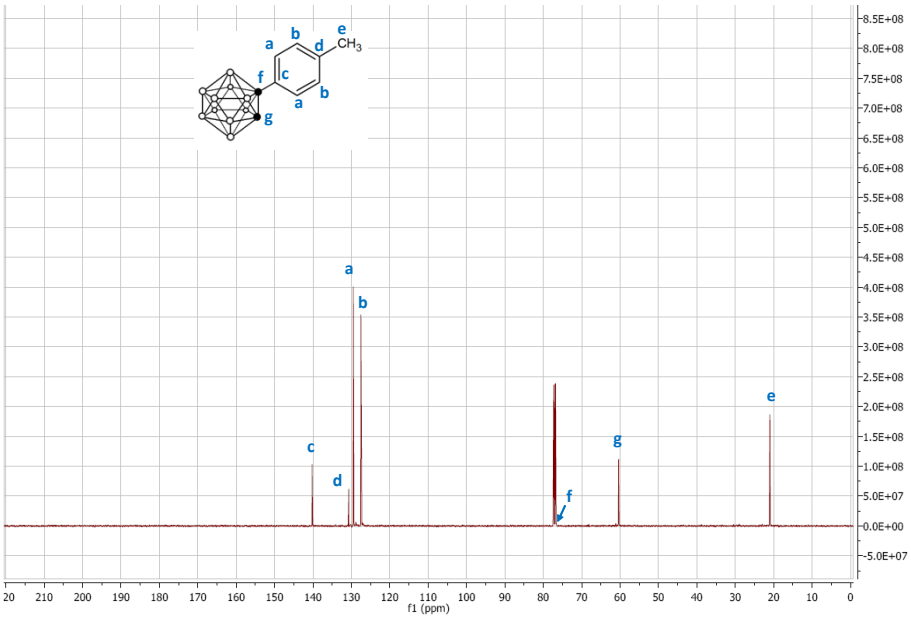


Figure S2: ^{13}C-NMR spectrum of compound **6**. The signal corresponding to the cluster carbon atom attached to the phenyl ring (f) is very small and appears very close to the signal of $CDCl_3$.

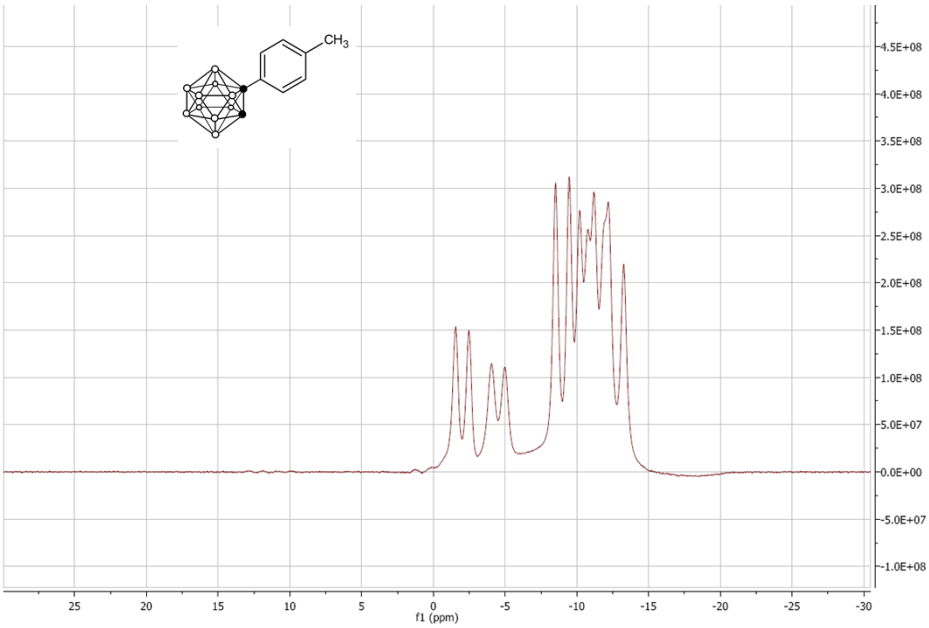
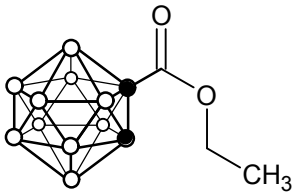


Figure S3: ^{11}B-NMR spectrum of compound **6**. All signals appear as singlets in the ^{11}B{^{1}H} spectrum (results not shown). They become doublets in the ^{11}B-NMR spectrum.

Compound 7: 1-C_2H_5OCO-1,2-$C_2B_{10}H_{11}$

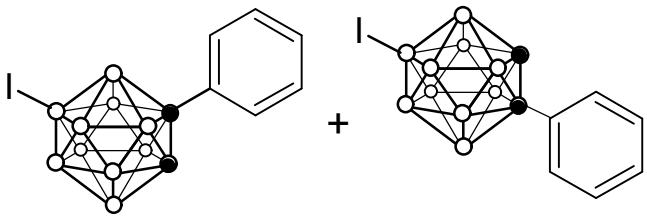


^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.29 – 4.25 (q, 2H, C*H*$_2$-O), 4.06 (s, 1H, cage C-*H*), 3.13 – 1.58 (m, 10B, B_{10}*H*$_{10}$), 1.31-1.28 (t, 3H, C*H*$_3$)

^{11}B NMR (160 MHz, $CDCl_3$, decoupled): -2.62 (d, 2*B*), -8.90 (d, 2*B*), -12.82 (dd, 6*B*).

Reported in Ref [12] in the manuscript.

Compound 8: 1-C_6H_5-9-I-*closo*-1,2-$C_2B_{10}H_{10}$



^{1}H NMR (500 MHz, $CDCl_3$): 7.51 (dd, 1H, C_{ar}*H*-C_{ar}H-C_{ar}H-C_{ar}-C_C), 7.49- 7.43 (m, 2H, C_{ar}*H*-C_{ar}-C_C), 7.43- 7.34 (m, 2H, C_{ar}*H*- C_{ar}H-C_{ar}-C_C), 4.29 (s, 0.3 H, cage C-*H*, isomer 1), 4.10 (s, 0.7 H, 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, 2*B*), -9.90 – -14.47 (m, 6*B*), -16.15– -17.05 (s, 1*B*).

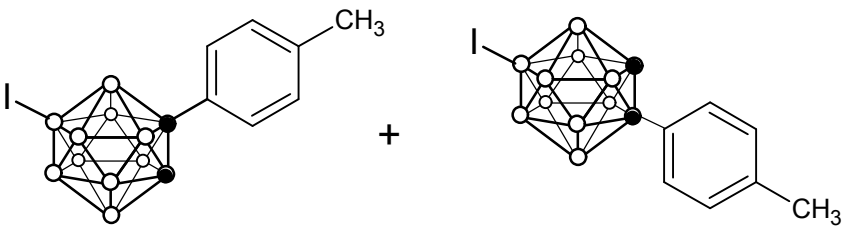
^{13}C NMR (126 MHz, $CDCl_3$): δ_C 130.36, 129.12, 127.49, 73.43, 61.06, 56.67.

LCMS (ESI) Experimental $[M]^-$ m/z = 344.44; theoretical $[M]^-$ 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-$C_6H_5CH_3$-9-I-*closo*-1,2-$C_2B_{10}H_{10}$



^{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, 1*B*), -6.73 – -7.71 (d, 2*B*), -9.37 – -12.22 (m, 6*B*), -16.12– -17.11(s, 1*B*).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C 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 $[M]^-$ m/z = 358.18; theoretical $[M]^-$ 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

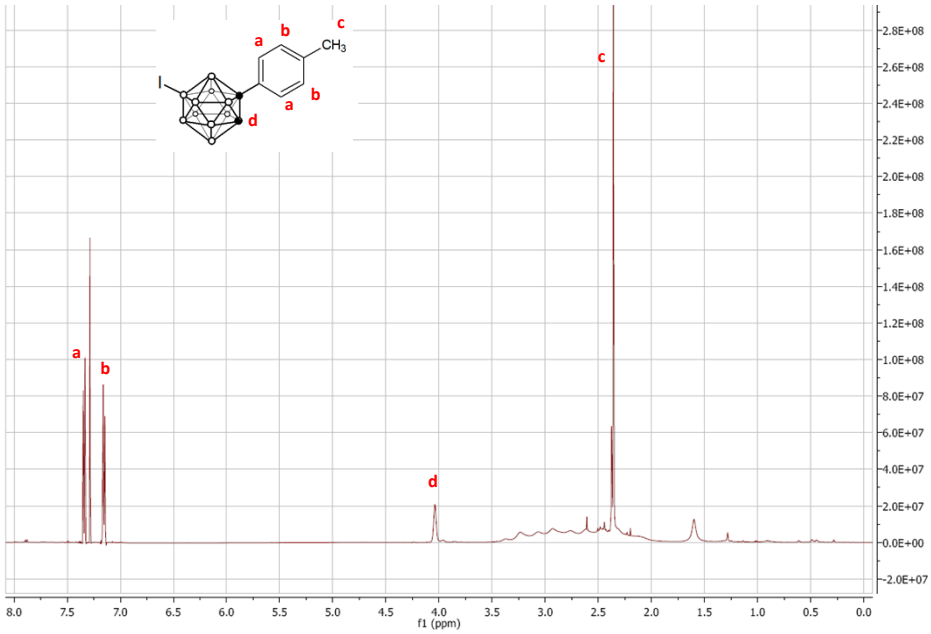


Figure S4: ^{1}H-NMR spectrum of compound **9**. Protons attached to boron atoms appear as broad signals in the range 1.5-3.3 ppm due to coupling with protons.

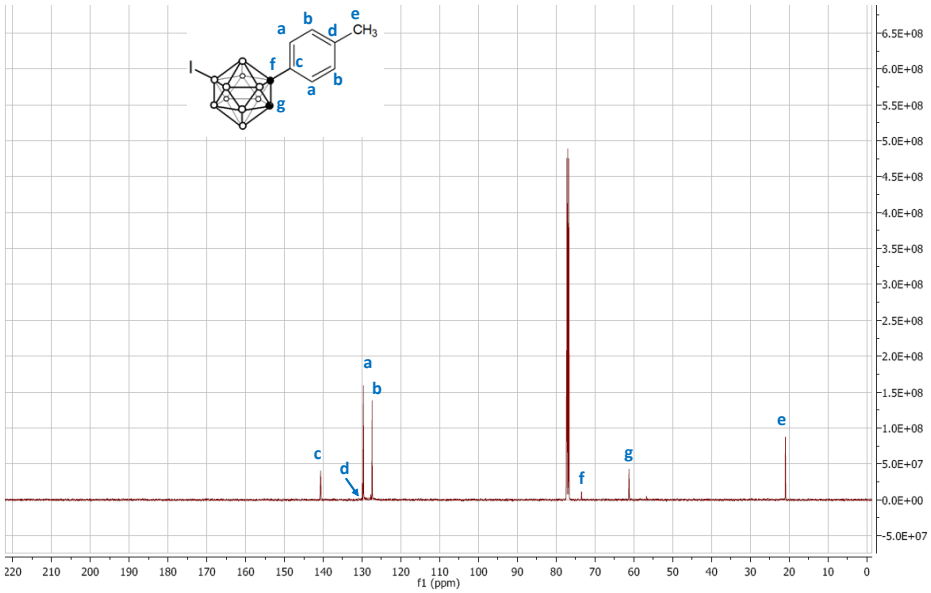


Figure S5: ^{13}C-NMR spectrum of compound **9**.

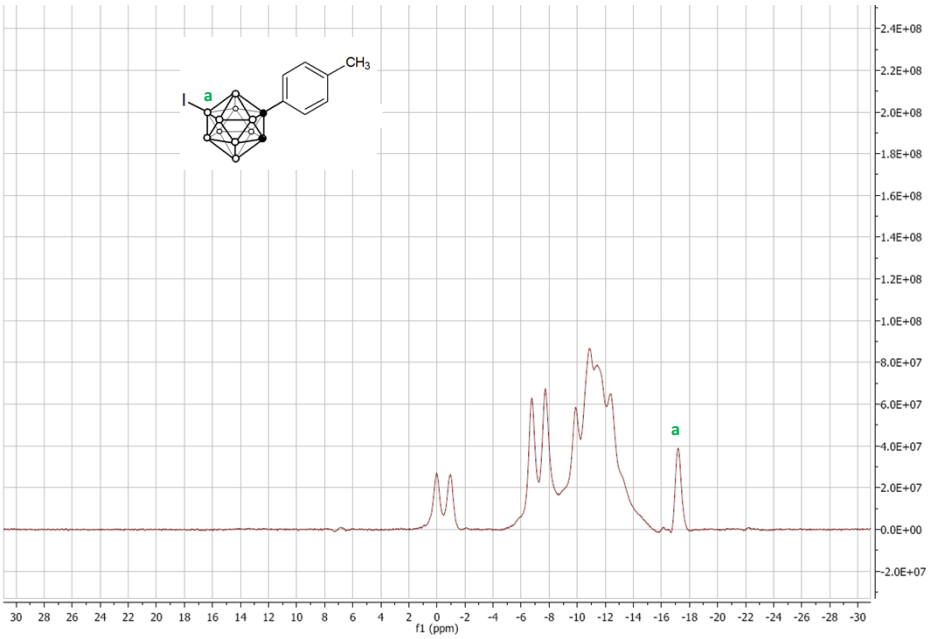
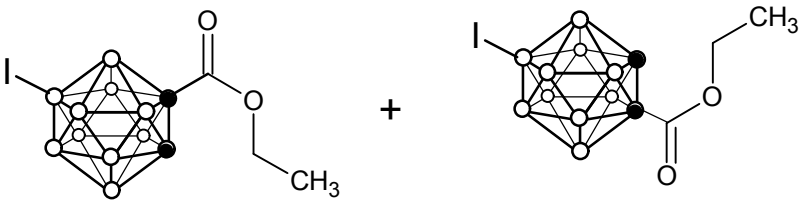


Figure S6: ^{11}B-NMR spectrum of compound **9**. All signals appear as singlets in the ^{11}B{^{1}H} spectrum (results not shown). All signals become doublets in the ^{11}B-NMR spectrum except the one corresponding to B-I, which appears upfield as a singlet, confirming the presence of the iodine atom.

Compound 10: 1-C_2H_5COO-9-I-*closo*-1,2-$C_2B_{10}H_{10}$



^{1}H NMR (500 MHz, $CDCl_3$): δ_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.

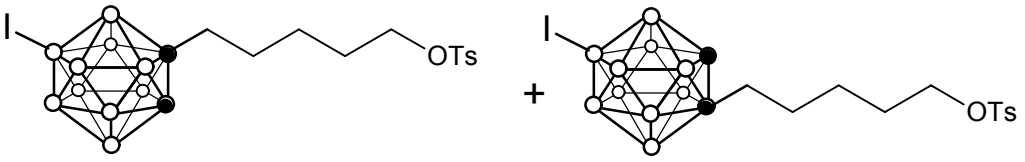
^{11}B NMR (160 MHz, $CDCl_3$, decoupled): -0.70 – -1.69 (d, 1*B*), -6.70 – -7.69 (d, 2*B*), -11.19 – -14.05 (m, 6*B*), -15.85(s, 0.4*B*), -16.79 (s, 0.6*B*).

^{13}C NMR (126 MHz, $CDCl_3$): δ_C 160.4 (*C*O), 64.35 (C_C-CO), 56.81 (C_C-H), 52.14 (CH_2-O), 12.75 (CH_3).

FTIR (KBr, cm^{-1}): ν 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: 1-$(CH_2)_5OSO_2C_6H_4CH_3$-9-I-*closo*-1,2-$C_2B_{10}H_{10}$



^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.79 (dd, 2H, $C_{ar}H$-C_{ar}-CH_3), 7.38 (dd, 2H, $C_{ar}H$-C_{ar}-S), 4.03 (q, 2H, CH_2-O), 3.88 (s, 0.3H, cage C-*H*), 3.69 (s, 0.7H, cage C-*H*), 2.48 (s, 3H, CH_3-C_{ar}), 2.28 – 2.14 (m, 2H, CH_2-CH_2O), 2.11 – 2.01 (t, 2H, CH_2- C_C), 1.66 (m, 2H, CH_2- CH_2- C_C), 1.53 – 1.30 (2H, m, CH_2-CH_2CH_2O).

^{11}B NMR (160 MHz, $CDCl_3$, decoupled): δ_B -0.72 (d, 1*B*), -7.56 (d, 2*B*), -12.39– -13.67 (hep, 6*B*), -16.48 (s, 0.3*B*), -18.45 (s, 0.7*B*). The presence of two peaks that remain as singlets in the ^{11}B NMR spectrum (-16.48 and -18.45 ppm, respectively) confirms the presence of two positional isomers in 0.3:0.7 ratio (as observed in the ^{1}H NMR spectrum.

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

Reported in Ref [13c] in the manuscript

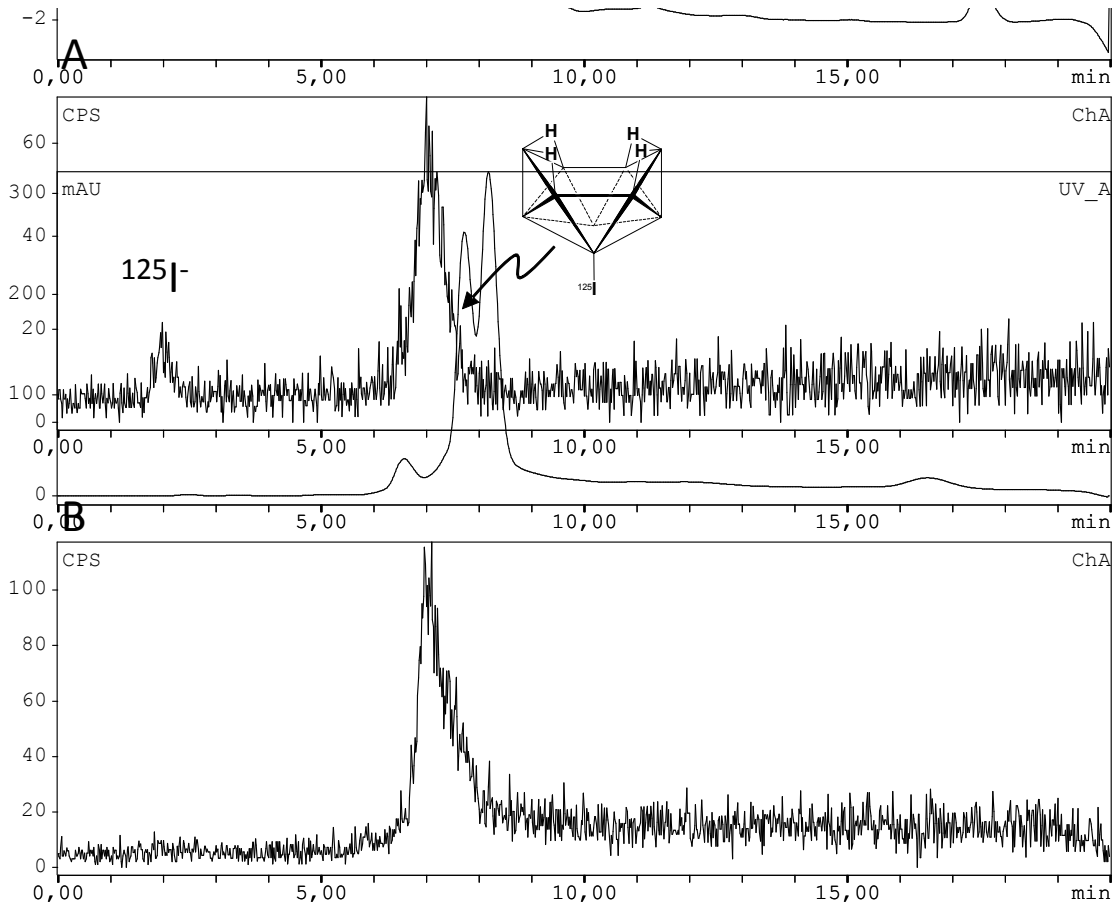


Figure S7: Chromatographic profiles (radiometric detection) for: (A) reaction crude and (B) pure 1-[^{125}I]decaborane.

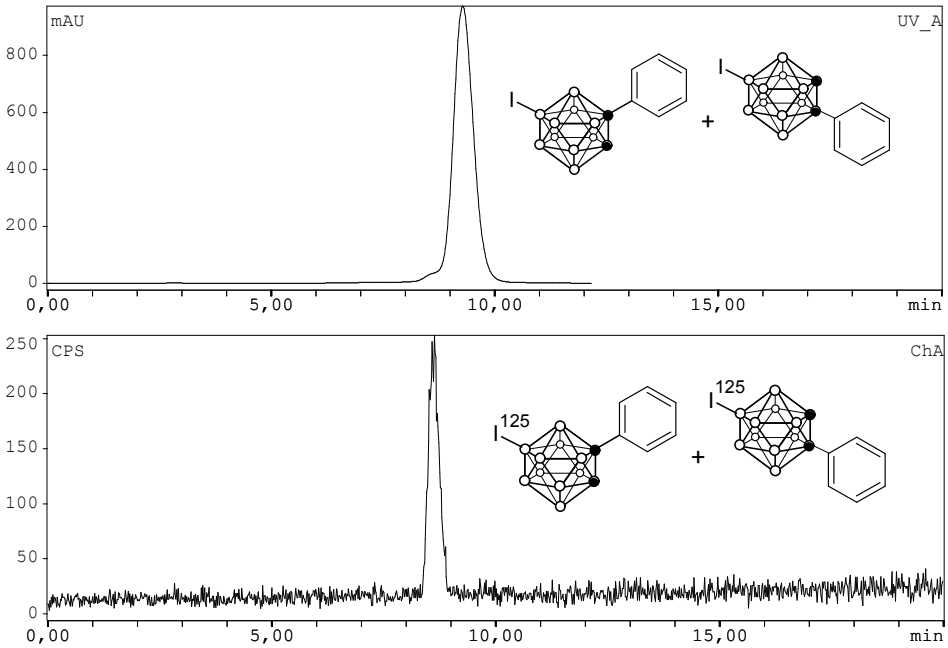


Figure S8: Chromatographic profiles (UV and radiometric detection) for reference compound **8** (top) and purified [^{125}I]**8** (bottom).

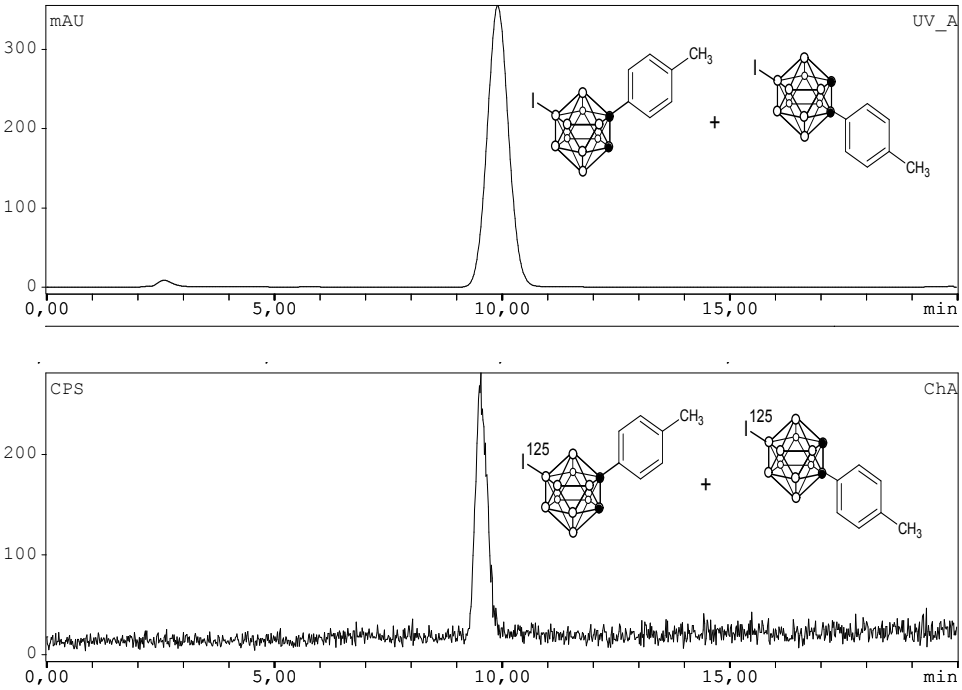


Figure S9: Chromatographic profiles (UV and radiometric detection) for reference compound **9** (top) and purified [^{125}I]**9** (bottom).

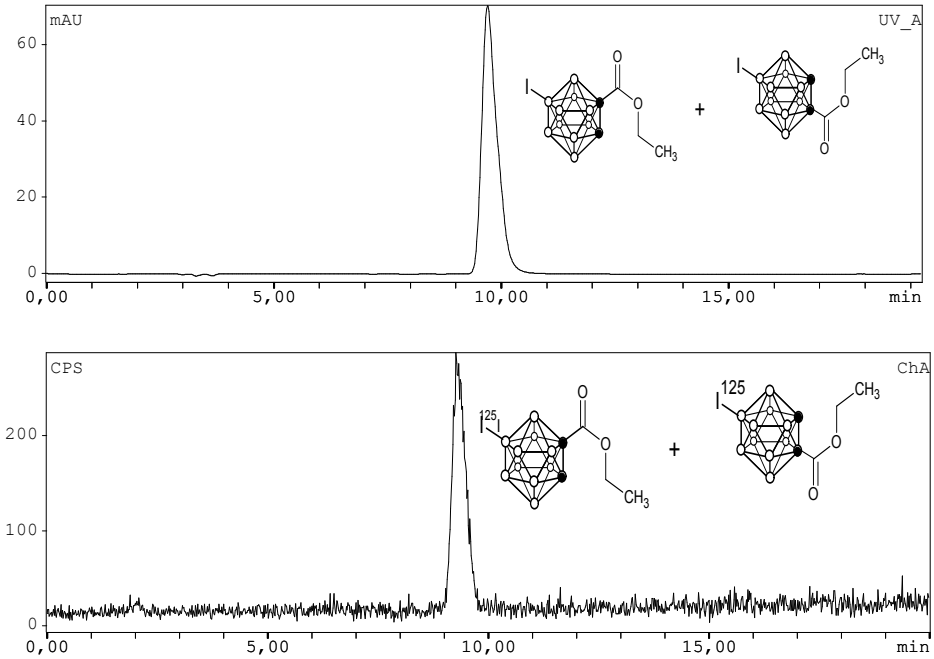


Figure S10: Chromatographic profiles (UV and radiometric detection) for reference compound **10** (top) and purified [^{125}I]**10** (bottom).

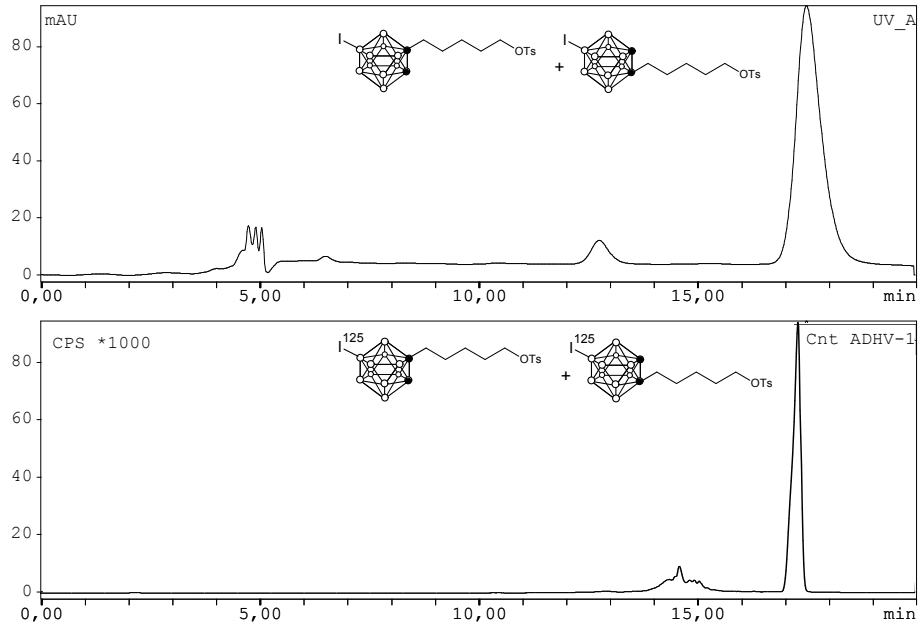


Figure S11: Chromatographic profiles (UV and radiometric detection) for reference compound **11** (top) and purified [^{125}I]**11** (bottom).