Supplementary Information for

# Selective Hydroboration of Electron-Rich Isocyanates by an NHC-Copper(I) Alkoxide

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**General Considerations and Starting Materials**

All reactions involving air- and moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line and glovebox techniques. NMR experiments using air-sensitive compounds were conducted in J. Young's tap NMR tubes prepared and sealed in a glovebox under argon. Hexane was purified using an MBraun Solvent Purification System and stored over 4 Å molecular sieves. $C_6D_6$ was dried over a potassium mirror prior to vacuum transfer into a sealed ampoule and storage in the glove box under argon, $CDCl_3$ was dried over $CaH_2$ prior to vacuum transfer into a sealed ampoule and storied over 4 Å molecular sieves. All NMR data were acquired at 298 K on an Agilent ProPulse or Bruker Avance 500 instruments for $^{1}H$ (500 MHz), $^{13}C$ (126 MHz), $^{19}F$ (470 MHz) and $^{11}B$ (160 MHz). $^{1}H$ and $^{13}C$ NMR spectra were referenced using residual solvent resonances. Data was processed using MestReNova software. Mass spectrometry was performed using a Bruker MicrOTOF Electrospray Time-Of-Flight Mass Spectrometer coupled to an Agilent High Performance Liquid Chromatography unit. Starting materials were purchased from standard suppliers and used without further purification unless otherwise stated. PinBH and heterocumulenes were distilled prior use. (IPr)CuOtBu and (6-Dipp)CuOtBu were prepared according to literature procedures.[1,2]

**General procedure for Hydroboration of Heterocumulenes**

1,3,5-trimethoxybenzene (3.3 mg, 20 µmol) was dissolved in 500 µL $C_6D_6$. Heterocumulene (0.13 mmol) was added, and the solution was transferred to a J. Young's NMR tube. $^{1}H$ NMR spectrum, with relaxation delay of 60 s, was collected to determine accurate ratio of heterocumulene to internal standard. (IPr)CuOtBu (0.02 eq.) was dissolved in 100 µL $C_6D_6$ and added to the NMR tube, followed by PinBH (1.3 eq.) Reactions were monitored by $^{1}H$ and $^{11}B$ NMR spectroscopy.

**Blank Reaction Between iPrNCO and Pinacolborane**

1,3,5-trimethoxybenzene (4.3 mg, 26 µmol) was dissolved in 500 µL $C_6D_6$. iPrNCO (0.13 mmol) was added, and the solution was transferred to a J. Young's NMR tube. $^{1}H$ NMR spectrum, with relaxation delay of 60 s, was collected to determine accurate ratio of isocyanate to internal standard. PinBH (1.3 eq.) was then added to the NMR tube. Reaction was monitored by $^{1}H$ and $^{11}B$ NMR spectroscopy after timepoints of 30 minutes at room temperature and 16 hours at 80 °C.

**Synthesis of (6-Dipp)CuN(iPr)C(O)H**

PinBH (17 µL, 0.12 mmol) was added to a solution of (6-Dipp)CuOtBu (65 mg, 0.12 mmol) in $C_6D_6$ (0.5 mL) to give an orange solution. To this solution was added iPrNCO (12 µL, 0,12 mmol). Crystalline material precipitated from the reaction mixture, suitable for XRD. The supernatant solution was decanted, and the product was washed with hexane and dried *in vacuo* to give (6-Dipp)CuN(iPr)C(O)H as a colourless crystalline solid. Yield 30 mg (45 %). $^{1}H$ NMR (500 MHz, $C_6D_6$) δ 7.27 (s, 1H, C(O)*H*), 7.15 – 7.11 (m, 2H, Ar-*H*), 7.01 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 4.57 (dh, *J* = 6.5, 1.2 Hz, 1H, NC*H*), 2.94 (hept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.73 (t, *J* = 5.8 Hz 4H, NC*H*$_2$), 1.50 (p, *J* = 5.8 Hz, 2H, $NCH_2CH_2$), 1.40 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.14 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 0.70 (d, *J* = 6.4 Hz, 6H, NCH(C*H*$_3)_2$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$) δ 202.3 (Cu*C*), 166.1 (*C*O), 145.7 (Ar-*C*), 142.0 (Ar-*C*), 129.7 (Ar-*C*), 125.0 (Ar-*C*), 46.0 (N*C*H$_2$), 42.3 (N*C*H$(CH_3)_2$), 28.9 (*C*H$(CH_3)_2$), 25.8 (NCH(*C*H$_3)_2$), 25.0 (CH(*C*H$_3)_2$), 24.8 (CH(*C*H$_3)_2$), 20.1 ($NCH_2CH_2$). MS (ESI) for [(6-Dipp)CuN(iPr)C(O)H]- Expected: 553.3093, found: 553.3097 (err [ppm] = 0.59).

**Reaction of (6-Dipp)CuN(iPr)C(O)H with Pinacolborane**

(6-Dipp)CuN(iPr)C(O)H (20 mg, 36 µmol) was suspended in 500 µL C6D6 and transferred to a J. Young's NMR tube. Pinacolatoborane (4.6 mg, 5.2 µL, 36 µmol) was added resulting in a colour change from colourless to orange and the dissolution of any remaining insoluble (6-Dipp)CuN(iPr)C(O)H. The reaction was monitored by 1H and 11B NMR spectroscopy.

**Spectroscopic Data for Boraformamides**

PinBN(iPr)C(O)H, 1a

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.03 (s, 1H), 4.68 (hept, *J* = 6.8 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 0.94 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 165.2, 83.5, 42.1, 24.3, 21.7. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.8. MS (ESI) for $[HN(iPr)C(O)H+H]^+$; Expected: 88.0757, found: 88.0756 (err [ppm] = -0.99). NMR data matches literature values.[3]

PinBN(Cy)C(O)H, 1b

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.10 (s, 1H), 4.39 – 4.31 (m, 1H), 2.04 – 1.97 (m, 2H), 1.69 – 1.62 (m, 4H), 1.53 – 1.42 (m, 1H), 1.23 – 1.15 (m, 2H), 1.11 – 1.06 (m, 1H), 0.96 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 165.4, 83.5, 50.2, 32.0, 26.6, 25.8, 24.4. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.8. MS (ESI) for $[HN(Cy)C(O)H+H]^+$; Expected: 128.1069, found: 128.1071 (err [ppm] = 1.33). NMR data matches literature values.[3]

PinBN(Ph)C(O)H, 1d

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.17 (s, 1H, NC(O)*H*), 7.22 – 7.21 (m, 2H, Ar-C*H*), 7.13 – 7.10 (m, 2H, Ar-C*H*), 6.99 – 6.95 (m, 1H, Ar-C*H*), 0.92 (s, 12H, $B(OC(CH_3)_2)_2$). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 164.3 (N*C*(O)H), 137.4 (Ar-*C*), 128.8 (Ar-*C*), 128.0 (Ar-*C*), 126.9 (Ar-*C*), 84.3 ($B(OC(CH_3)_2)_2$, 24.4 ($B(OC(CH_3)_2)_2$. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.7. MS (ESI) for [HN(Ph)C(O)H+H]+; Expected: 122.0601, found: 122.0600 (err [ppm] = -0.40).

PinBN(4-Me-$C_6H_4$)C(O)H, 1e

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.19 (s, 1H), 7.13 (d, J= 7.9 Hz, 2H), 6.94 (d, J= 7.9 Hz, 2H), 2.02 (s, 3H), 0.94 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 164.4, 136.4, 134.8, 129.5, 128.4, 84.2, 24.4, 20.9. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.7. MS (ESI) for $[HN(4\text{-}Me\text{-}C_6H_4)C(O)H+H]^+$; Expected: 136.0753, found: 136.0758 (err [ppm] = 1.15). NMR data matches literature values.[4]

PinBN(Dipp)C(O)H, 1f

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.24 (s, 1H), 7.18-7.16 (m, 1H), 7.11-7.10 (m, 2H), 3.04-3.01 (m, 2H), 1.23-1.22 (m, 12H), 0.95 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 164.6, 145.9, 132.6, 128.6, 123.8, 84.2, 29.2, 24.4, 24.2, 24.1. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.8. MS (ESI) for $[HN(Dipp)C(O)H+Na]^+$; Expected: 228.1358, found: 228.1360 (err [ppm] = 1.13). NMR data matches literature values.[4]

PinBN(4-MeO-$C_6H_4$)C(O)H, 1g

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 9.19 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 3.23 (s, 3H), 0.95 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 164.6, 158.8, 130.1, 129.0, 114.3, 84.2, 54.9, 24.4. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.8. MS (ESI) for $[HN(4\text{-}OMe\text{-}C_6H_4)C(O)H+Na]^+$; Expected: 174.0524, found: 174.0526 (err [ppm] = 1.27). NMR data matches literature values.[4]

PinBN(4-NC-$C_6H_4$)C(O)H, 1h

$^1$H NMR (500 MHz, $C_6D_6$) δ 8.96 (s, 1H), 7.01-6.99 (m, 2H), 6.92-6.90 (m, 2H), 0.93 (s, 12H). $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.1, 21.7. MS (ESI) for [HN(4-NC-$C_6H_4$)C(O)H-H]$^-$; Expected: 145.0407, found: 145.0412 (err [ppm] = 3.37). Due to mixture of products $^{13}$C NMR data was not collected and specific signals in the $^{11}$B NMR spectrum were not assigned. NMR data matches literature values.[4]

Single crystals suitable for XRD formed directly from the reaction mixture.

PinBN(4-NC-$C_6H_4$)$CH_3$, 1h'

$^1$H NMR (500 MHz, $C_6D_6$) δ 7.16-7.18 (m, 4H), 2.73 (s, 3H) 0.86 (s, 12H). $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.1, 21.7. MS (ESI) for [HN(4-NC-$C_6H_4$)$CH_3$-H]$^-$; Expected: 131.0617, found: 131.0622 (err [ppm] = 3.12). Due to mixture of products $^{13}$C NMR data was not collected and specific signals in the $^{11}$B NMR spectrum were not assigned. NMR data matches literature values.[4]

PinBN(4-N(BPin)$_2CH_2$-$C_6H_4$)C(O)H, 1h''

$^1$H NMR (500 MHz, $C_6D_6$) δ 7.84 (s, 1H), 7.08-7.06 (m, 2H), 6.33-6.31 (m, 2H), 5.36 (s, 2H), 1.01 (s, 36H). $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.1, 21.7. MS (ESI) for [HN(4-$CH_2$N(BPin)$_2$-$C_6H_4$)C(O)H-H]$^-$; Expected: 149.0719, found: 149.0720 (err [ppm] = 0.50). Due to mixture of products $^{13}$C NMR data was not collected and specific signals in the $^{11}$B NMR spectrum were not assigned.

PinBN(4-$CF_3$-$C_6H_4$)C(O)H, 1i

$^1$H NMR (500 MHz, $C_6D_6$) δ 9.03 (s, 1H), 7.31-7.29 (m, 2H), 7.09-7.07 (m, 2H), 0.93 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 163.9, 140.5, 128.9 (q, *J* = 31.2 Hz), 128.3, 125.9 (q, *J* = 3.7 Hz), 124.8 (assumed q, half of the signal is swamped by other resonances but repeated 2D NMR and movement of the peaks with field strength allow confirmation of the labelled peak at 123.7 and small peak at 121.5 ppm to be the upfield 2:1 component of the 1:2:2:1 quartet, resonance reported then reported as the derived centre of the peak based on the measured coupling constant, *J* = 272 Hz), 84.6, 24.3. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.6. $^{19}$F NMR (470 MHz, $C_6D_6$) δ -62.2. MS (ESI) for [HN(4-$CF_3$-$C_6H_4$)C(O)H+HCOO]$^-$; Expected: 234.0381, found: 234.0387 (err [ppm] = 2.90).

PinBN(4-$CF_3$-$C_6H_4$)$CH_3$, 1i'

$^1$H NMR (500 MHz, $C_6D_6$) δ 7.41-7.39 (m, 2H), 7.32-7.30 (m, 2H), 2.85 (s, 3H), 1.07 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 151.0, 126.0 (q, *J* = 3.8 Hz), 125.7 (q, *J* = 217.8 Hz), 122.4 (q, *J* = 34.3 Hz), 118.4, 83.3, 34.0, 24.7. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 24.6, 21.7. $^{19}$F NMR (470 MHz, $C_6D_6$) δ -61.2. MS (ESI) for [HN(4-$CF_3$-$C_6H_4$)$CH_3$+H]$^+$; Expected: 176.0681, found: 176.0682 (err [ppm] = -0.10). NMR data matches literature values.[5]

PinBN(3-$NO_2$-$C_6H_4$)C(O)H, 1j

$^1$H NMR (500 MHz, $C_6D_6$) δ 8.96 (s, 1H), 8.04 (t, *J* = 2.1 Hz, 1H), 7.63-7.61 (m, 1H), 7.21-7.18 (m, 1H), 6.72 (t, *J* = 8.1 Hz, 1H), 0.92 (s, 12H). $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.4. MS (ESI) for [HN(3-$NO_2$-$C_6H_4$)C(O)H-H]$^-$; Expected: 165.0305, found: 165.0309 (err [ppm] = 2.19). Due to mixture of products $^{13}$C NMR data was not collected. NMR data matches literature values.[4]

1-(H(O)CN(BPin))$C_6H_4$-4-(N(BPin)C(O)H), 1k

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 2H), 7.15 (s, 2H), 1.30 (s, 24H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.5, 134.9, 127.6, 84.7, 24.6. $^{11}$B NMR (160 MHz, $CDCl_3$) δ 25.8. MS (ESI) for [H(O)CNHPHNHC(O)H+Na]$^+$; Expected: 187.0475, found: 187.0479 (err [ppm] = 2.62). NMR data matches literature values.[4]

PinBN(iPr)C(NiPr)H, 3a

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 8.25 (s, 1H), 4.98 (hept, *J* = 6.9 Hz, 1H), 3.31 (hept, *J* = 6.3 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.3 Hz, 6H), 1.03 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 150.0, 82.8, 57.3, 43.7, 25.7, 24.6, 21.9. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.3. MS (ESI) for $[HN(iPr)C(NiPr)H+H]^+$; Expected: 129.1386, found: 129.1390 (err [ppm] = 2.70). NMR data matches literature values.[6]

PinBN(Cy)C(NCy)H, 3b

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 8.34 (s, 1H), 4.64 – 4.59 (m, 1H), 3.01 – 2.98 (m, 1H), 2.20 – 2.13 (m, 2H), 1.95 – 1.93 (m, 2H), 1.77 – 1.71 (m, 6H), 1.65 – 1.57 (m, 2H), 1.52 – 1.49 (m, 2H), 1.35 – 1.16 (m, 6H), 1.05 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 150.6, 82.8, 65.5, 51.8, 36.2, 32.1, 26.9, 26.3, 26.1, 25.4, 25.5. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.4. MS (ESI) for $[HN(Cy)C(NCy)H+H]^+$; Expected: 209.2010, found: 209.2015 (err [ppm] = 1.55). NMR data matches literature values.[6]

PinBN(4-Me-$C_6H_4$)C(N(4-Me-$C_6H_4$))H, 3c

$^{1}$H NMR (500 MHz, $C_6D_6$) δ 8.65 (s, 1H), 7.32-7.02 (br m, 4H), 6.96 (br s, 4H), 2.08 (s, 6H), 1.01 (s, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 151.5, 129.7, 128.4, 121.5, 83.9, 24.5, 20.9. $^{11}$B NMR (160 MHz, $C_6D_6$) δ 25.6. MS (ESI) for $[HN(4\text{-Me-}C_6H_4)C(N(4\text{-Me-}C_6H_4)H+H]^+$; Expected: 225.1398, found: 225.1320 (err [ppm] = 2.73). NMR data matches literature values.[6]

**Xray Crystallography**

Single crystals of [PinBN(4-NC-Ph)C(O)H] (1h) and [(6-Dipp)CuN(iPr)C(O)H] were run on a SuperNova, Dual, Cu at home/near, EosS2 diffractometer. The crystals were kept at 150.00(10) K during data collection. Using Olex2,[7] the structure was solved with the ShelXT[8] structure solution program using Intrinsic Phasing and refined with the ShelXL[9] refinement package using Least Squares minimisation.

1 guest molecule of benzene was present in the asymmetric unit of [(6-Dipp)CuN(iPr)C(O)H] and it was refined subject as 2 components, each treated as a rigid hexagon, to account for 60:40 disorder.

**Table S1:** Crystal data and structure refinement for PinBN(4-NC-$C_6H_4$)C(O)H and(6-Dipp)CuN(iPr)C(O)H.

| Identification code | PinBN(4-NC-$C_6H_4$)C(O)H | (6-Dipp)CuN(iPr)C(O)H |
|---|---|---|
| Empirical formula | $C_{14}H_{17}BN_2O_3$ | $C_{38}H_{54}CuN_3O$ |
| Formula weight | 272.10 | 632.38 |
| Temperature/K | 150.00(10) | 150.00(10) |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | $P2_1/n$ |
| a/Å | 7.9081(4) | 11.5493(1) |
| b/Å | 9.4286(4) | 16.0557(1) |
| c/Å | 9.6551(5) | 19.4851(2) |
| α/° | 76.504(4) | 90 |
| β/° | 86.081(4) | 94.4500(10) |
| γ/° | 83.312(4) | 90 |
| Volume/Å$^3$ | 694.63(6) | 3602.27(5) |
| Z | 2 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.301 | 1.166 |
| μ/mm$^{-1}$ | 0.740 | 1.082 |
| F(000) | 288.0 | 1360.0 |
| Crystal size/mm$^3$ | 0.241 × 0.145 × 0.078 | 0.274 × 0.217 × 0.092 |
| Radiation | Cu Kα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.428 to 144.482 | 7.142 to 146.144 |
| Index ranges | -8 ≤ h ≤ 9, -11 ≤ k ≤ 10, -11 ≤ l ≤ 10 | -14 ≤ h ≤ 9, -19 ≤ k ≤ 19, -24 ≤ l ≤ 20 |
| Reflections collected | 5451 | 24948 |
| Independent reflections | 2714 [$R_{int}$ = 0.0169, $R_{sigma}$ = 0.0241] | 7138 [$R_{int}$ = 0.0201, $R_{sigma}$ = 0.0181] |
| Data/restraints/parameters | 2714/0/185 | 7138/0/428 |
| Goodness-of-fit on $F^2$ | 1.027 | 1.031 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0341, $wR_2$ = 0.0893 | $R_1$ = 0.0301, $wR_2$ = 0.0805 |
| Final R indexes [all data] | $R_1$ = 0.0363, $wR_2$ = 0.0909 | $R_1$ = 0.0321, $wR_2$ = 0.0820 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.21 | 0.26/-0.40 |

**Computational Details**

DFT calculations were run with Gaussian 16 (C.01).[10] The Cu centres were described with the Stuttgart RECPs and associated basis sets,[11] and 6-31G** basis sets were used for all other atoms (BS1).[12] Initial BP86[13] optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues). Lowest energy conformers of the stationary points were found by performing systematic confirmational searches at the BP86/6-31G** level of theory. All energies were recomputed with 6-311++G** basis sets for all atoms except copper, for which the cc-pvtz-pp basis set and corresponding ECP was used (BS2).[14,15] Corrections for the effect of benzene (ε = 2.2706) solvent were run using the polarizable continuum model (PCM) and BS1.[16] Single-point dispersion corrections to the BP86 results employed Grimme's D3 parameter set with Becke-Johnson damping as implemented in Gaussian.[17]

Breakdown of Energy Contributions

The following tables detail the evolution of the relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

| | |
|---|---|
| $\Delta E_{BS1}$ | SCF energy computed with the BP86 functional with BS1 |
| $\Delta H_{BS1}$ | Enthalpy at 0 K with BS1 |
| $\Delta G_{BS1}$ | Free energy at 298.15 K and 1 atm with BS1 |
| $\Delta G_{BS1/bnz}$ | Free energy corrected for benzene solvent with BS1 |
| $\Delta G_{BS1/bnz+D3}$ | Free energy corrected for benzene and dispersion effects with BS1 |
| $\Delta E_{BS2}$ | SCF energy computed with the BP86 functional with BS2 |
| $\Delta G_{bnz}$ | Free energy corrected for basis set (BS2), dispersion effects and benzene solvent |

In each case the final data used in the main article is highlighted in bold.

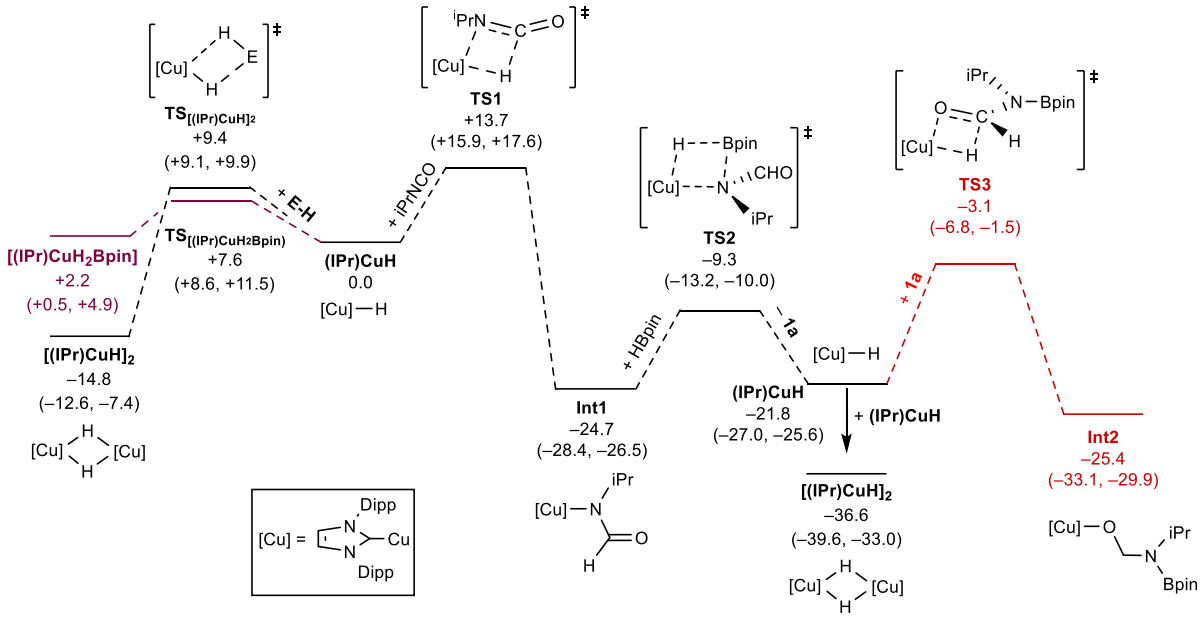


Figure S1: Computed pathway for hydroboration of iPrNCO, energies in brackets are calculated using other functionals (PBE0, wB97XD)

Table S2: Relative energies (kcal mol$^{-1}$) for computed stationary points and transition states in the hydroboration of iPrNCO. Data in bold are those used in the main text. All energies are quoted relative to two IPrCuH, iPrNCO and two HBPin at 0.0 kcal mol$^{-1}$.

| | $\Delta E_{BS1}$ | $\Delta H_{BS1}$ | $\Delta G_{BS1}$ | $\Delta G_{BS1/bnz}$ | $\Delta G_{BS1/bnz+D3}$ | $\Delta E_{BS2}$ | $\Delta G_{bnz}$ |
|---|---|---|---|---|---|---|---|
| **2 IPrCuH + iPrNCO + 2 HBPin** | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| **TS(IPrCuH) + iPrNCO + 2 HBPin** | 0.52 | 0.40 | -2.26 | 14.95 | 9.15 | 0.75 | **9.39** |
| **$[IPrCuH]_2$ + iPrNCO + 2PinBH** | -19.20 | -18.86 | -4.53 | 0.47 | -12.23 | -21.78 | **-14.81** |
| **TS($IPrCuH_2BPin$) + IPrCuH + 2 PinBH + iPrNCO** | 0.31 | 0.03 | 11.93 | 13.76 | 6.30 | 1.57 | **7.56** |
| **$IPrCuH_2BPin$ + IPrCuH + 2 PinBH + iPrNCO** | -5.36 | -4.51 | 7.43 | 9.24 | 2.55 | -5.75 | **2.16** |
| **TS1 + 2 HBPin + IPrCuH** | 7.93 | 7.53 | 20.50 | 22.25 | 12.46 | 9.17 | **13.70** |
| **IPrCuN(iPr)C(O)H + 2 HBPin + IPrCuH** | -32.12 | -28.56 | -16.30 | -15.81 | -25.36 | -31.46 | **-24.70** |
| **TS2 + HBPin + IPrCuH** | -23.58 | -19.44 | 7.63 | 10.00 | -15.42 | -17.50 | **-9.34** |
| **2 IPrCuH + PinBN(iPr)C(O)H + HBPin** | -35.08 | -31.86 | -18.55 | -18.45 | -25.15 | -31.73 | **-21.80** |
| **TS(IPrCuH) + PinBN(iPr)C(O)H + PinBH** | -34.57 | -31.46 | -6.31 | -3.50 | -16.01 | -30.98 | -12.41 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$[IPrCuH]_2$ + PinBN(iPr)C(O)H + PinBH** | - 54.28 | -50.71 | -23.08 | -17.98 | -37.38 | - 53.51 | **- 36.61** |
| **TS3 + HBPin + IPrCuH** | - 25.32 | -21.99 | 4.89 | 8.13 | -8.54 | - 19.85 | **-3.08** |
| **IPrCuOCH$_2$N(iPr)BPin + HBPin + IPrCuH** | - 49.04 | -42.27 | -17.30 | -14.83 | -31.22 | - 43.27 | **- 25.44** |

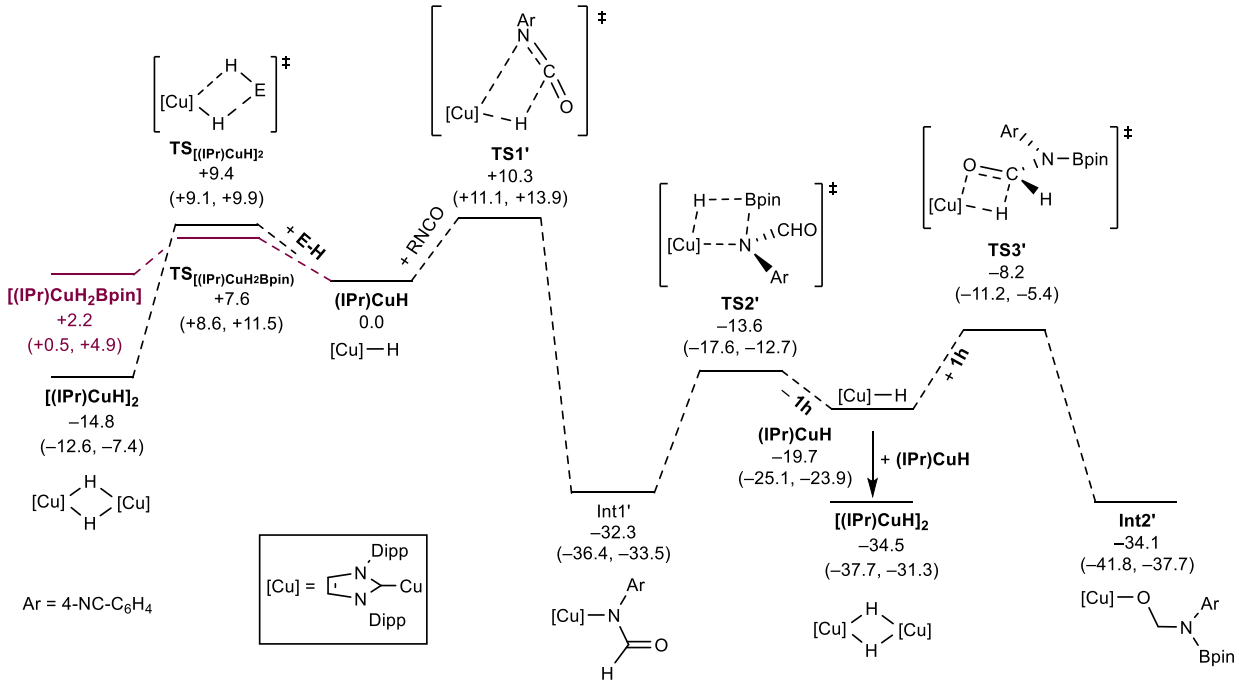


Figure S2: Computed pathway for hydroboration of 4-NC-$C_6H_4$NCO, energies in brackets are calculated using other functionals (PBE0, wB97XD)

Table S3: Relative energies (kcal mol$^{-1}$) for computed stationary points and transition states in the hydroboration of 4-NC-$C_6H_4$NCO. Data in bold are those used in the main text. All energies are quoted relative to two IPrCuH, 4-NC-$C_6H_4$NCO and HBPin at 0.0 kcal mol$^{-1}$.

| | $\Delta E_{BS1}$ | $\Delta H_{BS1}$ | $\Delta G_{BS1}$ | $\Delta G_{BS1/bnz}$ | $\Delta G_{BS1/bnz+D3}$ | $\Delta E_{BS2}$ | $\Delta G_{bnz}$ |
|---|---|---|---|---|---|---|---|
| **2 IPrCuH + 4-NC-$C_6H_4$NCO + HBPin** | 0 | 0 | 0 | 0 | 0 | 0 | **0** |
| **TS(IPrCuH) + 4-NC-$C_6H_4$NCO + HBPin** | 0.52 | 0.40 | 12.24 | 14.95 | -6.12 | 9.15 | **9.39** |
| **$[IPrCuH]_2$ + 4-NC-$C_6H_4$NCO + PinBH** | - 19.20 | -18.86 | -4.53 | 0.47 | 4.57 | - 12.23 | **- 14.81** |
| **TS(IPrCuH$_2$BPin) + IPrCuH + PinBH + 4-NC-$C_6H_4$NCO** | 0.31 | 0.03 | 11.93 | 13.76 | 6.30 | 1.57 | **7.56** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **$IPrCuH_2BPin$ + IPrCuH + PinBH + p-NC-$C_6H_4$NCO** | -5.36 | -4.51 | 7.43 | 9.24 | 2.55 | -5.75 | **2.16** |
| **TS1' + HBPin + IPrCuH** | 4.29 | 4.30 | 14.12 | 15.76 | 9.63 | 4.96 | **10.30** |
| **IPrCuN(4-NC-$C_6H_4$)C(O)H + HBPin + IPrCuH** | -38.76 | -34.98 | -23.17 | -22.66 | -33.16 | -37.87 | **-32.27** |
| **TS2' + IPrCuH** | -27.09 | -23.04 | 3.82 | 6.39 | -19.24 | -21.49 | **-13.63** |
| **2 IPrCuH + PinBN(4-NC-$C_6H_4$)C(O)H +** | -31.37 | -28.39 | -15.43 | -15.58 | -22.29 | -28.77 | **-19.70** |
| **TS(IPrCuH) + PinBN(4-NC-$C_6H_4$)C(O)H** | -30.85 | -28.00 | -3.19 | -0.63 | -13.14 | -28.02 | -10.31 |
| **[IPrCuH]2 + PinBN(4-NC-$C_6H_4$)C(O)H** | -50.56 | -47.25 | -19.96 | -15.10 | -34.52 | -50.55 | **-34.51** |
| **TS3' + IPrCuH** | -26.28 | -23.22 | 3.79 | 6.61 | -12.90 | -21.52 | **-8.15** |
| **IPrCuO$CH_2$N(4-NC-$C_6H_4$)BPin + IPrCuH** | -56.27 | -48.98 | -23.37 | -21.06 | -39.13 | -51.21 | **-34.07** |

**Cartesian Coordinates and Computed Energies [in Hartrees]**

IPrCuH
SCF (BP86) Energy = -1357.65730419
Enthalpy 0K = -1357.530864
Enthalpy 298K = -1357.529920
Free Energy 298K = -1357.633020
Lowest Frequency = 11.6670 cm-1
Second Frequency = 22.0948 cm-1
SCF (BP86-D3BJ) Energy = -1358.28187487
SCF (C6H6) Energy = -1358.13401638
SCF (BS2) Energy = -1358.40435178
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1356.929371
SCF (wB97XD-BS2-C6H6) Energy = -1357.97

| | | | |
|---|---|---|---|
| Cu | 0.00012 | -0.00012 | 1.96105 |
| N | -1.08184 | 0.00008 | -0.80884 |
| N | 1.08176 | 0.00014 | -0.80887 |
| C | -0.00003 | -0.00010 | 0.04864 |
| C | -0.68419 | 0.00048 | -2.14774 |
| H | -1.40288 | 0.00067 | -2.96270 |
| C | 0.68409 | 0.00049 | -2.14776 |
| H | 1.40275 | 0.00068 | -2.96274 |
| C | -2.46649 | -0.00001 | -0.37919 |
| C | -3.11721 | 1.24366 | -0.18534 |
| C | -4.46821 | 1.21287 | 0.21154 |
| H | -4.99755 | 2.15689 | 0.37761 |
| C | -5.13961 | -0.00014 | 0.40601 |
| H | -6.18963 | -0.00019 | 0.71686 |
| C | -4.46801 | -1.21308 | 0.21182 |
| H | -4.99720 | -2.15713 | 0.37813 |
| C | -3.11702 | -1.24374 | -0.18511 |
| C | -2.40027 | 2.58332 | -0.34822 |
| H | -1.39558 | 2.38367 | -0.75996 |
| C | -2.20763 | 3.26287 | 1.02753 |
| H | -3.18037 | 3.49320 | 1.49658 |
| H | -1.65341 | 4.21104 | 0.91520 |
| H | -1.64496 | 2.60941 | 1.71632 |
| C | -3.12920 | 3.51627 | -1.34041 |
| H | -4.13235 | 3.79664 | -0.97487 |
| H | -3.25310 | 3.04185 | -2.32875 |
| H | -2.55644 | 4.44966 | -1.47747 |
| C | -2.39995 | -2.58333 | -0.34796 |
| H | -1.39522 | -2.38356 | -0.75955 |
| C | -2.20744 | -3.26301 | 1.02775 |
| H | -1.64517 | -2.60944 | 1.71678 |
| H | -1.65285 | -4.21096 | 0.91543 |
| H | -3.18021 | -3.49377 | 1.49652 |
| C | -3.12868 | -3.51624 | -1.34033 |
| H | -4.13187 | -3.79670 | -0.97495 |
| H | -2.55585 | -4.44959 | -1.47739 |
| H | -3.25248 | -3.04174 | -2.32865 |
| C | 2.46639 | 0.00005 | -0.37919 |
| C | 3.11697 | -1.24370 | -0.18531 |
| C | 4.46792 | -1.21307 | 0.21171 |
| H | 4.99714 | -2.15713 | 0.37785 |
| C | 5.13946 | -0.00013 | 0.40623 |
| H | 6.18945 | -0.00021 | 0.71716 |
| C | 4.46802 | 1.21288 | 0.21196 |
| H | 4.99730 | 2.15688 | 0.37828 |
| C | 3.11705 | 1.24369 | -0.18502 |
| C | 2.40016 | 2.58338 | -0.34788 |
| H | 1.39528 | 2.38374 | -0.75915 |
| C | 2.20814 | 3.26335 | 1.02774 |
| H | 1.64609 | 2.60995 | 1.71709 |
| H | 1.65352 | 4.21129 | 0.91539 |
| H | 3.18106 | 3.49423 | 1.49614 |
| C | 3.12882 | 3.51595 | -1.34064 |
| H | 4.13224 | 3.79609 | -0.97567 |
| H | 2.55625 | 4.44947 | -1.47761 |
| H | 3.25208 | 3.04129 | -2.32896 |
| C | 2.39998 | -2.58330 | -0.34844 |
| H | 1.39525 | -2.38354 | -0.75999 |
| C | 2.20752 | -3.26330 | 1.02711 |
| H | 1.65270 | -4.21110 | 0.91459 |
| H | 1.64548 | -2.60981 | 1.71637 |
| H | 3.18029 | -3.49442 | 1.49570 |
| C | 3.12883 | -3.51592 | -1.34102 |
| H | 4.13232 | -3.79578 | -0.97601 |
| H | 3.25199 | -3.04140 | -2.32942 |
| H | 2.55644 | -4.44958 | -1.47781 |
| H | 0.00025 | 0.00006 | 3.47636 |

[IPrCuH]2
SCF (BP86) Energy = -2715.31978252
Enthalpy 0K = -2715.090422
Enthalpy 298K = -2715.089478
Free Energy 298K = -2715.273256
Lowest Frequency = 5.9974 cm-1
Second Frequency = 12.5657 cm-1
SCF (BP86-D3BJ) Energy = -2716.61458581
SCF (C6H6) Energy = -2716.29065827
SCF (BS2) Energy = -2716.84340985
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2713.90223
SCF (wB97XD-BS2-C6H6) Energy = -2715.977008

| | | | |
|---|---|---|---|
| Cu | -1.16732 | 0.00003 | 0.00005 |
| Cu | 1.16730 | 0.00004 | 0.00004 |
| N | -3.92546 | 1.06258 | 0.21097 |
| N | -3.92542 | -1.06266 | -0.21109 |
| N | 3.92542 | 1.06264 | -0.21101 |
| N | 3.92542 | -1.06260 | 0.21108 |
| C | -3.05897 | -0.00003 | -0.00003 |
| C | -5.26590 | 0.67015 | 0.13226 |
| H | -6.08114 | 1.37499 | 0.27126 |
| C | -5.26588 | -0.67026 | -0.13247 |
| H | -6.08109 | -1.37512 | -0.27152 |
| C | -3.49803 | 2.41323 | 0.49806 |
| C | -3.27883 | 3.30377 | -0.58263 |
| C | -2.88297 | 4.61936 | -0.27158 |
| H | -2.70131 | 5.32871 | -1.08620 |
| C | -2.71470 | 5.03122 | 1.05595 |
| H | -2.40681 | 6.05940 | 1.27507 |
| C | -2.93605 | 4.12898 | 2.10359 |
| H | -2.79608 | 4.45653 | 3.13944 |
| C | -3.33053 | 2.80060 | 1.85149 |
| C | -3.44369 | 2.88262 | -2.04225 |

```
H  -3.80517  1.83996 -2.05409
C  -2.08593  2.90401 -2.78030
H  -1.65283  3.92001 -2.79264
H  -2.21534  2.58009 -3.82809
H  -1.36467  2.22476 -2.29517
C  -4.49572  3.74959 -2.77020
H  -5.47426  3.71410 -2.26131
H  -4.63485  3.39366 -3.80587
H  -4.18409  4.80764 -2.82281
C  -3.55296  1.83821  3.01766
H  -3.86703  0.86683  2.59876
C  -2.24079  1.59527  3.79704
H  -1.46319  1.18239  3.13231
H  -2.41298  0.87850  4.61944
H  -1.85915  2.53100  4.24303
C  -4.68162  2.33179  3.95125
H  -4.42249  3.29494  4.42522
H  -4.85833  1.60088  4.75951
H  -5.62946  2.47300  3.40390
C  -3.49795 -2.41330 -0.49817
C  -3.33038 -2.80065 -1.85160
C  -2.93586 -4.12902 -2.10369
H  -2.79584 -4.45656 -3.13953
C  -2.71454 -5.03126 -1.05604
H  -2.40662 -6.05943 -1.27516
C  -2.88287 -4.61942  0.27148
H  -2.70123 -5.32876  1.08611
C  -3.27877 -3.30384  0.58252
C  -3.55276 -1.83825 -3.01777
H  -3.86680 -0.86687 -2.59886
C  -2.24056 -1.59535 -3.79711
H  -1.46295 -1.18251 -3.13235
H  -2.41269 -0.87854 -4.61949
H  -1.85894 -2.53108 -4.24313
C  -4.68140 -2.33179 -3.95138
H  -4.42230 -3.29496 -4.42533
H  -4.85806 -1.60088 -4.75966
H  -5.62927 -2.47295 -3.40406
C  -3.44368 -2.88270  2.04214
H  -3.80518 -1.84004  2.05398
C  -2.08595 -2.90407  2.78023
H  -2.21539 -2.58018  3.82802
H  -1.36469 -2.22479  2.29514
H  -1.65282 -3.92006  2.79256
C  -4.49573 -3.74969  2.77006
H  -5.47425 -3.71421  2.26113
H  -4.63490 -3.39376  3.80572
H  -4.18407 -4.80773  2.82268
C   3.05895  0.00001  0.00005
C   5.26587  0.67022 -0.13236
H   6.08109  1.37507 -0.27142
C   5.26588 -0.67018  0.13238
H   6.08109 -1.37505  0.27140
C   3.49800  2.41330 -0.49807
C   3.27878  3.30381  0.58264
C   2.88294  4.61942  0.27161
H   2.70127  5.32874  1.08624
C   2.71473  5.03131 -1.05591
H   2.40686  6.05950 -1.27502
C   2.93609  4.12909 -2.10357
H   2.79616  4.45667 -3.13942
C   3.33054  2.80070 -1.85149
C   3.44360  2.88263  2.04225
H   3.80509  1.83997  2.05408
C   2.08582  2.90399  2.78025
H   1.65266  3.91996  2.79251
H   2.21520  2.58014  3.82807
H   1.36460  2.22467  2.29515
C   4.49560  3.74959  2.77026
H   4.18394  4.80763  2.82290
H   5.47415  3.71413  2.26139
H   4.63470  3.39363  3.80592
C   3.55292  1.83832 -3.01768
H   3.86704  0.86695 -2.59880
C   2.24069  1.59537 -3.79695
H   1.46313  1.18249 -3.13216
H   2.41281  0.87858 -4.61936
H   1.85902  2.53110 -4.24292
C   4.68149  2.33191 -3.95136
H   4.42230  3.29504 -4.42535
H   4.85816  1.60098 -4.75962
H   5.62937  2.47315 -3.40410
C   3.49799 -2.41325  0.49815
C   3.27889 -3.30381 -0.58254
C   2.88302 -4.61940 -0.27150
H   2.70145 -5.32877 -1.08611
C   2.71464 -5.03123  1.05602
H   2.40674 -6.05941  1.27514
C   2.93588 -4.12897  2.10367
H   2.79583 -4.45650  3.13952
C   3.33037 -2.80059  1.85158
C   3.55269 -1.83817  3.01775
H   3.86670 -0.86678  2.59884
C   2.24047 -1.59533  3.79708
H   1.46287 -1.18246  3.13233
H   2.41259 -0.87856  4.61950
H   1.85886 -2.53108  4.24304
C   4.68135 -2.33167  3.95137
H   4.42228 -3.29485  4.42532
H   4.85797 -1.60075  4.75965
H   5.62922 -2.47279  3.40406
C   3.44388 -2.88269 -2.04215
H   3.80540 -1.84004 -2.05398
C   2.08618 -2.90405 -2.78031
H   2.21569 -2.58017 -3.82810
H   1.36491 -2.22474 -2.29527
H   1.65305 -3.92003 -2.79264
C   4.49594 -3.74970 -2.77001
H   4.18426 -4.80774 -2.82266
H   5.47444 -3.71425 -2.26103
H   4.63518 -3.39377 -3.80567
H   0.00001 -0.00002 -1.24681
H  -0.00005  0.00002  1.24692
```

IPrCuH2BPin
SCF (BP86) Energy = -1769.99185401
Enthalpy 0K = -1769.199047
Enthalpy 298K = -1769.198103
Free Energy 298K = -1769.326766
Lowest Frequency = 12.7789 cm-1
Second Frequency = 15.1854 cm-1
SCF (BP86-D3BJ) Energy = -1770.19160071
SCF (C6H6) Energy = -1769.99882302
SCF (BS2) Energy = -1770.37899407
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1768.459759

SCF (wB97XD-BS2-C6H6) Energy = -1769.841938

| | | | |
|---|---|---|---|
| Cu | 0.59125 | -0.00598 | 0.00120 |
| N | -2.12389 | 1.10028 | -0.02103 |
| N | -2.14186 | -1.06924 | 0.01782 |
| C | -1.27823 | 0.00844 | -0.00094 |
| C | -3.46601 | 0.71017 | -0.01544 |
| H | -4.27480 | 1.43543 | -0.02913 |
| C | -3.47734 | -0.65699 | 0.00920 |
| H | -4.29805 | -1.36876 | 0.02129 |
| C | -1.67037 | 2.47529 | -0.04439 |
| C | -1.45050 | 3.09709 | -1.29911 |
| C | -1.02058 | 4.43825 | -1.29075 |
| H | -0.83758 | 4.94582 | -2.24373 |
| C | -0.81681 | 5.12749 | -0.08936 |
| H | -0.47869 | 6.16892 | -0.10706 |
| C | -1.03831 | 4.48519 | 1.13471 |
| H | -0.86880 | 5.02912 | 2.06998 |
| C | -1.46916 | 3.14536 | 1.18846 |
| C | -1.65466 | 2.37181 | -2.62876 |
| H | -1.98529 | 1.34233 | -2.40681 |
| C | -0.32955 | 2.26737 | -3.41750 |
| H | 0.06257 | 3.26521 | -3.68128 |
| H | -0.48739 | 1.71055 | -4.35760 |
| H | 0.44075 | 1.74200 | -2.82881 |
| C | -2.76018 | 3.04492 | -3.47388 |
| H | -2.48389 | 4.07748 | -3.75024 |
| H | -3.71807 | 3.08993 | -2.92806 |
| H | -2.92478 | 2.48267 | -4.40934 |
| C | -1.68961 | 2.47075 | 2.54202 |
| H | -2.03703 | 1.43974 | 2.35541 |
| C | -0.36730 | 2.37235 | 3.33640 |
| H | 0.39376 | 1.81119 | 2.76907 |
| H | -0.53545 | 1.85476 | 4.29690 |
| H | 0.04222 | 3.37265 | 3.56163 |
| C | -2.78523 | 3.19004 | 3.36142 |
| H | -2.49213 | 4.22591 | 3.60616 |
| H | -2.96191 | 2.66092 | 4.31384 |
| H | -3.74078 | 3.23410 | 2.81149 |
| C | -1.71120 | -2.45150 | 0.04242 |
| C | -1.50471 | -3.07656 | 1.29784 |
| C | -1.09712 | -4.42469 | 1.29076 |
| H | -0.92470 | -4.93495 | 2.24428 |
| C | -0.90208 | -5.11748 | 0.08996 |
| H | -0.58137 | -6.16439 | 0.10863 |
| C | -1.11011 | -4.47192 | -1.13476 |
| H | -0.94759 | -5.01883 | -2.06954 |
| C | -1.51847 | -3.12509 | -1.18978 |
| C | -1.72430 | -2.44685 | -2.54382 |
| H | -2.05665 | -1.41075 | -2.35796 |
| C | -0.39784 | -2.36845 | -3.33358 |
| H | 0.36964 | -1.81893 | -2.76351 |
| H | -0.55468 | -1.84837 | -4.29466 |
| H | -0.00286 | -3.37495 | -3.55727 |
| C | -2.82789 | -3.14894 | -3.36733 |
| H | -2.54957 | -4.18884 | -3.61216 |
| H | -2.99353 | -2.61638 | -4.31982 |
| H | -3.78577 | -3.17916 | -2.82052 |
| C | -1.69884 | -2.34733 | 2.62688 |
| H | -2.01643 | -1.31392 | 2.40408 |
| C | -0.37163 | -2.25935 | 3.41421 |
| H | -0.52159 | -1.70105 | 4.35472 |
| H | 0.40443 | -1.74321 | 2.82488 |
| H | 0.00841 | -3.26216 | 3.67691 |
| C | -2.81212 | -3.00493 | 3.47402 |
| H | -2.54878 | -4.04031 | 3.75238 |
| H | -3.77097 | -3.03886 | 2.92907 |
| H | -2.96880 | -2.43882 | 4.40853 |
| H | 1.86348 | -0.03220 | -1.08339 |
| C | 4.84665 | -0.78982 | -0.22935 |
| C | 4.85503 | 0.72284 | 0.23306 |
| B | 2.68152 | -0.02209 | 0.00362 |
| O | 3.51082 | 1.14961 | -0.09193 |
| O | 3.49844 | -1.20239 | 0.09827 |
| C | 5.05584 | 0.87027 | 1.75620 |
| H | 6.09107 | 0.64207 | 2.06462 |
| H | 4.83026 | 1.91030 | 2.04533 |
| H | 4.37125 | 0.20375 | 2.30629 |
| C | 5.84187 | 1.62515 | -0.51835 |
| H | 6.88303 | 1.28919 | -0.36687 |
| H | 5.62815 | 1.63896 | -1.59791 |
| H | 5.76067 | 2.65971 | -0.14383 |
| C | 5.04277 | -0.93928 | -1.75284 |
| H | 6.07960 | -0.72153 | -2.06341 |
| H | 4.80608 | -1.97697 | -2.04146 |
| H | 4.36381 | -0.26587 | -2.30152 |
| C | 5.82525 | -1.70251 | 0.52018 |
| H | 5.73287 | -2.73607 | 0.14548 |
| H | 6.86954 | -1.37716 | 0.36718 |
| H | 5.61307 | -1.71449 | 1.60008 |
| H | 1.86197 | -0.00357 | 1.08985 |

iPrNCO
SCF (BP86) Energy = -286.624600900
Enthalpy 0K = -286.512862
Enthalpy 298K = -286.511918
Free Energy 298K = -286.551411
Lowest Frequency = 33.3619 cm-1
Second Frequency = 121.3205 cm-1
SCF (BP86-D3BJ) Energy = -286.639324976
SCF (C6H6) Energy = -286.626294929
SCF (BS2) Energy = -286.707993051
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -286.3768196
SCF (wB97XD-BS2-C6H6) Energy = -286.6092804

| | | | |
|---|---|---|---|
| N | 0.45342 | 0.00065 | 0.73866 |
| C | -0.97870 | -0.00006 | 0.44034 |
| H | -1.48462 | -0.00004 | 1.42326 |
| C | -1.38175 | 1.27849 | -0.31398 |
| H | -0.90818 | 1.30562 | -1.31088 |
| H | -2.47588 | 1.31284 | -0.45115 |
| H | -1.07227 | 2.17768 | 0.24213 |
| C | -1.38037 | -1.27922 | -0.31356 |
| H | -1.06966 | -2.17794 | 0.24264 |
| H | -2.47443 | -1.31503 | -0.45078 |
| H | -0.90678 | -1.30582 | -1.31046 |
| C | 1.49310 | 0.00027 | 0.09791 |
| O | 2.58803 | 0.00016 | -0.37745 |

IPrCuN(iPr)C(O)H
SCF (BP86) Energy = -1644.04548414
Enthalpy 0K = -1644.088369

Enthalpy 298K = -1644.087425
Free Energy 298K = -1644.210410
Lowest Frequency = 9.4738 cm-1
Second Frequency = 16.4640 cm-1
SCF (BP86-D3BJ) Energy = -1644.98759631
SCF (C6H6) Energy = -1644.81071355
SCF (BS2) Energy = -1645.16248196
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1643.376704
SCF (wB97XD-BS2-C6H6) Energy = -1644.647582

| | | | |
|---|---|---|---|
| Cu | -0.06318 | -0.92872 | 0.75476 |
| O | -1.72850 | -3.79844 | 2.98122 |
| N | 1.03435 | 1.26083 | -0.88937 |
| N | -1.13333 | 1.21486 | -0.89617 |
| N | -0.20885 | -2.40739 | 1.87286 |
| C | -0.03652 | 0.55874 | -0.37353 |
| C | 2.42341 | 0.95025 | -0.61889 |
| C | 3.10009 | 0.05585 | -1.48541 |
| C | 4.45170 | -0.22144 | -1.20170 |
| H | 5.00209 | -0.91277 | -1.84852 |
| C | 5.09880 | 0.36664 | -0.10813 |
| H | 6.14940 | 0.13412 | 0.09506 |
| C | 4.40436 | 1.25024 | 0.72696 |
| H | 4.91780 | 1.70331 | 1.58153 |
| C | 3.05179 | 1.56546 | 0.49255 |
| C | 2.42240 | -0.60509 | -2.68554 |
| H | 1.38304 | -0.23670 | -2.73514 |
| C | 2.35769 | -2.13963 | -2.51511 |
| H | 3.36776 | -2.58178 | -2.45983 |
| H | 1.83654 | -2.59978 | -3.37238 |
| H | 1.81561 | -2.41358 | -1.59461 |
| C | 3.11641 | -0.21760 | -4.01129 |
| H | 3.13809 | 0.87622 | -4.15371 |
| H | 2.58320 | -0.66442 | -4.86809 |
| H | 4.15872 | -0.57987 | -4.04290 |
| C | 2.32093 | 2.52951 | 1.42690 |
| H | 1.29655 | 2.66798 | 1.03962 |
| C | 2.19758 | 1.93968 | 2.85012 |
| H | 1.66246 | 0.97555 | 2.83396 |
| H | 1.64267 | 2.63240 | 3.50632 |
| H | 3.19054 | 1.77123 | 3.30247 |
| C | 2.99868 | 3.91840 | 1.45260 |
| H | 4.02292 | 3.86187 | 1.86047 |
| H | 2.42541 | 4.61244 | 2.09113 |
| H | 3.06459 | 4.35703 | 0.44243 |
| C | -2.50890 | 0.83898 | -0.63412 |
| C | -3.13275 | -0.09686 | -1.49651 |
| C | -4.47309 | -0.43306 | -1.22441 |
| H | -4.98207 | -1.15953 | -1.86643 |
| C | -5.15942 | 0.13618 | -0.14511 |
| H | -6.19991 | -0.14364 | 0.04983 |
| C | -4.51483 | 1.05619 | 0.69041 |
| H | -5.05635 | 1.48889 | 1.53810 |
| C | -3.17525 | 1.43014 | 0.46827 |
| C | -2.40608 | -0.75526 | -2.66881 |
| H | -1.39373 | -0.31910 | -2.73067 |
| C | -2.23932 | -2.27368 | -2.42988 |
| H | -1.69172 | -2.47030 | -1.49265 |
| H | -1.68022 | -2.73459 | -3.26273 |
| H | -3.21866 | -2.77865 | -2.36204 |
| C | -3.11513 | -0.47223 | -4.01243 |
| H | -4.12892 | -0.90833 | -4.03542 |
| H | -2.54515 | -0.91571 | -4.84704 |
| H | -3.21225 | 0.61059 | -4.20064 |
| C | -2.49453 | 2.41918 | 1.41396 |
| H | -1.46972 | 2.59521 | 1.04299 |
| C | -2.37327 | 1.82764 | 2.83709 |
| H | -3.36698 | 1.63415 | 3.27726 |
| H | -1.84280 | 2.53148 | 3.50176 |
| H | -1.81752 | 0.87498 | 2.82528 |
| C | -3.22167 | 3.78279 | 1.43290 |
| H | -3.28457 | 4.22395 | 0.42356 |
| H | -2.68606 | 4.49392 | 2.08527 |
| H | -4.25061 | 3.68713 | 1.82107 |
| C | 0.90934 | -3.27179 | 2.30977 |
| H | 0.66827 | -3.62497 | 3.33145 |
| C | 2.21752 | -2.47283 | 2.34664 |
| H | 2.47276 | -2.08414 | 1.34193 |
| H | 3.05695 | -3.10651 | 2.68450 |
| H | 2.13673 | -1.61228 | 3.03269 |
| C | 1.02607 | -4.51770 | 1.41000 |
| H | 0.08054 | -5.08140 | 1.43341 |
| H | 1.83834 | -5.18388 | 1.75393 |
| H | 1.23954 | -4.22278 | 0.36601 |
| C | -1.45312 | -2.80600 | 2.28606 |
| H | -2.25773 | -2.10787 | 1.92628 |
| C | -0.75413 | 2.28548 | -1.70724 |
| H | -1.48517 | 2.91722 | -2.20412 |
| C | 0.61370 | 2.31479 | -1.70350 |
| H | 1.31998 | 2.97730 | -2.19607 |

PinBH
SCF (BP86) Energy = -411.857276480
Enthalpy 0K = -411.662324
Enthalpy 298K = -411.661379
Free Energy 298K = -411.705588
Lowest Frequency = 87.9830 cm-1
Second Frequency = 214.9008 cm-1
SCF (BP86-D3BJ) Energy = -411.890528919
SCF (C6H6) Energy = -411.859141657
SCF (BS2) Energy = -411.965484248
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -411.5107886
SCF (wB97XD-BS2-C6H6) Energy = -411.8584391

| | | | |
|---|---|---|---|
| C | 0.79096 | 0.19447 | 0.04645 |
| C | -0.79102 | 0.19460 | -0.04645 |
| B | -0.00015 | -1.95002 | 0.00000 |
| O | -1.09223 | -1.20509 | -0.38673 |
| O | 1.09198 | -1.20518 | 0.38672 |
| C | -1.48266 | 0.46945 | 1.30009 |
| H | -1.37209 | 1.52289 | 1.60705 |
| H | -2.55757 | 0.24770 | 1.20199 |
| H | -1.07464 | -0.17310 | 2.09746 |
| C | -1.37864 | 1.09161 | -1.13987 |
| H | -1.13471 | 2.15108 | -0.95008 |
| H | -1.00336 | 0.81786 | -2.13710 |
| H | -2.47634 | 0.99207 | -1.15015 |
| C | 1.48280 | 0.46924 | -1.30003 |
| H | 1.37238 | 1.52269 | -1.60700 |
| H | 2.55768 | 0.24738 | -1.20175 |
| H | 1.07486 | -0.17326 | -2.09748 |

```
C   1.37882  1.09142  1.13982
H   2.47649  0.99155  1.15012
H   1.13516  2.15092  0.94993
H   1.00349  0.81785  2.13708
H  -0.00018 -3.14804 -0.00000
```

PinBN(iPr)C(O)H
SCF (BP86) Energy = -698.537787458
Enthalpy 0K = -698.225491
Enthalpy 298K = -698.224547
Free Energy 298K = -698.286559
Lowest Frequency = 36.2777 cm-1
Second Frequency = 55.2277 cm-1
SCF (BP86-D3BJ) Energy = -698.596445632
SCF (C6H6) Energy = -698.541193593
SCF (BS2) Energy = -698.724049796
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -697.9570337
SCF (wB97XD-BS2-C6H6) Energy = -698.5348924

```
O   3.39524  2.03440 -0.22073
N   1.69014  0.45079 -0.05508
C   2.67315 -0.66430  0.07524
H   3.65299 -0.16139  0.00685
C   2.53964 -1.65823 -1.09003
H   1.55940 -2.16201 -1.07144
H   3.32503 -2.43006 -1.01845
H   2.65451 -1.14475 -2.05915
C   2.55669 -1.34360  1.45000
H   2.68624 -0.60884  2.26202
H   3.34141 -2.11194  1.55827
H   1.57623 -1.83272  1.57045
C   2.20115  1.74492 -0.19048
H   1.39253  2.50504 -0.27198
B   0.25383  0.25283 -0.04262
O  -0.34448 -0.97783  0.17813
O  -0.64374  1.28995 -0.24715
C  -1.77563 -0.79672 -0.10754
C  -1.96775  0.76060  0.10477
C  -2.57069 -1.68590  0.85207
C  -1.99773 -1.24135 -1.56320
C  -3.00386  1.41725 -0.81125
C  -2.22478  1.14524  1.57202
H  -3.65528 -1.53707  0.71352
H  -2.34533 -2.74582  0.64988
H  -2.31854 -1.47843  1.90257
H  -3.06439 -1.20333 -1.84034
H  -1.43119 -0.60842 -2.26580
H  -1.64798 -2.27990 -1.67926
H  -4.00902  1.00162 -0.62514
H  -3.04219  2.50060 -0.61174
H  -2.75497  1.27565 -1.87338
H  -2.13215  2.23818  1.67722
H  -3.23591  0.85051  1.89881
H  -1.48884  0.67383  2.24410
```

IPrCuOCH2N(iPr)BPin
SCF (BP86) Energy = -2056.43692037
Enthalpy 0K = -2055.771685
Enthalpy 298K = -2055.770741
Free Energy 298K = -2055.917590
Lowest Frequency = 5.1528 cm-1
Second Frequency = 11.5302 cm-1
SCF (BP86-D3BJ) Energy = -2056.91600028
SCF (C6H6) Energy = -2056.69367200
SCF (BS2) Energy = -2057.14678472
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2054.920299
SCF (wB97XD-BS2-C6H6) Energy = -2056.536902

```
N   2.35651 -2.32979 -0.81367
C   2.09174 -3.60246 -0.10440
H   1.07864 -3.90290 -0.42943
C   2.04277 -3.41282  1.42178
H   3.01686 -3.06786  1.80517
H   1.78802 -4.36407  1.92266
H   1.27649 -2.66443  1.68559
C   3.09603 -4.69817 -0.51494
H   3.09806 -4.83462 -1.61019
H   2.83874 -5.66779 -0.05166
H   4.11625 -4.42225 -0.19876
B   3.51356 -1.54035 -0.60914
O   4.54639 -1.86773  0.28800
O   3.77185 -0.34312 -1.29820
C   5.43258 -0.71328  0.34971
C   5.16468 -0.00933 -1.04182
C   6.86554 -1.21483  0.56010
C   4.98810  0.14546  1.54888
C   5.30611  1.51659 -1.03360
C   5.99915 -0.61496 -2.18728
H   7.58359 -0.37637  0.54670
H   6.94475 -1.71418  1.54021
H   7.15676 -1.94051 -0.21401
H   5.66514  1.00129  1.71392
H   3.96546  0.52972  1.40184
H   4.99395 -0.48022  2.45653
H   6.33276  1.81660 -0.75958
H   5.09354  1.91426 -2.04008
H   4.59852  1.98062 -0.33011
H   5.60927 -0.24058 -3.14789
H   7.06486 -0.33874 -2.11319
H   5.92121 -1.71465 -2.19320
O   0.09472 -1.93325 -1.56342
Cu -0.68701 -0.59181 -0.64661
C  -1.77614  0.66345  0.16879
N  -3.14136  0.54089  0.35807
N  -1.50129  1.93100  0.64581
C  -3.68860  1.69106  0.92866
C  -3.91235 -0.63841  0.01884
C  -2.65498  2.56772  1.11050
C  -0.18922  2.54322  0.67736
H  -4.74931  1.77496  1.14839
C  -4.15012 -1.60389  1.02909
C  -4.41264 -0.77163 -1.30046
H  -2.62916  3.57379  1.51970
C   0.26741  3.23747 -0.47062
C   0.56666  2.45829  1.87323
C  -4.92706 -2.72641  0.68358
C  -3.57420 -1.48306  2.43971
C  -5.18216 -1.91571 -1.58816
C  -4.13828  0.25432 -2.39904
C   1.52668  3.86298 -0.38985
```

C -0.53950 3.31327 -1.76611
C 1.81535 3.10940 1.89873
C 0.07966 1.69647 3.10564
H -5.12356 -3.49331 1.44027
C -5.44108 -2.88222 -0.60929
H -3.04122 -0.51882 2.50923
C -2.53936 -2.60040 2.70587
C -4.68384 -1.47739 3.51496
H -5.57857 -2.05042 -2.60003
H -3.52544 1.06254 -1.96351
C -3.31902 -0.37305 -3.55037
C -5.44710 0.89050 -2.91978
H 1.91131 4.40231 -1.26166
C 2.29147 3.80725 0.78170
H -1.51771 2.83490 -1.58506
C 0.15815 2.51984 -2.89470
C -0.80966 4.77465 -2.18937
H 2.42237 3.06560 2.80916
H -0.89122 1.23397 2.85716
C 1.04996 0.55327 3.47834
C -0.14863 2.64754 4.30276
H -6.04065 -3.76454 -0.85687
H -3.00856 -3.59891 2.66278
H -2.09336 -2.48126 3.70866
H -1.72846 -2.57523 1.95925
H -5.24519 -2.42790 3.52309
H -5.40863 -0.66270 3.34645
H -4.24483 -1.34346 4.51875
H -2.36897 -0.79413 -3.17983
H -3.08841 0.38999 -4.31426
H -3.88071 -1.18390 -4.04677
H -6.10276 0.13713 -3.39039
H -5.22403 1.65836 -3.68070
H -6.01816 1.36980 -2.10630
H 3.26362 4.30967 0.82420
H -0.44306 2.55915 -3.81976
H 0.28836 1.46146 -2.61118
H 1.15492 2.93742 -3.12041
H 0.12642 5.30955 -2.42673
H -1.32631 5.33940 -1.39471
H -1.44179 4.79905 -3.09374
H 1.19461 -0.13922 2.63311
H 0.65370 -0.02193 4.33307
H 2.04076 0.94292 3.77037
H 0.79153 3.13745 4.61113
H -0.53418 2.08736 5.17219
H -0.87446 3.44184 4.05835
C 1.43417 -2.04930 -1.93602
H 1.83423 -1.15142 -2.44689
H 1.50512 -2.90513 -2.65050

TS(IPrCuH)
SCF (BP86) Energy = -2716.25125080
Enthalpy 0K = -2715.059515
Enthalpy 298K = -2715.058570
Free Energy 298K = -2715.246531
Lowest Frequency = -11.6355 cm-1
Second Frequency = 4.8322 cm-1
SCF (BP86-D3BJ) Energy = -2716.57217075
SCF (C6H6) Energy = -2716.26289990
SCF (BS2) Energy = -2716.80750050
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2713.862944
SCF (wB97XD-BS2-C6H6) Energy = -2715.944736

Cu 2.13594 0.00035 -0.94335
Cu -2.13411 0.00008 0.94051
N 4.29088 -1.08398 0.79313
N 4.29310 1.07976 0.79330
N -4.29372 -1.07994 -0.79262
N -4.29189 1.08379 -0.79292
C 3.59589 -0.00135 0.29048
C 5.37790 -0.68730 1.57481
H 6.03830 -1.40660 2.05131
C 5.37930 0.68075 1.57493
H 6.04115 1.39861 2.05157
C 3.92878 -2.46766 0.55931
C 4.37110 -3.09732 -0.63095
C 4.01386 -4.44633 -0.82116
H 4.33435 -4.95899 -1.73438
C 3.25802 -5.13834 0.13272
H 2.99223 -6.18746 -0.03605
C 2.84021 -4.49043 1.30105
H 2.24570 -5.03672 2.04080
C 3.16192 -3.14058 1.54343
C 5.19903 -2.37521 -1.69356
H 5.40667 -1.35499 -1.32706
C 4.40565 -2.23453 -3.01245
H 4.15435 -3.22322 -3.43592
H 5.00334 -1.68860 -3.76350
H 3.46409 -1.68097 -2.84752
C 6.55927 -3.07189 -1.92390
H 7.13973 -3.14928 -0.98869
H 7.16087 -2.50449 -2.65515
H 6.42973 -4.09317 -2.32298
C 2.69597 -2.46942 2.83560
H 2.98793 -1.40592 2.79240
C 1.15970 -2.51465 2.98948
H 0.64865 -1.99131 2.16518
H 0.86019 -2.01937 3.92906
H 0.78645 -3.55346 3.02754
C 3.39937 -3.09580 4.06294
H 3.13609 -4.16258 4.17330
H 3.09205 -2.57771 4.98785
H 4.49842 -3.03070 3.98244
C 3.93378 2.46421 0.55971
C 4.37794 3.09337 -0.63013
C 4.02340 4.44312 -0.82012
H 4.34536 4.95545 -1.73302
C 3.26833 5.13629 0.13353
H 3.00463 6.18596 -0.03508
C 2.84860 4.48882 1.30142
H 2.25467 5.03601 2.04097
C 3.16764 3.13830 1.54359
C 5.20489 2.36990 -1.69258
H 5.41050 1.34923 -1.32618
C 4.41164 2.23094 -3.01173
H 3.46898 1.67914 -2.84718
H 5.00852 1.68401 -3.76270
H 4.16233 3.22017 -3.43511
C 6.56650 3.06406 -1.92239
H 6.43901 4.08565 -2.32134
H 7.16726 2.49565 -2.65354

```
H    7.14681   3.14021 -0.98698
C    2.69930   2.46756  2.83510
H    2.99074   1.40389  2.79252
C    1.16277   2.51371  2.98625
H    0.86121   2.01864  3.92529
H    0.65290   1.99068  2.16103
H    0.79016   3.55278  3.02350
C    3.40094   3.09360  4.06360
H    4.50009   3.02798  3.98491
H    3.09183   2.57563  4.98799
H    3.13798   4.16050  4.17361
C   -3.59614   0.00141 -0.29083
C   -5.38084  -0.68130 -1.57315
H   -6.04307  -1.39940 -2.04891
C   -5.37969   0.68675 -1.57333
H   -6.04074   1.40582 -2.04927
C   -3.93395  -2.46426 -0.55896
C   -4.37734  -3.09328  0.63124
C   -4.02238  -4.44291  0.82133
H   -4.34373  -4.95512  1.73450
C   -3.26762  -5.13608 -0.13257
H   -3.00357  -6.18565  0.03612
C   -2.84861  -4.48874 -1.30079
H   -2.25487  -5.03592 -2.04051
C   -3.16812  -3.13835 -1.54308
C   -5.20368  -2.36967  1.69405
H   -5.41019  -1.34932  1.32728
C   -4.40918  -2.22958  3.01234
H   -4.15902  -3.21846  3.43601
H   -5.00555  -1.68247  3.76359
H   -3.46692  -1.67750  2.84652
C   -6.56471  -3.06437  1.92562
H   -6.43635  -4.08563  2.32512
H   -7.14589  -3.14142  0.99082
H   -7.16505  -2.49579  2.65698
C   -2.70039  -2.46768 -2.83485
H   -2.99286  -1.40428 -2.79270
C   -1.16379  -2.51245 -2.98572
H   -0.65458  -1.98877 -2.16051
H   -0.86248  -2.01735 -3.92482
H   -0.79021  -3.55118 -3.02259
C   -3.40130  -3.09484 -4.06319
H   -3.13730  -4.16151 -4.17283
H   -3.09258  -2.57688 -4.98771
H   -4.50052  -3.03023 -3.98462
C   -3.92989   2.46759 -0.55965
C   -3.16352   3.14038 -1.54424
C   -2.84190   4.49033 -1.30233
H   -2.24773   5.03652 -2.04244
C   -3.25936   5.13848 -0.13400
H   -2.99365   6.18768  0.03440
C   -4.01470   4.44659  0.82037
H   -4.33486   4.95944  1.73361
C   -4.37179   3.09748  0.63065
C   -5.19888   2.37535  1.69390
H   -5.40707   1.35524  1.32742
C   -4.40420   2.23433  3.01197
H   -3.46286   1.68072  2.84599
H   -5.00119   1.68833  3.76353
H   -4.15237   3.22291  3.43534
C   -6.55878   3.07220  1.92573
H   -6.42872   4.09334  2.32497
H   -7.15977   2.50469  2.65739
H   -7.14012   3.14994  0.99109
C   -2.69766   2.46887 -2.83625
H   -2.99052   1.40561 -2.79318
C   -1.16127   2.51290 -2.98932
H   -0.86155   2.01717 -3.92860
H   -0.65101   1.98946 -2.16460
H   -0.78727   3.55144 -3.02737
C   -3.39996   3.09577 -4.06395
H   -3.13573   4.16231 -4.17430
H   -4.49910   3.03159 -3.98394
H   -3.09264   2.57735 -4.98867
H    1.06398   0.00110 -2.01763
H   -1.05968  -0.00106  2.01230
```

TS(IPrCuH2BPin)
SCF (BP86) Energy = -1769.98281982
Enthalpy 0K = -1769.191836
Enthalpy 298K = -1769.190892
Free Energy 298K = -1769.319596
Lowest Frequency = -101.0561 cm-1
Second Frequency = 6.5093 cm-1
SCF (BP86-D3BJ) Energy = -1770.18380180
SCF (C6H6) Energy = -1769.98974857
SCF (BS2) Energy = -1770.36734105
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1768.44492
SCF (wB97XD-BS2-C6H6) Energy = -1769.829541

```
Cu -0.35310   0.33736 -0.74979
N   1.22664  -1.80723  0.53494
N   2.34825   0.04327  0.47036
C   1.11860  -0.48957  0.13920
C   2.47950  -2.08119  1.08855
H   2.74455  -3.07028  1.45176
C   3.18904  -0.91251  1.04634
H   4.19995  -0.67337  1.36469
C   0.17943  -2.79800  0.38253
C   0.13492  -3.55753 -0.81309
C  -0.86490  -4.54397 -0.91662
H  -0.92979  -5.14370 -1.83066
C  -1.77639  -4.76502  0.12266
H  -2.54404  -5.53960  0.02145
C  -1.71455  -3.99018  1.28696
H  -2.43933  -4.16074  2.08976
C  -0.74136  -2.98423  1.44369
C   1.09835  -3.32642 -1.97655
H   1.81887  -2.54758 -1.67185
C   0.34235  -2.79089 -3.21440
H  -0.39739  -3.52525 -3.57942
H   1.05003  -2.58909 -4.03759
H  -0.18982  -1.85442 -2.97452
C   1.90496  -4.60040 -2.31408
H   1.24692  -5.41806 -2.65672
H   2.46864  -4.96875 -1.43988
H   2.62555  -4.39401 -3.12433
C  -0.70407  -2.15094  2.72431
H   0.02163  -1.33299  2.57320
C  -2.07223  -1.49859  3.02478
H  -2.43464  -0.90138  2.17192
H  -1.98798  -0.83630  3.90404
H  -2.83908  -2.25792  3.26005
C  -0.21471  -2.99840  3.92194
```

```
H  -0.90194 -3.83992  4.11977
H  -0.16437 -2.38292  4.83704
H   0.78794 -3.42161  3.73914
C   2.72184  1.42708  0.25963
C   2.60217  2.33281  1.34387
C   2.99733  3.66624  1.12213
H   2.91647  4.39019  1.93986
C   3.47997  4.08163 -0.12463
H   3.77616  5.12495 -0.27658
C   3.57899  3.16589 -1.17866
H   3.95068  3.50028 -2.15295
C   3.20700  1.81728 -1.01378
C   3.33241  0.84743 -2.18826
H   3.02004 -0.15199 -1.83932
C   2.38184  1.24543 -3.34028
H   1.33226  1.25583 -2.99802
H   2.46657  0.52382 -4.17156
H   2.62809  2.24627 -3.73699
C   4.79511  0.73583 -2.67531
H   5.16555  1.69839 -3.06930
H   4.87161 -0.00647 -3.48860
H   5.47239  0.42416 -1.86181
C   2.07121  1.91568  2.71564
H   1.74660  0.86281  2.64903
C   0.83736  2.75021  3.12640
H   0.44158  2.39402  4.09339
H   0.03505  2.67184  2.37467
H   1.09049  3.81830  3.24463
C   3.17974  1.99548  3.79075
H   3.54463  3.03048  3.91229
H   4.04666  1.36514  3.52868
H   2.79487  1.65839  4.76889
H  -1.32803  0.75478 -1.84954
C  -4.06653  2.53019 -1.06371
C  -4.57227  1.27135 -0.23719
B  -2.29270  1.51378 -0.04237
O  -3.32974  0.59051  0.12495
O  -2.72440  2.74680 -0.52272
C  -5.25988  1.65247  1.08726
H  -6.24581  2.11883  0.91996
H  -5.40652  0.74028  1.68874
H  -4.63523  2.34872  1.67029
C  -5.44785  0.29190 -1.02672
H  -6.38031  0.77787 -1.36363
H  -4.91620 -0.10139 -1.90569
H  -5.72207 -0.56097 -0.38353
C  -3.91545  2.25163 -2.56973
H  -4.89377  2.10164 -3.05710
H  -3.42173  3.11680 -3.04225
H  -3.28122  1.36780 -2.74546
C  -4.87786  3.81220 -0.84303
H  -4.42927  4.63480 -1.42417
H  -5.91972  3.68305 -1.18470
H  -4.88859  4.11135  0.21594
H  -1.27915  1.43750  0.64423
```

TS1

SCF (BP86) Energy = -1644.20066543
Enthalpy 0K = -1644.030566
Enthalpy 298K = -1644.029622
Free Energy 298K = -1644.151766
Lowest Frequency = -69.5115 cm-1
Second Frequency = 14.3400 cm-1

SCF (BP86-D3BJ) Energy = -1644.92414479
SCF (C6H6) Energy = -1644.74488005
SCF (BS2) Energy = -1645.09773320
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1643.300945
SCF (wB97XD-BS2-C6H6) Energy = -1644.572123

```
N  -0.60561  1.03435 -3.01291
C  -1.38001  2.31126 -3.05867
H  -1.34653  2.70875 -4.09157
C  -2.83998  2.02567 -2.67921
H  -2.89510  1.57409 -1.67433
H  -3.42661  2.96085 -2.67966
H  -3.30442  1.32602 -3.39331
C  -0.70863  3.31460 -2.11666
H   0.31670  3.54191 -2.45016
H  -1.28229  4.25644 -2.08431
H  -0.65232  2.89478 -1.09789
C  -0.32621  0.34710 -4.01407
O  -0.07853 -0.23209 -5.02012
Cu  0.13283 -0.41726 -1.49045
N   1.31999 -0.17318  1.18161
N  -0.82319 -0.46442  1.33999
C   0.16916 -0.19610  0.40457
C   1.05061 -0.44066  2.52649
H   1.83756 -0.47973  3.27465
C  -0.29855 -0.62773  2.62690
H  -0.92777 -0.86433  3.48029
C   2.65716  0.03748  0.66711
C   3.17530  1.35781  0.63957
C   4.49624  1.52944  0.18313
H   4.92714  2.53522  0.15207
C   5.26625  0.43556 -0.23173
H   6.29122  0.59152 -0.58504
C   4.72755 -0.85546 -0.19673
H   5.33562 -1.70474 -0.52497
C   3.41262 -1.08840  0.25255
C   2.36317  2.55770  1.12861
H   1.29883  2.26272  1.11953
C   2.50651  3.79045  0.21179
H   3.52523  4.21477  0.24632
H   1.81346  4.58598  0.53564
H   2.27829  3.53967 -0.83675
C   2.74258  2.91838  2.58507
H   3.80845  3.19913  2.65364
H   2.57345  2.07132  3.27074
H   2.14209  3.77240  2.94489
C   2.87202 -2.51651  0.31952
H   1.79176 -2.45717  0.53682
C   3.01673 -3.25860 -1.02609
H   2.46692 -2.72420 -1.81852
H   2.59380 -4.27485 -0.93948
H   4.07397 -3.36667 -1.32700
C   3.54954 -3.29787  1.47037
H   4.63705 -3.39171  1.30170
H   3.13120 -4.31694  1.54245
H   3.40459 -2.79957  2.44465
C  -2.23646 -0.55108  1.04349
C  -2.75197 -1.74820  0.48319
C  -4.13704 -1.79930  0.22723
H  -4.56366 -2.70996 -0.20558
C  -4.97440 -0.71822  0.52491
```

H  -6.04815 -0.78409  0.31895
C  -4.44145  0.44504  1.09404
H  -5.10533  1.28205  1.33431
C  -3.06372  0.55822  1.36482
C  -2.51897  1.82371  2.03166
H  -1.41819  1.80116  1.94860
C  -3.00775  3.11959  1.34968
H  -2.76730  3.12709  0.27466
H  -2.52640  3.99695  1.81535
H  -4.09866  3.25304  1.45395
C  -2.87821  1.84505  3.53707
H  -3.97319  1.86346  3.67869
H  -2.45756  2.74166  4.02492
H  -2.48953  0.95749  4.06345
C  -1.88608 -2.98290  0.22956
H  -0.82862 -2.67854  0.30921
C  -2.07303 -3.56024 -1.18883
H  -1.42346 -4.44257 -1.32010
H  -1.78237 -2.81920 -1.95157
H  -3.11260 -3.88438 -1.37399
C  -2.16172 -4.05333  1.31310
H  -3.20874 -4.40284  1.27119
H  -1.98015 -3.66144  2.32876
H  -1.50722 -4.92932  1.16238
H   0.48908 -1.52094 -2.52507

TS2
SCF (BP86) Energy = -2056.63804994
Enthalpy 0K = -2055.735626
Enthalpy 298K = -2055.734682
Free Energy 298K = -2055.877864
Lowest Frequency = -143.8098 cm-1
Second Frequency = 9.0158 cm-1
SCF (BP86-D3BJ) Energy =  -
2056.88981527
SCF (C6H6) Energy =  -2056.65324295
SCF (BS2) Energy =  -2057.10571094
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -
2054.887744
SCF (wB97XD-BS2-C6H6) Energy = -
2056.504248

O  -1.33587 -3.94429  0.98756
N  -1.11464 -2.06583 -0.41596
C  -0.82371 -2.96867 -1.57627
H  -1.63110 -3.72458 -1.60802
C   0.51603 -3.70744 -1.39609
H   1.35089 -2.98397 -1.33525
H   0.70341 -4.37123 -2.25918
H   0.50510 -4.31723 -0.48156
C  -0.82881 -2.17558 -2.89113
H  -1.81452 -1.73234 -3.09273
H  -0.56016 -2.84207 -3.72939
H  -0.07689 -1.36204 -2.85668
C  -1.31441 -2.72031  0.79696
H  -1.50444 -1.99930  1.62599
C  -4.55099 -0.83647  0.50294
C  -4.65385 -1.70802 -0.82279
B  -2.55448 -0.71037 -0.69780
O  -3.51128 -1.25167 -1.59409
O  -3.13500 -0.52507  0.59552
C  -4.52548 -3.22592 -0.58358
H  -4.43508 -3.72775 -1.56173
H  -3.63998 -3.49108  0.01360
H  -5.41848 -3.63157 -0.07680
C  -5.91324 -1.44179 -1.66257
H  -6.82811 -1.70385 -1.10260
H  -5.97834 -0.38838 -1.97346
H  -5.88449 -2.06265 -2.57369
C  -5.29752  0.50918  0.39795
H  -6.39351  0.37888  0.38262
H  -5.03480  1.12843  1.27155
H  -4.99312  1.05695 -0.50850
C  -4.97868 -1.57016  1.78161
H  -4.84745 -0.90621  2.65296
H  -6.04342 -1.85939  1.73514
H  -4.37656 -2.47589  1.94861
H  -1.84572  0.18193 -1.15045
Cu  0.06959 -0.53542 -0.19233
C   1.31930  0.80907  0.18378
N   1.11888  2.16197  0.36103
N   2.66863  0.64717  0.42500
C  -0.14795  2.85447  0.20841
C   2.30316  2.81430  0.70347
C   3.38051 -0.61464  0.35063
C   3.28169  1.85860  0.74353
C  -0.99468  2.97817  1.33765
C  -0.46039  3.41727 -1.05361
H   2.33642  3.88546  0.88140
C   3.41370 -1.44790  1.49710
C   4.04633 -0.94176 -0.85744
H   4.34321  1.92492  0.96471
C  -2.18058  3.71989  1.17488
C  -0.65943  2.35974  2.69433
C  -1.66241  4.14357 -1.15698
C   0.43874  3.25886 -2.27946
C   4.15253 -2.64337  1.40349
C   2.71829 -1.07974  2.80751
C   4.77074 -2.14927 -0.89015
C   4.01731 -0.03645 -2.08936
H  -2.85737  3.83570  2.02729
C  -2.51135  4.30039 -0.05522
H   0.19361  1.67349  2.55034
C  -1.83202  1.52029  3.24896
C  -0.22136  3.44689  3.70369
H  -1.93606  4.58838 -2.11948
H   1.30362  2.63628 -1.99076
C  -0.29787  2.51934 -3.41933
C   0.98702  4.62244 -2.75842
H   4.19710 -3.31159  2.26933
C   4.82550 -2.99199  0.22640
H   2.05837 -0.21721  2.60947
C   1.82684 -2.22389  3.33752
C   3.75450 -0.64499  3.87107
H   5.29648 -2.43229 -1.80799
H   3.30125  0.78095 -1.89415
C   3.52270 -0.78711 -3.34549
C   5.40301  0.60422 -2.33767
H  -3.44044  4.87078 -0.15798
H  -2.68795  2.15998  3.52908
H  -1.51367  0.98716  4.16178
H  -2.18614  0.78280  2.50896
H   0.65675  4.01016  3.34345
H   0.03992  2.99058  4.67428
H  -1.03505  4.17219  3.88041
H  -0.67609  1.54117 -3.07965
H   0.38284  2.35571 -4.27286

```
H  -1.15955  3.10311 -3.78728
H   0.17045  5.29419 -3.07571
H   1.66108  4.48556 -3.62174
H   1.55126  5.13624 -1.96143
H   5.39240 -3.92755  0.17789
H   1.08861 -2.54600  2.58562
H   1.27986 -1.89028  4.23599
H   2.42242 -3.10722  3.62673
H   4.44769 -1.47091  4.10891
H   3.24761 -0.35000  4.80613
H   4.35928  0.21073  3.52524
H   4.21512 -1.59614 -3.63615
H   3.44968 -0.09233 -4.19986
H   2.52976 -1.23603 -3.17996
H   5.74387  1.18759 -1.46542
H   5.36633  1.28128 -3.20864
H   6.16629 -0.16688 -2.54211
```

TS3
SCF (BP86) Energy = -2055.92314629
Enthalpy 0K = -2055.739681
Enthalpy 298K = -2055.738737
Free Energy 298K = -2055.882225
Lowest Frequency = -599.9324 cm-1
Second Frequency = 10.0061 cm-1
SCF (BP86-D3BJ) Energy = -2056.87865173
SCF (C6H6) Energy = -2056.65465150
SCF (BS2) Energy = -2057.10946799
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2054.876036
SCF (wB97XD-BS2-C6H6) Energy = -2056.489185

```
O  -0.86388  0.09883  1.86826
N  -2.91318 -0.46774  0.81910
C  -2.66043 -1.92343  0.96147
H  -1.61875 -1.98903  1.31999
C  -2.77046 -2.64323 -0.39491
H  -3.80423 -2.60485 -0.77691
H  -2.47481 -3.70206 -0.29339
H  -2.10376 -2.17274 -1.13707
C  -3.56915 -2.54615  2.03506
H  -3.43298 -2.03238  3.00099
H  -3.32188 -3.61354  2.17263
H  -4.62962 -2.47272  1.74297
C  -1.80231  0.41487  1.00774
H  -2.14334  1.46397  0.94525
B  -4.16233  0.07370  0.37469
O  -5.27500 -0.70150  0.04552
O  -4.38931  1.44376  0.24225
C  -6.39773  0.22696 -0.09670
C  -5.66823  1.58645 -0.45098
C  -7.12278  0.26909  1.26058
C  -7.33195 -0.31207 -1.18417
C  -5.35457  1.72832 -1.95160
C  -6.36031  2.84932  0.07126
H  -8.03053  0.89447  1.22010
H  -7.42046 -0.75472  1.53976
H  -6.46208  0.66068  2.05135
H  -8.16393  0.38907 -1.36965
H  -6.79656 -0.48156 -2.13024
H  -7.76392 -1.27336 -0.86014
H  -6.26540  1.91717 -2.54463
H  -4.66557  2.57665 -2.09314
H  -4.86268  0.82191 -2.34115
H  -5.76361  3.73673 -0.19691
H  -7.36148  2.96351 -0.37919
H  -6.46605  2.82969  1.16619
N   3.04772  1.01004 -0.15294
N   2.83977 -1.13944 -0.36386
C   2.09766  0.00498 -0.13829
C   4.33064  0.50355 -0.38070
H   5.20370  1.14869 -0.42564
C   4.19999 -0.85091 -0.51388
H   4.93560 -1.62889 -0.69844
C   2.74159  2.41041  0.04714
C   2.71742  2.92041  1.36952
C   2.42318  4.28887  1.52998
H   2.39301  4.71228  2.53952
C   2.16360  5.11039  0.42665
H   1.93540  6.17115  0.57621
C   2.18966  4.57654 -0.86764
H   1.97559  5.22382 -1.72479
C   2.47761  3.21597 -1.08933
C   2.98820  2.05288  2.59832
H   3.20492  1.02847  2.24910
C   1.74450  1.97260  3.51342
H   1.46411  2.97118  3.89370
H   1.96045  1.33369  4.38778
H   0.87733  1.54481  2.98168
C   4.22883  2.55212  3.37414
H   4.07097  3.56780  3.77751
H   5.12633  2.58276  2.73265
H   4.44004  1.88530  4.22803
C   2.46543  2.65637 -2.51159
H   2.78380  1.60058 -2.46376
C   1.03365  2.67681 -3.09515
H   0.34492  2.09170 -2.46198
H   1.02675  2.24383 -4.11096
H   0.64633  3.70870 -3.16591
C   3.46001  3.39993 -3.43091
H   4.48740  3.36638 -3.02982
H   3.18374  4.46163 -3.55492
H   3.46894  2.94172 -4.43510
C   2.27246 -2.46893 -0.41957
C   1.87542 -2.98507 -1.67881
C   1.32457 -4.28095 -1.70433
H   1.00226 -4.70601 -2.66084
C   1.17575 -5.02837 -0.52944
H   0.74315 -6.03369 -0.57222
C   1.57740 -4.49189  0.69986
H   1.45465 -5.08181  1.61440
C   2.13575 -3.20124  0.78650
C   2.56830 -2.64845  2.14439
H   2.99275 -1.64278  1.98118
C   1.36373 -2.48898  3.10011
H   0.60944 -1.79699  2.68882
H   1.70304 -2.08763  4.07122
H   0.87759 -3.46154  3.29536
C   3.67609 -3.52278  2.77624
H   3.31168 -4.54216  2.99367
H   4.01459 -3.08119  3.72951
H   4.55174 -3.61539  2.11105
C   2.00372 -2.18386 -2.97425
H   2.52811 -1.24150 -2.73935
C   0.61089 -1.80653 -3.52906
```

H  0.71394 -1.21000 -4.45255
H  0.04442 -1.21061 -2.79345
H  0.02082 -2.70740 -3.77381
C  2.84627 -2.93262 -4.03113
H  2.36253 -3.87405 -4.34511
H  3.84972 -3.18395 -3.64729
H  2.97062 -2.30866 -4.93311
Cu 0.26736  0.19548  0.13693
H -1.19151  0.47877 -0.48759

4-NC-$C_6H_4$NCO
SCF (BP86) Energy = -491.975054717
Enthalpy 0K = -491.866583
Enthalpy 298K = -491.865639
Free Energy 298K = -491.910933
Lowest Frequency = 51.1656 cm-1
Second Frequency = 79.5687 cm-1
SCF (BP86-D3BJ) Energy = -492.002313066
SCF (C6H6) Energy = -491.978945693
SCF (BS2) Energy = -492.112136929
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -491.5484609
SCF (wB97XD-BS2-C6H6) Energy = -491.9228459

N -2.27477 -0.55726 -0.00000
C -3.31560  0.08875 -0.00000
O -4.40226  0.56807  0.00001
C -0.89904 -0.32153 -0.00000
C -0.03658 -1.43892 -0.00000
C -0.35878  0.98553 -0.00000
C  1.34739 -1.25557  0.00000
H -0.46919 -2.44273  0.00000
C  1.02451  1.16879 -0.00000
H -1.03015  1.84976 -0.00000
C  1.89296  0.05035 -0.00000
H  2.01710 -2.11974  0.00000
H  1.44482  2.17824 -0.00000
C  3.31385  0.24078  0.00000
N  4.48095  0.39737  0.00000

IPrCuN(4-NC-$C_6H_4$)C(O)H
SCF (BP86) Energy = -1850.16285784
Enthalpy 0K = -1849.452116
Enthalpy 298K = -1849.451172
Free Energy 298K = -1849.580881
Lowest Frequency = 7.2732 cm-1
Second Frequency = 9.7734 cm-1
SCF (BP86-D3BJ) Energy = -1850.36267969
SCF (C6H6) Energy = -1850.17391541
SCF (BS2) Energy = -1850.57684583
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1848.56064
SCF (wB97XD-BS2-C6H6) Energy = -1849.971959

Cu -0.01696 -0.78281 -0.19611
O -0.73438 -4.63931 -0.92800
N  0.66449  2.04214  0.17827
N  2.41863  0.76874  0.24698
N -1.05390 -2.33870 -0.45631
C  1.05186  0.72338  0.07999
C -0.70593  2.50342  0.06160
C -1.48115  2.63119  1.24181
C -2.80166  3.10092  1.09851
H -3.42815  3.21274  1.98939
C -3.32615  3.41960 -0.16028
H -4.35677  3.77870 -0.24779
C -2.53669  3.27528 -1.30768
H -2.95890  3.51846 -2.28816
C -1.20690  2.81798 -1.22668
C -0.93996  2.28845  2.62983
H  0.06263  1.84368  2.50330
C -1.82073  1.23760  3.34244
H -2.83084  1.62918  3.55360
H -1.36840  0.95393  4.30812
H -1.93435  0.32609  2.73288
C -0.78231  3.56084  3.49452
H -0.11489  4.29792  3.01641
H -0.36009  3.30644  4.48196
H -1.75673  4.05177  3.66239
C -0.37681  2.66100 -2.50050
H  0.64461  2.36082 -2.20781
C -0.94858  1.53777 -3.39605
H -0.97611  0.57456 -2.85867
H -0.32676  1.41189 -4.29916
H -1.97632  1.77079 -3.72438
C -0.26237  3.99283 -3.27609
H -1.24664  4.33936 -3.63561
H  0.38602  3.86529 -4.15987
H  0.16605  4.79287 -2.64887
C  3.28051 -0.39799  0.22611
C  3.51733 -1.08704  1.44188
C  4.36070 -2.21398  1.39064
H  4.55878 -2.77448  2.31012
C  4.94175 -2.63192  0.18736
H  5.59136 -3.51313  0.17137
C  4.68946 -1.92832 -0.99648
H  5.14365 -2.26619 -1.93375
C  3.85336 -0.79485 -1.00800
C  2.88705 -0.66784  2.76979
H  2.31264  0.25935  2.59773
C  1.89270 -1.73976  3.27263
H  1.09656 -1.92465  2.53152
H  1.41915 -1.41335  4.21461
H  2.40225 -2.69941  3.46732
C  3.96051 -0.35519  3.83685
H  4.55692 -1.24988  4.08608
H  3.48318 -0.00563  4.76838
H  4.65827  0.42762  3.49421
C  3.58516 -0.06039 -2.32146
H  2.93737  0.80649 -2.10235
C  2.82296 -0.96490 -3.31685
H  3.41811 -1.85371 -3.58919
H  2.60090 -0.41228 -4.24604
H  1.86970 -1.31632 -2.88751
C  4.89039  0.48303 -2.94596
H  5.42499  1.15295 -2.25136
H  4.66786  1.04997 -3.86624
H  5.57936 -0.33509 -3.21858
C -0.33168 -3.48599 -0.73364
H  0.76593 -3.25197 -0.77124
C  2.86576  2.07583  0.44268
H  3.91657  2.30754  0.59250

| | | | |
|---|---|---|---|
| C | 1.75850 | 2.87967 | 0.39933 |
| H | 1.64712 | 3.95557 | 0.50097 |
| C | -2.45670 | -2.32706 | -0.34720 |
| C | -3.08197 | -1.07737 | -0.08096 |
| C | -3.29635 | -3.46966 | -0.47979 |
| C | -4.46234 | -0.95763 | 0.05089 |
| H | -2.44963 | -0.18485 | 0.01817 |
| C | -4.68131 | -3.35082 | -0.34740 |
| H | -2.83237 | -4.43391 | -0.68696 |
| C | -5.29033 | -2.10053 | -0.08028 |
| H | -4.91316 | 0.01811 | 0.25422 |
| H | -5.31158 | -4.23956 | -0.45134 |
| C | -6.70995 | -1.98571 | 0.05456 |
| N | -7.87925 | -1.88258 | 0.16736 |

PinBN(4-NC-$C_6H_4$)C(O)H
SCF (BP86) Energy = -903.882318045
Enthalpy 0K = -903.573438
Enthalpy 298K = -903.572494
Free Energy 298K = -903.641116
Lowest Frequency = 25.1053 cm-1
Second Frequency = 38.3683 cm-1
SCF (BP86-D3BJ) Energy = -903.953531752
SCF (C6H6) Energy = -903.888301595
SCF (BS2) Energy = -904.123476142
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -903.1246805
SCF (wB97XD-BS2-C6H6) Energy = -903.8447165

| | | | |
|---|---|---|---|
| O | 0.97174 | 3.46286 | 0.17345 |
| N | 0.14875 | 1.26693 | 0.08942 |
| C | 0.03651 | 2.67422 | 0.15791 |
| H | -1.02965 | 2.98512 | 0.20313 |
| B | -1.08773 | 0.48572 | 0.03216 |
| O | -1.12161 | -0.89216 | 0.00757 |
| O | -2.32603 | 1.09695 | -0.01711 |
| C | -2.51381 | -1.25716 | -0.31641 |
| C | -3.31795 | 0.02128 | 0.15930 |
| C | -2.85238 | -2.55098 | 0.42699 |
| C | -2.56413 | -1.47766 | -1.83709 |
| C | -4.54807 | 0.36489 | -0.68354 |
| C | -3.67638 | -0.00519 | 1.65430 |
| H | -3.90592 | -2.83141 | 0.25769 |
| H | -2.21877 | -3.37131 | 0.05269 |
| H | -2.68422 | -2.45604 | 1.51000 |
| H | -3.55743 | -1.82934 | -2.16136 |
| H | -2.32505 | -0.55183 | -2.38574 |
| H | -1.81914 | -2.24063 | -2.11378 |
| H | -5.29448 | -0.44587 | -0.62996 |
| H | -5.01778 | 1.28433 | -0.29805 |
| H | -4.28540 | 0.53236 | -1.73846 |
| H | -4.03481 | 0.99214 | 1.95558 |
| H | -4.47300 | -0.73728 | 1.86623 |
| H | -2.79940 | -0.25493 | 2.27405 |
| C | 1.44564 | 0.65031 | 0.06430 |
| C | 1.67921 | -0.51252 | 0.82712 |
| C | 2.48910 | 1.19471 | -0.71455 |
| C | 2.92998 | -1.13422 | 0.80422 |
| H | 0.87225 | -0.93301 | 1.43085 |
| C | 3.74416 | 0.58050 | -0.73130 |
| H | 2.31797 | 2.10179 | -1.29467 |
| C | 3.97802 | -0.59144 | 0.02531 |
| H | 3.10658 | -2.03752 | 1.39455 |
| H | 4.55180 | 1.00232 | -1.33581 |
| C | 5.26441 | -1.22505 | 0.00247 |
| N | 6.31931 | -1.74819 | -0.01701 |

IPrCuOCH2N(4-NC-$C_6H_4$)BPin
SCF (BP86) Energy = -2262.04804684
Enthalpy 0K = -2261.136093
Enthalpy 298K = -2261.135148
Free Energy 298K = -2261.286790
Lowest Frequency = 6.1094 cm-1
Second Frequency = 8.9373 cm-1
SCF (BP86-D3BJ) Energy = -2262.29320354
SCF (C6H6) Energy = -2262.05809160
SCF (BS2) Energy = -2262.56358893
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2260.107615
SCF (wB97XD-BS2-C6H6) Energy = -2261.864727

| | | | |
|---|---|---|---|
| N | -2.42980 | 1.37541 | -1.36556 |
| B | -3.44361 | 0.39615 | -1.06593 |
| O | -4.55175 | 0.59131 | -0.24182 |
| O | -3.41634 | -0.87999 | -1.63076 |
| C | -5.21643 | -0.70540 | -0.09562 |
| C | -4.72616 | -1.47890 | -1.38501 |
| C | -6.72675 | -0.46163 | -0.01806 |
| C | -4.70676 | -1.32760 | 1.21557 |
| C | -4.54120 | -2.98830 | -1.20304 |
| C | -5.59094 | -1.19088 | -2.62620 |
| H | -7.27564 | -1.41814 | 0.02478 |
| H | -6.96582 | 0.10739 | 0.89551 |
| H | -7.09004 | 0.11441 | -0.88198 |
| H | -5.22271 | -2.27642 | 1.44050 |
| H | -3.62256 | -1.52028 | 1.17287 |
| H | -4.90045 | -0.62491 | 2.04246 |
| H | -5.49848 | -3.47126 | -0.94079 |
| H | -4.18406 | -3.43365 | -2.14627 |
| H | -3.80193 | -3.21285 | -0.41961 |
| H | -5.07666 | -1.58356 | -3.51825 |
| H | -6.58072 | -1.67252 | -2.55625 |
| H | -5.73818 | -0.10736 | -2.76698 |
| O | -0.12344 | 0.96663 | -2.07072 |
| Cu | 0.72840 | -0.01816 | -0.81755 |
| C | 1.91235 | -0.84575 | 0.34003 |
| N | 3.23003 | -0.46845 | 0.52076 |
| N | 1.77896 | -1.94758 | 1.16108 |
| C | 3.88685 | -1.30751 | 1.42096 |
| C | 3.85223 | 0.66901 | -0.12883 |
| C | 2.97254 | -2.24069 | 1.82565 |
| C | 0.56193 | -2.71175 | 1.33992 |
| H | 4.93059 | -1.16229 | 1.68521 |
| C | 3.85733 | 1.91442 | 0.54807 |
| C | 4.44542 | 0.48525 | -1.40284 |
| H | 3.05449 | -3.07645 | 2.51490 |
| C | 0.29618 | -3.78567 | 0.45441 |
| C | -0.29152 | -2.37784 | 2.42119 |
| C | 4.49521 | 2.99520 | -0.09122 |
| C | 3.19922 | 2.11974 | 1.91222 |
| C | 5.06513 | 1.60301 | -1.99450 |
| C | 4.41926 | -0.85046 | -2.14489 |

| | | | |
|---|---|---|---|
| C | -0.87329 | -4.53723 | 0.68218 |
| C | 1.21078 | -4.13441 | -0.71914 |
| C | -1.44405 | -3.16712 | 2.60312 |
| C | -0.01366 | -1.20517 | 3.36140 |
| H | 4.51406 | 3.97184 | 0.40364 |
| C | 5.09451 | 2.84408 | -1.34733 |
| H | 2.72836 | 1.16673 | 2.21039 |
| C | 2.07968 | 3.18265 | 1.84059 |
| C | 4.24488 | 2.48042 | 2.99239 |
| H | 5.52751 | 1.49628 | -2.98139 |
| H | 3.91087 | -1.58829 | -1.49988 |
| C | 3.60010 | -0.74028 | -3.45148 |
| C | 5.84620 | -1.37751 | -2.41814 |
| H | -1.10955 | -5.37254 | 0.01478 |
| C | -1.73264 | -4.23741 | 1.74658 |
| H | 2.10080 | -3.48416 | -0.66077 |
| C | 0.51276 | -3.83759 | -2.06625 |
| C | 1.70123 | -5.59809 | -0.65043 |
| H | -2.12358 | -2.93719 | 3.43045 |
| H | 0.95568 | -0.76172 | 3.07524 |
| C | -1.08691 | -0.10422 | 3.20225 |
| C | 0.10382 | -1.66524 | 4.83199 |
| H | 5.58192 | 3.69943 | -1.82686 |
| H | 2.48235 | 4.17607 | 1.57719 |
| H | 1.57918 | 3.27752 | 2.81957 |
| H | 1.31923 | 2.91617 | 1.08839 |
| H | 4.74711 | 3.43594 | 2.76127 |
| H | 5.02533 | 1.70507 | 3.07875 |
| H | 3.75893 | 2.58916 | 3.97736 |
| H | 2.57080 | -0.39918 | -3.24847 |
| H | 3.55017 | -1.72091 | -3.95624 |
| H | 4.06182 | -0.02482 | -4.15430 |
| H | 6.40811 | -0.69735 | -3.08169 |
| H | 5.80288 | -2.36308 | -2.91320 |
| H | 6.42444 | -1.48769 | -1.48495 |
| H | -2.63076 | -4.84217 | 1.91100 |
| H | 1.18973 | -4.06511 | -2.90794 |
| H | 0.21977 | -2.77616 | -2.13454 |
| H | -0.39687 | -4.45127 | -2.18890 |
| H | 0.86525 | -6.31293 | -0.74426 |
| H | 2.21797 | -5.80947 | 0.30110 |
| H | 2.40478 | -5.80342 | -1.47549 |
| H | -1.13902 | 0.25486 | 2.16122 |
| H | -0.85397 | 0.75696 | 3.85186 |
| H | -2.08728 | -0.47644 | 3.48438 |
| H | -0.84454 | -2.09372 | 5.20035 |
| H | 0.35419 | -0.80890 | 5.48139 |
| H | 0.88812 | -2.43105 | 4.95726 |
| C | -1.44919 | 1.02019 | -2.45490 |
| H | -1.82078 | 0.06998 | -2.87891 |
| H | -1.56627 | 1.81304 | -3.22926 |
| C | -2.34017 | 2.67415 | -0.82336 |
| C | -1.25697 | 3.52521 | -1.18388 |
| C | -3.31529 | 3.18864 | 0.07523 |
| C | -1.16868 | 4.82571 | -0.68633 |
| H | -0.45775 | 3.13075 | -1.81517 |
| C | -3.21826 | 4.48671 | 0.57505 |
| H | -4.15754 | 2.56230 | 0.37101 |
| C | -2.14644 | 5.33325 | 0.20188 |
| H | -0.32626 | 5.46042 | -0.97796 |
| H | -3.98474 | 4.86170 | 1.26033 |
| C | -2.04712 | 6.66292 | 0.72034 |
| N | -1.96237 | 7.75780 | 1.15008 |

TS1'
SCF (BP86) Energy = -1850.07802944
Enthalpy 0K = -1849.389067
Enthalpy 298K = -1849.388123
Free Energy 298K = -1849.521457
Lowest Frequency = -233.1015 cm-1
Second Frequency = 4.3020 cm-1
SCF (BP86-D3BJ) Energy = -1850.28711485
SCF (C6H6) Energy = -1850.10350531
SCF (BS2) Energy = -1850.50858747
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -1848.475791
SCF (wB97XD-BS2-C6H6) Energy = -1849.887274

| | | | |
|---|---|---|---|
| N | 2.78326 | -0.82019 | -1.47608 |
| C | 2.30020 | 0.06806 | -2.22726 |
| O | 2.20673 | 1.01266 | -2.95434 |
| Cu | -0.39846 | -0.20871 | -1.13247 |
| N | -2.64200 | -0.50126 | 0.76563 |
| N | -1.57154 | 1.35083 | 1.10220 |
| C | -1.56647 | 0.22692 | 0.30477 |
| C | -3.29309 | 0.14982 | 1.81470 |
| H | -4.16439 | -0.27618 | 2.30453 |
| C | -2.61640 | 1.32053 | 2.02718 |
| H | -2.77780 | 2.12482 | 2.73963 |
| C | -3.04850 | -1.78625 | 0.22933 |
| C | -2.50379 | -2.96229 | 0.80229 |
| C | -2.92628 | -4.19588 | 0.26996 |
| H | -2.51875 | -5.12387 | 0.68422 |
| C | -3.84861 | -4.25447 | -0.78175 |
| H | -4.16131 | -5.22500 | -1.18097 |
| C | -4.36674 | -3.07428 | -1.32821 |
| H | -5.08030 | -3.12942 | -2.15694 |
| C | -3.98066 | -1.81175 | -0.83751 |
| C | -1.46683 | -2.93006 | 1.92447 |
| H | -1.36285 | -1.88432 | 2.26312 |
| C | -0.08525 | -3.38349 | 1.39773 |
| H | -0.11962 | -4.42764 | 1.04043 |
| H | 0.67054 | -3.32490 | 2.20019 |
| H | 0.24850 | -2.74921 | 0.55873 |
| C | -1.90569 | -3.76844 | 3.14549 |
| H | -1.98815 | -4.84048 | 2.89601 |
| H | -2.88380 | -3.43858 | 3.53486 |
| H | -1.16435 | -3.67590 | 3.95770 |
| C | -4.53887 | -0.54178 | -1.47882 |
| H | -4.17131 | 0.32308 | -0.89927 |
| C | -4.01177 | -0.38500 | -2.92408 |
| H | -2.90848 | -0.36528 | -2.94431 |
| H | -4.38457 | 0.55323 | -3.37047 |
| H | -4.34749 | -1.21989 | -3.56383 |
| C | -6.08288 | -0.50453 | -1.43608 |
| H | -6.52604 | -1.32356 | -2.02872 |
| H | -6.45388 | 0.44567 | -1.85727 |
| H | -6.46326 | -0.59387 | -0.40435 |
| C | -0.60993 | 2.43203 | 0.99933 |
| C | -0.87083 | 3.48850 | 0.09154 |
| C | 0.07501 | 4.52989 | 0.02400 |
| H | -0.09114 | 5.35706 | -0.67390 |
| C | 1.22218 | 4.52196 | 0.82646 |
| H | 1.94416 | 5.34221 | 0.75603 |
| C | 1.45052 | 3.46441 | 1.71491 |

| | | | |
|---|---|---|---|
| H | 2.35382 | 3.46307 | 2.33387 |
| C | 0.54287 | 2.39270 | 1.82246 |
| C | 0.83225 | 1.24560 | 2.79028 |
| H | 0.00936 | 0.51417 | 2.70865 |
| C | 2.13844 | 0.51167 | 2.41105 |
| H | 2.09869 | 0.13004 | 1.37753 |
| H | 2.30787 | -0.34209 | 3.08985 |
| H | 3.01373 | 1.17939 | 2.49210 |
| C | 0.87191 | 1.73884 | 4.25479 |
| H | 1.68943 | 2.46347 | 4.41342 |
| H | 1.04045 | 0.89138 | 4.94145 |
| H | -0.07203 | 2.23166 | 4.54383 |
| C | -2.10438 | 3.52090 | -0.81014 |
| H | -2.74281 | 2.65981 | -0.54559 |
| C | -1.70315 | 3.35833 | -2.29432 |
| H | -2.60087 | 3.34738 | -2.93665 |
| H | -1.14869 | 2.41798 | -2.45568 |
| H | -1.05949 | 4.19088 | -2.62795 |
| C | -2.94138 | 4.80123 | -0.59089 |
| H | -2.37774 | 5.70804 | -0.87091 |
| H | -3.24947 | 4.91027 | 0.46286 |
| H | -3.85219 | 4.77332 | -1.21353 |
| H | 0.46862 | -0.58092 | -2.33762 |
| C | 4.16301 | -0.91343 | -1.20641 |
| C | 5.13239 | -0.01889 | -1.72587 |
| C | 4.58531 | -1.96862 | -0.36371 |
| C | 6.48157 | -0.17498 | -1.40556 |
| H | 4.81640 | 0.79772 | -2.38236 |
| C | 5.93318 | -2.12722 | -0.04166 |
| H | 3.82995 | -2.65696 | 0.02523 |
| C | 6.90032 | -1.22994 | -0.55780 |
| H | 7.22598 | 0.51811 | -1.80852 |
| H | 6.25274 | -2.94559 | 0.61004 |
| C | 8.28464 | -1.38611 | -0.22497 |
| N | 9.42287 | -1.51392 | 0.05210 |

TS2'
SCF (BP86) Energy = -2261.98631120
Enthalpy 0K = -2261.094663
Enthalpy 298K = -2261.093719
Free Energy 298K = -2261.243459
Lowest Frequency = -171.8631 cm-1
Second Frequency = 7.3439 cm-1
SCF (BP86-D3BJ) Energy = -2262.25871826
SCF (C6H6) Energy = -2262.01118296
SCF (BS2) Energy = -2262.51621551
SCF (PBE0-D3BJ-BS2-C6H6) Energy = -2260.065885
SCF (wB97XD-BS2-C6H6) Energy = -2261.821653

| | | | |
|---|---|---|---|
| O | -2.18772 | -1.03657 | -2.99735 |
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**NMR Spectra**

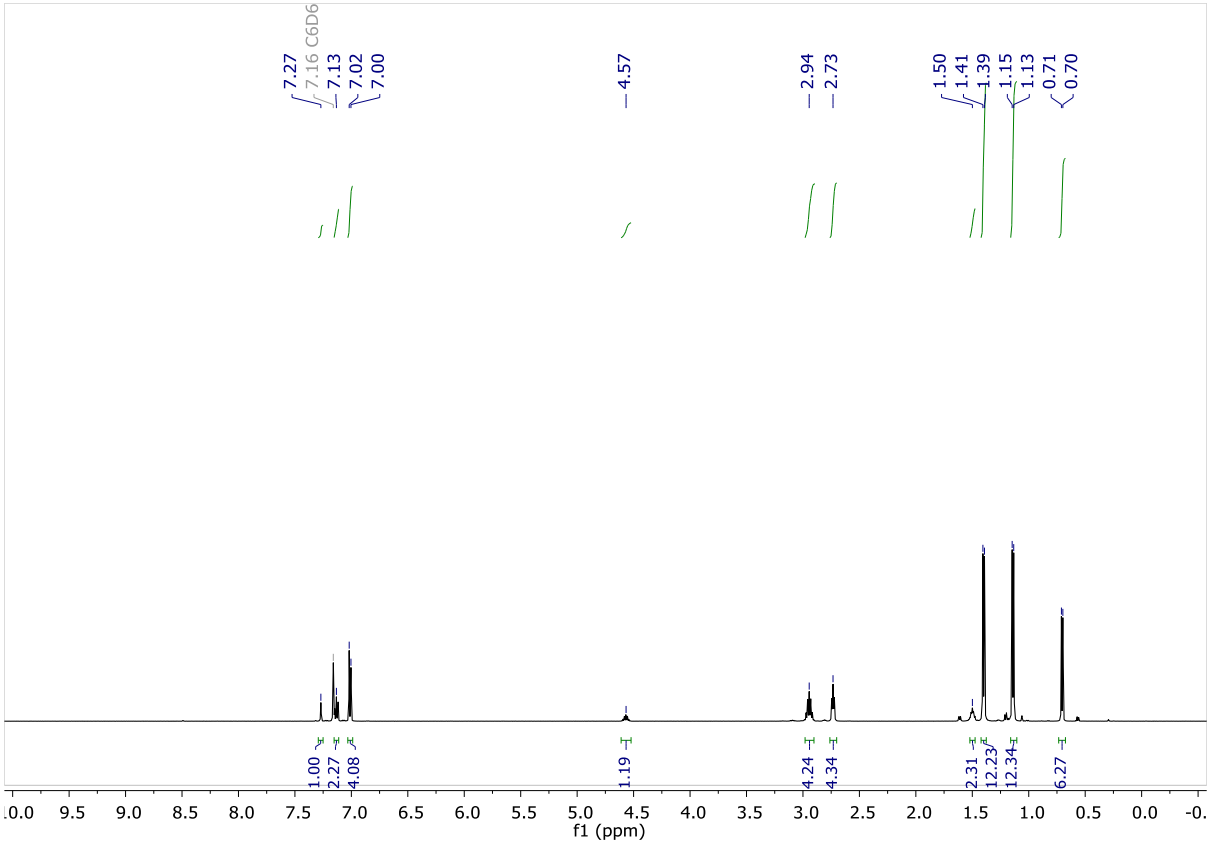


Figure S3: $^{1}$H NMR spectrum for (6-Dipp)CuN(iPr)C(O)H

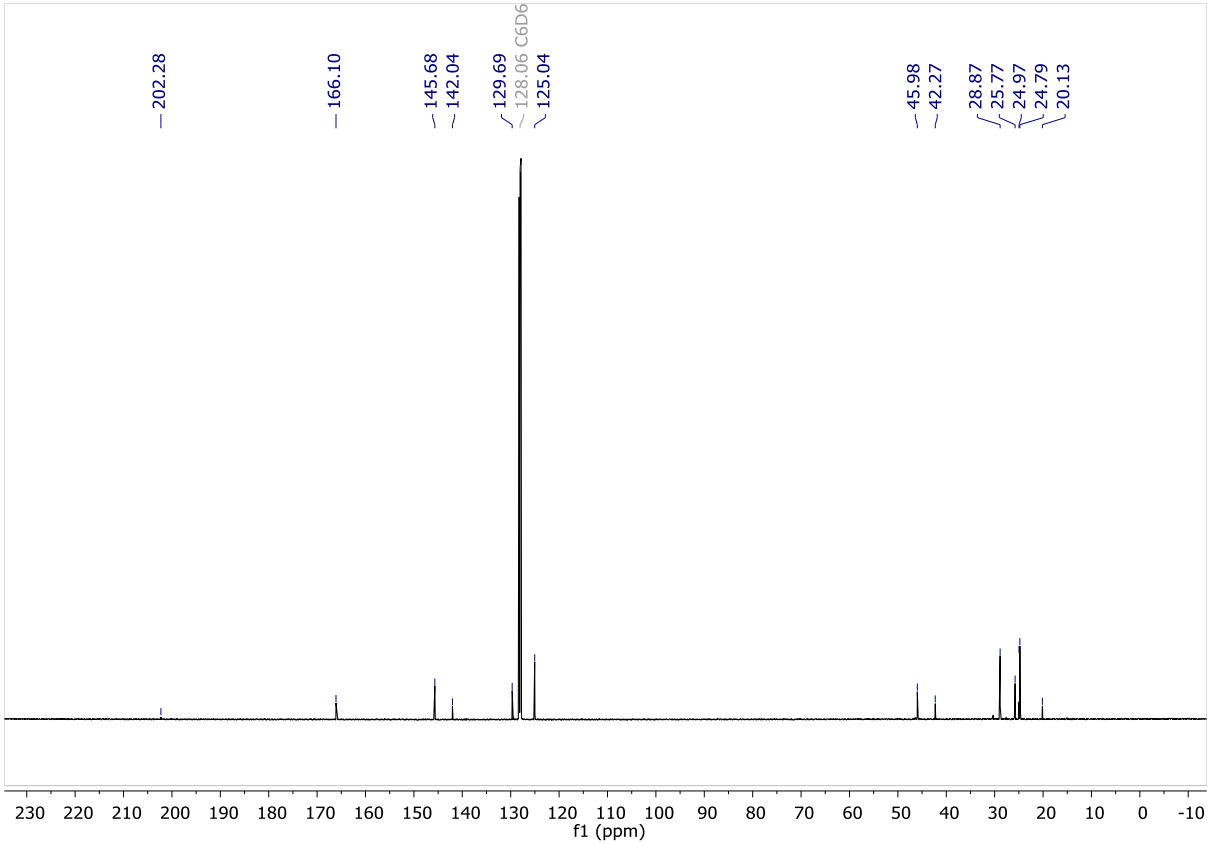


Figure S4: $^{13}$C NMR spectrum for (6-Dipp)CuN(iPr)C(O)H

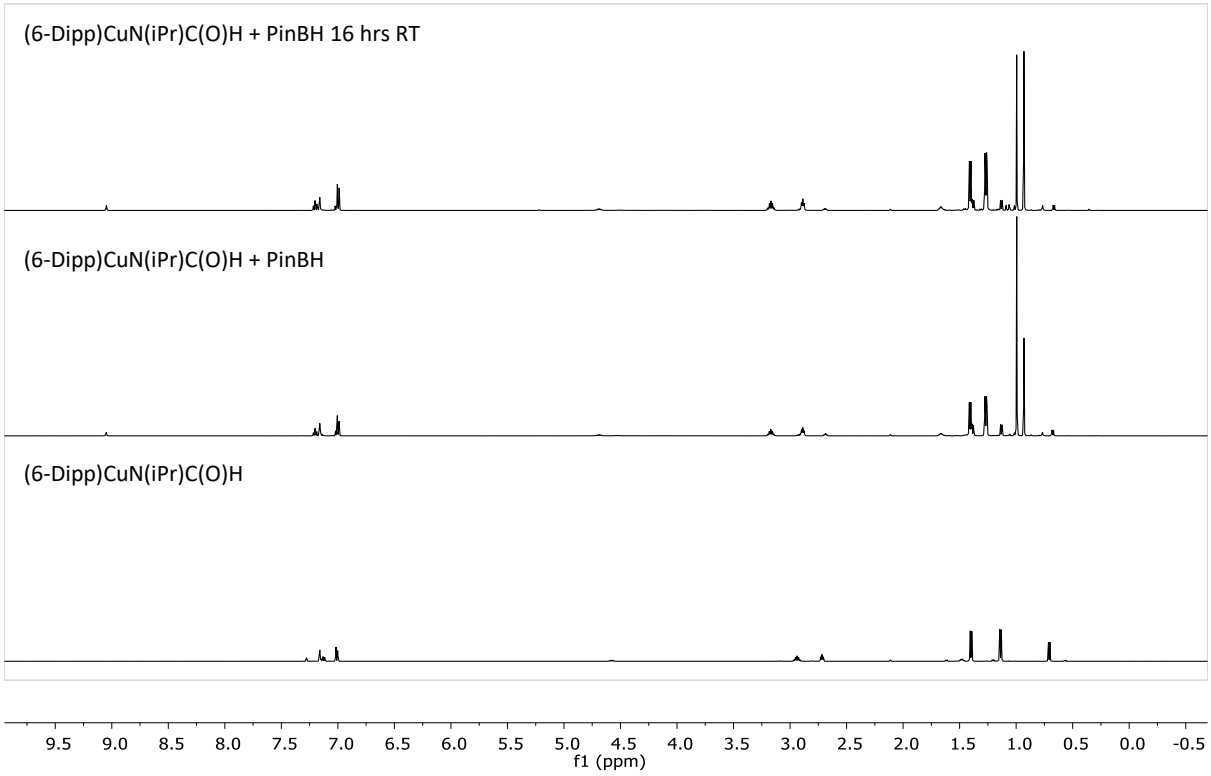


Figure S5: Stacked $^{1}H$ NMR Spectra for the reaction between (6-Dipp)CuN(iPr)C(O)H and Pinacolborane

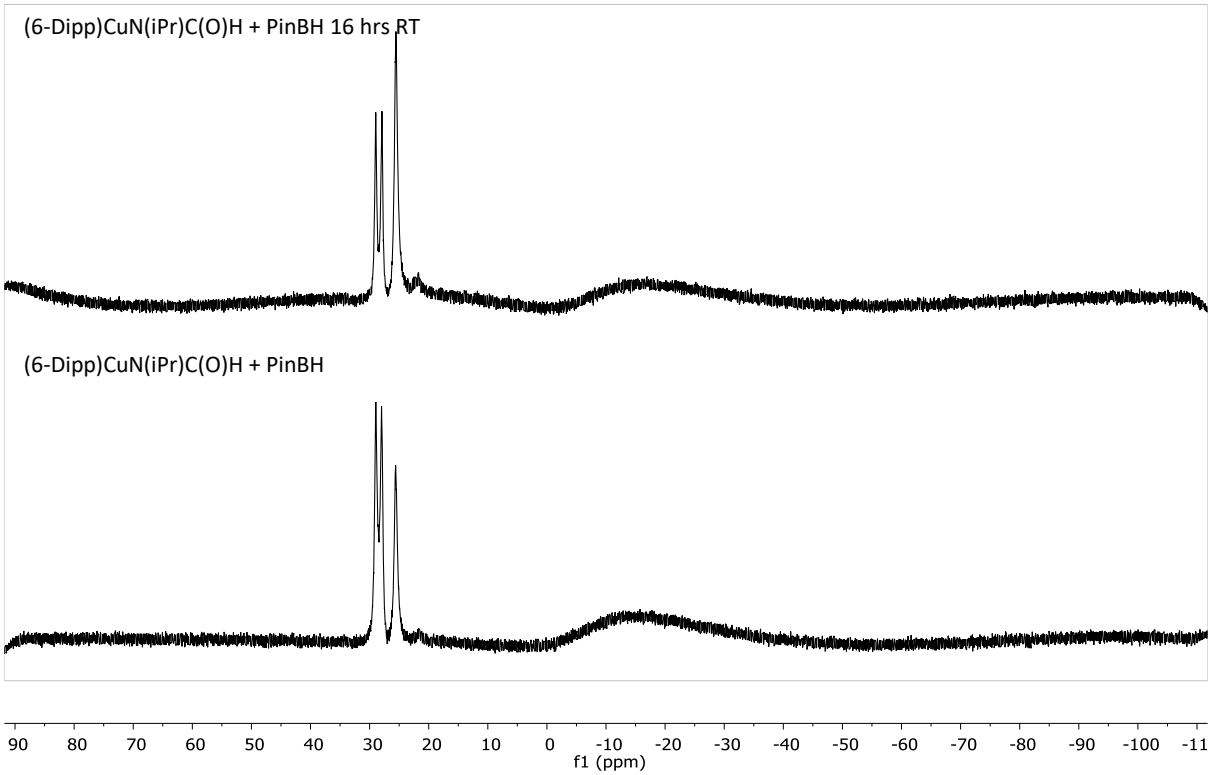


Figure S6: Stacked $^{11}B$ NMR Spectra for the reaction between (6-Dipp)CuN(iPr)C(O)H and Pinacolborane

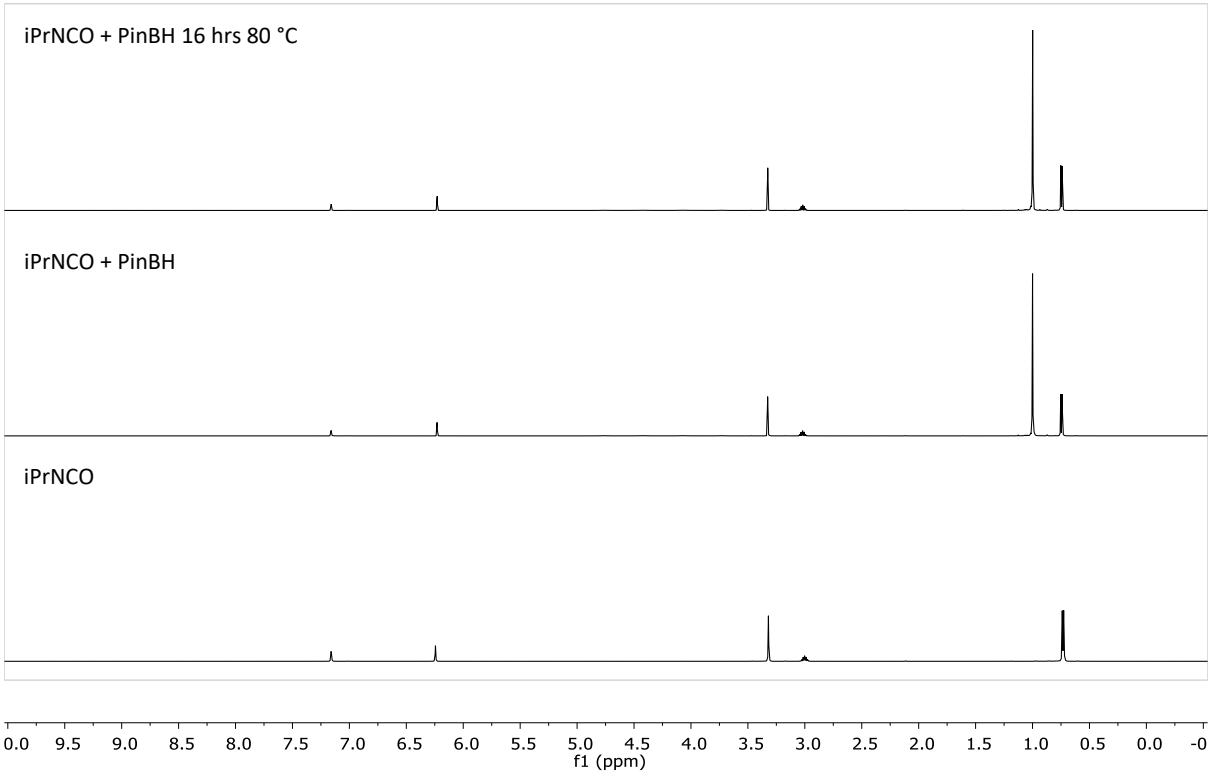


Figure S7: Stacked $^{1}$H NMR Spectra for the reaction between iPrNCO and Pinacolborane

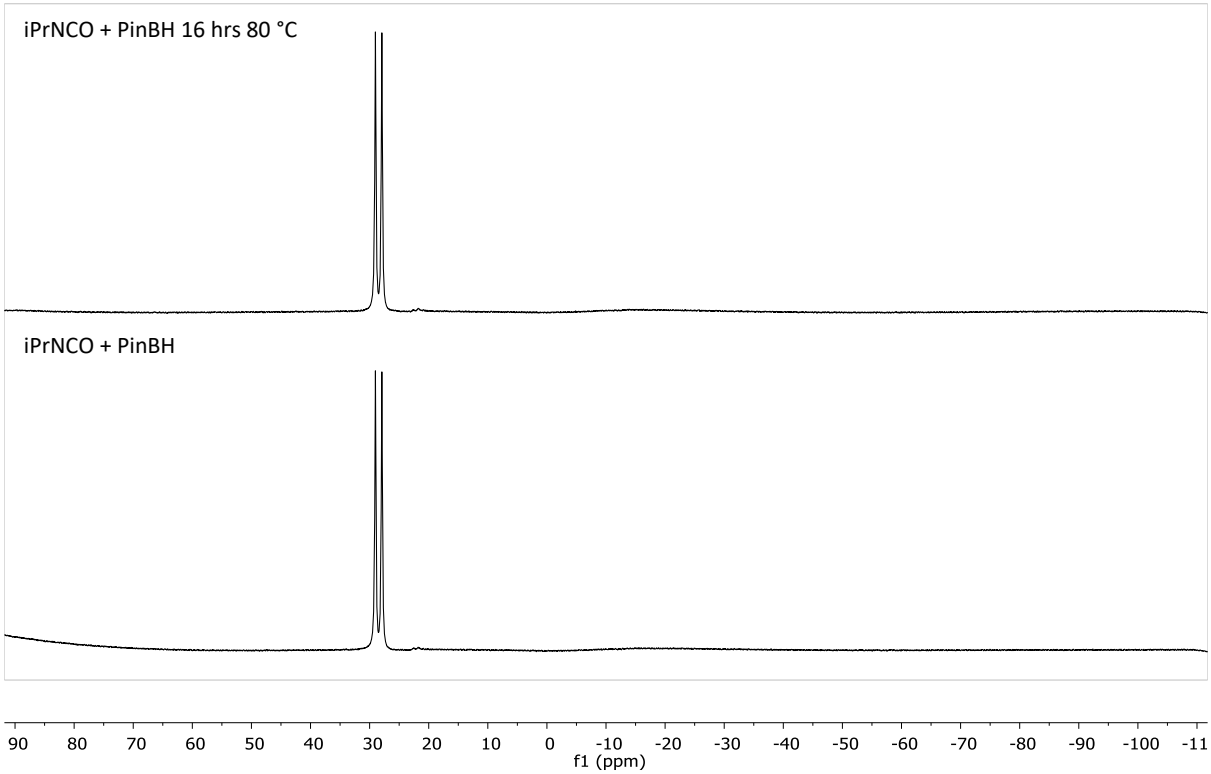


Figure S8: Stacked $^{1}$H NMR Spectra for the reaction between iPrNCO and Pinacolborane

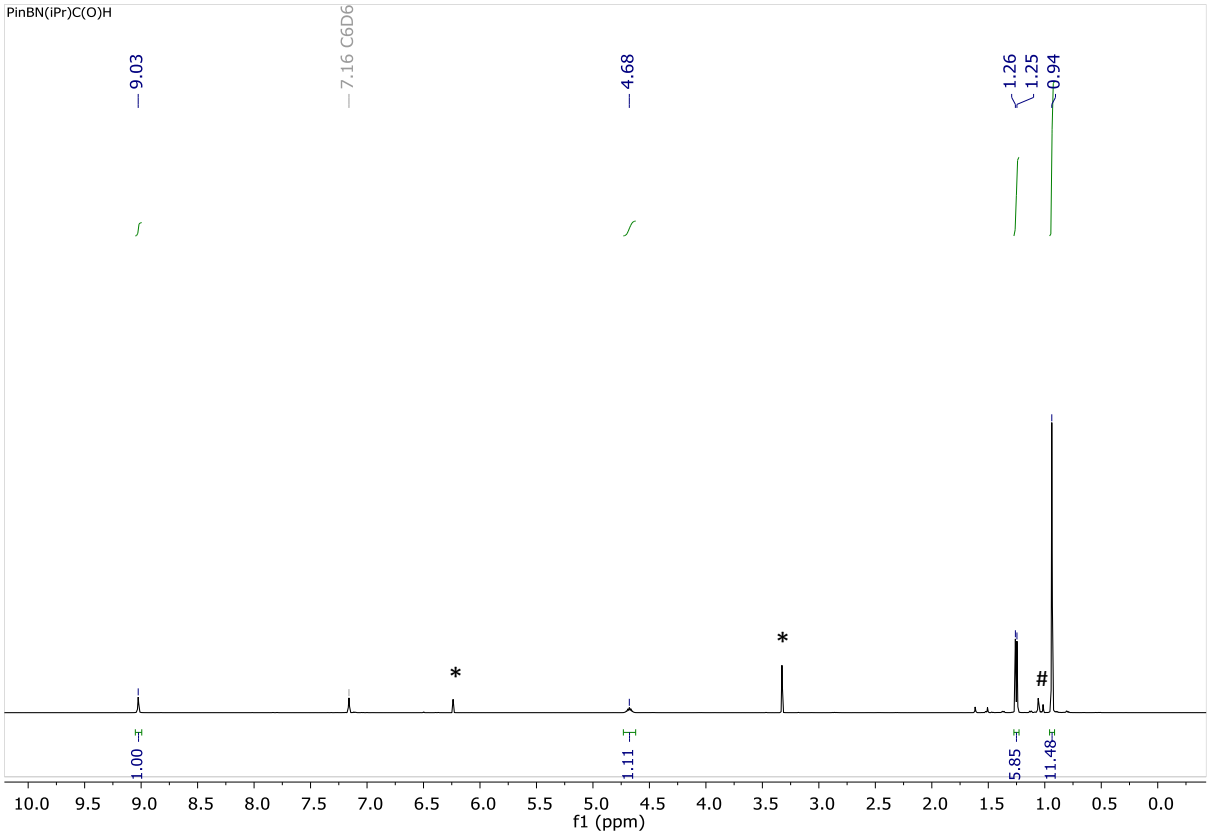


Figure S9: $^{1}H$ NMR spectrum for PinBN(iPr)C(O)H, 1a. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

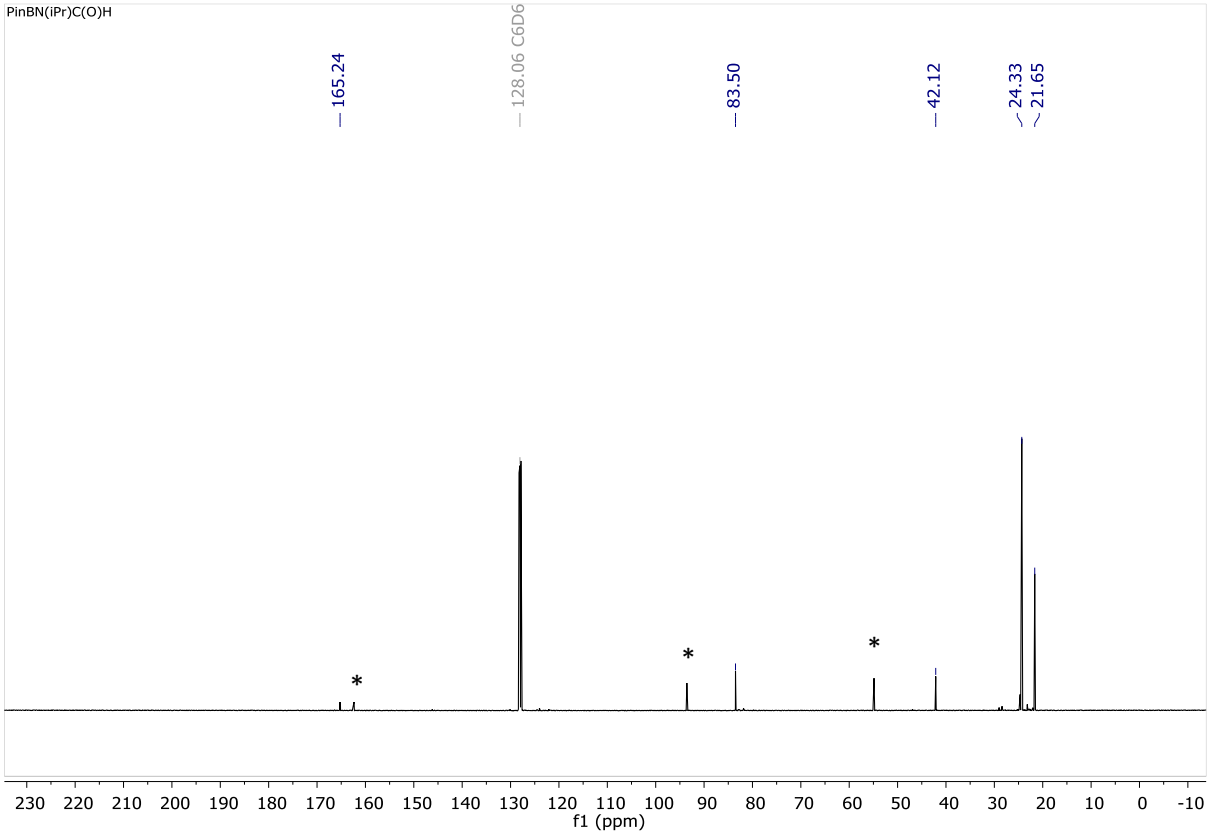


Figure S10: $^{13}C$ NMR spectrum for PinBN(iPr)C(O)H, 1a. $C_6H_3(OMe)_3$ internal standard indicated with *.

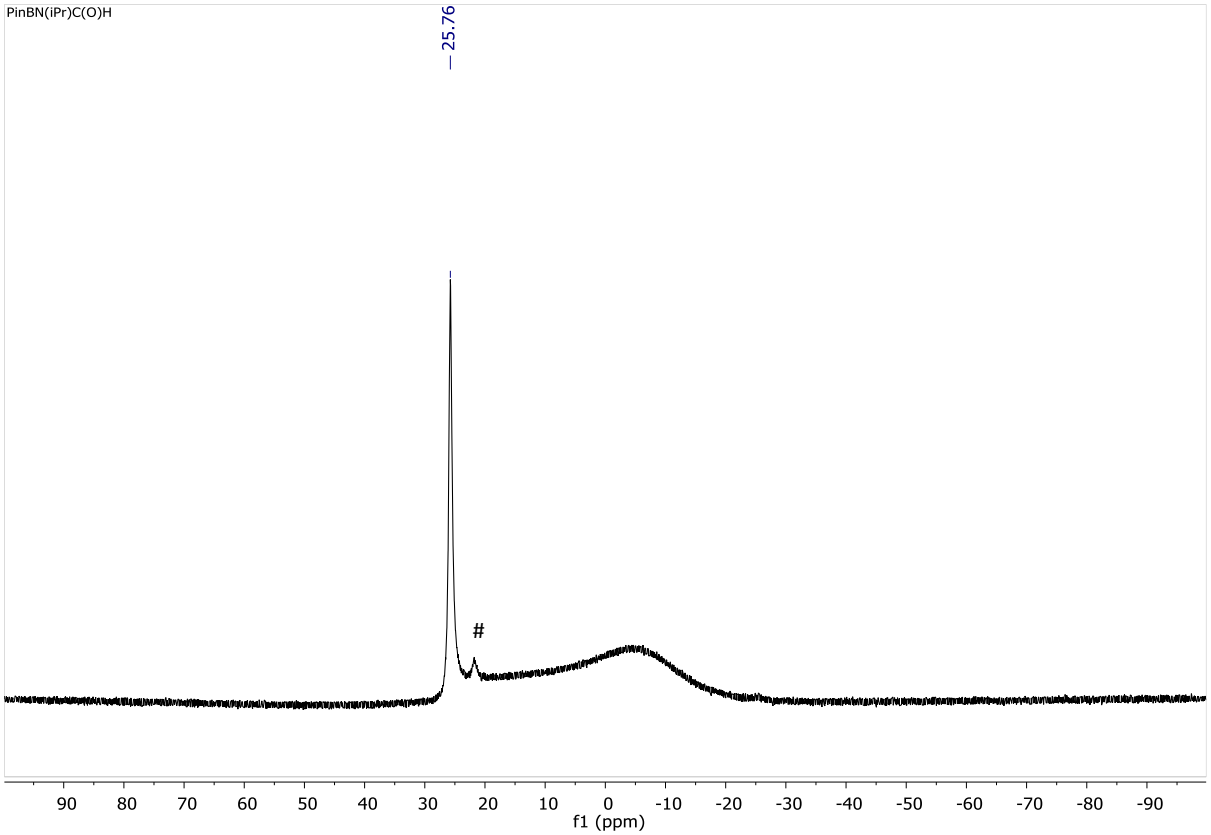


Figure S11: $^{11}B$ NMR spectrum for PinBN(iPr)C(O)H, 1a, PinBOtBu indicated with #.

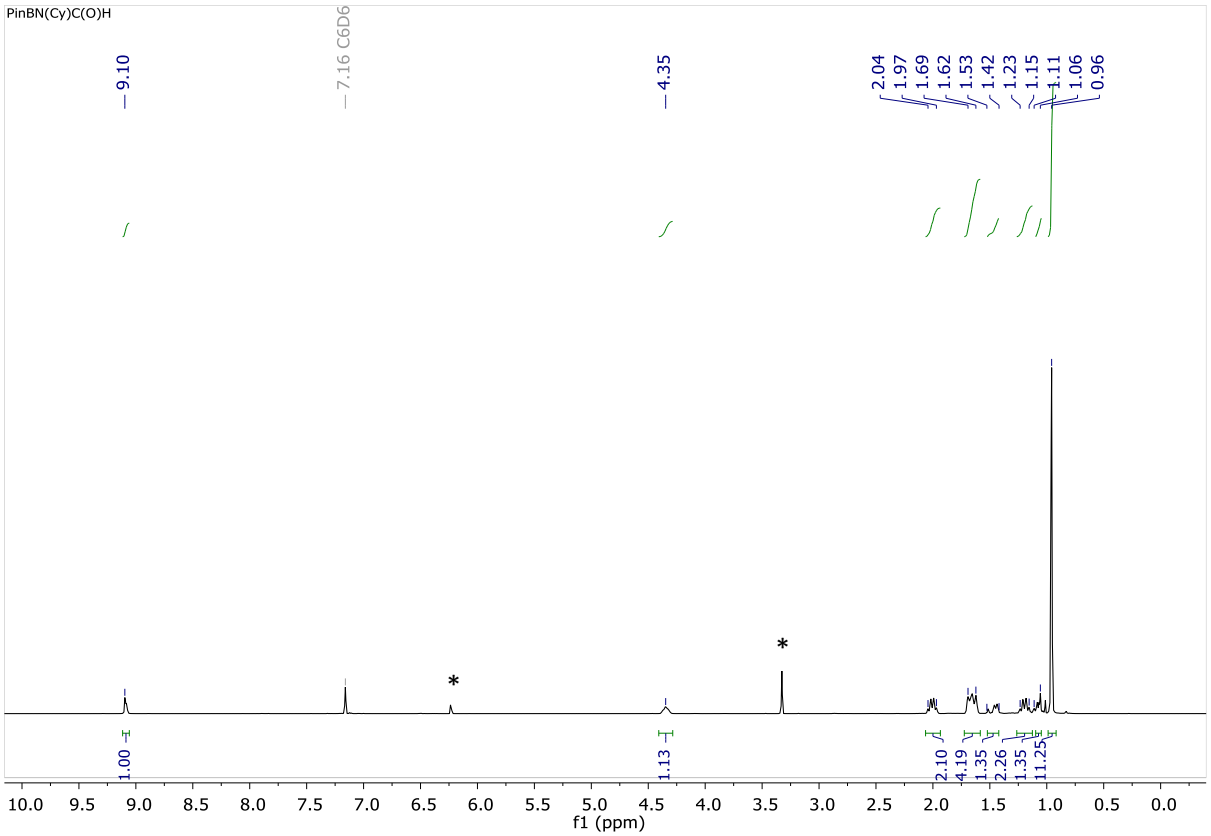


Figure S12: $^{1}H$ NMR spectrum for PinBN(Cy)C(O)H, 1b. $C_6H_3(OMe)_3$ internal standard indicated with *.

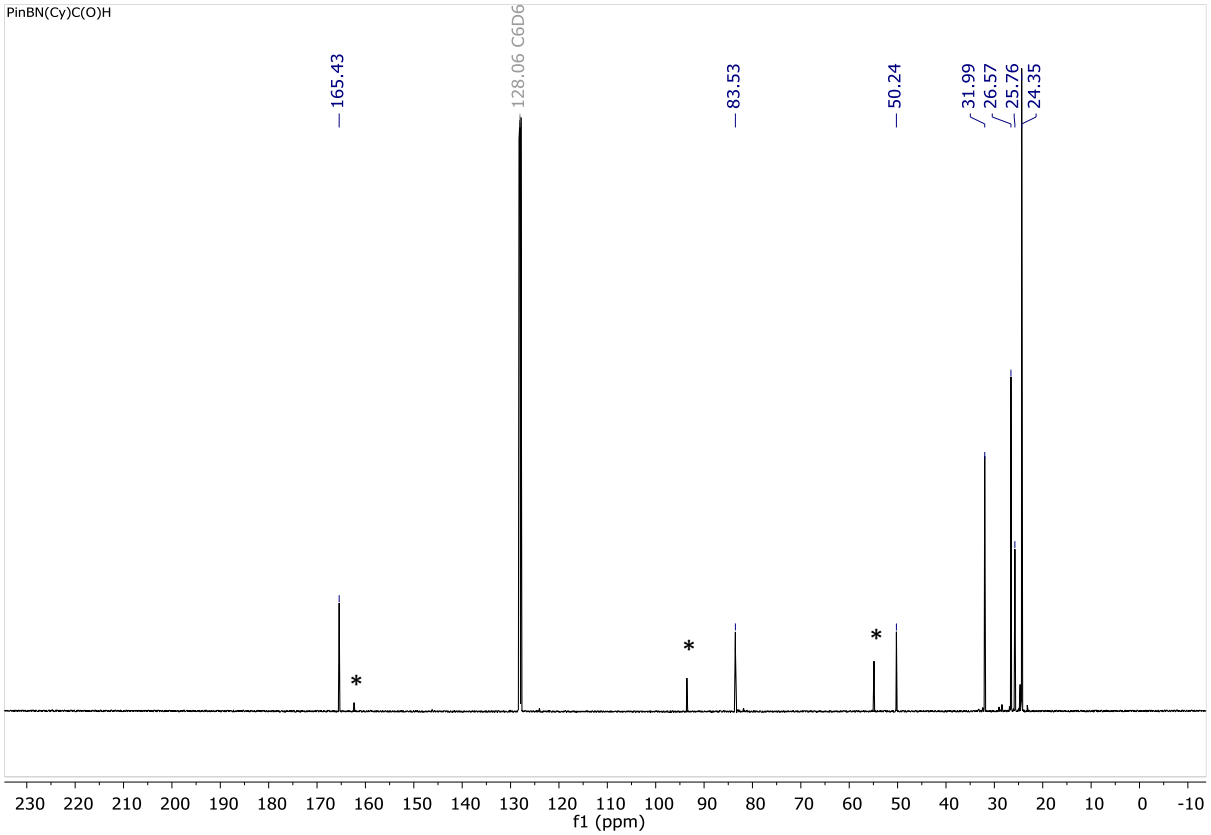


Figure S13: $^{13}C$ NMR spectrum for PinBN(Cy)C(O)H, 1b. $C_6H_3(OMe)_3$ internal standard indicated with *.

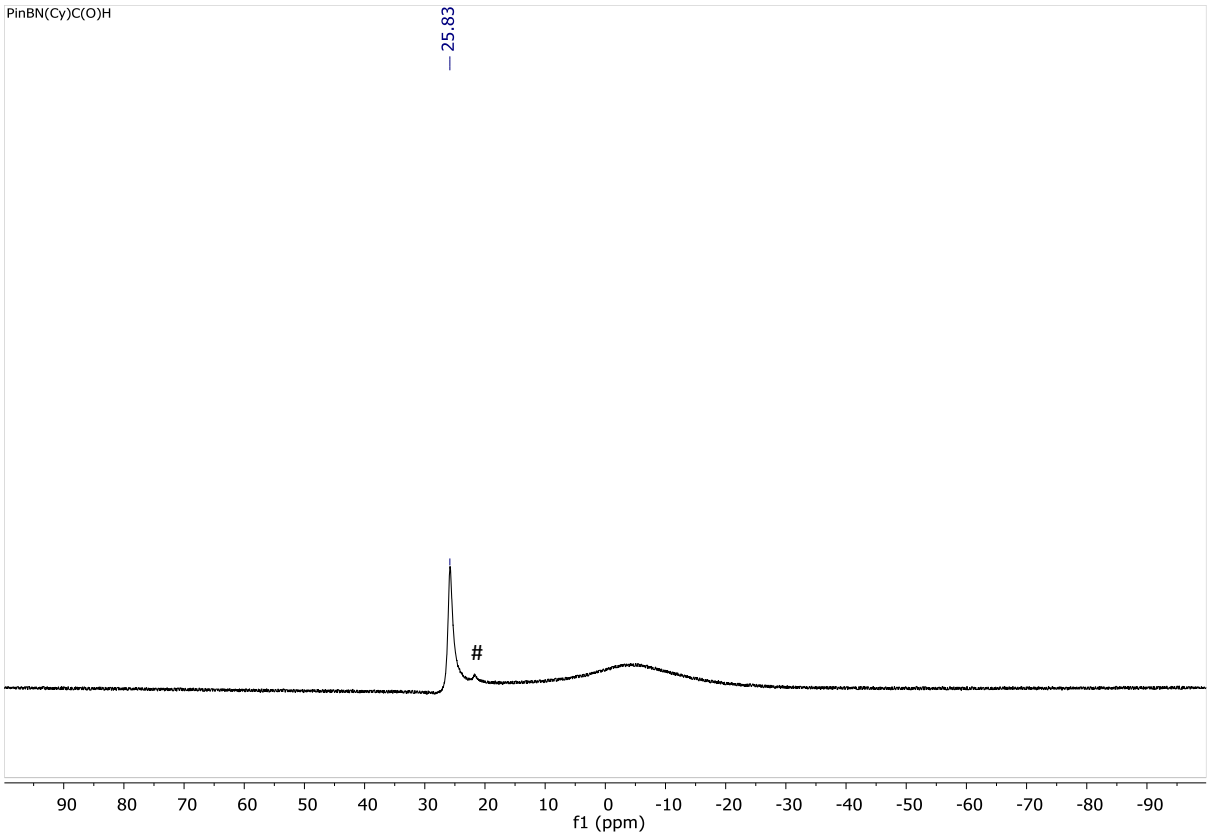


Figure S14: $^{11}B$ NMR spectrum for PinBN(Cy)C(O)H, 1b, PinBOtBu indicated with #.

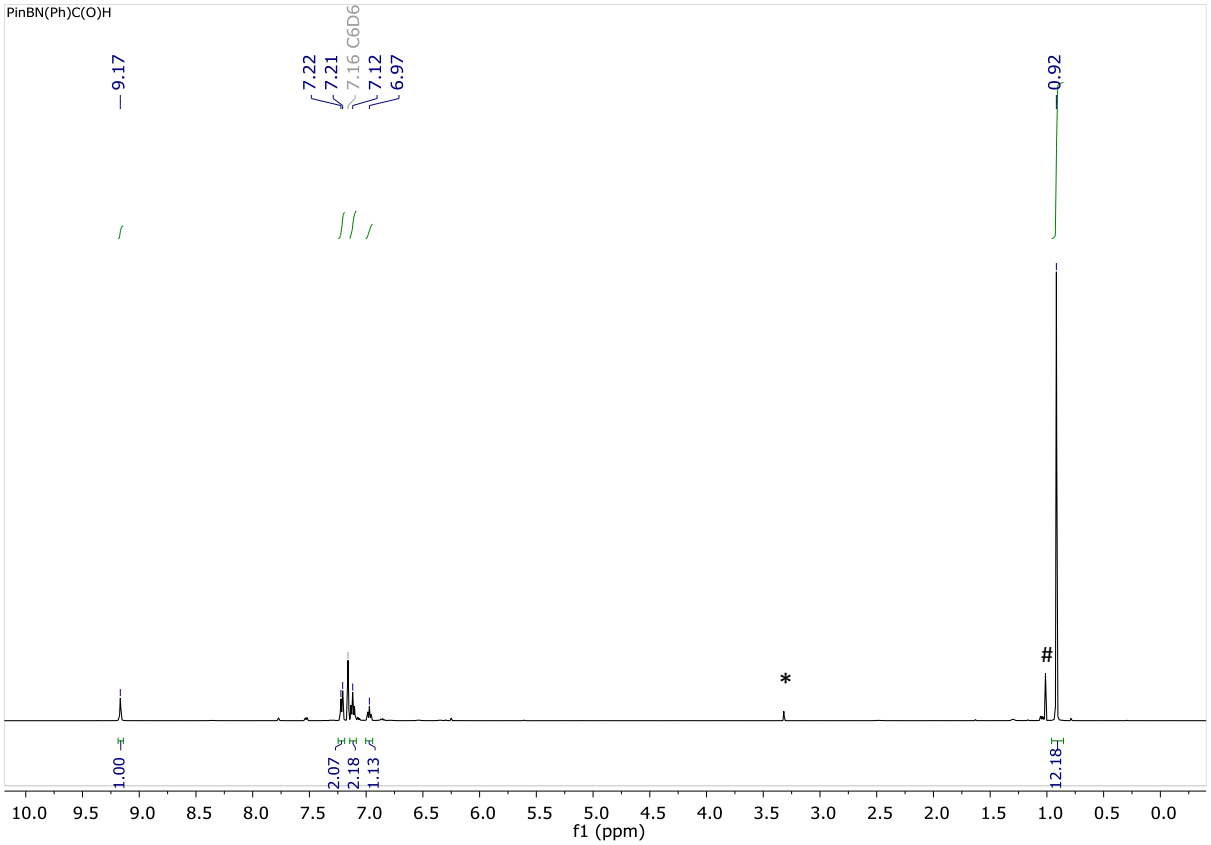


Figure S15: $^{1}$H NMR spectrum for PinBN(Ph)C(O)H, 1d. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

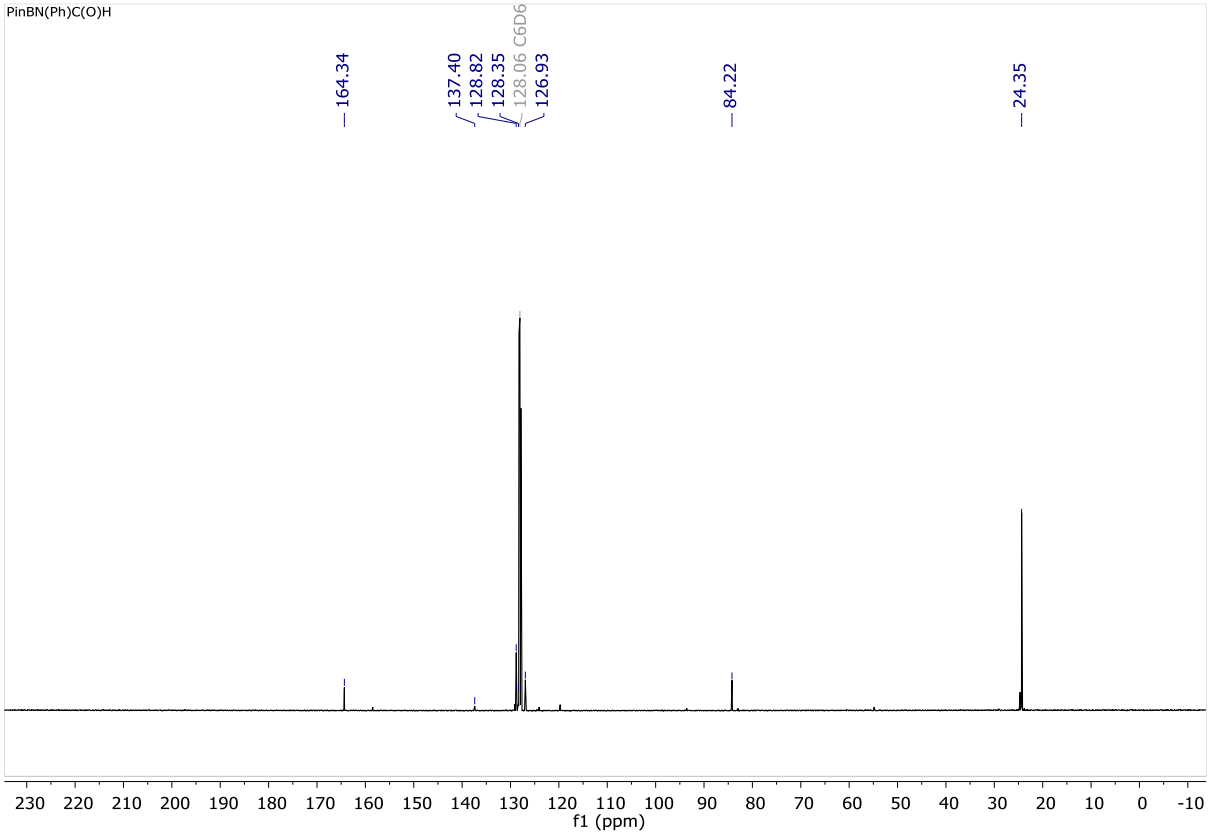


Figure S16: $^{13}$C NMR spectrum for PinBN(Ph)C(O)H, 1d.

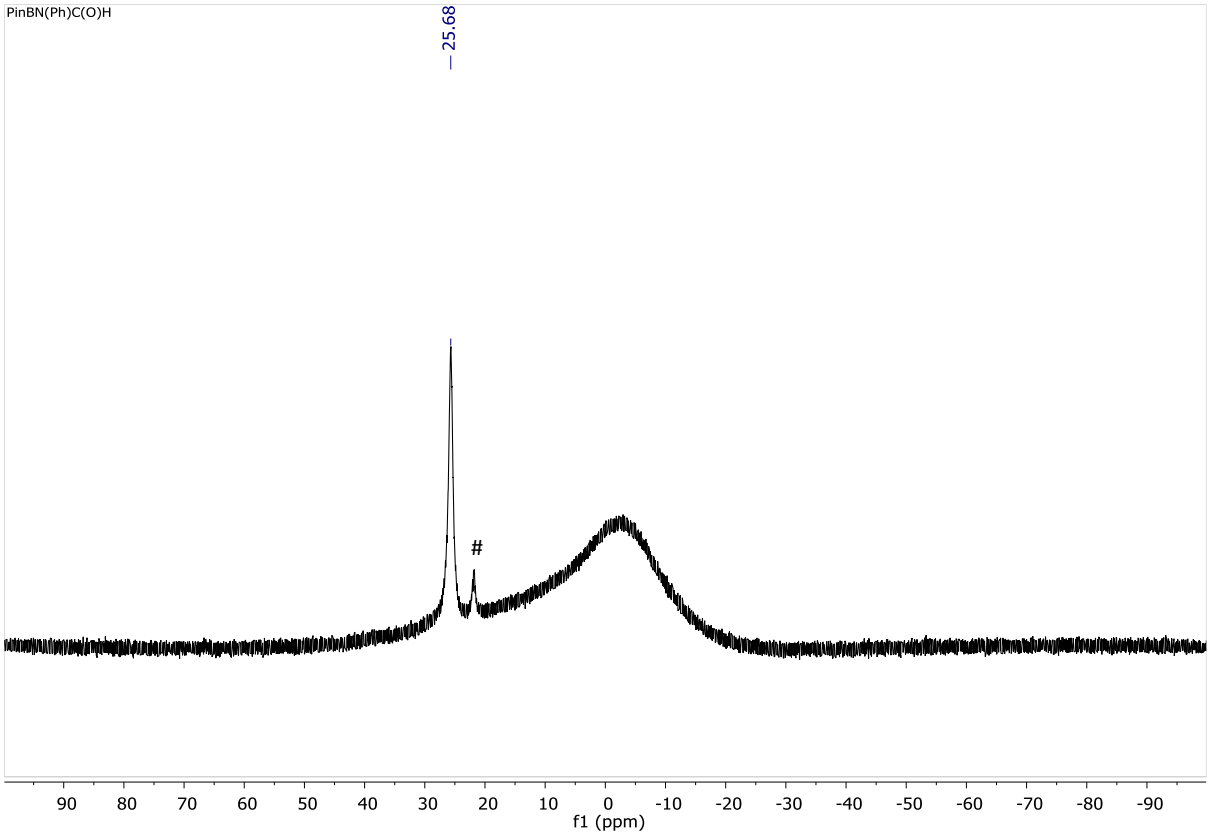


Figure S17: $^{11}$B NMR spectrum for PinBN(Ph)C(O)H, 1d, PinBOtBu indicated with #.

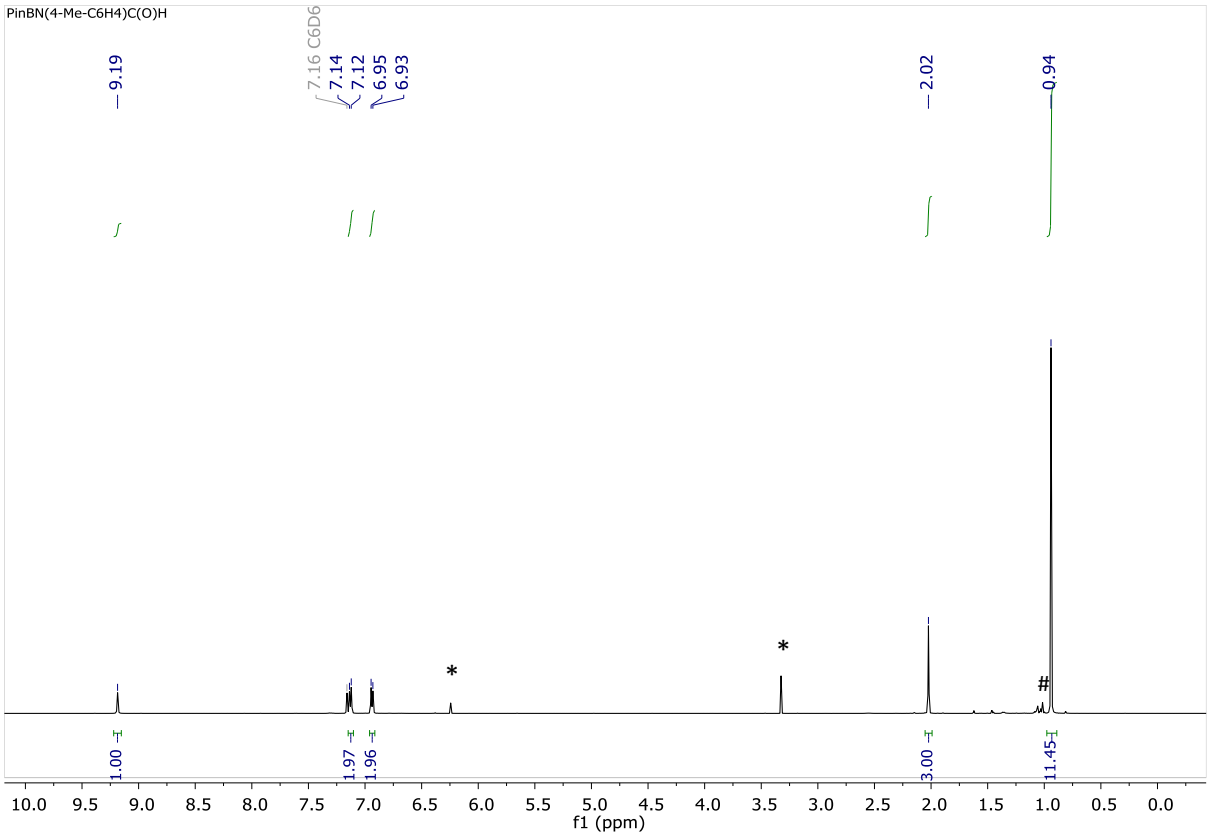


Figure S18: $^{1}$H NMR spectrum for PinBN(4-Me-$C_6H_4$)C(O)H, 1e. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

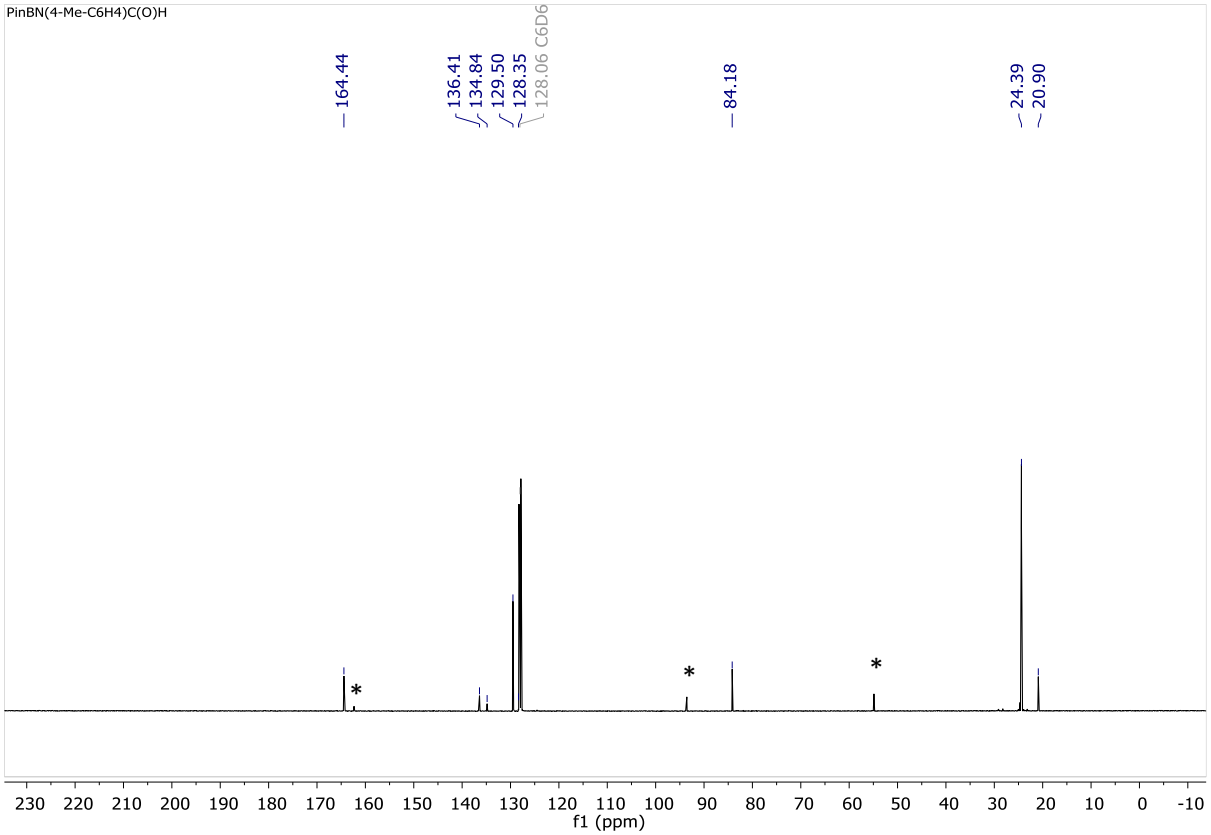


Figure S19: $^{13}C$ NMR spectrum for PinBN(4-Me-$C_6H_4$)C(O)H, 1e. $C_6H_3(OMe)_3$ internal standard indicated with *.

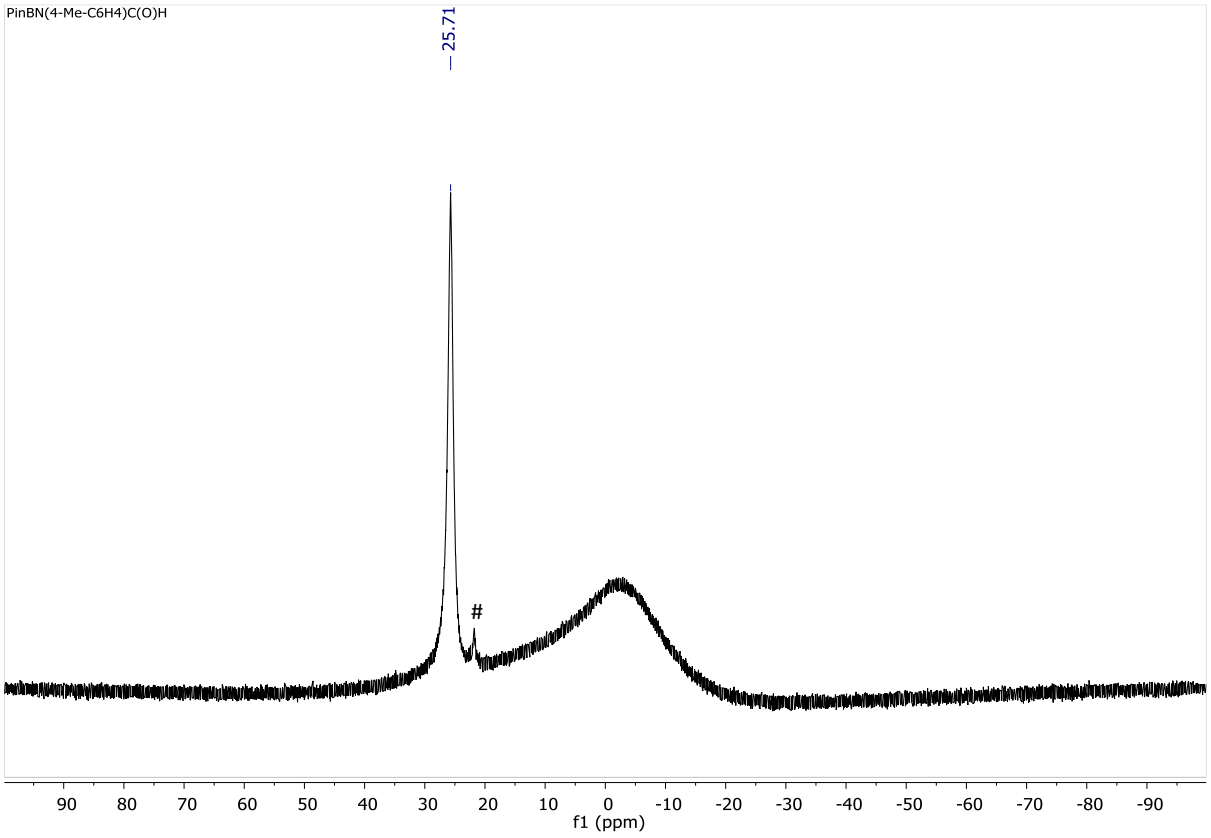


Figure S20: $^{11}B$ NMR spectrum for PinBN(4-Me-$C_6H_4$)C(O)H, 1e, PinBOtBu indicated with #.

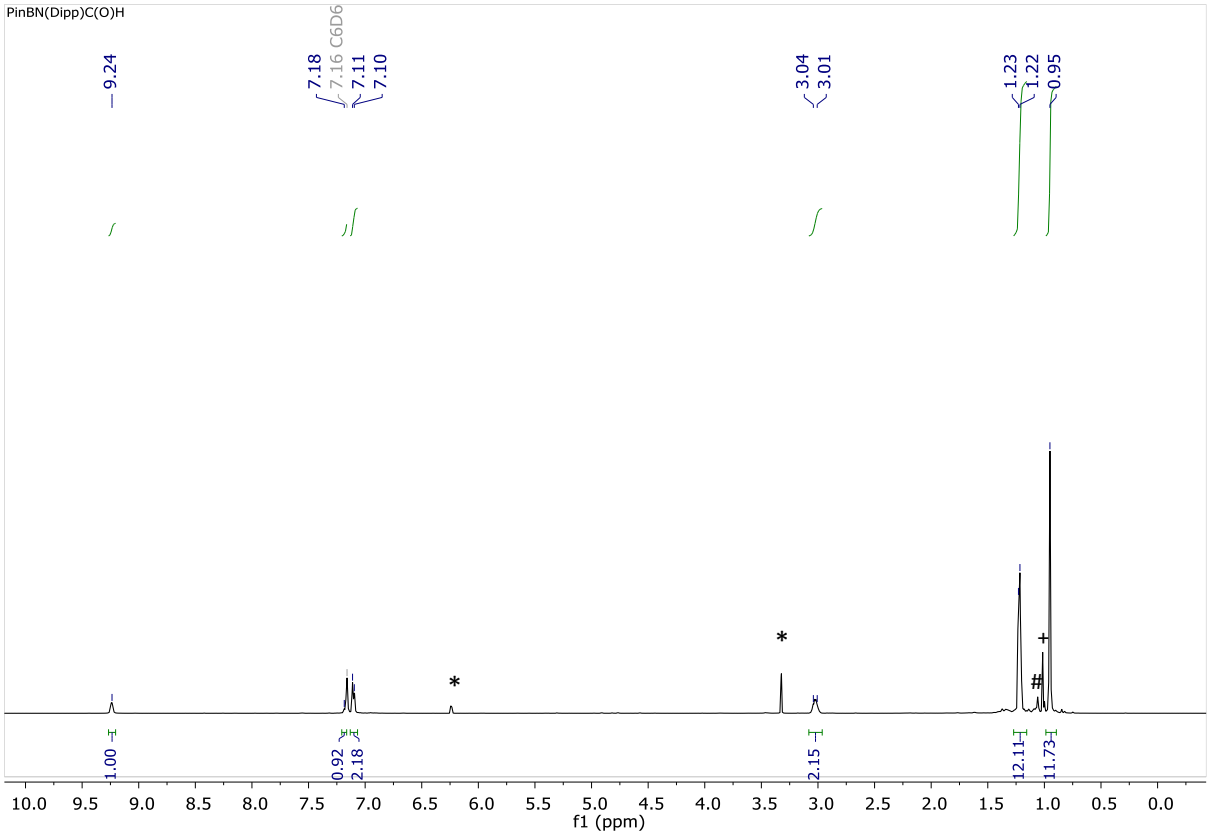


Figure S21: $^{1}$H NMR spectrum for PinBN(Dipp)C(O)H, 1f. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #, HBPin marked with +.

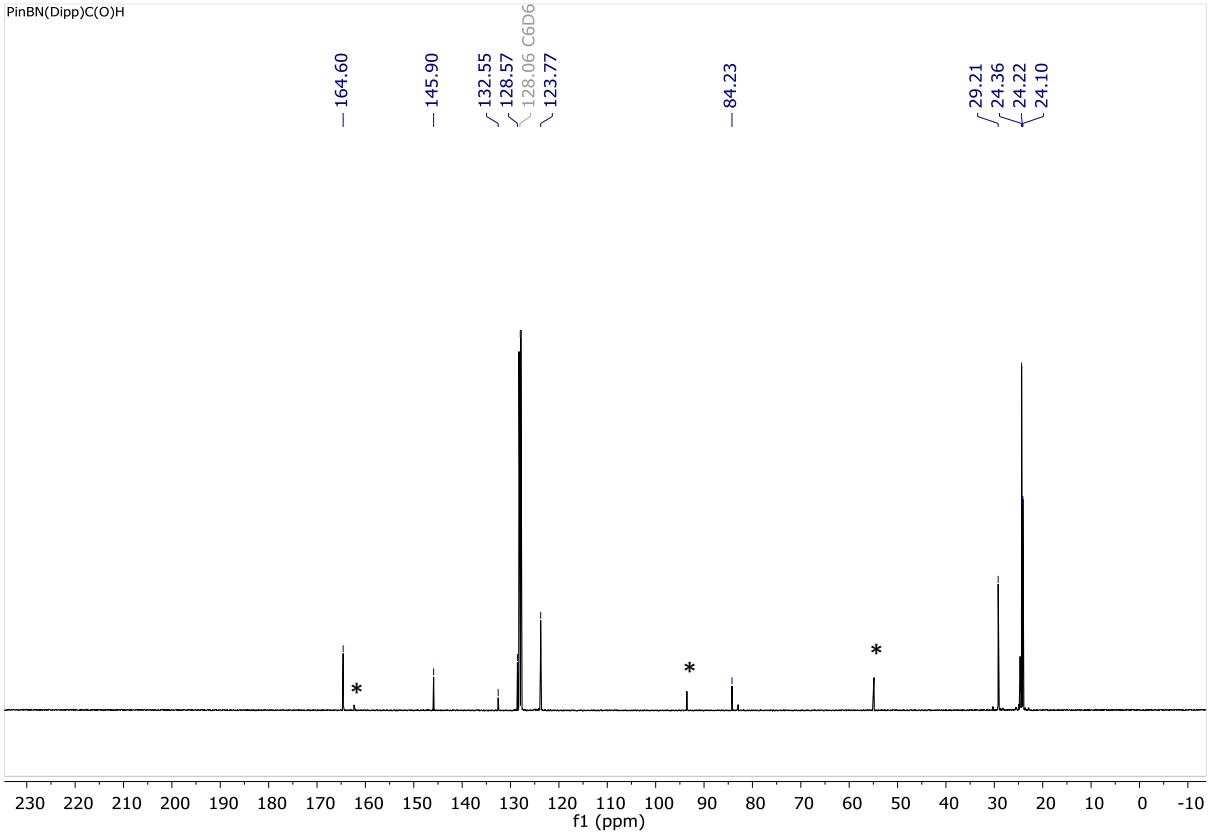


Figure S22: $^{13}$C NMR spectrum for PinBN(Dipp)C(O)H, 1f. $C_6H_3(OMe)_3$ internal standard indicated with *.

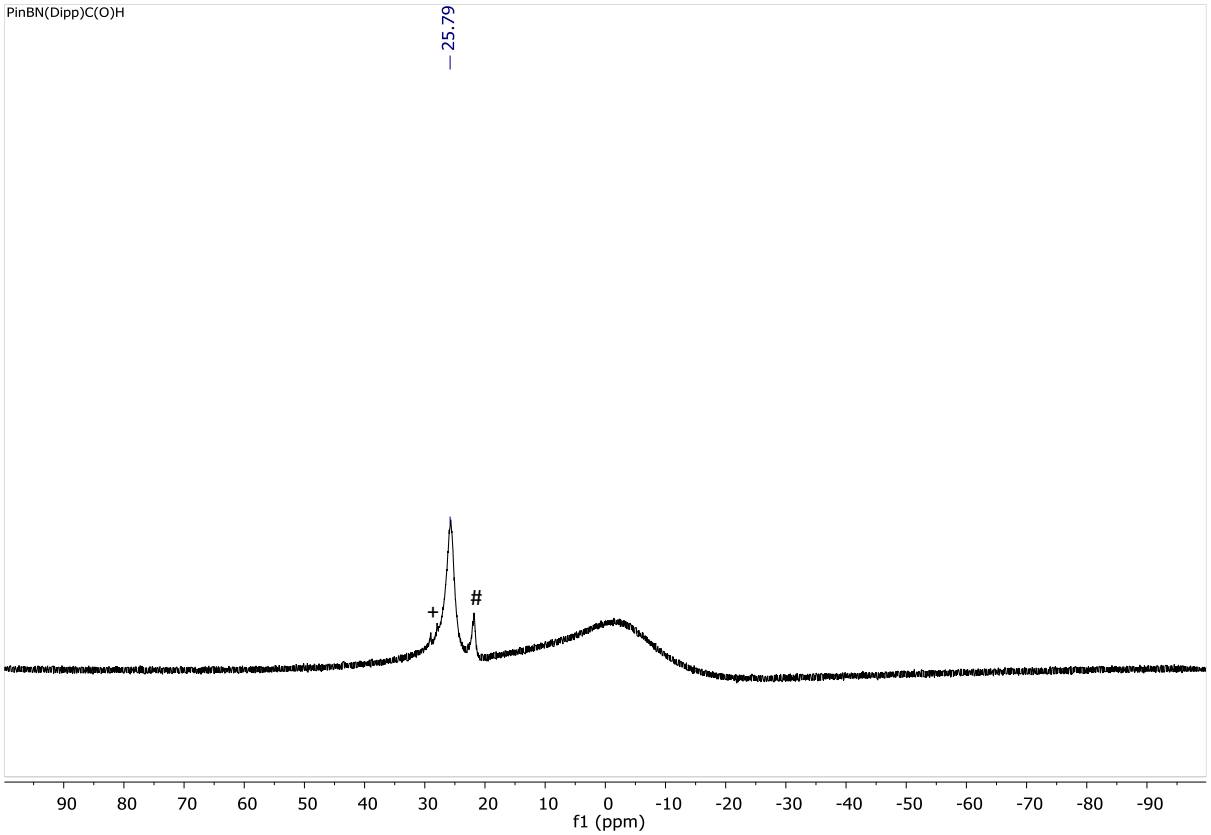


Figure S23: $^{11}$B NMR spectrum for PinBN(Dipp)C(O)H, 1f, PinBOtBu indicated with #, HBPin marked with +.

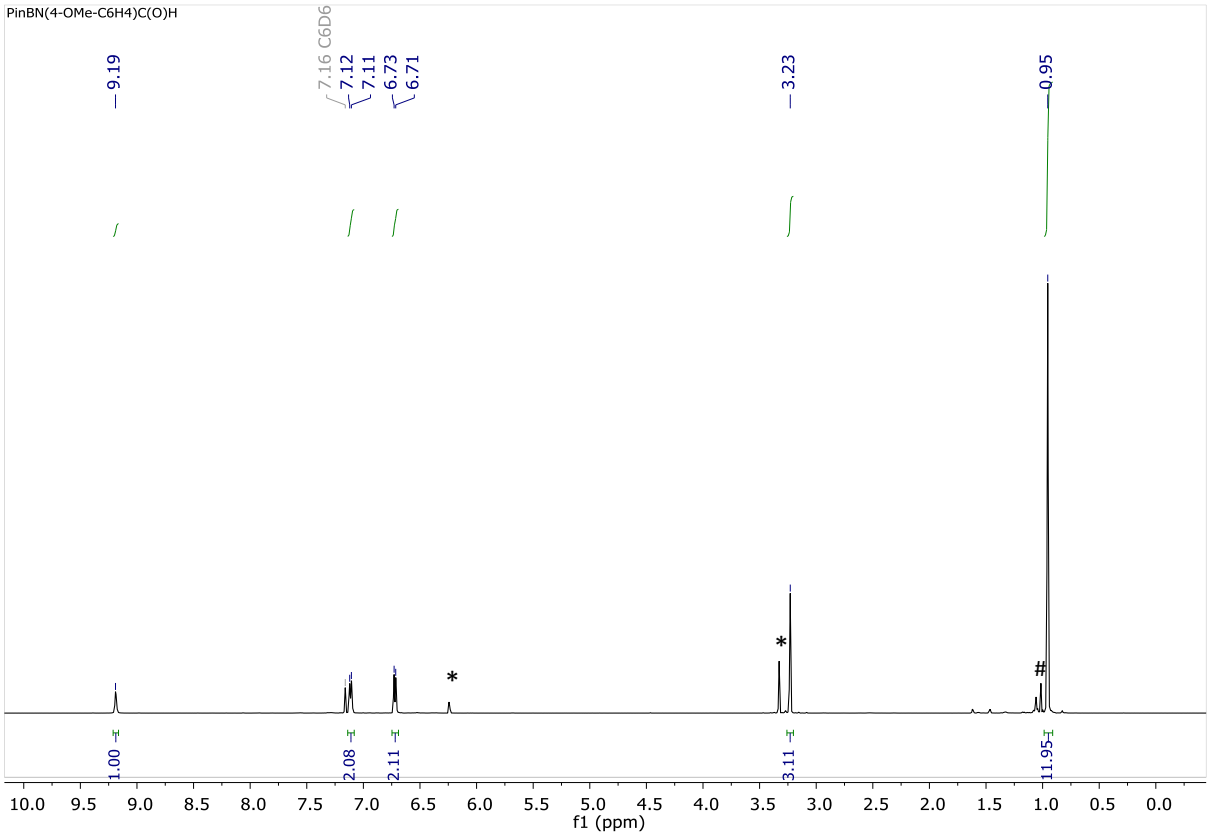


Figure S24: $^{1}$H NMR spectrum for PinBN(4-MeO-$C_6H_4$)C(O)H, 1g. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

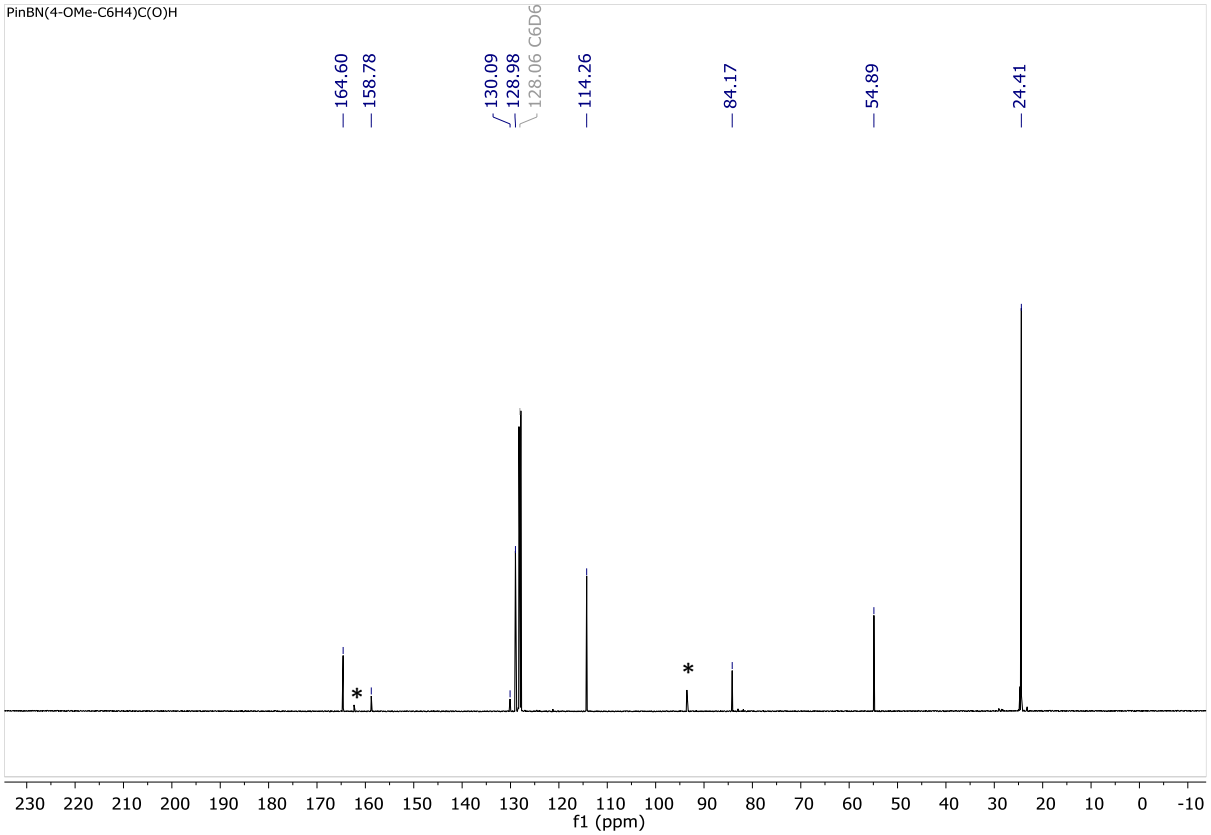


Figure S25: $^{13}C$ NMR spectrum for PinBN(4-MeO-$C_6H_4$)C(O)H, 1g. $C_6H_3(OMe)_3$ internal standard indicated with *.

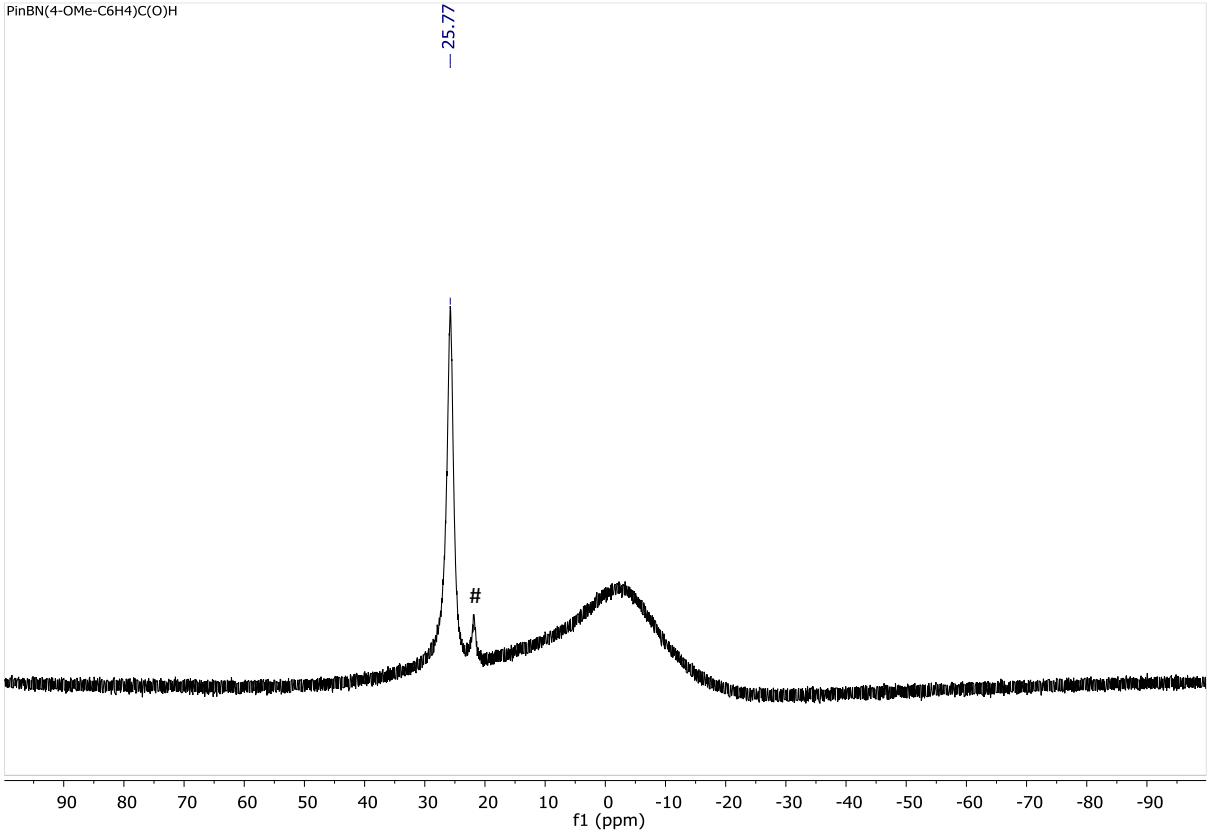


Figure S26: $^{11}B$ NMR spectrum for PinBN(4-MeO-$C_6H_4$)C(O)H, 1g, PinBOtBu indicated with #.

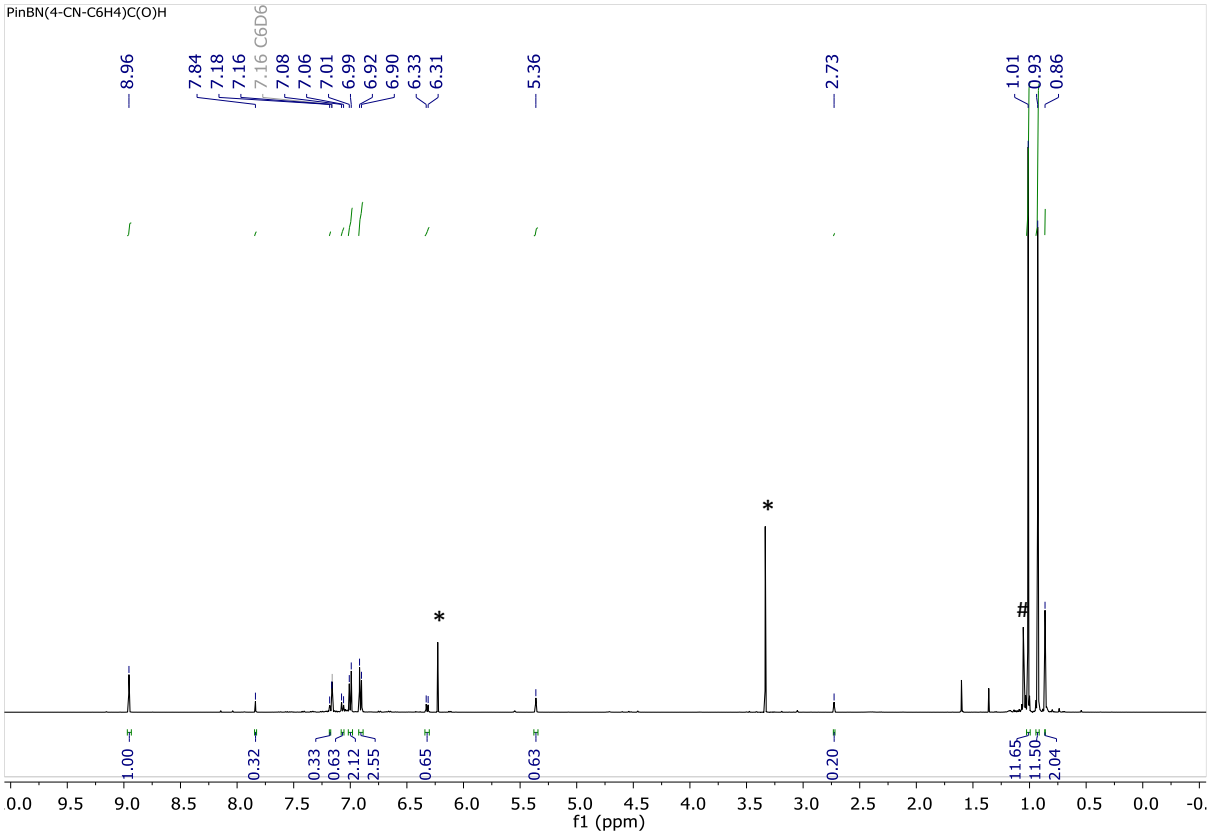


Figure S27: $^{1}$H NMR spectrum for PinBN(4-NC-$C_6H_4$)C(O)H, 1h, PinBN(4-NC-$C_6H_4$)$CH_3$, 1h' and PinBN(4-$CH_2N(BPin)_2$-$C_6H_4$)C(O)H, 1h''. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

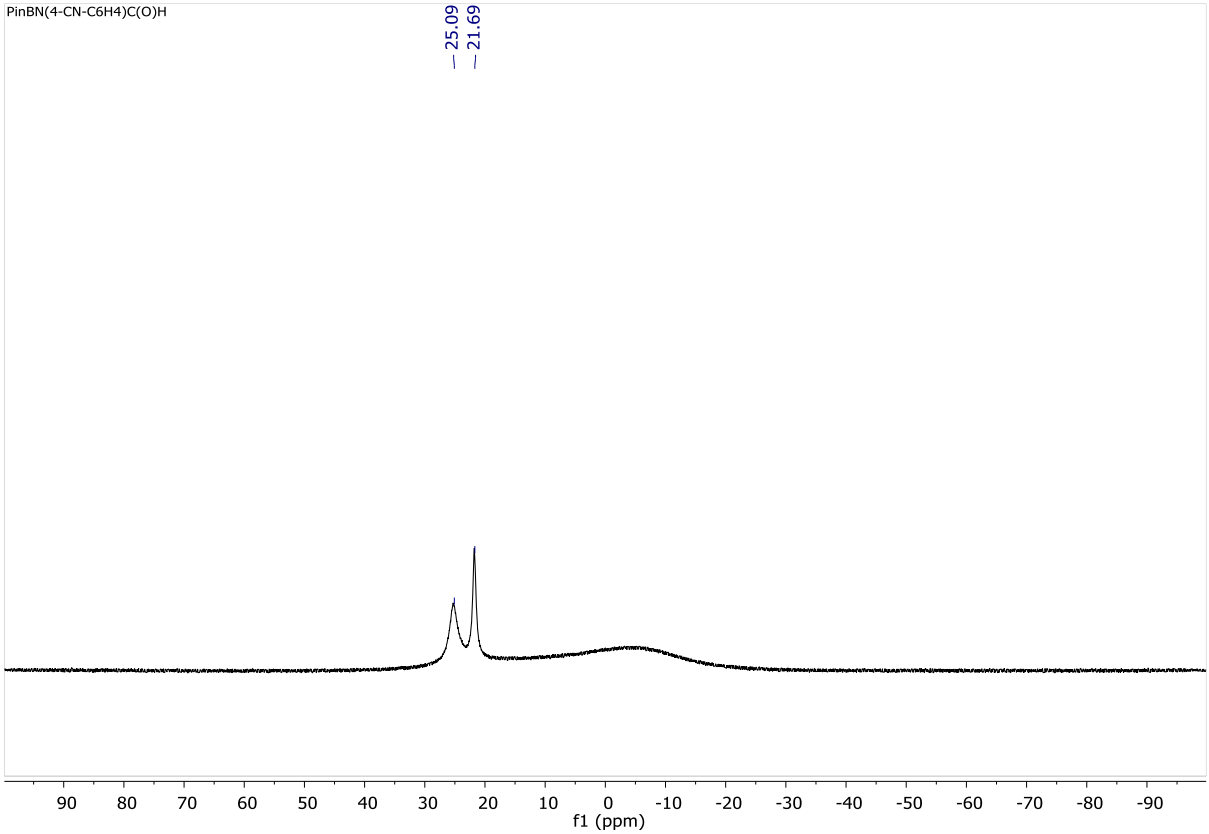


Figure S28: $^{11}$B NMR spectrum for PinBN(4-NC-$C_6H_4$)C(O)H, 1h, PinBN(4-NC-$C_6H_4$)$CH_3$, 1h' and PinBN(4-$CH_2N(BPin)_2$-$C_6H_4$)C(O)H, 1h''.

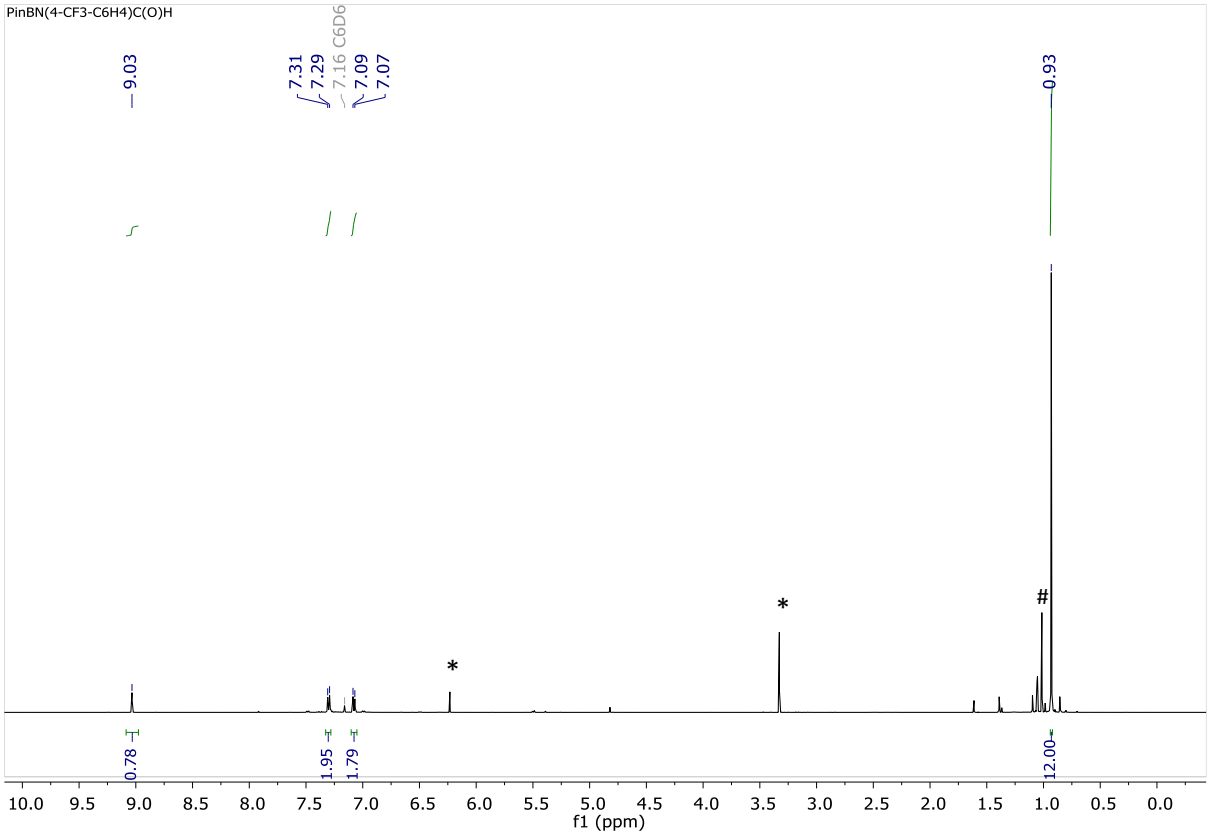


Figure S29: $^{1}$H NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)C(O)H, 1i. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

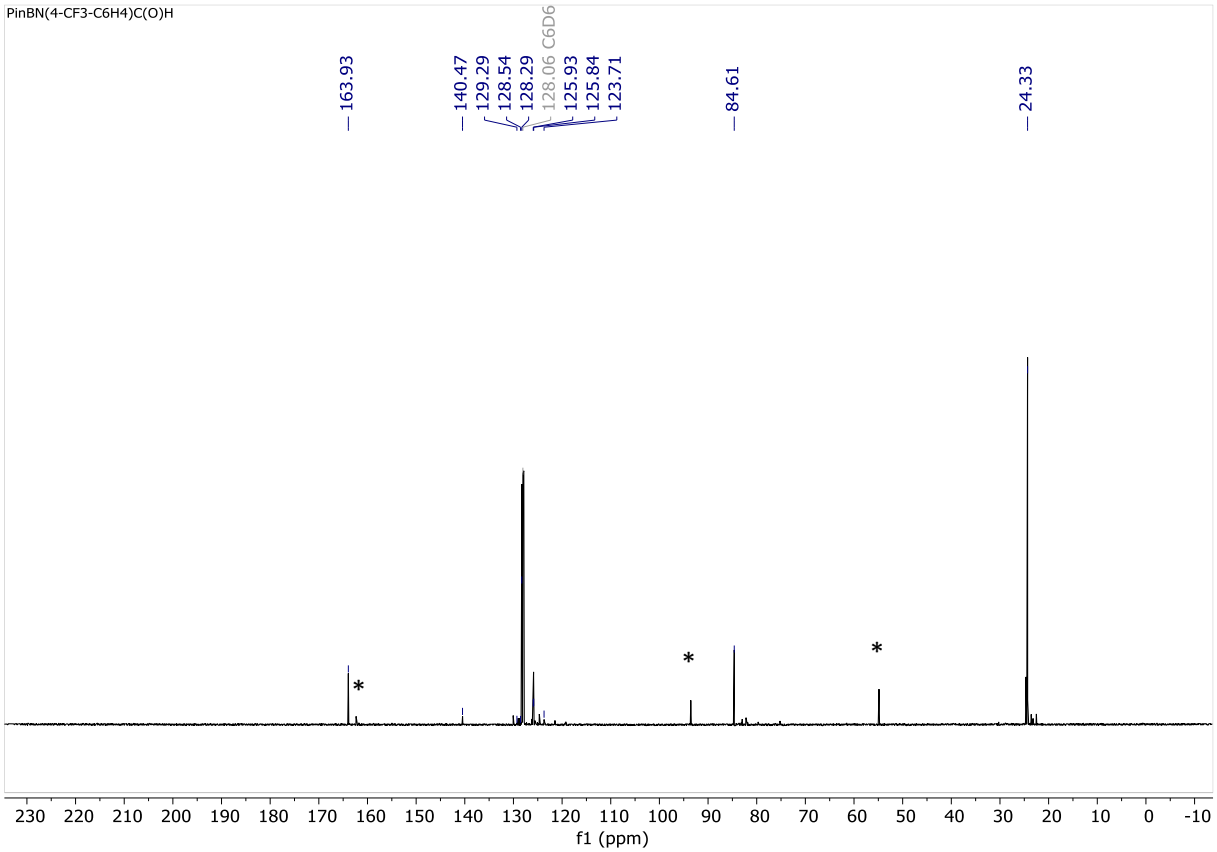


Figure S30: $^{13}$C NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)C(O)H, 1i. $C_6H_3(OMe)_3$ internal standard indicated with *.

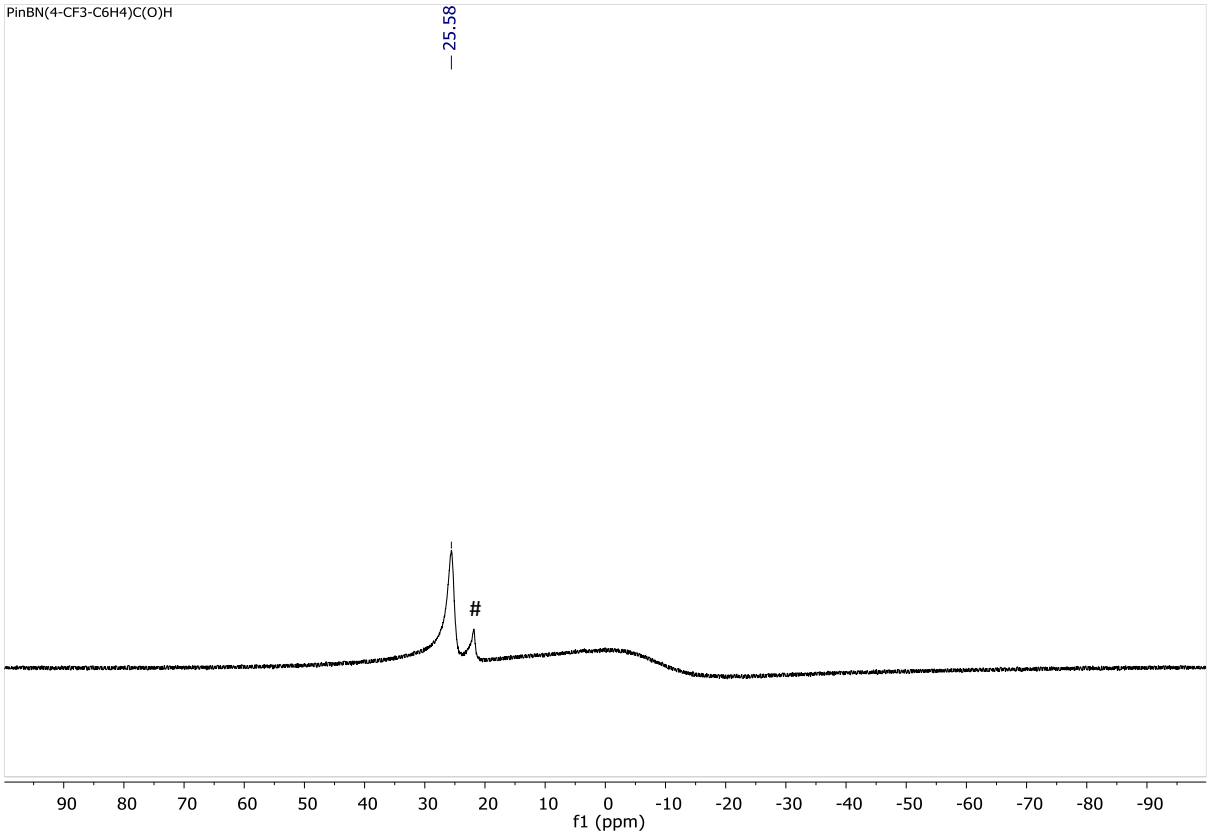


Figure S31: $^{11}$B NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)C(O)H, 1i, PinBOtBu indicated with #.

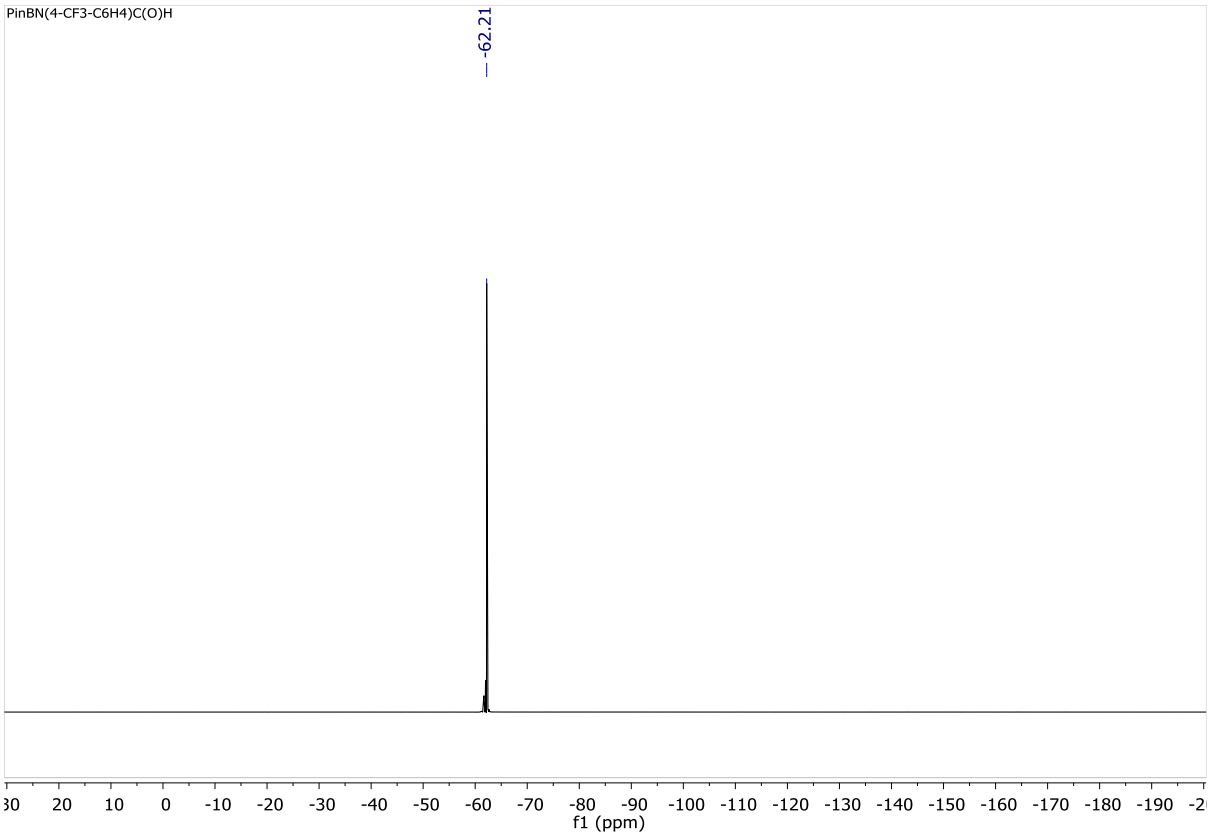


Figure S32: $^{19}$F NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)C(O)H, 1i.

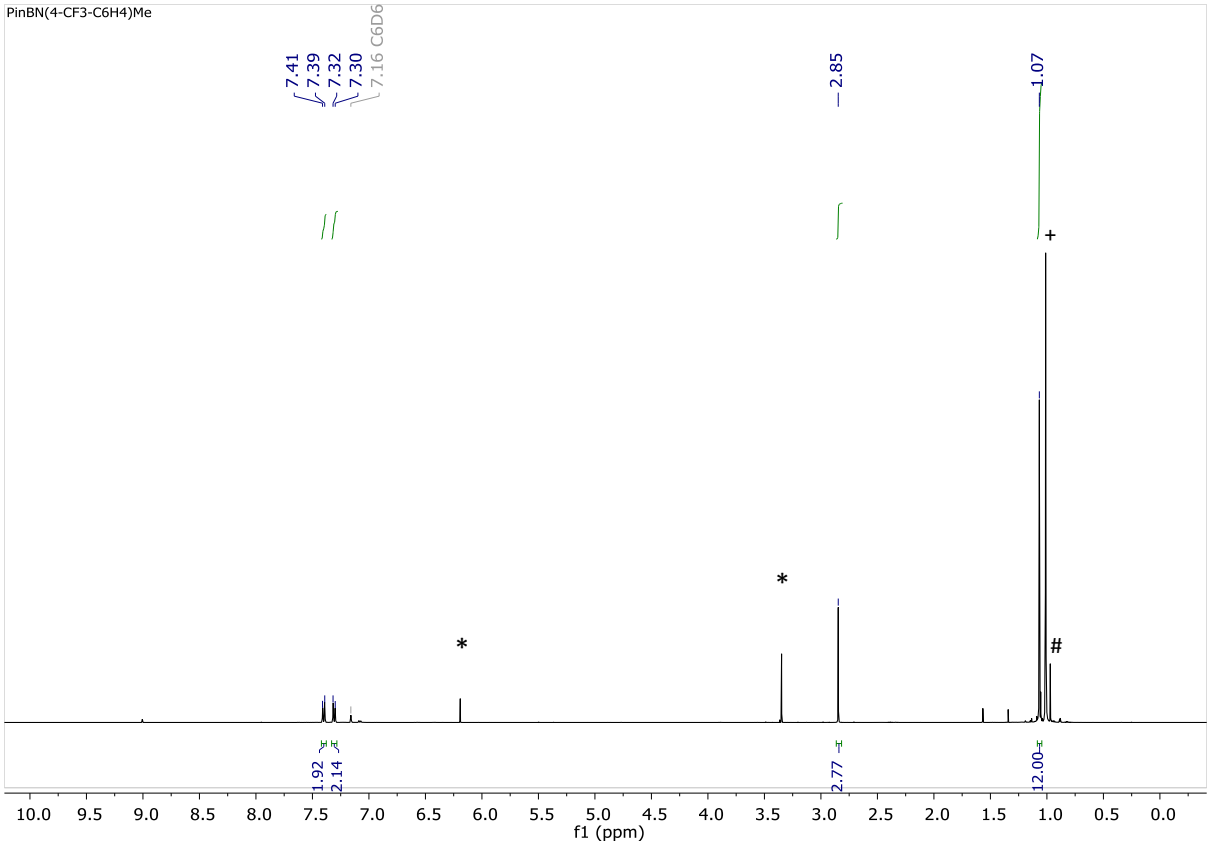


Figure S33: $^{1}$H NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)$CH_3$, 1i'. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #, PinBOBPin marked with +.

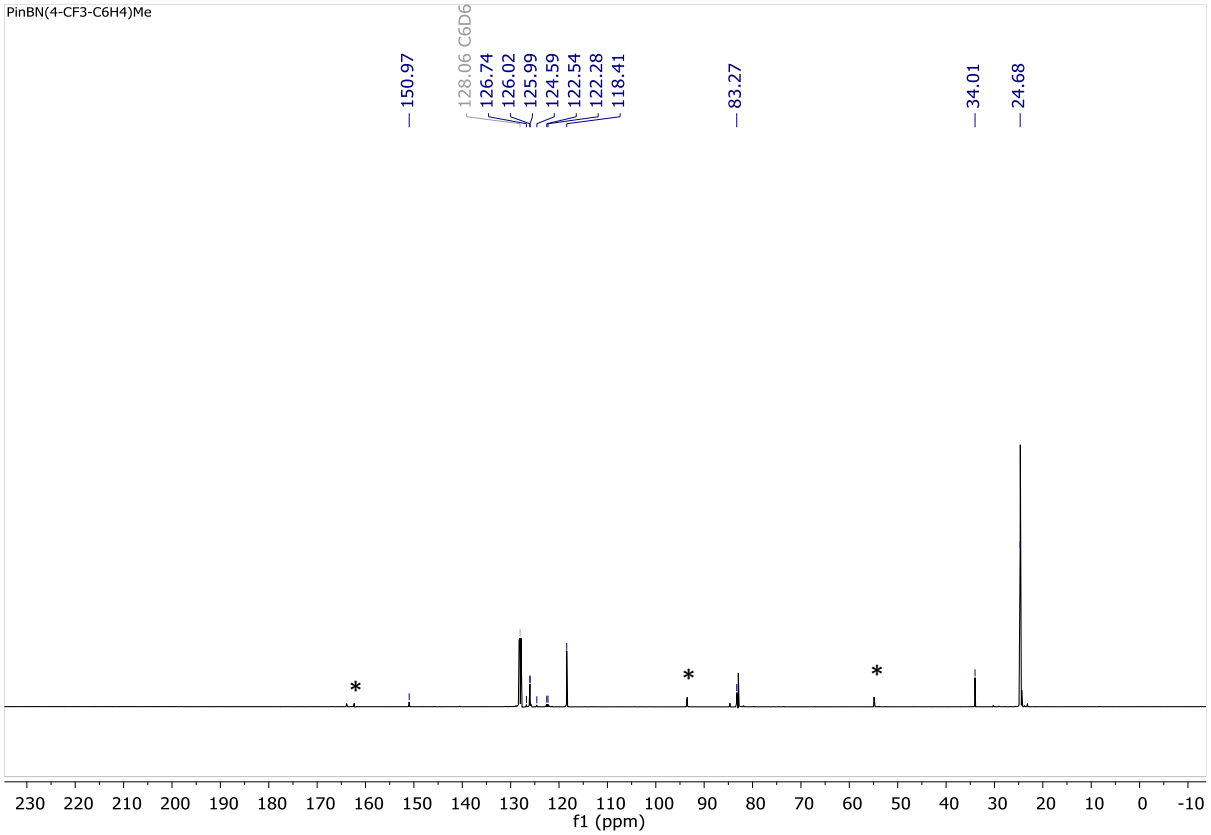


Figure S34: $^{13}$C NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)$CH_3$, 1i'. $C_6H_3(OMe)_3$ internal standard indicated with *.

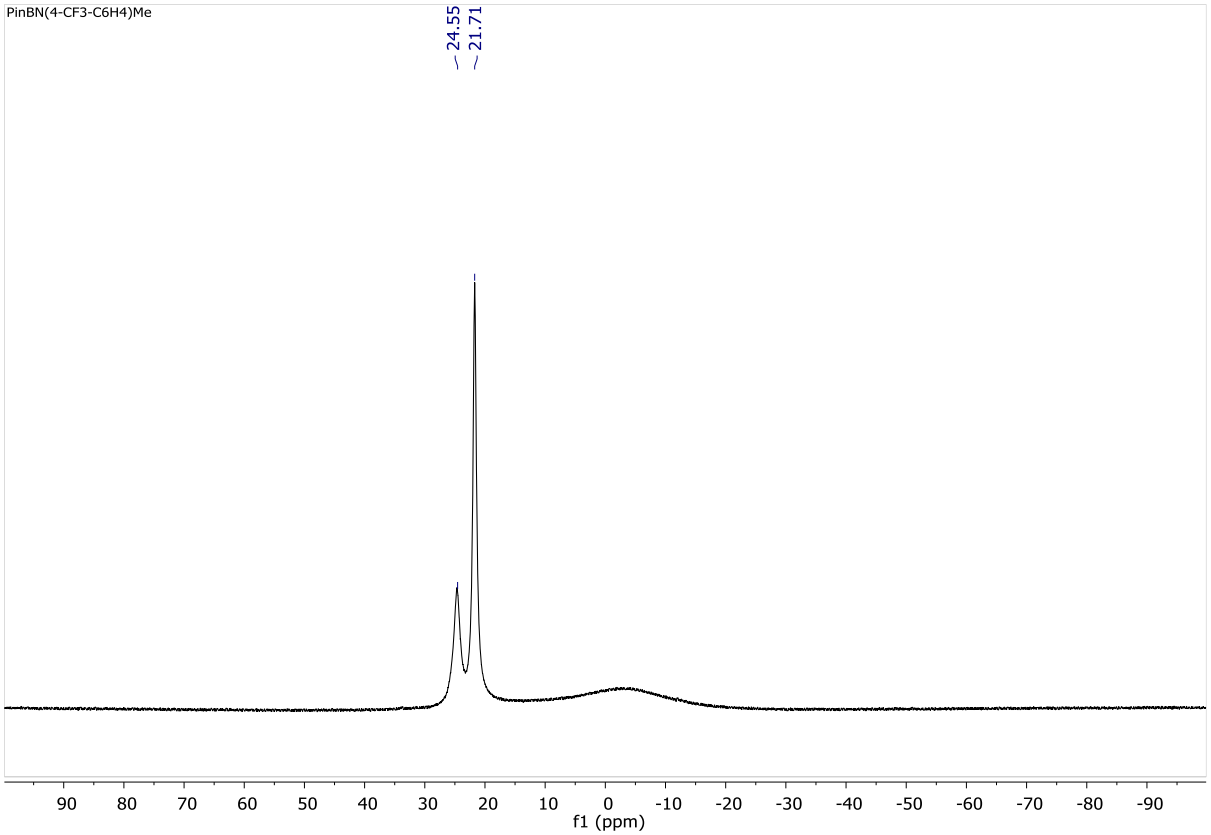


Figure S35: $^{11}B$ NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)$CH_3$, 1i'.

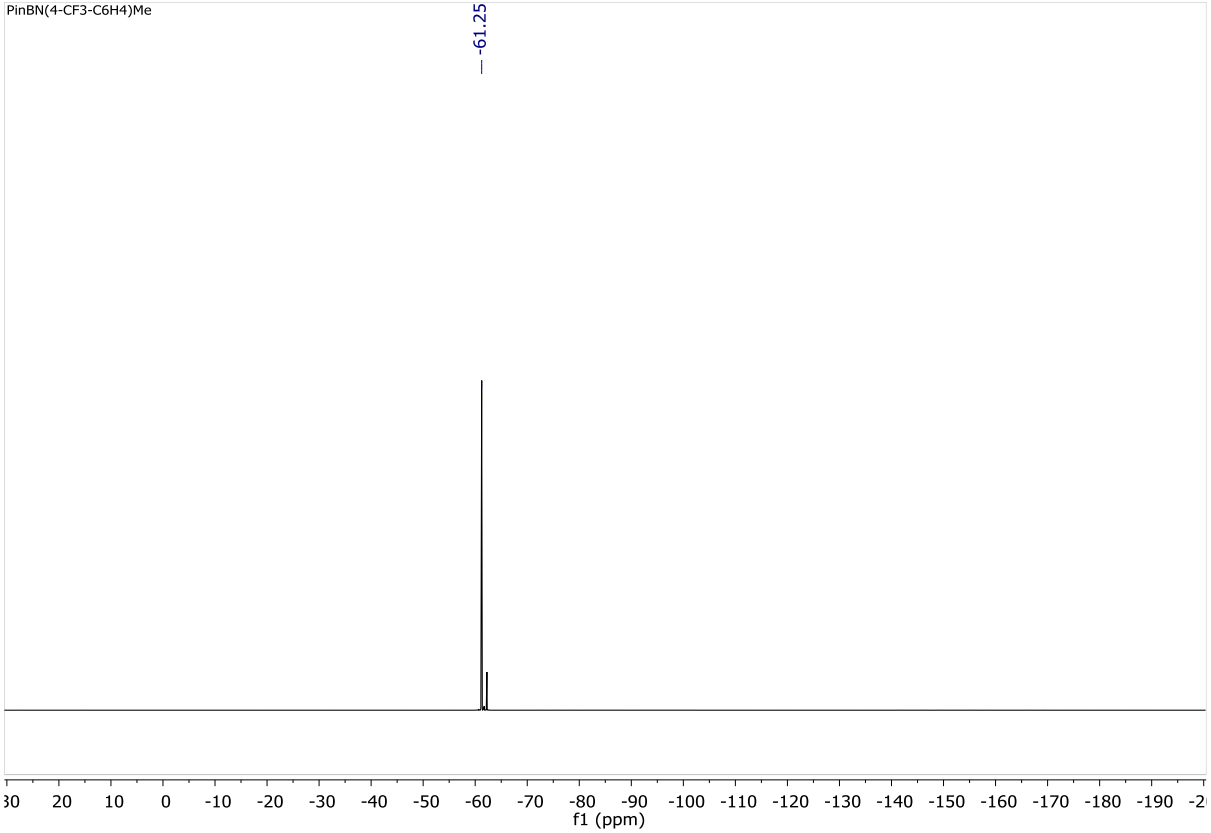


Figure S36: $^{19}F$ NMR spectrum for PinBN(4-$CF_3$-$C_6H_4$)$CH_3$, 1i'.

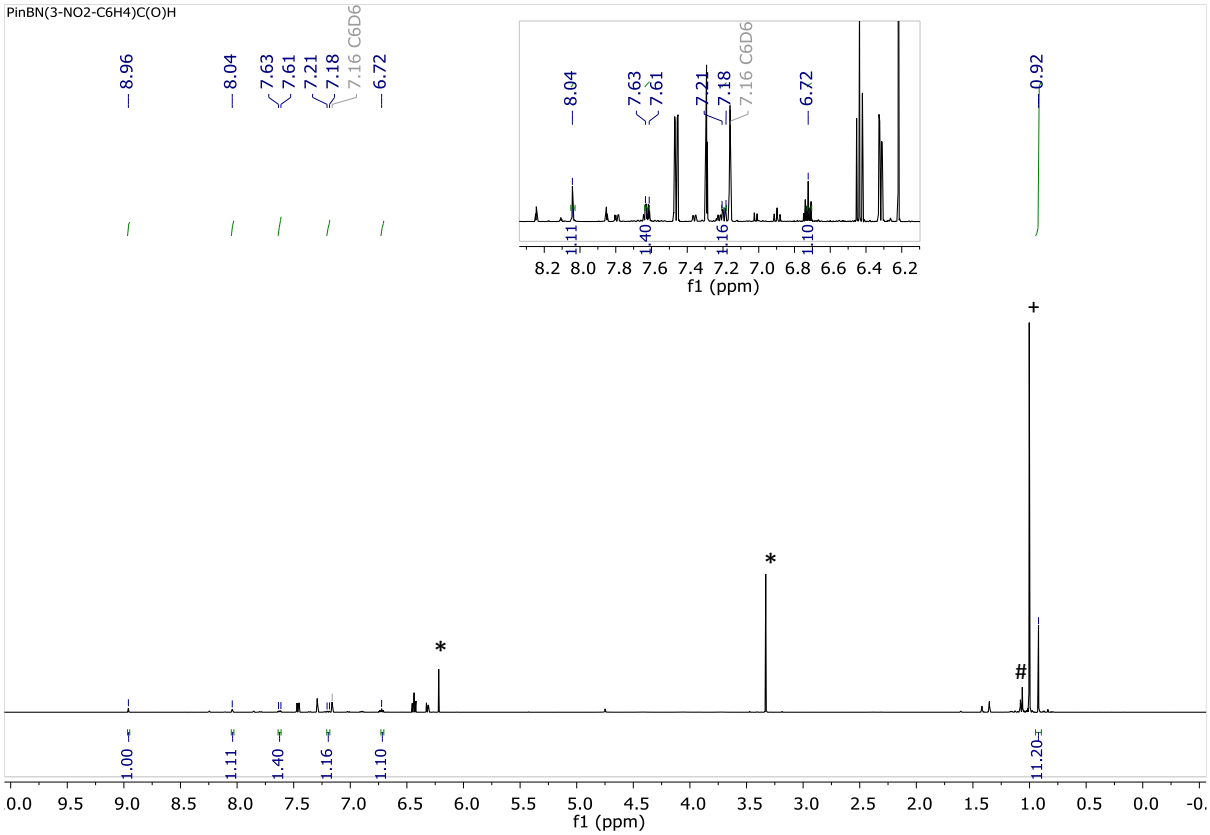


Figure S37: $^{1}$H NMR spectrum for PinBN(3-$NO_2$-$C_6H_4$)C(O)H, 1j, with inset showing expansion of the aromatic region. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #, HBPin marked with +.

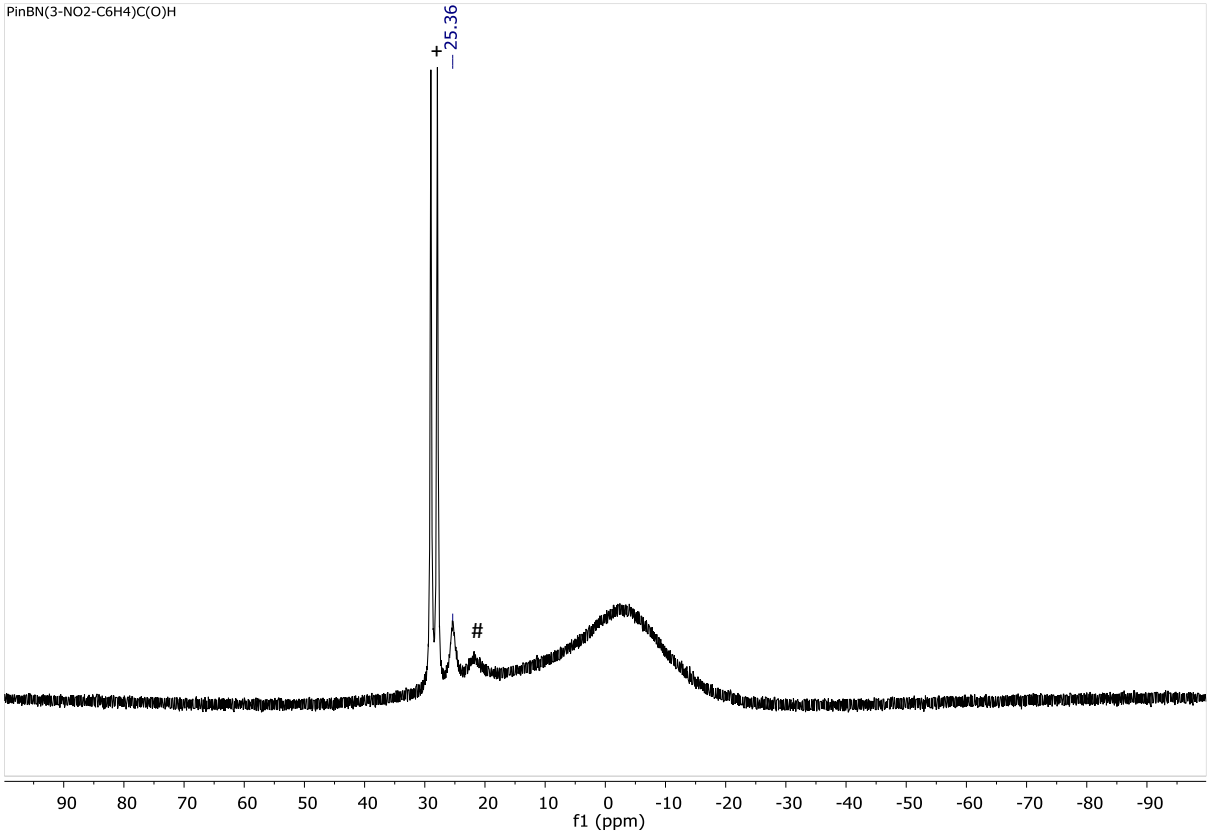


Figure S38: $^{11}$B NMR spectrum for PinBN(3-$NO_2$-$C_6H_4$)C(O)H, 1j, PinBOtBu indicated with #, HBPin marked with +.

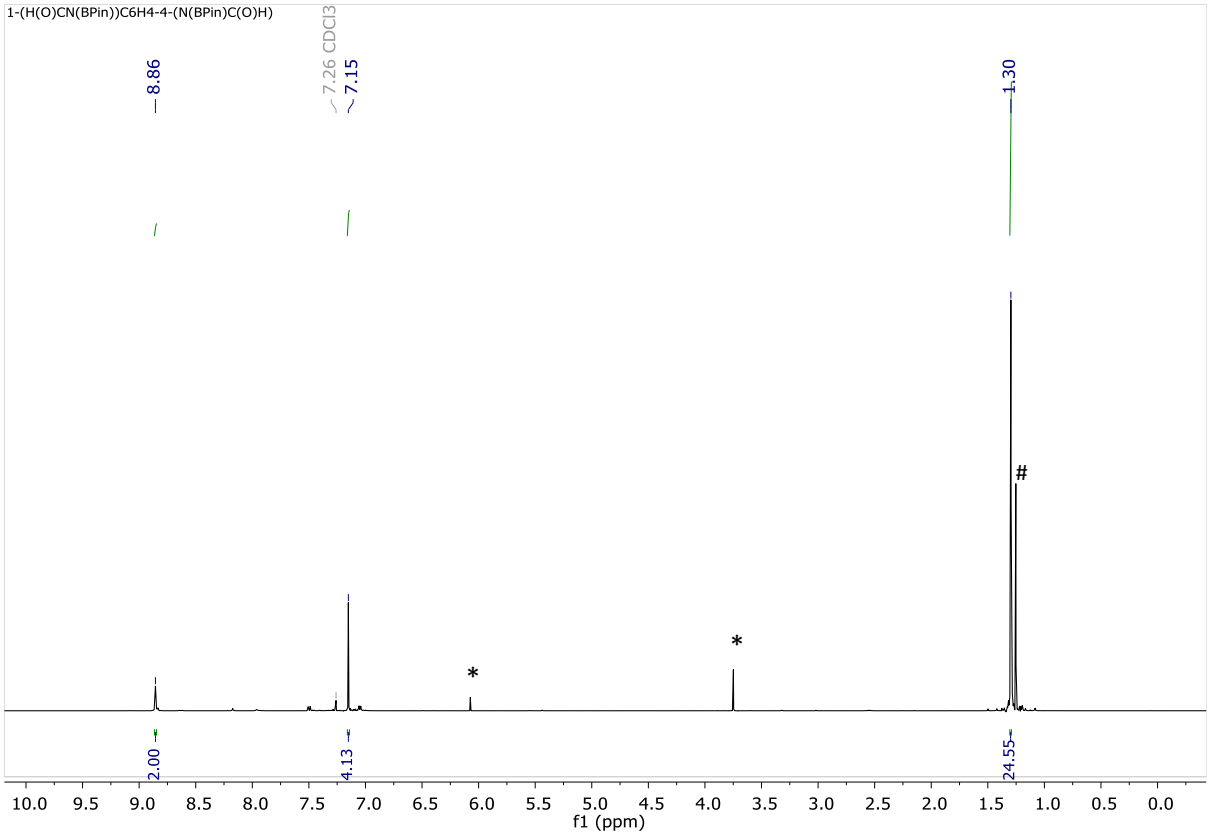


Figure S39: $^{1}$H NMR spectrum for 1-(H(O)CN(BPin))$C_6H_4$-4-(N(BPin)C(O)H), 1k. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

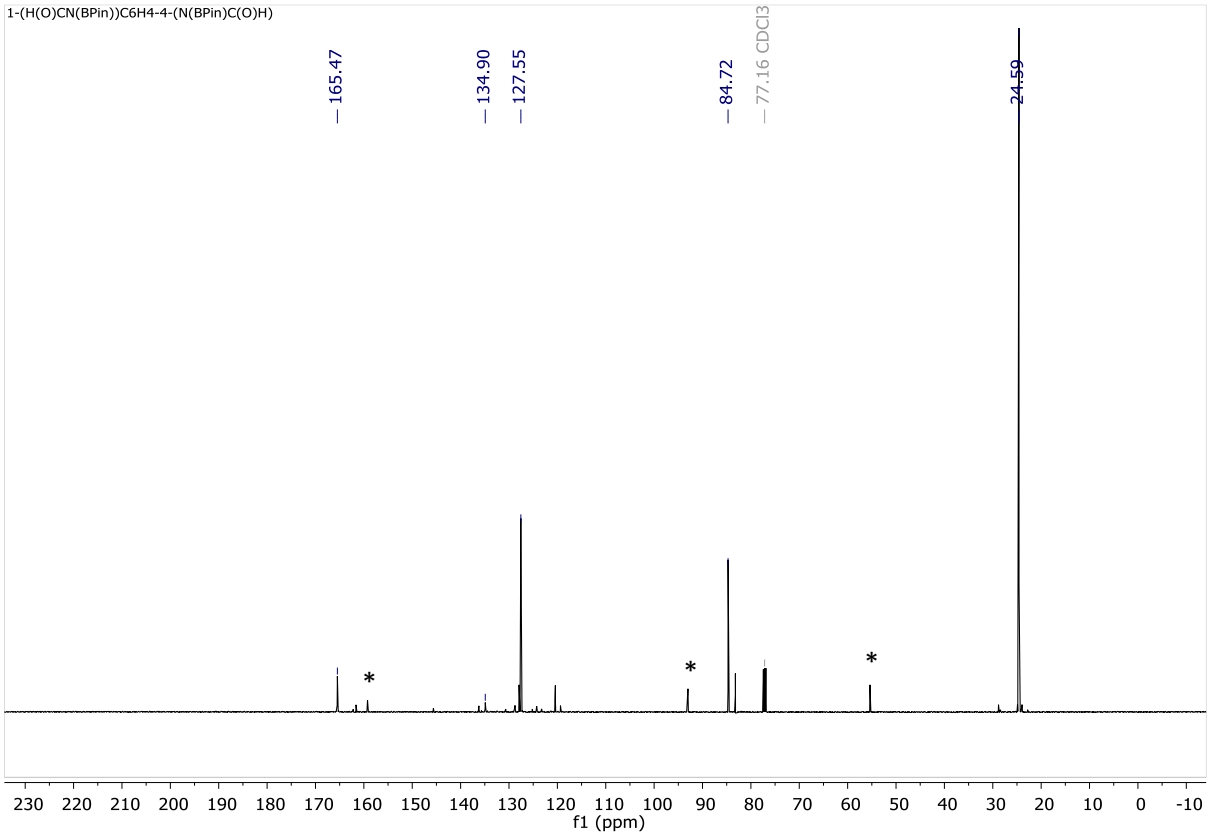


Figure S40: $^{13}$C NMR spectrum for 1-(H(O)CN(BPin))$C_6H_4$-4-(N(BPin)C(O)H), 1k. $C_6H_3(OMe)_3$ internal standard indicated with *.

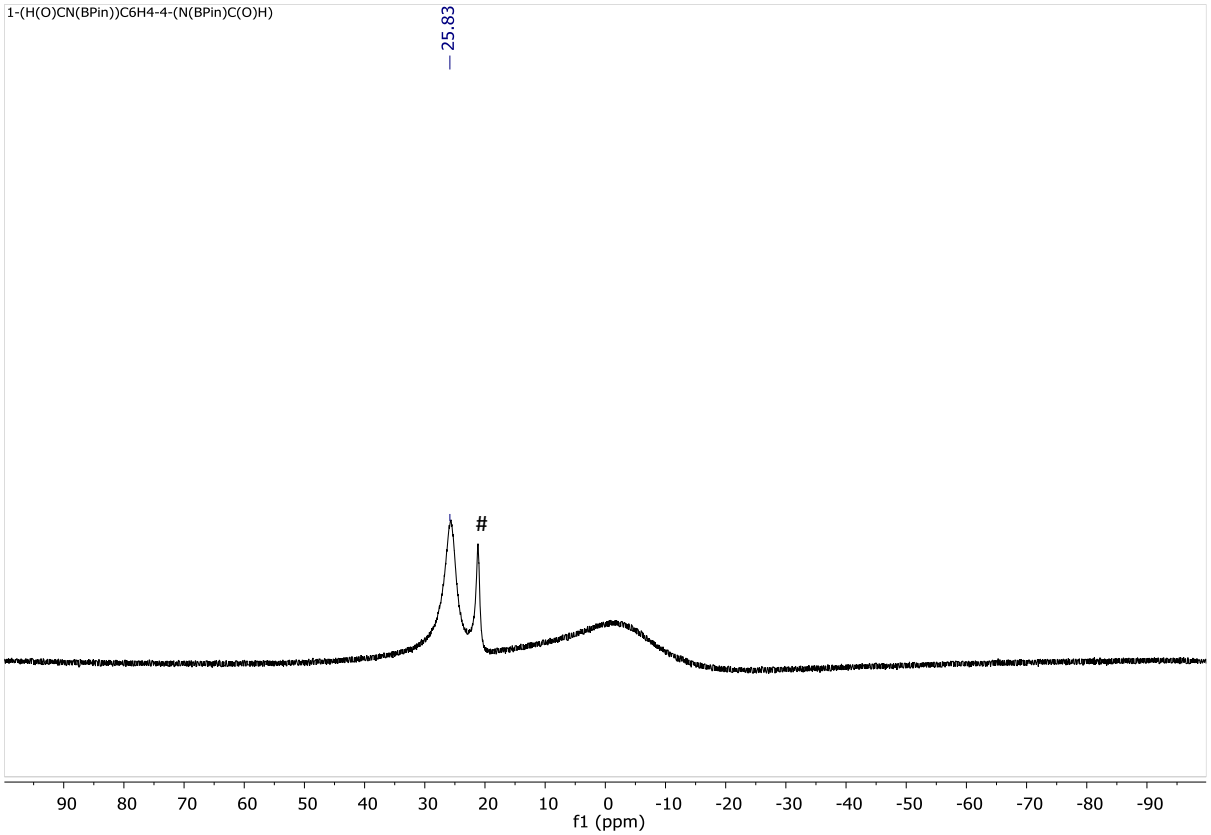


Figure S41: $^{11}$B NMR spectrum for 1-(H(O)CN(BPin))$C_6H_4$-4-(N(BPin)C(O)H), 1k, PinBOtBu indicated with #.

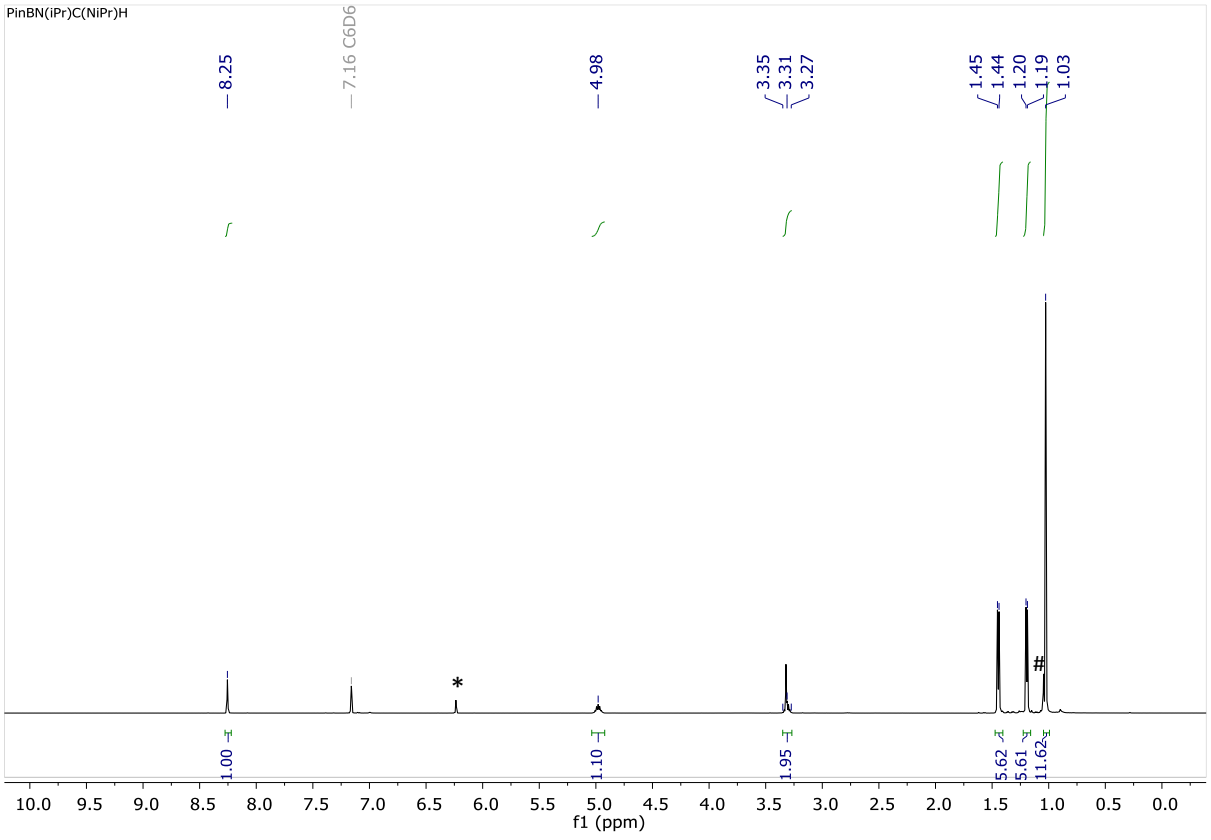


Figure S42: $^1$H NMR spectrum for PinBN(iPr)C(NiPr)H, 3a. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

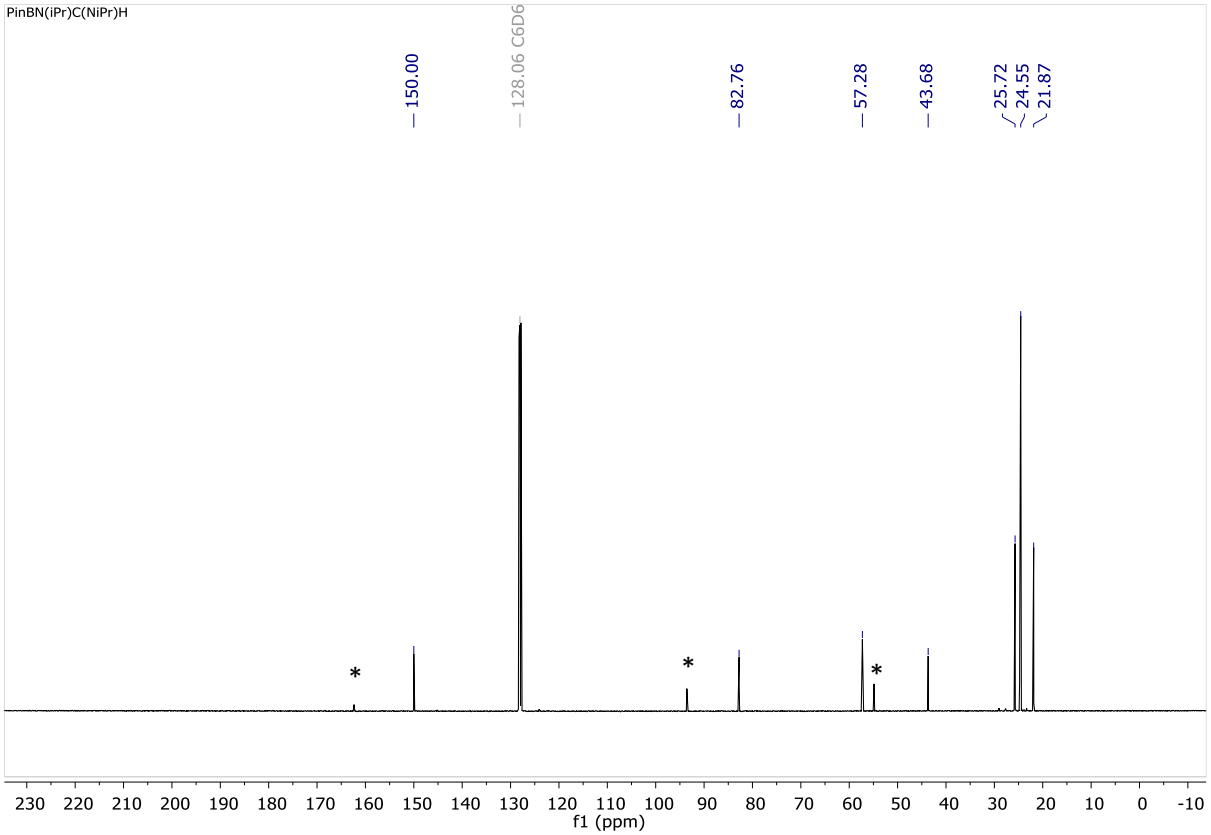


Figure S43: $^{13}C$ NMR spectrum for PinBN(iPr)C(NiPr)H, 3a. $C_6H_3(OMe)_3$ internal standard indicated with *.

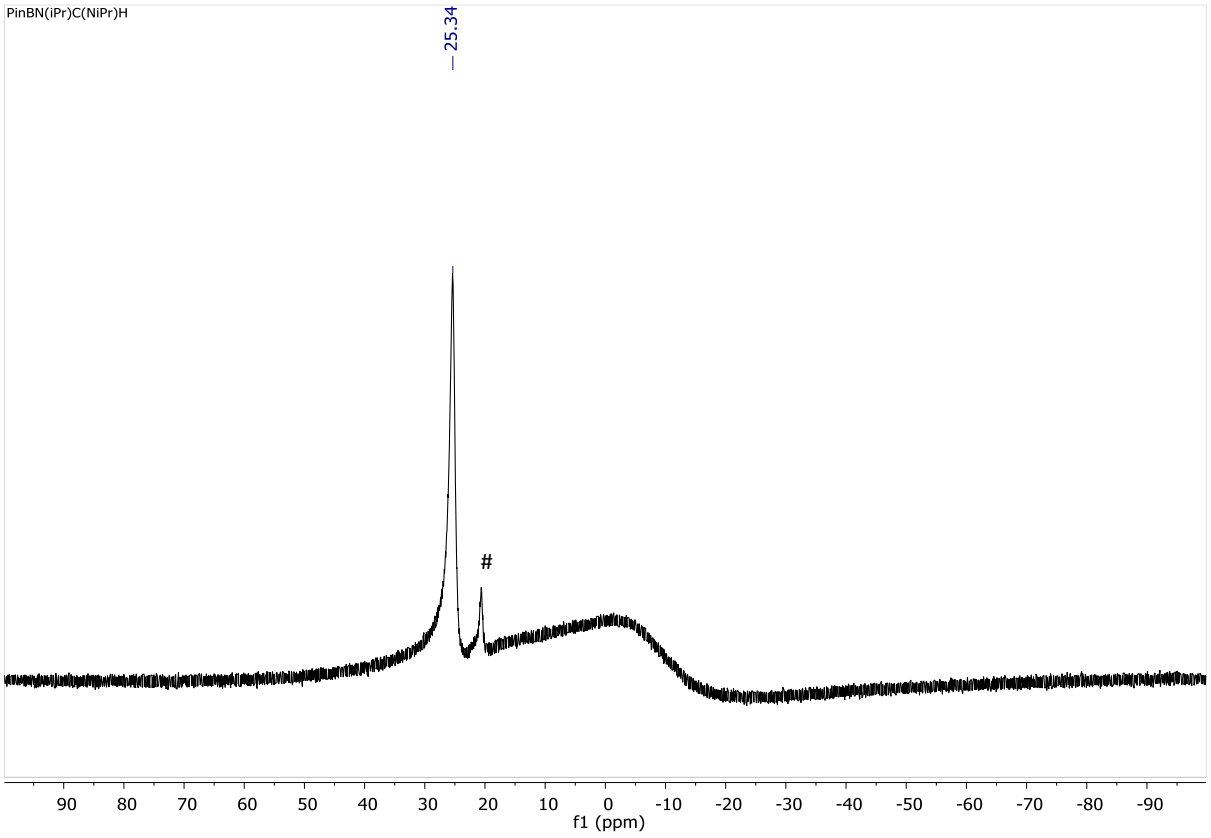


Figure S44: $^{11}B$ NMR spectrum for PinBN(iPr)C(NiPr)H, 3a, PinBOtBu indicated with #.

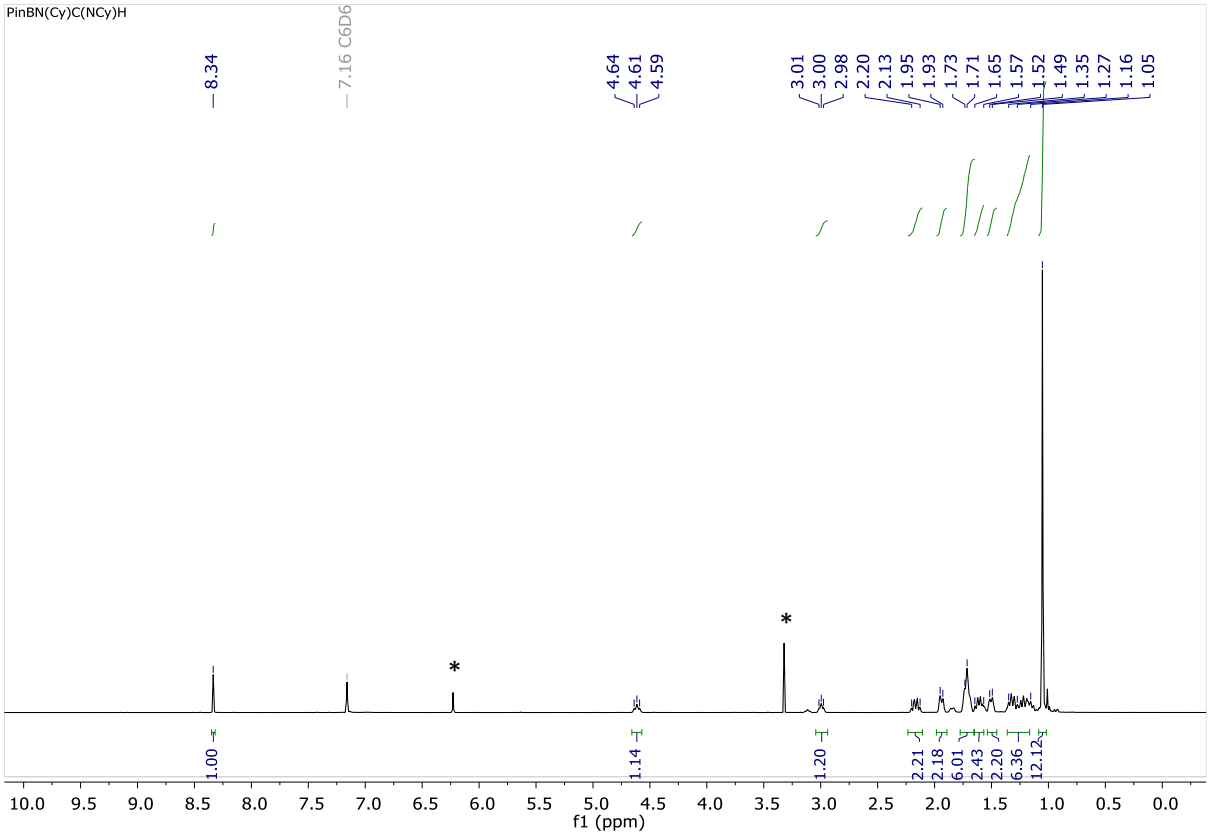


Figure S45: $^{1}H$ NMR spectrum for PinBN(Cy)C(NCy)H, 3b. $C_6H_3(OMe)_3$ internal standard indicated with *.

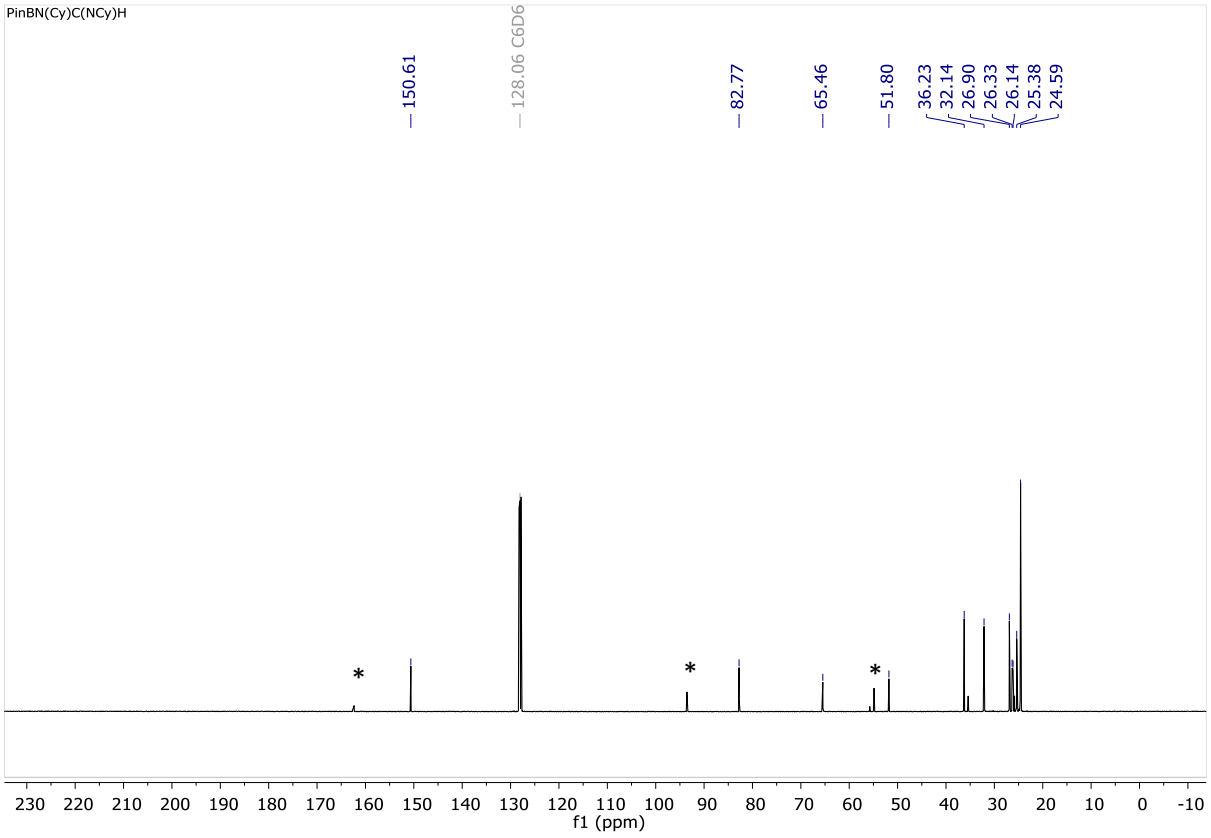


Figure S46: $^{13}C$ NMR spectrum for PinBN(Cy)C(NCy)H, 3b. $C_6H_3(OMe)_3$ internal standard indicated with *.

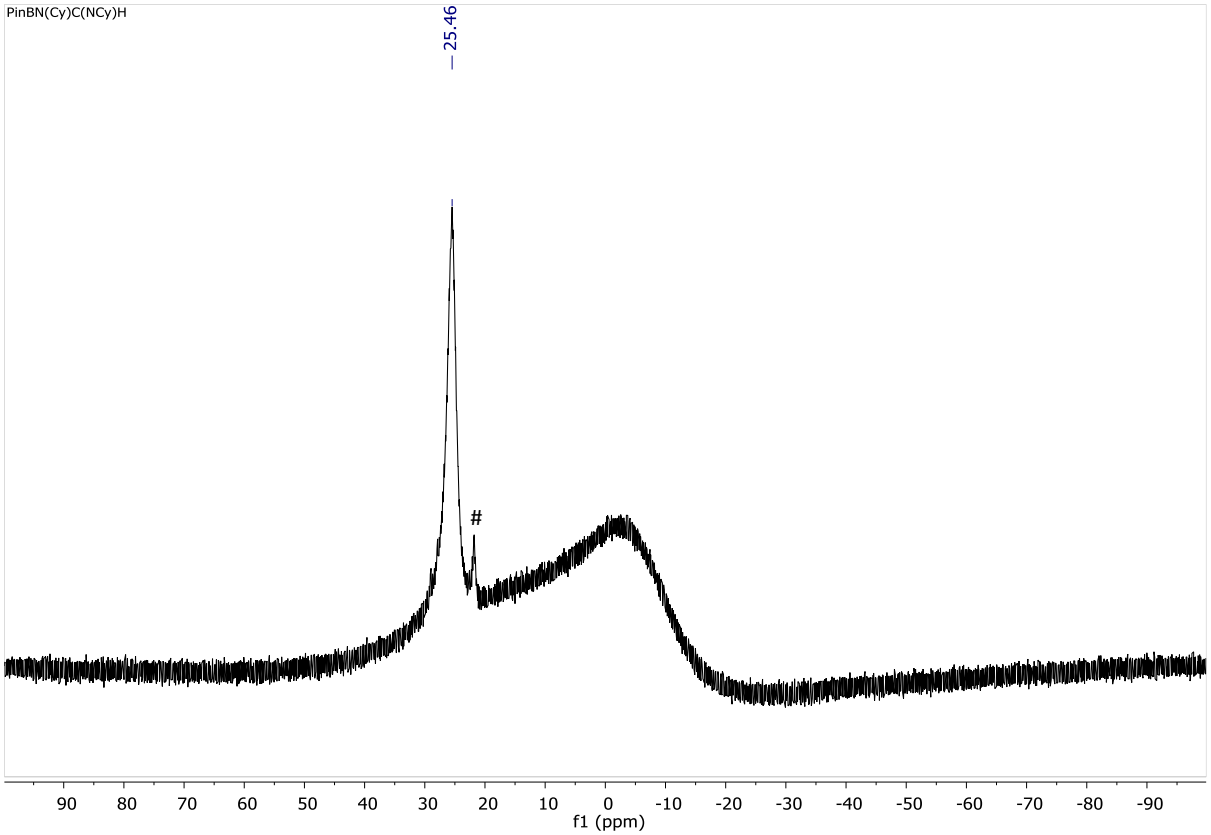


Figure S47: $^{11}$B NMR spectrum for PinBN(Cy)C(NCy)H, 3b, PinBOtBu indicated with #.

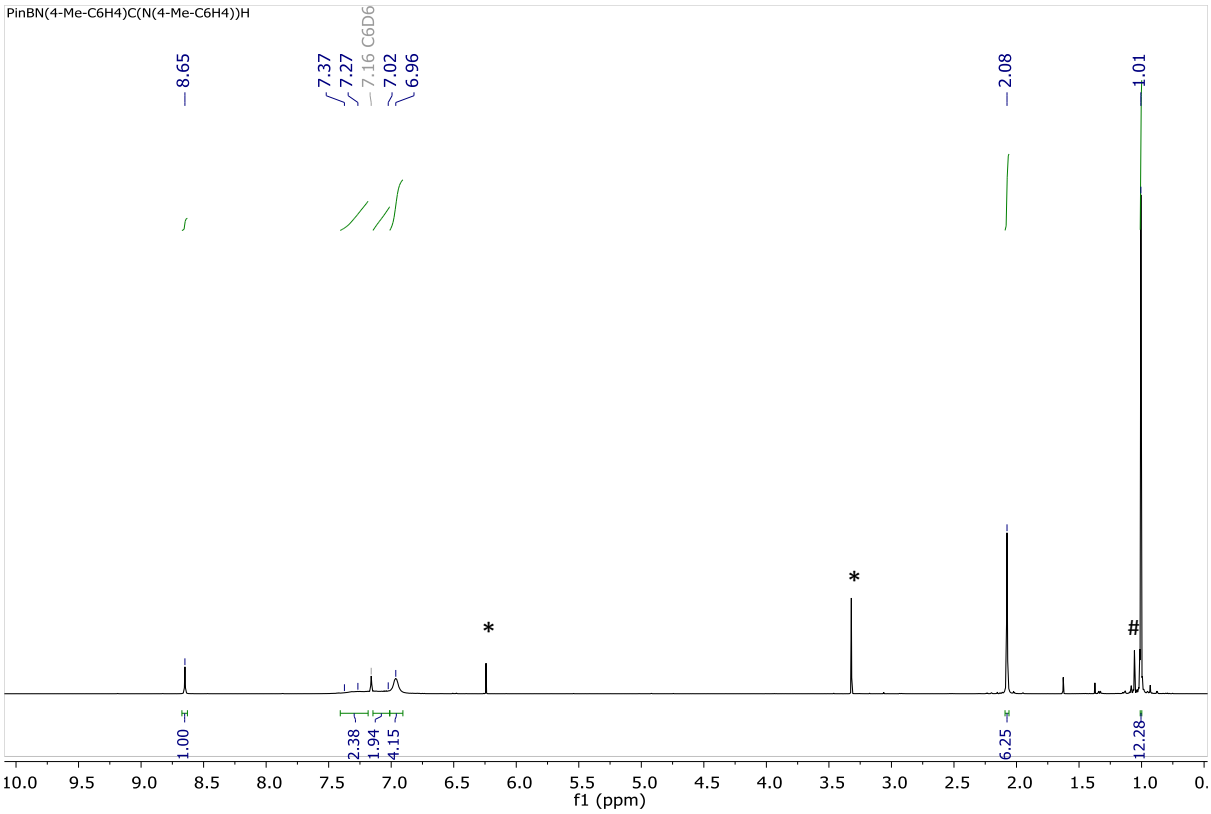


Figure S48: $^{1}$H NMR spectrum for PinBN(4-Me-$C_6H_4$)C(N(4-Me-$C_6H_4$))H, 3b. $C_6H_3(OMe)_3$ internal standard indicated with *, PinBOtBu indicated with #.

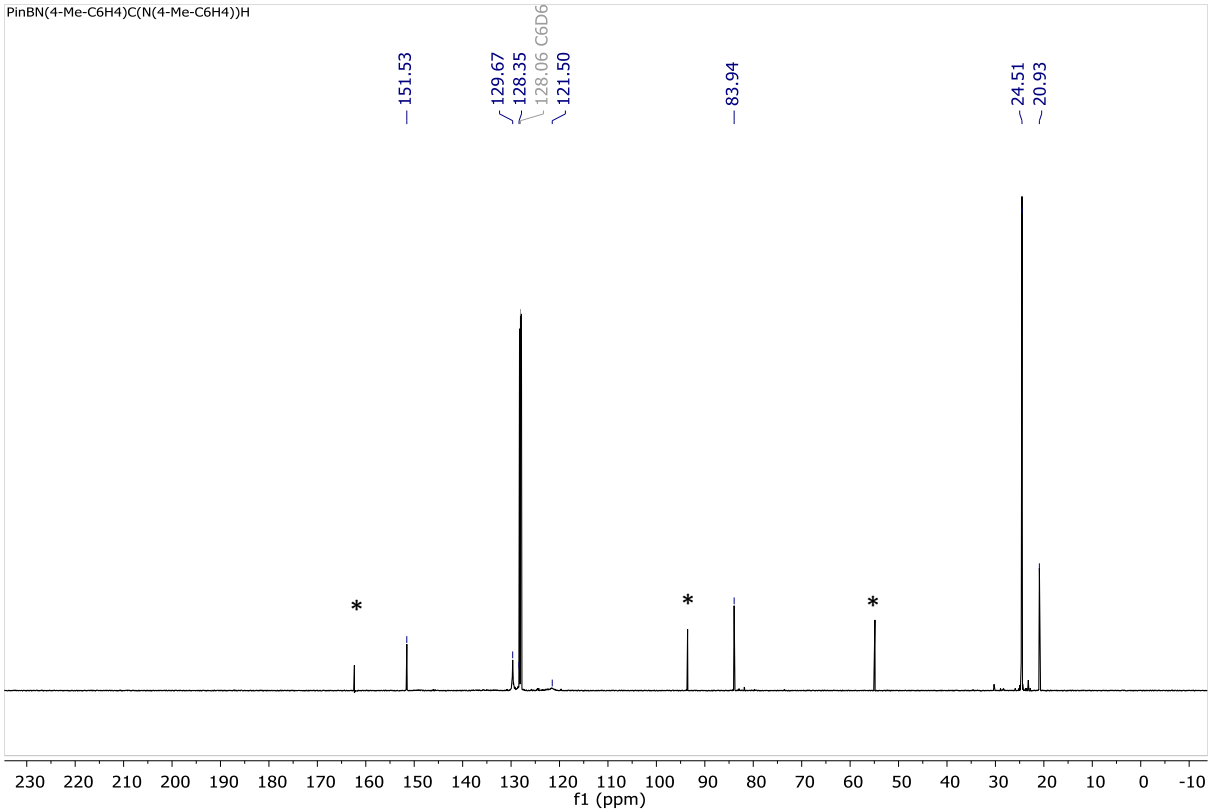


Figure S49: $^{13}C$ NMR spectrum for PinBN(4-Me-$C_6H_4$)C(N(4-Me-$C_6H_4$))H, 3b. $C_6H_3(OMe)_3$ internal standard indicated with *.

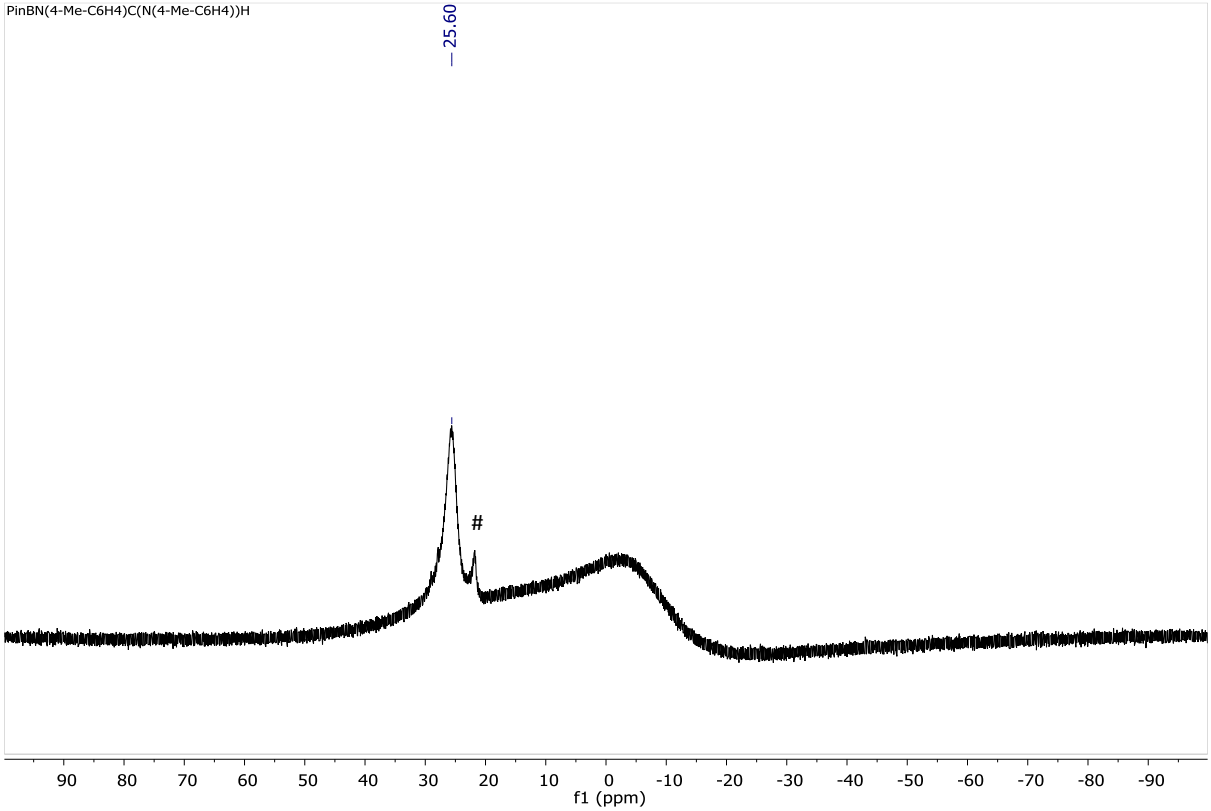


Figure S50: $^{11}B$ NMR spectrum for PinBN(4-Me-$C_6H_4$)C(N(4-Me-$C_6H_4$))H, 3b, PinBOtBu indicated with #.

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