Supplementary information

for

Bis(diiminate)-based boron difluoro complexes: Effective synthon for bis(borenium) cations

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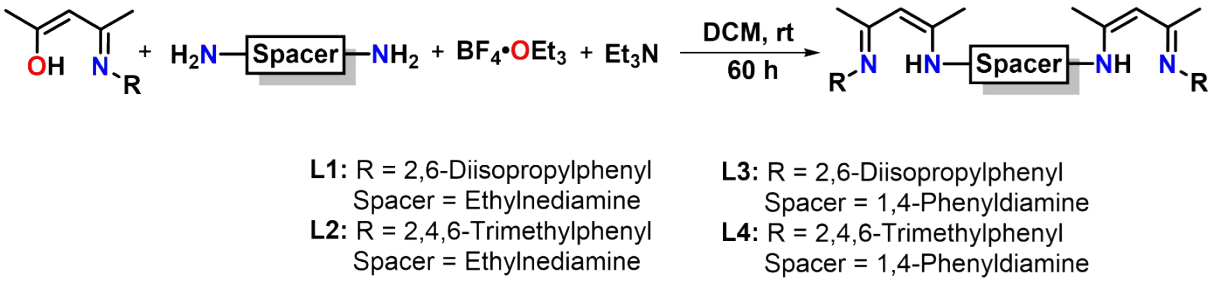
General Methods

The reactions were performed either under an atmosphere of argon using standard Schlenk techniques or in the open air. Chemicals were purchased from Spectrochem, Sigma-Aldrich, and TCI and used as received. All the solvents were purified by distillation using the appropriate drying agents, deoxygenated using three freeze–pump–thaw cycles, and stored over molecular sieves under dry argon before use. The deuterated solvents used for NMR spectroscopy were deoxygenated by freeze–pump–thaw cycles and stored under an argon atmosphere over molecular sieves. NMR chemical shifts are reported in ppm and coupling constants in Hz. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy data were obtained at ambient temperature using a Bruker 500 NMR spectrometer (operating at 500 MHz for ^{1}H, 126 MHz for ^{13}C, 160 MHz for ^{11}B and 471 MHz for ^{19}F). ^{1}H NMR spectra were referenced via residual proton resonances of $CDCl_3$ (^{1}H, 7.26 ppm) and ^{13}C NMR spectra were referenced to $CDCl_3$ (^{13}C, 77.16 ppm) and $BF_3{\cdot}OEt_2$ used as an internal standard used for ^{11}B. HRMS spectrum was obtained by Bruker micrOTOF-Q II Daltonik. Photoluminescence (PL) spectra were recorded by using a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon, model FM100) with an excitation and emission slit width at 2 nm. Quantum Yield was calculated in a liquid state using Quinine Hemisulphate in 0.5 M H_2SO_4 as a reference. Fluorescence lifetime was recorded using TCSPC HORIBA DeltaFlex™ using 390 nm diode laser· The emission was recorded at the respective emission maxima. Ludox was used to record the instrument response function (IRF) for each case. UV-Vis spectroscopy was performed on a 3 mL solution using the Varian UV−vis spectrophotometer (Cary 100 Bio) in a quartz cuvette (1 cm × 1 cm). Cyclic voltammetry was performed using a C-H instruments model CHI1103C in dichloromethane solvent using glassy carbon as the working electrode, Pt wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The scan rate was 100 $mV\,s^{-1}$ for cyclic voltammetry. A solution of Bu_4NPF_6 in dichloromethane (0.1 M) was used as the supporting electrolyte. The temperature was kept constant throughout each experiment at 25 °C. DFT calculations were implemented in the Gaussian 09 using the hybrid functional B3LYP in combination with the cc-pVDZ basis set for all atoms.

Synthetic Details.

General Synthesis of Ligands (L1-L4):

A solution of 2-hydroxy-4-imino-2-pentene in DCM (10 mL) was added to the solution of triethyloxonium tetrafluoroborate in dichloromethane under an argon atmosphere. The mixture was stirred at room temperature for 12 h. An equimolar portion of triethylamine was slowly added to the yellowish solution. After being stirred for another 20 min, the resulting mixture was added to a solution of diamines in 12 mL of triethylamine. The reaction mixture was stirred at room temperature for an additional 48 hours. The volatiles were removed under vacuum, resulting in an oily solid. Toluene was added to the resulting residue and filtered. Toluene was removed and obtained solid recrystallized from methanol at -20 ˚C (Scheme 1).



Scheme S1. Synthesis of ligands **L1**-**L4**.

Ethylene spacer ligands

L1: 2-hydroxy-4-(2,6-diisopropylphenyl)imino-2-pentene (2 g, 7.71 mmol), triethyloxonium tetrafluoroborate (1.46 g, 7.71 mmol), triethylamine (0.78 g, 7.71 mmol) and ethane-1,2-diamine (0.23 g, 3.85 mmol).

Yield: 82%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.93 (s, 2H, N*H*), 7.09 (d, J= 7.90 Hz, 4H, CH_{Aryl}), 7.02(t, 2H, CH_{Aryl}), 4.64 (s, 2H, C$H_{Pentene}$), 3.29 (s, 4H, CH_2), 2.84 (sept, 4H, CH_{Dipp}), 1.95 (s, 6H, CH_3), 1.61 (s, 6H, CH_3), 1.14 (d, J= 6.93 Hz, 12H, C$H_{3\ Dipp}$), 1.09 (d, J= 6.85 Hz, 12H, C$H_{3\ Dipp}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 166.3 (*C*N), 155.4 (*C*NH), 146.7 (C_{Aryl}), 138.1 (C_{Aryl}),

122.8 (CH$_{Aryl}$), 122.7 (CH$_{Aryl}$), 93.8 (CH), 44.5 (CH$_{pentene}$), 28.1 (CH$_{Dipp}$), 23.9 (CH$_3$), 22.8 (CH$_3$), 21.7 (CH$_3$), 19.1 (CH$_3$). **HRMS (ESI):** Calculated for $C_{36}H_{54}N_4$: 543.4421 $[M+H]^+$, found: 543.4421.

L2: 2-hydroxy-4-(2,4,6-trimethylphenyl)imino-2-pentene (2.00 g, 9.21 mmol), triethyloxonium tetrafluoroborate (1.75 g, 9.21 mmol), triethylamine (0.93 g, 9.21 mmol), and ethane-1,2-diamine (0.28 g, 4.61 mmol).

Yield: 78%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.83 (s, 2H, NH), 6.83 (s, 4H, CH_{Aryl}), 4.59 (s, 2H, C$H_{pentene}$), 3.31 (s, 4H, CH_2), 2.25 (s, 6H, C$H_{3\ Mes}$), 1.97 (s, 12H, C$H_{3\ Mes}$), 1.93 (s, 6H, CH_3), 1.57 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 166.2 (CN), 155.4 (CNH), 146.8 (C_{Aryl}), 131.1 (C_{Aryl}), 128.3 (CH$_{Aryl}$), 127.8 (CH$_{Aryl}$), 93.8 (CH), 44.6 (CH$_{pentene}$), 21.2 (CH$_3$), 20.8 (CH$_3$), 19.3 (CH$_3$), 18.4 (CH$_3$). **HRMS (ESI):** Calculated for $C_{30}H_{42}N_4$: 459.3482 $[M+H]^+$, found: 459.3506.

Phenyl spacer ligands

L3: 2-hydroxy-4-(2,6-diisopropylphenyl)imino-2-pentene (2.00 g, 7.71 mmol), triethyloxonium tetrafluoroborate (1.46 g, 7.71 mmol), triethylamine (0.78 g, 7.71 mmol) and p-phenylenediamine (0.42 g, 3.85 mmol).

Yield: 74%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.65 (s, 2H, NH), 7.13-7.07 (m, 6H, CH_{Aryl}), 6.85 (s, 4H, CH_{Phenyl}), 4.84 (s, 2H, C$H_{Pentene}$), 2.97 (sept, 4H, CH_{Dipp}), 2.03 (s, 6H, CH_3), 1.68 (s, 6H, CH_3), 1.19 (d, J= 6.95 Hz, 12H, C$H_{3\ Dipp}$), 1.12 (d, J= 6.82 Hz, 12H, C$H_{3\ Dipp}$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): 163.1 (CN), 157.1 (CNH), 142.9 (C_{Aryl}), 140.8 (C_{Aryl}), 139.8 (C_{Aryl}), 124.4 (CH$_{Aryl}$), 123.4 (CH$_{Aryl}$), 123.0 (CH$_{Aryl}$), 95.6 (CH), 28.3 (CH$_{Dipp}$), 24.2 (CH$_3$), 22.8 (CH$_3$), 21.2 (CH$_3$), 20.8 (CH$_3$). **HRMS (ESI):** Calculated for $C_{40}H_{54}N_4$: 591.4421 $[M+H]^+$, found: 591.4450.

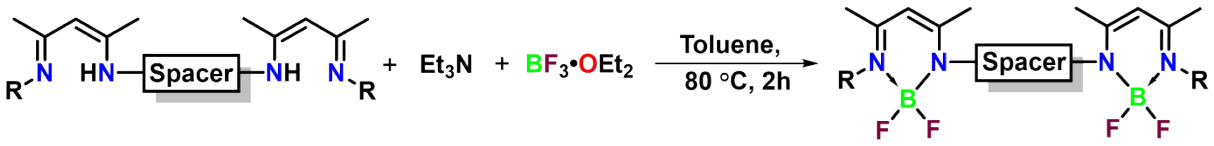
L4: 2-hydroxy-4-(2,4,6-trimethyl phenyl)imino-2-pentene (2 g, 9.21 mmol), triethyloxonium tetrafluoroborate (1.75 g, 9.21 mmol), triethylamine (0.93 g, 9.21 mmol) and p-phenylenediamine (0.49 g, 4.61 mmol).

Yield: 68%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.48 (s, 2H, N*H*), 6.85 (s, 8H, CH_{Aryl}), 4.83 (s, 2H, C$H_{pentene}$), 2.26 (s, 6H, C$H_{3\ Mes}$), 2.09 (s, 12H, C$H_{3\ Mes}$), 2.01 (s, 6H, CH_3), 1.66 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): 162.6 (*C*N), 157.6 (*C*N), 142.7 (C_{Aryl}), 140.2 (C_{Aryl}), 133.1 (C_{Aryl}), 130.7 (C_{Aryl}), 128.5 (C_{Aryl}), 123.4 (C_{Aryl}), 95.7 (*C*H), 20.9 (*C*H_3), 20.8 (*C*H_3), 20.7 (*C*H_3), 18.5 (*C*H_3). **HRMS (ESI):** Calculated for $C_{34}H_{42}N_4$: 507.3482 $[M+H]^+$, found: 507.3498.

General Synthesis of Complexes (1-4):

To a solution of ligand in toluene, triethylamine was added slowly, and the solution was allowed to be stirred for 10 minutes. $BF_3{\cdot}OEt_2$ was then added and the solution was heated at 80 °C for 2h. After cooling to rt, D.I. water was added to quench any excess boron compounds, and after aqueous workup light yellow solution was obtained. After the removal of toluene in vacuo off-white solid was obtained and recrystallization from methanol to give corresponding boron complexes (Scheme 2).



1: R = 2,6-Diisopropylphenyl
Spacer = Ethylnediamine
2: R = 2,4,6-Trimethylphenyl
Spacer = Ethylnediamine

3: R = 2,6-Diisopropylphenyl
Spacer = 1,4-Phenyldiamine
4: R = 2,4,6-Trimethylphenyl
Spacer = 1,4-Phenyldiamine

Scheme S2. Synthesis of boron difluoride complexes **1-4**.

Ethylene spacer Complexes (1 and 2)

1: L1 (0.5 g**,** 0.92 mmol), triethylamine (0.56 g, 0.77 mL, 5.53 mmol), and $BF_3{\cdot}OEt_2$ (1.30 g, 1.16 mL, 9.22 mmol).

Yield: 86%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (t, 2H, *C*H_{Aryl}), 7.19 (d, J=7.68 Hz, 4H, *C*H_{aryl}), 5.12 (s, 2H, *C*$H_{pentene}$), 3.68 (s, 4H, *C*H_2), 2.89 (sept, 4H, *C*H_{Dipp}), 2.24 (s, 6H, *C*H_3), 1.74 (s, 6H, *C*H_3), 1.24 (d, J= 6.65 Hz, 12H, *C*$H_{3\ Dipp}$), 1.13 (d, J=6.90 Hz, 12H, *C*$H_{3\ Dipp}$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 164.3 (*C*N), 163.7 (*C*N), 145.9 (C_{Aryl}), 135.9 (C_{Aryl}), 129.1 (*C*H_{Aryl}), 128.3 (*C*H_{Aryl}), 128.0 (*C*H_{Aryl}), 124.1 (*C*H_{Aryl}), 95.8 (*C*H), 45.1 (*C*H_2), 28.3 (*C*H), 24.6 (*C*H_3), 21.0 (*C*H_3), 19.7 (*C*H_3). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 1.17 (t). **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): δ -136.08 (q). **HRMS (ESI):** Calculated for $C_{36}H_{52}B_2F_4N_4$: 661.4218 $[M+Na]^+$, found: 661.4227.

2: L2 (0.5 g, 1.09 mmol), triethylamine (0.66 g, 0.91 mL, 6.54 mmol), and $BF_3{\cdot}OEt_2$ (1.54 g, 1.37 mL, 10.9 mmol).

Yield: 80%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.90 (s, 4H, C*H*$_{Aryl}$), 5.10 (s, 2H, $CH_{pentene}$), 3.72 (s, 4H, CH_2), 2.27 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 2.13 (s, 12H, $CH_{3\ Mes}$), 1.67 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 164.5 (*C*N), 163.3 (*C*N), 136.7 (C_{Aryl}), 136.6 (C_{Aryl}), 135.2 (CH_{Aryl}), 129.2 (C_{Aryl}), 95.6 (*C*H), 45.2 (*C*H_2), 21.0 (*C*H_3), 20.4 (*C*H_3), 19.7 (*C*H_3), 18.2 (*C*H_3). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 1.46 (t). **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): -134.68 (q). **HRMS (ESI):** Calculated for $C_{30}H_{40}B_2F_4N_4$: 577.3278 $[M+Na]^+$, found: 577.3278.

Phenyl spacer Complexes (3 and 4)

3: L3 (0.5 g, 0.846 mmol), triethylamine (0.51 g, 0.71 mL, 5.08 mmol), and $BF_3{\cdot}OEt_2$ (1.2 g, 1.06 mL, 8.46 mmol).

Yield: 75%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 (t, 2H, CH_{aryl}), 7.21 (s, 4H, C*H*), 7.18 (d, J= 7.64 Hz, 4H, CH_{aryl}), 5.30 (s, 2H, C$H_{pentene}$), 3.00 (sept, 4H, CH_{Dipp}), 1.91 (s, 6H, CH_3), 1.82 (s, 6H, CH_3), 1.23 (d, J= 6.70 Hz, 12H, C$H_{3\ Dipp}$), 1.17 (d, J= 6.91 Hz, 12H, C$H_{3\ Dipp}$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): 165.08 (*C*N), 163.53 (*C*N), 145.86 (C_{Aryl}), 140.3 (C_{Aryl}), 136.2 (C_{Aryl}), 128.1 (C_{Aryl}), 124.2 (CH_{Aryl}), 96.04 (*C*H), 28.4 (*C*H), 24.7 (*C*H_3), 24.6 (*C*H_3), 21.5 (*C*H_3), 21.4 (*C*H_3). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 0.78 (t). **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): -134.024 (q). **HRMS (ESI):** Calculated for $C_{40}H_{52}B_2F_4N_4$: 709.4220 $[M+Na]^+$, found: 709.4206.

4: L4 (0.5 g, 0.98 mmol) and triethylamine (0.6 g, 0.82 mL, 5.92 mmol), and $BF_3{\cdot}OEt_2$ (1.4 g, 1.24 mL, 9.87 mmol).

Yield: 81%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (s, 4H, CH_{Aryl}), 6.89 (s 4H, CH), 5.26 (s, 2H, $CH_{pentene}$), 2.26 (s, 6H, CH_3), 2.18 (s, 12H, CH_3), 1.89 (s, 6H, CH_3), 1.76 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz): δ 164.7 (*C*N), 163.6 (*C*N), 140.3 (C_{Aryl}), 136.75 (C_{Aryl}), 136.71 (C_{Aryl}), 135.0 (C_{Aryl}), 129.2 (C_{Aryl}), 128.0 (C_{Aryl}), 95.6 (*C*H), 21.4 (*C*H_3), 21.03 (*C*H_3), 20.7 (*C*H_3), 18.3 (*C*H_3). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 1.05 (t). **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): - 31.77 (q). **HRMS (ESI):** Calculated for $C_{34}H_{40}B_2F_4N_4$: 625.3279 $[M+Na]^+$, found: 625.3292.

Synthesis of Borenium cation:

5a: 1 (100 mg, 0.157 mmol) was dissolved in $CDCl_3$ in a vial in a glove box and TMSOTf (69.6 mg, 0.314 mmol) was added to this solution at room temperature. The reaction mixture was further stirred for 1 h at rt and then the solvent was removed in a vaccum followed by washing of the residue with hexane to afford a colourless solid.

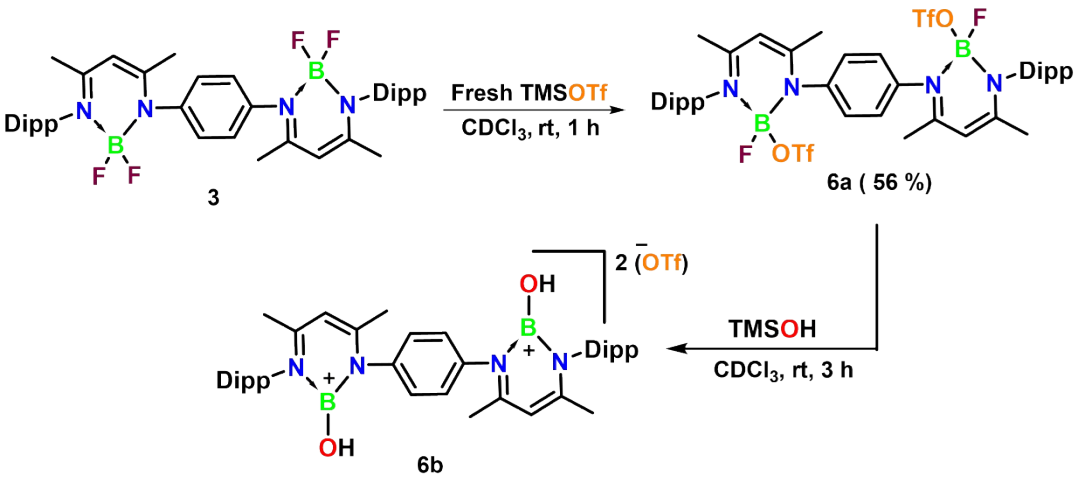
Yield: 78%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (t, 2H, C*H*$_{Aryl}$), 7.28 (d, J=7.65 Hz, 4H, C*H*$_{aryl}$), 5.73 (s, 2H, C*H*$_{pentene}$), 3.75 (s, 4H, C*H*$_2$), 2.71 (sept, 4H, C*H*$_{Dipp}$), 2.39 (s, 6H, C*H*$_3$), 1.91 (s, 6H, C*H*$_3$), 1.26 (d, J= 6.65 Hz, 12H, C*H*$_{3Dipp}$), 1.17 (d, J=6.94 Hz, 12H, C*H*$_{3Dipp}$). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 7.06 (bs) ppm. **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): δ - 77.31 (s) ppm. **HRMS (ESI):** Calculated for $C_{38}H_{52}F_8B_2N_4O_6S_2$: 899.3472 $[M+H]^+$, found: 899.3005. Calculated for $C_{37}H_{52}B_2F_5N_4O_3S_1$: 749.3873 $[M\text{-}OTf]^+$, found: 749.3667.

5b: 5a (100 mg, 0.11 mmol) was dissolved in $CDCl_3$ in a vial and TMSOH (20 mg, 0.22 mmol) was added to this solution at room temperature. The reaction mixture was further stirred for 3 h at rt then the solvent was removed in a vaccum followed by washing of the residue with hexane to afford a colourless solid.

Yield: 71%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.11 (m, 6H, C*H*$_{Aryl}$), 6.51 (s, 2H, C*H*$_{pentene}$), 5.23 (s, 4H, C*H*$_2$), 4.23 (s, 2H, B-O*H*), 3.11 (m, 4H, C*H*$_{Dipp}$), 2.85 (s, 12H, C*H*$_3$), 2.28 (bs, 24H, C*H*$_{3\ Dipp}$). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 22.57 (bs) ppm. **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): δ - 78.26 (s) ppm. **HRMS (ESI):** Calculated for $C_{36}H_{54}B_2O_2N_4$: 595.4361 $[M\text{-}H]^+$, found: 595.4360.



Scheme S3. Synthesis of OTf substituted complex **6a**; and bis(borenium) cation **6b**.

6a: 3 (100 mg, 0.146 mmol) was dissolved in $CDCl_3$ in a vial in a glove box and TMSOTf (34.6 mg, 0.292 mmol) was added to this solution at room temperature. The reaction mixture was further stirred for 1 h at rt and then the solvent was removed in a vaccum followed by washing of the residue with hexane affording a colourless solid.

Yield: 56%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39 (t, 2H, CH_{Aryl}), 7.34 (d, J=7.04 Hz, 2H, CH_{aryl}), 7.19 (t, 2H, CH_{aryl}), 7.11 (d, J=6.69 Hz, 2H, CH_{aryl}), 7.08 (d, J=6.69 Hz, 2H, CH_{Aryl}), 5.30 (s, 2H, $CH_{pentene}$), 3.03 (m, 4H, CH_{Dipp}), 1.79 (s, 6H, CH_3), 1.67 (s, 6H, CH_3), 1.13 (d, J=6.86 Hz, 24H, CH_{3Dipp}). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): δ 11 (bs) ppm. **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): δ – 77.53 (s) ppm.

6b: 6a (100 mg, 0.10 mmol) was dissolved in $CDCl_3$ in a vial in a glove box and TMSOH (19 mg, 0.21 mmol) was added to this solution at room temperature. The reaction mixture was further stirred for 3 h at rt then the solvent was removed in a vaccum followed by washing of the residue with hexane affording a colourless solid.

Yield: 52%

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 (t, 2H, CH_{Aryl}), 7.29 (s, 4H, CH_{aryl}), 7.22 (d, J=7.0 Hz, 4H, CH_{aryl}), 5.34 (s, 2H, $CH_{pentene}$), 3.06 (m, 4H, CH_{Dipp}), 1.96 (s, 6H, CH_3), 1.87 (s, 6H, CH_3), 1.27 (d, J=6.75 Hz, 12H, CH_{3Dipp}), 1.22 (d, J=6.77 Hz, 12H, CH_{3Dipp}). **^{11}B{^{1}H} NMR** ($CDCl_3$, 160 MHz): 21.13 (bs) ppm. **^{19}F{^{1}H} NMR** ($CDCl_3$, 470 MHz): δ - 78.75 (s) ppm. **HRMS (ESI):** Calculated for $C_{40}H_{54}B_2O_2N_4$: 643.4362 $[M-H]^+$, found: 643.4376.

NMR and Mass Spectra of Ligands and Complexes

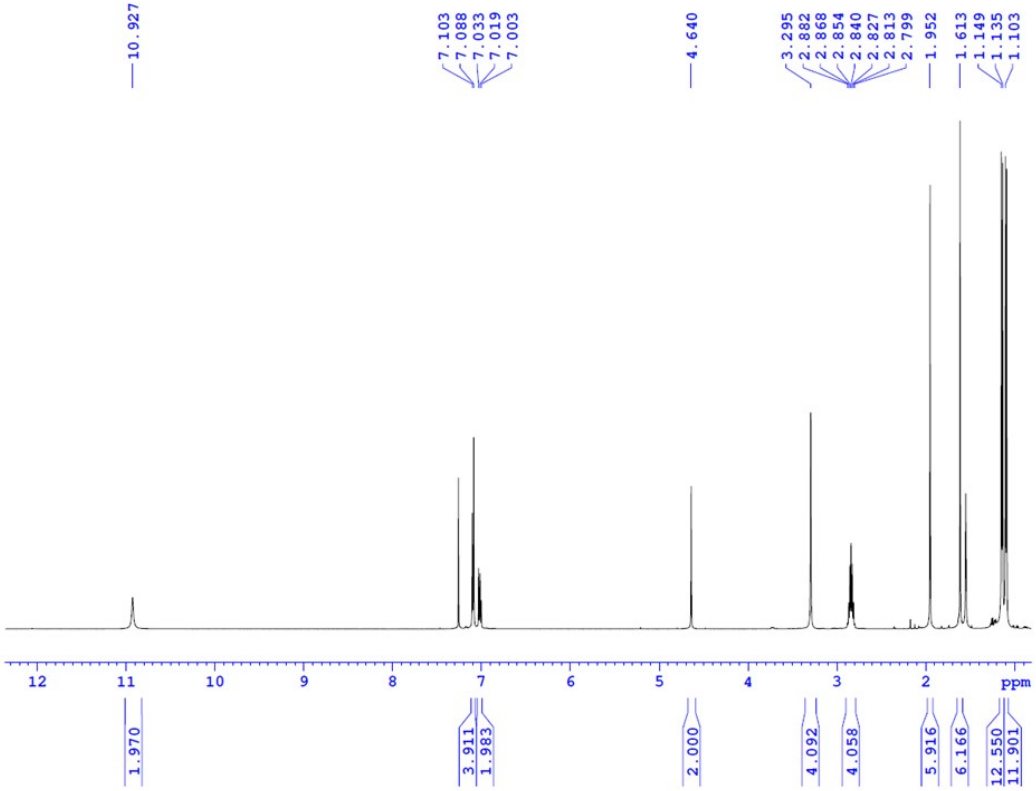


Figure S1. ^{1}H NMR spectrum of **L1.**

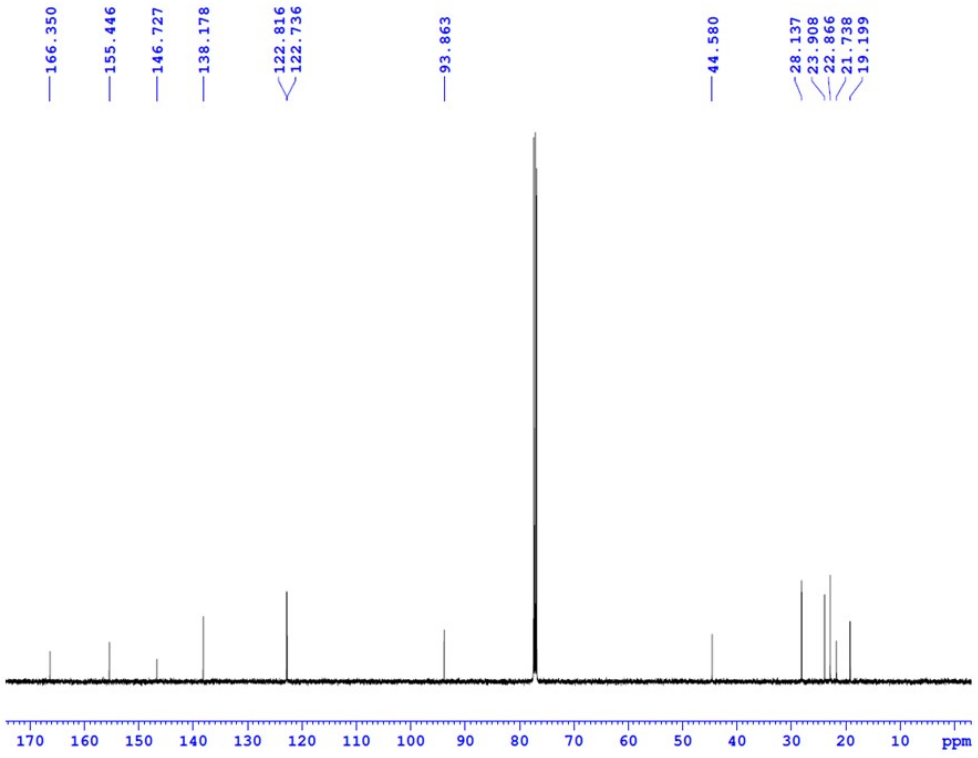


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **L1.**

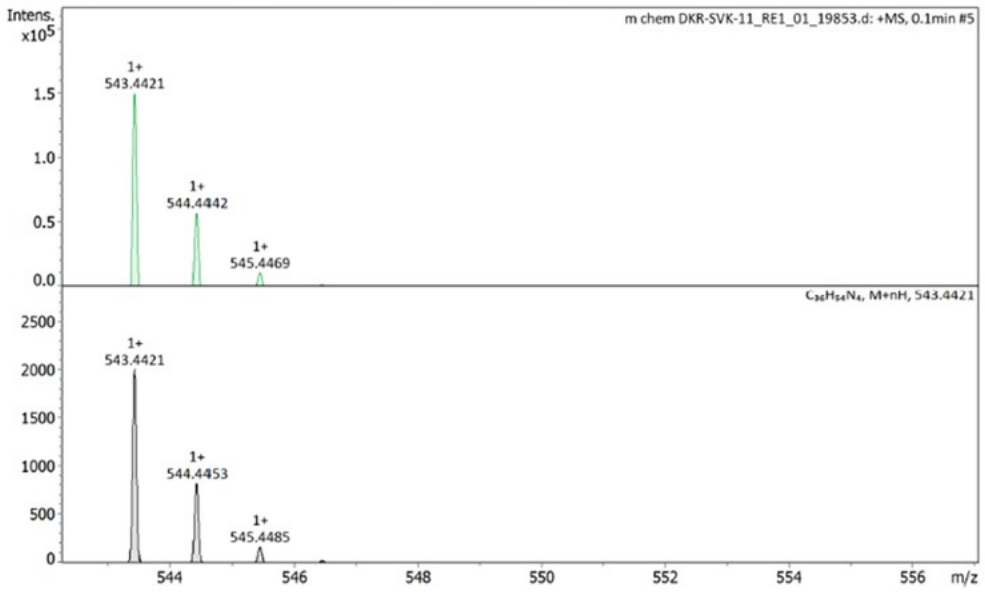


Figure S3. High-resolution mass spectrum of **L1**.

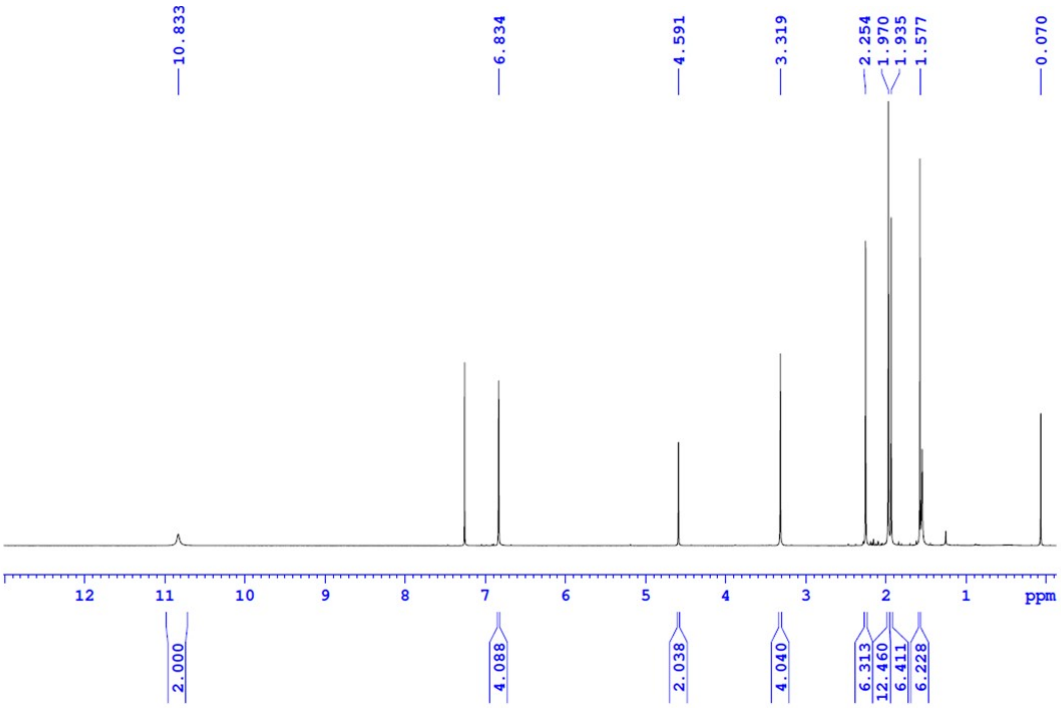


Figure S4. ^{1}H NMR spectrum of **L2.**

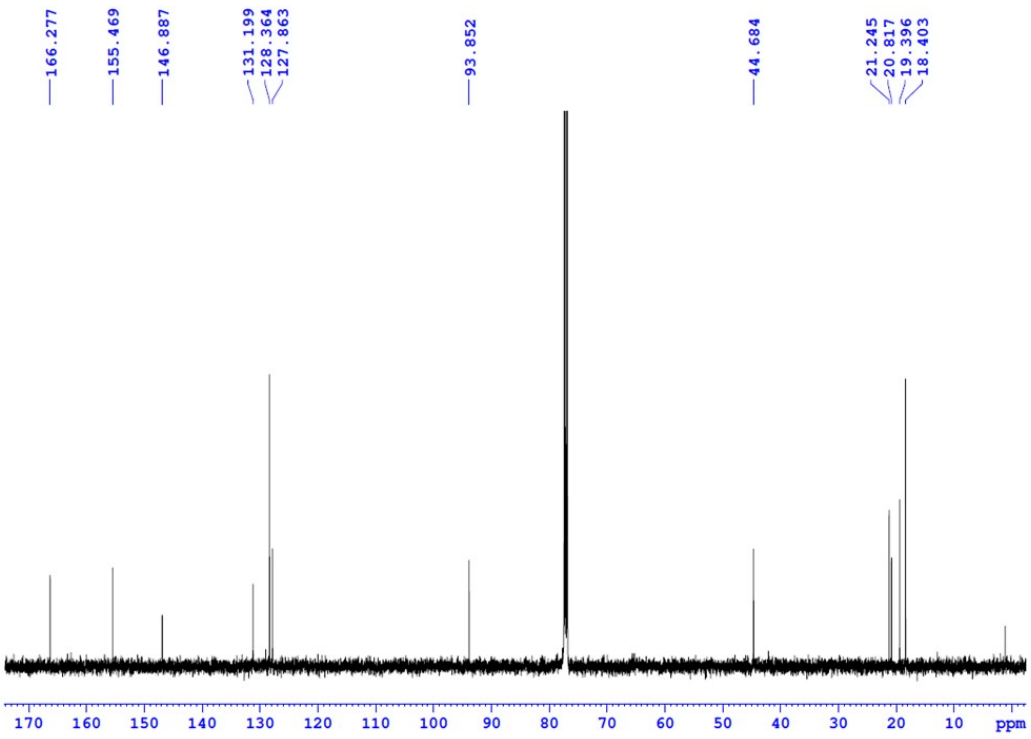


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **L2.**

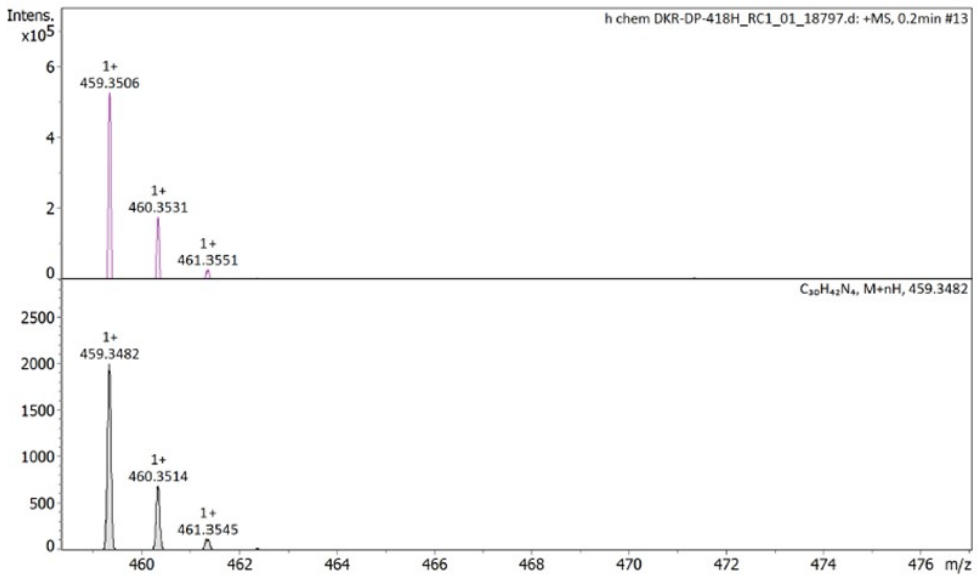


Figure S6. High-resolution mass spectrum of **L2**.

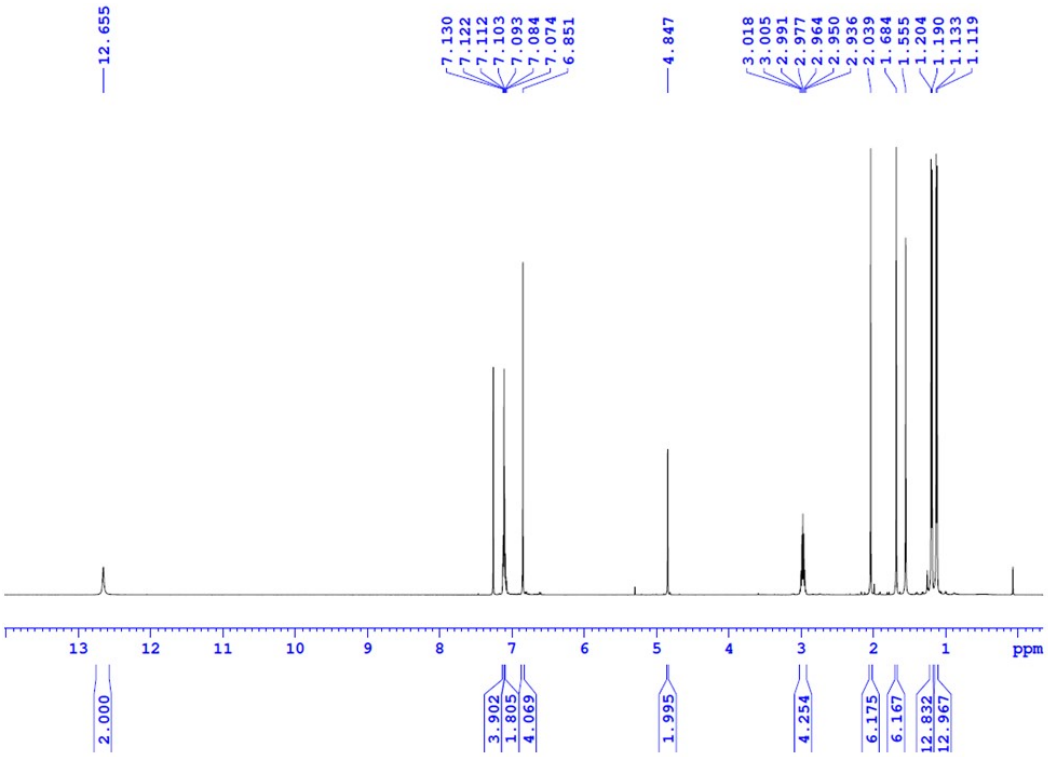


Figure S7. ^{1}H NMR spectrum of **L3.**

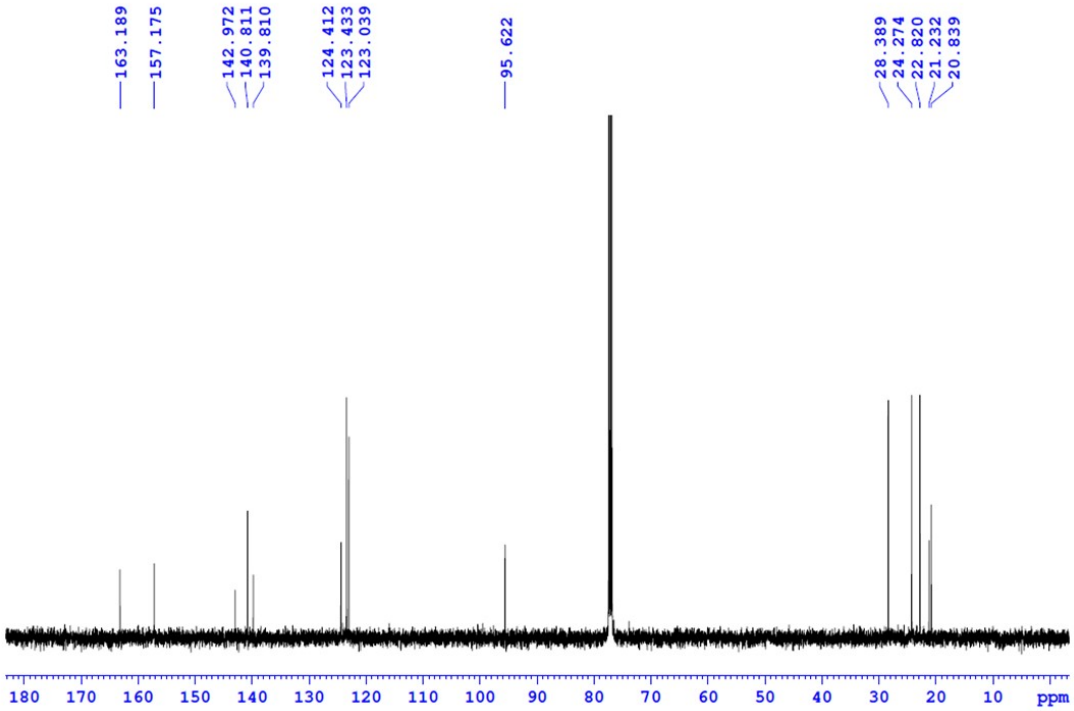


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **L3.**

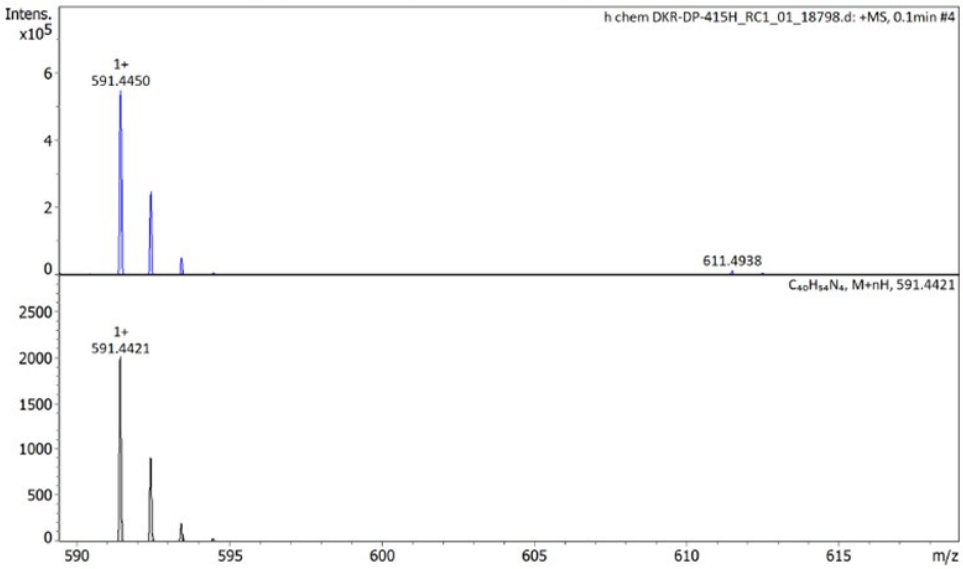


Figure S9. High-resolution mass spectrum of **L3**.

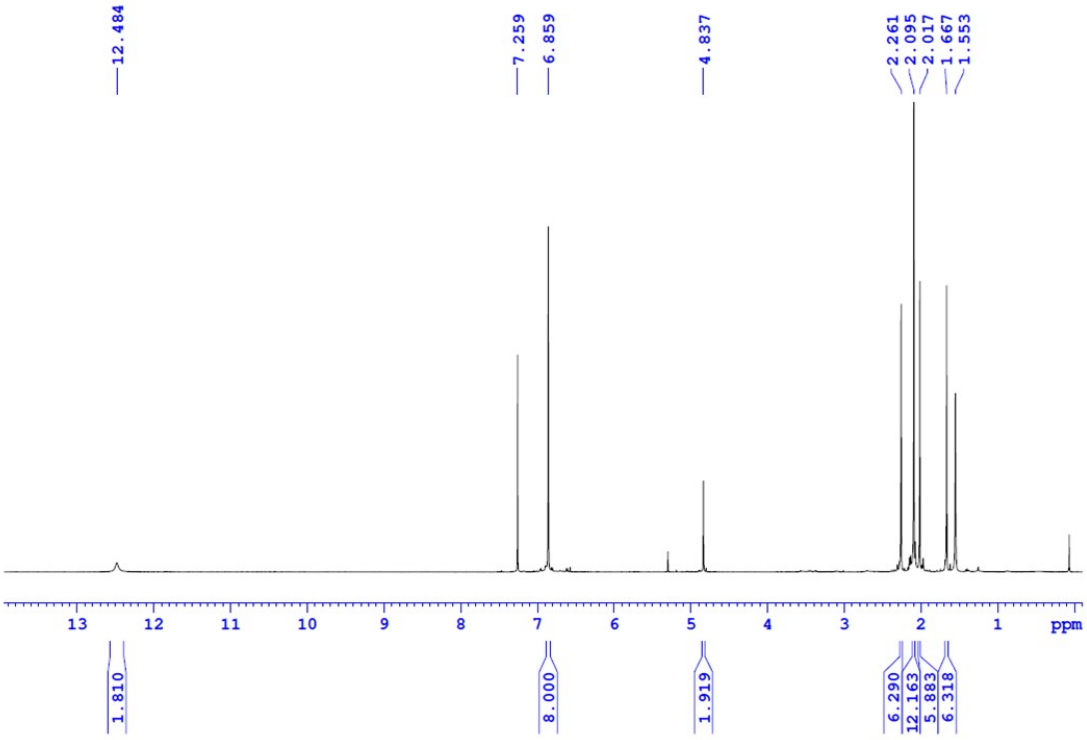


Figure S10. ^{1}H NMR spectrum of **L4.**

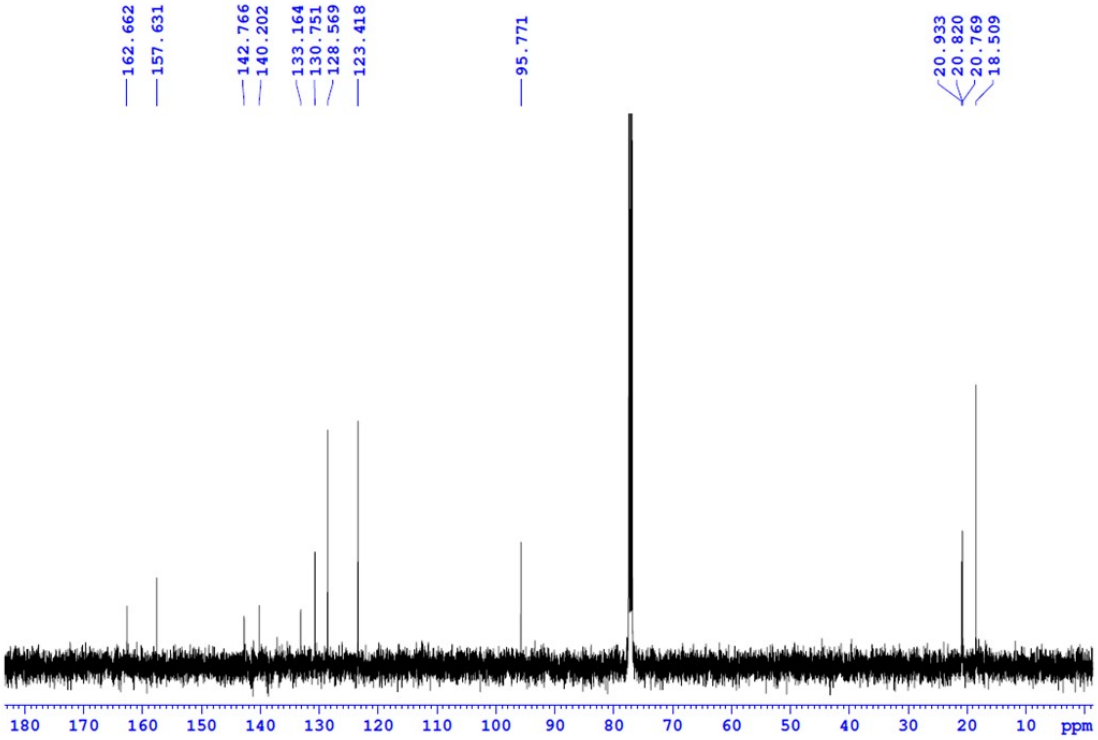


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **L4.**

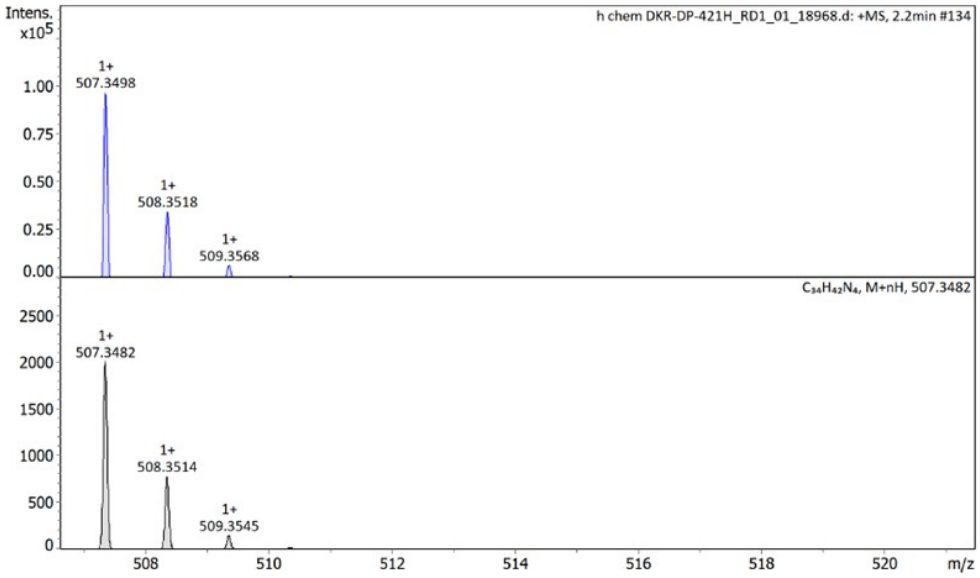


Figure S12. High-resolution mass spectrum of **L4**.

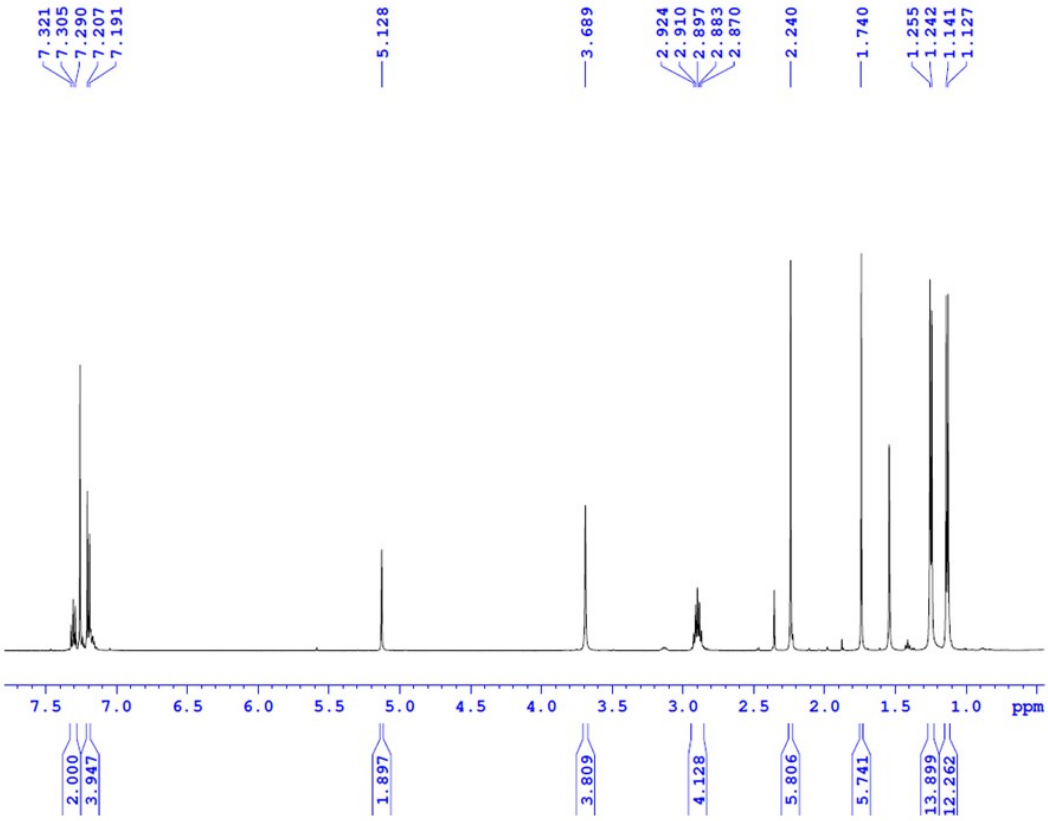


Figure S13. ^{1}H NMR spectrum of **1.**

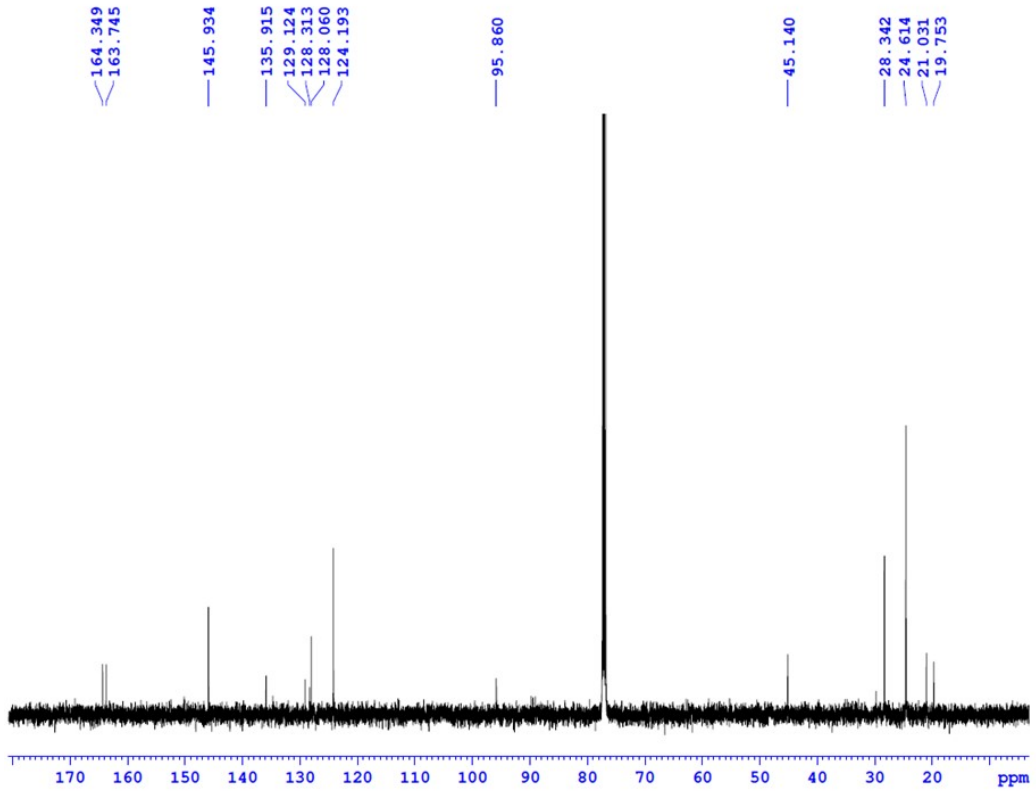


Figure S14. ^{13}C{^{1}H} NMR spectrum of **1.**

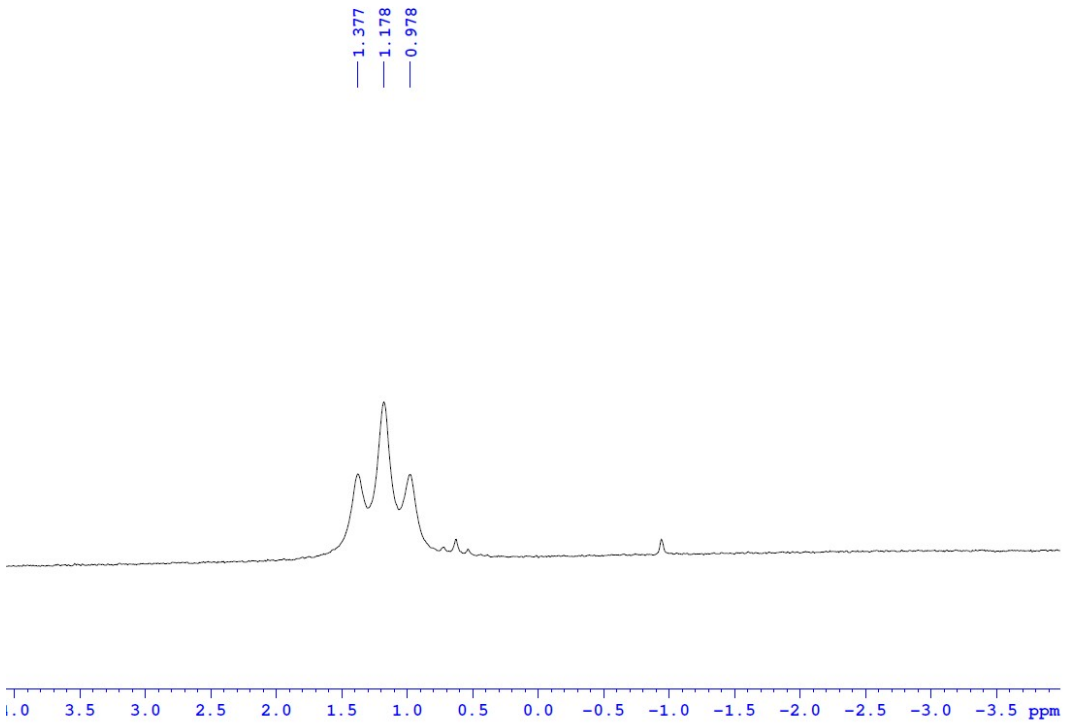


Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum of **1.**

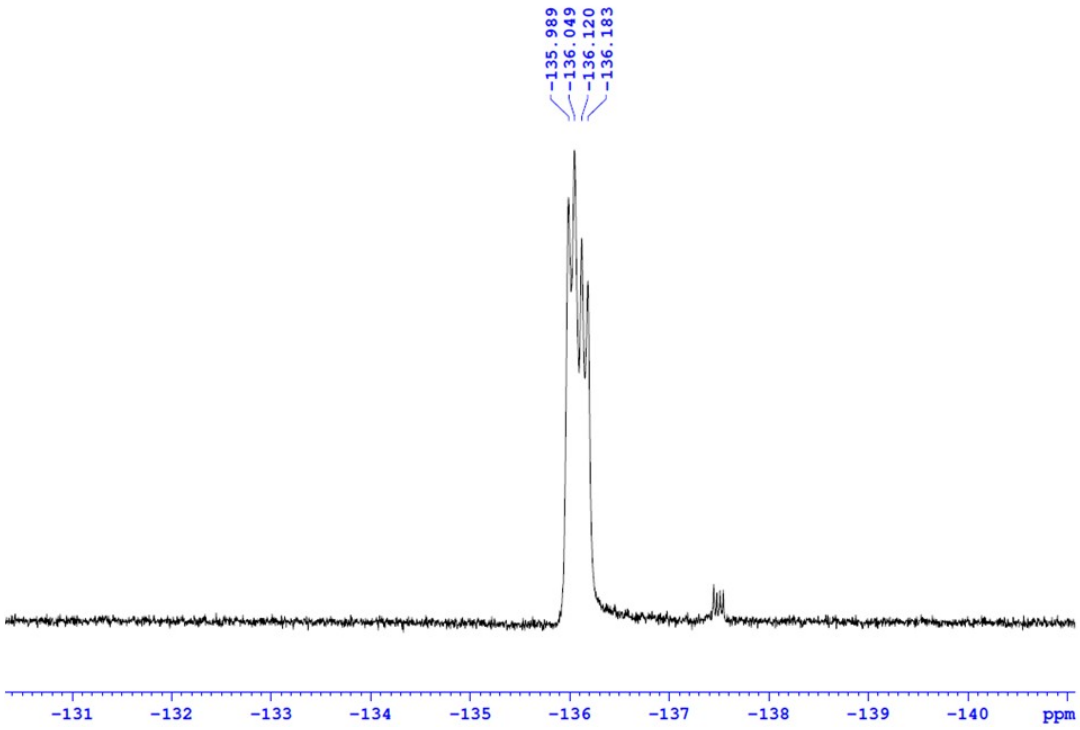


Figure S16. $^{19}F\{^{1}H\}$ NMR spectrum of **1.**

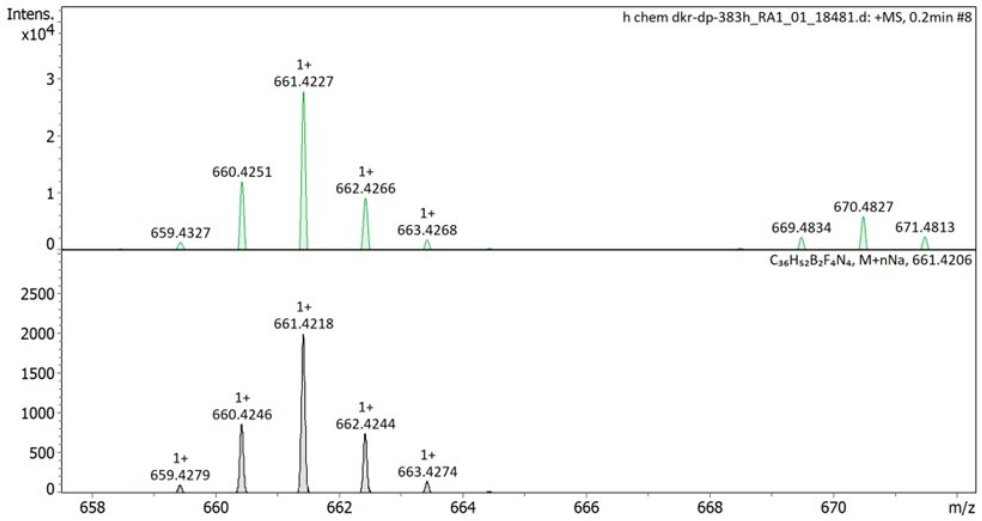


Figure S17. High-resolution mass spectrum of **1**.

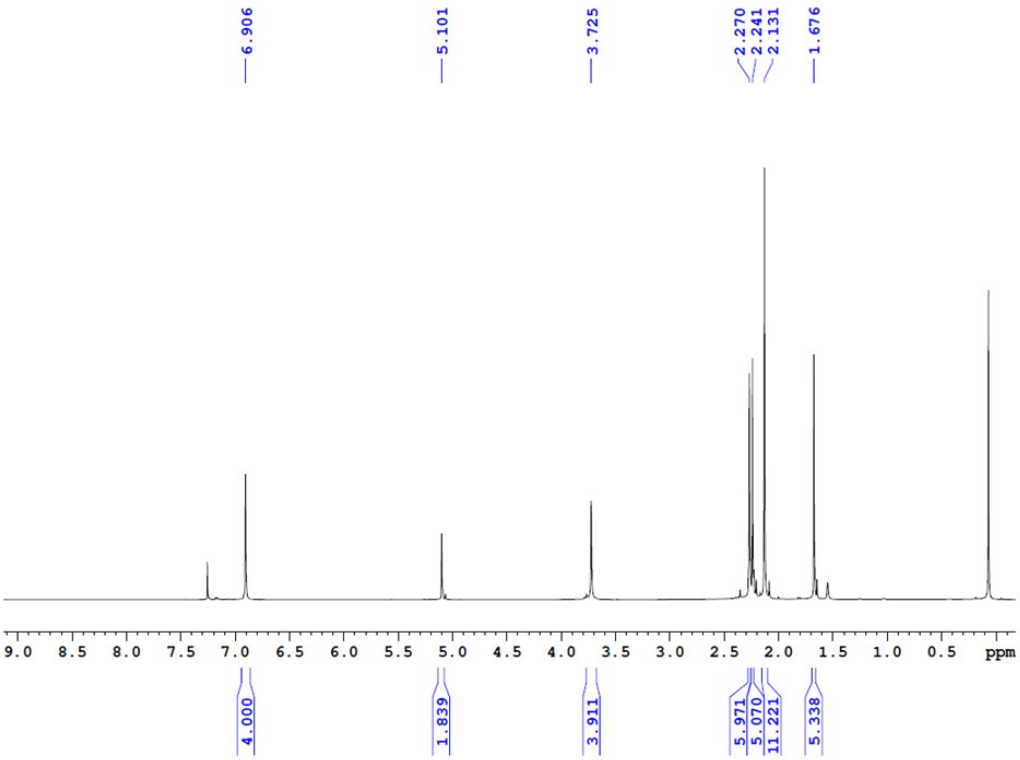


Figure S18. ^{1}H NMR spectrum of **2.**

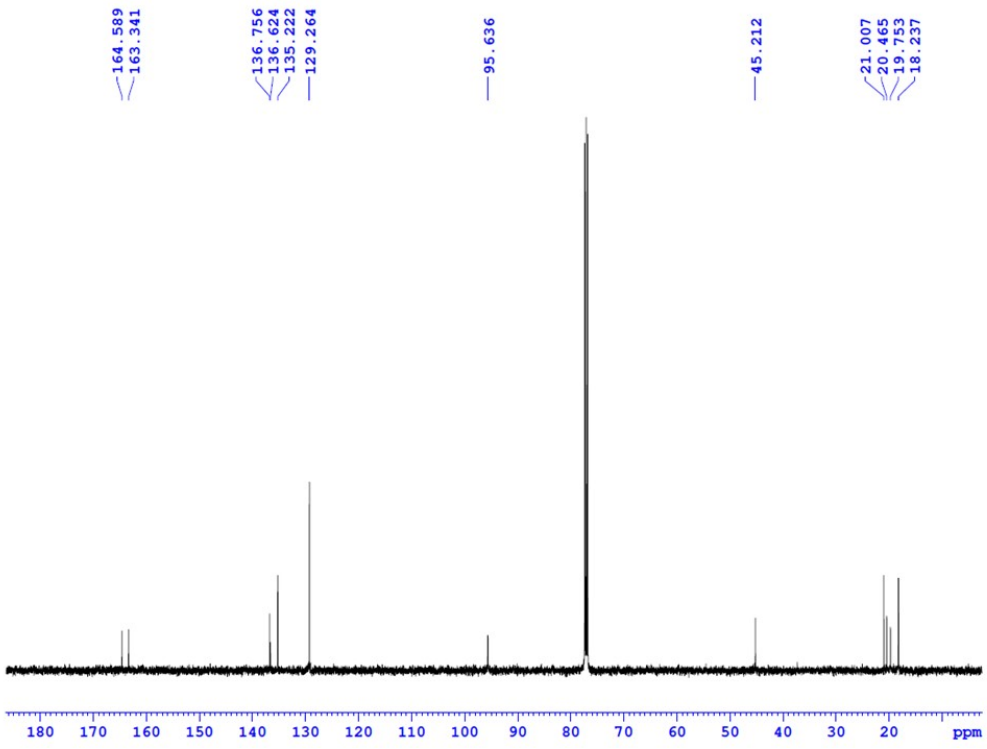


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **2.**

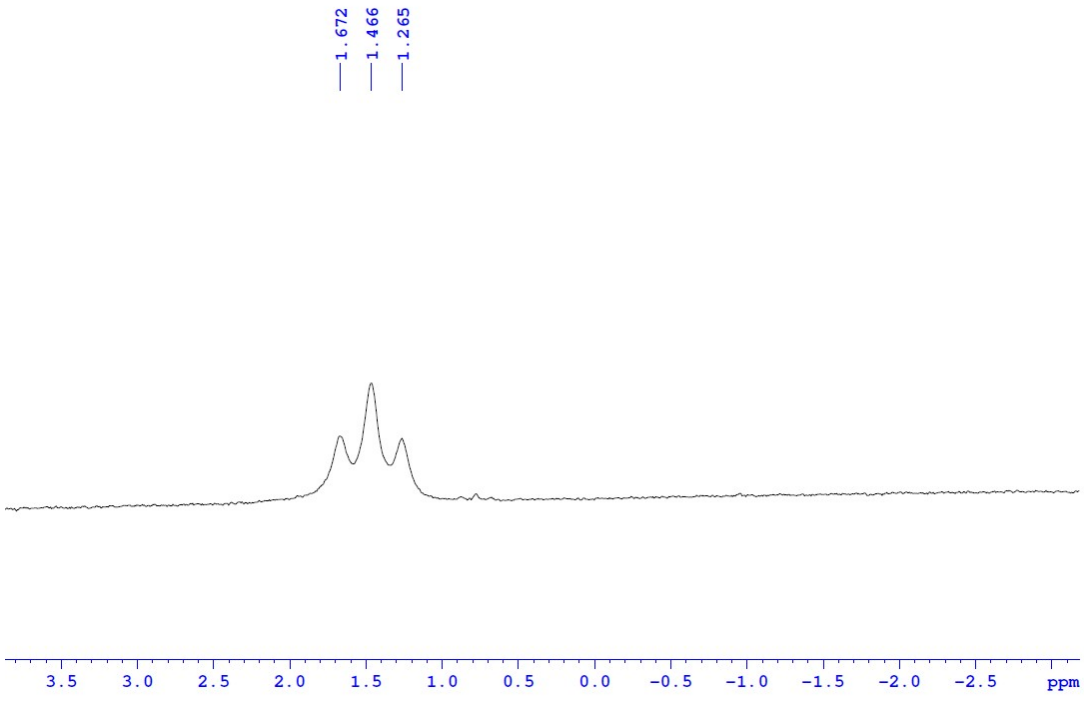


Figure S20. $^{11}B\{^{1}H\}$ NMR spectrum of **2.**

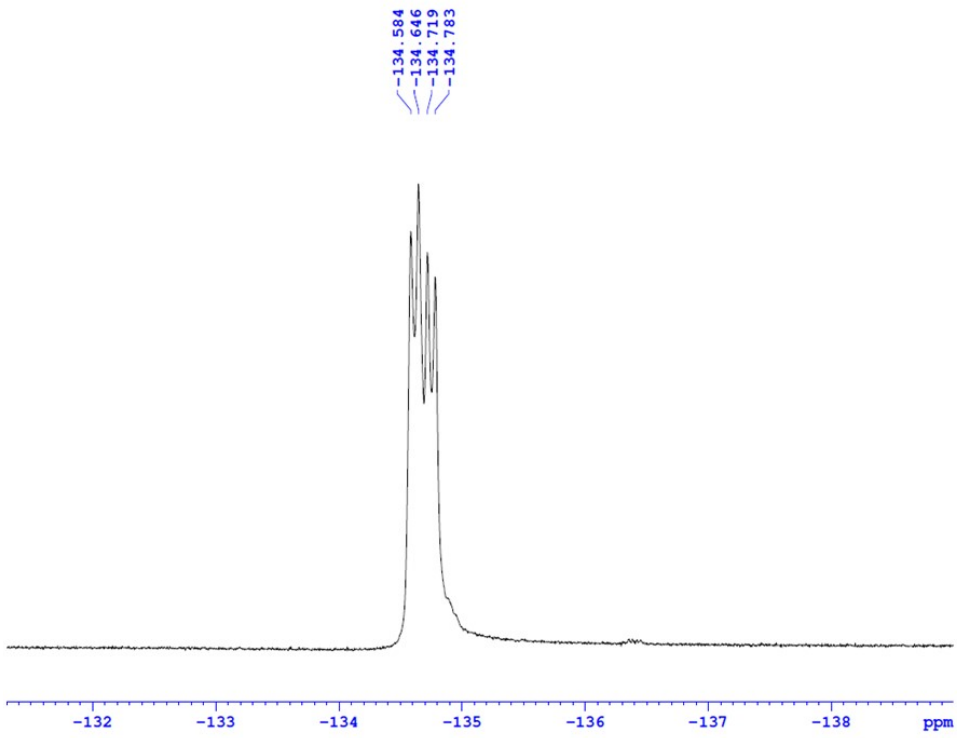


Figure S21. $^{19}F\{^{1}H\}$ NMR spectrum of **2.**

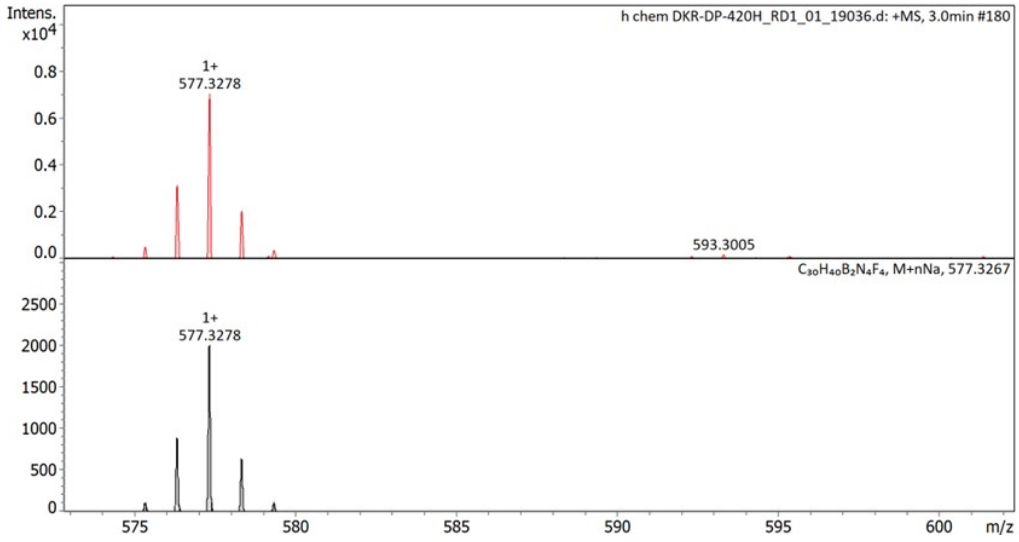


Figure S22. High-resolution mass spectrum of **2**.

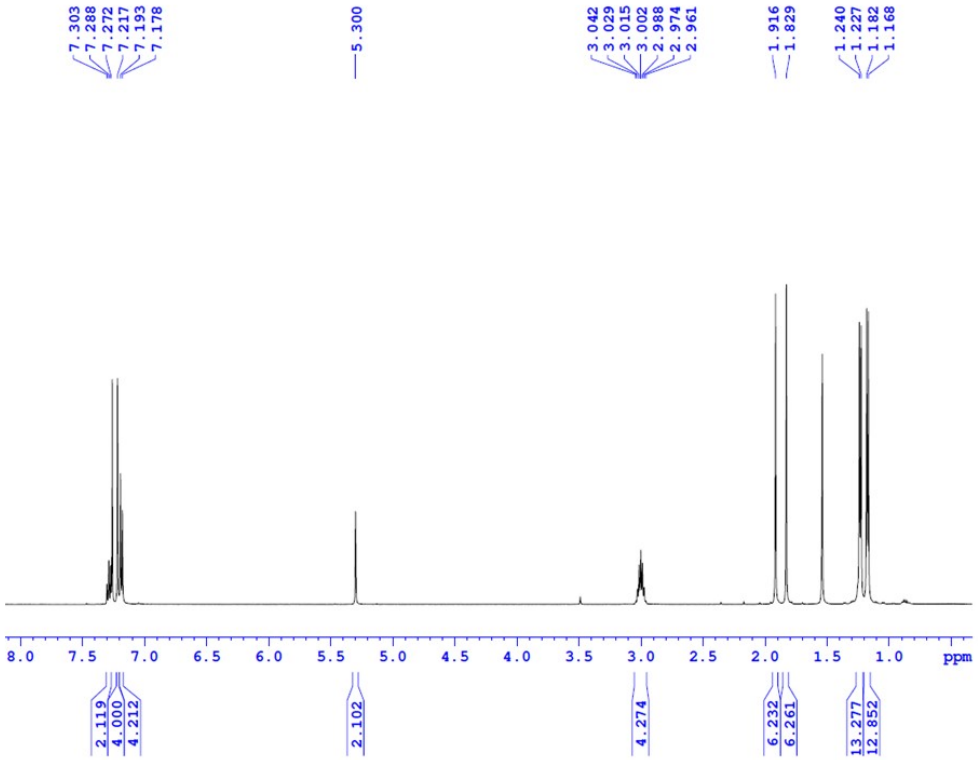


Figure S23. ^{1}H NMR spectrum of **3.**

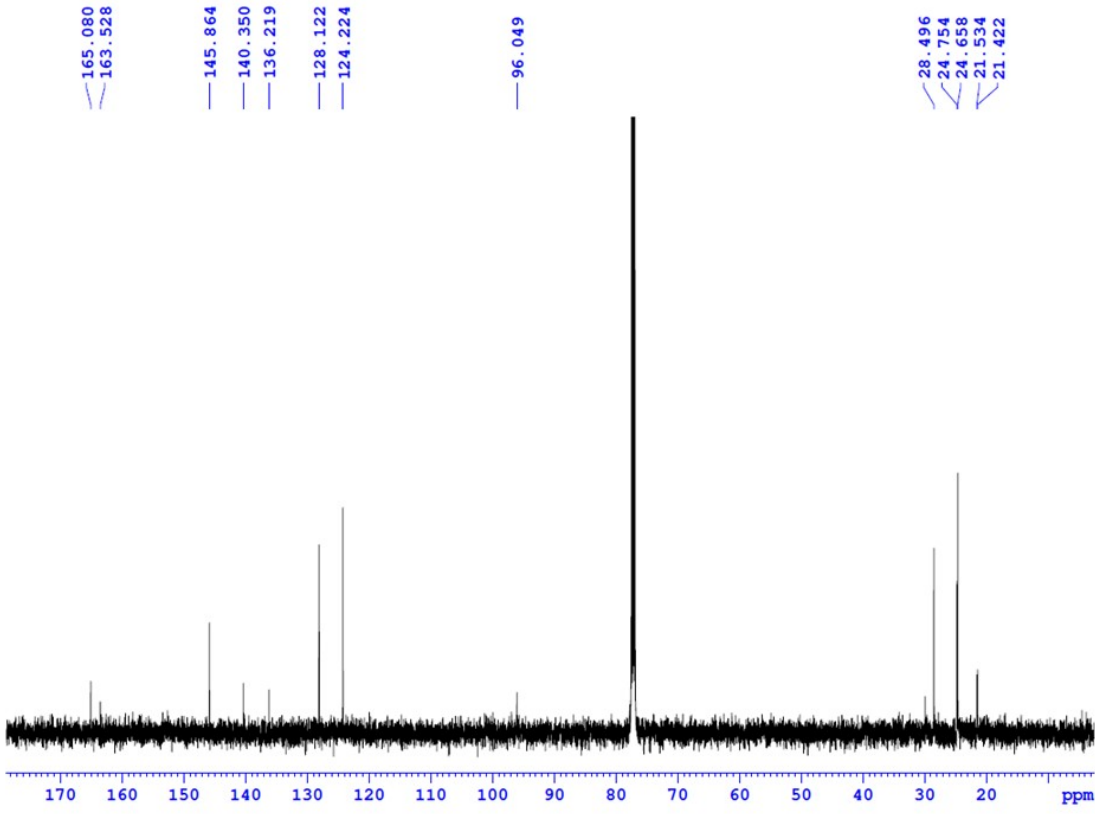


Figure S24. ^{13}C{^{1}H} NMR spectrum of **3.**

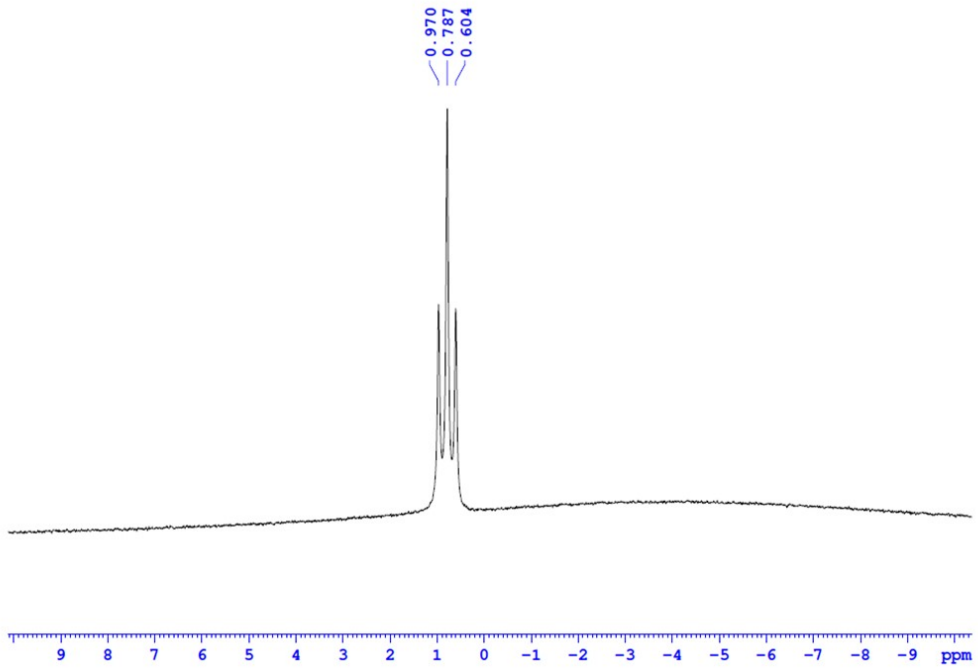


Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum of **3.**

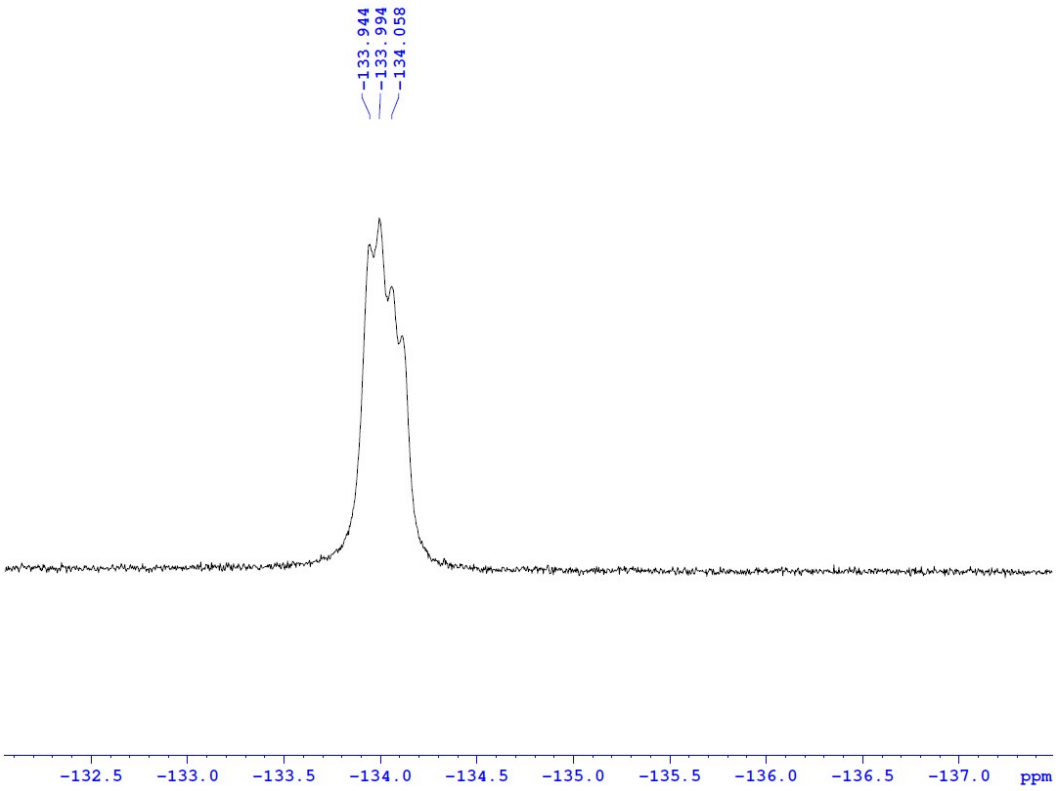


Figure S26. $^{19}F\{^{1}H\}$ NMR spectrum of **3.**

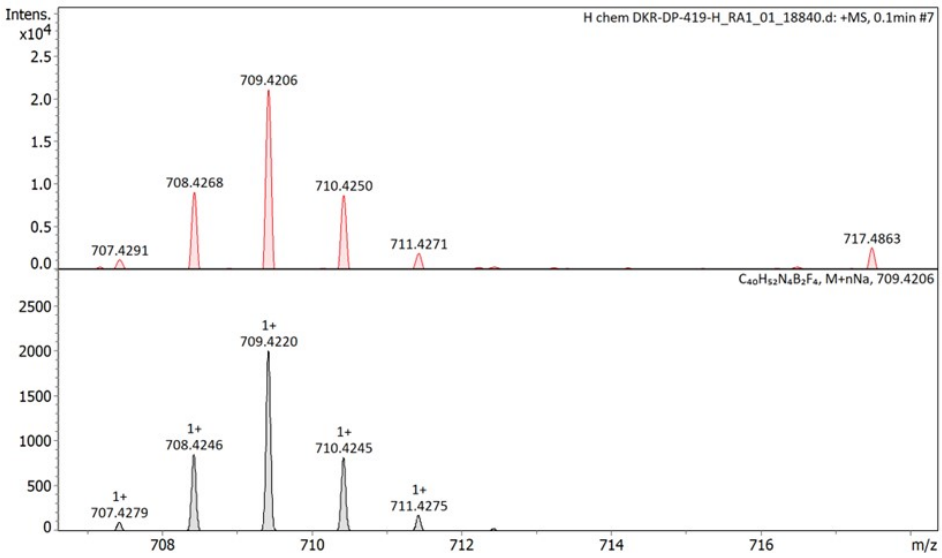


Figure S27. High-resolution mass spectrum of **3**.

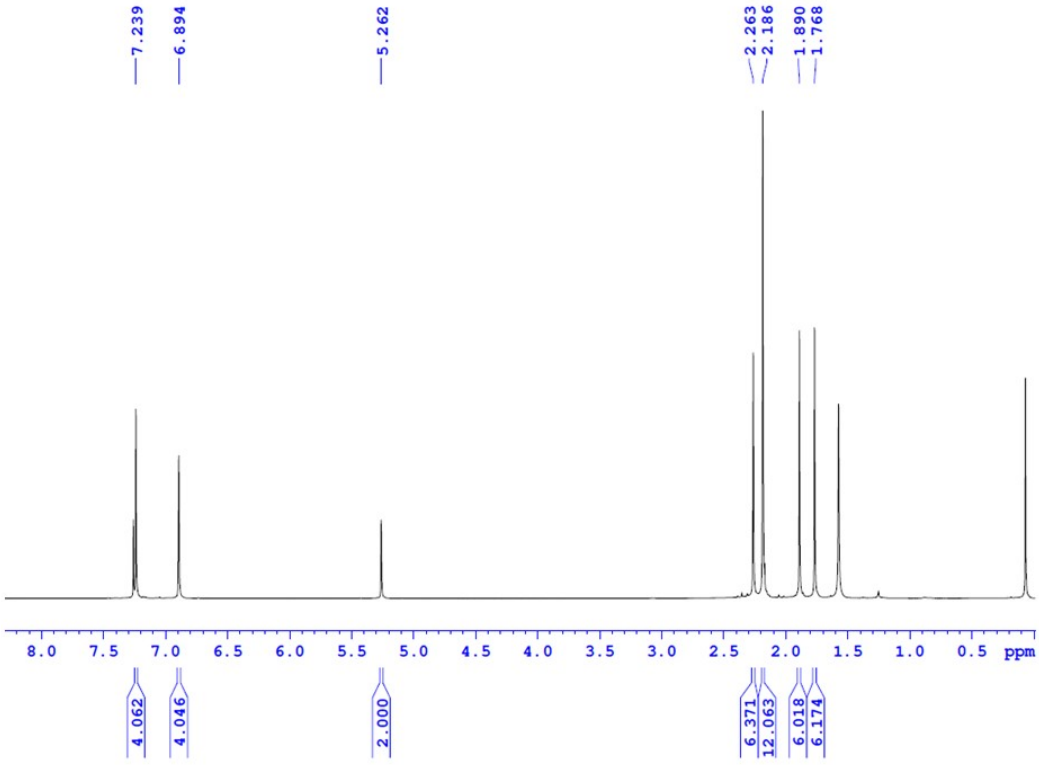


Figure S28. ^{1}H NMR spectrum of **4.**

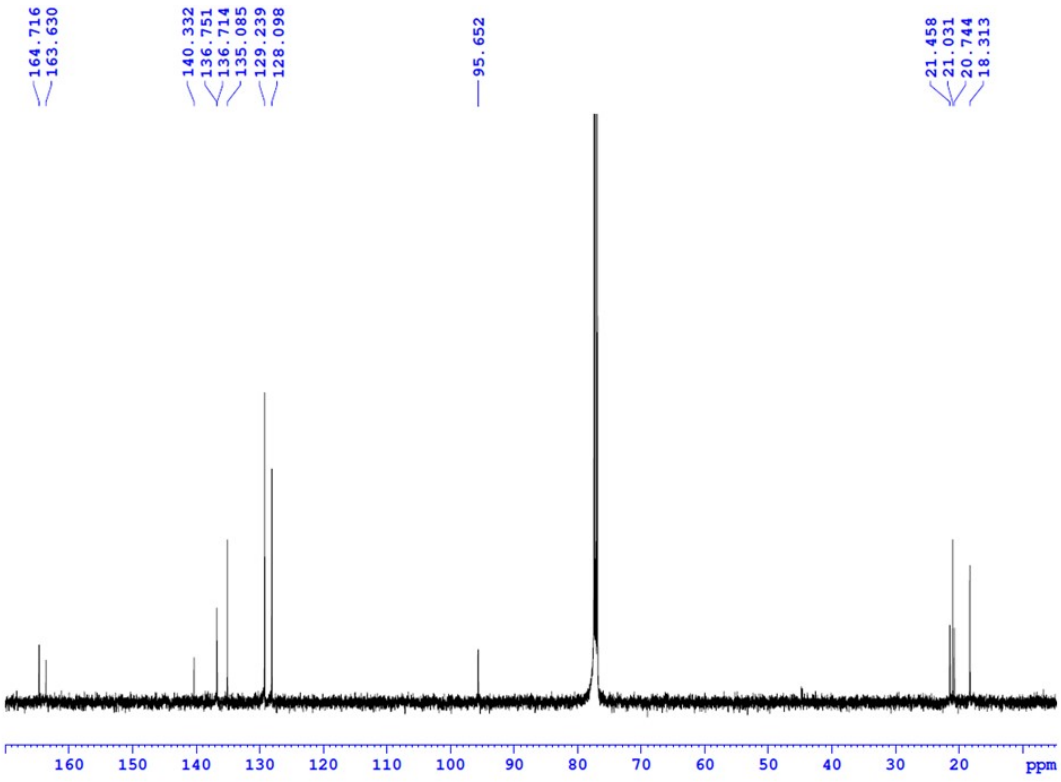


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **4.**

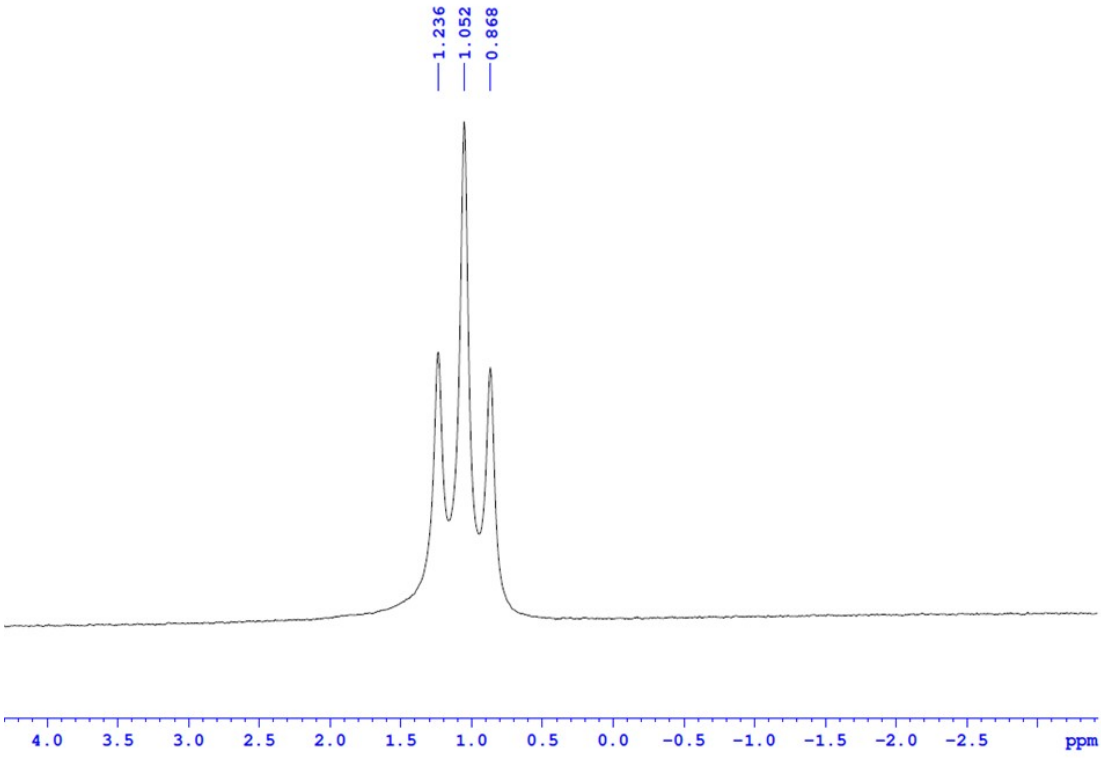


Figure S30. $^{11}B\{^{1}H\}$ NMR spectrum of **4.**

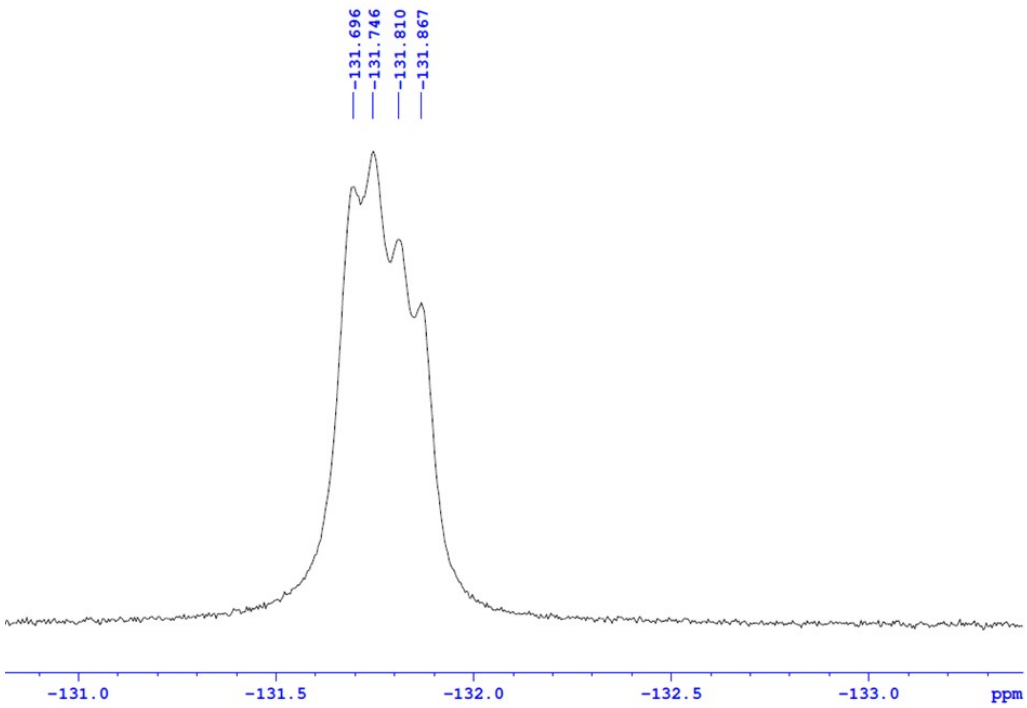


Figure S31. $^{19}F\{^{1}H\}$ NMR spectrum of **4.**

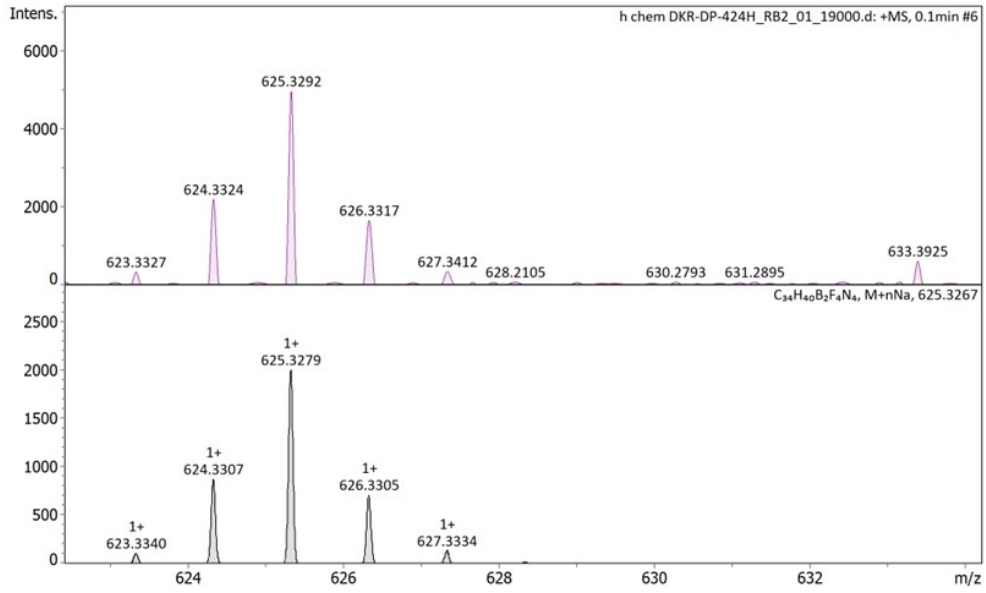


Figure S32. High-resolution mass spectrum of **4**.

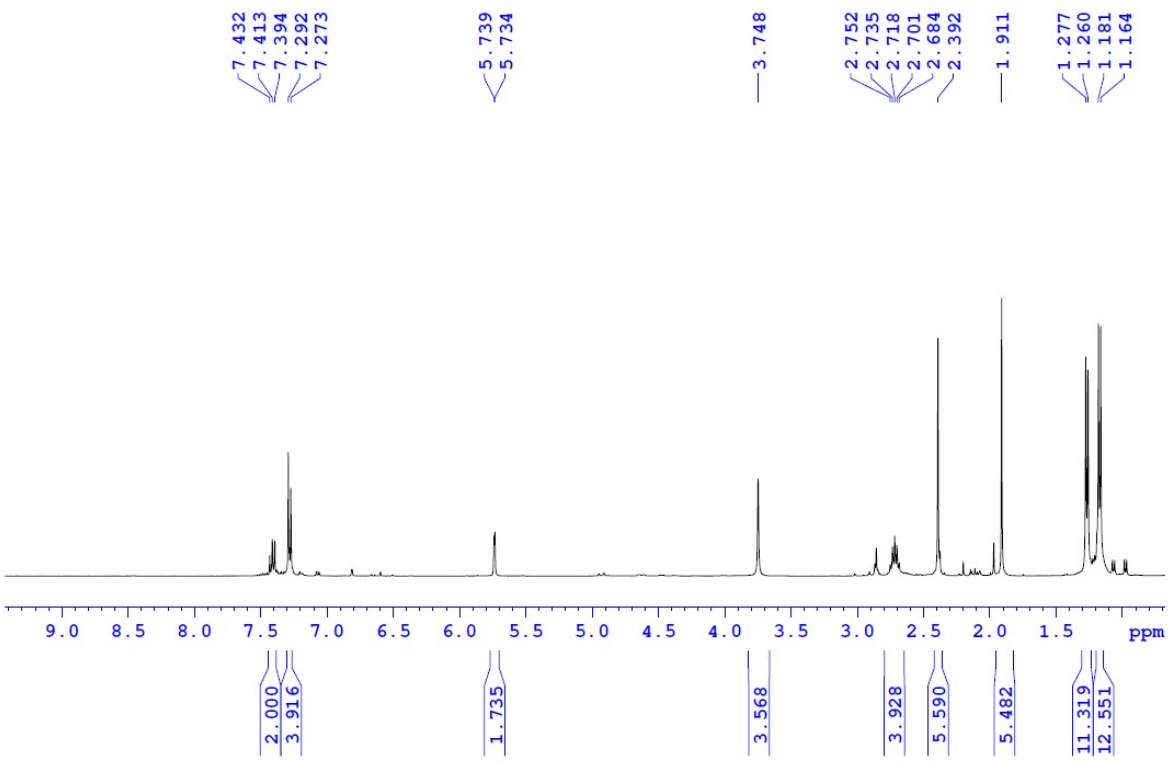


Figure S33. ^{1}H NMR spectrum of **5a.**

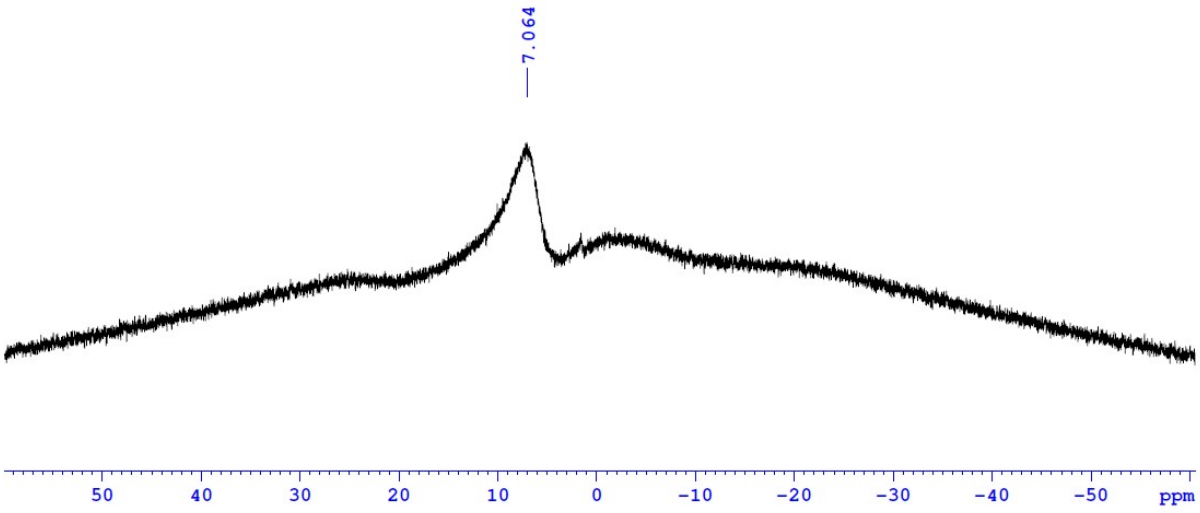


Figure S34. ^{11}B{^{1}H} NMR spectrum of **5a.**

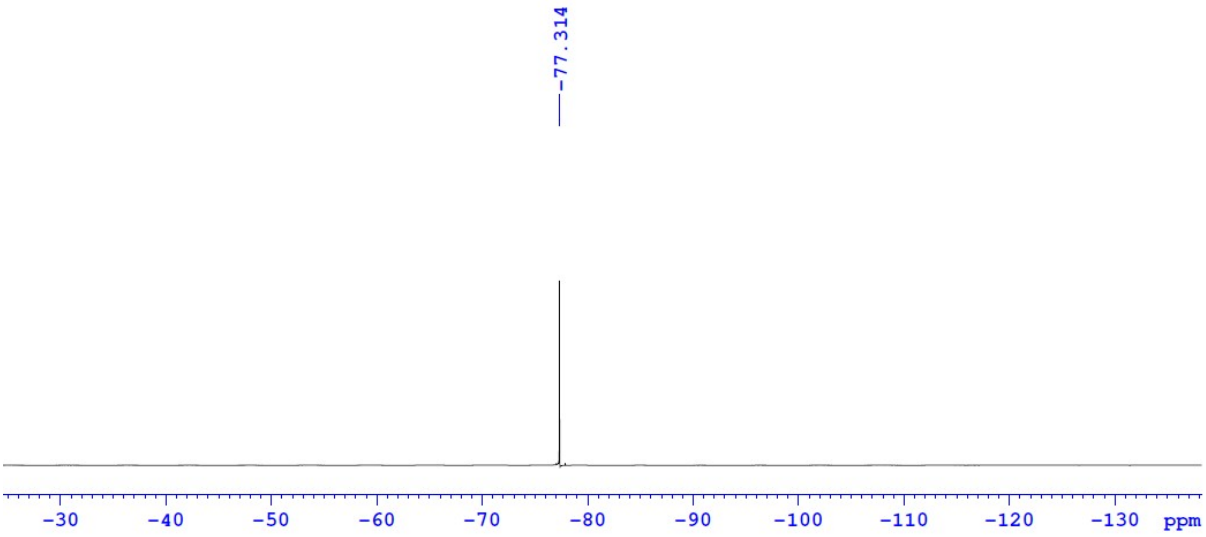


Figure S35. $^{19}F\{^{1}H\}$ NMR spectrum of **5a.**

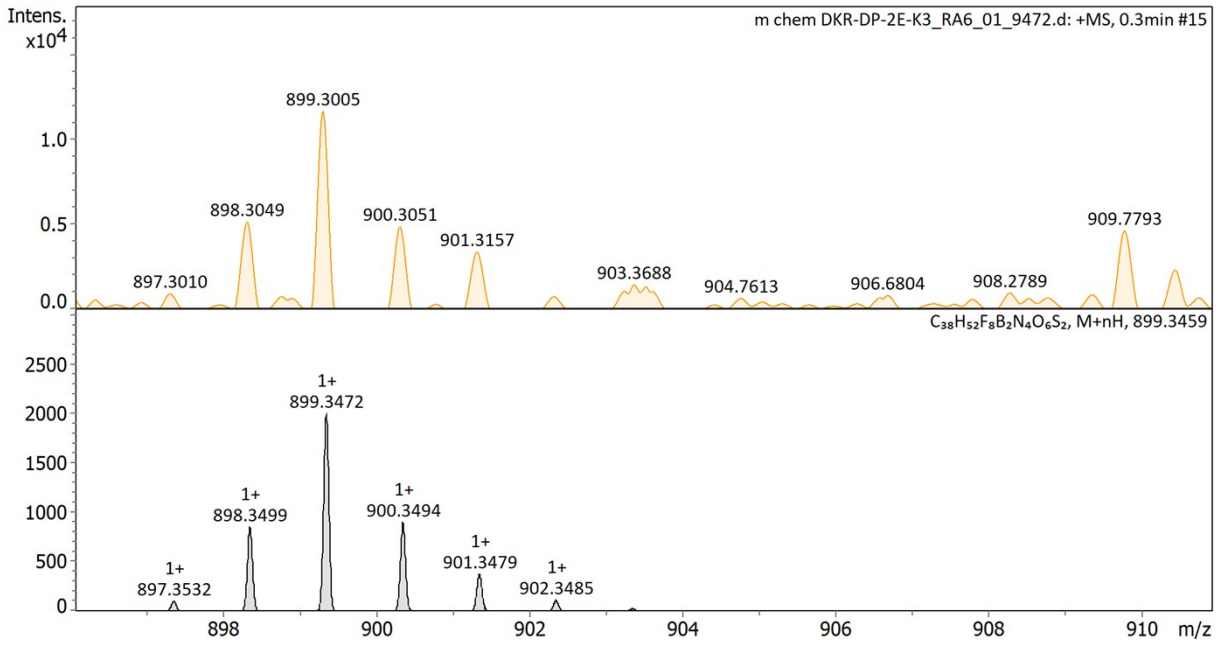


Figure S36. Liquid-chromatography mass spectrum of **5a [M+H]**$^{+}$.

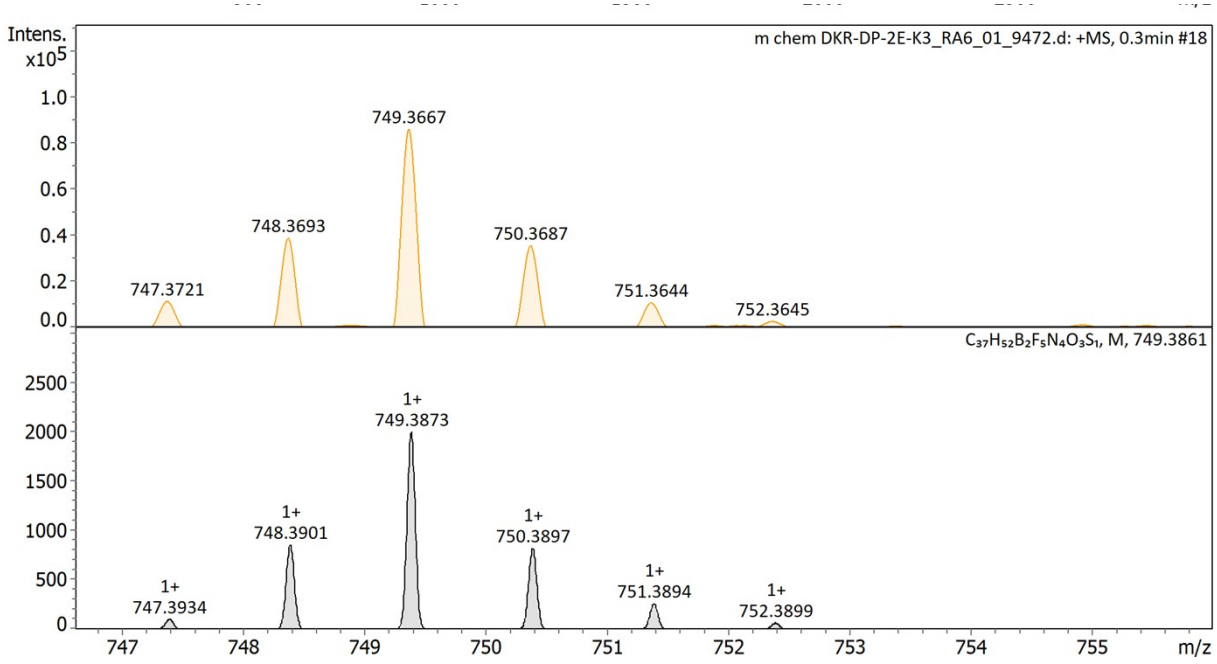


Figure S37. Liquid-chromatography mass spectrum of **5a [M-OTf]**$^{+}$.

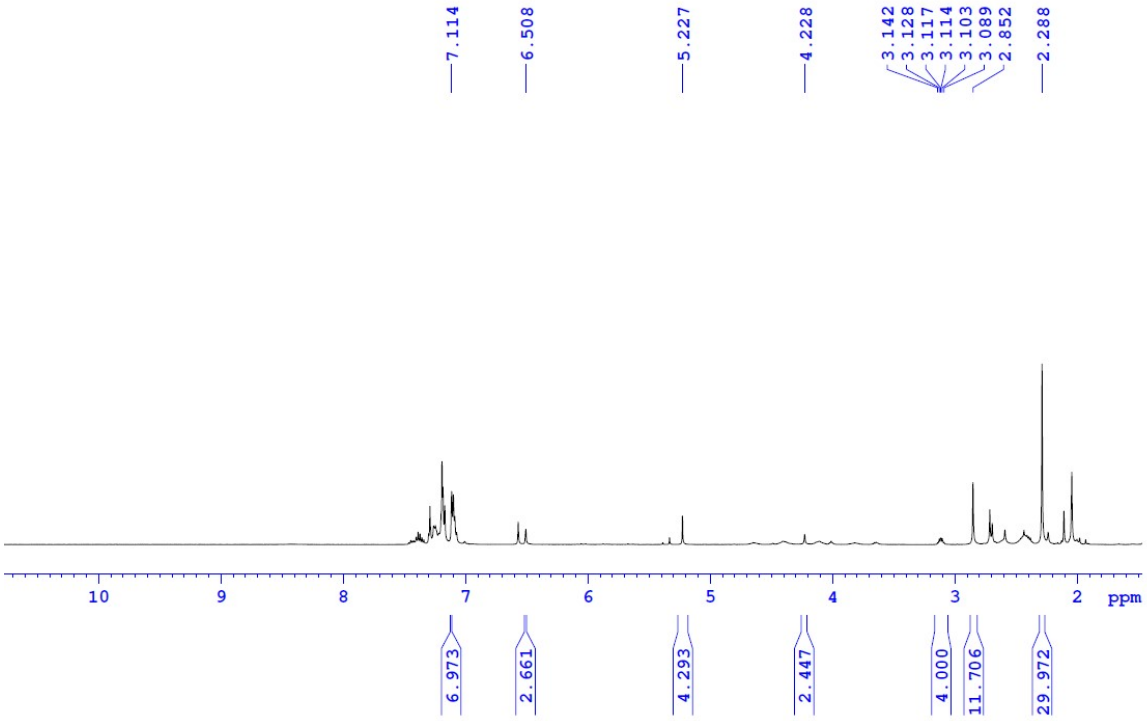


Figure S38. ^{1}H NMR spectrum of **5b.**

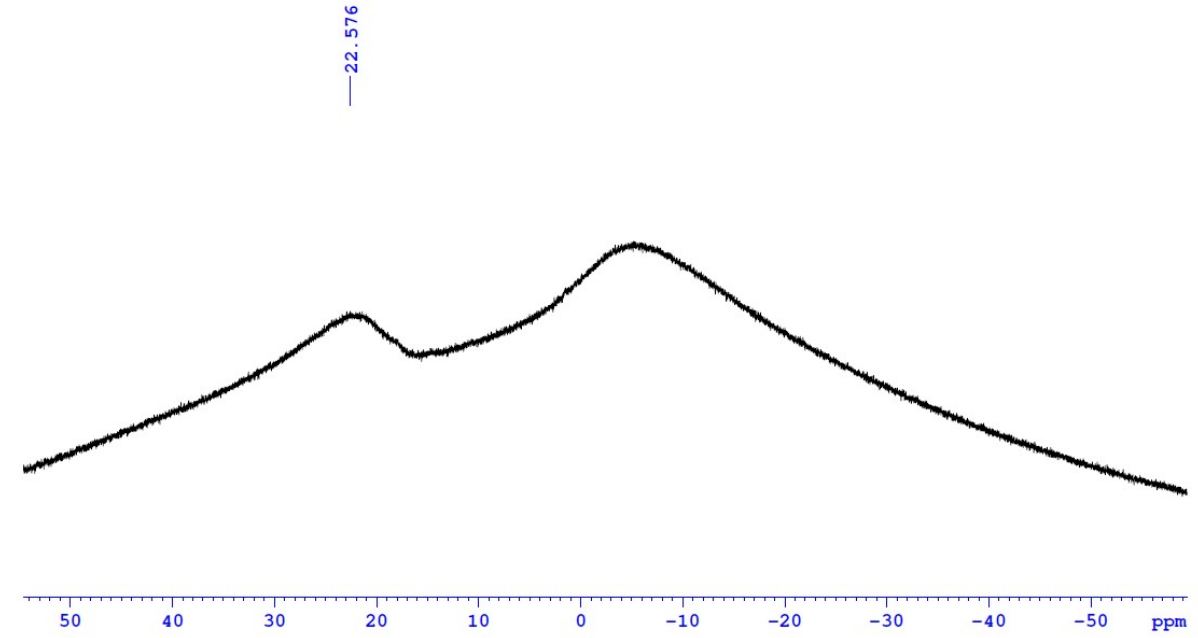


Figure S39a. $^{11}B\{^{1}H\}$ NMR spectrum of **5b.**

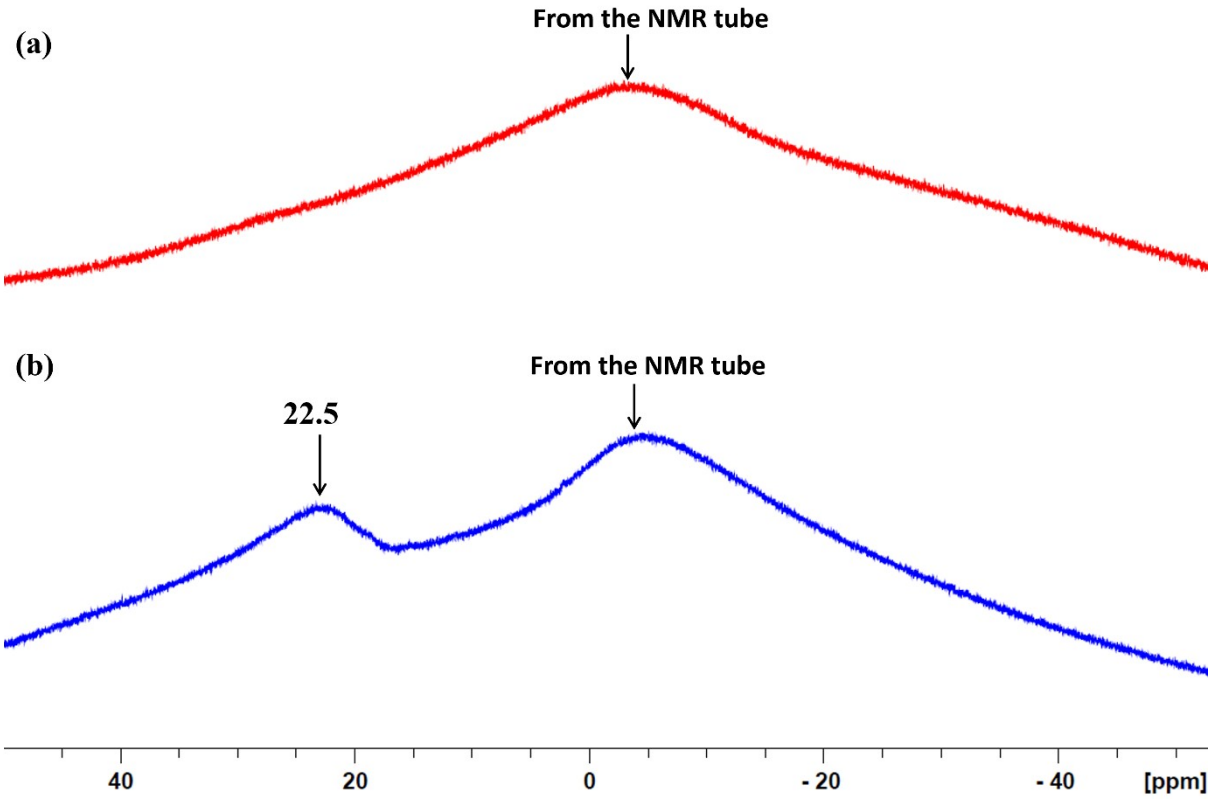


Figure S39b. Stacked $^{11}B\{^{1}H\}$ NMR spectrum of (a) blank and (b) with complex **5b.**

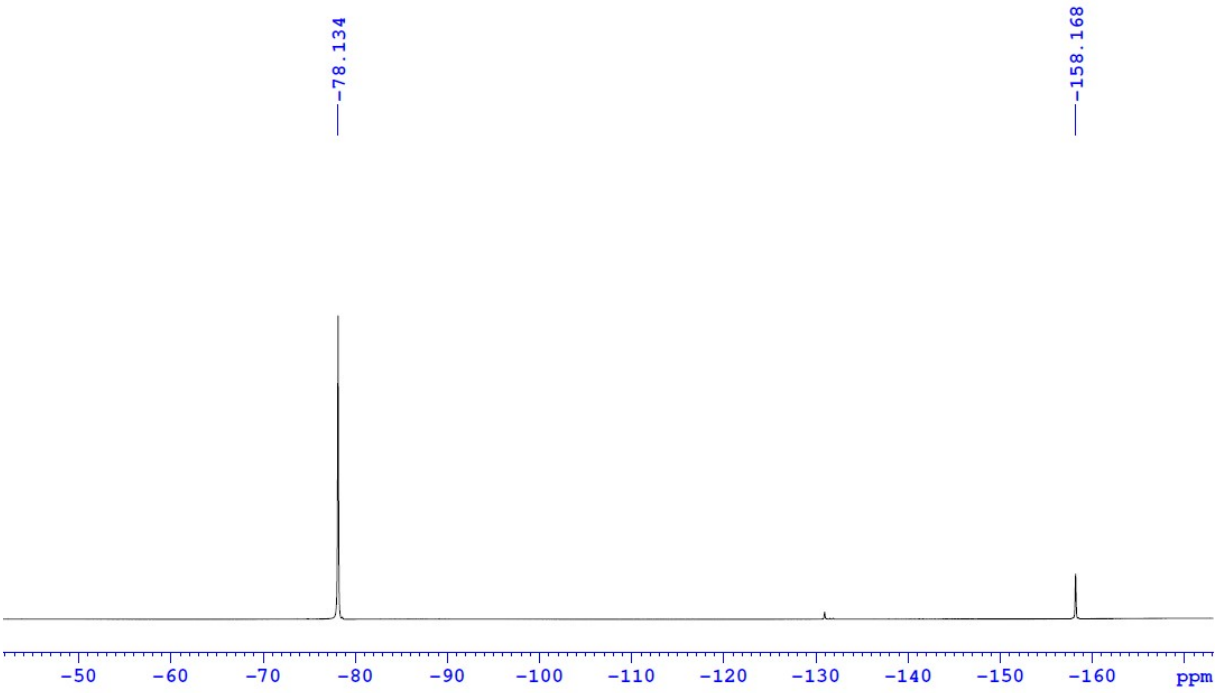


Figure S40. $^{19}F\{^{1}H\}$ NMR spectrum of **5b.**

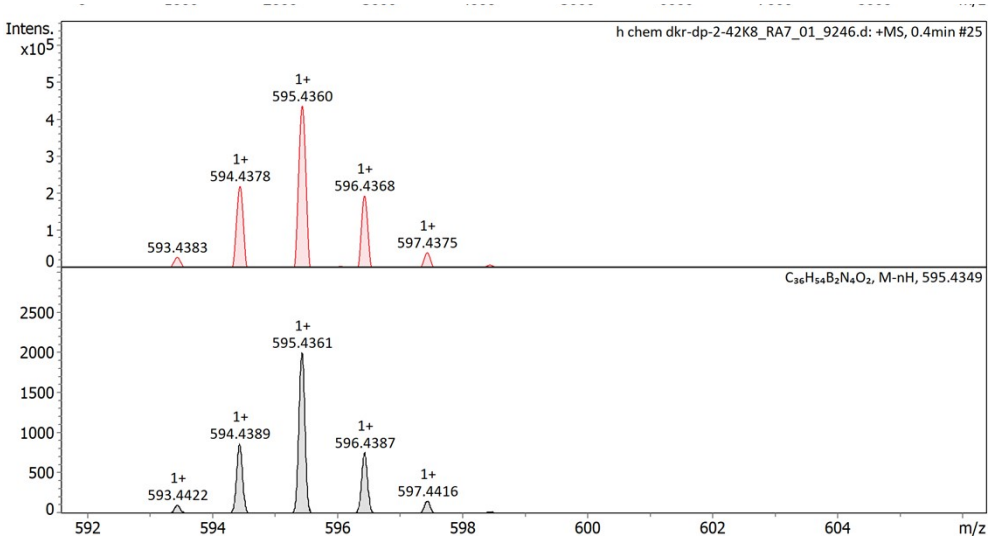


Figure S41. High-resolution mass spectrum of **5b**.

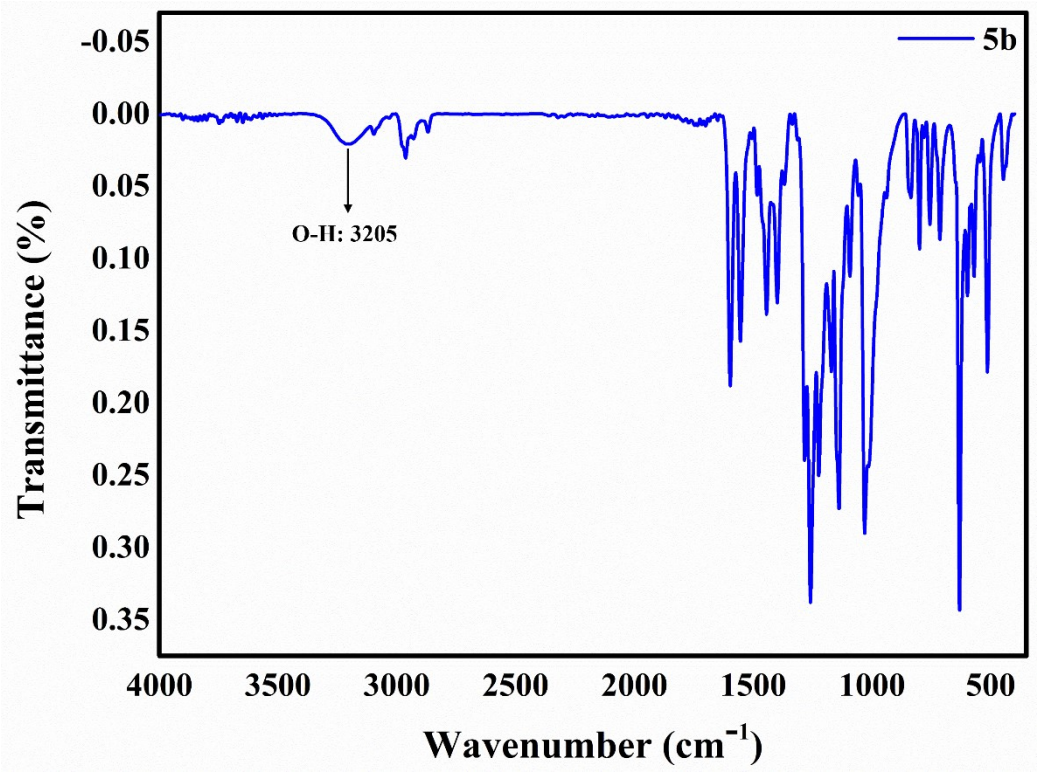


Figure S42. FT-IR spectrum of **5b**.

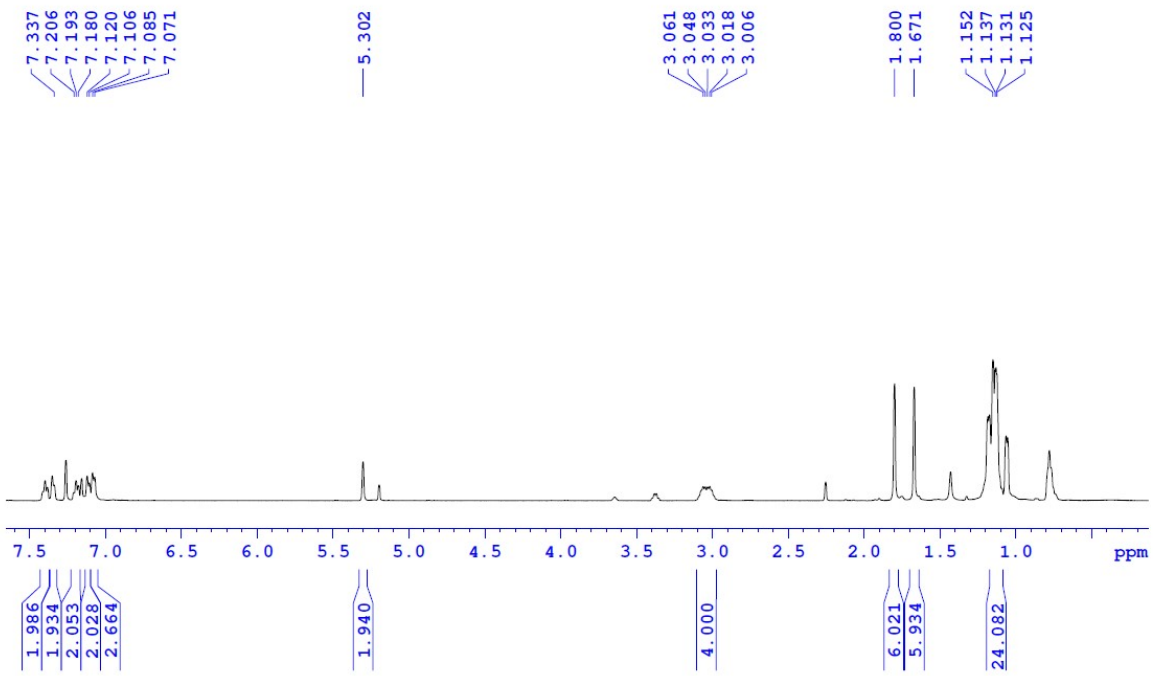


Figure S43. ^{1}H NMR spectrum of **6a.**

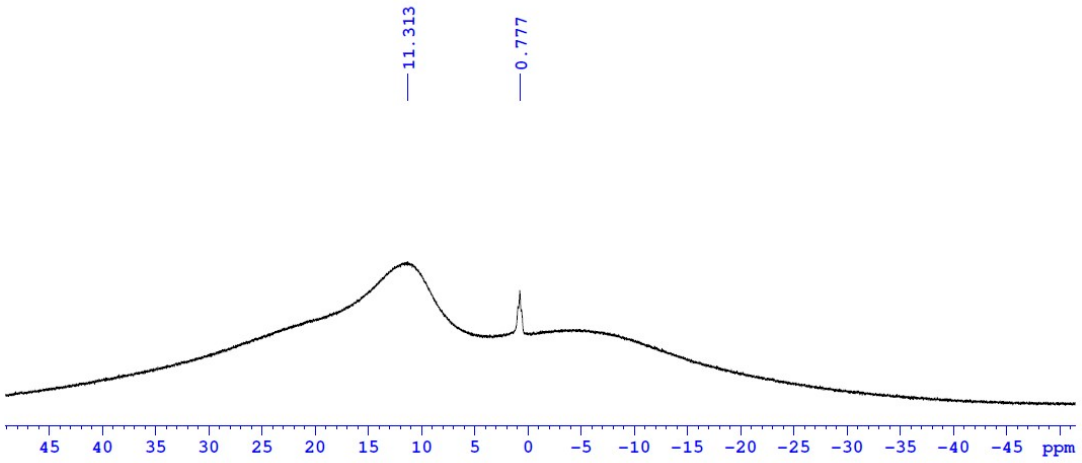


Figure S44. $^{11}B\{^{1}H\}$ NMR spectrum of **6a**. The peak (triplet) at 0.7 ppm is for the starting material **3**.

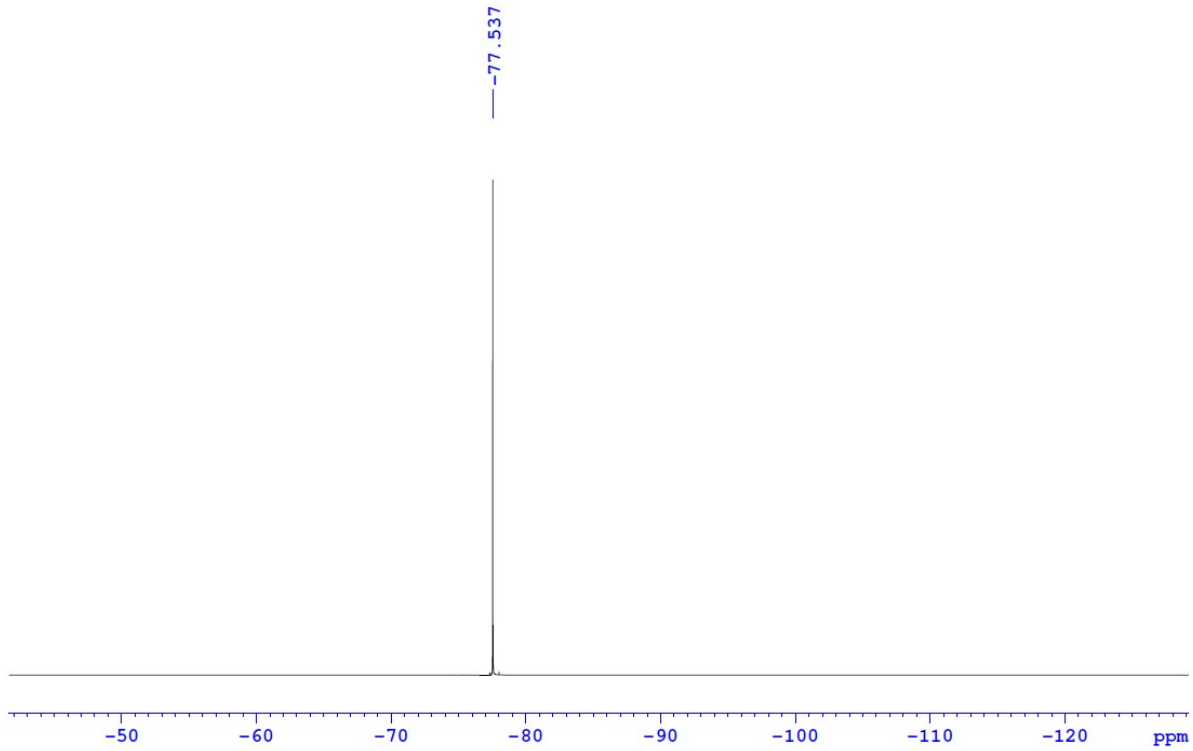


Figure S45. $^{19}F\{^{1}H\}$ NMR spectrum of **6a**.

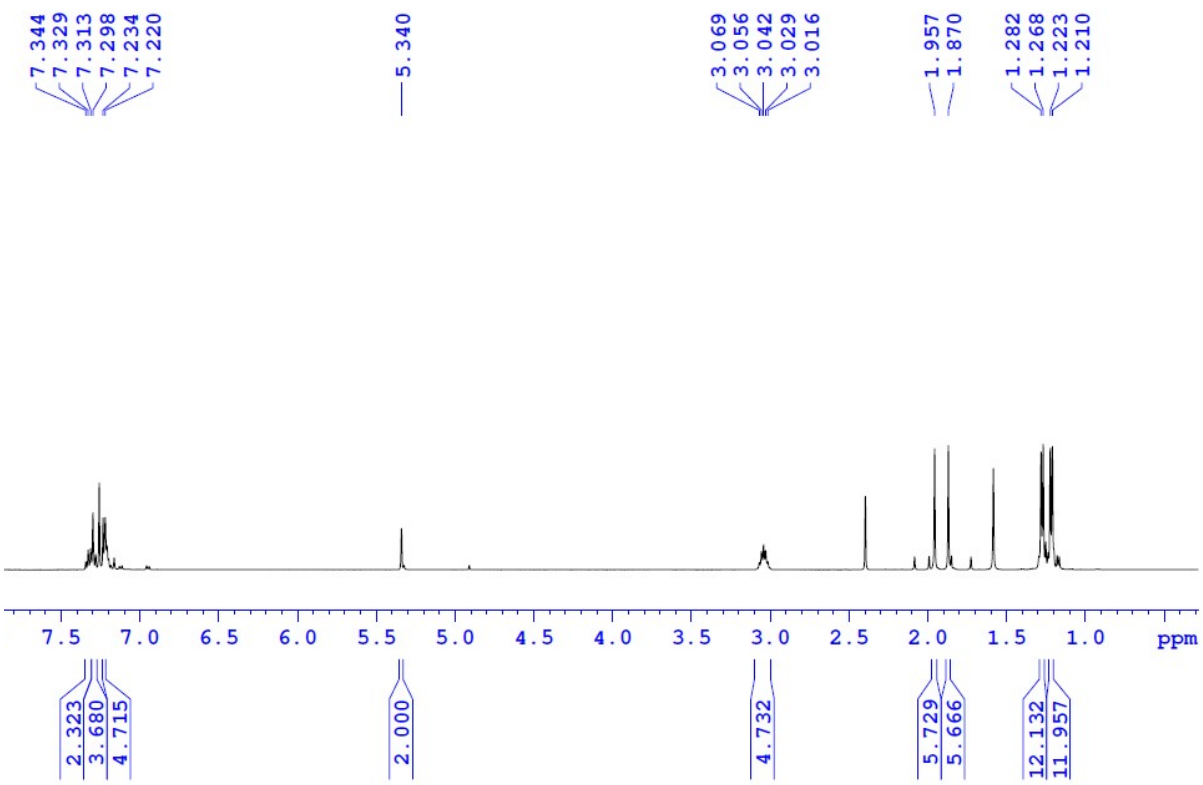


Figure S46. ^{1}H NMR spectrum of **6b.**

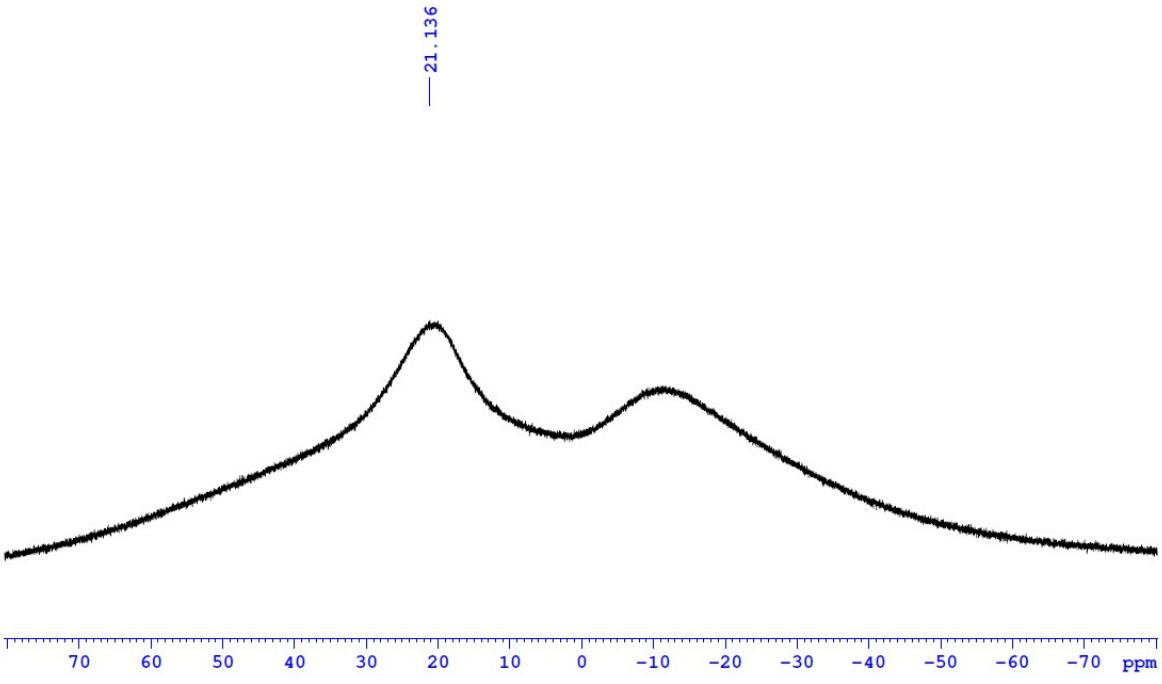


Figure S47. ^{11}B{^{1}H} NMR spectrum of **6b**.

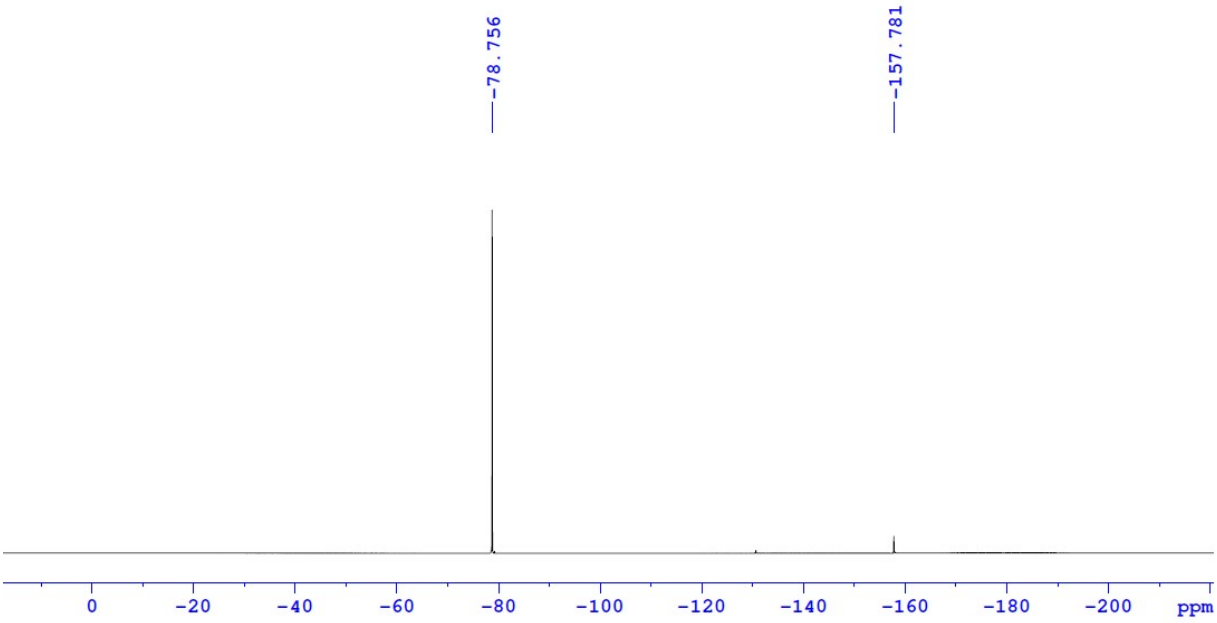


Figure S48. $^{19}F\{^{1}H\}$ NMR spectrum of **6b**.

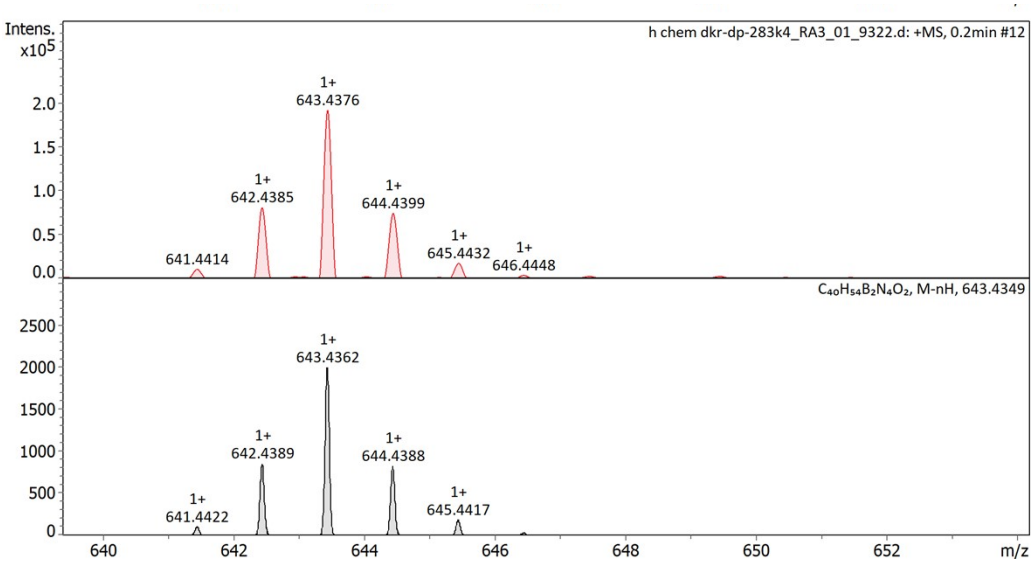


Figure S49. High-resolution mass spectrum of **6b**.

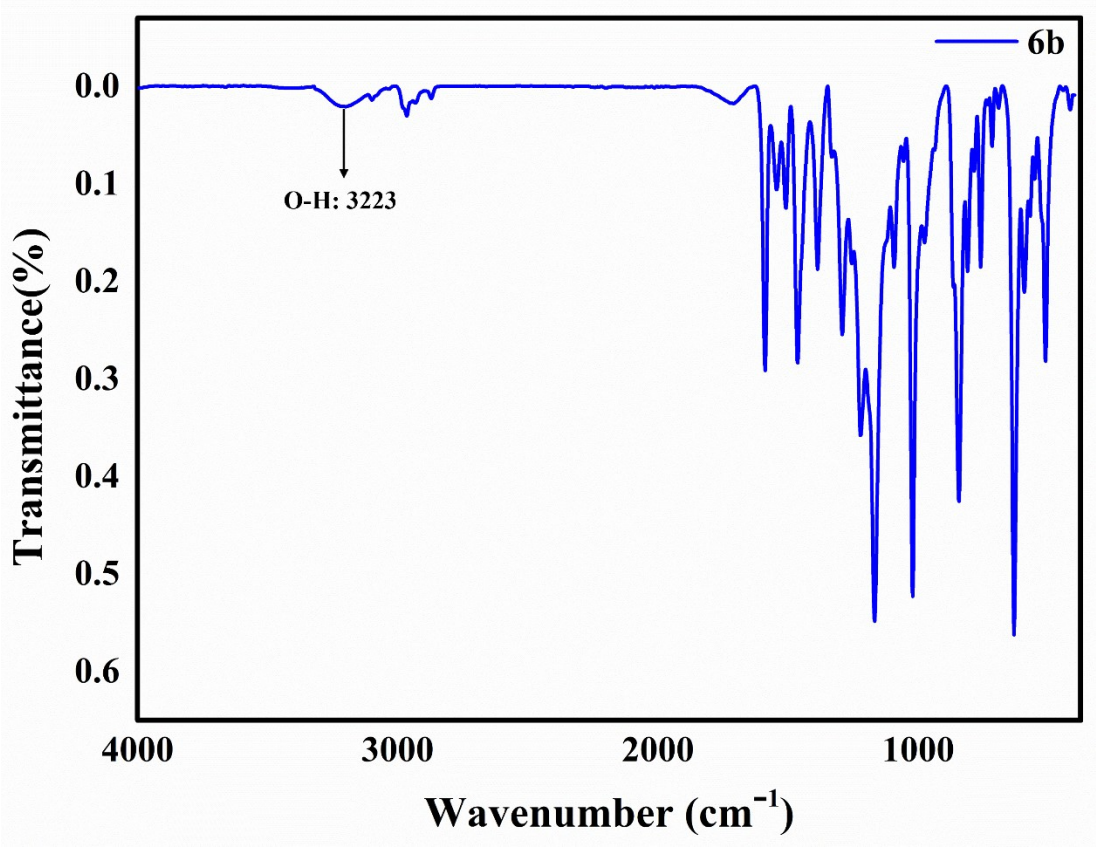


Figure S50. FT-IR spectrum of **6b**.

Photophysical and electrochemical properties:

The absorption spectra of complexes were performed in the solution phase, revealing a broad wavelength absorption band ranging from 338 to 345 nm (Figure S51(e)) with a molar extinction coefficient Ɛ between 67886 to 82756 $L.mol^{-1}$ cm^{-1} (Table S1). In order to investigate the redox properties of these complexes, the electrochemistry of complexes **1**-**4** was examined using cyclic voltammetry (CV). The cyclic voltammetry was carried out using a sample solution containing 0.1 M solution of Bu_4NPF_6 in DCM as a supporting electrolyte and a standard three-electrode system was employed for the measurements. The results of the voltammetric experiments are summarised in Figure S51(f).

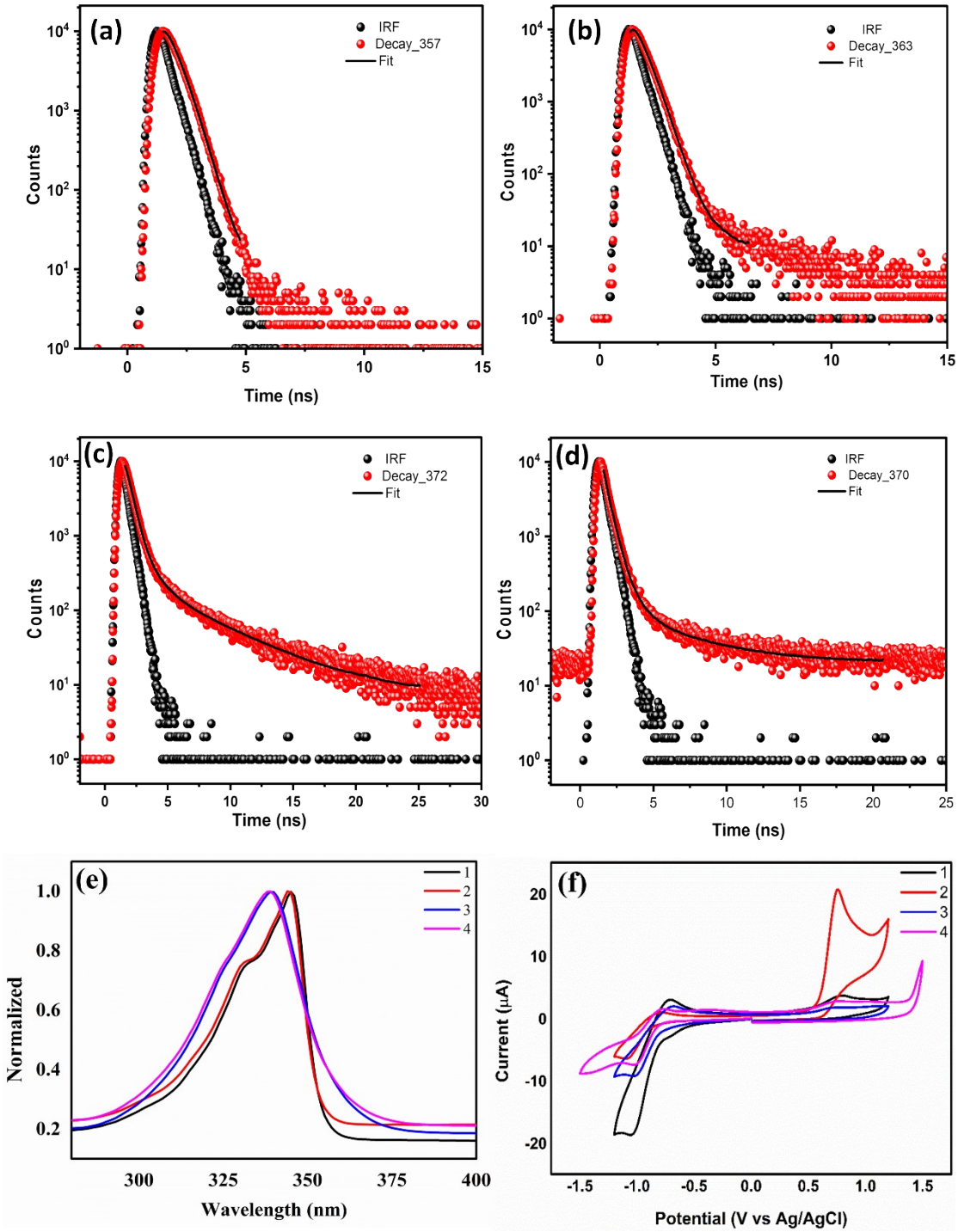


Figure S51. (a)–(d) Photoluminescence decay plots for complexes **1**–**4** (a-d respectively); **(e)** Absorption spectra of **1**–**4** in DCM solution; **(f)** Cyclic voltammograms of complex **1**–**4** in 0.1 M solution of Bu_4NPF_6 in DCM at 100 mV s^{-1} scan rate versus Ag/AgCl at 25 °C.

Table S1: Photophysical data of DBI complexes **1-4**.

S. No.	$\lambda_{max,abs}$ (nm)	Ɛ (L.mol^{-1}.cm^{-1}) [a]	λ_{exc} (nm)	λ_{em} (nm)	Stoke shift Δv (cm^{-1})[b]	Φ [c]	τ_{avg} (ns)
1	345	82756	342	358	1130	0.3	0.3
2	344	78854	341	360	1480	0.6	0.3
3	340	67886	338	376	2990	0.6	0.9
4	338	70310	336	381	3510	0.5	0.3

[a]Recorded in CH_2Cl_2, $c = 10^{-5}$ M at $T = 293$ K.

[b]$\Delta\tilde{V} = 1/\lambda_{exc} - 1/\lambda_{max,em}$ [cm^{-1}].

[c]Relative quantum yield was calculated concerning the standard Quinine Hemisulfate in 0.5 $M\ H_2SO_4$.

Crystallographic Details

The crystal data for **1** was collected on a CCD Agilent Technologies (Oxford Diffraction) SuperNova diffractometer at 293(2) K using a graphite-monochromated MoKα radiation. The crystal data for **2**, **4** and **5a** were collected D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K. The crystal data for **5b** was collected APEXII Kappa-CCD diffractometer equipped with a CCD plate detector, using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator) at 293(2) K. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization. The structures were solved by direct methods and refined by full-matrix least squares, based on *F*2, using SHELXL Crystal structures were refined using Olex2-1.0 software. All non-hydrogen atoms were refined anisotropically.

Table S2. Crystal data for Complex 1, 2, 4, 5a, and 5b.

Chemical Compound	**1**	**2**	**4**	**5a**	**5b**
Empirical formula	$C_{36}H_{52}B_2F_4N_4$	$C_{30}H_{40}B_2F_4N_4$	$C_{34}H_{40}B_2F_4N_4$	$C_{42}H_{56}B_2F_8N_4O_6S_2Cl_{12}$	$C_{38}H_{54}B_2F_6N_4O_8S_2$
Formula weight (g·mol^{-1})	638.43	554.28	602.32	1376.04	894.59
Temperature (K)	293 (2)	150 (2)	150 (2)	150 (2)	293(2)
Radiation, λ (Å)	MoK_α, 0.7107	MoK_α, 0.7107	MoK_α, 0.7107	MoK_α, 0.7107	MoK_α, 0.7107
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions					
***a* (Å)**	11.6320(7)	7.0540(10)	17.9364(15)	14.1344 (16)	8.627 (3)
***b* (Å)**	14.7782(7)	16.785(2)	7.0652(6)	11.0335 (12)	15.411 (5)
***c* (Å)**	10.9398(7)	12.4247(15)	13.0809(10)	20.579 (2)	16.562 (5)
α (°)	90	90	90	90	90
β (°)	109.606(7)	96.900(5)	104.394(3)	109.181 (4)	96.019(11)
γ (°)	90	90	90	90	90
Volume (Å^3)	1771.52(19)	1460.4(3)	1605.6 (2)	3031.2 (6)	2189.9 (12)

Z	2	2	2	2	2
Calculated density (g·cm^{-3})	1.197	1.260	1.246	1.508	1.357
Absorption coefficient (mm^{-1})	0.084	0.091	0.089	0.687	0.200
***F*(000)**	684.0	588.0	636.0	1404	940
Theta range for collection	6.65 to 49.994	4.098 to 55.06	6.226 to 54.918	4.192 to 54.986	4.748 to 49.99
Reflections collected	19815	15811	19534	32161	28532
Independent reflections	3116	3338	3664	6937	3850
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data /restraints/parameters	3116/0/214	3338/0/186	3664/0/203	6937/97/446	3850/0/278
Goodness-of-fit on F^2	1.067	1.038	1.040	1.036	1.028
Final R indices [I>2 σ (I)]	R_1 = 0.0577, wR^2 = 0.1459	R_1 = 0.0465, wR^2 = 0.1229	R_1 = 0.0440 wR^2 = 0.1155	R_1 = 0.0397 wR^2 = 0.0848	R_1 = 0.0496 wR^2 = 0.0987
R indices (all data)	R_1 = 0.0878, wR^2 = 0.1629	R_1 = 0.0532, wR^2 = 0.1287	R_1 = 0.0482 wR^2 = 0.1188	R_1 = 0.0559 wR^2 = 0.0936	R_1 = 0.0984 wR^2 = 0.1116
Maximum/minimum residual electron density (e·Å^{-3})	0.24 / –0.19	0.39/ -0.25	0.29 / –0s.25	0.34/ -0.36	0.26/ -0.39
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -13 ≤ l ≤ 13	-9 ≤ h ≤ 9, -21 ≤ k ≤ 20, -16 ≤ l ≤ 16	-23 ≤ h ≤ 23, - 8 ≤ k ≤ 9, -16 ≤ l ≤ 16	-18 ≤ h ≤ 18, -12 ≤ k ≤ 14, -24 ≤ l ≤ 26	-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
CCDC Number	2346141	2346147	2346142	2346139	2353046

Molecular Diagram of Complex 2 and 3

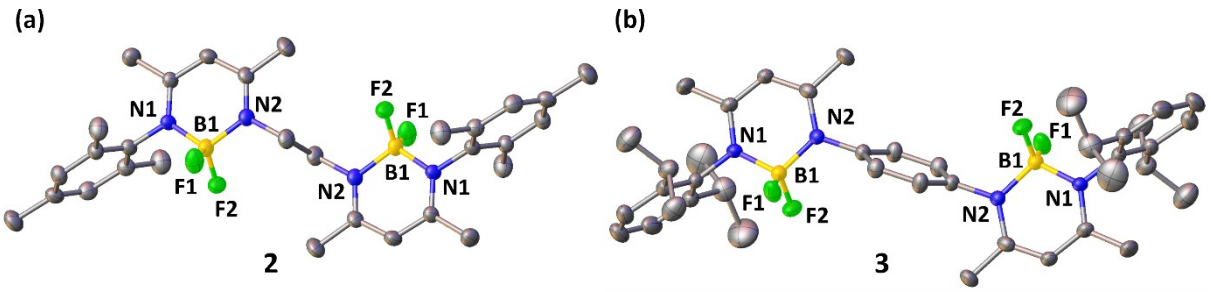


Figure S52. Molecular diagram of complexes **2** and **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and solvents are omitted for clarity. Selected bond length (Å), and bond angles (°)**: 2**: B1-N1 1.5427(17), B1-N2 1.5397(18), B1-F1 1.3986(17), B1-F2

1.4002(16); N2-B1-N1 109.63(10), F2-B1-N1 110.31(11), F1-B1-N2 109.47(11), F1-B1-F2 107.05(11), F2-B1-N2 109.46(11), F1-B1-N1 110.88(11).

Computational Study:

To illustrate the bonding scenario and the electronic structures, geometry optimizations of compounds **1**, **3**, **5a** and **5b** were carried out at the B3LYP/cc-pVDZ level of theory (see computational details). The geometrical parameters of compounds showed good agreement with the experimental crystal structures that can be seen from the alignments and superposition of the conformers (Figure S53). Further, the suitability of the calculation model was apparent from the satisfactory agreement between the experimentally observed and calculated $^{11}B\{^{1}H\}$ NMR values (within the error range of 9 ppm, Table S5). The boron atom occupies a trigonal planar geometry and therefore the C_3N_2B ring contains six π electrons in **5b**. To gain more insights into the electronic structure of **5b**, the DFT calculations were carried out on the cationic part of the **5b** and compared to **1**. The calculations reveal that the HOMO and HOMO-1 of **5b** (Figure S56) are the degenerate orbitals and are largely centered on the phenyl rings of the Dipp moieties, whereas the HOMO of **1** (Figure S54) describes the C-C-C allylic interaction within the C_3N_2B ring as well as the electron localizations over the N atoms due to non-planarity of the B atom. For both **1** and **5b** the LUMO is π* in nature (Figures S54 and S56) showing considerable N–C π* character in the C_3N_2B ring. The C_3N_2B ring π-bonding character of **5b** is found in the HOMO-4 and HOMO-5 orbitals which involves two π-allylic N–B–N and C–C–C fragments separated by a nodal plane that passes through the two N-C bonds, while the HOMO-18 features two N–C π-bonds. A comparable bonding situation was also observed in the borenium cation (**VIII**) reported by Cowley (Figure S59).[4] From the NBO analysis of **5b**, an analogous bonding description has been found (Figure S57, shows the pertinent NBO orbitals and corresponding electron occupancies). The NBO analysis of **5b** further showed the π-delocalization within the C_3N_2B moieties that contributes to the overall stabilizations as estimated by the second-order perturbation theory analysis (Figure S57). Noticeably, the second-order perturbation theory analysis also reveals the delocalization of the oxygen centered lone pair electron to the antibonding B-N orbital (which was majorly a boron centered 2p

orbital) of the C_3N_2B moiety providing an overall stabilization of 64.49 kcal/mol. This electron delocalization explains the partial quenching of the positive charge at the boron center (+1.38 in **1** and +1.29 in **5b**, Table S4) which is characteristic of the borenium cations.

With the degree of electron delocalization within the six-membered C_3N_2B rings of **5b**, the calculated NICS(1) values are more negative compared to **1** which are however nearly half of the corresponding values of the phenyl rings of the Dipp moieties in **5b** (Table S3). Comparable NICS(1) values were also observed for the borenium cation reported by the Cowley group **VIII** (Table S3).[4]

The Laplacian plot of electron densities of **1** and **5b** within the C_3N_2B ring resulted in nearly similar bonding description (polar B-N and non-polar C-C interactions), however, the extent of electron delocalizations in **5b** can be understood from the quantitative measurements of the properties at the bond critical points (bcp, (3,-1)). For example, a higher amount of electron density can be observed at the bcp bond along the B-N bonds of **5b**. However, the negative values of the energy density (H(r)) for both **1** and **5b** suggested a covalent character for the N-B interactions, which is again higher in **5b**. The electron density at the ring critical point (rcp, (3,+1)) of the C_3N_2B ring is higher in **5b** (Table S4).

Further, in order to understand the UV-vis spectra, time-dependent DFT (TD-DFT/ωB97XD /SMD(CH_2Cl_2)) calculations were performed on **1** and **3** including the solvent effect and the corresponding orbital transitions are provided in Tables S5. All the theoretical UV-vis plots corroborate with the experimentally obtained results. Major theoretical transition, for **1**, occurring at 295 nm majorly accounts for occupied molecular orbital HOMO (π orbitals located on C_3N_2B rings) to unoccupied molecular orbital LUMO (π* type orbitals of C_3N_2B ring) transition with an oscillator strength of f = 1.08 (Table S6). However, for **3**, the corresponding transitions from the degenerate HOMO and HOMO-1 (π orbitals located on C_3N_2B rings) orbitals to LUMO+1 and LUMO (π* type orbitals of C_3N_2B ring), respectively, was observed at 291 nm.

Computational details: All the calculations were carried out employing density functional theory (DFT) implemented in the Gaussian 09 (rev. E.01) program package.[5] Geometry optimizations of all the species were carried out in the gas phase using the hybrid functional B3LYP[6] in combination with the cc-pVDZ basis set for all atoms.[7] All the stationary points were fully characterized via analytical frequency calculations in order to establish their nature as minima (all positive eigenvalues). The electrostatic potentials (ESP), molecular orbitals (MO) and natural bond orbital (NBO6)[8] analyses were carried out using the Coulomb-attenuated CAM-B3LYP functional[9] in combination with the cc-pVDZ basis set. The lowest-energy vertical transitions (30) were calculated by TD-DFT, using a long-range dispersion corrected ωB97XD[10] functional in combination with the cc-pVDZ basis set including the solvent effect (CH_2Cl_2) by using the SMD continuum solvation model.[11] TD-DFT results were extracted using GaussSum 3.0 software. The gauge including atomic orbital (GIAO)[12] method has been used to compute the ^{11}B chemical shifts. The NMR chemical shifts were calculated using B3LYP and cc-pVDZ basis set on the optimized geometries. The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 94.78 ppm) and converted to the usual [$BF_3.OEt_2$] scale using the experimental δ (^{11}B) value of B_2H_6, 16.6 ppm.[13] The aromaticity of the compounds being investigated was evaluated by calculating Nucleus Independent Chemical Shift (NICS)[14] indices on the optimized geometry at the B3LYP/cc-pVDZ level of theory by using the GIAO method as implemented in Gaussian. As a normal routine, we placed ghost atoms at the ring critical point, the point of lowest density in the cage structure of each system,[15] to calculate the magnetic shielding tensor and measure aromaticity from the magnetic point of view. These values are denoted as NICS(0) as suggested by Schleyer et al.[14] Increasing aromaticity is indicated by more negative NICS values. Multiwfn (V. 3.8)[16] was used for topological analyses of the electron densities obtained from the DFT calculations.

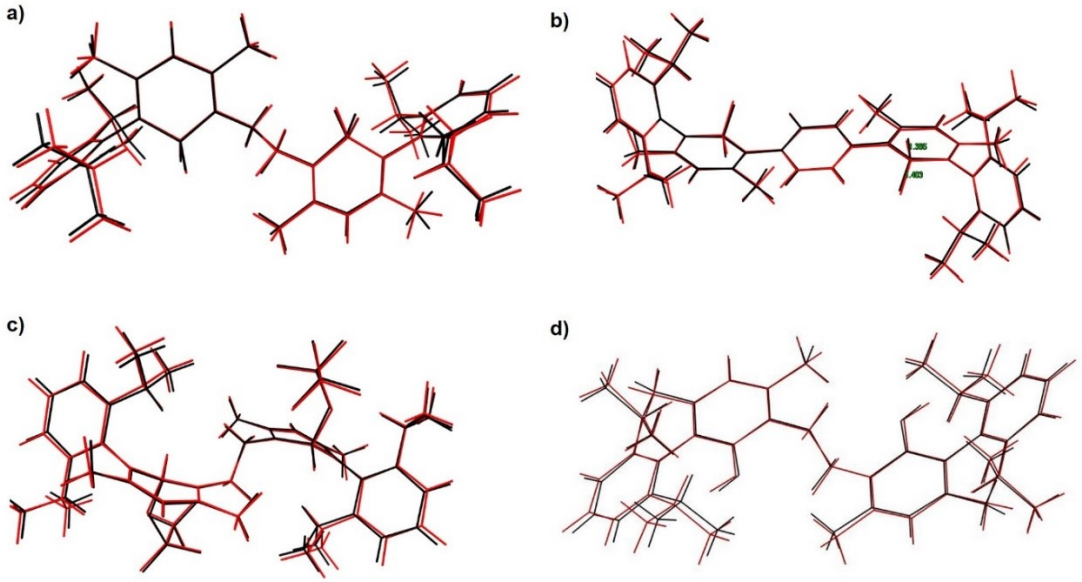


Figure S53. Superposition of crystal structures of a) **1**, b) **3**, c) **5a** and d) **5b** with optimized geometries at B3LYP/cc-pVDZ level (Black Line = Crystal Structure and red Line = Optimized Structure).

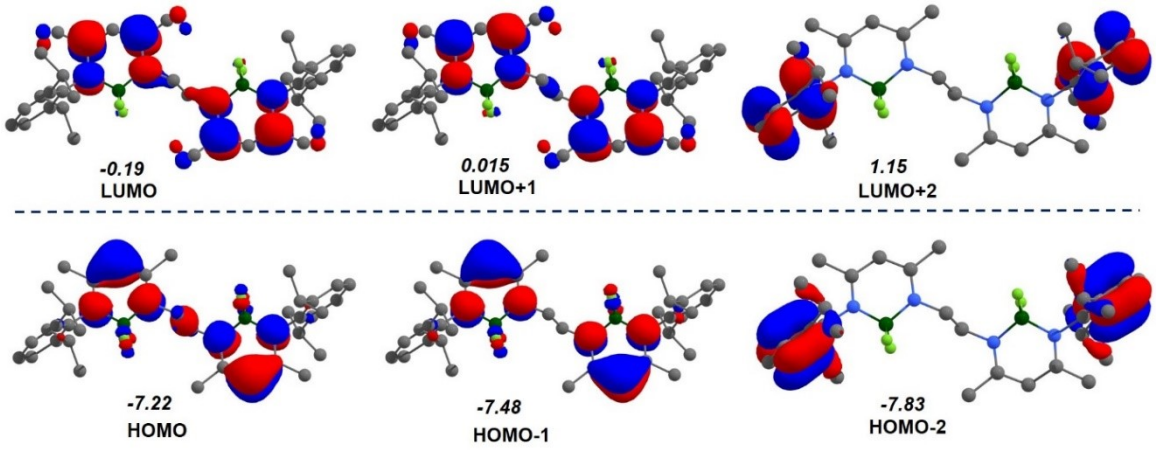


Figure S54. Selected frontier molecular orbitals of **1** calculated at the cam-B3LYP/cc-pVDZ//B3LYP/cc-pVDZ level. The H atoms are not shown for clarity (isosurfaces at 0.03 au)

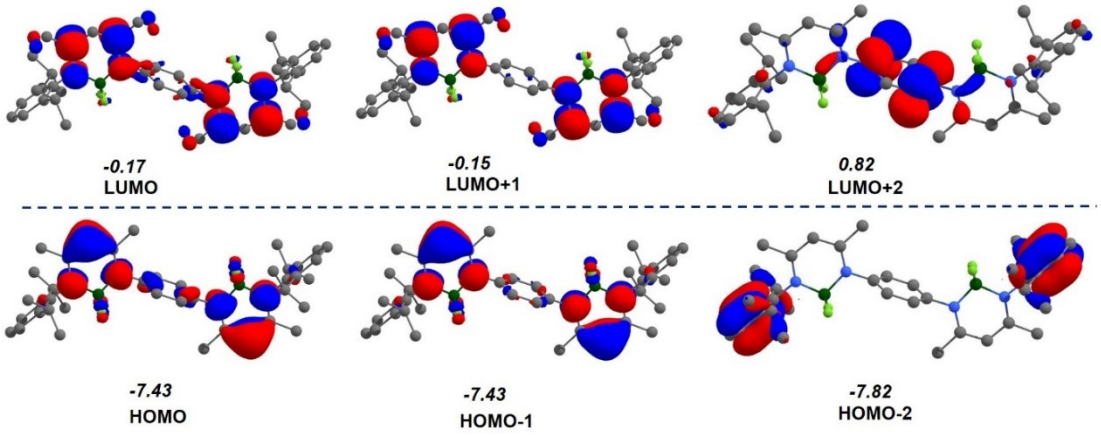


Figure S55. Selected frontier molecular orbitals of **3** calculated at the cam-B3LYP/cc-pVDZ//B3LYP/cc-pVDZ level. The H atoms are not shown for clarity (isosurfaces at 0.03 au)

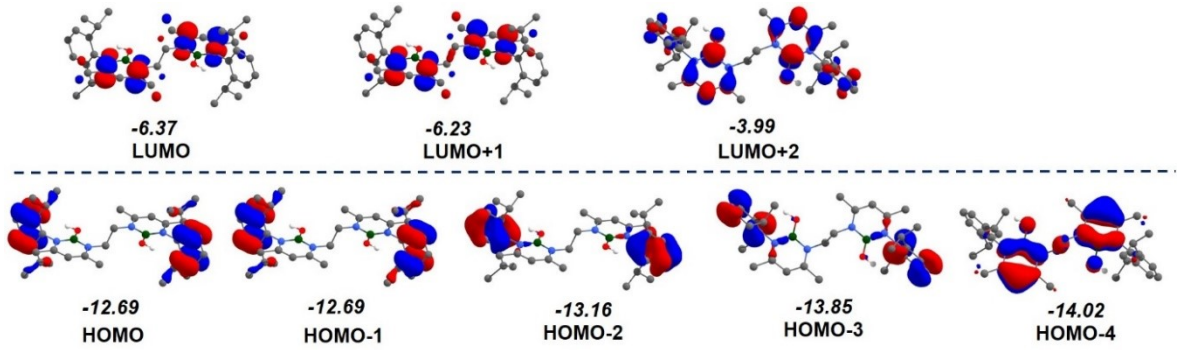


Figure S56. Selected frontier molecular orbitals of **5b** calculated at the cam-B3LYP/cc-pVDZ//B3LYP/cc-pVDZ level. The H atoms (except the one attached to oxygen atom) are not shown for clarity (isosurfaces at 0.03 au)

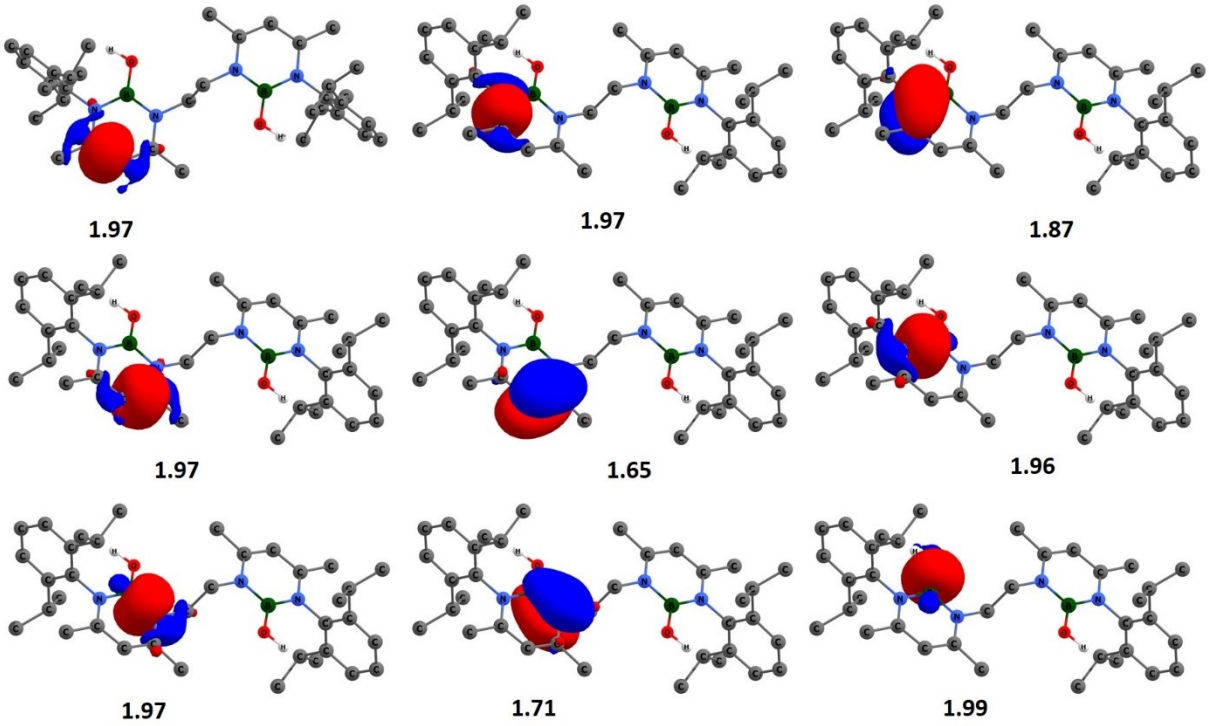


Figure S57(a). NLMOs (Natural localized molecular orbitals) and the corresponding electron occupancies of **5b** obtained from the NBO analysis. The H atoms (except the one attached to oxygen atom) are not shown for clarity (isosurfaces at 0.03 au)

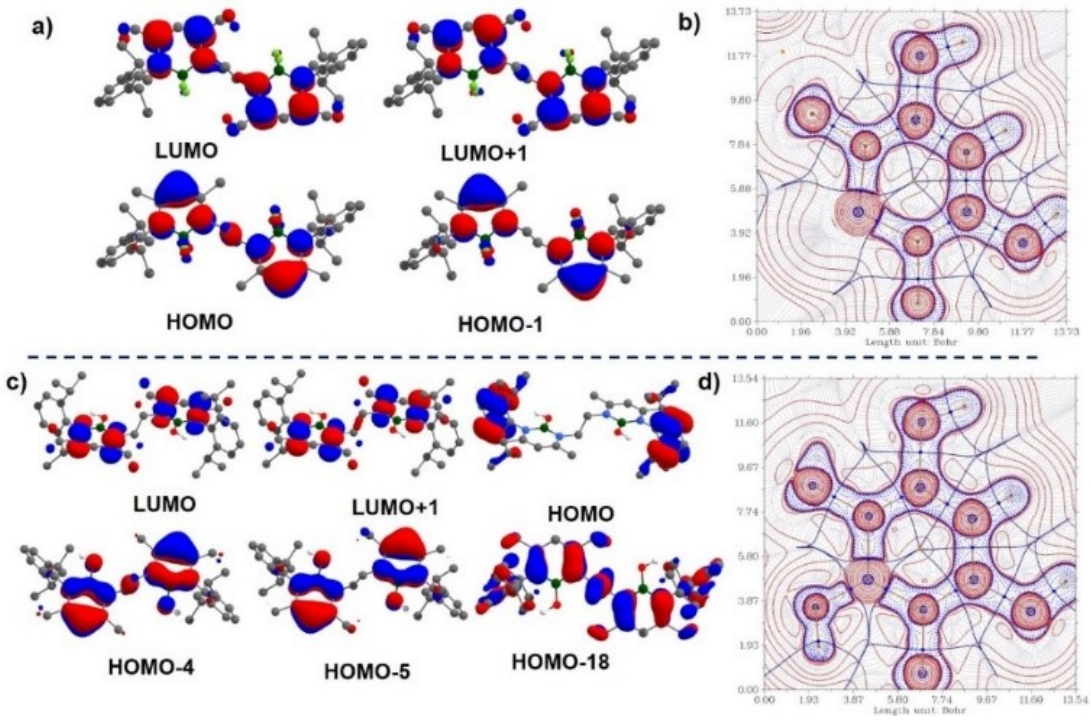


Figure S57(b). Selected frontier molecular orbitals of a) 1 and c) 5b; Topology of the Laplacian of the electron density in the C3N2B planes of (b) 1 and (d) 5b. Positive contour lines are depicted in crimson red and negative contour lines in blue dashes. The inter basin paths are shown in blue line bond paths (brown lines).

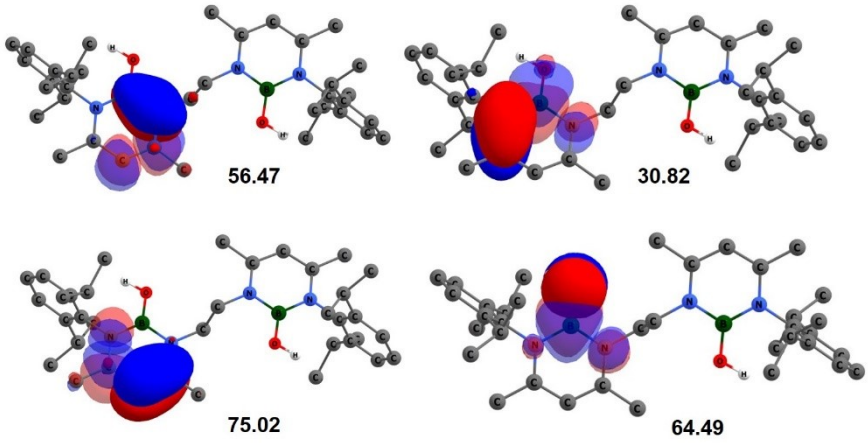


Figure S58. Donor acceptor interactions (energy values in kcal/mol) as obtained from the NBO analysis The H atoms (except the one attached to oxygen atom) are not shown for clarity (isosurfaces at 0.03 au).

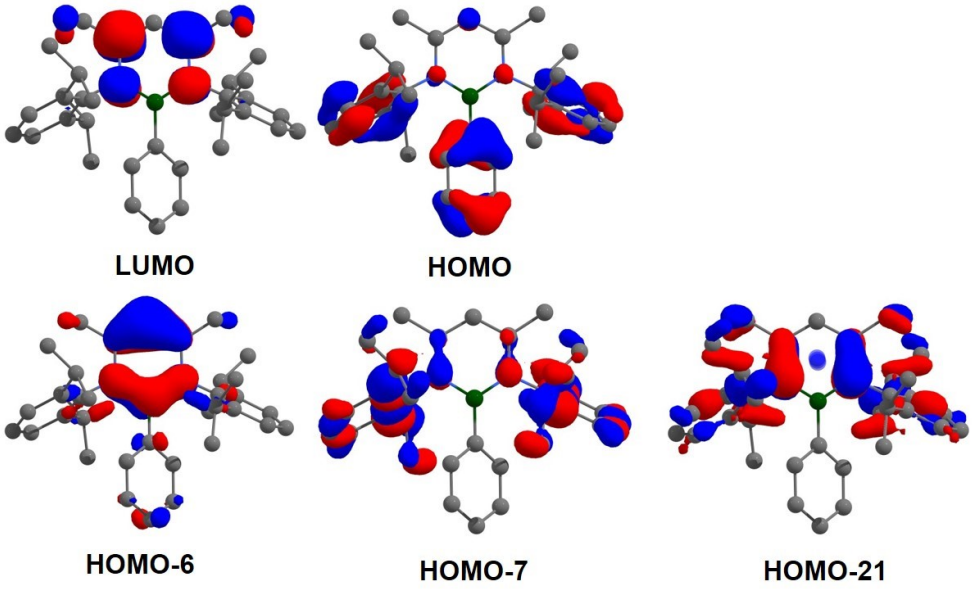


Figure S59. Selected frontier molecular orbitals of **VIII**.

Table S3. Nucleus independent chemical shifts (NICS) calculated at GIAO-B3LYP/cc-pVDZ//B3LYP/cc-pVDZ.

	1	**5a**	**5b**	**5b-Ph***	**VIII**
NICS(0)	0.07	-0.89	-2.41	-8.22	-1.3
NICS(1)	-1.1	-1.29	-4.02	-9.83	-3.5
NICS(-1)	-1.7	-2.66	-4.12	-10.05	-3.5

* phenyl rings of the Dipp moieties in **5b**

Table S4. Calculated charges and AIM (atoms in molecules) properties of selected atoms and bonds of **1** and **5b**.

parameters	**1**	**5b**
q_N	-0.68, -0.69	-0.69, -0.70
q_B	1.38	1.29
ρ(r) bcp B-N [e Å^{-3}]	0.152, 0.150	0.186, 0.189
∇^2(r) bcp B-N [e Å^{-5}]	0.379, 0.371	0.631, 0.636
H(r) bcp B-N [Hartree Å^{-3}]	-0.118, -0.117	-0.145, -0.151
ELF bcp B-M	0.252, 0.252	0.248, 0.253
$\rho(r)^{RCP}$	0.0182	0.0199
$\nabla^2(r)^{RCP}$	0.127	0.140
$H(r)^{RCP}$	0.0066	0.0069

Table S5. Experimentally observed and calculated $^{11}B\{^1H\}$ NMR (at GIAO-B3LYP/cc-pVDZ//B3LYP/cc-pVDZ), experimental (at room temperature in CH_2Cl_2) and calculated (at wB97XD/cc-pVDZ/SMD//B3LYP/cc-pVDZ level of theory) UV/vis data and corresponding orbital transitions for **1** and **3**.

Compound	^{11}B NMR (exp), ppm	^{11}B NMR (cal), ppm	λ(exp) nm	λ(cal) nm	Transitions	$E_{HOMO-LUMO}$ (eV)
1	1.17	1.79	345	295	H-1→L+1 (36%), HOMO→LUMO (62%)	7.03
3	0.78	1.02	340	291	H-1→LUMO (49%), HOMO→L+1 (48%)	7.26
5a	7.06	2.74	-	295	H-1→L+1 (35%), HOMO→LUMO (63%)	7.01
6a	10.98	2.15 1.95	-	295	-	-
VII[17]	25.4	19.9	-	-	-	-

Table S6. Energy, wavelength, oscillator strength and major contributions for each of the 20 mono-excitations calculated by TD-DFT methods at ωB97XD/cc-pVDZ/SMD(DCM) for **1**[a]

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strengths	Symmetry	Major contributions
1	33924.4858382	294.772337824	1.0801	Singlet-AU	H-1->L+1 (36%), HOMO->LUMO (62%)
2	35327.0839902	283.068933818	0.0	Singlet-AG	H-1->LUMO (48%), HOMO->L+1 (50%)
3	43093.396587	232.054114829	0.0	Singlet-AG	H-5->L+3 (22%), H-4->L+2 (21%), H-3->L+4 (27%), H-2->L+5 (26%)
4	43094.2031415	232.049771687	0.0116	Singlet-AU	H-5->L+2 (21%), H-4->L+3 (22%), H-3->L+5 (26%), H-2->L+4 (27%)
5	46087.3266275	216.979389602	0.003	Singlet-AU	H-5->L+1 (40%), H-4->LUMO (50%)
6	46117.1691414	216.838981798	0.0	Singlet-AG	H-5->LUMO (49%), H-4->L+1 (41%)
7	48042.4145634	208.149404872	0.0181	Singlet-AU	H-5->L+5 (14%), H-4->L+4 (14%), H-3->L+2 (29%), H-2->L+3 (30%)
8	48043.2211178	208.145910439	0.0	Singlet-AG	H-5->L+4 (14%), H-4->L+5 (14%), H-3->L+3 (30%), H-2->L+2 (29%)
9	48620.714089	205.673655506	0.0	Singlet-AG	H-3->LUMO (50%), H-2->L+1 (39%)
10	48621.5206434	205.670243704	0.0007	Singlet-AU	H-3->L+1 (39%), H-2->LUMO (51%)
11	48840.0968937	204.749798547	0.0023	Singlet-AU	H-1->L+5 (36%), HOMO->L+4 (46%)
12	48840.9034481	204.746417327	0.0	Singlet-AG	H-1->L+4 (38%), HOMO->L+5 (43%)

13	49709.5625681	201.168537468	0.0	Singlet-AG	H-1->LUMO (43%), HOMO->L+1 (43%)
14	49863.6144641	200.547034295	0.1319	Singlet-AU	H-1->L+1 (53%), HOMO->LUMO (31%)
15	50607.2576476	197.600116363	0.008	Singlet-AU	H-1->L+2 (39%), HOMO->L+3 (51%)
16	50611.2904198	197.584371334	0.0	Singlet-AG	H-1->L+3 (40%), HOMO->L+2 (48%)
17	53535.0502249	186.79351113	0.0	Singlet-AG	H-5->L+3 (23%), H-4->L+2 (21%), H-3->L+4 (18%), H-2->L+5 (17%)
18	53545.5354325	186.7569335	1.1575	Singlet-AU	H-8->LUMO (15%), H-5->L+2 (15%), H-4->L+3 (16%), H-3->L+5 (12%), H-2->L+4 (13%)
19	53764.9182371	185.994889007	1.4926	Singlet-AU	H-5->L+5 (27%), H-4->L+4 (29%), H-3->L+2 (13%), H-2->L+3 (14%)
20	53778.6296624	185.947467661	0.0	Singlet-AG	H-5->L+4 (29%), H-4->L+5 (28%), H-3->L+3 (14%), H-2->L+2 (14%)
21	54105.2842062	184.824830822	0.7924	Singlet-AU	H-17->L+1 (11%), H-12->LUMO (10%), H-8->LUMO (21%), H-4->L+3 (10%)
22	54249.657449	184.33296117	0.0	Singlet-AG	H-17->LUMO (18%), H-12->L+1 (11%), H-9->LUMO (10%), H-8->L+1 (26%)
23	55718.3930642	179.473948369	0.2061	Singlet-AU	H-7->L+1 (21%), H-6->LUMO (52%)
24	56387.8332402	177.343221496	0.0	Singlet-AG	H-7->LUMO (31%), H-6->L+1 (43%)
25	60918.2494679	164.154421497	0.3525	Singlet-AU	H-1->L+9 (27%), HOMO->L+8 (38%)
26	61064.2358196	163.761977298	0.0	Singlet-AG	H-1->L+8 (27%), HOMO->L+9 (34%)
27	61105.3700955	163.651737718	0.0	Singlet-AG	H-3->LUMO (43%), H-2->L+1 (56%)
28	61106.1766499	163.649577641	0.0015	Singlet-AU	H-3->L+1 (56%), H-2->LUMO (43%)
29	61548.168477	162.474371658	0.0009	Singlet-AU	H-11->L+5 (11%), H-10->L+4 (19%), H-7->L+5 (15%), H-6->L+4 (11%)
30	61570.752001	162.414777715	0.0	Singlet-AG	H-11->L+4 (16%), H-10->L+5 (23%), H-7->L+4 (21%), H-6->L+5 (13%)

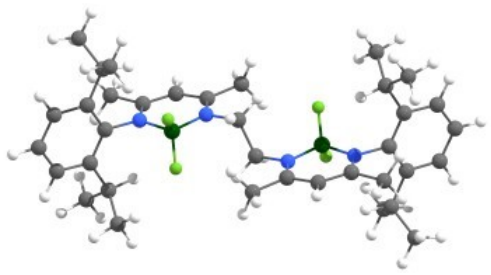
[a] Components with greater than 10 % contribution shown.

Table S7. Energy, wavelength, oscillator strength and major contributions for each of the 20 mono-excitations calculated by TD-DFT methods at ωB97XD/cc-pVDZ/SMD(DCM) for **3** [a]

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strengths	Symmetry	Major contributions
1	34362.4448931	291.015381214	1.3007	Singlet-AU	H-1->LUMO (49%), HOMO->L+1 (48%)
2	35164.96655	284.373937504	0.0	Singlet-AG	H-1->L+1 (48%), HOMO->LUMO (49%)
3	43090.9769238	232.067145233	0.0	Singlet-AG	H-5->L+5 (21%), H-4->L+4 (18%), H-3->L+7 (22%), H-2->L+6 (26%)
4	43090.9769238	232.067145233	0.0124	Singlet-AU	H-5->L+4 (21%), H-4->L+5 (19%), H-3->L+6 (26%), H-2->L+7 (22%)
5	43645.0798165	229.12090073	0.0003	Singlet-AU	H-7->L+2 (30%), H-6->L+3 (37%)
6	45283.9984162	220.828556438	0.0075	Singlet-AU	H-5->L+1 (38%), H-4->LUMO (49%)
7	45333.1982364	220.588892667	0.0	Singlet-AG	H-5->LUMO (40%), H-4->L+1 (50%)
8	46582.5510469	214.672656934	0.0622	Singlet-AU	H-6->LUMO (16%), H-1->L+2 (50%)
9	47203.5979572	211.84825803	0.0	Singlet-AG	HOMO->L+2 (72%)
10	47877.8774599	208.864731073	0.0045	Singlet-AU	H-3->L+1 (35%), H-2->LUMO (35%)
11	47879.4905687	208.857694207	0.0	Singlet-AG	H-3->LUMO (36%), H-2->L+1 (36%)
12	47910.9461915	208.720570035	0.0247	Singlet-AU	H-6->LUMO (55%), H-1->L+2 (21%)
13	48090.0012747	207.943433873	0.0	Singlet-AG	H-6->L+1 (66%)
14	48159.3649556	207.643934035	0.0105	Singlet-AU	H-5->L+6 (12%), H-3->L+1 (13%), H-3->L+4 (23%), H-2->LUMO (13%), H-2->L+5 (23%)
15	48173.8829353	207.581357173	0.0	Singlet-AG	H-6->L+1 (12%), H-3->LUMO (11%), H-3->L+5 (20%), H-2->L+1 (11%), H-2->L+4 (20%)
16	49778.926249	200.888222256	0.0026	Singlet-AU	H-1->L+7 (36%), HOMO->L+6 (33%)
17	49786.9917933	200.855678156	0.0	Singlet-AG	HOMO->L+3 (88%)
18	49900.7159678	200.397926283	0.0	Singlet-	H-1->L+6 (37%), HOMO->L+7

				AG	(46%)
19	49997.5024993	200.009990502	0.0141	Singlet-AU	H-1->L+3 (78%)
20	50365.2913189	198.54943232	0.0246	Singlet-AU	H-7->L+3 (25%), H-6->L+2 (27%)
21	51415.4251855	194.494161313	0.0	Singlet-AG	H-1->L+4 (42%), HOMO->L+5 (46%)
22	51416.2317399	194.491110329	0.012	Singlet-AU	H-1->L+5 (44%), HOMO->L+4 (43%)
23	52931.747512	188.922536475	0.0033	Singlet-AU	H-7->LUMO (83%)
24	53003.5308562	188.666676323	0.0	Singlet-AG	H-7->L+1 (98%)
25	53591.5090349	186.596723624	0.0	Singlet-AG	H-5->L+5 (26%), H-4->L+4 (24%), H-3->L+7 (16%), H-2->L+6 (20%)
26	53641.5154095	186.422772057	1.6654	Singlet-AU	H-5->L+4 (22%), H-4->L+5 (18%), H-3->L+6 (16%), H-2->L+7 (12%)
27	53661.6792702	186.352722017	1.7161	Singlet-AU	H-5->L+6 (24%), H-4->L+7 (15%), H-3->L+4 (13%), H-2->L+5 (11%)
28	53727.010179	186.126121046	0.0	Singlet-AG	H-5->L+7 (23%), H-4->L+6 (26%), H-3->L+5 (15%), H-2->L+4 (14%)
29	54740.0425418	182.681626386	0.996	Singlet-AU	H-9->L+1 (15%), H-8->LUMO (12%), H-7->L+3 (31%), H-6->L+2 (10%), H-1->LUMO (11%)
30	54936.8418225	182.027209214	0.169	Singlet-AU	H-19->L+1 (19%), H-18->LUMO (12%)

[a] Components with greater than 10 % contribution shown.



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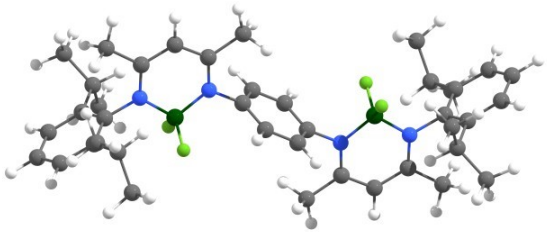

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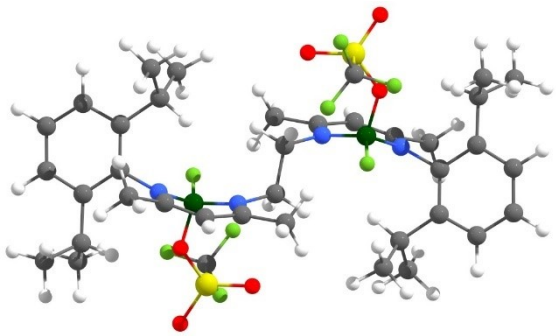

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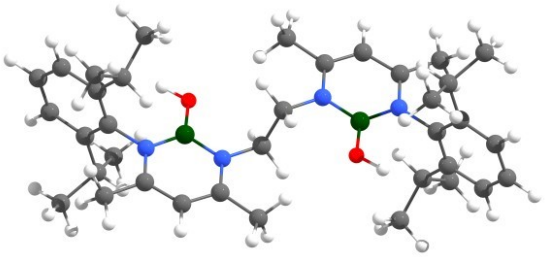

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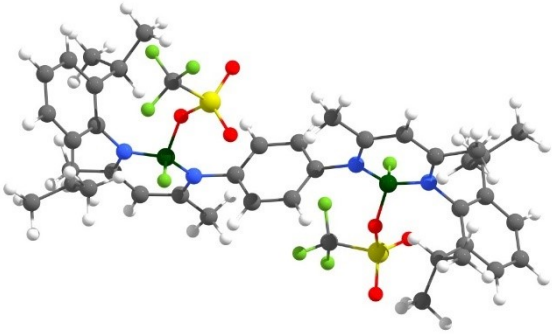

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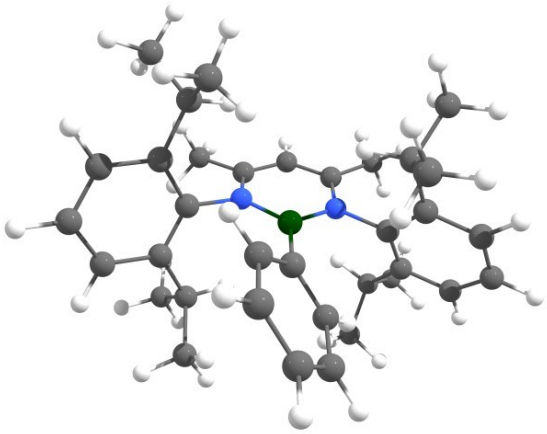

VIII

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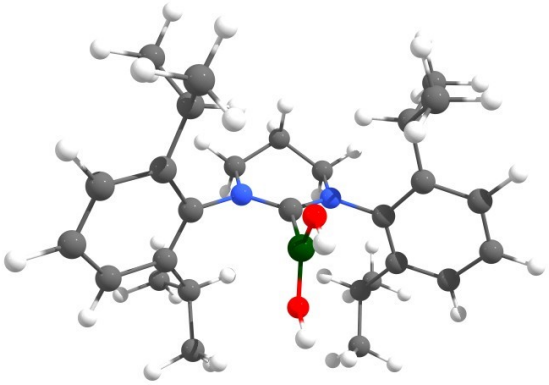

VII

7	-0.034302000	0.827698000	1.169522000
8	-1.221263000	-2.032955000	0.000000000
8	1.218394000	-2.014171000	0.000000000
6	3.198925000	1.427320000	3.188152000
1	4.119423000	1.799784000	2.710790000
1	3.458296000	1.105675000	4.209651000
1	2.494518000	2.269590000	3.279118000
6	2.603573000	0.259244000	2.374492000
1	2.398283000	0.631952000	1.358652000
6	1.283472000	-0.201235000	2.990566000
6	0.017938000	0.086740000	2.425801000
6	-0.024234000	0.182626000	0.000000000
6	3.628195000	-0.880482000	2.236276000
1	3.219455000	-1.715817000	1.650507000
1	3.945997000	-1.267132000	3.217501000
1	4.532065000	-0.513264000	1.724816000
6	-0.073113000	2.304370000	1.245390000
1	0.957223000	2.679021000	1.364591000
1	-0.627789000	2.569536000	2.154385000
6	-0.730308000	2.883474000	0.000000000
1	-0.629170000	3.978345000	0.000000000
1	-1.807327000	2.651235000	0.000000000
6	-1.199245000	-0.252170000	3.064704000
6	-2.572176000	0.148645000	2.526476000
1	-2.437778000	0.558993000	1.513688000
6	-3.196201000	1.256928000	3.399767000
1	-4.159207000	1.583922000	2.976131000
1	-2.542076000	2.140005000	3.481006000
1	-3.386802000	0.895752000	4.423193000
6	-3.534234000	-1.046405000	2.404369000
1	-4.484976000	-0.720206000	1.953622000
1	-3.773391000	-1.480267000	3.388163000
1	-3.109497000	-1.837670000	1.770813000
6	-1.114848000	-0.946612000	4.279940000
1	-2.031452000	-1.231266000	4.798848000
6	0.117515000	-1.271313000	4.843458000
1	0.156956000	-1.810845000	5.792058000
6	1.299582000	-0.896022000	4.208710000
1	2.256172000	-1.139780000	4.673228000
5	-0.005725000	-1.431405000	0.000000000
1	1.232178000	-2.982528000	0.000000000
1	-1.220076000	-3.001443000	0.000000000
7	-0.034302000	0.827698000	-1.169522000
6	3.198925000	1.427320000	-3.188152000
1	4.119423000	1.799784000	-2.710790000
1	3.458296000	1.105675000	-4.209651000
1	2.494518000	2.269590000	-3.279118000
6	2.603573000	0.259244000	-2.374492000
1	2.398283000	0.631952000	-1.358652000
6	1.283472000	-0.201235000	-2.990566000
6	0.017938000	0.086740000	-2.425801000
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1	3.219455000	-1.715817000	-1.650507000
1	3.945997000	-1.267132000	-3.217501000
1	4.532065000	-0.513264000	-1.724816000
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6	-2.572176000	0.148645000	-2.526476000
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6	-3.196201000	1.256928000	-3.399767000
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6	1.299582000	-0.896022000	-4.208710000
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