Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Difluoromethane as a Precursor to Difluoromethyl Borates

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General Considerations:

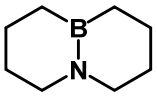
Hexamethylborazine,[1] Pd(TMEDA)PhI,[2] KN(^{i}Pr)$_2$,[3] 1,4,6,9-tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine, 1,2,3,4-tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine, and [1,2]azaborinino[1,2-a][1,2]azaborinine[4] were prepared according to literature procedures. THF was purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina and finally stored over activated molecular sieves for a minimum of 48 hours. All other reagents were used from commercial sources without further purification. Unless otherwise noted, all manipulations were performed under an inert nitrogen atmosphere. Column chromatography was performed using a Biotage Isolera One flash chromatography system.

NMR spectra were recorded on a Varian Vnmrs 700, Varian Vnmrs 500, or Varian MR400 spectrometer. ^{1}H, ^{13}C, ^{19}F, and ^{11}B shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{11}B and ^{19}F NMR spectra are referenced to fluorobenzene or, in spectra lacking internal standard, on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^{1}H NMR spectrum. Peaks not listed in the peak assignment correspond to residual solvent.[5] Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), septet (sp), and multiplet (m). Compounded splitting patterns are denoted through combinations of the above letters, e.g. dd for a doublet of doublets. Mass spectra were obtained on an electrospray Agilent Q-TOF mass spectrometer or a Micromass AutoSpec Ultima Magnetic Sector Mass Spectrometer electron ionization mass spectrometer. NMR spectra were processed using MestReNova version 10.0.2. For the purpose of labeling atoms for spectral assignments, hydrogen atoms are labeled with greek letters while carbon atoms are labeled with numbers. In spectra of *in-situ* reactions, fluorobenzene (internal standard) appears at -113.15 ppm. Water and H-grease also appear as trace contaminants in the ^{1}H-NMR spectra of isolated organic compounds (1.56 and 0.85 / 1.25 ppm, respectively)[5]

Computational Details:

Calculations were performed with the Gaussian 09[6] suite of programs using the M062X functional,[7] the IEFPCM polarizable continuum solvent model for tetrahydrofuran,[8] and an ultrafine (150,974 point) integration grid for all atoms. All reported compounds underwent geometry optimization with the 6-31G(d,p) basis set[9] followed by vibrational frequency calculations. These were used to verify that the structures were truly local energetic minima by the absence of imaginary vibrational modes and to provide entropies of formation at 25 °C. Theoretical NMR shifts were calculated using the GIAO methodology at the B3LYP/6-311+G(2d,p) level of theory, with the SDD ECP used for Pd. Optimized geometries appear at the end of the Supporting Information.

Preparation of Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine



1,4,6,9-tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine (4.00 g, 30.0 mmol) was dissolved in hexane (8 mL) with 1.2 g Pd/C (10%) in a Fisher-Porter tube. The reaction vessel was pressurized with H_2 (70 psi dynamic pressure) and heated at 80 °C for 16 hours. The resulting mixture was filtered and evaporated at 0 °C under vacuum to afford the title compound. 3.90 g colorless oil, 95%. ^{1}H-NMR (C_6D_6): 2.60 (4H, broad), 1.47 (8H, broad), 0.83 (4H, broad). ^{11}B-NMR: 42.95 (1B, broad). These spectroscopic features matched literature values reported in 1968 by Dewar and Jones.[10]

Fig. S1. ^{1}H NMR Spectrum:

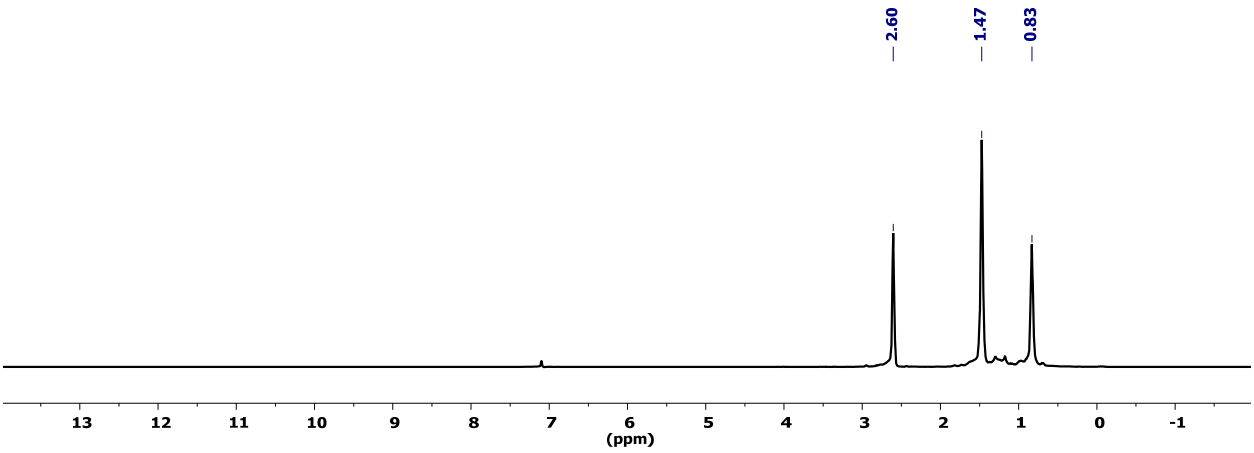
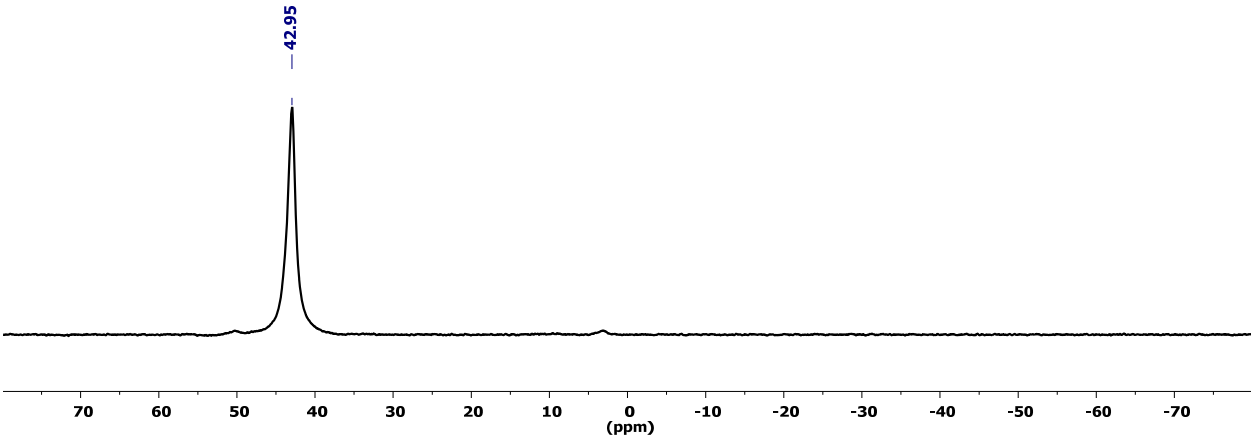
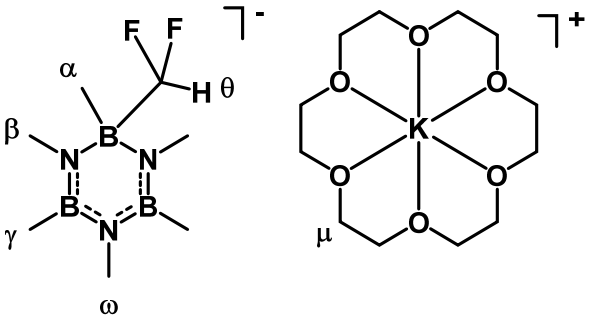


Fig. S2. ^{11}B NMR Spectrum:



Synthesis of 1-3



[K(18-crown-6)][$B_3N_3Me_6(CF_2H)$] (1)

Hexamethylborazine (328 mg, 2.0 mmol) and 18-crown-6 (528 mg, 2.0 mmol) were dissolved in 10 mL THF and cooled to 0 °C. Solid potassium toluide (260 mg, 2.0 mmol) was added in one portion and the mixture rapidly stirred for 10 minutes, providing a homogeneous red solution. Difluoromethane (50 mL gas, ~4.0 mmol) was added in one portion, and the solution stirred at room temperature for 90 minutes. The solution was poured into 100 mL pentane and stirred at room temperature for 15 minutes. The suspension was filtered and washed with pentane to provide the title compound as a white solid (970 mg, 95%). ^{1}H-NMR (THF-d_8): 5.20 (θ, 1H, (d, $J_{1H\text{-}19F}$=51.7)), 3.55 (μ, 24H, s), 2.51 (ß, 6H, s), 2.49 (ω, 3H, s), 0.05 (γ, 6H, s), 0.39 (α, 3H, s). ^{13}C-NMR: 136.87, 71.99, 35.80, 35.73, 3.54 (t, $J_{13C\text{-}19F}$=55.9), 0.48 (broad). ^{19}F-NMR: -128.23 (2F, ddd, $J_{19F\text{-}1H,\ 19F\text{-}11B}$=49.3, 32.2, 14.0). ^{11}B-NMR: 32.26 (2B, broad), -5.70 (1B, sharp). A single crystal was obtained by allowing pentane to diffuse into a saturated solution of **1** in THF at -30 °C.

Fig. S3. ^{1}H NMR Spectrum:

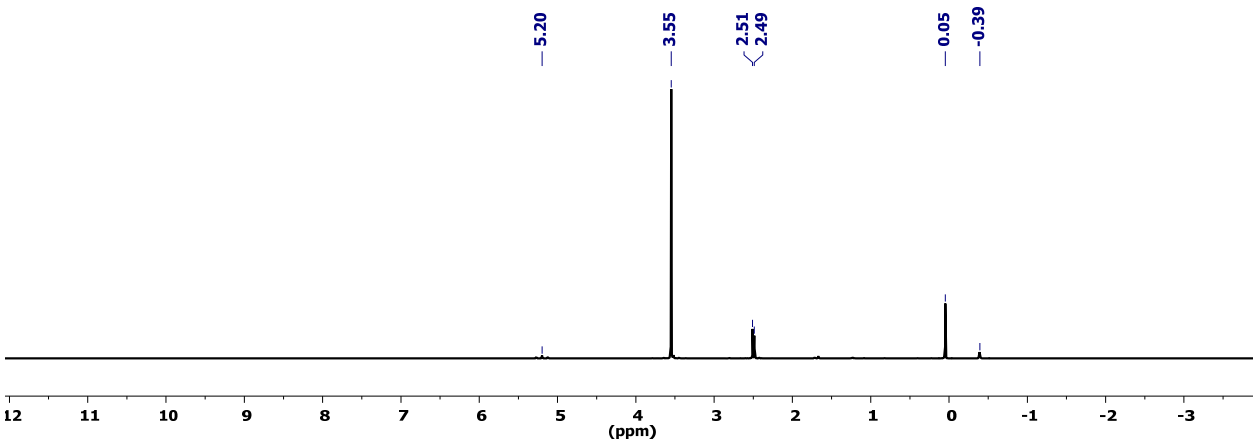


Fig. S4. ^{13}C NMR Spectrum:

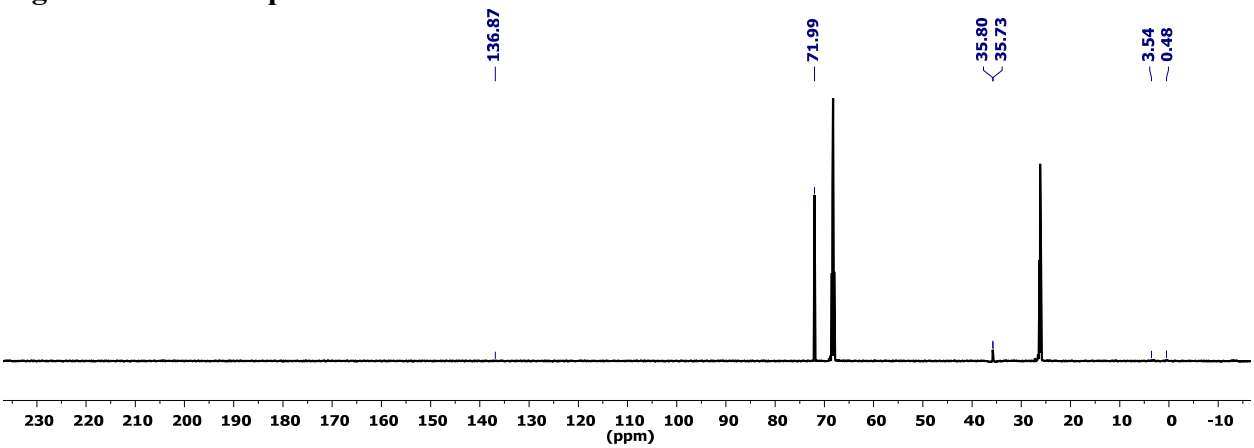


Fig. S5. ^{19}F NMR Spectrum:

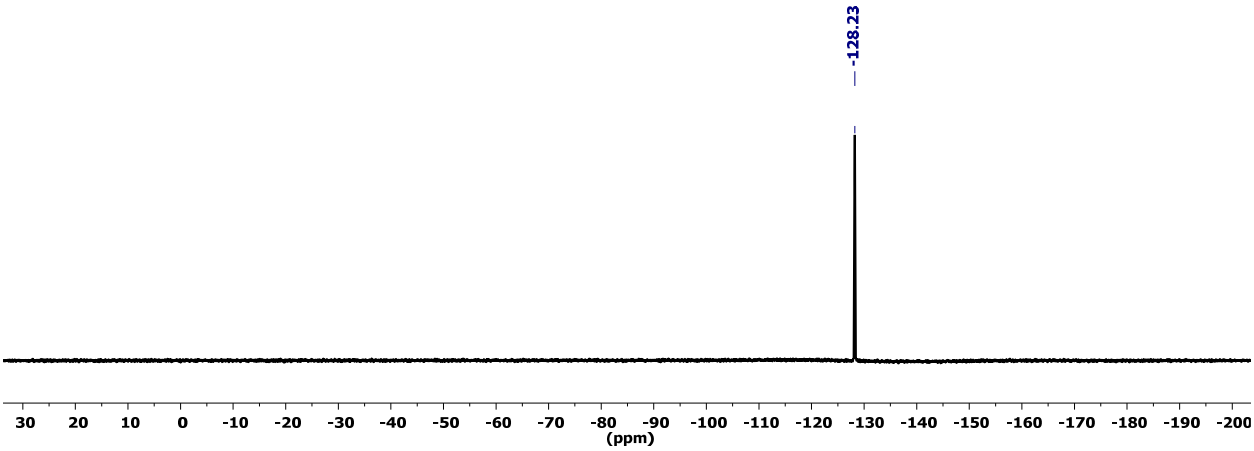


Fig. S6. ^{11}B NMR Spectrum:

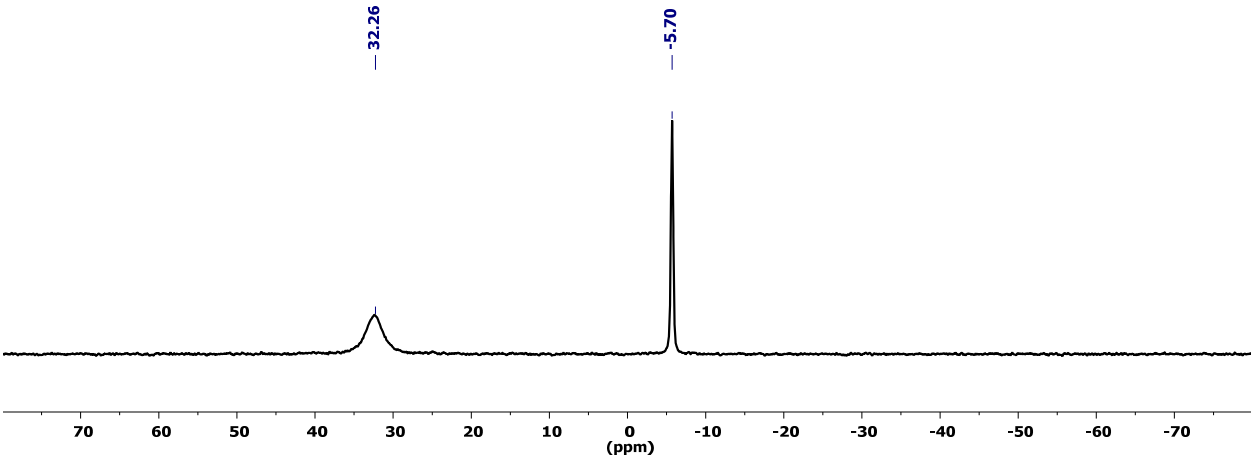


Fig. S7. ^{1}H- ^{1}H gCOSY Spectrum:

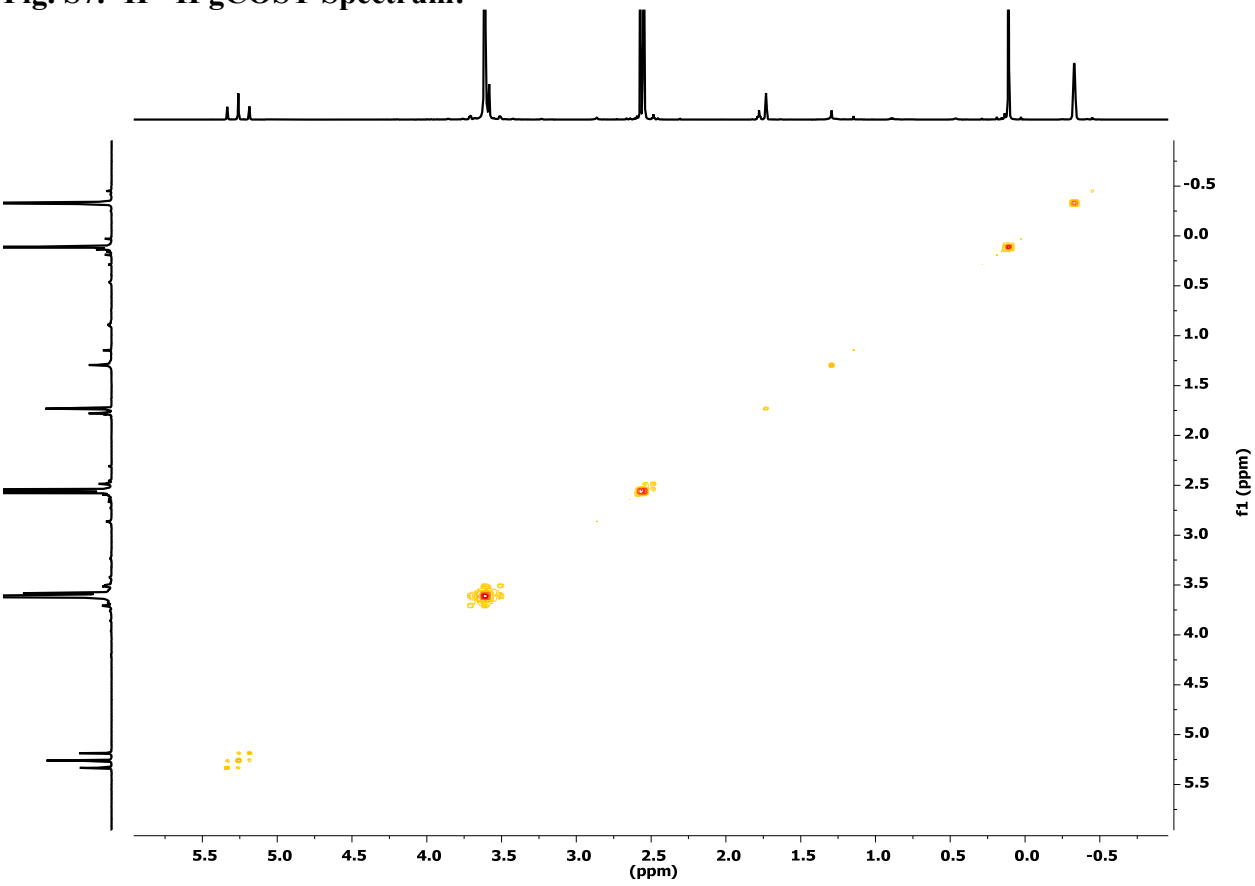
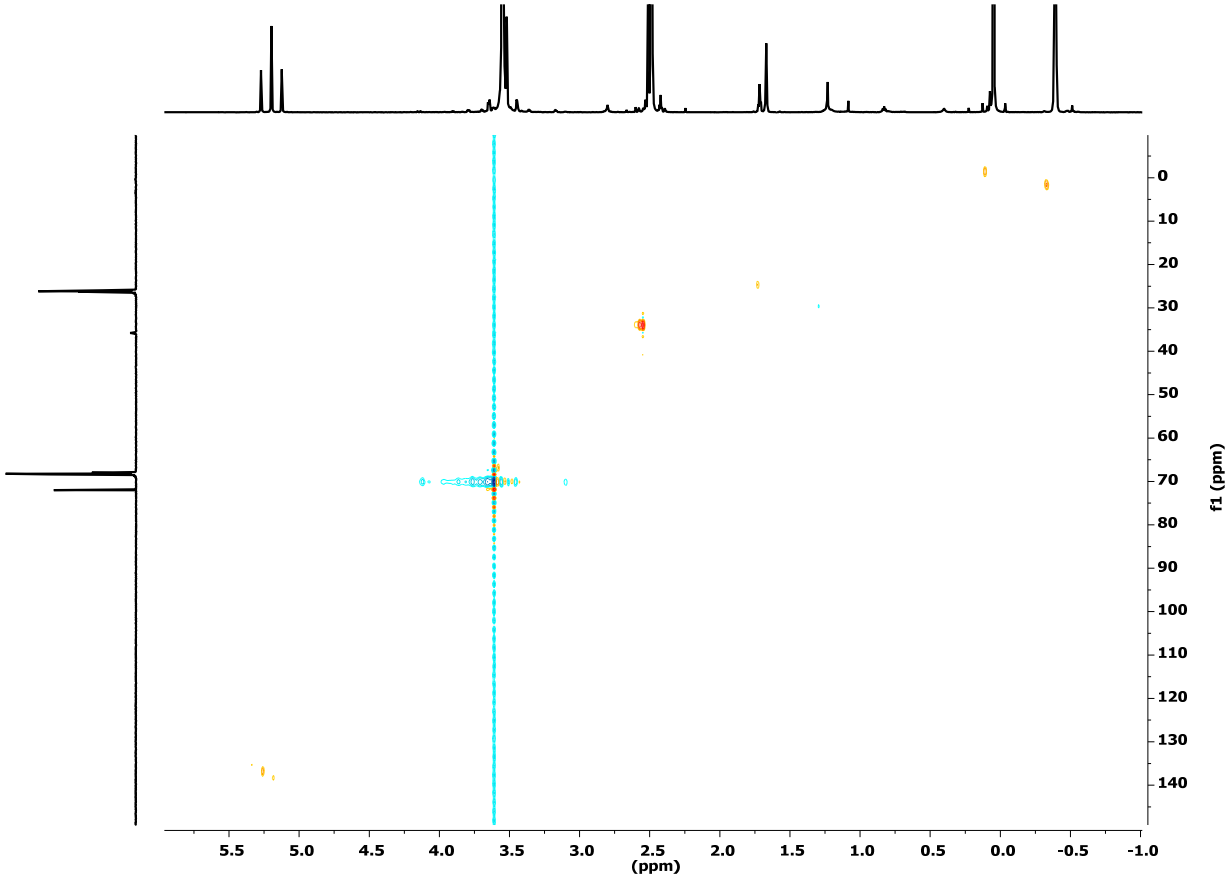
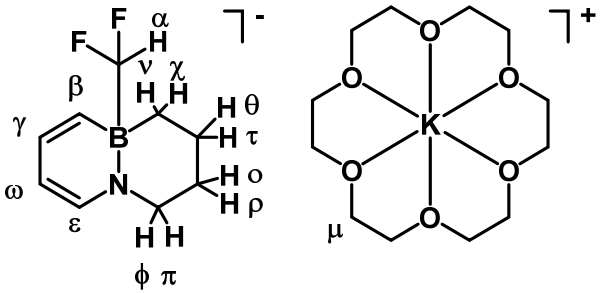


Fig. S8. ^{1}H- ^{13}C gHSQCAD Spectrum:





[K(18-crown-6)][1,2,3,4-tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine(CF_2H)] (2)

1,2,3,4-Tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine (471 mg, 3.59 mmol) and 18-crown-6 (934 mg, 3.59 mmol) were dissolved in 5 mL THF and cooled to 0 °C. Solid potassium toluide (466 mg, 3.58 mmol) was added in one portion and the mixture rapidly stirred for 10 minutes, providing a homogeneous red solution. Difluoromethane (180 mL gas, ~7 mmol) was added in one portion, and the solution stirred at room temperature for 30 minutes. The solution was poured into 100 mL pentane and stirred at room temperature for 15 minutes. The suspension was filtered and washed with pentane to provide the title compound as a red solid (1.091 mg, 62%). ^{1}H-NMR (THF-d_8): 5.78 (γ, 1H, (t, $J_{1H\text{-}1H}$=8.4)), 5.72 (α, 1H, (t, $J_{1H\text{-}19F}$=51.7)), 5.71 (ε, 1H, (d, $J_{1H\text{-}1H}$=6.6)), 4.66 (ß, 1H, (d, $J_{1H\text{-}1H}$=11.8)), 3.75 (ω, 1H, (ddd, $J_{1H\text{-}1H}$=6.6, 5.1, 1.4)), 3.61 (μ, 24H, s), 3.44 (π, 1H, (tt, $J_{1H\text{-}1H}$=11.9, 2.7)), 2.60 (ϕ, 1H, (dt, $J_{1H\text{-}1H}$=11.8, 2.7)), 1.73 (θ, 1H, overlap)), 1.67 (τ, 1H, overlap)), 1.41 (ο, 1H, overlap)), 1.36 (ρ, 1H, overlap)), 0.37 (ν, 1H, (d, $J_{1H\text{-}1H}$=12.5)), 0.11 (χ, 1H, broad). ^{13}C-NMR: 140.95, 136.68 (broad), 128.51 (broad), 127.26, 89.24, 70.06, 54.54, 31.24, 25.94, 18.28 (broad). ^{19}F-NMR: -127.10 (1F, ddd, $J_{19F\text{-}1H,\ 19F\text{-}11B}$=311.0, 54.0, 20.7), -131.96 (1F, ddd, $J_{19F\text{-}1H,\ 19F\text{-}11B}$=312.6, 51.9, 28.6). ^{11}B-NMR: -10.22 (1B, sharp).

Fig. S9. ^{1}H NMR Spectrum:

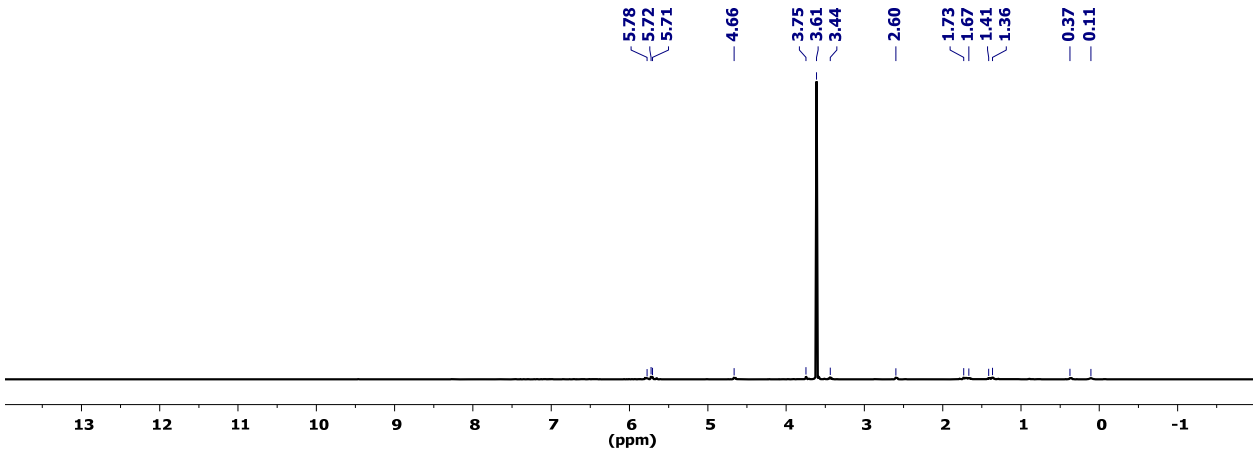


Fig. S10. ^{1}H NMR Spectrum (magnified):

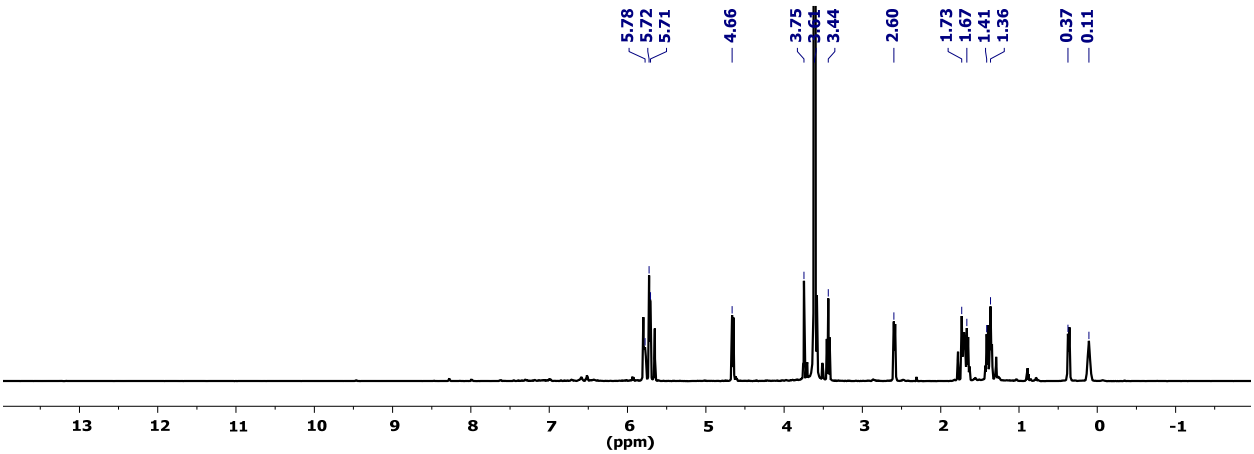


Fig. S11. ^{13}C NMR Spectrum:

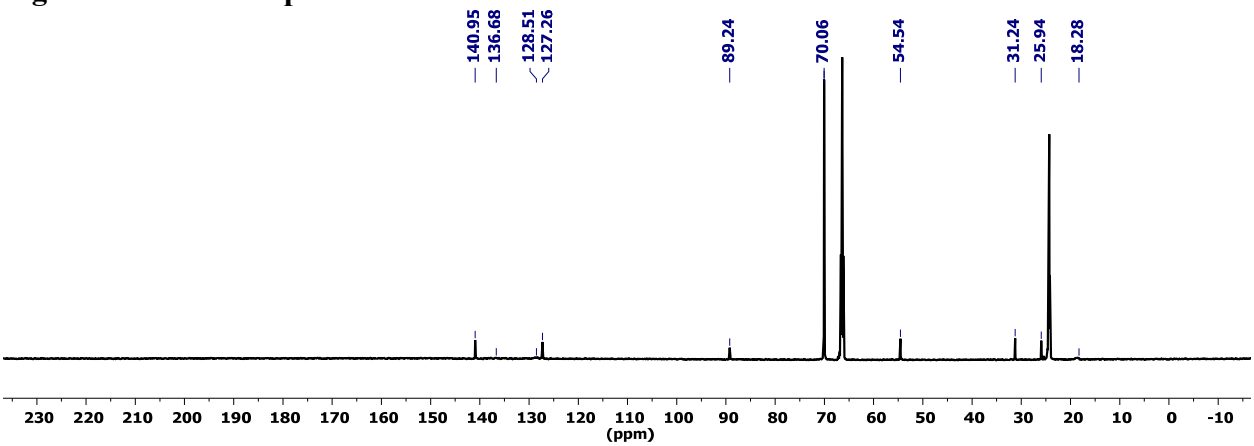


Fig. S12. ^{19}F NMR Spectrum:

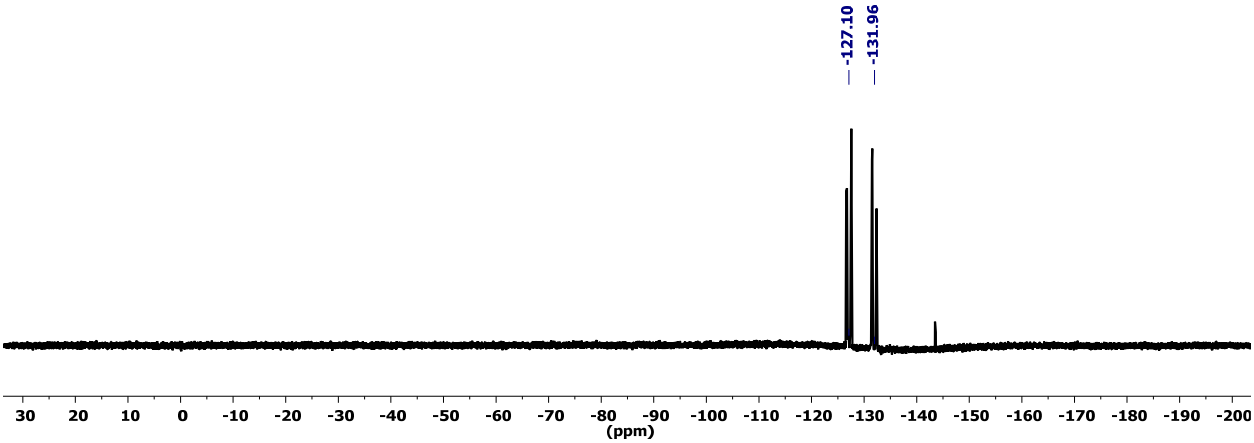


Fig. S13. ^{11}B NMR Spectrum:

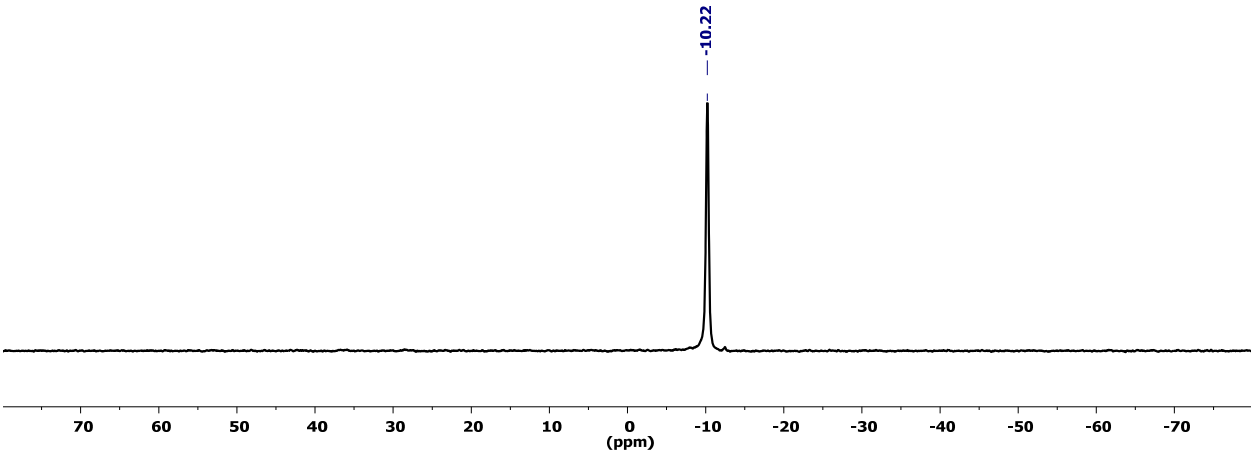


Fig. S14. ^{1}H- ^{1}H gCOSY Spectrum:

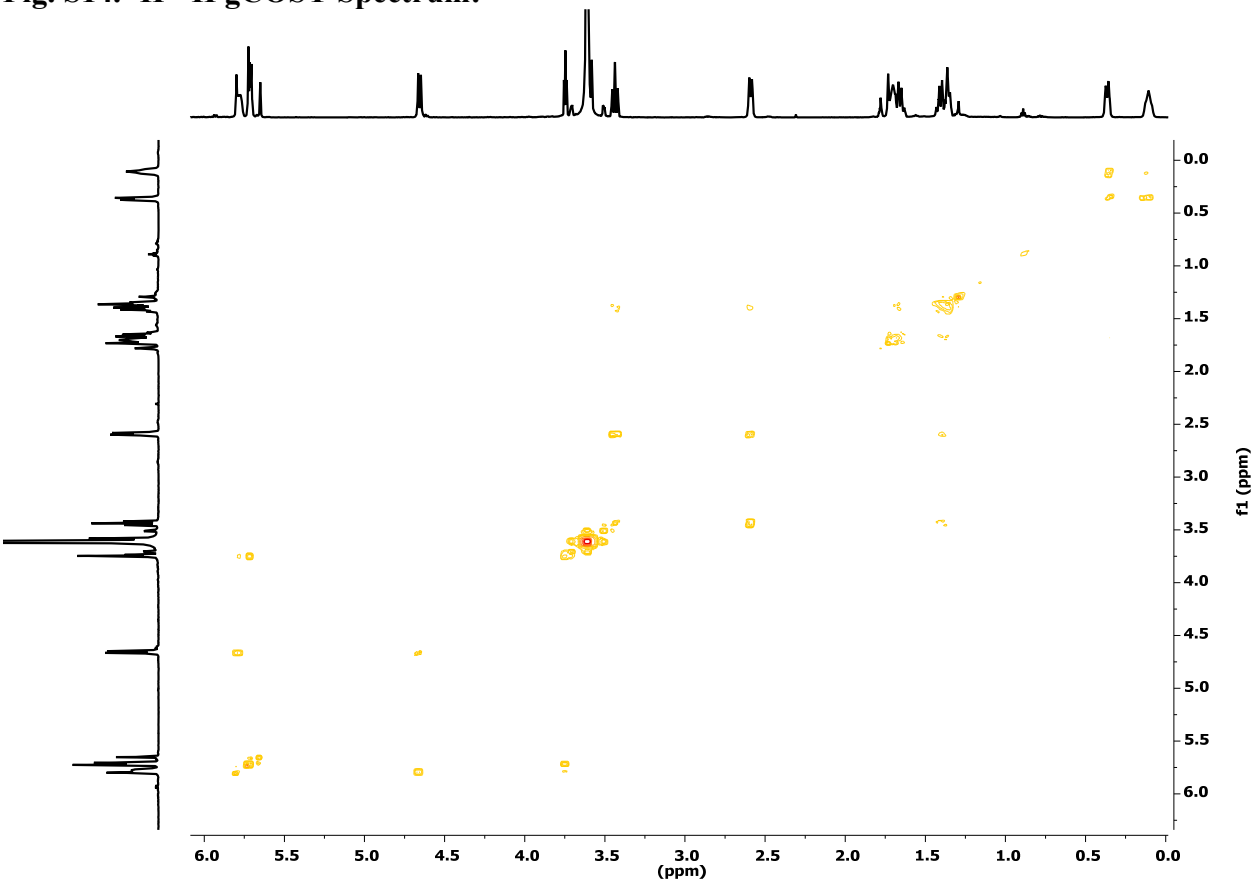
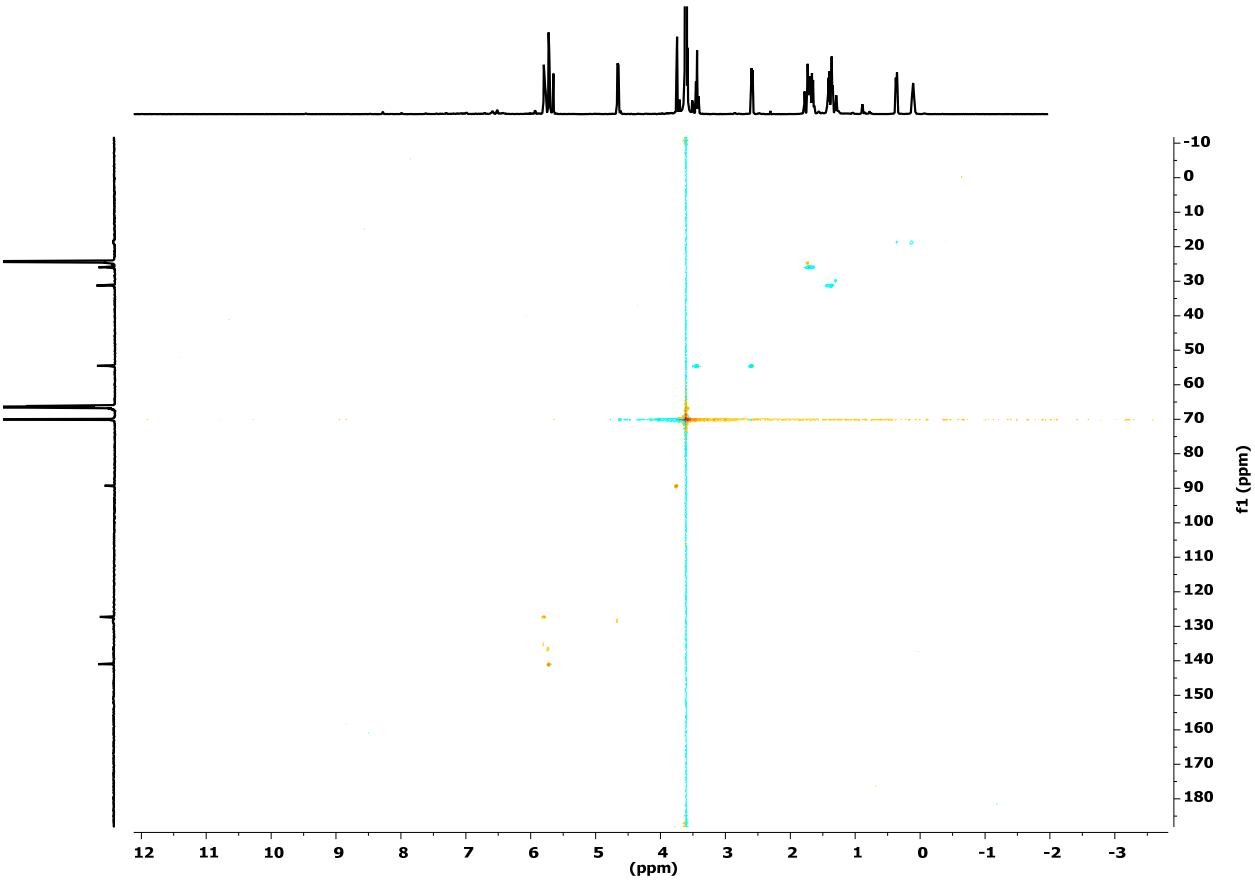
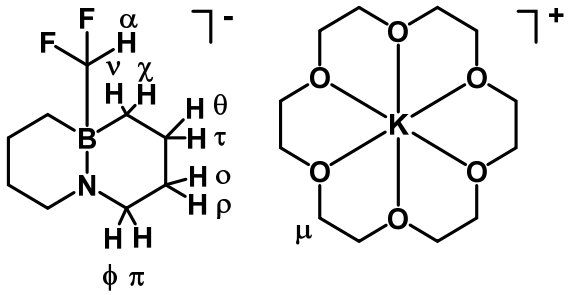


Fig. S15. ^{1}H- ^{13}C gHSQCAD Spectrum:





[K(18-crown-6)][octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine(CF_2H)] (3)

Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine (1.00 g, 7.23 mmol) was dissolved in 36 mL THF and cooled to -80 °C. A solution of $KN(iPr)_2$ (0.967 g, 6.95 mmol) in 10 mL THF cooled at -80 °C was then added in one portion, and the mixture stirred for one minute. The reaction vessel was sealed with a septum and difluoromethane (361 mL, 13.9 mmol) was added as a gas using a syringe with rapid stirring. After ten minutes, 18-crown-6 (1.908 g, 7.23 mmol) was then added, the mixture stirred until homogeneous at room temperature (15 minutes), and poured into 200 mL pentane. The suspension was stirred at room temperature for 15 minutes, filtered, and the filtercake washed with pentane (300 mL) to afford the title compound as a crystalline white solid (2.83 g, 78%). ^{1}H-NMR (THF-d_8): 5.93 (α, 1H, (t, $J_{1H\text{-}19F}$=51.3)), 3.62 (μ, 24H, s), 2.86 (π, 1H, (td, $J_{1H\text{-}1H}$=9.0, 4.6)), 2.48 (χ, 1H, (d, $J_{1H\text{-}1H}$=10.6)), 1.56 (o, 1H, overlap)), 1.55 (θ, 1H, overlap)), 1.51 (ρ, 1H, overlap)), 1.24 (τ, 1H, (td, $J_{1H\text{-}1H}$=9.1, 7.1, 4.5)), 0.10 (ν, 1H, (dd, $J_{1H\text{-}1H}$=12.9, 5.3)), 0.06 (χ, 1H, broad). ^{13}C-NMR: 70.03, 54.21, 29.72, 25.96, 18.80 (broad). ^{19}F-NMR: -127.04 (2F, dd, $J_{19F\text{-}1H,\ 19F\text{-}11B}$=51.9, 18.0). ^{11}B-NMR: -12.38 (1B, sharp). A single crystal was obtained by allowing pentane to diffuse into a saturated solution of **1** in THF at -30 °C.

Alternate Preparation:

Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine (274 mg, 2.00 mmol) and 18-crown-6 (528 mg, 2.00 mmol) were dissolved in 10 mL THF and cooled to 0 °C. Solid KCH_2Ph (260 mg, 2.00 mmol) was then added in one portion, and the mixture stirred for 15 minutes. The reaction vessel was sealed with a septum and difluoromethane (100 mL, ~4.0 mmol) was added as a gas using a syringe with rapid stirring. After ten minutes, the mixture was poured into 100 mL pentane. The suspension was stirred at room temperature for 15 minutes, filtered, and the filtercake washed with pentane (300 mL) to afford the title compound as a crystalline white solid (330 mg, 34%).

Fig. S16. ^{1}H NMR Spectrum:

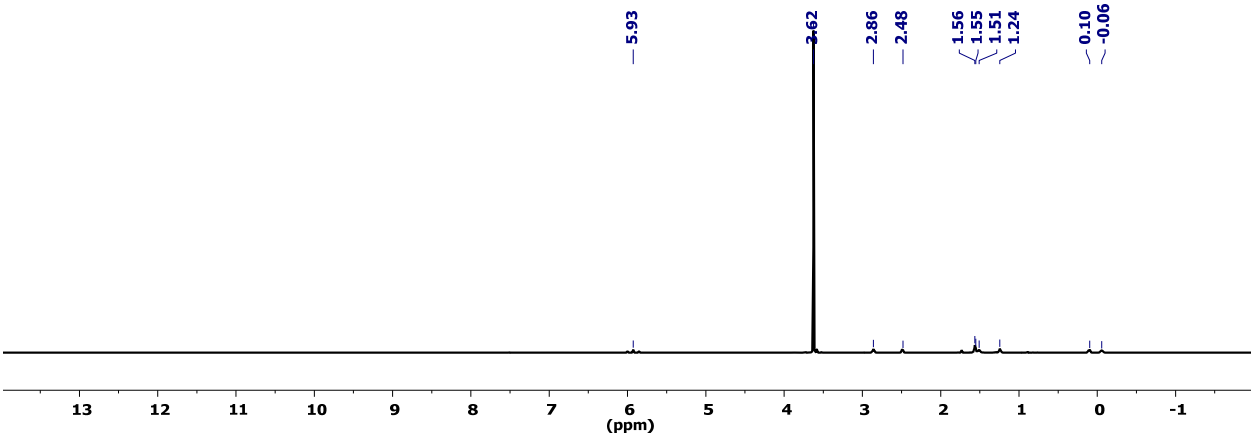


Fig. S17. ^{1}H NMR Spectrum (magnified):

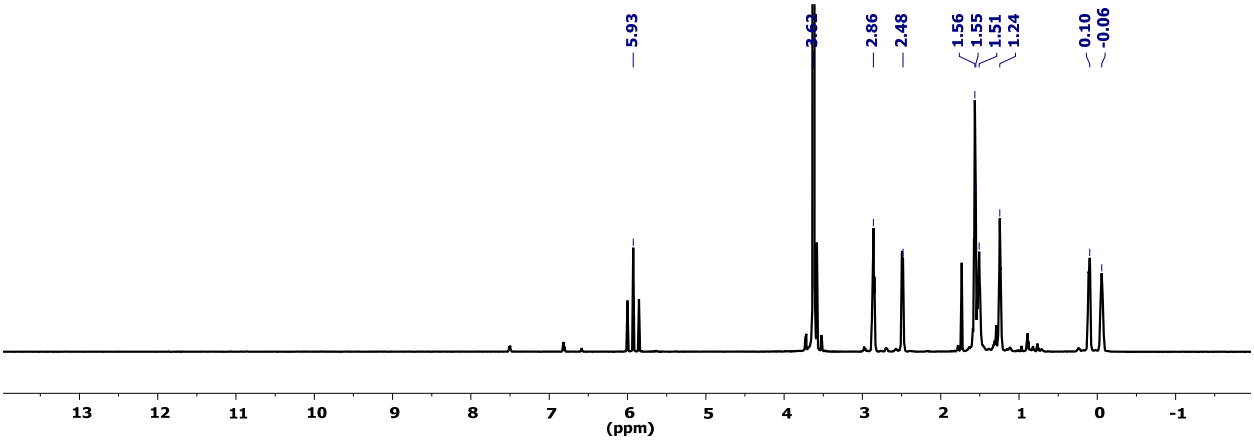


Fig. S18. ^{13}C NMR Spectrum:

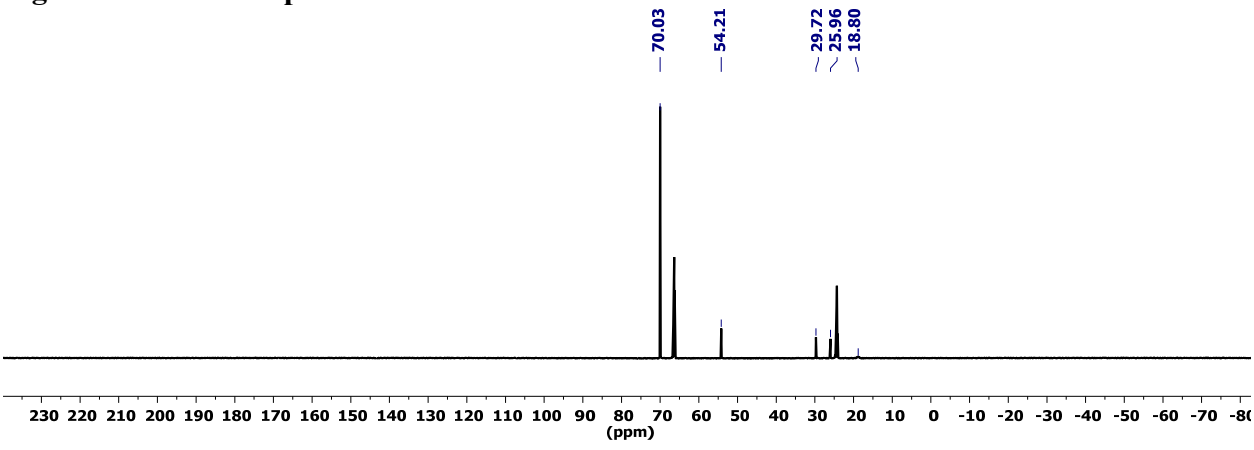


Fig. S19. ^{19}F NMR Spectrum:

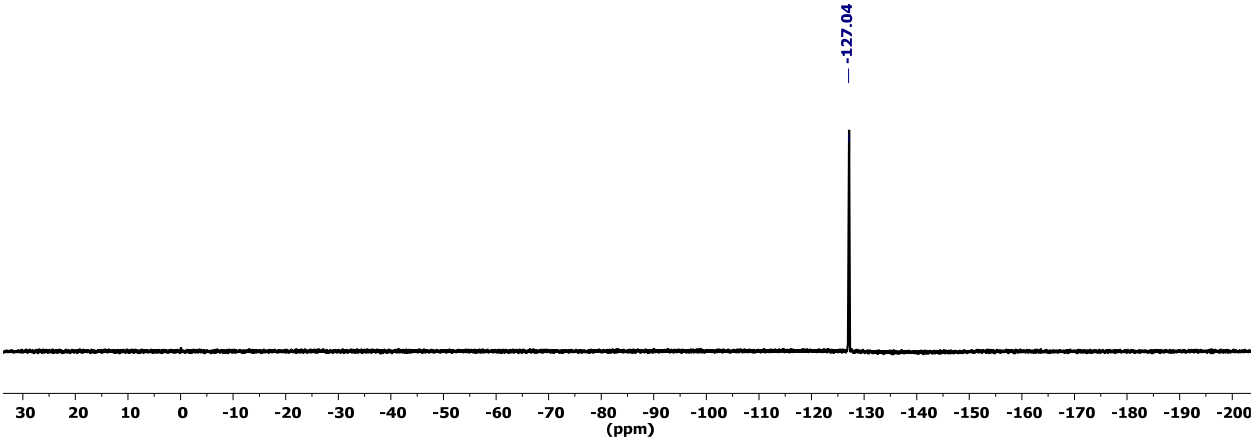


Fig. S20. ^{11}B NMR Spectrum:

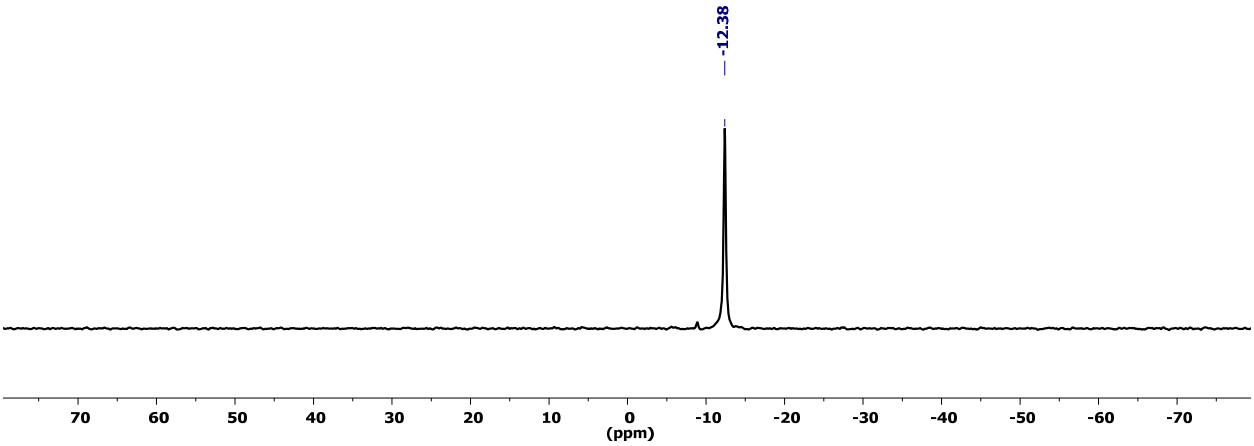


Fig. S21. ^{1}H- ^{1}H gCOSY Spectrum:

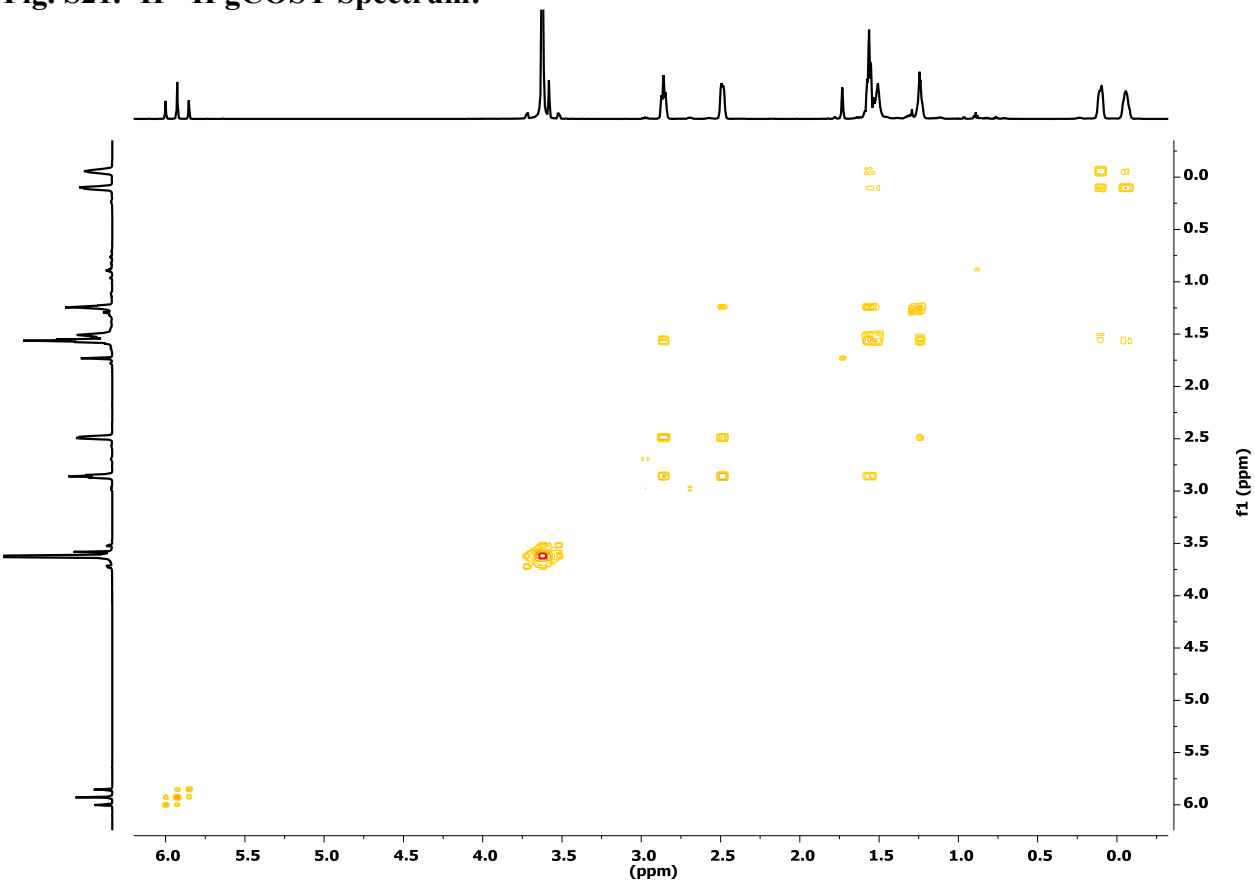
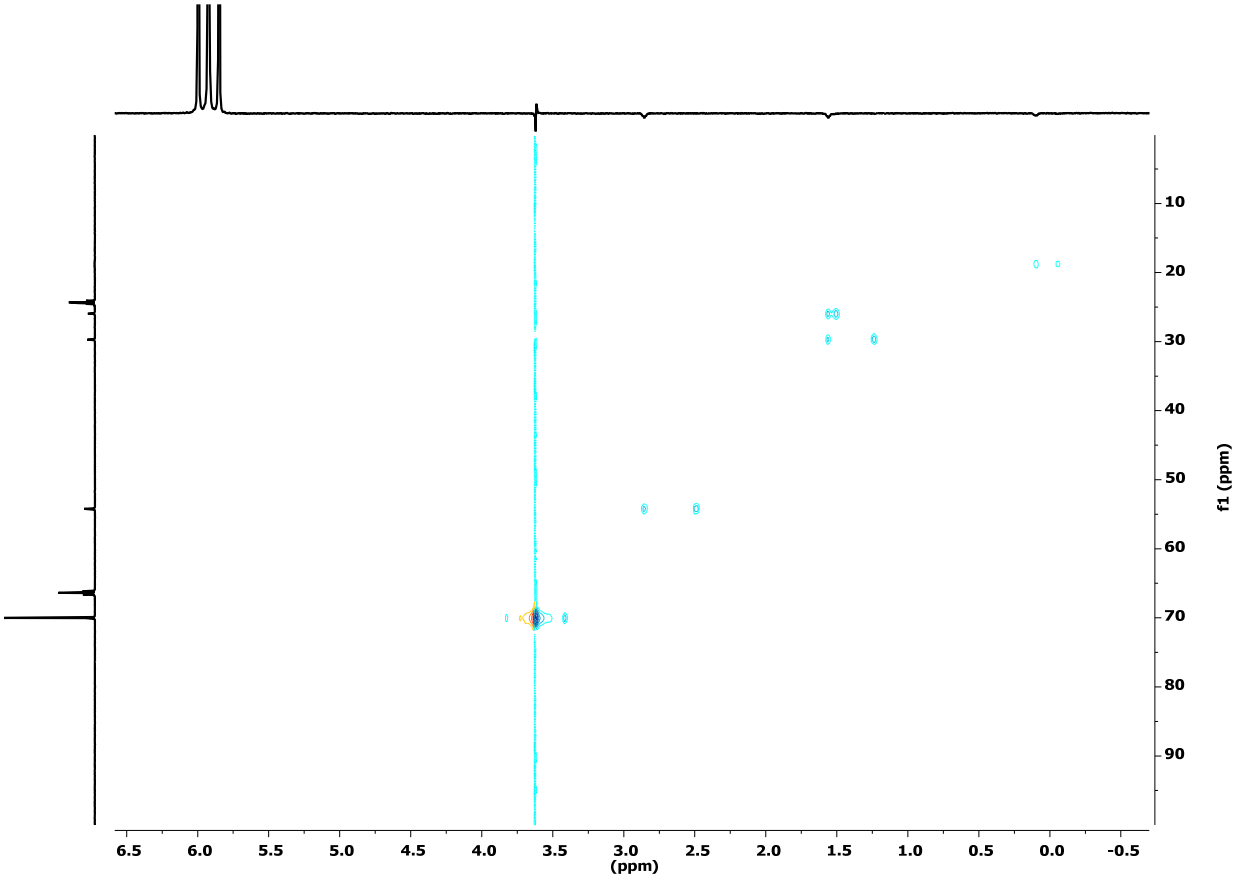


Fig. S22. ^{1}H- ^{13}C gHSQCAD Spectrum:



Reaction between 1 and 4, *in-situ* characterization of 7

1 (9.7 mg, 20 μmol) and **4** (8.4 mg, 20 μmol) were dissolved in 1 mL THF-d_8 at 25 °C, and the reaction mixture allowed to stand for one hour. The mixture was then analyzed by NMR spectroscopy. A new compound was observed in 97% chemical yield. ^{1}H-NMR (THF-d_8): 7.86 (ε, 1H), 7.60 (υ, 2H, (d, $J_{1H\text{-}1H}$=7.4)), 7.40 (ι, 2H, (t, $J_{1H\text{-}1H}$=7.7)), 7.29 (κ, 1H, (t, $J_{1H\text{-}1H}$=7.4)), 5.55 (α, 1H, (t, $J_{1H\text{-}19F}$=51.0)), 4.89 (ß, 1H), 4.85 (γ, 1H), 4.07 (ω, 1H), 3.24 (ϕ, 1H), 2.94 (π, 1H), 2.30 (ζ, 4H), 2.15 (ψ, 12H), 1.75 (ο, 1H), 1.60 (θ, 1H), 1.55 (τ, 1H), 1.35 (ρ, 1H), 0.89 (ν, 1H), 0.46 (χ, 1H). ^{19}F-NMR: -126.09 (1F, dd, $J_{19F\text{-}1H,\ 19F\text{-}19F}$=313.5, 51.6), -129.01 (1F, dd, $J_{19F\text{-}1H,\ 19F\text{-}19F}$=313.3, 51.0). ^{11}B-NMR: -10.66 (1B, sharp).

The resonances observed in the ^{1}H and ^{13}C NMR spectra were assigned primarily on the basis of H-H coupling observed in the ^{1}H-^{1}H COSY spectrum. The sp^3 α-C-H group adjacent to the boryl-CF_2H group (χ) was used as a starting point, permitting assignment of all the hydrogen atoms in the aliphatic ring. ε was then assigned on the basis of a crosspeak with ϕ, which enabled assignment of the resonances corresponding to the azaborine ring. The location of Pd binding was determined by comparing the energies and calculated ^{1}H-NMR shifts of the azaborine C-H groups in structures with varied Pd coordination.

Fig. S23. Proposed Structure of 7:

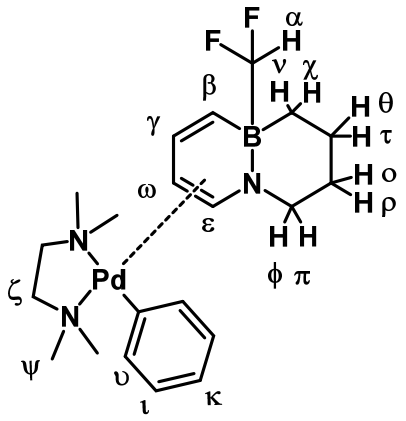


Fig. S24. ^{1}H NMR Spectrum:

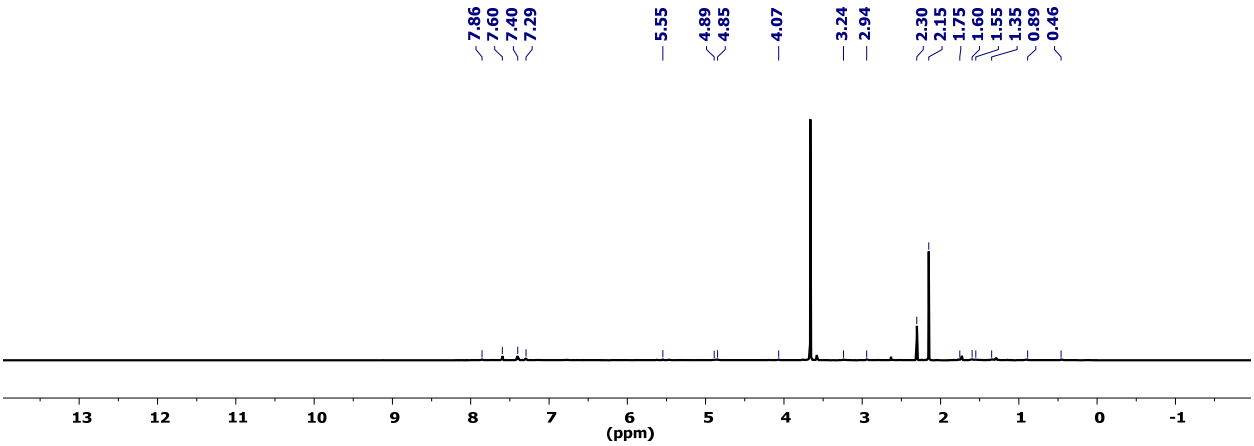
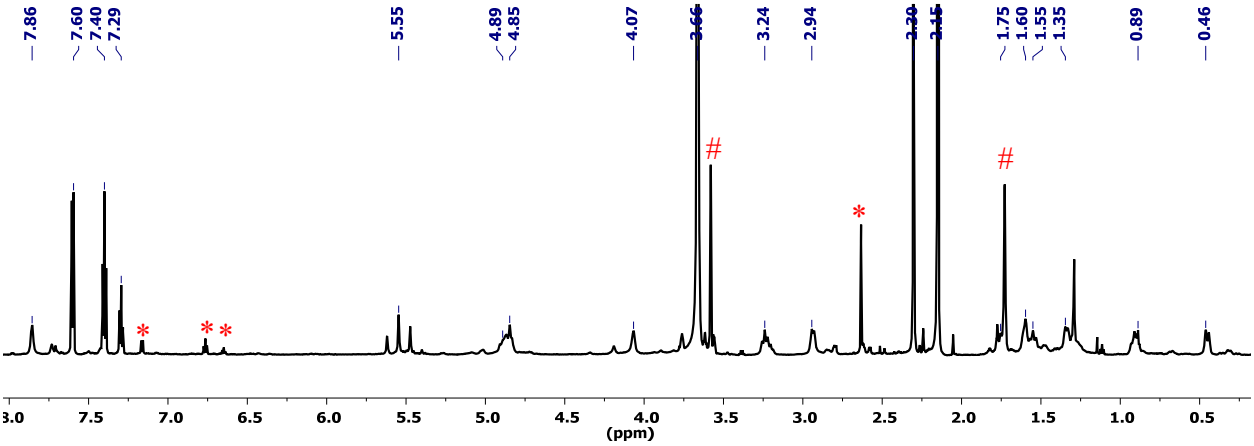


Fig. S25. ^{1}H NMR Spectrum (magnified):



***: Pd(TMEDA)(Ph)(I). #: THF**

Fig. S26. ^{13}C NMR Spectrum:

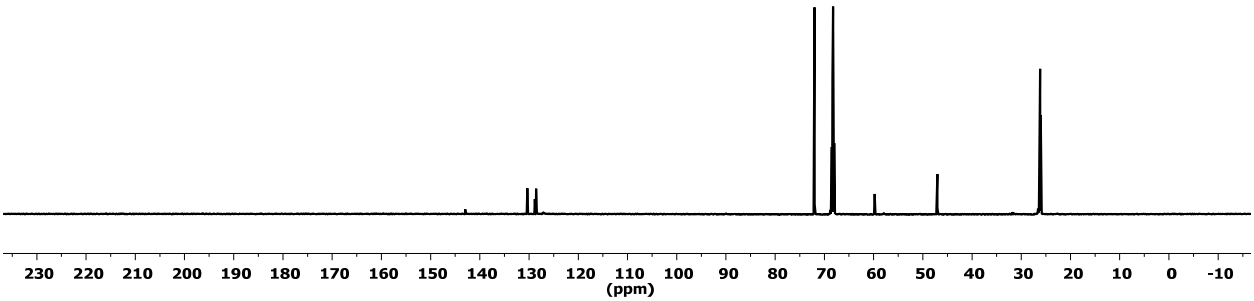


Fig. S27. ^{19}F NMR Spectrum:

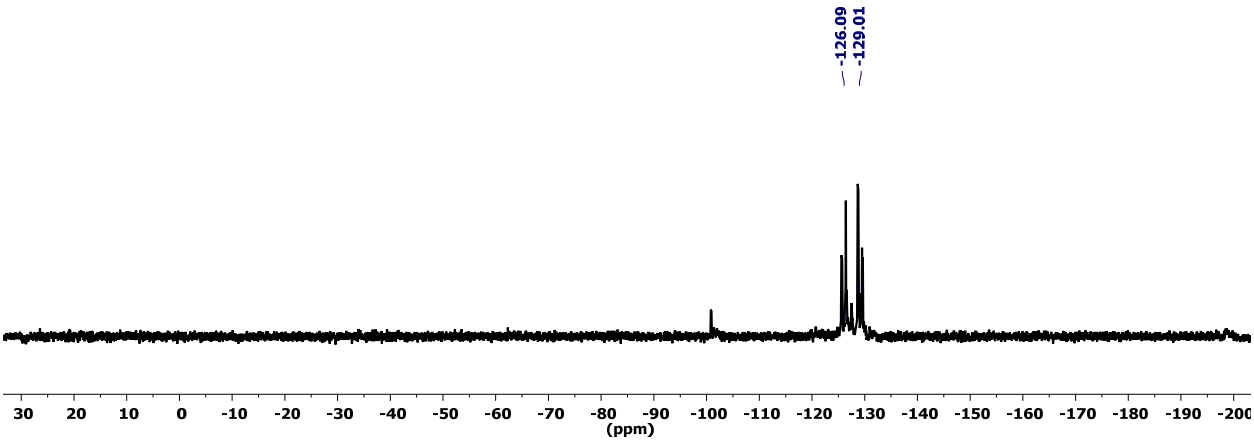


Fig. S28. ^{11}B NMR Spectrum:

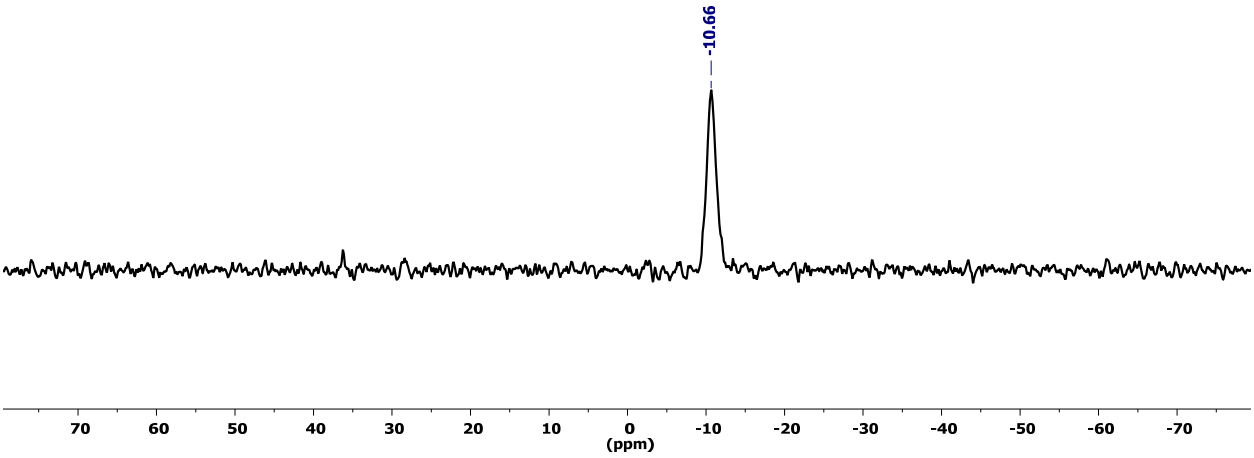


Fig. S29. ^{1}H-^{1}H gCOSY Spectrum:

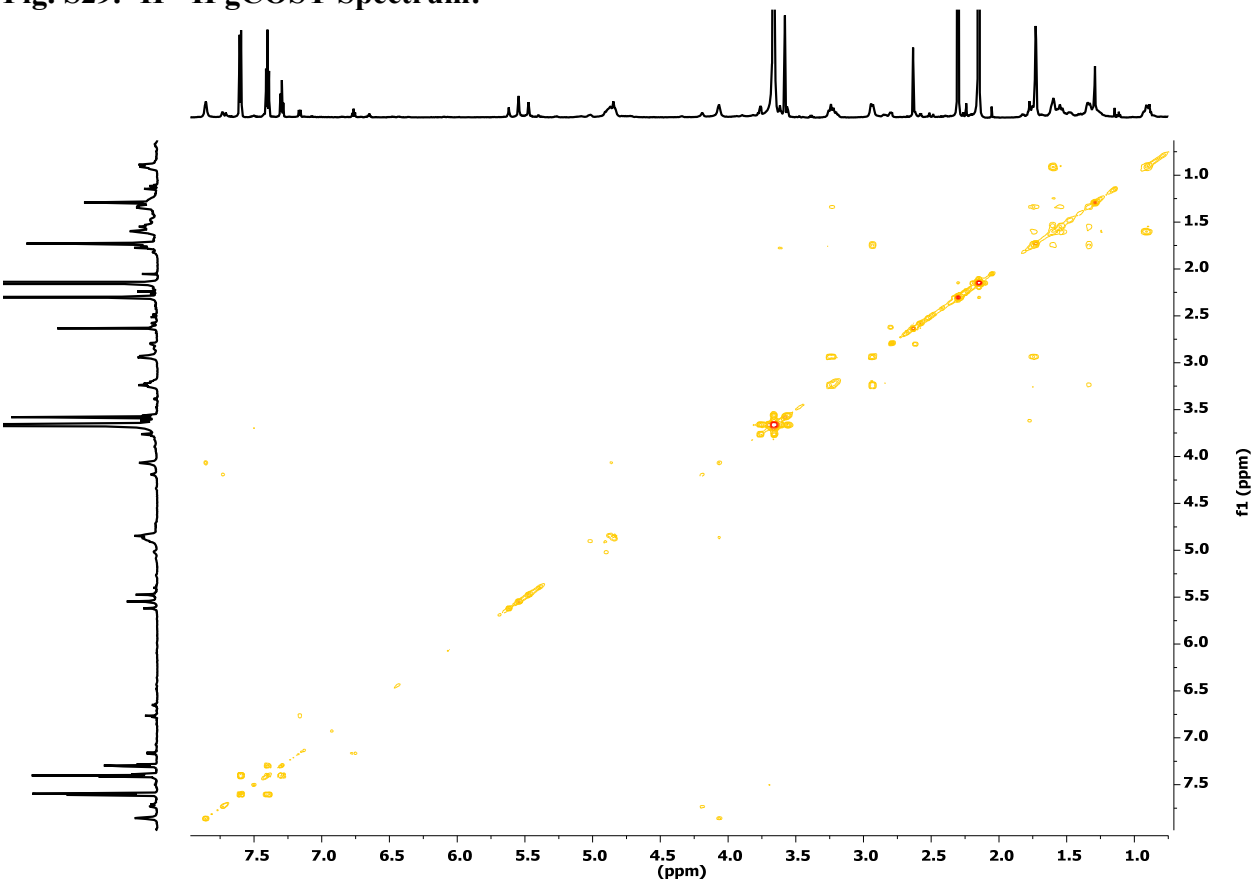
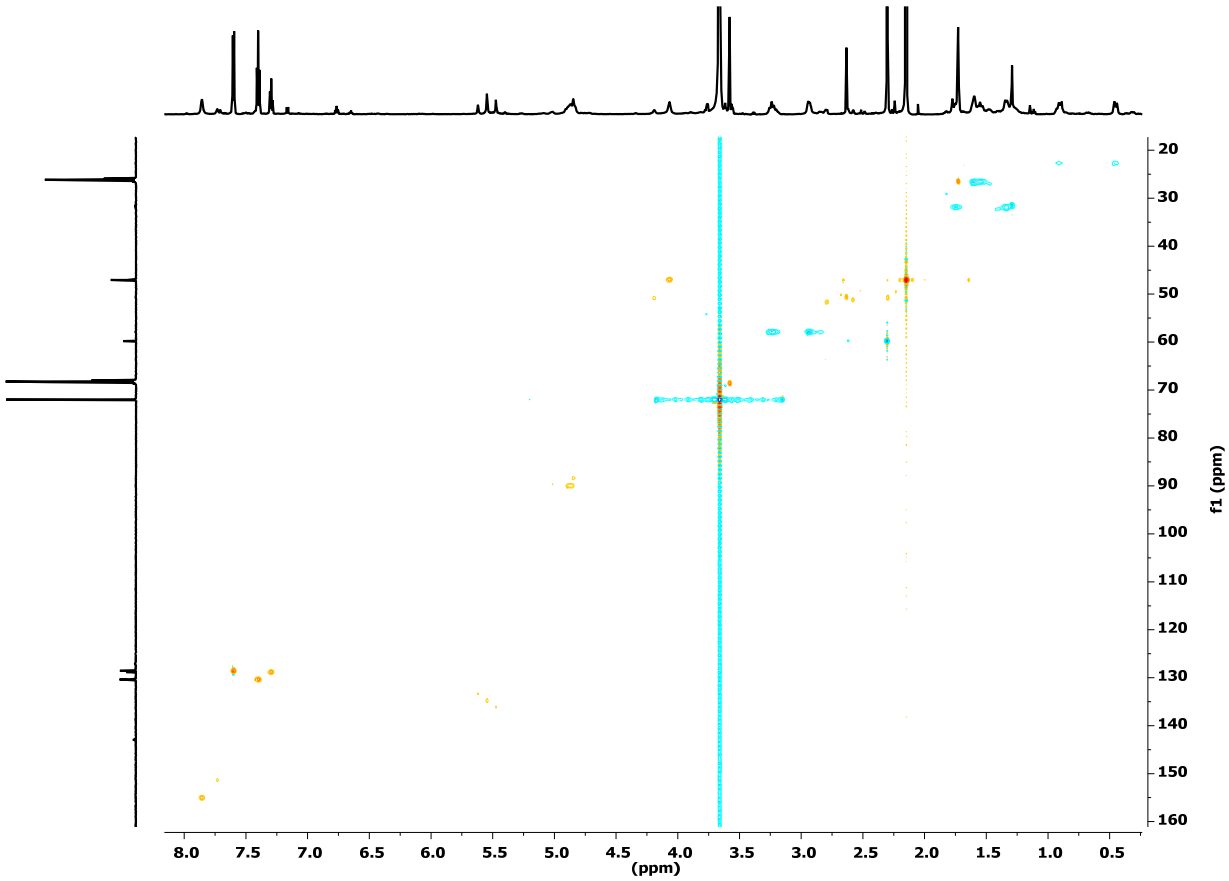


Fig. S30. ^{1}H- ^{13}C gHSQCAD Spectrum:

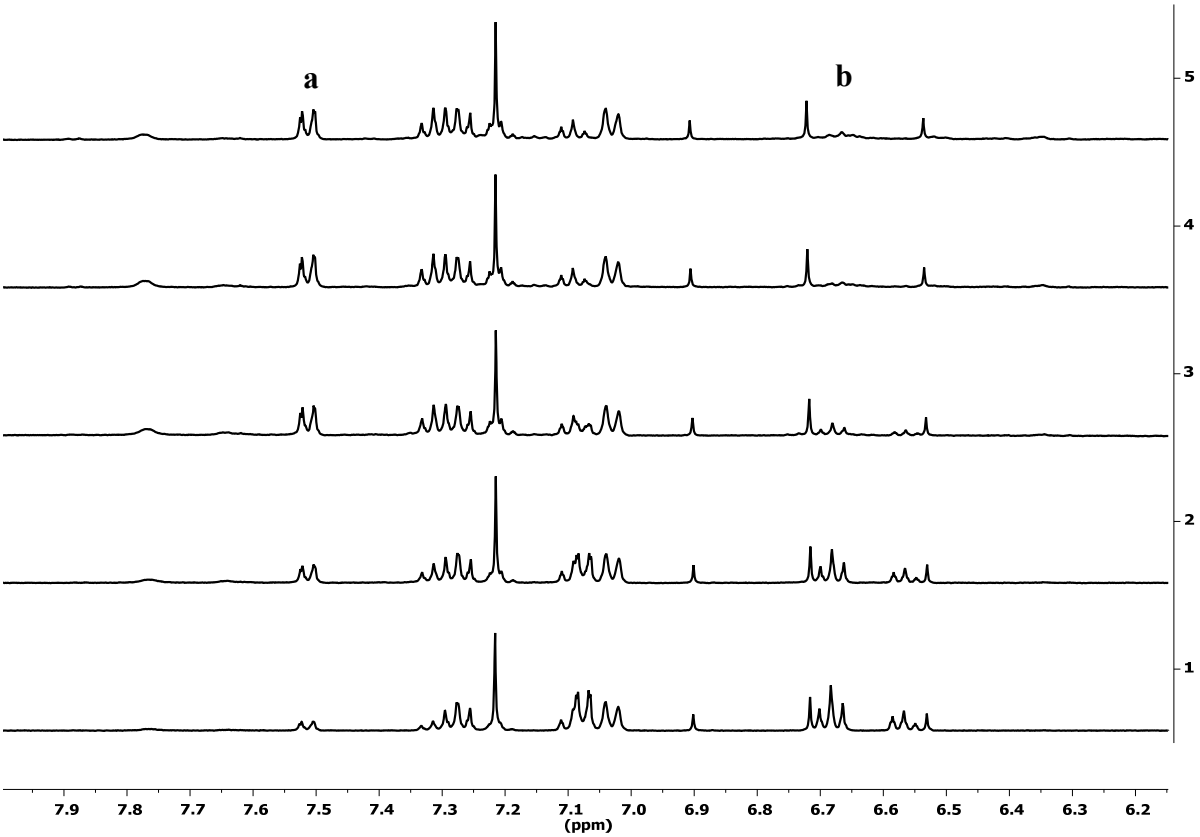


Titration of 1 with 4

1 and **4** were combined as stock solutions in THF to produce solutions with desired concentrations in the presence of 10.0 mM difluoromethyl phenyl ether as internal standard. Conversion to **5** was monitored by ^{1}H NMR spectroscopy. The *o*- protons in C_6H_5-OCF_2H and the *o*- protons in the Pd-C_6H_5 unit in **5** were integrated in the ^{1}H NMR spectrum to provide the concentration of **5**.

Conc. **1**	Conc. **4**	Yield **7** (vs. **4**)
2.50 mM	10.0 mM	29%
5.00 mM	10.0 mM	58%
10.0 mM	10.0 mM	97%
15.0 mM	10.0 mM	98%
20.0 mM	10.0 mM	87%

Fig. S31. Stacked ^{1}H-NMR spectra used to determine yield of 7:



1: 2.5 mM **1**; 2: 5.0 mM **1**; 3: 10.0 mM **1**; 4: 15 mM **1**; 5: 20 mM **1**.
a: resonance used for quantification of **7**. b: resonance used to quantify **4**.

Reaction of 1 or 3 with 4

1 (10.4 mg, 20 µmol) or **3** (9.7 mg, 20 µmol) and **4** (8.4 mg, 20 µmol) were dissolved in 1 mL THF-d_8 at 25 °C, and the reaction mixture allowed to stand for one hour. The mixture was then analyzed by NMR spectroscopy. No new products were observed. After heating these mixtures at 80 °C for 12 hours, Pd(TMEDA)(CF_2H)$_2$ (^{19}F NMR: -101; lit: -100.5) was observed in trace yield (**2**: 1.4%; **3**: 3.4%).

Preparation of Pd(TMEDA)(Ph)(CF_2H) and Pd(TMEDA)(CF_2H)$_2$ from 2 and 4

1 and **4** were dissolved in 1 mL THF at 25 °C, and the reaction mixture heated at 80 °C for two hours. The mixture was then analyzed by NMR spectroscopy. Pd(TMEDA)(CF_2H)$_2$ (^{19}F NMR: -100.5 in DMF-d_7)[11] and Pd(TMEDA)(Ph)(CF_2H) (^{19}F NMR: -100.3 in $CDCl_3$)[12] were observed. When 20 µmol **1** and 20 µmol **4** were combined, the yields of these products were 54% and 5%. When 20 µmol **1** and 30 µmol **4** were combined, the product distribution changed and the yields were 28% and 26%. DPPF (40 µmol, 22.2 mg) was then added to each reaction, and the reactions were then heated to 80 °C for a further two hours, and ^{19}F-NMR spectra were recorded to measure the yield of difluoromethylbenzene (-111.24 ppm, 99%, 26% combined yield). The presence of difluoromethylbenzene was validated by GC-MS with comparison to an authentic sample.

We found that the steric profile of the palladium-coordinated ligands dramatically influences the success of the transmetalation. For instance, when using Pd(DPPF)(I)(Ph), we did not observe CF_2H^- transfer, in contrast to the result using Pd(TMEDA)(I)(Ph). This result is consistent with the proposed mechanism that operates through an associative pathway – the more sterically encumbered ligand inhibits association.

Fig. S32. ^{19}F Spectrum after heating 1 (20 µmol) and 4 (20 µmol) in 1 mL THF:

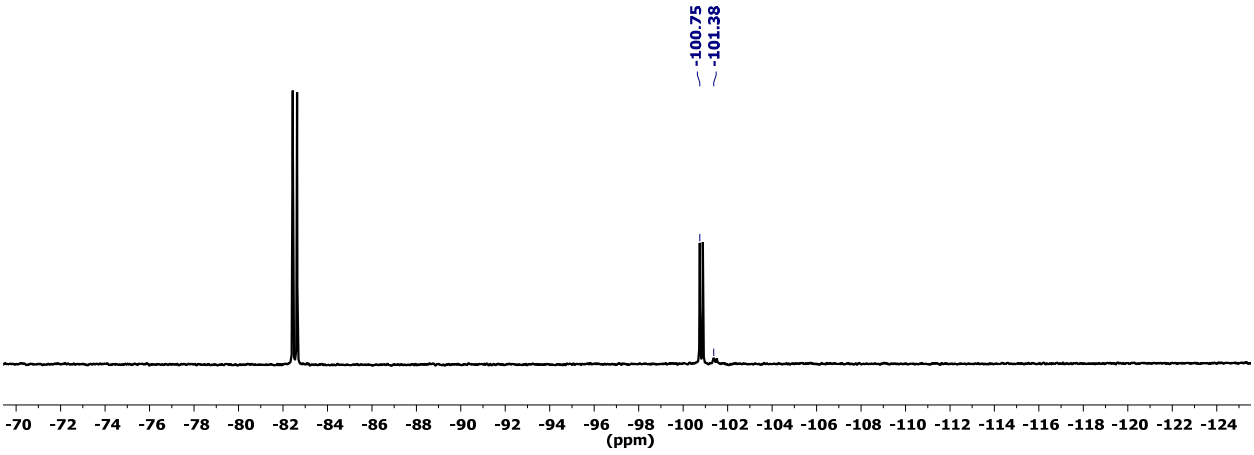


Fig. S33. ^{19}F Spectrum after addition of DPPF, heating at 80 °C for 2 hours:

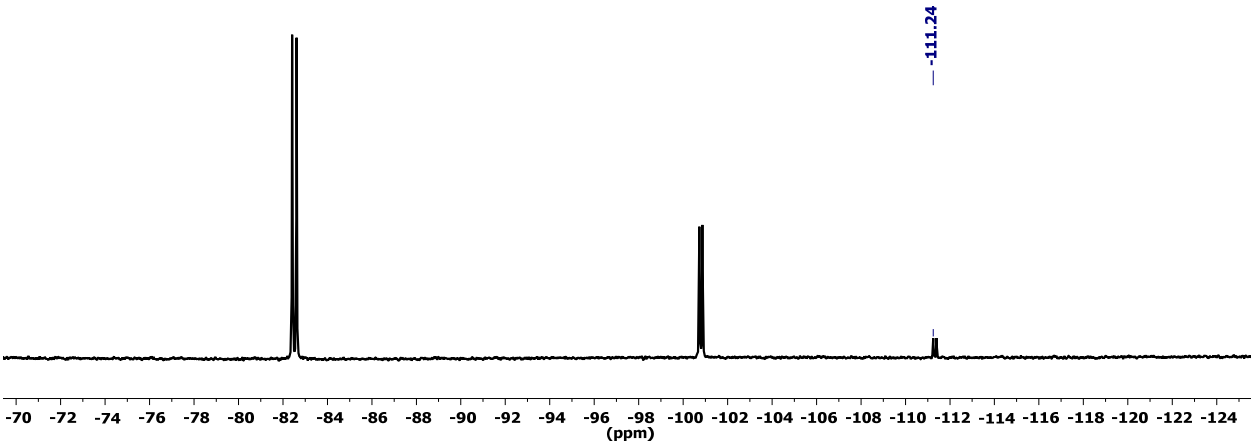


Fig. S34. ^{19}F Spectrum after heating 1 (20 µmol) and 4 (30 µmol) in 1 mL THF:

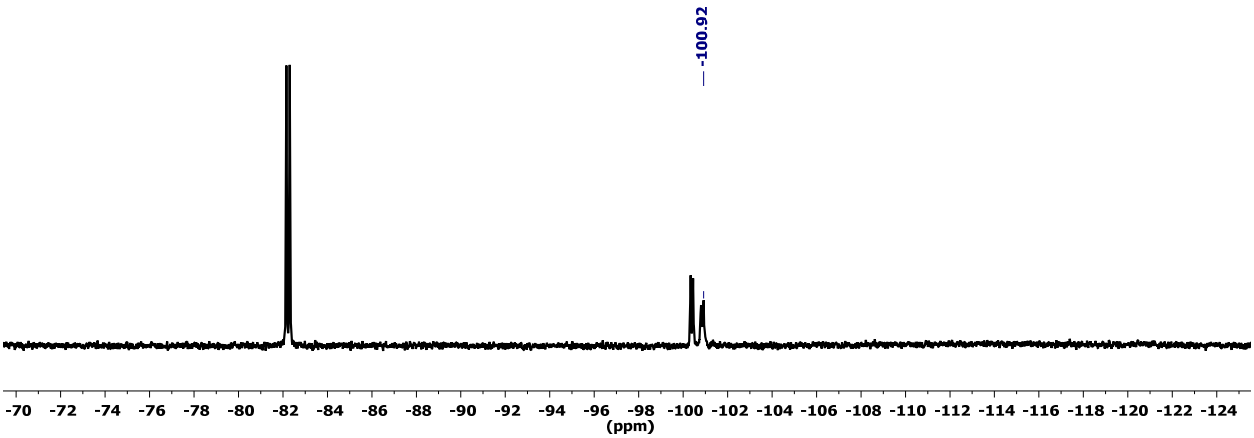


Fig. S35. ^{19}F Spectrum after addition of DPPF, heating at 80 °C for 2 hours:

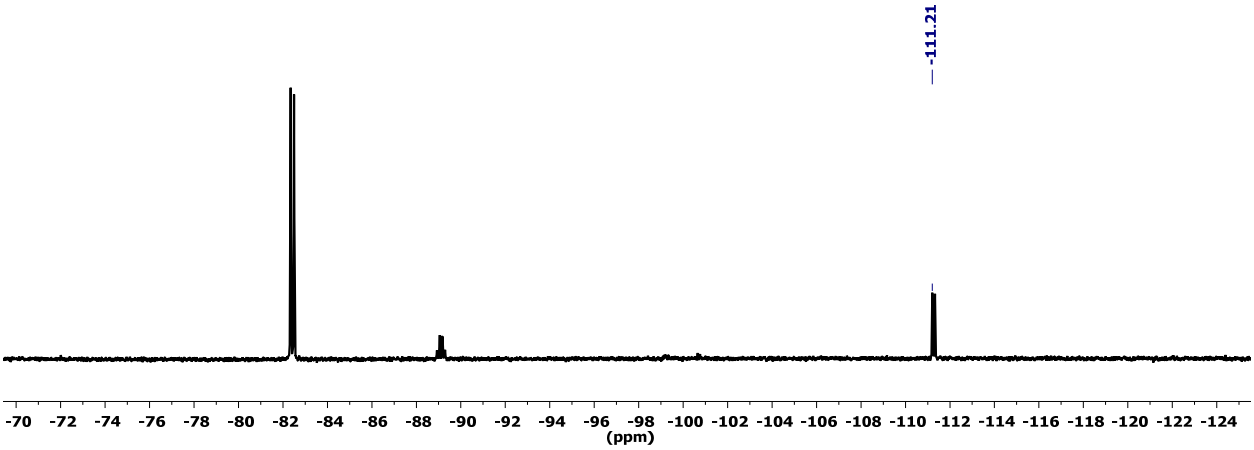


Fig. S36. GC-MS chromatogram for $PhCF_2H$ generated from reductive elimination:

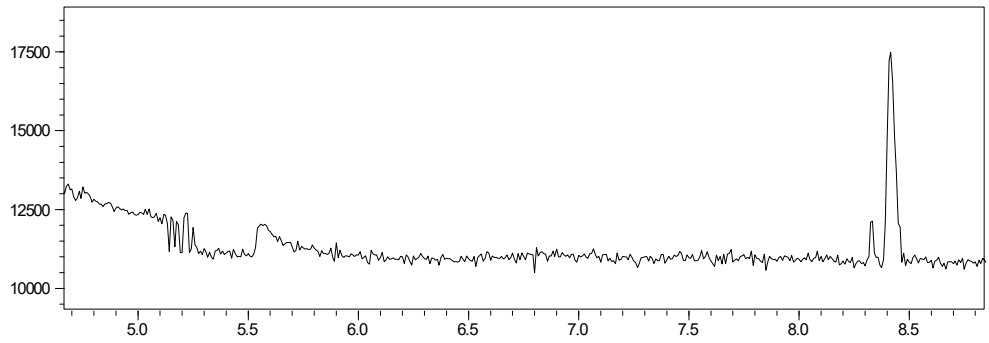


Fig. S37. GC-MS mass spectrum for $PhCF_2H$ generated from reductive elimination:

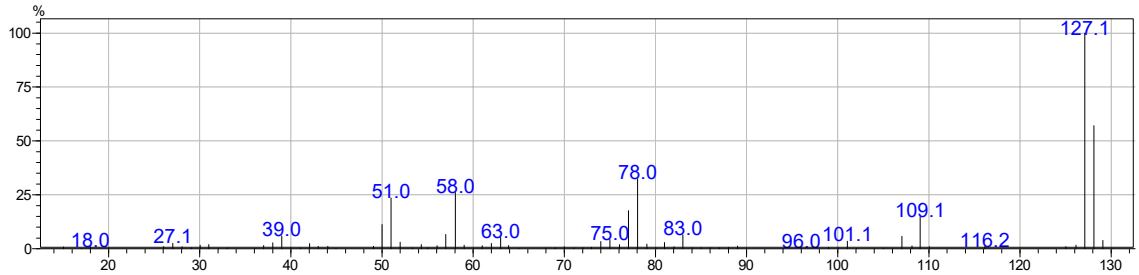


Fig. S38. GC-MS chromatogram for authentic $PhCF_2H$:

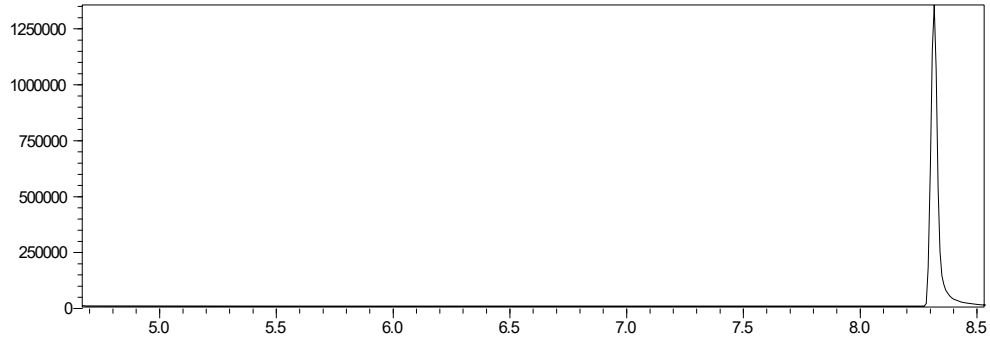
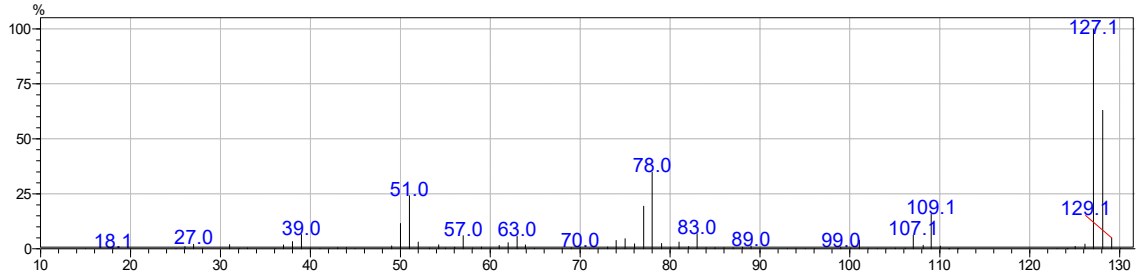


Fig. S39. GC-MS mass spectrum for authentic $PhCF_2H$:



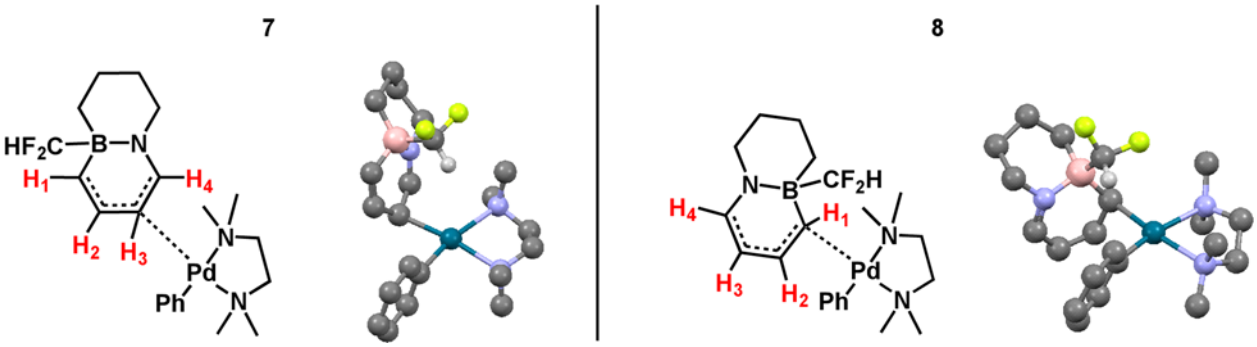
Calculated Energies of Optimized Structures

Name	Free Energy (Hartrees)
$B_3N_3Me_6$	-478.129782
1,2,3,4-Tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine	-391.409358
Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine	-393.779312
1	-716.499774
2	-629.767710
3	-632.140679
CF_2H^-	-238.307892
$B_3N_3Me_6CF_3^-$	-815.736660
CF_3^-	-337.568602
Pd(TMEDA)PhI (**4**)	-718.131841
7	-1336.342718
8	-1336.340669
9	-1336.281395
$Pd(TMEDA)PhCF_2H$	-944.976449
I^-	-11.562841

Calculated Binding Affinities

[LA]-CF_2H^-	CF_2H^- Affinity (Hartrees)	CF_2H^- Affinity (kcal/mol)	CF_3^- Affinity (Hartrees)	CF_3^- Affinity (kcal/mol)
$B_3N_3Me_6$	-0.052892	-33.19	-0.036617	-22.9
1,2,3,4-Tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine	-0.05046	-31.79	Not Calculated	Not Calculated
Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine	-0.053475	-33.689	Not Calculated	Not Calculated

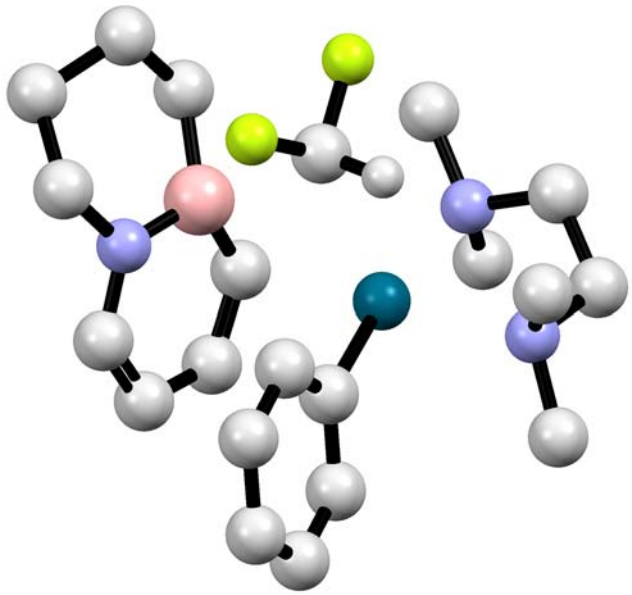
Calculated NMR shifts for possible isomers of 7



	Expt.			Calculated				
Atom	**2**	**7**	Δ(δH2/7)	**2**	**7**	Δ(δH2/7)	**8**	Δ(δH2/8)
H1	4.66	4.89	-0.23	4.8588	5.4002	-0.5414	2.5823	2.2765
H2	5.78	4.85	0.93	6.3579	5.0173	1.3406	7.6327	-1.2748
H3	3.75	4.07	-0.32	3.9618	3.152	0.8098	5.2937	-1.3319
H4	5.71	7.86	-2.15	6.1441	8.2015	-2.0574	6.2689	-0.1248

We calculated the change in NMR shift for H_{1-4} between free **2** and the two isomers identified as local minima **7** and **8**, and compared these shifts to that observed experimentally between **2** and the addition product. **7** was in better agreement with the data, and was predicted to be more stable than **8** by -1.4 kcal/mol.

Calculated Structure of 9



Calculated Structures

$B_3N_3Me_6$

¶

B	1.20092400	-0.81877000	0.01129100
N	1.28459700	0.61874300	-0.03097000
B	0.10865200	1.44947700	0.01124600
B	-1.30941200	-0.63066700	0.01112100
N	-1.17801400	0.80315400	-0.03123600
N	-0.10655400	-1.42190100	-0.03071300
C	0.22751200	3.03123800	0.11656900
H	1.13426800	3.34344400	0.64088200
H	0.26330800	3.49233200	-0.87923000
H	-0.62323100	3.47592100	0.63906200
C	2.60257700	1.25285400	-0.09535300
H	3.30895400	0.61887300	-0.63368300
H	2.54716000	2.20305900	-0.62892800
H	3.01652300	1.44876900	0.90136100
C	2.51158400	-1.71241400	0.11516900
H	2.89317700	-1.97144100	-0.88124900
H	3.32194600	-1.19900800	0.63879200
H	2.32898600	-2.65511400	0.63717400
C	-0.21625200	-2.88047600	-0.09440900
H	0.63324200	-3.30759400	-0.62979500
H	-0.25093900	-3.33669400	0.90257100
H	-1.11971700	-3.17559000	-0.63041100
C	-2.73893000	-1.31819400	0.11567400
H	-3.15635700	-1.51584400	-0.88044700
H	-2.69961500	-2.27810400	0.63678500
H	-3.46232600	-0.68917400	0.64071600
C	-2.38653200	1.62692600	-0.09579300
H	-3.18049300	1.10454000	-0.63193100
H	-2.76518800	1.88476400	0.90088600
H	-2.19047300	2.55709100	-0.63155600

1,2,3,4-Tetrahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine

C	2.31048600	-0.70911000	0.39465000
C	1.08793200	-1.46031900	-0.11263000
C	1.28653300	1.54687900	0.03601800
C	2.46680000	0.63507600	-0.31532400
H	-1.23654900	-2.42223100	-0.09280000
H	3.18711900	-1.34574700	0.24075300
H	0.93383500	-2.37482300	0.46774200
C	-1.31970700	-1.33939000	-0.05225900
C	-1.47848100	1.46667300	0.05508200

H	1.25610500	2.42387400	-0.62122900
H	3.42389000	1.09460700	-0.04726800
C	-2.61152400	0.69838800	0.03532100
C	-2.53577100	-0.72275300	-0.01987100
H	-1.59397500	2.54860900	0.09493300
H	-3.60108100	1.15227000	0.06113900
H	-3.43313100	-1.32948400	-0.03163600
B	-0.11296900	0.79640400	0.01268700
N	-0.14186400	-0.64704900	-0.03277600
H	1.43274400	1.94974000	1.04923700
H	2.49479400	0.45795400	-1.39843100
H	2.21312900	-0.54435800	1.47520400
H	1.24340400	-1.75576000	-1.15758000

Octahydro-[1,2]azaborinino[1,2-a][1,2]azaborinine

N	0.00018800	-0.63925600	0.00042900
C	-1.21382000	-1.45436700	-0.02273500
H	-1.36221000	-1.91094900	0.96807700
H	-1.06219200	-2.28368800	-0.72695600
C	2.45424600	-0.66202200	0.41887100
H	3.33333600	-1.29928700	0.27966000
H	2.39903300	-0.41485100	1.48696100
C	-1.38386600	1.54307800	0.05061300
H	-1.31472600	2.38302200	0.75357600
H	-1.54407400	2.00647400	-0.93485300
C	1.38365400	1.54336300	-0.04962300
H	1.31292400	2.38328000	-0.75259800
H	1.54571400	2.00688300	0.93536000
C	-2.45352500	-0.66239400	-0.42001500
H	-2.39645300	-0.41518300	-1.48801800
H	-3.33263500	-1.29988800	-0.28220300
C	-2.56714500	0.63062400	0.38609600
H	-2.55525900	0.38181600	1.45555700
H	-3.52737300	1.11905000	0.18741300
C	1.21412800	-1.45439000	0.02362300
H	1.36157900	-1.91231900	-0.96669300
H	1.06285700	-2.28275700	0.72904600
B	-0.00003900	0.76457100	0.00088900
C	2.56624300	0.63090100	-0.38750800
H	2.55205600	0.38211900	-1.45690500
H	3.52681400	1.11946300	-0.19080200

1

F	-2.41004700	-1.11090800	-1.36905500

F	-2.45591800	1.08762200	-1.34797700
N	-0.08403500	-1.26810600	0.51586200
N	1.88216000	0.00090900	-0.26624500
N	-0.08332500	1.27323000	0.51442600
C	-1.61140300	0.00301100	-1.10808700
C	-0.76850800	-2.49523000	0.87470700
H	-0.13684100	-3.37401800	0.71848400
H	-1.67304300	-2.62954500	0.26937200
H	-1.08871600	-2.50274800	1.92753700
C	2.16633200	-2.59662100	0.13131300
H	1.94174900	-3.23586200	0.99069300
H	3.23944300	-2.38776600	0.15940200
H	1.98489200	-3.20673000	-0.76368400
C	3.20924300	-0.00039600	-0.85903500
H	4.02542200	-0.00186200	-0.11851100
H	3.35532900	0.87908300	-1.49361100
H	3.35306300	-0.87959900	-1.49456000
C	2.16958100	2.59799800	0.12234100
H	3.24154600	2.38534100	0.16575800
H	1.93784800	3.24993000	0.97003300
H	2.00172600	3.19591500	-0.78349700
C	-0.76924800	2.50255600	0.86323400
H	-1.66970100	2.63544800	0.25119600
H	-0.13576600	3.38013400	0.70775200
H	-1.09678500	2.51478400	1.91368400
B	1.26896700	-1.26262900	0.12882000
B	-0.97906800	0.00259100	0.40324000
C	-2.20746400	0.00260600	1.48449800
H	-2.85466500	-0.87438000	1.36361200
H	-2.85397000	0.88037500	1.36624100
H	-1.85199700	0.00065900	2.52467600
B	1.26960300	1.26574700	0.12599900
H	-0.85815100	0.02609300	-1.91371900

2

C	-0.70883400	-1.75823900	-0.78620200
C	-1.06875600	0.18795400	1.46432400
C	-2.22408500	-0.66219200	0.91999500
H	1.73527800	-2.26048100	-1.32278000
H	-1.23515900	-1.24051600	-1.60459300
C	1.67838300	-1.36786600	-0.69507800
C	1.54277000	0.88453100	1.02610900
H	-0.66997600	-0.30516300	2.36553400
H	-2.72627900	-0.11577300	0.11203300
C	2.72965700	0.36132800	0.65202200

C	2.82151100	-0.74628500	-0.28948300
H	1.56202600	1.68382500	1.77342500
H	3.66843800	0.72589500	1.07767400
H	3.78212900	-1.14360300	-0.59669700
B	0.14686500	0.38693700	0.38176000
N	0.43023300	-0.97608400	-0.34185800
C	-0.29839700	1.48746200	-0.74955100
F	-0.56285700	2.72788400	-0.17736100
F	-1.47447200	1.16907800	-1.43889900
H	-1.45230200	1.16338600	1.79767200
H	-2.98611600	-0.86800900	1.68565300
H	-0.36216700	-2.72322800	-1.17937100
H	0.45382400	1.67389100	-1.53467800
C	-1.70956800	-1.98748200	0.34810900
H	-1.21399600	-2.56311900	1.14219700
H	-2.54178500	-2.59712100	-0.02700300

3

F	-2.42023200	-1.48676800	0.46584900
F	-1.47434300	-1.67441800	-1.51257200
N	0.61104800	0.44260400	-0.86640900
C	0.03293400	1.73397300	-1.21040100
H	-0.93488800	1.56869900	-1.70847600
H	0.67465300	2.24210400	-1.94947900
C	-1.64773600	-0.78048100	-0.45767000
H	-2.32157600	-0.00387100	-0.85462900
C	2.68322700	-0.75312200	-0.25038100
H	3.75625200	-0.59788000	-0.08113700
H	2.58019200	-1.38682300	-1.14199200
C	-0.57396400	0.68021700	1.48427300
H	-1.28009700	0.20904400	2.18439400
H	0.34141300	0.87476100	2.06837200
C	0.54750500	-1.68479300	0.67456800
H	0.06952000	-2.12887300	1.56027100
H	0.46272000	-2.43936300	-0.12359300
C	-0.21381400	2.67919300	-0.02137700
H	0.74478100	2.93134400	0.45229500
H	-0.63942200	3.62313400	-0.38705400
C	-1.13479100	2.03258300	1.01747100
H	-2.12166900	1.88208800	0.55225000
H	-1.30104800	2.73130800	1.85066900
C	2.01422500	0.59109700	-0.52235900
H	2.18292700	1.22317700	0.37607300
H	2.53794800	1.10422300	-1.34730300
B	-0.23292200	-0.31741400	0.21545200

C	2.03507400	-1.45049400	0.94552800
H	2.15783600	-0.80063200	1.82516200
H	2.57295100	-2.38196100	1.17437200

CF_2H^-

C	0.04382400	0.66033800	0.00000000
H	-1.05177000	0.94430700	0.00000000
F	0.04382400	-0.27257400	1.11555400
F	0.04382400	-0.27257400	-1.11555400

$B_3N_3Me_6CF_3^-$

F	-0.90028600	0.00002300	1.96083600
F	-2.52643000	-1.07944000	1.03784300
F	-2.52646100	1.07942300	1.03782500
N	0.01242600	1.26878700	-0.60430900
N	1.96918200	0.00000300	0.21117000
N	0.01243000	-1.26878700	-0.60430100
C	-1.69718800	0.00000100	0.85246600
C	-0.64852200	2.50274700	-0.98866500
H	-0.04869800	3.37980800	-0.73313400
H	-1.61219800	2.60912600	-0.47745800
H	-0.85667300	2.54847600	-2.06851400
C	2.24029700	2.60305500	-0.14531500
H	2.04249100	3.23592100	-1.01617600
H	3.31536500	2.40408800	-0.13234600
H	2.01908900	3.21594600	0.73861400
C	3.27932600	0.00001500	0.84121100
H	4.11475200	-0.00006500	0.12273800
H	3.40613800	-0.87875200	1.48040700
H	3.40618500	0.87888000	1.48026300
C	2.24026200	-2.60307500	-0.14526800
H	3.31533700	-2.40415700	-0.13224400
H	2.04246600	-3.23591100	-1.01615500
H	2.01897800	-3.21598100	0.73863000
C	-0.64848400	-2.50274800	-0.98871000
H	-1.61218000	-2.60915600	-0.47755000
H	-0.04865200	-3.37980300	-0.73317000
H	-0.85658200	-2.54846200	-2.06857000
B	1.35512300	1.26185200	-0.17547900
B	-0.87796200	-0.00000200	-0.58203800
C	-1.99425800	-0.00000100	-1.78098300
H	-2.65057600	0.87752900	-1.74272900
H	-2.65056700	-0.87753800	-1.74274700
H	-1.51434400	0.00001300	-2.76991000

B	1.35511800	-1.26185200	-0.17544800

CF_3^-

C	0.00060400	-0.00007700	0.55588100
F	-0.59658200	1.10150800	-0.12344300
F	-0.65688300	-1.06669700	-0.12346900
F	1.25306200	-0.03475900	-0.12367500

Pd(TMEDA)PhI (4)

Pd	0.22336700	0.22136300	-0.01625900
N	2.47931700	0.64002000	-0.04020300
N	0.12614500	2.43597200	0.08135400
C	-1.72844900	0.08457700	-0.01898200
C	-2.42732400	0.24193900	-1.21934200
C	-2.44717700	-0.06807800	1.17018800
C	-3.82388800	0.27259300	-1.22687500
H	-1.88624200	0.34181800	-2.15812700
C	-3.84223800	-0.03659200	1.16062300
H	-1.92176000	-0.21099300	2.11142200
C	-4.53454400	0.13757600	-0.03674600
H	-4.35331200	0.39842000	-2.16700000
H	-4.38794700	-0.15413000	2.09253000
H	-5.61959800	0.16047800	-0.04229900
I	0.41937700	-2.49368400	-0.00053500
C	-0.22287000	2.98269100	-1.24289700
H	-1.23722000	2.66897700	-1.49500800
H	-0.17539000	4.08076500	-1.22795300
H	0.45751200	2.60202300	-2.00589600
C	-0.84094200	2.94803500	1.06903000
H	-0.76825800	4.04220500	1.13993300
H	-1.85039900	2.66898200	0.76483000
H	-0.63425600	2.50522300	2.04557600
C	2.57053100	2.09511800	-0.26927000
H	3.55938100	2.47294800	0.03129600
H	2.47363000	2.27220300	-1.34423600
C	3.05155300	0.27247500	1.26365600
H	4.11975900	0.53132900	1.30807200
H	2.52566500	0.78719400	2.07013200
H	2.93231300	-0.80310600	1.40959200
C	1.49045500	2.85339500	0.48353900
H	1.61231000	3.93419900	0.32023100
H	1.58362200	2.67355900	1.55842000
C	3.20319800	-0.07456900	-1.10145600
H	3.14140500	-1.14802100	-0.91511000

H	2.73961100	0.13997300	-2.06736200
H	4.25921700	0.23159700	-1.12966800

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Pd	-1.06185300	0.35954500	-0.34829400
N	-0.06439900	2.51954700	-0.30543400
N	-2.67798900	1.52747000	0.75090500
C	-2.18870600	-1.25305000	-0.29499000
C	-3.11546800	-1.50683300	-1.31164400
C	-2.15845900	-2.11502800	0.80798100
C	-4.00533400	-2.58099400	-1.21936000
H	-3.15221800	-0.86325400	-2.18862400
C	-3.04770600	-3.18464100	0.90427600
H	-1.42274400	-1.96059800	1.59492100
C	-3.97636300	-3.42098200	-0.10965100
H	-4.71872300	-2.75962200	-2.01915600
H	-3.00992200	-3.84014400	1.76990000
H	-4.66573100	-4.25626800	-0.03681700
C	-3.81703300	1.72138200	-0.16228000
H	-4.23748000	0.74649900	-0.41470100
H	-4.59147600	2.34086000	0.31382800
H	-3.49003800	2.20423600	-1.08500500
C	-3.16130700	0.85994000	1.97029300
H	-3.87574200	1.50390900	2.50352600
H	-3.64986300	-0.07715800	1.70190200
H	-2.31536000	0.63883400	2.62574100
C	-1.21362600	3.38927600	0.01364700
H	-0.85767100	4.39014600	0.30536400
H	-1.80078300	3.51131900	-0.90185500
C	0.94182100	2.57960300	0.76367200
H	1.29914800	3.61078600	0.91125200
H	0.53115300	2.20829800	1.70452300
H	1.78489000	1.94243400	0.49989500
C	-2.08225300	2.82583200	1.12038200
H	-2.87383800	3.54847500	1.37035900
H	-1.48907300	2.67477300	2.02630500
C	0.54033300	3.02501500	-1.54653200
H	1.49586100	2.52974400	-1.71833700
H	-0.12592300	2.83104000	-2.39086300
H	0.72825900	4.10685400	-1.47645500
C	1.67367200	-2.43760600	0.02837500
B	2.74117300	-1.26415500	0.26837200
C	0.57985400	-2.26059200	-0.72408100
N	2.56149300	-0.22466100	-0.93845000
C	2.32053000	-0.45574100	1.61222500

C	4.28367400	-1.78056900	0.33097800
C	0.30315800	-0.97587000	-1.42636100
H	-0.15114500	-3.05196700	-0.88351200
C	3.65943100	0.70311400	-1.23220900
C	1.46603500	-0.16141400	-1.63823300
F	3.12289500	0.66164000	1.86135800
F	2.46065200	-1.25231300	2.73095300
H	1.28275500	-0.08202800	1.62794900
H	4.46851700	-2.22476200	1.31806700
H	4.42101800	-2.59356800	-0.39771200
C	5.32555800	-0.69710700	0.03601900
H	-0.26836800	-1.08204600	-2.35161700
H	3.69922400	1.45116700	-0.42924200
H	3.44692400	1.22143100	-2.17444300
C	5.00733100	-0.00791600	-1.29105600
H	1.44349300	0.55702700	-2.46019700
H	5.31371300	0.05798100	0.83205500
H	6.34253500	-1.10728000	-0.00122400
H	4.98771800	-0.74774900	-2.10176200
H	5.76984000	0.73624900	-1.54589600
H	1.82393900	-3.41928400	0.48282200

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Pd	1.05401300	-0.18164900	0.20530700
N	2.15964600	-2.22576700	0.39672000
N	3.13681000	0.45044400	-0.49638100
C	0.41446200	1.67822800	-0.00414600
C	0.25021700	2.23430000	-1.28257300
C	0.37710100	2.55472600	1.08820100
C	0.03325800	3.60253800	-1.46014600
H	0.29288600	1.60103400	-2.16624400
C	0.17497300	3.92509700	0.91601900
H	0.50485000	2.16649800	2.09483000
C	-0.00432900	4.45590700	-0.35958500
H	-0.10431500	3.99963200	-2.46232800
H	0.16131200	4.57937400	1.78389400
H	-0.16740200	5.52063600	-0.49555400
C	3.19106900	0.48487200	-1.96612800
H	2.59501400	1.32840800	-2.31762100
H	4.22696900	0.60852600	-2.31640500
H	2.77287000	-0.42971800	-2.39019800
C	3.57505300	1.75449200	0.02404200
H	4.61825100	1.95444100	-0.26240700
H	2.93005000	2.53821000	-0.37649700
H	3.49125300	1.75914300	1.11330000

C	3.48074000	-1.99917000	-0.22204000
H	4.20592400	-2.74379800	0.14063700
H	3.37531100	-2.15704800	-1.29883900
C	2.30042300	-2.50046000	1.83364800
H	2.89763600	-3.40870700	2.00555600
H	2.77915800	-1.65762200	2.33671700
H	1.30895200	-2.64093300	2.27097200
C	4.01778100	-0.60359800	0.04389300
H	5.02596400	-0.51376800	-0.39059400
H	4.11263800	-0.43240100	1.12063900
C	1.52453100	-3.37866600	-0.25773700
H	0.55840400	-3.58387100	0.20536500
H	1.35597700	-3.15156400	-1.31126200
H	2.15759000	-4.27408200	-0.16764100
C	-0.81138600	-1.03313000	0.97235500
B	-2.12275300	-0.86461600	0.03281200
C	-0.79656600	-0.36605600	2.22511300
N	-2.80108900	0.51702000	0.42368000
C	-1.64652800	-0.82710900	-1.52313800
C	-3.27864900	-2.00088400	0.28194200
C	-1.63258500	0.69976700	2.52226600
H	-0.10135800	-0.69341200	3.00305100
C	-4.02879000	0.82756100	-0.30729100
C	-2.59686800	1.10318900	1.57875100
F	-2.65763700	-0.97210800	-2.46636600
F	-0.79462600	-1.90529200	-1.77059800
H	-1.08954600	0.06873500	-1.82117500
H	-2.94605200	-2.98046300	-0.09075300
H	-3.41470200	-2.11754700	1.36935100
C	-4.63799600	-1.64415200	-0.34600500
H	-1.55413800	1.25174600	3.45036800
H	-3.80682700	0.81368000	-1.37899000
H	-4.37478900	1.83111800	-0.03684700
C	-5.09230500	-0.22612800	0.02115900
H	-3.25019400	1.94474500	1.81988700
H	-4.55939400	-1.70757100	-1.43579900
H	-5.42120100	-2.35217200	-0.04389100
H	-5.29945800	-0.16672800	1.09879900
H	-6.02178000	0.02878600	-0.50084200
H	-0.40951200	-2.04759300	1.03526400

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Pd	0.89249400	-0.10952700	0.28261000
N	1.70207700	-2.24187400	0.70180800
N	2.93181900	0.06666600	-0.74254500

C	0.52942800	1.77329700	-0.07398700
C	-0.31837200	2.19823800	-1.09753300
C	1.15763100	2.72642000	0.73349100
C	-0.53149000	3.56418200	-1.30495700
H	-0.84667800	1.47667200	-1.71138800
C	0.94358400	4.08781600	0.52165700
H	1.80811400	2.40966900	1.54656700
C	0.09548400	4.51136700	-0.50045100
H	-1.19770200	3.88380400	-2.10169500
H	1.43370000	4.81590900	1.16201100
H	-0.07673300	5.57042000	-0.66511100
C	2.68828500	0.16941700	-2.19310700
H	2.07329900	1.04981700	-2.39294200
H	3.64171500	0.25644600	-2.73370700
H	2.15875800	-0.71456700	-2.55158700
C	3.77613200	1.20183300	-0.33554800
H	4.75882000	1.13831200	-0.82475800
H	3.29279400	2.13627700	-0.62096500
H	3.91171000	1.18979300	0.74830500
C	2.71750900	-2.38957700	-0.35749200
H	3.31699600	-3.29854800	-0.18806800
H	2.18229300	-2.52257600	-1.30374600
C	2.32178400	-2.25632100	2.03501700
H	2.92791900	-3.16353200	2.17915000
H	2.95032400	-1.37588200	2.18205800
H	1.53644200	-2.23629500	2.79329500
C	3.64839800	-1.19271700	-0.43726900
H	4.41879500	-1.37626500	-1.20039600
H	4.16944500	-1.06043700	0.51418200
C	0.75435900	-3.36131900	0.59847700
H	0.00519700	-3.28005300	1.38783200
H	0.24668700	-3.31521900	-0.36516600
H	1.27855300	-4.32264200	0.70812800
C	-0.93292400	-0.56424600	1.81489200
B	-1.95805200	-0.72868600	0.64686100
C	-0.81652800	0.62760000	2.49806200
N	-2.79705900	0.48484400	0.48253000
C	-0.81999800	-0.95084900	-1.54738500
C	-2.68183900	-2.12860500	0.38317700
C	-1.61934700	1.75536600	2.15824600
H	-0.14833800	0.70862600	3.35652100
C	-3.98117600	0.46902700	-0.39008600
C	-2.56586600	1.62696700	1.18174500
F	-1.91723700	-0.37760300	-2.23988000
F	-0.91603800	-2.31957900	-1.88726700
H	0.02395300	-0.61894500	-2.18543700

H	-1.97360400	-2.90022600	0.07422600
H	-3.07793000	-2.44243200	1.36412800
C	-3.84785900	-2.05246100	-0.60625000
H	-1.50736400	2.70203500	2.67107900
H	-3.66798500	0.63324000	-1.42482100
H	-4.63737200	1.29468800	-0.09640900
C	-4.74094700	-0.85142100	-0.28923600
H	-3.21898200	2.46525800	0.94624500
H	-3.45017600	-1.94486000	-1.61923400
H	-4.44817500	-2.97038200	-0.58522400
H	-5.14350400	-0.95198200	0.72792800
H	-5.59700200	-0.80814000	-0.97208000
H	-0.42427200	-1.42320200	2.24972600

Pd(TMEDA)PhCF$_2$H

Pd	-0.23539900	-0.22575700	-0.03310400
N	-2.51118700	-0.05993000	-0.01514200
N	-0.44249500	2.04522800	0.00012900
C	1.76043800	-0.21492600	-0.03466300
C	2.48890700	0.07766700	1.13015900
C	2.49640100	-0.39961300	-1.21653800
C	3.87978200	0.20426400	1.11268600
H	1.96626400	0.20593300	2.07649300
C	3.88562500	-0.26750700	-1.24384400
H	1.97745900	-0.64986600	-2.14040300
C	4.58430600	0.03839600	-0.07738300
H	4.41287000	0.42935900	2.03272300
H	4.42319700	-0.40861600	-2.17790400
H	5.66526400	0.13856300	-0.09442100
C	-0.09791800	2.54369200	1.33865000
H	0.95079700	2.31608800	1.53906500
H	-0.25088100	3.63146200	1.40448800
H	-0.70695000	2.05093400	2.09913800
C	0.43240000	2.68717200	-0.99041400
H	0.27993100	3.77668000	-1.00506500
H	1.47258900	2.46861700	-0.74175900
H	0.21991700	2.27904400	-1.98143400
C	-2.79205000	1.33767100	0.36888600
H	-3.83634100	1.59732300	0.13628600
H	-2.67620400	1.41329800	1.45417500
C	-3.03178000	-0.35017000	-1.35999900
H	-4.12126300	-0.19863500	-1.39909500
H	-2.55581900	0.29593700	-2.10007900
H	-2.79764400	-1.38580500	-1.60577600
C	-1.85656600	2.31818500	-0.32183300

H	-2.12604900	3.34761700	-0.03986700
H	-1.97071500	2.24297700	-1.40712600
C	-3.13801800	-0.97285800	0.95203400
H	-2.91855600	-1.99861700	0.65738200
H	-2.71920800	-0.79189600	1.94458000
H	-4.22763100	-0.82314700	0.98655500
C	-0.06875900	-2.20278200	-0.07399300
H	0.77775300	-2.63232800	-0.62091300
F	-0.01685000	-2.72952800	1.20613600
F	-1.20440300	-2.78295300	-0.63854200

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