Supporting Information

Direct C–H electrophilic borylation with $(C_6F_5)_2B$-NTf_2 to generate B-N dibenzo[a,h]pyrenes

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Contents

Procedure for the **Attempted borylation of 2-PhPy with $(C_6F_5)_2$BCl:** An NMR spectrum was taken of **$(C_6F_5)_2$BCl** (5 mg, 0.013 mmol), with 2,6-di-tertbutylpyridine (5 mg, 0.026 mmol), and a hexamethylbenzene internal standard (1 mg, 0.0065 mmol) in C_6D_5Br. Then, 2-phenylpyridine (2 mg, 0.013 mmol) was diluted in a 0.5 mL volumetric flask with C_6D_5Br. Aliquots of 0.1 mL of the 2-phenylpyridine solution was added to the J-Young tube and an NMR was taken immediately after every aliquot.

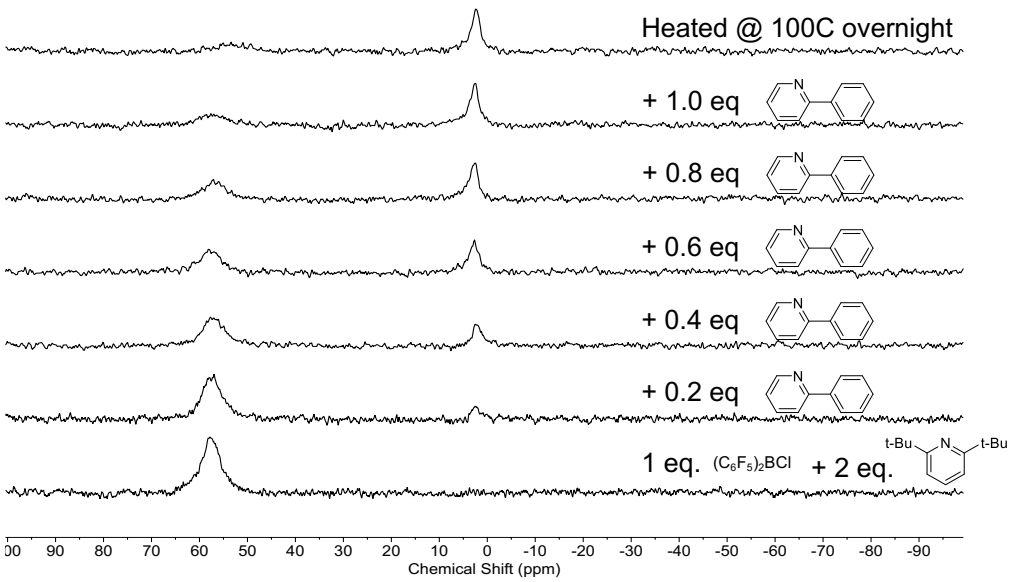


Figure S1. Attempted borylation of 2-PhPy with $(C_6F_5)_2BCl$ monitored by ^{11}B NMR spectroscopy in C_6D_5Br.

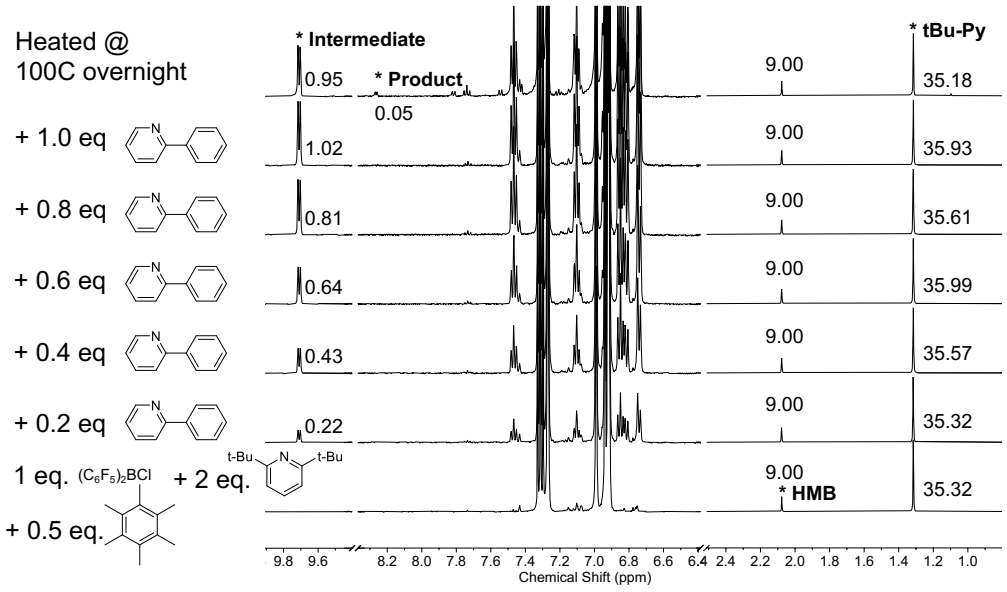


Figure S2. Attempted borylation of 2-PhPy with $(C_6F_5)_2BCl$ monitored by ^{11}B NMR spectroscopy in C_6D_5Br. *Spectra that are stitched together are not to scale to each other so signals can be easily seen.*

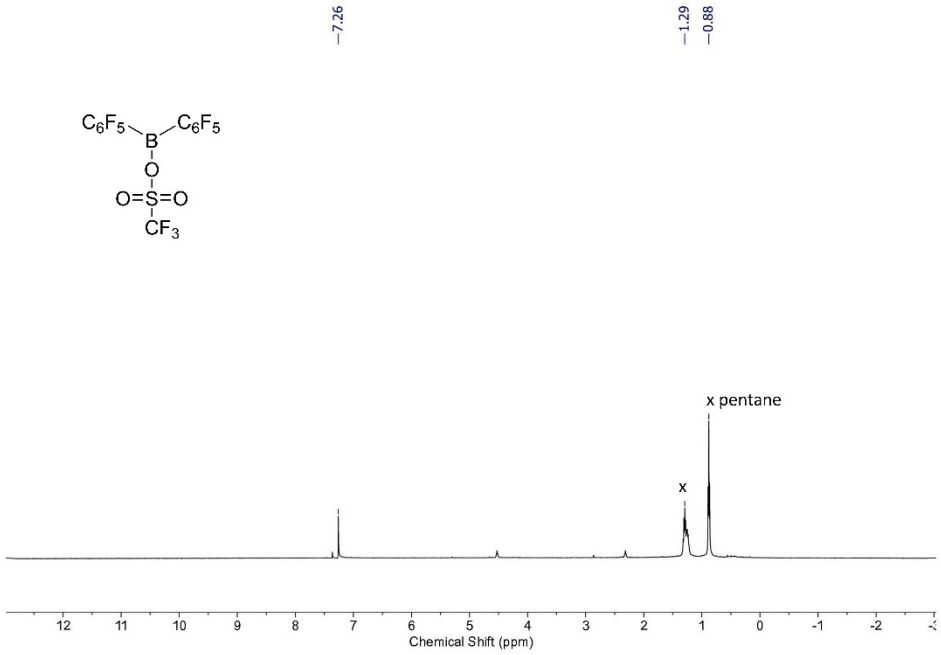


Figure S3. ^{1}H NMR of **$(C_6F_5)_2$B-OTf** in $CDCl_3$

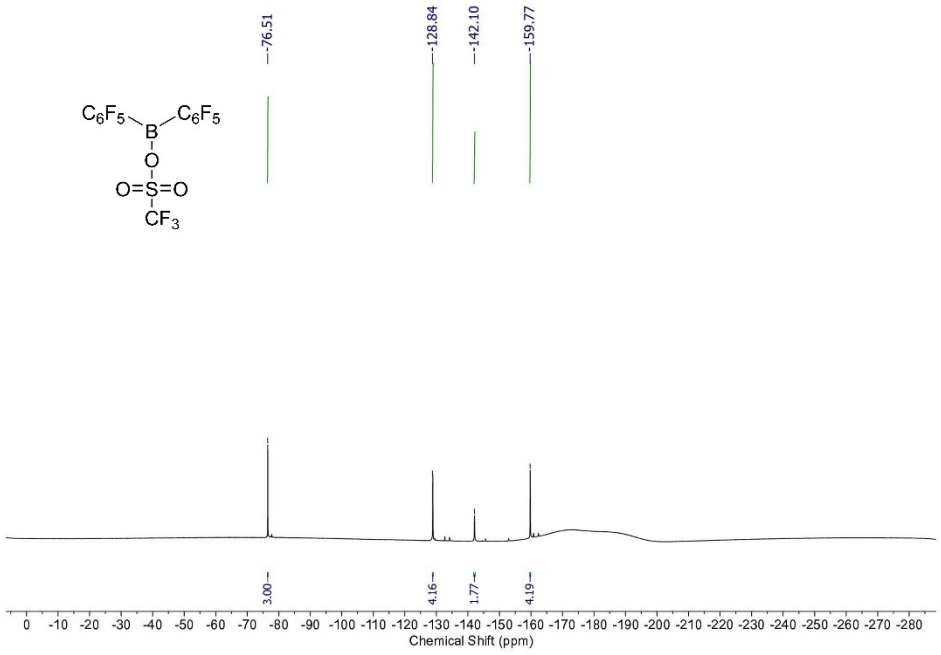


Figure S4. ^{19}F NMR of **$(C_6F_5)_2$B-OTf** in $CDCl_3$

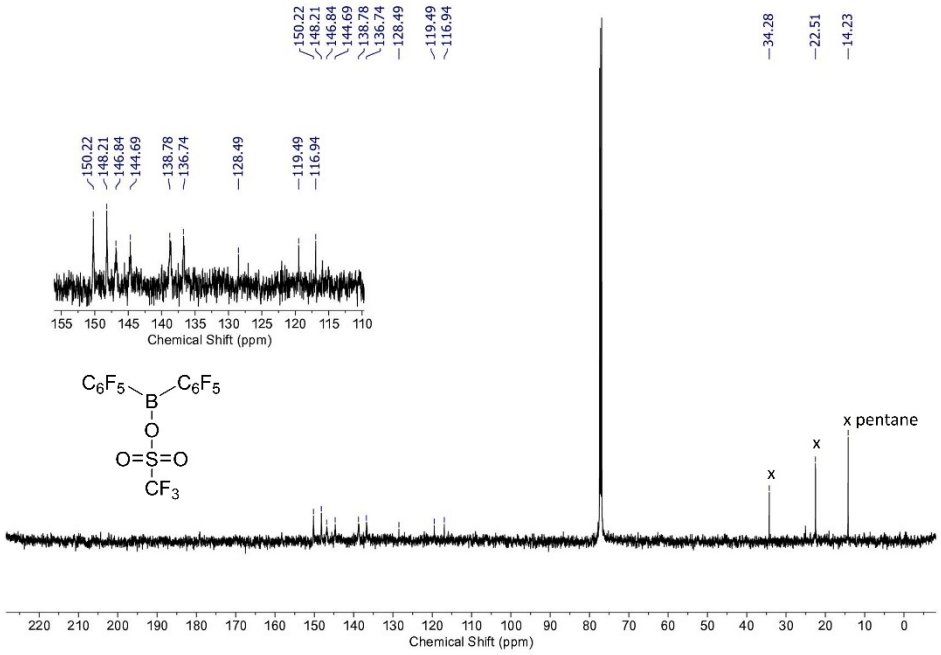


Figure S5. $^{13}C\{^{1}H\}$ NMR of **$(C_6F_5)_2B$-OTf** in $CDCl_3$

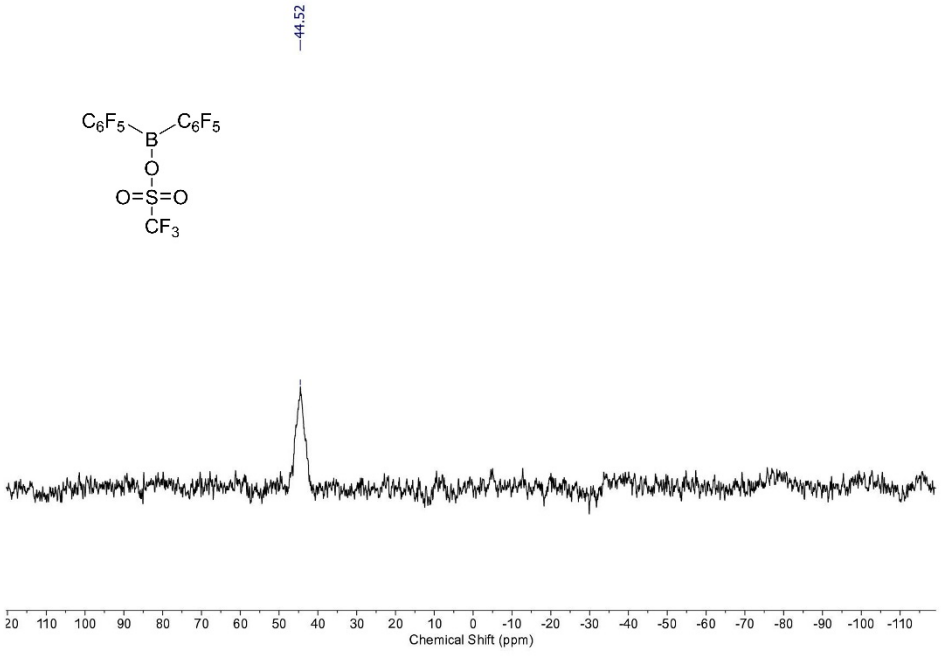


Figure S6. ^{11}B NMR of **$(C_6F_5)_2B$-OTf** in $CDCl_3$

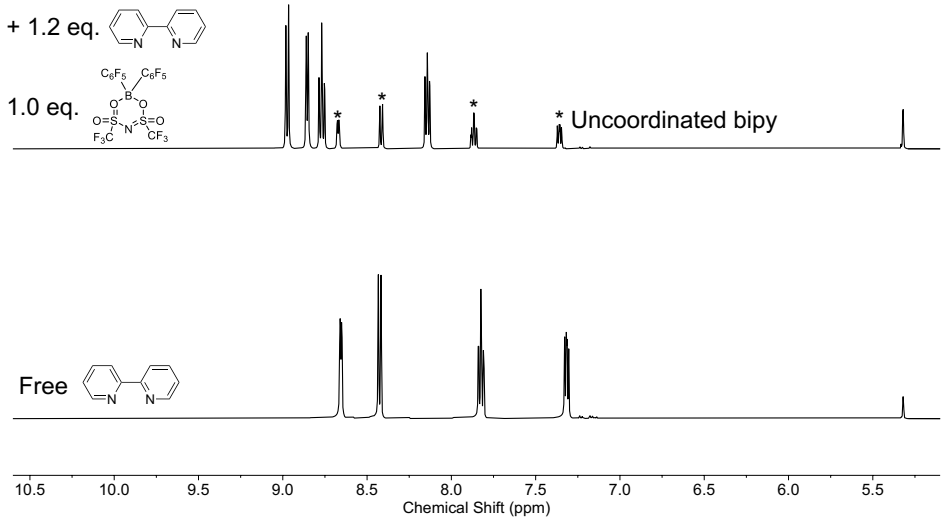


Figure S7. ^{1}H NMR spectra of 2,2-bipyridine coordination to $(C_6F_5)_2BNTf_2$ in CD_2Cl_2.

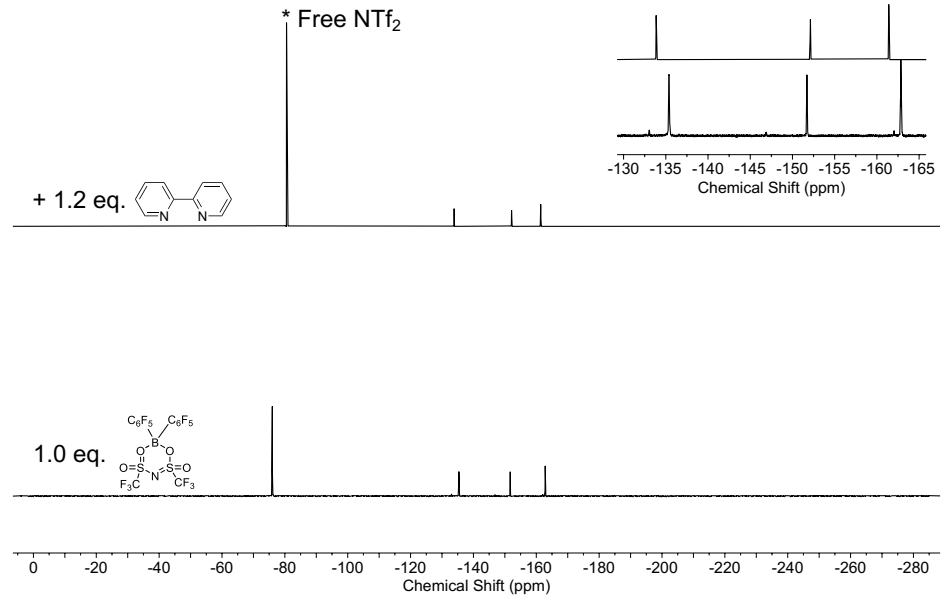


Figure S8. ^{19}F NMR spectra of 2,2-bipyridine coordination to $(C_6F_5)_2BNTf_2$ in CD_2Cl_2.

Procedure for the **PhPy First NMR experiment:** An NMR spectrum was taken of **$(C_6F_5)_2B$-NTf_2** (8 mg, 0.013 mmol) in C_6D_5Br, then 2-phenylpyridine (2 mg, 0.013 mmol) and a hexamethylbenzene internal standard (1 mg, 0.0065 mmol) were added into the NMR tube and another NMR spectrum was taken. Then, 2,6-di-tertbutylpyridine (2.5 mg, 0.013 mmol) was added and an NMR spectrum was taken. The J-Young tube was then heated at 100°C for 16 hours to allow the reaction to go to completion. The reaction was cooled to room temperature and the final NMR spectrum was taken.

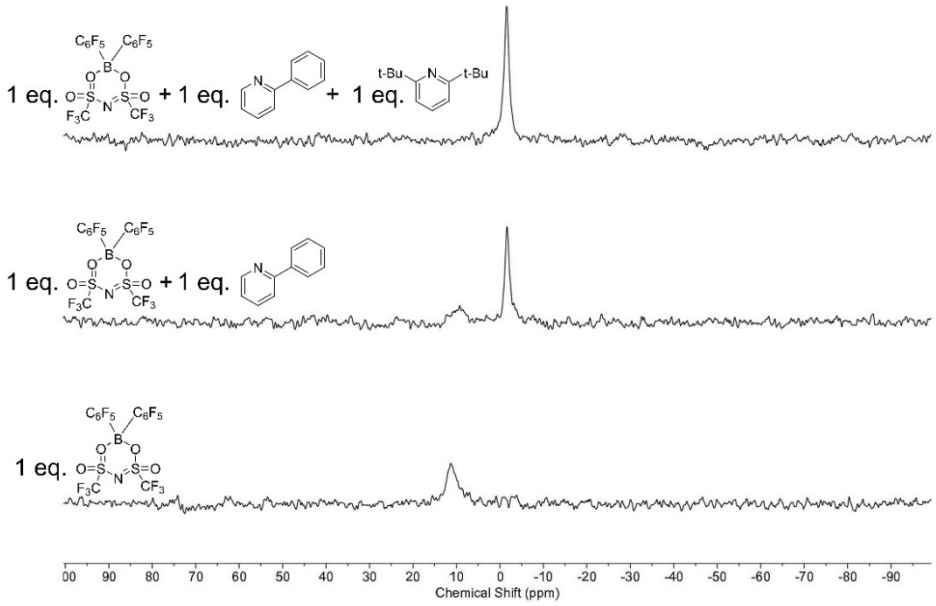


Figure S9. PhPy first experiment monitored by ^{11}B NMR spectroscopy in C_6D_5Br.

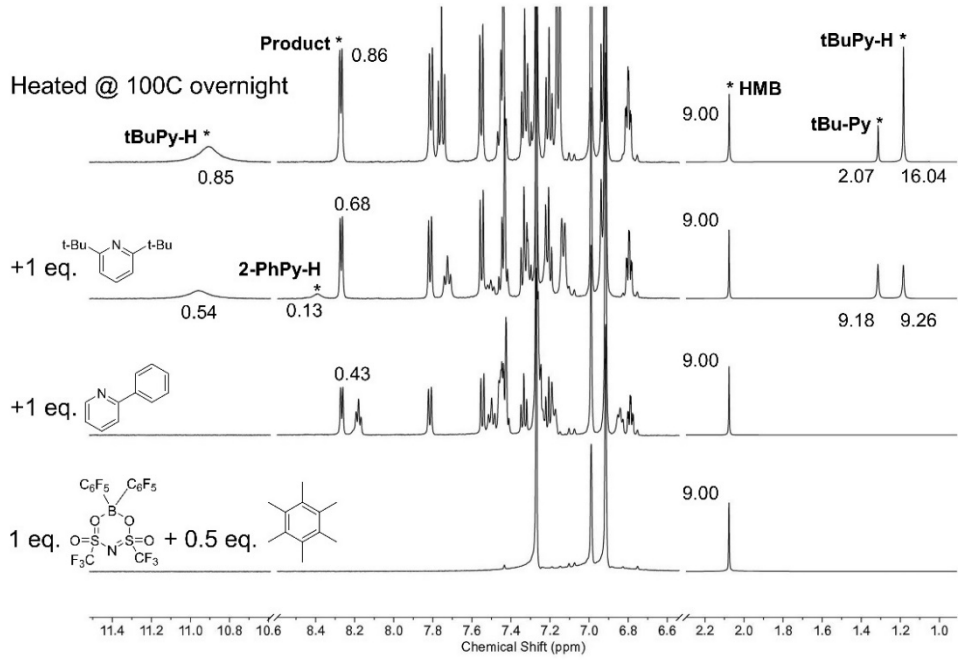


Figure S10. PhPy first experiment monitored by ^{1}H NMR spectroscopy in C_6D_5Br. *Spectra that are stitched together are not to scale to each other so signals can be easily seen.*

Procedure for the **DTBP First NMR experiment:** An NMR spectrum was taken of **$(C_6F_5)_2B$-NTf_2** (8 mg, 0.013 mmol), with 2,6-di-tertbutylpyridine (2.5 mg, 0.013 mmol), and a hexamethylbenzene internal standard (1 mg, 0.0065 mmol) in C_6D_5Br. Then, 2-phenylpyridine (2 mg, 0.013 mmol) was diluted in a 0.5 mL volumetric flask with C_6D_5Br. Aliquots of 0.1 mL of the 2-phenylpyridine solution was added to the J-Young tube and an NMR was taken immediately after every aliquot.

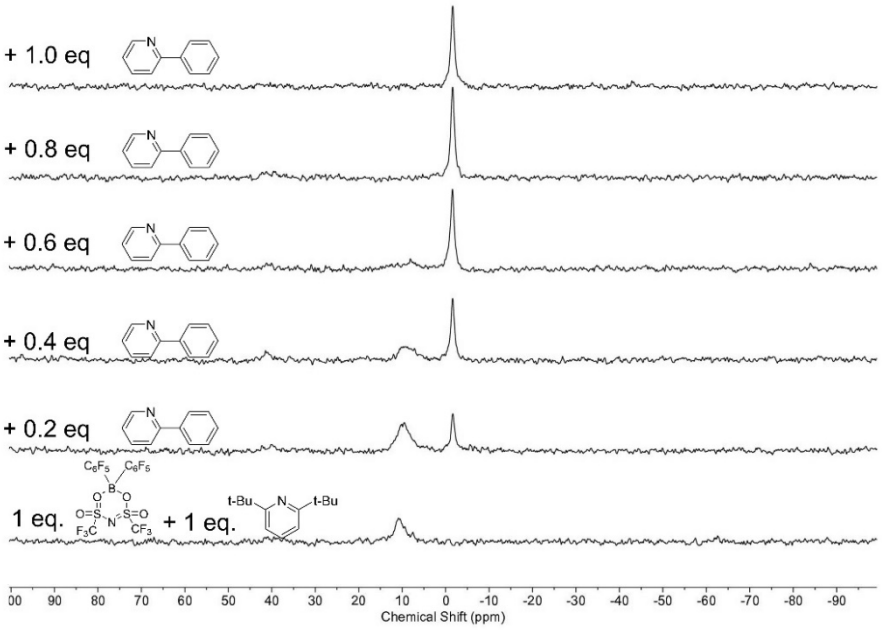


Figure S11. DTBP first experiment monitored by ^{11}B NMR spectroscopy in C_6D_5Br.

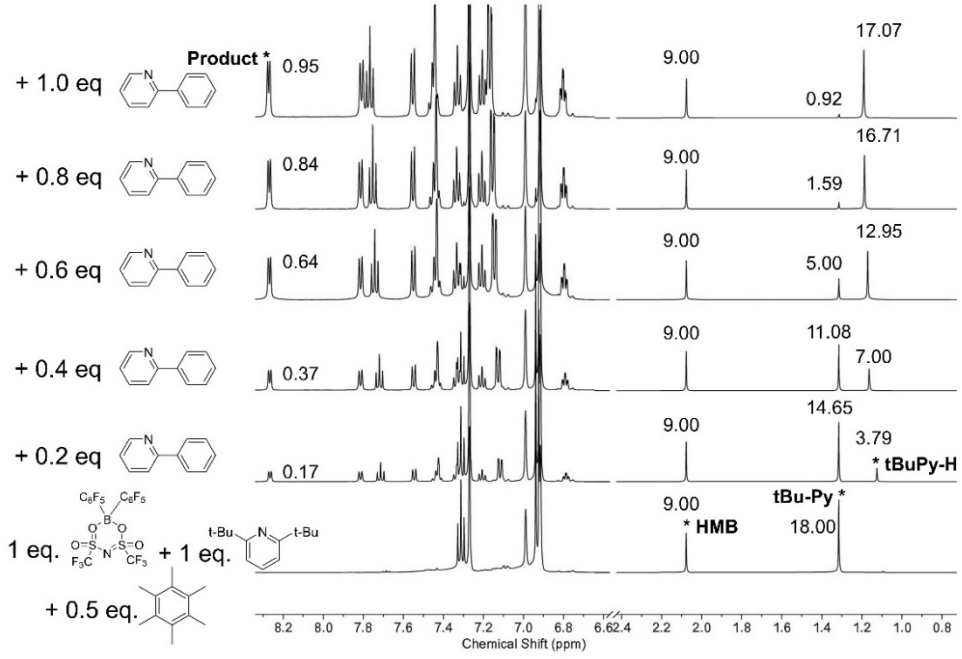


Figure S12. DTBP first experiment monitored by ^{1}H NMR spectroscopy in C_6D_5Br. *Spectra that are stitched together are not to scale to each other so signals can be easily seen.*

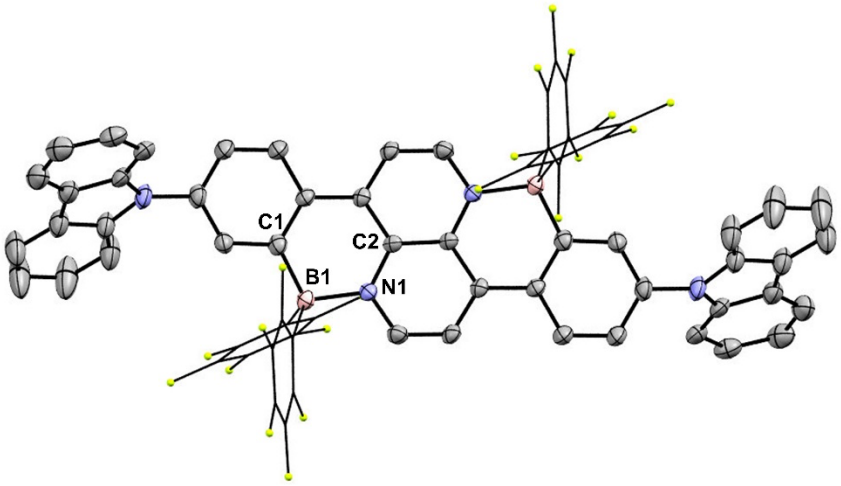


Figure S13. Molecular structure of **1-carb**. Hydrogen atoms and solvent molecules were omitted for clarity. Thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) B(1)-N(1) 1.619(5), B(1)-C(1) 1.595(6), N(1)-C(2) 1.382(4).

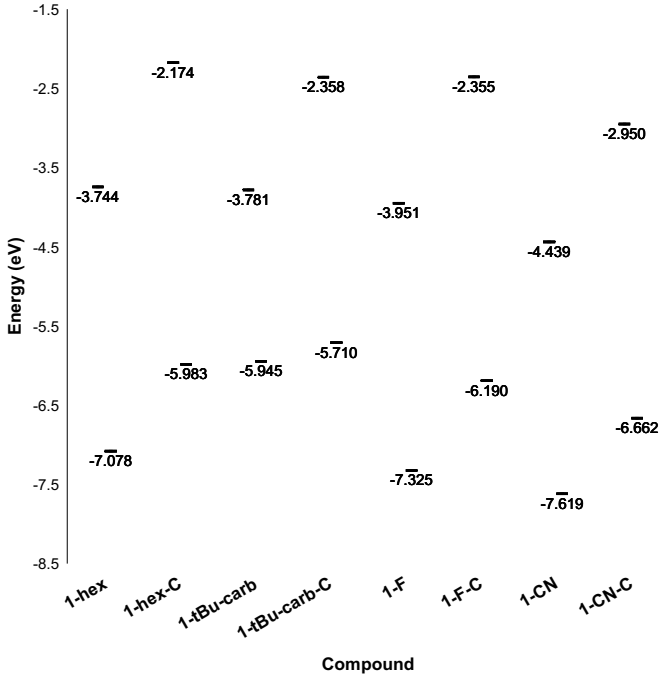


Figure S14. DFT (PBE0/Def-TZVP)-calculated energy levels of selected compounds **1-hex**, **1-F**, **1-^{t}Bu-carb**, **1-CN**, and their all-carbon analogues.

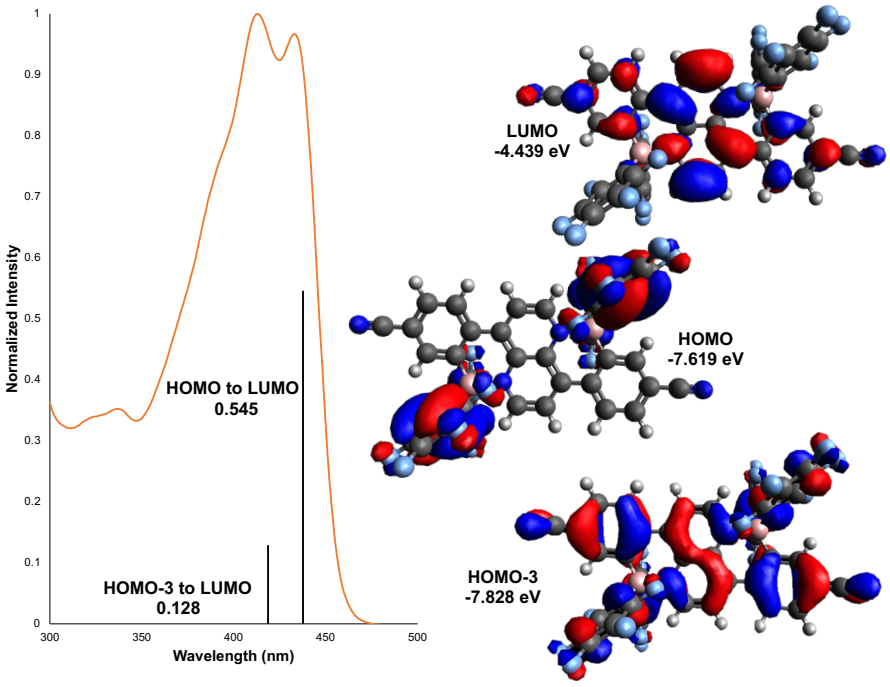


Figure S15. Frontier molecular orbitals and TD-DFT calculated electronic transitions for **1-CN** with oscillator strengths > 0.1. The experimental UV-Vis spectrum is overlaid for comparison.

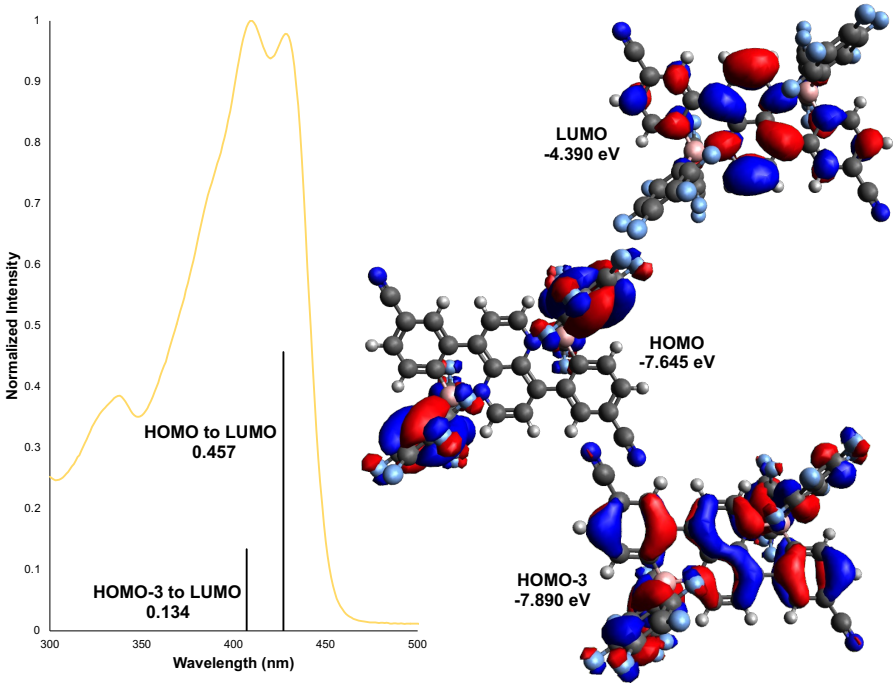


Figure S16. Frontier molecular orbitals and TD-DFT calculated electronic transitions for **2-CN** with oscillator strengths > 0.1. The experimental UV-Vis spectrum is overlaid for comparison.

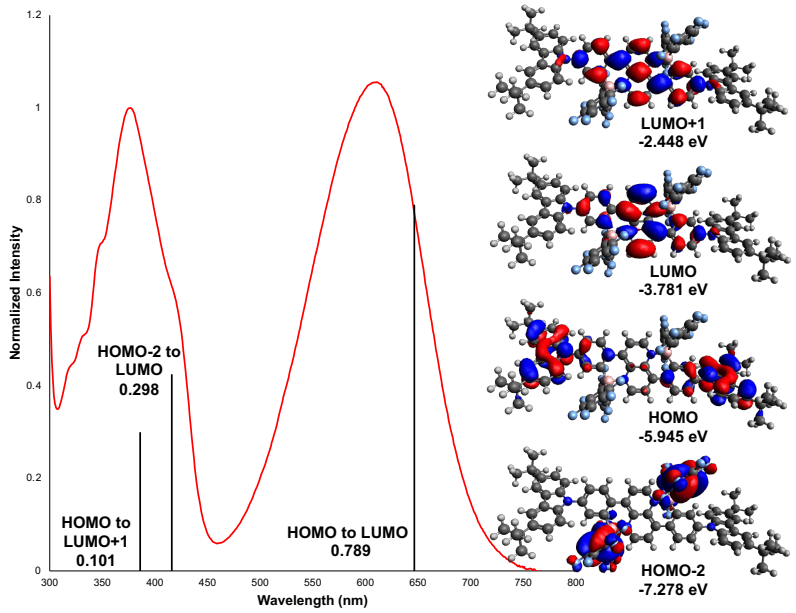


Figure S17. Frontier molecular orbitals and TD-DFT calculated electronic transitions for **1-^{t}Bu-carb** with oscillator strengths > 0.1. The experimental UV-Vis spectrum is overlaid for comparison.

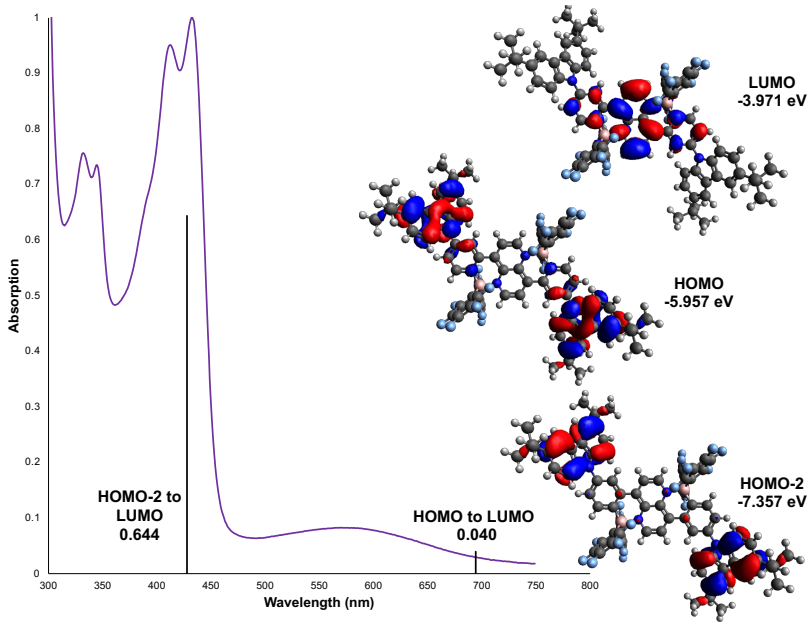


Figure S18. Frontier molecular orbitals and TD-DFT calculated electronic transitions for **2-^{t}Bu-carb** with oscillator strengths > 0.1 except for the HOMO-LUMO transition. The experimental UV-Vis spectrum is overlaid for comparison.

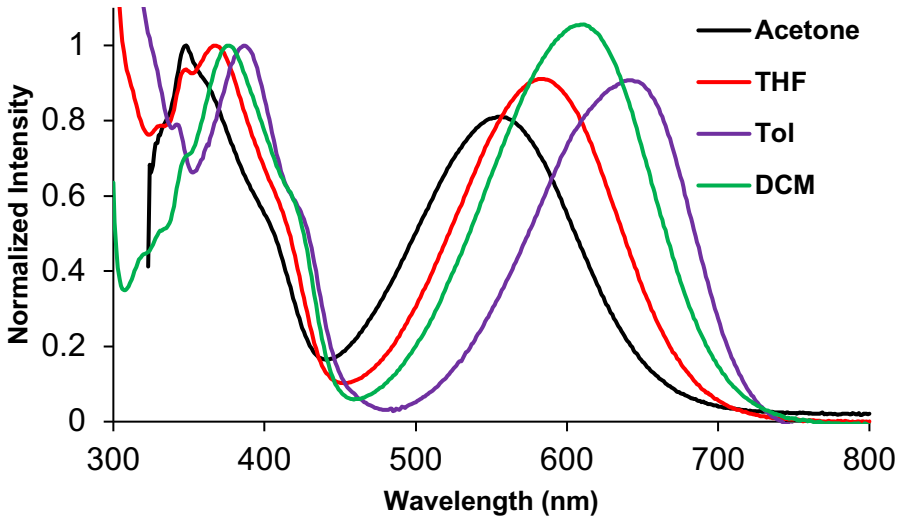


Figure S19. The absorption spectra of **1-^{t}Bu-carb** in 10^{-5} M solutions of different solvents.

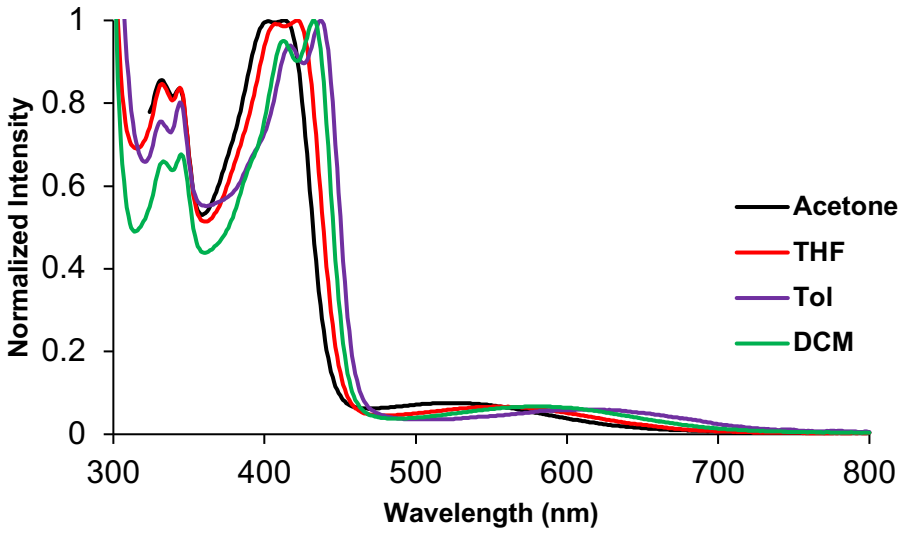


Figure S20. The absorption spectra of **1-^{t}Bu-carb** in 10^{-5} M solutions of different solvents.

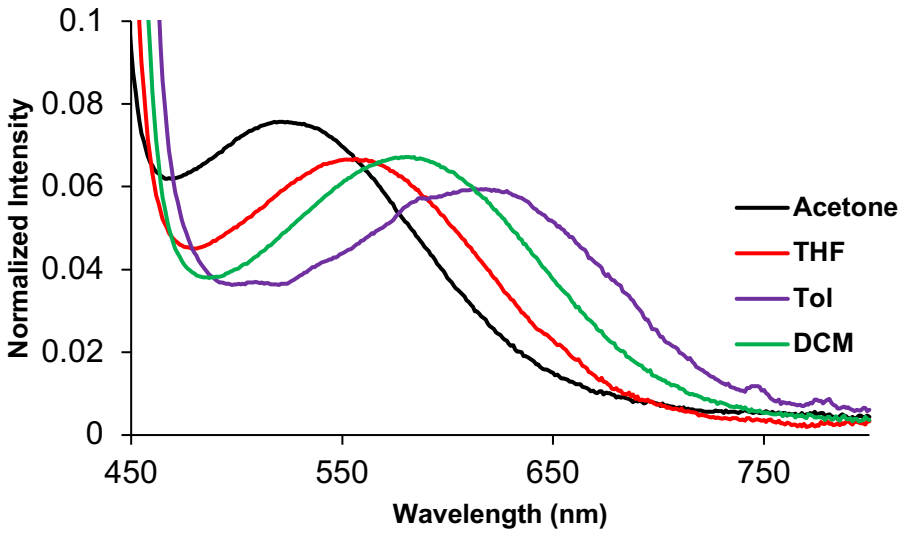


Figure S21. The absorption spectra of **2-^{t}Bu-carb** in 10^{-5} M solutions of different solvents, zoomed into the 450-800 nm region.

Materials: All experiments were performed under a purified argon atmosphere either using a MBraun Unilab glove box or a double manifold high vacuum line fitted with an OxisorBW scrubber (Matheson Gas products) argon purification cartridge, unless otherwise specified. Hexanes, pentane, tetrahydrofuran, diethyl ether, and toluene were dried and purified using a Grubbs/Dow solvent purification system and stored in 500ml thick-walled Kontes flasks over sodium/benzophenone ketal as an indicator. Chlorobenzene, benzene, bromobenzene, *o*-dichlorobenzene, dichloromethane, and chloroform were dried and stored over calcium dihydride. All dried solvents were degassed, and vacuum distilled prior to use. 1,5-naphthyridine and 4,8-dibromo-1,5-naphthyridine were synthesized according to previously reported procedures.[1] All other commercially available starting materials were used without further purification.

Nuclear Magnetic Resonance (NMR) Spectroscopy: NMR spectra were obtained using a BrukerRDQ-400 or a Bruker Ascend-500 NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent protons and naturally abundant ^{13}C resonances for all

deuterated solvents. Chemical shifts (referenced to residual solvent) were reported in parts per million (ppm). Resonances of carbon atoms directly bonded to boron atoms were not always observed due to quadrupolar relaxation effects. ^{11}B NMR spectra were acquired using boron-free quartz NMR tubes and probes. Multiplicities were reported as follows: singlet (s), doublets (d), triplets (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of doublets (td), triplet of triplets (tt), doublet of doublet of doublets (ddd), and multiplets (m).

UV-Vis Absorption Spectroscopy: Absorption spectra were measured using an Agilent Technologies Cary 60 UV-Vis spectrometer at ambient conditions. All solution UV-Vis spectra were measured with 10 mm quartz cuvettes, using dichloromethane (DCM) as the solvent, unless otherwise specified. Stock solutions (1 mg/mL) were prepared, serially diluted to concentrations of 10^{-5} to 10^{-6} M and then used to construct calibration curves with at least five data points for molar absorptivity. Wavelengths of the onset of absorption maxima were used to estimate the optical bandgap using the equation:

$$E_g^{opt} = \frac{1240}{\lambda_{onset}}$$

Photoluminescence (PL) Spectroscopy & Quantum Yield Calculation: All PL data were recorded with and Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature. Samples were recorded in dichloromethane solutions, and excited at the highest wavelength of absorption maxima for each compound. The excitation and emission slit widths were maintained at 5 nm. The PL quantum yields were estimated by using the comparative method proposed by Williams et. al.[2]

$$\phi_X = \phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X}{\eta_{ST}}\right)^2$$

Φ is the PL quantum yield, Grad is the slope of the integrated PL vs. absorption line, and η is the refractive index of solution. Subscripts X and ST refer to the sample and standard, respectively. Fluorescein in 0.1M NaOH aqueous solutions were used as the standard for PL quantum yield calculation. To minimize reabsorption effects, the absorbance of both the standard and sample compounds were maintained to be less than 0.1 absorbance at the respective excitation wavelengths. When making the PL vs. absorption plots, the same excitation and absorption wavelengths were used for both the sample and standard.

X-Ray Crystallography: X-ray crystallographic analyses were performed on a Nonius system equipped with a Bruker Apex-II CCD detector using samples coated in Fomblin Y HVAC 140/13 oil or Fomblin YR-1800 and mounted on a glass fibre. Full crystallography details can be found in independently uploaded .cif files CCDC 2333166-2333175.

Cyclic Voltammetry (CV): Cyclic voltammetry was collected with a CHI660D potentiostat using a three-electrode setup. Glassy carbon, platinum mesh, and silver wire-half cell were used as the working, counter, and reference electrodes, respectively. Ionic strength of the solution was maintained by using a 0.1M solution of $[nBu_4N][PF_6]$ in THF solvent. All cyclic voltammograms were externally referenced to the Fc/Fc^+. Scan rates were maintained at 100 mV/s, unless otherwise specified. Potentials of reduction and oxidations were used to calculate the electrochemical LUMO and HOMO energy levels, respectively, using the equations:

$$E_{LUMO} = -(4.8 + E_{red}) \quad E_{HOMO} = -(4.8 + E_{ox})$$

CHN Elemental Analyses and High-Resolution Mass Spectrometry: Elemental and mass spectrometric analyses were performed Jian Jun Li, Wade White and Michelle Thibault, at the Instrumentation Facility in the Department of Chemistry, University of Calgary.

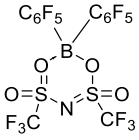
Density Functional Theory Calculations: Geometries of minimum structures were optimized with Gaussian 09 program package[C1] using PBE0 hybrid density functional[C2] and Ahlrichs' small triple-ζ valence quality def2-TZVP basis sets.[C3] Nature of the stationary points was ascertained by frequency calculations and none of the optimized structures showed negative eigenfrequencies.

C1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö.; Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, GAUSSIAN 09 (Revision D.01), Gaussian, Inc., Wallingford CT, 2013.

C2 (a) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868; Erratum, Phys. Rev. Lett., 1997, 78, 1396; (b) J. P. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys., 1996, 105, 9982–9985; (c) C. Adamo and V. Barone, J. Chem. Phys., 1999, 110, 6158–6170.

C3 A. Schaefer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829−5836

Synthesis



Synthesis of bis(pentafluorophenyl) (bis(trifluoromethanesulfonyl)imide-κ^{2}O borane (C_6F_5)$_2$B-NTf$_2$: In an argon atmosphere glovebox, a vial was loaded with (C_6F_5)$_2$B-Cl (400 mg, 1.05 mmol) and dissolved in DCM. TMS-NTf$_2$ (370 mg, 1.05 mmol) was added dropwise to the reaction mixture. Pentane was layered on top of the DCM mixture and stored in the freezer at -30°C. After 24 hours, crystalline needles precipitated out of solution. The mother liquor was

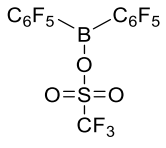
removed, and the crystals were washed with pentane/toluene and dried *in vacuo*, resulting in a 77% yield (508 mg, 0.81 mmol).

^{19}F {^{1}H} NMR (471 MHz, CD_2Cl_2) δ -76.02 (s 6F), -135.38 (m, 4F), -151.73 (t, J = 28 Hz, 2F), -162.87 (m, 4F).

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ 149.44 (d, $^{1}J_{CF}$ = 248 Hz), 143.03 (d, $^{1}J_{CF}$ = 256 Hz), 138.00 (d, $^{1}J_{CF}$ = 251 Hz), 118.73 (q, $^{1}J_{CF}$ = 322 Hz), 109.22 (br).

^{11}B {^{1}H} NMR (161 MHz CD_2Cl_2) δ 10.74.

Elemental Analysis calcd C 26.90; H 0.00; N 2.24. Found C 27.29; H 0.29; N. 2.38.



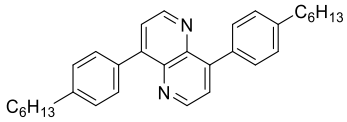
Synthesis of bis(pentafluorophenyl) ((trifluoromethylsulfonyl)oxyl) borane, $(C_6F_5)_2$B-OTf: In an argon atmosphere glovebox, a vial was loaded with $(C_6F_5)_2$B-Cl (100 mg, 0.263 mmol) and dissolved in DCM. TMS-OTf (58 mg, 0.263 mmol) was added dropwise to the reaction mixture. Pentane was layered on top of the DCM mixture and stored in the freezer at -30°C. After 24 hours, crystalline needles precipitated out of solution. The mother liquor was removed, resulting in a 64% yield (83 mg, 0.168 mmol). **NOTE**: $(C_6F_5)_2$B-OTf does not seem to be stable in the solid-state and turns into a brown oil *in vacuo*, as well as a slow decomposition even at -30°C in a pentane solution.

^{19}F NMR (471 MHz, $CDCl_3$) δ -76.51, -128.84, -142.10, -159.77.

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.22 (d, $^{1}J_{CF}$ = 252.9 Hz), 145.76 (d, $^{1}J_{CF}$ = 271.1 Hz), 137.76 (d, $^{1}J_{CF}$ = 257.0 Hz), 118.22 (d, $^{1}J_{CF}$ = 320.2 Hz).

^{11}B NMR (161 MHz $CDCl_3$) δ 44.52.

HRMS (ESI): m/z $[M-H]^-$ calcd for $C_{13}HBF_{13}O_3S$, 494.9532; found 494.9586.

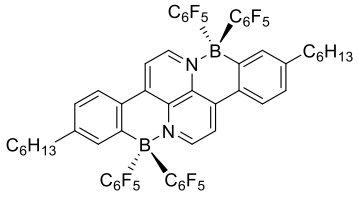


Synthesis of 4,8-(4-hexylphenyl)-1,5-naphthyridine (C_6-Naphth): Synthesis was adapted using previously reported procedures.[3] 4,8-dibromo-1,5-naphthyridine (**Br_2-Naphth**) (0.35 g, 1.22 mmol), 4-hexylphenylboronic acid (1.00 g, 4.85 mmol), and palladium acetate (14 mg, 0.06 mmol) were loaded into a round bottom flask. K_2CO_3 (0.67 g, 4.86 mmol) was dissolved in a DMF/H_2O (30 mL, 1:1) solvent mixture, degassed with argon for 30 minutes, and cannula transferred into the reaction flask. The reaction mixture was sealed and heated at 80°C for 48 h. After the reaction has completed, the mixture is filtered and extracted with DCM, and washed with brine. The organic phase was dried over Na_2SO_4 and solvent was removed *in vacuo*. The crude product was recrystallized in THF/MeOH (1:1) solution to obtain **C_6-Naphth** in a 46% yield (0.25 g, 0.56 mmol) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, J = 4.4 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 4.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 2.71 (t, J = 8.1 Hz, 2H), 1.70 (m, 2H), 1.42 (m, 2H), 1.35 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.83, 148.07, 143.05, 142.05, 133.91, 129.86, 127.81, 123.29, 35.31, 31.22, 30.76, 28.63, 22.09, 13.58.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{39}N_2$, 451.3116; found 451.3108.



Synthesis of 1-hex: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (128 mg, 0.67 mmol) and **(C_6F_5)B-NTf_2** (347 mg, 0.56 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **C_6-Naphth** (100 mg, 0.22 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was taken up in DCM (10 mL) and ran through a short silica plug and the remaining solvent was removed *in vacuo*. The resulting residue was recrystallized in hot hexanes resulting in **1-hex** as a yellow solid with an 88% yield (73 mg, 0.064 mmol). X-ray quality crystals were obtained via a slow evaporation of a DCM/pentane mixture.

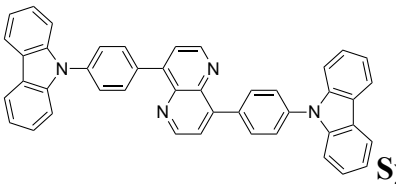
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.92 (d, J = 6.4 Hz, 1H), 8.43 (d, J = 6.4 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.34 (s, 1H), 7.27 (dd, ^{1}J = 8.63 Hz, 1.53 Hz 1H), 2.62 (t, J = 7.5 Hz, 2H), 1.56 (t, J = 7.04 Hz, 2H), 1.23 (m, 6H), 0.83 (m, 3H).

^{19}F {^{1}H} NMR (471 MHz, CD_2Cl_2) δ -132.40 (dd, J = 23.6 Hz, 7.6 Hz, 2F), -156.96 (t, J = 20.5 Hz, 1H), -163.40 (td, J = 24.2 Hz, 5.4 Hz, 2F).

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2) δ 150.69, 150.32, 148.51 (d, $^1J_{CF}$ = 242.9), 140.47 (d, $^1J_{CF}$ = 249.9), 137.74 (d, $^1J_{CF}$ = 259.5), 137.23, 134.86, 133.14, 128.89, 126.42, 125.91, 121.04 (br), 119.87, 36.45, 31.99, 31.08, 29.00, 22.92, 14.14. (Carbon attached to boron on the phenylnaphthyridine core not observed).

^{11}B {^{1}H} NMR (161 MHz, CD_2Cl_2) δ -3.59.

HRMS (ESI): m/z $[M-H]^-$ calcd for $C_{56}H_{36}B_2F_{20}N_2$, 1137.2672; found 1137.2653.

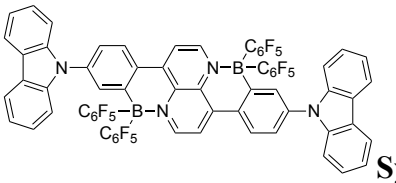


Synthesis of 4,8-bis(4-(9H-carbazol-9-yl)phenyl)-1,5-naphthyridine (Cz-Naphth): The same procedure for **C_6-Naphth** was performed using (4-(9H-carbazol-9-yl)phenyl)boronic acid, except purification involved column chromatography using 1:1 $CHCl_3$/hexanes to obtain a pale yellow solid in a 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (d, *J* = 4.3 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 4.3 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 150.88, 140.79, 138.46, 136.01, 132.34, 126.75, 126.18, 124.43, 123.73, 120.51, 120.33, 110.18, 109.92.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{44}H_{29}N_4$, 613.23922; found 613.23627.



Synthesis of 1-carb: 2,6-di-tert-butylpyridine (8.1 mg, 0.04 mmol) and **$(C_6F_5)B$-NTf_2** (26.5 mg, 0.04 mmol) were loaded into a J-Young NMR tube and dissolved in *o*-dichlorobenzene-d_4. Then, **Cz-Naphth** (13 mg, 0.02 mmol) was added in two portions, the tube was sealed and heated at 100°C for 16 hours. The reaction was cooled to room temperature and filtered, and the resulting crystalline solid was washed with $CHCl_3$. The crystals were dried, resulting in **1-carb** with a 60% yield (16.5 mg, 0.01 mmol).

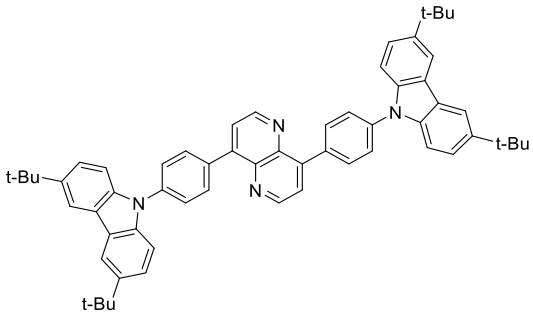
^{1}H NMR (400 MHz, Acetone) δ 9.57 (d, *J* = 6.3 Hz, 2H), 9.12 (d, *J* = 6.6 Hz, 2H), 8.73 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 7.7 Hz, 4H), 7.88 (s, 2H), 7.86 (d, *J* = 2.3 Hz, 1H), 7.48 – 7.38 (m, 6H), 7.36 – 7.29 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.10 (m, 3H).

^{13}C {^{1}H} NMR (A suitable ^{13}C spectrum was not able to be obtained due to limited solubility).

^{19}F NMR (376 MHz, Acetone) δ -132.09 (dd, *J* = 23.8, 7.8 Hz), -158.54 (t, *J* = 20.3 Hz), -164.10 – -165.63 (m).

^{11}B NMR (161 MHz, Acetone) δ -3.34.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{68}H_{26}B_2F_{20}N_4$, 1301.2102; found 1301.2128.

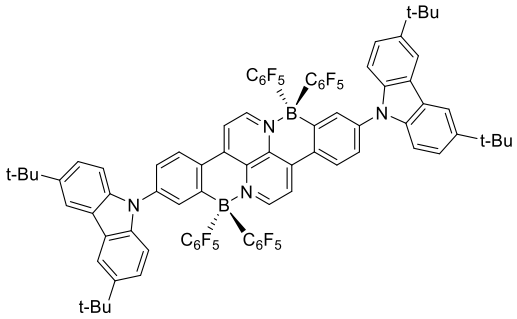


Synthesis of 4,8-bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-1,5-naphthyridine (^{t}BuCz-Naphth): The same procedure for **C_6-Naphth** was performed using (4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)boronic acid, except purification involved column chromatography using 1:1 $CHCl_3$/hexanes to obtain a pale yellow solid in a 56% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (d, *J* = 4.3 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 4.3 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.51 (dd, *J* = 8.7, 2.0 Hz, 2H), 1.49 (s, 18H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.83, 148.05, 143.28, 142.72, 139.17, 139.03, 135.50, 132.24, 126.32, 124.39, 123.83, 116.44, 109.64, 34.93, 32.19.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{60}H_{61}N_4$, 837.48907; found 837.49087.



Synthesis of 1-^{t}Bu-carb: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (17.4 mg, 0.09 mmol) and **$(C_6F_5)B$-NTf_2** (38 mg, 0.06 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **^{t}BuCz-Naphth** (19 mg, 0.03 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was extracted with $CHCl_3$ and put through a plug of silica. The solvent was removed, resulting in **1-^{t}Bu-carb** with a 37% yield as a blue solid (17 mg, 0.01 mmol).

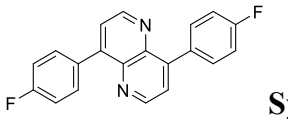
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, J = 6.4 Hz, 2H), 8.51 (d, J = 6.6 Hz, 2H), 8.29 (d, J = 8.9 Hz, 2H), 8.11 (s, 4H), 7.84 (s, 2H), 7.75 (dd, J = 8.7, 2.3 Hz, 2H), 7.45 (dd, J = 8.7, 2.1 Hz, 4H), 7.35 (d, J = 8.7 Hz, 4H), 1.47 (s, 36H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.31, 148.21 (d, J_{CF} = 240.1 Hz), 146.02, 144.37, 143.86, 140.06 (d, J_{CF} = 260.7 Hz), 138.23, 137.64 (d, J_{CF} = 249.0 Hz), 137.37, 129.09, 128.00, 125.23, 125.15, 124.49, 124.05, 119.98 (br), 119.55, 116.68, 109.75, 34.95, 32.07 (Carbon attached to boron on the phenylnaphthyridine core not observed).

^{19}F NMR (471 MHz, $CDCl_3$) δ -132.15 (dd, J = 24.4, 8.5 Hz), -156.15 (t, J = 20.7 Hz), -162.87 (td, J = 22.8, 8.5 Hz).

^{11}B NMR (161 MHz, $CDCl_3$) δ -4.41.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{84}H_{59}B_2F_{20}N_4$, 1525.4601; found 1525.4613.



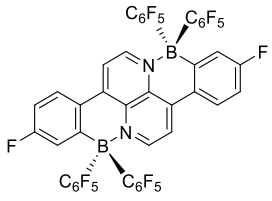
Synthesis of 4,8-(4-fluorophenyl)-1,5-naphthyridine (F-Naphth): The same procedure for **C_6-Naphth** was performed using 4-fluorophenylboronic acid in a 50% yield as a grey-white solid.

^{1}H NMR (500 MHz, C_6D_6) δ 8.67 (d, J = 4.3 Hz, 0H), 7.62 – 7.54 (m, 1H), 7.04 – 6.92 (m, 1H).

^{13}C {^{1}H} NMR (126 MHz, C_6D_6) δ 163.61, 161.64, 149.53, 146.58, 141.84, 132.19, 132.12, 122.92, 114.29, 114.12.

^{19}F NMR (471 MHz, C_6D_6) δ -114.02.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{13}F_2N_2$, 318.1041; found 318.1047.



Synthesis of 1-F: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (90 mg, 0.47 mmol) and **$(C_6F_5)B$-NTf_2** (246 mg, 0.39 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **F-Naphth** (50 mg, 0.16 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was taken up in $CHCl_3$ (10 mL) and stored at -10°C resulting in a yellow-green precipitate. The resulting precipitate was washed with 2 mL of cold acetone, resulting in **1-F** with a 29% yield (47 mg, 0.047 mmol). X-ray quality crystals were obtained from a concentrated solution of acetone.

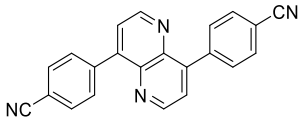
^{1}H NMR (500 MHz, Acetone) δ 9.45 (d, J = 6.2 Hz, 2H), 8.94 (d, J = 6.4 Hz, 2H), 8.47 (dd, J = 9.7, 5.1 Hz, 2H), 7.32 – 7.24 (m, 4H).

^{13}C {^{1}H} NMR (126 MHz, Acetone) δ 167.89, 165.86, 155.97 (br), 153.18, 149.15 (d, J_{CF} = 240.7 Hz), 146.21, 141.01 (d, J_{CF} = 249.3 Hz), 138.21 (d, J_{CF} = 249.9 Hz), 137.84, 130.96 (d, J_{CF} = 9.1 Hz), 126.07, 122.03, 120.92 (br), 119.30 (d, J_{CF} = 20.4 Hz), 116.58 (d, J_{CF} = 23.2 Hz).

^{19}F NMR (471 MHz, Acetone) δ -107.89 (dd, J = 14.7, 8.5 Hz), -133.32 (dd, J = 24.0, 8.2 Hz), -159.64 (t, J = 19.8 Hz), -162.71 – -175.55 (m).

^{11}B NMR (161 MHz, Acetone) δ -3.71.

HRMS (APCI): m/z $[M^*]^+$ calcd for $C_{44}H_{10}B_2F_{22}N_2$, 1006.0673; found 1006.0698.



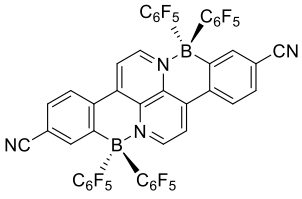
Synthesis of 4,8-bis(4-cyanophenyl)-1,5-naphthyridine (CN-Naphth):

The same procedure for **C_6-Naphth** was performed using 4-cyanophenylboronic acid, to obtain a white solid in an 87% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, J = 4.3 Hz, 1H), 7.99 – 7.79 (m, 8H), 7.68 (d, J = 4.3 Hz, 2H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.08, 147.02, 142.07, 141.58, 132.15, 131.41, 124.35, 118.79, 112.79.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{22}H_{13}N_4$, 333.11347; found 333.11238.



Synthesis of 1-CN: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (12 mg, 0.06 mmol) and **(C_6F_5)B-NTf_2** (38 mg, 0.06 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **CN-Naphth** (10 mg, 0.03 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was extracted with $CHCl_3$ and put through a plug of silica. The solvent was removed and recrystallized in acetonitrile obtaining a 26% yield (8 mg, 0.008 mmol).

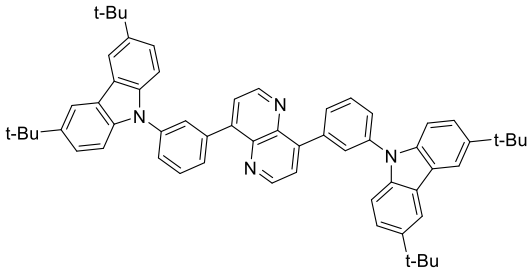
^{1}H NMR (500 MHz, Acetone) δ 9.66 (d, J = 6.1 Hz, 1H), 9.13 (d, J = 6.4 Hz, 1H), 8.56 (d, J = 8.3 Hz, 1H), 7.94 (s, 1H), 7.90 (dd, J = 8.3, 1.7 Hz, 1H).

^{13}C {^{1}H} NMR (126 MHz, Acetone) δ 154.02, 149.20 (d, J_{CF} = 238.4 Hz), 141.15 (d, J_{CF} = 257.0 Hz), 138.26 (d, J_{CF} = 249.4 Hz), 137.15, 133.34, 131.90, 128.16, 123.71, 119.10, 116.76 (Carbons attached to boron not observed).

^{19}F NMR (471 MHz, Acetone) δ -133.26 (dd, J = 22.8, 9.0 Hz), -159.23 (t, J = 19.1 Hz), -165.63 – -165.81 (m).

^{11}B NMR (161 MHz, Acetone) δ -3.06.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{46}H_{10}B_2F_{20}N_4$, 1021.0845; found 1021.0833.

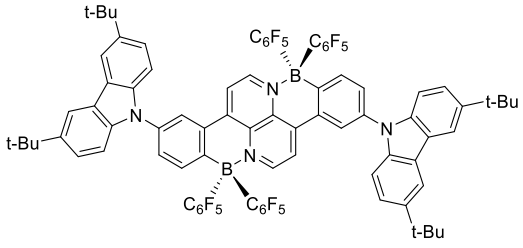


Synthesis of 4,8-bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-1,5-naphthyridine (ᵗBuCz′-Naphth): The same procedure for **C_6-Naphth** was performed using (3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)boronic acid, except purification involved column chromatography using CHCl3 to obtain a pale brown solid in a 40% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, *J* = 4.4 Hz, 1H), 8.17 (s, 1H), 8.08 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.76 (dd, *J* = 12.0, 4.6 Hz, 3H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 1H), 1.48 (s, 18H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.92, 147.80, 143.11, 142.46, 139.12, 138.67, 138.16, 129.81, 129.10, 128.80, 126.53, 124.24, 123.79, 123.60, 116.40, 109.56, 34.89, 32.16.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{60}H_{61}N_4$, 837.4891; found 837.4899.



Synthesis of 2-ᵗBu-carb: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (9.6 mg, 0.05 mmol) and **$(C_6F_5)B$-NTf_2** (31 mg, 0.05 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **ᵗBuCz′-Naphth** (20 mg, 0.024 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was

extracted with $CHCl_3$ and put through a plug of silica. The solvent was removed, resulting in **2-^{t}Bu-carb** with a 53% yield as a green solid (19 mg, 0.012 mmol).

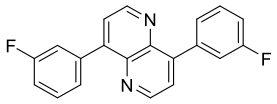
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, J = 6.4 Hz, 2H), 8.48 (d, J = 6.5 Hz, 2H), 8.29 (d, J = 1.4 Hz, 2H), 8.16 (d, J = 1.7 Hz, 4H), 7.83 – 7.72 (m, 4H), 7.47 (dd, J = 8.6, 1.9 Hz, 4H), 7.39 (d, J = 8.6 Hz, 4H), 1.47 (s, 38H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.10, 150.47 (br), 148.23 (d, J_{CF} = 238.9 Hz), 146.21, 143.68, 140.57 (d, J_{CF} = 253.4 Hz), 139.01, 138.61, 137.61 (d, J_{CF} = 251.9 Hz), 137.26, 132.47, 134.79, 129.09, 124.05, 123.78, 123.54, 120.41, 119.82, 116.64, 109.09, 34.93, 32.13.

^{19}F NMR (471 MHz, $CDCl_3$) δ -132.30 (dd, J = 23.8, 9.0 Hz), -156.00 (t, J = 20.7 Hz), -162.74 (td, J = 23.3, 8.5 Hz).

^{11}B NMR (161 MHz, $CDCl_3$) δ -2.44.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{84}H_{59}B_2F_{20}N_4$, 1525.4601; found 1525.4583.



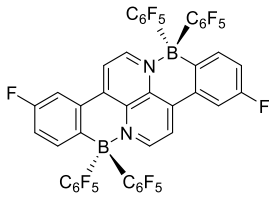
Synthesis of 4,8-(3-fluorophenyl)-1,5-naphthyridine (F′-Naphth): The same procedure for **C$_6$-Naphth** was performed using 3-fluorophenylboronic acid in a 46% yield as a white solid.

^{1}H NMR (400 MHz, Acetone) δ 9.07 (d, J = 4.4 Hz, 2H), 7.86 (d, J = 4.3 Hz, 2H), 7.70 – 7.65 (m, 4H), 7.59 (td, J = 8.1, 6.0 Hz, 2H), 7.32 – 7.26 (m, 2H).

^{13}C {^{1}H} NMR (101 MHz, Acetone) δ 163.18 (d, J_{CF} = 243.2 Hz), 151.69, 147.73, 142.86, 140.42 (d, J_{CF} = 8.4 Hz), 130.70 (d, J_{CF} = 8.4 Hz), 127.49 (d, J_{CF} = 3.3 Hz), 125.08, 118.70 (d, J_{CF} = 23.1 Hz), 115.98 (d, J_{CF} = 21.3 Hz).

^{19}F NMR (376 MHz, Acetone) δ -115.55.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{13}F_2N_2$, 319.1041; found 319.1056.



Synthesis of 2-F: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (90 mg, 0.47 mmol) and **(C_6F_5)B-NTf_2** (246 mg, 0.39 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **F′-Naphth** (50 mg, 0.16 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was taken up in $CHCl_3$ (10 mL) and filtered hot. The resulting precipitate was washed with 2 mL of cold $CHCl_3$ and hexanes, resulting in **2-F** with a 26% yield (41 mg, 0.041 mmol). X-ray quality crystals were obtained from $CHCl_3$/hexanes.

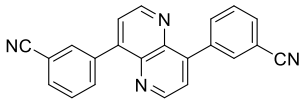
^{1}H NMR (500 MHz, Acetone) δ 9.55 (d, J = 6.4 Hz, 2H), 9.01 (d, J = 6.4 Hz, 2H), 8.13 (dd, J = 10.8, 2.6 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.37 (td, J = 8.6, 2.4 Hz, 2H).

^{13}C {^{1}H} NMR (126 MHz, Acetone) δ 164.51, 162.57, 153.55, 149.10 (d, J_{CF} = 241.1 Hz), 146.07, 140.93 (d, J_{CF} = 251.1 Hz), 138.1 (d, J_{CF} = 245.2 Hz), 138.02, 135.80, 122.83, 121.32 (d, J_{CF} = 20.9 Hz), 113.27 (d, J_{CF} = 22.3 Hz). (Carbons attached to boron not observed).

^{19}F {^{1}H} NMR (376 MHz, Acetone) δ -115.62, -132.28 (dd, J = 23.5, 8.6 Hz), -158.84 (t, J = 20.0 Hz), -164.92 – -165.13 (m).

^{11}B NMR (161 MHz, Acetone) δ -3.84.

HRMS (MALDI): m/z $[M^*]^-$ calcd for $C_{44}H_{10}B_2F_{22}N_2$, 1006.0679; found 1006.0626.

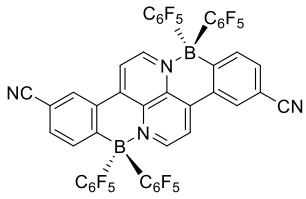


Synthesis of 4,8-bis(3-cyanophenyl)-1,5-naphthyridine (CN′-Naphth): 4,8-dibromo-1,5-naphthyridine (**Br_2-Naphth**) (0.05 g, 0.17 mmol), 3-tributylstannylbenzonitrile (0.17 g, 0.43mmol), $Pd(PPh_3)_4$ (0.02 g, 0.017 mmol), and 4 mL of toluene were loaded into a microwave reactor vessel. The solvent mixture was degassed with argon for 30 minutes and was heated with a microwave reactor at 165°C for 45 minutes while stirring. After the reaction has completed, the mixture is filtered and washed with toluene and hexanes, and dried *in vacuo* to obtain CN'-Naphth in a 69% yield (40 mg, 0.12 mmol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (d, *J* = 4.3 Hz, 1H), 8.13 (t, *J* = 1.8 Hz, 1H), 8.02 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.80 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.74 – 7.64 (m, 2H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 151.12, 146.51, 142.07, 138.10, 134.89, 134.46, 132.37, 129.34, 124.36, 118.83, 112.78.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{22}H_{13}N_4$, 333.1135; found 333.1143.



Synthesis of 2-CN: Synthesis was adapted using previously reported procedures.[4] 2,6-di-tert-butylpyridine (24 mg, 0.12 mmol) and **(C_6F_5)B-NTf_2** (79 mg, 0.12 mmol) were dissolved in chlorobenzene (20 mL) and loaded into a round bottom flask. Then, **CN′-Naphth** (20 mg, 0.06 mmol) was added to the reaction mixture, the flask was sealed and heated at 100°C for 16 hours. Volatiles were removed *in vacuo* and the residue was extracted with $CHCl_3$ and purified with column chromatography (9:1 $CHCl_3$/hexanes). The solvent was removed and washed with minimal cold $CHCl_3$ 18% yield (11 mg, 0.01 mmol).

^{1}H NMR (500 MHz, Acetone) δ 9.66 (d, J = 6.2 Hz, 1H), 9.20 (d, J = 6.2 Hz, 1H), 8.81 (s, 1H), 7.91 (d, J = 7.9 Hz, 0H), 7.79 (d, J = 7.8 Hz, 1H).

^{13}C {^{1}H} NMR (126 MHz, CDCl3) δ 153.95 (d, J = 19.5 Hz), 149.16 (d, J_{CF} = 240.7 Hz), 145.40, 141.17 (d, J_{CF} = 243.4 Hz), 138.23 (d, J_{CF} = 261.4), 138.04, 135.75, 134.62, 131.31, 130.63, 123.41 (d, J = 13.2 Hz), 118.81, 112.90 (Carbons attached to boron not observed).

^{19}F NMR (471 MHz, Acetone) δ -132.99 (dd, J = 23.3, 9.5 Hz), -159.22 (t, J = 19.6 Hz), -165.73 (td, J = 23.8, 9.0 Hz).

^{11}B NMR (161 MHz, Acetone) δ -3.30.

HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{46}H_{10}B_2F_{20}N_4$ 1021.0845; found 1021.0852.

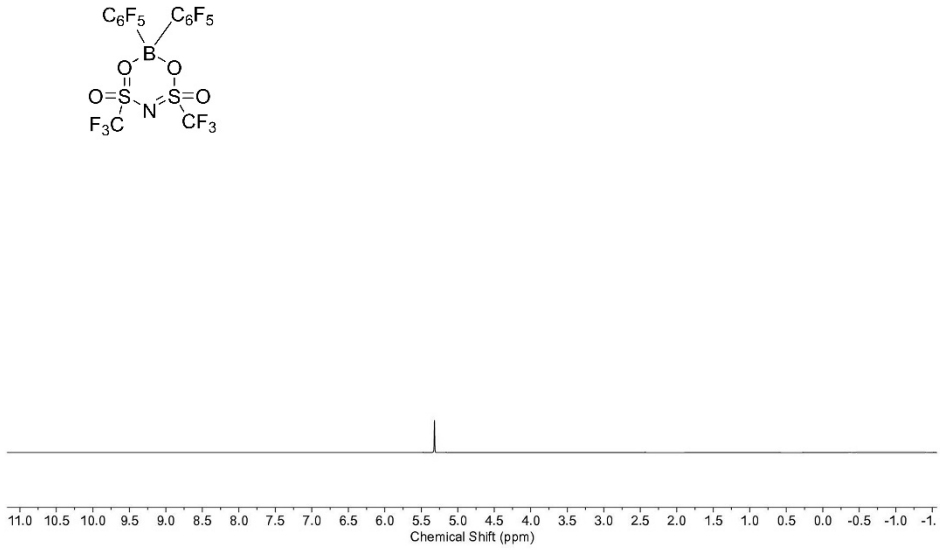


Figure S22. ^{1}H NMR of **$(C_6F_5)_2B$-NTf_2** in CD_2Cl_2

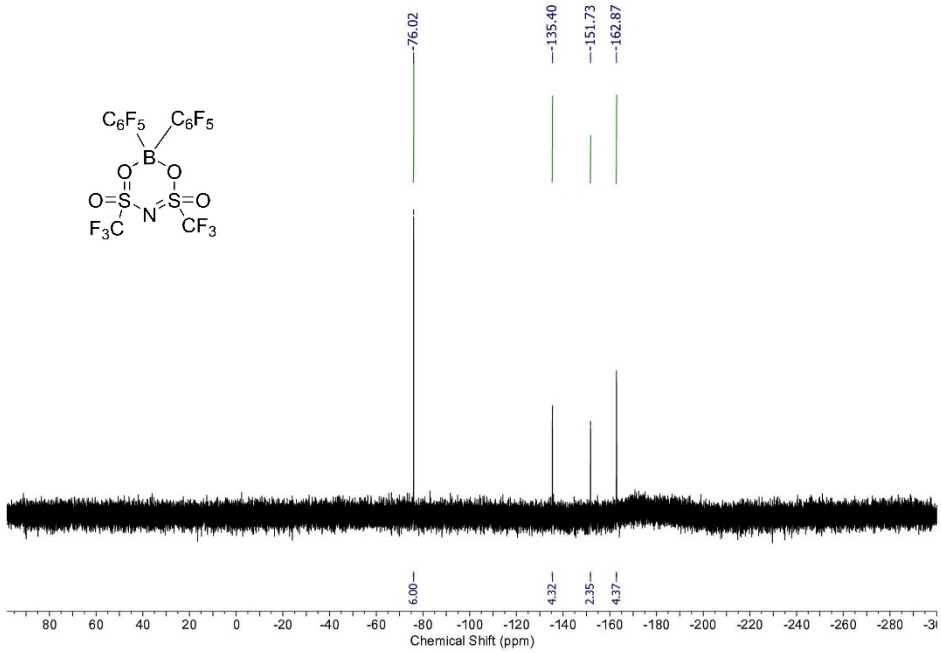


Figure S23. ^{19}F $\{^{1}H\}$ NMR of **$(C_6F_5)_2B$-NTf_2** in CD_2Cl_2

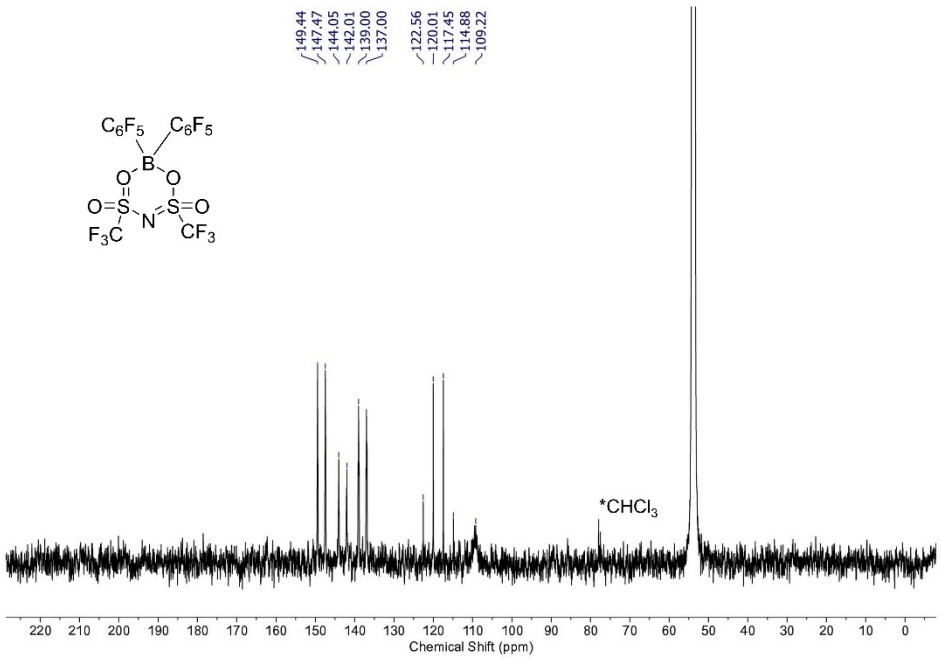


Figure S24. ^{13}C $\{^{1}H\}$ NMR of **$(C_6F_5)_2B$-NTf_2** in CD_2Cl_2

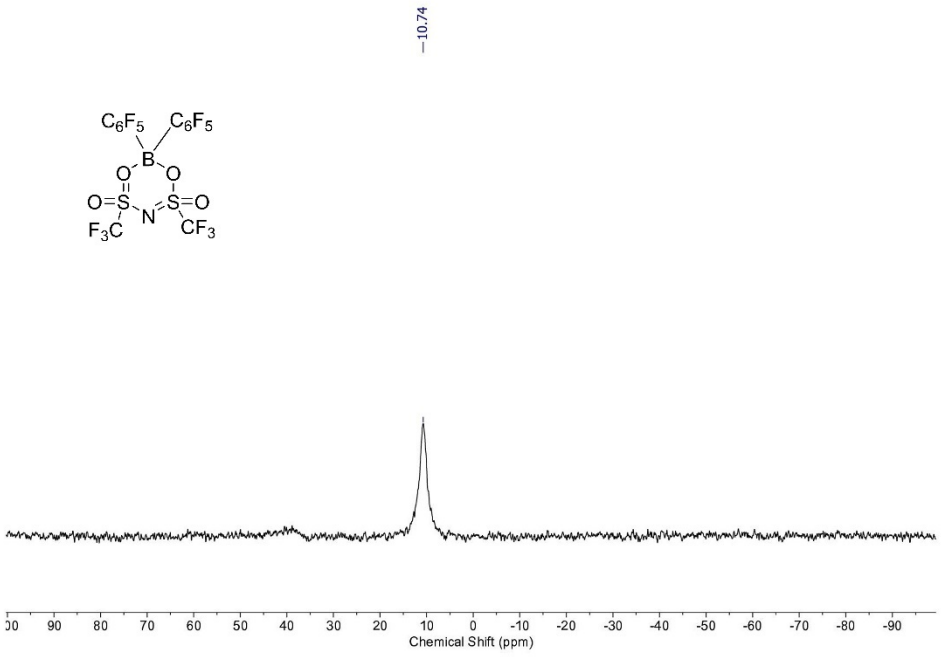


Figure S25. ^{11}B $\{^{1}H\}$ NMR of **$(C_6F_5)_2B$-NTf_2** in CD_2Cl_2

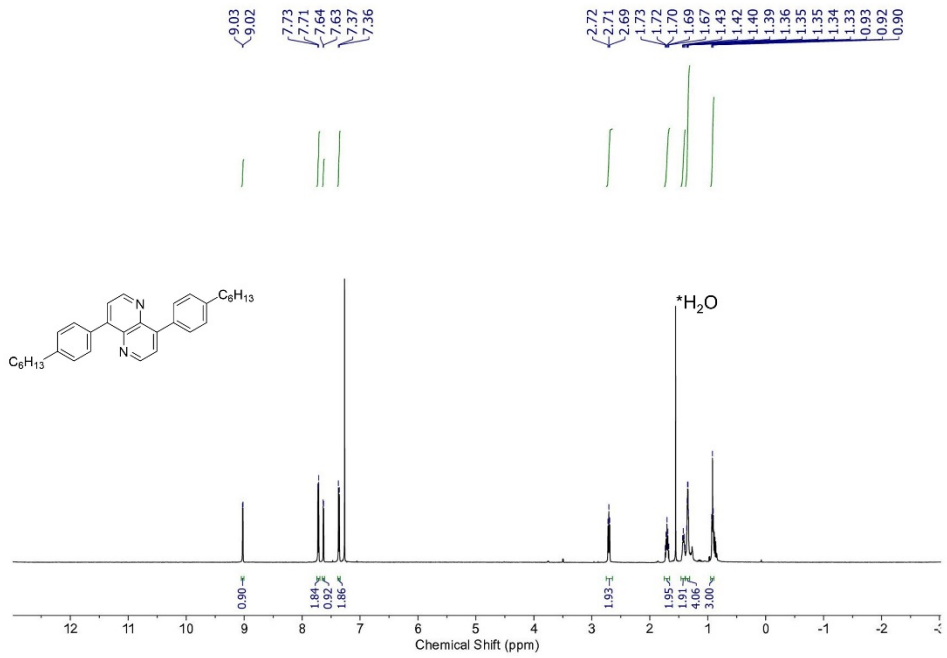


Figure S26. ^{1}H NMR of **C_6-Naphth** in $CDCl_3$

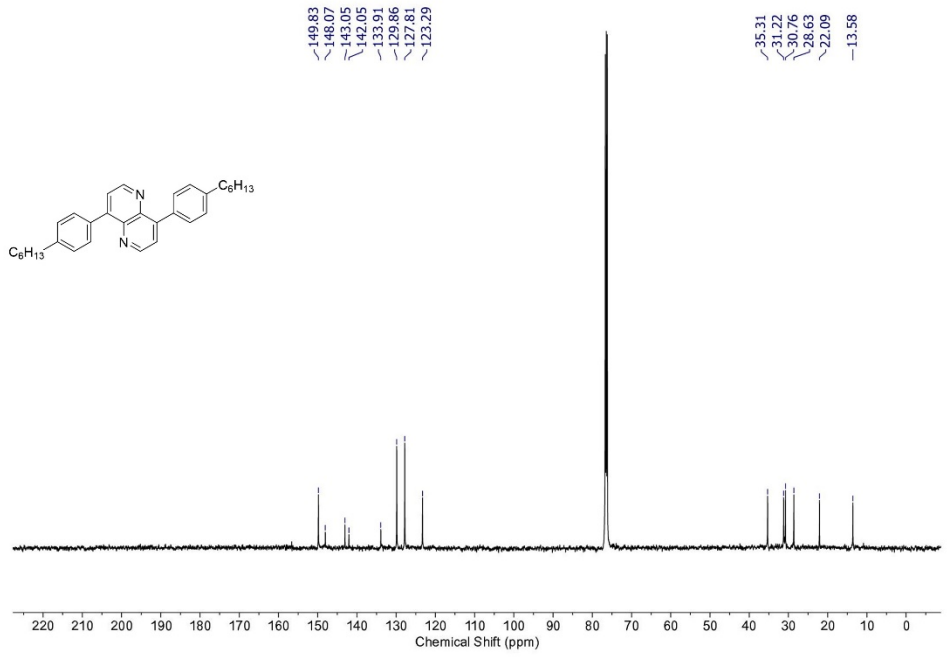


Figure S27. ^{13}C {^{1}H} NMR of **C_6-Naphth** in $CDCl_3$

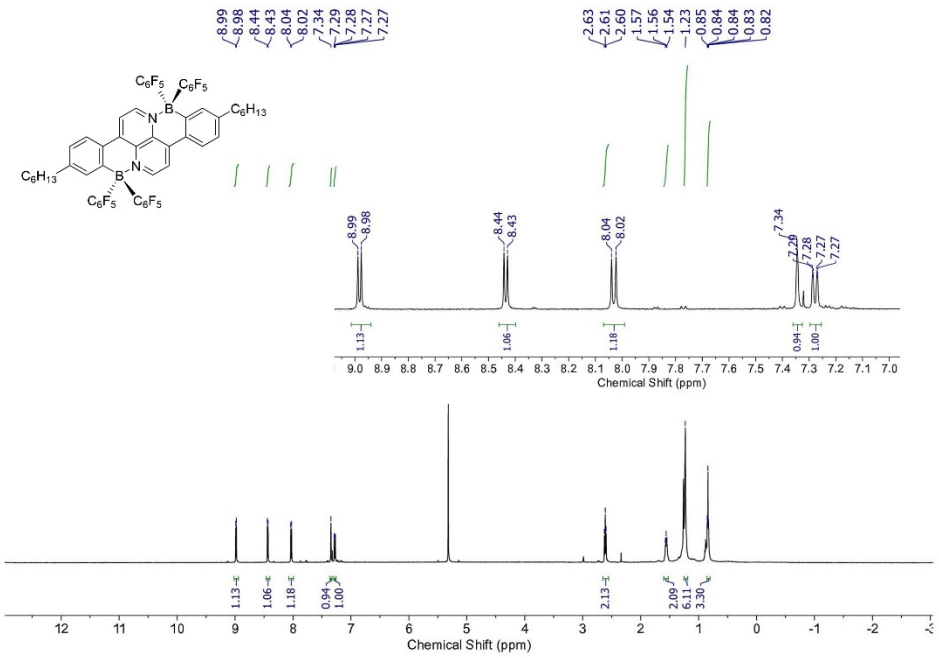


Figure S28. ^{1}H NMR of **1-hex** in CD_2Cl_2

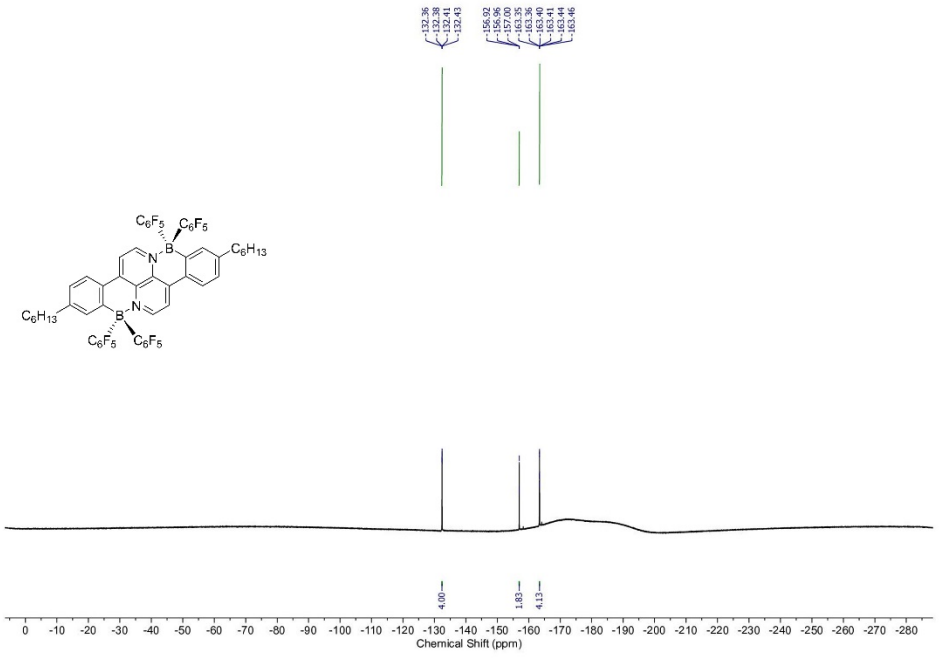


Figure S29. ^{19}F $\{^{1}H\}$ NMR of **1-hex** in CD_2Cl_2

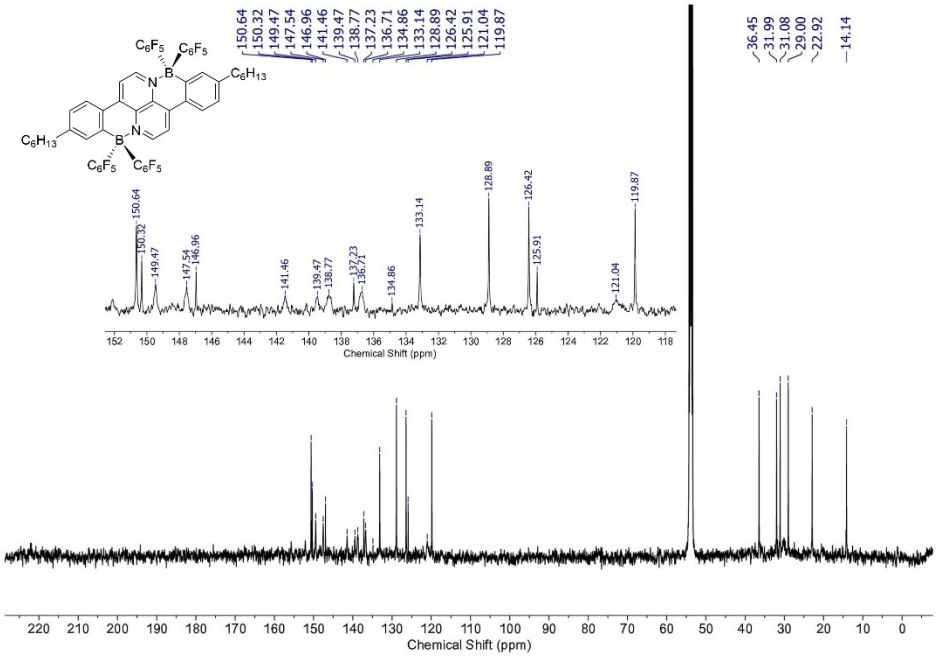


Figure S30. ^{13}C {^{1}H} NMR of **1-hex** in CD_2Cl_2

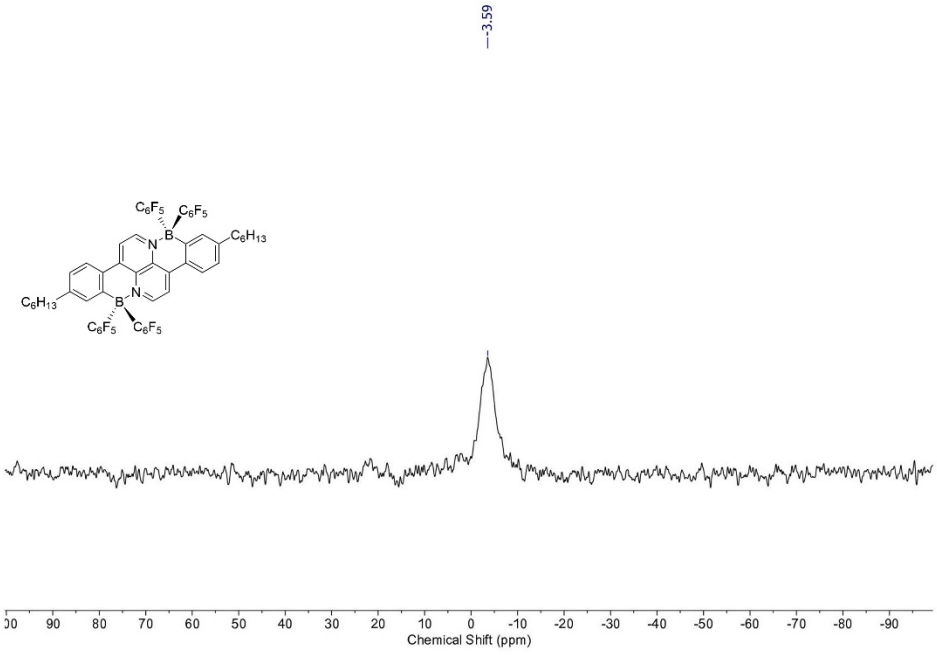


Figure S31. ^{11}B {^{1}H} NMR of **1-hex** in CD_2Cl_2

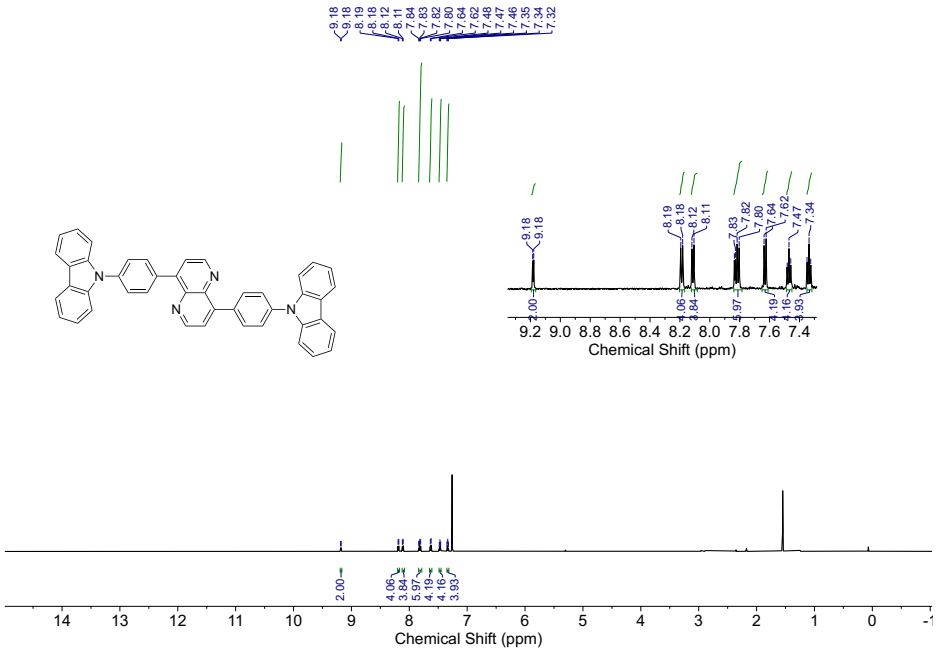


Figure S32. ^{1}H NMR of **Cz-Naphth** in $CDCl_3$

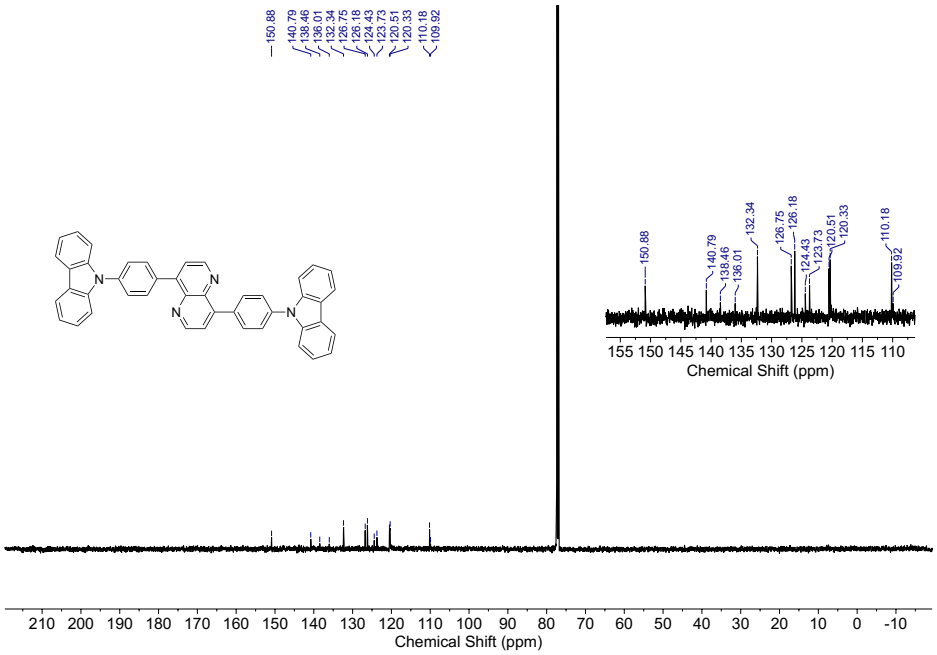


Figure S33. ^{13}C NMR of **Cz-Naphth** in $CDCl_3$

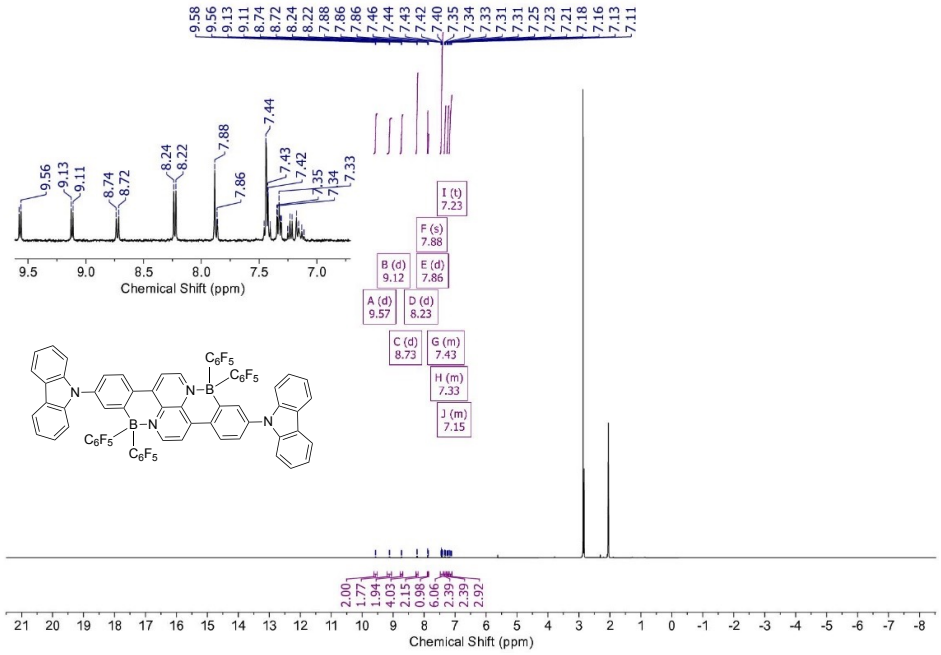


Figure S34. ^{1}H NMR spectrum of **1-carb** in acetone-d_6

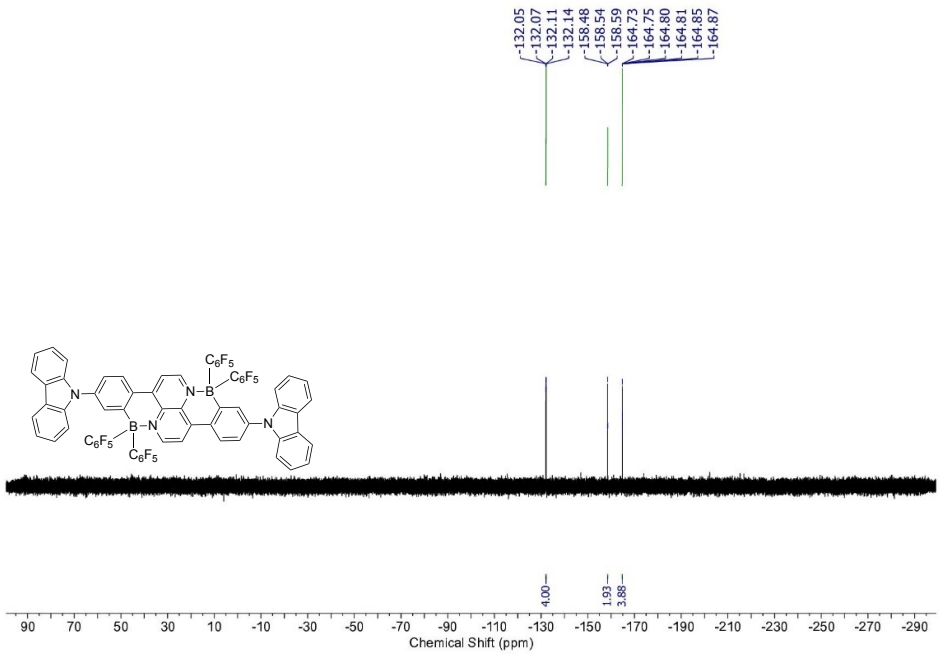


Figure S35. ^{19}F NMR spectrum of **1-carb** in acetone-d_6

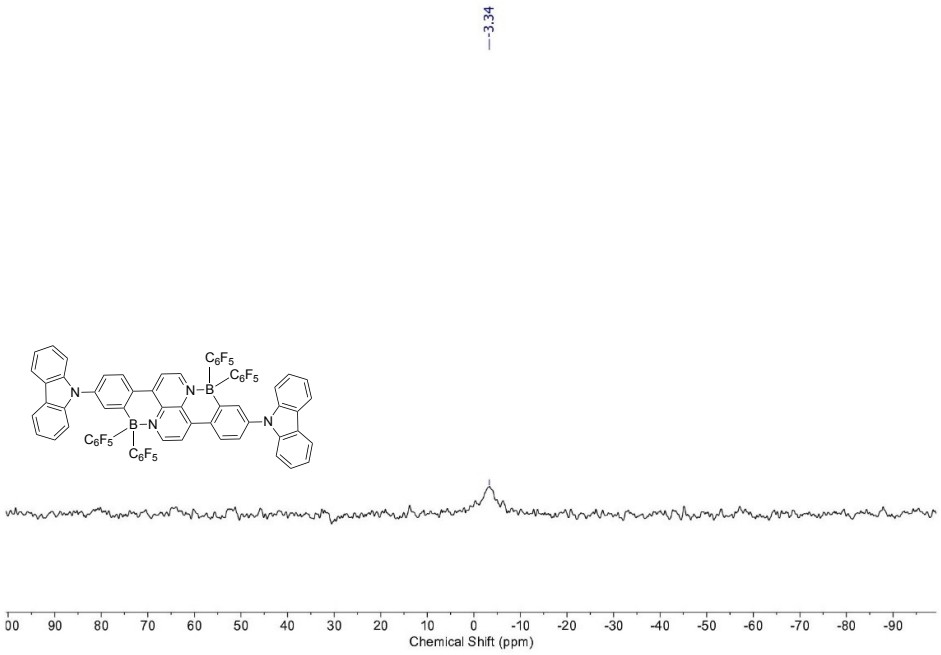


Figure S36. ^{11}B NMR spectrum of **1-carb** in acetone-d_6

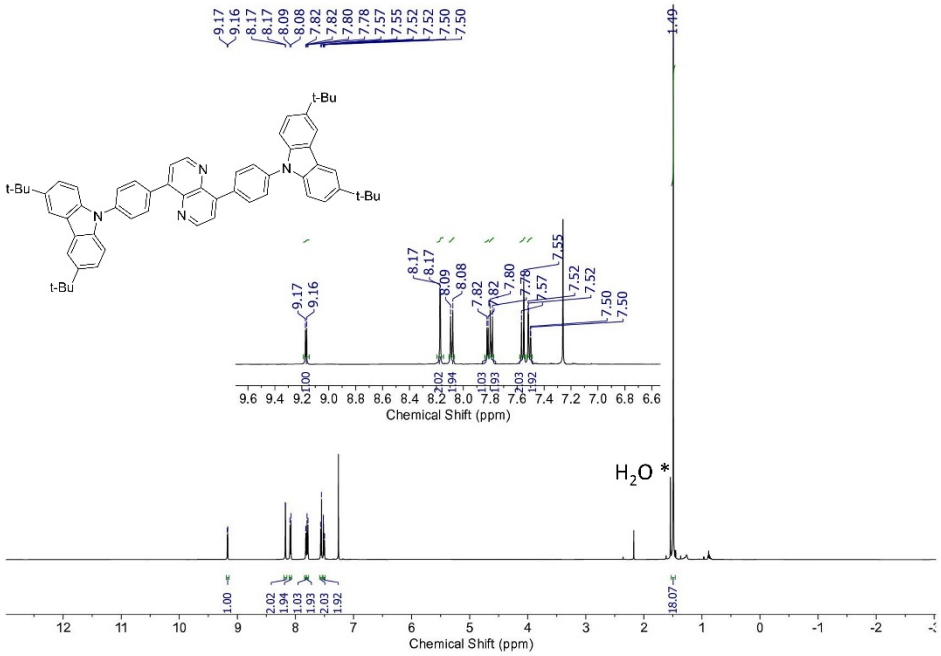


Figure S37. ^{1}H NMR of **^{t}BuCz-Naphth** in $CDCl_3$

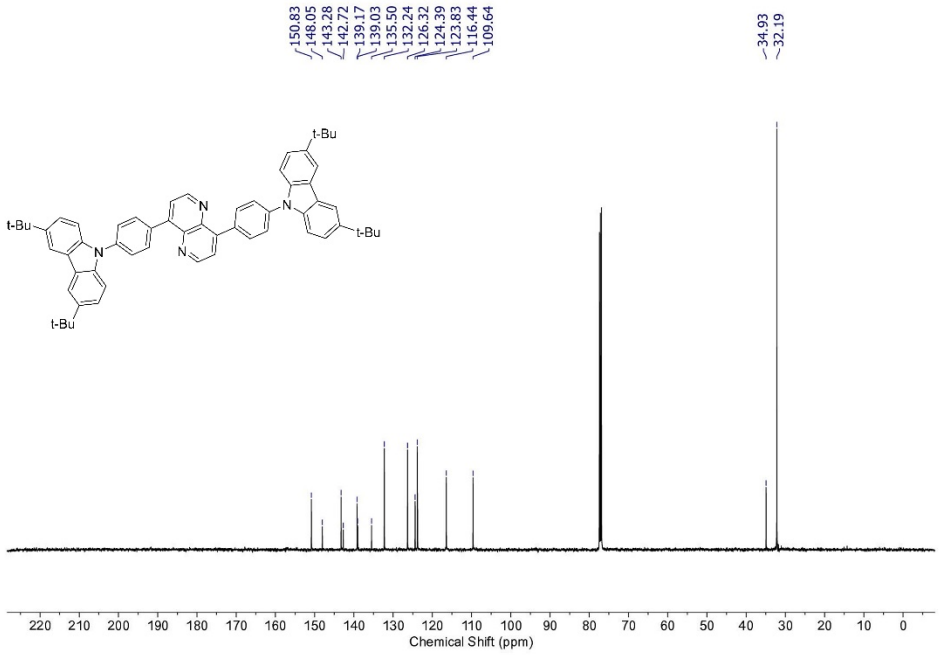


Figure S38. ^{13}C {^{1}H} NMR of **^{t}BuCz-Naphth** in $CDCl_3$

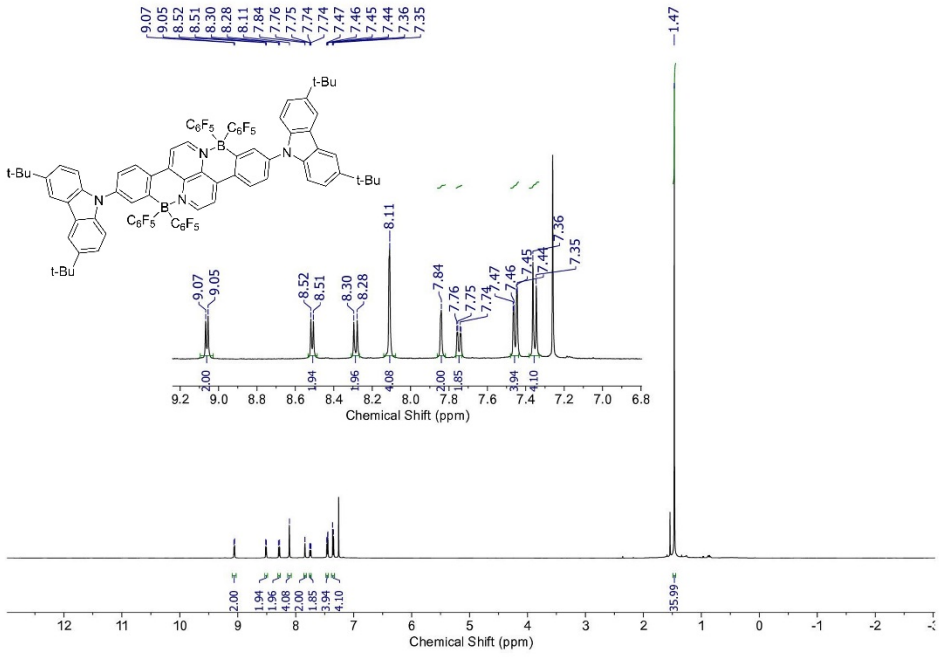


Figure S39. ^{1}H NMR of **1-^{t}Bu-carb** in $CDCl_3$

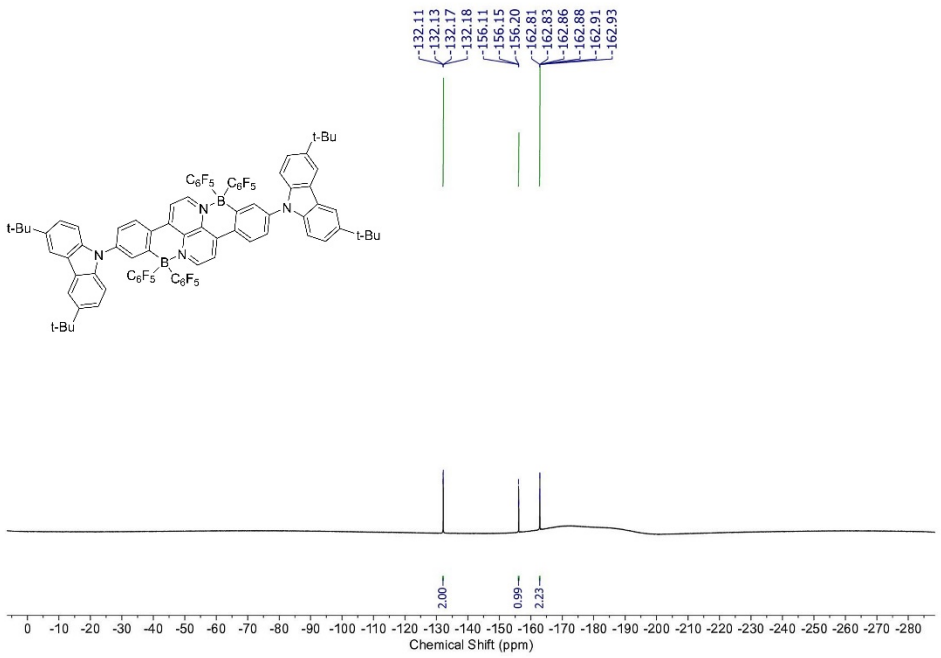


Figure S40. ^{19}F NMR of **1-^{t}Bu-carb** in $CDCl_3$

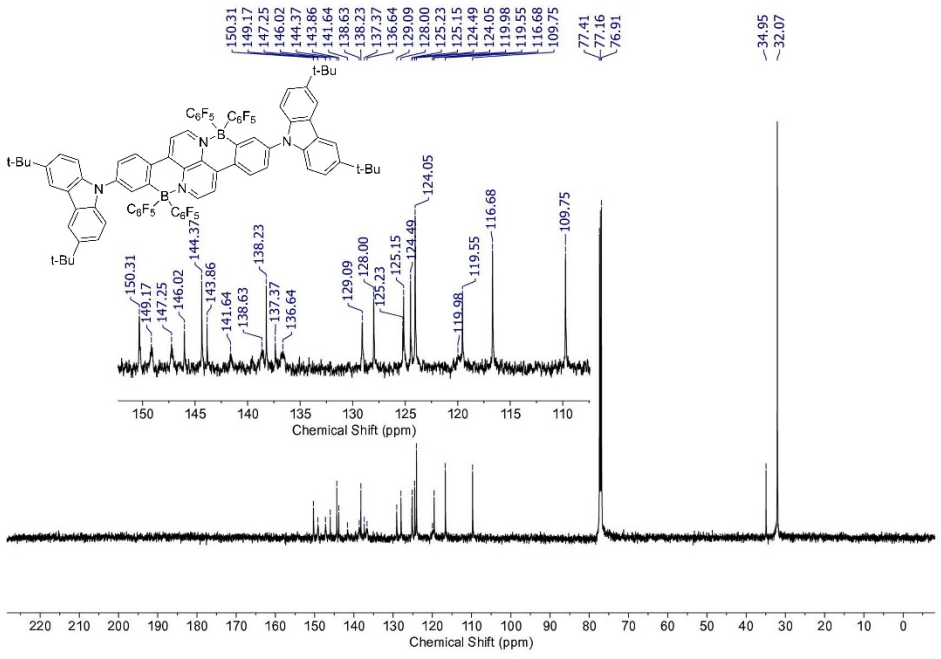


Figure S41. ^{13}C {^{1}H} NMR of **1-^{t}Bu-carb** in $CDCl_3$

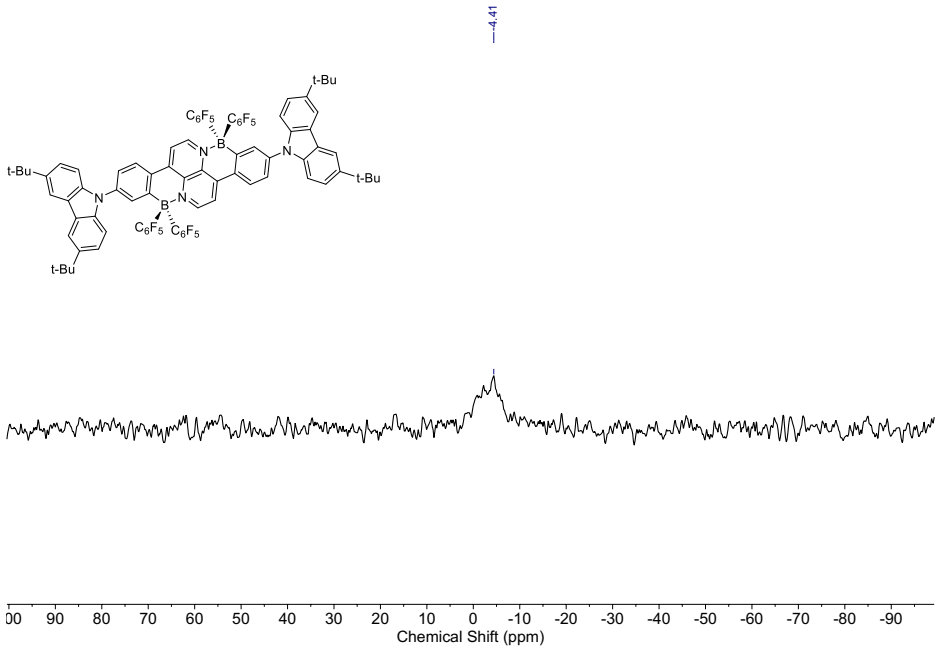


Figure S42. ^{11}B NMR of **1-*t*Bu-carb** in $CDCl_3$

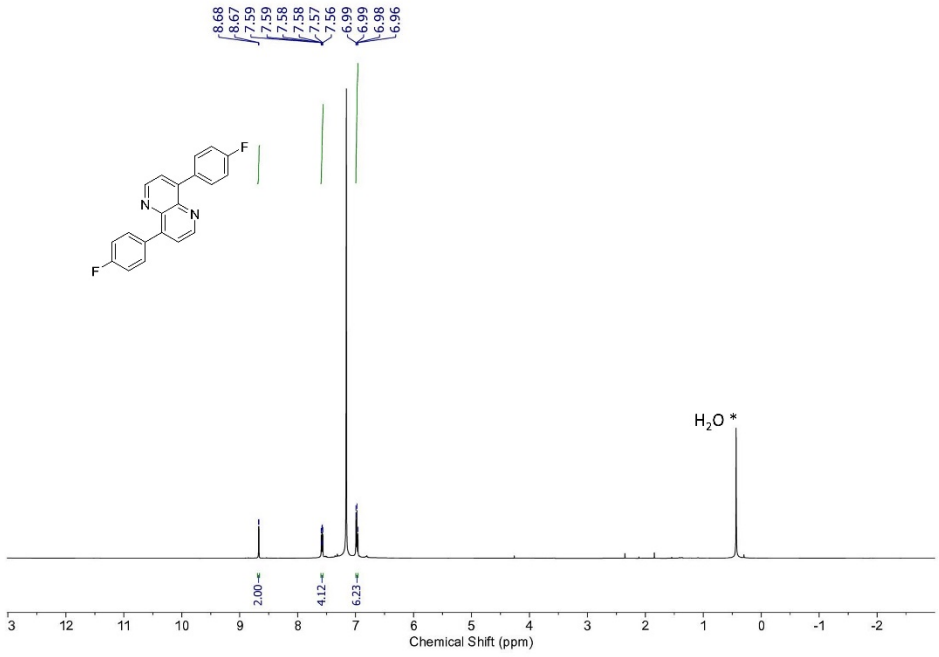


Figure S43. ^{1}H NMR of **F-Naphth** in C_6D_6

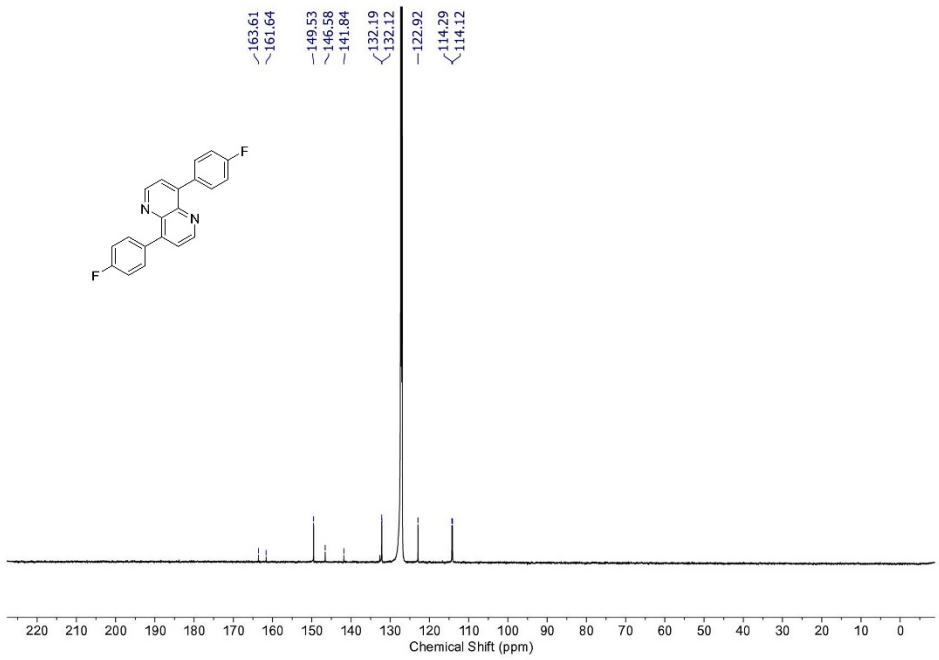


Figure S44. ^{13}C {^{1}H} NMR of **F-Naphth** in C_6D_6

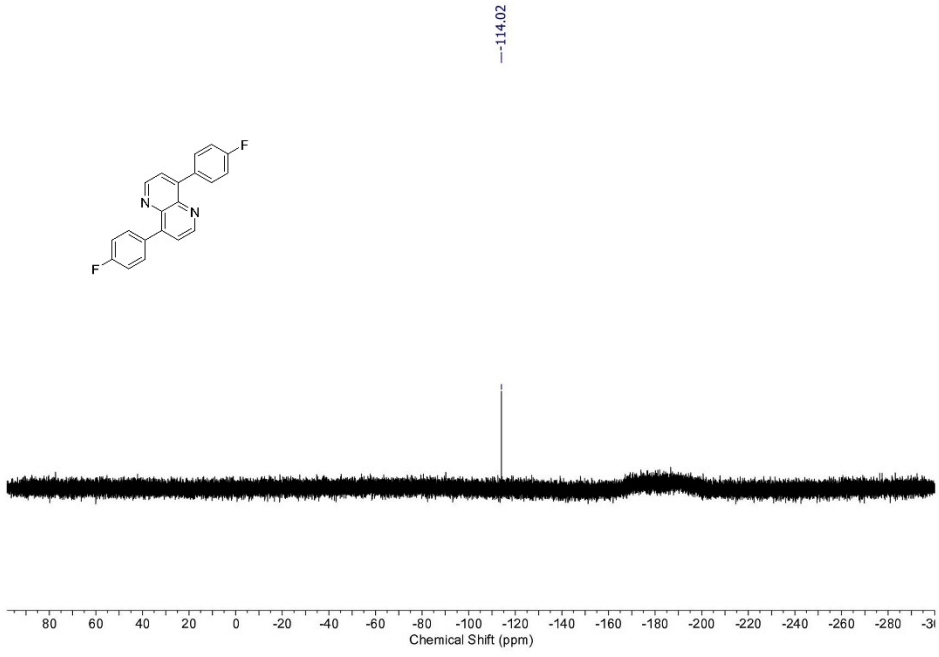


Figure S45. ^{19}F {^{1}H} NMR of **F-Naphth** in C_6D_6

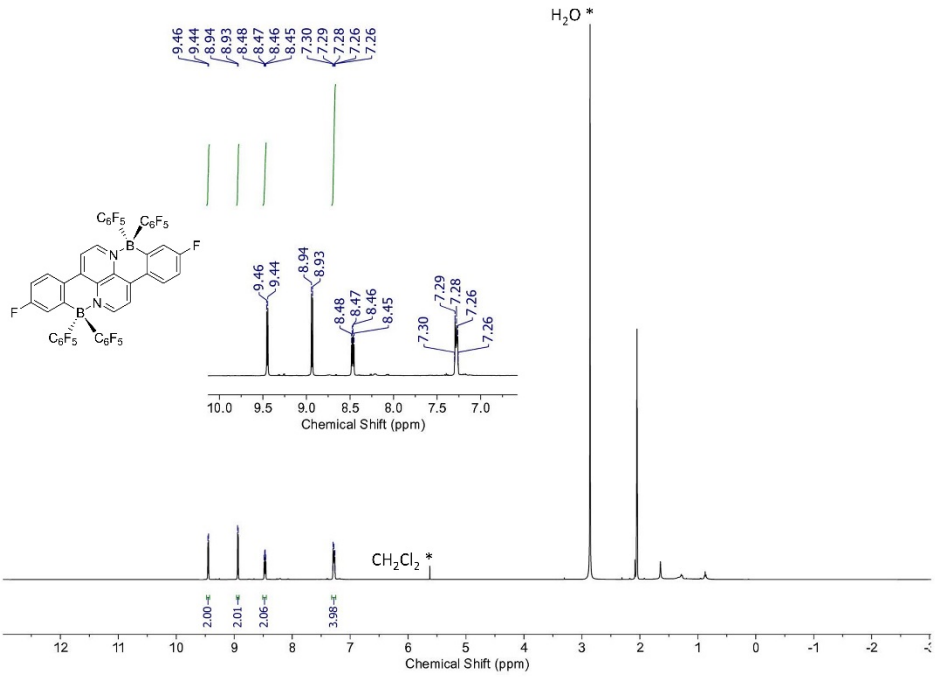


Figure S46. ^{1}H NMR of **1-F** in acetone-d_6

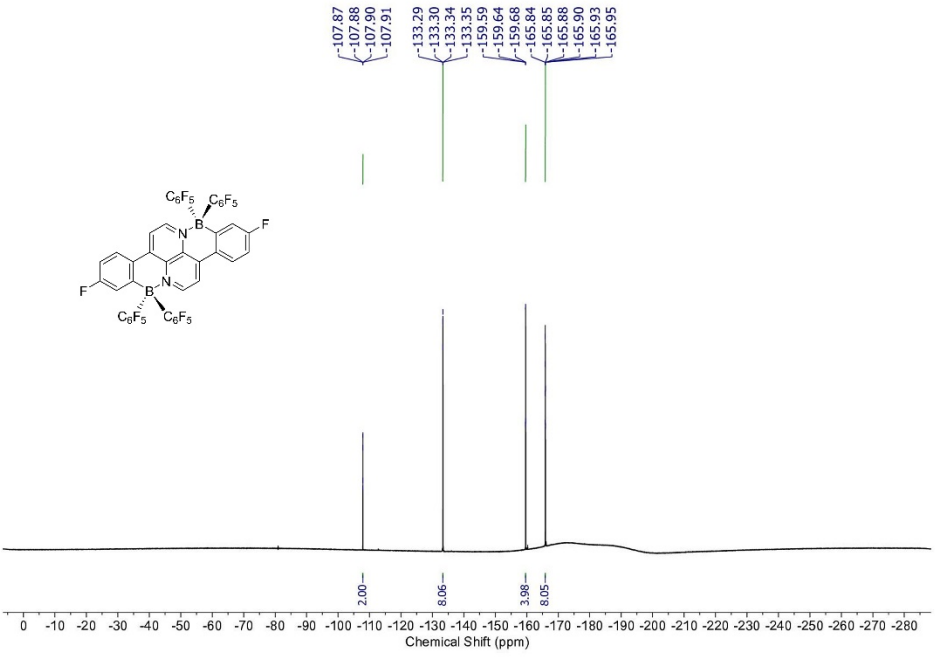


Figure S47. ^{19}F NMR of **1-F** in acetone-d_6

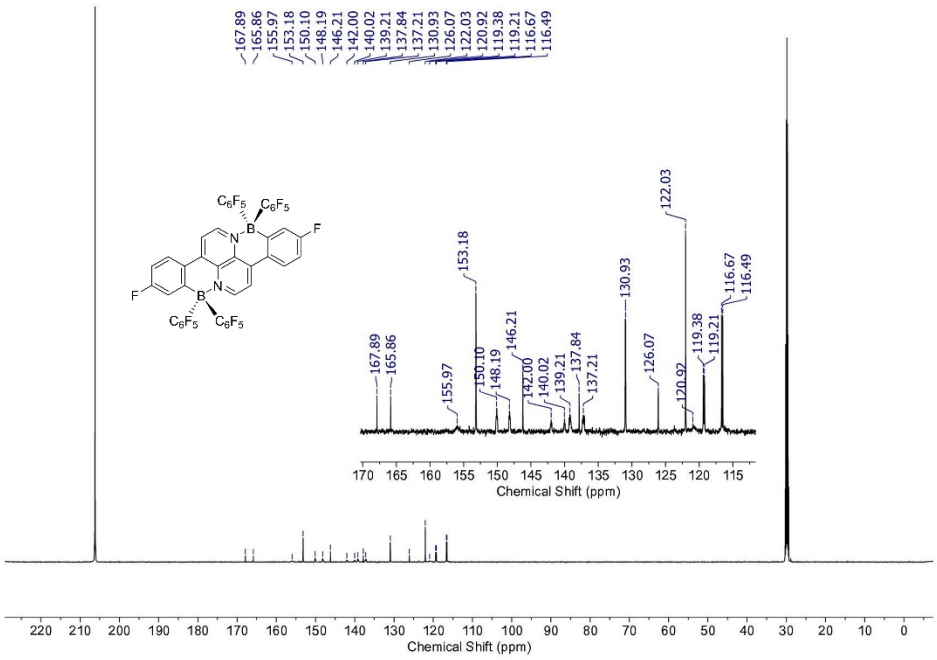


Figure S48. ^{13}C {^{1}H} NMR of **1-F** in acetone-d_6

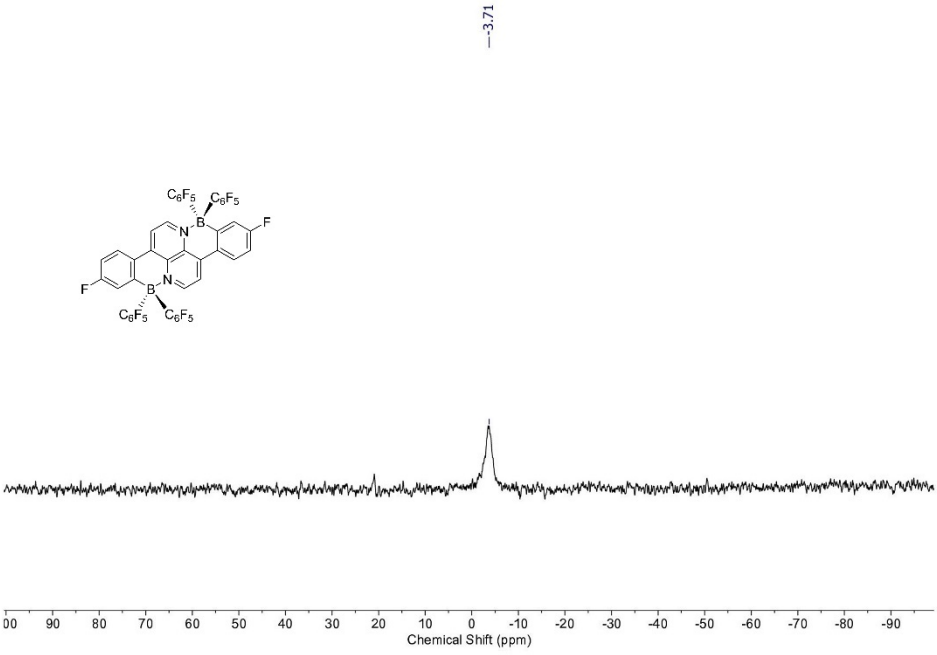


Figure S49. ^{11}B NMR of **1-F** in acetone-d_6

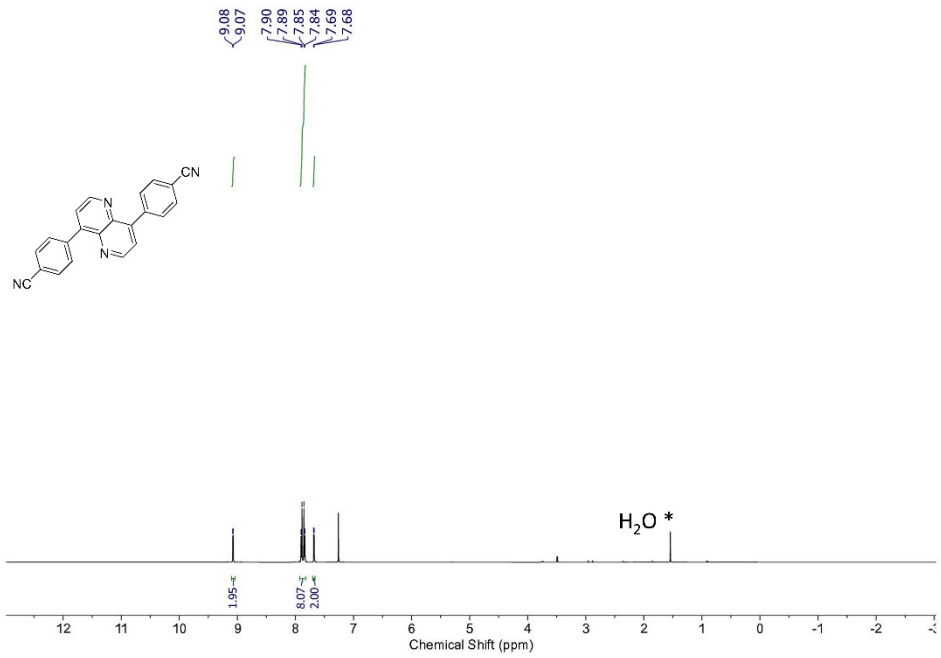


Figure S50. ^{1}H NMR of **CN-Naphth** in $CDCl_3$

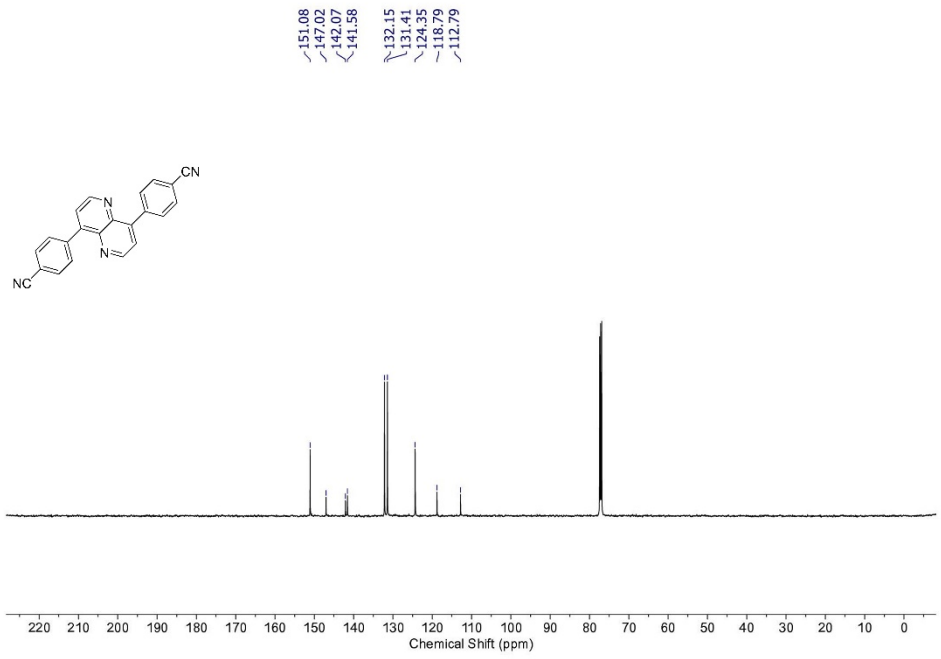


Figure S51. ^{13}C $\{^{1}H\}$ NMR of **CN-Naphth** in $CDCl_3$

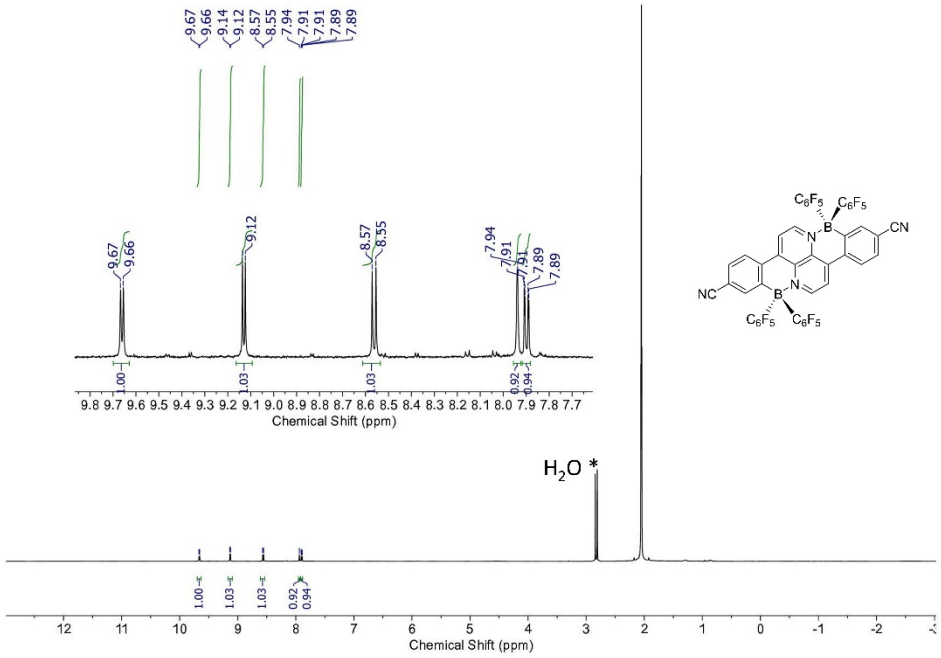


Figure S52. ^{1}H NMR of **1-CN** in acetone-d_6

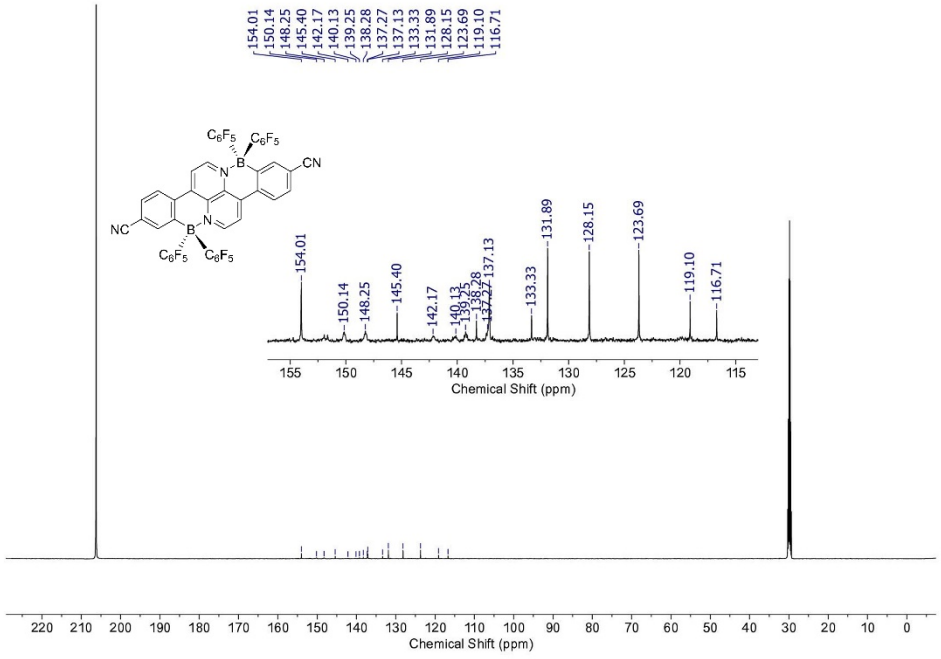


Figure S53. ^{13}C {^{1}H} NMR of **1-CN** in acetone-d_6

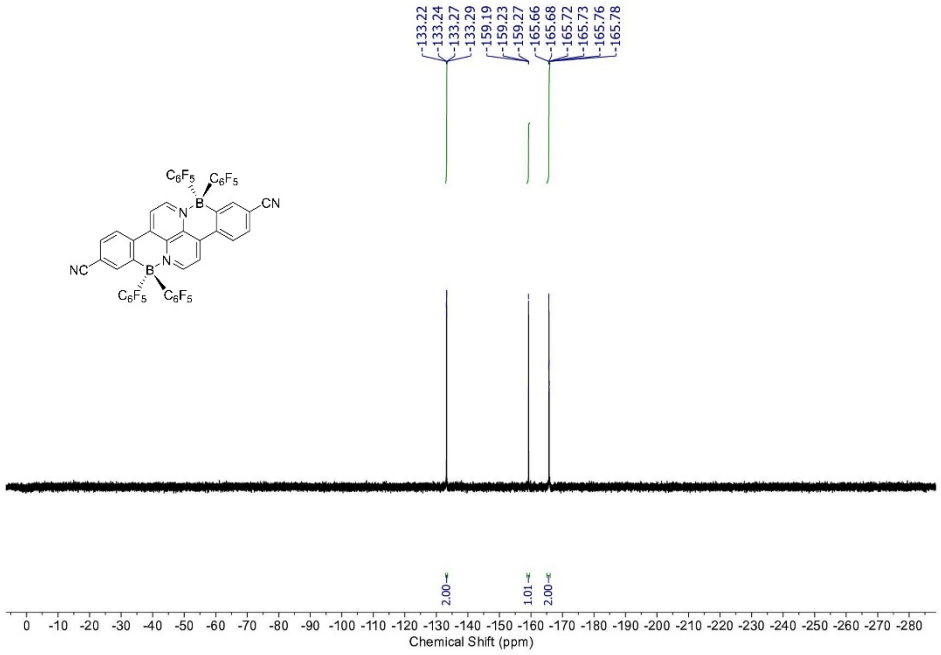


Figure S54. ^{19}F NMR of **1-CN** in acetone-d_6

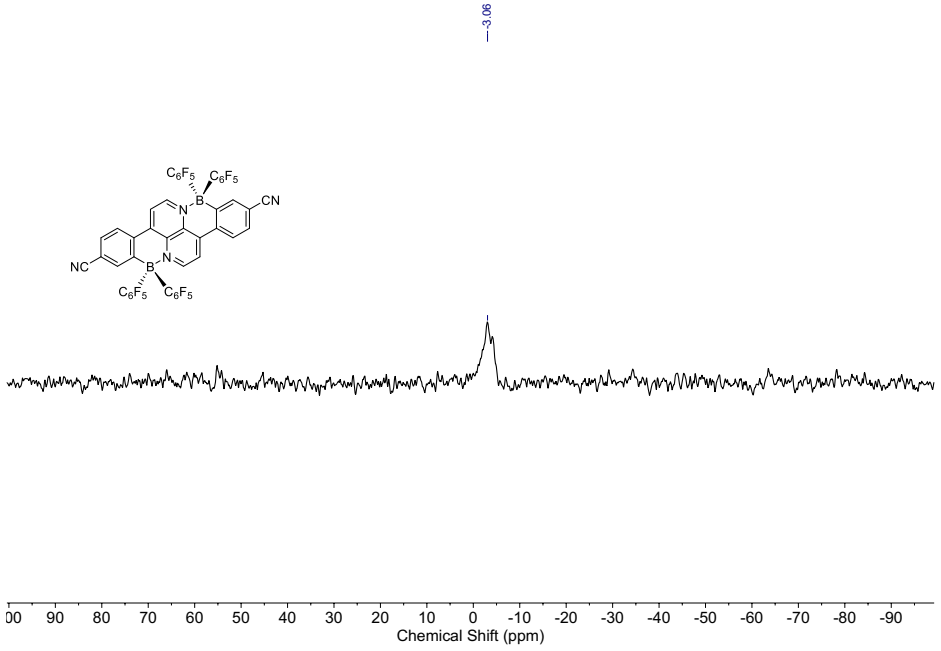


Figure S55. ^{11}B NMR of **1-CN** in acetone-d_6

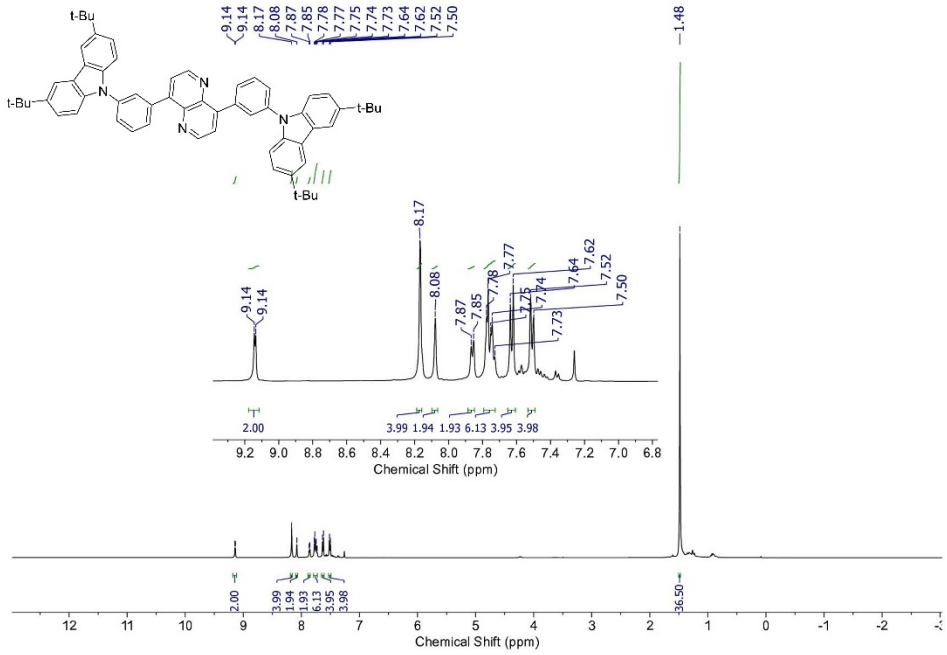


Figure S56. ^{1}H NMR of **'BuCz'-Naphth** in $CDCl_3$

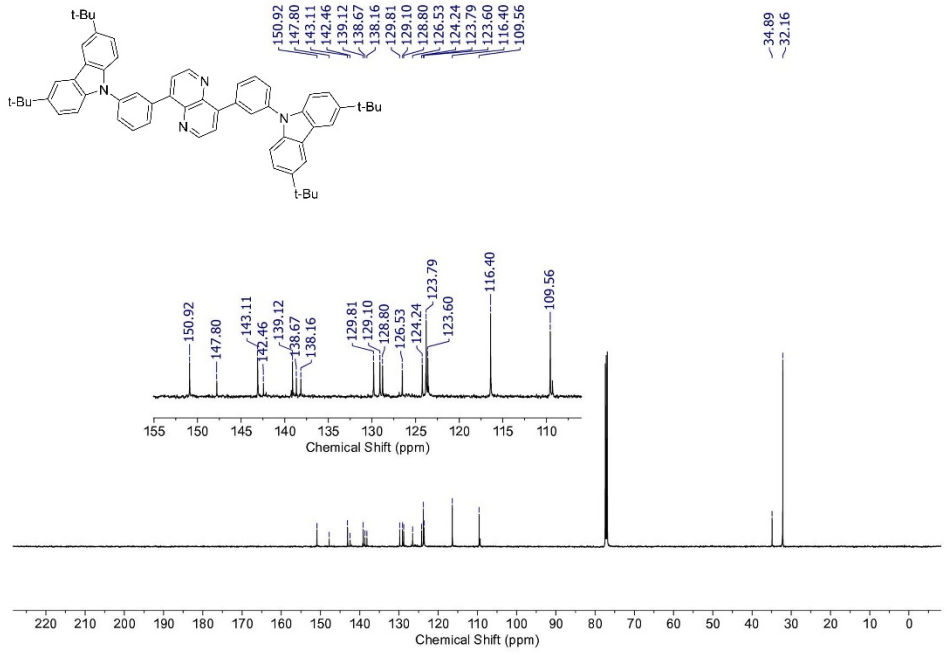


Figure S57. ^{13}C {^{1}H} NMR of **'BuCz'-Naphth** in $CDCl_3$

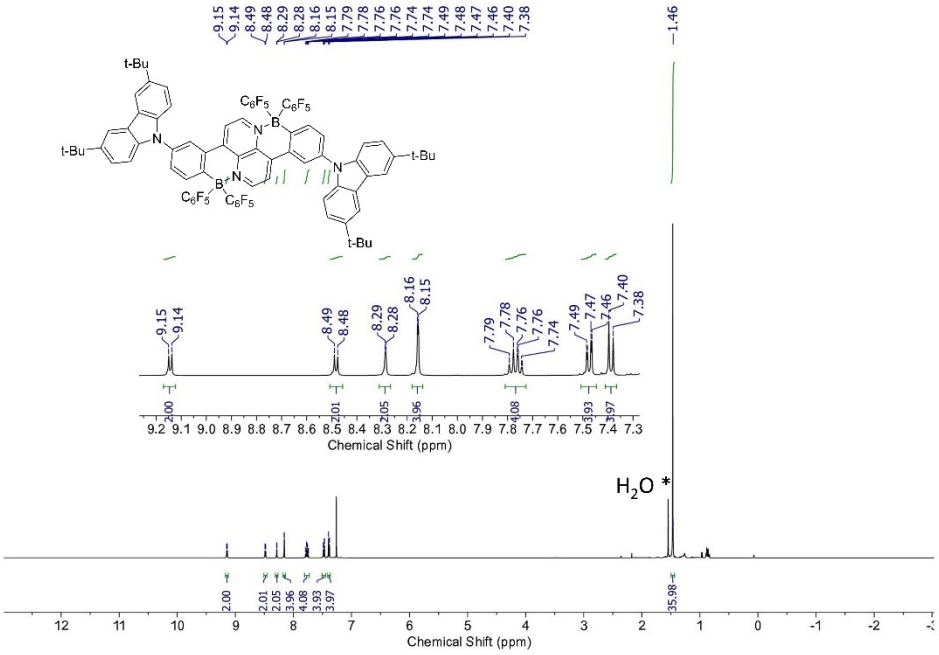


Figure S58. ^{1}H NMR of **2-^{t}Bu-carb** in $CDCl_3$

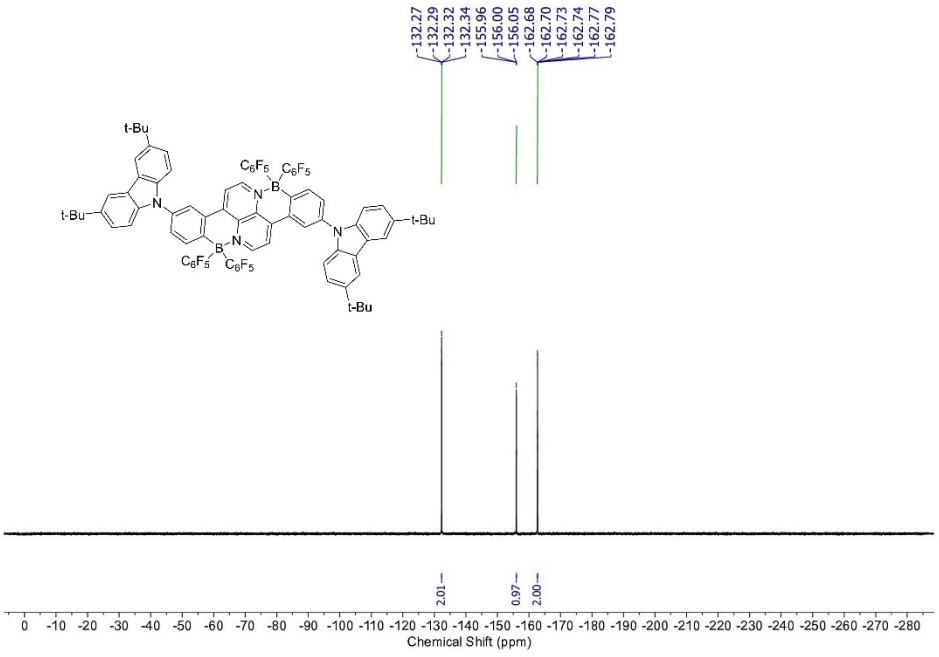


Figure S59. ^{19}F NMR of **2-^{t}Bu-carb** in $CDCl_3$

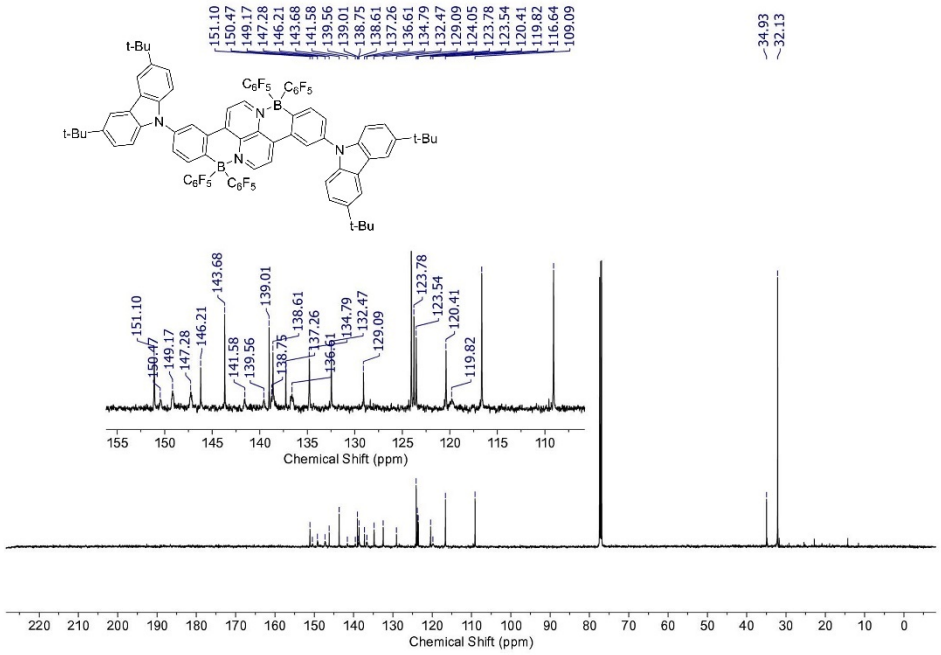


Figure S60. ^{13}C {^{1}H} NMR of **2-*t*Bu-carb** in $CDCl_3$

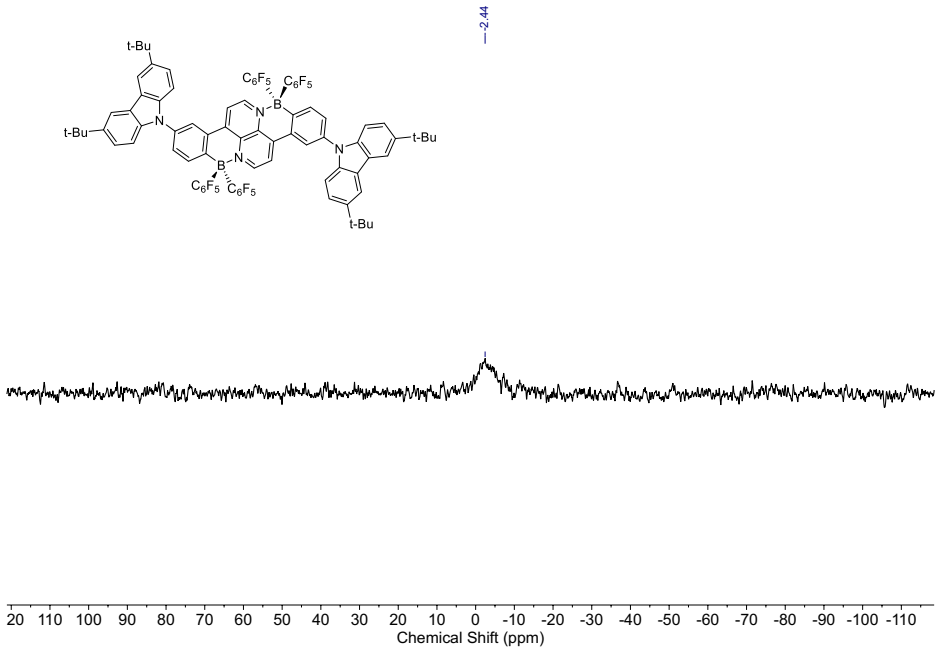


Figure S61. ^{11}B NMR of **2-*t*Bu-carb** in $CDCl_3$

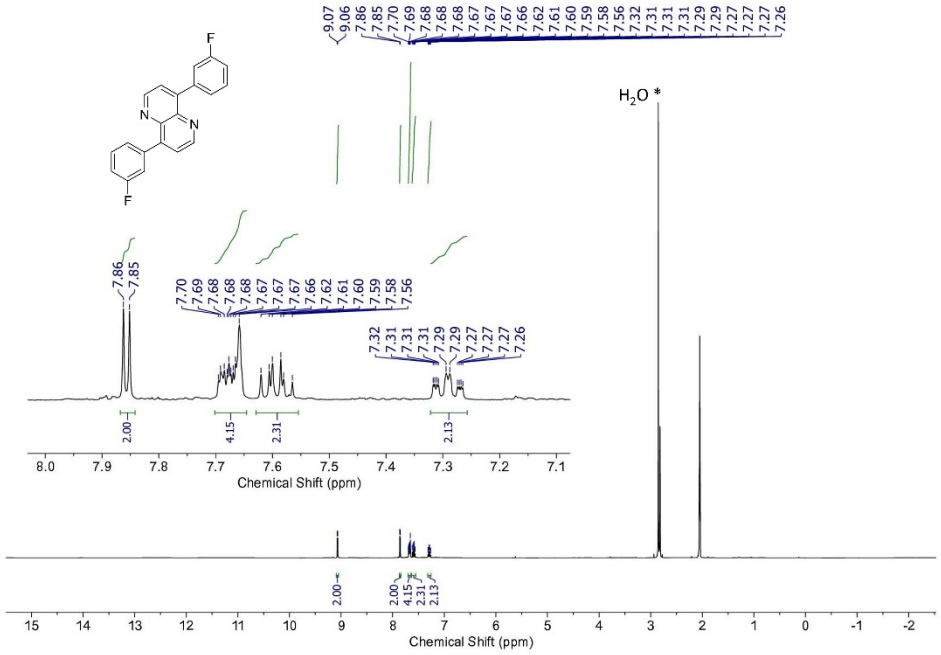


Figure S62. ^{1}H NMR of **F′-Naphth** in acetone-d$_6$

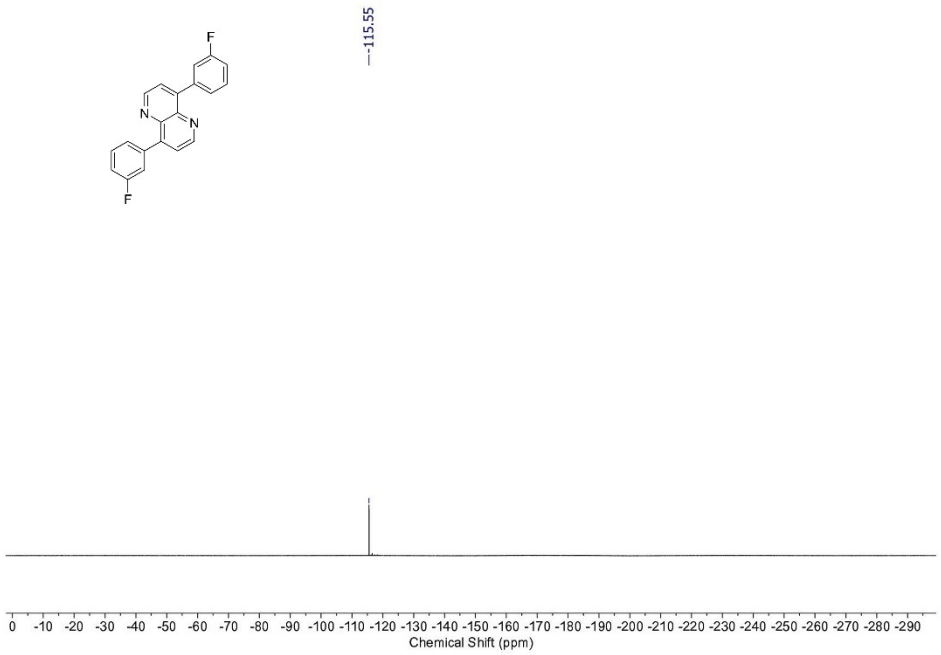


Figure S63. ^{19}F {^{1}H} NMR of **F′-Naphth** in acetone-d$_6$

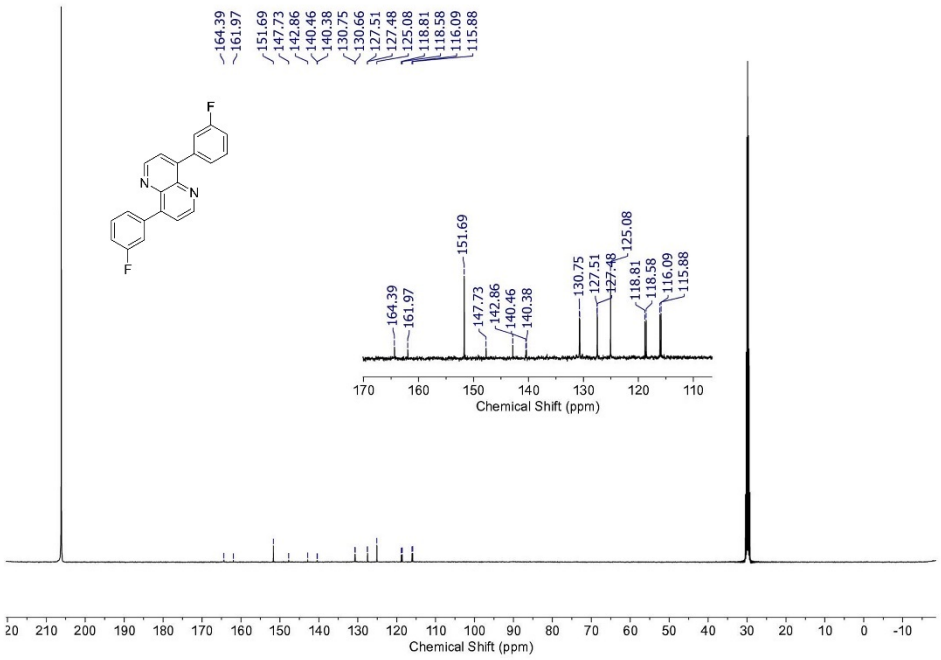


Figure S64. ^{13}C {^{1}H} NMR of **F′-Naphth** in acetone-d_6

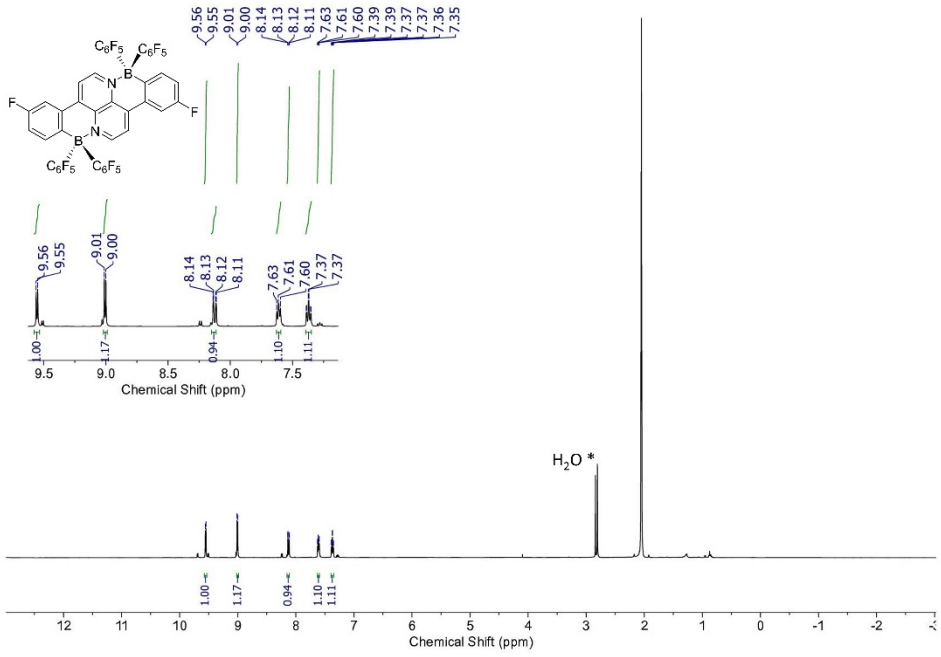


Figure S65. ^{1}H NMR of **2-F** in acetone-d_6

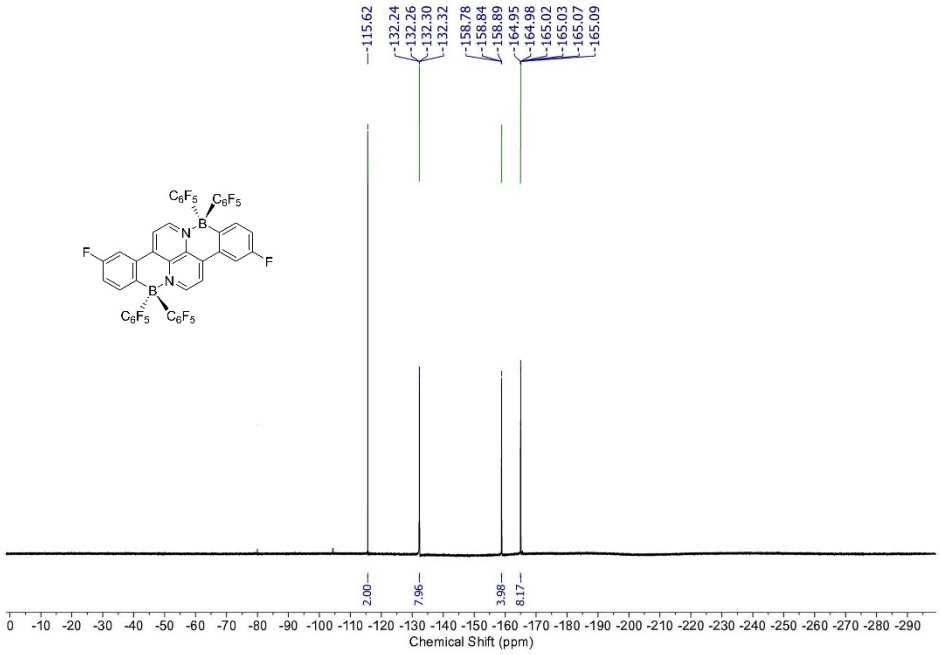


Figure S66. ^{19}F $\{^{1}H\}$ NMR of **2-F** in acetone-d_6

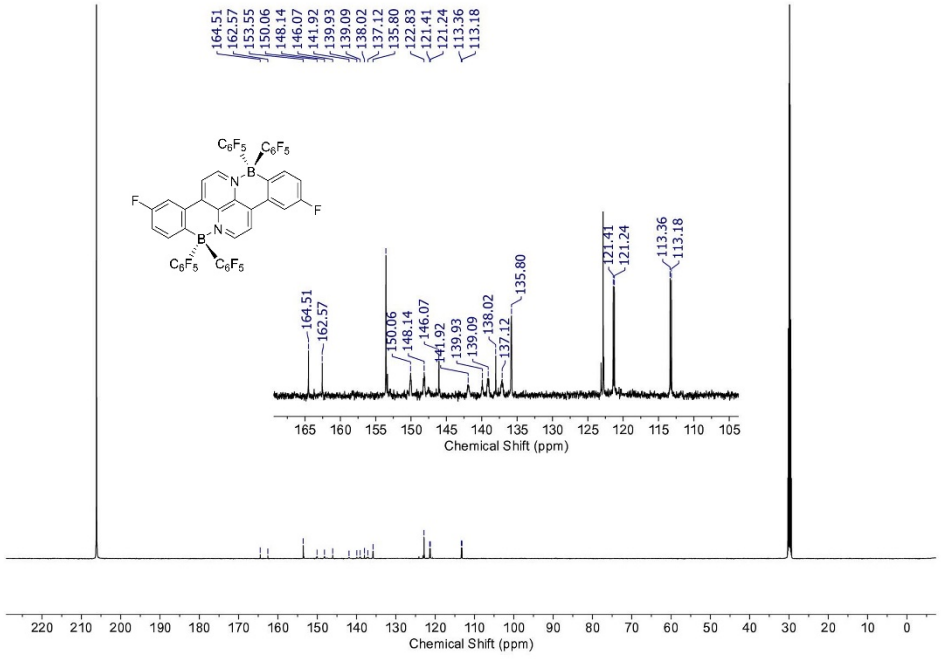


Figure S67. ^{13}C $\{^{1}H\}$ NMR of **2-F** in acetone-d_6

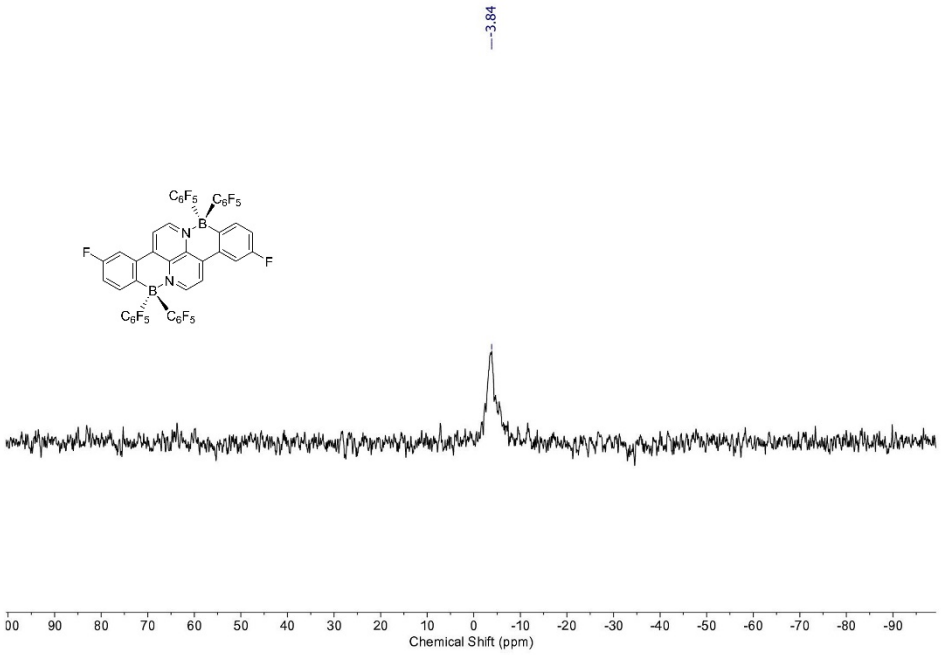


Figure S68. ^{11}B NMR of **2-F** in acetone-d_6

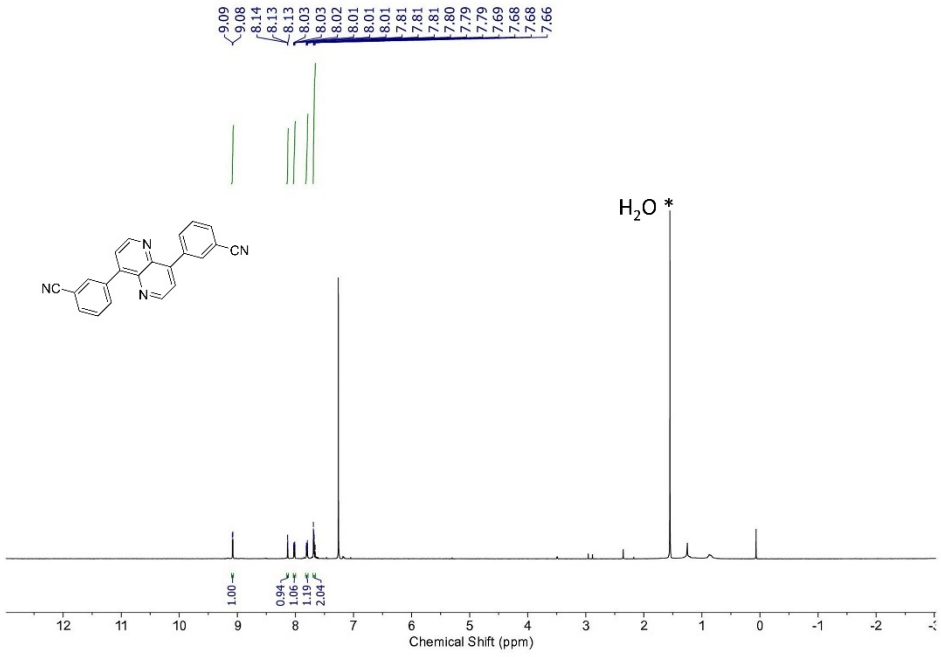


Figure S69. ^{1}H NMR of **CN′-Naphth** in $CDCl_3$

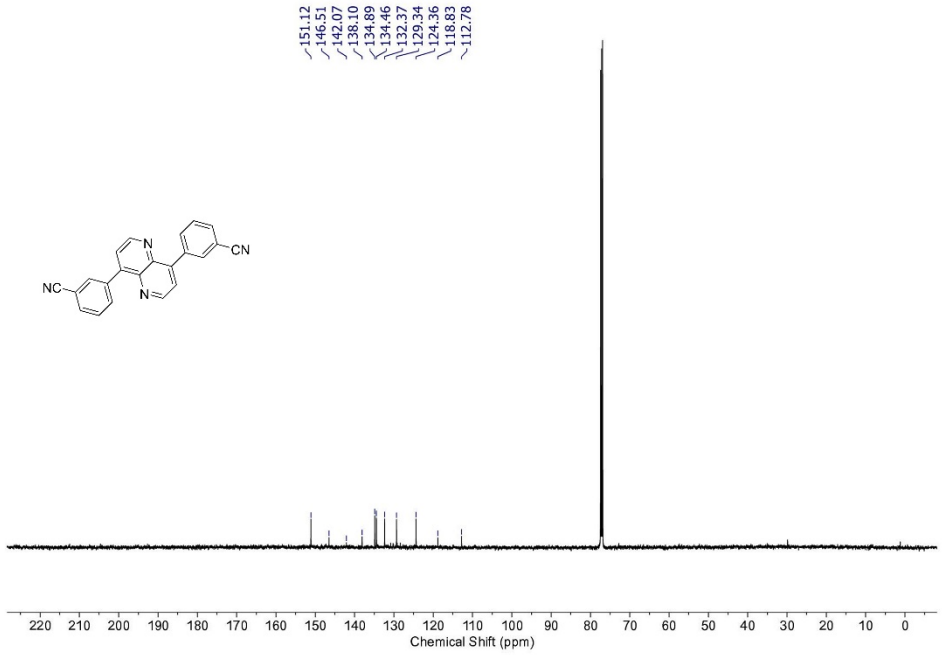


Figure S70. ^{13}C {^{1}H} NMR of **CN′-Naphth** in $CDCl_3$

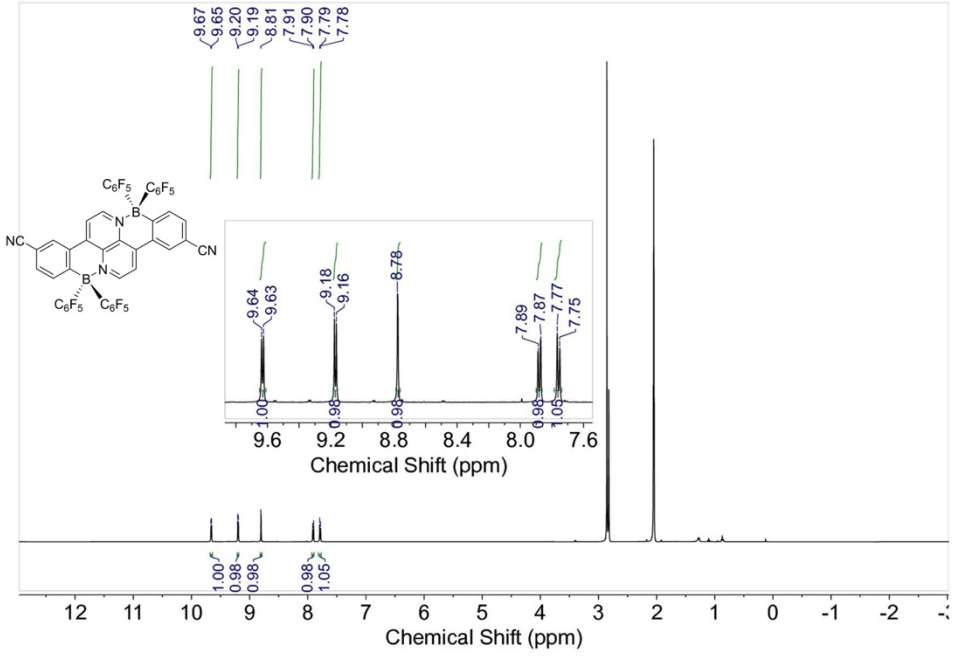


Figure S71. ^{1}H NMR of **2-CN** in acetone-d_6

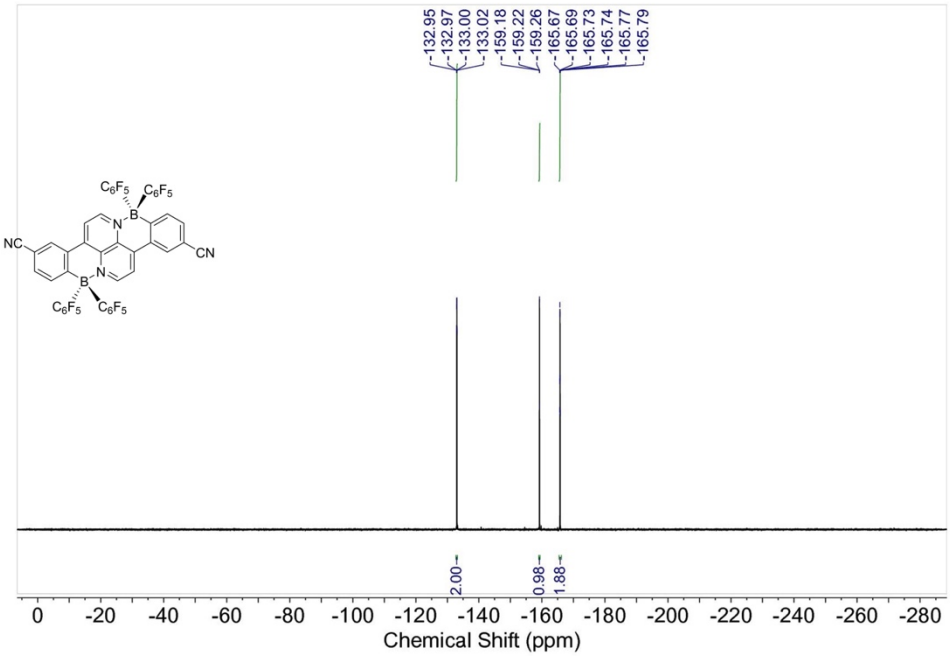


Figure S72. ^{19}F NMR of **2-CN** in acetone-d_6

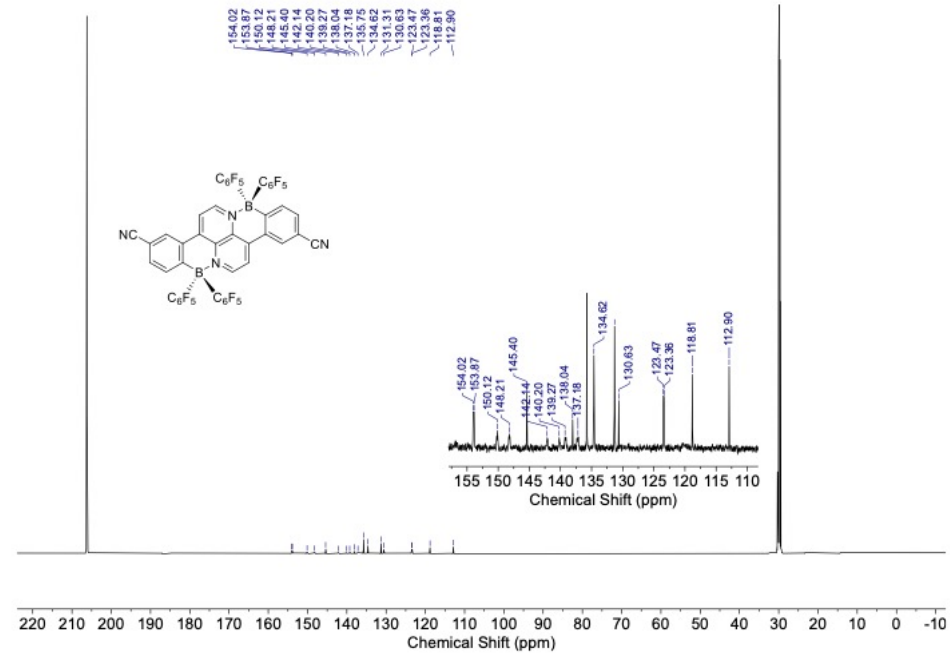


Figure S73. ^{13}C $\{^1H\}$ NMR of **2-CN** in acetone-d_6

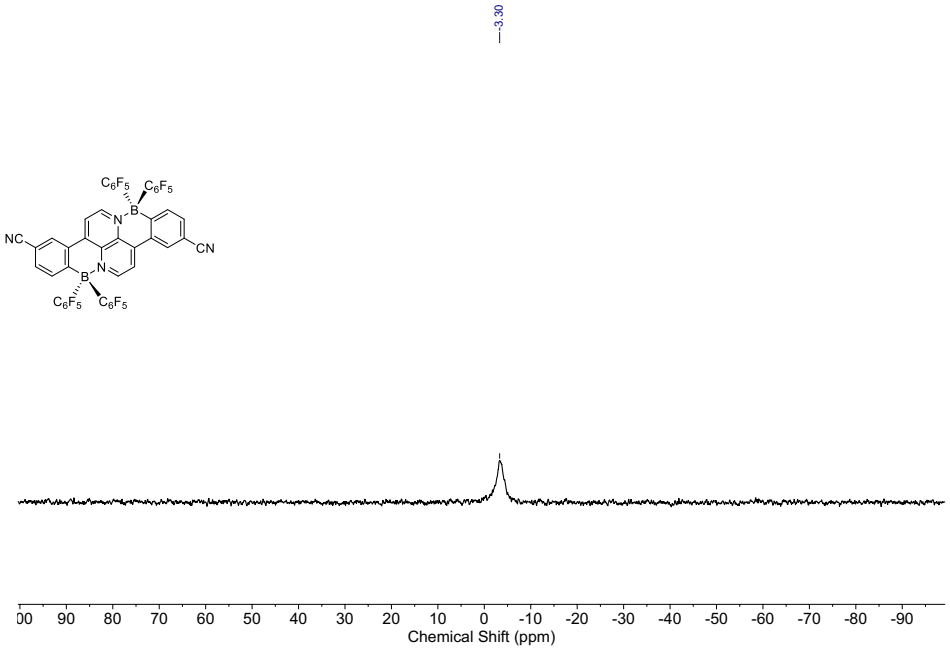


Figure S74. ^{11}B NMR of **2-CN** in acetone-d_6

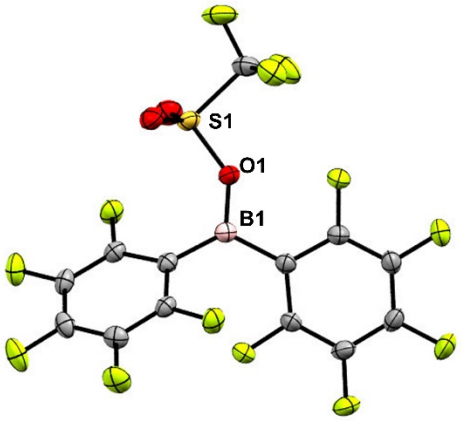


Figure S75. Molecular structure of **$(C_6F_5)_2$BOTf**. Thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) B(1)-O(1) 1.396(2), O(1)-S(1) 1.562(1).

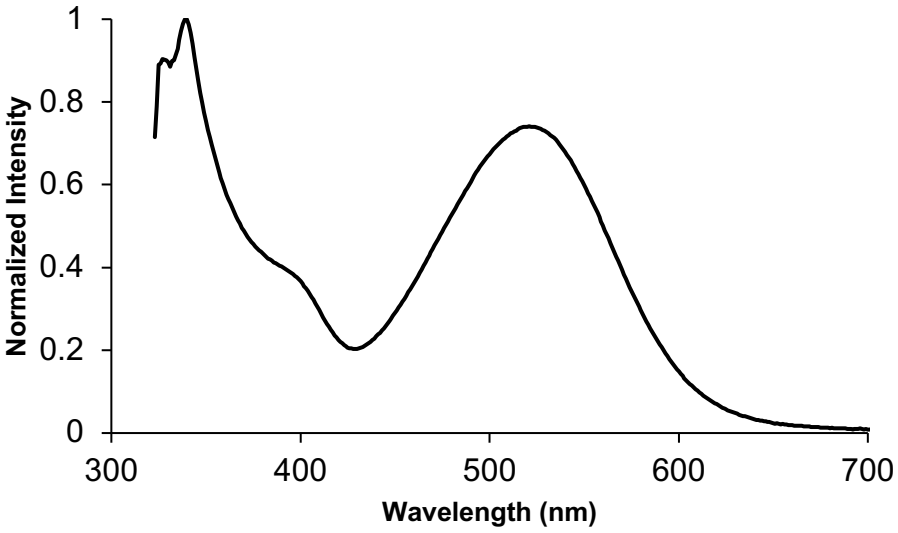


Figure S76. The absorption spectrum of **1-carb** in a 10^{-5} M acetone solution.

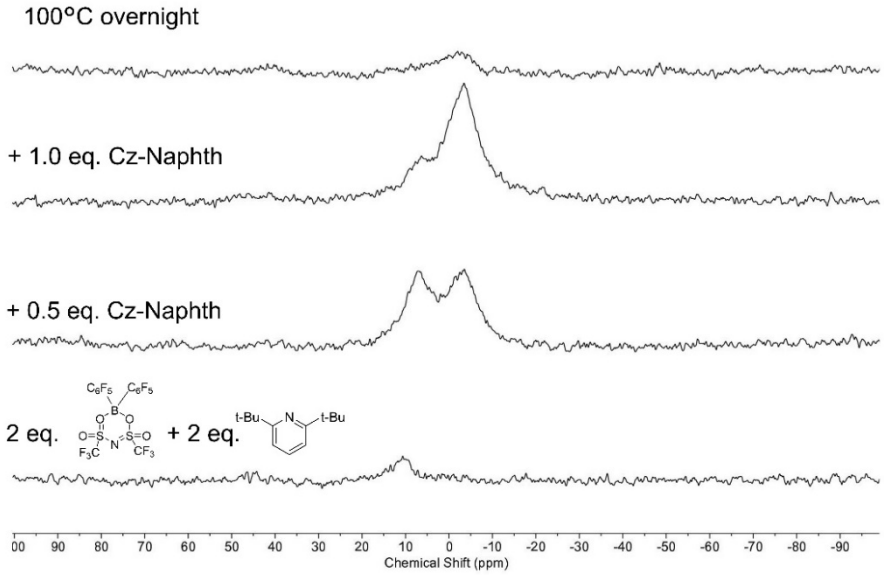


Figure S77. Borylation of Cz-Naphth monitored by ^{11}B NMR spectroscopy in *o*-$Cl_2C_6D_4$.

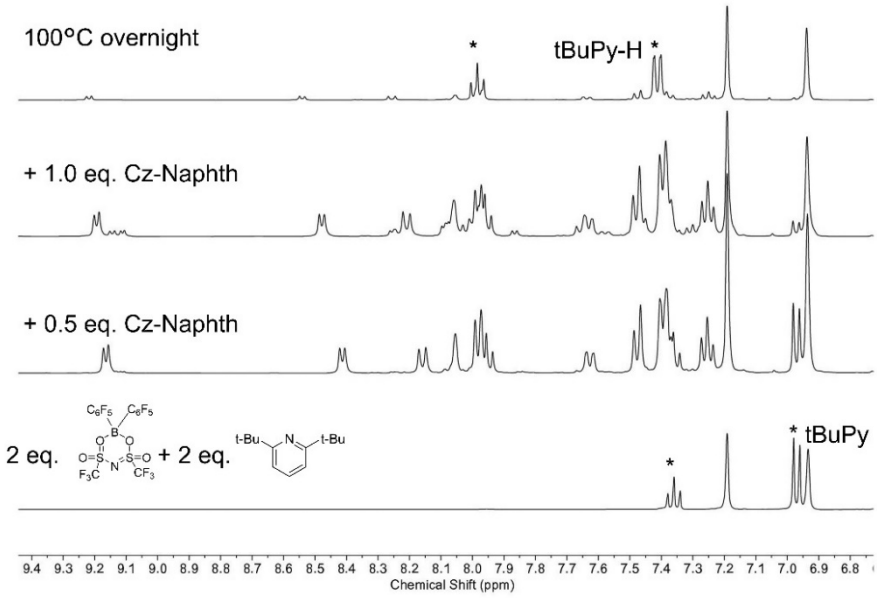


Figure S78. Borylation of Cz-Naphth monitored by ^{1}H NMR spectroscopy in *o*-$Cl_2C_6D_4$

Table S1. Summary of DFT calculated electronic data for compounds in the ***meta*-B series** and ***para*-B series** and their all-carbon analogues.

Compound	HOMO (eV)	LUMO (eV)	E_g^{calc} (eV)
1-hex	-7.078	-3.744	3.334
1-^{t}Bu-carb	-5.945	-3.781	2.164
2-^{t}Bu-carb	-5.957	-3.971	1.986
1-F	-7.325	-3.951	3.374
2-F	-7.335	-4.069	3.266
1-CN	-7.619	-4.439	3.180
2-CN	-7.645	-4.390	3.255
1-hex-C	-2.174	-5.983	3.809
1-^{t}Bu-carb-C	-2.358	-5.710	3.352
2-^{t}Bu-carb-C	-2.393	-5.811	3.418
1-F-C	-2.355	-6.190	3.835
2-F-C	-2.465	-6.318	3.853
1-CN-C	-2.950	-6.662	3.712
2-CN-C	-2.801	-6.656	3.855

Table S2. Crystal data and structure refinement for **$(C_6F_5)_2B$-NTf_2**, **$(C_6F_5)_2B$-OTf** and **1-hex**.

Compound	**$(C_6F_5)_2B$-NTf_2**	**$(C_6F_5)_2B$-OTf**	**1-hex**
Empirical formula	$C_{14}BNO_4F_{16}S_2$	$BC_{13}F_{13}O_3S$	$C_{56}H_{36}B_2N_2F_{20}$
Formula weight	625.08	494.00	1138.49
Temperature/K	296.15	296.15	296.15
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1	Pbcn	$P2_1/c$
a/Å	9.6324(9)	33.0522(15)	16.8525(4)
b/Å	10.7924(10)	11.2332(6)	15.3208(5)
c/Å	10.8665(10)	8.4733(4)	9.5674(3)
α/°	65.7390(10)	90	90
β/°	86.565(2)	90	99.2810(10)
γ/°	69.970(2)	90	90
Volume/Å^3	963.27(16)	3146.0(3)	2437.91(12)
Z	2	8	2
ρ_{calc}g/cm^3	2.155	2.086	1.551
μ/mm^{-1}	0.458	3.450	1.267
F(000)	608.0	1920.0	1152.0
Crystal size/mm^3	0.19 × 0.184 × 0.113	0.567 × 0.104 × 0.092	0.302 × 0.149 × 0.026
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range /°	4.13 to 58.098	5.348 to 133.358	5.314 to 145.334
Index ranges	$-12 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-39 \le h \le 37$, $-11 \le k \le 13$, $-9 \le l \le 10$	$-20 \le h \le 20$, $0 \le k \le 18$, $0 \le l \le 11$
Reflections collected	16696	17899	7899
Independent reflections	5136 [R_{int} = 0.0306, R_{sigma} = 0.0361]	2781 [R_{int} = 0.0375, R_{sigma} = 0.0299]	7899 [R_{int} = 0.0470, R_{sigma} = 0.0449]
Data/restraints/parameters	5136/0/343	2781/0/280	7899/0/362
GooF	1.030	1.050	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0842	R_1 = 0.0324, wR_2 = 0.0861	R_1 = 0.0592, wR_2 = 0.1586
Final R indexes [all data]	R_1 = 0.0598, wR_2 = 0.0929	R_1 = 0.0350, wR_2 = 0.0881	R_1 = 0.0684, wR_2 = 0.1670
Largest diff. peak/hole / e Å^{-3}	0.41/-0.43	0.30/-0.35	0.24/-0.42

Table S3. Crystal data and structure refinement for **1-carb**, **1-^{t}Bu-carb**, and **1-F**.

Compound	**1-carb**	**1-^{t}Bu-carb**	**1-F**
Empirical formula	$C_{68}H_{26}B_2F_{20}N_4$	$C_{96}H_{82}B_2F_{20}N_4O_4$	$C_{50}H_{22}B_2F_{22}N_2O_2$
Formula weight	1300.55	1757.27	1122.31
Temperature/K	296.15	173	296.15
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	10.2642(5)	10.9839(7)	9.0598(6)
b/Å	10.8711(6)	13.2502(10)	10.5792(7)
c/Å	12.8590(7)	17.5105(12)	12.1126(8)
α/°	71.888(4)	71.475(4)	94.889(5)
β/°	78.885(4)	77.749(4)	97.993(5)
γ/°	84.992(4)	70.273(4)	102.729(5)
Volume/Å^3	1337.60(13)	2258.8(3)	1113.31(13)
Z	1	1	1
ρ_{calc}g/cm^3	1.615	1.292	1.674
μ/mm^{-1}	1.261	0.914	1.482
F(000)	652.0	908	560.0
Crystal size/mm^3	0.15 × 0.045 × 0.038	0.283 × 0.124 × 0.043	0.221 × 0.064 × 0.053
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range /°	7.346 to 133.886	5.36 to 133.648	7.424 to 133.152
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-15 \le l \le 15$	$-13 \le h \le 13$, $-14 \le k \le 13$, $-20 \le l \le 20$	$-10 \le h \le 10$, $-12 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	22874	27687	12542
Independent reflections	4575 [R_{int} = 0.1425, R_{sigma} = 0.1071]	7665 [R_{int} = 0.0918, R_{sigma} = 0.1012]	3791 [R_{int} = 0.0627, R_{sigma} = 0.0667]
Data/restraints/parameters	4575/0/424	7665/348/715	3791/0/354
GooF	0.996	1.082	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0610, wR_2 = 0.1440	R_1 = 0.0982, wR_2 = 0.2530	R_1 = 0.0463, wR_2 = 0.1275
Final R indexes [all data]	R_1 = 0.1072, wR_2 = 0.1717	R_1 = 0.1057, wR_2 = 0.2629	R_1 = 0.0614, wR_2 = 0.1380
Largest diff. peak/hole / e Å^{-3}	0.26/-0.36	0.73/-0.67	0.27/-0.34

Table S4. Crystal data and structure refinement for **1-CN**, **2-*t*Bu-carb**, and **2-F**.

Compound	1-CN	2-*t*Bu-carb	2-F
Empirical formula	$C_{54}H_{22}B_2F_{20}N_8$	$C_{102}H_{87.47}B_2F_{20}N_4O_6$	$C_{46}H_{12}B_2Cl_6F_{22}N_2$
Formula weight	1184.447	1866.84	1244.90
Temperature/K	173	296.15	296.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P21/n	P21/c	P21/n
a/Å	9.4453(13)	13.2106(9)	14.8212(13)
b/Å	20.727(3)	10.7119(7)	10.0171(8)
c/Å	12.4957(19)	32.530(2)	17.0876(12)
α/°	90	90	90
β/°	100.146(8)	95.306(4)	115.304(6)
γ/°	90	90	90
Volume/Å^3	2408.1(6)	4583.6(5)	2293.5(3)
Z	2	2	2
ρ_{calc}g/cm^3	1.634	1.353	1.803
μ/mm^{-1}	1.353	0.951	4.619
F(000)	1189.7	1931	1224.0
Crystal size/mm^3	0.198 × 0.147 × 0.126	0.535 × 0.216 × 0.206	0.290 × 0.072 × 0.037
Radiation	Cu Kα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range /°	8.36 to 144.94	6.72 to 145.406	6.632 to 133.182
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 23, -15 ≤ l ≤ 15	-16 ≤ h ≤ 15, -12 ≤ k ≤ 13, -39 ≤ l ≤ 40	-17 ≤ h ≤ 17, -11 ≤ k ≤ 10, -20 ≤ l ≤ 16
Reflections collected	17519	26188	16361
Independent reflections	4682 [Rint = 0.0505, Rsigma = 0.0455]	8811 [R_{int} = 0.0392, R_{sigma} = 0.0429]	4017 [R_{int} = 0.0587, R_{sigma} = 0.0519]
Data/restraints/parameters	4682/78/439	8811/116/682	4017/36/380
GooF	1.062	1.11	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1658	R_1 = 0.0681, wR_2 = 0.2032	R_1 = 0.0668, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.0661, wR_2 = 0.1787	R_1 = 0.0842, wR_2 = 0.2417	R_1 = 0.0821, wR_2 = 0.1985
Largest diff. peak/hole / e Å^{-3}	0.39/-0.53	0.47/-0.44	1.61/-0.51

Table S5. Crystal data and structure refinement for **2-CN**.

Compound	**2-CN**
Empirical formula	$C_{92}H_{20}B_4F_{40}N_8$
Formula weight	2040.40
Temperature/K	273.15
Crystal system	orthorhombic
Space group	$C222_1$
a/Å	24.0995(17)
b/Å	31.488(3)
c/Å	12.9587(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9833.8(12)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	1.210
F(000)	4032.0
Crystal size/mm^3	0.182 × 0.078 × 0.058
Radiation	CuKα (λ = 1.54178)
2Θ range /°	8.24 to 146.46
Index ranges	$-28 \le h \le 29$, $-38 \le k \le 37$, $-15 \le l \le 14$
Reflections collected	26063
Independent reflections	9346 [R_{int} = 0.0885, R_{sigma} = 0.1025]
Data/restraints/parameters	9346/1523/850
GooF	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0834, wR_2 = 0.2053
Final R indexes [all data]	R_1 = 0.1374, wR_2 = 0.2420
Largest diff. peak/hole / e Å^{-3}	0.54/-0.49

Table S6. Cartesian Coordinates for **1-hex** (PBE0/def2-TZVP).

F	-5.46744	3.14211	-2.96147	H	-6.44995	-0.26899	4.14436
F	-4.91934	5.27404	-1.37344	H	-5.69232	-1.29666	5.37031
F	-3.5555	4.89849	0.94206	H	-5.5679	0.45274	5.49523
F	-2.76272	2.48914	1.66182	C	-5.57554	-0.38013	4.78589
F	-4.70014	0.71504	-2.27159	H	5.5679	0.45264	-5.49528
F	-6.52718	-4.6048	-1.2444	H	5.69234	-1.29676	-5.3703
F	-7.67713	-2.19126	-0.77857	H	6.44996	-0.26904	-4.14439
F	-3.83476	-4.86864	-1.00197	C	5.57555	-0.38021	-4.78592
F	-2.33526	-2.80887	-0.31527	C	-3.15245	-0.20694	1.84901
F	-6.20744	-0.10356	-0.10645	C	-4.31498	-0.20397	2.61875
F	3.83483	-4.86861	1.00198	C	-4.31075	-0.40838	3.9892
F	6.52723	-4.60473	1.24449	C	-3.0832	-0.65407	4.61419
F	7.67715	-2.19116	0.7787	C	-1.91902	-0.64877	3.88753
F	6.20745	-0.1035	0.10654	C	3.0832	-0.65416	-4.61419
F	2.3353	-2.80887	0.31523	C	4.31076	-0.40844	-3.98922
F	3.55547	4.8985	-0.94212	C	4.31499	-0.20401	-2.61877
F	4.91925	5.27408	1.37341	C	1.91903	-0.64885	-3.88753
F	2.76274	2.48913	-1.66189	C	3.15246	-0.20696	-1.84902
F	5.46733	3.14217	2.96147	C	1.93039	-0.40492	-2.50235
F	4.70008	0.71508	2.27158	C	-1.93038	-0.40488	2.50234
N	-1.78325	-0.20284	-0.3843	C	-1.72008	-0.21627	-1.70682
N	1.78326	-0.20285	0.38428	C	-0.54049	-0.28824	-2.40823
C	-4.82318	2.96928	-1.81501	C	0.68431	-0.31891	-1.76224
C	-4.54465	4.0591	-1.00999	C	-0.62796	-0.24841	0.33543
C	-3.85377	3.86139	0.17105	C	0.62797	-0.24842	-0.33544
C	-3.46563	2.57983	0.53001	C	1.72009	-0.21629	1.7068
C	-4.41811	1.70758	-1.4143	C	-0.6843	-0.31889	1.76223
C	-5.78007	-3.56111	-0.92322	C	0.54051	-0.28824	2.40822
C	-4.40899	-3.68922	-0.80382	C	3.75037	1.4444	0.22297
C	-6.36104	-2.32778	-0.68724	C	4.17565	-1.31246	0.25017
C	-5.56101	-1.24849	-0.35293	C	-4.17562	-1.31248	-0.25017
C	-3.6487	-2.58261	-0.46018	H	0.60122	-0.29701	3.48545
C	5.78011	-3.56105	0.92329	B	3.25257	-0.05031	-0.25926

C	6.36107	-2.32771	0.68733	B	-3.25256	-0.05032	0.25924
C	4.40904	-3.68919	0.80384	H	-5.26825	-0.0333	2.12923
C	3.64874	-2.58259	0.46017	H	-3.05092	-0.85137	5.68044
C	5.56103	-1.24843	0.35299	H	-0.99298	-0.85907	4.40686
C	3.85373	3.8614	-0.1711	H	3.05093	-0.85149	-5.68044
C	4.54459	4.05913	1.00995	H	0.99299	-0.85916	-4.40685
C	4.8231	2.96932	1.81499	H	5.26826	-0.03332	-2.12926
C	3.46562	2.57984	-0.53006	H	-0.6012	-0.297	-3.48547
C	4.41806	1.70761	1.41428	H	-2.66837	-0.17707	-2.22546
C	-3.75038	1.44438	-0.223	H	2.66839	-0.17709	2.22544

Table S7. Cartesian Coordinates for **1-^{t}Bu-carb** (PBE0/def2TZVP).

F	-3.14227	6.2539	-0.85518	C	-9.95679	1.83487	1.59923
F	-3.55989	6.31157	1.82613	C	-8.59365	2.16269	1.69627
F	-3.6198	3.98252	3.21789	H	-6.54524	1.58275	1.45503
F	-3.27661	1.67361	1.99395	H	-11.3258	0.26329	1.07024
F	-2.80804	3.96409	-2.11839	H	-8.3102	3.14154	2.06576
F	-4.81119	0.68098	-6.34598	C	-7.98997	-2.10171	0.1487
F	-6.07343	2.34519	-4.6137	C	-9.32338	-1.69874	0.31835
F	-2.64975	-0.73138	-5.50415	C	-7.69115	-3.36222	-0.35296
F	-1.77261	-0.50369	-3.02576	C	-8.74396	-4.21058	-0.64001
F	-5.21636	2.60906	-2.12947	C	-10.3621	-2.57658	0.01961
F	2.77444	-5.12601	-2.05928	C	-10.0896	-3.85048	-0.45634
F	4.93857	-6.25315	-0.86508	H	-6.67181	-3.67822	-0.53465
F	6.1369	-4.97283	1.20353	H	-8.50819	-5.19428	-1.0298
F	5.215	-2.65464	2.07241	H	-11.384	-2.24654	0.15708
F	1.83874	-2.80131	-1.23342	C	7.97935	-0.36267	-0.79091
F	3.47477	2.18265	4.6758	C	7.96301	1.89142	-0.89902
F	3.41562	0.26407	6.59376	C	7.62391	3.23848	-0.8983
F	3.19928	1.5501	2.13022	C	9.30844	1.49407	-0.87386
F	3.06532	-2.33022	5.87751	C	8.6505	4.16397	-0.91076
F	2.79517	-3.00371	3.34147	C	10.00805	3.80185	-0.91395
N	-1.31202	0.95285	-0.84275	C	10.31998	2.45069	-0.88634
N	1.31344	-1.05064	0.70905	H	11.35183	2.12353	-0.86626
C	-3.19734	5.12206	-0.16642	H	6.59319	3.56812	-0.87095
C	-3.40837	5.15682	1.20015	H	8.38342	5.21459	-0.91188
C	-3.44198	3.96716	1.90367	C	7.65999	-1.71428	-0.7921
C	-3.2753	2.76826	1.22775	C	9.31862	0.05393	-0.80899
C	-3.04016	3.90067	-0.79911	C	8.69905	-2.62488	-0.77096

C	-4.36468	0.81876	-5.1084	C	10.05132	-2.2432	-0.75915
C	-3.26158	0.10616	-4.67701	C	10.34412	-0.888	-0.7884
C	-5.00352	1.66765	-4.22196	H	8.44629	-3.67897	-0.76151
C	-4.51901	1.79717	-2.93153	H	6.63428	-2.05859	-0.8197
C	-2.81567	0.26342	-3.3744	H	11.37137	-0.54619	-0.80125
C	4.45848	-5.10047	-0.42757	C	11.13182	-3.32064	-0.72154
C	5.06377	-4.44475	0.62989	C	10.96803	-4.16122	0.55044
C	3.3552	-4.52497	-1.02949	H	11.07289	-3.54057	1.44369
C	2.87758	-3.31218	-0.55824	H	11.73077	-4.94431	0.58727
C	4.54778	-3.23802	1.07213	H	9.99035	-4.64532	0.5937
C	3.33299	0.90856	4.33688	C	10.99485	-4.22878	-1.94935
C	3.29853	-0.06448	5.31846	H	10.02134	-4.72189	-1.98291
C	3.12163	-1.38557	4.94833	H	11.76205	-5.00805	-1.93048
C	3.20253	0.54193	3.00642	H	11.11254	-3.65648	-2.87284
C	2.9983	-1.70454	3.60693	C	12.53792	-2.72731	-0.72311
N	-7.14757	-1.04247	0.48177	H	12.71065	-2.0897	0.14768
N	7.15145	0.75892	-0.84729	H	12.73034	-2.13987	-1.62463
C	-3.65366	0.0166	-0.13503	H	13.27425	-3.53399	-0.69215
C	-5.04301	-0.00723	-0.11069	C	11.07422	4.89419	-0.93494
C	-5.75342	-1.06099	0.45104	C	10.90769	5.74589	-2.19906
C	-5.05094	-2.14777	0.98404	H	11.02326	5.13565	-3.0982
C	-3.67957	-2.13472	0.98011	H	11.66204	6.53749	-2.22457
C	5.05639	1.55583	-1.76394	H	9.92523	6.22058	-2.24102
C	5.75755	0.75031	-0.85841	C	10.91821	5.78788	0.3012
C	5.04426	-0.07289	0.00445	H	9.93734	6.26632	0.3351
C	3.68542	1.54414	-1.7616	H	11.67434	6.57812	0.29467
C	3.65513	-0.10926	0.00968	H	11.03903	5.20774	1.21926
C	2.95995	0.73378	-0.86948	C	12.48824	4.31989	-0.93124
C	-2.95679	-1.05351	0.4452	H	12.67391	3.69189	-1.80634
C	-0.56005	1.81332	-1.51421	H	12.68388	3.7275	-0.03382
C	0.81149	1.76064	-1.54068	H	13.21386	5.13657	-0.95133
C	1.51305	0.79743	-0.83179	C	-11.1866	-4.85674	-0.79487
C	-0.70974	-0.03932	-0.13034	C	-12.5826	-4.29659	-0.53637
C	0.7115	-0.10727	-0.06675	H	-12.7244	-4.02808	0.51359
C	0.56216	-1.93291	1.35244	H	-13.3312	-5.05174	-0.78788
C	-1.50988	-1.02477	0.52876	H	-12.7863	-3.41435	-1.14853
C	-0.80806	-1.95978	1.27434	C	-11.0921	-5.23977	-2.27654
C	3.05878	-0.77363	2.57548	H	-11.2221	-4.36248	-2.91487
C	3.42404	-2.6287	0.52326	H	-11.8704	-5.9651	-2.53041
C	-3.3955	1.13068	-2.45431	H	-10.1268	-5.68905	-2.51873
C	-3.09623	2.67218	-0.14918	C	-11.0094	-6.1139	0.06488
B	2.89805	-1.13738	0.97758	H	-11.0816	-5.87222	1.12817
B	-2.89976	1.21242	-0.88858	H	-10.0405	-6.58776	-0.10543
H	-5.60106	0.80443	-0.56156	H	-11.7857	-6.8472	-0.1719

H	-5.59009	-2.97466	1.42756	C	-11.0053	2.86845	2.00256
H	-3.1691	-2.98833	1.40618	C	-12.4279	2.34117	1.83701
H	5.59893	2.15437	-2.4842	H	-12.6437	2.07373	0.79943
H	3.17662	2.15234	-2.49809	H	-13.1405	3.11469	2.13321
H	5.59719	-0.67965	0.71095	H	-12.6125	1.46548	2.46459
H	1.32657	2.51274	-2.11788	C	-10.8066	3.2543	3.47313
H	-1.09255	2.57657	-2.06482	H	-10.9174	2.3829	4.12318
H	1.09443	-2.65894	1.95175	H	-11.5488	3.99991	3.77221
H	-1.32207	-2.72489	1.83507	H	-9.8171	3.68023	3.65085
C	-7.94248	0.03743	0.86569	C	-10.8534	4.11771	1.1266
C	-9.29257	-0.33388	0.78114	H	-10.9985	3.87397	0.07133
C	-7.58153	1.2906	1.34347	H	-9.86476	4.56878	1.2322
C	-10.2896	0.56826	1.14347	H	-11.5954	4.87022	1.40856

Table S8. Cartesian Coordinates for **1-F** (PBE0/def2TZVP).

F	-5.48771	3.15453	-2.91046	C	-5.78696	-3.5535	-0.90387
F	-4.92035	5.27969	-1.32099	C	-4.41486	-3.68344	-0.79694
F	-3.53631	4.8941	0.98087	C	-6.36608	-2.32211	-0.65221
F	-2.7433	2.47916	1.68607	C	-5.56264	-1.24632	-0.315
F	-4.71935	0.72296	-2.23516	C	-3.65121	-2.58014	-0.45046
F	-6.53646	-4.59364	-1.22779	C	5.78833	-3.55214	0.90464
F	-7.68182	-2.18439	-0.7314	C	6.36698	-2.32055	0.65295
F	-3.84274	-4.86086	-1.00961	C	4.41629	-3.68266	0.79751
F	-2.33619	-2.80733	-0.31818	C	3.65224	-2.57971	0.45082
F	-6.20429	-0.103	-0.05061	C	5.56315	-1.24512	0.31551
F	3.84464	-4.8603	1.01022	C	3.84335	3.86116	-0.21079
F	6.5382	-4.59195	1.22877	C	4.54415	4.06429	0.96369
F	7.68265	-2.18229	0.73231	C	4.83279	2.97789	1.77016
F	6.20436	-0.10156	0.05105	C	3.4559	2.57732	-0.56147
F	2.33734	-2.80743	0.31836	C	4.42773	1.71367	1.37763
F	3.53503	4.89413	-0.98228	F	-5.35959	-0.41106	4.70883
F	4.91833	5.28081	1.31984	F	5.35959	-0.41252	-4.70875
F	2.74301	2.47874	-1.68705	C	-3.14072	-0.20996	1.86869
F	5.48599	3.15627	2.91002	C	-4.30185	-0.20829	2.63669
F	4.71863	0.72425	2.23517	C	-4.23636	-0.4225	3.99449

N	-1.78546	-0.2023	-0.37183	C	-3.03793	-0.67111	4.64711
N	1.78557	-0.20257	0.37194	C	-1.88506	-0.66032	3.89987
C	-4.83419	2.97668	-1.77069	C	3.03795	-0.67265	-4.64684
C	-4.54571	4.06339	-0.96459	C	4.23638	-0.4237	-3.99435
C	-3.84452	3.86081	0.20975	C	4.3019	-0.20896	-2.63664
C	-3.45658	2.57719	0.56068	C	1.88508	-0.66156	-3.89958
C	-4.42863	1.71269	-1.37792	C	3.14079	-0.21034	-1.86862
H	-0.9537	-0.87143	4.40828	C	1.91291	-0.41136	-2.51626
H	3.02957	-0.87031	-5.71094	C	-1.91284	-0.41076	2.51643
H	0.9537	-0.87299	-4.40783	C	-1.73179	-0.21186	-1.69455
H	5.27252	-0.04059	-2.1855	C	-0.55704	-0.28469	-2.40423
H	-0.6272	-0.28904	-3.48092	C	0.6719	-0.32069	-1.76693
H	-2.68352	-0.16891	-2.20671	C	-0.62564	-0.24962	0.33988
H	2.68367	-0.16952	2.2068	C	0.62574	-0.24972	-0.33974
H	0.62738	-0.28951	3.48102	C	1.73193	-0.2123	1.69466
C	-3.75081	1.44499	-0.19332	C	-0.67181	-0.32056	1.76707
B	3.25125	-0.05051	-0.27865	C	0.55717	-0.28497	2.40434
B	-3.25119	-0.05063	0.27868	C	3.75026	1.44543	0.19295
H	-5.27244	-0.04009	2.18547	C	4.17685	-1.31116	0.22647
H	-3.02956	-0.86825	5.71131	C	-4.17629	-1.31178	-0.22615

Table S9. Cartesian Coordinates for **1-CN** (PBE0/def2TZVP).

F	4.555989	0.798769	2.444692	C	4.43928	-0.51299	-3.80293
F	5.235233	3.258866	3.113015	C	3.250005	-0.78736	-4.48584
F	2.784913	2.435834	-1.62348	C	-2.06392	-0.76091	3.796058
F	4.723615	5.339298	1.448136	C	-3.25004	-0.78519	4.486248
F	3.487562	4.879852	-0.92323	C	-4.43931	-0.51148	3.803067
F	2.373855	-2.81824	0.432519	C	-4.41547	-0.26259	2.437436
F	6.189664	-0.03109	0.371275	C	-3.2213	-0.24916	1.720639
F	7.66884	-2.07161	1.167497	C	5.678903	-0.51271	-4.51023
F	6.548541	-4.50034	1.619941	C	-5.67899	-0.51098	4.510259
F	3.880588	-4.83218	1.239069	C	4.298115	1.76588	1.551952
F	-6.18969	-0.03293	-0.37117	C	3.427893	2.571622	-0.45957

F	-2.37247	-2.81819	-0.43155	C	4.65514	3.045317	1.94109
F	-3.87817	-4.83312	-1.23745	C	4.394876	4.109709	1.095932
F	-7.66781	-2.07443	-1.16674	C	3.76939	3.869677	-0.11378
F	-6.54631	-4.50275	-1.61841	C	5.560477	-1.18551	0.611631
F	-4.55657	0.797006	-2.44484	C	3.673963	-2.5626	0.644643
F	-2.78547	2.436485	1.622348	C	4.438409	-3.64475	1.049293
F	-3.48941	4.879886	0.921296	C	6.365144	-2.23985	1.009412
F	-4.72616	5.337835	-1.44998	C	5.798441	-3.48161	1.238964
F	-5.23712	3.256514	-3.11397	C	-3.6727	-2.56324	-0.64377
N	-6.67619	-0.51213	5.086314	C	-5.5599	-1.18709	-0.61118
N	6.67606	-0.51404	-5.08636	C	-6.36403	-2.24197	-1.00862
N	1.765187	-0.22889	0.4563	C	-4.43659	-3.64591	-1.04807
N	-1.76502	-0.22868	-0.45616	C	-5.79671	-3.48352	-1.23778
C	-3.69841	1.460525	-0.3351	C	-4.29906	1.764575	-1.55247
C	-4.18311	-1.28533	-0.43993	C	-3.42881	2.571497	0.458557
C	4.18374	-1.28451	0.440386	C	-3.77097	3.869257	0.112315
C	3.697797	1.461098	0.334594	C	-4.39681	4.108529	-1.09736
C	0.441743	-0.31885	2.427557	C	-4.65675	3.043691	-1.94206
C	-0.75113	-0.36206	1.730953	B	-3.26005	-0.05392	0.130921
C	1.651003	-0.23556	1.773677	B	3.26017	-0.05371	-0.1309
C	0.641355	-0.28418	-0.30956	H	0.458574	-0.3247	3.506589
C	-0.64122	-0.28404	0.309754	H	2.577555	-0.18167	2.329322
C	0.751266	-0.3624	-1.73073	H	-2.57734	-0.18127	-2.32921
C	-0.44155	-0.31881	-2.4274	H	-0.4583	-0.32457	-3.50644
C	-1.65081	-0.23529	-1.77354	H	5.353558	-0.07552	-1.92875
C	-2.03047	-0.46909	2.422213	H	1.157044	-0.99562	-4.33747
C	2.030573	-0.46999	-2.42194	H	3.272348	-1.01652	-5.54342
C	3.221433	-0.24963	-1.72054	H	-1.15708	-0.99323	4.338247
C	2.06393	-0.76275	-3.79558	H	-3.27241	-1.0136	5.543989
C	4.415537	-0.26329	-2.43744	H	-5.35347	-0.07525	1.928539

Table S10. Cartesian Coordinates for **2-^{t}Bu-carb** (PBE0/def2TZVP).

F	-0.48348	-6.05357	3.87642	H	-11.0735	1.51318	-6.35732
F	0.77583	-4.8473	5.95597	C	-7.46798	-2.6253	1.69037
F	2.358	-2.69258	5.49049	C	-6.71788	-1.55517	1.24071
F	2.68382	-1.76469	3.04493	C	-9.46631	-4.17973	1.69339
F	-0.17494	-5.1622	1.41354	C	-8.71127	-2.97574	1.1351
F	1.48348	-6.62509	-3.86699	H	-11.6556	-0.61939	-4.26422
F	2.37934	-7.40423	-1.42726	C	-7.22533	-0.80269	0.18893
F	0.6264	-4.07252	-4.22144	C	-10.7922	-4.41278	0.97423
F	0.66167	-2.3493	-2.2211	C	-9.20411	-2.19682	0.09924
F	2.41451	-5.71186	0.6008	H	-7.07284	-3.21067	2.51292
F	-0.62683	4.07208	-4.22186	C	-8.4734	-1.11011	-0.37683
F	-1.48398	6.62468	-3.86775	N	-6.7074	0.32508	-0.43562
F	-2.37974	7.40415	-1.42808	H	-5.77481	-1.30764	1.71324
F	-2.41473	5.71208	0.60023	C	-7.61572	0.74215	-1.40093
F	-0.66192	2.34916	-2.22127	C	-8.7227	-0.12173	-1.39531
F	-2.35769	2.69334	5.49039	H	-11.2926	-5.28366	1.40443
F	-0.77569	4.84827	5.95551	C	-7.53523	1.78907	-2.31018
F	-2.68361	1.76515	3.04494	C	-9.76861	0.08216	-2.29305
F	0.48337	6.05441	3.87573	C	-8.58876	1.96339	-3.18712
F	0.17473	5.16273	1.41297	H	-10.1642	-2.42031	-0.34868
N	0.37324	-1.78507	0.36802	C	-9.72151	1.13042	-3.1993
N	-0.37334	1.7853	0.36796	H	-6.67569	2.44725	-2.3465
C	0.31151	-5.01467	3.66013	C	-10.8394	1.4041	-4.20264
C	0.9502	-4.40229	4.72359	C	-11.9861	0.40508	-4.07487
C	1.75922	-3.30793	4.48026	H	-10.6153	-0.59244	-2.27479
C	1.92324	-2.85457	3.18047	H	-8.52672	2.7814	-3.89585
C	0.50727	-4.52845	2.37895	H	-12.7604	0.64233	-4.80848
C	1.48152	-5.77507	-2.85379	C	-9.76287	-3.95513	3.18087
C	1.04115	-4.47621	-3.0283	H	-11.467	-3.55953	1.07972
C	1.93469	-6.16831	-1.60688	H	-8.84776	-3.8232	3.76172
C	1.9238	-5.26289	-0.55943	H	-10.2989	-4.81423	3.59432
C	1.05488	-3.60279	-1.95262	H	-12.4476	0.44105	-3.08472
C	-1.48191	5.77481	-2.85441	C	-11.4034	2.81065	-3.96932
C	-1.93503	6.16822	-1.60754	H	-10.637	3.57927	-4.08767
C	-1.04151	4.47595	-3.02875	H	-12.2018	3.02263	-4.68627
C	-1.05513	3.60269	-1.95294	H	-10.3812	-3.06574	3.32474
C	-1.92403	5.26296	-0.55995	H	-11.8165	2.90257	-2.96179
C	-1.75904	3.30863	4.48004	H	-6.28542	2.88605	0.13152
C	-0.9501	4.4031	4.7232	H	8.3899	5.63134	0.48012
C	-0.31155	5.01541	3.65962	H	9.88183	-0.31662	-5.82658
C	-1.92312	2.85511	3.18032	C	8.60961	5.44049	1.53348
C	-0.50736	4.52903	2.37851	H	9.13666	6.31068	1.93507

C	2.96916	-2.12606	0.35236	H	7.65879	5.35395	2.06341
C	4.15034	-2.87006	0.33563	H	10.64828	4.60753	-0.0913
C	5.3805	-2.28981	0.10737	C	10.28345	-1.31339	-5.6284
C	5.4673	-0.92232	-0.16138	H	11.07406	-1.51407	-6.35711
C	4.3141	-0.16403	-0.14975	H	11.65627	0.61834	-4.2639
C	-5.46746	0.92254	-0.16096	H	9.48283	-2.03603	-5.79865
C	-5.38062	2.29004	0.10767	C	10.79285	4.41204	0.97432
C	-4.15043	2.8703	0.33574	H	11.2934	5.2828	1.40459
C	-4.31427	0.16423	-0.14938	C	9.46683	4.17928	1.69328
C	-2.96926	2.12629	0.35241	C	11.98653	-0.40621	-4.0745
C	-3.07125	0.74749	0.13859	H	12.76087	-0.64366	-4.80797
C	3.07112	-0.74728	0.13841	C	8.71161	2.97546	1.13488
C	-0.85941	-2.26561	0.35711	C	9.20444	2.1964	0.09911
C	-1.98078	-1.47207	0.2764	H	10.16463	2.41967	-0.34865
C	-1.88564	-0.09259	0.23867	C	10.83956	-1.40495	-4.20247
C	0.56174	-0.43743	0.31429	C	9.76881	-0.08274	-2.29306
C	-0.56185	0.43765	0.3143	H	10.61567	0.59166	-2.27466
C	0.85932	2.26583	0.35701	C	7.46815	2.62531	1.68995
C	1.88552	0.0928	0.23857	C	8.47357	1.10986	-0.37706
C	1.98068	1.47228	0.27629	C	9.7216	-1.13098	-3.19933
C	-1.3339	3.45348	2.07041	C	8.72281	0.12142	-1.3955
C	-1.4618	3.95612	-0.67045	H	7.07301	3.21077	2.51243
C	1.46164	-3.95604	-0.67011	C	6.71787	1.55536	1.24016
C	1.33388	-3.453	2.07067	C	7.22532	0.80275	0.18848
B	-1.56231	2.86136	0.55062	C	7.6156	-0.74219	-1.40131
B	1.56223	-2.8611	0.55079	C	8.58864	-1.96368	-3.18734
H	4.10845	-3.93656	0.52554	H	11.46749	3.55863	1.07991
H	4.40217	0.8849	-0.39846	C	7.535	-1.78909	-2.31058
H	-4.40239	-0.88472	-0.39797	N	6.70719	-0.32486	-0.43621
H	-4.10851	3.93681	0.52555	H	12.44785	-0.44231	-3.08427
H	-2.94105	-1.96494	0.26676	H	5.77466	1.30806	1.71254
H	-0.94746	-3.34255	0.40688	C	9.76311	3.95463	3.1808
H	0.94738	3.34277	0.40672	H	8.52654	-2.78167	-3.89606
H	2.94096	1.96514	0.26661	H	10.29926	4.81363	3.59433
H	-8.38888	-5.63157	0.48042	H	6.67531	-2.44705	-2.34704
C	-8.60878	-5.44075	1.53374	H	8.84789	3.8229	3.76151
H	-9.88108	0.31602	-5.82659	C	11.40324	-2.81164	-3.96905
H	-7.65806	-5.35399	2.06381	H	12.20169	-3.02382	-4.68587
H	-9.1357	-6.31105	1.93527	H	10.6366	-3.58006	-4.08753
C	-10.283	1.31269	-5.62847	H	10.38124	3.06512	3.32477
H	-10.6474	-4.60825	-0.09136	H	11.81611	-2.90366	-2.96145
H	-9.4825	2.03552	-5.79858	H	6.2853	-2.88581	0.13114

Table S11. Cartesian Coordinates for **2-F** (PBE0/def2TZVP).

F	-5.48756	3.20456	-2.80149	C	3.42052	2.58828	-0.6424
F	-4.884	5.31495	-1.20537	C	4.42186	1.74497	1.29051
F	-3.47673	4.90302	1.07753	C	-3.1045	-0.21708	1.92486
F	-2.69549	2.47909	1.7587	C	-4.24968	-0.22516	2.72471
F	-4.73204	0.76286	-2.15049	C	-4.19637	-0.4453	4.08615
F	-6.6037	-4.5409	-1.13517	C	-2.9609	-0.68466	4.66632
F	-7.71475	-2.11975	-0.61926	C	-1.80553	-0.67496	3.93074
F	-3.91029	-4.83909	-0.9535	C	2.96091	-0.68517	-4.66622
F	-2.3716	-2.8032	-0.27782	C	4.19637	-0.44573	-4.08609
F	-6.20516	-0.05623	0.04407	C	4.24969	-0.22542	-2.72467
F	3.91075	-4.83894	0.95377	C	1.80554	-0.67536	-3.93064
F	6.60412	-4.54047	1.1355	C	3.10451	-0.21723	-1.92482
F	7.71495	-2.11924	0.61948	C	1.86999	-0.42033	-2.55027
F	6.20517	-0.0559	-0.04401	C	-1.86998	-0.42011	2.55033
F	2.37188	-2.80324	0.27793	C	-1.76201	-0.21713	-1.66344
F	3.47643	4.90298	-1.078	C	-0.59826	-0.29383	-2.39378
F	4.88353	5.31524	1.20494	C	0.63881	-0.32731	-1.77687
F	2.69542	2.47894	-1.75899	C	-0.61999	-0.25496	0.35075
F	5.48716	3.20505	2.80129	C	0.62001	-0.255	-0.3507
F	4.73186	0.76323	2.15048	C	1.76203	-0.21713	1.66347
N	-1.79162	-0.20558	-0.34108	C	-0.63879	-0.32721	1.77692
N	1.79164	-0.20562	0.34111	C	0.59828	-0.29377	2.39383
C	-4.82193	3.01425	-1.67086	C	3.73279	1.46329	0.11548
C	-4.51524	4.09337	-0.86127	C	4.19327	-1.28754	0.16005
C	-3.80231	3.87723	0.30348	C	-4.19314	-1.28768	-0.15993
C	-3.42067	2.58827	0.64215	C	-3.73291	1.46319	-0.11561
C	-4.42207	1.7447	-1.29063	B	3.24521	-0.04204	-0.34074
C	-5.83801	-3.50997	-0.81986	B	-3.2452	-0.04206	0.34076
C	-4.46606	-3.65577	-0.73141	H	-5.21711	-0.0517	2.26792
C	-6.39947	-2.27247	-0.55857	H	-0.87902	-0.88483	4.44712
C	-5.57957	-1.2061	-0.23079	H	0.87901	-0.88531	-4.44698
C	-3.68585	-2.56169	-0.39318	H	5.21712	-0.05191	-2.26791
C	5.83834	-3.50963	0.82012	H	-0.68534	-0.30389	-3.46931

C	6.39968	-2.27209	0.55878	H	-2.72269	-0.17268	-2.15855
C	4.46641	-3.65558	0.73165	H	2.72272	-0.17269	2.15858
C	3.68609	-2.56159	0.39334	H	0.68537	-0.30381	3.46935
C	5.57968	-1.20581	0.23093	H	-5.08878	-0.44969	4.70024
C	3.80204	3.8773	-0.30383	H	5.08878	-0.4502	-4.70018
C	4.51488	4.0936	0.86094	F	-2.89522	-0.93389	5.97737
C	4.82161	3.01459	1.67065	F	2.89522	-0.93458	-5.97724

Table S12. Cartesian Coordinates for **2-CN** (PBE0/def2TZVP).

F	-4.66757	0.79084	-2.29522	C	-1.93679	-0.67393	3.860702
F	-5.40523	3.234557	-2.96534	C	-4.33706	-0.18348	2.587964
F	-2.74928	2.500309	1.674048	C	-4.32642	-0.41692	3.944838
F	-4.84943	5.342095	-1.34967	C	-3.1136	-0.68662	4.588087
F	-3.50988	4.928373	0.973255	C	1.936774	-0.67441	-3.86058
F	-2.35053	-2.76969	-0.3312	C	3.113581	-0.68719	-4.58797
F	-6.20298	-0.03738	-0.14968	C	4.326401	-0.41736	-3.94477
F	-7.68115	-2.10885	-0.85972	C	4.33704	-0.18374	-2.58792
F	-6.54369	-4.52625	-1.32962	C	3.165673	-0.18236	-1.82621
F	-3.85745	-4.8142	-1.05363	C	-4.38561	1.772638	-1.42664
F	6.202965	-0.03722	0.149571	C	-3.44164	2.614963	0.536507
F	2.350642	-2.76969	0.331556	C	-4.77397	3.042857	-1.81648
F	3.857685	-4.81403	1.054165	C	-4.49117	4.121051	-0.99638
F	7.681259	-2.10855	0.859781	C	-3.81265	3.904342	0.189041
F	6.543923	-4.52594	1.330014	C	-5.5654	-1.18558	-0.40066
F	4.667641	0.79117	2.295113	C	-3.66134	-2.53511	-0.49372
F	2.749126	2.500135	-1.67427	C	-4.42498	-3.63324	-0.85528
F	3.509638	4.92831	-0.97376	C	-6.36909	-2.25619	-0.75348
F	4.849243	5.342335	1.349074	C	-5.79378	-3.49239	-0.99158
F	5.405202	3.234993	2.964948	C	3.661442	-2.53502	0.494028
N	-3.05574	-1.20564	7.113192	C	5.565439	-1.18542	0.400724
N	3.055712	-1.20659	-7.113	C	6.369196	-2.25595	0.753634
N	-1.77961	-0.17428	-0.39724	C	4.425155	-3.63307	0.85567
N	1.779603	-0.17424	0.397285	C	5.793948	-3.49215	0.991903

C	-3.08302	-0.97443	5.985353	C	4.385587	1.772866	1.42645
C	3.082997	-0.9752	-5.98519	C	3.441513	2.614943	-0.53676
C	3.731403	1.491457	0.231569	C	3.812477	3.904375	-0.18944
C	4.181686	-1.26219	0.283332	C	4.491022	4.121239	0.995931
C	-4.18165	-1.26229	-0.28318	C	4.773906	3.043143	1.81614
C	-3.73146	1.491382	-0.23171	B	3.255641	-0.01026	-0.23727
C	-0.52218	-0.26229	-2.41149	B	-3.25565	-0.01027	0.237301
C	0.693115	-0.30123	-1.75502	H	-5.24629	-0.41069	4.516844
C	-1.70918	-0.18321	-1.71755	H	-0.57659	-0.26875	-3.48939
C	-0.63059	-0.22637	0.331014	H	-2.65358	-0.13458	-2.2429
C	0.630574	-0.2264	-0.33095	H	2.65357	-0.13437	2.242941
C	-0.69313	-0.30105	1.755086	H	0.576588	-0.26842	3.489452
C	0.522174	-0.26205	2.411553	H	-5.28641	0.00403	2.100167
C	1.709172	-0.18304	1.7176	H	-1.01819	-0.90074	4.384151
C	1.950746	-0.39856	-2.4882	H	1.01818	-0.90133	-4.38399
C	-1.95076	-0.39828	2.48828	H	5.286399	0.003843	-2.10015
C	-3.16568	-0.18218	1.826255	H	5.24627	-0.41121	-4.51677

Table S13. Cartesian Coordinates for **1-hex-C** (PBE0/def2-TZVP).

C	1.82127	-0.21426	-0.43219	C	-4.69973	2.84095	1.87908
C	1.72921	-0.2675	-1.80021	C	-4.39026	3.94356	1.10536
C	0.49908	-0.33779	-2.4485	C	-5.50547	-1.1643	0.36849
C	-0.68779	-0.32248	-1.75244	C	-3.59663	-2.53407	0.31873
C	0.63361	-0.24593	0.33487	C	-4.3666	-3.64039	0.64114
C	-0.63364	-0.24597	-0.33483	C	-6.29751	-2.25338	0.68936
C	0.68776	-0.32227	1.75249	C	-5.72706	-3.50322	0.838
C	-1.8213	-0.21419	0.43222	F	-2.31597	-2.77613	0.07187
C	-0.49913	-0.33755	2.44855	F	-3.80192	-4.83368	0.73917
C	-1.72924	-0.26731	1.80025	F	-6.15838	-0.01393	0.19521
C	1.98274	-0.37504	2.43725	F	-7.60386	-2.09937	0.84525
C	3.1745	-0.17773	1.74238	F	-6.47262	-4.55039	1.14168
C	3.20783	-0.07308	0.21288	F	-2.65254	2.40052	-1.6031
C	4.37818	-0.10547	2.43976	F	-3.37333	4.79087	-0.82628

C	4.45253	-0.2616	3.81315	F	-4.72513	5.15824	1.50092
C	3.26507	-0.52272	4.49538	F	-4.65753	0.58336	2.28959
C	2.06615	-0.57285	3.82189	F	-5.33728	2.99774	3.02932
C	3.69066	1.32492	-0.245	C	5.50542	-1.164511	-0.36834
C	4.12277	-1.24502	-0.21219	C	3.59651	-2.53419	-0.3185
C	-1.98278	-0.37533	-2.43719	C	4.36642	-3.64056	-0.64086
C	-2.06618	-0.57345	-3.82177	C	5.72688	-3.503461	-0.83773
C	-3.2651	-0.52343	-4.49528	C	6.29741	-2.253641	-0.68917
C	-4.45254	-0.26209	-3.8131	F	6.15836	-0.014141	-0.19523
C	-3.17454	-0.17783	-1.74235	F	2.31582	-2.77616	-0.07168
C	-4.37821	-0.10564	-2.43974	F	3.80169	-4.83383	-0.73884
C	-3.20785	-0.07302	-0.21286	F	6.47239	-4.550681	-1.14138
H	-1.16876	-0.77598	-4.39082	F	7.60375	-2.099701	-0.84511
H	-3.28286	-0.6824	-5.5686	C	4.34087	1.57395	-1.45413
C	-5.75706	-0.16429	-4.54124	C	3.361	2.46995	0.48303
H	-5.29545	0.09047	-1.89792	C	3.71036	3.75005	0.08
H	2.62543	-0.27062	-2.40578	C	4.39049	3.94335	-1.10571
H	0.5024	-0.38278	-3.52882	C	4.69987	2.84065	-1.87933
H	-0.50246	-0.38248	3.52887	F	5.33743	2.997289	-3.02959
H	-2.62548	-0.27036	2.4058	F	4.65753	0.58305	-2.28967
H	5.29545	0.090459	1.89793	F	3.37365	4.79089	0.82588
C	5.75703	-0.163851	4.54131	F	4.72545	5.15798	-1.50137
H	3.28274	-0.68145	5.56874	F	2.65271	2.40069	1.60292
H	1.16874	-0.77514	4.39103	H	-5.75	0.67043	-5.24789
C	-4.12283	-1.24488	0.21234	H	-6.58883	-0.01311	-3.8521
C	-3.69061	1.32502	0.24488	H	-5.956	-1.07162	-5.11784
C	-3.36087	2.46995	-0.48325	H	6.58871	-0.012061	3.85221
C	-3.71012	3.75011	-0.08032	H	5.95626	-1.071411	5.11747
C	-4.34082	1.57418	1.45399	H	5.74974	0.670479	5.24843

Table S14. Cartesian Coordinates for **1-^{t}Bu-carb-C** (PBE0/def2TZVP).

C	-1.460241	-0.730985	0.92993	C	-7.705761	-3.138505	0.573104
C	-0.772755	-1.375026	1.93319	C	-10.11114	-3.604116	0.533938

C	0.618309	-1.375394	1.982819	C	-8.768747	-4.015534	0.467953
C	1.373698	-0.732577	1.034306	H	-6.687111	-3.499358	0.502194
C	-0.715916	0.014533	-0.022962	H	-8.544678	-5.066663	0.325377
C	0.71694	0.005849	0.022949	C	-11.21979	-4.647275	0.414946
C	-1.372589	0.752244	-1.034912	H	-11.38764	-1.886487	0.742091
C	1.461263	0.752086	-0.929357	C	-7.906931	0.447002	0.987192
C	-0.617106	1.395329	-1.983192	C	-9.268551	0.091555	0.957771
C	0.773953	1.395975	-1.932807	C	-10.24092	1.074423	1.083404
H	-1.304259	-1.904287	2.712169	C	-7.523575	1.766199	1.166746
H	1.099324	-1.904886	2.793961	C	-8.519409	2.723237	1.289936
H	-1.098044	1.924289	-2.794728	C	-9.884026	2.409117	1.245151
H	1.305663	1.925546	-2.711456	H	-11.28695	0.788227	1.05903
C	2.922227	0.805933	-0.842496	C	-10.97380	3.472678	1.374826
C	-2.921253	-0.784282	0.843629	H	-6.48053	2.051779	1.226301
C	-3.665772	-1.62994	1.67498	H	-8.212878	3.751658	1.429232
C	-5.042075	-1.62111	1.690923	C	-10.39882	4.876402	1.545787
C	-5.733239	-0.753548	0.849756	C	-11.84805	3.164112	2.595927
C	-5.012127	0.052866	-0.017286	H	-9.790886	4.960154	2.450167
C	-3.622832	0.038061	-0.039732	H	-11.21608	5.596838	1.6305
H	-5.587529	-2.266776	2.367951	H	-9.786237	5.171978	0.690275
H	-3.156108	-2.31138	2.342591	H	-11.25298	3.169157	3.512432
H	-5.563058	0.700803	-0.685788	H	-12.32630	2.185938	2.513844
C	3.623739	-0.01869	0.038725	H	-12.63754	3.914482	2.697063
C	3.666613	1.654493	-1.671075	C	-11.84647	3.465591	0.114277
C	5.013019	-0.034205	0.015295	H	-11.25051	3.690661	-0.773591
C	5.733921	0.774359	-0.849841	H	-12.63665	4.217732	0.194988
C	5.042947	1.645617	-1.687251	H	-12.32341	2.495706	-0.041189
H	5.564047	-0.684291	0.681708	C	-12.60999	-4.024016	0.505555
H	3.156699	2.338501	-2.335885	C	-11.08154	-5.672214	1.546914
H	5.588699	2.29414	-2.361299	C	-11.10615	-5.366371	-0.934471
C	-2.901131	0.900356	-1.083139	H	-11.20985	-4.66024	-1.761946
C	-3.141128	2.407858	-0.823769	H	-11.89201	-6.121309	-1.029192
C	-3.118999	3.388547	-1.816138	H	-10.14444	-5.871478	-1.045001
C	-3.25461	2.901821	0.477185	H	-12.76662	-3.518182	1.46172
C	-3.4053	4.249907	0.765682	H	-13.36755	-4.806667	0.418295
C	-3.417101	5.180451	-0.254109	H	-12.78553	-3.304246	-0.298022
C	-3.265069	4.739398	-1.555178	H	-11.16823	-5.188438	2.522949
F	-2.94941	3.073095	-3.101017	H	-10.11839	-6.185493	1.512726
F	-3.19195	2.098781	1.532549	H	-11.86653	-6.430154	1.470479
F	-3.520853	4.645551	2.023479	C	7.906513	-0.427022	-0.995903
F	-3.256927	5.610618	-2.552034	C	7.993082	1.809093	-0.744793
F	-3.556127	6.466873	0.007977	C	9.323879	1.352469	-0.794668
C	-3.45128	0.381611	-2.432423	C	9.26606	-0.078934	-0.957805
C	-2.900499	-0.760281	-3.01751	C	10.24139	-1.064481	-1.089613

C	-3.378159	-1.310177	-4.196361	C	7.517056	-1.745925	-1.190962
C	-4.469876	-0.748168	-4.829711	C	8.508938	-2.699444	-1.319751
C	-5.078812	0.351842	-4.255816	C	9.879433	-2.391474	-1.26627
C	-4.581094	0.881955	-3.077769	H	6.472919	-2.026048	-1.257287
F	-5.268695	1.90779	-2.575267	H	8.204445	-3.728732	-1.472292
F	-1.898334	-1.412765	-2.441579	H	11.28511	-0.778145	-1.057048
F	-2.801433	-2.387709	-4.70459	C	10.90407	-3.514179	-1.41098
F	-4.936039	-1.264754	-5.951585	C	10.36885	2.258243	-0.67239
F	-6.14194	0.893274	-4.828409	C	7.712339	3.15198	-0.550844
C	2.902121	-0.882093	1.081211	C	8.779031	4.030182	-0.432028
C	3.453715	-0.365718	2.430796	C	10.11544	3.614454	-0.49441
C	4.583427	-0.868062	3.074734	H	11.39002	1.894415	-0.711758
C	5.082552	-0.339896	4.253057	H	8.552343	5.077677	-0.2824
C	4.475189	0.760087	4.828675	C	11.28337	4.591739	-0.366548
C	2.90455	0.776072	3.017604	H	6.694701	3.51618	-0.482148
C	3.383621	1.324033	4.19678	C	10.81736	6.032759	-0.175188
F	6.145508	-0.883135	4.824241	C	12.14031	4.532888	-1.636535
F	4.9427	1.274831	5.95083	C	12.14467	4.20561	0.841682
F	5.269584	-1.894009	2.570424	C	12.33862	-2.999427	-1.330648
F	1.902721	1.430289	2.443094	C	10.72022	-4.20569	-2.767033
F	2.808423	2.401556	4.706712	C	10.70147	-4.539533	-0.2891
C	3.14068	-2.389415	0.819607	H	12.55933	-2.285645	-2.128446
C	3.117729	-3.371453	1.81064	H	13.03326	-3.836363	-1.435813
C	3.262605	-4.722084	1.547861	H	12.54420	-2.518439	-0.370936
C	3.414402	-5.161474	0.2462	H	10.83469	-4.075656	0.691313
C	3.403566	-4.229505	-0.772283	H	11.42645	-5.353149	-0.383484
C	3.253898	-2.881691	-0.48199	H	9.702262	-4.978868	-0.317742
F	3.519299	-4.623502	-2.03065	H	11.56116	4.245153	1.764752
F	3.19236	-2.077189	-1.536348	H	12.98905	4.893804	0.941572
F	3.253681	-5.594651	2.543498	H	12.54756	3.195406	0.744611
F	3.552498	-6.447659	-0.017682	H	10.22008	6.382927	-1.02089
F	2.948695	-3.057579	3.095936	H	11.68729	6.688811	-0.09185
N	-7.134996	-0.702503	0.865224	H	10.22653	6.151722	0.736551
N	7.135744	0.722142	-0.866522	H	11.55392	4.811471	-2.515598
C	-7.991466	-1.791636	0.757515	H	12.54168	3.531774	-1.806815
C	-9.320518	-1.341557	0.808695	H	12.98541	5.222881	-1.557012
C	-10.36917	-2.251631	0.69998	H	10.86813	-3.499312	-3.587575
H	11.44484	-5.017243	-2.880104	H	9.721482	-4.634372	-2.871405

Table S15. Cartesian Coordinates for **1-F-C** (PBE0/def2TZVP).

C	0.673794	-0.203685	-1.747607	F	2.769487	2.428548	-1.790483

C	-0.515269	-0.187739	-2.43974	F	3.623552	4.828286	-1.19176
C	-1.741082	-0.097609	-1.786187	F	5.544544	3.208052	2.760552
C	-1.824759	-0.015583	-0.419188	F	5.024255	5.28519	1.09024
C	0.631429	-0.043141	-0.33684	C	4.067415	-1.151014	0.267465
C	-0.631382	0.042518	0.336894	C	3.475181	-2.396977	0.483166
C	1.824801	0.015014	0.419236	C	4.190841	-3.514119	0.884128
C	-0.673755	0.202959	1.747664	C	5.559705	-3.435481	1.053087
C	1.741127	0.09691	1.786249	C	6.193697	-2.234115	0.797545
C	0.515314	0.186941	2.439799	C	5.455041	-1.133344	0.399274
H	-0.525291	-0.247945	-3.519361	F	6.16286	-0.036325	0.126117
H	-2.640319	-0.095944	-2.387312	F	2.1791	-2.589024	0.272719
H	2.640374	0.09524	2.387357	F	3.565149	-4.662974	1.08396
H	0.525326	0.247014	3.519426	F	6.252846	-4.493389	1.43093
C	-1.960274	0.357482	2.433798	F	7.507556	-2.138783	0.925777
C	1.960307	-0.358313	-2.433719	C	-3.213483	-0.036931	0.236203
C	2.016659	-0.655341	-3.801385	C	-4.066973	1.151204	-0.267175
C	3.205082	-0.710549	-4.496922	C	-5.454636	1.134048	-0.398804
C	4.373149	-0.458737	-3.80379	C	-6.192981	2.235163	-0.796691
C	4.368819	-0.203038	-2.45276	C	-5.558621	3.436377	-1.052035
C	3.165469	-0.170124	-1.754567	C	-3.474357	2.397012	-0.482681
H	3.23665	-0.939705	-5.554493	C	-4.189712	3.514495	-0.88326
H	1.103873	-0.85627	-4.345189	F	-7.50689	2.140305	-0.924755
H	5.315242	-0.021453	-1.961683	F	-6.25145	4.494624	-1.429507
C	-3.165449	0.169454	1.75462	F	-6.162819	0.037208	-0.125859
C	-2.016613	0.654213	3.801535	F	-2.178187	2.588635	-0.272395
C	-4.368792	0.202235	2.452835	F	-3.563659	4.663187	-1.082901
C	-4.373104	0.457657	3.803913	C	-3.776259	-1.434853	-0.11867
C	-3.205025	0.7093	4.497091	C	-4.455889	-1.731596	-1.30037
H	-5.315215	0.020742	1.961734	C	-4.885787	-3.004303	-1.631497
H	-1.103819	0.85499	4.345378	C	-4.623103	-4.065327	-0.785368
H	-3.236589	0.938213	5.554715	C	-3.917095	-3.826764	0.376975
C	3.213496	0.036652	-0.236225	C	-3.496254	-2.541863	0.684647
C	3.775809	1.434865	0.118259	F	-3.624513	-4.828733	1.190227
C	4.455144	1.732151	1.29999	F	-2.769641	-2.429369	1.789467
C	3.495752	2.541555	-0.685481	F	-5.545933	-3.206801	-2.761167

C	3.916186	3.826661	-0.378104	F	-5.025869	-5.284546	-1.091565
C	4.621861	4.06578	0.784331	F	-4.731128	-0.785471	-2.199878
C	4.884646	3.005073	1.630819	F	5.539184	-0.479924	-4.455126
F	4.730606	0.786354	2.199777	F	-5.53912	0.478736	4.455263

Table S16. Cartesian Coordinates for **1-CN-C** (PBE0/def2TZVP).

C	0.749585	-0.223426	-1.712575	F	3.592111	4.825937	-1.173854
C	-0.406322	-0.211876	-2.459351	F	5.331642	3.356859	2.918591
C	-1.659883	-0.114158	-1.862921	F	4.864586	5.374109	1.162472
C	-1.803463	-0.023542	-0.500869	C	4.071447	-1.098903	0.477654
C	0.645876	-0.045722	-0.307136	C	3.493896	-2.352398	0.688574
C	-0.645817	0.045101	0.307227	C	4.208688	-3.444892	1.152364
C	1.803532	0.023005	0.500945	C	5.56489	-3.331871	1.392997
C	-0.749531	0.222711	1.71268	C	6.187774	-2.122954	1.144022
C	1.65995	0.113556	1.863	C	5.449464	-1.047009	0.681334
C	0.406385	0.211157	2.459441	F	6.146306	0.058264	0.417072
H	-0.366479	-0.282289	-3.53761	F	2.214263	-2.573395	0.410575
H	-2.532195	-0.118475	-2.502212	F	3.596948	-4.601891	1.343847
H	2.532266	0.117926	2.502285	F	6.257257	-4.365129	1.831599
H	0.366558	0.281489	3.537705	F	7.489218	-1.996619	1.339955
C	-2.062383	0.395638	2.338018	C	-3.218268	-0.056374	0.09572
C	2.062431	-0.396503	-2.337882	C	-4.070999	1.09914	-0.477333
C	2.175491	-0.737832	-3.692554	C	-5.449058	1.047801	-0.680928
C	3.391847	-0.811412	-4.328527	C	-6.187011	2.124117	-1.143309
C	4.554777	-0.539042	-3.608061	C	-5.563709	3.332867	-1.392064
C	4.464704	-0.245009	-2.253859	C	-3.493014	2.352466	-0.688041
C	3.236931	-0.193109	-1.608628	C	-4.207449	3.445327	-1.151529
H	3.452469	-1.07363	-5.377161	F	-7.488515	1.9983	-1.339177
H	1.28676	-0.957273	-4.267746	F	-6.255739	4.366473	-1.830375
H	5.377957	-0.044727	-1.709935	F	-6.146291	-0.057286	-0.416909
C	-3.236886	0.19243	1.608715	F	-2.213274	2.57296	-0.410127
C	-2.17545	0.736614	3.692781	F	-3.595289	4.602139	-1.342808
C	-4.464661	0.244167	2.253959	C	-3.734516	-1.476217	-0.243479

C	-4.554735	0.537861	3.608233	C	-4.345935	-1.819289	-1.450004
C	-3.391804	0.81004	4.328771	C	-4.736814	-3.108569	-1.76425
H	-5.377908	0.04402	1.709979	C	-4.501147	-4.139729	-0.873772
H	-1.286722	0.955885	4.268044	C	-3.860775	-3.854954	0.315983
H	-3.452424	1.071979	5.377474	C	-3.478154	-2.55405	0.605861
C	3.218306	0.056131	-0.095708	F	-3.593226	-4.826356	1.172415
C	3.734075	1.476264	0.243064	F	-2.811135	-2.396057	1.743179
C	4.345192	1.819879	1.449597	F	-5.333101	-3.355556	-2.919267
C	3.477592	2.553767	-0.606652	F	-4.866341	-5.37345	-1.163813
C	3.859769	3.854874	-0.317071	F	-4.589738	-0.904223	-2.389347
C	4.499816	4.140197	0.872722	C	5.828763	-0.579908	-4.247221
C	4.735628	3.109361	1.763543	C	-5.828722	0.578571	4.247402
F	4.58916	0.905154	2.389228	N	6.856684	-0.61416	-4.766064
F	2.810889	2.395276	-1.744087	N	-6.856641	0.612694	4.766258

Table S17. Cartesian Coordinates for **2-^{t}Bu-carb-C** (PBE0/def2TZVP).

C	1.87632	0.120012	0.14718	H	5.489329	1.633279	-1.867579
C	1.961817	1.342402	0.772433	H	6.643728	3.635909	-2.639599
C	0.829051	2.102095	1.050654	C	9.143285	4.541883	-2.117428
C	-0.429203	1.669013	0.716304	H	10.163007	2.567034	-0.439116
C	0.585907	-0.397433	-0.144842	C	7.813939	-0.743599	0.63059
C	-0.580494	0.389142	0.134065	C	8.90851	0.137866	0.548835
C	0.434418	-1.676368	-0.729145	C	10.079766	-0.150991	1.236166
C	-1.870972	-0.129019	-0.156248	C	7.882734	-1.887181	1.410005
C	-0.823872	-2.108945	-1.064091	C	9.066798	-2.146116	2.083628
C	-1.956784	-1.350364	-0.783409	C	10.182227	-1.301376	2.01144
H	2.921413	1.748414	1.061404	H	10.916069	0.536323	1.165857
H	0.963496	3.057701	1.539038	C	11.483474	-1.598581	2.755789
H	-0.958276	-3.063474	-1.55461	H	7.039948	-2.560247	1.507871
H	-2.916648	-1.755975	-1.072139	H	9.113754	-3.041405	2.68958
C	-3.069821	0.640033	0.196985	C	11.414796	-2.90064	3.549743
C	3.075273	-0.651018	-0.201774	C	11.784151	-0.45846	3.735895
C	4.349322	-0.099369	-0.039501	H	10.634351	-2.870731	4.314264
C	5.500852	-0.82763	-0.279535	H	12.367509	-3.067781	4.058224
C	5.390772	-2.156607	-0.678814	H	11.230528	-3.76223	2.903006
C	4.138557	-2.704631	-0.859786	H	10.982942	-0.355975	4.471888
C	2.975623	-1.968264	-0.652256	H	11.889336	0.499032	3.221651

H	4.464371	0.922396	0.293585	H	12.717417	-0.654234	4.2719
H	4.071751	-3.737249	-1.176529	C	12.633707	-1.71499	1.748898
C	-2.970752	1.958675	0.643483	H	12.450524	-2.526327	1.040115
C	-4.343214	0.084401	0.044059	H	13.574035	-1.921156	2.268387
C	-4.134257	2.693069	0.854435	H	12.763841	-0.79458	1.176054
C	-5.386122	2.141328	0.68202	C	10.571352	4.709678	-1.605824
C	-5.495178	0.810597	0.288292	C	8.328634	5.760283	-1.667064
H	-4.06833	3.726819	1.167708	C	9.186867	4.501717	-3.649571
H	-4.457416	-0.939256	-0.283484	H	9.769436	3.646293	-4.000248
C	1.624123	-2.620606	-0.956818	H	9.649302	5.41296	-4.039787
C	1.347541	-3.808192	-0.001954	H	8.187125	4.424666	-4.081749
C	0.553146	-4.908335	-0.326865	H	10.606948	4.774926	-0.51535
C	1.77416	-3.77236	1.327105	H	10.996384	5.633527	-2.005693
C	1.496323	-4.779638	2.238922	H	11.215788	3.885854	-1.923083
C	0.739758	-5.870234	1.859034	H	8.288418	5.820417	-0.57666
C	0.260535	-5.925869	0.563742	H	7.302317	5.720462	-2.037725
F	0.016021	-5.042838	-1.540642	H	8.783632	6.681128	-2.043217
F	2.451958	-2.73909	1.811036	C	-7.816333	0.716777	-0.6011
F	1.942167	-4.685116	3.481496	C	-7.159356	-0.989818	0.712655
F	-0.481321	-6.951815	0.176384	C	-8.49113	-1.252296	0.338936
F	0.465593	-6.833554	2.719182	C	-8.908961	-0.159682	-0.503758
C	1.730767	-3.004404	-2.45138	C	-10.09278	0.124609	-1.180413
C	1.472612	-2.049461	-3.43685	C	-7.891095	1.858767	-1.388568
C	1.601814	-2.307678	-4.792187	C	-9.079271	2.111595	-2.047453
C	2.038261	-3.546029	-5.2221	C	-10.19986	1.267579	-1.958395
C	2.356757	-4.503477	-4.277655	H	-7.047892	2.529358	-1.499108
C	2.217193	-4.219826	-2.929902	H	-9.137036	3.003298	-2.661419
F	2.600345	-5.189587	-2.097846	H	-10.92527	-0.562261	-1.093231
F	1.12336	-0.809342	-3.117429	C	-11.47317	1.632825	-2.717732
F	1.328368	-1.360181	-5.674758	C	-9.127255	-2.393683	0.808265
F	2.169571	-3.803409	-6.510243	C	-6.481281	-1.84757	1.56398
F	2.803573	-5.68901	-4.661779	C	-7.145823	-2.977986	2.015292
C	-1.619033	2.614017	0.940639	C	-8.464382	-3.28022	1.650657
C	-1.722262	3.006921	2.432967	H	-10.15350	-2.584844	0.513297
C	-2.206428	4.225582	2.905335	H	-6.609722	-3.643484	2.67917
C	-2.342705	4.517262	4.251726	C	-9.184935	-4.532343	2.149315
C	-2.023093	3.564986	5.201007	H	-5.466095	-1.646607	1.88348
C	-1.463029	2.057357	3.423344	C	-8.30782	-5.38171	3.065581
C	-1.588953	2.323612	4.777415	C	-9.59787	-5.394977	0.950985
F	-2.787579	5.705439	4.629905	C	-10.43772	-4.124859	2.933578
F	-2.15125	3.830026	6.487914	C	-12.58357	0.606805	-2.508908
F	-2.590824	5.190564	2.068298	C	-11.17160	1.710903	-4.219029
F	-1.115939	0.815079	3.110128	C	-11.98486	2.994746	-2.233663
F	-1.314587	1.381053	5.664938	H	-12.29327	-0.384408	-2.866495

C	-1.345071	3.79587	-0.022111	H	-13.47209	0.911457	-3.067285
C	-0.548341	4.896937	0.294033	H	-12.86724	0.524166	-1.456594
C	-0.257714	5.909318	-0.603042	H	-12.21769	2.966286	-1.166338
C	-0.74166	5.847299	-1.896296	H	-12.89431	3.272454	-2.774326
C	-1.501059	4.755718	-2.267484	H	-11.24783	3.784283	-2.393921
C	-1.776867	3.753652	-1.349287	H	-10.17337	-3.512558	3.799213
F	-1.951768	4.655204	-3.507862	H	-10.96684	-5.012659	3.29191
F	-2.458278	2.719074	-1.825322	H	-11.13144	-3.549529	2.317158
F	0.486579	6.936526	-0.223835	H	-7.407617	-5.733838	2.555496
F	-0.469437	6.805641	-2.762628	H	-8.867185	-6.261877	3.391974
F	-0.007323	5.037704	1.505334	H	-8.004113	-4.833544	3.960997
N	6.761772	-0.231215	-0.118506	H	-8.722673	-5.708185	0.376393
N	-6.755288	0.209518	0.138623	H	-10.26459	-4.854936	0.275577
C	7.172946	0.971438	-0.680057	H	-10.12199	-6.292809	1.291292
C	8.496911	1.233846	-0.292551	H	-10.81227	0.749642	-4.594488
C	9.142174	2.380947	-0.748483	H	-10.41055	2.461667	-4.441149
C	6.500749	1.83446	-1.536467	H	-12.07553	1.978119	-4.774005
C	8.48786	3.267369	-1.59069	H	-6.276922	2.724843	0.8781
C	7.169439	2.963057	-1.971515	H	6.281286	-2.741677	-0.871375

Table S18. Cartesian Coordinates for **2-F-C** (PBE0/def2TZVP).

C	0.645213	0.272516	-1.747882	F	7.533243	2.060839	0.924881
C	-0.55334	0.281714	-2.422684	F	6.301956	4.399139	1.549826
C	-1.768896	0.161955	-1.75511	F	3.611733	4.603157	1.240088
C	-1.831182	0.027855	-0.390867	H	1.035809	1.028254	-4.347987
C	0.626278	0.057057	-0.344206	H	5.267082	0.131921	-2.023866
C	-0.626311	-0.056932	0.34425	C	-1.920485	-0.461201	2.446952
C	1.831153	-0.027817	0.390886	C	-3.136839	-0.255384	1.793117
C	-0.645246	-0.272401	1.747924	C	-1.943081	-0.81363	3.800998
C	1.768882	-0.162115	1.755108	C	-4.324509	-0.332167	2.515824
C	0.553327	-0.281823	2.422691	C	-3.134587	-0.900072	4.47733
H	2.677388	-0.182307	2.341585	H	-1.035888	-1.027568	4.348205
H	0.578709	-0.387184	3.498621	H	5.268312	0.702323	-4.420427
H	-0.57869	0.386911	-3.498632	C	-4.343875	-0.643939	3.860573
H	-2.677393	0.181969	-2.341606	H	-5.2671	-0.131398	2.023924
C	1.920443	0.461525	-2.44687	H	-5.268351	-0.701345	4.420603
C	1.943021	0.814228	-3.800842	F	3.120628	1.23887	-5.770227

C	3.134529	0.900882	-4.477151	F	-3.120701	-1.237796	5.770476
C	4.343829	0.644721	-3.86043	C	-3.208605	0.026408	0.288912
C	4.324474	0.332697	-2.515736	C	-3.763667	1.445421	0.009959
C	3.136805	0.255678	-1.79306	C	-4.078829	-1.127804	-0.26128
C	3.208565	-0.026368	-0.288908	C	-3.468919	2.510751	0.863249
C	3.763552	-1.445447	-0.010167	C	-3.887094	3.811111	0.62329
C	3.468789	-2.510646	-0.863619	C	-4.604804	4.110014	-0.51762
C	4.454336	-1.804194	1.147947	C	-4.882043	3.093052	-1.411786
C	4.881836	-3.093333	1.411357	C	-4.454491	1.80397	-1.148194
C	3.88692	-3.811054	-0.623851	F	-4.745674	0.904549	-2.089777
F	2.730034	-2.343656	-1.953346	F	-5.005011	5.344582	-0.758663
C	4.60459	-4.110153	0.517035	F	-5.554229	3.353452	-2.52227
F	4.745512	-0.904935	2.089688	F	-2.730145	2.34394	1.952989
F	5.553982	-3.353917	2.521824	F	-3.580222	4.770693	1.481299
F	3.580032	-4.770496	-1.482011	C	-3.498695	-2.367197	-0.538928
F	5.004748	-5.344771	0.757902	C	-5.467366	-1.094337	-0.377569
C	4.0789	1.127676	0.261448	C	-6.218261	-2.171458	-0.816201
C	5.467441	1.094068	0.377671	C	-5.596333	-3.364579	-1.132197
C	3.498899	2.367082	0.539307	C	-4.226251	-3.460351	-0.981699
C	6.21845	2.171043	0.816453	F	-2.201751	-2.576445	-0.349714
C	5.596647	3.364175	1.132676	F	-3.611308	-4.6034	-1.239347
C	4.226573	3.460098	0.982238	F	-6.30152	-4.399688	-1.549202
F	2.201973	2.576504	0.350155	F	-6.164895	-0.006262	-0.047073
F	6.164859	0.005991	0.046932	F	-7.53306	-2.061388	-0.924704

Table S19. Cartesian Coordinates for **2-CN-C** (PBE0/def2TZVP).

C	0.705582	0.568683	-1.649387	F	6.280508	3.972348	2.47758
C	-0.468417	0.713944	-2.351177	F	3.604604	4.264905	2.120796
C	-1.7072	0.497645	-1.753806	H	1.188703	1.796585	-4.022362
C	-1.816157	0.126533	-0.437327	H	5.331757	0.365497	-1.809839
C	0.637811	0.106886	-0.308519	C	-2.006513	-0.859963	2.26139
C	-0.638002	-0.107693	0.308368	C	-3.198212	-0.509299	1.622877
C	1.815949	-0.127152	0.437256	C	-2.084441	-1.463127	3.518627

C	-0.705773	-0.569677	1.649137	C	-4.412185	-0.682389	2.284123
C	1.706983	-0.498333	1.753715	C	-3.299004	-1.654608	4.15819
C	0.468212	-0.714889	2.350983	H	-1.188637	-1.798814	4.021473
H	2.594822	-0.635875	2.355843	H	5.429553	1.358196	-4.04571
H	0.457094	-1.006463	3.392308	C	-4.478675	-1.236568	3.543086
H	-0.457361	1.005329	-3.392551	H	-5.331965	-0.367412	1.809599
H	-2.595065	0.6353	-2.355858	H	-5.429579	-1.361477	4.044934
C	2.006387	0.858516	-2.261777	C	3.335218	2.270115	-5.445226
C	2.084439	1.460963	-3.51936	C	-3.335117	-2.273528	5.444025
C	3.299025	1.651865	-4.159078	C	-3.215585	0.029515	0.188148
C	4.478611	1.233871	-3.543789	C	-3.749588	1.481661	0.145557
C	4.412014	0.680437	-2.284497	C	-4.077833	-1.002834	-0.575951
C	3.19805	0.508039	-1.623079	C	-3.470363	2.375546	1.180682
C	3.215418	-0.029793	-0.188013	C	-3.866413	3.70416	1.161751
C	3.750082	-1.481617	-0.144513	C	-4.545085	4.208729	0.069978
C	3.470895	-2.376226	-1.179019	C	-4.804964	3.36864	-0.99706
C	4.400804	-2.045536	0.953255	C	-4.399598	2.04658	-0.952148
C	4.806873	-3.36738	0.998774	F	-4.668219	1.329251	-2.043947
C	3.86764	-3.7046	-1.15949	F	-4.924471	5.47155	0.037641
F	2.767531	-2.005012	-2.2424	F	-5.438523	3.830034	-2.062885
C	4.547031	-4.208195	-0.067686	F	-2.767599	2.003477	2.244147
F	4.669393	-1.327462	2.044581	F	-3.576446	4.492785	2.182998
F	5.44105	-3.827828	2.064642	C	-3.498928	-2.184137	-1.044064
F	3.577745	-4.493975	-2.180178	C	-5.46165	-0.929305	-0.727972
F	4.927096	-5.470793	-0.034832	C	-6.206023	-1.903464	-1.370684
C	4.077051	1.003514	0.575499	C	-5.583463	-3.033114	-1.868335
C	5.460918	0.930656	0.727587	C	-4.220088	-3.173882	-1.692617
C	3.497694	2.184869	1.042863	F	-2.210844	-2.440633	-0.851178
C	6.20491	1.905548	1.369586	F	-3.606701	-4.263419	-2.123381
C	5.581899	3.035298	1.866516	F	-6.282453	-3.969467	-2.480052
C	4.218481	3.175349	1.690752	F	-6.159459	0.095245	-0.236157
F	2.209493	2.440777	0.84992	F	-7.514417	-1.757542	-1.500647
F	6.159164	-0.093901	0.236372	N	3.364758	2.769009	-6.482775
F	7.51336	1.760255	1.499592	N	-3.364588	-2.77297	6.481312

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