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Published in:
Chemistry: A European Journal

DOI:
10.1002/chem.202003319

Publication date:
2020

Document Version
Other version

Chemistry–A European Journal

Supporting Information

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Thu-Hong Doan, Aurélien Chardon, Arnaud Osi, Damien Mahaut, Nikolay Tumanov, Johan Wouters, Benoît Champagne, and Guillaume Berionni*[a]

Supporting Information

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Content

General laboratory procedure

1.1. Analytical methods

^{1}H (400 MHz), ^{1}H (500 MHz), ^{13}C (101 MHz), ^{13}C (125 MHz), ^{19}F (376 MHz), ^{31}P NMR (162 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on 400 or 500 MHz NMR JEOL spectrometer. The observed signals are reported in parts per million (ppm) relative to the residual signal of the non-deuterated solvent for ^{1}H and ^{13}C NMR spectra.

The following abbreviations are used to describe multiplicities s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, br = broad, m = multiplet. The chemical shifts are calibrated to residual proton resonance of tetramethylsilane (TMS) (δ_H 0 ppm) and carbon resonance of the solvent $CDCl_3$ (δ_C 77.16 ppm). The external references considered as 0.0 ppm are borontrifluoride etherate ($BF_3{\cdot}Et_2O$) for ^{11}B NMR and trichloromonofluoromethane ($CFCl_3$) for ^{19}F NMR.

Flash chromatography was performed using silica gel Silica Flash® 40-63 micron (230-400 mesh) from Sigma-Aldrich. TLC detection was accomplished by irradiation with a UV lamp at 265 or 313 nm.

Melting points were determined on a Büchi B-545 device and are not corrected.

Infrared spectra were recorded on a PerkinElmer FT-IR Spectrometer.

UV-VIS absorption spectra were recorded by Cary 5000 UV-Vis-NIR Spectrophotometer. Photoluminescence spectra were recorded by Cary Eclipse Fluorescence Spectrophotometer.

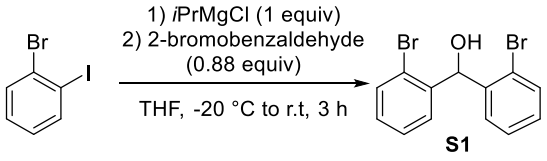
1.2. Materials

Diethylether, tetrahydrofuran and dichloromethane were dried with an MBraun solvent purification system and stored under argon. Others reagents and chemicals were purchased from Sigma-Aldrich, Alfa Aesar, TCI and Fluorochem and used without further purification. Unless otherwise stated all the reactions were performed under an atmosphere of argon using classical Schlenk line technique or in a high-performance glovebox.

2. Preparation of starting materials.

2.1. Synthesis of bis(2-bromophenyl)methanol derivatives

Bis(2-bromophenyl)methanol S1



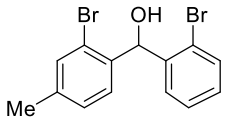
S1

Prepared according to a literature procedure.[1]
Under Ar atmosphere, a solution of *i*-PrMgCl (117 mL, 117 mmol, 2.0 M in THF, 1.0 equiv) was added to a solution 1-iodo-2-bromobenzene (30.0 mL, 234 mmol, 1.0 equiv) in THF (200 mL) at -20 °C. The mixture was stirred at -20 °C for 1,5 h. At the same temperature, 2-bromobenzaldehyde (24 mL, 206 mmol, 0.88 equiv) was added over 45 min. The mixture was stirred at -15 °C for further 45 min. Saturated aqueous NH_4Cl (100 mL) and H_2O (700 mL) were added and the reaction mixture was allowed to warm at room temperature. The mixture was diluted with Et_2O, the organic phase was collected and the aqueous phase was extracted using Et_2O (2 x 200 mL). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduced pressure. Precipitation from *n*-hexane, followed by filtration afforded bis(2-bromophenyl)methanol **S1** as a white powder (55.7 g, 162 mmol, 69% yield). ^1H and ^{13}C NMR data are in good agreement with the one reported in the literature. [1]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 – 7.44 (m, 2H), 7.29 − 7.20 (m, 4H), 7.15 – 7.08 (m, 2H), 6.34 (s, 1H), 2.50 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 141.0 (C_q), 133.1 (CH), 129.6 (CH), 128.8 (CH), 127.8 (CH), 124.0 (C_q), 74.4 (CH).

(2-bromo-4-methylphenyl)(2-bromophenyl)methanol S2



S2

Following the procedure for the synthesis of bis(2-bromophenyl)methanol **S1**, the product **S2** was prepared from 1-iodo-2-bromo-4-methylbenzene (4.8 mL, 33.7 mmol, 1.0 equiv) in THF (84 mL), *i*-PrMgCl (16.8 mL, 33.7 mmol, 2M in THF, 1.0 equiv) and bromobenzaldehyde (3.5 mL, 30.3 mmol, 0.9 equiv). The product was purified by flash

[1] C. Sparr, A. Link, C. Fisher, *Synthesis*, **2017**, *49*, 397.

chromatography (SiO_2, EtOAc / *n*-pentane = 1/10) to afford **S2** as a pale yellow oil, which became a pale yellow sticky foam under vacuum line (10.5 g, 29.5 mmol, 99% yield).

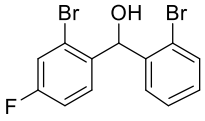
R_f = 0.57 (SiO_2, EtOAc / *n*-pentane = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.29 (m, 1H), 7.22 – 7.16 (m, 1H), 7.16 – 7.05 (m, 2H), 6.37 (d, *J* = 4.0 Hz, 1H, CH), 2.53 (d, *J* = 4.0 Hz, 1H, OH), 2.33 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 141.2 (C_q), 139.8 (C_q), 138.0 (C_q), 133.5 (CH), 133.0 (CH), 129.4 (CH), 128.7 (CH), 128.5 (2 x CH), 127.7 (CH), 123.82 (C_q), 123.80 (C_q), 74.1 (CH), 20.9 (CH_3).

HRMS (ESI) (m/z): calcd. for [$C_{14}H_{11}{}^{79}Br_2$] ([M-OH]$^+$): 336.92220; found: 336.92509.

(2-bromo-4-fluorophenyl)(2-bromophenyl)methanol S3



S3

Following the procedure for the synthesis of bis(2-bromophenyl)methanol **S1**, the product **S3** was prepared from 1-iodo-2-bromo-4-fluorobenzene (4.3 mL, 33.2 mmol, 1.0 equiv) in anhydrous THF (84 mL), *i*-PrMgCl (16.6 mL, 33.2 mmol, 2M in THF, 1.0 equiv) and bromobenzaldehyde (3.5 mL, 29.9 mmol, 0.9 equiv). The crude was crystallized in CH_2Cl_2/*n*-pentane in a fridge to afford the desired compound **S3** as colorless crystals (6.89 g). The yellow mother liqueur was purified by flash chromatography (SiO_2, EtOAc /*n*-pentane = 1/10) to give **S3** as a white solid (3.61 g). The total amount of the obtained product is 10.5 g (29.1 mmol, 99% yield).

R_f = 0.56 (SiO_2, EtOAc/*n*-pentane = 1/10)

M.p.: 87 – 89°C (CH_2Cl_2/*n*-pentane)

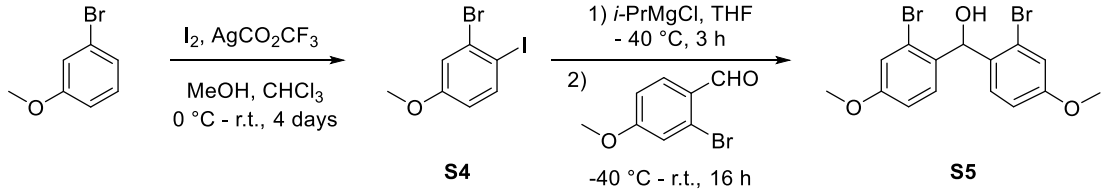
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 – 7.53 (m, 1H), 7.38 – 7.27 (m, 4H), 7.24 – 7.16 (m, 1H), 7.07 – 6.97 (m, 1H), 6.37 (d, *J* = 4.0 Hz, 1H, CH), 2.57 (d, *J* = 4.0 Hz, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 162.0 (d, $J_{C\text{-}F}$ = 251.2 Hz, C_q), 140.9 (C_q), 137.1 (d, $J_{C\text{-}F}$ = 3.5 Hz, C_q), 133.2 (CH), 129.9 (d, $J_{C\text{-}F}$ = 8.5 Hz, CH), 129.7 (CH), 128.6 (CH), 127.8 (CH), 124.0 (d, $J_{C\text{-}F}$ = 9.6 Hz, C_q), 123.8 (C_q), 120.3 (d, $J_{C\text{-}F}$ = 24.6 Hz, CH), 114.8 (d, $J_{C\text{-}F}$ = 20.9 Hz, CH), 73.8 (CH).

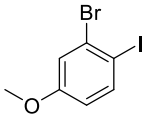
^{19}F NMR (471 MHz, $CDCl_3$): δ (ppm) -112.1 (m).

HRMS (ESI) (m/z): calcd. for $[C_{13}H_{18}{}^{79}Br_2F]$ ($[M\text{-}OH]^+$): 340.89713; found: 340.89740.

Synthesis of bis(2-bromo-4-methoxyphenyl)methanol S5



2-Bromo-1-iodo-4-methoxymethane S4



S4

Following the reported procedure,[2] to a solution of 3-bromoanisole (3.39 mL, 26.7 mmol, 1.0 equiv) and $AgCO_2CF_3$ (8.27 g, 37.4 mmol, 1.4 equiv) in MeOH (135 mL) was added dropwise a solution of I_2 (9.50 g, 37.4 mmol, 1.4 equiv) in $CHCl_3$ (75 mL) via a dropping funnel at 0°C by using an ice bath. The reaction was carried out in a dark hood and the flask containing reaction mixture was covered by aluminum foil. After the addition finished, the ice bath was removed and the reaction mixture was stirred at room temperature for 4 days. The reaction mixture was then filtered through a plug of Celite to remove a yellow solid and the Celite plug was washed with $CHCl_3$. The filtrate was concentrated under reduced pressure. The brown oil residue was dissolved in CH_2Cl_2 and the solution was washed 3 times with saturated $Na_2S_2O_5$, then extracted with CH_2Cl_2. The organic layer was washed with brine, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. The product was purified by flash chromatography (SiO_2, *n*-pentane) to afford **S4** as a transparent oil (6.57 g, 21.0 mmol, 79% yield).

$\mathbf{R_f}$ = 0.39 (SiO_2, *n*-pentane)

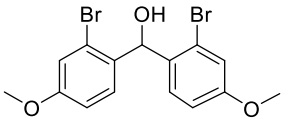
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 2.9 Hz, 1H), 6.60 (dd, *J* = 8.8, 2.9 Hz, 1H), 3.78 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 160.4 (C_q), 140.4 (CH), 130.1 (C_q), 118.5 (CH), 115.6 (CH), 89.7 (C_q), 55.8 (CH_3).

HRMS (ESI) (m/z): calcd. for $[C_7H_6O^{79}Br^{127}I]$ ($[M]^+$): 311.86412; found: 311.86418.

[2] M. Matveenko, G. Liang, E. M. W. Lauterwasser, E. Zubía, D. Trauner, *J. Am. Chem. Soc*. **2012**, *134*, 9291.

Bis(2-bromo-4-methoxyphenyl)methanol S5



S5

Following the procedure for the synthesis of bis(2-bromophenyl)methanol **S1**, the product **S5** was prepared from 1-iodo-2-bromo-4-methoxybenzene **S4** (6.00 g, 19.17 mmol, 1.0 equiv) in THF (42 mL), *i*-PrMgCl (9.6 mL, 19.17 mmol, 2M in THF, 1.0 equiv) and 2-bromo-4-methoxybenzaldehyde (3.71 g, 17.25 mmol, 0.9 equiv). The product was purified by flash chromatography (SiO_2, EtOAc / *n*-pentane = 1/20, then 1/4) to afford **S5** as a yellow oil, which became a yellow sticky foam under vacuum line (6.57 g, 16.34 mmol, 85% yield).

R_f = 0.46 (SiO_2, EtOAc/*n*-pentane = 1/4)

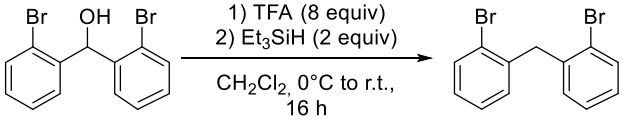
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.6 Hz, 2H), 6.29 (d, *J* = 3.5 Hz, 1H, CH), 3.80 (s, 6H, OCH_3), 2.43 (d, *J* = 3.8 Hz, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 159.7 (C_q), 133.5 (C_q), 129.3 (CH), 124.1 (C_q), 118.3 (CH), 113.5 (CH), 73.5 (CH), 55.7 (CH_3).

HRMS(ESI) (m/z): calcd. for [$C_{15}H_{12}O_2{}^{79}Br_2$] ([M+H-$H_2O$]$^+$): 382.92768; found: 382.92740.

2.2. Synthesis of bis(2-bromophenyl)methane derivatives

Bis(2-bromophenyl)methane 1a



S1 **1a**

Prepared according to the literature.[3] Trifluoroacetic acid (36.0 mL, 469 mmol, 8 equiv) was added dropwise to a solution of bis(2-bromophenyl)methanol **S1** (20.1 g, 58.8 mmol, 1 equiv) in CH_2Cl_2 (150 mL) at 0 °C. After 5 min at 0 °C, triethylsilane (19 mL, 119 mmol, 2 equiv) was added dropwise. The mixture was allowed to warm at room temperature and stirred overnight. The crude mixture was concentrated under reduce pressure. Filtration through a plug of silica gel afforded the title compound as colorless

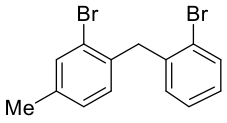
[3] T. J. A. Corrie, L. T. Ball, C. A. Russell, G. C. Lloyd-Jones, *J. Am. Chem. Soc*. **2016**, *138*, 45.

oil (19.0 g, 58.2 mmol, 99% yield). ^{1}H and ^{13}C NMR data are in good agreement with the one reported in the literature. [3]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.23 (td, *J* = 7.5, 1.3 Hz, 2H), 7.12 (td, *J* = 8.5, 7.7, 1.7 Hz, 2H), 7.04 – 6.96 (m, 2H), 4.21 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 139.0 (C_q), 133.0 (CH), 130.8 (CH), 128.2 (CH), 127.7 (CH), 125.2 (C_q), 42.2 (CH_2).

(2-bromo-4-methylphenyl)(2-bromophenyl)methane 1b



1b

Following the procedure for the synthesis of bis(2-bromophenyl)methane **1a**, the product **1b** was prepared from the corresponding alcohol **S2** (9.50 g, 26.7 mmol, 1.0 equiv), trifluoroacetic acid (16.3 mL, 213.4 mmol, 8.0 equiv) and triethylsilane (8.5 mL, 53.4 mmol, 2.0 equiv) in CH_2Cl_2 (67 mL). The product was purified by filtered through a plug of silica gel with *n*-pentane as eluent. The product was obtained as a colorless oil (9.04 g, 26.6 mmol, 99% yield) and dried under vacuum line overnight to remove the traces of triethylsilane.

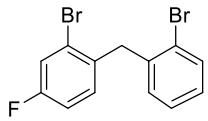
R_f = 0.54 (SiO_2, *n*-pentane)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43 (d, *J* = 1.0 Hz, 1H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.16 (s, 2H, CH_2), 2.32 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 139.3 (C_q), 138.3 (C_q), 135.8 (C_q), 133.4 (CH), 132.9 (CH), 130.8 (CH), 130.6 (CH), 128.5 (CH), 128.1 (CH), 127.6 (CH), 125.2 (C_q), 124.9 (C_q), 41.8 (CH_2), 20.8 (CH_3).

HRMS (ESI) (m/z): calcd. for [$C_{14}H_{11}{}^{79}Br_2$] ([M+H]$^+$): 336.92220; found: 336.92216.

(2-bromo-4-fluorophenyl)(2-bromophenyl)methane 1c



1c

Following the procedure for the synthesis of bis(2-bromophenyl)methane **1a**, the product **1c** was prepared from the corresponding alcohol **S3** (9.50 g, 26.4 mmol, 1.0 equiv), trifluoroacetic acid (16.2 mL, 211.1 mmol, 8.0 equiv) and triethylsilane (8.4 mL, 52.8 mmol, 2.0 equiv) in CH_2Cl_2 (67 mL). The product was purified by filtered through a plug of silica gel with *n*-pentane as eluent. The product was obtained as a colorless oil (9.05 g, 26.3 mmol, 99% yield) and dried under vacuum line overnight to remove the traces of triethylsilane.

R_f = 0.59 (SiO_2, *n*-pentane)

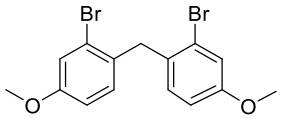
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.27 – 7.21 (m, 1H, partly overlapped with $CDCl_3$), 7.17 – 7.09 (m, 1H), 7.01 – 6.96 (m, 1H), 6.96 – 6.90, m, 2H), 4.16 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 161.2 (d, J_{C-F} = 249.3 Hz, C_q), 138.8 (C_q), 134.9 (d, J_{C-F} = 3.6 Hz, C_q), 133.1 (CH), 131.4 (d, J_{C-F} = 8.2 Hz, CH), 130.8 (CH), 128.4 (CH), 127.8 (CH), 125.2 (C_q), 124.9 (d, J_{C-F} = 9.3 Hz, C_q), 120.1 (d, J_{C-F} = 24.3 Hz, CH), 114.8 (d, J_{C-F} = 20.9 Hz, CH), 41.4 (CH_2).

^{19}F NMR (471 MHz, $CDCl_3$): δ (ppm) -114.3 (m).

HRMS (ESI) (m/z): calcd. for [$C_{13}H_8{}^{79}Br_2F$] ([M]$^+$): 340.89713; found: 340.89729.

Bis(2-bromo-4-methoxyphenyl)methane 1d



1d

Following the procedure for the synthesis of bis(2-bromophenyl)methane **1a**, the product **1d** was prepared from the corresponding alcohol **S5** (2.55 g, 6.34 mmol, 1.0 equiv), trifluoroacetic acid (3.9 mL, 50.72 mmol, 8.0 equiv) and triethylsilane (2.0 mL, 12.7 mmol, 2.0 equiv) in CH_2Cl_2 (16 mL). The product was purified by filtered through a plug of silica gel with *n*-pentane as eluent. The product was obtained as a colorless oil (2.42 g, 6.27 mmol, 99% yield) and dried under vacuum line overnight to remove the traces of triethylsilane.

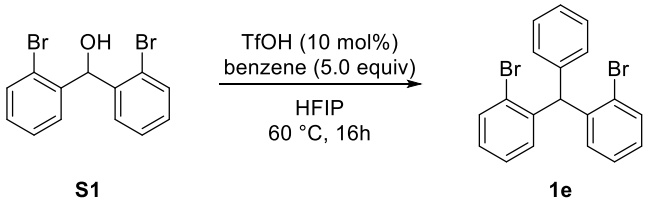
R_f = 0.31 (SiO_2, EtOAc/*n*-pentane = 1/20)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15 (d, *J* = 2.6 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.06 (s, 2H, CH_2), 3.79 (s, 6H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 158.7 (C_q), 131.3 (C_q), 131.0 (CH), 125.1 (C_q), 118.1 (CH), 113.6 (CH), 55.6 (CH_3), 40.3 (CH_2).

HRMS (ESI) (m/z): calcd. for [$C_{15}H_{14}O_2{}^{79}Br_2$] ([M]$^+$): 383.93551; found: 383.93534.

2.3. Synthesis of 2,2'-dibromotriphenylmethane 1e



S1 **1e**

Compound **1e** was prepared using the modified procedure described by our lab.[4] In a sealed tube, "neat" triflic acid (90.0 μL, 1.02 mmol, 0.10 equiv) was added rapidly to a solution of bis(2-bromophenyl)methanol **S1** (3.50 g, 10.2 mmol, 1.0 equiv) and benzene (4.5 mL, 51.0 mmol, 5.0 equiv) in HFIP (10 mL). The tube was then sealed and the resulting mixture was heated at 60 °C for 16 h. The reaction mixture was concentrated under reduced pressure. Methanol was then poured into the residue to form a pale yellow precipitate. The solid was purified by by flash chromatography (SiO_2, *n*-pentane) to afford **1e** as a transparent oil, which became white solid while standing (3.7 g, 9.2 mmol, 90% yield). ^{1}H NMR data is in good agreement with the one reported in the literature. [5]

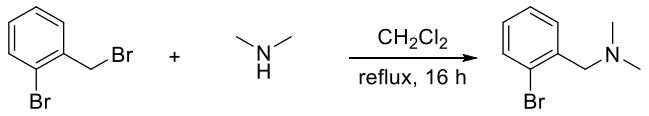
R_f = 0.23 (SiO_2, *n*-pentane)

M.p. : 130 – 132°C (*n*-pentane)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.59 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H, partly overlapped with $CDCl_3$), 7.20 (td, *J* = 7.5, 1.3 Hz, 2H), 7.12 (td, *J* = 7.7, 1.7 Hz, 2H), 7.06 – 7.00 (m, 2H), 6.81 (dd, *J* = 7.7, 1.7 Hz), 6.17 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 142.3 (C_q), 141.2 (C_q), 133.4 (CH), 131.2 (CH), 130.0 (CH), 128.6 (CH), 128.4 (CH), 127.3 (CH), 126.9 (CH), 126.1 (C_q), 56.2 (CH).

2.4. Synthesis of 1-(2-bromophenyl)-*N*,*N*-dimethylmethanamine S6:



S6

[4] A. Chardon, A. Osi, D. Mahaut, T.-D. Doan, N. Tumanov, J. Wouters, L. Fusaro, B. Champagne, G. Berionni, *Angew. Chem. Int. Ed*. **2020**, DOI: 10.1002/anie.202003119

[5] Y. Van Den Winkel, L. M. Van Ben Barr, H. M. M. Bastiaans, M. Schenkel, H. B. Stegmann, F. Bickelhaupt, *Tetrahedron*. **1990**, *46*, 1009.

Following the reported procedure,[6] dimethylamine (30.0 mL, 60.0 mmol, 2M in THF, 3.0 equiv) was added dropwise into a solution of 2-bromobenzylbromide (5.0 g, 20.0 mmol, 1.0 equiv) in CH_2Cl_2 (80 mL). The mixture was refluxed at 40°C for 16h. The reaction mixture was then washed saturated $NaHCO_3$, extracted with CH_2Cl_2. The organic layer was washed with brine, dried with $MgSO_4$, filtered and then concentrated by using rotavapor. The product was purified by flash chromatography (SiO_2, EtOAc/*n*-pentane = 1/1) to afford **S6** as a transparent oil (3.96 g, 18.5 mmol, 92% yield).

$\mathbf{R_f}$ = 0.51 (SiO_2, EtOAC/*n*-pentane = 1/1)

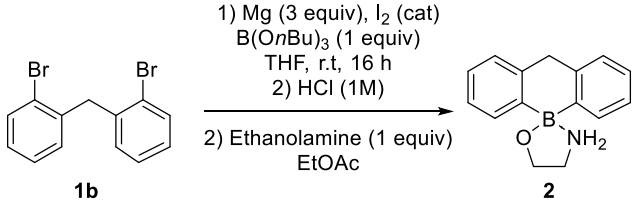
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.28 (td, *J* = 7.7, 1.2 Hz, 1H, partly overlapped with $CDCl_3$), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 3.53 (s, 2H, CH_2), 2.31 (s, 6H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 138.3 (C_q), 132.9 (CH), 131.1 (CH), 128.6 (CH), 127.4 (CH), 124.9 (C_q), 63.4 (CH_2), 45.7 (CH_3).

HRMS (ESI) (m/z): calcd. for [$C_9H_{13}N^{79}Br$] ([M+H]$^+$): 214.02259; found: 214.02272.

3. Synthesis of 9-aminoethyl-9,10-dihydro-9-boraanthracene 2

9-Aminoethyl-9,10-dihydro-9-boraanthracene 2



1b **2**

Under an Ar atmosphere, bis(2-bromophenyl)methane **1b** (5.1 g, 15.6 mmol, 1.0 equiv) was mixed with B(O*n*Bu)$_3$ (4.2 mL, 15.6 mmol, 1.0 equiv) and THF (40 mL) in a dropping funnel and added over a suspension of magnesium turnings (1.14 g, 46.7 mmol, 3.0 equiv) and a small crystal of I_2 in THF (10 mL) over 1 h at 20 °C. The mixture was left stirring at 20 °C for 72 h. Diluted hydrochloric acid (1.5 M, 50 mL) was added dropwise. The organic phase was collected and washed with brine, and the aqueous phase was back extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and then filtered. The solution was concentrated under reduced pressure. Ethyl acetate (20 mL) and ethanolamine (0.94 mL, 15.6 mmol, 1.0 equiv) was added and the mixture was stirred at room temperature overnight. The crude mixture was concentrated under reduced pressure followed by final precipitation of a solid by adding dichloromethane. The 9-aminoethoxy-9,10-dihydro-9-boraanthracene **3** was obtained as

[6] R. Ruzziconi, S. Lepri, F. Buonerba, M. Schlosser, M. Mancinelli, S. Ranieri, L. Prati, A. Mazzanti, *Org. Lett.* **2015**, *17*, 2740.

an off-white powder (2.77g, 11.3 mmol, 75% yield) after filtration and washing with dichloromethane. Crystals suitable for X-ray structure analysis were obtained by slow evaporation of saturated solution of the 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** in methanol.

M.p.: 147-151 °C (MeOH).

IR (neat) cm^{-1}: 3277, 3055, 3001, 2862, 1608, 1428

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.60 - 7.56 (m, 2H), 7.22 - 7.04 (m, 6H), 4.27 (t, *J* = 6.1 Hz, 2H), 4.07 (AB, *J* = 17.1 Hz, 2H), 3.03 (t, *J* = 6.1 Hz, 2H).

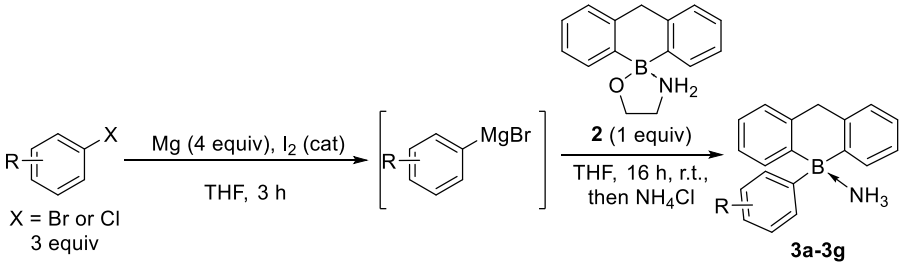
^{13}C NMR (101 MHz, CD_3OD): δ (ppm) 148.6 (C_q), 143.0 (C_q), 130.3 (CH), 126.1 (CH), 125.3 (CH), 124.4 (CH), 64.7 (CH_2), 59.7 (CH_2), 42.3 (CH_2).

^{11}B NMR (128 MHz, DMSO-d_6): δ (ppm) 0.68

Table S1: Optimization for the synthesis of 9-aminoethyl-9,10-dihydro-9-boraanthracene **2**.

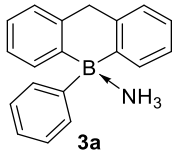
Entry	Metal source	Boron source	Amount of Metal Source	Temperature	Reaction time (h)	Isolated yield (%)
1	*n*BuLi	B(O*i*Pr)$_3$	2 equiv	−94 °C to r.t.	16	0
2	*t*BuLi	B(O*i*Pr)$_3$	4 equiv	−94 °C to r.t.	16	0
3	*t*BuLi	B(O*n*Bu)$_3$	4 equiv	−94 °C to r.t.	16	0
4	*t*BuLi	B(OMe)$_3$	4 equiv	−94 °C to r.t.	16	0
5	*t*BuLi	B(O*n*Bu)$_3$	4 equiv	−94 °C to 40 °C	16	0
6	Mg	B(O*i*Pr)$_3$	3 equiv	40 °C	16	54
7	Mg	B(O*n*Bu)$_3$	3 equiv	40 °C	16	60
8	Mg	B(O*n*Bu)$_3$	3 equiv	66 °C	72	17
9	Mg	B(O*n*Bu)$_3$	3 equiv	20 °C	72	75
10	Mg	B(O*n*Bu)$_3$	3 equiv	20 °C	3	53

4. General procedure A for synthesis of 9-aryl-9,10-dihydro-9-boraanthracene ammonia complexes 3.



Under an Ar atmosphere, a solution of the corresponding halogenoaryl (3 equiv) in THF was added over a suspension of magnesium turnings (4 equiv) and a small crystal of I_2 in THF (10 mL). After 2h of stirring at room temperature the above Grignard solution was transferred dropwise (at -94 °C in the case of **3b**-**3g** and at 0°C for **3a**) into a THF solution of 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (1 equiv). The mixture was let warm up at room temperature overnight. After 16h at room temperature, excess of saturated aqueous NH_4Cl was added. The mixture was stirred at room temperature for 30 min. The organic phase was collected and the aqueous phase was extracted using ethyl acetate (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduced pressure. Precipitation from *n*-hexane, followed by filtration and washing with *n*-hexane afforded the 9-aryl-9,10-dihydro-9-boraanthracene ammonia complexes **3a**-**3g** as white powder.

9-Phenyl-9,10-dihydro-9-boraanthracene ammonia complex 3a



3a

The title compound **3a** was prepared according to general procedure **A** from 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (200 mg, 0.85 mmol, 1 equiv), 1-bromobenzene (0.35 mL, 3.15 mmol, 3.7 equiv) and magnesium turnings (82 mg, 3.40 mmol, 4 equiv). The 9-phenyl-9,10-dihydro-9-boraanthracene ammonia complex **3a** (190 mg, 0.71 mmol, 82% yield) was obtained as a white powder. Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-phenyl-9,10-dihydro-9-boraanthracene ammonia complex **3a** in methanol.

M.p.: 227 - 231 °C (MeOH)

IR (neat) cm^{-1}: 3282, 3222, 3050, 1600, 1430, 1370, 1166

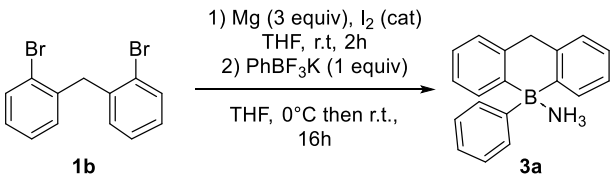
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ (ppm) 7.56 (d, *J* = 7.1 Hz, 2H), 7.12- 6.82 (m, 11H), 5.60 (br, 3H), 3.68 (AB, *J* = 12.0 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ (ppm) 152.0 (C_q), 141.3 (C_q), 132.5 (CH), 129.8 (CH), 126.3 (CH), 125.8 (CH), 124.3 (CH), 124.1 (CH), 124.0 (CH), 30.7 (CH_2).

^{11}B NMR (128 MHz, DMSO-*d*$_6$): δ (ppm) -9.4 (br, s)

HRMS (ESI) (m/z): The mass of the title compound **3a** cannot be detected due to its sensitivity to moisture and acidic conditions.

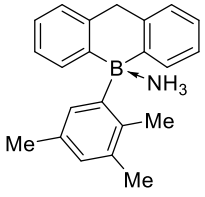
Synthesis of 9-phenyl-9,10-dihydro-9-boraanthracene ammonia complex 3a using potassium phenyltrifluoroborate as a boron source.



1b **3a**

To a mixture of Mg^0 powder (330 mg, 14.0 mmol, 3.0 equiv) and I_2 (traces amount for initiating the Grignard reaction) was added dry THF (10 mL). The mixture was cooled down to 0 °C. A solution of bis(2-bromophenyl)methane **1a** (1.5 g, 4.6 mmol, 1.0 equiv) in THF (5 mL) was then added dropwise under argon atmosphere. After finishing the addition, the ice bath was removed and the mixture was warmed to room temperature and stirred for 3h. After 3h, the whole THF suspension containing the bis-organomagnesium reagents was added dropwise to a suspension of potassium phenyltrifluoroborate (846 mg, 4.6 mmol, 1.0 equiv) in THF (10 mL) at 0 °C. The reaction mixture was then warmed up to room temperature and stirred for 16 h. After 16h at room temperature, a saturated ammonium chloride solution was then added (15 mL). The reaction mixture was then extracted with ethylacetate (50 mL). The organic layer was washed with brine, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. Precipitation from *n*-hexane, followed by filtration and washing with *n*-hexane afforded 9-phenyl-9,10-dihydro-9-boraanthracene ammonia complex **3a** as a white powder (250 mg, 0.92 mmol, 20% yield). ^1H and ^{11}B NMR data were in good agreement with the one reported above.

9-(2,4,5-Trimethylphenyl)-9,10-dihydro-9-boraanthracene ammonia complex 3b



3b

The title compound **3b** was prepared according to the general procedure **A** with 9-aminoethoxy-9,10- dihydro-9-boraanthracene **2** (700 mg, 2.95 mmol, 1 equiv), 1-bromo-2,6-difluorobenzene (1.81 g, 9.09 mmol, 3 equiv) and magnesium turnings (400 mg, 16.5 mmol, 5.6 equiv). 9-(2,4,5-trimethylphenyl)-9,10-dihydro-9-boraanthracene ammoniate **3b** (245 mg, 0.79 mmol, 27% yield) was isolated as a white powder.

M.p.: 162 - 166°C (MeOH).

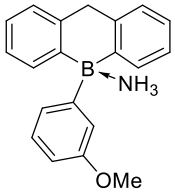
IR (neat) cm^{-1}: 3675, 3313, 3294, 3228, 2987, 2901, 1598, 1353.

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.17 – 7.13 (m, 3H), 7.07 – 6.98 (m, 6H), 6.62 (s, 1H), 3.90 (br, 3H), 4.15 (AB, *J* = 12.3 Hz, 2H), 2.29 (s, 3H), 2.17 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD): δ (ppm) 141.9 (C_q), 139.0 (C_q), 132.5 (CH), 132.1, 131.0, 130.4, 126.3 (CH), 124.7 (CH), 124.4 (CH), 39.0 (CH_2), 21.3 (CH_3), 18.4 (CH_3), 18.1 (CH_3).

^{11}B NMR (128 MHz, CD_3OD): δ (ppm) -9.3 (br, s).

9-(3-Anisole)-9,10-dihydro-9-boraanthracene ammonia complex 3c



3c

The title compound **3c** was prepared according to the general procedure **A** with 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (700 mg, 2.95 mmol, 1.0 equiv), 3-bromoanisole (1.1 mL, 8.69 mmol, 3 equiv) and magnesium turnings (400 mg, 16.5 mmol, 5.5 equiv). 9-(3-anisole)-9,10-dihydro-9-boraanthracene ammoniate **3c** (441 mg, 1.46 mmol, 50% yield) was isolated as a pale yellow powder.

M.p.: 177 - 181 °C (MeOH).

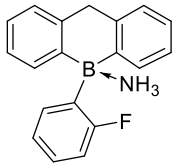
IR (neat) cm^{-1}: 3322, 3285, 3224, 3057, 2997, 2935, 1573, 1352.

^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.45 (dd, *J* = 7.2, 0.9 Hz, 2H), 7.16 - 6.97 (m, 6H), 6.97 - 6.94 (m, 1H), 6.72 – 6.66 (m, 2H), 6.69 - 6.66 (m, 1H), 4.90 (br, 3H), 3.77 (br, 2H), 3.60 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD): δ (ppm) 158.6 (C_q), 142.2 (C_q), 129.4, 127.2, 125.9, 125.4, 124.4, 124.2, 118.3, 109.5, 53.9 (CH_3), 40.2 (CH_2).

^{11}B NMR (128 MHz, CD_3OD): δ (ppm) -9.5 (br, s)

9-(2-Fluorophenyl)-9,10-dihydro-9-boraanthracene ammonia complex 3d



3d

The title compound **3d** was prepared according to the general procedure **A** with 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (3.00 g, 12.7 mmol, 1 equiv), 1-iodo-2-

fluorobenzene (5.21 mL, 44.6 mmol, 3.5 equiv) and magnesium turnings (1.20 g, 49.5 mmol, 4 equiv). 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3d** (2.09 g, 5.68 mmol, 45% yield) was isolated as a pale yellow powder. Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(2-fluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3d** in methanol.

M.p.: 166 - 170 °C (MeOH).

IR (neat) cm^{-1}: 3662, 3333, 3302, 3228, 3063, 2997, 1463, 1355.

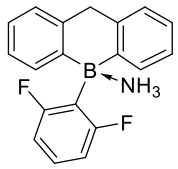
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ (ppm) 7.51 (d, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 7.06 - 6.92 (m, 5H), 6.77 - 6.71 (m, 2H), 6.61 (d, *J* = 7.2, 1.7 Hz, 1H), 5.65 (br, 2H), 3.77 (AB, *J* = 16.0 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ (ppm) 168.8 (d, J_{C-F} = 237.6 Hz), 142.1, 135.4 (d, J_{C-F} = 12.5 Hz), 131.1 (d, J_{C-F} = 1.8 Hz), 127.1 (d, J_{C-F} = 8.2 Hz), 126.4, 124.9 (d, J_{C-F} = 5.7 Hz), 123.2 (d, J_{C-F} = 2.4 Hz), 114.3 (d, J_{C-F} = 26.4 Hz), the benzhydryl CH_2 was not observed due to an overlap with the solvent peak.

^{11}B NMR (128 MHz, DMSO-*d*$_6$): δ (ppm) -10.3.

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ (ppm) -103.5 (d, *J* = 5.2 Hz, 1F).

9-(2,6-Difluorophenyl)-9,10-dihydro-9-boraanthracene ammonia complex 3e



3e

The title compound **3e** was prepared according to the general procedure **A** with 9-aminoethoxy-9,10- dihydro-9-boraanthracene **2** (300 mg, 1.27 mmol, 1 equiv), 1-bromo-2,6-difluorobenzene (0.43 mL, 3.81 mmol, 3 equiv) and magnesium turnings (119 mg, 4.95 mmol, 3.9 equiv). 9-(2,6-difluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3e** (270 mg, 0.88 mmol, 69% yield) was isolated as a pale yellow powder.

M.p.: 182 - 186°C (MeOH);

IR (neat) cm^{-1}: 3675, 3341, 2988, 2901, 1610, 1440.

^{1}H NMR (400 MHz, CD): δ (ppm) 7.25 (d, *J* = 7.1 Hz, 2H), 7.16 (d, *J* = 7.1 Hz, 2H), 7.06 - 6.92 (m, 5H), 6.77 - 6.71 (m, 2H), 4.87 (br, 3H), 4.22 - 4.08 (m, 2H).

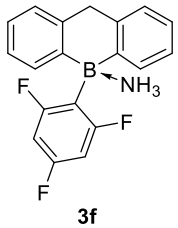
^{13}C NMR (101 MHz, acetone-d_6): δ (ppm) 168.5 – 165.9 (m), 142.3, 132.9, 132.2 (t, J_{C-F} = 1.7 Hz), 127.5, 126.3 (d, J_{C-F} = 192 Hz), 126.0, 125.6 (d, J_{C-F} = 4.0 Hz), 111.6 – 111.1 (m), 40.0 (CH_2).

^{11}B NMR (128 MHz, CD_3OD): δ (ppm) -10.1 (br s)

^{19}F NMR (376 MHz, CD_3OD): δ (ppm) -102.3 (d, J = 5.2 Hz, 2F).

HRMS (ESI) (m/z): calcd. for $[C_{19}H_{12}{}^{10}BF_2]$ $([M\text{-}H\text{-}NH_3])^+$: 288.10310; found: 288.10291.

9-(2,4,6-Trifluorophenyl)-9,10-dihydro-9-boraanthracene ammonia complex 3f



3f

The title compound **3f** was prepared according to the general procedure **A** with 9-aminoethoxy-9,10- dihydro-9-boraanthracene **2** (400 g, 1.69 mmol, 1 equiv), 1-bromo-2,4,6-trifluorobenzene (0.6 mL, 5.07 mmol, 3 equiv) and magnesium turnings (162 mg, 6.76 mmol, 4 equiv). 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3f** (350 mg, 1.08 mmol, 64% yield) was isolated as a yellow powder. Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3f** in methanol.

M.p.: 153 -157 °C (decomposed) (MeOH).

IR (neat) cm^{-1}: 3675, 3301, 3250, 2988, 2901, 1730, 1600, 1585.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.26 - 7.17 (m, 4H), 7.12 - 7.03 (m, 4H), 6.60 - 6.52 (m, 2H), 4.44 (br, 3H), 4.24 - 4.05 (m, 2H).

^{13}C NMR (101 MHz, CD_3CN): δ (ppm) 142.5, 132.9, 127.9, 126.6, 126.0, 100.2 (dd, J_{C-F} = 23.2, 1.0 Hz), 100.0 (d, J_{C-F} = 61.6 Hz), 99.9, 39.7 (CH_2).

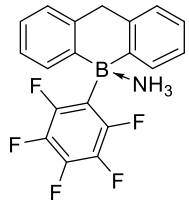
^{11}B NMR (128 MHz, CD_3CN): δ (ppm) -9.8 (br).

^{19}F NMR (376 MHz, CD_3CN): δ (ppm) -100.3 (br, 2F), -116.0 (m, 1F).

HRMS (ESI) (m/z): calcd. for $[C_{19}H_{11}{}^{10}BF_3]$ $([M\text{-}H\text{-}NH_3])^+$: 306.09372; found: 306.09367.

4.

9-(Pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammonia complex 3g



3g

The title compound **3g** was prepared according to the modified general procedure **A** with 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (1.25 g, 5.25 mmol, 1 equiv), 1-chloro-pentafluorobenzene (2.5 mL, 19.4 mmol, 3.7 equiv) and magnesium turnings (500 mg, 20.6 mmol, 3.9 equiv). The dropwise addition of the solution of 1-chloro-pentafluorobenzene in THF over magnesium turnings was performed at 0 °C and the reaction was stirred at 0 °C for 3h. After 16h of stirring at room temperature 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3g** (907 mg, 2.51 mmol, 48% yield) was isolated as a colorless solid.

M.p.: 116 - 120 °C (MeOH).

IR (neat) cm^{-1}: 3675, 3293, 2970, 2901, 1727, 1513, 1457.

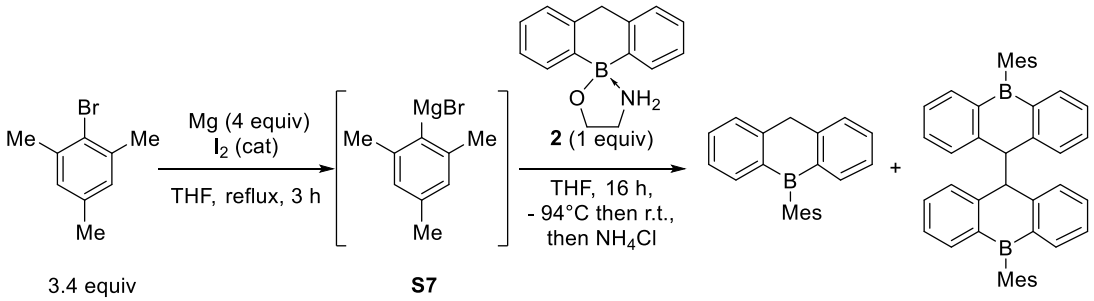
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ (ppm) 7.28 (d, *J* = 6.8 Hz, 2H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.10 - 6.94 (m, 4H), 5.57 (br, 3H), 4.17 - 3.92 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$): δ (ppm) 141.9, 132.4, 126.9, 125.6, 125.1. The benzydryl CH_2 carbon was overlap with the solvent peak. The carbons attached to the pentafluorophenyl ring were not observed due to intensive coupling and poor solubility of the compound.

^{11}B NMR (128 MHz, DMSO-*d*$_6$): δ (ppm) -10.6 (br, s).

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ (ppm) -130.9 (dd, *J* = 26.4, 8.4 Hz, 1F), -160.6 (t, *J* = 21.4 Hz, 2F), -165.2 - (-165.6) (m, 2F).

9-Mesityl-9,10-dihydro-9-boraanthracene 4a and the corresponding dimer 5



3.4 equiv **S7** **4a** **5**

Under an Ar atmosphere, a solution of bromomesitylene (2.6 mL, 17.0 mmol, 3.4 equiv) in THF (15 mL) was added over a suspension of magnesium turnings (500 mg, 20.6 mmol, 4 equiv) and a small crystal of I_2 in THF (10 mL). The suspension was then refluxed. After 3h of stirring the Grignard solution was transferred dropwise into a THF (10 mL) solution of 9-aminoethoxy-9,10-dihydro-9-boraanthracene **2** (1.17g, 4.93 mmol, 1 equiv) at -94 °C. The mixture was stirred at -94 °C for 2h then allowed to warm at room temperature overnight. Excess of saturated aqueous NH_4Cl was added. The mixture was stirred at room temperature for 30 min. The organic phase was collected and the aqueous phase was extracted using ethyl acetate (3 x 30 mL). The combined organic layers were dried over $MgSO_4$ and then filtered. The crude mixture was concentrated under reduced pressure. Precipitation from *n*-hexane, followed by filtration afforded the dimer of 9-mesityl-9,10-dihydro-9-boraanthracene **5** as a white powder (230 mg, 0.39 mmol, 8% yield). Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-mesityl-9,10-dihydro-9-boraanthracene dimer **5** in a solution of CH_2Cl_2/*n*-pentane 1:1. The filtrate was concentrated under reduced pressure. Purification by silica gel chromatography using *n*-hexane as solvent afforded 9-mesityl-9,10-dihydro-9-boraanthracene **4a** as colorless crystals (387 mg, 1.30 mmol, 26% yield). Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-mesityl-9,10-dihydro-9-boraanthracene **4a** in a solution of CH_2Cl_2/*n*-pentane 1:1.

9-mesityl-9,10-dihydro-9-boraanthracene **4a**: For full characterization see the page S22.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 – 7.66 (m, 2H), 7.59 – 7.55 (m, 4H), 7.33 – 7.26 (m, 2H), 6.92 (s, 2H), 4.56 (s, 2H), 2.39 (s, 3H), 1.98 (s, 6H).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 64.3.

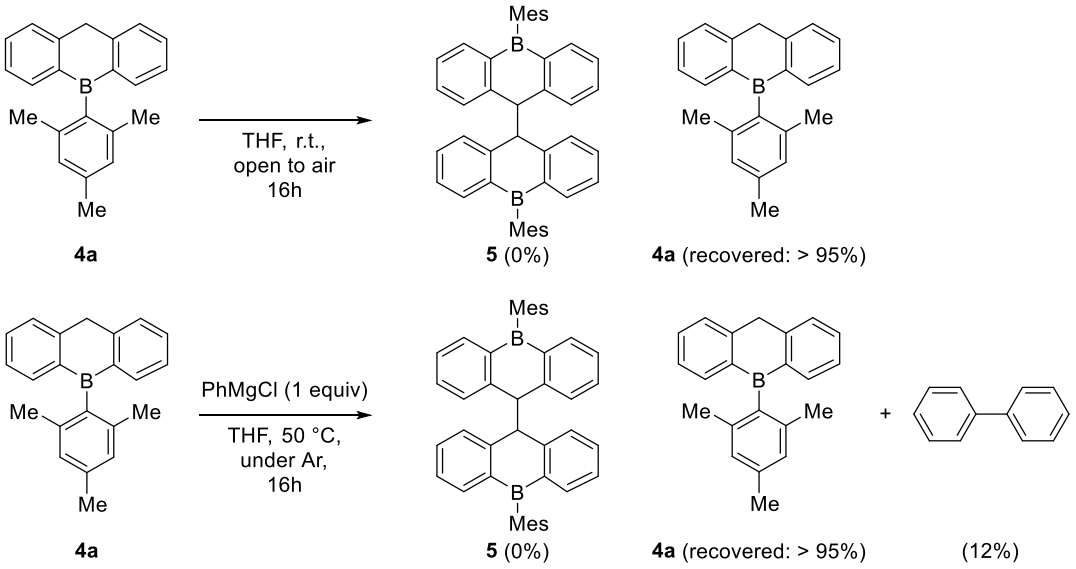
9-mesityl-9,10-dihydro-9-boraanthracene dimer **5**:

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46 (dd, *J* = 7.3, 1.5 Hz, 4H), 7.28 - 7.15 (m, 8H), 6.86 - 6.77 (m, 8H), 4.98 (s, 2H), 2.35 (s, 6H), 1.78 (s, 6H), 1.49 (s, 6H).

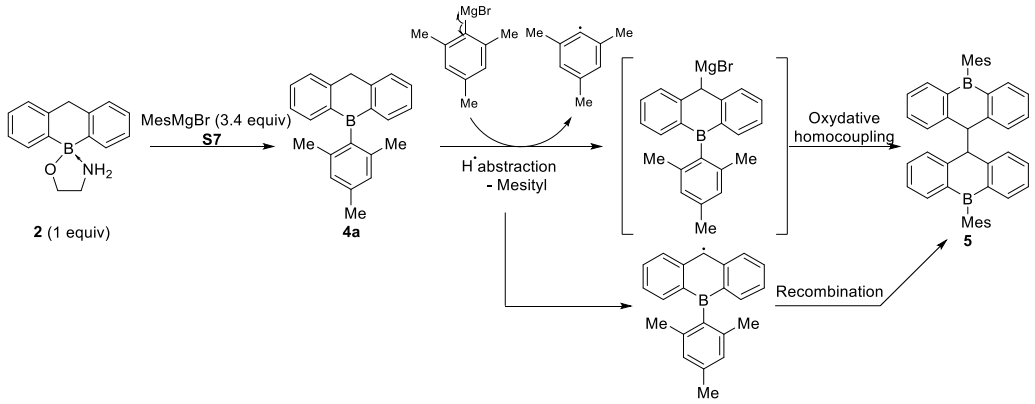
^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 64.0.

Control experiments and proposed mechanism for the formation of 5

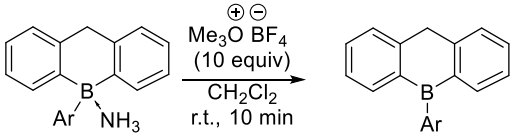
a) Controlled experiments



b) Proposed mechanism



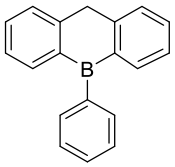
5. General procedure B for synthesis of 9-aryl-9,10-dihydro-9-boraanthracene 4b-4d.



In a glove-box, trimethyloxonium tetrafluoroborate (10 equiv) was added over a solution of 9-aryl-9,10-dihydro-9-boraanthracene (1 equiv) in CH_2Cl_2 at 20°C. The reaction was stirred for 10 min at room temperature and the suspension was filtered. The filtrate was

evaporated to dryness and diluted with a mixture of (*n*-pentane/CH_2Cl_2 10:1) and then again. Evaporation to dryness of the second filtrate afforded 9-aryl-9,10-dihydro-9-boraanthracene **4b** - **4d**.

9-Phenyl-9,10-dihydro-9-boraanthracene 4b



4b

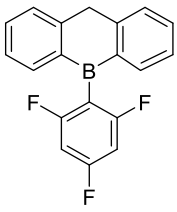
The title compound **4b** was prepared according to the general procedure **B** with trimethyloxonium trifluoroborate (100 mg, 0.67 mmol, 10 equiv), 9-phenyl-9,10-dihydro-9-boraanthracene ammoniate **3a** (17.5 mg, 0.065 mmol, 1 equiv). 9-phenyl-9,10-dihydro-9-boraanthracene **4b** (11.6 mg, 0.046 mmol, 71% yield) was isolated as a white solid. The title compound was found to be extremely sensitive to moisture. Accordingly, some degradation into the corresponding borinic acid was detected by ^{1}H and ^{13}C NMR analysis. For that reason, only ^{13}C and ^{11}B NMR spectra data were reported. The ^{1}H signals were tentatively assigned.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 – 7.83 (m, 2H), 7.66 – 7.60 (m, 2H), 4.57 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 148.5 (C_q), 138.8 (C_q), 138.7 (CH), 132.7 (CH), 129.1 (CH), 128.2 (CH), 128.16 (CH), 127.5 (CH), 125.8 (CH), 38.6 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 59.7

9-(2,4,6-Trifluorophenyl)-9,10-dihydro-9-boraanthracene 4c



4c

The title compound **4c** was prepared according to the general procedure **B** with trimethyloxonium tetrafluoroborate (105 mg, 0.71 mmol, 10 equiv) and 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **3f** (23.2 mg, 0.071 mmol, 1 equiv). 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene **4c** (15.4 mg, 0.05 mmol, 70% yield) was isolated as an orange solid. Crystals suitable for X-ray structure analysis

have been obtained by slow evaporation of a saturated solution of 9-(2,4,6-trifluorophenyl)-9,10-dihydro-9-boraanthracene **3c** in a solution of CH_2Cl_2/*n*-pentane 1:1.

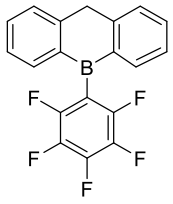
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (d, *J* = 7.7 Hz, 2H), 7.67 - 7.57 (m, 4H), 7.44 - 7.33 (m, 2H), 6.79 (dd, *J* = 9.0, 6.9 Hz, 2H), 4.59 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 165.1 - 163.3 (m), 162.5, 148.5, 138.0, 133.6, 128.2, 125.9, 100.4 - 99.7 (m), 38.6 (CH_2).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 59.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -97.8 (s, 2F), -108.6 (t, *J* = 7.3 Hz, 1F).

9-(Pentafluorophenyl)-9,10-dihydro-9-boraanthracene 4d



4d

The title compound **4d** was prepared according to the general procedure **B** with trimethyloxonium trifluoroborate (90 mg, 0.61 mmol, 10 equiv), 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene ammoniate **4g** (20.3 mg, 0.056 mmol, 1 equiv). 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene **4d** (12.8 mg, 0.037 mmol, 66% yield) was isolated as a yellow solid. Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of 9-(pentafluorophenyl)-9,10-dihydro-9-boraanthracene **4d** in a solution of CH_2Cl_2/*n*-pentane 1:1.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 7.4 Hz, 2H), 7.69 - 7.60 (m, 4H), 7.42 - 7.37 (m, 2H), 4.62 (s, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 148.7, 141.2, 137.8, 134.2, 131.6, 128.8 (d, *J* = 48.5 Hz), 128.4, 127.6 (d, *J* = 85.2 Hz), 127.1, 38.5 (CH_2).

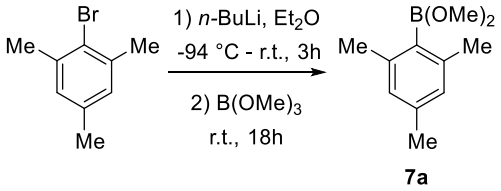
^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 58.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) (-129.8) – (-129.9) (m), (-153.5) – (-153.6) (m), (-161.3) – (-161.4) (m).

6. Synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene derivatives:

6.1. One-pot synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene 4a using lithium reagent:

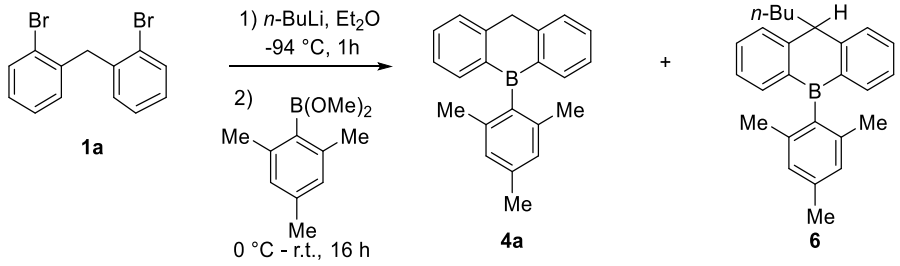
Step 1: Synthesis of dimethyl-mesitylborate **7a** as starting material



7a

A solution of 2-bromomesitylene (1.5 mL, 10.1 mmol, 1.0 equiv) in Et_2O (20 mL) under argon atmosphere was cooled down to -94 °C using an acetone/liquid nitrogen bath. *n*-BuLi (4.0 mL, 10.1 mmol, 2.5 M in hexane, 1.0 equiv) was added dropwise. After the addition finished, the acetone/liquid nitrogen bath was removed and the mixture was stirred at room temperature. A yellow solution with white precipitation appeared after 1 hour of stirring. The reaction mixture was kept stirring in an additional time of 2h. Thereafter, trimethylborate (1.1 mL, 10.1 mmol, 1.0 equiv) was added dropwise and the mixture was stirred at room temperature for 18h. The reaction mixture was filtered through a plug of Celite under argon atmosphere to remove the white precipitate. The Celite plug was washed with *n*-pentane and the filtrate was then concentrated under vacuum line. The residue as a transparent oil containing the desired product **7a** and mesitylene was used directly to the next step without further purification due to its sensitivity to moisture. The presence of the product **7a** in the residue was confirmed by ^{1}H and ^{11}B NMR.

Step 2: Synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene **4a**



A solution of bis(2-bromophenyl)methane **1a** (1.34 g, 4.1 mmol, 1.0 equiv) in Et_2O (36 mL) under argon atmosphere was cooled down to -94 °C using an acetone/liquid nitrogen bath. *n*-BuLi (3.5 mL, 8.6 mmol, 2.5 M in hexane, 2.1 equiv) was added dropwise. A yellow solution appeared immediately. The mixture was stirred at -94 °C for

1 hour. After 1h, the acetone/liquid nitrogen bath was replaced by an ice bath. The product **7a** prepared in the step 1 was dissolved in 10 mL of Et_2O and the solution was added into the above reaction mixture at 0 °C. Thereafter, the mixture was warmed up to room temperature and stirred for 16h. The reaction mixture was washed with water and extracted with EtOAc (50 mL). The organic layer was washed with brine, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. The product was purified by flash chromatography (SiO_2, *n*-pentane) to afford **4a** as a white solid (784 mg, 2.65 mmol, 65% yield). This compound was stored in the glovebox due to its slow decomposition under ambient atmosphere.
R_f = 0.26 (SiO_2, *n*-pentane).

M.p.: 127 – 131°C (*n*-pentane/CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 – 7.65 (m, 2H), 7.59 – 7.56 (m, 4H), 7.31 – 7.26 (m, 2H), 6.92 (s, 2H, $CH_{(mesityl)}$), 4.56 (s, 2H, $CH_{2\ (boraanthracene)}$), 2.39 (s, 3H, *para*-$CH_{3\ (mesityl)}$), 1.98 (s, 6H, *ortho*-$CH_{3\ (mesityl)}$).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 147.7 (C_q), 138.4 (C_q), 138.1 (CH), 136.8 (C_q), 132.9 (CH), 128.2 (CH), 127.0 (CH), 125.9 (CH), 38.3 (CH_2), 22.8 (CH_3), 21.4 (CH_3). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 62.5

HRMS (ESI) (m/z): calcd. for [$C_{22}H_{22}{}^{10}B$] ([M+H]$^+$): 296.18454; found: 296.18477.

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) 2920, 2852, 1609, 1595, 1165, 1484, 1142, 1396, 1270, 1256, 1168, 1157, 1087, 1028, 900, 891, 846, 772, 712, 671, 651, 572.

Beside the main product **4a**, the side product **6** was obtained as a white solid (108 mg, 0.31 mmol, 8% yield). This compound was crystallized in *n*-pentane/CH_2Cl_2 to give **6** as colorless crystals.

R_f = 0.30 (SiO_2, *n*-pentane)

M.p.: 88 – 91°C (*n*-pentane/CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, *J* = 7.3 Hz, 2H), 7.58 – 7.49 (m, 4H), 7.31 – 7.20 (m, 2H, overlapped with $CDCl_3$), 6.94 (s, 1H, $CH_{(mesityl)}$), 6.90 (s, 1H, $CH_{(mesityl)}$), 4.46 (t, *J* = 5.5 Hz, 1H, $CH_{(boraanthracene)}$), 2.39 (s, 3H, *para*-$CH_{3(mesityl)}$), 2.04 – 1.94 (m, 8H, containing *ortho*-$CH_{3\ (mesityl)}$ at 2.02, *ortho*-$CH_{3\ (mesityl)}$) at 1.98 and $CH_{2\ (n\text{-butyl})}$)), 1.15 – 1.02 (m, 2H, $CH_{2\ (n\text{-butyl})}$)), 0.94 – 0.82 (m, 2H, $CH_{2\ (n\text{-butyl})}$), 0.69 (t, *J* = 7.3 Hz, 3H, $CH_{3\ (n\text{-butyl})}$).

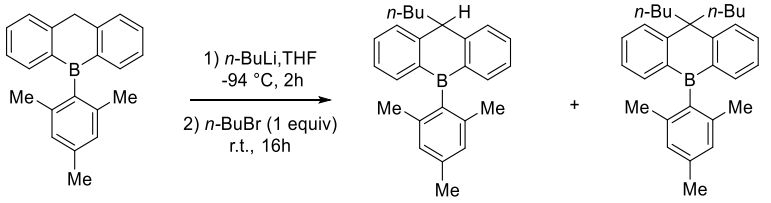
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 152.8 (C_q), 138.5 (C_q), 138.2 (C_q), 137.7 (CH), 136.7 (C_q), 132.8 (CH), 128.1 (CH), 127.0 (CH), 126.9 (CH), 125.8 (CH), 48.4 (CH), 43.9 (CH_2), 27.3 (CH_2), 22.9 (CH_3), 22.9 (CH_2), 22.7 (CH_3), 21.4 (CH_3), 14.0 (CH_3). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 65.5

HRMS (ESI) (m/z): calcd. for [$C_{26}H_{28}{}^{10}B$] ([M-H]$^+$): 350.23149; found: 350.23146.

IR (neat, ATR): ṽ (cm^{-1}) 3053, 3010, 2966, 2953, 2930, 2852, 1608, 1594, 1568, 1463, 1440, 1354, 1303, 1286, 1271, 1250, 1200, 1166, 1081, 1027, 900, 873, 843, 808, 768, 724, 679, 657, 618, 588.

6.2. Independent synthesis of 9-mesityl-9-butyl,10-hydro-9-boraanthracene 6:



4a **6a** **6b** (detected by NMR)

A solution of **4a** (60 mg, 0.20 mmol, 1.0 equiv) in THF (5 mL) under argon atmosphere was cooled down to -94 °C using an acetone/liquid nitrogen bath. *n*-BuLi (80 μL, 0.20 mmol, 2.5 M in hexane, 1 equiv) was added dropwise. A bright orange solution appeared immediately. The mixture was stirred at -94 °C for 2 hours. Then bromobutane (22 μL, 0.20 mmol, 1 equiv) was added at -94 °C. The acetone/liquid nitrogen bath was removed and the reaction mixture was warmed up to room temperature and kept stirring for 16 hours to give a light-yellow solution. The reaction mixture was then concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, *n*-pentane) to afford **6a** as a white solid (69 mg, 0.195 mmol, 96% yield) and **6b** as a white solid (traces amount detected by NMR).

The ^{1}H, ^{13}C and ^{11}B NMR data of **6a** are in agreement with the data presented in section 6.1.

The formation of **6b** was confirmed by ^{1}H and ^{11}B NMR.

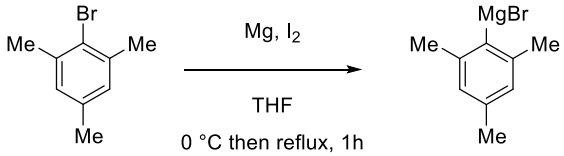
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 7.9 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.22 (td, *J* = 7.3, 1.0 Hz, 2H), 6.92 (s, 2H, $CH_{(mesityl)}$), 2.39 (s, 3H, *para*-$CH_{3(mesityl)}$), 2.31 – 2.16 (m, 4H, $CH_{2\ (n\text{-butyl})}$), 1.96 (s, 6H, *ortho*-$CH_{3(mesityl)}$), 0.99 (dt, *J* = 14.5, 7.3 Hz, 4H, $CH_{2\ (n\text{-butyl})}$), 0.60 (t, *J* = 7.3 Hz, 6H, $CH_{3\ (n\text{-butyl})}$), 0.52 – 0.35 (m, 4H, $CH_{2\ (n\text{-butyl})}$).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 64.4

6.3. One-pot synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene derivatives using Grignard reagent:

Synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene

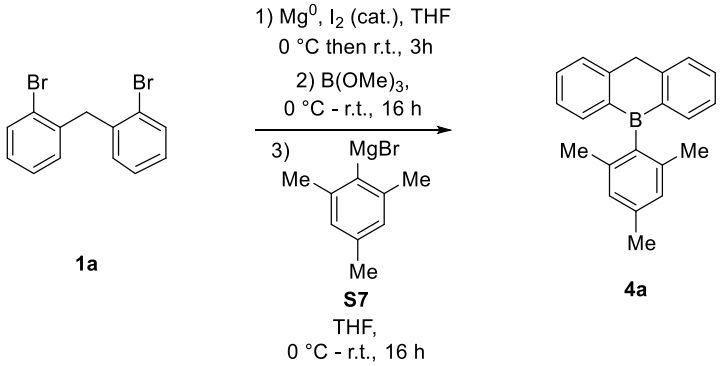
Step 1: Synthesis mesityl-magnesiumbromide **S7** as the starting material



S7

To a mixture of Mg^0 powder (295 mg, 12.3 mmol, 4.0 equiv) and I_2 (catalytic amount) was added THF (10 mL). The mixture was cooled down to 0 °C using an ice bath. A solution of 2-bromomesitylene (1.4 mL, 9.2 mmol, 3.0 equiv) in THF (5 mL) was then added dropwise under argon atmosphere into the above mixture. After the addition finished, the ice bath was removed and the mixture was refluxed for 1 hour using an oil bath. Thereafter, the reaction mixture was cooled down to room temperature and used directly for the next step without further purification.

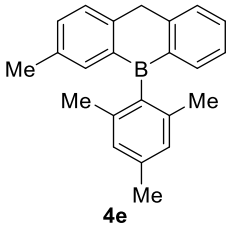
Step 2: Synthesis of 9-mesityl-9,10-dihydro-9-boraanthracene **4a**



To a mixture of Mg^0 powder (220 mg, 9.2 mmol, 3.0 equiv) and I_2 (catalytic amount) was added THF (10 mL). The mixture was cooled down to 0 °C using an ice bath. A solution of bis(2-bromophenyl)methane **1a** (1.0 g, 3.1 mmol, 1.0 equiv) in THF (5 mL) was then added dropwise under argon atmosphere into the above mixture. After the addition

finished, the ice bath was removed and the mixture was warmed to room temperature and stirred for 3h. After 3h, the mixture was cooled down to 0 °C and trimethylborate (0.7 mL, 6.1 mmol, 2.0 equiv) was added dropwise. The reaction mixture was then warmed up slowly to room temperature and stirred for 16h. The product **S7** prepared in the step 1 in THF was then added dropwise into the above reaction mixture at 0 °C. The mixture was kept stirring at room temperature for 16h. The reaction mixture was then washed with water and extracted with ethylacetate (50 mL). The organic layer was washed with brine, dried with $MgSO_4$, filtered and then concentrated under reduced pressure. The product was purified by flash chromatography (SiO_2, *n*-pentane) to afford **4a** as a white solid (185 mg, 0.62 mmol, 20% yield over 4 steps). This compound was stored in the glovebox due to its slow decomposition under ambient atmosphere. The ^{1}H, ^{13}C and ^{11}B NMR data are in agreement with the data presented in section 6.1 (method using lithium reagent).

9-Mesityl-7-methyl-9,10-dihydro-9-boraanthracene 4e



4e

Following the procedure for the synthesis of compound **4a** using Grignard reagent, the compound **4e** was synthesized from the starting material **1b** (1.0 g, 2.9 mmol, 1.0 equiv) in THF (5 mL), Mg^0 powder (212 mg, 8.8 mmol, 3.0 equiv) and I_2 (catalytic amount) in THF (10 mL), trimethylborate (0.7 mL, 5.9 mmol, 2.0 equiv) and mesitylmagnesiumbromide, which was prepared from 2-bromomesitylene (1.4 mL, 8.8 mmol, 3.0 equiv) in THF (5 mL) and Mg^0 powder (282 mg, 11.8 mmol, 4.0 equiv) and I_2 (catalytic amount) in THF (10 mL). The desired compound **4e** was obtained as a pale yellow oil after purification, which then became a pale yellow solid while standing (336 mg, 1.1 mmol, 37 % yield). This compound was stored in the glovebox due to its slow decomposition under ambient atmosphere. The product was crystallized in CH_2Cl_2 by slow evaporation in the glovebox to afford colorless single crystals.

R_f = 0.24 (SiO_2, *n*-pentane).

M.p.: 134 – 137°C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 – 7.60 (m, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.45 (m, 2H), 7.40 (dd, *J* = 7.8 Hz, *J* = 2.0 Hz, 1H), 7.31 – 7.24 (m, 1H, partly overlapped

with $CDCl_3$), 6.95 – 6.91 (m, 2H, $CH_{(mesityl)}$), 4.51 (s, 2H, $CH_{2\ (boraanthracene)}$), 2.40 (s, 3H, *para*-$CH_{3\ (mesityl)}$), 2.32 (s, 3H, $CH_{3\ (boraanthracene)}$), 1.98 (s, 6H, *ortho*-$CH_{3\ (mesityl)}$).

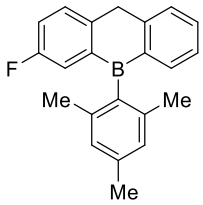
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 147.8 (C_q), 144.9 (C_q), 138.4 (C_q), 138.0 (CH), 137.9 (CH), 136.7 (C_q), 135.2 (C_q), 134.1 (CH), 132.7 (CH), 128.2 (CH), 128.1 (CH), 126.9 (CH), 125.8 (CH), 38.0 (CH_2), 22.9 (CH_3), 21.5 (CH_3), 21.2 (CH_3). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 63.9.

HRMS (ESI) (m/z): calcd. for [$C_{23}H_{22}{}^{10}B$] ([M-H]$^+$): 308.18454; found: 308.18471.

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) 2917, 2851, 1594, 1566, 1552, 1489, 1447, 1399, 1294, 1279, 1251, 1198, 1182, 1161, 1094, 1036, 959, 922, 903, 892, 875, 848, 817, 803, 773, 711, 655, 628, 602, 537, 509.

9-Mesityl-7-fluoro-9,10-dihydro-9-boraanthracene 4f



4f

Following the procedure for the synthesis of compound **4a** using Grignard reagent, the compound **4f** was synthesized from the starting material **1c** (1.0 g, 2.9 mmol, 1.0 equiv) in THF (5 mL), Mg^0 powder (210 mg, 8.7 mmol, 3.0 equiv) and I_2 (catalytic amount) in THF (10 mL), trimethylborate (0.7 mL, 5.8 mmol, 2.0 equiv) and mesitylmagnesiumbromide, which was prepared from 2-bromomesitylene (1.3 mL, 8.7 mmol, 3.0 equiv) in THF (5 mL) and Mg^0 powder (279 mg, 11.6 mmol, 4.0 equiv) and I_2 (catalytic amount) in THF (10 mL). The desired compound **4f** was obtained as a pale yellow solid after purification (135 mg, 0.43 mmol, 15% yield). This compound was stored in the glovebox due to its slow decomposition under ambient atmosphere. The product was crystallized in CH_2Cl_2 by slow evaporation in the glovebox to afford colorless single crystals.

R_f = 0.18 (SiO_2, *n*-pentane).

M.p.: 124 – 137 °C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 – 7.66 (m, 1H), 7.63 – 7.51 (m, 3H), 7.35 – 7.24 (m, 3H, partly overlapped with $CDCl_3$), 6.94 – 6.90 (m, 2H, $CH_{(mesityl)}$), 4.52 (s, 2H, $CH_{2\ (boraanthracene)}$), 2.39 (s, 3H, *para*-$CH_{3\ (mesityl)}$), 1.97 (s, 6H, *ortho*-$CH_{3\ (mesityl)}$).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 161.3 (d, $J_{C\text{-}F}$ = 247.1 Hz, C_q), 147.8 (C_q), 143.1 (C_q), 138.3 (C_q), 138.27 (CH), 137.1 (C_q), 133.2 (CH), 129.9 (d, $J_{C\text{-}F}$ = 6.7 Hz, CH), 128.3 (CH), 127.1 (CH), 126.1 (CH), 122.4 (d, $J_{C\text{-}F}$ = 17.1 Hz, CH), 120.4 (d, $J_{C\text{-}F}$ = 22.1 Hz, CH), 37.7 (CH_2), 22.8 (CH_3), 21.4 (CH_3). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

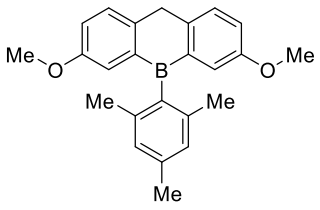
^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 63.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -117.2 (br).

HRMS (ESI) (m/z): calcd. for [$C_{22}H_{19}{}^{10}BF$] ([M-H]$^+$): 312.15947; found: 312.15955.

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) 2955, 2914, 1607, 1596, 1558, 1485, 1473, 1447, 1404, 1376, 1342, 1287, 1272, 1262, 1190, 1157, 1131, 1092, 969, 919, 894, 845, 818, 806, 724, 706, 676, 599, 539, 519, 452.

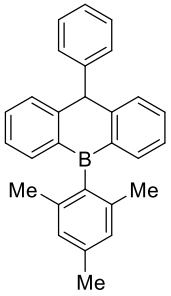
9-Mesityl-2,7-dimethoxy-9,10-dihydro-9-boraanthracene 4g



4g

Following the procedure for the synthesis of compound **4a** using Grignard reagent, the compound **4g** was synthesized from the starting material **1d** (1.0 g, 2.6 mmol, 1.0 equiv) in THF (5 mL), Mg^0 powder (287 mg, 7.8 mmol, 3.0 equiv) and I_2 (catalytic amount) in THF (10 mL), trimethylborate (0.6 mL, 5.2 mmol, 2.0 equiv) and mesitylmagnesiumbromide, which was prepared from 2-bromomesitylene (1.2 mL, 7.8 mmol, 3.0 equiv) in THF (5 mL) and Mg^0 powder (249 mg, 10.4 mmol, 4.0 equiv) and I_2 (catalytic amount) in THF (10 mL). The desired compound **4g** was purified by flash chromatography (SiO_2, EtOAc / *n*-pentane = 2/100). However, the pure compound **4g** was not obtained due to the same R_f of 0.67 (SiO_2, EtOAc / *n*-pentane = 2/100) with the formed bis-(2-bromo-4-methoxyphenyl)methane **S8** as a side product. The presence of these two compounds **4g** and **S8** was confirmed by ^{1}H NMR (see in the section 8).

9-Mesityl-10-phenyl-9-boraanthracene 4h



4h

Following the procedure for the synthesis of compound **4a** using Grignard reagent, the compound **4h** was synthesized from the starting material **1e** (1.2 g, 3.0 mmol, 1.0 equiv) in THF (5 mL), Mg^0 powder (215 mg, 9.0 mmol, 3.0 equiv) and I_2 (catalytic amount) in THF (10 mL), trimethylborate (0.7 mL, 6.0 mmol, 2.0 equiv) and mesitylmagnesiumbromide, which was prepared from 2-bromomesitylene (1.4 mL, 8.95 mmol, 3.0 equiv) in THF (5 mL) and Mg^0 powder (287 mg, 11.9 mmol, 4.0 equiv) and I_2 (catalytic amount) in THF (10 mL). The desired compound **4h** was obtained as a white solid after purification (282 mg, 0.76 mmol, 25% yield). This compound was stored in the glovebox due to its slow decomposition in the air. The product was crystallized in CH_2Cl_2 by slow evaporation in the glovebox to afford colorless single crystals.

R_f = 0.19 (SiO_2, *n*-pentane).

M.p.: 189 – 191°C (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (dd, *J* = 7.5 Hz, *J* = 1.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.42 – 7.35 (m, 2H), 7.27 – 7.19 (m, 4H, partly overlapped with $CDCl_3$), 7.18 – 7.11 (m, 3H), 6.98 – 6.93 (m, 2H, $CH_{(mesityl)}$), 5.61 (s, 1H, $CH_{(boraanthracene)}$), 2.41 (s, 3H, *para*-$CH_{3\ (mesityl)}$), 2.14 (s, 3H, *ortho*-$CH_{3\ (mesityl)}$), 2.02 (s, 3H, *ortho*-$CH_{3\ (mesityl)}$).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 151.3 (C_q), 146.2 (C_q), 138.5 (C_q), 138.3 (C_q), 137.8 (CH), 136.9 (C_q), 133.4 (CH), 129.7 (CH), 128.9 (CH), 128.9 (CH), 127.1 (CH), 127.06 (CH), 126.3 (CH), 126.1 (CH), 54.0 (CH), 23.0 (CH_3), 22.9 (CH_3), 21.5 (CH_3). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

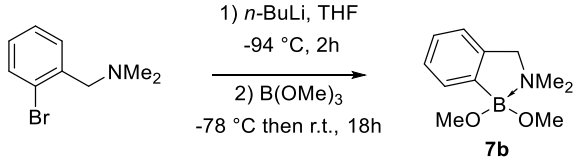
^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) 64.1.

HRMS (ESI) (m/z): calcd. for [$C_{28}H_{24}{}^{10}B$] ([M-H]$^+$): 370.20019; found: 370.20006.

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) 2907, 2853, 1610, 1594, 1566, 1491, 1439, 1304, 1274, 1246, 1167, 1159, 1072, 951, 896, 849, 771, 697, 679, 654, 620, 611.

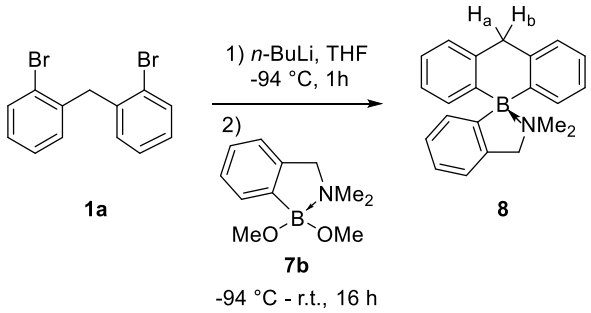
7. Synthesis of the spirocyclic amino boraanthracene 8

Step 1: Synthesis of 1-(2-(dimethylborate)phenyl)-*N*,*N*-dimethylmethanamine **7b** as starting material



A solution of 1-(2-bromophenyl)-*N*,*N*-dimethylmethanamine (550 mg, 2.6 mmol, 1.0 equiv) in THF (10 mL) under argon atmosphere was cooled down to -94 °C using an acetone/liquid nitrogen bath. *n*-BuLi (1.2 mL, 3.1 mmol, 2.5 M in hexane, 1.2 equiv) was added dropwise. The mixture was stirred at -94°C for 2h. Thereafter, trimethylborate (0.9 mL, 7.7 mmol, 3.0 equiv) was added dropwise at -94°C. The reaction mixture was warmed up slowly to room temperature and stirred for 18h. The mixture was then filtered through a plug of Celite under argon atmosphere to remove the white precipitate. The Celite plug was washed with *n*-pentane and the filtrate was then concentrated under vacuum line. The residue was used directly to the next step without further purification due to its sensitivity to moisture.

Step 2: Synthesis of the spirocyclic amino boraanthracene **8**



A solution of bis(2-bromophenyl)methane **1a** (350 mg, 1.1 mmol, 1.0 equiv) in THF (10 mL) under argon atmosphere was cooled down to -94 °C using an acetone/liquid nitrogen bath. *n*-BuLi (0.9 mL, 2.1 mmol, 2.5 M in hexane, 2.0 equiv) was added dropwise. The mixture was stirred at -78 °C for 1h. The product **7b** prepared in the step 1 was dissolved in 10 mL of THF and the solution was added into the above reaction mixture at -94 °C. The mixture was slowly warmed up to room temperature and stirred for 16h. The mixture was then filtered many times through cotton to remove totally a white solid and concentrated under reduced pressure. The residue was crystallized from *n*-pentane to afford **8** as a white solid (230 mg, 0.74 mmol, 69% yield). The product was recrystallized from CH_2Cl_2/*n*-pentane to give **8** as colorless crystals.

$\mathbf{R_f}$: this compound is decomposed on SiO_2 or Al_2O_3

M.p.: 187 – 194 °C (CH_2Cl_2/*n*-pentane).

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 7.23 – 7.16 (m, 3H), 7.15 – 7.11 (m, 2H), 7.06 – 6.99 (m, 3H), 6.94 – 6.87 (m, 4H), 4.27 (d, *J* = 19.2 Hz, 1H, H_a or H_b), 4.04 (s, 2H, $CH_{2(spiroamino)}$), 3.86 (d, *J* = 19.2 Hz, 1H, H_a or H_b), 2.22 (s, 6H, CH_3).

^{13}C NMR (126 MHz, $(CD_3)_2CO$): δ (ppm) 145.3 (C_q), 142.2 (C_q), 135.3 (CH), 132.2 (CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 126.6 (CH), 125.6 (CH), 122.9 (CH), 68.1 (CH_2), 48.0 (CH_3), 41.3 (CH_2). (The carbon atoms directly attached to the boron atom of the boraanthracene scaffold were not detected due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $(CD_3)_2CO$): δ (ppm) 2.62

HRMS(ESI) (m/z): calcd. for [$C_{22}H_{23}N^{10}B$] ([M+H]$^+$): 311.19544; found: 311.19550.

8. NMR spectra

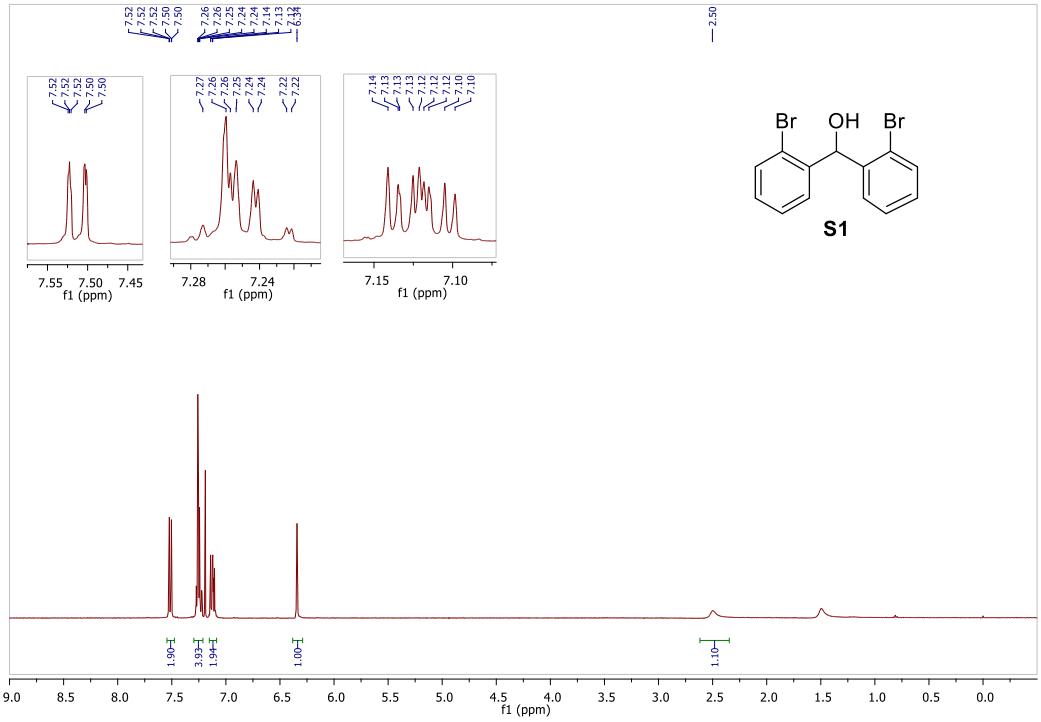


Figure S1. ^{1}H NMR (400 MHz) spectrum of **S1** in $CDCl_3$ with TMS as the internal reference.

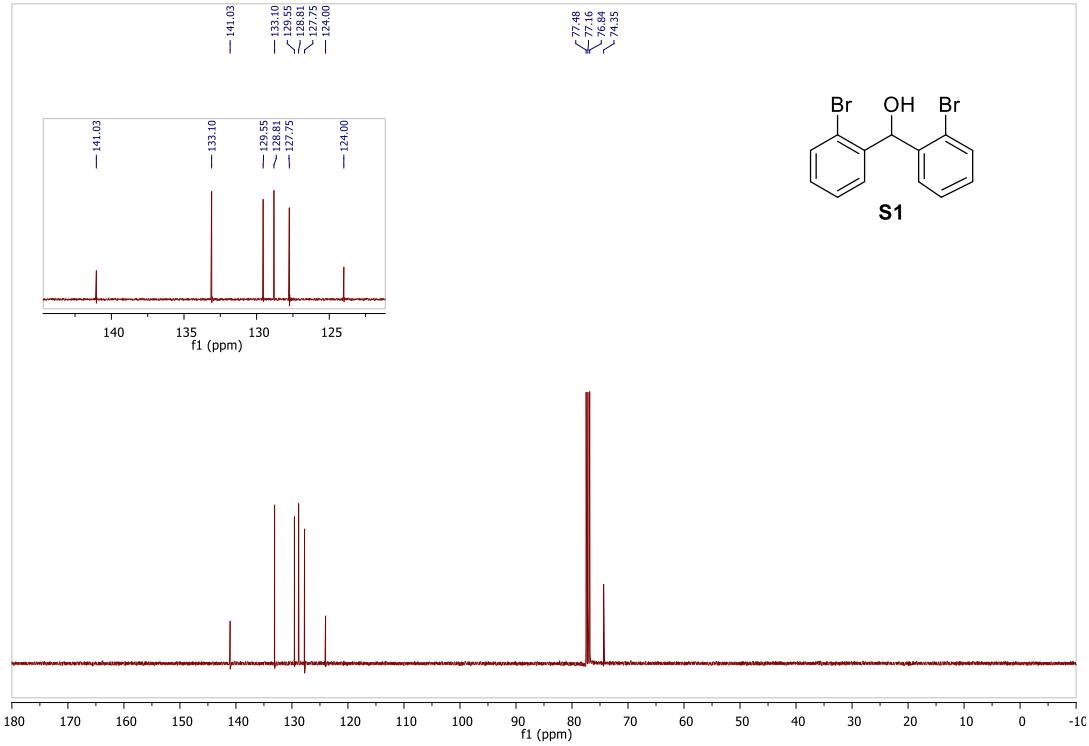


Figure S2. ^{13}C NMR (400 MHz) spectrum of **S1** in $CDCl_3$.

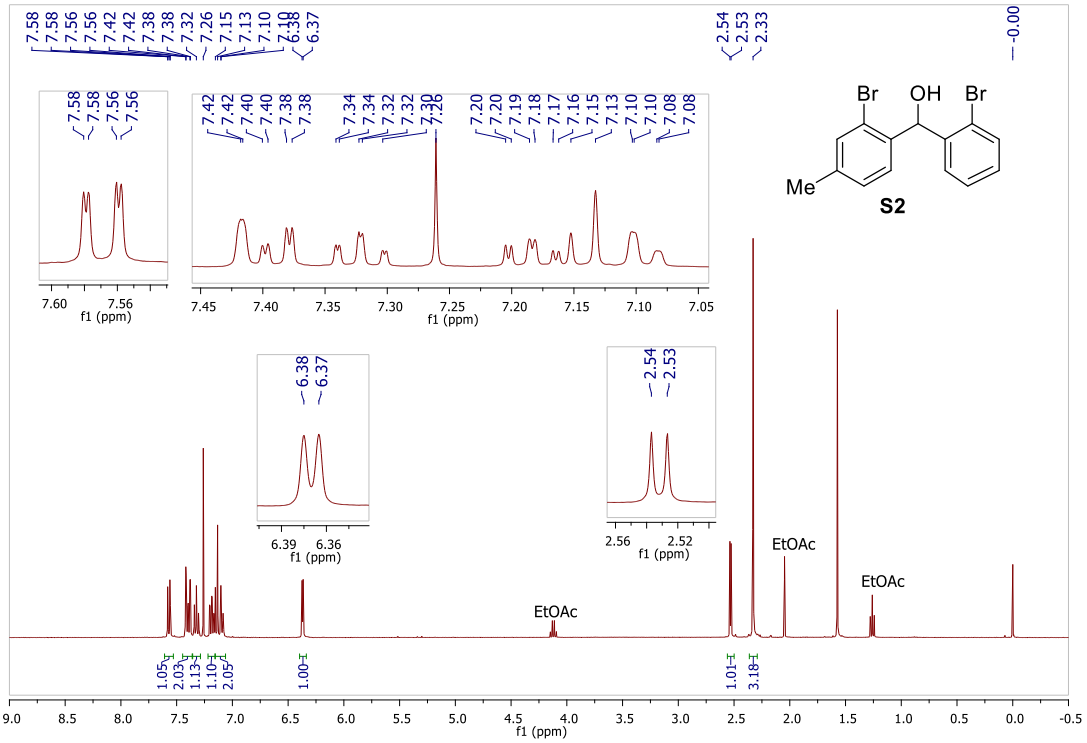


Figure S3. ^{1}H NMR (400 MHz) spectrum of **S2** in $CDCl_3$ with TMS as the internal reference.

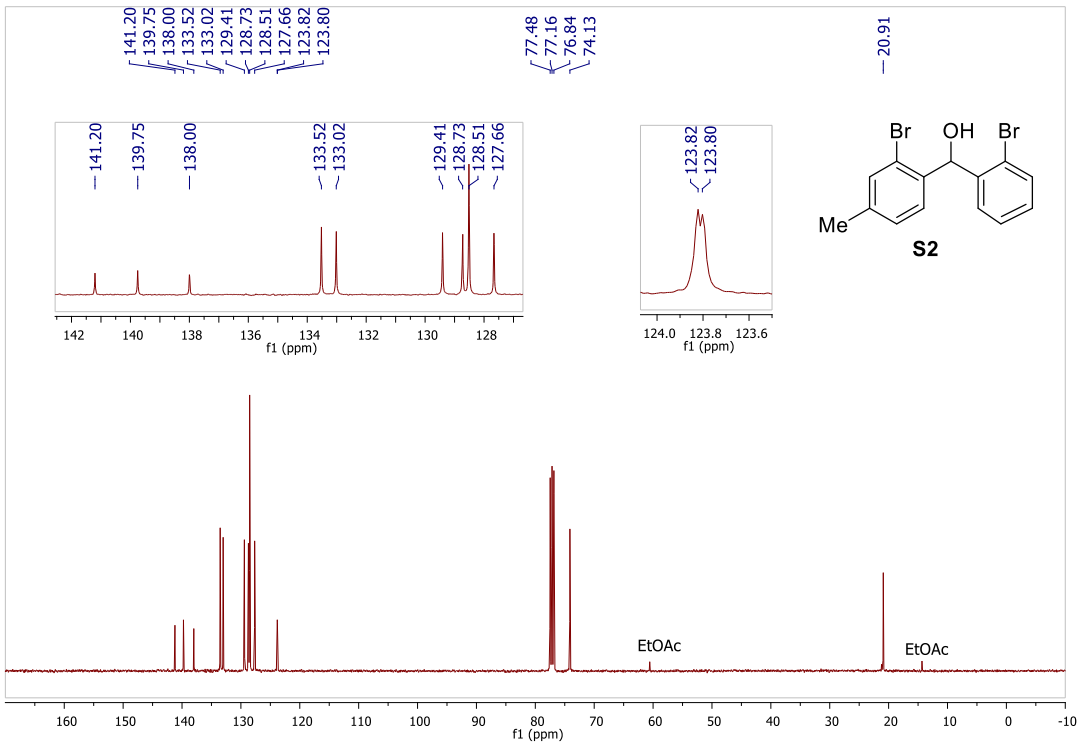


Figure S4. ^{13}C NMR (101 MHz) spectrum of **S2** in $CDCl_3$.

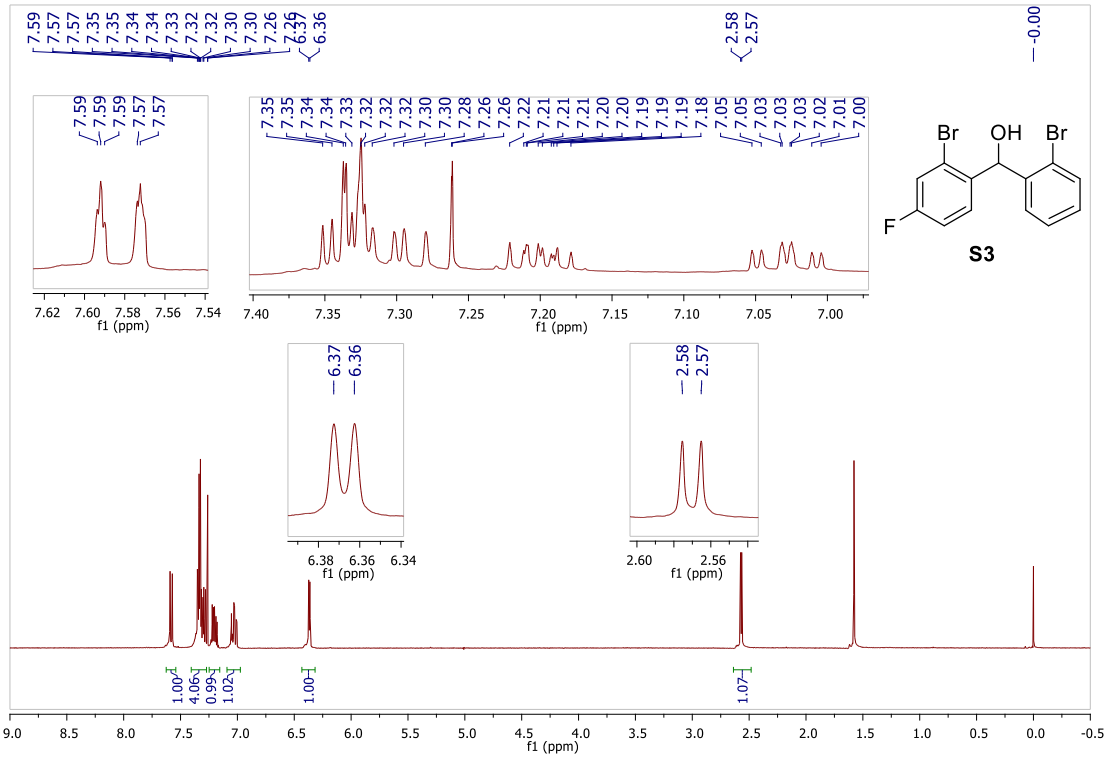


Figure S5. ^{1}H NMR (400 MHz) spectrum of **S3** in $CDCl_3$ with TMS as the internal reference.

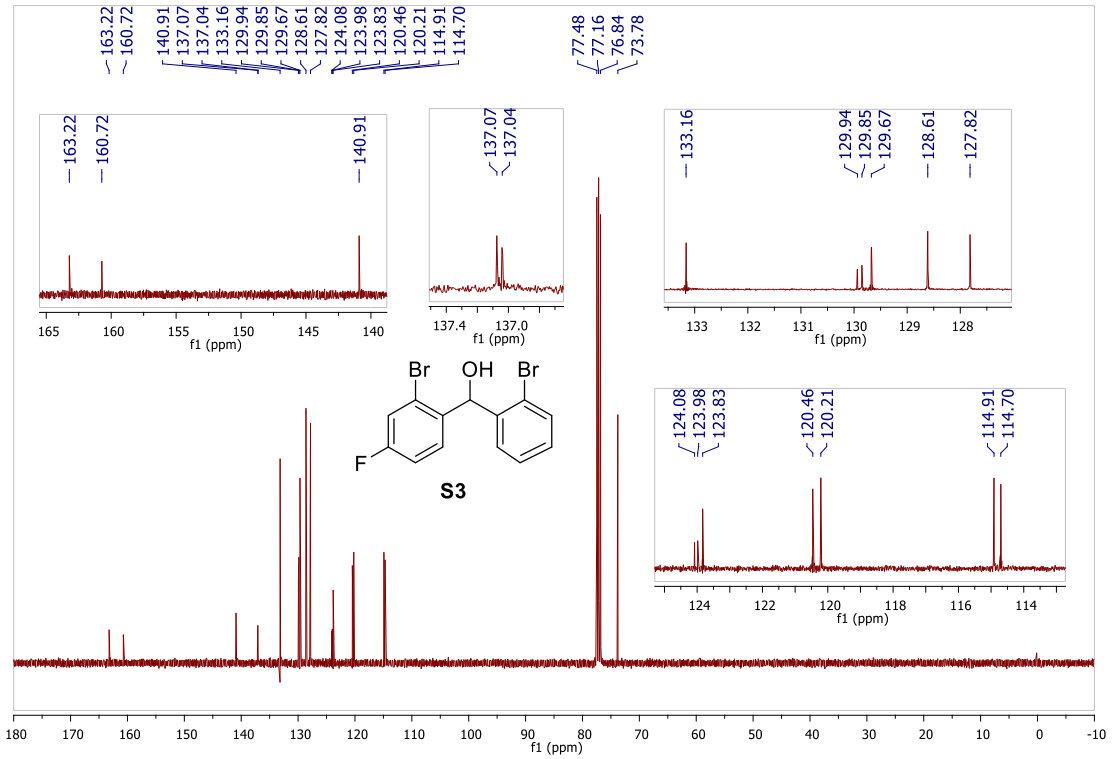


Figure S6. ^{13}C NMR (101 MHz) spectrum of **S3** in $CDCl_3$.

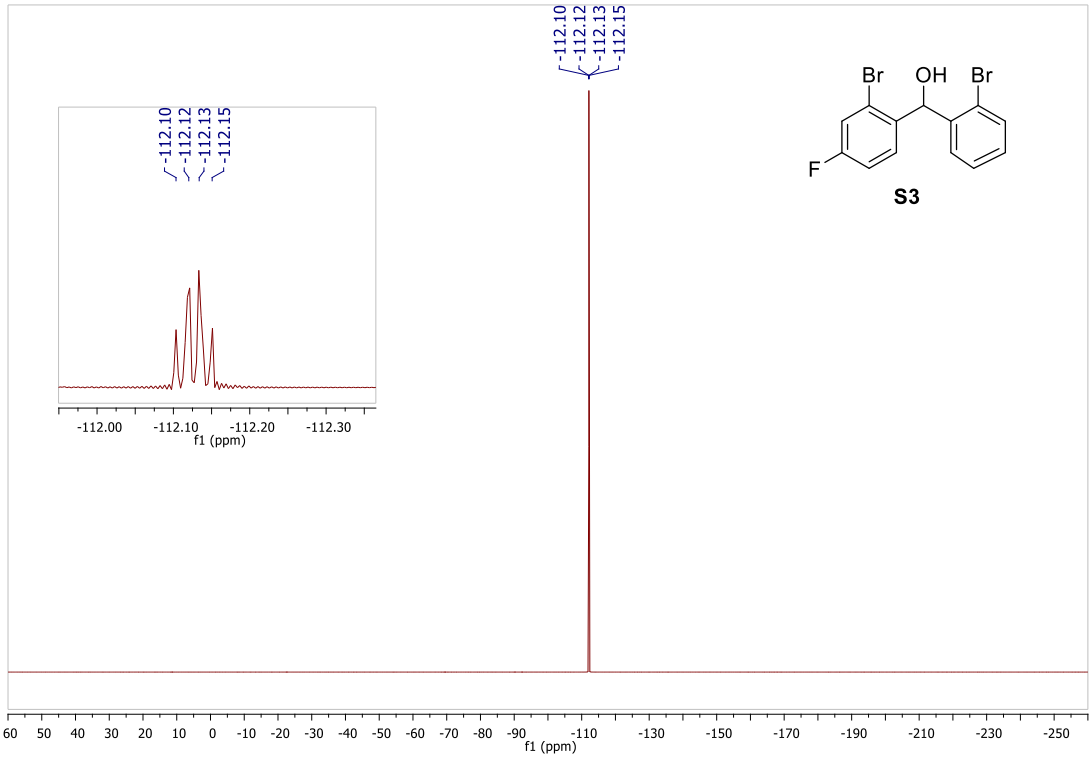


Figure S7. ^{19}F NMR (471 MHz) spectrum of **S3** in $CDCl_3$.

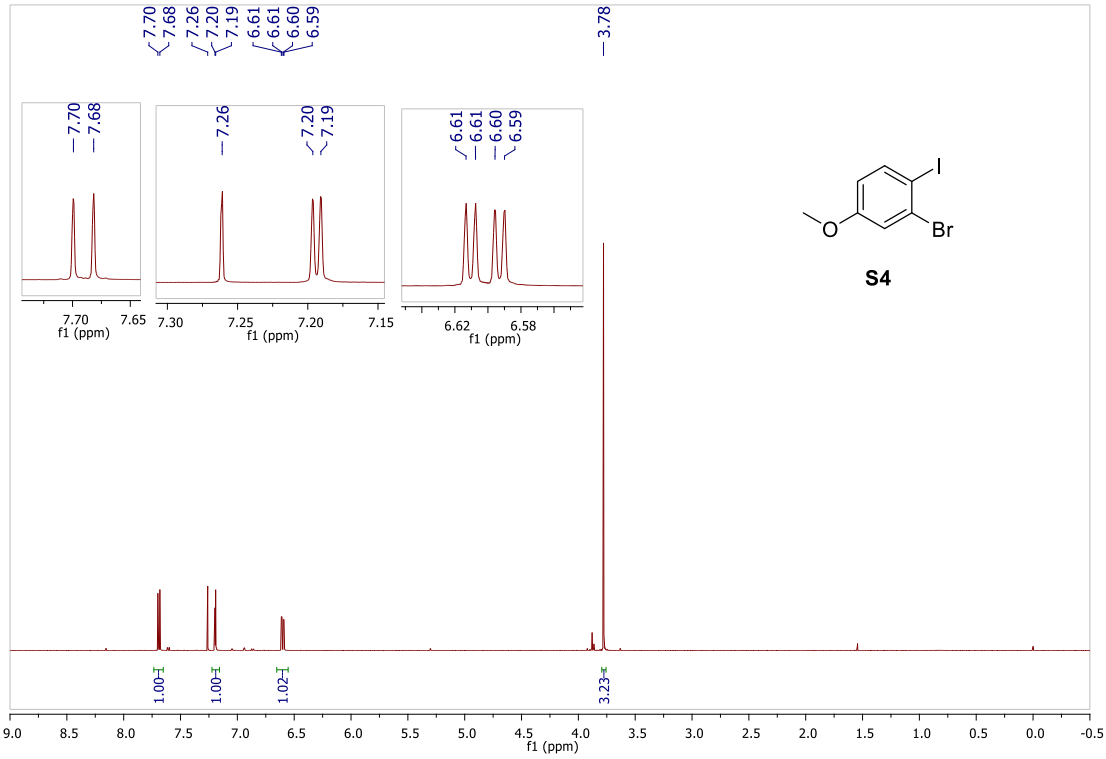


Figure S8. ^{1}H NMR (500 MHz) spectrum of **S4** in $CDCl_3$ with TMS as the internal reference.

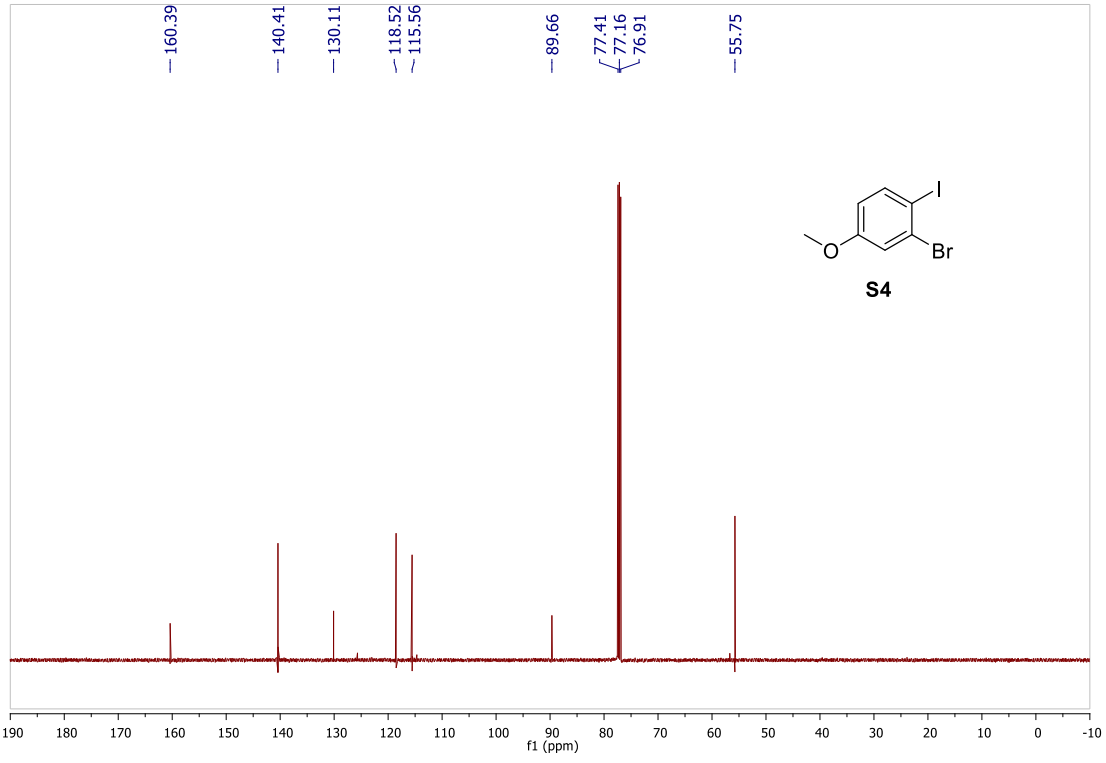


Figure S9. ^{13}C NMR (125 MHz) spectrum of **S4** in $CDCl_3$.

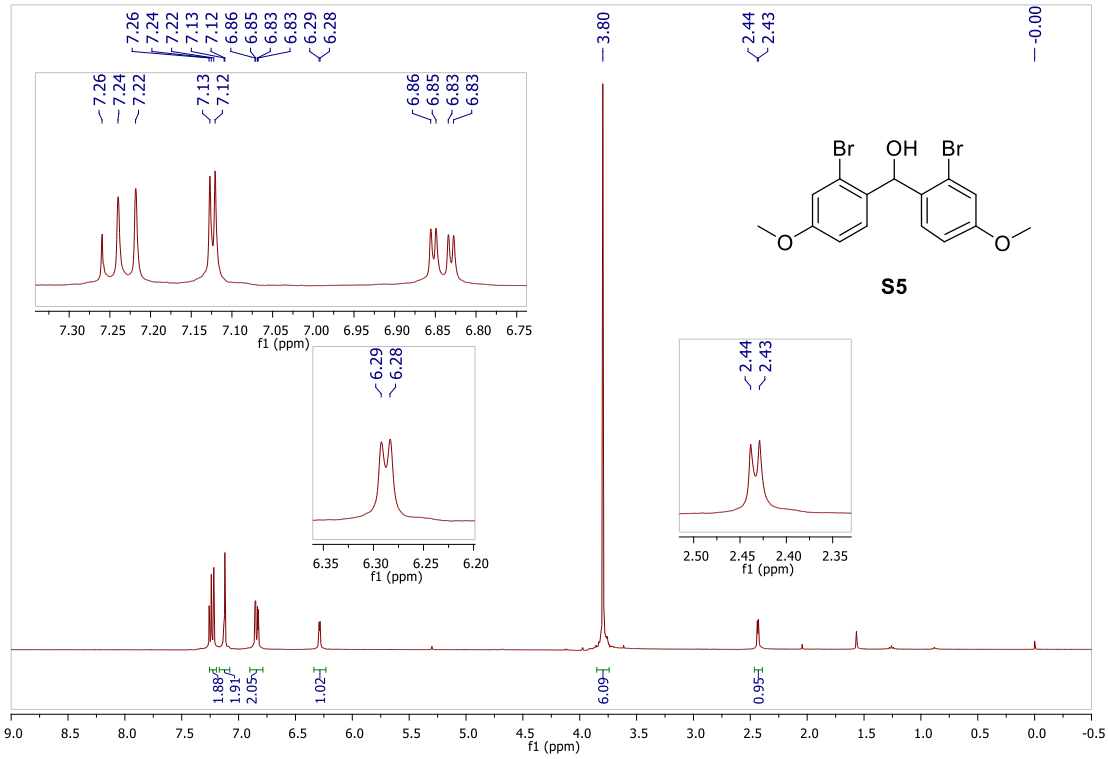


Figure S10. ^{1}H NMR (400 MHz) spectrum of **S5** in $CDCl_3$ with TMS as the internal reference.

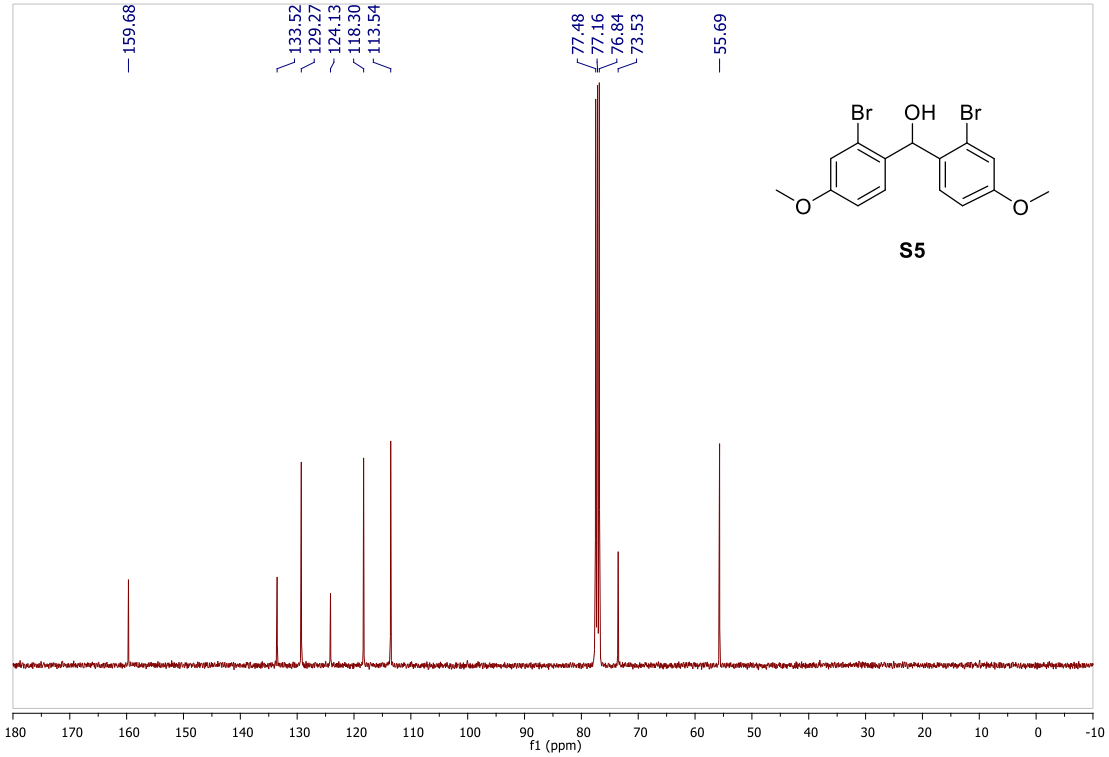


Figure S11. ^{13}C NMR (101 MHz) spectrum of **S5** in $CDCl_3$.

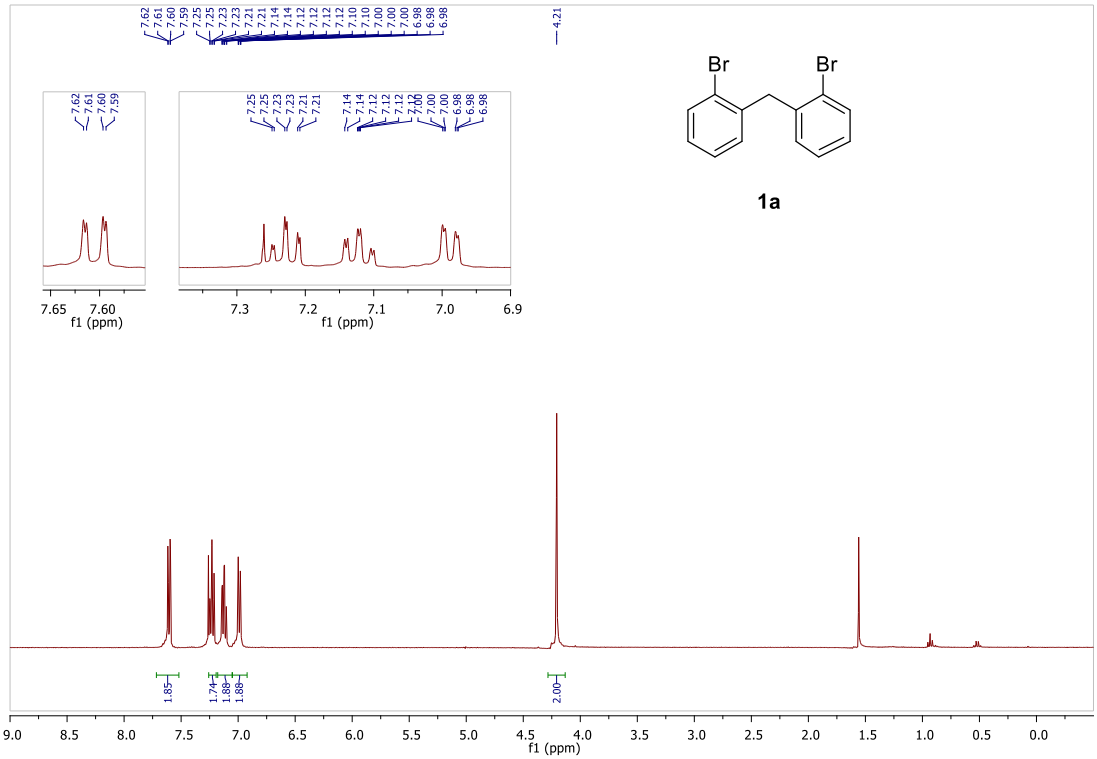


Figure S12. ^{1}H NMR (400 MHz) spectrum of **1a** in $CDCl_3$.

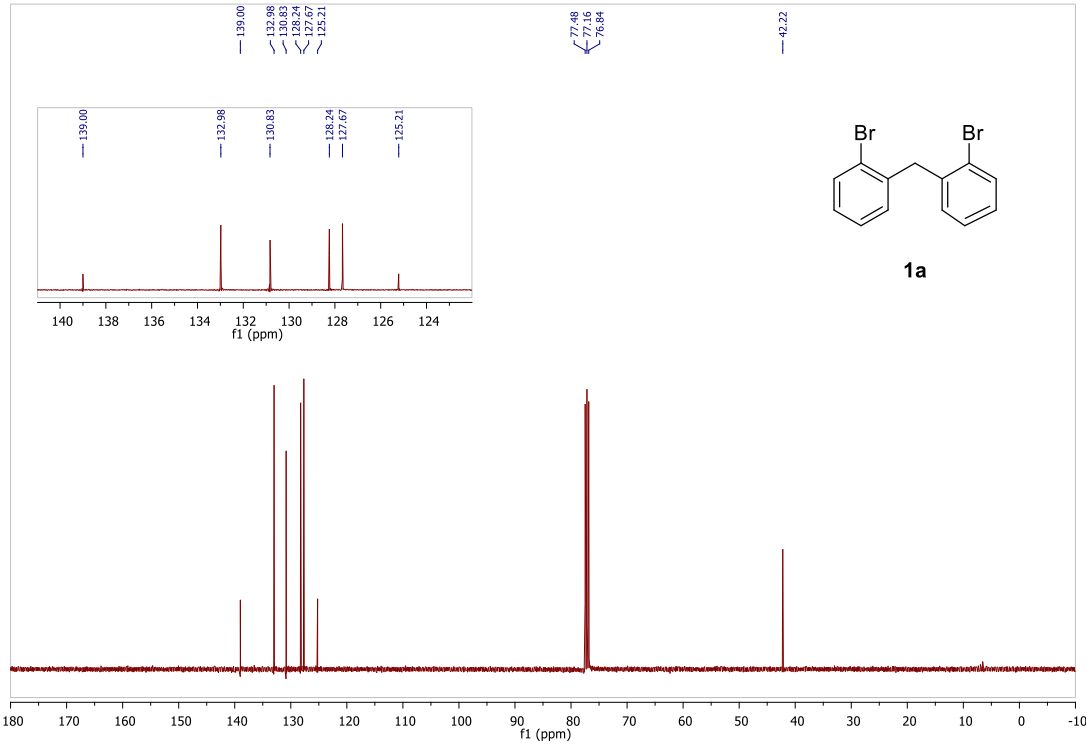


Figure S13. ^{13}C NMR (101 MHz) spectrum of **1a** in $CDCl_3$.

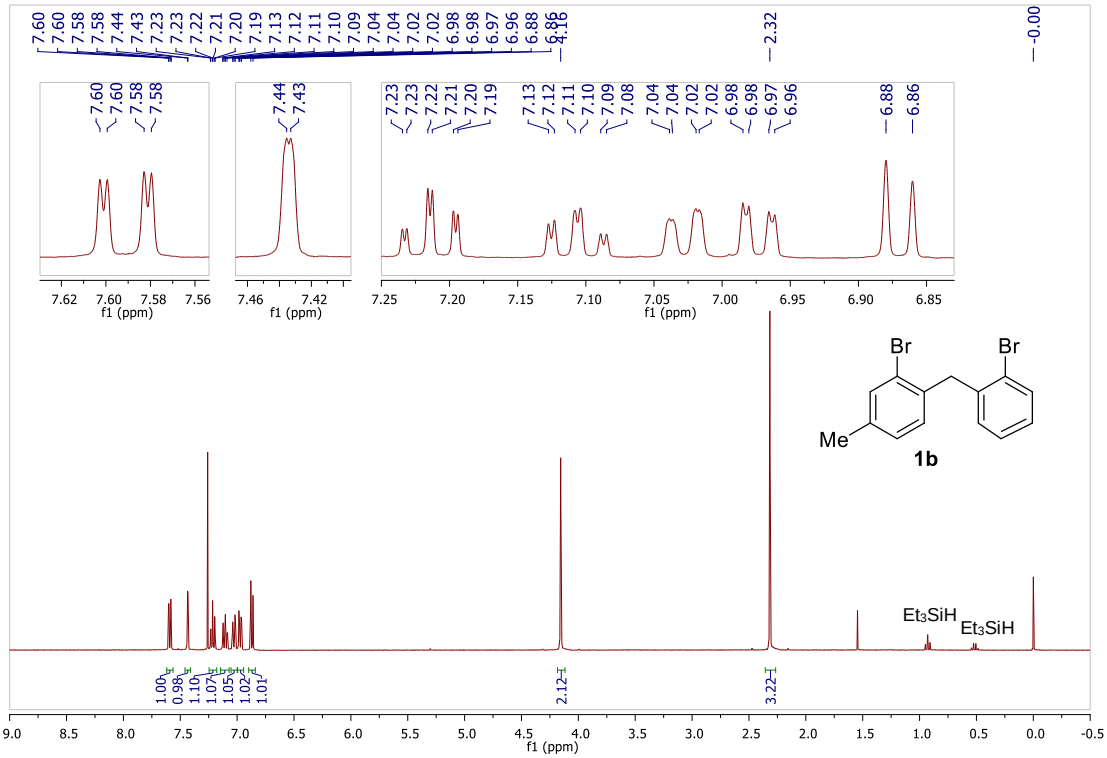


Figure S14. ^{1}H NMR (400 MHz) spectrum of **1b** in $CDCl_3$ with TMS as the internal reference.

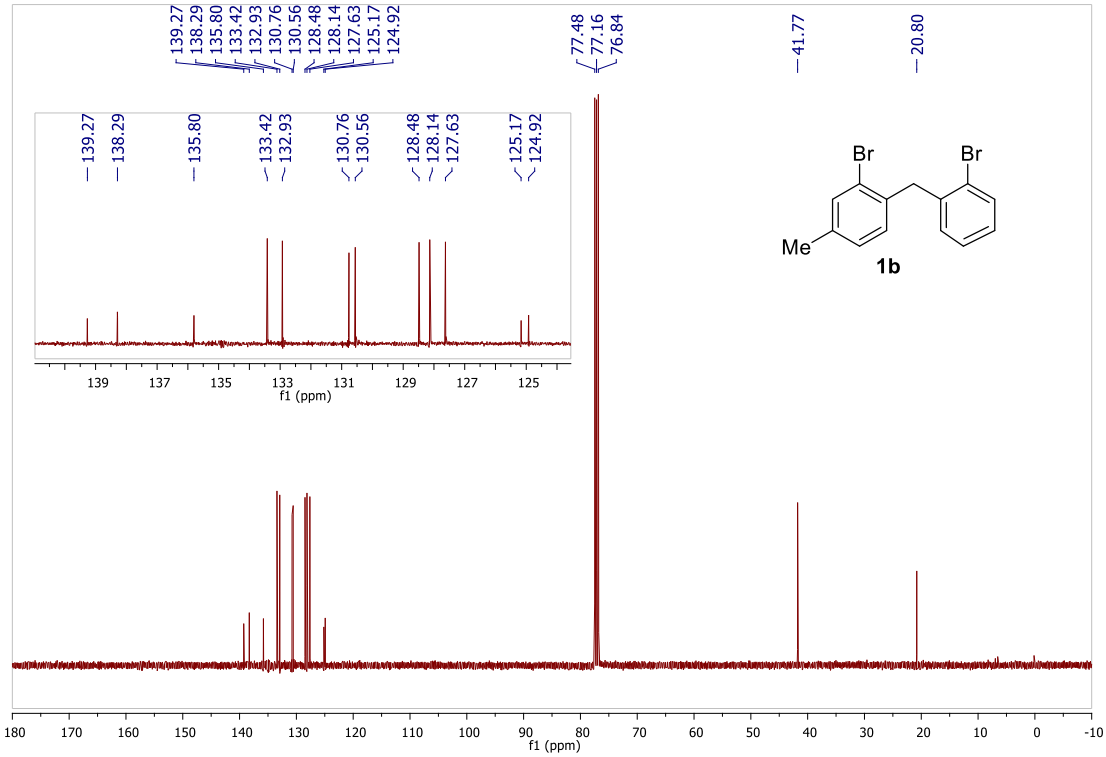


Figure S15. ^{13}C NMR (101 MHz) spectrum of **1b** in $CDCl_3$.

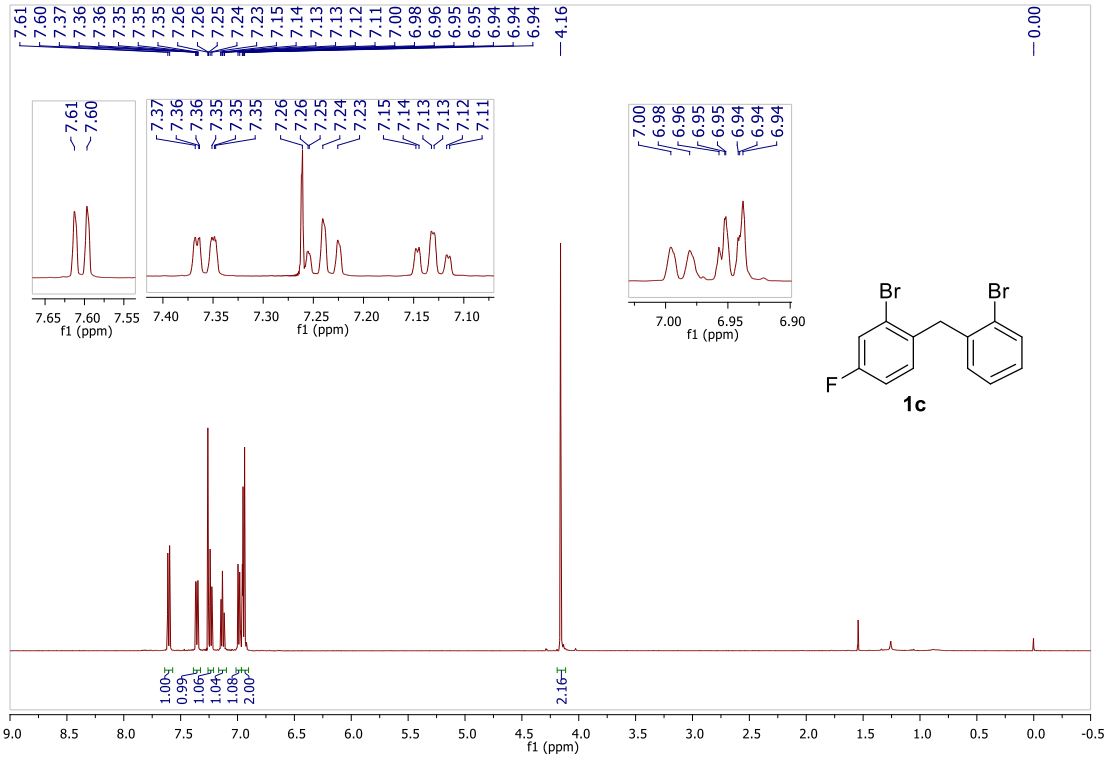


Figure S16. ^{1}H NMR (500 MHz) spectrum of **1c** in $CDCl_3$ with TMS as the internal reference.

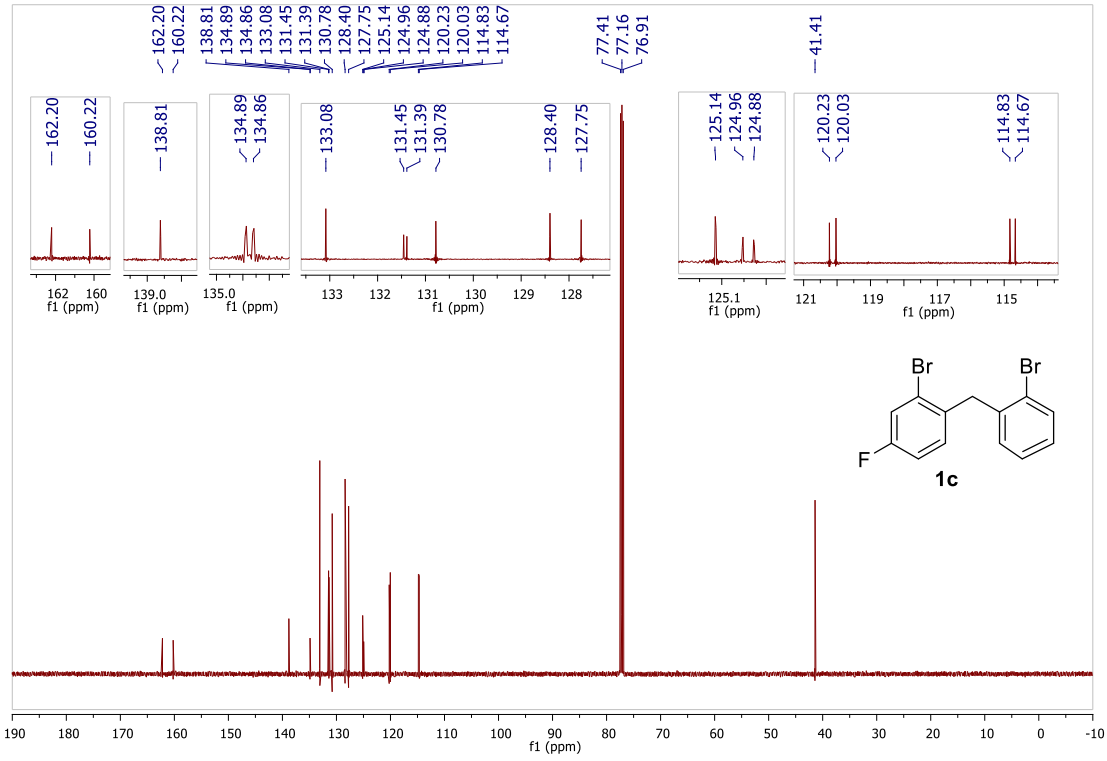


Figure S17. ^{13}C NMR (125 MHz) spectrum of **1c** in $CDCl_3$.

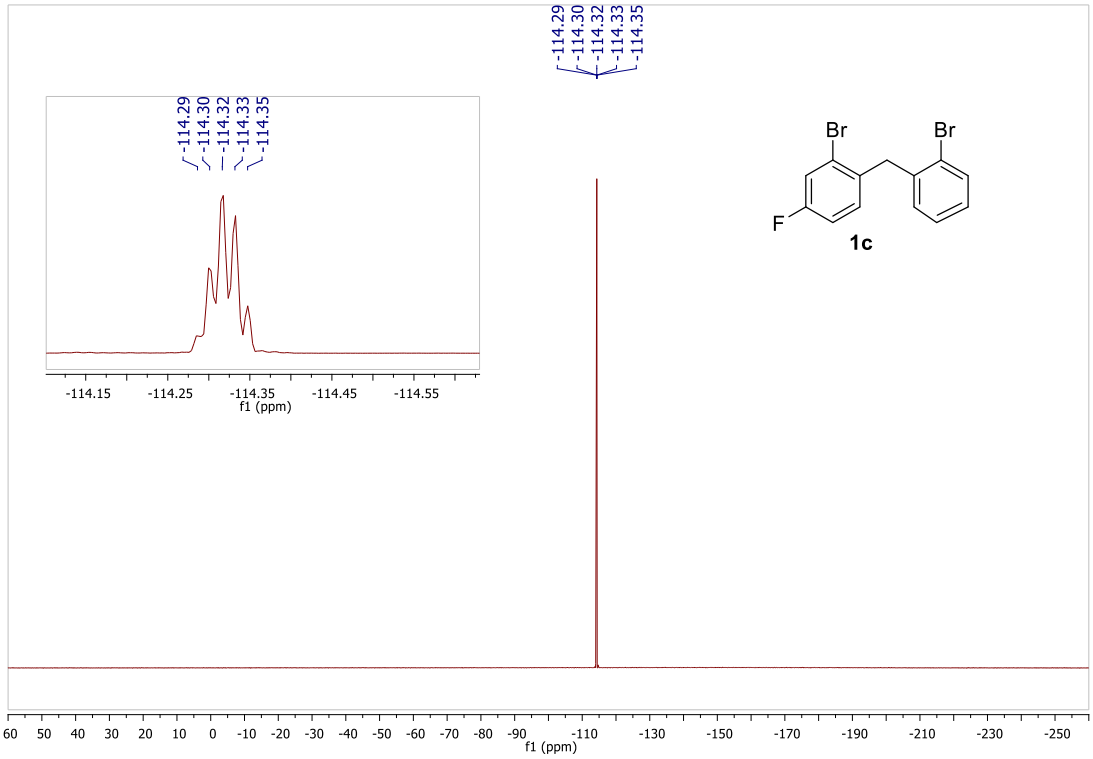


Figure S18. ^{19}F NMR (471 MHz) spectrum of **1c** in $CDCl_3$.

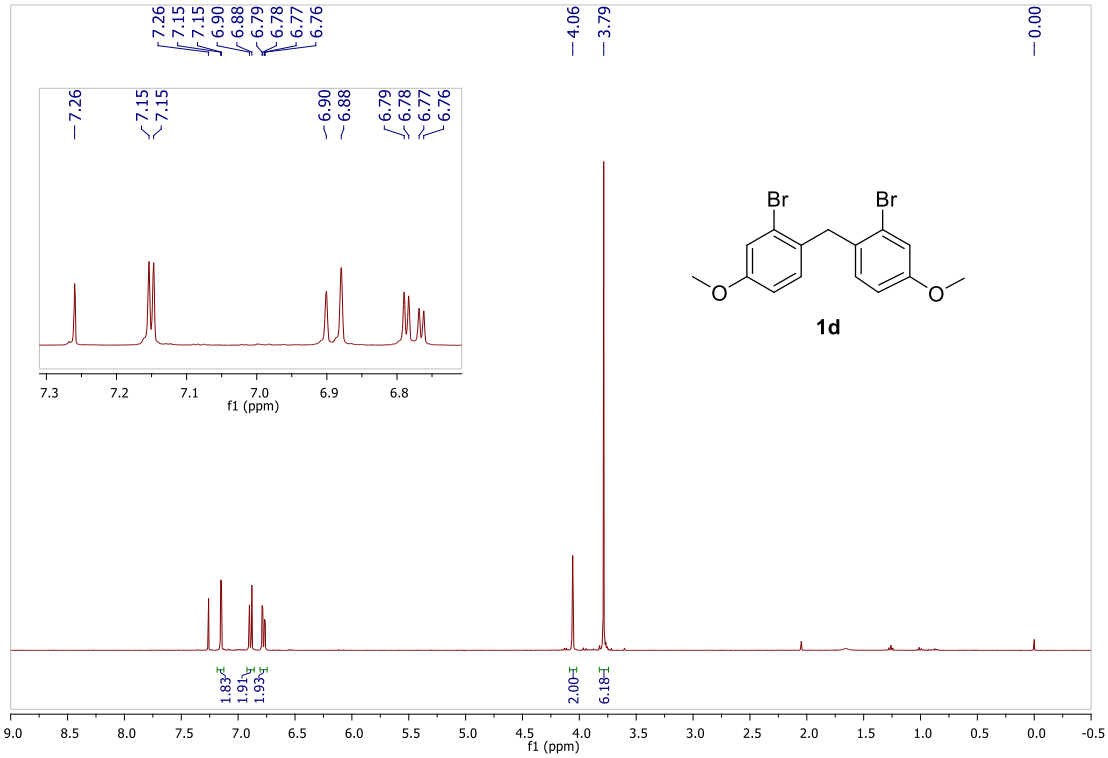


Figure S19. ^{1}H NMR (400 MHz) spectrum of **1d** in $CDCl_3$ with TMS as the internal reference.

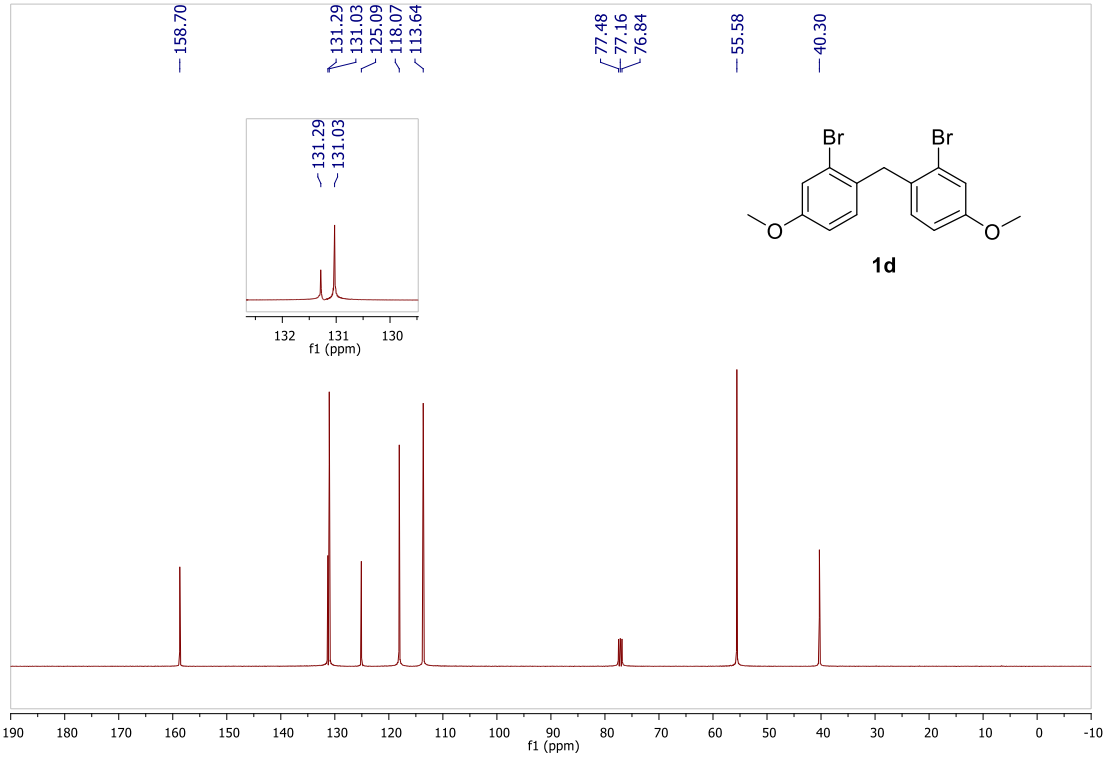


Figure S20. ^{13}C NMR (101 MHz) spectrum of **1d** in $CDCl_3$.

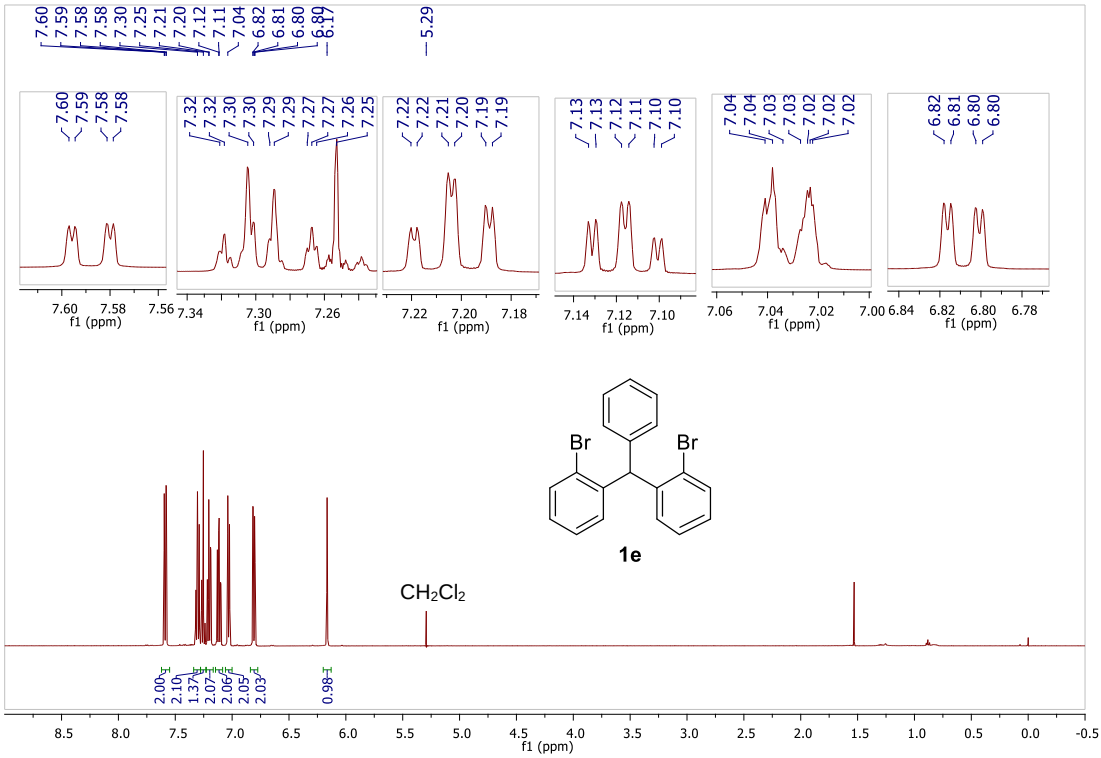


Figure S21. ^{1}H NMR (500 MHz) spectrum of **1e** in $CDCl_3$ with TMS as the internal reference.

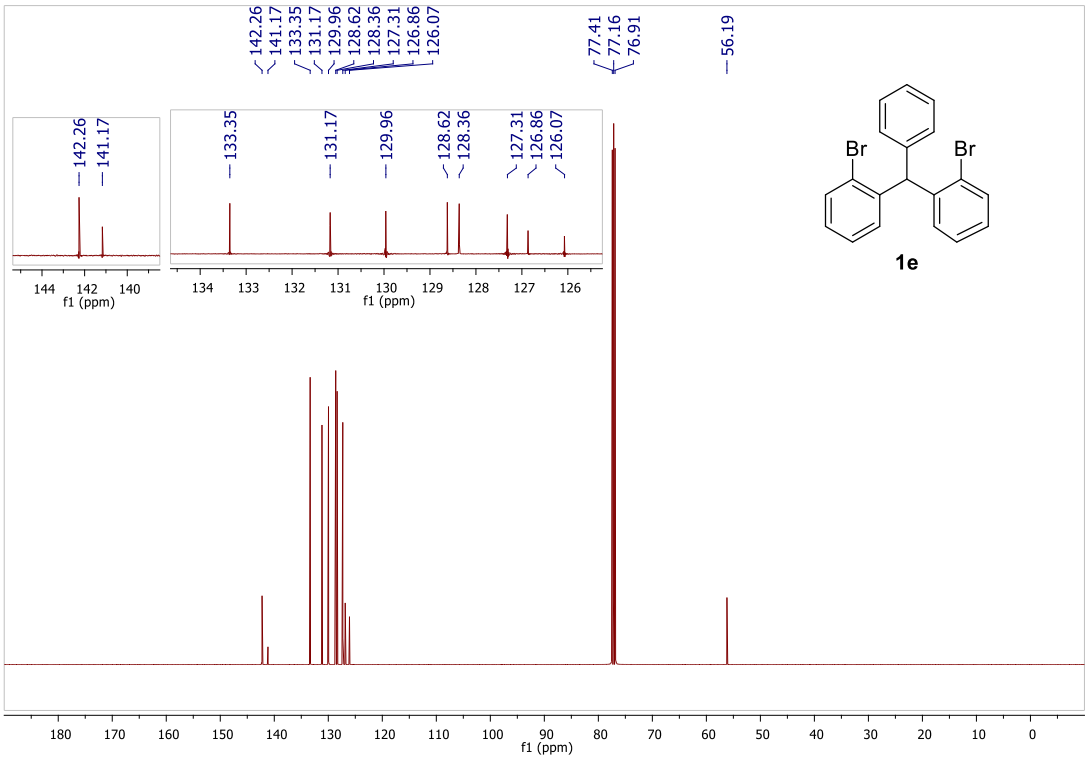


Figure S22. ^{13}C NMR (125 MHz) spectrum of **1e** in $CDCl_3$.

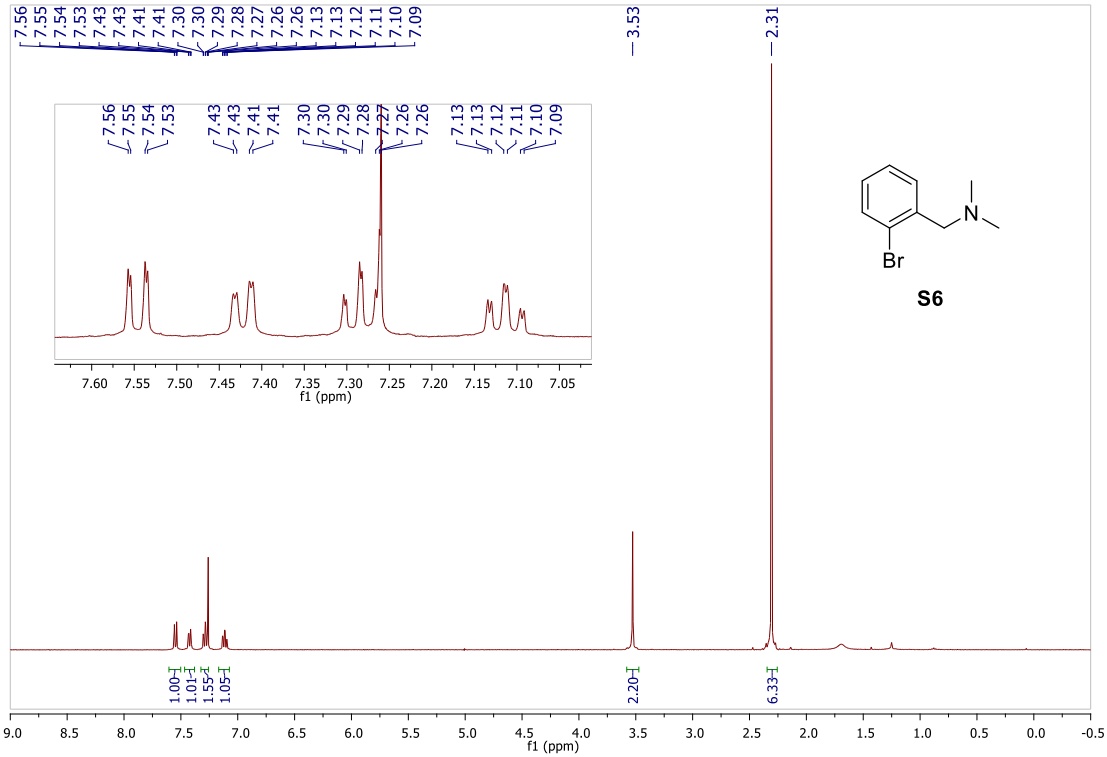


Figure S23. ^{1}H NMR (400 MHz) spectrum of **S6** in $CDCl_3$.

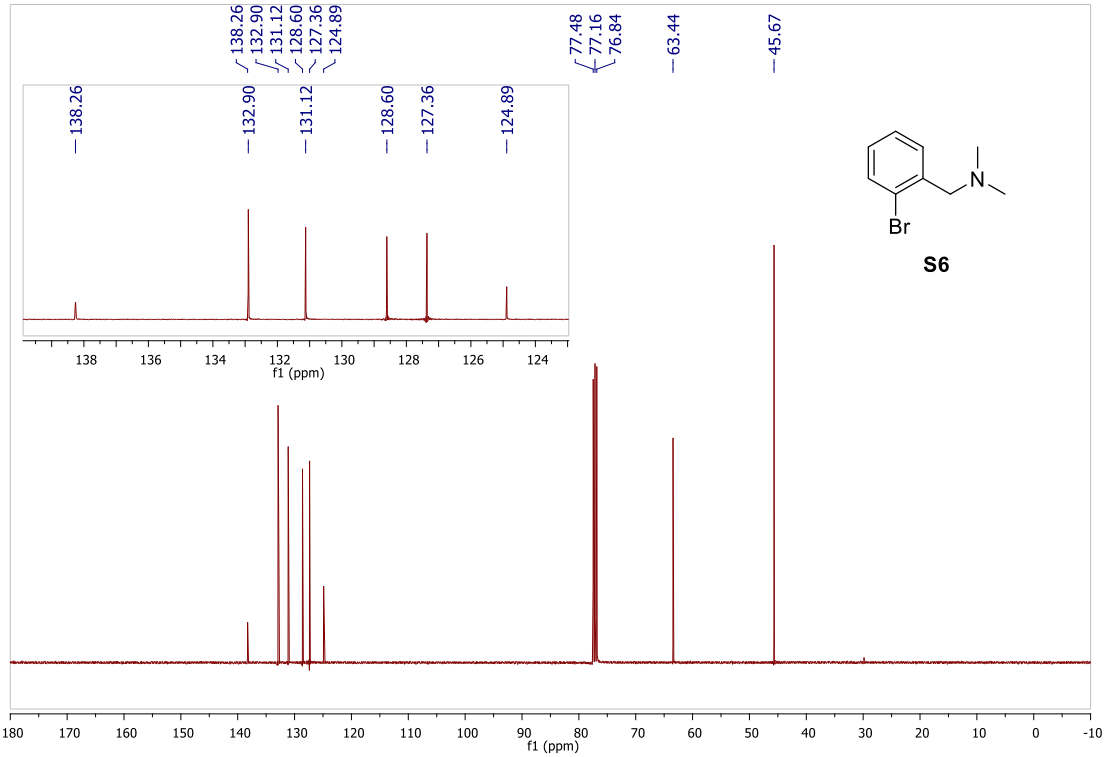


Figure S24. ^{13}C NMR (101 MHz) spectrum of **S6** in $CDCl_3$.

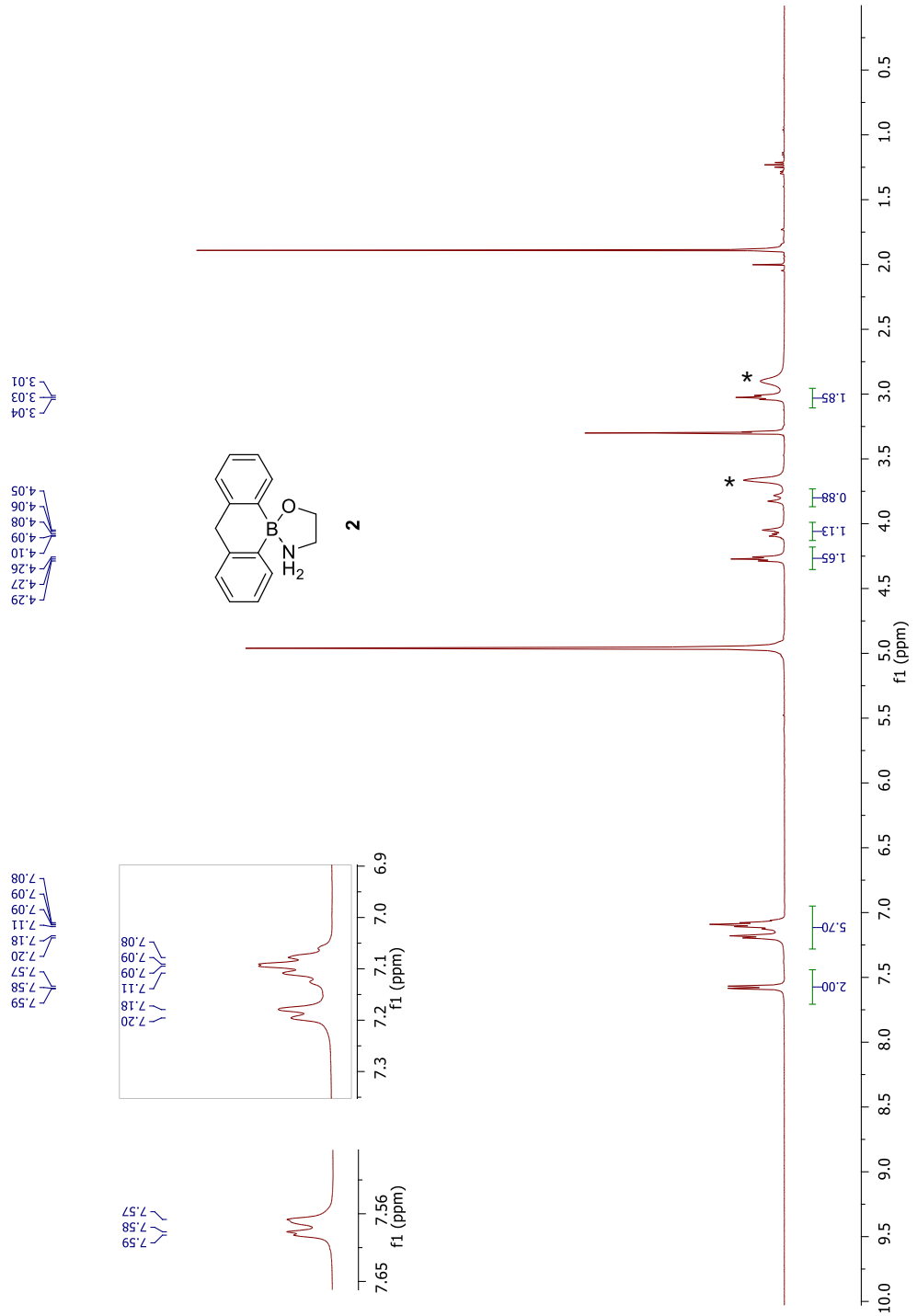


Figure S25. ^{1}H NMR (400 MHz) spectrum of **2** in CD_3OD (*: residue of ethanolamine).

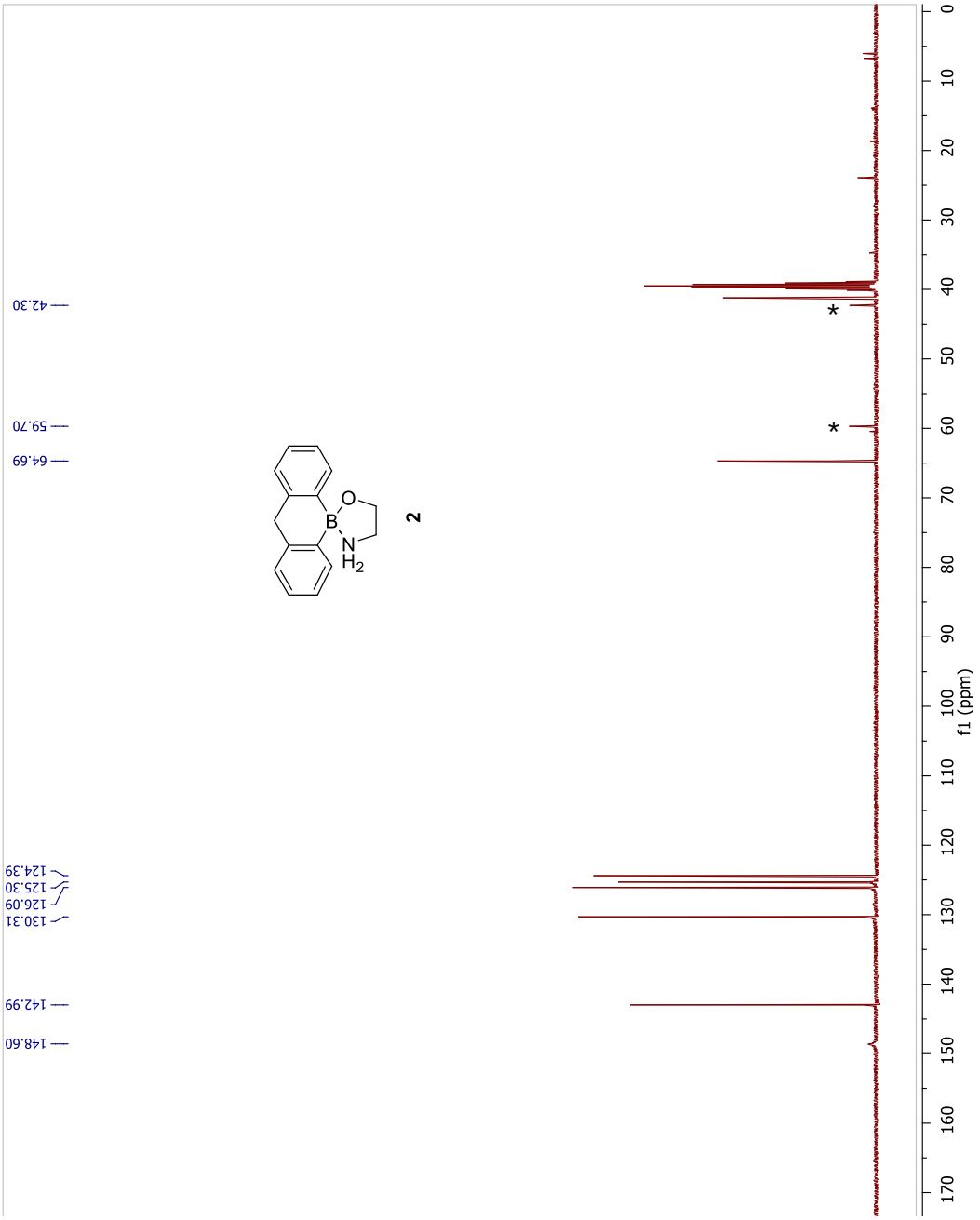


Figure S26. ^{13}C NMR (101 MHz) spectrum of **2** in CD_3OD (*: residue of ethanolamine).

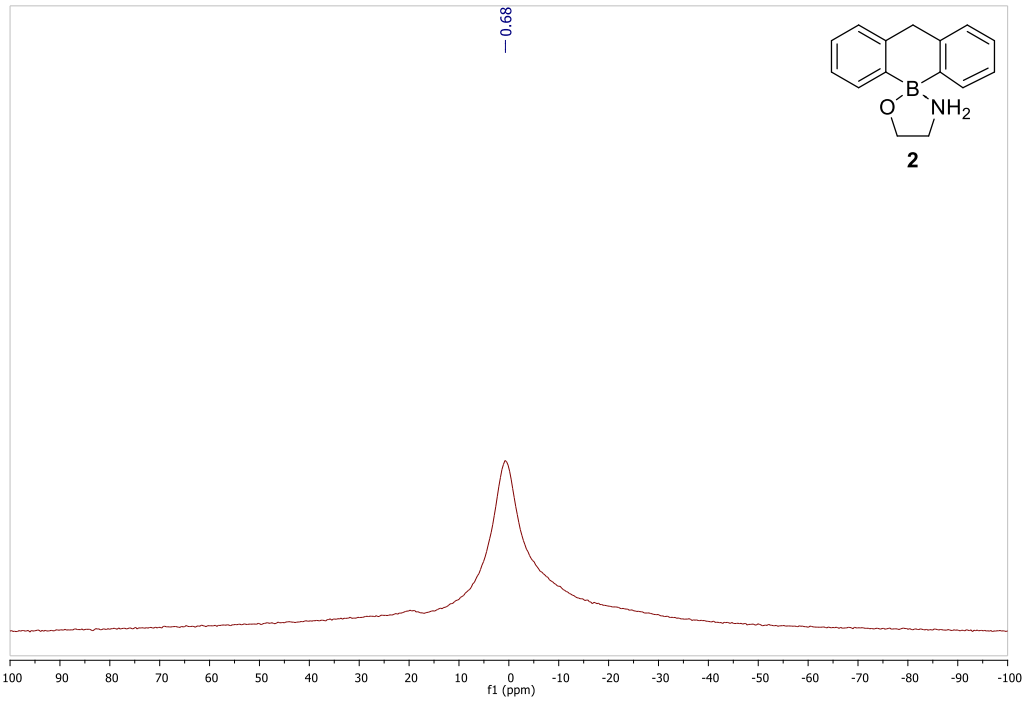


Figure S27. ^{11}B NMR (128 MHz) spectrum of **2** in DMSO-d_6.

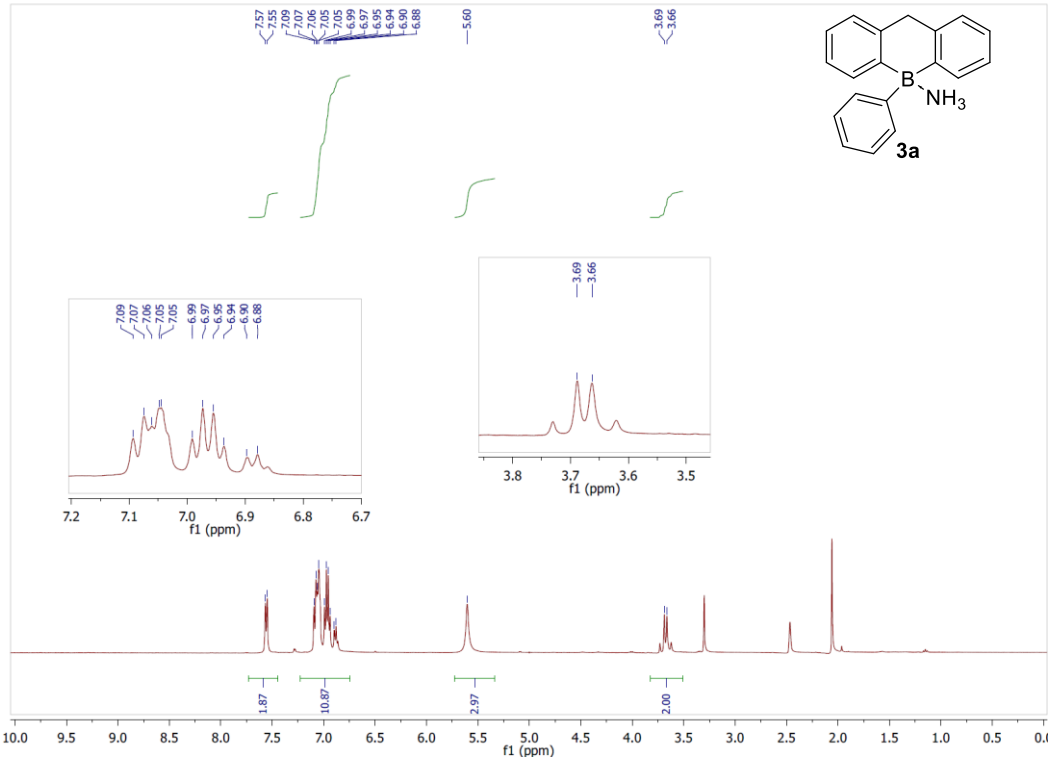


Figure S28. ^{1}H NMR (400 MHz) spectrum of **3a** in DMSO-d_6.

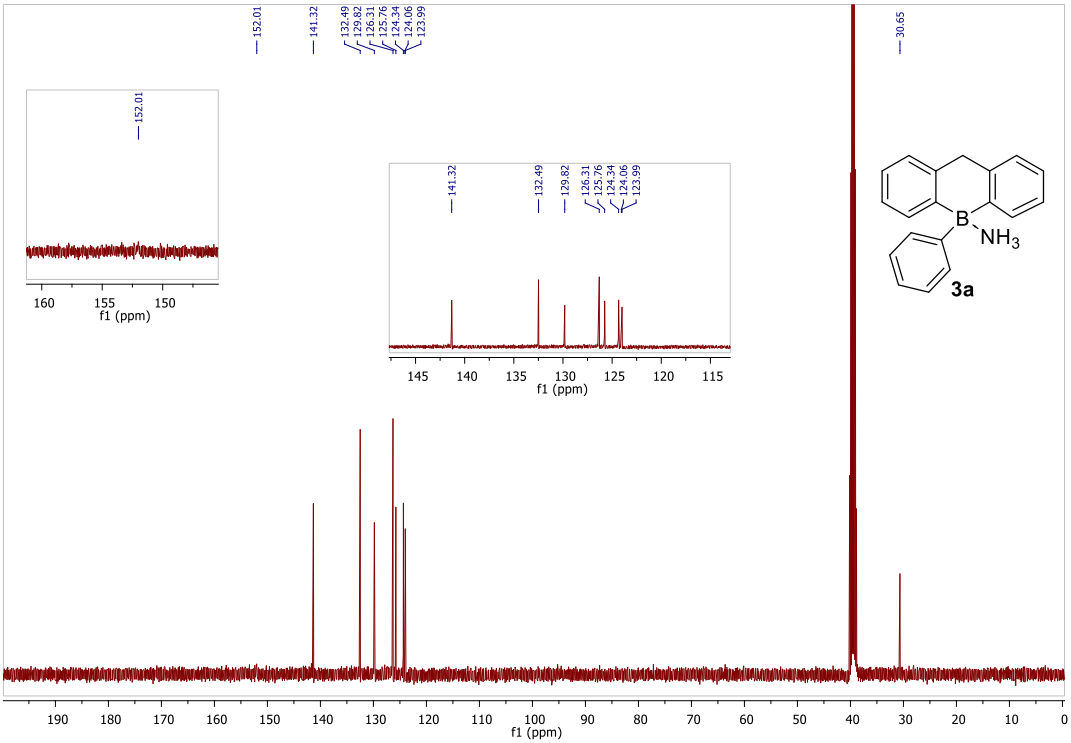


Figure S29. ^{13}C NMR (101 MHz) spectrum of **3a** in DMSO-d_6.

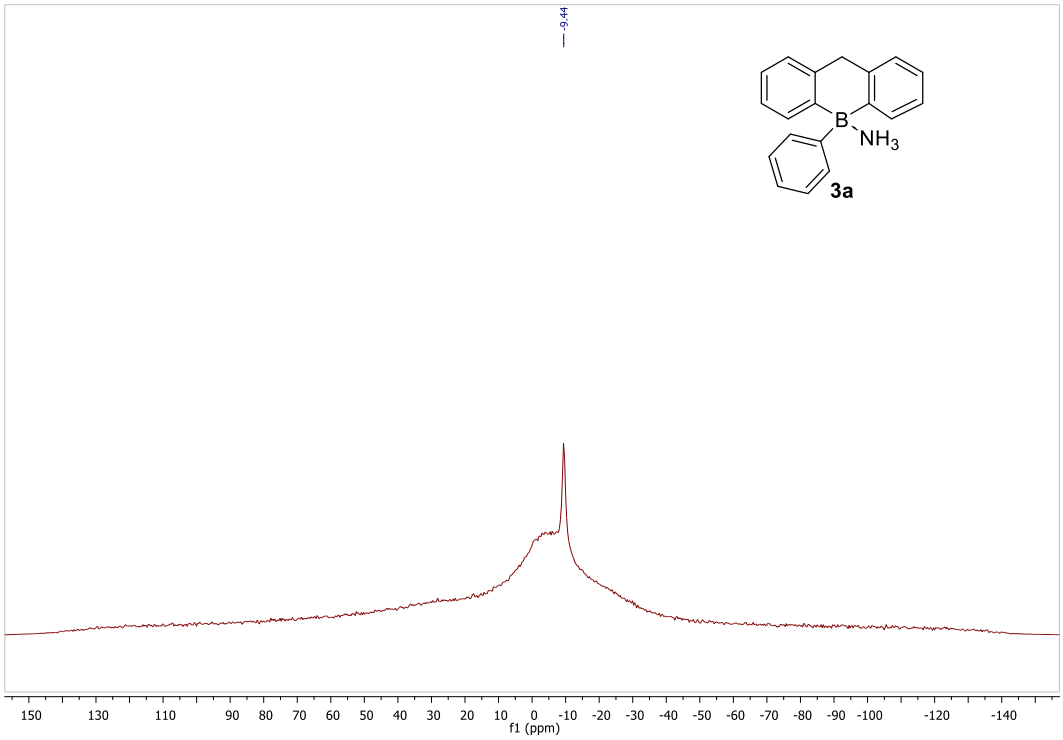


Figure S30. ^{11}B NMR (128 MHz) spectrum of **3a** in DMSO-d_6.

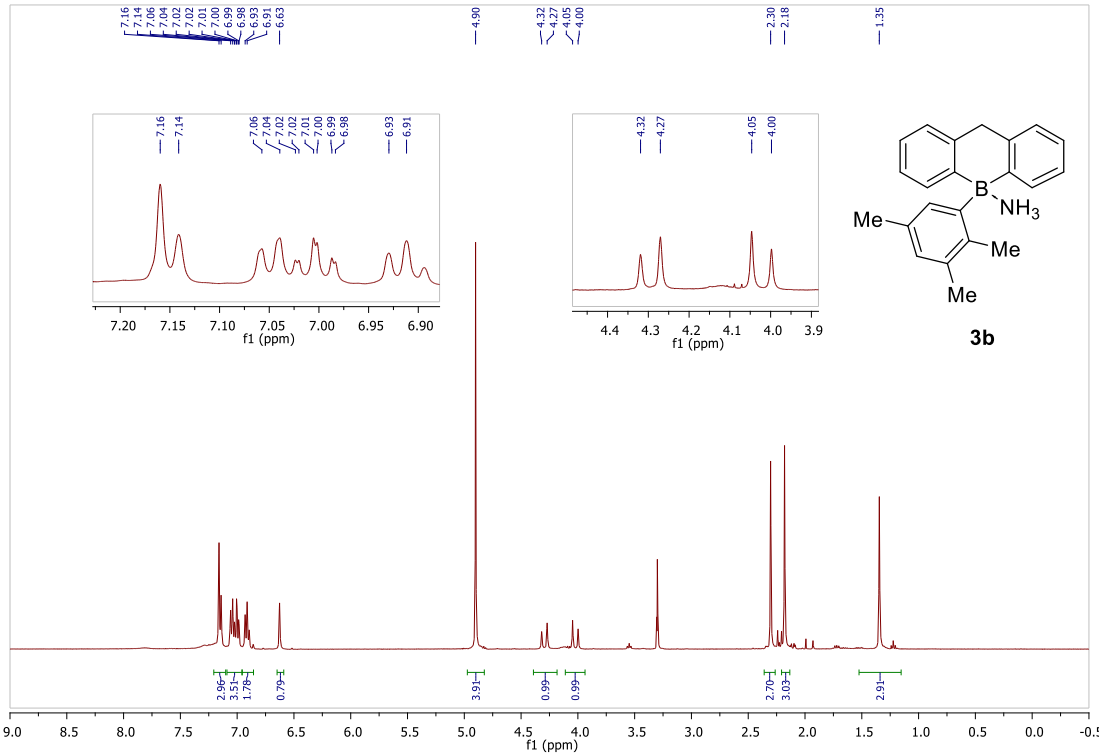


Figure S31. ^{1}H NMR (400 MHz) spectrum of **3b** in CD_3OD.

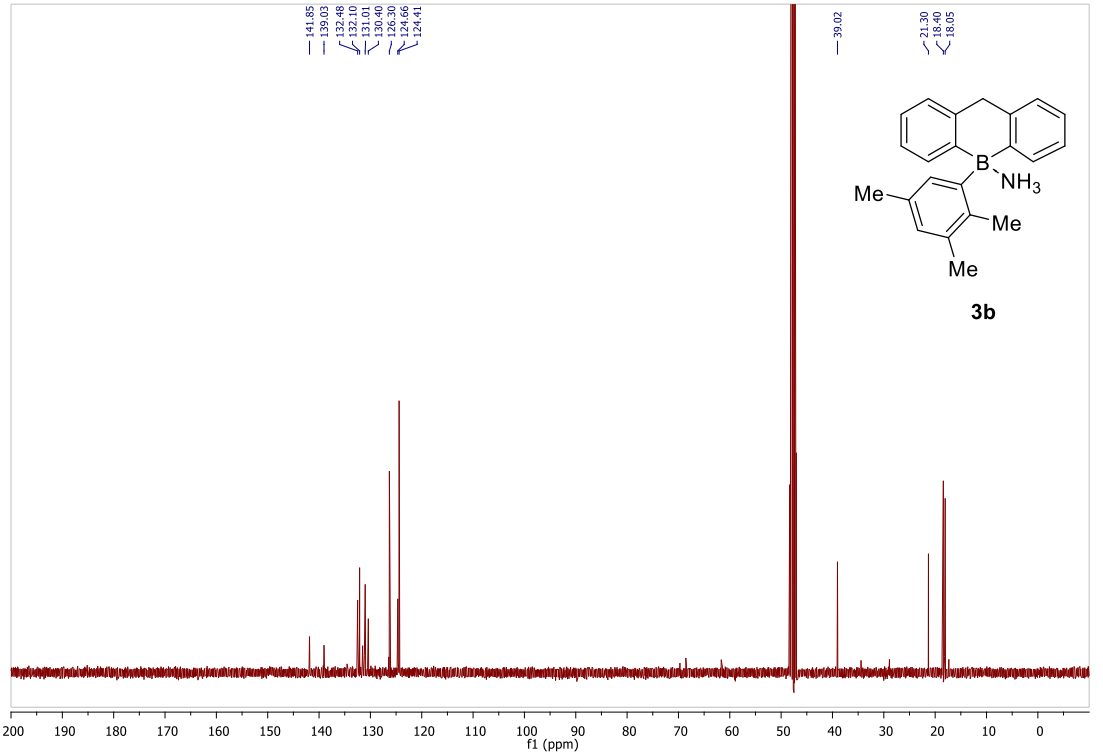


Figure S32. ^{13}C NMR (101 MHz) spectrum of **3b** in CD_3OD.

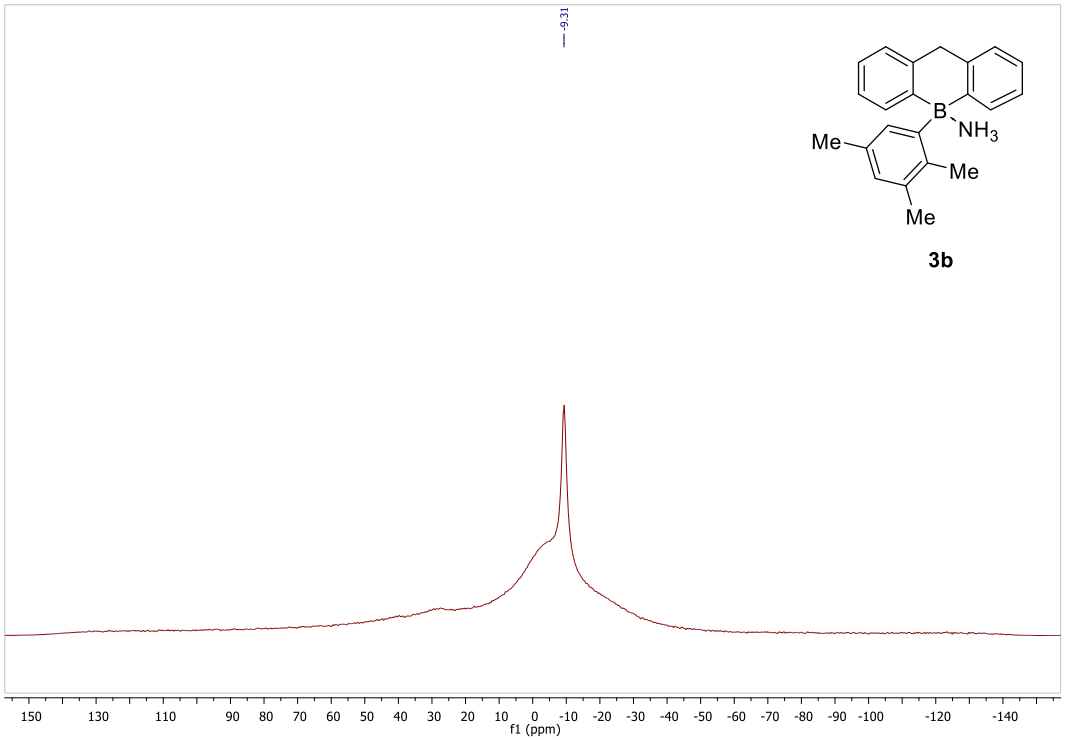


Figure S33. ^{11}B NMR (128 MHz) spectrum of **3b** in CD_3OD.

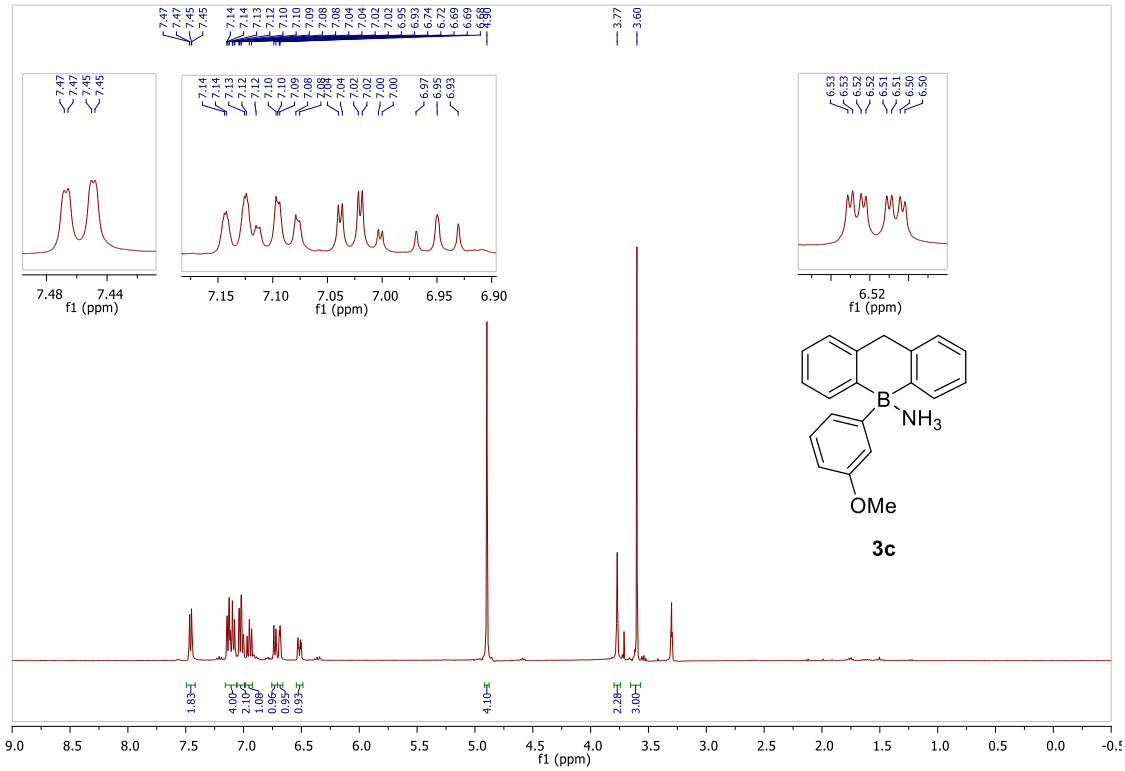


Figure S34. ^{1}H NMR (400 MHz) spectrum of **3c** in CD_3OD.

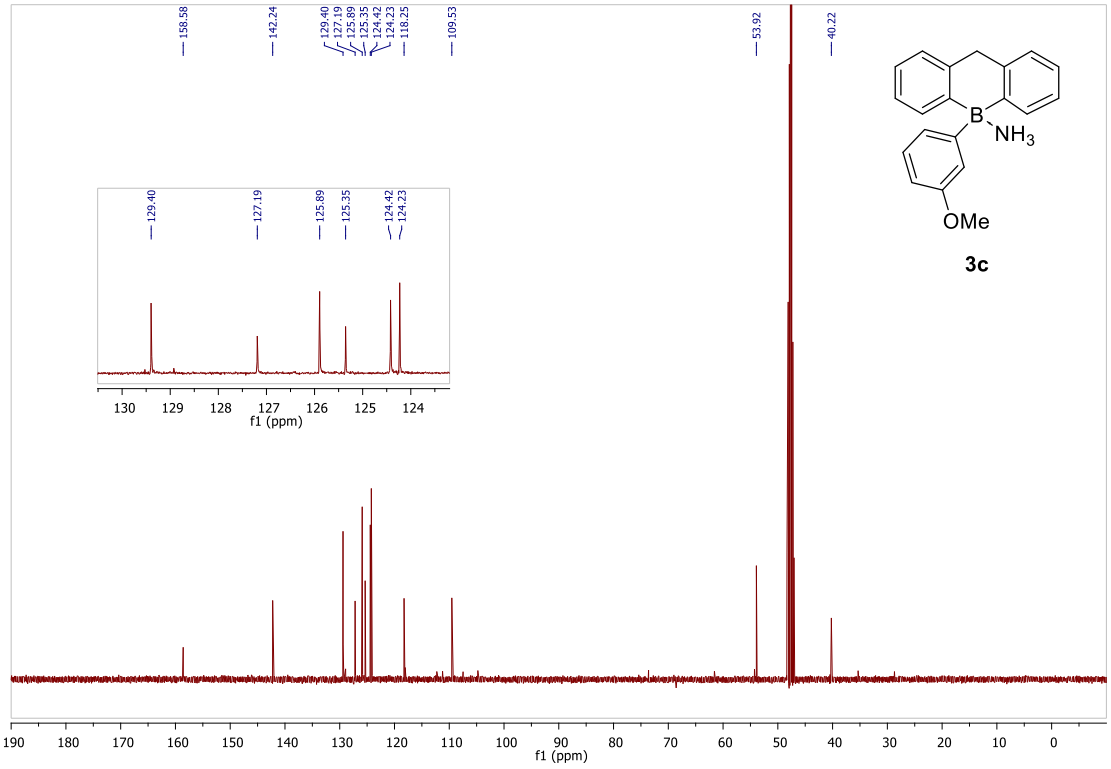


Figure S35. ^{13}C NMR (101 MHz) spectrum of **3c** in CD_3OD.

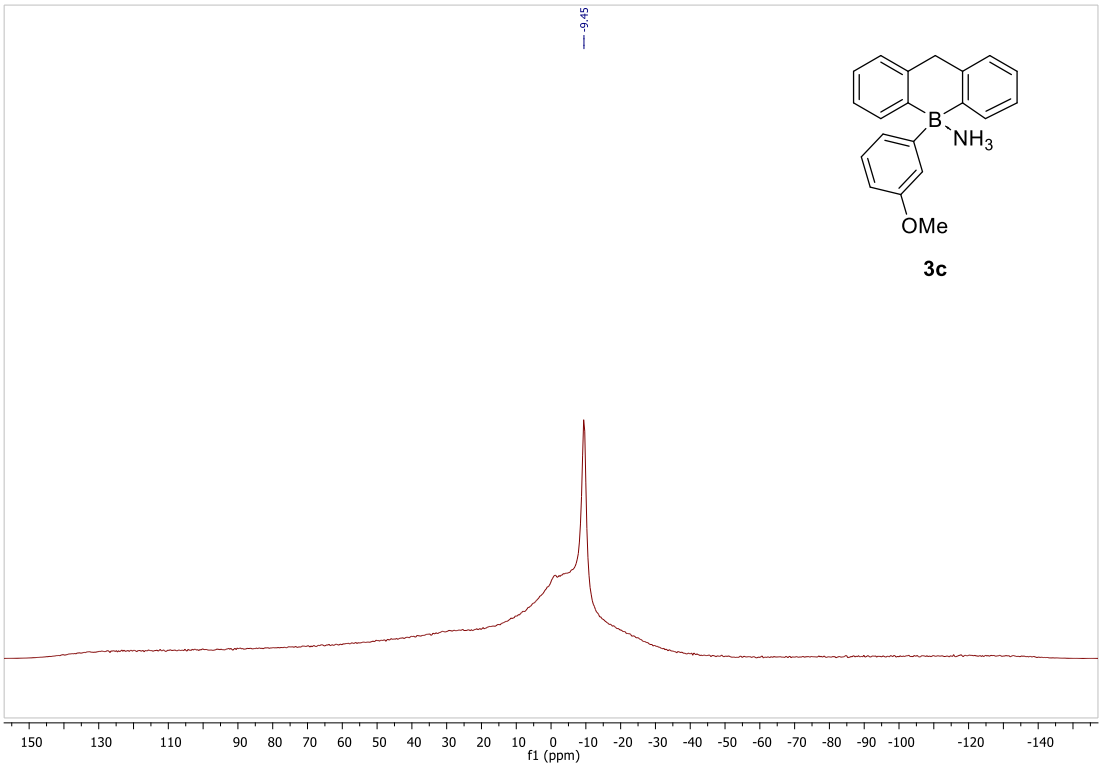


Figure S36. ^{11}B NMR (128 MHz) spectrum of **3c** in CD_3OD.

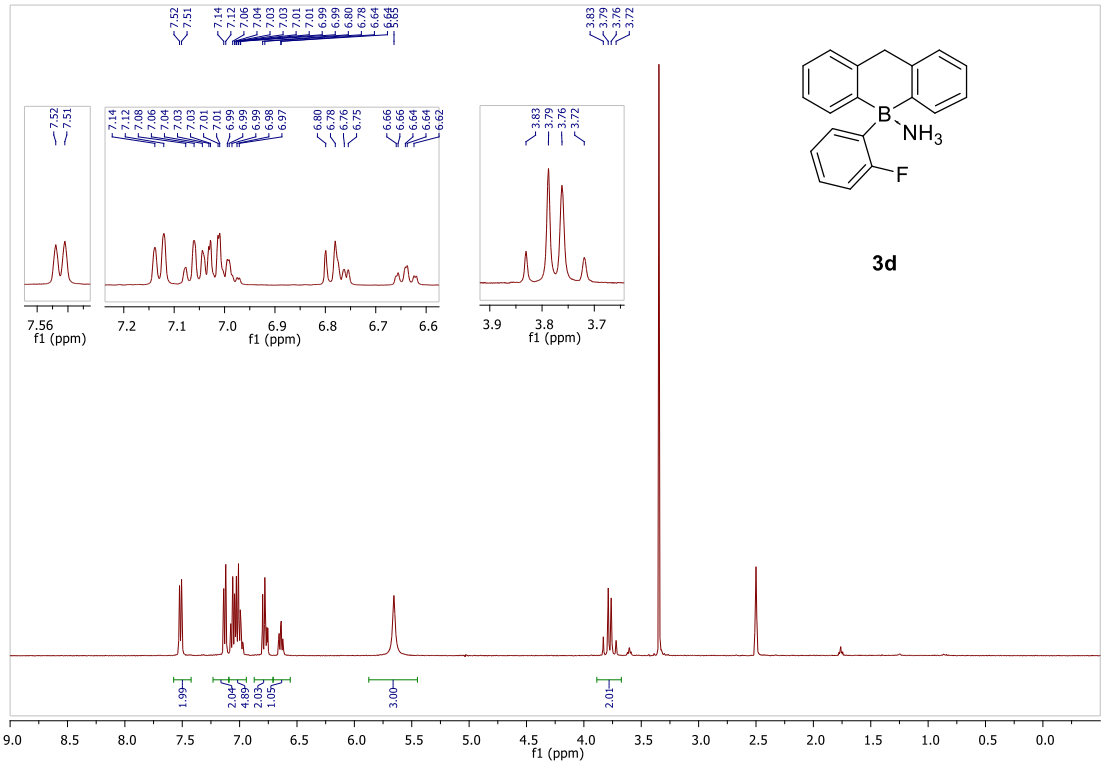


Figure S37. ^{1}H NMR (400 MHz) spectrum of **3d** in DMSO-d_6.

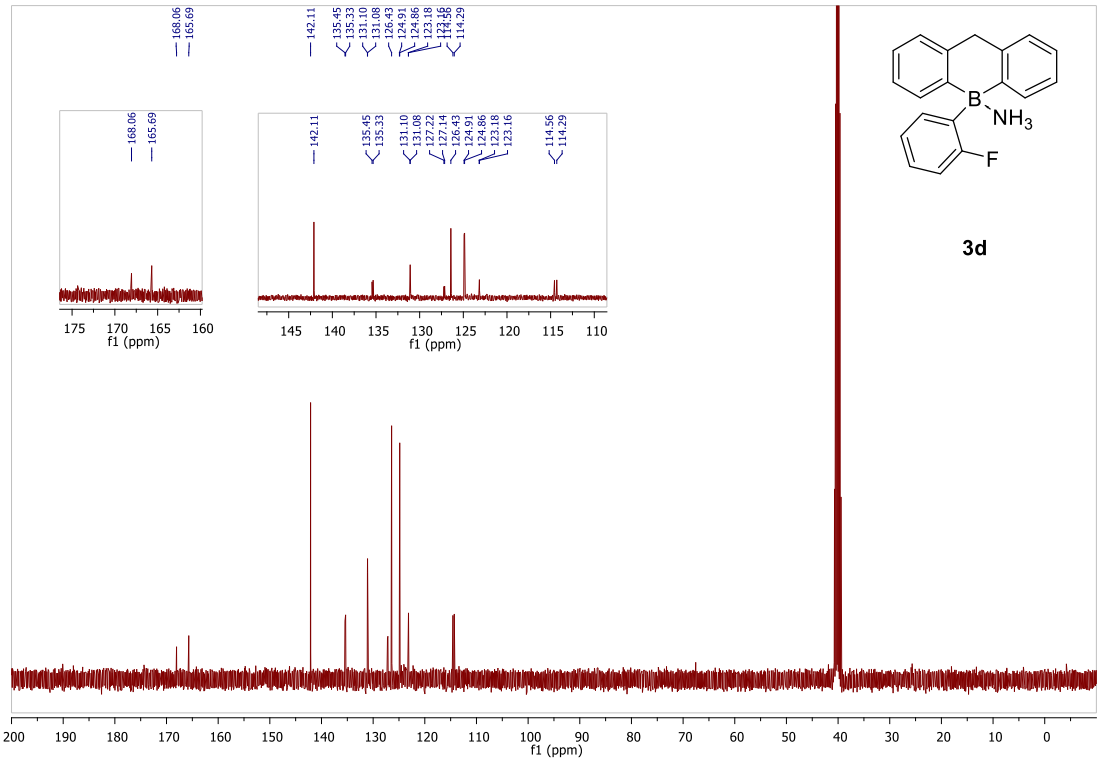


Figure S38. ^{13}C NMR (101 MHz) spectrum of **3d** in DMSO-d_6.

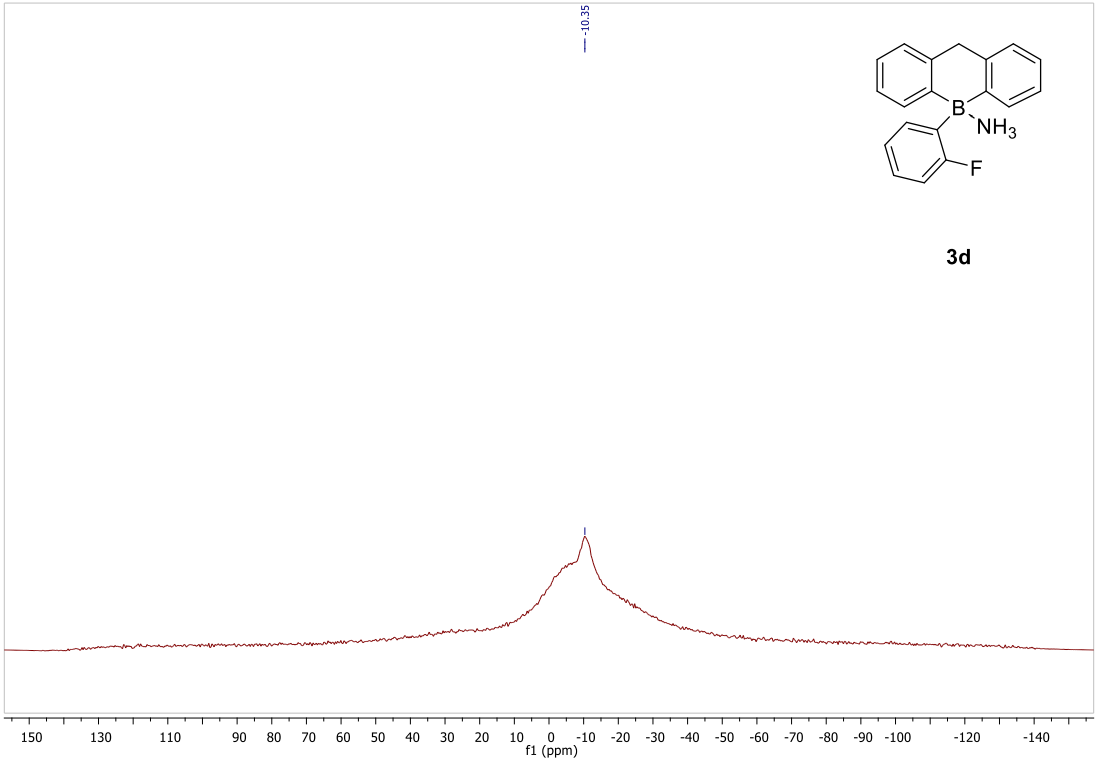


Figure S39. ^{11}B NMR (128 MHz) spectrum of **3d** in DMSO-d_6.

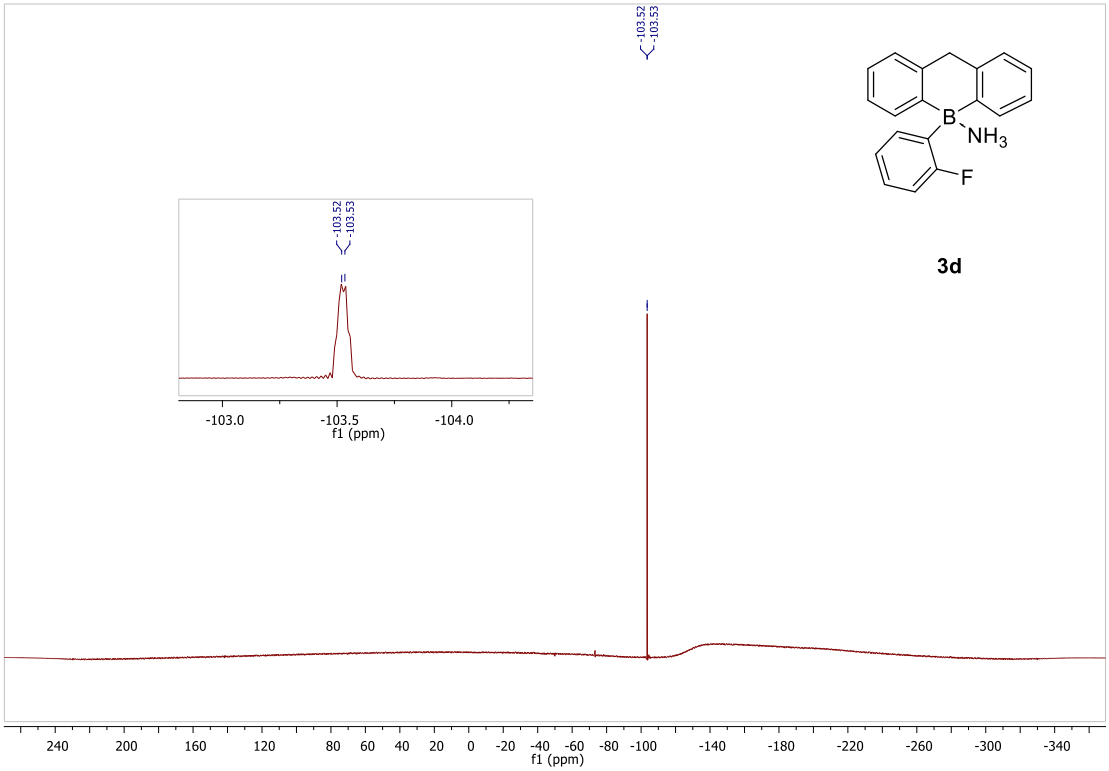


Figure S40. ^{19}F NMR (376 MHz) spectrum of **3d** in DMSO-d_6.

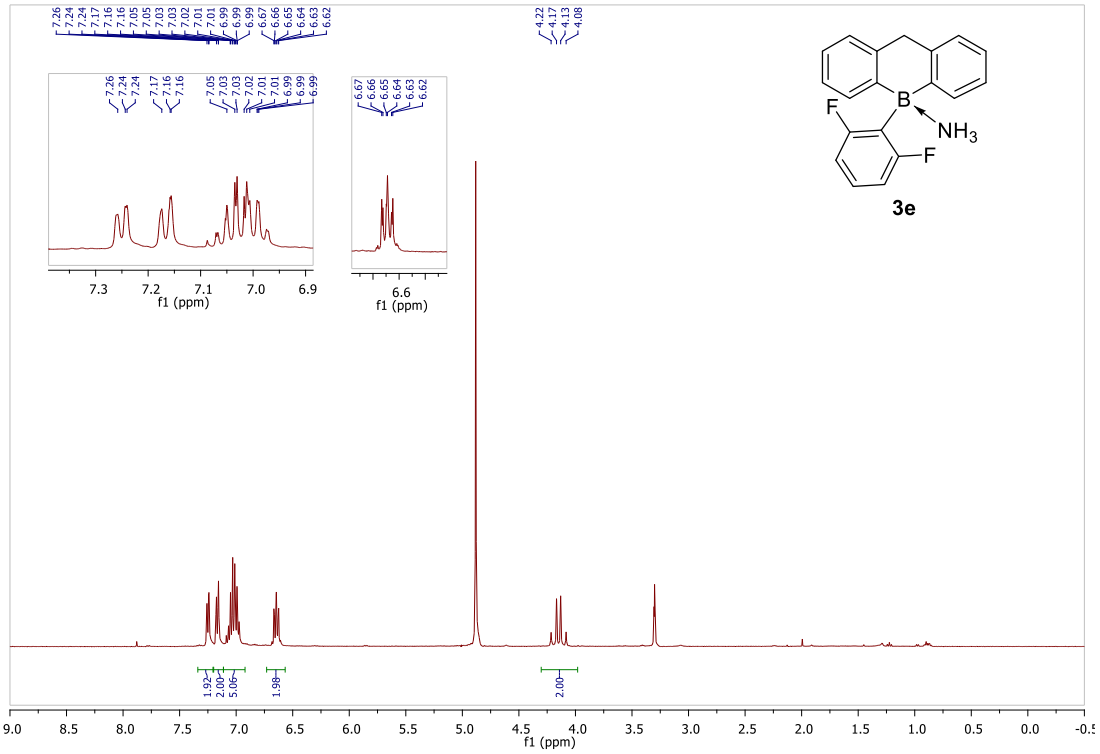


Figure S41. ^{1}H NMR (400 MHz) spectrum of **3e** in CD_3OD.

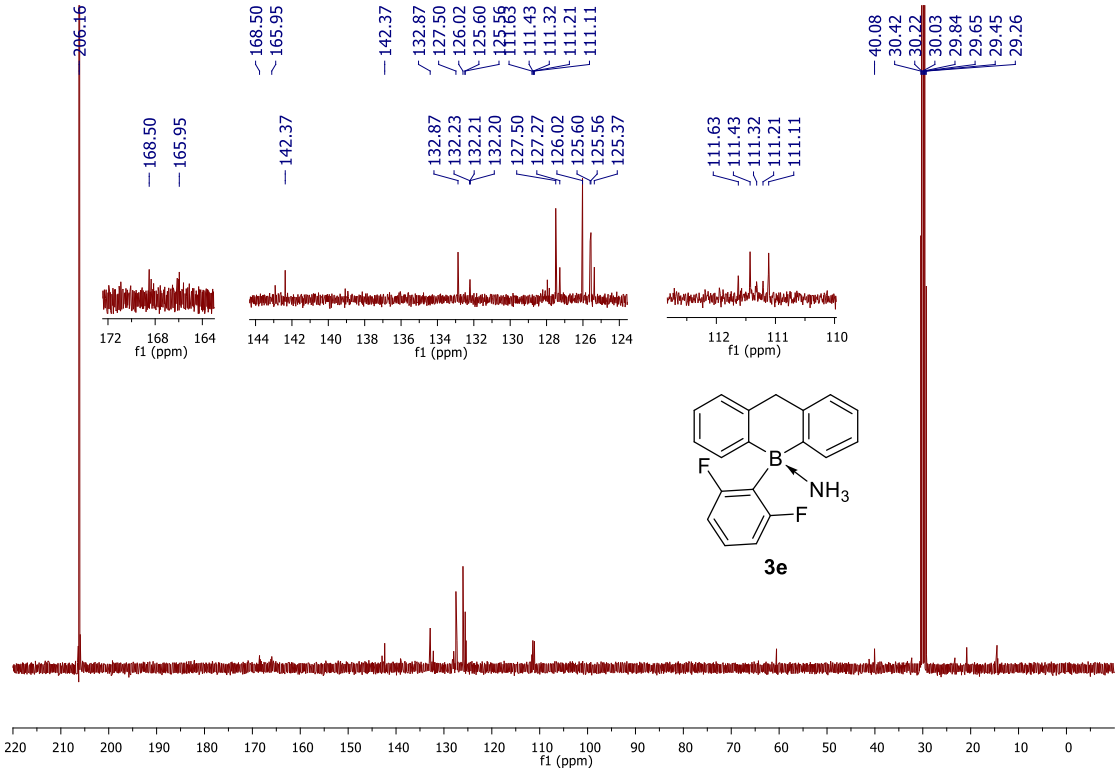


Figure S42. ^{13}C NMR (101 MHz) spectrum of **3e** in $(CD_3)_2CO$.

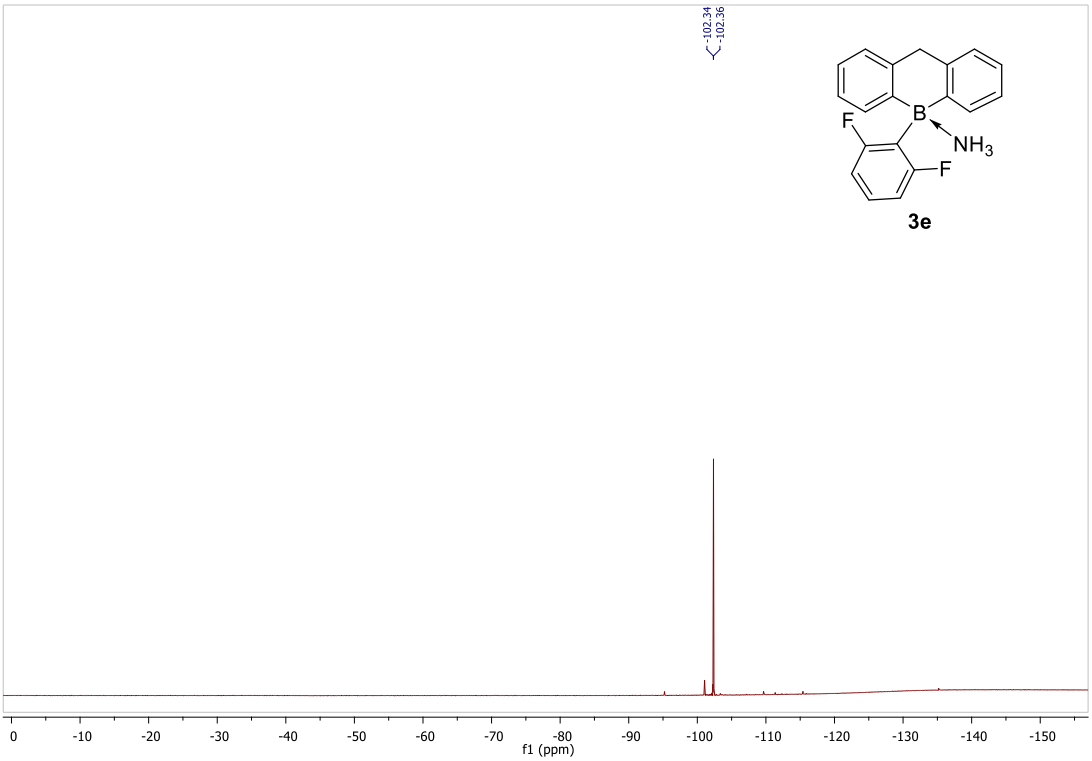


Figure S43. ^{19}F NMR (376 MHz) spectrum of **3e** in CD_3OD.

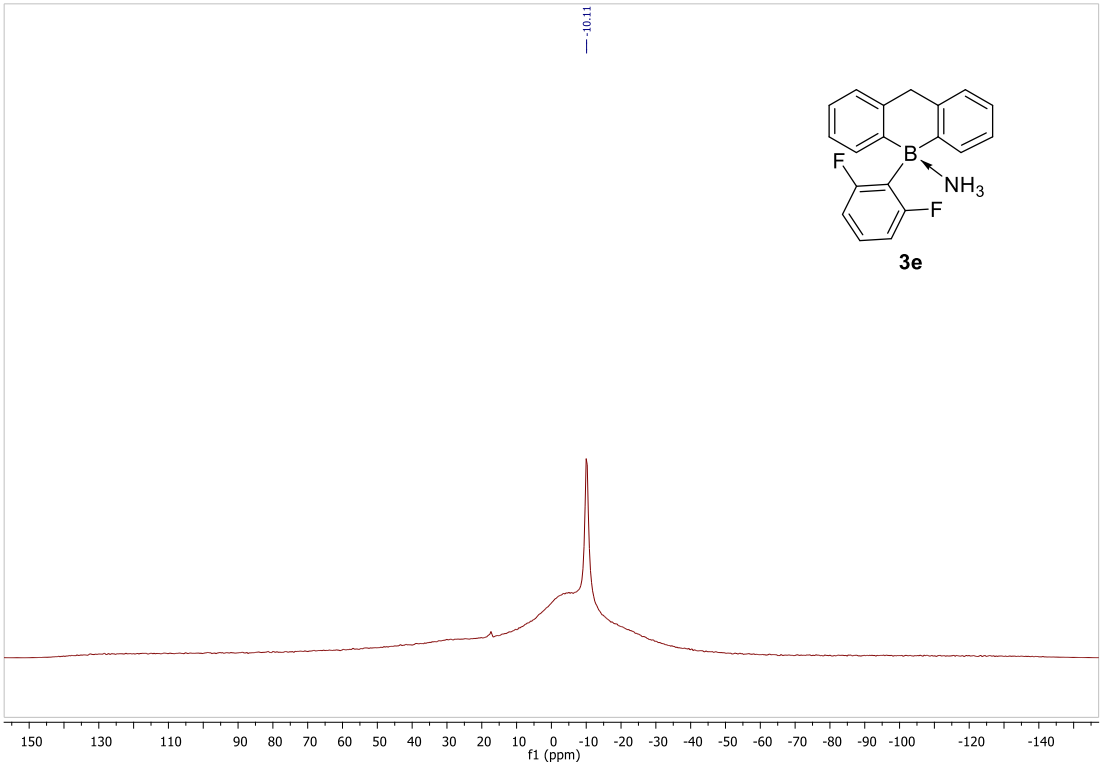


Figure S44. ^{11}B NMR (128 MHz) spectrum of **3e** in CD_3OD.

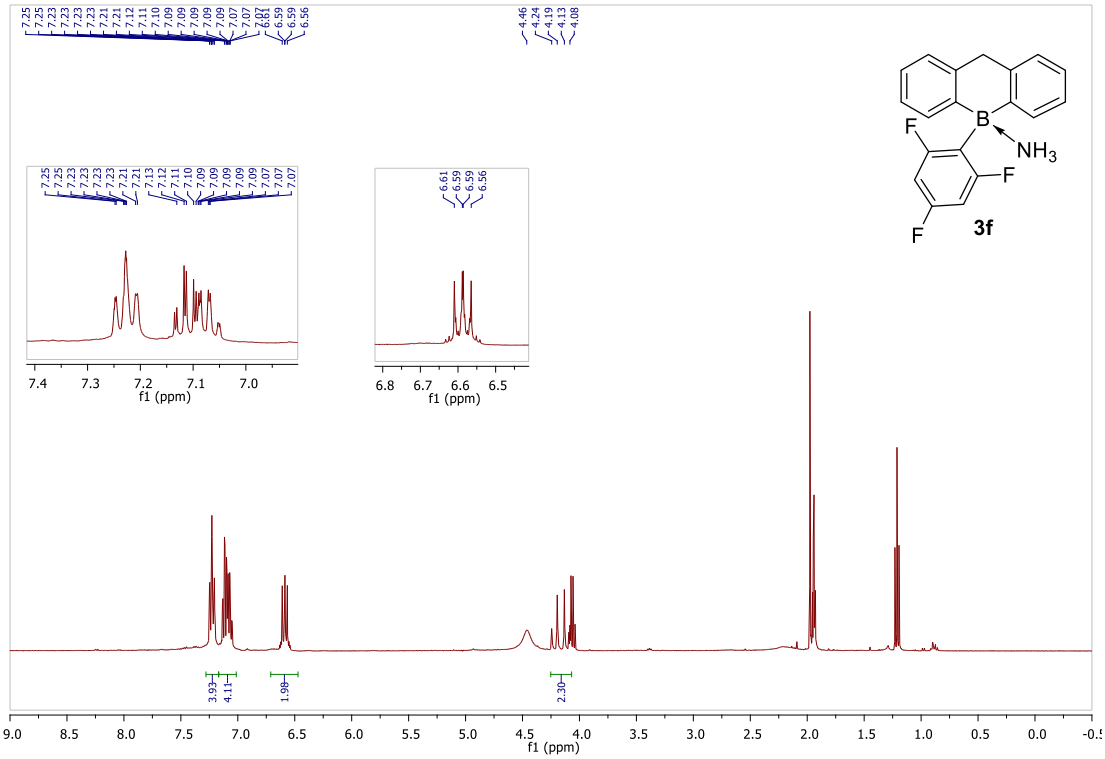


Figure S45. ^{1}H NMR (400 MHz) spectrum of **3f** in CD_3CN.

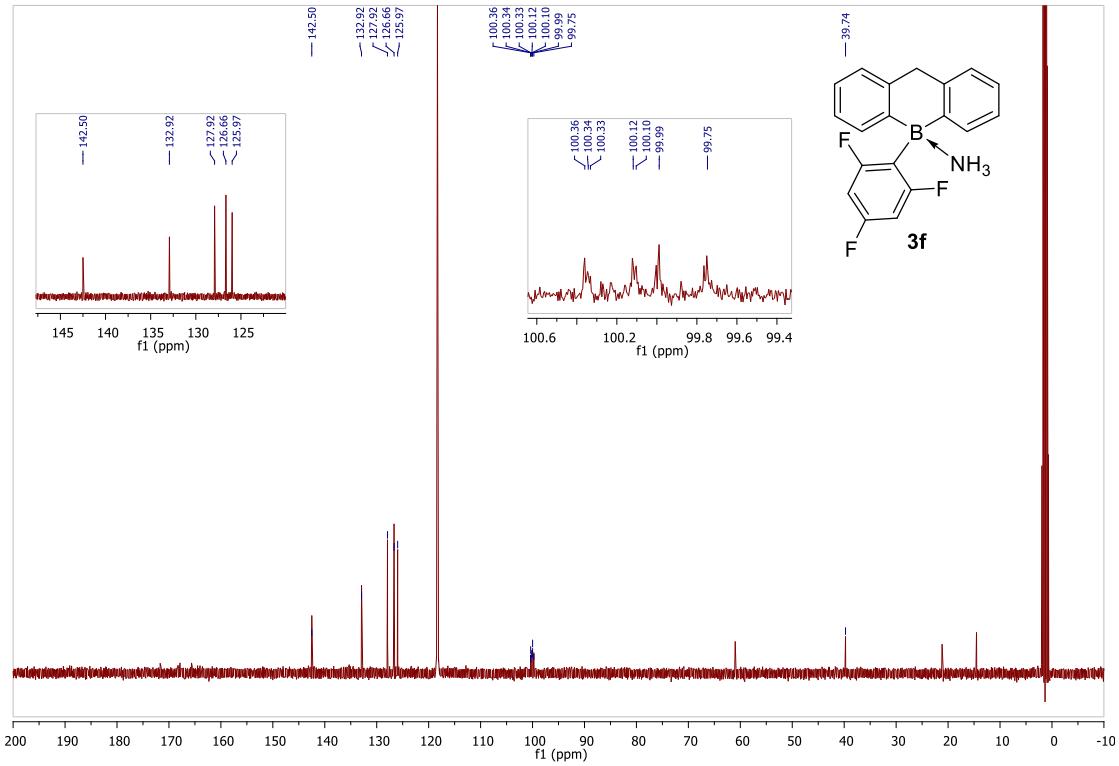


Figure S46. ^{13}C NMR (101 MHz) spectrum of **3f** in CD_3CN.

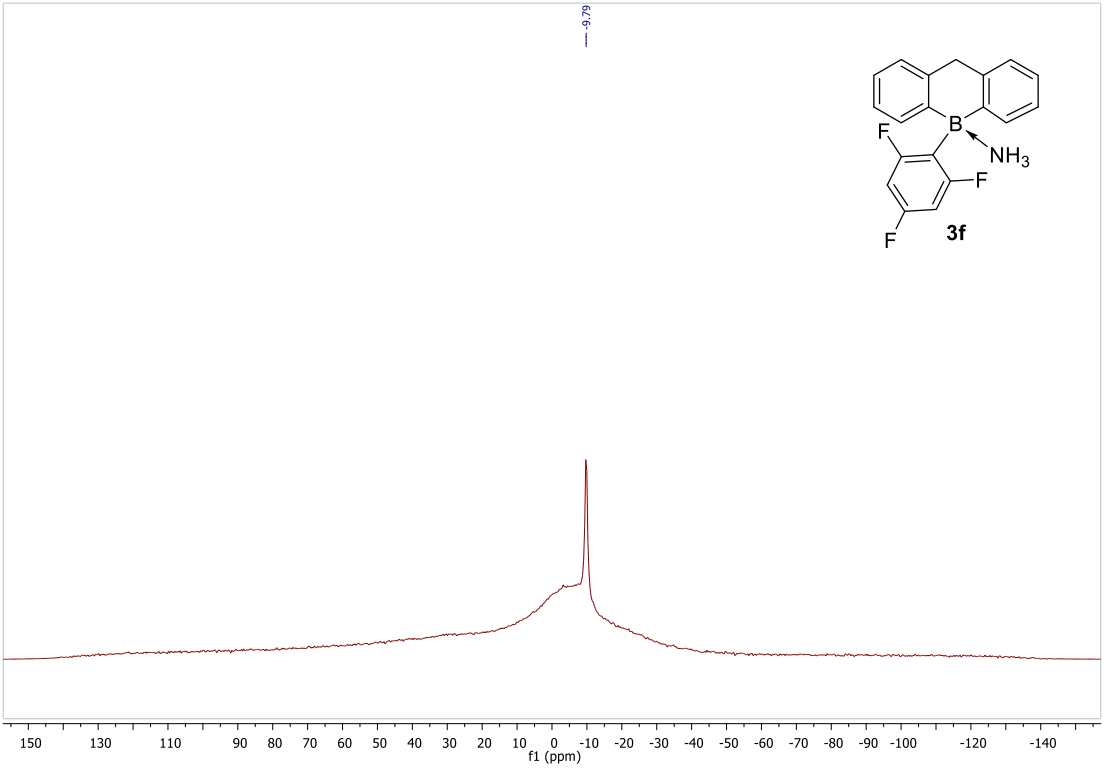


Figure S47. ^{11}B NMR (128 MHz) spectrum of **3f** in CD_3CN.

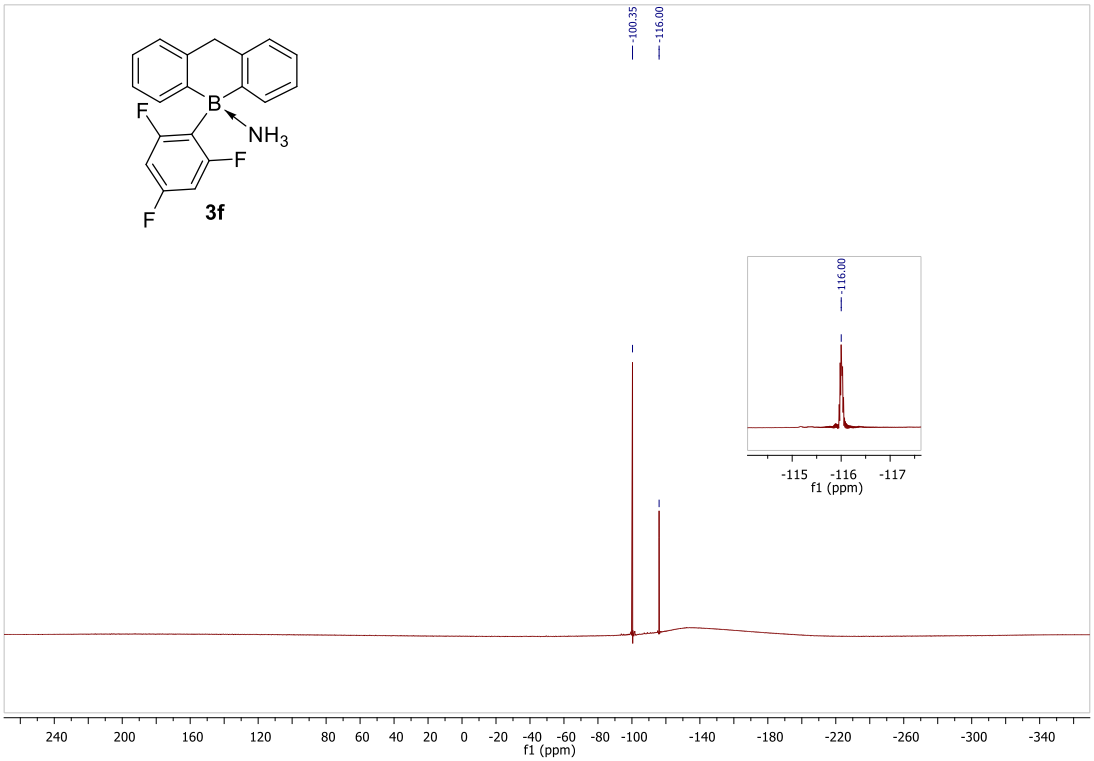


Figure S48. ^{19}F NMR (376 MHz) spectrum of **3f** in CD_3CN.

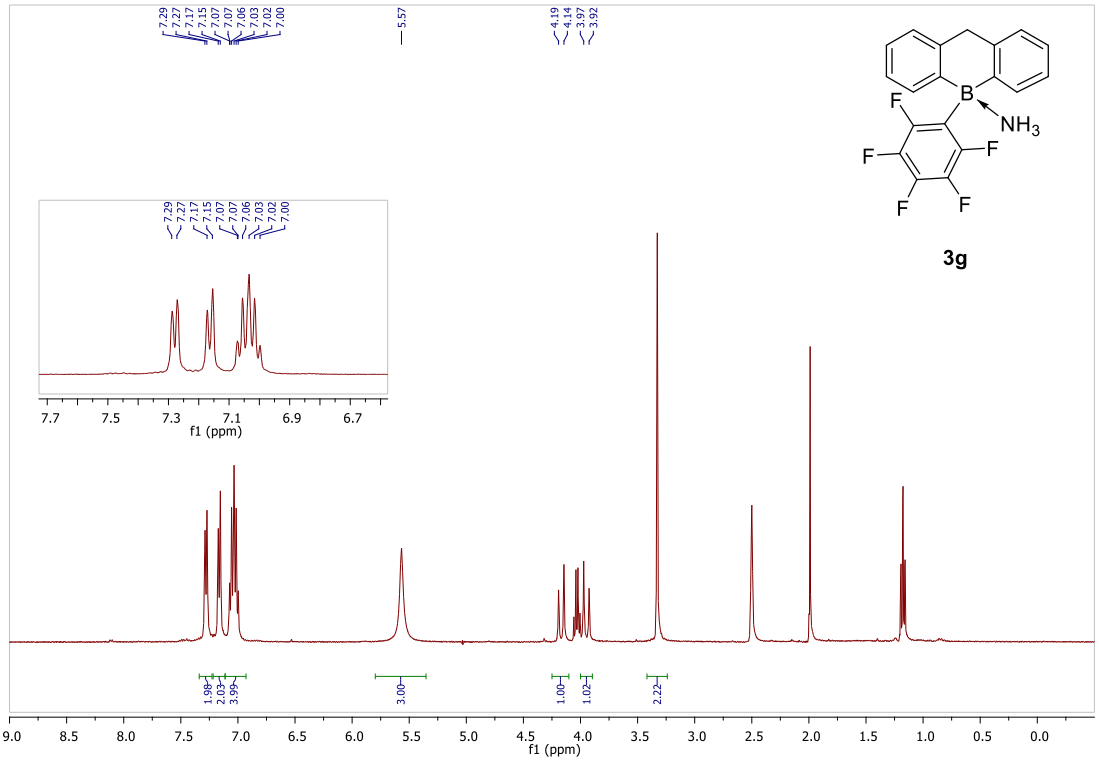


Figure S49. ^{1}H NMR (400 MHz) spectrum of **3g** in DMSO-d_6.

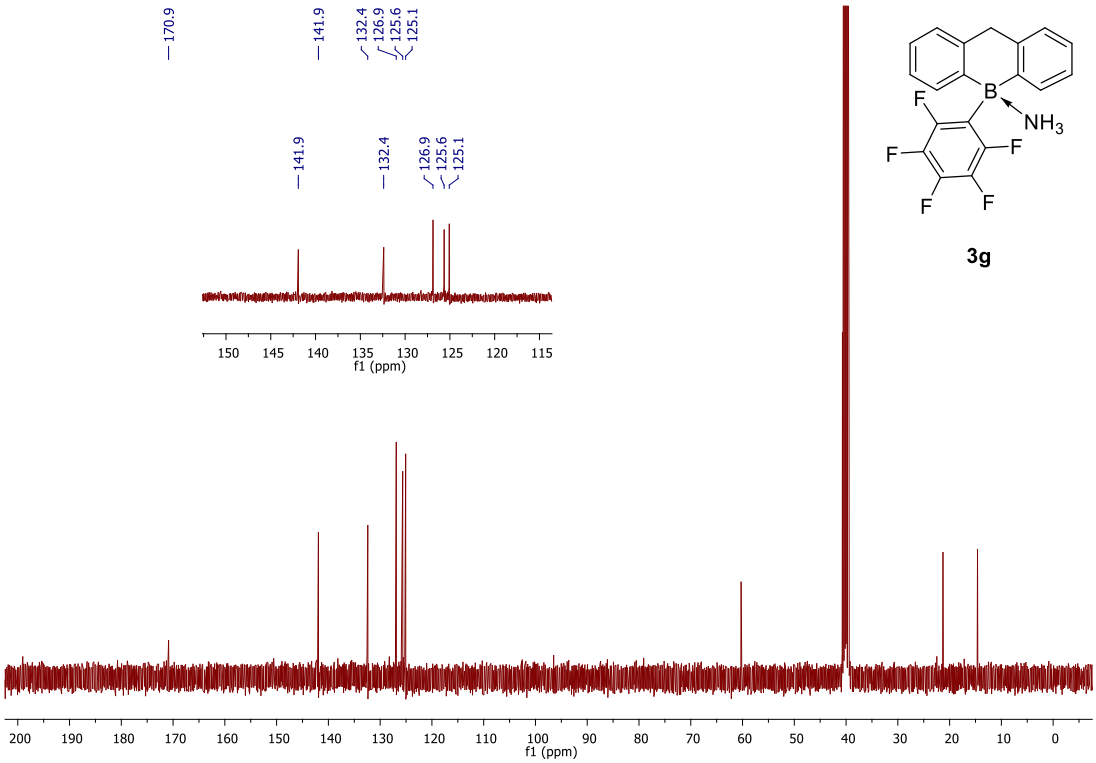


Figure S50. ^{13}C NMR (101 MHz) spectrum of **3g** in DMSO-d_6.

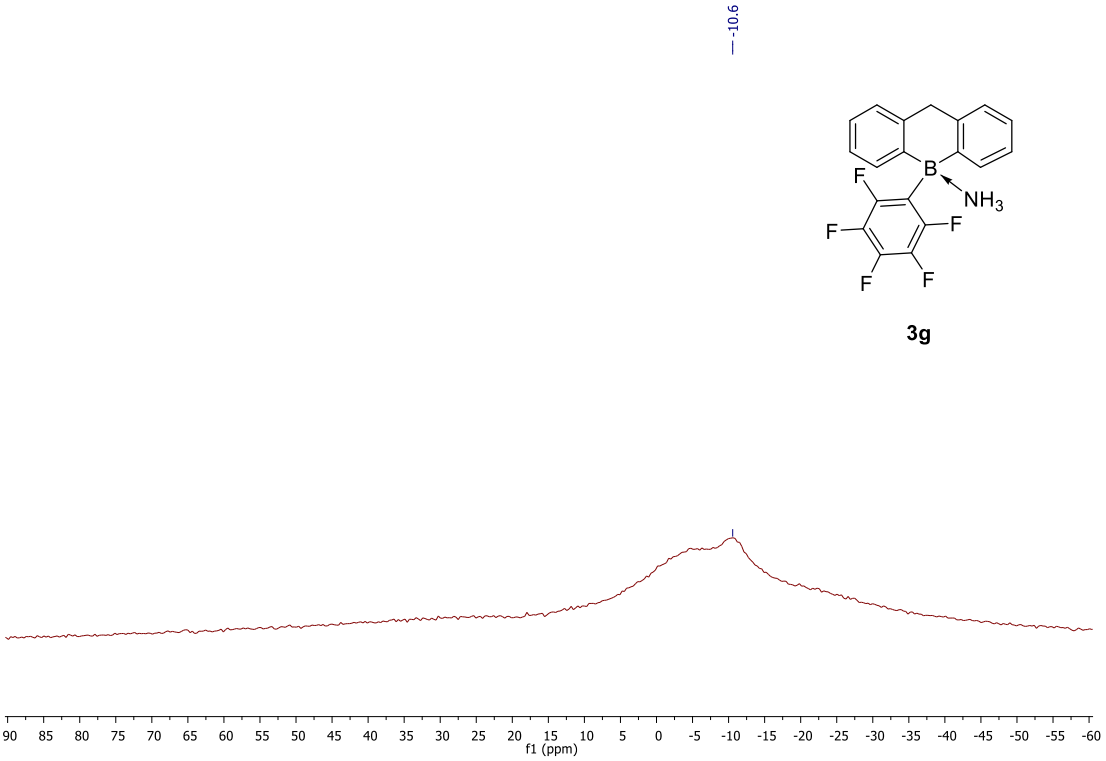


Figure S51. ^{11}B NMR (128 MHz) spectrum of **3g** in DMSO-d_6.

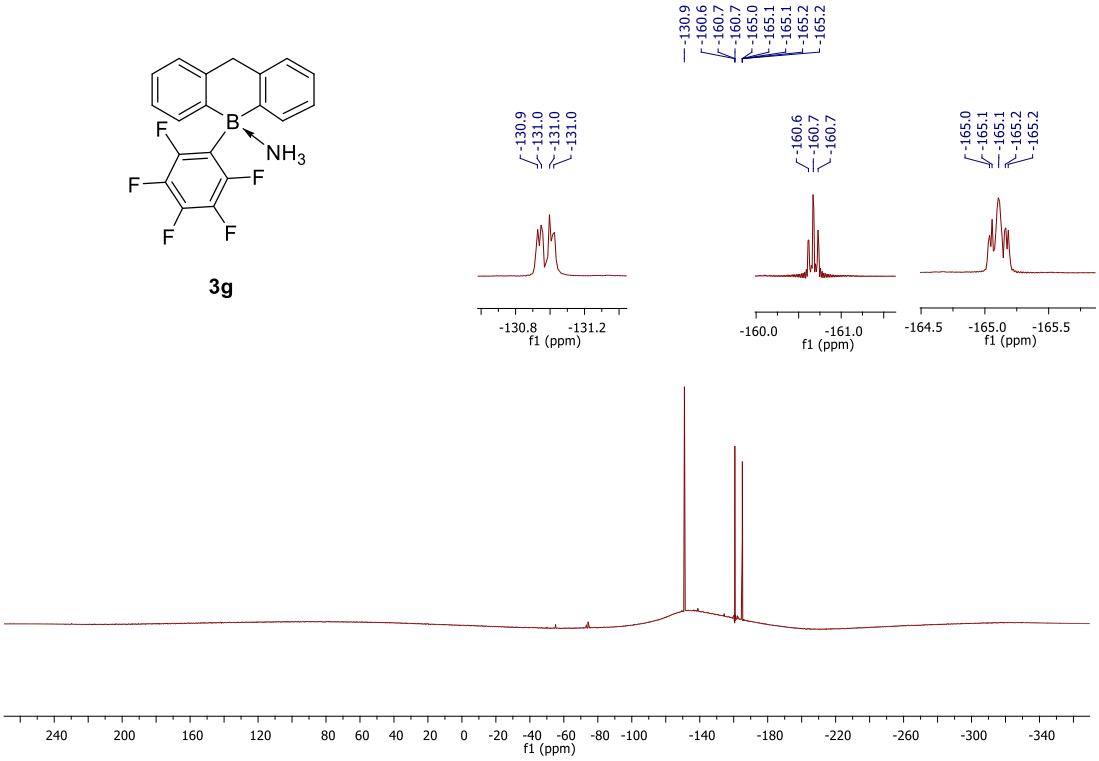


Figure S52. ^{19}F NMR (376 MHz) spectrum of **3g** in DMSO-d_6.

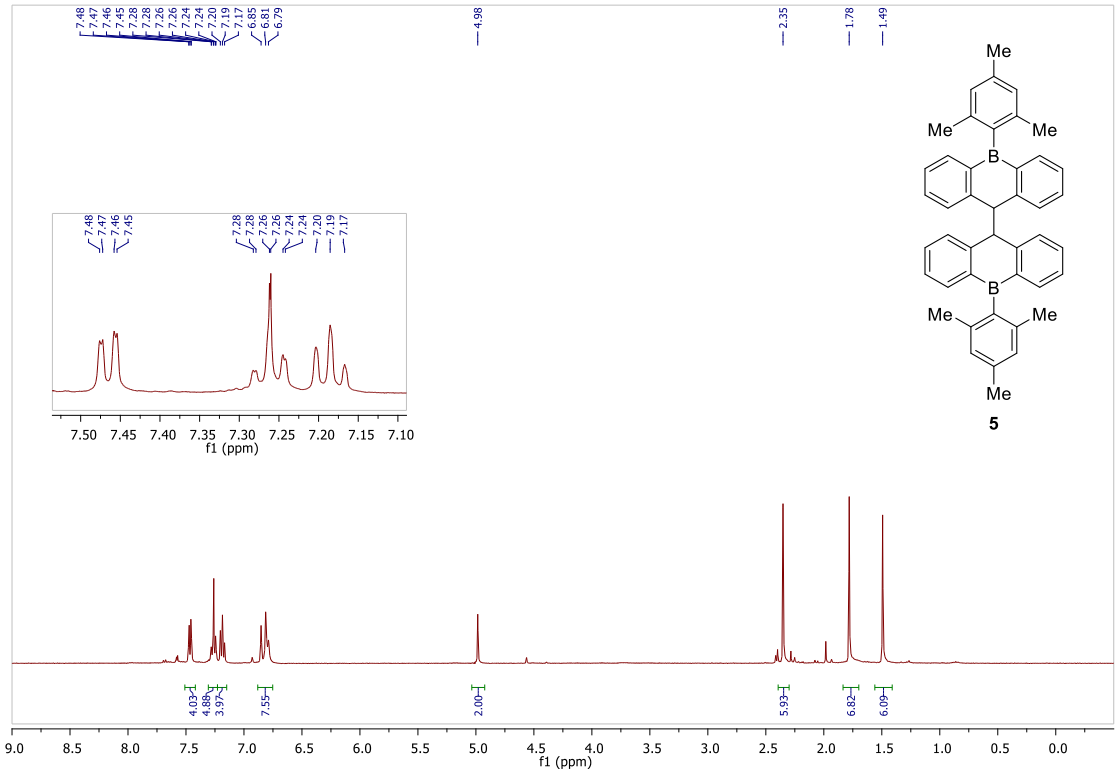


Figure S53. ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$.

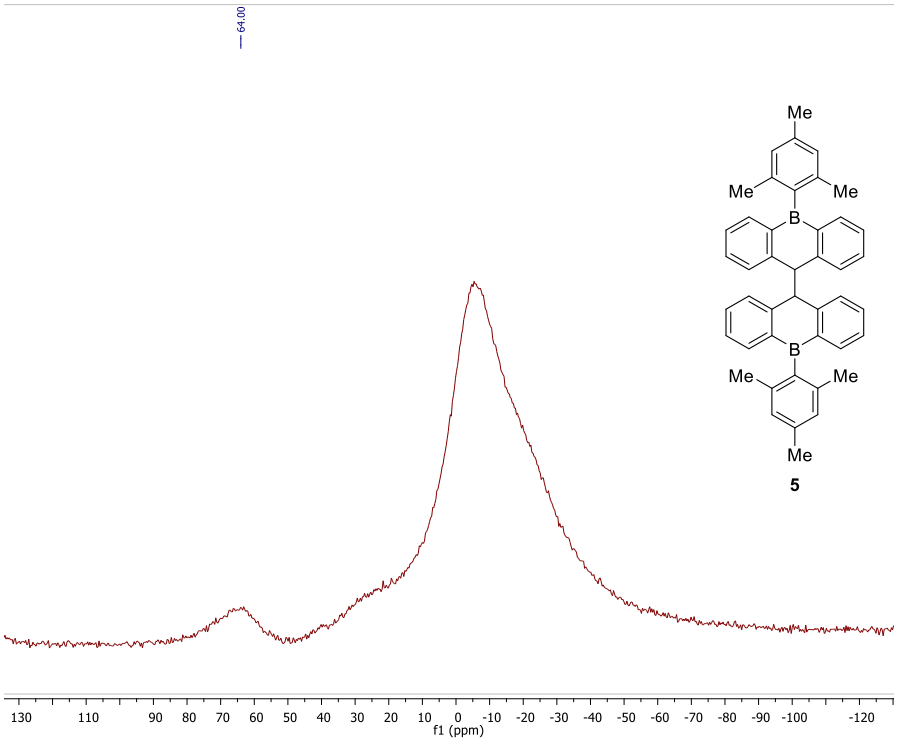


Figure S54. ^{11}B NMR (128 MHz) spectrum of **5** in $CDCl_3$.

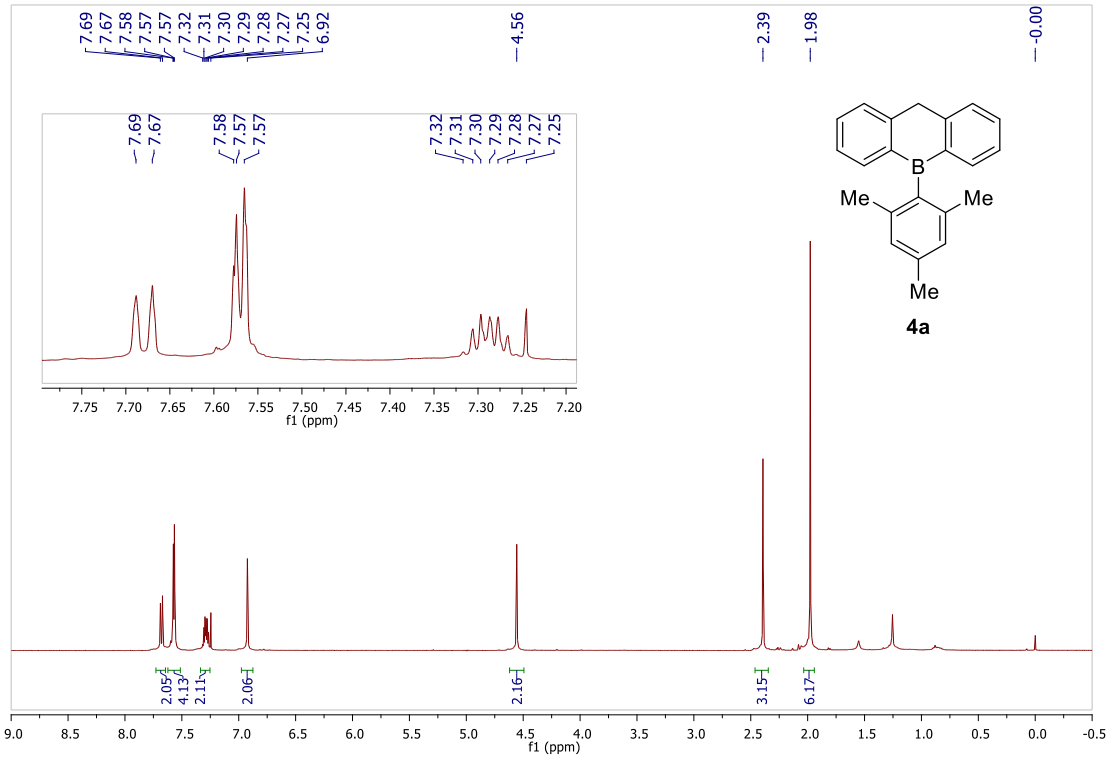


Figure S55. ^{1}H NMR (400 MHz) spectrum of **4a** in $CDCl_3$ with TMS as the internal reference.

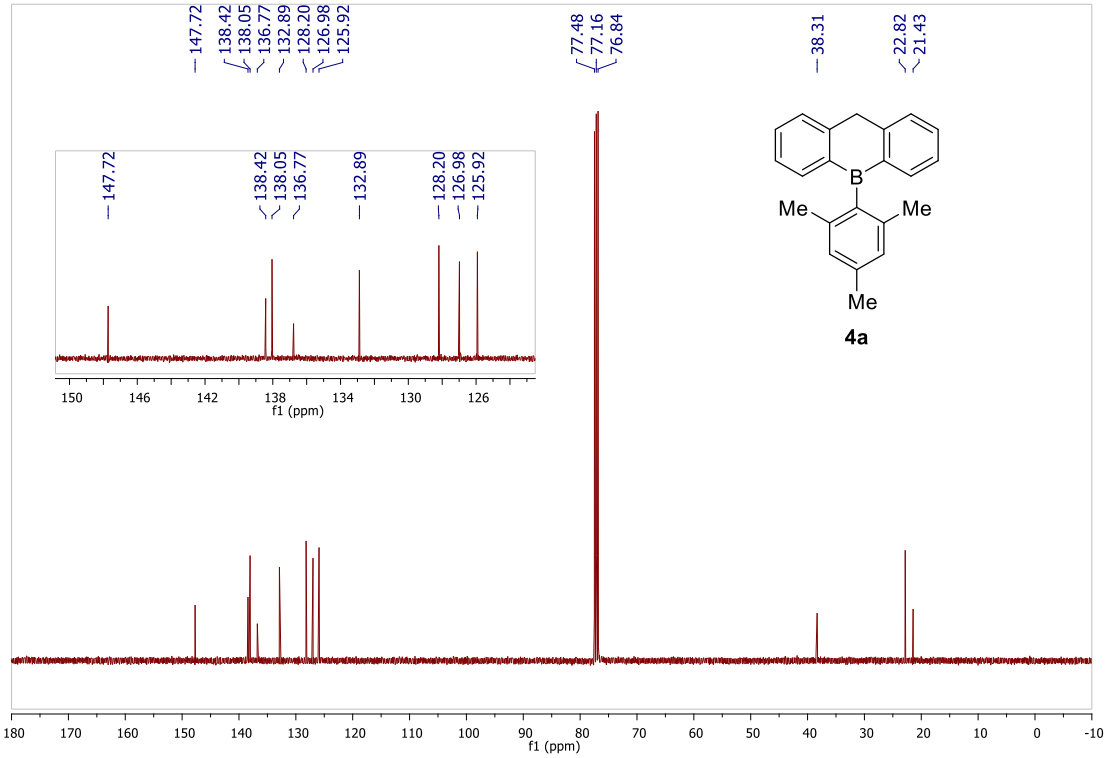


Figure S56. ^{13}C NMR (101 MHz) spectrum of **4a** in $CDCl_3$.

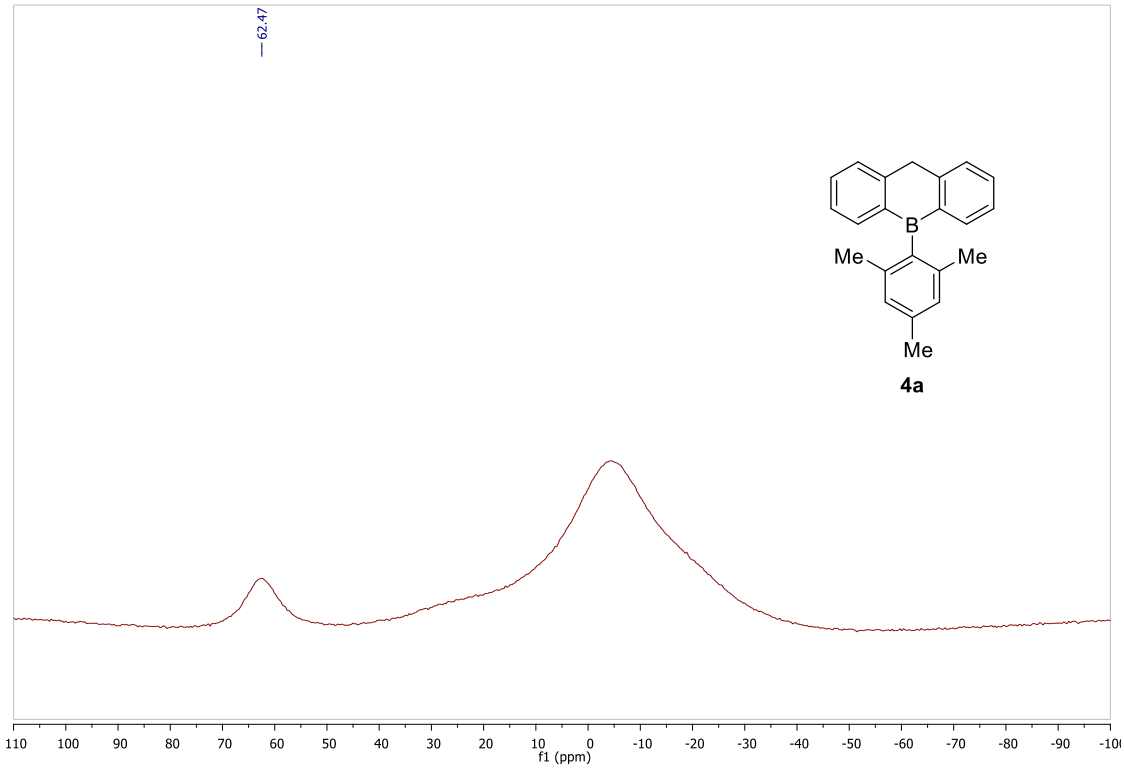


Figure S57. ^{11}B NMR (128 MHz) spectrum of **4a** in $CDCl_3$.

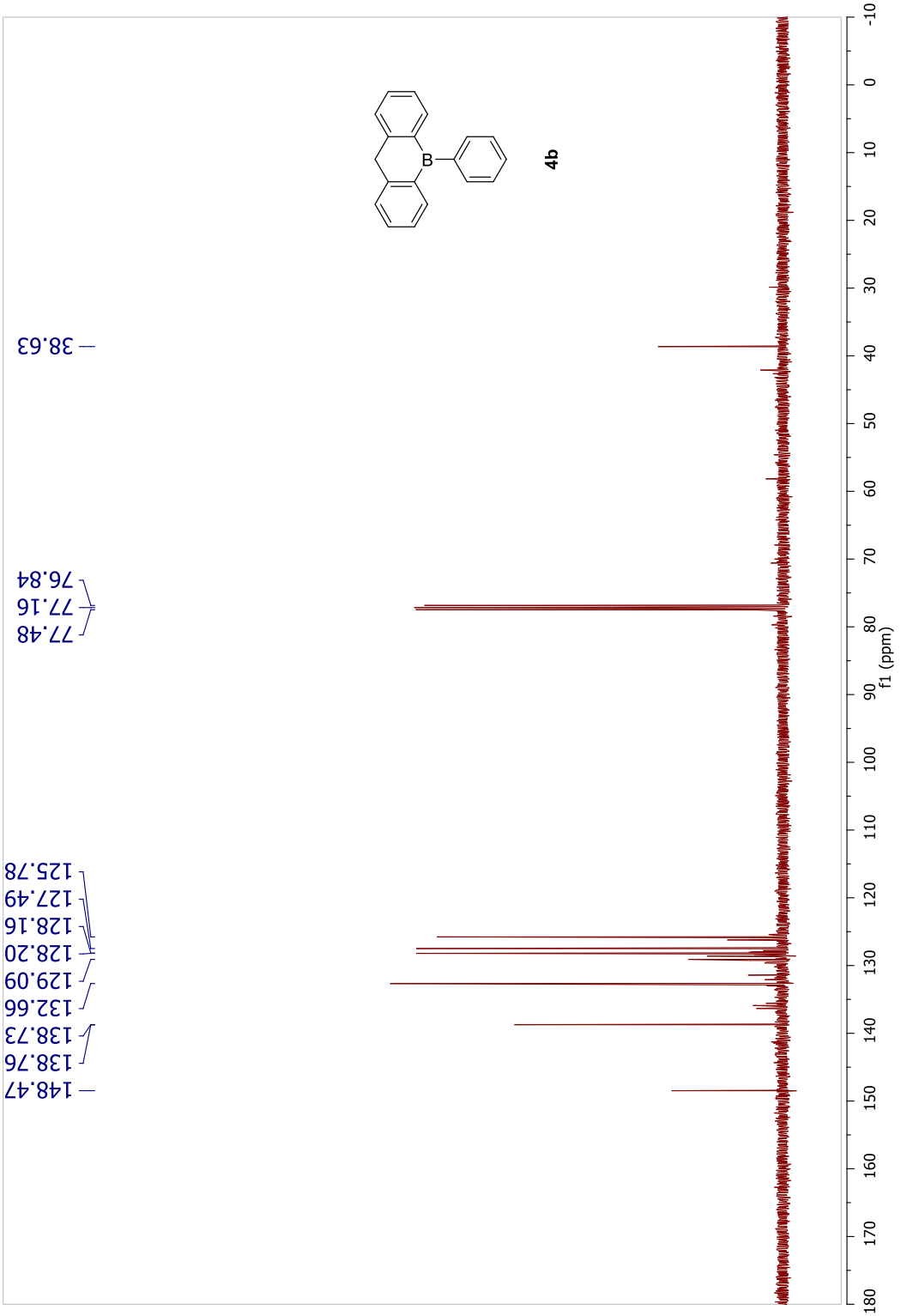


Figure S58. ^{13}C NMR (101 MHz) spectrum of **4b** in $CDCl_3$, some impurities are due to the rapid decomposition into the corresponding borinic acid.

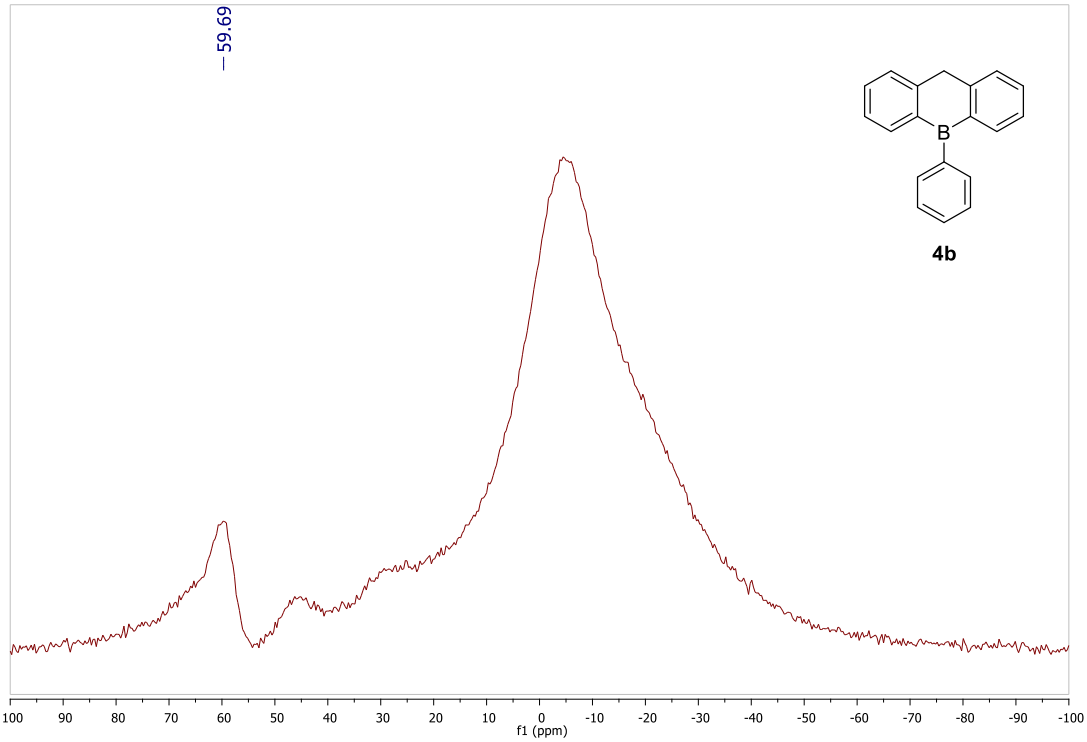


Figure S59. ^{11}B NMR (128 MHz) spectrum of **4b** in $CDCl_3$.

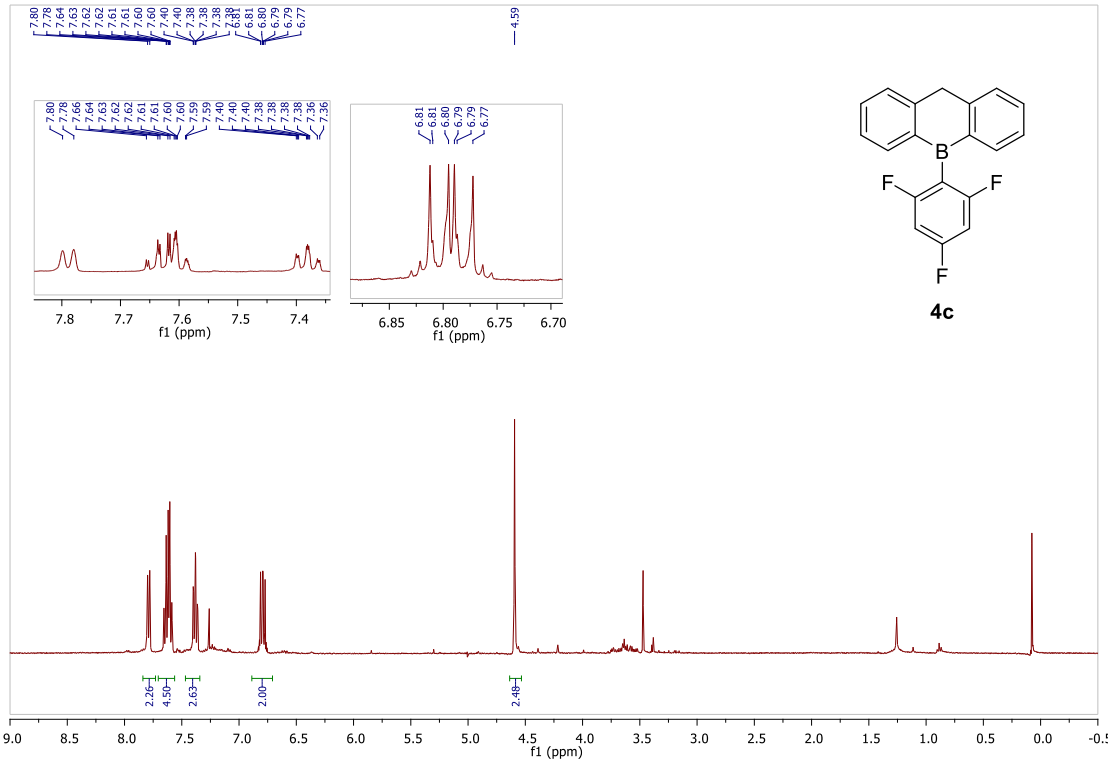


Figure S60. ^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$.

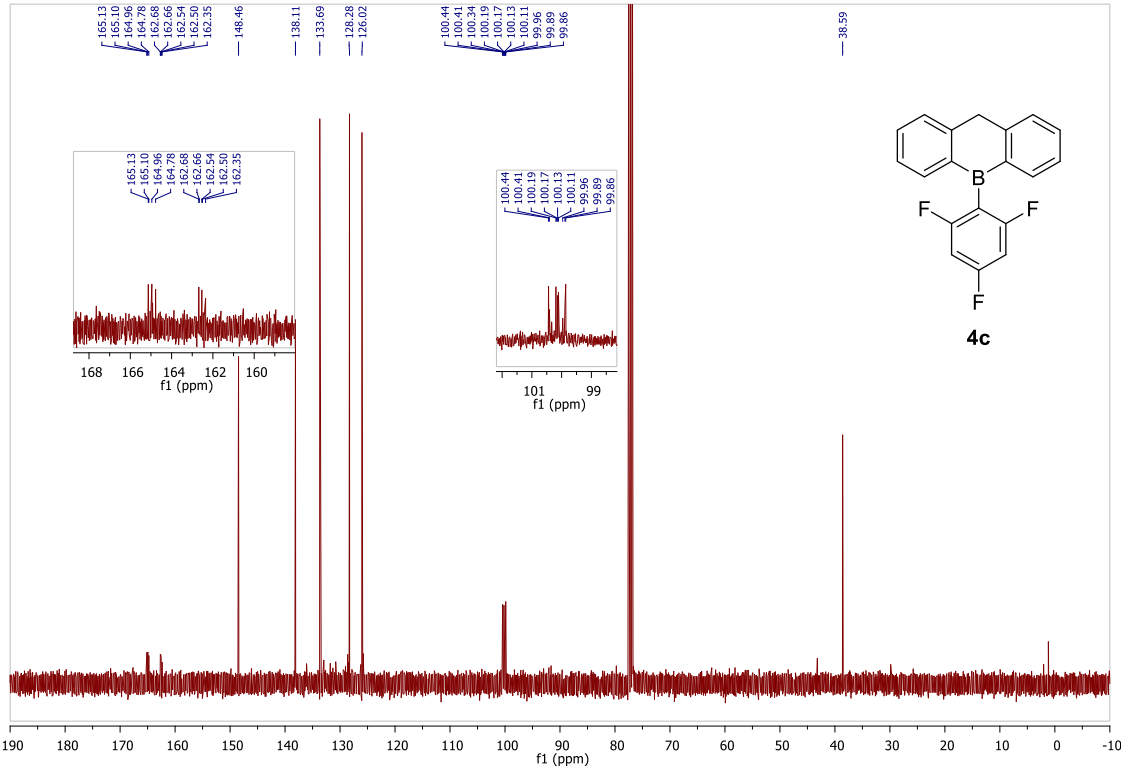


Figure S61. ^{13}C NMR (101 MHz) spectrum of **4c** in $CDCl_3$.

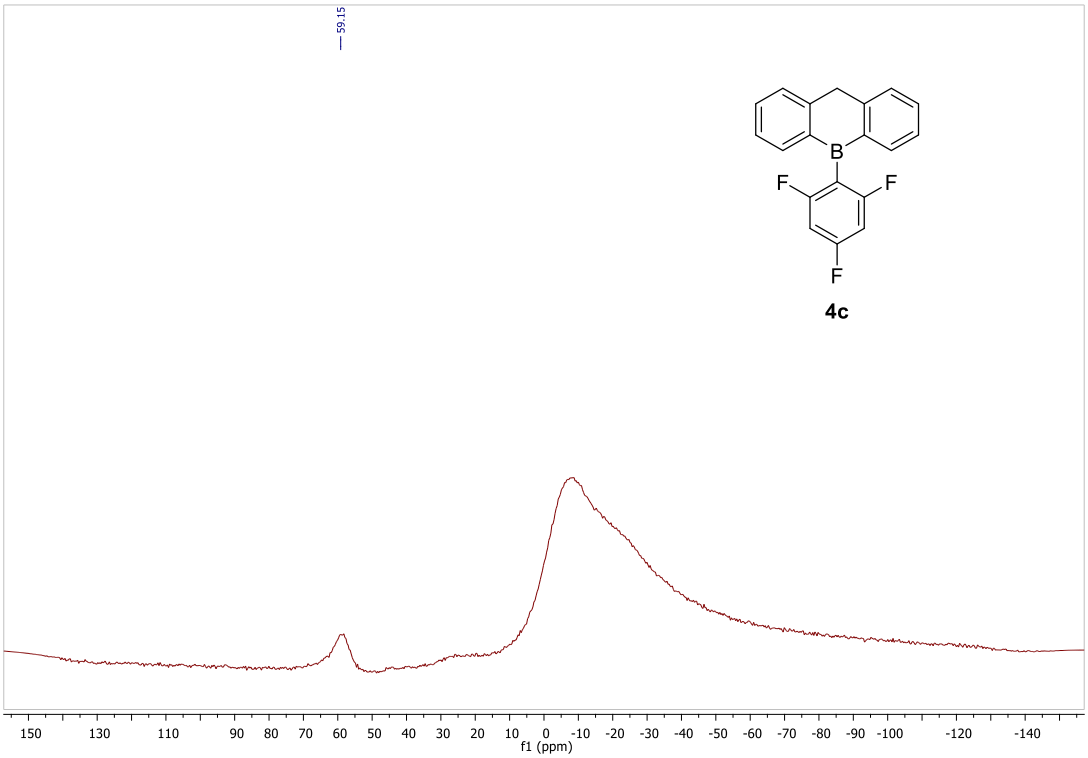


Figure S62. ^{11}B NMR (128 MHz) spectrum of **4c** in $CDCl_3$.

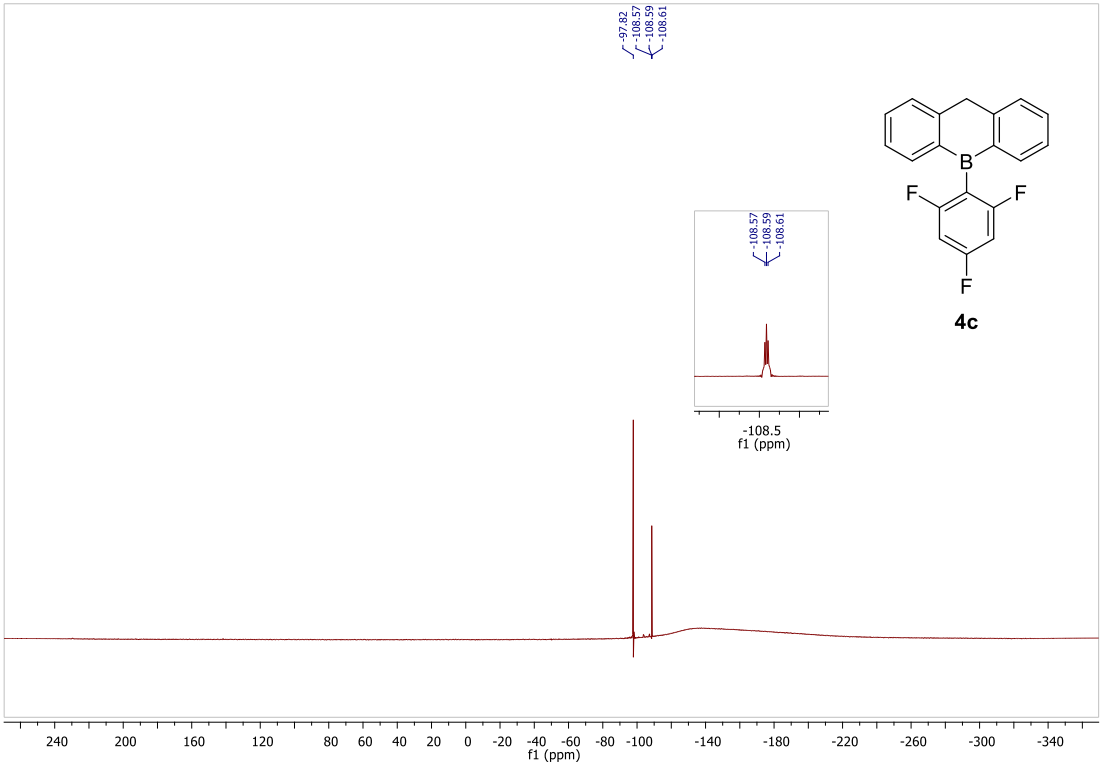


Figure S63. ^{19}F NMR (376 MHz) spectrum of **4c** in $CDCl_3$.

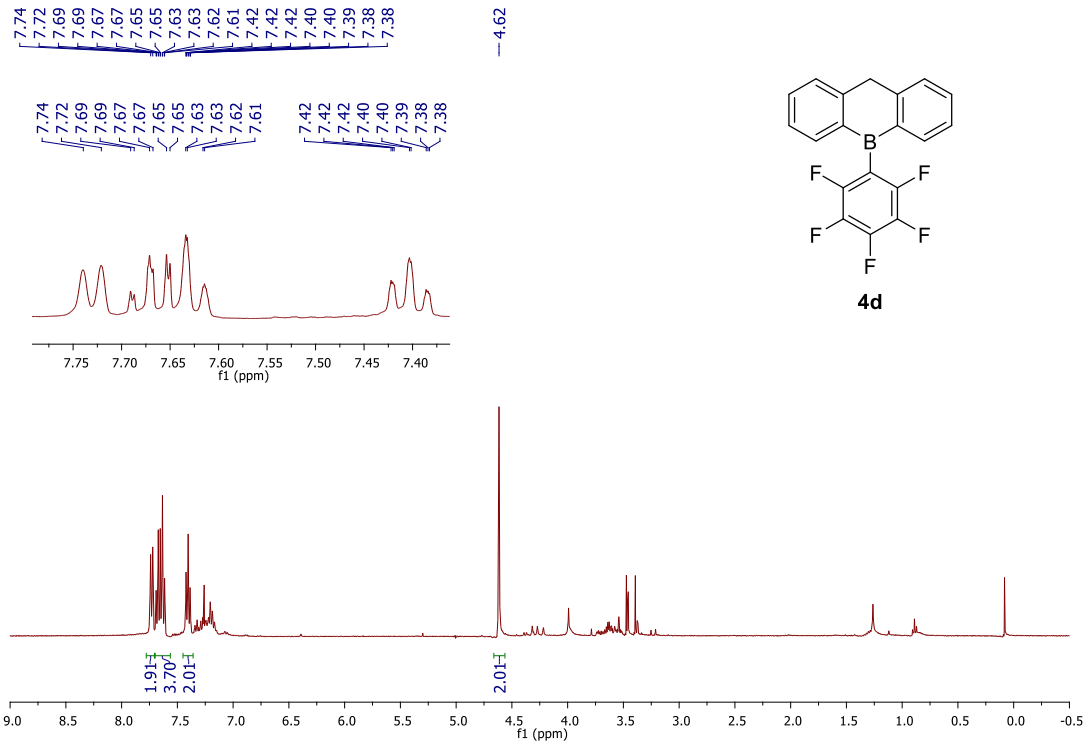


Figure S64. ^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$.

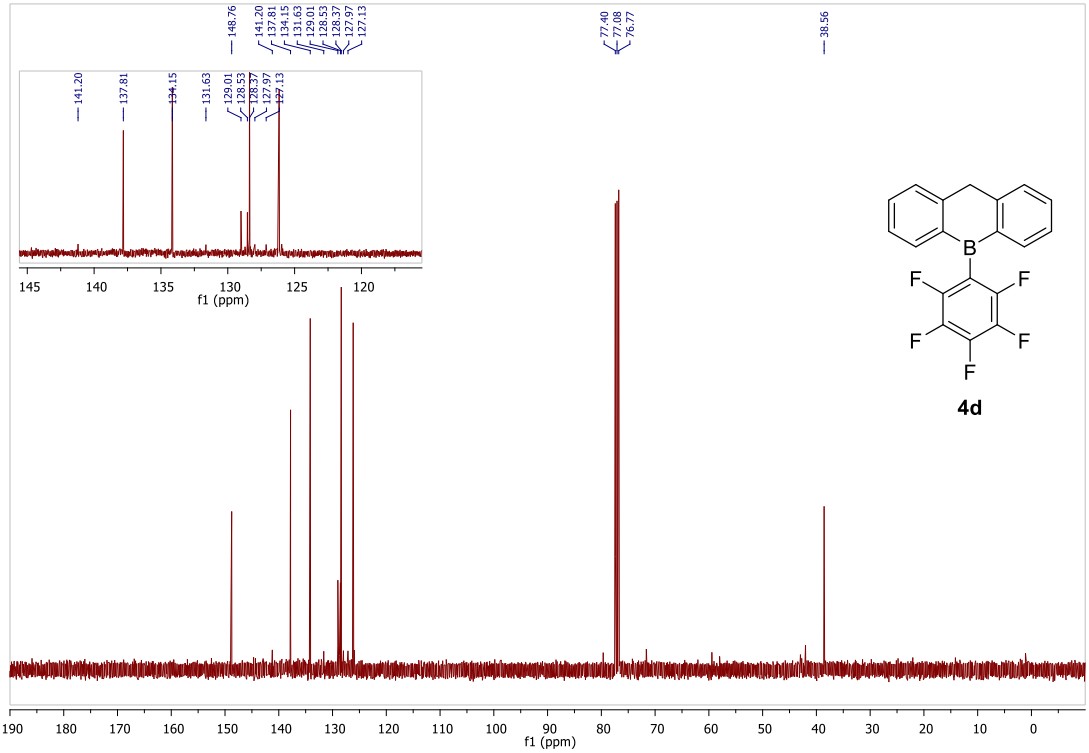


Figure S65. ^{13}C NMR (101 MHz) spectrum of **4d** in $CDCl_3$.

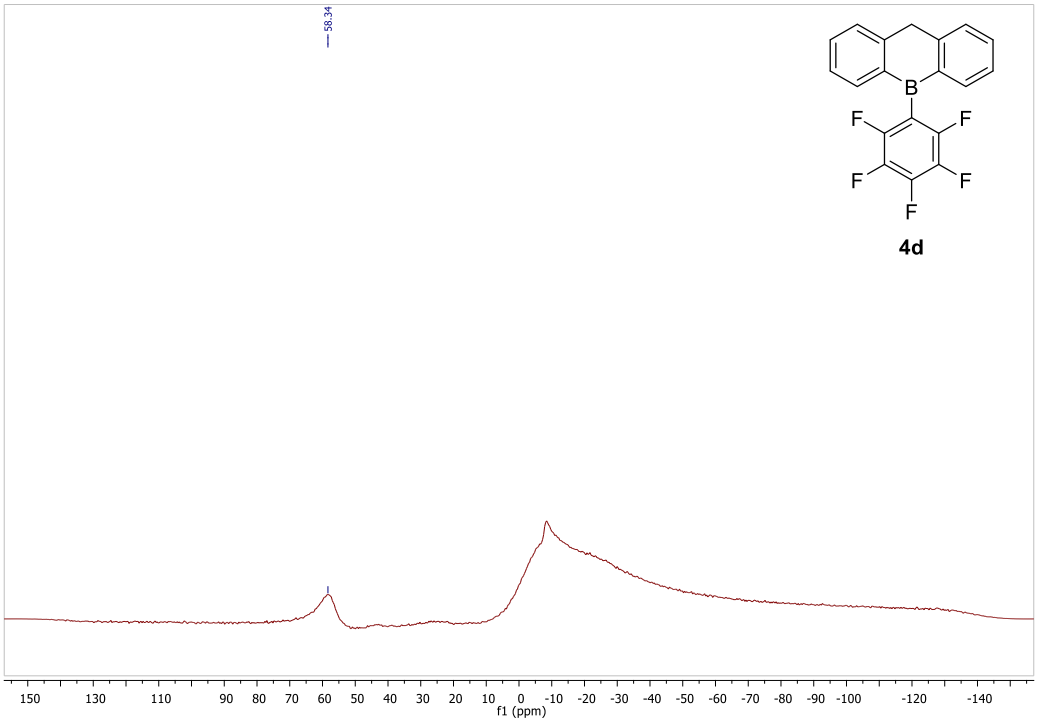


Figure S66. ^{11}B NMR (128 MHz) spectrum of **4d** in $CDCl_3$.

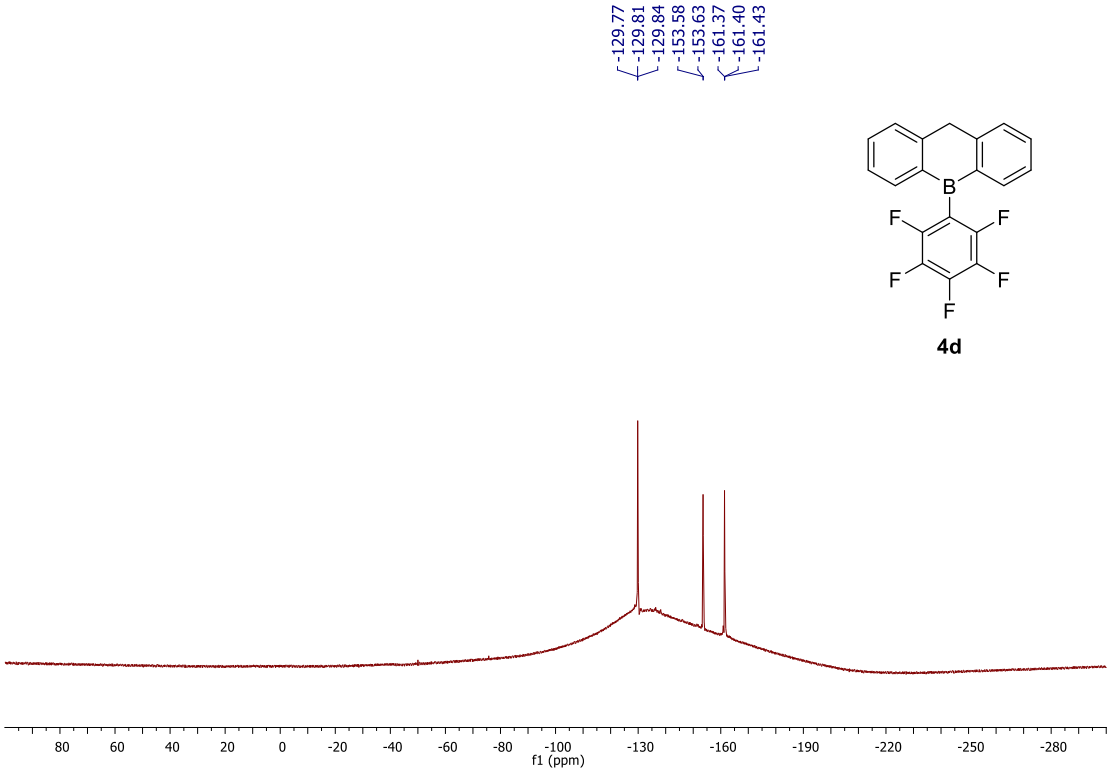


Figure S67. ^{19}F NMR (376 MHz) spectrum of **4d** in $CDCl_3$.

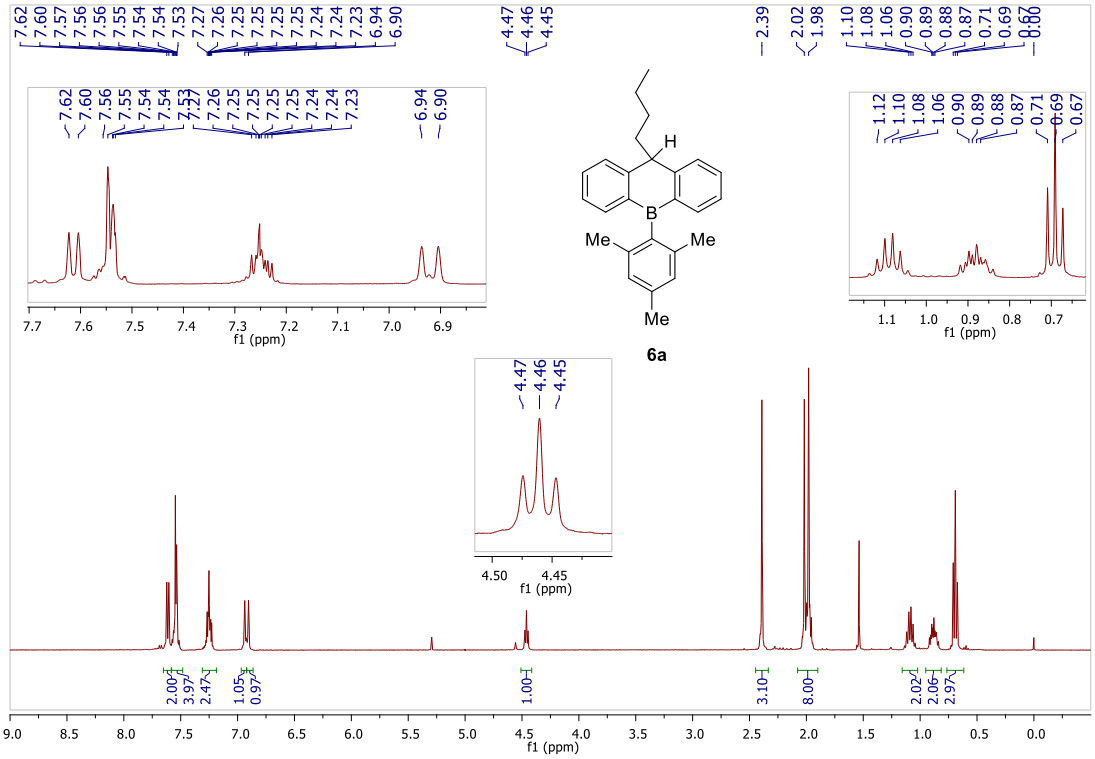


Figure S68. ^{1}H NMR (400 MHz) spectrum of **6a** in $CDCl_3$ with TMS as the internal reference.

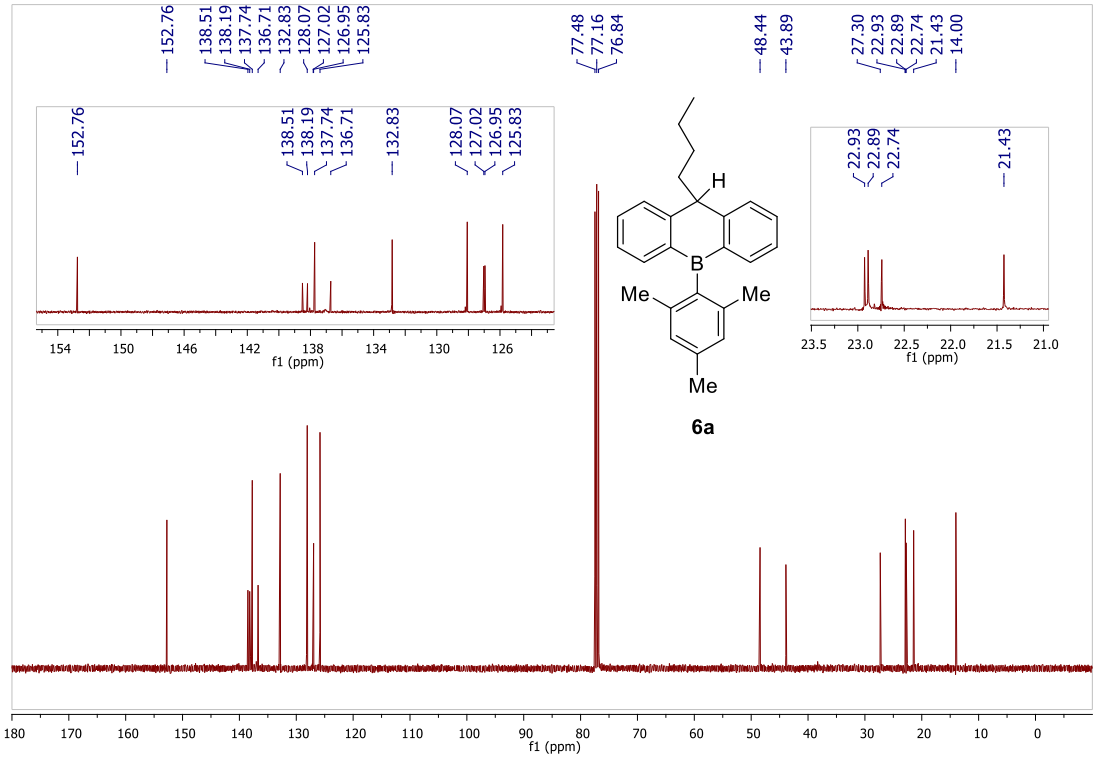


Figure S69. ^{13}C NMR (101 MHz) spectrum of **6a** in $CDCl_3$.

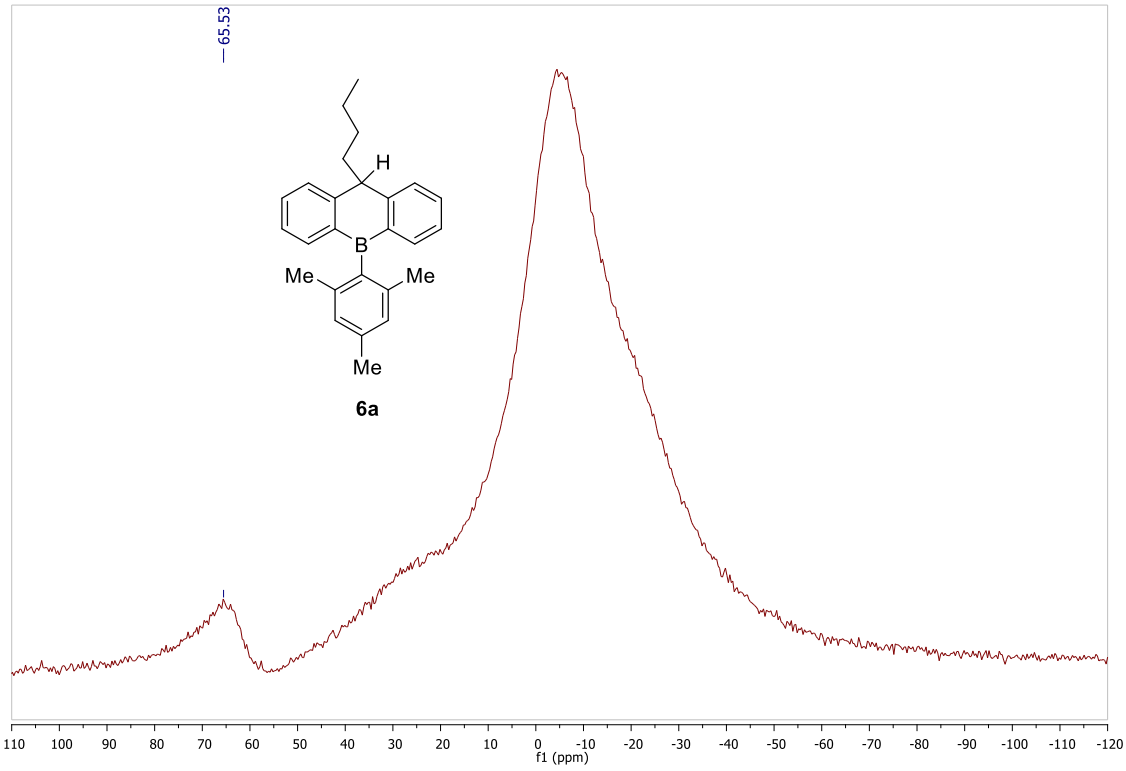


Figure S70. ^{11}B NMR (128 MHz) spectrum of **6a** in $CDCl_3$.

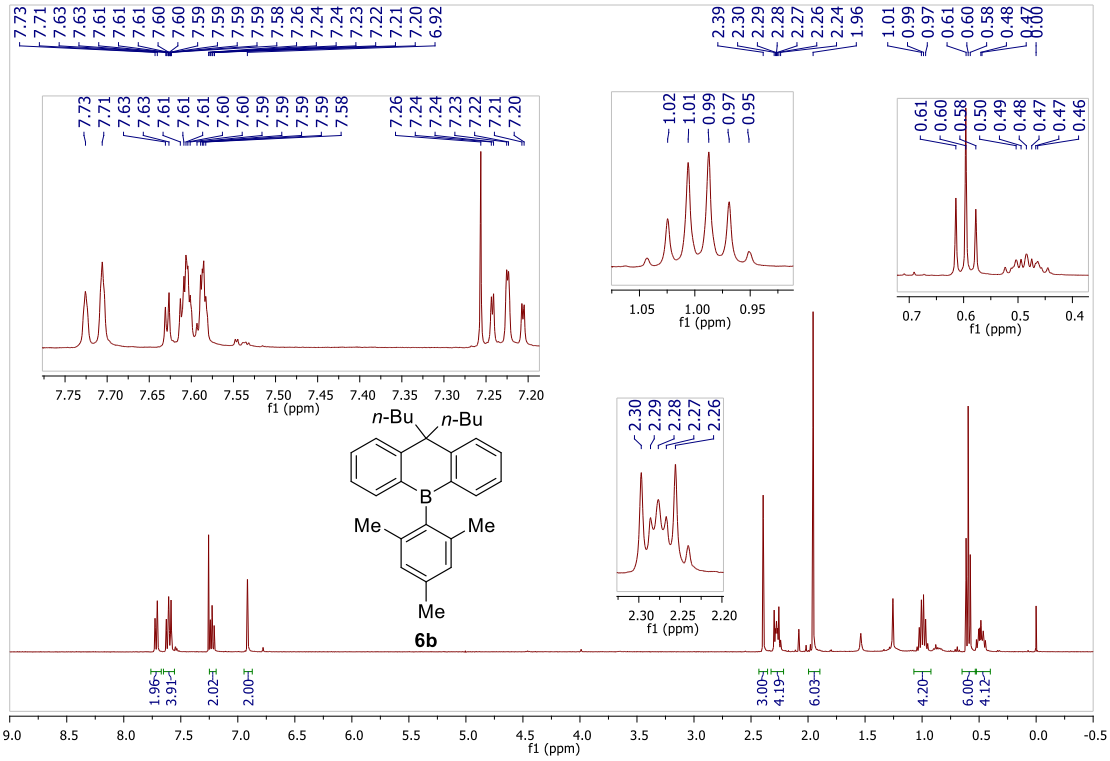


Figure S71. ^{1}H NMR (400 MHz) spectrum of **6b** in $CDCl_3$ with TMS as the internal reference.

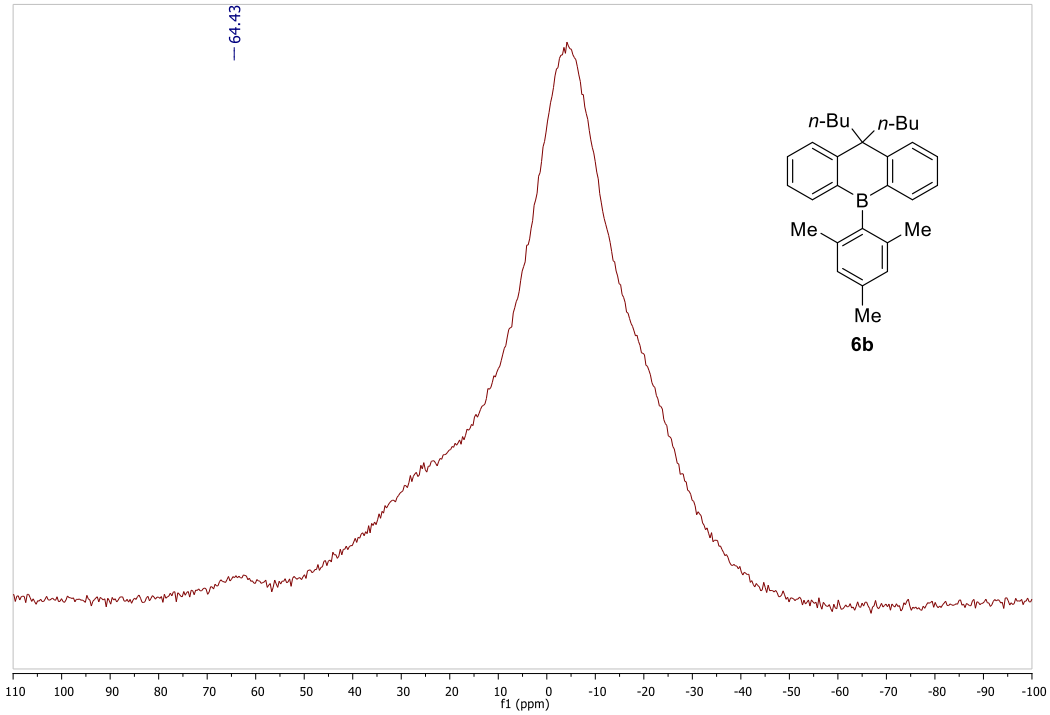


Figure S72. ^{11}B NMR (128 MHz) spectrum of **6b** in $CDCl_3$.

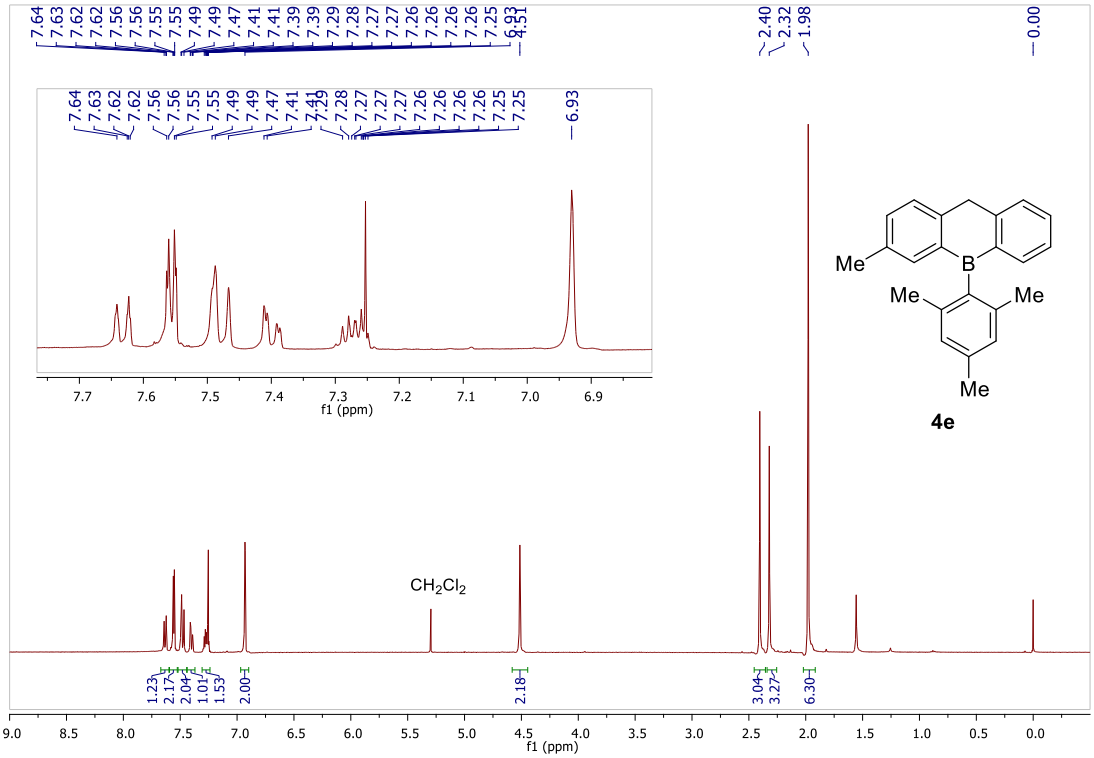


Figure S73. ^{1}H NMR (400 MHz) spectrum of **4e** in $CDCl_3$ with TMS as the internal reference.

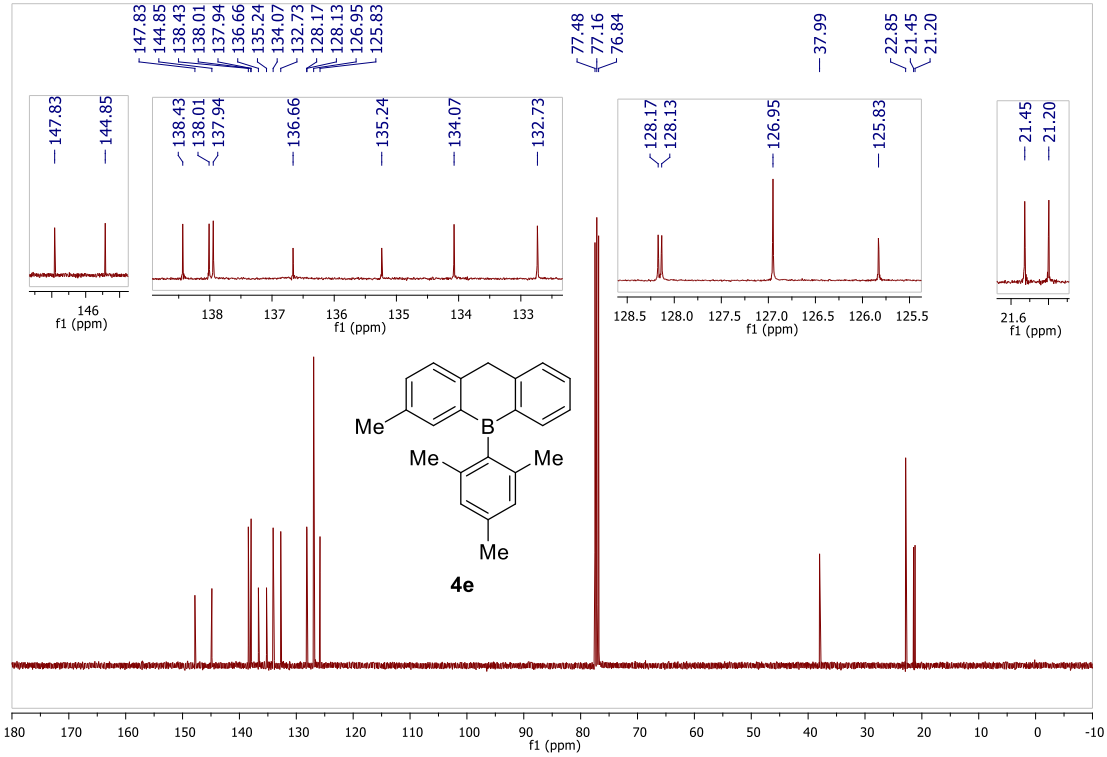


Figure S74. ^{13}C NMR (101 MHz) spectrum of **4e** in $CDCl_3$.

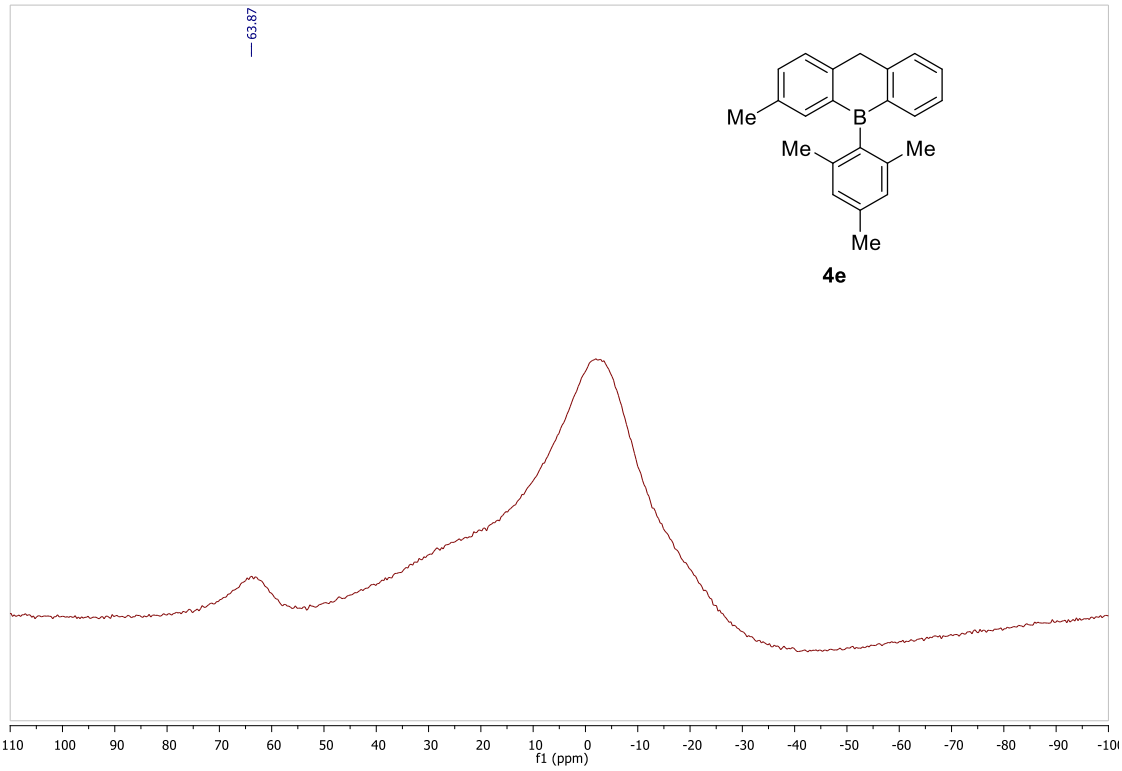


Figure S75. ^{11}B NMR (128 MHz) spectrum of **4e** in $CDCl_3$.

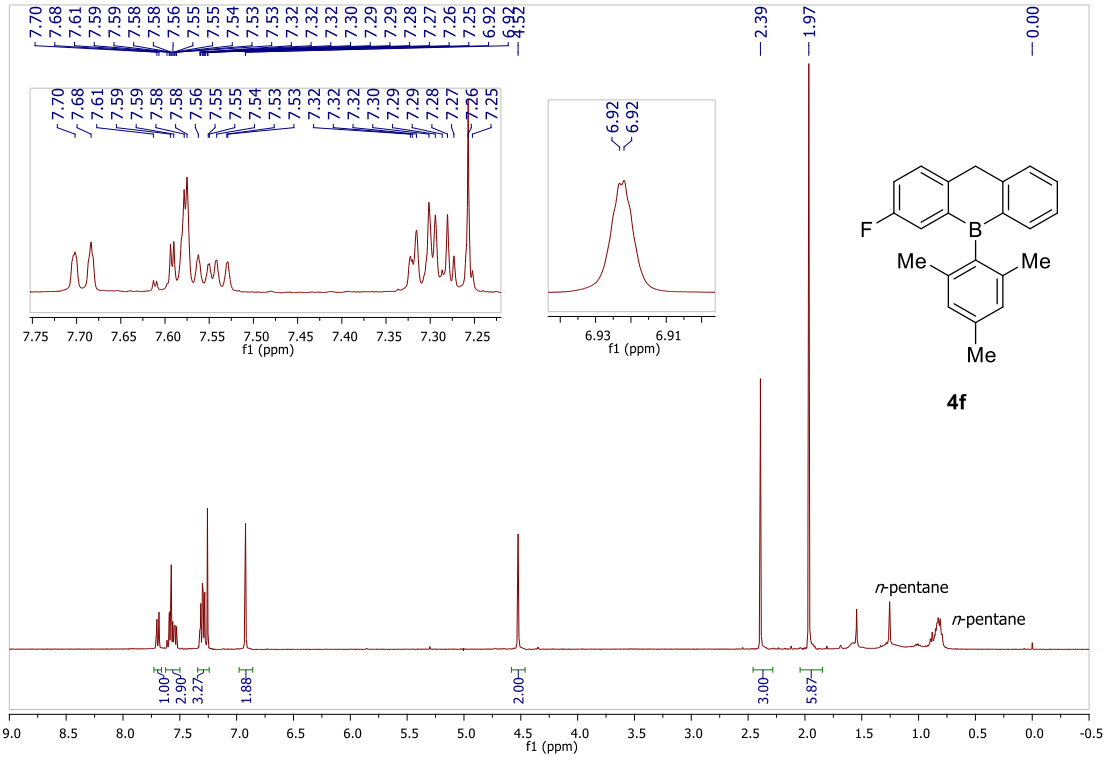


Figure S76. ^{1}H NMR (400 MHz) spectrum of **4f** in $CDCl_3$ with TMS as the internal reference.

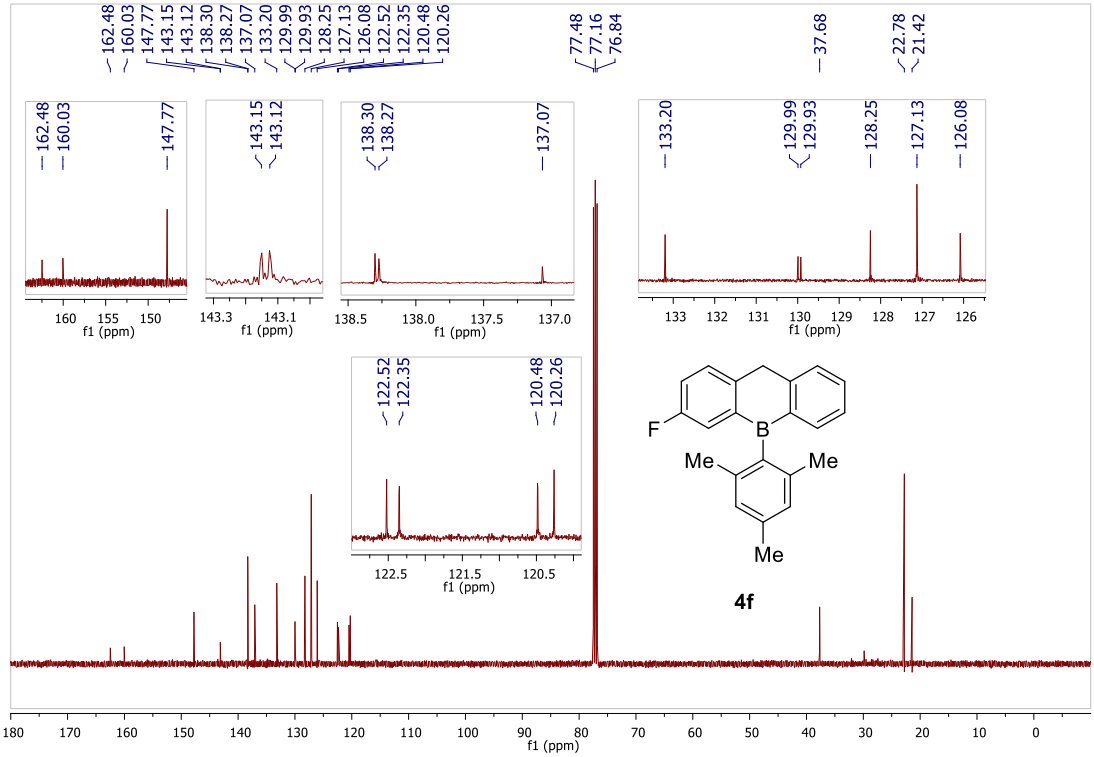


Figure S77. ^{13}C NMR (101 MHz) spectrum of **4f** in $CDCl_3$.

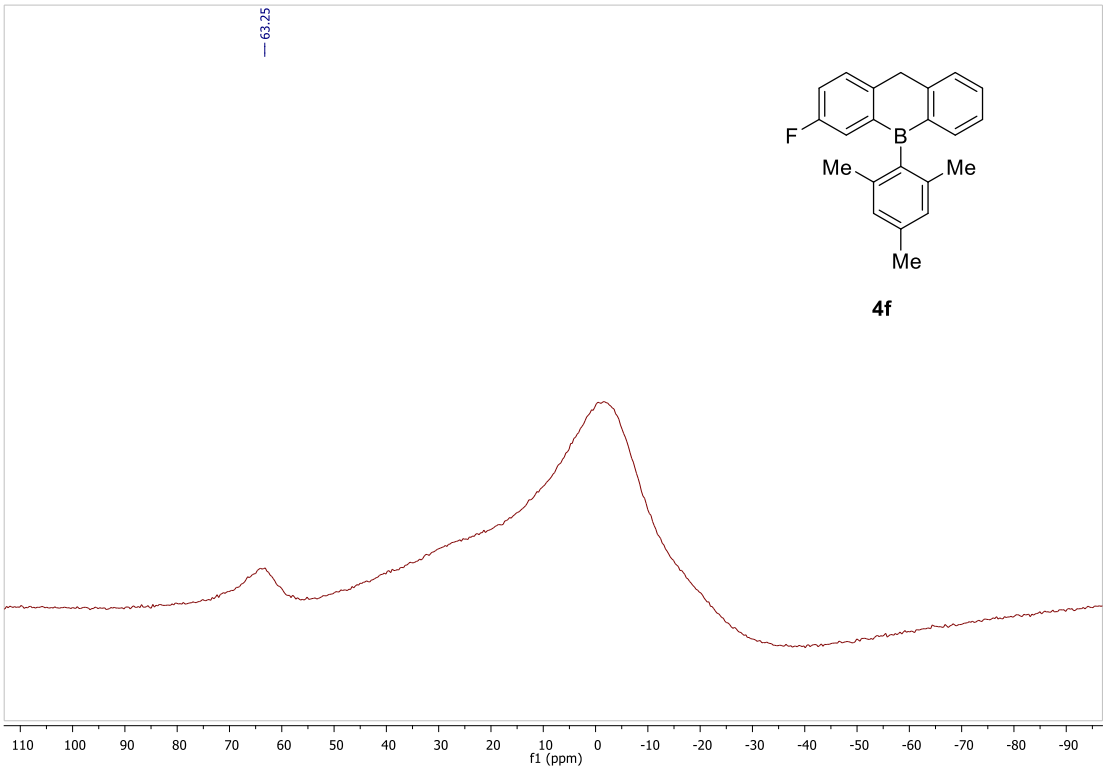


Figure S78. ^{11}B NMR (128 MHz) spectrum of **4f** in $CDCl_3$.

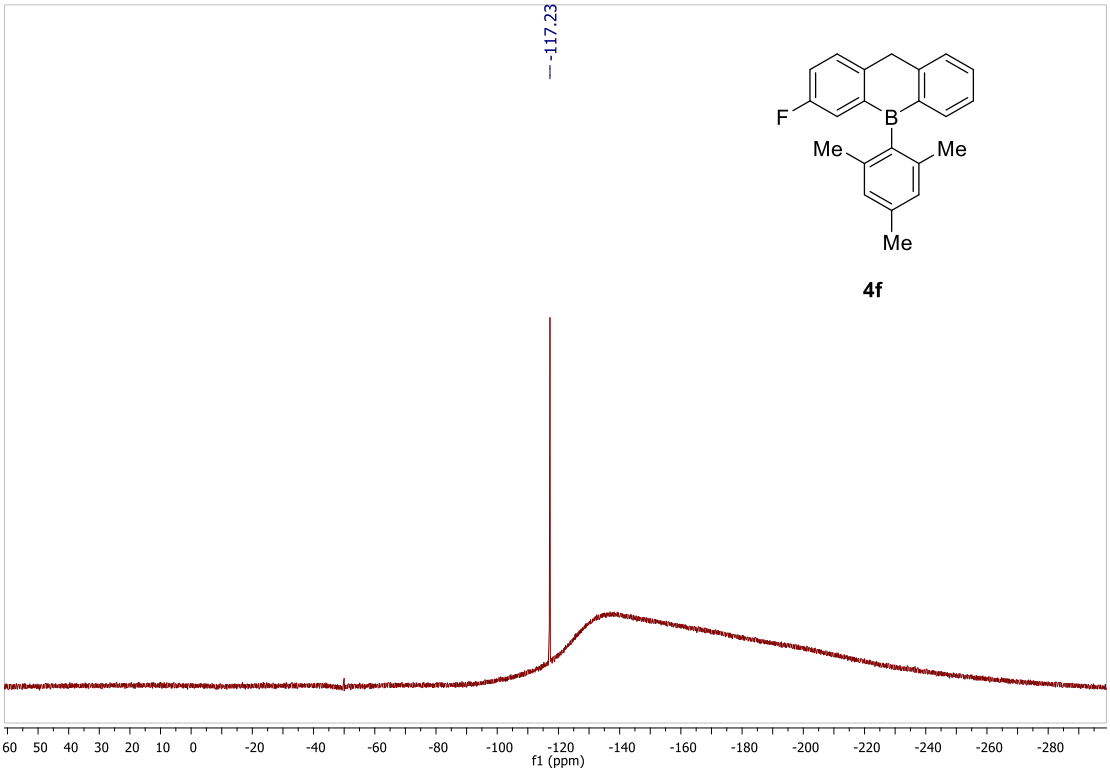


Figure S79. ^{19}F NMR (376 MHz) spectrum of **4f** in $CDCl_3$.

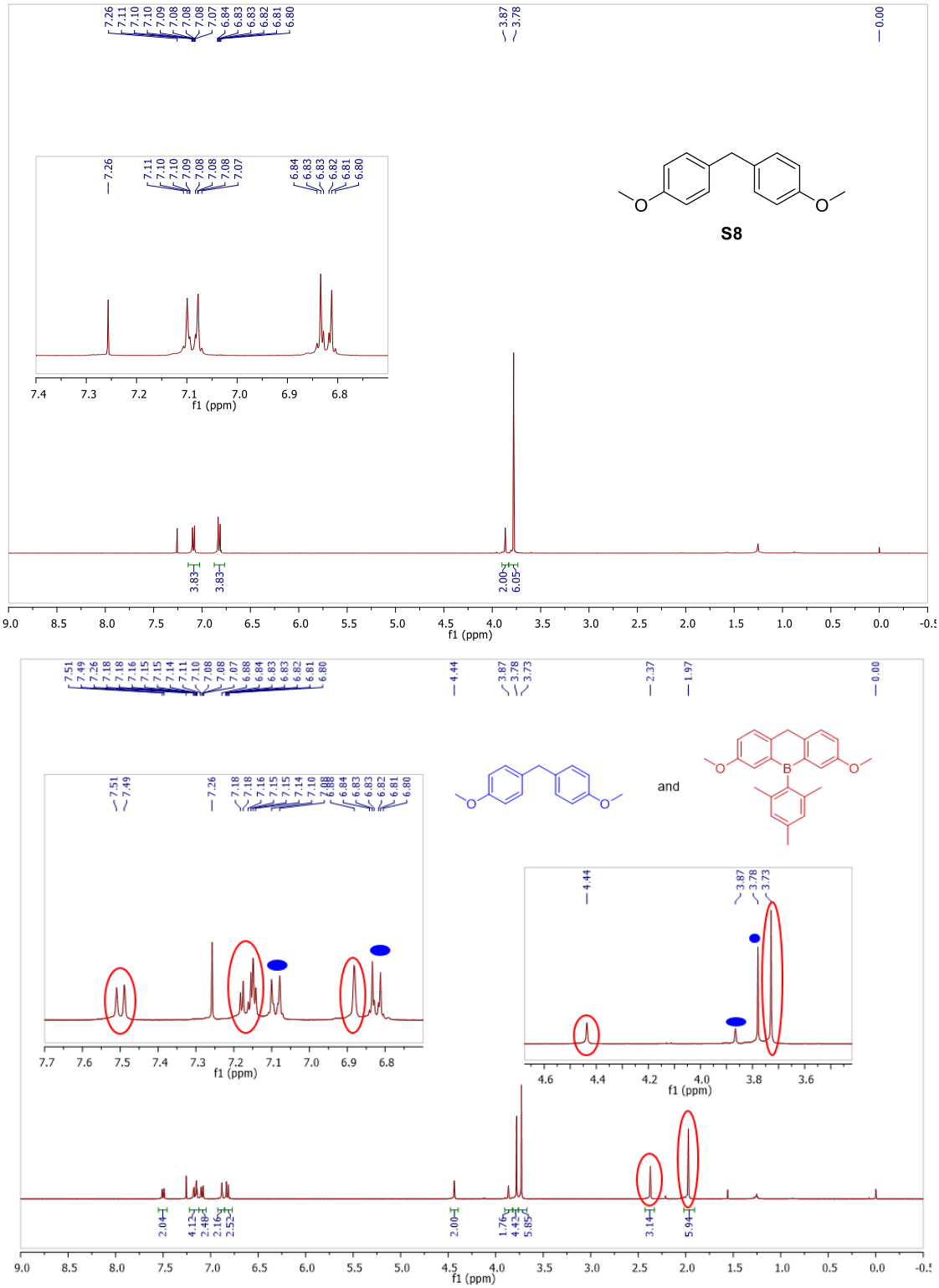


Figure S80. ^{1}H NMR (400 MHz) spectra of **S8** (top), and the mixture of **4g** (red marked) and **S8** as the side product (blue marked) (bottom) in $CDCl_3$ with TMS as the internal reference.

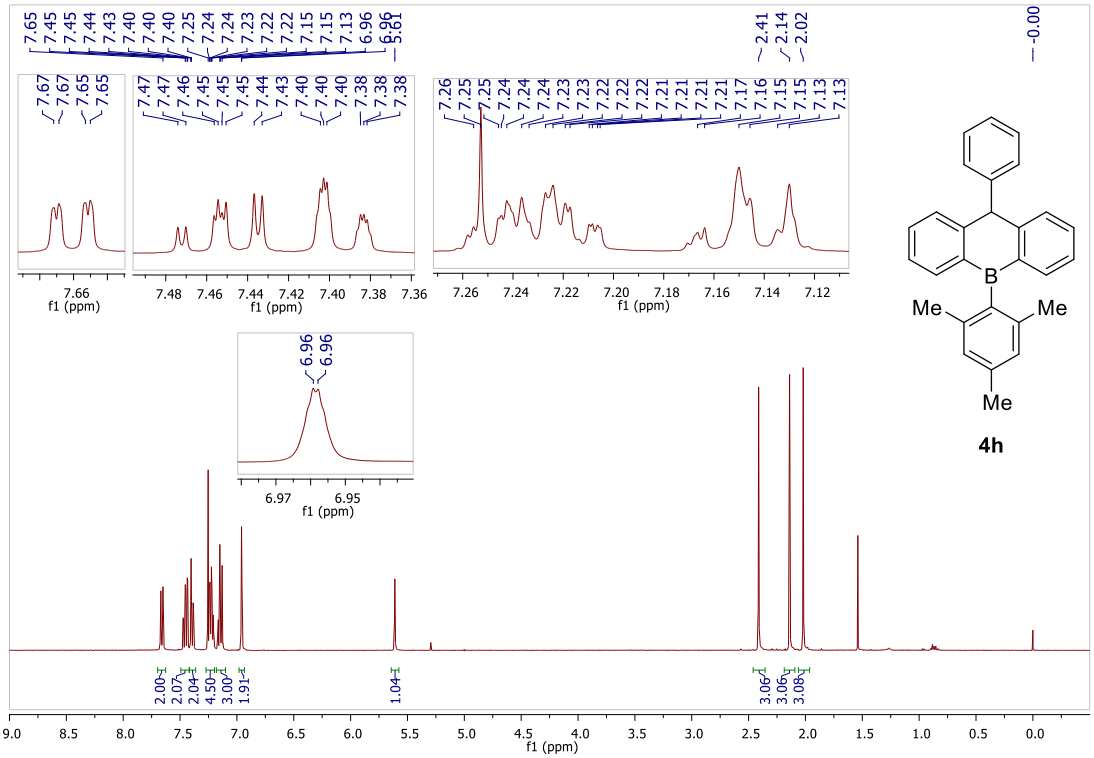


Figure S81. ^{1}H NMR (400 MHz) spectrum of **4h** in $CDCl_3$ with TMS as the internal reference.

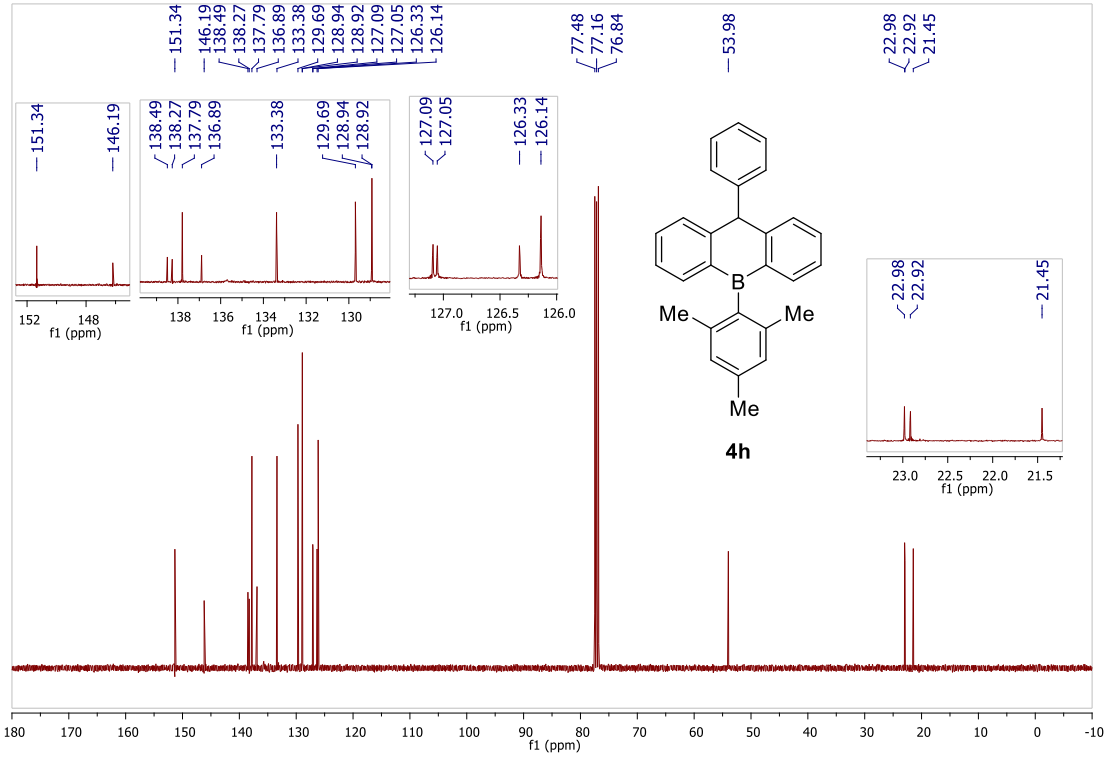


Figure S82. ^{13}C NMR (101 MHz) spectrum of **4h** in $CDCl_3$.

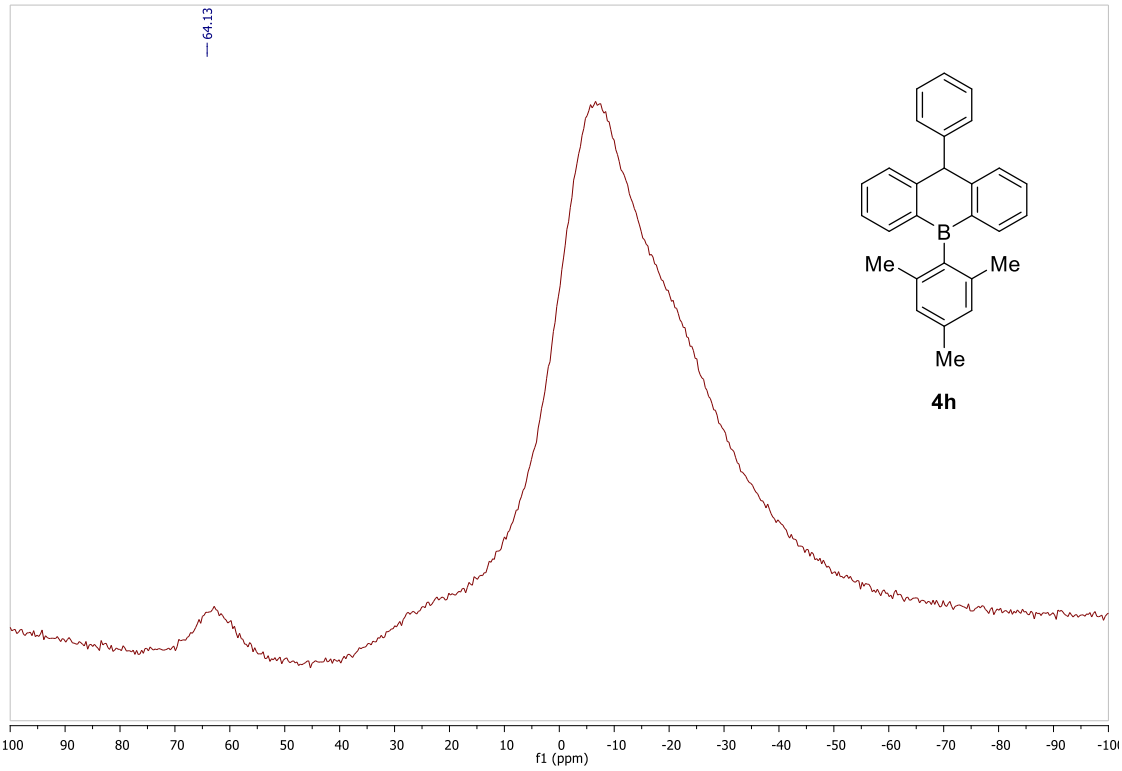


Figure S83. ^{11}B NMR (128 MHz) spectrum of **4h** in $CDCl_3$.

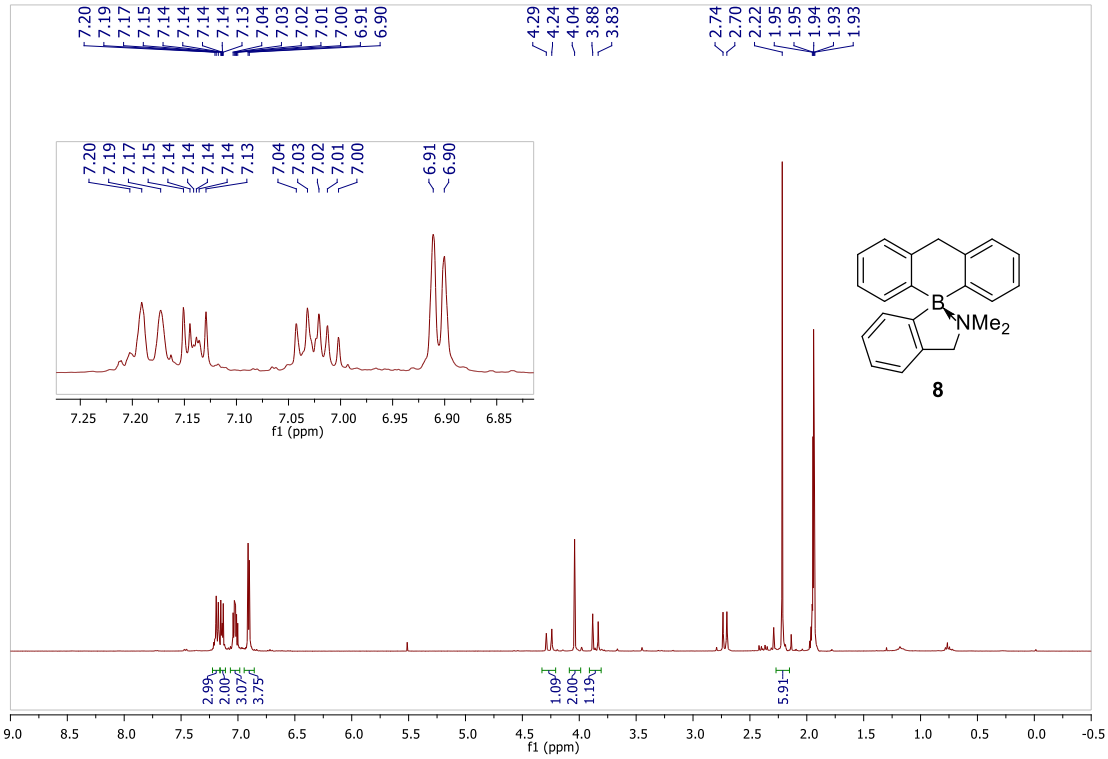


Figure S84. ^{1}H NMR (400 MHz) spectrum of **8** in CD_3CN.

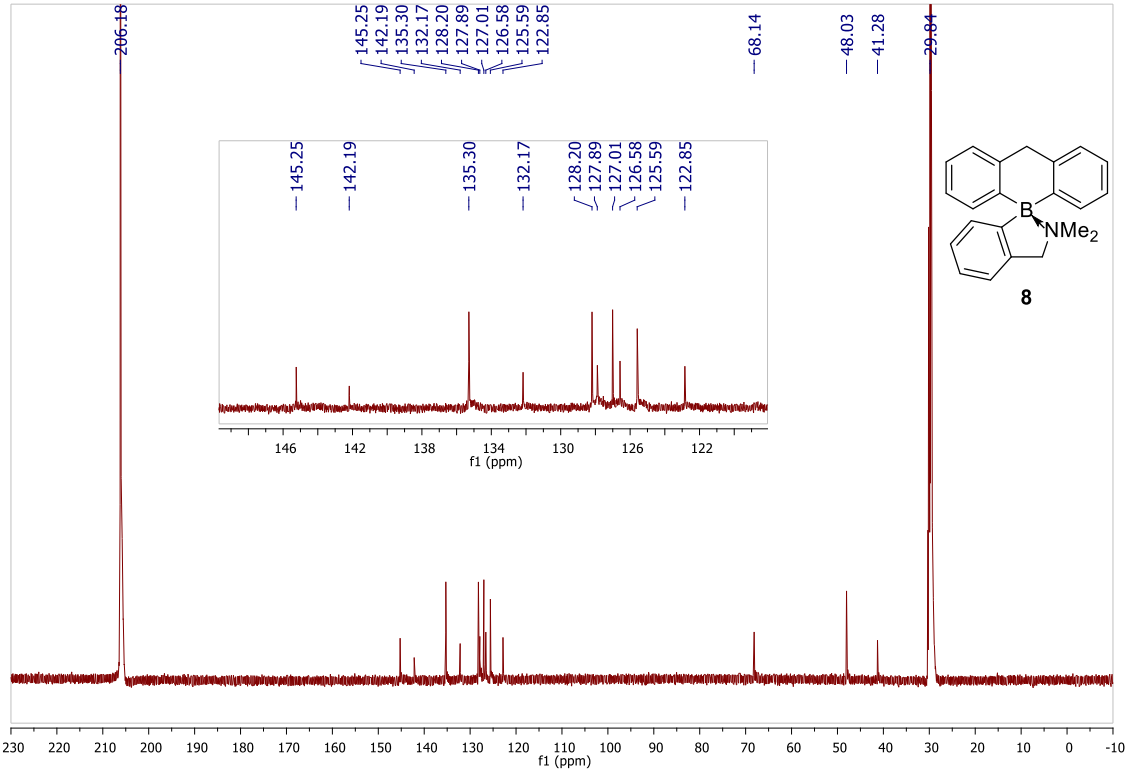


Figure S85. ^{13}C NMR (126 MHz) spectrum of **8** in $(CD_3)_2CO$.

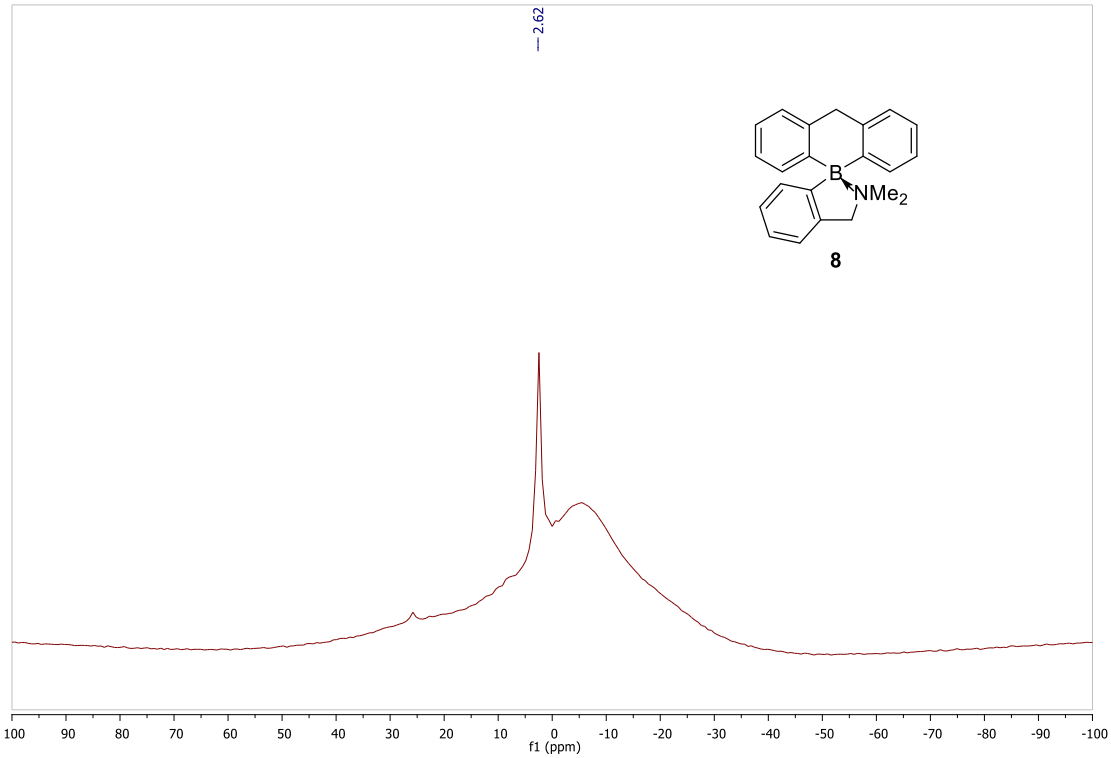


Figure S86. ^{11}B NMR (128 MHz) spectrum of **8** in $(CD_3)_2CO$.

9. NMR spectra the additional reactions

9.1. NMR spectra of Lewis-acid base interaction for 4c and 4d in a presence of PPh_3 and P(*o*-tolyl)$_3$

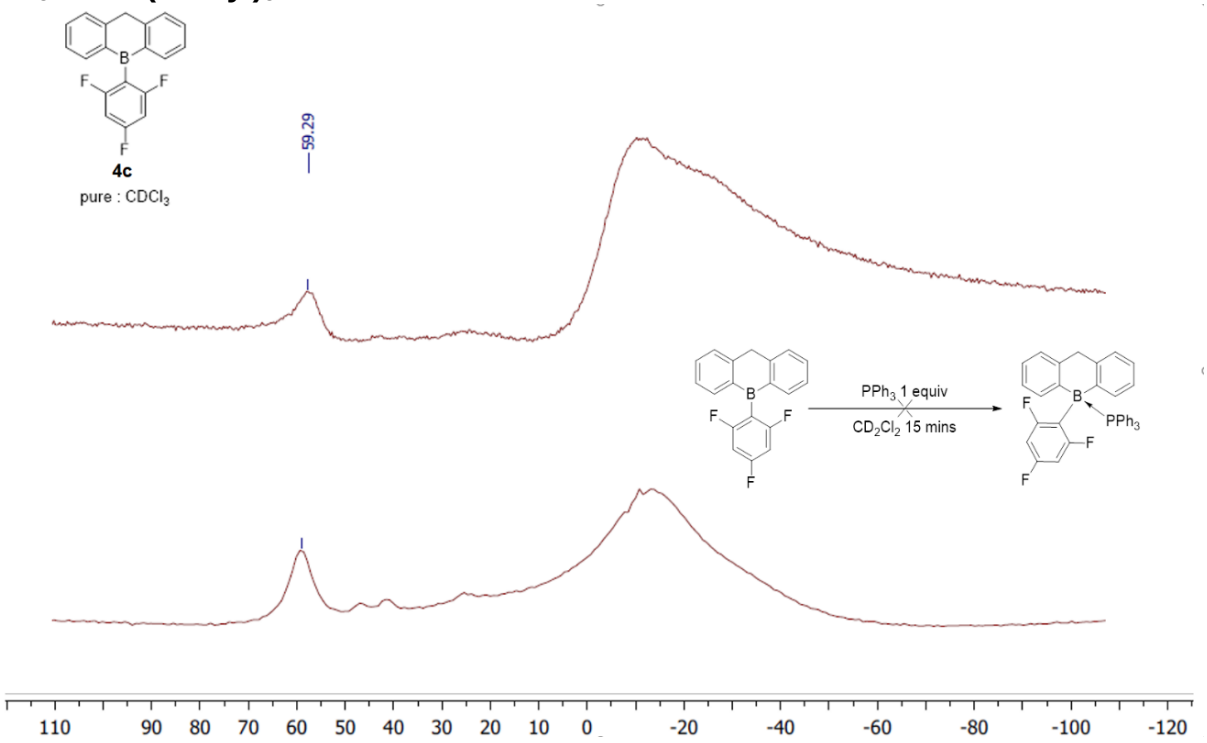


Figure S87. ^{11}B NMR (128 MHz) spectra of **4c** in $CDCl_3$ (top) and the reaction mixture of **4c** and PPh_3 in CD_2Cl_2 after 15 min (bottom).

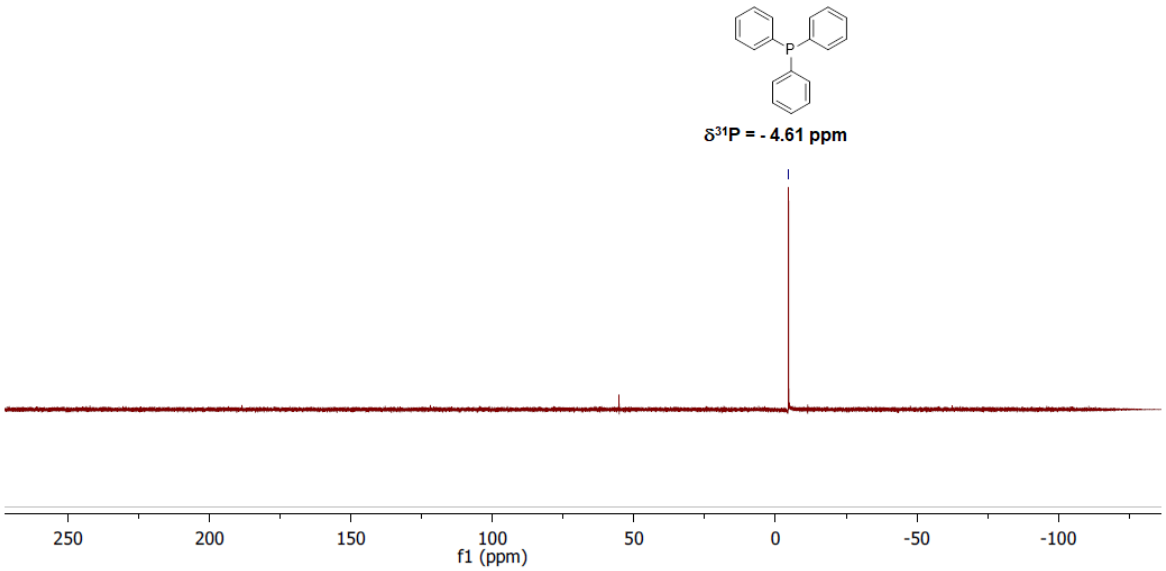


Figure S88. ^{31}P NMR (162 MHz) spectrum of the reaction mixture of **4c** and PPh_3 in CD_2Cl_2 after 15 min.

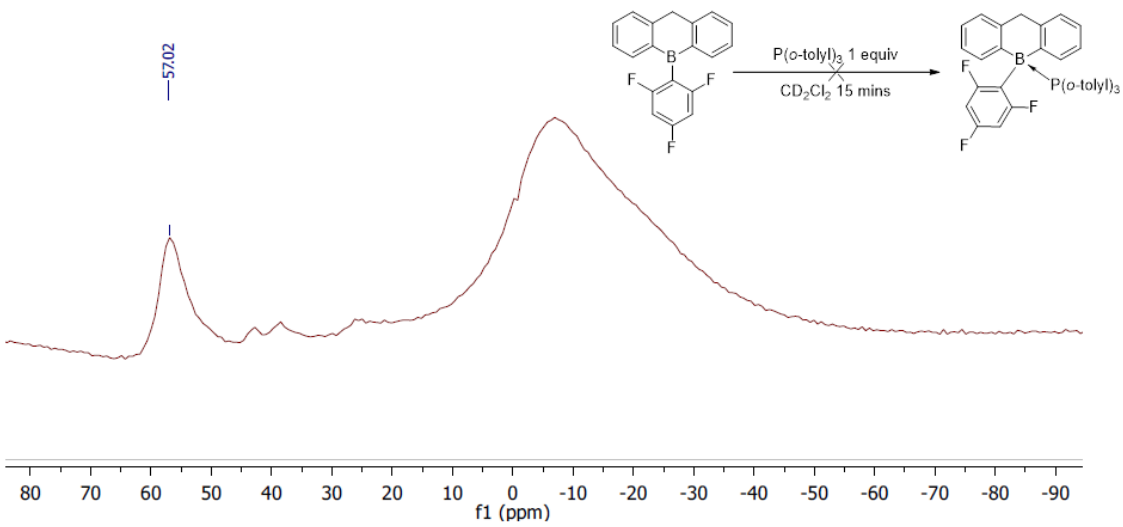


Figure S89. ^{11}B NMR (128 MHz) spectrum of the reaction mixture of **4c** and P(*o*-tolyl)$_3$ in CD_2Cl_2 after 15 min.

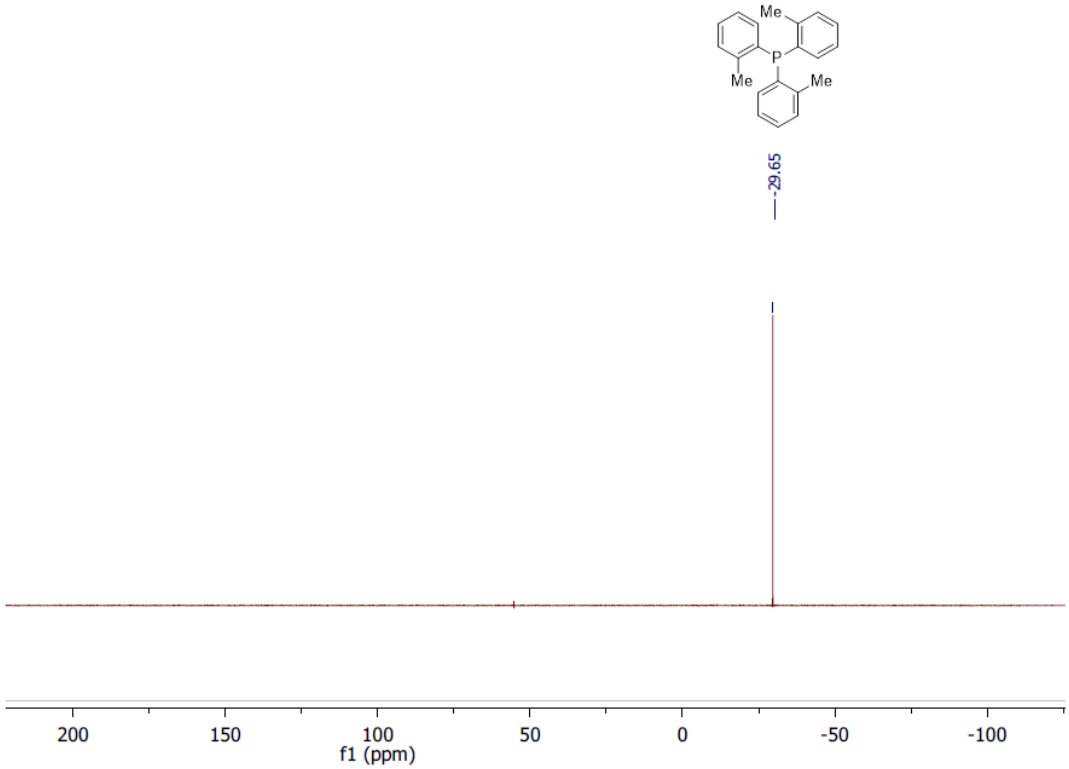


Figure S90. ^{31}P NMR (162 MHz) spectrum of the reaction mixture of **4c** and P(*o*-tolyl)$_3$ in CD_2Cl_2 after 15 min.

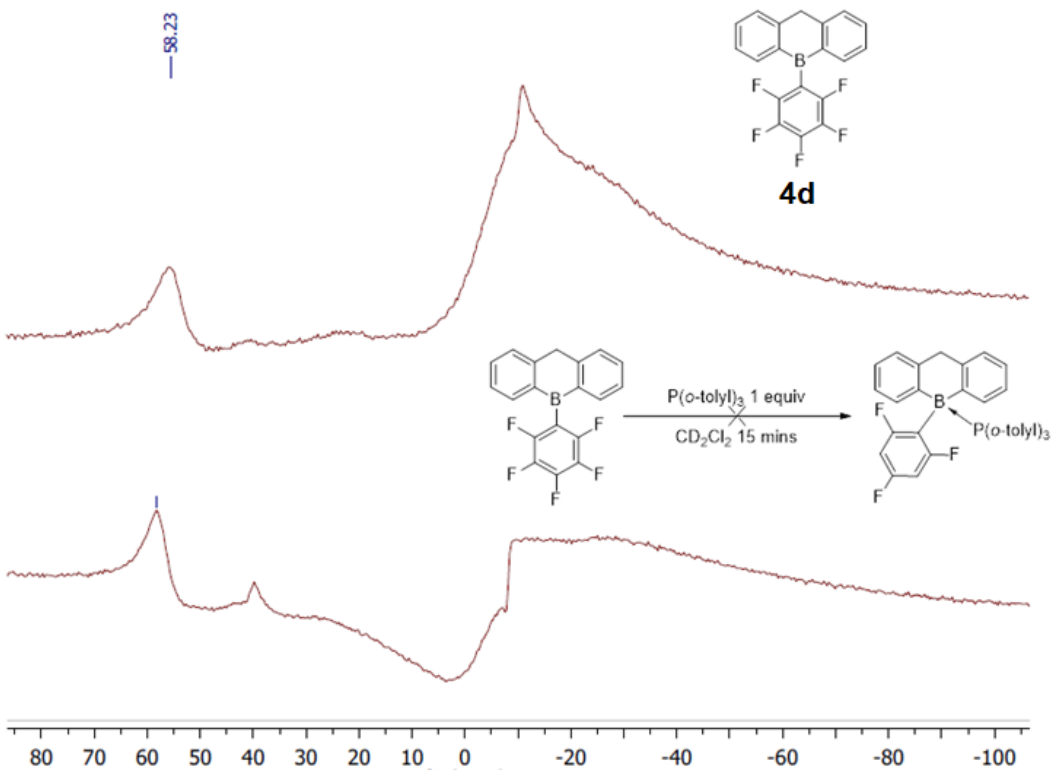


Figure S91. ^{11}B NMR (128 MHz) spectrum of **4d** in $CDCl_3$ (top) and the mixture of **4d** and P(*o*-tolyl)$_3$ in CD_2Cl_2 after 15 min (bottom).

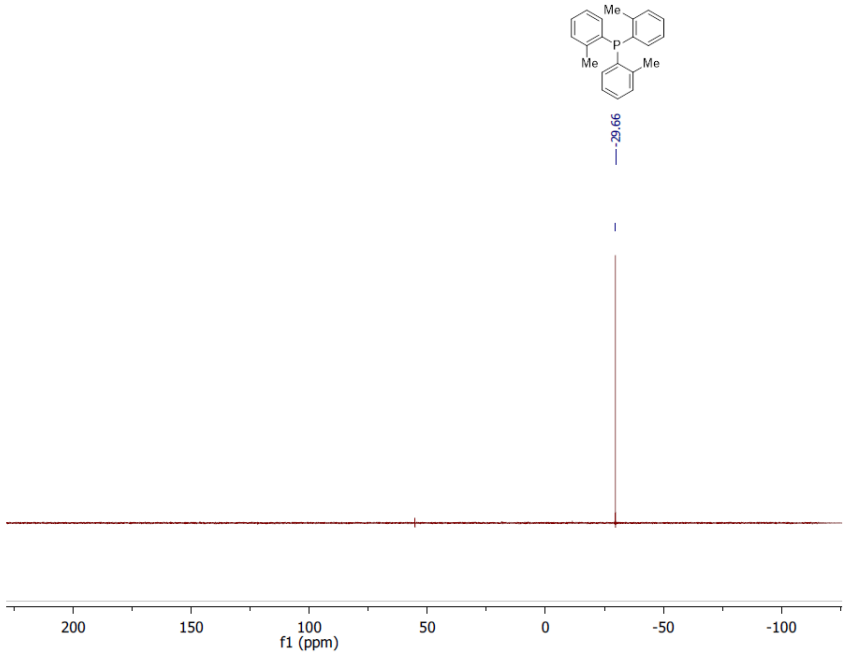


Figure S92. ^{31}P NMR (162 MHz) spectrum of the reaction mixture of **4d** and P(*o*-tolyl)$_3$ in CD_2Cl_2 after 15 min.

9.2. NMR spectra of the controlled reaction for the formation of 5

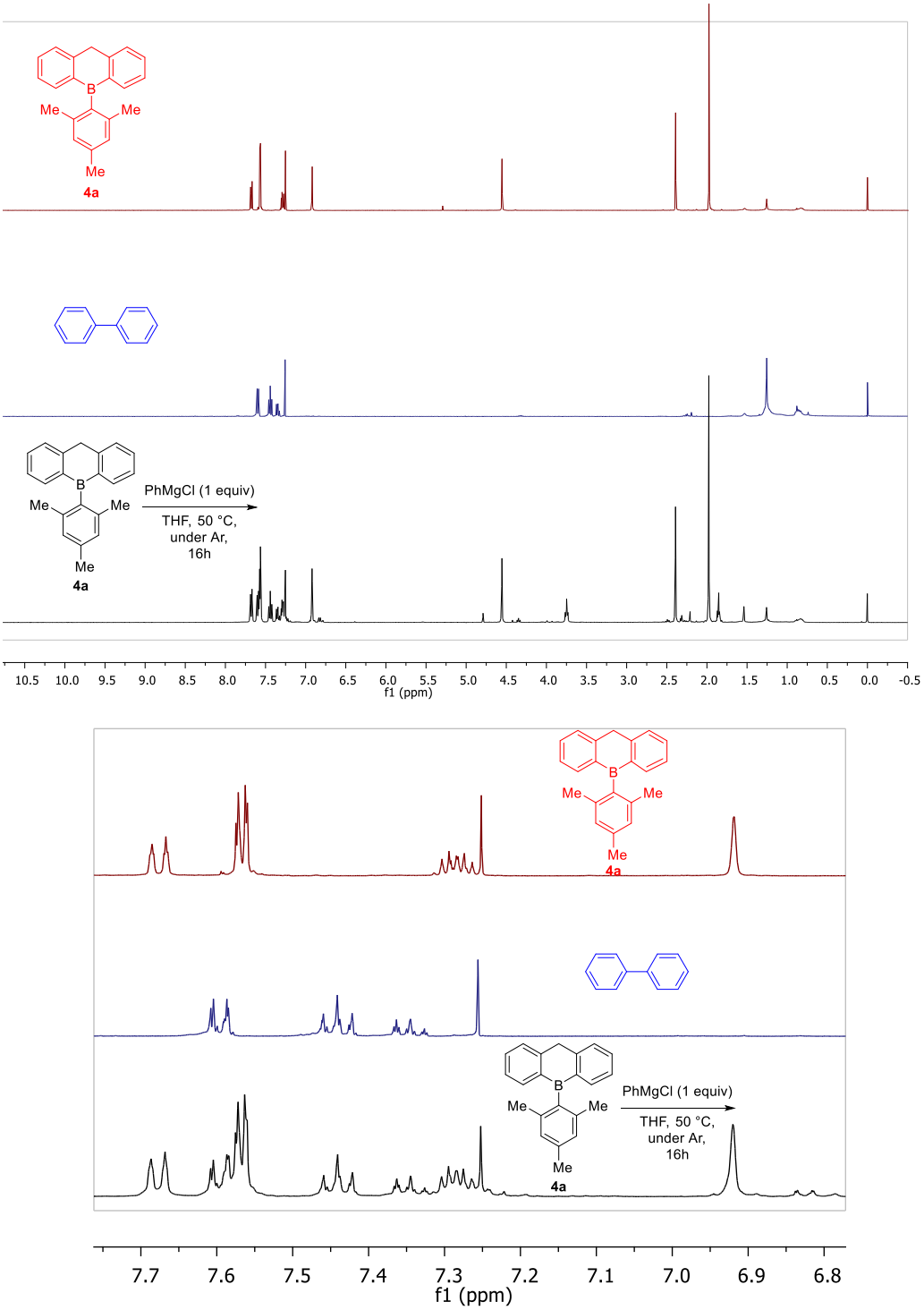


Figure S93. NMR spectra of the controlled reaction between **4a** and PhMgCl (top) and the enlarged NMR spectra for the aromatic area (bottom). The NMR spectra of **4a**, the formed biphenyl and the crude of the reaction between **4a** and PhMgCl are shown in red, blue and black lines, respectively.

9.3. NMR spectra of the independent synthesis of 9-mesityl-9-butyl,10-hydro-9-boraanthracene 6:

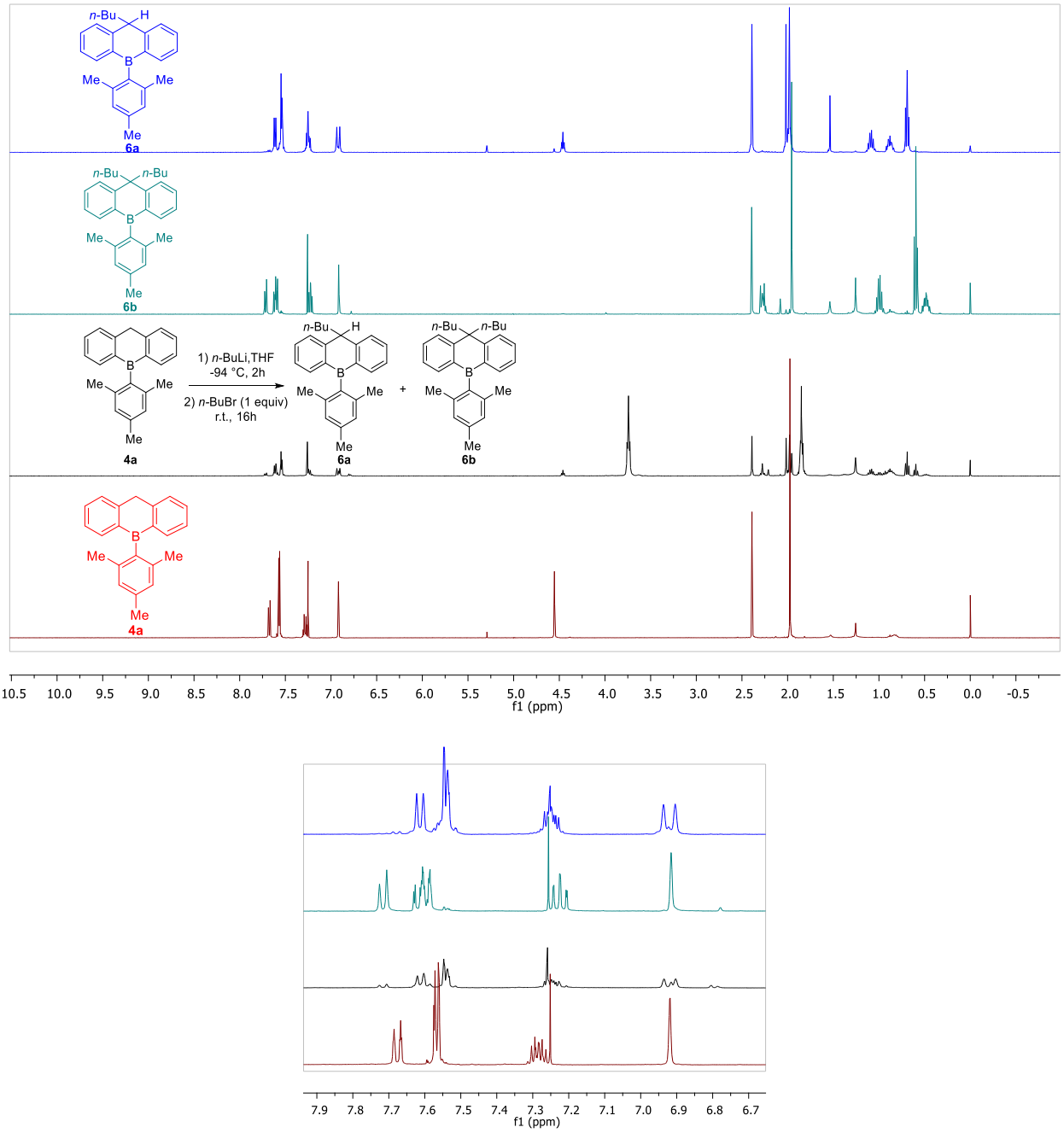
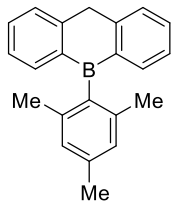


Figure S94. NMR spectra of the independent synthesis of **6** (top) and the enlarged NMR spectra for the aromatic area (bottom). The NMR spectra of the starting material **4a**, the crude, the products **6a** and **6b** are shown in red, black, blue and olive lines, respectively.

10. UV-Vis and Photoluminescence spectra



4a

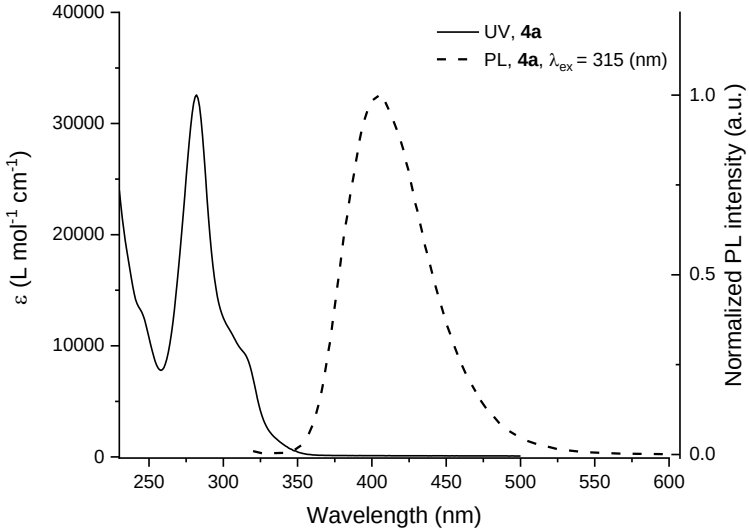
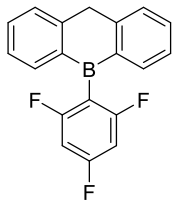


Figure S95. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 315 nm) of **4a** in CH_2Cl_2.



4c

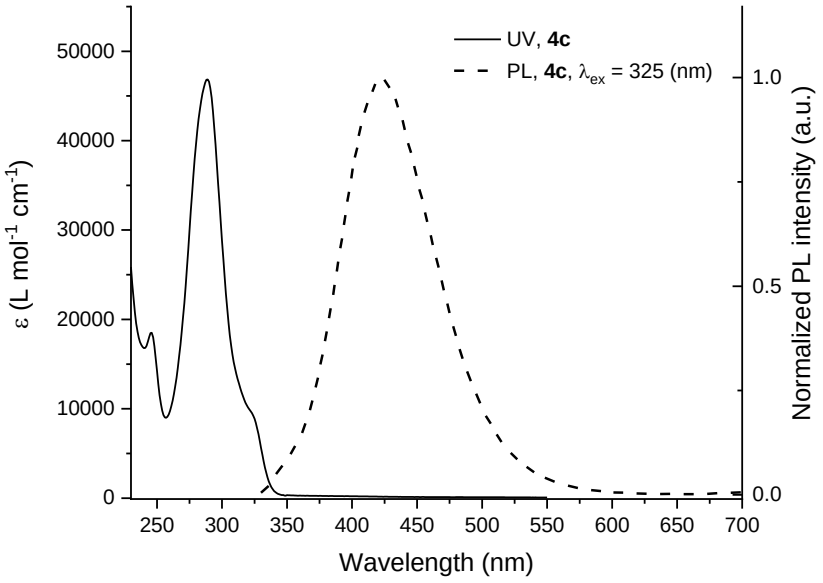


Figure S96. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 325 nm) of **4c** in CH_2Cl_2.

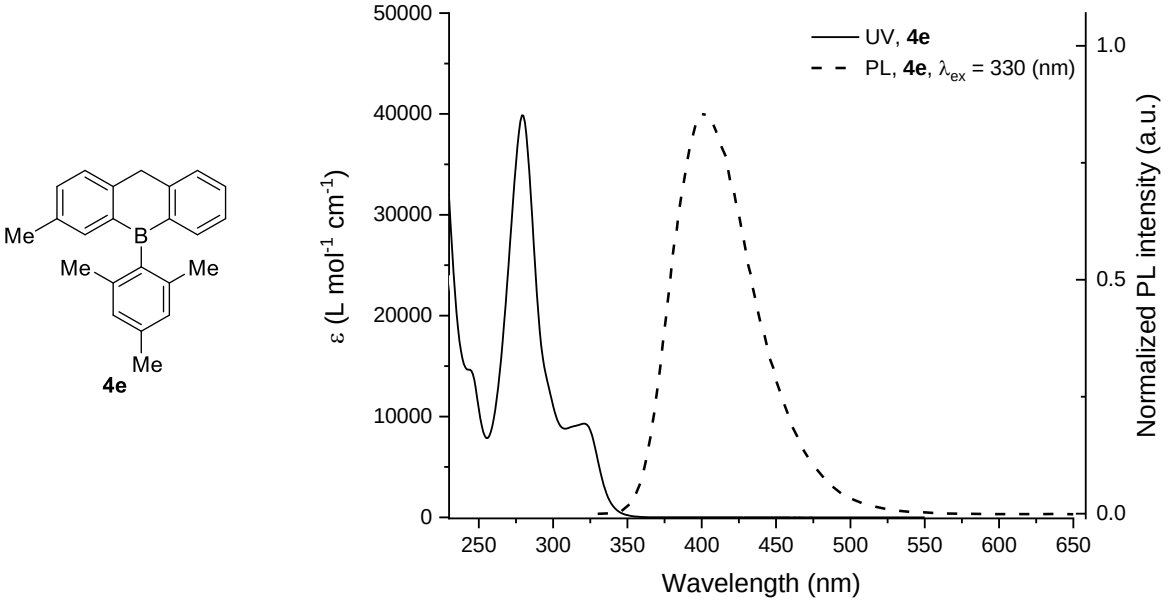


Figure S97. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 330 nm) of **4e** in CH_2Cl_2.

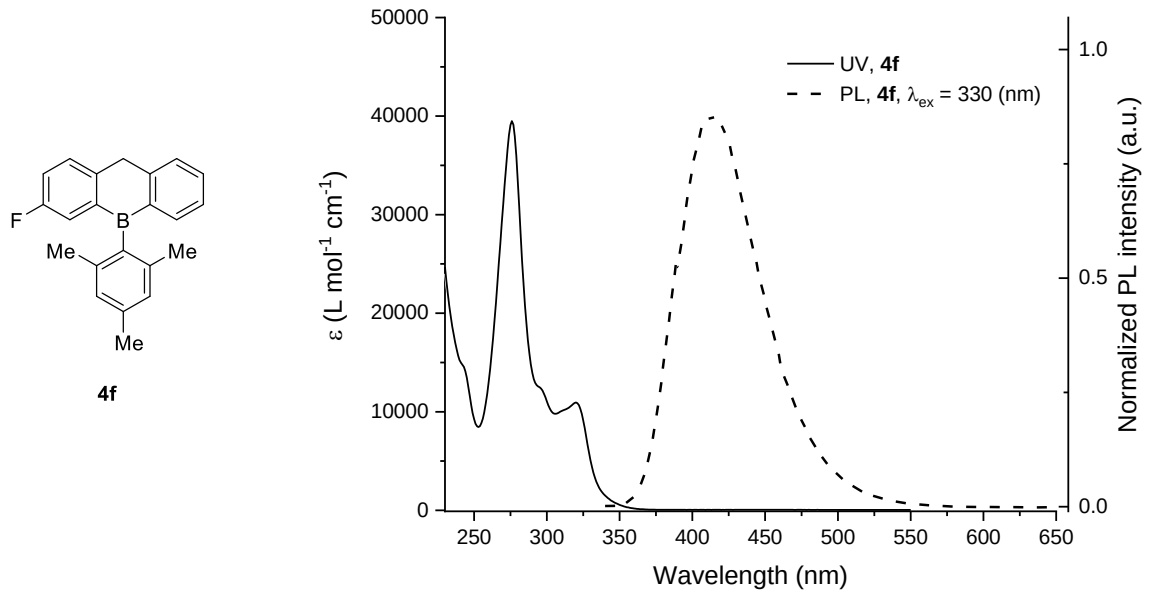


Figure S98. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 330 nm) of **4f** in CH_2Cl_2.

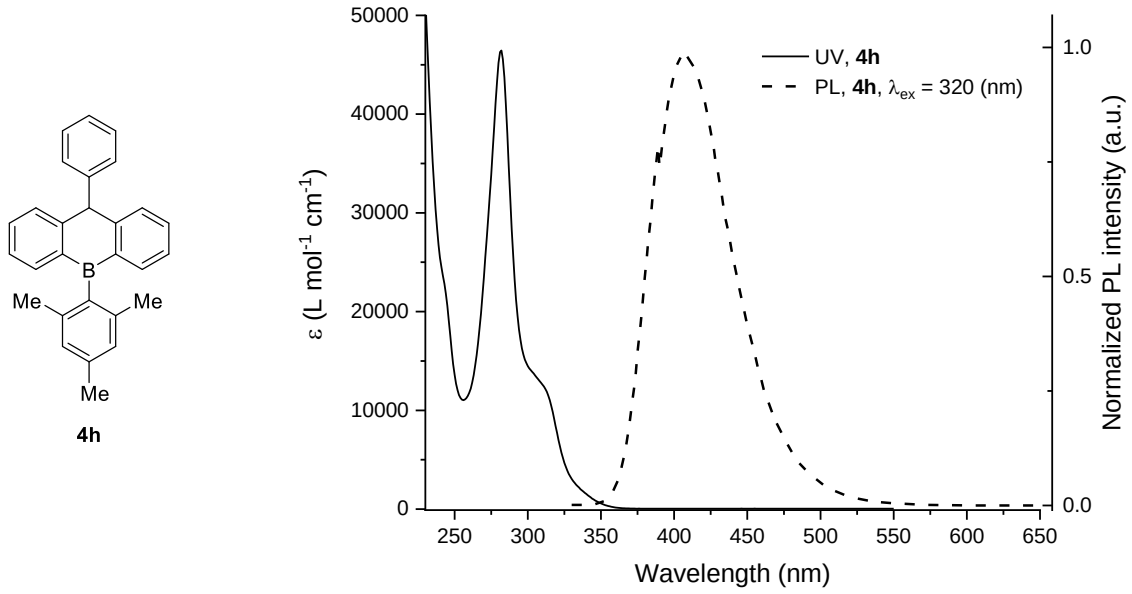


Figure S99. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 320 nm) of **4h** in CH_2Cl_2.

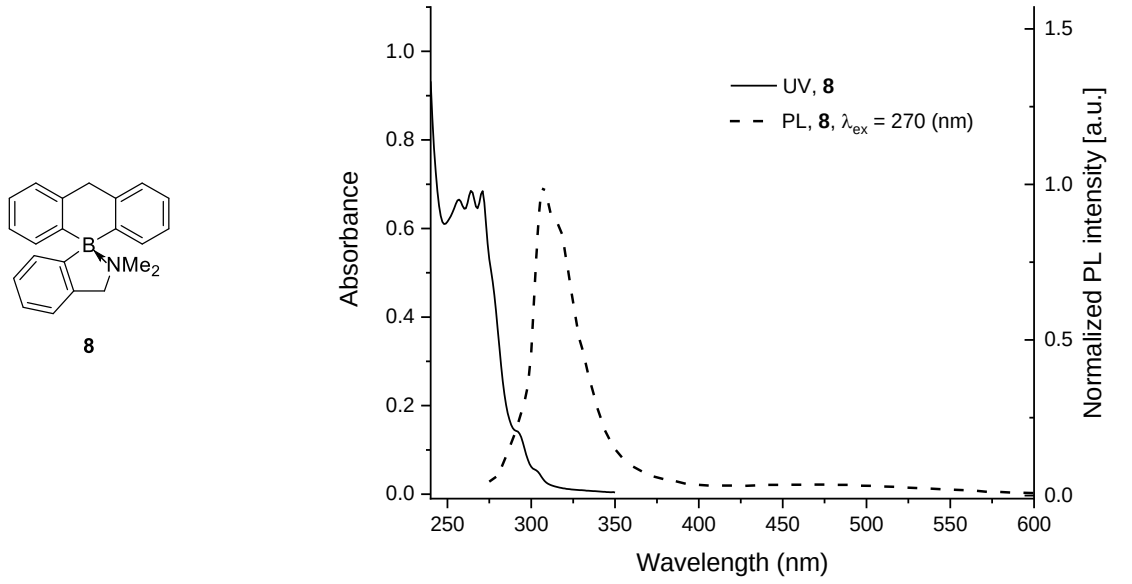


Figure S100. UV-Vis absorption spectrum (straight line) and normalized photoluminescence spectrum (dash line, λ_{ex} = 270 nm) of **8** in CH_2Cl_2.

11. Crystallographic data

Single-crystal X-ray diffraction data for all compounds were collected on an Oxford Diffraction Gemini Ultra R diffractometer (4-circle kappa platform, Ruby CCD detector) using Mo Kα and Cu Kα radiation. The structures solved by SHELXT and then refined by full-matrix least-squares refinement of $|F|^2$ in SHELXL-2015 (different versions) using Olex2 and ShelXle. Non-hydrogen atoms were refined anisotripically; hydrogen atoms were located from a difference Fourier map. Hydrogen atoms not involved in hydrogen bonding were refined in the riding mode with isotropic temperature factors fixed at 1.2U of the parents atoms (1.5U for methyl group). Coordinates of the hydrogen atoms implicated in hydrogen bonds were refined. The program Mercury was used for molecular graphics. Experiments were carried out at 295 K.[7]

[7] Computer programs: *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015), *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018), *CrysAlis PRO* 1.171.40.16b (Rigaku OD, 2018), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXT* (Sheldrick, 2015), *SHELXT* 2015 (Sheldrick, 2015), *SHELXL2018*/1 (Sheldrick, 2018), *SHELXL2018*/3 (Sheldrick, 2018).

	4a	4c	4d	4e

	2	3a	3d	3f
Chemical formula	$2(C_{15}H_{16}BNO)\cdot H_2O$	$C_{19}H_{18}BN$	$C_{19}H_{17}BFN$	$C_{19}H_{15}BF_3N\cdot CH_4O$
M_r	492.21	271.15	289.14	357.17
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, *Cm*	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	11.42896 (9), 11.89780 (12), 19.5241 (2)	10.2532 (3), 16.6961 (6), 9.2515 (3)	17.4338 (5), 9.7707 (2), 18.1986 (5)	9.41756 (8), 11.20545 (11), 18.07441 (17)
α, β, λ (°)	90, 90, 90	90, 101.132 (3), 90	90, 90, 90	90, 102.9088 (9), 90
V (Å^3)	2654.88 (4)	1553.95 (9)	3099.95 (14)	1859.15 (3)
Z	4	4	8	4
Radiation type	Cu *K*α	Mo *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	0.61	0.07	0.63	0.82
Crystal size (mm)	0.43 × 0.39 × 0.17	0.58 × 0.22 × 0.15	0.33 × 0.14 × 0.04	0.45 × 0.28 × 0.23
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini Ultra			
Absorption correction	Analytical			
T_{min}, T_{max}	0.820, 0.909	0.974, 0.991	0.881, 0.977	0.780, 0.868
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14290, 4687, 4533	9422, 4070, 3324	9892, 2731, 2176	16343, 3286, 3029
R_{int}	0.019	0.016	0.032	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.597	0.762	0.597	0.598
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.102, 1.03	0.039, 0.105, 1.01	0.049, 0.150, 1.05	0.043, 0.125, 1.05
No. of reflections	4687	4070	2731	3286
No. of parameters	340	215	400	258
No. of restraints	0	2	328	3
H-atom treatment	mixed		constrained	mixed
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, -0.20	0.12, -0.19	0.16, -0.14	0.20, -0.16
CCDC deposition number	1894695	1894696	1894697	1894698

Chemical formula	$C_{22}H_{21}B$	$C_{19}H_{12}BF_3$	$C_{19}H_{10}BF_5$	$C_{23}H_{23}B$
M_r	296.20	308.10	344.08	310.22
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	9.08944 (19), 8.22672 (18), 23.3444 (5)	8.6286 (5), 9.4523 (5), 10.2633 (6)	7.7665 (6), 9.5509 (8), 11.5367 (9)	14.7715 (5), 8.0057 (2), 16.2672 (6)
α, β, λ (°)	90, 94.4692 (19), 90	67.393 (5), 75.518 (5), 79.118 (5)	69.971 (8), 77.865 (7), 79.307 (7)	90, 104.309 (4), 90
V (Å^3)	1740.30 (6)	744.17 (8)	780.02 (12)	1864.02 (12)
Z	4	2	2	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.06	0.87	1.09	0.06
Crystal size (mm)	0.68 × 0.49 × 0.35	0.42 × 0.27 × 0.09	0.43 × 0.27 × 0.09	0.63 × 0.50 × 0.40
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini Ultra			
Absorption correction	Gaussian	Analytical		
T_{min}, T_{max}	0.464, 1.000	0.786, 0.939	0.747, 0.911	0.973, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29431, 3562, 3075	7806, 2611, 2012	6195, 2749, 2182	9006, 3804, 2724
R_{int}	0.020	0.046	0.028	0.016
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.598	0.597	0.625
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.146, 1.05	0.043, 0.131, 1.04	0.047, 0.147, 1.06	0.058, 0.181, 1.06
No. of reflections	3562	2611	2749	3804
No. of parameters	212	209	227	221
No. of restraints	0	0	0	0
H-atom treatment	constrained			
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, -0.15	0.16, -0.13	0.17, -0.16	0.22, -0.19
CCDC deposition number	1894700	1894702	1894703	2011740

	4f	**4h**	**5**	**6**	**8**
Chemical formula	$C_{22}H_{20}BF$	$C_{28}H_{25}B$	$C_{44}H_{40}B_2$	$C_{26}H_{29}B$	$C_{22}H_{22}BN$
M_r	314.19	372.29	590.38	352.30	311.21
Crystal system, space group	Monoclinic, *I*2/*a*	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	10.9794 (2), 12.4100 (2), 13.5748 (3)	9.1984 (4), 11.4289 (5), 12.5518 (5)	8.6797 (4), 8.9094 (4), 12.9370 (7)	9.3068 (4), 10.7789 (5), 11.7604 (6)	8.22059 (17), 16.6674 (3), 13.7231 (2)
α, β, λ (°)	90, 105.533 (2), 90	64.187 (4), 74.088 (4), 67.803 (4)	92.906 (4), 99.390 (4), 119.093 (5)	110.616 (5), 90.436 (4), 101.968 (4)	90, 106.515 (2), 90
V (Å^3)	1782.07 (6)	1090.29 (9)	852.63 (9)	1076.02 (10)	1802.71 (6)
Z	4	2	1	2	4
Radiation type	Cu *K*α	Mo *K*α	Cu *Kα*		
μ (mm^{-1})	0.57	0.06	0.48	0.45	0.49
Crystal size (mm)	0.40 × 0.20 × 0.13	0.69 × 0.45 × 0.17	0.27 × 0.24 × 0.05	0.70 × 0.32 × 0.05	0.30 × 0.11 × 0.08
Diffractometer	Oxford Diffraction Xcalibur, Ruby, Gemini Ultra				
Absorption correction	Gaussian	Analytical	Analytical	Gaussian .	Analytical
T_{min}, T_{max}	0.884, 0.950	0.972, 0.990	0.909, 0.975	0.528, 1.000	0.921, 0.974
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7905, 1569, 1399	11382, 5406, 4039	8341, 3013, 2480	9226, 3785, 3202	8483, 3169, 2694
R_{int}	0.019	0.015	0.032	0.018	0.027
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.597	0.667	0.597	0.597	0.597
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.055, 0.177, 1.12	0.047, 0.146, 1.04	0.053, 0.162, 1.05	0.048, 0.154, 1.07	0.048, 0.148, 1.05
No. of reflections	1569	5406	3013	3785	3169
No. of parameters	118	320	212	249	219
No. of restraints	0	12	0	0	0
H-atom treatment	constrained				
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, -0.10	0.19, -0.15	0.20, -0.15	0.21, -0.14	0.35, -0.12
CCDC deposition number	2011741	2011742	1894701	2011743	2011744

12. Quantum chemical calculations

The geometries of all compounds were fully optimized using density functional theory with the M06-2X exchange-correlation (XC) functional and the 6-311G(d) atomic basis set.[8] The equilibrium geometries, obtained with a TIGHT convergence threshold on the residual forces on the atoms (1.5 x 10^{-5} Hartree/Bohr or Hartree/radian), were used as starting point for Hessian and then vibrational frequency calculations. All compounds (besides the fluoride anion) are characterized by 3N-6 real vibrational frequencies, demonstrating these structures are minima on the potential energy surface. Gas phase reference enthalpies ($H^{\ominus}$) and Gibbs enthalpies ($G^{\ominus}$) were calculated at T = 298.15 K and P = 1.0 atm. For fluoride affinities (FIA), isodesmic reactions were employed, using G3 $FSiMe_3 \rightarrow SiMe_3^+ + F^-$ as anchor point, according to the scheme of Krossing.[9] All calculations were performed using the Gaussian16 package.[10]

B-X distances and binding energies

Table S2. B-X distances (in Å) in the Lewis adduct for eight boranes of presented in the Scheme 9 of the manuscript.

X	**9a**	**9b**	**9c**	**9d**	**4a**	**4b**	**4c**	**4d**
F^-	1.450	1.455	1.436	1.433	1.450	1.442	1.433	1.430
NH_3	1.674	1.686	1.652	1.651	1.674	1.646	1.650	1.648
PPh_3	2.127	2.220	2.114	2.116	2.171	2.047	2.046	2.074

[8] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
[9] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489.
[10] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

Table S3. Binding and reorganization energies for fluoride, ammonia and triphenylphosphine of the boranes **9a**-**9d** and **4a**-**4d**. The reorganization energy is defined as the amount of energy necessary to change the geometry of the borane from isolated to that in the product.

	9a	**9b**	**9c**	**9d**	**4a**	**4b**	**4c**	**4d**
				ΔE (kJ mol^{-1})				
F^-	-448.9	-441.5	-470.7	-496.4	-421.5	-450.0	-466.5	-490.3
NH_3	-98.2	-85.5	-121.8	-127.4	-71.3	-95.4	-113.9	-118.8
PPh_3	-79.2	-45.9	-80.6	-68.0	-48.1	-54.3	-49.3	-80.5
				ΔH^θ (kJ mol^{-1})				
F^-	-451.6	-442.8	-472.3	-497.8	-425.0	-452.3	-467.5	-490.9
F^- (corrected)[11]	-332.6	-323.7	-353.3	-378.7	-306.0	-333.3	-348.5	-371.9
NH_3	-88.2	-73.5	-110.5	-115.9	-58.6	-85.2	-102.3	-107.1
PPh_3	-71.7	-37.0	-73.1	-61.3	-39.6	-47.6	-42.0	-73.5
				ΔG^θ (kJ mol^{-1})				
F^-	-419.2	-403.4	-439.8	-464.6	-372.7	-414.2	-426.6	-449.9
NH_3	-42.5	-19.0	-62.5	-67.3	-0.2	-38.5	-54.6	-57.9
PPh_3	-7.2	40.1	-3.1	8.1	43.0	20.2	30.9	-5.3
				Reorganization energies (kJ mol^{-1})				
F^-	173.6	135.0	158.6	158.7	140.6	168.6	176.3	179.2
NH_3	74.1	88.7	91.8	91.1	95.5	106.5	101.5	102.2
PPh_3	69.3	92.0	93.2	102.8	99.7	136.0	159.4	97.4

[11] The FIA (**1**) is generally estimated using an isodesmic reaction (**3**), of which ΔH^θ is evaluated at a given level of approximation [here, M06-2X/6-311G(d)] whereas (**2**), the anchorpoint, is evaluated at a reference level (here, G3, where ΔH^θ = 958.4 kJ mol^{-1}).[9] In such a case, the above ΔH^θ values should be corrected by +119 kJ mol^{-1}.

$LA + F^- \rightarrow LAF^-$ (**1**) [FIA]

$SiMe_3F \rightarrow SiMe_3^+ + F^-$ (**2**)

$LA + SiMe_3F \rightarrow LAF^- + SiMe_3^+$ (**3**)

Global and local electrophilicity indexes

The global electrophilicity index (ω, in eV) is defined as:[12]

$$\omega\ (eV) = {\chi^2}/{2\eta} \text{ with } \chi\ (eV) = {-1}/{2}\,(\varepsilon_{HOMO} + \varepsilon_{LUMO}) \text{ and } \eta\ (eV) = \varepsilon_{LUMO} - \varepsilon_{HOMO}$$

where χ is the electronegativity of Mulliken and η the chemical hardness.

The local electrophilicity index ω_X is defined as the product of the global electrophilicity ω with a local Fukui function f_k^+ (on the atomic site *k*):[13]

$$\omega_X(eV) = \omega\, f_k^+$$

the latter can itself be conveniently expressed from the electron population of atom *k* in the system of N and N+1 electrons:[14]

$$f_k^+ = Q_k(N+1) - Q_k(N) = \Delta Q_k$$

Table S4: Global (ω) and local (ω_B, on the boron atom) electrophilicity indexes for several Lewis acids. Structures are optimized at the M06-2X/6-311G(d) level of theory. The energies of the frontier orbitals are obtained as the energies of the corresponding Kohn-Sham orbitals. The natural charges of the boron Q_B (N) and Q_B (N+1) are obtained after NBO analysis (respectively with charge=0, spin multiplicity=1 and charge=-1, spin multiplicity=2) on the same geometrical structures and at the same level of theory.

Compounds	Global Electrophilicity Index			Local (boron) electrophilicity index			
	ε_{HOMO} (eV)	ε_{LUMO} (eV)	**ω (eV)**	Q_B (N+1)	Q_B (N)	ΔQ_B	**ω_B (eV)**
9a	-8.17	-1.12	**1.53**	0.50	0.93	-0.42	-0.65
9b	-7.55	-1.06	**1.43**	0.54	1.02	-0.49	-0.69
9c	-8.25	-1.36	**1.68**	0.48	0.92	-0.44	-0.74
9d	-8.42	-1.63	**1.86**	0.49	0.92	-0.44	-0.81
4a	-7.44	-1.00	**1.38**	0.52	0.98	-0.45	-0.63
4b	-7.90	-1.08	**1.48**	0.49	0.90	-0.41	-0.61
4c	-8.03	-1.29	**1.61**	0.47	0.89	-0.41	-0.67
4d	-8.20	-1.53	**1.77**	0.47	0.88	-0.41	-0.73
$B(C_6F_5)_3$	-9.00	-2.78	**2.79**	0.44	0.88	-0.44	**-1.23**

[12] R. G. Parr, L. V. Szentpály, S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 1922

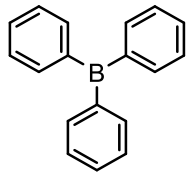
[13] a) P. Pérez, A. Toro-Labbé, A. Aizman, R. Contreras, *J. Org. Chem.* **2002**, *67*, 4747; b) E. Chamorro, P. K. Chattaraj, P. Fuentealba, *J. Phys. Chem. A.* **2003**, *107*, 7068; c) P. K. Chattaraj, U. Sarkar, D. R. Roy, *Chem. Rev.* **2006**, *106*, 2065

[14] W. Yang, W. J. Mortier, *J. Am. Chem. Soc.* **1986**, *108*, 5708

Cartesian coordinates, electronic energies, charge and multiplicities of the optimized structures

The structures coordinates are given in the same order as in scheme 9 in the manuscript.

Structure 9a



9a

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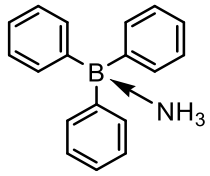
B	-0.000077	0.000241	0.000120
C	1.539721	-0.278404	0.005631
C	2.078697	-1.408689	-0.631501
H	1.412391	-2.099438	-1.138768
C	3.446860	-1.651573	-0.641396
H	3.840473	-2.522097	-1.154490
C	4.310341	-0.780568	0.015937
H	5.377617	-0.973987	0.019980
C	3.802653	0.338992	0.668109
H	4.472901	1.016635	1.185378
C	2.436359	0.591642	0.648069
H	2.051315	1.472823	1.151693
C	-0.528864	1.473010	-0.000447
C	-1.733785	1.815764	0.635415
H	-2.306500	1.042646	1.138070
C	-2.198302	3.125396	0.650389
H	-3.122708	3.368324	1.162690
C	-1.479600	4.123321	-0.000688
H	-1.845747	5.144294	-0.000795
C	-0.290540	3.809648	-0.651844
H	0.268508	4.584745	-1.164389
C	0.183346	2.503430	-0.636666
H	1.116987	2.270490	-1.139111
C	-1.011295	-1.193999	-0.004917
C	-0.709651	-2.408109	0.634366
H	0.242946	-2.516690	1.143432
C	-1.611163	-3.465543	0.644104
H	-1.362512	-4.386992	1.158999
C	-2.830261	-3.343228	-0.015529
H	-3.530710	-4.171348	-0.019749

C	-3.149270	-2.157256	-0.669758
H	-4.096622	-2.061372	-1.188737
C	-2.255519	-1.093387	-0.649539
H	-2.517601	-0.169018	-1.154757



9a-NH_3

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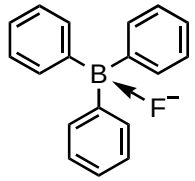
B	0.124723	0.131600	-0.617379
C	1.647058	-0.194244	-0.169730
C	2.029214	-1.417459	0.392470
H	1.279162	-2.187370	0.543694
C	3.345922	-1.672870	0.769791
H	3.605436	-2.631180	1.207417
C	4.326822	-0.705749	0.587529
H	5.353060	-0.903683	0.877155
C	3.977358	0.524847	0.039389
H	4.729859	1.295238	-0.093238
C	2.657577	0.768792	-0.323662
H	2.404795	1.759636	-0.701245
C	-0.523770	1.432770	0.096927
C	0.054355	2.058520	1.207151
H	0.976385	1.659626	1.618248
C	-0.524269	3.176520	1.804288
H	-0.050938	3.632802	2.667399
C	-1.704295	3.708304	1.299046
H	-2.154912	4.580317	1.760315
C	-2.309293	3.103595	0.201327
H	-3.239653	3.498399	-0.193522
C	-1.725104	1.983040	-0.378435
H	-2.249796	1.500776	-1.203153
C	-0.850756	-1.160229	-0.677336
C	-2.034275	-1.255105	0.063406
H	-2.318517	-0.433846	0.713788
C	-2.855976	-2.378267	-0.005439
H	-3.763916	-2.419360	0.587171
C	-2.517018	-3.444543	-0.829343
H	-3.156749	-4.318429	-0.887222
C	-1.341310	-3.385381	-1.571596
H	-1.055686	-4.217722	-2.206417

C	-0.526727	-2.261901	-1.485771
H	0.412862	-2.266938	-2.038119
N	0.272358	0.591166	-2.219947
H	0.630065	-0.175789	-2.785371
H	0.911700	1.377465	-2.314100
H	-0.629151	0.870329	-2.601136



9a-F^-

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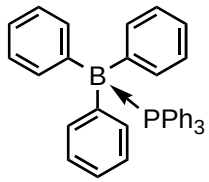
B	0.143312	0.187372	-0.816468
C	1.637142	-0.143693	-0.242878
C	1.891532	-0.990864	0.843157
H	1.059393	-1.511506	1.312282
C	3.180186	-1.206485	1.328019
H	3.338207	-1.871773	2.172817
C	4.267135	-0.582089	0.724467
H	5.274285	-0.749954	1.094932
C	4.045583	0.254906	-0.366327
H	4.886188	0.743877	-0.852128
C	2.752016	0.465969	-0.834233
H	2.586338	1.115281	-1.688971
C	-0.532255	1.426091	0.007412
C	-0.379563	1.628961	1.384816
H	0.268962	0.960861	1.947599
C	-1.013606	2.674070	2.054077
H	-0.870397	2.799614	3.124121
C	-1.819624	3.565261	1.352889
H	-2.312592	4.384517	1.868187
C	-1.977914	3.396616	-0.020421
H	-2.598663	4.090001	-0.582167
C	-1.343881	2.343737	-0.673258
H	-1.466800	2.220909	-1.745339
C	-0.809670	-1.138454	-0.753643
C	-1.543446	-1.525695	0.374765
H	-1.531485	-0.887602	1.255852
C	-2.307422	-2.691035	0.397402
H	-2.864361	-2.957847	1.291798
C	-2.369689	-3.507168	-0.727679
H	-2.967517	-4.413958	-0.717745

C	-1.661344	-3.139665	-1.868953
H	-1.706638	-3.764200	-2.757522
C	-0.897385	-1.976436	-1.873588
H	-0.352115	-1.692112	-2.768782
F	0.271226	0.585489	-2.204929



9a-PPh_3

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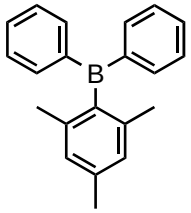
B	0.000366	0.000379	-1.399623
C	-1.561414	-0.252398	-1.752070
C	-1.985986	-1.379775	-2.467272
H	-1.248074	-2.075532	-2.850591
C	-3.334388	-1.641782	-2.703168
H	-3.620457	-2.529084	-3.258392
C	-4.310300	-0.773658	-2.229607
H	-5.361050	-0.979430	-2.403216
C	-3.920154	0.375991	-1.547271
H	-4.666715	1.076559	-1.187747
C	-2.571607	0.629680	-1.324707
H	-2.301916	1.537648	-0.794268
C	0.562279	1.479670	-1.750330
C	-0.202377	2.412288	-2.463272
H	-1.174240	2.121797	-2.846201
C	0.244780	3.711395	-2.697381
H	-0.380981	4.403789	-3.250938
C	1.484990	4.121620	-2.224148
H	1.832108	5.134721	-2.396442
C	2.286066	3.207770	-1.543950
H	3.266386	3.503452	-1.184847
C	1.831615	1.912685	-1.323145
H	2.483228	1.224042	-0.794351
C	1.000596	-1.225678	-1.751173
C	2.190975	-1.029470	-2.463311
H	2.425849	-0.042270	-2.845174
C	3.092179	-2.066347	-2.698247
H	4.005005	-1.870213	-3.251143
C	2.826724	-3.345971	-2.226669
H	3.530326	-4.153193	-2.399563
C	1.634371	-3.583103	-1.547291

H	1.399690	-4.580259	-1.189480
C	0.740336	-2.541912	-1.325666
H	-0.182092	-2.762450	-0.797484
P	-0.000194	-0.000476	0.727222
C	1.673406	0.121056	1.462637
C	2.004043	1.131491	2.366857
C	2.659557	-0.793071	1.065298
C	3.303239	1.238938	2.854654
H	1.253073	1.841205	2.692049
C	3.952704	-0.680861	1.559200
H	2.424502	-1.591324	0.370599
C	4.279859	0.338667	2.448727
H	3.547845	2.030958	3.553251
H	4.706406	-1.391130	1.239089
H	5.292486	0.427441	2.825833
C	-0.942605	1.387737	1.462929
C	-1.981662	1.168156	2.368515
C	-0.645607	2.699087	1.064986
C	-2.724525	2.239039	2.857191
H	-2.219692	0.162771	2.694028
C	-1.389477	3.762351	1.559942
H	0.162114	2.895420	0.369167
C	-2.434680	3.535156	2.450825
H	-3.531777	2.054227	3.556725
H	-1.152346	4.770406	1.239577
H	-3.018054	4.367285	2.828641
C	-0.731603	-1.510772	1.462397
C	-0.023202	-2.300101	2.369630
C	-2.015273	-1.909336	1.063141
C	-0.580176	-3.478154	2.858860
H	0.966116	-2.003396	2.696180
C	-2.565125	-3.084531	1.558522
H	-2.587849	-1.308540	0.365785
C	-1.847216	-3.875207	2.451378
H	-0.017685	-4.084222	3.559898
H	-3.556277	-3.383376	1.237044
H	-2.276917	-4.795940	2.829691

Structure 9b



9b

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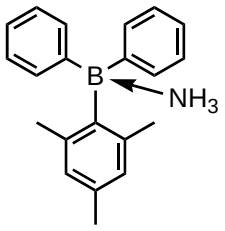
B	0.518546	0.001187	-0.000779
C	1.276969	1.362854	-0.114742
C	0.663280	2.456179	-0.748083
C	1.305496	3.683231	-0.855643
C	2.569612	3.853823	-0.298007
C	3.189679	2.794371	0.357518
C	2.553535	1.561159	0.435806
C	-1.055605	-0.001998	-0.000105
C	-1.769084	0.569813	1.068040
C	-3.162024	0.544223	1.062242
C	-3.876580	-0.013867	0.005672
C	-3.161510	-0.569085	-1.052392
C	-1.768723	-0.581350	-1.064750
C	1.282612	-1.357323	0.113085
C	2.559670	-1.550494	-0.438092
C	3.200907	-2.781085	-0.359916
C	2.585539	-3.842919	0.296168
C	1.321040	-3.677395	0.854474
C	0.673725	-2.453013	0.747010
C	-1.036646	1.200278	2.230220
C	-5.383031	0.008873	-0.007822
C	-1.035788	-1.212767	-2.226056
H	-0.335029	2.333934	-1.158529
H	0.819277	4.510350	-1.361011
H	3.068274	4.814508	-0.368062
H	4.168192	2.931236	0.804492
H	3.042899	0.742631	0.954224
H	-3.703918	0.973236	1.901603
H	-3.703447	-1.009006	-1.886146
H	3.045399	-0.730062	-0.956920
H	4.179725	-2.914037	-0.807403
H	3.088156	-4.801547	0.366154
H	0.838472	-4.506396	1.360255
H	-0.324915	-2.334839	1.157892
H	-0.233196	0.556193	2.599601

H	-1.713730	1.396913	3.062733
H	-0.575661	2.147507	1.937250
H	-5.789113	-0.853061	-0.540144
H	-5.753086	0.908426	-0.508049
H	-5.789963	0.005304	1.004759
H	-1.712932	-1.412046	-3.057901
H	-0.572701	-2.158564	-1.931752
H	-0.233860	-0.567663	-2.596898

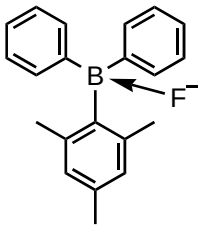


9b-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -894.141699

C	-1.198672	1.377241	0.260972
C	-0.629618	2.544469	0.794754
C	-1.213523	3.795028	0.626786
C	-2.399072	3.914135	-0.093357
C	-2.984508	2.775409	-0.634025
C	-2.392680	1.527136	-0.451352
C	1.112847	-0.083972	0.195270
C	1.618190	0.621197	-0.923950
C	2.990547	0.686751	-1.161515
C	3.916644	0.046182	-0.346123
C	3.418525	-0.740019	0.683127
C	2.049592	-0.829967	0.944605
C	-1.298957	-1.348360	0.006625
C	-2.594017	-1.639419	0.463954
C	-3.301186	-2.753982	0.025376
C	-2.727275	-3.615001	-0.904916
C	-1.449685	-3.348430	-1.383498
C	-0.749086	-2.234334	-0.927639
B	-0.481637	-0.058564	0.538595
N	-0.648487	-0.109032	2.215250
C	1.640377	-1.841049	2.001472
C	0.717890	1.264095	-1.959003
C	5.396693	0.176737	-0.592495
H	0.326478	2.481403	1.313367
H	-0.739182	4.677902	1.042801

H	-2.856890	4.886790	-0.236718
H	-3.903623	2.858782	-1.204750
H	-2.859235	0.652845	-0.895541
H	3.346158	1.242967	-2.025945
H	4.110914	-1.322458	1.286899
H	-3.083810	-0.964605	1.165184
H	-4.300716	-2.946991	0.400946
H	-3.273545	-4.484107	-1.254811
H	-0.994624	-4.012557	-2.110834
H	0.254053	-2.047516	-1.301114
H	-1.548083	0.298568	2.458715
H	-0.605163	-1.048450	2.599687
H	2.415081	-2.601313	2.106833
H	0.723798	-2.365962	1.718823
H	1.511146	-1.404325	2.998624
H	1.245800	1.334790	-2.912002
H	-0.189499	0.680692	-2.122321
H	0.403829	2.270889	-1.674546
H	5.946174	-0.670493	-0.178280
H	5.790433	1.084706	-0.126655
H	5.618259	0.235525	-1.659921
H	0.071695	0.455871	2.661425

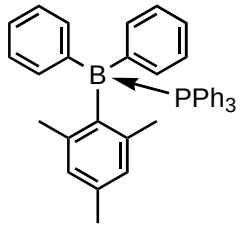


9b-F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -937.533143

C	-1.343625	1.263472	0.341842
C	-1.011716	2.470816	0.973757
C	-1.712793	3.648107	0.737036
C	-2.792729	3.651040	-0.144589
C	-3.159938	2.463185	-0.767178
C	-2.445195	1.291807	-0.518542
C	1.127821	0.047309	0.259249
C	1.582194	0.740458	-0.884177
C	2.945853	0.818997	-1.186832
C	3.910414	0.210769	-0.396194
C	3.466890	-0.529111	0.694093
C	2.113190	-0.628793	1.018174

C	-1.134418	-1.417763	0.073831
C	-2.210846	-2.019464	0.742107
C	-2.860112	-3.141955	0.237575
C	-2.448294	-3.703473	-0.969219
C	-1.378273	-3.133115	-1.650519
C	-0.733363	-2.012470	-1.128427
B	-0.458657	-0.069715	0.703242
C	1.749496	-1.528717	2.180383
C	0.634061	1.397620	-1.867413
C	5.380581	0.342094	-0.705934
H	-0.170492	2.477758	1.662544
H	-1.419857	4.567829	1.236741
H	-3.343116	4.567313	-0.337702
H	-4.006603	2.448434	-1.448503
H	-2.745576	0.373900	-1.018970
H	3.258403	1.366198	-2.075116
H	4.196754	-1.060520	1.303706
H	-2.533111	-1.586598	1.685134
H	-3.689984	-3.582881	0.783768
H	-2.951861	-4.578702	-1.369353
H	-1.039050	-3.567576	-2.587115
H	0.119167	-1.597530	-1.661870
H	2.601449	-2.159993	2.448956
H	0.903725	-2.170873	1.927854
H	1.443895	-0.953626	3.054199
H	1.151466	1.602248	-2.808869
H	-0.226865	0.763444	-2.084786
H	0.233411	2.340443	-1.487209
H	5.922595	-0.575347	-0.461887
H	5.838250	1.153063	-0.129746
H	5.546081	0.559457	-1.763996
F	-0.541175	-0.158083	2.153542



9b-PPh_3

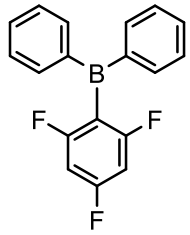
Charge = 0; Multiplicity = 1; E (u.a.) = -1873.730946

C	0.220571	1.126954	-1.979231
C	0.922723	2.326609	-2.172117

C	0.425334	3.356145	-2.967245
C	-0.800701	3.215241	-3.607698
C	-1.511302	2.027619	-3.457724
C	-1.004343	1.005864	-2.661446
C	2.283103	0.341286	-0.362322
C	3.379944	-0.243827	-1.050495
C	4.679755	-0.107013	-0.565329
C	4.975257	0.628578	0.576017
C	3.925052	1.308537	1.174316
C	2.611157	1.201054	0.709127
C	0.612786	-1.549915	-1.311401
C	0.047305	-2.022437	-2.501997
C	-0.086853	-3.382938	-2.766739
C	0.347022	-4.324367	-1.840415
C	0.950698	-3.886990	-0.664209
C	1.084779	-2.525434	-0.417393
B	0.786892	0.022084	-0.942314
P	-0.838518	0.055641	0.569718
C	-1.515410	1.652049	1.199885
C	-2.335319	-0.738564	-0.152066
C	-0.564950	-0.938836	2.089335
C	-1.830329	1.826967	2.548526
C	-2.322834	3.046048	3.004209
C	-2.506462	4.102374	2.120930
C	-2.193138	3.935949	0.776088
C	-1.697104	2.722386	0.314882
C	-3.457671	0.009102	-0.517082
C	-2.337310	-2.120142	-0.378517
C	-4.551588	-0.608848	-1.114621
C	-3.434021	-2.732096	-0.971963
C	-4.540980	-1.978640	-1.347965
C	-1.633605	-1.562926	2.740909
C	0.717566	-1.039344	2.634514
C	-1.421621	-2.270964	3.917881
C	-0.142001	-2.365149	4.455531
C	0.925307	-1.749396	3.812383
C	6.380837	0.712620	1.109863
C	3.241613	-0.961558	-2.378724
C	1.594002	2.099764	1.369525
H	1.880854	2.460825	-1.679434
H	0.996872	4.270951	-3.083911
H	-1.194116	4.016294	-4.224165
H	-2.465834	1.896760	-3.957124
H	-1.600234	0.107737	-2.548517

H	5.492627	-0.577198	-1.114342
H	4.129752	1.966813	2.015413
H	-0.269650	-1.319679	-3.263477
H	-0.529352	-3.706997	-3.703011
H	0.239832	-5.384757	-2.042002
H	1.325832	-4.606212	0.056393
H	1.594390	-2.212743	0.487325
H	-1.680461	1.019715	3.255645
H	-2.558752	3.166816	4.055475
H	-2.887350	5.052260	2.478767
H	-2.325106	4.754091	0.077134
H	-1.448563	2.620355	-0.735028
H	-3.486590	1.077360	-0.342487
H	-1.485503	-2.726210	-0.091111
H	-5.413541	-0.013661	-1.394042
H	-3.412839	-3.801879	-1.146203
H	-5.393660	-2.458216	-1.815551
H	-2.634333	-1.494014	2.328841
H	1.563514	-0.580359	2.134116
H	-2.258058	-2.751006	4.412998
H	0.022456	-2.920879	5.371853
H	1.926500	-1.823664	4.220986
H	7.110342	0.773931	0.299620
H	6.626589	-0.172854	1.703141
H	6.511876	1.586147	1.750903
H	4.174949	-0.870722	-2.937796
H	3.023547	-2.025449	-2.260789
H	2.446159	-0.534233	-2.990408
H	0.901271	2.521420	0.641459
H	1.001510	1.595274	2.138325
H	2.094762	2.934372	1.863458

Structure 9c

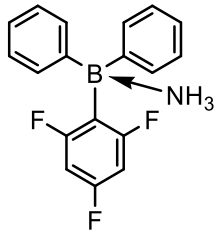


9c

Charge = 0; Multiplicity = 1; E (u.a.) = -1017.382578041178

B	0.828396	-0.001199	-0.047926
C	1.586767	1.349062	0.114147

C	1.021882	2.550378	-0.344161
C	1.694733	3.758466	-0.223837
C	2.941756	3.797294	0.393497
C	3.514040	2.625981	0.879220
C	2.847954	1.415966	0.728473
C	-0.748825	0.005897	-0.081416
C	-1.521302	0.714590	0.839426
C	-2.905190	0.739194	0.846814
C	-3.552468	0.018528	-0.140958
C	-2.870355	-0.708128	-1.100497
C	-1.487864	-0.695987	-1.034359
C	1.580796	-1.358253	-0.177924
C	2.866283	-1.436596	-0.738149
C	3.527266	-2.652577	-0.860725
C	2.924365	-3.818613	-0.399987
C	1.652650	-3.768470	0.163840
C	0.986182	-2.554361	0.255731
F	-0.895582	1.397917	1.804677
F	-0.827907	-1.385107	-1.972305
F	-4.887342	0.024539	-0.169306
H	0.042432	2.532335	-0.813070
H	1.245892	4.671423	-0.598838
H	3.464375	4.741564	0.500933
H	4.479158	2.657248	1.372426
H	3.301089	0.508262	1.113420
H	-3.454169	1.294524	1.595118
H	-3.392051	-1.258636	-1.871537
H	3.343498	-0.533069	-1.103314
H	4.512137	-2.692606	-1.312508
H	3.442566	-4.767562	-0.485327
H	1.180101	-4.677290	0.519251
H	-0.012099	-2.527431	0.682622

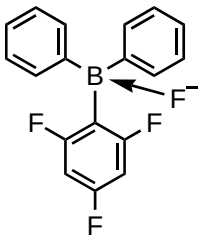


9c-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1073.961769296858

C	1.150454	-1.399627	0.262044
C	0.668743	-2.562191	0.880769

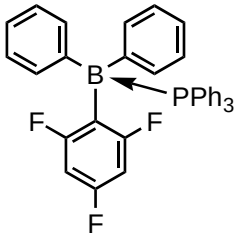
C	1.223959	-3.813870	0.638869
C	2.282054	-3.937547	-0.255596
C	2.761754	-2.806012	-0.905419
C	2.201487	-1.557884	-0.647352
C	-1.095316	0.026469	0.095066
C	-1.363063	-0.080419	-1.270210
C	-2.625068	-0.127039	-1.835444
C	-3.705438	-0.070287	-0.972441
C	-3.545122	0.031949	0.395011
C	-2.243251	0.075810	0.869332
C	1.287639	1.341825	0.119231
C	2.650187	1.455872	0.438432
C	3.386956	2.596068	0.136983
C	2.772958	3.666906	-0.504994
C	1.425920	3.581859	-0.835702
C	0.698927	2.435976	-0.522945
F	-0.318196	-0.128691	-2.108580
F	-2.111852	0.173142	2.223838
F	-4.943645	-0.114801	-1.479121
H	-0.193653	-2.504813	1.545670
H	0.824613	-4.692144	1.135032
H	2.718891	-4.910078	-0.454199
H	3.572901	-2.895667	-1.620271
H	2.579904	-0.688274	-1.174969
H	-2.758081	-0.208151	-2.905883
H	-4.392556	0.075063	1.065671
H	3.161348	0.617939	0.910678
H	4.439985	2.646409	0.393229
H	3.341679	4.557630	-0.748353
H	0.938703	4.409578	-1.340095
H	-0.353499	2.396537	-0.788634
B	0.458940	0.030614	0.579616
N	0.485422	0.149752	2.227573
H	1.458866	0.172188	2.523910
H	0.036466	1.005736	2.545263
H	0.026424	-0.628172	2.695274



9c-F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -1117.350539531175

C	1.325331	-1.297607	0.305347
C	0.934597	-2.495681	0.919331
C	1.493581	-3.721542	0.574530
C	2.479537	-3.785205	-0.407315
C	2.893626	-2.610881	-1.026256
C	2.323089	-1.390284	-0.668920
C	-0.980200	0.118205	0.387388
C	-1.471107	-0.364231	-0.820466
C	-2.804218	-0.373825	-1.214262
C	-3.721233	0.154172	-0.329276
C	-3.336284	0.681325	0.886054
C	-1.980282	0.651565	1.196615
C	1.352265	1.427860	0.247639
C	2.085175	2.248633	1.111735
C	2.731395	3.398669	0.663556
C	2.662249	3.762466	-0.677438
C	1.937001	2.964824	-1.559142
C	1.292604	1.821004	-1.096811
F	-0.602503	-0.858122	-1.728310
F	-1.656353	1.209433	2.374884
F	-5.029895	0.165628	-0.666426
H	0.175246	-2.454780	1.696433
H	1.163931	-4.630455	1.070998
H	2.920896	-4.738563	-0.683189
H	3.667286	-2.644822	-1.788762
H	2.665897	-0.484362	-1.161445
H	-3.102376	-0.775604	-2.173612
H	-4.055154	1.110327	1.571851
H	2.136351	1.970315	2.159728
H	3.289897	4.015289	1.362918
H	3.163966	4.657998	-1.032208
H	1.870822	3.238714	-2.608620
H	0.729528	1.211770	-1.800281
B	0.626599	0.089652	0.819679
F	0.701172	0.082718	2.254180



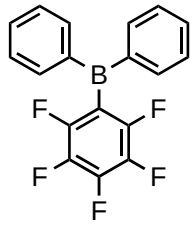
9c-PPh_3

Charge = 0; Multiplicity = 1; E (u.a.) = -2053.550400901341

C	0.312609	-1.974910	0.966548
C	0.570312	-2.832617	-0.114097
C	0.228332	-4.180035	-0.089111
C	-0.370852	-4.723372	1.043598
C	-0.581340	-3.911162	2.151937
C	-0.238871	-2.562093	2.111025
C	2.176900	-0.164659	0.314231
C	3.215436	-0.880308	0.918265
C	4.560749	-0.745652	0.613075
C	4.905069	0.183348	-0.349944
C	3.956222	0.961949	-0.982489
C	2.634961	0.763770	-0.611372
C	0.303150	0.554576	2.111859
C	-0.919364	0.479877	2.804571
C	-1.256830	1.384576	3.805803
C	-0.371339	2.398206	4.160521
C	0.855105	2.482864	3.511706
C	1.179410	1.575667	2.506678
F	2.917232	-1.749838	1.890866
F	1.727417	1.547443	-1.235070
F	6.195231	0.340494	-0.672098
H	1.050960	-2.440137	-1.004219
H	0.433080	-4.806112	-0.951256
H	-0.644775	-5.772499	1.070429
H	-1.010769	-4.329118	3.056510
H	-0.390173	-1.963905	3.001423
H	5.308322	-1.338302	1.123027
H	4.226049	1.702702	-1.723000
H	-1.643611	-0.283639	2.543388
H	-2.215674	1.298425	4.306342
H	-0.631711	3.107132	4.938968
H	1.560720	3.261107	3.782637
H	2.137521	1.680017	2.008176
B	0.653796	-0.395769	0.847494
P	-0.789624	0.255080	-0.553418

C	-0.954949	2.062357	-0.829986
C	-0.985896	2.584085	-2.125090
C	-1.015220	2.938009	0.260689
C	-1.082212	3.956324	-2.326969
H	-0.922354	1.925165	-2.982796
C	-1.111989	4.308542	0.049970
H	-0.997329	2.563672	1.276581
C	-1.144645	4.821692	-1.241642
H	-1.103027	4.346998	-3.337998
H	-1.156389	4.973036	0.905413
H	-1.215739	5.891696	-1.401475
C	-0.732287	-0.459612	-2.241948
C	-1.917401	-0.694472	-2.945350
C	0.490721	-0.714235	-2.866826
C	-1.877289	-1.177119	-4.248432
H	-2.874966	-0.498863	-2.476299
C	0.526923	-1.199805	-4.168763
H	1.421398	-0.547215	-2.340318
C	-0.655836	-1.431344	-4.861981
H	-2.803641	-1.355754	-4.782234
H	1.483103	-1.399130	-4.638652
H	-0.625692	-1.811229	-5.876933
C	-2.441188	-0.273181	0.046094
C	-3.402960	0.647362	0.466001
C	-2.723184	-1.642989	0.126121
C	-4.617443	0.206360	0.982557
H	-3.211490	1.710893	0.396901
C	-3.937480	-2.075801	0.643140
H	-2.000822	-2.376346	-0.214244
C	-4.883569	-1.153834	1.080428
H	-5.354134	0.931872	1.308232
H	-4.136910	-3.139277	0.708128
H	-5.828011	-1.495616	1.488882

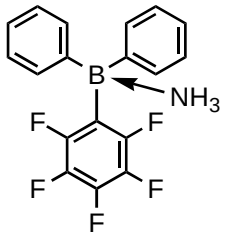
Structure 9d



9d

Charge = 0; Multiplicity = 1; E (u.a.) = -1215.828867

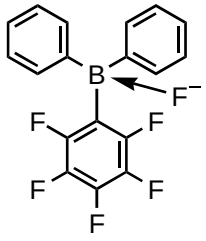
B	0.897708	0.000000	0.000000
C	1.641637	-1.349192	0.201935
C	1.046434	-2.398595	0.921422
C	1.706173	-3.602782	1.122435
C	2.970941	-3.797855	0.574681
C	3.573763	-2.784705	-0.164192
C	2.920056	-1.571328	-0.336900
C	-0.686867	0.000000	0.000000
C	-1.422131	-0.903290	-0.762028
C	-2.807492	-0.912399	-0.780212
C	-3.500088	0.000000	0.000000
C	-2.807491	0.912415	0.780212
C	-1.422129	0.903300	0.762029
C	1.641649	1.349185	-0.201932
C	2.920068	1.571308	0.336909
C	3.573790	2.784677	0.164197
C	2.970982	3.797832	-0.574681
C	1.706213	3.602771	-1.122439
C	1.046460	2.398592	-0.921425
F	-0.797560	-1.789849	-1.537602
F	-0.797557	1.789863	1.537599
F	-4.825045	0.000000	0.000000
H	0.053944	-2.261800	1.340639
H	1.233772	-4.393742	1.693831
H	3.483586	-4.742728	0.718064
H	4.552442	-2.941917	-0.603410
H	3.395344	-0.789608	-0.920195
H	3.395343	0.789587	0.920210
H	4.552469	2.941879	0.603418
H	3.483639	4.742698	-0.718066
H	1.233823	4.393735	-1.693839
H	0.053971	2.261807	-1.340647
F	-3.476509	1.778984	1.532885
F	-3.476515	-1.778963	-1.532887



9d-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1272.410198

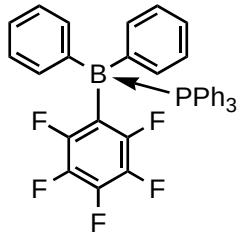
C	-1.398542	1.467599	0.186085
C	-0.892461	2.644453	0.756339
C	-1.326822	3.904277	0.359709
C	-2.282121	4.019098	-0.644822
C	-2.781288	2.869976	-1.247207
C	-2.343260	1.614463	-0.834945
C	0.742160	-0.103000	0.329945
C	1.105231	-0.138825	-1.013691
C	2.418034	-0.208326	-1.447167
C	3.442486	-0.236930	-0.512292
C	3.134295	-0.199432	0.834796
C	1.802650	-0.134343	1.218404
C	-1.717404	-1.264068	0.251300
C	-3.108395	-1.260573	0.442457
C	-3.893327	-2.375368	0.169649
C	-3.300467	-3.538270	-0.311978
C	-1.925922	-3.570436	-0.512858
C	-1.150991	-2.448473	-0.230510
F	0.155332	-0.117799	-1.951912
F	1.576099	-0.095938	2.555706
F	4.708176	-0.301286	-0.908887
H	-0.105238	2.589072	1.509025
H	-0.912379	4.793868	0.821886
H	-2.623605	4.997438	-0.964409
H	-3.511306	2.950943	-2.045494
H	-2.733514	0.729366	-1.326866
H	-3.599381	-0.351449	0.786841
H	-4.966539	-2.334935	0.322759
H	-3.906612	-4.409938	-0.532505
H	-1.454528	-4.470727	-0.892181
H	-0.078373	-2.502209	-0.393235
B	-0.847258	0.028488	0.679696
N	-1.014881	0.050247	2.321911
H	-2.010156	0.108557	2.528132
H	-0.654798	-0.801312	2.747391
H	-0.551089	0.837409	2.769496
F	4.106124	-0.224575	1.743698
F	2.710363	-0.247199	-2.743270



9d-F^{-}

Charge = -1; Multiplicity = 1; E (u.a.) = -1315.806615

C	-1.514952	1.449418	0.032940
C	-2.145192	2.454747	0.773912
C	-2.717981	3.568383	0.163471
C	-2.675227	3.707046	-1.219993
C	-2.050862	2.722298	-1.981377
C	-1.479396	1.616611	-1.358499
C	0.728150	0.028250	0.337023
C	1.133375	-0.651880	-0.804034
C	2.456280	-0.780609	-1.201483
C	3.451280	-0.201537	-0.436247
C	3.100828	0.503124	0.700335
C	1.763474	0.610005	1.060246
C	-1.659205	-1.236488	0.505876
C	-2.692539	-1.407122	-0.419234
C	-3.340238	-2.630539	-0.581839
C	-2.969950	-3.726512	0.189387
C	-1.950030	-3.582093	1.126815
C	-1.313774	-2.354709	1.276950
F	0.229257	-1.220875	-1.619962
F	1.526448	1.339963	2.156339
F	4.735652	-0.311310	-0.797355
H	-2.175411	2.351867	1.854037
H	-3.198179	4.332419	0.768868
H	-3.119911	4.573373	-1.700615
H	-2.006757	2.819315	-3.062583
H	-0.996136	0.858314	-1.970435
H	-3.002011	-0.562167	-1.028120
H	-4.139398	-2.727549	-1.311657
H	-3.471321	-4.681800	0.064865
H	-1.654163	-4.428563	1.740647
H	-0.528567	-2.248483	2.021603
B	-0.873846	0.166207	0.795488
F	4.061874	1.079269	1.435932
F	2.784936	-1.451907	-2.313465
F	-0.902964	0.381736	2.211894



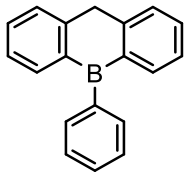
9d-PPh_3

Charge = 0; Multiplicity = 1; E (u.a.) = -2251.991904

C	0.570527	-0.142608	2.198280
C	1.022347	-1.471403	2.274874
C	1.261600	-2.103807	3.487488
C	1.077650	-1.410566	4.680585
C	0.676953	-0.081784	4.636329
C	0.433145	0.540305	3.413011
C	1.857794	0.345009	0.002822
C	2.909188	1.189551	0.358056
C	4.204771	1.034984	-0.110282
C	4.505907	-0.020645	-0.954822
C	3.506114	-0.907741	-1.309380
C	2.225599	-0.711101	-0.816648
C	-0.134909	2.085619	0.680942
C	-1.159211	2.536788	1.526812
C	-1.678393	3.824286	1.441291
C	-1.204407	4.704139	0.475757
C	-0.201474	4.282661	-0.391512
C	0.322489	2.999255	-0.279788
F	2.703409	2.198927	1.206595
F	1.310350	-1.633628	-1.177188
F	5.743011	-0.184190	-1.411172
B	0.413101	0.567483	0.747110
F	3.780583	-1.938913	-2.105476
F	5.165078	1.881043	0.252662
P	-1.134841	-0.430993	-0.294208
C	-1.319051	-2.217525	0.044134
C	-2.791768	0.292941	0.056407
C	-1.129624	-0.250529	-2.117620
C	-1.137046	-3.179470	-0.951156
C	-1.242072	-4.531275	-0.643731
C	-1.523461	-4.934822	0.656389
C	-1.687706	-3.982749	1.656606
C	-1.579594	-2.630903	1.355884
C	-3.772493	-0.338904	0.820042
C	-3.074308	1.538921	-0.517949

C	-5.005676	0.275003	1.026189
C	-4.305671	2.142944	-0.315009
C	-5.273394	1.515668	0.464209
C	-2.218299	-0.746863	-2.843650
C	-0.116547	0.432793	-2.785491
C	-2.272767	-0.586276	-4.220349
C	-1.251274	0.089536	-4.884032
C	-0.179888	0.602853	-4.166128
H	1.188224	-2.034513	1.359787
H	1.600430	-3.134432	3.500320
H	1.267303	-1.895491	5.632015
H	0.564989	0.482490	5.556109
H	0.168097	1.590453	3.413343
H	-1.595958	1.854375	2.249303
H	-2.470806	4.130114	2.116210
H	-1.609369	5.707393	0.399671
H	0.182068	4.958097	-1.148795
H	1.121571	2.711754	-0.957277
H	-0.893658	-2.878197	-1.962909
H	-1.095148	-5.269360	-1.423722
H	-1.602189	-5.989945	0.892690
H	-1.883308	-4.287877	2.678061
H	-1.665691	-1.901606	2.153858
H	-3.601991	-1.319840	1.242114
H	-2.325847	2.047515	-1.117878
H	-5.758296	-0.228901	1.621708
H	-4.502093	3.111719	-0.759640
H	-6.234852	1.990200	0.625150
H	-3.026806	-1.254154	-2.326255
H	0.719855	0.843957	-2.235730
H	-3.116408	-0.980277	-4.775208
H	-1.297349	0.220629	-5.959176
H	0.612174	1.138509	-4.676320

Structure 4b

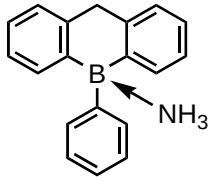


4b

Charge = 0; Multiplicity = 1; E (u.a.) = -757.781142316

B	-0.176517	0.122723	0.063546

C	1.320456	-0.217043	0.298418
C	2.342175	0.734765	0.115859
H	2.073947	1.739080	-0.194200
C	3.672899	0.425085	0.336253
H	4.442779	1.174122	0.189469
C	4.015144	-0.859471	0.758540
H	5.054344	-1.115244	0.935602
C	3.026758	-1.808686	0.965052
H	3.297722	-2.803788	1.307180
C	1.681959	-1.501170	0.743776
C	-0.617473	1.542860	-0.437656
C	-1.535087	2.317874	0.286665
H	-1.949360	1.928081	1.212212
C	-1.916346	3.583010	-0.146759
H	-2.615771	4.168374	0.440145
C	-1.409166	4.092582	-1.337513
H	-1.713890	5.073974	-1.683869
C	-0.509163	3.337030	-2.081775
H	-0.112570	3.726966	-3.012886
C	-0.108942	2.085334	-1.626950
H	0.604300	1.512271	-2.212681
C	-1.222106	-0.991228	0.341735
C	-0.793446	-2.251889	0.794497
C	-1.729738	-3.260003	1.037555
H	-1.390370	-4.230524	1.389151
C	-3.081889	-3.037683	0.830615
H	-3.795098	-3.831790	1.024095
C	-3.522843	-1.799882	0.362695
H	-4.578460	-1.628678	0.184709
C	-2.599346	-0.798055	0.120212
H	-2.939949	0.158415	-0.261739
C	0.661782	-2.577090	1.016373
H	0.787622	-2.911608	2.053598
H	0.912139	-3.454143	0.406722

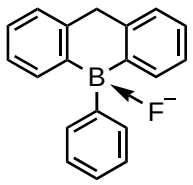


4b-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -814.350267907

B	0.097666	-0.008441	-0.805987
C	1.448349	-0.386182	-0.017629

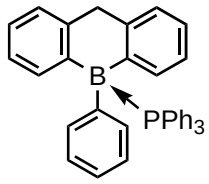
C	2.752507	-0.178772	-0.472979
H	2.934610	0.277397	-1.446138
C	3.865659	-0.528641	0.289491
H	4.865884	-0.354363	-0.092562
C	3.684576	-1.101773	1.540412
H	4.541264	-1.382528	2.143216
C	2.394330	-1.320158	2.015813
H	2.250261	-1.774373	2.992042
C	1.286488	-0.969351	1.251386
C	-0.467965	1.476577	-0.477098
C	0.385388	2.513106	-0.075105
H	1.436682	2.297389	0.098420
C	-0.083597	3.807362	0.132688
H	0.600149	4.587484	0.451089
C	-1.430739	4.098058	-0.054912
H	-1.801277	5.103790	0.111776
C	-2.301865	3.085898	-0.444500
H	-3.357097	3.300493	-0.578395
C	-1.822416	1.795183	-0.648663
H	-2.520913	1.009810	-0.927107
C	-0.979970	-1.182926	-0.588609
C	-1.047378	-1.736073	0.702085
C	-1.954970	-2.749641	0.991299
H	-1.989471	-3.168924	1.992854
C	-2.814168	-3.236409	0.009751
H	-3.515512	-4.029354	0.245274
C	-2.762654	-2.704124	-1.270889
H	-3.426313	-3.075416	-2.044507
C	-1.851266	-1.688784	-1.556094
H	-1.846424	-1.289171	-2.570297
C	-0.118803	-1.193827	1.767584
H	-0.516594	-0.228471	2.110424
H	-0.106044	-1.855292	2.637186
N	0.457723	0.044150	-2.410749
H	0.822564	-0.849001	-2.738896
H	1.149027	0.768462	-2.593643
H	-0.371035	0.278689	-2.952911



4b-F^{-}

Charge = -1; Multiplicity = 1; E (u.a.) = -857.7411936725657

B	0.122958	-0.054890	-0.948160
C	1.472015	-0.415179	-0.128177
C	2.752037	-0.280350	-0.668452
H	2.842316	0.075021	-1.691502
C	3.894740	-0.595942	0.063459
H	4.879618	-0.480931	-0.381319
C	3.771674	-1.064477	1.367730
H	4.654651	-1.318428	1.947122
C	2.503594	-1.218620	1.922677
H	2.401089	-1.599861	2.936718
C	1.363493	-0.900759	1.186205
C	-0.446513	1.432567	-0.548282
C	0.041031	2.226876	0.495516
H	0.874375	1.860740	1.091454
C	-0.496130	3.481885	0.784872
H	-0.090509	4.069593	1.604236
C	-1.541824	3.986862	0.021450
H	-1.962183	4.964170	0.240386
C	-2.041924	3.222589	-1.031815
H	-2.857108	3.606831	-1.639487
C	-1.501132	1.970931	-1.301128
H	-1.899416	1.383808	-2.125183
C	-0.981413	-1.171187	-0.529534
C	-1.018831	-1.636652	0.795002
C	-1.948999	-2.596911	1.186090
H	-1.957380	-2.952064	2.214699
C	-2.861809	-3.113693	0.269360
H	-3.582932	-3.863551	0.581610
C	-2.830351	-2.671583	-1.049132
H	-3.529991	-3.078115	-1.774686
C	-1.893605	-1.714968	-1.435803
H	-1.849721	-1.385498	-2.470837
C	-0.020738	-1.067508	1.783987
H	-0.382047	-0.079137	2.101723
H	0.024650	-1.689818	2.683877
F	0.341826	-0.083976	-2.373198



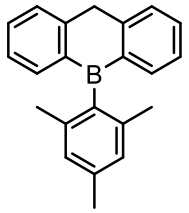
4b-PPh_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1793.938949776583

B	1.033643	0.298838	0.008623
C	1.823631	-0.451740	-1.197282
C	1.303334	-1.168836	-2.280213
H	0.231905	-1.316324	-2.382726
C	2.119366	-1.738340	-3.255710
H	1.673767	-2.288638	-4.077506
C	3.497451	-1.606501	-3.165946
H	4.143300	-2.046040	-3.918297
C	4.044665	-0.920295	-2.087030
H	5.123386	-0.830524	-1.995147
C	3.227650	-0.355475	-1.112053
C	1.012371	1.921583	-0.136697
C	1.343698	2.581127	-1.328004
H	1.638778	1.994943	-2.194731
C	1.347261	3.969755	-1.423401
H	1.616032	4.446714	-2.360285
C	1.018787	4.745810	-0.317253
H	1.020958	5.828216	-0.387288
C	0.713063	4.119701	0.886900
H	0.484717	4.714068	1.765827
C	0.723284	2.730798	0.972107
H	0.519934	2.260124	1.930591
C	1.752362	-0.110882	1.407483
C	3.159883	-0.042550	1.369177
C	3.919082	-0.323686	2.500516
H	5.002494	-0.268000	2.442523
C	3.308527	-0.675777	3.700169
H	3.910452	-0.895430	4.575270
C	1.924594	-0.743566	3.760624
H	1.429397	-1.013993	4.687364
C	1.164608	-0.461556	2.626310
H	0.086176	-0.516187	2.718853
C	3.834130	0.355519	0.075474
H	3.712281	1.438924	-0.059267
H	4.907691	0.160400	0.128654
P	-0.929767	-0.280084	-0.034650
C	-1.112529	-2.092581	-0.175806
C	-2.249839	-2.679254	-0.735143
C	-0.083191	-2.900803	0.313822
C	-2.361701	-4.063185	-0.791649
H	-3.042857	-2.060472	-1.139765
C	-0.204363	-4.285149	0.257553
H	0.813992	-2.452503	0.726076

C	-1.341224	-4.866503	-0.292026
H	-3.244027	-4.513661	-1.231722
H	0.598955	-4.906815	0.635139
H	-1.429380	-5.946057	-0.340040
C	-1.950345	0.168901	1.418814
C	-2.254481	1.517103	1.630936
C	-2.428130	-0.795429	2.307088
C	-3.010015	1.893150	2.734093
H	-1.907638	2.269809	0.931181
C	-3.186845	-0.411832	3.408489
H	-2.203091	-1.844259	2.146165
C	-3.474265	0.930594	3.625751
H	-3.238373	2.940582	2.894353
H	-3.553180	-1.166072	4.095408
H	-4.064043	1.227031	4.485722
C	-1.914337	0.451322	-1.396415
C	-3.308217	0.537231	-1.291541
C	-1.287802	0.929853	-2.547772
C	-4.058380	1.072009	-2.330456
H	-3.809001	0.199471	-0.390513
C	-2.042917	1.472283	-3.582554
H	-0.211499	0.887841	-2.638541
C	-3.426056	1.540488	-3.478230
H	-5.136819	1.131302	-2.238487
H	-1.542569	1.847294	-4.467731
H	-4.012133	1.965604	-4.285208

Structure 4a

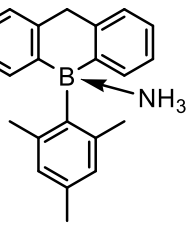


4a

Charge = 0; Multiplicity = 1; E (u.a.) = -875.697546662878

B	0.256465	-0.009477	0.180628
C	1.071720	1.308172	0.170400
C	0.444129	2.559386	0.313671
H	-0.635430	2.587416	0.433195
C	1.170434	3.737432	0.304865
H	0.671966	4.693674	0.416346
C	2.556540	3.682750	0.151023
H	3.137776	4.598656	0.142598

C	3.196440	2.461050	0.008910
H	4.276045	2.428719	-0.110012
C	2.468108	1.268645	0.016759
C	-1.307933	0.000900	0.349967
C	-1.885578	-0.112732	1.623644
C	-3.272443	-0.095941	1.759214
C	-4.109921	0.028728	0.653881
C	-3.526120	0.142625	-0.605970
C	-2.143281	0.130295	-0.771030
C	1.038525	-1.337175	0.017932
C	2.435697	-1.315116	-0.132235
C	3.133954	-2.516492	-0.278781
H	4.214196	-2.497671	-0.394789
C	2.463502	-3.730051	-0.277548
H	3.021667	-4.653116	-0.392410
C	1.076179	-3.767391	-0.129688
H	0.553708	-4.717299	-0.129424
C	0.379506	-2.580384	0.015429
H	-0.700739	-2.594836	0.130867
C	3.222989	-0.028039	-0.142152
H	3.982604	-0.083057	0.647495
H	3.794241	0.018680	-1.077622
C	-5.608808	0.011686	0.809932
C	-0.996353	-0.247802	2.836284
C	-1.531467	0.260011	-2.145155
H	-6.092125	0.658310	0.075142
H	-6.003849	-0.998336	0.668058
H	-5.909032	0.345663	1.804508
H	-2.295111	0.322664	-2.921586
H	-0.906293	1.155657	-2.214040
H	-0.890225	-0.597343	-2.372335
H	-4.164621	0.245312	-1.480267
H	-3.709917	-0.180928	2.751037
H	-1.577672	-0.303639	3.757629
H	-0.313747	0.603604	2.920186
H	-0.378977	-1.149182	2.772203

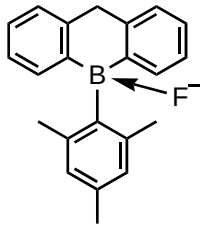


4a-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -932.2575155322747

B	0.283832	0.009174	-0.637318
C	1.094340	1.332207	-0.199930
C	0.456641	2.572394	-0.060883
H	-0.618123	2.628120	-0.217343
C	1.151565	3.719276	0.303126
H	0.631002	4.665400	0.406217
C	2.518113	3.641259	0.553940
H	3.072098	4.524794	0.852354
C	3.168389	2.420204	0.437218
H	4.232511	2.355874	0.649120
C	2.472019	1.269796	0.059043
C	-1.295804	0.035262	-0.246710
C	-1.618522	-0.234588	1.108720
C	-2.945182	-0.293405	1.528600
C	-4.008644	-0.075804	0.659912
C	-3.697947	0.263734	-0.647598
C	-2.377167	0.337737	-1.101561
C	1.060384	-1.340671	-0.194480
C	2.440208	-1.310139	0.053105
C	3.118321	-2.483400	0.396667
H	4.184190	-2.442393	0.605773
C	2.450209	-3.696959	0.476169
H	2.989775	-4.597531	0.748778
C	1.084417	-3.747577	0.209923
H	0.550905	-4.690186	0.271293
C	0.408647	-2.579247	-0.117577
H	-0.665452	-2.615503	-0.287051
C	3.240574	-0.028582	-0.081312
H	4.059073	-0.040320	0.644791
H	3.742282	-0.033584	-1.061502
N	0.522653	-0.078034	-2.291694
H	1.519817	-0.225317	-2.435353
H	0.252050	0.757295	-2.802585
H	0.038689	-0.879923	-2.690884
C	-5.434491	-0.186367	1.132531
C	-0.562705	-0.438037	2.175940
C	-2.207554	0.835506	-2.526465
H	-6.126377	0.269747	0.422513
H	-5.725853	-1.233454	1.253776
H	-5.570506	0.303086	2.099388
H	-3.159627	1.201431	-2.911346
H	-1.513416	1.680404	-2.578767
H	-1.876653	0.063230	-3.227898

H	-4.506134	0.496149	-1.336858
H	-3.154472	-0.505336	2.574871
H	-0.970711	-0.177500	3.154338
H	0.320110	0.179081	2.007293
H	-0.225375	-1.476355	2.220368

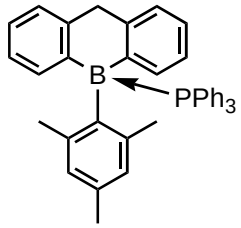


4a-F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -975.6467463419019

B	0.256157	0.049930	-0.772674
C	1.101780	1.340407	-0.251002
C	0.669445	2.628927	-0.595722
H	-0.263627	2.724695	-1.146995
C	1.384337	3.770275	-0.259423
H	1.017541	4.753246	-0.541749
C	2.581931	3.645962	0.443734
H	3.158414	4.526602	0.711918
C	3.031954	2.382225	0.797388
H	3.965801	2.277949	1.347275
C	2.303951	1.234784	0.459496
C	-1.288577	0.036346	-0.178897
C	-1.517898	-0.049728	1.213304
C	-2.810159	-0.063230	1.743266
C	-3.933071	0.007042	0.931602
C	-3.721757	0.092005	-0.438960
C	-2.441569	0.107680	-0.999637
C	1.059200	-1.323097	-0.422713
C	2.262665	-1.347876	0.292995
C	2.953080	-2.551786	0.479296
H	3.888644	-2.548742	1.036099
C	2.463786	-3.744696	-0.032737
H	3.011394	-4.670378	0.118992
C	1.264285	-3.739532	-0.743573
H	0.866965	-4.665949	-1.148994
C	0.586776	-2.542283	-0.929101
H	-0.347739	-2.536741	-1.486189
C	2.826821	-0.101788	0.943233
H	2.625845	-0.168246	2.023924

H	3.919627	-0.113536	0.854500
F	0.221663	0.143764	-2.219613
C	-5.329302	-0.007415	1.502396
C	-0.372774	-0.131450	2.197055
C	-2.380340	0.204223	-2.512641
H	-5.879038	0.901044	1.237917
H	-5.907221	-0.856319	1.124469
H	-5.309578	-0.078088	2.592281
H	-3.392902	0.246924	-2.924201
H	-1.831804	1.087544	-2.839475
H	-1.859508	-0.646841	-2.951265
H	-4.586253	0.148405	-1.099566
H	-2.938684	-0.130736	2.822399
H	-0.746728	-0.191572	3.222260
H	0.276326	0.744340	2.123697
H	0.248281	-1.010781	2.010540



4a-PPh_3

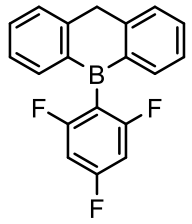
Charge = 0; Multiplicity = 1; E (u.a.) = -1911.852990384193

B	0.752135	0.682882	0.430013
C	0.230982	0.977194	1.918194
C	0.762706	0.288840	3.020525
H	1.583756	-0.403565	2.857861
C	0.273265	0.468934	4.306572
H	0.701196	-0.082258	5.137120
C	-0.770679	1.366563	4.521742
H	-1.170540	1.515285	5.519139
C	-1.270420	2.101781	3.455802
H	-2.052143	2.837084	3.629082
C	-0.770323	1.930466	2.160560
C	2.310757	0.205197	0.352448
C	3.278169	1.246858	0.348274
C	4.634383	0.957164	0.206732
C	5.111020	-0.343689	0.100637
C	4.182227	-1.365838	0.223471
C	2.814994	-1.114005	0.372297
C	0.369157	1.863792	-0.598407

C	-0.552496	2.857321	-0.239614
C	-0.847283	3.895006	-1.129222
H	-1.557782	4.661707	-0.830484
C	-0.271863	3.946741	-2.389614
H	-0.519139	4.755054	-3.069555
C	0.634321	2.957491	-2.768457
H	1.101297	2.987870	-3.747092
C	0.950677	1.945339	-1.873624
H	1.696181	1.208878	-2.158033
C	-1.312587	2.827090	1.067989
H	-1.369161	3.847665	1.462634
H	-2.352341	2.547607	0.849500
C	6.576288	-0.625107	-0.104211
C	2.932684	2.706903	0.568397
C	1.940500	-2.321732	0.617246
H	6.831605	-1.643491	0.193957
H	6.853121	-0.509409	-1.156110
H	7.197251	0.062910	0.473294
H	2.552273	-3.177253	0.908659
H	1.225996	-2.149001	1.422475
H	1.375042	-2.632542	-0.265292
H	4.527755	-2.396853	0.227328
H	5.344774	1.780950	0.199117
H	3.789702	3.219340	1.009665
H	2.087296	2.830033	1.245852
H	2.678414	3.220425	-0.361573
P	-0.747681	-0.717317	-0.278086
C	-1.232135	-2.140197	0.776508
C	-1.258122	-3.448373	0.289796
C	-1.515411	-1.908642	2.128281
C	-1.563831	-4.506667	1.138460
H	-1.023055	-3.649817	-0.749172
C	-1.821556	-2.971016	2.971026
H	-1.489465	-0.903326	2.533319
C	-1.844409	-4.271585	2.479575
H	-1.576196	-5.518146	0.748513
H	-2.033203	-2.775248	4.016116
H	-2.076338	-5.099435	3.140049
C	-0.470175	-1.414358	-1.950531
C	-1.544404	-1.913781	-2.695696
C	0.814087	-1.444737	-2.495133
C	-1.331403	-2.446265	-3.959995
H	-2.548386	-1.880996	-2.284959
C	1.022645	-1.974163	-3.765591

H	1.654577	-1.057207	-1.929530
C	-0.046610	-2.475587	-4.496762
H	-2.168905	-2.833400	-4.529043
H	2.023930	-1.990294	-4.180172
H	0.117509	-2.886306	-5.486682
C	-2.343367	0.168135	-0.523597
C	-3.414045	0.047724	0.364682
C	-2.469823	1.017218	-1.629573
C	-4.577562	0.785531	0.168163
H	-3.357650	-0.622644	1.211684
C	-3.632224	1.751486	-1.820986
H	-1.653527	1.120884	-2.337169
C	-4.685764	1.645537	-0.917791
H	-5.398281	0.684066	0.869024
H	-3.704819	2.416767	-2.673744
H	-5.590430	2.224606	-1.065994

Structure 4c

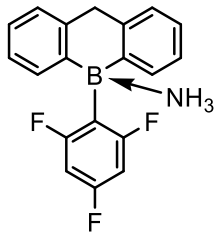


4c

Charge = 0; Multiplicity = 1; E (u.a.) = -1055.503184214954

B	-0.170375	0.102939	0.070530
C	1.319155	-0.216864	0.320485
C	2.334653	0.739312	0.132972
H	2.064865	1.735810	-0.202050
C	3.663540	0.441153	0.371890
H	4.431560	1.190938	0.220659
C	4.007879	-0.837612	0.812220
H	5.046774	-1.084145	1.003236
C	3.025485	-1.794372	1.011464
H	3.300779	-2.786232	1.358989
C	1.681342	-1.498365	0.771535
C	-0.614801	1.534250	-0.434614
C	-1.434226	2.373466	0.311781
C	-1.841771	3.633563	-0.091650
H	-2.473214	4.249728	0.533981
C	-1.401788	4.068822	-1.329121

C	-0.587781	3.299502	-2.141469
H	-0.257148	3.652127	-3.109008
C	-0.217643	2.054990	-1.660967
C	-1.217141	-1.003212	0.323828
C	-0.789371	-2.265831	0.770679
C	-1.727617	-3.277052	0.992118
H	-1.392576	-4.250824	1.338328
C	-3.077253	-3.051076	0.773939
H	-3.792400	-3.847201	0.950914
C	-3.516736	-1.805479	0.323337
H	-4.571964	-1.630285	0.148116
C	-2.592251	-0.801229	0.102590
H	-2.932042	0.165475	-0.255263
C	0.663457	-2.582483	1.018288
H	0.769808	-2.922509	2.055856
H	0.933090	-3.453344	0.408063
F	-1.851053	1.941310	1.511861
F	0.568577	1.297487	-2.441189
F	-1.777398	5.278512	-1.756047

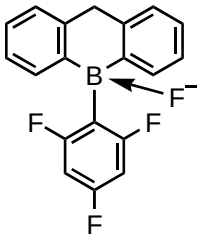


4c-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1112.079369986871

B	0.013272	-0.106892	-0.742775
C	1.433063	-0.321594	-0.023706
C	2.584526	0.320341	-0.500103
H	2.496636	1.037853	-1.316420
C	3.836583	0.104594	0.058708
H	4.708845	0.619008	-0.329814
C	3.957883	-0.772852	1.132740
H	4.927721	-0.957699	1.581630
C	2.828036	-1.402024	1.635164
H	2.921390	-2.073730	2.484277
C	1.567309	-1.181894	1.072745
C	-0.486688	1.438618	-0.709550
C	-0.770820	2.004119	0.532967
C	-1.204879	3.300830	0.738156
H	-1.407491	3.676494	1.732098

C	-1.368156	4.095215	-0.383958
C	-1.112899	3.627468	-1.657763
H	-1.242643	4.253742	-2.529999
C	-0.681615	2.314157	-1.764285
C	-1.106592	-1.138664	-0.232569
C	-0.878024	-1.968619	0.871639
C	-1.844069	-2.905158	1.250926
H	-1.655389	-3.546196	2.107878
C	-3.039687	-3.024146	0.557255
H	-3.776253	-3.757987	0.865807
C	-3.291887	-2.188813	-0.527542
H	-4.231454	-2.257309	-1.065070
C	-2.330785	-1.261037	-0.904341
H	-2.555249	-0.587463	-1.731889
C	0.364298	-1.827755	1.720964
H	0.095866	-1.216391	2.593284
H	0.646277	-2.806538	2.121251
N	0.281434	-0.539092	-2.312706
H	0.592892	-1.508093	-2.309174
H	0.998980	0.027723	-2.758601
H	-0.556013	-0.472551	-2.886489
F	-0.611592	1.231427	1.619498
F	-0.434322	1.869378	-3.031093
F	-1.787031	5.357459	-0.228566

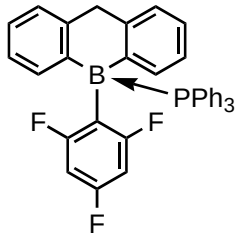


4c-F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -1155.469542508547

B	0.140410	-0.031540	-0.905912
C	1.494767	-0.409481	-0.104449
C	2.760661	-0.292995	-0.676417
H	2.835311	0.093599	-1.689141
C	3.911899	-0.669873	0.013601
H	4.888144	-0.566360	-0.452352
C	3.807557	-1.186651	1.299981
H	4.696974	-1.489304	1.845096
C	2.549160	-1.327750	1.882176
H	2.460389	-1.745568	2.882814

C	1.404467	-0.945960	1.189442
C	-0.464984	1.470531	-0.506326
C	-0.031794	2.342279	0.484266
C	-0.573205	3.597641	0.751525
H	-0.175977	4.218737	1.543535
C	-1.624481	4.012844	-0.036588
C	-2.132594	3.220739	-1.047615
H	-2.960941	3.545104	-1.663647
C	-1.533928	1.982854	-1.239526
C	-0.966264	-1.148801	-0.496200
C	-0.986234	-1.632654	0.822004
C	-1.904829	-2.606585	1.208040
H	-1.900520	-2.975781	2.231524
C	-2.817646	-3.120891	0.290948
H	-3.528630	-3.882435	0.598165
C	-2.800123	-2.661613	-1.022149
H	-3.500986	-3.065560	-1.747701
C	-1.879560	-1.688204	-1.403769
H	-1.857193	-1.331412	-2.428948
C	0.028188	-1.083808	1.806333
H	-0.299736	-0.086870	2.132654
H	0.067874	-1.709756	2.703644
F	0.379972	-0.019899	-2.319011
F	0.990662	1.987986	1.288573
F	-2.060581	1.233292	-2.223949
F	-2.175901	5.225997	0.186307



4c-PPh_3

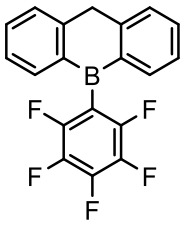
Charge = 0; Multiplicity = 1; E (u.a.) = -2091.659079250746

B	-0.496922	0.804365	-0.033278
C	-0.431513	1.655300	-1.415906
C	0.384831	1.443496	-2.527597
H	1.082106	0.613295	-2.537135
C	0.327878	2.260705	-3.652073
H	0.980739	2.066483	-4.496444
C	-0.569220	3.320030	-3.690671
H	-0.623538	3.963288	-4.562223

C	-1.393174	3.554523	-2.595765
H	-2.090709	4.387117	-2.612021
C	-1.325692	2.740427	-1.468430
C	-1.822354	-0.171493	-0.038473
C	-2.180655	-0.909863	-1.171873
C	-3.296160	-1.723768	-1.285207
H	-3.495006	-2.268797	-2.198206
C	-4.135708	-1.801591	-0.191737
C	-3.882899	-1.099974	0.969987
H	-4.548297	-1.150045	1.821348
C	-2.742493	-0.311114	1.001737
C	-0.450315	1.903158	1.165650
C	-1.349016	2.975849	1.001202
C	-1.424899	3.996193	1.942828
H	-2.131319	4.807714	1.793487
C	-0.593358	3.998967	3.058046
H	-0.657086	4.801150	3.785144
C	0.336603	2.981321	3.210884
H	1.016125	2.982270	4.056438
C	0.401789	1.953341	2.272405
H	1.155210	1.186897	2.425658
C	-2.186313	3.025464	-0.256496
H	-2.986163	2.275665	-0.195991
H	-2.673386	3.998199	-0.352993
F	-1.388302	-0.859701	-2.252236
F	-2.545573	0.361691	2.151662
F	-5.224613	-2.578117	-0.259873
P	1.067946	-0.505444	0.118889
C	0.946375	-1.940366	-1.010618
C	1.579202	-1.977336	-2.254141
C	0.096838	-2.987313	-0.641319
C	1.357873	-3.042601	-3.118480
H	2.249308	-1.180426	-2.555015
C	-0.128872	-4.044581	-1.513456
H	-0.397567	-2.975390	0.324652
C	0.498569	-4.072738	-2.753791
H	1.854053	-3.061976	-4.081891
H	-0.797441	-4.845904	-1.220595
H	0.321497	-4.898195	-3.433836
C	1.161900	-1.361846	1.740935
C	2.208528	-2.253048	1.995615
C	0.148978	-1.208185	2.686836
C	2.246869	-2.968770	3.183629
H	2.995872	-2.398727	1.266063

C	0.186660	-1.934868	3.874012
H	-0.656162	-0.506079	2.521243
C	1.232598	-2.812859	4.124657
H	3.066612	-3.652131	3.373111
H	-0.605229	-1.803510	4.602141
H	1.260929	-3.375625	5.050852
C	2.697587	0.256675	-0.188966
C	3.834939	-0.507097	-0.475491
C	2.800805	1.649302	-0.133258
C	5.060335	0.113158	-0.679553
H	3.763469	-1.584883	-0.569404
C	4.031645	2.263689	-0.337936
H	1.923123	2.255280	0.058209
C	5.160322	1.499324	-0.605619
H	5.935535	-0.486120	-0.902792
H	4.100818	3.344139	-0.294753
H	6.117408	1.982251	-0.767378

Structure 4d

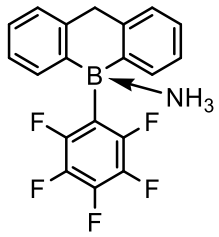


4d

Charge = 0; Multiplicity = 1; E (u.a.) = -1253.949978891904

B	-0.169377	0.099737	0.071679
C	1.318337	-0.212523	0.322752
C	2.333350	0.744490	0.135182
H	2.064858	1.741325	-0.200147
C	3.661983	0.446334	0.373632
H	4.430012	1.195867	0.222149
C	4.006136	-0.832953	0.812881
H	5.045100	-1.079504	1.003004
C	3.024417	-1.790530	1.011450
H	3.300485	-2.782607	1.357407
C	1.680337	-1.495018	0.772480
C	-0.615226	1.535631	-0.435092
C	-1.428278	2.360979	0.328810
C	-1.824561	3.619648	-0.093944
C	-1.404893	4.078796	-1.332663
C	-0.595610	3.283169	-2.128529

C	-0.213238	2.034137	-1.666229
C	-1.218253	-1.001321	0.319402
C	-0.790054	-2.263730	0.767804
C	-1.728670	-3.274056	0.989683
H	-1.394449	-4.247466	1.337369
C	-3.078034	-3.047597	0.770394
H	-3.793389	-3.843256	0.948082
C	-3.517748	-1.802369	0.318712
H	-4.572903	-1.627188	0.143855
C	-2.593392	-0.798515	0.097662
H	-2.934504	0.167933	-0.259877
C	0.662461	-2.579273	1.017141
H	0.767333	-2.919834	2.054647
H	0.933597	-3.449677	0.406994
F	-1.849603	1.948960	1.528381
F	0.566440	1.292053	-2.458479
F	-1.777568	5.279010	-1.756262
F	-2.597732	4.386066	0.667880
F	-0.197607	3.724992	-3.316785

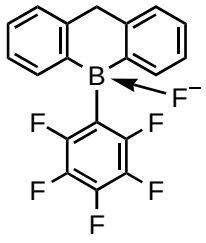


4d-NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1310.528036301421

B	0.016159	-0.114168	-0.749398
C	1.433894	-0.321431	-0.028634
C	2.584281	0.322663	-0.504944
H	2.497547	1.035643	-1.325455
C	3.834981	0.113492	0.058863
H	4.706780	0.629062	-0.328831
C	3.955194	-0.759170	1.136995
H	4.924029	-0.938311	1.590143
C	2.826327	-1.390742	1.638188
H	2.919549	-2.058713	2.490125
C	1.566441	-1.177572	1.071116
C	-0.485789	1.435533	-0.708404
C	-0.762980	1.977201	0.542822
C	-1.196684	3.277550	0.729454
C	-1.370719	4.100697	-0.374269

C	-1.108381	3.608742	-1.639351
C	-0.675486	2.297412	-1.773194
C	-1.106622	-1.138778	-0.237565
C	-0.879591	-1.964521	0.869955
C	-1.849685	-2.895130	1.253633
H	-1.663481	-3.533187	2.113216
C	-3.046091	-3.011656	0.561209
H	-3.785791	-3.740476	0.873846
C	-3.295783	-2.180651	-0.527571
H	-4.235771	-2.247978	-1.064267
C	-2.331217	-1.258774	-0.909194
H	-2.553360	-0.589358	-1.740842
C	0.364546	-1.827557	1.717191
H	0.097835	-1.222839	2.594602
H	0.647909	-2.808793	2.110240
N	0.282050	-0.539261	-2.319564
H	0.593517	-1.508528	-2.315024
H	1.001273	0.024669	-2.767047
H	-0.554841	-0.475976	-2.895019
F	-0.609171	1.220045	1.634373
F	-0.435732	1.876468	-3.041451
F	-1.786442	5.352129	-0.214899
F	-1.271034	4.387240	-2.706810
F	-1.448635	3.749536	1.946409

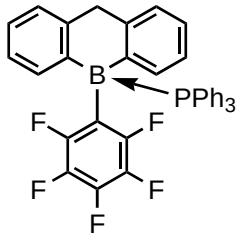


4d-F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -1353.925378283708

B	0.143380	-0.043399	-0.906879
C	1.497707	-0.410553	-0.105233
C	2.761703	-0.281484	-0.678516
H	2.832522	0.108560	-1.690118
C	3.916307	-0.650830	0.009453
H	4.891275	-0.537572	-0.456448
C	3.816511	-1.172187	1.294330
H	4.708691	-1.468507	1.838155
C	2.560250	-1.325251	1.877370
H	2.476169	-1.745833	2.877084

C	1.411474	-0.951234	1.186889
C	-0.465821	1.467371	-0.509790
C	-0.034894	2.313271	0.501650
C	-0.593894	3.561992	0.750436
C	-1.630986	4.014755	-0.040707
C	-2.099479	3.208397	-1.063673
C	-1.516872	1.968623	-1.272133
C	-0.968999	-1.149257	-0.491178
C	-0.984077	-1.635698	0.825872
C	-1.909295	-2.602589	1.214322
H	-1.902621	-2.974463	2.236662
C	-2.832011	-3.105884	0.301375
H	-3.547963	-3.861497	0.611217
C	-2.818811	-2.643780	-1.010671
H	-3.527637	-3.039451	-1.732701
C	-1.892042	-1.677776	-1.395426
H	-1.872389	-1.320175	-2.420308
C	0.038284	-1.098546	1.808334
H	-0.287690	-0.106793	2.152145
H	0.084191	-1.735607	2.697264
F	0.377622	-0.023859	-2.317559
F	0.966043	1.968046	1.327401
F	-2.037364	1.243874	-2.270993
F	-2.179832	5.215354	0.180022
F	-0.137395	4.336255	1.744401
F	-3.108474	3.641701	-1.831531



4d-PPh_3

Charge = 0; Multiplicity = 1; E (u.a.) = -2290.117769772489

B	0.430106	-0.752412	-0.000027
C	0.050973	-1.567067	-1.337419
C	0.625245	-1.264430	-2.581345
H	1.385524	-0.491587	-2.639608
C	0.280082	-1.938640	-3.743623
H	0.744805	-1.673931	-4.687133
C	-0.657224	-2.965927	-3.683794
H	-0.939365	-3.505688	-4.581297

C	-1.205507	-3.313870	-2.459093
H	-1.912972	-4.137015	-2.400433
C	-0.859475	-2.633102	-1.287908
C	1.979851	-0.249053	0.000002
C	2.945335	-1.258186	0.000056
C	4.307294	-1.010649	0.000066
C	4.764240	0.298916	0.000017
C	3.849869	1.334159	-0.000042
C	2.492467	1.038337	-0.000051
C	0.050915	-1.567105	1.337325
C	-0.859521	-2.633147	1.287741
C	-1.205606	-3.313947	2.458892
H	-1.913059	-4.137098	2.400175
C	-0.657396	-2.966022	3.683631
H	-0.939578	-3.505807	4.581106
C	0.279885	-1.938716	3.743536
H	0.744543	-1.674013	4.687079
C	0.625106	-1.264478	2.581292
H	1.385356	-0.491612	2.639616
C	-1.496378	-3.099792	-0.000103
H	-1.499716	-4.194990	-0.000123
H	-2.555107	-2.811554	-0.000115
F	2.569229	-2.536366	0.000095
F	1.666881	2.105489	-0.000109
F	6.068092	0.553249	0.000026
F	4.270525	2.597247	-0.000090
F	5.183959	-2.010363	0.000120
P	-0.962356	0.784740	0.000008
C	-1.065740	1.886380	1.464930
C	-2.247666	2.583707	1.738139
C	0.023508	2.042399	2.320632
C	-2.328956	3.428864	2.836126
H	-3.119434	2.452214	1.107881
C	-0.061201	2.885017	3.423858
H	0.945478	1.513133	2.129289
C	-1.234333	3.581434	3.681553
H	-3.250474	3.963995	3.034424
H	0.794208	2.994395	4.080230
H	-1.299145	4.239070	4.540924
C	-1.065801	1.886466	-1.464843
C	-2.247695	2.583920	-1.737863
C	0.023347	2.042410	-2.320683
C	-2.329050	3.429129	-2.835804
H	-3.119388	2.452493	-1.107488

C	-0.061427	2.885079	-3.423866
H	0.945290	1.513047	-2.129478
C	-1.234525	3.581621	-3.681374
H	-3.250540	3.964363	-3.033955
H	0.793904	2.994397	-4.080349
H	-1.299387	4.239298	-4.540710
C	-2.586986	-0.050779	0.000005
C	-3.181721	-0.423487	1.208474
C	-3.181765	-0.423375	-1.208477
C	-4.376600	-1.133483	1.205603
H	-2.705312	-0.174413	2.150972
C	-4.376644	-1.133373	-1.205628
H	-2.705392	-0.174211	-2.150969
C	-4.977452	-1.483463	-0.000018
H	-4.830478	-1.421793	2.146622
H	-4.830557	-1.421596	-2.146657
H	-5.909243	-2.037909	-0.000026

NH_3

NH_3

Charge = 0; Multiplicity = 1; E (u.a.) = -56.5328010001

N	0.000000	-0.000000	0.114054
H	-0.000000	0.939355	-0.266127
H	-0.813505	-0.469677	-0.266127
H	0.813505	-0.469677	-0.266127

F^-

F^-

Charge = -1; Multiplicity = 1; E (u.a.) = -99.78866634324905

F	0.000000	0.000000	0.000000

PPh_3

PPh_3

Charge = 0; Multiplicity = 1; E (u.a.) = -1036.137136053904

P	0.000172	-0.001776	-1.299877
C	1.497140	-0.673211	-0.457413
C	2.046234	-1.846080	-0.985461
C	2.093575	-0.094889	0.664753
C	3.154014	-2.440382	-0.393670
H	1.598887	-2.297294	-1.866311

C	3.211336	-0.683650	1.249178
H	1.685994	0.817691	1.086101
C	3.740819	-1.857531	0.725467
H	3.565100	-3.352542	-0.811630
H	3.667205	-0.222949	2.118645
H	4.610657	-2.314529	1.183809
C	-0.166402	1.631024	-0.458426
C	-0.964865	1.860019	0.663851
C	0.577218	2.691285	-0.986329
C	-1.010485	3.122372	1.248720
H	-1.553086	1.051926	1.085149
C	0.541328	3.947709	-0.394194
H	1.191322	2.528096	-1.867144
C	-0.255942	4.166082	0.725277
H	-1.636609	3.288076	2.118522
H	1.127777	4.758456	-0.811885
H	-0.292353	5.147704	1.184226
C	-1.331508	-0.961108	-0.458562
C	-2.622549	-0.839867	-0.982581
C	-1.130672	-1.773474	0.659021
C	-3.693603	-1.498031	-0.390930
H	-2.788326	-0.221445	-1.859904
C	-2.202135	-2.443291	1.243193
H	-0.136101	-1.884779	1.077270
C	-3.484159	-2.304173	0.723918
H	-4.689691	-1.389502	-0.805346
H	-2.032560	-3.073458	2.109320
H	-4.316857	-2.825629	1.182452