■ EXPERIMENTAL AND COMPUTATIONAL SECTION

Synthesis. A solution of 1 (260 mg, 1.26 mmol) prepared according to the literature procedure{1} in benzene (30 ml) was treated with $AlCl_3$ (200 mg, 1.50 mmol) and then with I_2 (500 mg, 1.96 mmol) and the mixture was left stirring at ambient temperature for 24 h. The mixture was then treated carefully with water (20 ml) and CH_2Cl_2 (20 ml) under cooling to 0°C. The organic layer was separated, evaporated, and the residual solid was separated by column (2.5 × 30 cm) chromatography using a mixture of CH_2Cl_2 : hexane (1:1). The elution resulted in the separation of the main fraction of R_F(hexane) = 0.05. This solution was evaporated to dryness and identified by ^{11}B NMR spectroscopy as **4**.

Crystallography. A colorless block-like specimen of C2H7B7ClIP2, approximate dimensions 0.165 mm × 0.278 mm × 0.325 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. Full-sets of diffraction data for **4** were collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K_α radiation; λ = 0.71073 Å) microfocus X-ray (IµS) source, Photon CMOS detector and Oxford Cryosystems cooling device.

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS) Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.730. Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.{2}

A total of 1674 frames were collected. The total exposure time was 1.71 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32315 reflections to a maximum θ angle of 28.32° (0.75 Å resolution), of which 2657 were independent (average redundancy 12.162, completeness = 99.8%, R_{int} = 2.27%, R_{sig} = 1.25%) and 2613 (98.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.9909(6) Å, b = 7.4346(4) Å, c = 13.3364(7) Å, β = 115.7460(10)°, volume = 1070.88(10) Å^3, are based upon the refinement of the XYZ-centroids of 147 reflections above 20 σ(I) with 13.67° < 2θ < 59.91°. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4. The final anisotropic full-matrix least-squares refinement on F^2 with 126 variables converged at R_1 = 1.89%, for the observed data and wR_2 = 5.53% for all data. The goodness-of-fit was 1.379. The largest peak in the final difference electron density synthesis was 0.621 $e^-/Å^3$ and the largest hole was -1.677 $e^-/Å^3$ with an RMS deviation of 0.206 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.053 g/cm^3 and F(000), 616 e^-.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) with C-H and B-H distances of 1.1Å.

Table S1 Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	**y/b**	**z/c**	**U(eq)**
I1	0.39772(2)	0.70440(2)	0.53770(2)	0.01834(6)
Cl1	0.05161(4)	0.73518(7)	0.92019(4)	0.02255(10)
B1	0.78463(17)	0.8683(2)	0.84934(15)	0.0150(3)
B2	0.81303(18)	0.9127(3)	0.73222(16)	0.0177(3)
B3	0.89053(18)	0.7262(2)	0.82726(16)	0.0145(3)
B4	0.77536(17)	0.6345(3)	0.86920(15)	0.0148(3)
B5	0.63681(17)	0.7602(3)	0.80037(16)	0.0144(3)
B6	0.65952(17)	0.9262(2)	0.71893(15)	0.0151(3)
C9	0.65582(15)	0.5590(2)	0.74679(13)	0.0148(3)
B10	0.59340(18)	0.7136(2)	0.65495(16)	0.0142(4)
C11	0.69043(17)	0.8146(2)	0.62125(15)	0.0157(3)
P8	0.80830(4)	0.47697(6)	0.75859(4)	0.01706(10)
P7	0.83665(4)	0.68611(6)	0.65556(4)	0.01806(10)

Table S2 Bond lengths (Å) for **4**

I1-B10	2.184(2)	Cl1-B3	1.786(2)
B1-B2	1.768(3)	B1-B4	1.769(2)
B1-B3	1.772(3)	B1-B6	1.787(3)
B1-B5	1.791(3)	B1-H1	1.12
B2-C11	1.730(3)	B2-B6	1.774(3)
B2-B3	1.836(3)	B2-P7	2.053(2)
B2-H2	1.12	B3-B4	1.832(3)
B3-P8	2.1117(19)	B3-P7	2.113(2)
B4-C9	1.732(2)	B4-B5	1.775(3)
B4-P8	2.0516(18)	B4-H4	1.12
B5-C9	1.715(3)	B5-B6	1.742(3)
B5-B10	1.810(3)	B5-H5	1.12
B6-C11	1.715(2)	B6-B10	1.807(3)
B6-H6	1.12	C9-B10	1.608(2)
C9-P8	1.8681(17)	C9-H9	0.91(3)
B10-C11	1.604(3)	C11-P7	1.8706(19)
C11-H11	0.91(3)	P8-P7	2.1970(6)

Table S3 Bond angles (°) for **4**

B2-B1-B4	111.35(13)	B2-B1-B3	62.45(11)
B4-B1-B3	62.30(10)	B2-B1-B6	59.85(10)

B4-B1-B6	107.55(13)	B3-B1-B6	109.94(13)
B2-B1-B5	107.54(13)	B4-B1-B5	59.81(11)
B3-B1-B5	109.81(13)	B6-B1-B5	58.26(10)
B2-B1-H1	120.3	B4-B1-H1	120.4
B3-B1-H1	119.0	B6-B1-H1	122.6
B5-B1-H1	122.7	C11-B2-B1	105.01(13)
C11-B2-B6	58.60(10)	B1-B2-B6	60.60(10)
C11-B2-B3	105.05(13)	B1-B2-B3	58.88(10)
B6-B2-B3	107.69(13)	C11-B2-P7	58.54(8)
B1-B2-P7	114.09(11)	B6-B2-P7	111.00(12)
B3-B2-P7	65.56(9)	C11-B2-H2	125.9
B1-B2-H2	121.1	B6-B2-H2	121.3
B3-B2-H2	121.7	P7-B2-H2	116.7
B1-B3-Cl1	119.95(12)	B1-B3-B4	58.77(10)
Cl1-B3-B4	122.24(12)	B1-B3-B2	58.67(10)
Cl1-B3-B2	121.42(12)	B4-B3-B2	105.62(13)
B1-B3-P8	111.22(11)	Cl1-B3-P8	119.62(10)
B4-B3-P8	62.22(8)	B2-B3-P8	111.24(11)
B1-B3-P7	111.12(11)	Cl1-B3-P7	119.12(10)
B4-B3-P7	111.24(11)	B2-B3-P7	62.18(9)
P8-B3-P7	62.67(6)	C9-B4-B1	104.90(12)
C9-B4-B5	58.52(10)	B1-B4-B5	60.71(11)
C9-B4-B3	104.94(12)	B1-B4-B3	58.93(10)
B5-B4-B3	107.85(13)	C9-B4-P8	58.44(8)
B1-B4-P8	114.14(11)	B5-B4-P8	110.97(11)
B3-B4-P8	65.60(8)	C9-B4-H4	126.1
B1-B4-H4	121.0	B5-B4-H4	121.2
B3-B4-H4	121.7	P8-B4-H4	116.8
C9-B5-B6	105.84(13)	C9-B5-B4	59.49(10)
B6-B5-B4	109.31(13)	C9-B5-B1	104.70(13)
B6-B5-B1	60.75(11)	B4-B5-B1	59.48(10)
C9-B5-B10	54.19(10)	B6-B5-B10	61.15(10)
B4-B5-B10	102.84(13)	B1-B5-B10	104.77(13)
C9-B5-H5	124.9	B6-B5-H5	120.0
B4-B5-H5	122.3	B1-B5-H5	123.0
B10-B5-H5	125.6	C11-B6-B5	105.95(13)
C11-B6-B2	59.42(11)	B5-B6-B2	109.52(13)
C11-B6-B1	104.82(13)	B5-B6-B1	60.99(11)
B2-B6-B1	59.55(10)	C11-B6-B10	54.11(10)
B5-B6-B10	61.28(11)	B2-B6-B10	102.77(13)
B1-B6-B10	105.04(13)	C11-B6-H6	125.0
B5-B6-H6	119.8	B2-B6-H6	122.4
B1-B6-H6	122.8	B10-B6-H6	125.5
B10-C9-B5	65.92(11)	B10-C9-B4	114.04(13)
B5-C9-B4	61.99(11)	B10-C9-P8	114.35(12)
B5-C9-P8	123.51(11)	B4-C9-P8	69.36(8)

B10-C9-H9	123.3(16)	B5-C9-H9	113.9(16)
B4-C9-H9	113.2(15)	P8-C9-H9	110.3(16)
C11-B10-C9	113.19(15)	C11-B10-B6	60.01(10)
C9-B10-B6	107.56(13)	C11-B10-B5	107.73(14)
C9-B10-B5	59.89(10)	B6-B10-B5	57.57(11)
C11-B10-I1	119.91(12)	C9-B10-I1	121.54(12)
B6-B10-I1	118.69(11)	B5-B10-I1	119.52(12)
B10-C11-B6	65.88(11)	B10-C11-B2	114.07(14)
B6-C11-B2	61.98(11)	B10-C11-P7	114.15(11)
B6-C11-P7	123.37(12)	B2-C11-P7	69.39(9)
B10-C11-H11	124.1(15)	B6-C11-H11	113.9(16)
B2-C11-H11	112.4(16)	P7-C11-H11	110.0(15)
C9-P8-B4	52.20(7)	C9-P8-B3	90.32(7)
B4-P8-B3	52.18(7)	C9-P8-P7	97.35(5)
B4-P8-P7	100.15(6)	B3-P8-P7	58.69(5)
C11-P7-B2	52.07(8)	C11-P7-B3	90.34(8)
B2-P7-B3	52.26(8)	C11-P7-P8	97.54(6)
B2-P7-P8	100.19(6)	B3-P7-P8	58.64(5)

Table S4 Anisotropic atomic displacement parameters (Å2) for **4**. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
I1	0.01330(8)	0.02104(9)	0.01519(8)	0.00033(3)	0.00108(6)	0.00131(3)
Cl1	0.0128(2)	0.0279(2)	0.0216(2)	-0.00378(17)	0.00248(17)	0.00061(16)
B1	0.0167(8)	0.0135(8)	0.0143(8)	-0.0011(6)	0.0065(7)	0.0006(6)
B2	0.0181(9)	0.0164(8)	0.0200(9)	0.0014(7)	0.0095(7)	-0.0009(7)
B3	0.0130(8)	0.0160(8)	0.0139(8)	-0.0009(6)	0.0051(7)	0.0009(6)
B4	0.0150(8)	0.0166(9)	0.0118(7)	0.0004(6)	0.0051(6)	-0.0002(7)
B5	0.0134(8)	0.0162(8)	0.0135(8)	0.0010(7)	0.0057(7)	0.0003(7)
B6	0.0157(8)	0.0144(8)	0.0157(8)	0.0003(6)	0.0073(7)	0.0012(6)
C9	0.0152(7)	0.0125(7)	0.0143(7)	0.0005(6)	0.0042(6)	-0.0019(6)
B10	0.0131(9)	0.0161(9)	0.0111(8)	0.0004(6)	0.0033(7)	0.0010(6)
C11	0.0160(8)	0.0188(8)	0.0120(8)	0.0044(6)	0.0058(6)	0.0032(6)
P8	0.0184(2)	0.01265(19)	0.0165(2)	-0.00144(15)	0.00422(17)	0.00343(15)
P7	0.0179(2)	0.0244(2)	0.0140(2)	-0.00045(15)	0.00891(18)	0.00355(16)

Table **S5** Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **4**

	x/a	**y/b**	**z/c**	**U(eq)**
H1	0.8203	0.9620	0.9224	0.018
H2	0.8647	1.0360	0.7283	0.021
H4	0.8025	0.5773	0.9543	0.018
H5	0.5710	0.7840	0.8382	0.017
H6	0.6082	1.0567	0.7046	0.018
H9	0.612(2)	0.467(4)	0.757(2)	0.027(6)
H11	0.669(2)	0.877(3)	0.557(2)	0.024(6)

Computational details. Magnetic shielding was calculated using the GIAO-MP2 method incorporated into Gaussian09{3} utilizing the IGLO-II basis with the MP2/cc-pVTZ geometry. Electrostatic potentials were computed at the HF/cc-pVDZ level (for I basis set in Ref. {4}) using Gaussian09 and Molekel4.3{5} programs. It has recently been shown that this basis set size is sufficient for these purposes. {6}

Interaction energy (ΔE) values were calculated for all pairwise interactions the crystal structures of 4. All hydrogen atoms were optimized using DFT-D3/BLYP/DZVP method prior the energy calculations.{7} ΔE were evaluated at MP2.5/CBS using the Turbomole 6.6{8} and Cuby4{9} programs. MP2.5/CBS was calculated as the sum of MP2/CBS energy and MP2.5 correction. MP2/CBS was estimated by the extrapolation from cc-pVTZ to cc-pVQZ (for I atoms cc-pVTZ-PP basis set with pseudopotential was used).{10} The MP2.5 correction term was calculated using the aug-cc-pVDZ basis set. Counterpoise corrections for basis set superposition error (BSSE) were used for all energy calculations.

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