Substituent-Directed Reactivity Switch in the Fluorination of NHC-Boranes

Malika Makhlouf Brahmi, Dennis P. Curran, Max Malacria, Louis Fensterbank, Emmanuel Lacôte*

Supporting information

General Remarks

Chemicals and solvents were purchased from commercial suppliers and used as received. Reactions were carried out under argon, with magnetic stirring and redistilled solvents when necessary. CH₂Cl₂ was distilled from CaH₂. Thin layer chromatography (TLC) was conducted on silica mesh 60 plates and column chromatography was performed on silica gel 60 (35–70 mm). The melting points reported were measured with a melting point apparatus and were uncorrected. IR spectra were recorded on a FT-IR spectrometer equipped with a diamond pike. ¹H, ¹³C, ¹¹B and ¹⁹F NMR spectra were recorded on a 400 MHz NMR device (400, 100, 133 and 376 MHz respectively). COSY and HSQC measurements were used to assign signals. Chemical shifts are given in ppm. Unless otherwise noted, the NMR spectra were recorded in CDCl₃. Chloroform (δ = 7.26 ppm) was used as internal standard in ¹H NMR spectra, whereas CDCl₃ (δ = 77.2 ppm) was used as internal standard in ¹³C NMR spectra. ¹¹B chemical shifts are relative to Et₂O•BF₃ (δ = 0 ppm). ¹⁹F chemical shifts are relative to CFCl₃ (δ = 0 ppm). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q, quint., sept. represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, septet, respectively. Exact masses and X-ray diffraction were obtained at Institut Parisien de Chimie Moléculaire (UMR 7201) of Université Pierre et Marie Curie, Paris. Elemental analyses were performed by Service de Microanalyse, Institut de Chimie des Substances Naturelles (ICSN CNRS, Gif-sur-Yvette).

Compounds 1a, 1c, 1d, 1f, 1g, 1h, 1i, 5, 2 have been prepared according to the literature procedures. 7a, 3 and 7b, 3 are known products in the literature. Their spectroscopic data were consistent with those previously reported.

NB: all ¹³C signals adjacent to a boron in all carbene-boranes are not visible because of the quadrupolar couplings.

General Procedure 1 (GP1): Preparation of monosubstituted NHC-boranes complexes

LiAlH₄ (1 M in Et₂O, 1.5 equiv) was added to a solution of boronic acid (1 equiv.) in dry diethyl ether (0.43 M) at 0 °C. The NHC (1.1 equiv.) was added to the suspension at 0°C and the resulting reaction mixture was stirred overnight at room temperature. The crude mixture was filtrated through a short pad of celite and washed with diethyl ether. After concentration in vacuo, the residue was purified by flash column chromatography and recrystallized when necessary to afford the NHC-borane complex as a pure white solid.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene 4-methoxycarbonylphenylborane complex (1b)

Following GP1 using 4-methoxycarbonylphenylboronic acid (671 mg, 3.73 mmol) and 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (1.6 g, 4.10 mmol), substrate 1b was obtained as a pure white solid (214 mg, 10%), after purification by flash column chromatography (SiO2, pentane/AcOEt: 90/10) and recrystallization from hexanes/CH2Cl2 (10/1).

Mp 181-184 °C. IR (diamond): v = 3165, 3015, 2965, 2900, 2315 (B–H), 1716 (C=O), 1470, 1270, 750 cm–1.

1H NMR (CDCl3, 400 MHz): δ 7.49-7.43 (m, 4H, CH=CH–CH= arom. + CH=CH–CO2Me arom.), 7.25 (d, 4H, J = 7.6 Hz, CH=CH–CH= arom.), 7.04 (s, 2H, NCH), 6.73 (d, 2H, J = 7.9 Hz, CH–CH=C–CO2Me arom.), 3.81 (s, 3H, CO2Me), 2.55 (sept., 4H, J = 6.8 Hz, CHMe2), 1.17 (d, 12H, J = 6.8 Hz, CHMeMe), 1.13 (d, 12H, J = 6.8 Hz, CHMeMe). 13C NMR (CDCl3, 100 MHz): δ 168.7 (C=O), 145.6 (C arom.), 136.1 (CH arom.), 134.3 (C arom.), 130.3 (CH arom.), 127.3 (CH arom.), 124.9 (C arom.), 124.0 (CH arom.), 122.6 (NCH), 51.5 (CO2Me), 28.9 (CHMe2), 25.6 (CHMeMe), 22.3 (CHMeMe). 11B NMR (BF3•OEt2, 133 MHz): δ –23.4 (t, J_B–H = 82.5 Hz). Anal. Calcd for C35H45BN2O2: C, 78.35; H, 8.45; N, 5.22. Found: C, 78.06; H, 8.36; N, 5.21.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene 4-methoxyphenylborane complex (1e)

Following GP1 using 4-methoxyphenylboronic acid (630 mg, 4.1 mmol) and 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (1.6 g, 4.1 mmol), substrate 1e was obtained as a pure white solid (400 mg, 19%), after purification by flash column chromatography (SiO2, pentane/AcOEt: 95/5) and recrystallization from hexanes/CH2Cl2 (10/1).

Mp 227-232.2 °C. IR (diamond): ν = 2960, 2900, 2300 (B–H), 1420, 1265, 1040, 735 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.48 (t, 2H, \(J = 7.6\) Hz, CH=CH–CH= arom.), 7.25 (d, 4H, \(J = 7.6\) Hz, CH=CH–CH= arom.), 7.02 (s, 2H, NCH), 6.55 (d, 2H, \(J = 8.1\) Hz, CH–CH=C(OMe) arom.), 6.37 (d, 2H, \(J = 8.6\) Hz, CH=C(OMe) arom.), 3.67 (s, 3H, OMe), 2.60 (sept., 4H, \(J = 6.8\) Hz, CHMe\(_2\)), 1.21 (d, 12H, \(J = 6.8\) Hz, CHMe\(_2\)), 1.15 (d, 12H, \(J = 6.8\) Hz, CHMeMe). \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 156.4 (C arom.), 145.6 (C arom.), 137.1 (CH arom.), 134.5 (C arom.), 130.0 (CH arom.), 123.9 (CH arom.), 122.4 (NCH), 122.4 (CH arom.), 55.2 (OMe), 28.9 (CHMe\(_2\)), 25.6 (CHMeMe), 22.4 (CHMeMe). \(^11\)B NMR (BF\(_3\)•OEt\(_2\), 133 MHz): \(\delta\) –23.2 (t, \(J_{B-H} = 85.9\) Hz). Anal. Calcd for C\(_{34}\)H\(_{45}\)BN\(_2\)O: C, 80.30; H, 8.92; N, 5.51. Found: C, 80.28; H, 9.09; N, 5.51.
General Procedure 2 (GP 2): Fluorination reaction

To a solution of NHC-borane complex 1a-j (1 equiv.) in CH₂Cl₂ (0.07 M), was added the triphenylcarbenium derivative (1 equiv.), then phenol (1 equiv.). The reaction mixture was stirred at room temperature for 5 min. The solvent was then evaporated in vacuo and the residue was purified by flash chromatography.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluorophenylborane complex (2a)

Following GP2 using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenylborane complex 1a (50 mg, 0.104 mmol), triphenylcarbenium tetrafluoroborate (34.4 mg, 0.104 mmol) and phenol (9.8 mg, 0.104 mmol), substrate 2a was obtained as a pure white solid (36.4 mg, 68%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 90/10).

Mp 222–227°C. IR (diamond): ν = 2960, 2930, 2870, 2360 (B-F), 1460, 1260, 1060, 1015, 930, 800, 760, 735 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.50 (t, J = 7.8 Hz, 2H, CH=CH–CH= arom.), 7.28 (d, J = 7.8 Hz, 4H, CH=CH–CH= arom.), 7.04 (s, 2H, NCH), 6.94 (t, J = 6.9 Hz, 1H, H arom.), 6.88 (t, J = 6.8 Hz, 2H, H arom.), 6.77 (d, J = 6.6 Hz, 2H, H arom.), 2.61-2.55 (m, 4H, CHMe₂), 1.20 (d, J = 6.8 Hz, 12H, CHMe₂), 1.13 (d, J = 6.8 Hz, 12H, CHMe₂). ¹³C NMR (CDCl₃, 100 MHz): δ 145.5 (C arom.), 134.2 (C arom.), 131.7 (CH arom.), 130.4 (CH arom.), 126.6 (CH arom.), 125.9 (CH arom.), 123.8 (NCH), 123.8 (CH arom.), 29.0 (CHMe₂), 25.9 (CHMeMe), 22.3 (CHMeMe). ¹¹B NMR (BF₃·OEt₂, 133 MHz): δ 4.8 (br s). ¹⁹F NMR (CFCl₃, 376 MHz): δ –153.2 (br s). HRMS calcd. for C₃₃H₄₁N₂₁¹¹BF₂Na ([M + Na]+): 537.3223, found 537.3224.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluoro-(4-methoxycarbonylphenyl)borane complex (2b)

Following GP2 using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene 4-methoxycarbonyl-phenylborane complex 1b (30 mg, 0.056 mmol), triphenylcarbenium tetrafluoroborate (18.5 mg, 0.056 mmol) and phenol (5.3 mg, 0.056 mmol), substrate 2b was obtained as a pure white solid (32 mg, quantitative), after purification by flash chromatography (SiO$_2$, pentane/AcOEt: 85/15). Mp 153–155.5°C. IR (diamond): $\nu = 2965, 2930, 2870, 1720$ (C=O), 1460, 1175, 1105, 730 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.57 (d, $J = 8.0$ Hz, 2H, CH arom.), 7.50 (t, $J = 7.8$ Hz, 2H, CH=CH–CH= arom.), 7.25 (d, $J = 7.8$ Hz, 4H, CH=CH–CH= arom.), 7.06 (s, 2H, NCH), 6.85 (d, $J = 8.1$ Hz, 2H, CH arom.), 3.85 (s, 3H, CO$_2$Me), 2.55–2.48 (m, 4H, CHMe$_2$), 1.18 (d, $J = 6.8$ Hz, 12H, CHMe$_2$), 1.13 (d, $J = 6.9$ Hz, 12H, CHMe$_2$). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.2 (C=O), 145.4 (C arom.), 134.0 (C arom.), 131.7 (CH arom.), 130.6 (CH arom.), 127.8 (CH arom.), 125.5 (C arom.), 123.9 (NCH + CH arom.), 51.7 (CO$_2$Me), 29.0 (CHMe$_2$), 25.9 (CHMeMe), 22.2 (CHMeMe). $^{11}$B NMR (BF$_3$$\cdot$OEt$_2$, 133 MHz): $\delta$ 4.2 (br s). $^{19}$F NMR (CFCl$_3$, 376 MHz): $\delta$ −154.5 (s). HRMS calcd. for C$_{35}$H$_{43}$O$_2$N$_2^{11}$BF$_2$Na ([M + Na]$^+$): 595.3284, found 595.3291.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluoro-[4-(trifluoromethyl)phenyl]borane complex (2c)

Following GP2 using 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene 4-(trifluoromethyl)phenyl-borane complex 1c (50 mg, 0.091 mmol), triphenylcarbenium tetrafluoroborate (30.2 mg, 0.091 mmol) and phenol (8.6 mg, 0.091 mmol), substrate 2c was obtained as a pure white solid (44 mg, 83%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 90/10).

**Mp 172.2–174.6°C. IR (diamond):** ν = 2965, 2930, 2870, 1470, 1160, 1120, 1105, 1065, 820 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.49 (t, J = 7.8 Hz, 2H, CH=CH–CH= arom.), 7.25 (d, J = 7.8 Hz, 4H, CH=CH-CH= arom.), 7.11 (d, J = 7.7 Hz, 2H, CH arom.), 7.06 (s, 2H, NCH), 6.86 (d, J = 7.7 Hz, 2H, CH arom.), 2.54-2.47 (m, 4H, C₆HMe₂), 1.16 (d, J = 6.8 Hz, 12H, CHMe₂), 1.10 (d, J = 6.9 Hz, 12H, CHMe₂). ¹³C NMR (CDCl₃, 100 MHz): δ 145.3 (C arom.), 133.8 (C arom.), 131.8 (t, J₃-F = 4.0 Hz, F₂B–C=CH), 130.5 (CH arom.), 126.9 (q, J₃-F = 137.3 Hz, CF₃), 125.1 (q, J₃-F = 32.8 Hz, C–CF₃ arom.), 123.9 (CH arom. + NCH), 123.0 (q, J₃-F = 4.0 Hz, CH=C–CF₃), 29.3 (CHMe₂), 24.5 (CHMeMe), 23.9 (CHMeMe). ¹¹B NMR (BF₃•OEt₂, 133 MHz): δ 3.2 (br s). ¹⁹F NMR (CFCl₃, 376 MHz): δ −62.9 (s, CF₃), −154.7 (br s, BF₂). Anal. Calcd for C₃₄H₄₆BF₅N₂: C, 70.11; H, 6.92; N, 4.81. Found: C, 70.04; H, 7.04; N, 4.63.
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluoro-(3-bromophenyl)borane complex (2d)

Following GP2 using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene 3-bromophenylborane complex 1d (25 mg, 0.044 mmol), triphenylcarbenium tetrafluoroborate (14.5 mg, 0.044 mmol) and phenol (4 mg, 0.441 mmol), substrate 2d was obtained as a pure white solid (22.4 mg, 86%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 95/5).

Mp 186–189°C. IR (diamond): ν = 2965, 2930, 2870, 1470, 1160, 1120, 1105, 1065, 820 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.42 (t, J = 7.8 Hz, 2H, CH=CH–CH= arom.), 7.18 (d, J = 7.8 Hz, 4H, CH=CH–CH= arom.), 6.99-6.95 (m, 3H, NCH + B–C–CH=CH–Br), 6.71-6.62 (m, 3H, H arom.), 2.46-2.42 (m, 4H, CHMe₂), 1.11 (d, J = 6.8 Hz, 12H, CHMe₂), 1.03 (d, J = 6.9 Hz, 12H, CHMe₂). ¹³C NMR (CDCl₃, 100 MHz): δ 145.4 (C arom.), 134.7 (CH arom.), 133.9 (C arom.), 130.7 (CH arom.) 130.2 (CH arom.), 129.1 (B–C–CH=CH–Br), 128.4 (CH arom.), 123.9 (CH–CH–CH arom.), 123.8 (NCH), 121.9 (C arom.), 29.0 (CHMe₂), 25.9 (CHMeMe), 22.2 (CHMeMe). ¹¹B NMR (BF₃•OEt₂, 133 MHz): δ 2.9 (br s). ¹⁹F NMR (CFCl₃, 376 MHz): δ –154.1 (br s). HRMS calcd. for C₃₃H₄₀N₂¹¹BF₂Na (M + Na⁺): 616.2362, found 616.2358.

1,3-Dimethylimidazol-2-ylidene difluorophenylborane complex (2g)

Following GP2 using 1,3-dimethylimidazol-2-ylidene phenylborane complex 1g (16 mg, 0.086 mmol), triphenylcarbenium tetrafluoroborate (28.4 mg, 0.086 mmol) and phenol (8.1 mg, 0.086 mmol), substrate 2g was obtained as a colorless oil (9.8 mg, 51%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 40/60).

IR (diamond): ν = 3135, 3005, 2960, 1175, 1000, 970, 840 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.45 (d, J = 7.0 Hz, 2H, B–C=CH arom.), 7.29-7.20 (m, 3H, CH arom.) 6.82 (s, 2H, NCH), 3.88 (s, 6H, NMe). ¹³C NMR (CDCl₃, 100 MHz): δ 131.1 (t, J_C-F = 3.5 Hz, F₂B–C=CH), 127.6 (CH arom.), 126.9 (CH arom.), 122.8 (NCH), 36.7 (t, J_C-F = 5.0 Hz, NMe). ¹¹B NMR (BF₃•OEt₂, 133 MHz): δ 5.4 (t, J_B-F = 42.9 Hz). ¹⁹F
NMR (CFCl₃, 376 MHz): δ −157.8 (bq, Jₓ₋ₓ = 33.5 Hz). HRMS calcd. for C₁₁H₁₃N₂₁¹BF₂Na ([M + Na]⁺): 245.1032, found 245.1026.

1,3-Dimethylimidazol-2-ylidene difluoro-[4-(trifluoromethyl)phenyl]borane complex (2h)

Following GP2 using 1,3-dimethylimidazol-2-ylidene 4-(trifluoromethane)phenylborane complex 1h (25 mg, 0.98 mmol), triphenylcarbenium tetrafluoroborate (32.5 mg, 0.098 mmol) and phenol (9.2 mg, 0.098 mmol), substrate 2h was obtained as a pure white solid (23 mg, 81%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 40/60).

Mp 65–67.5°C. IR (diamond): ν = 3140, 2960, 2930, 1320, 1160, 1120, 1060, 970, 820 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ 7.58–7.52 (m, 4H, CH₆arom.), 6.85 (s, 2H, NCH), 3.86 (s, 6H, NMe). ¹³C NMR (CDCl₃, 100 MHz): δ 131.1 (t, Jₓ₋ₓ = 3.4 Hz, FₓB–C=CHₓ), 128.8 (q, Jₓ= 31.7 Hz, C–CF₃), 124.7 (q, Jₓ= 270 Hz, CF₃), 124.1 (q, Jₓ= 3.6 Hz, CHₓ=C–CFₓ₃), 121.9 (NCH), 36.5 (t, Jₓ₋ₓ = 4.5 Hz, NMe). ¹¹B NMR (BF₃•OEt₂, 133 MHz): δ 5.0 (br s). ¹⁹F NMR (CFCl₃, 376 MHz): δ −62.8 (s, CF₃), −157.8 (br s, BF₂).

Anal. Calcd for C₁₂H₁₂BF₅N₂: C, 49.69; H, 4.17; N, 9.66. Found: C, 49.56; H, 4.12; N, 9.41.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene trifluoroborane complex (3)

A) Following GP2 using NHC-boranes complexes 1e (50 mg, 0.098 mmol), triphenylcarbenium tetrafluoroborate (32.5 mg, 0.098 mmol) and phenol (9.2 mg, 0.098 mmol), 3 was obtained as a pure white solid (35.8 mg, 80%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 80/20).

B) Following GP2 using NHC-boranes complexes 1f (50 mg, 0.103 mmol), triphenylcarbenium tetrafluoroborate (34 mg, 0.103 mmol) and phenol (9.6 mg, 0.103 mmol), 3 was obtained as a pure white solid (27.7 mg, 59%), after purification by flash chromatography (SiO₂, pentane/AcOEt: 80/20).
Decomposition at 264°C. $^{11}$B NMR (BF$_3$•OEt$_2$, 133 MHz): $\delta$ –0.8 (q, $J_{B,F}$ = 35.2 Hz). $^{19}$F NMR (CFCl$_3$, 376 MHz): $\delta$ –140.3 (q, $J_{F,B}$ = 33.7 Hz). HRMS calc. for C$_{27}$H$_{36}$BF$_3$N$_2$Na ([M + Na]$^+$): 479.2821, found 479.2819.

1,3-Dimethylimidazol-2-ylidene trifluoroborane complex (4)

Following GP2 using 1,3-dimethylimidazol-2-ylidene 4-methoxyphenylborane complex 1i (25 mg, 0.116 mmol), triphenylcarbenium tetrafluoroborate (38 mg, 0.116 mmol) and phenol (10.9 mg, 0.116 mmol), substrate 4 was obtained as a pure white solid (15.3 mg, 80%), after purification by flash chromatography (SiO$_2$, pentane/AcOEt: 20/80).

$\text{Mp }$209–213°C. IR (diamond): $\nu = 3150, 2920, 2850, 1030, 940 \text{ cm}^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.90 (s, 2H, NCH), 3.92 (s, 6H, NMe). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 122.0 (NCH), 36.6 (q, $J_{C,F}$ = 3.0 Hz, NMe). $^{11}$B NMR (BF$_3$•OEt$_2$, 133 MHz): $\delta$ 0.5 (q, $J_{B,F}$ = 37.1 Hz). $^{19}$F NMR (CFCl$_3$, 376 MHz): $\delta$ –157.8 (q, $J_{F,B}$ = 36.5 Hz). HRMS calc. for C$_5$H$_8$N$_2$BF$_3$Na ([M + Na]$^+$): 187.0625, found 187.0623.

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene difluorophenoxyborane complex (6)

Following GP using 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene borane complex 5 (50 mg, 0.124 mmol), triphenylcarbenium tetrafluoroborate (41 mg, 0.124 mmol) and phenol (11.6 mg, 0.124 mmol), 6 was obtained as a pure white solid (33.2 mg, 50%) after purification by flash chromatography (SiO$_2$, pentane/AcOEt: 95/5 then 90/10).

$\text{Mp }$177.7–180.3°C. IR (neat): $\nu = 2960, 2920, 2855, 2360$ (B-O), 2340 (B–O), 1460, 1260, 1060, 1015, 930, 800, 760, 735 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.51 (t, $J$ = 7.8 Hz, 2H, CH=CH–CH= arom.), 7.31
(d, J = 7.8 Hz, 4H, CH=CH–CH= arom.), 7.10 (s, 2H, NCH), 6.92 (t, J = 7.9 Hz, 2H, CH arom.), 6.61 (t, J = 7.3 Hz, 1H, CH arom.), 6.32 (d, J = 7.9 Hz, 2H, O–C=CH arom.), 2.69-2.56 (m, 4H, CHMe2), 1.29 (d, J = 6.8 Hz, 12H, CHMe2), 1.19 (d, J = 6.8 Hz, 12H, CHMe2). ¹³C NMR (CDCl₃, 100 MHz): δ 156.6 (O–C arom.), 145.5 (C arom.), 134.1 (C arom.), 130.4 (CH arom.), 128.5 (CH arom.), 123.9 (CH arom.), 123.5 (NCH), 119.4 (CH arom.), 118.6 (CH arom.), 29.1 (CHMe₂), 25.3 (CHMeMe), 23.0 (CHMeMe). ¹¹B NMR (BF₃•OEt₂, 133 MHz): δ 0.5 (t, J₈₋₉ = 47.0 Hz). ¹⁹F NMR (CFCl₃, 376 MHz): δ –142.1 (q, J₁₉₋₂₁ = 46.8 Hz).

HRMS calc'd. for C₃₃H₄₁ON₂¹¹BF₂Na ([M + Na]⁺): 553.3178, found 553.3225.
2b