Electronic Supplementary Material (ESI) for Dalton Transactions.

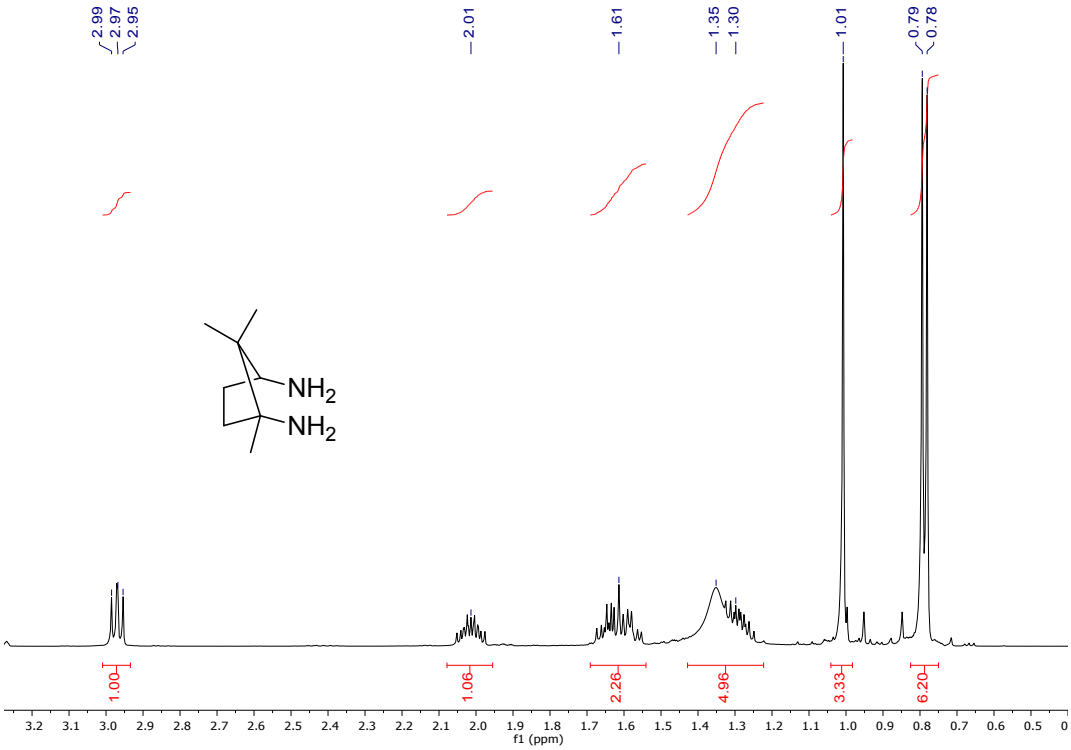
Chiral Carbene–Borane Adducts: Precursors for Borenium Catalysts for Asymmetric FLP Hydrogenations

Jolie Lam,[a] Benjamin A. R. Günther,[ab] Jeffrey M. Farrell,[a] Patrick Eisenberger,[c] Brian P. Bestvater,[c] Paul D. Newman,[b] Rebecca L. Melen,*[b] Cathleen M. Crudden,*[cd] Douglas W. Stephan*[a]*

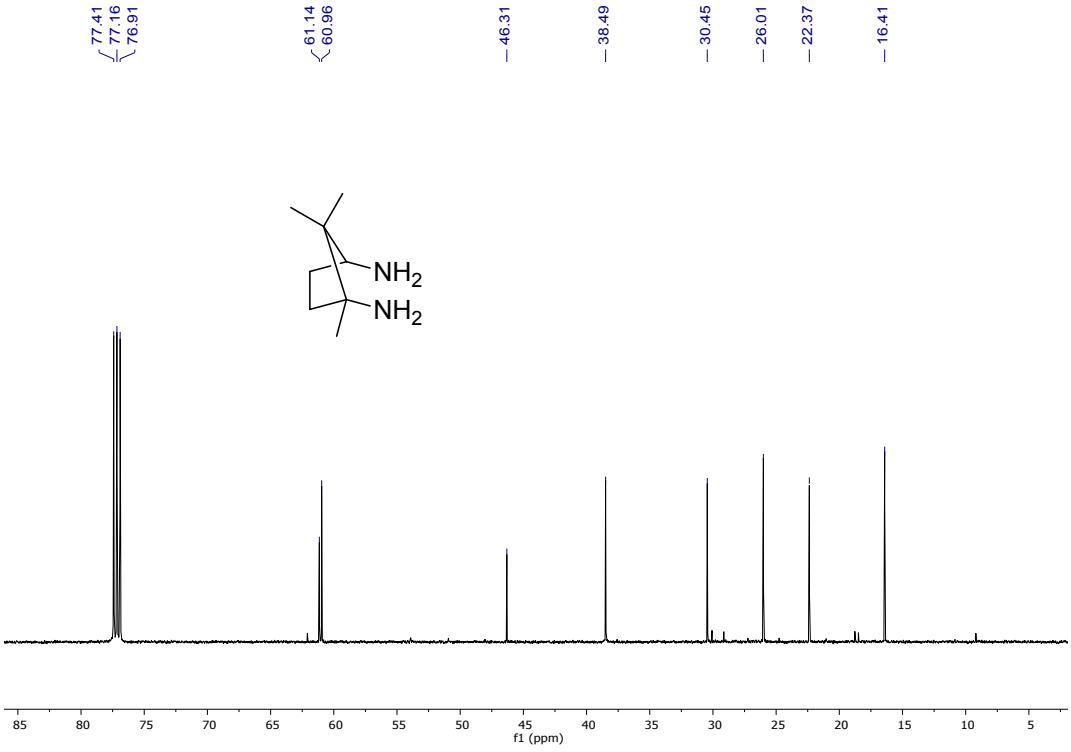
Supporting Information

Table of Contents

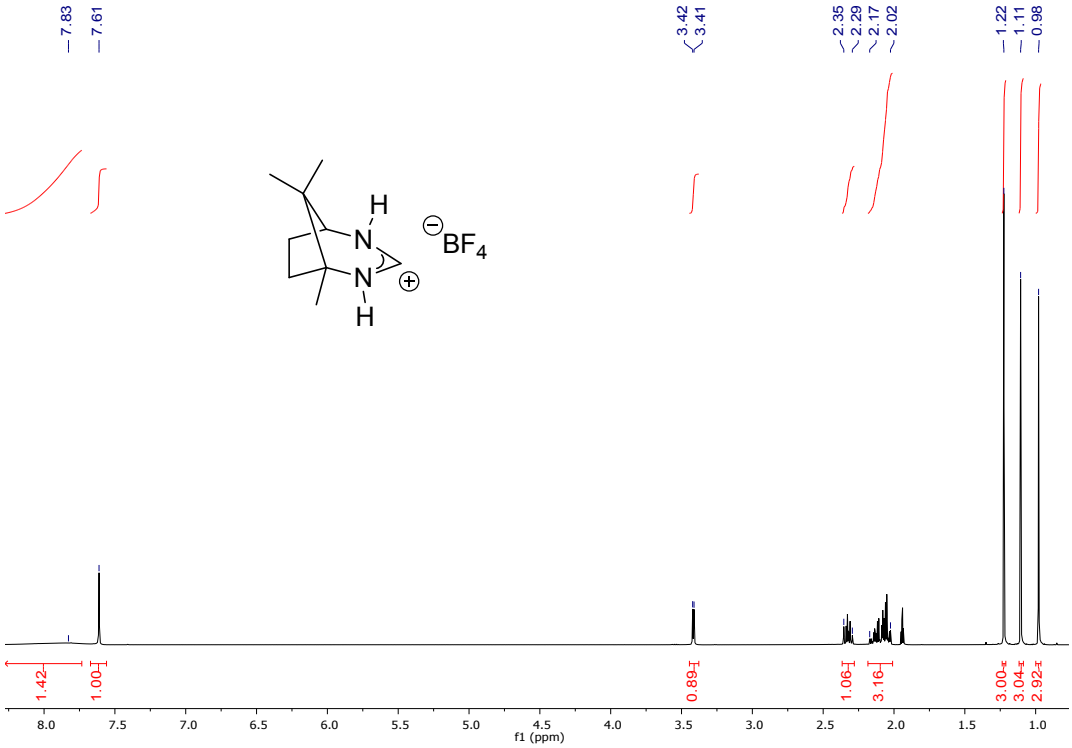
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **2**



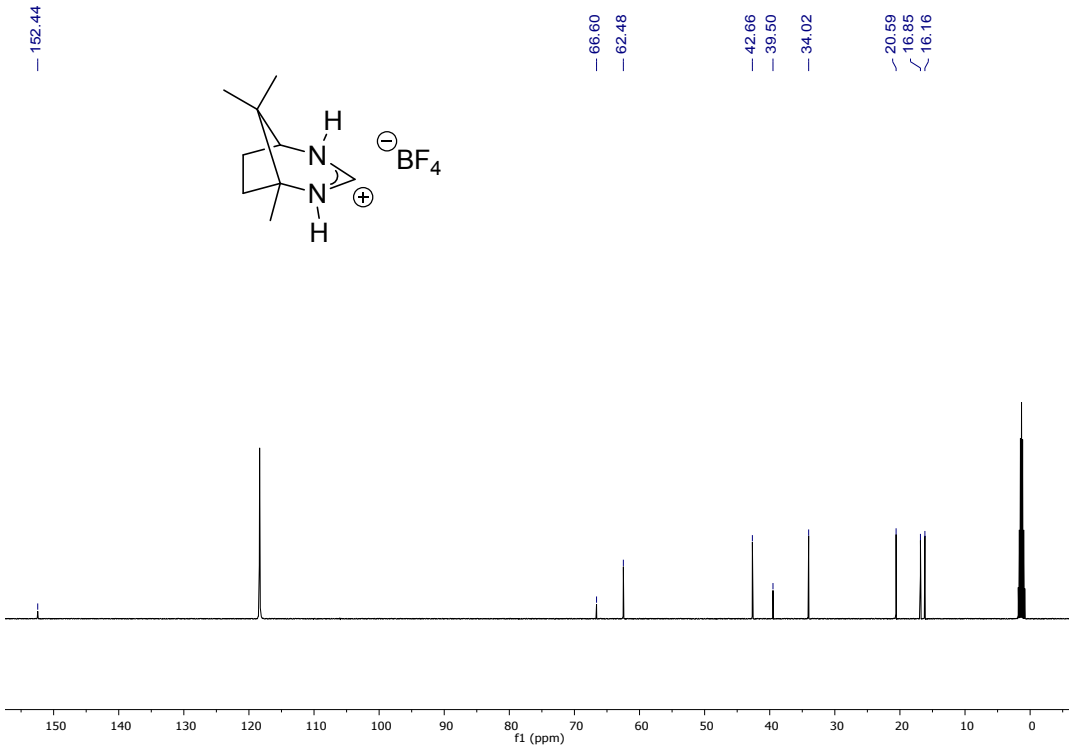
^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **2**



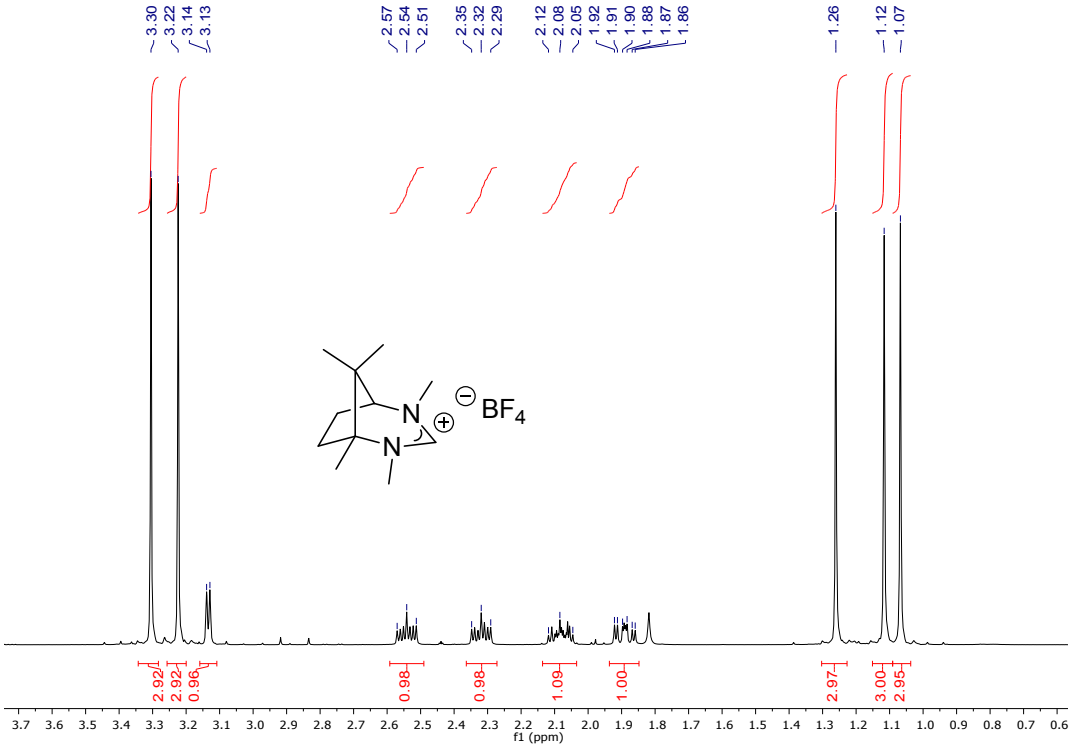
^{1}H NMR (500 MHz, CD_3CN, 298 K) spectrum of **3**



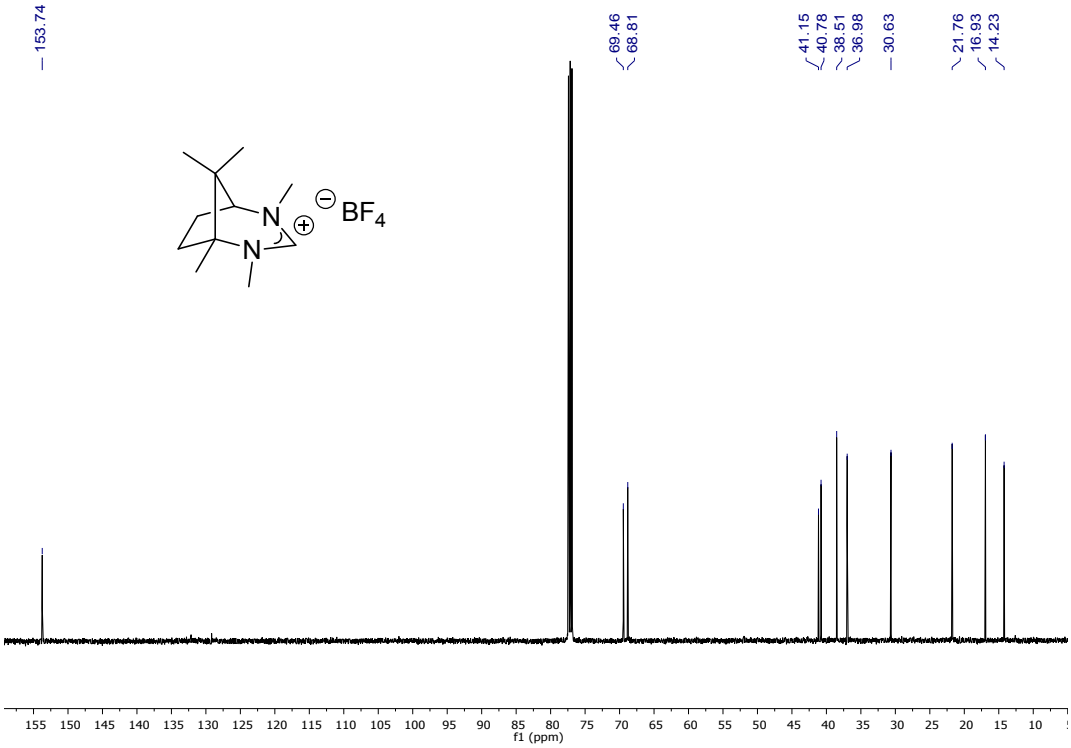
^{13}C NMR (126 MHz, CD_3CN, 298 K) spectrum of **3**



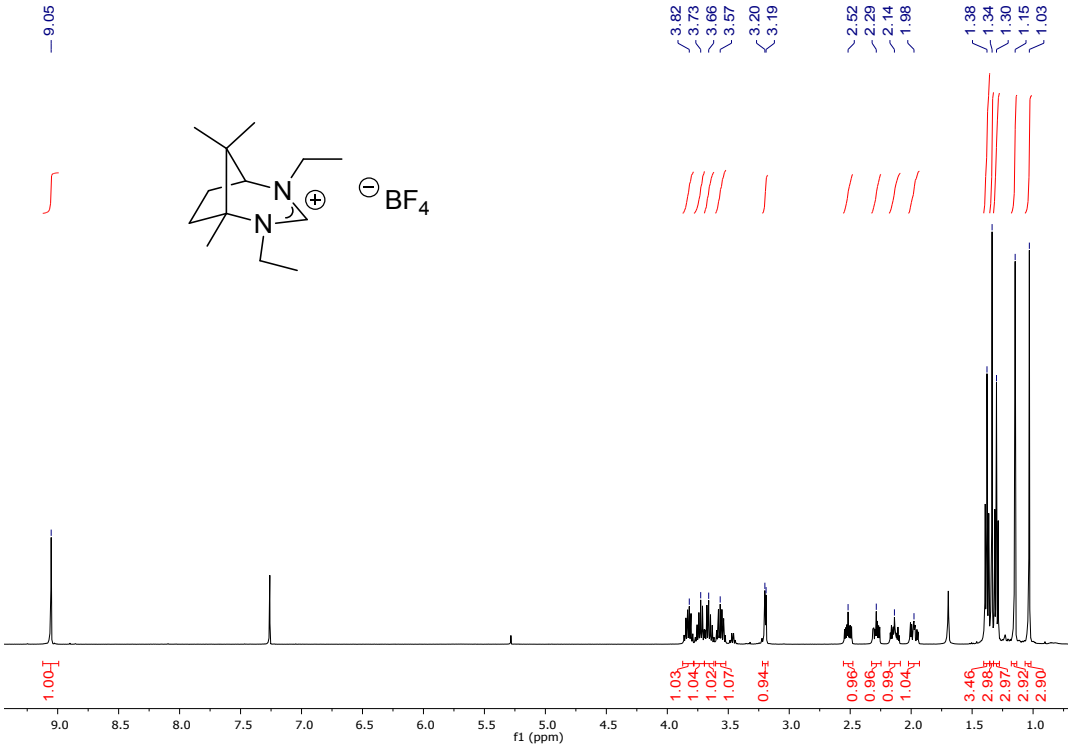
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **4**



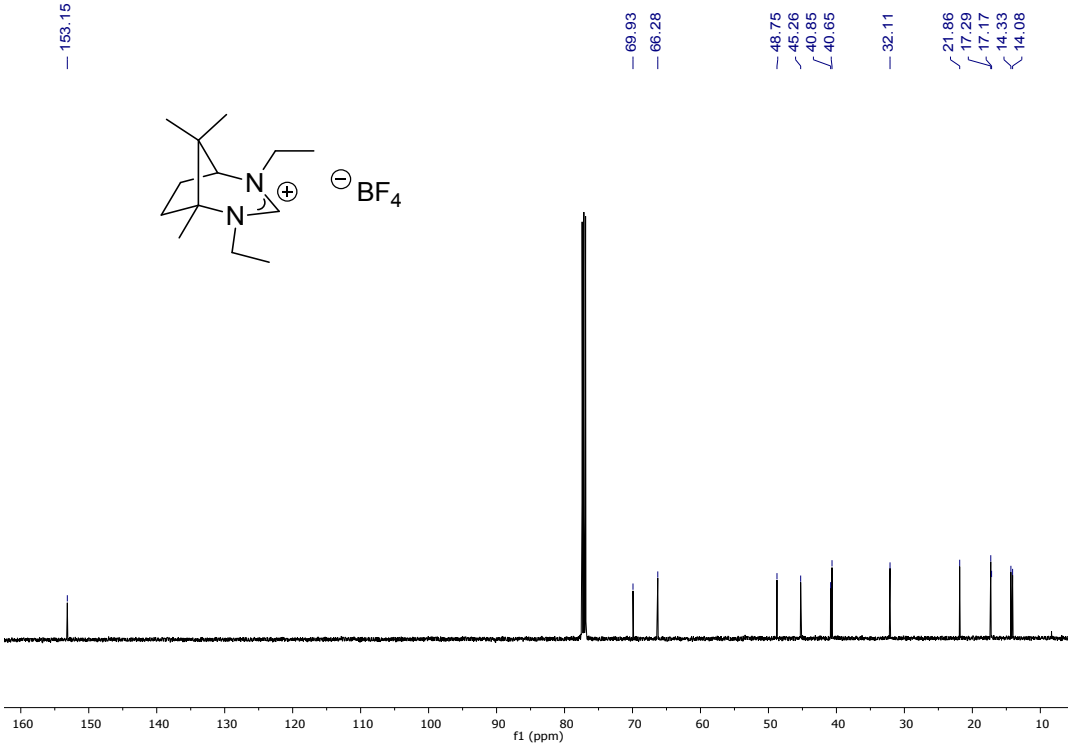
^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **4**



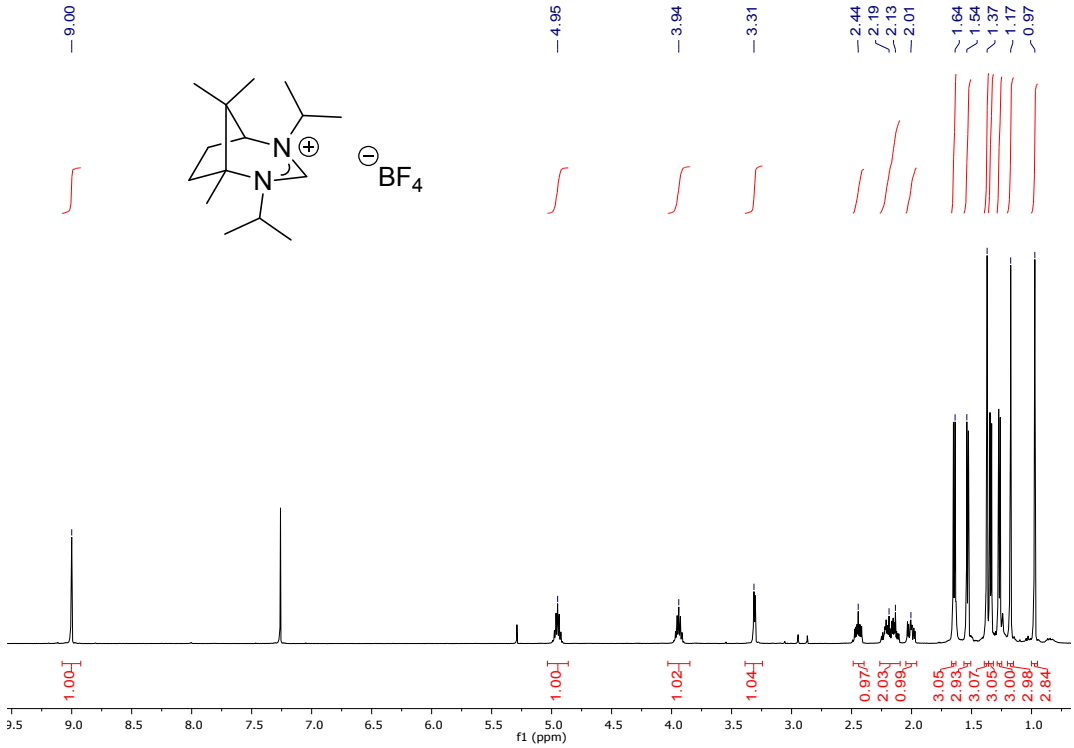
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **5**



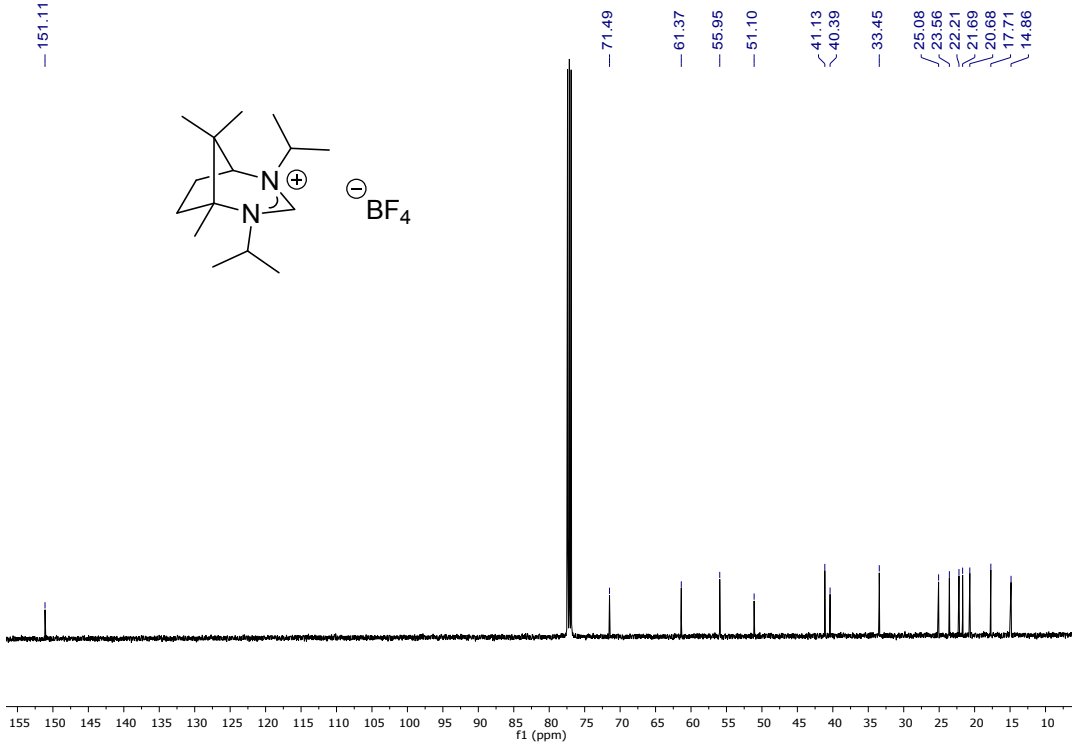
^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **5**



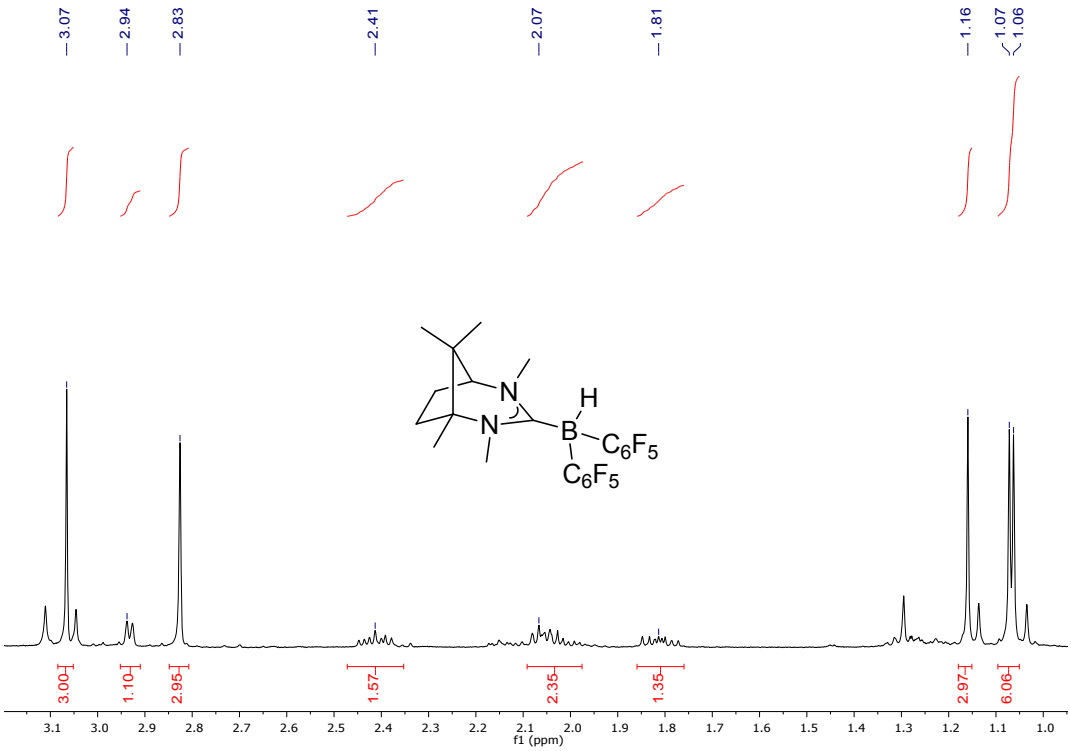
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **6**



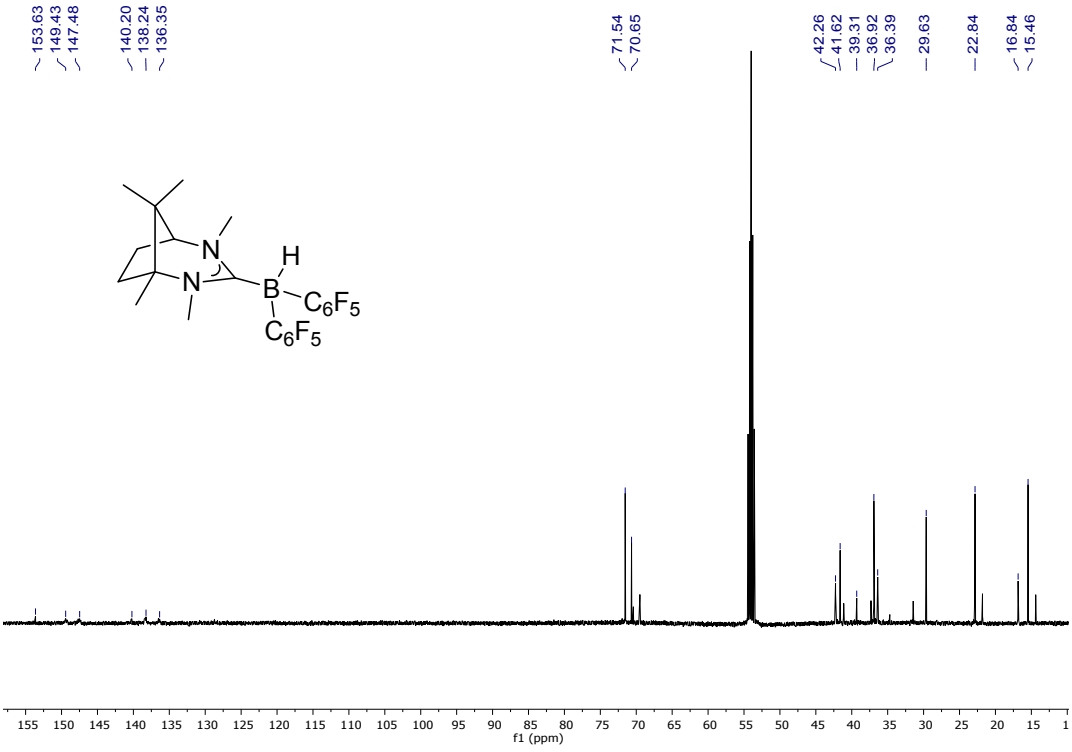
^{13}C NMR (126 MHz, CDCl3, 298 K) spectrum of **6**



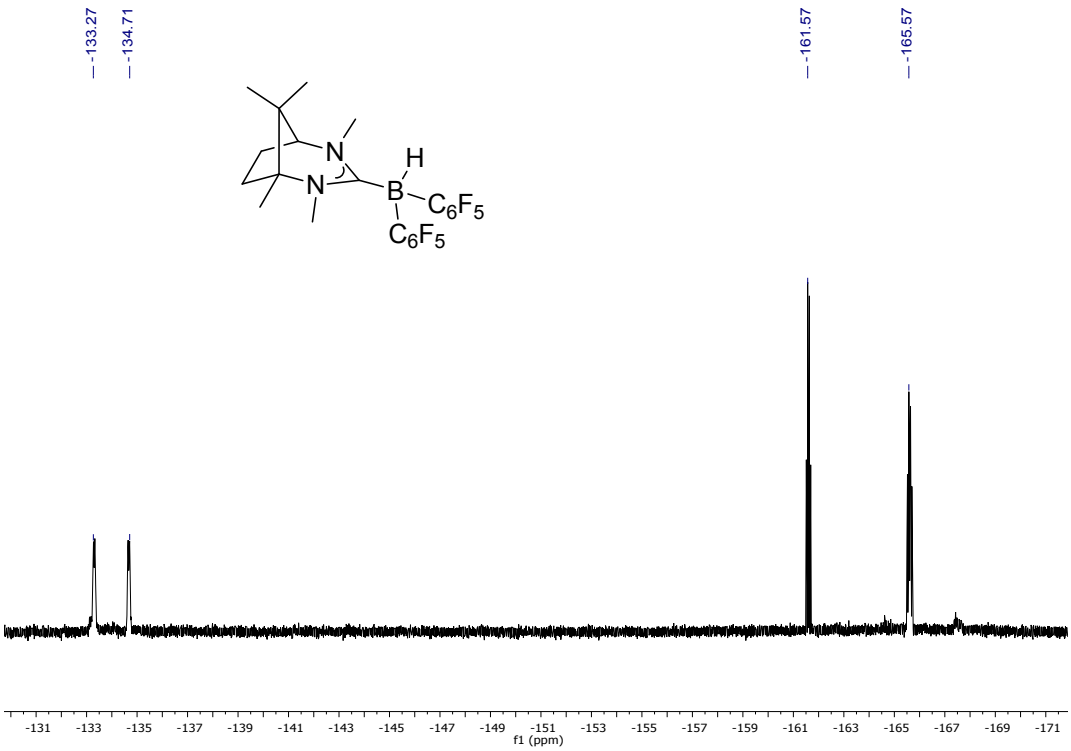
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of **7**



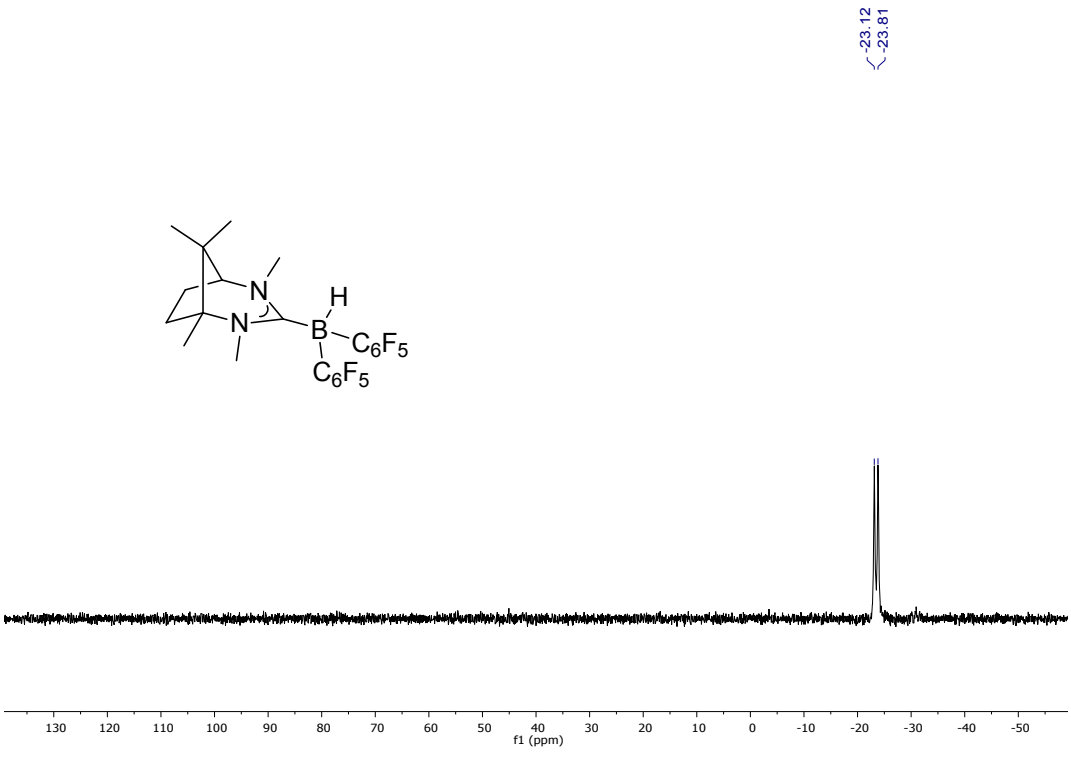
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **7**



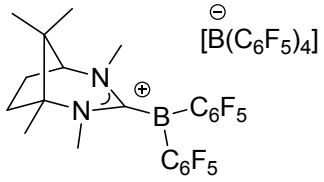
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of **7**

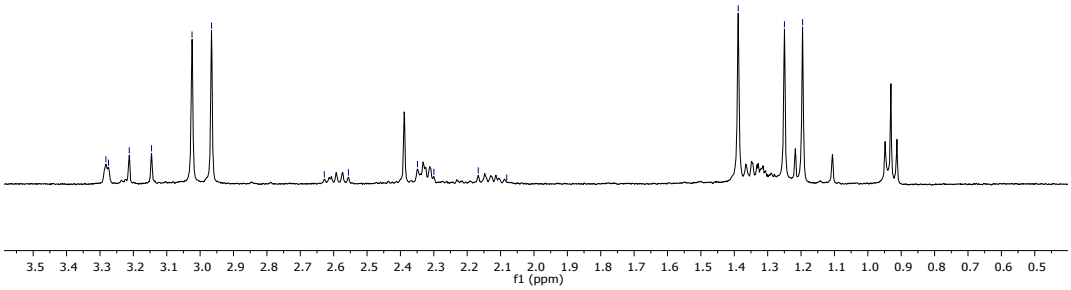


^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **7**

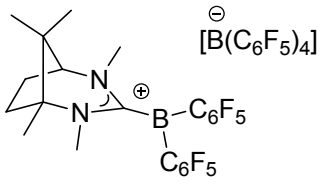


^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **8**

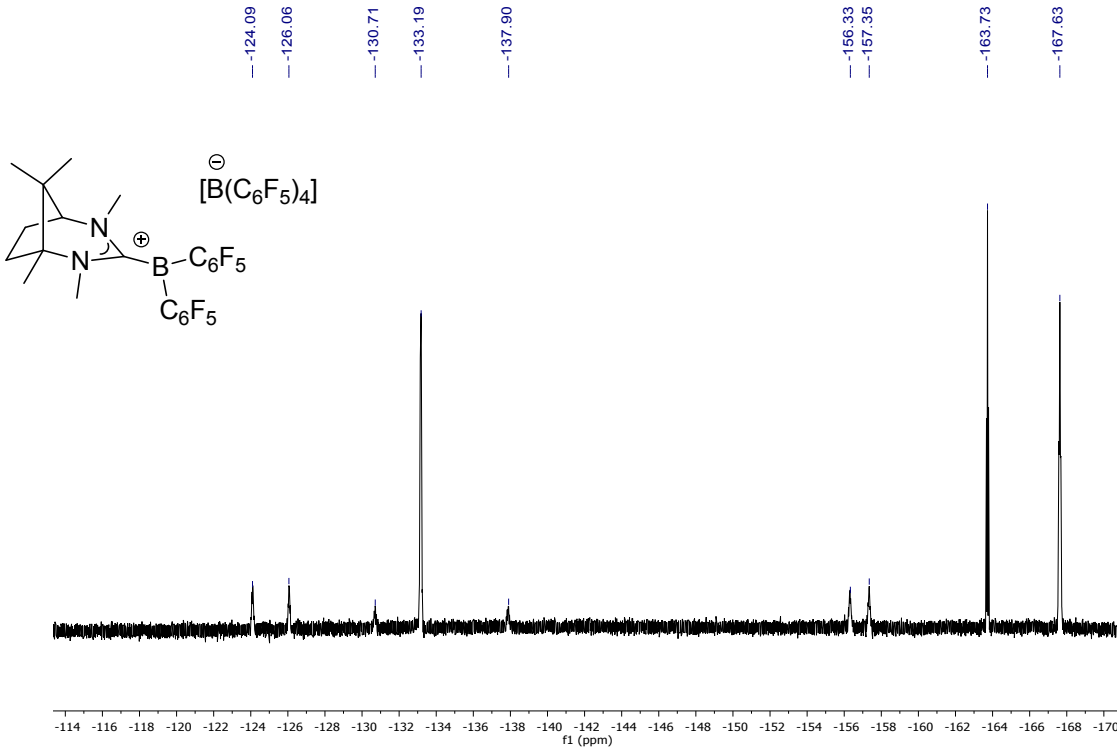




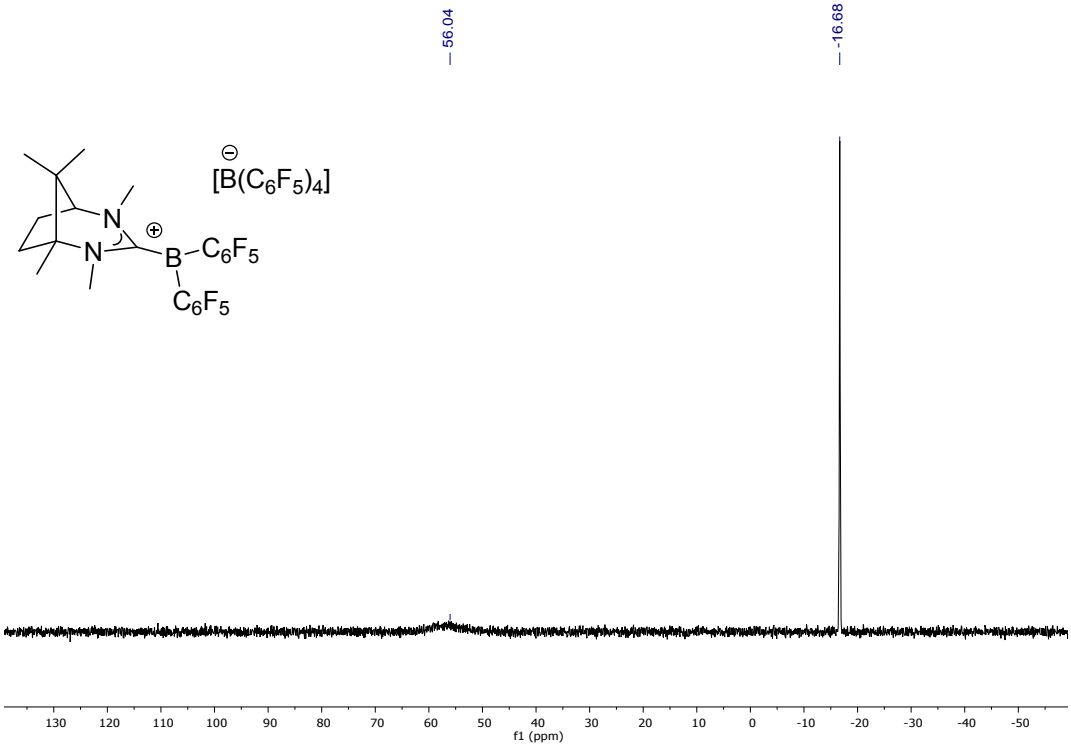
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **8**



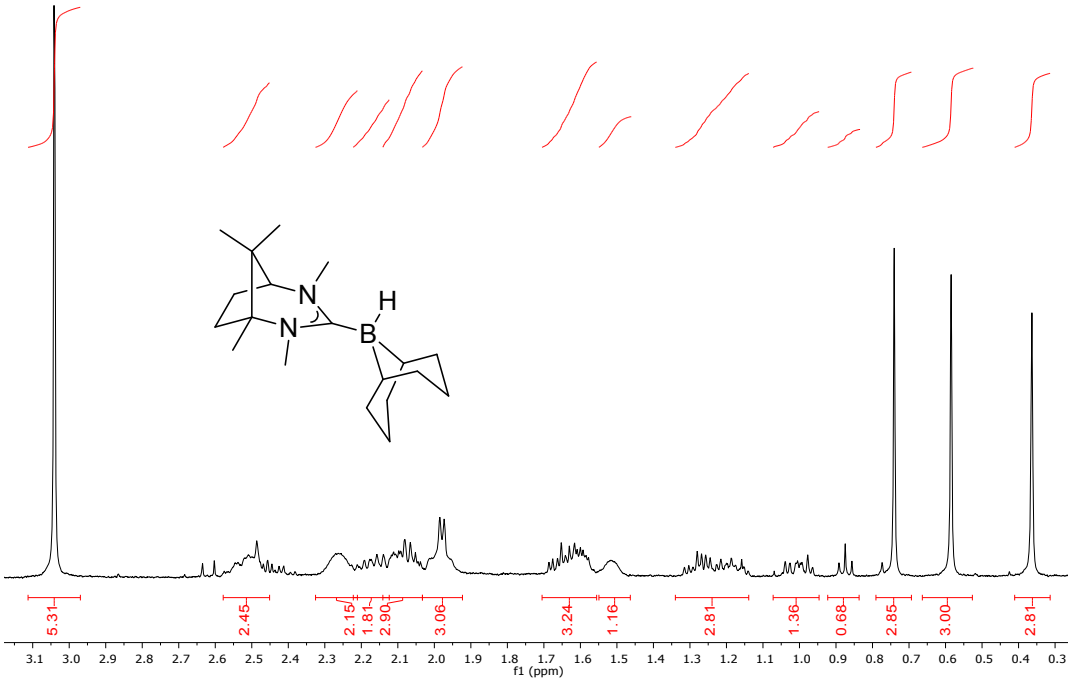
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of **8**



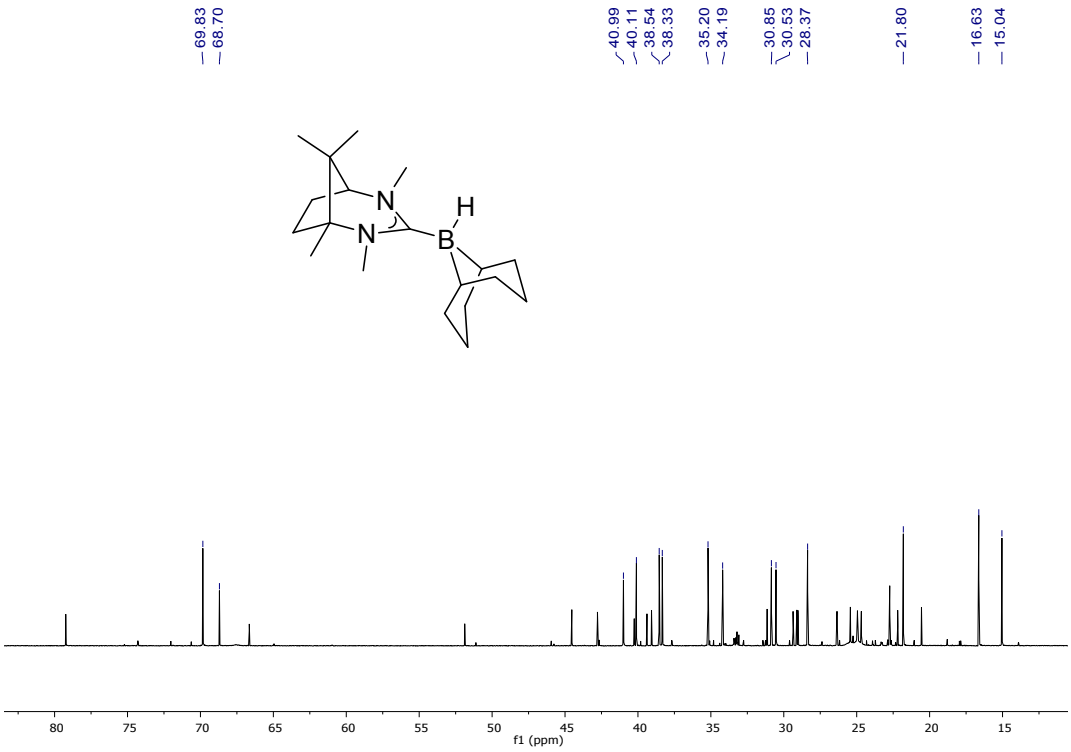
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **8**



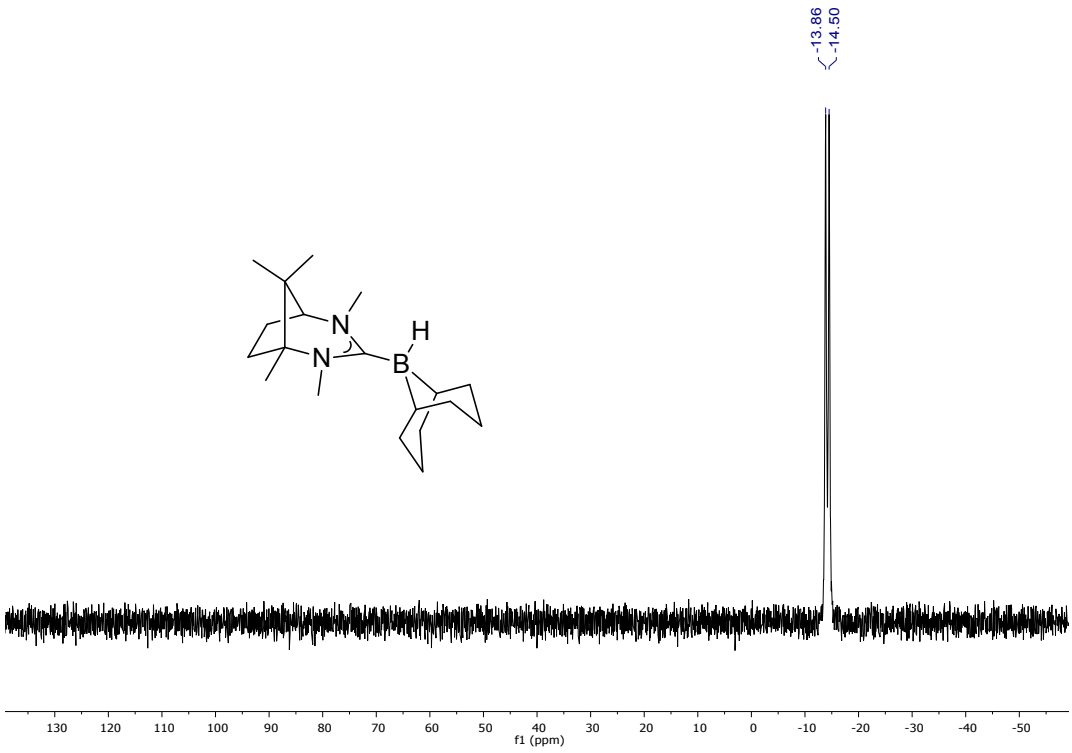
^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **9**



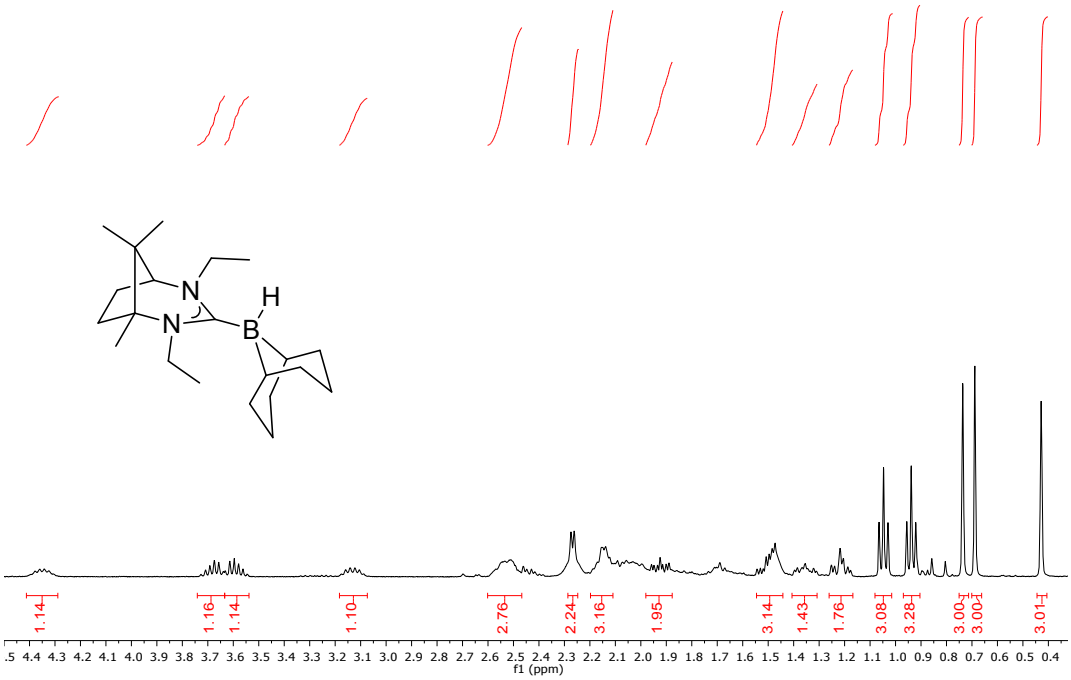
^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **9**



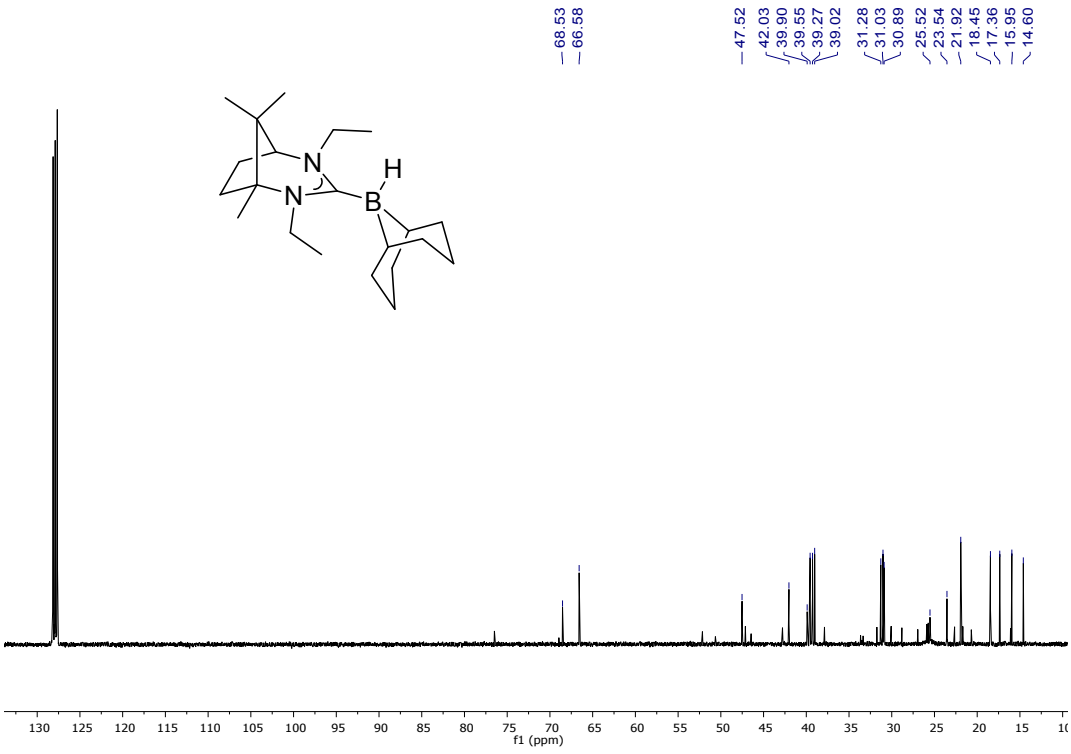
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **9**



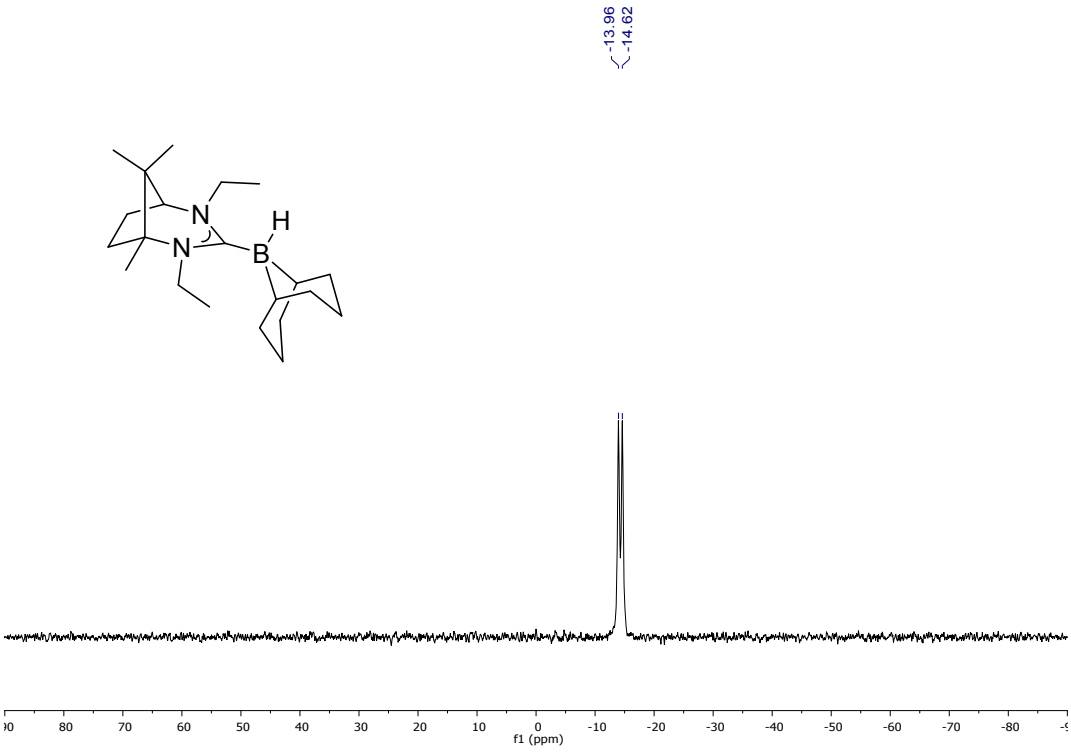
^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **10**



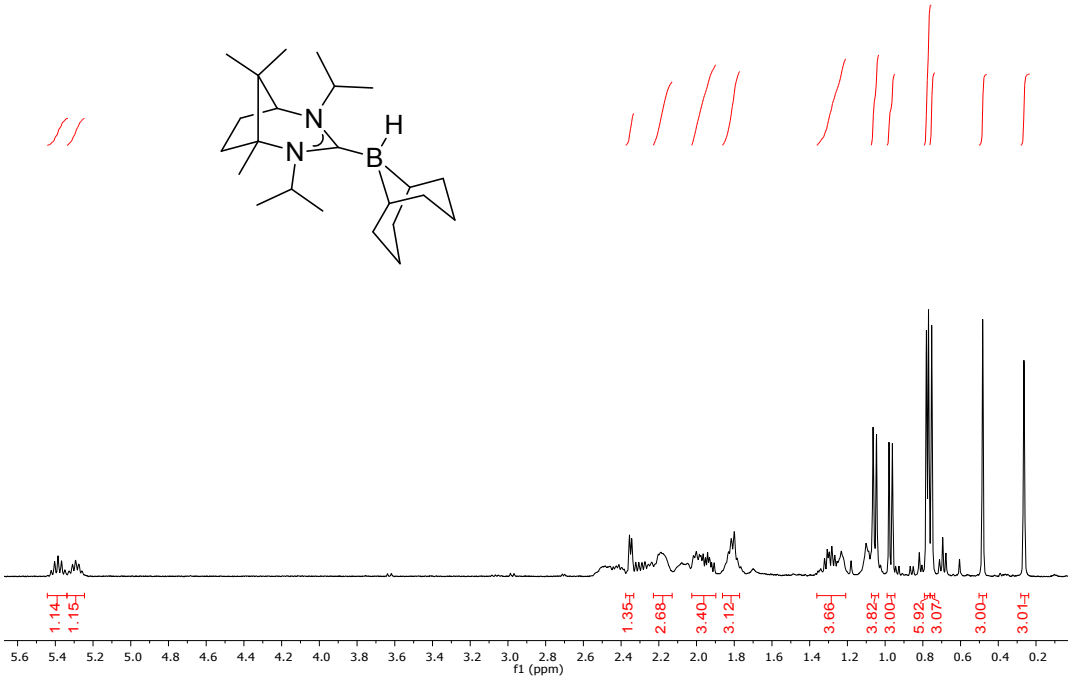
^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **10**



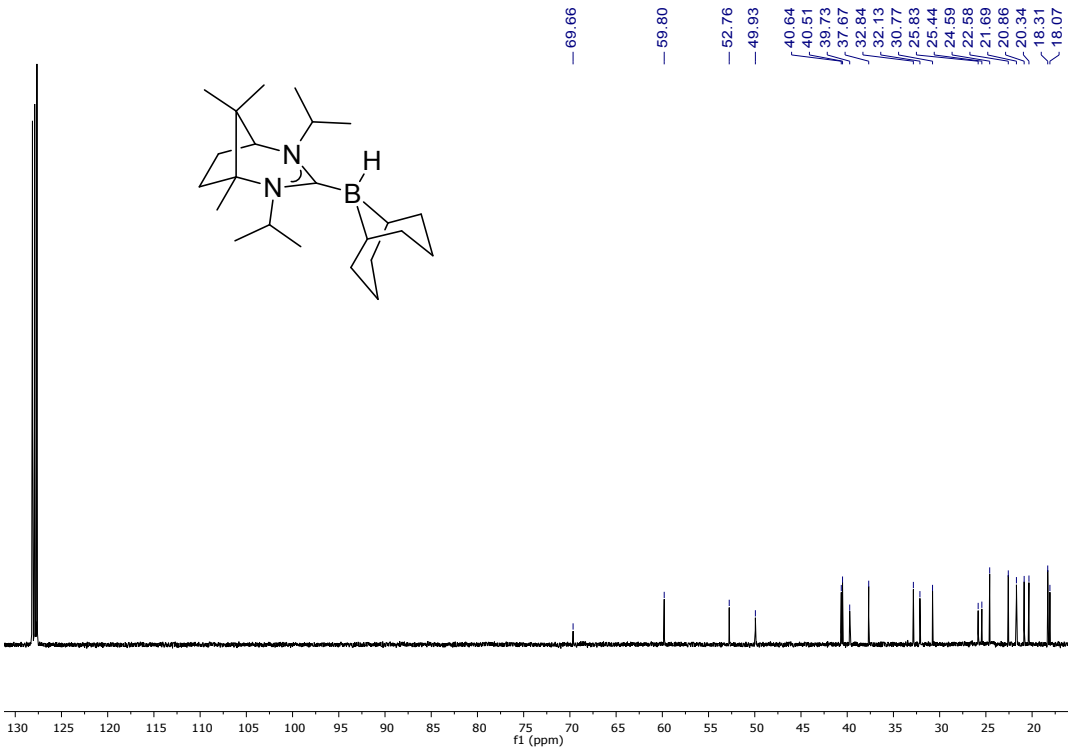
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **10**



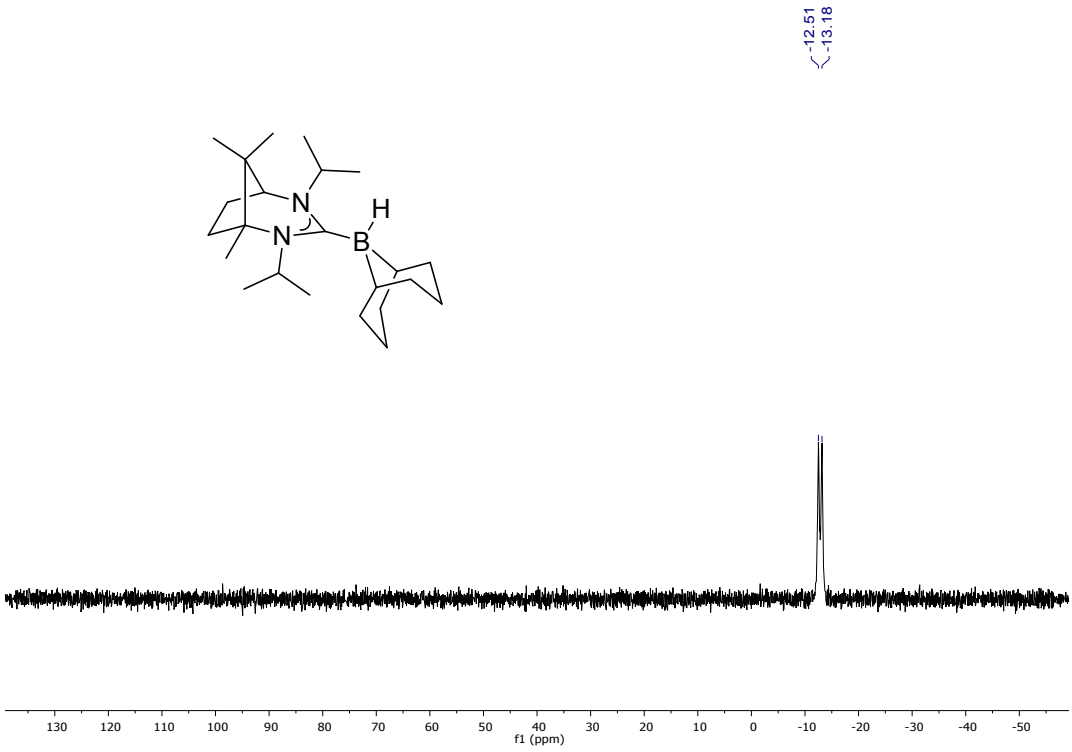
^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **11**



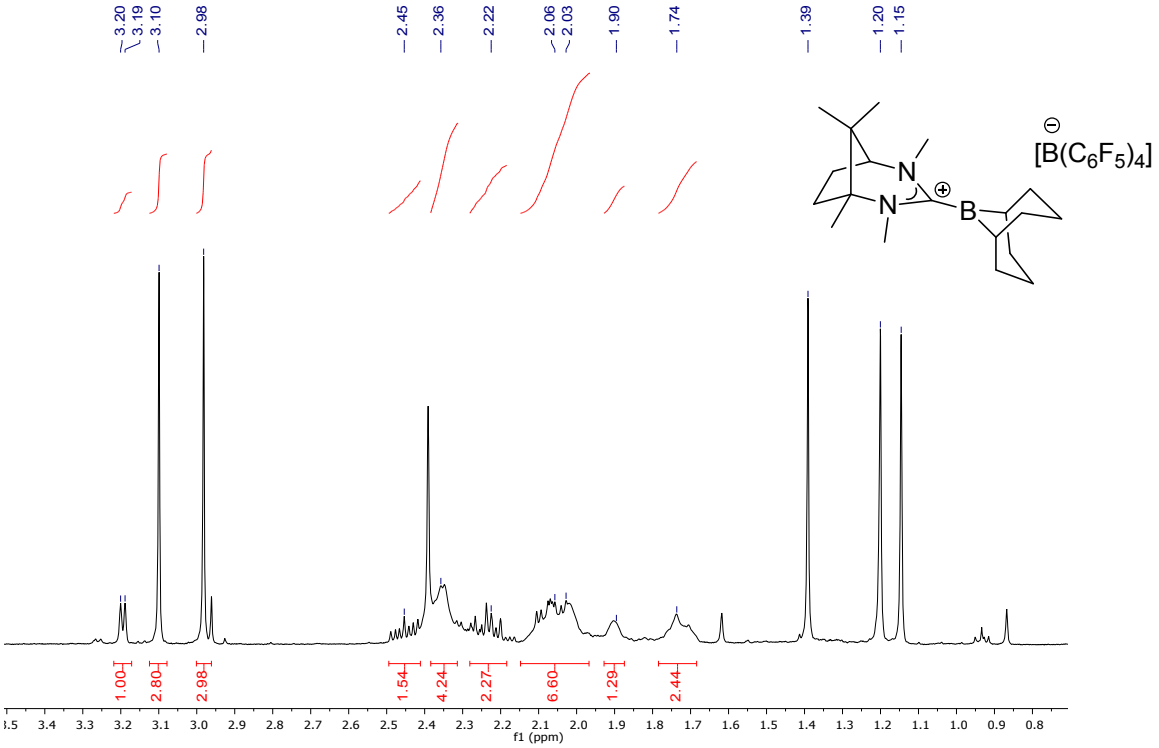
^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **11**



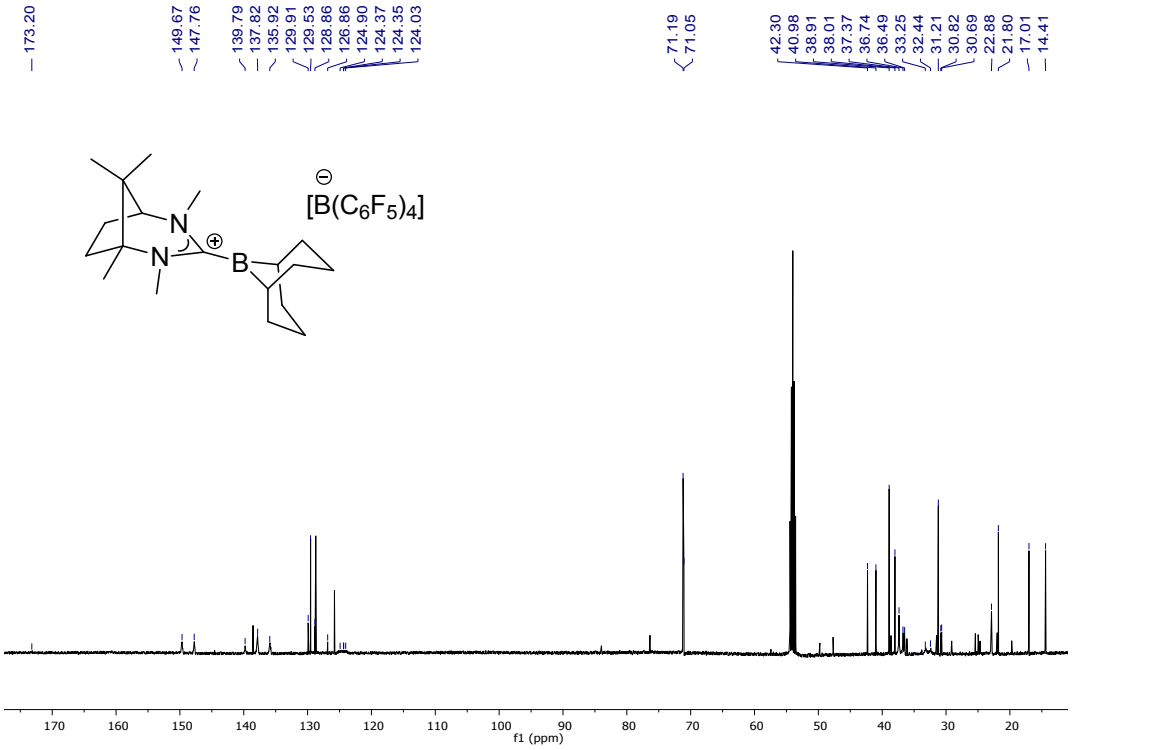
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **11**



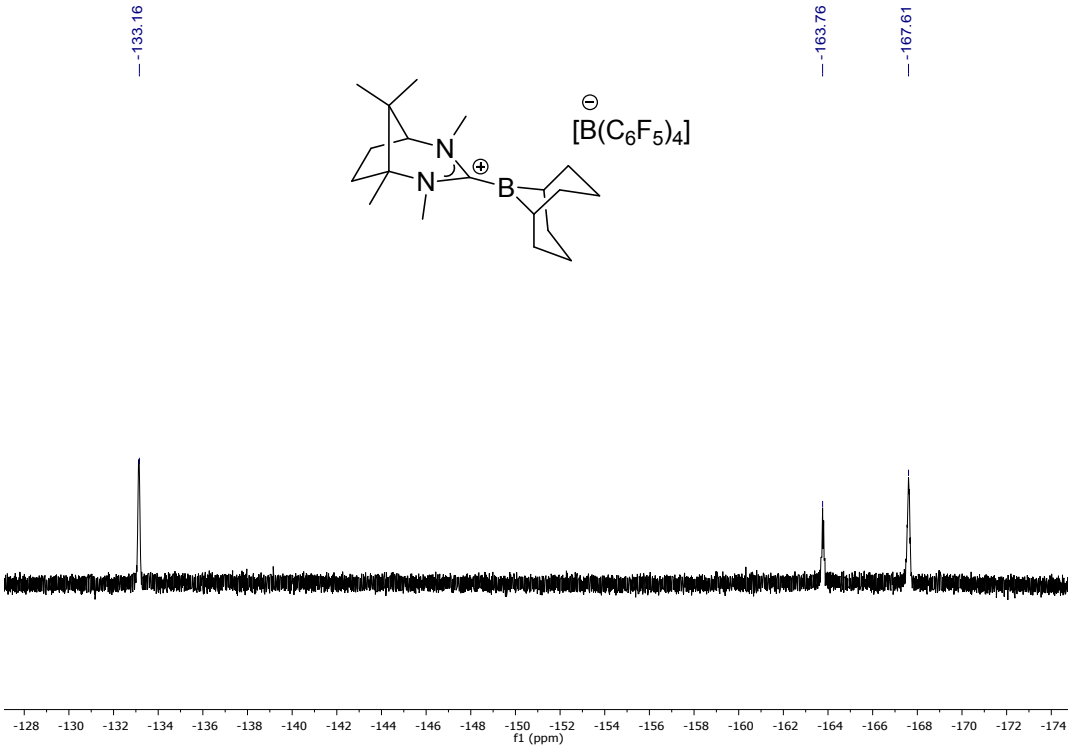
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **12**



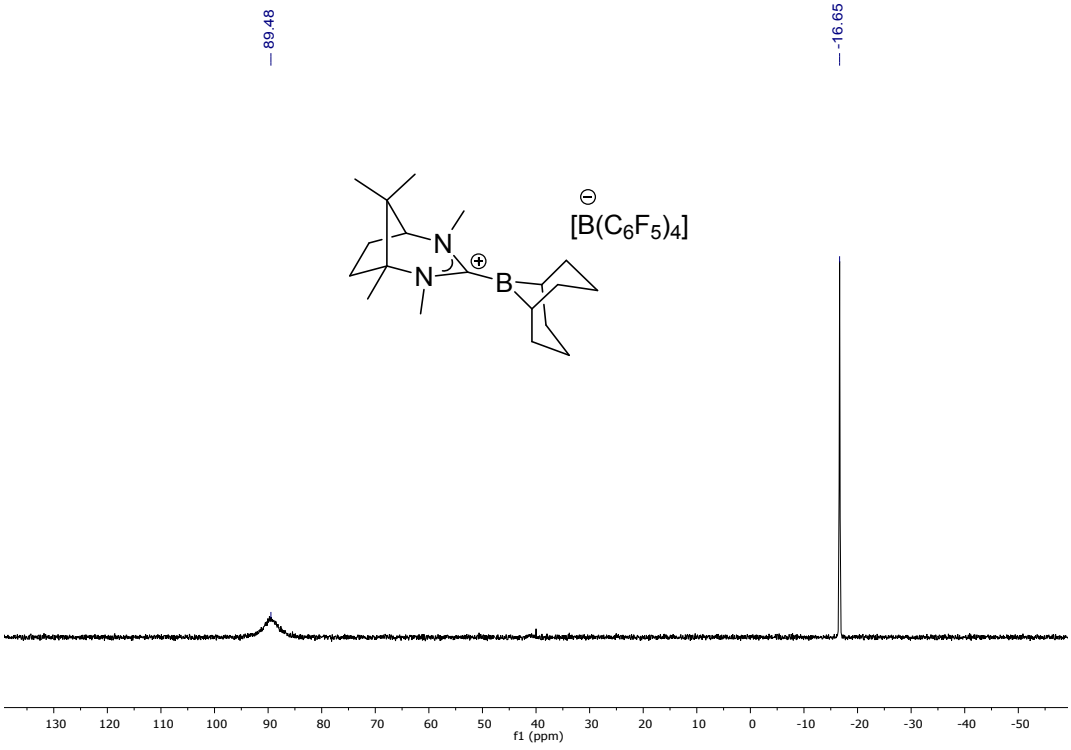
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **12**



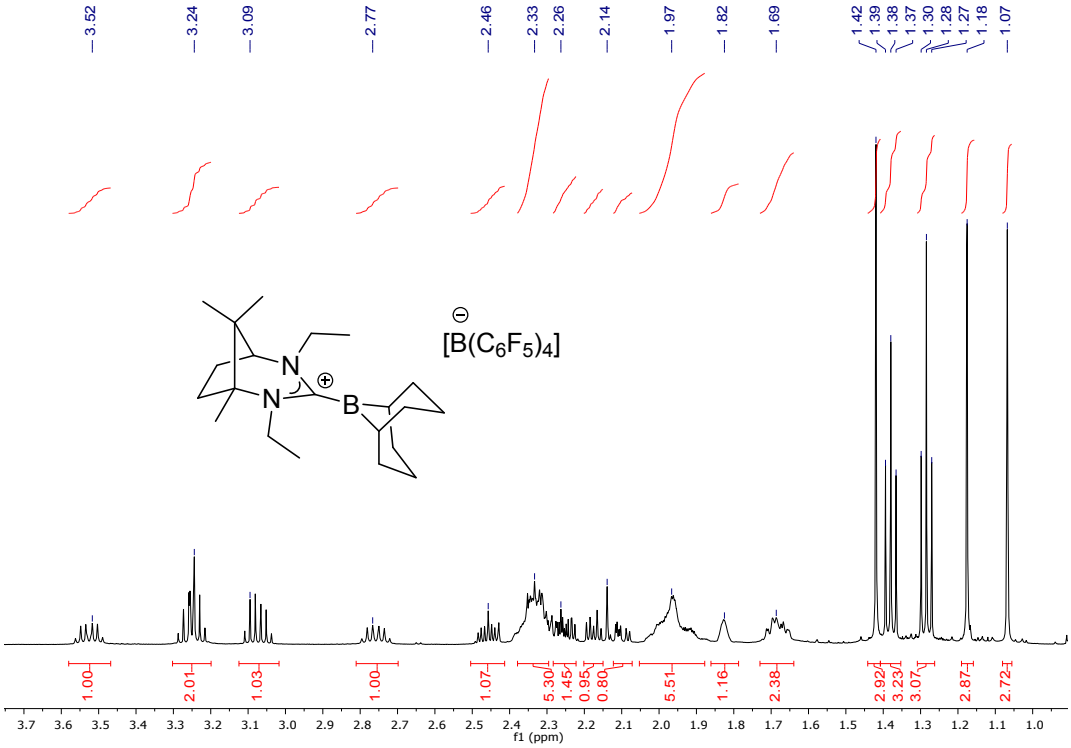
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of **12**



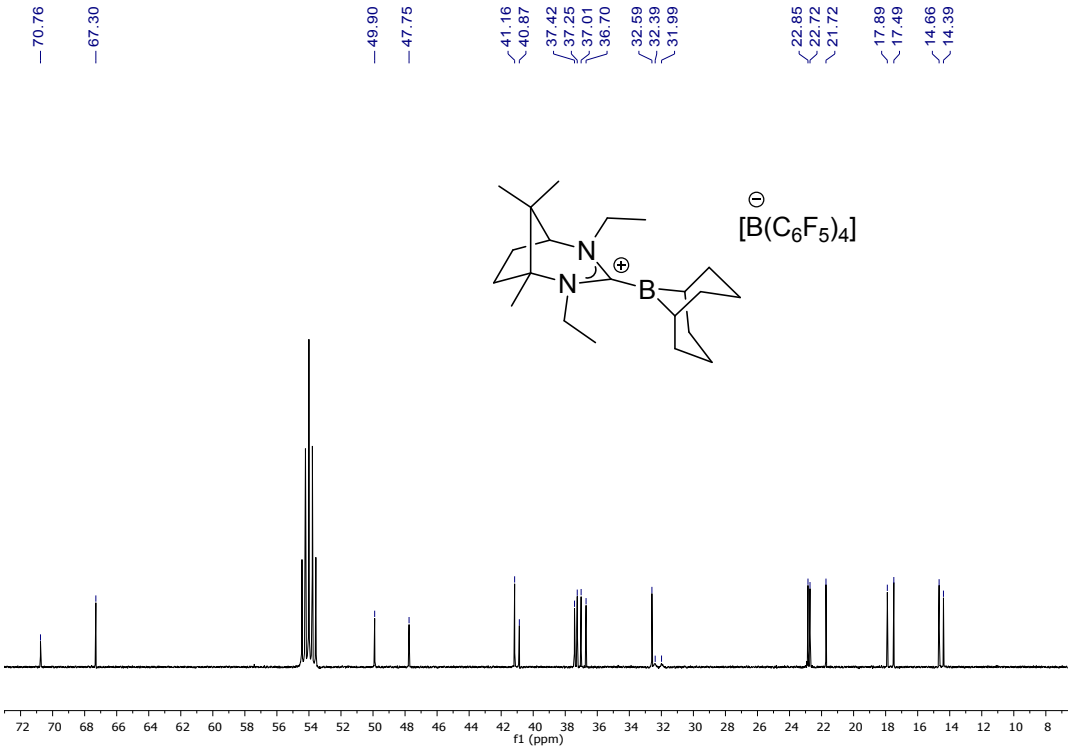
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **12**



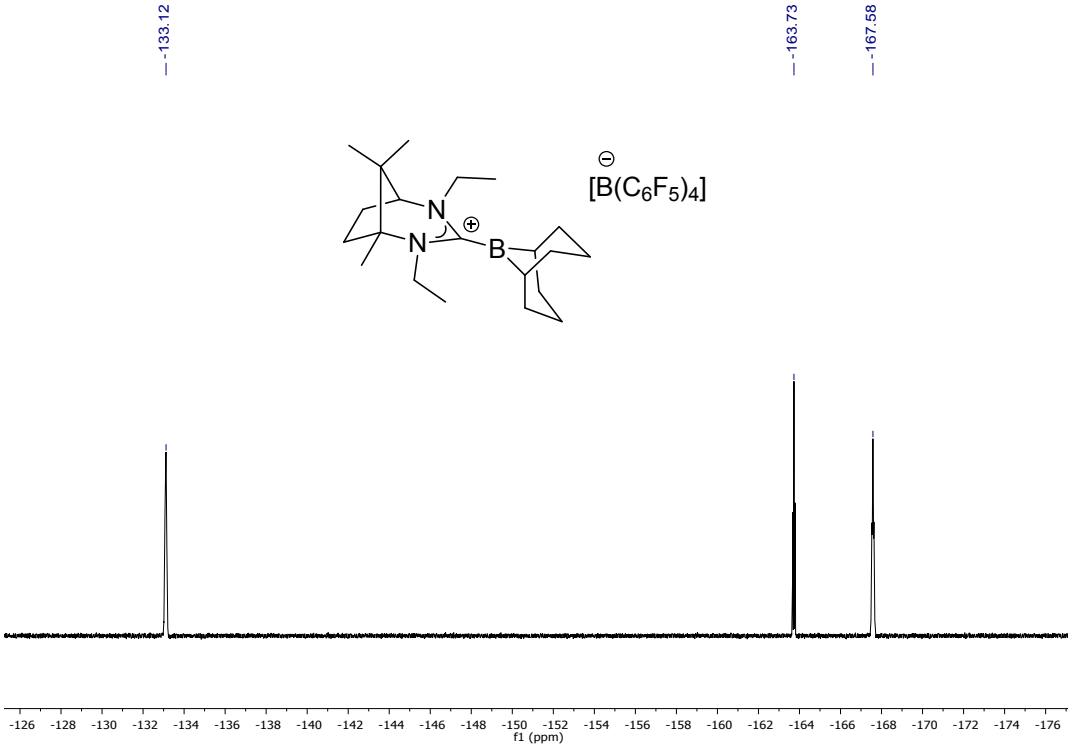
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **13**



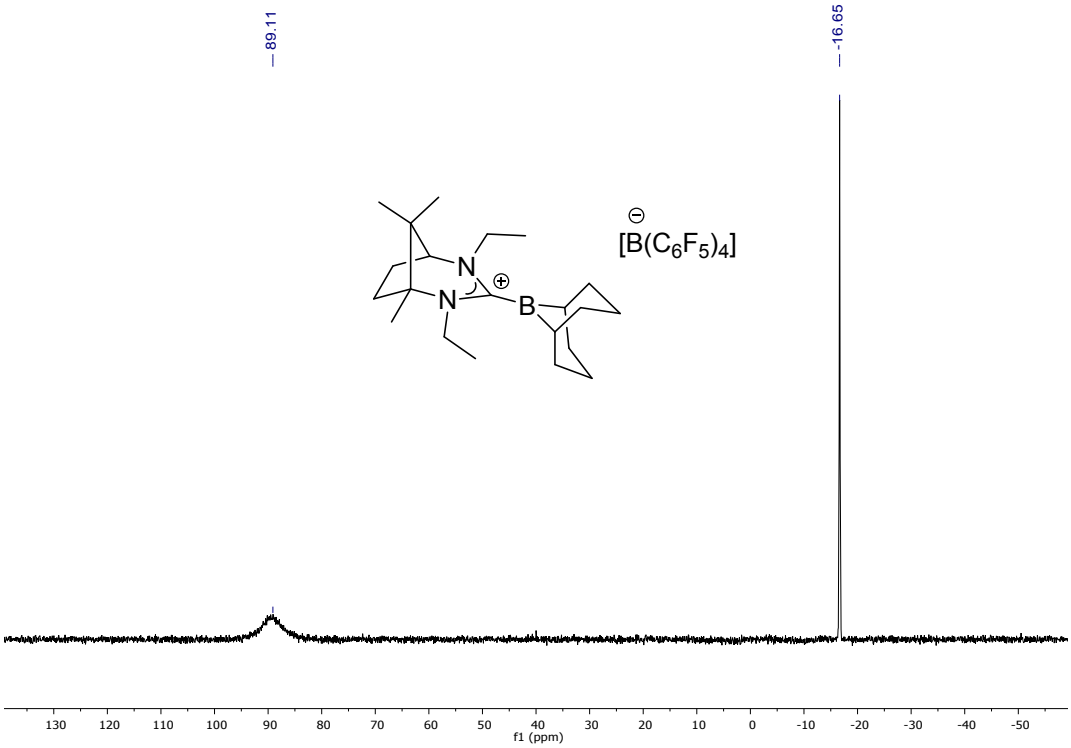
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **13**



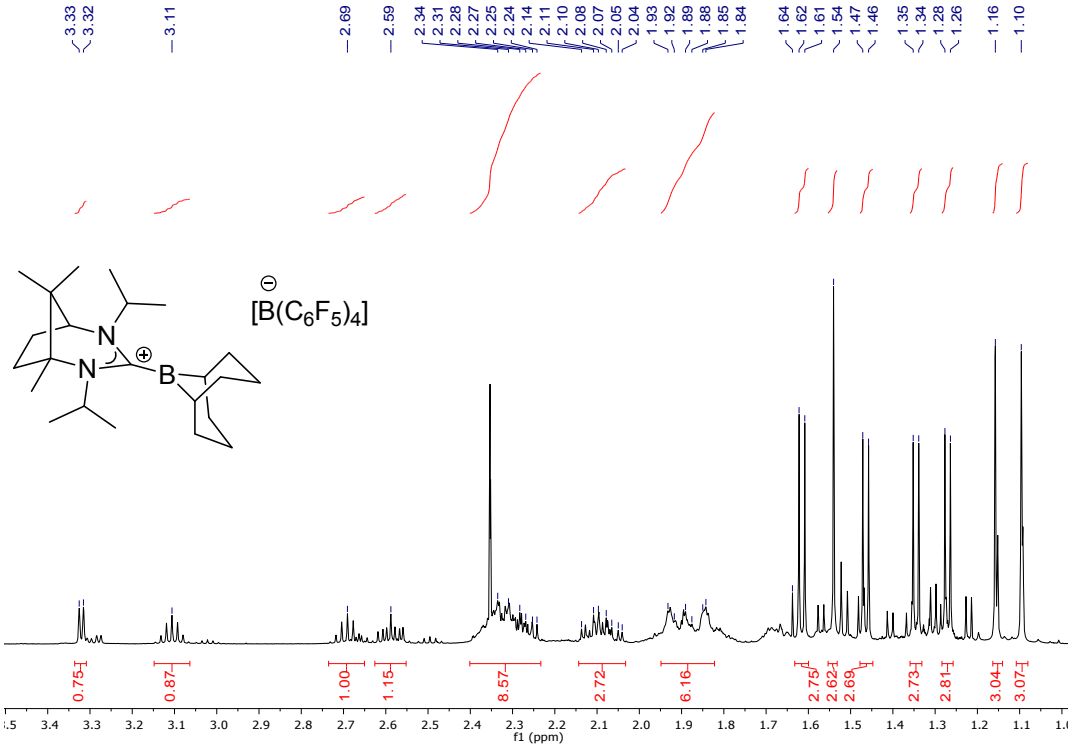
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of **13**



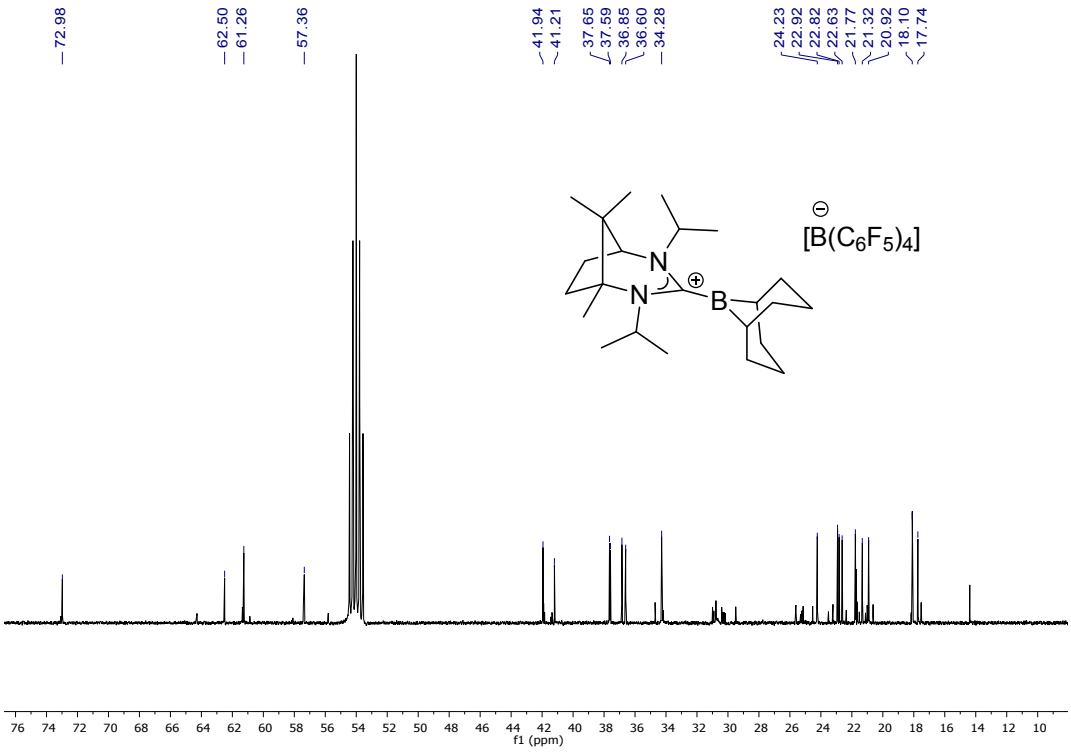
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **13**



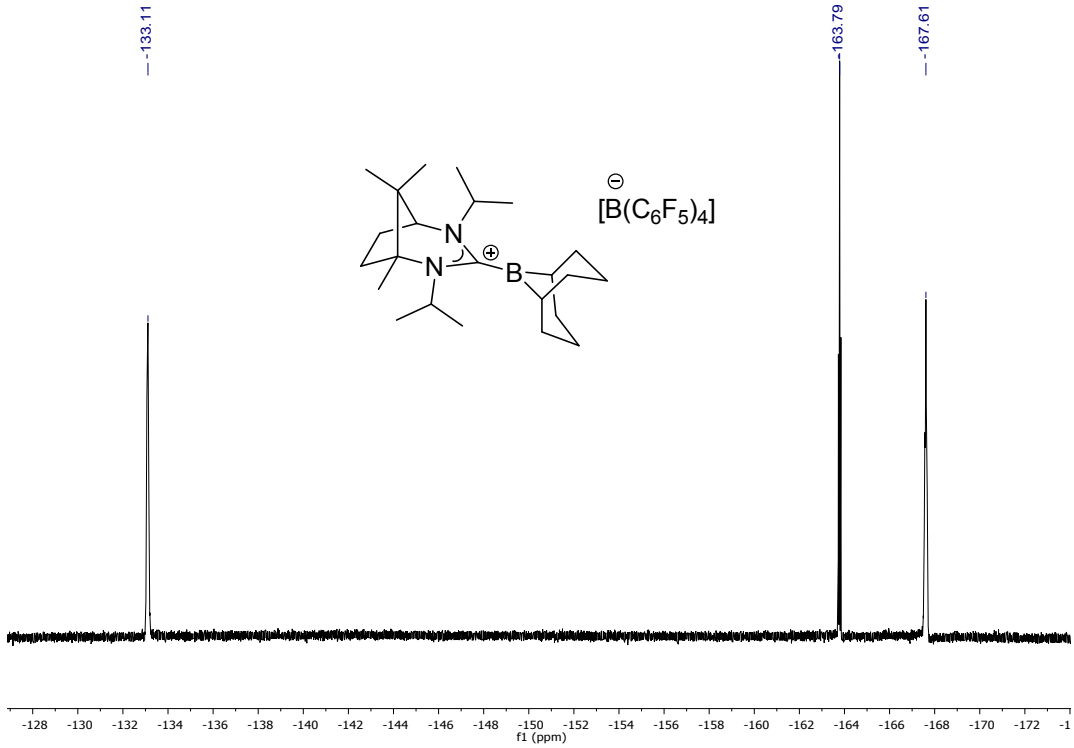
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **14**



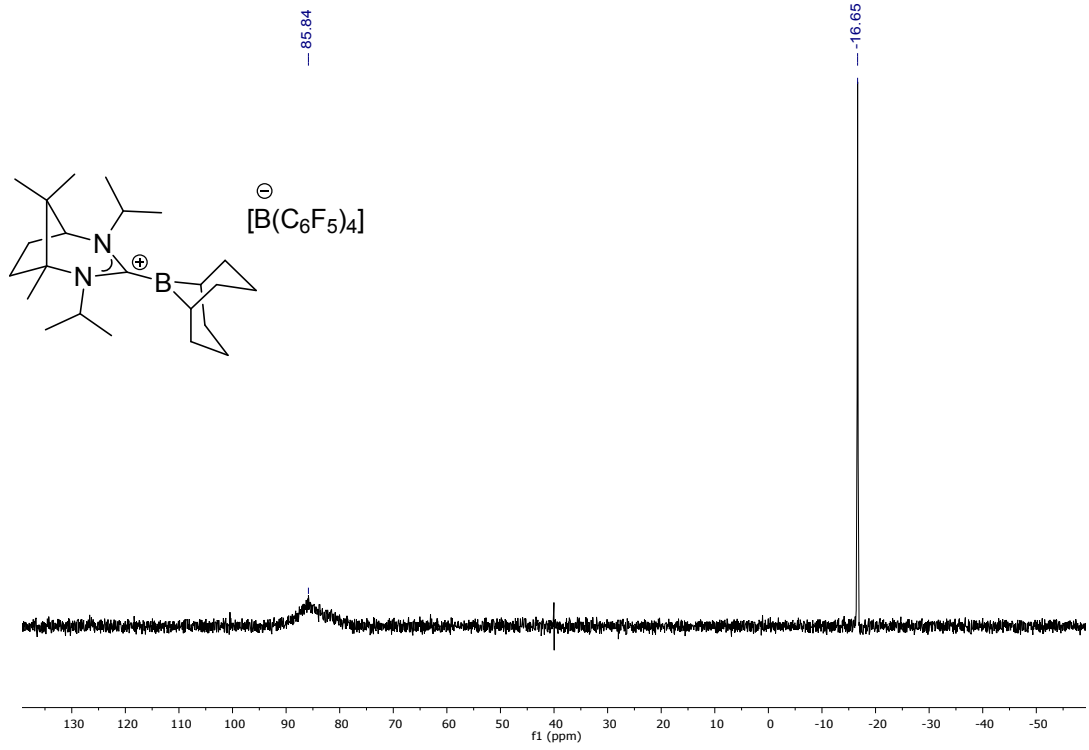
^{13}C NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **14**



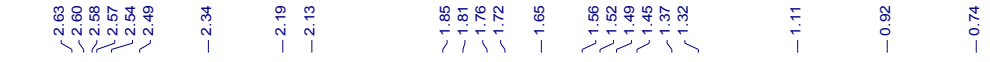
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of **14**

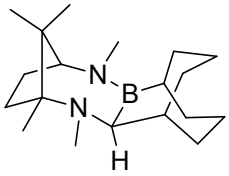


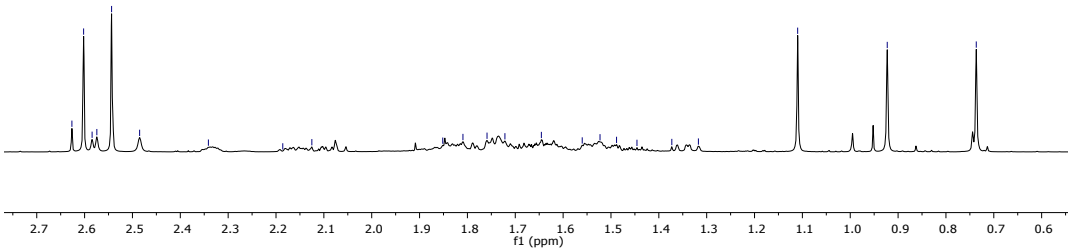
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **14**



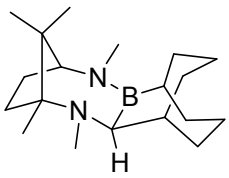
^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **15**

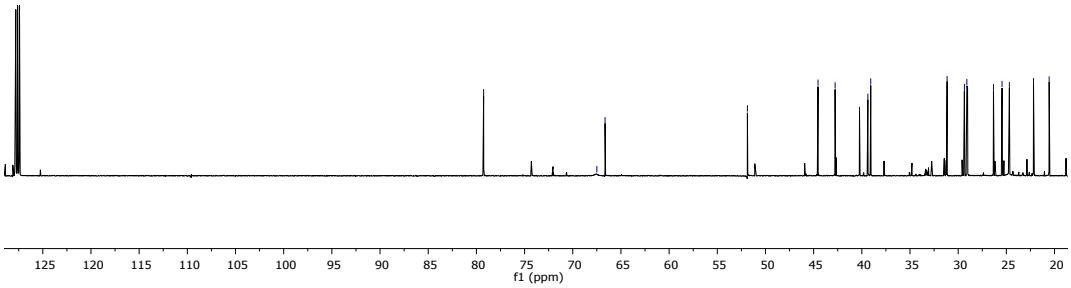




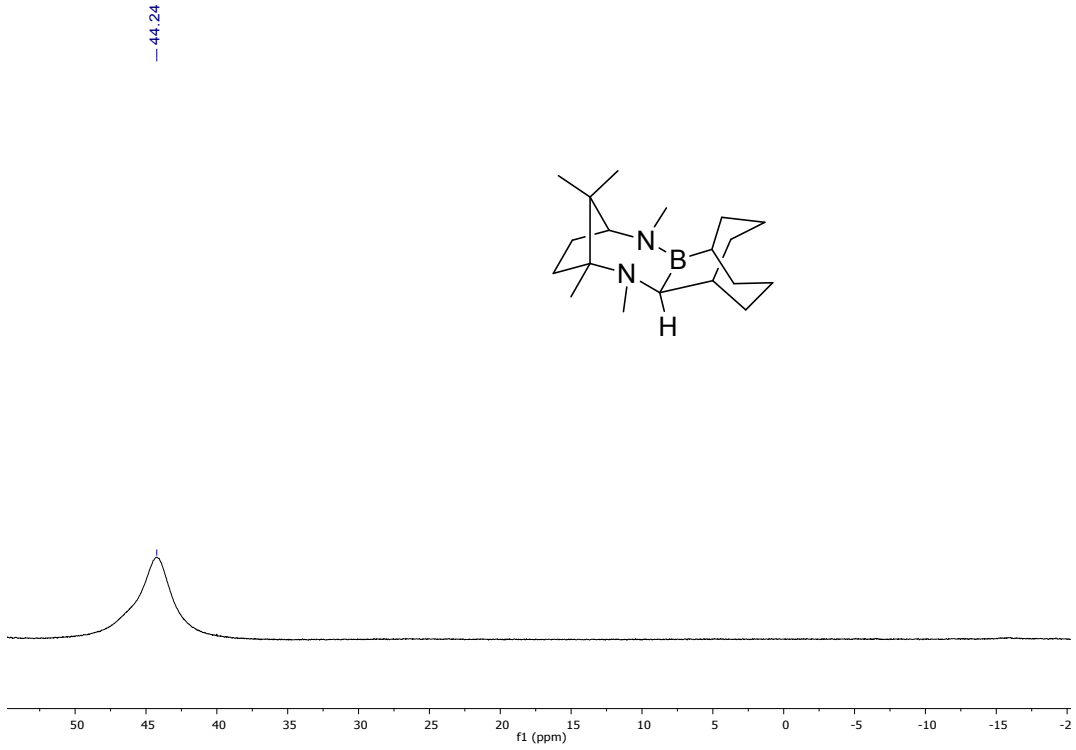


^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **15**

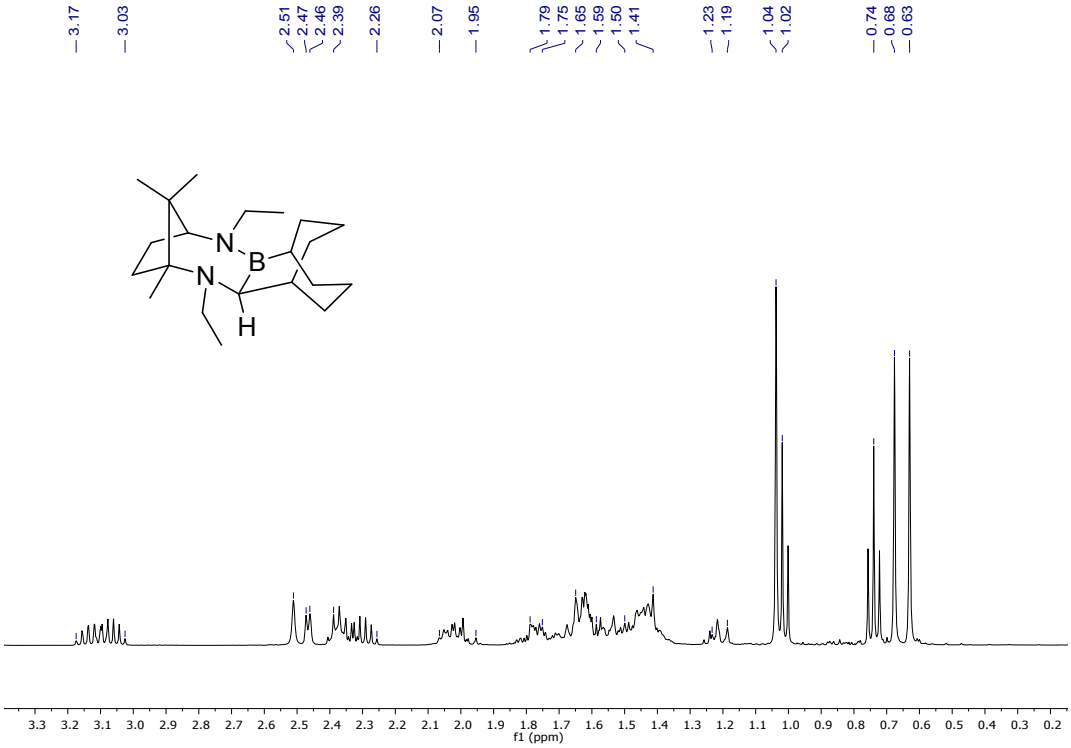




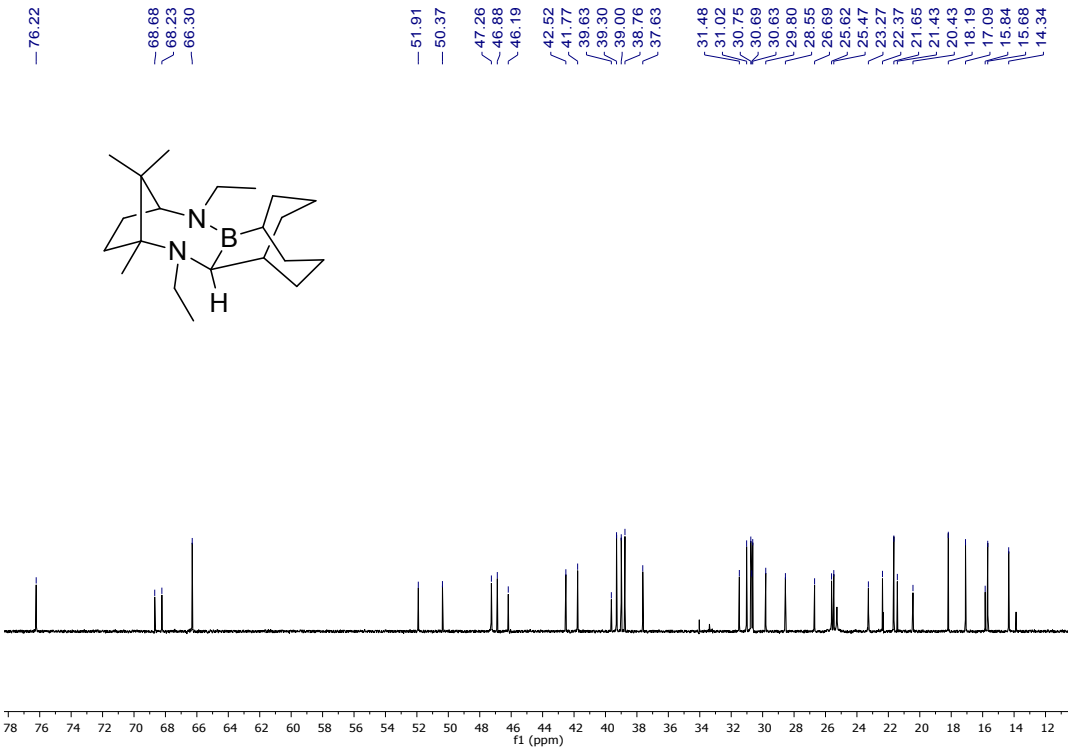
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **15**



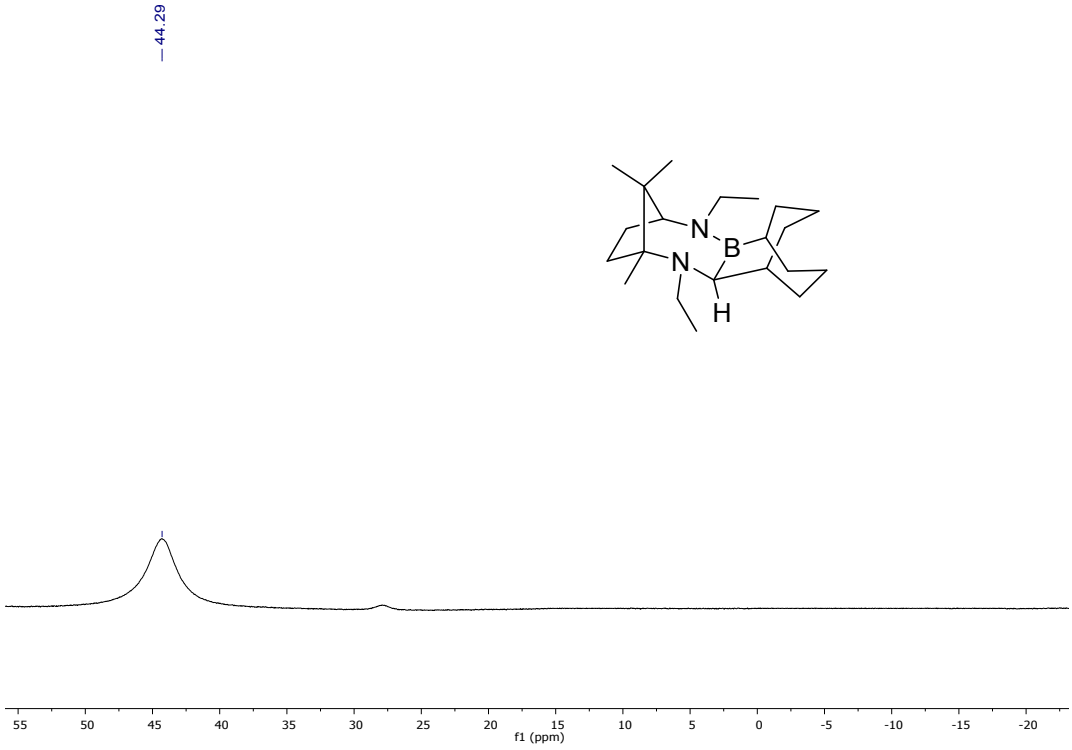
^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **16**



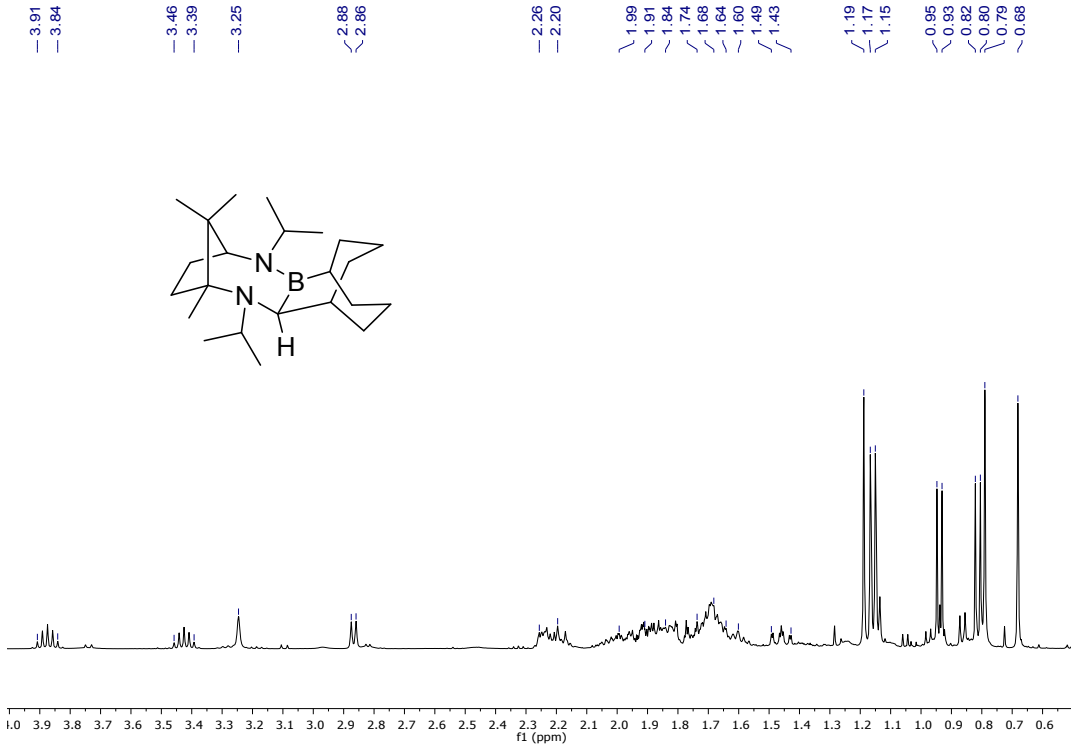
^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **16**



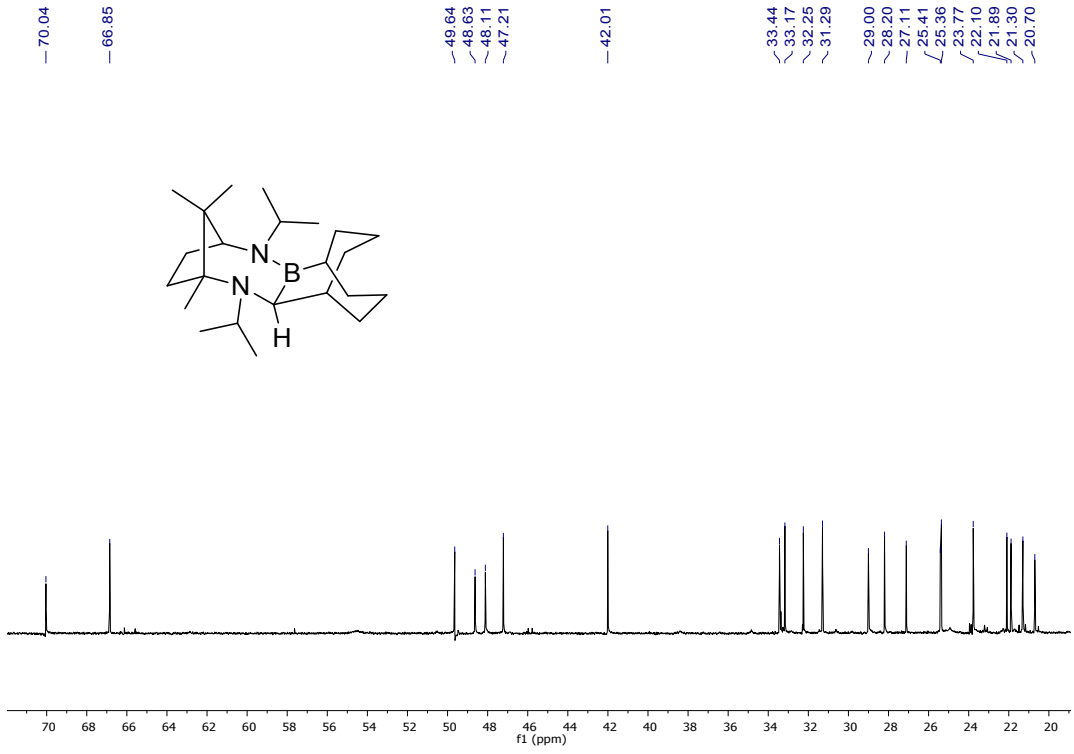
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **16**



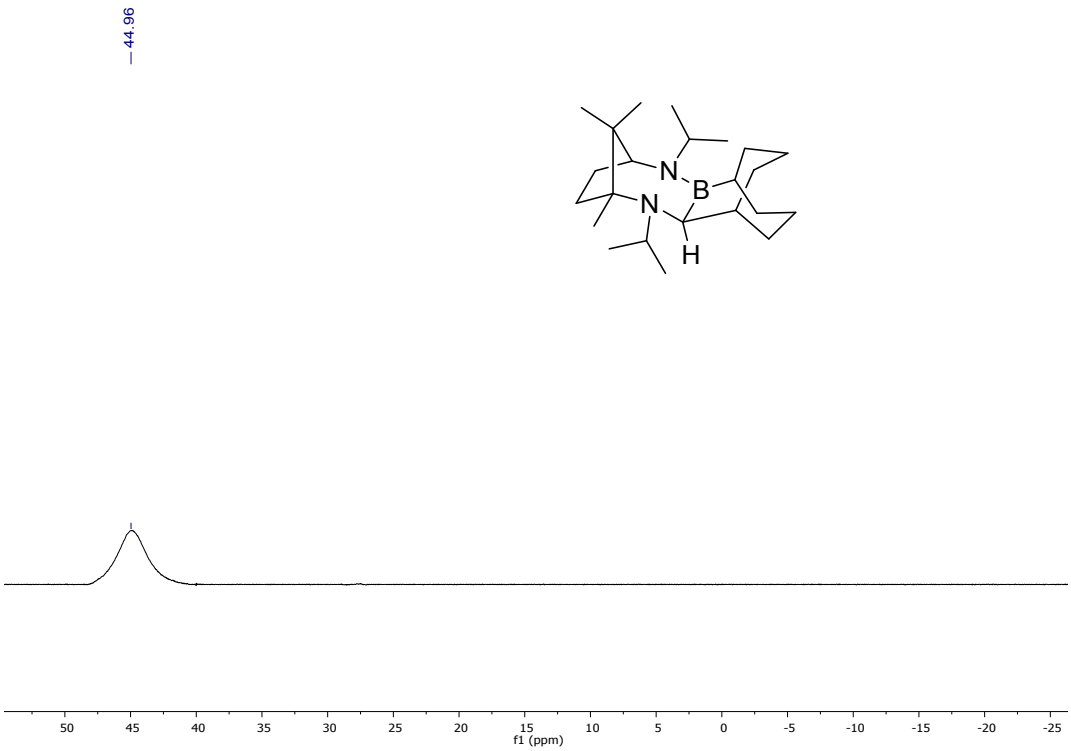
^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **17**



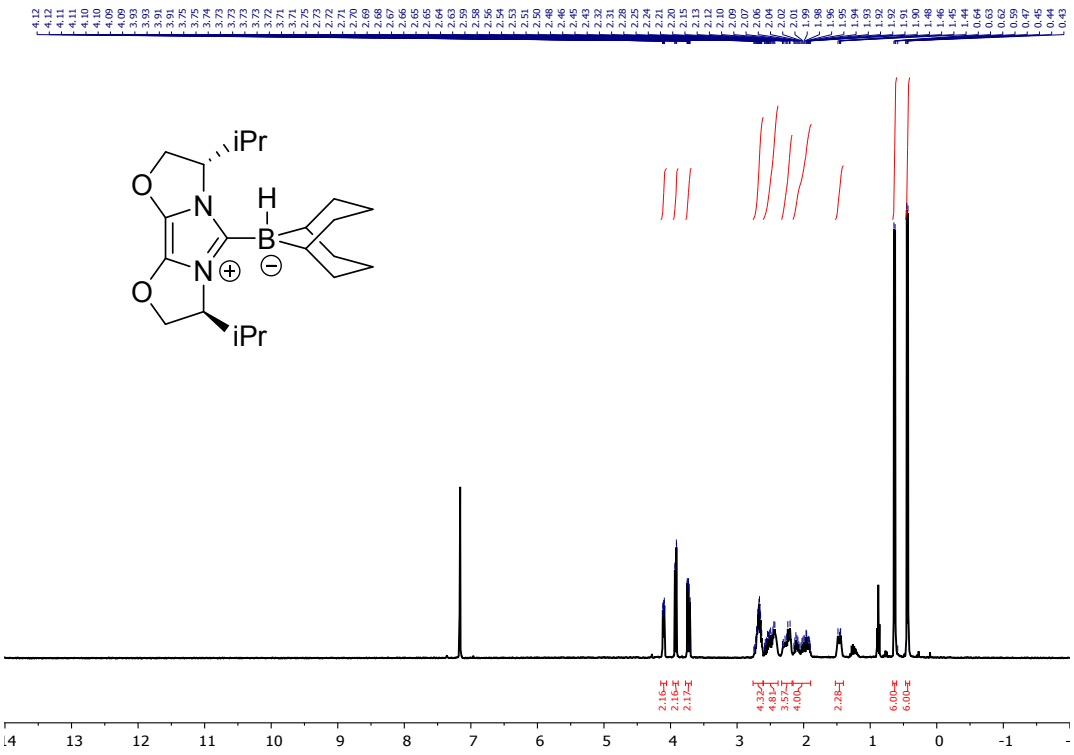
^{13}C NMR (126 MHz, C_6D_6, 298 K) spectrum of **17**



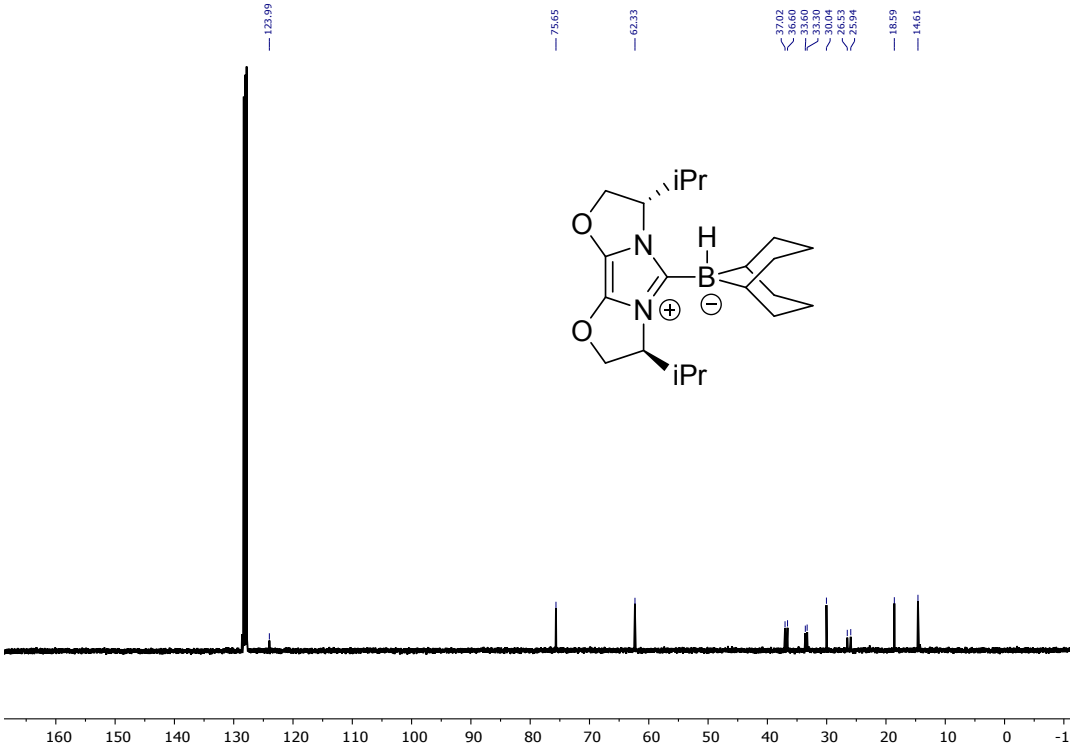
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **17**



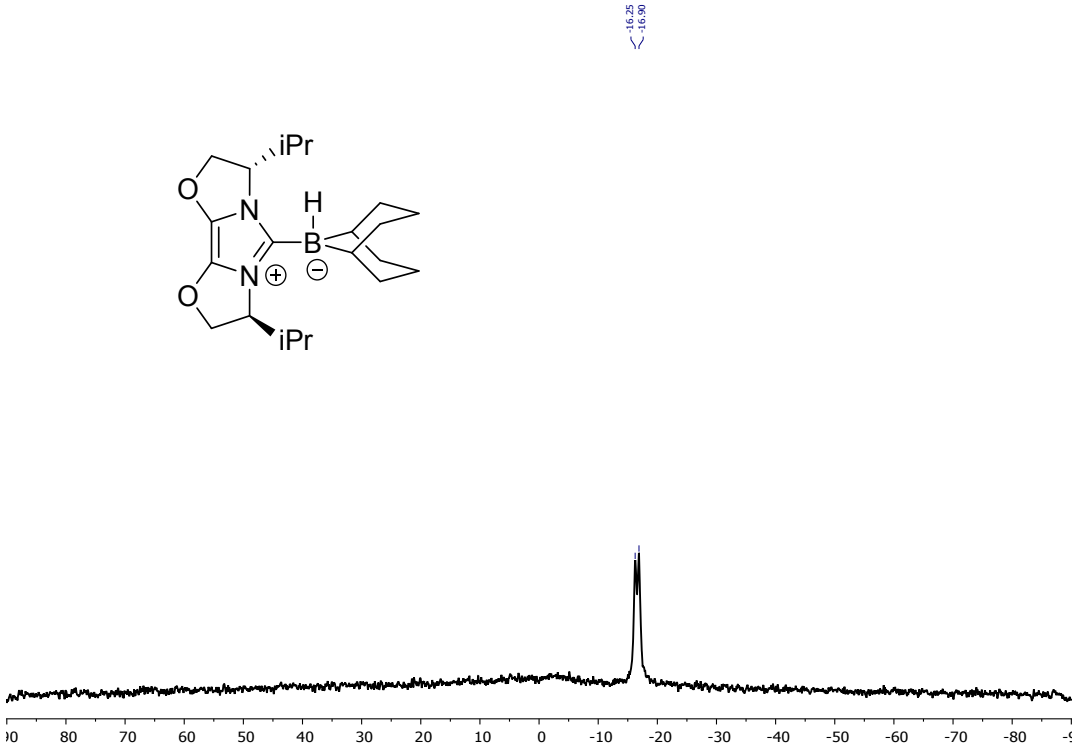
^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **20**



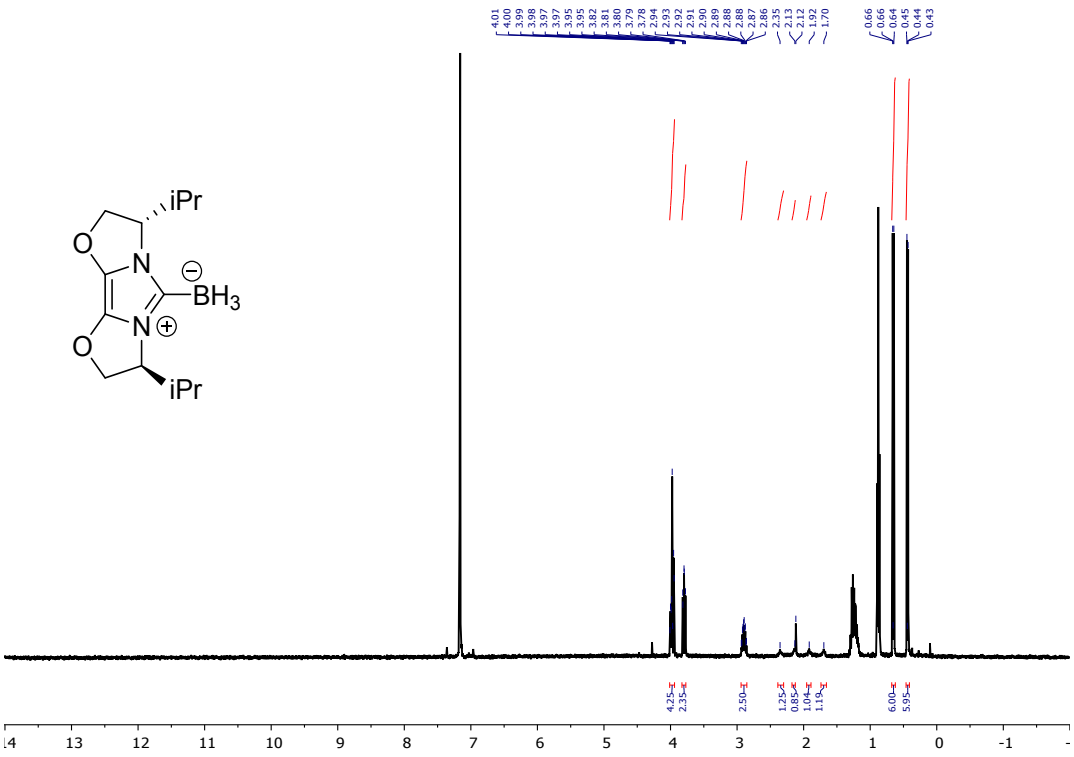
^{13}C NMR (125 MHz, C_6D_6, 298 K) spectrum of **20**



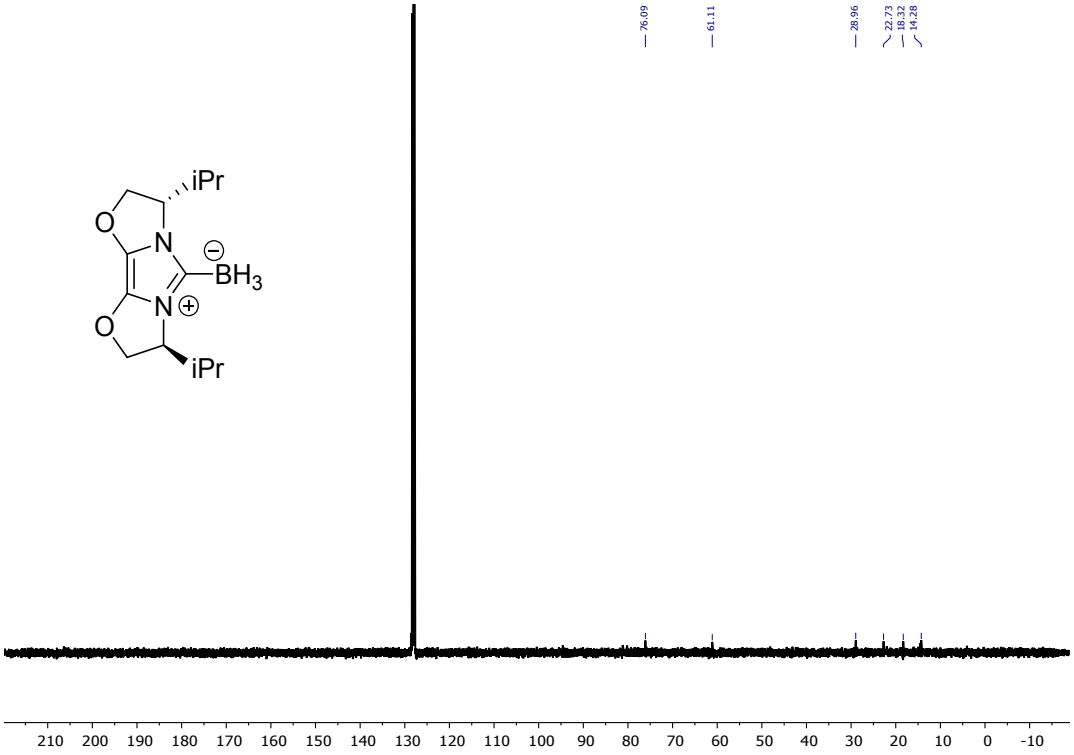
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **20**



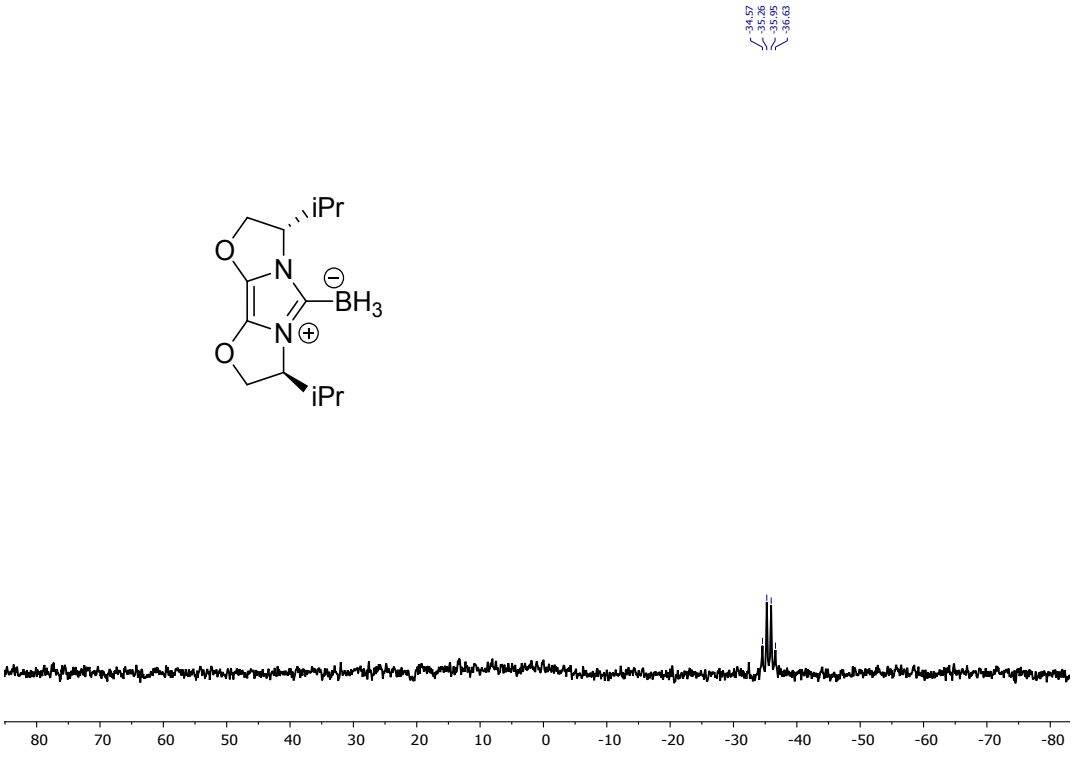
^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **21**



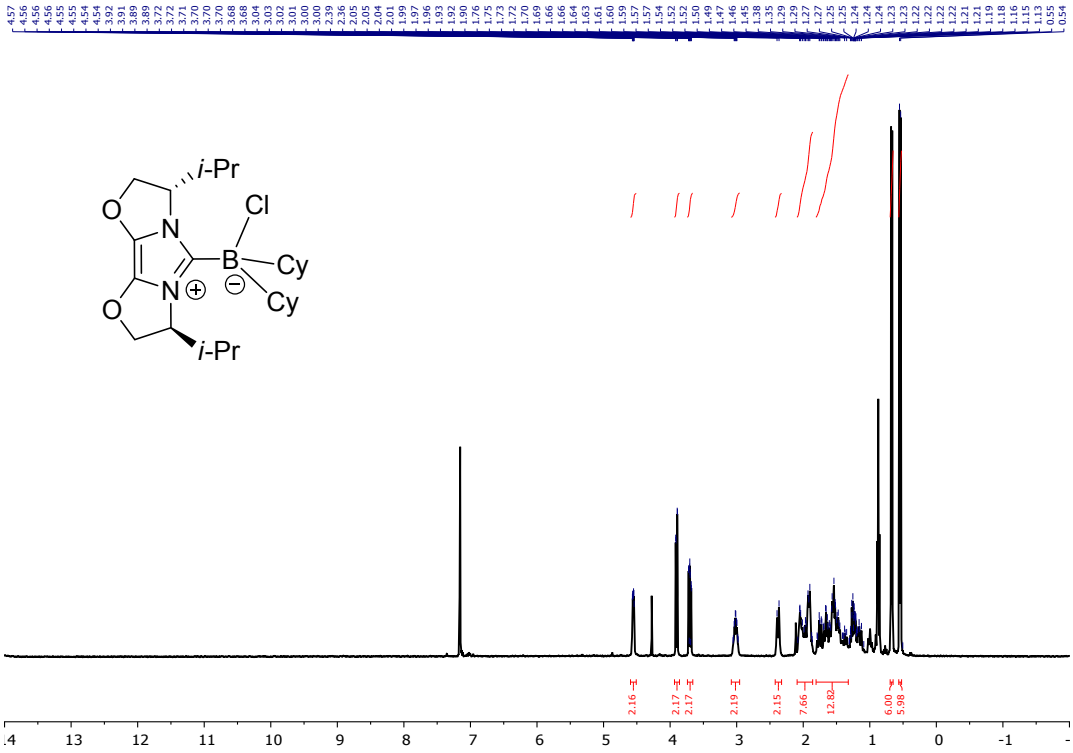
^{13}C NMR (125 MHz, C_6D_6, 298 K) spectrum of **21**



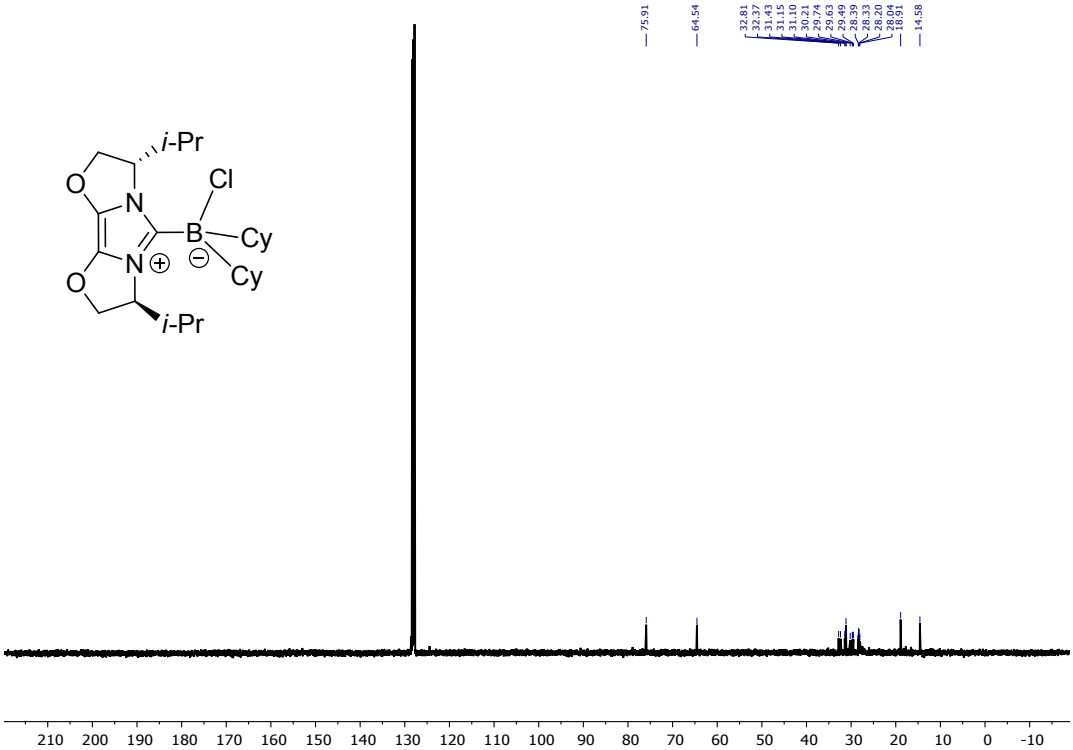
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **21**



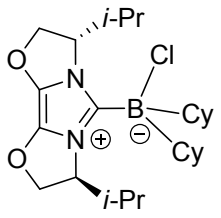
^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **22**

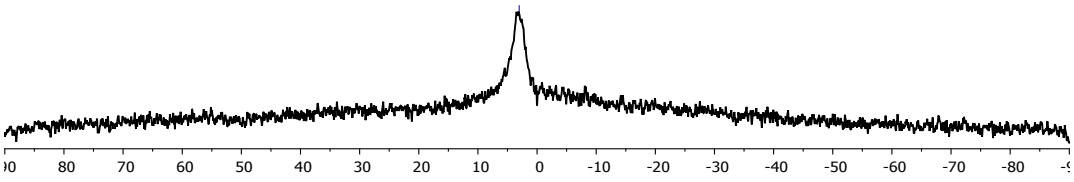


^{13}C NMR (125 MHz, C_6D_6, 298 K) spectrum of **22**

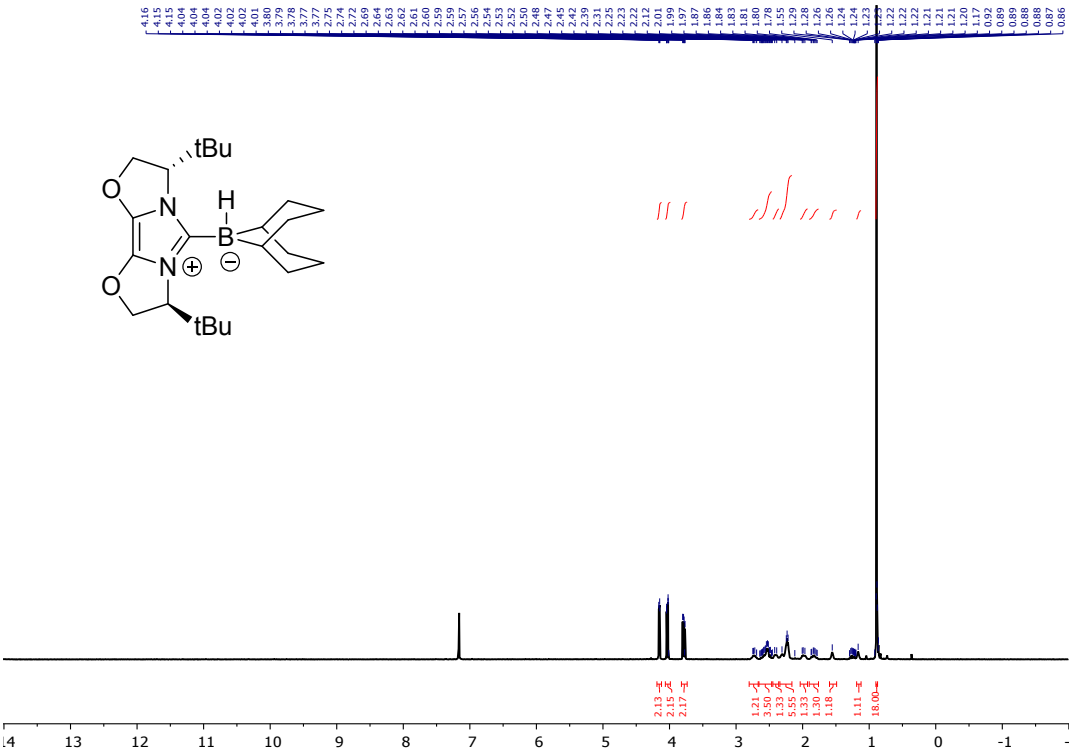


^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **22**

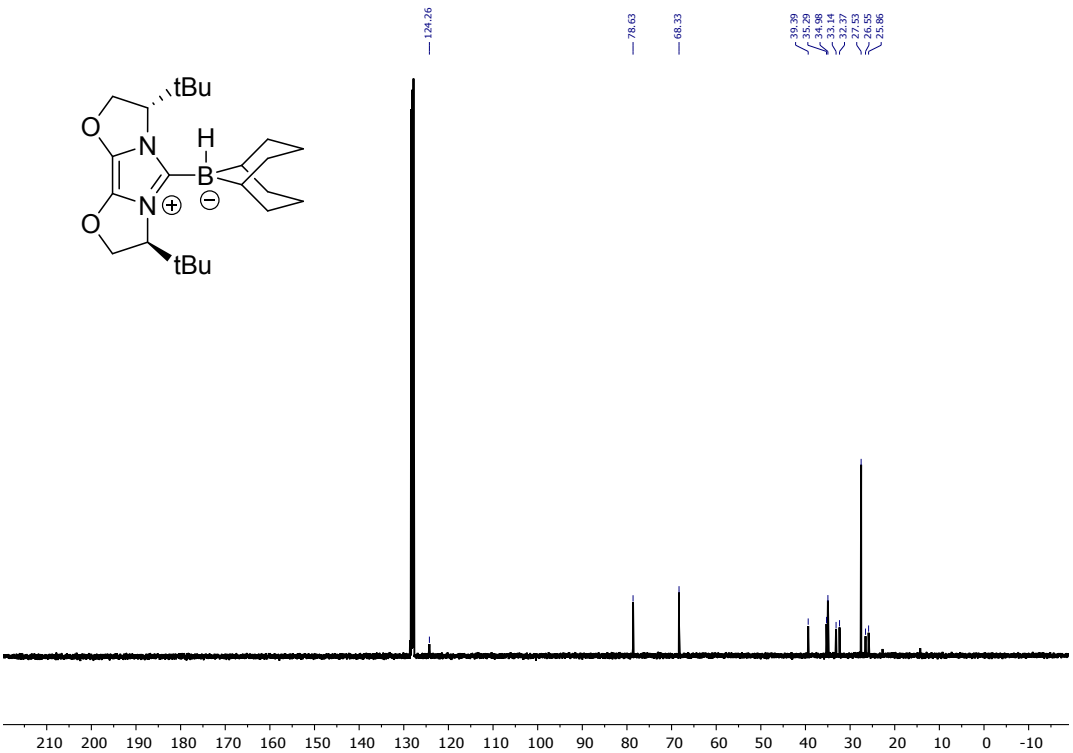




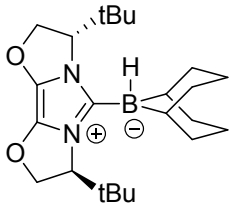
^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **23**



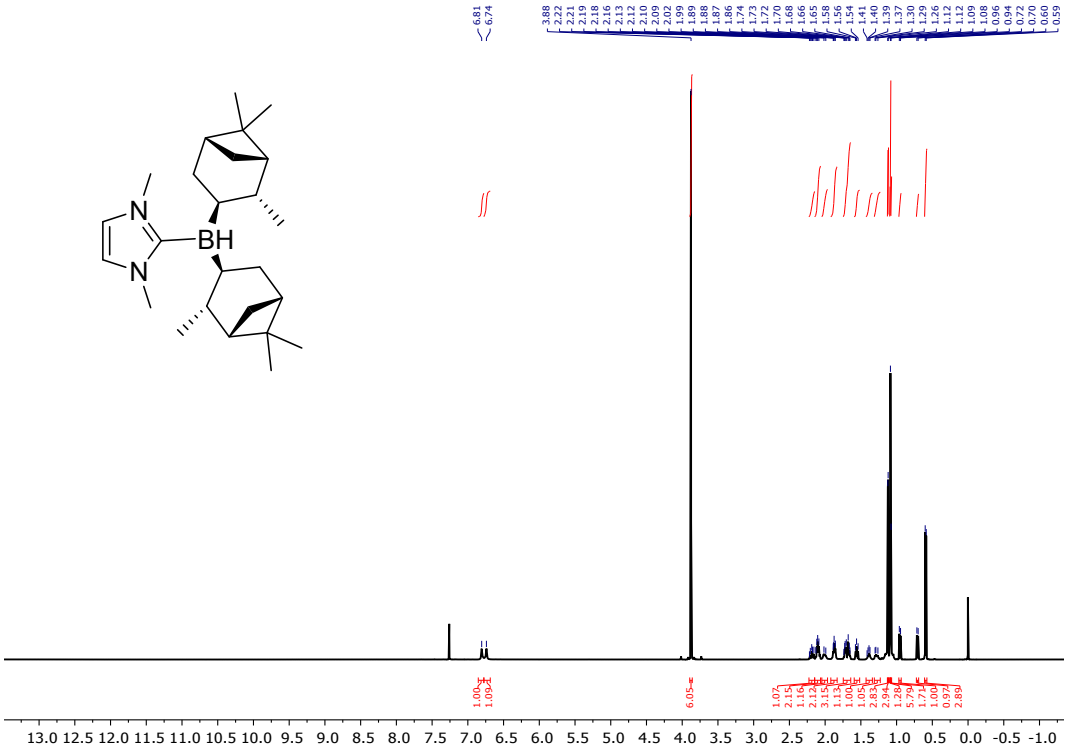
^{13}C NMR (125 MHz, C_6D_6, 298 K) spectrum of **23**



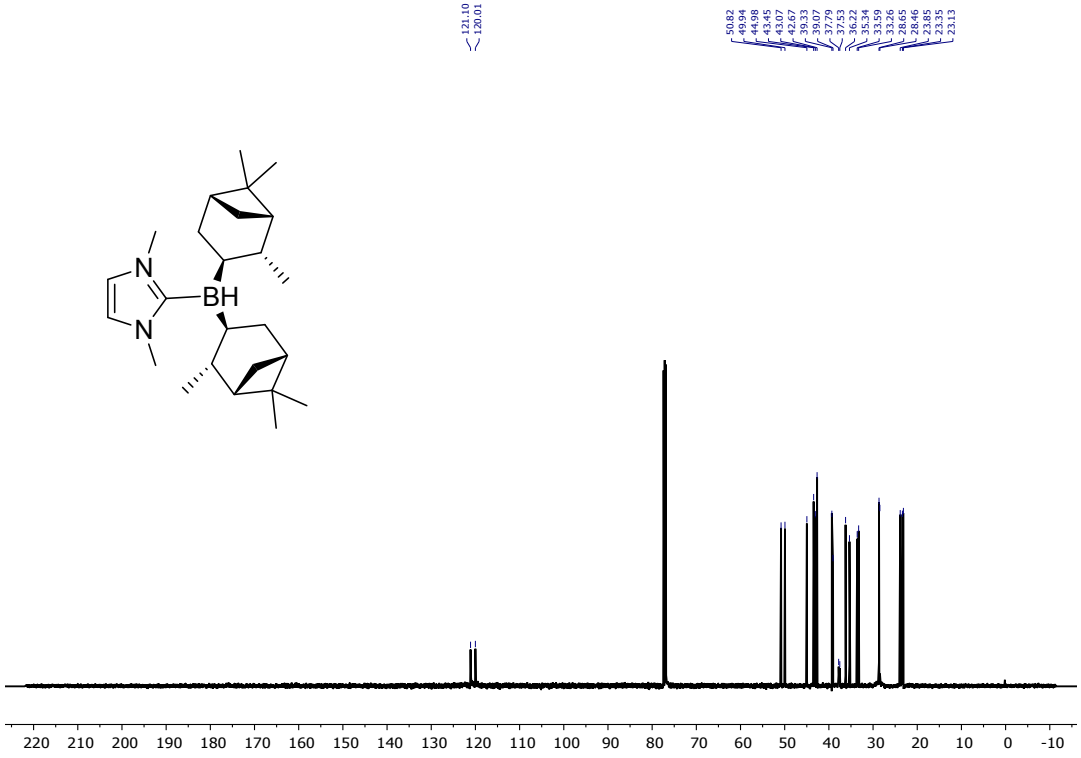
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **23**



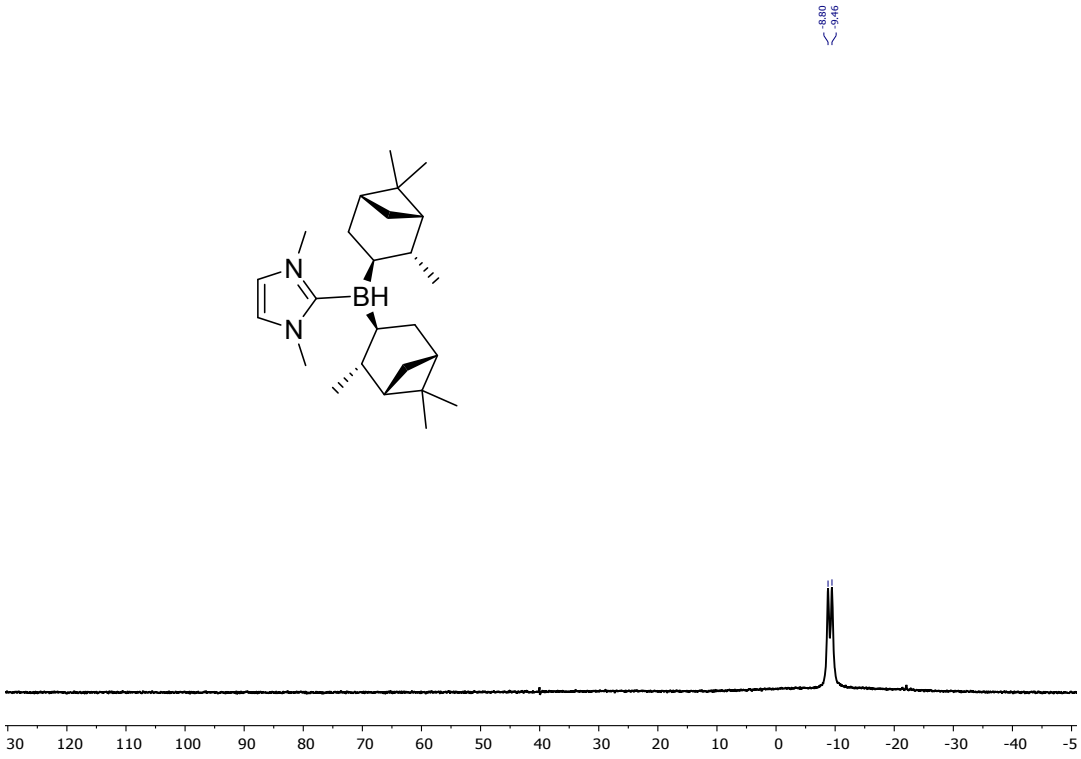
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **24**



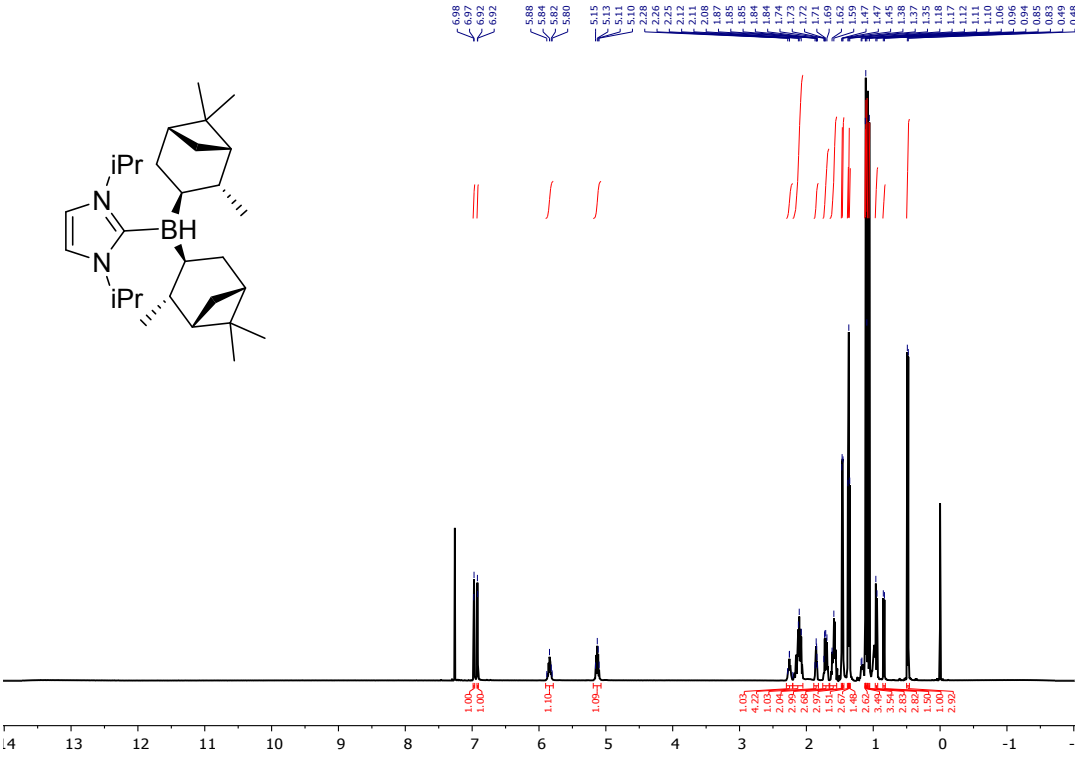
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **24**



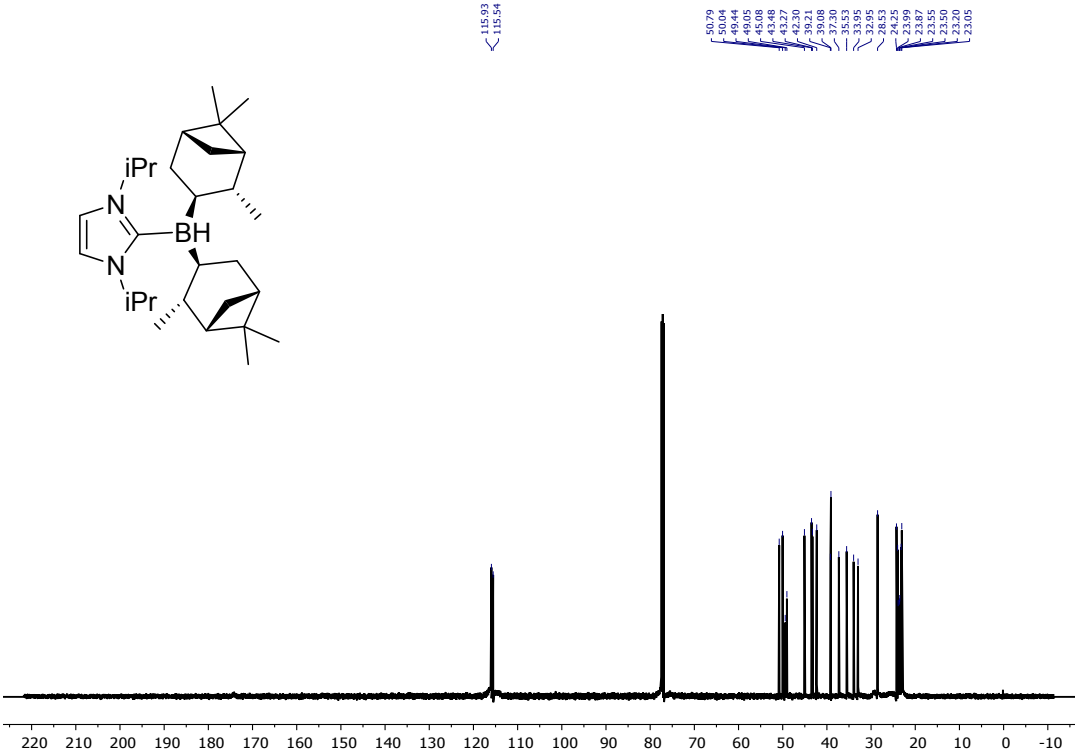
^{11}B NMR (128 MHz, d^{8}-toluene, 298 K) spectrum of **24**



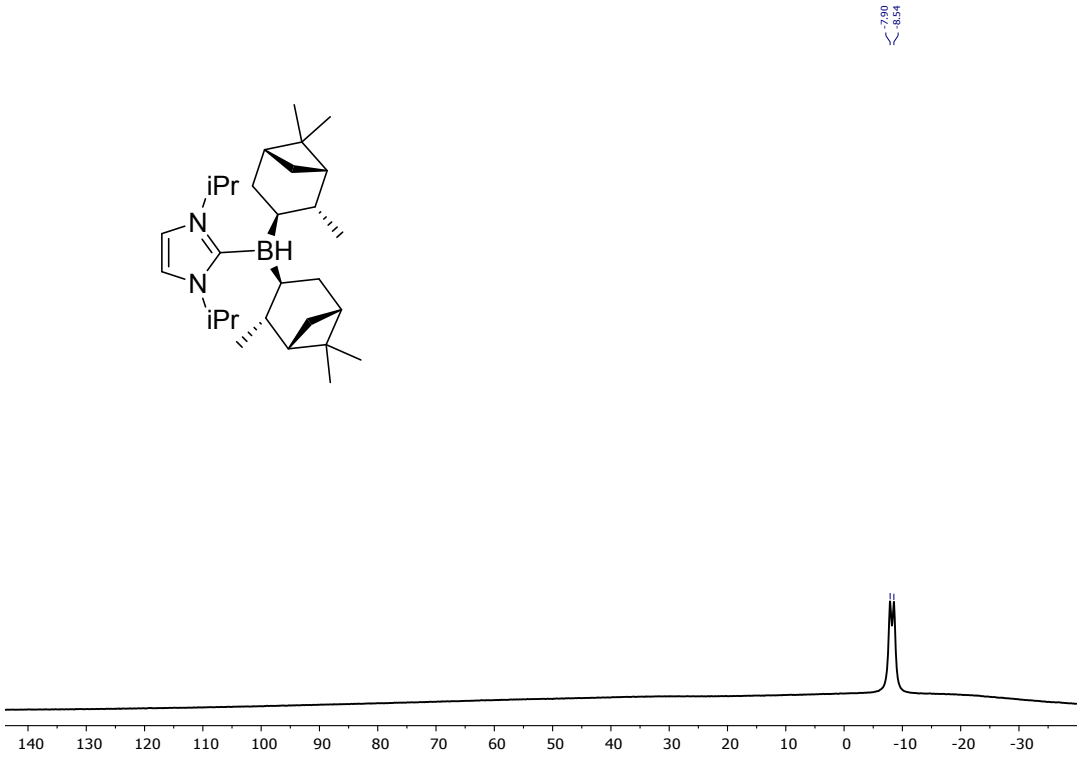
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **25**



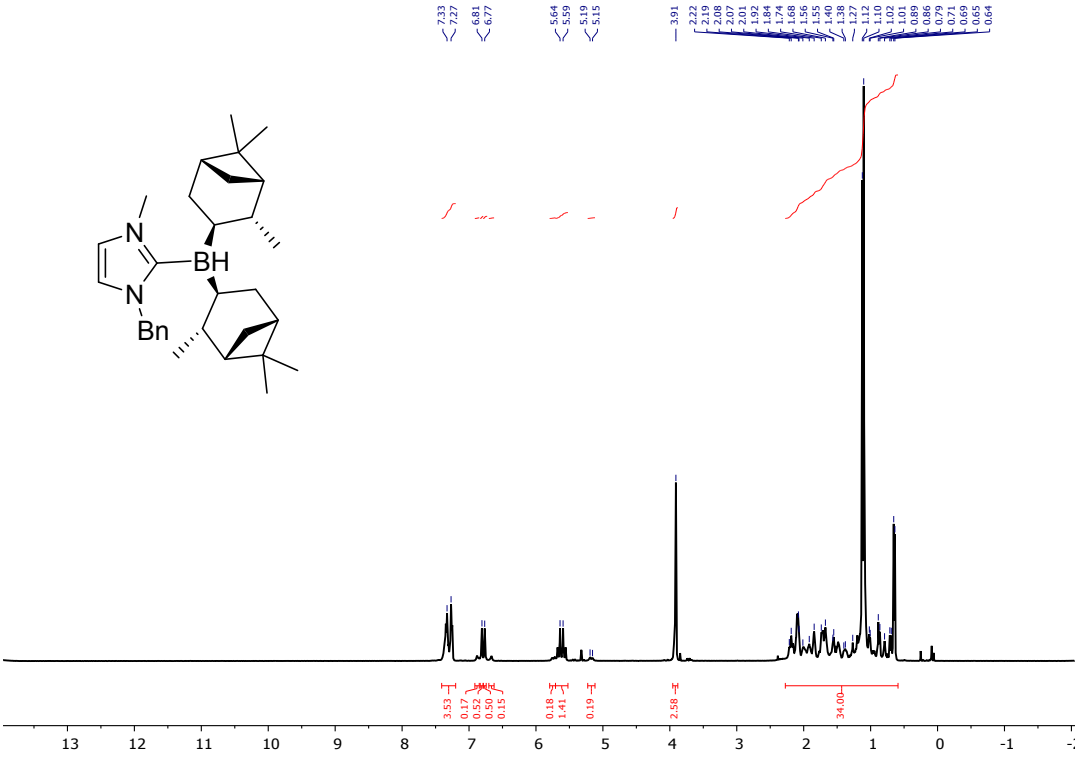
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **25**



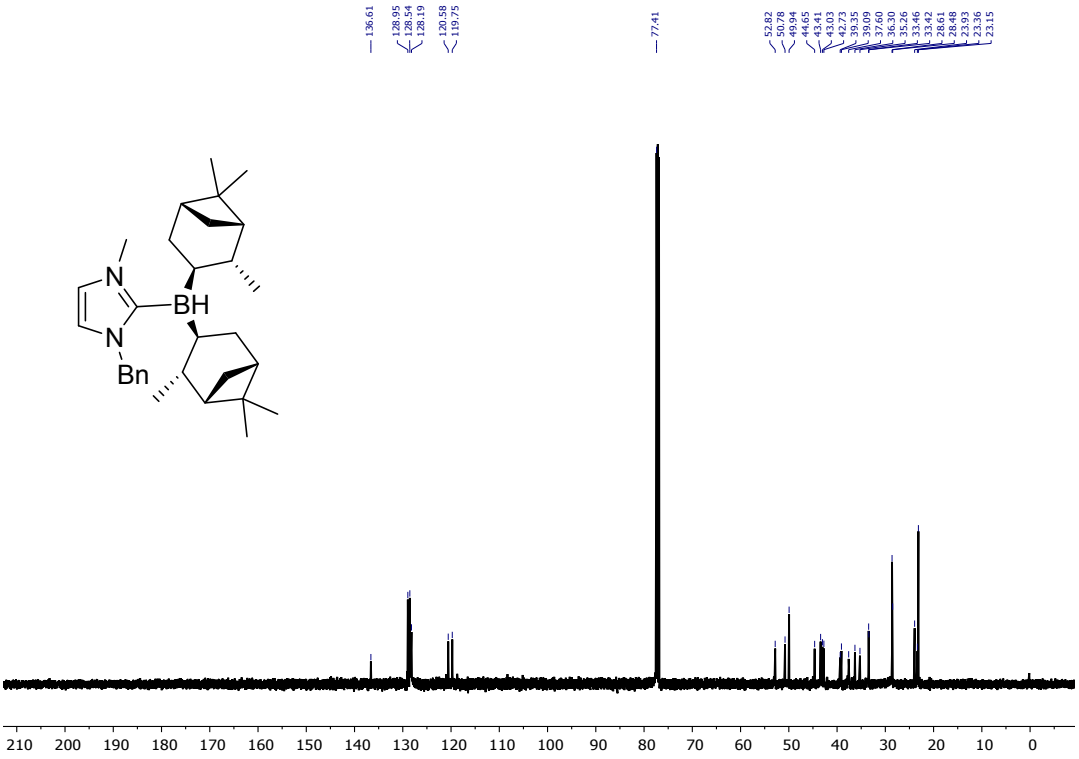
^{11}B NMR (128 MHz, d^{8}-toluene, 298 K) spectrum of **25**



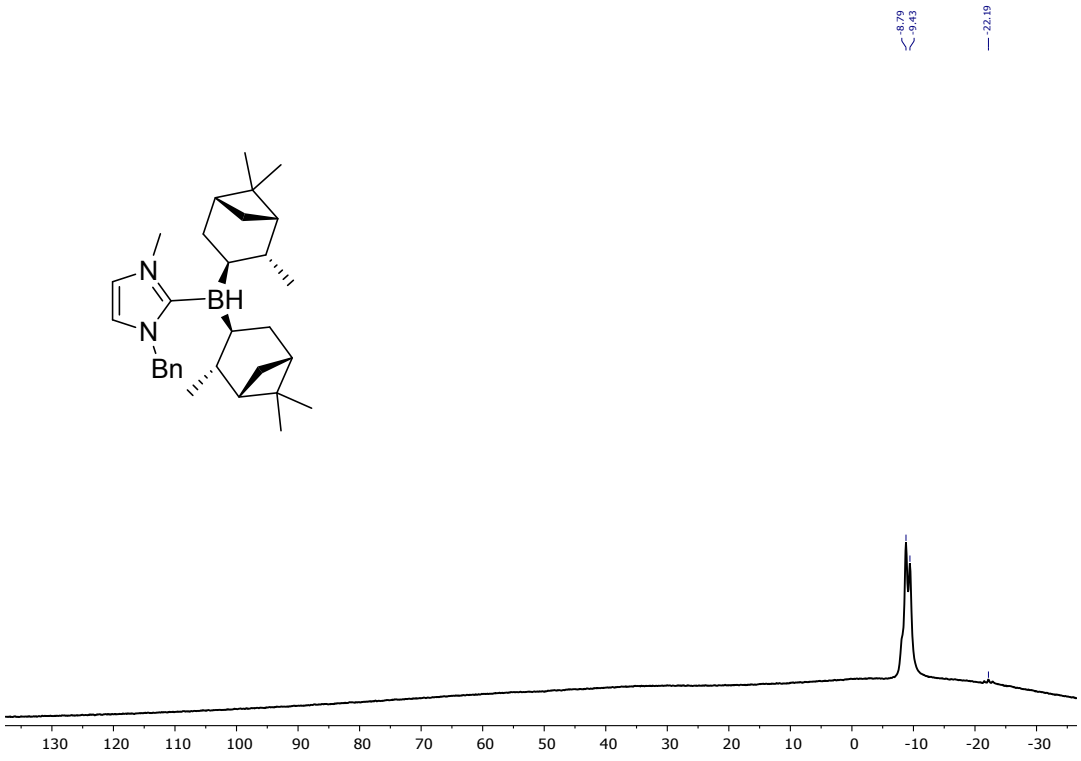
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of **26**



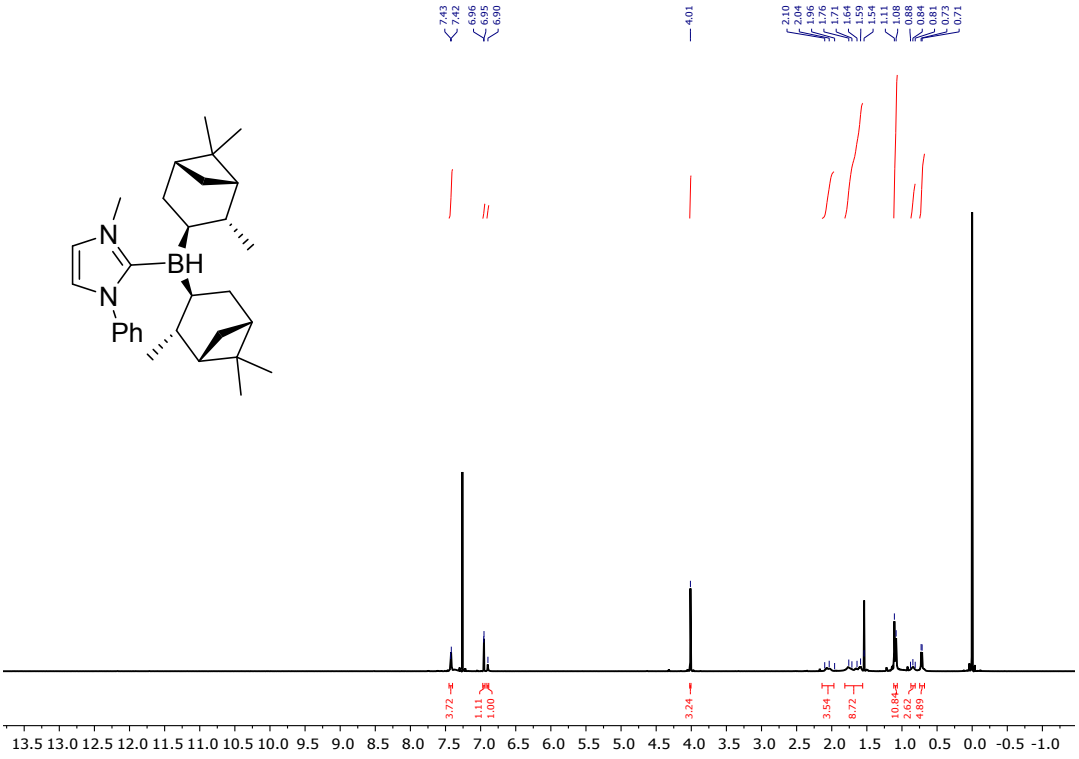
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **26**



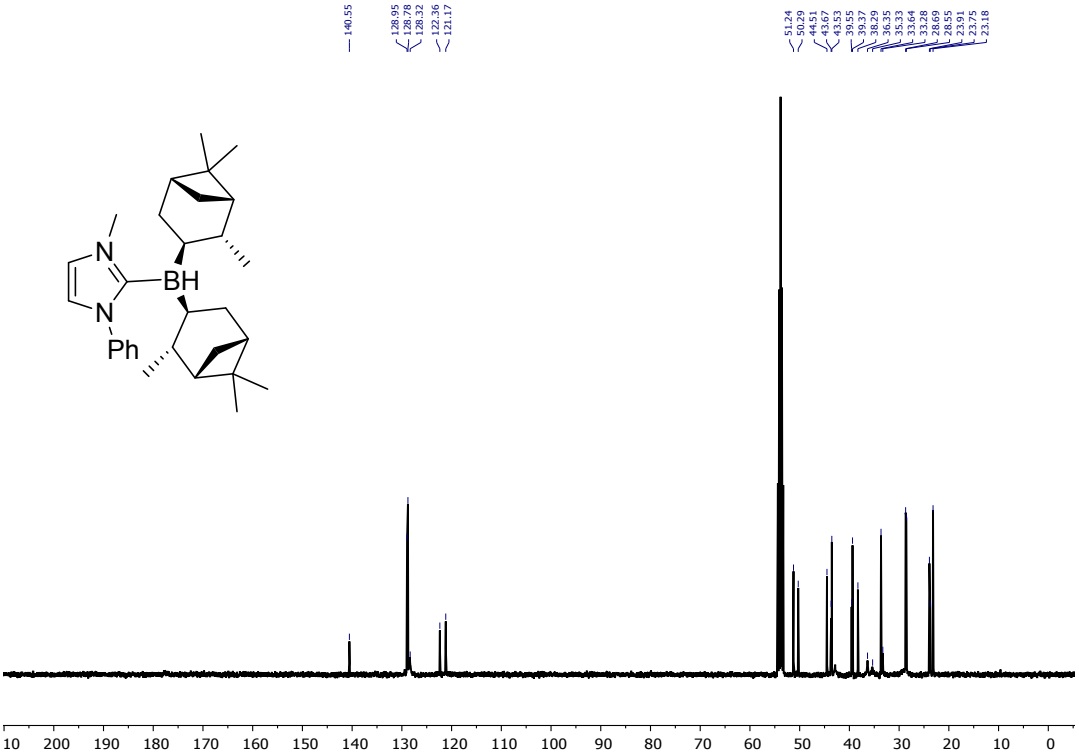
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **26**



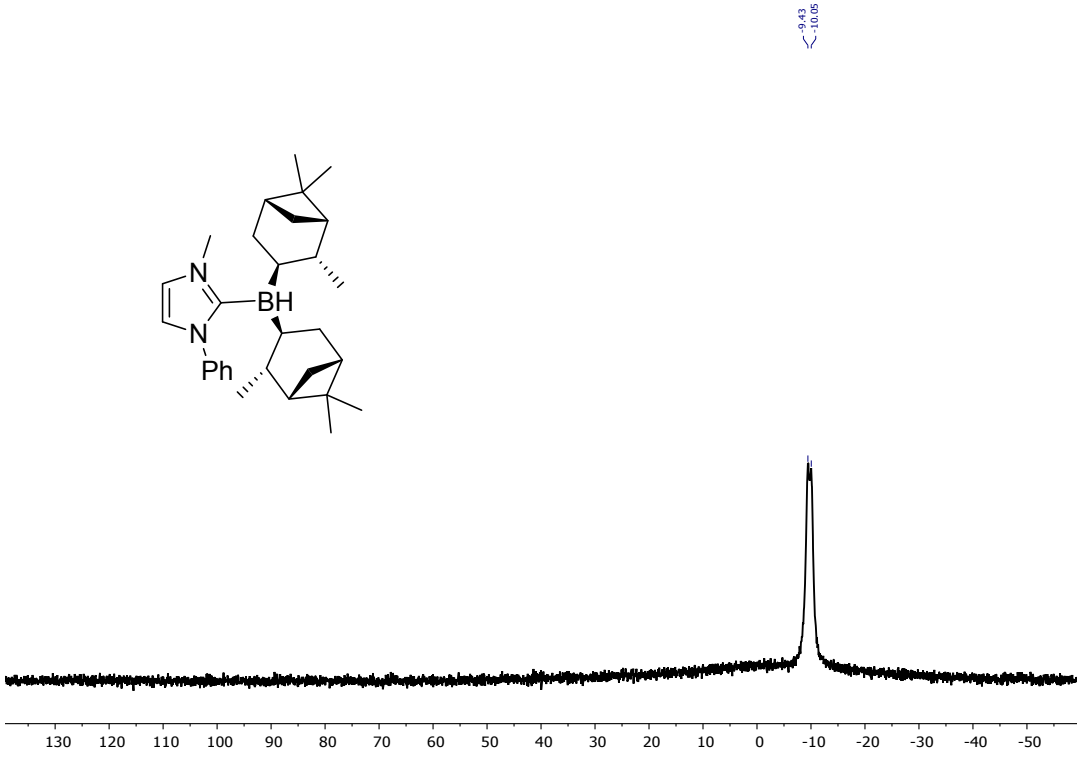
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **27**



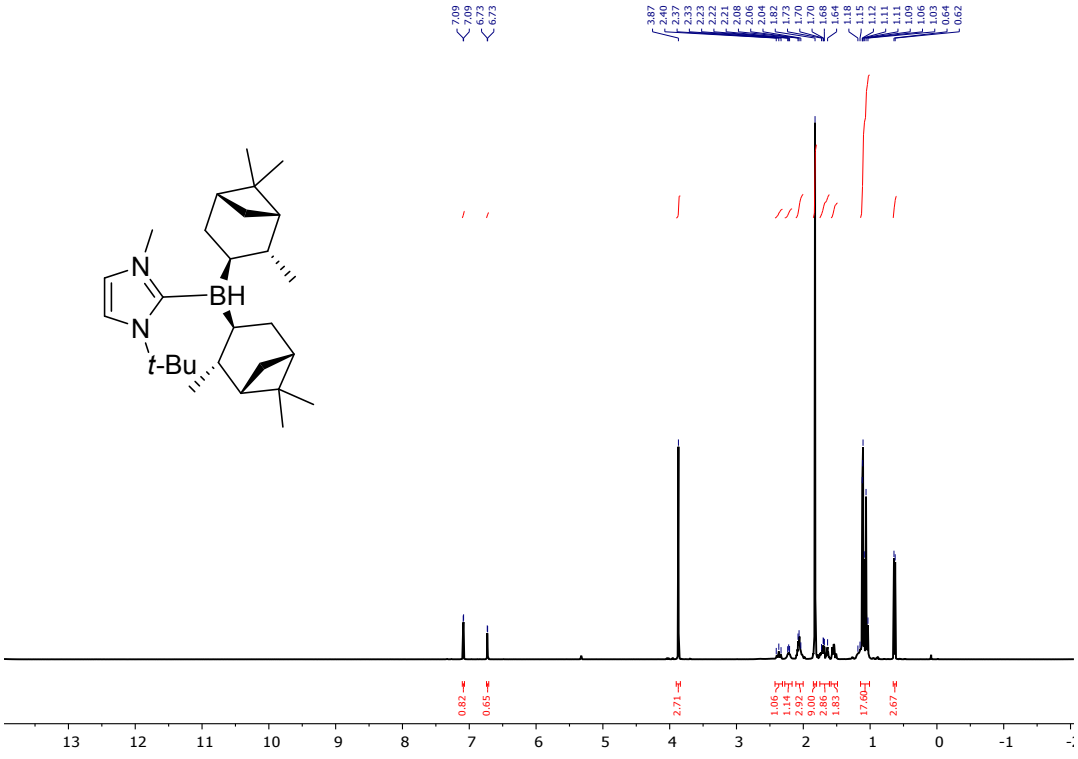
^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) spectrum of **27**



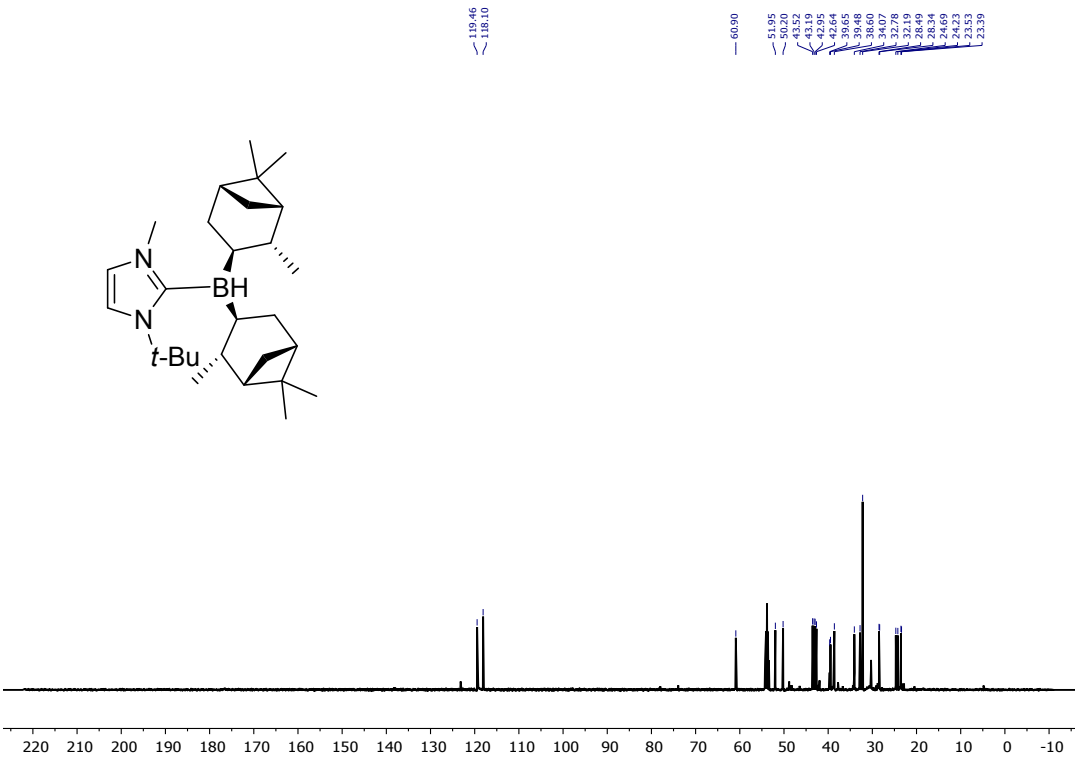
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **27**



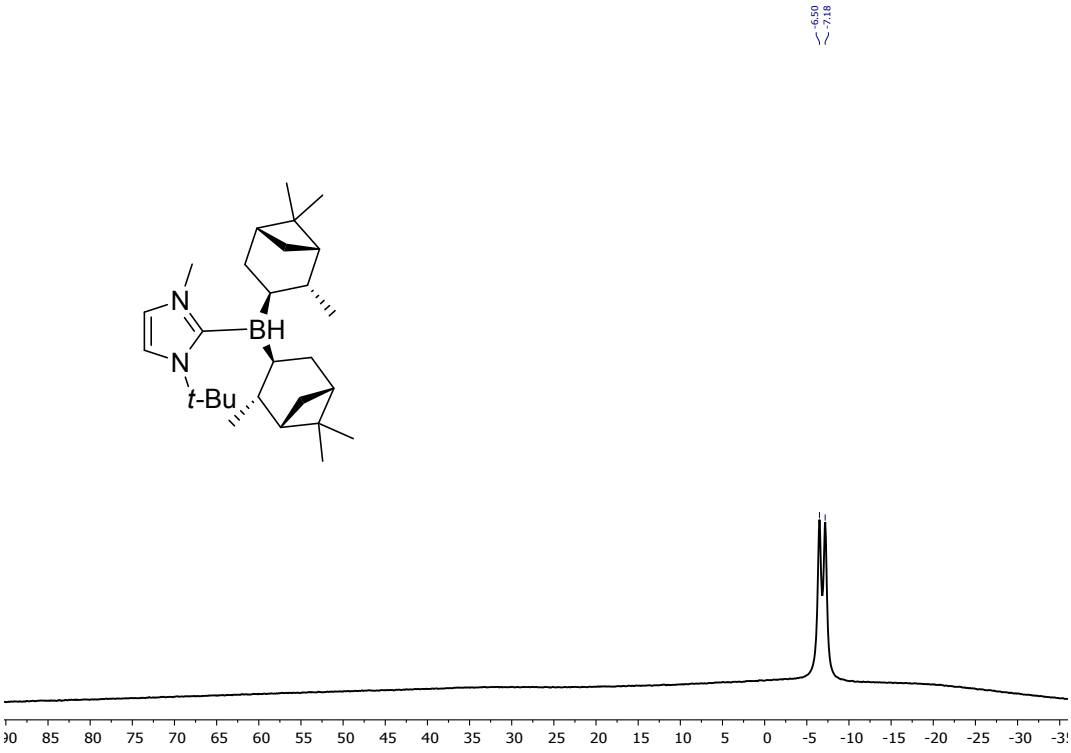
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of **28**



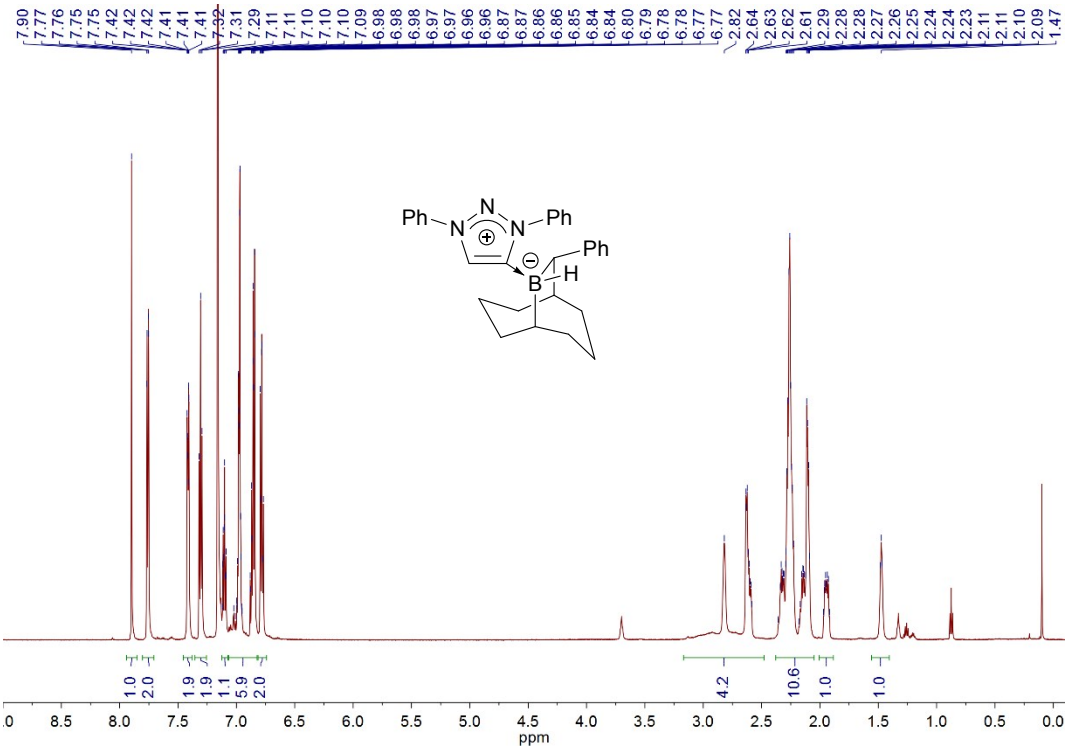
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **28**



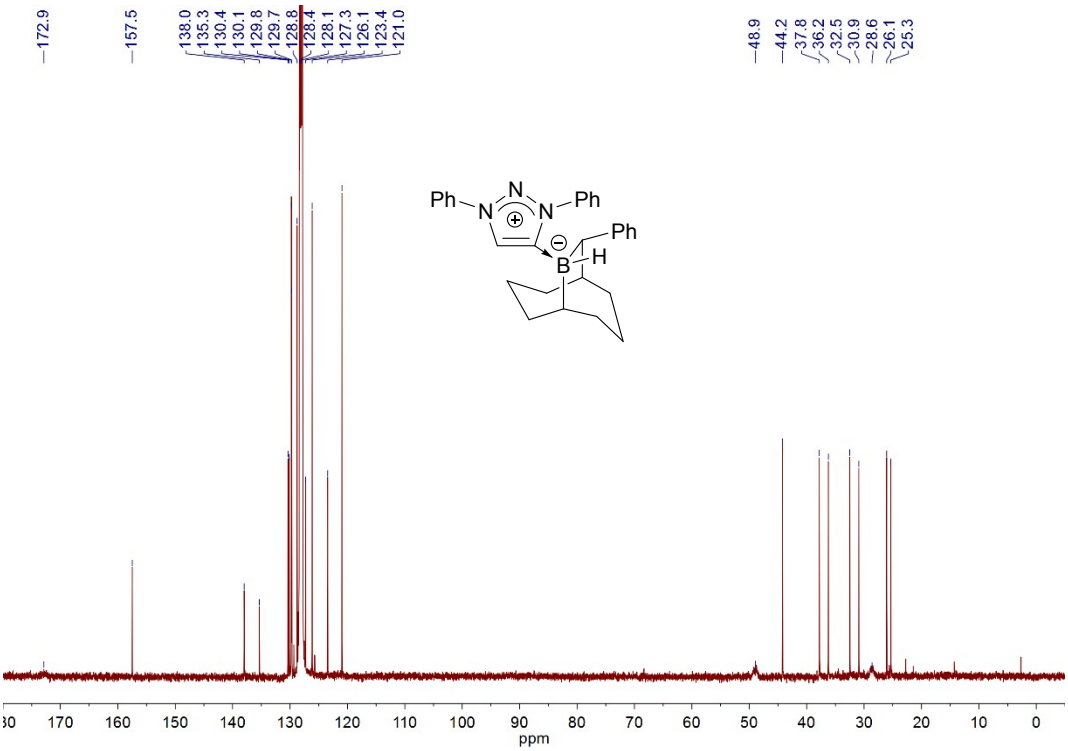
^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **28**



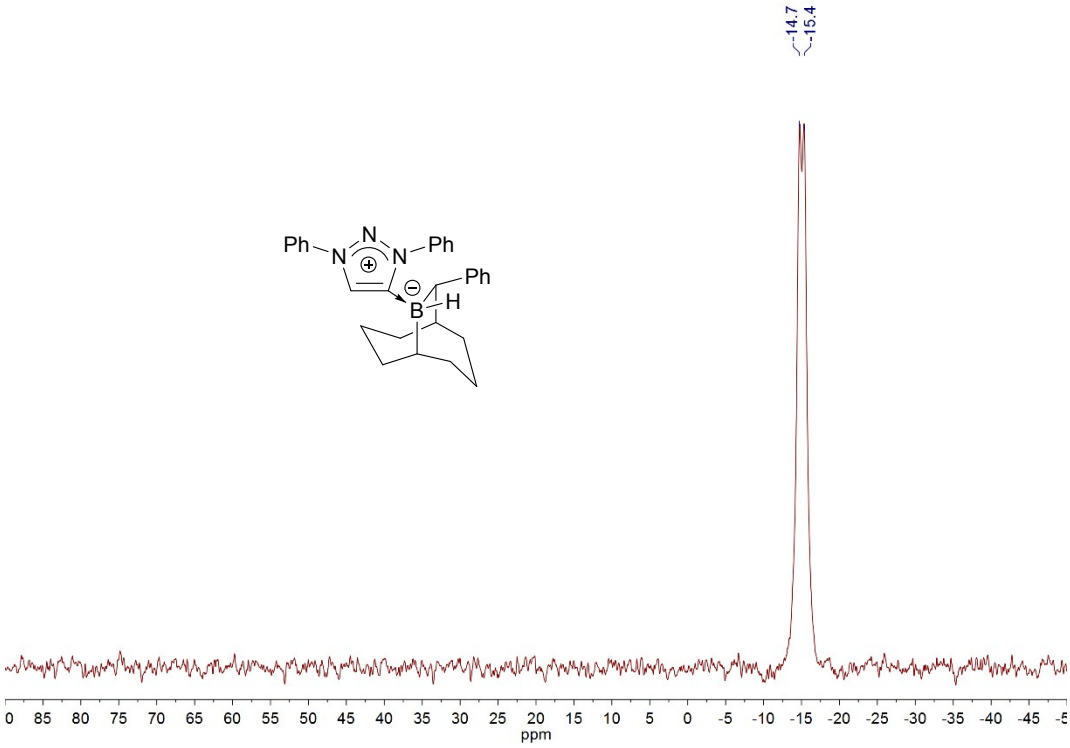
^{1}H NMR (600 MHz, C_6D_6, 298 K) spectrum of **29**



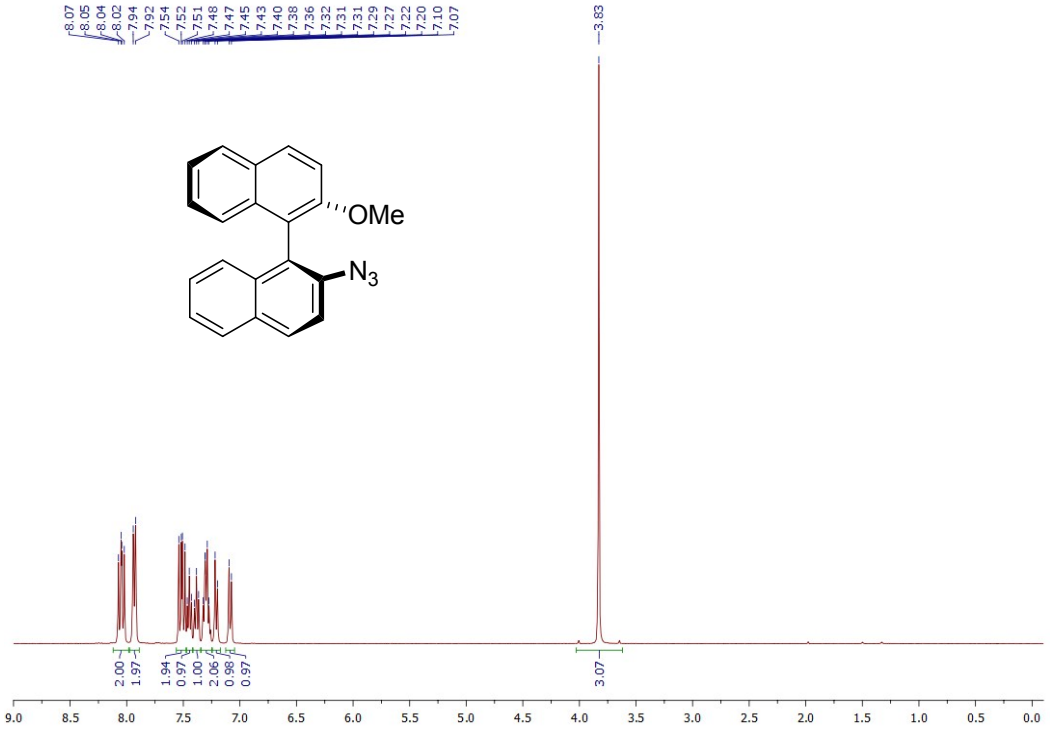
^{13}C NMR (125 MHz, C_6D_6, 298 K) spectrum of **29**



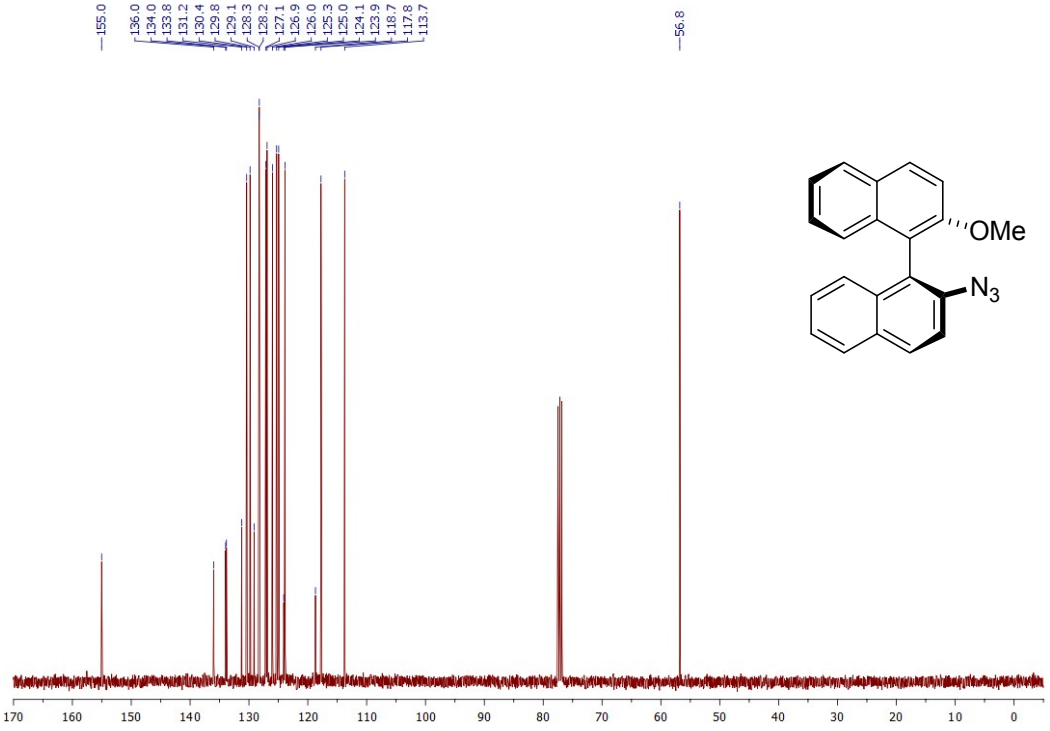
^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of **29**



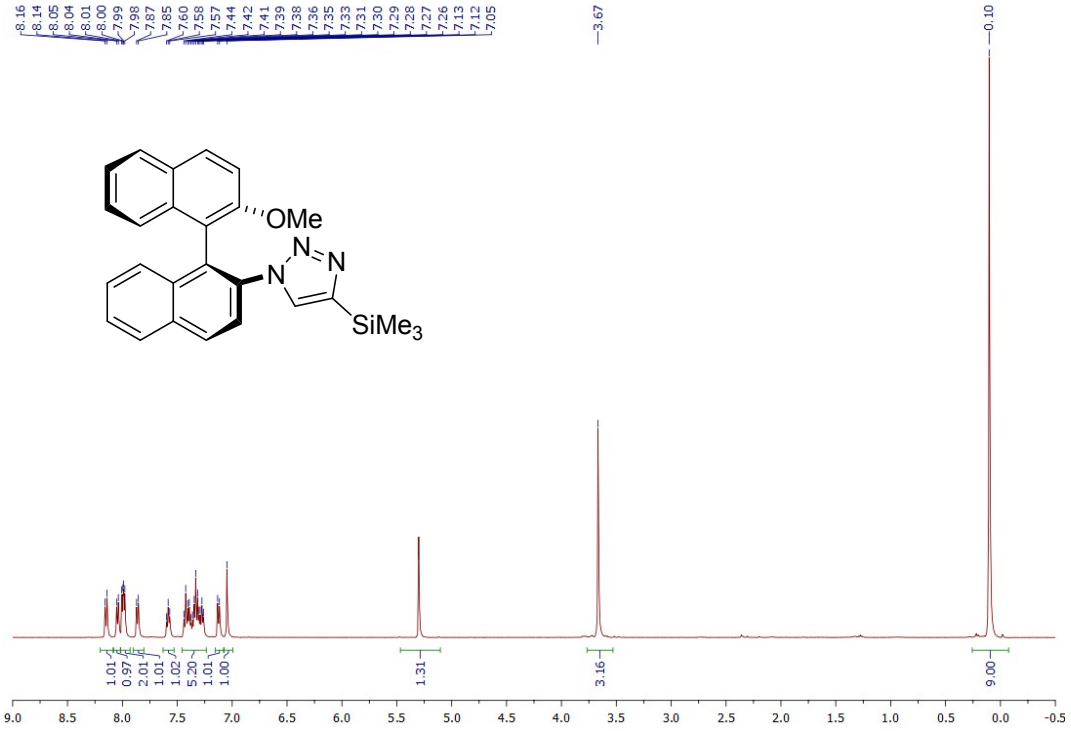
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **30**



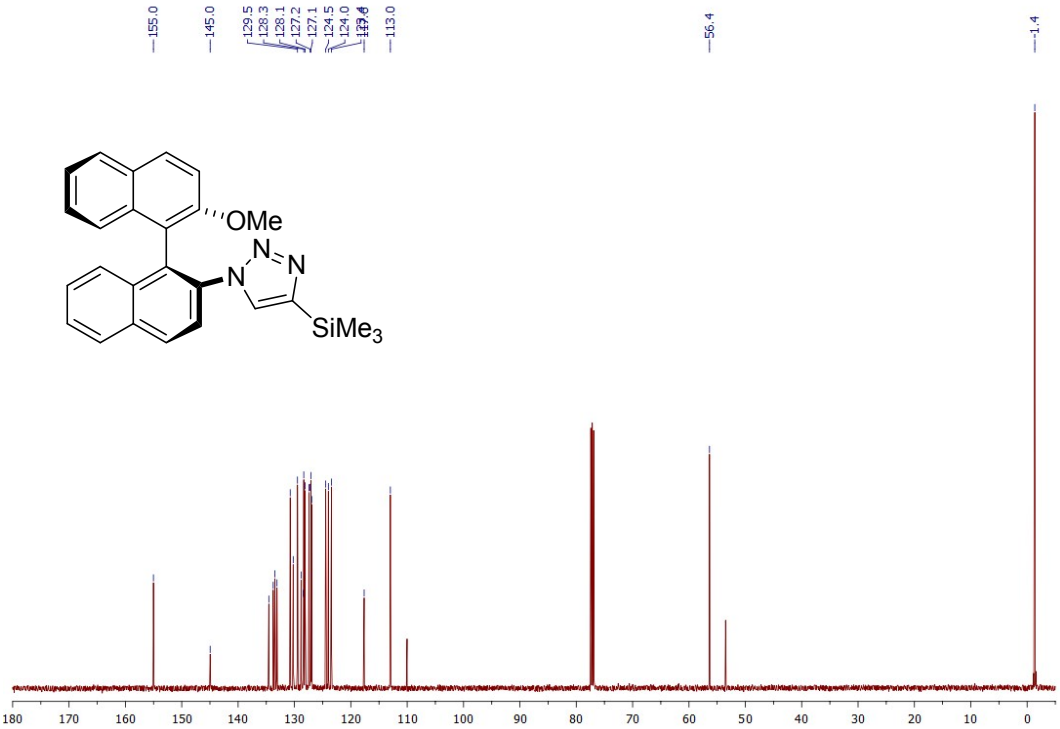
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **30**



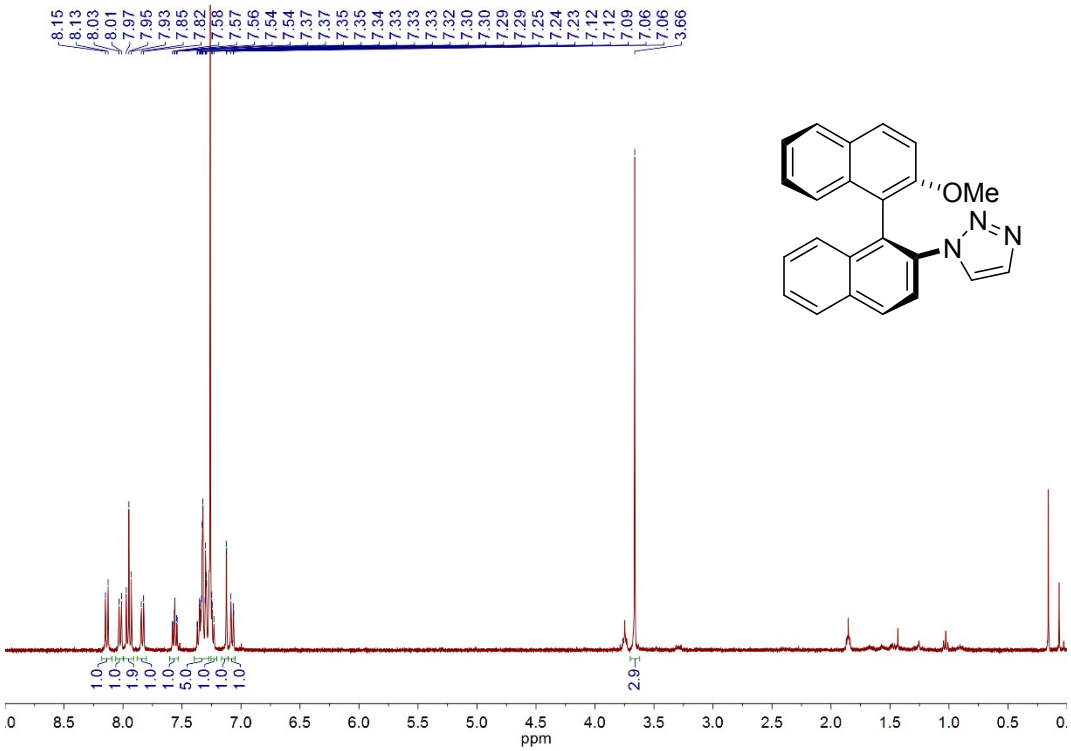
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **31**



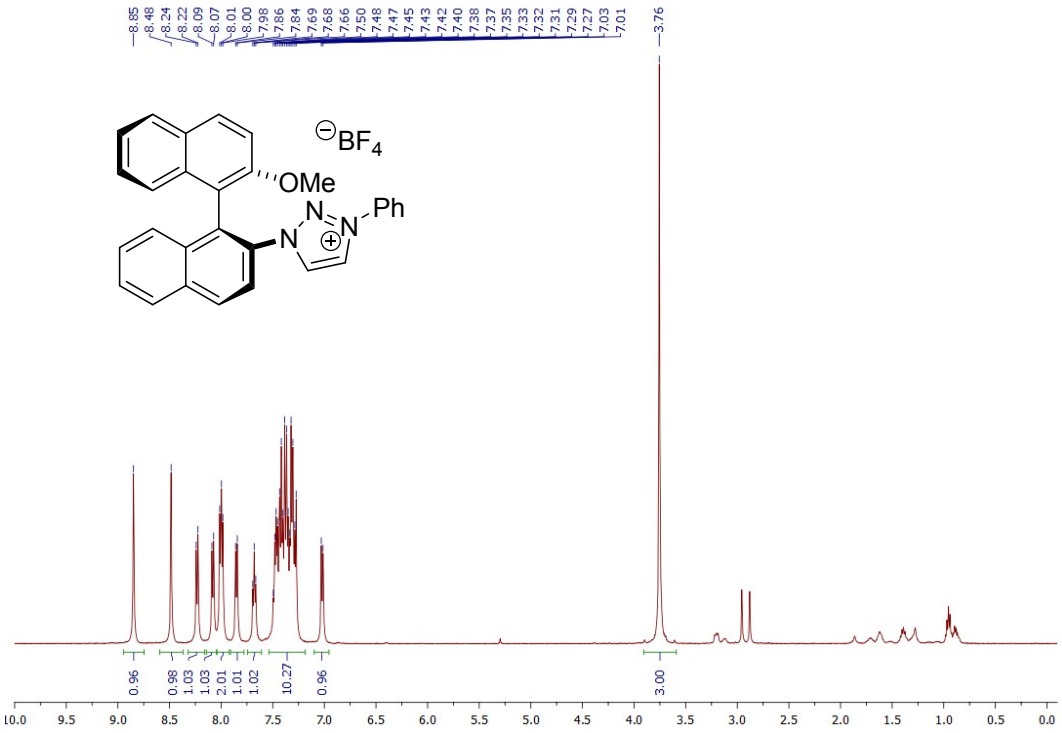
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) spectrum of **31**



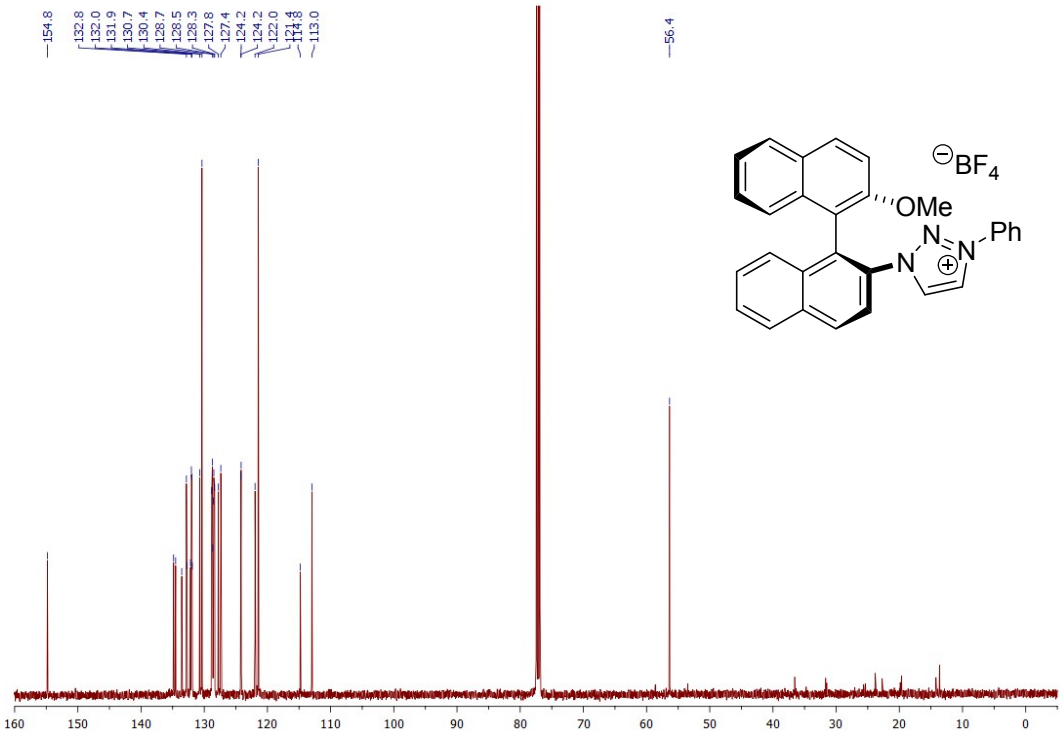
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **32**



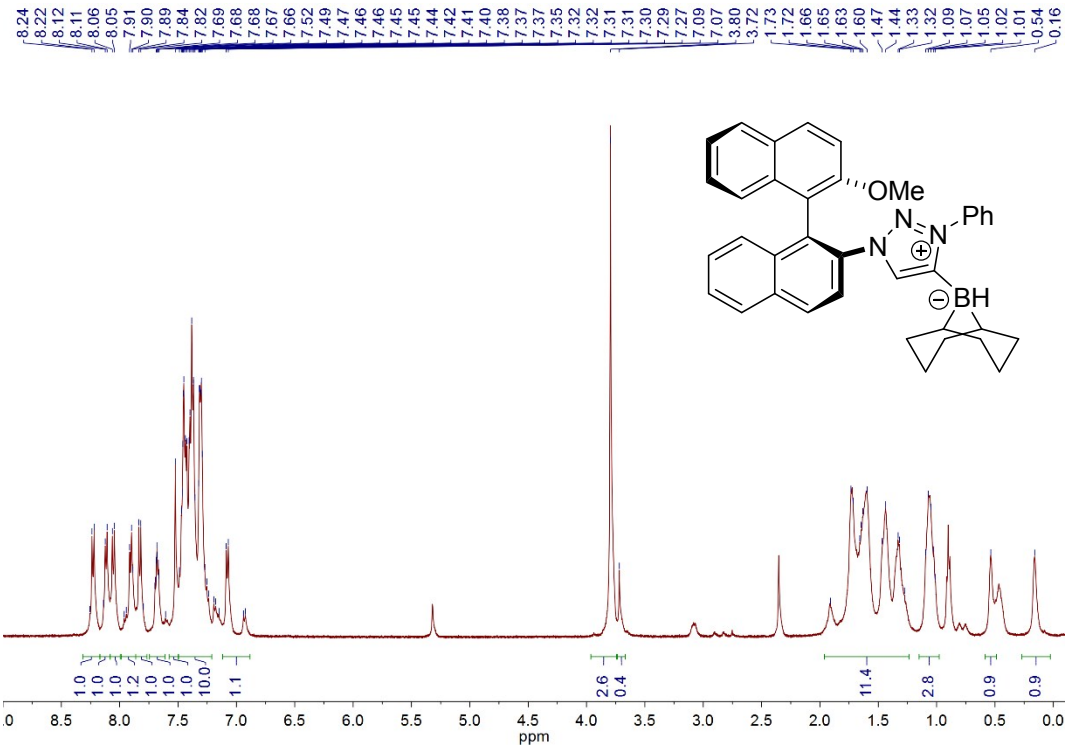
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **33**



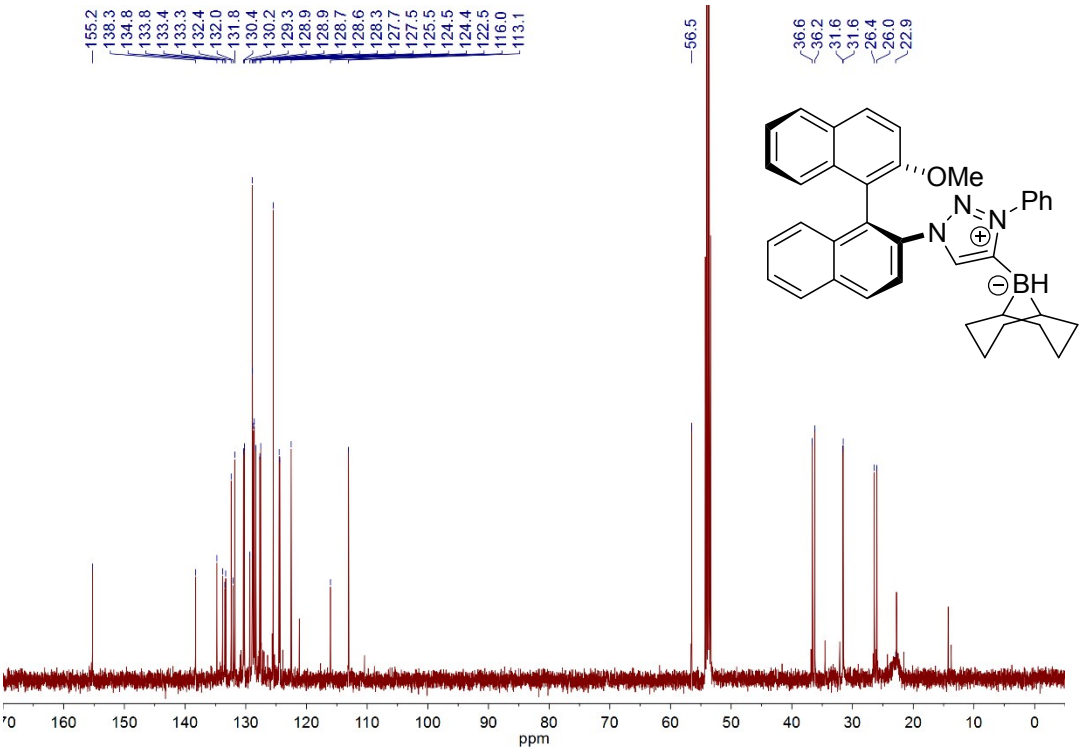
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of **33**



^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **34a**



^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) spectrum of **34a**



^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of **34a**

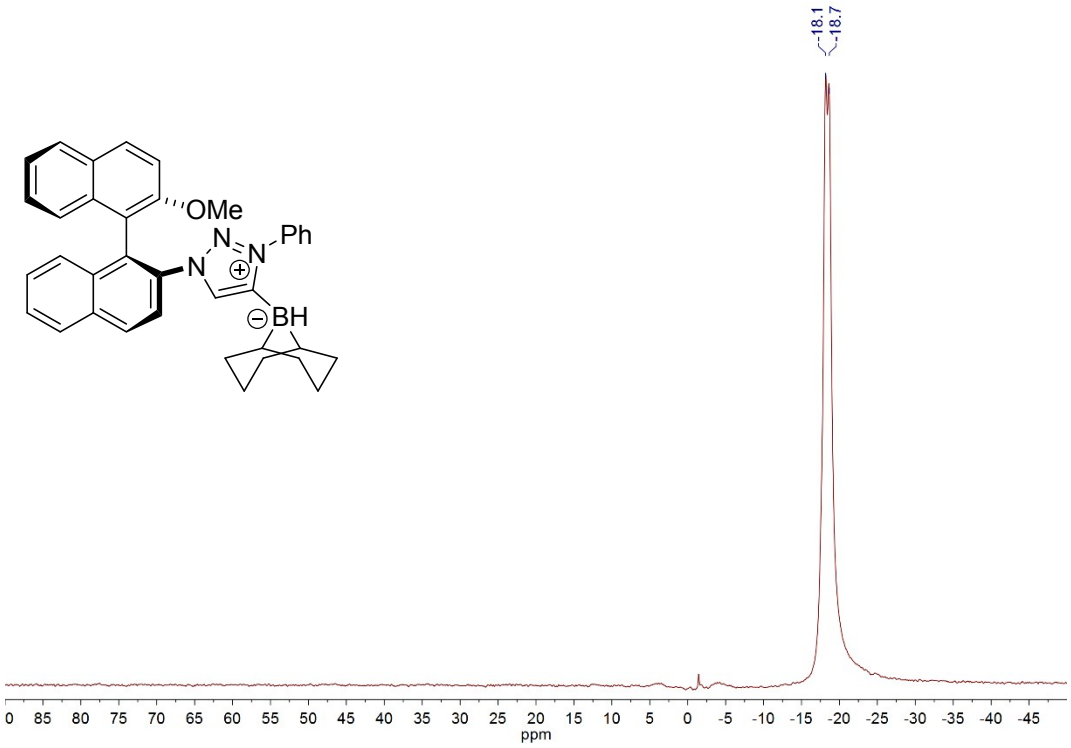
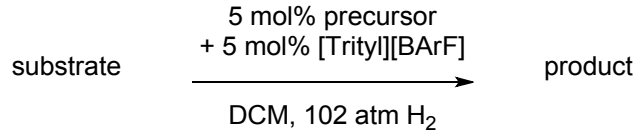
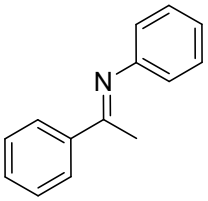
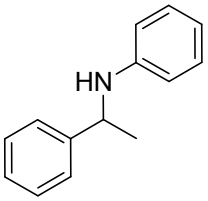
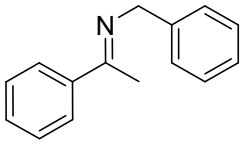
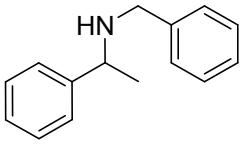
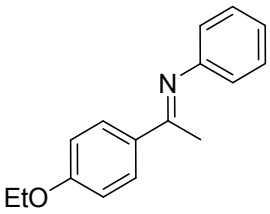
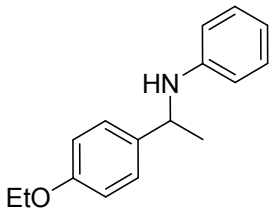
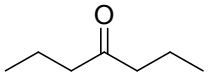
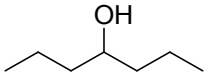
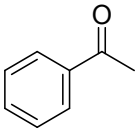
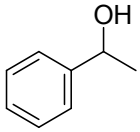


Table for catalytic hydrogenations of **20**, **21, 23**, **24**, **25**, **26**, **27**, **28**, and **34**



Entry	Substrate	Precursor	t (h)	Temp.	Product	Yield (%)	e.e.
1		20	24	r.t.		100	7
2		20	6	r.t.		88	9
3		20	3	r.t.		50	12
4		20	12	0 ºC		94	1
5		20	3	50 ºC		71	8
6		21	24	r.t.		3	5
7		21	3	50 ºC		6	7
8		23	24	r.t.		0	-
9		23	48	r.t.		0	-
10		24	4	r.t.		55	12
11		24	20	-30		5	20
12		24[a]	24	25		0	-
13		24[b]	24	25		12	15
14		25	24	-30		<5	8
15		26	4	25		47	13
16		26	24	25		5	13
17		27	20	-30		<5	-
18		28	4	25		0	-
19		28	20	-30		0	-
20		34	18	25		100	6
10		20	6	r.t.		0	-
11		20	6	r.t.		91	11
12		20[c]	24	r.t.		0	-
13		20[c]	24	70 ºC		0	-
14		21[c]	24	r.t.		0	-
15		21[c]	24	70 ºC		0	-
16		20	48	r.t.		0	-
17		23	48	r.t.		0	-

Carried out in [a] toluene, [b] chlorobenzene, [c] diethyl ether