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Electronic Supporting Information

Microwave-assisted direct synthesis of BODIPY dyes and derivatives

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General methods

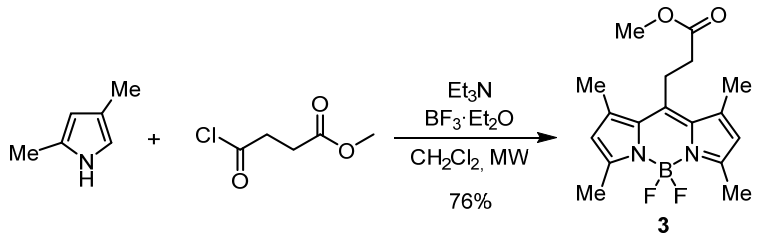
All reactions were carried out in dried glassware microwave tube, under argon atmosphere, using standard gas-tight syringes and septa. Toluene was distilled from sodium/benzophenone. Dichloromethane was dried *via* MBraun MB-SPS 800 Solvent Purification System. Available reagents were used as received. Microwave-assisted reactions were performed in an Anton Paar Monowave 300 reactor operating at 2455 MHz using a 6 mL (30 mL for scalable reaction) sealed microwave tube with stirring. The mixtures were irradiated with the appropriate power (the system operates at 0-850 W power) to reach the temperature of 40 ºC or 80 ºC using the "as fast as possible" heating mode (hold time: 2 min, approximately).[1] Completion of the reactions and reaction times were estimated by thin layer chromatography (TLC), pre-coated silica gel foils with fluorescent indicator 254 nm (Alugram® Xtra SIL G/UV_{254}, 0.20 mm thick), UV light as the visualizing agent, and ethanolic phosphomolybdic acid as the developing agent. Flash column chromatography was performed using 230-400 mesh silica gel. ^{1}H NMR and $^{13}C\{H\}$ NMR spectra were recorded at room temperature in $CDCl_3$ using a 300 and 400 MHz Bruker Advance 300 MHz, 400 Mz or a Bruker Advance 500 MHz spectrometer and calibrated to the solvent peak. DEPT data were used to assign carbon types. Chemical shifts are reported in ppm (δ) relative to the solvent $CDCl_3$ (δ_H 7.26 ppm and δ_C 77.1 ppm). Mass spectra were obtained with a MAT 95XP Magnetic Sector EI spectrometer operating in the positive ionization mode. The IR spectra were taken with ATR ("attenuated total reflectance"). Ultraviolet/Visible (UV/Vis) absorption and fluorescence spectra was recorded with standard 1 cm quartz cells. Emission spectra was recorded using a spectrofluorometer equipped with a pulsed xenon flash-lamp as a light source.

General procedure for the microwave assisted synthesis of BODIPYs. In an oven-dried microwave tube equipped with a magnetic stir bar, a solution of the appropriated pyrrole (2.0 mmol), acyl chloride (0.7 mmol), Et_3N (2.7 mmol) and $BF_3{\cdot}OEt_2$ (4.0 mmol) in dry CH_2Cl_2 (1.0 mL) was irradiated with microwaves at 40 °C for 15 min under argon. (reaction complete by TLC test). The reaction was diluted with CH_2Cl_2 (15.0 mL) and the organic phase was washed with water (15.0 mL), dried ($MgSO_4$ anhyd.), filtered and concentrated. The resulting crude was purified by flash column chromatography

[1] E. M. López-Vidal, V. Blanco, M. D. García, C. Peinador and J. M. Quintela, *Org. Lett.*, 2012, **14**, 580–683.

(EtOAc/hexanes) to afford, after concentration and high vacuum drying, the corresponding BODIPY.

Methyl 3-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1-*f*][1,3,2]diazaborinin-10-yl)propanoate (3).[2]

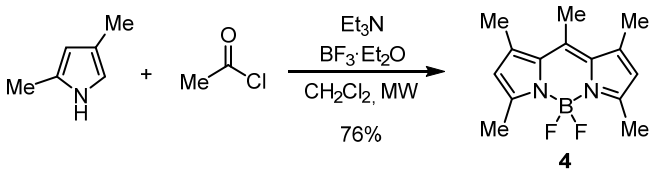


According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.210 mL, 1.99 mmol), methyl 4-chloro-4-oxobutanoate (820 µL, 0.660 mmol), Et_3N (0.370 mL, 2.66 mmol) and $BF_3{\cdot}Et_2O$ (0.500 mL, 3.98 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (5-10% AcOEt/hexanes), compound **3** (162 mg, 73%) was obtained as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (s, 2H), 3.73 (s, 3H), 3.29 (t, *J*=8.8 Hz, 2H), 2.59 (t, *J*=8.8 Hz, 2H), 2.51 (s, 6H), 2.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1 (C), 154.7 (2 x C), 143.3 (2 x C), 140.4 (2 x C), 131.2 (C), 122.0 (2 x CH), 52.1 (CH_3), 35.2 (CH_2), 23.6 (CH_2), 16.5 (2 x CH_3), 14.5 (2 x CH_3); MS (EI) m/z (%) 334 $[M]^+$ (38); HRMS (EI) calcd for $C_{17}H_{21}O_2N_2BF_2$ $[M]^+$ 334.1659, found 334.1652.

For the scale up: According to the general procedure, the mixture of 2,4-dimethylpyrrole (2.05 mL, 19.9 mmol), methyl 4-chloro-4-oxobutanoate (0.820 mL, 6.64 mmol), Et_3N (3.70 mL, 26.6 mmol) and $BF_3{\cdot}Et_2O$ (5.00 mL, 39.8 mmol) in CH_2Cl_2 (3.00 mL) was irradiated. After purification by column chromatography (5-10% AcOEt/hexanes), compound **3** (1.45 g, 63%) was obtained as a brown solid.

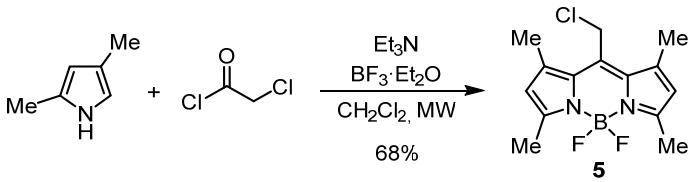
[2] (a) A. A. Pakhomov, Y. N. Knononevich, M. V. Stukalova, E. A. Suidchenko, N. M. Surin, G. V. Cherkaev, O. I. Shchegolikina, V. I. Martynov and A. M. Muzafarov, *Tetrahedron Lett.*, 2016, **57**, 979–982. (b) J. Agramunt, R. Ginesi, E. Pedroso and A. Grandas, *J. Org. Chem.*, 2020, **85**, 6593–6604.

5,5-Difluoro-1,3,7,9,10-pentamethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*][1,3,2]diaza-borinine (4).[3]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.390 mL, 3.81 mmol), acetyl chloride (910 µL, 1.27 mmol), Et_3N (0.710 mL, 5.08 mmol) and $BF_3{\cdot}Et_2O$ (0.960 mL, 7.64 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (30% CH_2Cl_2/hexanes), compound **4** (254 mg, 76%) was obtained as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (s, 2H), 2.56 (s, 3H), 2.51 (s, 6H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0 (2 x C), 141.9 (2 x C), 141.5 (2 x C), 132.5 (C), 121.7 (2 x CH), 17.7 (2 x CH_3), 16.8 (CH_3), 14.9 (2 x CH_3); MS (EI) m/z (%) 263 $[M + H]^+$ (14), 262 $[M]^+$ (100); HRMS (EI) calcd for $C_{14}H_{17}N_2BF_2$ $[M]^+$ 262.1447, found 262.1450.

10-(Chloromethyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (5).[4]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.270 mL, 2.66 mmol), 2-chloroacetyl chloride (700 µL, 0.890 mmol), Et_3N (0.490 mL, 3.54 mmol) and $BF_3{\cdot}Et_2O$ (0.670 mL, 5.31 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (50% CH_2Cl_2/hexanes), compound **5** (178 mg, 68%) was obtained as a red solid. ^{1}H RMN (400 MHz, $CDCl_3$) δ 6.09 (s, 2H), 4.77 (s, 2H), 2.53 (s, 12H); ^{13}C RMN (100 MHz, $CDCl_3$) δ 156.7 (2 x C), 141.1 (2 x C), 136.0 (2 x C), 131.4

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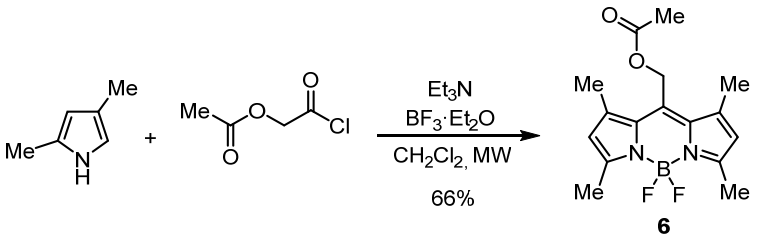
[3] A. B. Nepomnyashchii, M. Bröring, J. Ahrens and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 8633–8645.

[4] Y. Wu, X. Peng, B. Guo, J. Fan, Z. Zhang, J. Wang, A. Cui and Y. Gao, *Org. Biomol. Chem.*, 2005, **3**, 1387–1392.

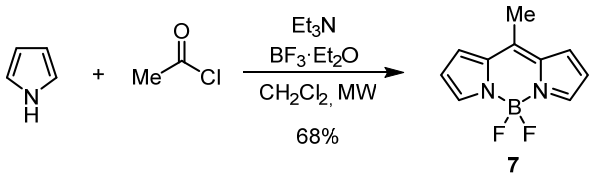
(C), 122.3 (2 x CH), 37.2 (CH_2), 15.5 (2 x CH_3), 14.7 (2 x CH_3); MS (EI) m/z (%) 296 $[M]^+$ (31); HRMS (EI) calcd for $C_{14}H_{16}N_2BCl_2F_2$ $[M]^+$ 296.1058, found 296.1056.

(5,5-Difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'*f*][1,3,2]diazaborinin-10-yl)methyl acetate (6).[5]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.230 mL, 2.20 mmol), acetoxyacetyl chloride (790 µL, 0.730 mmol), Et_3N (0.410 mL, 2.93 mmol) and $BF_3{\cdot}Et_2O$ (0.550 mL, 4.39 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (15-30% AcOEt/hexanes), compound **6** (155 mg, 66%) was obtained as an orange solid. ^{1}H RMN (300 MHz, $CDCl_3$) δ 6.08 (s, 2H), 5.29 (s, 2H), 2.53 (s, 6H), 2.35 (s, 6H), 2.12 (s, 3H); ^{13}C RMN (75 MHz, $CDCl_3$) δ 170.5 (C), 156.6 (2 x C), 141.5 (2 x C), 133.3 (2 x C), 132.7 (C), 122.3 (2 x CH), 57.9 (CH_2), 20.6 (CH_3), 15.6 (2 x CH_3), 14.7 (2 x CH_3). MS (EI) m/z (%) 320 $[M]^+$ (55); HRMS (EI) calcd for $C_{16}H_{19}O_2N_2BF_2$ $[M]^+$ 320.1502, found 320.1510.

5,5-Difluoro-10-methyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (7).[6]



According to the general procedure, the mixture of 1*H*-pyrrole (0.270 mL, 3.81 mmol), acetyl chloride (910 µL, 1.27 mmol), Et_3N (0.710 mL, 5.08 mmol) and $BF_3{\cdot}Et_2O$ (0.960 mL, 7.64 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (15-20% AcOEt/hexanes), compound **7** (177 mg, 68%) was obtained as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.27 (s, 2H), 6.45 (s, 2H),

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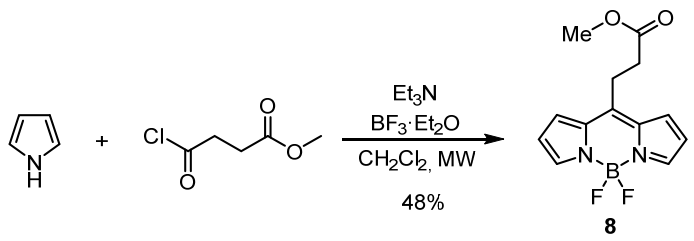
5 K. Krumova and G. Cosa, *J. Am. Chem. Soc.*, 2010, **132**, 17560–17569.

6 L. Jiao, C. Yu, J. Wang, E. A. Briggs, N. A. Besley, D. Robinson, M. J. Ruedas-Rama, A. Orte, L. Crovetto, E. M. Talavera, J. M. Álvarez-Pez, M. V. der Auweraer and N. Boens, *RSC Adv.*, 2015, **5**, 89375–89388.

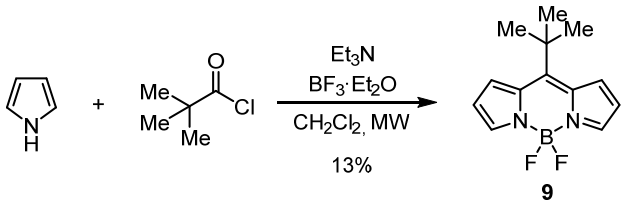
2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4 (C), 143.8 (2 x CH), 137.3 (2 x C), 128.1 (2 x CH), 119.1 (2 x CH), 16.1 (CH_3); MS (EI) m/z (%) 206 $[M]^+$ (100); HRMS (EI) calcd for $C_{10}H_9N_2BF_2$ $[M]^+$ 206.0821, found 206.0819.

Methyl 3-(5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)propanoate (8).



According to the general procedure, the mixture of 1*H*-pyrrole (0.140 mL, 1.99 mmol), methyl 4-chloro-4-oxobutanoate (820 µL, 0.660 mmol), Et_3N (0.370 mL, 2.66 mmol) and $BF_3{\cdot}Et_2O$ (0.500 mL, 3.98 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (20% AcOEt/hexanes), compound **8** (88.2 mg, 48%) was obtained as a brown solid. λ_{max}^{abs} ($CHCl_3$)/nm = 502 (Ɛ/$M^{-1}cm^{-1}$ 52532); λ_{exc} ($CHCl_3$)/nm = 502; λ_{max}^{em} ($CHCl_3$)/nm = 509; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.31 (d, *J*=4.2 Hz, 2H), 6.54 (d, *J*=4.2 Hz, 2H), 3.68 (s, 3H), 3.25 (t, *J*=8.1 Hz, 2H), 2.76 (t, *J*=8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (C), 147.8 (C), 144.2 (2 x CH), 134.9 (2 x C), 128.1 (2 x CH), 118.4 (2 x CH), 52.1 (CH_3), 36.8 (CH_2), 25.9 (CH_2); MS (EI) m/z (%) 278 $[M]^+$ (42); HRMS (EI) calcd for $C_{13}H_{13}O_2N_2BF_2$ $[M]^+$ 278.1033, found 278.1029.

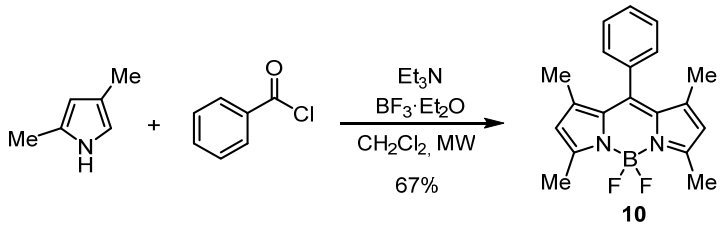
10-(*tert*-Butyl)-5,5-difluoro-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (9).[6]



According to the general procedure, the reaction of 1*H*-pyrrole (0.170 mL, 2.49 mmol), pivaloyl chloride (100 µL, 0.830 mmol), Et_3N (0.460 mL, 3.32 mmol) and $BF_3{\cdot}Et_2O$ (0.630 mL, 5.58 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (15% AcOEt/hexanes), compound **9** (27.4 mg, 13%) was obtained as a

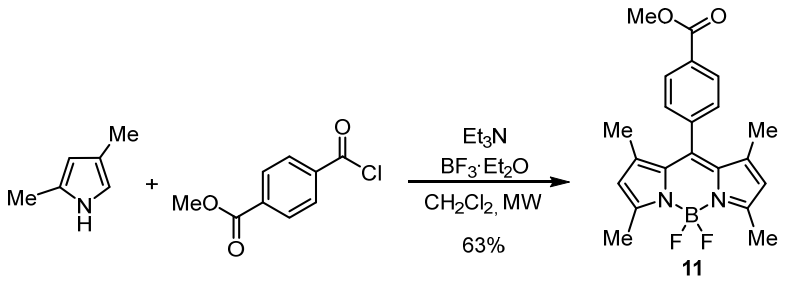
brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.66 (d, *J*= 4.3 Hz, 2H), 6.54 (d, *J*=4.4 Hz, 2H), 1.73 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (C), 142.6 (2 x CH), 135.0 (2 x C), 132.8 (2 x CH), 117.9 (2 x CH), 40.8 (C), 36.2 (3 x CH_3); MS (EI) m/z (%) 248 $[M]^+$ (50); HRMS (EI) calcd for $C_{13}H_{15}BF_2N_2$ $[M]^+$ 248.1291, found 248.1298.

5,5-Difluoro-1,3,7,9-tetramethyl-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (10).[7]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.220 mL, 2.13 mmol), benzoyl chloride (830 µL, 0.710 mmol), Et_3N (0.400 mL, 2.84 mmol) and $BF_3{\cdot}Et_2O$ (0.540 mL, 4.27 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (15-20% AcOEt/hexanes), compound **10** (154 mg, 67%) was obtained as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.50 (m, 3H), 7.29-7.31 (m, 2H), 6.00 (s, 2H), 2.58 (s, 6H), 1.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4 (2 x C), 143.2 (2 x C), 141.8 (C), 135.0 (2 x C), 131.5 (C), 129.1 (2 x CH), 129.0 (CH), 128.0 (2 x CH), 121.2 (2 x CH), 14.6 (2 x CH_3), 14.3 (2 x CH_3); MS (EI) m/z (%) 325 $[M + H]^+$ (25), 324 $[M]^+$ (100); HRMS (EI) calcd for $C_{19}H_{19}N_2BF_2$ $[M]^+$ 324.1604, found 324.1603.

Methyl 4-(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)benzoate (11).[8]

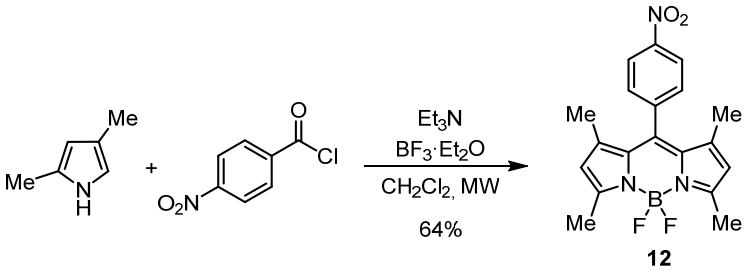


[7] K. Guzow, K. Kornowska and W. Wiczk, *Tetrahedron Lett.*, 2009, **50**, 2908–2910.

[8] W. Quin, M. Baruah, W. M. De Borgg and N. Boens, *J. Photochem. Photobiol., A: Chem.*, 2006, **183**, 190–197.

According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.160 mL, 1.51 mmol), methyl 4-(chlorocarbonyl)benzoate (101 mg, 0.500 mmol), Et_3N (0.280 mL, 2.01 mmol) and $BF_3 \cdot Et_2O$ (0.380 mL, 3.02 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (10% AcOEt/hexanes), compound **11** (121 mg, 63%) was obtained as a dark red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J*=8.4 Hz, 2H), 7.40 (d, *J*=8.4 Hz, 2H), 5.98 (s, 2H), 3.98 (s, 3H), 2.55 (s, 6H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9 (C), 157.0 (2 x C), 141.6 (2 x C), 140.2 (C), 139.8 (2 x C), 132.3 (C), 130.9 (C), 130.8 (2 x CH), 128.4 (2 x CH), 119.5 (2 x CH), 52.4 (CH_3), 14.6 (4 x CH_3); MS (EI) m/z (%) 383 $[M + H]^+$ (29), 382 $[M]^+$ (100); HRMS (EI) calcd for $C_{21}H_{21}O_2N_2BF_2$ $[M]^+$ 382.1659, found 382.1662.

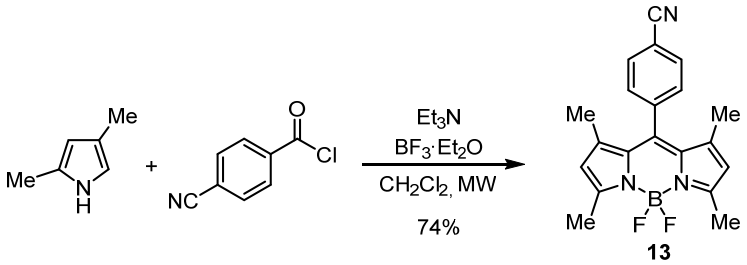
5,5-Difluoro-1,3,7,9-tetramethyl-10-(4-nitrophenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (12).[9]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.250 mL, 2.24 mmol), 4-nitrobenzoyl chloride (151 mg, 0.810 mmol), Et_3N (0.45 mL, 3.23 mmol) and $BF_3 \cdot Et_2O$ (0.610 mL, 4.85 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (10-20% AcOEt/hexanes), compound **12** (190 mg, 64%) was obtained as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J*=7.8 Hz, 2H), 7.54 (d, *J*=7.8 Hz, 2H), 6.01 (s, 2H), 2.56 (s, 6H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (2 x C), 148.4 (C), 142.6 (2 x C), 142.0 (2 x C), 138.4 (C), 130.7 (C), 129.7 (2 x CH), 124.4 (2 x CH), 121.9 (2 x CH), 14.7 (4 x CH_3); MS (EI) m/z (%) 370 $[M + H]^+$ (20), 369 $[M]^+$ (100); HRMS (EI) calcd for $C_{19}H_{18}O_2N_3BF_2$ $[M]^+$ 369.1455, found 369.1465.

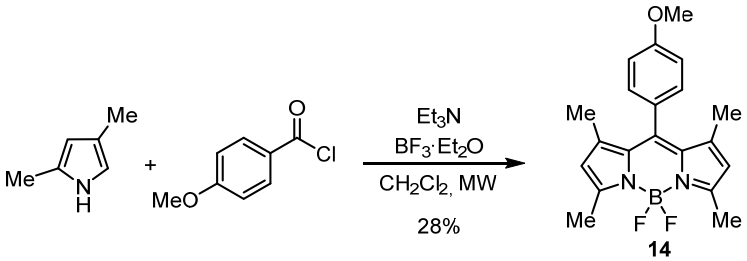
[9] T. Ueno, Y. Urano, H. Kojima and T. Nugano, *J. Am. Chem. Soc.*, 2006, **128**, 10640–10641.

4-(5,5-Difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diaza-borinin-10-yl)benzonitrile (13).[10]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.190 mL, 1.81 mmol), 4-cyanobenzoyl chloride (103 mg, 0.600 mmol), Et_3N (0.340 mL, 2.42 mmol) and $BF_3{\cdot}Et_2O$ (0.460 mL, 3.62 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (7-10% AcOEt/hexanes), compound **13** (156 mg, 74%) was obtained as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dt, *J*=8.3, 1.8 Hz, 2H), 7.44 (dt, *J*=8.3, 1.8 Hz, 2H), 6.00 (s, 2H), 2.55 (s, 6H), 1.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 (2 x C), 142.6 (2 x C), 140.0 (2 x C), 138.7 (C), 132.9 (2 x CH), 130.7 (C), 129.4 (2 x CH), 121.8 (2 x CH), 118.1 (C), 113.3 (C), 14.6 (4 x CH_3); MS (EI) m/z (%) 350 $[M + H]^+$ (23), 349 $[M]^+$ (100); HRMS (EI) calcd for $C_{20}H_{18}N_3BF_2$ $[M]^+$ 349.1556, found 349.1558.

5,5-Difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (14).[11]



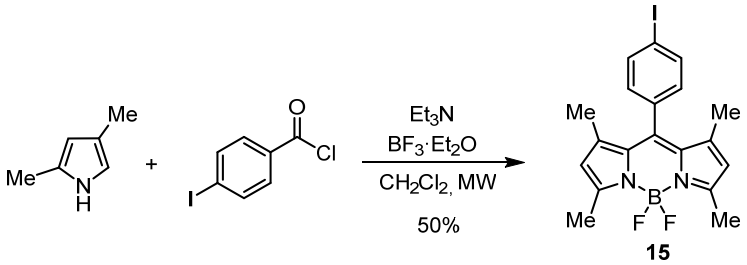
According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.180 mL, 1.76 mmol), 4-methoxybenzoyl chloride (101 mg, 0.590 mmol), Et_3N (0.330 mL, 2.34 mmol) and $BF_3{\cdot}Et_2O$ (0.440 mL, 3.52 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (7-20% AcOEt/hexanes), compound **14** (58.2

[10] E. Caruso, M. Gariboldi, A. Sangion, P. Gramatica and S. Banfi, *J. Photochem. Photobiol. B*, 2017, **167**, 269–281.

[11] S. Zhu, J. Zhang, G. Vegesna, A. Tiwari, F.-T. Luo, M. Zeller, R. Luck, H. Li, S. Green and H. Liu, *RSC Adv.*, 2011, **2**, 404–407.

mg, 28%) was obtained as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (dt, *J*=8.8, 2.2 Hz, 2H), 6.99 (dt, *J*=8.8, 2.2 Hz, 2H), 5.97 (s, 2H), 3.87 (s, 3H), 2.55 (s, 6H), 1.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (2 x C), 155.3 (2 x C), 143.2 (2 x C), 141.9 (C), 131.9 (C), 129.2 (2 x CH), 127.0 (C), 121.1 (2 x CH), 114.5 (2 x CH), 55.3 (CH_3), 14.6 (4 x CH_3); MS (EI) m/z (%) 355 $[M + H]^+$ (26), 354 $[M]^+$ (100); HRMS (EI) calcd for $C_{20}H_{21}ON_2BF_2$ $[M]^+$ 354.1710, found 354.1709.

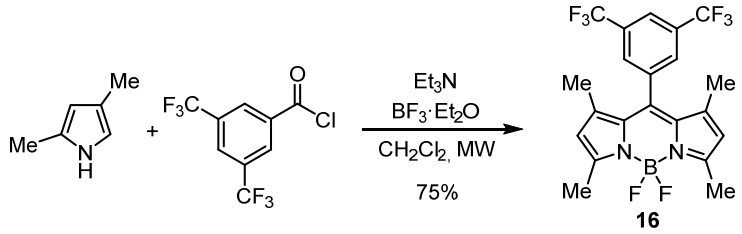
5,5-Difluoro-10-(4-iodophenyl)-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (15).[12]



According to the modified general procedure, the mixture of 2,4-dimethylpyrrole (0.120 mL, 1.13 mmol), 4-iodobenzoyl chloride (101 mg, 0.380 mmol), Et_3N (0.210 mL, 1.50 mmol) and $BF_3 \cdot Et_2O$ (0.280 mL, 2.25 mmol) in CH_2Cl_2 (1.00 mL) was irradiated 15 min at 40 ºC. After purification by column chromatography (7% AcOEt/hexanes), compound **15** (86.5 mg, 50%) obtained as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J*=8.3 Hz, 2H), 7.03 (d, *J*=8.3 Hz, 2H), 6.03 (s, 2H), 2.54 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (2 x C), 142.3 (2 x C), 140.1 (C), 138.4 (2 x CH), 135.0 (2 x C), 131.7 (C), 130.0 (2 x CH), 121.5 (2 x CH), 94.0 (2 x C), 14.7 (2 x CH_3), 14.6 (2 x CH_3); MS (EI) m/z (%) 451 $[M + H]^+$ (19), 450 $[M]^+$ (100); HRMS (EI) calcd for $C_{19}H_{18}N_2BF_2I$ $[M]^+$ 450.0570, found 450.0572.

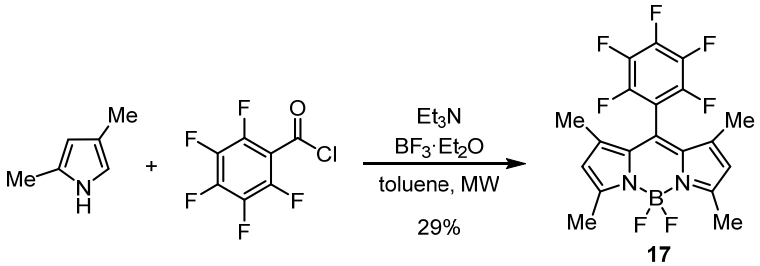
[12] T. N. Singh-Rachford, A. Haefele, R. Ziessel and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164–16165.

10-(3,5-Bis(trifluoromethyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (16).[13]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.110 mL, 1.08 mmol), 3,5-bis(trifluoromethyl)benzoyl chloride (660 µL, 0.360 mmol), Et_3N (0.200 mL, 1.45 mmol) and $BF_3{\cdot}Et_2O$ (0.270 mL, 2.17 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (30% CH_2Cl_2/hexanes), compound **16** (125 mg, 75%) was obtained as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.85 (s, 2H), 6.04 (s, 2H), 2.57 (s, 6H), 1.33 (s, 6H); ^{13}C RMN (75 MHz, $CDCl_3$) δ 157.1 (C), 142.3 (2 x C), 137.3 (2 x C), 136.8 (C), 132.8 (q, $^2J_{CF}$= 34.1 Hz, 2 x C), 130.9 (2 x C), 129.1 (2 x CH), 122.9 (q, $^1J_{CF}$= 273.2 Hz, 2 x C), 122.8 (m, $^3J_{CF}$= 3.8 Hz, CH), 122.1 (2 x CH), 14.8 (2 x CH_3), 14.7 (2 x CH_3). MS (EI) m/z (%) 460 $[M]^+$ (100); HRMS (EI) calcd for $C_{21}H_{17}N_2BF_8$ $[M]^+$ 460.1352, found 460.1341.

5,5-Difluoro-1,3,7,9-tetramethyl-10-(perfluorophenyl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (17).[14]



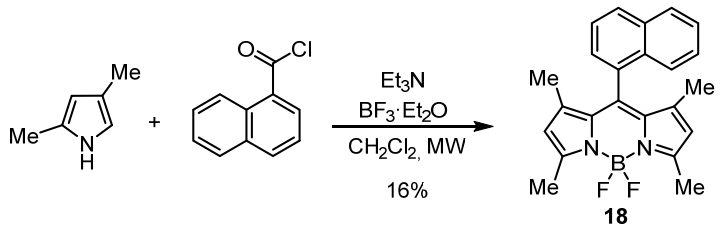
According to the modified general procedure, the mixture of 2,4-dimethylpyrrole (0.130 mL, 1.30 mmol), 2,3,4,5,6-pentafluorobenzoyl chloride (620 µL, 0.430 mmol), Et_3N (0.240 mL, 1.74 mmol) and $BF_3{\cdot}Et_2O$ (0.330 mL, 2.60 mmol) in toluene (1.00 mL) was irradiated 15 min at 80 ºC. After purification by column chromatography (4-10%

[13] M. Hecht, T. Fischer, P. Dietrich, W. Kraus, A. B. Descalzo, W. E. S. Unger and K. Rurack, *ChemistryOpen*, 2013, **2**, 25–38.

[14] G. Vives, C. Giarsante, R. Bofinger, G. Raffy, A. Del Guerzo, B. Kauffann, P. Batat, G. Jonusauskas, N. D. Mcdenaghan, *Chem. Comm*., 2011, **47**, 10425–10427.

AcOEt/hexanes), compound **17** (52.9 mg, 29%) was obtained as a red solid. ^{1}H-RMN (400 MHz, $CDCl_3$) δ 6.06 (s, 2H), 2.57 (s, 6H), 1.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8 (2 x C), 145.1 (C), 136.5 (C), 131.0 (2 x C), 122.7 (2 x C), 122.3 (2 x CH), 14.8 (2 x CH_3), 13.6 (2 x CH_3). MS (EI) m/z (%) 415 $[M + H]^+$ (16), 414 $[M]^+$ (100); HRMS (EI) calcd for $C_{19}H_{14}N_2BF_7$ $[M]^+$ 414.1133, found 414.1131.

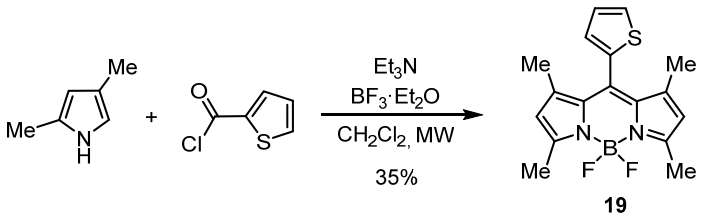
5,5-Difluoro-1,3,7,9-tetramethyl-10-(naphthalen-1-yl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (18).[15]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.160 mL, 1.57 mmol), 1-naphthoyl chloride (790 µL, 0.530 mmol), Et_3N (0.290 mL, 2.10 mmol) and $BF_3{\cdot}Et_2O$ (0.400 mL, 3.15 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (10% AcOEt/hexanes), compound **18** (31.6 mg, 16%) was obtained as a brown solid. ^{1}H RMN (300 MHz, $CDCl_3$) δ 7.95 (d, *J*= 8.3 Hz, 1H), 7.88 (d, *J*= 8.2 Hz, 1H), 7.79 (d, *J*= 8.2 Hz, 1H), 7.50-7.59 (m, 2H), 7.39-7.46 (m, 2H), 5.94 (s, 2H), 2.60 (s, 6H), 1.06 (s, 6H); ^{13}C RMN (75 MHz, $CDCl_3$) δ 155.6 (C), 143.0 (2 x C), 140.2 (C), 133.5 (2 x C), 132.5 (C), 132.0 (C), 131.7 (2 x C), 129.2 (CH), 128.2 (CH), 127.3 (CH), 126.6 (CH), 126.0 (CH), 125.8 (CH), 124.9 (CH), 121.2 (2 x CH), 14.6 (2 x CH_3), 13.9 (2 x CH_3). MS (EI) m/z (%) 375 $[M + H]^+$ (23), 374 $[M]^+$ (100); HRMS (EI) calcd for $C_{23}H_{21}N_2BF_2$ $[M]^+$ 374.1760, found 374.1775.

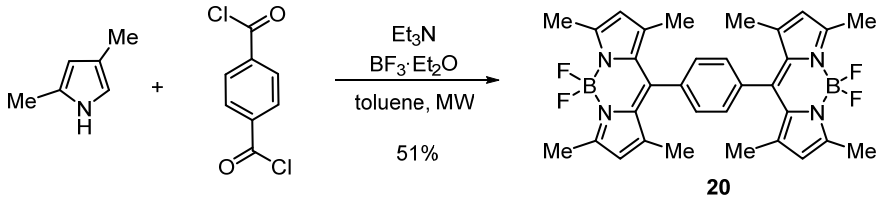
[15] H. Sunahara, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc.*, 2007, **129**, 5597–5604.

5,5-Difluoro-1,3,7,9-tetramethyl-10-(thiophen-2-yl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (19).[16]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.210 mL, 2.05 mmol), thiophene-2-carbonyl chloride (730 µL, 0.680 mmol), Et_3N (0.380 mL, 2.73 mmol) and $BF_3 \cdot Et_2O$ (0.510 mL, 4.09 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (30% CH_2Cl_2/hexanes), compound **19** (78.5 mg, 35%) was obtained as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J*= 1.3, 5.1 Hz, 1H), 7.13 (dd, *J*= 3.4, 5.1 Hz, 1H), 6.98 (dd, *J*= 1.2, 3.4 Hz, 1H), 6.00 (s, 2H), 2.56 (s, 6H), 1.59 (s, 6H); ^{13}C RMN (75 MHz, $CDCl_3$) δ 156.1 (2 x C), 143.5 (2 x C), 134.6 (2 x C), 134.0 (C), 132.4 (C), 127.8 (CH), 127.6 (CH), 127.4 (CH), 121.5 (2 x CH), 14.6 (s, 2 x CH_3), 13.5 (s, 2 x CH_3). MS (EI) m/z (%) 331 $[M + H]^+$ (27), 330 $[M]^+$ (100); HRMS (EI) calcd for $C_{17}H_{17}N_2BF_2S$ $[M]^+$ 330.1168, found 330.1154.

1,4-Bis(5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)benzene (20).[17]



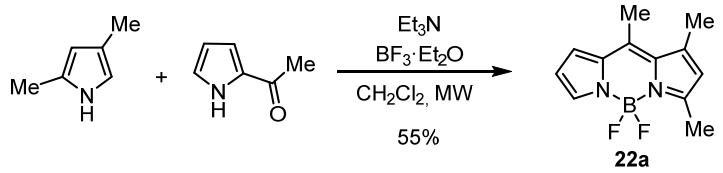
According to the modified general procedure, the mixture of 2,4-dimethylpyrrole (0.250 mL, 2.41 mmol), terephthaloyl dichloride (700 mg, 0.350 mmol), Et_3N (0.290 mL, 2.07 mmol) and $BF_3 \cdot Et_2O$ (0.350 mL, 2.76 mmol) in toluene (1.00 mL) was irradiated 4 h at 80 ºC. After purification by column chromatography (20% AcOEt/hexanes), compound **20** (99.6 mg, 51%) was obtained as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 4H), 6.01 (s, 4H), 2.57 (s, 12H), 1.53 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0 (4 x

[16] T. Jun, K. Kim, K. Mun Lee, A. C. Benniston and D. G. Churchill, *J. Coord. Chem.*, 2012, **65**, 4299–4314.

[17] T. Li, W. Gu, C. Yu, X. Lv, H. Wang, E. Hao and L. Jiao, *Chin. J. Chem.*, 2016, **34**, 989–996.

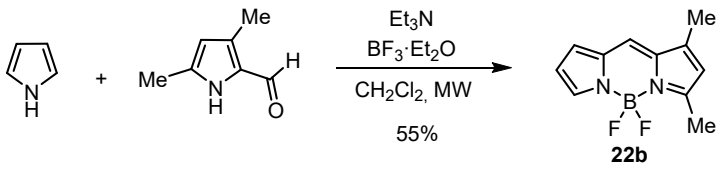
C), 142.6 (4 x C), 140.6 (2 x C), 136.2 (4 x C), 131.4 (2 x C), 129.6 (4 x CH), 121.5 (4 x CH), 15.8 (4 x CH_3), 14.7 (4 x CH_3). MS (EI) m/z (%) 571 $[M + H]^+$ (27), 570 $[M]^+$ (100); HRMS (EI) calcd for $C_{32}H_{32}N_4B_2F_4$ $[M]^+$ 570.2744, found 570.2763.

5,5-Difluoro-1,3,10-trimethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diaza-borinine (22a).[18]



According to the general procedure, the mixture of 2,4-dimethylpyrrole (0.190 mL, 1.83 mmol), 2-acetylpyrrole (101 mg, 0.920 mmol), Et_3N (0.510 mL, 3.66 mmol) and $BF_3{\cdot}Et_2O$ (0.690 mL, 5.50 mmol) in CH_2Cl_2 (1 mL) was irradiated. After purification by column chromatography (10% AcOEt/hexanes), compound **22a** (117 mg, 55%) was obtained as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.07 (d, *J*= 4.0 Hz, 1H), 6.41-6.43 (m, 1H), 6.14 (s, 1H), 2.57 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0 (C), 145.5 (C), 142.0 (C), 137.9 (CH), 134.3 (C), 134.2 (C), 123.9 (CH), 122.8 (CH), 115.6 (CH), 16.9 (CH_3), 16.4 (CH_3), 14.9 (CH_3). MS (EI) m/z (%) 234 $[M]^+$ (100); HRMS (EI) calcd for $C_{12}H_{13}N_2BF_2$ $[M]^+$ 234.1134, found 234.1142.

5,5-Difluoro-1,3-dimethyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (22b).[19]



According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (70.3 mg, 0.570 mmol), 1*H*-pyrrole (790 µL, 1.14 mmol), Et_3N (0.320 mL, 2.27 mmol) and $BF_3{\cdot}Et_2O$ (0.430 mL, 3.41 mmol) in CH_2Cl_2 (1.00 mL) was irradiated. After purification by column chromatography (10% AcOEt/hexanes), compound **22b** (68.9 mg, 55%) was obtained as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H),

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18 J. Al Anshori, T. Slanina, E. Palao and P. Klán, *Photochem. Photobiol. Sci*., 2016, **15**, 250–259.

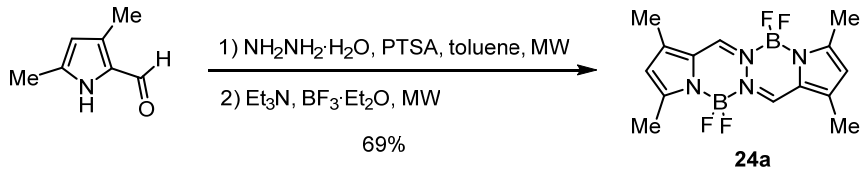
19 A. de J. Gómez-Infante, J. Bañuelos, I. Valois-Escamilla, D. Cruz-Cruz, R. Prieto-Montero, I. López-Arbeloa, T. Arbeloa, and E. Peña-Cabrera, *Eur. J. Org. Chem*., 2016, 5009–5023.

7.18 (s, 1H), 6.91 (d, *J*= 3.4 Hz, 1H), 6.42 (s, 1H), 6.15 (s, 1H), 2.58 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (C), 145.9 (C), 139.2 (CH), 136.5 (C), 132.7 (C), 126.5 (CH), 124.8 (CH), 121.3 (CH), 116.3 (CH), 15.2 (CH_3), 11.4 (CH_3). MS (EI) m/z (%) 220 $[M]^+$ (51); HRMS (EI) calcd for $C_{11}H_{11}N_2BF_2$ $[M]^+$ 220.0978, found 220.0989.

General procedure for the microwave assisted synthesis of BOPHYs, BOAHYs and BOPAHYs.

In an oven-dried microwave tube equipped with a magnetic stir bar, 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde or pyrrole-2-carboxaldehyde (0.50-0.60 mmol), the corresponding hydrazine (0.30-2.4 mmol), toluene (1.0 mL) and *p*-toluenesulfonic acid (0.012-0.016 mmol) were added. The microwave tube was closed and put into the microwave at 80 ºC and irradiated for 30 minutes (reaction complete by TLC test). Afterward, Et_3N (2.3-9.5 mmol) and $BF_3{\cdot}Et_2O$ (2-3-9.5 mmol) were added and the mixture was irradiated at 80-120 °C for further 30 minutes-4 hours under argon. The reaction was diluted with CH_2Cl_2 (10 mL), washed with water (15 mL), dried ($MgSO_4$ anhyd.), filtered and concentrated. The resulting crude was purified by flash column chromatography to afford, after concentration and high vacuum drying, the corresponding BOPHY, BOAHY or BOPAHY.

5,5,12,12-Tetrafluoro-1,3,8,10-tetramethyl-5*H*,12*H*-5λ^4,6λ^4,12λ^4,13λ^4-pyrrolo[1,2-d]pyrrolo[1',2':4,5][1,2,4,3]triazaborinino[2,1-*a*][1,2,4,3]triazaborinine (24a).[20]

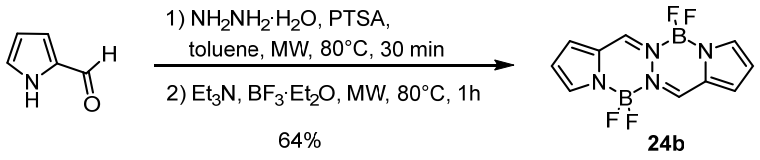


According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (60.4 mg, 0.490 mmol), hydrazine hydrate (0.120 mL, 2.43 mmol), and *p*-toluenesulfonic acid (2.50 mg, 0.0120 mmol) in toluene (1.00 mL) was irradiated. Et_3N (1.00 mL, 7.31 mmol) and $BF_3{\cdot}Et_2O$ (0.920 mL, 7.31 mmol) were added and the mixture was irradiated at 80 ºC for further 2 hours. After purification by column chromatography (15-30-50% CH_2Cl_2/hexanes), compound **24a** (114 mg, 69%) was obtained as an orange

[20] I.-S. Tamgho, A. Hasheminasab, J. T. Engle, V. N. Nemykin and C. J. Ziegler, *J. Am. Chem. Soc*. 2014, **136**, 5623−5626.

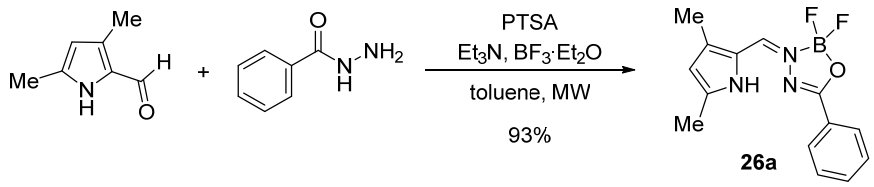
solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 2H), 6.18 (s, 2H), 2.49 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2 (2 x CH), 141.0 (2 x C), 134.6 (2 x C), 123.4 (2 x C), 117.9 (2 x CH), 14.1 (2 x CH_3), 11.1 (2 x CH_3); MS (EI) m/z (%) 338 $[M]^+$ (52); HRMS (EI) calcd for $C_{14}H_{16}N_4B_2F_4$ $[M]^+$ 338.1492, found 338.1507.

5,5,12,12-Tetrafluoro-5*H*,12*H*-5λ^4,6λ^4,12λ^4,13λ^4-pyrrolo[1,2-d]pyrrolo-[1',2':4,51,2,4,3]-triazaborinino[2,1-*a*][1,2,4,3]triazaborinine (24b).[20]



According to the general procedure, the mixture of pyrrole-2-carboxaldehyde (60.1 mg, 0.630 mmol), hydrazine hydrate (0.150 mL, 0.320 mmol), and *p*-toluenesulfonic acid (3.10 mg, 0.0160 mmol) in toluene (1.00 mL) was irradiated. Et_3N (1.30 mL, 9.45 mmol) and $BF_3{\cdot}Et_2O$ (1.20 mL, 9.45 mmol) were added and the mixture was irradiated at 80 ºC for further 1 hour. After purification by column chromatography (50-80% CH_2Cl_2/hexanes), compound **24b** (113 mg, 64%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, $(CD)_3CO$) δ 8.72 (s, 2H), 7.87 (s, 2H), 7.60 (d, *J*=, 4.0 Hz, 2H), 6.72 (dd, *J*= 2.0, 3.9 Hz, 2H); ^{13}C NMR (75 MHz, $(CD)_3CO$) δ 141.9 (2 x CH), 137.2 (2 x CH), 129.2 (2 x CH), 124.9 (2 x C), 117.1 (2 x CH). MS (EI) m/z (%) 282 $[M]^+$ (19); HRMS (EI) calcd for $C_{10}H_8N_4B_2F_4$ $[M]^+$ 282.0866, found 282.0872.

(*Z*)-3-((3,5-Dimethyl-1*H*-pyrrol-2-yl)methylene)-2,2-difluoro-5-phenyl-2,3dihydro-1,3λ^4,4,2λ^4-oxadiazaborole (26a).[21]

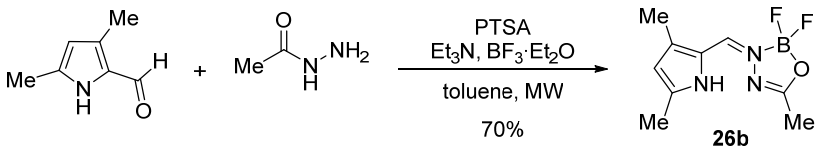


According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (70.5 mg, 0.57 mmol), benzohydrazide (86.1 mg, 0.63 mmol), toluene (1 mL) and *p*-toluenesulfonic acid (2.9 mg, 0.014 mmol) was irradiated for 30 minutes. Et_3N

[21] C. Yu, X. Fang, Q. Wu, L. Jiao, L. Sun, Z. Li, P.-K. So, W.-Y. Wong and E. Hao, *Org. Lett.*, 2020, **22**, 4588−4592.

(0.32 mL, 2.27 mmol) and $BF_3 \cdot Et_2O$ (0.29 mL, 2.27 mmol) were added and the mixture was irradiated at 80 ºC for further 30 minutes. After purification by column chromatography (10% AcOEt/hexanes), compound **26a** was obtained as a yellow solid (150.6 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.74 (s, 1H), 7.95 (d, *J*=7.4 Hz, 2H), 7.36-7.55 (m, 4H), 5.99 (s, 1H), 2.45 (s, 3H), 2.14 (s, 3H); NMR (75 MHz, $CDCl_3$) δ 167.8 (C), 142.5 (C), 138.9 (C), 134.5 (CH), 132.4 (CH), 128.5 (2 x CH), 128.0 (2 x CH), 127.2 (C), 121.7 (C), 113.8 (CH), 14.1 (CH_3), 11.2 (CH_3); MS (EI) m/z (%) 289 $[M]^+$ (47); HRMS (EI) calcd for $C_{14}H_{14}ON_3BF_2$ $[M]^+$ 289.1193, found 289.1189.

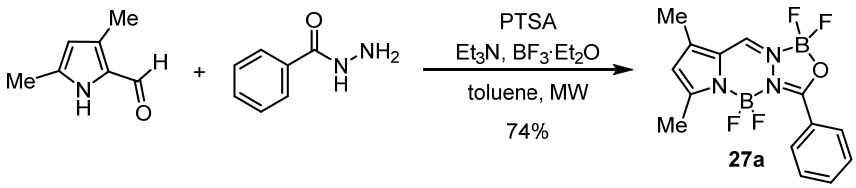
(*Z*)-3-((3,5-Dimethyl-1-*H*-2-yl)methylene)-2,2-difluoro-5-methyl-2,3-dihydro-1,3λ^4.4,2λ^4-oxadiazaborole (26b).[22]



According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (71.1 mg, 0.57 mmol), acetohydrazide (46.3 mg, 0.63 mmol), toluene (1 mL) and *p*-toluenesulfonic acid (2.7 mg, 0.014 mmol) was irradiated. Et_3N (0.32 mL, 2.27 mmol) and $BF_3 \cdot Et_2O$ (0.29 mL, 2.27 mmol) were added and the mixture was irradiated at 80 ºC for further 30 minutes. After purification by column chromatography (10% AcOEt/hexanes), compound **26b** (90.0 mg, 70%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.44 (s, 1H), 6.00 (d, *J*= 2.5 Hz, 1H), 2.38 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H); NMR (75 MHz, $CDCl_3$) δ 171.5 (C), 141.6 (C), 138.5 (C), 134.7 (CH), 121.5 (C), 113.6 (CH), 14.0 (CH_3), 11.3 (CH_3), 8.8 (CH_3); MS (EI) m/z (%) 227 $[M]^+$ (47); HRMS (EI) calcd for $C_9H_{12}ON_3BF_2$ $[M]^+$ 227.1036, found 227.1043.

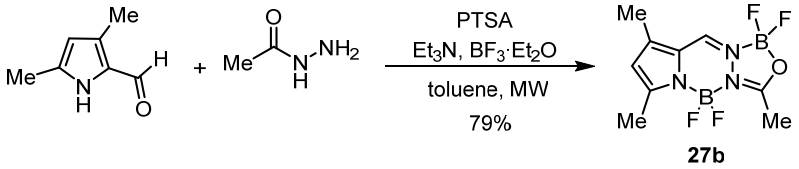
[22] P. P. Shandev, F. de Jong, K. Veys, J. Huang, P. V. Santhini, D. Verhaeghe, L. Van Meervelt, D. Escudero, M. Van der Auweraer, and W. Dehaen, *Chem. Comm.*, 2020, **56**, 5791–5794.

1,1,5,5-Tetrafluoro-7,9-dimethyl-3-phenyl-1*H*,5*H*-1λ^4,4λ^4,5λ^4,11λ^4-[1,3,4,2]oxa-diazaborolo[3,4-*a*]pyrrolo[1,2-*d*][1,2,4,3]triazaborinine (27a).[21]



According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (60.2 mg, 0.490 mmol), benzohydrazide (72.6 mg, 0.530 mmol), and *p*-toluenesulfonic acid (2.40 mg, 0.0120 mmol) in toluene (1.00 mL) was irradiated. Et_3N (0.680 mL, 4.85 mmol) and $BF_3 \cdot Et_2O$ (0.610 mL, 4.85 mmol) were added and the mixture was irradiated at 120 ºC for further 4 h. After purification by column chromatography (10-30% AcOEt/hexanes), compound **27a** (142 mg, 74%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, *J*= 7.5 Hz, 2H), 7.68-7.74 (m, 2H), 7.57 (t, *J*= 7.6 Hz, 2H), 6.22 (s, 1H), 2.46 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 (C), 153.3 (C), 141.3 (C), 134.7 (CH), 132.9 (CH), 130.8 (CH), 130.7 (CH), 130.7 (CH), 128.6 (CH), 124.4 (C), 123.3 (C), 119.4 (CH), 14.3 (CH_3), 11.0 (CH_3); MS (EI) m/z (%) 337 $[M]^+$ (40); HRMS (EI) calcd for $C_{14}H_{13}ON_3B_2F_4$ $[M]^+$ 337.1175, found 337.1180.

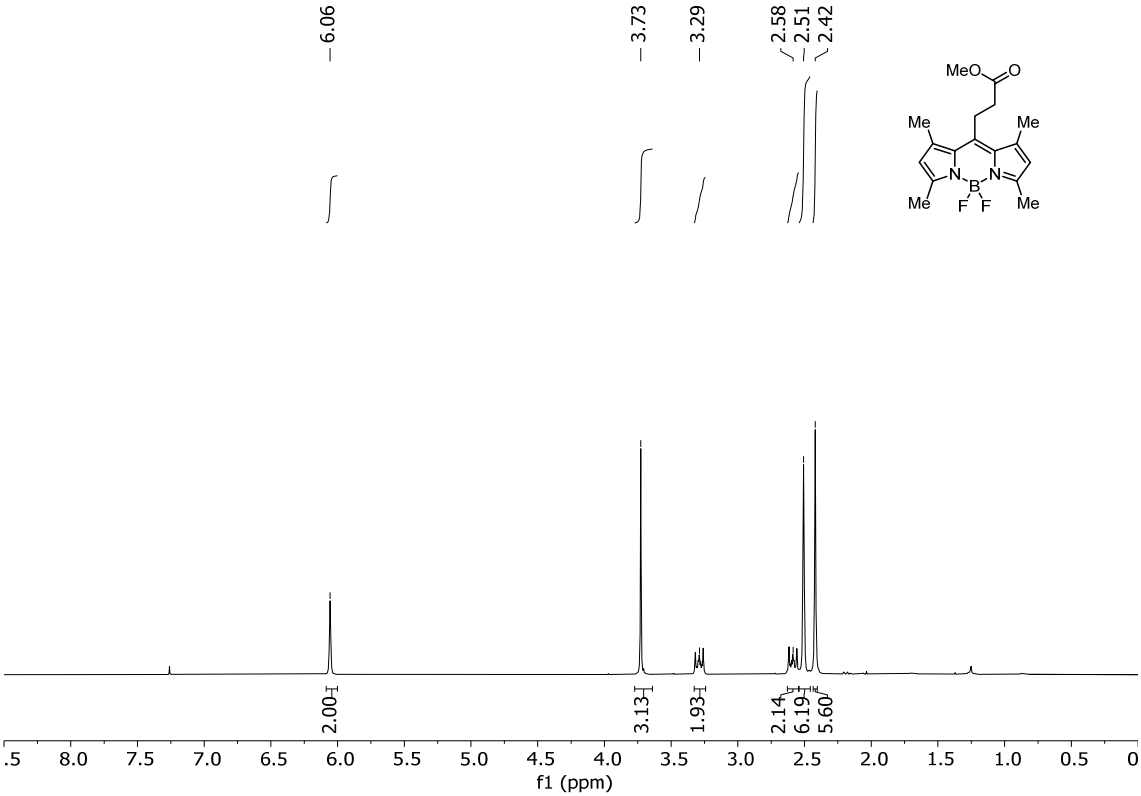
1,1,5,5-Tetrafluoro-3,7,9-trimethyl-1*H*,5*H*-1l^4,4λ^4,5λ^4,11λ^4-[1,3,4,2]oxa-diazaborolo[3,4-*a*]pyrrolo[1,2-*d*][1,2,4,3]triazaborinine (27b).[22]



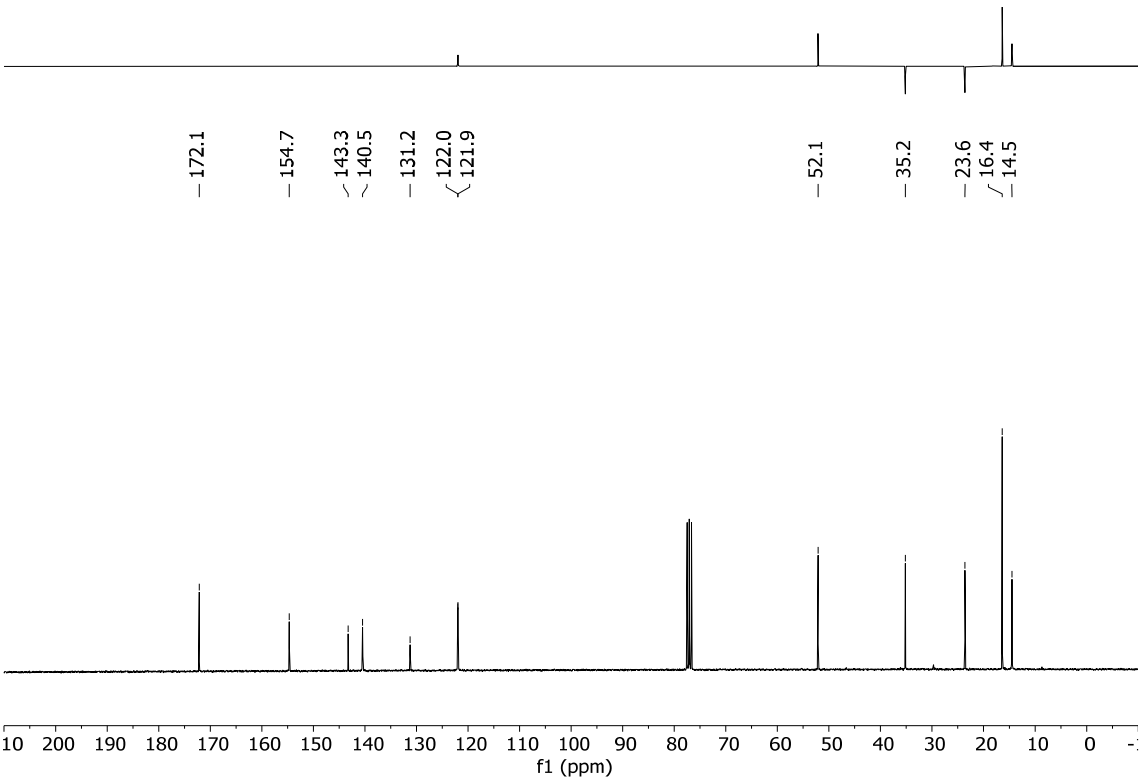
According to the general procedure, the mixture of 3,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (70.1 mg, 0.570 mmol), acetohydrazide (47.1 mg, 0.630 mmol), and *p*-toluenesulfonic acid (2.70 mg, 0.0140 mmol) in toluene (1.00 mL) was irradiated. Et_3N (0.790 mL, 5.68 mmol) and $BF_3 \cdot Et_2O$ (0.710 mL, 5.68 mmol) were added and the mixture was irradiated at 120 ºC for further 4 h. After purification by column chromatography (20-30% CH_2Cl_2/hexanes), compound **27b** (123 mg, 79%) was obtained as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 6.20 (s, 1H), 2.63 (s, 3H), 2.47 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (C), 152.7 (C), 141.3 (C), 132.4 (CH),

123.2 (C), 119.1 (CH), 15.6 (CH_3), 14.2 (CH_3), 11.0 (CH_3). MS (EI) m/z (%) 275 $[M]^+$ (21); HRMS (EI) calcd for $C_9H_{11}ON_3B_2F_4$ $[M]^+$ 275.1019, found 275.1028.

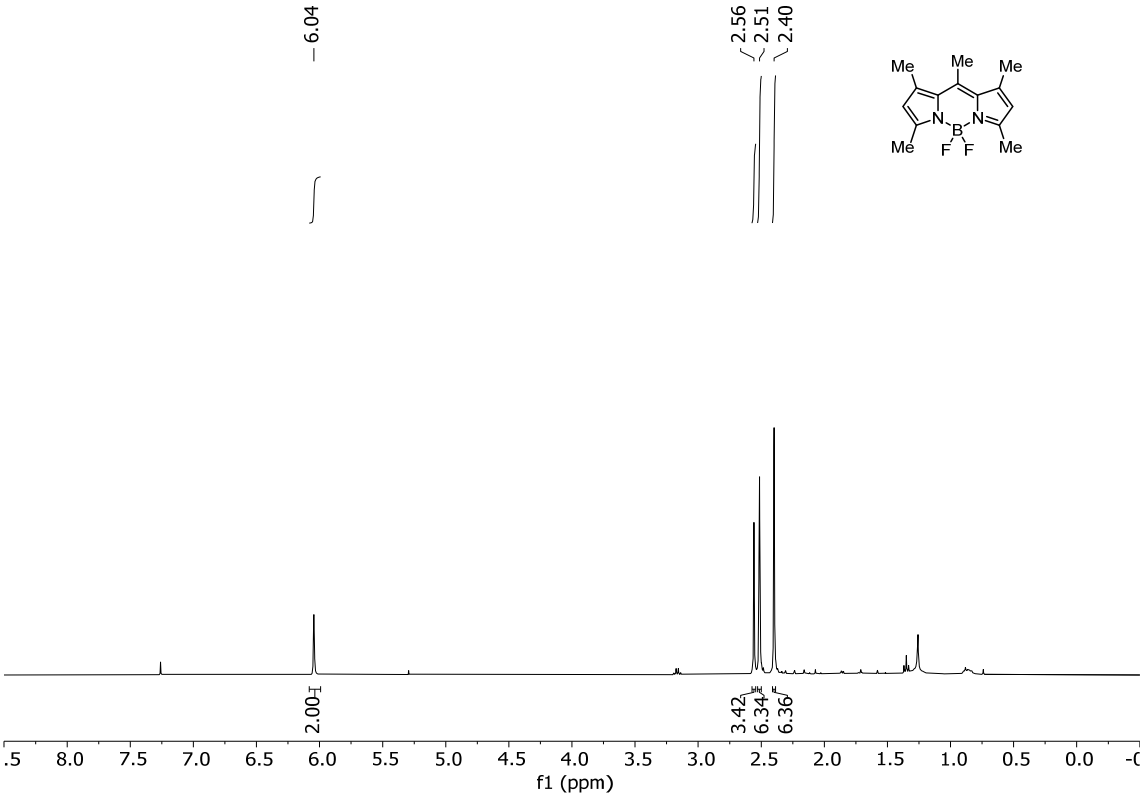
300 MHz ^{1}H-NMR Spectrum of compound **3** ($CDCl_3$, 300 K)



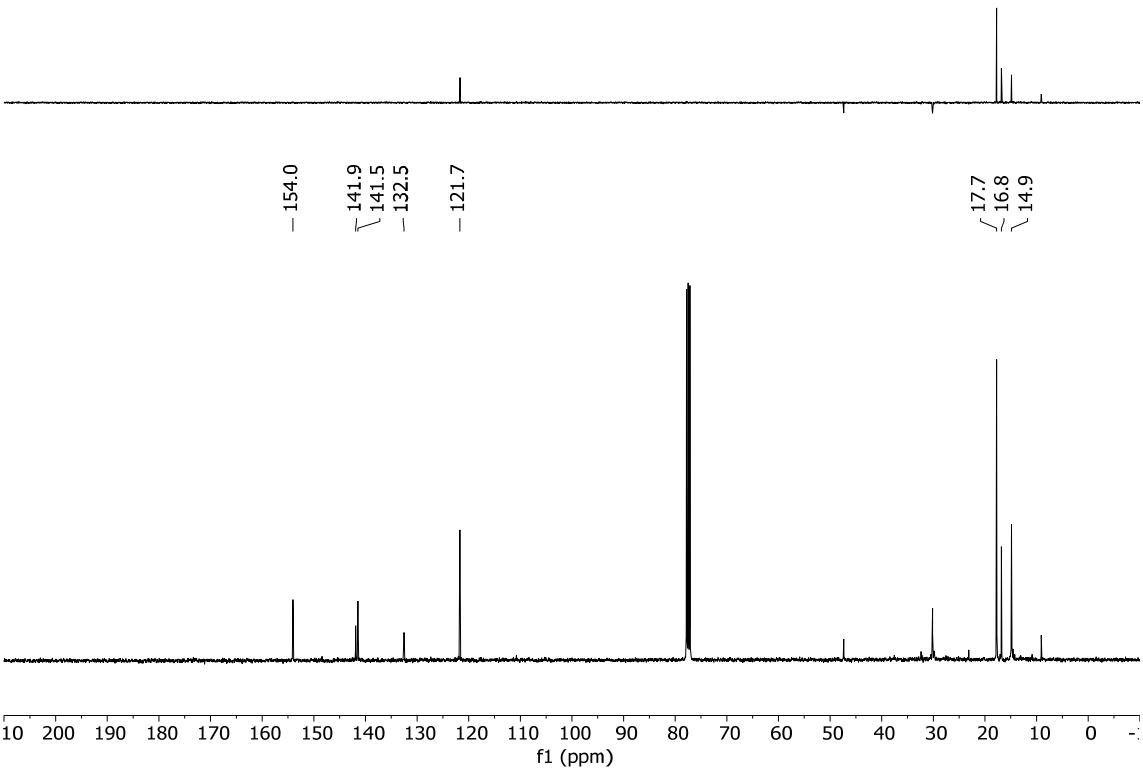
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **3** ($CDCl_3$, 300 K)



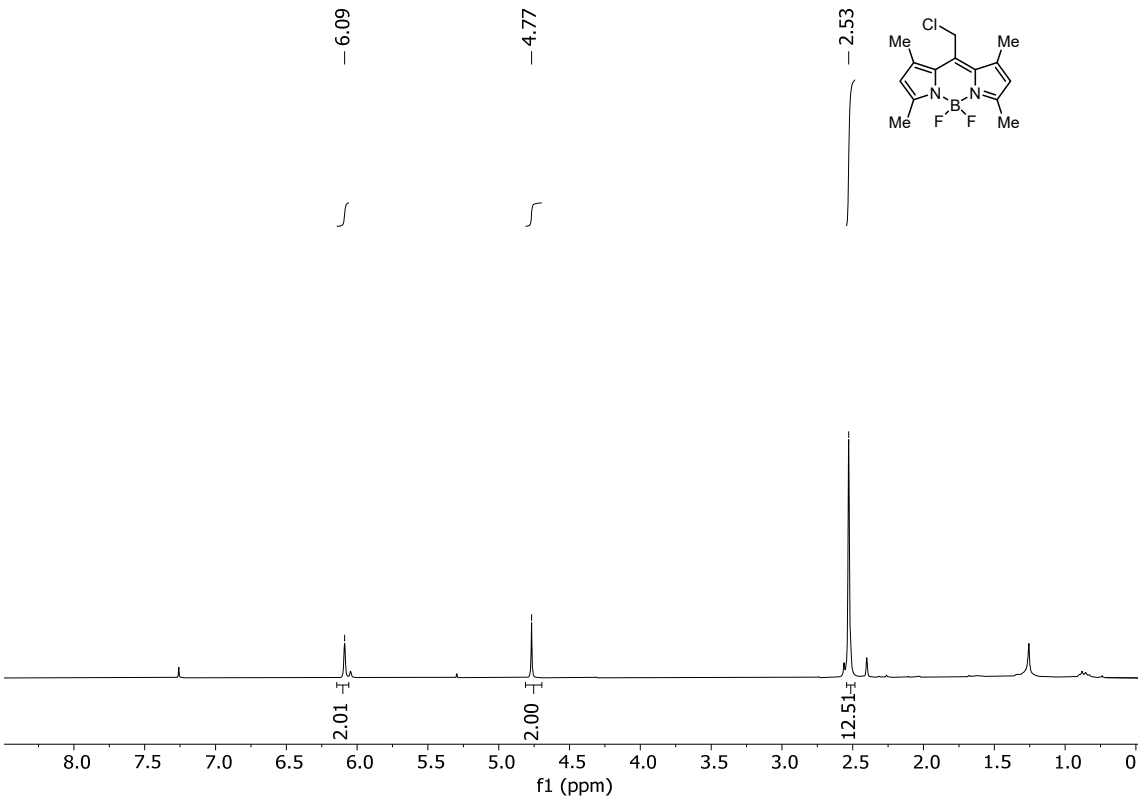
300 MHz ^{1}H-NMR Spectrum of compound **4** ($CDCl_3$, 300 K)



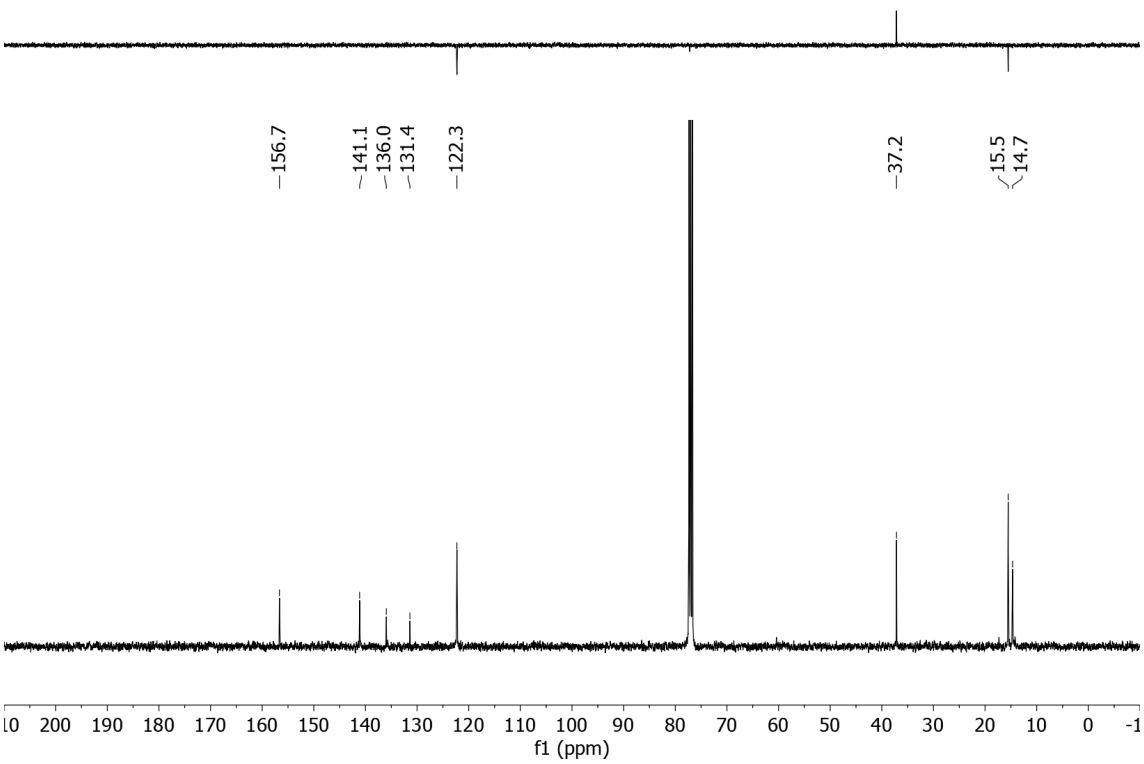
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **4** ($CDCl_3$, 300 K)



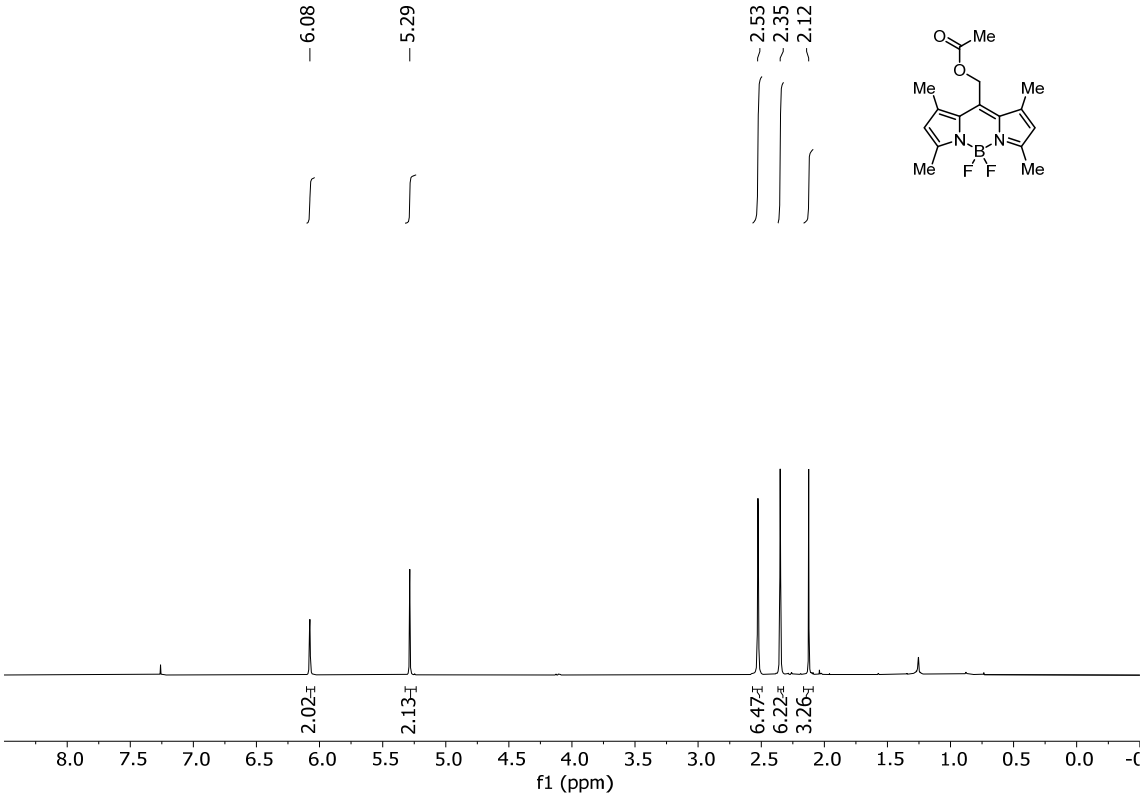
300 MHz ^{1}H-NMR Spectrum of compound **5** ($CDCl_3$, 300 K)



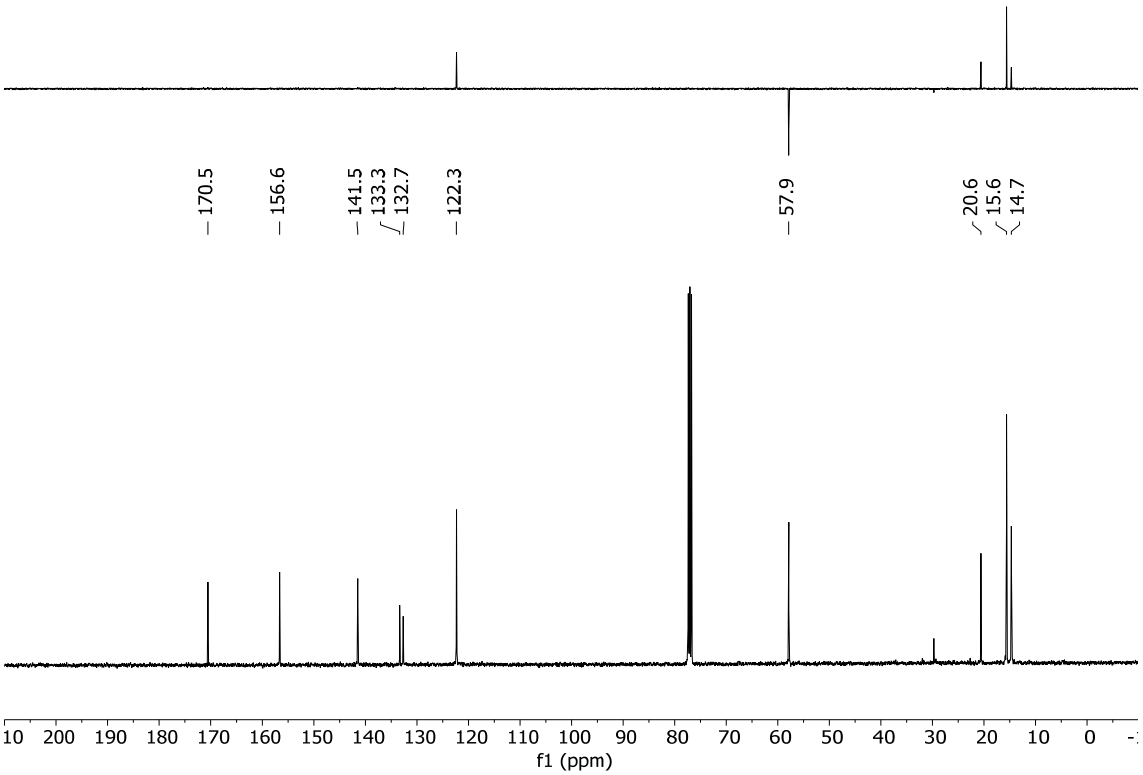
100 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **5** ($CDCl_3$, 300 K)



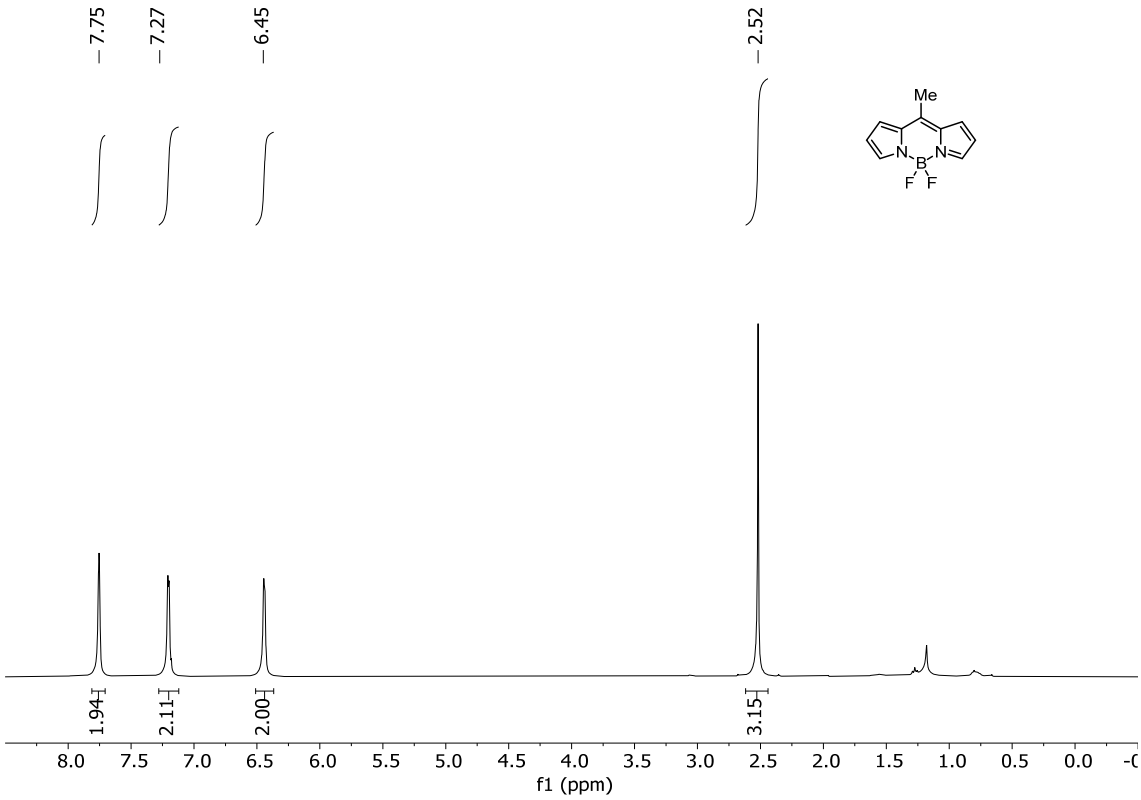
300 MHz ^{1}H-NMR Spectrum of compound **6** ($CDCl_3$, 300 K)



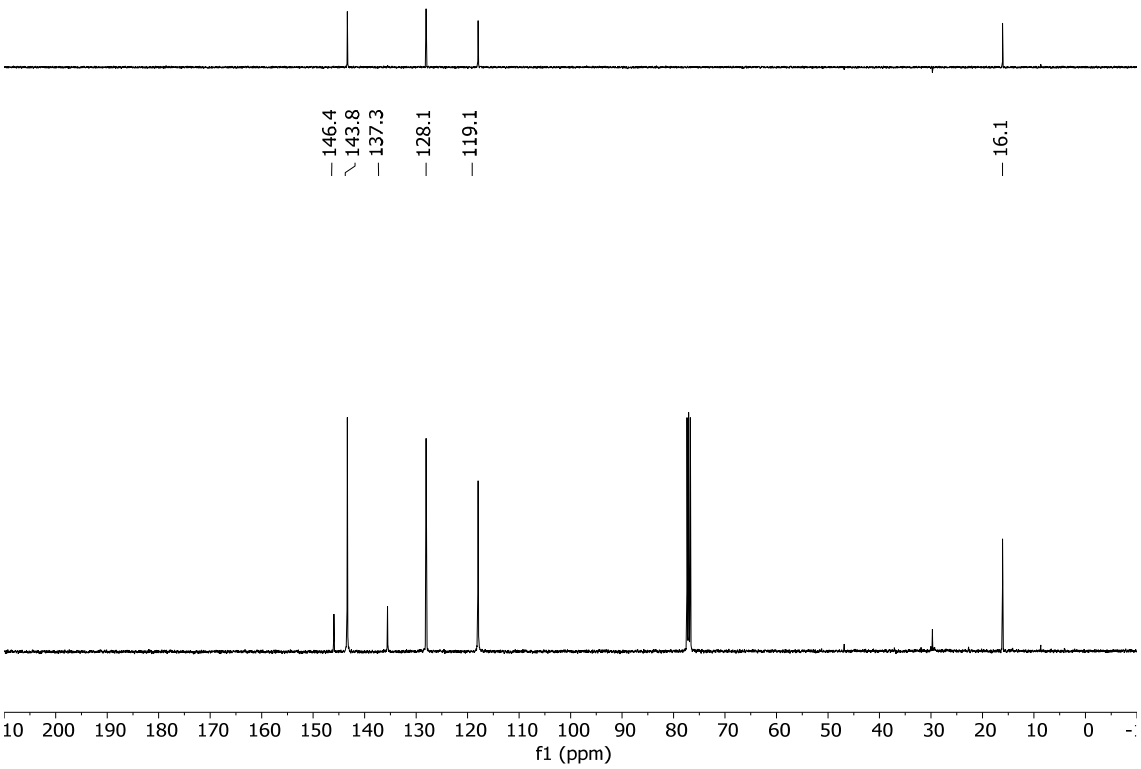
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **6** ($CDCl_3$, 300 K)



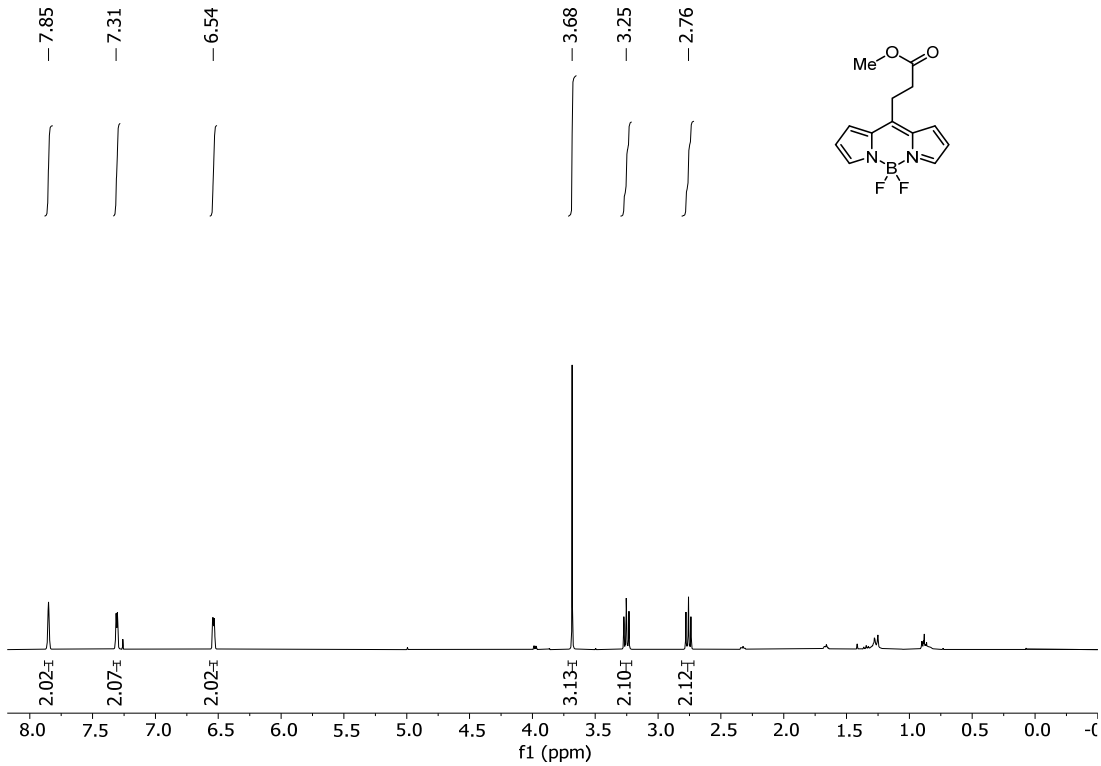
300 MHz ^{1}H-NMR Spectrum of compound **7** ($CDCl_3$, 300 K)



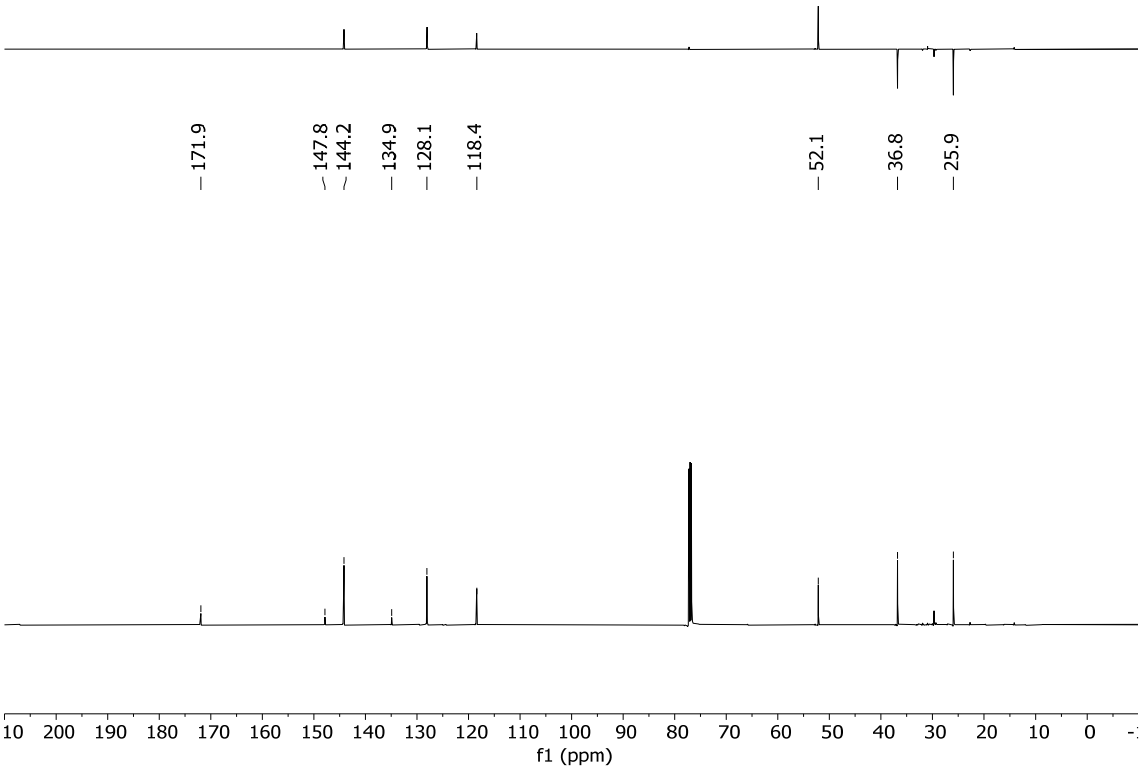
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **7** ($CDCl_3$, 300 K)



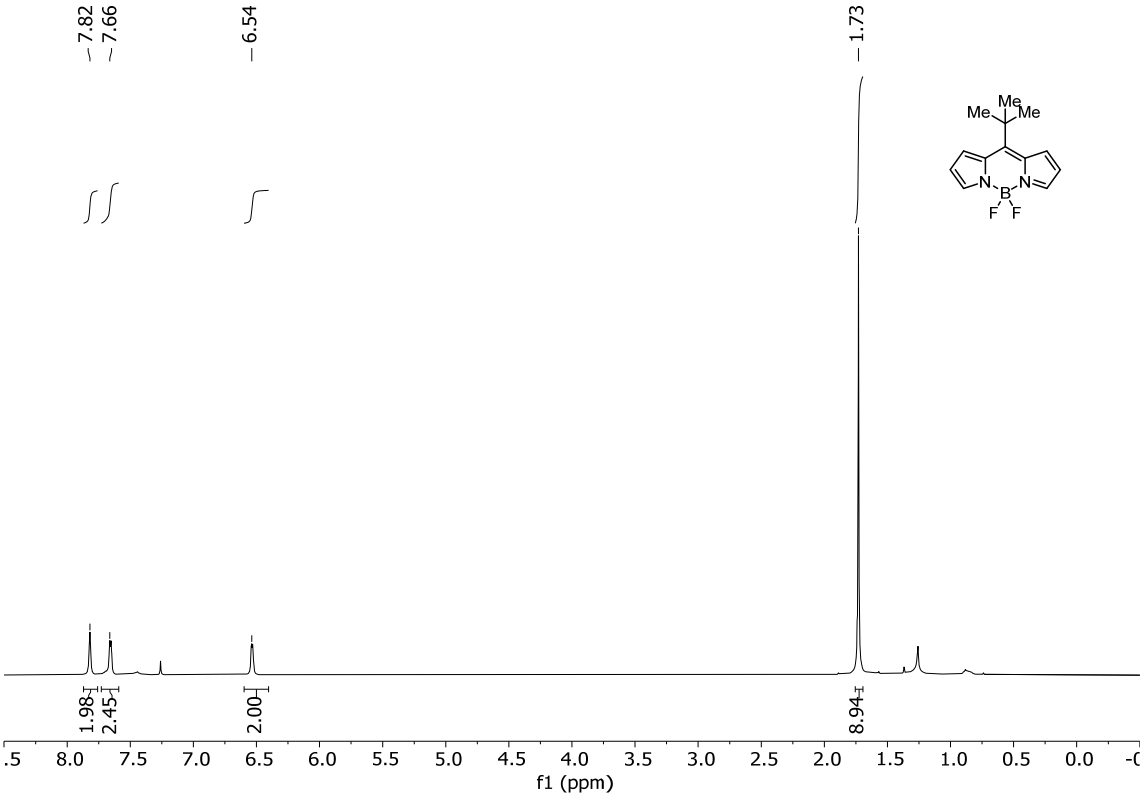
300 MHz ^{1}H-NMR Spectrum of compound **8** ($CDCl_3$, 300 K)



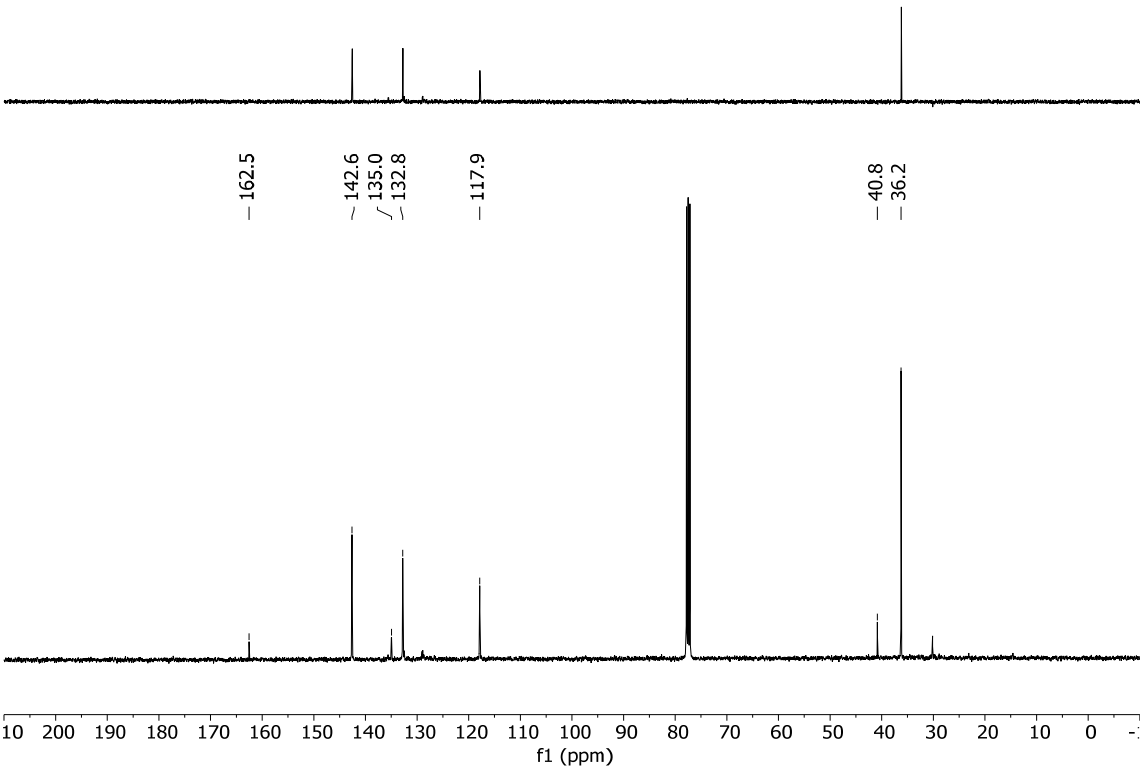
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **8** ($CDCl_3$, 300 K)



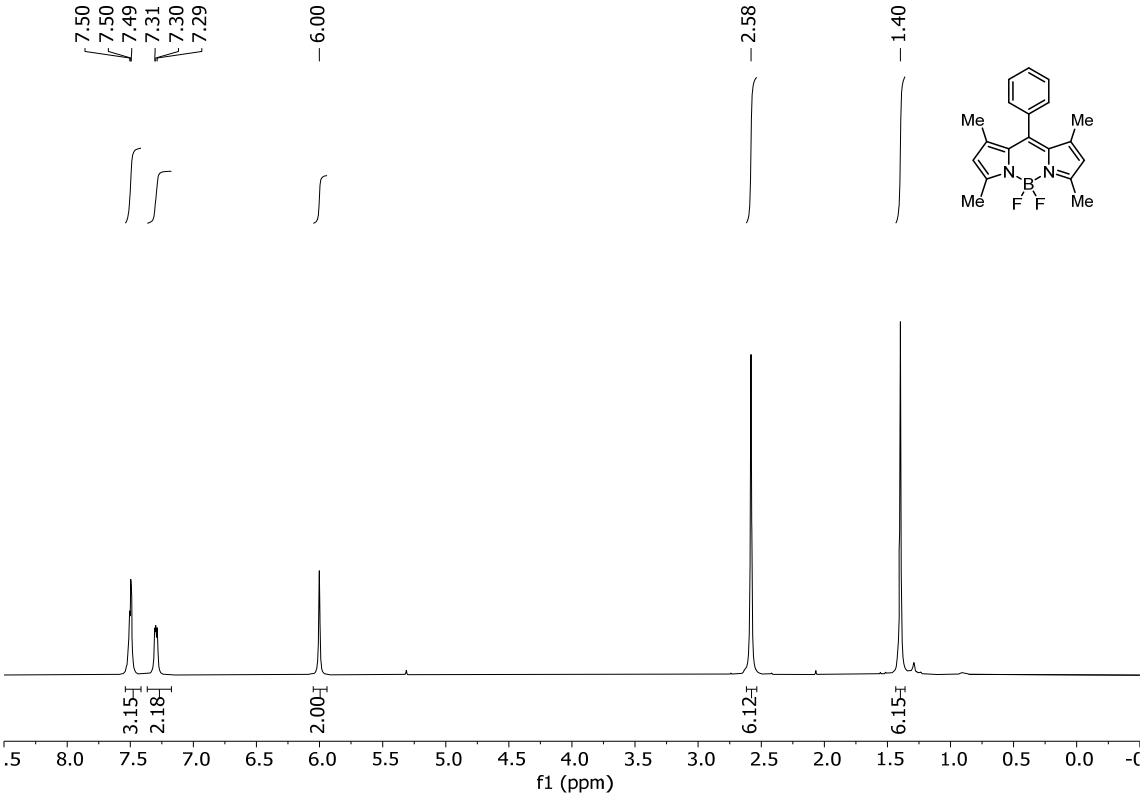
300 MHz ^{1}H-NMR Spectrum of compound **9** ($CDCl_3$, 300 K)



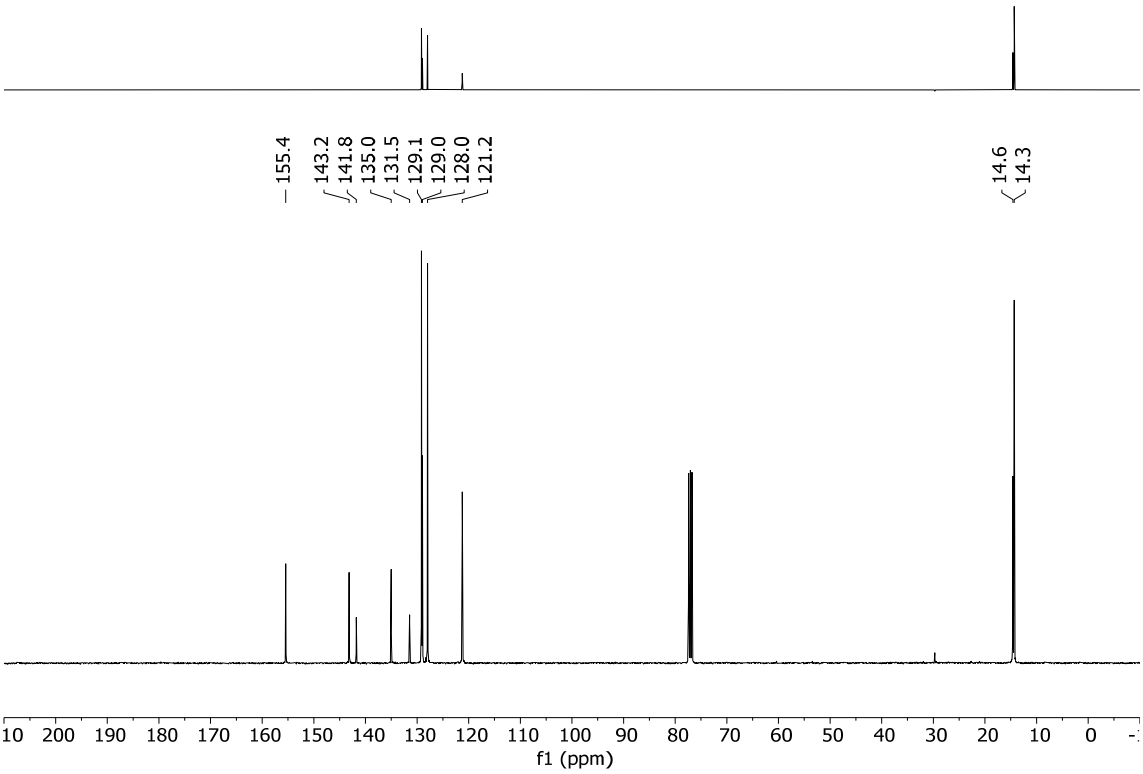
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **9** ($CDCl_3$, 300 K)



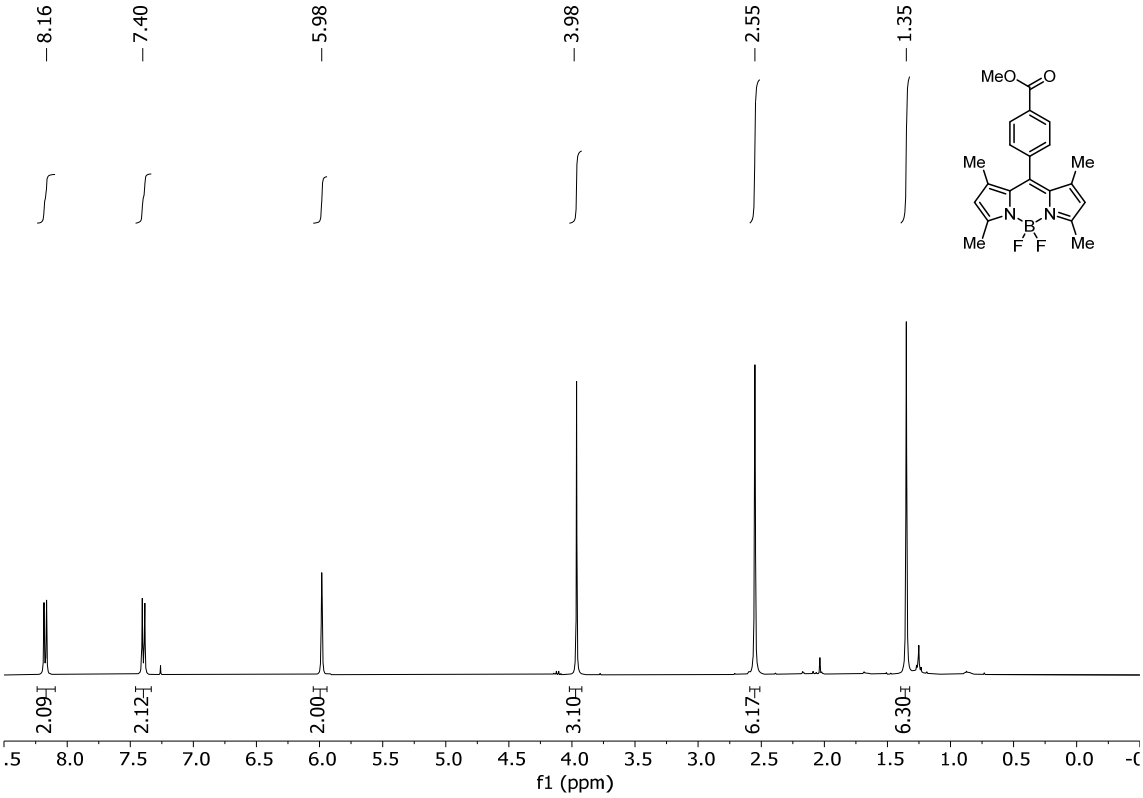
300 MHz ^{1}H-NMR Spectrum of compound **10** ($CDCl_3$, 300 K)



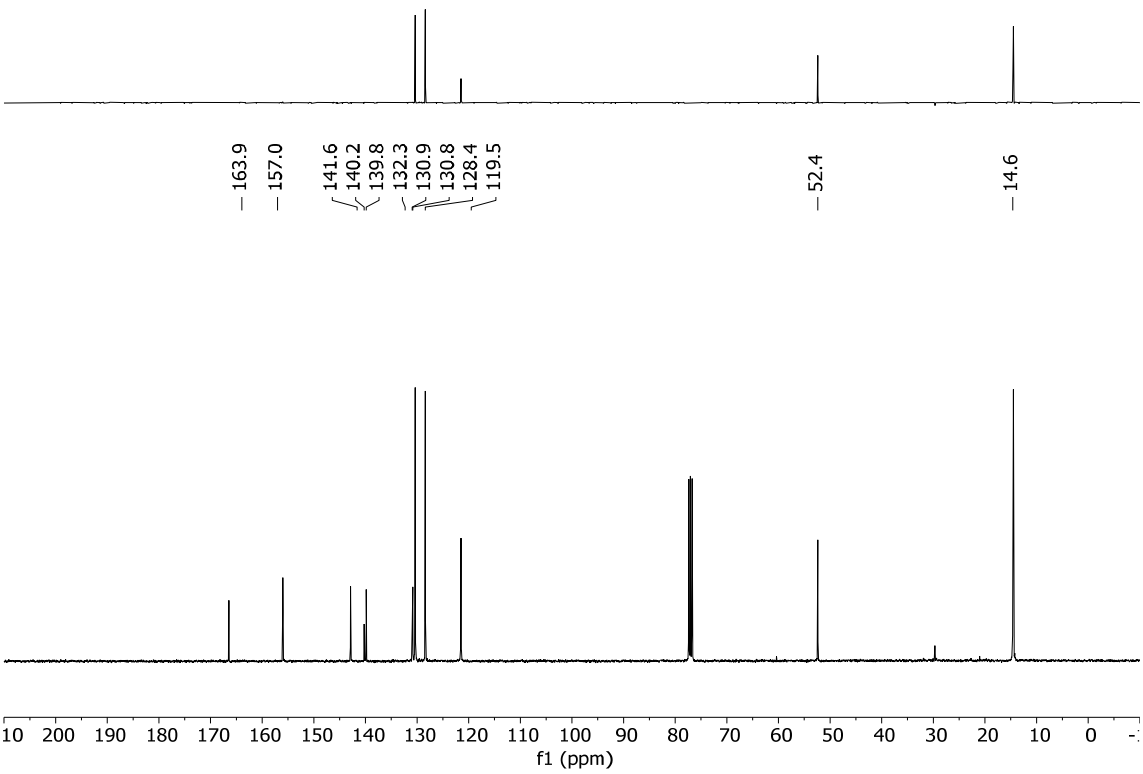
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **10** ($CDCl_3$, 300 K)



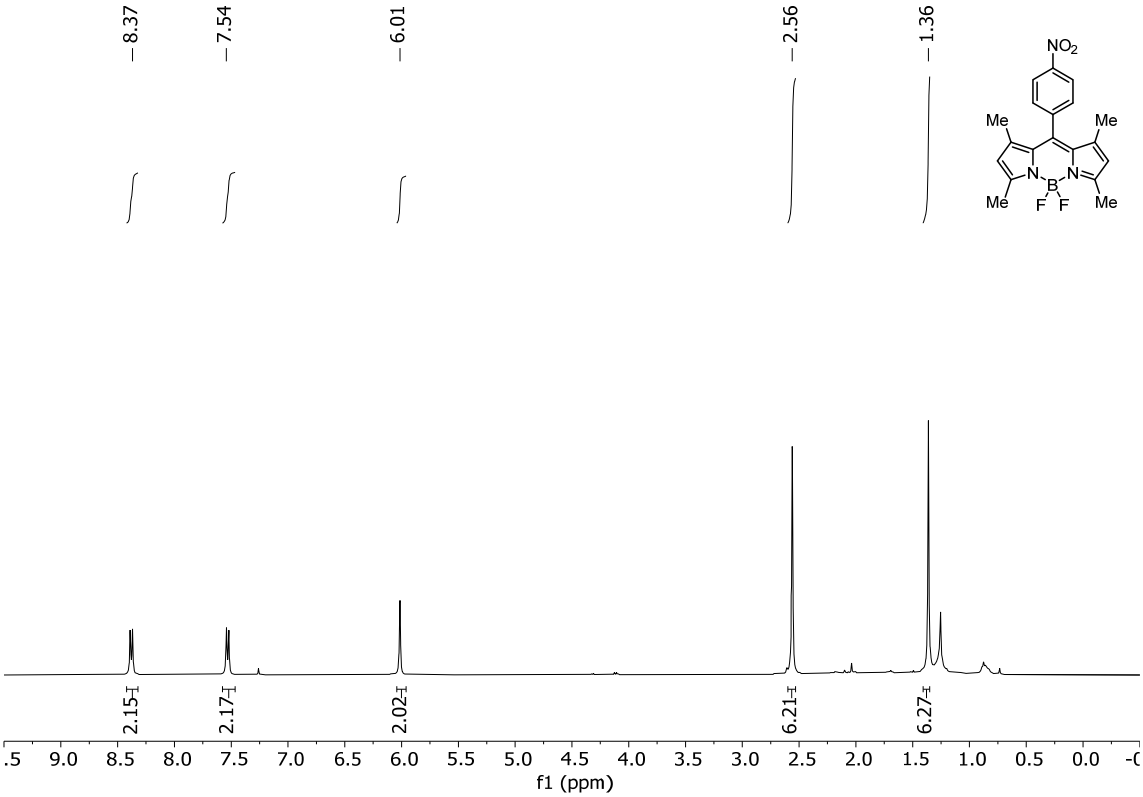
300 MHz ^{1}H-NMR Spectrum of compound **11** ($CDCl_3$, 300 K)



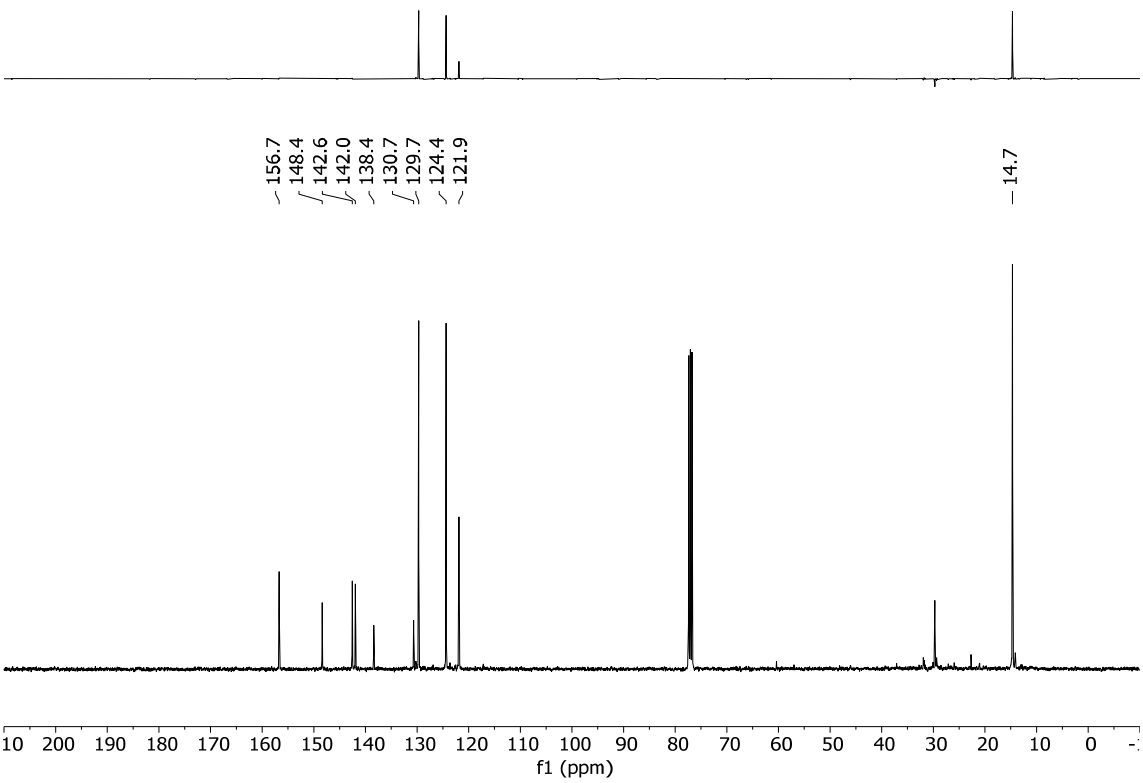
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **11** ($CDCl_3$, 300 K)



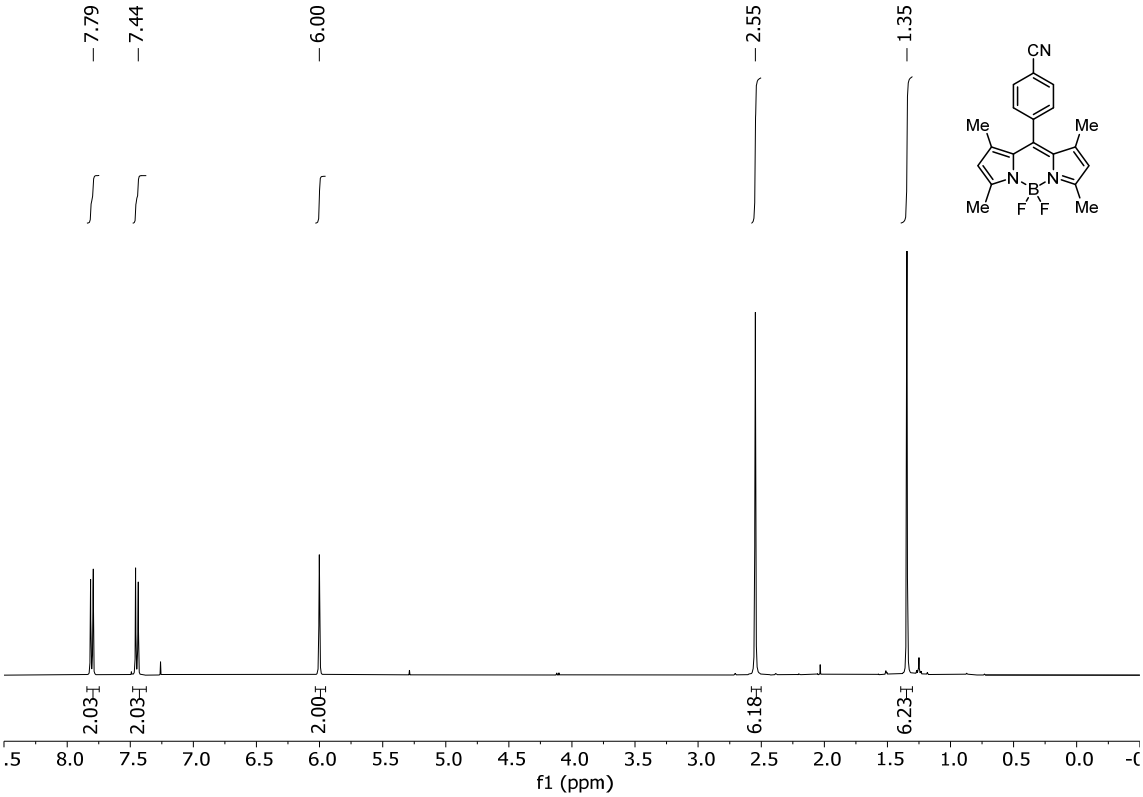
300 MHz ^{1}H-NMR Spectrum of compound **12** ($CDCl_3$, 300 K)



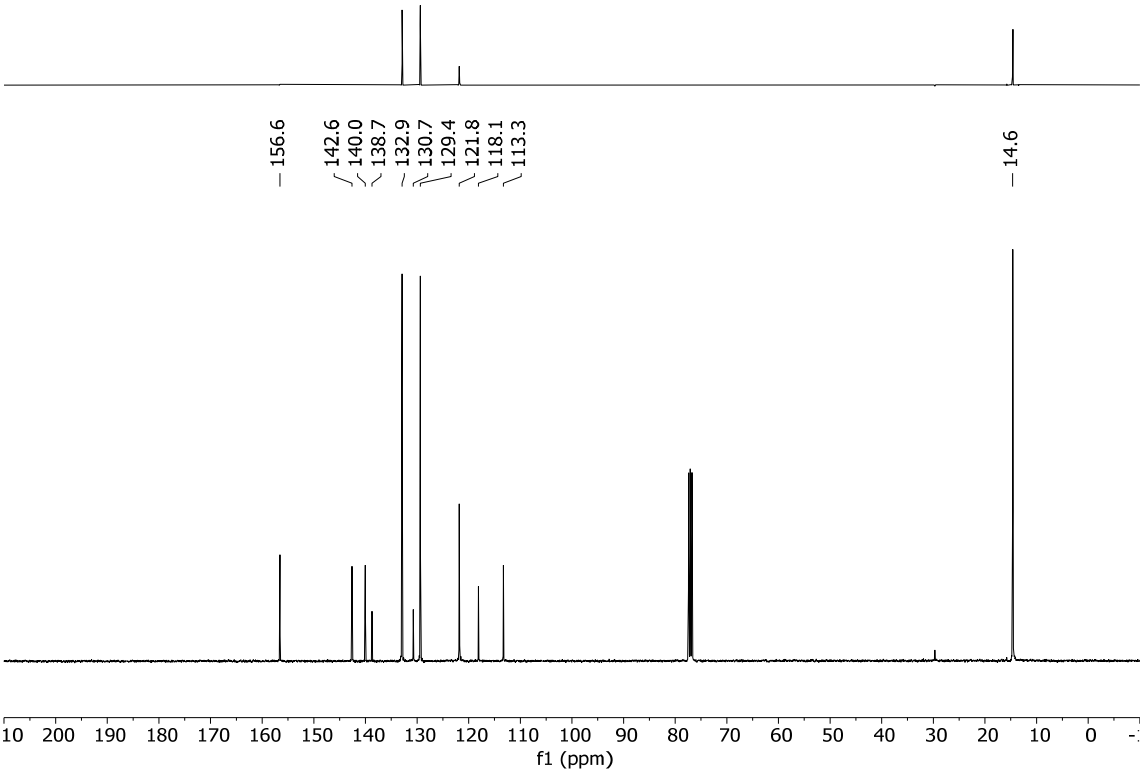
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **12** ($CDCl_3$, 300 K)



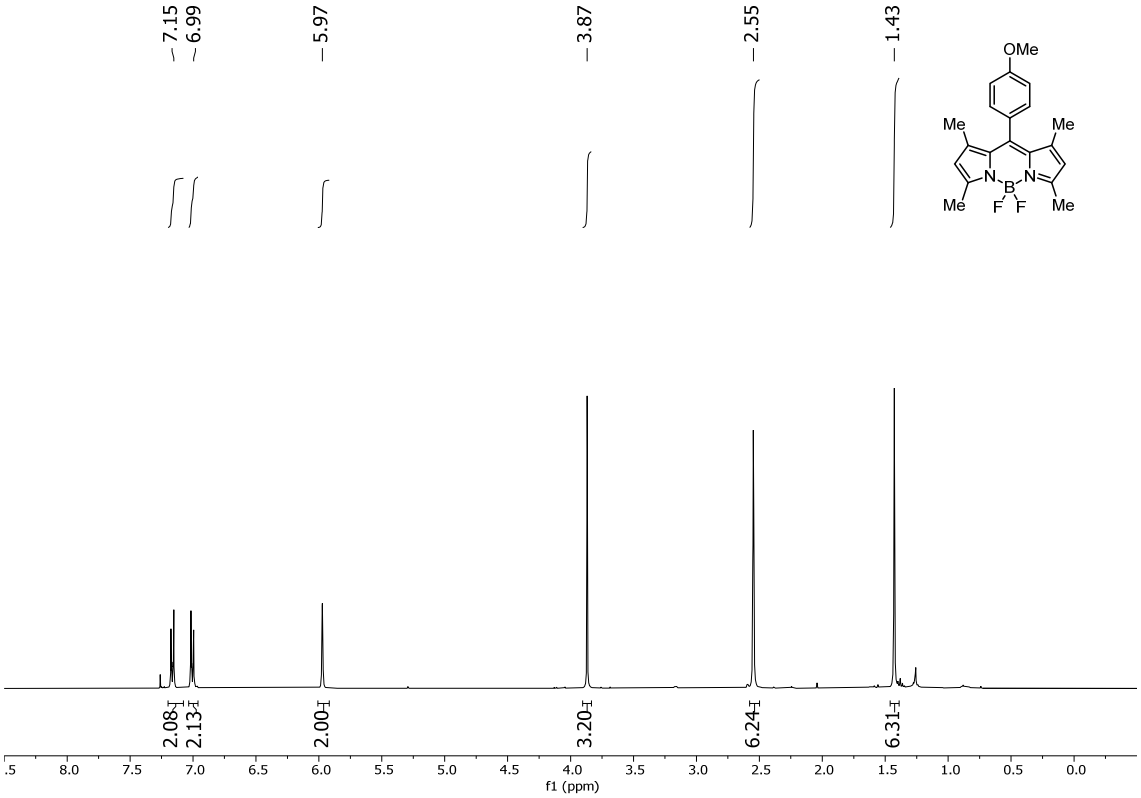
300 MHz ^{1}H-NMR Spectrum of compound **13** ($CDCl_3$, 300 K)



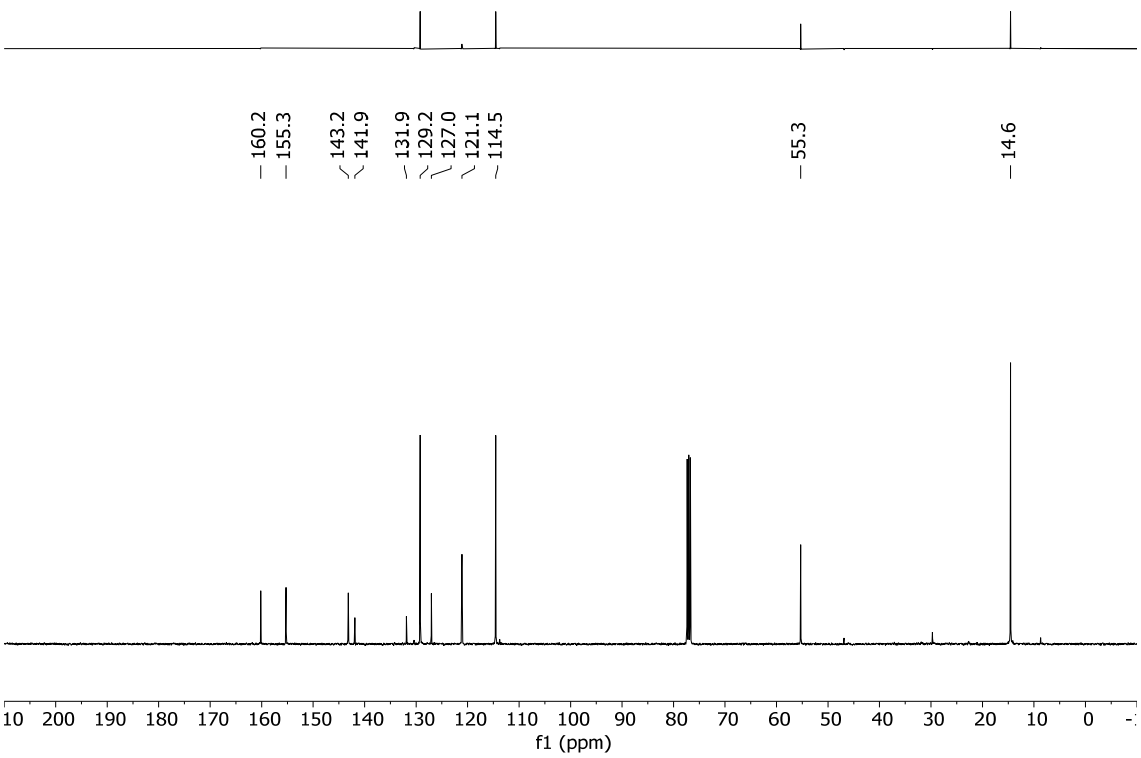
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **13** ($CDCl_3$, 300 K)



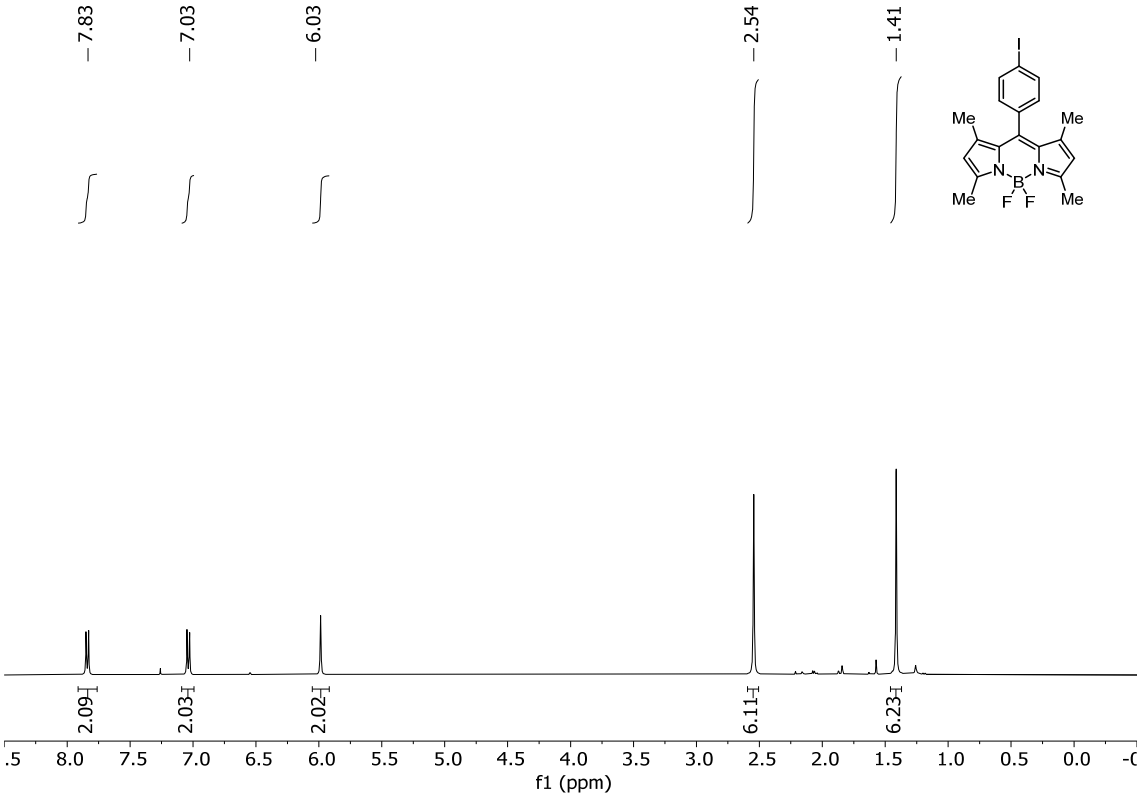
300 MHz ^{1}H-NMR Spectrum of compound **14** ($CDCl_3$, 300 K)



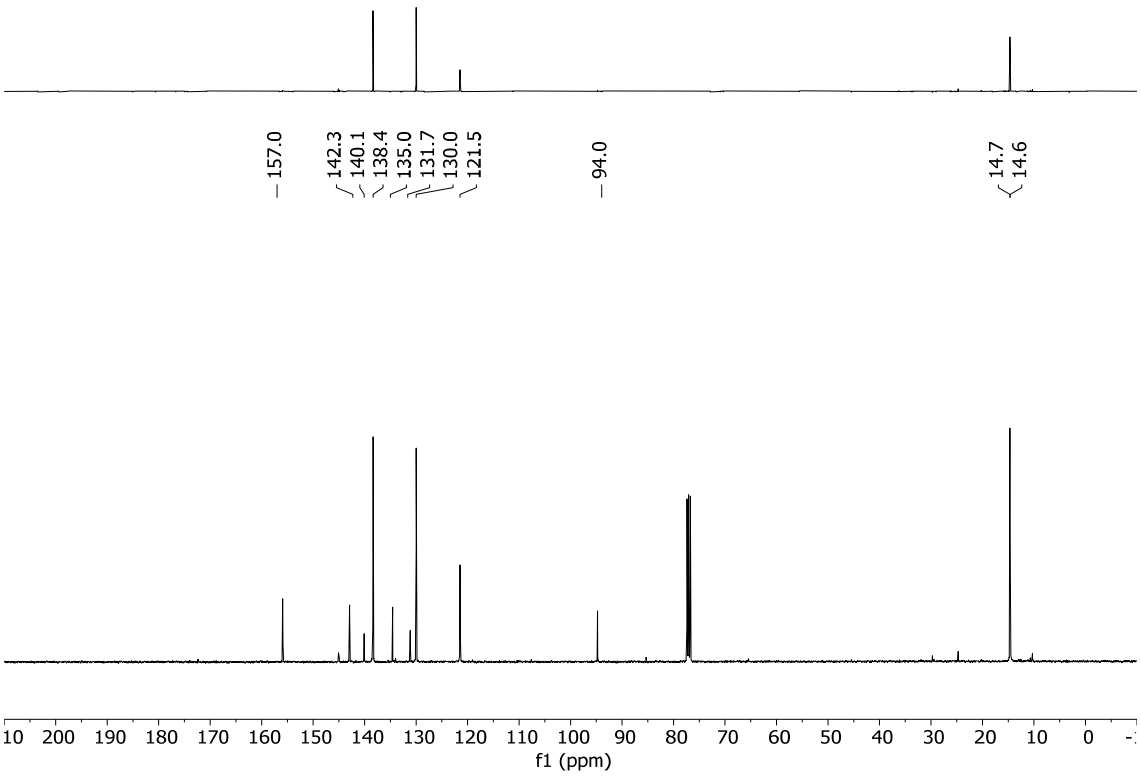
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **14** ($CDCl_3$, 300 K)



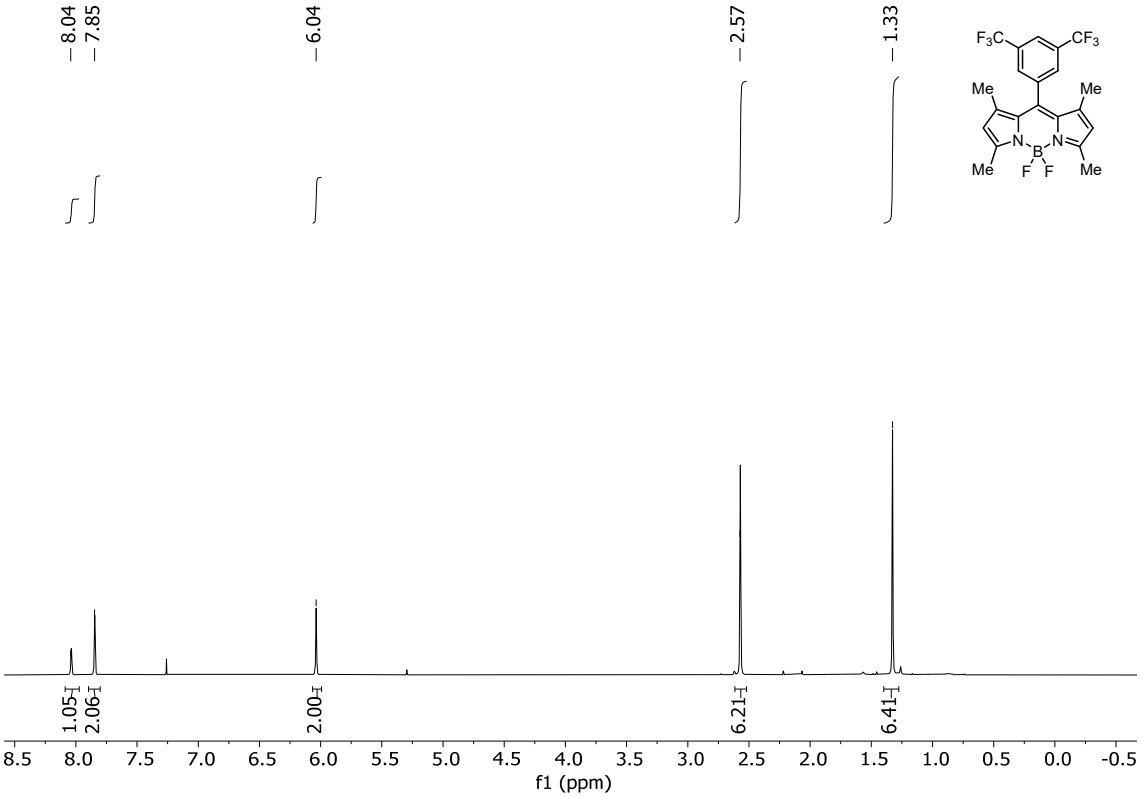
300 MHz ^{1}H-NMR Spectrum of compound **15** ($CDCl_3$, 300 K)



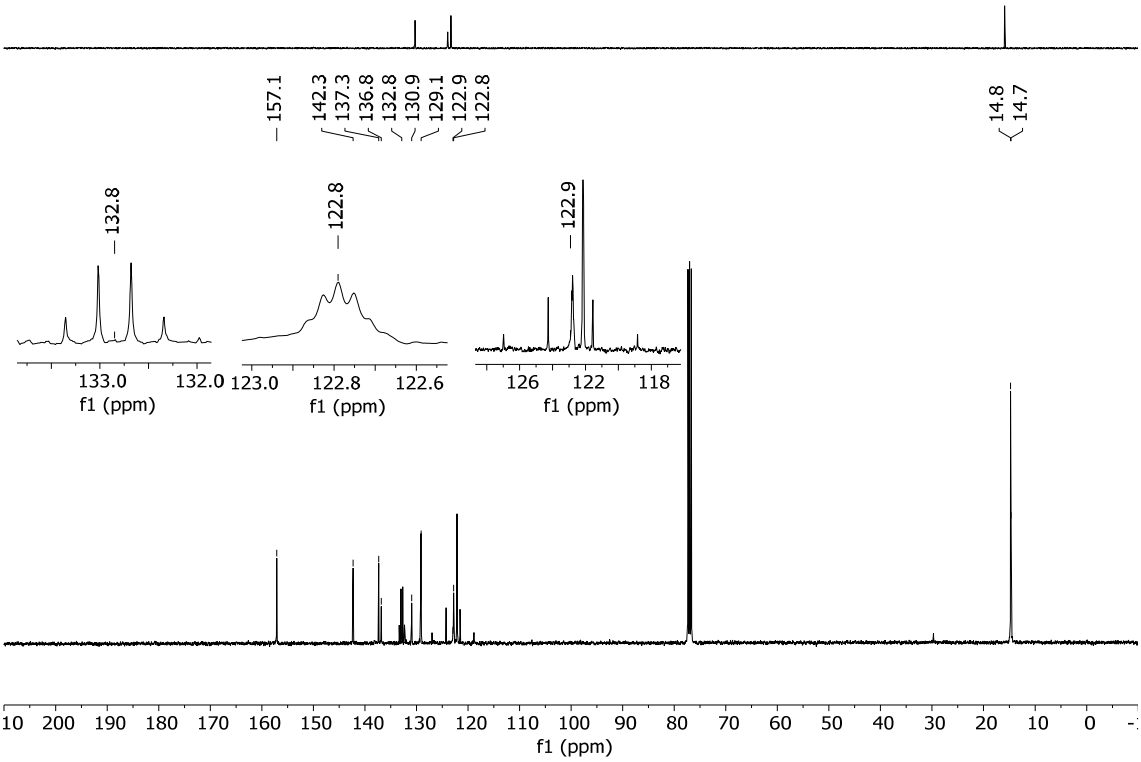
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **15** ($CDCl_3$, 300 K)



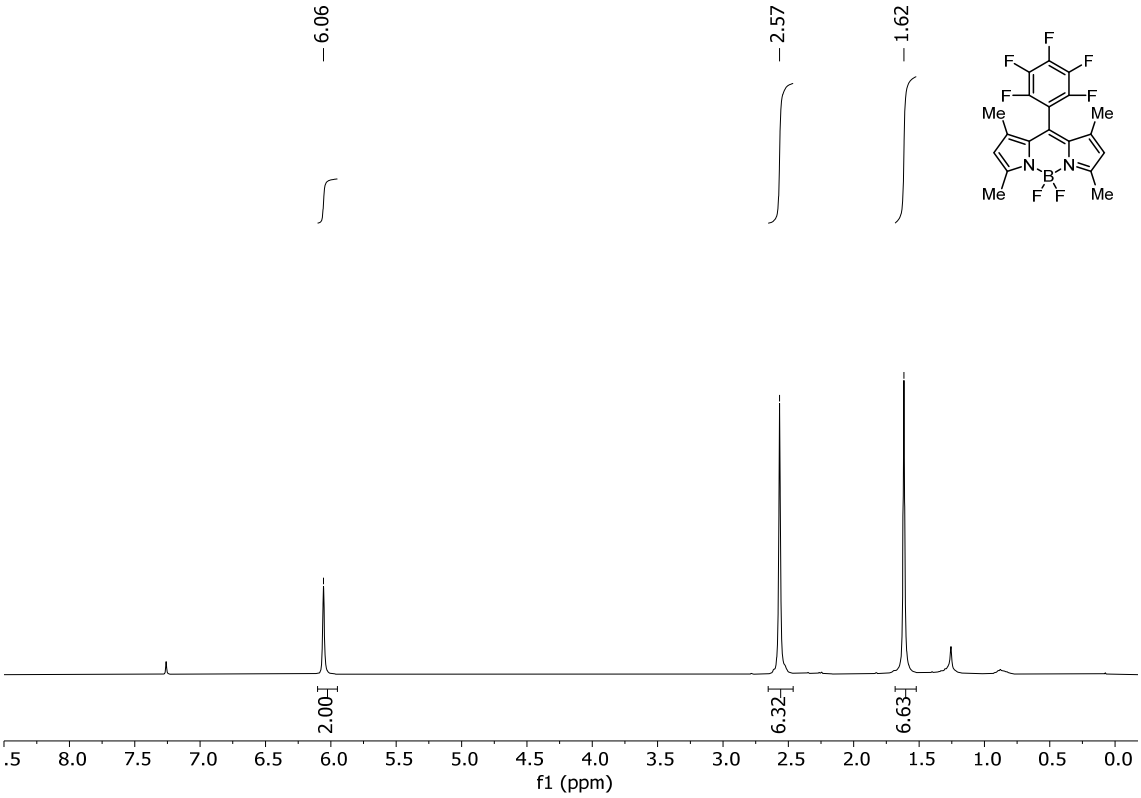
300 MHz ^{1}H-NMR Spectrum of compound **16** ($CDCl_3$, 300 K)



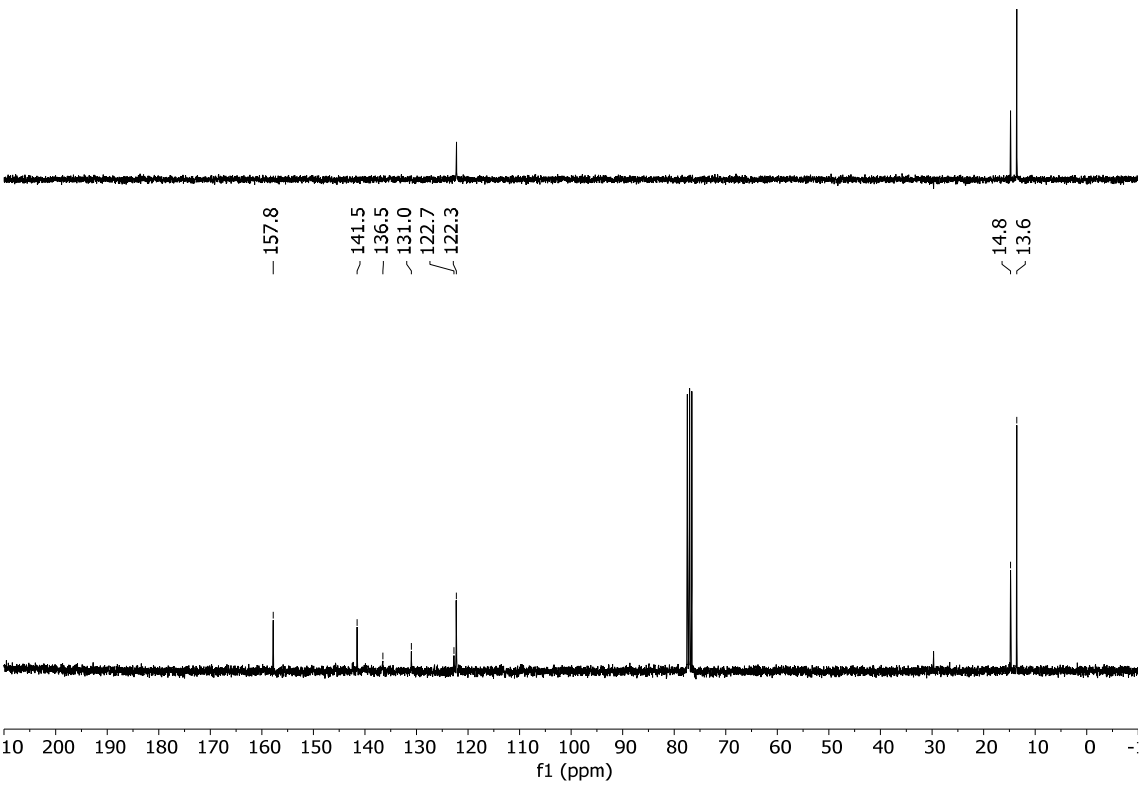
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **16** ($CDCl_3$, 300 K)



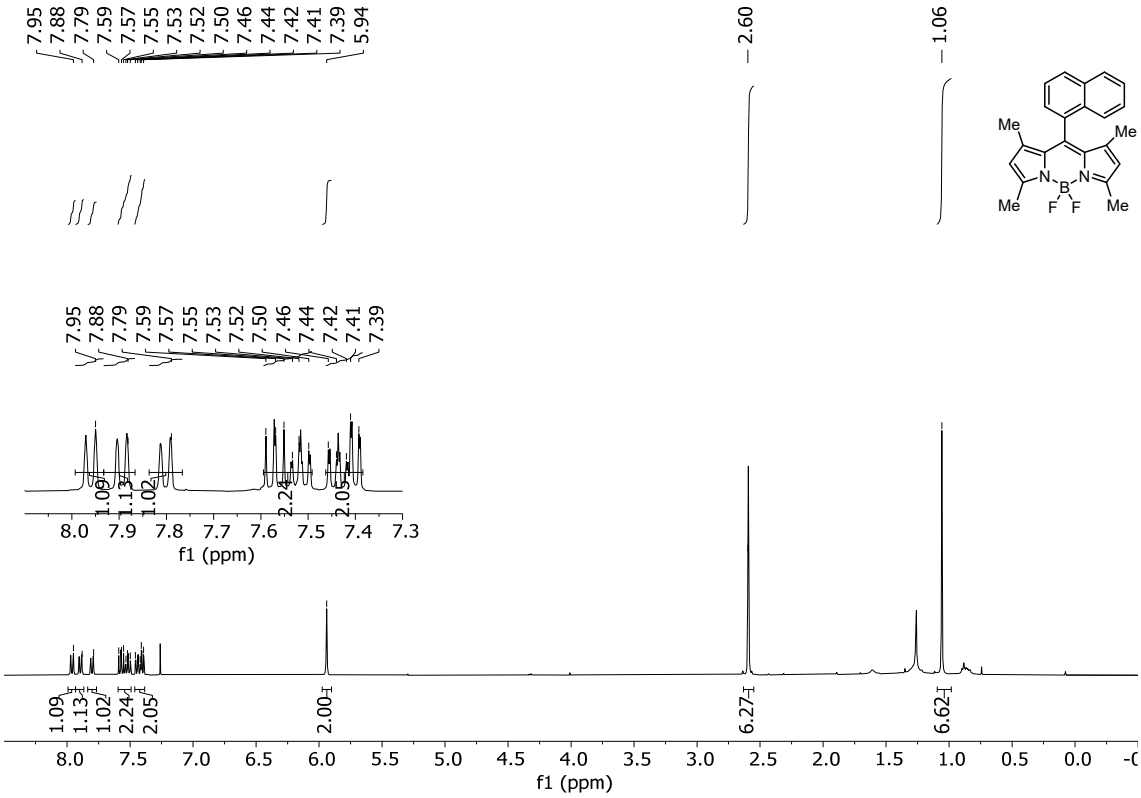
400 MHz ^{1}H-NMR Spectrum of compound **17** ($CDCl_3$, 300 K)



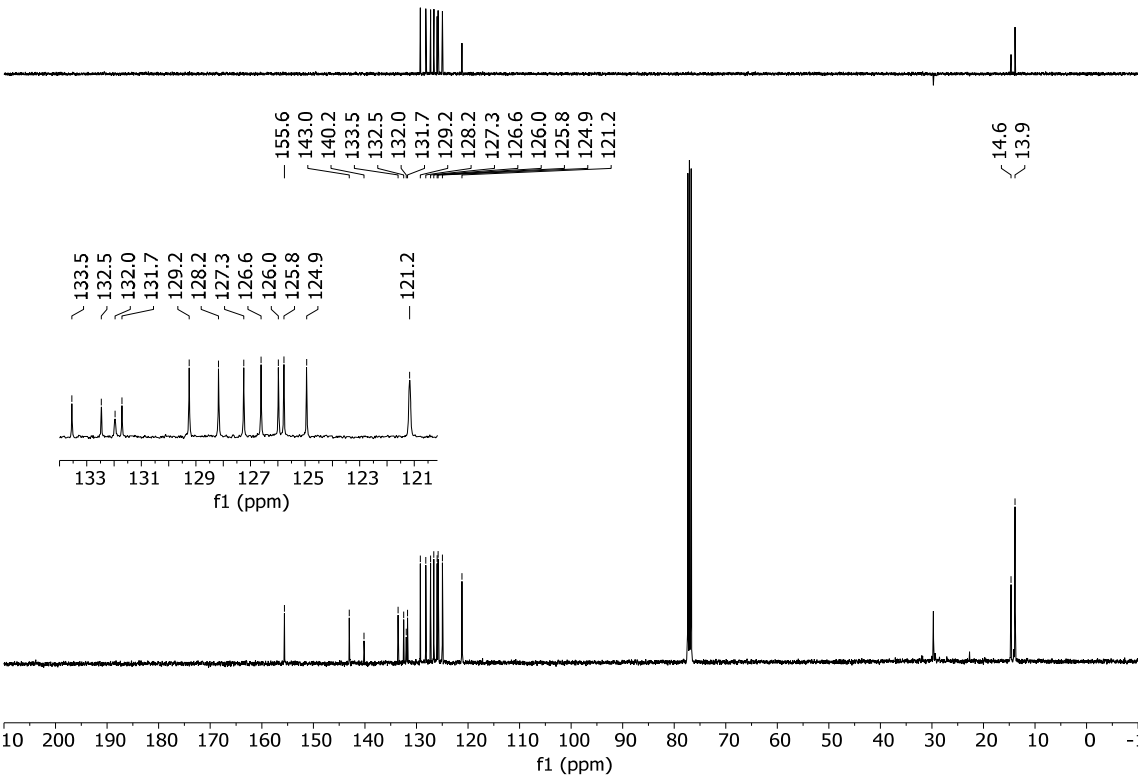
100 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **17** ($CDCl_3$, 300 K)



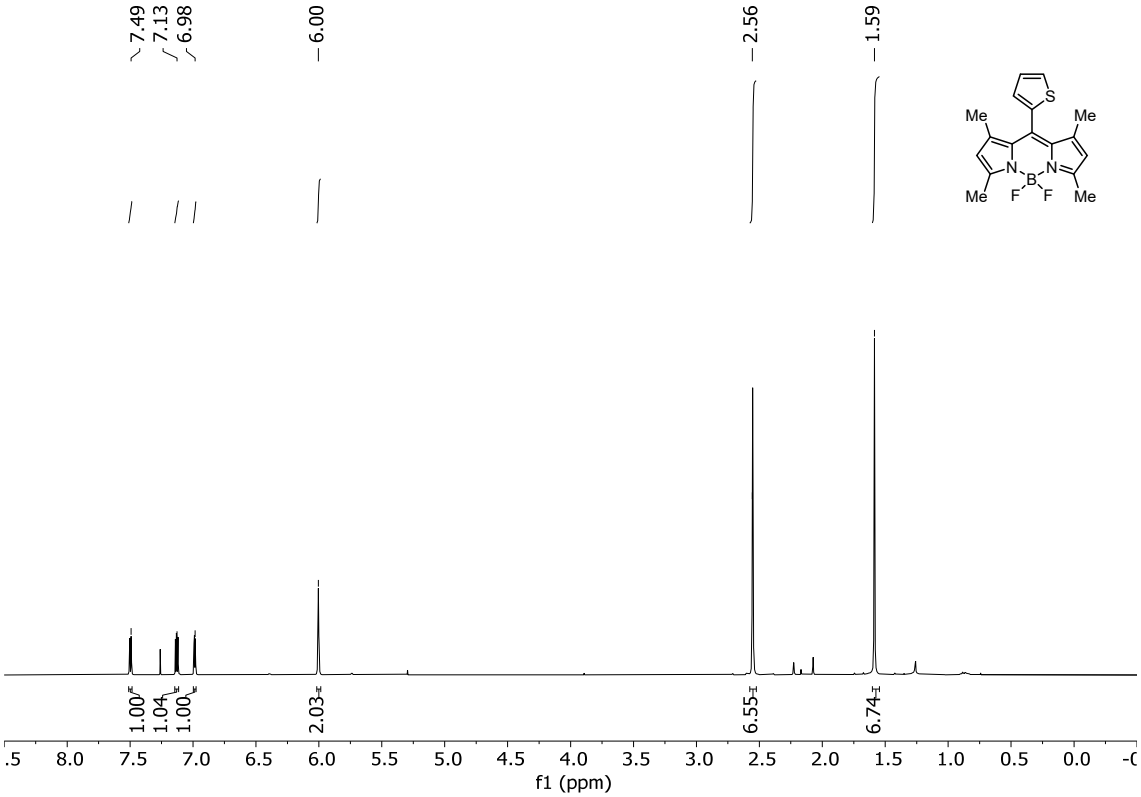
300 MHz ^{1}H-NMR Spectrum of compound **18** ($CDCl_3$, 300 K)



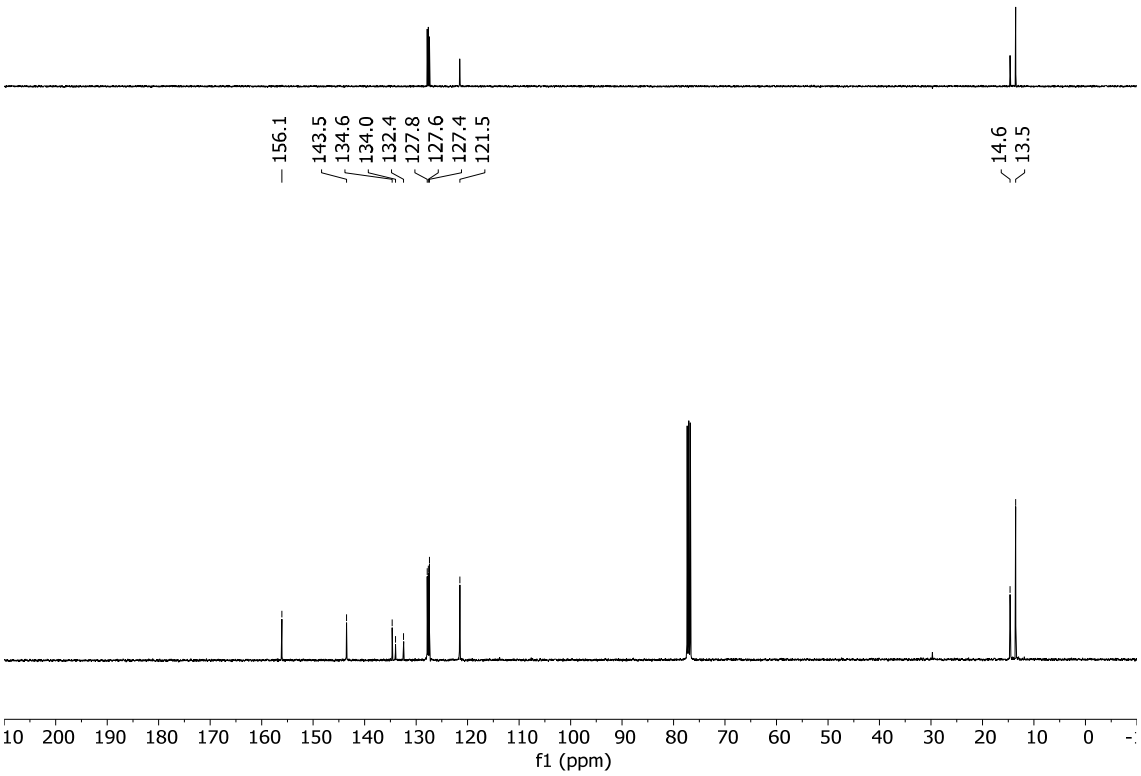
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **18** ($CDCl_3$, 300 K)



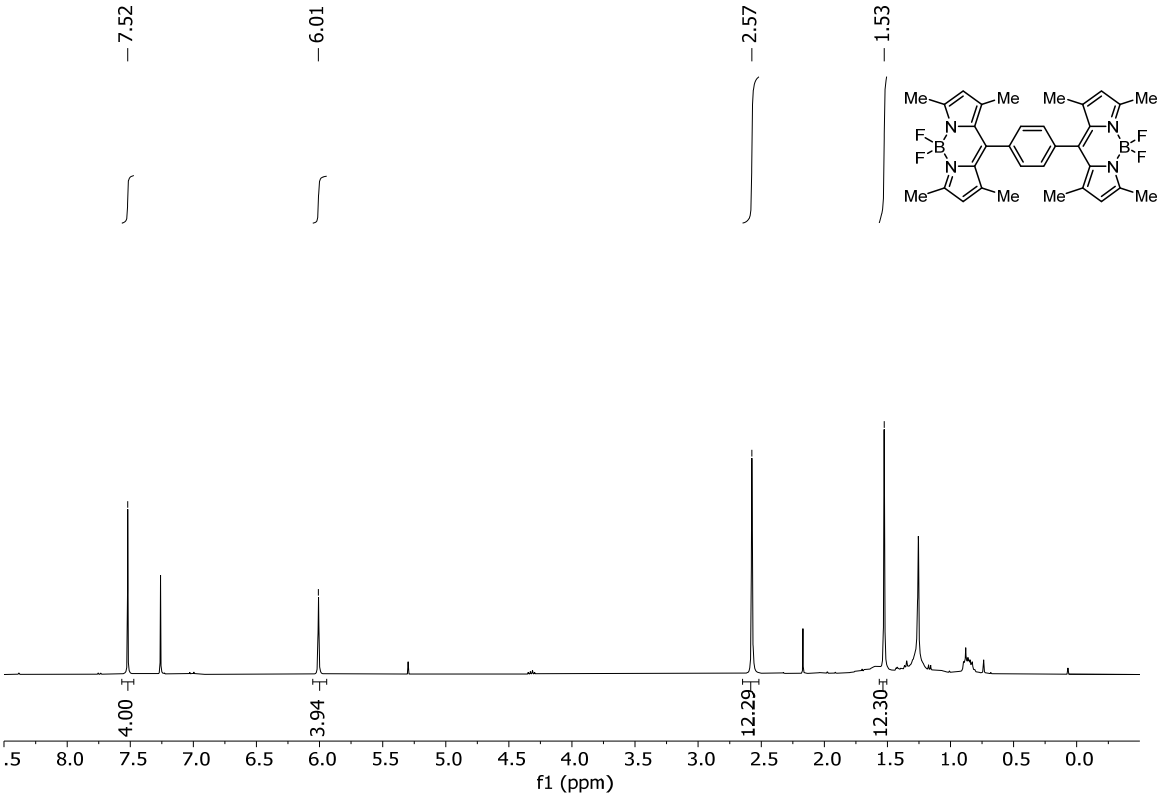
300 MHz ^{1}H-NMR Spectrum of compound **19** ($CDCl_3$, 300 K)



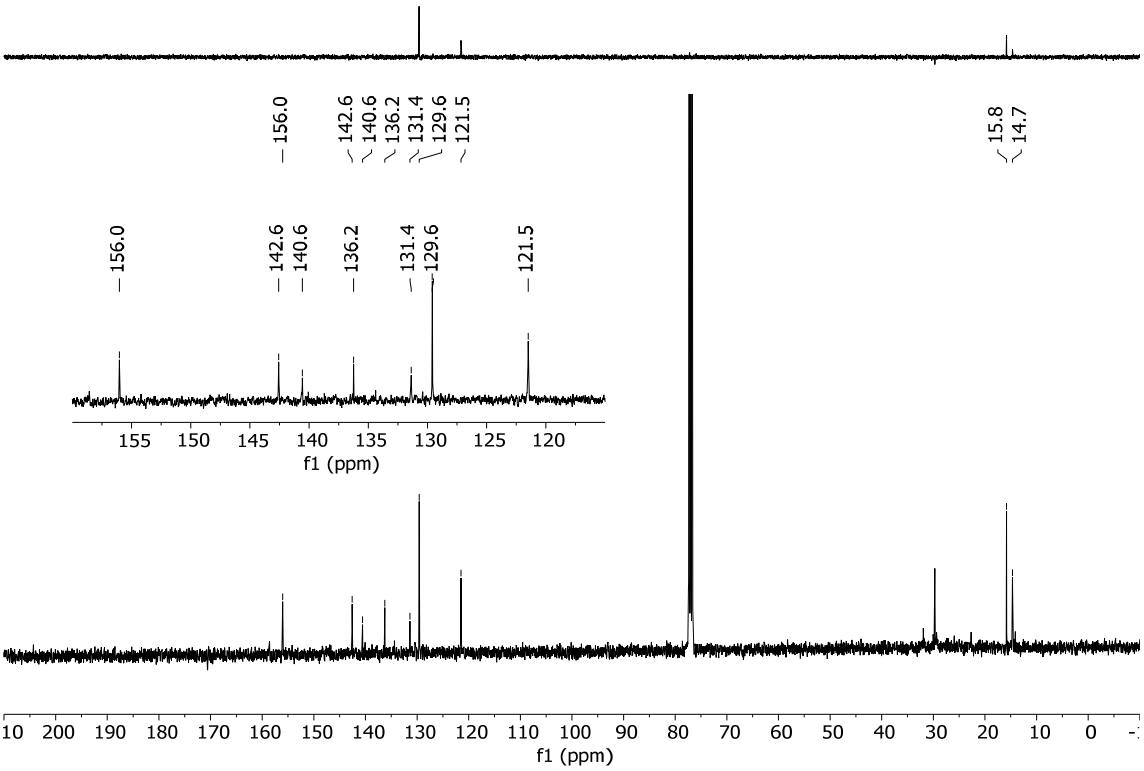
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **19** ($CDCl_3$, 300 K)



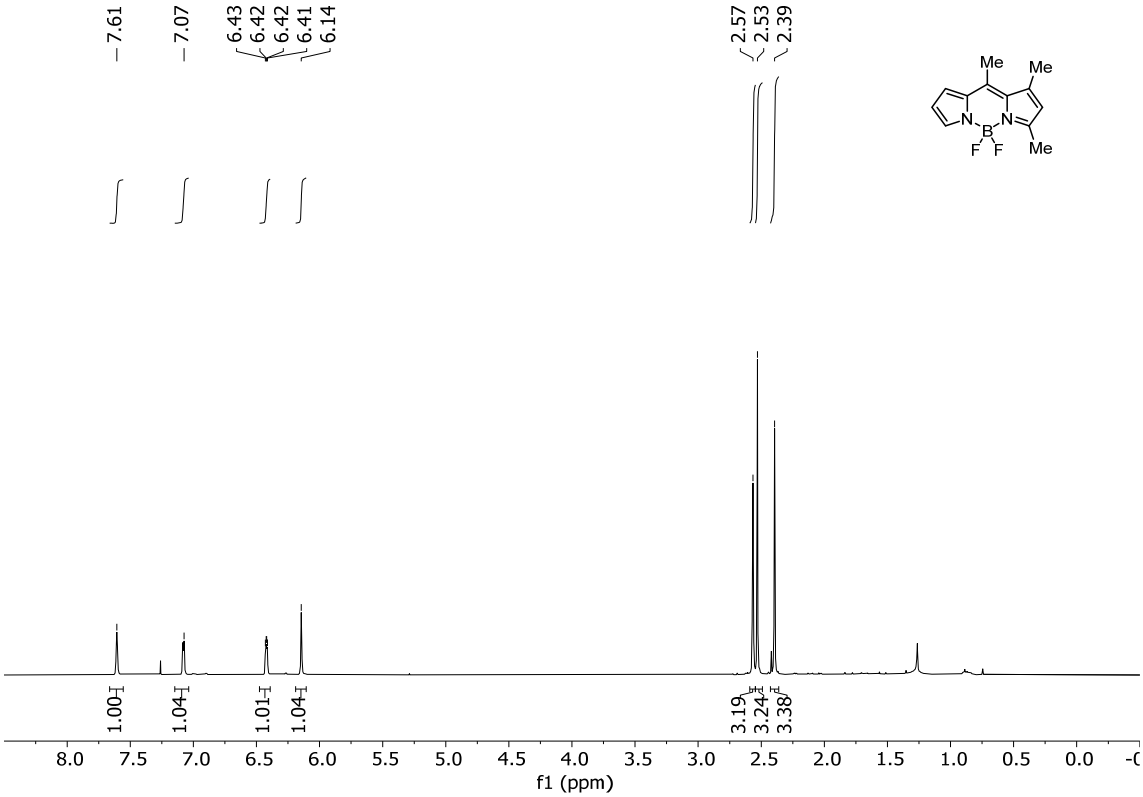
300 MHz ^{1}H-NMR Spectrum of compound **20** ($CDCl_3$, 300 K)



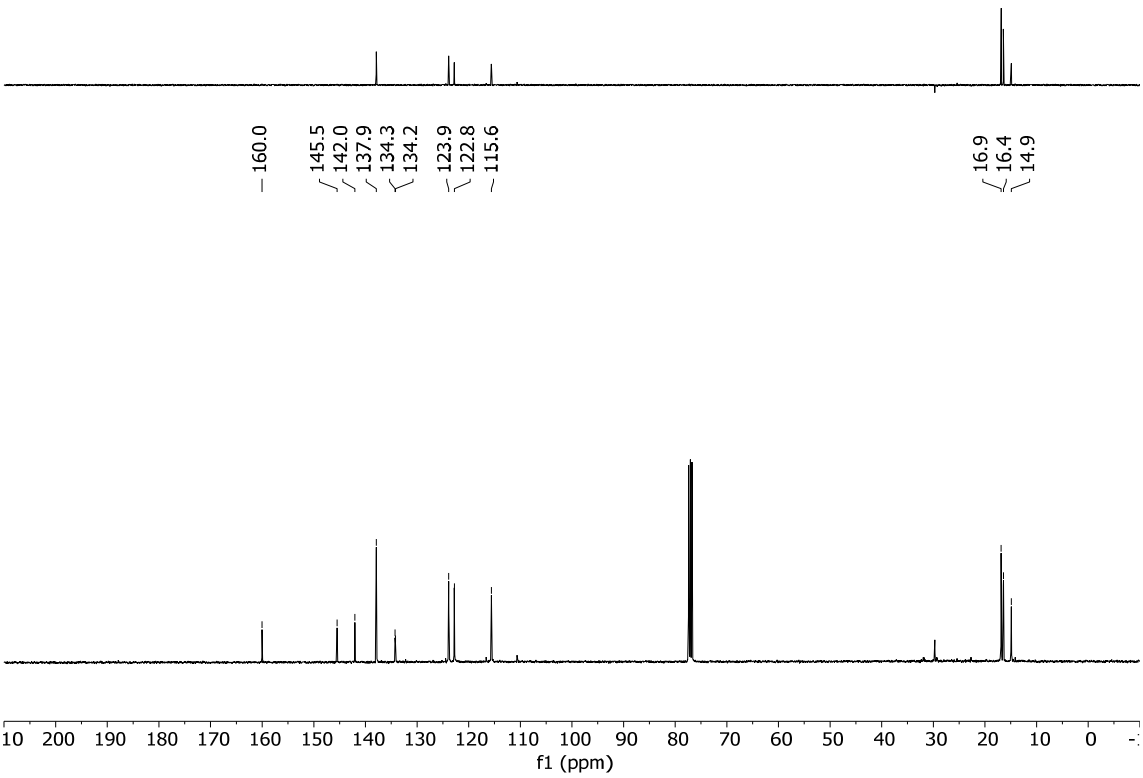
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **20** ($CDCl_3$, 300 K)



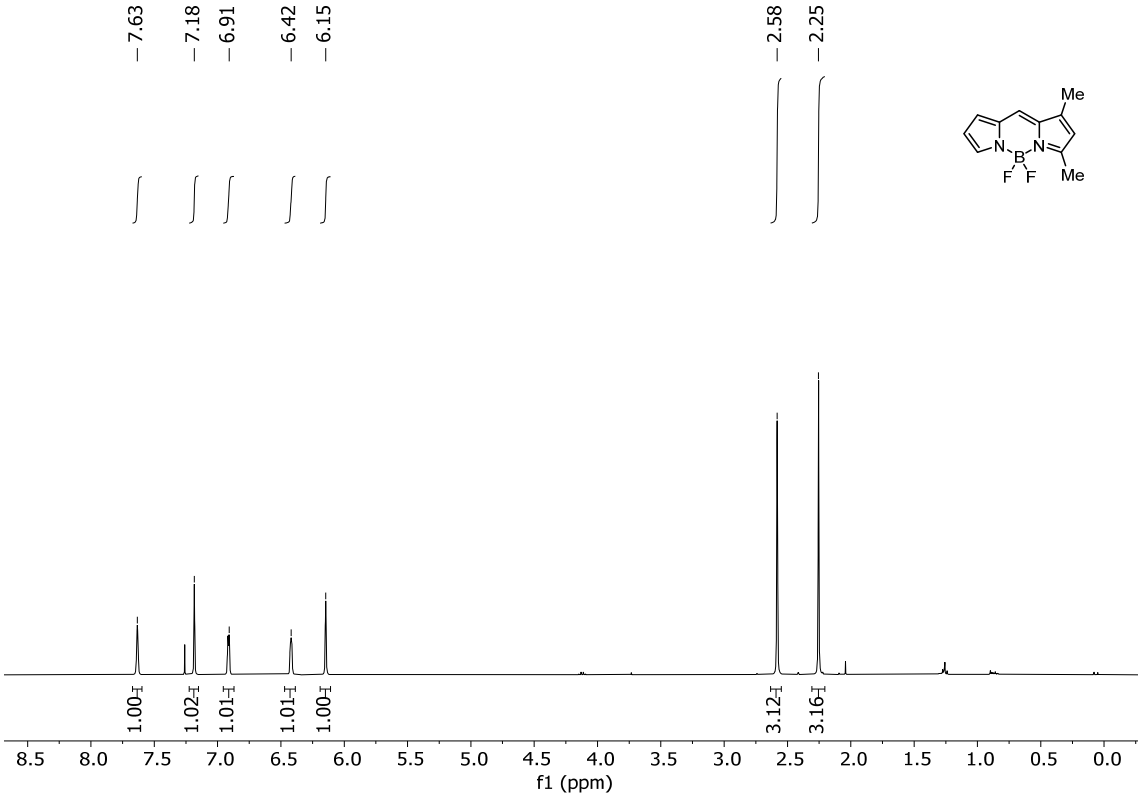
300 MHz ^{1}H-NMR Spectrum of compound **22a** ($CDCl_3$, 300 K)



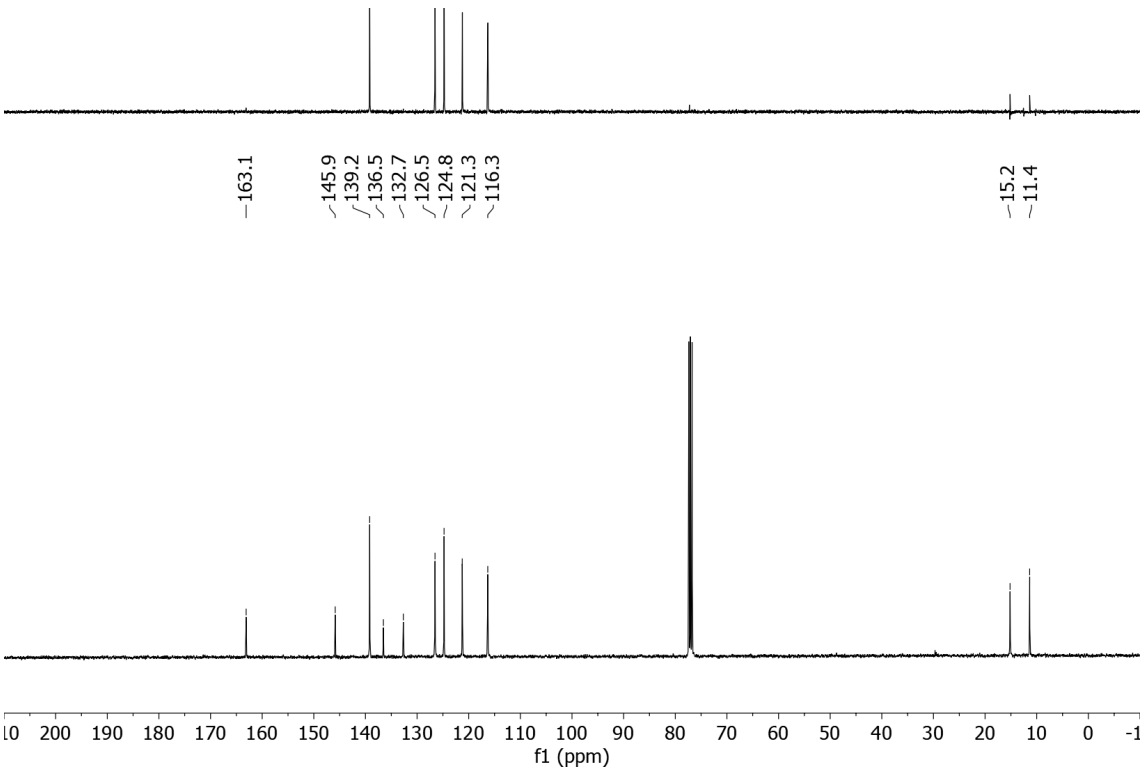
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **22a** ($CDCl_3$, 300 K)



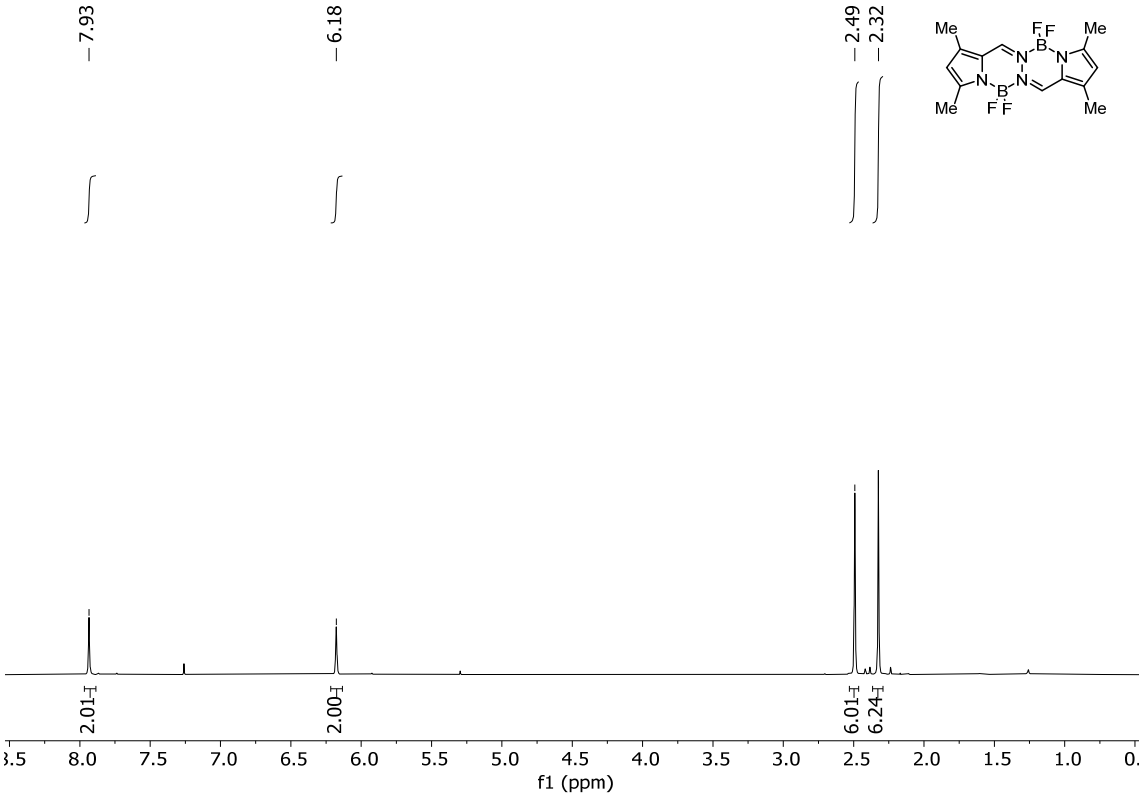
400 MHz ^{1}H-NMR Spectrum of compound **22b** ($CDCl_3$, 300 K)



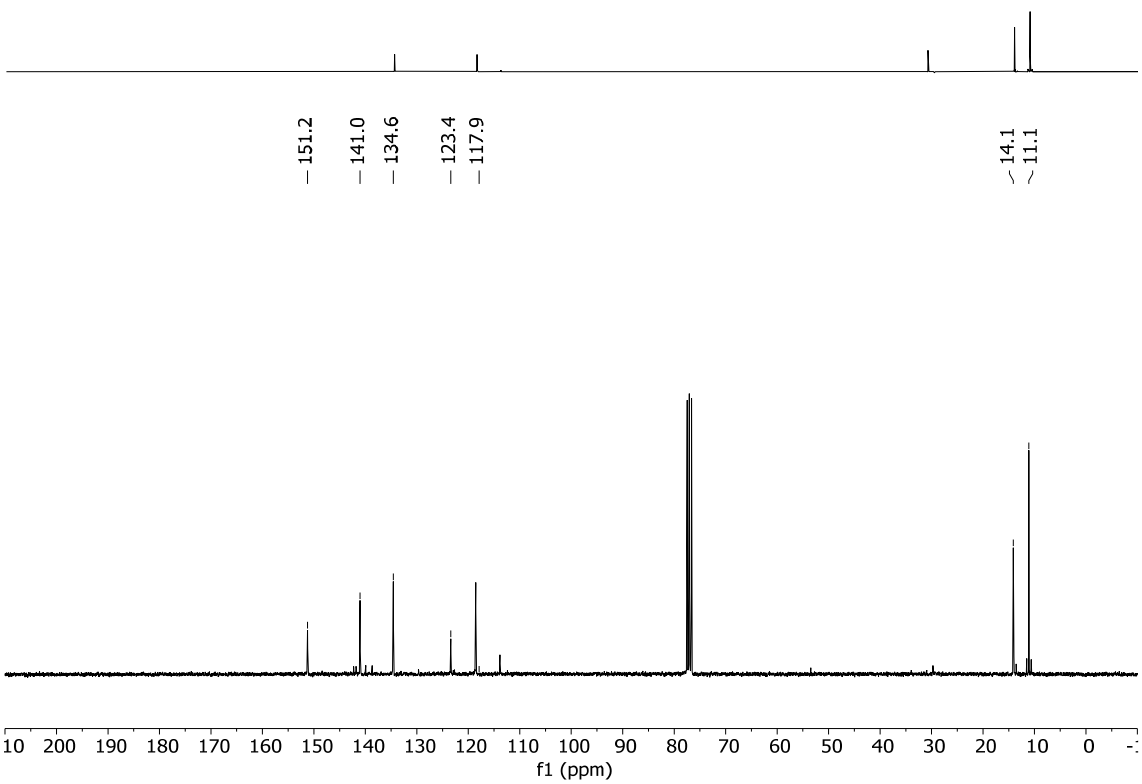
100 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **22b** ($CDCl_3$, 300 K)



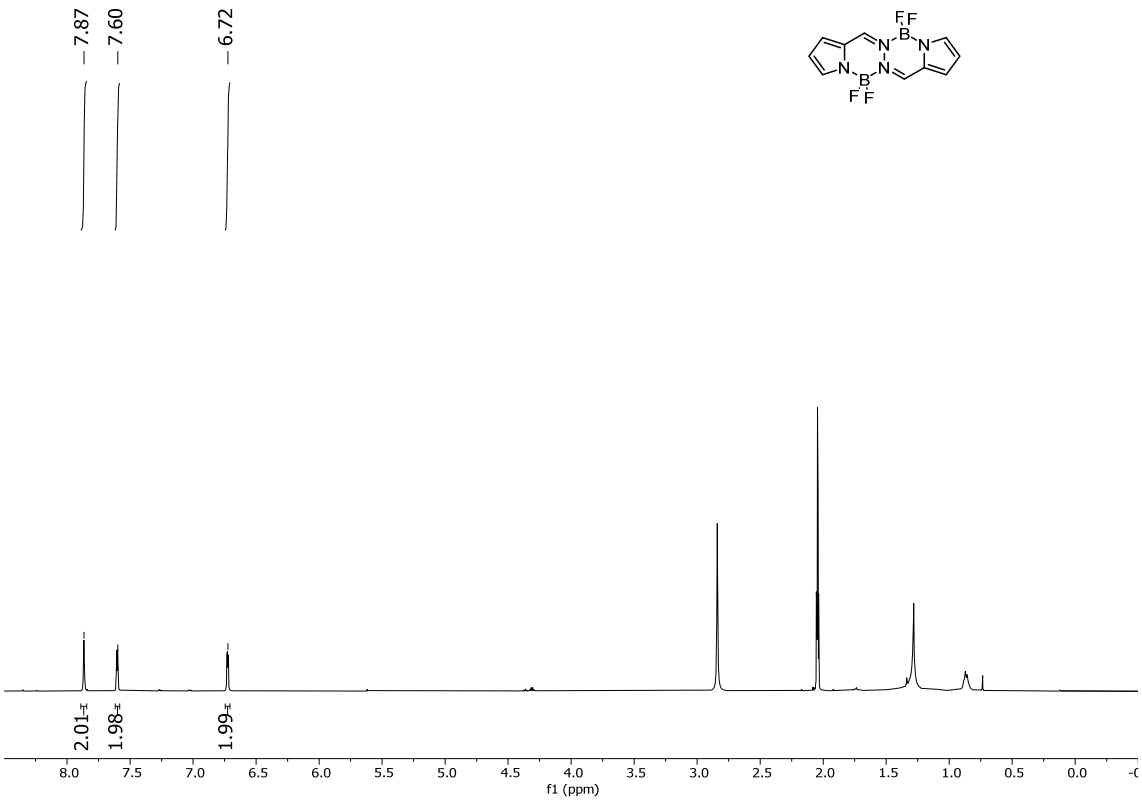
300 MHz ^{1}H-NMR Spectrum of compound **24a** ($CDCl_3$, 300 K)



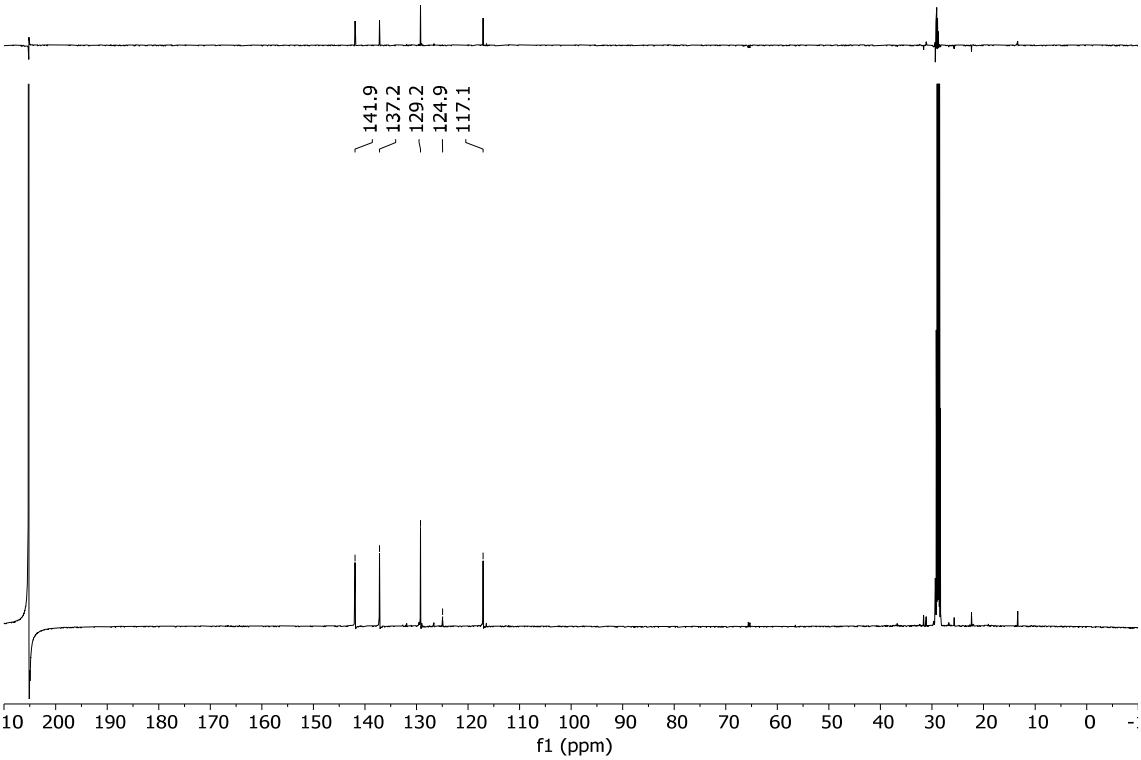
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **24a** ($CDCl_3$, 300 K)



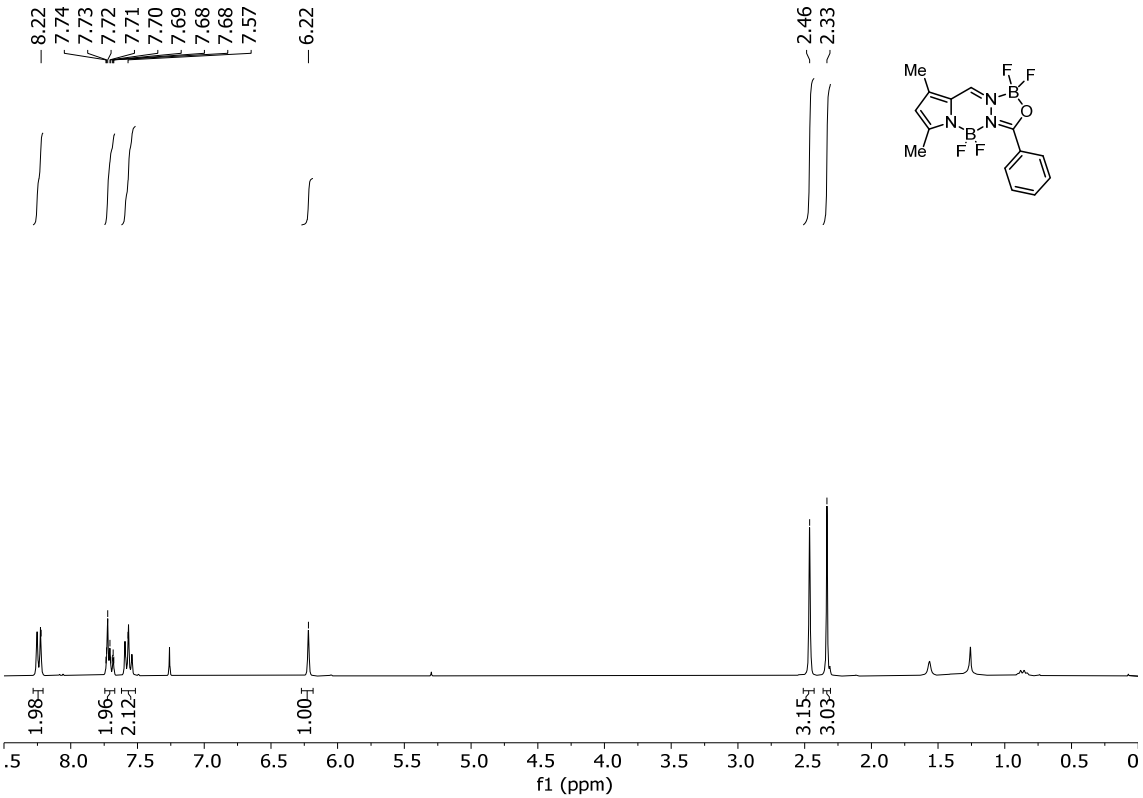
300 MHz ^{1}H-NMR Spectrum of compound **24b** ($(CD)_3CO$, 300 K)



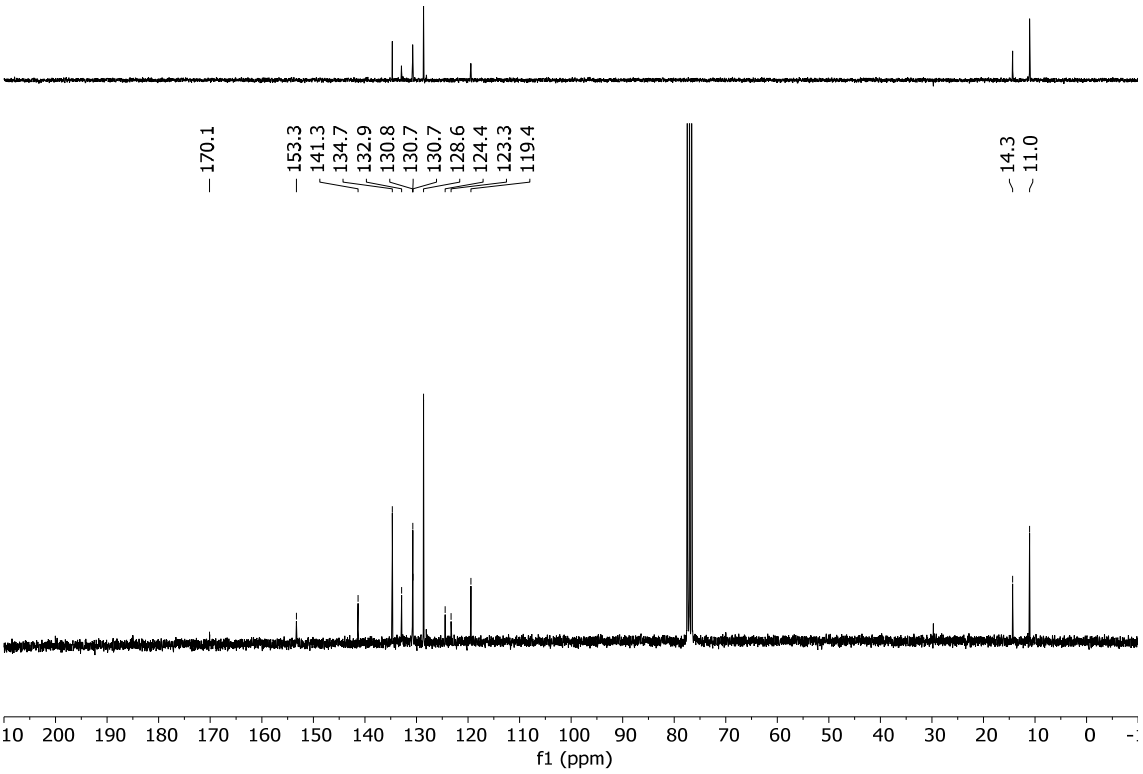
75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **24b** $(CD)_3CO$, 300 K)



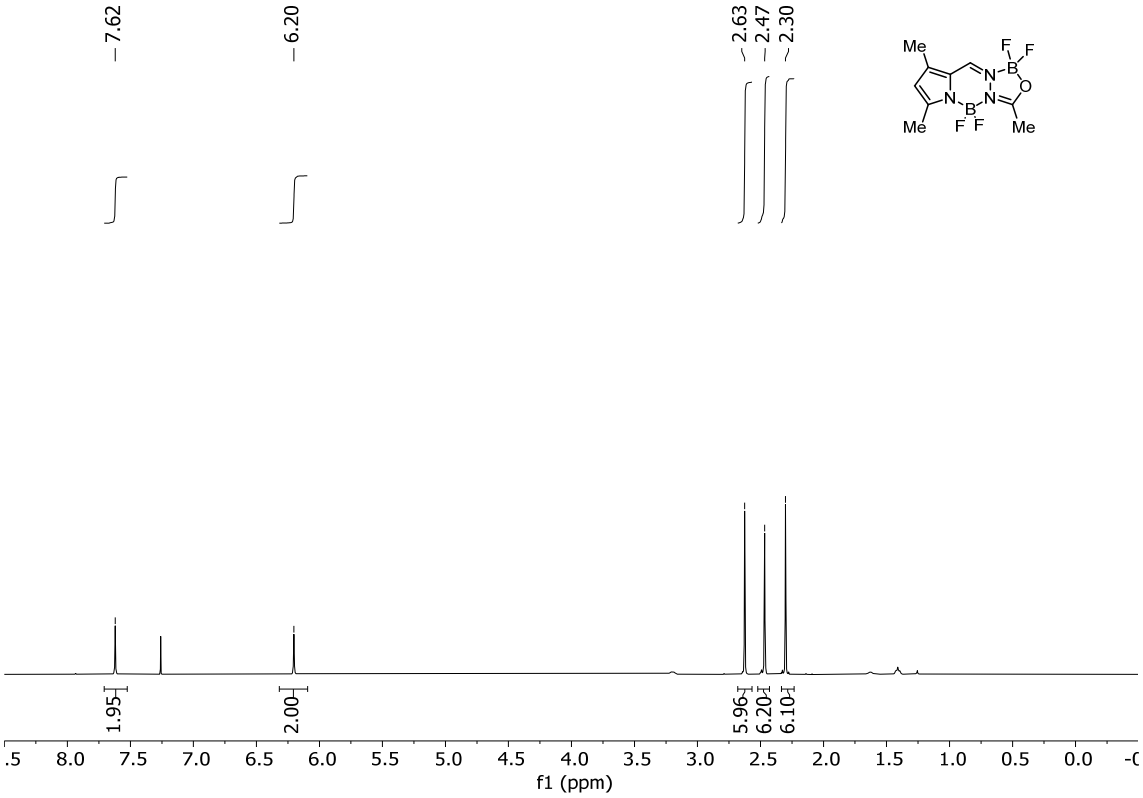
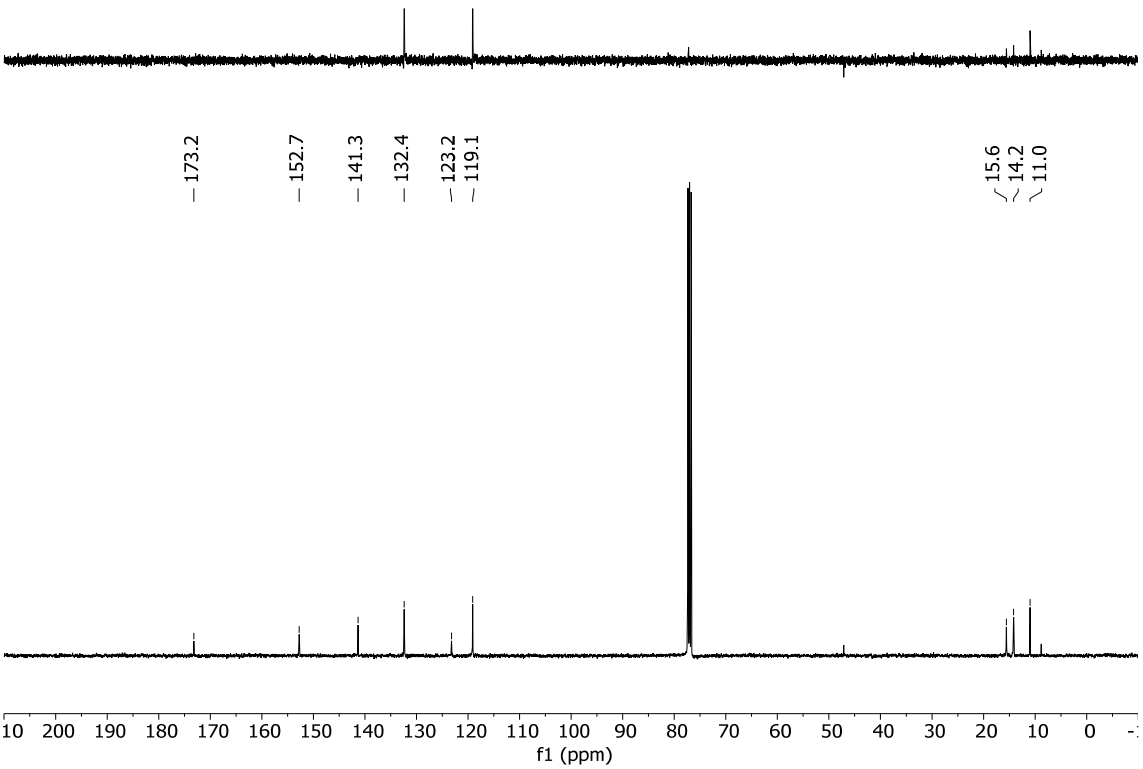
300 MHz ^{1}H-NMR Spectrum of compound **27a** ($CDCl_3$, 300 K)



75 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **27a** ($CDCl_3$, 300 K)



400 MHz ^{1}H-NMR Spectrum of compound **27b** ($CDCl_3$, 300 K)



100 MHz ^{13}C{^{1}H}-NMR Spectrum of compound **27b** ($CDCl_3$, 300 K)