Electronic Supporting Information

New members of fluorescent 1,8-naphthyridine-based BF_2 compounds: Selective binding of BF_2 with terminal bidentate N^N^O and N^C^O groups and tunable spectroscopy properties

Mei-Ling Du,[a] Cun-Yan Hu,[a] Liu-Fang Wang,[a] Cong Li,[a] Yang-Yang Han,[a] Xin Gan,[a] Yong Chen,[c] Wei-Hua Mu,[a] Michael L. Huang*[b] and Wen-Fu Fu*[a,c]

Experimental procedures

General Comments

All reactions were performed under nitrogen atmosphere. The solvents used for spectroscopic measurements were HPLC grade. ^{1}H NMR spectra were recorded on a Bruker 400 (^{19}F NMR, 376 MHz) or 500 MHz AVANCE II spectrometer at 298 K. ESI-MS data were obtained with an APEX II Model FT-ICR mass spectrograph. Elemental analyses were performed with an Elementar Vario EL instrument. UV-Vis spectra were obtained using a Hitachi U-3010 spectrophotometer. Corrected emission spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer adapted to a right-angle configuration at room temperature. The emission lifetimes of samples were determined by single-photon counting on a FL920 spectrometer. The fluorescence quantum yields were measured relative to rhodamin 6G in methanol (λ_{ex} = 488 nm, Φ_F = 0.86) at room temperature and corrected for changes in the refractive index.[1] All 1,8-naphthyridine derivatives, 2,4-dimethyl-7-amino-1,8-naphthyridine, 2-methyl-7-amino-1,8-naphthyridine, 2-chloro-7-amino-1,8-naphthyridine, and 2-hydroxyl-7-amino-1,8-naphthyridine were prepared according to reported methods.[2-5]

X-ray crystallography

X-ray diffraction measurements for compounds **1**, **4**, and **6–9** were carried out on a Bruker SMART or Rigaku SATURN diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.071073 nm) at 113 K or room temperature. The structures of the compounds were solved by direct methods using SHELXL-97. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method using F^2 data.[6,7]

Theoretical calculations

All optimizations were carried out in CH_2Cl_2 solution with the Gaussian 03 program package at the SCRF-B3LYP/6-311++G(d,p) level employing the PCM/Bader model. TD-DFT at the SCRF-TD-DFT B3LYP/6-311++G(d,p) level was carried out in CH_2Cl_2 solution to predict and verify the absorption spectra of various species. [8-11]

References

1 J. Olmsted, *J. Phys. Chem.,* 1979, **83**, 2581–2584.

2 H. F. J. Li, W. F. Fu, L. Li, X. Gan, W. H. Mu, W. Q. Chen, X. M. Duan and H. B. Song, *Org. Lett.*, 2010, **12**, 2924–2927.

3 L. Quan, Y. Chen, X. J. Lv and W. F. Fu, *Chem. Eur. J.*, 2012, **18**, 14599–14604.

4 Y. Y. Wu, Y. Chen, G. Z. Gou, W. H. Mu, X. J. Lv, M. L. Du and W. F. Fu, *Org. Lett.*, 2012, **14**, 5226–5229.

5 Y. Y. Wu, Y. Chen, W. H. Mu, X. J. Lv and W. F. Fu, *J. Photochem. Photobio. A Chemistry,* 2013, **272**, 73–79.

6 W. F. Fu, L. F. Jia, W. H. Mu, X. Gan, J. B. Zhang, P. H. Liu, Q. Y. Cao, G. J. Zhang, L. Quan, X. J. Lv and Q. Q. Xu, *Inorg. Chem.*, 2010, **49**, 4524–4533.

7 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

8 G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

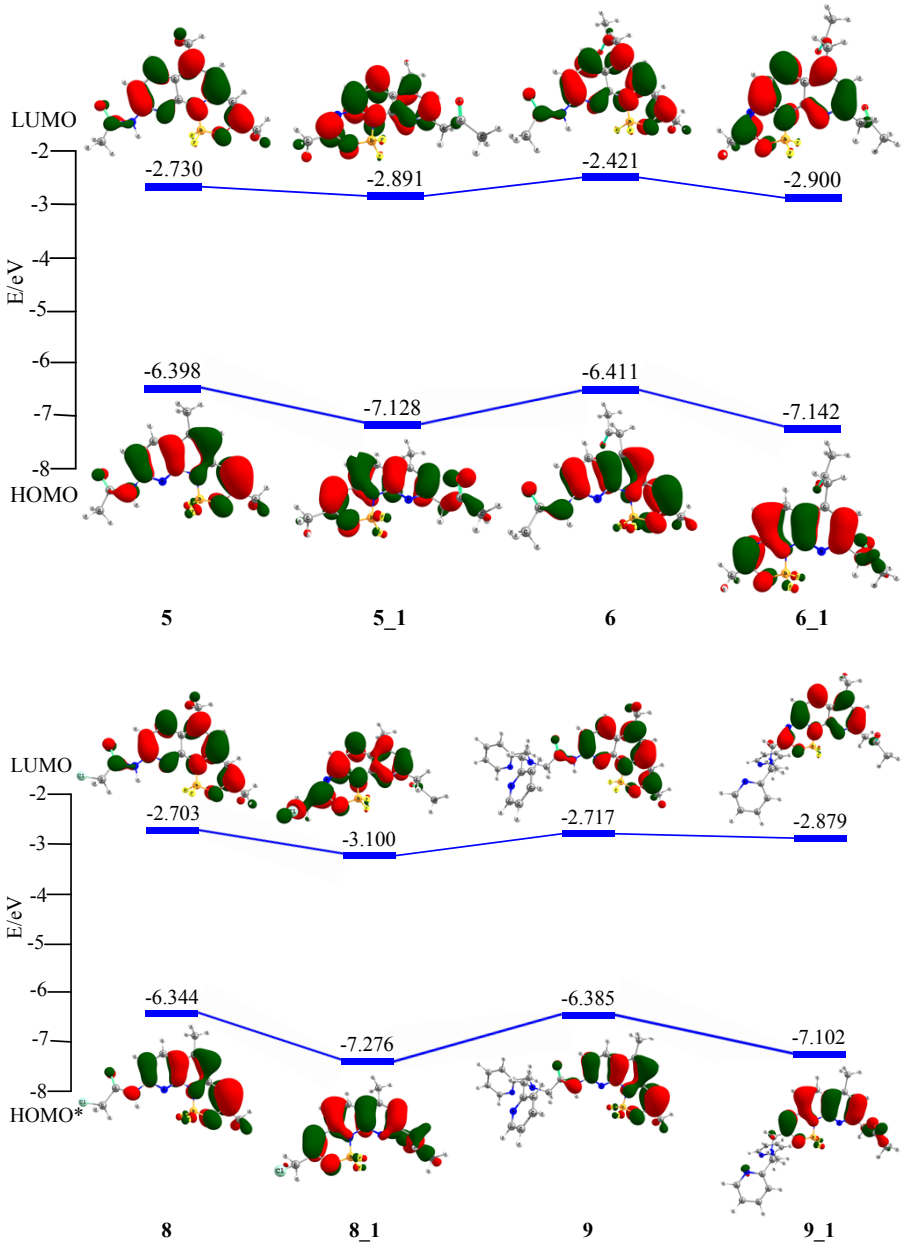
9 M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria,M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J.M.Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov,G. Liu,A. Liashenko, P. Piskorz, I. Komaromi, R. L.Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara,M. Challacombe, P.M.W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03* (*Revision C.02*), Gaussian, Inc., Wallingford, CT, 2004.

10 A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648–5652.
11 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
12 M. P. Andersson and P. Uvdal, *J. Phys. Chem. A*, 2005, **109**, 2937–2941。

Table S1. X-ray crystallographic date for complexes 1, 4, 6–9.

Compounds	**1**	**4**	**6**•0.5H_2O	**7**•1/3CH_2Cl_2	**8**	**9**
formula	$C_{12}H_{12}BF_2N_3O$	$C_{10}H_{20}BF_2N_3O_2$	$C_{16}H_{17}BF_2N_3O_{3.5}$	$C_{12}H_{13}BF_2N_3O$	$C_{14}H_{13}BClF_2N_3O_2$	$C_{26}H_{25}BF_2N_6O_2$
formula weight	263.06	263.10	356.14	292.37	339.53	502.33
T [K]	113(2)	113(2)	113(2)	113(2)	293(2)	113(2)
crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	P-1	P1 21/c1	P2(1)/c	P-1	P-1	P-1
crystal size [mm]	0.32×0.24×0.22	0.24×0.06×0.05	0.22×0.20×0.12	0.20×0.18×0.10	0.20×0.15×0.10	0.22×0.20×0.18
a [Å]	7.2978(8)	4.6470(8)	20.167(6)	11.461(3)	7.645(2)	8.506(1)
b [Å]	8.114(1)	19.0559(3)	17.717(5)	12.130(3)	12.310(3)	8.810(1)
c [Å]	10.499(1)	11.323(2)	9.387(3)	14.451(4)	16.339(3)	17.414(2)
α [°]	93.34(2)	90	90	83.107(7)	94.37(3)	96.487(5)
β/ [°]	107.60(2)	96.138(8)	99.038	82.118(7)	99.76(3)	103.927(3)
γ [°]	94.49(3)	90	90	73.049(6)	95.76(3)	105.669(4)
V [Å]^3	588.57(12)	996.9(3)	3312,2(17)	1896.9(8)	1500.9(5)	1197.2(2)
Z	2	4	8	2	2	2
D_c/g cm^{-3}	1.484	1.753	1.428	1.536	1.503	1.393
μ [mm^{-1}]	0.118	0.145	0.115	0.254	0.288	0.101
$2\theta_{max}$ [°]	60.06	55.78	55.76	50.04	52.00	55.86
unique reflections	3324	2350	7848	6688	5758	5705
parameters	175	168	481	542	415	341
R_{int}	0.0504	0.0426	0.0573	0.0413	0.0361	0.0412
goodness of fit	1.041	1.007	1.038	1.039	1.122	0.909
$R1$, w$R2$[$I>2\alpha(I)$]	0.0476, 0.1337	0.0368, 0.0830	0.0471, 0.0980	0.0640, 0.2047	0.0524, 0.1678	0.0371, 0.0939
$R1$, w$R2$[all data]	0.0503, 0.1369	0.0537, 0.0910	0.0676, 0.1067	0.0846, 0.2227	0.0662, 0.1865	0.0582, 0.1001
max, min peaks (e Å^{-3})	0.463, -0.320	0.283, -0.235	0.268, -0.258	1.960, -1.578	0.588, -0.490	0.181, -0.315

$R1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{1/2}$

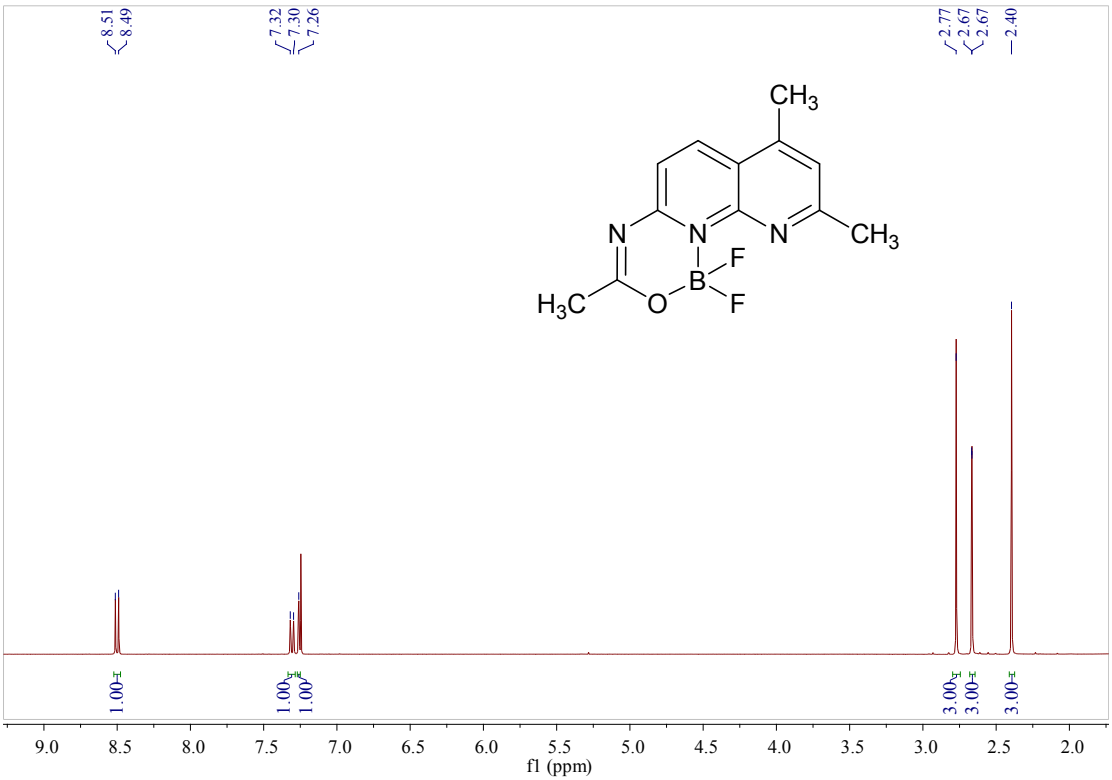


* For compound **9** and **9_1**, it's HOMO-1.

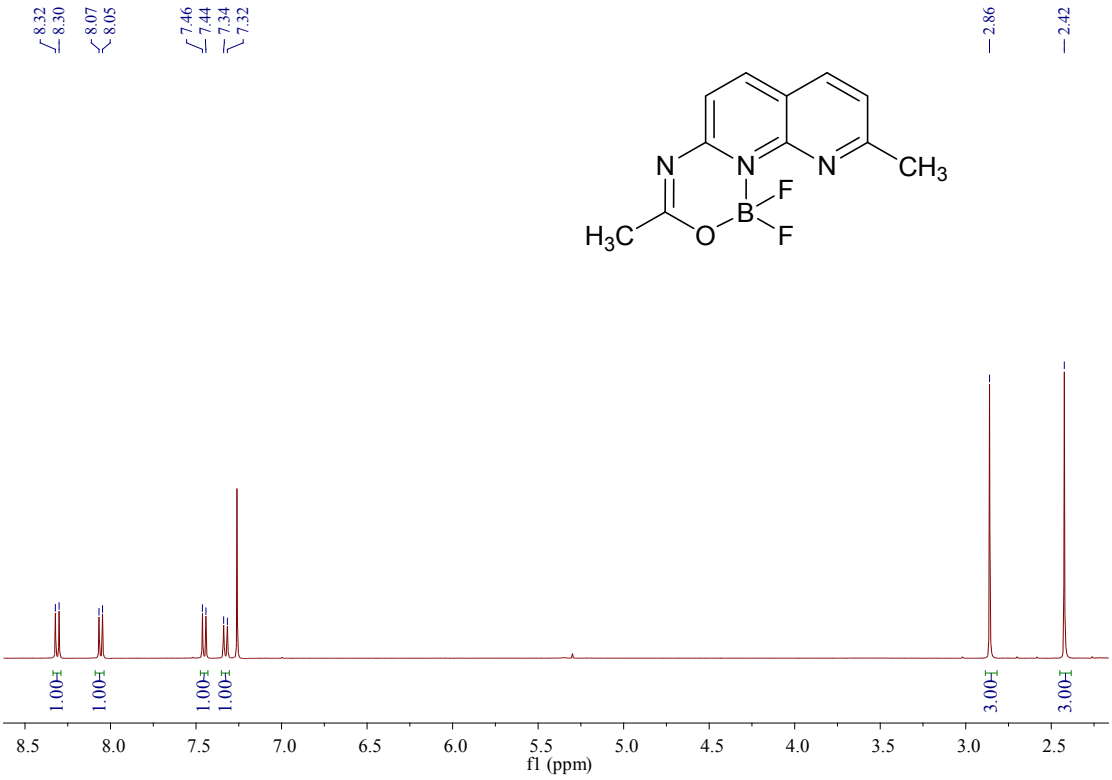
Figure S1. Molecular orbital energy diagrams of **5, 6, 8** and **9** and their corresponding compounds.

Table S2. Optical transitions with oscillator strength (*f*) calculated by the TD-DFT (SCRF(PCM/Bader)-B3LYP/6-311++G(d,p)) level in CH_2Cl_2 solution.

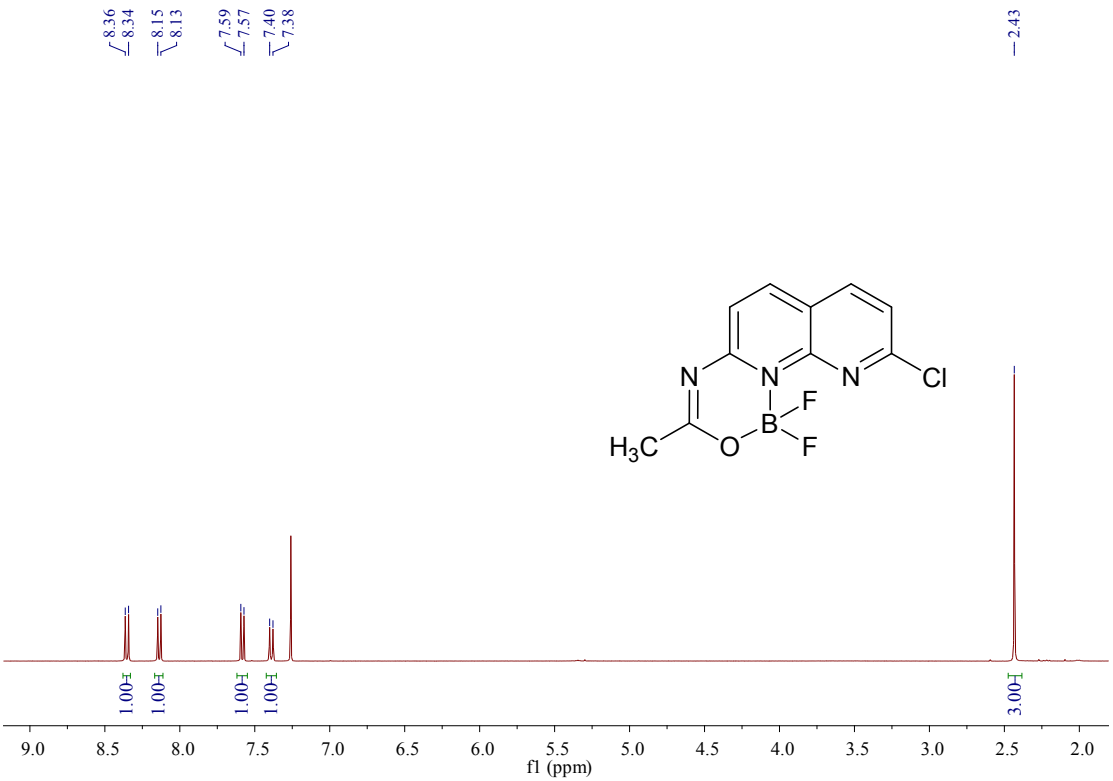
cpd.	electronic transitions	energy (eV)	λ_{ab}/nm(cal.)	λ_{ab}/nm(exp.)	*f*	composition
1	S_0-S_1	3.77	329	344, 361	0.47	HOMO to LUMO (0.69)
	S_0-S_6	5.05	245		0.35	HOMO to LUMO+1 (0.65)
2	S_0-S_1	3.79	327	343, 360	0.48	HOMO to LUMO (0.70)
	S_0-S_6	5.10	243		0.28	HOMO to LUMO+1 (0.63)
3	S_0-S_1	3.73	332	345, 362	0.50	HOMO to LUMO (0.69)
	S_0-S_6	5.18	239		0.42	HOMO to LUMO+1 (0.42)
4	S_0-S_1	3.70	335	365, 383	0.52	HOMO to LUMO (0.70)
5	S_0-S_1	3.26	380	390, 410	0.60	HOMO to LUMO (0.70)
	S_0-S_6	4.70	263	263	0.36	HOMO-3 to LUMO (0.54)
5_1	S_0-S_1	3.73	332		0.43	HOMO to LUMO (0.68)
	S_0-S_8	5.06	245		0.34	HOMO to LUMO+1 (0.56)
6	S_0-S_1	3.22	385	392, 412	0.58	HOMO to LUMO (0.70)
	S_0-S_{12}	5.2	238	254	0.56	HOMO-1 to LUMO+1 (0.55)
6_1	S_0-S_1	3.74	331		0.45	HOMO to LUMO (0.68)
	S_0-S_{10}	5.04	246		0.38	HOMO to LUMO+1 (0.62)
7	S_0-S_1	3.25	381	390, 412	0.56	HOMO to LUMO (0.70)
	S_0-S_6	4.90	253	256	0.38	HOMO-3 to LUMO (0.50)
8	S_0-S_1	3.22	385	391, 412	0.58	HOMO to LUMO (0.70)
	S_0-S_8	5.15	241	268	0.43	HOMO to LUMO+3 (0.51)
8_1	S_0-S_1	3.66	338		0.36	HOMO to LUMO (0.66)
	S_0-S_{10}	4.96	250		0.31	HOMO to LUMO+1 (0.52)
9	S_0-S_1	2.95	420	392, 413	0.0001	HOMO to LUMO (0.70)
	S_0-S_2	3.26	381	261	0.64	HOMO-1 to LUMO (0.69)
9_1	S_0-S_1	2.72	456		0.0093	HOMO to LUMO (0.70)
	S_0-S_2	3.71	333		0.5269	HOMO-1 to LUMO (0.69)



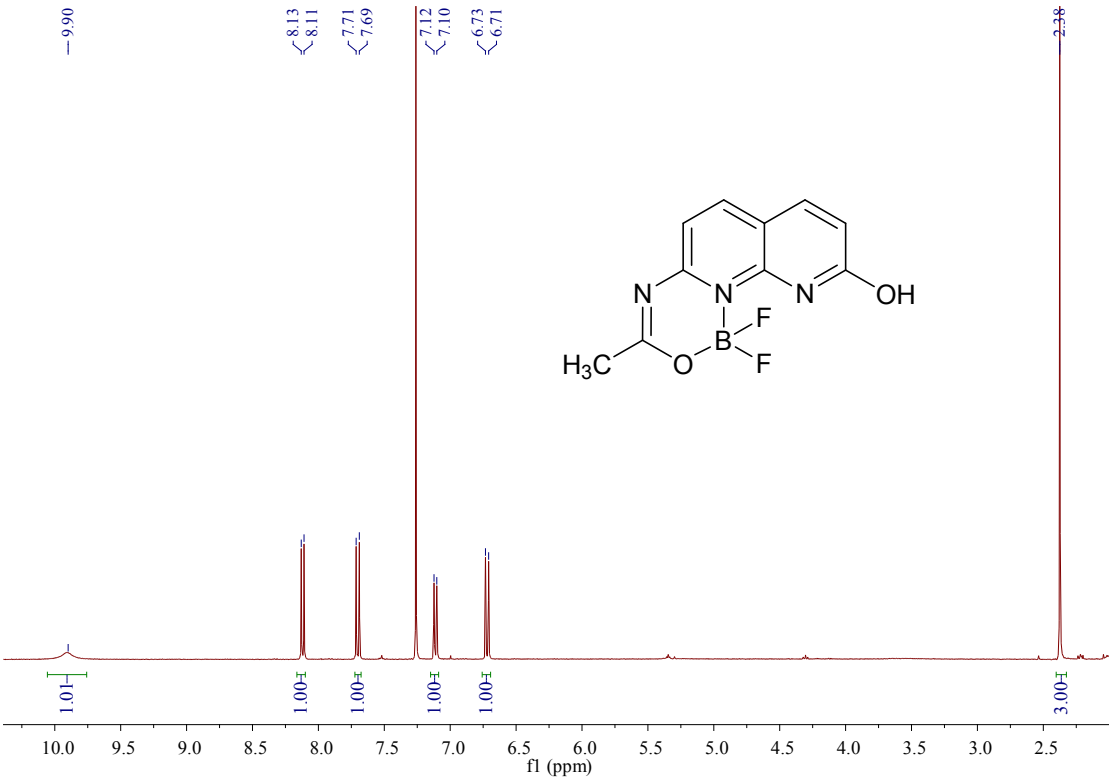
^{1}H NMR spectra of **1** in $CDCl_3$



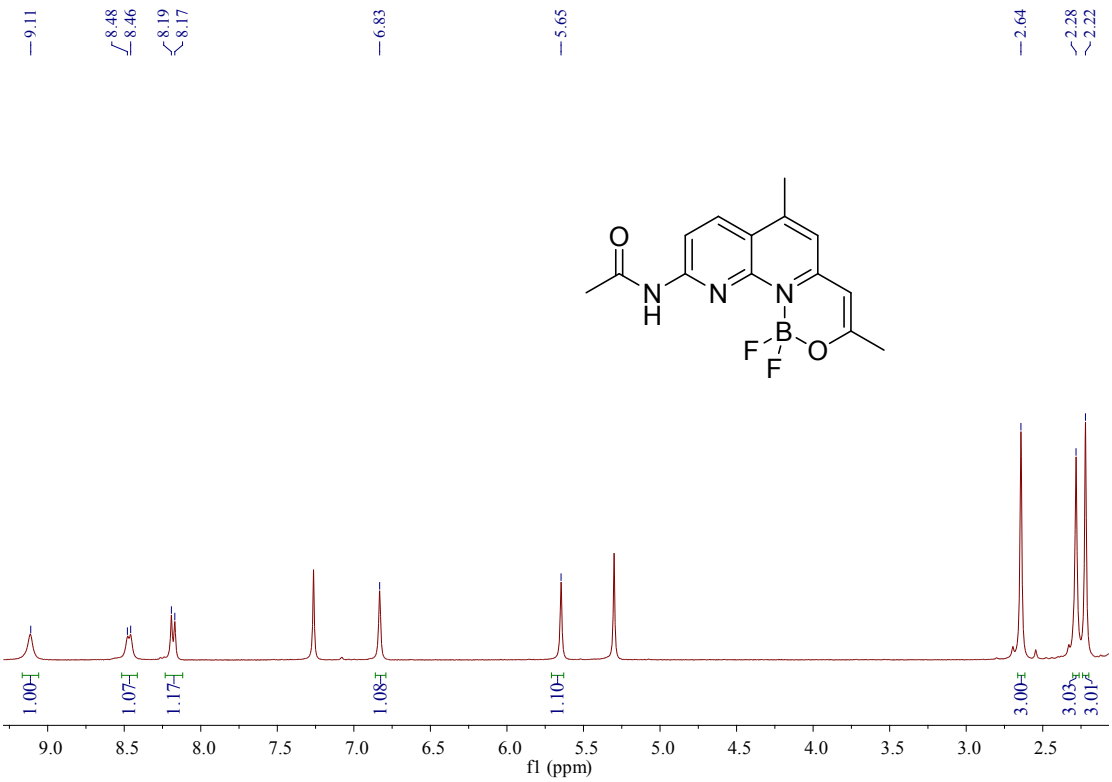
^{1}H NMR spectra of **2** in $CDCl_3$

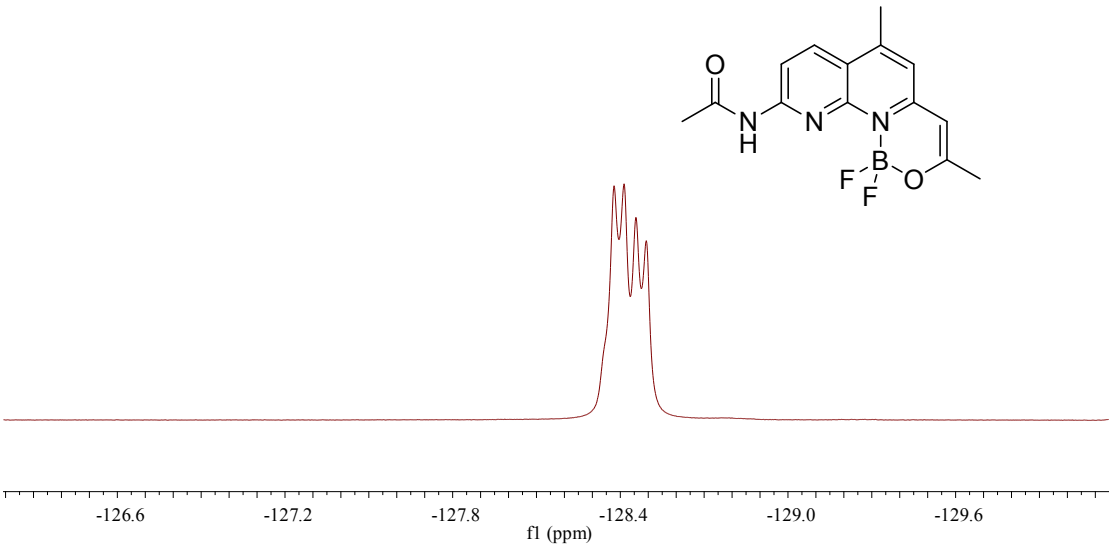


^{1}H NMR spectra of **3** in $CDCl_3$

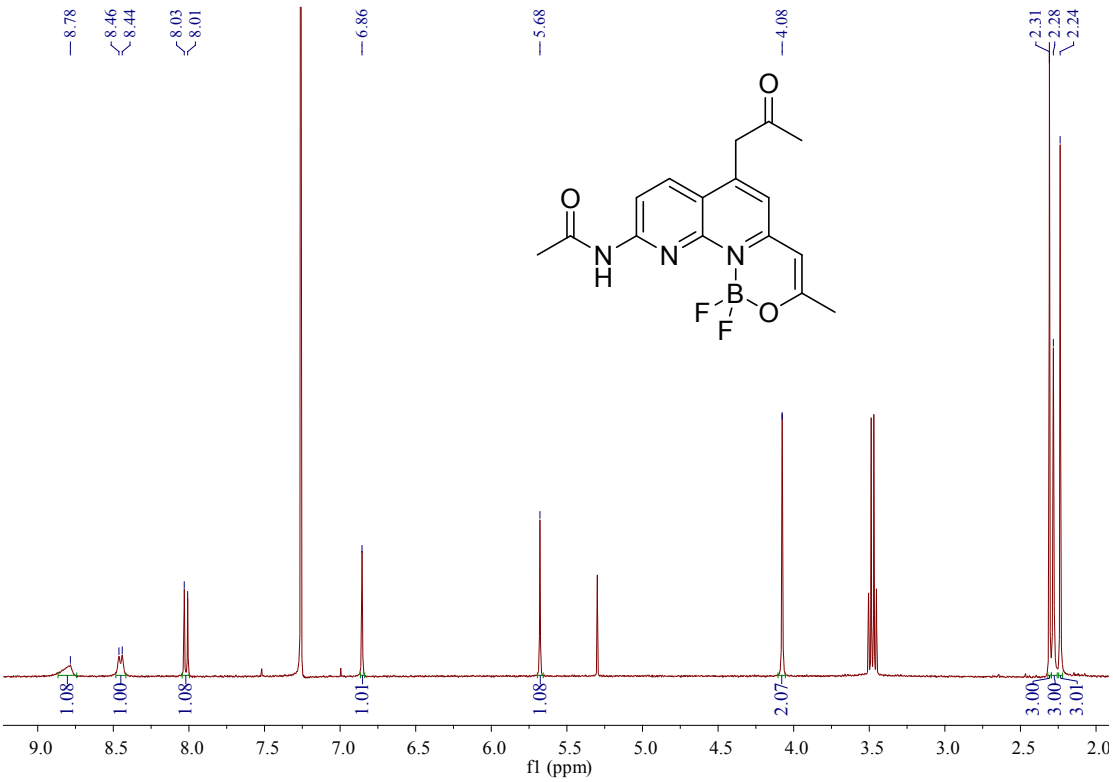


^{1}H NMR spectra of **4** in $CDCl_3$

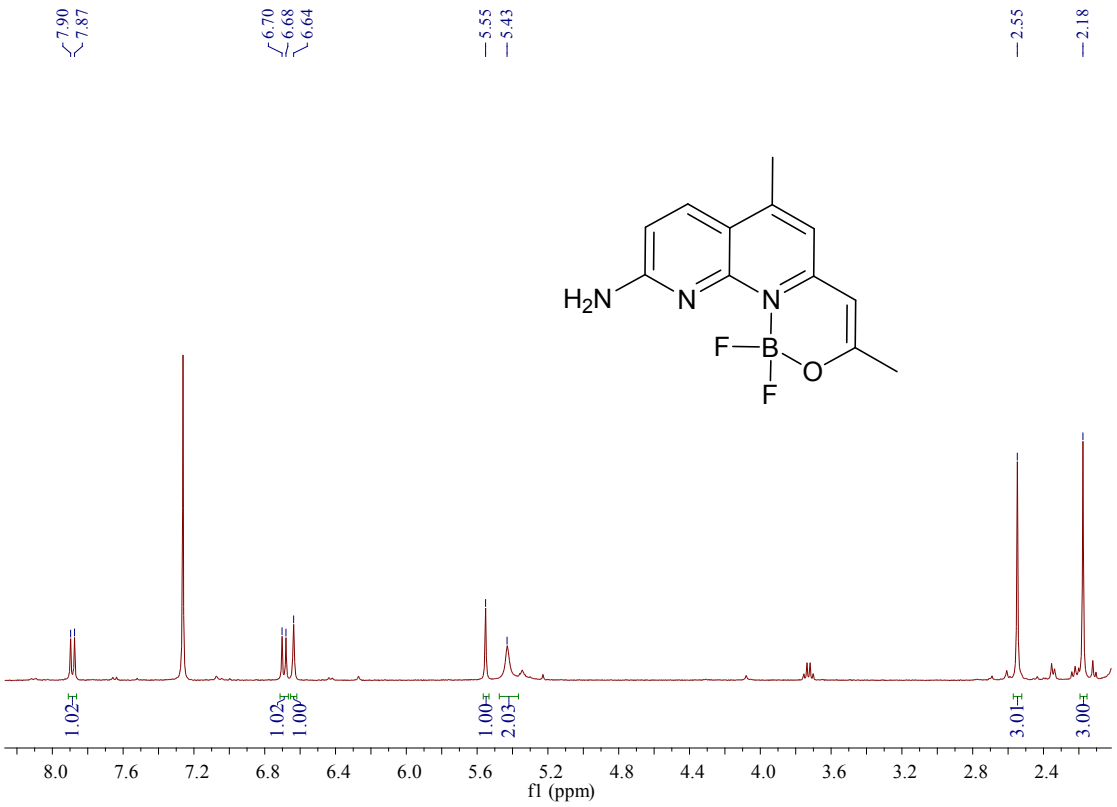


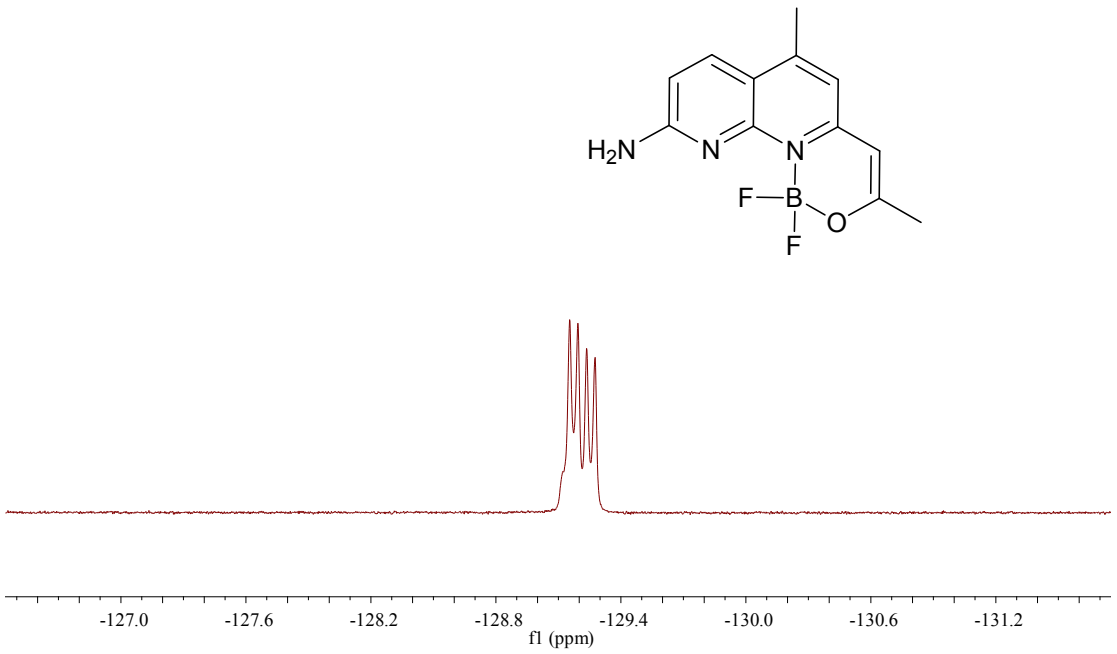


^{1}H, ^{19}F NMR spectra of **5** in $CDCl_3$

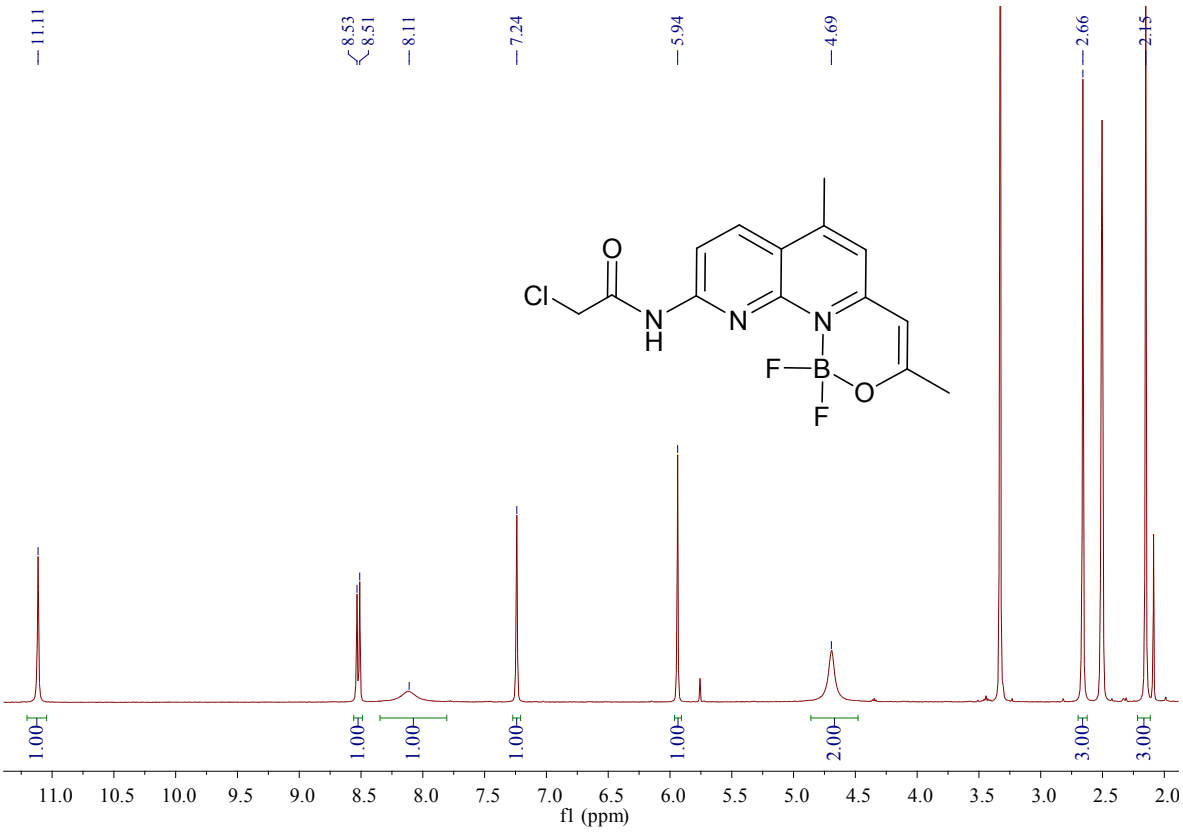


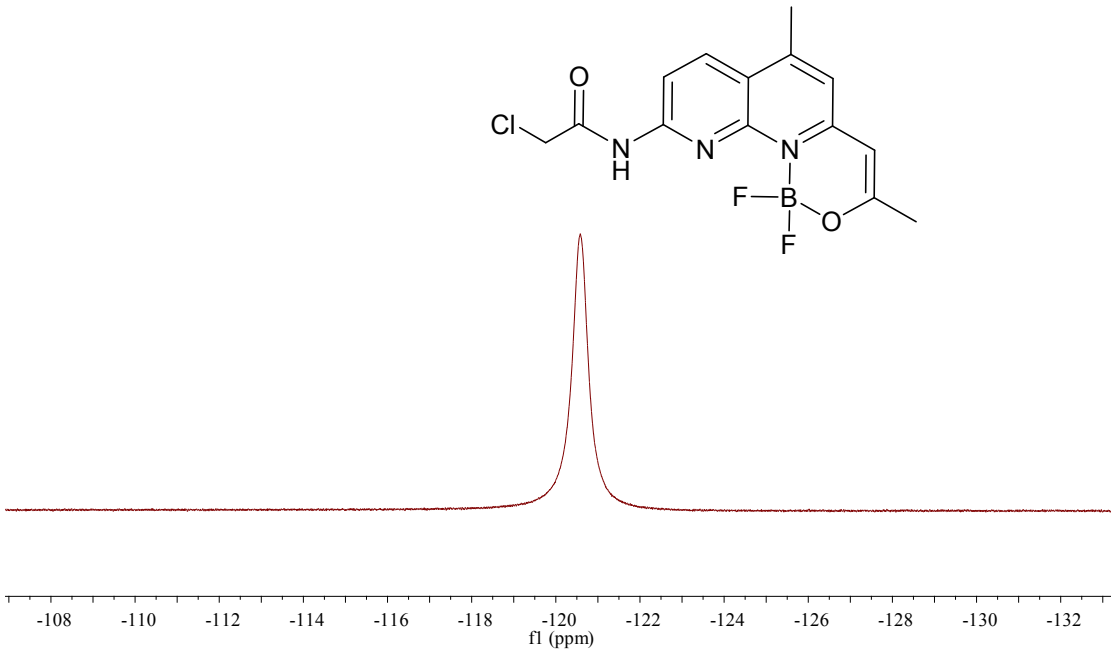
^{1}H NMR spectra of **6** in $CDCl_3$



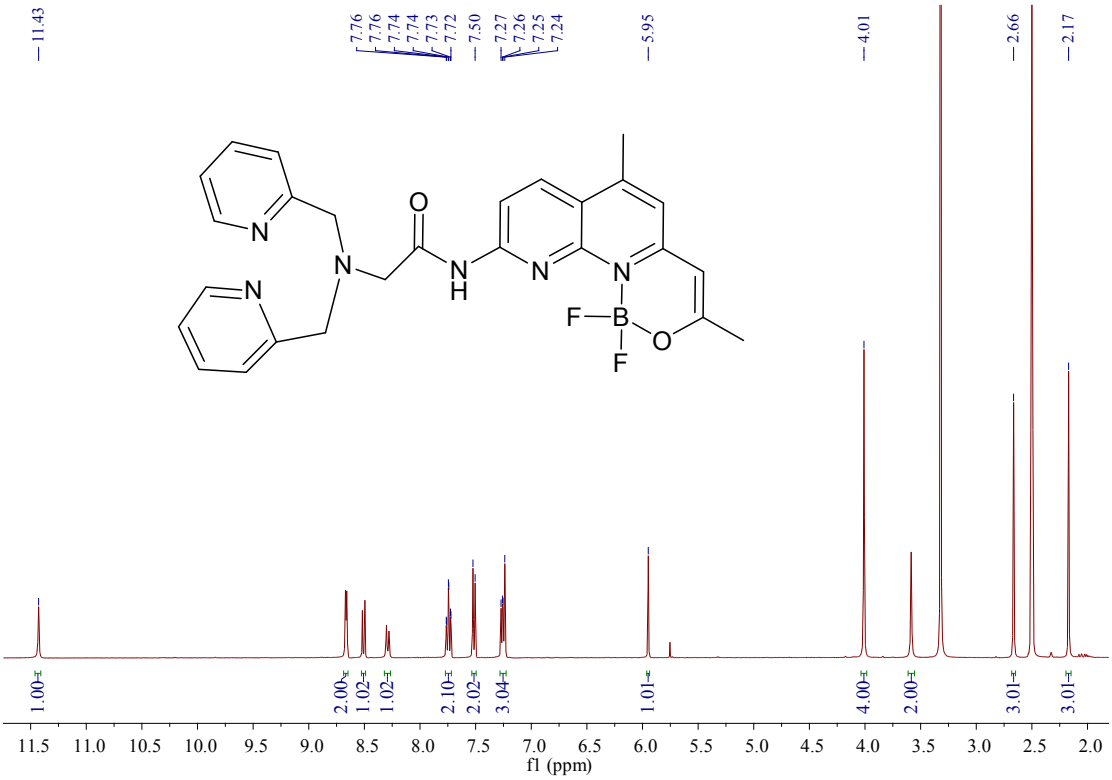


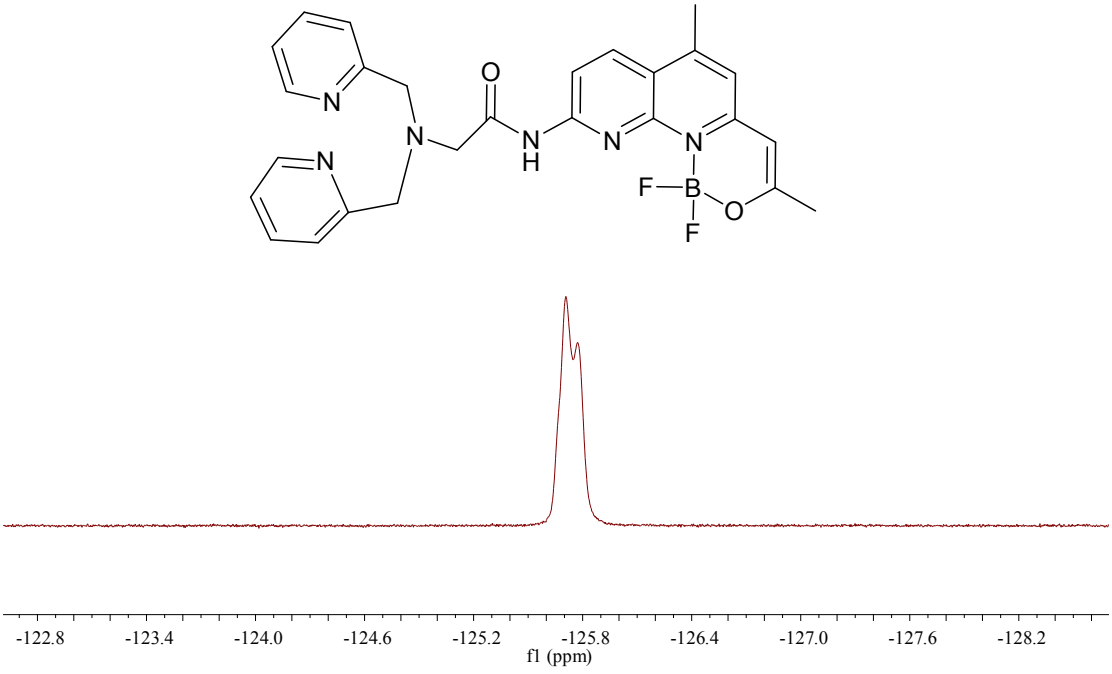
^{1}H, ^{19}F NMR spectra of **7** in $CDCl_3$





^{1}H, ^{19}F NMR spectra of **8** in DMSO-d_6





^{1}H, ^{19}F NMR spectra of **9** in DMSO-d_6