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Electronic Supplementary Information for the article

Catalytic insertion of nitrenes into B–H bonds

Nikita M. Ankudinov, Nikita V. Alexeev, Evgeniya S. Podyacheva,
Denis A. Chusov, Konstantin A. Lyssenko, Dmitry S. Perekalin

Table of Contents

General Information

Unless stated otherwise, all reactions were carried out under argon in flame-dried glassware. The solvents used for the reactions were purified using MBraun Solvent Purification System and were stored under argon. Other solvents – benzene, chlorobenzene (PhCl), 1,2-difluorobenzene (o-DFB), 1,2-dichlorobenzene (o-DCB), chloroform, 1,1,1-trifluorotoluene ($PhCF_3$) and hexafluoroisopropanol (HFIP) were purchased from the local suppliers and used as received. All reagents were obtained from commercial sources and used without further purification. Starting materials (borane adducts **1**, sulfonamides **5** and sulfonates **6**) were prepared following modified literature procedures (see below for details). Macherey-Nagel silica gel 60 (230–400 mesh) was used for column chromatography, for thin layer chromatography (TLC) analysis either Macherey-Nagel POLYGRAM SIL G/UV_{254} pre-coated polyester TLC plates (0.2 mm) or Sorbfil TLC-A-UV plates (0.09-0.12 mm) were used. NMR spectra were measured on Bruker Avance 300/400/600/800 and Varian Inova 400 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS (^{1}H and ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B) or $CFCl_3$ (^{19}F), coupling constants (*J*) are given in Hz. High-resolution mass spectra were recorded on SCIEX TripleTOF 5600+ instrument using electrospray ionization (ESI). Interface capillary voltage was set to 5500 V in a positive ion mode and to 4500 V in a negative mode with mass range from m/z 100 to 3000 Da; external or internal calibration was done with the Electrospray Calibrant Solution (Fluka). Molecular ions in the spectra were analyzed and matched with the appropriately calculated m/z and isotopic profiles in the LabSolutions v.5.114 program. IR spectra (KBr pellets) were measured on a Shimadzu IR Prestige 21 FT-IR Spectrophotometer. Enantiomeric excess values of the insertion products were measured using Shimadzu HPLC equipped with Daicel Chiralpak IB-3 or IJ-3 (both are 4.6 × 150 mm) columns and diode array detector; flow rate 1 mL/min was adjusted in all experiments.

Synthesis of Substrates

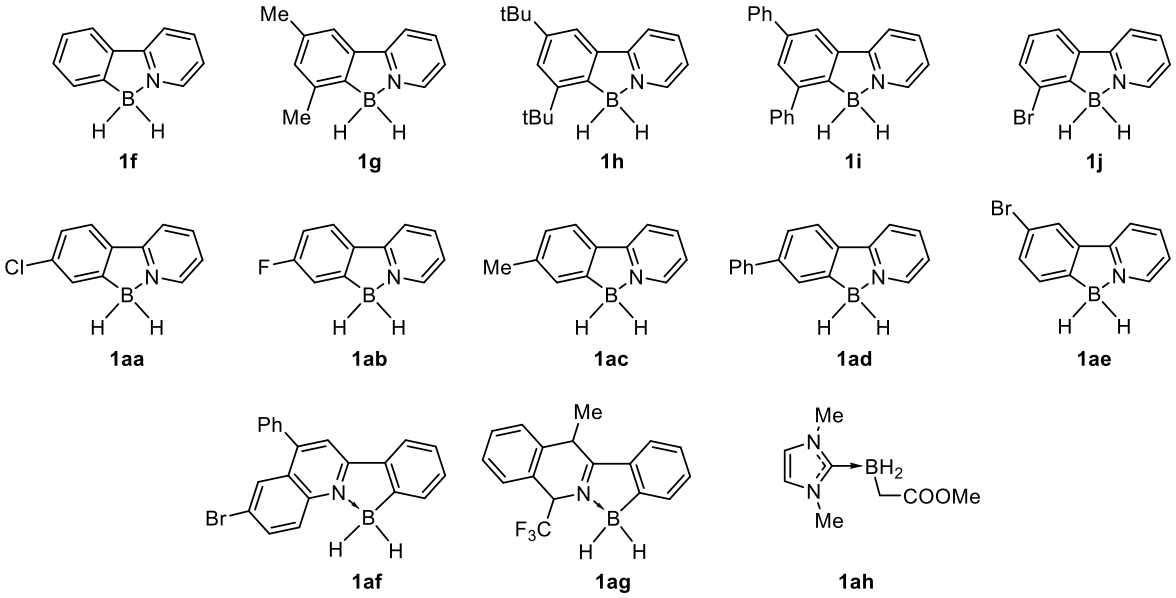
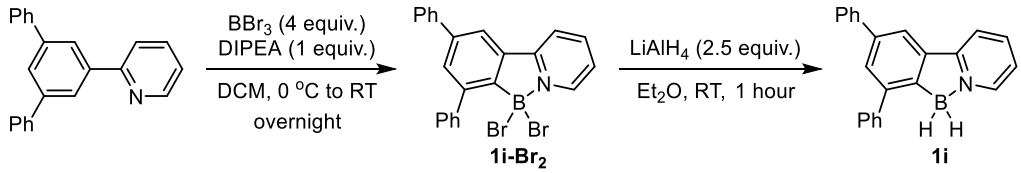


Fig. S1. List of boranes used in this study. All aryl-pyridine boranes were synthesized following to the general literature procedure.[1] Compounds **1i**, **1af**, **1ag** are new, other substrates were reported elsewhere.[2,3] Carbene-borane **1ah** was synthesized according to the literature procedure.[4,5]

Synthesis of 2-(2-boraneyl-3,5-diphenylphenyl)pyridine (**1i**)



CAUTION! BBr_3 is highly moisture sensitive and readily decomposes in air with an evolution of HBr vapors. It should be handled in a well-ventilated hood. An exceptional care must be taken during the quenching step.

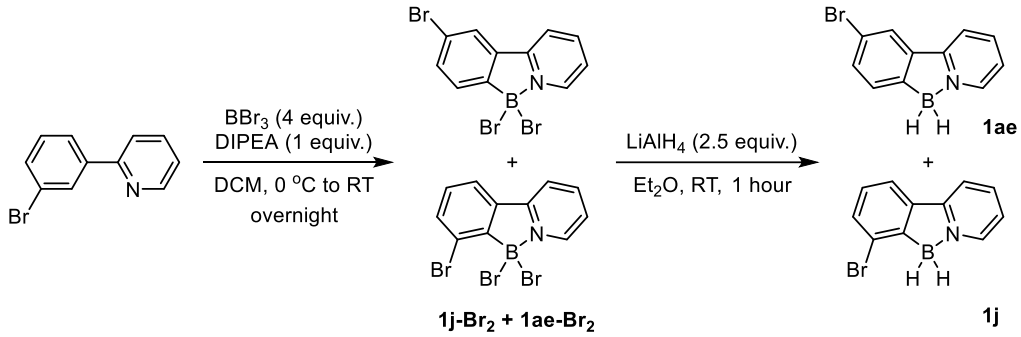
An oven-dried 25 ml Schlenk flask was charged with 2-(3,5-diphenylphenyl)pyridine (227 mg, 0.74 mmol), DIPEA (95.5 mg, 129 µL, 0.74 mmol, 1 equiv.) and DCM (2 ml). The reaction mixture was cooled with an ice-bath and solution of BBr_3 in DCM (3 ml, 1.0M in DCM) was added dropwise in argon flow. After being stirred overnight at room temperature, the mixture was poured to a saturated aqueous K_2CO_3 solution dropwise to quench an excess of BBr_3. After stirring for 10 minutes the mixture was diluted with an additional DCM (10 ml) and transferred to a separatory funnel. The organic phase was decanted and the aqueous one was extracted with an additional DCM (2 x 10 ml). The combined organic washings were dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting yellow solid (345 mg, 98% crude yield) was dried in vacuum and used for the next step without further purification.

An oven-dried 50 ml Schlenk flask was charged with dibromide **1i-Br_2** (345 mg, 0.74 mmol) and Et_2O (20 ml) to give a suspension. Then freshly purified $LiAlH_4$ (70.3 mg, 1.85 mmol, 2.5 equiv.) was added in argon flow in one portion (cooling is not necessary on small scales). *With other phenylpyridines, the suspension usually dissolves*

since the products are soluble in ether unlike the starting dibromides. However, this particular substrate poorly dissolves in ether, so a yellow precipitate gradually forms. After being stirred for 1 hour, water (4 ml) was carefully added dropwise. The resulting mixture was filtered through Celite and the filter cake was thoroughly washed with DCM. The solution was dried over Na_2SO_4, filtered and concentrated in vacuum. The crude product was purified by flash column chromatography (hexane/DCM 1:1) to give **1i** as a white solid in 78% overall yield (186 mg).

R_f (Hexane/DCM 2:1): 0.25 **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 8.80 (d, *J* = 5.6 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 1.5 Hz, 1H), 8.27 (t, *J* = 7.8 Hz, 1H), 8.03 – 7.96 (m, 2H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.61 (ddd, *J* = 7.3, 5.8, 1.1 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.43 – 7.30 (m, 2H), 3.69 (br, 2H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -8.0. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 158.7, 144.7, 144.2, 143.9, 142.1, 141.1, 140.4, 139.6, 129.7, 129.1, 129.98, 128.96, 128.1, 127.9, 127.7, 123.0, 120.2, 119.7. **HRMS** (ESI-TOF, m/z) calcd for $C_{23}H_{17}BN$ $[M - H]^+$: 318.1454; Found: 318.1458.

Synthesis of 2-(2-boraneyl-3-bromophenyl)pyridine (**1j**) and 2-(2-boraneyl-5-bromophenyl)pyridine (**1ae**)



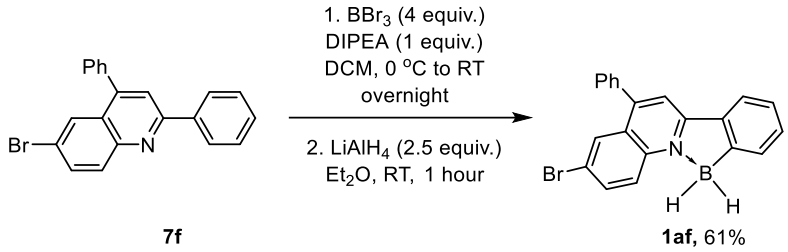
*Synthesis of both **1j** and **1ae** was reported previously.*[2] *However, no details were given on the separation of these isomers.* An oven-dried 25 ml Schlenk flask was charged with 2-(3-bromophenyl)pyridine (362 mg, 1.547 mmol), DIPEA (200 mg, 269 µL, 1.547 mmol, 1 equiv.) and DCM (2 ml). The reaction mixture was cooled with an ice bath and solution of BBr_3 in DCM (8 ml, 1.0M in DCM) was added dropwise in argon flow. After being stirred overnight at room temperature, the mixture was poured to a saturated aqueous K_2CO_3 solution dropwise to quench an excess of BBr_3. After stirring for 10 minutes the mixture was diluted with additional DCM (10 ml) and transferred to a separatory funnel. The organic phase was decanted and the aqueous one was extracted with DCM (2 x 50 ml). The combined organic washings were dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting yellow solid (450 mg, 72% crude yield) was dried in vacuo and used for the next step without further purification as a mixture of two isomers.

An oven-dried 50 ml Schlenk flask was charged with the mixture of **1j-Br$_2$** and **1ae-Br$_2$** (450 mg, 1.12 mmol) and Et_2O (20 ml) to give a suspension. Then freshly purified $LiAlH_4$ (106 mg, 2.8 mmol, 2.5 equiv.) was added in argon flow in one portion. After being stirred for 1 hour almost all solids dissolved and water (10 ml) was carefully added dropwise. The resulting mixture was filtered through Celite and the filter cake was thoroughly washed with DCM. The solution was dried over Na_2SO_4, filtered and concentrated in vacuo. The mixture was purified by column chromatography (gradient elution with hexane/DCM 5:1 to 2:1) to give the p-substituted isomer **1ae** as a first band in 22% yield (62 mg) and then the o-substituted product **1j** as a second band in 59% yield (162 mg). Analytical data are consistent with previously reported.

2-(2-boraneyl-5-bromophenyl)pyridine (**1ae**): **R_f** (Hexane/DCM 2:1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 5.7 Hz, 1H), 8.05 – 7.91 (m, 3H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 6.6 Hz, 1H), 3.35 (br, 2H).

2-(2-boraneyl-3-bromophenyl)pyridine (**1j**): R_f (Hexane/DCM 2:1): 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 5.7 Hz, 1H), 8.05 – 7.91 (m, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 6.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 3.39 (br, 2H).

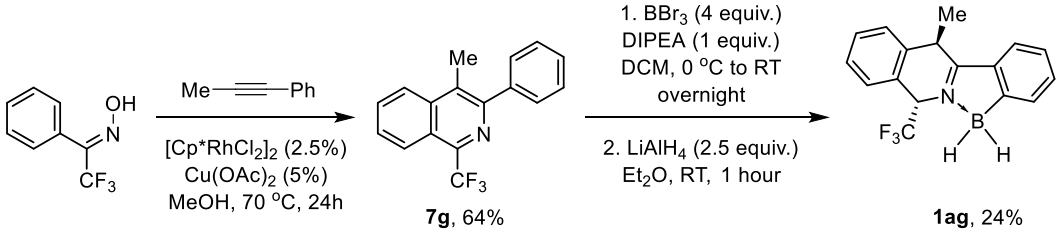
Synthesis of 2-(2-boraneylphenyl)-6-bromo-4-phenylquinoline (**1af**)



Starting quinoline **7f** was prepared from *p*-bromoaniline, benzaldehyde and phenylacetylene using $Cu(OTf)_2$ as catalyst according to the literature procedure.[6] It was then converted into borane **1af** following the general procedure[1] as described above for **1i**. Yield: 61% yield (170 mg from 0.74 mmol pf **7f**).

R_f (Hexane/DCM 1:1): 0.5. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 9.1 Hz, 1H), 8.04 (s, 1H), 7.97 (s, 1H), 7.97 – 7.85 (m, 3H), 7.72 – 7.53 (m, 5H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 3.69 (br, 1H). **^{11}B NMR** (128 MHz, $CDCl_3$): δ -9.6. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.8, 152.0, 141.2, 137.6, 136.8, 136.2, 135.3, 131.2, 130.4, 129.8, 129.5, 129.2, 126.9, 125.5, 125.4, 122.7, 121.1, 117.0. **HRMS** (ESI-TOF, m/z) calcd for $C_{22}H_{16}B^{79}BrNO^+$ $[M+MeOH-H_2]^+$: 400.0503, found: 400.0495; calcd for $C_{23}H_{20}B^{79}BrNO_2^+$ $[M+2MeOH+H-2H_2]^+$: 432.0765, found: 432.0759.

Synthesis of 3-(2-boraneylphenyl)-4-methyl-1-(trifluoromethyl)-1,4-dihydroisoquinoline (**1ag**)



7g was prepared following the modified literature procedure.[7] An oven-dried 10 ml Schlenk flask was filled with argon and charged with 2,2,2-trifluoro-1-phenylethanone oxime (255 mg, 1.35 mmol), prop-1-yn-1-ylbenzene (3.4 mmol, 430 µL, 2.5 equiv.), $[Cp^*RhCl_2]_2$ (20.8 mg, 0.034 mmol, 2.5 mol%), $Cu(OAc)_2 \times H_2O$ (14 mg, 0.068 mmol, 5 mol%) and dry MeOH (3 ml). To the resulting solution 3Å MS were added and it was heated to 75 °C (oil bath temp.) with vigorous stirring for 24 h. The reaction mixture was filtered through Celite and the filter cake was thoroughly washed with DCM. Then 20 ml of water was added to the filtrate, mixture was thoroughly shaken in a separatory funnel and the organic layer was separated. The aqueous phase was extracted with an additional DCM (3 × 15 ml). Combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography (gradient elution with Hexane/DCM 10:1 to 2:1) to give **7g** as a white solid in 64% yield (247 mg).

R_f (Hexane/DCM 2:1): 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.40 (m, 1H), 2.75 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −62.44. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.1, 144.0 (q, *J* = 33.1 Hz), 140.2, 137.7, 130.8, 130.2, 128.5, 128.4, 128.2, 128.0, 125.1 (q, *J* = 2.7 Hz), 124.6, 123.2, 122.5 (q, *J* = 276.2 Hz), 16.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{13}F_3N^+$ $[M + H]^+$: 288.0995; Found: 288.0989.

1ag was prepared following the general procedure from 0.87 mmol of isoquinoline **7g** in 24% yield (61 mg). Final reduction by $LiAlH_4$ was apparently accompanied by reduction of the nitrogen heterocycle. This was clearly indicated by appearance of two quartet signals due to CH groups at 4.7 and 5.7 ppm. It was additionally confirmed by ^{1}H-^{13}C HSQC and HMBC spectra of the insertion product **2ag** (vide infra). Compound **1ag** was isolated as a single isomer, most probably with trans-position of CH_3 and CF_3 groups. However, cis-arrangement cannot be excluded. So far, the attempts to establish configuration by NOESY NMR did not give unambiguous results. **R_f** (Hexane/DCM 2:1): 0.37. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.9 (dd, *J* = 14.2, 7.6 Hz, 2H), 7.5 (t, *J* = 7.4 Hz, 1H), 7.5 (d, *J* = 7.4 Hz, 1H), 7.5 – 7.3 (m, 4H), 5.7 (q, *J* = 7.1 Hz, 1H), 4.7 (q, *J* = 7.5 Hz, 1H), 3.24 (br, 2H), 1.8 (d, *J* = 7.5 Hz, 3H). **^{11}B NMR** (128 MHz, $CDCl_3$): δ -7.28. **^{19}F NMR** (376 MHz, $CDCl_3$): δ −70.47 (t, *J* = 5.9 Hz).**^{13}C NMR** (101 MHz, $CDCl_3$): δ 180.6, 137.4, 135.7, 131.8, 130.2, 130.0, 128.9, 127.8, 127.6, 125.3, 125.2, 124.4, 123.14 (q, *J* = 283.5 Hz), 61.8 (q, *J* = 31.6 Hz), 35.0, 22.4 (q, *J* = 2.8 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{14}BF_3N^-$ $[M - H]^-$: 300.1177; Found: 300.1180.

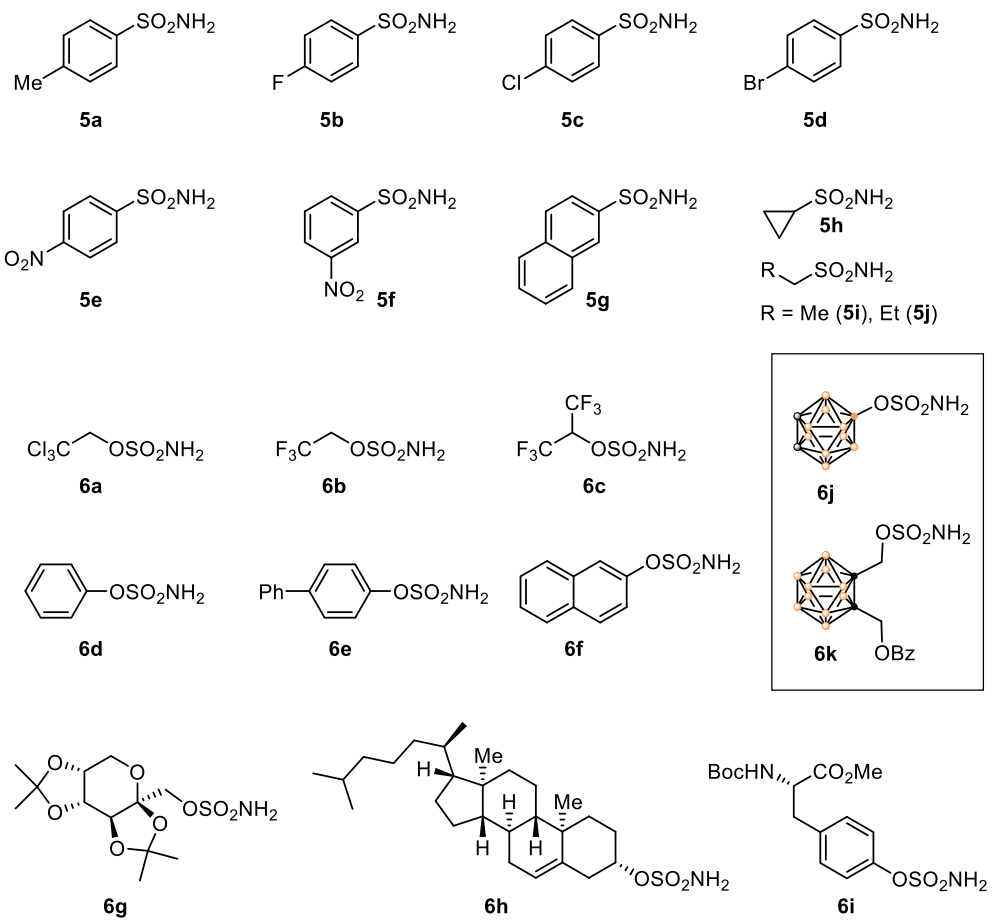
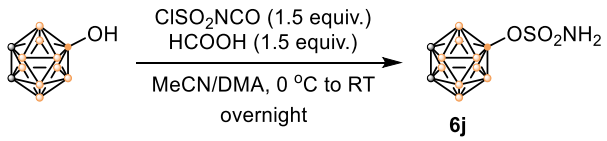
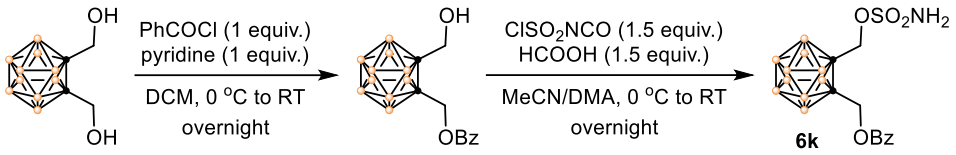


Fig. S2. List of sulfonamides **5** and sulfonates **6** used in this study. Compounds **6j** and **6k** are the new ones, other substrates were reported elsewhere. Sulfonamides **5** were prepared starting from corresponding sulfonyl chlorides, sulfonates **6** were synthesized starting from corresponding alcohols (see below for examples). Compounds **6g**, **6h** and **6i** were prepared using hexafluoroisopropyl sulfamate.[8]



In an oven-dried 10 ml Schlenk flask in argon flow chlorosulfonyl isocyanate (212 mg, 131 µL, 1.5 mmol) was added. The flask was cooled in an ice-bath and then formic acid (69 mg, 57 µl, 1.5 mmol) was carefully added. The mixture solidified within 5 minutes. The solid was redissolved in MeCN (1 ml) and was left to stir for 3 hours at ambient temperature. Then the mixture was cooled again and 9-hydroxy-o-carborane[9] (161 mg, 1 mmol) in DMA (1 ml) was added dropwise. The resulting solution was gradually warmed up and stirred overnight, diluted with water (10 ml), extracted with EtOAc (3 x 10 ml), washed with saturated $NaHCO_3$ (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (DCM/EA 10:1) to give **6j** as viscous colorless oil, which quickly solidified upon trituration with n-pentane (63% yield, 152 mg).

R_f (DCM/EA 10:1): 0.63 (K_2PtCl_4 + HCl methanolic stain). **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 6.36 (s, 2H, -NH_2), 4.48 (s, 2H), 2.91 – 1.35 (m, 9H). **^{11}B{^{1}H} NMR** (128 MHz, $(CD_3)_2CO$): δ 9.9 (1B), -4.6 (1B), -10.9 (2B), -15.0 (2B), -16.8 (4B). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 52.6, 44.7. **HRMS** (ESI-TOF, m/z) calcd for $C_2H_{14}B_{10}NO_3S$ $[M + H]^+$: 242.1624; Found: 242.1628.

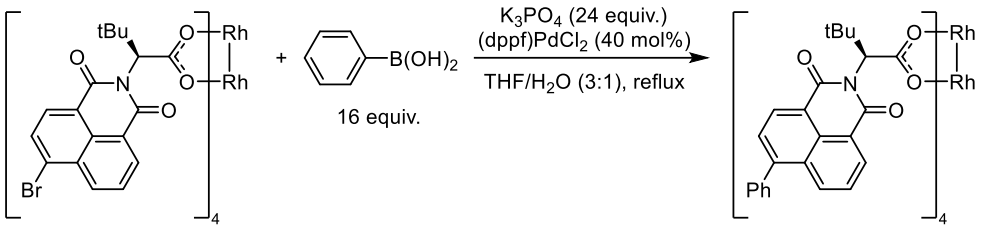


Without exclusion of air an oven-dried 100 ml RBF was charged with 1,2-bis(hydroxymethyl)-*o*-carborane (1030 mg, 5 mmol). Then DCM (50 ml) and pyridine (402 µL, 5 mmol) were added to give a pale-yellow solution. The mixture was cooled in an ice-bath and then benzoyl chloride (585 µL, 5 mmol) was added dropwise. The reaction mixture was stirred at ambient temperature overnight, washed with water (2 x 20 ml) and brine (10 ml), dried over Na_2SO_4 and concentrated on a rotavap to give a viscous pale-yellow oil. The crude product was purified by column chromatography (hexane/DCM 1:1 to DCM, R_f (DCM) = 0.5) to give a mono-benzylation product as white crystals in 47% yield (731 mg), which was used for the next step without characterization.

In an oven-dried 10 ml Schlenk flask in argon flow chlorosulfonyl isocyanate (623 mg, 383 µL, 4.4 mmol) was added. The flask was cooled in an ice-bath and then formic acid (206 mg, 169 µl, 4.48 mmol) was carefully added. The mixture solidified within 5 minutes. The solid was redissolved in MeCN (3 ml) and was left to stir for 4 hours at ambient temperature. Then the mixture was cooled again and mono-benzylated carborane (616 mg, 2 mmol) in DMA (2 ml) was added dropwise. The resulting solution was gradually warmed up and stirred overnight, diluted with water (10 ml), extracted with EtOAc (3 x 10 ml), washed with saturated $NaHCO_3$ (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (gradient elution with DCM to DCM/EtOAc 10:1) to give **6k** as viscous white oil, which quickly solidified upon trituration with n-pentane (63% yield, 195 mg).

R_f (DCM/EA 10:1): 0.69 (K_2PtCl_4 + HCl methanolic stain). **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.09 (d, *J* = 7.1 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.17 (s, 2H, -NH_2), 5.09 (s, 2H), 4.90 (s, 2H), 2.87 – 2.07 (m, 10H). **^{11}B{^{1}H} NMR** (192 MHz, $(CD_3)_2CO$): δ -3.3 (2B), -11.0 (8B). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 165.3, 134.8, 130.6, 129.7, 129.6, 77.6, 76.5, 68.1, 63.5. **HRMS** (ESI-TOF, m/z) calcd for $C_{11}H_{22}B_{10}NO_5S$ $[M + H]^+$: 390.2149; Found: 390.2166.

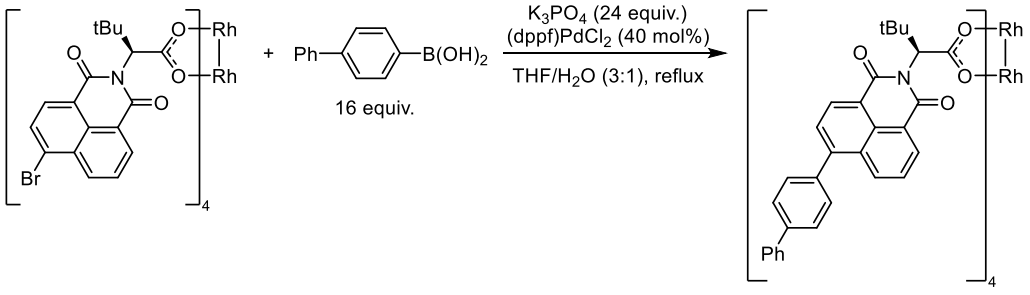
Synthesis of Catalysts



Rh_2[(*S*)-4-Ph-NTTL]$_4$

All Rh_2[(*S*)-4-Ar-NTTL]$_4$ complexes were prepared following the literature cross-coupling protocol.[10] An oven-dried 10 ml Schlenk flask was charged with Rh_2[(*S*)-4-Br-NTTL]$_4$[11] (61.7 mg, 0.035 mmol, 1 equiv.), phenylboronic acid (68 mg, 0.56 mmol, 16 equiv.) and K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.). Then THF/H_2O (6 + 2 ml) were added in an argon flow followed by (dppf)$PdCl_2$ (10 mg, 0.0014 mmol, 40 mol%). The flask was capped and the resulting biphasic system was stirred for 16 hours at 80 °C. After the indicated time the solution was cooled to room temperature and THF was removed under reduced pressure. The residue was diluted with water (20 ml) and extracted with DCM (3 x 10 ml). The organic phases were combined, washed with water (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane/DCM 1:1, then pure DCM, then DCM/EA 50:1) to give a green solid in 61% yield (38 mg). The same reaction on a 3-fold scale (0.105 mmol) afforded the product in 64% yield (118 mg).

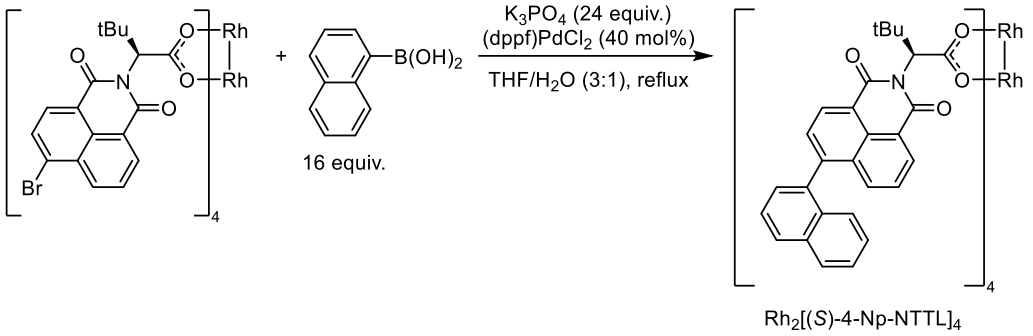
Rh_2[(*S*)-4-Ph-NTTL]$_4$: **R_f** (DCM): 0.52. **^{1}H NMR** (500 MHz, $CDCl_3$): 8.92 – 8.82 (m, 4H), 8.58 – 8.49 (m, 4H), 8.20 – 8.09 (m, 4H), 7.91 – 7.80 (m, 4H), 7.61 – 7.34 (m, 24H), 5.87 (s, 4H), 1.33 (s, 36H). **^{13}C NMR** (126 MHz, $CDCl_3$, *mixture of conformers*): δ 187.4, 165.0, 164.8, 163.3, 163.0, 146.3, 146.0, 139.4, 139.2, 132.5, 132.1, 132.0, 131.9, 131.0, 130.6, 130.1, 129.93, 129.88, 128.7, 128.64, 128.62, 128.57, 128.33, 128.28, 127.6, 127.4, 126.4, 123.3, 123.2, 122.4, 122.1, 62.1, 60.6, 36.3, 31.7, 29.0, 22.8, 21.2, 14.31, 14.27. **HRMS** (ESI-TOF, m/z) calcd for $C_{100}H_{86}N_6O_{16}Rh_2$ [M + 2MeCN]$^+$: 1833.4243; Found: 1833.3326.



Rh_2[(*S*)-4-PhPh-NTTL]$_4$

An oven-dried 10 ml Schlenk flask was charged with Rh_2[(*S*)-4-Br-NTTL]$_4$ (61.7 mg, 0.035 mmol, 1 equiv.), 4-biphenylboronic acid (111 mg, 0.56 mmol, 16 equiv.) and K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.). Then THF/H_2O (6 + 2 ml) were added in an argon flow followed by (dppf)$PdCl_2$ (10 mg, 0.0014 mmol, 40 mol%). The flask was capped and the resulting biphasic system was stirred for 16 hours at 80 °C. After the indicated time the solution was cooled to room temperature and THF was removed under reduced pressure. The residue was diluted with water (20 ml) and extracted with DCM (3 x 10 ml). The organic phases were combined, washed with water (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane/DCM 1:1, then pure DCM, then DCM/EA 50:1) to give a green solid in 53% yield (38.2 mg).

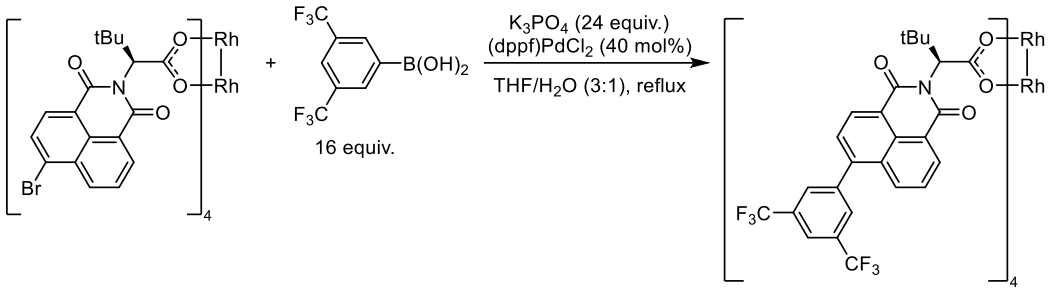
Rh_2[(*S*)-4-PhPh-NTTL]$_4$: **R_f** (Hexane/DCM 1:2): 0.47. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.91 – 8.86 (m, 4H), 8.59 – 8.52 (m, 4H), 8.29 – 8.20 (m, 4H), 7.94 – 7.86 (m, 4H), 7.79 – 7.64 (m, 16H), 7.64 – 7.55 (m, 8H), 7.55 – 7.45 (m, 12H), 7.44 – 7.37 (m, 4H), 5.88 (t, *J* = 4.8 Hz, 4H), 1.34 (s, 36H). **^{13}C NMR** (126 MHz, $CDCl_3$, *mixture of conformers*): δ 187.3, 165.0, 164.8, 163.4, 163.1, 146.0, 145.6, 141.3, 141.2, 140.5, 138.3, 138.2, 132.5, 132.2, 132.0, 131.9, 131.1, 130.6, 130.4, 130.0, 129.9, 129.08, 129.07, 128.8, 128.6, 127.8, 127.7, 127.5, 127.4, 127.3, 126.5, 123.4, 123.3, 122.4, 122.3, 66.1, 62.1, 36.3, 31.1, 29.0, 26.1, 15.4. **HRMS** (ESI-TOF, m/z) calcd for $C_{122}H_{100}N_5O_{16}Rh_2$ $[M + MeCN + H]^+$: 2097.5309; Found: 2097.5324.



Rh_2[(*S*)-4-Np-NTTL]$_4$

An oven-dried 10 ml Schlenk flask was charged with Rh_2[(*S*)-4-Br-NTTL]$_4$ (61.7 mg, 0.035 mmol, 1 equiv.), 1-naphthylboronic acid (96.3 mg, 0.56 mmol, 16 equiv.) and K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.). Then THF/H_2O (6 + 2 ml) were added in an argon flow followed by (dppf)$PdCl_2$ (10 mg, 0.0014 mmol, 40 mol%). The flask was capped and the resulting biphasic system was stirred for 16 hours at 80 °C. After the indicated time the solution was cooled to room temperature and THF was removed under reduced pressure. The residue was diluted with water (20 ml) and extracted with DCM (3 x 10 ml). The organic phases were combined, washed with water (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane/DCM 1:1, then pure DCM, then DCM/EA 50:1) to give a green solid in 53% yield (43.5 mg).

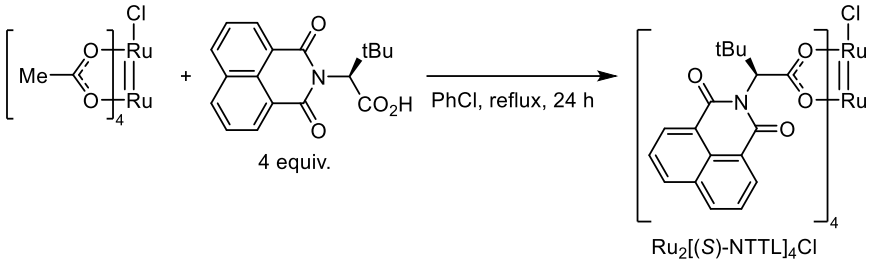
Rh_2[(*S*)-4-Np-NTTL]$_4$: **R_f** (Hexane/DCM 1:2): 0.40. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.98 – 8.87 (m, 4H), 8.62 – 8.50 (m, 4H), 8.23 – 8.08 (m, 4H), 8.00 – 7.67 (m, 20H), 7.65 – 7.36 (m, 16H), 5.89 (s, 4H), 1.35 (s, 36H). **^{13}C NMR** (126 MHz, $CDCl_3$, *mixture of conformers*): δ 187.2, 165.1, 164.9, 163.3, 163.0, 146.3, 145.9, 136.7, 136.6, 133.3, 133.2, 132.1, 132.0, 131.1, 130.6, 130.0, 129.2, 129.0, 128.9, 128.8, 128.28, 128.26, 128.16, 127.9, 127.74, 127.70, 127.6, 126.8, 126.5, 126.4, 123.4, 123.3, 122.5, 122.3, 70.8, 62.2, 36.3, 29.1, 26.1, 22.8, 14.3. **HRMS** (ESI-TOF, m/z) calcd for $C_{114}H_{91}N_5O_{16}Rh_2$ $[M + MeCN]^+$: 1992.4604; Found: 1992.4677.



$Rh_2[(S)\text{-}4\text{-}Ar^F\text{-}NTTL]_4$

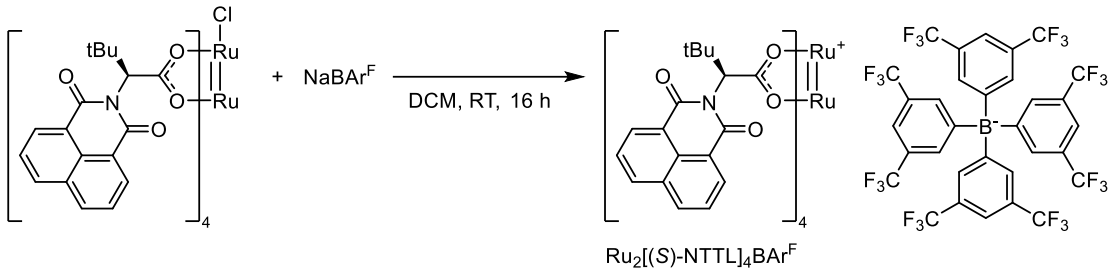
An oven-dried 10 ml Schlenk flask was charged with $Rh_2[(S)\text{-}4\text{-}Br\text{-}NTTL]_4$ (61.7 mg, 0.035 mmol, 1 equiv.), 3,5-bis(trifluoromethyl)phenylboronic acid (143.4 mg, 0.56 mmol, 16 equiv.) and K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.). Then THF/H_2O (6 + 2 ml) were added in an argon flow followed by (dppf)$PdCl_2$ (10 mg, 0.0014 mmol, 40 mol%). The flask was capped and the resulting biphasic system was stirred for 16 hours at 80 °C. After the indicated time the solution was cooled to room temperature and THF was removed under reduced pressure. The residue was diluted with water (20 ml) and extracted with DCM (3 x 10 ml). The organic phases were combined, washed with water (10 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (hexane, then hexane/Et_2O 5:1) to give a green solid in 55% yield (44.5 mg).

$Rh_2[(S)\text{-}4\text{-}Ar^F\text{-}NTTL]_4$: **$R_f$** (Hexane/DCM 1:2): 0.78. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.90 (dd, *J* = 7.3, 3.7 Hz, 4H), 8.61 – 7.87 (m, 4H), 8.05 – 7.87 (m, 20H), 7.70 – 7.58 (m, 4H), 5.84 (s, 1H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$, *mixture of conformers*): δ 187.3, 164.9 – 164.2 (m), 163.0, 162.8, 142.8 – 142.5 (m), 142.4 – 142.1 (m), 134.8, 132.7, 132.3 (q, *J* = 33.4 Hz), 131.9, 131.4, 130.9 – 130.6 (m), 130.7 – 130.3 (m), 130.1, 130.0, 129.6 – 129.4 (m), 129.1, 129.0, 128.7, 128.6, 127.9, 127.5, 126.6, 126.5, 124.4, 124.3, 123.6, 123.5, 122.4, 122.2, 122.1, 120.1, 120.0, 66.2, 62.3, 36.3, 31.7, 29.0, 22.8, 21.1, 15.3, 14.3. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.79, -62.82. **HRMS** (ESI-TOF, m/z) calcd for $C_{106}H_{75}F_{24}N_5O_{16}Rh_2$ $[M + MeCN]^+$: 2336.2969; Found: 2336.2983.



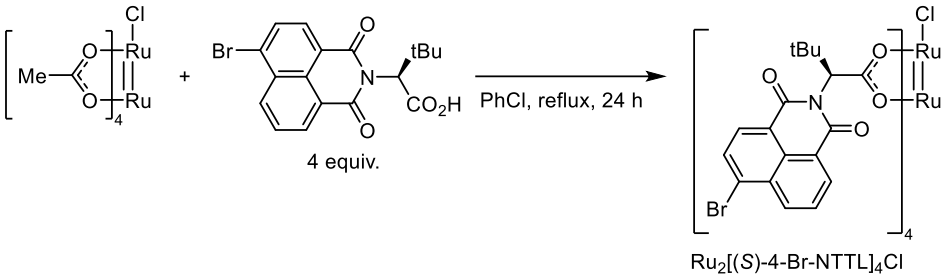
$Ru_2[(S)\text{-}NTTL]_4Cl$

Without exclusion of air an oven-dried 10 ml RBF was charged with $Ru_2(OAc)_4Cl$ (94.7 mg, 0.2 mmol) and *N*-1,8-naphthaloyl-(*S*)-tert-leucine (250 mg, 0.8 mmol, 4 equiv.). Then 4 ml of chlorobenzene was added. A small Hickman distill head was charged with K_2CO_3 (500 mg) and connected to a reflux condenser. The resulting setup was placed on top of the reaction flask and the reaction mixture was brought to reflux (oil bath temp = 165 °C). After being stirred for 24 hours at this temperature flakelike brown precipitate formed. The mixture was concentrated on a rotavap and redissolved in a large amount of DCM/MeOH (10:1) mixture (aprox. 100 ml) and evaporated with a portion of silica gel (***NOTE**: the product poorly dissolves in both chlorobenzene and eluent, dry loading is highly recommended, otherwise a large amount of solvent is required to elute the complex*). The residue was dry loaded on a pre-packed silica column and eluted with DCM and then DCM/MeOH (10:1). Orange fractions were collected, concentrated on a rotavap and dried in vacuo to give beige/dusty rose solid in 73% yield (216 mg). Analytical data are consistent with the previously reported.[12]



$Ru_2[(S)\text{-NTTL}]_4BAr^F$

An oven-dried 10 ml Schlenk flask was charged with $Ru_2[(S)\text{-NTTL}]_4Cl$ (73.9 mg, 0.05 mmol) and DCM (2 ml). To the resulting suspension $NaBAr^F \bullet 3H_2O$ (47 mg, 0.05 mmol) was added in a flow of argon. All solids dissolved within a minute and the resulting orange solution was stirred overnight at ambient temperature. The solution was directly transferred to a pre-packed silica column and the product was eluted with DCM/EtOAc 40:1 as orange band. The solution was concentrated on a rotavap and dried in vacuo to afford mustard-colored solid in 97% yield (112 mg). Analytical data are consistent with the previously reported.[12]



$Ru_2[(S)\text{-4-Br-NTTL}]_4Cl$

Without exclusion of air an oven-dried 10 ml RBF was charged with $Ru_2(OAc)_4Cl$ (94.7 mg, 0.2 mmol) and *N*-4-bromo-1,8-naphthaloyl-(*S*)-tert-leucine (312 mg, 0.8 mmol, 4 equiv.). Then 4 ml of chlorobenzene was added. A small Hickman distill head was charged with K_2CO_3 (500 mg) and connected to a reflux condenser. The resulting setup was placed on top of the reaction flask and the reaction mixture was brought to reflux (oil bath temp = 165 °C). After being stirred for 24 hours at this temperature orange solution formed. The solution was directly transferred to a pre-packed silica column and the product was eluted with DCM/MeOH 60:1. Orange fractions were collected, concentrated on a rotavap and dried in vacuo to give brown solid in 98% yield (350 mg).

$Ru_2[(S)\text{-4-Br-NTTL}]_4Cl$: $\mathbf{R_f}$ (DCM/EA 10:1): 0.82. **HRMS** (ESI-TOF, m/z) calcd for $C_{74}H_{63}Br_4N_5O_{16}Ru_2$ [M - Cl + MeCN]$^+$: 1796.9094; Found: 1796.9081. **IR** (KBr, cm^{-1}): 2958, 1708, 1670, 1589, 1571, 1507, 1482, 1461, 1399, 1367, 1343, 1325, 1299, 1238, 1203, 1180, 1126, 1046, 1020, 997, 948, 909, 850, 786, 750, 732, 721, 708.

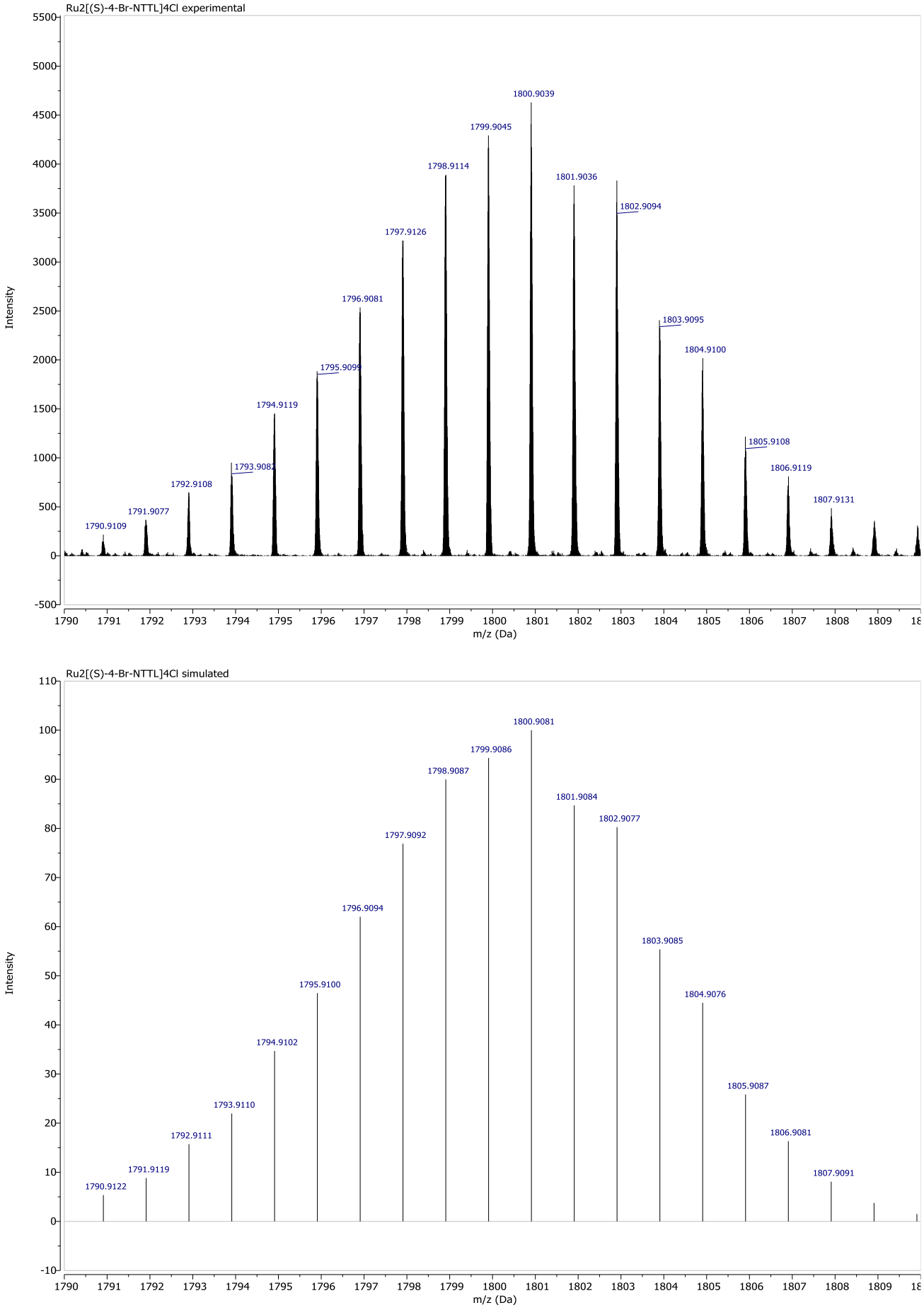
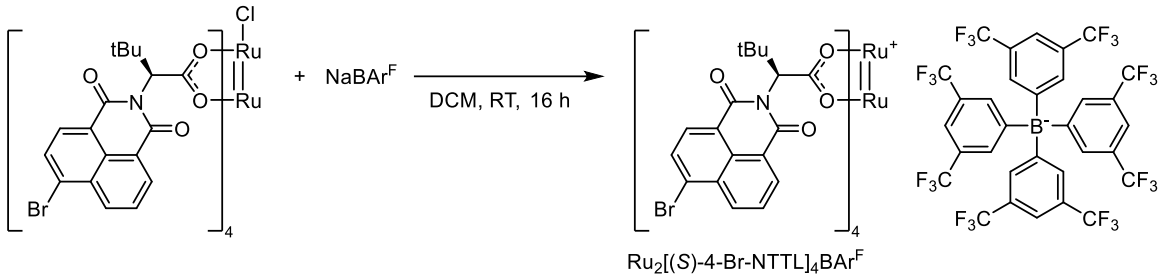


Fig. S3. HRMS of $Ru_2[(S)\text{-4-Br-NTTL}]_4Cl$ (top: observed, bottom: simulated $[M - Cl + MeCN]^+$).



Ru_2[(*S*)-4-Br-NTTL]$_4$$BAr^F$

An oven-dried 10 ml Schlenk flask was charged with Ru_2[(*S*)-4-BrNTTL]$_4$Cl (269 mg, 0.15 mmol) and DCM (5 ml). To the resulting suspension $NaBAr^F$•3H_2O (141 mg, 0.15 mmol) was added in a flow of argon. The solution became slightly lighter in color and was allowed to stir at ambient temperature overnight. The mixture was directly transferred to a pre-packed silica column and the product was eluted with DCM/MeOH 100:1 as orange band. The solution was concentrated on a rotavap and dried in vacuo to afford mustard-colored solid in 98% yield (338 mg).

Ru_2[(*S*)-4-Br-NTTL]$_4$$BAr^F$: **$R_f$** (DCM/hexane 10:3): 0.83. **HRMS** (ESI-TOF, m/z) calcd for $C_{74}H_{63}Br_4N_5O_{16}Ru_2$ [M - BAr^F + MeCN]$^+$: 1796.9094; Found: 1796.9055. **HRMS** (-p ESI, m/z) calcd for $C_{32}H_{12}BF_{24}$ [BAr^F]$^-$: 862.0691; Found 862.0660. **IR** (KBr, cm^{-1}): 2971, 1707, 1670, 1590, 1572, 1507, 1480, 1462, 1414, 1401, 1368, 1354, 1280, 1238, 1180, 1163, 1128, 1046, 1022, 997, 948, 887, 852, 839, 786, 751, 711.

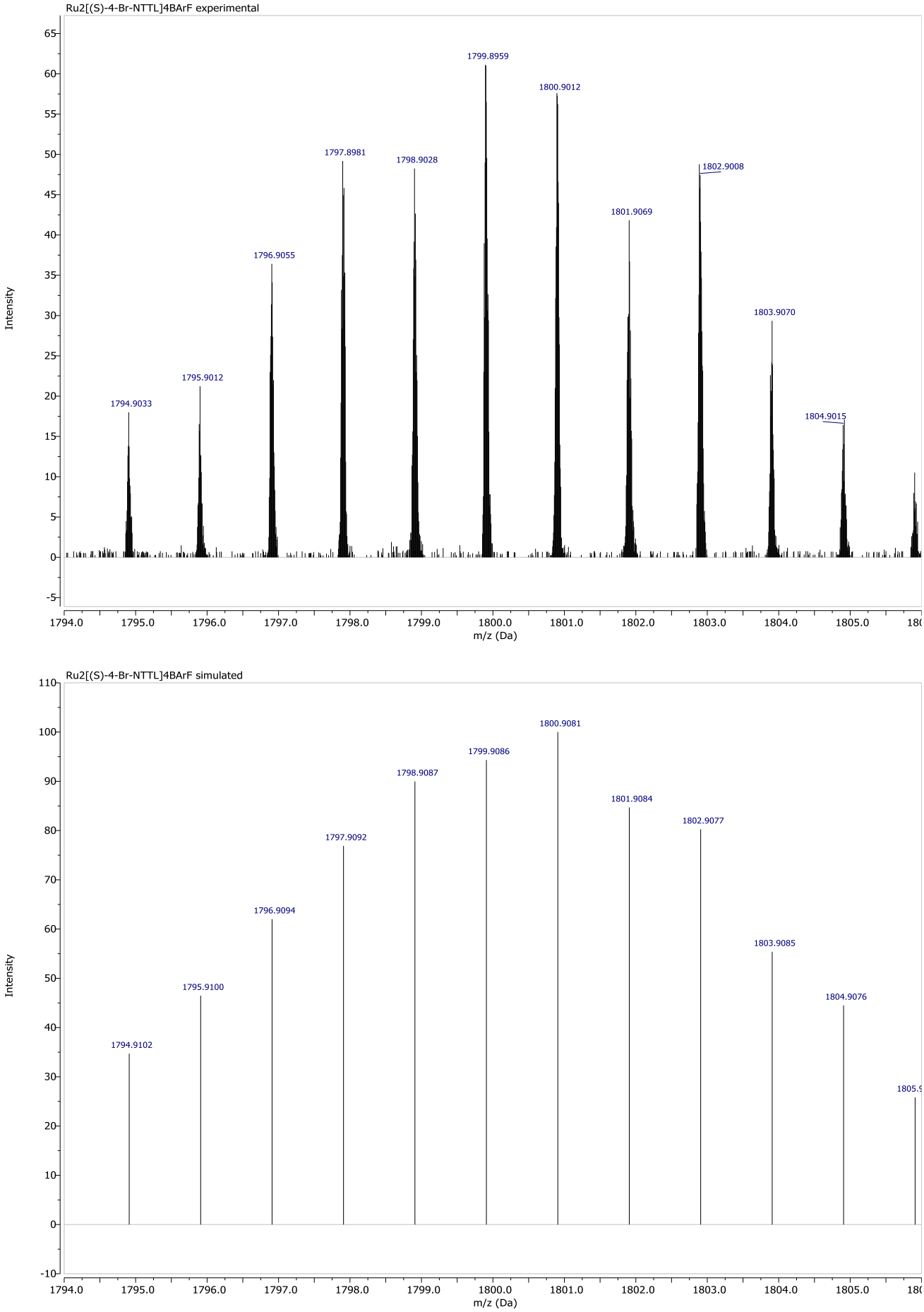
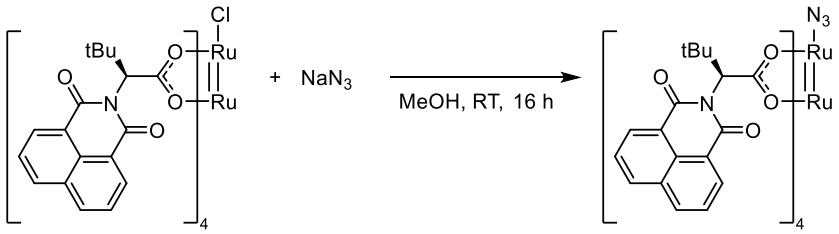


Fig. S4. HRMS of Ru_2[(*S*)-4-Br-NTTL]$_4$BAr^F (top: observed, bottom: simulated [M - BAr^F + MeCN]$^+$).



$Ru_2[(S)\text{-NTTL}]_4N_3$

Without exclusion of air a 10 ml vial was charged with $Ru_2[(S)\text{-NTTL}]_4Cl$ (22.1 mg, 0.015 mmol), sodium azide (9.8 mg, 0.15 mmol, 10 equiv.) and MeOH (2 ml). The mixture was stirred at ambient temperature overnight. The resulting violet solid was filtered and washed with H_2O (2 x 1 ml), MeOH (2 x 1 ml) and cold DCM (1 ml). The precipitate was dried, redissolved in DCM (aprox. 20 ml), transferred to a preweighted storage vial, concentrated on a rotavap and dried in vacuo to afford violet solid in 65% yield (13.7 mg).

$Ru_2[(S)\text{-NTTL}]_4N_3$: **$R_f$** (DCM/EA 10:1): 0.28. **HRMS** (ESI-TOF, m/z) calcd for $C_{72}H_{64}N_4O_{16}Ru_2$ $[M - N_3]^+$: 1442.2434; Found: 1442.2413. **IR** (KBr, cm^{-1}): 2958, **2053**, **2024** (N_3^-), 1705, 1667, 1589, 1481, 1414, 1399, 1377, 1357, 1341, 1300, 1279, 1239, 1180, 1149, 1126, 1112, 1075, 1029, 996, 906, 847, 786, 710.

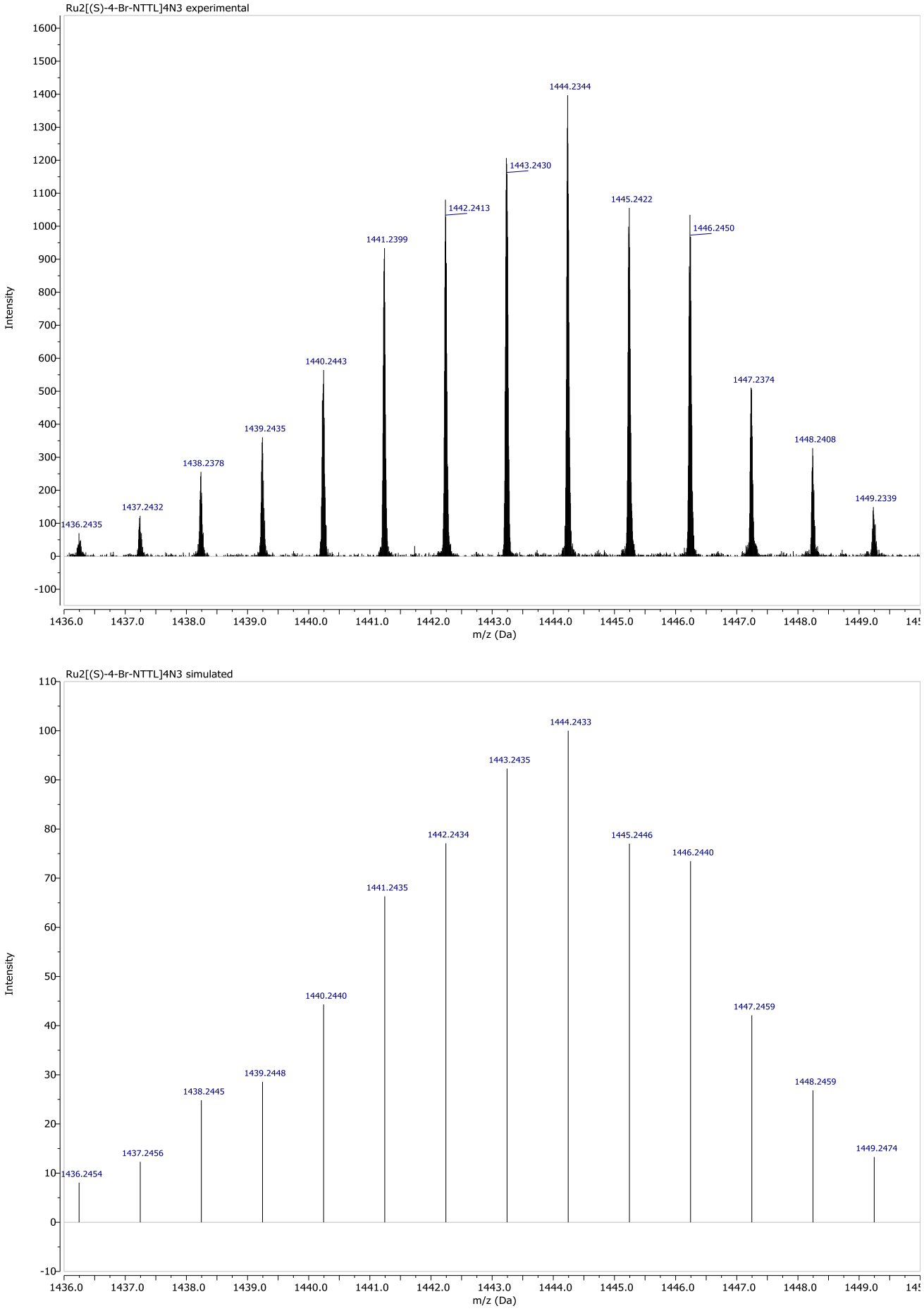


Fig. S5. HRMS of $Ru_2[(S)\text{-NTTL}]_4N_3$ (top: observed, bottom: simulated $[M - N_3]^+$).

$Ru_2[(S)\text{-NTTL}]_4NO_3$

Without exclusion of air a 10 ml vial was charged with $Ru_2[(S)\text{-NTTL}]_4Cl$ (22.1 mg, 0.015 mmol), silver nitrate (2.6 mg, 0.015 mmol, 1 equiv.) and MeOH (2 ml). The resulting mixture was stirred at ambient temperature for 3 hours in dark. Then DCM (2 ml) was added and the solution was passed through Celite. The solvents were removed in vacuo to afford the desired product as orange solid in quantitative yield (22 mg).

$Ru_2[(S)\text{-NTTL}]_4NO_3$: $\mathbf{R_f}$ (DCM/EA 1:1): 0.13. **HRMS** (ESI-TOF, m/z) calcd for $C_{72}H_{64}N_4O_{16}Ru_2$ $[M - NO_3]^+$: 1442.2434; Found: 1442.2451. **IR** (KBr, cm^{-1}): 2958, 1705, 1667, 1589, 1481, **1457** (NO_3^-), 1416, 1399, 1377, 1358, 1340, 1299, 1279, 1240, 1180, 1150, 1112, 1079, 1029, 997, 931, 906, 866, 846, 786, 710.

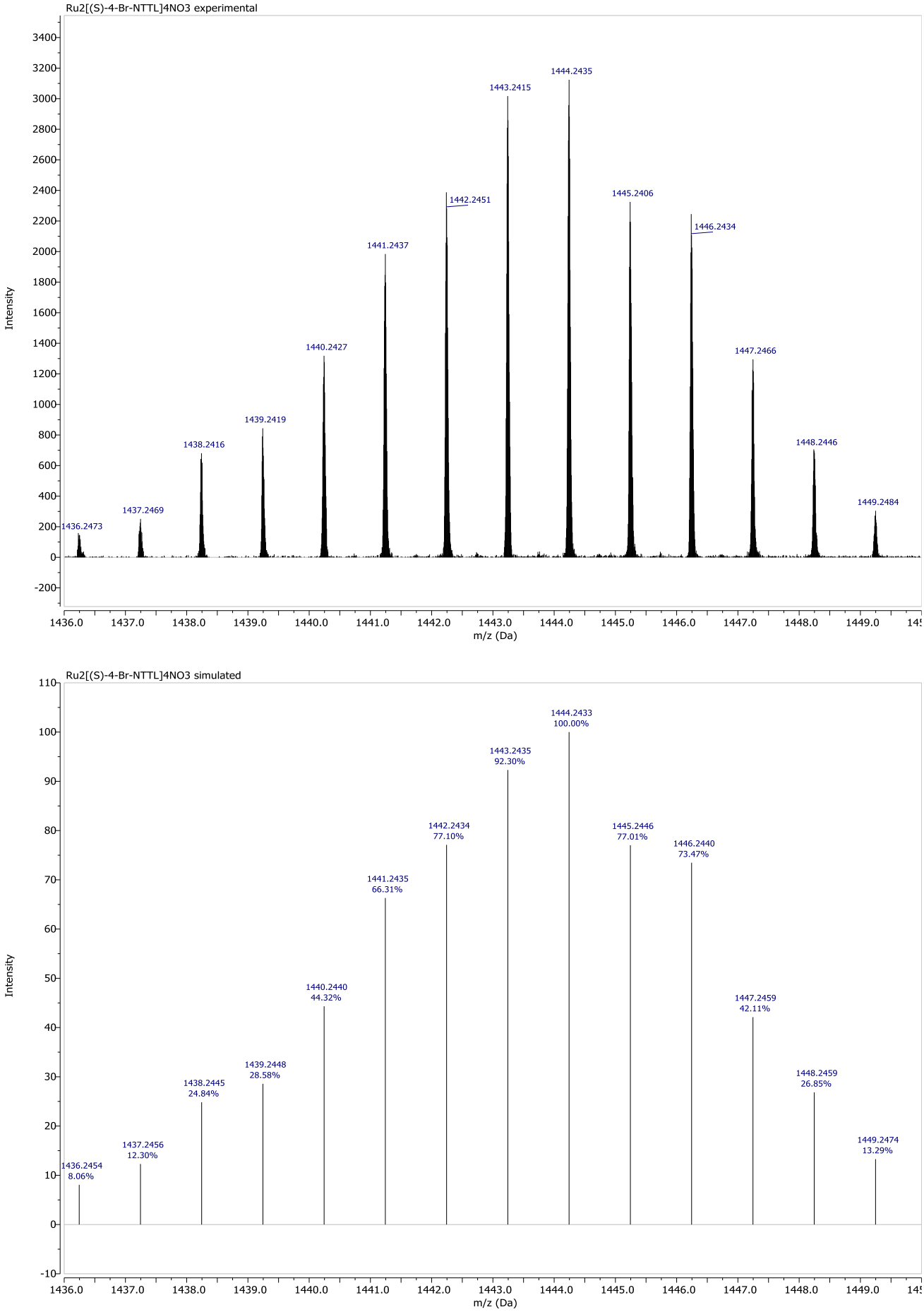
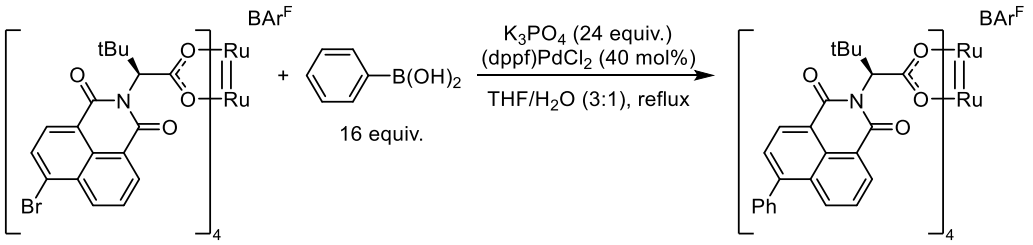


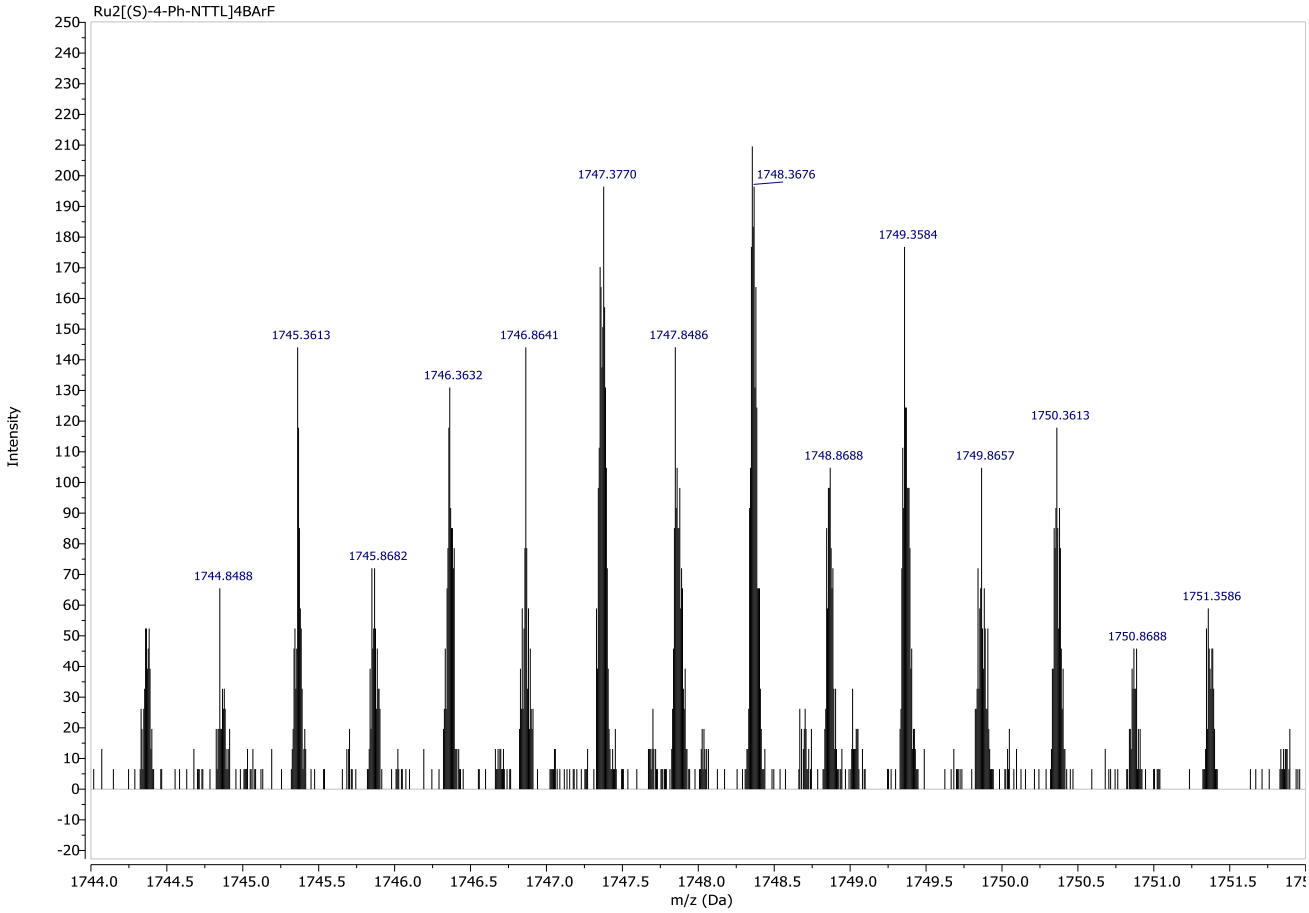
Fig. S6. HRMS of $Ru_2[(S)\text{-NTTL}]_4NO_3$ (top: observed, bottom: simulated $[M - NO_3]^+$).



$Ru_2[(S)\text{-}4\text{-}Ph\text{-}NTTL]_4BAr^F$

An oven-dried 10 ml Schlenk flask was charged with $Ru_2[(S)\text{-}4\text{-}Br\text{-}NTTL]_4BAr^F$ (91.7 mg, 0.035 mmol, 1 equiv.), phenylboronic acid (68 mg, 0.56 mmol, 16 equiv.) and K_3PO_4 (178 mg, 0.84 mmol, 24 equiv.). Then THF/H_2O (6 + 2 ml) were added in an argon flow followed by (dppf)$PdCl_2$ (10 mg, 0.0014 mmol, 40 mol%). The flask was capped and the resulting red biphasic system was stirred for 16 hours at 80 °C. After the indicated time the solution was cooled to room temperature and filtered through Celite. The residue was washed with water (20 ml) and brine (10 ml), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was redissolved in DCM (4 ml) in air and stirred with $NaBAr^F \bullet 3H_2O$ (49.4 mg, 0.0525 mmol, 1.5 equiv.) for 3 hours. The solution was directly transferred to SiO_2 column. The first orange band was collected using gradient elution (DCM, then DCM/MeOH 80:1) to give an orange solid in 45% yield (41.5 mg).

$Ru_2[(S)\text{-}4\text{-}Ph\text{-}NTTL]_4BAr^F$: **$R_f$** (DCM/hexane 10:3): 0.65. **HRMS** (ESI-TOF, m/z) calcd for $C_{96}H_{80}N_5O_{16}Ru_2$ [M - BAr^F]$^+$: 1746.3676; Found: 1746.3632. **HRMS** (-p ESI, m/z) calcd for $C_{32}H_{12}BF_{24}$ [BAr^F]$^-$: 862.0691; Found 862.0659. **IR** (KBr, cm^{-1}): 2968, 1705, 1667, 1589, 1481, 1457, 1416, 1400, 1369, 1355, 1278, 1238, 1180, 1164, 1126, 999, 911, 866, 864, 839, 787, 768, 710, 702.



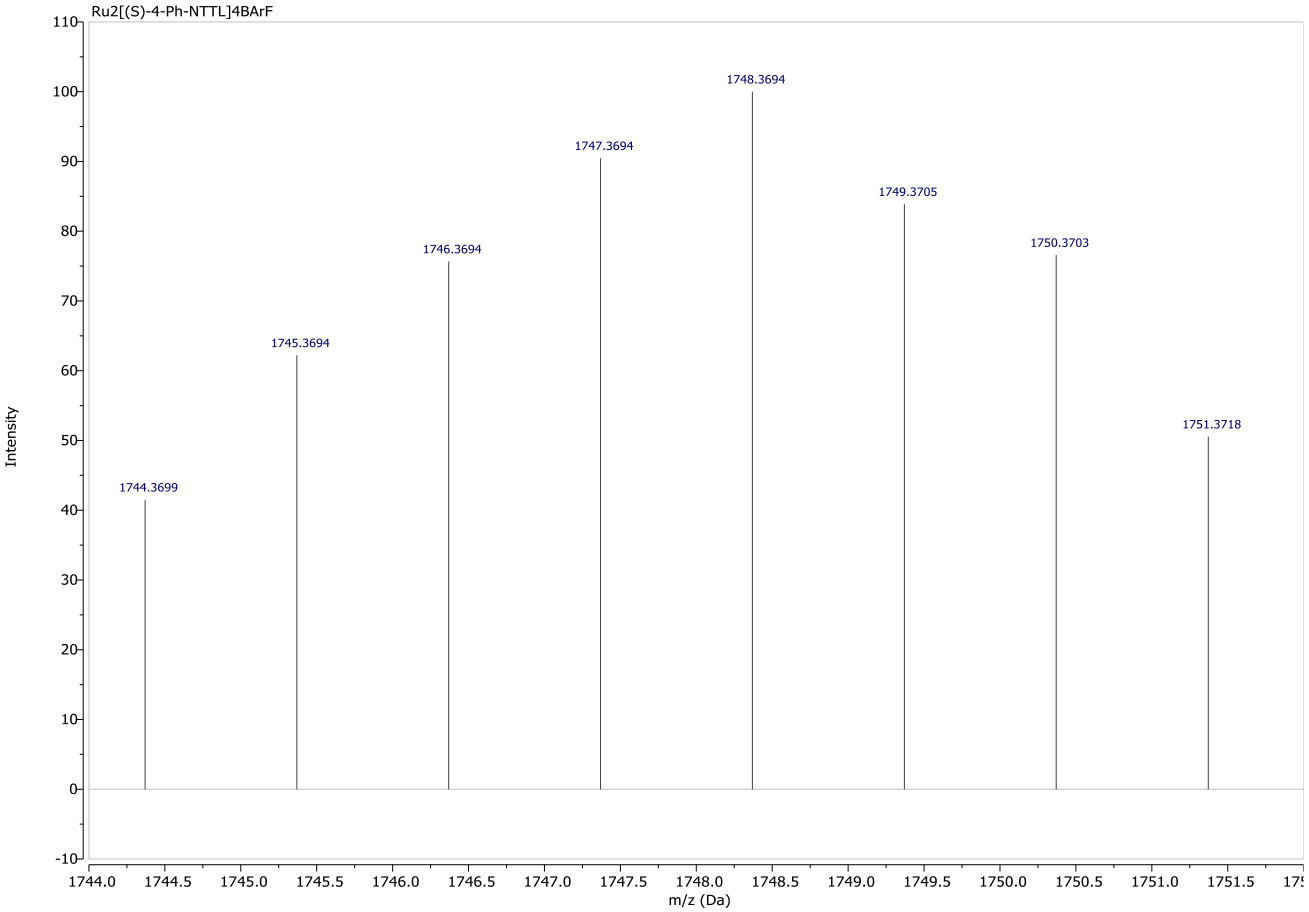
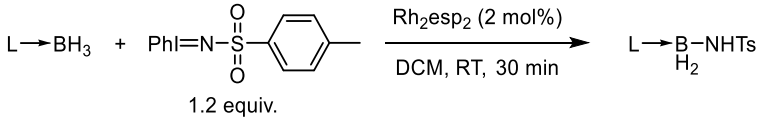
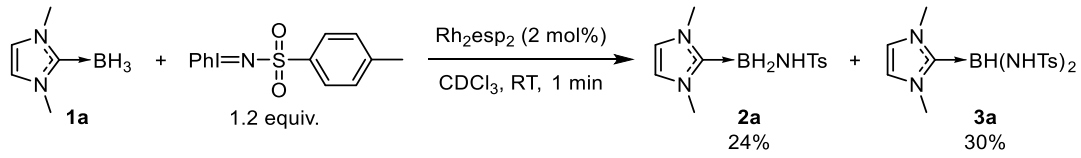


Fig. S7. HRMS of Ru_2[(*S*)-4-Ph-NTTL]$_4$BAr^F (top: observed, bottom: simulated [M - BAr^F]$^+$).

Screening of Boranes



An oven-dried 10 ml Schlenk flask was charged with corresponding borane adduct **1a-f** (0.1 mmol), Rh_2esp_2 (2 mol%, 1.5 mg, 0.02 mmol) and $CDCl_3$ (0.6 ml). To the resulting solution PhINTs (44.8 mg, 0.12 mmol, 1.2 equiv.) was added in one portion and the reaction mixture was stirred until all solids dissolved (up to 30 minutes). Then 1,3,5-tribromobenzene was added as an internal standard, the content of the flask was transferred to an NMR tube under argon and immediately thereafter ^{1}H and ^{11}B NMR spectra were recorded.



11 mg (0.1 mmol) of **1a** and 17 mg (0.054 mmol) of 1,3,5-tribromobenzene were used. According to ^{1}H NMR, products **2a** (δ_{NHC} = 6.70 ppm, 0.024 mmol, 24% yield) and **3a** (δ_{NHC} = 6.77 ppm, 0.03 mmol, 30% yield) were formed, and starting borane **1a** (δ_{NHC} = 6.80 ppm, 0.012 mmol, 12%) remained. The residual borane (ca. 34%)

was apparently converted into unidentified, insoluble materials) Both products **2a** and **3a** are stable on silica and in solution for at least one week (see detailed isolation procedure below).

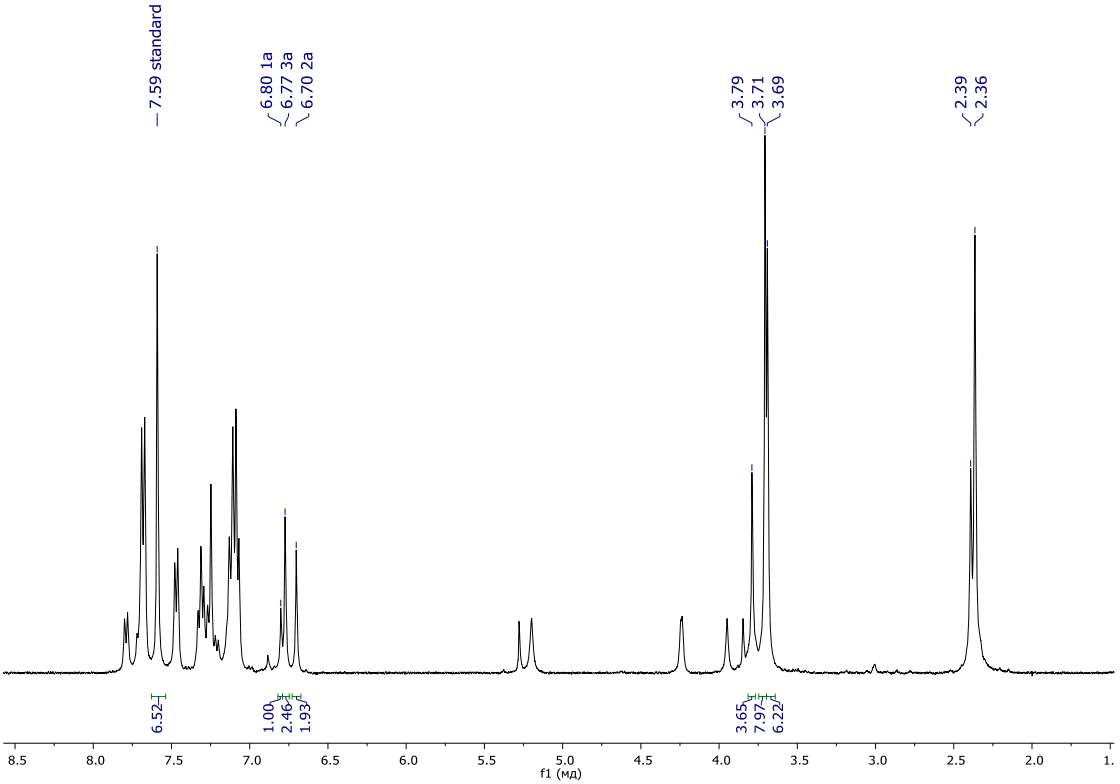


Fig. S8. ^{1}H NMR spectrum of the reaction mixture of **1a** and PhINTs. Only characteristic signals of NHC fragment and 1,3,5-tribromobenzene are integrated. See Figures S65-S70 for pure and fully assigned spectra.

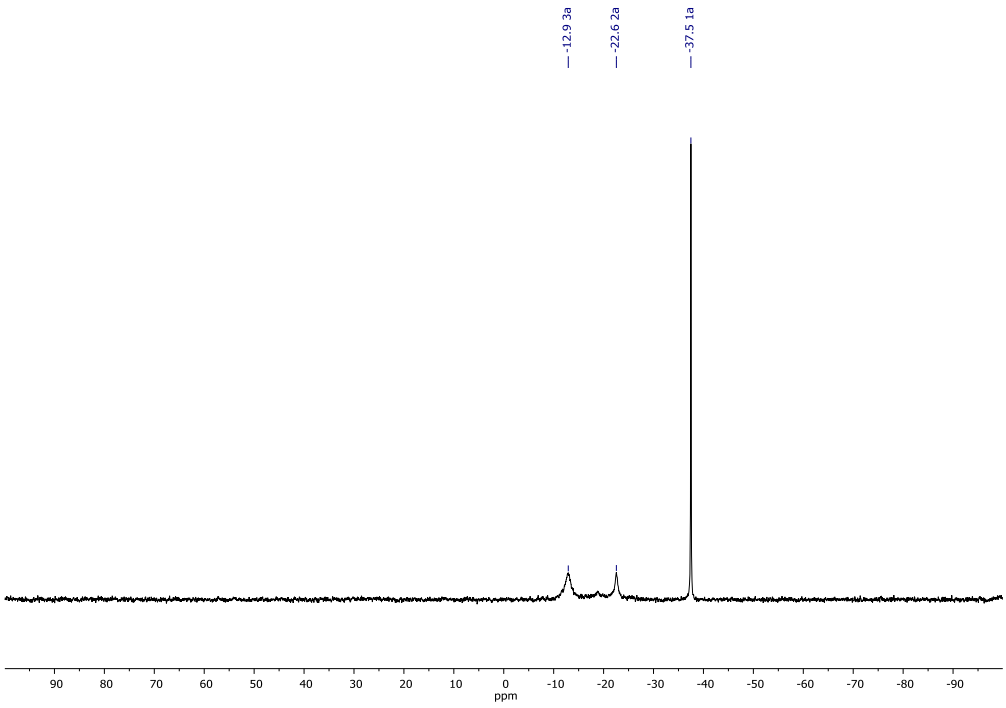
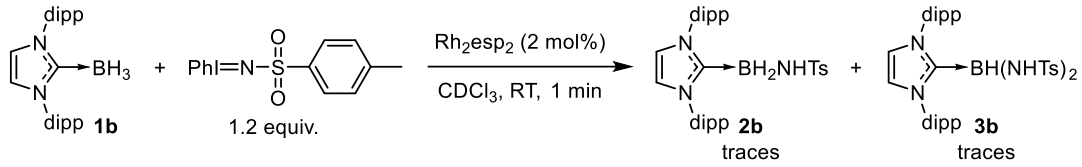


Fig. S9. ^{11}B NMR spectrum of the reaction mixture of **1a** and PhINTs.



40.2 mg of **1b** and 22 mg of 1,3,5-tribromobenzene were used. According to ^{1}H and ^{11}B NMR, there are only trace amount of the insertion products **2b** and **3b** with 4% conversion of starting borane.

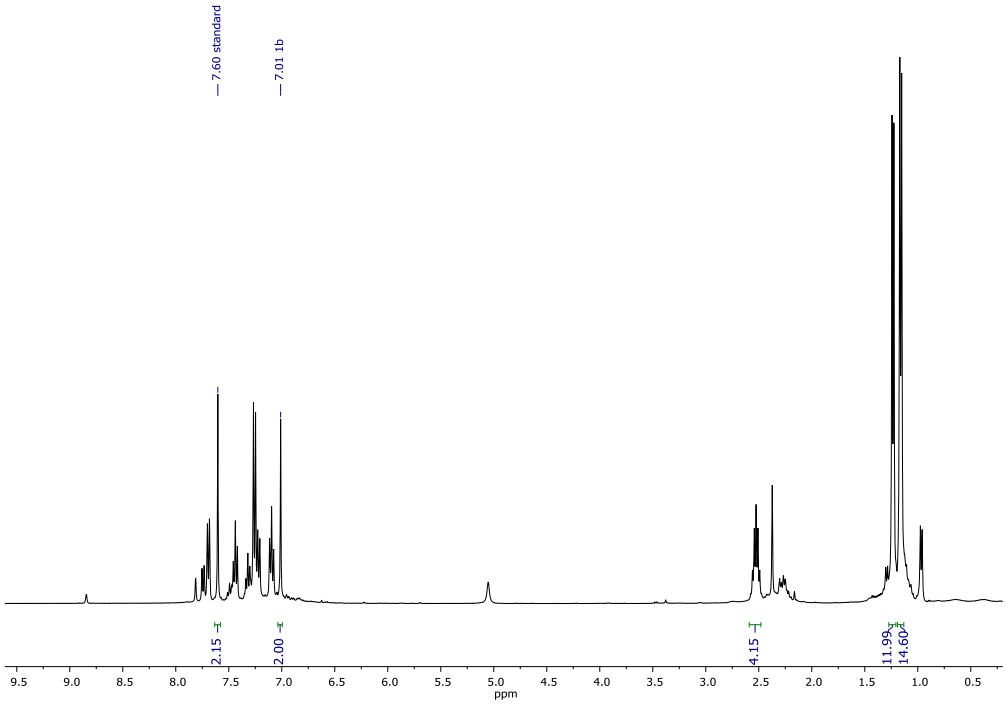


Fig. S10. ^{1}H NMR spectrum of the reaction mixture of **1b** and PhINTs. Only characteristic signals of NHC fragment and 1,3,5-tribromobenzene are integrated.

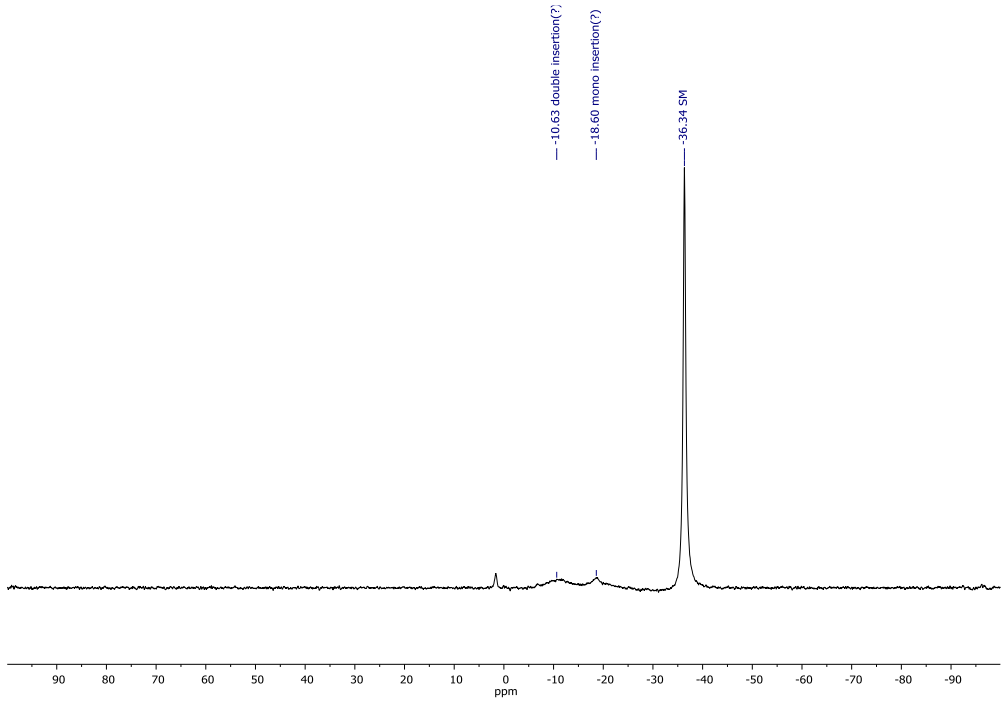
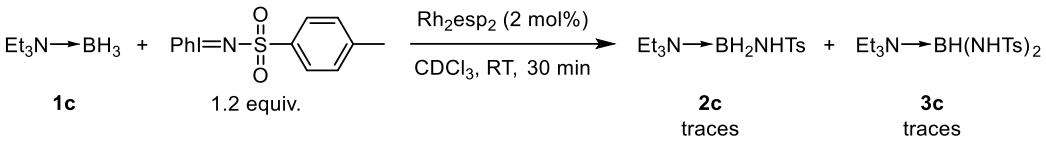


Fig. S11. ^{11}B NMR spectrum of the reaction mixture of **1b** and PhINTs. The major signal corresponds to the starting borane **1b**.



11.5 mg of **1c** and 10.4 mg of 1,3,5-tribromobenzene were used. According to ^{1}H and ^{11}B NMR, there are only trace amount of the insertion products **2c** and **3c** with 14% conversion of starting borane.

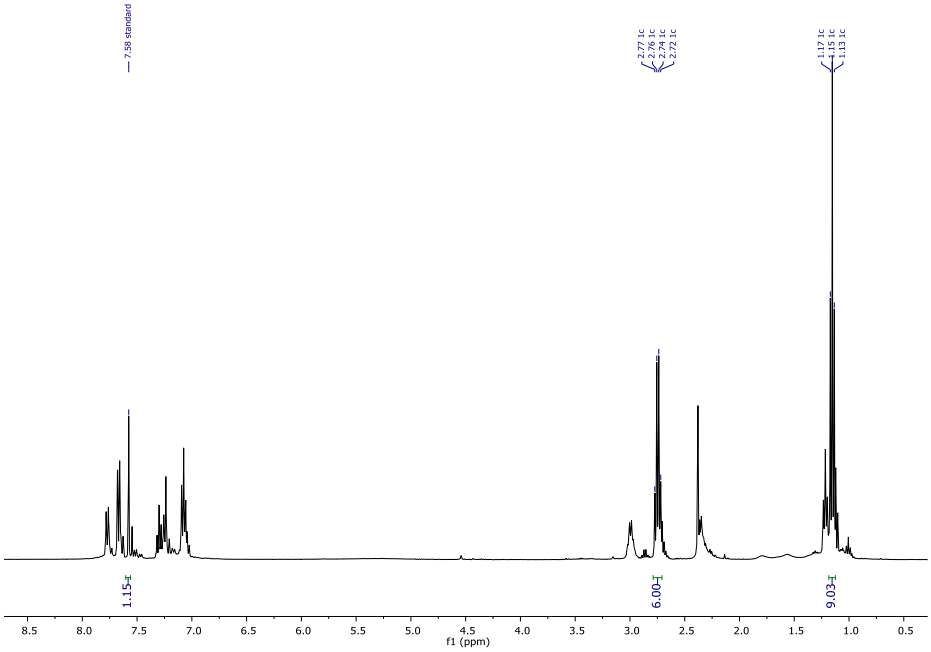


Fig. S12. ^{1}H NMR spectrum of the reaction mixture of **1c** and PhINTs. Only characteristic signals of Et_3N fragment and 1,3,5-tribromobenzene are integrated.

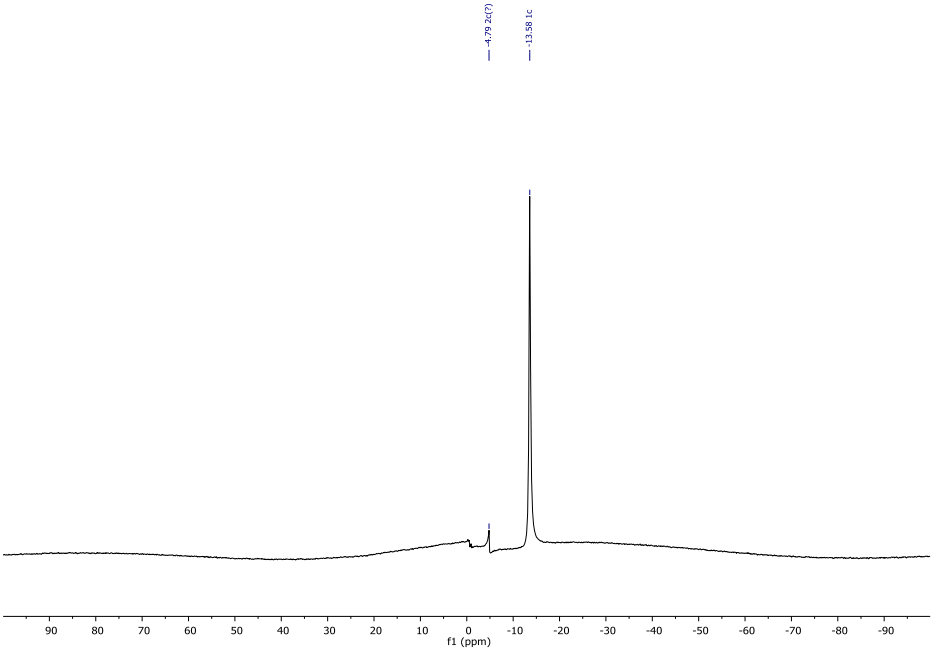
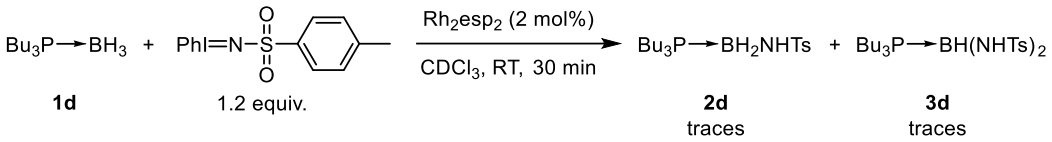


Fig. S13. ^{11}B NMR spectrum of the reaction mixture of **1c** and PhINTs. The major signal corresponds to the starting borane **1c**.



15.4 mg of **1d** and 11.4 mg of 1,3,5-tribromobenzene were used. According to ^{1}H, ^{11}B and ^{31}P NMR, there are only trace amount of the insertion products **2d** and **3d** with 9% conversion of starting borane.

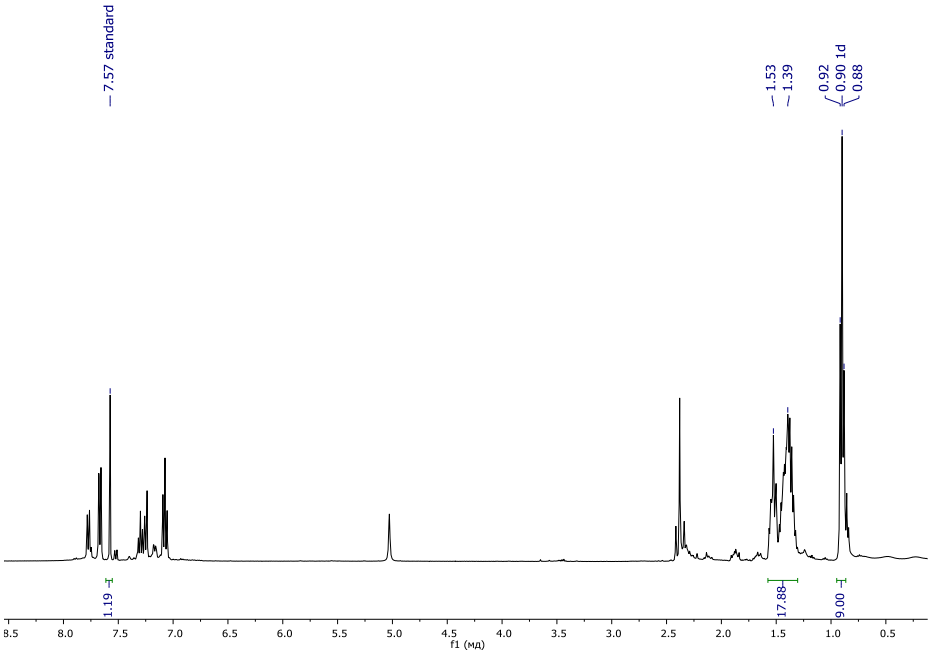


Fig. S14. ^{1}H NMR spectrum of the reaction mixture of **1d** and PhINTs. Only characteristic signals of Bu_3P fragment and 1,3,5-tribromobenzene are integrated.

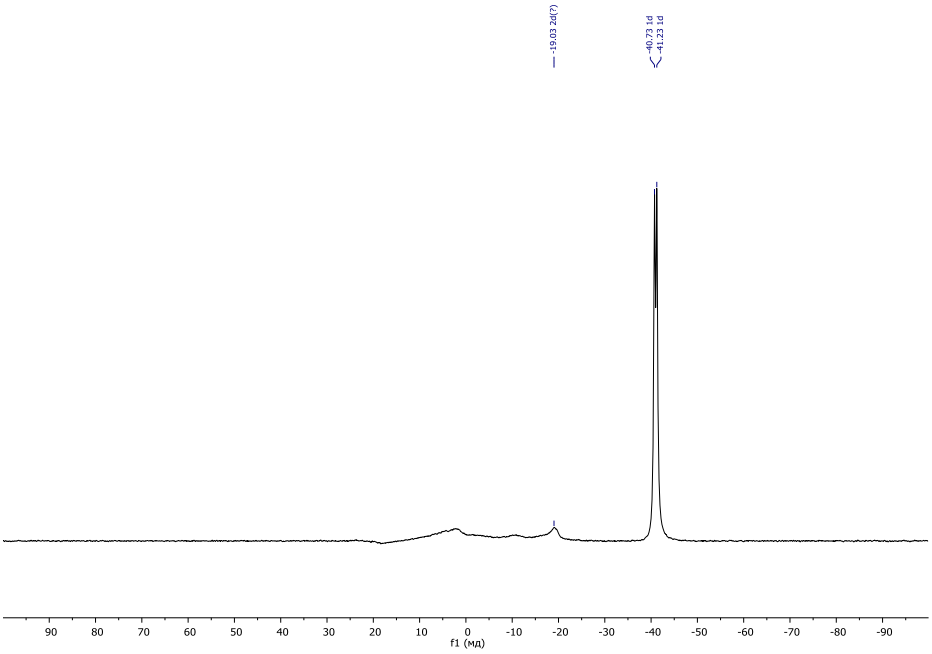
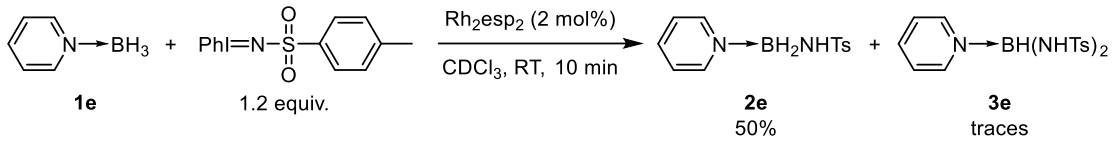


Fig. S15. ^{11}B NMR spectrum of the reaction mixture of **1d** and PhINTs. The major signal corresponds to the starting borane **1d**.



9.3 mg of **1e** and 13 mg of 1,3,5-tribromobenzene were used. According to ^{1}H and ^{11}B NMR, there was mainly **2e** (50% yield), conversion of starting borane was 52%. The product quickly degrades upon standing in solution and completely decomposes when passed through a short silica pad.

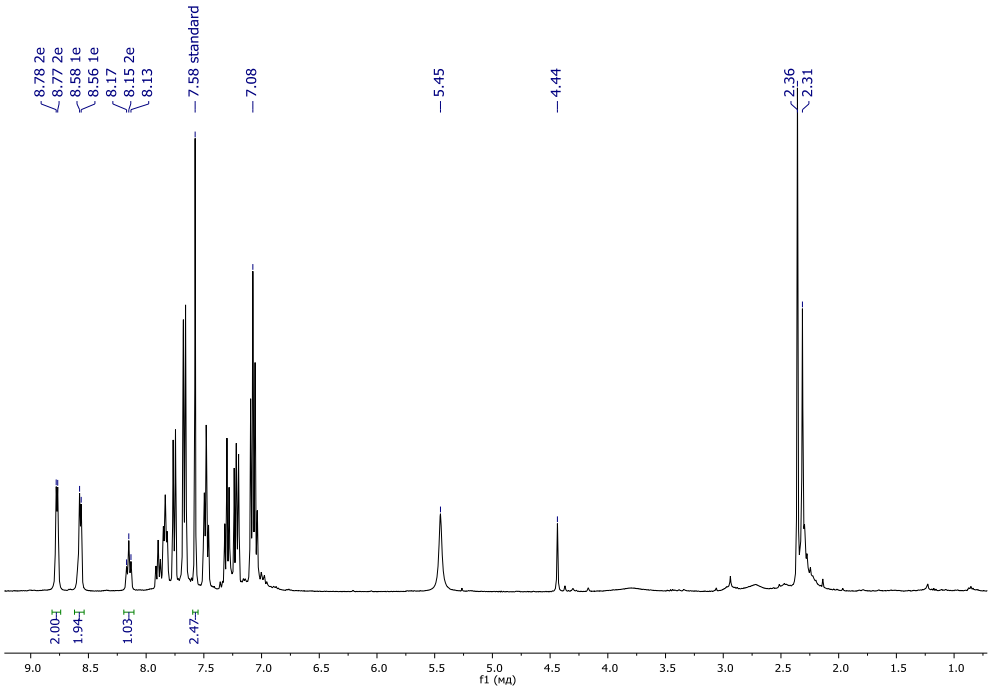


Fig. S16. ^{1}H NMR spectrum of the reaction mixture of **1e** and PhINTs.

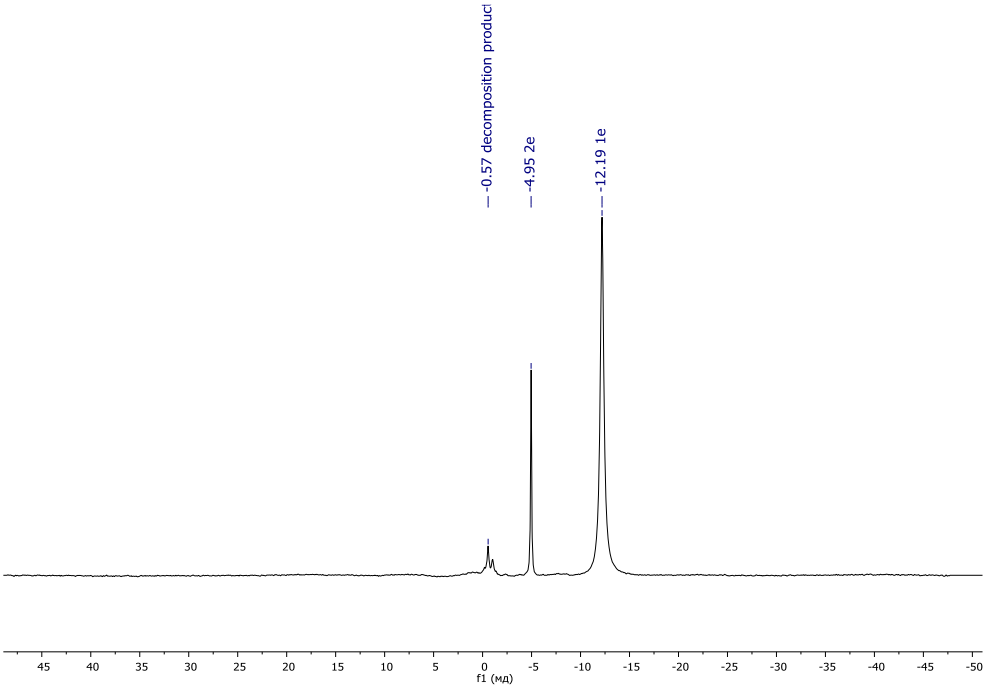
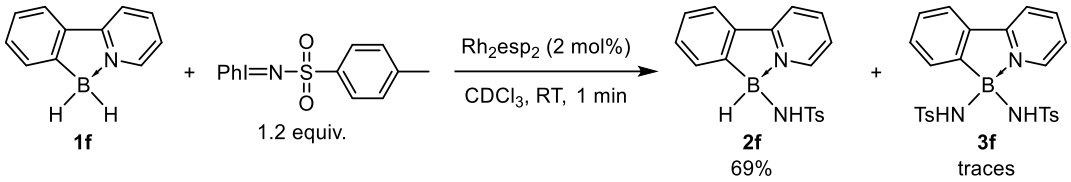


Fig. S17. ^{11}B NMR spectrum of the reaction mixture of **1e** and PhINTs.



16.7 mg of **1f** and 11.7 mg of 1,3,5-tribromobenzene were used. According to ^{1}H and ^{11}B NMR, the main product was **2f** (69% yield), the conversion of the starting borane was 77%. The product decomposes by 5% upon standing for 3 days in $(CD_3)_2CO$ solution in air at ambient temperature. It can be purified by standard column chromatography on silica without significant decomposition.

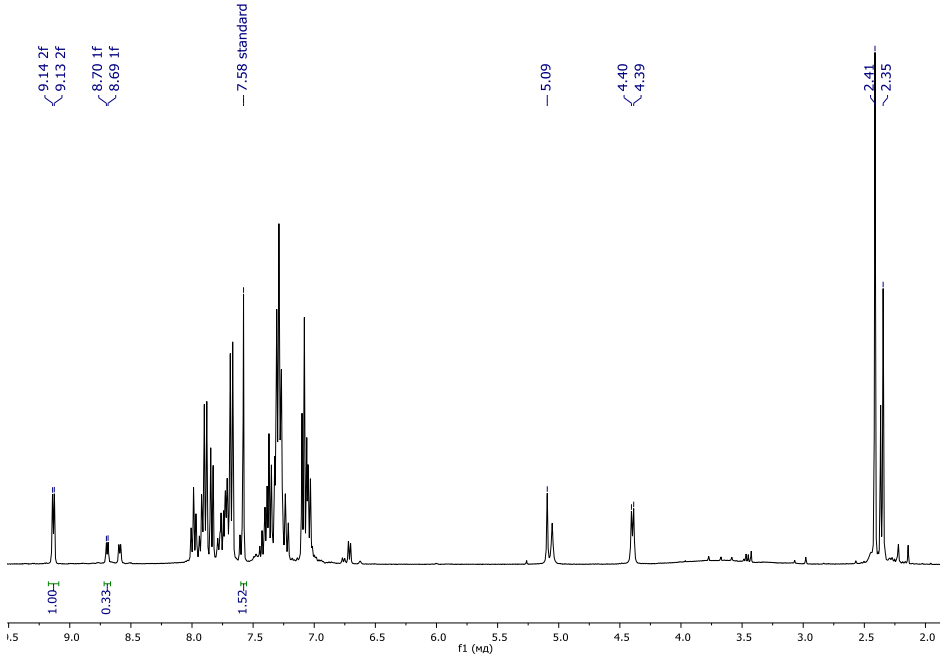


Fig. S18. ^{1}H NMR spectrum of the reaction mixture of **1f** and PhINTs. Only characteristic signals of PhPy fragment and 1,3,5-tribromobenzene are integrated. See Figures S71-S73 for pure and fully assigned spectra.

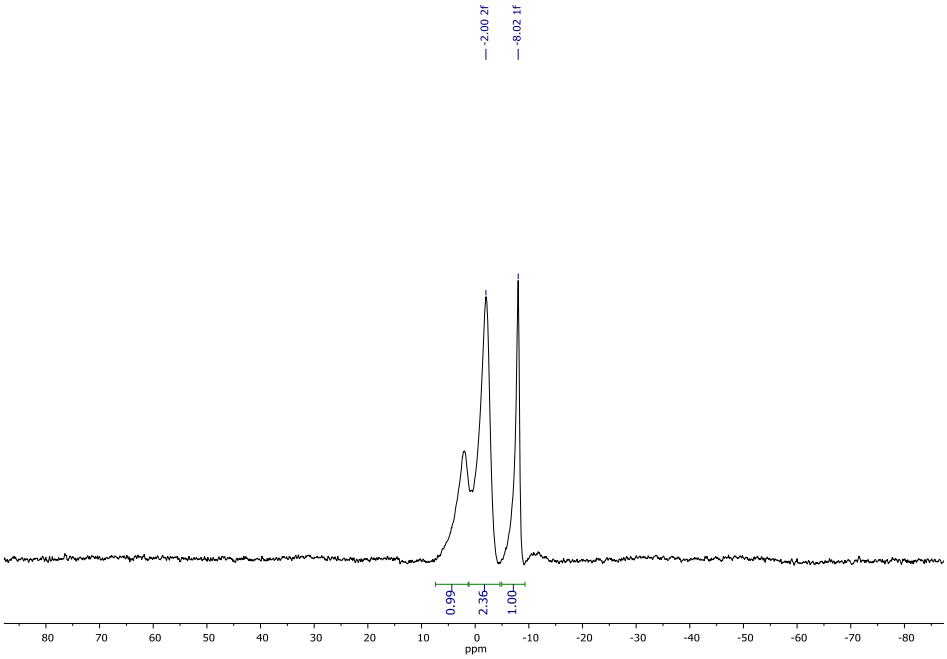


Fig. S19. ^{11}B NMR spectrum of the reaction mixture of **1f** and PhINTs.

Control experiments

NMR tube was charged with borane **1f** (9 mg, 0.05 mmol) and other solid reagents (0.05 mmol) as well as catalyst $Rh_2(NTTL)_4$ (2 mg, 2 mol%), then $CDCl_3$ (0.6 ml) was added and the sample was thoroughly shaken. ^1H and ^{11}B NMR spectra were recorded after 10 min and after 20 h at 20 °C. In case the reaction was observed 1,3,5-tribromobenzene was subsequently added as the internal standard.

CAUTION! TsN_3 and BnN_3 are potentially explosive upon heating. Although we did not have any incidents, it is recommended to follow safety precautions when working with organic azides.

entry	Reagents	results
1	**1f** + $TsNH_2$ + $Rh_2(NTTL)_4$	no reaction
2	**1f** + $TcesNH_2$ + $Rh_2(NTTL)_4$	no reaction
3	**1f** + PhIO, with or without catalyst	very slow oxidation of borane (ca. 5% in 20 h)
4	**1f** + TsN=IPh, no catalyst	no reaction after 10 min, non-selective reaction after 20 h: ca. 30% of the product **2f** was formed, ca. 60% of the unreacted borane **1f** remained. No further changes observed after 72 h.
5	**1f** + $TcesNH_2$ + PhIO, no catalyst	fast non-selective reaction after 10 min: ca. 20% of the product **2p** was formed, ca. 60% of the unreacted borane **1f** remained. No further changes observed after 20 h.
6	**1f** + BnN_3, no catalyst	no reaction after 72 h at 60 °C
7	**1f** +TsN_3, no catalyst	mixture **1f** and **2f** in 1:1 ratio + byproducts after 120 h at 60 °C

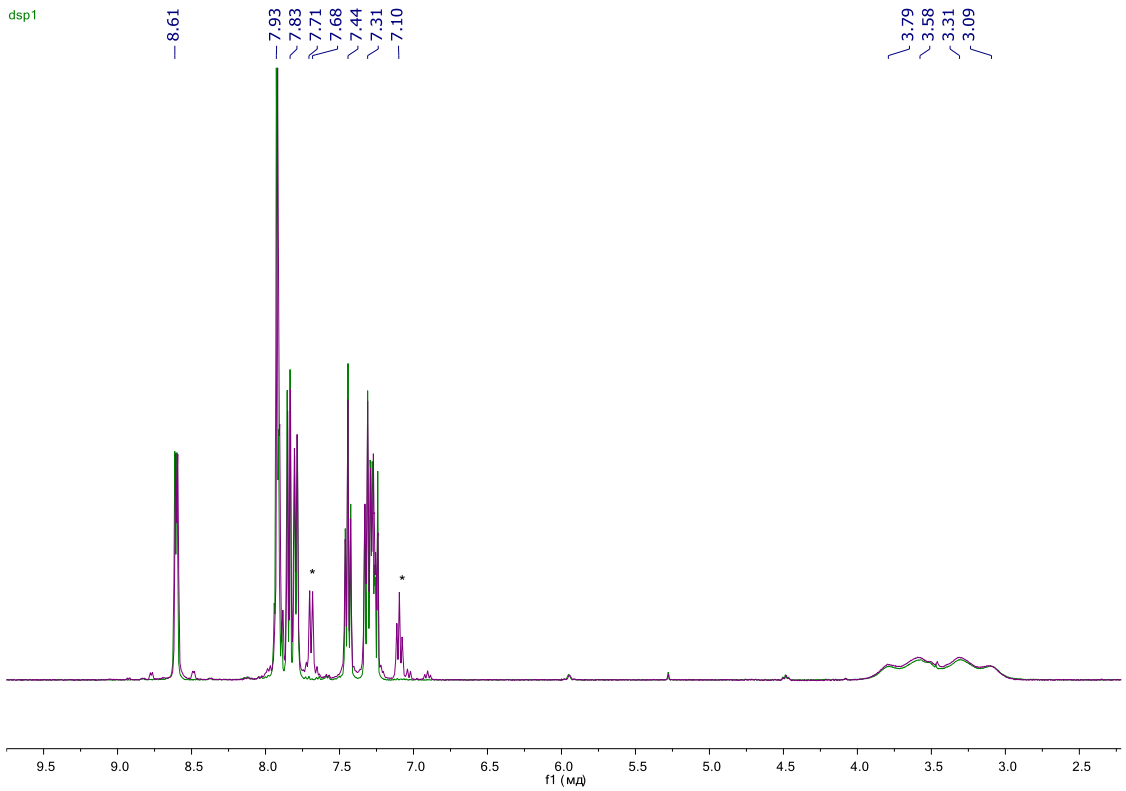


Fig. S20. ^1H NMR spectra of the borane **1f** (green) and the reaction mixture of **1f** + PhIO (purple) after 20 hours at RT in $CDCl_3$. Asterisks marks new signals that appear as the result of oxidation. PhIO remains largely insoluble.

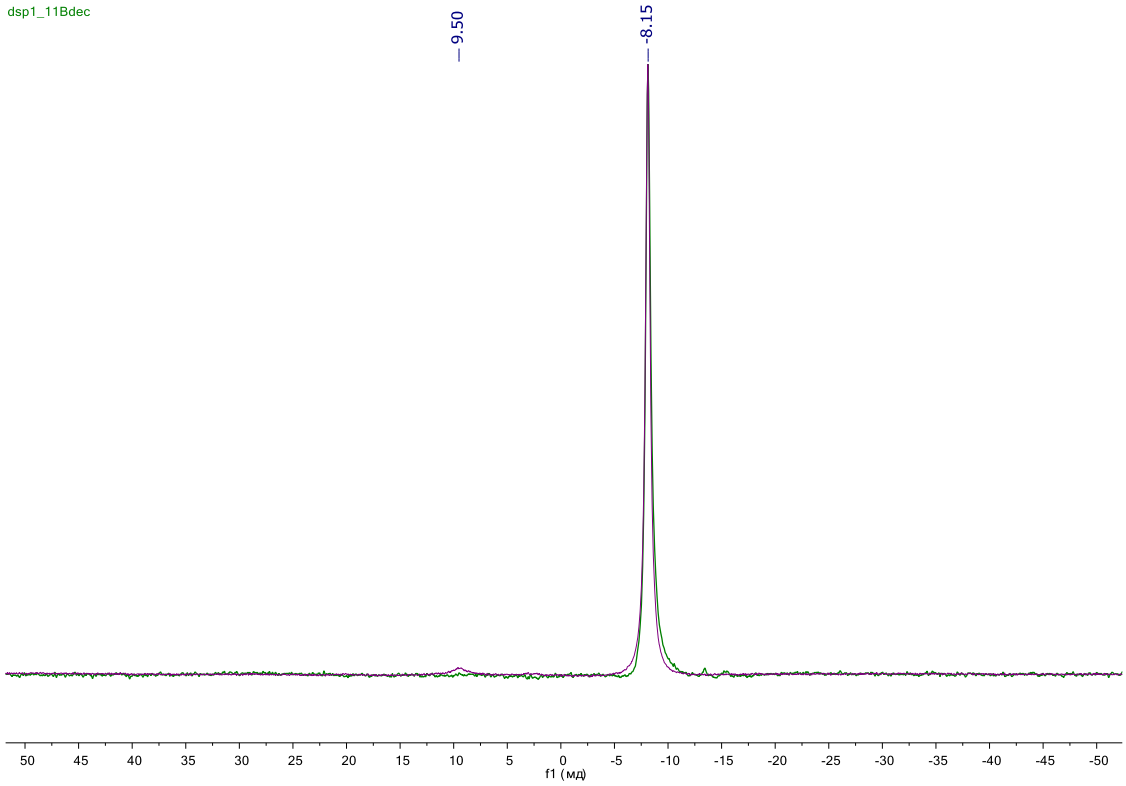


Fig. S21. ^{11}B NMR spectra of the borane **1f** (green) and the reaction mixture of **1f** + PhIO (purple) after 20 hours at RT in $CDCl_3$.

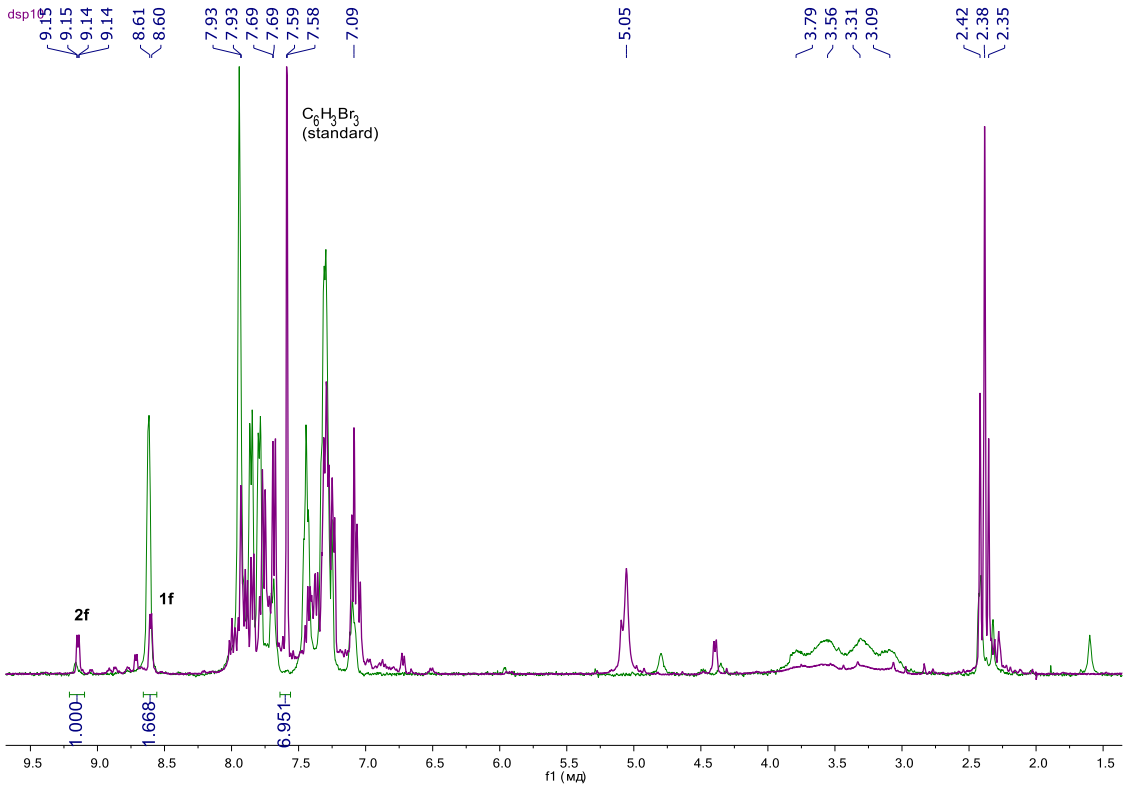


Fig. S22. ^{1}H NMR spectra of the borane **1f** + TsN=IPh after 10 min (green, essentially no reaction) and after 20 hours (purple) at RT in $CDCl_3$. 1,3,5-tribromobenzene standard (0.05 mmol, 1 equiv.) was added for the second spectrum. Only characteristic signals of PhPy fragment of **1f**, **2f**, and $C_6H_3Br_3$ are integrated. According to the integration ca. 40% conversion of **1f** and 40% yield of **2f** was observed. These numbers should be treated only as estimates because of the signal overlap.

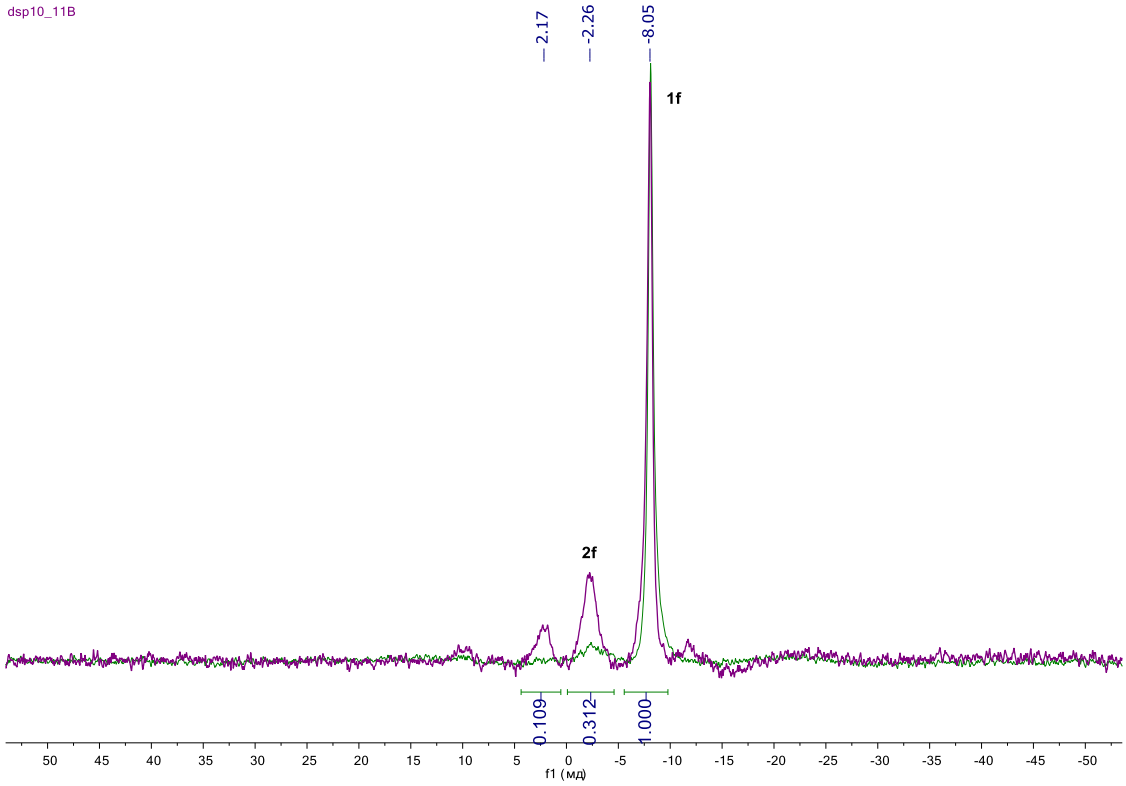


Fig. S23. ^{11}B NMR spectra of the borane **1f** + TsN=IPh after 10 min (green, essentially no reaction) and after 20 hours (purple) at RT in $CDCl_3$. According to the integration ca. 30% conversion of **1f** and 20% yield of **2f** was observed.

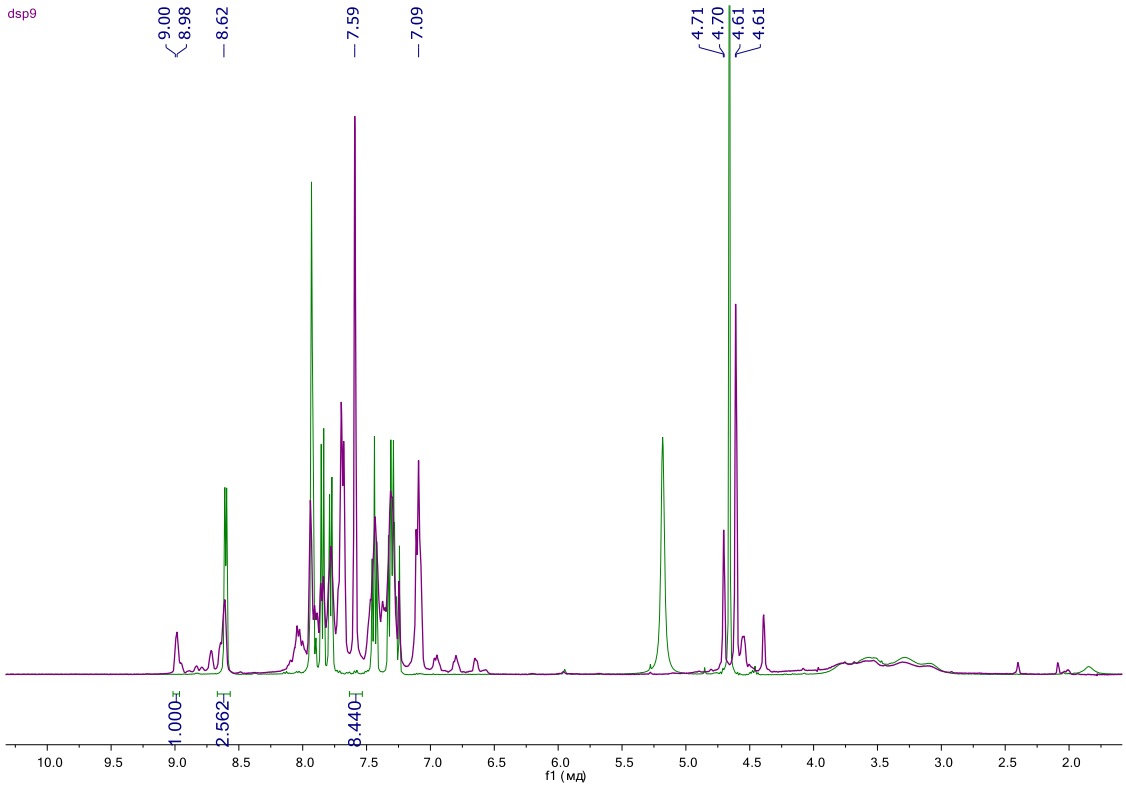


Fig. S24. ^{1}H NMR spectra of the borane **1f** + $TcesNH_2$ (green, no reaction) and **1f** + $TcesNH_2$ + PhIO after 10 min (purple) at RT in $CDCl_3$. 1,3,5-tribromobenzene standard (0.04 mmol) was added for the second spectrum. Only characteristic signals of PhPy fragment of **1f**, **2f**, and $C_6H_3Br_3$ are integrated. According to the integration ca. 30% conversion of **1f** and 25% yield of **2p** was observed. These numbers should be treated only as estimates because of the signal overlap.

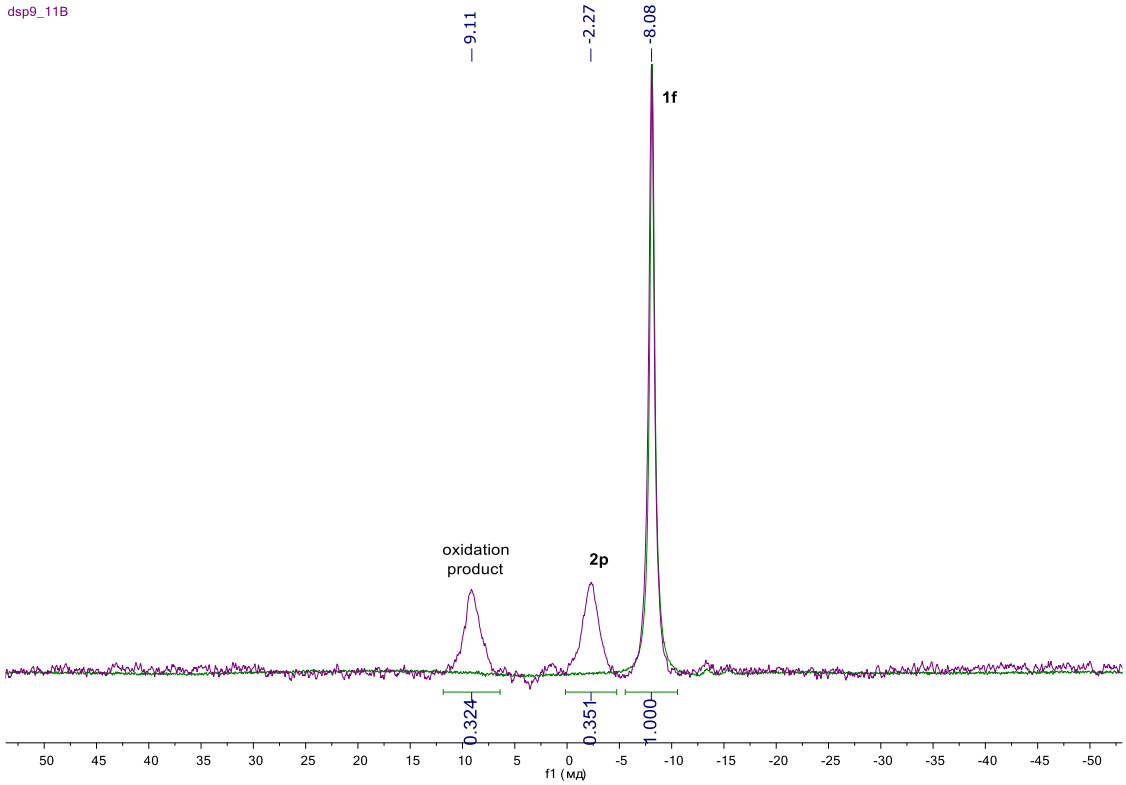


Fig. S25. ^{11}B NMR spectra of the borane **1f** + $TcesNH_2$ (green, no reaction) and **1f** + $TcesNH_2$ + PhIO after 10 min (purple) at RT in $CDCl_3$. According to the integration ca. 40% conversion of **1f** and 20% yield of **2p** was observed.

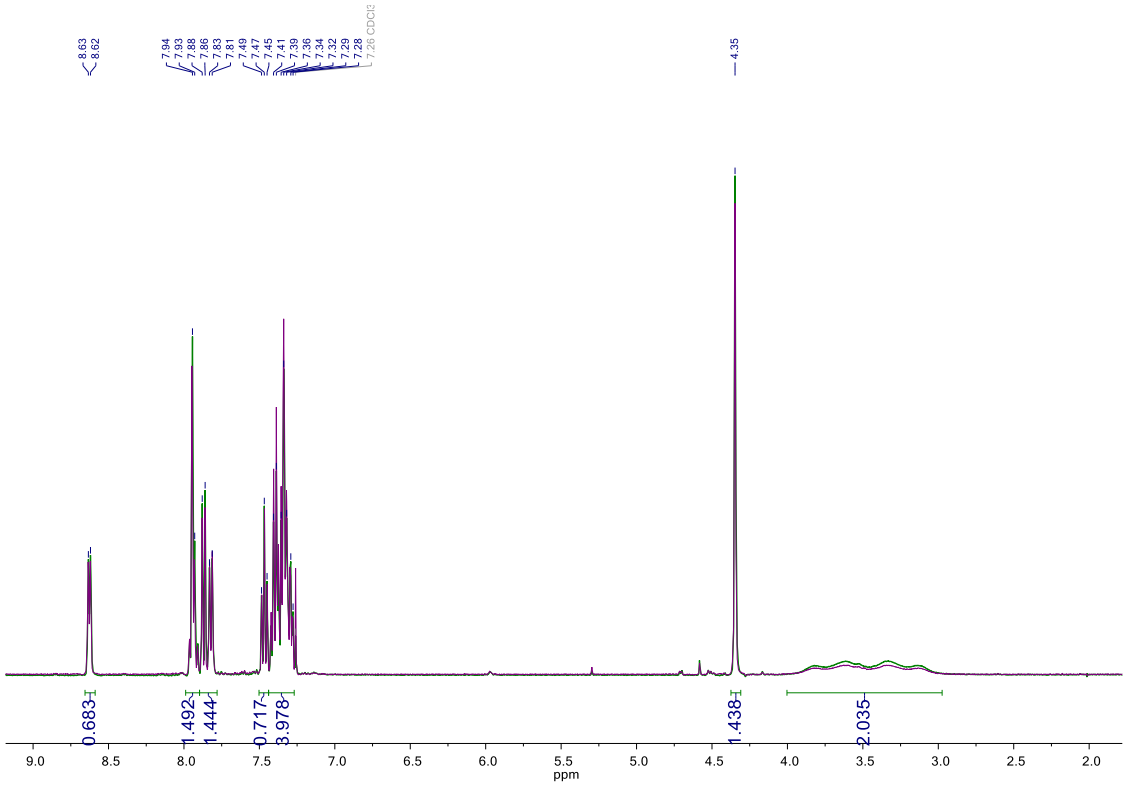


Fig. S26. ^{1}H NMR spectra **1f** + BnN_3 at RT (green) and after 72 h at 60 °C (violet) in $CDCl_3$.

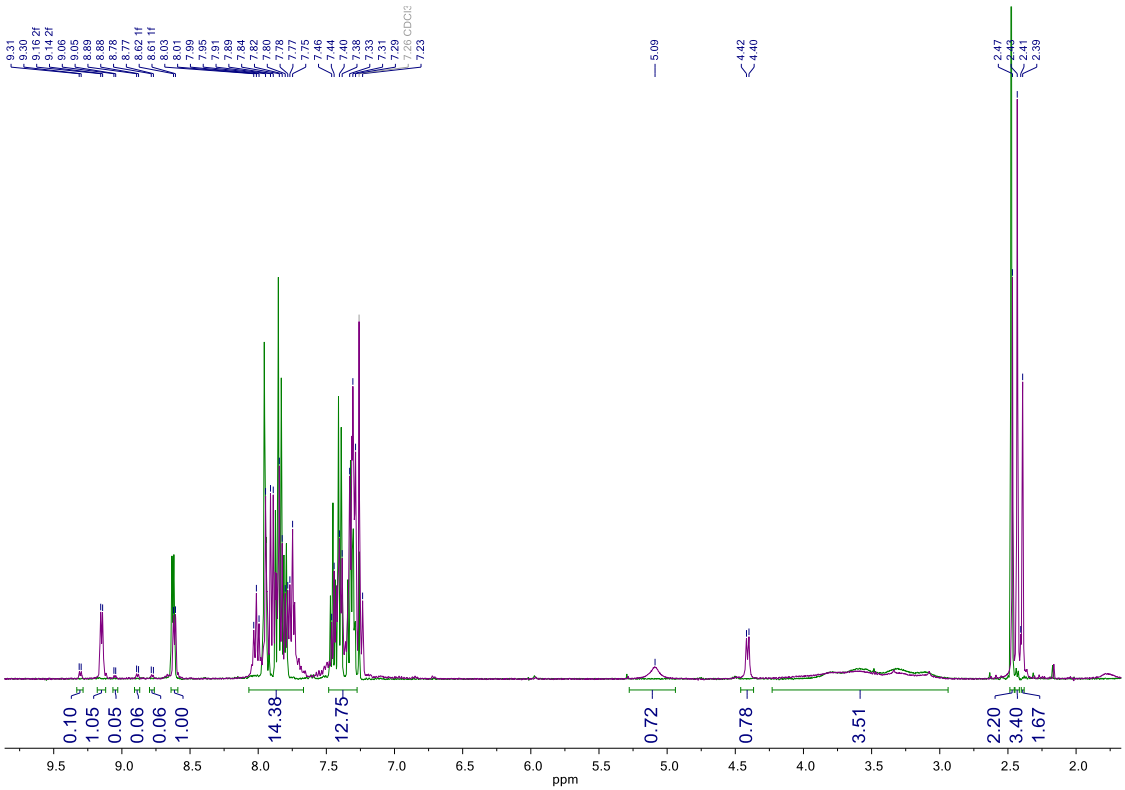


Fig. S27. ^{1}H NMR spectra **1f** + TsN_3 at RT (green) and after 120 h at 60 °C (violet) in $CDCl_3$.

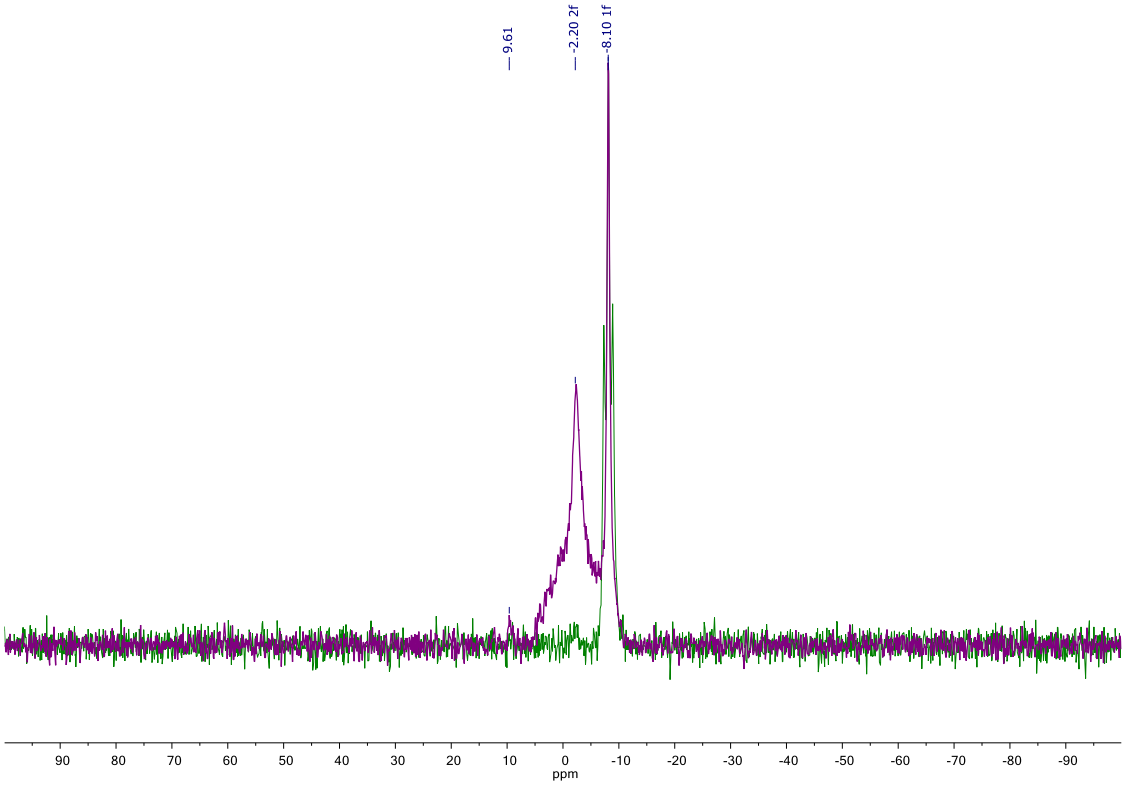
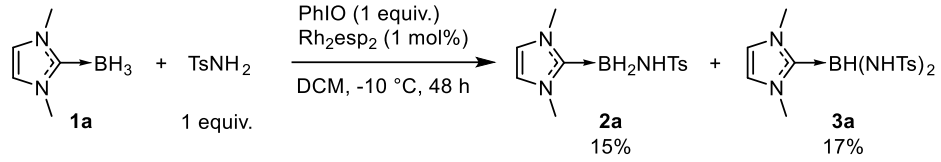
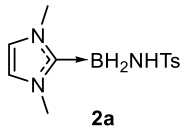


Fig. S28. ^{11}B NMR spectra **1f** + TsN_3 at RT (green) and after 120 h at 60 °C (violet) in $CDCl_3$.

Nitrene insertion into NHC-BH_3

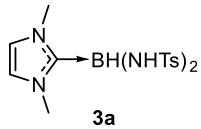


An oven-dried 25 ml Schlenk flask was charged with Rh_2esp_2 (8 mg, 0.01 mmol, 1 mol%), **1a** (110 mg, 1 mmol), $TsNH_2$ (171 mg, 1 mmol) and DCM (8 ml). The resulting solution was cooled to -20 °C and then PhIO (220 mg, 1 mmol) was added at once. The suspension was placed in a freezer and stirred at -10 °C for 48 hours and then at room temperature overnight. The mixture was filtered through Celite, concentrated in vacuo and then purified by column chromatography. Elution with pure DCM gave 41.3 mg of starting borane **1a** (38% recovery), then mono-insertion product **2a** was eluted using DCM/EtOAc 1:1 in 15% yield (42 mg). Finally, elution with pure EtOAc afforded double-insertion product **3a** in 17% yield (75.5 mg). X-ray quality crystals of both products were grown by slow diffusion of hexane into DCM solutions.



2a

2a: **R_f** (DCM/EA 10:1): 0.16 (visualized with ceric ammonium molybdate). **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 2H, NHC), 4.62 (s, NH), 3.78 (s, 6H), 2.36 (s, 3H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -22.74 (t, *J* = 94.1 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 142.5, 140.2, 128.5, 126.3, 121.0, 35.2, 20.4. A carbon directly attached to the boron atom was not detected, possibly due to quadrupole relaxation.[13] **HRMS** (ESI-TOF, m/z) calcd for $C_{12}H_{17}BN_3O_2S$ $[M-H]^+$: 278.1134; Found: 278.1133.

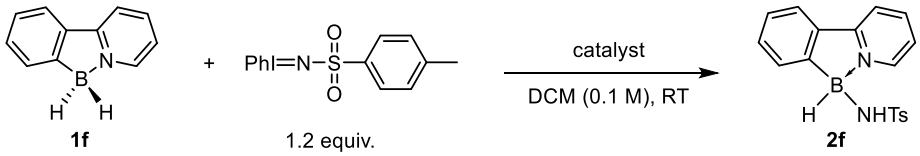


3a

3a: R_f (DCM/EA 1:1): 0.13 (visualized with ceric ammonium molybdate). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.40 (d, *J* = 7.9 Hz, 4H), 7.19 (s, 2H), 7.15 (d, *J* = 7.9 Hz, 4H), 5.52 (s, NH), 3.58 (s, 6H), 2.91 (br, 1H), 2.33 (s, 6H). **^{11}B NMR** (128 MHz, DMSO-d_6): δ -13.15. **^{13}C NMR** (101 MHz, DMSO-d_6): δ 141.2, 140.6, 128.7, 125.7, 121.7, 35.4, 20.9. A carbon directly attached to the boron atom was not detected, possibly due to quadrupole relaxation.[13] **HRMS** (ESI-TOF, m/z) calcd for $C_{19}H_{25}BN_4O_4S_2Na$ $[M+Na]^+$: 471.1308; Found: 471.1304.

Racemic insertion reactions

Table S1. Catalyst scope for the racemic B–H nitrene insertion.



1f 1.2 equiv. **2f**

entry	catalyst (loading, %)	time, min	conversion, %[a]	yield, %[a]
1	Rh_2esp_2 (2 mol%)	1	77	69
2	$Rh_2(OAc)_4$ (2 mol%)	1	79	25
3	$Rh_2(OPiv)_4$ (2 mol%)	1	78	28
4	Co(TPP) (5 mol%)	10	53	23
5	PPh_3AuCl (5 mol%) + $NaBAr^F$ (10 mol%)	1	49	14
6	$Cu(MeCN)_4PF_6$ (10 mol%)	1	85	35
7	$Cu(MeCN)_4PF_6$ (10 mol%) + bpy (12 mol%)	5	76	29
8	$Cu(MeCN)_4PF_6$ (10 mol%) + phen (12 mol%)	10	73	20
9	$Cu(MeCN)_4PF_6$ (10 mol%) + dppe (12 mol%)	30	55	14
10	$Cu(MeCN)_4PF_6$ (10 mol%) + BOX (12 mol%)	1	40	16
11	Rh_2esp_2 (1 mol%)	1	75	65
12[b]	**Rh_2esp_2 (1 mol%)**	**60**	**69**	**54**
13[b,c]	Rh_2esp_2 (1 mol%)	4320	82	43

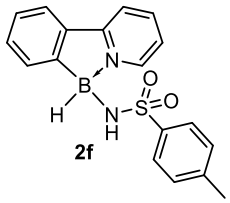
[a] Both yield and conversion were determined by ^1H using 1,1,2,2-tetrachloroethane as internal standard. [b] PhINTs was generated *in situ* using $TsNH_2$ (1.2 equiv.) and PhIO (1.2 equiv.). [c] Benzene used as a solvent.

1 **5** or **6** **2**

General procedure: An oven-dried 10 ml Schlenk flask was charged with Rh_2esp_2 (1.5 mg, 0.002 mmol, 1 mol%), arylpyridineborane **1** (0.2 mmol, 1 equiv.), corresponding sulfonamide **5** or sulfamate **6** (0.24 mmol, 1.2 equiv.) and DCM (2 ml). To this solution iodosobenzene (52.8 mg, 0.24 mmol, 1.2 equiv.) was added in one portion and the resulting suspension was stirred until all solids dissolved or for 24 hours.

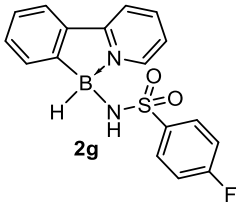
For electron-poor sulfamates, the reaction in usually complete within an hour, in case of electron-rich sulfonamides up to 24 hours were required. For sulfonamides, the suspension is commonly observed after 24 hours, suggesting incomplete conversion. However, prolonged reaction times do not result in increased yields.

The reaction mixture was directly transferred to a prepacked SiO_2 column and the desired product was eluted using either pure DCM (for most sulfamate derivatives) or a mixture of DCM/EtOAc (20:1) (for most sulfonamide derivatives) as eluent. All products were additionally purified by liquid diffusion crystallization: amidoborane was dissolved in minimum amount of DCM and on top of that 10-fold volume excess of PE was added. Resulting colorless crystals were additionally washed with PE and dried in vacuo.



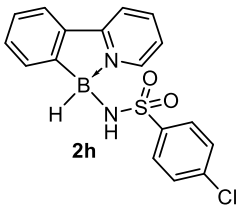
2f

B-(4-tolylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2f**) was prepared following the general procedure in 54% yield (36.3 mg). The same protocol on a 6 mmol scale afforded **2f** in 57% yield (1155 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.63. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 9.06 (d, *J* = 5.6 Hz, 1H), 8.33 – 8.27 (m, 1H), 8.26 – 8.22 (m, 1H), 7.99 – 7.93 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.68 (ddd, *J* = 7.2, 5.7, 1.3 Hz, 1H), 7.38 – 7.24 (m, 5H), 5.67 (d, *J* = 7.3 Hz, 1H), 3.76 (br, 1H), 2.42 (s, 3H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -2.29. **^{13}C NMR** (100.4 MHz, $CDCl_3$): δ 156.6, 144.9, 141.8, 141.5, 141.3, 136.7, 131.0, 130.2, 129.2, 127.3, 126.8, 122.6, 121.6, 117.7, 21.5. **HRMS** (ESI-TOF, m/z) calcd for $C_{18}H_{16}BN_2O_2S$ $[M - H]^+$: 335.1025; Found: 335.1024. X-ray quality crystals were grown by slow diffusion of hexane into DCM solution.



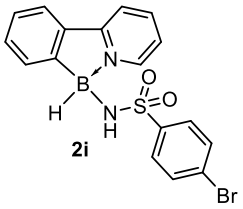
2g

B-(4-fluorophenylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2g**) was prepared following the general procedure in 67% yield (45.5 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.71. **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.5 Hz, 1H), 8.32 – 8.28 (m, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.03 – 7.91 (m, 3H), 7.72 – 7.63 (m, 1H), 7.36 – 7.20 (m, 5H), 5.76 (d, J = 6.9 Hz, 1H), 3.76 (br, 1H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -2.26 (d, *J* = 98.0 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 164.9 (d, *J* = 249.3 Hz), 157.5, 145.2, 143.2, 142.8 (d, *J* = 3.1 Hz), 137.8, 131.4, 131.1, 130.2 (d, *J* = 9.0 Hz), 127.9, 124.0, 122.7, 119.2, 116.1 (d, *J* = 22.6 Hz). **^{19}F NMR** (376.5 MHz, $(CD_3)_2CO$): δ -111.06. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{14}BFN_2O_2S$ $[M - H]^+$: 339.0774; Found: 339.0775.



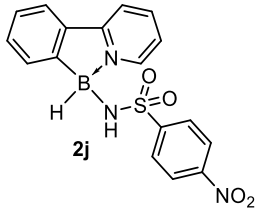
2h

B-(4-chlorophenylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2h**) was prepared following the general procedure in 67% yield (47.8 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.77. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.2 Hz, 1H), 8.32 – 8.29 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.99 – 7.88 (m, 3H), 7.72 – 7.65 (m, 1H), 7.60 – 7.52 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 (d, *J* = 6.2 Hz, 1H), 5.84 (d, *J* = 5.4 Hz, 1H), 3.76 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.32 (d, *J* = 103.6 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.6, 145.2, 143.2, 137.9, 137.3, 131.4, 131.1, 129.9 (2C, overlapped), 129.4, 129.3, 127.9, 124.0, 122.7, 119.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{13}B^{35}ClN_2O_2S$ $[M - H]^+$: 355.0479; Found: 355.0472.



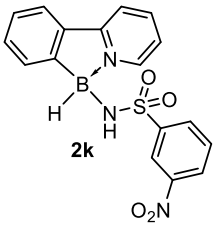
2i

B-(4-bromophenylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2i**) was prepared following the general procedure in 69% yield (55.4 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.74. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.2 Hz, 1H), 8.33 – 8.28 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 6.0, 1.8 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.71 – 7.68 (m, 1H), 7.38 – 7.28 (m, 2H), 7.26 (d, *J* = 6.2 Hz, 1H), 5.84 (d, *J* = 6.2 Hz, 1H), 3.75 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.27 (d, *J* = 102.5 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.6, 145.7, 145.3, 143.3, 137.9, 132.5, 131.4, 131.1, 129.5, 127.9, 125.7, 124.0, 122.7, 119.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{13}B^{79}BrN_2O_2S$ $[M - H]^+$: 398.9974; Found: 398.9968.



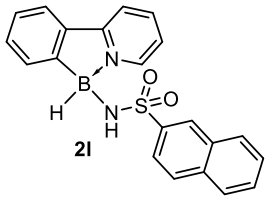
2j

B-(4-nitrophenylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2j**) was prepared following the general procedure in 56% yield (41.0 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.83. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.6 Hz, 1H), 8.43 – 8.38 (m, 2H), 8.33 (td, *J* = 7.9, 1.4 Hz, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 8.19 – 8.15 (m, 2H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.72 (ddd, *J* = 7.2, 5.7, 1.2 Hz, 1H), 7.33 (td, *J* = 7.3, 1.3 Hz, 1H), 7.29 (td, *J* = 7.2, 1.1 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 6.15 (d, *J* = 6.6 Hz, 1H), 3.77 (br, 1H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -2.33 (d, *J* = 90.8 Hz) **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 157.6, 151.9, 150.2, 145.2, 143.4, 137.9, 131.4, 131.1, 128.8, 128.0, 124.7, 124.1, 122.7, 119.3. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{13}BN_3O_4S$ $[M - H]^+$: 366.0719; Found: 366.0717.



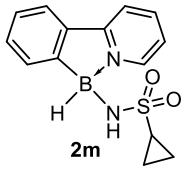
2k

B-(3-nitrophenylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2k**) was prepared following the general procedure in 65% yield (47.8 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.74. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.04 (d, *J* = 5.4 Hz, 1H), 8.66 – 8.62 (m, 1H), 8.42 (m, 1H), 8.33 – 8.29 (m, 2H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.9 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.25 (m, 1H), 7.20 (d, *J* = 7.1 Hz, 1H), 6.17 (d, *J* = 5.9 Hz, 1H), 3.76 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.41 (d, *J* = 99.4 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$: δ 157.7, 149.0, 148.1, 145.2, 143.4, 137.9, 133.3, 131.3, 131.2, 131.1, 128.0, 126.4, 124.1, 122.8, 122.3, 119.3. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{13}BN_3O_4S$ $[M - H]^+$: 366.0719; Found: 366.0714.



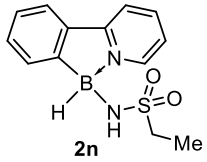
2l

B-(2-naphthylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2l**) was prepared following the general procedure in 66% yield (49.3 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.69. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.09 (d, *J* = 5.1 Hz, 1H), 8.42 (s, 1H), 8.24 (t, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.10 – 8.06 (m, 2H), 8.03 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.69 – 7.60 (m, 3H), 7.28 (dt, *J* = 7.8, 4.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 5.83 (d, *J* = 6.4 Hz, 1H), 3.82 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.21 (d, *J* = 84.2 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.5, 145.2, 143.3, 143.1, 137.8, 135.1, 133.2, 131.3, 131.1, 129.9, 129.4, 128.7, 128.7, 127.9, 127.8, 127.6, 124.1, 123.9, 122.6, 119.1. **HRMS** (ESI-TOF, m/z) calcd for $C_{21}H_{16}BN_2O_2S$ [M - H]$^+$: 371.1025; Found: 371.1018.



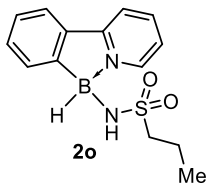
2m

B-(cyclopropylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2m**) was prepared following the general procedure in 65% yield (37.2 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.51. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.06 (d, *J* = 5.5 Hz, 1H), 8.33 – 8.28 (m, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.34 (m, 1H), 5.16 (d, *J* = 6.0 Hz, 1H), 3.93 (br, 1H), 2.68 – 2.60 (m, 1H), 1.12 – 0.91 (m, 4H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -2.04 (d, *J* = 96.7 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 157.3, 145.3, 143.1, 137.9, 131.5, 131.2, 127.8, 123.9, 122.7, 119.1, 32.4, 5.9, 5.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{14}H_{14}BN_2O_2S$ [M - H]$^+$: 285.0869; Found: 285.0870.



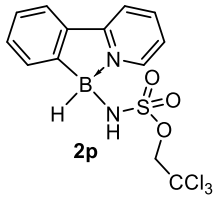
2n

B-(ethylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2n**) was prepared following the general procedure in 56% yield (30.5 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.31. **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 9.15 (d, *J* = 5.7 Hz, 1H), 8.32 – 8.27 (m, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.07 (d, *J* = 5.4 Hz, 1H), 3.85 (br, 1H), 3.21 – 3.12 (m, 1H), 3.08 – 3.00 (m, 1H), 1.42 (t, *J* = 7.4 Hz, 3H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.15 (d, *J* = 106.0 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.4, 145.5, 143.1, 138.0, 131.5, 131.1, 127.9, 123.9, 122.8, 119.1, 47.8, 9.3. **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{14}BN_2O_2S$ [M−H]$^+$: 273.0869; Found: 273.0869.



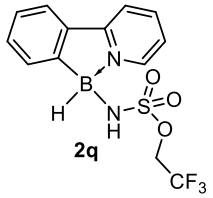
2o

B-(butylsulfonamido)-(2-(2-pyridyl)phenyl)borane (**2o**) was prepared following the general procedure in 80% yield (46.0 mg). **R_f** (DCM/EA 10:1): 0.46. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 9.14 (d, *J* = 5.7 Hz, 1H), 8.33 – 8.23 (m, 2H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.45 (td, *J* = 7.3, 1.0 Hz, 1H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 5.15 (d, *J* = 5.9 Hz, 1H), 3.84 (br, 1H), 3.19 – 3.09 (m, 1H), 3.08 – 2.98 (m, 1H), 2.00 – 1.88 (m, 2H), 1.10 (t, *J* = 7.5 Hz, 3H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -2.23 (d, *J* = 103.5 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 157.3, 145.5, 143.1, 137.9, 131.5, 131.0, 127.9, 123.9, 122.7, 119.1, 55.5, 18.8, 13.5. **HRMS** (ESI-TOF, m/z) calcd for $C_{14}H_{16}BN_2O_2S$ $[M-H]^+$: 287.1025; Found: 287.1025.



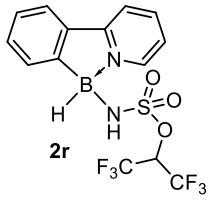
2p

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)phenyl)borane (**2p**) was prepared following the general procedure in 65% yield (48.4 mg). **R_f** (Hexane/DCM 1:2): 0.20. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.02 (d, *J* = 5.4 Hz, 1H), 8.36 – 8.31 (m, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.49 – 7.44 (m, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 6.23 (d, *J* = 6.1 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 3.95 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.24 (d, *J* = 95.3 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.7, 145.2, 143.6, 138.0, 131.7, 131.4, 128.1, 124.2, 122.8, 119.3, 95.6, 78.6 (t, *J* = 4.0 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{12}B^{35}Cl_3N_2O_3S$ $[M-H]^+$: 390.9649; Found: 390.9657.



2q

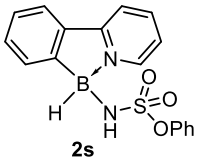
B-(2,2,2-trifluoroethoxysulfonamido)-(2-(2-pyridyl)phenyl)borane (**2q**) was prepared following the general procedure in 65% yield (44.3 mg). **R_f** (Hexane/DCM 3:1): 0.34. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 8.98 (d, *J* = 5.6 Hz, 1H), 8.33 (td, *J* = 8.0, 1.3 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.46 (td, *J* = 7.3, 0.9 Hz, 1H), 7.39 (td, *J* = 7.5, 0.9 Hz, 1H), 6.25 (d, *J* = 6.0 Hz, 1H), 4.66 – 4.58 (m, 2H), 3.90 (br, 1H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -2.35 (d, *J* = 92.2 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 157.7, 145.1, 143.6, 137.9, 131.7, 131.3, 128.1, 124.2 (q, *J* = 276.8 Hz), 124.2, 122.8, 119.3, 64.9 (q, *J* = 36.3 Hz). **^{19}F NMR** (376.5 MHz, $(CD_3)_2CO$): δ -74.41 (t, *J* = 8.6 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{11}BF_3N_2O_3S$ $[M-H]^+$: 343.0535; Found: 343.0533.



2r

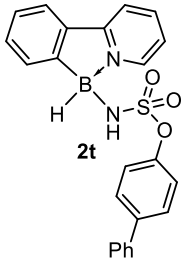
B-(1,1,1,3,3,3-hexafluoro-isopropoxy-sulfonamido)-(2-(2-pyridyl)phenyl)borane (**2r**) was prepared following the general procedure in 63% yield (44.3 mg). **R_f** (Hexane/DCM 3:1): 0.54. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.95 (d, *J* = 5.4 Hz, 1H), 8.36 – 8.32 (m, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.66

(d, *J* = 7.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 (t, *J* = 7.1 Hz, 1H), 6.59 (d, *J* = 5.7 Hz, 1H), 5.74 (hept, *J* = 5.9 Hz, 1H). 3.95 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.24 (d, *J* = 99.8 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.0, 144.2, 142.9, 137.1, 130.9, 130.4, 127.4, 123.3, 123.14 – 118.93 (m), 121.9, 118.5, 71.8 (dt, *J* = 68.0, 34.2 Hz). **^{19}F NMR** (376.5 MHz, $(CD_3)_2CO$): δ -73.64 (d, *J* = 5.1 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{14}H_{11}BF_6N_2O_3SNa$ $[M + Na]^+$: 435.0385; Found: 435.0378.



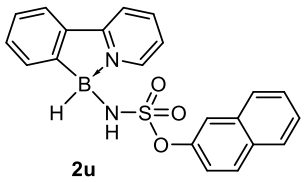
2s

B-(phenoxysulfonamido)-(2-(2-pyridyl)phenyl)borane (**2s**) was prepared following the general procedure in 56% yield (37.9 mg). **R_f** (Hexane/DCM 3:1): 0.31 **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.00 (d, *J* = 5.0 Hz, 1H), 8.29 (t, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 6.1 Hz, 1H), 7.51 – 7.25 (m, 9H), 6.16 (d, *J* = 6.6 Hz, 1H), 3.98 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.22 (d, *J* = 98.9 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.6, 152.5, 145.2, 143.4, 137.9, 131.5, 131.4, 130.3, 128.0, 126.6, 124.1, 123.0, 122.7, 119.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{14}BN_2O_3S$ $[M - H]^+$: 337.0818; Found: 337.0817.



2t

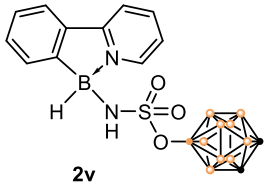
B-(4-phenyl-phenoxysulfonamido)-(2-(2-pyridyl)phenyl)borane (**2t**) was prepared following the general procedure in 53% yield (43.9 mg). **R_f** (Hexane/DCM 3:1): 0.28. **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 9.01 (d, *J* = 5.4 Hz, 1H), 8.28 (t, *J* = 7.7 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.69 – 7.64 (m, 3H), 7.54 – 7.44 (m, 5H), 7.40 – 7.33 (m, 3H), 6.15 (d, *J* = 6.8 Hz, 1H), 4.01 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.41. **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.7, 152.0, 145.2, 143.4, 141.1, 139.6, 138.0, 131.6, 131.5, 129.8, 128.8, 128.3, 128.0, 127.8, 124.1, 123.5, 122.7, 119.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{23}H_{18}BN_2O_3S$ $[M - H]^+$: 413.1131; Found: 413.1117.



2u

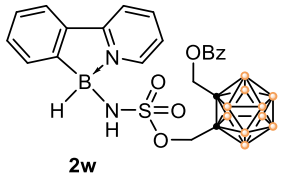
B-(2-naphthyloxysulfonamido)-(2-(2-pyridyl)phenyl)borane (**2u**) was prepared following the general procedure in 43% yield (33.1 mg). **R_f** (Hexane/DCM 3:1): 0.34. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.00 (d, *J* = 5.2 Hz, 1H), 8.26 (t, *J* = 7.3 Hz, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.03 – 7.84 (m, 5H), 7.62 – 7.48 (m, 4H), 7.45 (d, *J* = 6.1 Hz, 1H), 7.33 (m, 2H), 6.19 (d, *J* = 6.3 Hz, 1H), 4.02 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.17 (d, *J* = 84.1 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.7, 150.1, 145.2, 143.4, 138.0, 134.8, 132.5, 131.50, 131.45, 130.2, 128.6,

128.5, 128.0, 127.5, 126.6, 124.0, 122.9, 122.7, 119.9, 119.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{21}H_{16}BN_2O_3S$ [M - H]$^+$: 387.0974; Found: 387.0970.



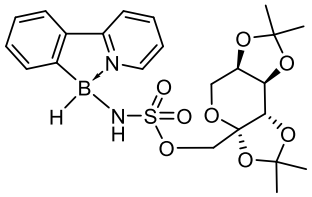
2v

2v was prepared following the general procedure on 0.1 mmol scale in 63% yield (25.6 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.57. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 9.02 (d, *J* = 5.7 Hz, 1H), 8.31 – 8.21 (m, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 5.37 (d, *J* = 6.6 Hz, 1H), 4.45 (s, 2H), 4.30 – 3.48 (br, 1H) 3.13 – 1.48 (m, 9H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ 10.34 (1B), -2.27 (1B), -4.47 (1B), -10.77 (2B), -15.79 (6B). **^{11}B{^{1}H} NMR** (128.4 MHz, $(CD_3)_2CO$): δ 10.35 (1B), -2.09 (1B), -4.48 (1B), -10.77 (2B), -14.96 (2B), -16.65 (4B). **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 157.5, 145.3, 143.0, 137.9, 131.5, 131.4, 127.7, 123.7, 122.5, 119.0, 52.3, 44.1. **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{21}{}^{11}B_{11}N_2O_3SK$ [M + K]$^+$: 445.1933; Found: 445.1950.



2w

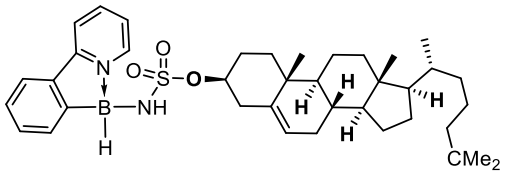
2w was prepared following the general procedure in 61% yield (67.4 mg). $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.20. **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ 8.97 (d, *J* = 5.6 Hz, 1H), 8.34 – 8.30 (m, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.11 – 8.07 (m, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.35 (m, 1H), 6.18 (d, *J* = 6.4 Hz, 1H), 5.15 – 5.06 (m, 2H), 4.87 (s, 1H), 3.92 (br, 1H), 2.79 – 1.65 (m, 10H). **^{11}B{^{1}H} NMR** (192 MHz, $(CD_3)_2CO$): δ -2.33 (1B), -3.32 (2B), -10.57 (8B). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 165.3, 157.7, 145.1, 143.6, 138. 0, 134.8, 131.7, 131.3, 130.7, 129.7, 129.6, 128.2, 124.2, 122.8, 119.4, 77. 5, 77.2, 67.7, 63.6. **HRMS** (ESI-TOF, m/z) calcd for $C_{22}H_{29}{}^{11}B_{11}N_2O_5SNa$ [M + Na]$^+$: 577.2718; Found: 577.2735. X-ray quality crystals were grown by slow diffusion of hexane into DCM solution.



2x (dr = 1:1)

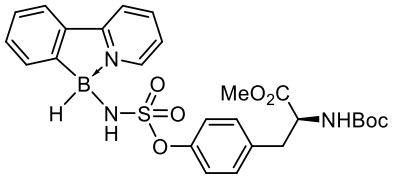
2x was prepared following the general procedure on 0.1 mmol scale in 55% yield (27.6 mg). $\mathbf{R_f}$ (DCM/EA 10:1): 0.57. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$, *1:1 mixture of diastereomers*): δ 9.10 (d, *J* = 5.7 Hz, 1H), 9.03 (d, *J* = 5.7 Hz, 1H), 8.35 – 8.30 (m, 2H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.48 – 7.43 (m, 2H), 7.40 – 7.36 (m, 2H) 5.91 (d, *J* = 6.9 Hz, 1H), 5.88 (d, *J* = 6.9 Hz, 1H), 4.71 – 4.65 (m, 2H), 4.48 (d, *J* = 2.7 Hz, 1H), 4.44 (d, *J* = 2.6 Hz, 1H), 4.31 – 4.26 (m, 2H), 4.24 – 4.22 (m, 2H), 4.19 – 4.15 (m, 2H), 3.95 (d, *J* = 1.9 Hz, 1H), 3.92 (d, *J* = 1.9 Hz, 1H), 3.67 (d, *J* = 2.3 Hz, 1H), 3.64 (d, *J* = 2.3 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H),

1.34 (s, 3H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -2.22. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$, *1:1 mixture of diastereomers*): δ 157.57, 157.55, 145.45, 145.26, 143.36, 143.32, 137.90, 137.87, 131.63, 131.58, 131.53, 131.46, 128.01, 127.98, 124.10, 122.66, 122.64, 119.20, 109.62, 109.54, 109.50, 102.40, 102.34, 71.74, 71.72, 71.08, 71.05, 71.03, 70.85, 69.06, 62.07, 61.98, 26.81, 26.79, 26.46, 26.35, 25.84, 25.79, 24.54, 24.43. **HRMS** (ESI-TOF, m/z) calcd for $C_{23}H_{30}BN_2O_8S$ $[M + H]^+$: 505.1815; Found: 505.1820.



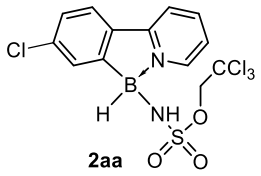
2y (dr = 1:1)

2y was prepared following the general procedure on 0.1 mmol scale in 45% yield (28.4 mg). **R_f** (Hexane/DCM 3:1): 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$, *1:1 mixture of diastereomers*): δ 9.12 (d, *J* = 5.7 Hz, 2H), 8.04 (t, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.43 (m, 6H), 5.46 (d, *J* = 4.9 Hz, 1H), 5.41 (d, *J* = 5.0 Hz, 1H), 4.50 – 4.40 (m, 2H), 4.28 (t, *J* = 6.3 Hz, 2H), 3.94 (br, 2H), 2.70 – 2.61 (m, 2H), 2.60 – 2.49 (m, 2H), 2.24 – 2.13 (m, 2H), 2.07 – 1.73 (m, 10H), 1.70 – 0.77 (m, 64H), 0.68 (s, 6H). **^{11}B NMR** (128.4 MHz, $CDCl_3$): δ -1.35. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$, *1:1 mixture of diastereomers*): δ 157.49, 145.43, 145.41, 143.28, 141.04, 140.92, 137.97, 131.57, 131.52, 131.32, 131.25, 127.96, 124.02, 123.29, 122.76, 119.17, 80.08, 57.59, 57.04, 51.09, 51.07, 43.10, 40.62, 40.24, 39.88, 38.04, 37.97, 37.35, 37.33, 36.95, 36.60, 32.71, 32.67, 32.63, 28.92, 28.68, 24.92, 24.51, 23.07, 22.83, 21.77, 19.67, 19.13, 12.23. **HRMS** (ESI-TOF, m/z) calcd for $C_{38}H_{55}BN_2O_3SNa$ $[M + Na]^+$: 653.3924; Found: 653.3900.



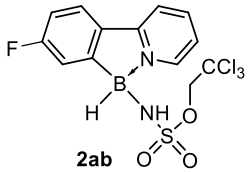
2z (dr = 1.5:1)

2z was prepared following the general procedure on 0.1 mmol scale in 76% yield (41.0 mg). **R_f** (DCM/EA 10:1): 0.63. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$, *1.5:1 mixture of diastereomers*): δ 8.99 (t, *J* = 5.4 Hz, 2H), 8.29 (t, *J* = 7.7 Hz, 2H), 8.26 – 8.22 (m, 2H), 7.99 – 7.94 (m, 2H), 7.71 – 7.64 (m, 2H), 7.47 – 7.39 (m, 4H), 7.38 – 7.28 (m, 10H), 6.23 (t, *J* = 7.5 Hz, 2H), 6.10 (d, *J* = 6.2 Hz, 2H), 4.45 (td, *J* = 8.5, 5.7 Hz, 2H), 3.69 (s, 3H), 3.19 (d, *J* = 4.8 Hz, 1H, *minor*), 3.16 (d, *J* = 4.7 Hz, 1H, *major*), 3.09 – 2.99 (m, 2H), 1.37 (s, 9H, *minor*), 1.36 (s, 9H, *major*). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -2.22. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$, *1.5:1 mixture of diastereomers*): δ 173.16, 157.58, 156.26, 151.24, 145.15, 143.36, 137.86, 135.88, 135.86, 131.60, 131.45, 131, 43, 131.07, 127.95, 124.04, 122.81, 122.64, 119.18, 79.47, 56.01, 52.29, 37.54, 28.49. **HRMS** (ESI-TOF, m/z) calcd for $C_{26}H_{31}BN_3O_7S$ $[M + H]^+$: 540.1975; Found: 540.1974.



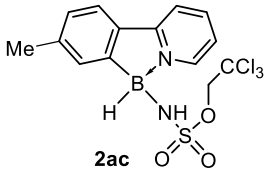
2aa

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-5-chloro-phenyl)borane (**2aa**) was prepared following the general procedure in 70% yield (60.0 mg). $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.40. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.99 (d, *J* = 5.3 Hz, 1H), 8.40 – 8.33 (m, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.76 (m, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.40 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.38 (d, *J* = 6.4 Hz, 1H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 3.90 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.56 (d, *J* = 97.7 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 156.7, 145.2, 143.8, 137.7, 136.6, 131.3, 128.3, 124.5, 124.4, 119.6, 95.5, 78.55 (t, *J* = 3.9 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{10}B^{35}Cl_4N_2O_3S$ [M - H]$^+$: 424.9259; Found: 424.9253.



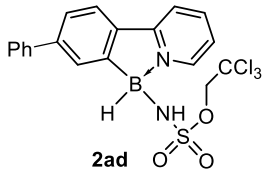
2ab

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-5-fluoro-phenyl)borane (**2ab**) was prepared following the general procedure in 66% yield (54.1 mg). $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.37. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.99 (d, *J* = 5.4 Hz, 1H), 8.33 (t, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.06 (dd, *J* = 8.3, 4.7 Hz, 1H), 7.71 (t, *J* = 6.2 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.13 (td, *J* = 9.0, 2.4 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 3.91 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.61 (d, *J* = 104.9 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 165.9 (d, *J* = 250.1 Hz), 156.8, 145.2, 143.7, 134.1, 125.1 (d, *J* = 8.9 Hz), 123.9, 119.3, 117.7 (d, *J* = 20.5 Hz), 115.3 (d, *J* = 24.1 Hz), 95.6, 78.6 (t, *J* = 3.8 Hz). **^{19}F NMR** (376.5 MHz, $(CD_3)_2CO$): δ -111.38. **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{10}B^{35}Cl_3FN_2O_3S$ [M - H]$^+$: 408.9554; Found: 408.9546.



2ac

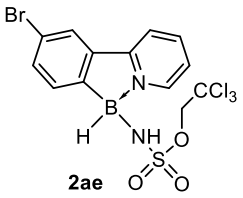
B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-5-methyl-phenyl)borane (**2ac**) was prepared following the general procedure in 65% yield (53.0 mg). $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.37. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.96 (d, *J* = 5.4 Hz, 1H), 8.28 (t, *J* = 7.7 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.66 (t, *J* = 6.5 Hz, 1H), 7.53 (s, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 4.71 (d, *J* = 11.1 Hz, 1H), 3.92 (br, 1H), 2.39 (s, 3H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.39 (d, *J* = 95.8 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 157.9, 145.0, 143.4, 141.8, 135.6, 132.1, 129.0, 123.6, 122.7, 119.0, 95.6, 78.62 (t, *J* = 3.8 Hz), 21.94. **HRMS** (ESI-TOF, m/z) calcd for $C_{14}H_{13}B^{35}Cl_3N_2O_3S$ [M−H]$^+$: 404.9805; Found: 404.9799.



2ad

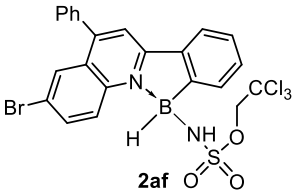
B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-5-phenyl-phenyl)borane (**2ad**) was prepared following the general procedure in 65% yield (61.1 mg). $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.34. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.02 (d, *J* = 5.7 Hz, 1H), 8.37 – 8.27 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 1.1 Hz, 1H), 7.72 (m, 3H), 7.67 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.35 (m, 1H), 6.33 (d, *J* = 6.5 Hz, 1H), 4.80 (d, *J* = 11.1 Hz, 1H), 4.75 (d, *J* = 11.1 Hz, 1H), 4.03 (br, 1H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ -1.94. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$):

δ 157.4, 145.2, 144.1, 143.6, 141.9, 137.2, 129.9, 129.7, 128.5, 127.9, 127.1, 124.1, 123.3, 119.4, 95.6, 78.6. **HRMS** (ESI-TOF, m/z) calcd for $C_{19}H_{16}B^{35}Cl_3N_2O_3SNa$ [M + Na]$^+$: 490.9937; Found: 490.9915.



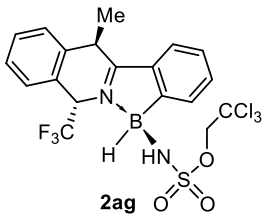
2ae

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-4-bromo-phenyl)borane (**2ae**) was prepared following the general procedure in 55% yield (52.1 mg). **R_f** (Hexane/DCM 3:1): 0.40. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.03 (d, *J* = 5.5 Hz, 1H), 8.43 – 8.34 (m, 2H), 8.20 (d, *J* = 1.3 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.32 (d, *J* = 6.4 Hz, 1H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 3.91 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.32 (d, *J* = 80.1 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 156.2, 145.4, 143.8, 140.3, 134.2, 133.3, 125.7, 125.0, 121.7, 119.9, 95.5, 78.6 (t, *J* = 3.9 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{10}B^{79}Br^{35}Cl_3N_2O_3S$ [M−H]$^+$: 468.8754; Found: 468.8740.



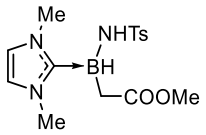
2af

2af was prepared following the general procedure from 0.13 mmol of **1af** in 52% yield (38.0 mg). **R_f** (DCM/Hexane 3:1): 0.23. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 9.1 Hz, 1H), 8.09 (s, 1H), 8.02 – 7.91 (m, 3H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.50 (m, 6H), 7.40 (t, *J* = 7.2 Hz, 1H), 4.57 (q, *J* = 12.2, 11.5 Hz, 2H), 4.50 (s, 1H), 4.30 (br, 1H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.93. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.7, 155.1, 140.8, 137.0, 136.4, 136.2, 132.6, 131.2, 130.2, 129.5, 129.4, 127.9, 127.8, 125.3, 122.7, 121.8, 116.7, 99.1, 94.4, 77.8. **HRMS** (ESI-TOF, m/z) calcd for $C_{23}H_{17}B^{79}Br^{35}Cl_3N_2NaO_3S^+$ [M+Na]$^+$ 620.9175, found: 620.9175; calcd for $C_{23}H_{17}B^{79}Br^{35}Cl_3KN_2O_3S^+$ [M+K]$^+$ 636.8914, found: 636.8913.



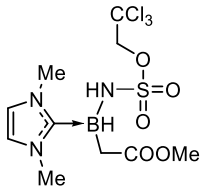
2ag

2ag was prepared following the general procedure from 0.2 mmol of **1ag** in 53% yield (56.5 mg). Only one isomer was formed, presumably with trans-arrangement of CF_3 and NHTces groups to avoid steric hindrance. **R_f** (DCM/Hexane 2:1): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (t, *J* = 6.8 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 6.7 Hz, 2H), 7.47 – 7.38 (m, 3H), 5.93 (q, *J* = 6.5 Hz, 1H), 4.65 (q, *J* = 7.2 Hz, 1H), 4.55 – 4.39 (m, 3H), 3.72 (br, 1H), 1.82 (d, *J* = 7.6 Hz, 3H). **^{11}B NMR** (128 MHz, $CDCl_3$): δ -2.21. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -70.08. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 184.5 (C=N), 158.9 (C-B, broad due to quadrupolar splitting), 136.6, 134.7, 133.7, 130.7, 130.4, 129.3, 127.9, 127.7, 127.4, 124.8, 124.5, 123.0 (q, *J* = 283.9 Hz, CF_3), 94.2 (CCl_3), 78.0 (CH_2), 58.7 (q, *J* = 31.5 Hz, CH-CF_3), 35.2 (CH-CH_3), 22.5 (CH_3). **HRMS** (ESI-TOF, m/z) calcd for $C_{19}H_{16}B^{35}Cl_3F_3N_2O_3S^+$ [M−H]$^+$: 524.9987; Found: 524.9984.



2ah

2ah was prepared following the general procedure from 0.1 mmol of **1ah** in 43% yield (15.0 mg). $\mathbf{R_f}$ (DCM/EA 5:3): 0.17 (visualized with ceric ammonium molybdate).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.81 (s, 2H), 4.02 (s, 1H), 3.82 (s, 6H), 3.43 (s, 3H), 2.67 (br, 1H) 2.38 (s, 3H), 1.53 (s, 2H). **^{11}B NMR** (128 MHz, $CDCl_3$): δ -16.01 (d, *J* = 93.8 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 178.4, 141.3, 140.3, 129.0, 126.6, 121.5, 51.0, 36.5, 21.5. **HRMS** (ESI-TOF, m/z) calcd for $C_{15}H_{22}BN_3NaO_4S^+$ $[M+Na]^+$: 374.1316; Found: 374.1320.



2ai

2ai was prepared following the general procedure from 0.07 mmol of **1ai** in 58% yield (19.4 mg). $\mathbf{R_f}$ (DCM/EA 1:1): 0.34 (visualized with ceric ammonium molybdate). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.85 (s, 2H), 4.58 (d, *J* = 10.7 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.38 (s, 1H), 3.84 (s, 6H), 3.58 (s, 3H), 2.98 (br, 1H), 1.66 (d, J = 5.8 Hz, 2H). **^{11}B NMR** (128 MHz, $CDCl_3$): δ -15.67 (d, *J* = 93.8 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 178.5, 121.8, 94.7, 77.8, 51.3, 36.5. **HRMS** (ESI-TOF, m/z) calcd for $C_{10}H_{17}B^{35}Cl_3N_3NaO_5S^+$ $[M+Na]^+$ 429.9940; Found: 429.9944.

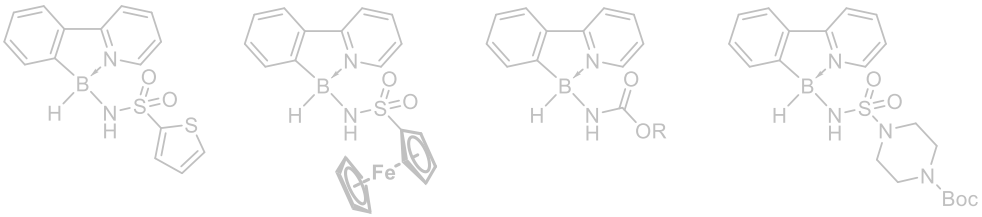
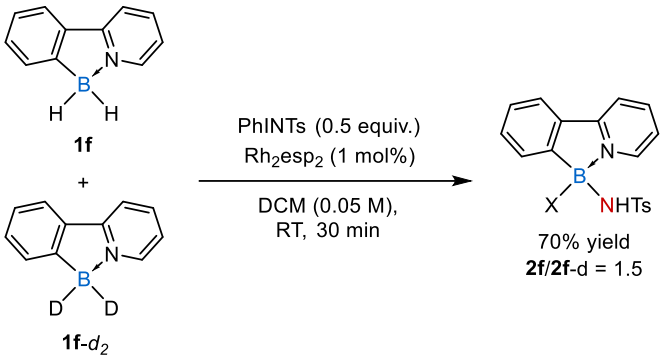


Fig. S29. List of unsuccessful substrates.

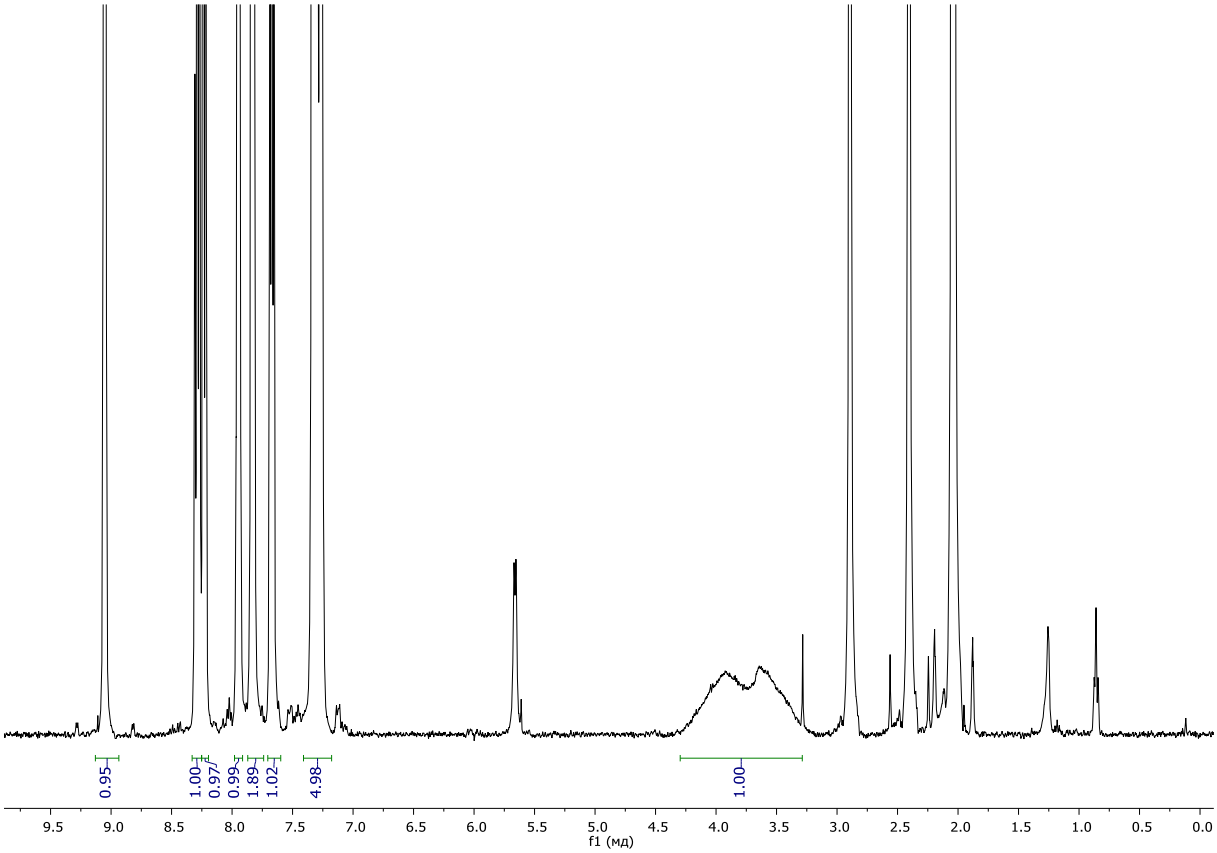
In case of thiophenesulfonamide catalyst degradation was observed, the yield of the target B–H insertion product was < 10%. In case of ferrocenesulfonamide the intramolecular C–H insertion product was the only Fe-containing compound aside from starting material, albeit it is formed in low yields (15-20%). In case of inactivated carbamates (R = Ph, tBu) the reaction does not take place even at elevated temperatures. In case of sulfamides usually a complex mixture of B-containing products forms (at least 5 different compounds according to crude ^{11}B NMR).

Mechanistic Studies

KIE experiment



An oven-dried 10 ml Schlenk flask was charged with Rh_2esp_2 (1.5 mg, 0.002 mmol, 1 mol%), **1f** (0.1 mmol), **1f**-d_2 (0.1 mmol) and DCM (1 ml). To this solution PhINTs (37.3 mg, 0.1 mmol, 0.5 equiv.) was added portionwise during the course of 15 minutes. The resulting solution was stirred for additional 15 minutes, then in was directly transferred to a SiO_2 column and the products were eluted with DCM to DCM/EA (40:1) to afford 25.3 mg of **2f** and **2f**-*d* mixture (70% yield). The product ratio was determined based on ^{1}H NMR by comparing broad B–H signal intensities of thus obtained **2f** + **2f**-*d* mixture and pure **2f**. With standard ^{1}H NMR parameters (relaxation delay = 1s) the intensity of B–H peak in **2f** is equal to 1±0.02 with respect to aromatic C–H protons (based on 3 independent measurements). The intensity of B–H peak of **2f** + **2f**-*d* mixture was 0.6, which corresponds to their ratio 1.5:1. The same results were obtained at lower conversions using 0.1 equiv. of PhINTs.



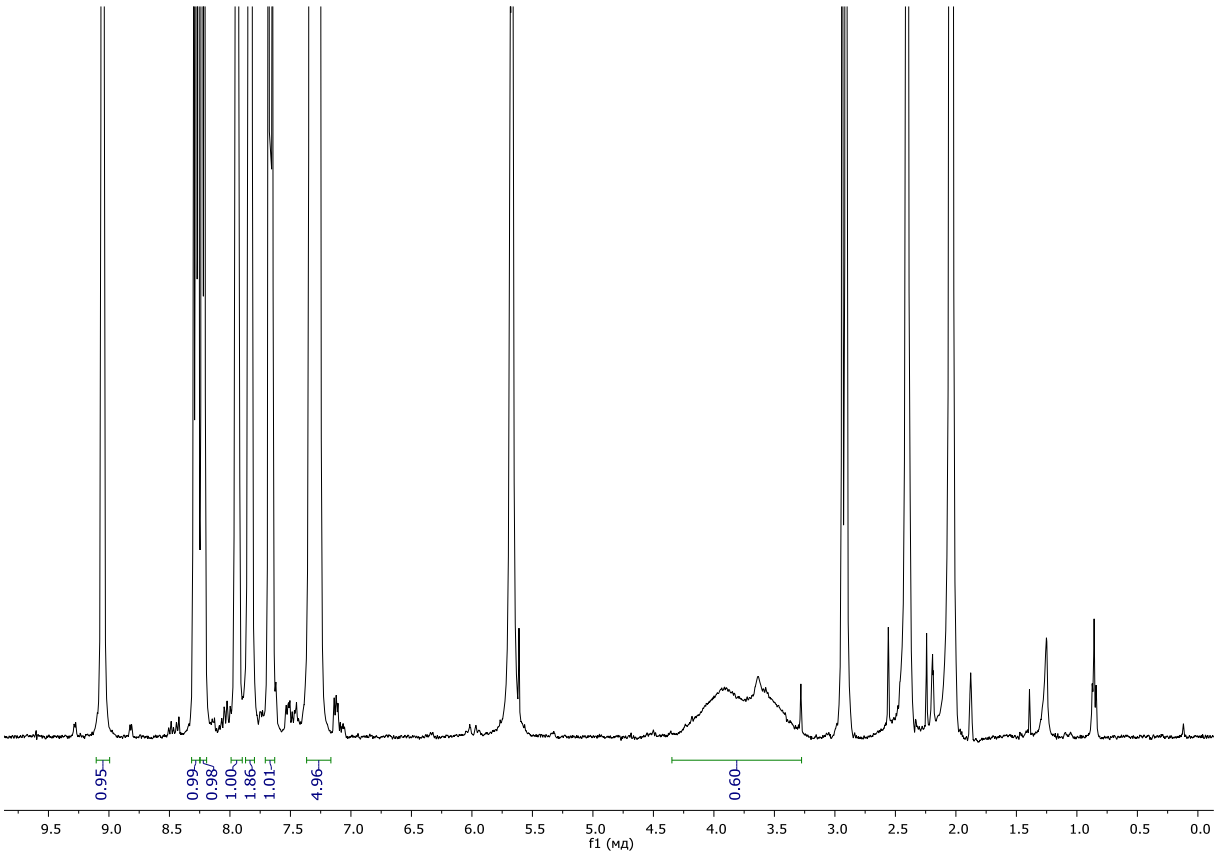
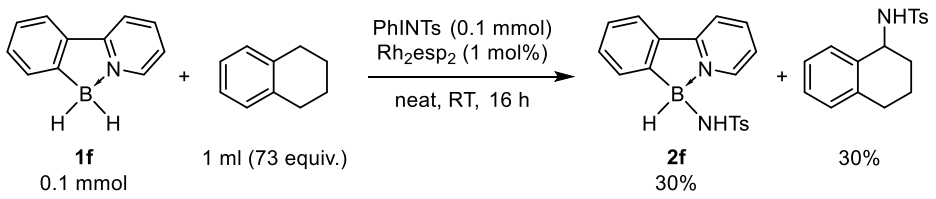


Fig. S30. ^{1}H NMR spectra of pure **2f** (top) and a mixture of **2f** and **2f**-*d* in 1.6:1 ratio (bottom).

Competitive Reactions



An oven-dried 10 ml Schlenk flask was charged with Rh_2esp_2 (1.5 mg, 0.002 mmol, 1 mol%), **1f** (0.1 mmol, 1 equiv.), and tetralin (1 ml, 73 equiv.). The resulting solution was purged with argon for 15 minutes. To the resulting solution PhINTs (37.3 mg, 0.1 mmol, 1 equiv.) was added in one portion and the resulting suspension was stirred overnight. The reaction mixture was directly transferred to a prepacked SiO_2 column and first eluted with PE to remove an excess of tetralin and then with DCM/EA (20:1) to collect a mixture of **2f** and C–H insertion products. The product ratio and yields were determined to be 1:1 based on ^{1}H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as internal standard. Conversion of starting borane **1f** was 65%.

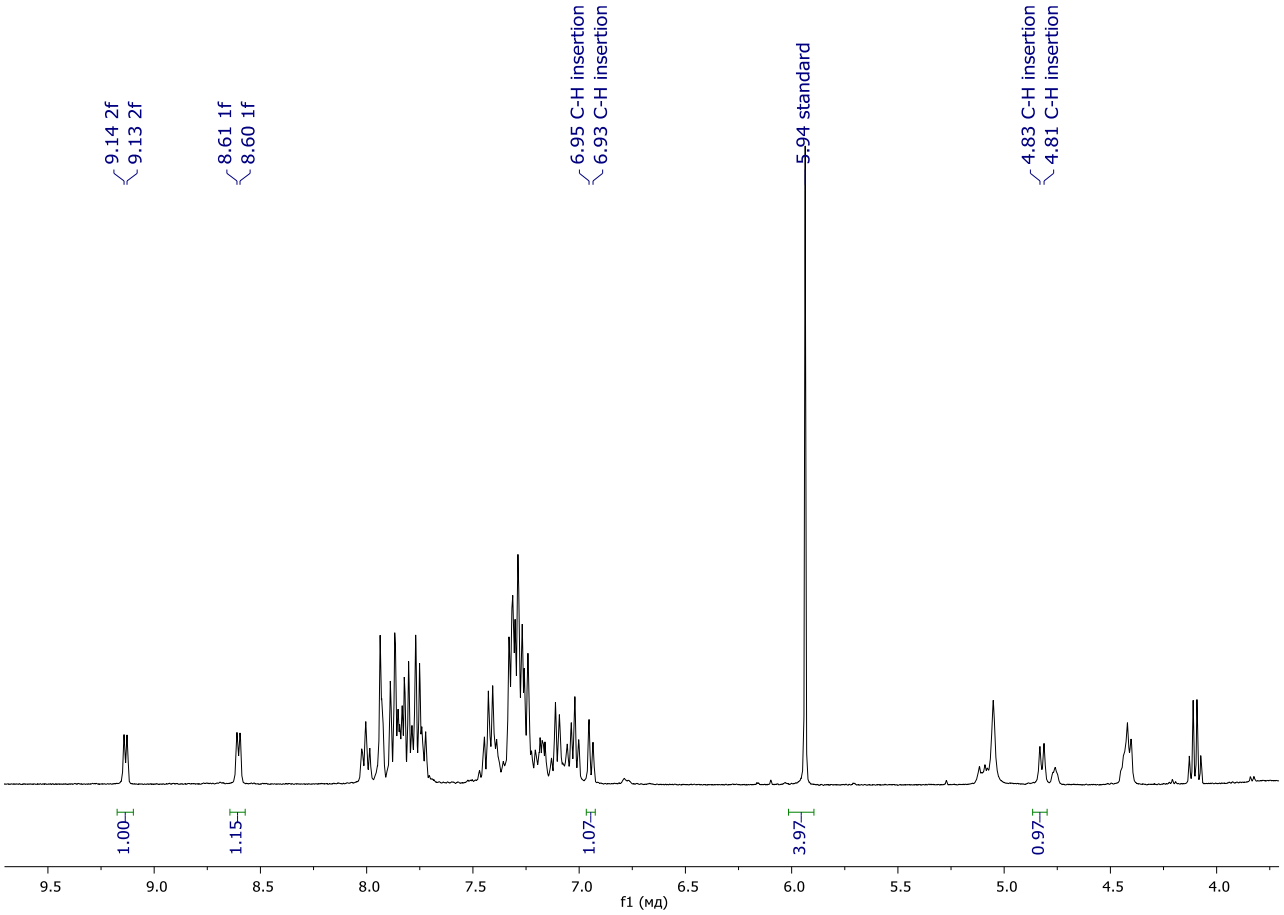
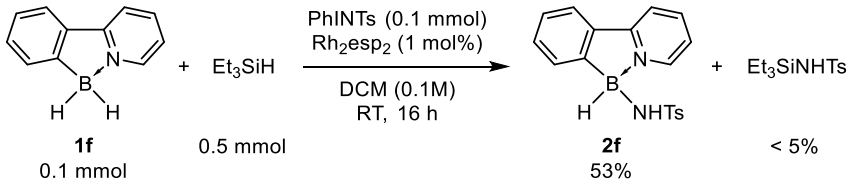


Fig. S31. ^{1}H NMR spectrum of the mixture of **2f** and tetralin C–H insertion product.



An oven-dried 10 ml Schlenk flask was charged with Rh_2esp_2 (1.5 mg, 0.002 mmol, 1 mol%), **1f** (0.1 mmol, 1 equiv.) and DCM (1 ml). To the resulting solution Et_3SiH was added (58 mg, 0.5 mmol, 5 equiv.) followed by PhINTs (37.3 mg, 0.1 mmol, 1 equiv.). The resulting suspension was stirred overnight, filtered through Celite and concentrated in vacuo. The yield of **2f** (53%) and conversion of **1f** (76%) were determined based on ^{1}H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as internal standard. There were only trace amounts of Si–H insertion product.

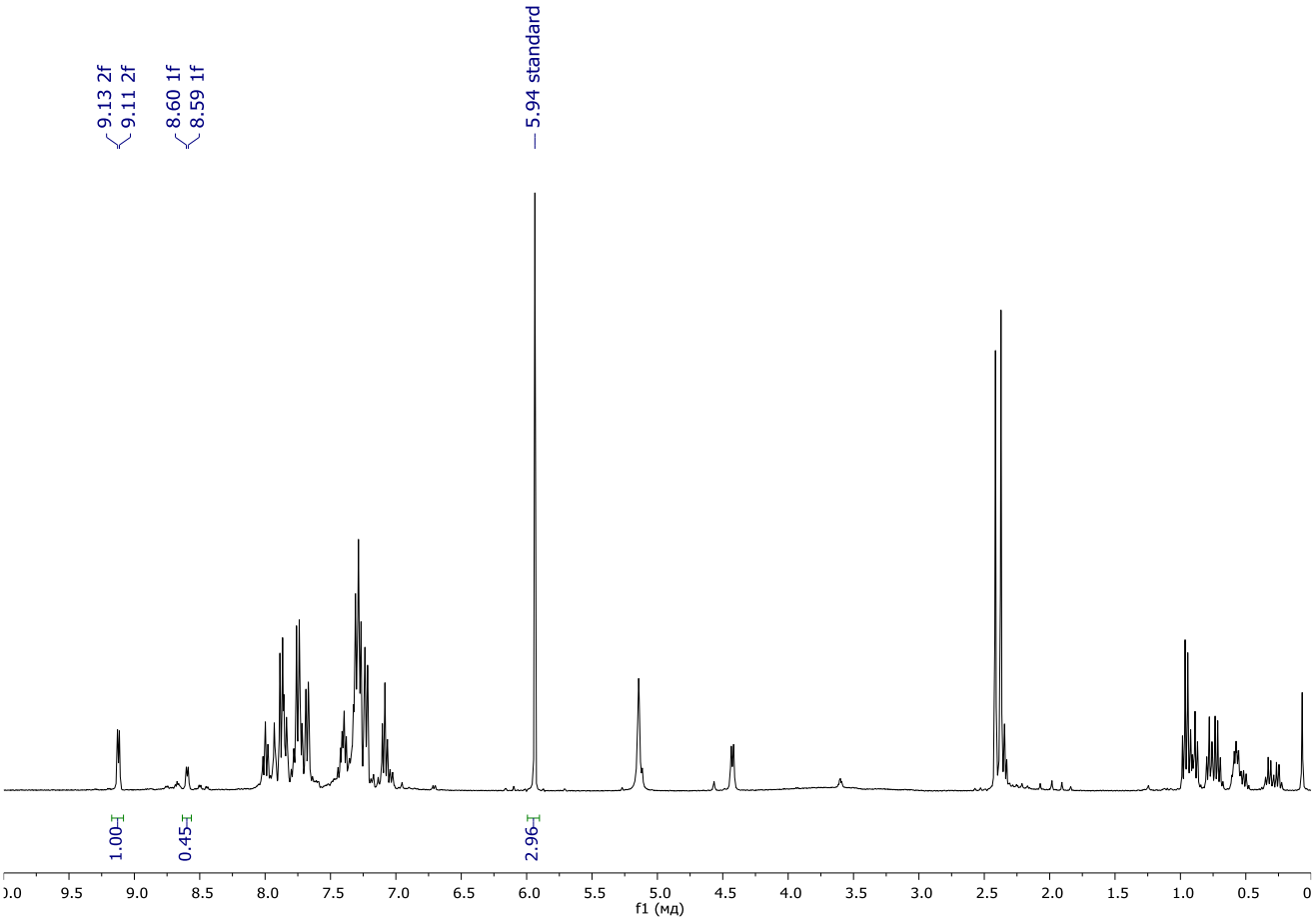
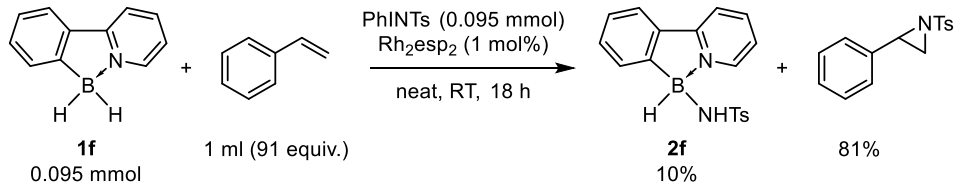


Fig. S32. ^{1}H NMR spectrum of **2f** and trace amounts of $Et_3SiNHTs$.



An oven-dried 10 ml Schlenk flask was filled with argon and charged with Rh_2esp_2 (0.8 mg, 9.5×10^{-4} mmol, 1 mol%), **1f** (16 mg, 0.095 mmol, 1 equiv.), and styrene (1 ml, 91 equiv.), that was flushed with argon for 15 minutes prior to use. To the resulting solution PhINTs (35.5 mg, 0.095 mmol, 1 equiv.) was added in one portion and the resulting suspension was stirred overnight. The reaction mixture was directly transferred to a prepacked SiO_2 column and first eluted with hexane to remove an excess of styrene and then with DCM/EA (10:1) to collect a mixture of **1f**, **2f** and aziridine product. The yield of **2f** (10%) and conversion of **1f** (14%) were determined based on ^{1}H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as the internal standard. The yield of aziridine product was 81%.

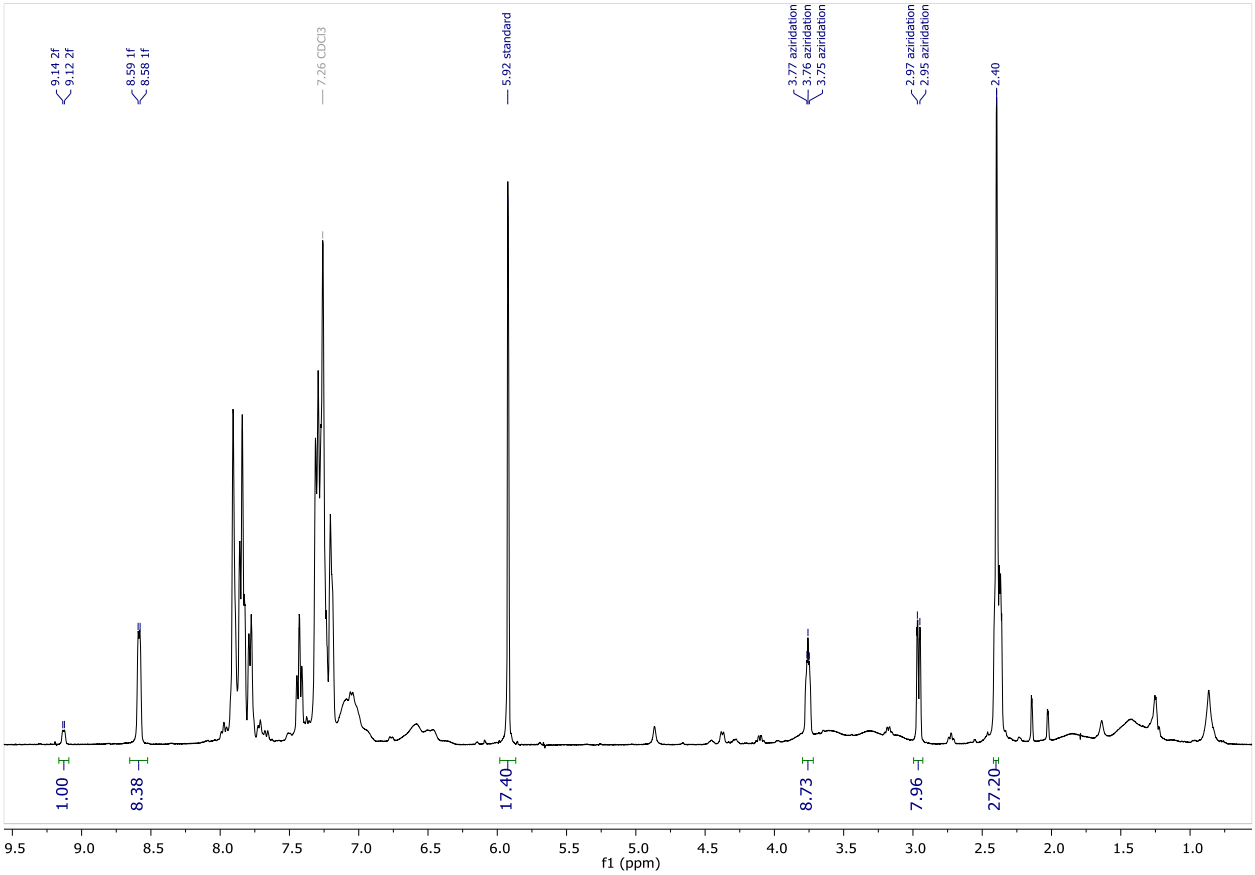
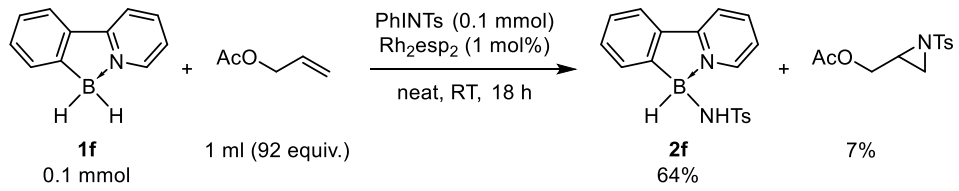


Fig. S33. ^{1}H NMR spectrum of the products of competitive reaction of **1f** with PhI=NTs in neat styrene.



An oven-dried 10 ml Schlenk flask was filled with argon and charged with Rh_2esp_2 (0.8 mg, 1×10^{-3} mmol, 1 mol%), **1f** (16.7 mg, 0.1 mmol, 1 equiv.), and freshly distilled allyl acetate (1 ml, 92 equiv.), that was flushed with argon for 15 minutes prior to use. To the resulting solution PhINTs (37.3 mg, 0.1 mmol, 1 equiv.) was added in one portion and the resulting suspension was stirred overnight. The reaction mixture was concentrated by rotary evaporation and then dried in vacuo (oil pump) for 1h at rt. The yield of **2f** (64%) and conversion of **1f** (75%) were determined based on ^{1}H NMR ($CDCl_3$) using 1,1,2,2-tetrachloroethane as the internal standard. The yield of aziridine product was 7%.

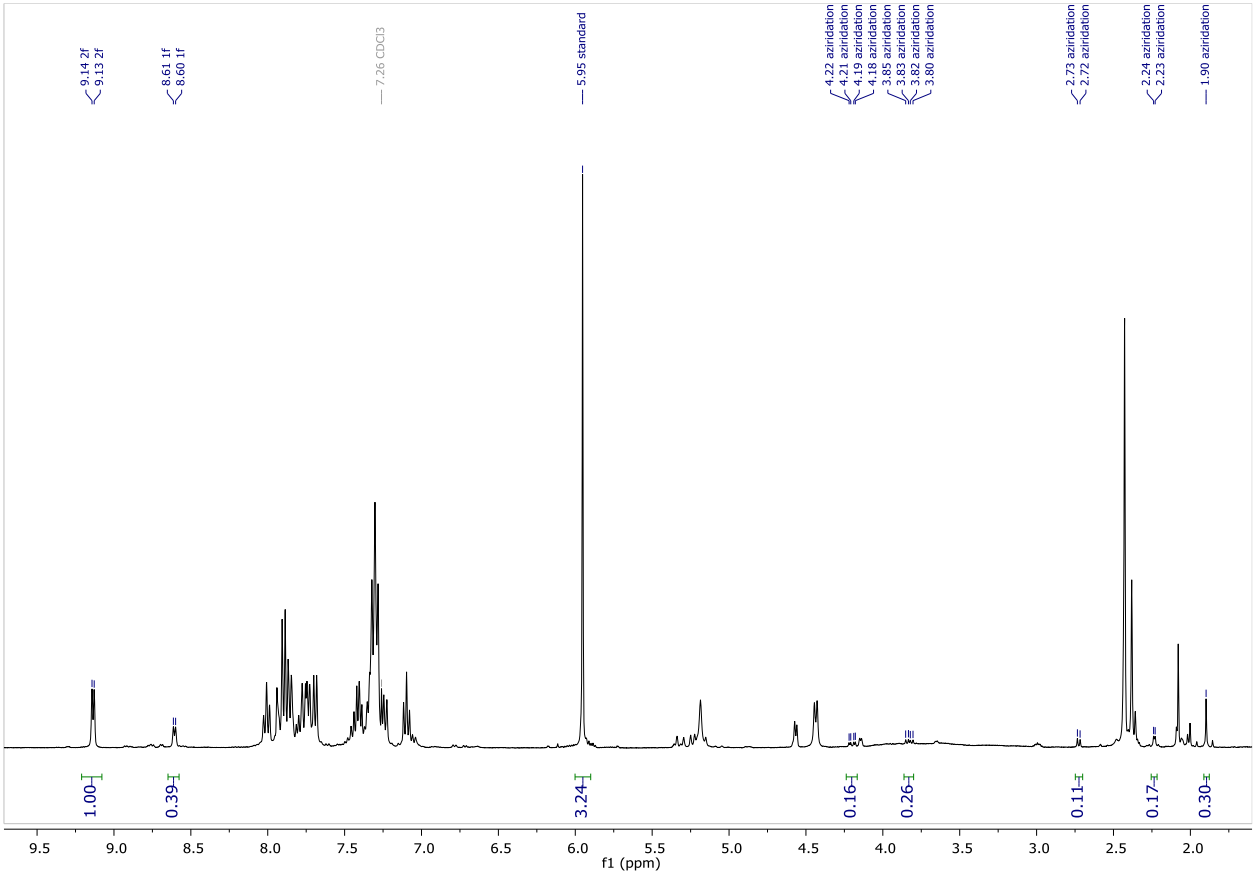
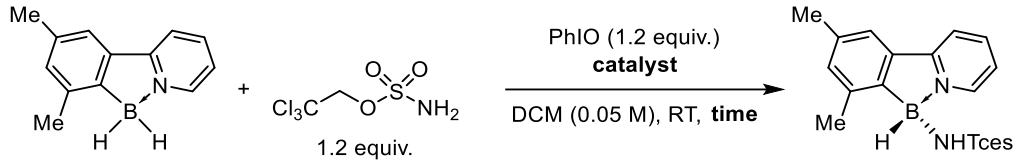
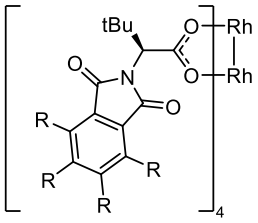


Fig. S34. ^{1}H NMR spectrum of the products of the competitive reaction of **1f** with PhI=NTs in neat allyl acetate.

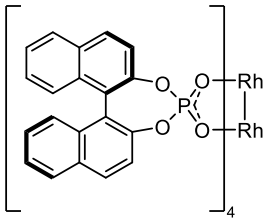
Optimization of Enantioselective B–H nitrene insertion

Table S2. Catalysts screening for enantioselective B–H nitrene insertion.

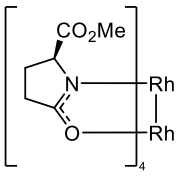




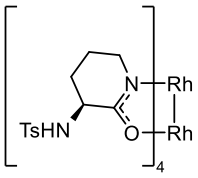
R = H, Rh_2[(*S*)-PTTL]$_4$
R = Ph, Rh_2[(*S*)-TPPTTL]$_4$



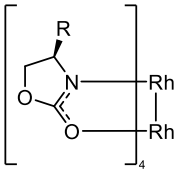
Rh_2[(*R*)-BNP]$_4$



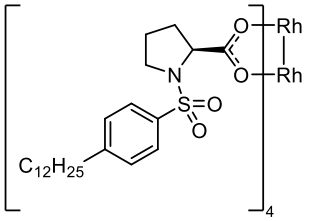
Rh_2[(5*S*)-MEPY]$_4$



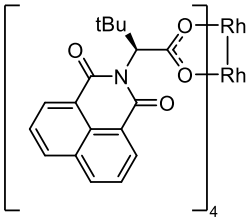
Rh_2[(*S*)-NAP]$_4$



R = iPr, Rh_2[(4*R*)-IPOX]$_4$
R = Bn, Rh_2[(4*R*)-BNOX]$_4$

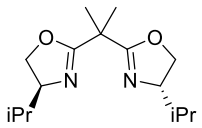


Rh_2[(*S*)-DOSP]$_4$



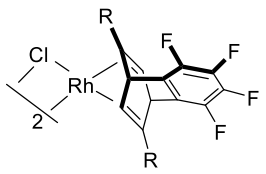
Rh_2[(*S*)-NTTL]$_4$

$Cu(MeCN)_4PF_6$ +



BOX

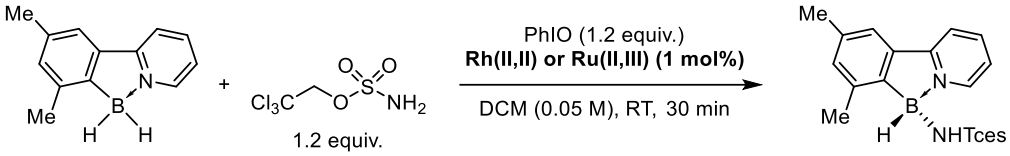
mixed *in situ* in 1:1 ratio



R = tBu, [(*R,R*-tBu$_2$-TFB)RhCl]$_2$
R = Ph, [(*R,R*-Ph$_2$-TFB)RhCl]$_2$

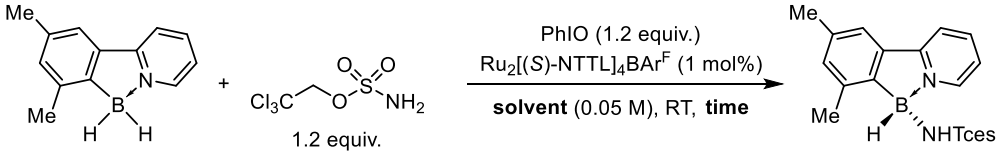
entry	catalyst (loading, %)	time, min	yield, %	e.r.
1	Rh_2[(*S*)-PTTL]$_4$ (1 mol%)	30	36	53:47
2	Rh_2[(*S*)-TPPTTL]$_4$ (1 mol%)	45	90	54:46
3	Rh_2[(*R*)-BNP]$_4$ (1 mol%)	240	44	52:48
4	Rh_2[(5*S*)-MEPY]$_4$ (1 mol%)	20	37	51:49
5	Rh_2[(*S*)-NAP]$_4$ (1 mol%)	20	48	52:48
6	Rh_2[(*4R*)-IPOX]$_4$ (1 mol%)	45	56	52:48
7	Rh_2[(*4R*)-BNOX]$_4$ (1 mol%)	60	48	52:48
8	Rh_2[(*S*)-DOSP]$_4$ (1 mol%)	30	42	51:49
9	**Rh_2[(*S*)-NTTL]$_4$ (1 mol%)**	**30**	**85**	**62:38**
10	[(BOX)Cu(MeCN)$_2$]PF_6 (5 mol%)	60	24	51:49
11	[(*R*,*R*-tBu$_2$-TFB)RhCl]$_2$ (2.5 mol%)	30	29	52:48
12	[(*R*,*R*-Ph$_2$-TFB)RhCl]$_2$ (2.5 mol%)	30	86	52:48

Table S3. NTTL-based catalysts screening for enantioselective B–H nitrene insertion.



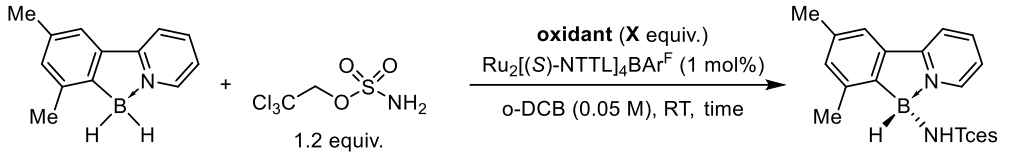
entry	catalyst (loading, %)	yield, %	e.r.
1	Rh_2[(*S*)-NTTL]$_4$ (1 mol%)	85	62:38
2	Rh_2[(*S*)-4-Br-NTTL]$_4$ (1 mol%)	78	59:41
3	**Rh_2[(*S*)-4-Ph-NTTL]$_4$ (1 mol%)**	**77**	**67:33**
4	Rh_2[(*S*)-4-PhPh-NTTL]$_4$ (1 mol%)	69	66:34
5	Rh_2[(*S*)-4-Np-NTTL]$_4$ (1 mol%)	64	65:35
6	Rh_2[(*S*)-4-Ar^F-NTTL]$_4$ (1 mol%)	71	55:45
7	Ru_2[(*S*)-NTTL]$_4$$BAr^F$ (1 mol%)	71	70:30
8	Ru_2[(*S*)-4-Br-NTTL]$_4$$BAr^F$ (1 mol%)	60	68:32
9	Ru_2[(*S*)-4-Ph-NTTL]$_4$$BAr^F$ (1 mol%)	44	60:40
10	**Ru_2[(*S*)-NTTL]$_4$Cl (1 mol%)**	**63**	**72:28**
11	Ru_2[(*S*)-NTTL]$_4$$N_3$ (1 mol%)	69	71:29
12	Ru_2[(*S*)-NTTL]$_4$$NO_3$ (1 mol%)	63	72:28

Table S4. Solvent screening for enantioselective B–H nitrene insertion.



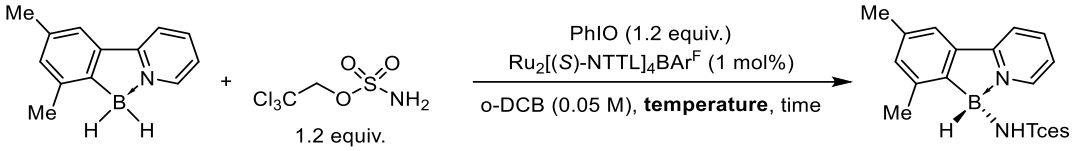
entry	solvent	time, min	yield, %	e.r.
1	CH_2Cl_2	30	71	70:30
2	$CHCl_3$	30	75	60:40
3	o-DFB	60	62	75:25
4	**o-DCB**	**60**	**73**	**75:25**
5	$PhCF_3$	60	65	75:25
6	PhCl	15	62	74:26
7	EtOAc	720	59	76:24
8	iPrOH	30	< 5	-
9	CH_3NO_2	30	17	-
10	acetone	60	22	-

Table S5. Hypervalent iodine reagent screening for enantioselective B–H nitrene insertion.



entry	oxidant (equiv.)	additive (equiv.)	time, min	yield, %	e.r.
1	**PhIO (1.2)**	**-**	**30**	**73**	**75:25**
2	$PhI(OAc)_2$ (1.2)	MgO (2.5)	60	26	77:23
3	$PhI(OPiv)_2$ (1.2)	MgO (2.5)	60	38	75:25
4	$PhI(OOCCF_3)_2$ (1.2)	MgO (2.5)	720	< 5	-
5	PhIO (1.5)	-	30	72	75:25
6	PhIO (3)	-	30	28	63:27

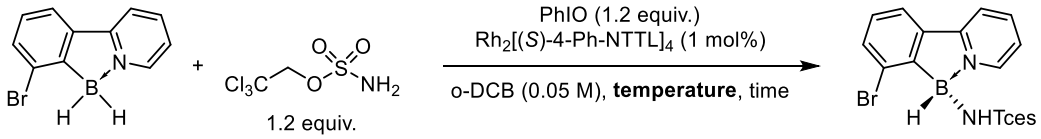
Table S6. Temperature screening for Ru(II,III) catalyzed enantioselective B–H nitrene insertion.



entry	temp. °C	time, min	yield, %	e.r.
1	+ 22	30	73	70:30
2	**+ 4**	**180**	**57**	**81:19**
3	- 10	1440 (24h)	41	81:19
4[a]	- 30	7200 (120h)	37	80:20

[a]PhCl used as solvent.

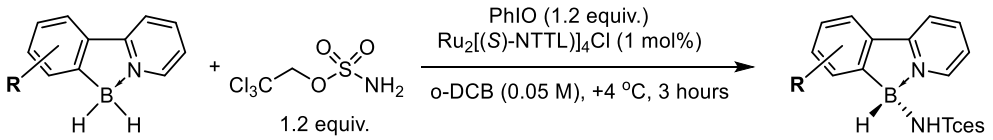
Table S7. Temperature screening for Rh(II,II) catalyzed enantioselective B–H nitrene insertion.



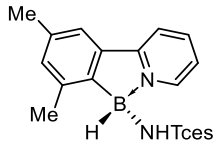
entry	temp. °C	time, min	yield, %	e.r.
1	+22	30	79	71:29
2	+4	360	84	80:20
3	−10	2160 (36h)	97	79:21
4[a]	**−30**	**2880 (48h)**	**89**	**89:11**

[a]PhCl used as solvent.

Enantioselective B–H Nitrene Insertion (Borane Scope)

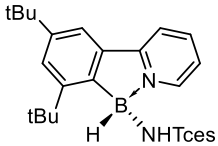


An oven-dried 10 ml Schlenk flask was charged with $Ru_2[(S)\text{-NTTL}]_4Cl$ (1.5 mg, 0.001 mmol, 1 mol%), phenylpyridineborane **1f** or **1g-j** (0.1 mmol, 1 equiv.), 2,2,2-Trichloroethyl sulfamate **6a** (27.4 mg, 0.12 mmol, 1.2 equiv.) and o-DCB (2 ml). The resulting solution was cooled in an ice-bath and then iodosobenzene (26.4 mg, 0.12 mmol, 1.2 equiv.) was added in one portion. The resulting suspension was stirred for 3 hours. The mixture was then diluted with hexane (2 ml) and directly transferred to a short prepacked silica column. The product was eluted using either pure DCM.



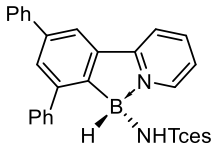
2ga

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-4,6-dimethyl-phenyl)borane (**2ga**) was prepared following the general procedure in 81% yield (34.1 mg) with 83:17 e.r. $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.27. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$: δ 9.01 (d, *J* = 5.3 Hz, 1H), 8.29 (t, *J* = 7.7 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.62 (s, 1H), 7.07 (s, 1H), 6.15 (d, *J* = 6.0 Hz, 1H), 4.65 (s, 2H), 3.96 (br, 1H), 2.48 (s, 3H), 2.36 (s, 3H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -2.37 (d, *J* = 83.3 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 158.2, 145.2, 143.4, 141.6, 138.1, 138.1, 133.7, 123.8, 120.5, 119.2, 95.7, 78.5, 21.3, 21.2. **HRMS** (ESI-TOF, m/z) calcd for $C_{15}H_{16}B^{35}Cl_3N_2O_3SNa$ $[M + Na]^+$: 442.9937; Found: 442.9928. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 80:20, t_R = 6.06 min for *R*-enantiomer; t_R = 6.62 min for *S*-enantiomer



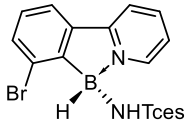
2ha

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-4,6-di-*tert*-butyl-phenyl)borane (**2ha**) was prepared following the general procedure in 37% yield (18.6 mg) with 78:22 e.r. $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.43. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.7 Hz, 1H), 8.35 (d, *J* = 8.1 Hz, 1H), 8.27 (td, *J* = 7.9, 1.4 Hz, 1H), 7.94 (d, *J* = 1.7 Hz, 1H), 7.68 – 7.61 (m, 2H), 6.06 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.10 (br, 1H), 1.53 (s, 9H), 1.39 (s, 9H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.61. **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 158.2, 155.4, 151.3, 144.7, 143.2, 139.2, 127.3, 123.7, 118.9, 117.5, 95.7, 78.3, 38.0, 35.4, 32.5, 31.7. **HRMS** (ESI-TOF, m/z) calcd for $C_{21}H_{28}B^{35}Cl_3N_2O_3SNa$ $[M + Na]^+$: 527.0876; Found: 527.0853. **Chiral HPLC**: Chiralpak IJ-3, heptane/IPA = 95:5, t_R = 9.80 min for *R*-enantiomer; t_R = 11.99 min for *S*-enantiomer.



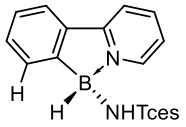
2ia

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-4,6-diphenyl-phenyl)borane (**2ia**) was prepared following the general procedure in 48% yield (26.7 mg) with 91:9 e.r. $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.23. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 8.92 (s, 1H), 8.60 (d, J = 7.9 Hz, 1H), 8.49 – 8.33 (m, 2H), 7.92 – 7.81 (m, 4H), 7.77 (s, 2H), 7.60 – 7.32 (m, 6H), 7.15 (s, 1H), 4.17 (s, 1H), 3.68 (s, 2H). **^{11}B NMR** (128 MHz, DMSO-d_6): δ -1.29. **^{13}C NMR** (101 MHz, DMSO-d_6): δ 155.8, 144.4, 143.6, 142.9, 141.9, 140.4, 139.8, 138.9, 129.5, 128.9, 128.4, 127.6, 127.2, 126.9, 123.9, 119.5, 119.1, 94.7, 76.0. **HRMS** (ESI-TOF, m/z) calcd for $C_{25}H_{20}B^{35}Cl_3N_2O_3SNa$ $[M + Na]^+$: 567.0250; Found: 567.0243. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 5.48 min for *R*-enantiomer; t_R = 7.19 min for *S*-enantiomer.



2ja

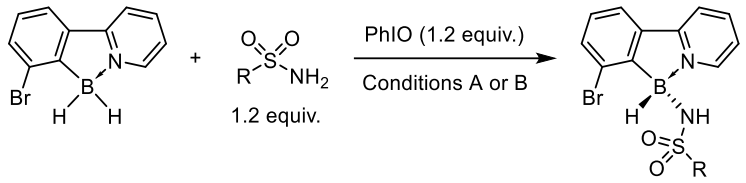
B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2ja**) was prepared following the general procedure in 60% yield (28.4 mg) with 91:9 e.r. $\mathbf{R_f}$ (Hexane/DCM 3:1): 0.35. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.08 (d, J = 5.7 Hz, 1H), 8.41 – 8.35 (m, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.79 (ddd, J = 7.1, 5.8, 1.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 6.33 (d, J = 6.3 Hz, 1H), 4.85 (d, J = 11.0 Hz, 1H), 4.80 (d, J = 11.0 Hz, 1H), 3.93 (br, 1H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.87 (d, J = 78.9 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 156.4, 145.3, 143.9, 140.0, 135.1, 130.4, 127.1, 125.0, 122.0, 119.9, 95.5, 78.6. **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{11}B^{79}Br^{35}Cl_3N_2O_3SK$ $[M + K]^+$: 508.8469; Found: 508.8456. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 5.60 min for *R*-enantiomer; t_R = 6.29 min for *S*-enantiomer.



***R*-2p**

B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-phenyl)borane (*R*-**2p**) was prepared following the general procedure in 51% yield (20.1 mg) with 83:17 e.r. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 4.83 min for *R*-enantiomer; t_R = 6.16 min for *S*-enantiomer. Other analytical data are identical to those of the racemic sample reported above.

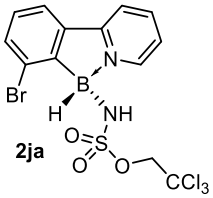
Enantioselective B–H Nitrene Insertion (Nitrene Scope)



Conditions A: $Ru_2[(S)\text{-NTTL})]_4Cl$ (1 mol%), o-DCB (0.05 M), +4 °C
Conditions B: $Rh_2[(S)\text{-4-Ph-NTTL}]_4$ (1 mol%), PhCl (0.05 M), -30 °C

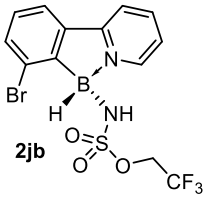
Conditions A: An oven-dried 10 ml Schlenk flask was charged with $Ru_2[(S)\text{-NTTL}]_4Cl$ (1.5 mg, 0.001 mmol, 1 mol%), 3-bromophenylpyridineborane (24.6 mg, 0.1 mmol, 1 equiv.), corresponding sulfonamide or sulfamate (0.24 mmol, 1.2 equiv.) and o-DCB (2 ml). The resulting solution was cooled in an ice-bath and then iodosobenzene (26.4 mg, 0.12 mmol, 1.2 equiv.) was added in one portion. The resulting suspension was placed in a fridge (internal temperature +4 °C) and stirred until all solids dissolved and high conversion of starting borane was observed. The mixture was diluted with hexane (2 ml) and directly transferred to a short prepacked silica column. The product was eluted using either pure DCM (for most sulfamate derivatives) or a mixture of DCM/EtOAc (20:1) (for most sulfonamide derivatives) as eluent.

Conditions B: An oven-dried 10 ml Schlenk flask was charged with $Rh_2[(S)\text{-4-Ph-NTTL}]_4$ (1.8 mg, 0.001 mmol, 1 mol%), 3-bromophenylpyridineborane (24.6 mg, 0.1 mmol, 1 equiv.), corresponding sulfamate (0.24 mmol, 1.2 equiv.) and PhCl (2 ml). The resulting solution was cooled in a dry ice/isopropanol bath (internal temperature -30 °C) and then iodosobenzene (26.4 mg, 0.12 mmol, 1.2 equiv.) was added in one portion. The resulting suspension was placed in a freezer (internal temperature -30 °C) and stirred until high conversion of starting borane was observed (up to 2 weeks). The mixture was diluted with hexane (2 ml) and directly transferred to a short prepacked silica column. The product was eluted using pure DCM.



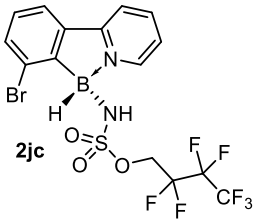
B-(2,2,2-trichloroethoxysulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2ja**). Conditions A: 6 h, 60% yield, 91:9 e.r. (as above). Conditions B: 48 h, 89% yield, 89:11 e.r.

Analytical data are identical to those reported in the previous section.



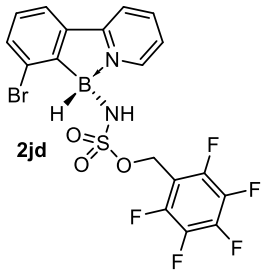
B-(2,2,2-trifluoroethoxysulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2jb**). Conditions A: 48 h, 66% yield, 91:9 e.r. Conditions B: 7 days, 88% yield, 71:29 e.r.

R_f (Hexane/DCM 3:1): 0.33. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.04 (d, *J* = 5.6 Hz, 1H), 8.42 – 8.35 (m, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.04 – 8.01 (m, 1H), 7.79 (ddd, *J* = 7.2, 5.8, 1.2 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 6.3 Hz, 1H), 4.73 – 4.60 (m, 2H), 3.89 (br, 1H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.88 (d, *J* = 91.5 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 156.4, 145.3, 143.9, 140.0, 135.1, 130.5, 127.0, 125.0, 124.1 (q, *J* = 276.8 Hz), 122.0, 119.9, 65.1 (q, *J* = 36.3 Hz). **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -74.32 (t, *J* = 8.5 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{13}H_{10}B^{79}BrF_3N_2O_3S$ $[M - H]^+$: 420.9640; Found: 420.9629. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 4.85 min for *R*-enantiomer; t_R = 5.47 min for *S*-enantiomer.



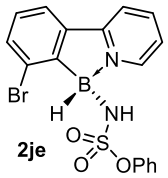
B-(2,2,3,3,4,4,4-heptafluorobutoxy-sulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2jc**). Conditions A: 48 h, 68% yield, 90:10 e.r. Conditions B: 5 days, 78% yield, 77:23 e.r.

R_f (Hexane/DCM 3:1): 0.44. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.5 Hz, 1H), 8.44 – 8.37 (m, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 1H), 7.80 (ddd, *J* = 7.1, 5.7, 1.1 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 6.35 (d, *J* = 6.0 Hz, 1H), 4.83 – 4.69 (m, 2H), 3.90 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -1.92 (d, *J* = 99.6 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 156.5, 145.3, 144.0, 140.1, 135.2, 130.6, 127.0, 125.1, 122.1, 120. 0, 64.4 (t, *J* = 26.1 Hz). 3 C-F coupled carbon atoms are not visible due to their low intensity. **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -81.75 (3F), -121.03 (2F), -128.10 (2F). **HRMS** (ESI-TOF, m/z) calcd for $C_{15}H_{11}B^{79}BrF_7N_2O_3SNa$ $[M + Na]^+$: 544.9552; Found: 544.9540. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 4.06 min for *R*-enantiomer; t_R = 4.57 min for *S*-enantiomer.



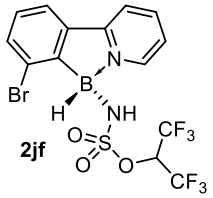
B-(pentafluorophenoxy-sulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2jd**). Conditions A: 72 h, 74% yield, 89:11 e.r. Conditions B: 14 days, 68% yield, 80:20 e.r.

R_f (Hexane/DCM 3:1): 0.25. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 9.05 (d, *J* = 5.6 Hz, 1H), 8.40 – 8.34 (m, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.76 (ddd, *J* = 7.1, 5.8, 1.2 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 6.4 Hz, 1H), 5.37 – 5.34 (m, 2H), 3.89 (br, 1H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.86 (d, 78.5 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 156.42, 147.88 – 145.46 (m), 145.34, 143.77, 142.52 (d, *J* = 252.7 Hz), 139.98, 138.29 (d, *J* = 249.5 Hz), 135.00, 130.30, 127.12, 124.86, 121.88, 119.81, 111.02 (td, *J* = 17.9, 3.9 Hz), 58.06. **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -142.94 (dd, *J* = 21.6, 7.5 Hz, 2F), -155.45 (t, *J* = 20.4 Hz, 1F), -164.53 (td, *J* = 21.5, 8.0 Hz, 2F). **HRMS** (ESI-TOF, m/z) calcd for $C_{18}H_{11}B^{79}BrF_5N_2O_3SNa$ $[M + Na]^+$: 542.9584; Found: 542.9548. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 80:20, t_R = 18.59 min for *R*-enantiomer; t_R = 22.07 min for *S*-enantiomer. X-ray quality crystals were grown by slow diffusion of hexane into DCM solution.



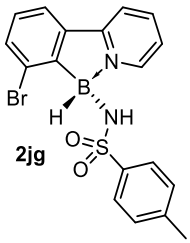
B-(phenoxysulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2je**). Conditions A: 24 h, 24% yield, 62:38 e.r. Conditions B: 10 days, 84% yield, 62:38 e.r.

R_f (Hexane/DCM 3:1): 0.30. **^{1}H NMR** (800 MHz, $(CD_3)_2CO$): δ 8.85 (d, *J* = 5.5 Hz, 1H), 8.33 (t, *J* = 7.3 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 6.5 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 3H), 7.21 – 7.16 (m, 3H), 6.36 (d, *J* = 5.7 Hz, 1H), 3.92 (br, 1H). **^{11}B NMR** (192 MHz, $(CD_3)_2CO$): δ -1.81 (d, *J* = 106.3 Hz). **^{13}C NMR** (201 MHz, $(CD_3)_2CO$): δ 156.6, 152.6, 145.2, 143.7, 139.9, 135.0, 130.2, 130.1, 127.3, 126.2, 124.7, 122.4, 121.8, 119.8. **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{15}BBrN_2O_3S$ $[M + H]^+$: 417.0079; Found: 417.0064. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 17.67 min for *R*-enantiomer; t_R = 18.81 min for *S*-enantiomer.



B-(1,1,1,3,3,3-hexafluoro-isopropoxy-sulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2jf**). Conditions A: 24 h, 41% yield, 54:46 e.r.

R_f (Hexane/DCM 3:1): 0.50. **^{1}H NMR** (500 MHz, $(CD_3)_2CO$): δ 8.92 (d, *J* = 5.7 Hz, 1H), 8.45 – 8.39 (m, 1H), 8.37 – 8.33 (m, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.81 (ddd, *J* = 7.1, 5.8, 1.2 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 6.76 (s, 1H), 5.66 (dq, *J* = 12.1, 6.0 Hz, 1H), 3.89 (br, 1H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -2.00 (d, *J* = 101.3 Hz). **^{13}C NMR** (126 MHz, $(CD_3)_2CO$): δ 156.7, 145.0, 144.1, 139.8, 135.2, 130.4, 127.1, 125.21 – 118.37 (m), 125.0, 121.9, 120.1, 72.2 (septet, *J* = 34.0 Hz). **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -73.55 – -73.84 (m). **HRMS** (ESI-TOF, m/z) calcd for $C_{14}H_{10}B^{79}BrF_6N_2O_3SK$ $[M + K]^+$: 528.9229; Found: 528.9221. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 4.02 min for *R*-enantiomer; t_R = 4.36 min for *S*-enantiomer.

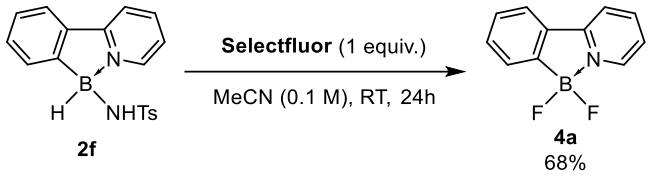


B-(4-methylphenyl-sulfonamido)-(2-(2-pyridyl)-6-bromo-phenyl)borane (**2jg**). Conditions A: 48 h, 48% yield, 53:47 e.r.

R_f (DCM/EA 10:1): 0.69. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 9.18 (d, *J* = 5.5 Hz, 1H), 8.40 – 8.31 (m, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.23 (m, 3H), 5.58 (d, *J* = 6.5 Hz, 1H), 3.77 (br, 1H), 2.38 (s, 3H). **^{11}B NMR** (128 MHz, $(CD_3)_2CO$): δ -1.89 (d, *J* = 90.0 Hz). **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 145.5, 143.4, 142.0, 139.8, 134.8, 130.1, 129.4, 128.05, 127.1, 124.7, 121.7, 119.7, 21.3.

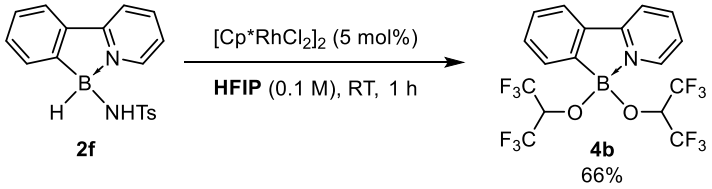
Two quaternary carbons were not detected due to their low intensity. **HRMS** (ESI-TOF, m/z) calcd for $C_{18}H_{17}B^{79}BrN_2O_2S$ [M + H]$^+$: 415.0287; Found: 415.0285. **Chiral HPLC**: Chiralpak IB-3, heptane/IPA = 60:40, t_R = 7.44 min for *R*-enantiomer; t_R = 9.16 min for *S*-enantiomer.

Reactions of Amidoborane Products



An oven-dried 10 ml Schlenk flask was charged with **2f** (67.2 mg, 0.2 mmol), Selectfluor (70.8 mg, 0.2 mmol, 1 equiv.) and MeCN (2 ml). The resulting suspension was stirred for 24 hours, at which point full conversion of **2f** was achieved. The reaction mixture was concentrated in vacuo and purified via SiO_2 column chromatography (using DCM/EA 20:1), affording **4a** as colorless crystals (27.5 mg, 68% yield).

R_f (DCM/EA 10:1): 0.86. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 8.64 (d, *J* = 5.6 Hz, 1H), 8.44 – 8.36 (m, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.80 – 7.70 (m, 1H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.44 (dt, J = 22.7, 7.3 Hz, 2H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ 8.00 (t, *J* = 50.9 Hz). **^{13}C NMR** (100.4 MHz, $(CD_3)_2CO$): δ 156.1, 145.4, 142.6, 137.8, 132.4, 130.5, 129.4, 125.2, 122.9, 119.4. **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -160.15, -160.26, -160.40, -160.53. Additional peak at δ = −151.55 corresponds to BF_4^- likely due to side hydrolysis of **4a**. Analytical data are consistent with the previously reported.[14]



An oven-dried 10 ml Schlenk flask was charged with **2f** (67.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%) and argon purged HFIP (2 ml, 7.44 mmol, excess). The resulting solution was stirred for 1 hour, at which point full conversion of **2f** was achieved. The reaction mixture was concentrated in vacuo and purified via SiO_2 column chromatography (using hexane/DCM 1:1), affording **4b** as colorless crystals (66.0 mg, 66% yield).

R_f (Hexane/DCM 2:1): 0.39. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 8.61 (d, *J* = 5.5 Hz, 1H), 8.44 (t, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.81 (t, *J* = 6.6 Hz, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.60 – 7.48 (m, 2H), 4.71 (septet, *J* = 6.2 Hz, 2H). **^{11}B NMR** (128.4 MHz, $(CD_3)_2CO$): δ 9.33. **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 156.1, 145.7, 143.3, 139.2, 132.6, 132.1, 130.4, 125.3, 123.6, 124.9 – 121.6 (m), 119.45, 71.34 (septet, *J* = 32.7 Hz). **^{19}F NMR** (376 MHz, $(CD_3)_2CO$): δ -75.53 (d, *J* = 5.6 Hz). **HRMS** (ESI-TOF, m/z) calcd for $C_{17}H_{11}BF_{12}NO_2$ [M + H]$^+$: 500.0691; Found: 500.0703.

Crystallographic Details

Single crystals of **2a, 2f, 2w, 2jd** and **3a** were investigated using Bruker D8 QUEST single-crystal X-ray diffractometer equipped with PHOTONII detector, charge-integrating pixel array detector (CPAD), laterally graded multilayer (Goebel) mirror and microfocus Mo-target X-ray tube (λ = 0.73071 Å). The frame width of 0.4º were employed for data collection. Data reduction and integration were performed with the Bruker software package SAINT (Version 8.40B).[15] The data were corrected for Lorentz and polarization effects. The absorption correction was performed using multi-scan routine as implemented in SADABS (Version 2016/2).[16] Crystal structure solution and refinement were performed using SHELX-2018 package.[17] Atomic positions were located using dual t methods and refined using a combination of Fourier synthesis and least-square refinement in isotropic and anisotropic approximations. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as U_{iso}(H)=1.5U_{eq}(C) for methyl H atoms and U_{iso}(H)=1.2U_{eq}(C) otherwise. The hydrogen atoms of NH and BH groups were located from the Fourier density synthesis. The only exception was crystal stricture of **2jd** in which in one of independent molecules there is a superposition of two enantiomers and as the result N-H and B-H atoms were placed in ideal calculated positions (Fig. S35). Upon the refinement of disordered **2jd** the EADP and SADI constraints were employed. The absolute configuration of ordered and main contribution of disordered molecule in **2jd** was established in accordance with Flack parameter which was equal to 0.08(2). Despite the presence of a possible translation in the crystal structure of **2f**, a twofold reduction of the cell volume is impossible. The translation is observed only for **2f** molecules, whereas for solvate methylene chloride molecules with a population of about 0.9, the indicated symmetry is not fulfilled. The analysis of the reflection intensities shows that the hkl reflections with odd sum h+k are three times weaker than the average reflection intensity, but among them (30 thousand reflections) there are 8579 observed reflections. On this basis the description of this structure in the P-1 group with Z' =4 is quite reasonable.

Crystallographic parameters and final residuals for the single-crystal XRD experiments are given in Table S8.

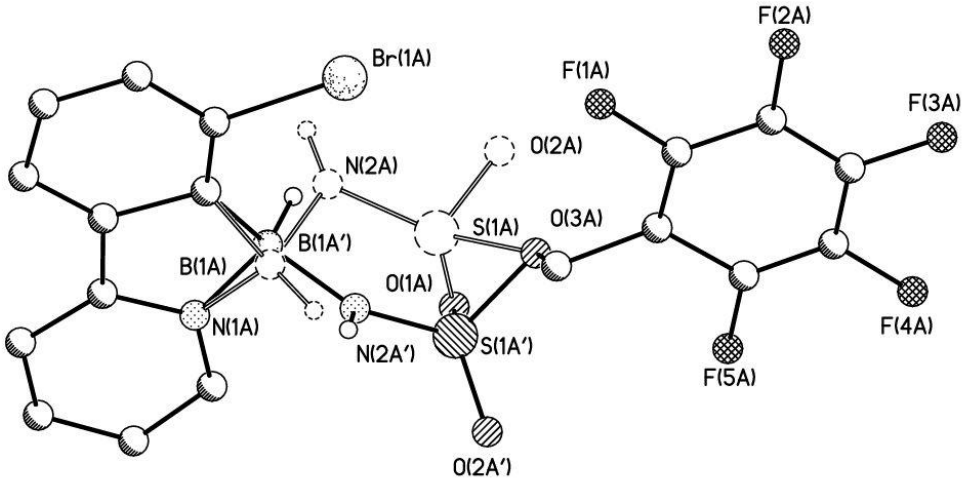


Fig. S35. The superposition of two enantiomers (0.88 and 0.12) in one of the independent molecules in **2jd**.

Table S8. Crystal data, data collection and structure refinement for **2a, 2f, 2w, 2jd** and **3a**.

	2a	**2f**	**2w**	**2jd**	**3a**
CCDC	2347444	2347448	2347446	2347445	2347447
Formula	$C_{12}H_{18}BN_3O_2S$	$C_{18.86}H_{18.72}BCl_{1.72}N_2O_2S$	$C_{22}H_{29}B_{11}N_2O_5S$	$C_{18}H_{11}BBrF_5N_2O_3S$	$C_{19}H_{25}BN_4O_4S_2$
FW	279.16	409.09	552.44	521.07	448.36
T, K	100	110	100	100	110
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	P-1	P 1	$P2_1/n$
Z (Z')	4(1)	8(4)	2(1)	2(2)	4(1)
a, Å	10.0323(4)	15.0095(9)	7.0532(8)	7.948(2)	15.6010(13)
b, Å	14.0039(5)	15.3676(9)	13.9162(15)	8.047(2)	8.9989(11)
c, Å	10.9141(4)	17.4816(10)	14.4394(16)	16.160(4)	15.8836(16)
α, °	90	78.015(2)	80.019(4)	92.793(9)	90
β, °	116.185(2)	77.183(2)	81.480(4)	100.437(8)	107.422(3)
γ, °	90	81.734(2)	81.506(4)	107.826(9)	90
V, Å^3	1375.98(9)	3825.9(4)	1369.6(3)	961.6(5)	2127.6(4)
d_{calc}, g cm^{-3}	1.348	1.420	1.340	1.800	1.400
μ, cm^{-1}	2.36	4.66	1.57	23.18	2.84
F(000)	592	1696	572	516	944
$2\theta_{max}$, °	58	56	55	52	52
Reflections collected	12514	49308	24177	10427	20668
Reflections unique	3648	18369	6170	6810	4176
Reflections with I > 2σ(I)	3108	10144	4785	3870	2835
Variables	187	1058	415	575	286
R1	0.0435	0.0643	0.0762	0.0872	0.0519
wR2	0.1204	0.2074	0.1995	0.2037	0.1251
GOF	1.071	0.992	0.999	1.011	1.041
Largest difference in peak/hole (e/Å^3)	0.397/-0.541	0.707/-0.428	0.385/-0.529	0.887/-0.824	0.360/-0.329

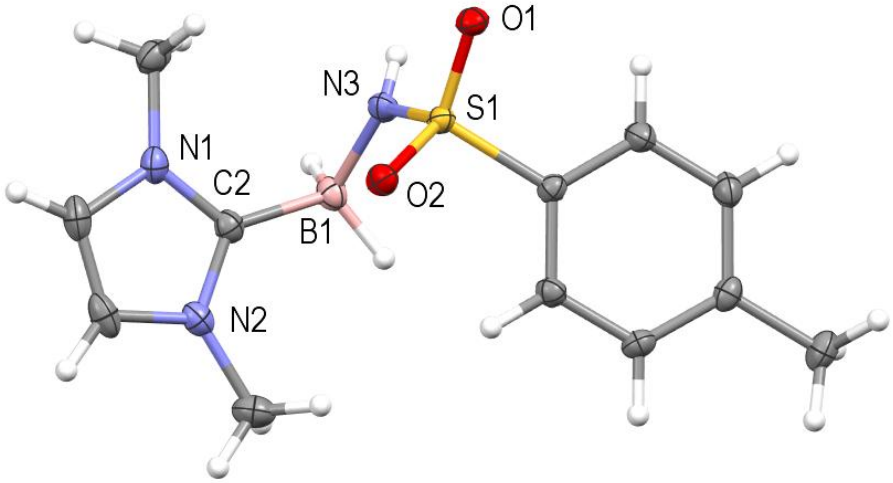


Fig. S36. Crystal structure of **2a**. All atoms (except hydrogens) are shown as 50% thermal ellipsoids.

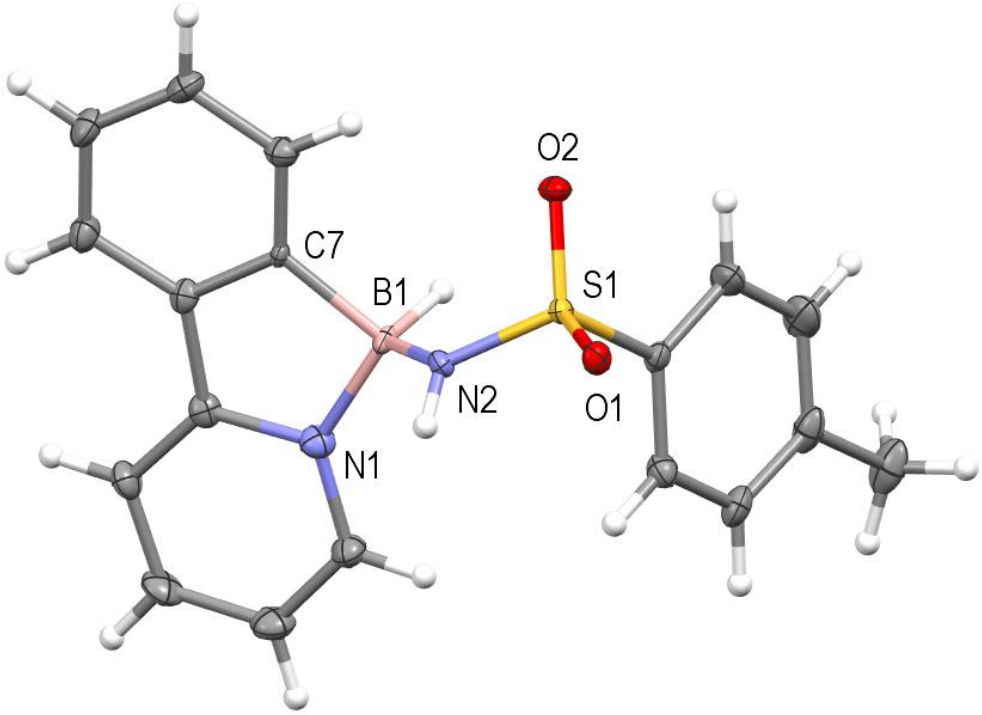


Fig. S37. Crystal structure of **2f**. All atoms (except hydrogens) are shown as 50% thermal ellipsoids. Only one independent molecule is shown. Disordered solvent molecules are omitted for clarity.

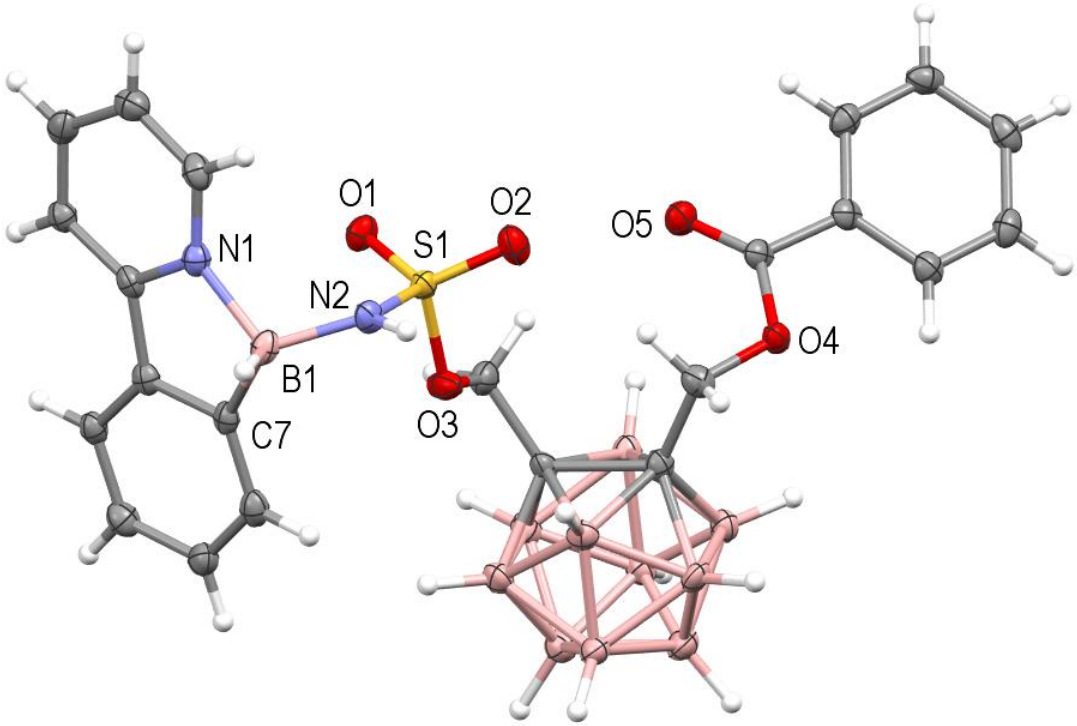


Fig. S38. Crystal structure of **2w**. All atoms (except hydrogens) are shown as 50% thermal ellipsoids.

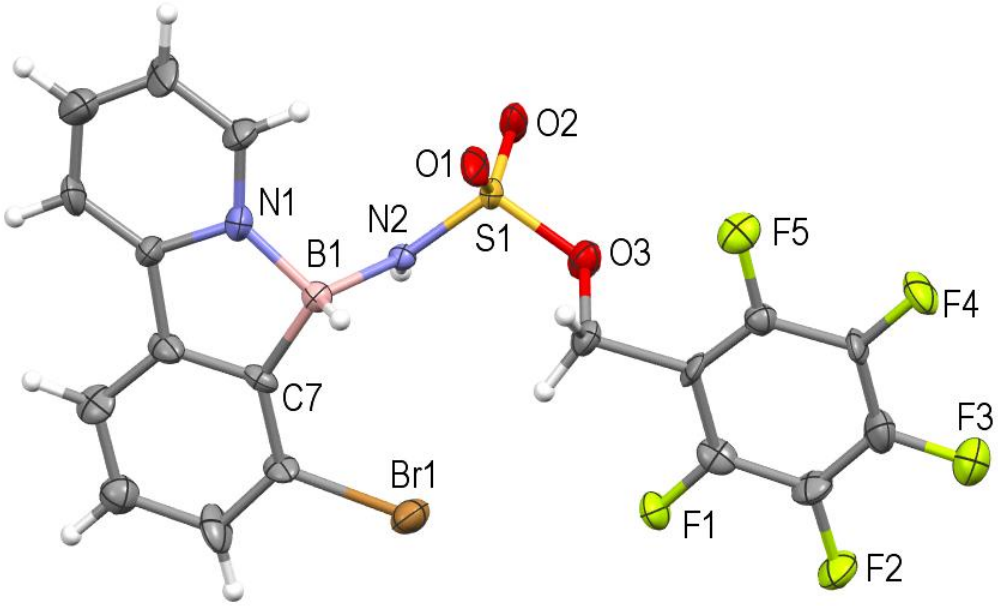


Fig. S39. Crystal structure of **2jd**. All atoms (except hydrogens) are shown as 50% thermal ellipsoids. Second disordered molecule is shown in Fig. S24A.

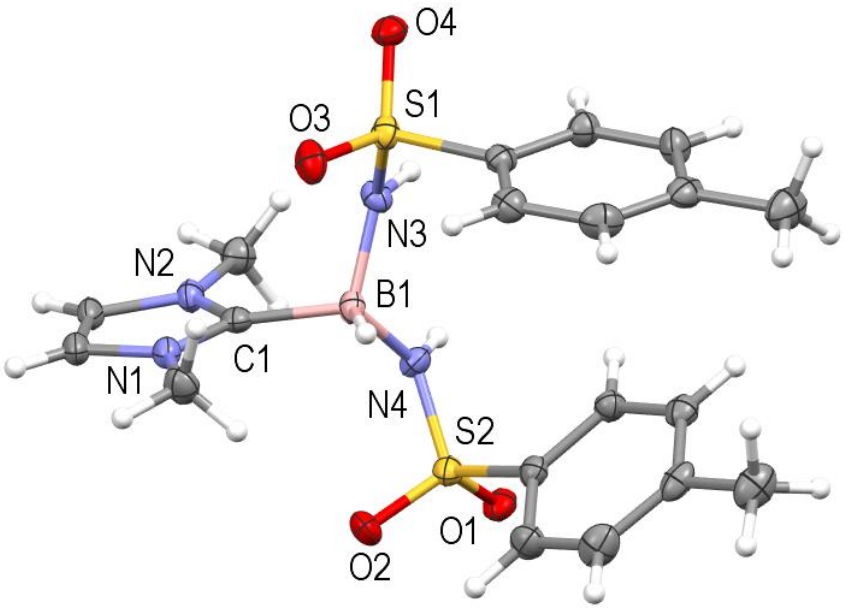
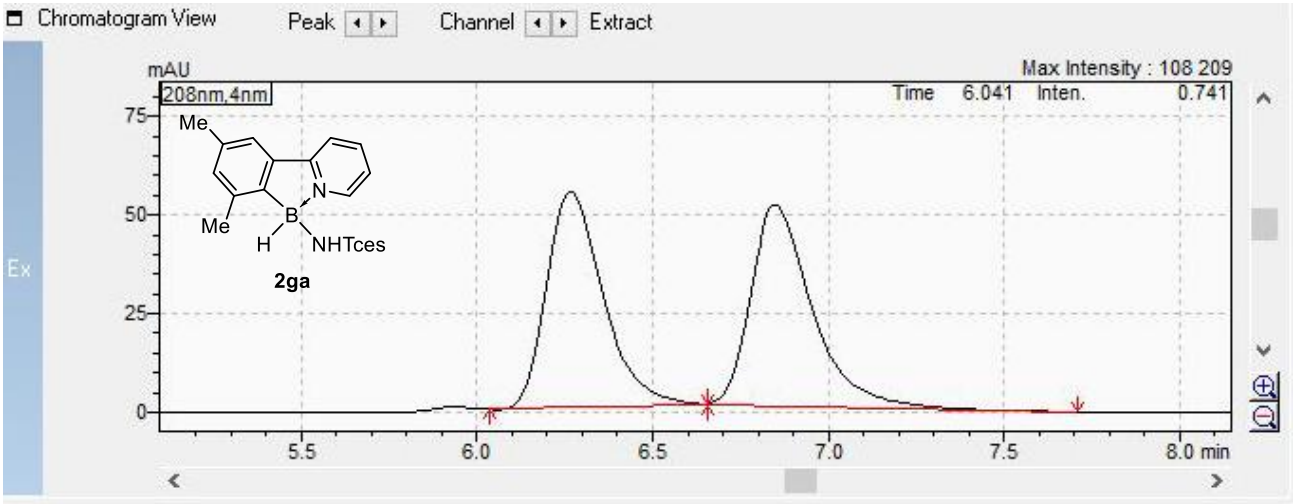


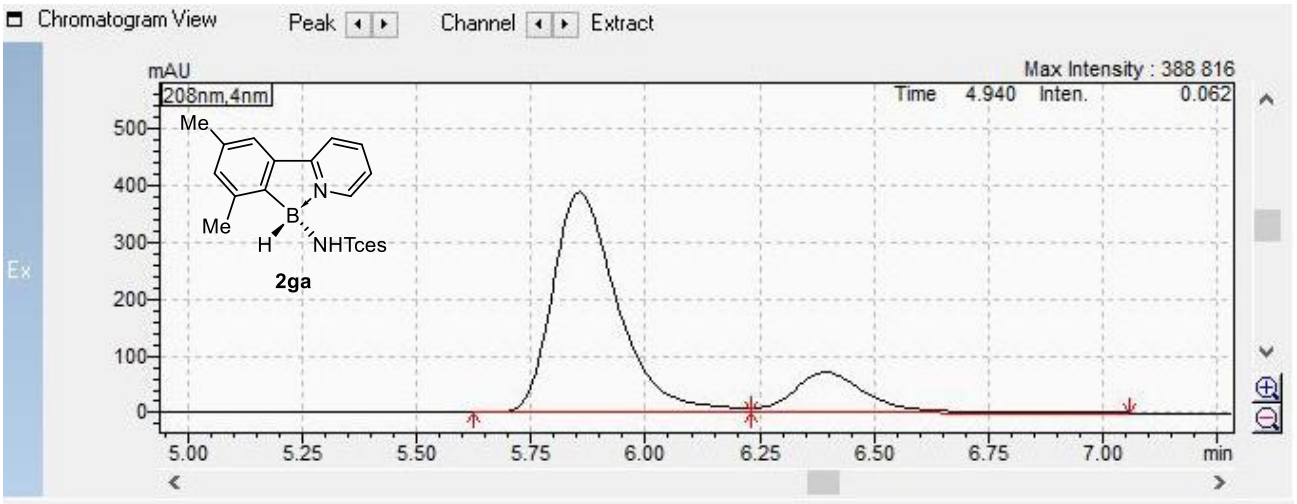
Fig. S40. Crystal structure of **3a**. All atoms (except hydrogens) are shown as 50% thermal ellipsoids.

HPLC Traces



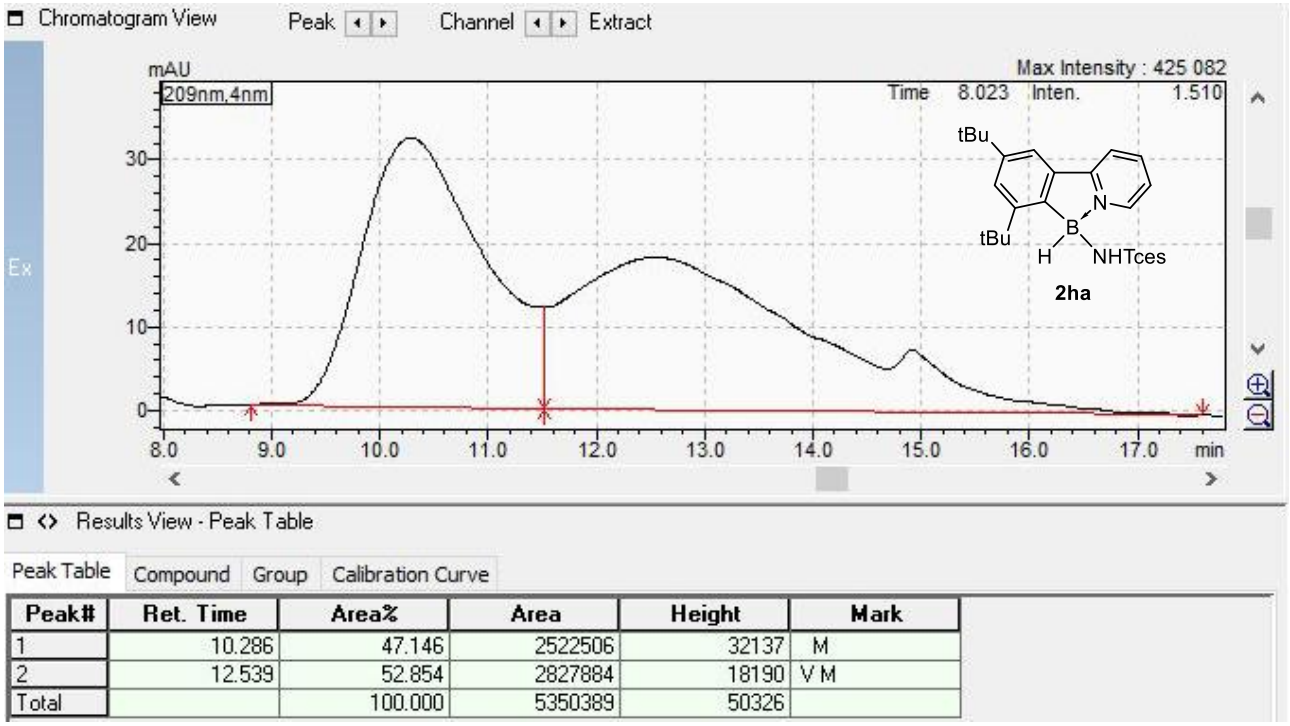
Peak#	Ret. Time	Area%	Area	Height	Mark
1	6.265	49.668	609788	54834	M
2	6.851	50.332	617936	50833	M
Total		100.000	1227724	105667	

Fig. S41. HPLC chromatogram for racemic **2ga**.



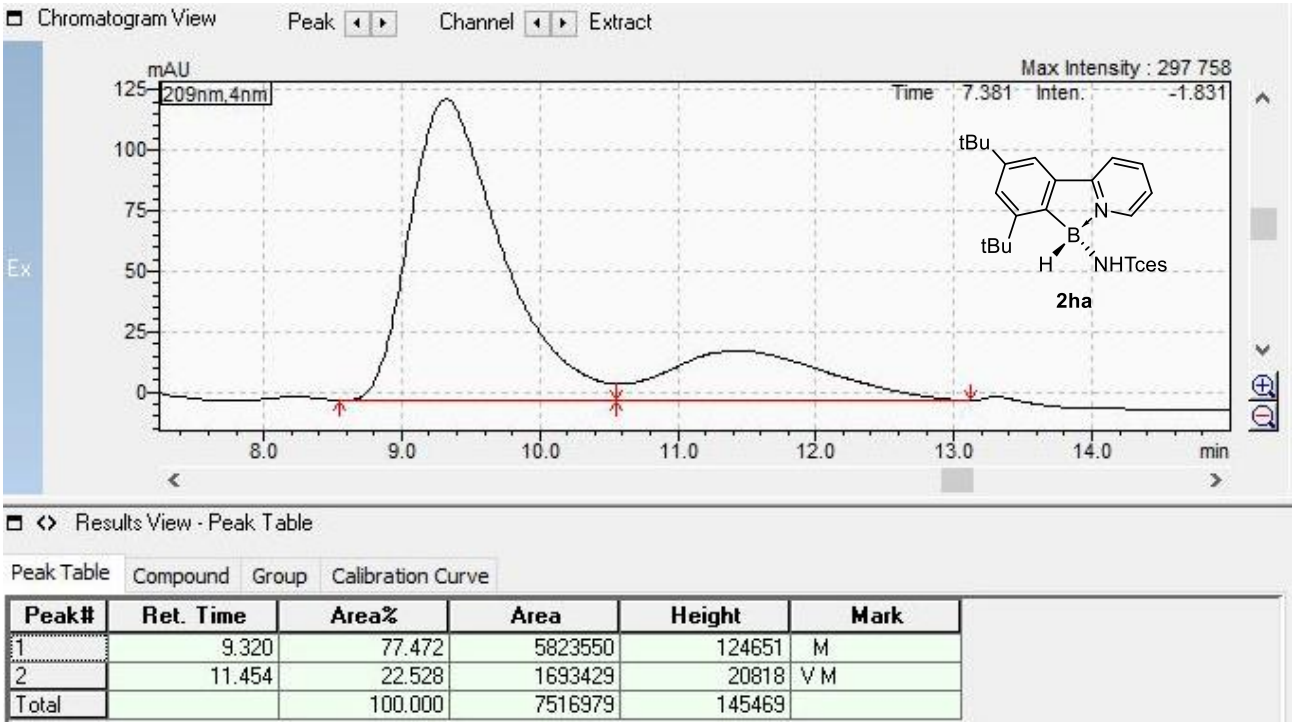
Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.855	82.584	3864278	388874	M
2	6.394	17.416	814930	71380	V M
Total		100.000	4679208	460254	

Fig. S42. HPLC chromatogram for *R*-enriched **2ga**.



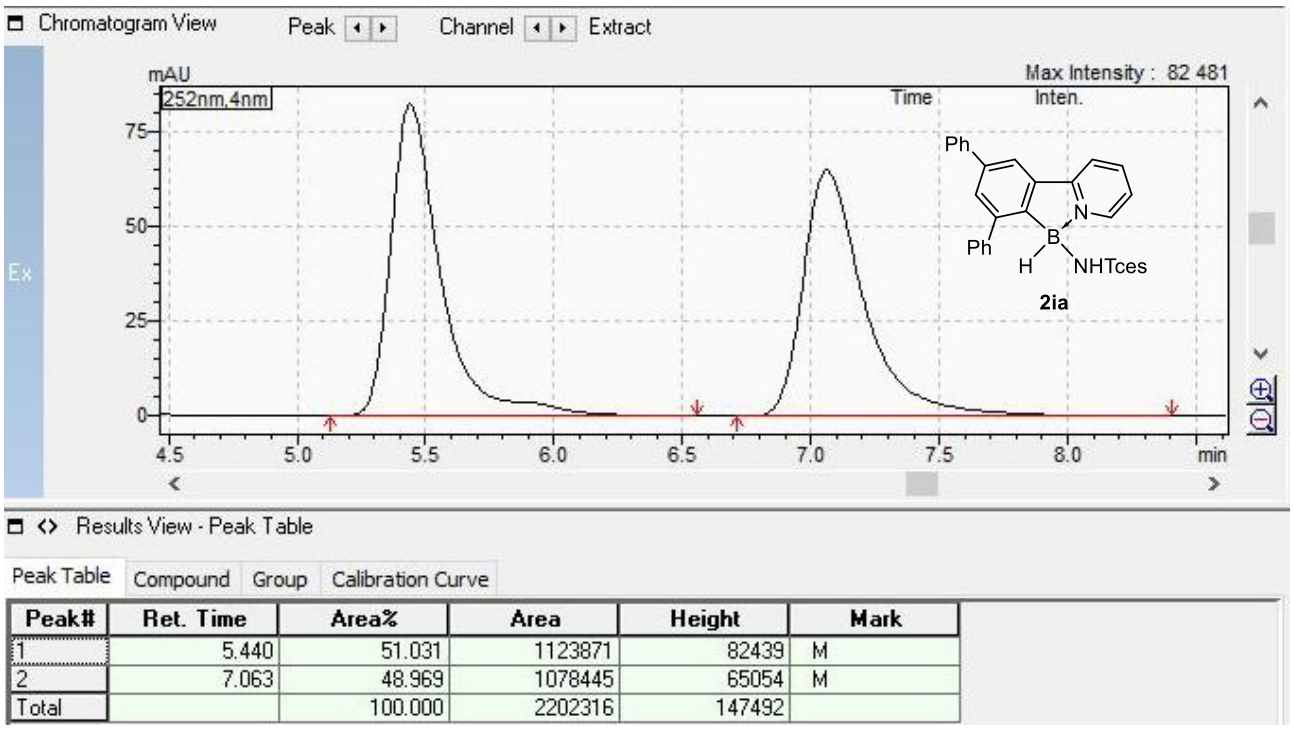
Peak#	Ret. Time	Area%	Area	Height	Mark
1	10.286	47.146	2522506	32137	M
2	12.539	52.854	2827884	18190	V M
Total		100.000	5350389	50326	

Fig. S43. HPLC chromatogram for racemic **2ha**.



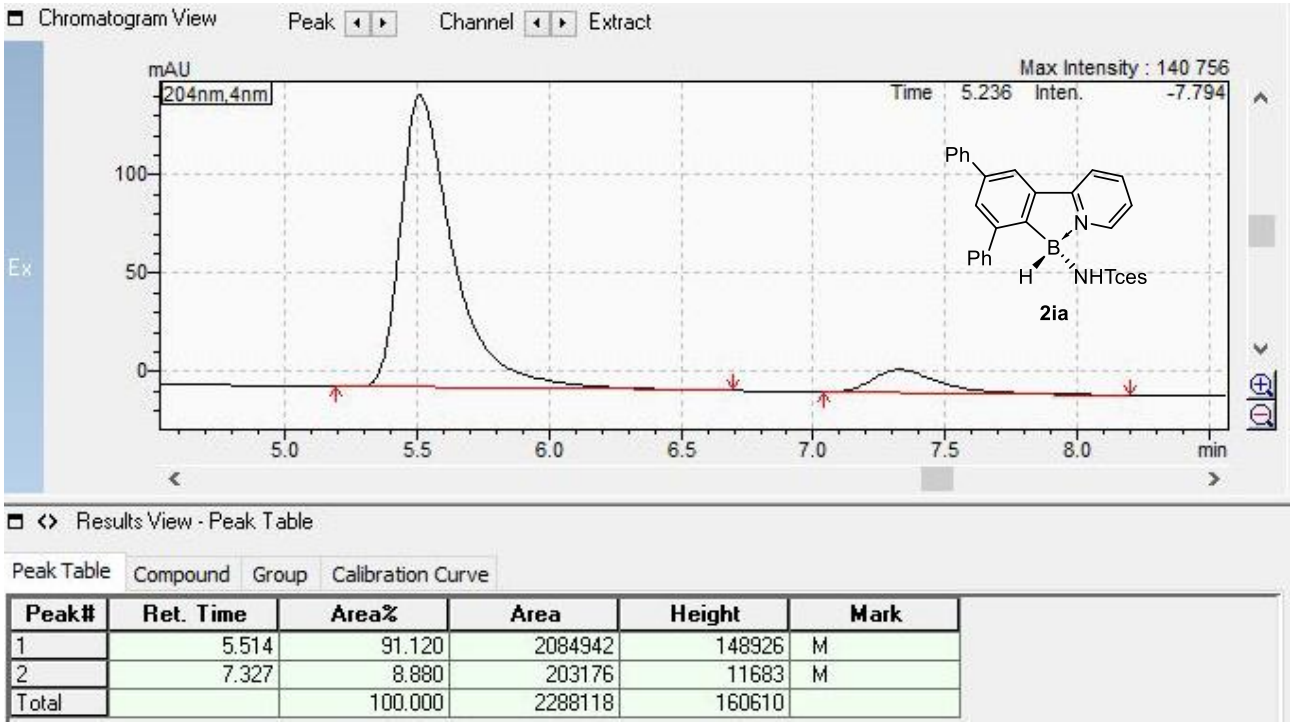
Peak#	Ret. Time	Area%	Area	Height	Mark
1	9.320	77.472	5823550	124651	M
2	11.454	22.528	1693429	20818	V M
Total		100.000	7516979	145469	

Fig. S44. HPLC chromatogram for *R*-enriched **2ha**.



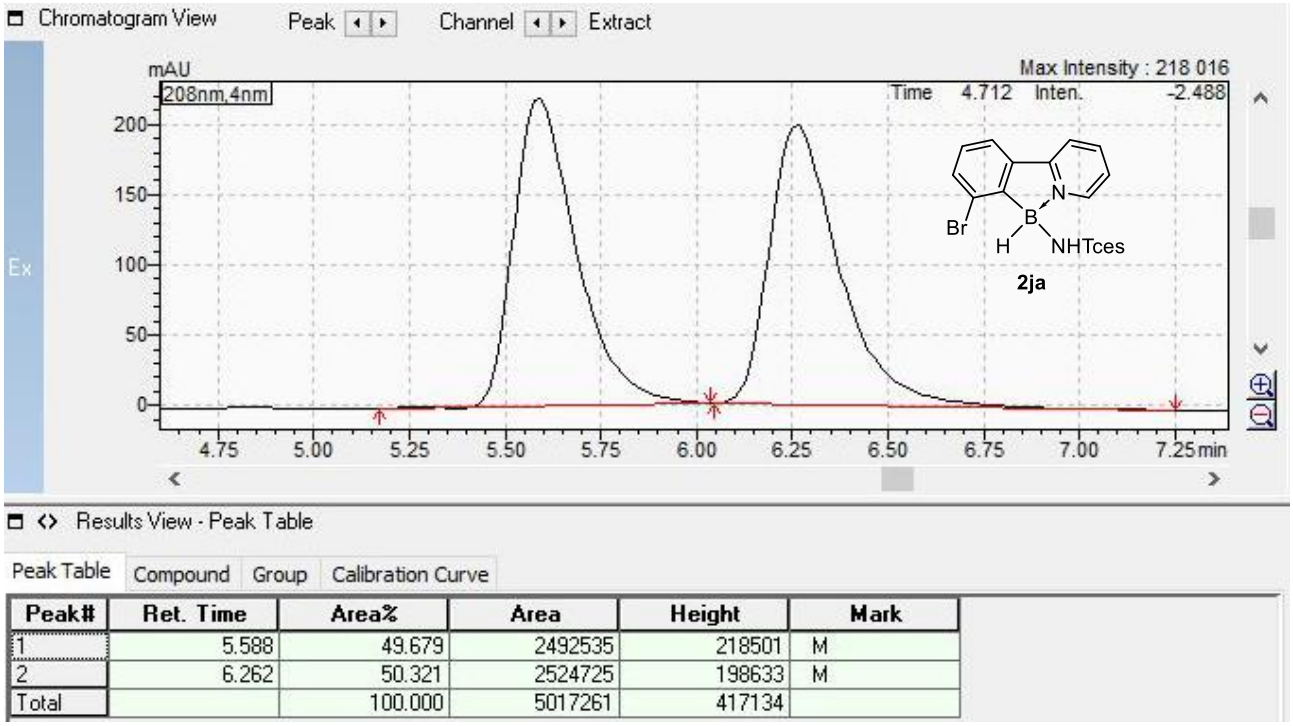
Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.440	51.031	1123871	82439	M
2	7.063	48.969	1078445	65054	M
Total		100.000	2202316	147492	

Fig. S45. HPLC chromatogram for racemic **2ia**.



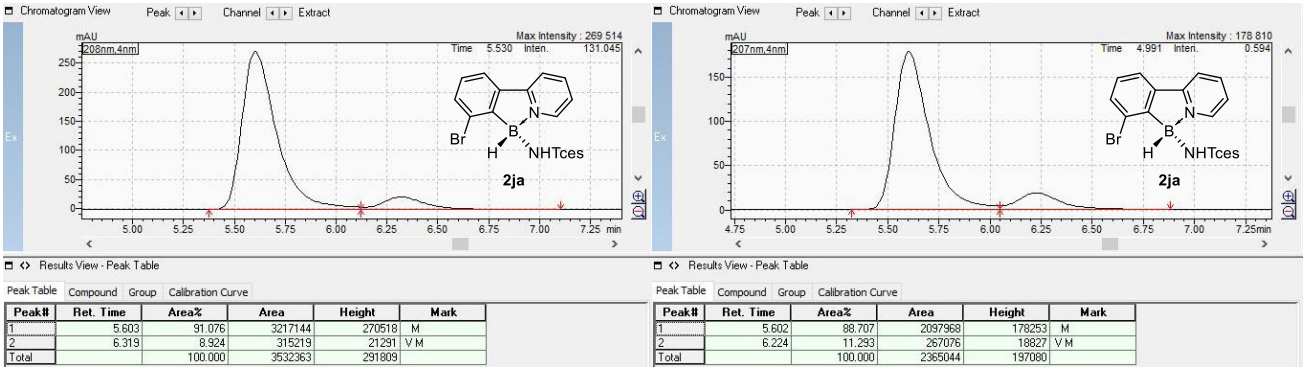
Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.514	91.120	2084942	148926	M
2	7.327	8.880	203176	11683	M
Total		100.000	2288118	160610	

Fig. S46. HPLC chromatogram for *R*-enriched **2ia**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.588	49.679	2492535	218501	M
2	6.262	50.321	2524725	198633	M
Total		100.000	5017261	417134	

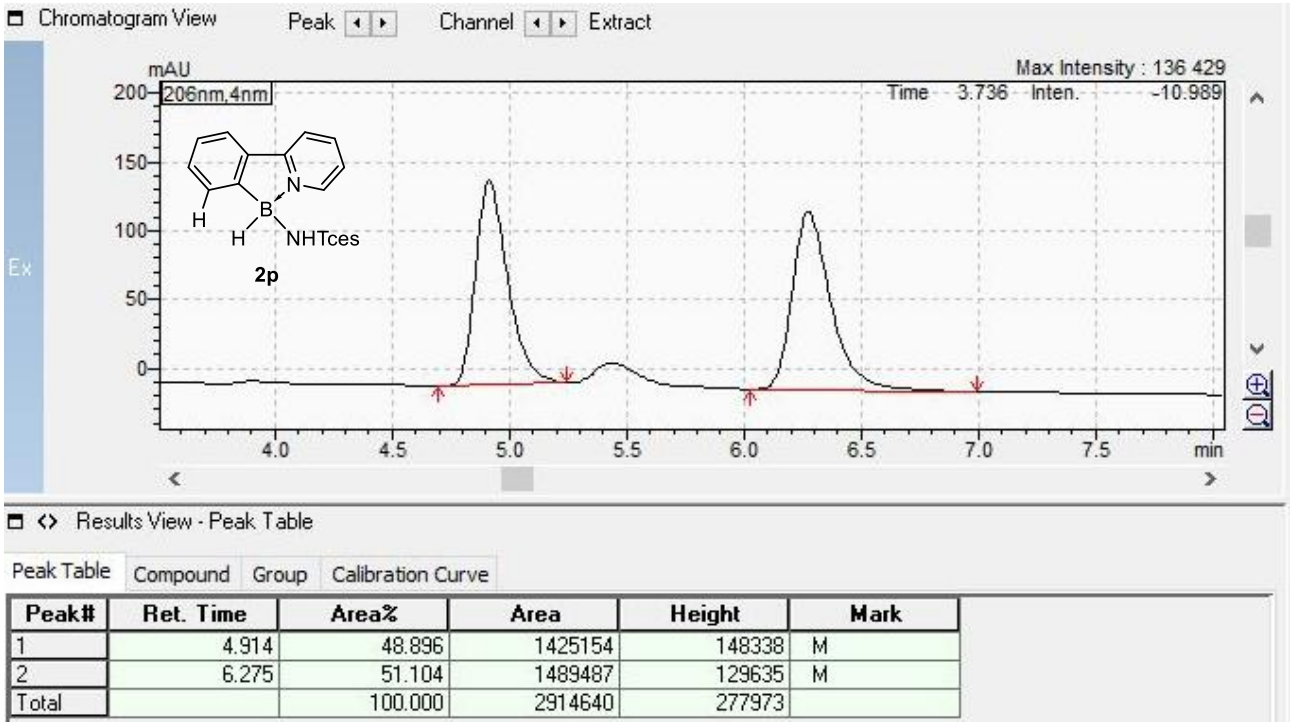
Fig. S47. HPLC chromatogram for racemic **2ja**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.603	91.076	3217144	270518	M
2	6.319	8.924	315219	21291	V M
Total		100.000	3532363	291809	

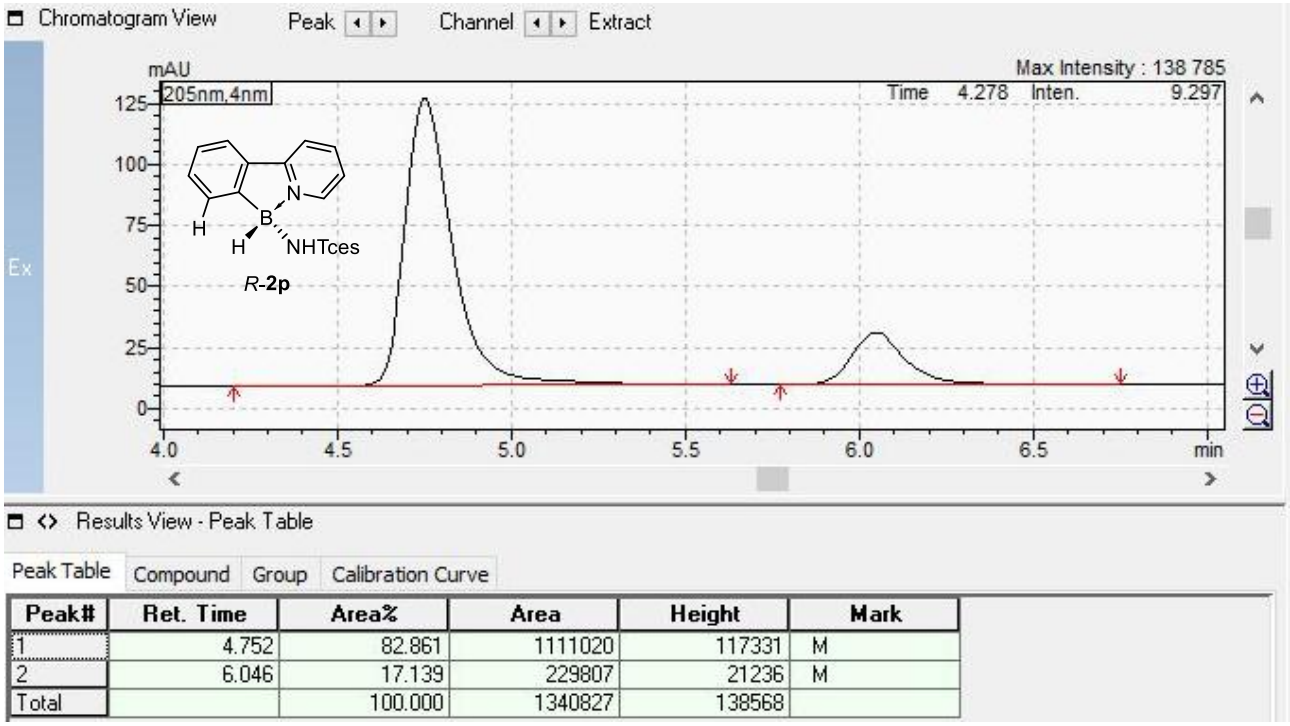
Peak#	Ret. Time	Area%	Area	Height	Mark
1	5.602	88.707	2097968	178253	M
2	6.224	11.293	267076	18827	V M
Total		100.000	2365044	197080	

Fig. S48. HPLC chromatograms for *R*-enriched **2ja** (left: Ru(II,III) catalyzed, conditions A; right: Rh(II,II) catalyzed, conditions B).



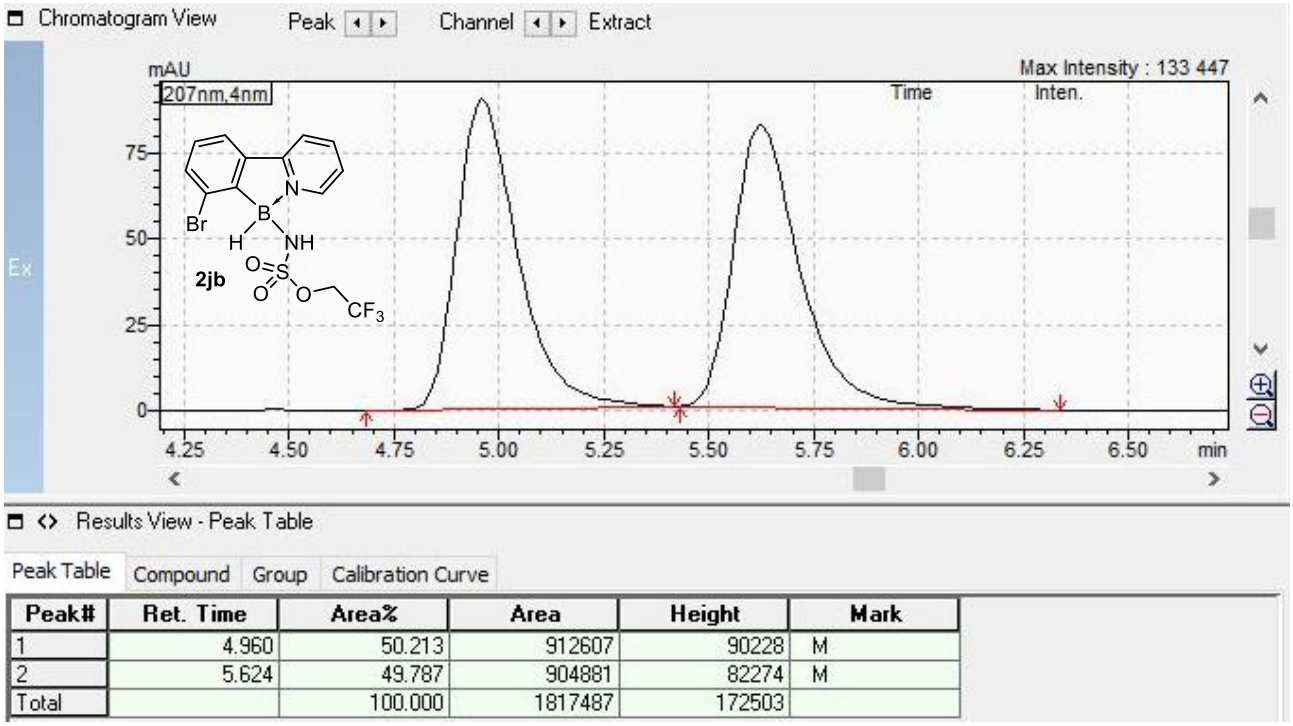
Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.914	48.896	1425154	148338	M
2	6.275	51.104	1489487	129635	M
Total		100.000	2914640	277973	

Fig. S49. HPLC chromatogram for racemic **2p**.



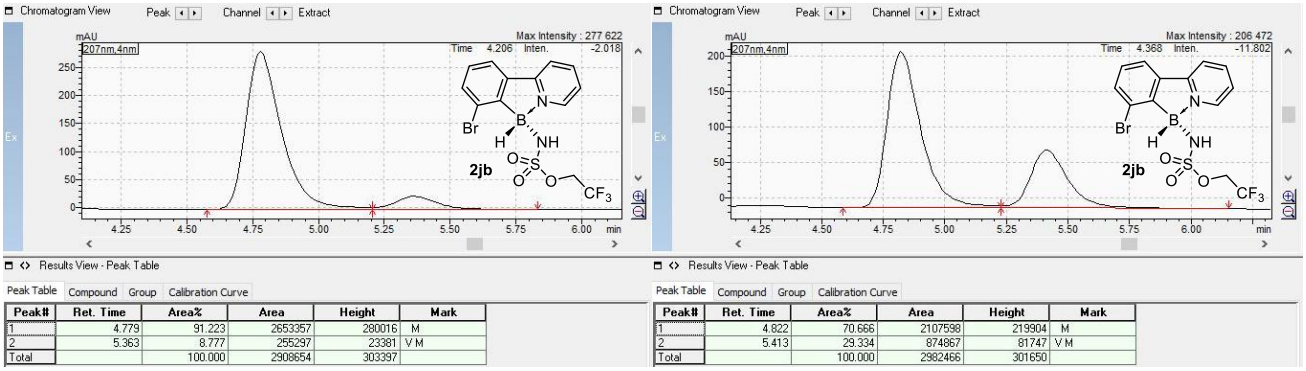
Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.752	82.861	1111020	117331	M
2	6.046	17.139	229807	21236	M
Total		100.000	1340827	138568	

Fig. S50. HPLC chromatogram for *R*-**2p**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.960	50.213	912607	90228	M
2	5.624	49.787	904881	82274	M
Total		100.000	1817487	172503	

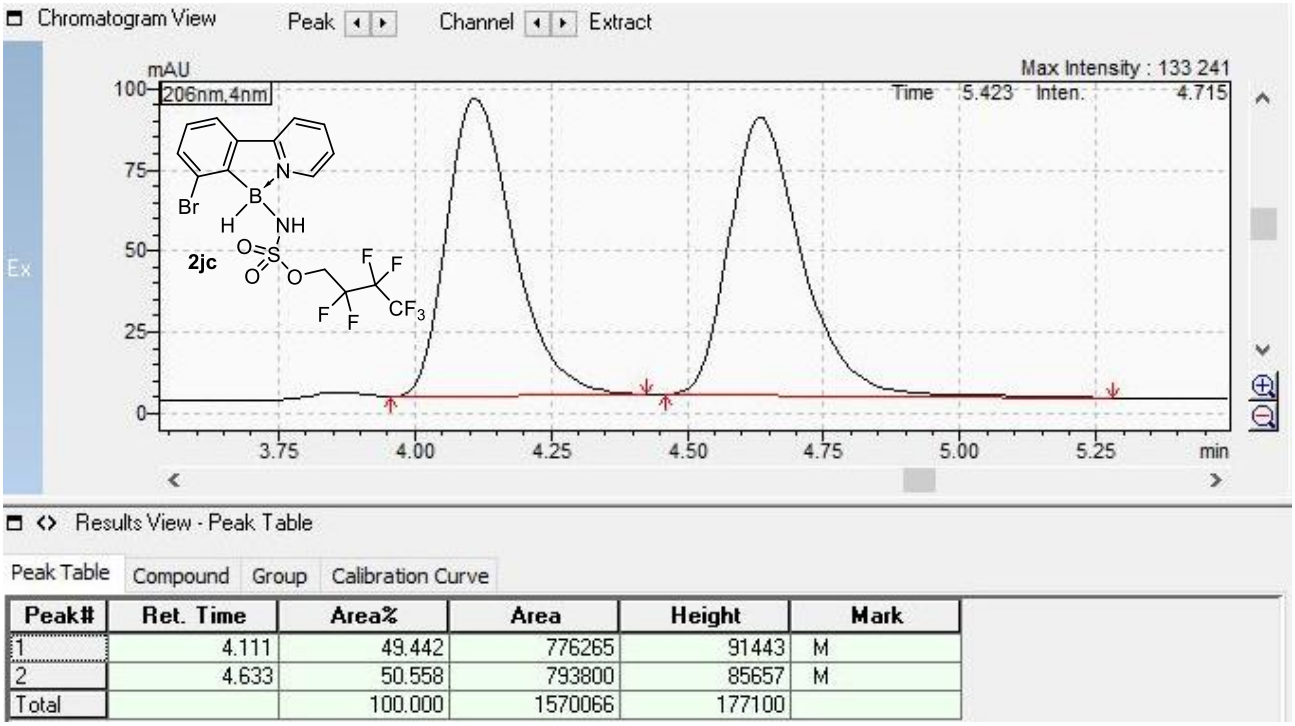
Fig. S51. HPLC chromatograms for racemic **2jb**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.779	91.223	2653357	280016	M
2	5.363	8.777	255297	23381	V M
Total		100.000	2908654	303397	

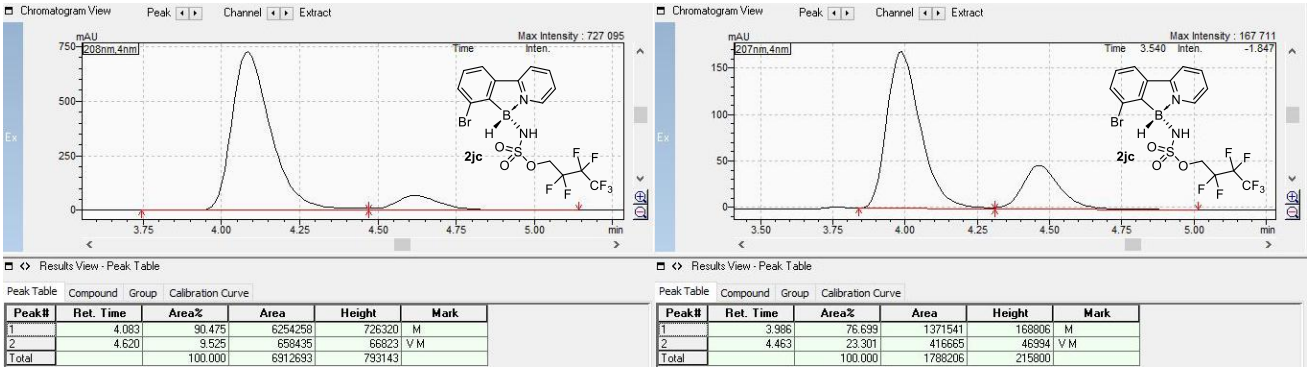
Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.822	70.666	2107598	219904	M
2	5.413	29.334	874867	81747	V M
Total		100.000	2982466	301650	

Fig. S52. HPLC chromatograms for *R*-enriched **2jb** (left: Ru(II,III) catalyzed, conditions A; right: Rh(II,II) catalyzed, conditions B).



Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.111	49.442	776265	91443	M
2	4.633	50.558	793800	85657	M
Total		100.000	1570066	177100	

Fig. S53. HPLC chromatograms racemic **2jc**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.083	90.475	6254258	726320	M
2	4.620	9.525	658435	66823	V M
Total		100.000	6912693	793143	

Peak#	Ret. Time	Area%	Area	Height	Mark
1	3.986	76.699	1371541	168806	M
2	4.463	23.301	416665	46994	V M
Total		100.000	1788206	215800	

Fig. S54. HPLC chromatograms for *R*-enriched **2jc** (left: Ru(II,III) catalyzed, conditions A; right: Rh(II,II) catalyzed, conditions B).

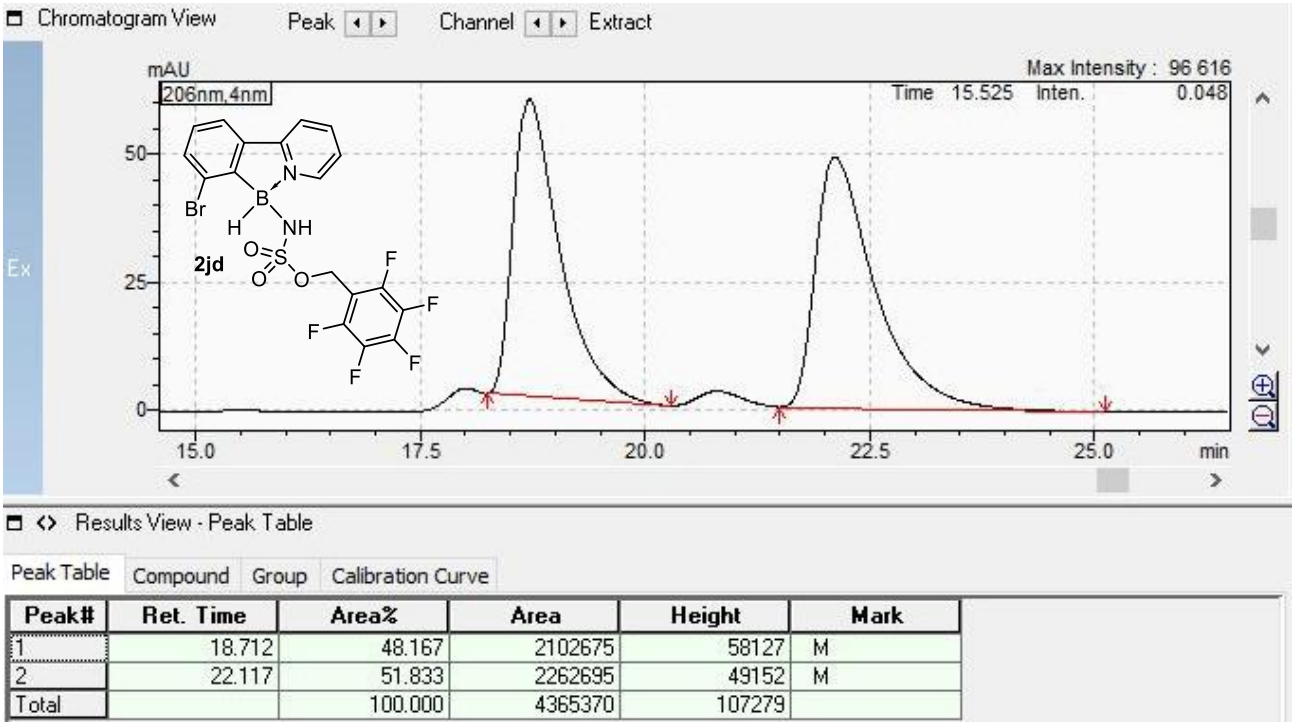


Fig. S55. HPLC chromatograms for racemic **2jd**.

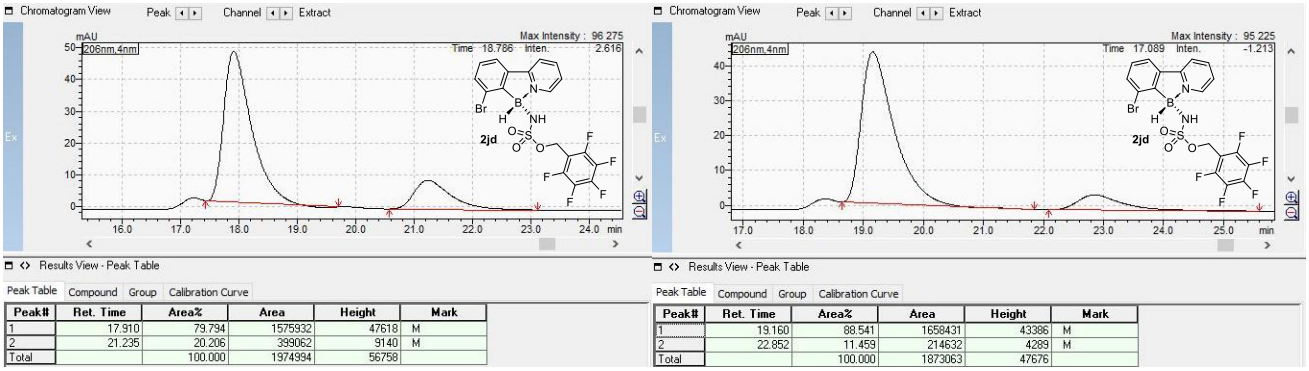
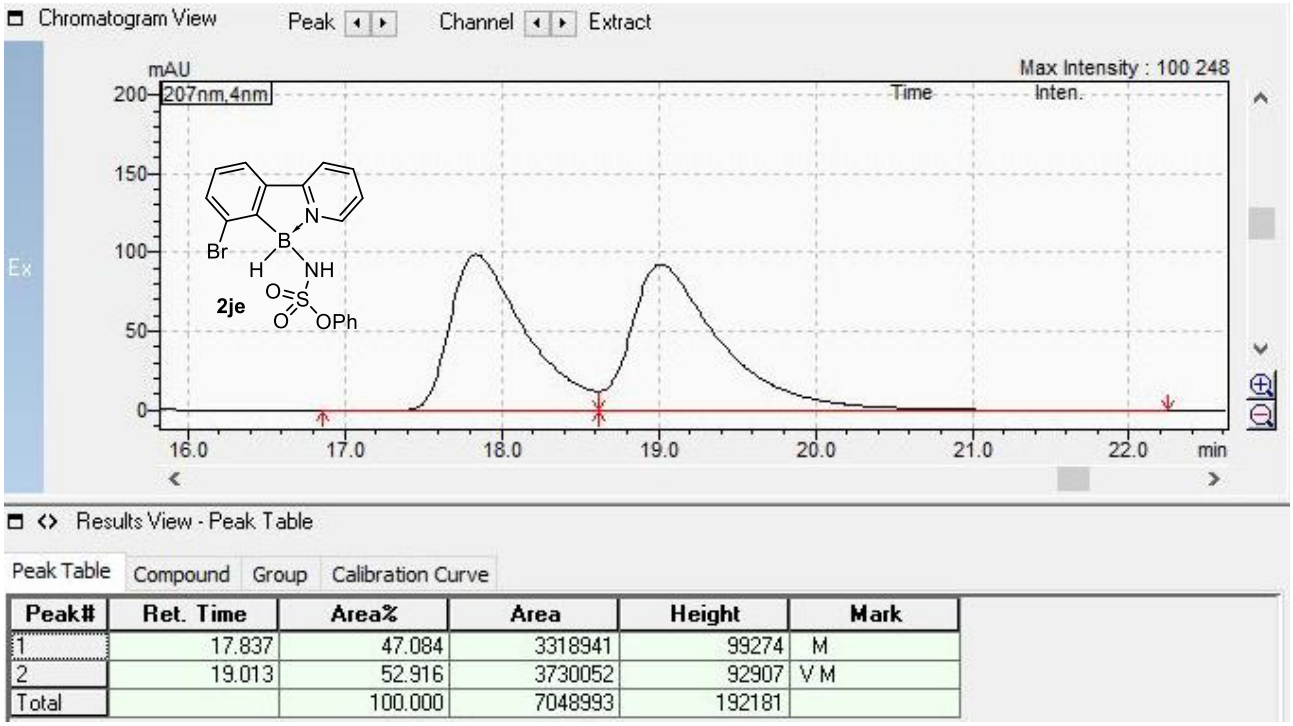
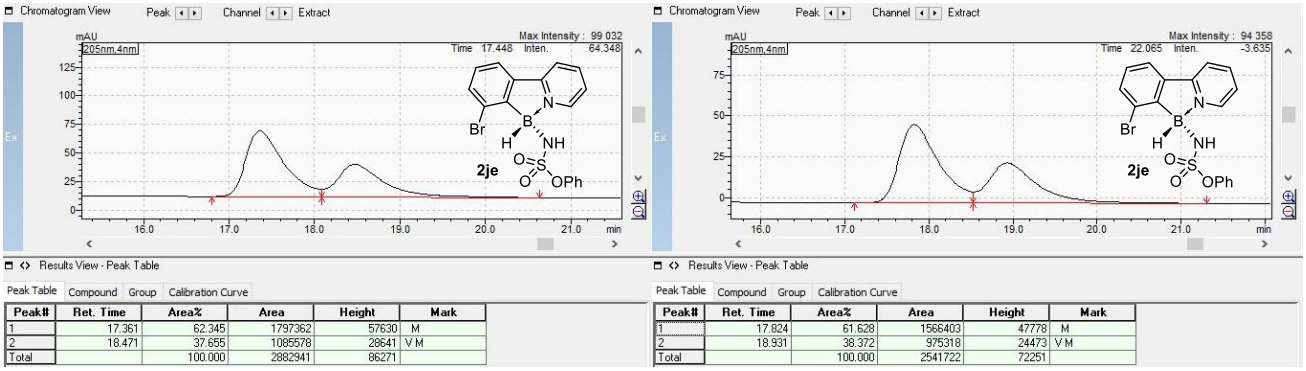


Fig. S56. HPLC chromatograms for *R*-enriched **2jd** (left: Ru(II,III) catalyzed, conditions A; right: Rh(II,II) catalyzed, conditions B).



Peak#	Ret. Time	Area%	Area	Height	Mark
1	17.837	47.084	3318941	99274	M
2	19.013	52.916	3730052	92907	V M
Total		100.000	7048993	192181	

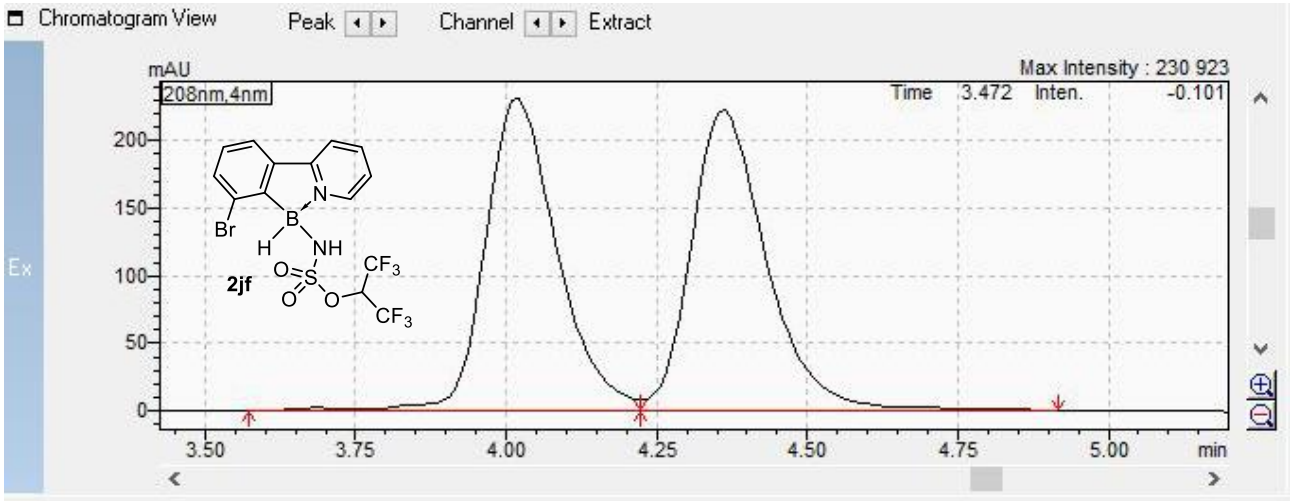
Fig. S57. HPLC chromatograms for racemic **2je**.



Peak#	Ret. Time	Area%	Area	Height	Mark
1	17.361	62.345	1797362	57630	M
2	18.471	37.655	1085578	28641	V M
Total		100.000	2882941	86271	

Peak#	Ret. Time	Area%	Area	Height	Mark
1	17.824	61.628	1566403	47778	M
2	18.931	38.372	975318	24473	V M
Total		100.000	2541722	72251	

Fig. S58. HPLC chromatograms for *R*-enriched **2je** (left: Ru(II,III) catalyzed, conditions A; right: Rh(II,II) catalyzed, conditions B).

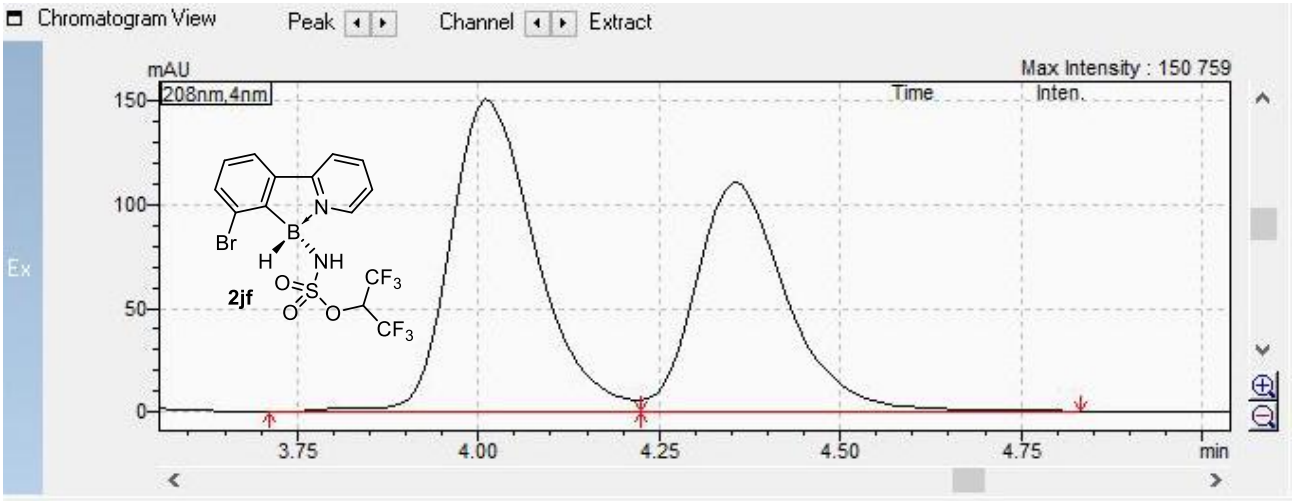


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.017	49.788	1920684	230852	M
2	4.360	50.212	1937004	222666	V M
Total		100.000	3857688	453518	

Fig. S59. HPLC chromatograms for racemic **2jf**.

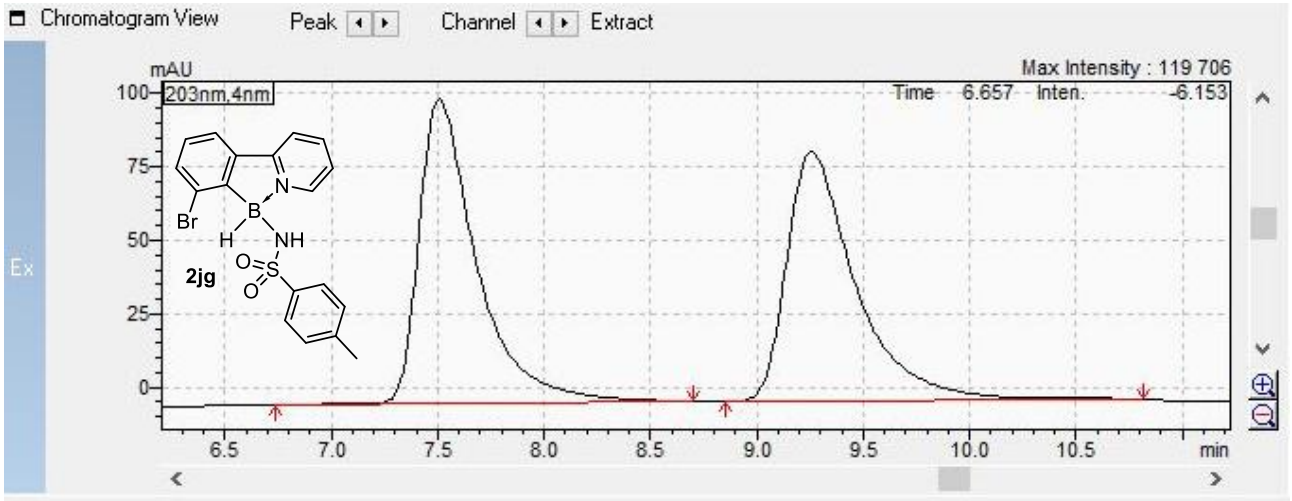


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area%	Area	Height	Mark
1	4.013	56.247	1223188	150238	M
2	4.355	43.753	951494	109984	V M
Total		100.000	2174682	260222	

Fig. S60. HPLC chromatograms for *R*-enriched **2jf** (Ru(II,III) catalyzed, conditions A).

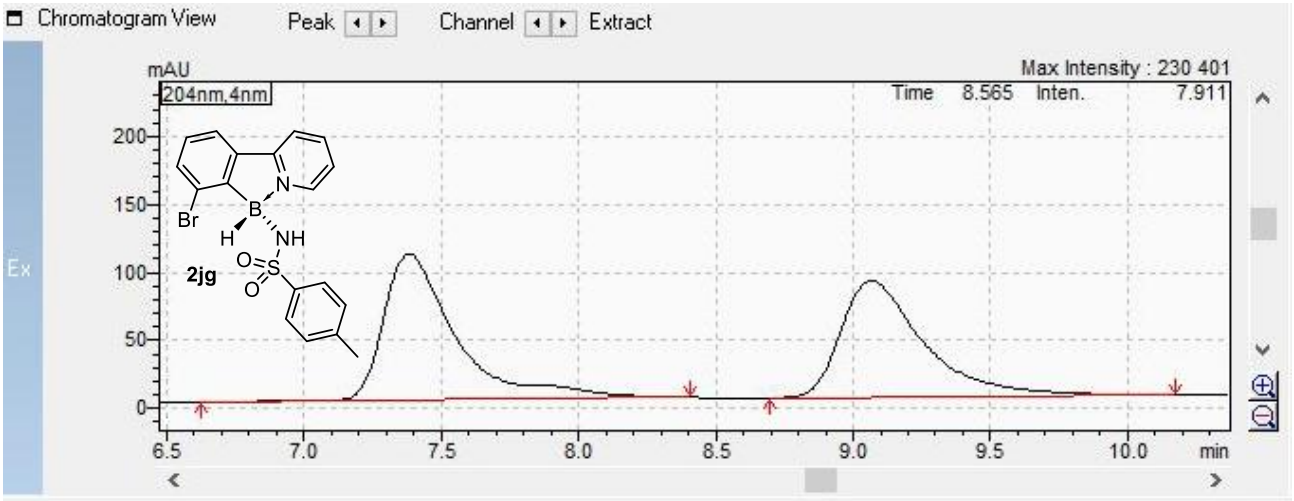


Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area%	Area	Height	Mark
1	7.509	50.360	1955945	103659	M
2	9.257	49.640	1928008	84841	M
Total		100.000	3883953	188500	

Fig. S61. HPLC chromatograms for racemic **2jg**.



Results View - Peak Table

Peak Table | Compound | Group | Calibration Curve

Peak#	Ret. Time	Area%	Area	Height	Mark
1	7.381	52.520	1998510	107737	M
2	9.066	47.480	1806754	85798	M
Total		100.000	3805264	193535	

Fig. S62. HPLC chromatograms for *R*-enriched **2jg** (Ru(II,III) catalyzed, conditions A).

NMR Spectra

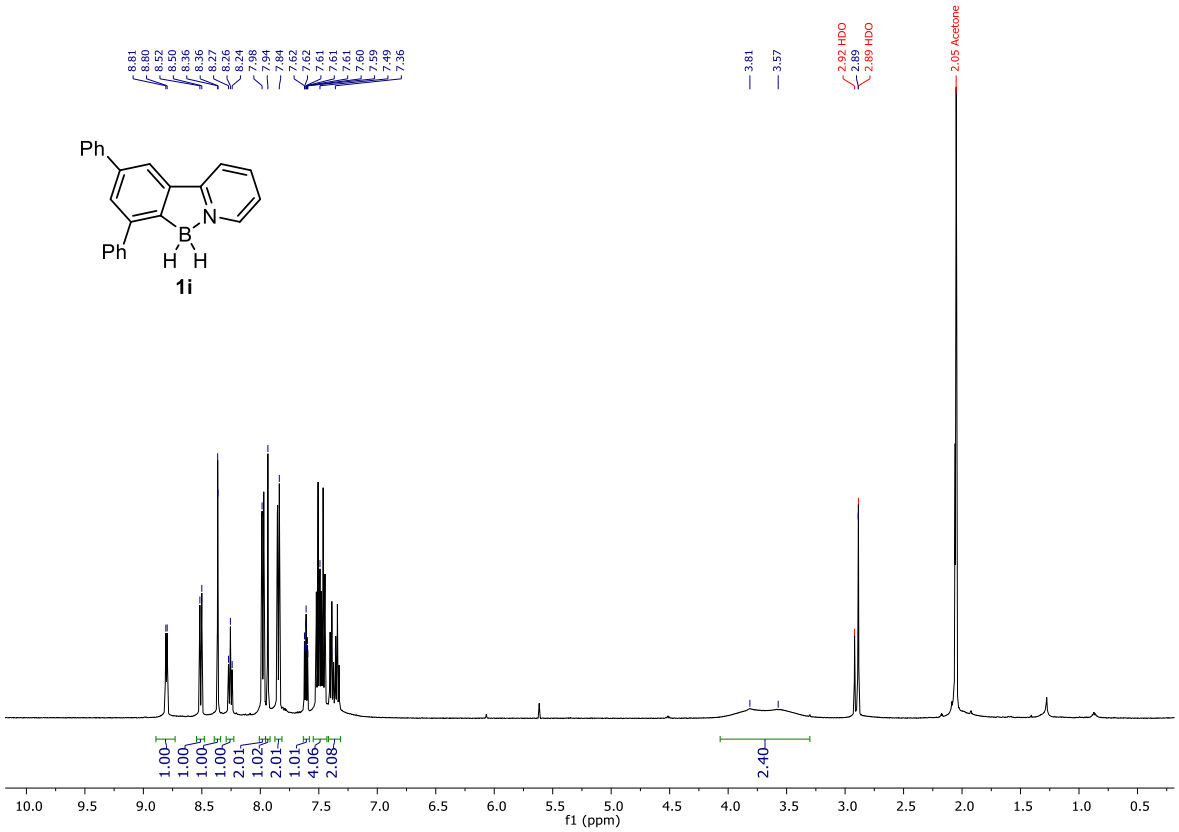


Fig. S63. ^{1}H NMR spectrum of **1i** in acetone-d_6.

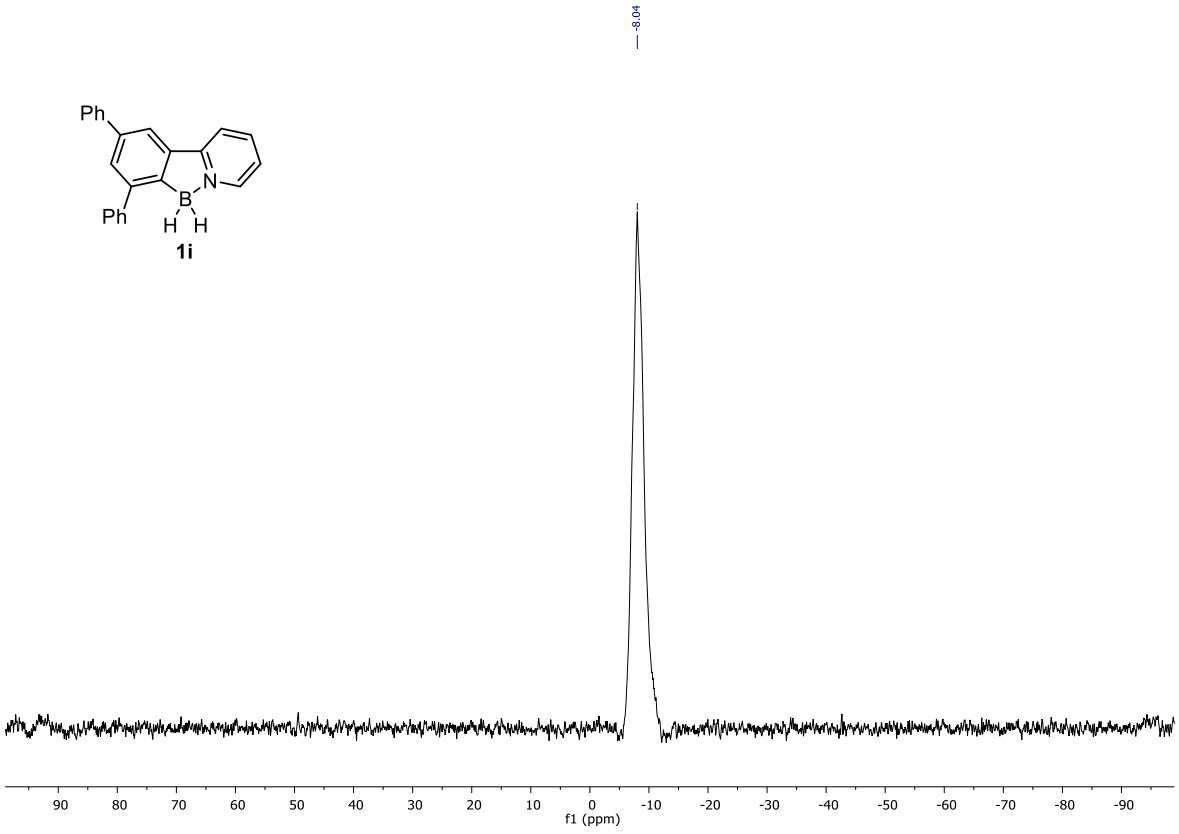


Fig. S64. ^{11}B NMR spectrum of **1i** in acetone-d_6.

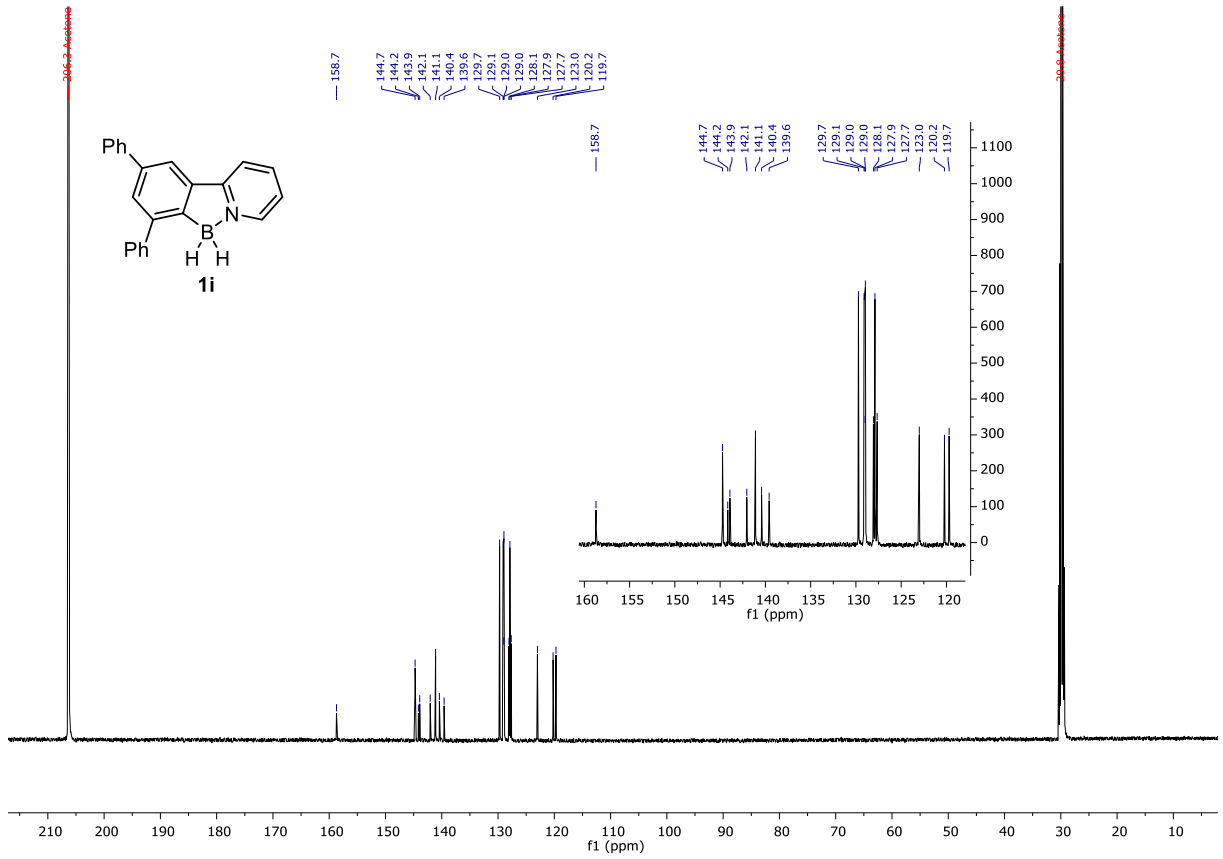


Fig. S65. ^{13}C NMR spectrum of **1i** in acetone-d_6.

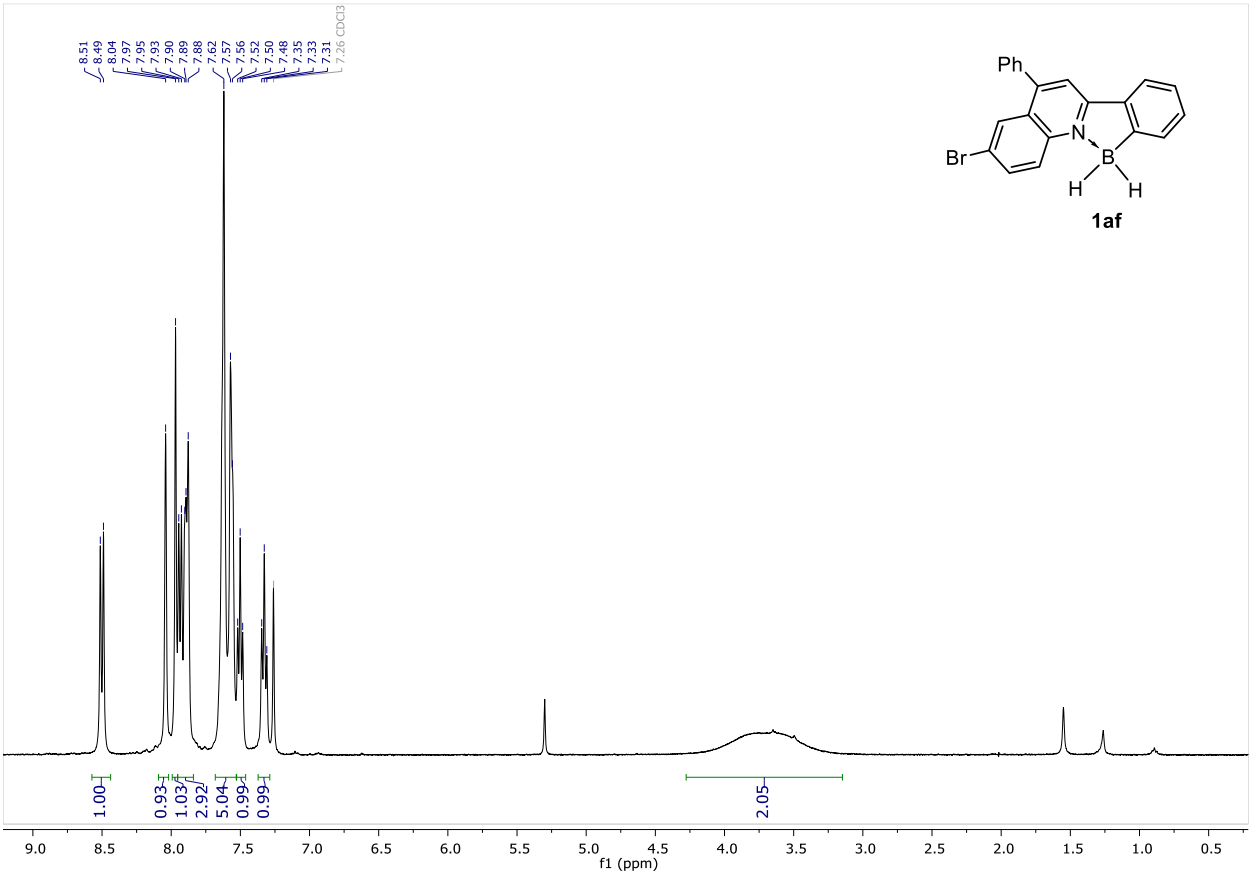


Fig. S66. ^{1}H NMR spectrum of **1af** in $CDCl_3$.

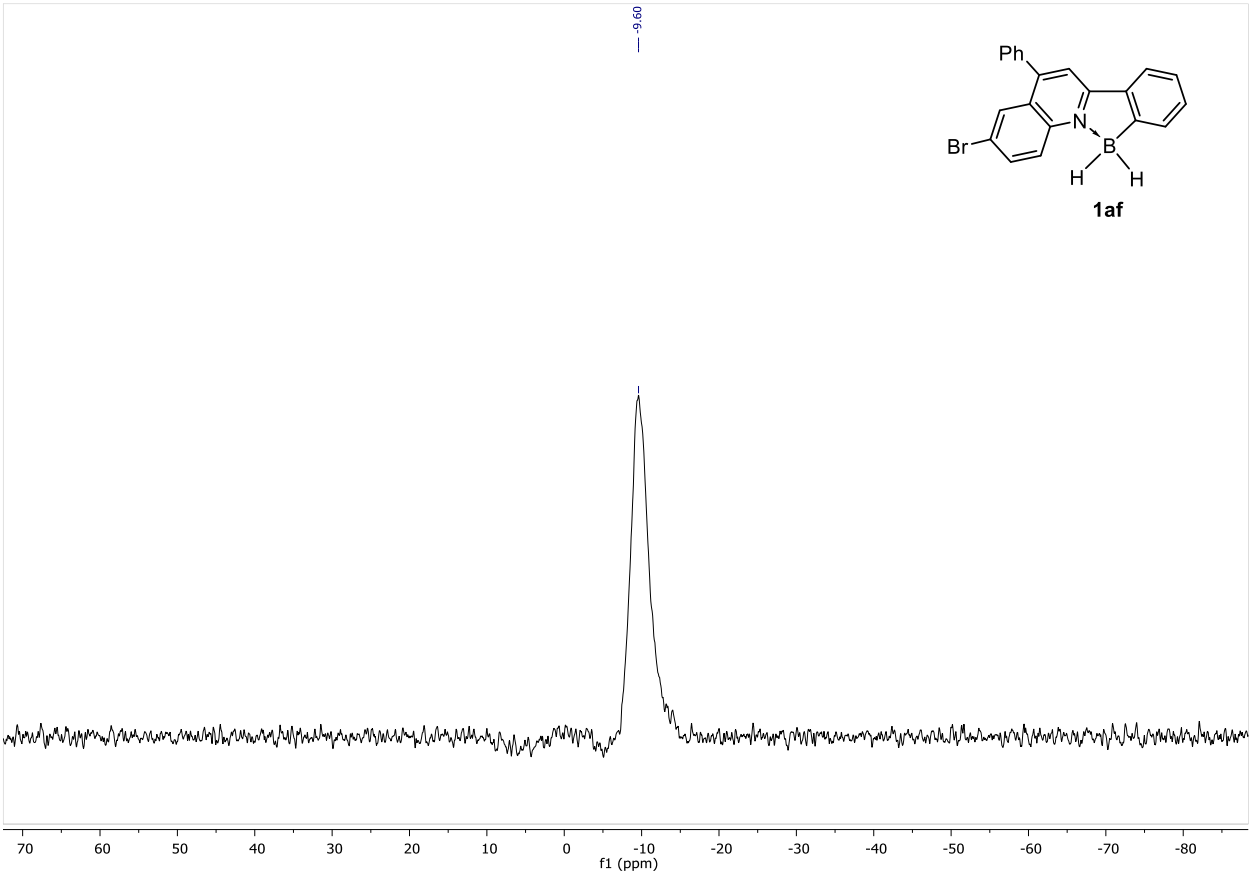


Fig. S67. ^{11}B NMR spectrum of **1af** in $CDCl_3$.

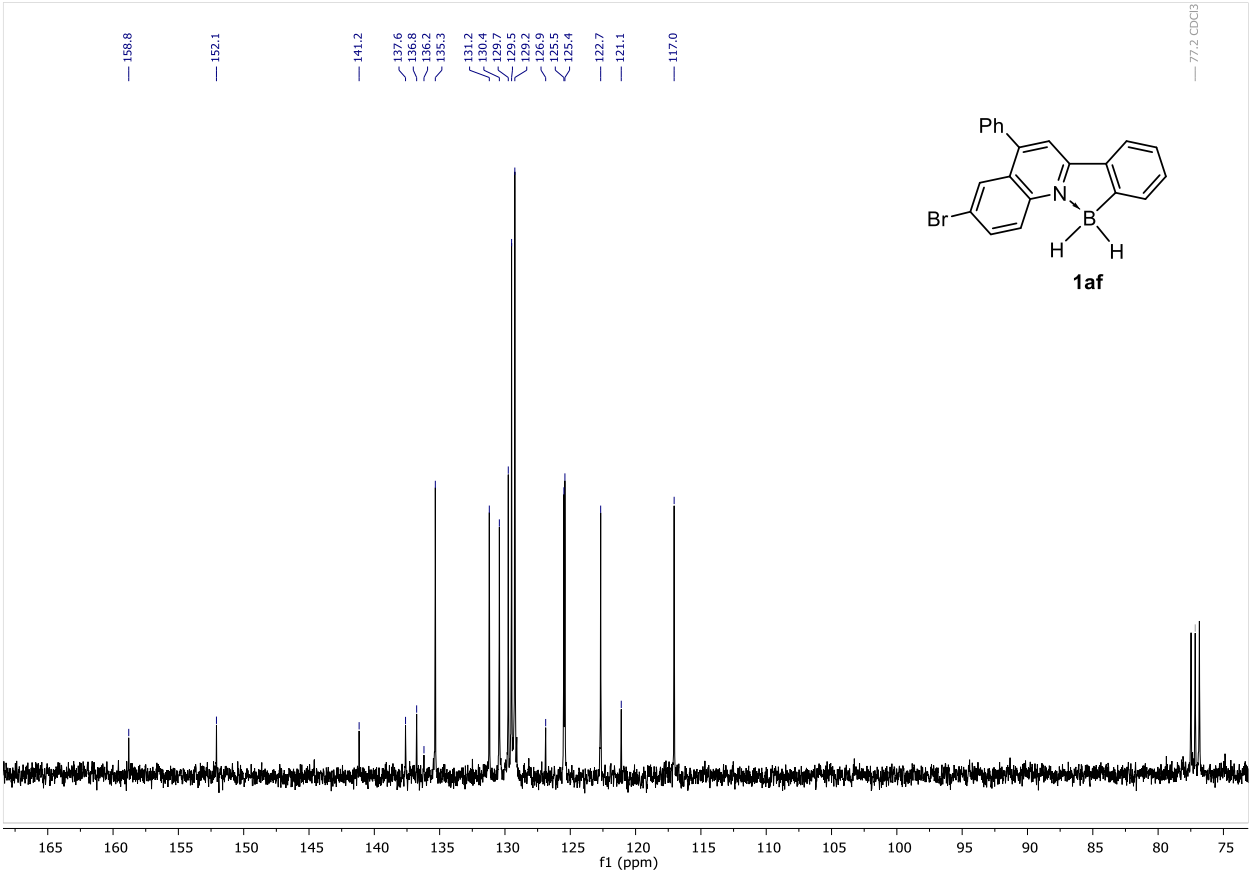


Fig. S68. ^{13}C NMR spectrum of **1af** in $CDCl_3$.

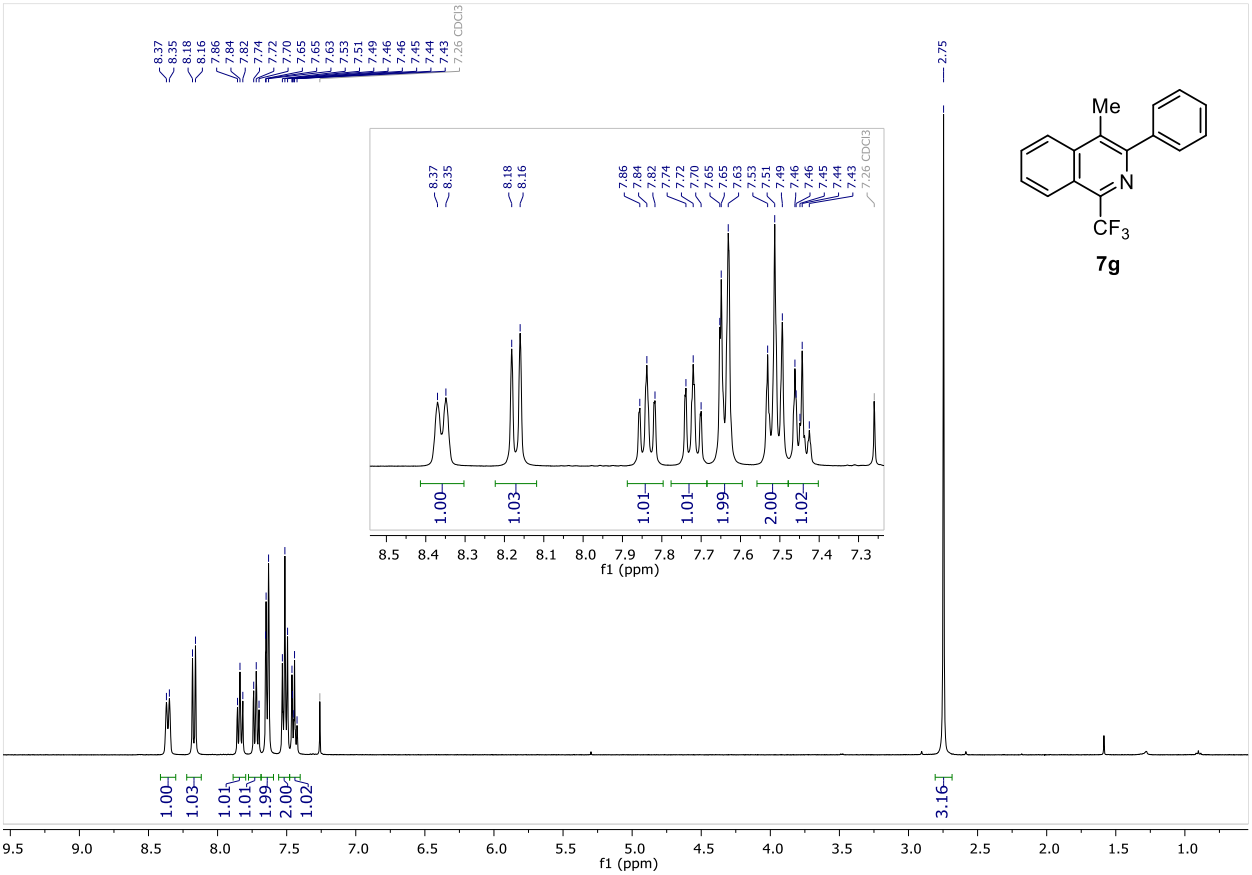


Fig. S69. ^{1}H NMR spectrum of **7g** in $CDCl_3$.

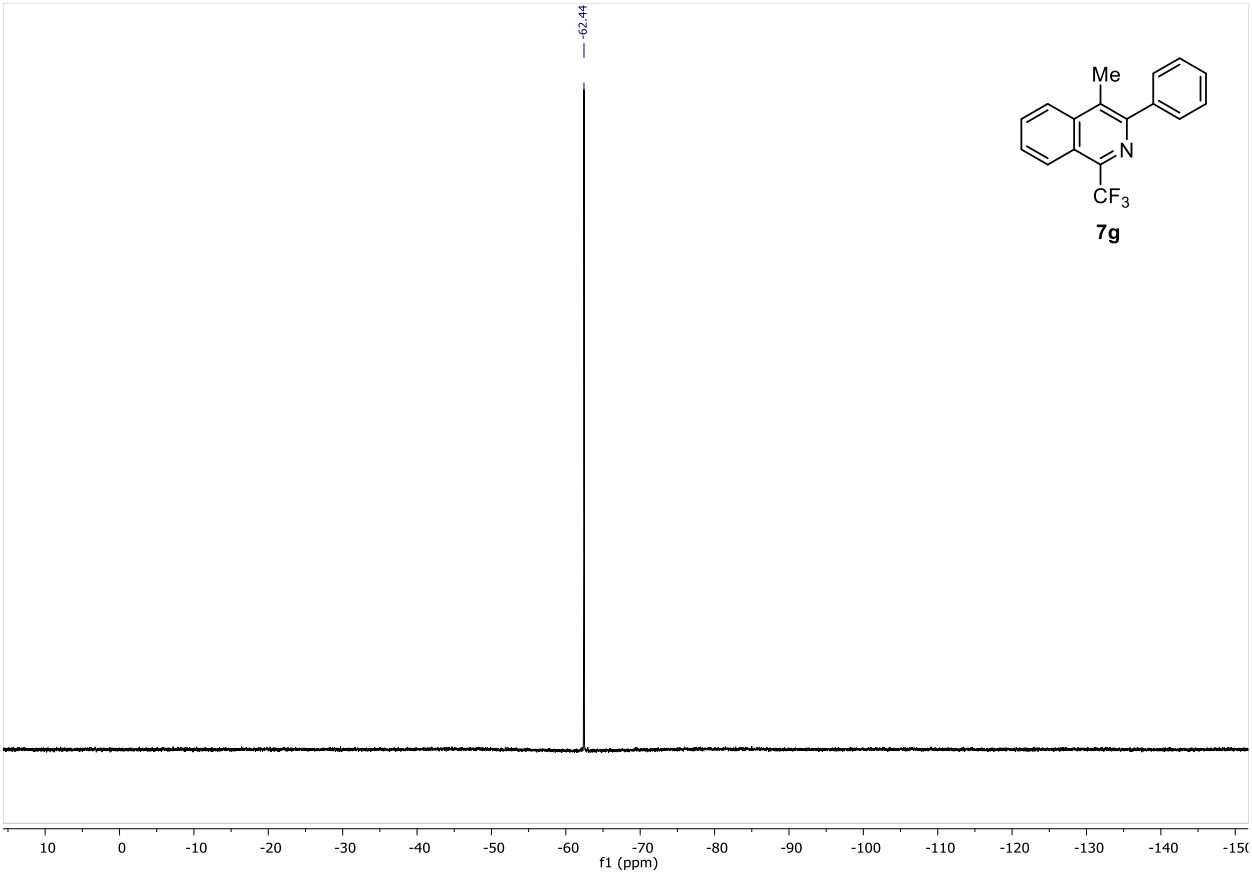


Fig. S70. ^{19}F NMR spectrum of **7g** in $CDCl_3$.

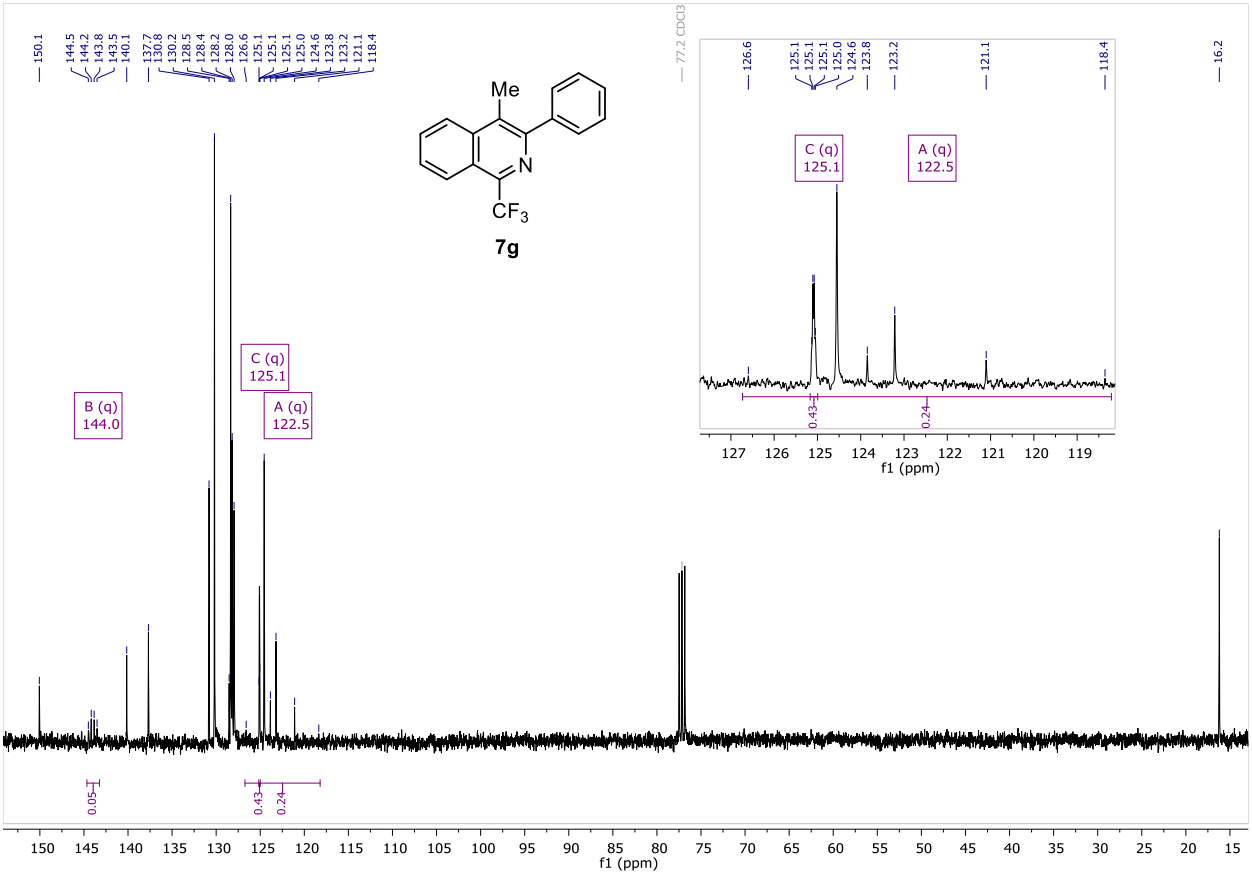


Fig. S71. ^{13}C NMR spectrum of **7g** in $CDCl_3$.

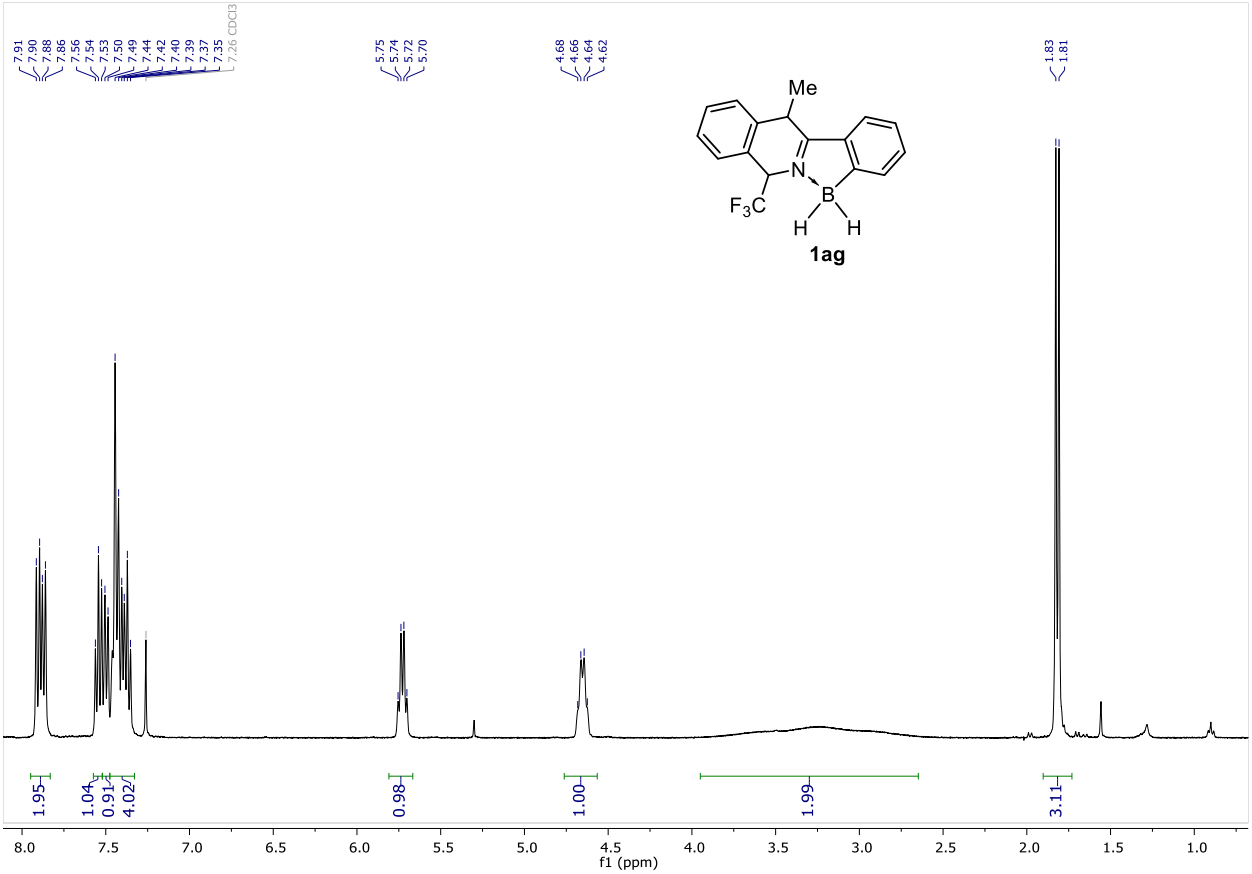


Fig. S72. ^{1}H NMR spectrum of **1ag** in $CDCl_3$.

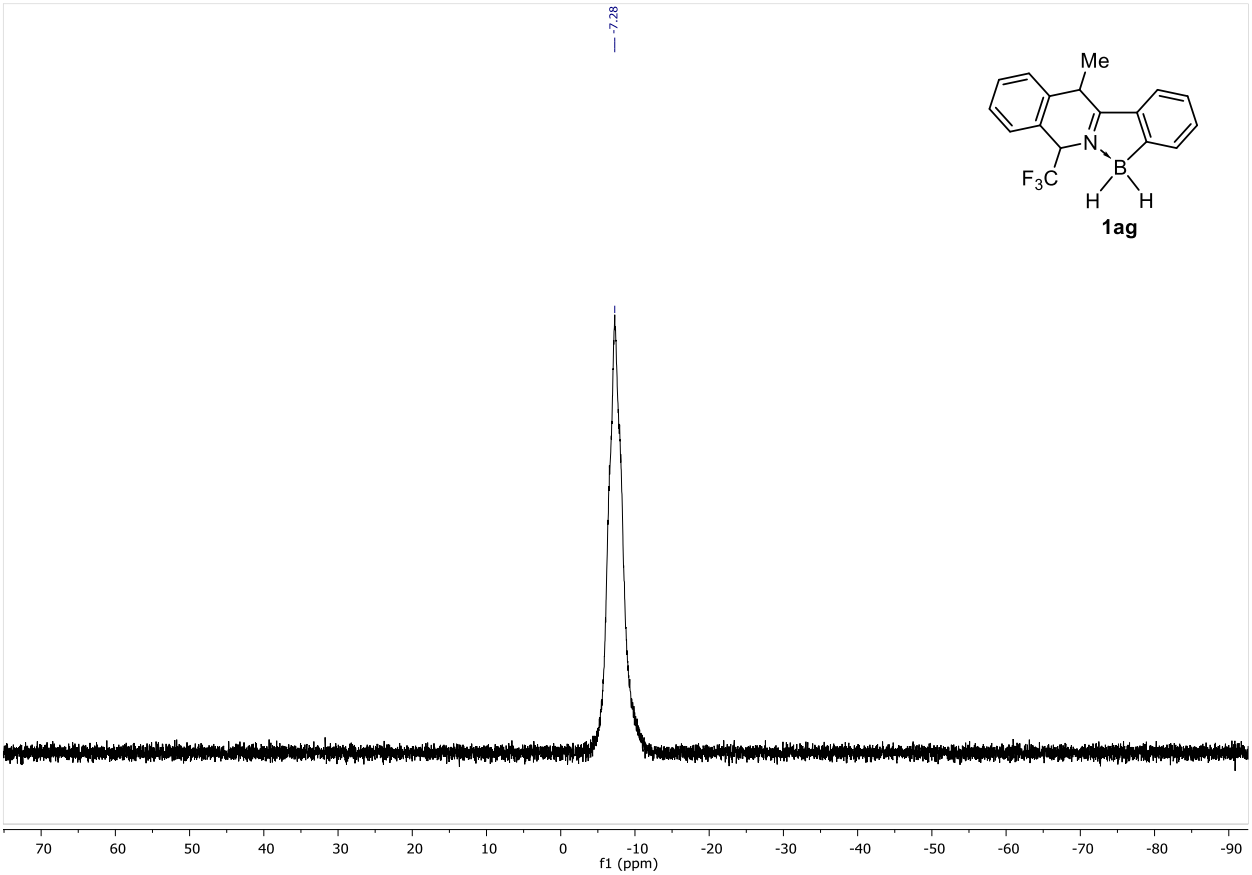


Fig. S73. ^{11}B NMR spectrum of **1ag** in $CDCl_3$.

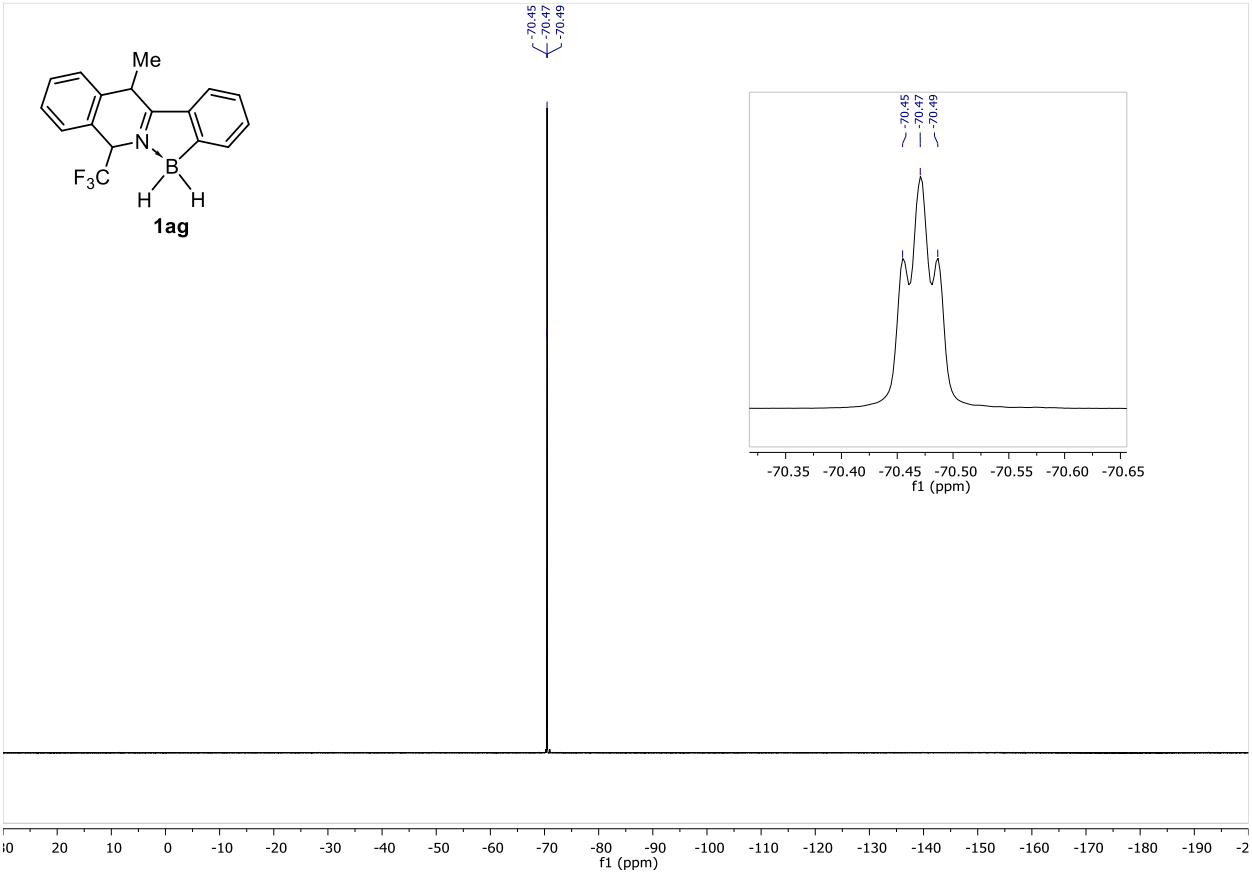


Fig. S74. ^{19}F NMR spectrum of **1ag** in $CDCl_3$.

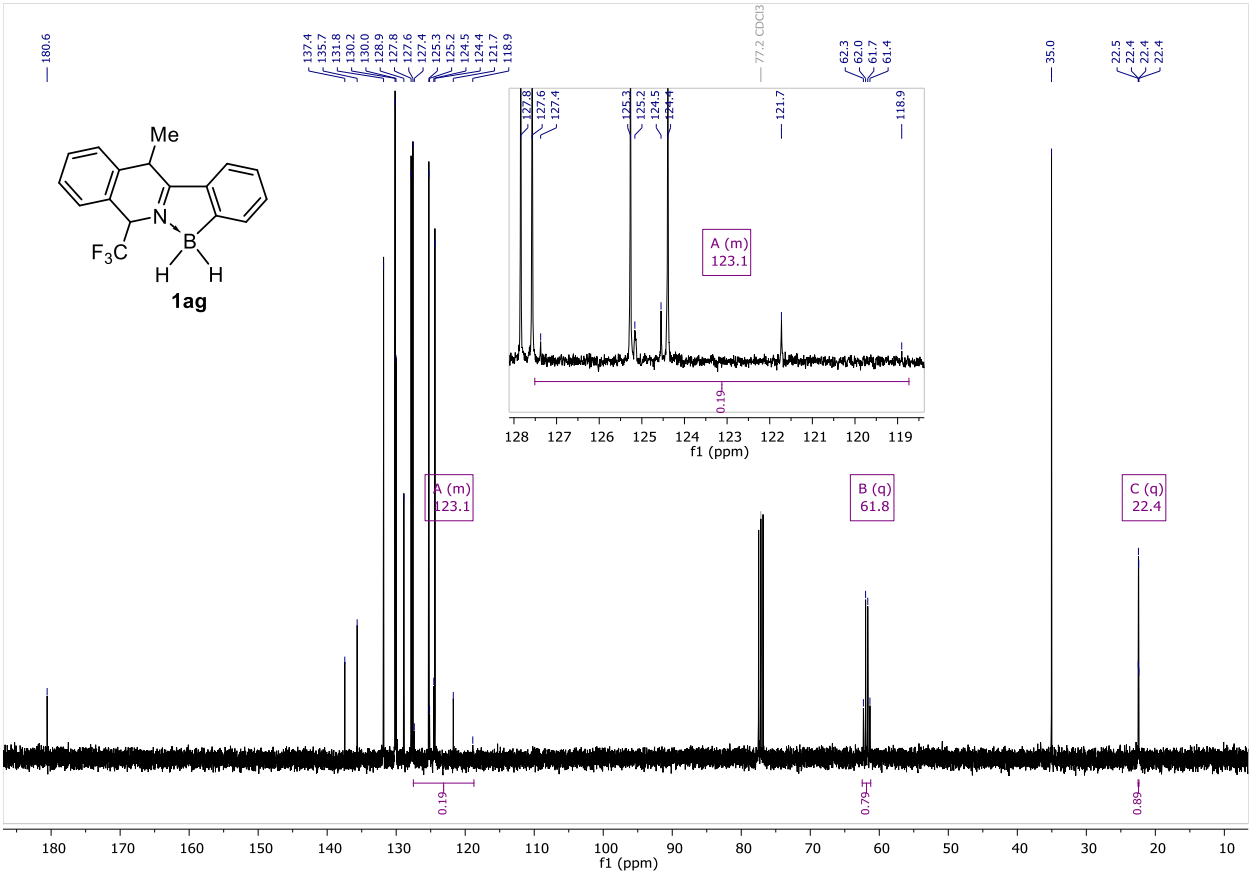


Fig. S75. ^{13}C NMR spectrum of **1ag** in $CDCl_3$.

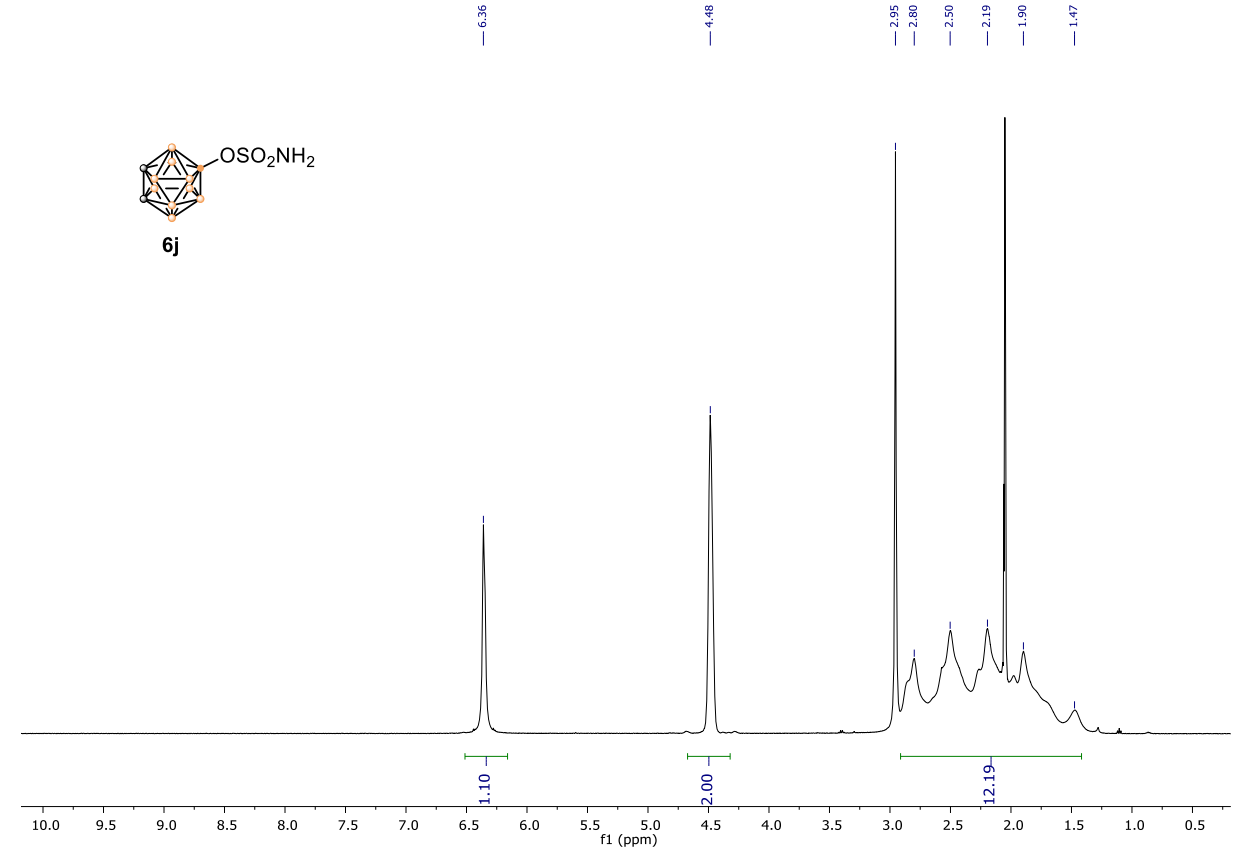


Fig. S76. ^{1}H NMR spectrum of **6j** in acetone-d_6.

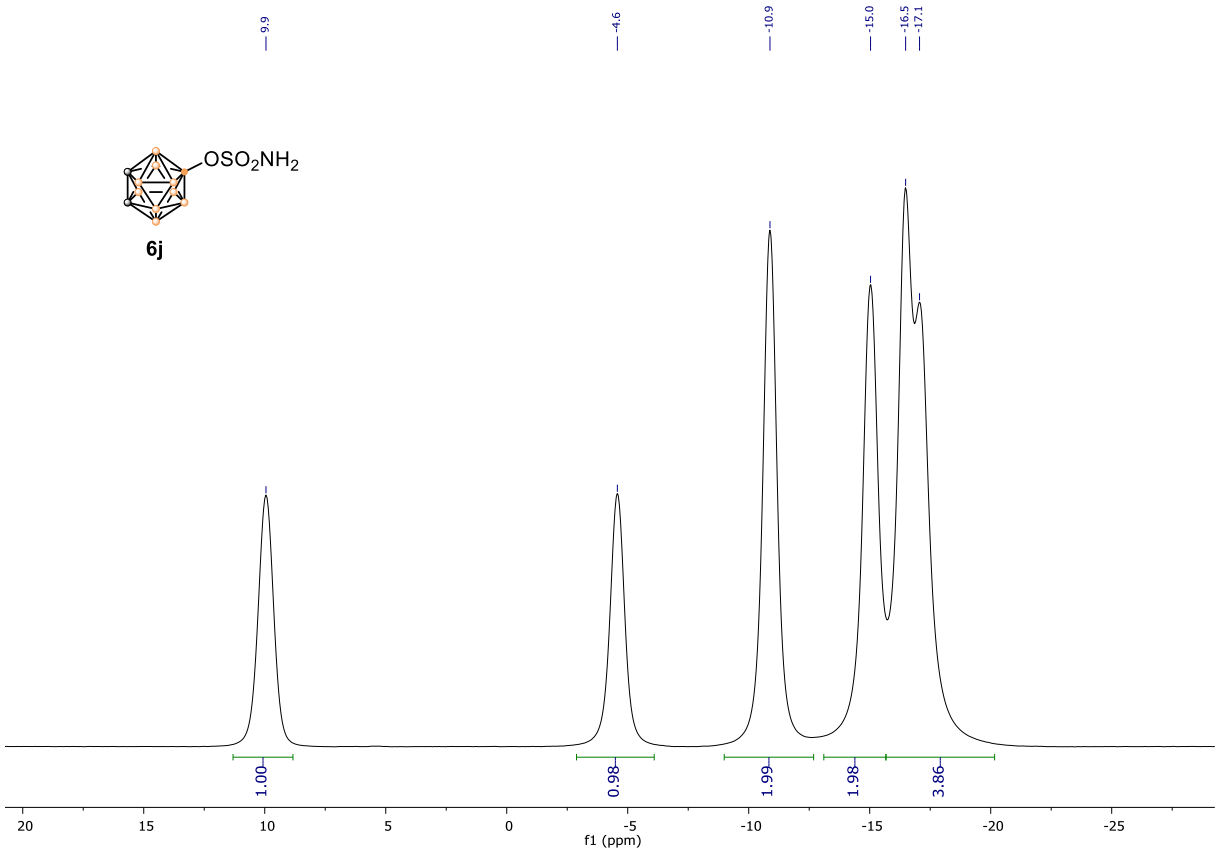


Fig. S77. $^{11}B\{^{1}H\}$ NMR spectrum of **6j** in acetone-d_6.

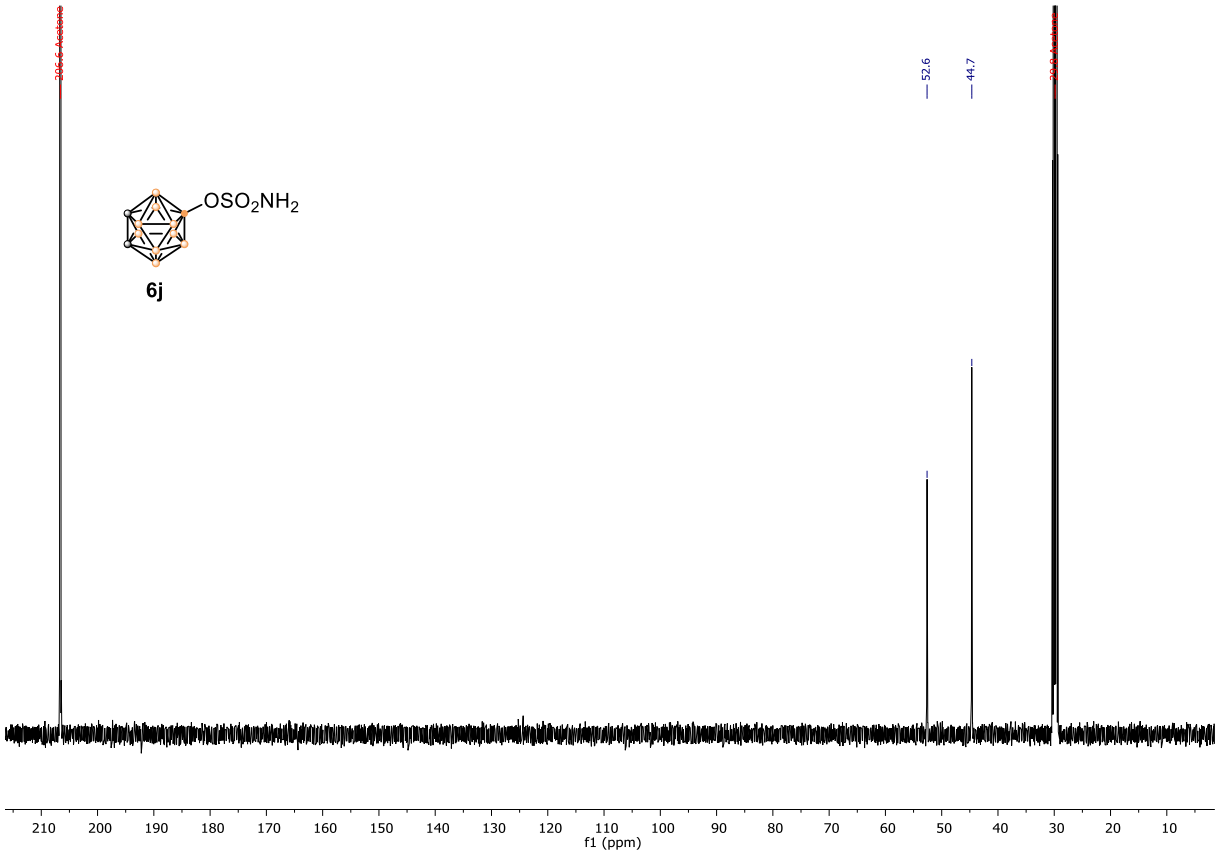


Fig. S78. ^{13}C NMR spectrum of **6j** in acetone-d_6.

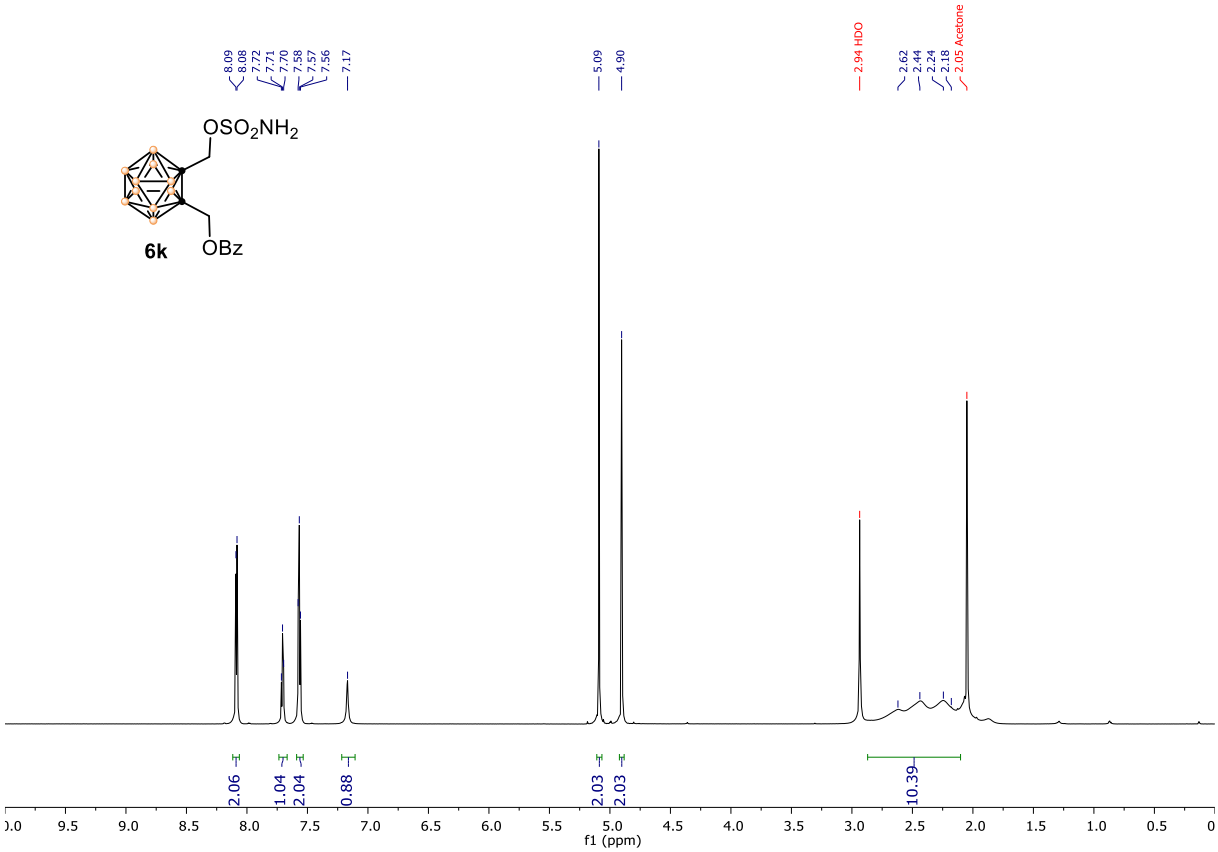


Fig. S79. ^{1}H NMR spectrum of **6k** in acetone-d_6.

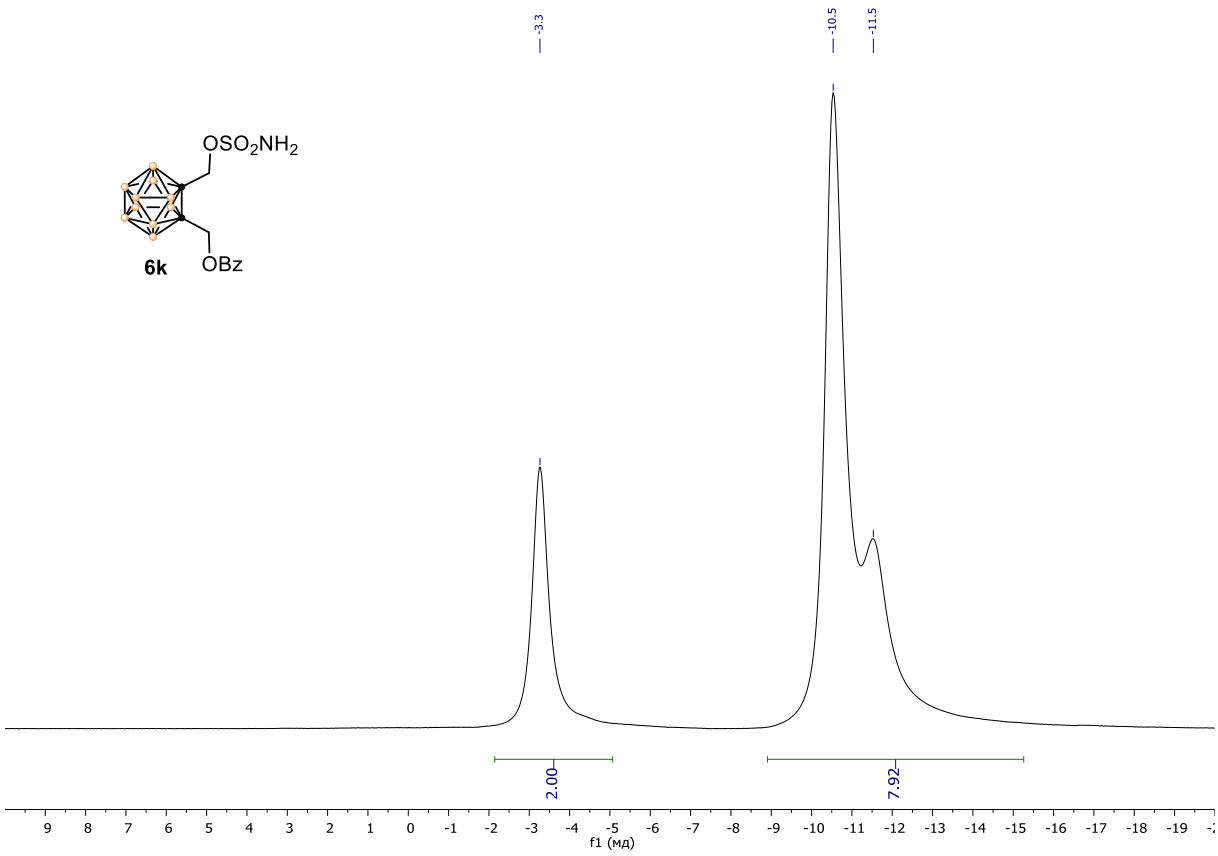


Fig. S80. ^{11}B{^{1}H} NMR spectrum of **6k** in acetone-d_6.

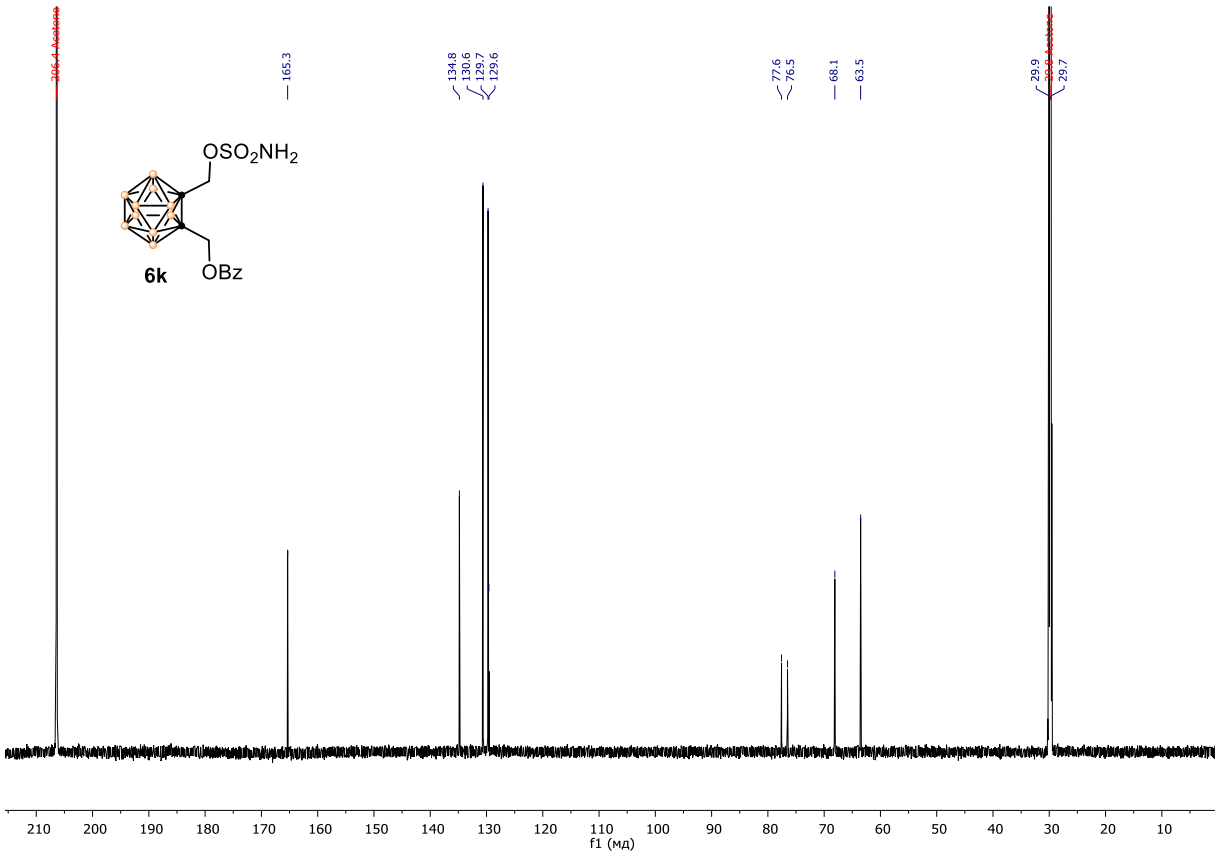


Fig. S81. ^{13}C NMR spectrum of **6k** in acetone-d_6.

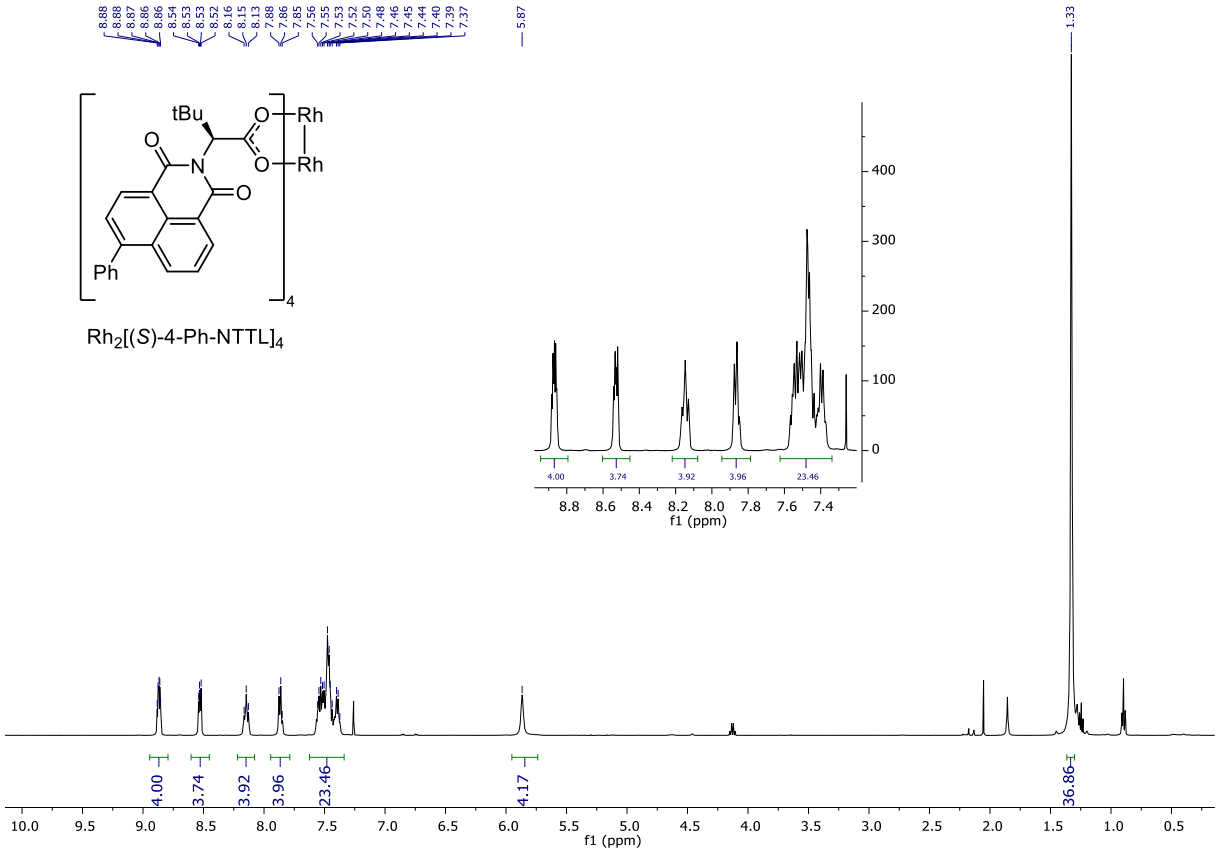
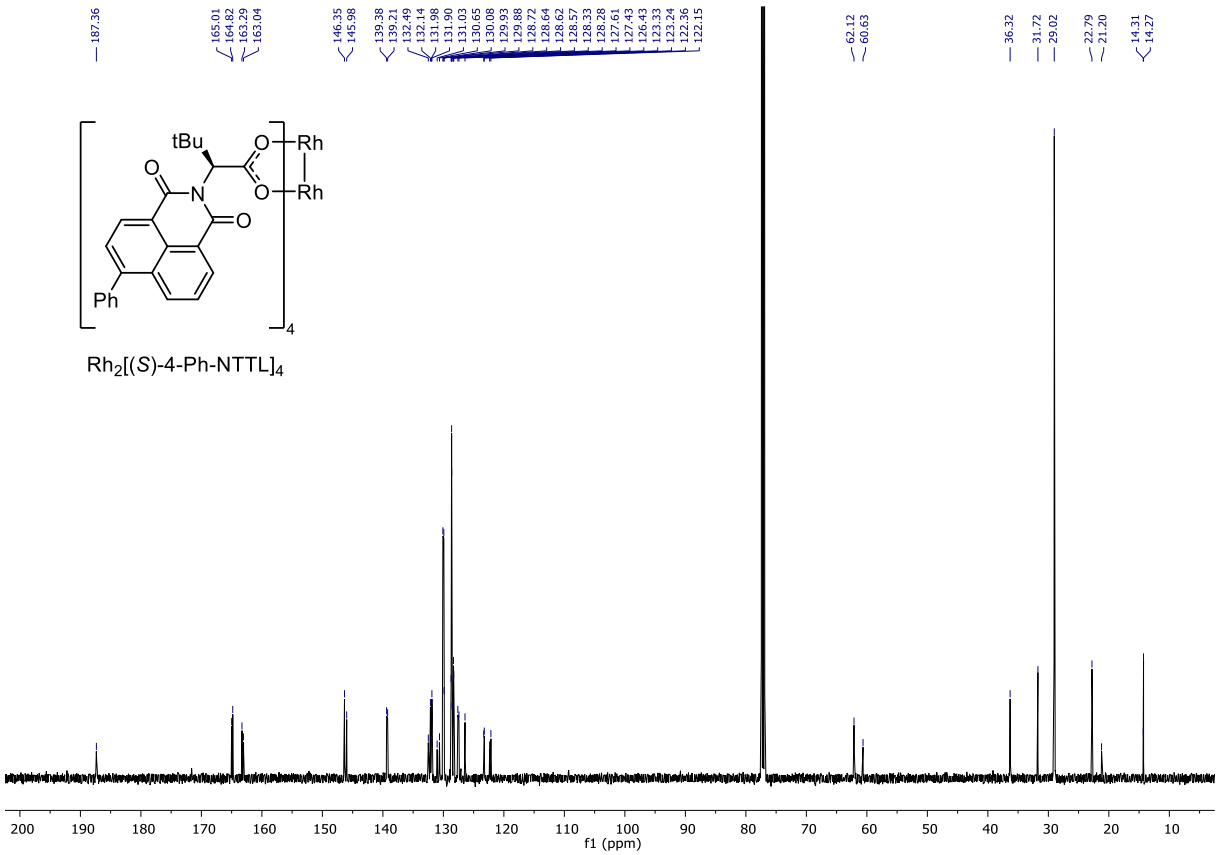
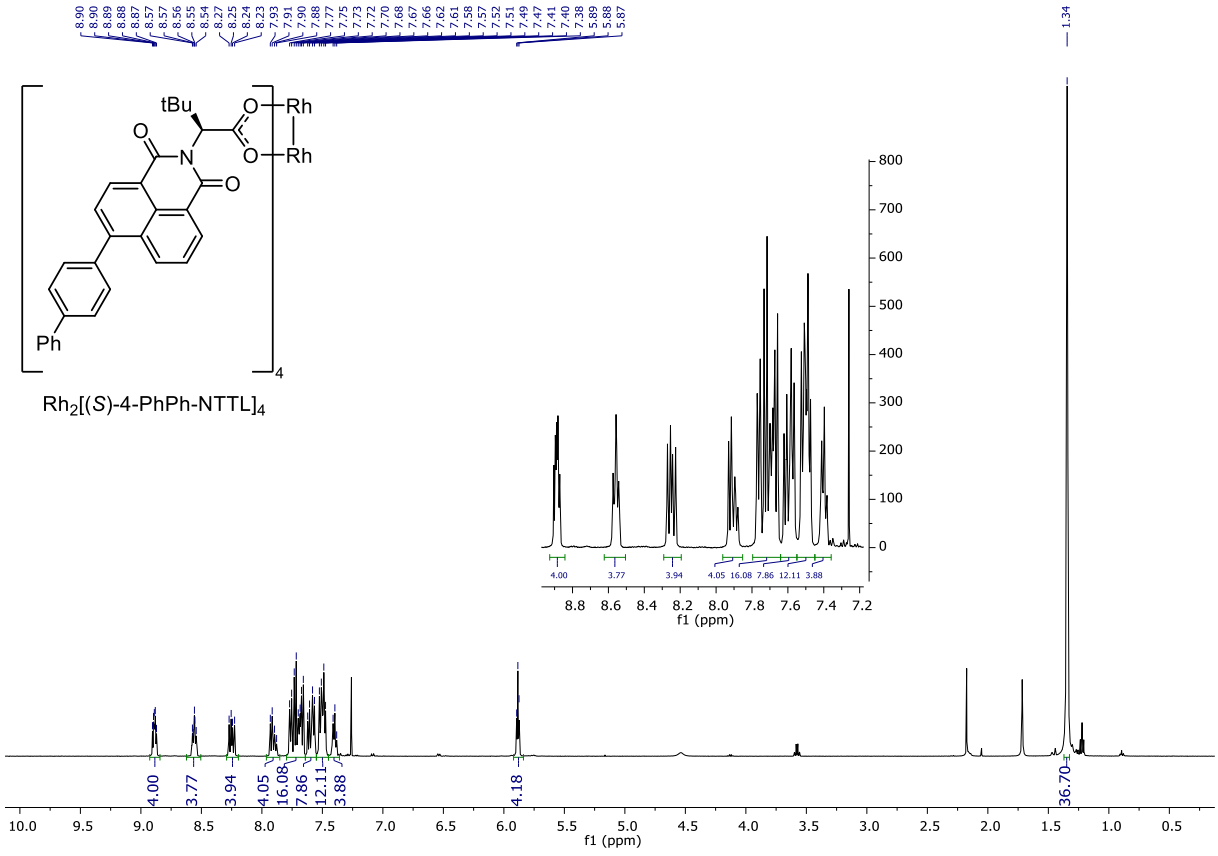


Fig. S82. ^{1}H NMR spectrum of $Rh_2[(S)$-4-Ph-NTTL$]_4$ in $CDCl_3$.



$Rh_2[(S)\text{-}4\text{-}Ph\text{-}NTTL]_4$

Fig. S83. ^{13}C NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Ph\text{-}NTTL]_4$ in $CDCl_3$.



$Rh_2[(S)\text{-}4\text{-}PhPh\text{-}NTTL]_4$

Fig. S84. ^{1}H NMR spectrum of $Rh_2[(S)\text{-}4\text{-}PhPh\text{-}NTTL]_4$ in $CDCl_3$.

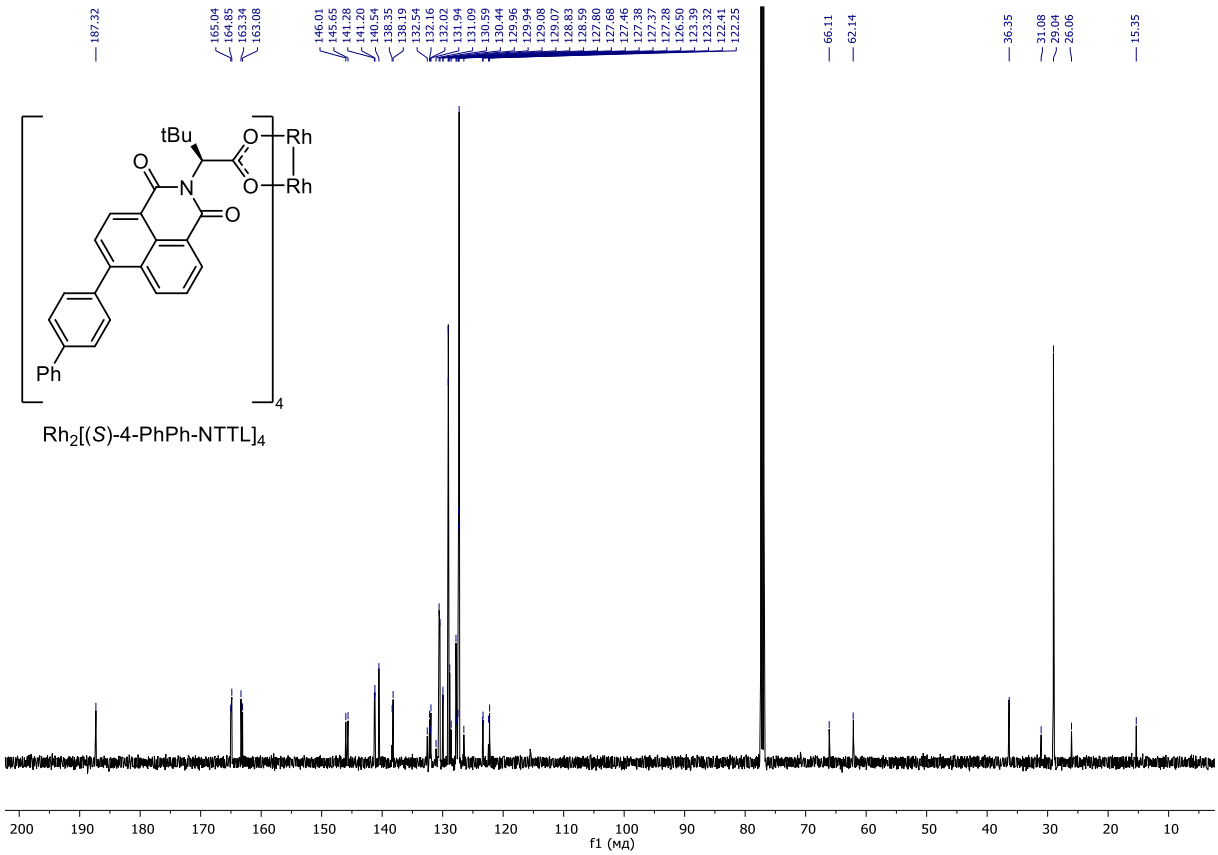


Fig. S85. ^{13}C NMR spectrum of $Rh_2[(S)\text{-}4\text{-}PhPh\text{-}NTTL]_4$ in $CDCl_3$.

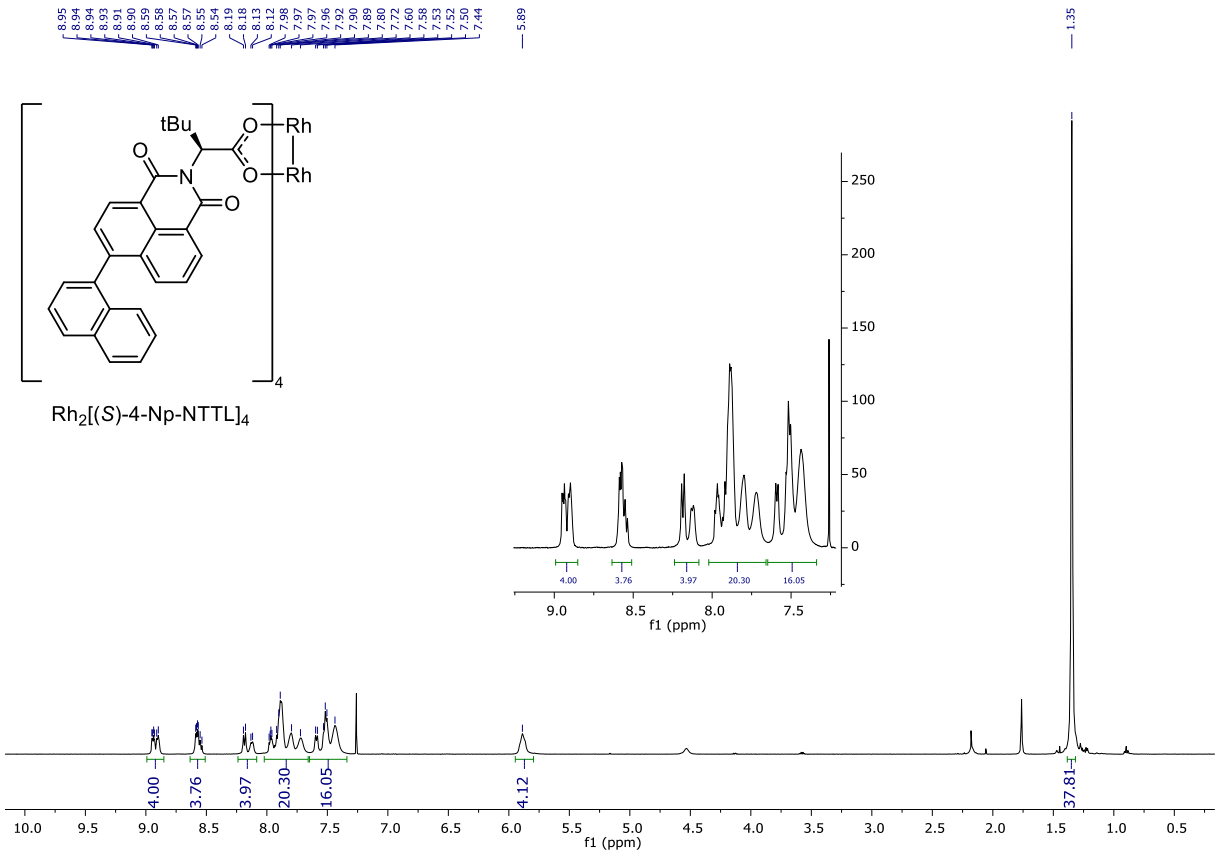


Fig. S86. ^{1}H NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Np\text{-}NTTL]_4$ in $CDCl_3$.

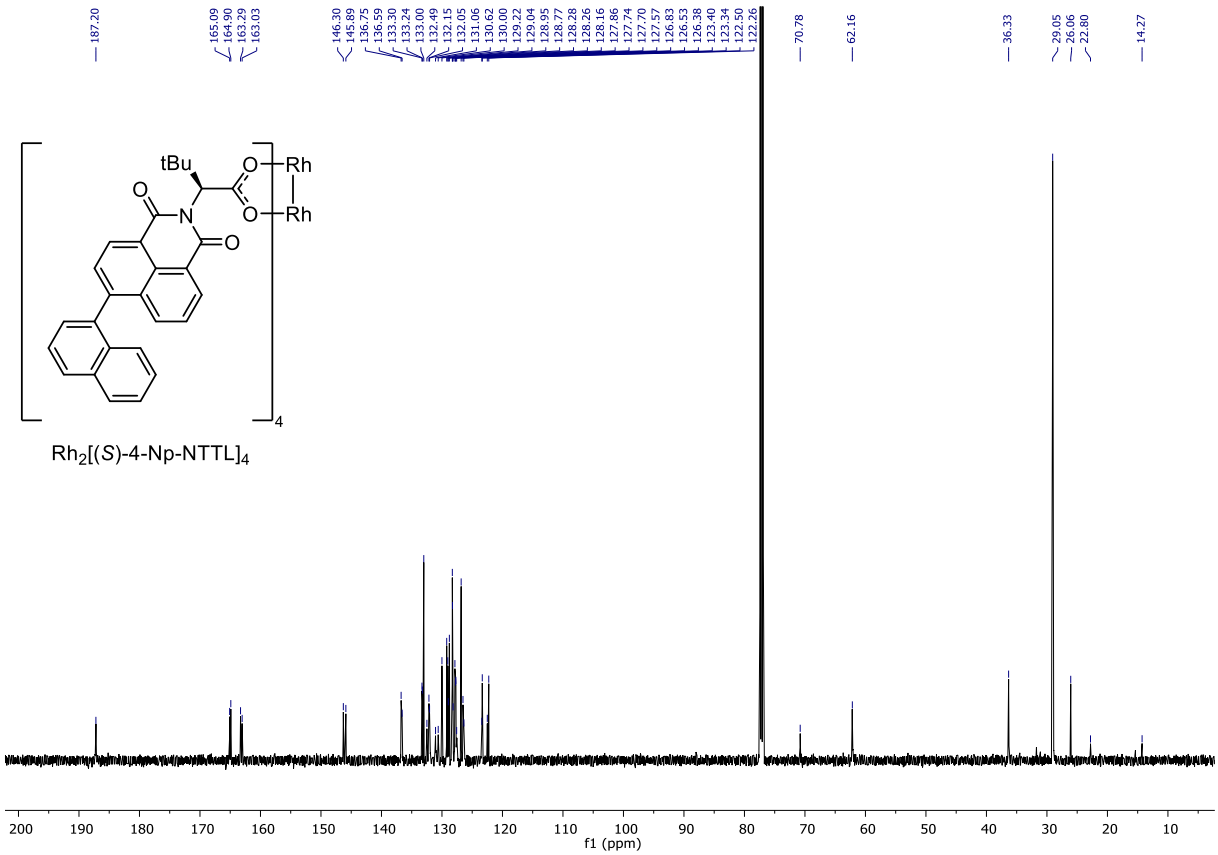


Fig. S87. ^{13}C NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Np\text{-}NTTL]_4$ in $CDCl_3$.

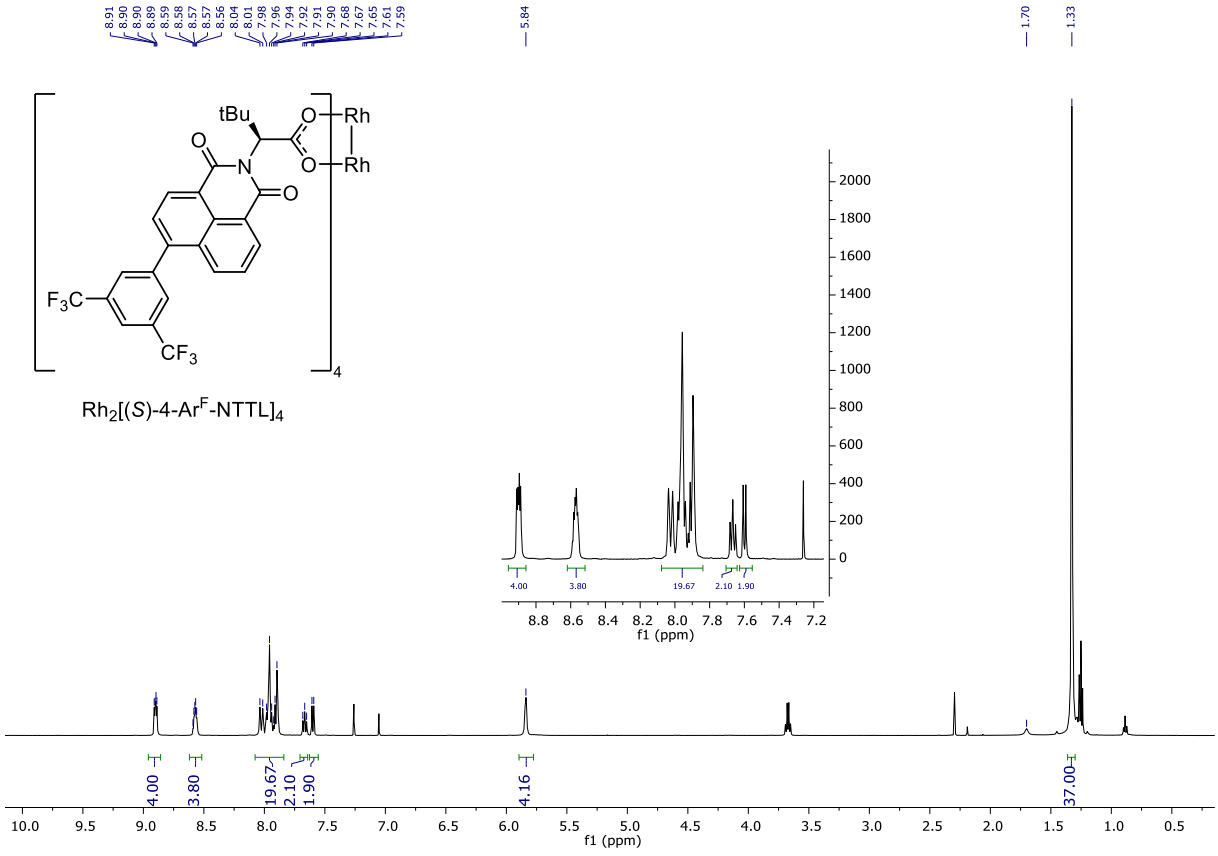


Fig. S88. ^{1}H NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Ar^F\text{-}NTTL]_4$ in $CDCl_3$.

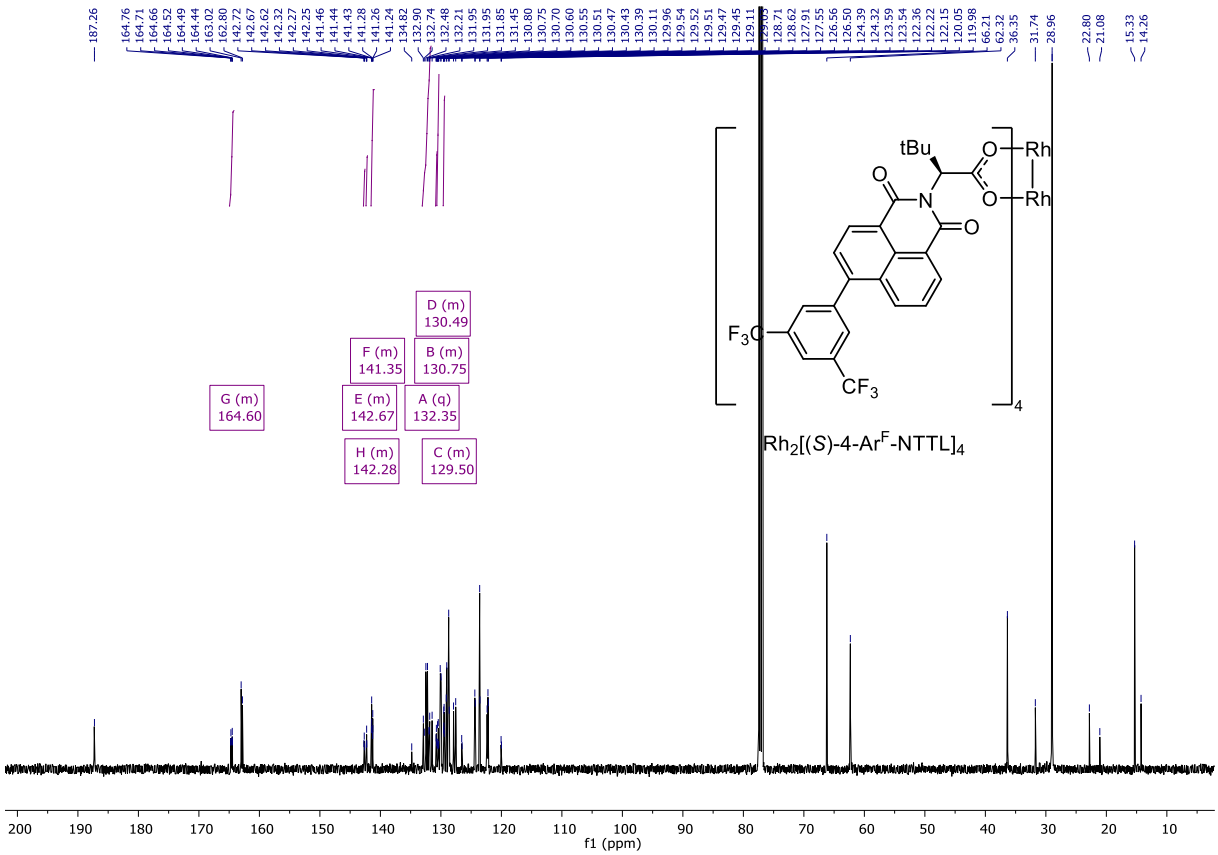


Fig. S89. ^{13}C NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Ar^F\text{-}NTTL]_4$ in $CDCl_3$.

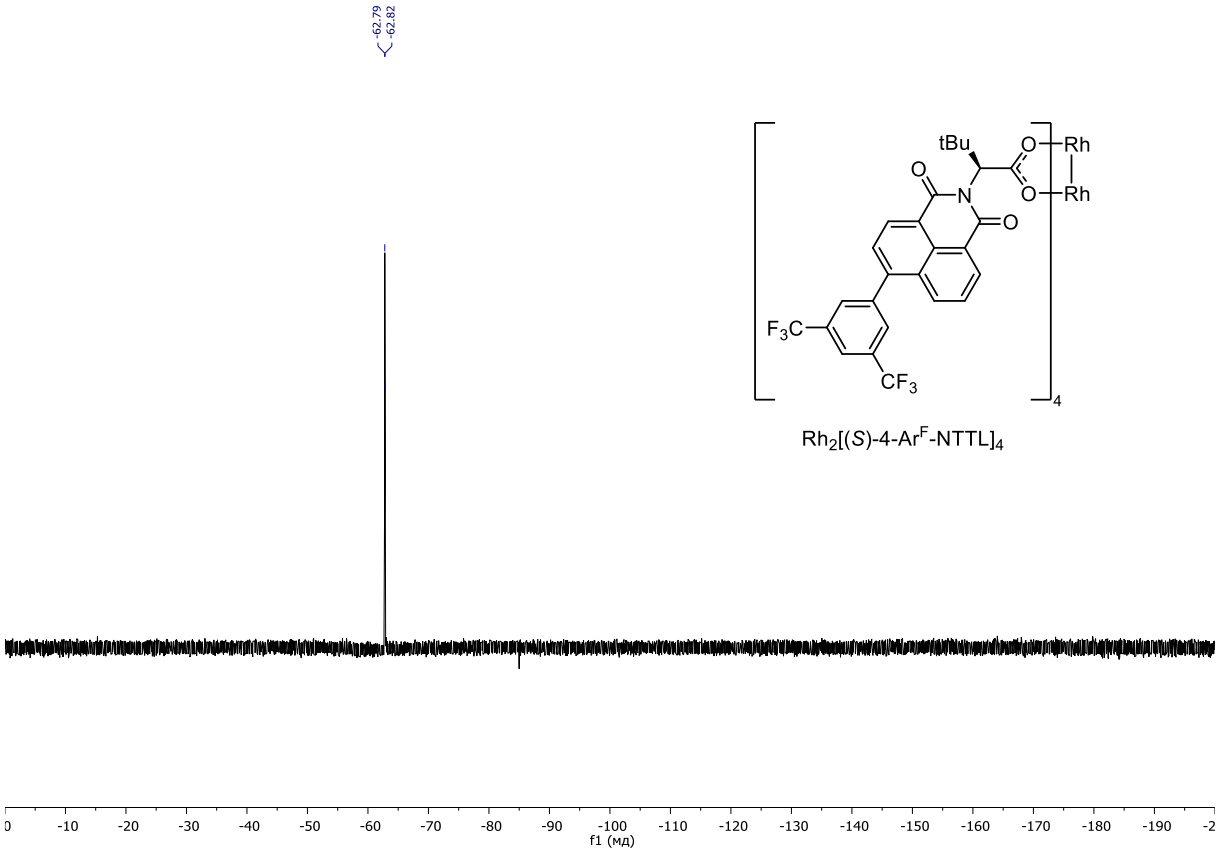


Fig. S90. ^{19}F NMR spectrum of $Rh_2[(S)\text{-}4\text{-}Ar^F\text{-}NTTL]_4$ in $CDCl_3$.

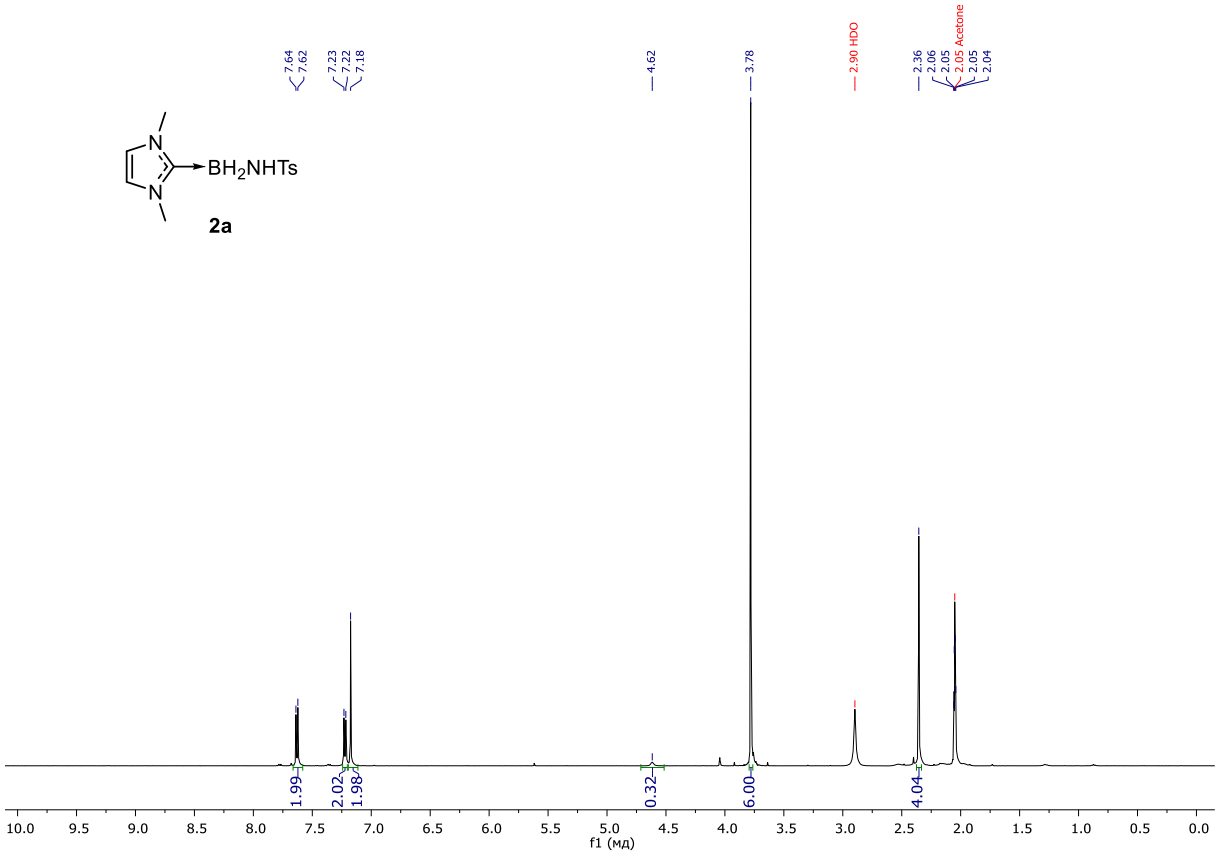


Fig. S91. ^{1}H NMR spectrum of **2a** in acetone-d_6.

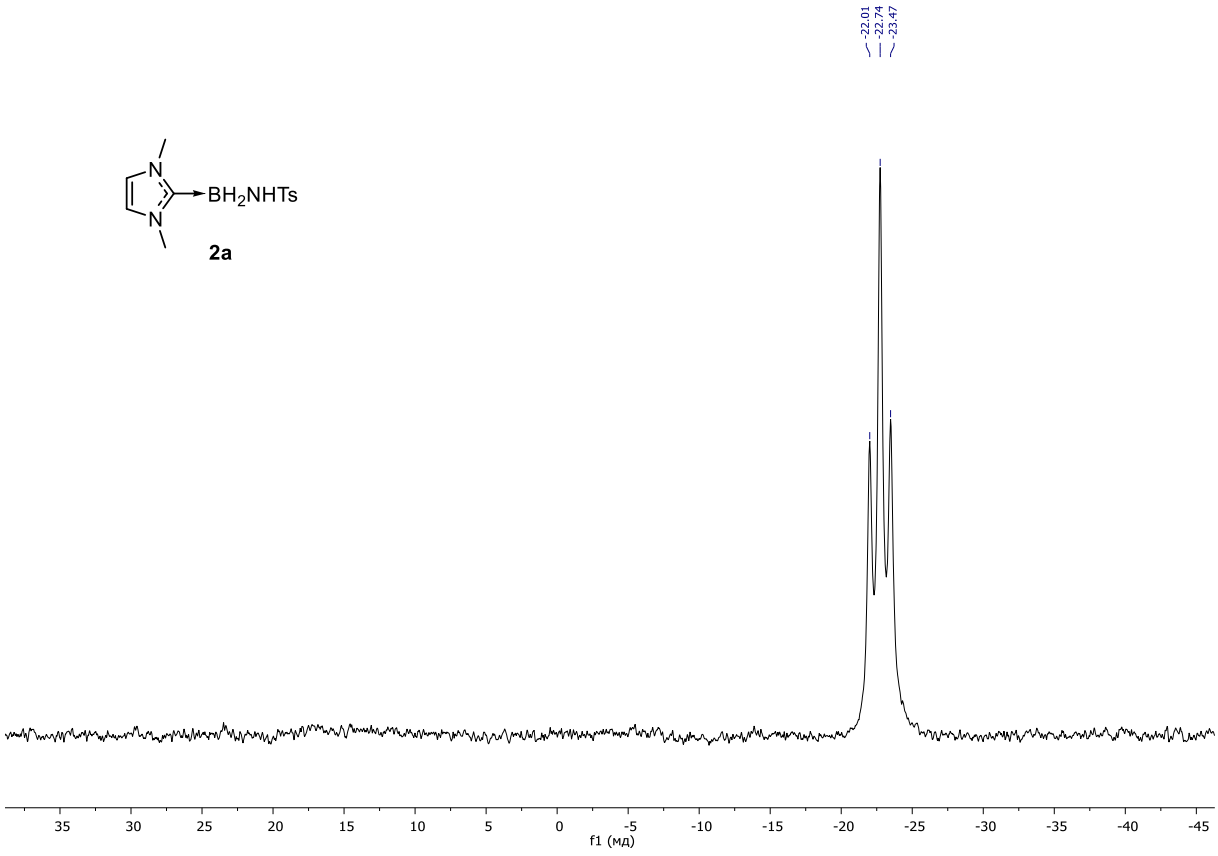


Fig. S92. ^{11}B NMR spectrum of **2a** in acetone-d_6.

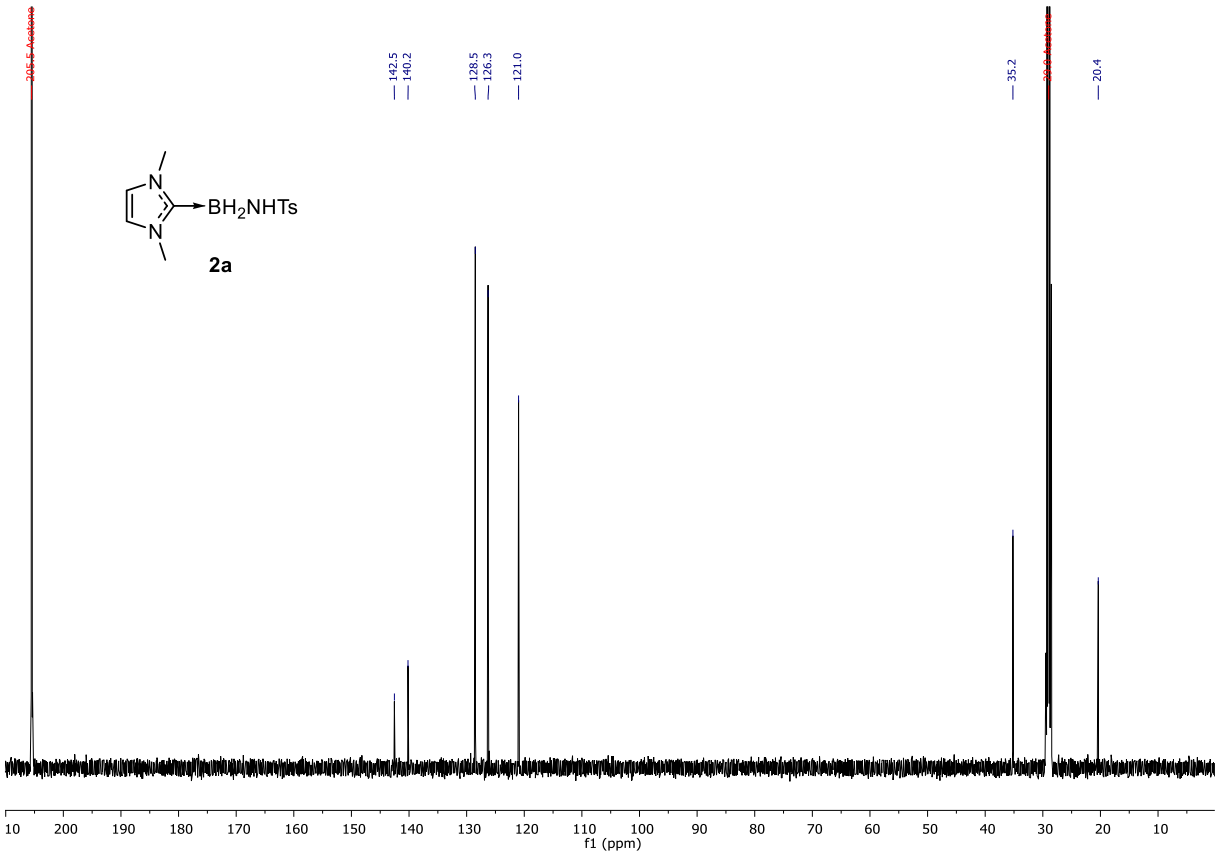


Fig. S93. ^{13}C NMR spectrum of **2a** in acetone-d_6.

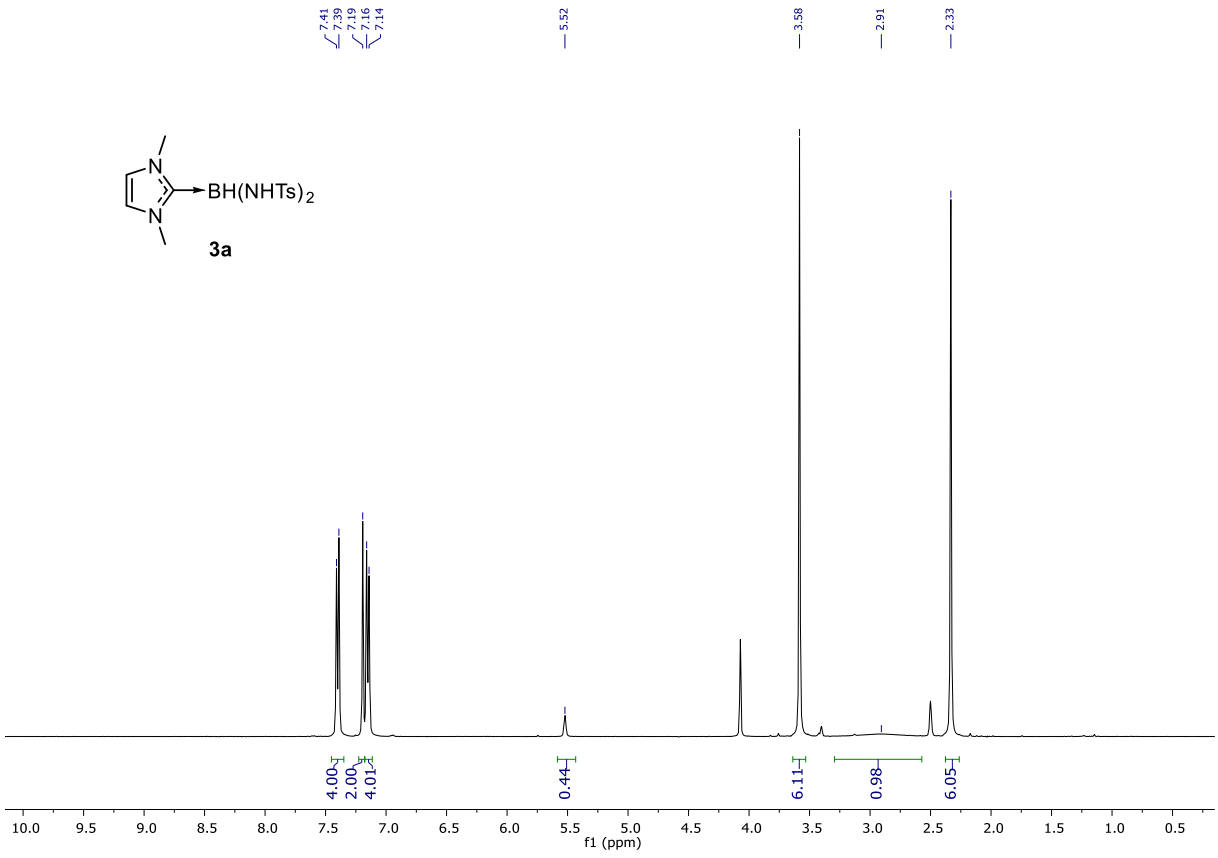


Fig. S94. ^{1}H NMR spectrum of **3a** in DMSO-d_6.

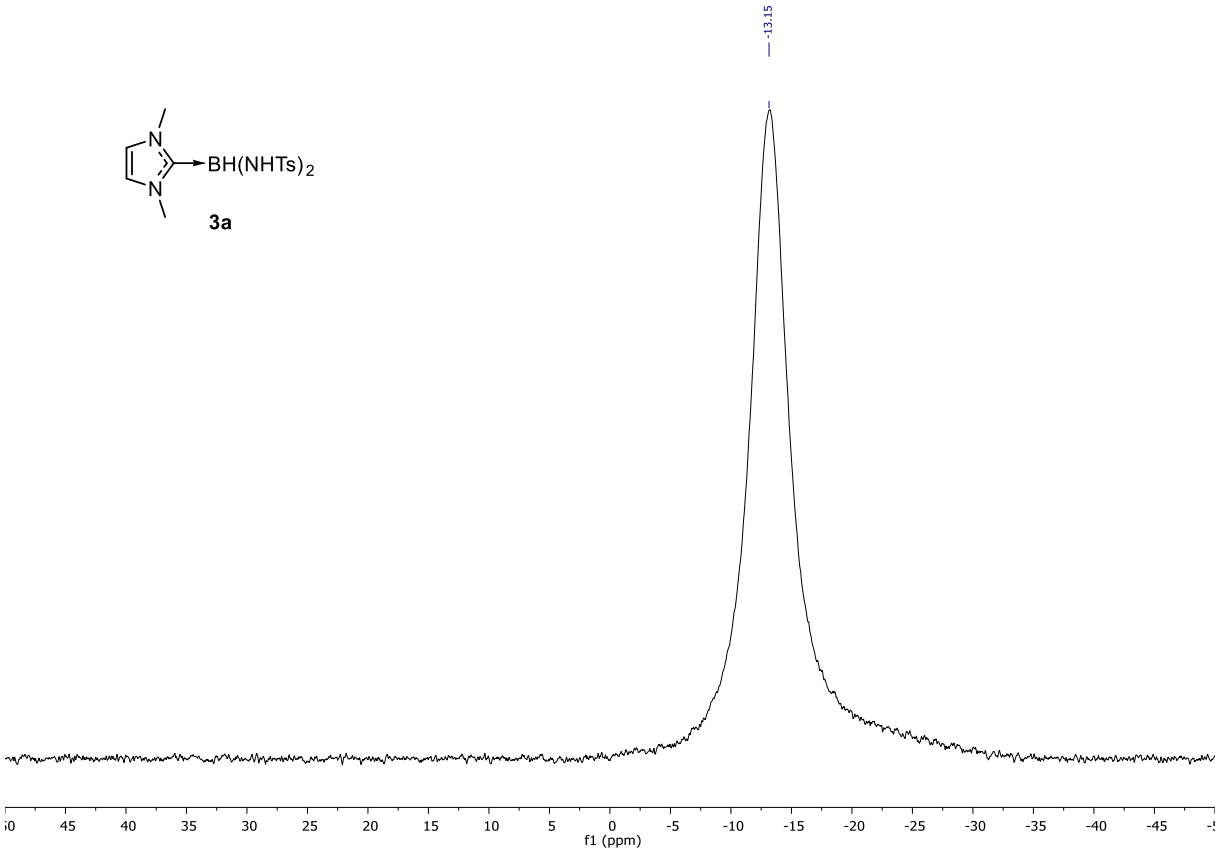


Fig. S95. ^{11}B NMR spectrum of **3a** in DMSO-d$_6$.

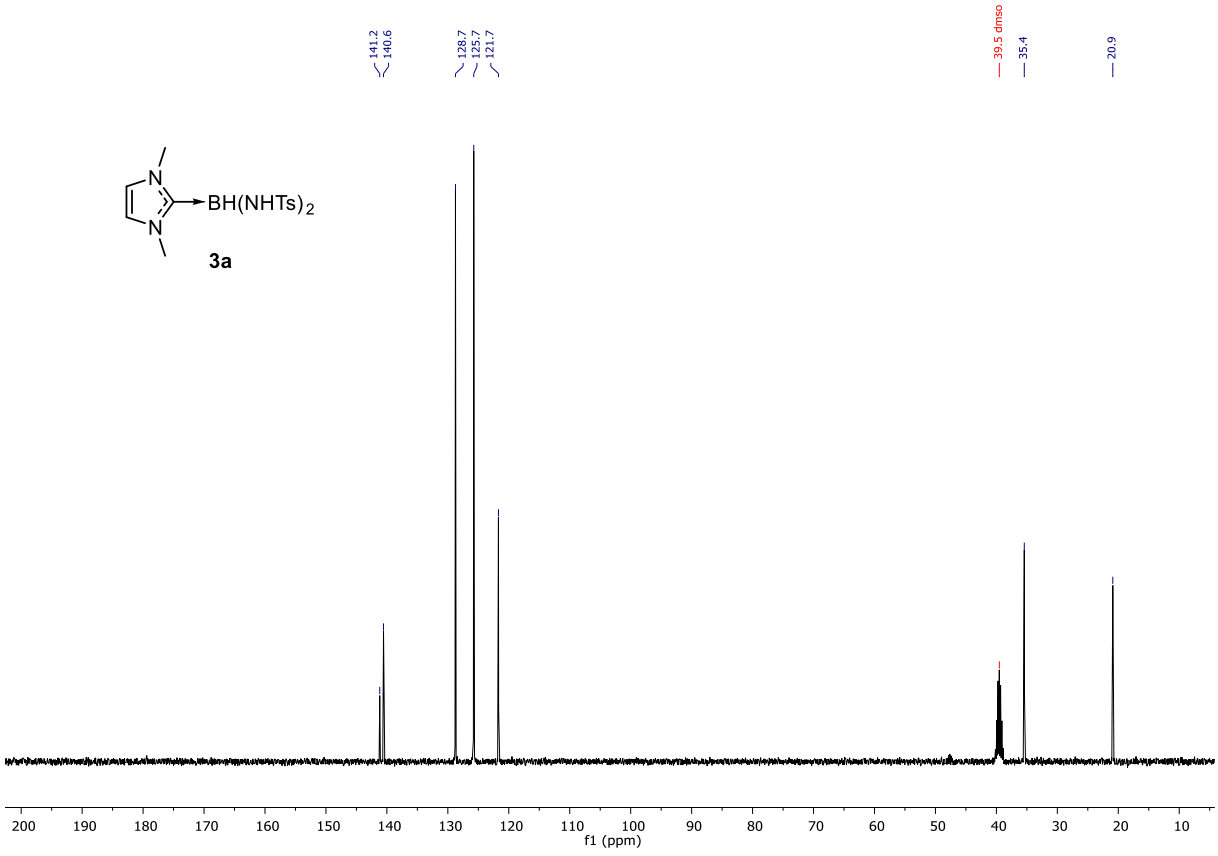


Fig. S96. ^{13}C NMR spectrum of **3a** in DMSO-d$_6$.

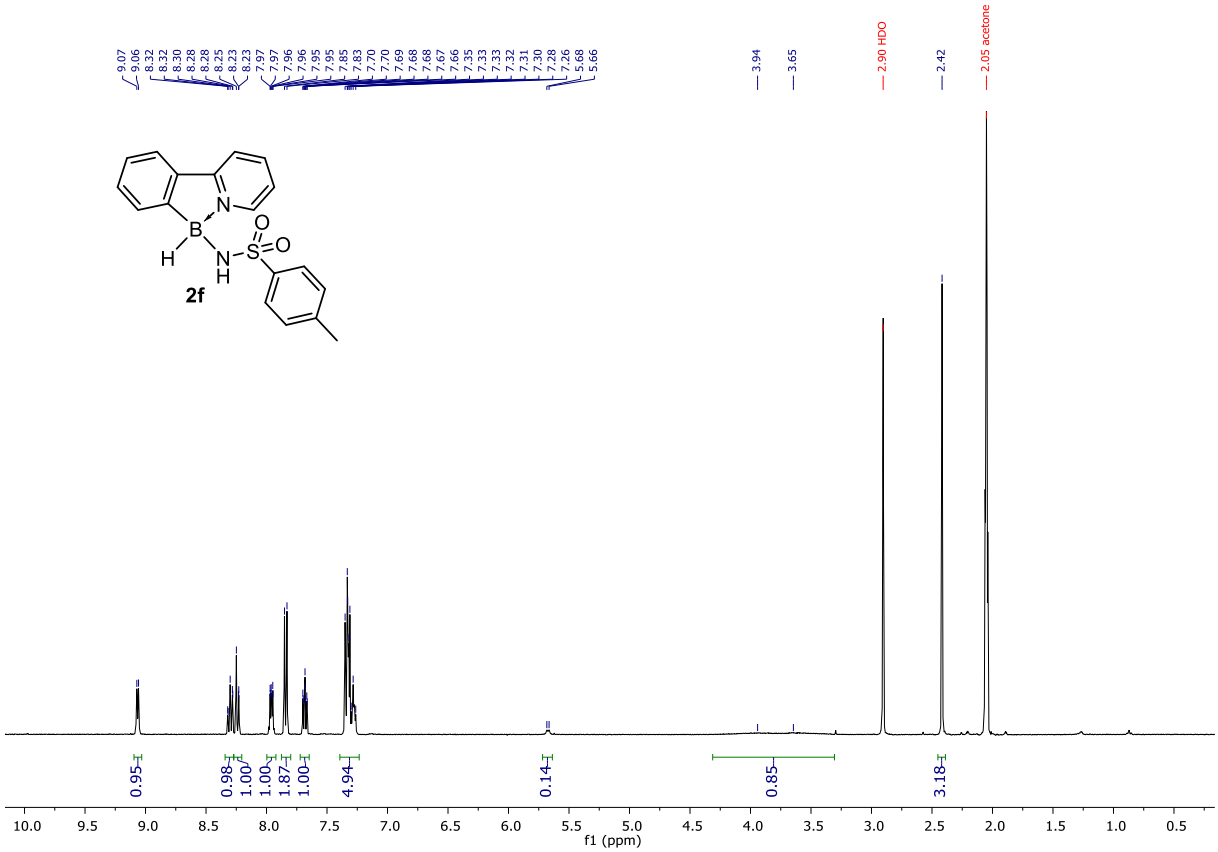


Fig. S97. ^{1}H NMR spectrum of **2f** in acetone-d_6.

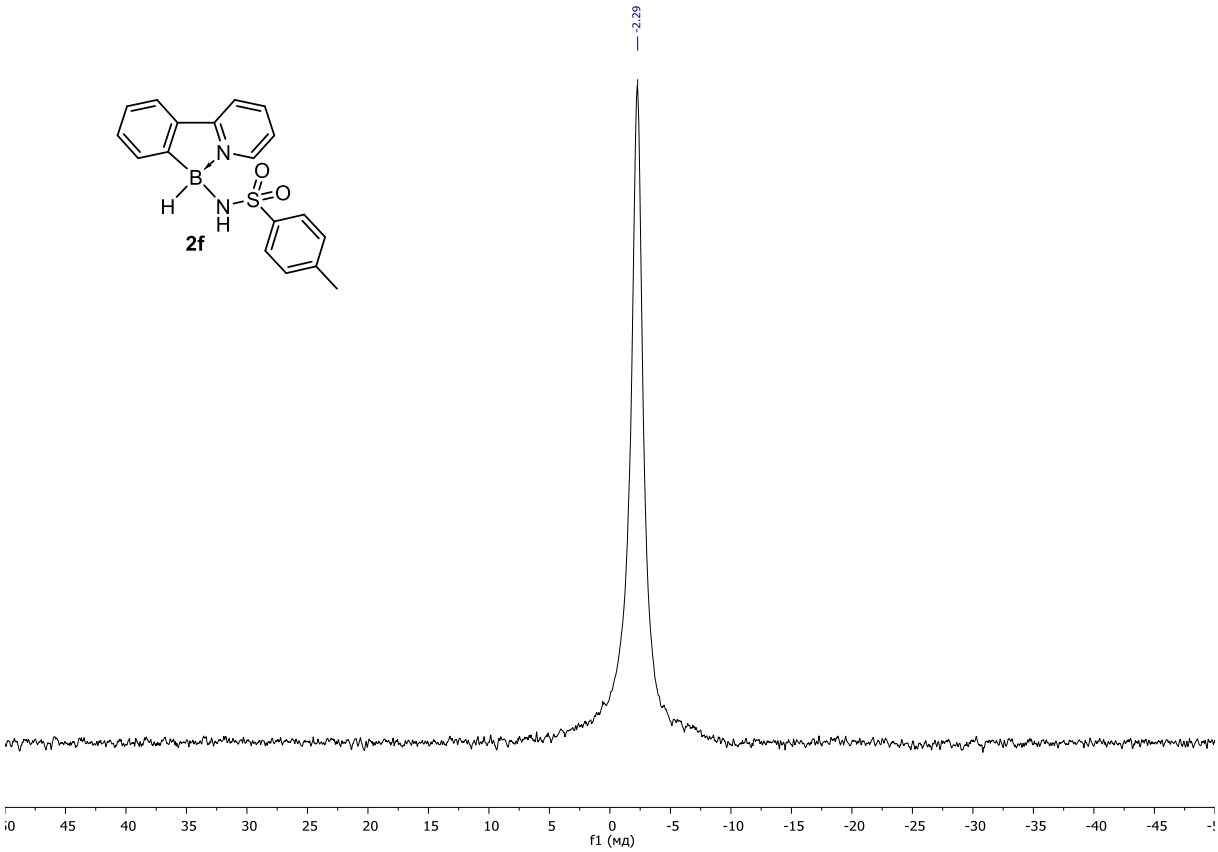


Fig. S98. ^{11}B NMR spectrum of **2f** in acetone-d_6.

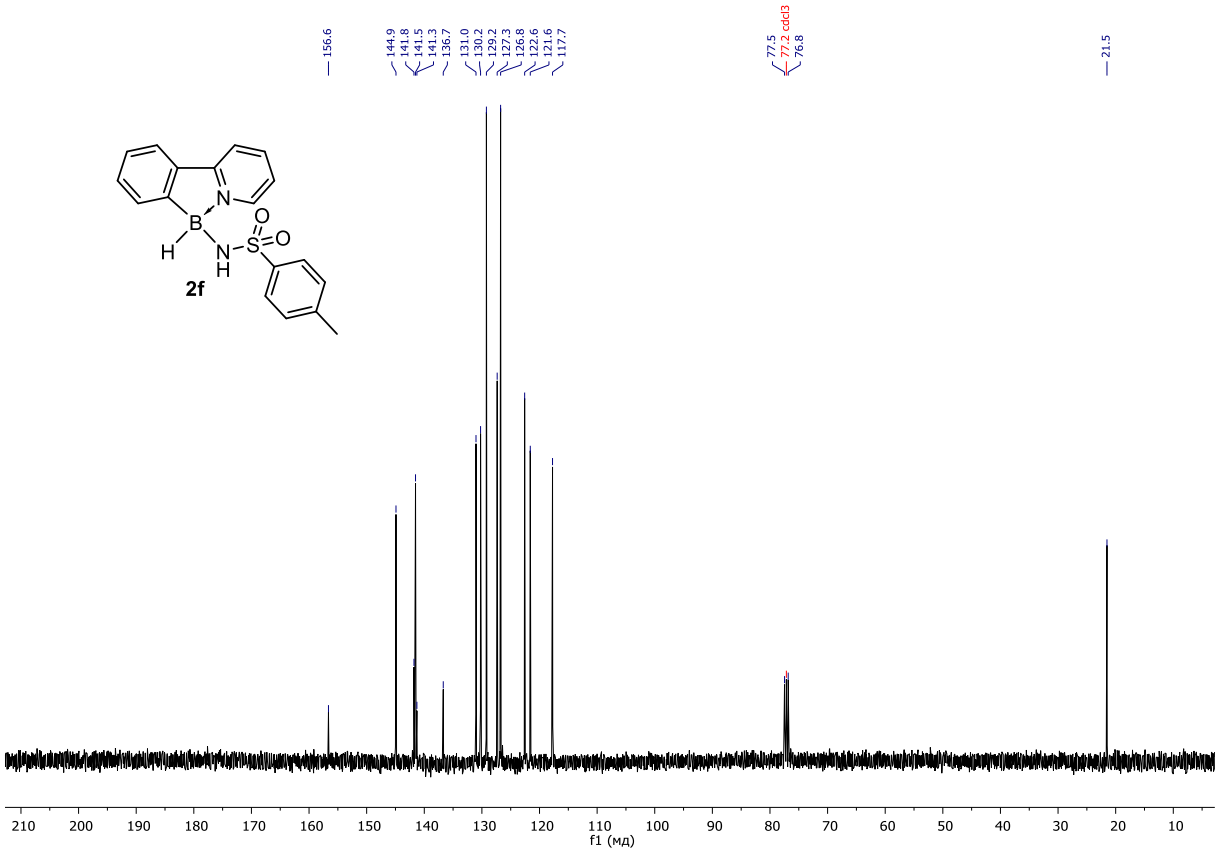


Fig. S99. ^{13}C NMR spectrum of **2f** in $CDCl_3$.

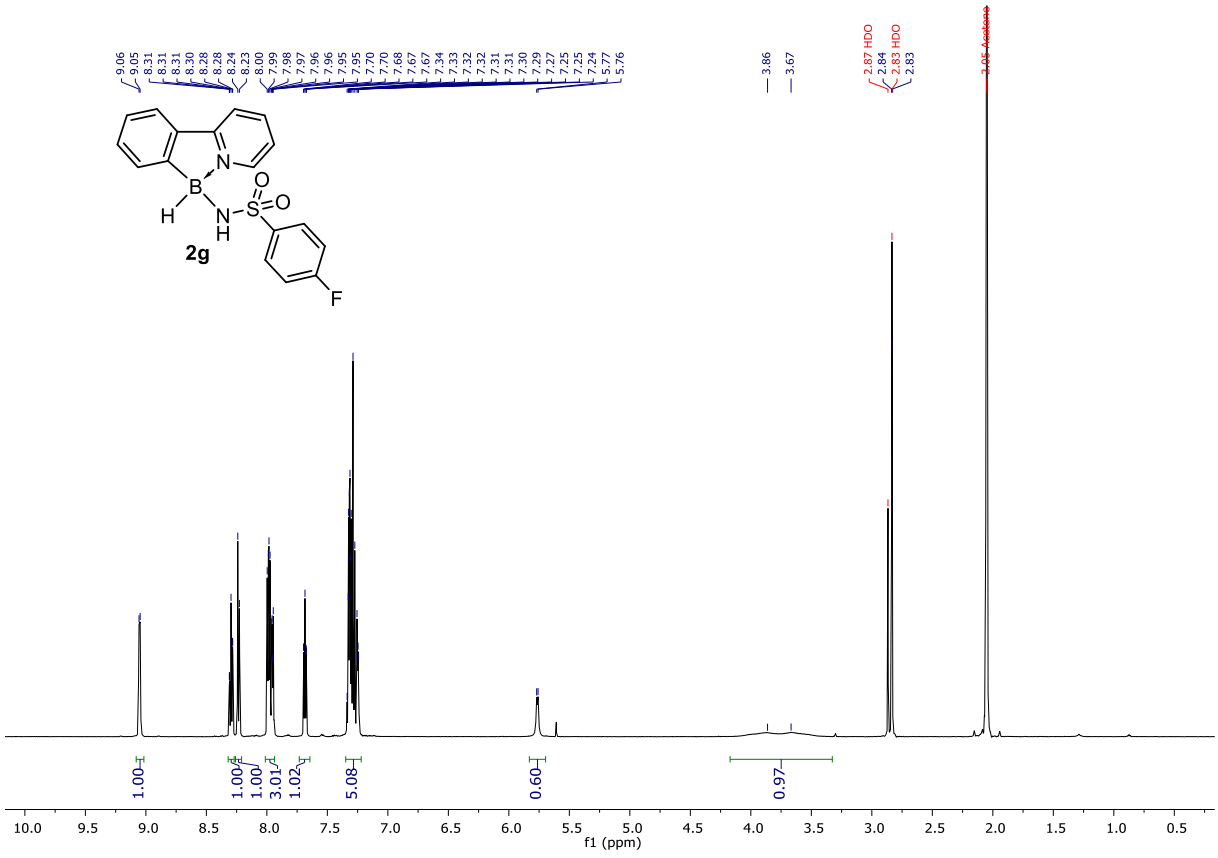


Fig. S100. ^{1}H NMR spectrum of **2g** in acetone-d_6.

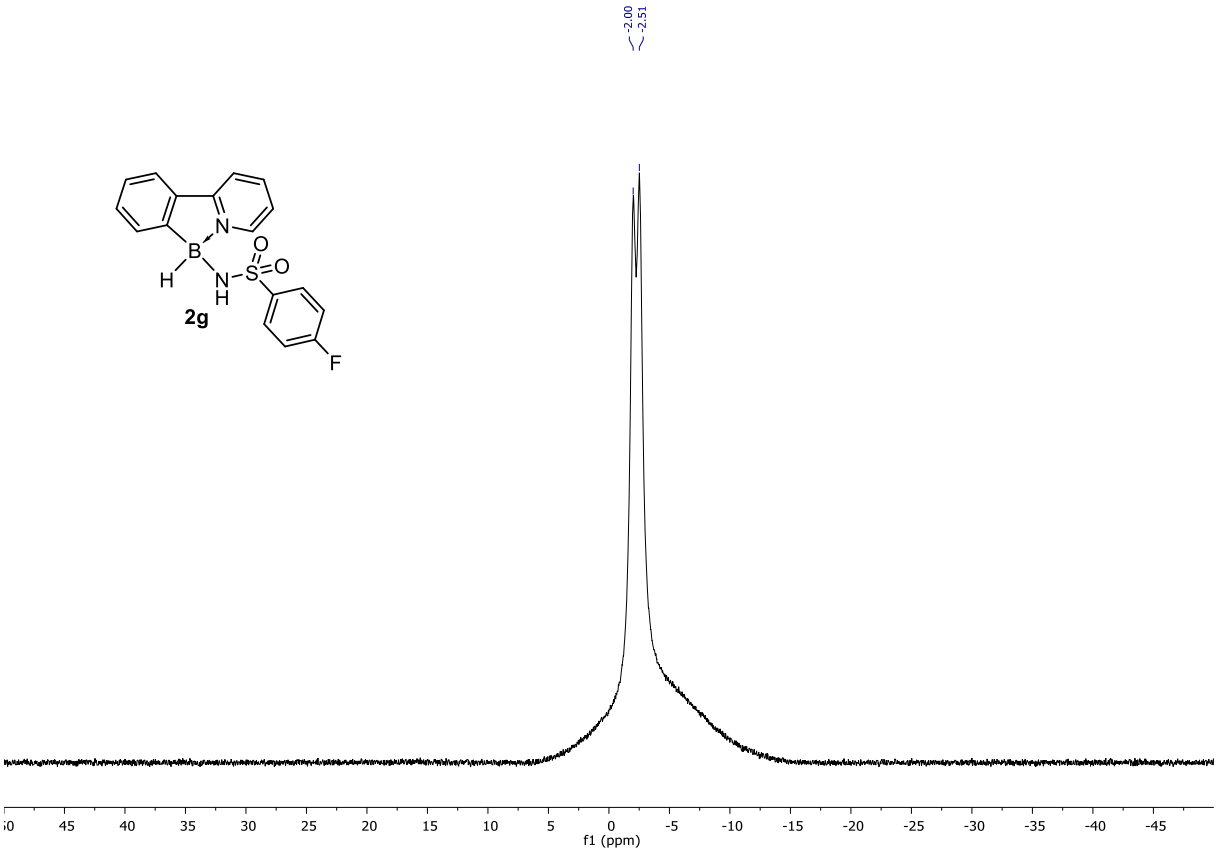


Fig. S101. ^{11}B NMR spectrum of **2g** in acetone-d_6.

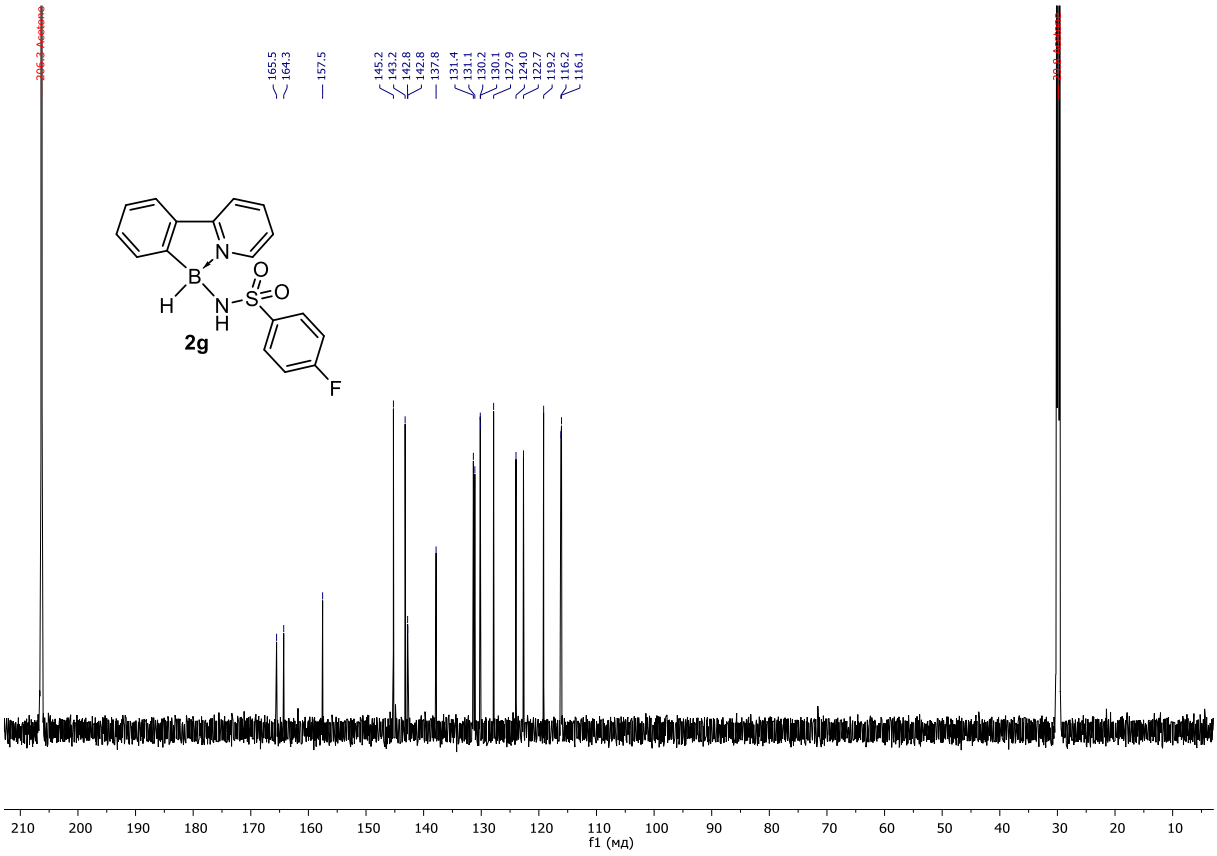


Fig. S102. ^{13}C NMR spectrum of **2g** in acetone-d_6.

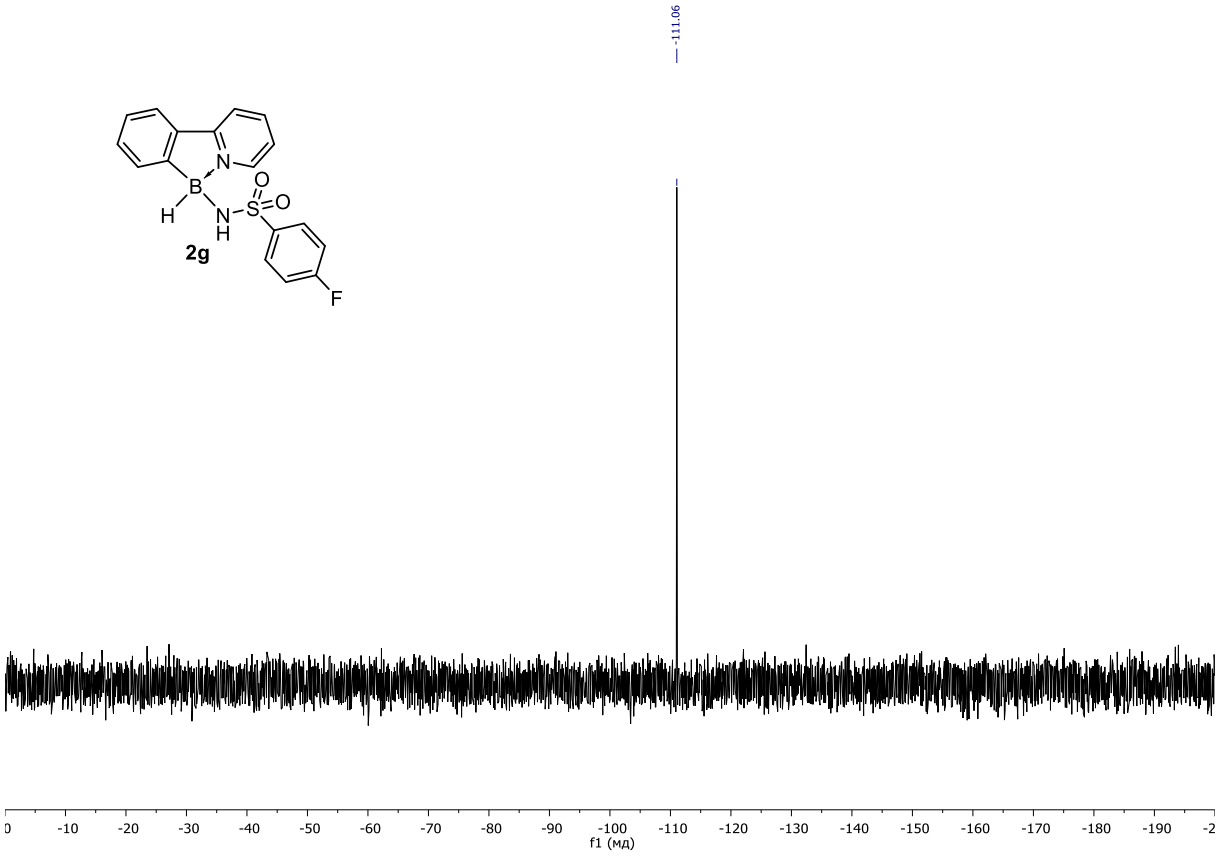


Fig. S103. ^{19}F NMR spectrum of **2g** in acetone-d_6.

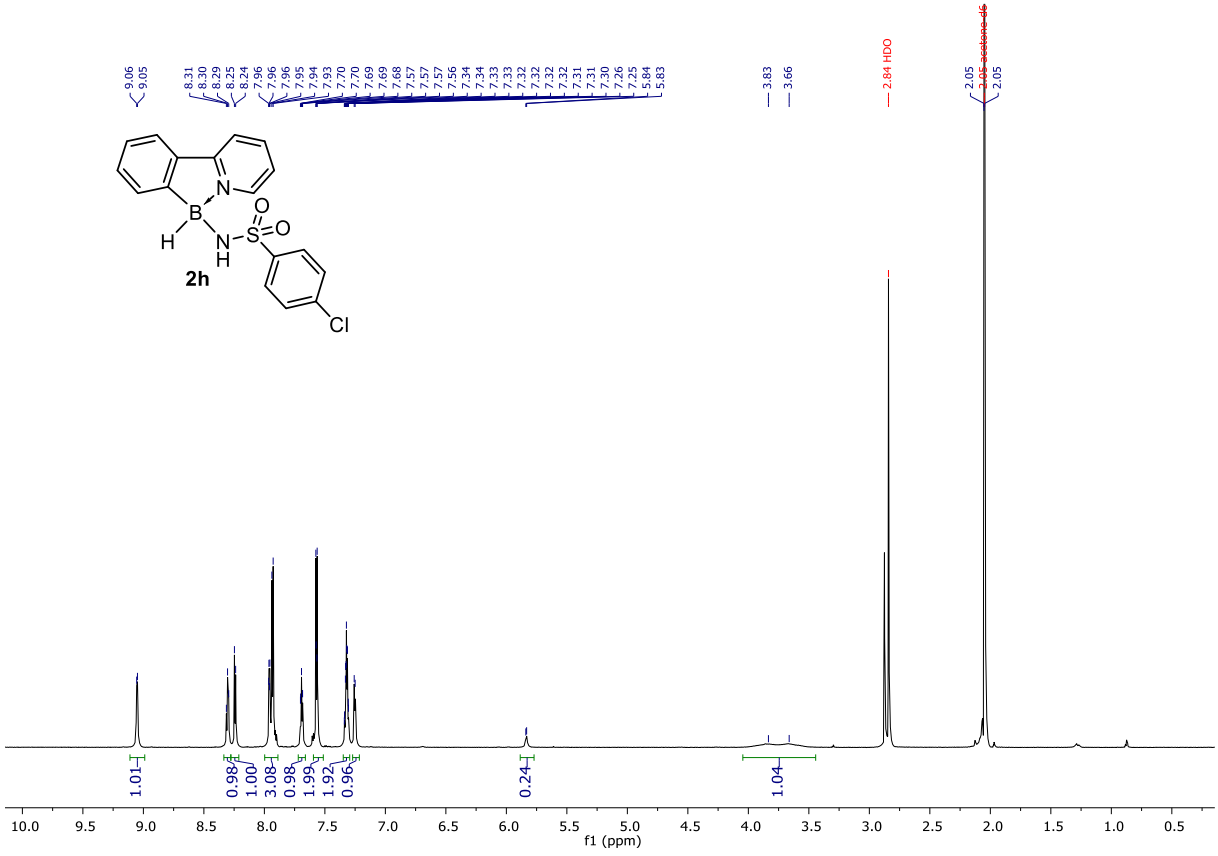


Fig. S104. ^{1}H NMR spectrum of **2h** in acetone-d_6.

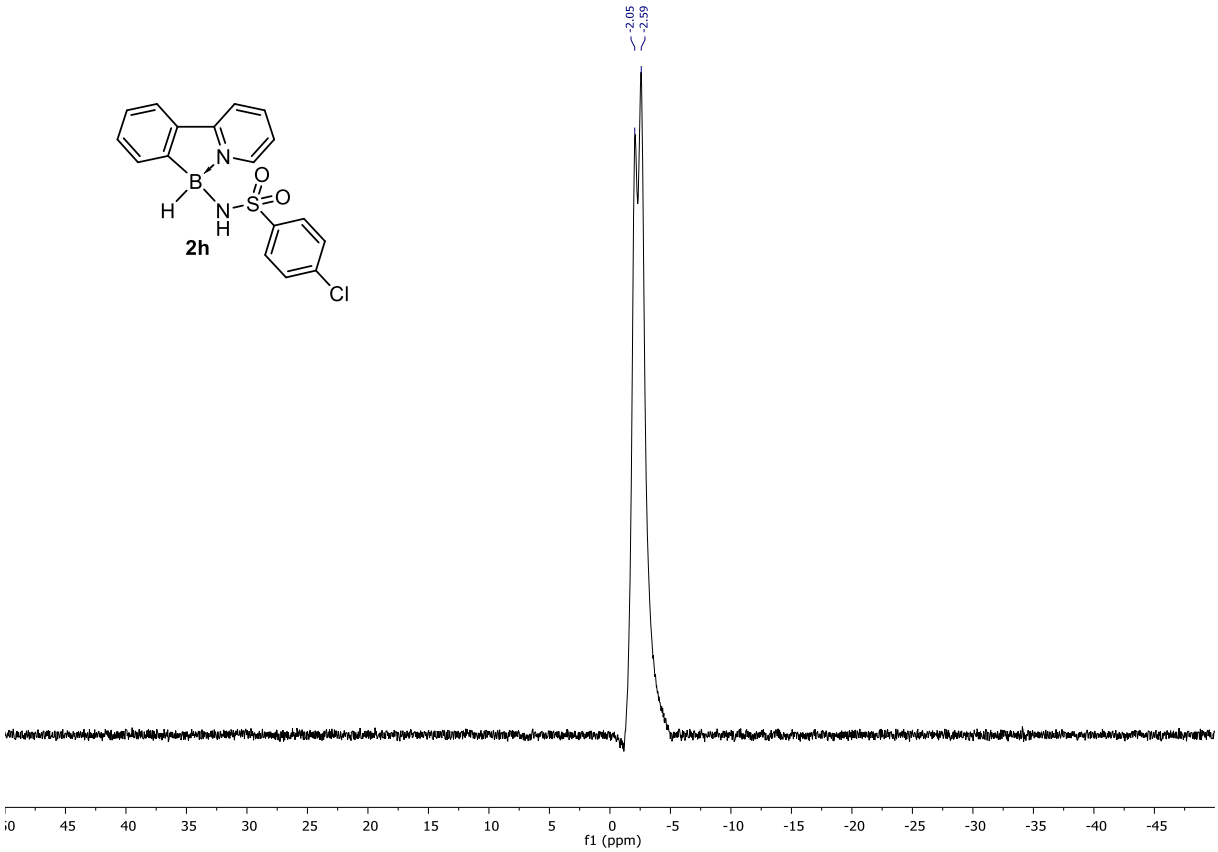


Fig. S105. ^{11}B NMR spectrum of **2h** in acetone-d_6.

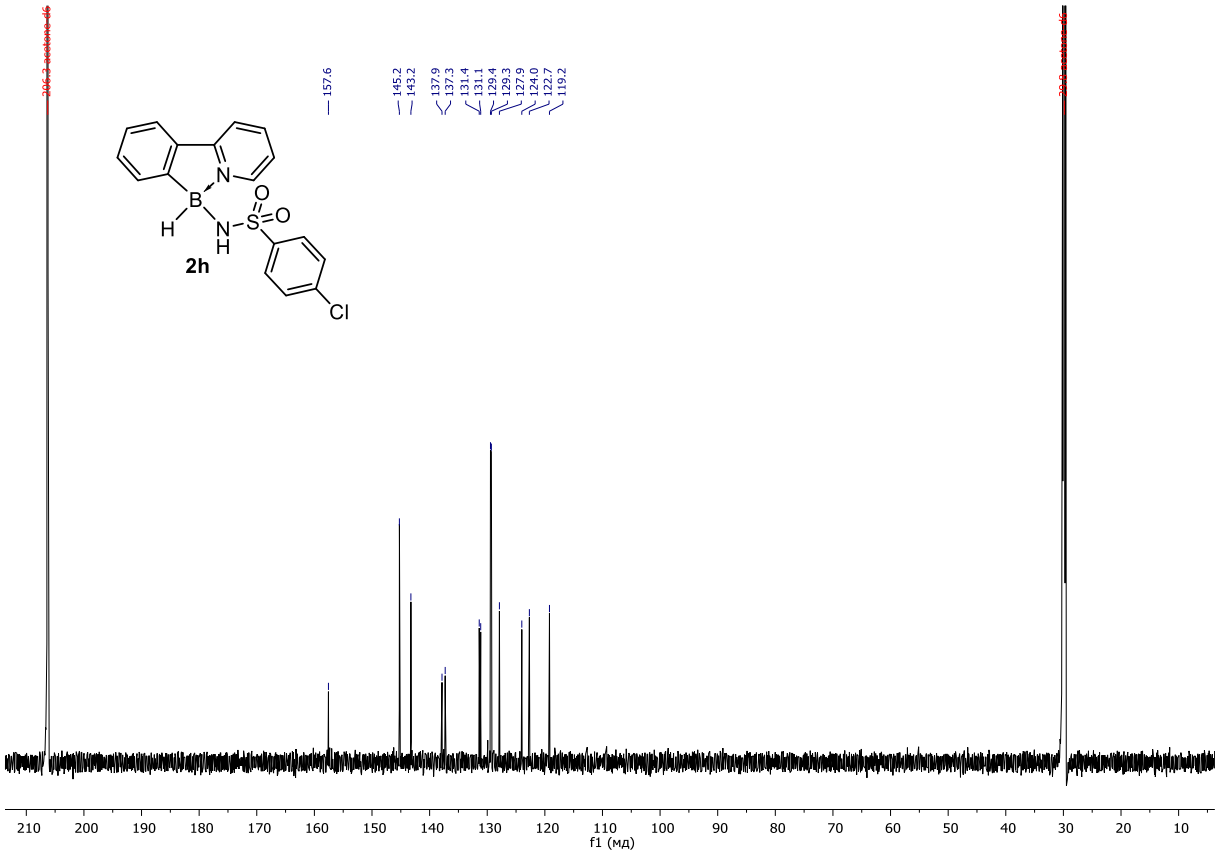


Fig. S106. ^{13}C NMR spectrum of **2h** in acetone-d_6.

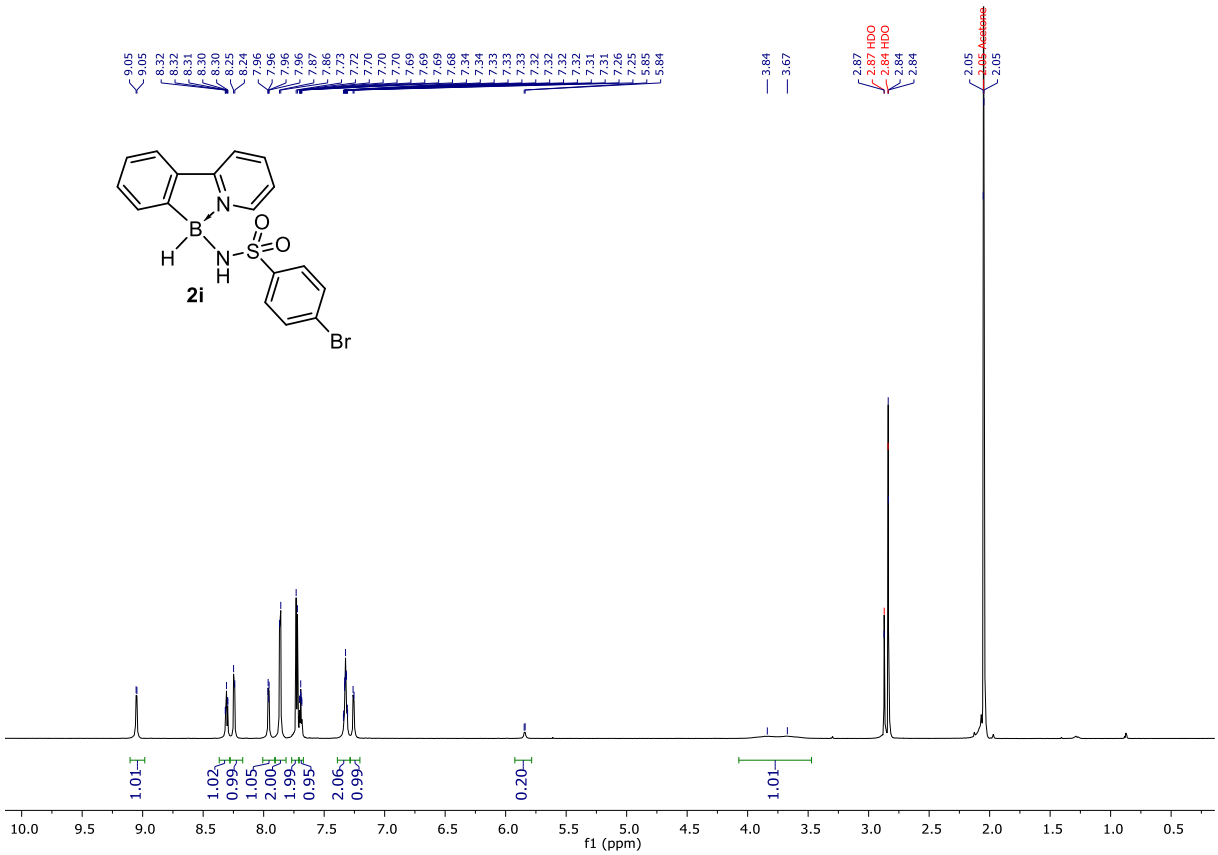


Fig. S107. ^{1}H NMR spectrum of **2i** in acetone-d_6.

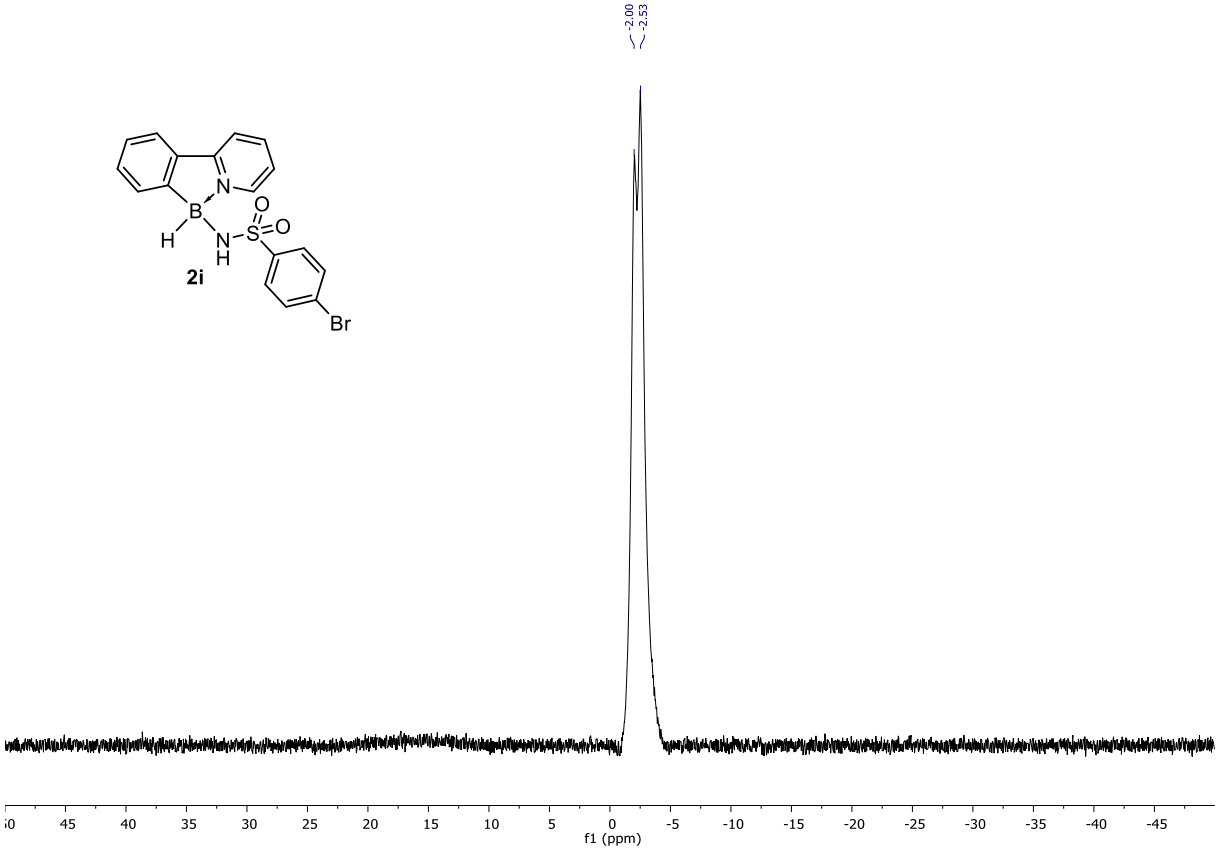


Fig. S108. ^{11}B NMR spectrum of **2i** in acetone-d_6.

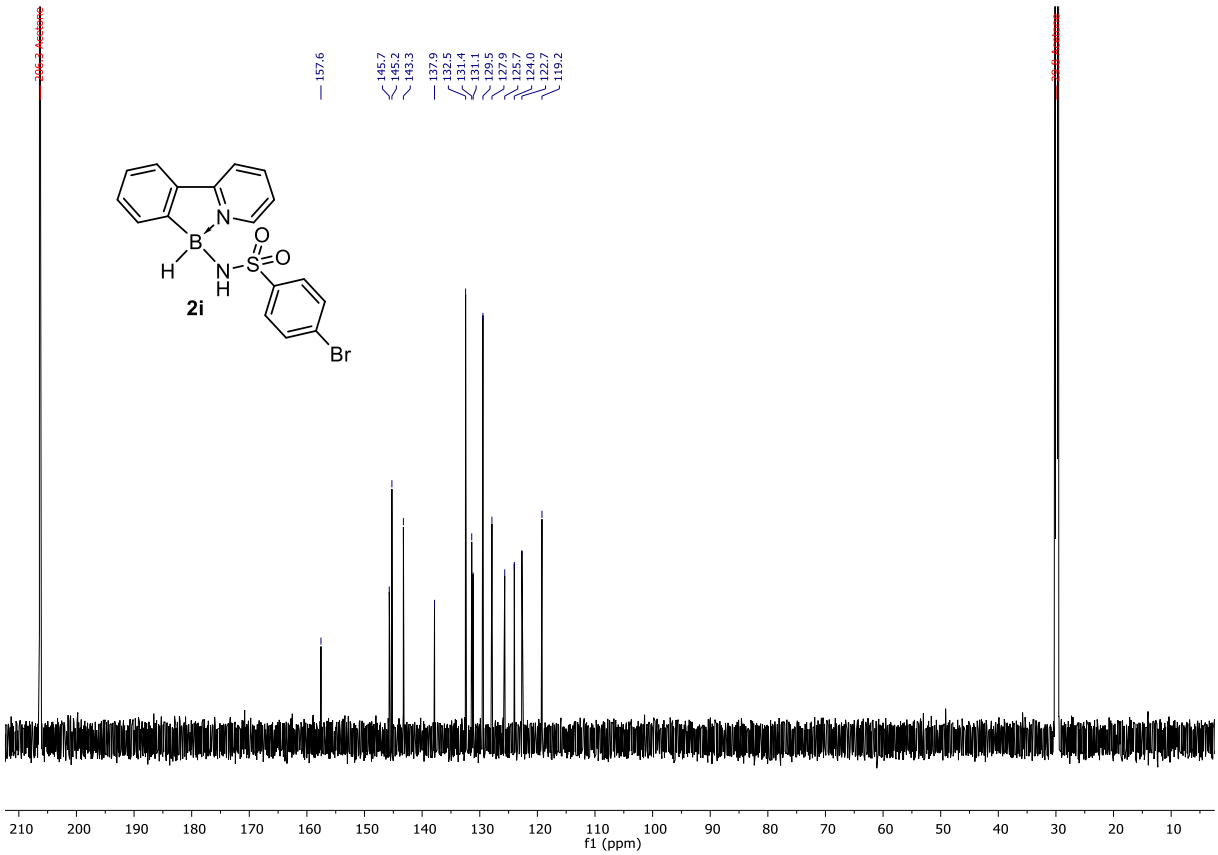


Fig. S109. ^{13}C NMR spectrum of **2i** in acetone-d_6.

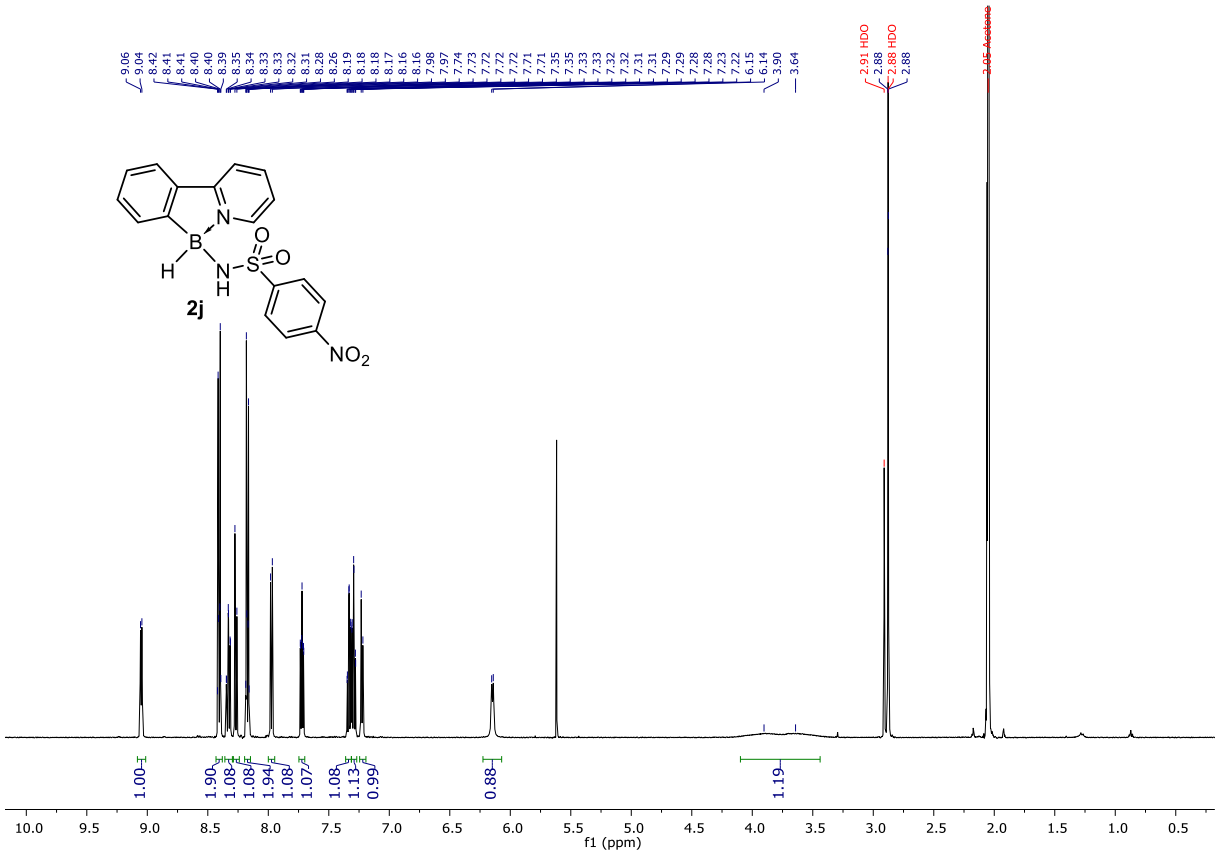


Fig. S110. ^{1}H NMR spectrum of **2j** in acetone-d_6.

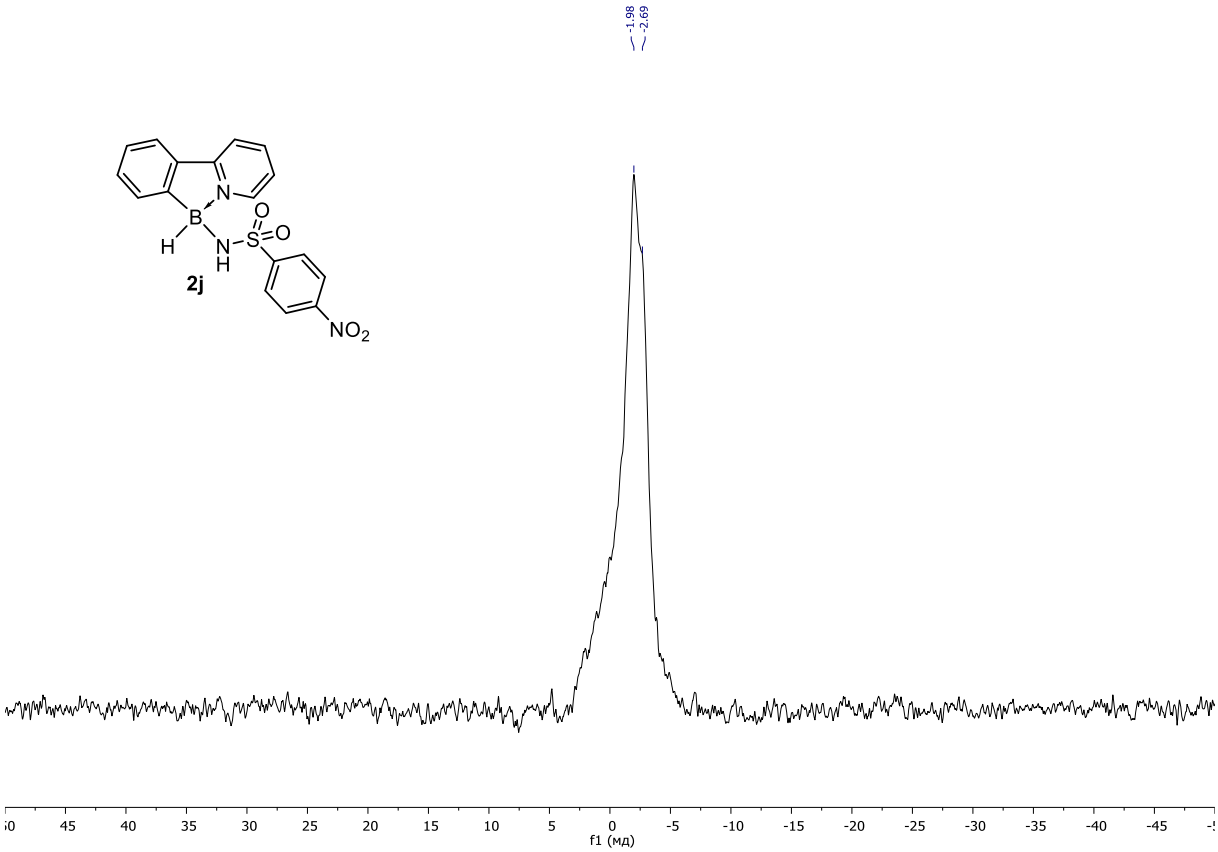


Fig. S111. ^{11}B NMR spectrum of **2j** in acetone-d_6.

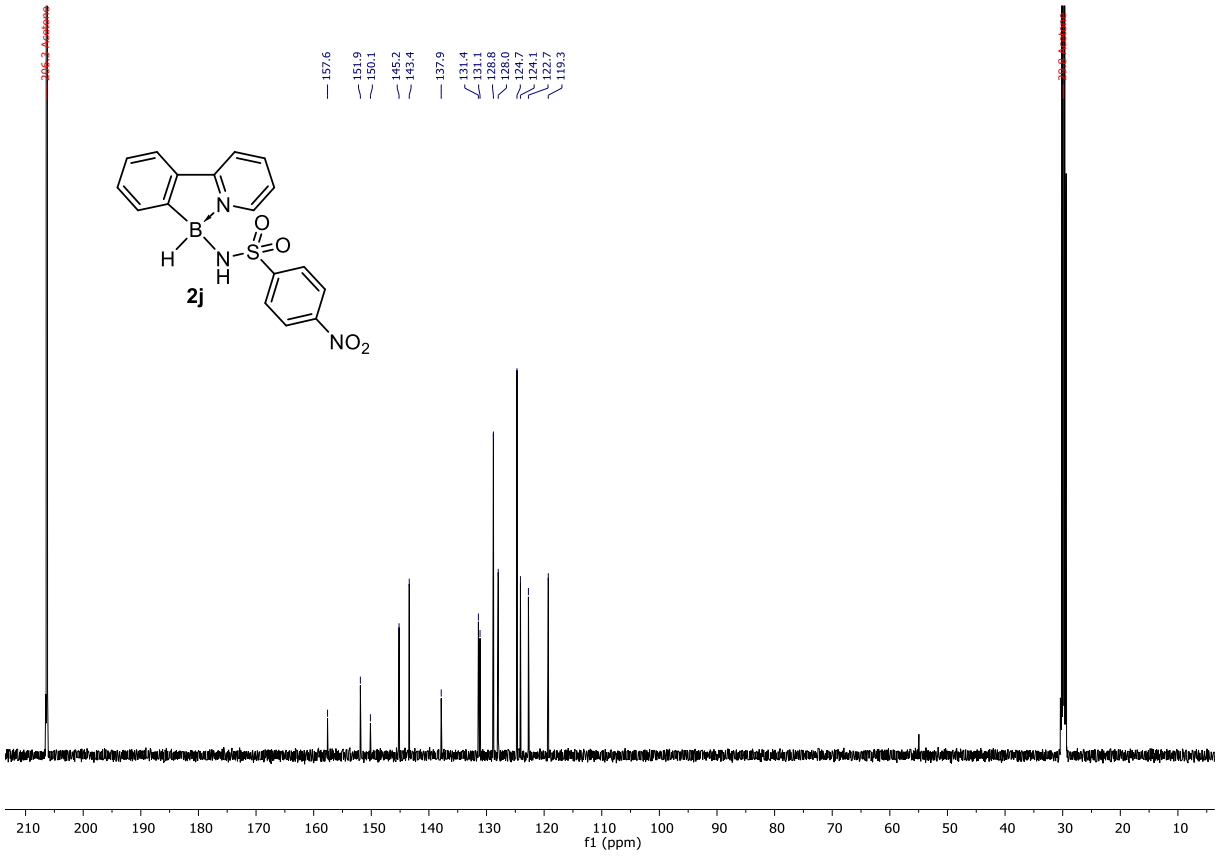


Fig. S112. ^{13}C NMR spectrum of **2j** in acetone-d_6.

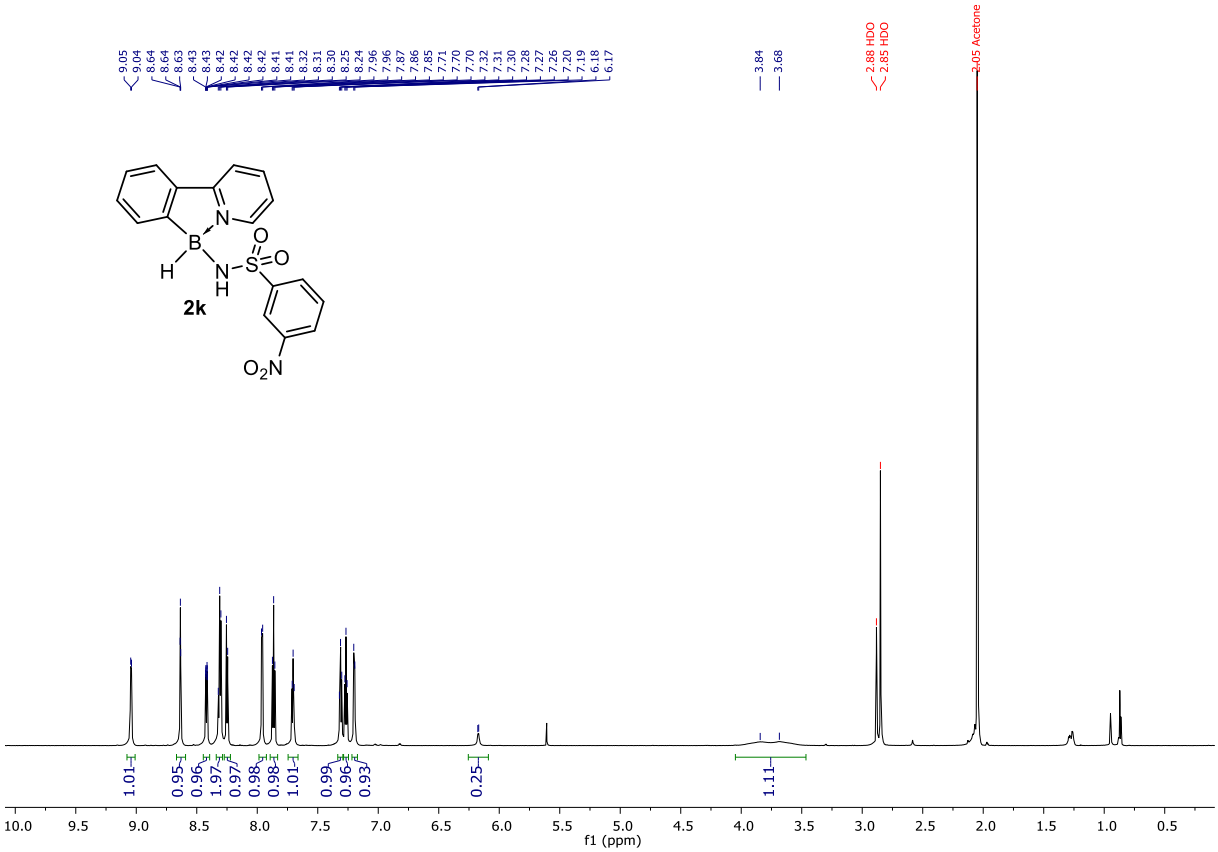


Fig. S113. ^{1}H NMR spectrum of **2k** in acetone-d_6.

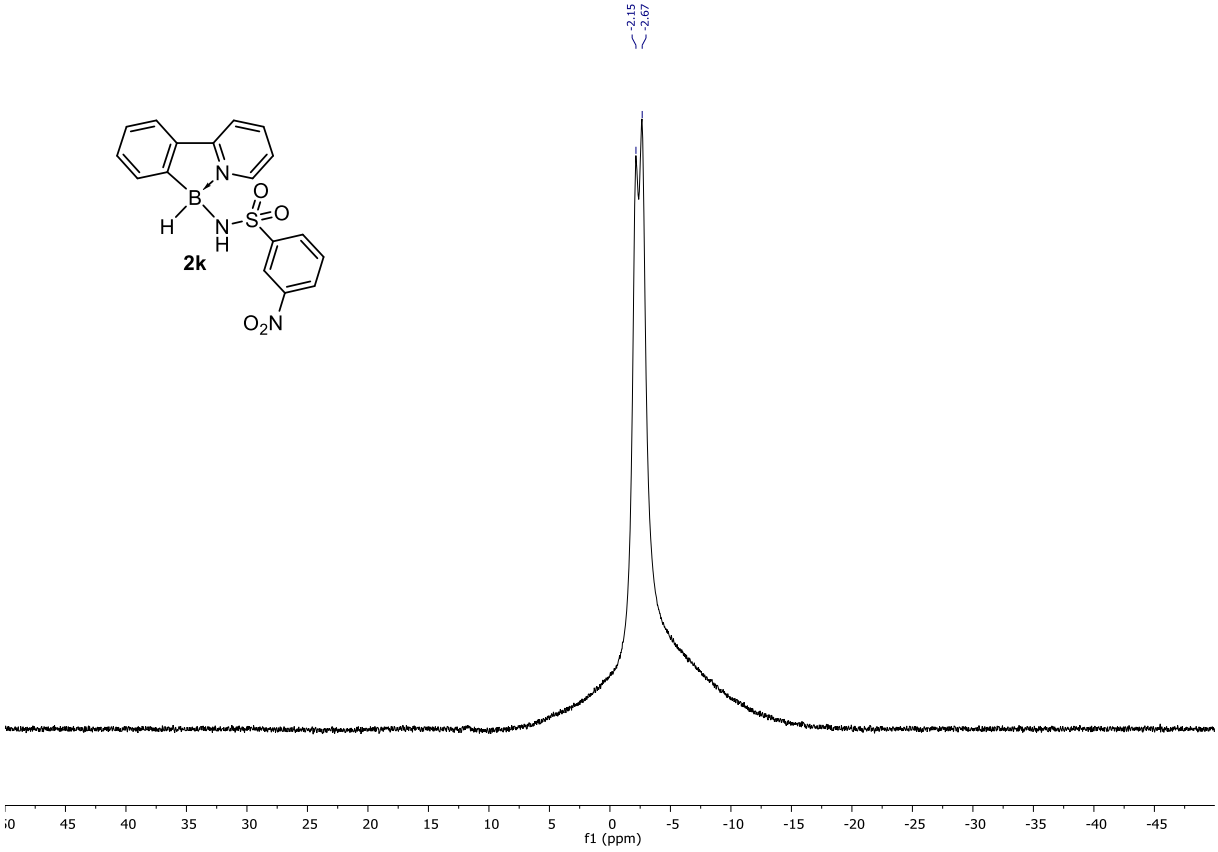


Fig. S114. ^{11}B NMR spectrum of **2k** in acetone-d_6.

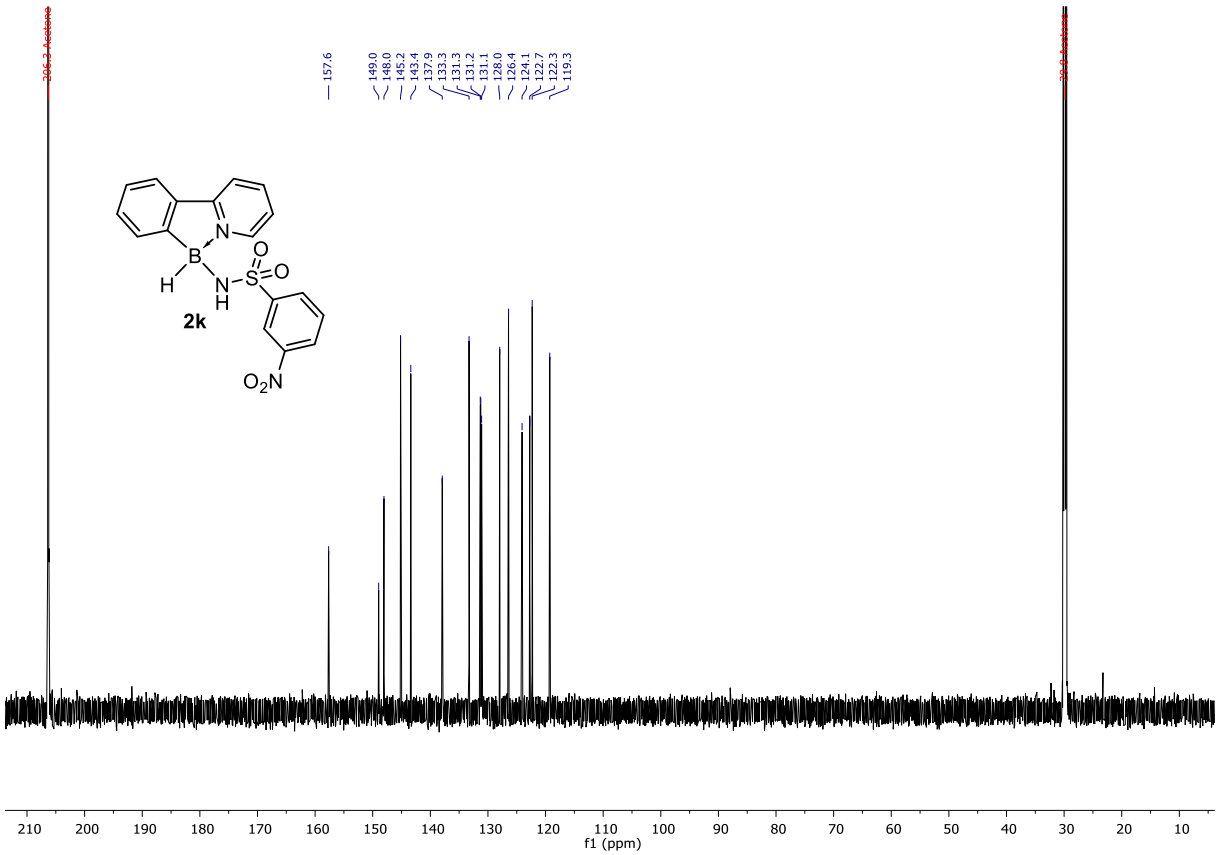


Fig. S115. ^{13}C NMR spectrum of **2k** in acetone-d$_6$.

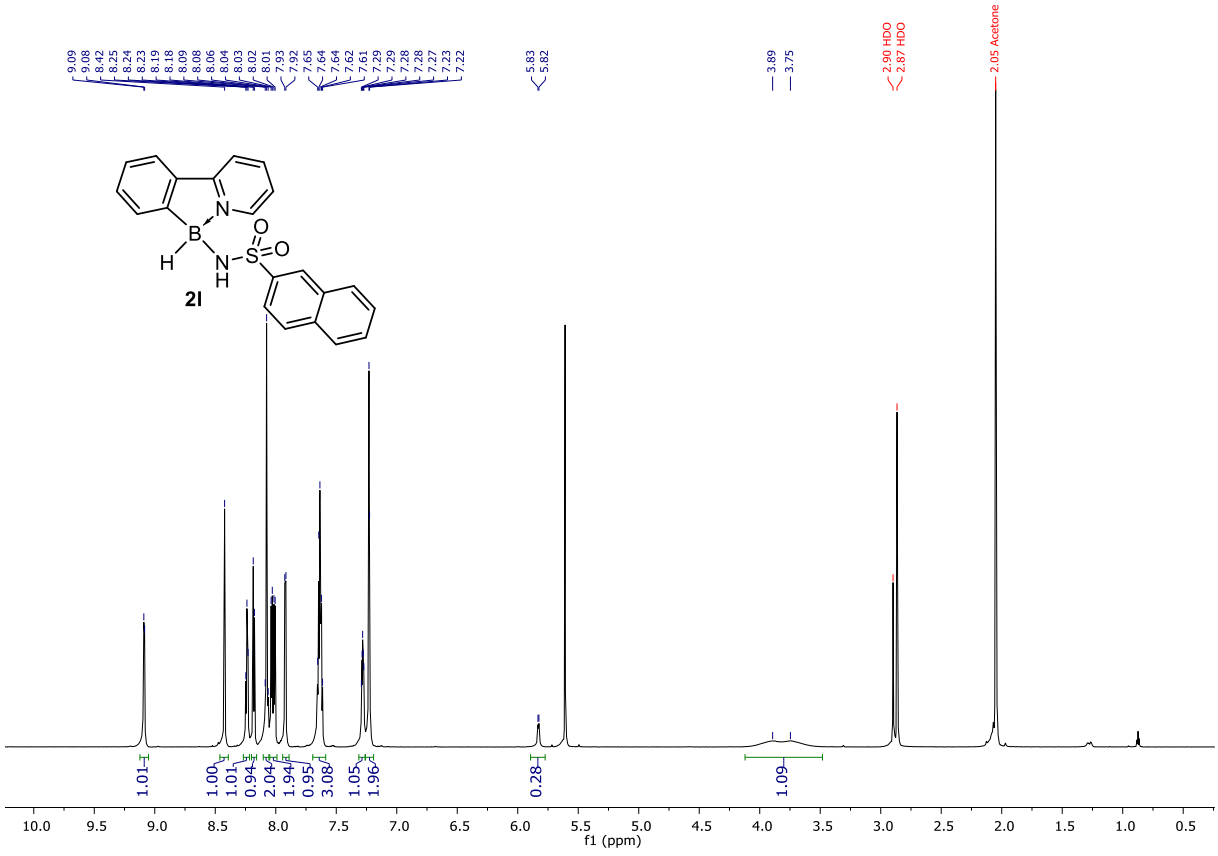


Fig. S116. ^{1}H NMR spectrum of **2l** in acetone-d$_6$.

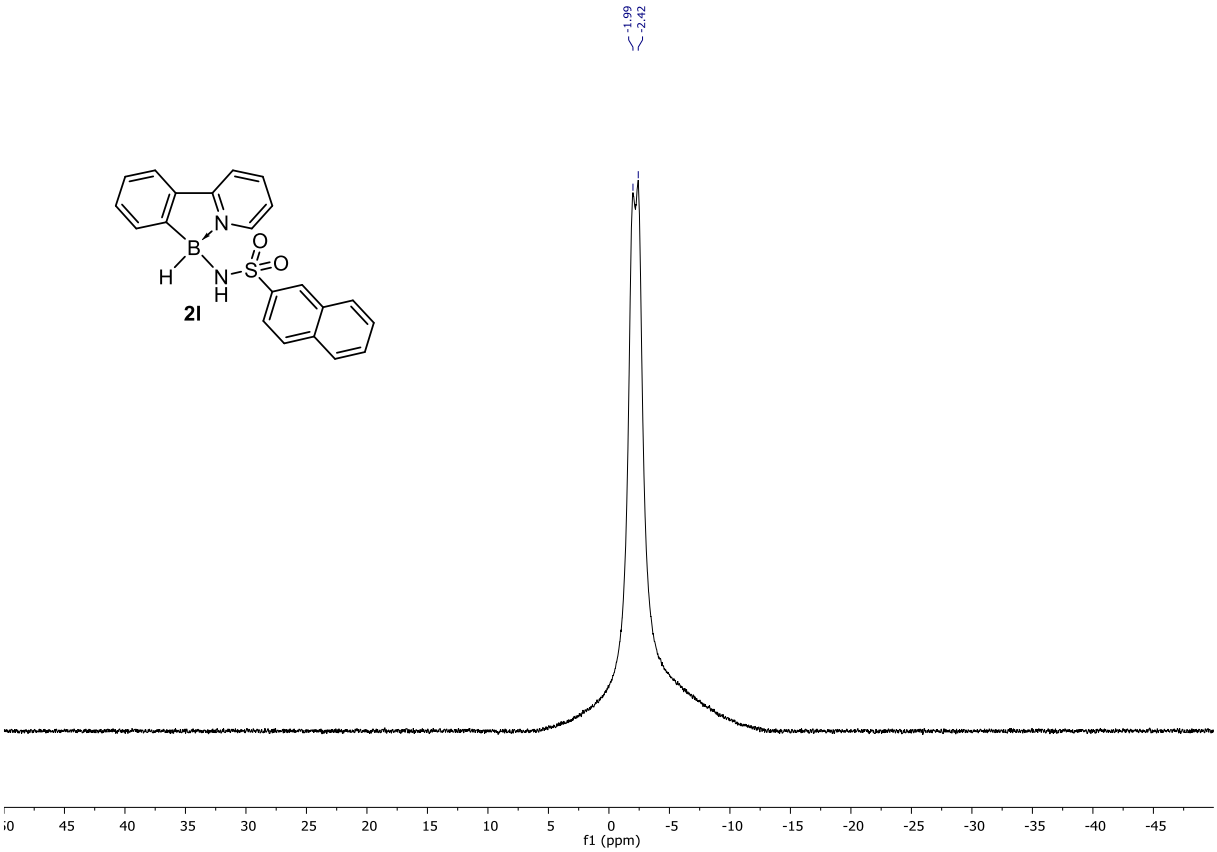


Fig. S117. ^{11}B NMR spectrum of **2l** in acetone-d_6.

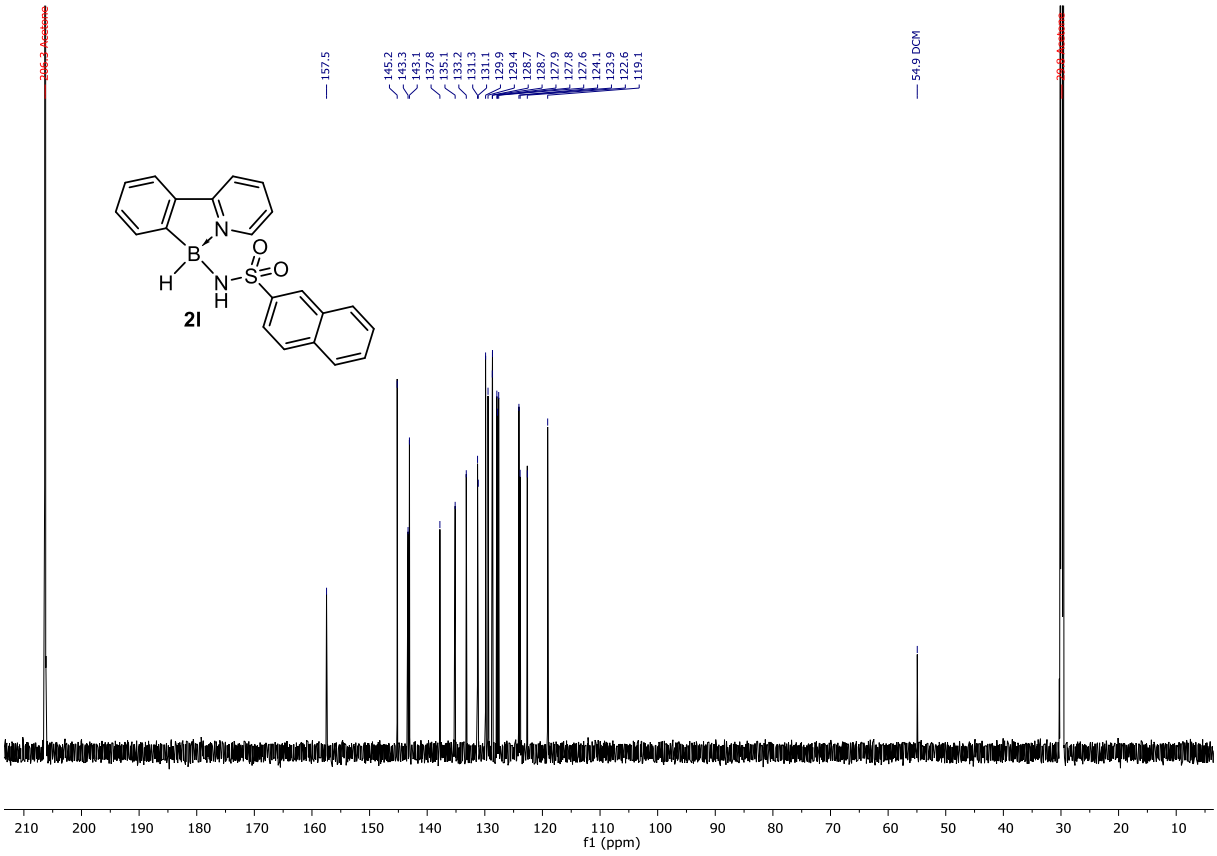


Fig. S118. ^{13}C NMR spectrum of **2l** in acetone-d_6.

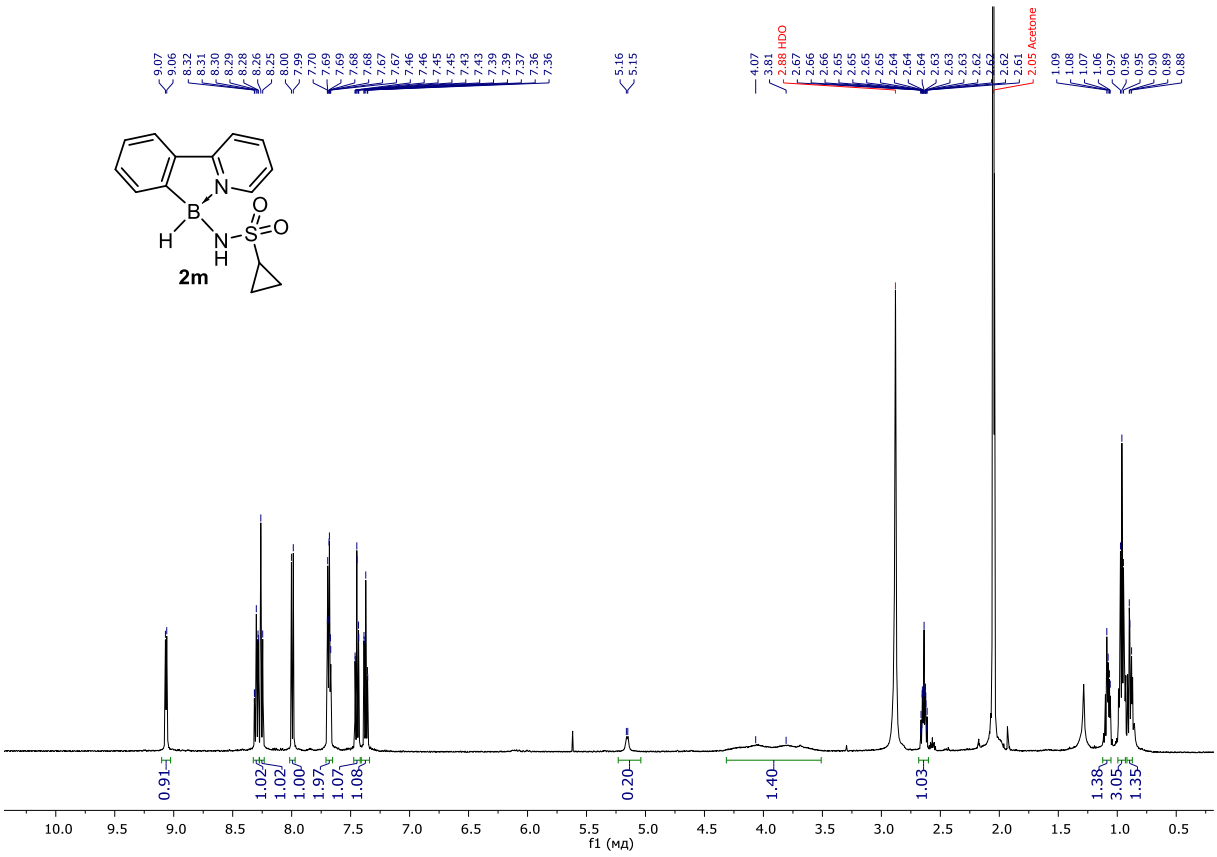


Fig. S119. ^{1}H NMR spectrum of **2m** in acetone-d_6.

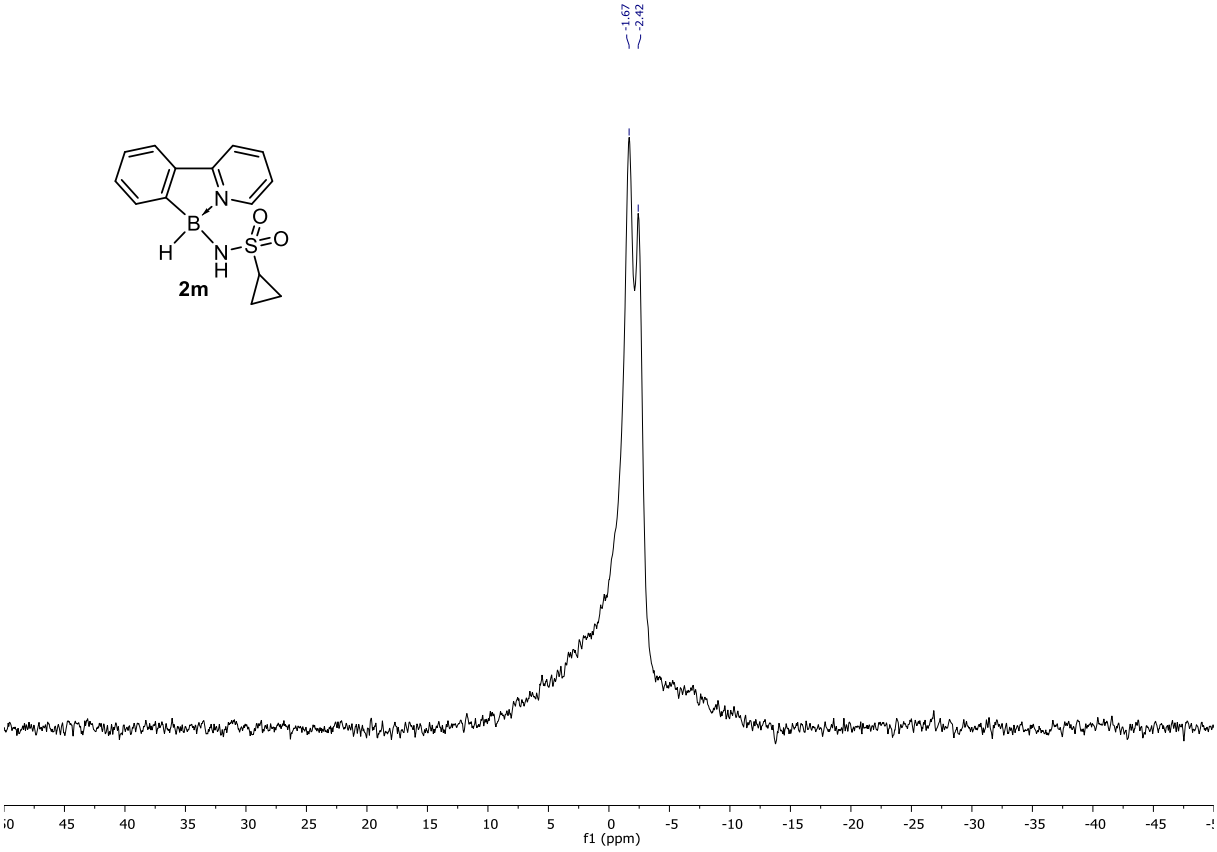


Fig. S120. ^{11}B NMR spectrum of **2m** in acetone-d_6.

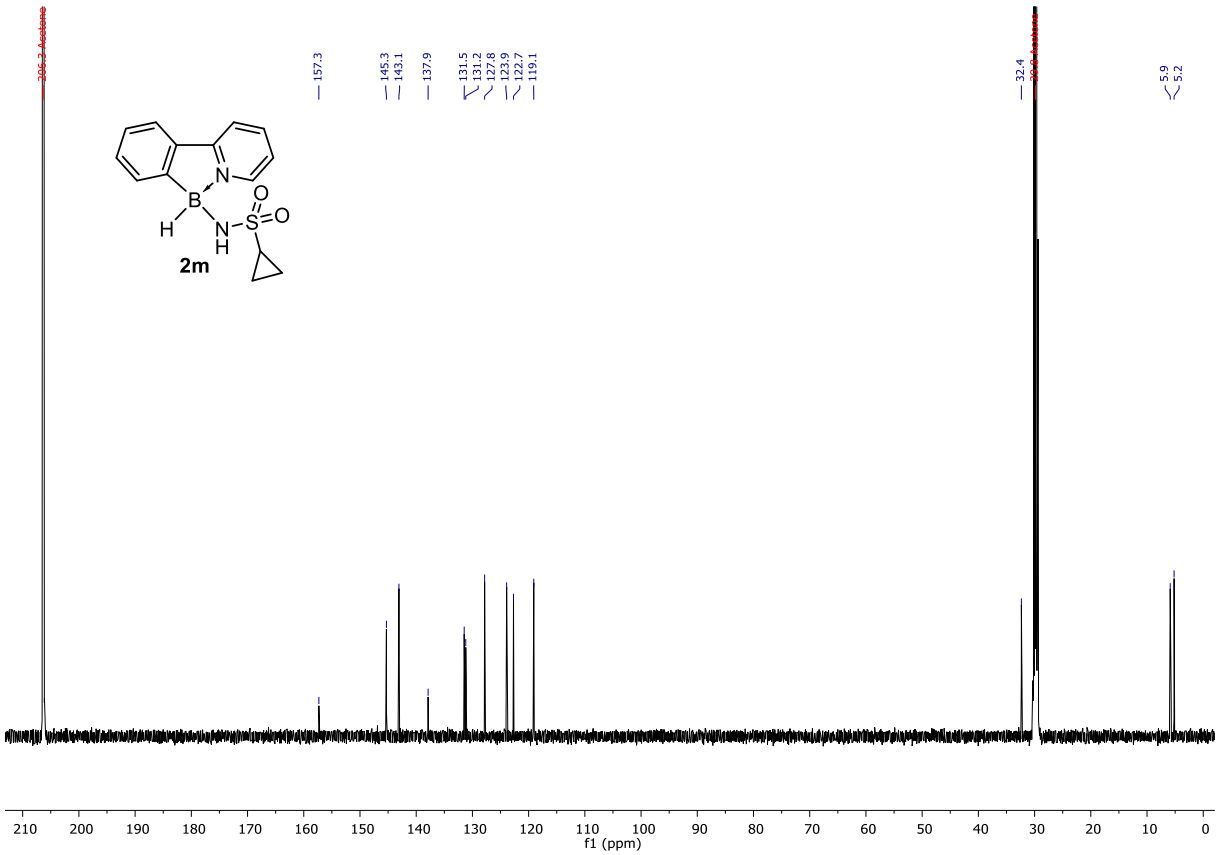


Fig. S121. ^{13}C NMR spectrum of **2m** in acetone-d_6.

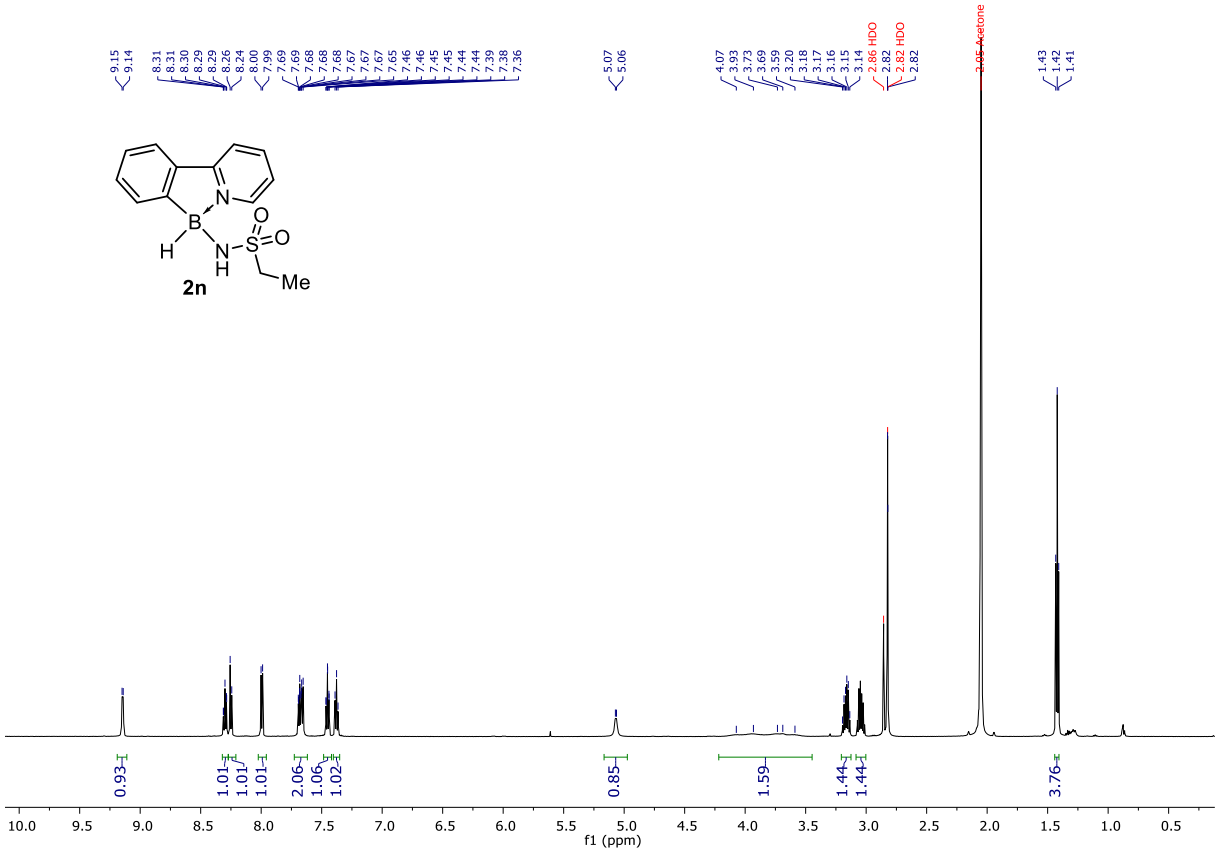


Fig. S122. ^{1}H NMR spectrum of **2n** in acetone-d_6.

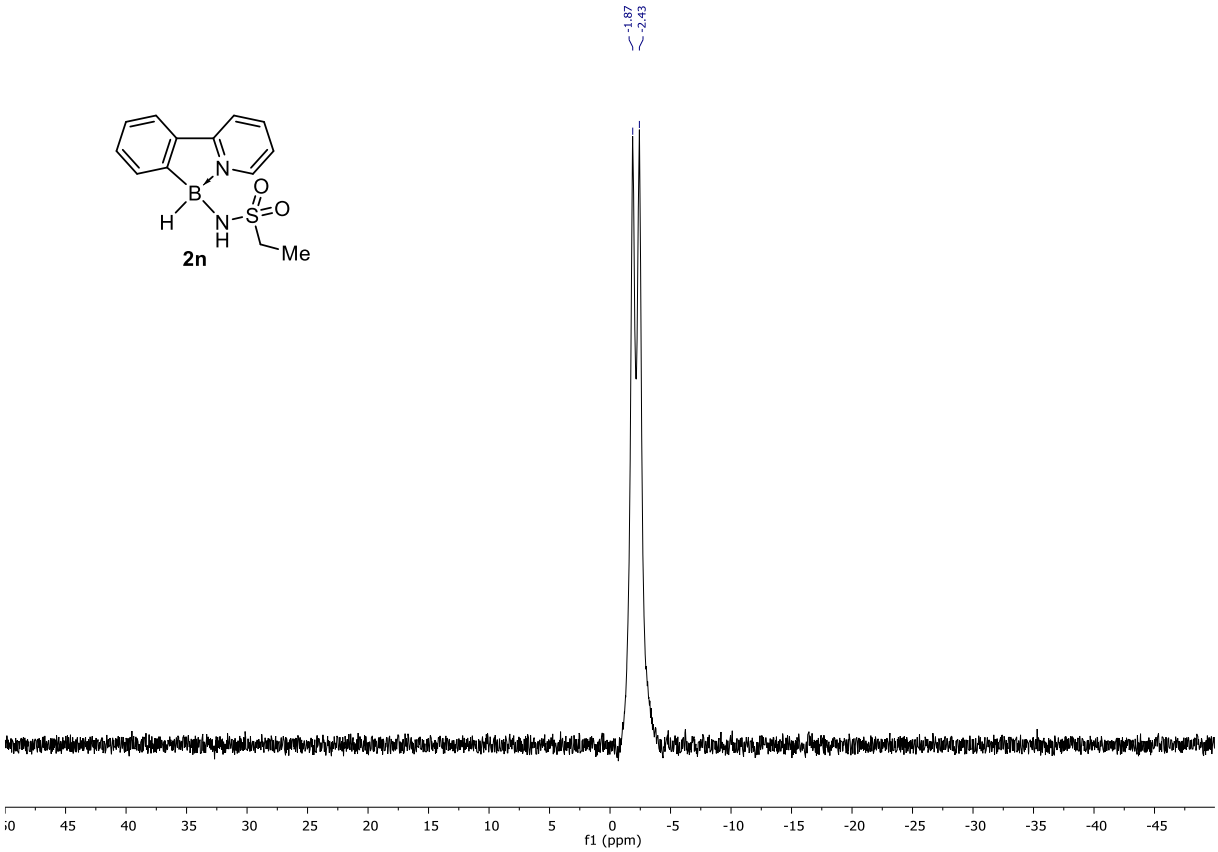


Fig. S123. ^{11}B NMR spectrum of **2n** in acetone-d_6.

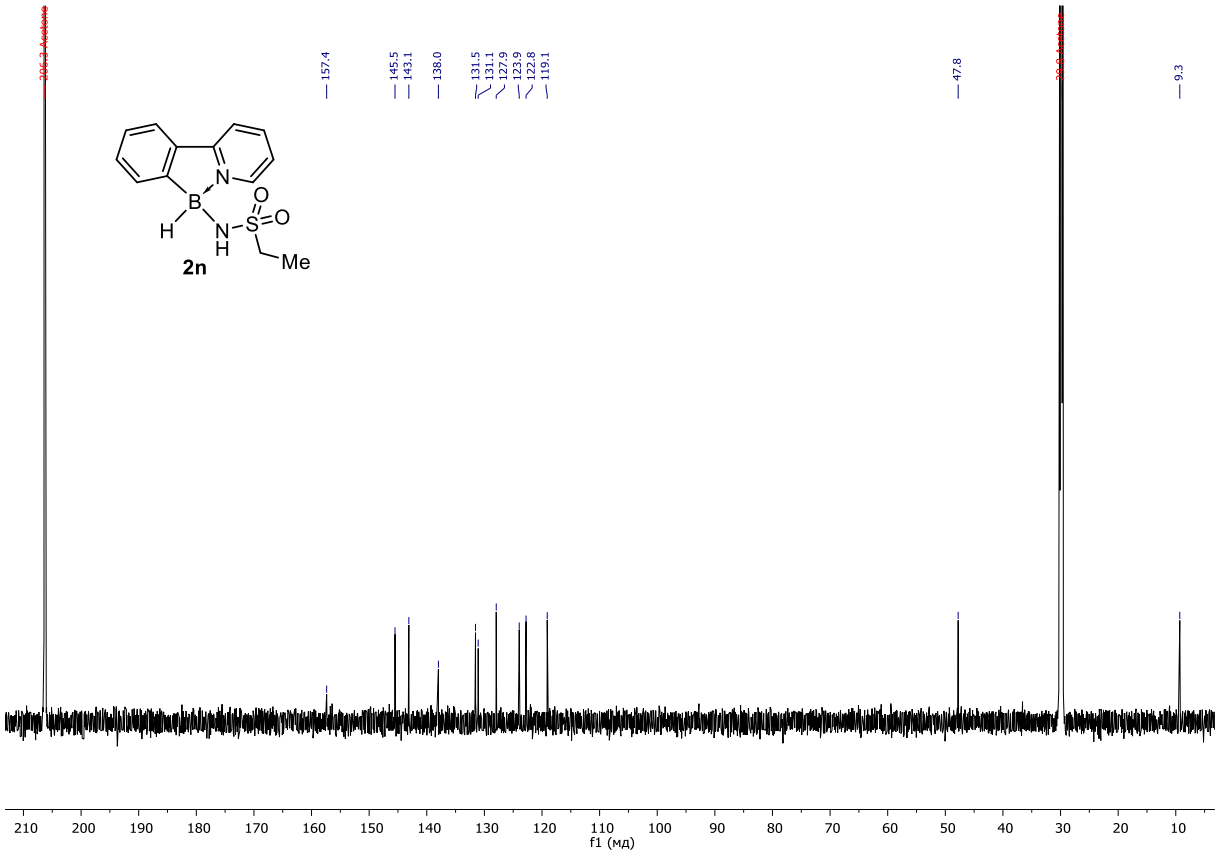


Fig. S124. ^{13}C NMR spectrum of **2n** in acetone-d_6.

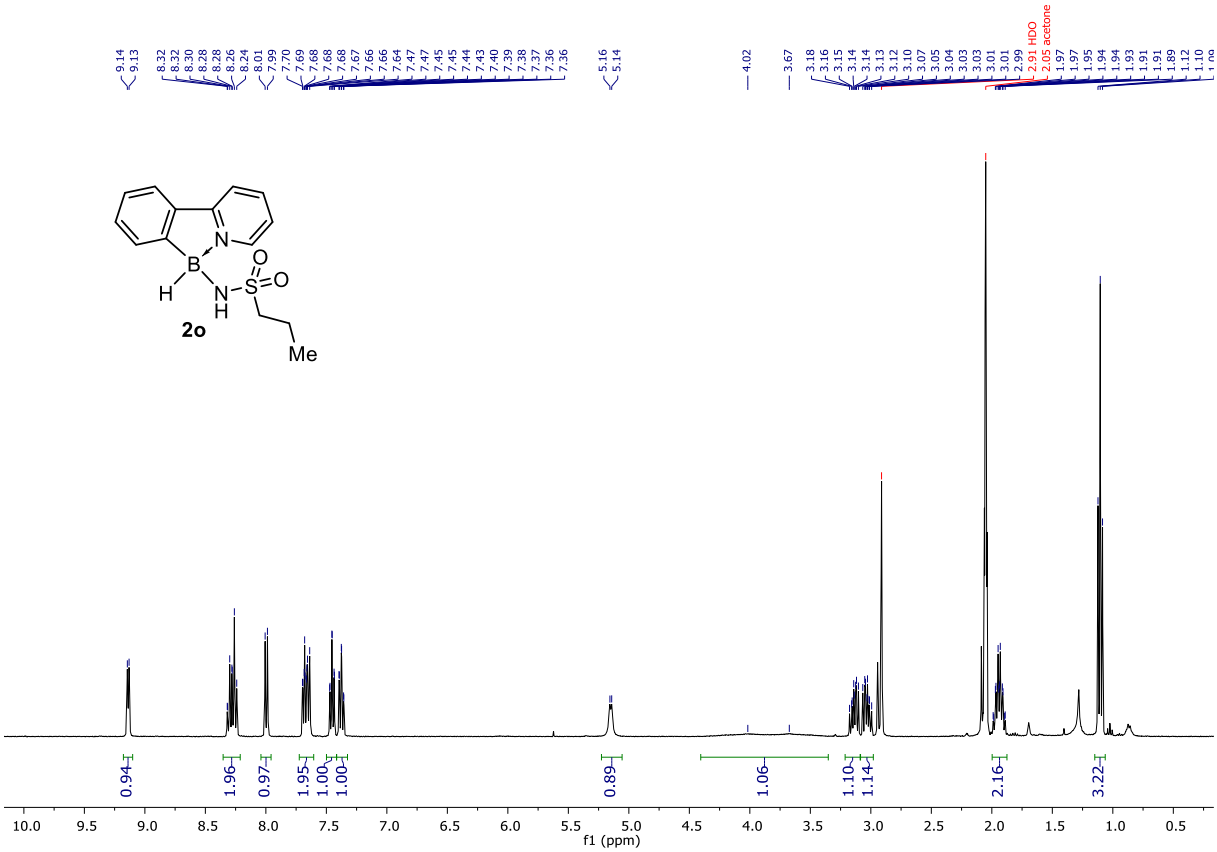


Fig. S125. ^{1}H NMR spectrum of **2o** in acetone-d_6.

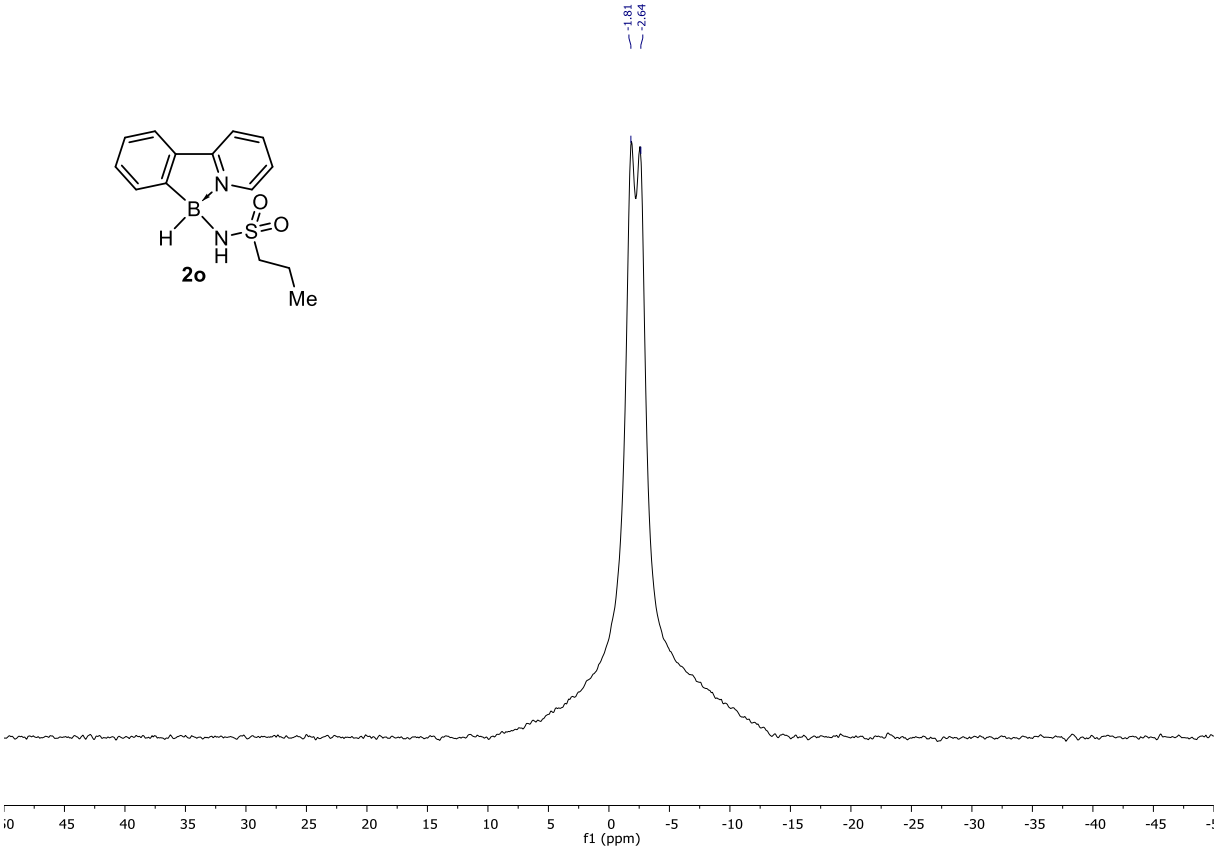


Fig. S126. ^{11}B NMR spectrum of **2o** in acetone-d_6.

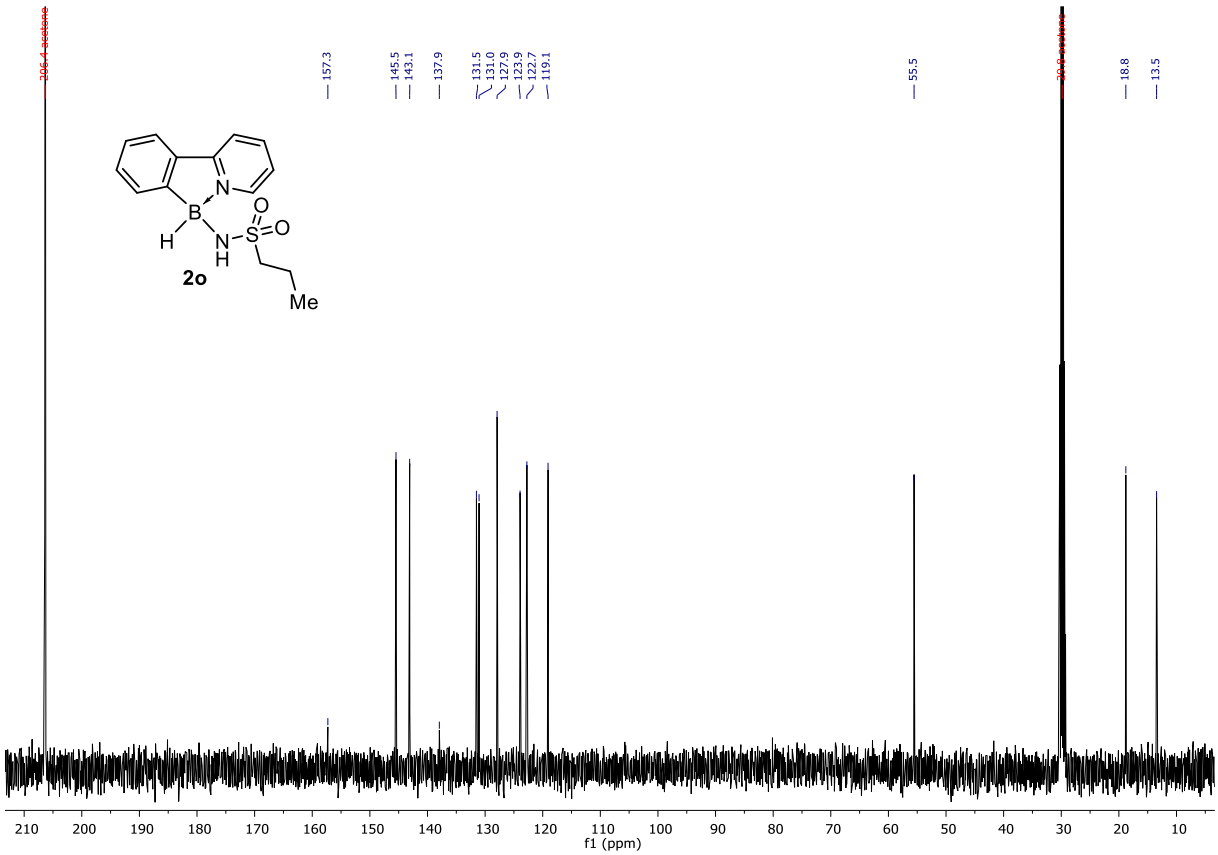


Fig. S127. ^{13}C NMR spectrum of **2o** in acetone-d_6.

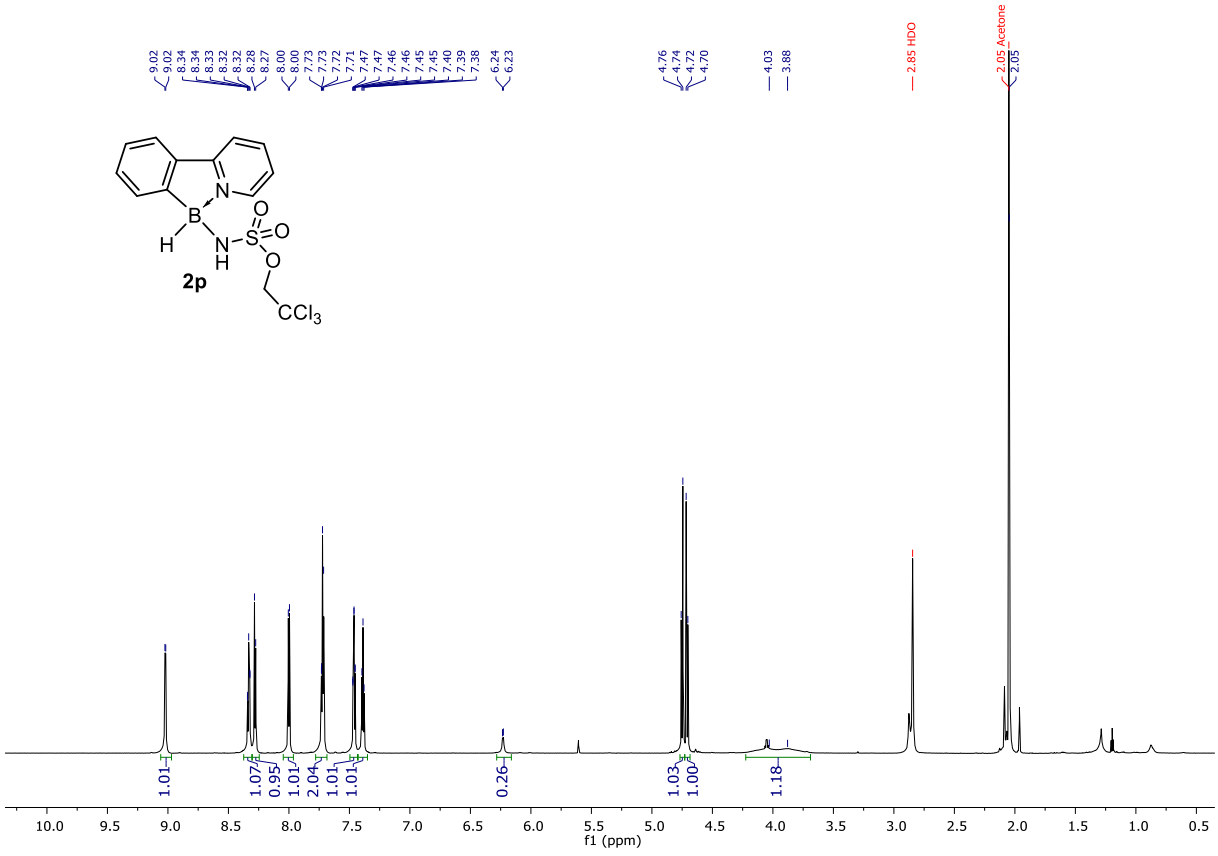


Fig. S128. ^{1}H NMR spectrum of **2p** in acetone-d_6.

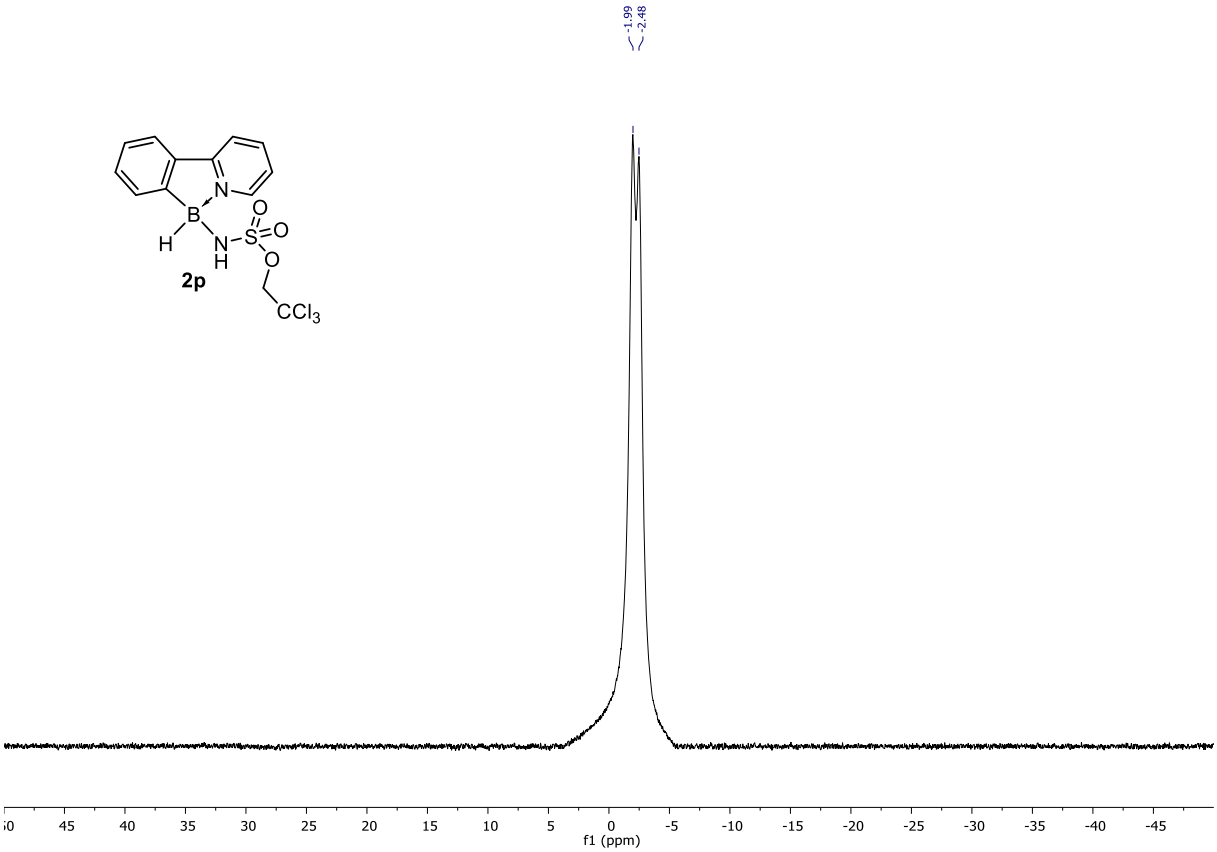


Fig. S129. ^{11}B NMR spectrum of **2p** in acetone-d_6.

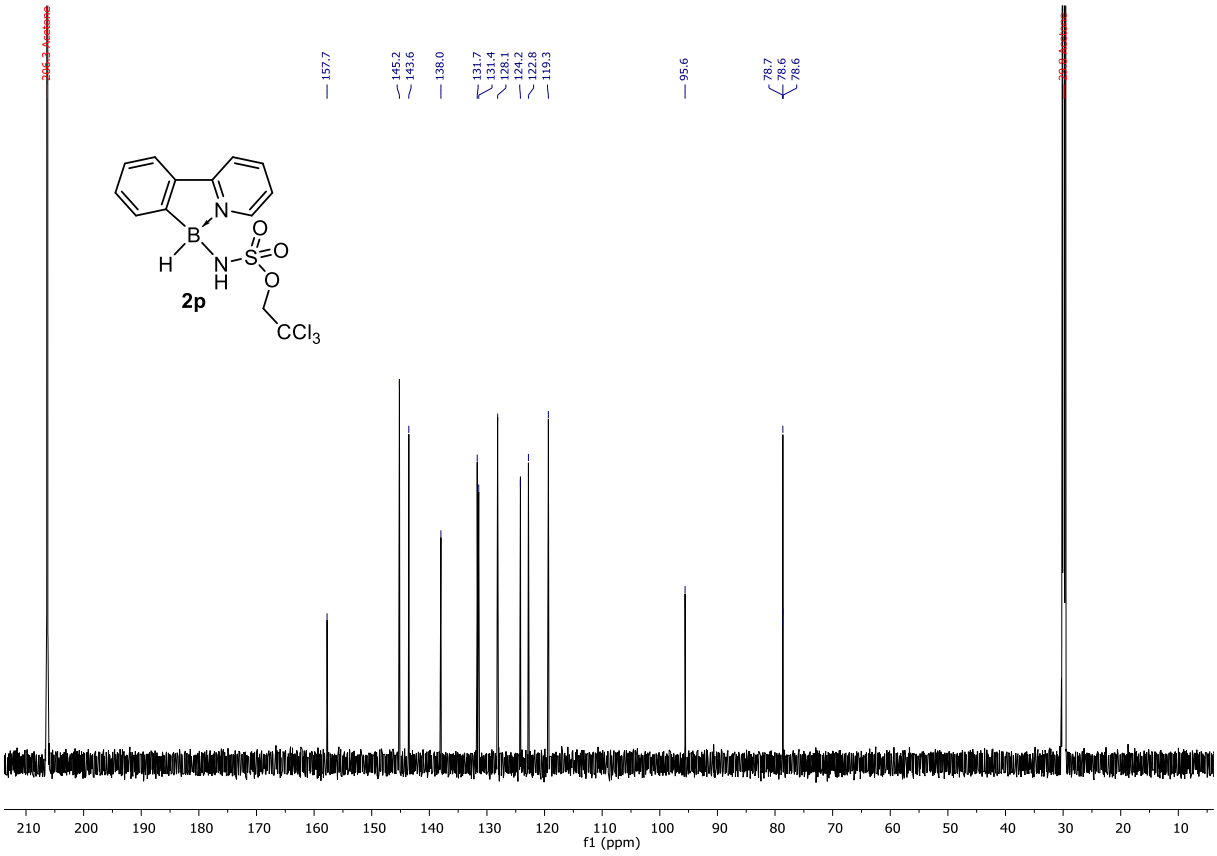


Fig. S130. ^{13}C NMR spectrum of **2p** in acetone-d_6.

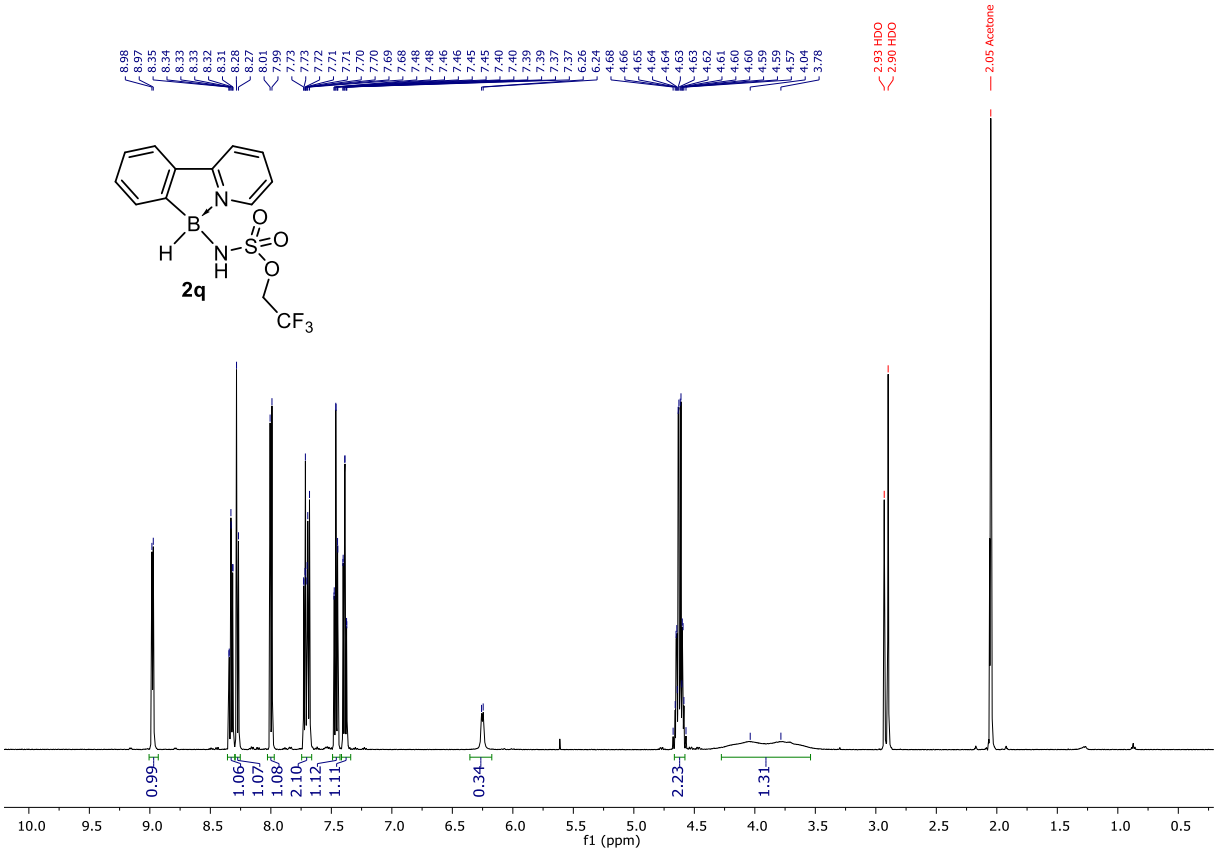


Fig. S131. ^{1}H NMR spectrum of **2q** in acetone-d_6.

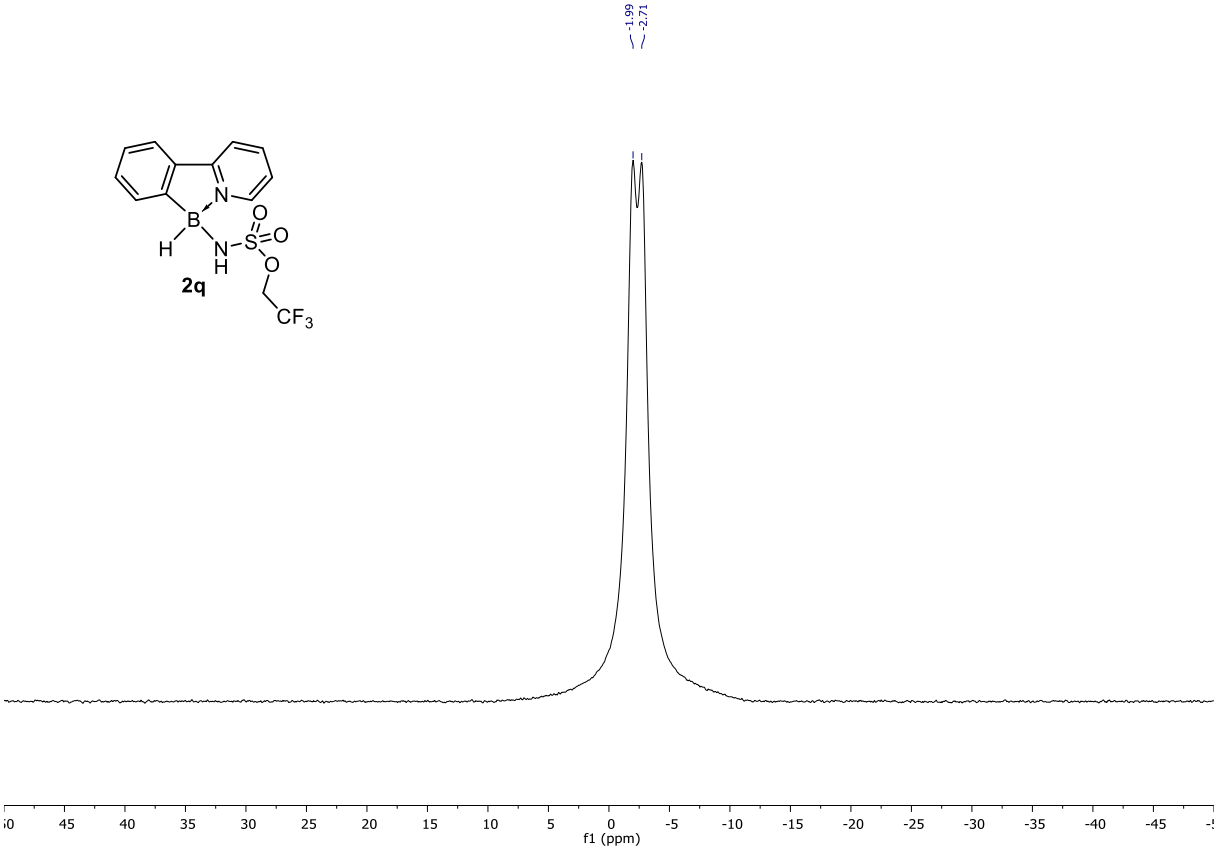


Fig. S132. ^{11}B NMR spectrum of **2q** in acetone-d_6.

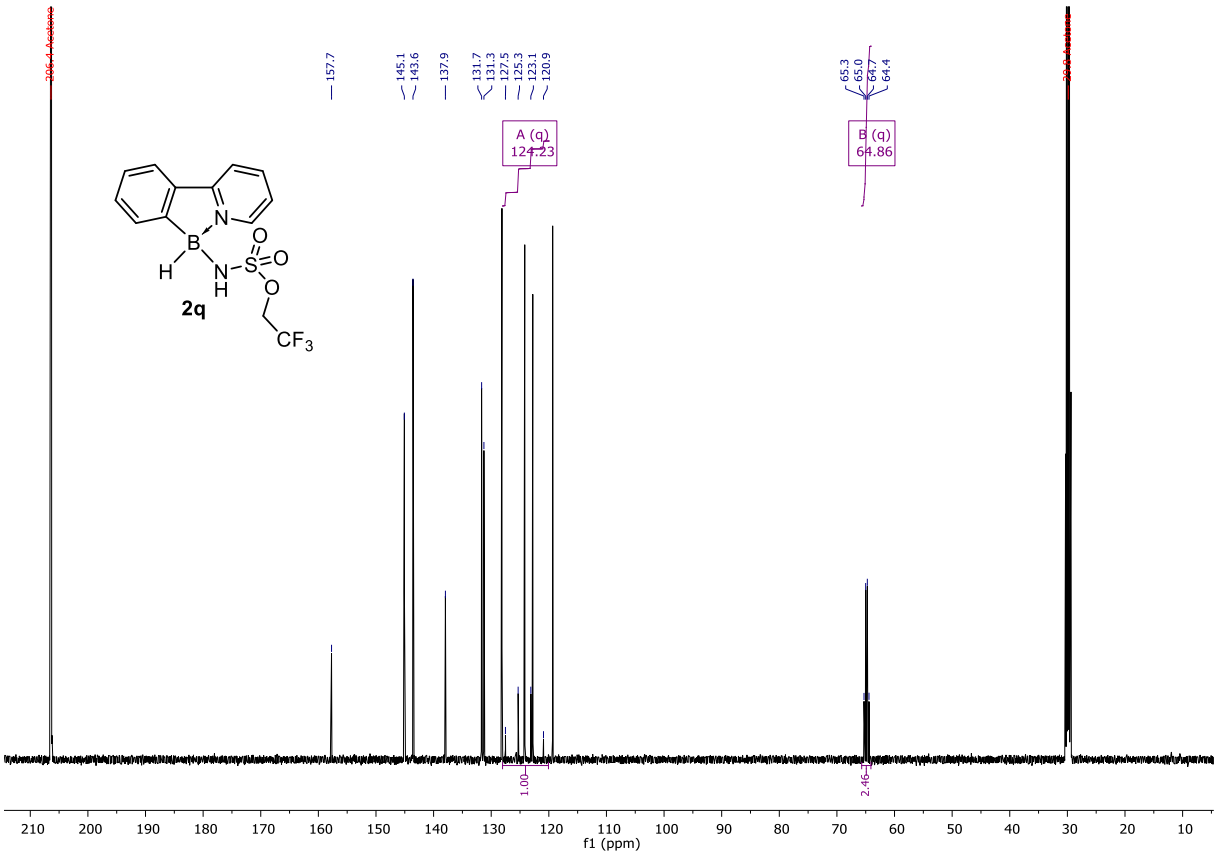


Fig. S133. ^{13}C NMR spectrum of **2q** in acetone-d_6.

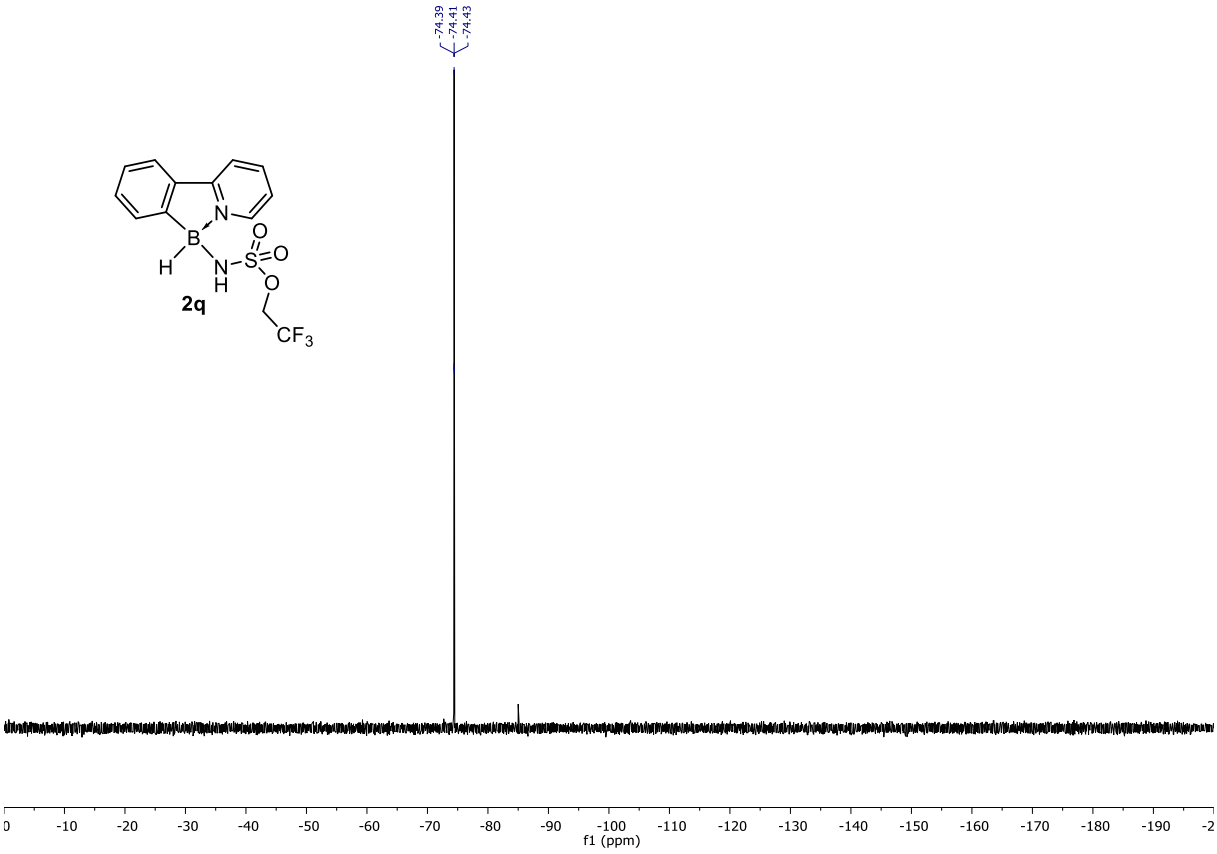


Fig. S134. ^{19}F NMR spectrum of **2q** in acetone-d_6.

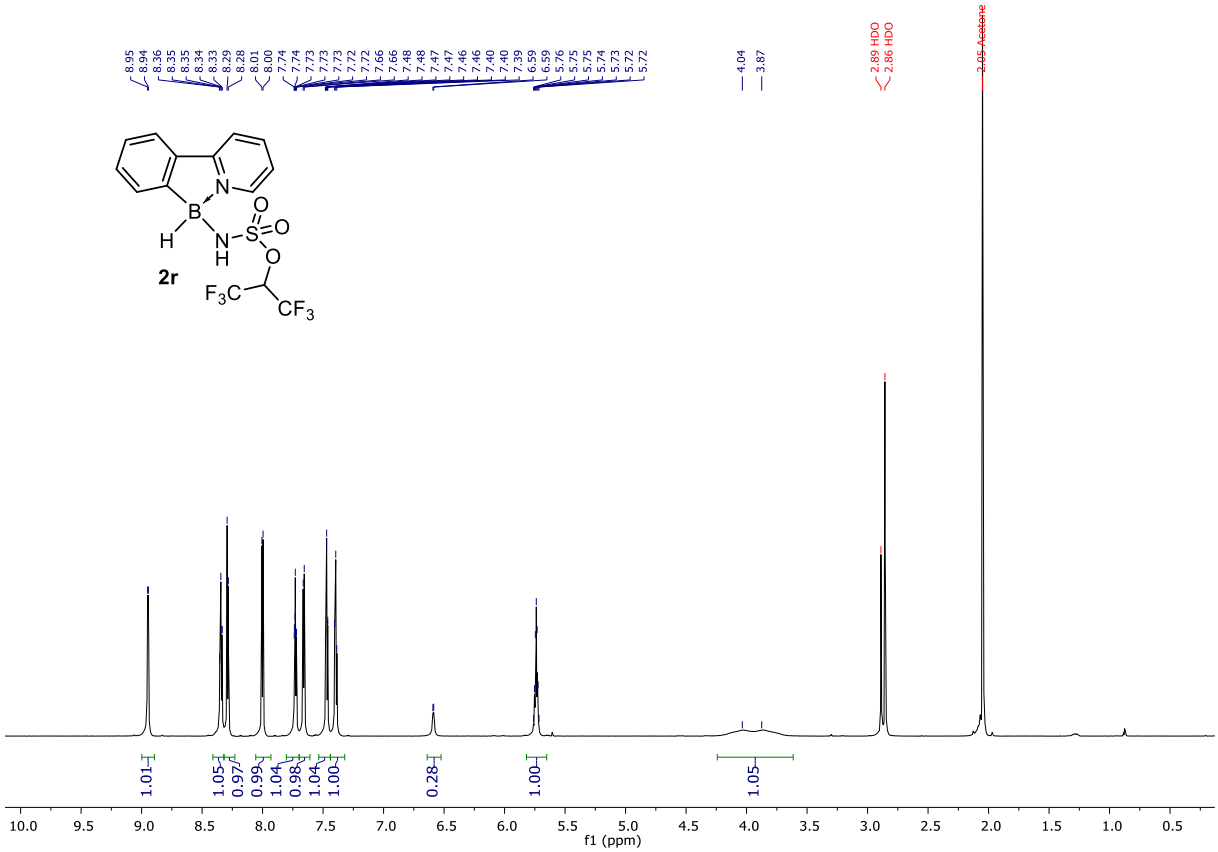


Fig. S135. ^{1}H NMR spectrum of **2r** in acetone-d_6.

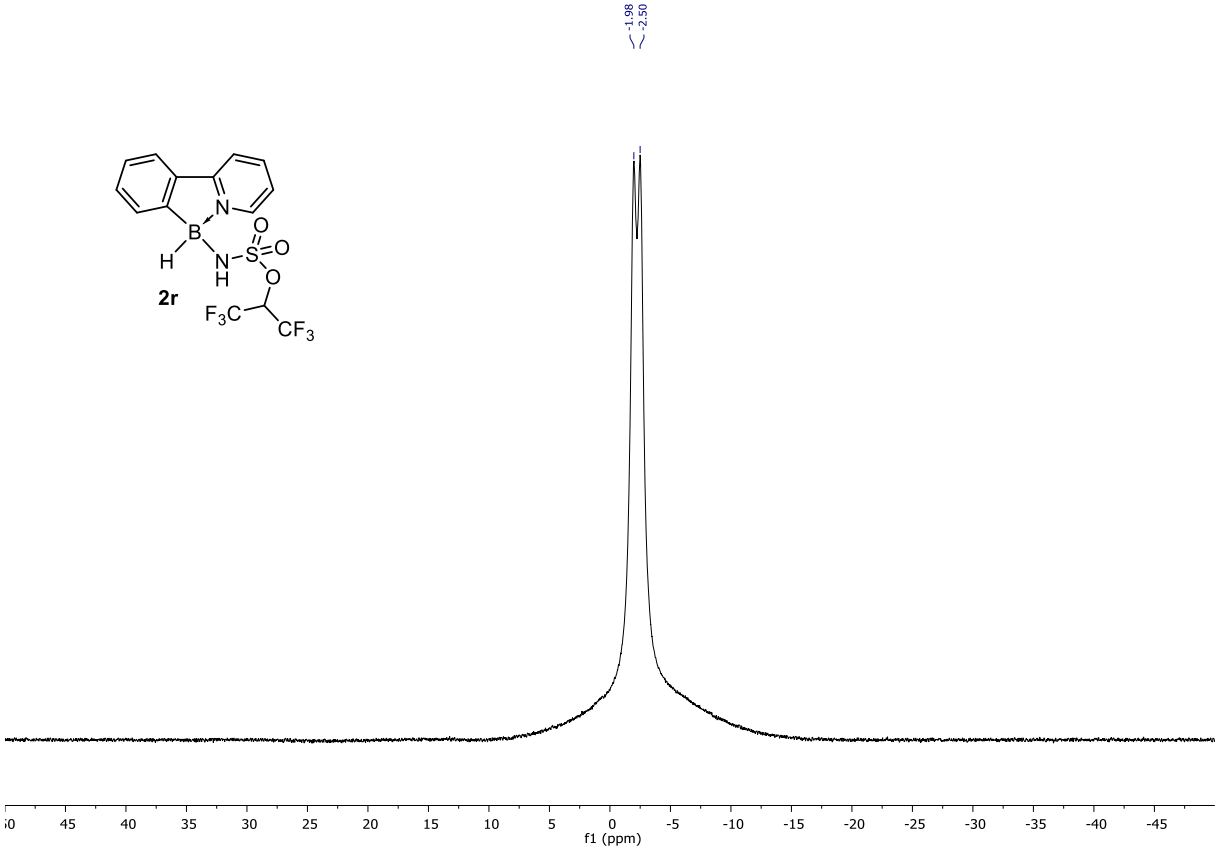


Fig. S136. ^{11}B NMR spectrum of **2r** in acetone-d_6.

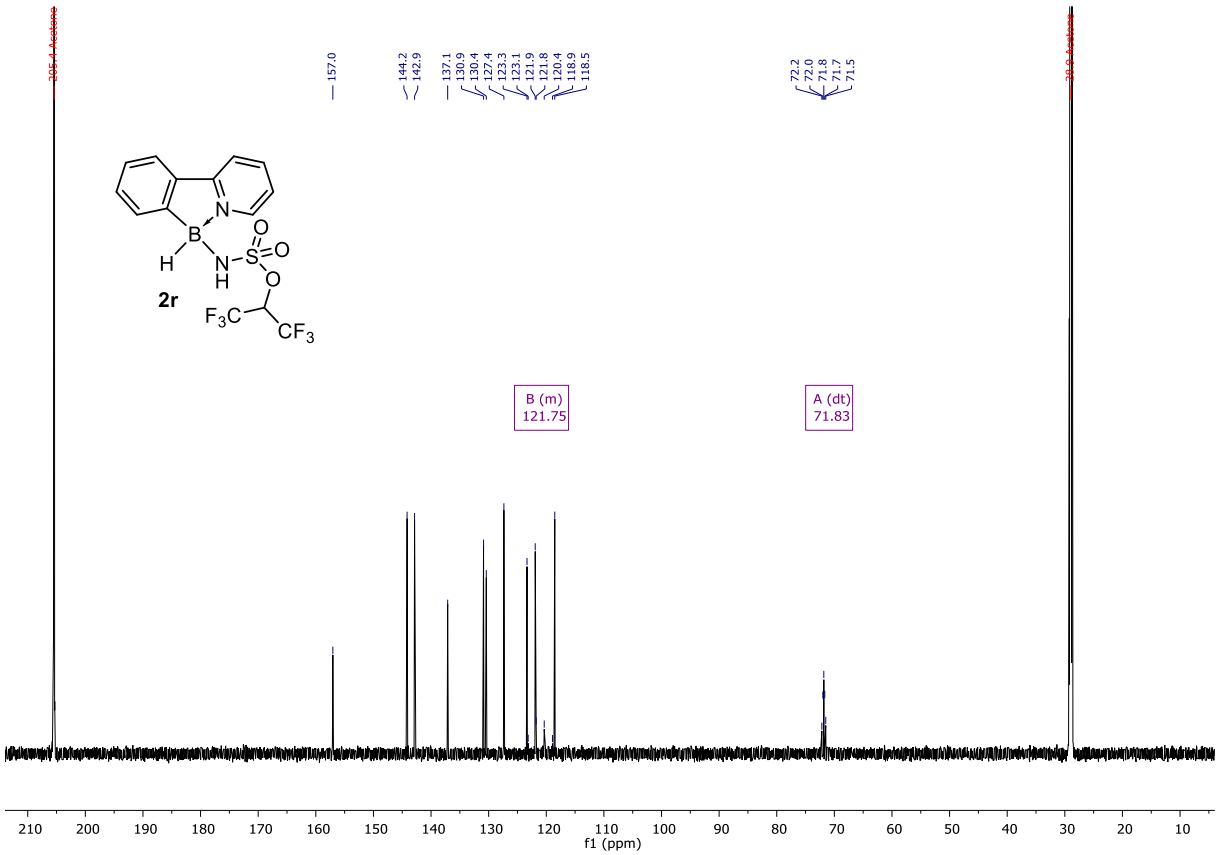


Fig. S137. ^{13}C NMR spectrum of **2r** in acetone-d_6.

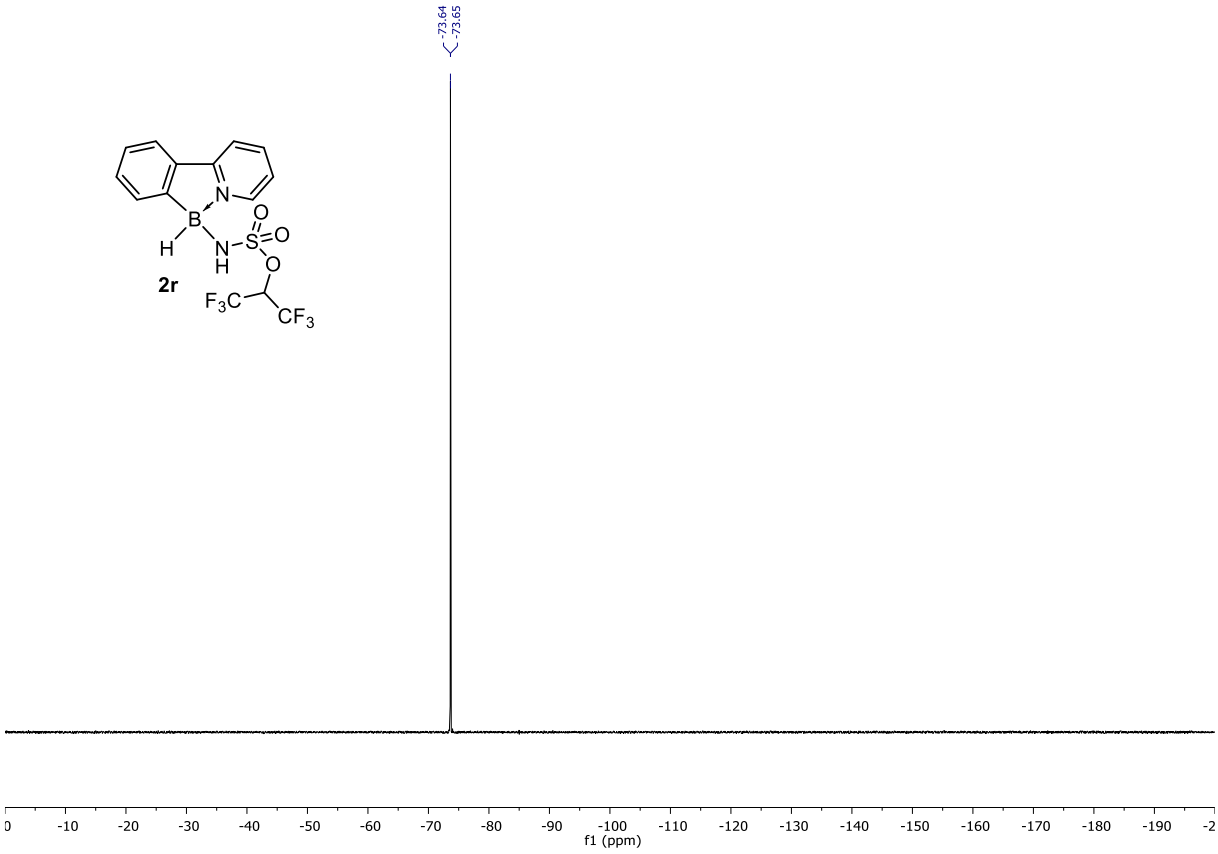


Fig. S138. ^{19}F NMR spectrum of **2r** in acetone-d_6.

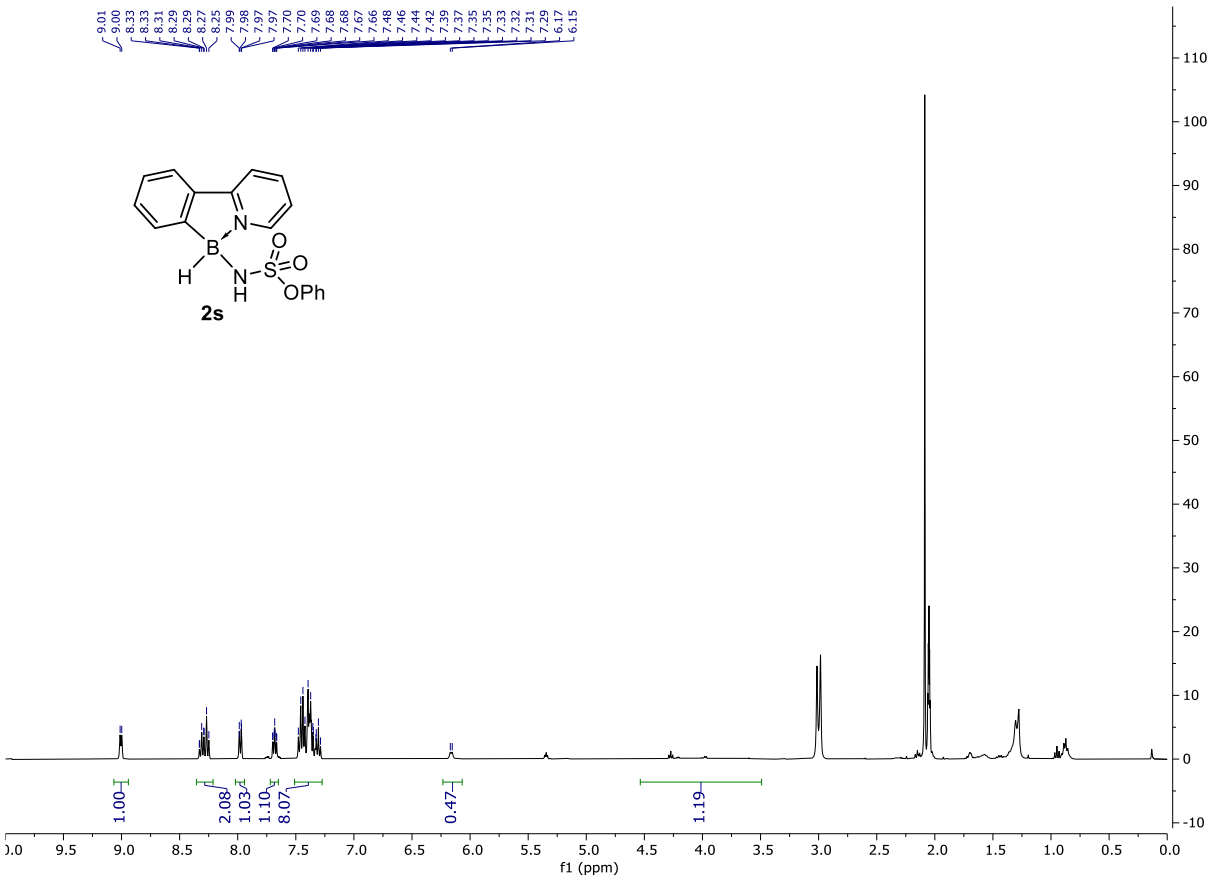


Fig. S139. ^{1}H NMR spectrum of **2s** in acetone-d_6.

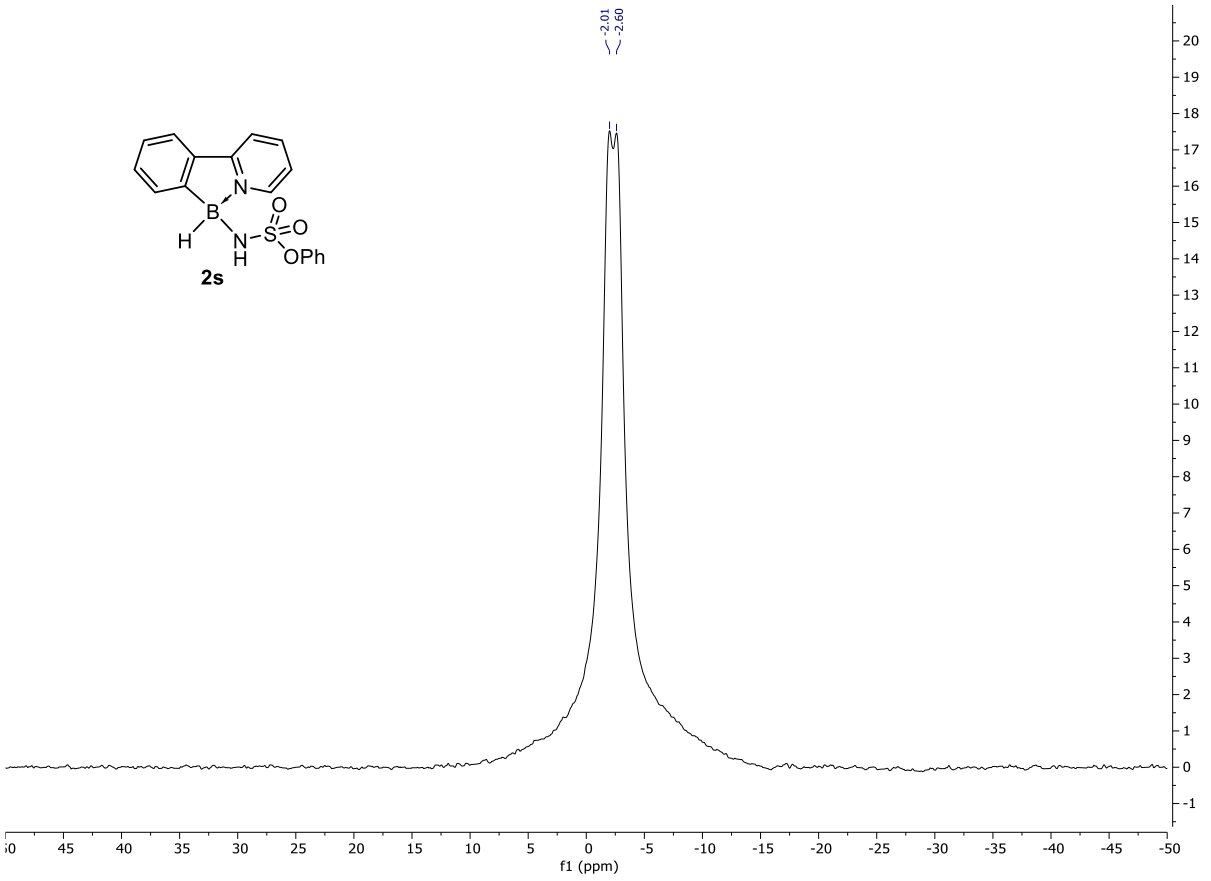


Fig. S140. ^{11}B NMR spectrum of **2s** in acetone-d_6.

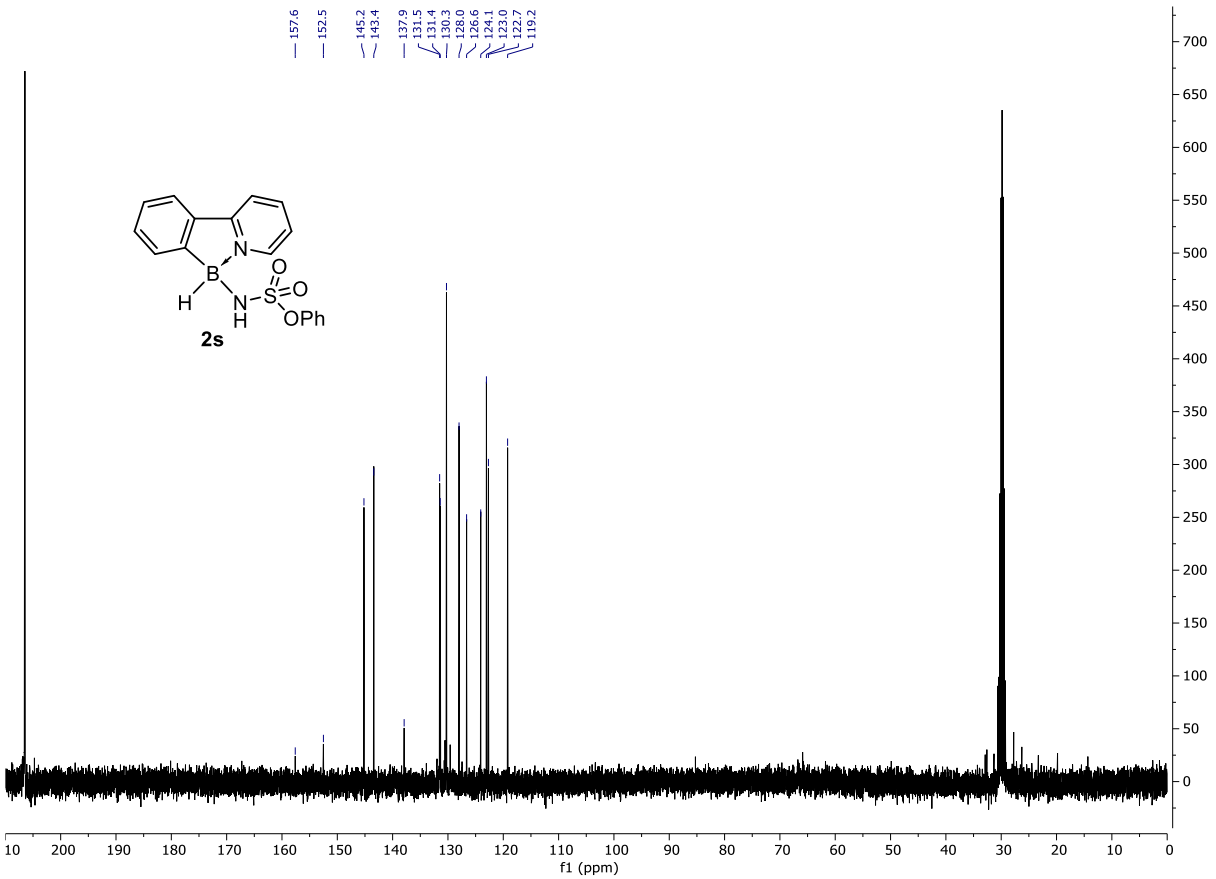


Fig. S141. ^{13}C NMR spectrum of **2s** in acetone-d_6.

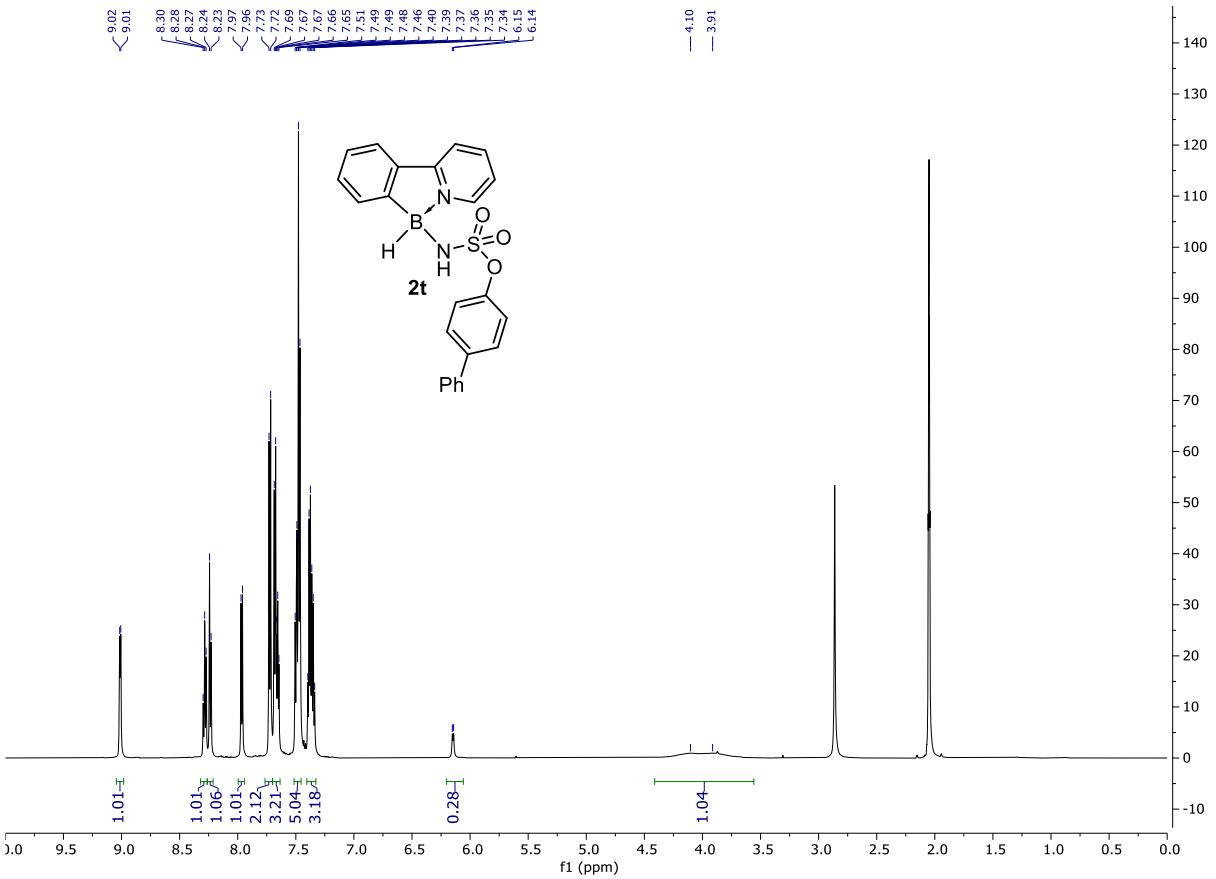


Fig. S142. ^{1}H NMR spectrum of **2t** in acetone-d_6.

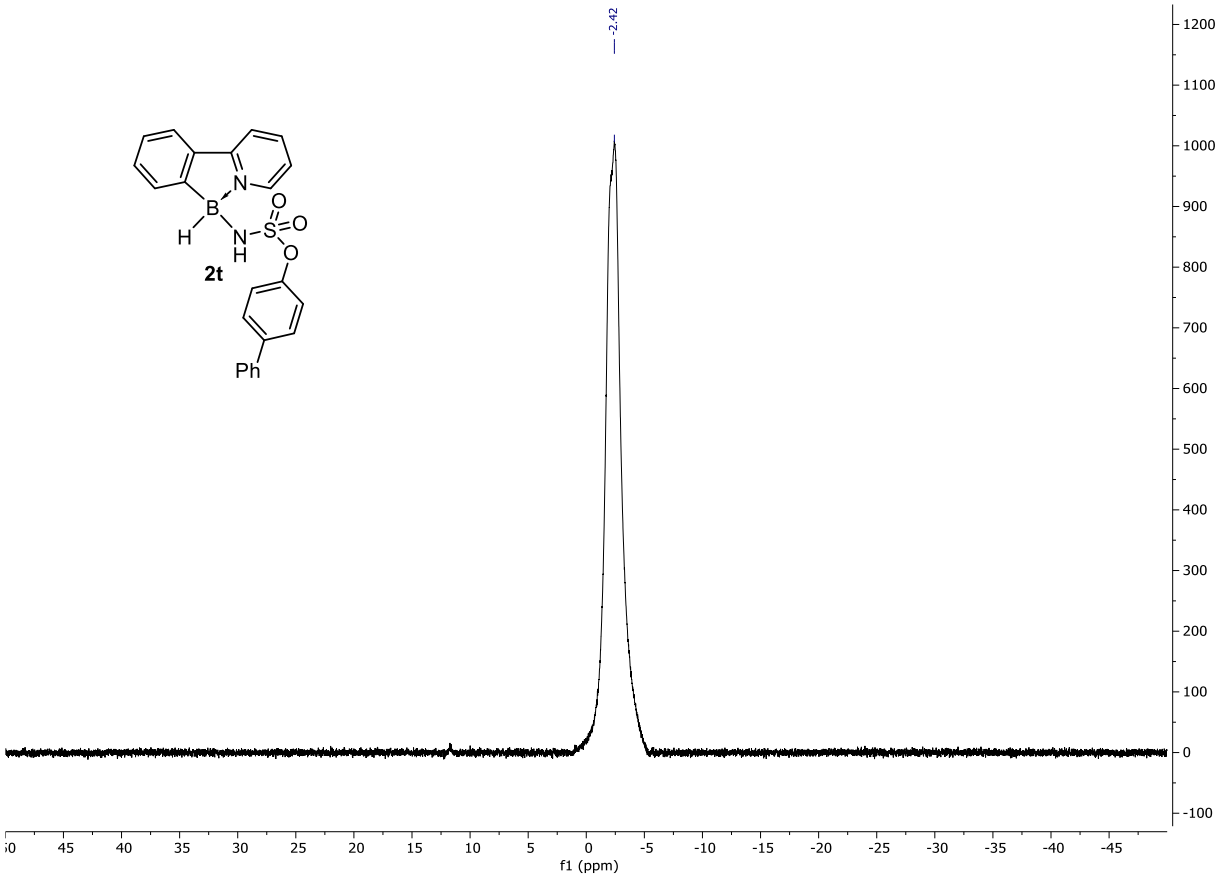


Fig. S143. ^{11}B NMR spectrum of **2t** in acetone-d_6.

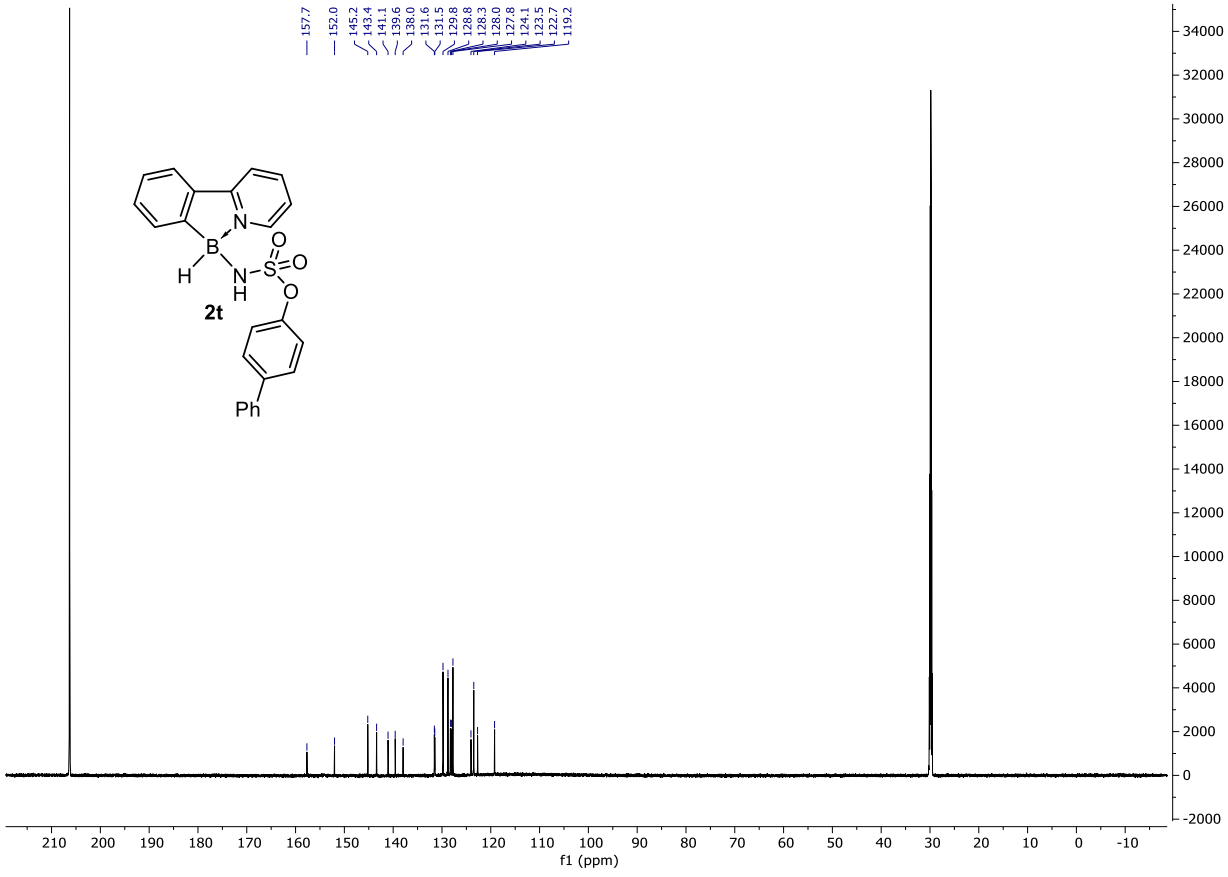


Fig. S144. ^{13}C NMR spectrum of **2t** in acetone-d_6.

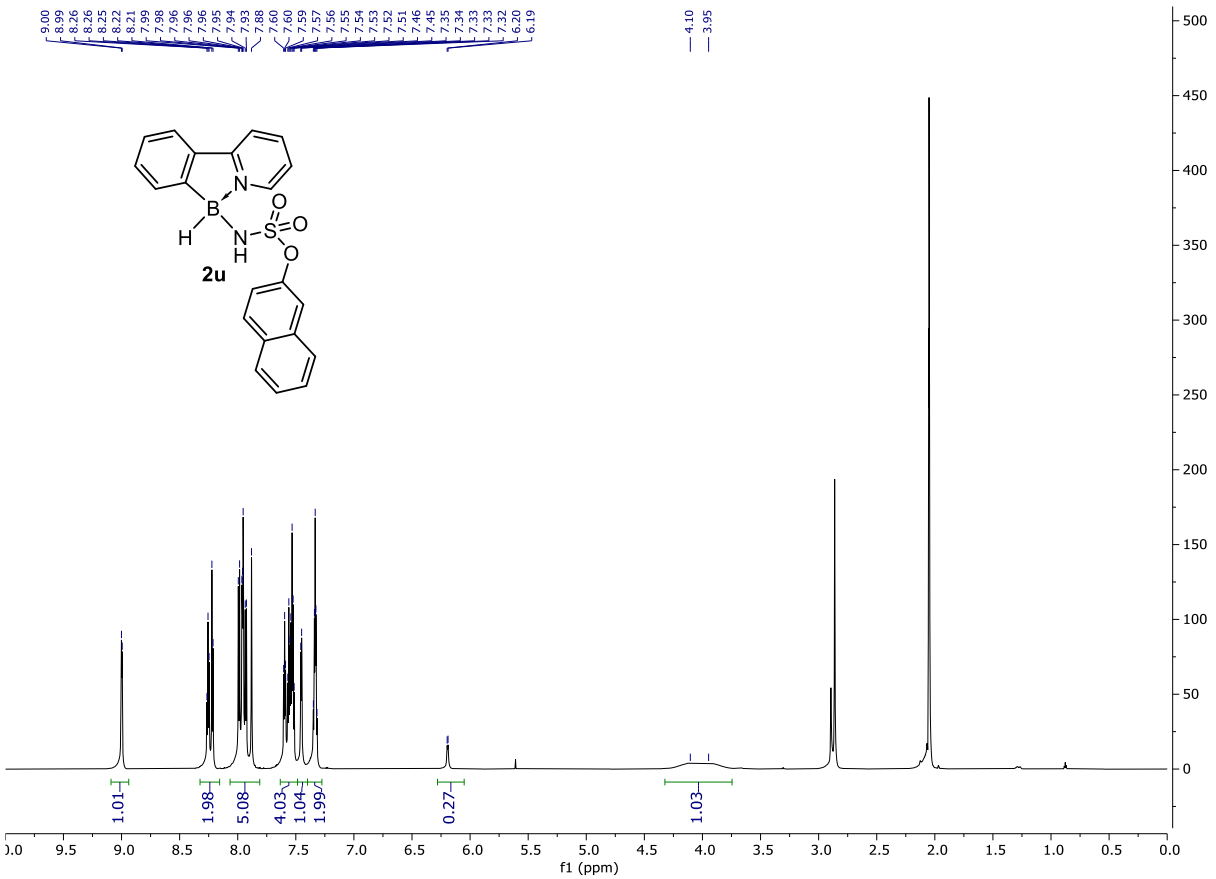


Fig. S145. ^{1}H NMR spectrum of **2u** in acetone-d_6.

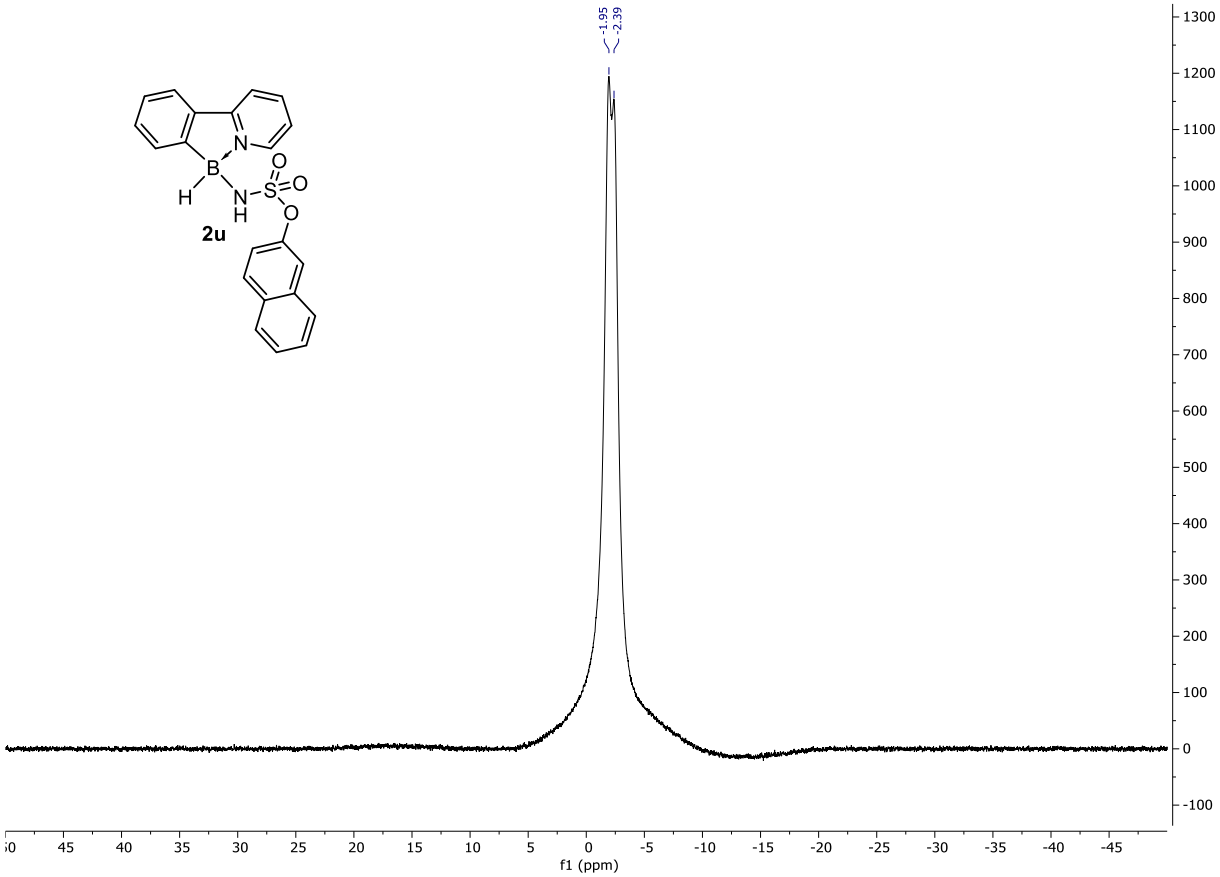


Fig. S146. ^{11}B NMR spectrum of **2u** in acetone-d_6.

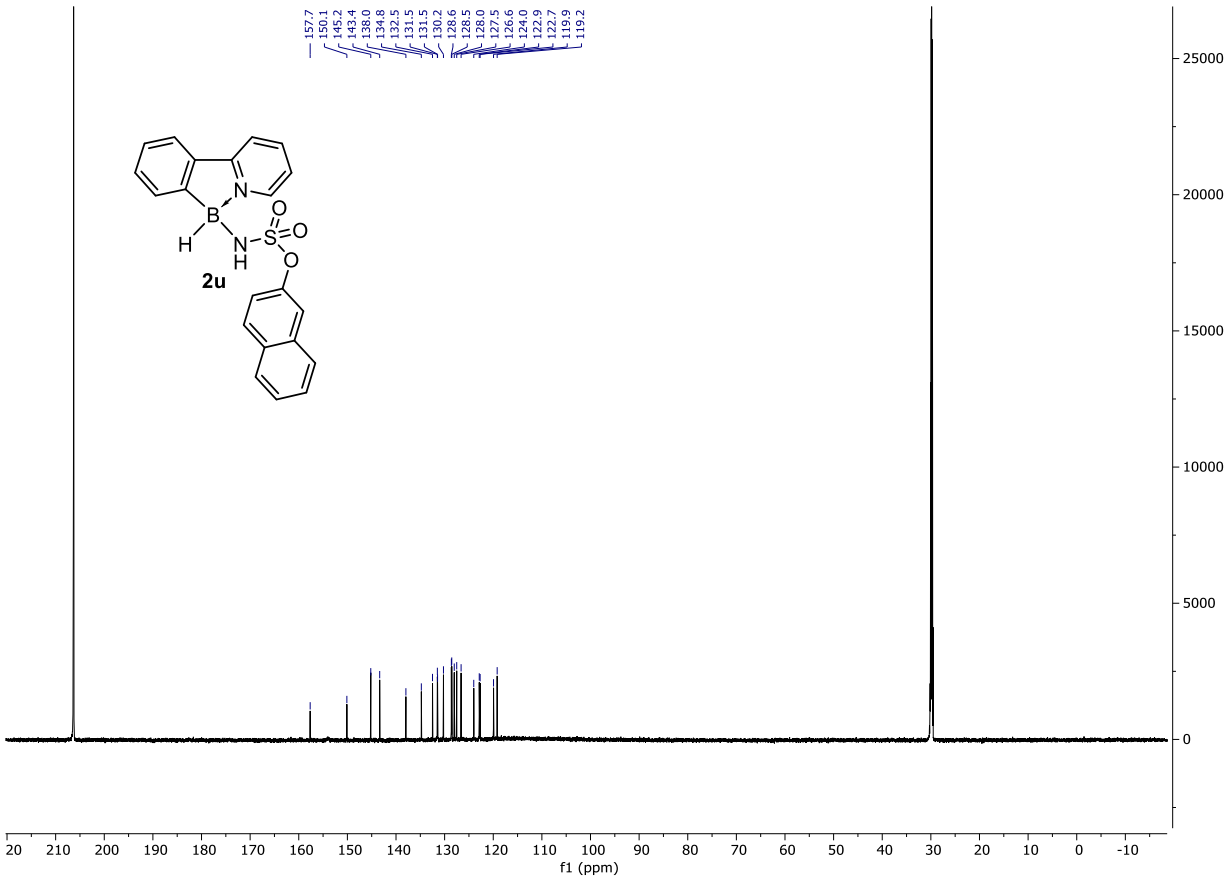


Fig. S147. ^{13}C NMR spectrum of **2u** in acetone-d_6.

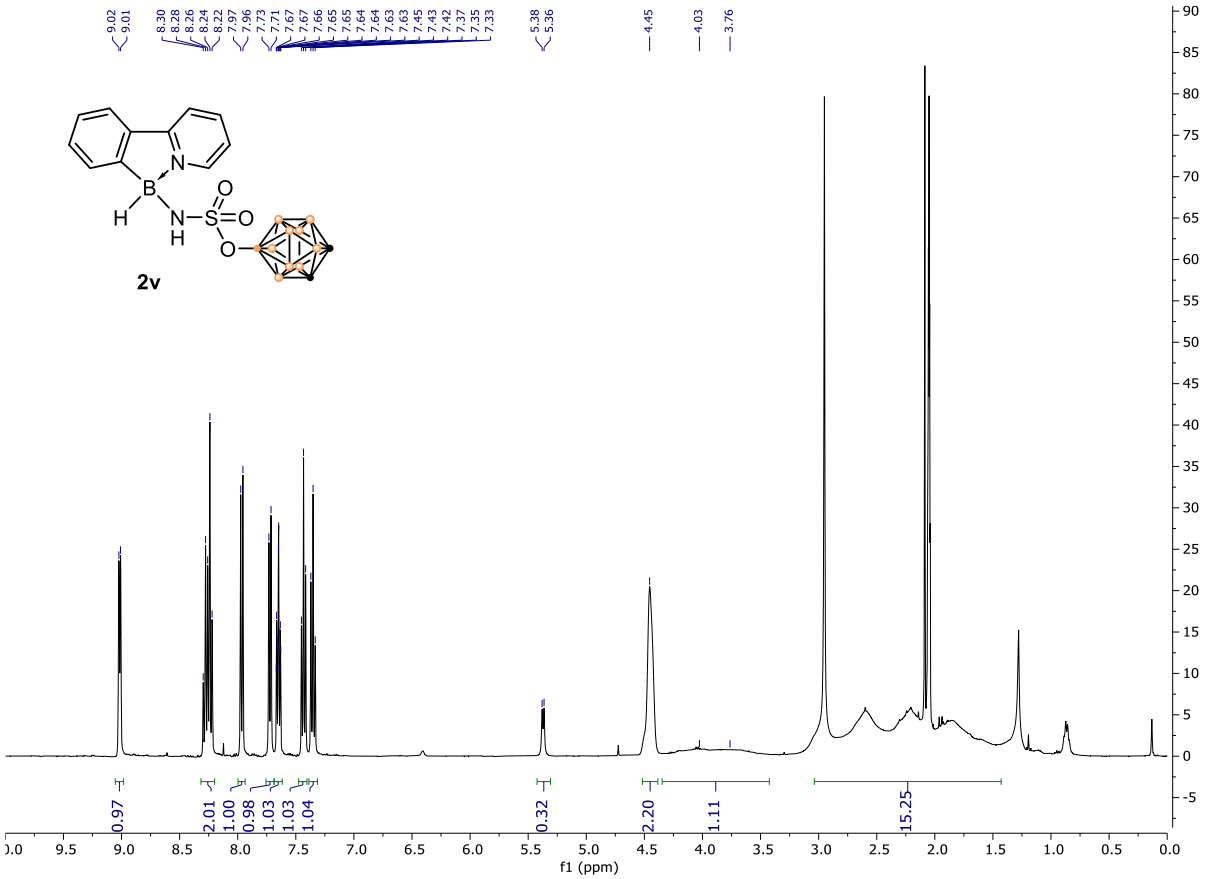


Fig. S148. ^{1}H NMR spectrum of **2v** in acetone-d_6.

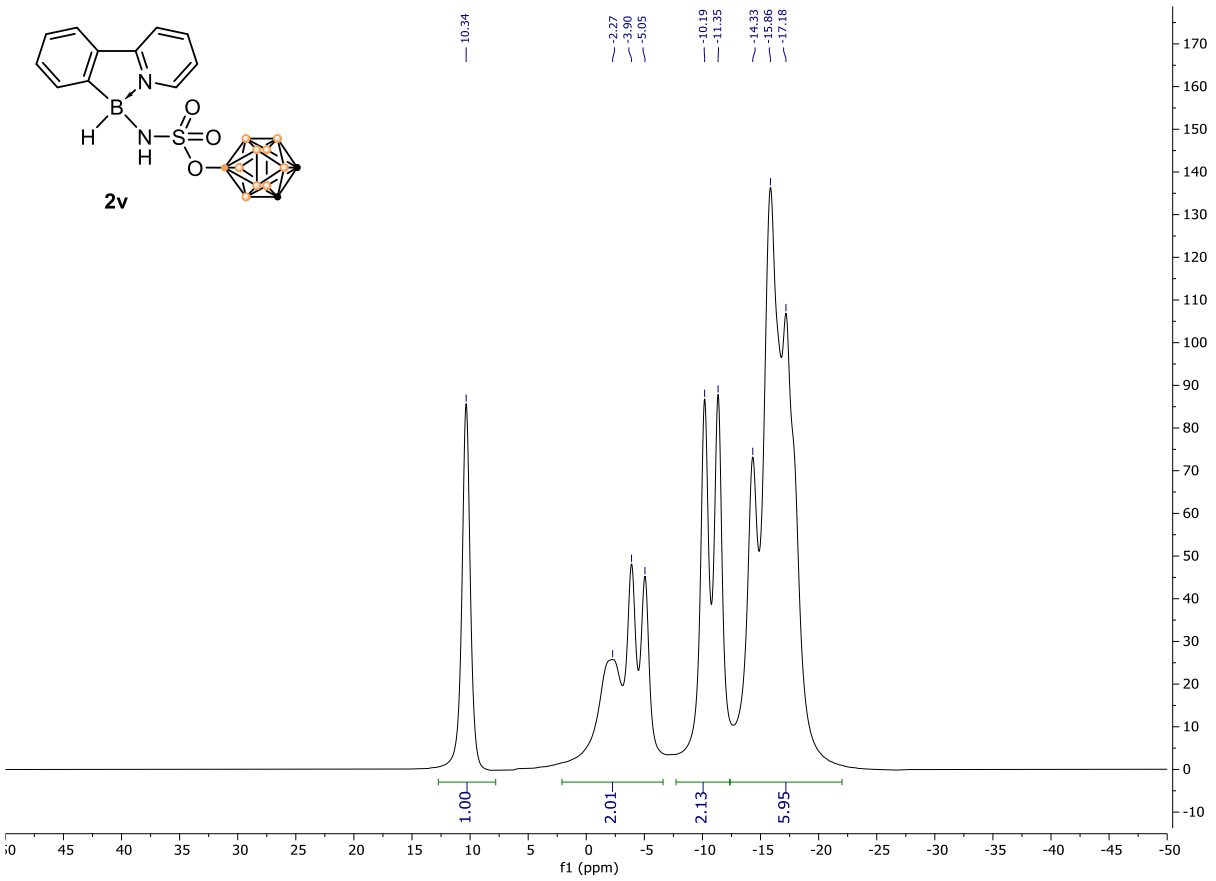


Fig. S149. ^{11}B NMR spectrum of **2v** in acetone-d_6.

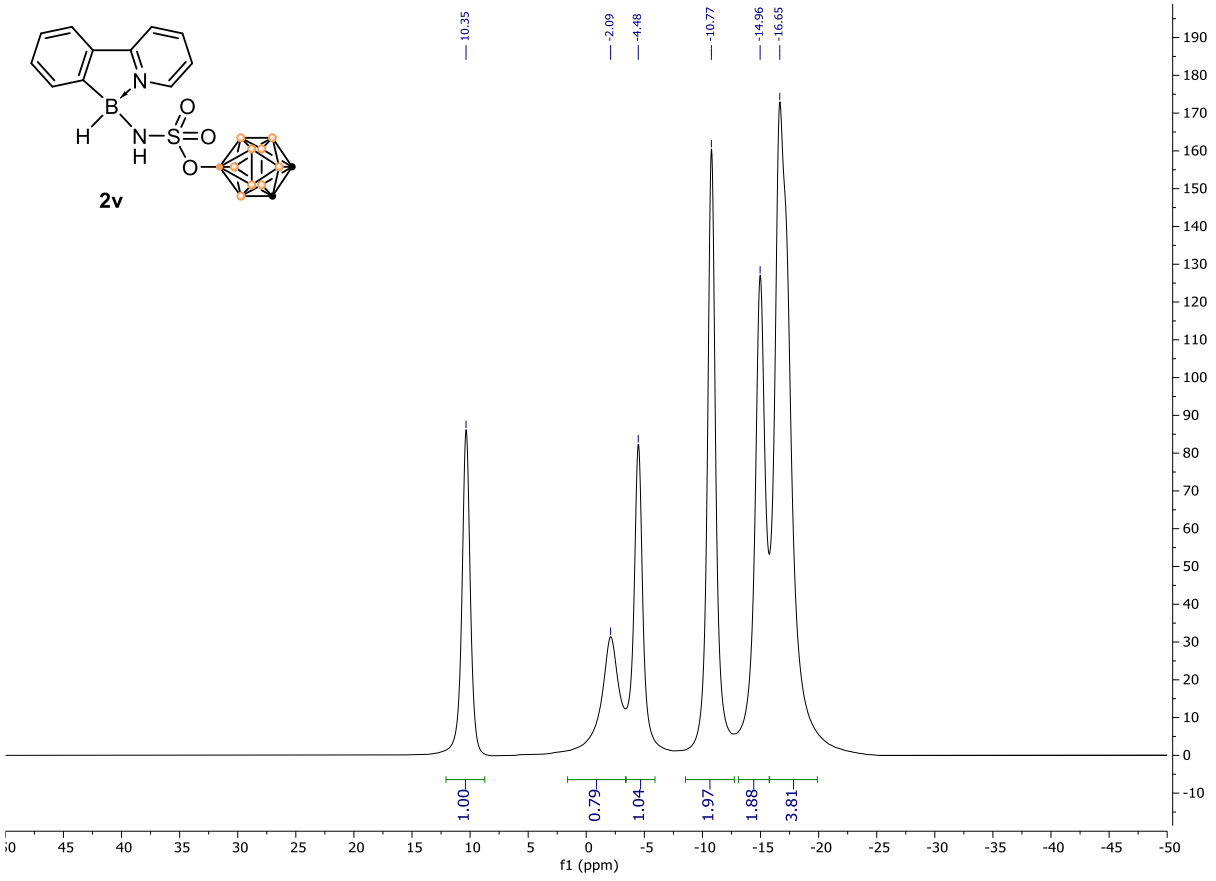


Fig. S150. $^{11}B\{^1H\}$ NMR spectrum of **2v** in acetone-d_6.

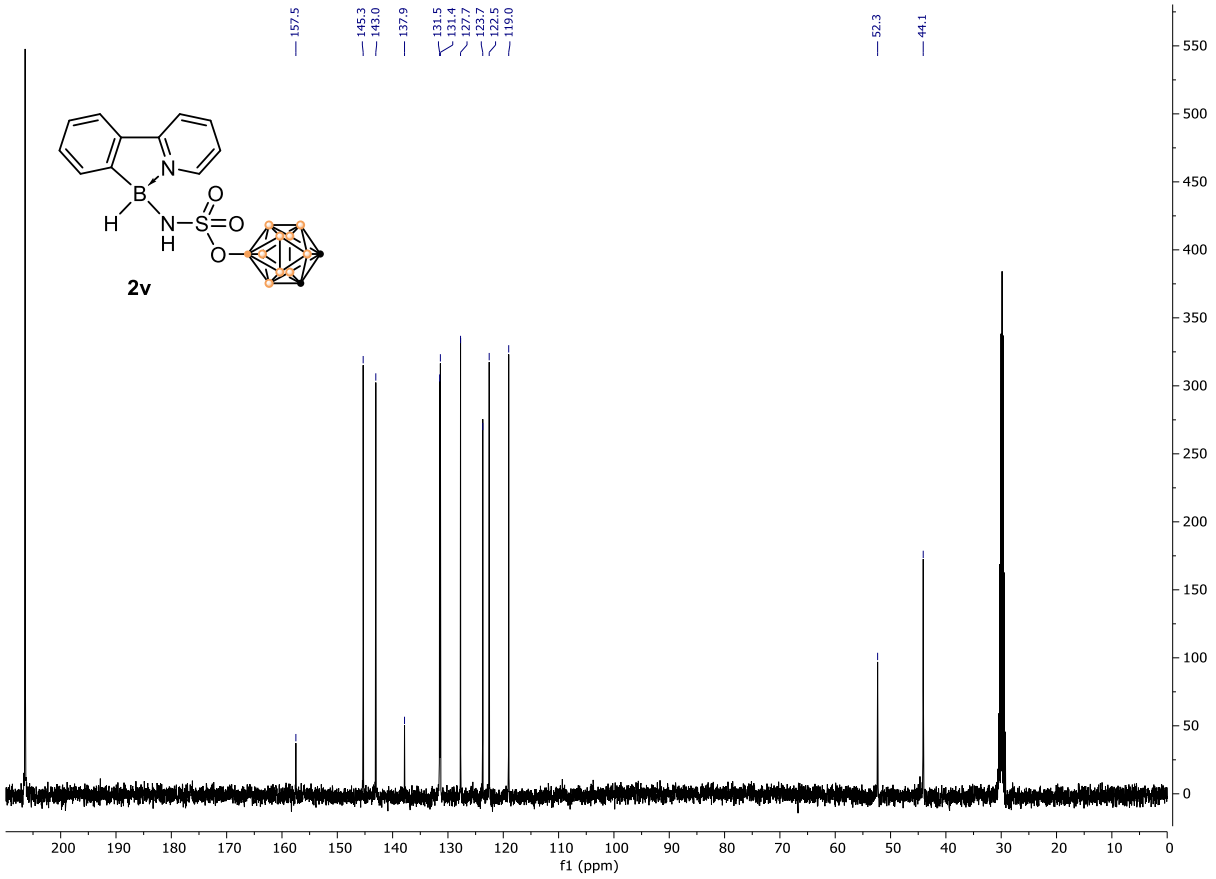


Fig. S151. ^{13}C NMR spectrum of **2v** in acetone-d_6.

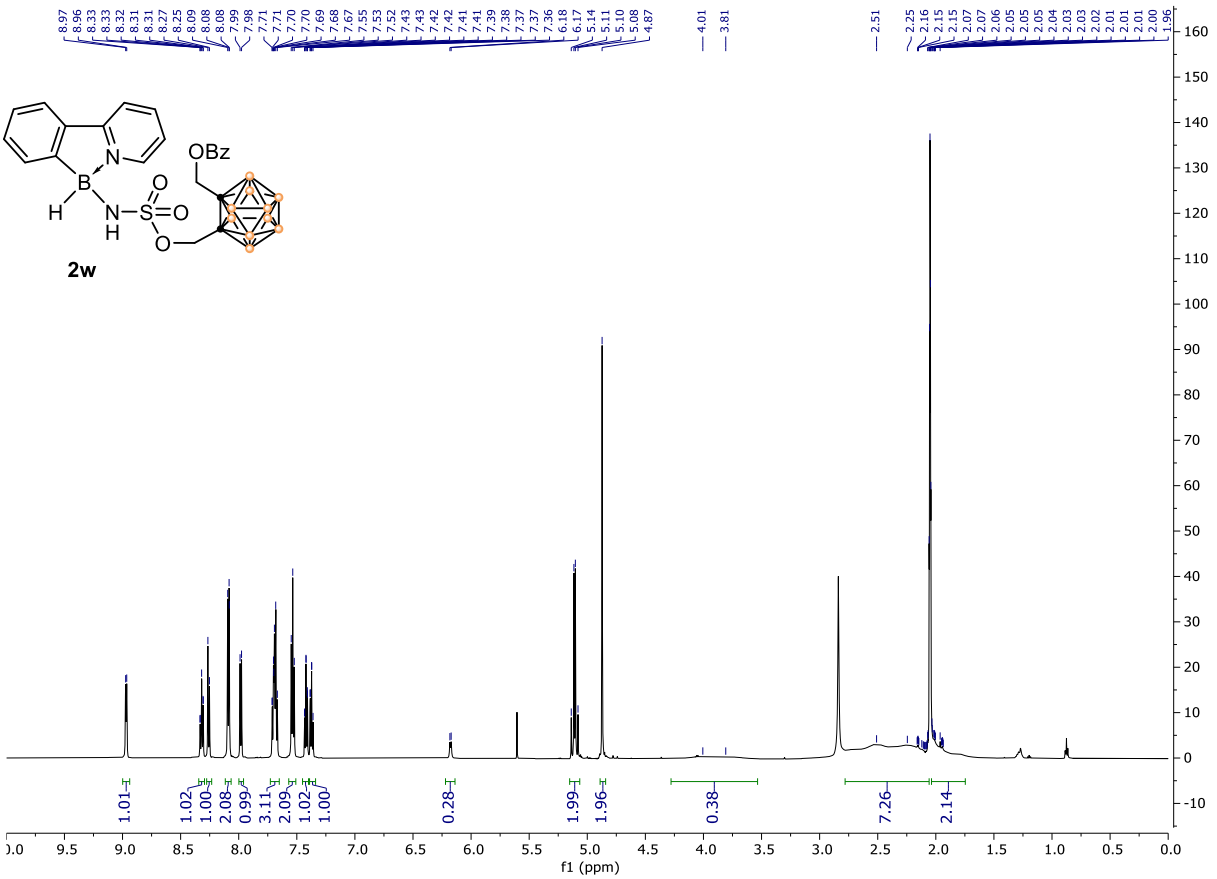


Fig. S152. ^{1}H NMR spectrum of **2w** in acetone-d_6.

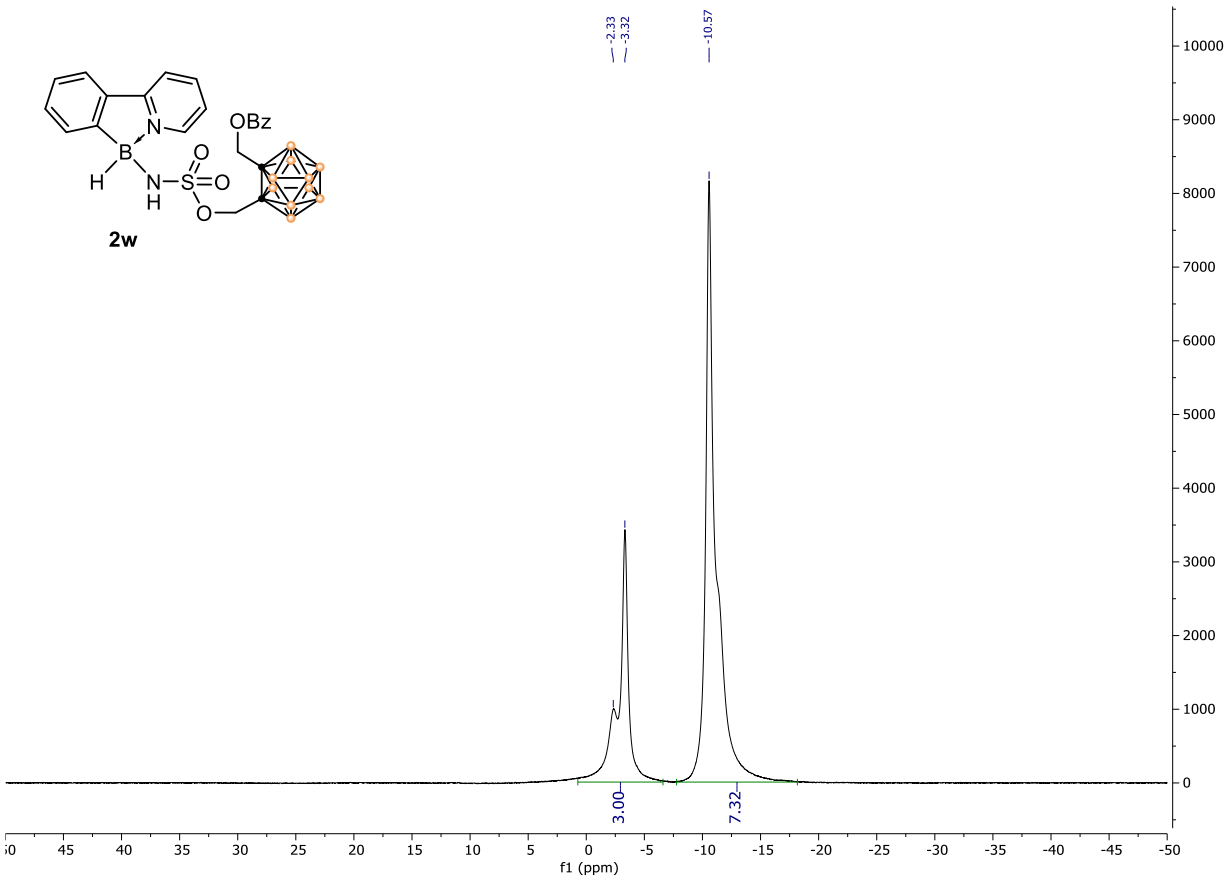


Fig. S153. $^{11}B\{^{1}H\}$ NMR spectrum of **2w** in acetone-d_6.

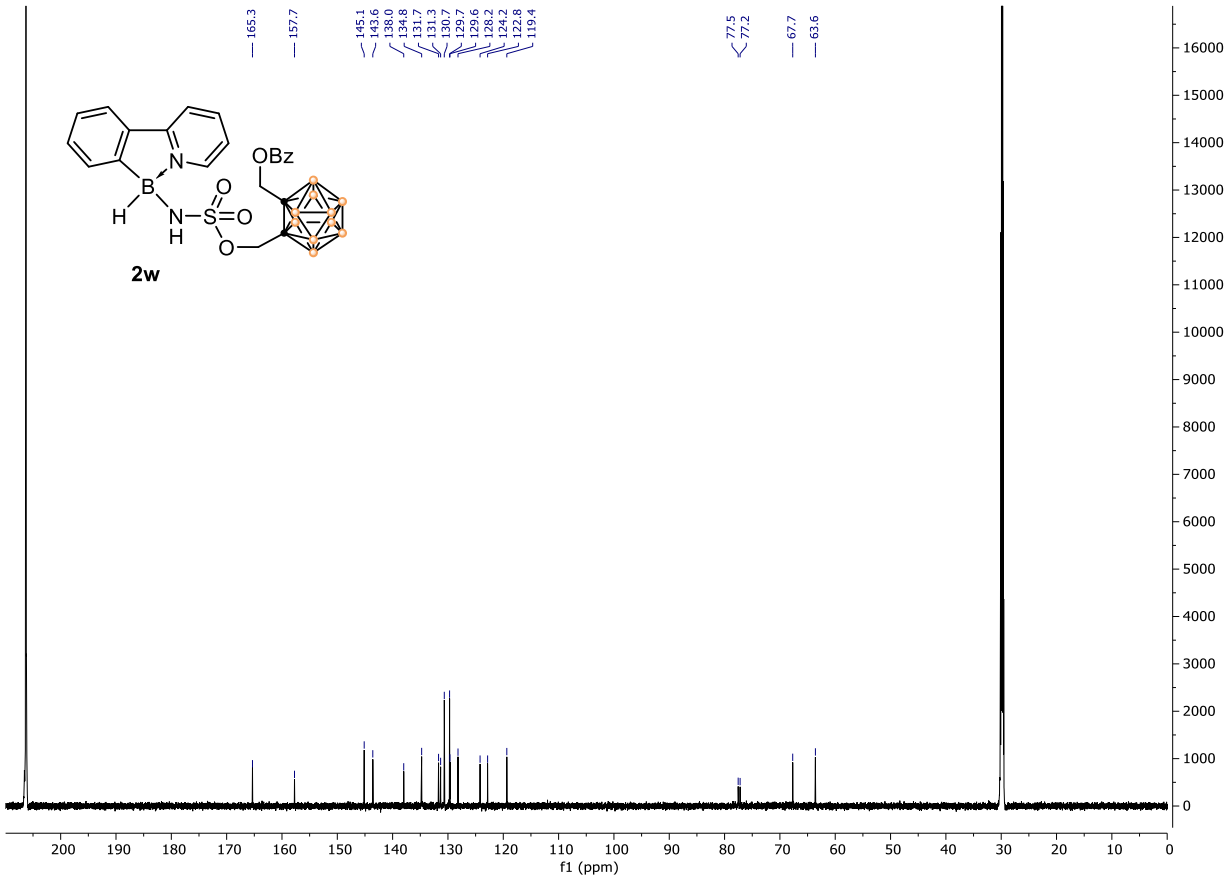


Fig. S154. ^{13}C NMR spectrum of **2w** in acetone-d_6.

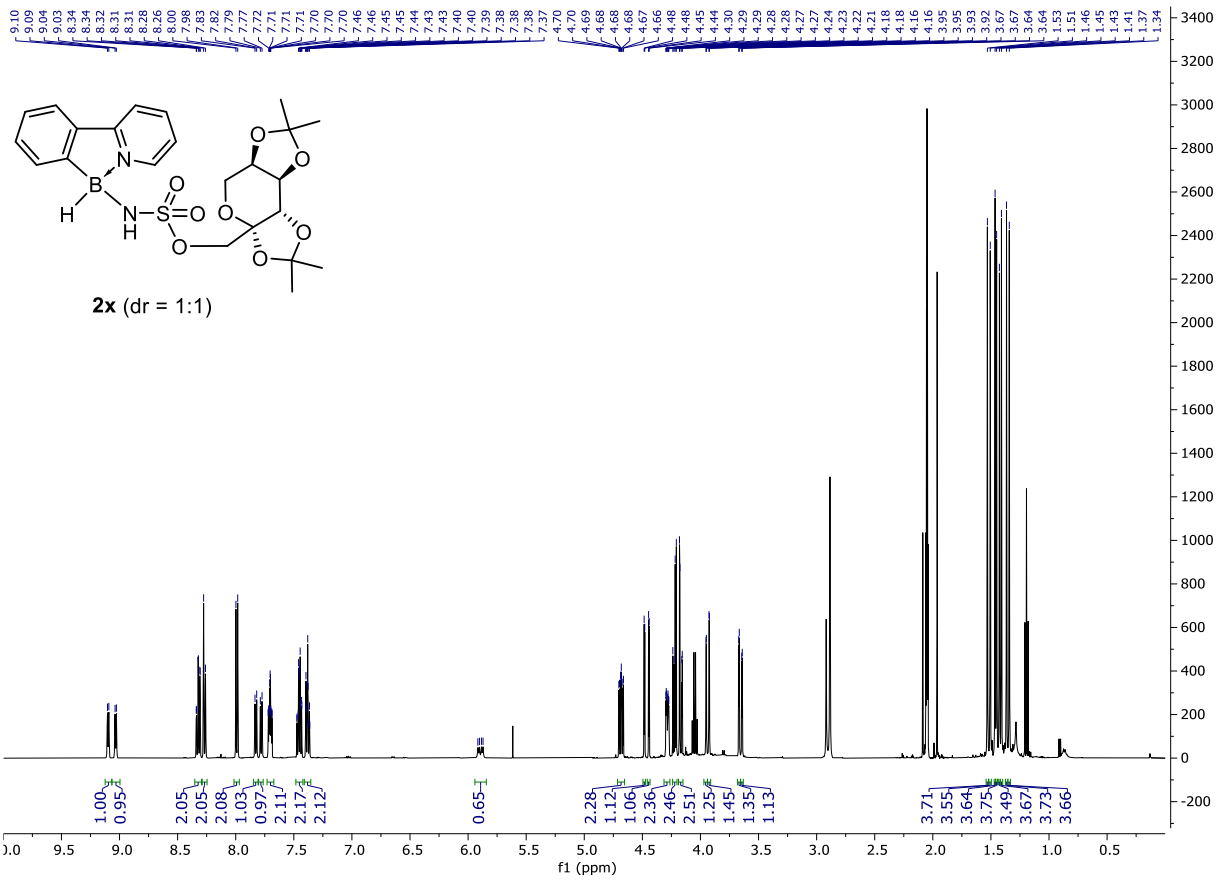


Fig. S155. ^{1}H NMR spectrum of **2x** in acetone-d_6.

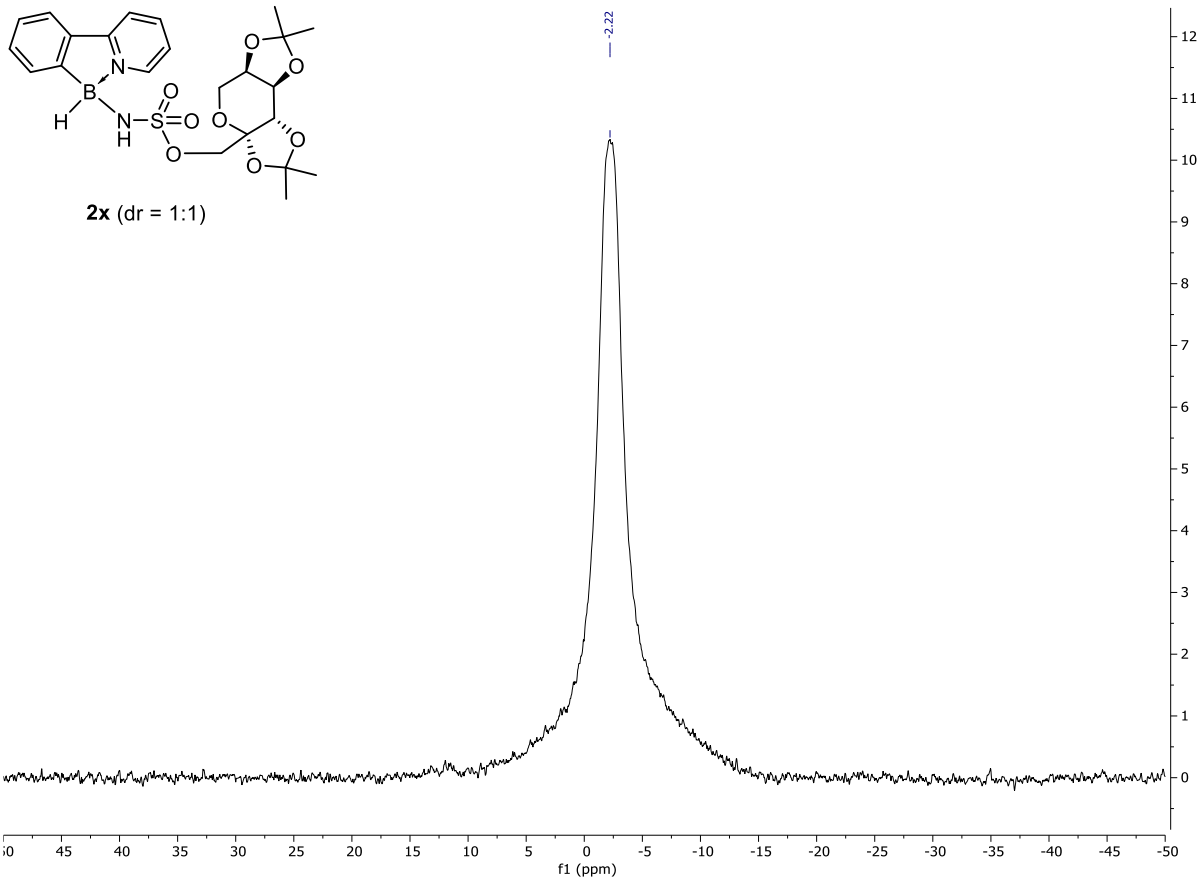


Fig. S156. ^{11}B NMR spectrum of **2x** in acetone-d_6.

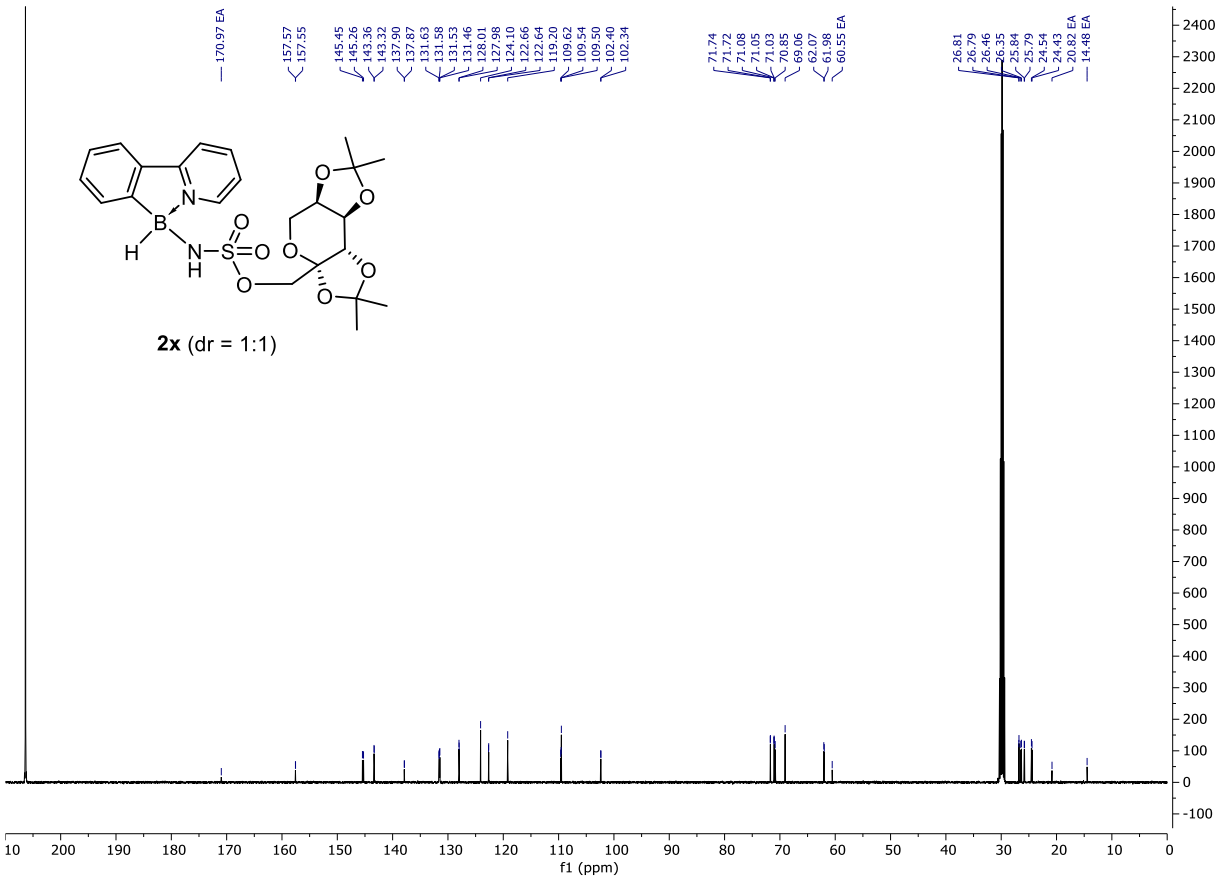


Fig. S157. ^{13}C NMR spectrum of **2x** in acetone-d_6.

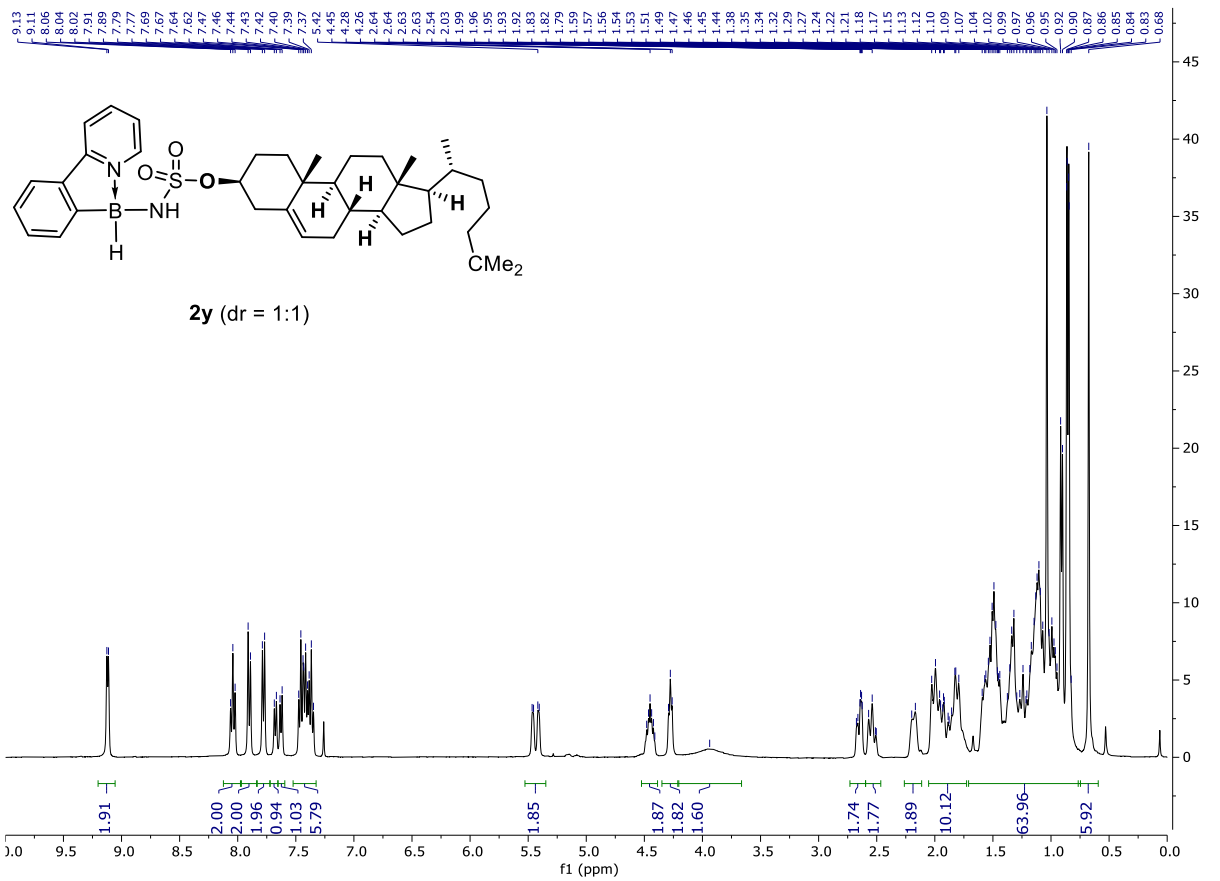


Fig. S158. ^{1}H NMR spectrum of **2y** in $CDCl_3$.

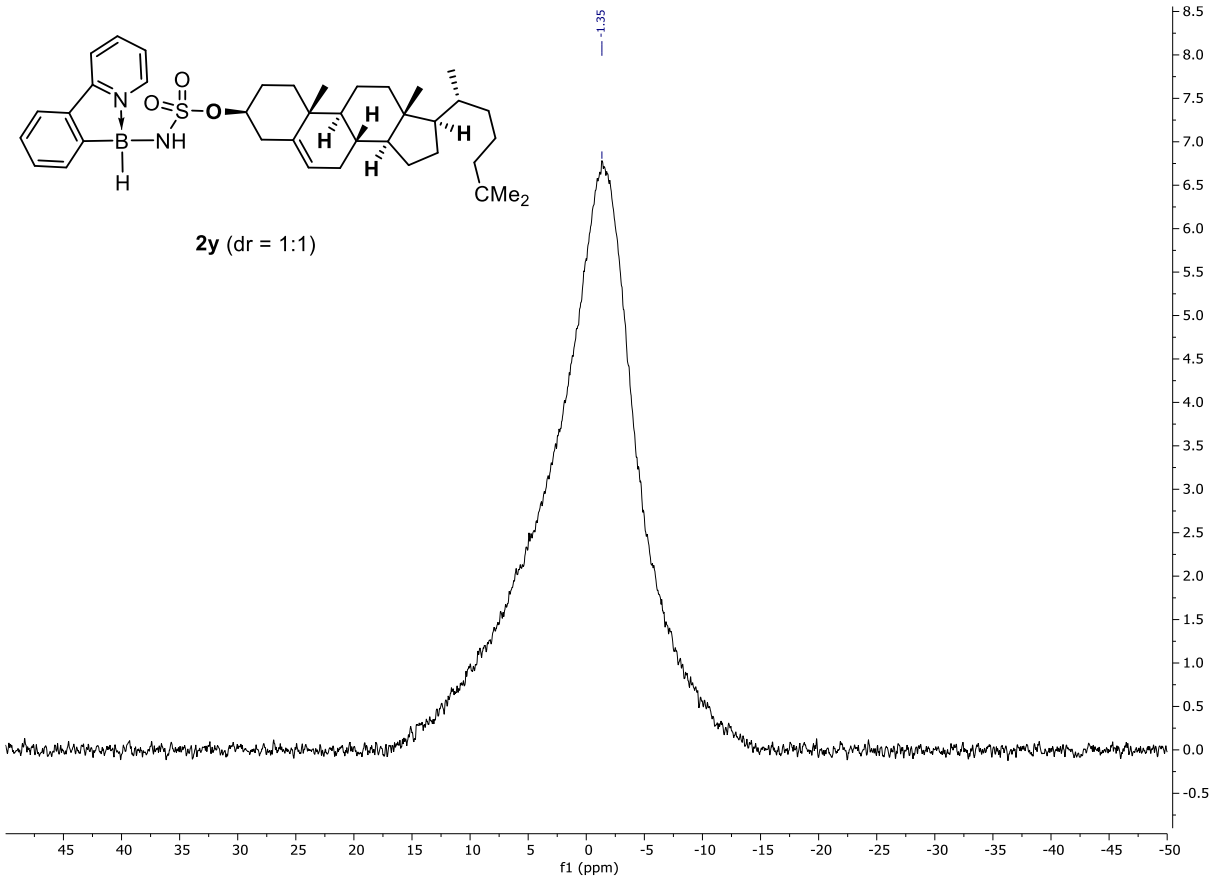


Fig. S159. ^{11}B NMR spectrum of **2y** in $CDCl_3$.

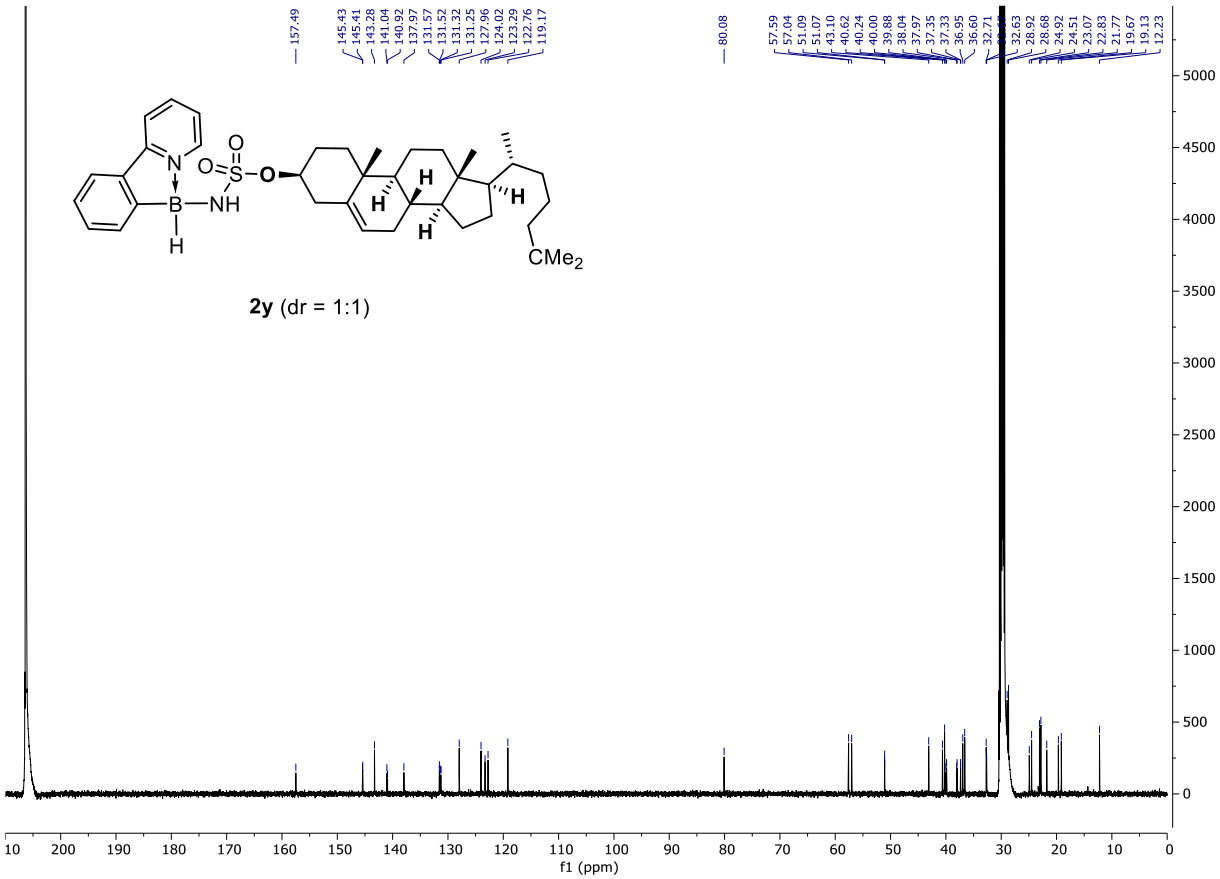


Fig. S160. ^{13}C NMR spectrum of **2y** in acetone-d_6.

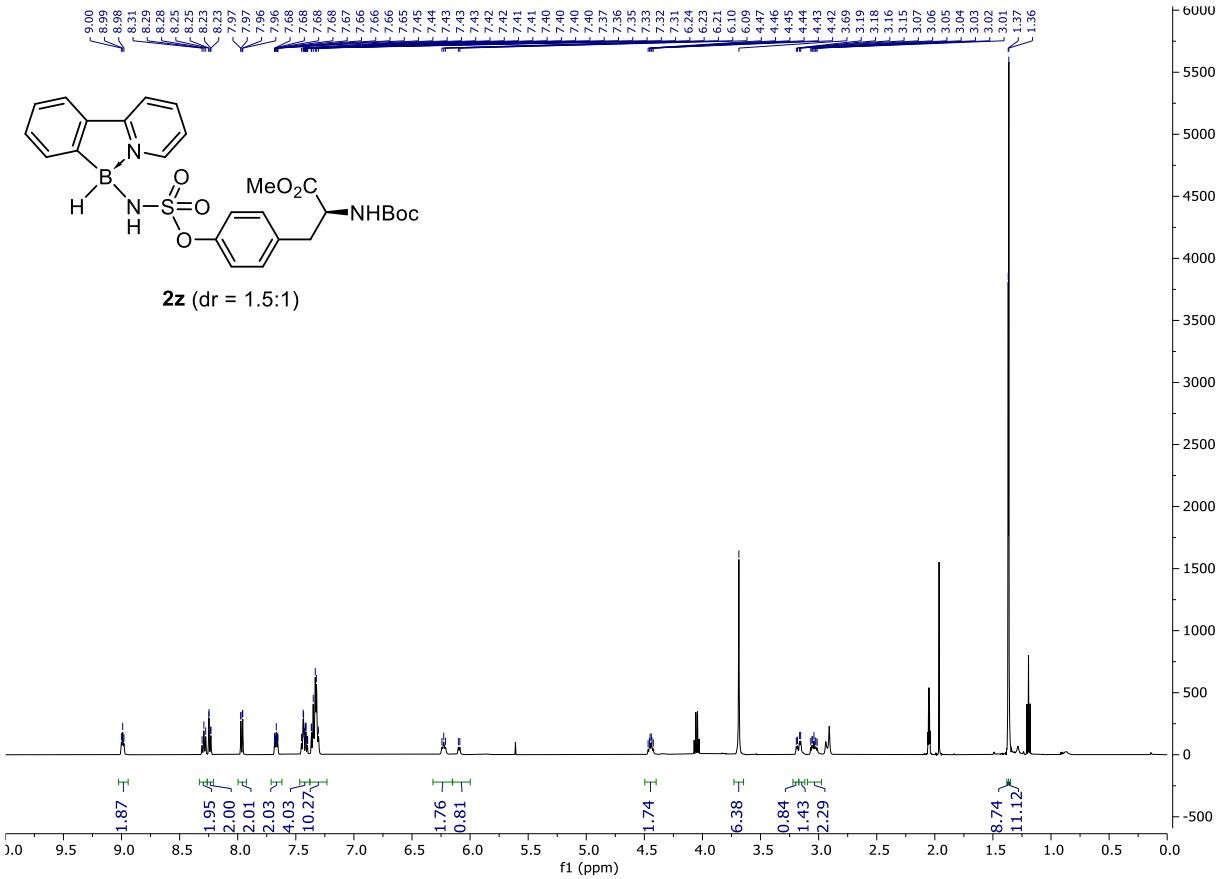


Fig. S161. ^{1}H NMR spectrum of **2z** in acetone-d_6.

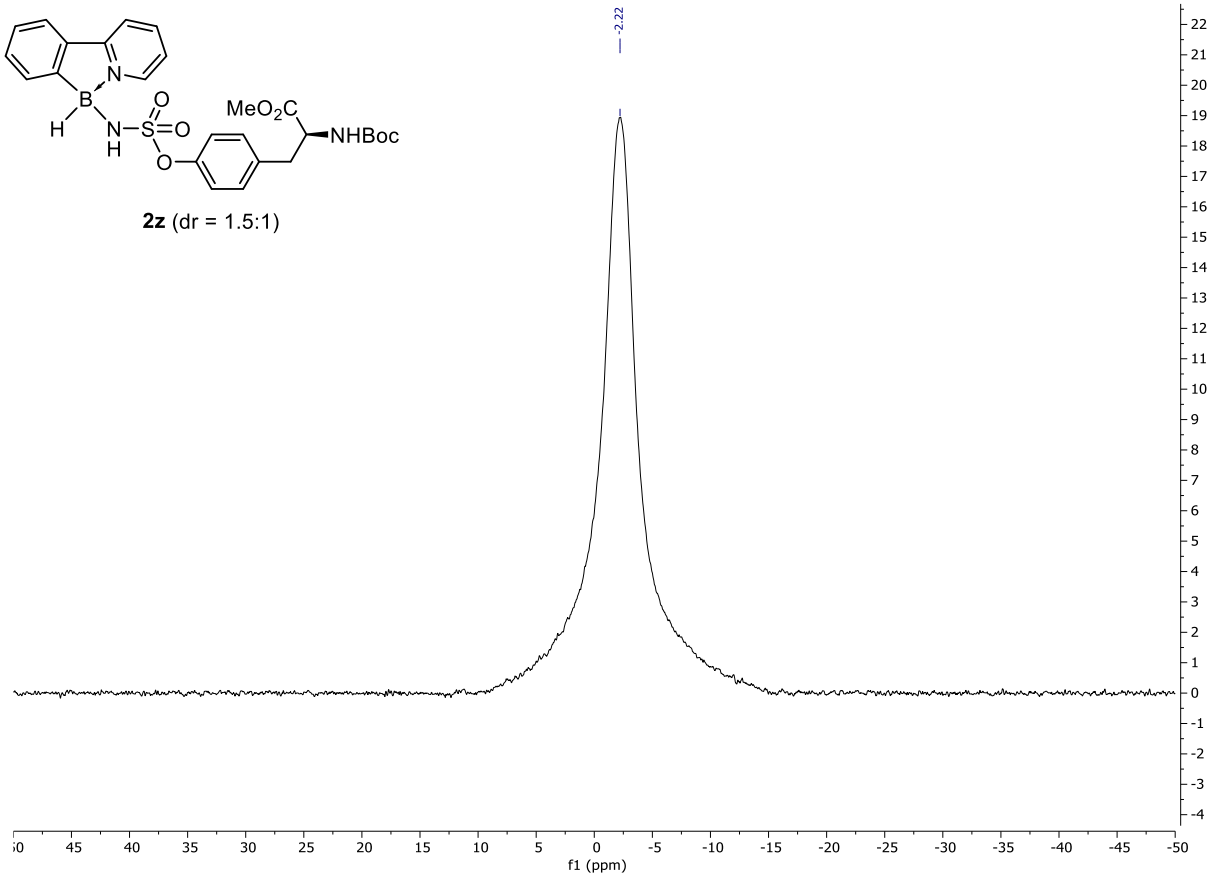


Fig. S162. ^{11}B NMR spectrum of **2z** in acetone-d_6.

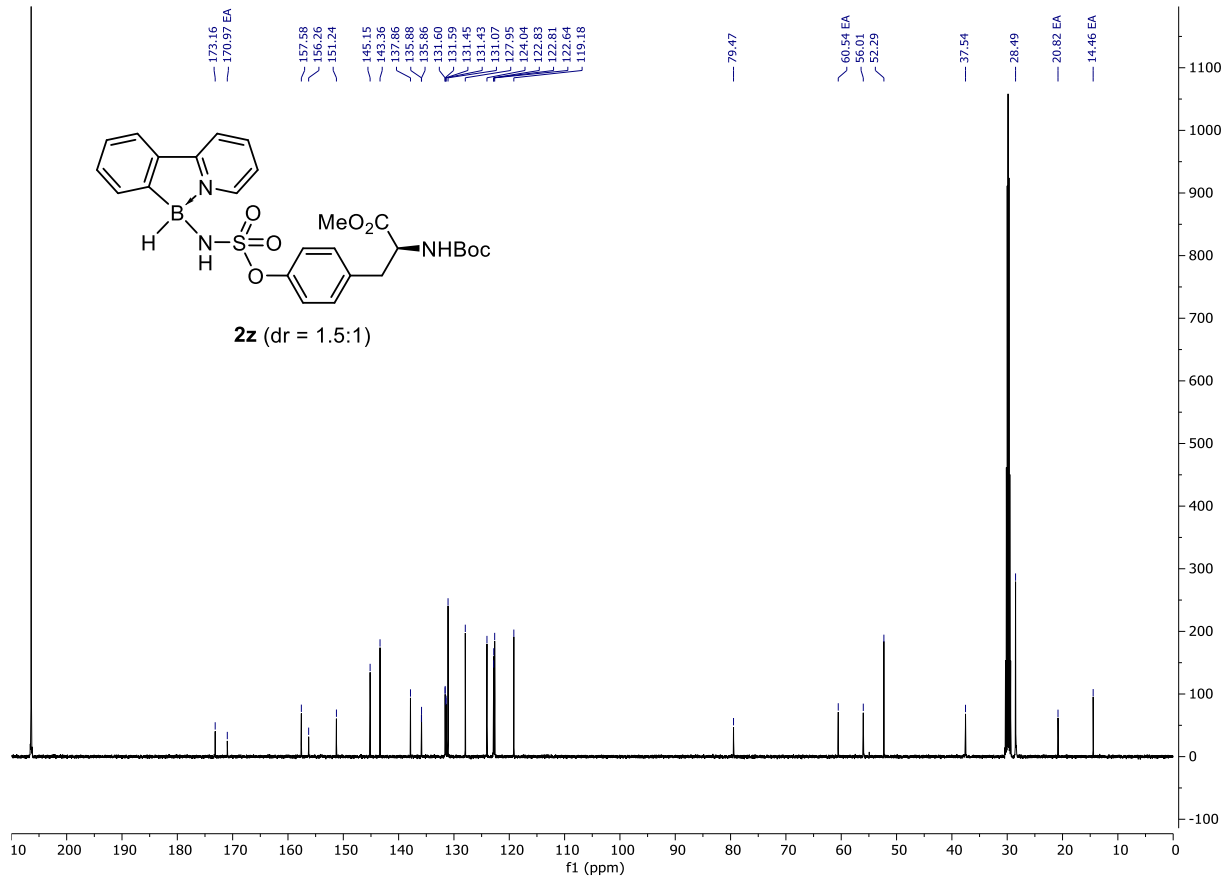


Fig. S163. ^{13}C NMR spectrum of **2z** in acetone-d_6.

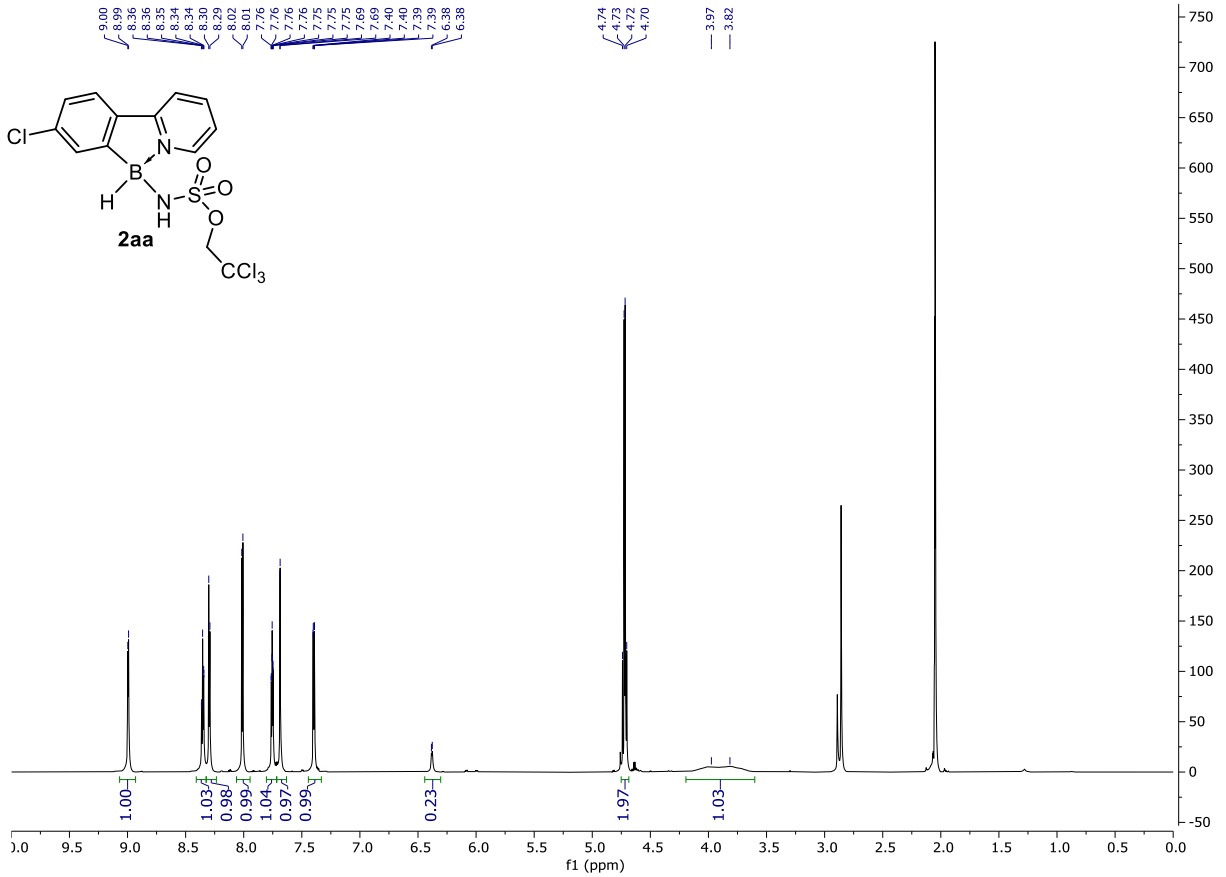


Fig. S164. ^{1}H NMR spectrum of **2aa** in acetone-d_6.

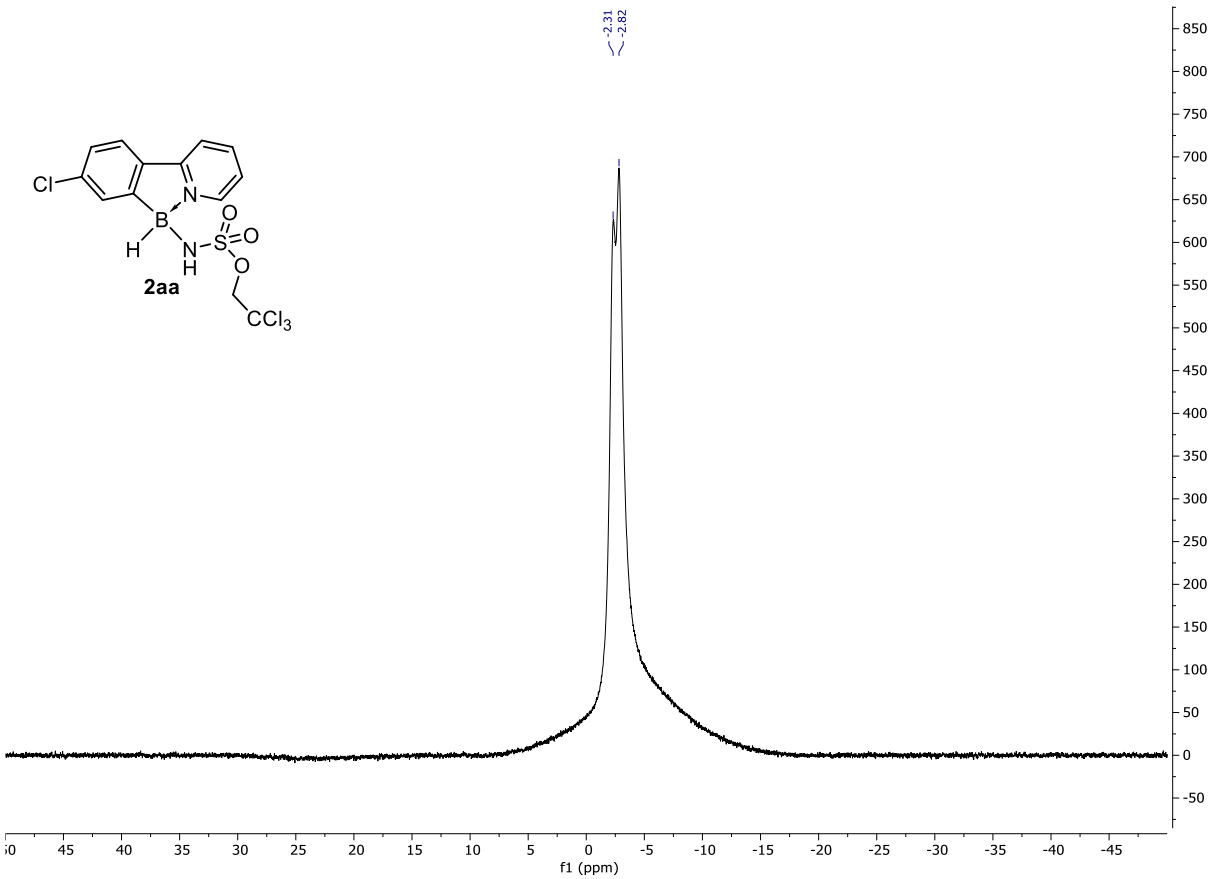


Fig. S165. ^{11}B NMR spectrum of **2aa** in acetone-d_6.

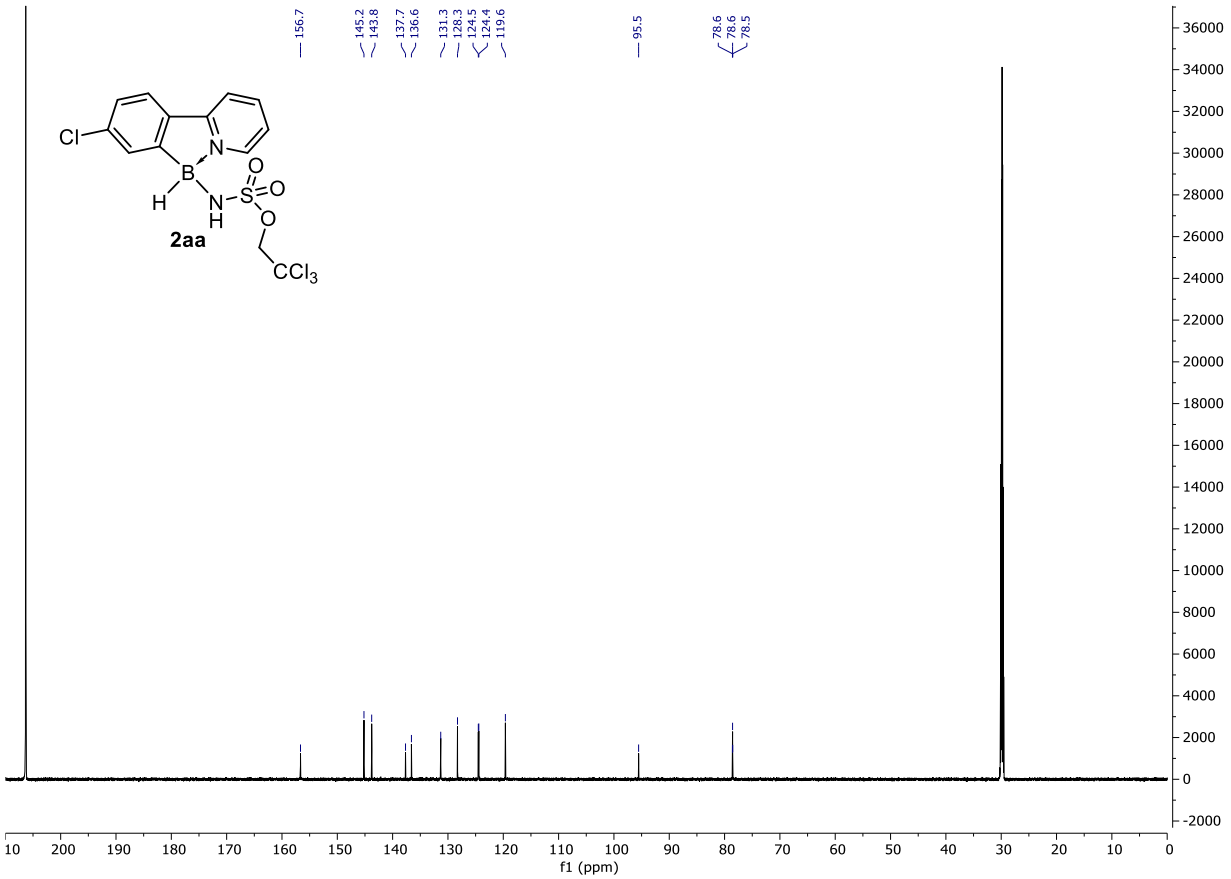


Fig. S166. ^{13}C NMR spectrum of **2aa** in acetone-d_6.

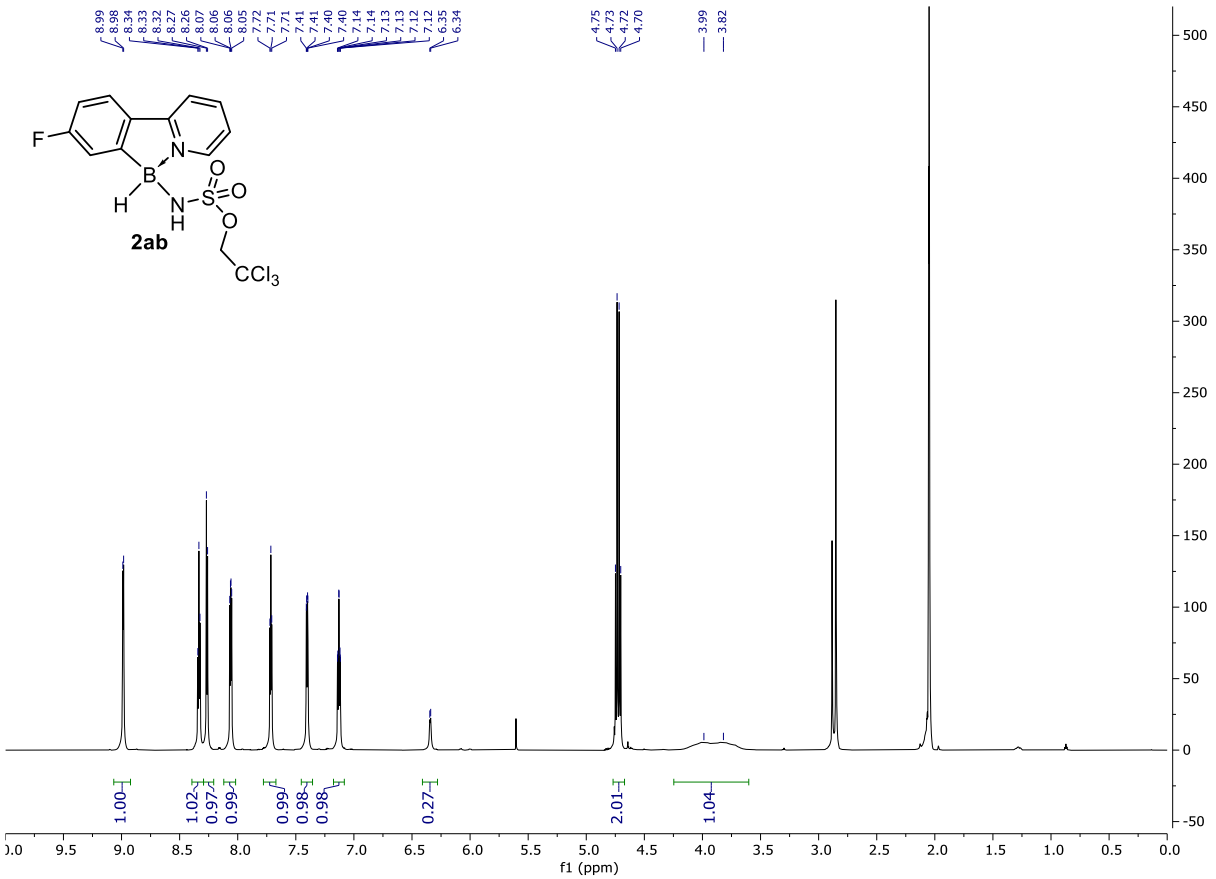


Fig. S167. ^{1}H NMR spectrum of **2ab** in acetone-d_6.

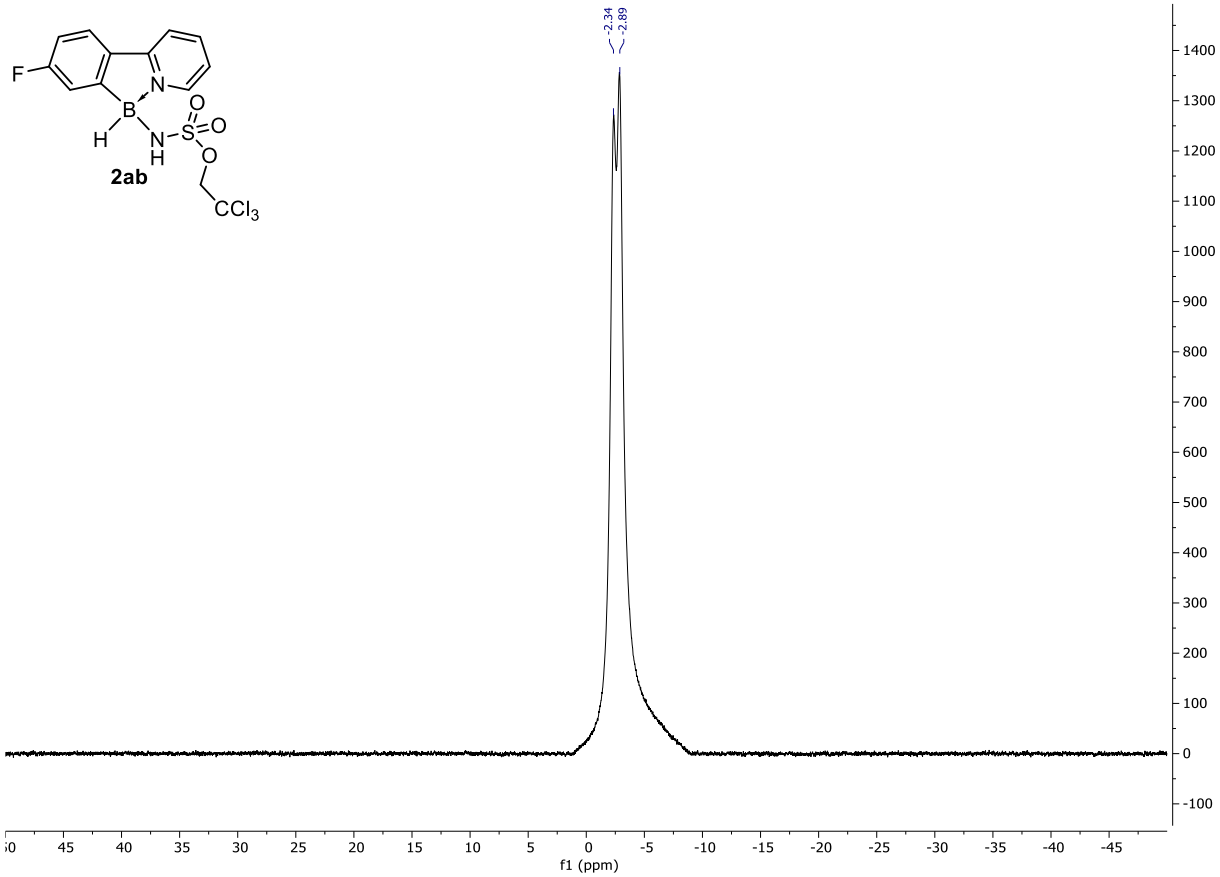


Fig. S168. ^{11}B NMR spectrum of **2ab** in acetone-d_6.

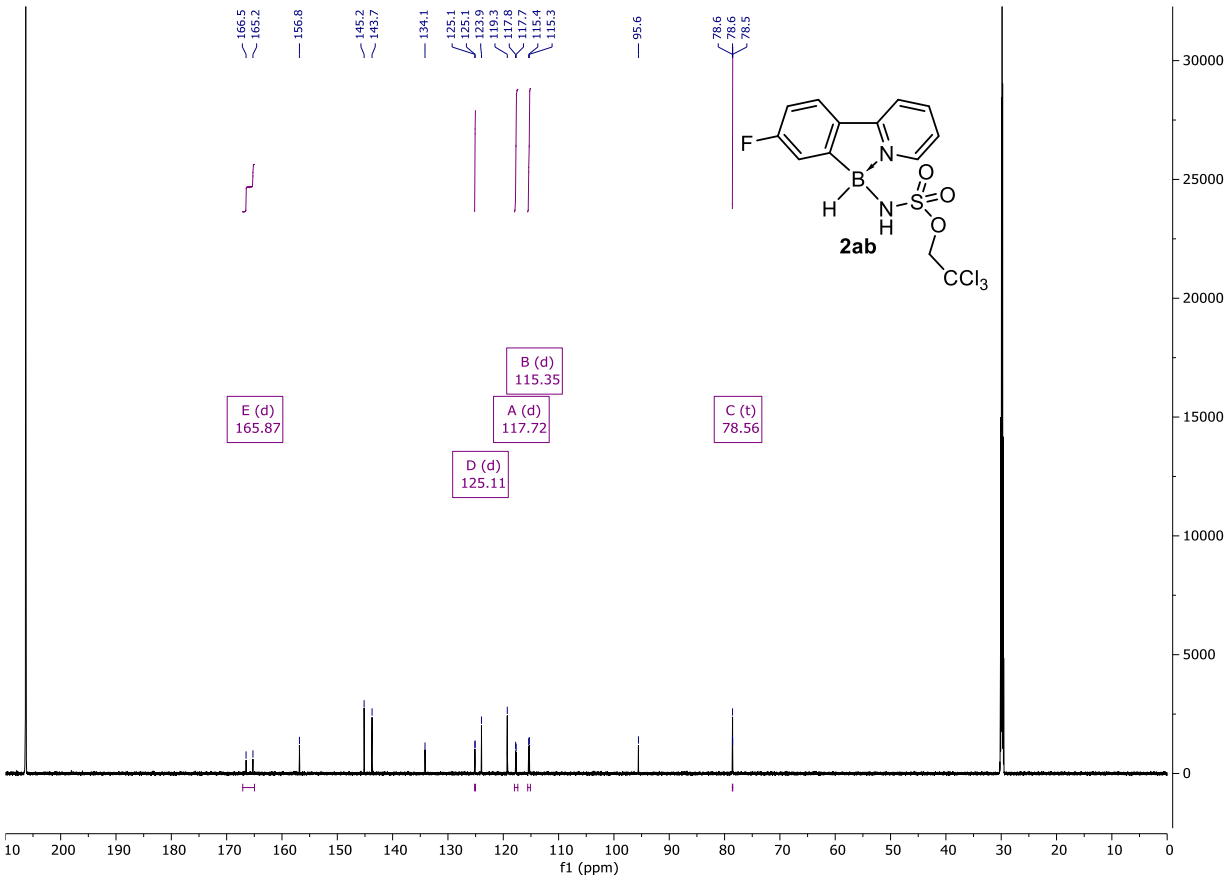


Fig. S169. ^{13}C NMR spectrum of **2ab** in acetone-d_6.

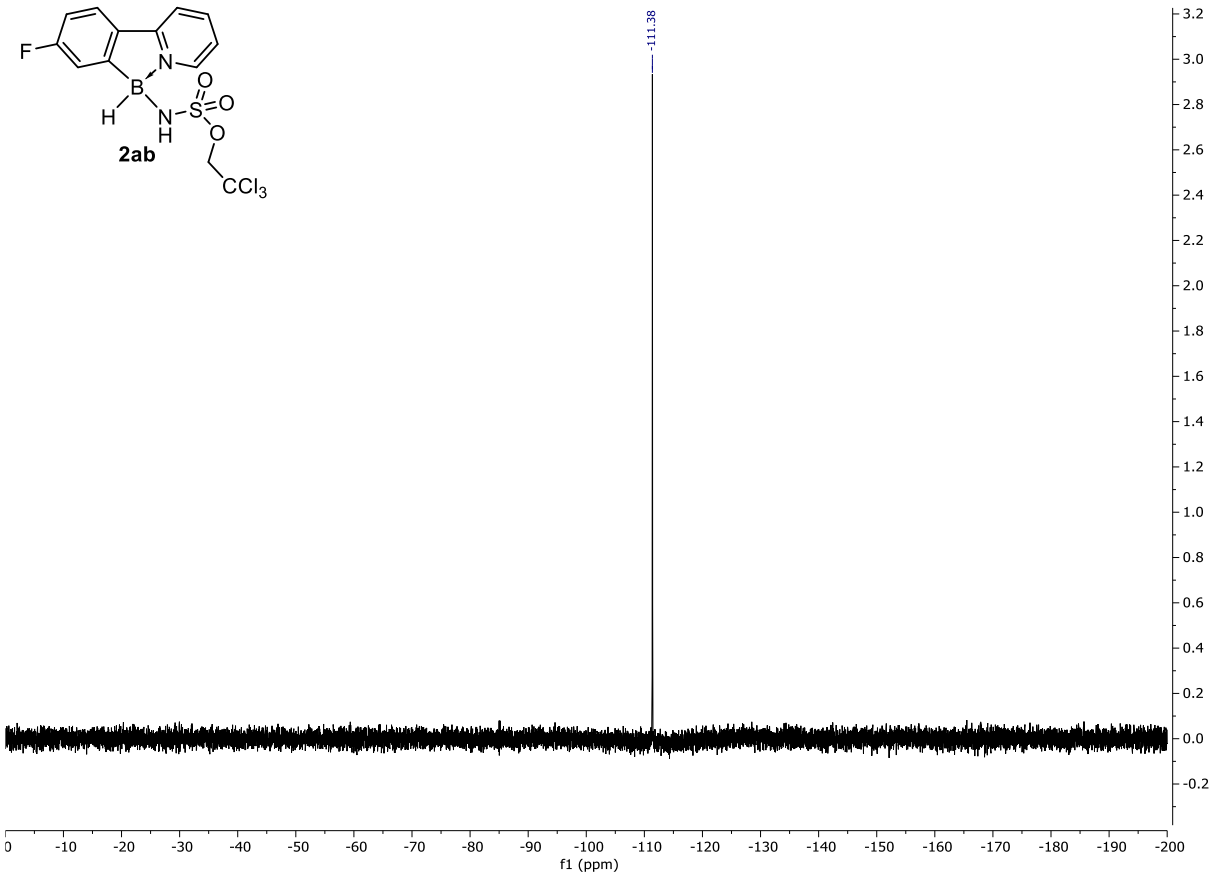


Fig. S170. ^{19}F NMR spectrum of **2ab** in acetone-d_6.

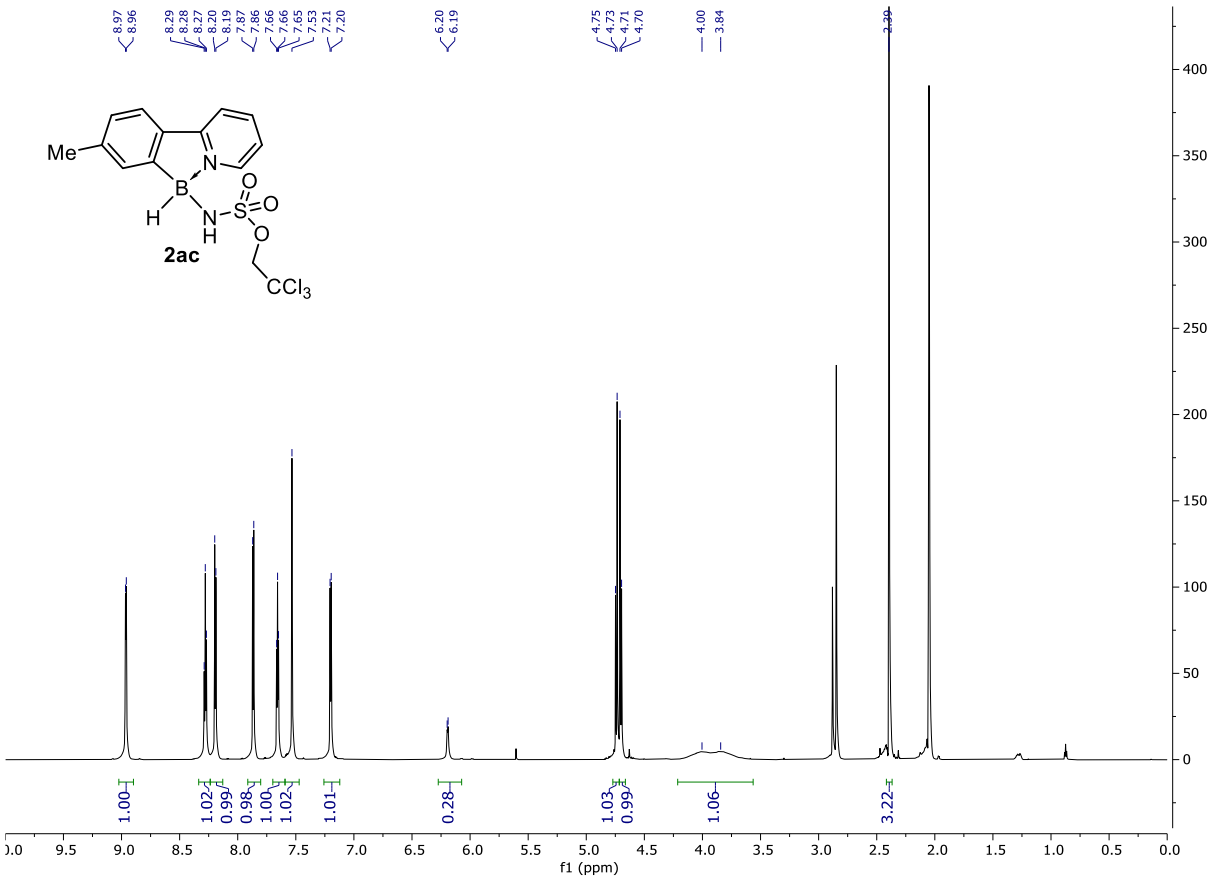


Fig. S171. ^{1}H NMR spectrum of **2ac** in acetone-d_6.

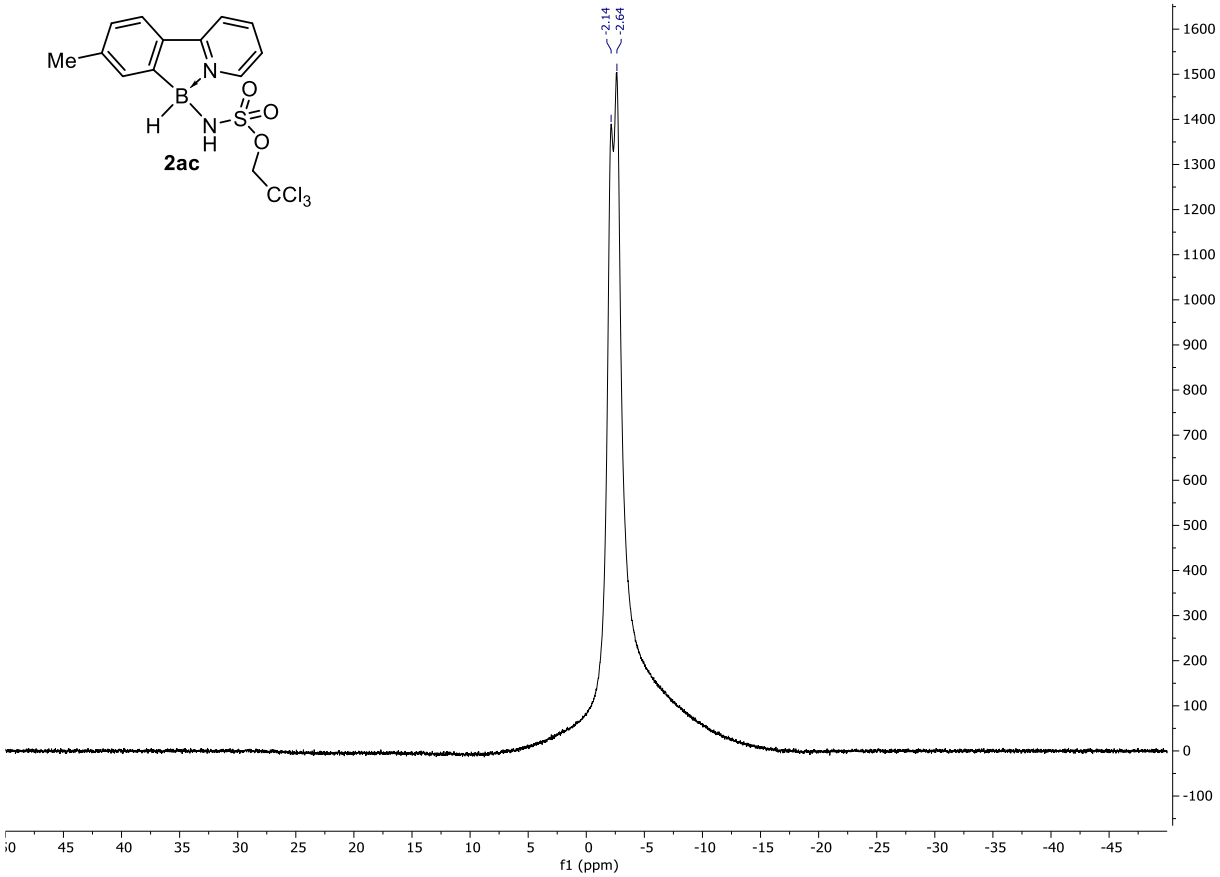


Fig. S172. ^{11}B NMR spectrum of **2ac** in acetone-d_6.

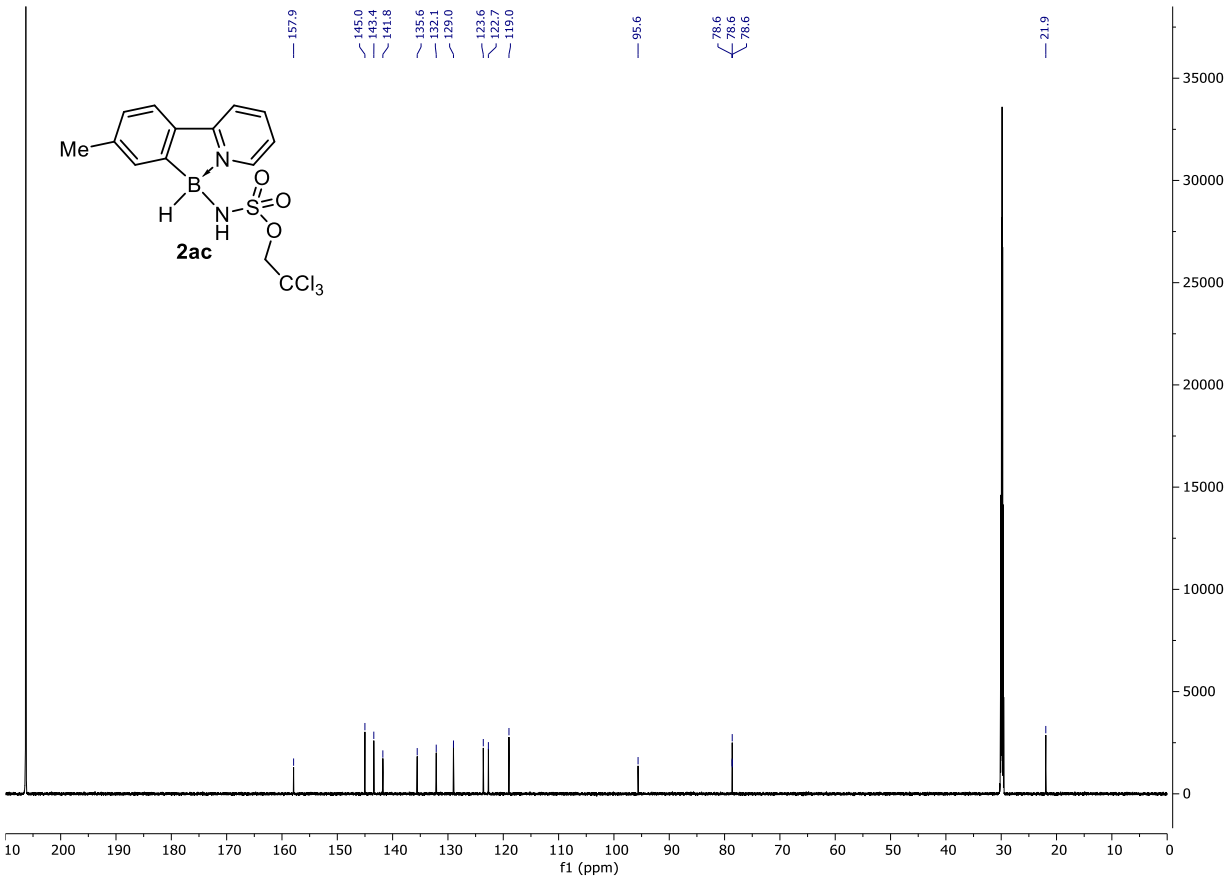


Fig. S173. ^{13}C NMR spectrum of **2ac** in acetone-d_6.

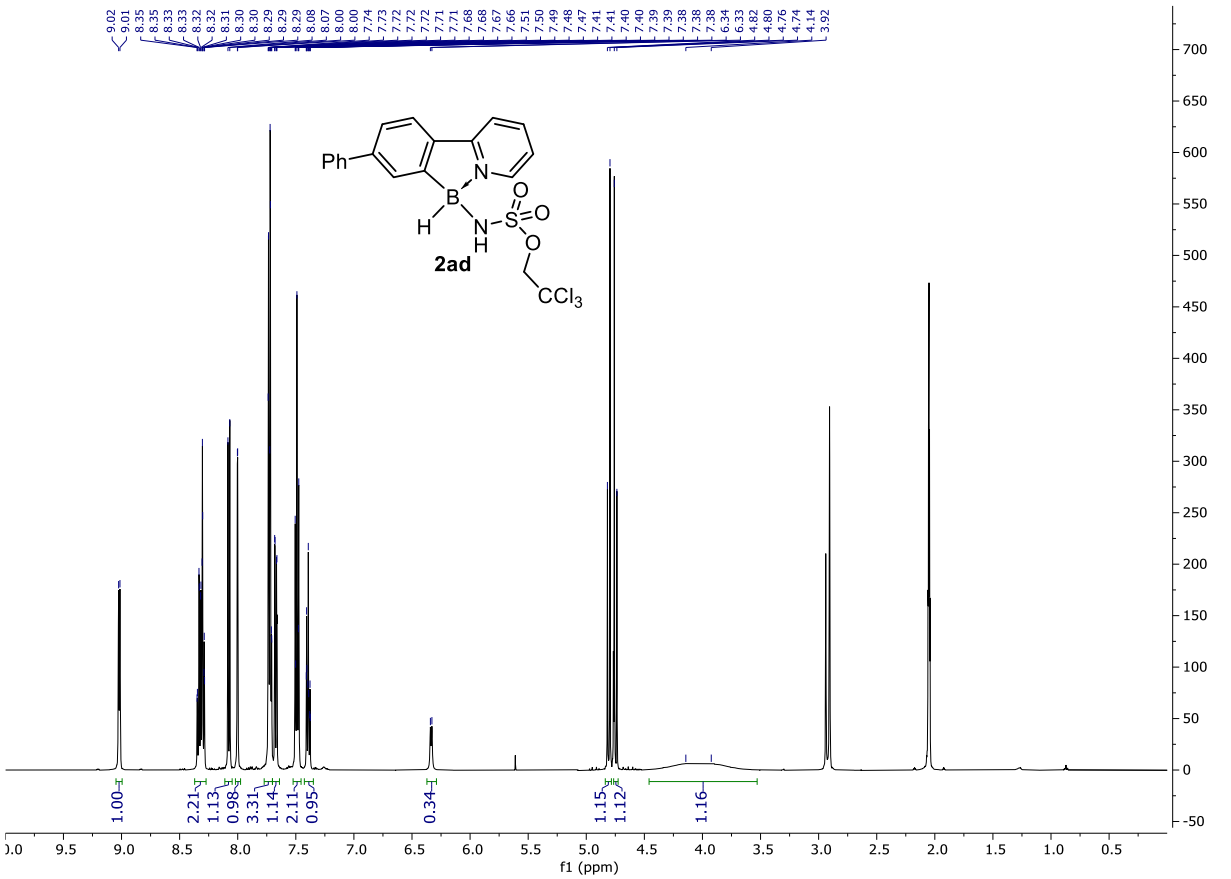


Fig. S174. ^{1}H NMR spectrum of **2ad** in acetone-d_6.

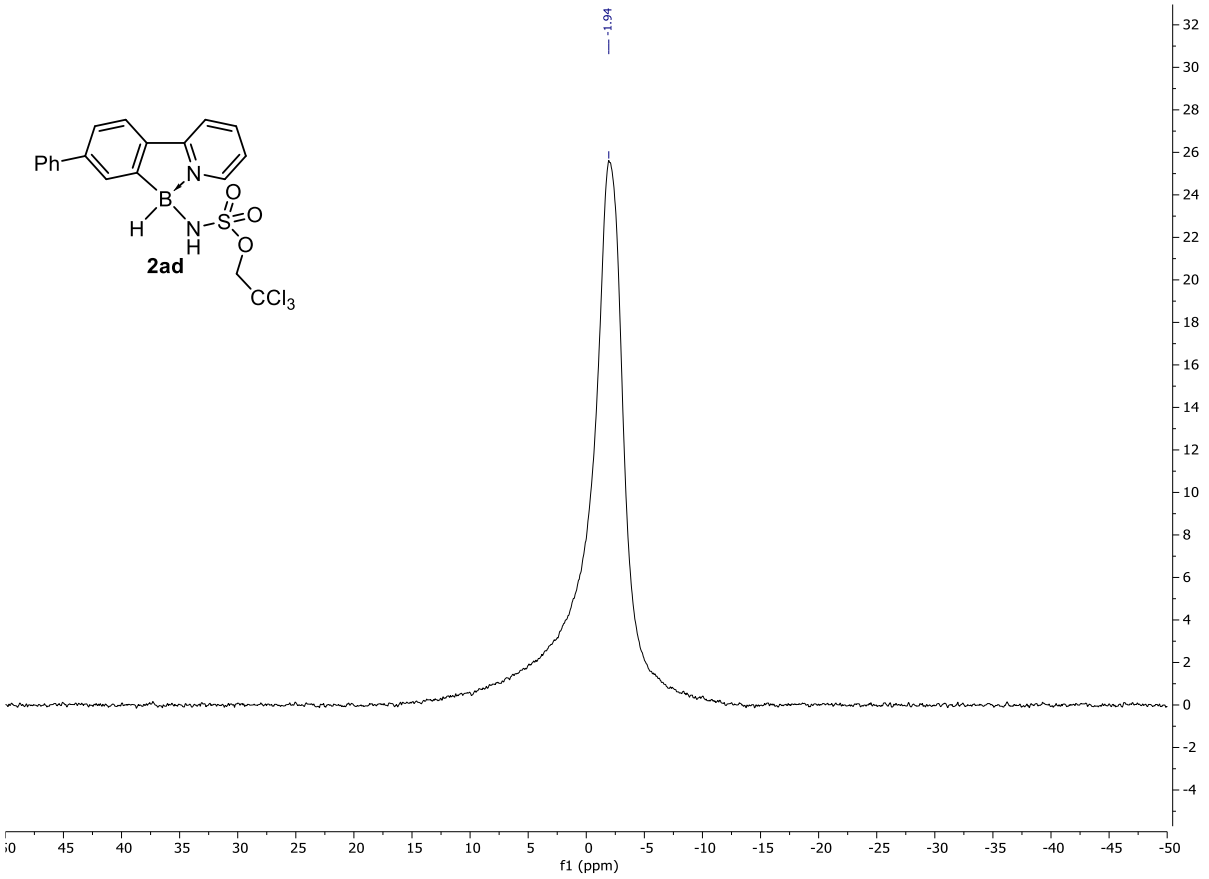


Fig. S175. ^{11}B NMR spectrum of **2ad** in acetone-d_6.

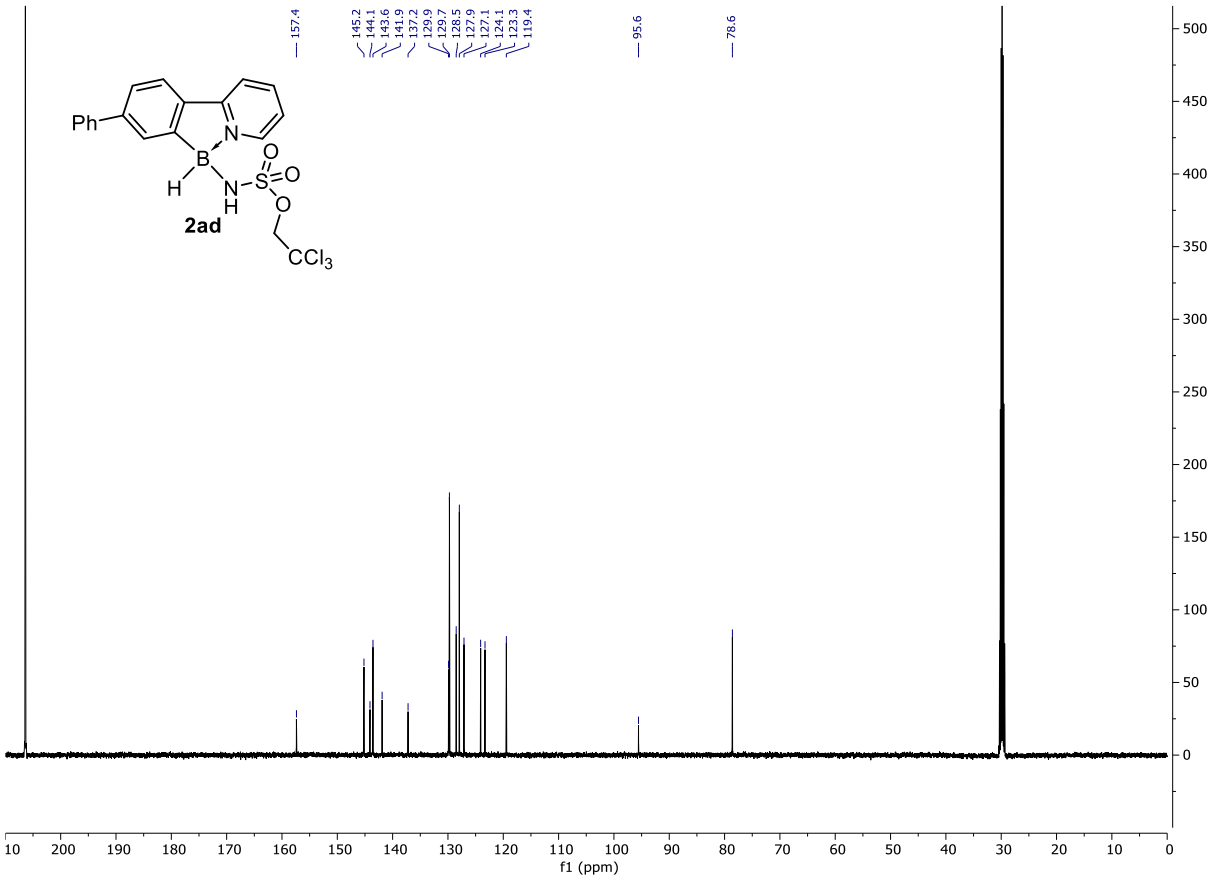


Fig. S176. ^{13}C NMR spectrum of **2ad** in acetone-d_6.

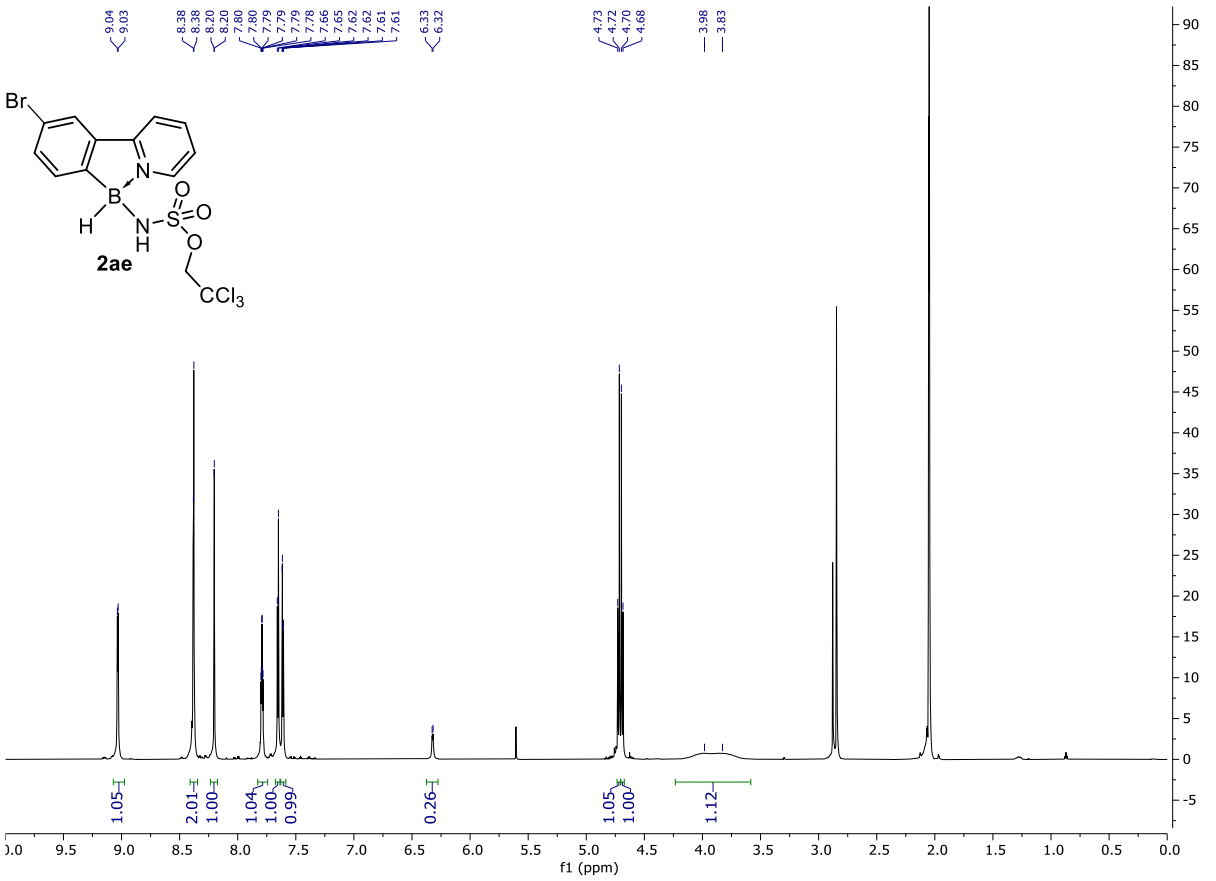


Fig. S177. ^{1}H NMR spectrum of **2ae** in acetone-d_6.

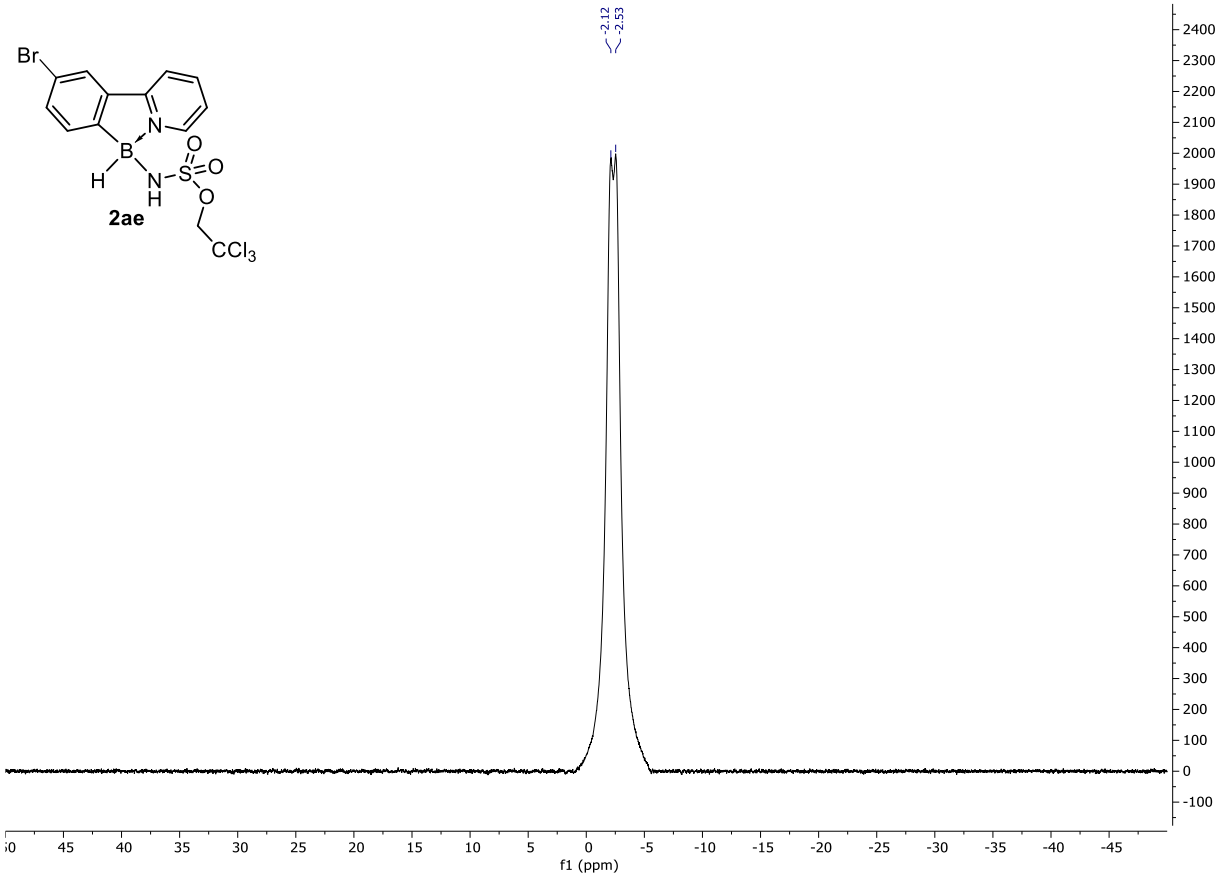


Fig. S178. ^{11}B NMR spectrum of **2ae** in acetone-d_6.

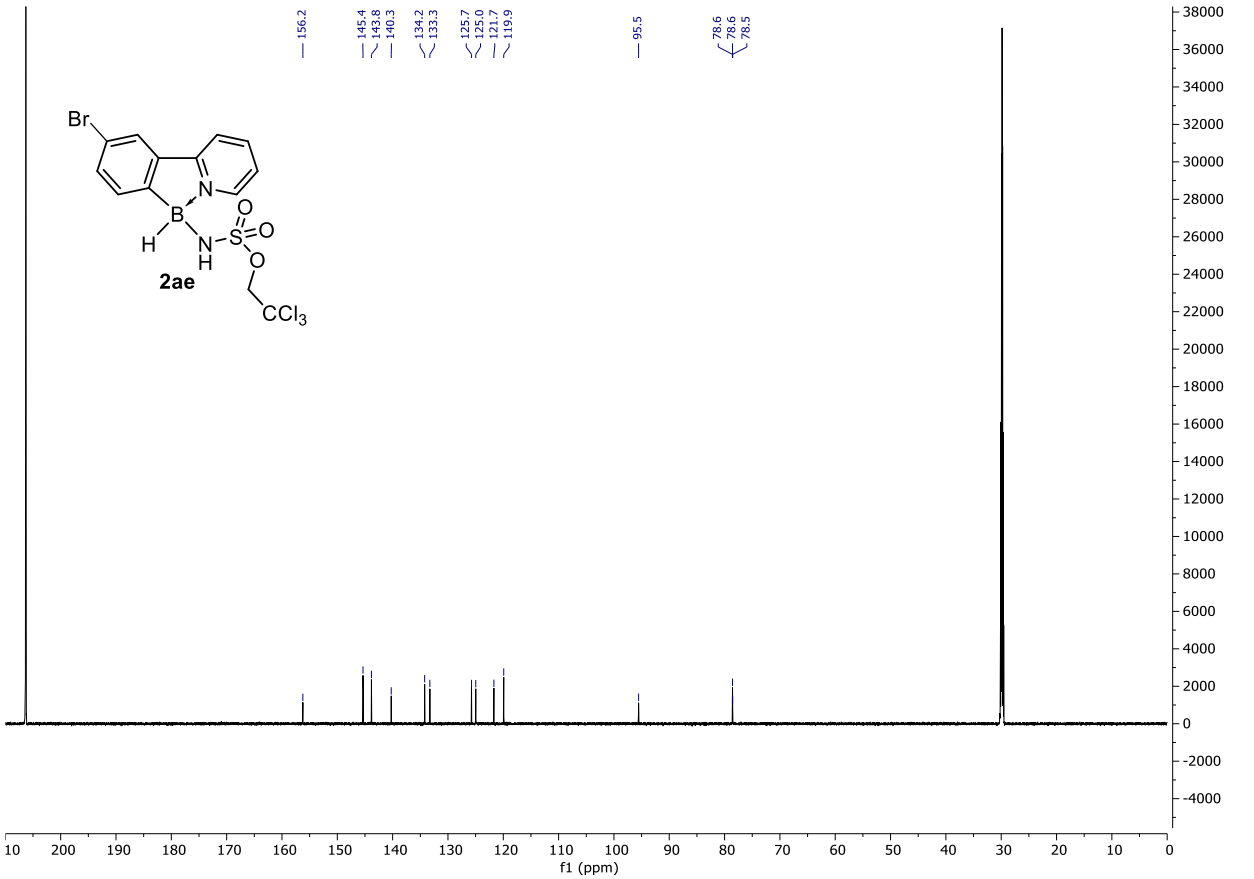


Fig. S179. ^{13}C NMR spectrum of **2ae** in acetone-d_6.

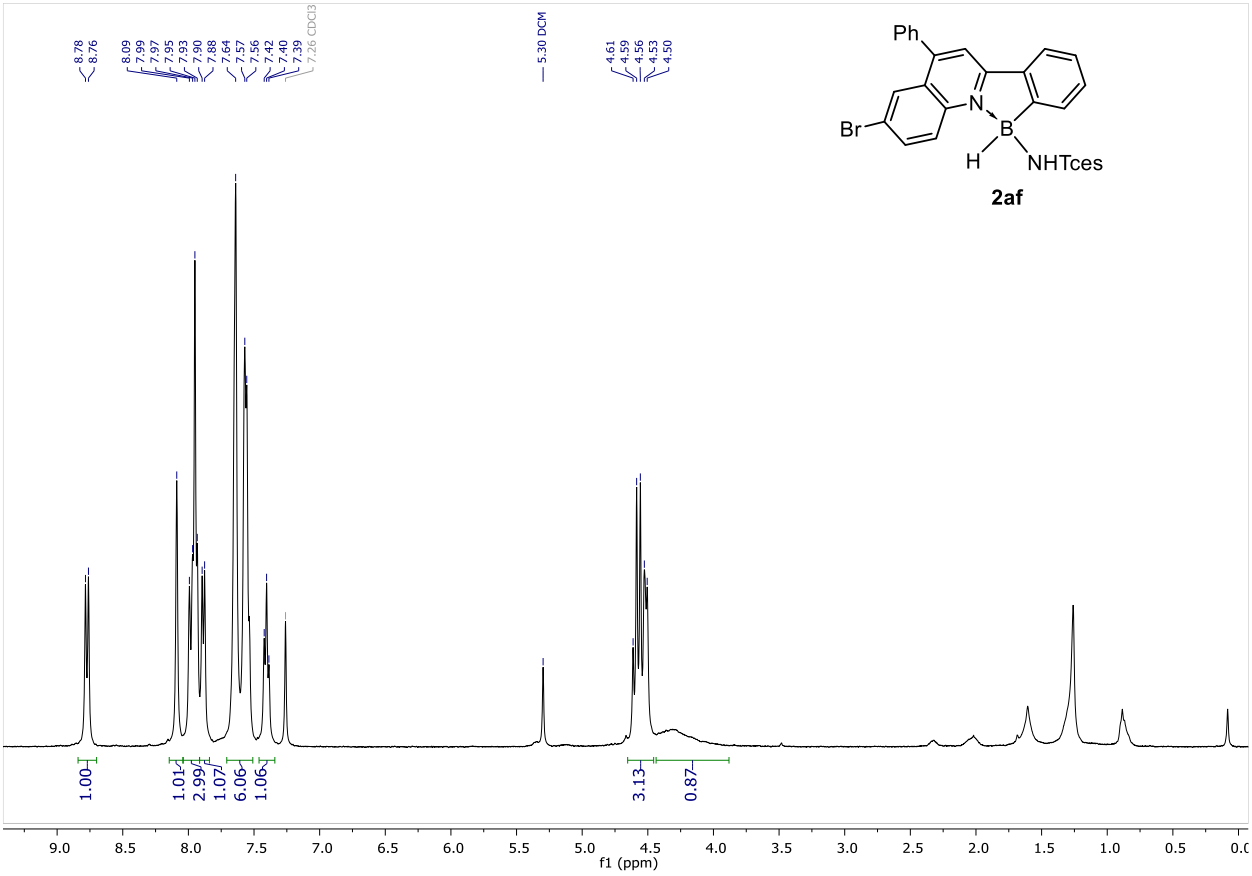


Fig. S180. ^{1}H NMR spectrum of **2af**.

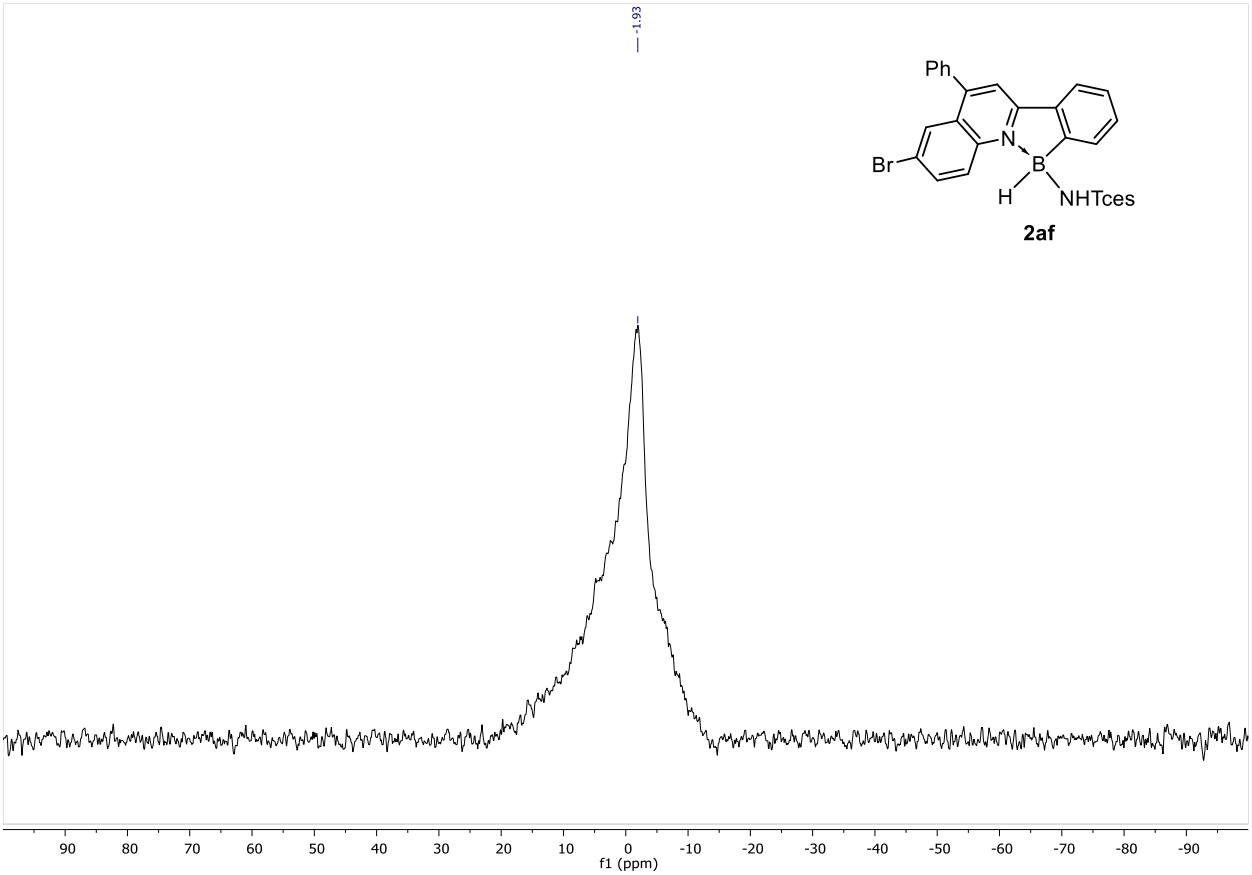


Fig. S181. ^{11}B NMR spectrum of **2af**.

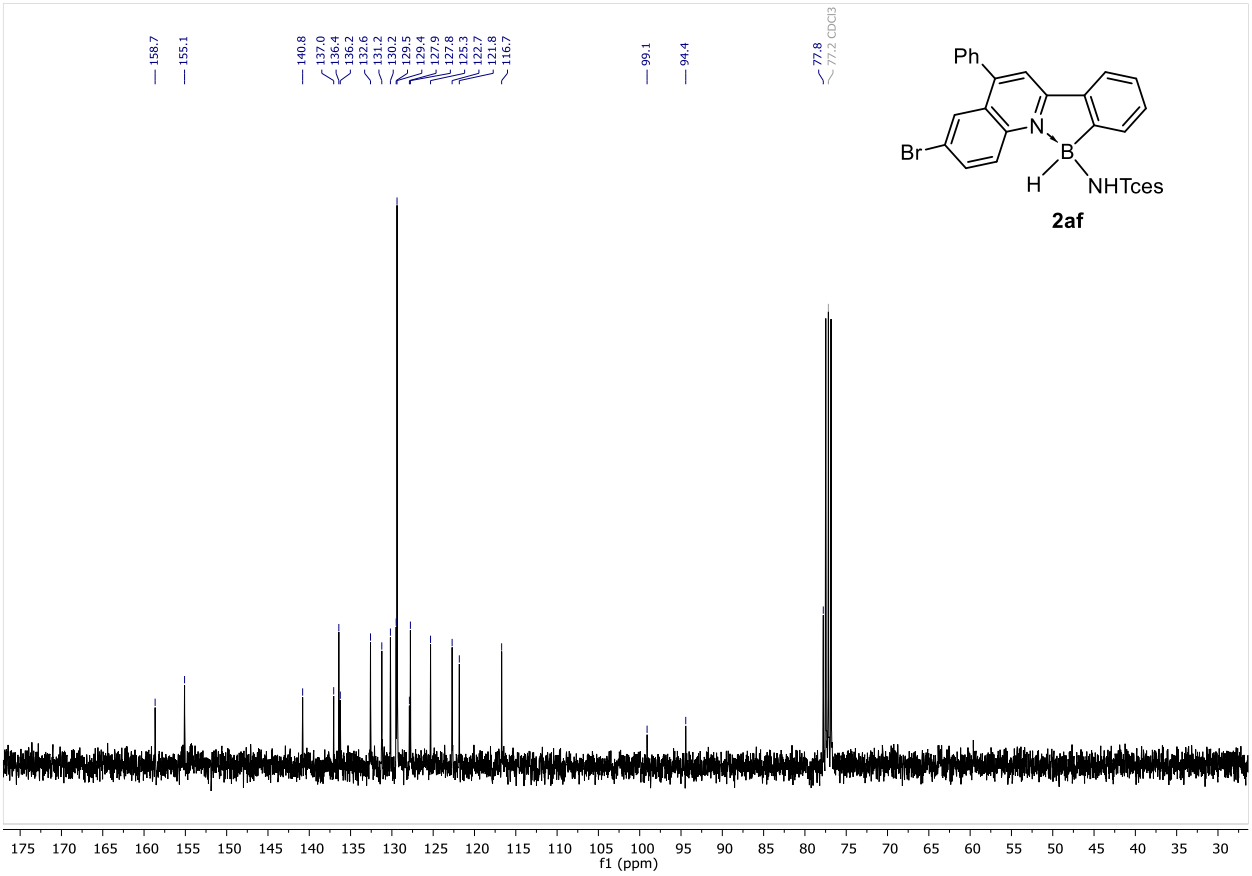


Fig. S182. ^{13}C NMR spectrum of **2af**.

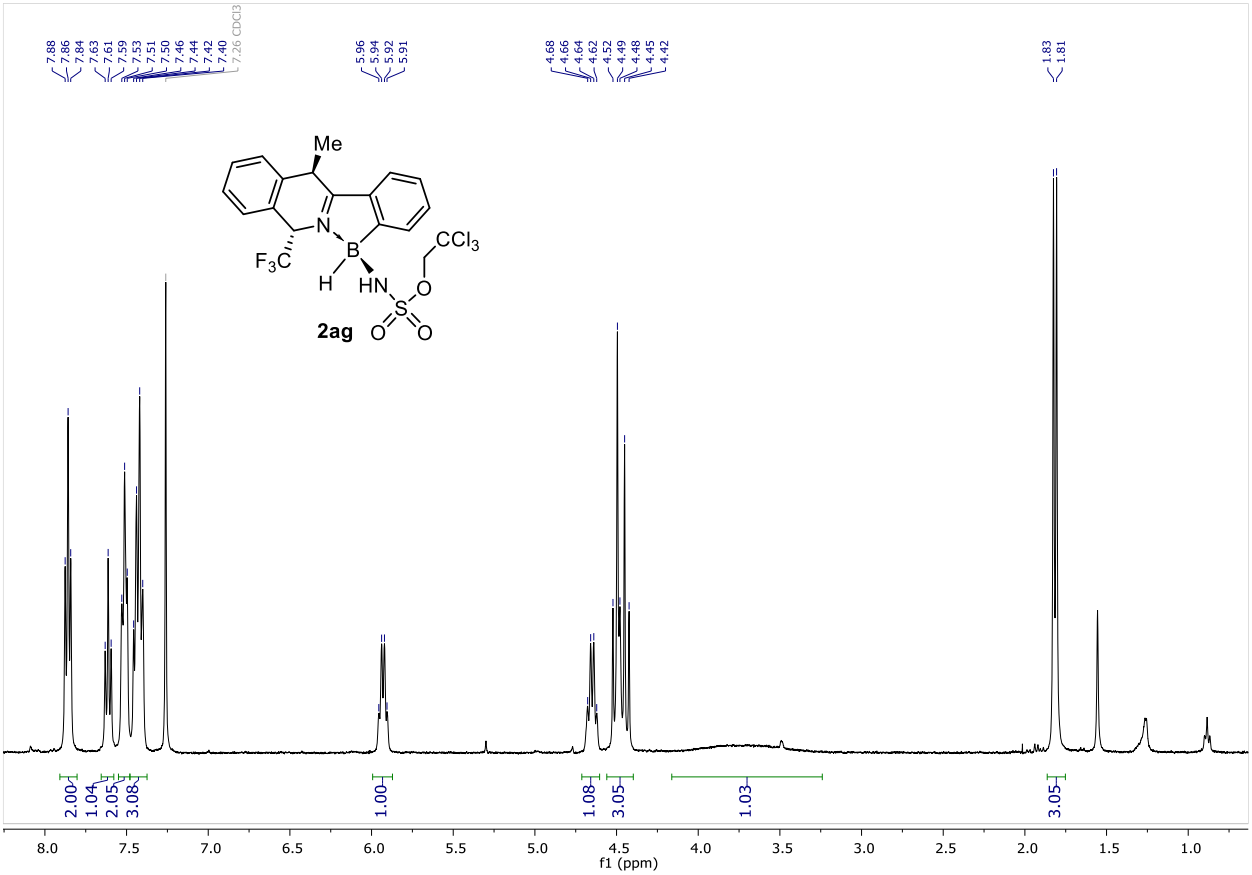


Fig. S183. ^{1}H NMR spectrum of **2ag**.

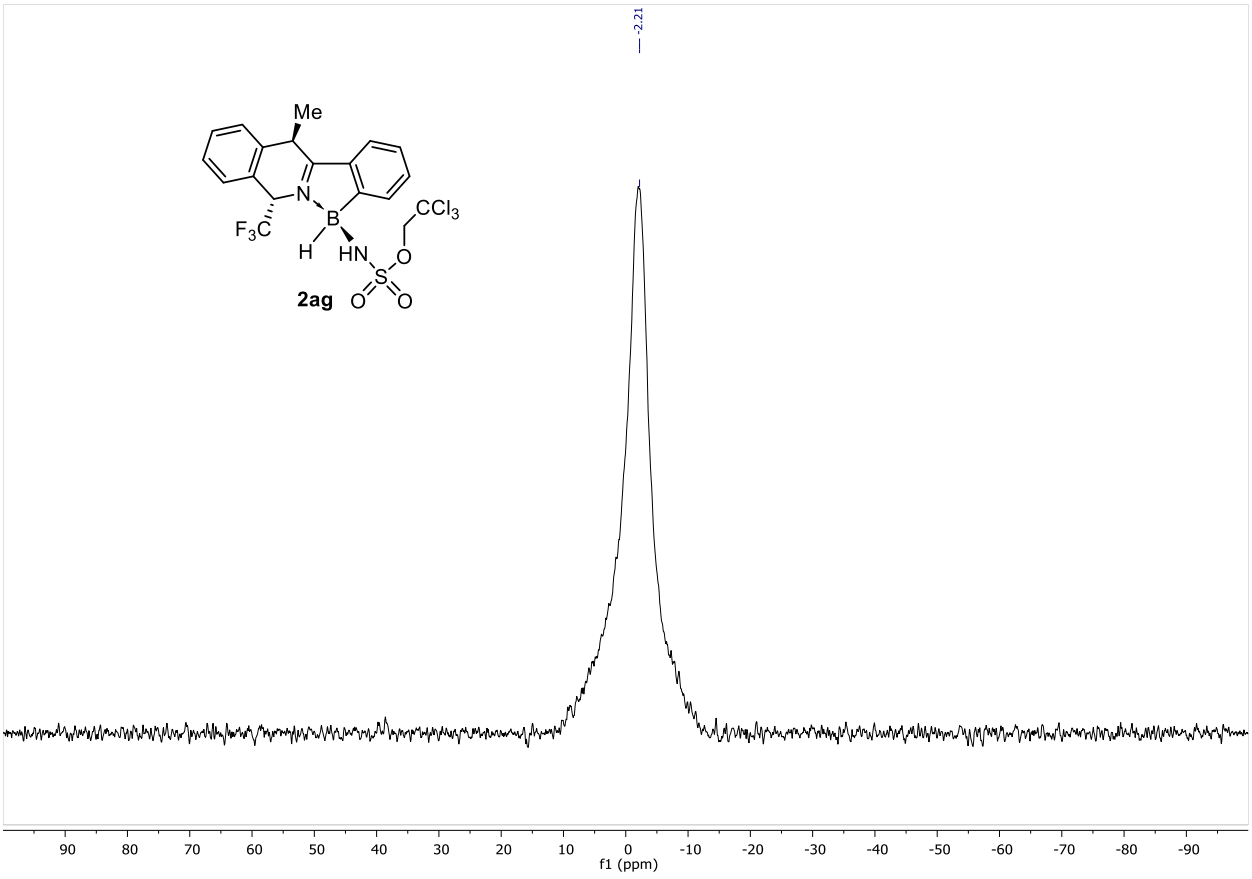


Fig. S184. ^{11}B NMR spectrum of **2ag**.

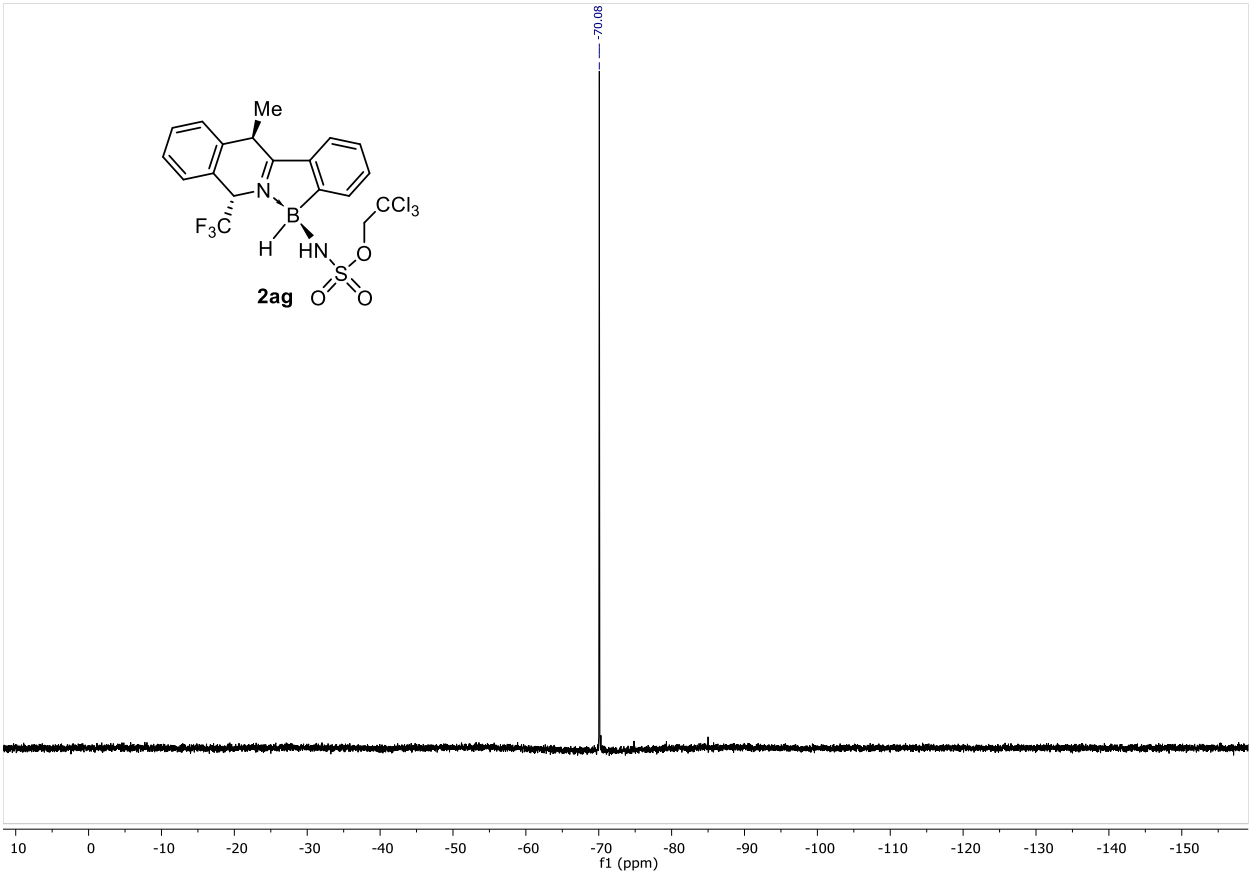


Fig. S185. ^{19}F NMR spectrum of **2ag**.

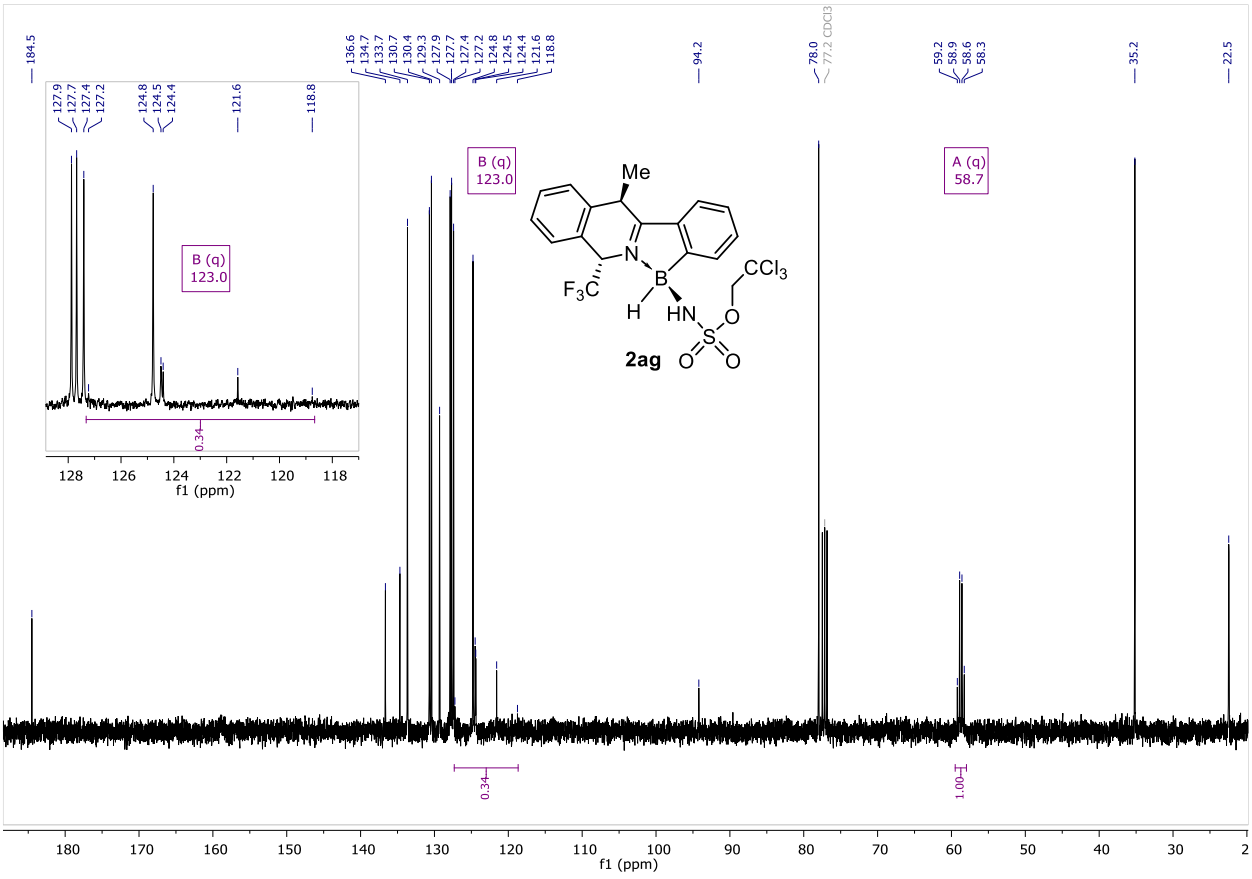


Fig. S186 ^{13}C NMR spectrum of **2ag**.

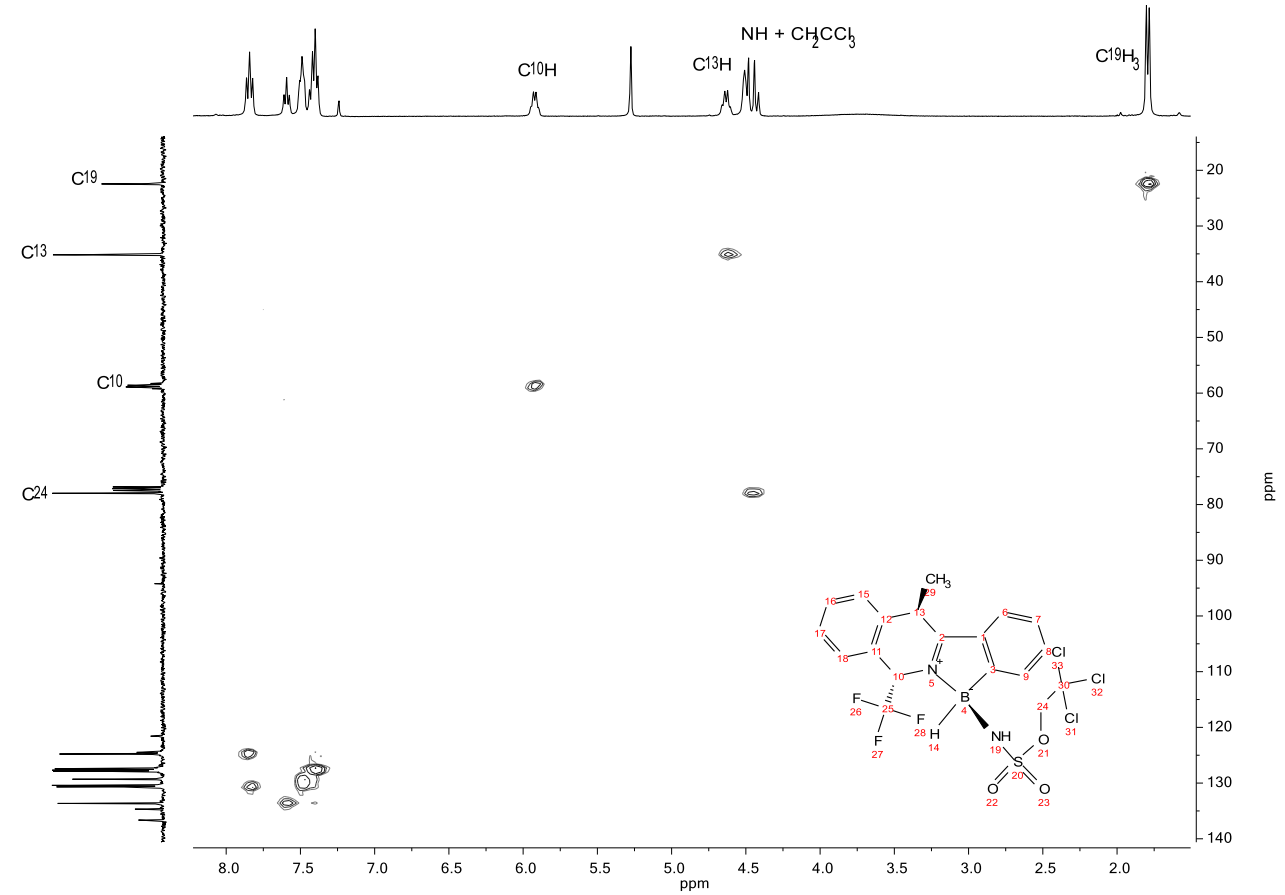


Fig. S187. ^{1}H-^{13}C HSQC NMR spectrum of **2ag**.

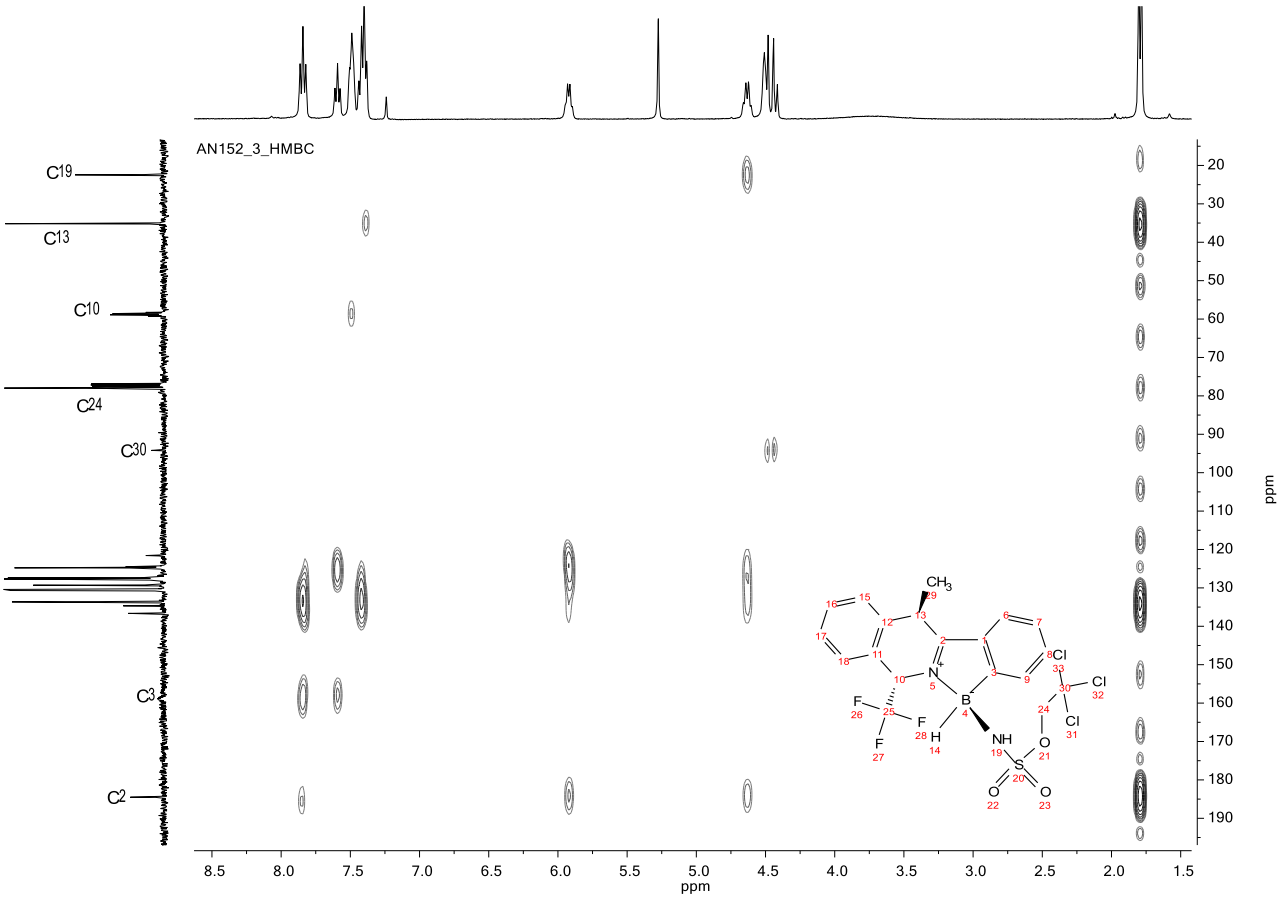


Fig. S188. ^{1}H-^{13}C HMBC NMR spectrum of **2ag**.

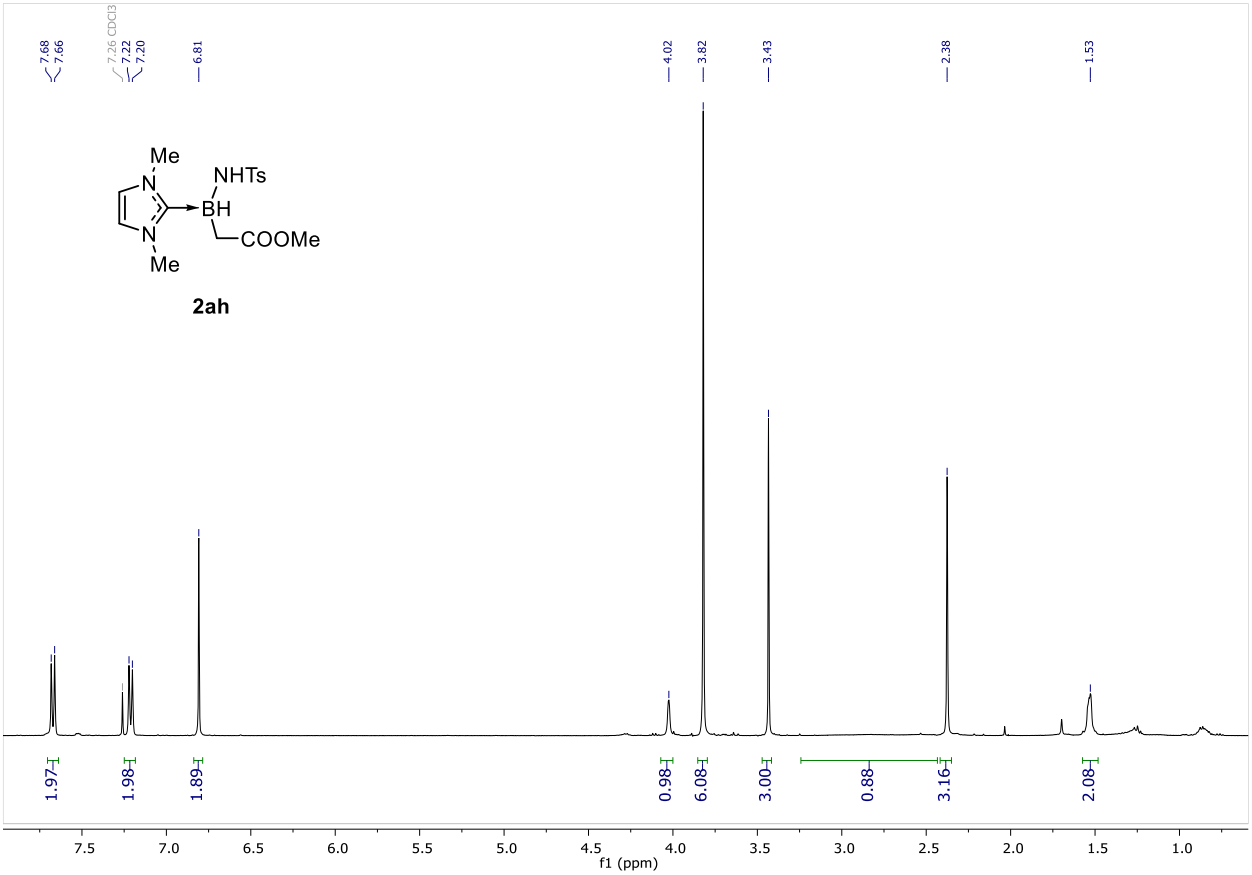


Fig. S189. ^{1}H NMR spectrum of **2ah**.

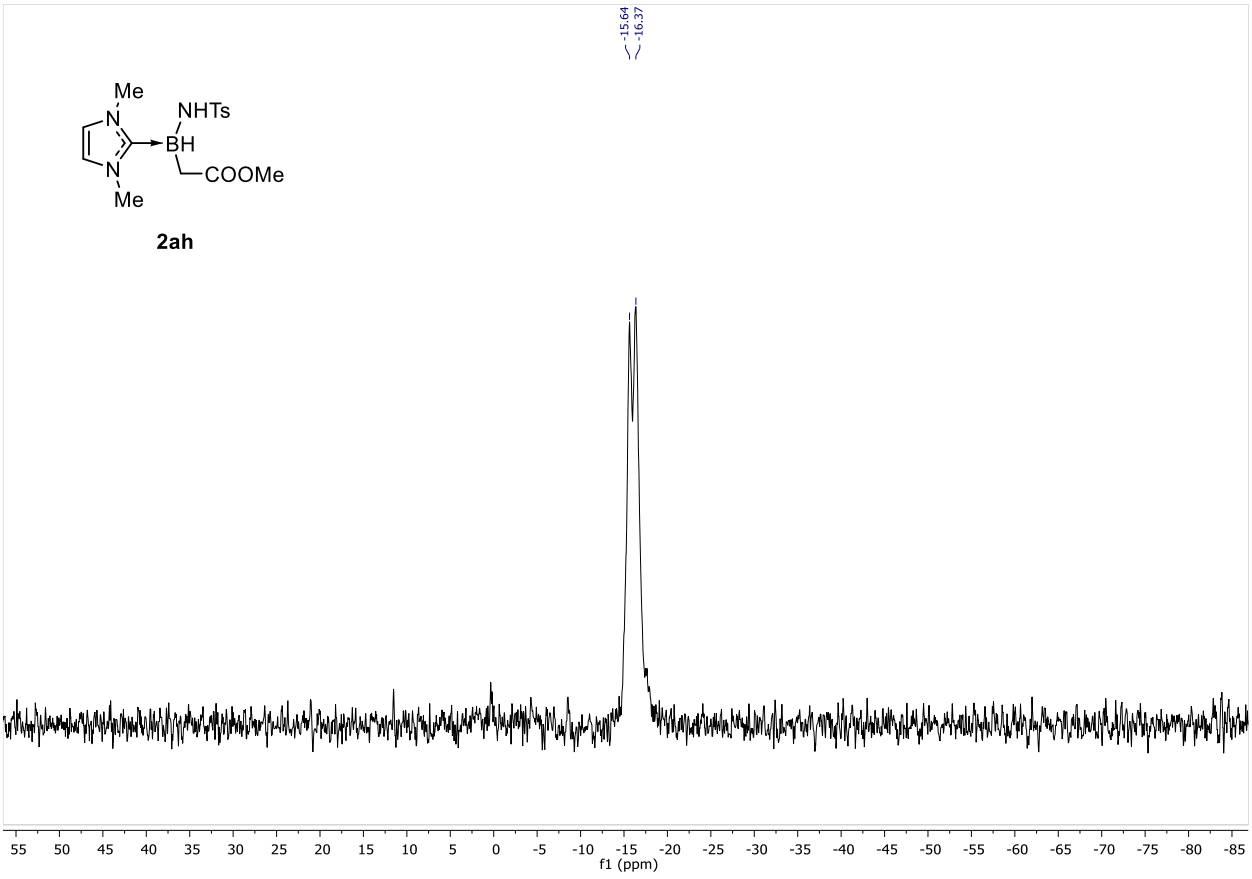


Fig. S190. ^{11}B NMR spectrum of **2ah**.

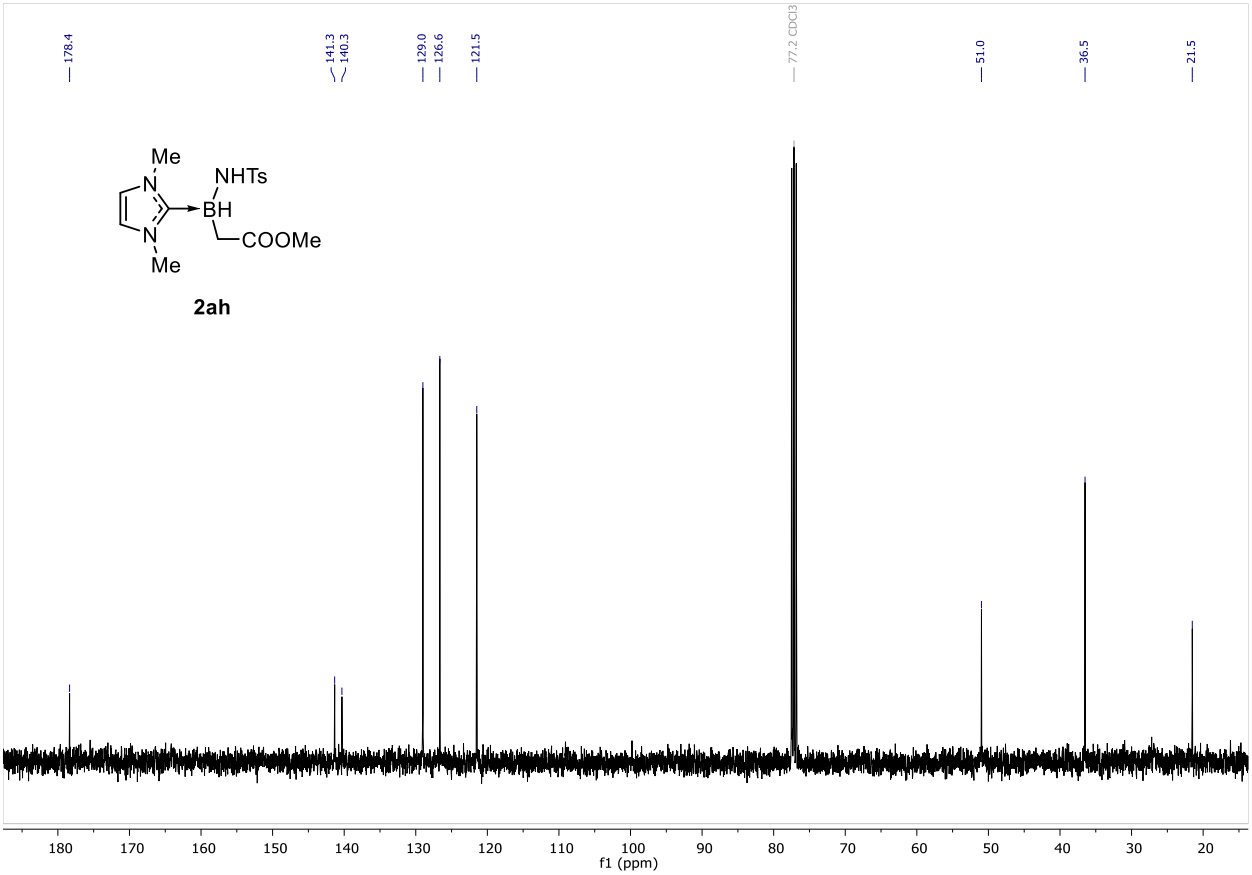


Fig. S191. ^{13}C NMR spectrum of **2ah**.

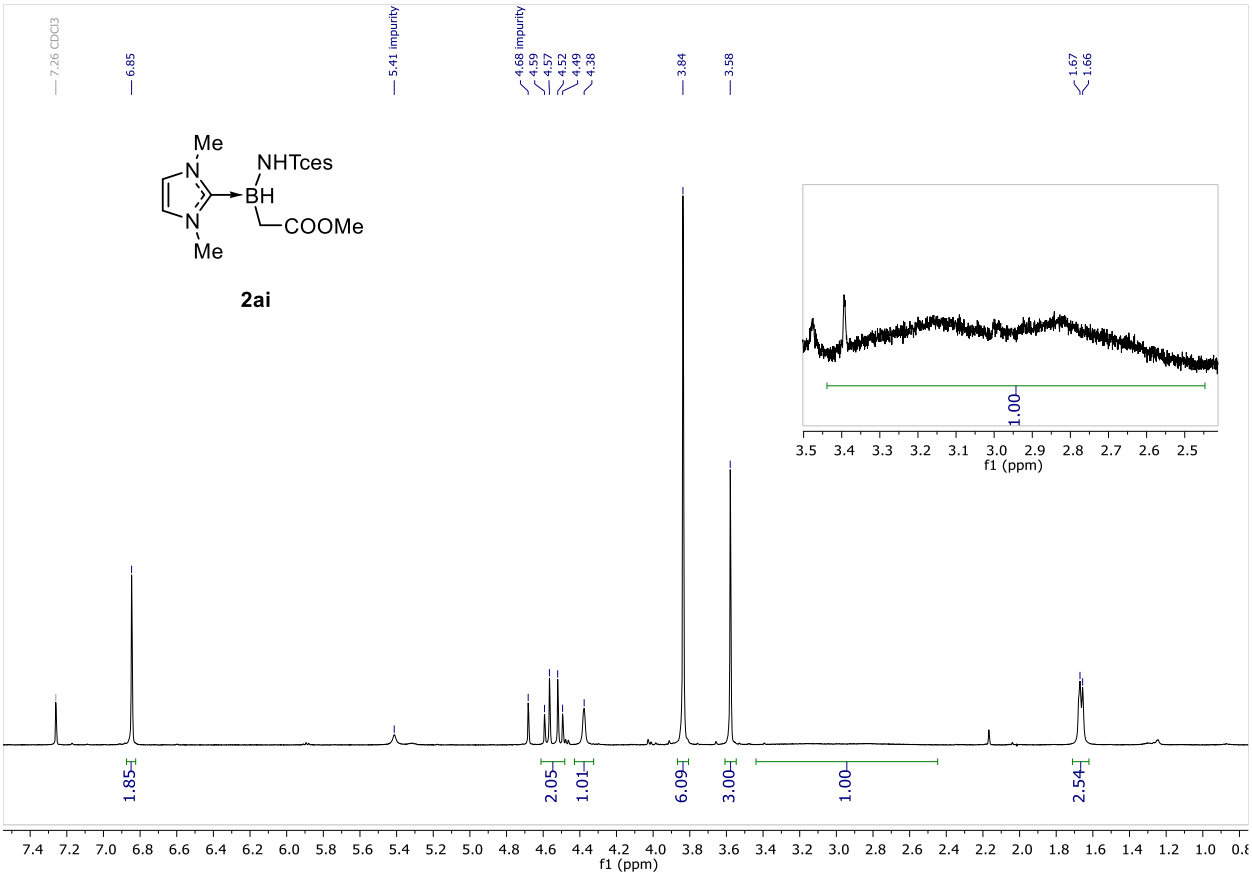


Fig. S192. ^{1}H NMR spectrum of **2ai**.

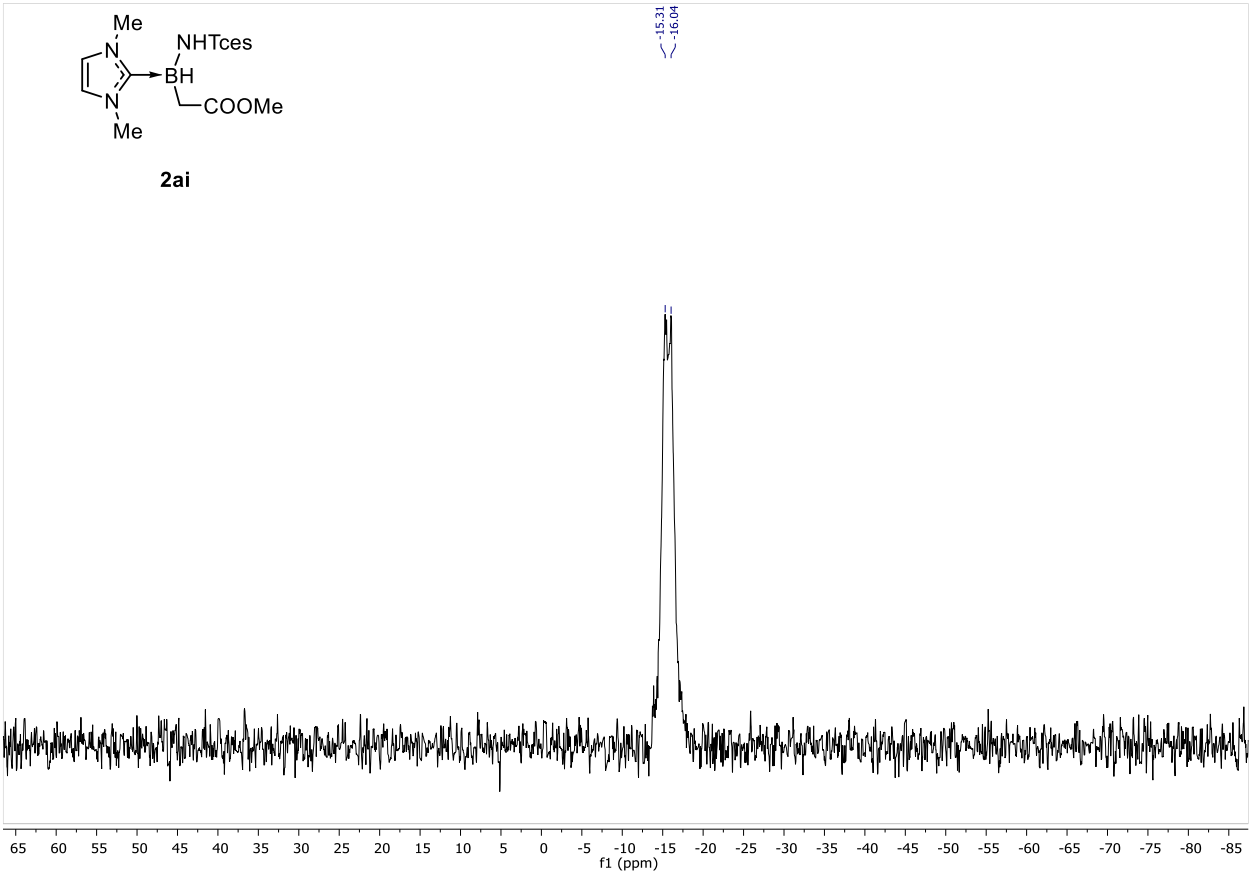


Fig. S193. ^{11}B NMR spectrum of **2ai**.

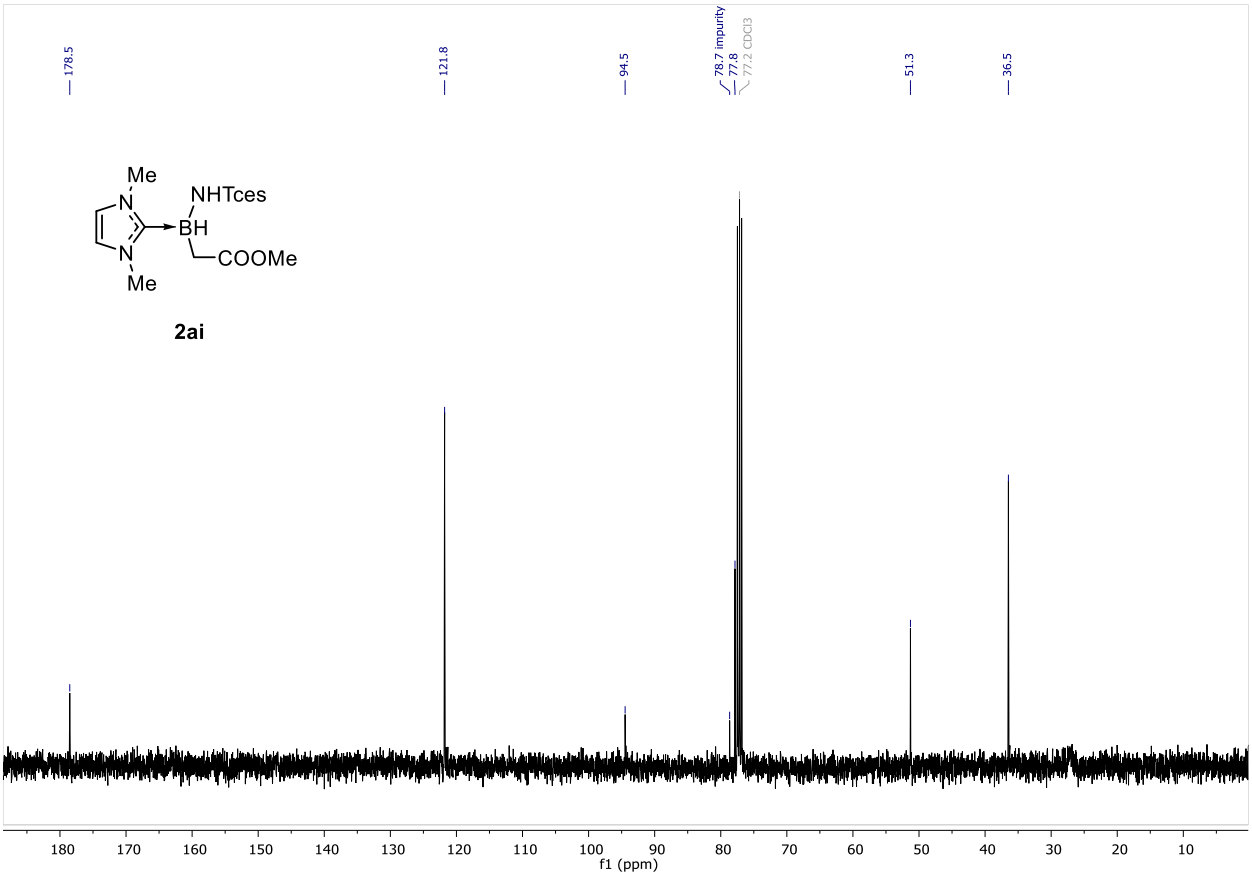


Fig. S194. ^{13}C NMR spectrum of **2ai**.

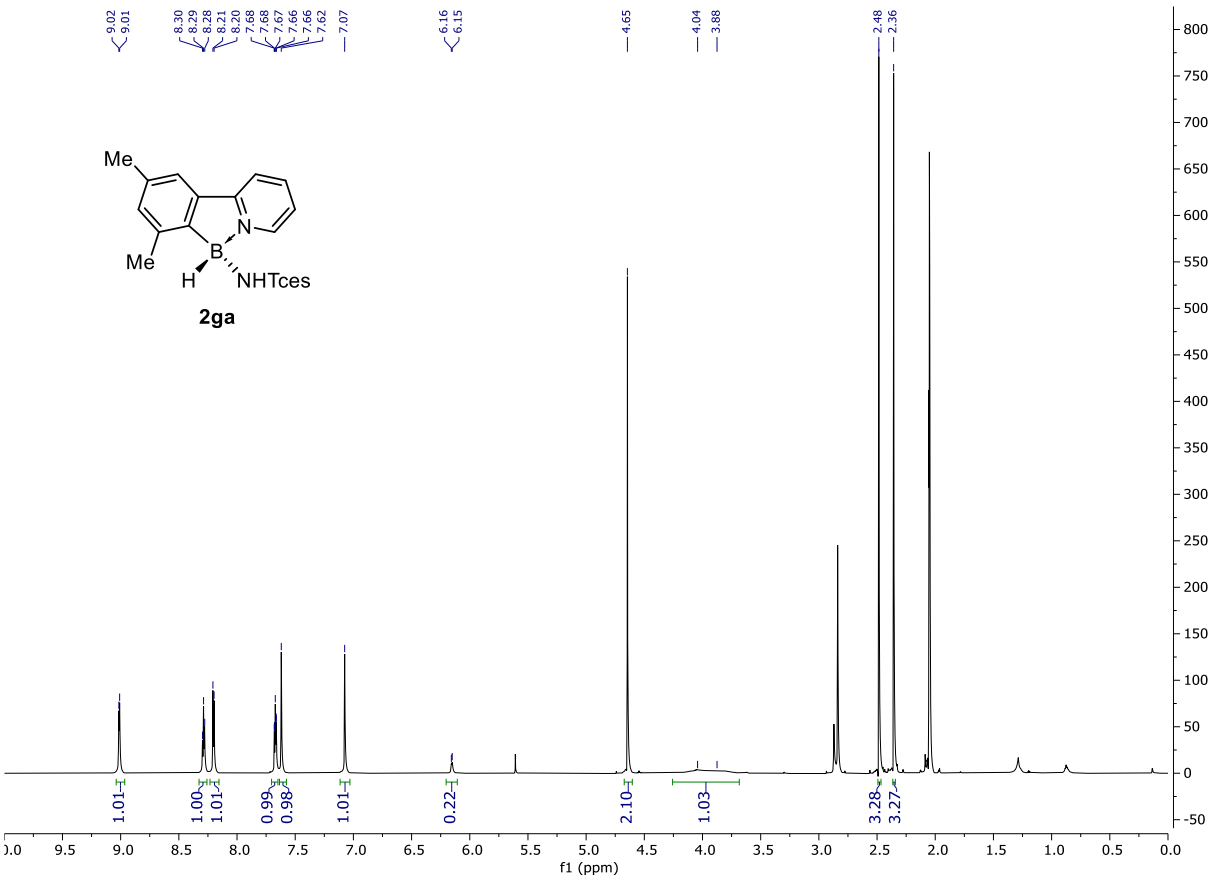


Fig. S195. ^{1}H NMR spectrum of **2ga** in acetone-d_6.

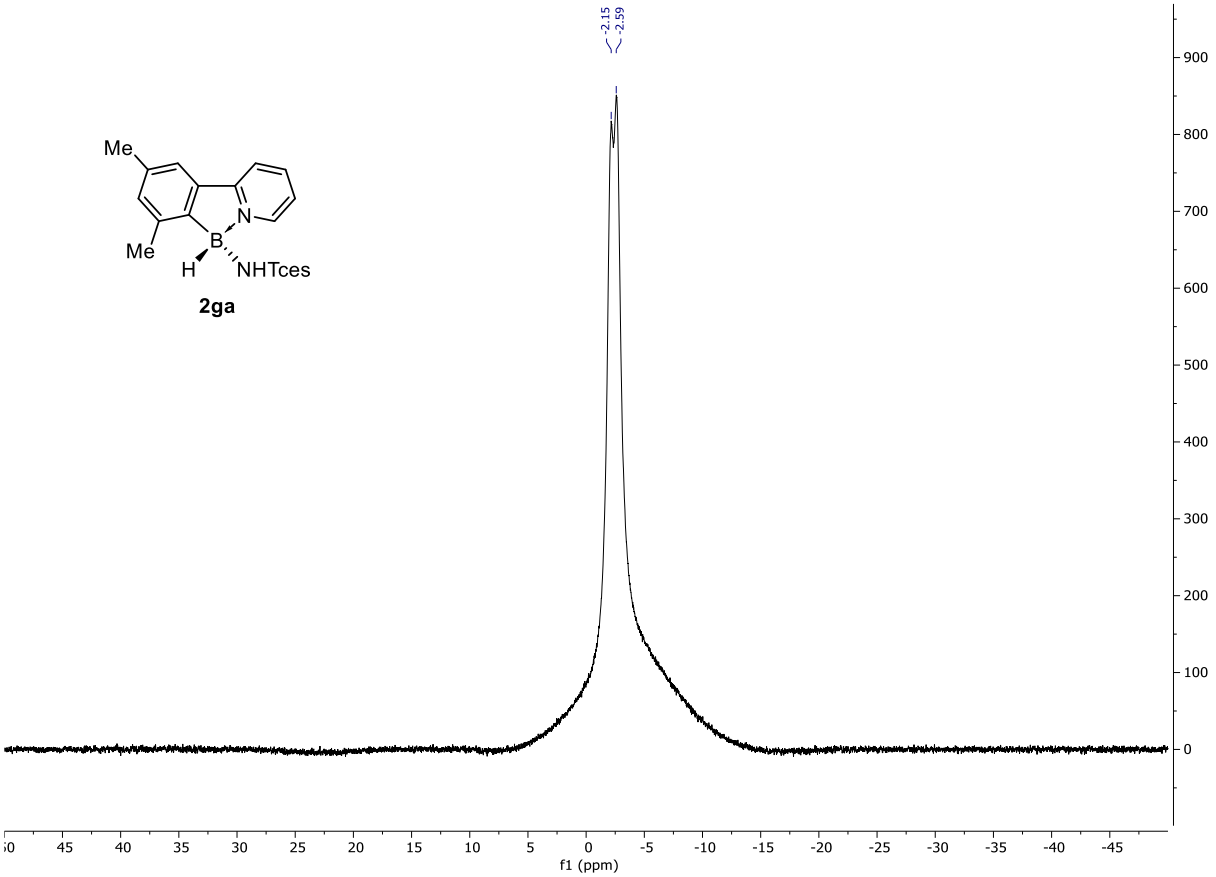


Fig. S196. ^{11}B NMR spectrum of **2ga** in acetone-d_6.

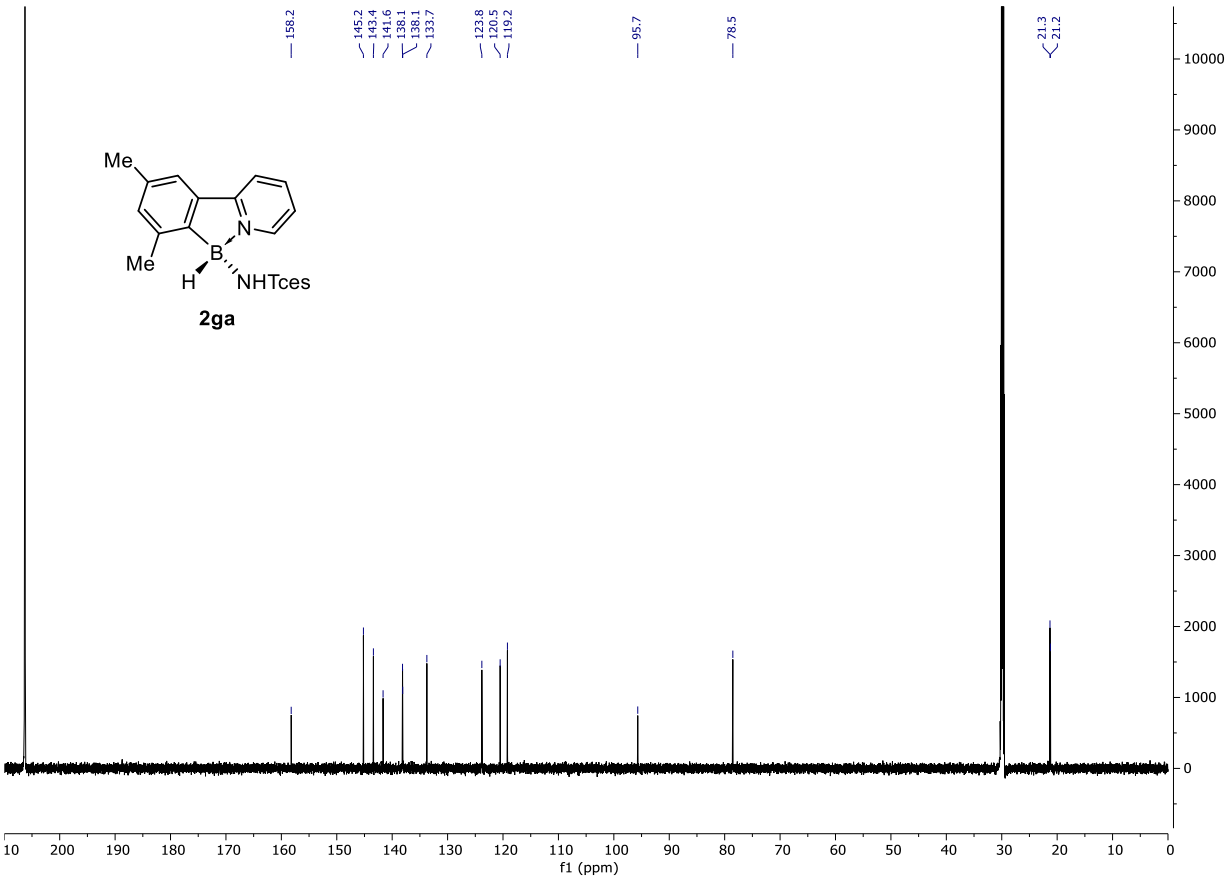


Fig. S197. ^{13}C NMR spectrum of **2ga** in acetone-d_6.

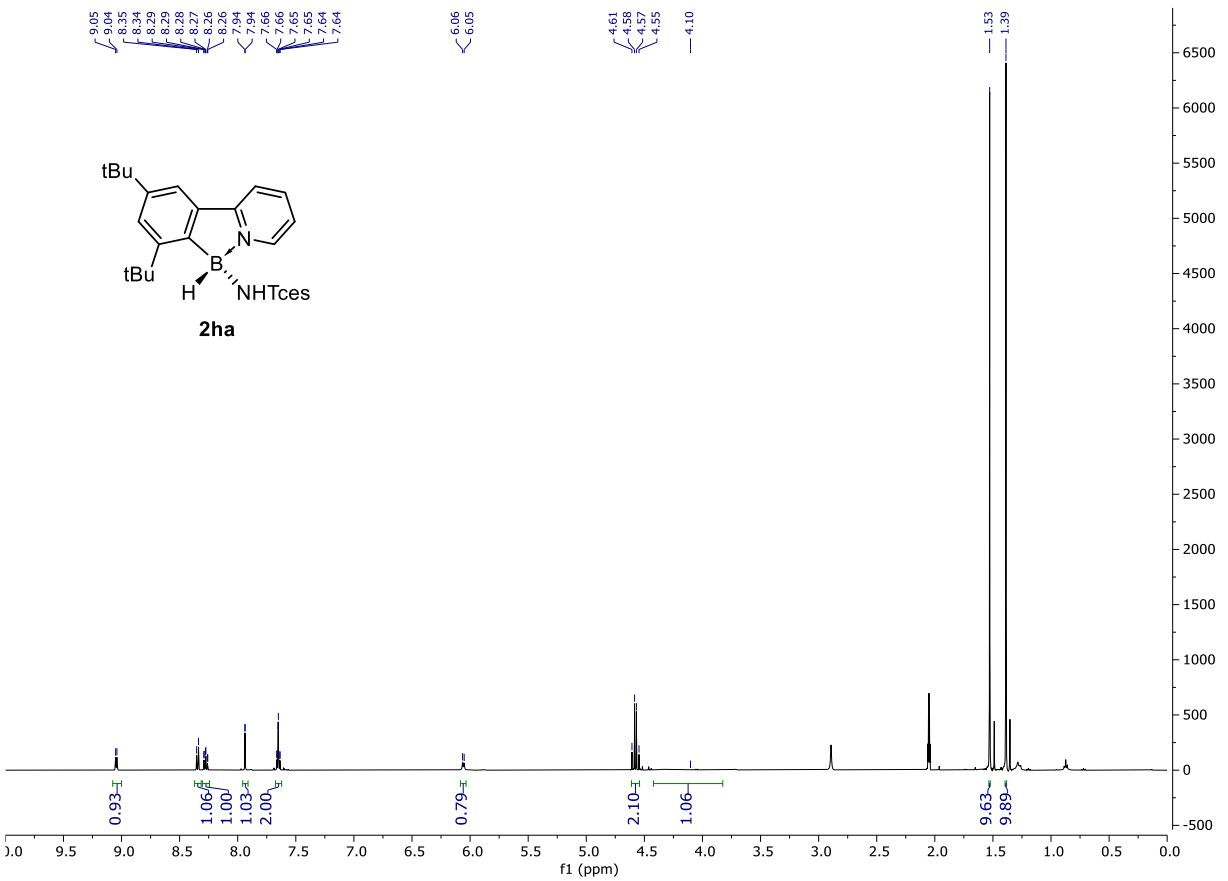


Fig. S198. ^{1}H NMR spectrum of **2ha** in acetone-d_6.

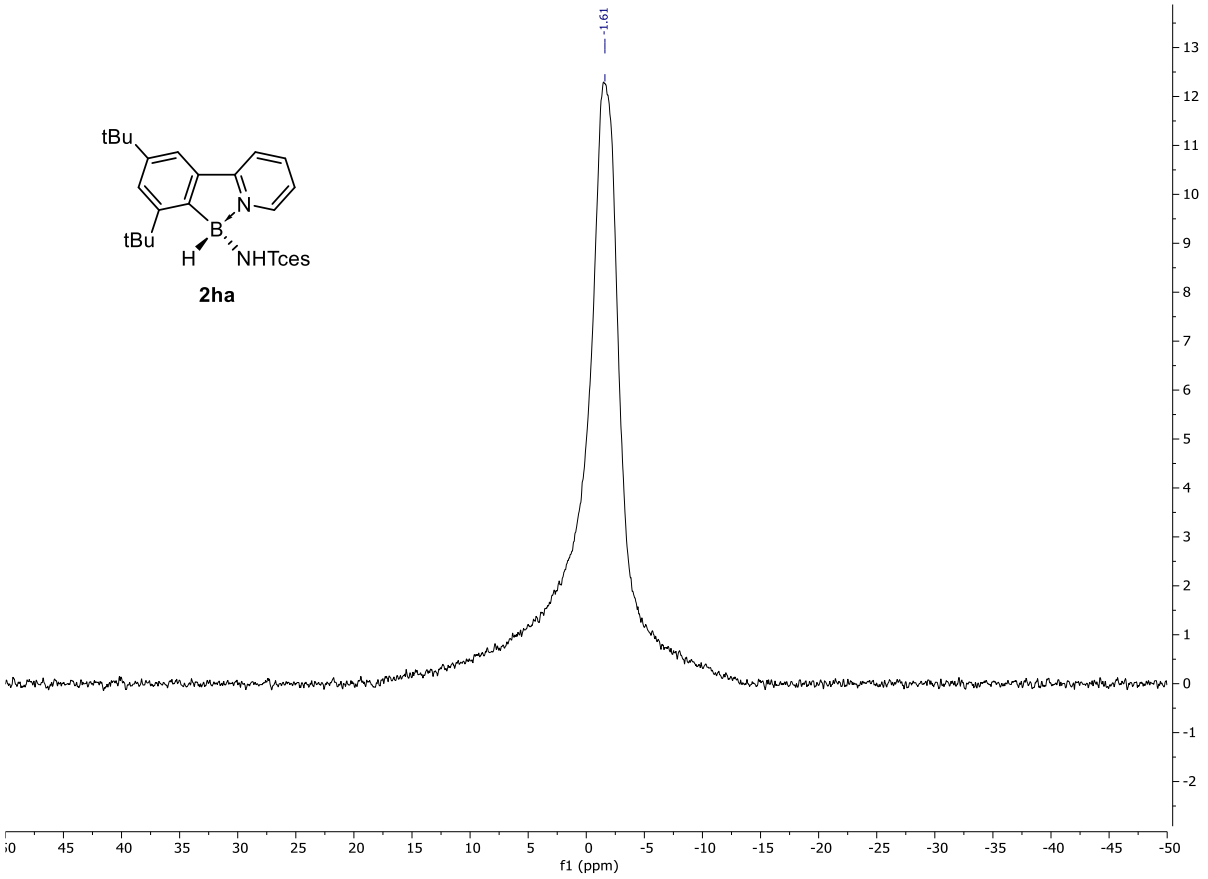


Fig. S199. ^{11}B NMR spectrum of **2ha** in acetone-d_6.

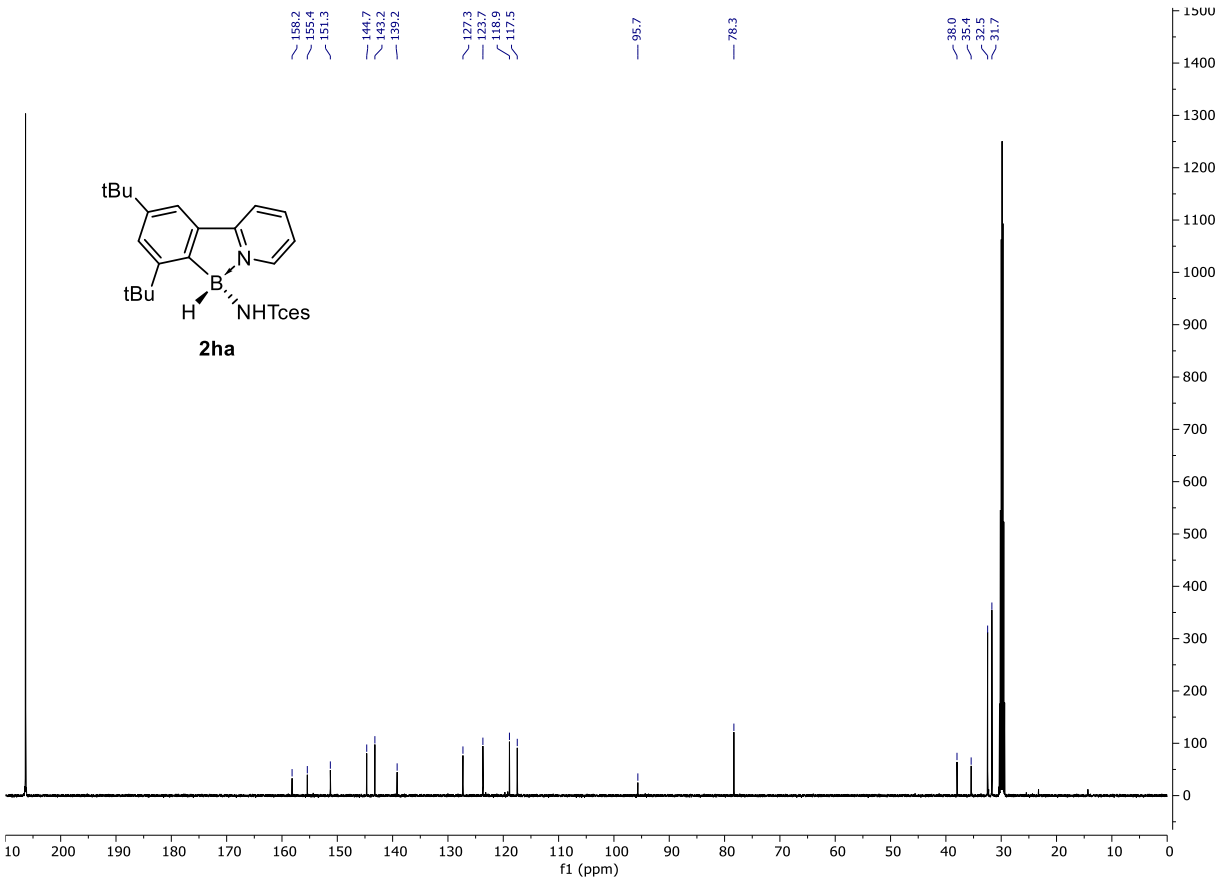


Fig. S200. ^{13}C NMR spectrum of **2ha** in acetone-d_6.

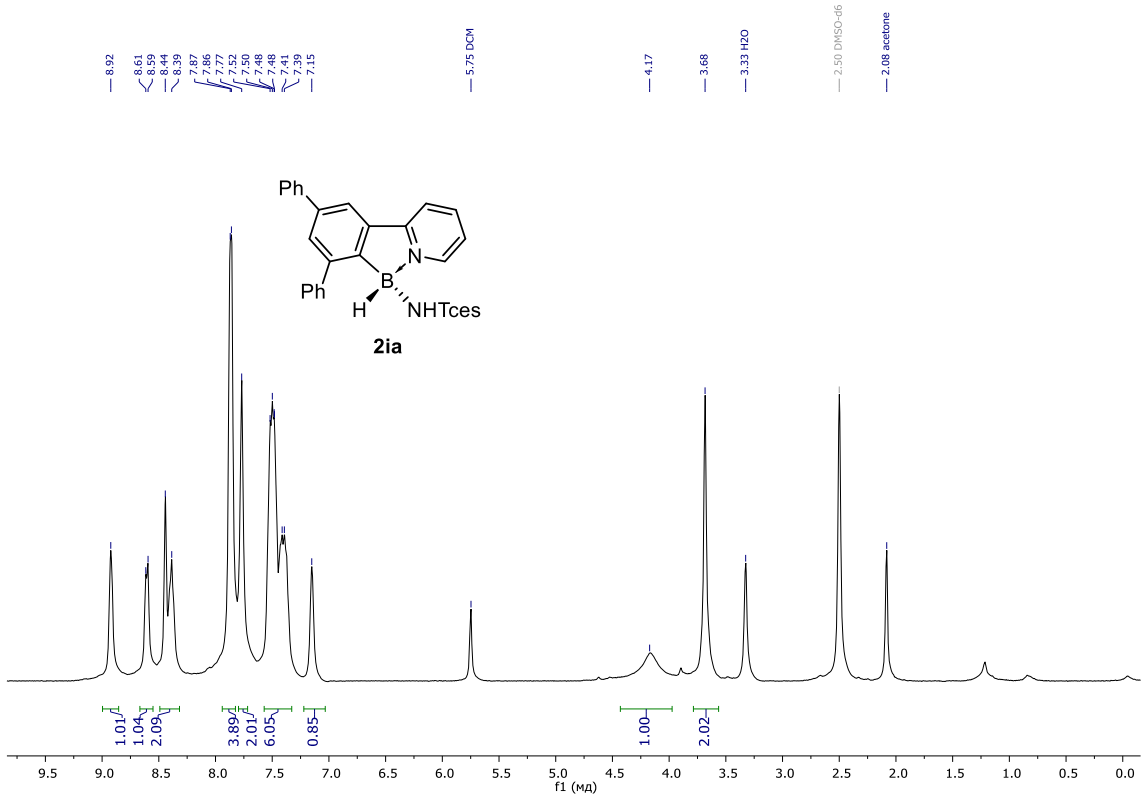


Fig. S201. ^{1}H NMR spectrum of **2ia** in DMSO-d_6.

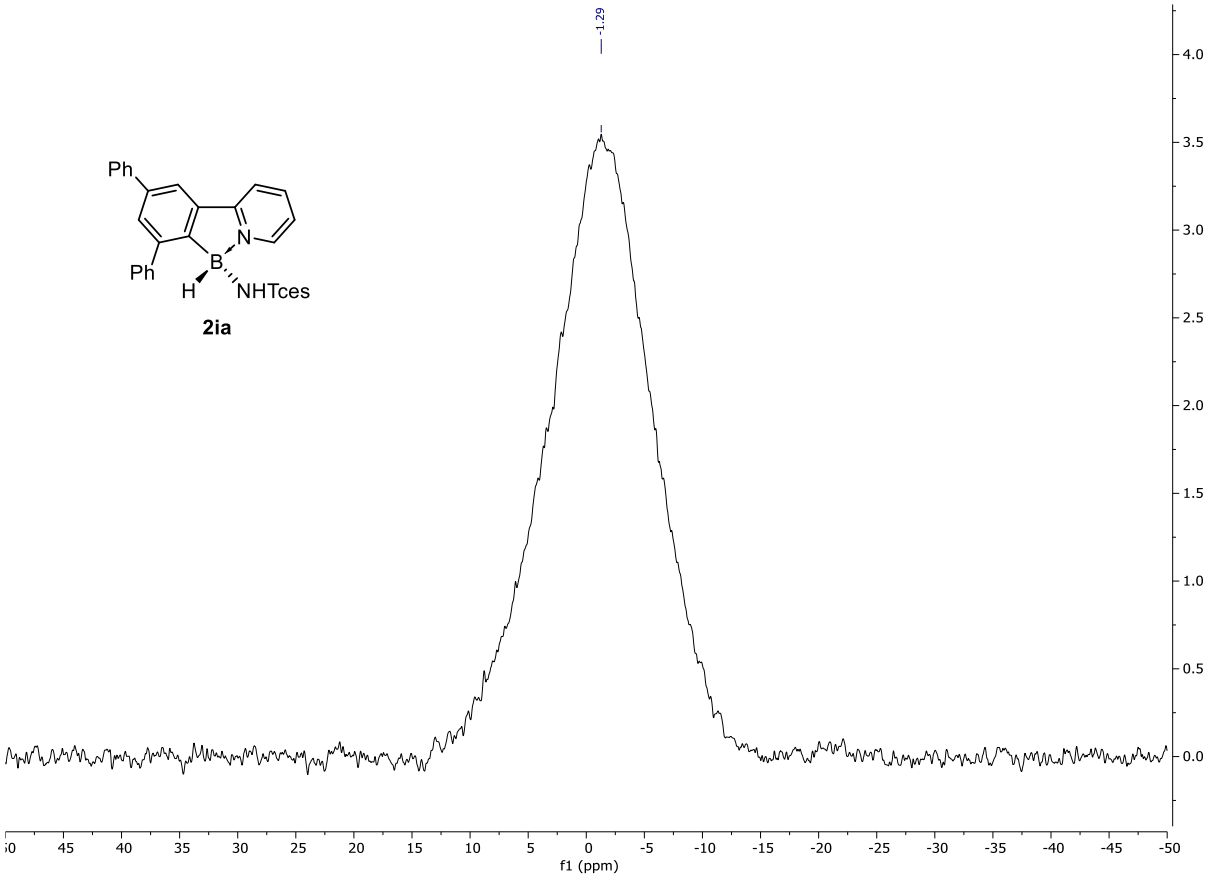


Fig. S202. ^{11}B NMR spectrum of **2ia** in DMSO-d_6.

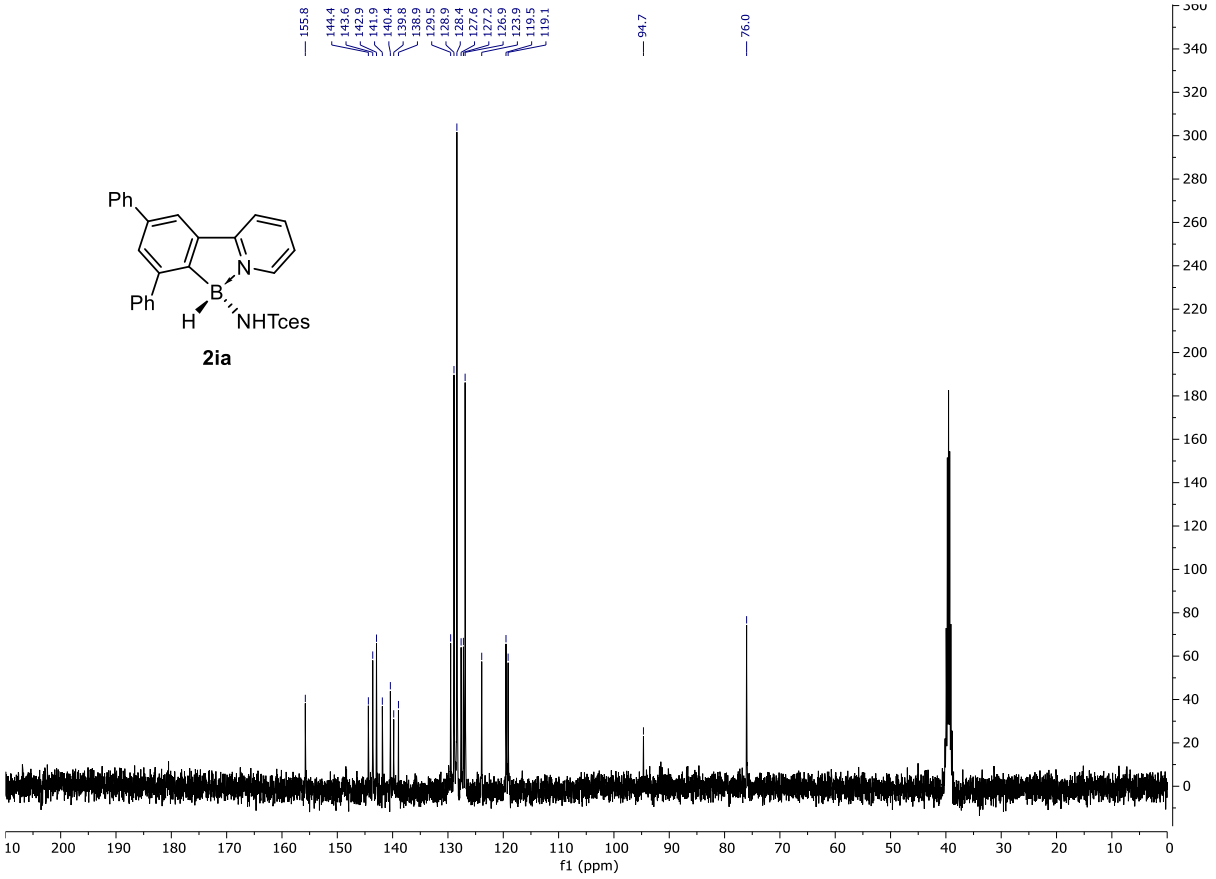


Fig. S203. ^{13}C NMR spectrum of **2ia** in DMSO-d_6.

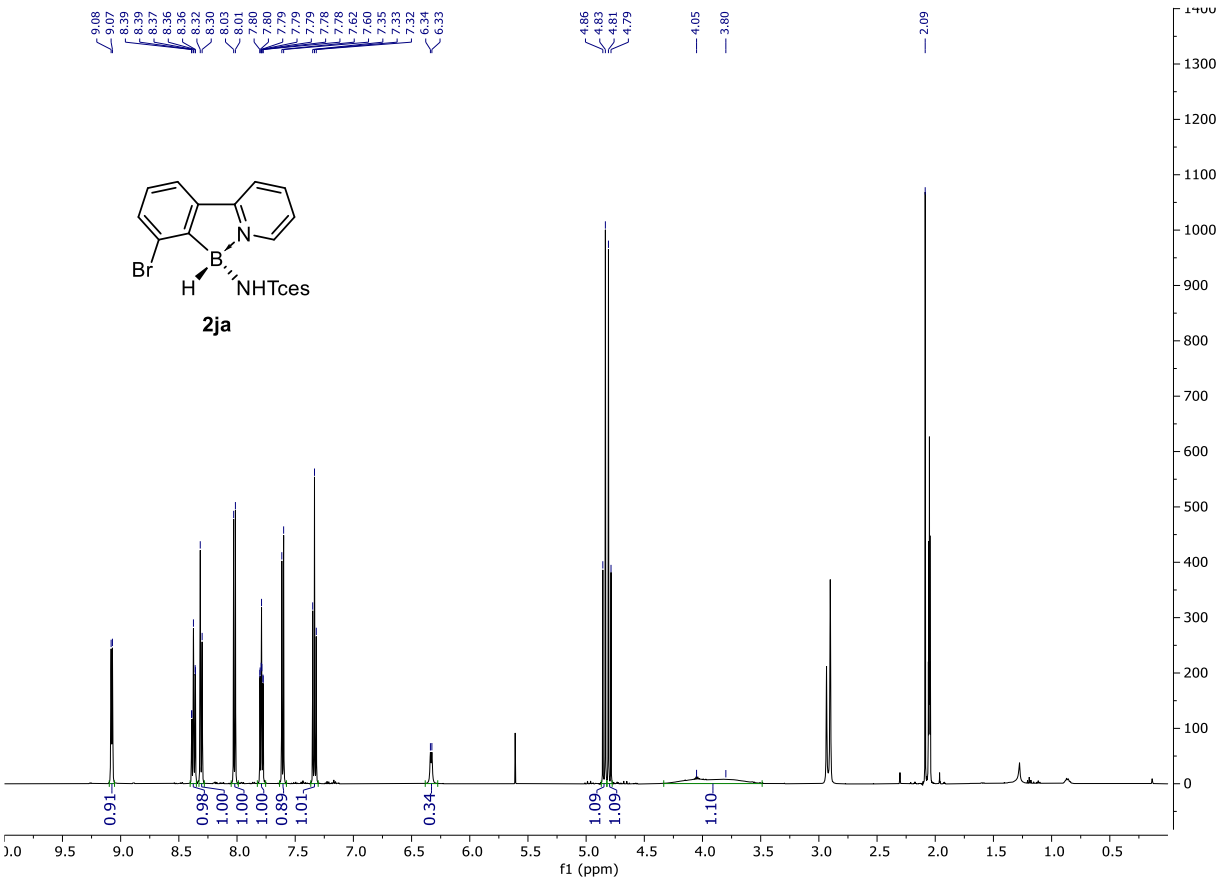


Fig. S204. ^{1}H NMR spectrum of **2ja** in acetone-d_6.

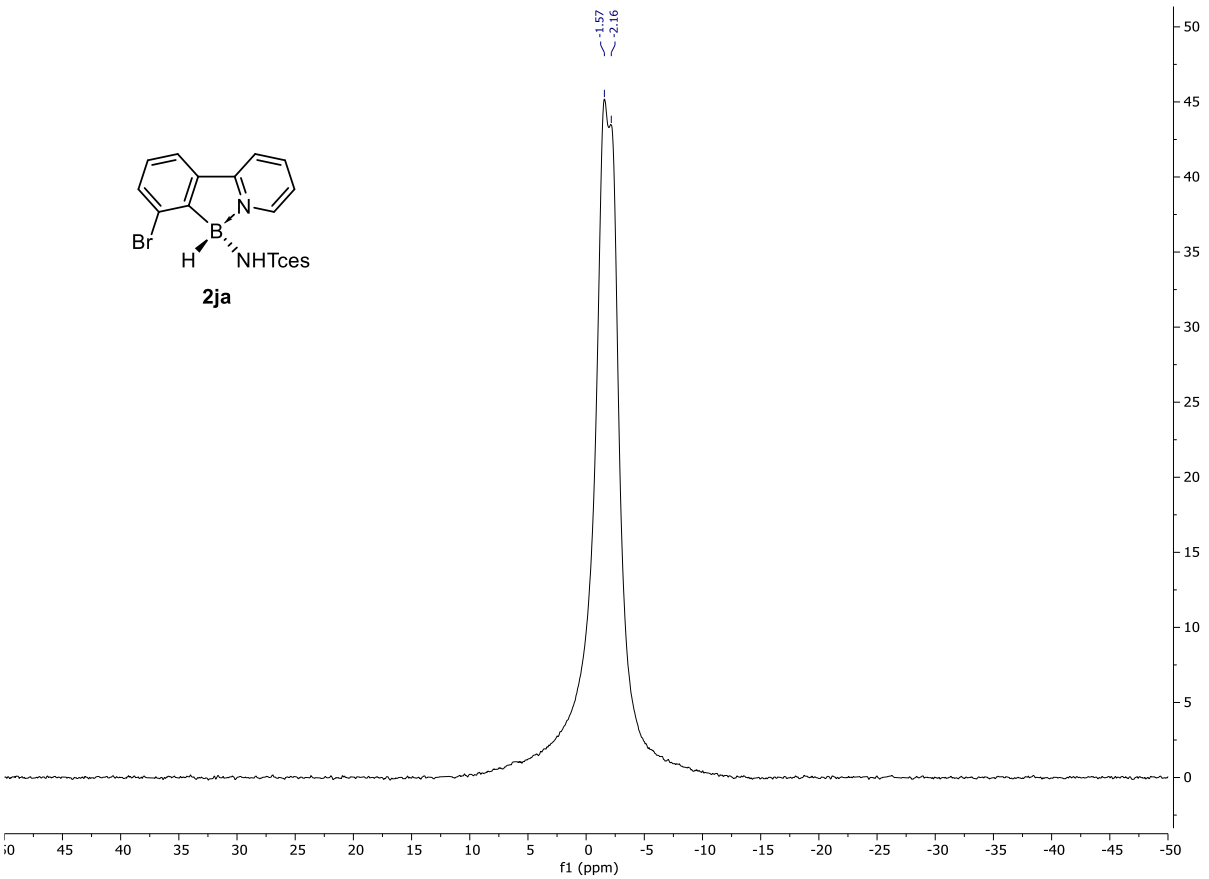


Fig. S205. ^{11}B NMR spectrum of **2ja** in acetone-d_6.

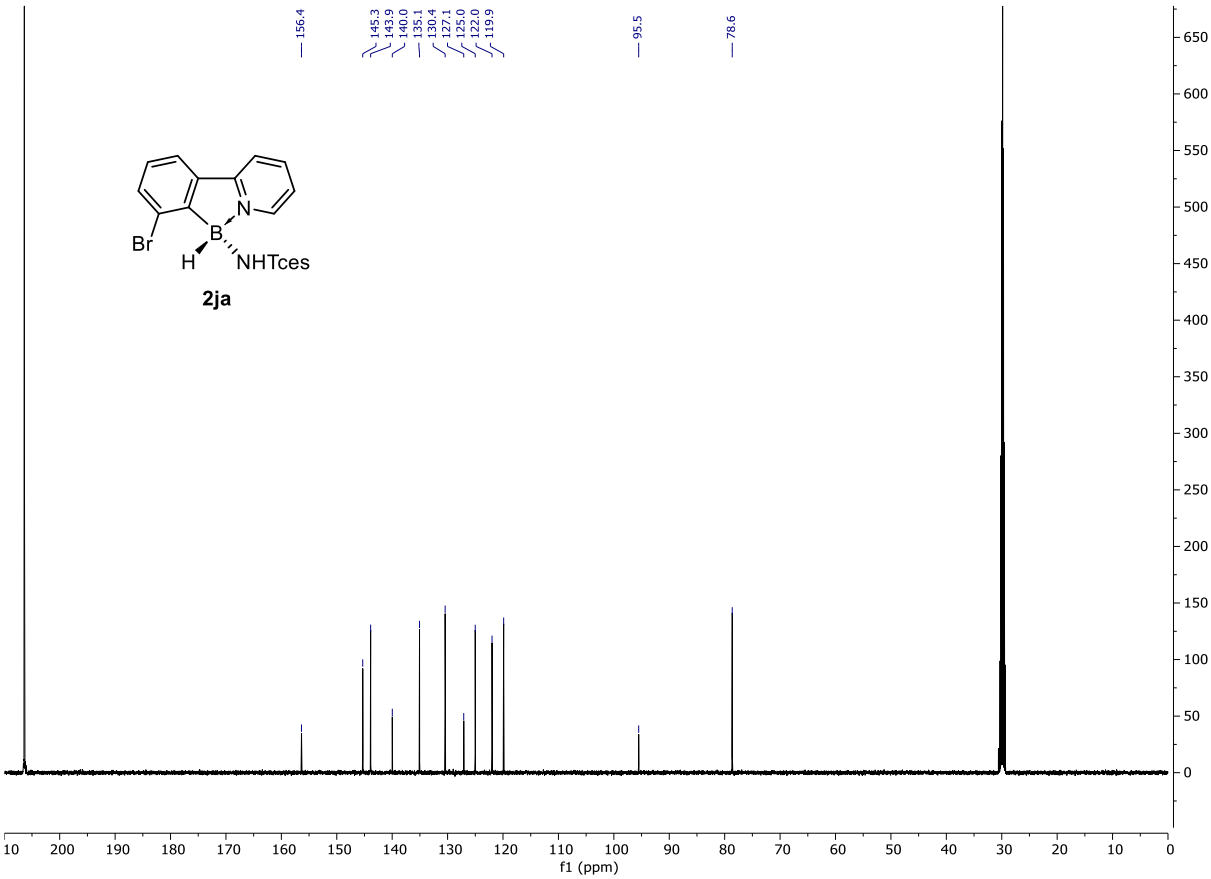


Fig. S206. ^{13}C NMR spectrum of **2ja** in acetone-d_6.

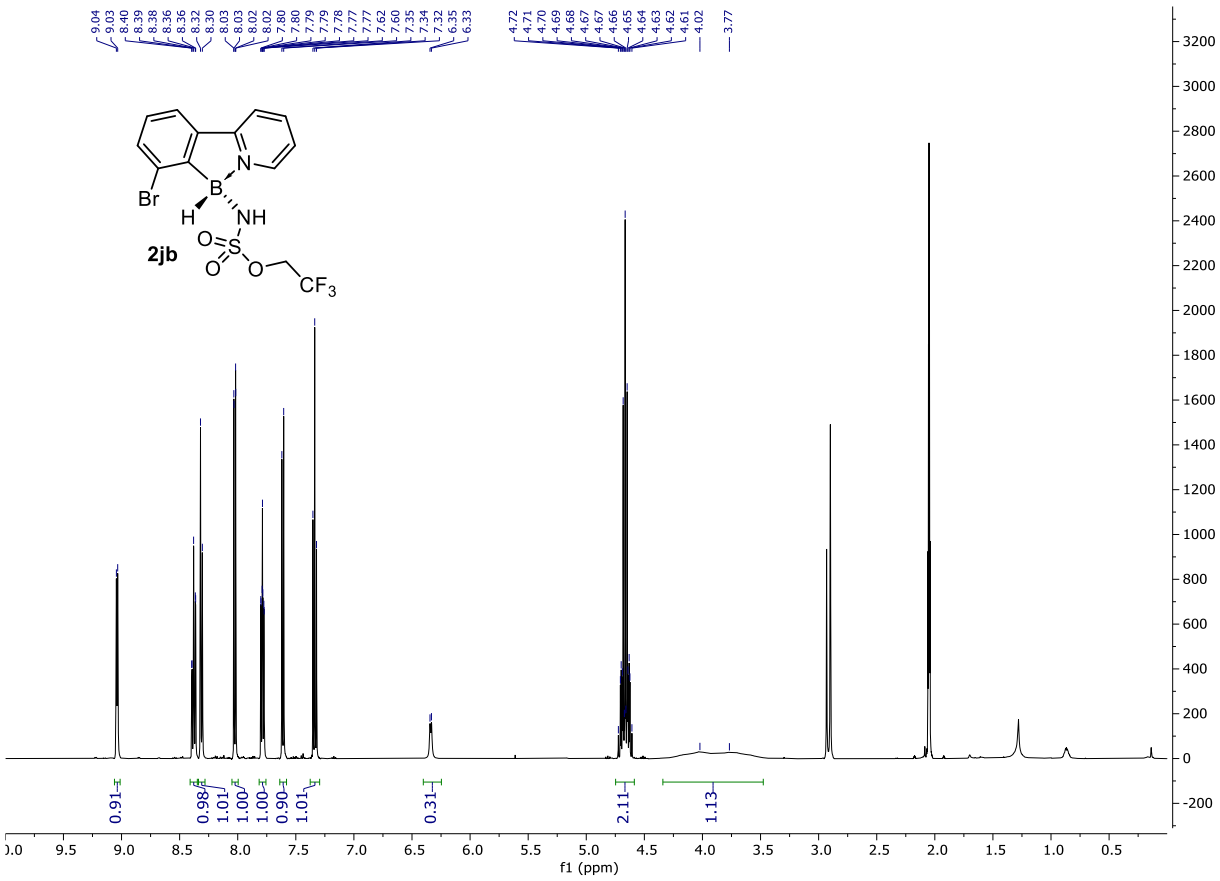


Fig. S207. ^{1}H NMR spectrum of **2jb** in acetone-d_6.

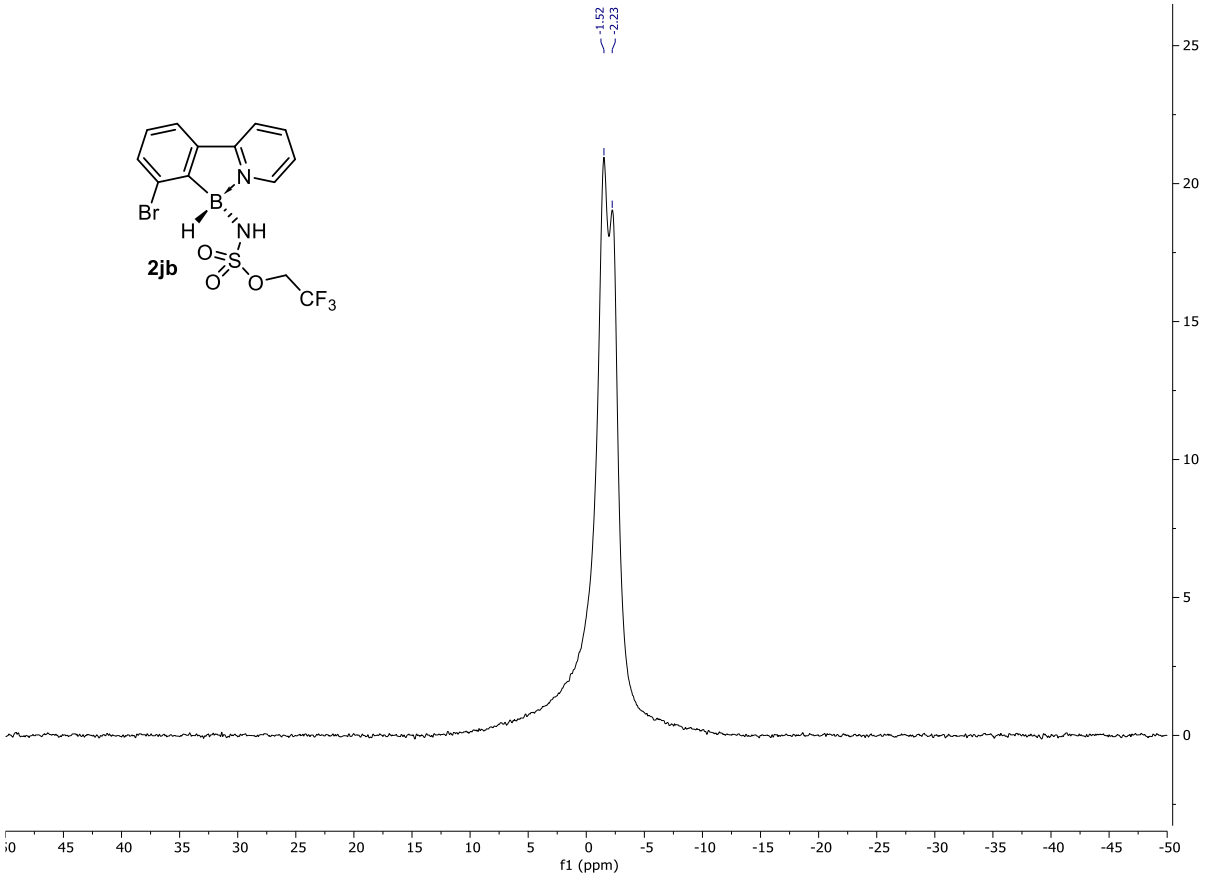


Fig. S208. ^{11}B NMR spectrum of **2jb** in acetone-d_6.

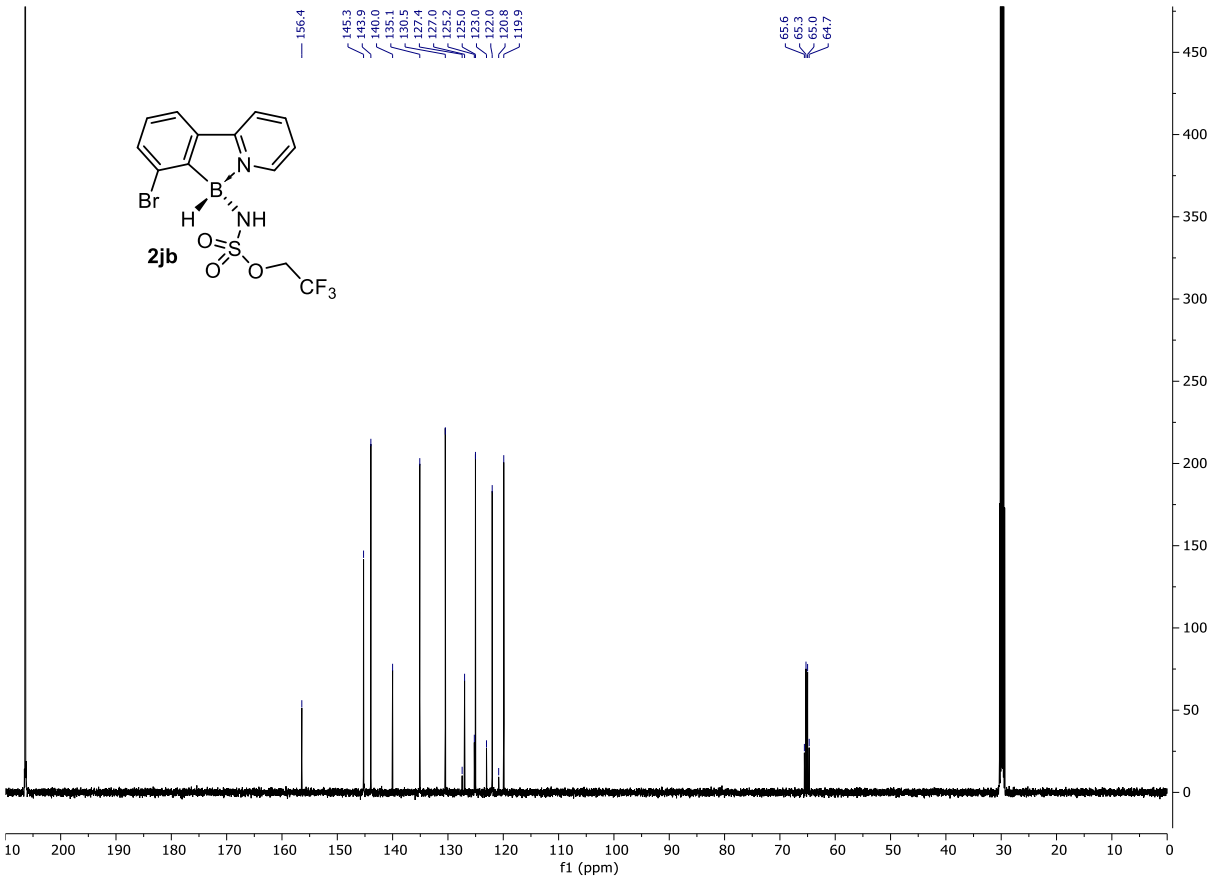


Fig. S209. ^{13}C NMR spectrum of **2jb** in acetone-d_6.

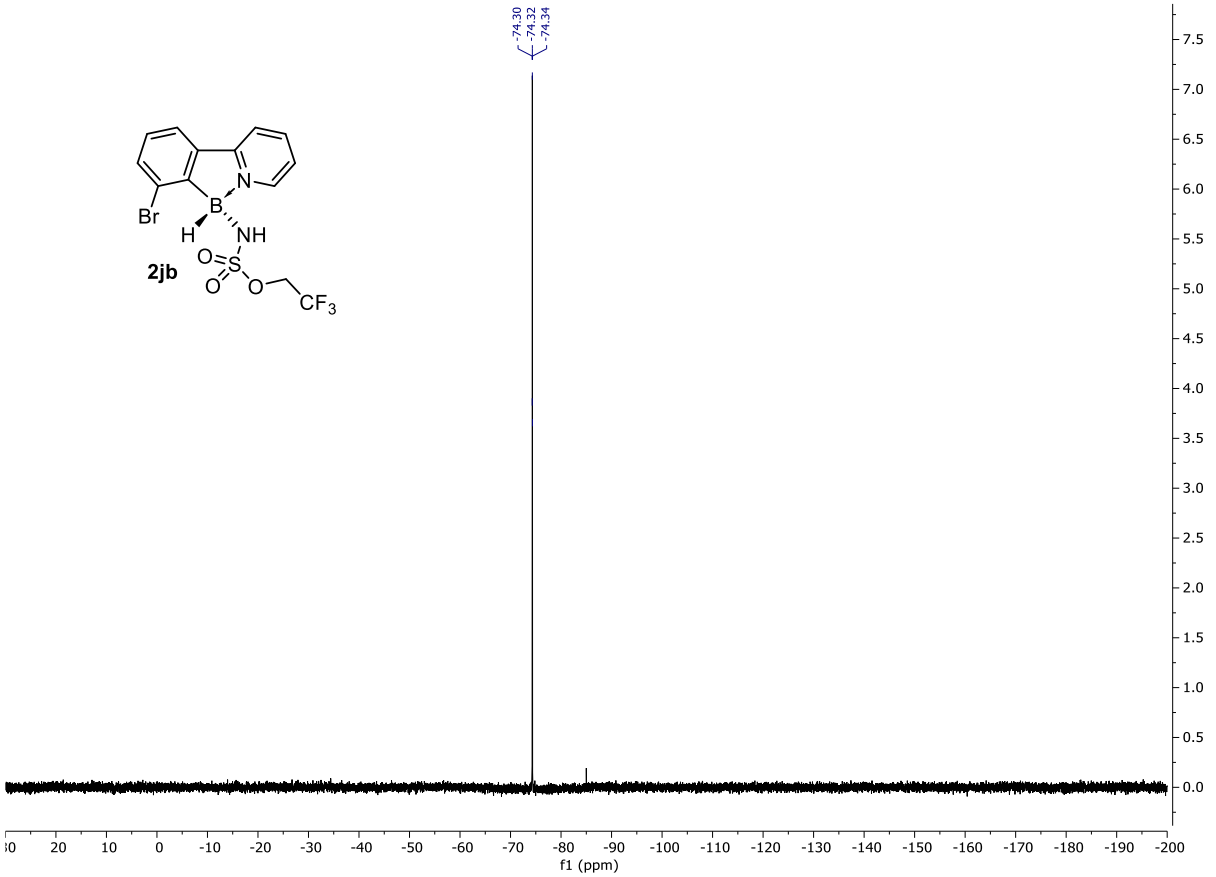


Fig. S210. ^{19}F NMR spectrum of **2jb** in acetone-d_6.

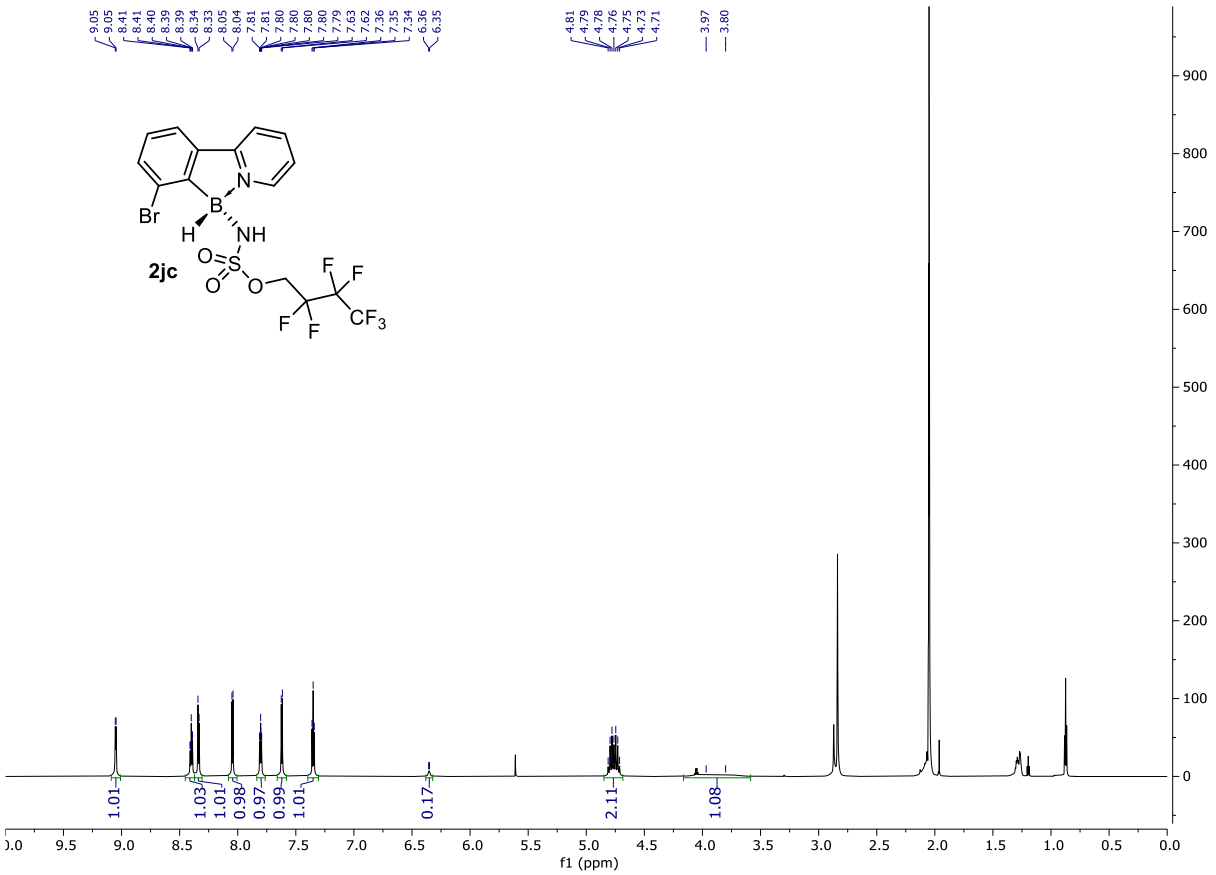


Fig. S211. ^{1}H NMR spectrum of **2jc** in acetone-d_6.

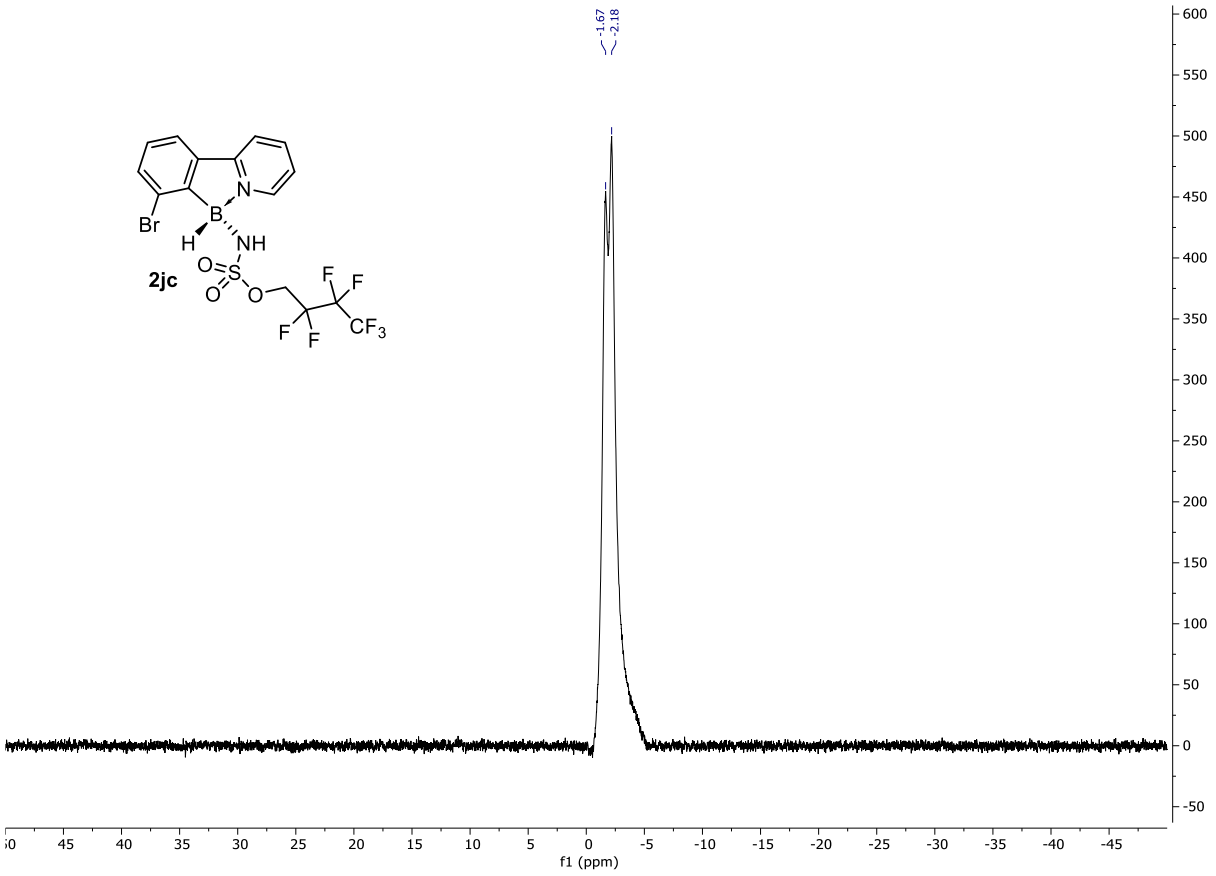


Fig. S212. ^{11}B NMR spectrum of **2jc** in acetone-d_6.

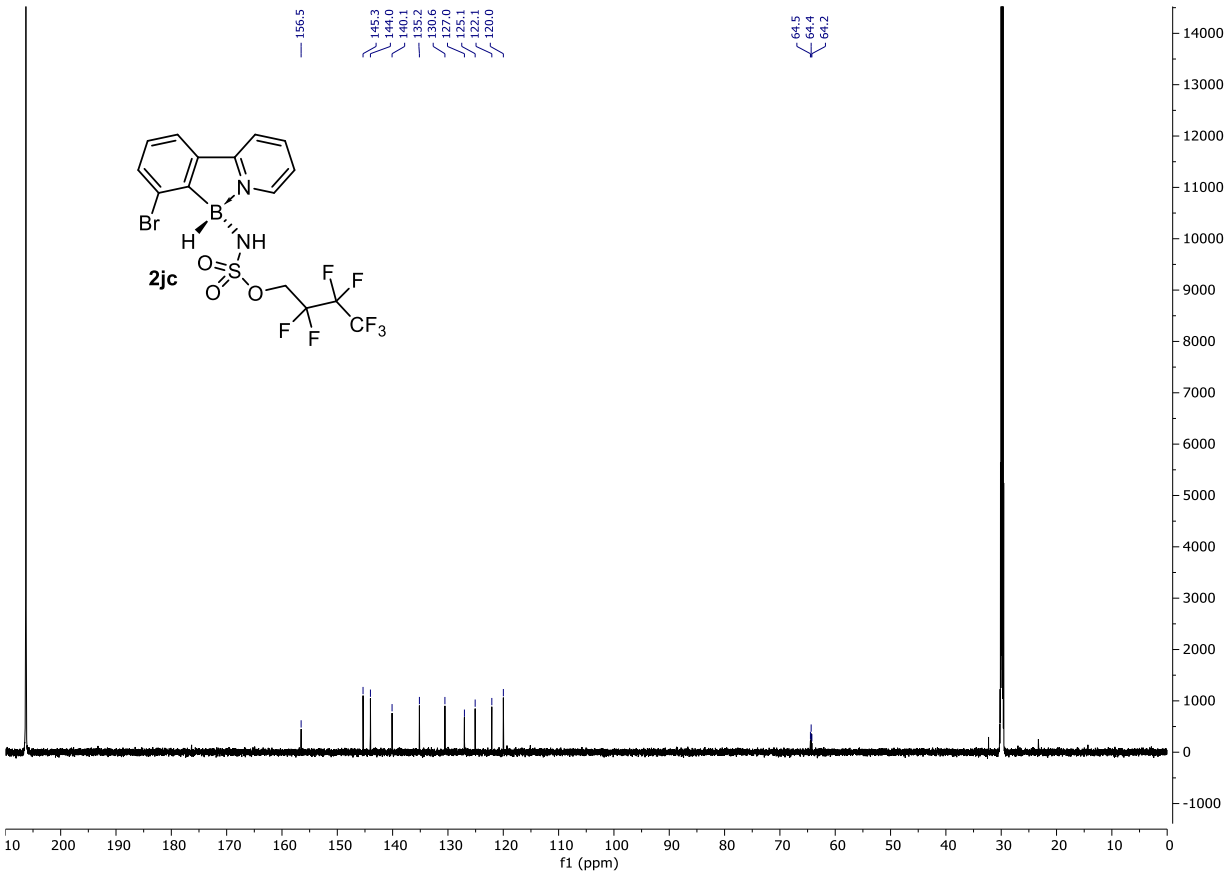


Fig. S213. ^{13}C NMR spectrum of **2jc** in acetone-d_6.

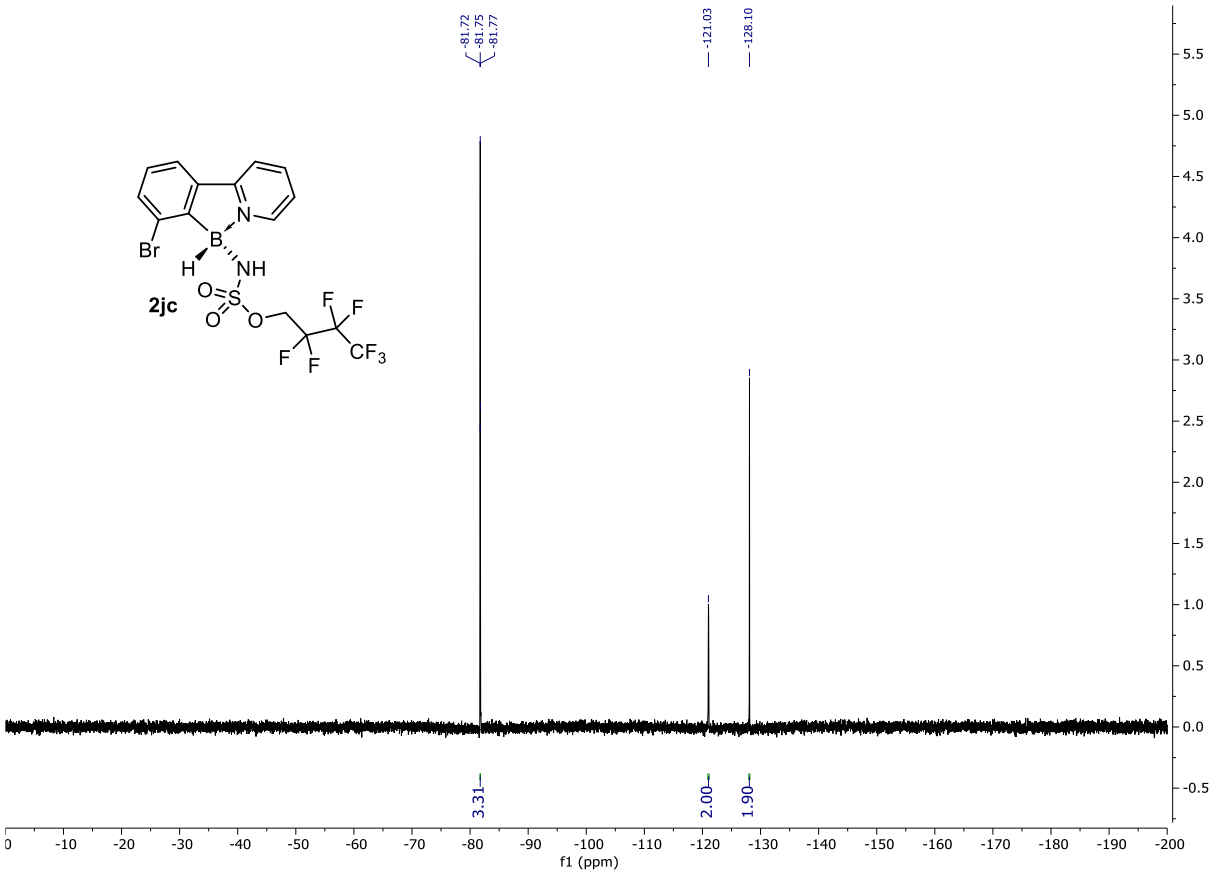


Fig. S214. ^{19}F NMR spectrum of **2jc** in acetone-d_6.

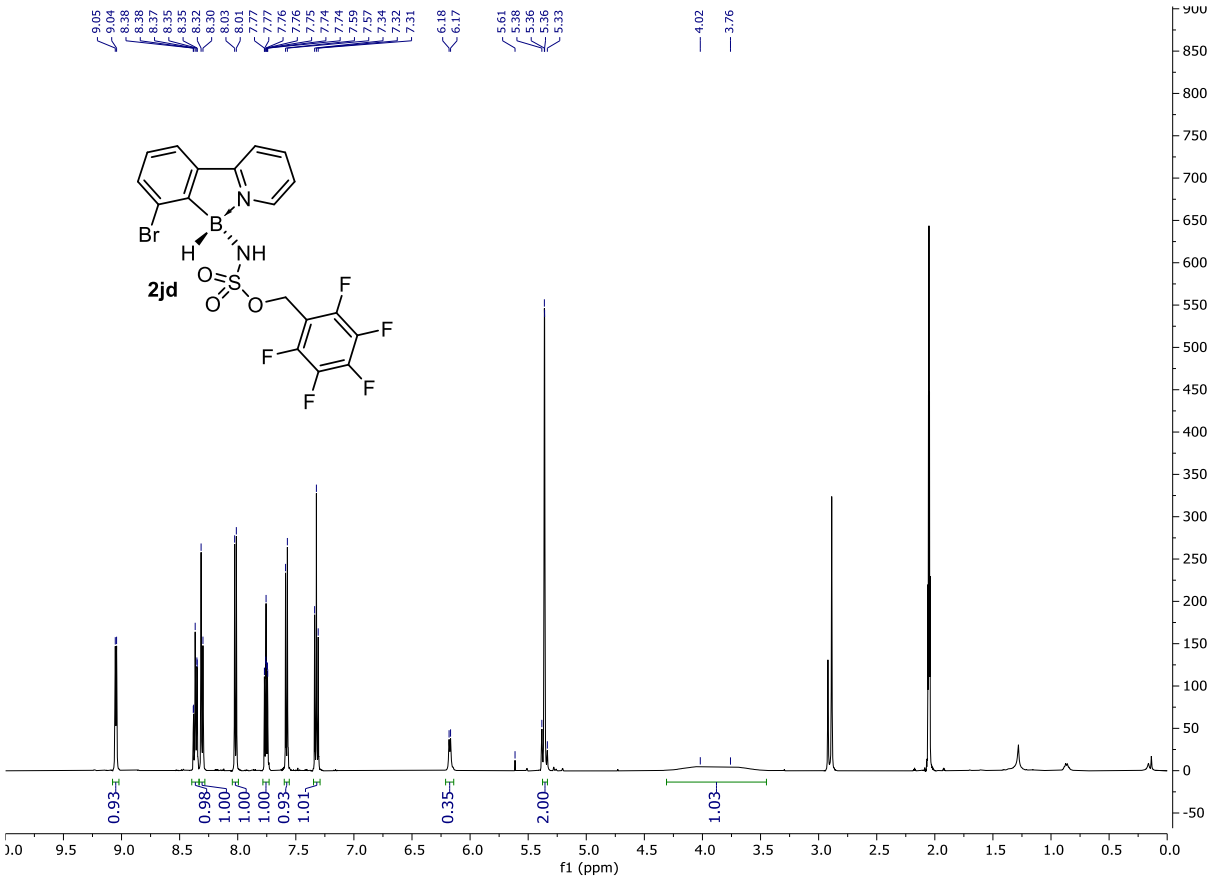


Fig. S215. ^{1}H NMR spectrum of **2jd** in acetone-d_6.

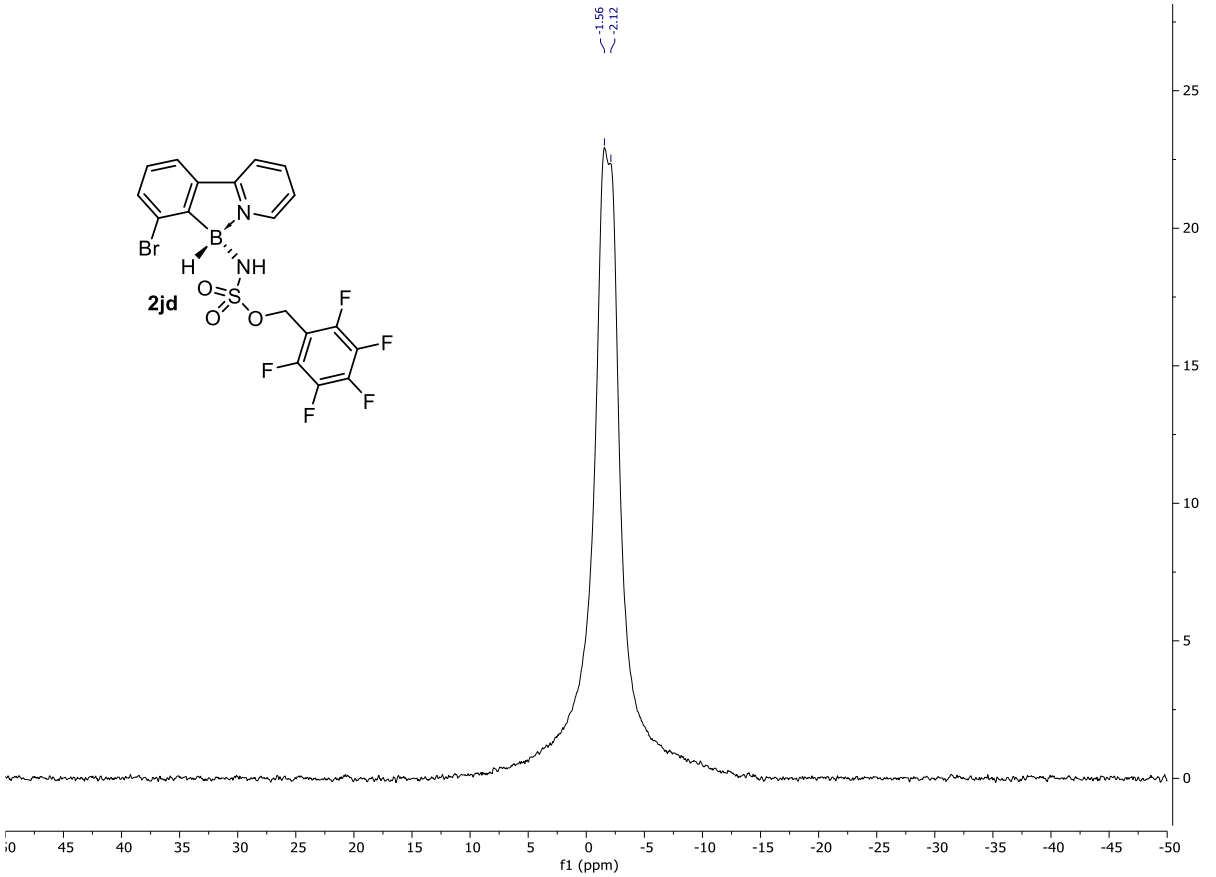


Fig. S216. ^{11}B NMR spectrum of **2jd** in acetone-d_6.

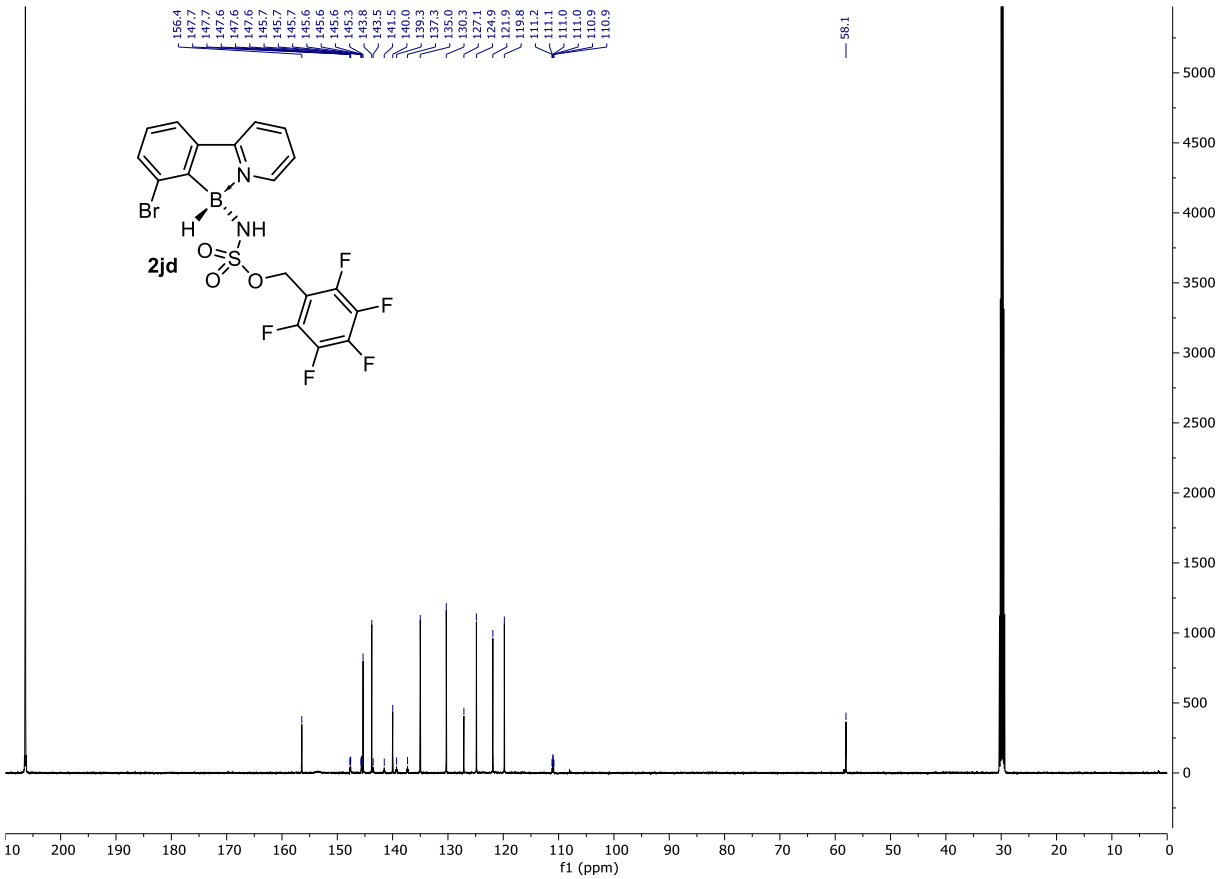


Fig. S217. ^{13}C NMR spectrum of **2jd** in acetone-d_6.

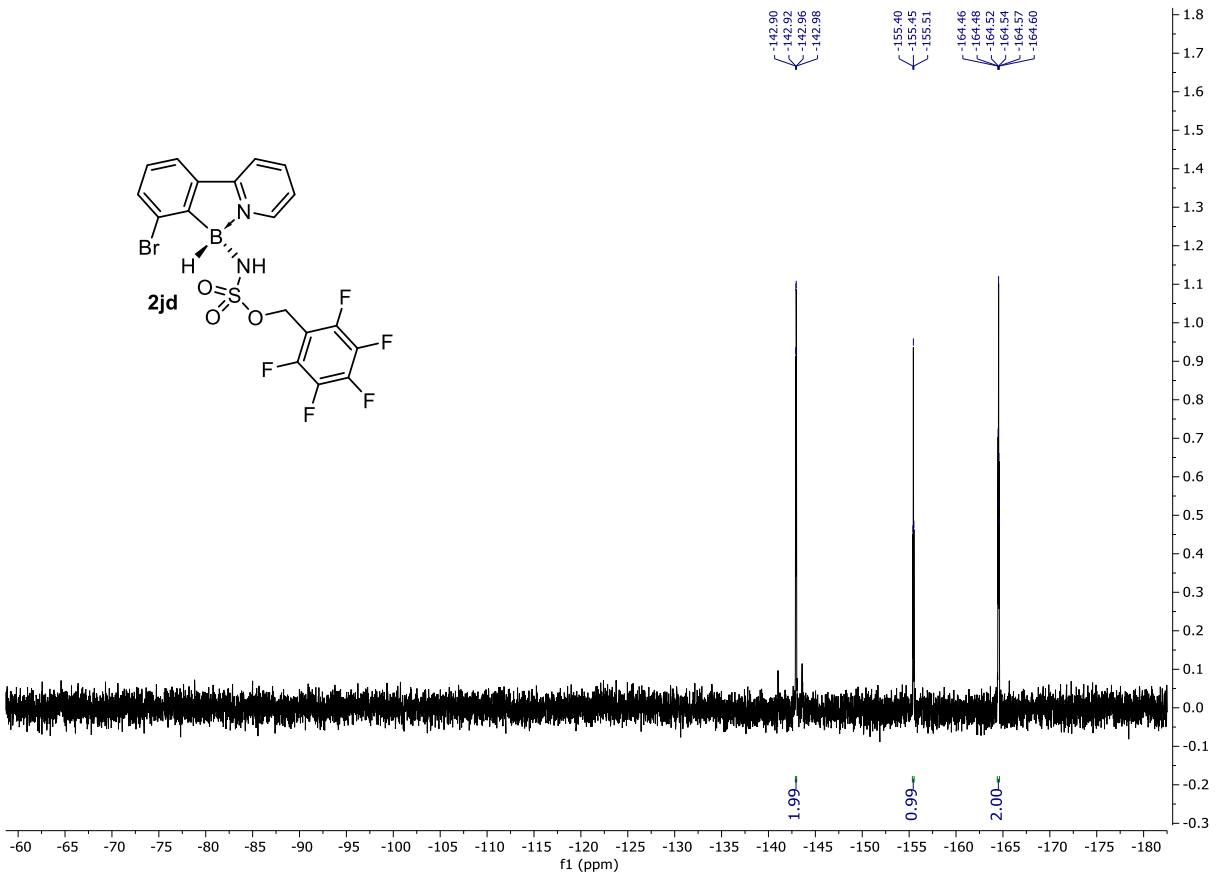


Fig. S218. ^{19}F NMR spectrum of **2jd** in acetone-d_6.

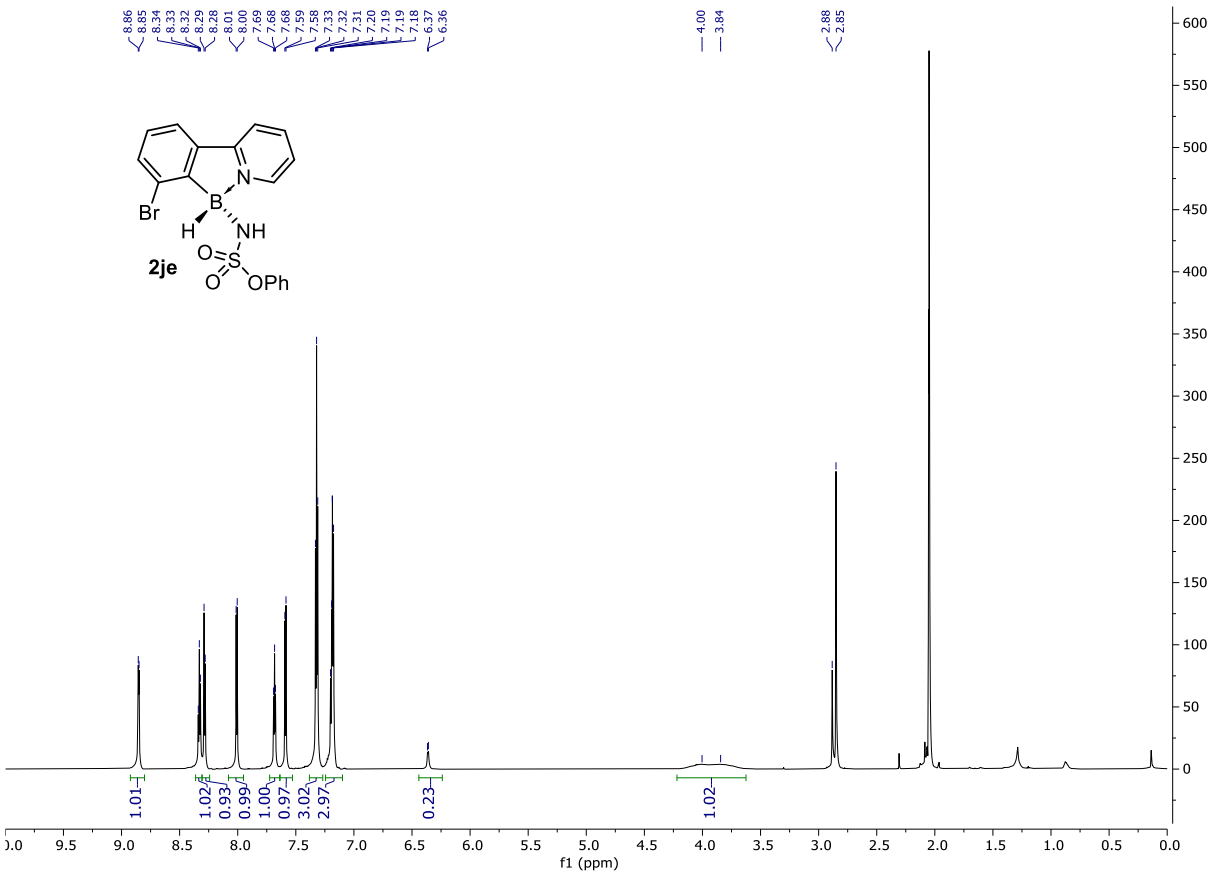


Fig. S219. ^{1}H NMR spectrum of **2je** in acetone-d_6.

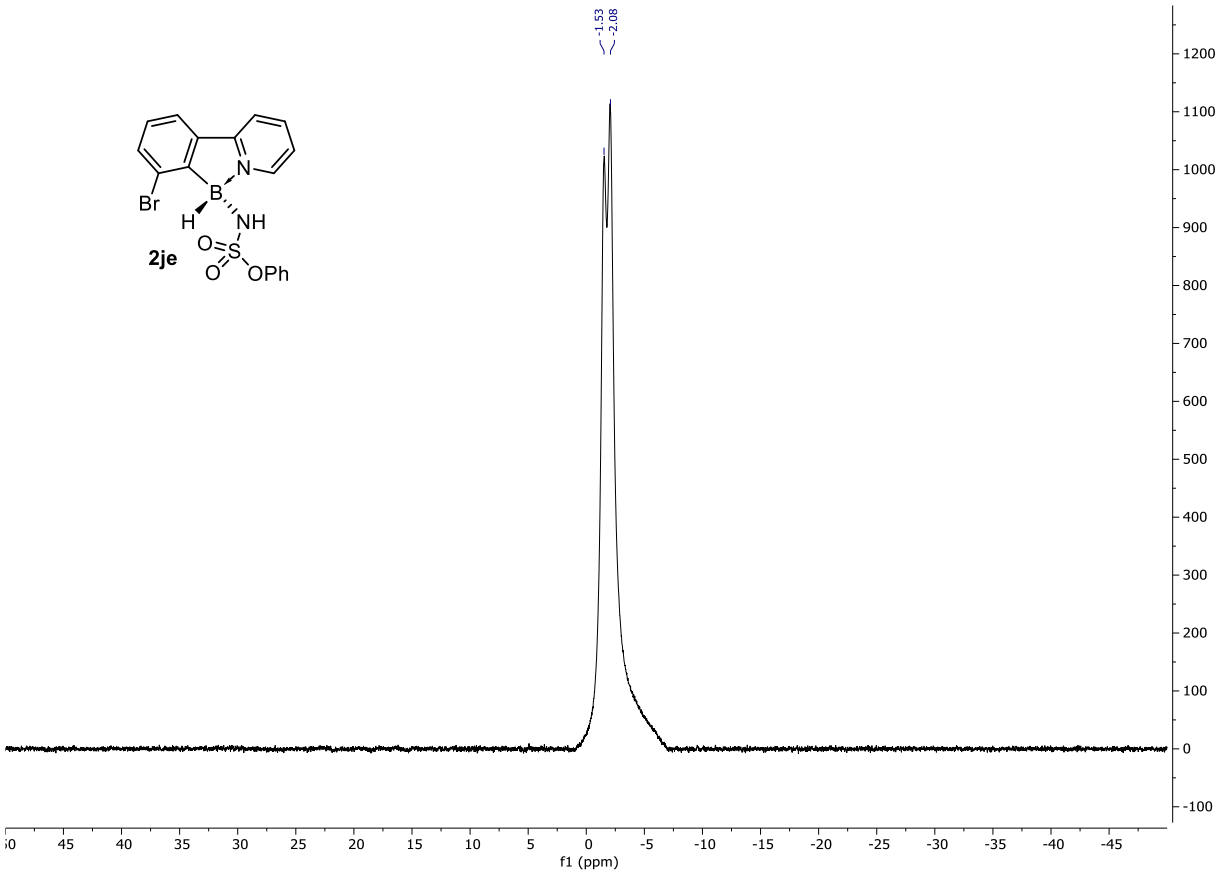


Fig. S220. ^{11}B NMR spectrum of **2je** in acetone-d_6.

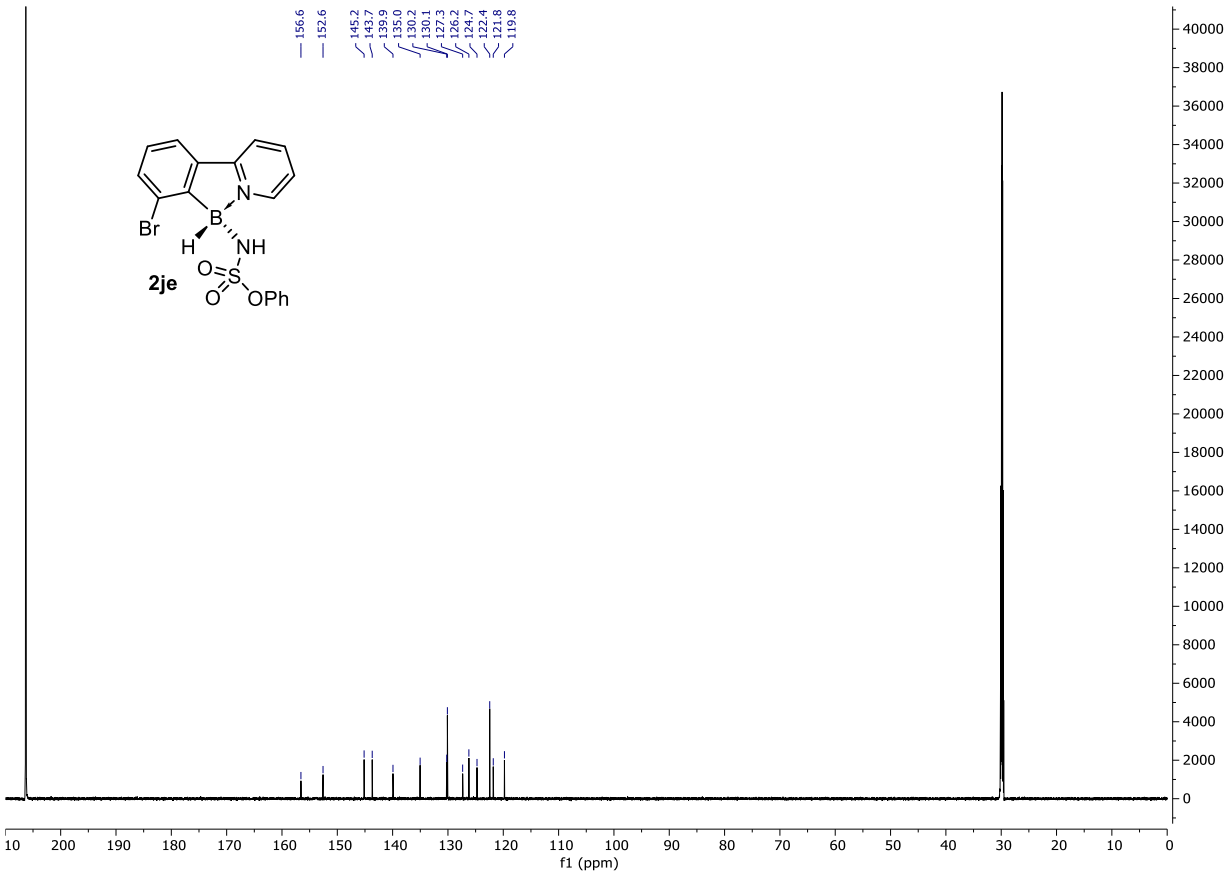


Fig. S221. ^{13}C NMR spectrum of **2je** in acetone-d_6.

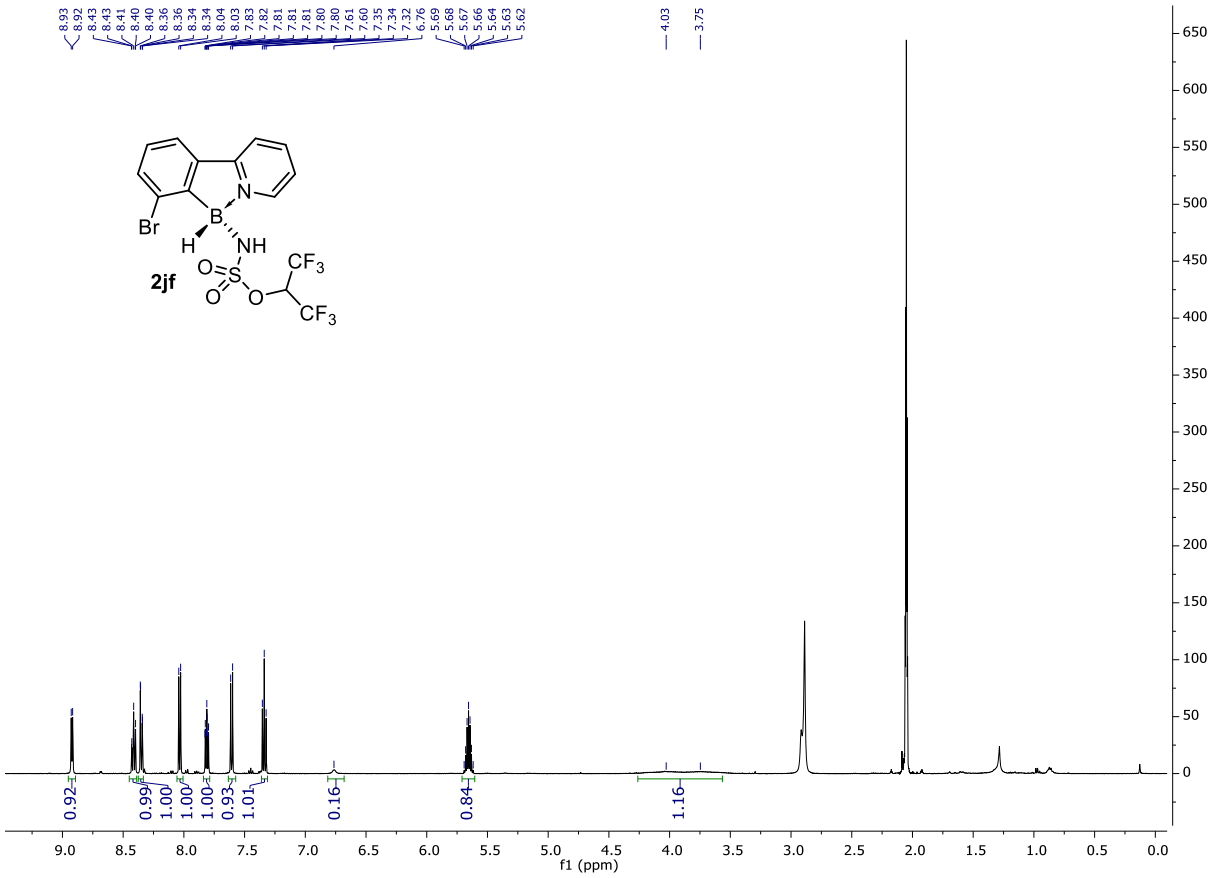


Fig. S222. ^{1}H NMR spectrum of **2jf** in acetone-d_6.

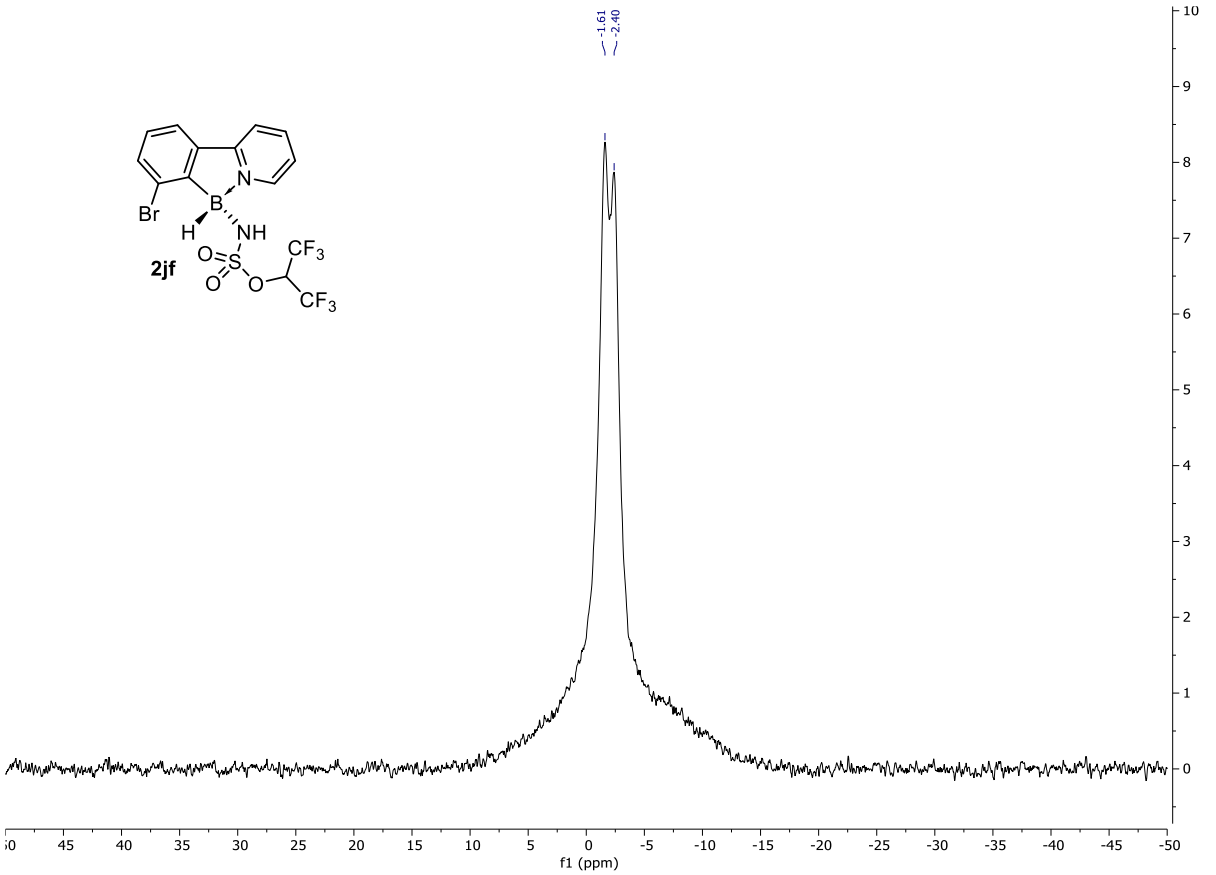


Fig. S223. ^{11}B NMR spectrum of **2jf** in acetone-d_6.

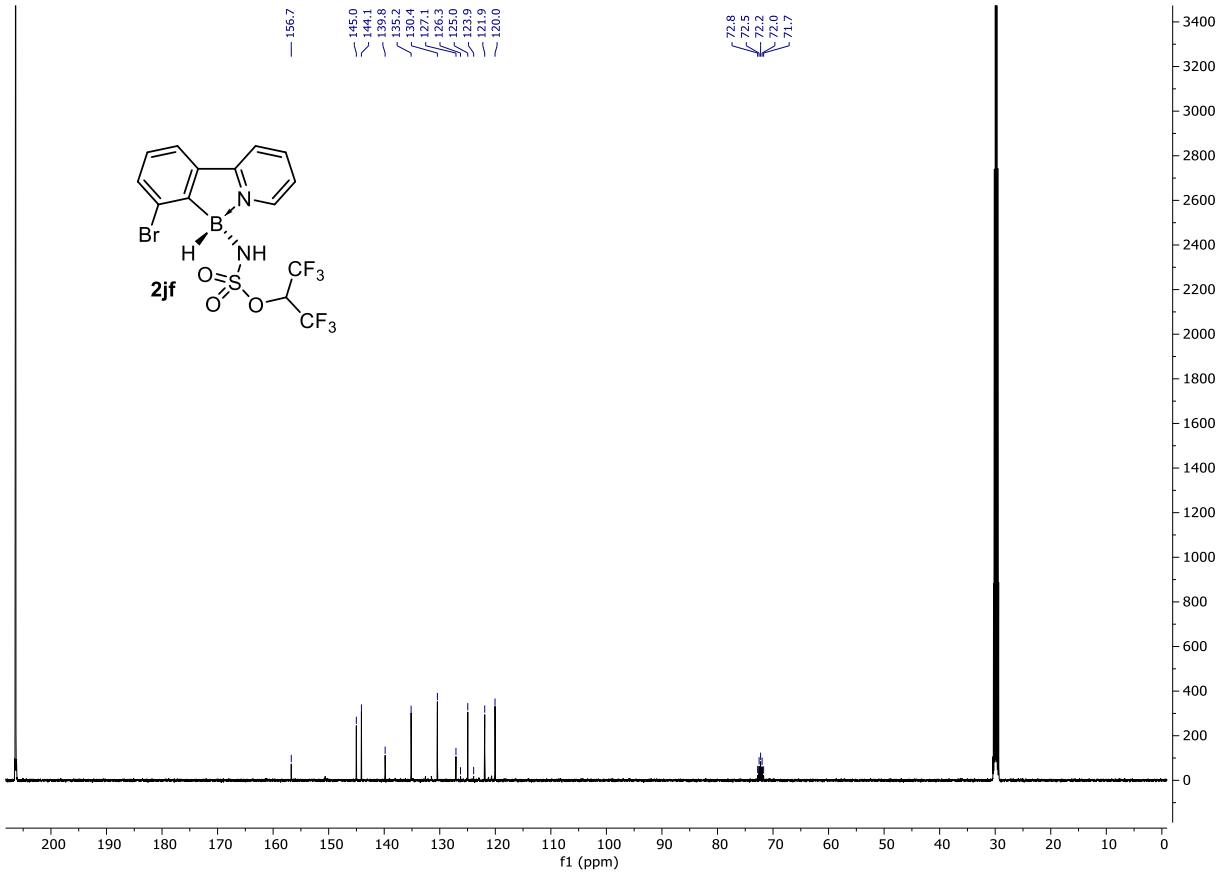


Fig. S224. ^{13}C NMR spectrum of **2jf** in acetone-d_6.

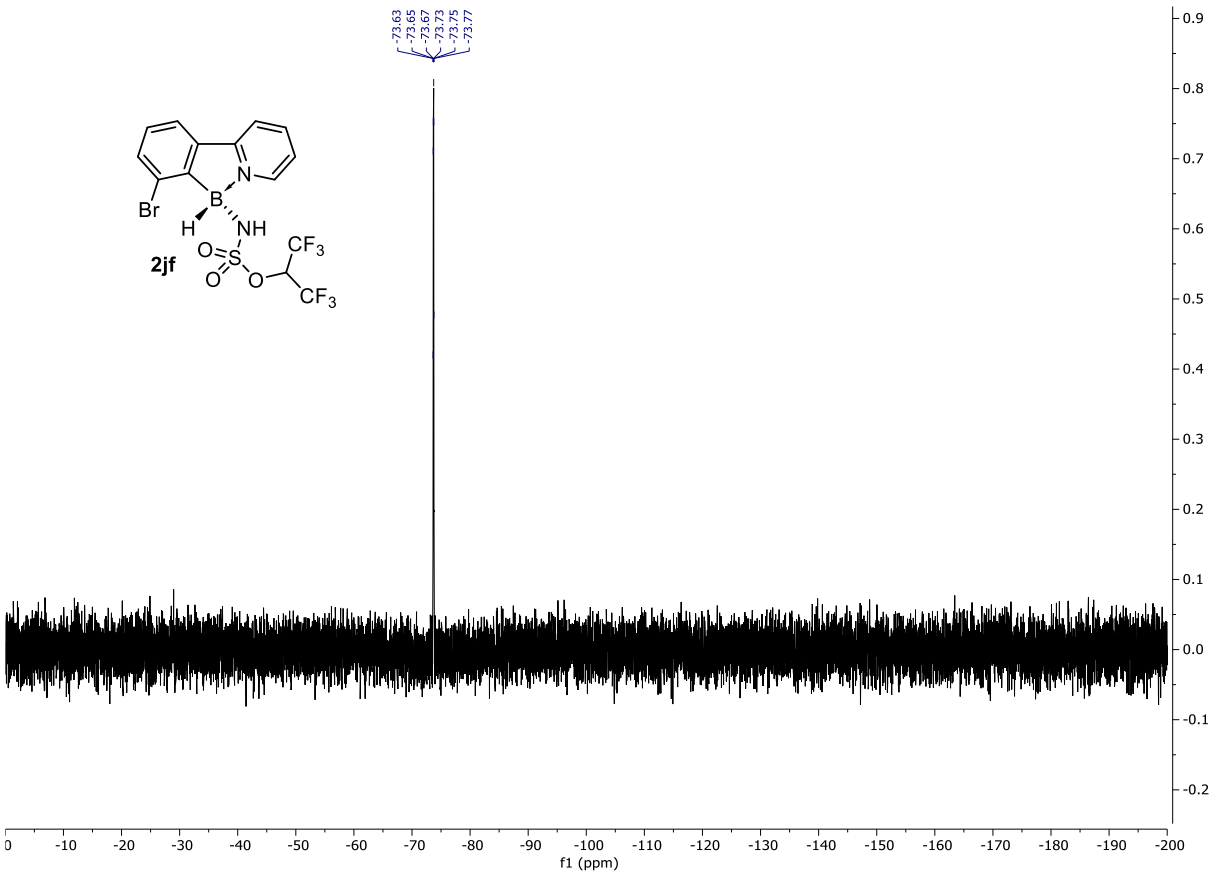


Fig. S225. ^{19}F NMR spectrum of **2jf** in acetone-d_6.

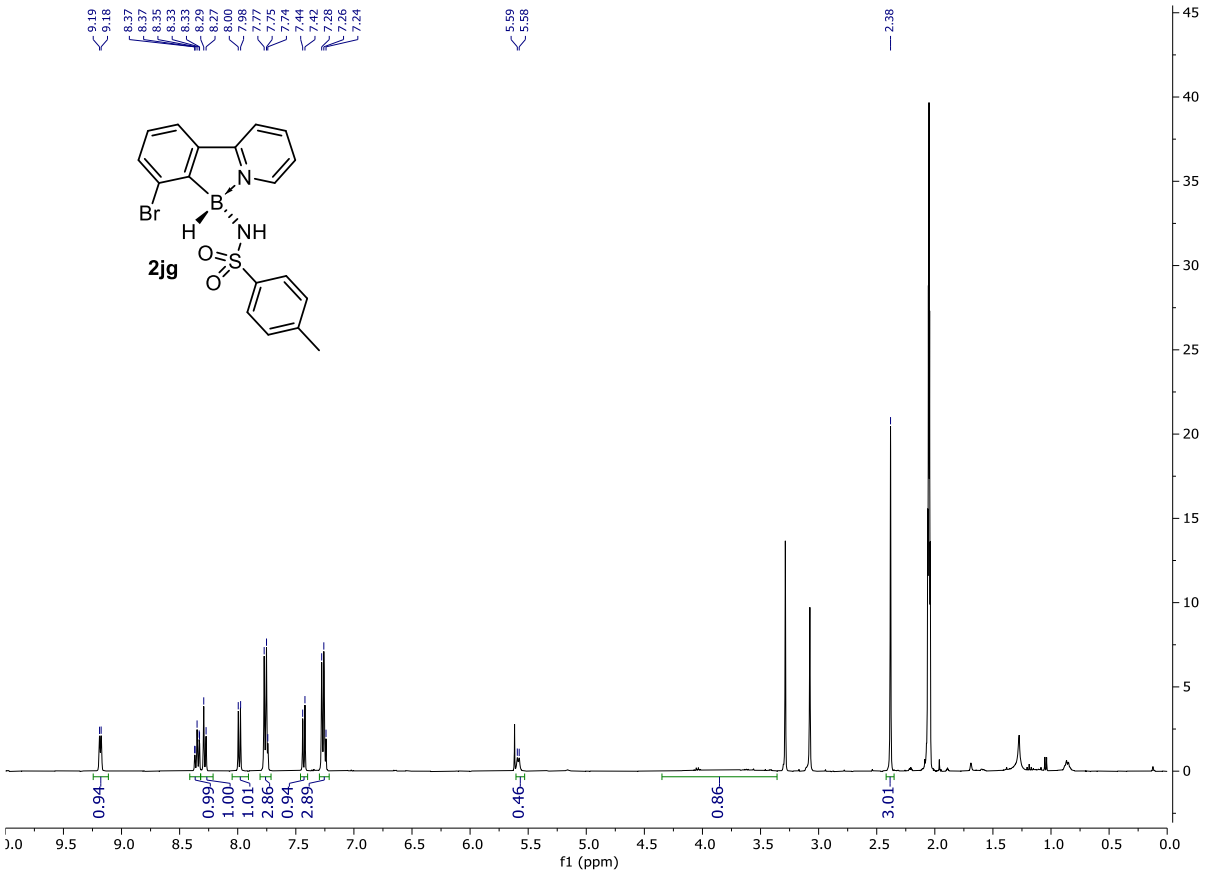


Fig. S226. ^{1}H NMR spectrum of **2jg** in acetone-d_6.

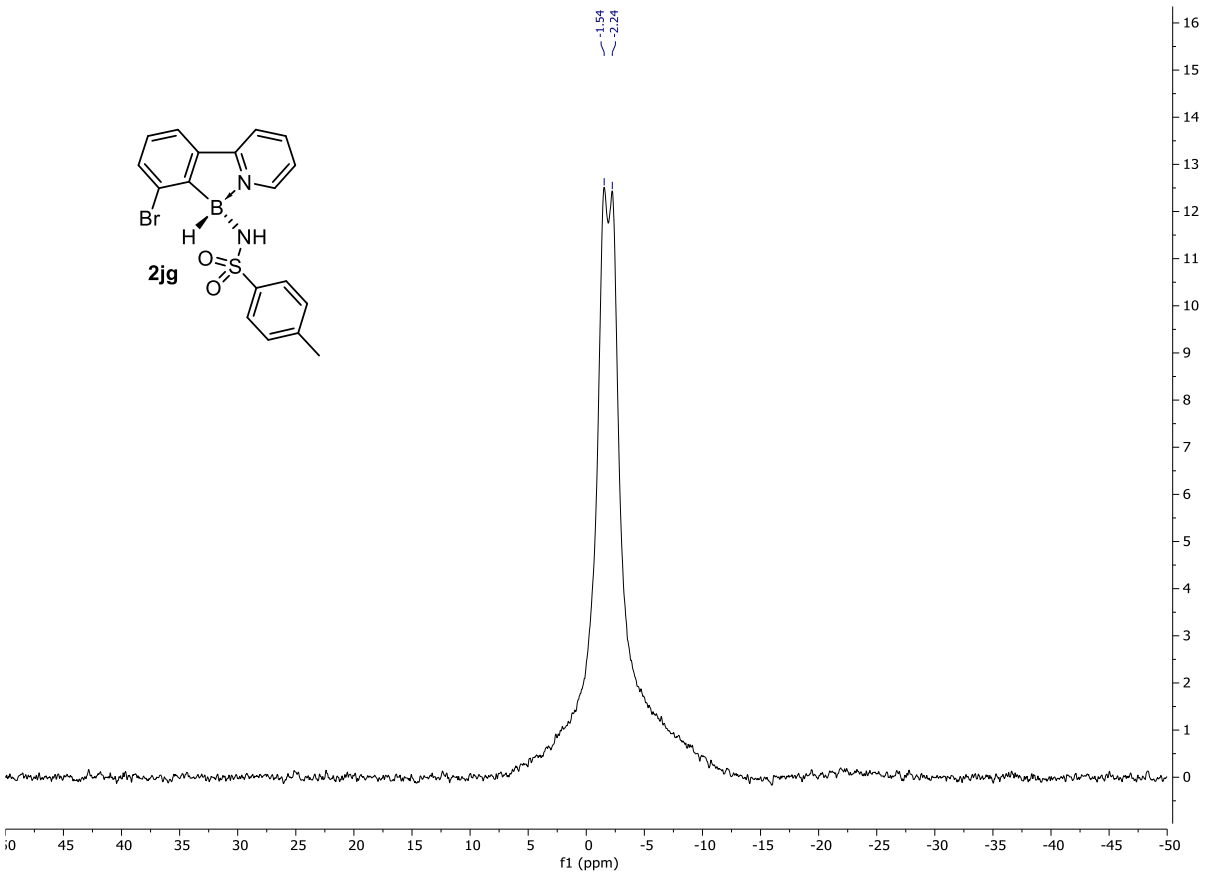


Fig. S227. ^{11}B NMR spectrum of **2jg** in acetone-d_6.

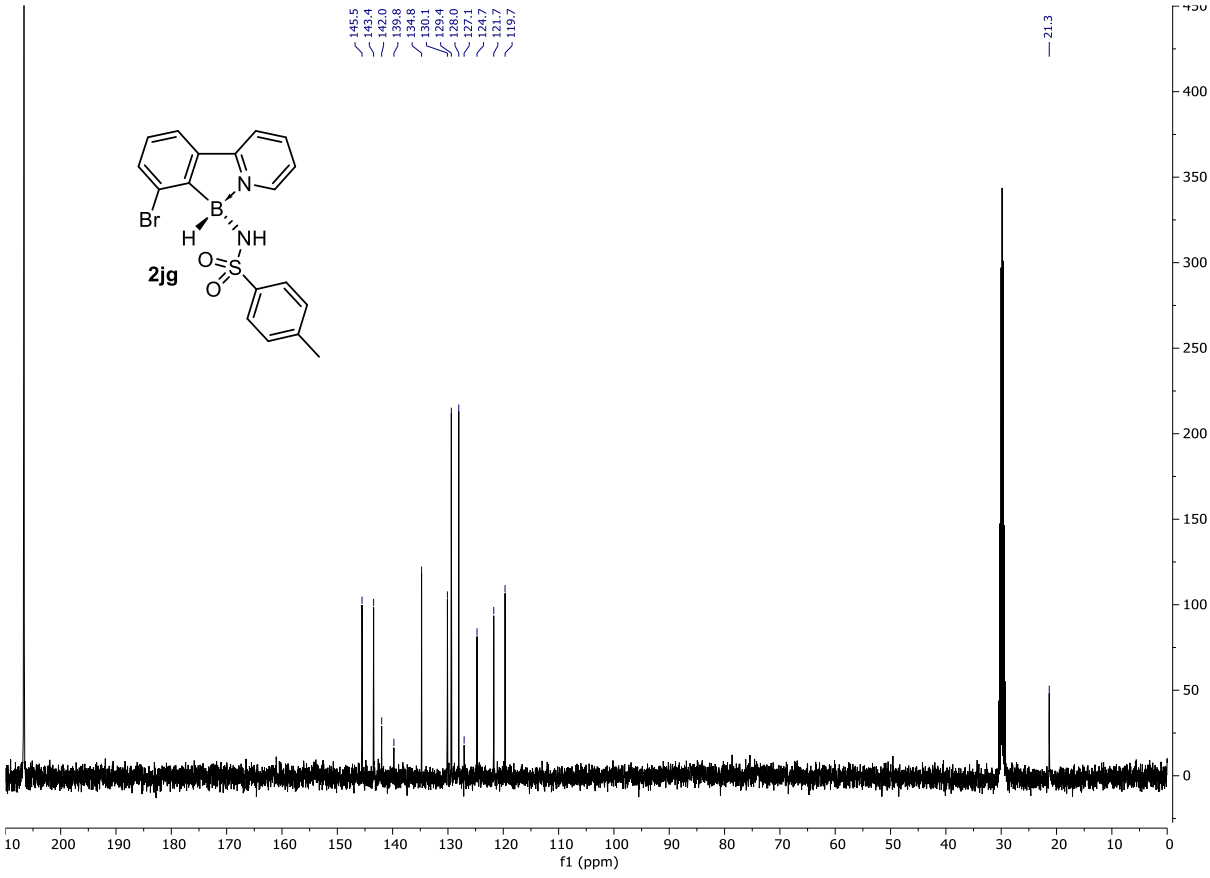


Fig. S228. ^{13}C NMR spectrum of **2jg** in acetone-d_6.

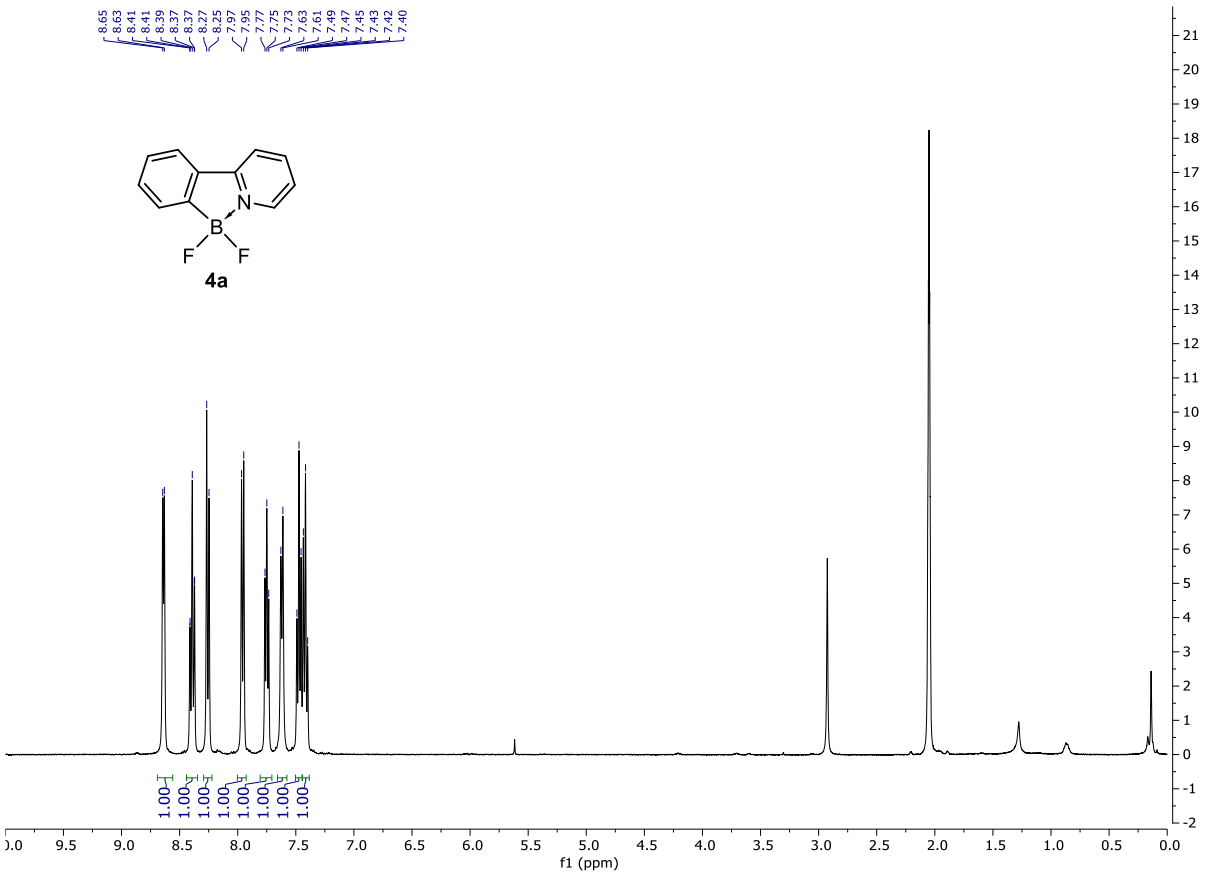


Fig. S229. ^{1}H NMR spectrum of **4a** in acetone-d_6.

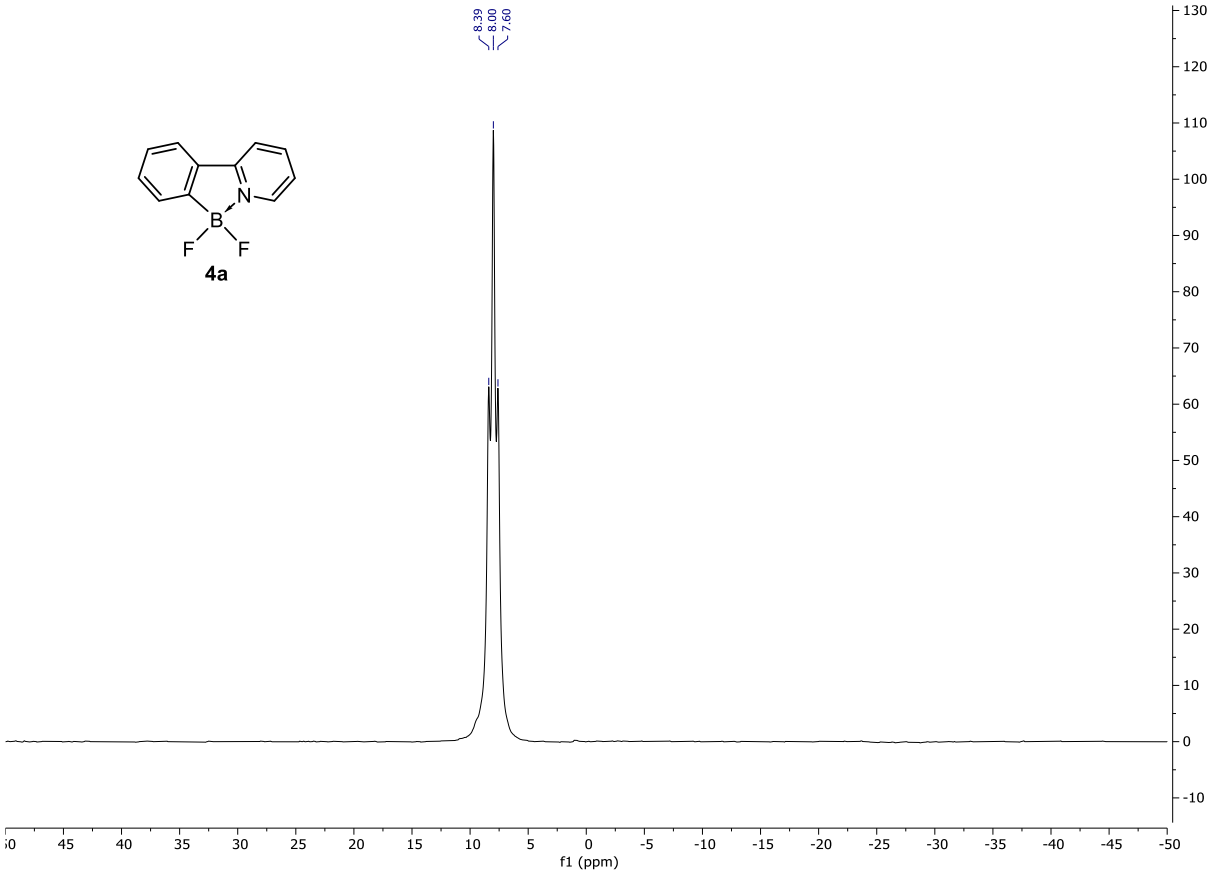


Fig. S230. ^{11}B NMR spectrum of **4a** in acetone-d_6.

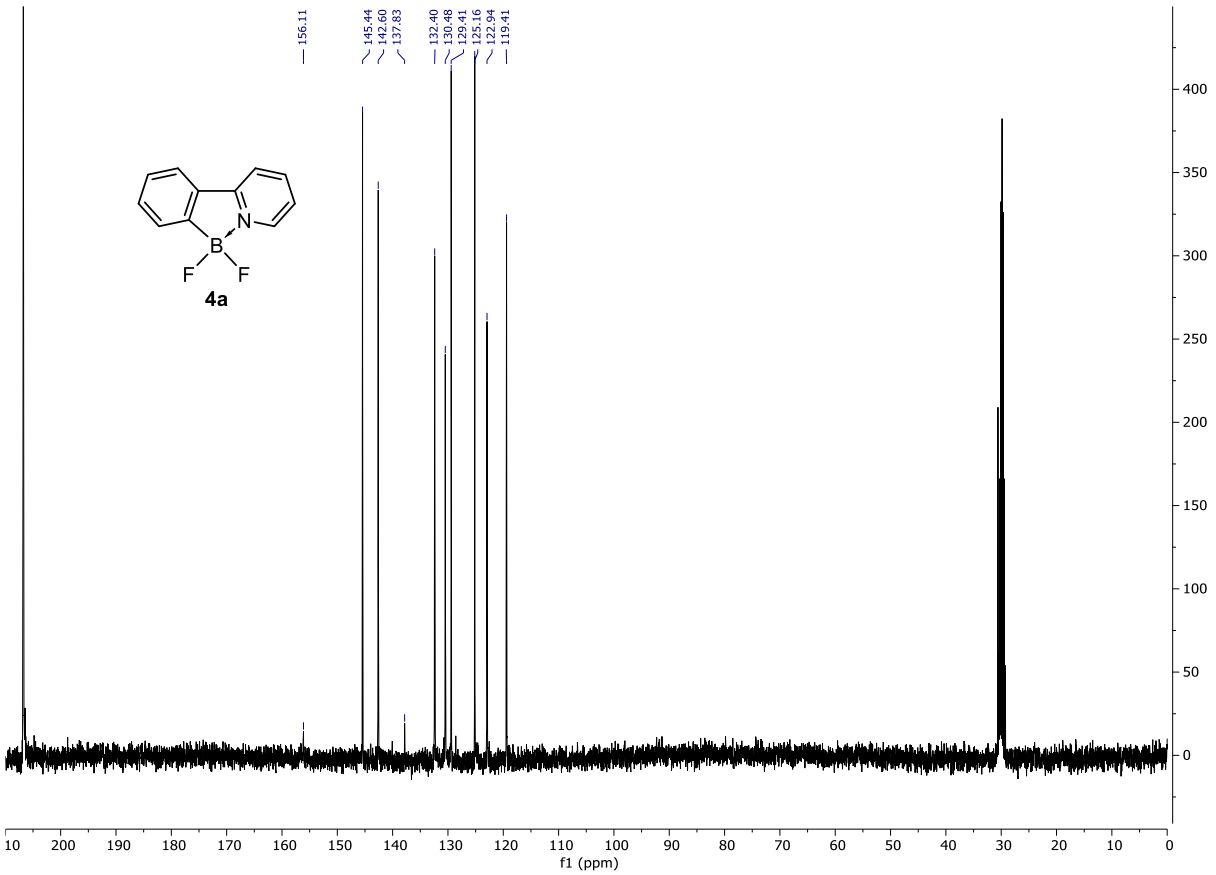


Fig. S231. ^{13}C NMR spectrum of **4a** in acetone-d_6.

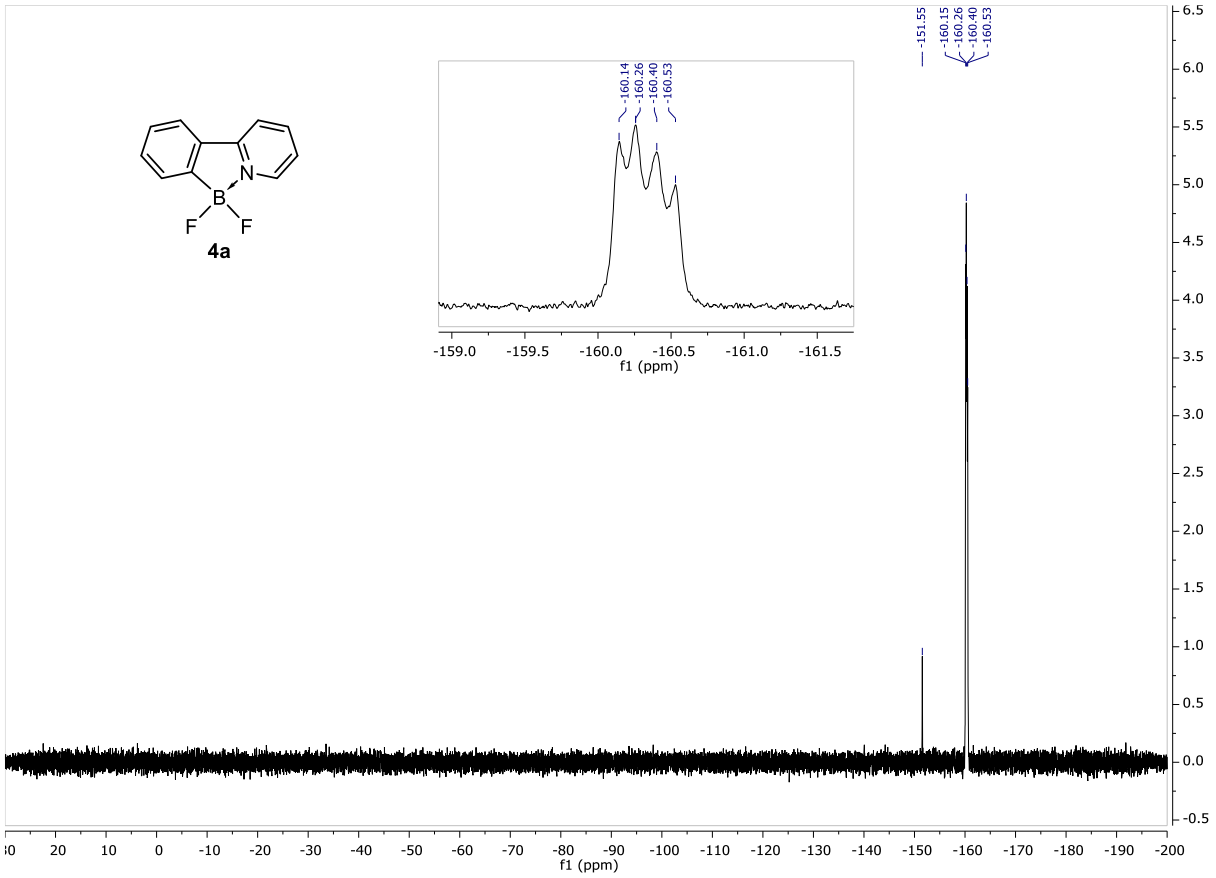


Fig. S232. ^{19}F NMR spectrum of **4a** in acetone-d_6.

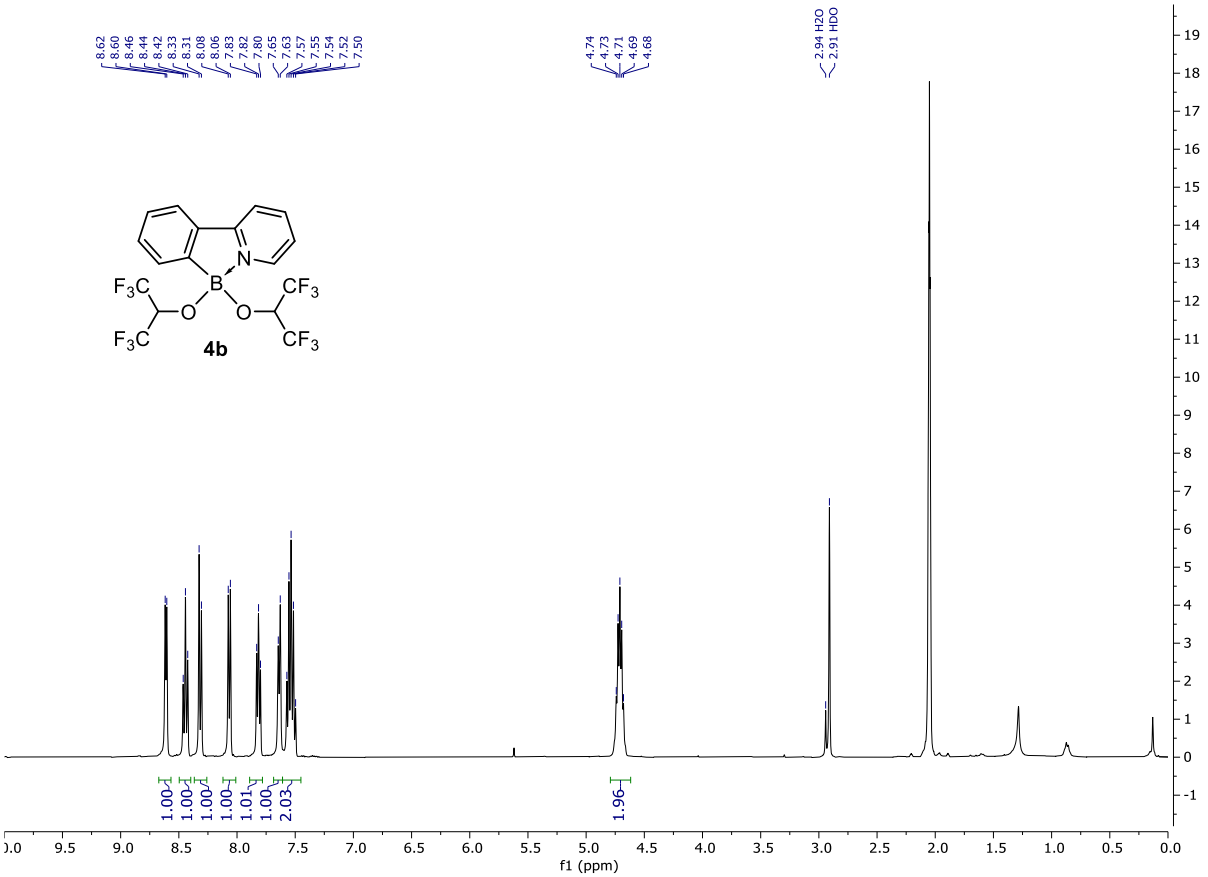


Fig. S233. ^{1}H NMR spectrum of **4b** in acetone-d_6.

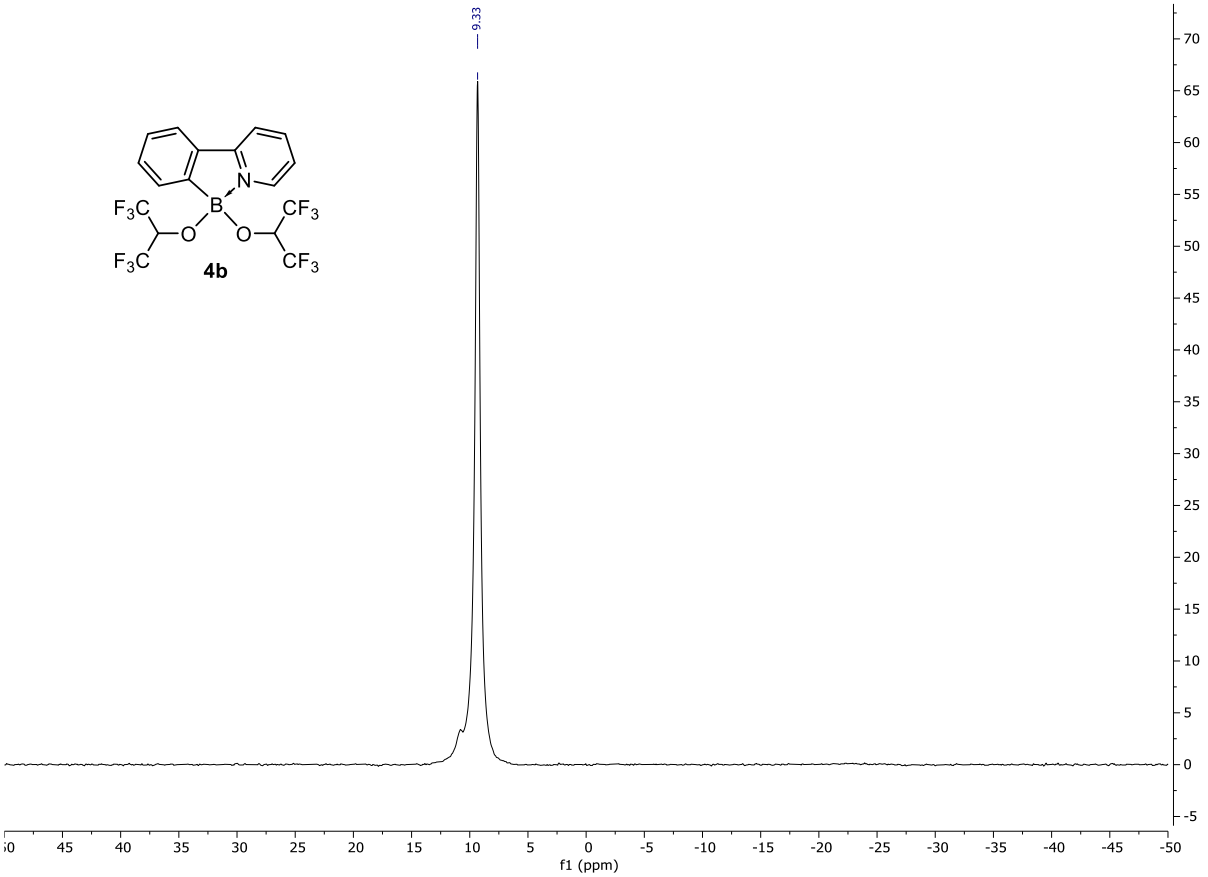


Fig. S234. ^{11}B NMR spectrum of **4b** in acetone-d_6.

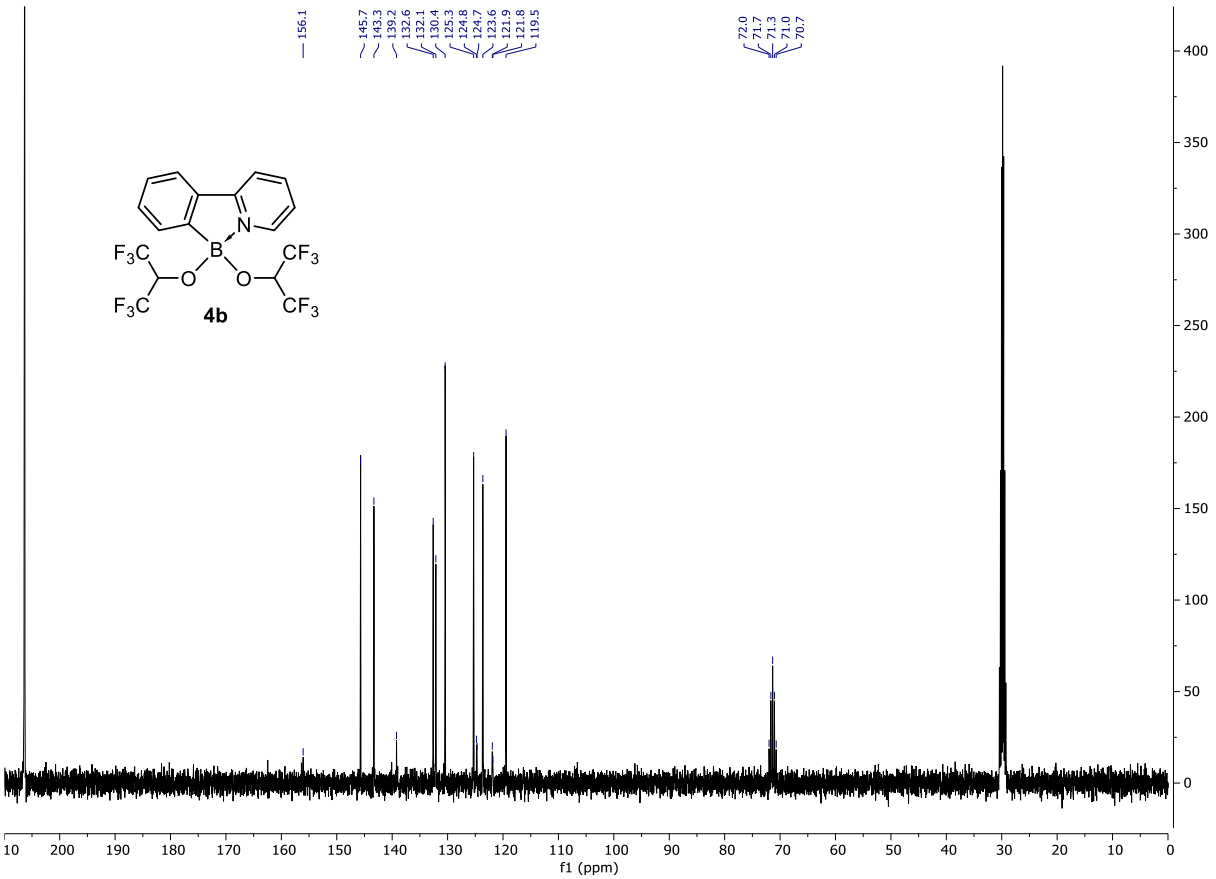


Fig. S235. ^{13}C NMR spectrum of **4b** in acetone-d_6.

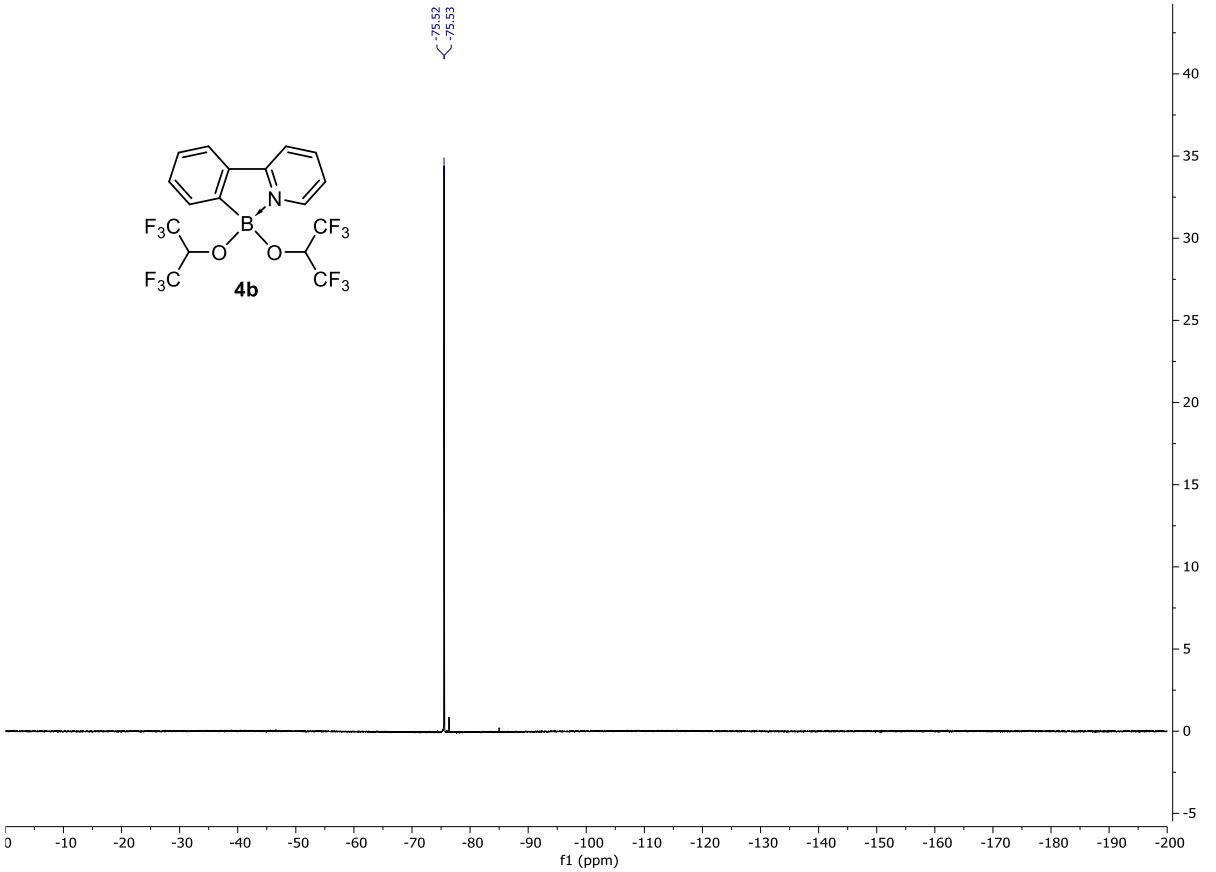


Fig. S236. ^{19}F NMR spectrum of **4b** in acetone-d_6.

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