Observation of Aliphatic C-H···X Hydrogen Bonds in Imidazolium Ionic Liquids

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Supporting Information

1. Synthesis

1.1. General

Deuterated 1-*n*-butyl-3-methylimidazolium chloride isotopologues **1a**-**1e** were prepared as described.[8] Potassium hexafluorophosphate and sodium tetrafluoroborate were purchased from Sigma-Aldrich, Inc. (St. Louis, MO, USA) and used as received. IR spectra were recorded on a Thermo Electron Nicolet Avatar 370 DTGS FT-IR spectrophotometer. Routine NMR experiments were performed on Bruker AVANCE 400 and AVANCE III 400 spectrometers operating at ^{1}H and ^{13}C frequencies of 400.13 and 100.62 MHz, respectively, using CD_2Cl_2 as solvent. Chemical shifts (δ) are in ppm relative to the residual solvent signal (5.32 and 54.0 ppm for ^{1}H and ^{13}C, respectively), and coupling constants (*J*) are reported in Hz. HR-MS spectra were recorded on a Thermo Scientific Exactive Orbitrap mass spectrometer using ASAP ionization.[S1]

1.2. Preparation of 1-n-butyl-3-methylimidazolium hexafluorophosphate isotopologues.[S2]

Potassium hexafluorophosphate (1.1 g, 6.0 mmol) was added to a solution of the appropriate 1-*n*-butyl-3-methylimidazolium chloride isotopologue (1.0 g, 5.7 mmol) in distilled water (1.0 mL) in a 10 mL vial fitted with a teflon-lined cap. Following phase separation, the reaction was stirred vigorously for 3 h, diluted with dichloromethane (1 mL) and washed with distilled water (3 × 0.5 mL). The organic layer was further diluted with dichloromethane (5.0 mL), and the resulting solution was dried with $MgSO_4$. The solvent was then removed *in vacuo* to yield the desired hexafluorophosphate salts as colorless to pale yellow oils. A Mohr titration of the product indicated that it was free of chloride ion.[S2]

*1.2.1. [1",1",1"-d_3]-1-n-Butyl-3-methylimidazolium hexafluorophosphate (**2a**)*: Obtained from **1a** in 88% yield. IR (NaCl plate, cm^{-1}): 3169, 3117, 2966, 2939, 2878, 1568, 1468, 1386, 1336, 1172, 1114, 840. ^{1}H NMR: δ 8.46 (1H, bdd, *J* = 2.0, *J* = 2.0, H2), 7.29 (1H, ABX, J_{AX} = 2.0, J_{AB} = 1.7, H4), 7.28 (1H, ABX, J_{AX} = 2.0, J_{AB} = 1.7, H5), 4.15 (3H, t, *J* = 7.4, H1"), 1.86 (2H, tt, *J* = 7.6, *J* = 7.4, H2'), 1.37 (2H, tq, *J* = 7.6, *J* = 7.4, H3'), 0.96 (3H, t, *J* = 7.4, H4'). ^{13}C NMR: δ 136.2 (C2), 124.2 (C4), 122.8 (C5), 50.6 (C1'), 36.3 (hep, $^{1}J_{CD}$ = 21.9, C1"), 32.3 (C2'), 19.9 (C3'), 13.6 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ([M-PF_6]$^+$): 142.1419, found: 142.1416.

*1.2.2. [1',1'-d_2]-1-n-Butyl-3-methylimidazolium hexafluorophosphate (**2b**)*: Obtained from **1b** in 91% yield. IR (NaCl plate, cm^{-1}): 3171, 3118, 2966, 2938, 2878, 1575, 1563, 1469, 1432, 1179, 1140, 1113, 841. ^{1}H NMR: δ 8.46 (1H, ddq, *J* = 2.0, *J* = 2.0, *J* = 0.6, H2), 7.29 (1H, ABX, J_{Ax} = 2.0, J_{AB} = 1.7, H4), 7.28 (1H, ABX, J_{AX} = 2.0, J_{AB} = 1.7, H5), 3.91 (3H, d, *J* = 0.6, H1"), 1.84 (2H, bt, *J* = 7.5, H2'), 1.36 (2H, tq, *J* = 7.5, *J* = 7.4, H3'), 0.96 (3H, t, *J* = 7.4, H4'). ^{13}C NMR: δ 136.2 (C2), 124.2 (C4), 122.8 (C5), 50.0 (quin, $^{1}J_{CD}$ = 21.8, C1'), 36.9 (C1"), 32.1 (C2'), 19.8 (C3'), 13.6 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ([M-PF_6]$^+$): 141.1352, found: 141.1352.

*1.2.3. [2',2'-d_2]-1-n-Butyl-3-methylimidazolium hexafluorophosphate (**2c**)*: Obtained from **1c** in 85% yield. IR (NaCl plate, cm^{-1}): 3172, 3124, 2965, 2937, 2878, 1576, 1463, 1432, 1385, 1336, 1171, 1113, 839. ^{1}H NMR: δ 8.46 (1H, ddq, J = 2.0, J = 2.0, J = 0.6, H2), 7.29 (1H, ABX, J_{AX} = 2.0, J_{AB} = 1.7, H4), 7.28 (1H, ABX, J_{AX} = 2.0, J_{AB} = 1.7, H5), 4.14 (2H, bs, H1'), 3.91 (3H, d, J = 0.6, H1"), 1.35 (2H, bq, J = 7.4, H3'), 0.96 (3H, t, J = 7.4, H4'). ^{13}C NMR: δ 136.2 (C2), 124.2 (C4), 122.8 (C5), 50.4 (C1'), 36.9 (C1"), 31.6 (quin, $^1J_{CD}$ = 19.7, C2'), 19.7 (C3'), 13.5 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ($[M\text{-}PF_6]^+$): 141.1352, found: 141.1353.

*1.2.4. [3',3'-d_2]-1-n-Butyl-3-methylimidazolium hexafluorophosphate (**2d**)*: Obtained from **1d** in 88% yield. IR (NaCl plate, cm^{-1}): 3172, 3125, 2965, 2937, 2877, 1575, 1461, 1432, 1385, 1168, 1113, 841. ^{1}H NMR: δ 8.47 (1H, bdd, J = 1.9, J = 1.9, H2), 7.29 (1H, ABX, J_{AX} = 1.9, J_{AB} = 1.8, H4), 7.28 (1H, ABX, J_{AX} = 1.9, J_{AB} = 1.8, H5), 4.15 (2H, bt, J = 7.4, H1'), 3.92 (3H, bs, H1"), 1.83 (2H, tt, J = 7.4, $^3J_{HD}$ = 1.1, H2'), 0.94 (3H, t, $^3J_{HD}$ = 1.1, H4'). ^{13}C NMR: δ 136.2 (C2), 124.2 (C4), 122.8 (C5), 50.6 (C1'), 36.9 (C1"), 32.1 (C2'), 19.2 (quin, $^1J_{CD}$ = 19.3, C3'), 13.4 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ($[M\text{-}PF_6]^+$): 141.1352, found: 141.1353.

*1.2.5. [4',4',4',-d_3]-1-n-Butyl-3-methylimidazolium hexafluorophosphate (**2e**)*: Obtained from **1e** in 86% yield. IR (NaCl plate, cm^{-1}): 3171, 3125, 2939, 2872, 2225, 2079, 1575, 1462, 1432, 1390, 1340, 1168, 1114, 839. ^{1}H NMR: δ 8.46 (1H, bdd, J = 1.9, J = 1.9, H2), 7.29 (1H, ABX, J_{AX} = 1.9, J_{AB} = 1.8, H4), 7.28 (1H, ABX, J_{AX} = 1.9, J_{AB} = 1.8, H5), 4.15 (2H, t, J = 7.4, H1'), 3.91 (3H, s, H1"), 1.85 (2H, tt, J = 7.7, J = 7.4, H2'), 1.34 (2H, tt, J = 7.7, $^3J_{HD}$ = 1.1, H3'). ^{13}C NMR: δ 136.2 (C2), 124.2 (C4), 122.8 (C5), 50.6 (C1"), 36.8 (C1'), 32.2 (C2'), 19.6 (C3'), 12.7 (hep, $^1J_{CD}$ = 19.2, C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ($[M\text{-}PF_6]^+$): 142.1419, found: 142.1416.

1.3. Preparation of 1-n-butyl-3-methylimidazolium tetrafluoroborate isotopologues.[S2]

Sodium tetrafluoroborate (0.8 g, 7.3 mmol) was added to a solution of the appropriate 1-*n*-butyl-3-methylimidazolium chloride isotopologue (1.2 g, 6.8 mmol) in distilled water (1.4 mL) in a 10 mL vial fitted with a teflon-lined cap. The mixture was stirred until phase separation occurred, shaken vigorously for an additional 10 min, and extracted with dichloromethane (2 × 1.5 mL). The combined organic layers were washed with a 4.5 M solution of sodium tetrafluoroborate (0.8 mL), dried with $MgSO_4$, and filtered through celite. The solvent was removed under reduced pressure to yield the desired tetrafluororborate salts as colorless to pale yellow oils. A Mohr titration of the product indicated that it was free of chloride ion.[S2]

*1.3.1. [1",1",1"-d_3]-1-n-Butyl-3-methylimidazolium tetrafluoroborate (**3a**)*: Obtained from **1a** in 91% yield. IR (NaCl plate, cm^{-1}): 3155, 3114, 2964, 2939, 2879, 1568, 1466, 1386, 1336, 1285, 1174, 1064. ^{1}H NMR: δ 8.74 (1H, bdd, J = 1.9, J = 1.9, H2), 7.32 (1H, dd, J = 1.9, J = 1.8, H4), 7.30 (1H, dd, J = 1.9, J = 1.8, H5), 4.17 (2H, t, J = 7.4, H1'), 1.85 (2H, tt, J = 7.6, J = 7.4, H2'), 1.36 (2H, tq, J = 7.6, J = 7.4, H3'), 0.95 (3H, t, J = 7.4, H4'). ^{13}C NMR: δ 136.3 (C2), 123.6 (C4), 122.1 (C5), 49.9 (C1'), 35.6 (hep, $^1J_{CD}$ = 22.0, C1"), 31.8 (C2'), 19.3 (C3'), 13.1 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ($[M\text{-}BF_4]^+$): 142.1419, found: 142.1411.

*1.3.2. [1',1'-d_2]-1-n-Butyl-3-methylimidazolium tetrafluoroborate (**3b**)*: Obtained from **1b** in 89% yield. IR (NaCl plate, cm^{-1}): 3157, 3115, 2964, 2937, 2877, 1575, 1562, 1468, 1433, 1374, 1331, 1285, 1249, 1180. ^{1}H NMR: δ 8.75 (1H, bdd, J = 1.9, J = 1.9, H2), 7.32 (1H, dd, J = 1.9, J = 1.8, H4), 7.30 (1H, dd, J = 1.9, J = 1.8, H5), 3.93 (3H, bs, H1"), 1.84 (2H, bt, J = 7.6, H2'), 1.36 (2H, tq, J = 7.6, J =

7.4, H3'), 0.96 (3H, t, J = 7.4, H4'). ^{13}C NMR: δ 136.9 (C2), 124.1 (C4), 122.6 (C5), 49.9 (quin, $^{1}J_{CD}$ = 21.8, C1'), 36.8 (C1"), 32.2 (C2'), 19.8 (C3'), 13.6 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{13}D_2N_2$ ([M-BF_4]$^+$): 141.1356, found: 141.1350.

*1.3.3. [2',2'-d_2]-1-n-Butyl-3-methylimidazolium tetrafluoroborate (**3c**)*: Obtained from **1c** in 90% yield. IR (NaCl plate, cm^{-1}): 3166, 3124, 2965, 2938, 2876, 1575, 1464, 1431, 1385, 1335, 1286, 1173, 1049. ^{1}H NMR: δ 8.74 (1H, bdd, J = 1.9, J = 1.9, H2), 7.32 (1H, dd, J = 1.9, J = 1.8, H4), 7.30 (1H, dd, J = 1.9, J = 1.8, H5), 4.16 (2H, bs, H1'), 3.93 (3H, s, H1"), 1.35 (2H, bq, J = 7.4, H3'), 0.95 (3H, t, J = 7.4, H4'). ^{13}C NMR: δ 136.9 (C2), 124.1 (C4), 122.7 (C5), 50.3 (C1'), 36.8 (C1"), 31.6 (quin, $^{1}J_{CD}$ = 19.7, C2'), 19.7 (C3'), 13.6 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{13}D_2N_2$ ([M-BF_4]$^+$): 141.1356, found: 141.1351.

*1.3.4. [3',3'-d_2]-1-n-Butyl-3-methylimidazolium tetrafluoroborate (**3d**)*: Obtained from **1d** in 88% yield. IR (NaCl plate, cm^{-1}): 3157, 3132, 2964, 2935, 2874 1575, 1461, 1432, 1383, 1286, 1171, 1051. ^{1}H NMR: δ 8.74 (1H, bdd, J = 1.9, J = 1.9, H2), 7.32 (1H, dd, J = 1.9, J = 1.8, H4), 7.30 (1H, dd, J = 1.9, J = 1.8, H5), 4.17 (2H, bt, J = 7.4, H1'), 3.93 (3H, s, H1"), 1.84 (2H, tt, J = 7.4, $^{3}J_{HD}$ = 1.1, H2'), 0.94 (3H, t, $^{3}J_{HD}$ = 1.1, H4'). ^{13}C NMR: δ 136.9 (C2), 124.1 (C4), 122.7 (C5), 50.4 (C1'), 36.8 (C1"), 32.2 (C2'), 19.2 (quin, $^{1}J_{CD}$ = 19.3, C3'), 13.4 (C4'). HR-MS (ASAP): m/z calcd for $C_8H_{13}D_2N_2$ ([M-BF_4]$^+$): 141.1356, found: 141.1352.

*1.3.5. [4',4',4',-d_3]-1-n-Butyl-3-methylimidazolium tetrafluoroborate (**3e**)*: Obtained from **1e** in 88% yield. IR (NaCl plate, cm^{-1}): 3164, 3122, 2937, 2870, 2222, 2077, 1574, 1462, 1432, 1339, 1286, 1170, 1061. ^{1}H NMR: δ 8.75 (1H, bdd, J = 1.9, J = 1.9, H2), 7.32 (1H, dd, J = 1.9, J = 1.8, H4), 7.30 (1H, dd, J = 1.9, J = 1.8, H5), 4.17 (2H, t, J = 7.4, H1'), 3.93 (3H, s, H1"), 1.85 (2H, tt, J = 7.7, J = 7.4, H2'), 1.34 (2H, tt, J = 7.7, $^{3}J_{HD}$ = 1.1, H3'). ^{13}C NMR: δ 136.9 (C2), 124.1 (C4), 122.7 (C5), 50.5 (C1"), 36.8 (C1'), 32.3 (C2'), 19.6 (C3'), 12.7 (hep, $^{1}J_{CD}$ = 19.2, C4'). HR-MS (ASAP): m/z calcd for $C_8H_{12}D_3N_2$ ([M-BF_4]$^+$): 142.1419, found: 142.1415.

2. Isotope Effect on Nuclear Shielding Measurements

2.1. Sample preparation

All imidazolium isotopologues were dried under reduced pressure (< 1 x 10^{-3} mBar) at 50 ºC with constant stirring and regular argon exchanges for 48 hours. The samples were then placed in an argon-filled glove box and allowed to equilibrate for 24 hours. After that time they were transferred to 5 mm NMR tubes, and these were subsequently fitted with 60 μL coaxial inserts containing reference solutions. For hexafluorophosphate salts **2**-**2e**, the reference was 1M Na_2HPO_4 and trifluoroacetic acid in D_2O, while for tetrafluoroborate salts **3**-**3e** it was 1M $NaBF_4$ and trifluoroacetic acid in D_2O. In addition, systems containing **2e** and **2** or **3e** and **3** in the outer tube and coaxial insert, respectively, were prepared. All sample systems were tightly sealed and used in NMR measurements within two hours following preparation.

2.3. NMR experiments

NMR experiments were carried out at 30.0 ºC on a Bruker Avance III 400 NMR spectrometer operating at ^{1}H, ^{11}B, ^{19}F, and ^{31}P frequencies of 400.13, 128.39, 376.50, and 161.98 MHz, respectively. ^{1}H, ^{11}B, ^{19}F, and ^{31}P spectra were referenced against the ^{1}H resonance of HDO, the ^{11}B resonance of 1M $NaBF_4$ in D_2O, the ^{19}F resonance of 1M trifluoroacetic acid or 1M $NaBF_4$ in D_2O, and the ^{31}P

resonance of 1M Na_2HPO_4 in D_2O, respectively. In all cases the reference signal was arbitrarily set to 0 ppm. Acquisition times, spectral widths, and data sizes were adjusted to obtain a minimum resolution of 0.2 Hz per point. The data was zero-filled to a final resolution of 0.1 Hz per point prior to Fourier transformation. For the samples that contained **2e** and **2** or **3e** and **3** in the outer tube and coaxial insert, respectively, field-frequency lock was achieved against the deuterium signal of the labeled imidazolium salt. The data recorded for three different samples of each isotopologue was averaged in the estimation of Δ(H,D) values, and the results are summarized in **Tables S1-S6** and **Tables S7-S12**.

3. References

S1. C. N. McEwen, R. G. McKay and B. S. Larsen, *Anal. Chem*., 2005, **77**, 7826.
S2. X. Creary and E. D. Willis, *Org. Synth.*, 2005, **82***,* 166.

Table S1. ^{1}H, ^{31}P, and ^{19}F chemical shifts for **2**. Data for repeats obtained for three different samples and their averages are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1428.5	1428.7	1428.6	1428.6 ± 0.1	-
H-4	1031.3	1031.5	1031.3	1031.4 ± 0.1	-
H-5	1016.4	1016.6	1016.5	1016.5 ± 0.1	-
H-1’	-276.8	-276.6	-276.7	-276.7 ± 0.1	-
H-2’	-1206.5	-1206.3	-1206.4	-1206.4 ± 0.1	-
H-3’	-1425.0	-1424.8	-1424.9	-1424.9 ± 0.1	-
H-4’	-1600.8	-1600.6	-1600.7	-1600.7 ± 0.1	-
H-1”	-384.0	-383.8	-383.9	-383.9 ± 0.1	-
^{31}P	-23411.3	-23411.4	-23410.9	-23411.2 ± 0.3	-
^{19}F	1422.4	1422.3	1422.4	1422.4 ± 0.1	-

Table S2. ^{1}H, ^{31}P, and ^{19}F chemical shift data for **2a**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **2** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1427.9	1427.8	1427.9	1427.9 ± 0.1	1.7 ± 0.5
H-4	1030.0	1029.9	1030.1	1030.0 ± 0.1	3.5 ± 0.5
H-5	1015.2	1015.1	1015.2	1015.2 ± 0.1	3.2 ± 0.5
H-1’	-278.7	-278.8	-278.7	-278.7 ± 0.1	5.0 ± 0.5
H-2’	-1209.2	-1209.3	-1209.2	-1209.2 ± 0.1	7.0 ± 0.5
H-3’	-1435.4	-1435.6	-1435.5	-1435.5 ± 0.1	26.5 ± 0.5
H-4’	-	-	-	-	-
H-1”	-385.4	-385.5	-385.4	-385.4 ± 0.1	3.7 ± 0.5
^{31}P	-23411.9	-23411.6	-23411.7	-23411.7 ± 0.2	3.1 ± 3.1
^{19}F	1419.6	1419.7	1419.8	1419.7 ± 0.1	7.2 ± 0.5

Table S3. ^{1}H, ^{31}P, and ^{19}F chemical shift data for **2b**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **2** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1427.9	1428.4	1428.3	1428.2 ± 0.3	1.0 ± 1.0
H-4	1030.2	1030.7	1030.7	1030.5 ± 0.3	2.0 ± 1.0
H-5	1015.6	1016.1	1016.0	1015.9 ± 0.3	1.5 ± 1.0
H-1’	-278.4	-277.9	-278.0	-278.1 ± 0.3	3.5 ± 1.0
H-2’	-1213.5	-1213.0	-1213.1	-1213.2 ± 0.3	17.0 ± 1.0
H-3’	-	-	-	-	-
H-4’	-1608.8	-1608.3	-1608.3	-1608.5 ± 0.3	19.5 ± 1.0
H-1”	-384.9	-384.4	-384.5	-384.6 ± 0.3	1.7 ± 1.0
^{31}P	-23410.8	-23410.8	-23411.0	-23410.9 ± 0.1	-1.9 ± 2.5
^{19}F	1418.9	1419.1	1418.5	1418.8 ± 0.3	9.6 ± 1.1

Table S4. ^{1}H, ^{31}P, and ^{19}F chemical shift data for **2c**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **2** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1429.6	1429.1	1429.6	1429.4 ± 0.3	-2.0 ± 1.0
H-4	1031.9	1031.4	1031.9	1031.7 ± 0.3	-1.0 ± 1.0
H-5	1017.3	1016.8	1017.3	1017.1 ± 0.3	-1.5 ± 1.0
H-1’	-280.6	-281.1	-280.5	-280.7 ± 0.3	10.0 ± 1.0
H-2’	-	-	-	-	-
H-3’	-1429.1	-1429.6	-1429	-1429.2 ± 0.3	10.7 ± 1.0
H-4’	-1600.8	-1601.3	-1600.8	-1601.0 ± 0.3	0.7 ± 1.0
H-1”	-383.3	-384.1	-383.2	-383.5 ± 0.5	-1.0 ± 1.5
^{31}P	-23410.4	-23410.7	-23410.4	-23410.5 ± 0.2	-4.3 ± 3.1
^{19}F	1418.9	1418.8	1418.6	1418.8 ± 0.2	9.6 ± 0.8

Table S5. ^{1}H, ^{31}P, and ^{19}F chemical shift data for **2d**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **2** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1428.8	1428.9	1429.1	1428.9 ± 0.2	-0.7 ± 0.7
H-4	1031.4	1031.5	1031.7	1031.5 ± 0.2	-0.2 ± 0.7
H-5	1016.8	1017.0	1017.1	1017.0 ± 0.2	-1.2 ± 0.7
H-1’	-	-	-	-	-
H-2’	-1211.7	-1211.4	-1211.3	-1211.5 ± 0.2	12.7 ± 0.7
H-3’	-1425.2	-1425.0	-1424.9	-1425.0 ± 0.2	0.2 ± 0.7
H-4’	-1600.5	-1600.3	1600.2	-1600.3 ± 0.2	-1.0 ± 0.7
H-1”	-383.5	-383.3	-383.2	-383.3 ± 0.2	-1.5 ± 0.7
^{31}P	23411.3	23411.5	23411.4	23411.4 ± 0.1	-1.2 ± 2.5
^{19}F	1418.9	1418.8	1418.5	1418.7 ± 0.2	9.8 ± 0.8

Table S6. ^{1}H, ^{31}P, and ^{19}F chemical shift data for **2e**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **2** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1427.5	1427.5	1427.9	1427.6 ± 0.2	2.5 ± 0.7
H-4	1030.8	1030.7	1031.1	1030.9 ± 0.2	1.2 ± 0.7
H-5	1015.5	1015.4	1015.8	1015.6 ± 0.2	2.2 ± 0.7
H-1’	-277.1	-277.2	-276.8	-277.0 ± 0.2	0.7 ± 0.7
H-2’	-1207.1	-1207.1	-1206.7	-1207.0 ± 0.2	1.5 ± 0.7
H-3’	-1425.5	-1425.5	-1425.1	-1425.4 ± 0.2	1.2 ± 0.7
H-4’	-1601.2	-1601.2	-1600.8	-1601.1 ± 0.2	1.0 ± 0.7
H-1”	-	-	-	-	-
^{31}P	-23410.8	-23410.8	-23410.8	-23410.8 ± 0.0	-2.5 ± 1.9
^{19}F	1412.6	1412.7	1412.6	1412.6 ± 0.1	26.0 ± 0.5

Table S7. ^{1}H, ^{11}B, and ^{19}F chemical shifts for **3**. Data for repeats obtained for three different samples and their averages are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1362.6	1362.5	1362.6	1362.6 ± 0.1	-
H-4	927.9	927.8	927.9	927.9 ± 0.1	-
H-5	907.0	906.9	907.0	907.0 ± 0.1	-
H-1’	-420.5	-420.6	-420.5	-420.5 ± 0.1	-
H-2’	-1375.5	-1375.6	-1375.4	-1375.5 ± 0.1	-
H-3’	-1595.8	-1596.0	-1595.8	-1595.9 ± 0.1	-
H-4’	-1770.7	-1770.8	-1770.7	-1770.7 ± 0.1	-
H-1”	-531.2	-531.3	-531.1	-531.2 ± 0.1	-
^{11}B	42.8	42.8	42.9	42.8 ± 0.1	-
^{19}F	-27941.0	-27940.9	-27940.9	-27940.9 ± 0.1	-

Table S8. ^{1}H, ^{11}B, and ^{19}F chemical shift data for **3a**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **3** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1362.8	1362.3	1362.9	1362.7 ± 0.3	-0.2 ± 1.0
H-4	928.3	927.8	927.4	927.8 ± 0.5	0.0 ± 1.5
H-5	907.4	906.9	906.5	906.9 ± 0.5	0.0 ± 1.5
H-1’	-420.4	-420.9	-421.3	-420.9 ± 0.5	0.7 ± 1.5
H-2’	-1375.8	-1376.3	-1376.7	-1376.3 ± 0.5	2.0 ± 1.5
H-3’	-1604.0	-1604.6	-1604.9	-1604.5 ± 0.5	21.5 ± 1.5
H-4’	-	-	-	-	-
H-1”	-530.5	-531.1	-531.5	-531.0 ± 0.5	-0.5 ± 1.5
^{11}B	43.1	42.9	42.8	42.9 ± 0.2	0.8 ± 2.3
^{19}F	-27944.2	-27944.2	-27944.5	-27944.3 ± 0.2	9.0 ± 0.8

Table S9. ^{1}H, ^{11}B, and ^{19}F chemical shift data for **3b**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **3** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1361.6	1361.4	1361.3	1361.4 ± 0.2	2.7 ± 0.7
H-4	927.3	927.0	926.9	927.1 ± 0.2	2.0 ± 0.7
H-5	906.5	906.3	906.2	906.3 ± 0.2	1.5 ± 0.7
H-1’	-421.4	-421.6	-421.7	-421.6 ± 0.2	2.5 ± 0.7
H-2’	-1381.7	-1381.9	-1381.9	-1381.8 ± 0.1	15.7 ± 0.5
H-3’	-	-	-	-	-
H-4’	-1777.8	-1778.0	-1778.1	-1778.0 ± 0.2	18.0 ± 0.7
H-1”	-531.3	-531.5	-531.7	-531.5 ± 0.2	0.7 ± 0.7
^{11}B	42.6	42.6	42.6	42.6 ± 0.0	-1.6 ± 0.8
^{19}F	-27945.0	-27944.7	-27944.6	-27944.8 ± 0.2	10.1 ± 0.8

Table S10. ^{1}H, ^{11}B, and ^{19}F chemical shift data for **3c**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **3** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1362.6	1362.1	1362.5	1362.4 ± 0.3	0.5 ± 1.0
H-4	928.4	927.9	928.3	928.2 ± 0.3	-0.7 ± 1.0
H-5	907.6	907.1	907.5	907.4 ± 0.3	-1.0 ± 1.0
H-1’	-424.3	-424.8	-424.4	-424.5 ± 0.3	10.0 ± 1.0
H-2’	-	-	-	-	-
H-3’	-1599.5	-1600.1	-1599.6	-1599.7 ± 0.3	9.7 ± 1.0
H-4’	-1770.2	-1770.7	-1770.3	-1770.4 ± 0.3	-0.7 ± 1.0
H-1”	-530.2	-530.7	-530.4	-530.4 ± 0.3	-2.0 ± 1.0
^{11}B	43.1	43.0	43.0	43.0 ± 0.1	1.6 ± 1.6
^{19}F	-27945.7	-27945.2	-27945.7	-27945.5 ± 0.3	12.2 ± 1.1

Table S11. ^{1}H, ^{11}B, and ^{19}F chemical shift data for **3d**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **3** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1363.3	1363.4	1363.6	1363.4 ± 0.2	-2.2 ± 0.7
H-4	928.4	928.4	928.6	928.5 ± 0.1	-1.5 ± 0.5
H-5	907.8	907.9	908.1	907.9 ± 0.2	-2.5 ± 0.7
H-1’	-	-	-	-	-
H-2’	-1379.8	-1380.0	-1379.6	-1379.8 ± 0.2	10.7 ± 0.7
H-3’	-1595.4	-1595.2	-1595.1	-1595.2 ± 0.2	-1.5 ± 0.7
H-4’	-1769.9	-1769.8	-1769.6	-1769.8 ± 0.2	-2.5 ± 0.7
H-1”	-530.1	-530.0	-529.9	-530.0 ± 0.1	-3.0 ± 0.5
^{11}B	43.1	43.0	43.3	43.1 ± 0.2	2.3 ± 2.3
^{19}F	-27950.8	-27950.7	-27950.9	-27950.8 ± 0.1	26.3 ± 0.5

Table S12. ^{1}H, ^{11}B, and ^{19}F chemical shift data for **3e**. Data for repeats obtained for three different samples, their averages, and H/D isotope effects observed with respect to **3** for all nuclei are reported.

Nuclei	δ (Hz)				Δ(H,D) ± s.d. (ppb)
	Repeat 1	Repeat 2	Repeat 3	Average ± s.d.	
H-2	1361.2	1361.0	1361.2	1361.1 ± 0.1	3.5 ± 0.5
H-4	927.2	927.0	927.3	927.2 ± 0.2	1.7 ± 0.7
H-5	905.8	905.6	905.8	905.7 ± 0.1	3.0 ± 0.5
H-1’	-420.9	-421.1	-420.8	-420.9 ± 0.2	1.0 ± 0.7
H-2’	-1375.8	-1376.1	-1375.8	-1375.9 ± 0.2	1.0 ± 0.7
H-3’	-1596.0	-1596.4	-1596.0	-1596.1 ± 0.2	0.7 ± 0.7
H-4’	-1771.0	-1771.2	-1770.9	-1771.0 ± 0.2	0.7 ± 0.7
H-1”	-	-	-	-	-
^{11}B	42.7	42.6	42.7	42.7 ± 0.1	-1.6 ± 1.6
^{19}F	-27955.5	-27955.1	-27955.5	-27955.4 ± 0.2	38.2 ± 0.8