Supporting Information

ortho-Dialkylamino Arylboranes as Efficient Reagents for Difluorocarbene Trapping

Egor A. Ilin, [a,b] Vladimir O. Smirnov, [a] Alexander D. Volodin, [c] Alexander A. Korlyukov, [c] Alexander D. Dilman*[a]

[a] N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation

[b] Department of Chemistry, Lomonosov Moscow State University, 119991, Moscow, Leninskie Gory 1-3, Russian Federation

[c] A. N. Nesmeyanov Institute of Organoelement Compounds, 119991 Moscow, Vavilov str. 28, Russian Federation

adil25@mail.ru

Content

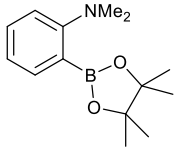
General Methods: All reactions, except when explicit use of aqueous media, were performed under an argon atmosphere. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or aq. $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage –4500V) or in a negative ion mode (3200V); mass range from m/z 50 to m/z 3000.

For NMR measurements, regular acquisition conditions were used. In ^{13}C NMR spectra, signals of carbons directly attached to boron atom are not observed. This phenomenon is typical for organoboron compounds.[1]

Reagents. Starting compounds were prepared according to literature procedures: 1-(2-bromophenyl)pyrrolidine (**1b**),[2] 2-(dimethylamino)phenol (**4a**),[3] 2-(pyrrolidin-1-yl)phenol (**4b**),[4] 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (*i*-PrOBPin).[5]

[1] (a) S. Bruns, V. Sinnwell and J. Voss, *Magn. Reson. Chem.*, 2003, **41**, 269–272. (b) B. Wrackmeyer, *Z. Naturforsch.*, 2015, **70**, 421–424. (c) B. Wrackmeyer, *Progress in NMR Spectroscopy*, 1979, **12**, 227–259.
[2] B. Xu, M.-L. Li, X.-D. Zuo, S.-F. Zhu and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 8700–8703.
[3] H. Wang, Y. Li, F. Sun, Y. Feng, K. Jin and X. Wang, *J. Org. Chem.*, 2008, **73**, 8639–8642.
[4] K. C. Nicolaou and S. T. Harrison, *J. Am. Chem. Soc.*, 2007, **129**, 429–440.
[5] Q. Lin, D. Meloni, Y. Pan, M. Xia, J. Rodgers, S. Shepard, M. Li, L. Galya, B. Metcalf, T.-Y. Yue, P. Liu and J. Zhou, *Org. Lett.*, 2009, **11**, 1999–2002.

N,N-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2a).[6]



A solution of n-BuLi in hexane (8.8 mL, 2.4 M, 21.0 mmol) was added dropwise to a mixture of dimethylaniline (2.42 g; 20.0 mmol) and TMEDA (3.2 mL; 21.1 mmol) at 0 °C, and the mixture was stirred at room temperature for 20 hours. Then the mixture was diluted with THF (8.0 mL), cooled to -78 °C; *i*-PrOBpin (2.84 g, 21.1 mmol) was added, and the mixture was stirred for 15 minutes at -78 °C and for 1 hour at room temperature. Then, TMSCl (2.41 g, 22.2 mmol) was added, and the mixture was stirred at room temperature for 2 hours. The mixture was diluted with hexane (8.0 mL) and left without stirring to allow the precipitate to settle down. The supernatant solution was separated, the precipitate was washed with hexane (2×5 mL). The combined supernatant solution and hexane washings were evaporated under vacuum. The residue was distilled under vacuum (113-114 °C /1.3 Torr) to give opalescent viscous liquid (the obtained material contains minor impurities according to ^{1}H NMR). The liquid was dissolved in hexane (3 mL) with moderate heating (*ca.* 40-50 °C), the solution is filtered, and the filtrate was kept in a fridge (ca. 0 °C) until formation of first crystals, and then put in a freezer (*ca.* -20 °C) to complete crystallization. Compound **2a** is prone to supersaturation in hexane solution but crystalizes readily in the presence of a seed or on scratching. The liquid phase was separated, and the crystals were dried under vacuum.

Aminoboronate **2a** was found to be rather stable to ambient conditions. Thus, no change in proton NMR was found for a sample of **2a**, which was stored in an open vial in air at room temperature after five months. However, after such a long-term storage, this sample gave some insoluble white material upon dissolution in hexane. Therefore, storage of **2a** under an argon blanket is recommended, while brief handling in air (weighing, transferring) does not compromise results using this compound.

If **2a** is deteriorated, it could be readily purified by dissolution in small amount of hexane (*ca.* 1 mL per gram) with moderate heating, filtering through a cotton plug and crystallization of the filtrate as described above.

Yield 3.30 g (67 %).

White crystals. Mp 44-45 °C.

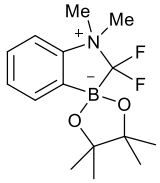
^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.66 (d, *J* = 7.3 Hz, 1H); 7.32 (m, 2H); 6.85 (t, *J* = 7.7 Hz, 1 H); 2.9 (s, 6H); 1.39 (s, 12 H).

^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 157.9; 136.5; 131.4; 118.9; 114.9; 83.5; 44.8; 24.8.

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: 31.65 (s).

[6] C. R. Wade, H. Zhao and F. P. Gabbaï, *Chem. Commun.*, 2010, **46**, 6380–6381.

2,2-Difluoro-1,1,4',4',5',5'-hexamethyl-1,2-dihydrospiro[benzo[d][1,3]azaborole-3,2'-[1,3,2]dioxaborolan]-1-ium-3-uide (3a).



Reaction in MeCN. A mixture of potassium bromodifluroacetate (427 mg; 2.00 mmol; 2.00 equiv), compound **2a** (247 mg, 1.00 mmol) and MeCN (2 mL) was stirred at 60 °C for 5 hours, and then cooled to room temperature. Ethyl acetate (4 mL) and saturated aqueous $NaHCO_3$ (4 mL) were added with stirring, the organic layer was separated, aqueous layer was extracted with ethyl acetate (3×2 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum, and the residue was subjected to column chromatography on silica gel eluting with ethyl acetate. Yield 271 mg (91%).

Reaction in DMF. A mixture of potassium bromodifluroacetate (426 mg; 2.00 mmol; 2.0 equiv), compound **2a** (247 mg, 1.00 mmol) and DMF (2 mL) was stirred at room temperature for 45 hours. The solvent was evaporated under vacuum (*ca.* 1 Torr), and the residue was partitioned between ethyl acetate (4 mL) and water (8 mL). The upper layer was separated, the aqueous layer was extracted with ethyl acetate (3×2 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum, and the residue was subjected to column chromatography on silica gel eluting with ethyl acetate. Yield 233 mg (78%).

White crystals. Mp 168-171 °C. R_f = 0.20 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.63 (d; *J* = 7.2, 1.5 Hz, 1H); 7.27 (t, *J* = 7.2 Hz, 1H); 7.17 (t, *J* = 7.7, 1H); 7.08 (d, *J* = 8.1 Hz, 1H); 3.14 (s, 6H); 1.23(s; 6H); 1.15(s; 6H).

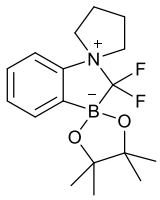
^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 150.5; 133.1; 129.8; 128.4; 114.3; 79.2; 48.0 (t, *J* = 4.9 Hz); 26.1; 25.0.

^{19}F NMR (282.4 MHz; $CDCl_3$) δ: -110.6 (s).

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: 3.32 (s).

HRMS (ESI): calcd for $C_{15}H_{23}BF_2NO_2$ (M+H): 298.1787; found: 298.1785.

2',2'-Difluoro-4'',4'',5'',5''-tetramethyl-2'H-dispiro[pyrrolidine-1,1'-benzo[d][1,3]azaborole-3',2''-[1,3,2]dioxaborolan]-1-ium-3'-uide (3b).



A solution of n-BuLi in hexane (0.45 mL, C = 2.4 M, 1.05 mmol) was added to a solution of *N*-(2-bromophenyl)pyrrolidine (227.0 mg, 1.00 mmol) in THF (2 mL) at -78 °C, and the mixture was stirred at -78 °C for 1 hour. Then, *i*-PrOBpin (191.6 mg, 1.03 mmol) was added, and the mixture was stirred at -78 °C for 1.5 hours and at room temperature for 30 min. Then, TMSCl (116.4 mg, 1.07 mmol) was added, the stirring was discontinued, and the mixture was kept overnight at room temperature to allow precipitate to settle down. The supernatant solution was separated, the precipitate was washed with hexane (6 mL). The combined supernatant solution and hexane washings were evaporated under vacuum. The residue was dissolved in MeCN (2 mL) followed by addition of potassium bromodifluroacetate (426.0 mg, 2.00 mmol), and the mixture was stirred at 60 °C for 5 hours. The mixture was cooled to room temperature. Saturated aqueous $NaHCO_3$ (4 mL) and ethyl acetate (4 mL) were added, organic layer was separated, and the aqueous layer was extracted with ethyl acetate (5×2 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum, and the residue was subjected to column chromatography on silica gel eluting with ethyl acetate. Yield 207 mg (64%).

White crystals. Mp 150-153 °C. R_f = 0.20 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.71(d, *J* = 7.0 Hz, 1H); 7.02 (d, *J* = 7.9 Hz, 1H); 7.30(m; 2H); 4.32 (m, 2H); 3.54(m, 2H); 2.27 (s, 4H); 1.31 (s, 6H); 1.25 (s, 6H).

^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 152.2; 133.2; 129.4; 128.6; 114.2; 79.4; 61.5 (t, *J* = 3.5 Hz); 26.2; 25.6; 25.1.

^{19}F NMR (282.4 MHz; $CDCl_3$) δ: -109.9 (s).

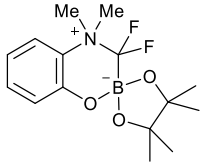
^{11}B NMR (96.3 MHz; $CDCl_3$) δ:3.49 (s).

HRMS (ESI): calcd for $C_{17}H_{25}BF_2NO_2$ (M+H): 324.1944; found: 324.1946.

Preparation of 6 (General Procedure).

Pinacolborane (192 mg, 1.5 mmol) was added to a solution of aminophenol **4** (1.00 mmol) in THF (0.5 mL) at room temperature with stirring (CAUTION! Frothing!), and the mixture was stirred for 40 min. The solvent and an excess of pinacolborane were removed under vacuum into a cold trap of Schlenk line, and the reaction vessel was refilled with argon. Then, potassium bromodifluroacetate (426 mg, 2.00 mmol) and MeCN (2.0 mL) were added, and the mixture was stirred at 60 °C for 5 hours. The mixture was cooled to room temperature. Saturated aqueous $NaHCO_3$ (4 mL) and ethyl acetate (4 mL) were added, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (5×3 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum, and the residue was subjected to column chromatography on silica gel eluting with ethyl acetate.

3,3-Difluoro-4,4,4',4',5',5'-hexamethyl-3,4-dihydrospiro[benzo[e][1,4,2]oxazaborinine-2,2'-[1,3,2]dioxaborolan]-4-ium-2-uide (6a).



Yield 257 mg (82%).

White crystals. Mp 138-141 °C. R_f = 0.20 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.26 (m, 1H); 7.17 (d, *J* = 8.4 Hz, 1H;); 7.06 (d, *J* = 8.3 Hz, 1H); 6.80 (t, *J* = 7.8 Hz, 1H); 3.46 (s, 6H); 1.30 (s, 6H); 1.19 (s, 6H).

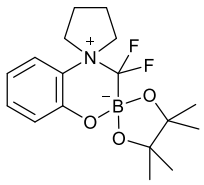
^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 151.7; 131.6; 130.4; 123.5; 118.8; 118.5; 80.0; 48.1; 26.0; 25.4.

^{19}F NMR (282.4 MHz; $CDCl_3$) δ: -108.4 (s).

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: 3.03(s).

HRMS (ESI): calcd for $C_{15}H_{23}BF_2NO_3$ (M+H): 314.1736; found: 314.1743.

3',3'-Difluoro-4'',4'',5'',5''-tetramethyl-3'H-dispiro[pyrrolidine-1,4'-benzo[e][1,4,2]oxazaborinine-2',2''-[1,3,2]dioxaborolan]-1-ium-2'-uide (6b).



Yield 305 mg (90%).

White crystals. Mp 160-163 °C. R_f = 0.20 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.28 (t, *J* = 7.7 Hz, 1H); 6.99(d, *J* = 8.3 Hz, 2H); 6.72 (t, *J* = 7.8 Hz, 1H); 4.49 (m, 2H); 3.74 (m,2H); 2.21 (br s, 4H); 1.26(s ;6H); 1.14(s ;6H).

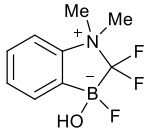
^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 151.7; 131.7; 131.1; 123.4; 119.3; 118.3; 79.9; 61.0 (br); 25.9; 25.3; 24.7.

^{19}F NMR (282.4 MHz; $CDCl_3$) δ: -106.3 (br s).

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: 3.06 (s)

HRMS (ESI): calcd for $C_{17}H_{25}BF_2NO_3$ (M+H): 340.1893; found: 340.1895.

2,2,3-Trifluoro-3-hydroxy-1,1-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azaborol-1-ium-3-uide (8a).



Hydrochloric acid (2.0 mL; 38%; 24.8 mmol) was added to KHF_2 (1.576 g; 20.2 mmol) in a plastic test tube with stirring. Then, a solution of compound **3a** (297.0 mg; 1.00 mmol) in THF (4.0 mL) was added, and the mixture was stirred at room temperature for 4 hours. The mixture was neutralized by careful addition (*Caution*! Gas evolution!) of saturated aqueous K_2CO_3 (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×2 mL). The combined organic layers were dried over Na_2SO_4, evaporated under vacuum, and the residue was subjected to column chromatography on silica gel (ethyl acetate/MeOH, 10/1). For crystallization, the product was dissolved in CH_2Cl_2 (5 mL), and then diluted with hexane (5 mL) followed by evaporation of CH_2Cl_2 under moderate vacuum on a rotary evaporator (to approximately 4 mL of final volume). The precipitate was filtered, washed with small amount of hexane, and dried under vacuum. Yield 158 mg (73%).

White solid. Mp 87-88 °C. R_f = 0.32 (ethyl acetate/MeOH, 10/1).

^{1}H NMR (300.1 MHz; DMSO-d_6) δ: 7.62 (m, 1H); 7.47 (m, 1H); 7.38 (m, 2H); 3.32 (d, *J* = 3.9 Hz, 3H); 3.28 (d, *J* = 3.8, 3H).

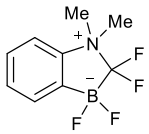
^{13}C NMR (75.5 MHz; DMSO-d_6) δ: 150.5; 130.8; 129.3; 128.4; 116.5; 48.1 (d, *J* = 7.9); 47.9 (d, *J* = 7.4 Hz).

^{19}F NMR (282.4 MHz; DMSO-d_6) δ: -112.40 (d, *J* = 185.5 Hz, 1F); -113.33 (d, *J* = 186.4 Hz, 1F); -162.03 (s, 1F).

^{11}B NMR (96.3 MHz; DMSO-d_6) δ: 2.06 (s).

HRMS (ESI): calcd for $C_9H_{11}BF_3NNaO$ (M+Na): 240.0780; found: 240.0784.

2,2,3,3-Tetrafluoro-1,1-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azaborol-1-ium-3-uide (8b).



Hydrochloric acid (2.0 mL, 38%, 24.80 mmol) was added to KHF_2 (1.544 g, 19.80 mmol) in a plastic test tube with stirring. Then, a solution of compound **3a** (297.0 mg; 1.00 mmol) in MeCN (4.0 mL) was added, and the mixture was stirred at room temperature for two weeks and for two additional weeks the tube was kept without stirring. The mixture was neutralized by careful addition (*Caution*! Gas evolution!) of saturated aqueous K_2CO_3 (6 mL). The organic layer was separated, and the aqueous layer was extracted with acetonitrile (3×2 mL). The combined organic layers were dried over Na_2SO_4, evaporated under vacuum. According to ^{19}F NMR with internal standard (m-$BrC_6H_4CF_3$), the residue consists of the mixture of **8b** (0.40 mmol) and compound **8a** (0.58 mmol). The residue was subjected to column chromatography on silica gel eluting with ethyl acetate. Yield 83 mg (38%).

White solid. Mp 113-115 °C. R_f = 0.38 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.72 (m, 1H); 7.44 (m, 2H); 7.3 (m, 1H); 3.32 (s, 6H).

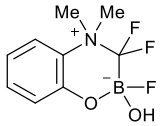
^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 150.8; 132.0; 130.7; 130.2; 115.4; 48.7.

^{19}F NMR (282.4 MHz; $CDCl_3$) δ: -113.87 (s, 2F); -169.80 (q, *J* = 54.5 Hz; 2F).

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: 3.20 (t, *J* = 54.5 Hz).

HRMS (ESI): calcd for $C_9H_{10}BF_4NNa$ (M+Na): 242.0736; found: 242.0738.

2,3,3-Trifluoro-2-hydroxy-4,4-dimethyl-3,4-dihydro-2H-benzo[e][1,4,2]oxazaborinin-4-ium-2-uide (9a).



Hydrochloric acid (1.0 mL; 38%; 12.4 mmol) was added to KHF_2 (789 g; 10.1 mmol) in a plastic test tube. Then, a solution of compound **6a** (313.0 mg; 1.00 mmol) in MeCN (3.0 mL) was added, and the mixture was stirred at room temperature for 1 hour. The mixture was neutralized by careful addition (*Caution*! Gas evolution!) of saturated aqueous K_2CO_3 (10 mL). The organic layer was separated, and the aqueous layer was extracted with MeCN (3×2 mL). The combined organic layers were dried over Na_2SO_4, evaporated under vacuum, and the residue was subjected to column chromatography on silica gel (ethyl acetate/MeOH, 10/1). Yield 182 mg 78%).

Colorless crystals. Mp 124–125 °C. R_f = 0.20 (ethyl acetate/MeOH, 10/1).

^{1}H NMR (300.1 MHz; DMSO-d_6) δ: 7.67 (d; *J* = 8.3 Hz, 1H), 7.33 (m; 1H), 6.89 (m, 2H); 3.82(d, 1H); 3.49 (s; 3H), 3.44 (s, 3H).

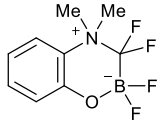
^{13}C NMR (75.5 MHz; DMSO-d_6) δ: 150.2; 131.9; 130.9; 121.22; 121.19; 118.8; 47.9; 47.7.

^{19}F NMR (282.4 MHz; DMSO-d_6) δ: -112.03 (d, *J* = 206.1, 1F); -110.04 (d, *J* = 207.0 Hz; 1F); -148.55 (s, 1F)

^{11}B NMR (96.3 MHz; DMSO-d_6) δ: 0.01 (s).

HRMS (ESI): calcd for $C_9H_{11}BF_3NNaO_2$ (M+Na): 256.0729; found: 256.0735.

2,2,3,3-Tetrafluoro-4,4-dimethyl-3,4-dihydro-2H-benzo[e][1,4,2]oxazaborinin-4-ium-2-uide (9b).



Hydrochloric acid (2.0 mL; 38%; 24.8 mmol) was added to KHF_2 (1.58 g; 20.3 mmol) in a plastic test tube. Then, a solution of compound **6a** (313.0 mg; 1.00 mmol) in MeCN (3.0 mL) was added, and the mixture was stirred at room temperature for 7 days. The mixture was neutralized by careful addition (*Caution*! Gas evolution!) of saturated aqueous K_2CO_3 (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×2 mL). The combined organic layers were dried over Na_2SO_4, evaporated under vacuum, and the residue was subjected to column chromatography on silica gel eluting with ethyl acetate. Yield 214 mg (91%).

Colorless crystals. Mp 135-136 °C. R_f = 0.20 (ethyl acetate).

^{1}H NMR (300.1 MHz; $CDCl_3$) δ: 7.72 (d, *J* = 8.4, 1H); 7.41 (t, *J* = 7.8, 1H); 7.02 (m, 2H); 3.49 (s, 3H); 3.34 (s, 3H).

^{13}C NMR (75.5 MHz; $CDCl_3$) δ: 148.8; 132.0; 130.6; 121.25; 121.09; 120.2; 47.2.

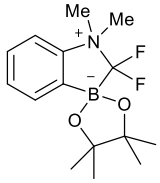
^{19}F NMR (282.4 MHz) δ: -112.71 (s, 2F); -153.50 (q, *J* = 34.9 Hz, 2F).

^{11}B NMR (96.3 MHz; $CDCl_3$) δ: -0.81 (tt, *J* = 34.9, 20.5 Hz).

HRMS (ESI): calcd for $C_9H_{10}BF_4NNaO$ (M+Na): 258.0685; found: 258.0691.

Mechanistic experiments

Evaluation of 3a toward heating with or without 1,1-diphenylethylene.

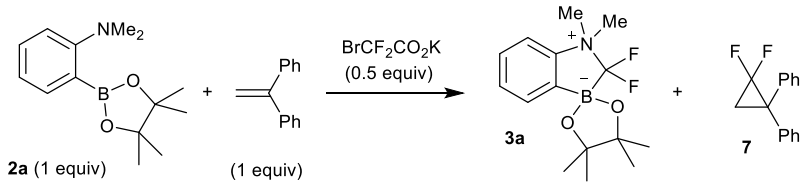


(a) A solution of compound **3a** (25.8 mg, 0.087 mmol) and 1,1-diphenylethylene (124 mg, 0.689 eq, 7.9 eq) in *p*-xylene (0.150 mL) was stirred at 100 °C for 3 hours. The mixture was cooled to room temperature and analyzed ^{19}F NMR with internal standard (3-Br$C_6H_4CF_3$):
starting **3a**, 29%; cyclopropane **7**, 48 %.

(b) Experiment (a) performed at 80 °C:
starting **3a**, 90%; cyclopropane **7**, 10 %.

(c) Experiment (a) when 1,1-diphenylethylene was replaced with p-xylene:
starting **3a**, 77%.

Competition **2a**/1,1-diphenylethylene.

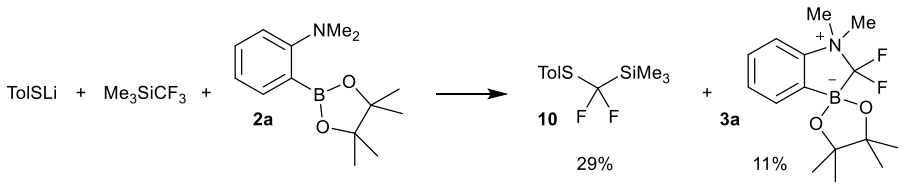


In MeCN. A mixture of potassium bromodifluroacetate (20.0 mg; 0.094 mmol), compound **2a** (49 mg, 0.198 mmol, 2.0 eq), 1,1-diphenylethylene (36.0 mg, 0.200 mmol, 2.0 eq) and MeCN (0.2 mL) was stirred at 60 °C for 4.5 hours and then cooled to room temperature. The mixture was analyzed by ^{19}F NMR using 3-Br$C_6H_4CF_3$ as internal standard.

In DMF. A mixture of potassium bromodifluroacetate (113 mg; 0.53 mmol), compound **2a** (267 mg, 1.08 mmol, 2.0 eq), 1,1-diphenylethylene (183 mg, 1.02 mmol, 1.9 eq) and DMF (1 mL) was stirred at room temperature for 45 hours. The mixture was analyzed by ^{19}F NMR using 3-Br$C_6H_4CF_3$ as internal standard.

Trapping of diflurocarbene in reaction of lithium thiolate with $TMSCF_3$.

The interaction of lithium thiolate with $TMSCF_3$ was adopted from the literature.[7]

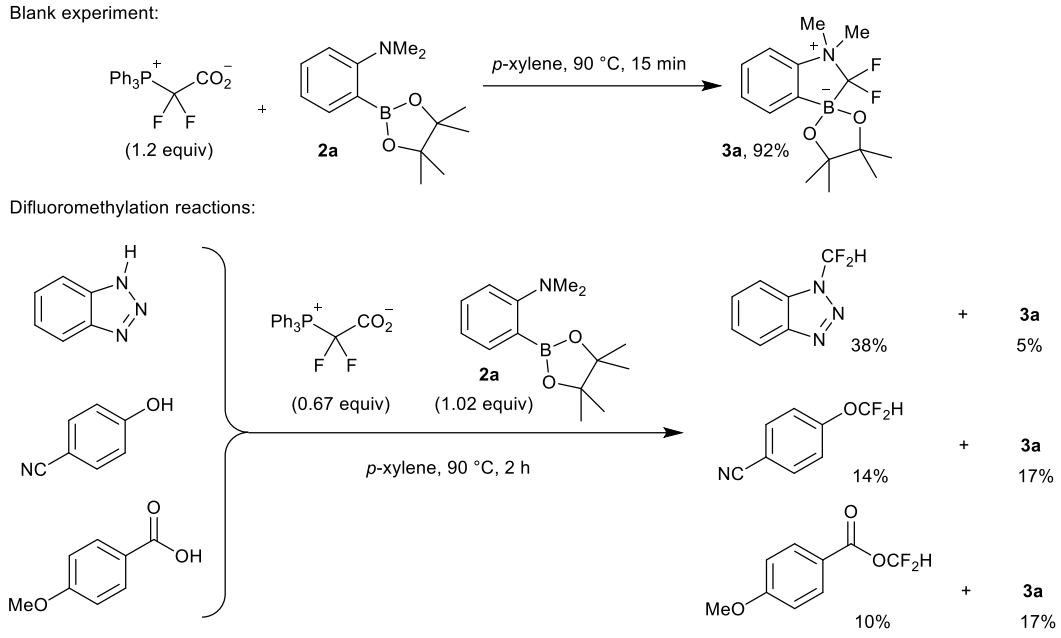


A mixture of *p*-thiocresol (24.1 mg, 0.194 mmol), LiCl (66 mg, 1.56 mmol) and several crystals of 1,10-phenanthroline in hexane (0.60 mL) and THF (0.15 mL) was stirred in an ice bath. Thiocresol was neutralized by addition of *n*-BuLi (2.5M in hexanes, *ca.* 0.08 mL) until steady crimson color appeared. Then, solvents were evaporated under vacuum into a cold trap of Schlenk line, the reaction vessel was filled with argon, and the residue was dissolved in DMF (1.0 mL) followed by addition of compound **2a** (338 mg, 1.37 mmol, 7.0 equiv). The resulting solution was cooled in an ice bath, $TMSCF_3$ (23 mg; 0.162 mmol) was added, and the stirring was continued at room temperature for one hour. The mixture was analyzed by ^{19}F NMR using 3-$BrC_6H_4CF_3$ as internal standard. As internal standard, 3-$BrC_6H_4CF_3$ (16.0 mg) was added, and the mixture was transferred into NMR tube under argon. ^{19}F NMR was taken in 45 minutes (total reaction time: 1 hour 45 minutes), and it revealed *p*-$MeC_6H_4SCF_2TMS$ (**10**, 29 % yield based on $TMSCF_3$) and **3a** (11 % yield based on $TMSCF_3$). The same procedure performed without addition of compound **2a** gave silane **10** in 42 % yield based on $TMSCF_3$.

[7] G. K. S. Prakash, S. Krishnamoorthy, S. Kar and G. A. Olah, *J. Fluorine Chem.*, 2015, **180**, 186-191.

Trapping difluorocarbene in difluoromethylation reactions.

Phosphobetaine ($Ph_3PCF_2CO_2$) was obtained according a literature procedure.[8] Experiments were performed according using phosphobetaine as a source of difluorocarbene as described in the literature.[9]



Blank experiment. A mixture of phosphobetaine (216 mg; 0.607 mmol) and compound **2a** (124 mg; 0.502 mmol) was stirred in *p*-xylene (0.5 mL) at 90 °C for 15 min. The mixture was cooled and analyzed by ^{19}F NMR with internal standard.

Reaction of benzotriazole.

A mixture of phosphobetaine (97.0 mg; 0.272 mmol), compound **2a** (102.6 mg; 0.415 mmol) and benzotriazole (48.6 mg; 0.407 mmol) was stirred in *p*-xylene (0.7 mL) at 90 °C for 2 hours. The mixture was cooled and analyzed by ^{19}F NMR with internal standard.

Reaction of *p*-cyanophenol.

A mixture of phosphobetaine (113.0 mg; 0.317 mmol), compound **2a** (120.1 mg; 0.486 mmol) and *p*-cyanophenol (57.0 mg; 0.478 mmol) was stirred in *p*-xylene (1.0 mL) at 90 °C for 2 hours. and cooled to room temperature. The mixture was cooled and analyzed by ^{19}F NMR with internal standard.

Reaction of *p*-anisic acid.

A mixture of phosphobetaine (105.7 mg; 0.297 mmol), compound **2a** (111.0 mg; 0.449 mmol) and 4-methoxybenzoic acid (68.0 mg; 0.447 mmol) was stirred in *p*-xylene (0.75 mL) at 90 °C for 2 hours. and cooled to room temperature. The mixture was cooled and analyzed by ^{19}F NMR with internal standard.

[8] J. Zheng, J. Cai, J.-H. Lin, Y. Guo and J.-C. Xiao, *Chem. Commun.*, 2013, **49**, 7513–7515.
[9] X.-Y. Deng, J.-H. Lin, J. Zheng and J.-C. Xiao, *Chem. Commun.*, 2015, **51**, 8805–8808.

X-ray data

Table 1S. Crystallographic data for **2a**, **3a**, **6b**.

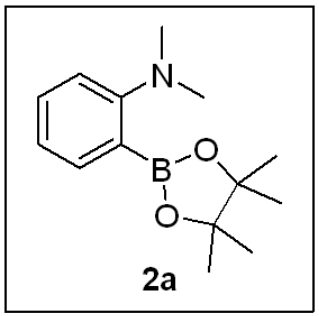
	2a	**3a**	**6b**
Brutto formula	$C_{14}H_{22}BNO_2$	$C_{15}H_{22}BF_2NO_2$	$C_{17}H_{24}BF_2NO_3$
Formula weight	247.13	297.14	339.18
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Scan mode	ω and ϕ scans	ϕ and ω scans	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube	CuKα [1.54178] sealed tube	MoKα [0.71073] sealed tube
Crystal Dimensions, mm	0.22 × 0.34 × 0.41	0.14 × 0.22 × 0.31	0.17 × 0.25 × 0.3
Crystal color	colourless	colourless	colourless
Crystal system	orthorhombic	orthorhombic	monoclinic
a, Å	17.0129(10)	10.6561(16)	9.0809(5)
b, Å	12.3612(7)	15.0608(13)	11.7860(6)
c, Å	27.5884(16)	19.6214(17)	15.8425(9)
β, °	90	90	95.2640(10)
Volume, Å³	5801.8(6)	3149.0(6)	1688.43(16)
Density, gcm^{-3}	1.132	1.254	1.334
Temperature, K	120	120	120
T_{min}/T_{max}	0.6317/0.7461	0.6282/0.7536	0.6863/0.7461
μ, mm^{-1}	0.073	0.808	0.104
Space group	Pbca	Pbca	$P12_1/c1$
Z	16	8	4
F(000)	2144	1264	720
Reflections collected	70012	35164	22877
Independent reflections	8906	3095	5142
Reflections (I>2σ(I))	6565	2821	3910
Parameters	337	196	313
R_{int}	0.0483	0.0365	0.0490
$2\theta_{min}$ - $2\theta_{max}$, °	2.952 - 61.248	9.014 - 144.506	4.314 - 61.090
wR_2 (all reflections)	0.1640	0.0877	0.1072
R_1(I>σ(I))	0.0567	0.0323	0.0415
GOF	1.089	1.038	1.006
ρ_{min}/ρ_{max}, eÅ^{-3}	-0.295/0.465	-0.206/0.329	-0.210/0.400
CCDC number	1995215	1995216	1995217

Single crystal X-ray studies of **2a, 3a, 6b** were carried out in a Center for molecule composition studies of INEOS RAS.

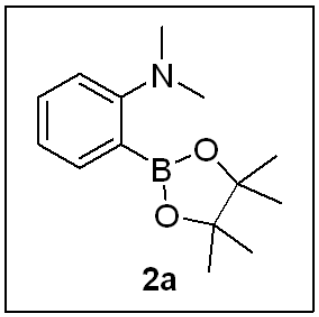
The structures were solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogens atoms of methyl, methylene and aromatic fragments were calculated according to those idealized geometry and refined with constraints applied to C-H bond lengths and equivalent displacement parameters (U_{eq}(H) = 1.2U_{eq}(C), C - cental atom of CH_2 group; U_{eq}(C) = 1.5U_{eq}(C), C - central atom of CH_3 group. All structures were solved with the ShelXT[10] program and refined with the ShelXL[11] program.

Crystal data were deposited at The Cambridge Crystallographic Data Centre (CCDC): CCDC 1995215 (**2a**), 1995216 (**3a**), 1995217 (**6b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

[10] G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
[11] G. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.



^{1}H NMR
300 MHz
$CDCl_3$

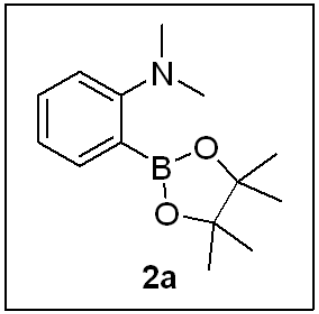


2a

^{13}C {^{1}H} NMR

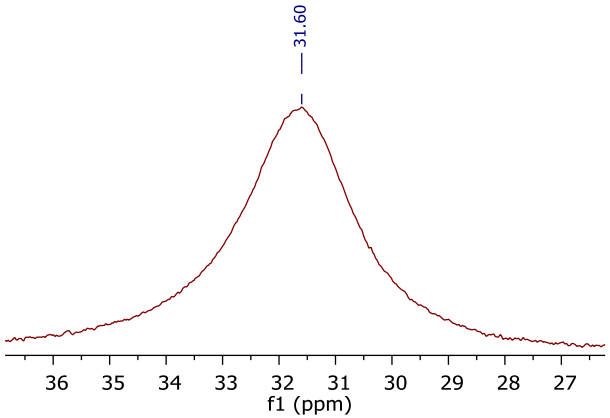
75 MHz

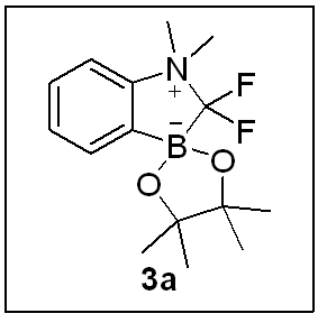
$CDCl_3$



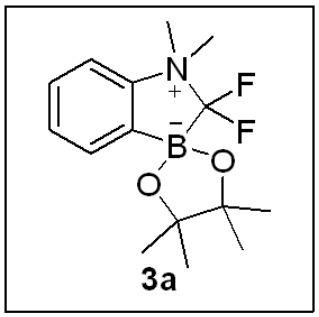
2a

^{11}B {^{1}H} NMR
96 MHz
$CDCl_3$





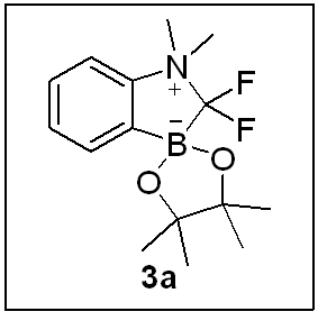
^{1}H NMR
300 MHz
$CDCl_3$



^{13}C {^{1}H} NMR

75 MHz

$CDCl_3$

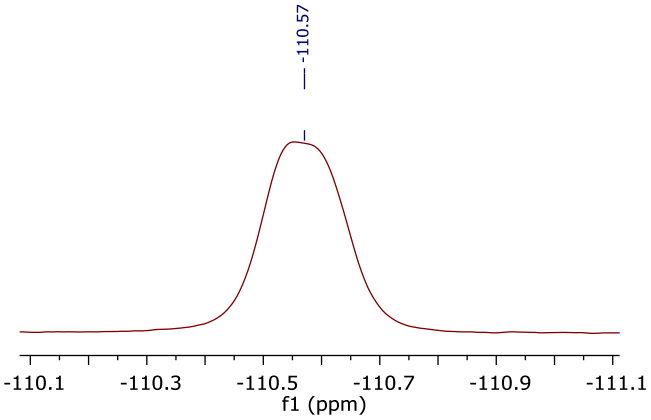


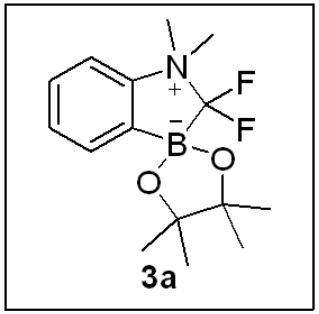
3a

^{19}F NMR

282 MHz

$CDCl_3$

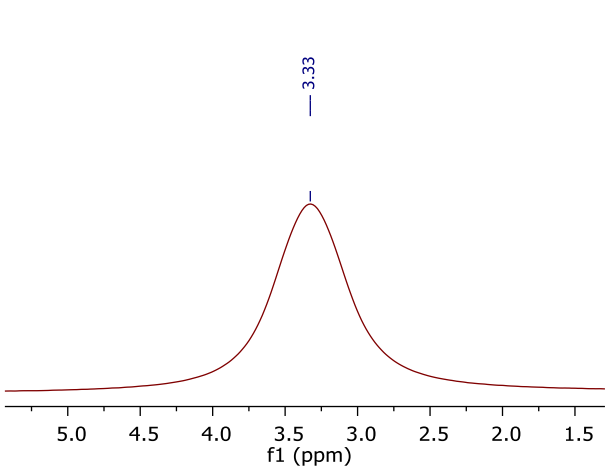


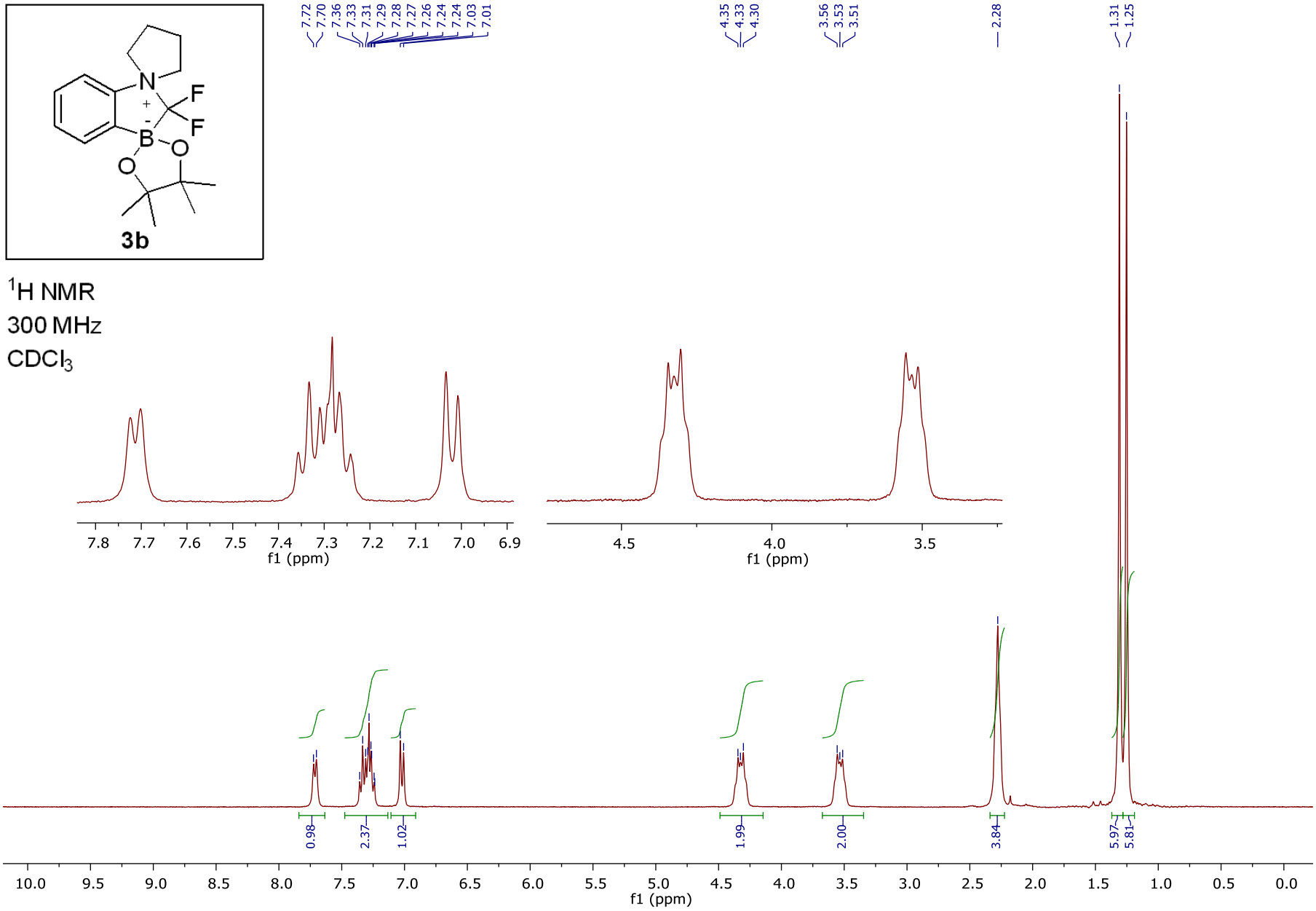


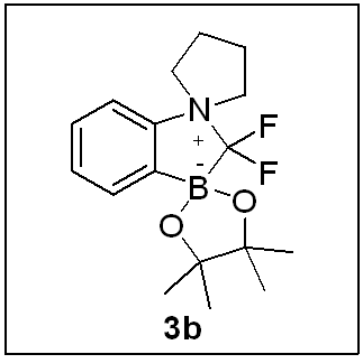
^{11}B {^{1}H} NMR

96 MHz

$CDCl_3$



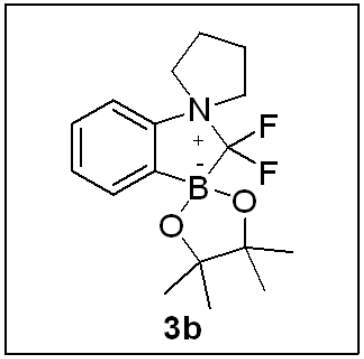

3b
1H NMR
300 MHz
CDCl3
7.72
7.70
7.36
7.33
7.31
7.29
7.28
7.27
7.26
7.24
7.24
7.03
7.01
4.35
4.33
4.30
3.56
3.53
3.51
2.28
1.31
1.25
f1 (ppm)
0.98
2.37
1.02
1.99
2.00
3.84
5.97
5.81



^{13}C {^{1}H} NMR

75 MHz

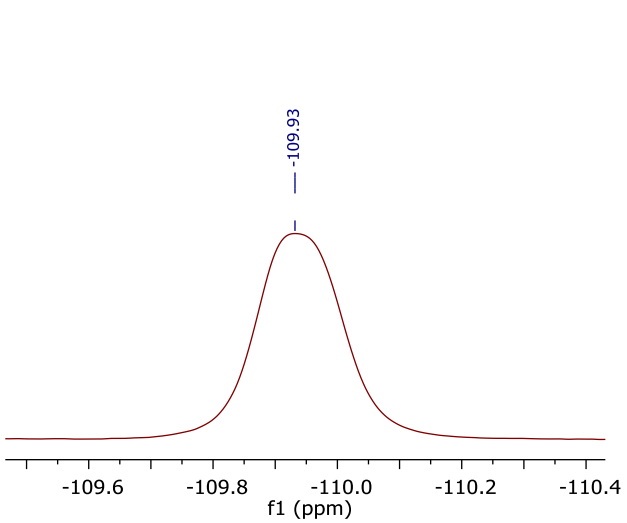
$CDCl_3$

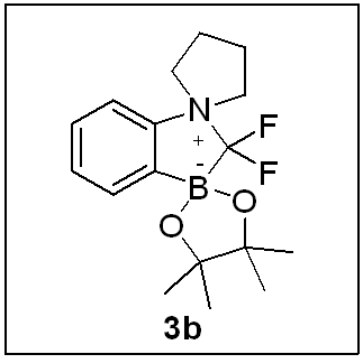


^{19}F NMR

282 MHz

$CDCl_3$



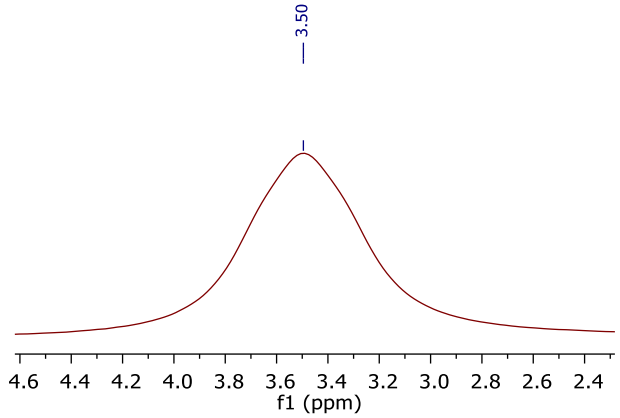


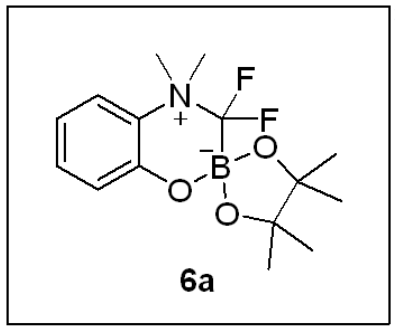
3b

^{11}B {^{1}H} NMR

96 MHz

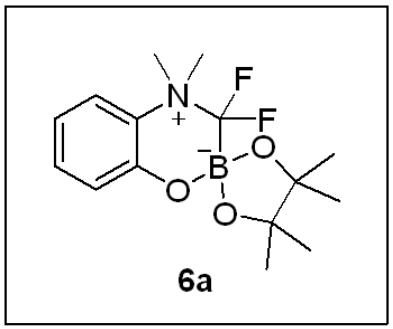
$CDCl_3$





6a

^{1}H NMR
300 MHz
$CDCl_3$

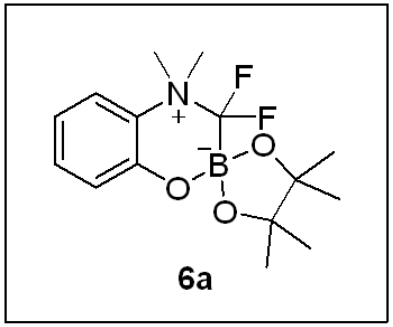


6a

^{13}C {^{1}H} NMR

75 MHz

$CDCl_3$

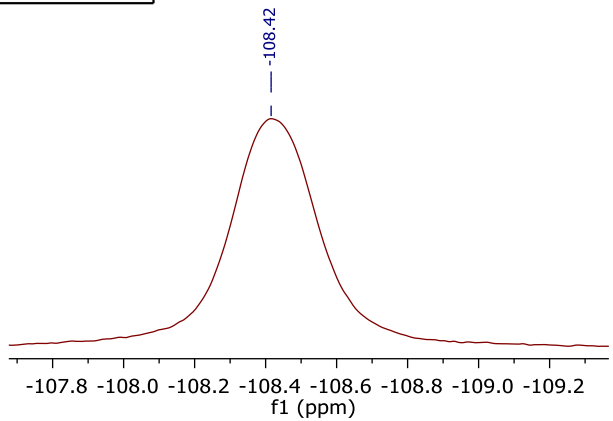


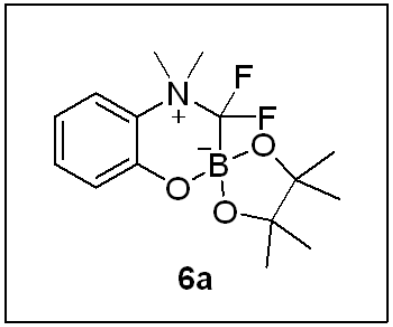
6a

^{19}F NMR

282 MHz

$CDCl_3$



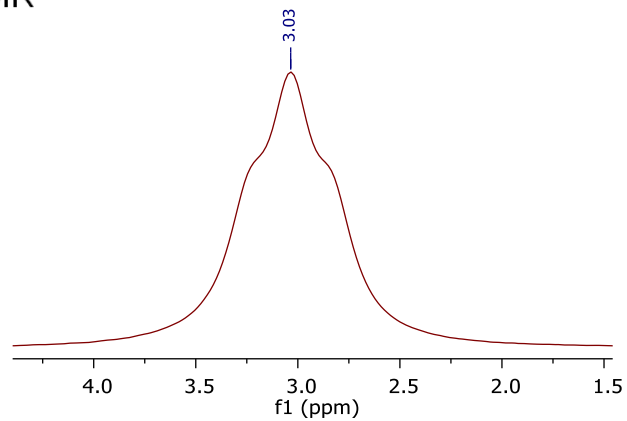


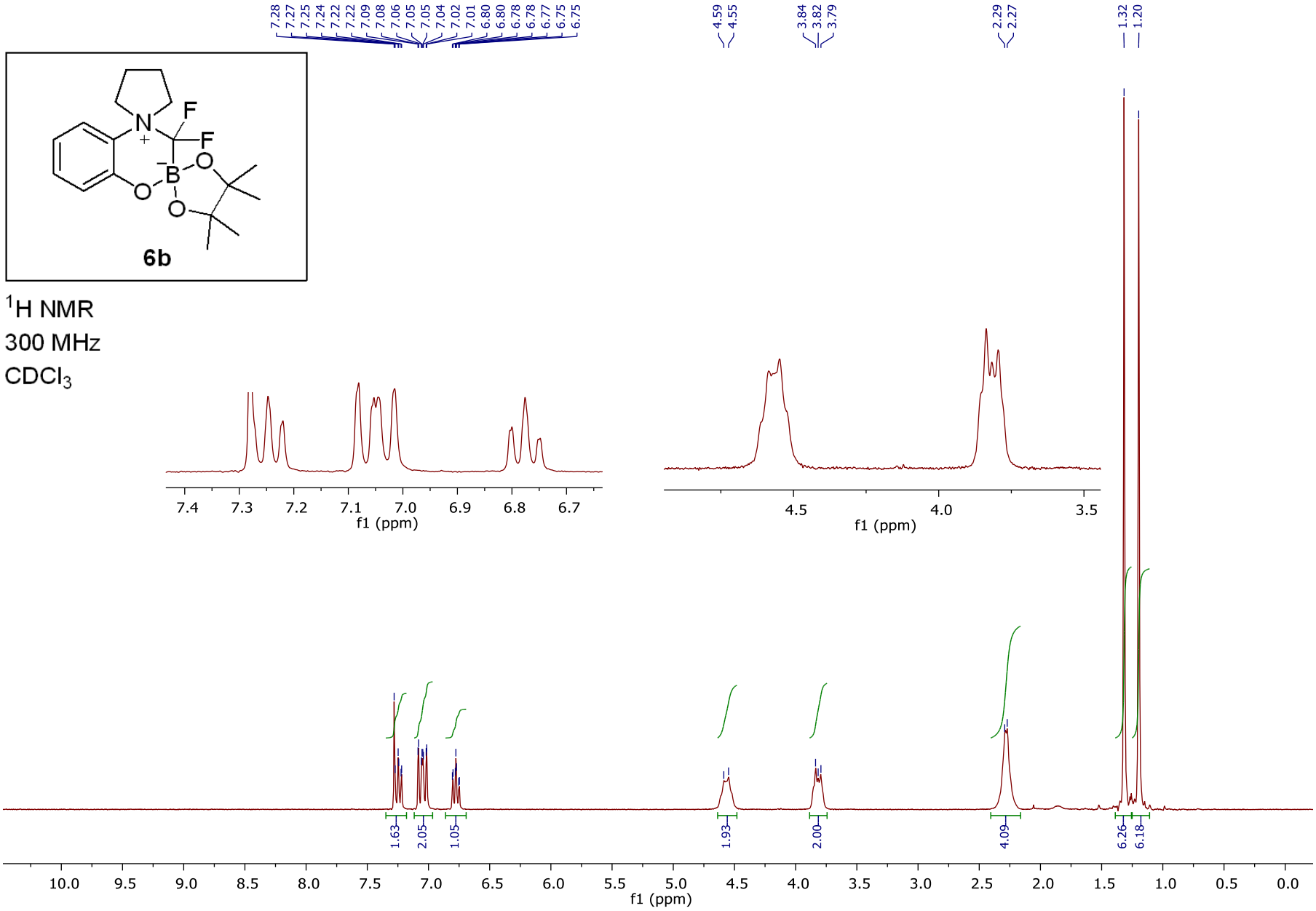
6a

^{11}B {^{1}H} NMR

96 MHz

$CDCl_3$




7.28
7.27
7.25
7.24
7.22
7.22
7.09
7.08
7.06
7.05
7.05
7.04
7.02
7.01
6.80
6.80
6.78
6.78
6.77
6.75
6.75
4.59
4.55
3.84
3.82
3.79
2.29
2.27
1.32
1.20
F
F
N
+
B
O
O
O
6b
1H NMR
300 MHz
CDCl3
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
4.5
4.0
3.5
f1 (ppm)
1.63
2.05
1.05
1.93
2.00
4.09
6.26
6.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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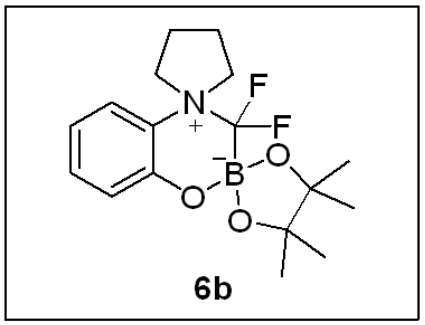
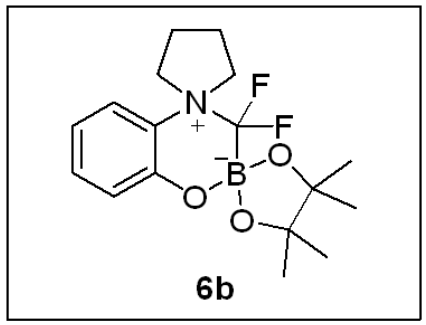
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



^{13}C {^{1}H} NMR

75 MHz

$CDCl_3$

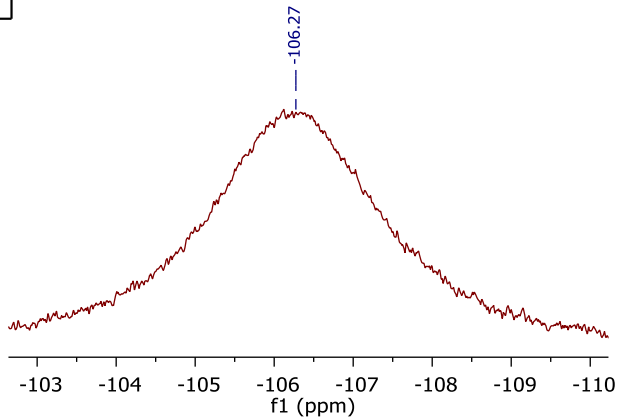


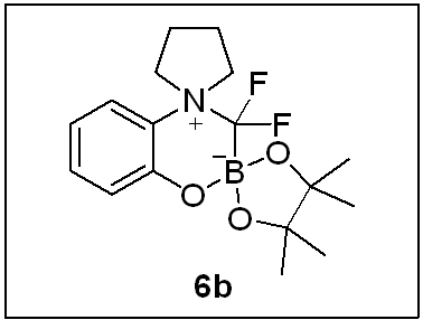
6b

^{19}F NMR

282 MHz

$CDCl_3$



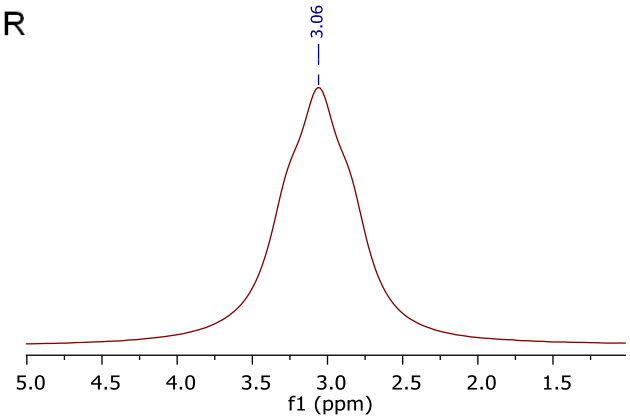


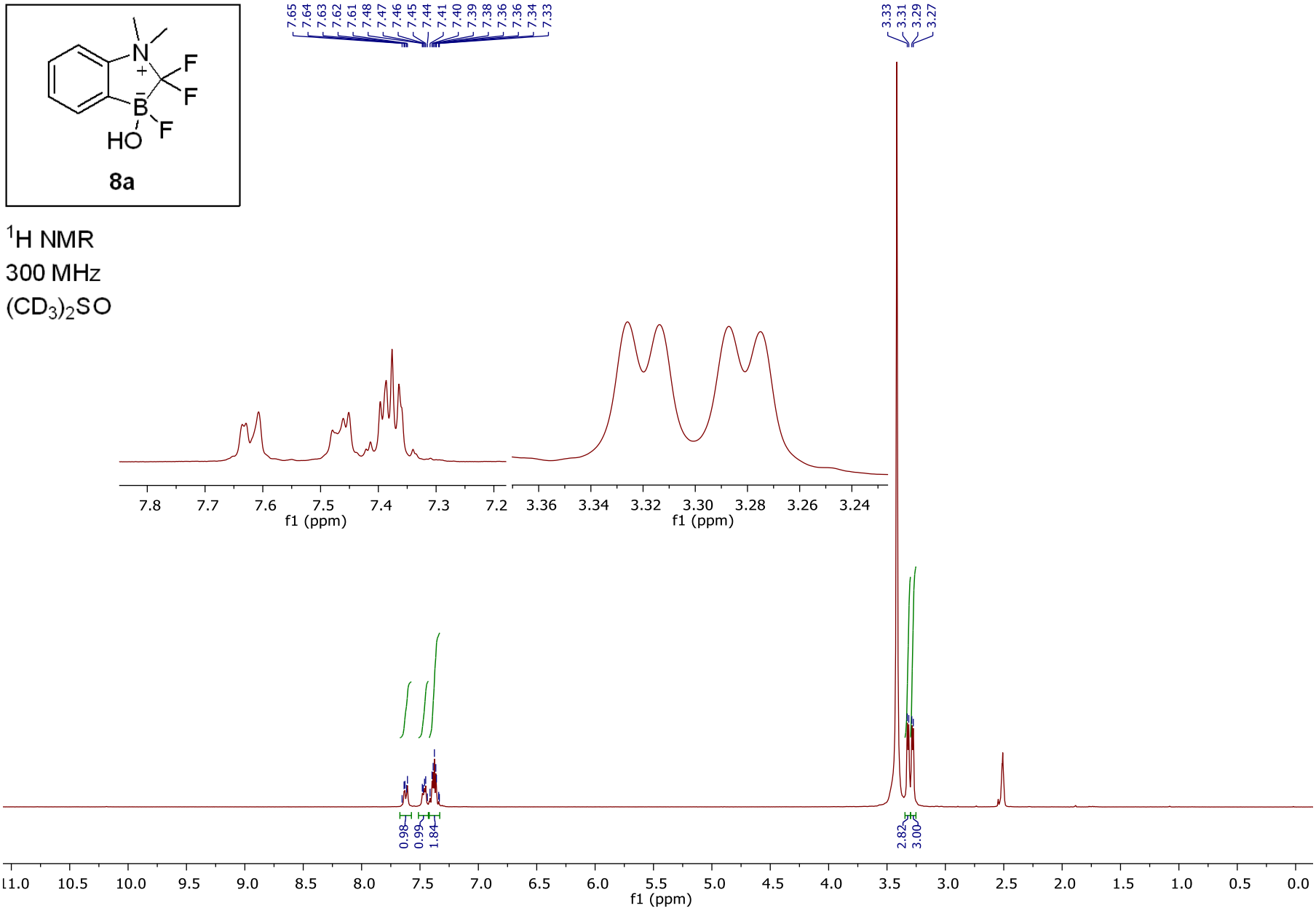
6b

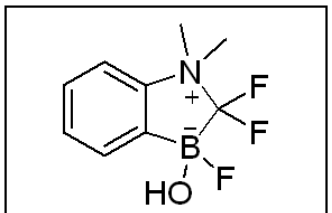
^{11}B {^{1}H} NMR

96 MHz

$CDCl_3$

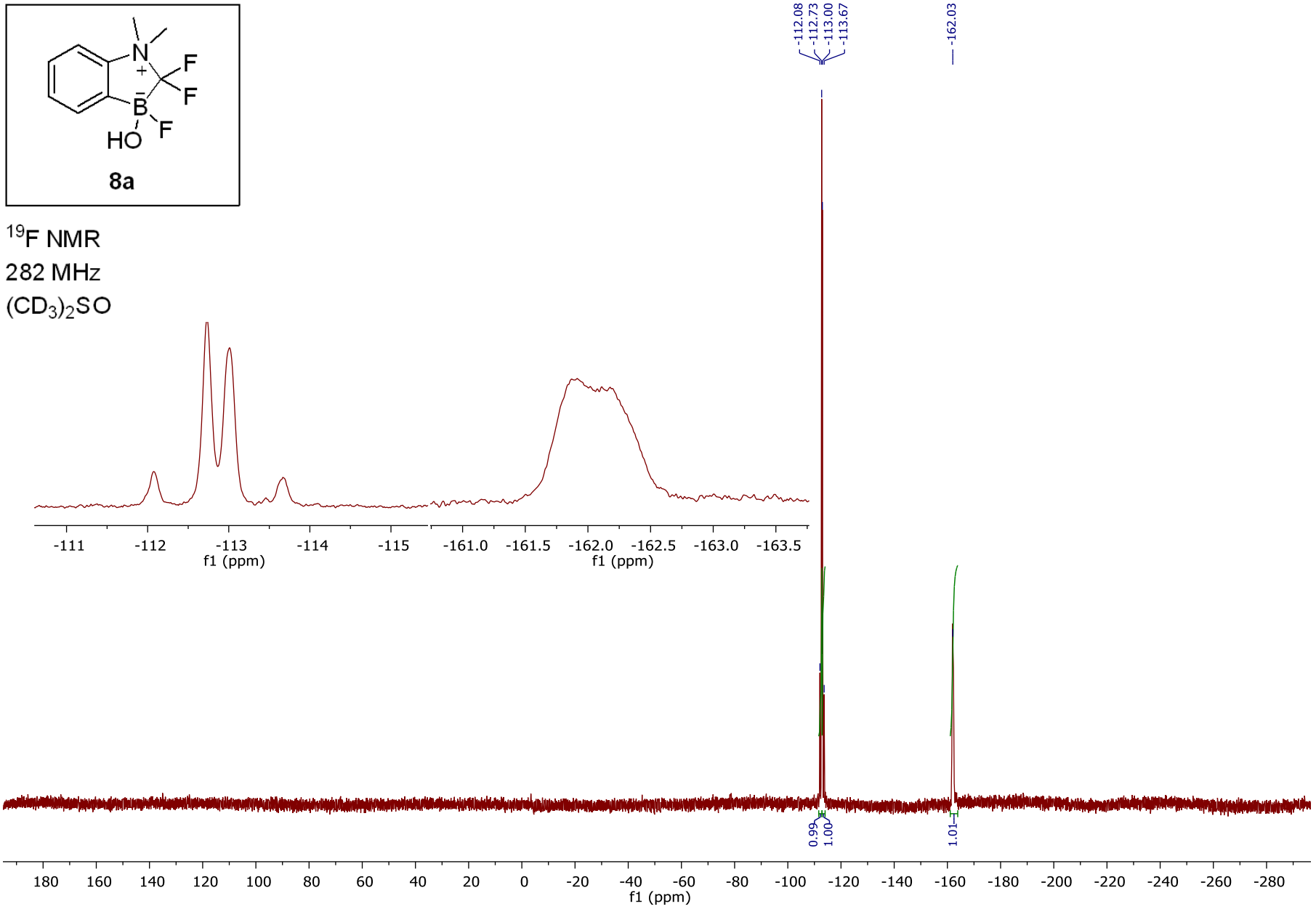


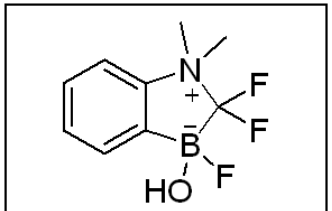

8a
1H NMR
300 MHz
(CD3)2SO
f1 (ppm)
f1 (ppm)
f1 (ppm)



8a

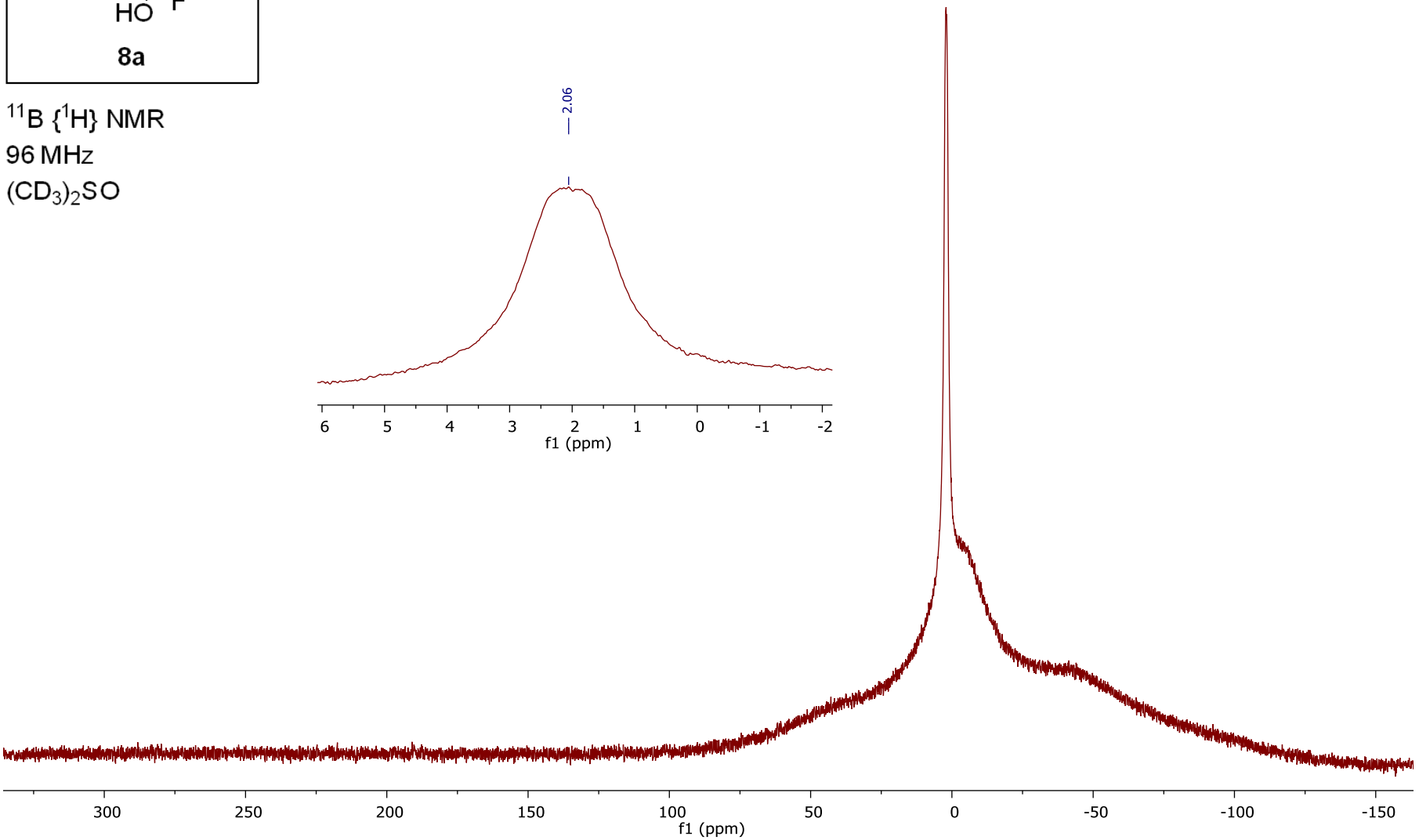
^{13}C {^{1}H} NMR
75 MHz
$(CD_3)_2SO$

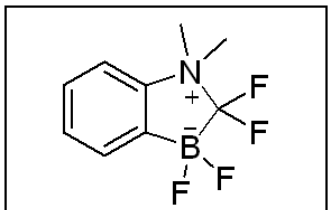

8a
19F NMR
282 MHz
(CD3)2SO
-112.08
-112.73
-113.00
-113.67
-162.03
f1 (ppm)
0.99
1.00
1.01



8a

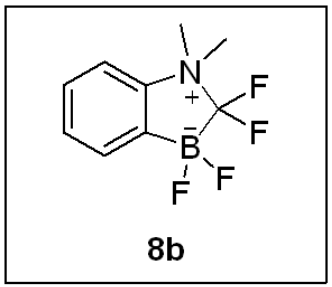
^{11}B {^{1}H} NMR
96 MHz
$(CD_3)_2SO$





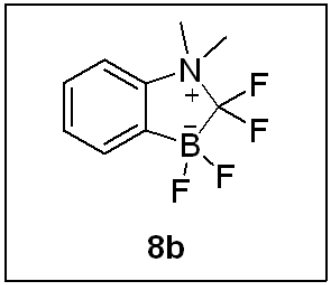
8b

^{1}H NMR
300 MHz
$CDCl_3$



8b

^{13}C {^{1}H} NMR
75 MHz
$CDCl_3$

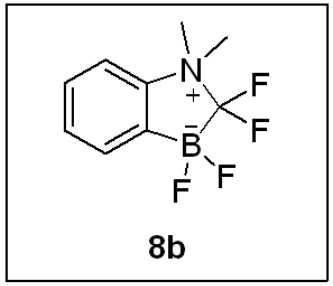


8b

^{19}F NMR

282 MHz

$CDCl_3$

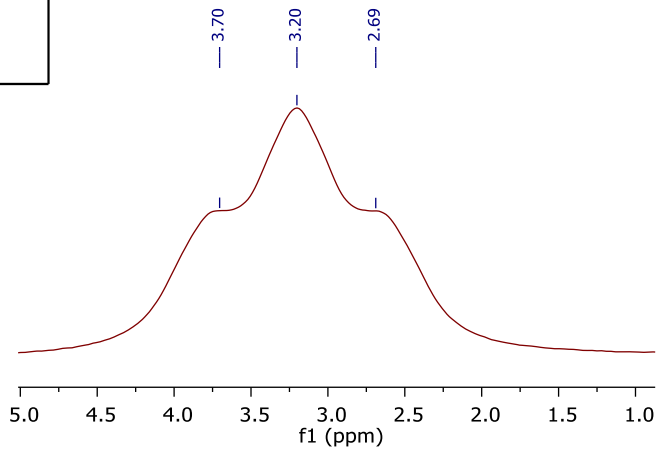


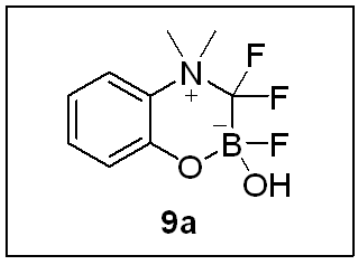
8b

^{11}B {^{1}H} NMR

96 MHz

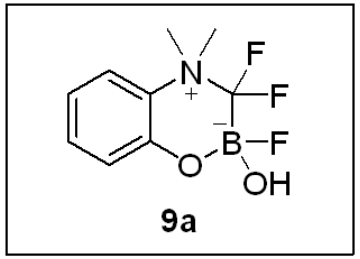
$CDCl_3$





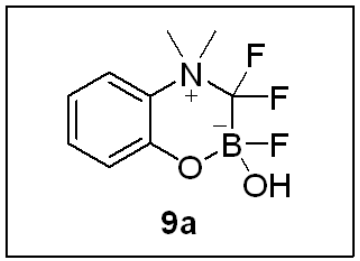
9a

^{1}H NMR
300 MHz
$(CD_3)_2SO$



9a

^{13}C {^{1}H} NMR
75 MHz
$(CD_3)_2SO$

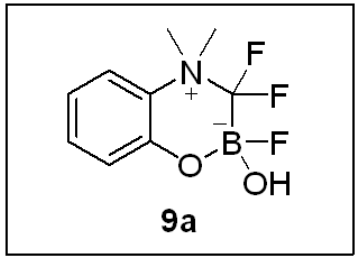


9a

^{19}F NMR

282 MHz

$(CD_3)_2SO$

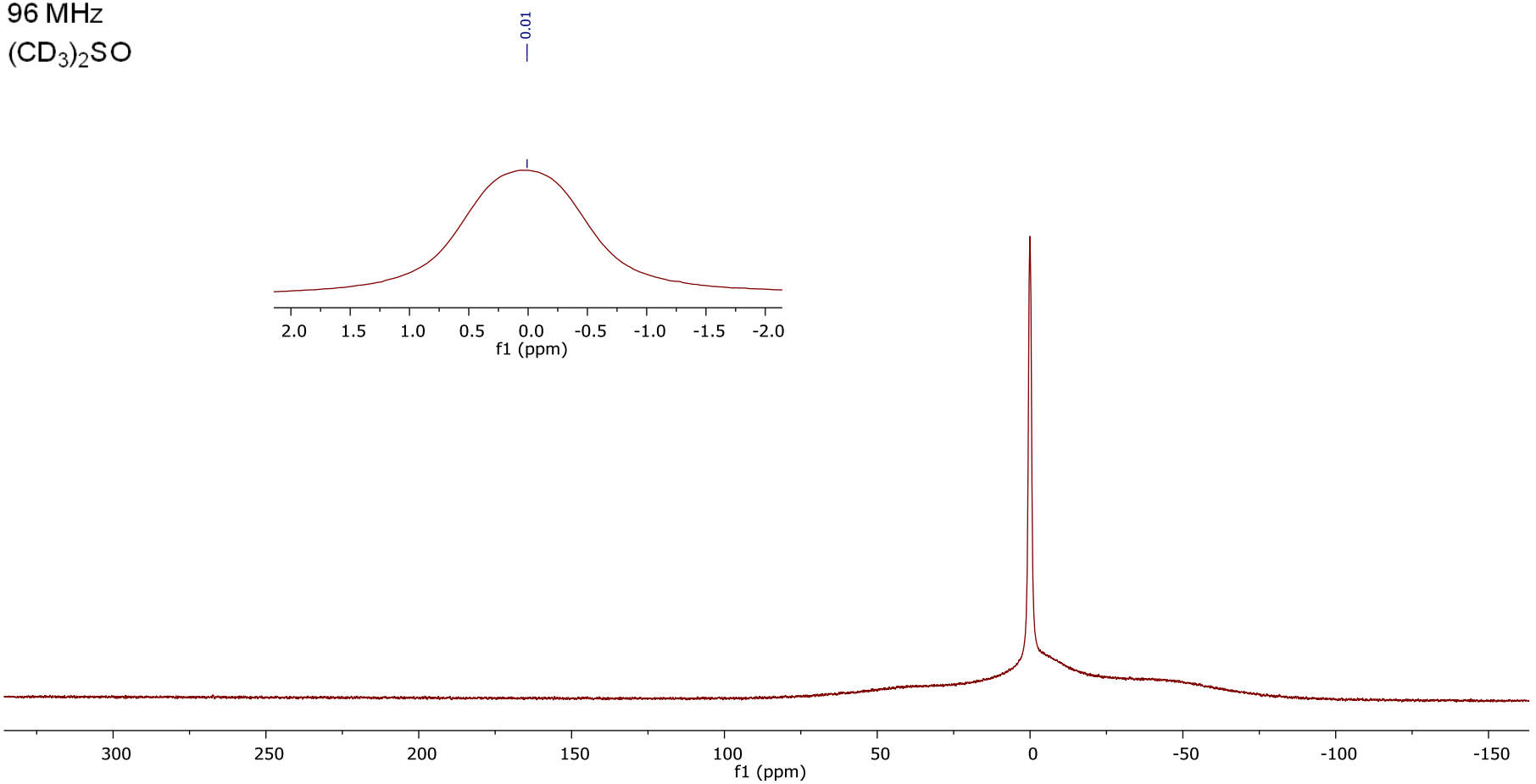


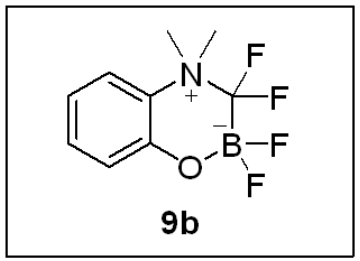
9a

^{11}B {^{1}H} NMR

96 MHz

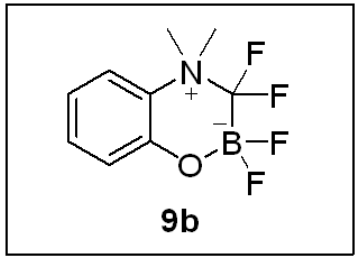
$(CD_3)_2SO$





9b

^{1}H NMR
300 MHz
$(CD_3)_2SO$

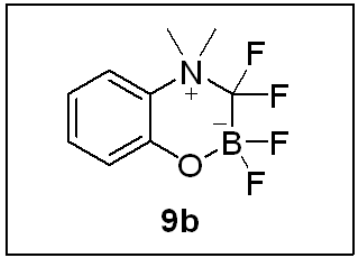


9b

^{13}C {^{1}H} NMR

75 MHz

$(CD_3)_2SO$

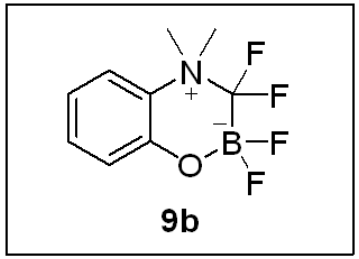


9b

^{19}F NMR

282 MHz

$(CD_3)_2SO$



9b

^{11}B {^{1}H} NMR

96 MHz

$(CD_3)_2SO$