# Selective C-O Cleavage and C=O Deoxygenation of Carbamates and Polyurethane Catalyzed by Organoactinide Complexes

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## 1. Material, methods, and general remarks

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or J-Young Teflon valve-sealed NMR tubes on a dual manifold Schlenk line interfaced to a high vacuum ($10^{-5}$ Torr) line, or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1 – 2 ppm of $O_2$). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4Å molecular sieve column. The actinide complexes $[(Me_3Si)_2N]_2An$ $[\kappa^2\text{-}(N,C)CH_2Si(CH_3)_2N(SiMe_3)]$ (An = U, Th), imidazolin-2-iminato thorium complex, and deuterated pinacolborane (DBpin) were prepared according to published procedures.[1-4] All carbamates are commercially available compounds obtained from commercial suppliers (Sigma Aldrich, TCI America, Aaronchem, Tzamal D-Chem, and AA Blocks) and were used without any further purifications, unless otherwise noted. Pinacolborane ester (CAS# = 25015-63-8) was purchased from Tzamal D-Chem and Sigma Aldrich and distilled under high vacuum ($10^{-5}$ Torr) before use. Tris[N,N-bis(trimethylsilyl)amide]lanthanum(III) (CAS# = 175923-07-6) was purchased from Sigma-Aldrich and used as received. All catalytic reactions were carried out under an $N_2$ atmosphere in a glovebox. Hydrocarbon solvent toluene-$d_8$ (Cambridge Isotopes) was distilled under vacuum from a Na/K alloy and degassed by three freeze-pump-thaw cycles before use. Thin-layer chromatography (TLC) was performed using silica gel 60 F-254 pre-coated plates (0.25 mm) and visualized by UV irradiation, CAM stain, $KMnO_4$ stain, and $I_2$, stain. Column chromatography was performed using silica gel 60 (0.063-0.200mm) purchased from Merck KGaA. $^1H$ and $^{13}C$ NMR spectra were recorded on 400 MHz spectrometers with $^{13}C$ operating frequencies of 101 MHz, $^{11}B$ operating frequencies of 128 MHz, and $^{19}F$ operating frequencies of 377 MHz. $^1H$ and $^{13}C$ NMR spectra were referenced to TMS as an internal standard with a deuterated solvent unless otherwise stated. Chemical shifts ($\delta$) are reported in ppm relative to the residual solvents ($CDCl_3$) signal ($\delta$ = 7.26 for $^1H$ NMR and $\delta$ = 77.16 for $^{13}C$ NMR), (Toluene-$d_8$) signal ($\delta$ = 2.08 (p) for $^1H$ NMR; $\delta$ = 21.4 (dp) for $^{13}C$ NMR. Data for $^1H$ NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), brs (broad signal). The full assignment for every compound's $^1H$ and $^{13}C$ signals appears in color in the spectral graphic.

## 2. Optimization of the reaction conditions for the selective C-O cleavage and C=O deoxygenation of carbamates

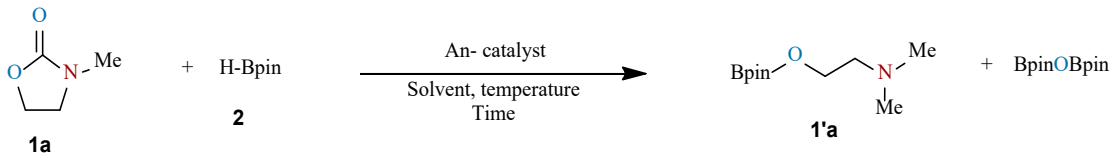
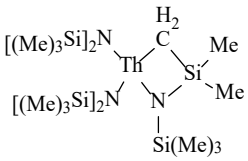


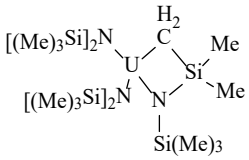

**Table S1.** *Optimization of the reaction conditions*.[a]

| Entry | Catalyst | Solvent | H- source | Temp [°C] | Time [h] | yield |
|---|---|---|---|---|---|---|
| 1 | **I** | THF | HBpin | 66 | 48 | - |
| 2 | **I** | Benzene | HBpin | 80 | 24 | 20 |
| 3 | **II** | Benzene | HBpin | 80 | 24 | 16 |
| 4 | **III** | Benzene | HBpin | 80 | 24 | 14 |
| 5 | **I** | Toluene | HBpin | 110 | 24 | 72 |
| 6 | **II** | Toluene | HBpin | 110 | 24 | 70 |
| 7 | **III** | Toluene | HBpin | 110 | 24 | 62 |
| 8 | **II** | Toluene | 9BBN | 110 | 24 | 84 |
| 9 | **II** | Toluene | $BH_3$*THF | 110 | 24 | 8 |
| 10 | **II** | Toluene | HBCat | 110 | 24 | trace |
| 11 | **I** | Toluene | H-Si(Et)$_3$ | 110 | 24 | - |
| 12 | **I** | Toluene | HBcat | 110 | 24 | trace |
| 13 | **II** | Toluene | $PhSiH_3$ | 110 | 24 | 13 |
| 14 | **II** | Toluene | $Et_3SiH$ | 110 | 24 | 0 |
| 15 | - | Toluene | HBpin | 110 | 48 | - |
| 16 | **I** | Toluene | HBpin[b] | 110 | 48 | 90 |

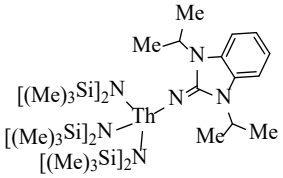
[a] The reactions were carried out with **1a** (0.2 mmol), **2** (0.63 mmol, 3.1 equiv), and 3%mmol of actinide catalyst. heated in oil bath for 2- 48 h. [b] Addition of one more equivalent of HBpin after 24h.




**I**




**II**




**III**

## 3. Procedure and characterization data for carbamate C-O cleavage and C=O deoxygenation reaction

### 3.1 Typical NMR-scale reaction procedure for the catalytic C-O cleavage and C=O deoxygenation of carbamate

In a typical experiment, a J. Young Teflon-sealed NMR tube was loaded inside the glovebox with carbamate (0.2 mmol, 1 equiv) and HBpin (0.63 mmol, 3 equiv), followed by the addition of the catalyst (3% mmol). The reaction was diluted to 650 μL with toluene-$d_8$, sealed, and placed in an oil bath, preheated to 110 °C for the specific amount of time. After completion, the crude reaction mixture was analyzed using $^{1}$H-NMR, $^{13}$C-NMR, $^{11}$B-NMR, and if relevant, $^{19}$F-NMR. The isolated compounds of relevant carbamate derivatives [ 1'y-(H), 1'ab-(H), and (1'ac-H)] were diluted with toluene and purified via column chromatography using silica gel (gradient eluent of hexane/EtOAc from ratio of 100:0 up to 20:80, respectively) to give the corresponding products.

### 3.2 Typical 1 gram-scale reaction procedure for the catalytic C-O cleavage and C=O deoxygenation of carbamates

Inside the glovebox, a 100 mL ACE pressure tube equipped with a magnetic stir bar was charged with carbamate (**1y**) (0.96 g, 5.4 mmol, 1 equiv), HBpin (**2**) (2.43 mL, 3.1 equiv). and either the uranium(IV) metallacycle (**II**) (1 mmol%) catalyst or the tris[N,N-bis(trimethylsilyl)amide]lanthanum(III) (1 mol%). The reaction mixture was diluted to a total volume of 40 mL with toluene, which had been dried using Na/K alloy and distilled under high vacuum ($10^{-5}$ Torr) prior to use. The pressure tube was then sealed, removed from the glovebox, and placed in an oil bath, preheated to 110 °C for 48 hours. After completion, the reaction mixture was loaded onto silica and purified by column chromatography on silica gel (gradient elution with hexane/EtOAc from a ratio of 100:0 up to 0:100, respectively) to afford the corresponding drug molecule **1'y-(H)**. with 91% and 82% of isolated yields for catalyst **II** and tris[N,N-bis(trimethylsilyl)amide]lanthanum(III), respectively.

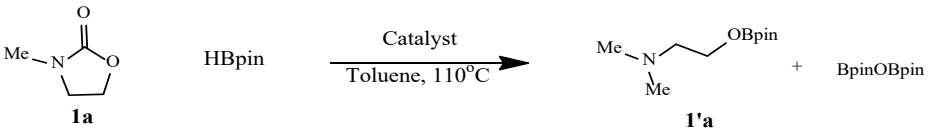
### 3.3 Typical 2-gram-scale reaction procedure for the catalytic C-O cleavage and C=O deoxygenation of carbamate

Inside the glovebox, a 100 mL ACE pressure tube equipped with a magnetic stir bar was charged with carbamate (**1y**) (1.9 g, 10.7 mmol, 1 equiv), HBpin (**2**) (4.87 mL, 3.1 equiv). and the uranium(IV) metallacycle (**II**) catalyst (1 mmol%). The reaction mixture was diluted to a total volume of 40 mL with toluene, which had been dried using Na/K alloy and distilled under

high vacuum ($10^{-5}$ Torr) prior to use. The pressure tube was then sealed, removed from the glovebox, and placed in an oil bath, preheated to 110 °C for 48 hours. After completion, the reaction mixture was loaded onto silica and purified by column chromatography on silica gel (gradient elution with hexane/EtOAc from a ratio of 100:0 to 0:100, respectively) to afford the corresponding drug molecule 1'y-(H) with an isolated yield of 90%.

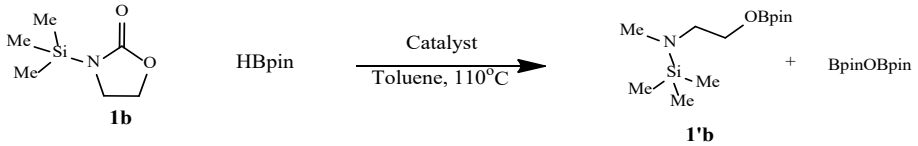
### 3.4 Characterization data for the catalytic C-O cleavage and C=O deoxygenation of carbamate reaction

**Synthesis of 1'a:** 20 mg (17 $\mu$L) of **1a** were reacted with 80 mg (91 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′a** in 72%, 70%, and 62% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.



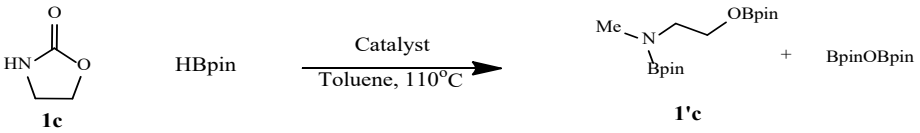

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.82 (t, $J$ = 6.0 Hz, 2H, O-$CH_2$-), 2.33 (t, $J$ = 6.0 Hz, 2H, N-$CH_2$-), 2.10 (s, 6H- N[Me]$_2$), 1.10 (s, 12H- OBpin), (BpinOBpin) 1.04 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 79.60, 60.02, 58.39, 43.51, 22.58. (BpinOBpin) δ 80.46, 22.30.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 21.39 (O-B), 20.78 (B-O-B).
**HRMS** (ESI) calcd. for $[C_{10}H_{22}BNO_5+H]^+$ $[M+H]^+$ : 216.1766, found: 216.1773.

**Synthesis of 1'b:** 32 mg (30 $\mu$L) of **1b** were reacted with 80 mg (91 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′b** in 48%, 84%, and >95% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.68 (t, $J$ = 5.6 Hz, 2H, O-$CH_2$-), 2.88 (t, $J$ = 5.7 Hz, 2H, N-$CH_2$-), 2.47 (s, 3H, N-$CH_3$), 0.94 (s, 12H,OBpin), 0.00 (s, 9H, Si($CH_3$)$_3$). (BpinOBpin) 0.83 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 81.20, 62.58, 49.82, 33.45, 24.09, 0.35.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.46 (O-B), 20.97 (B-O-B).
**HRMS** (ESI) calcd. for $[C_{12}H_{28}BNO_3Si+H]^+$ $[M+H]^+$ : 274.2004, found: 274.2020.

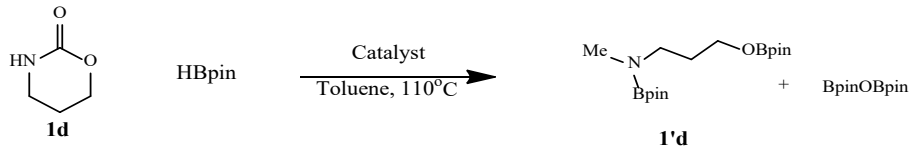
**Synthesis of 1'c:** 18 mg of **1c** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′c** in 94%, 90%, and 90% yield for catalysts **I**, **II**, and **III**, respectively, in 2h.




**1c** **1'c**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 4.09 (t, $J$ = 5.7 Hz, 2H, O-$CH_2$-), 3.29 (t, $J$ = 5.7 Hz, 2H, N-$CH_2$-), 2.88 (s, 3H, N-$CH_3$), 1.34 (s, 12H, O-Bpin), 1.32 (s, 12H, N-Bpin), (BpinOBpin) 1.25 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 81.83, 81.64, 62.78, 50.01, 33.64, 24.38, 24.28. (BpinOBpin) δ 82.33, 24.14.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.46 (N-B), 22.50 (O-B), 21.59 (B-O-B).
**HRMS** (ESI) calcd. for $[C_{15}H_{31}B_2NO_5+H]^+$ $[M+H]^+$ : 328.2461, found: 328.2460.

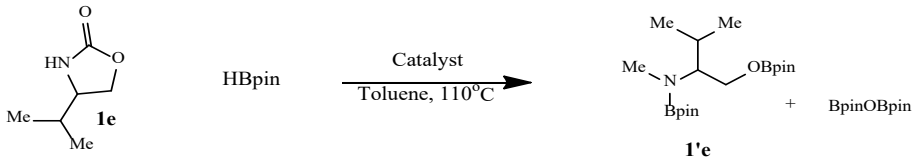
**Synthesis of 1'd:** 20 mg of **1d** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′d** in 90%, 93%, and 85% yield for catalysts **I**, **II**, and **III**, respectively, in 4h.




**1d** **1'd**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.83 (t, J = 6.8 Hz, 2H, O-$CH_2$-), 2.94 (t, J = 7.0 Hz, 2H, N-$CH_2$-), 2.51 (s, 3H, N-$CH_3$), 1.66 (p, J = 6.9 Hz, 2H -$CH_2$-), 1.01 (s, 12H, O-Bpin), 0.98 (s, 12H, N-Bpin), (BpinOBpin) δ 0.95 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 79.97, 79.71, 60.91, 43.52, 31.29, 28.83, 22.47, 22.39. (BpinOBpin) δ 80.50, 22.29.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.28 (N-B), 21.63 (O-B).
**HRMS** (ESI) calcd. for $[C_{21}H_{35}B_2NO_5+H]^+$ $[M+H]^+$ : 342.2618, found: 342.2667.

**Synthesis of 1'e:** 26 mg of **1e** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′e** in 87%, 92%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.

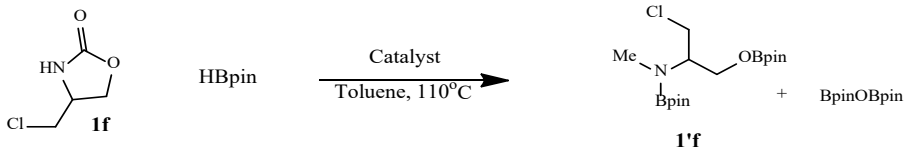



**1e** **1'e**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.93 (d, $J$ = 6.4 Hz, 2H, O-$CH_2$- ), 3.13 (dt, $J$ = 10.3, 6.4 Hz, 1H, N-CH-), 2.58 (s, 3H, N-$CH_3$), 1.64 (dp, $J$ = 10.2, 6.6 Hz, 1H,-CH-), 1.18 (s, 12H, OBPin), 1.13 (s, 12H, NBpin), , 0.92 (d, $J$ = 6.6 Hz, 3H, -$CH_3$), 0.80 (d, $J$ = 6.6 Hz, 3H, -$CH_3$). (BpinOBpin) 1.05 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 79.92, 79.41, 61.57, 60.57, 25.78, 24.36, 22.53, 22.48, 22.46, (BpinOBpin) δ 80.47, 22.30.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.78 (N-B), 21.58(O-B).

**HRMS** (ESI) calcd. for $[C_{18}H_{37}B_2NO_5+H]^+$ $[M+H]^+$ : 370.2931, found: 370.2935.

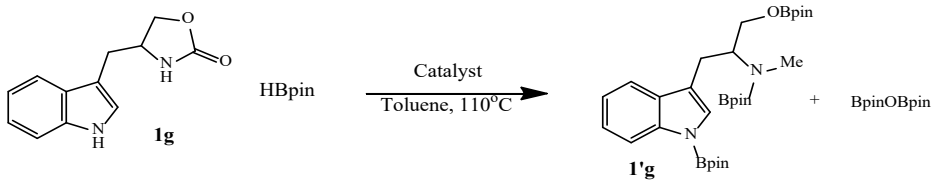
**Synthesis of 1'f:** 27 mg of **1f** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′f** in 88%, 94%, and 81% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.




**1f** **1'f**

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 4.22 (dt, J = 7.6, 3.3 Hz, 1H, NCH-), 3.11 (dd, J = 5.8, 3.8 Hz, 2H-$CH_2$-), 2.76 (ddd, J = 56.2, 13.9, 6.2 Hz, 2H-$CH_2$-), 2.46 (s, 3H, $NCH_3$), 0.92 (s, 24H, OBpin + NBpin), (BpinOBpin) 0.85 (s, 24H).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 81.99, 81.69, 72.51, 51.93, 46.01, 33.97, 24.10, 24.01. (BpinOBpin) δ 82.15, 23.95.
**$^{11}$B{$^1$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.24 (N-B), 21.57 (O-B).
**HRMS** (ESI) calcd. for $[C_{16}H_{32}B_2ClNO_5+H]^+$ $[M+H]^+$ : 376.2228, found: 376.2243.

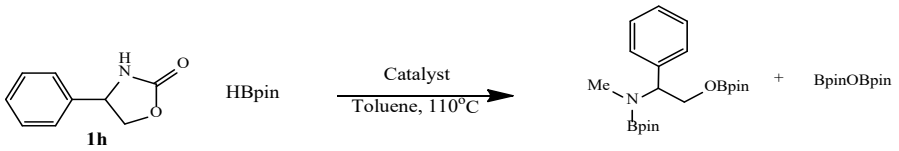
**Synthesis of 1'g:** 43 mg of **1g** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′g** in 80%, 81%, and 78% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.




**1g** **1'g**

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 8.07 (d, J = 8.0 Hz, 1H,[Ar]), 7.49 (d, J = 7.6 Hz, 1H, [Ar]), 7.40 (s, 1H, [Ar]), 7.18 – 7.13 (m, 1H, [Ar]), 7.12 – 7.06 (m, 1H, [Ar]), 4.11 – 4.02 (m, 1H, N-CH-), 3.97 (dd, J = 10.5, 8.5 Hz, 1H, O-$CH_2$-), 3.76 (dd, J = 10.5, 4.8 Hz, 1H, O-$CH_2$-), 2.80 – 2.69 (m, 1H, Ar-$CH_2$-), 2.62 – 2.52 (m, 1H, Ar-$CH_2$-), 2.46 (s, 3H), 1.04 (m, 24H (NBpin), 1.02 (s, 12H, OBpin), (BpinOBpin) δ 0.94 (s, 24H).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 139.78, 131.85, 126.12, 122.50, 120.80, 118.62, 117.67, 114.56, 82.34, 81.89, 81.31, 65.24, 55.34, 27.21, 24.31, 24.23, 24.18, 24.12. (BpinOBpin) δ 83.51, 22.62.
**$^{11}$B{$^1$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.93 (N-B), 21.63 (O-B).
**HRMS** (ESI) calcd. for $[C_{30}H_{49}B_3N_2O_7+H]^+$ $[M+H]^+$ : 583.3892, found: 583.3928.

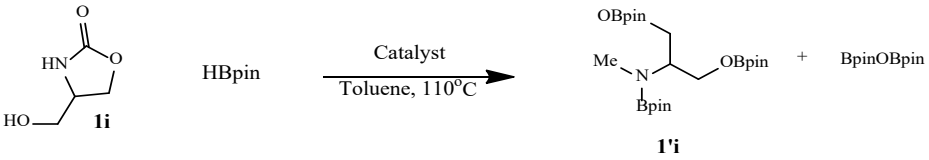
**Synthesis of 1'h:** 32 mg of **1h** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′h** in 95%, 90%, and 80% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.




**1h** **1'h**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.49 – 7.24 (m, 5H, Ar), 5.02 (dd, *J* = 9.5, 5.3 Hz, 1H,O-$CH_2$), 4.63 (t, 1H, PhCH-N), 4.43 (dd, *J* = 10.8, 5.3 Hz, 1H, $OCH_2$), 2.71 (s, 3H, $NCH_3$), 1.39 (s, 12H. OBpin), 1.33 (s, 12H, NBpin), (BpinOBpin) 1.26 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 141.29, 129.38, 129.07, 128.02, 83.35, 83.15, 64.55, 61.13, 29.67, 25.85, 25.75, (BpinOBpin) δ 83.73, 25.54.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.60 (N-B), 21.55 (O-B).
**HRMS** (ESI) calcd. for $[C_{21}H_{35}B_2NO_5+H]^+$ $[M+H]^+$ : 404.2774, found: 404.2815.

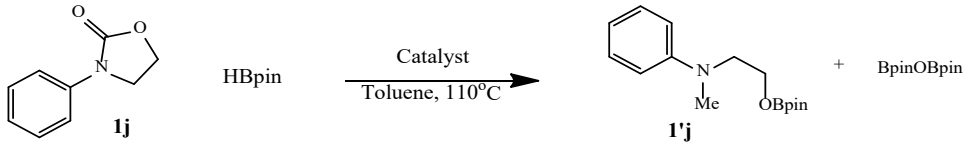
**Synthesis of 1'i:** 23 mg of **1i** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′i** in 84%, 79%, and 82% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**1i** **1'i**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 4.48 – 4.34 (m, 1H,CHN), 3.83 (m, 2H, $OCH_2$-), 2.94 (dd, *J* = 30.8, 6.2 Hz, 2H, $OCH_2$-), 2.62 (s, 3H, $NCH_3$), 1.05 (s, 24H, OBpin), 1.01 (s, 12H, NBpin), (BpinOBpin) 0.96 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 80.12, 80.03, 79.87, 70.88, 64.81, 49.17, 32.35, 22.62, 22.44, 22.40, (BpinOBpin) δ 80.48, 22.30.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.49 (N-B), 21.59 (O-B).
**HRMS** (ESI) calcd. for $[C_{22}H_{44}B_3NO_8+H]^+$ $[M+H]^+$ : 484.3419, found: 484.3420.

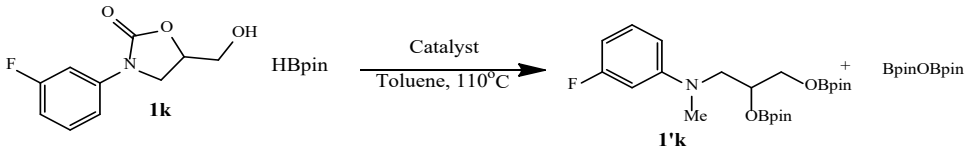
**Synthesis of 1'j:** 32mg of **1j** were reacted with 80 mg (91 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′j** in 87%, 78%, and 79% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**1j** **1'j**

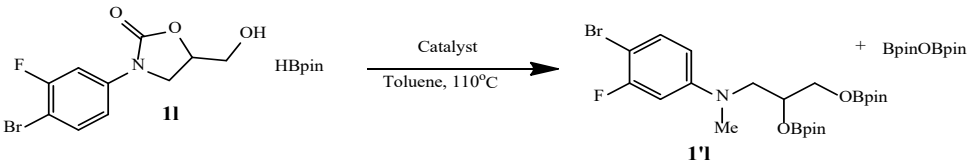
**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.13 (dd, *J* = 8.8, 7.2 Hz, 2H, Ar), 6.69 – 6.63 (m, 1H, Ar), 6.61 (d, *J* = 7.8 Hz, 2H, Ar), 3.89 (t, *J* = 6.1 Hz, 2H, $OCH_2$-), 3.22 (t, *J* = 6.1 Hz, 2H, $NCH_2$-), 2.66 (s, 3H, $NCH_3$), 1.00 (s, 12H, OBpin). (BpinOBpin) 1.02 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 147.41, 127.05, 114.34, 110.22, 80.19, 60.19, 51.66, 36.25, 22.60, (BpinOBpin) δ 80.50, 22.29.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.46 (OBpin), 21.63 (BpinOBpin).
**HRMS** (ESI) calcd. for $[C_{15}H_{24}BNO_3+H]^+$ $[M+H]^+$ : 278.1922, found: 278.2106.

**Synthesis of 1'k:** 42 mg of **1k** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′k** in 90%, 92%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.



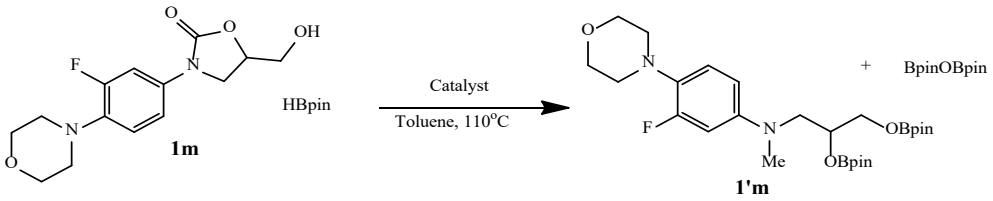

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.08 – 6.80 (m, 1H, Ar), 6.47 (dt, *J* = 13.0, 2.5 Hz, 1H, Ar), 6.36 (dd, *J* = 8.3, 2.4 Hz, 2H, Ar), 4.74 – 4.19 (m, 1H, OCH-), 3.93 (dd, *J* = 11.2, 3.9 Hz, 1H, $OCH_2$), 3.75 (dd, *J* = 11.2, 5.1 Hz, 1H, $OCH_2$), 3.20 (d, *J* = 6.5 Hz, 2H, $NCH_2$), 2.59 (s, 3H, $NCH_3$), 1.00 (s, 24, OBpin) (BpinOBpin) 1.01 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 162.53 (d, *J* = 240.9 Hz), 149.21 (d, *J* = 10.7 Hz), 127.98 (d, *J* = 10.3 Hz), 105.80, 100.52 (d, *J* = 21.6 Hz), 97.12 (d, *J* = 26.2 Hz), 80.41, 80.35, 69.99, 63.76, 52.25, 36.74, 22.33, 22.25. (BpinOBpin) δ 80.51, 22.29.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.48 (O-B), 21.64 (BpinOBpin).
**$^{19}$F NMR** (377 MHz, Toluene-$d_8$) δ -112.86.
**HRMS** (ESI) calcd. for $[C_{22}H_{36}B_2NO_6+H]^+$ $[M+H]^+$ : 452.2786, found: 452.2854.

**Synthesis of 1'l:** 58 mg of **1l** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′l** in 84%, 79%, and 74% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.08 (t, *J* = 8.6 Hz, 1H, Ar), 6.42 (dd, *J* = 12.5, 2.9 Hz, 1H, Ar), 6.15 (dd, *J* = 9.0, 2.9 Hz, 1H, Ar), 4.38 – 4.28 (m, 1H, OCH-), 3.89 (dd, *J* = 11.2, 4.0 Hz, 1H, $OCH_2$), 3.71 (dd, *J* = 11.2, 5.0 Hz, 1H, $OCH_2$), 3.12 (d, *J* = 6.5 Hz, 2H, $NCH_2$), 2.51 (s, 3H, $NCH_3$), (O-Bpin + BpinOBpin) 1.01 (s, 48H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 160.87 (d, *J* = 242.4 Hz), 151.12 (d, *J* = 9.8 Hz), 133.84 (d, *J* = 2.5 Hz), 110.00 (d, *J* = 2.5 Hz), 101.00 (d, *J* = 26.8 Hz), 94.44 (d, *J* = 21.4 Hz), 83.30, 83.26, 72.58, 66.44, 54.94, 39.53, 25.44, (BpinOBpin) δ 83.33, 25.13.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.43 (OBpin), 21.58 (BpinOBpin).
**$^{19}$F NMR** (377 MHz, Toluene-$d_8$) δ -107.62.
**HRMS** (ESI) calcd. for $[C_{22}H_{35}B_2BrFNO_6+H]^+$ $[M+H]^+$ : 530.1891, found: 530.1890.

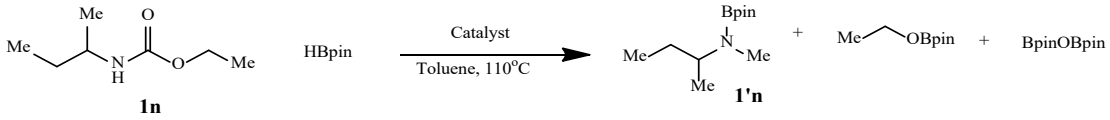
**Synthesis of 1'm:** 59 mg of **1m** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′m** in 84%, 79%, and 70% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**1m** **1'm**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 6.58 (t, J = 9.3 Hz, 1H, Ar), 6.48 (dd, J = 15.6, 2.8 Hz, 1H, Ar), 6.29 (dd, J = 8.9, 2.9 Hz, 1H, Ar), 4.44 – 4.32 (m, 1H, OCH-), 3.81 (ddd, J = 65.4, 11.2, 4.5 Hz, 2H, $OCH_2$-), 3.62 – 3.53 (m, 4H, -$CH_2OCH_2$-), 3.15 (d, J = 6.5 Hz, 2H, $NCH_2$-), 2.72 (dd, J = 5.5, 3.5 Hz, 4H, -$CH_2NCH_2$-), 2.57 (s, 3H), 0.96 (d, J = 1.3 Hz, 48H OBpin & BpinOBpin ).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 155.41 (d, *J* = 243.4 Hz), 144.51 (d, *J* = 10.2 Hz), 128.13 (d, *J* = 9.9 Hz), 118.30 (d, *J* = 4.9 Hz), 105.77 (d, *J* = 2.6 Hz), 99.02 (d, *J* = 25.2 Hz), 80.39, 80.32, 70.14, 64.98, 63.81, 52.74, 49.95, 36.83, 22.61. (BpinOBpin) δ 80.49, 22.29.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.44 (O-B), 21.58 (B-O-B).
**$^{19}$F NMR** (377 MHz, Toluene-$d_8$) δ -122.61.
**HRMS** (ESI) calcd. for $[C_{26}H_{43}B_2FN_2O_7+H]^+$ $[M+H]^+$ : 537.3313, found: 537.3359.

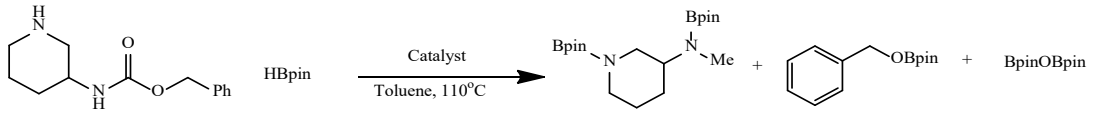
**Synthesis of 1'n:** 29 mg of **1n** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′n** in 84%, 91%, and 92% yield for catalysts **I**, **II**, and **III**, respectively, in 12h.




**1n** **1'n**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.38-3.32 (m, 1H, NCH-), 2.39 (s, 3H,$NCH_3$), 1.36-1.30 (m, 1H, -$CH_2$-), 1.16 – 1.10 (m, 1H, -$CH_2$-), 1.03 (s, 12H, OBpin), 0.94 (m, 3H, $CH_3$), 0.78 (t, *J* = 7.3 Hz, 3H, $CH_3$). (EtOBpin) δ 3.78 (q, *J* = 7.1 Hz, 2H), 1.05-1.01 inside pin peak (m, 3H), 0.99 (s, 12H), (BpinOBpin) δ 0.95 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 79.46, 49.80, 24.79, 24.22, 22.56, 15.22, 9.14, (EtOBpin) δ 79.96, 58.26, 22.39, 17.27**,** (BpinOBpin) δ 80.49, 22.30.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.37 (N-B), 22.39 (O-B), 21.64 (O-B).
**HRMS** (ESI) calcd. for $[C_{11}H_{24}BNO_2+H]^+$ $[M+H]^+$ : 214.1973, found: 214.2008.

**Synthesis of 1'o:** 47 mg of **1o** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′o** in 90%, 93%, and 90% yield for catalysts **I**, **II**, and **III**, respectively, in 12h.

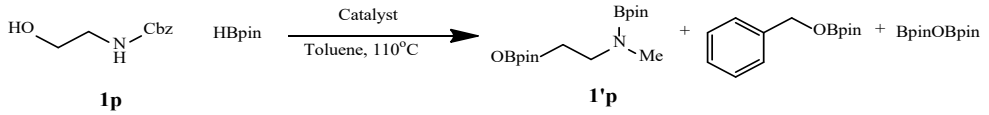



**1o** **1'o**

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 3.62 (ddd, *J* = 49.8, 13.1, 4.2 Hz, 2H. $CH_2$), 3.08 (tt, *J* = 11.2, 4.3 Hz, 1H, NCH-), 2.81 (t, *J* = 11.5 Hz, 1H), 2.57 (s, 3H, $NCH_3$), 2.42 (t, *J* = 11.2 Hz, 1H), 1.75 – 1.55 (m, 2H), 1.50 – 1.34 (m, 2H), 1.07 (d, *J* = 9.1 Hz, 24H), (PH$CH_2$OBpin) δ 7.24 (d, *J* = 7.4 Hz, 2H, Ar),

7.12 (t, $J$ = 7.4 Hz, 2H, Ar), 7.06 (d, $J$ = 7.2 Hz, 1H, Ar), 4.87 (s, 2H, $OCH_2$-), 0.86 (s, 12H, OBpin), (BpinOBpin) δ 1.01 (s, 24H).
**$^{13}C\{^1H\}$ NMR** (101 MHz, Toluene-$d_8$) δ 81.24, 81.21, 54.80, 48.47, 43.84, 30.17, 29.90, 27.15, 24.10, 24.06, ($PHCH_2OBpin$) δ 139.40, 127.84, 126.84, 126.32, 81.99, 66.18, 24.00, (BpinOBpin) δ 82.14, 23.94.
**$^{11}B\{^1H\}$ NMR** (128 MHz, Toluene-$d_8$) δ 23.78 (N-B), 22.70 (O-B), 21.70 (O-B).
**HRMS** (ESI) calcd. for $[C_{18}H_{36}B_2N_2O_4+H]^+$ $[M+H]^+$ : 367.2934, found: 367.2956.

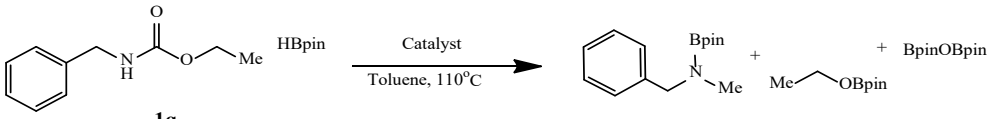
**Synthesis of 1'p:** 39 mg of **1p** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′p** in 95%, 91%, and 90% yield for catalysts **I**, **II**, and **III**, respectively, in 12h.



**1p** **1'p**

**$^1H$ NMR** (400 MHz, Toluene-$d_8$) δ 3.80 (t, $J$ = 5.7 Hz, 2H,$OCH_2$), 3.00 (t, $J$ = 5.7 Hz, 2H, $NCH_2$), 2.59 (s, 3H, $NCH_3$), 1.04 (s, 12H, OBpin), 1.01 (s, 12H, NBpin), ($PHCH_2OBpin$) δ 7.21 – 7.02 (m, 5H, Ar), 4.80 (s, 2H, $CH_2O$), 0.98 (s, 12H ,OBpin), (BpinOBpin) δ .95 (s, 24H).
**$^{13}C\{^1H\}$ NMR** (101 MHz, Toluene-$d_8$) δ 81.83, 81.64, 62.77, 50.00, 33.63, 24.37, 24.26, ($PHCH_2OBpin$) δ139.58, 128.03, 127.03, 126.51, 82.19, 66.36, 24.18, (BpinOBpin) δ 82.33, 24.12.
**$^{11}B\{^1H\}$ NMR** (128 MHz, Toluene-$d_8$) δ 24.37 (N-B), 22.68 (O-B), 21.63 (O-B).
**HRMS** (ESI) calcd. for $[C_{15}H_{31}B_2NO_5+H]^+$ $[M+H]^+$ : 328.2461, found: 328.2472.

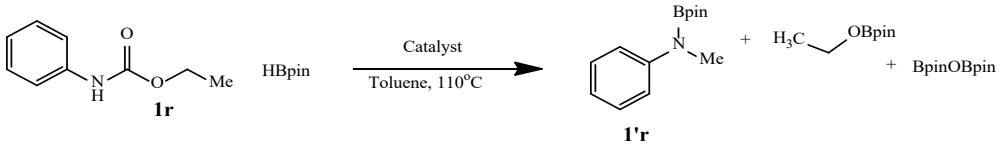
**Synthesis of 1'q:** 36 mg of **1q** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′q** in 90%, 85%, and 95% yield for catalysts **I**, **II**, and **III**, respectively, in 4h.



**1q** **1'q**

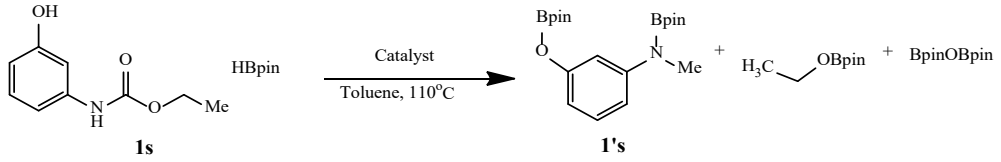
**$^1H$ NMR** (400 MHz, Toluene-$d_8$) δ 7.18 – 6.96 (m, 5H, Ar), 3.99 (s, 2H, $CH_2N$), 2.44 (s, 3H, $NCH_3$), 0.98 (s, 12H, NBpin), (EtOBpin) δ 3.78 (q, $J$ = 7.0 Hz, 2H), 1.02 (t, $J$ = 7.1 Hz, 3H), 1.06 (s, 12H, OBpin), (BpinOBpin) δ0.95 (s, 25H).
**$^{13}C\{^1H\}$ NMR** (101 MHz, Toluene-$d_8$) δ 140.27, 128.09, 127.58, 126.50, 82.32, 52.75, 32.77, 24.34, (EtOBpin) δ 81.88, 60.09, 24.22, 17.05, (BpinOBpin) δ 81.79, 24.13.
**$^{11}B\{^1H\}$ NMR** (128 MHz, Toluene-$d_8$) δ 24.59 (N-B), 22.40 (O-B), 21.61 (O-B).
**HRMS** (ESI) calcd. for $[C_{14}H_{22}BNO_2+H]^+$ $[M+H]^+$ : 248.1816, found: 248.1822.

**Synthesis of 1'r:** 33 mg of **1r** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′r** in 84%, 79%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 4h.



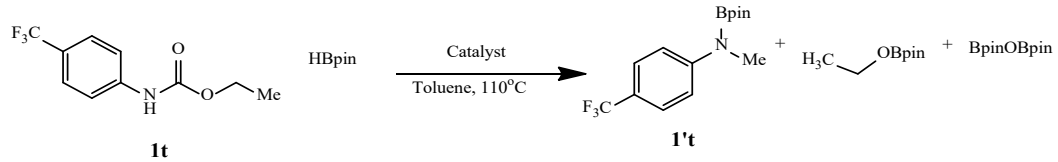

**$^{1}$H NMR (**400 MHz, Toluene-$d_8$) δ 7.30 (d, *J* = 1.1 Hz, 2H, Ar), 7.15 – 7.05 (m, 2H, Ar), 6.83 – 6.70 (m, 1H, Ar), 2.91 (s, 3H, $CH_3$), 0.98 (s, 12H, NBpin), (EtOBpin) 3.78 (q, *J* = 7.1 Hz, 2H), 1.06 – 1.03 (m, 3H), 1.01 (s, 12H, OBpin), (BpinOBpin) 0.95 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 147.43, 128.28, 120.46, 118.70, 81.79, 33.76, 24.24, (EtOBpin) δ 82.26, 60.09, 24.21, 17.05. (BpinOBpin) δ 82.33, 24.12.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.63 (N-B), 22.40 (O-B), 21.65 (O-B).
**HRMS** (ESI) calcd. for $[C_{13}H_{20}BNO_2+H]^+$ $[M+H]^+$ : 234.1660, found: 234.1660.

**Synthesis of 1's:** 36 mg of **1s** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′s** in 92%, 86%, and 79% yield for catalysts **I**, **II**, and **III**, respectively, in 12h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.13 (t, J = 2.3 Hz, 1H, Ar), 6.93 – 6.82 (m, 2H, Ar), 6.64 (ddd, J = 7.8, 2.3, 1.1 Hz, 1H, Ar), 2.75 (s, 3H, $NCH_3$), 0.88 (s, 12H, OBpin), 0.84 (s, 12H, NBpin). (EtOBpin) 3.67 (q, J = 7.0 Hz, 2H, $OCH_2$-), 0.94 – 0.91 (m, 3H, $CH_3C$-), 0.88 (s, 12H, OBpin), (BpinOBpin) 0.84 (s, 23H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 154.02, 148.39, 128.41, 113.11, 111.56, 110.14, 82.34, 81.63, 33.51, 24.26, (EtOBpin) δ 82.12, 59.91, 24.04, 16.87. (BpinOBpin) δ 82.16, 23.95.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ (N-B)24.53, 22.37 (O-B), 21.64 (O-B).
**HRMS** (ESI) calcd. for $[C_{19}H_{31}B_2NO_5+H]^+$ $[M+H]^+$ : 376.2461, found: 376.2504.

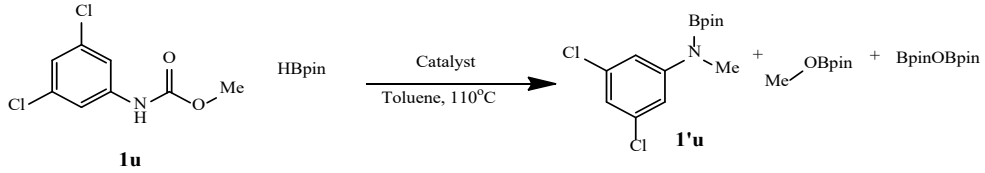
**Synthesis of 1't:** 46 mg of **1t** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′t** in 46%, 94%, and 70% yield for catalysts **I**, **II**, and **III**, respectively, in 12h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.65 – 7.45 (m, 4H, Ar), 3.09 (s, 3H, $NCH_3$), 1.29 (s, 12H, NBpin), (EtOBpin) 4.08 (q, J = 7.0 Hz, 2H, $OCH_2$-), 1.36 – 1.33 (m, 3H, $CH_3C$-), 1.32 (s, 12H, OBpin). (BpinOBpin) 1.26 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 150.44, 125.46 (q, *J* = 3.8 Hz), 117.73, 81.80, 33.42, 24.18. (EtOBpin) δ 82.34, 60.08, 24.15, 17.01.(BpinOBpin) δ 82.76, 24.09.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.77 (N-B), 22.41 (O-B), 21.59 (O-B).

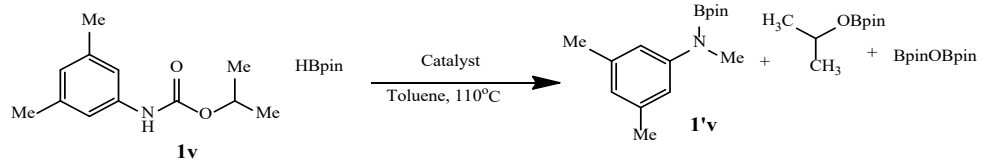
**$^{19}$F NMR** (377 MHz, Toluene-$d_8$) δ -61.26.
**HRMS** (ESI) calcd. for $[C_{14}H_{20}BF_3NO_2+H]^+$ $[M+H]^+$ : 302.1534, found: 301.1463.

**Synthesis of 1'u:** 44 mg of **1u** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′u** in 90%, 95%, and 95% yield for catalysts **I**, **II**, and **III**, respectively, in 4h.



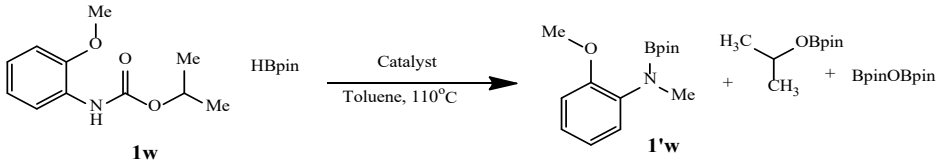

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 7.28 – 7.15 (m, 2H, Ar), 6.75 (s, 1H, Ar), 2.61 (s, 3H, $NCH_3$), 0.98 (s, 12H, NBpin), (MeOBpin + BpinOBpin) 3.41 (s, 3H- Me-O), 0.95 (s, 36H, OBpin).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 149.52, 134.67, 120.02, 116.52, 81.97, 51.80, 33.30, 24.07. (MeOBpin) δ 82.90, 24.22, (BpinOBpin) δ 82.33, 24.12,
**$^{11}$B{$^1$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.52 (N-B), 22.57 (O-B), 21.59 (O-B).
**HRMS** (ESI) calcd. for $[C_{13}H_{18}BCl_2NO_2+H]^+$ $[M+H]^+$ : 302.0880, found: 301.0838.

**Synthesis of 1'v:** 41 mg of **1v** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′v** in 93%, 90%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.



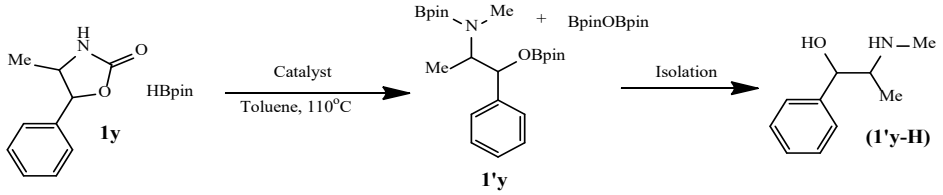

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 6.87 (s, 2H, Ar), 6.32 (s, 1H, Ar), 2.84 (s, 3H, $NCH_3$), 2.02 (s, 6H, $ArCH_3$), 0.88 (s, 12H, NBpin), (*iso*-PropOBpin) 4.26 – 4.11 (m, 1H, -CH-), 0.95 (d, $J$ = 6.2 Hz, 6H, $(CH_3)_2$C-), 0.92 (s, 12H, OBpin), (BpinOBpin) 0.84 (s, 24H).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 147.52, 137.04, 122.67, 117.23, 81.69, 34.17, 24.32, 21.40, (*iso*-PropOBpin) δ 82.19, 66.76, 24.50, 24.25, (BpinOBpin) δ 82.37, 24.19.
**$^{11}$B{$^1$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.59 (N-B), 22.11 (O-B), 21.64 (O-B).
**HRMS** (ESI) calcd. for $[C_{15}H_{24}BO_2+H]^+$ $[M+H]^+$: 262.1973, found: 262.1989.

**Synthesis of 1'w:** 42 mg of **1w** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′w** in 85%, 90%, and 86% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.



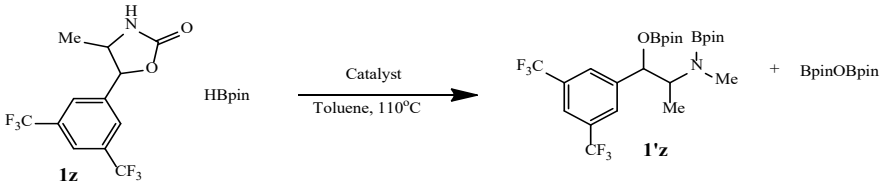

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.18 (dd, J = 7.7, 1.8 Hz, 1H, Ar), 6.92 (td, J = 7.8, 1.8 Hz, 1H, Ar), 6.78 (td, J = 7.6, 1.4 Hz, 1H, Ar), 6.58 (dd, J = 8.1, 1.4 Hz, 1H, Ar), 3.41 (s, 3H, $OCH_3$), 3.08 (s, 3H, $NCH_3$), 1.01 (s, 12H, NBpin), (*iso*-PropOBpin) 4.38 (hept, J = 6.1 Hz, 1H, -CH-), 1.13 (d, J = 6.1 Hz, 6H, $(CH_3)_2C$-), 1.06 (s, 12H, OBpin). (BpinOBpin) 1.02 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 155.35, 136.72, 128.38, 125.27, 120.42, 111.66, 81.69, 54.54, 36.48, 24.34, (*iso*-PropOBpin) δ 81.91, 66.78, 24.49, 24.24 (BpinOBpin) δ 82.38, 24.18.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.30 (N-B), 22.14 (O-B), 21.65 (O-B).
**HRMS** (ESI) calcd. for $[C_{14}H_{22}BNO_3+H]^+$ $[M+H]^+$ : 264.1766, found: 264.1759.

**Synthesis of 1'y-H:** 35 mg of **1y** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′y-H** in 80%, 95%, and 0% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.40 – 7.24 (m, 5H, Ar), 4.81 (d, J = 3.9 Hz, 1H -OCH-), 2.84 (dt, J = 6.3, 3.2 Hz, 1H, -NCH-), 2.52 (s, 3H, $NCH_3$), 2.35 (s, 2H, NH+OH), 0.88 (d, J = 6.5 Hz, 3H, $CH_3C$-).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Chloroform-d) δ 141.53, 128.12, 127.08, 126.14, 73.04, 60.46, 34.02, 14.23.
**HRMS** (ESI) calcd. for $[C_{10}H_{15}NO+H]^+$ $[M+H]^+$ : 166.1226, found: 166.1237.

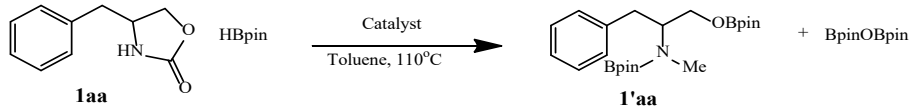
**Synthesis of 1'z:** 62 mg of **1z** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′z** in 93%, 95%, and 82% yield for catalysts **I**, **II**, and **III**, respectively, in 16h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 8.01 (s, 2H, Ar), 7.85 (s, 1H, Ar), 5.27 (d, J = 8.9 Hz, 1H, -OCH-), 3.74 – 3.60 (m, 1H, -NCH-), 2.44 (s, 3H, $NCH_3$), 1.36 (d, J = 6.7 Hz, 3H, $CH_3C$-), 1.11 (s, 12H, OBpin), 1.07 (s, 12H, NBpin). (BpinOBpin) 1.14 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 146.58, 131.95 (q, J = 33.1 Hz), 128.21 (d, J = 4.5 Hz), 126.05, 123.35, 122.29 – 121.19 (m), 83.35, 82.60, 78.84, 57.71, 29.49, 25.45, 25.01, 15.99. (BpinOBpin) 83.63, 25.14.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 23. 19 (N-B), 21.61(O-B).
**$^{19}$F NMR** (377 MHz, Toluene-$d_8$) δ -62.65.

**HRMS** (ESI) calcd. for $[C_{24}H_{35}B_2F_6NO_5+H]^+$ $[M+H]^+$ : 554.2678, found: 554.2695

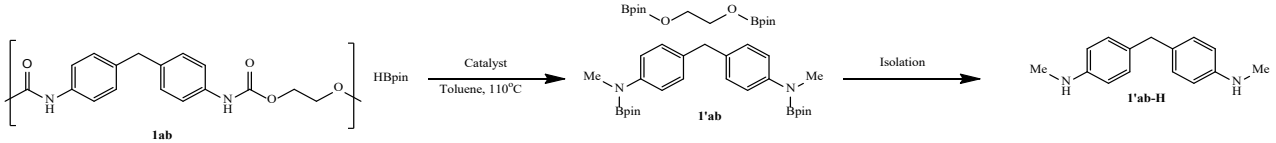
**Synthesis of 1'aa:** 35 mg of **1aa** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′aa** in 99%, 94%, and 99% yield for catalysts **I**, **II**, and **III**, respectively, in 2h.




**1aa** **1'aa**

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 7.04 – 6.91 (m, 5H, Ar), 3.95 – 3.84 (m, 1H, NCH-), 3.80 – 3.64 (m, 2H, $OCH_2$-), 2.51 (d, $J$ = 7.5 Hz, 2H, $ArCH_2$-), 2.43 (s, 3H, $NCH_3$), 1.03 (s, 12H, OBpin), 0.96 (s, 12H, NBpin), (BpinOBpin) δ 0.95 (s, 24H).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 139.43, 129.06, 127.80, 125.52, 82.32, 81.91, 65.19, 57.65, 34.68, 28.09, 24.31, 24.27. (BpinOBpin) δ 82.63, 24.14.
**$^{11}$B{$^1$H} NMR** (128 MHz, Toluene-$d_8$) δ 23.77 (N-B), 21.55(O-B).
**HRMS** (ESI) calcd. for $[C_{22}H_{37}B_2NO_5+H]^+$ $[M+H]^+$ : 418.2931, found: 418.2948.

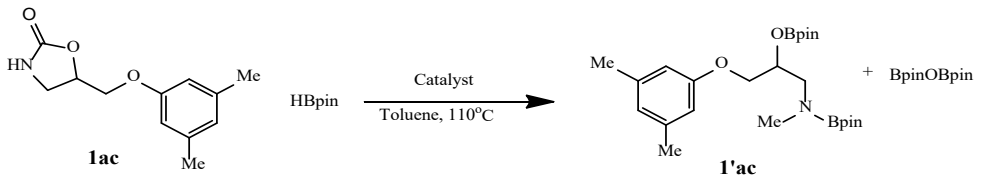
**Synthesis of 1'ab-H:** 63 mg of **1ab** were reacted with 214 mg (242 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ab-H** in 61 % yield using catalysts **II**.




**1ab** **1'ab** **1'ab-H**

**$^1$H NMR** (400 MHz, Chloroform-d) δ 6.82 (d, $J$ = 8.4 Hz, 4H, Ar), 6.40 (d, $J$ = 8.2 Hz, 4H, Ar), 3.60 (s, 2H, $CH_2(Ar)_2$-), 2.95 (s, 2H, NH), 2.63 (s, 6H, $NCH_3$).
**$^{13}$C{$^1$H} NMR** (101 MHz, Chloroform-d) δ 146.94, 131.43, 129.61, 113.06, 40.17, 31.31.
**HRMS** (ESI) calcd. for $[C_{15}H_{18}N_2+H]^+$ $[M+H]^+$ : 227.1543, found: 227.1542

**Synthesis of 1'ac:** 44 mg of **1ac** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ac** in >99%, >99%, and >99% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.

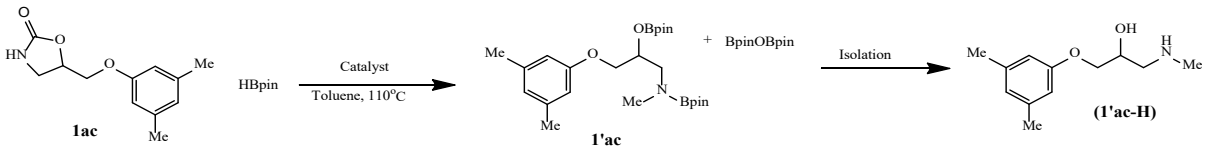



**1ac** **1'ac**

**$^1$H NMR** (400 MHz, Toluene-$d_8$) δ 6.43 (s, 2H, Ar), 6.39 (s, 1H, Ar), 4.69 – 4.53 (m, 1H, OCH-), 3.75 (dq, J = 9.8, 5.3, 4.2 Hz, 2H, -$CH_2$OAr), 3.20 – 2.96 (m, 2H, $NCH_2$-), 2.67 (s, 3H, $NCH_3$), 2.07 (s, 6H, $ArCH_3$), 1.05 (s, 23H, NBpin, OBpin), (BpinOBpin) δ 0.95 (s, 24H).
**$^{13}$C{$^1$H} NMR** (101 MHz, Toluene-$d_8$) δ 159.18, 138.38, 122.28, 112.45, 82.00, 81.80, 71.19, 69.47, 51.57, 34.30, 24.30, 24.20, 21.03. (BpinOBpin) δ 82.33, 24.14.

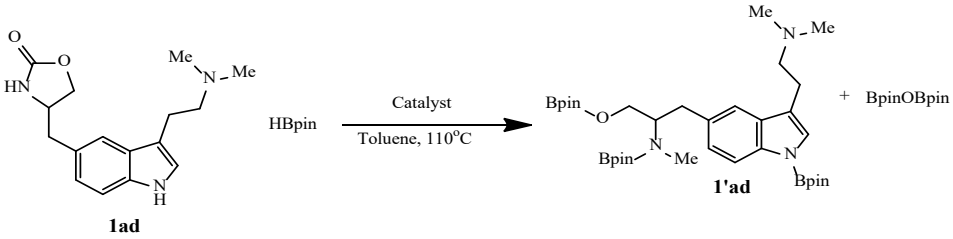
**$^{11}B\{^1H\}$ NMR** (128 MHz, Toluene-$d_8$) δ 24.62(N-B), 21.61 (O-B).
**HRMS** (ESI) calcd. for $[C_{24}H_{41}B_2NO_5+H]^+$ $[M+H]^+$ : 462.3193, found: 462.3230.

**Synthesis of 1'ac-H:** 44 mg of **1ac** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford the corresponding product **1′ac-H**.



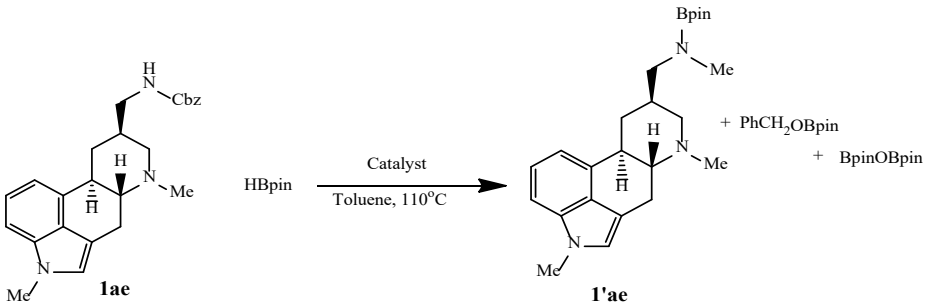

**$^1H$ NMR** (400 MHz, Chloroform-d) δ 6.62 – 6.47 (m, 3H, Ar), 4.21 – 3.86 (m, 5H), 2.89 – 2.74 (m, 2H), 2.51 (s, 3H, $NCH_3$), 2.26 (s, 6H, $ArCH_3$).
**$^{13}C\{^1H\}$ NMR** (101 MHz, Chloroform-d) δ 157.58, 138.21, 121.81, 111.25, 69.26, 66.66, 52.89, 34.85, 20.38.

**Synthesis of 1'ad:** 57 mg of **1ad** were reacted with 133 mg (151 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ad** in 90%, 91%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.



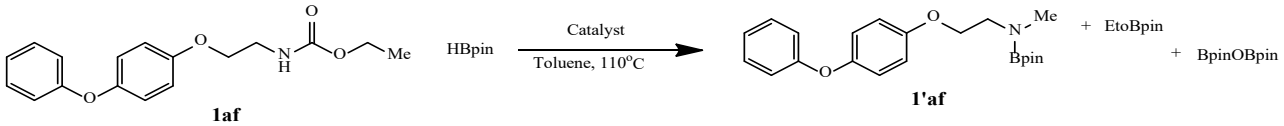

**$^1H$ NMR** (400 MHz, Toluene-$d_8$) δ  δ 7.98 (d, J = 8.4 Hz, 1H, Ar), 7.41 (s, 1H, Ar), 7.26 (s, 1H, Ar), 7.08 (d, J = 8.4 Hz, 1H, Ar), 4.14 – 3.95 (m, 1H, NCH-), 3.84 (td, J = 13.5, 5.7 Hz, 2H, ArCH2-), 2.89 – 2.69 (m, 4H, $OCH_2$-, $NCH_2$-), 2.53 (s, 3H, $NCH_3$), 2.49 (d, J = 13.7 Hz, 2H), 2.11 (s, 6H, $N(CH_3)_2$), 1.02 (s, 24H, N-Bpin), O-Bpin 0.94 (s, 36H).
**$^{13}C\{^1H\}$ NMR** (101 MHz, Toluene-$d_8$) δ 138.50, 131.95, 131.69, 125.59, 124.35, 118.95, 118.78, 114.26, 82.32, 81.83, 81.29, 65.32, 59.62, 58.66, 45.14, 35.28, 28.82, 24.29, 24.26, 24.17, 24.12, (BpinOBpin) δ83.46, 22.63.
**$^{11}B\{^1H\}$ NMR** (128 MHz, Toluene-$d_8$) δ 25.04 (N-B), 21.67 (O-B).
**HRMS** (ESI) calcd. for $[C_{34}H_{58}B_3N_3O_7+H]^+$ $[M+H]^+$ : 654.4627, found: 654.4656.

**Synthesis of 1'ae:** 80 mg of **1ae** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ae** in 89%, 92%, and 80% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.



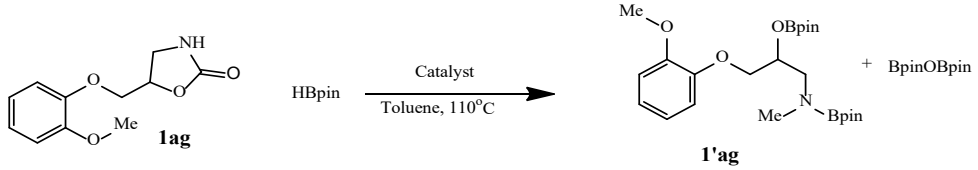

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 6.98 – 6.74 (m, 3H, Ar), 6.24 (s, 1H, Ar), 3.21 (dd, *J* = 14.5, 4.3 Hz, 1H, NCH-), 3.10 (s, 3H, $NCH_3$), 2.82 (m, 4H), 2.61 (s, 3H, $NCH_3$), 2.46 (d, *J* = 12.9 Hz, 1H), 2.25 (s, 3H, $NCH_3$), 2.21 – 1.82 (m, 3H), 1.72 (t, *J* = 11.1 Hz, 1H,), 0.97 (s, 12H, NBpin), 0.84 – 0.72 (m, 1H, -CH-). ($PHCH_2OBpin$) δ 7.25 – 6.99 (m, 5H), 4.80 (s, 2H, $ArCH_2$-), 1.08 (s, 12H, OBpin), (BpinOBpin) δ 0.94 (s, 24H),
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 135.53, 134.89, 128.01, 123.41, 122.79, 113.50, 111.97, 107.29, 82.62, 68.56, 62.88, 54.13, 44.10, 41.79, 34.84, 34.67, 33.17, 32.68, 25.44, 23.60. ($PHCH_2OBpin$) δ 140.55, 129.01, 128.02, 127.50, 83.18, 67.33, 25.19, (BpinOBpin) δ83.32, 25.13.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.76(N-B), 22.64 (O-B), 21.61 (O-B).
**HRMS** (ESI) calcd. for $[C_{24}H_{36}BN_3O_2+H]^+$ $[M+H]^+$ : 410.2973, found: 410.2999.

**Synthesis of 1'af:** 60 mg of **1af** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′af** in >99%, >95%, and >99% yield for catalysts **I**, **II**, and **III**, respectively in 24h.



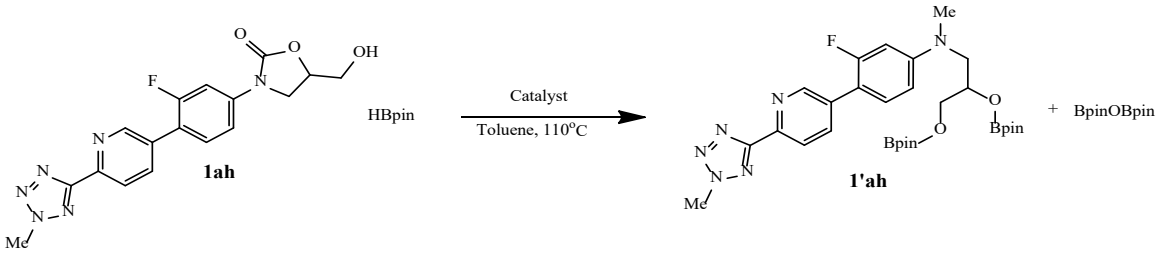

**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 7.01 (t, J = 7.7 Hz, 2H, Ar), 6.89 – 6.71 (m, 5H, Ar), 6.62 (d, J = 8.6 Hz, 2H, Ar), 3.66 (t, J = 6.0 Hz, 2H $ArOCH_2$-), 3.18 (t, J = 6.0 Hz, 2H, $NCH_2$-), 2.63 (s, 3H, $NCH_3$), 0.98 (s, 12H, NBpin). (EtOBpin) 3.78 (q, J = 7.1 Hz, 2H), 1.01 (m, 3H), 1.03 (s, 12H, OBpin). (BpinOBpin) δ0.94 (d, J = 3.9 Hz, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 157.07, 153.61, 148.15, 127.58, 120.20, 118.91, 115.54, 113.47, 80.50, 79.97, 65.45, 46.17, 32.43, 22.52, (EtOBpin) δ 58.27, 22.38, 15.22. (BpinOBpin) δ 80.79, 22.29.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.43 (N-B), 22.38 (O-B), 22.60 (O-B).
**HRMS** (ESI) calcd. for $[C_{21}H_{28}BNO_4+H]^+$ $[M+H]^+$ : 370.2184, found: 370.2206.

**Synthesis of 1'ag:** 44 mg of **1ag** were reacted with 107 mg (121 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ag** in 90%, 90%, and 88% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.



**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 6.72 – 6.56 (m, 4H, Ar), 4.66 (tt, J = 7.7, 4.6 Hz, 1H, O-CH-), 3.78 (t, J = 6.4 Hz, 2H), 3.40 (s, 3H,OMe), 3.08 (ddd, J = 47.0, 13.9, 6.2 Hz, 2H, $ArOCH_2$-), 2.66 (s, 3H, $NCH_3$), 1.04 (m, 24H, NBpin, OBpin), (BpinOBpin) 0.95 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 150.22, 149.24, 121.09, 120.76, 114.45, 112.89, 81.95, 81.74, 71.17, 70.94, 55.35, 51.51, 34.16, 24.44, 24.31. (BpinOBpin) 82.33, 24.12.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 24.55 (N-B), 21.60 (O-B).
**HRMS** (ESI) calcd. for $[C_{23}H_{39}B_2NO_7+H]^+$ $[M+H]^+$ : 464.2985, found: 464.3006

**Synthesis of 1'ah:** 74 mg of **1ah** were reacted with 80 mg (91 $\mu$L) of HBpin **2** following the procedure described above, to afford **1′ah** in 79%, 71%, and 73% yield for catalysts **I**, **II**, and **III**, respectively, in 24h.




**$^{1}$H NMR** (400 MHz, Toluene-$d_8$) δ 9.04 – 8.94 (m, 1H, Ar), 8.17 (d, J = 8.2 Hz, 1H, Ar), 7.72 – 7.64 (m, 1H, Ar), 7.08 – 7.02 (m, 1H, Ar), 6.54 – 6.35 (m, 2H, Ar), 4.43 (dq, J = 6.6, 4.5, 3.2 Hz, 1H, O-CH-), 3.95 (dd, J = 11.2, 4.1 Hz, 1H, $OCH_2$-), 3.78 (dd, J = 11.2, 5.0 Hz, 1H, $OCH_2$-), 3.58 (s, 3H, $NCH_3$), 3.24 (d, J = 6.5 Hz, 2H, $NCH_3$), 2.62 (s, 3H, $NCH_3$), 1.08 (s, 12H, OBpin), 0.98 (s, 12H, OBpin), (BpinOBpin) δ 0.99 (s, 24H).
**$^{13}$C{$^{1}$H} NMR** (101 MHz, Toluene-$d_8$) δ 160.71, 158.28, 149.17 (d, J = 11.2 Hz), 147.54 (d, J = 4.1 Hz), 143.32, 133.61 (d, J = 4.1 Hz), 131.13 (d, J = 2.2 Hz), 128.47 (d, J = 5.5 Hz), 120.02, 110.18 (d, J = 13.7 Hz), 106.56 (d, J = 2.2 Hz), 97.47 (d, J = 27.7 Hz), 80.48, 70.01, 63.75, 52.05, 36.73, 36.31, 29.75, 22.61, 22.36, (BpinOBpin) 80.52, 22.30.
**$^{11}$B{$^{1}$H} NMR** (128 MHz, Toluene-$d_8$) δ 22.651 (O-B), 21.61 (B-O-B).
**HRMS** (ESI) calcd. for $[C_{29}H_{41}B_2FN_6O_6+H]^+$ $[M+H]^+$ : 611.3330, found: 611.3332.

## 3.5 NMR spectral

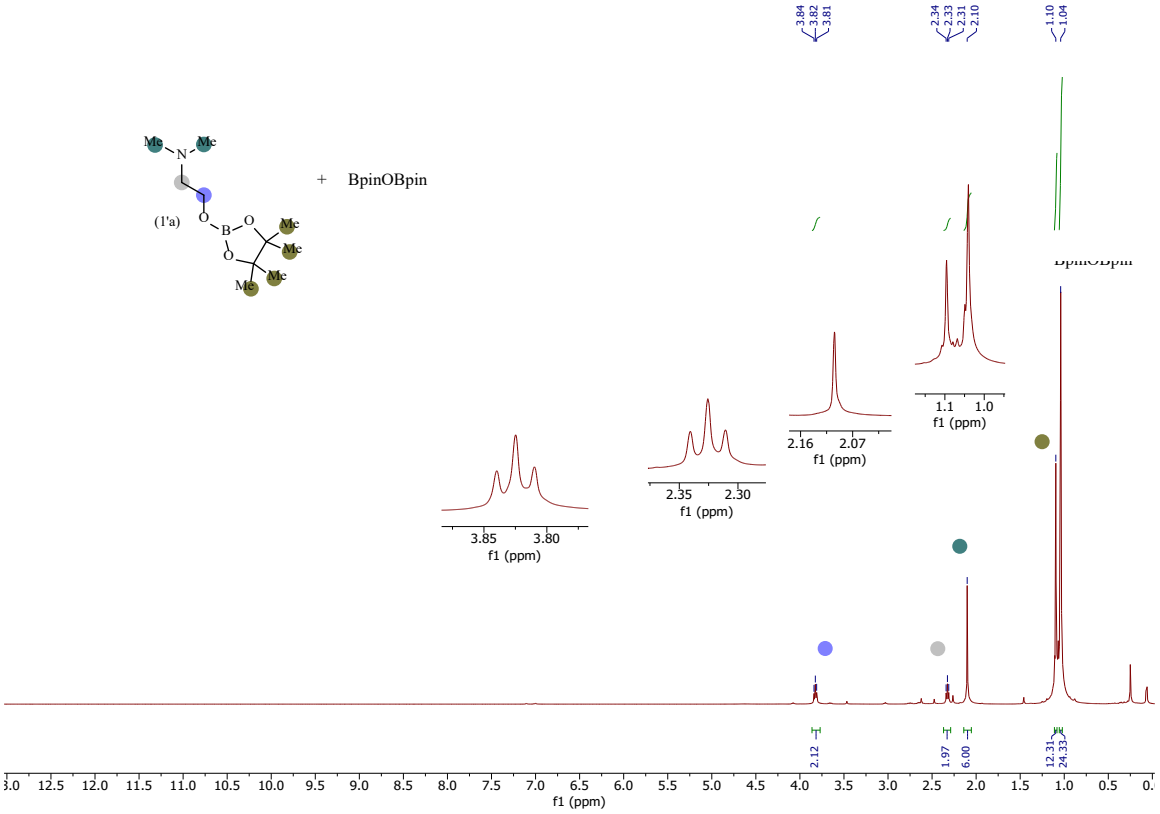



Figure S1: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'a**

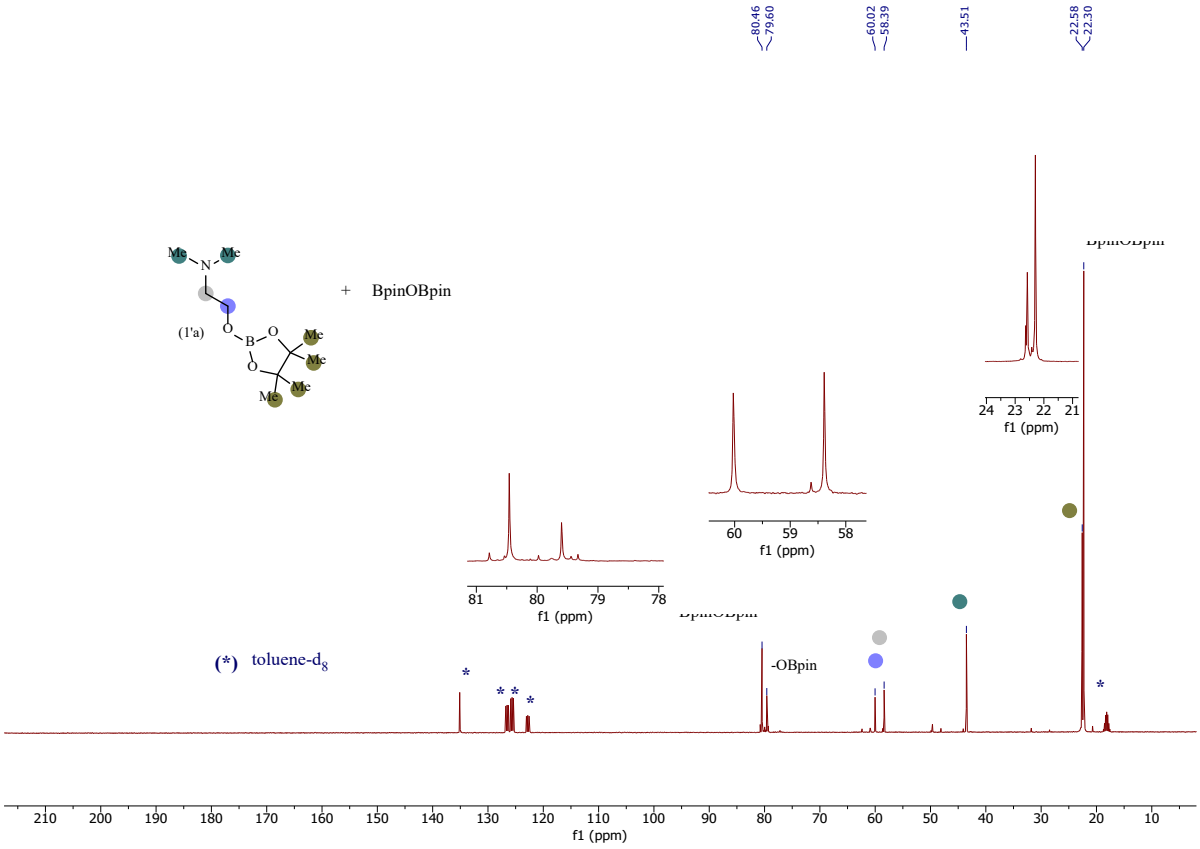



Figure S2: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'a**

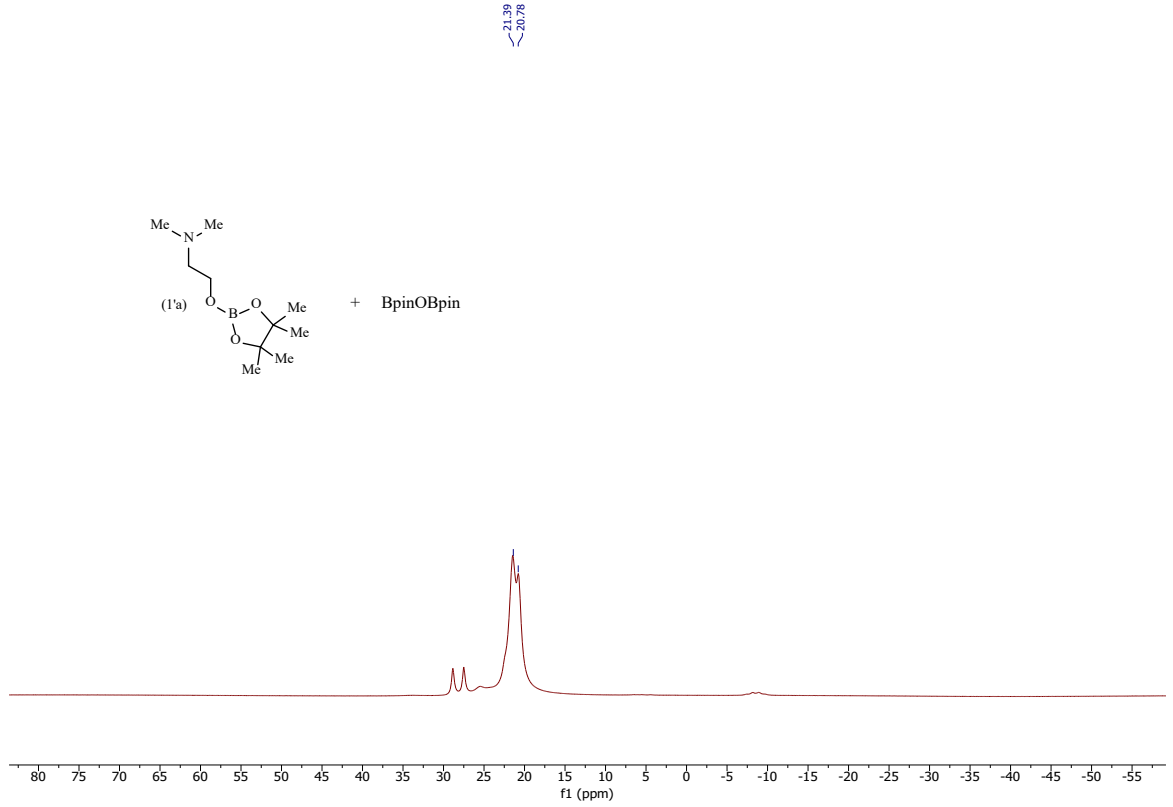



Figure S3: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'a**

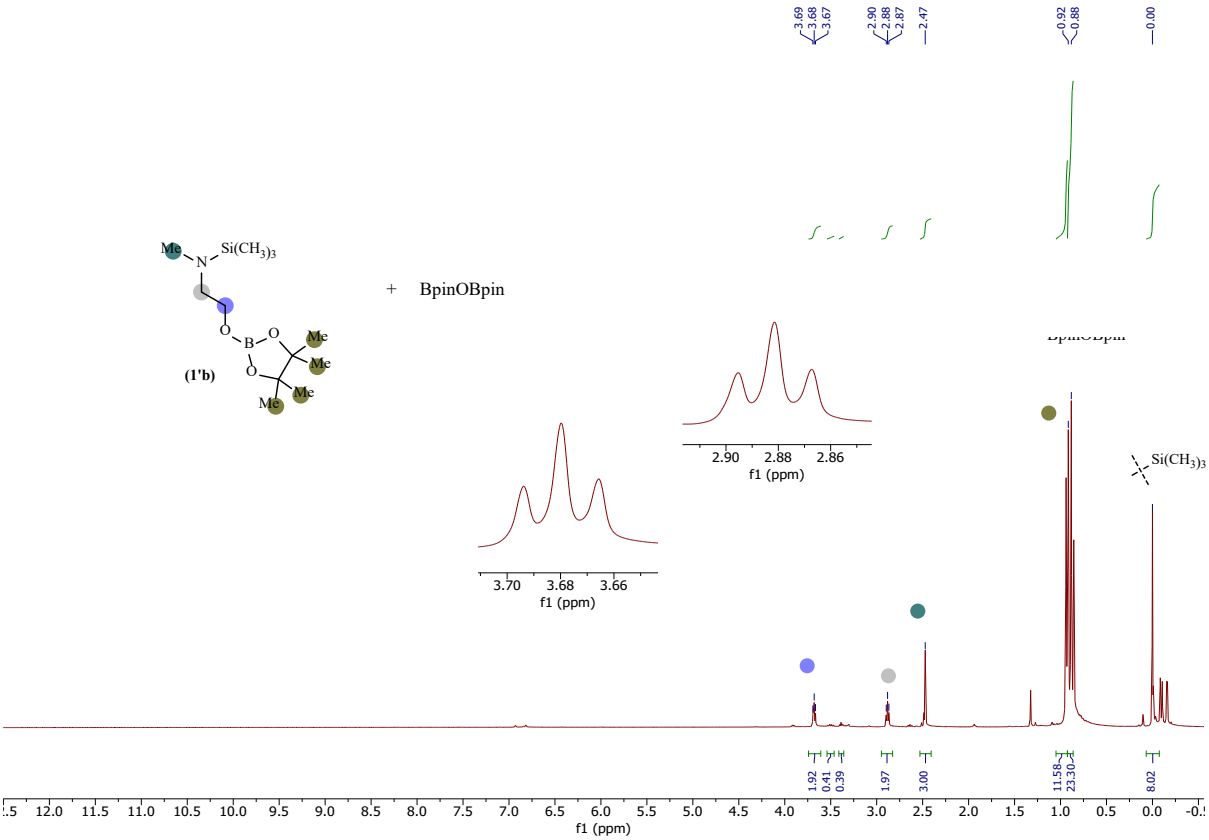



Figure S4: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'b**

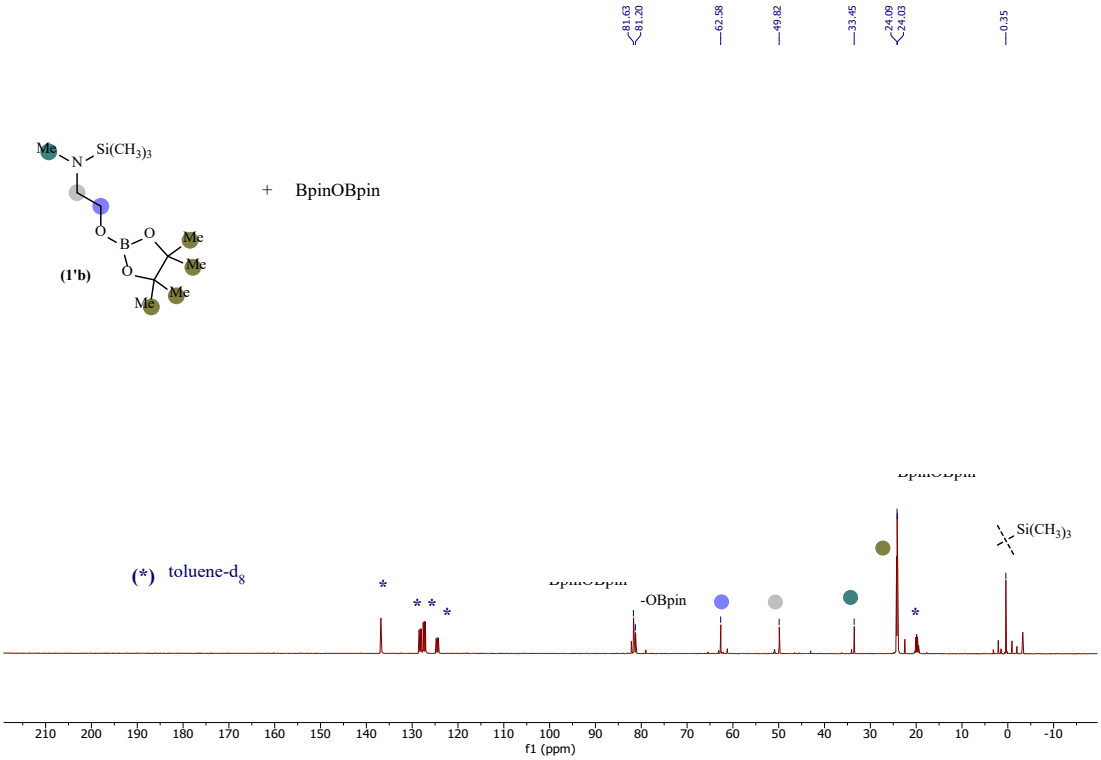



Figure S5: $^{13}C\{^1H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'b**

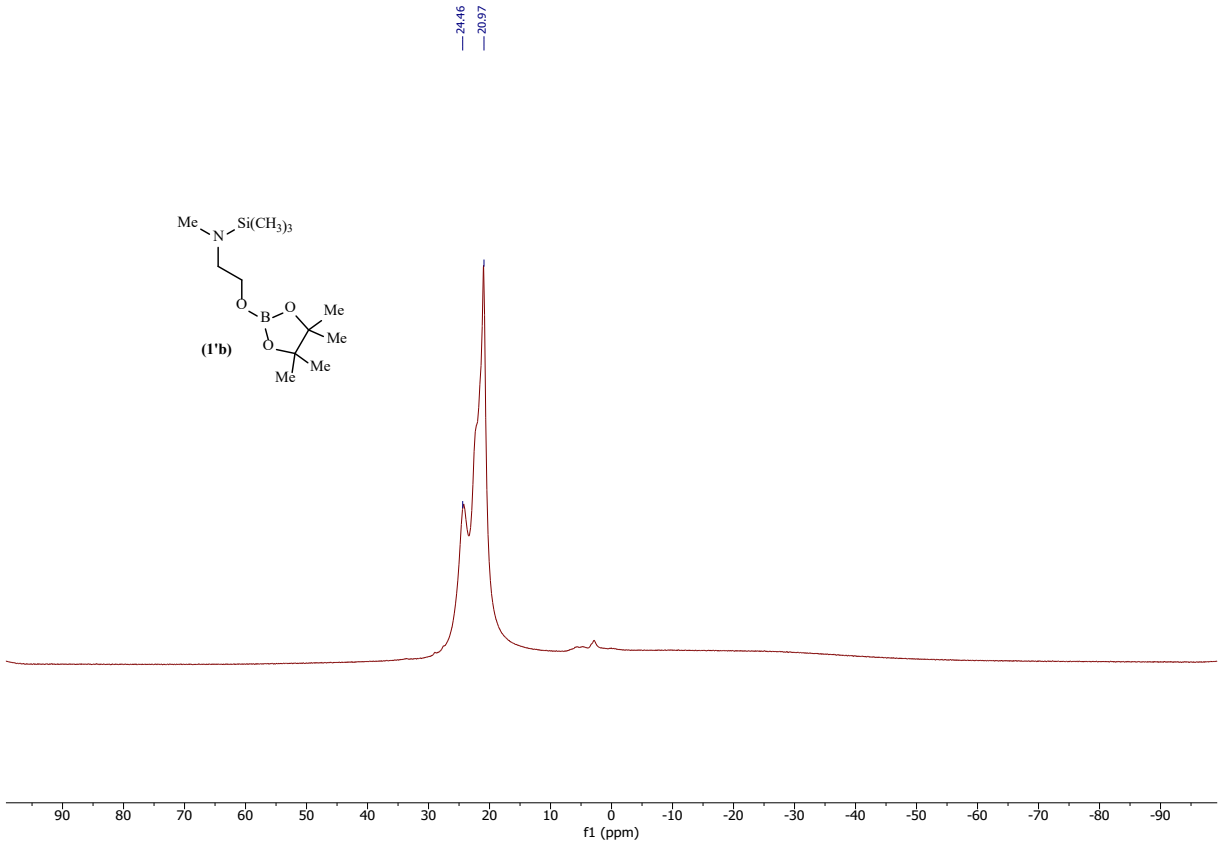



Figure S6: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'b**

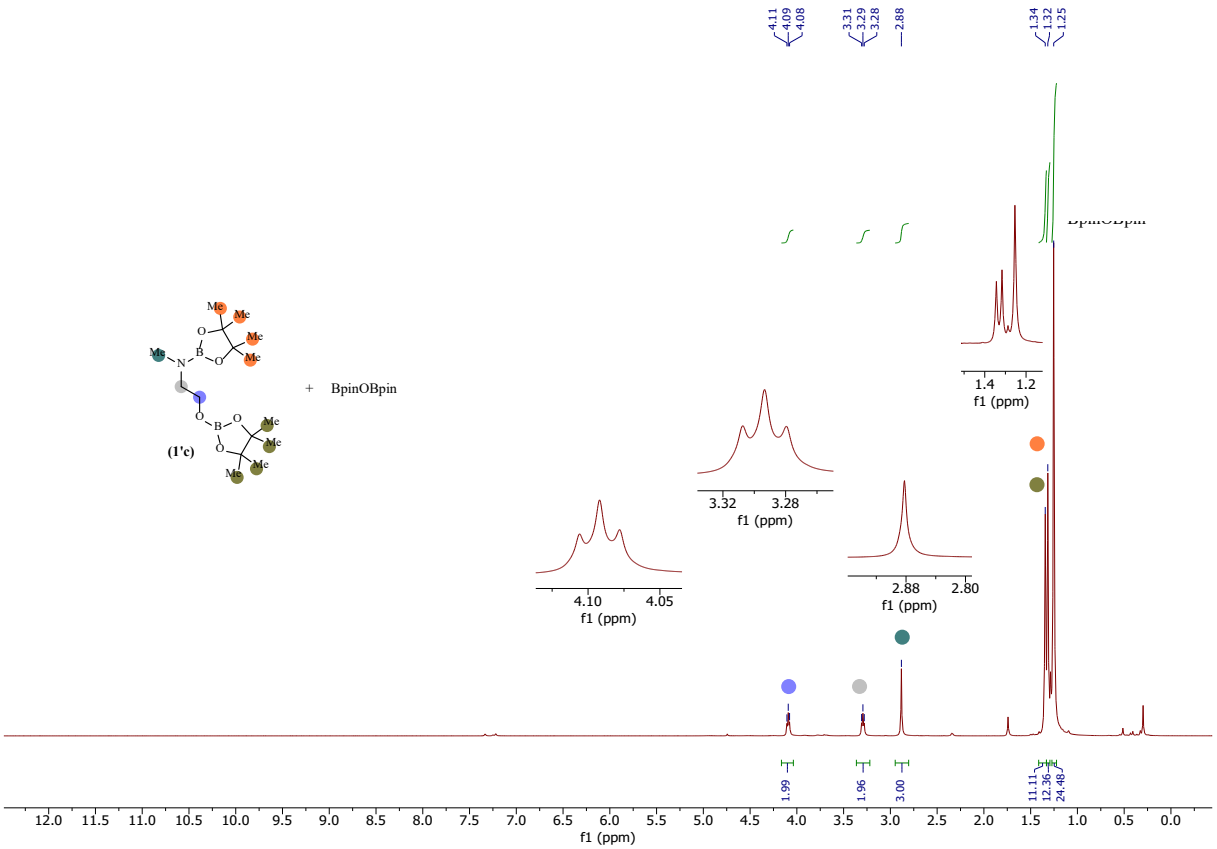



Figure S7: $^{1}$H NMR (400 MHz, Toluene-d$_8$) of compound **1'c**

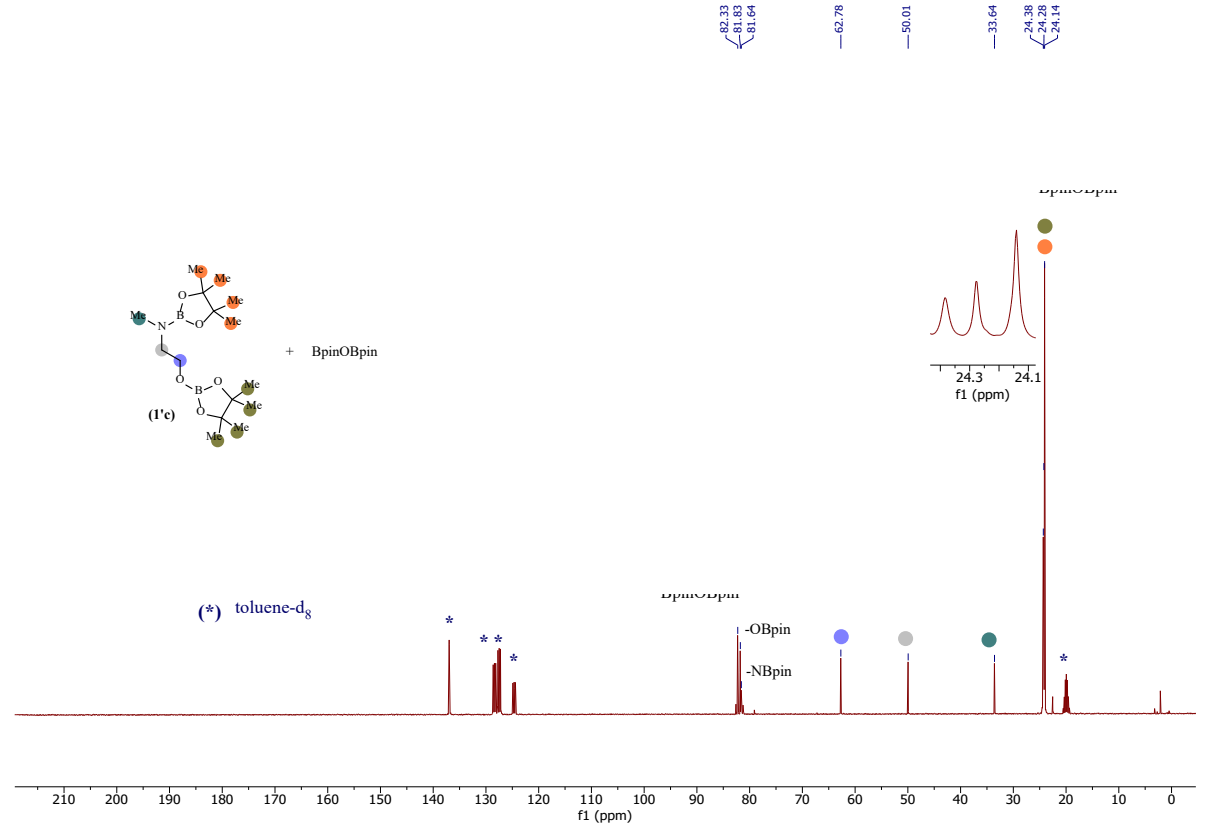



Figure S8: $^{13}$C{$^{1}$H} NMR (101 MHz, Toluene-d$_8$) of compound **1'c**

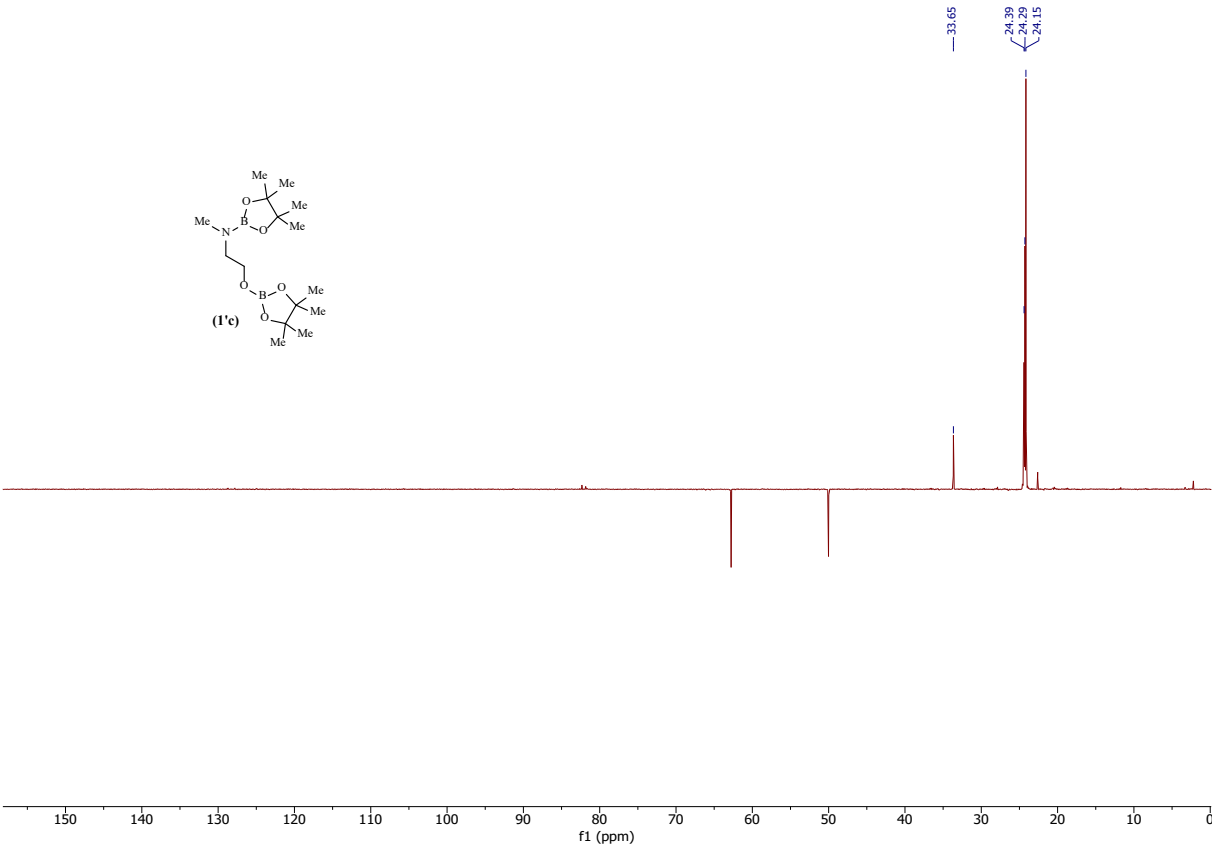



Figure S9: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'c**

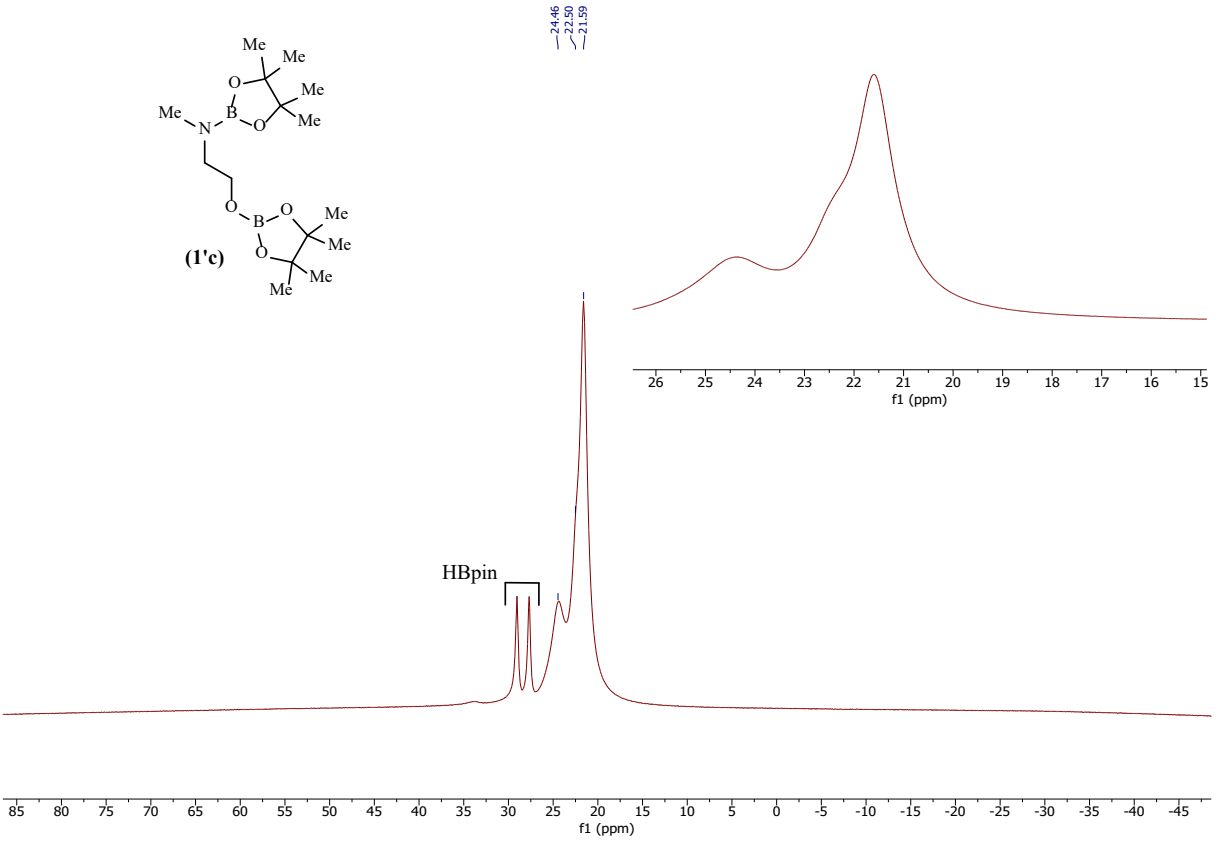



Figure S10: $^{11}B$ NMR (128 MHz, Toluene-$d_8$) of compound **1'c**

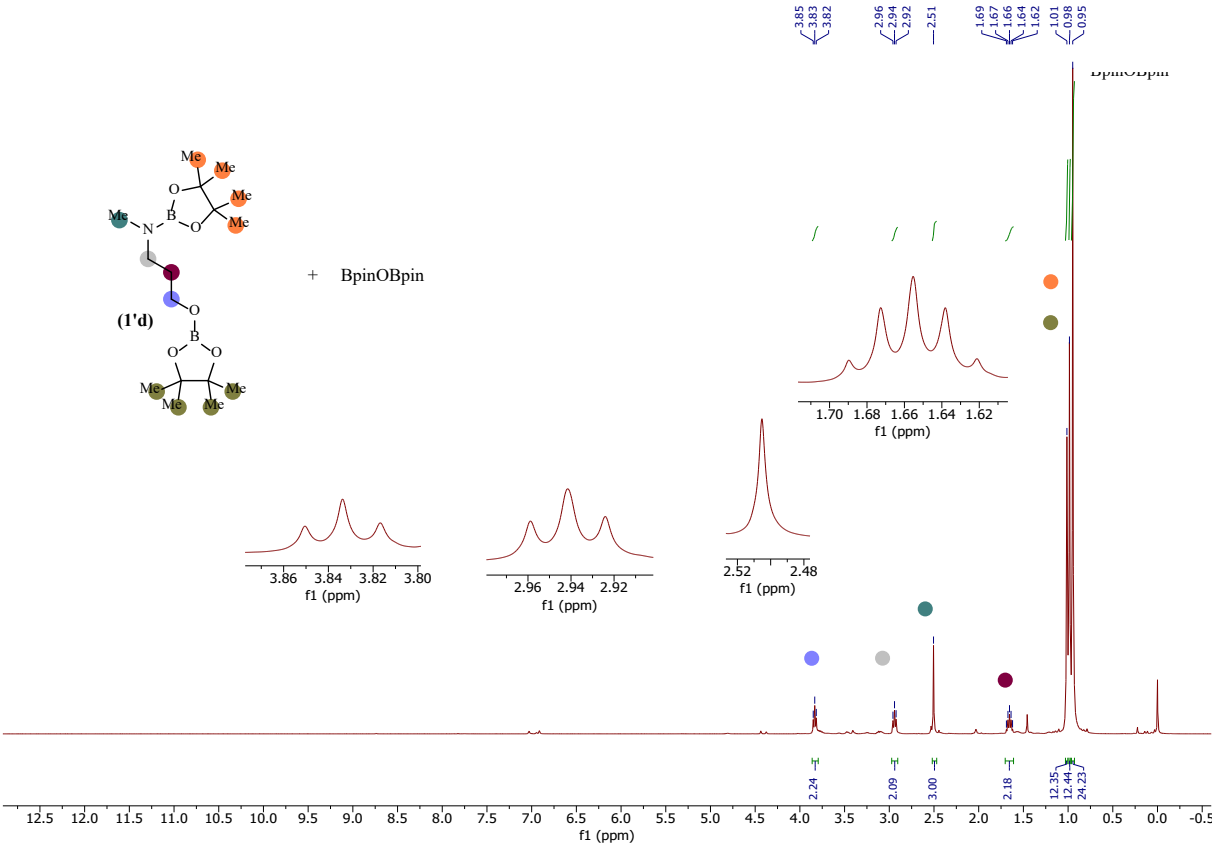



Figure S11: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'd**

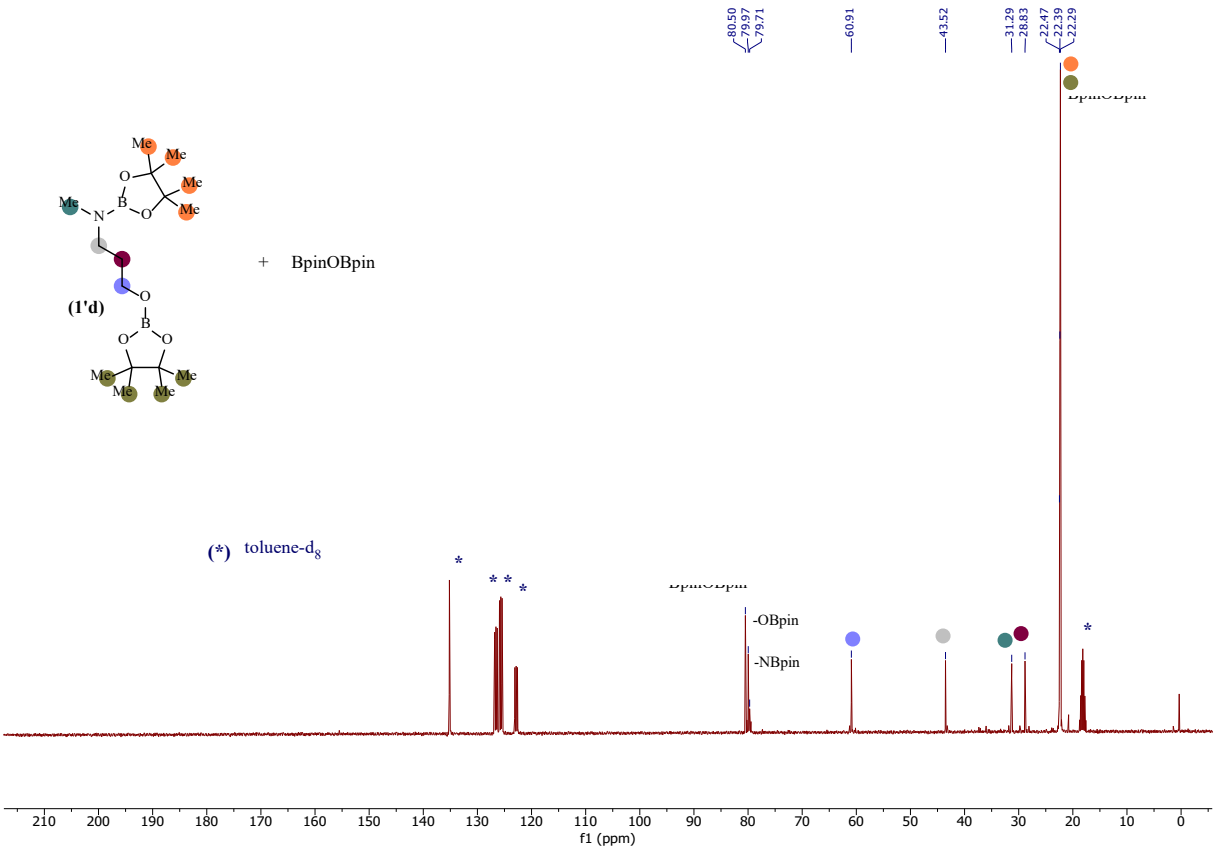



Figure S12: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'd**

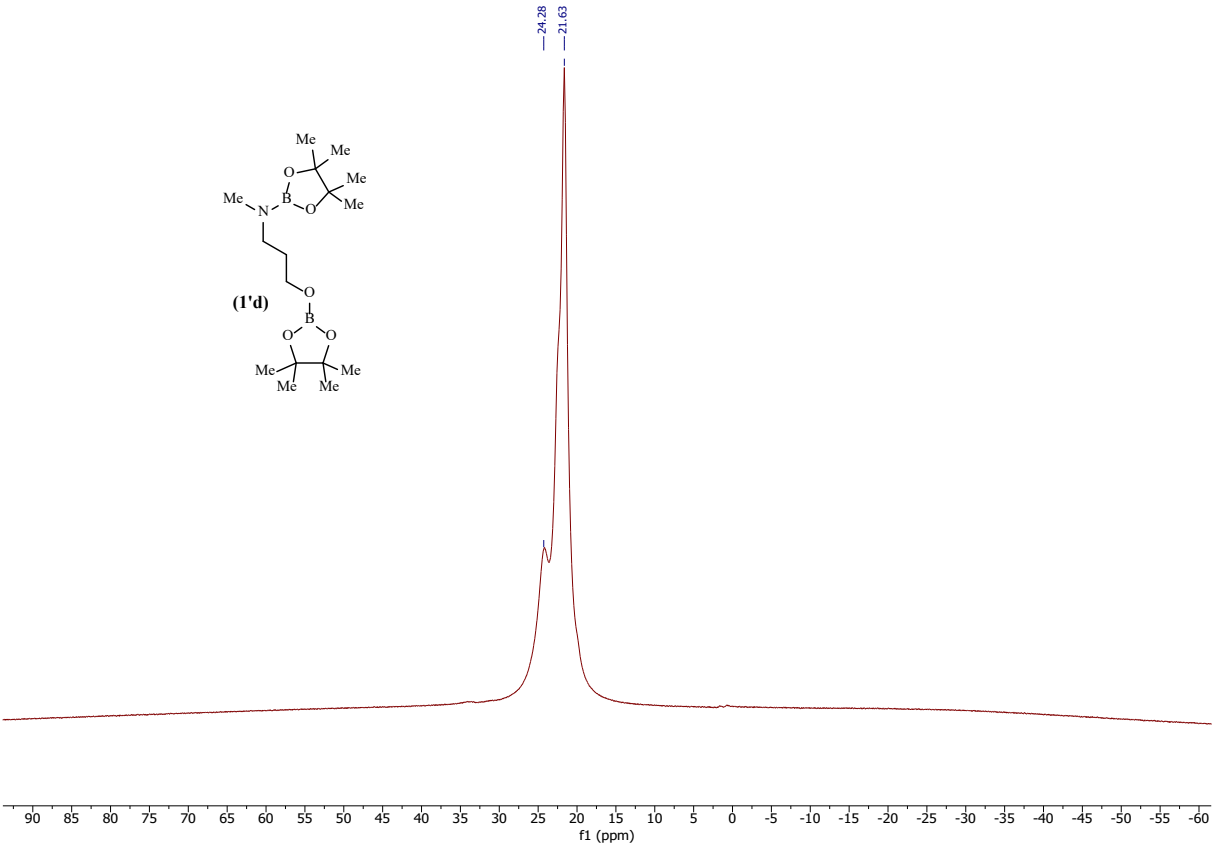



Figure S13: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'd**

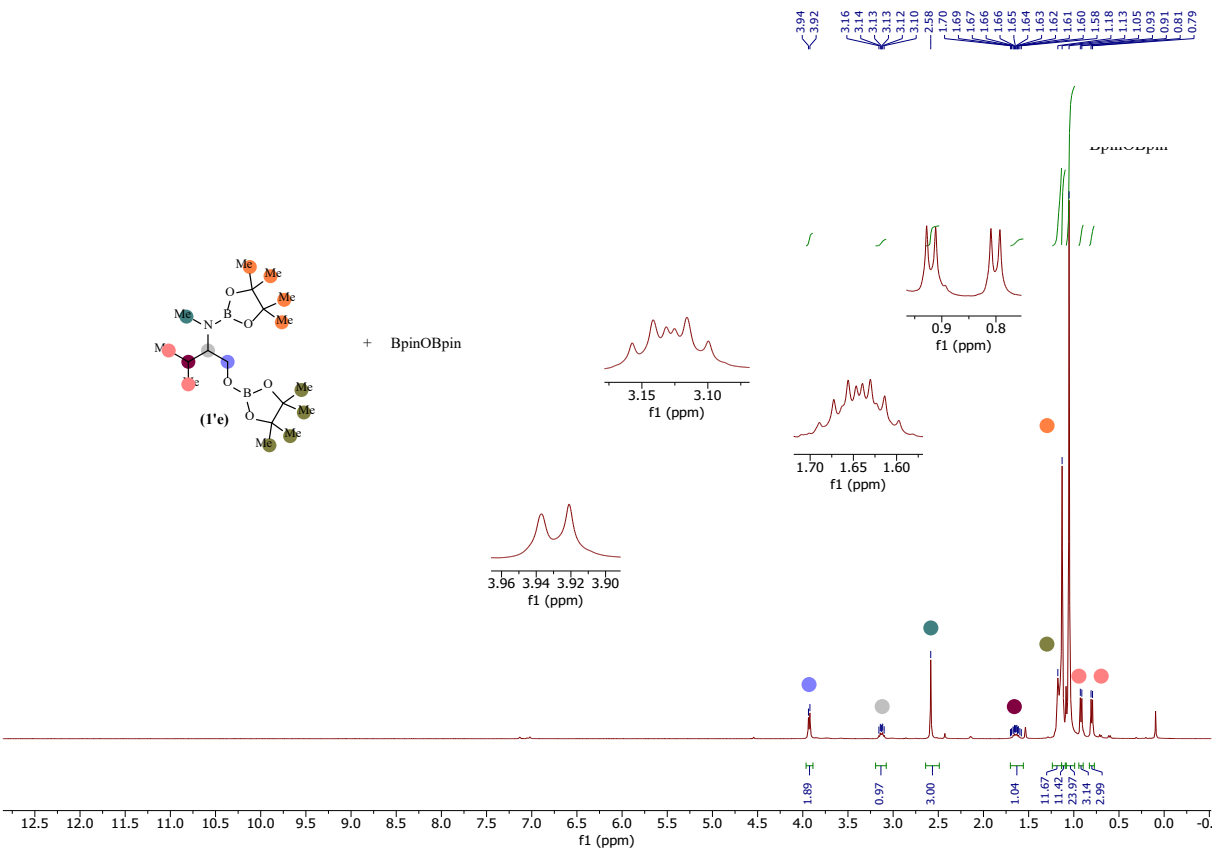



Figure S14: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'e**

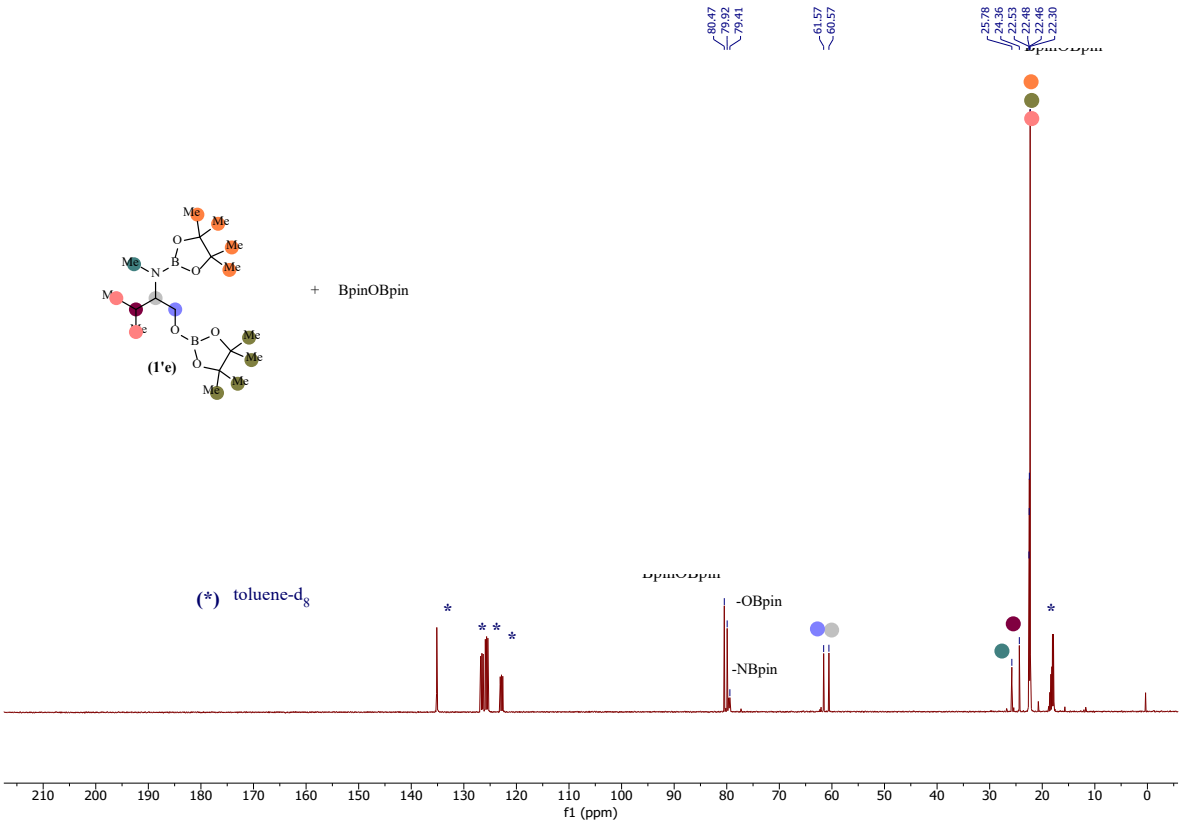



Figure S15: $^{13}C\{^1H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'e**

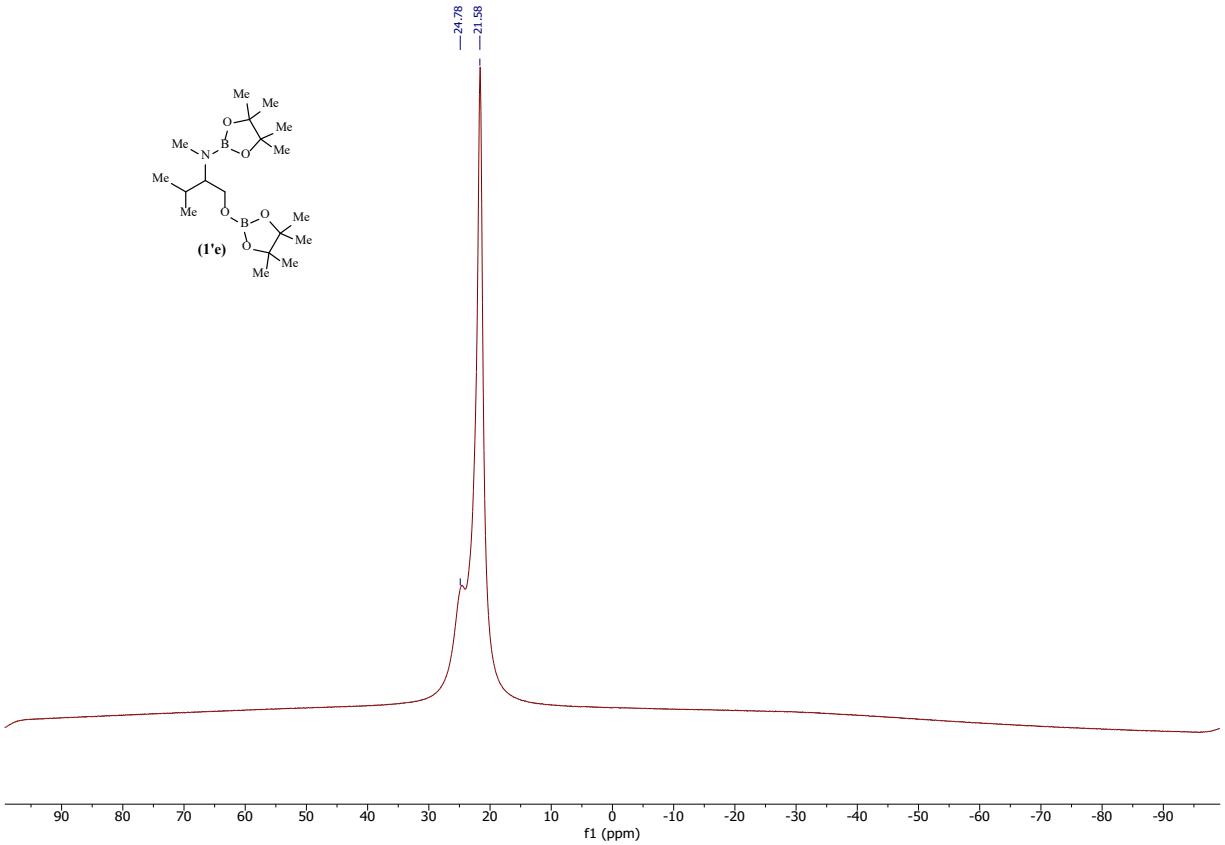



Figure S16: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'e**

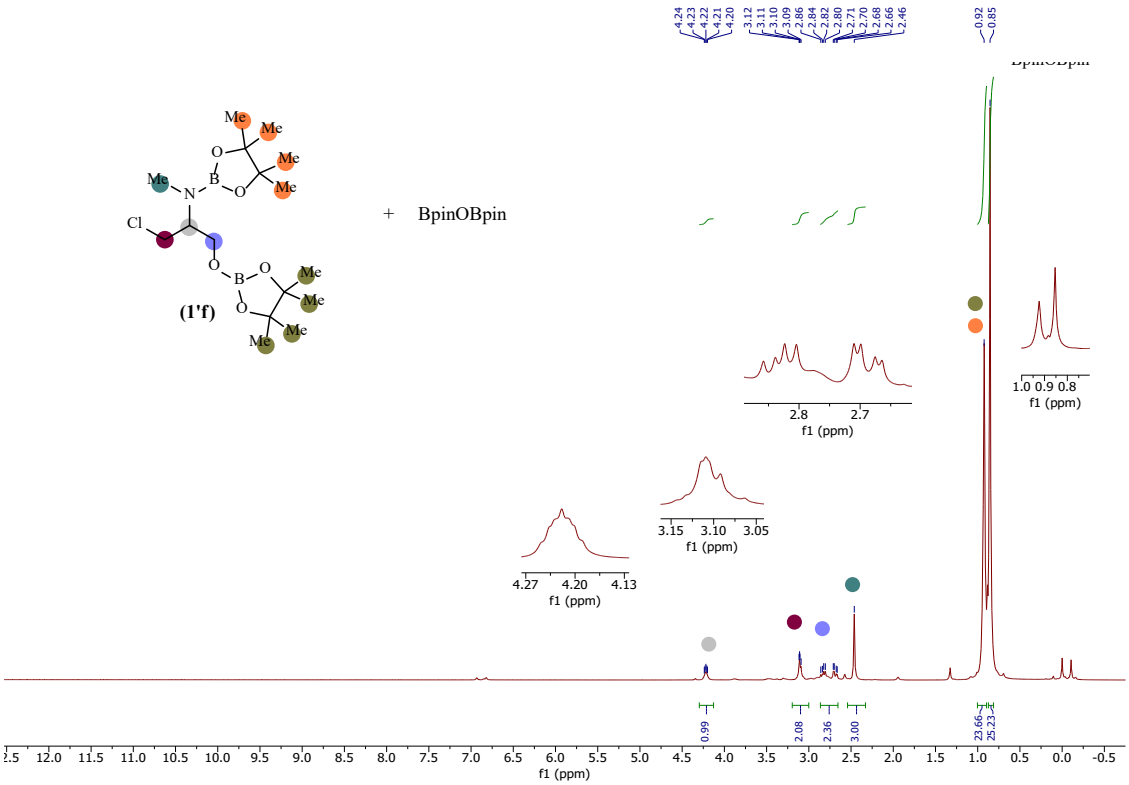



Figure S17: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'f**

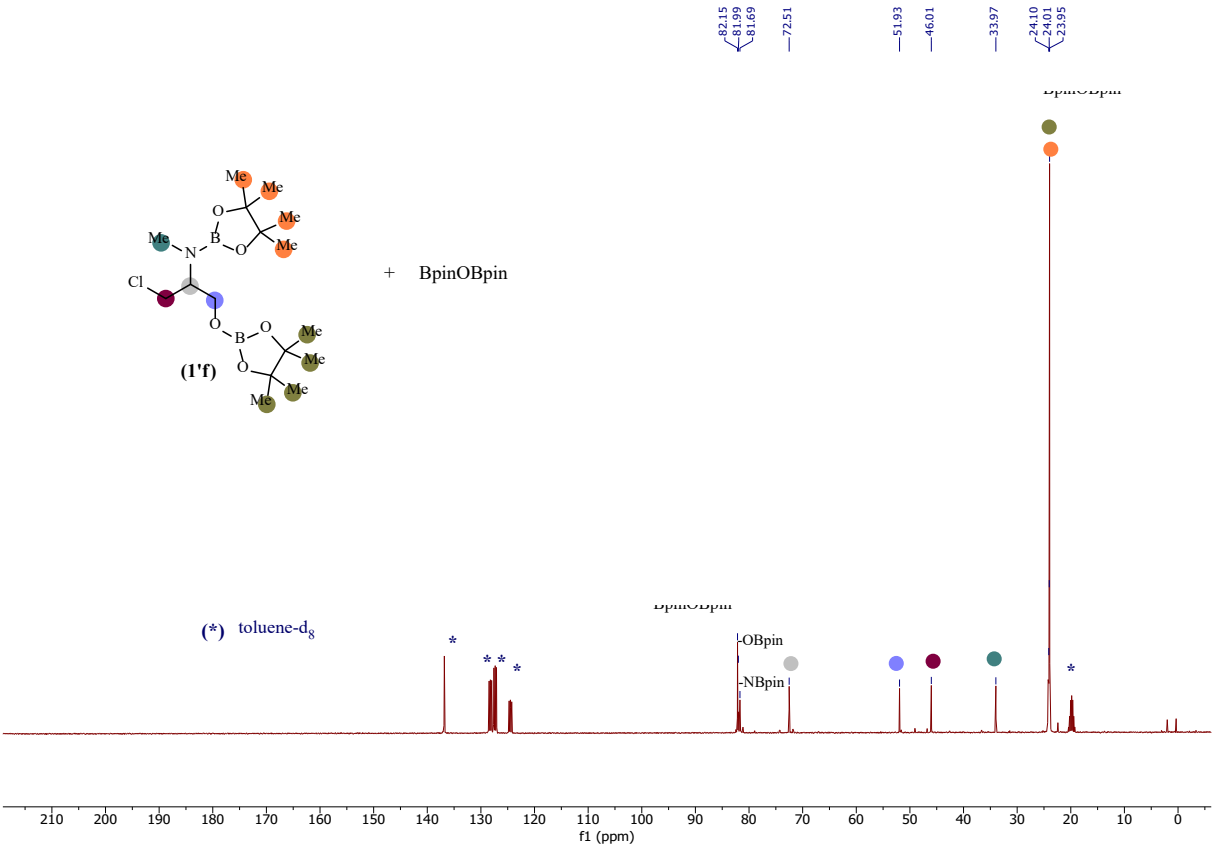



Figure S18: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'f**

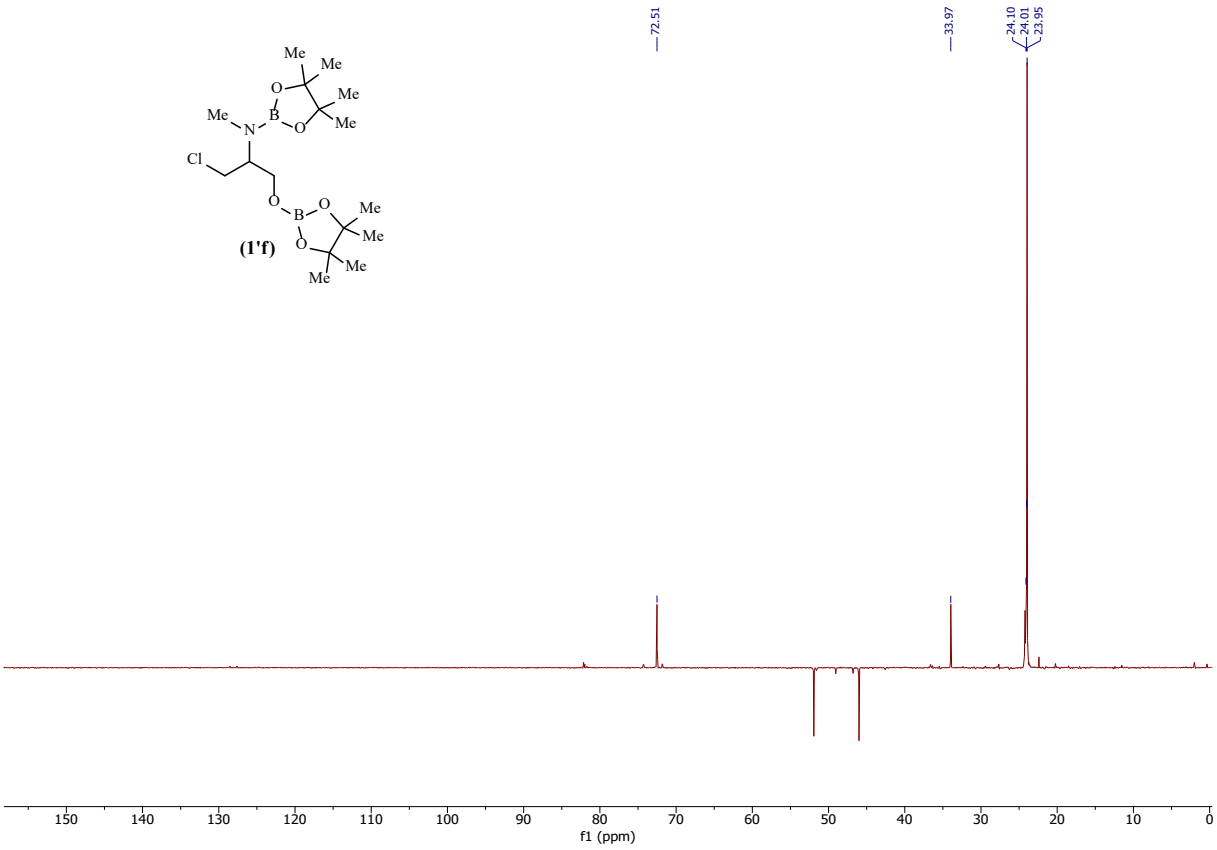



Figure S19: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'f**

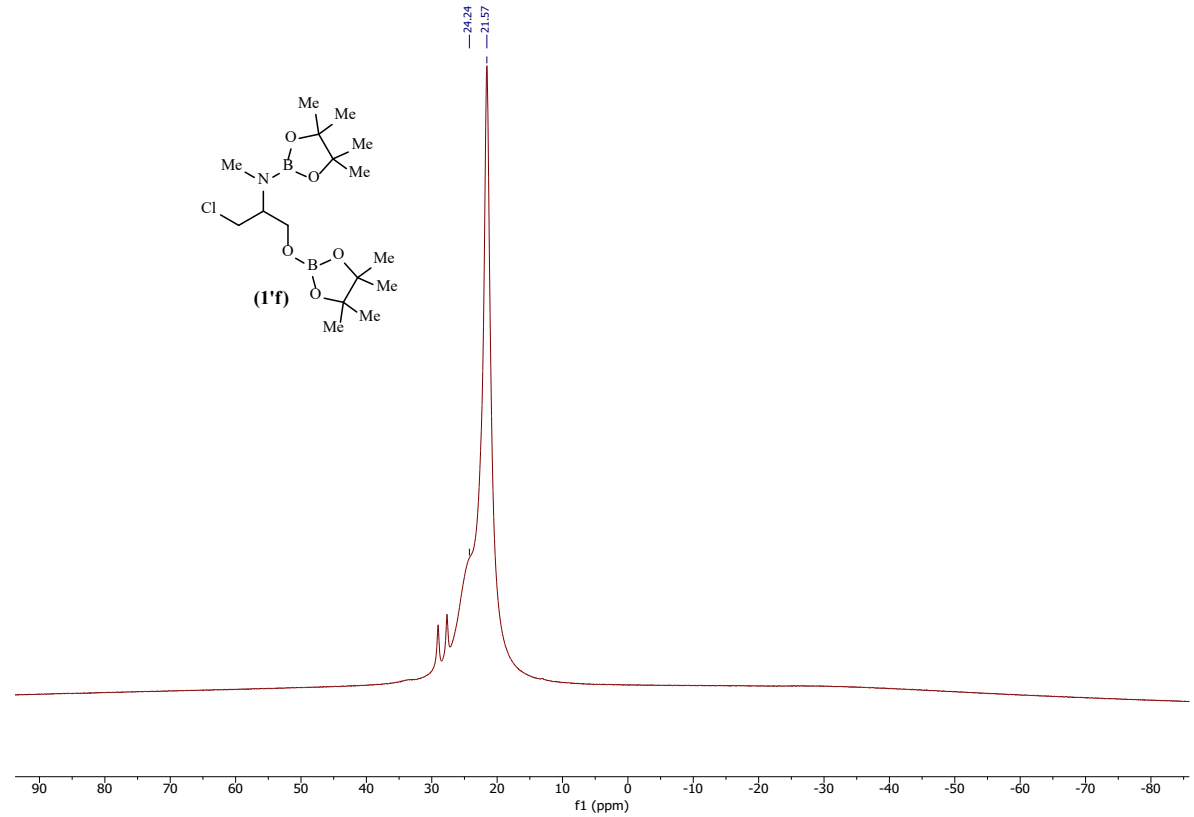



Figure S20: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'f**

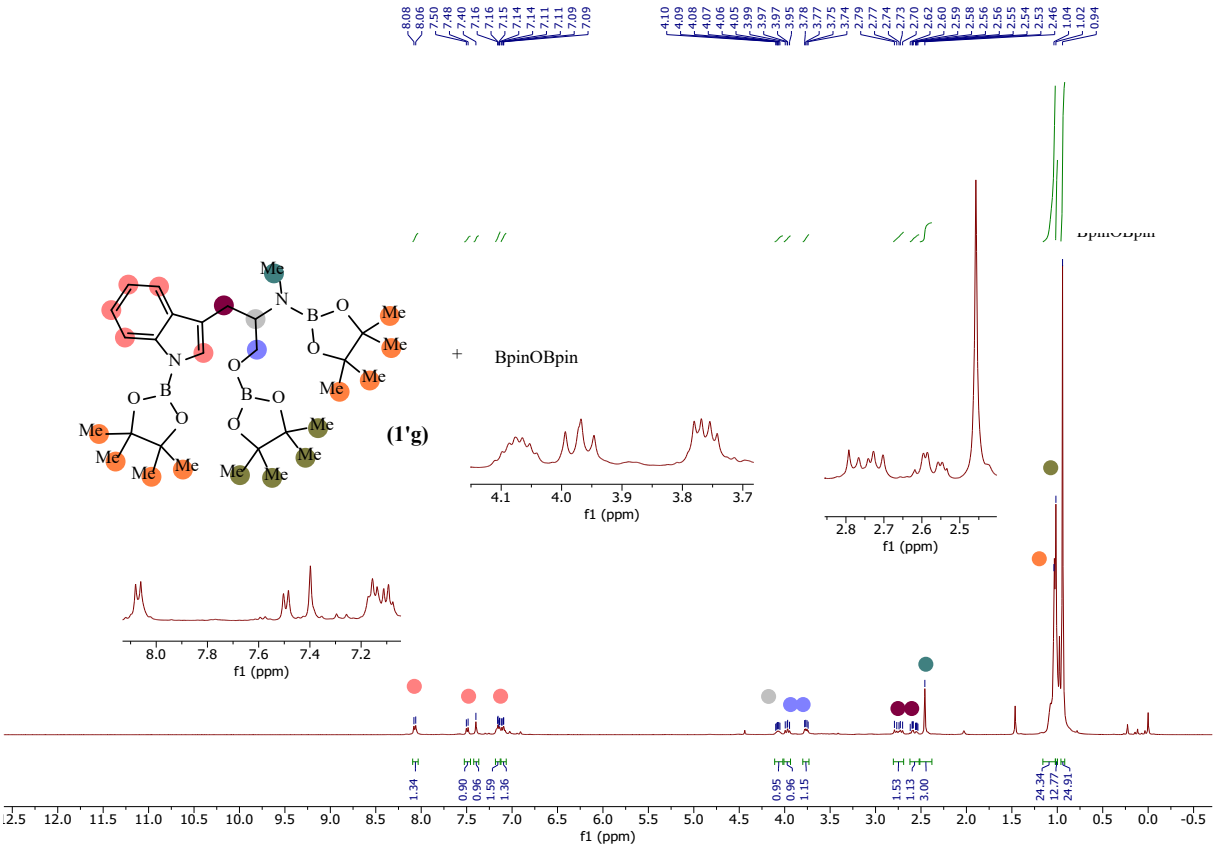



Figure S21: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'g**

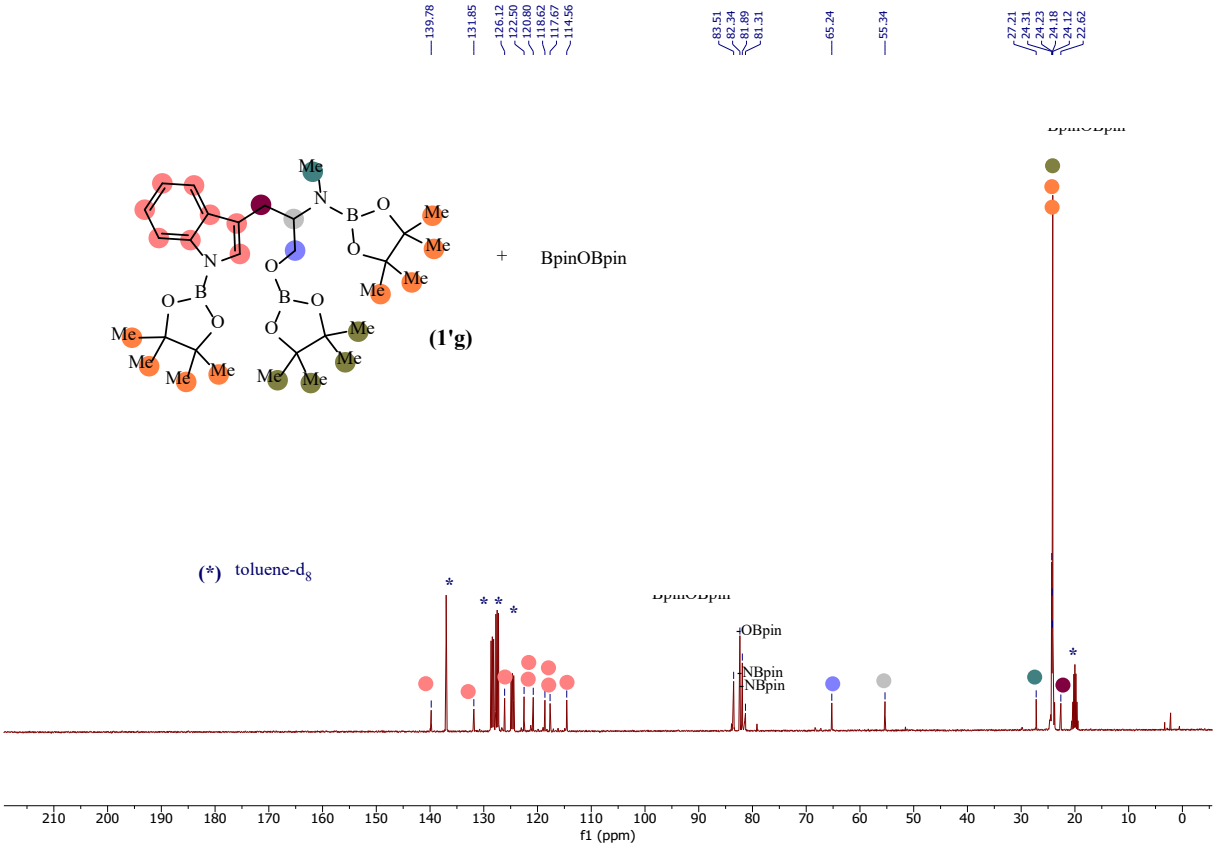



Figure S22: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'g**

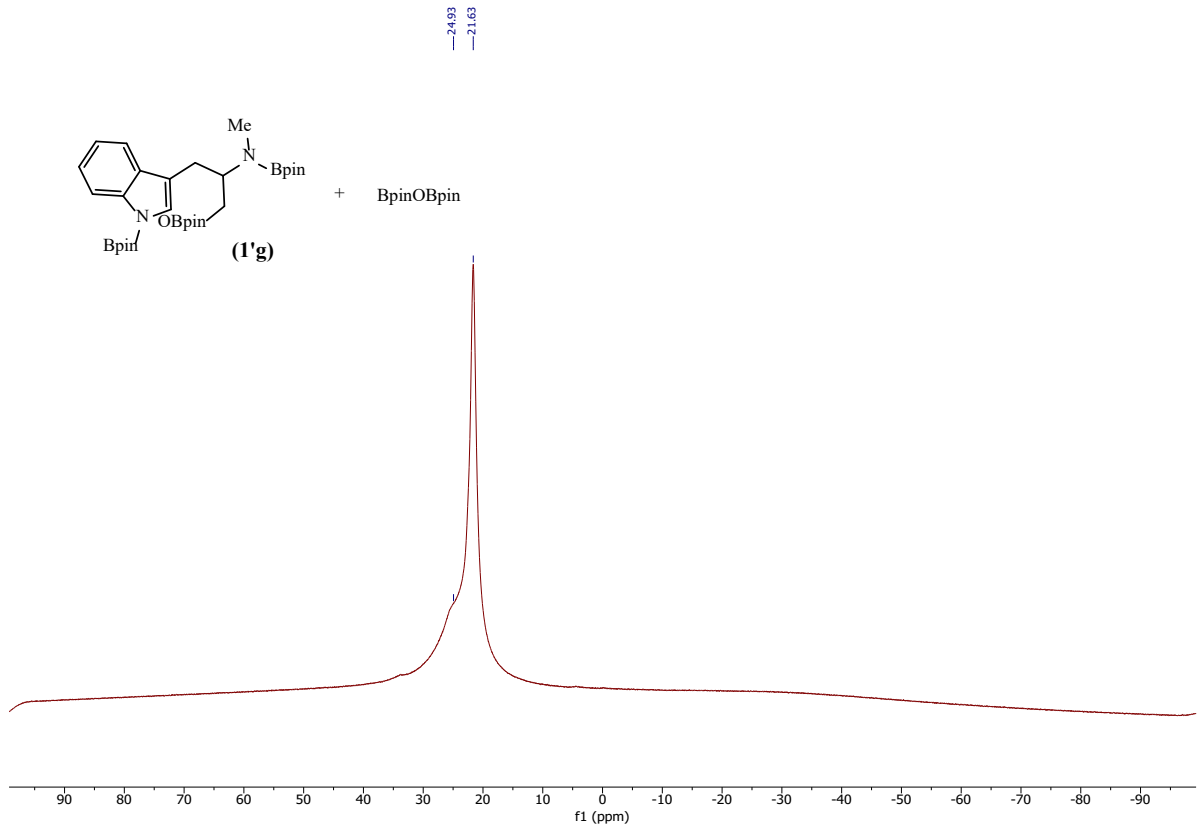



Figure S23: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'g**

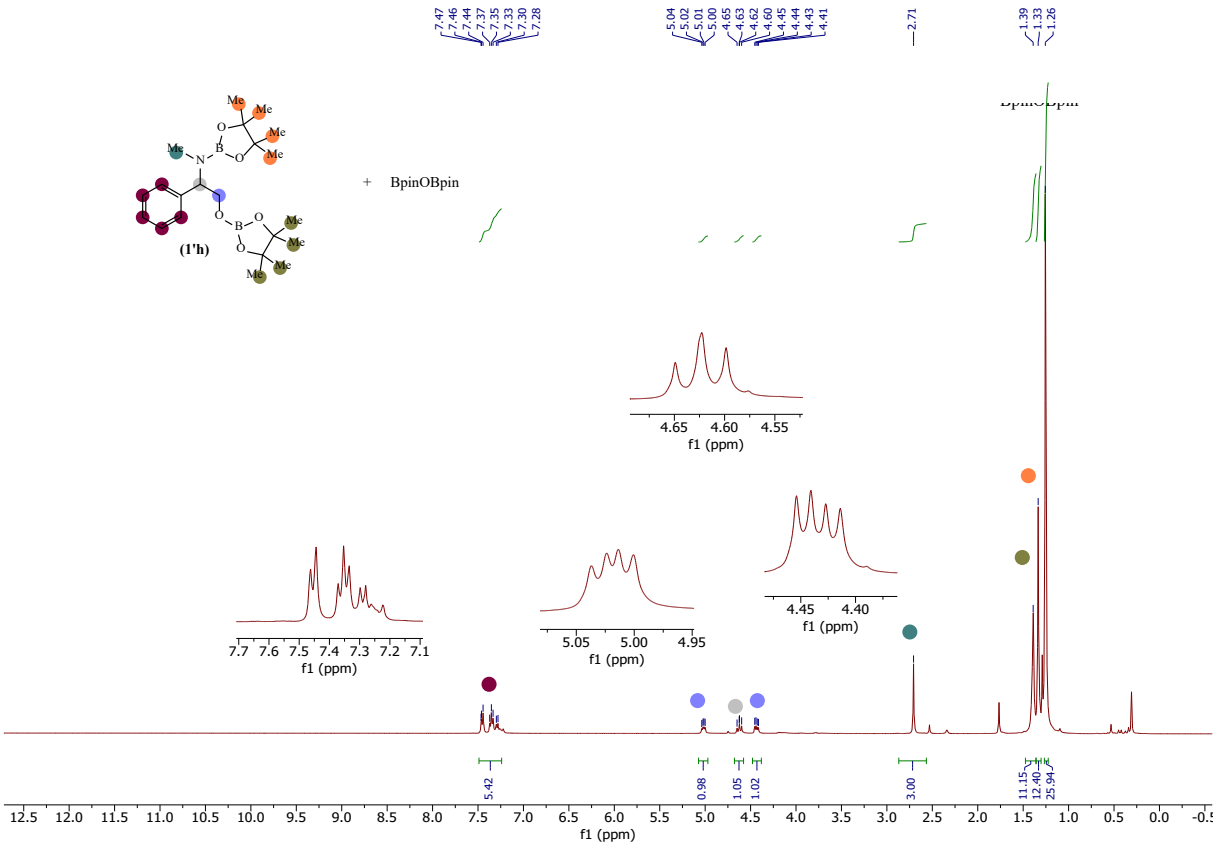



Figure S24: $^1H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'h**

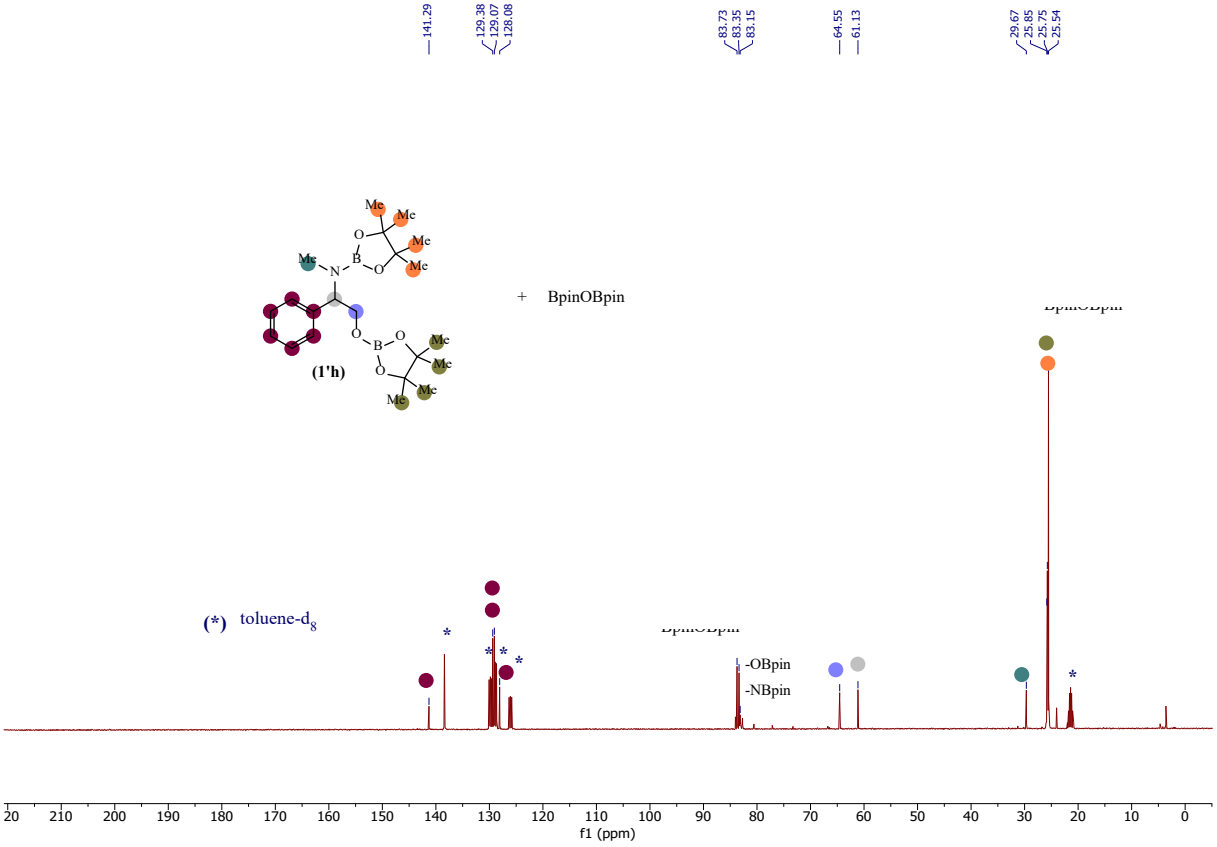



Figure S25: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'h**

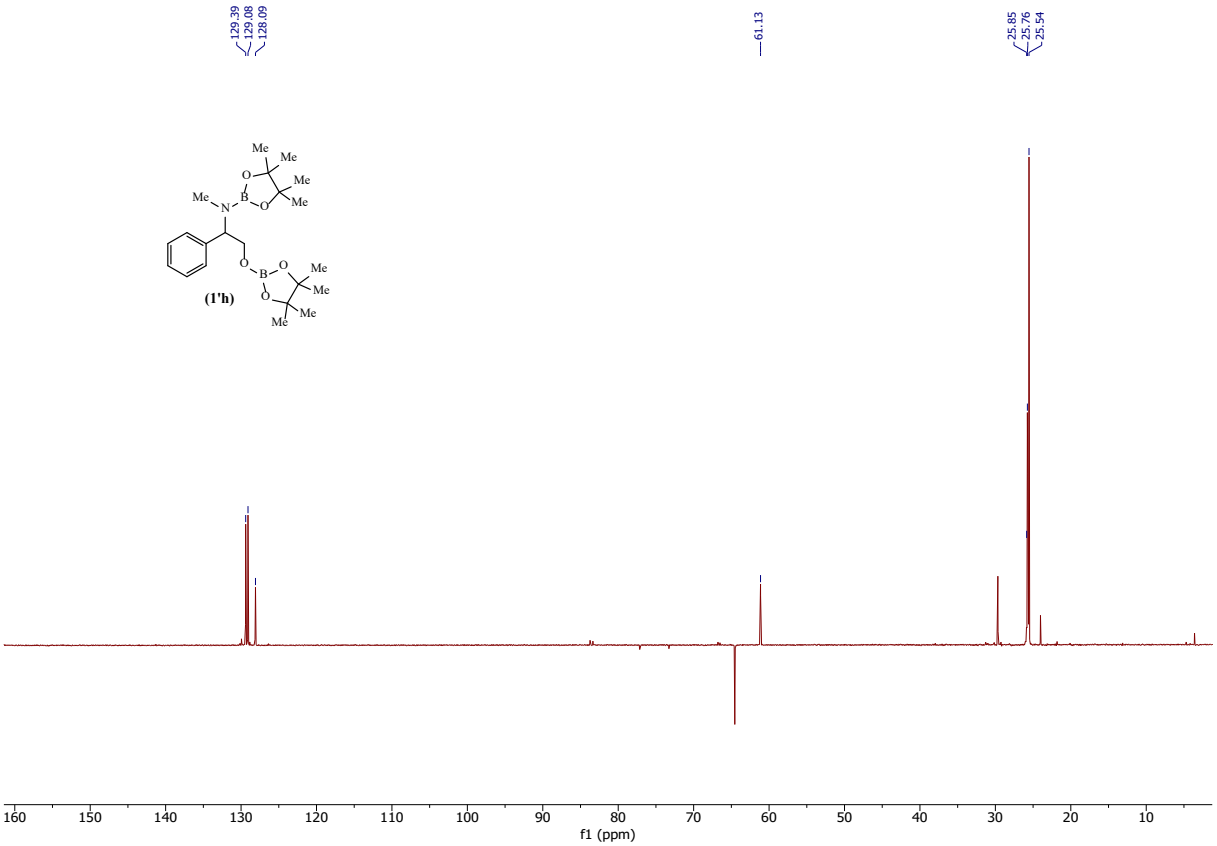



Figure S26: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'h**

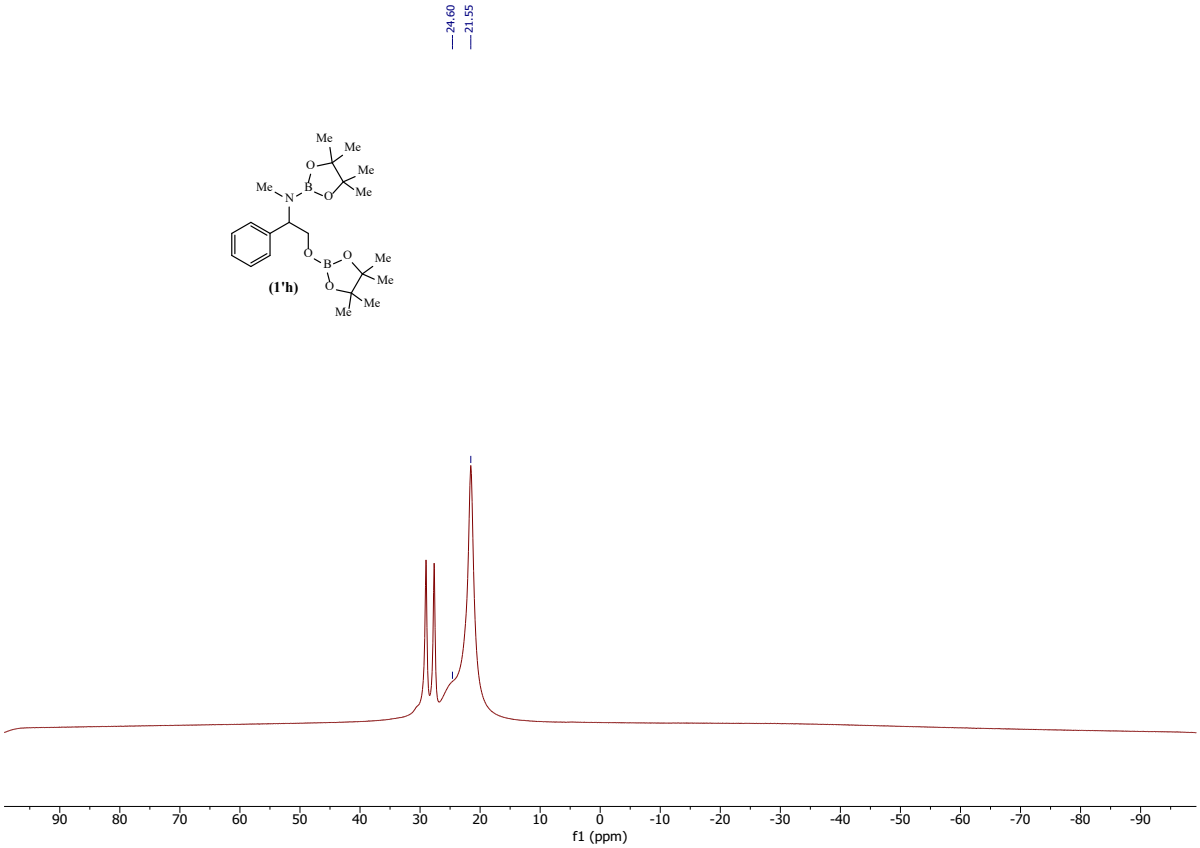



Figure S27: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'h**

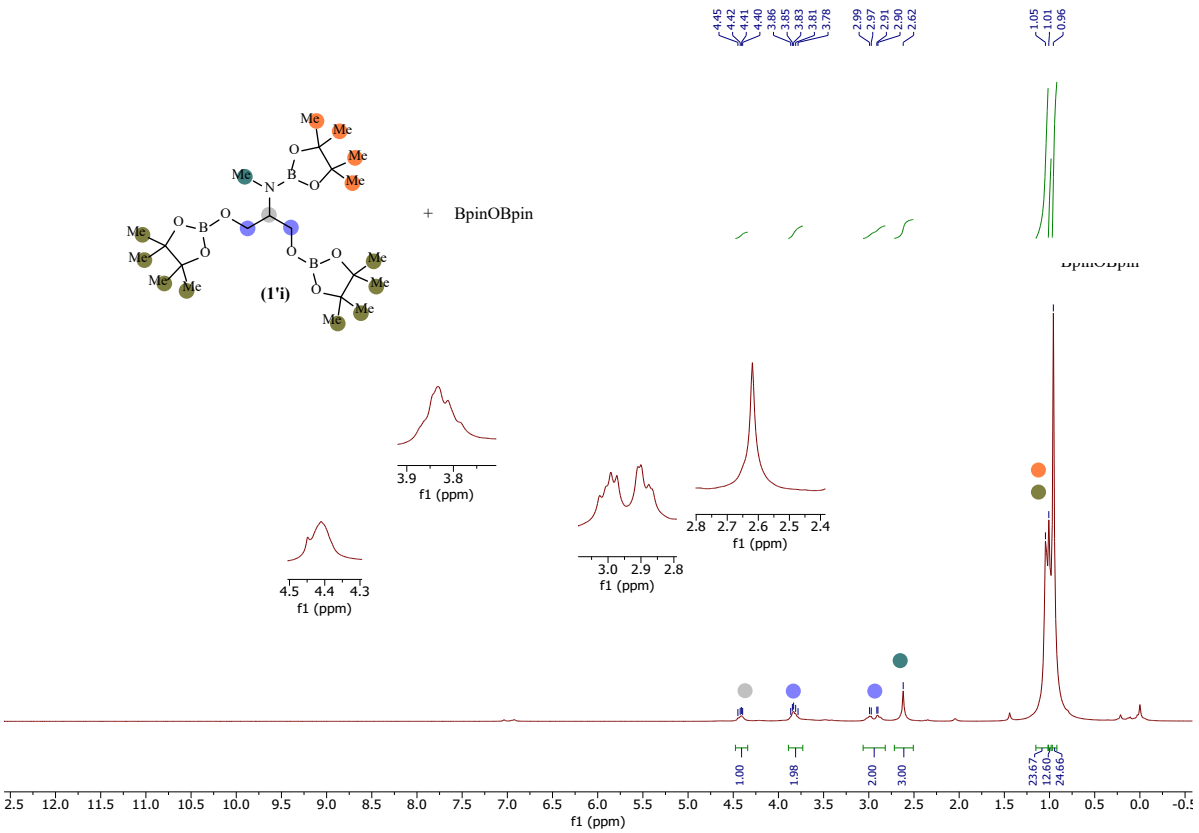



Figure S28: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'i**

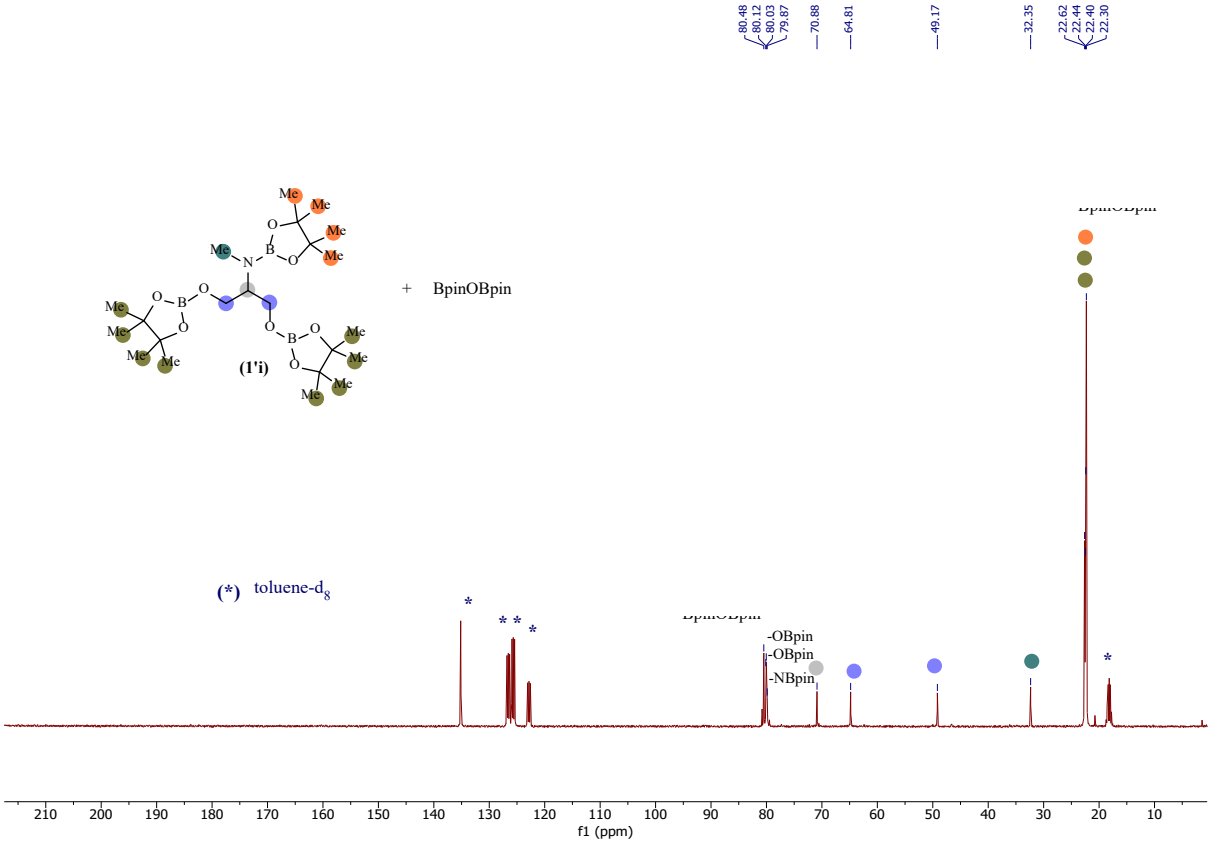



Figure S29: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound 1'**i**

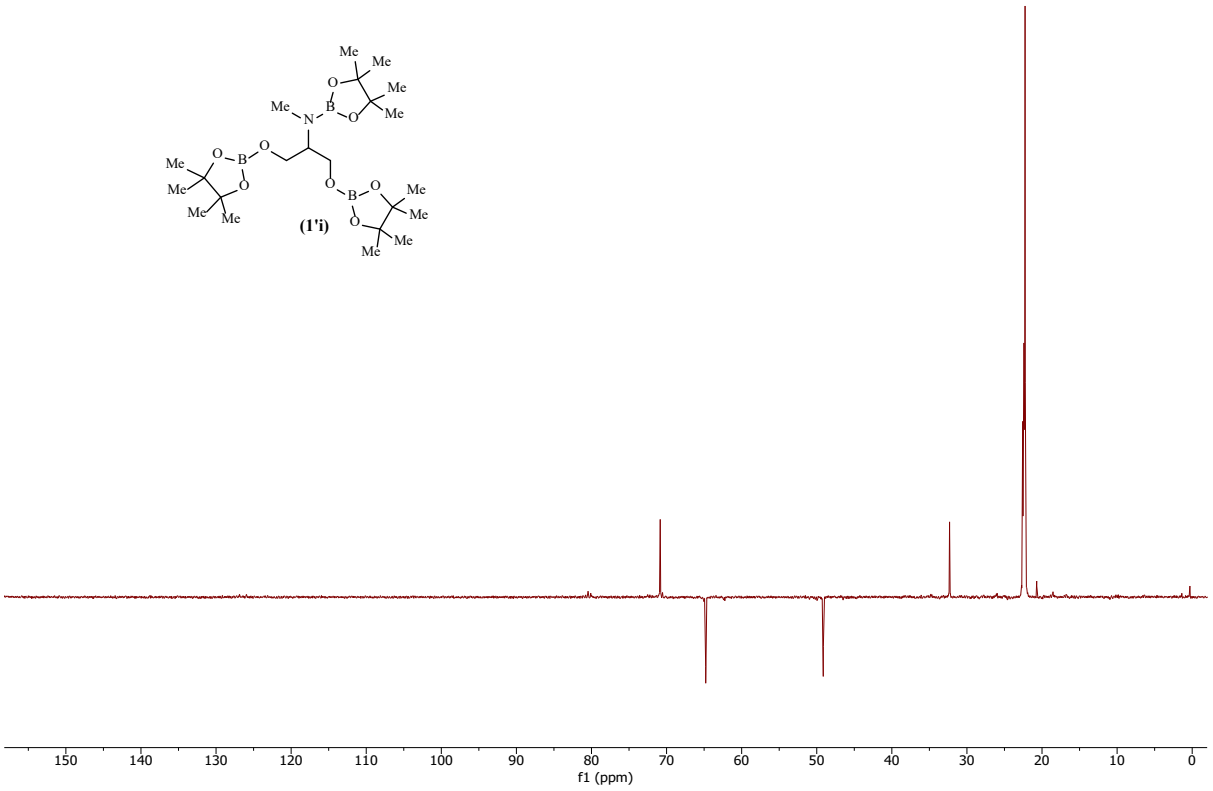



Figure S30: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'i**

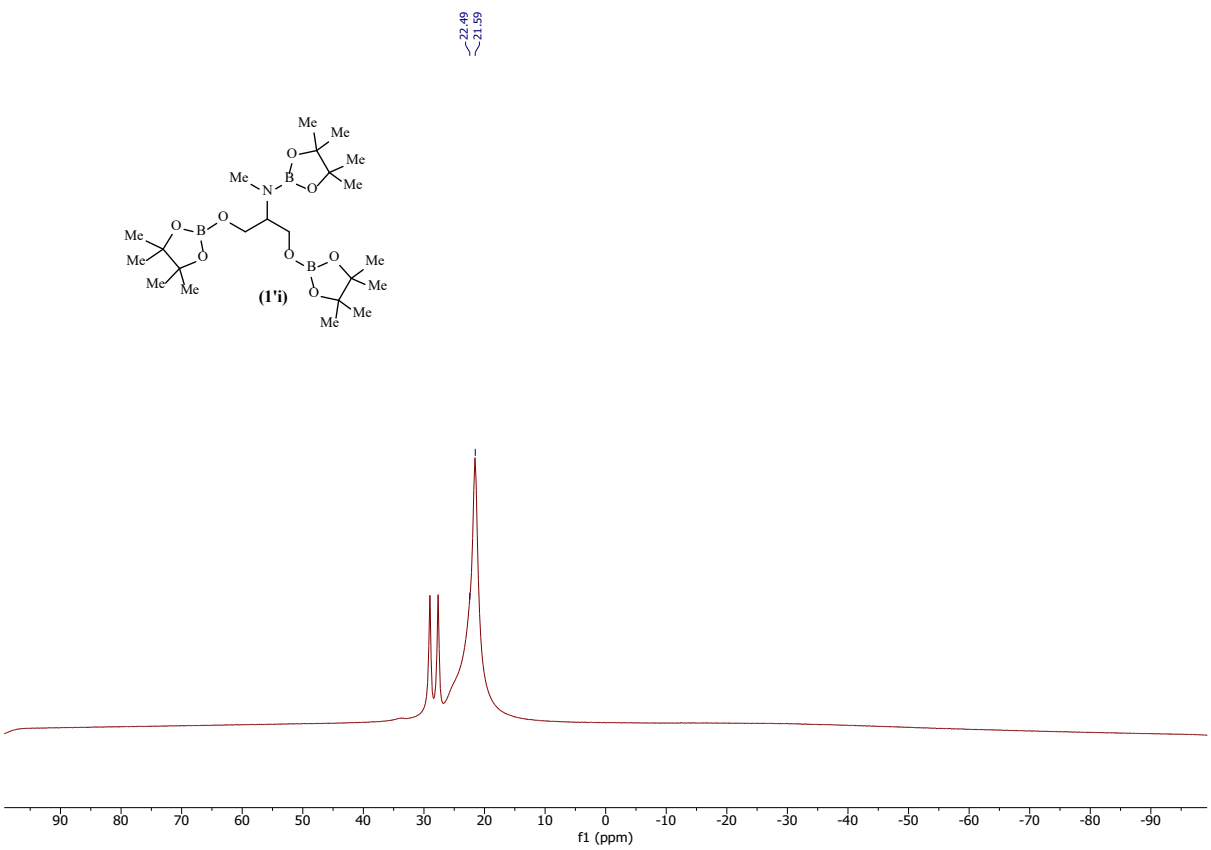



Figure S31: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'i**

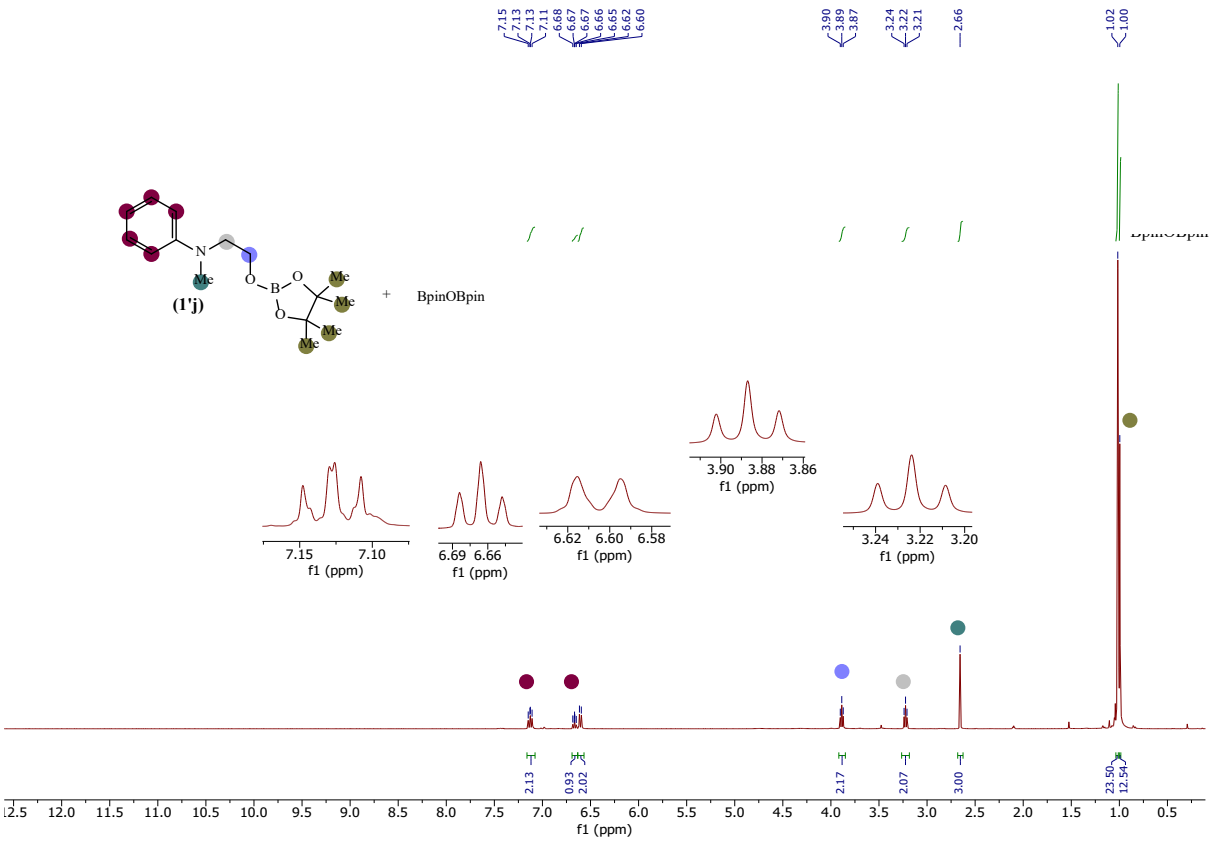



Figure S32: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'j**

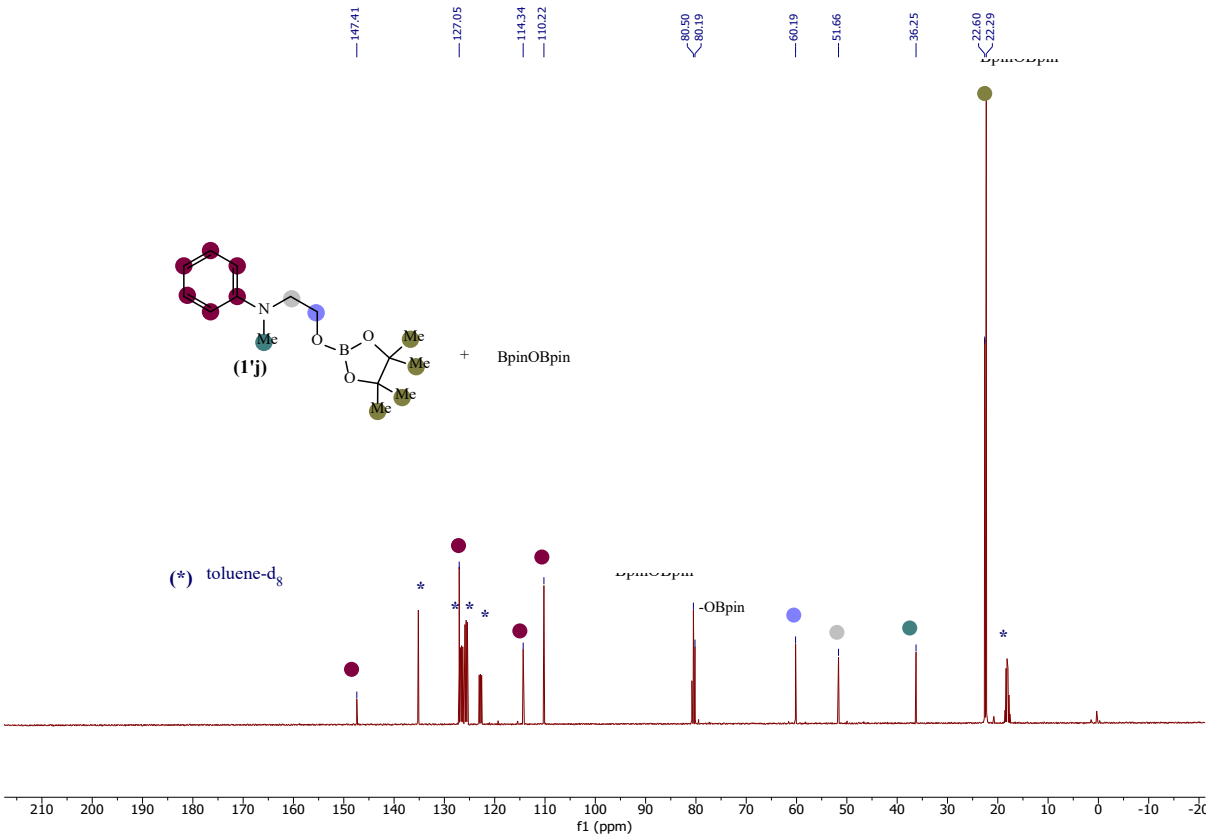



Figure S33: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'j**

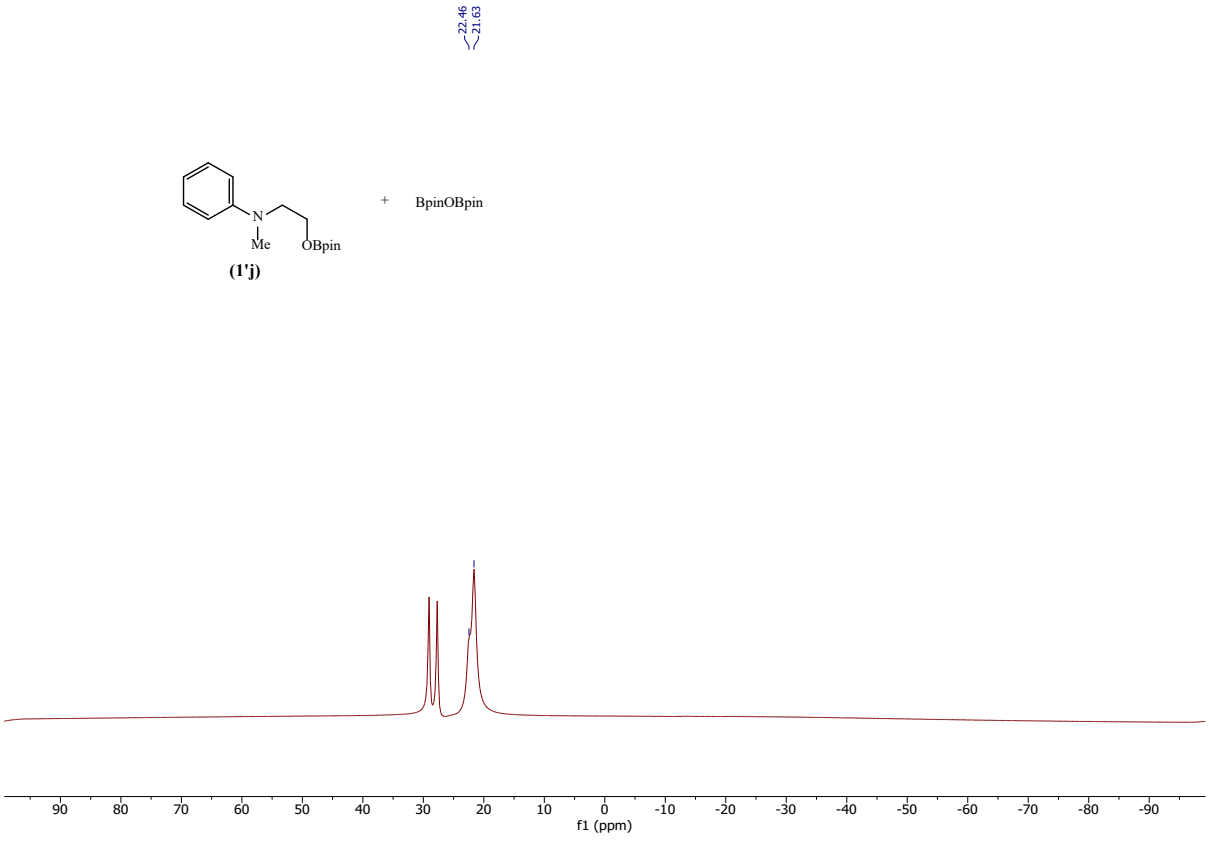



Figure S34: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'j**

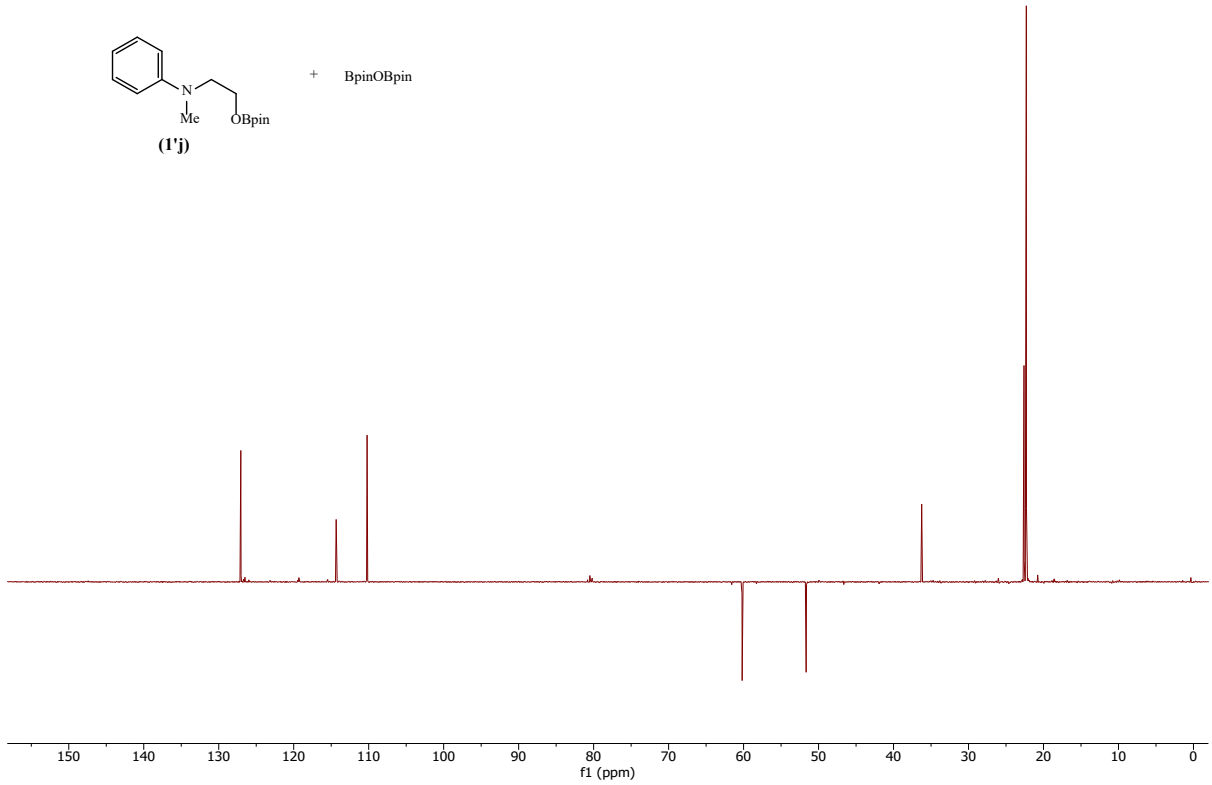



Figure S35: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'j**

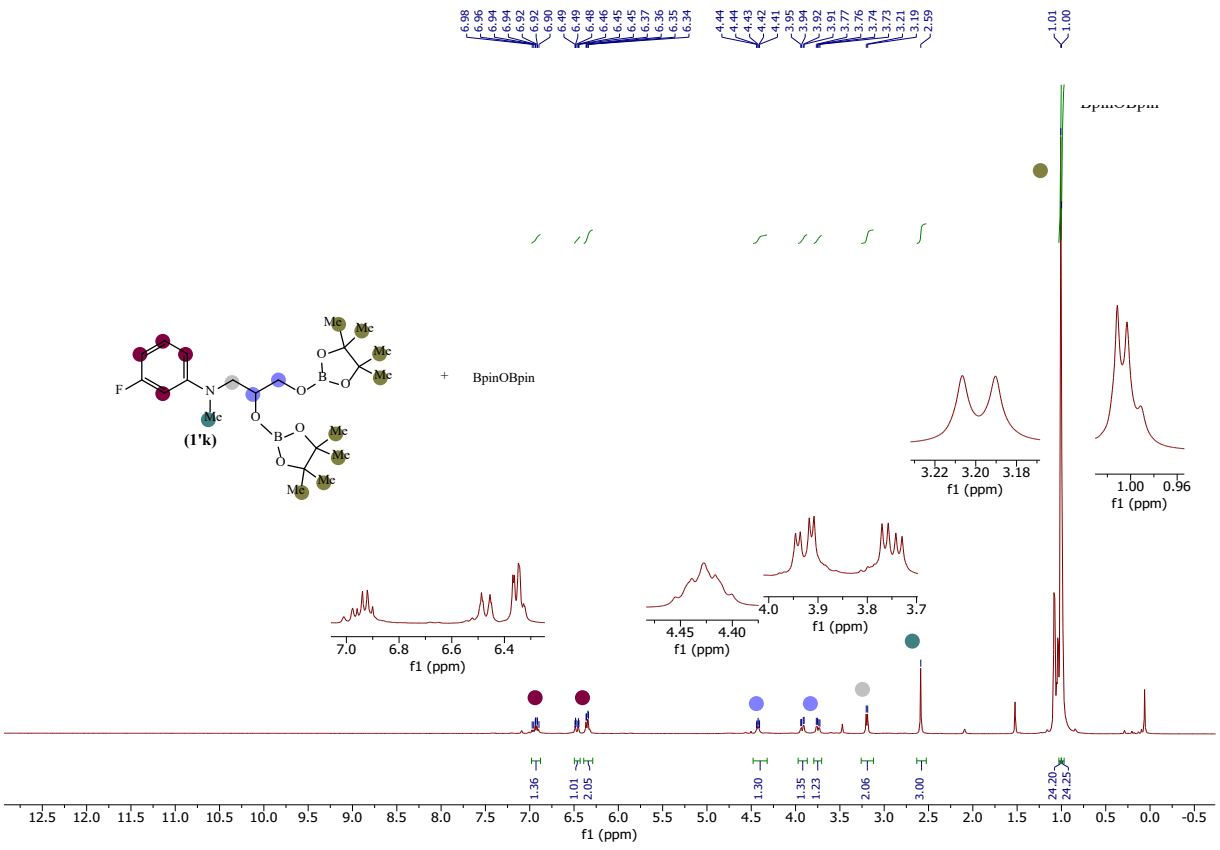



Figure S36: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'k**

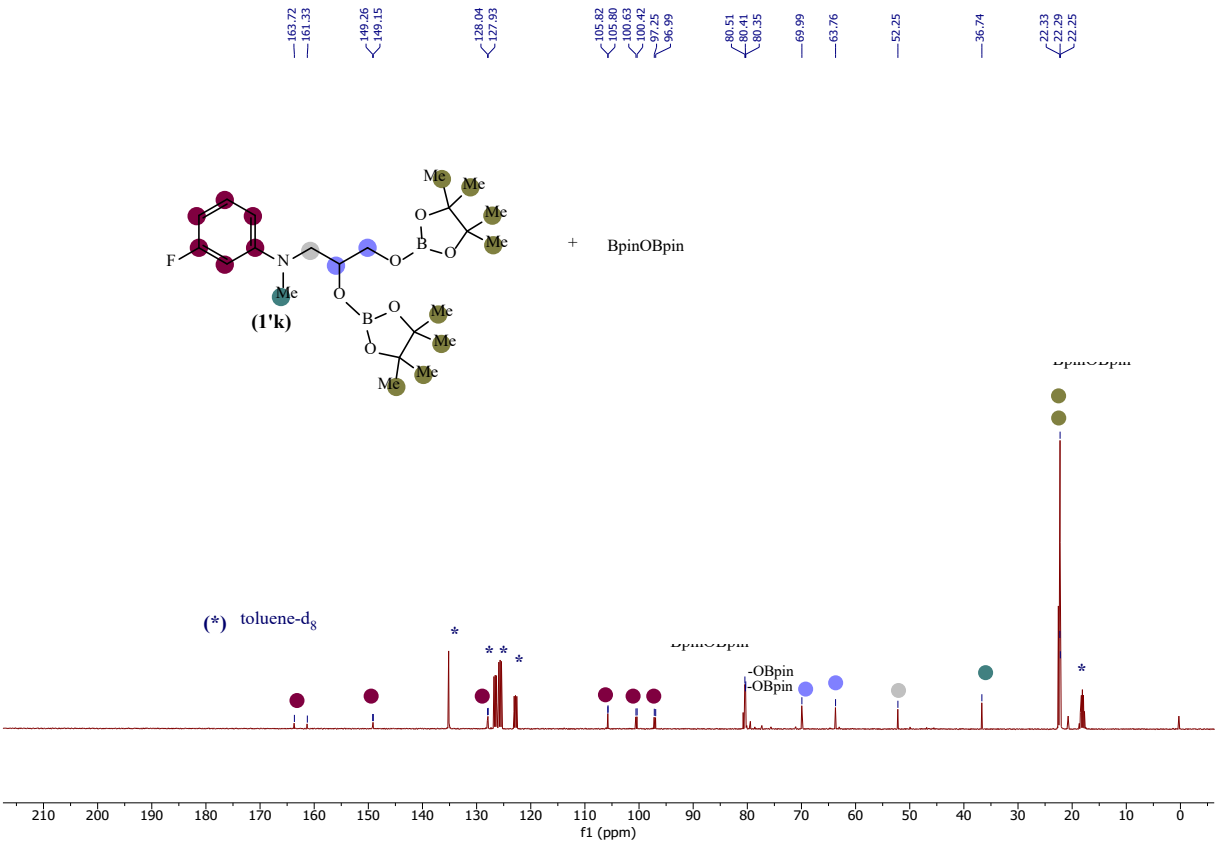



Figure S37: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'k**

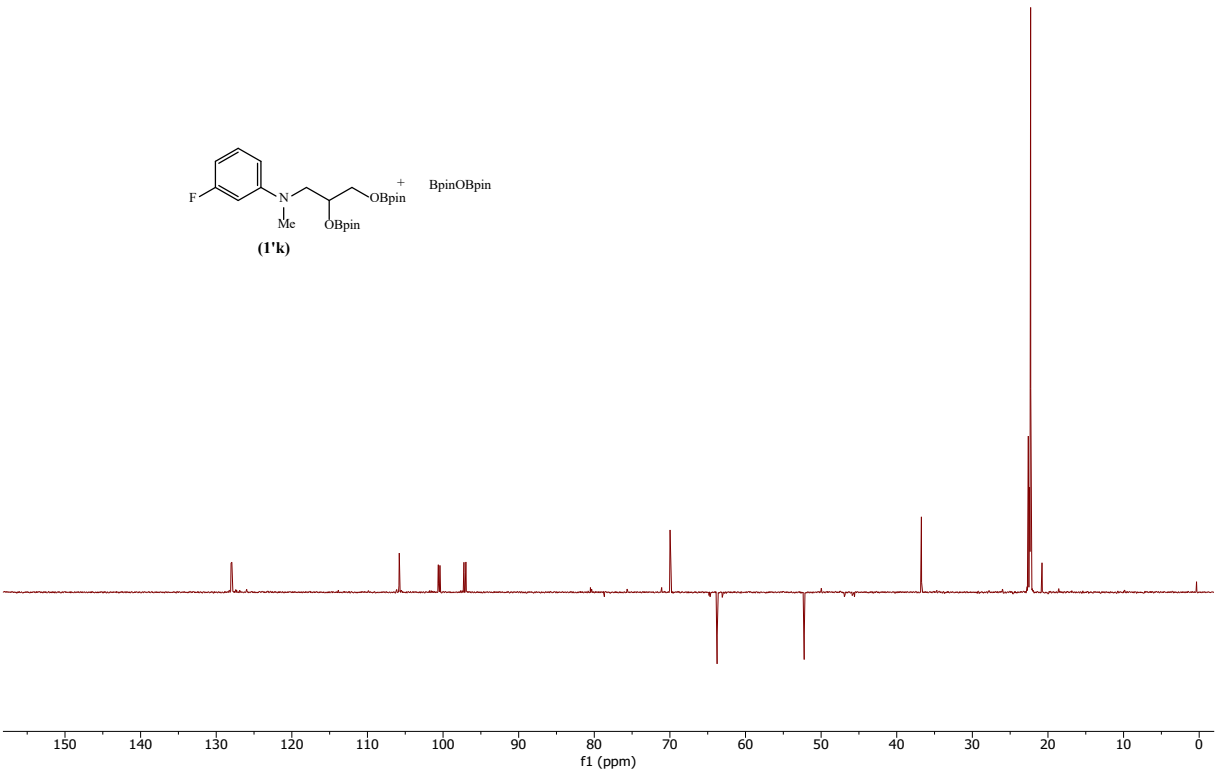



Figure S38: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'k**

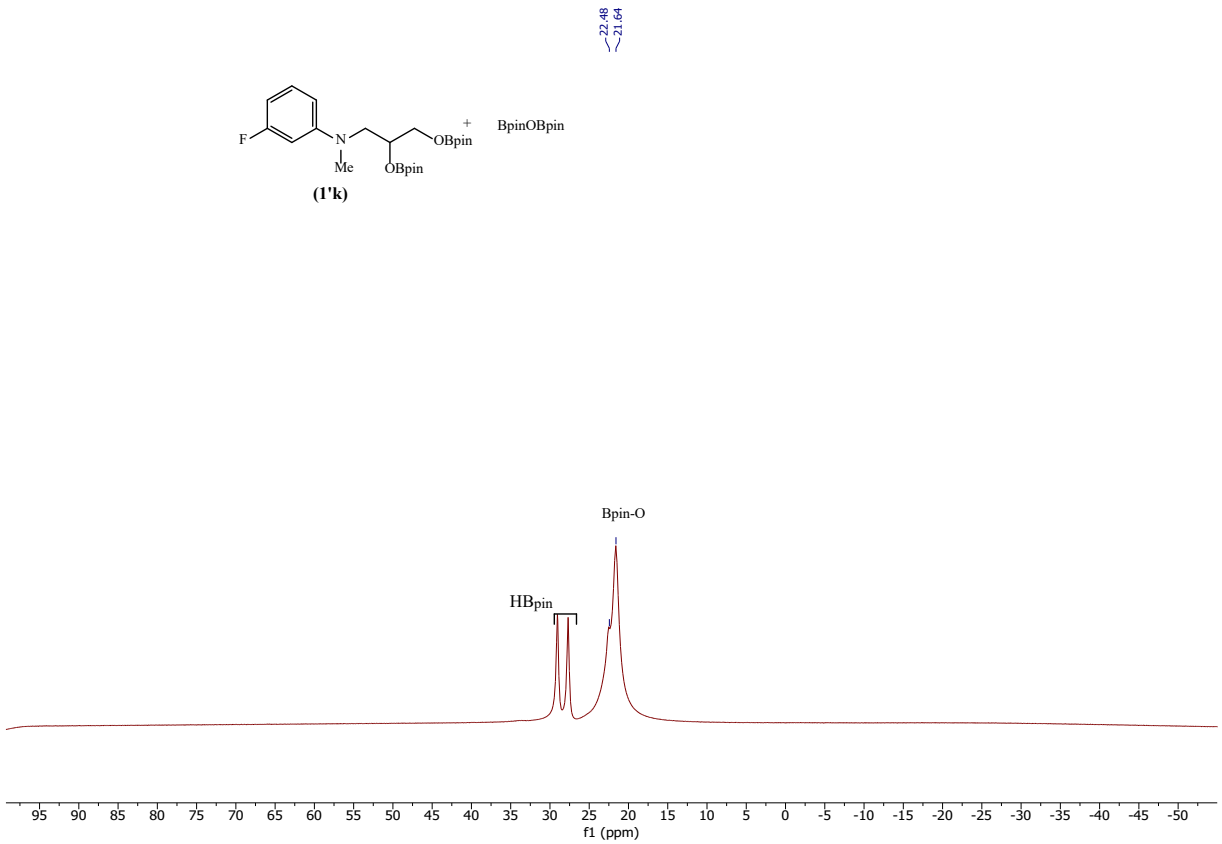



Figure S39: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'k**

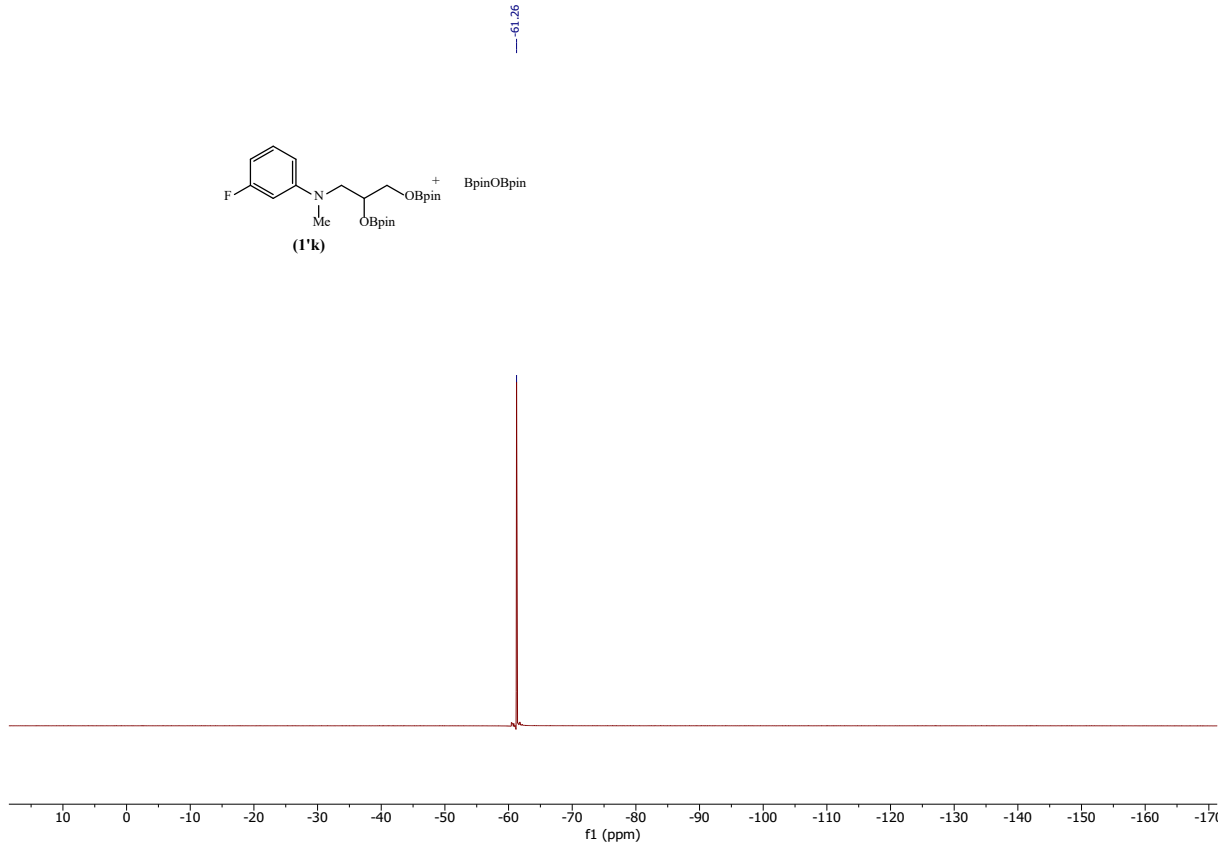



Figure S40: $^{19}F$ NMR (377 MHz, Toluene-$d_8$) of compound **1'k**

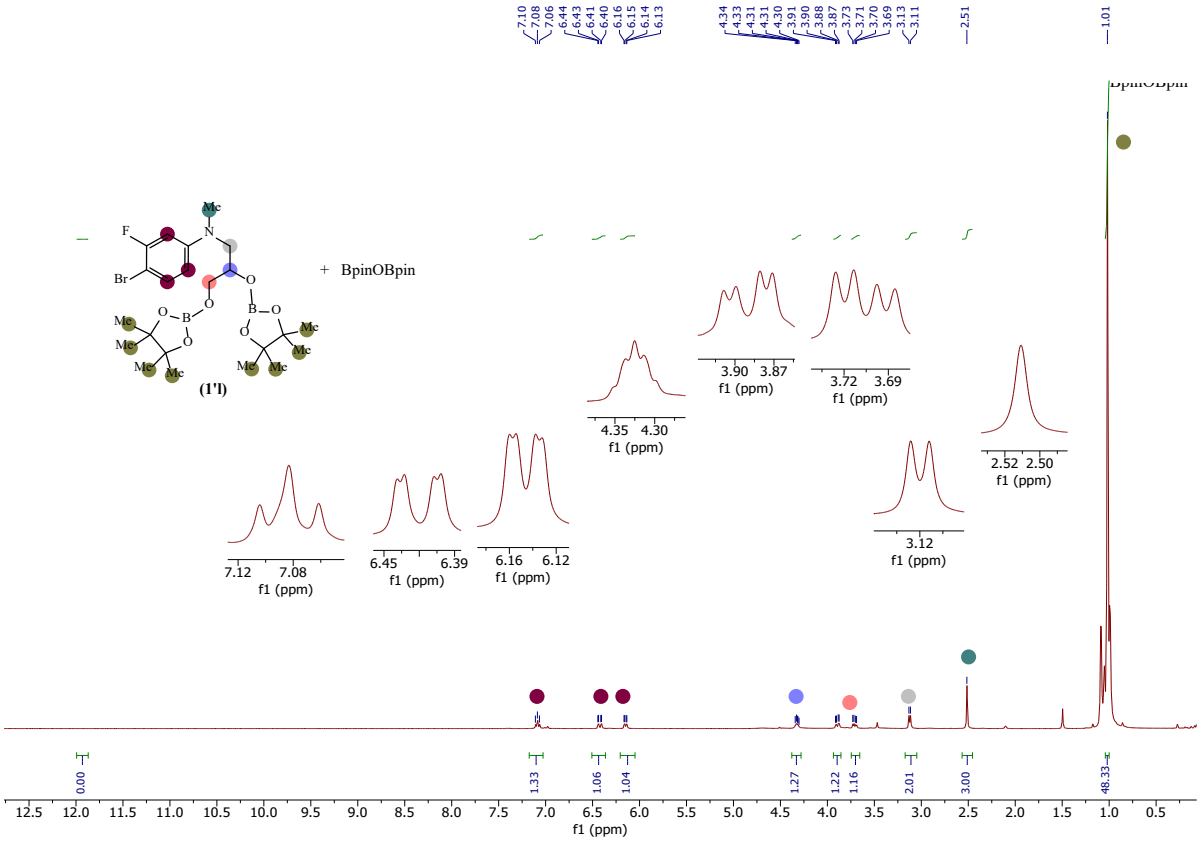



Figure S41: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'l**

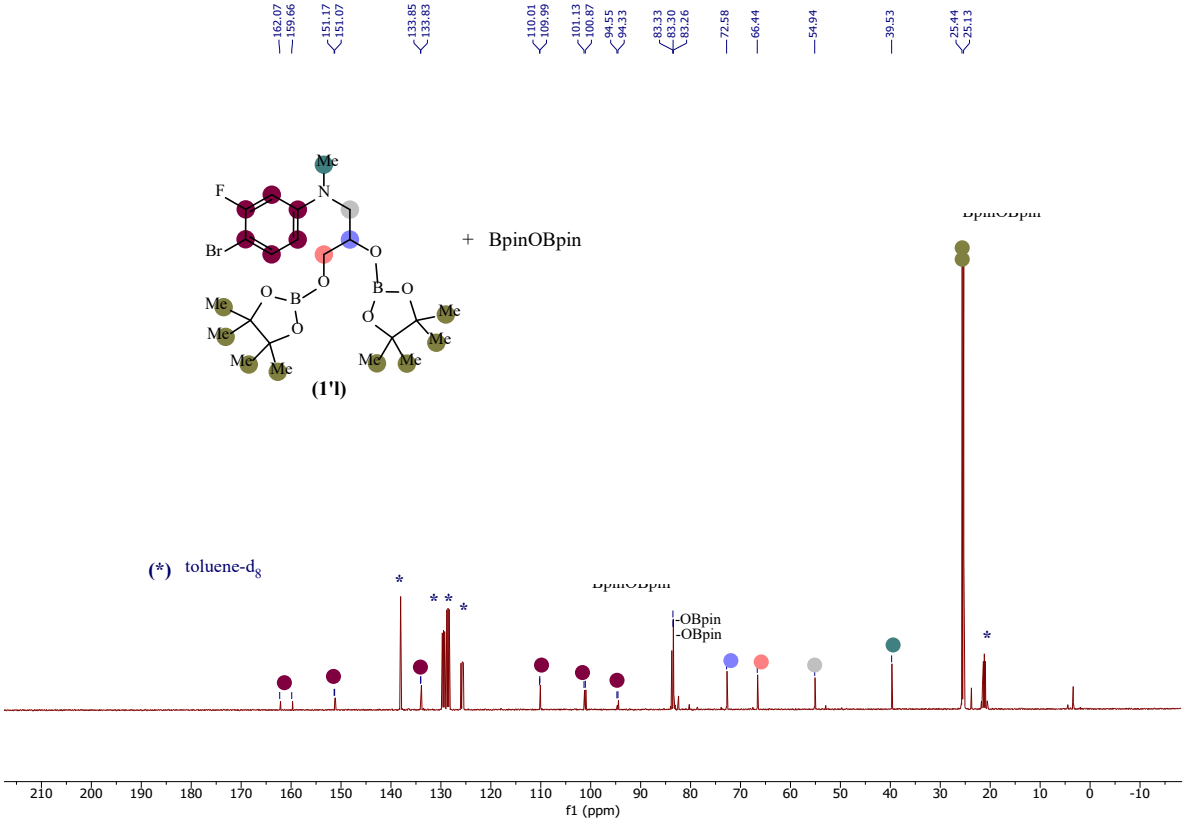



Figure S42: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'l**

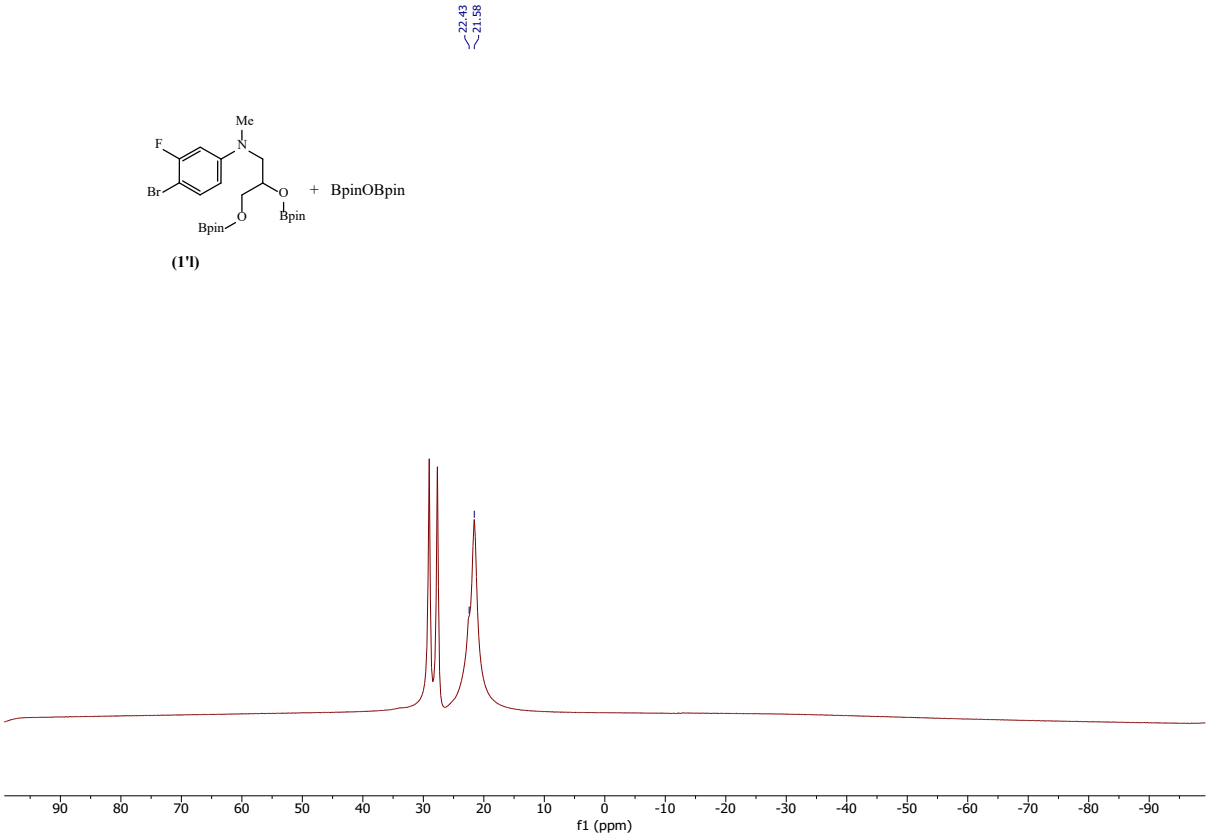



Figure S43: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'l**

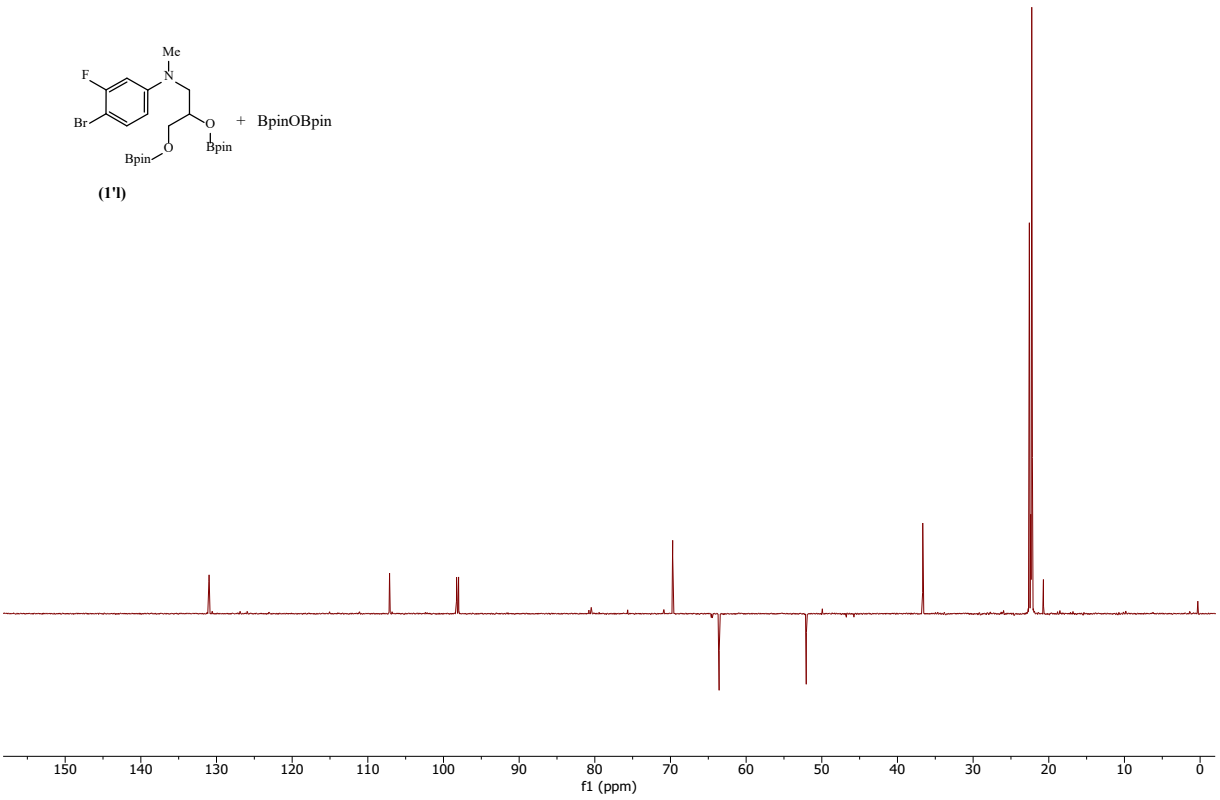



Figure S44: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'l**

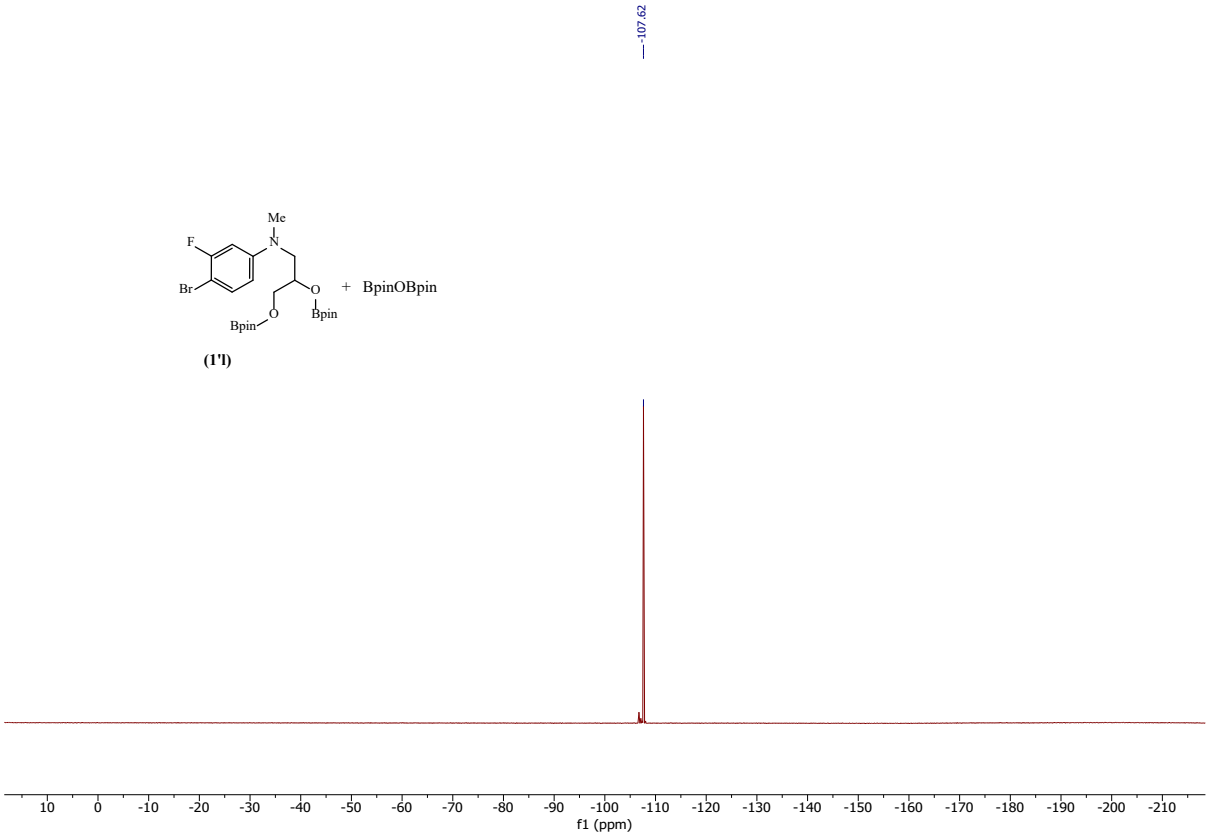



Figure S45: $^{19}$F NMR (377 MHz, Toluene-$d_8$) of compound **1'l**

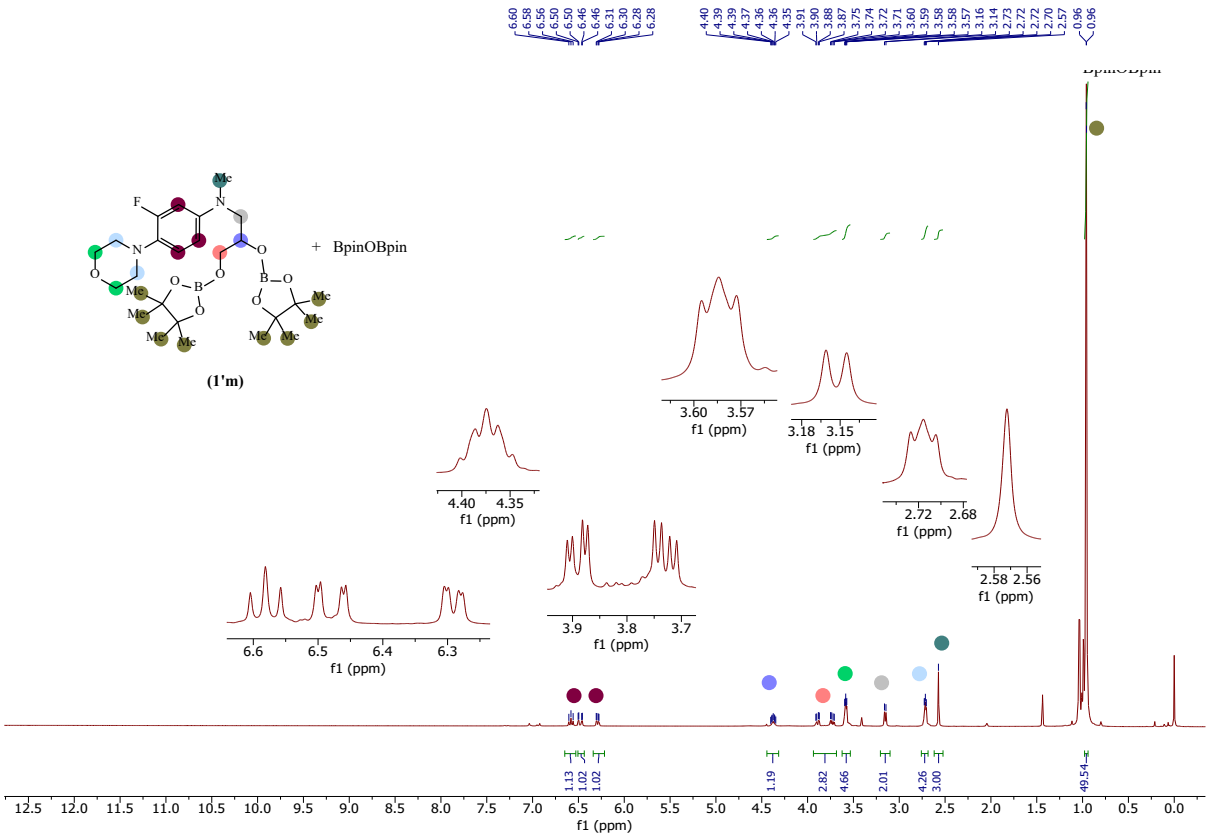



Figure S46: $^{1}$H NMR (400 MHz, Toluene-$d_8$) of compound **1'm**

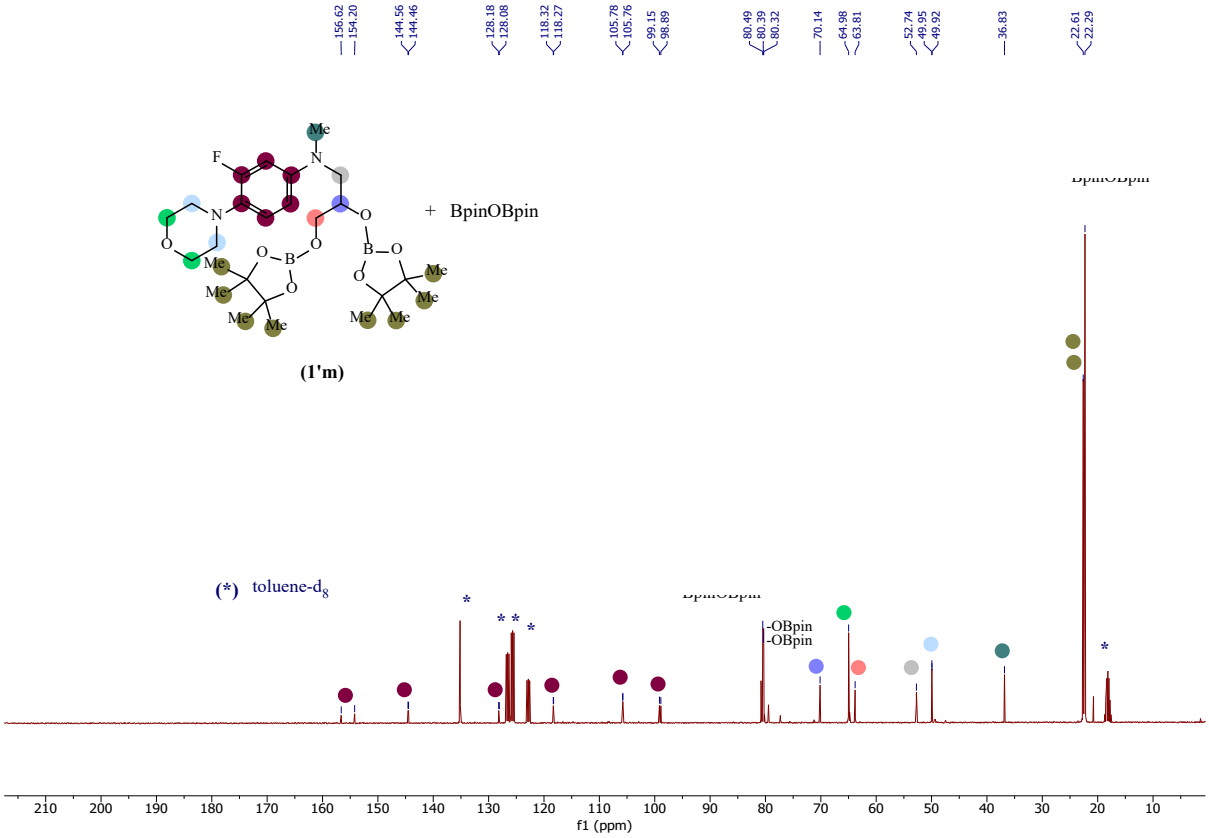



Figure S47: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'm**

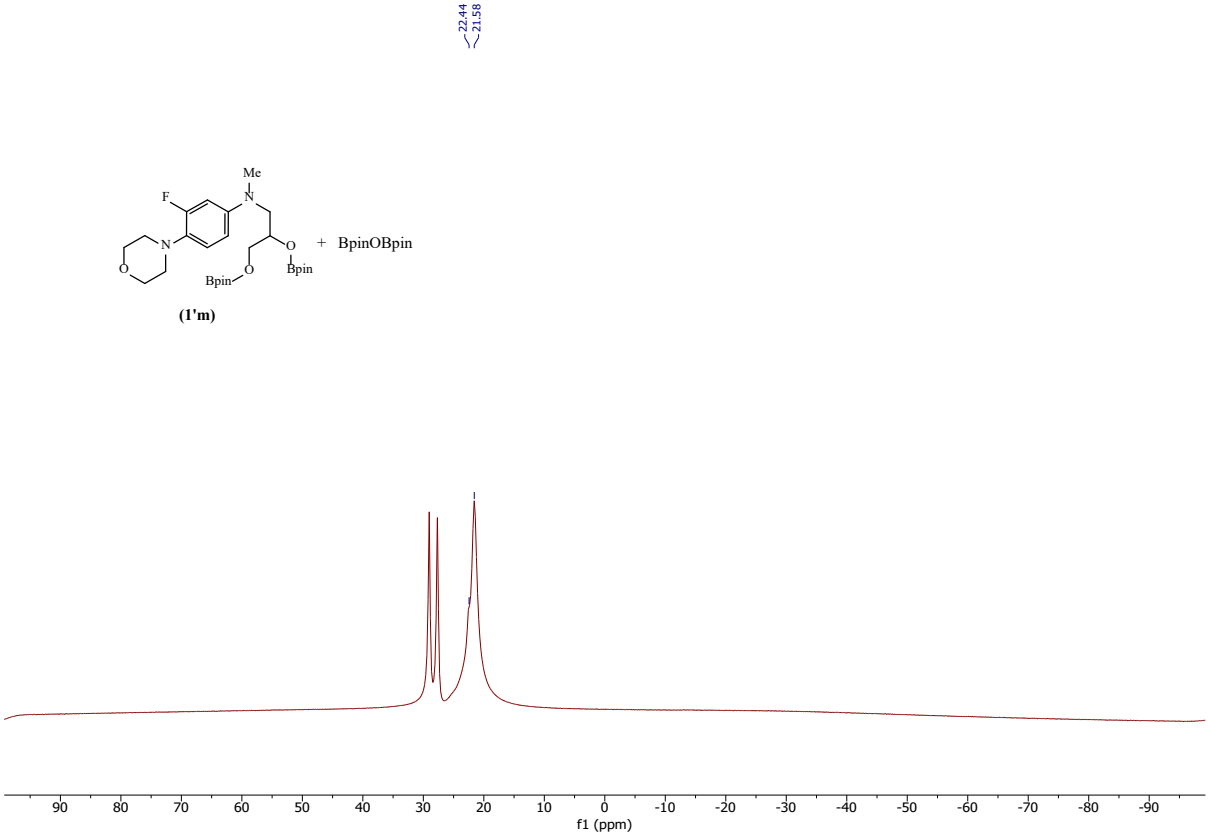



Figure S48: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'm**

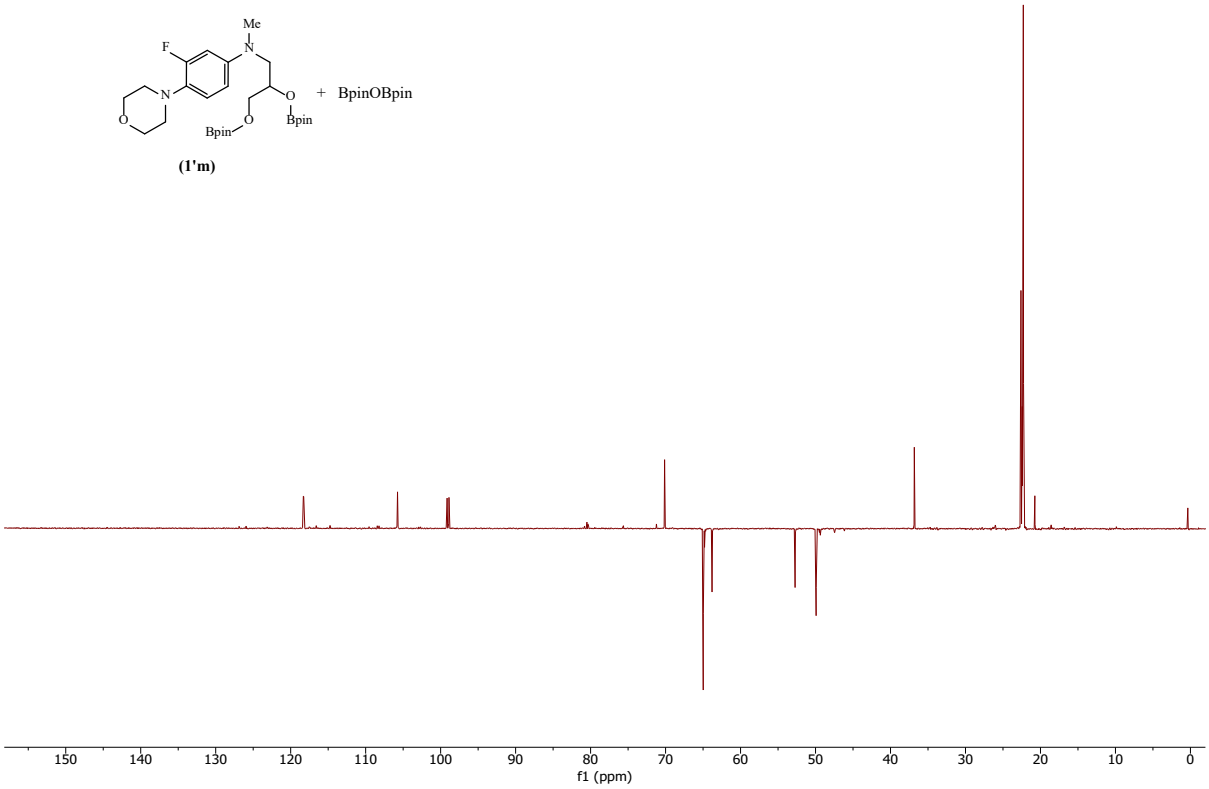



Figure S49: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'm**

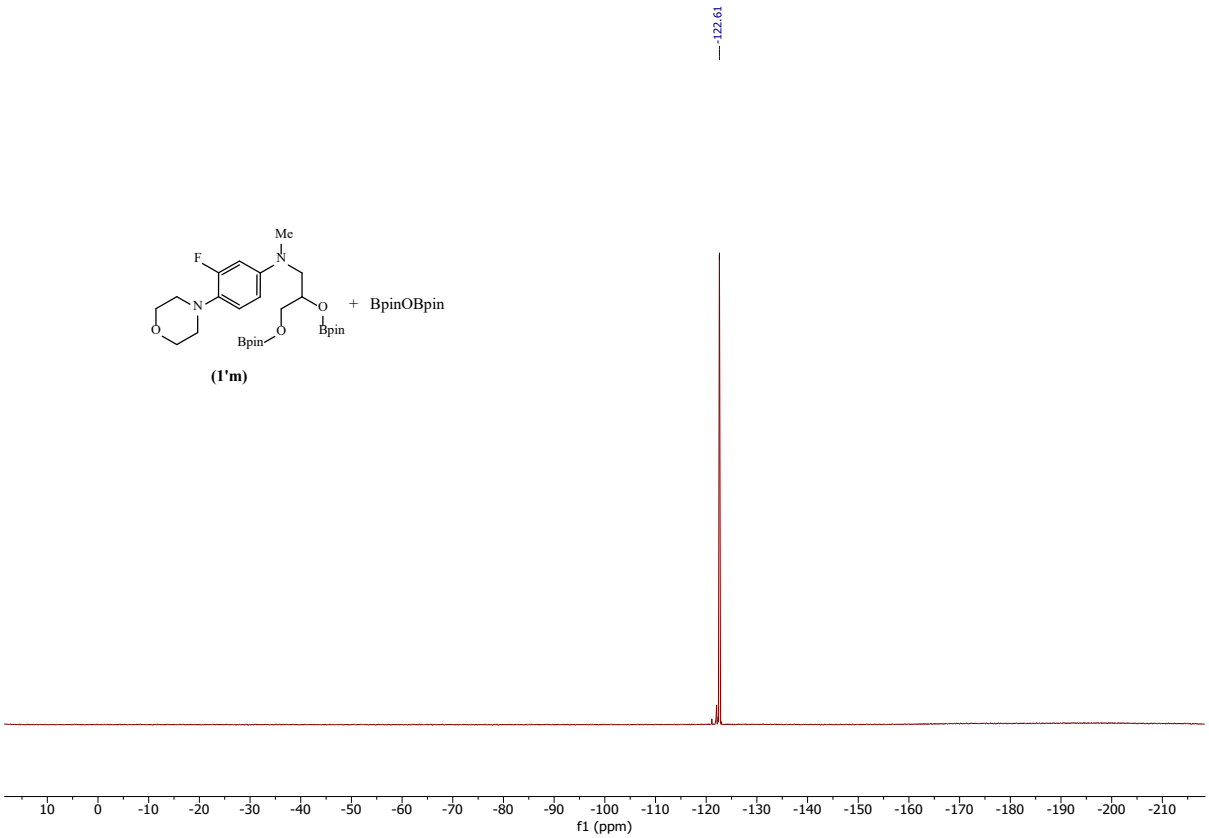



Figure S50: $^{19}F$ NMR (377 MHz, Toluene-$d_8$) of compound **1'm**

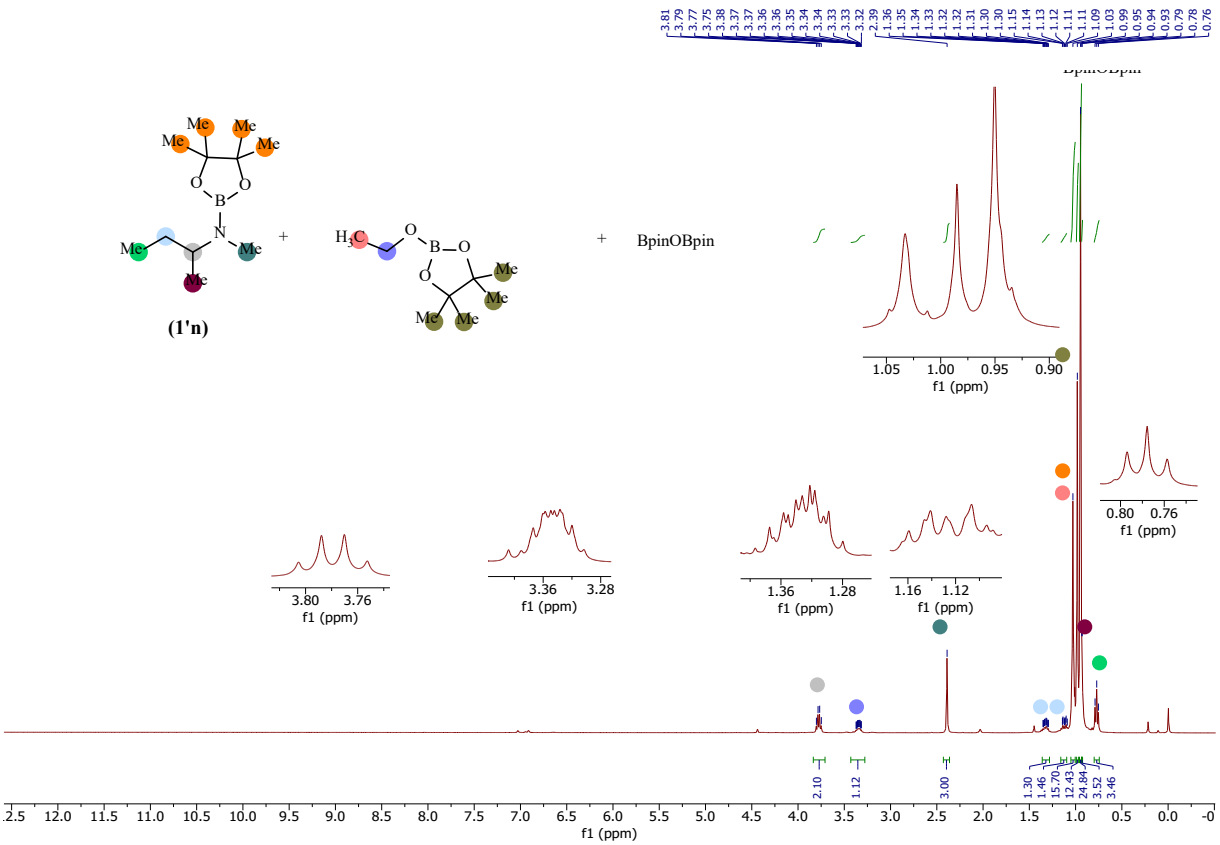



Figure S51: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'n**

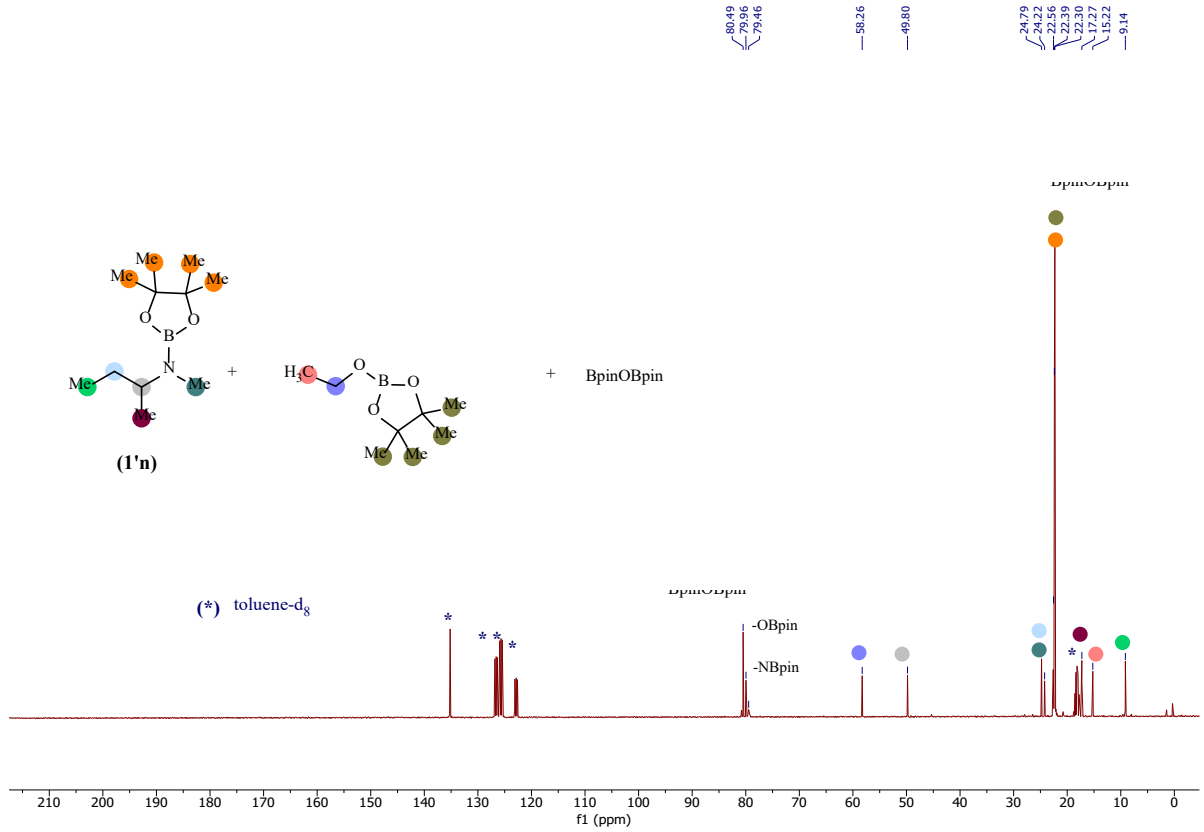



Figure S52: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'n**

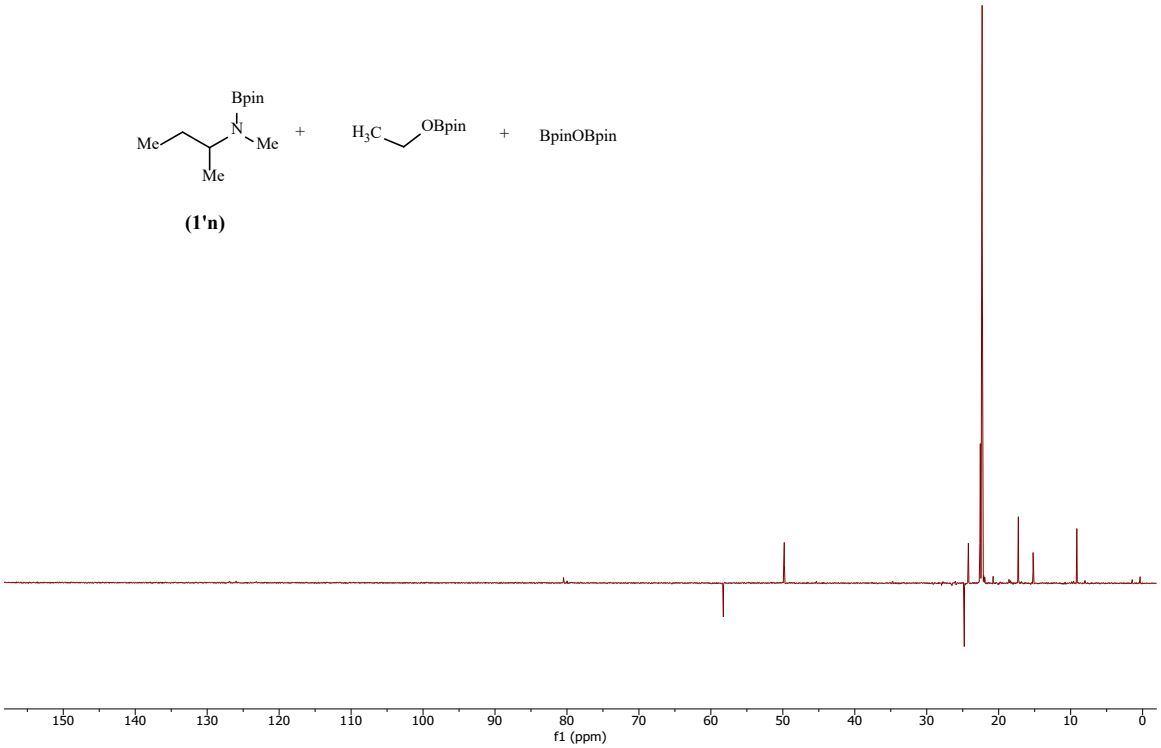



Figure S53: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'n**

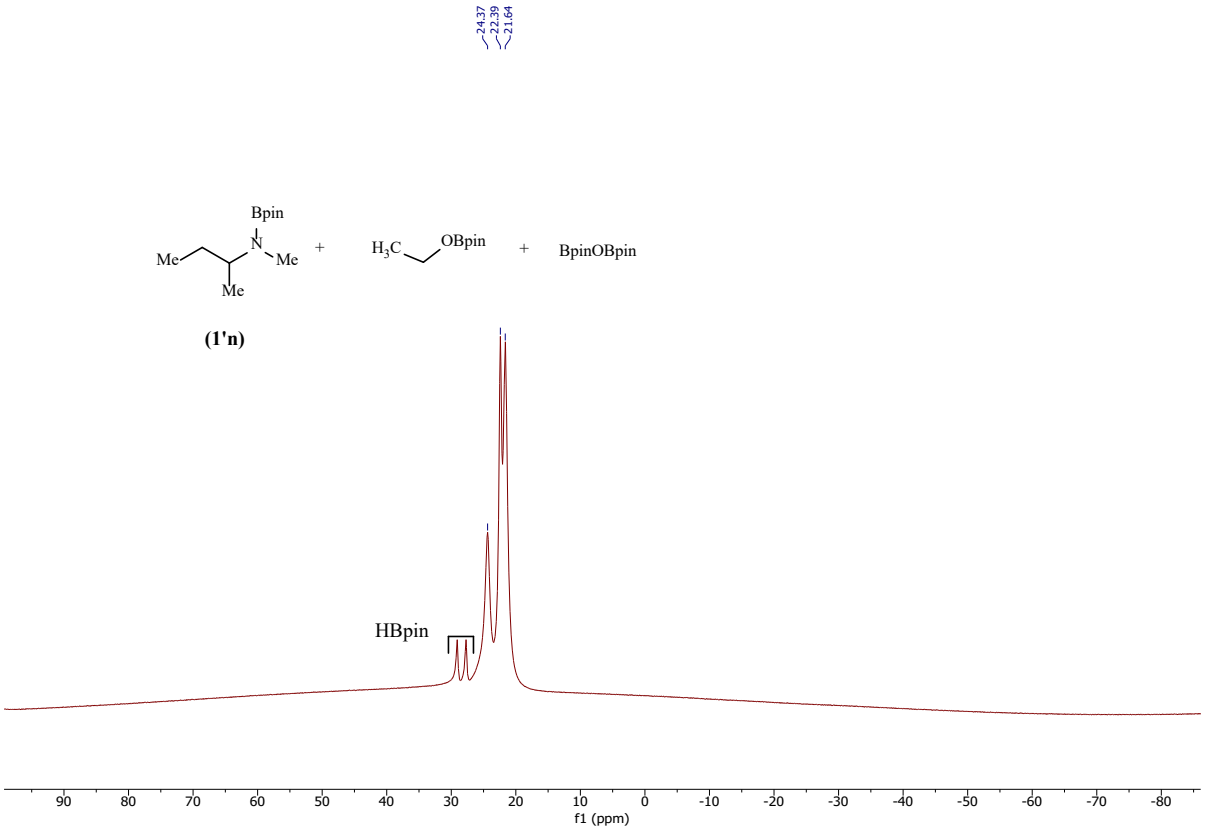



Figure S54: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'n**

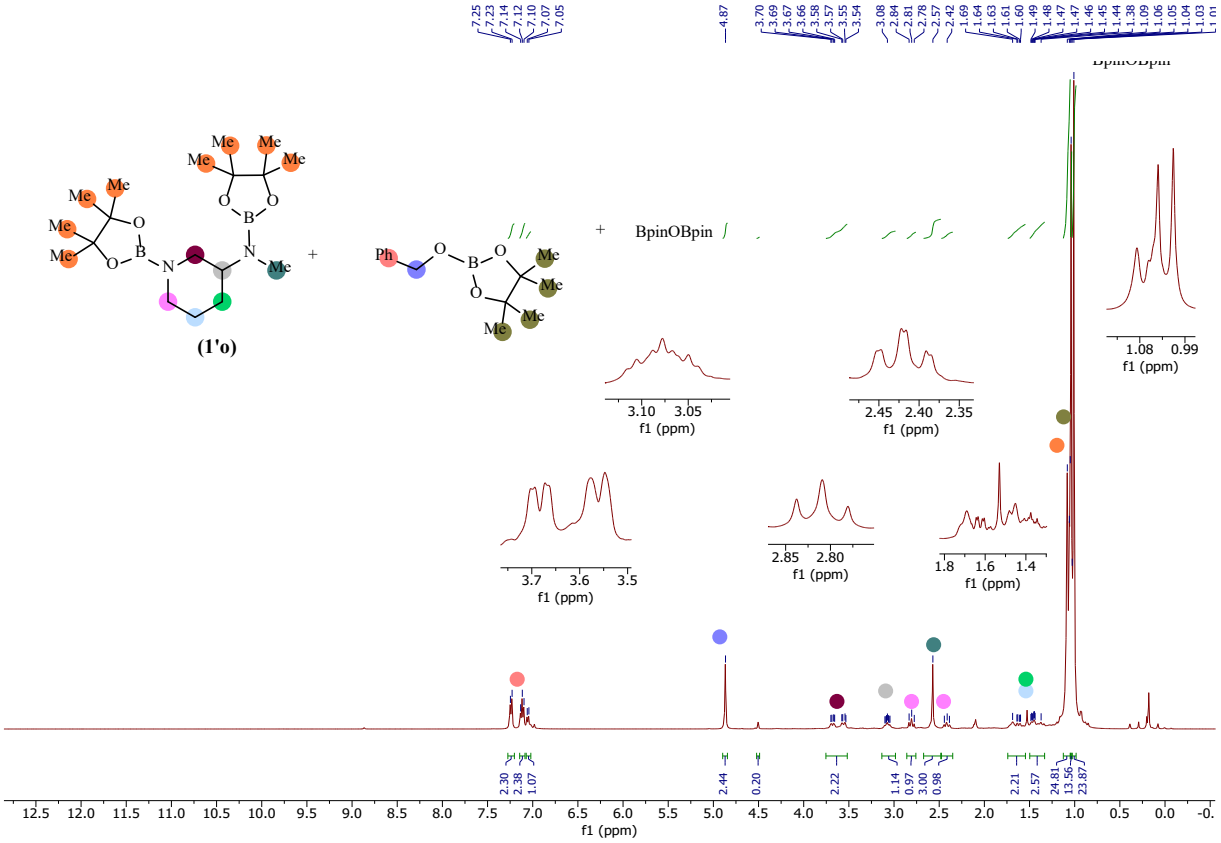



Figure S55: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'o**

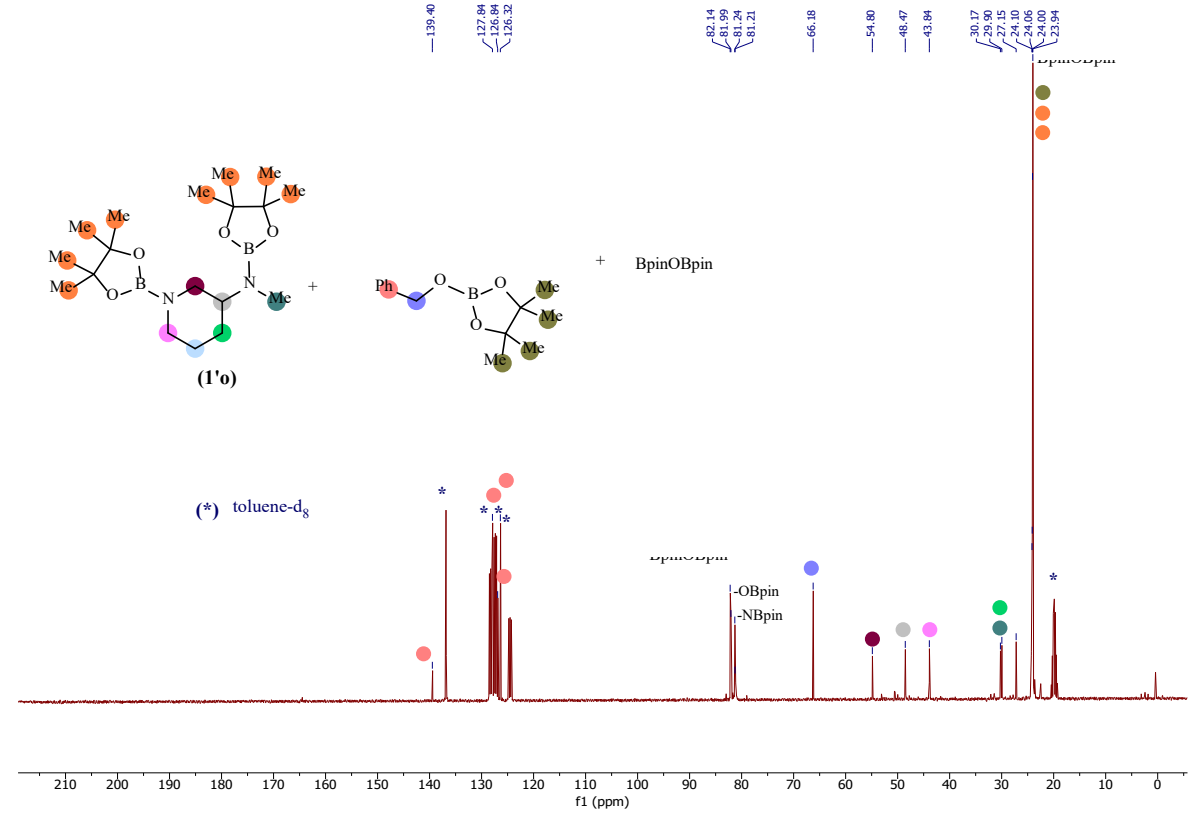



Figure S56: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'o**

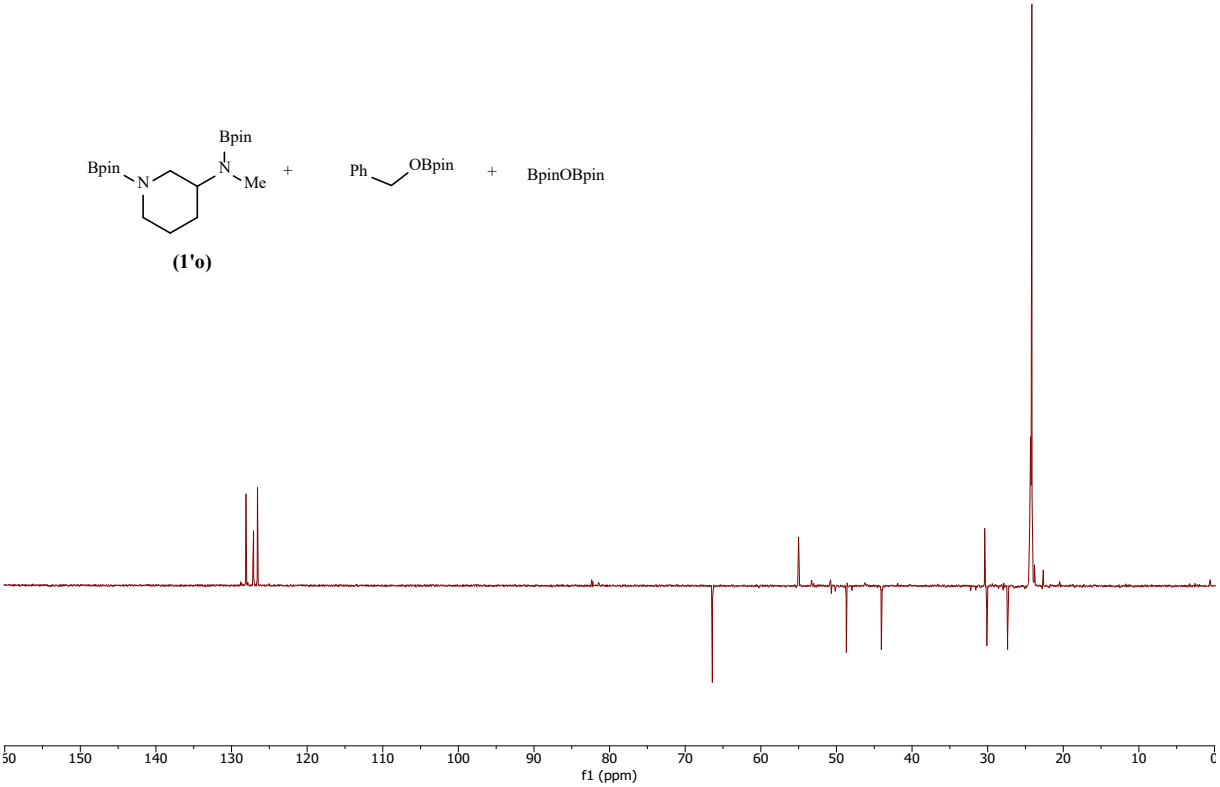



Figure S57: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'o**

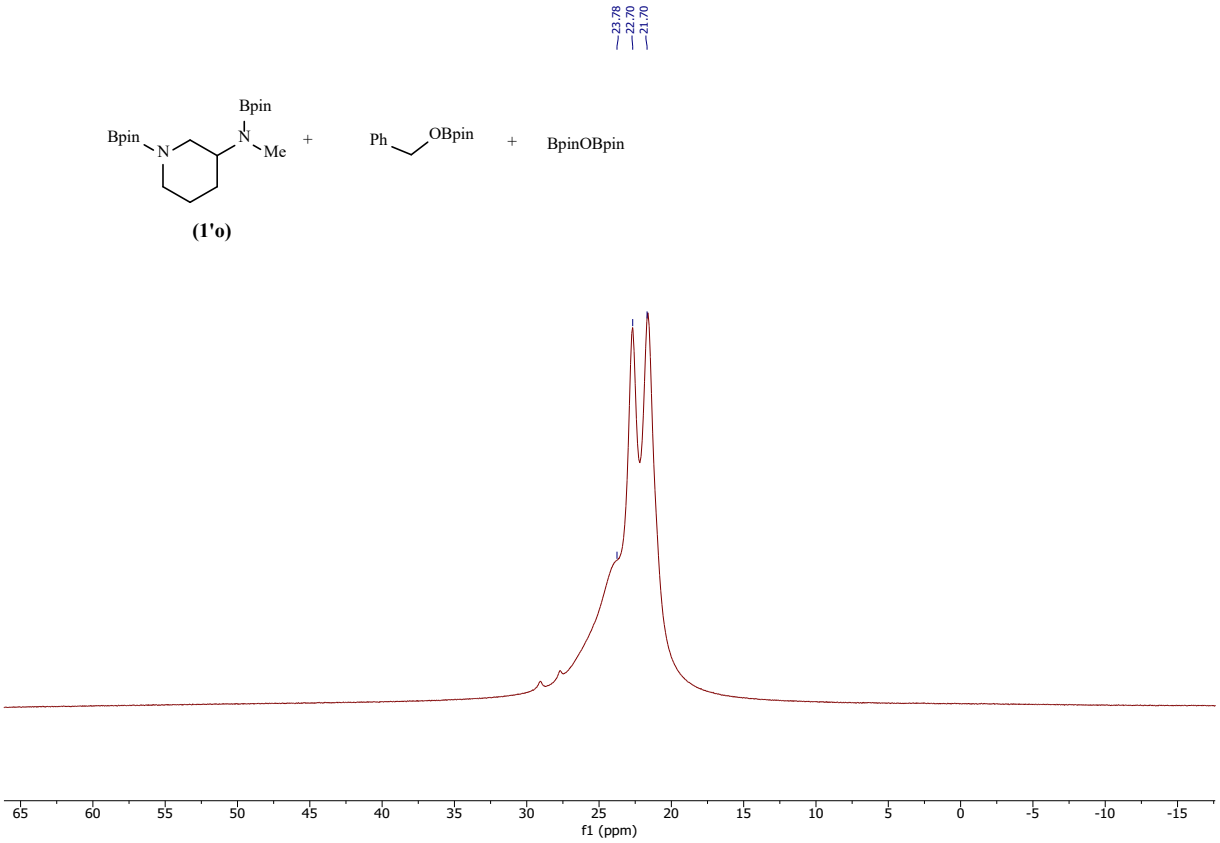



Figure S58: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'o**

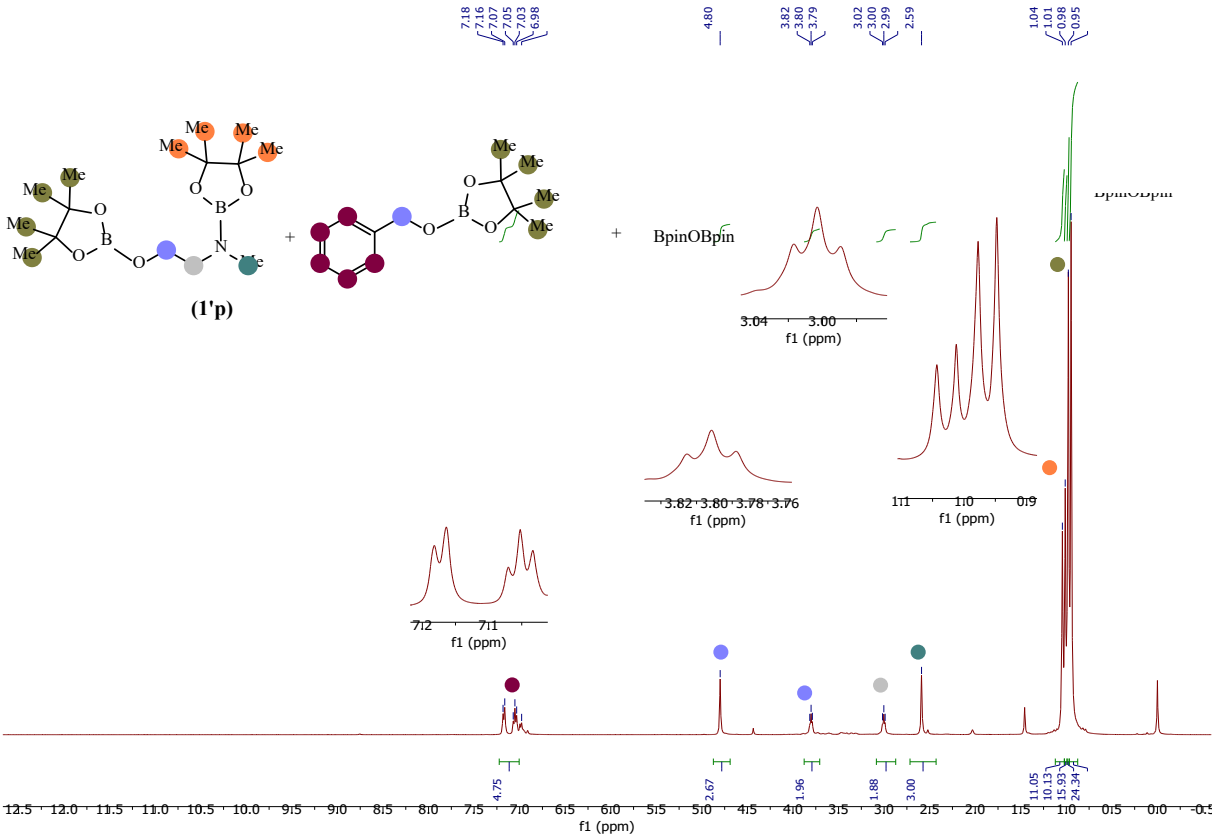



Figure S59: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'p**

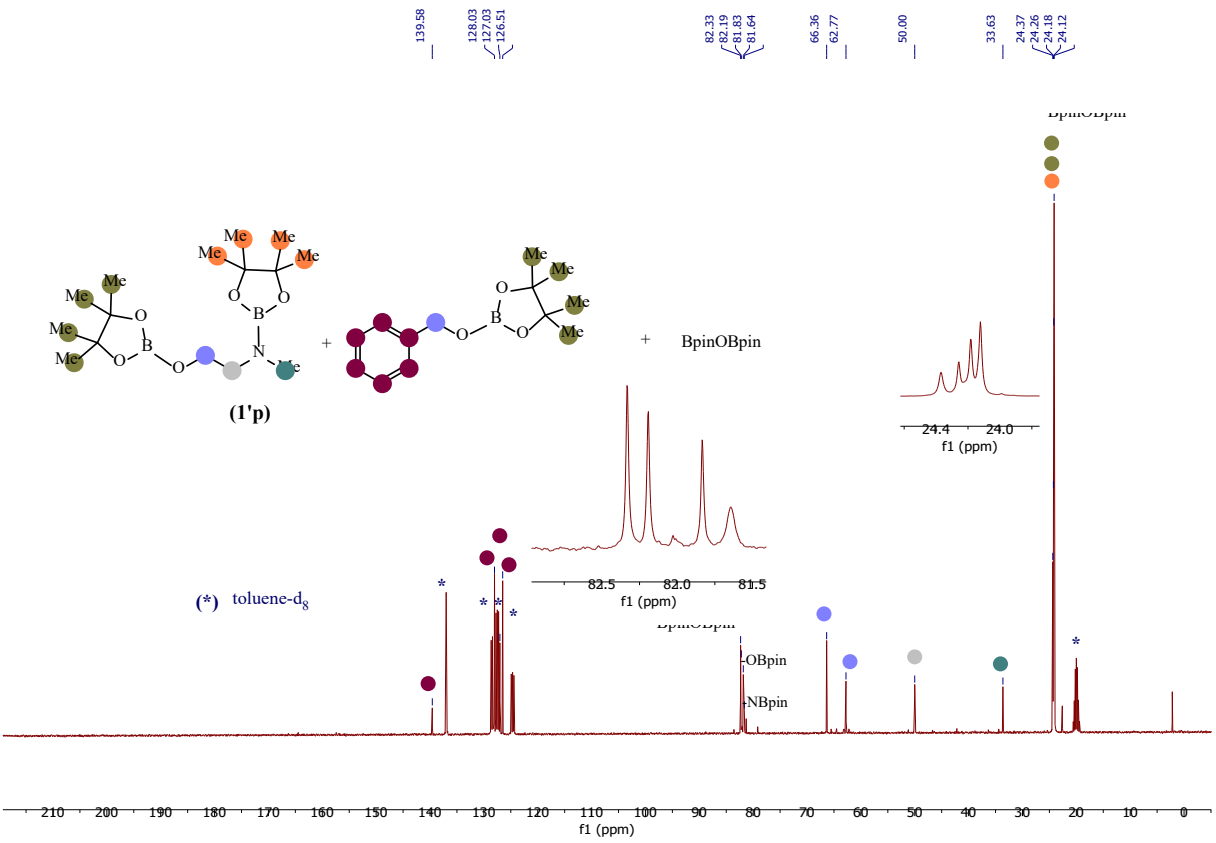



Figure S60: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'p**

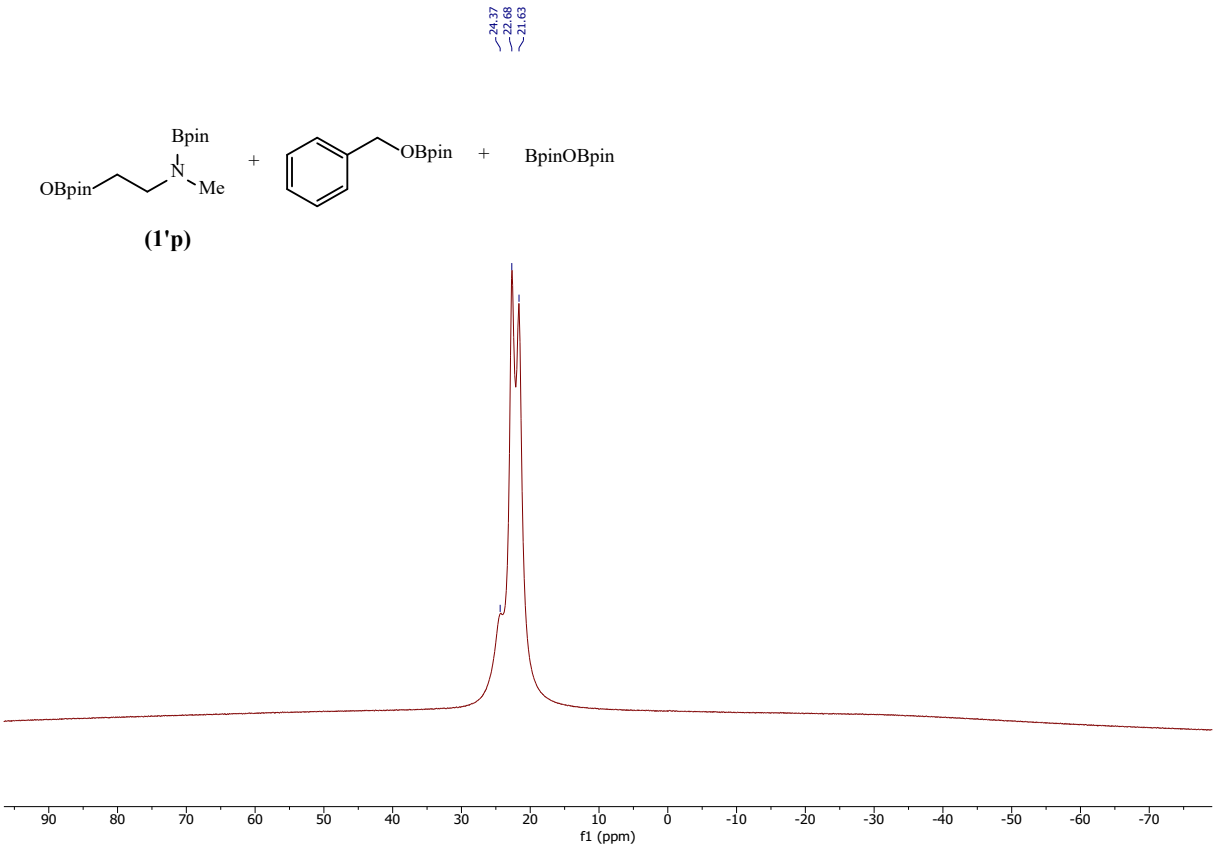



Figure S61: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'p**

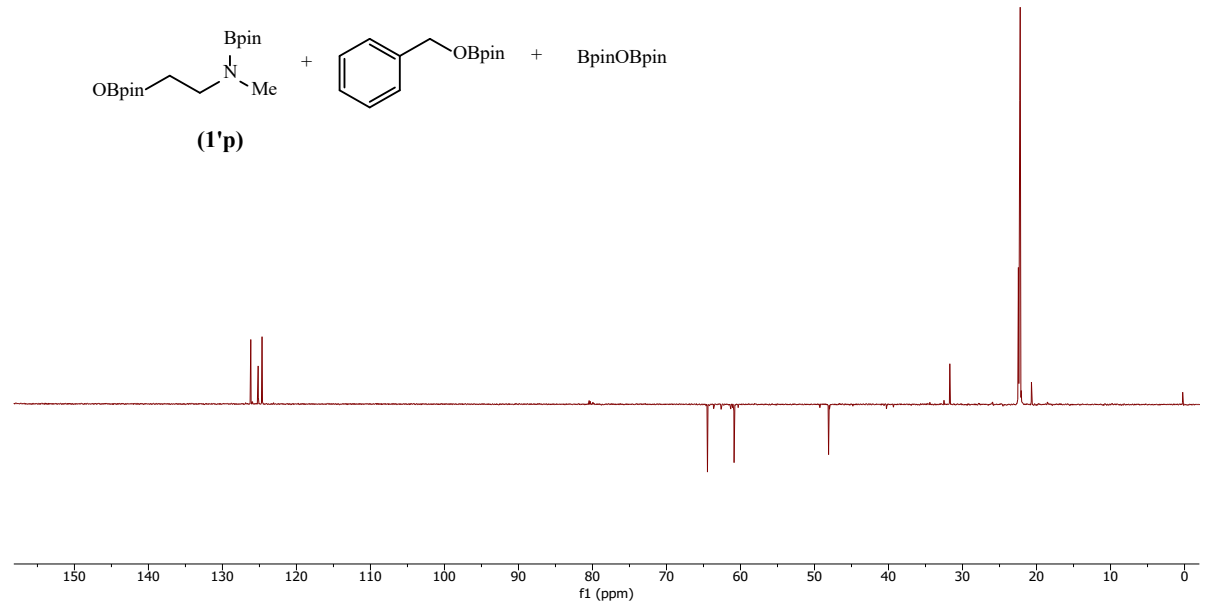



Figure S62: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'p**

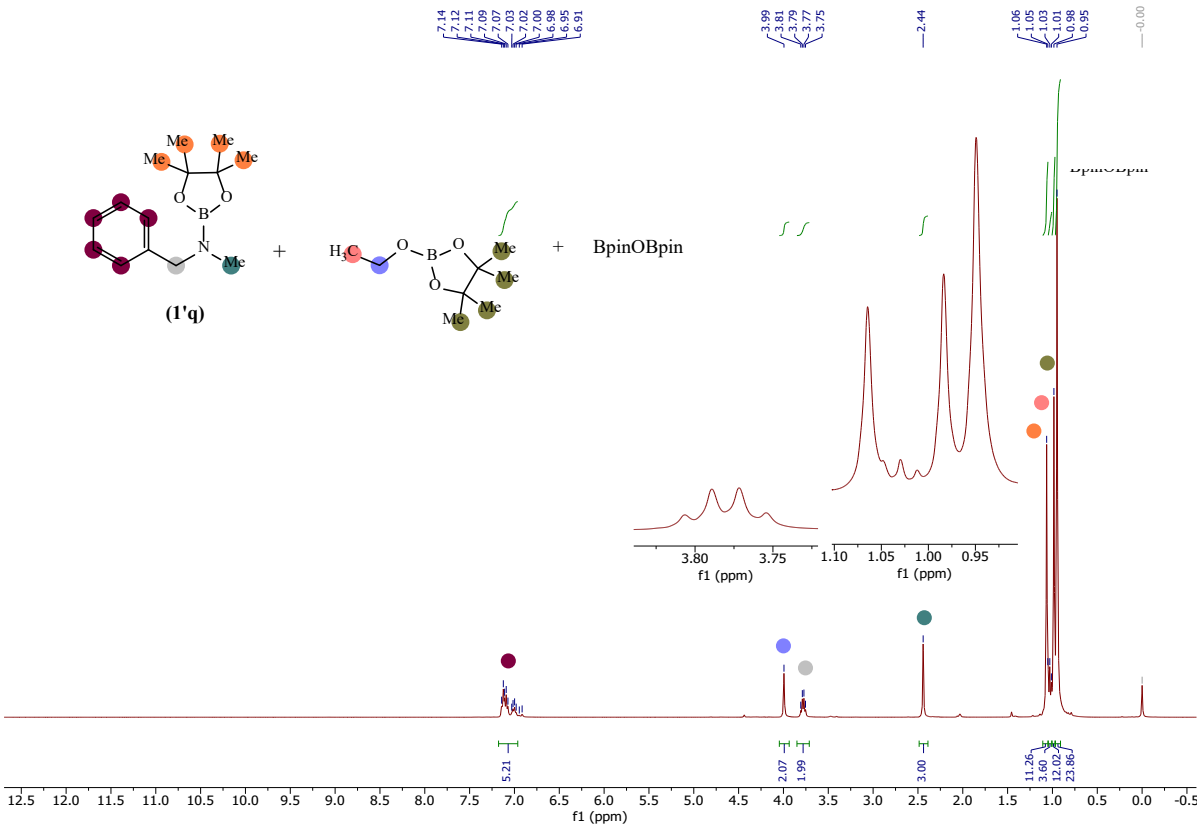



Figure S63: $^{1}$H NMR (400 MHz, Toluene-$d_8$) of compound **1'q**

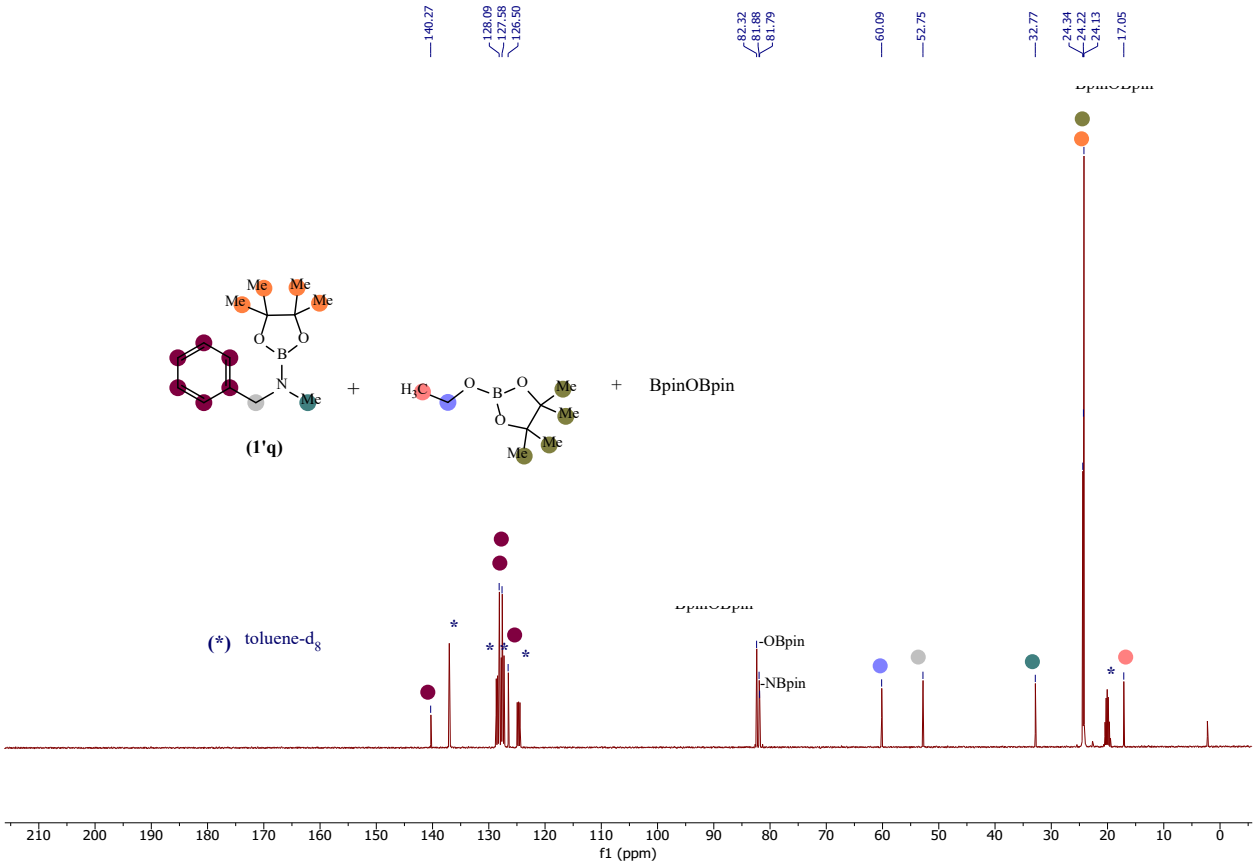



Figure S64: $^{13}$C{$^{1}$H} NMR (101 MHz, Toluene-$d_8$) of compound **1'q**

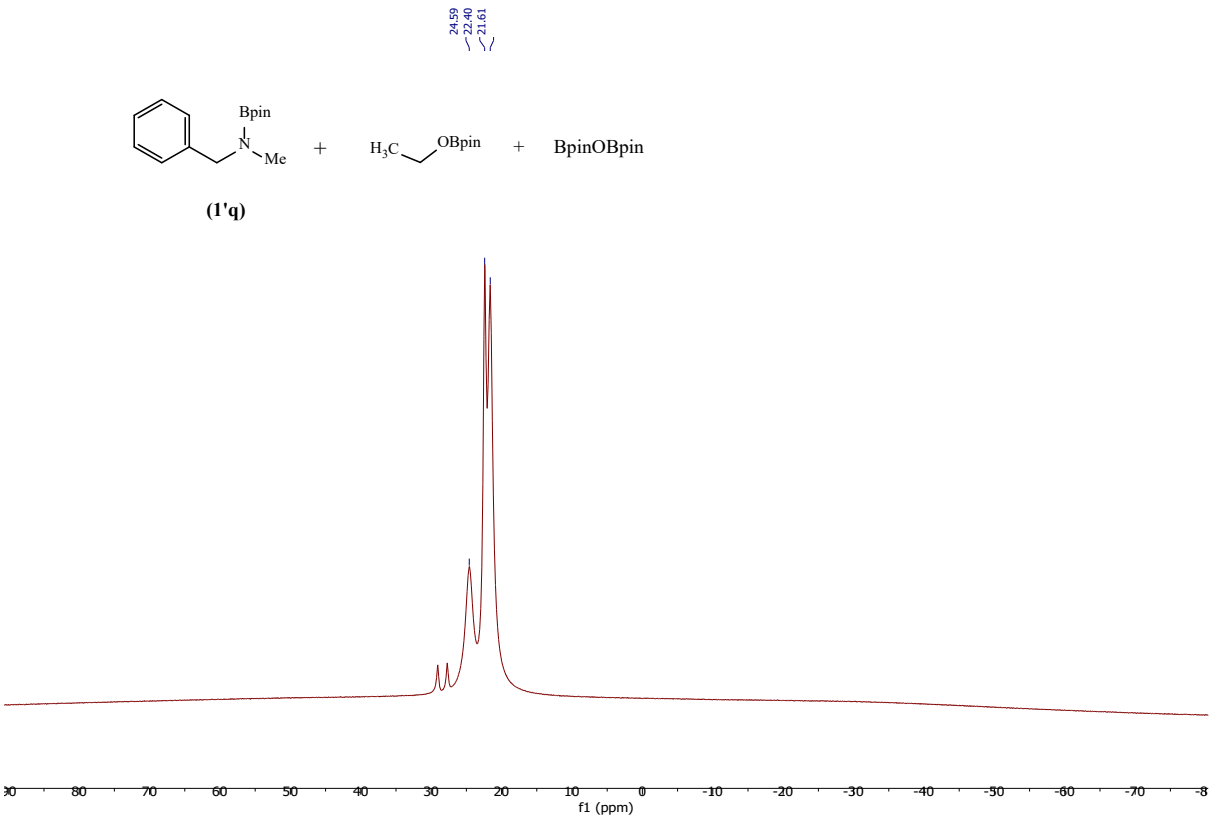



Figure S65: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'q**

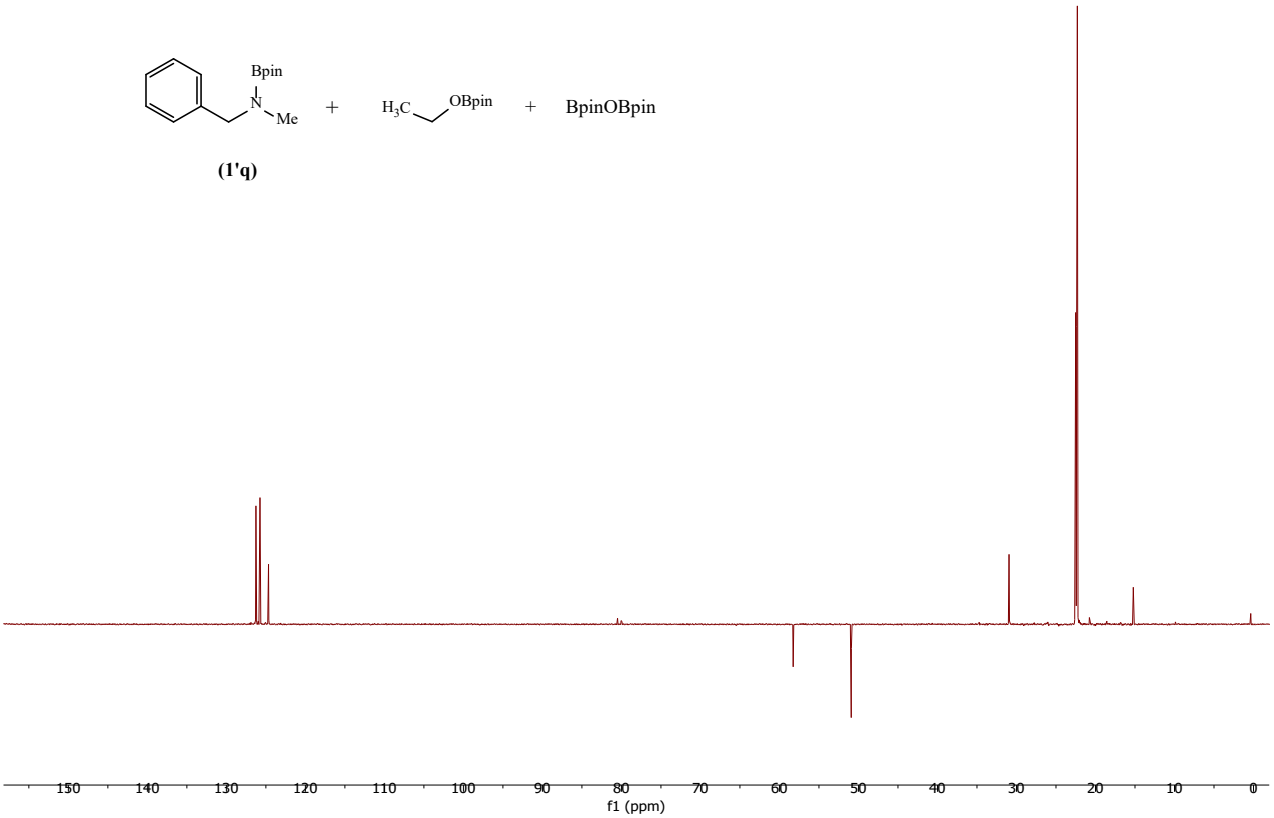



Figure S66: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'q**

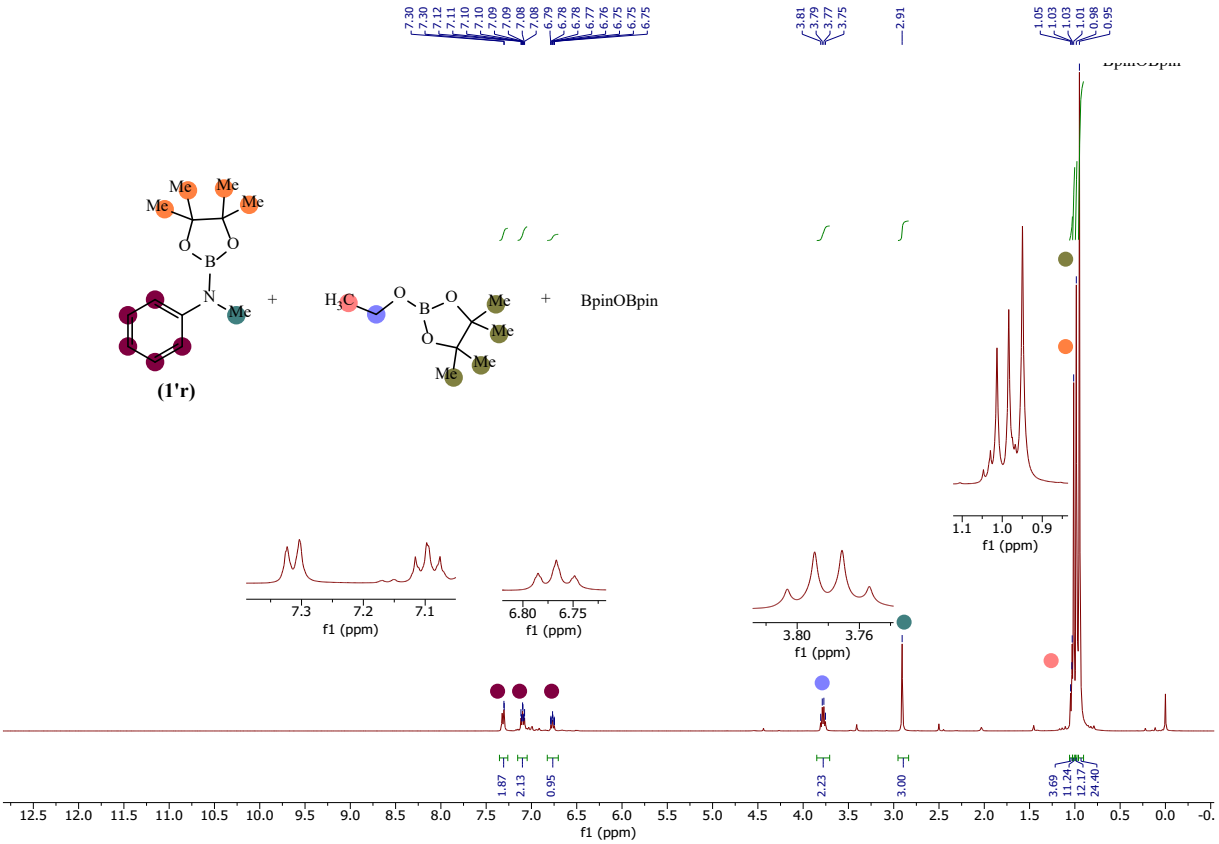



Figure S67: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'r**

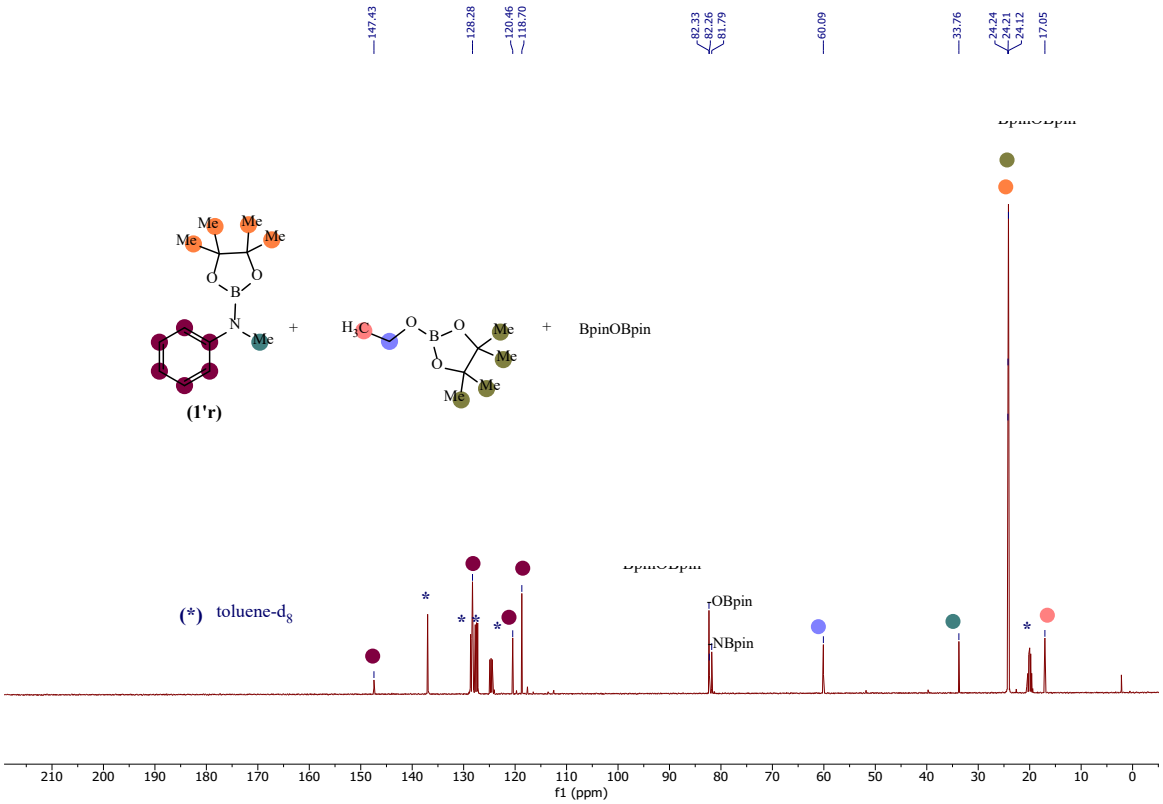



Figure S68: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'r**

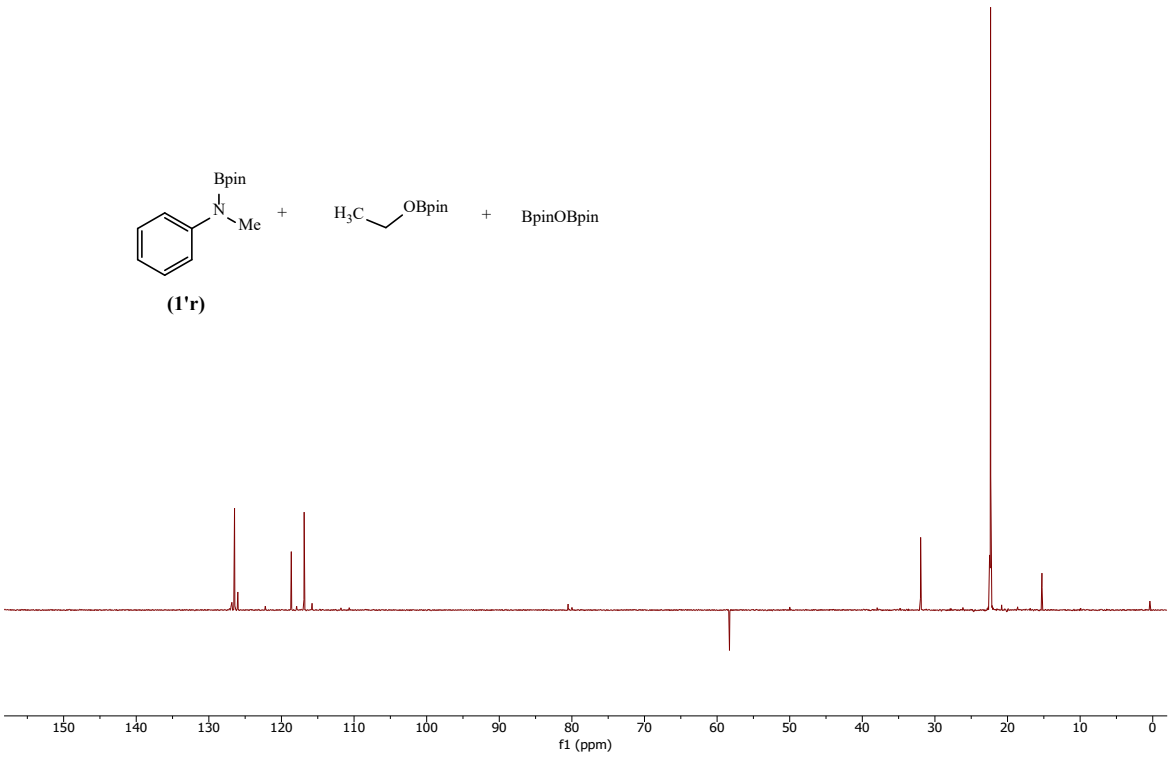



Figure S69: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'r**

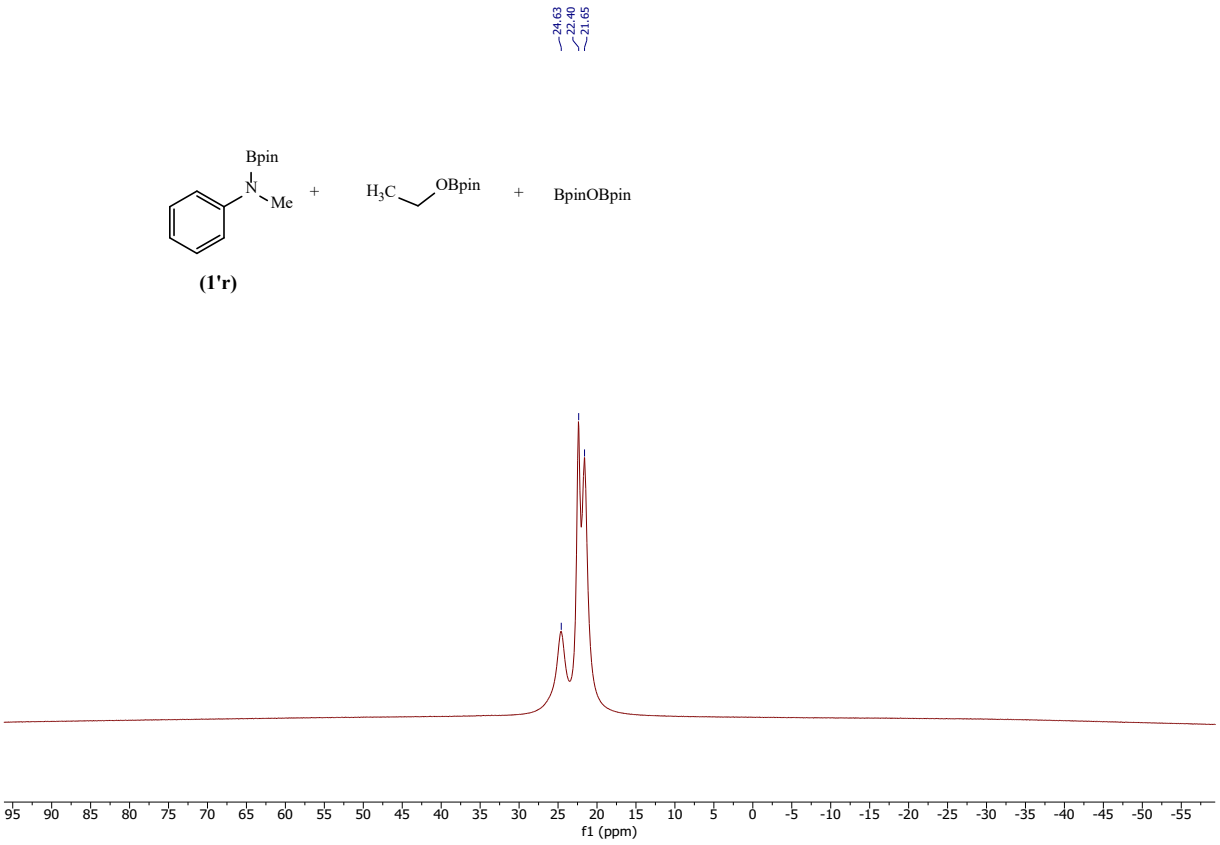



Figure S70: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'r**

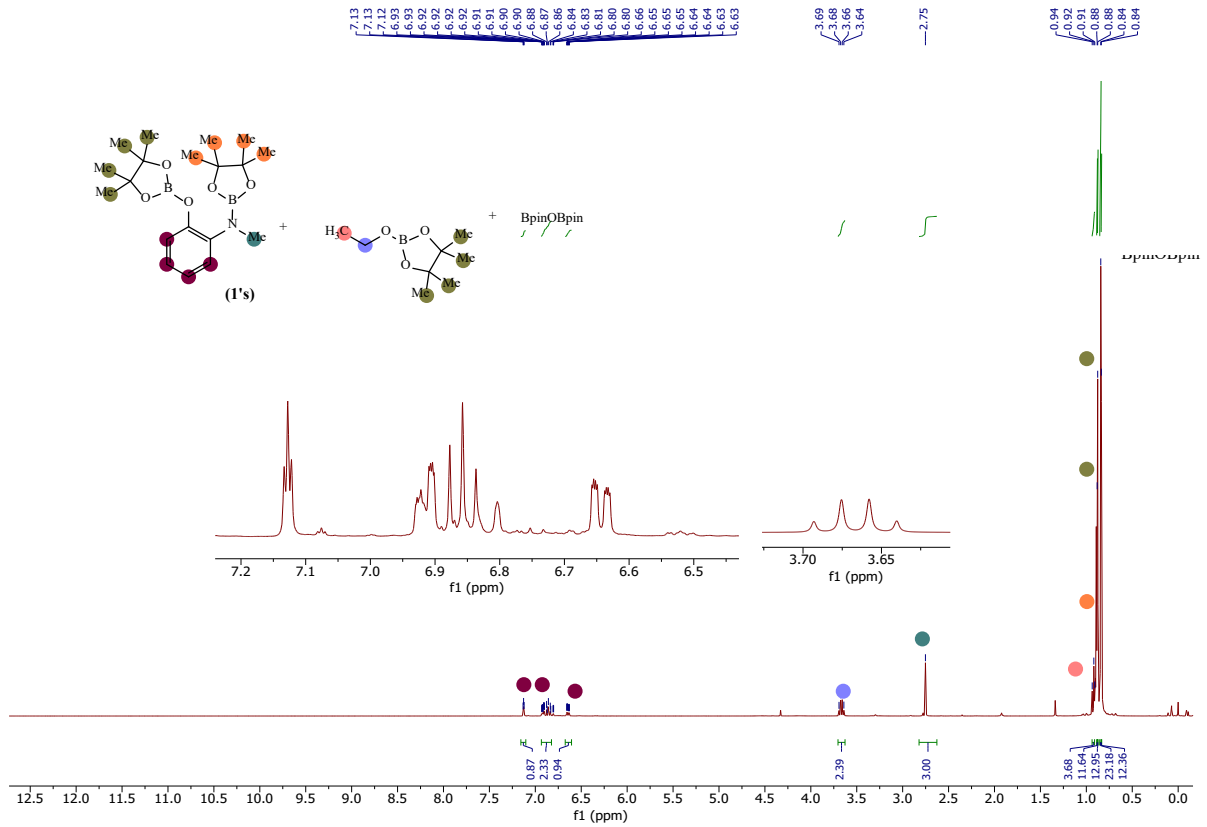



Figure S71: $^{1}$H NMR (400 MHz, Toluene-$d_8$) of compound **1's**

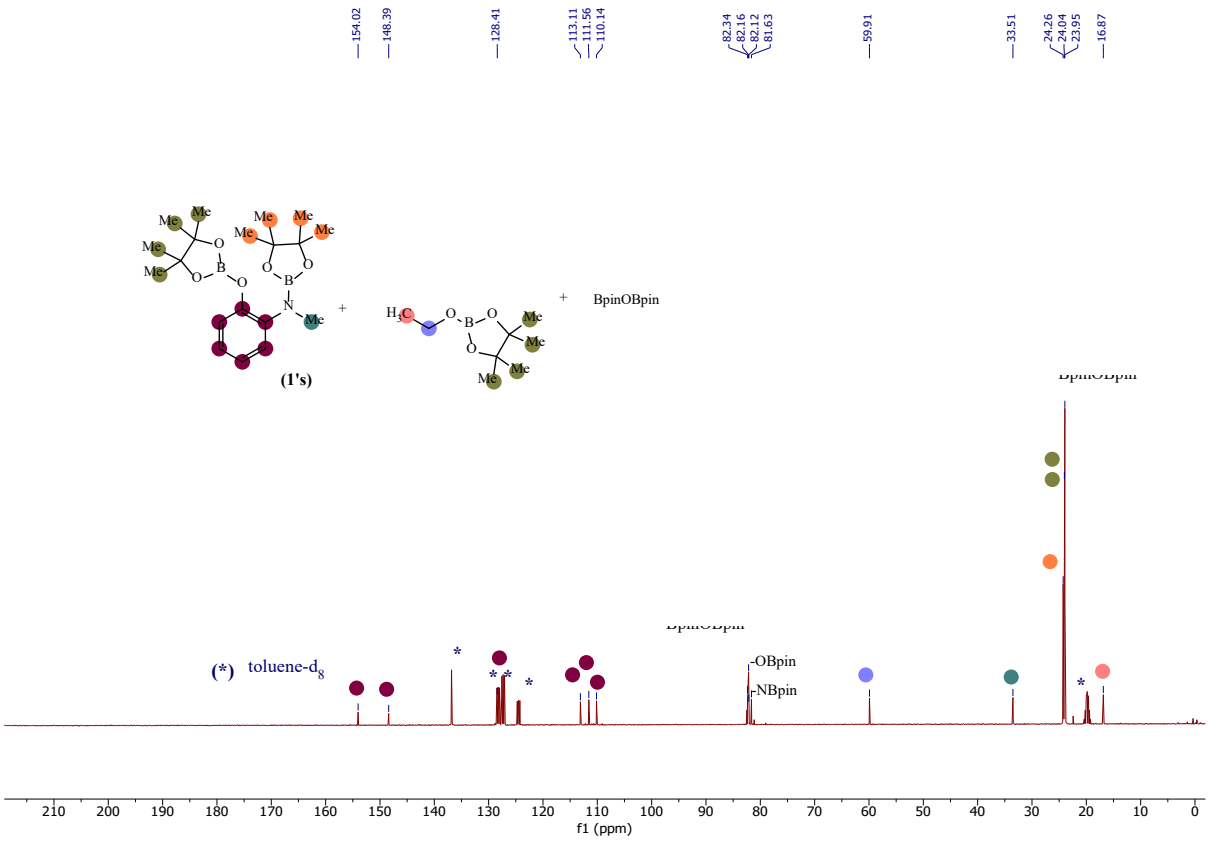



Figure S72: $^{13}$C{$^{1}$H} NMR (101 MHz, Toluene-$d_8$) of compound **1's**

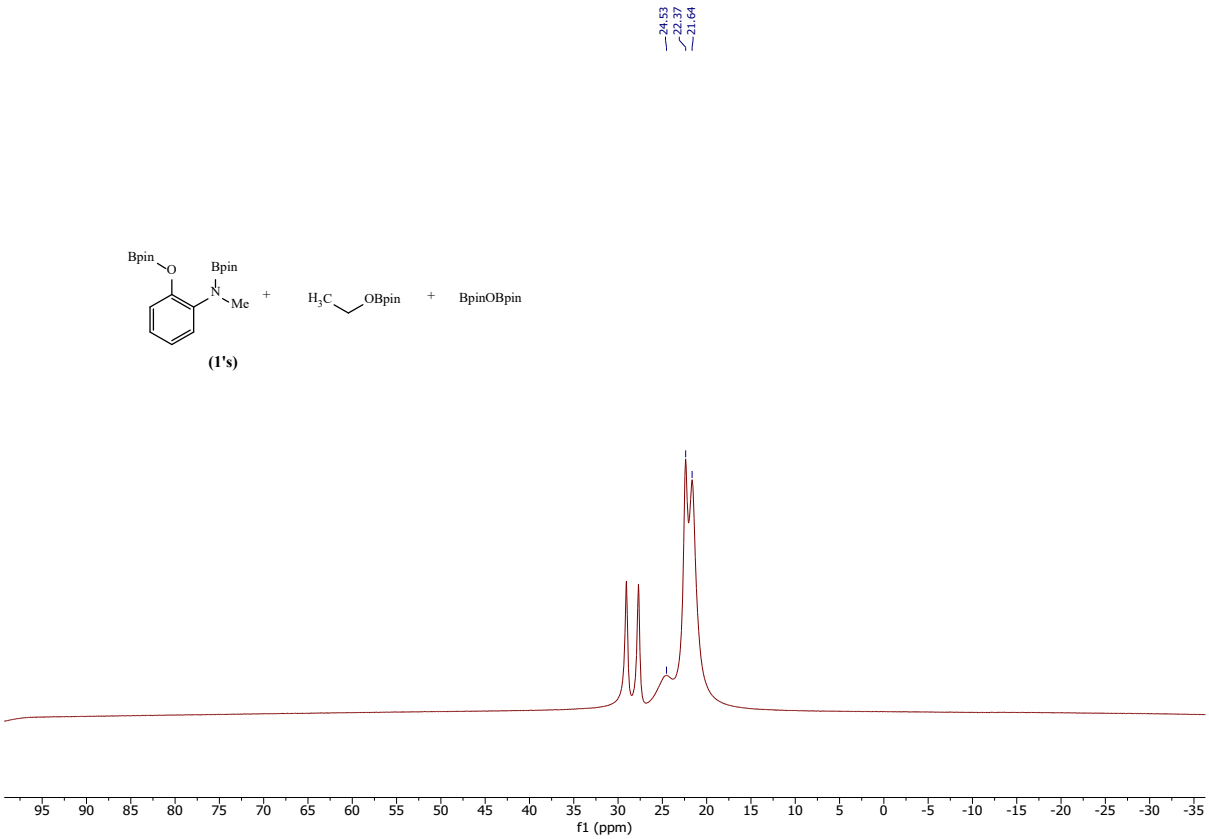



Figure S73: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1's**

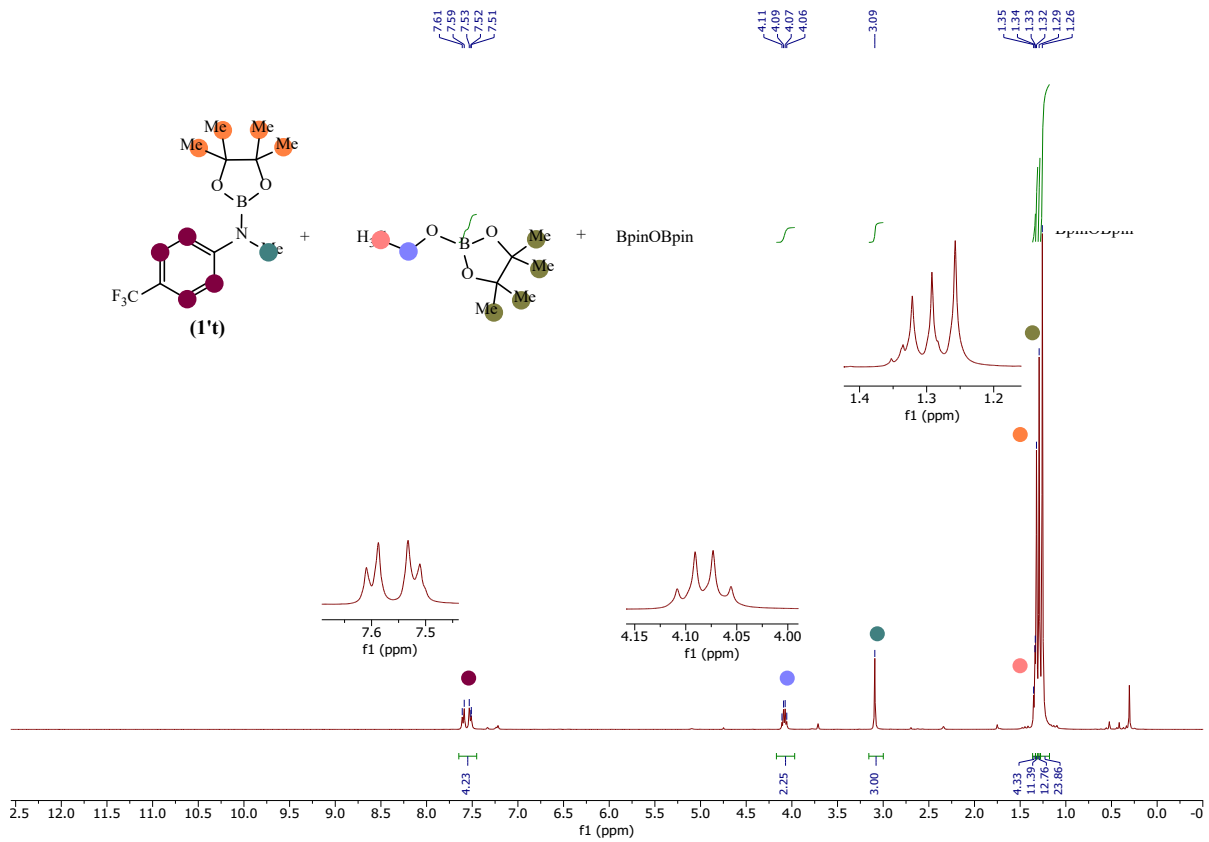



Figure S74: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1't**

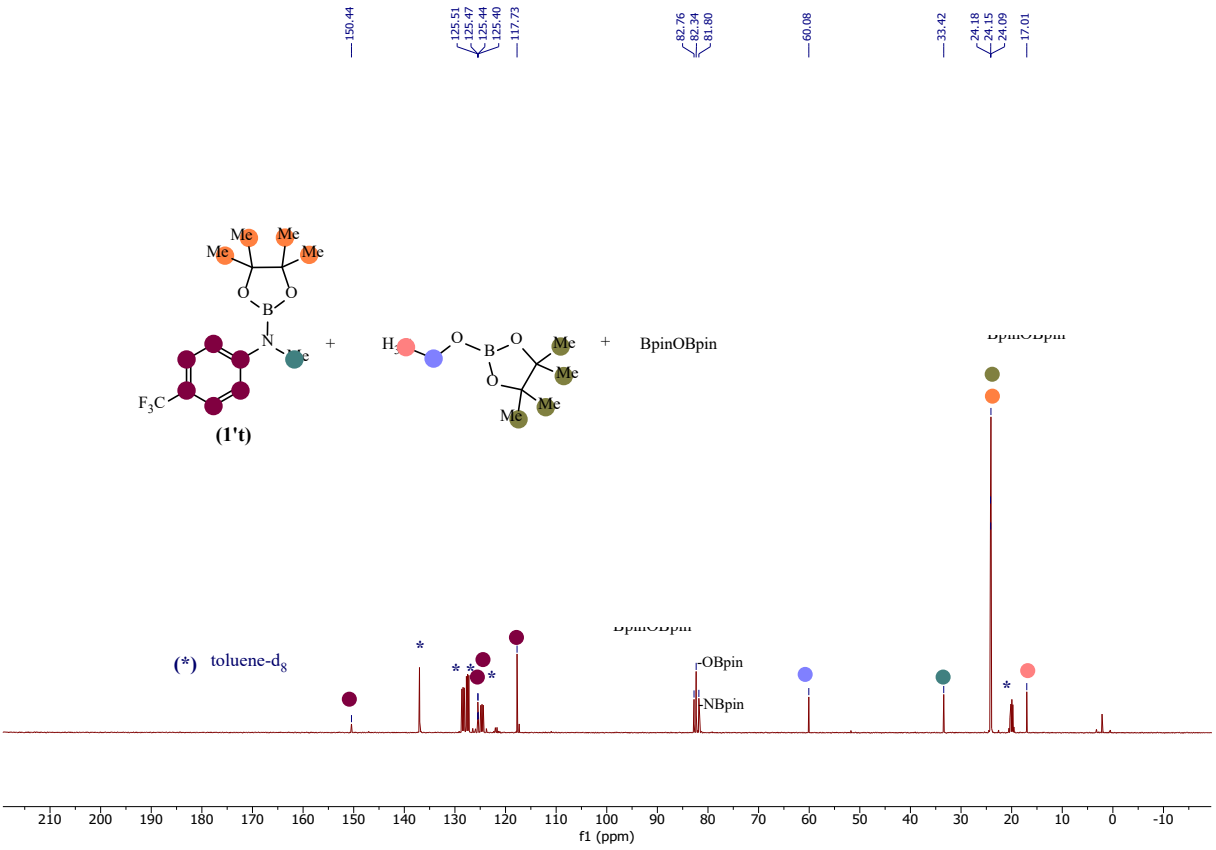



Figure S75: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1't**

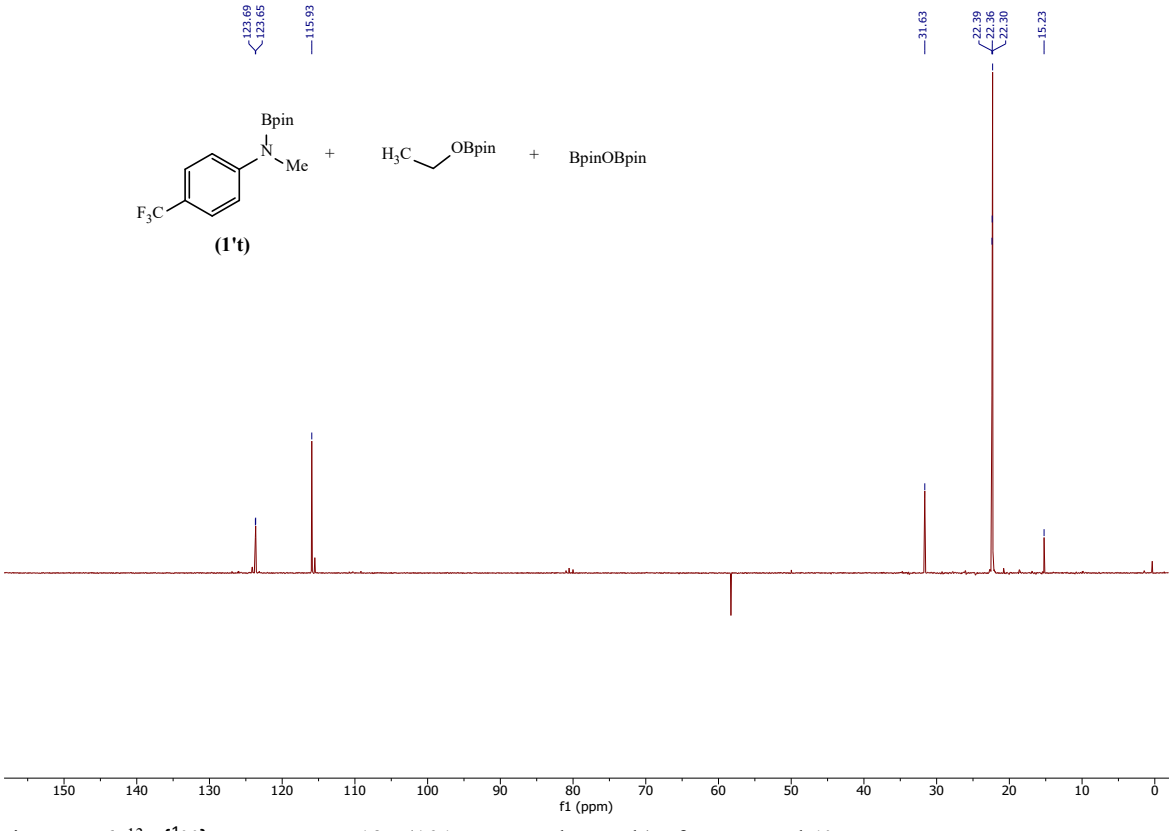



Figure S76: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1't**

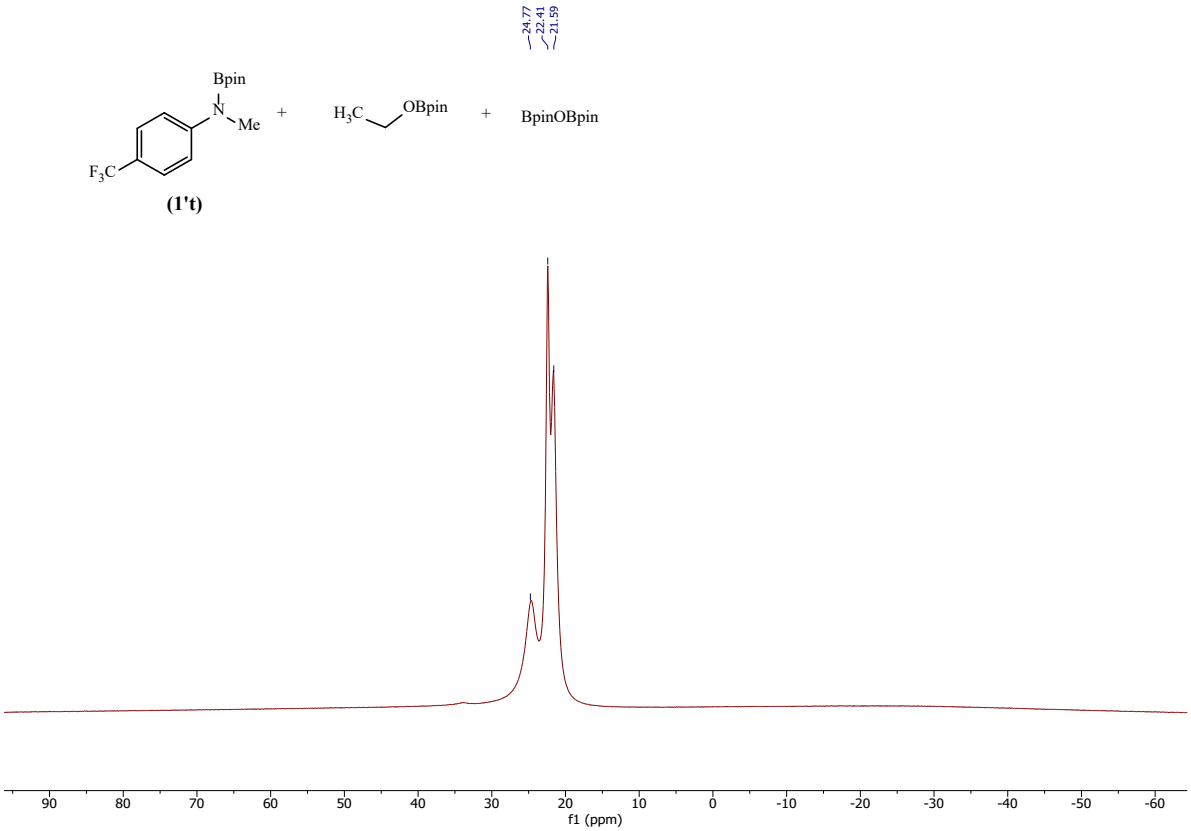



Figure S77: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1't**

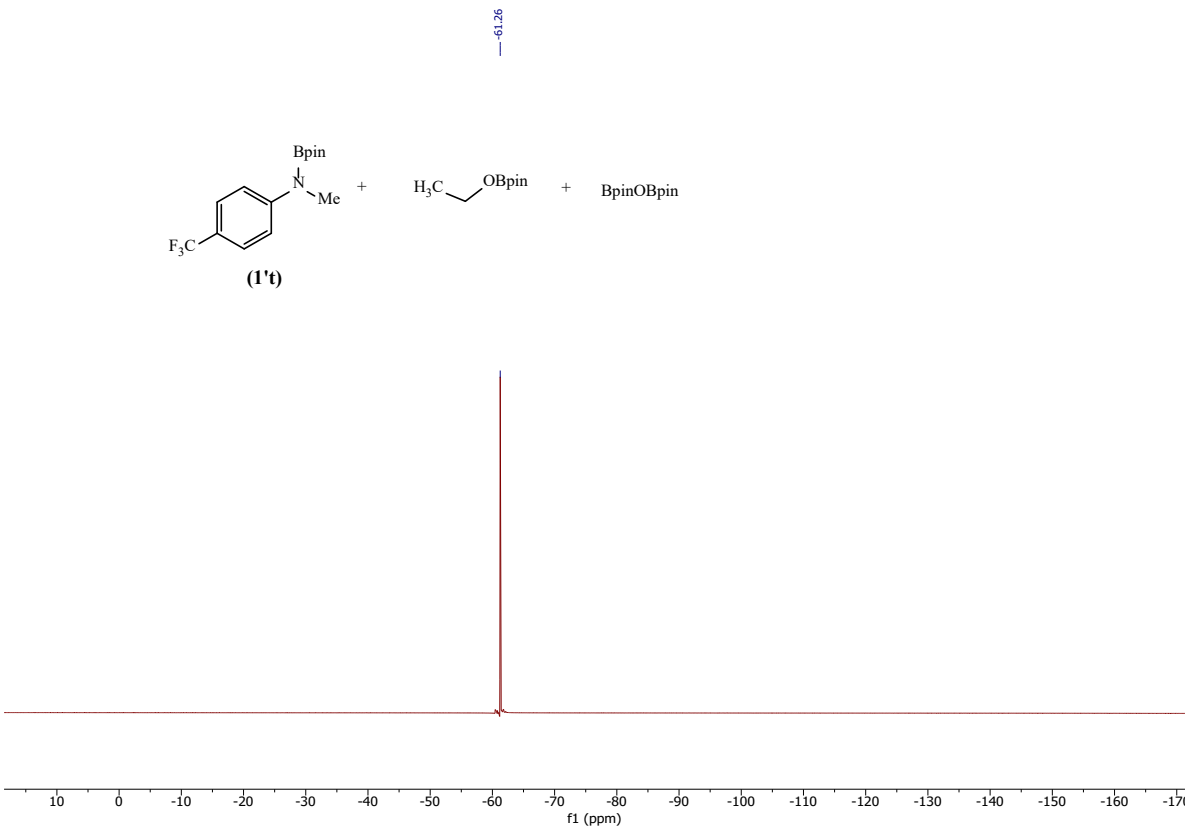



Figure S78: $^{19}F$ NMR (377 MHz, Toluene-$d_8$) of compound **1't**

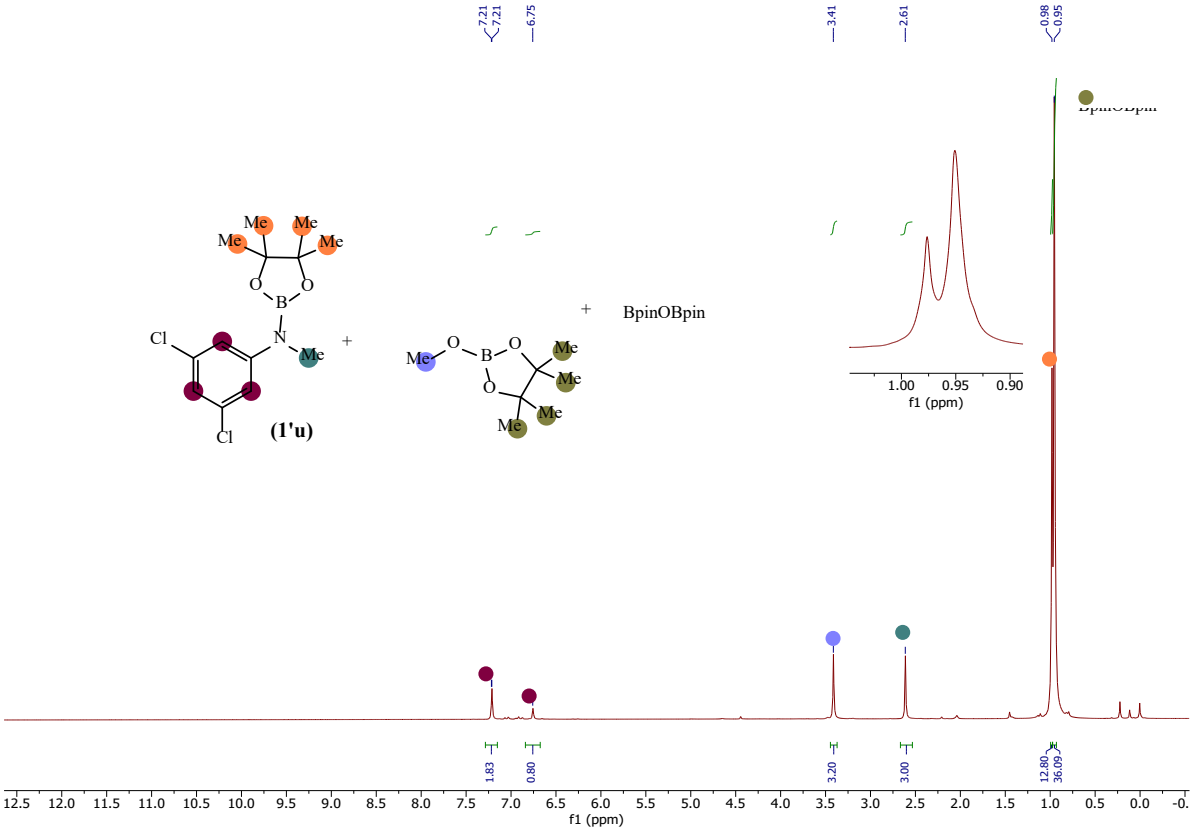



Figure S79: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'u**

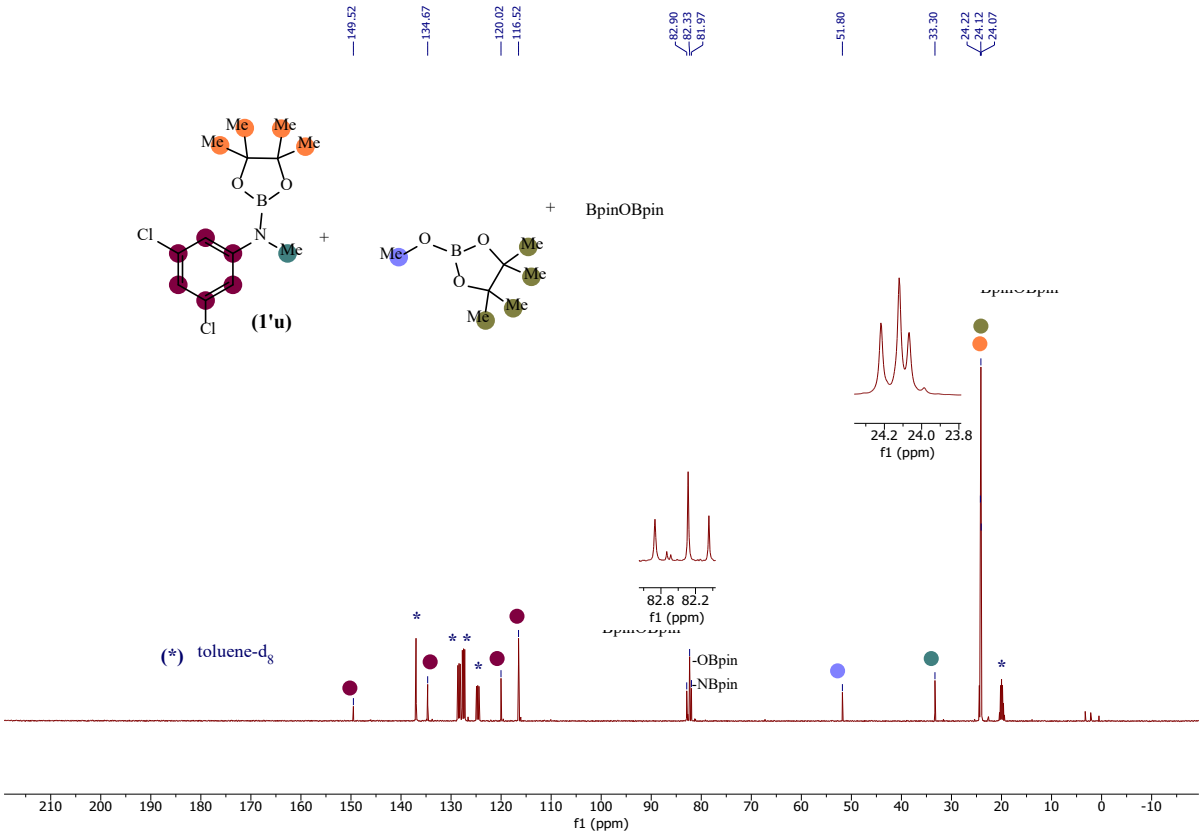



Figure S80: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'u**

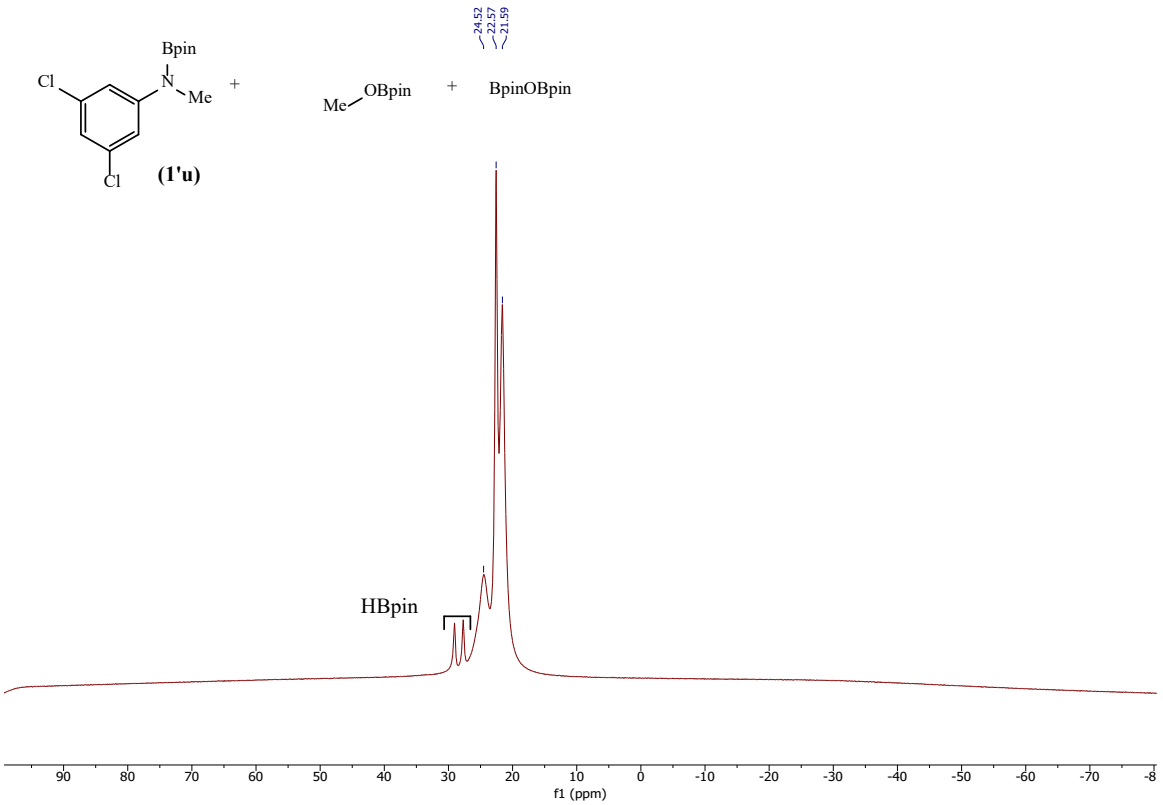



Figure S81: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'u**

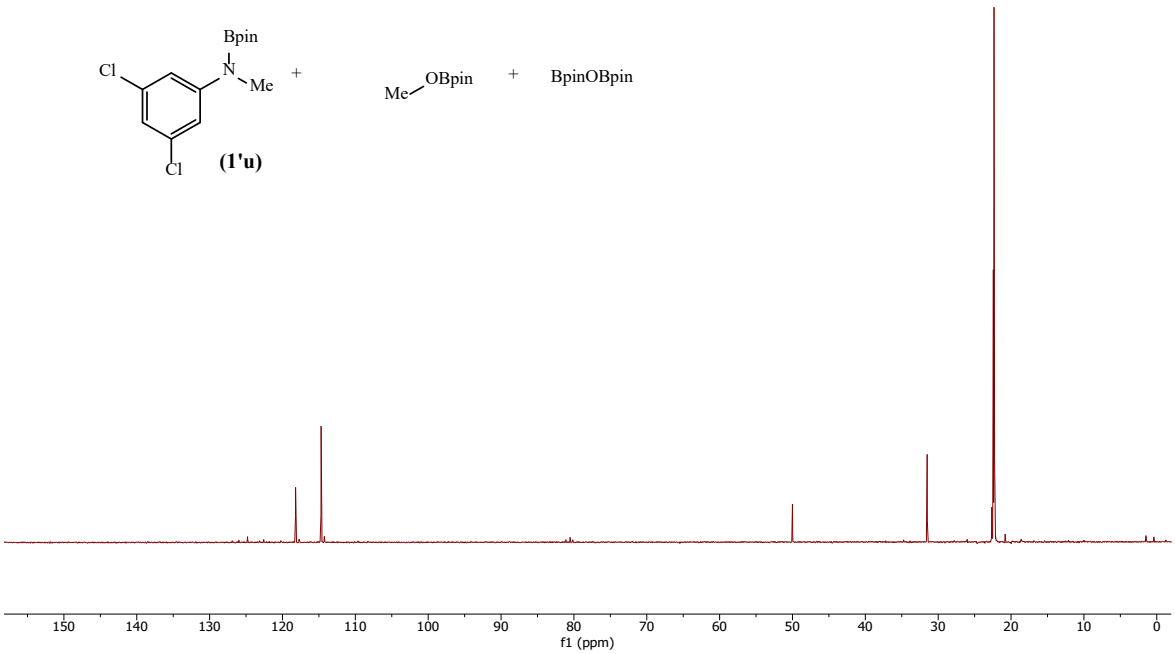



Figure S82: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'u**

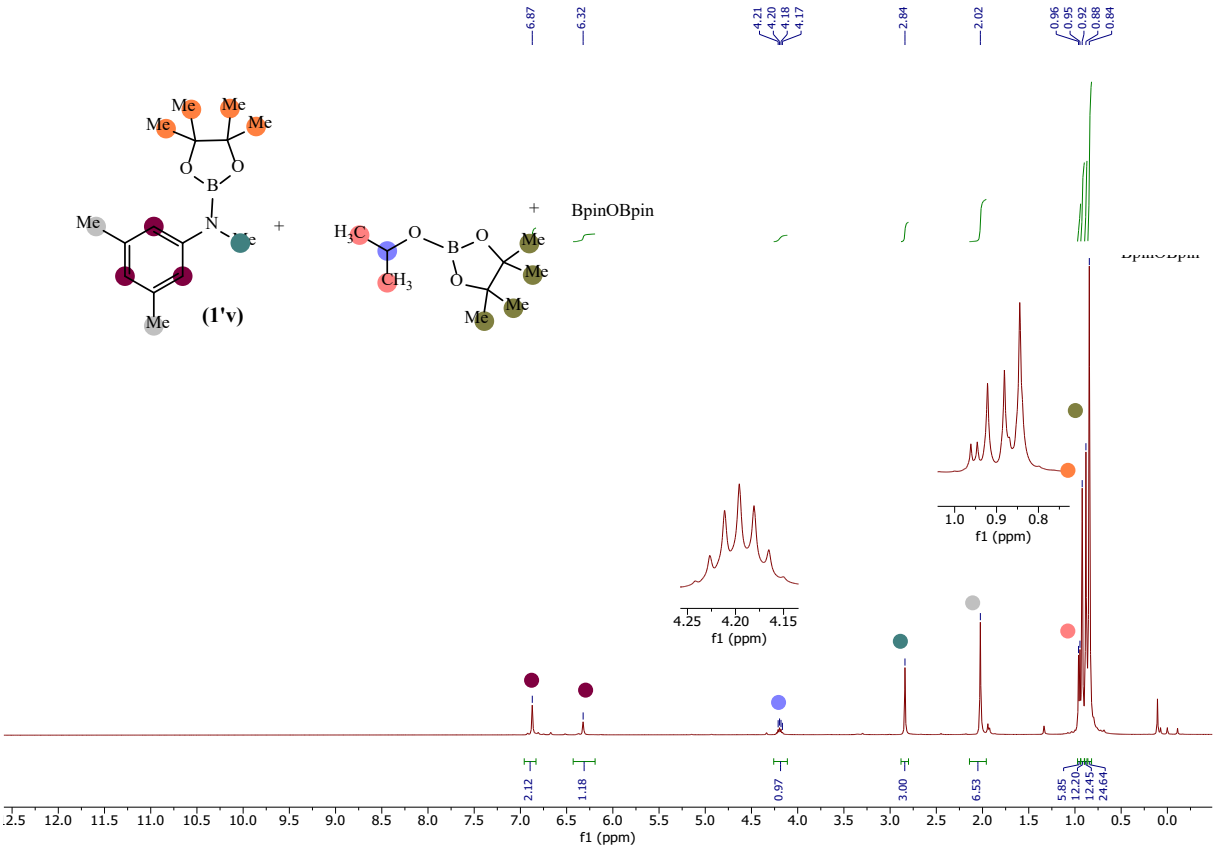



Figure S83: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'v**

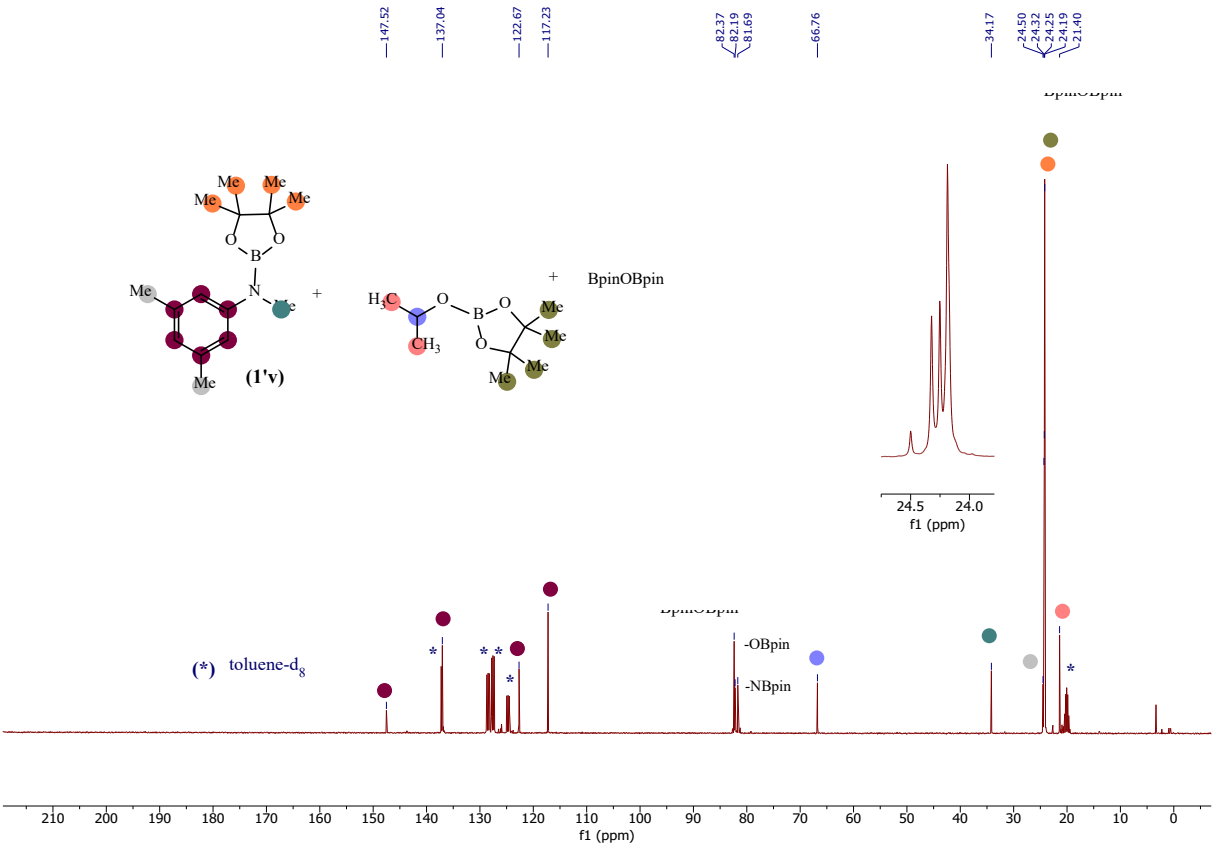



Figure S84: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'v**

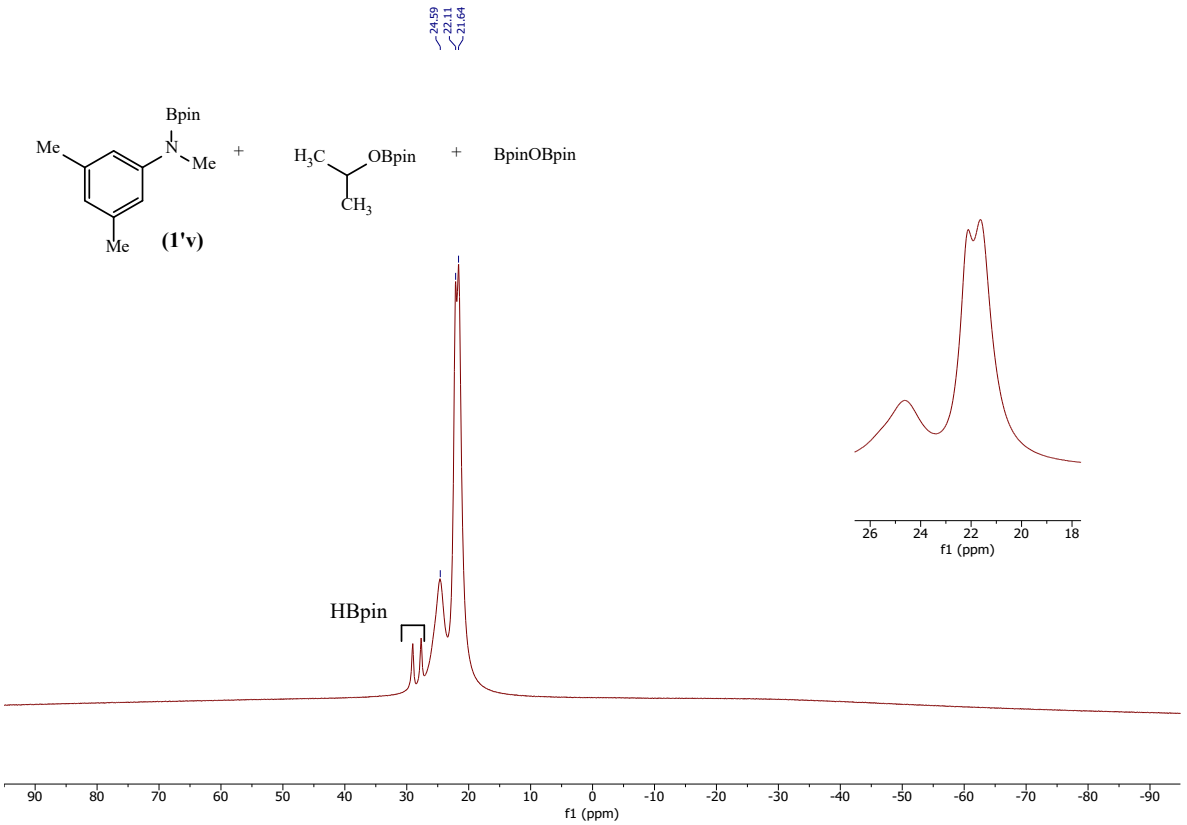



Figure S85: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'v**

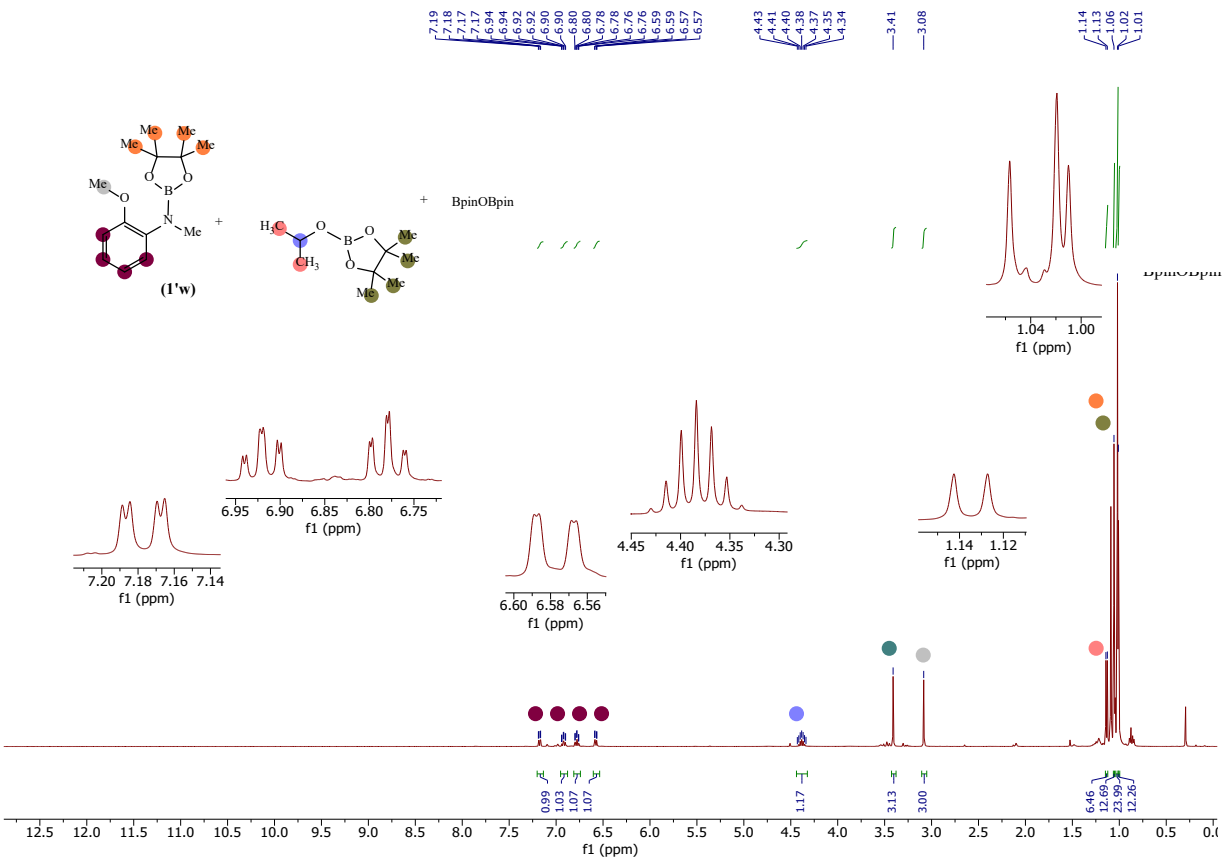



Figure S86: $^1H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'w**

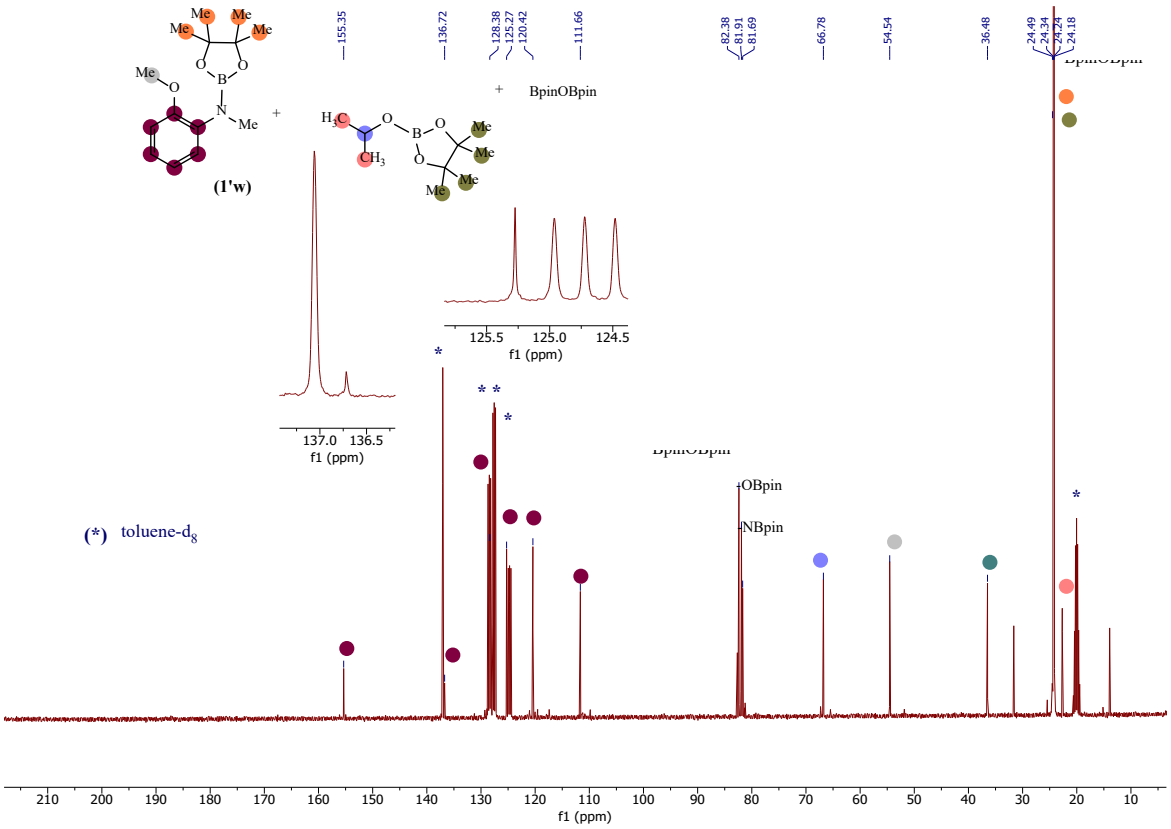



Figure S87: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'w**

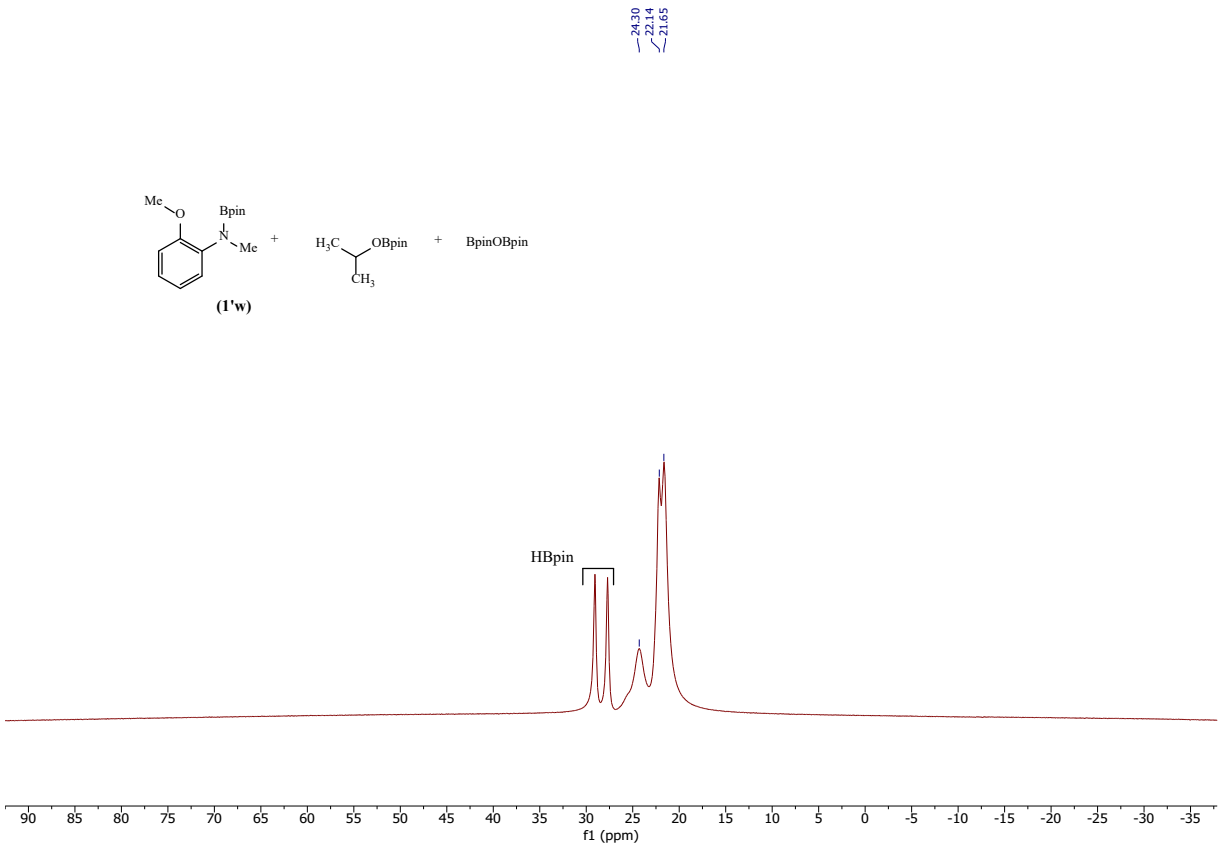



Figure S88: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'w**

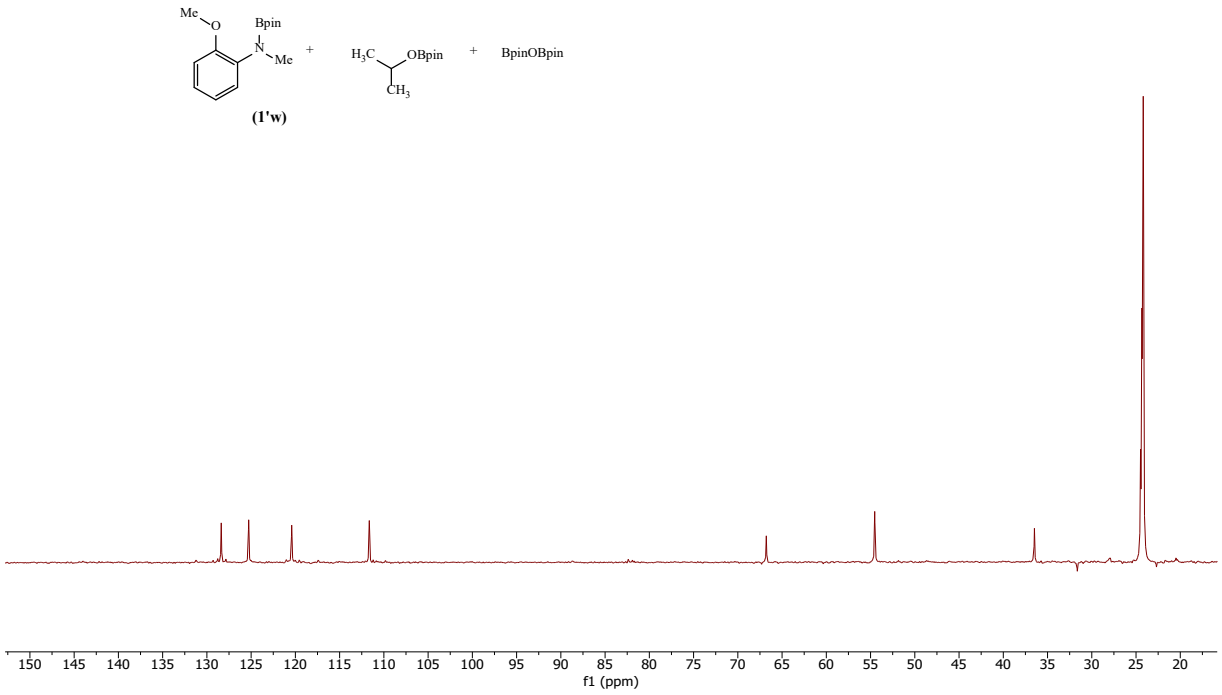



Figure S89: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'w**

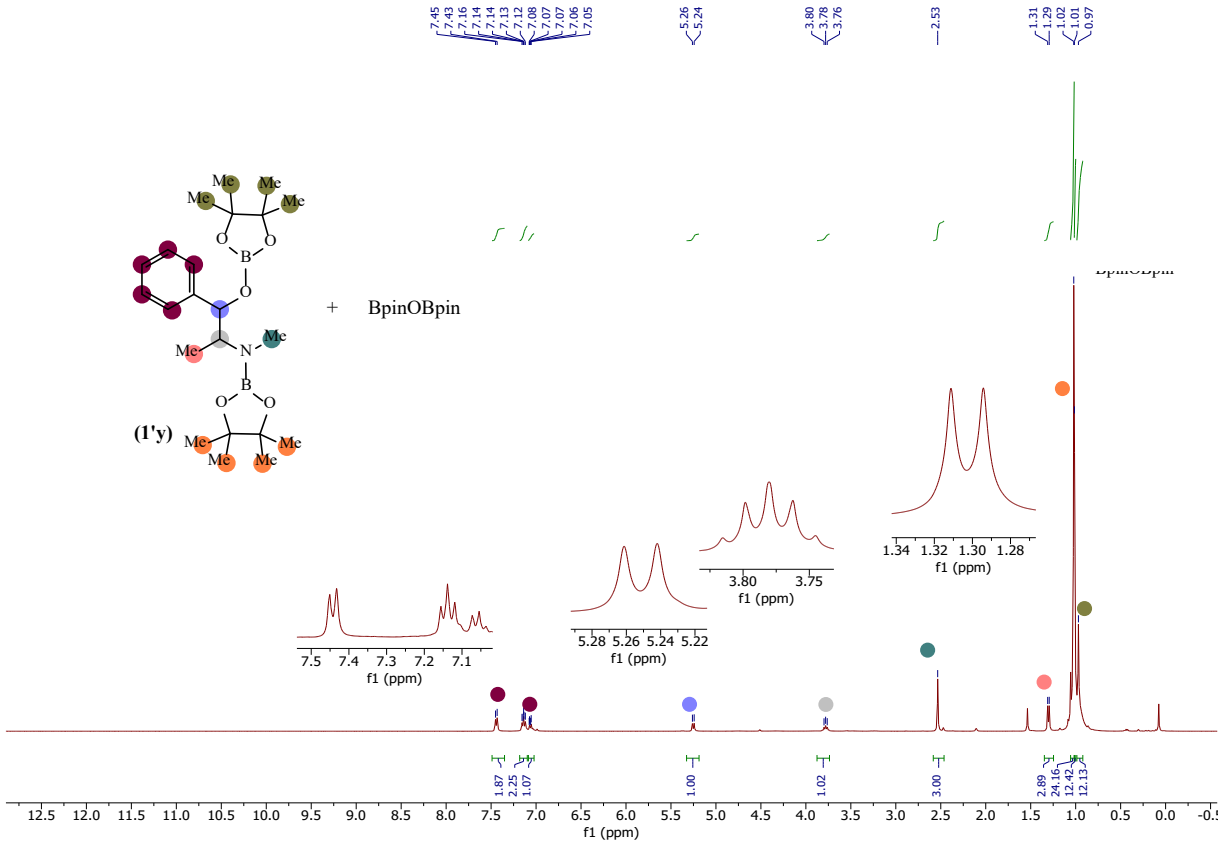



Figure S90: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'y**

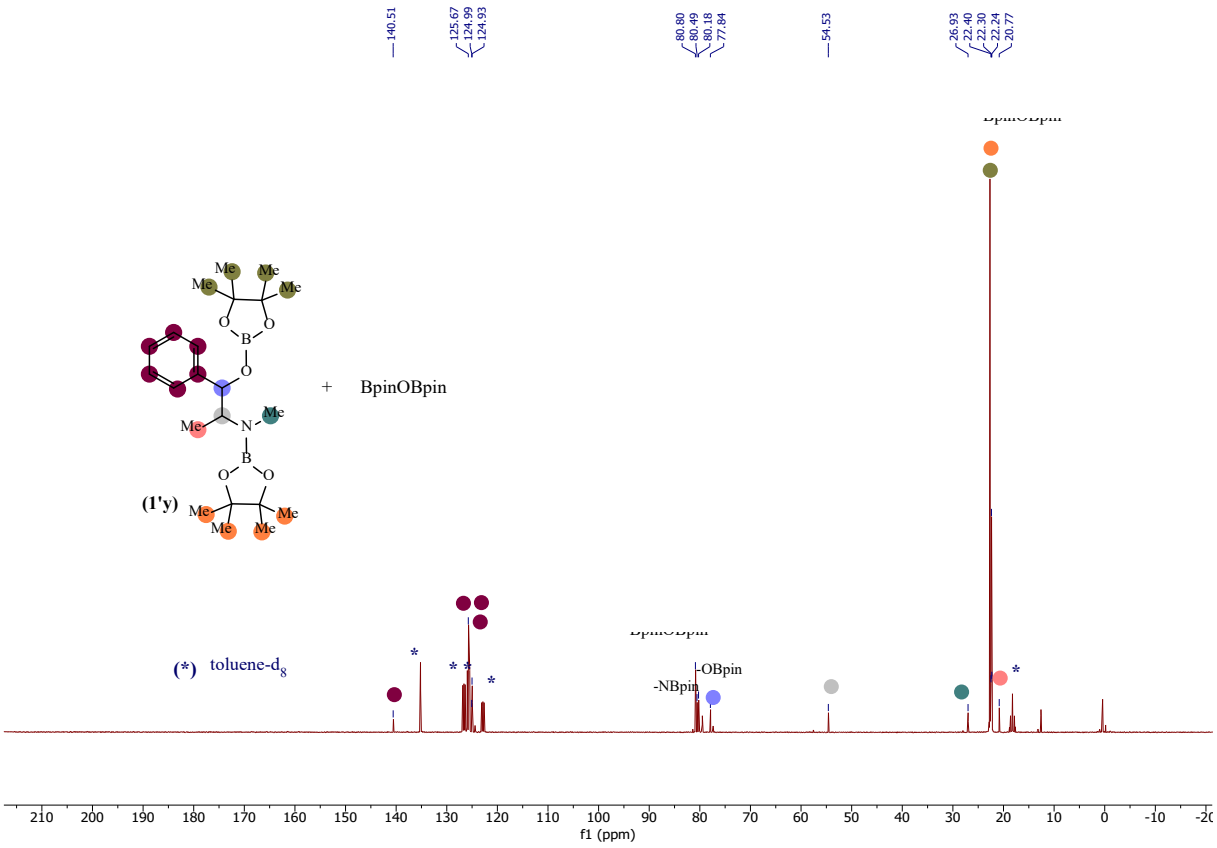



Figure S91: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'y**

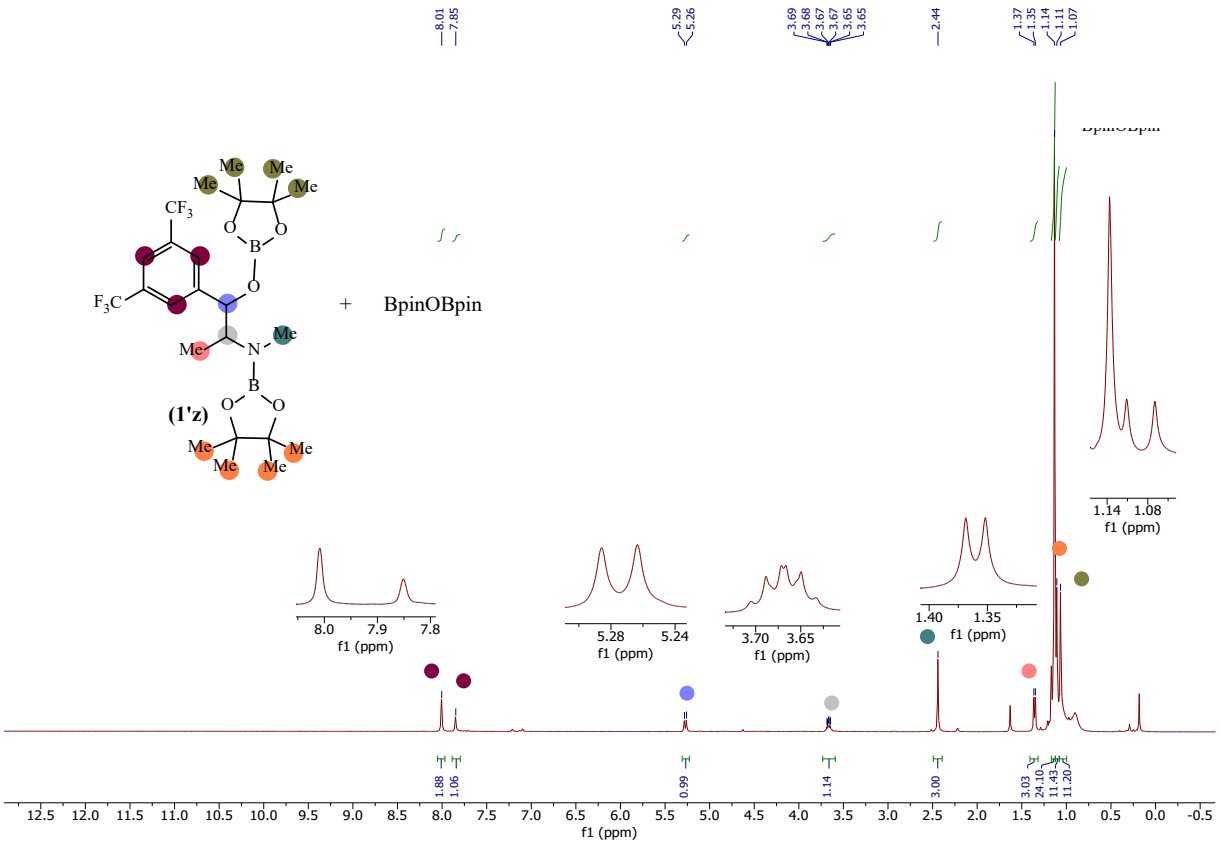



Figure S92: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'z**

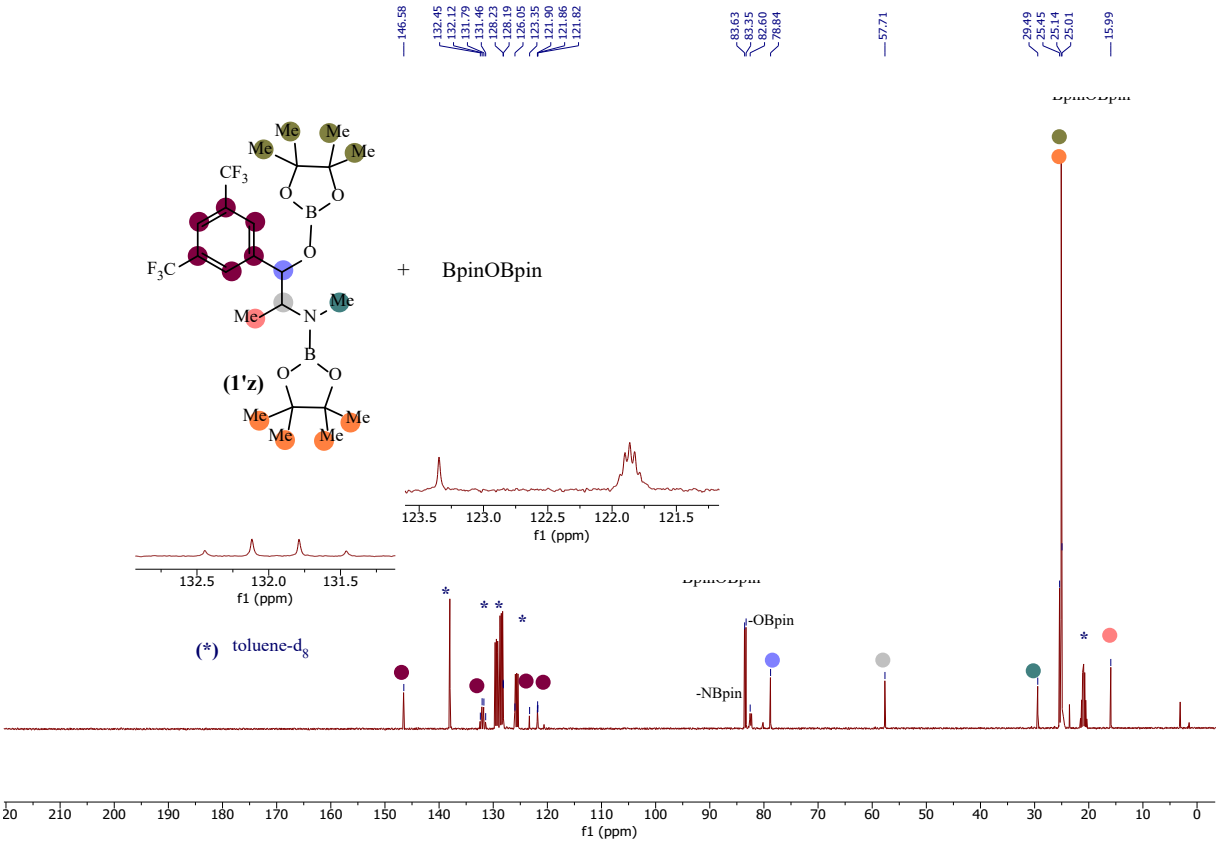



Figure S93: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'z**

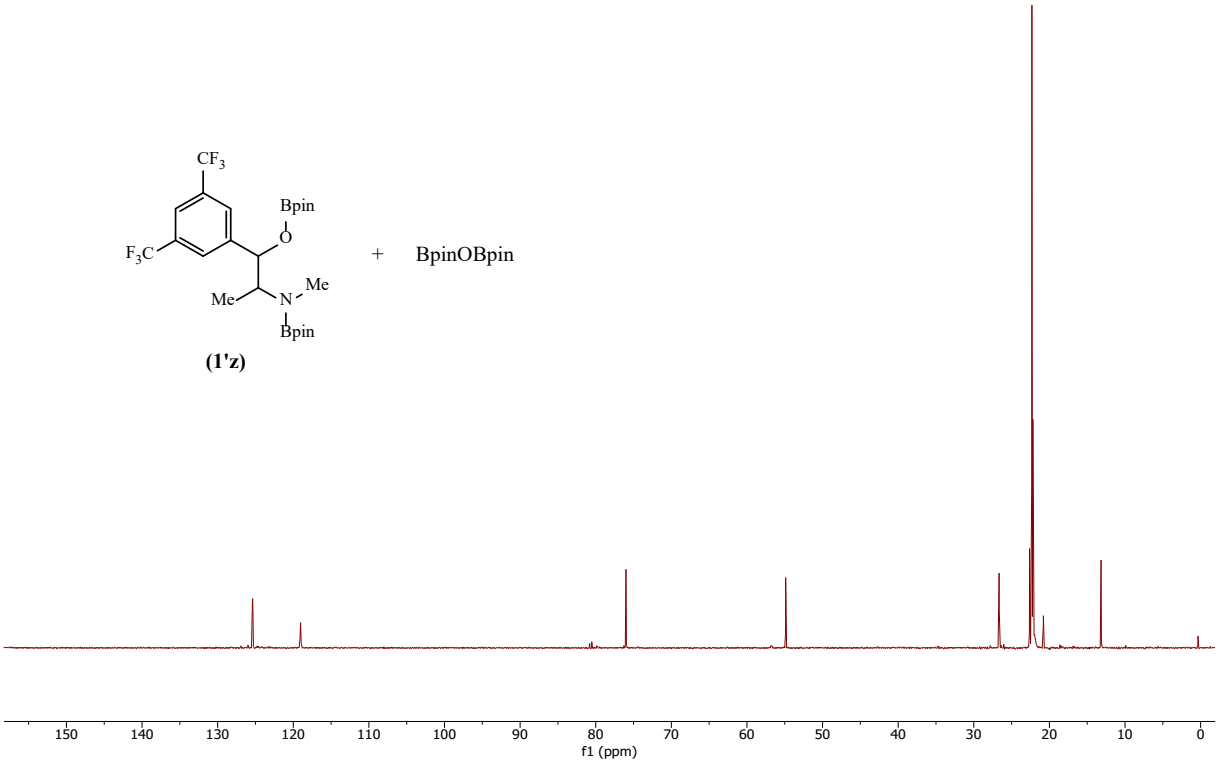



Figure S94: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'z**

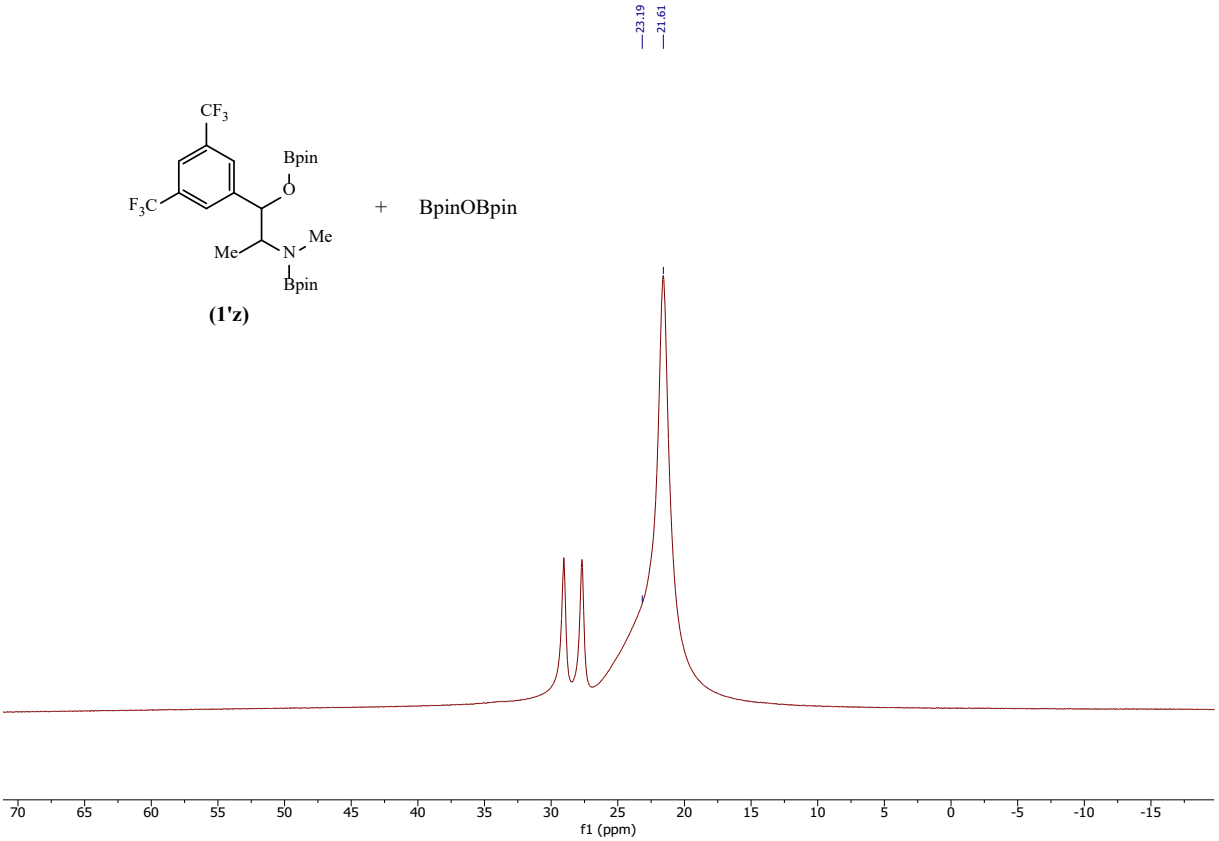



Figure S95: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'z**

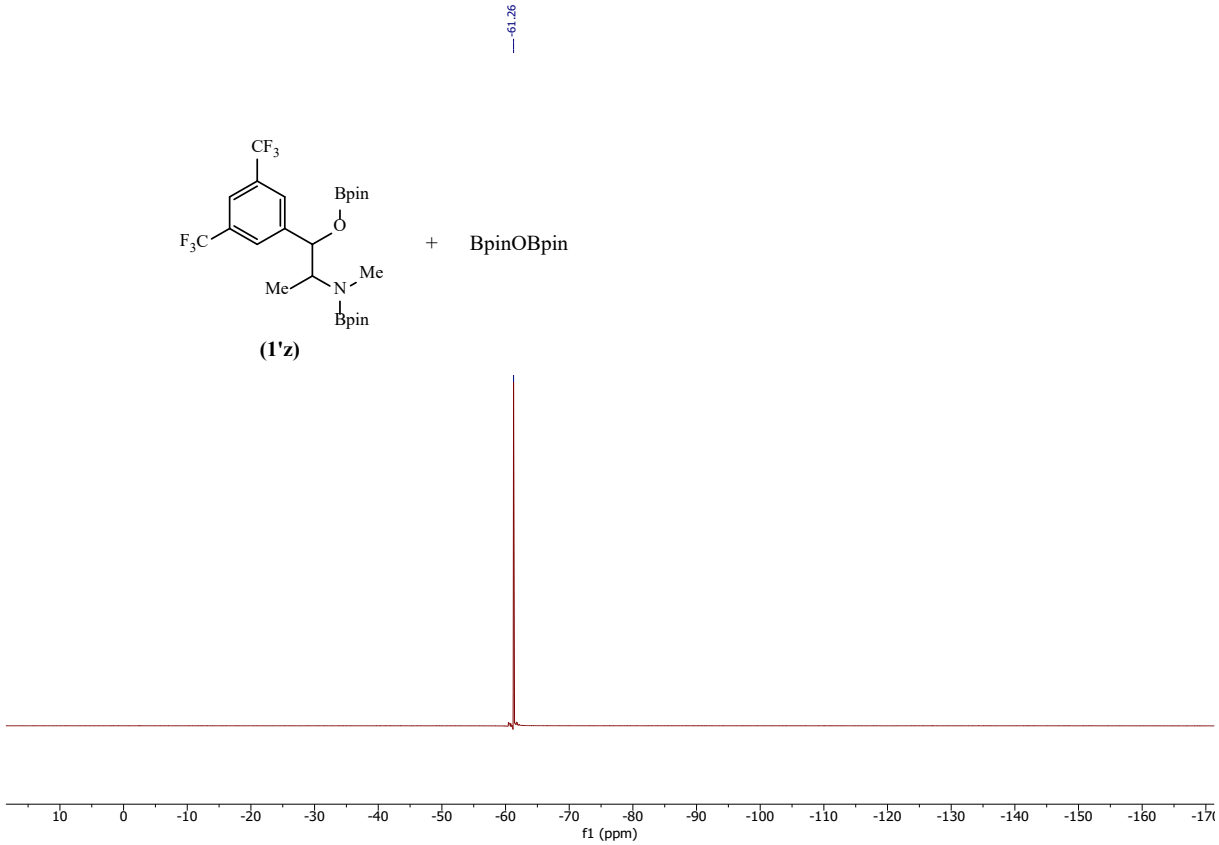



Figure S96: $^{19}F$ NMR (377 MHz, Toluene-$d_8$) of compound **1'z**

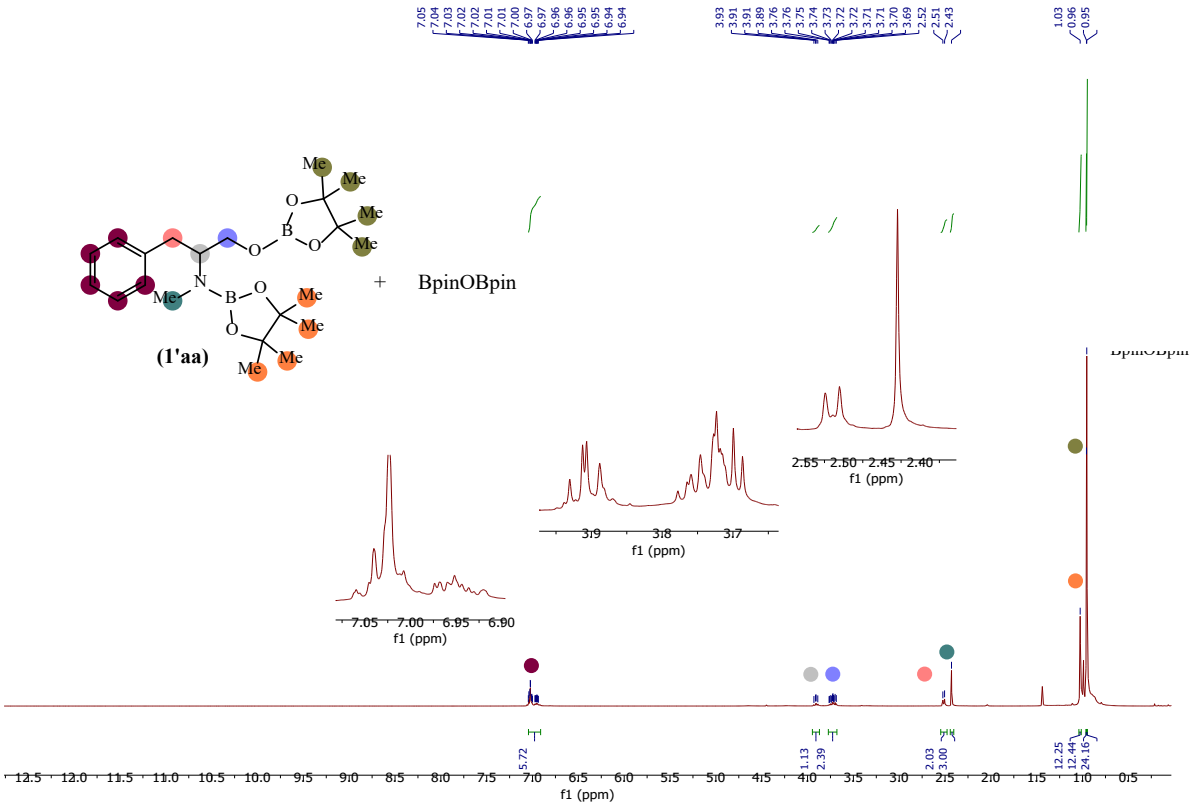



Figure S97: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'aa**

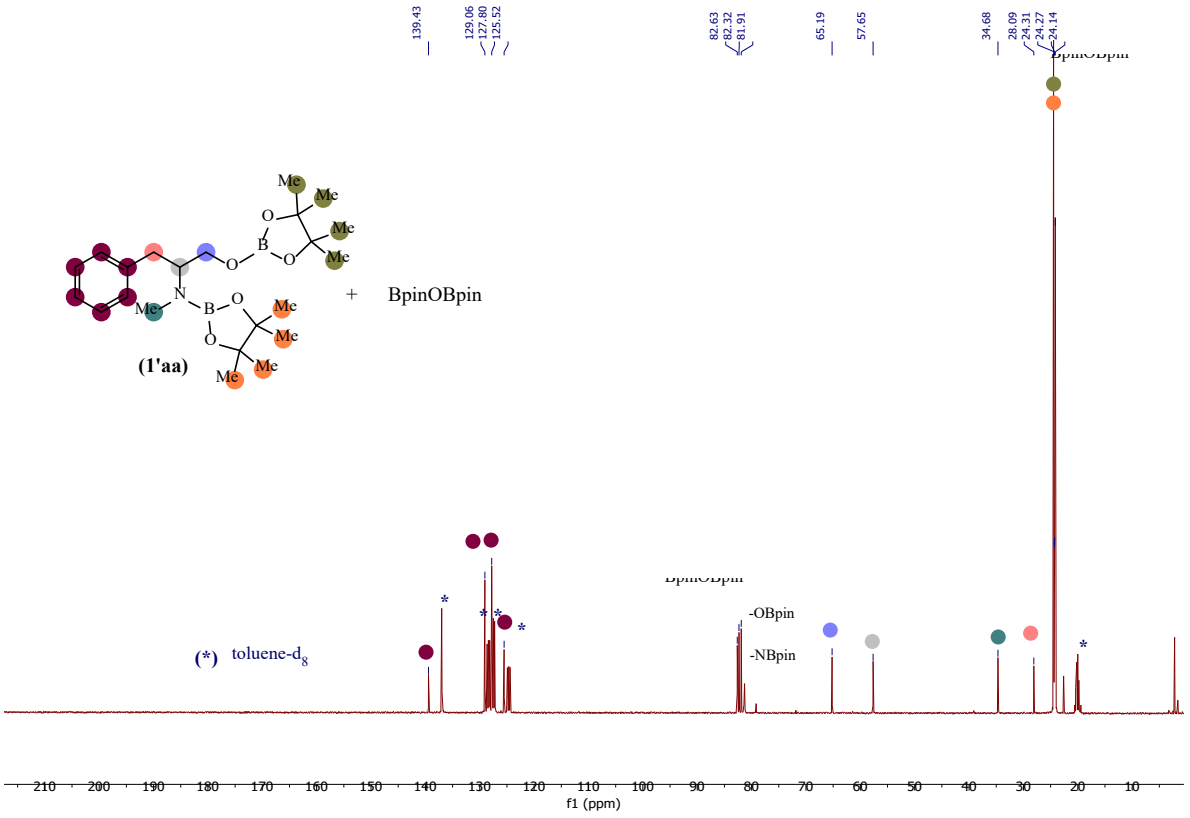



Figure S98: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'aa**

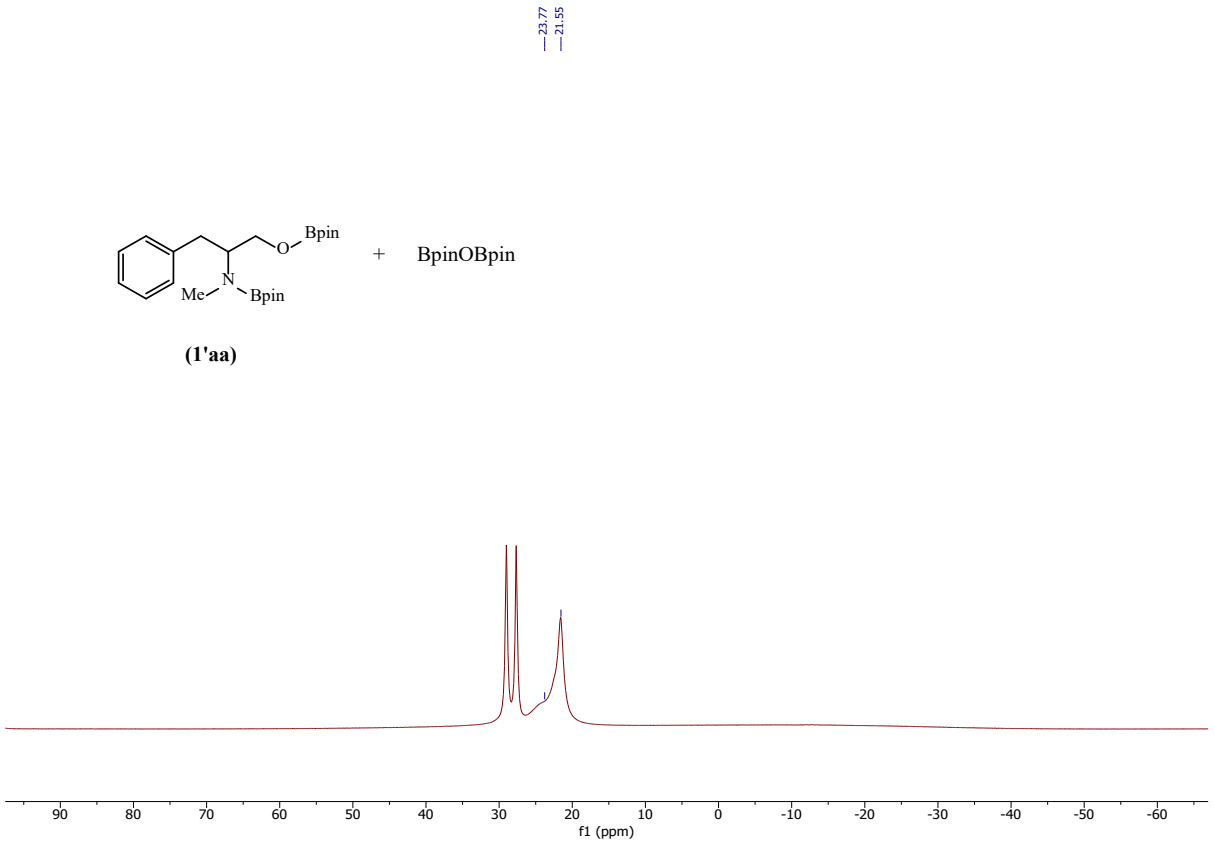



Figure S99: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'aa**

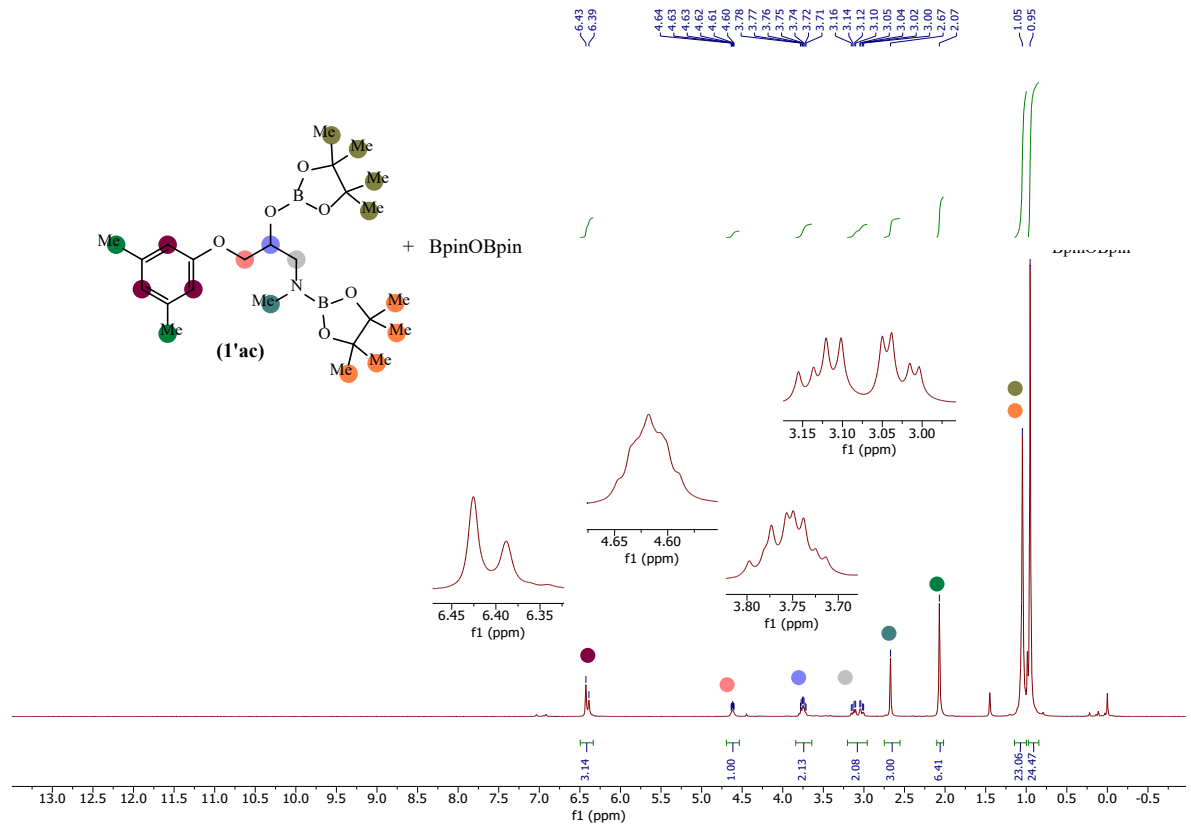



Figure S100: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'ac**

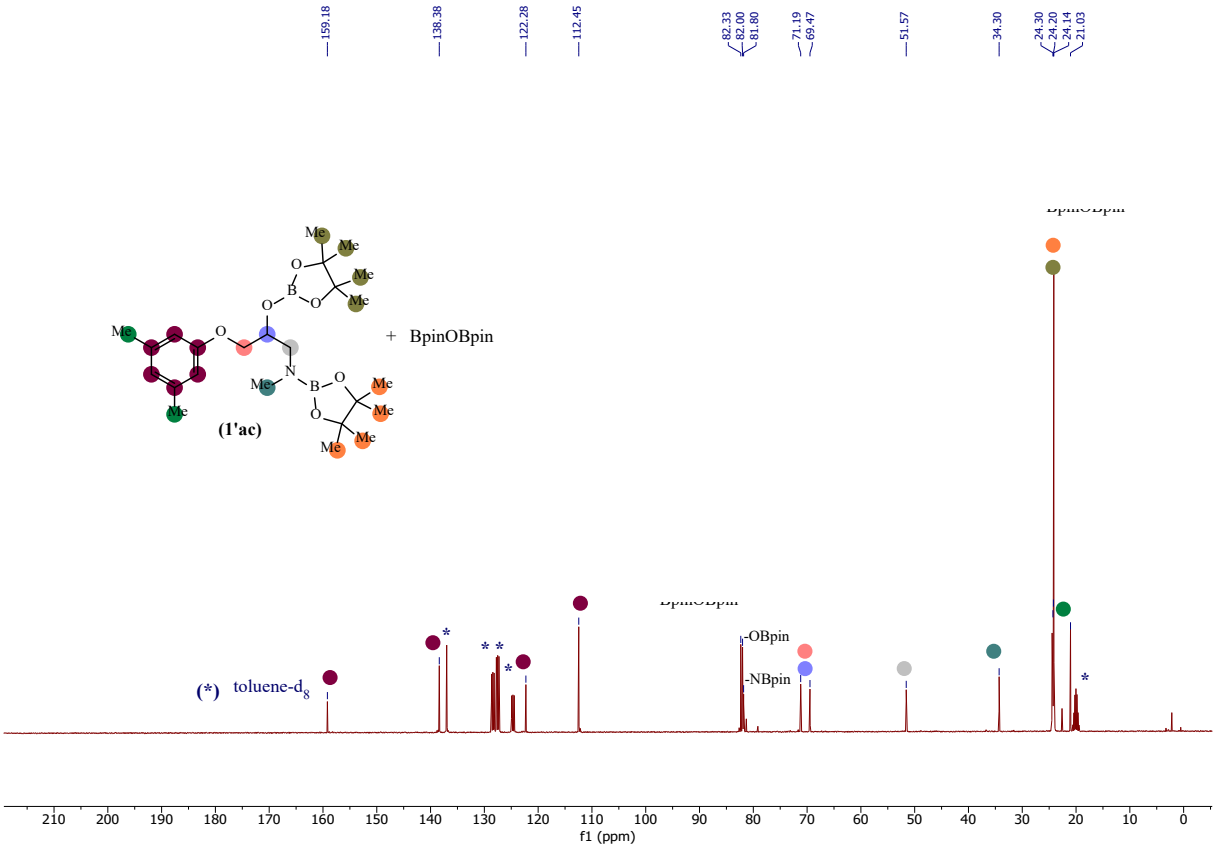



Figure S101: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'ac**

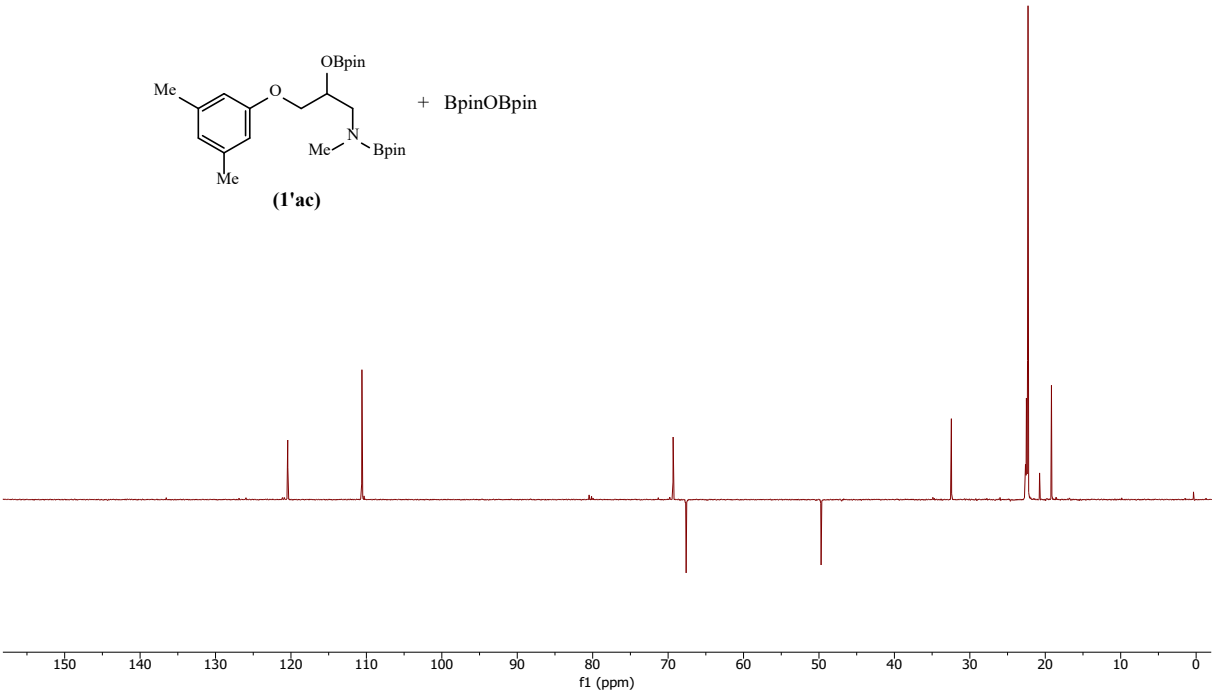



Figure S102: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'ac**

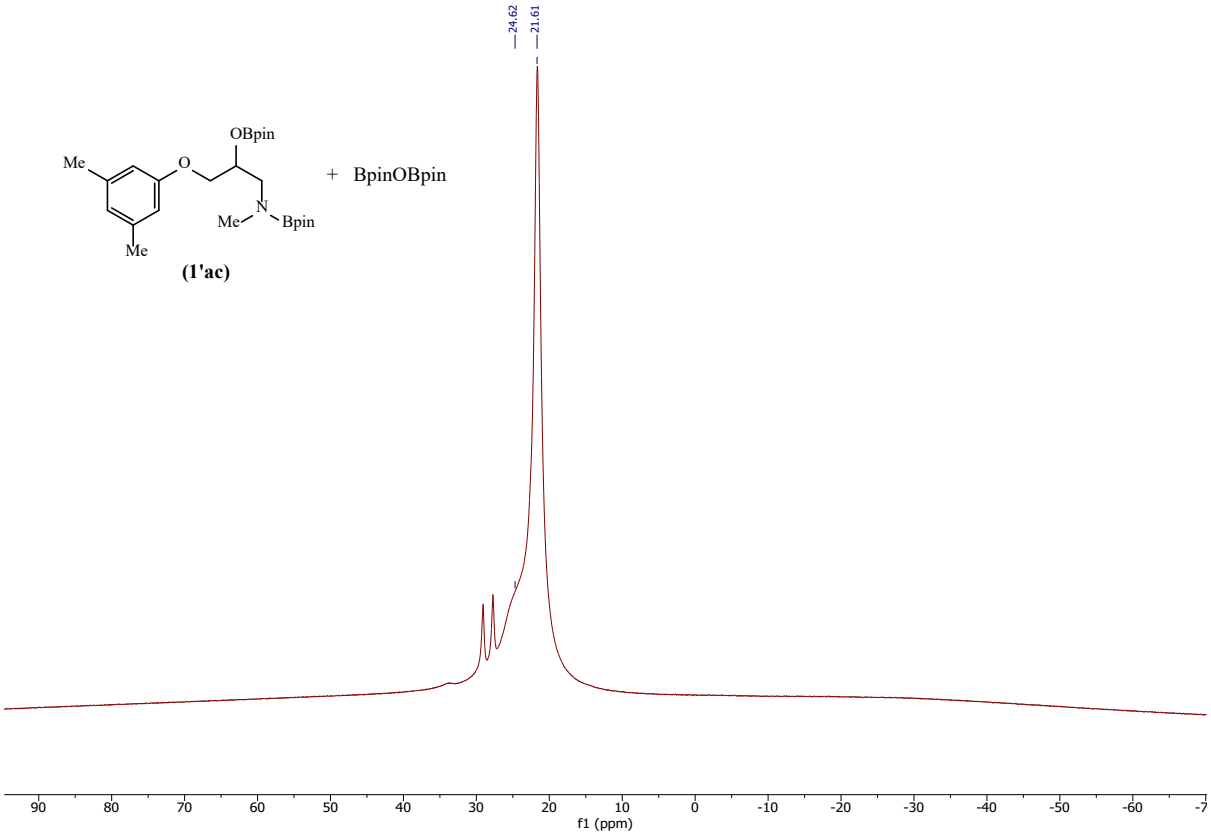



Figure S103: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'ac**

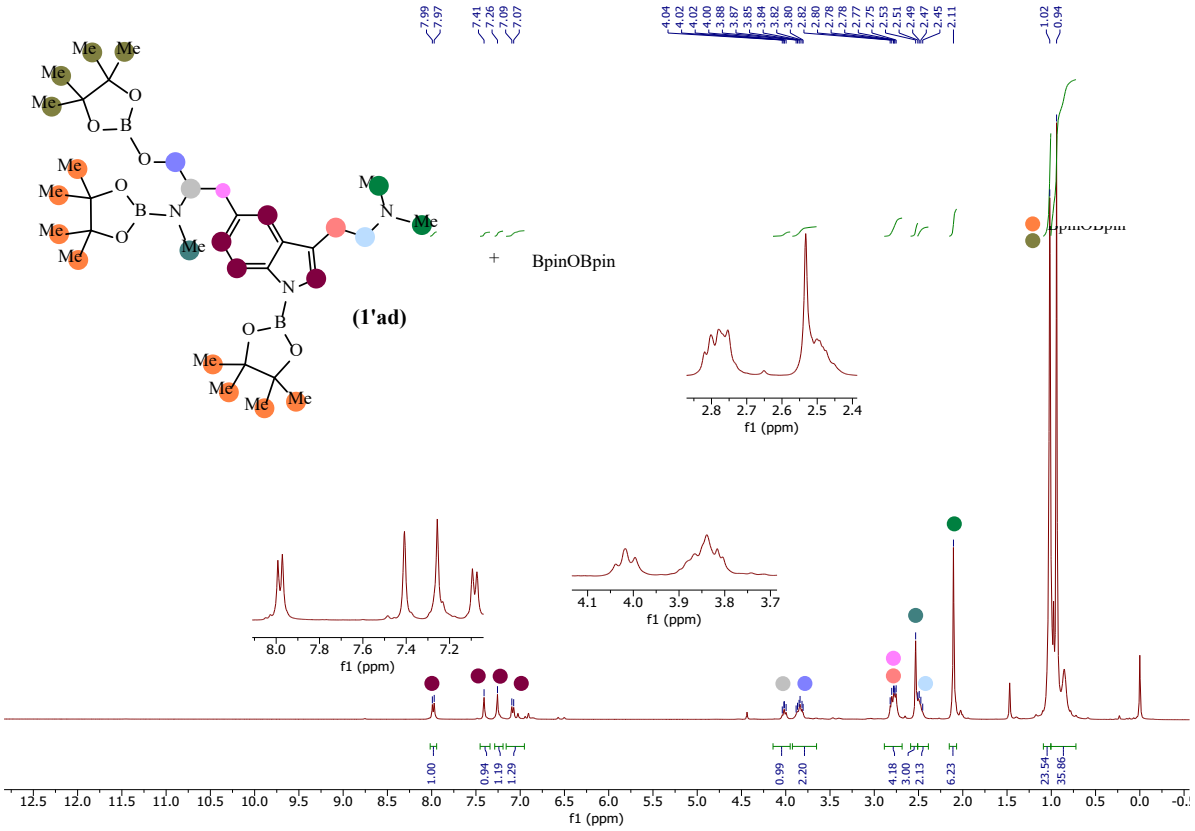



Figure S104: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'ad**

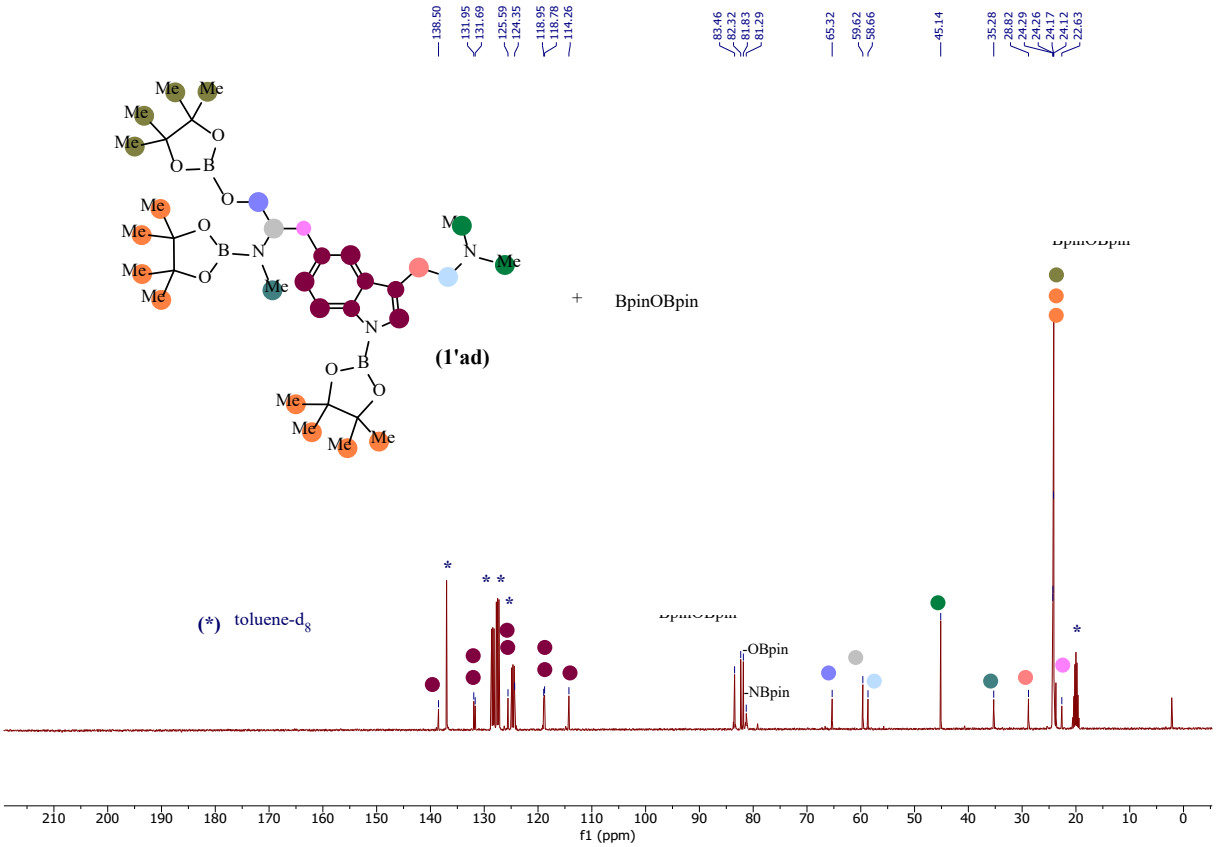



Figure S105: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'ad**

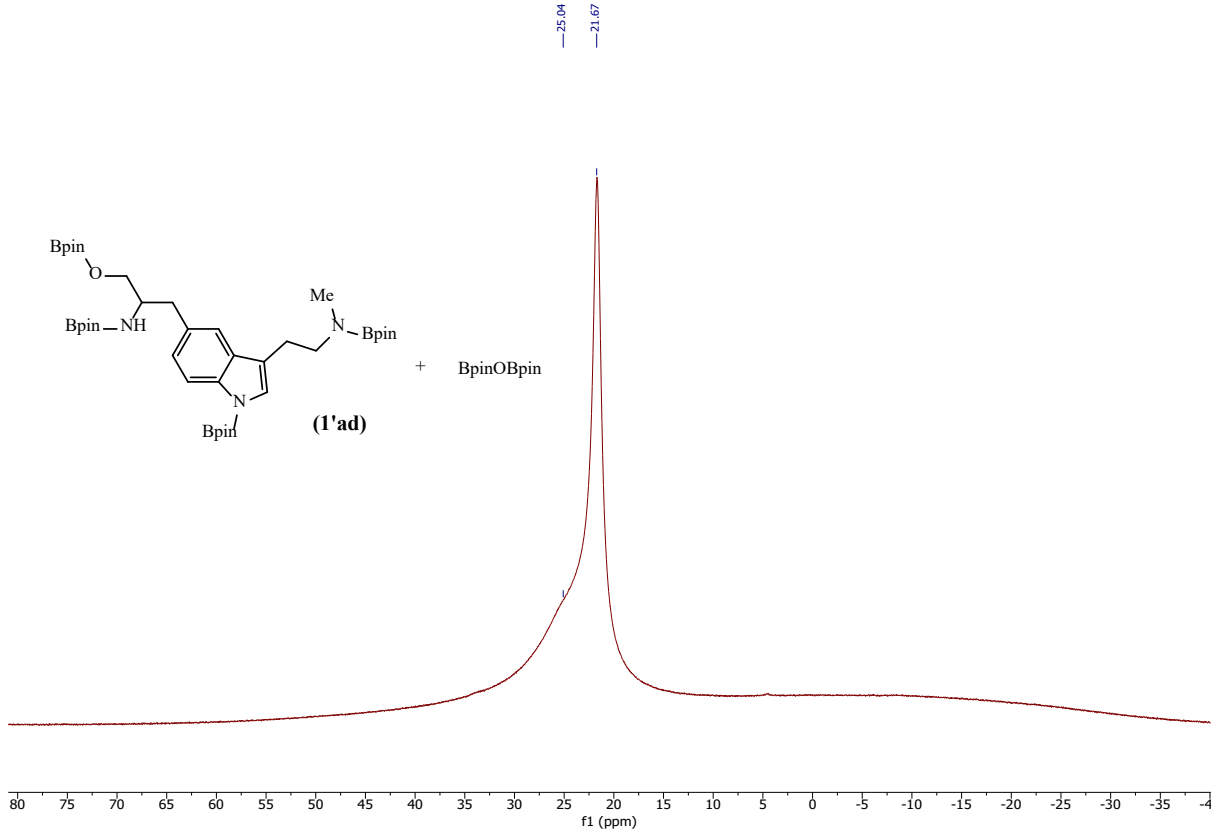



Figure S106: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'ad**

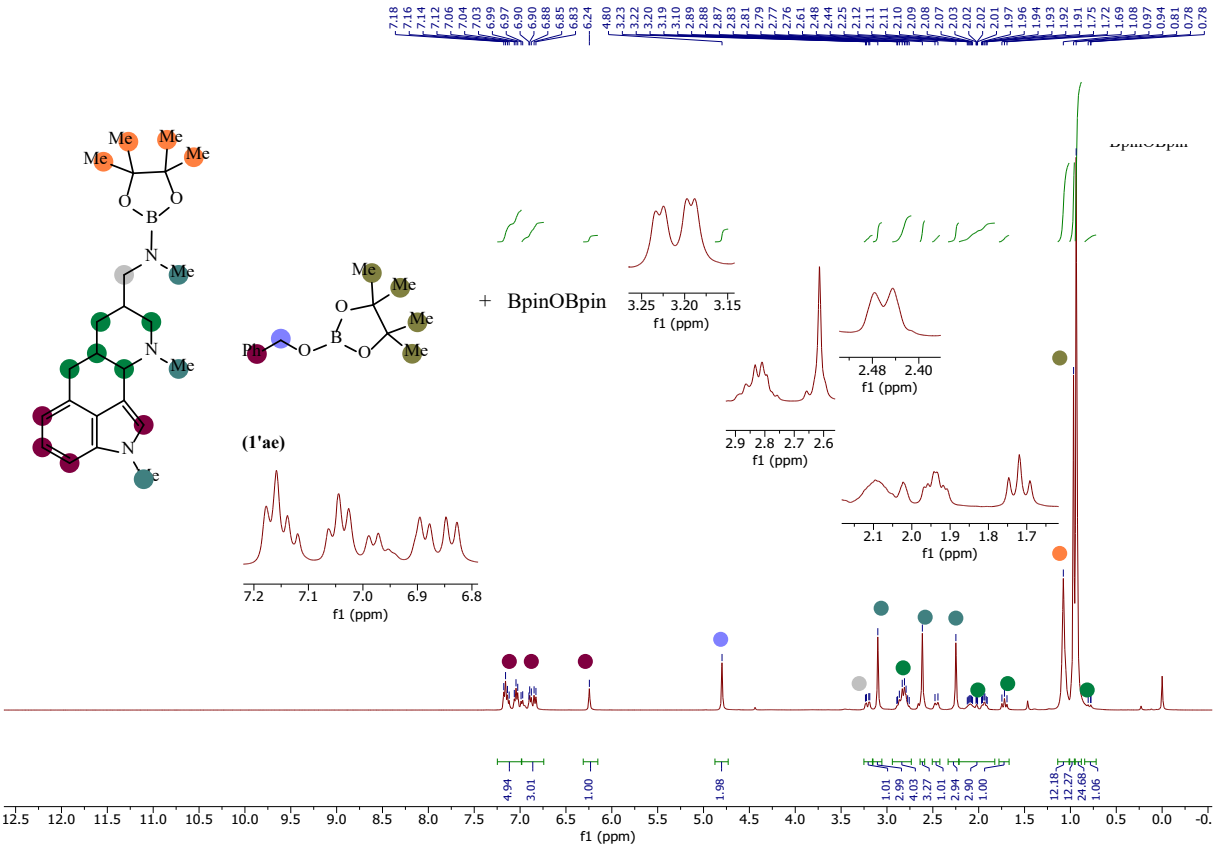



Figure S107: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'ae**

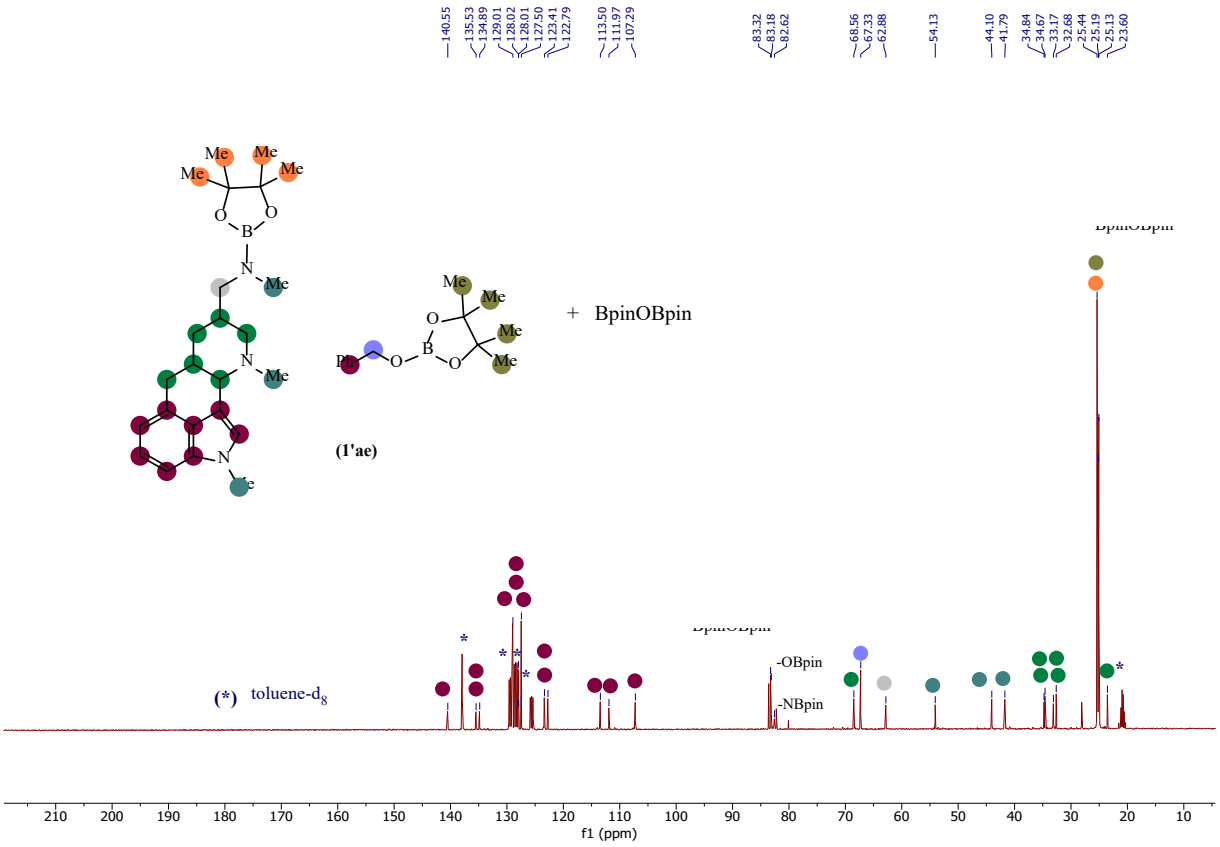



Figure S108: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'ae**

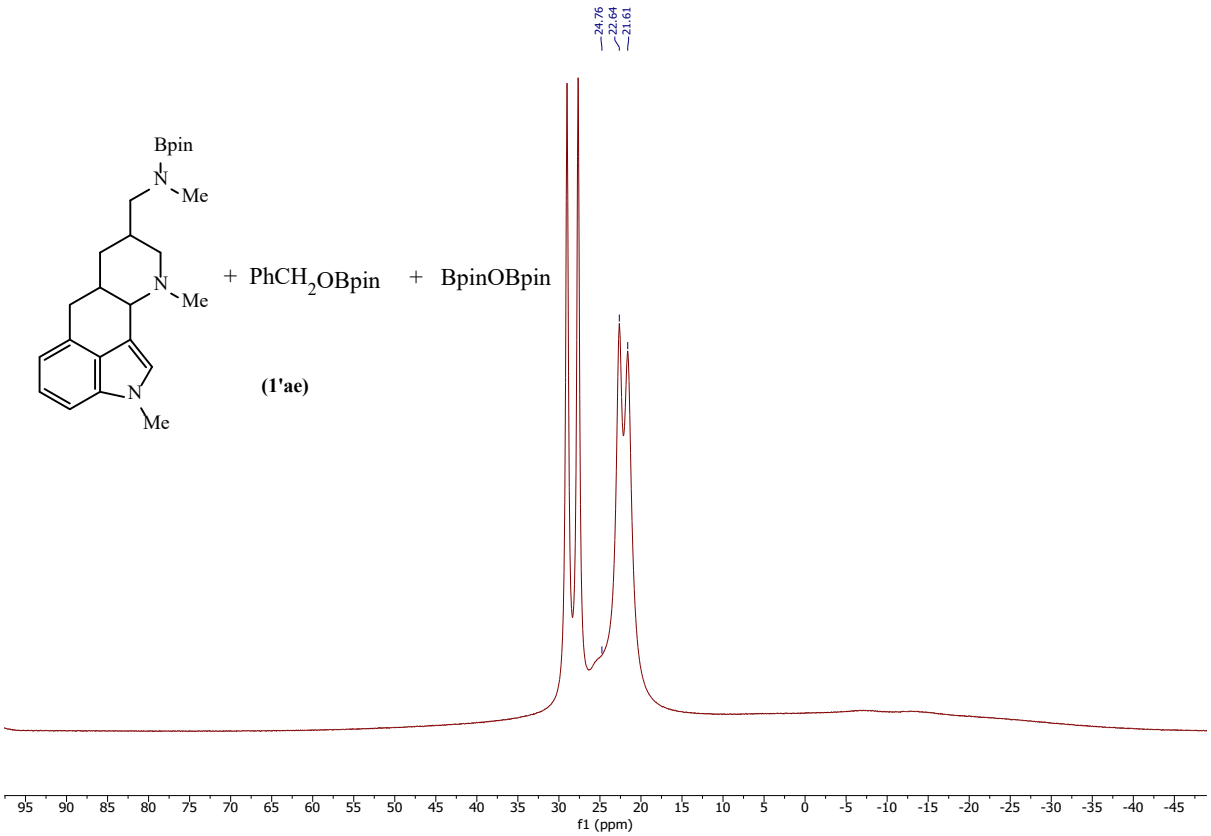



Figure S109: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'ae**

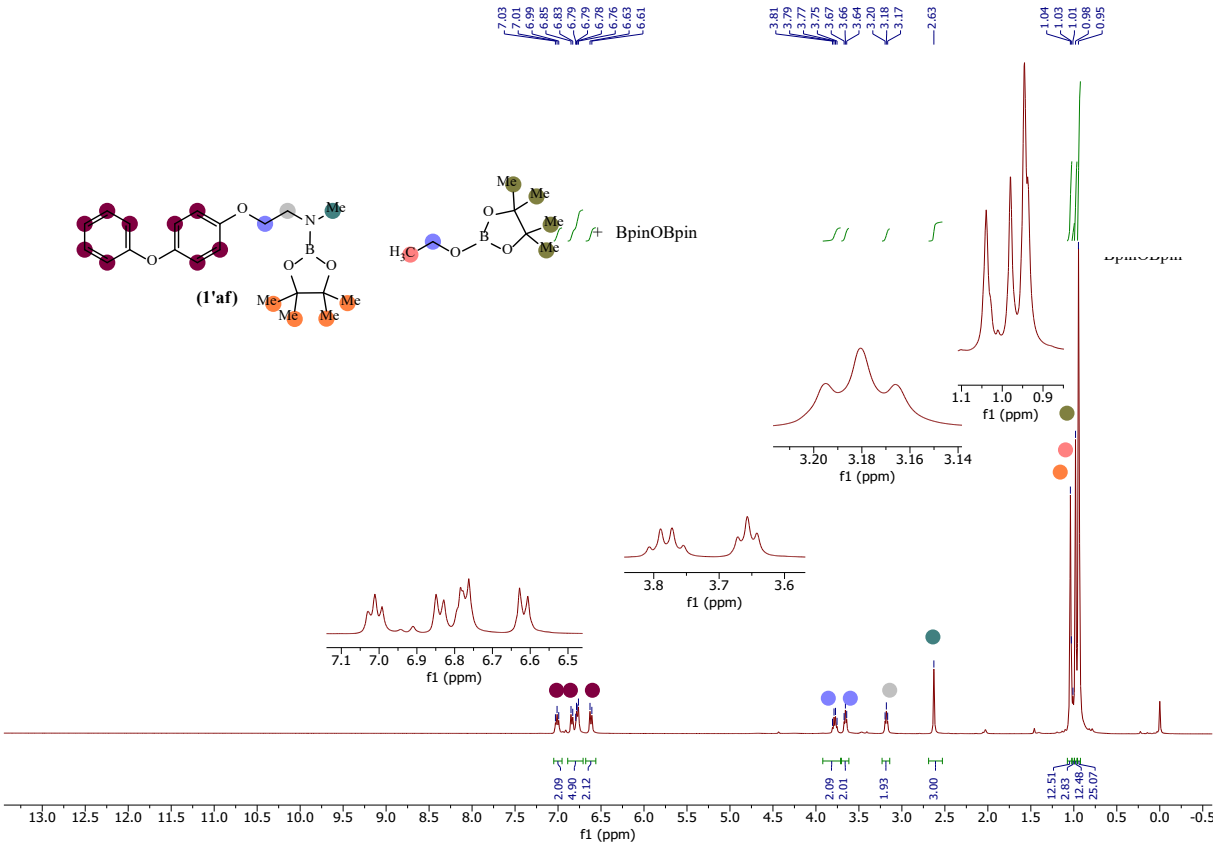



Figure S110: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'af**

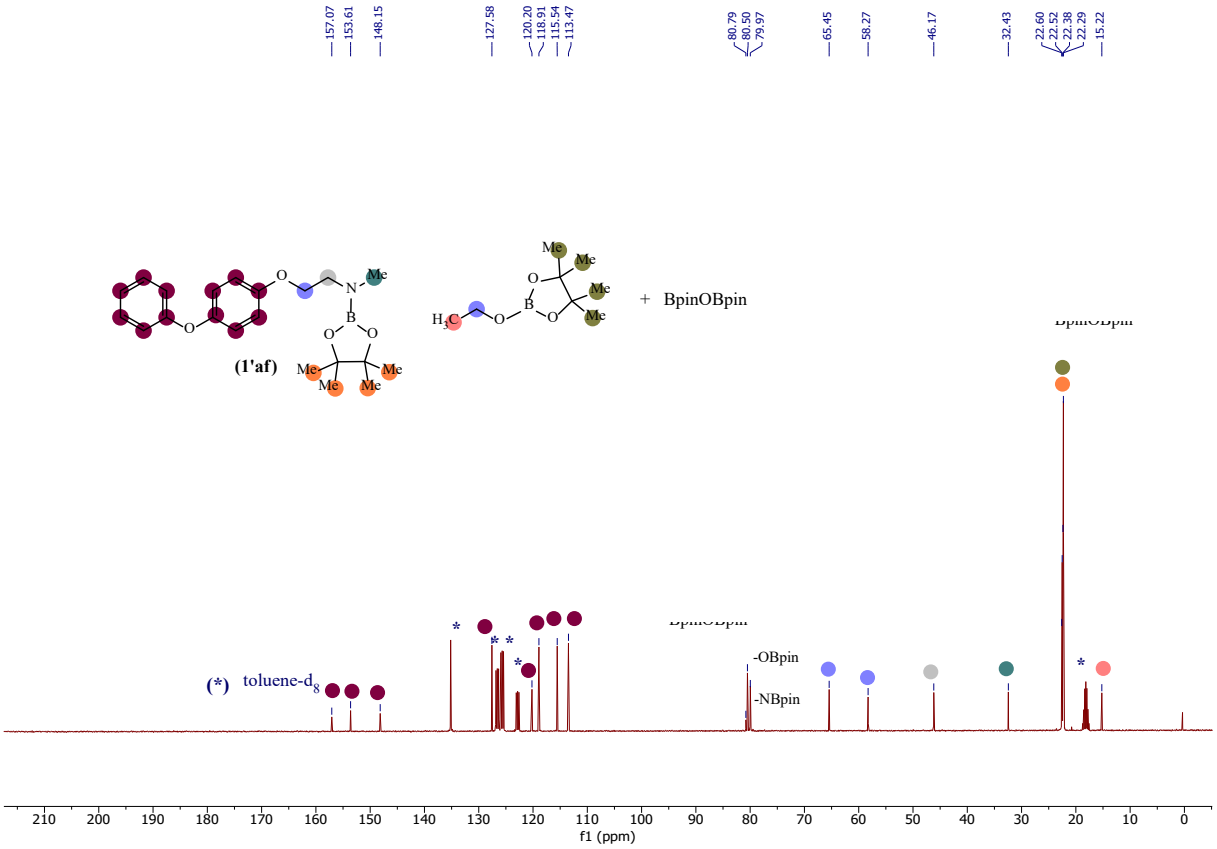



Figure S111: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'af**

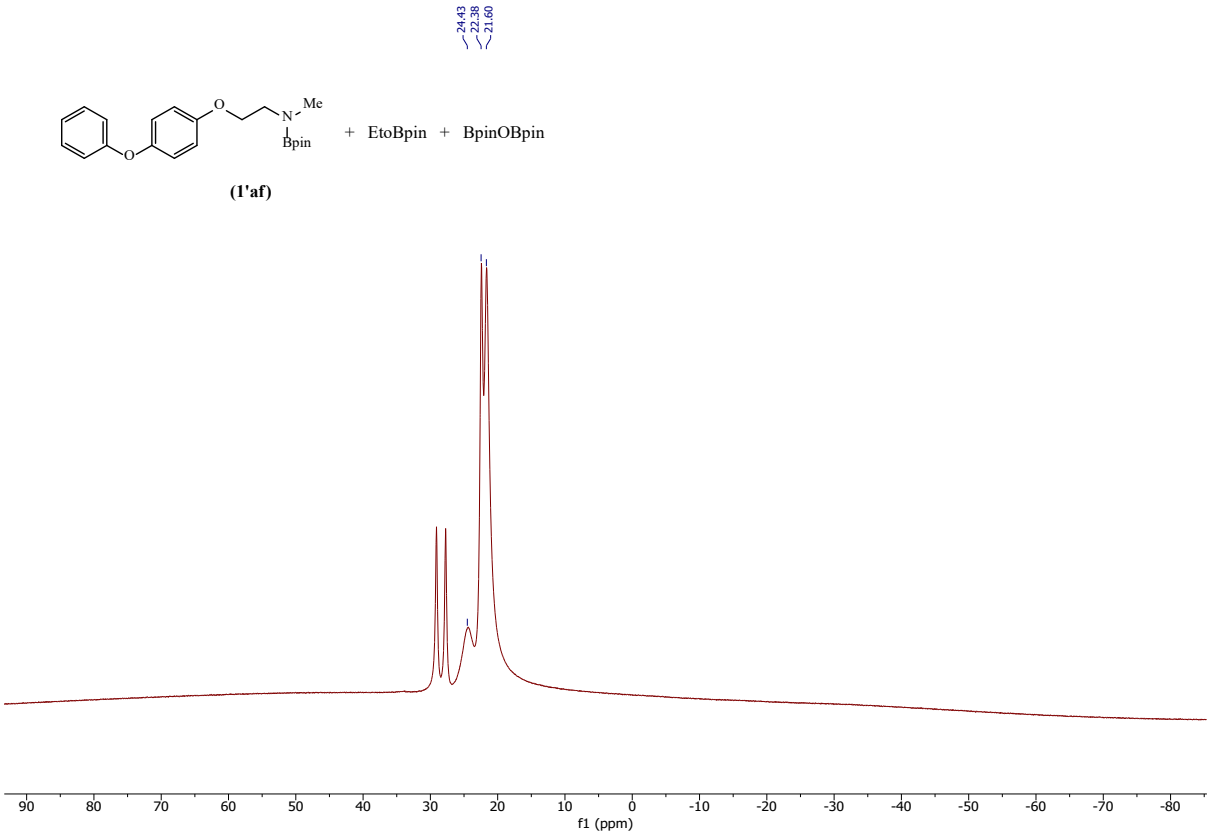



Figure S112: $^{11}B\{^{1}H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'af**

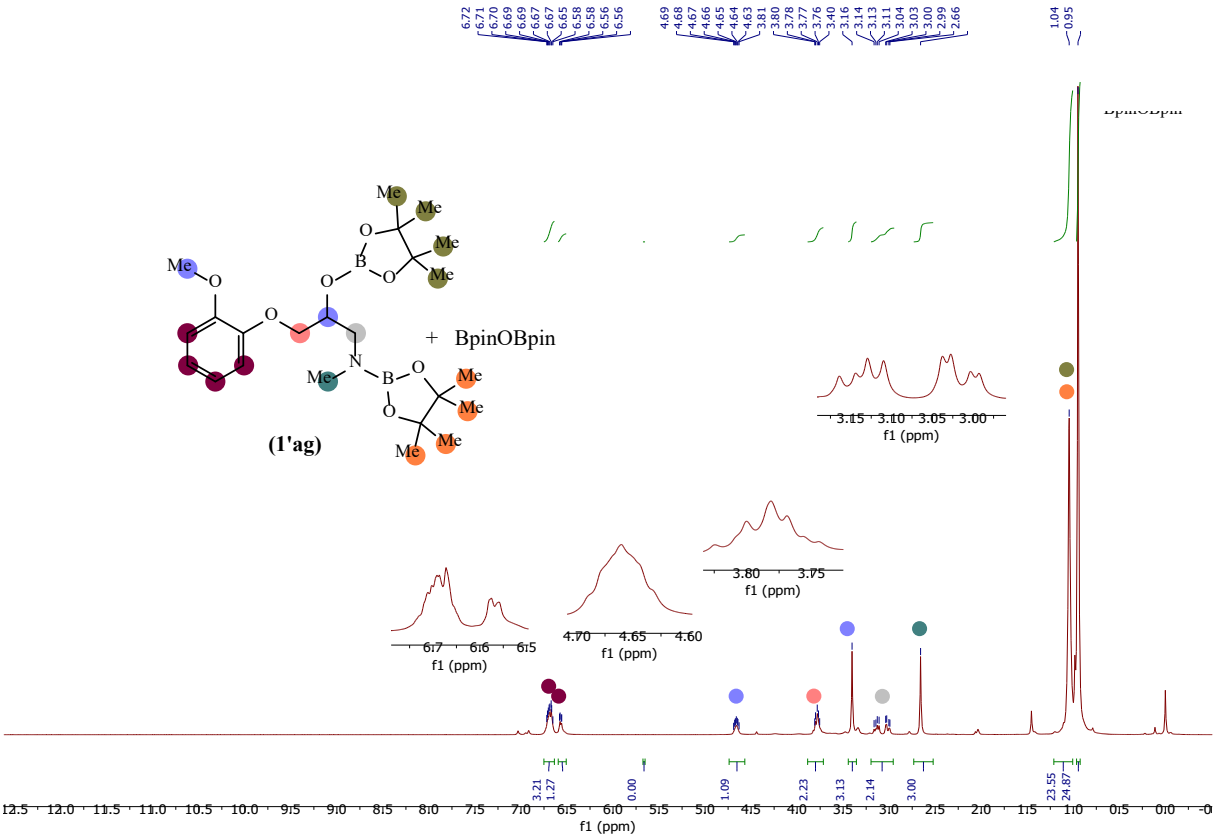



Figure S113: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'ag**

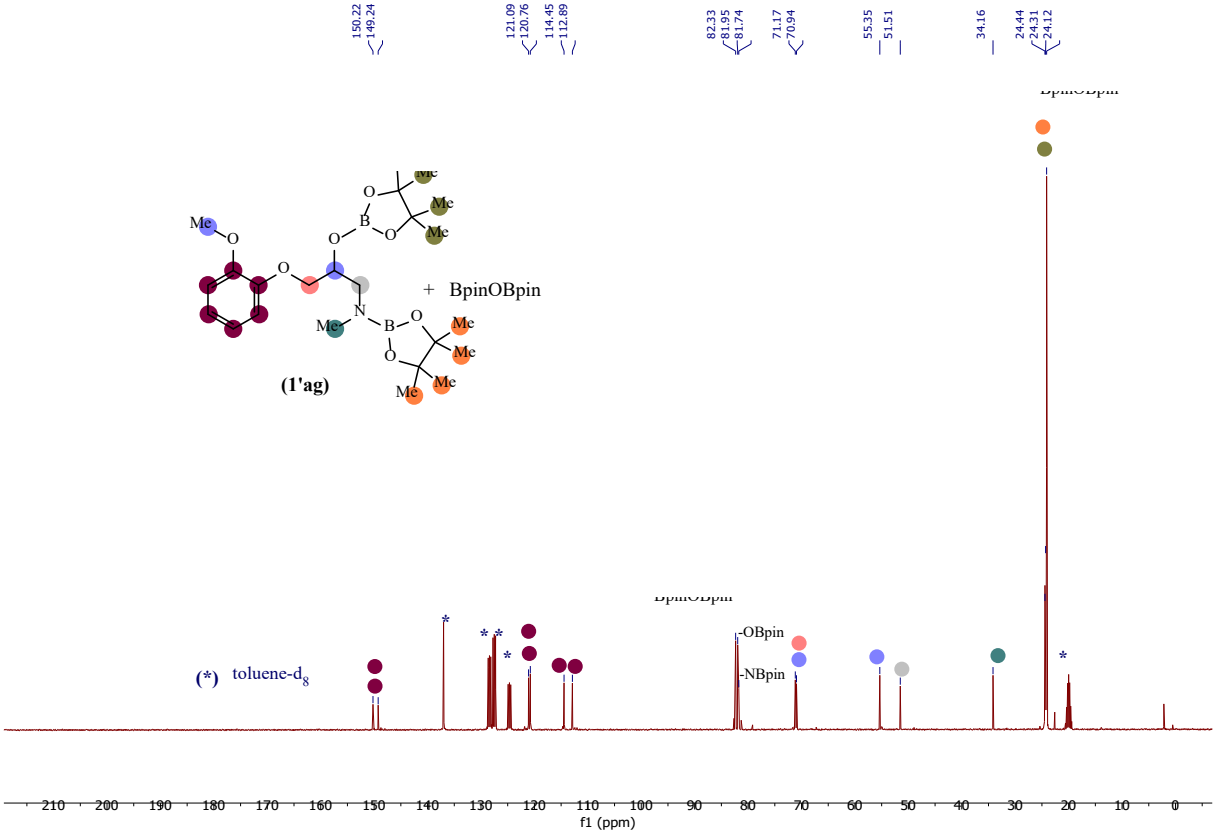



Figure S114: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'ag**

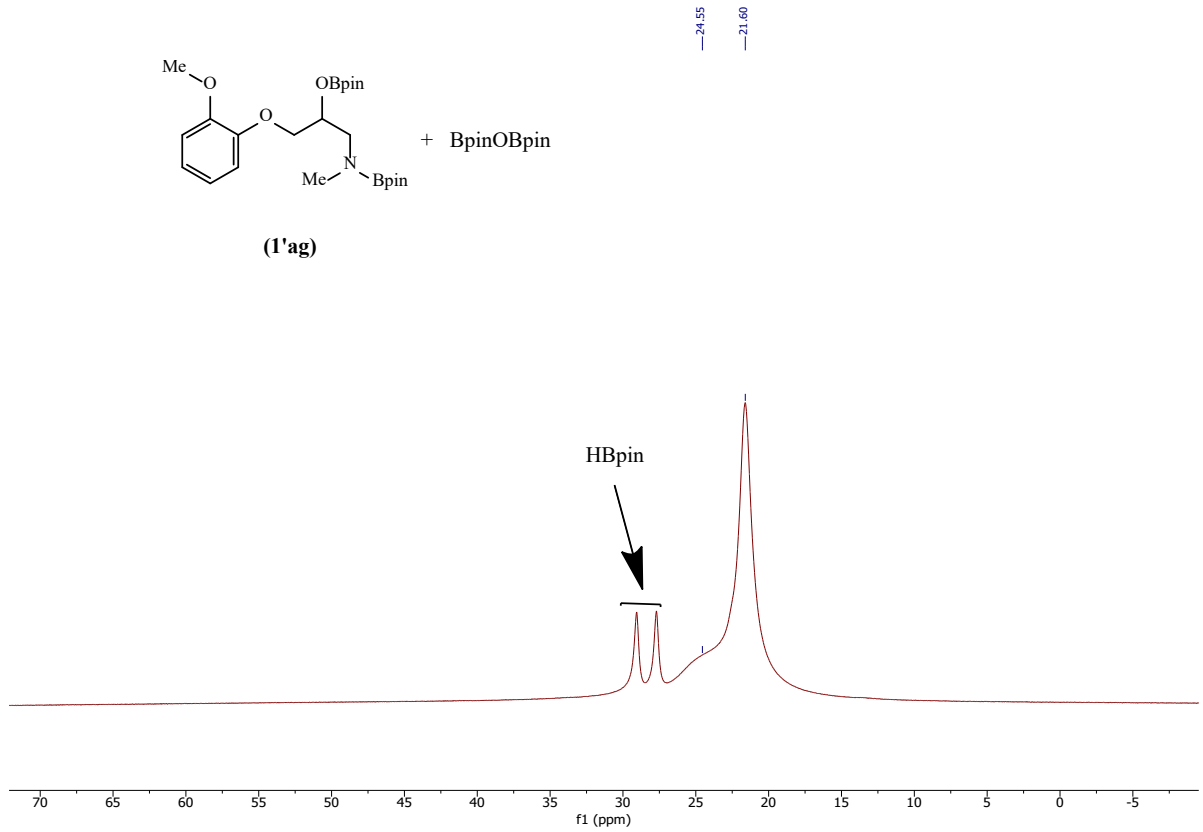



Figure S115: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'ag**

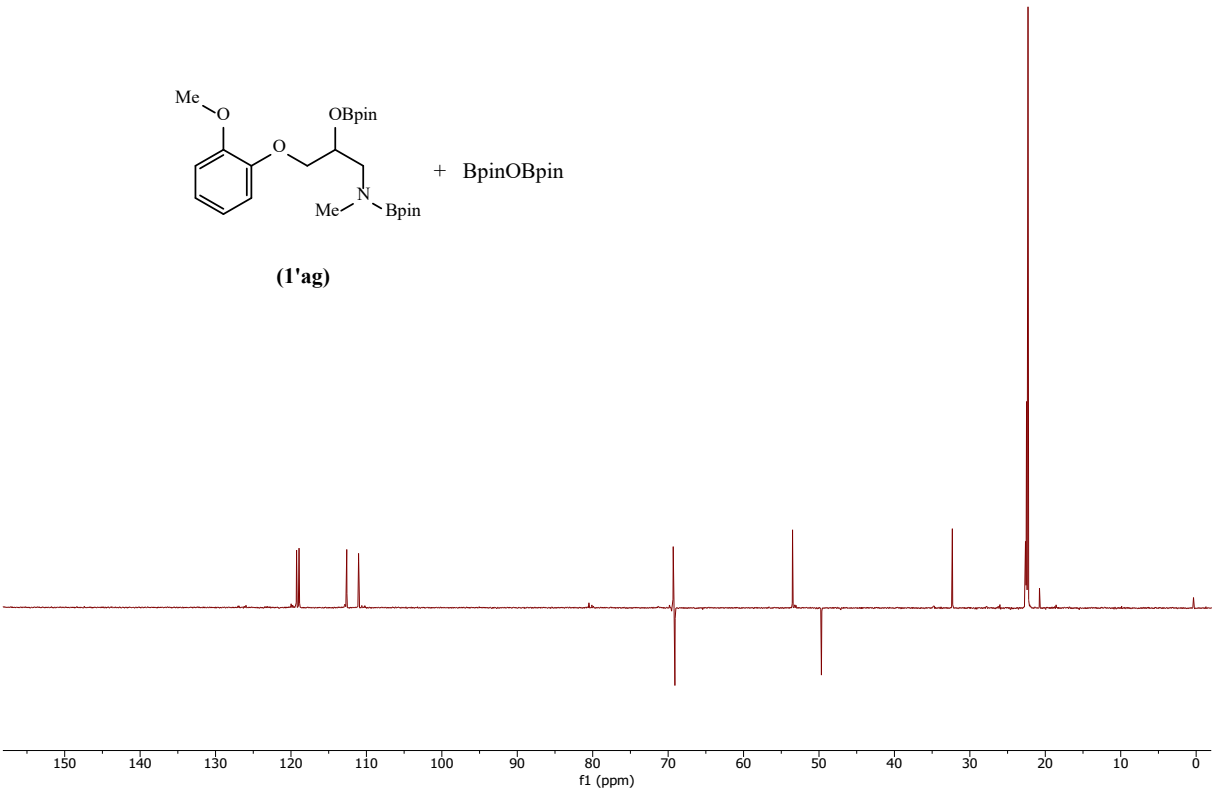



Figure S116: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'ag**

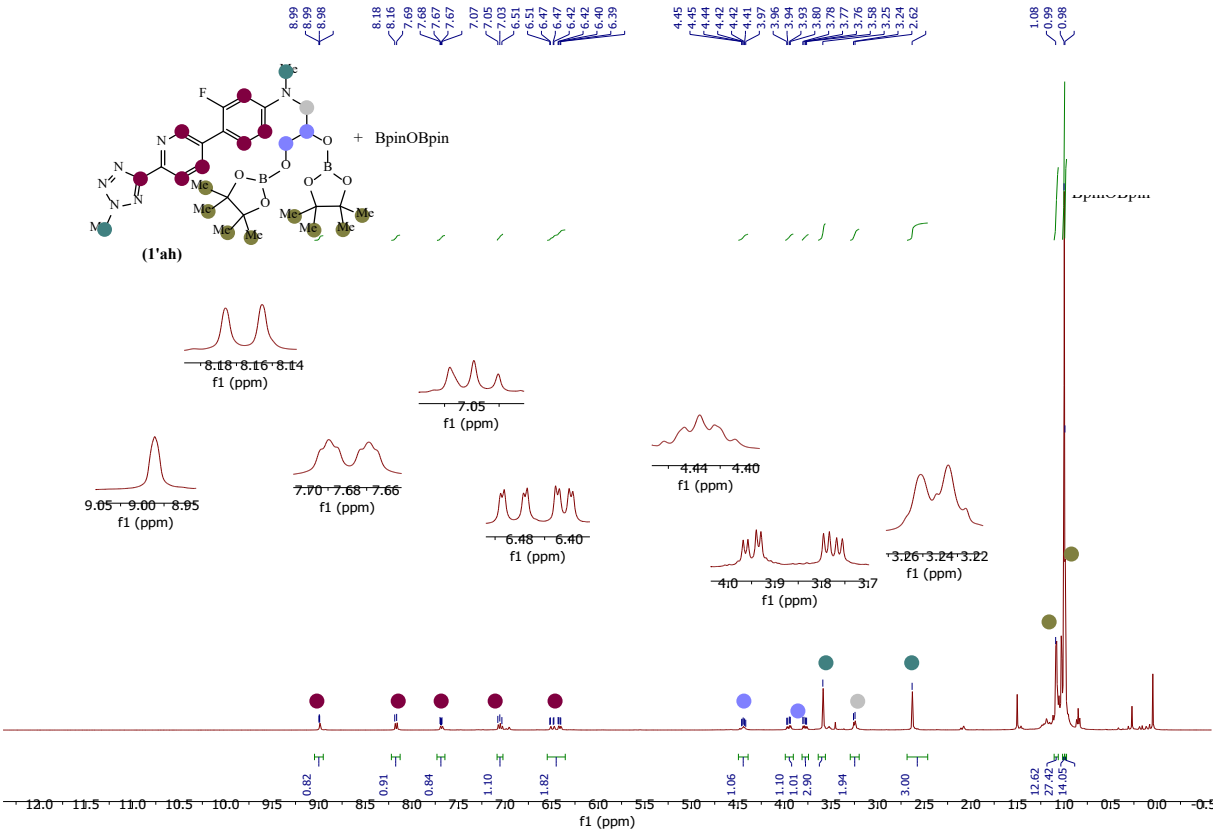



Figure S117: $^{1}$H NMR (400 MHz, Toluene-d$_8$) of compound **1'ah**

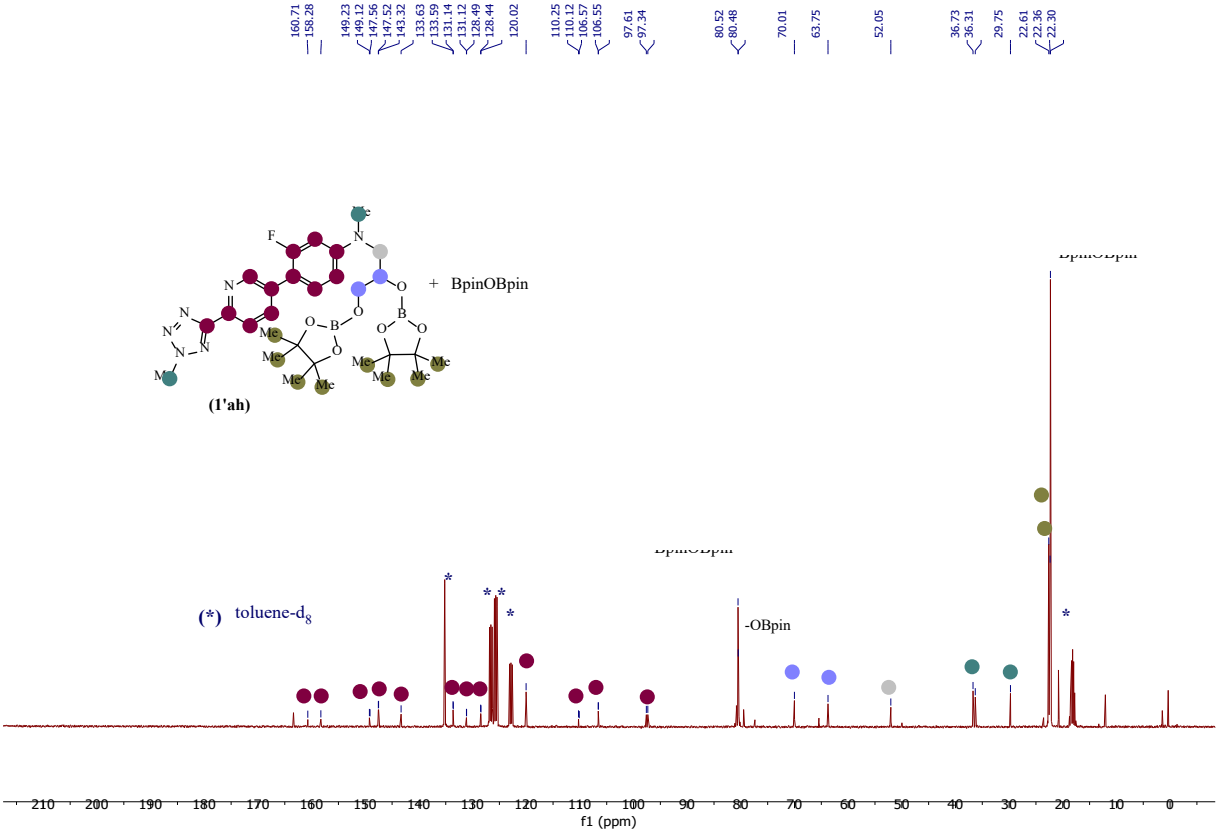



Figure S118: $^{13}$C{$^{1}$H} NMR (101 MHz, Toluene-d$_8$) of compound **1'ah**

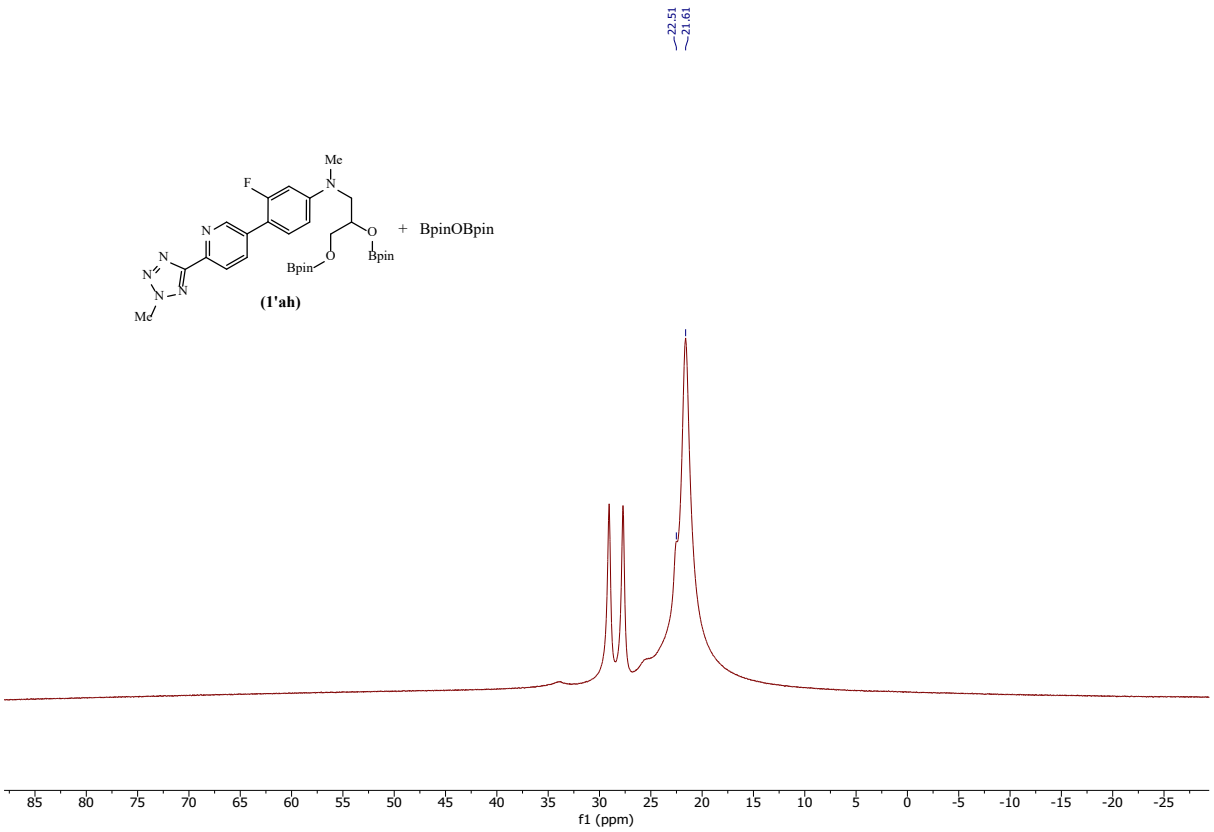



Figure S119: $^{11}B\{^1H\}$ NMR (128 MHz, Toluene-$d_8$) of compound **1'ah**

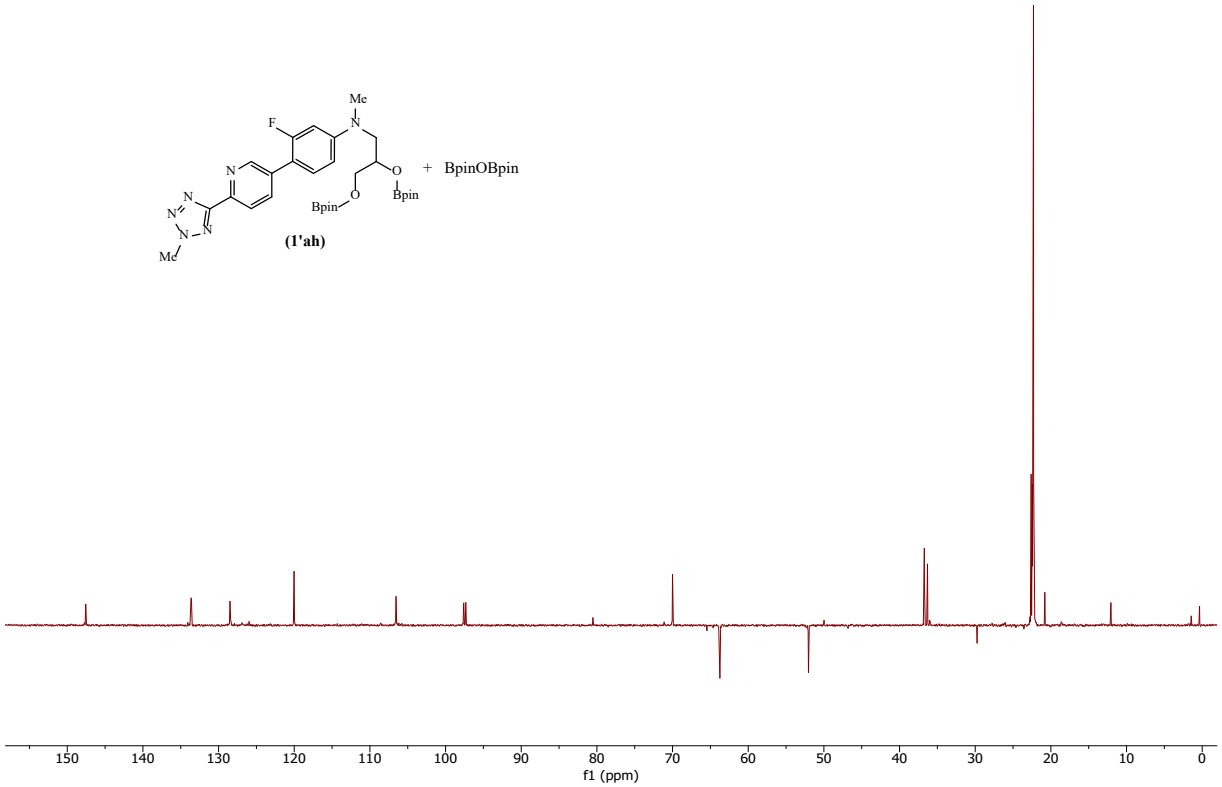



Figure S120: $^{13}C\{^1H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'ah**

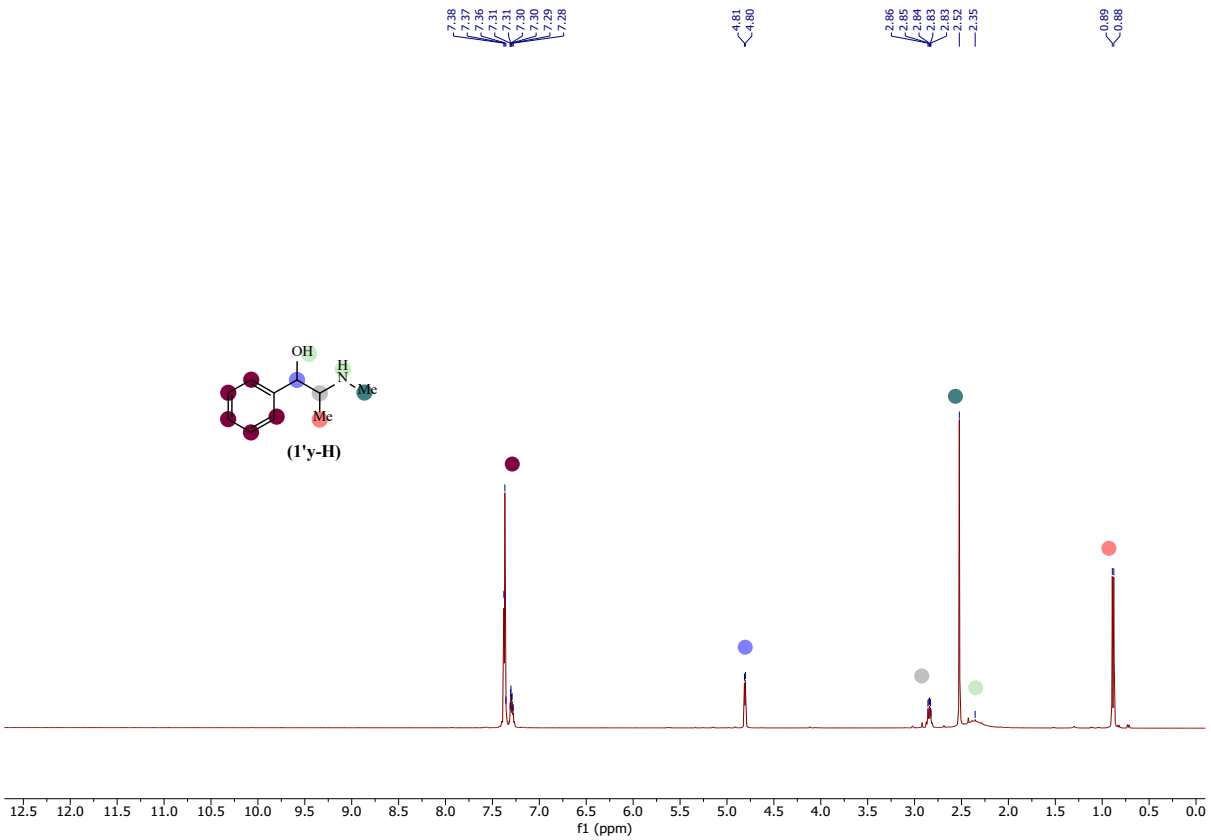



Figure S121: $^{1}$H NMR (400 MHz, Toluene-d$_8$) of compound **1'y-H**

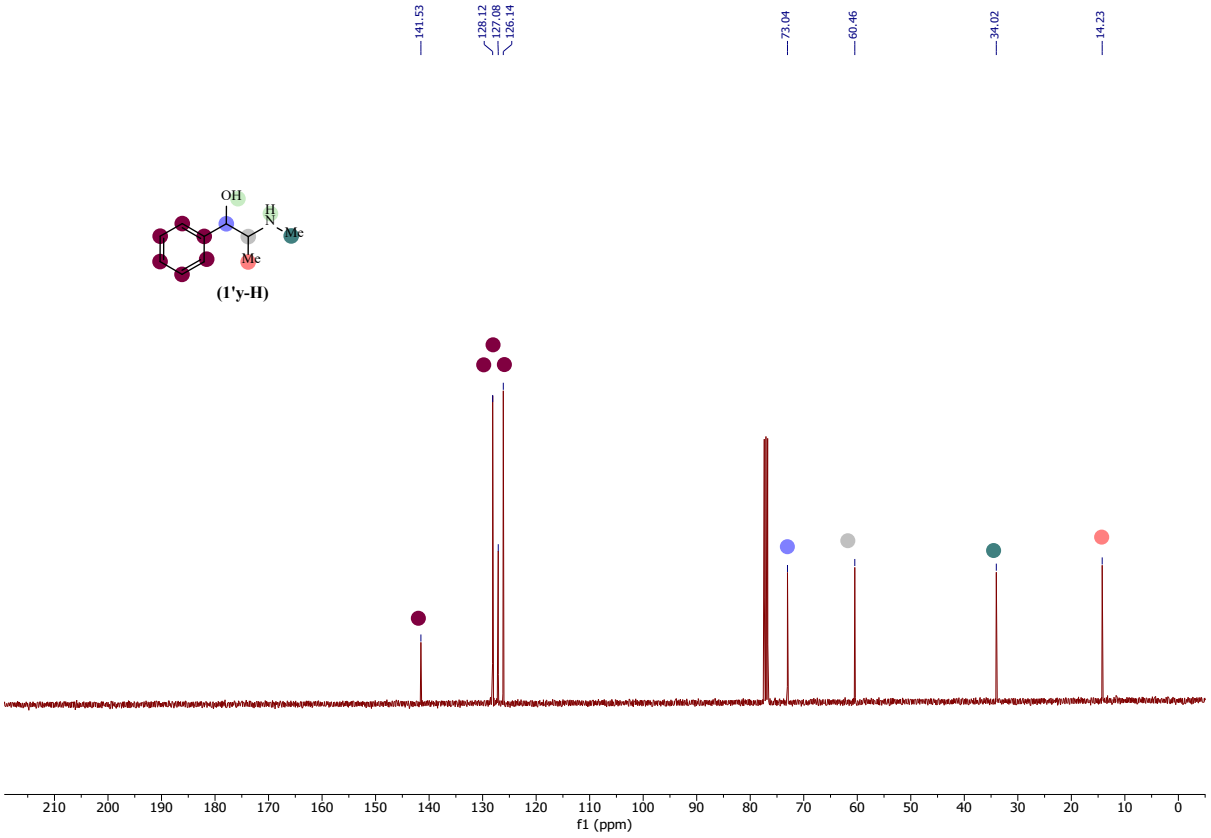



Figure S122: $^{13}$C{$^{1}$H} NMR (101 MHz, Toluene-d$_8$) of compound **1'y-H**

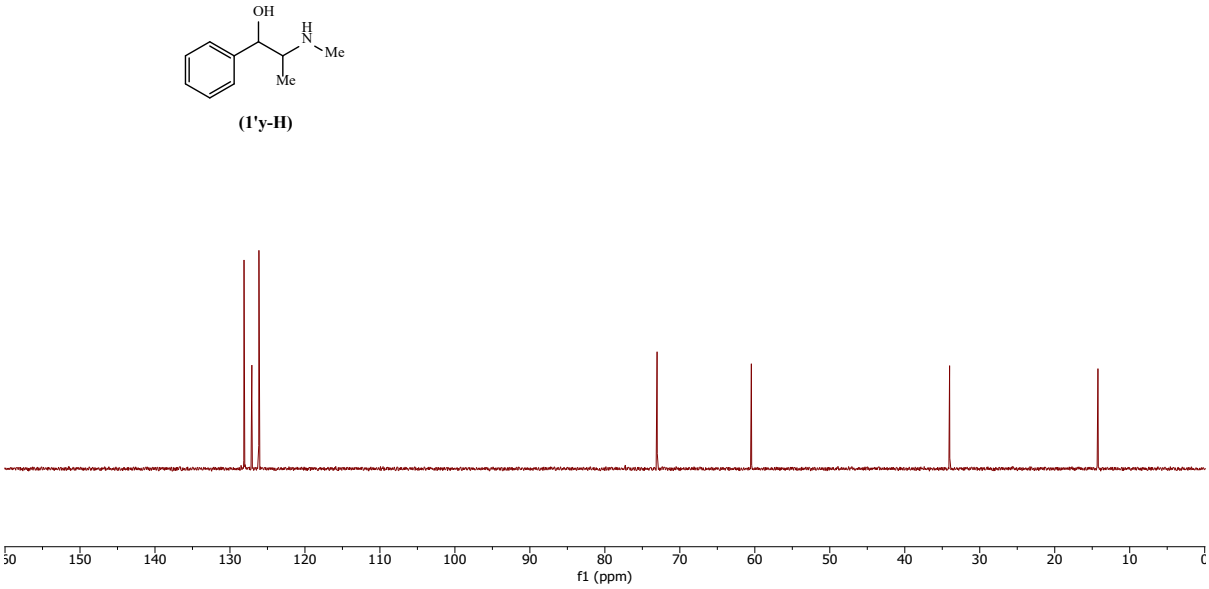



Figure S123: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'y-H**

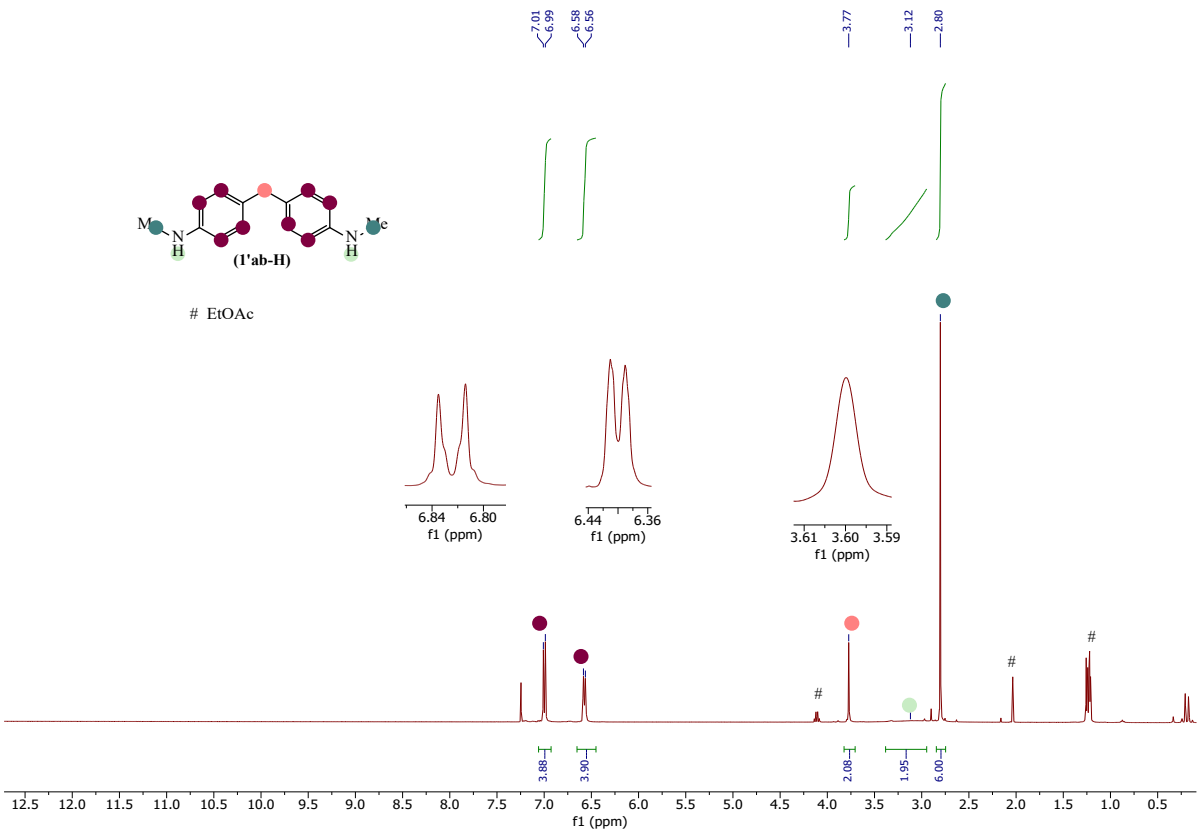



Figure S124: $^{1}H$ NMR (400 MHz, Toluene-$d_8$) of compound **1'ab-H**

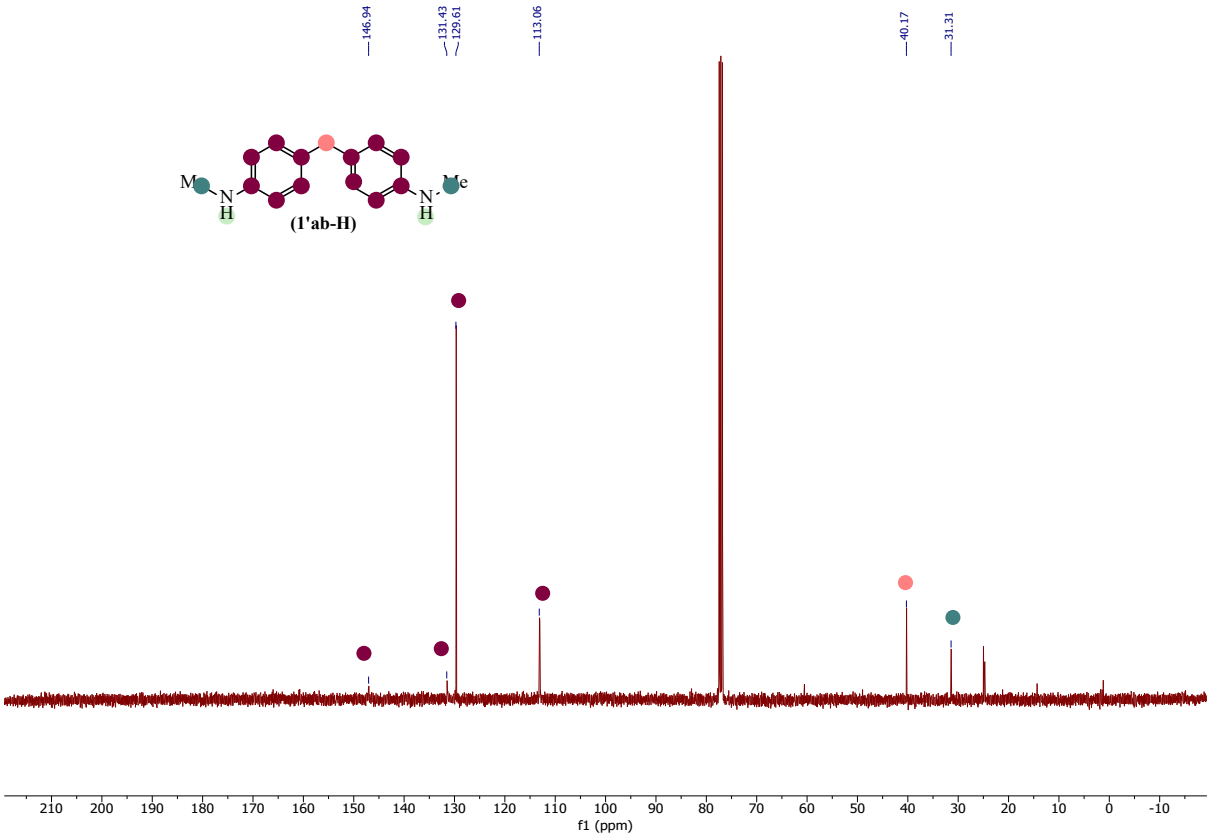



Figure S125: $^{13}C\{^{1}H\}$ NMR (101 MHz, Toluene-$d_8$) of compound **1'ab-H**

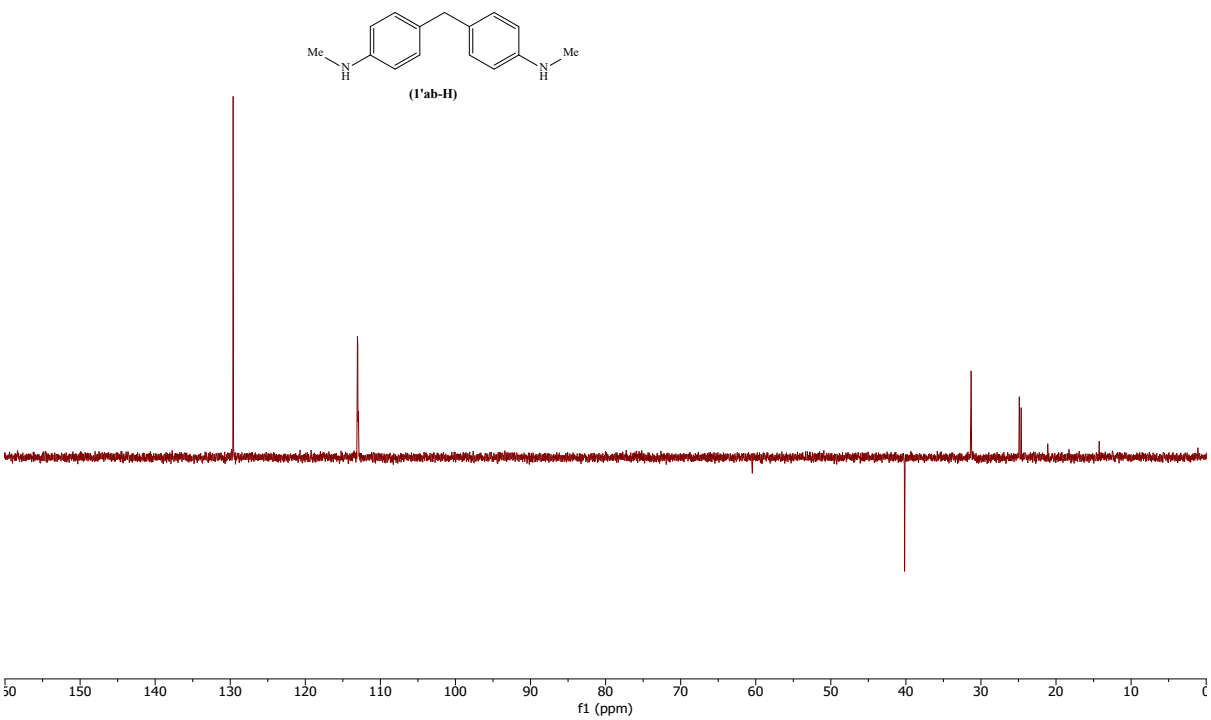



Figure S126: $^{13}C\{^{1}H\}$ NMR DEPT-135 (101 MHz, Toluene-$d_8$) of compound **1'ab-H**

## 4 Kinetic studies

### 4.1 Kinetic experiments

All the kinetic experiments were performed similarly. In the glovebox, to a J. Young NMR tube, a typical amount of uranium catalyst **II** from a stock solution (2 - 20 µmol), 3-methyl-2-oxazolidinone **1a** (0.1 – 0.40 mmol), HBpin **2** (0.45 – 2.00 mmol), 1,2,3,4,5,6-hexamethylbenzene (29.8 µmol, as internal standard) from a stock solution, were added to the NMR tube and diluted to a final volume of 0.80 mL of toluene-$d_8$. Then, the NMR tube was sealed. The NMR tube was taken out of the glovebox, and the $^1$H NMR experiment began at 110 °C. All the experiments were done by changing either one substrate or the catalyst while keeping the other reagents constant, and the data was collected early in the reaction (conversion less than 20%) in constant intervals. The product concentrations were measured by the signal area ratio [N-$(CH_3)_2$] group of the product, a singlet at 2.21 ppm, and compared to the signal at 2.07 ppm, which corresponds to the benzene-Me singlet of the internal standard. The least-square fit of the initial product concentration versus time determined reaction rates.

Figures for kinetic studies of the reaction between 3-methyl-2-oxazolidinone and HBpin using uranium catalyst **II**:

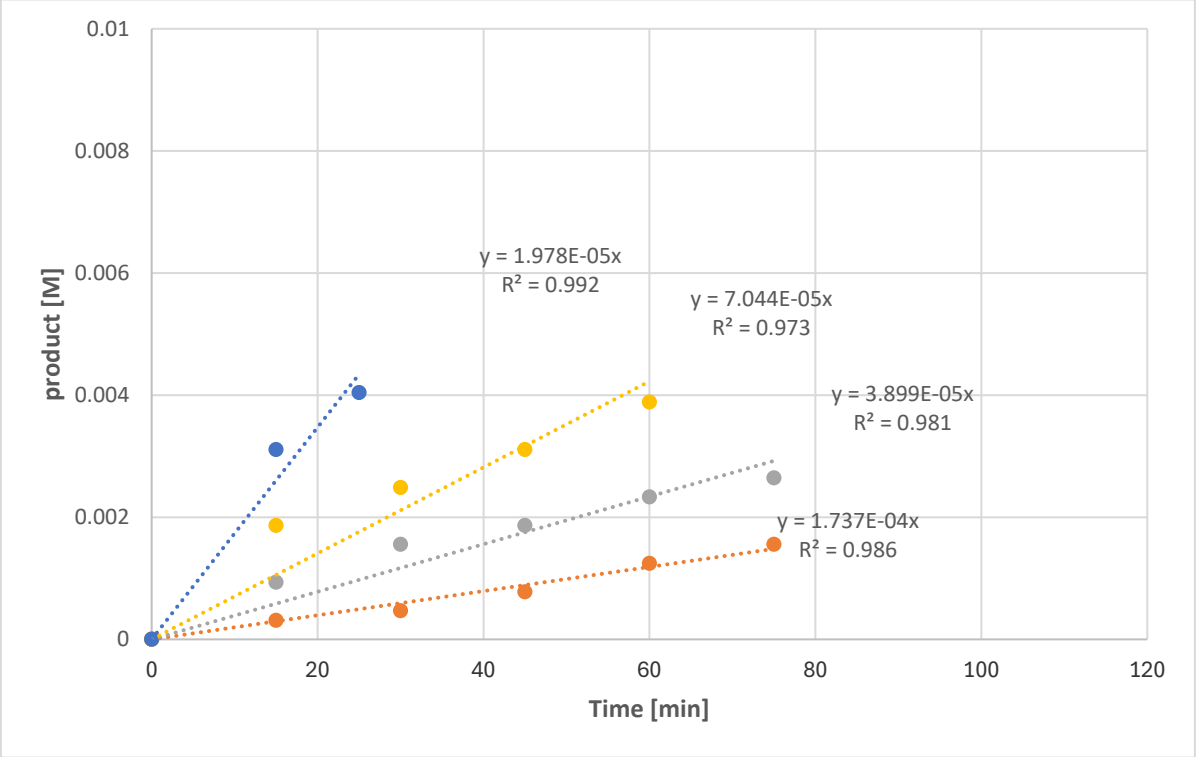



Figure S127. Initial reaction progresses at different concentrations of uranium catalyst **II**. (20.0 µmol (●), 12 µmol (●), 6.0 µmol (●), 2.0 µmol (●).

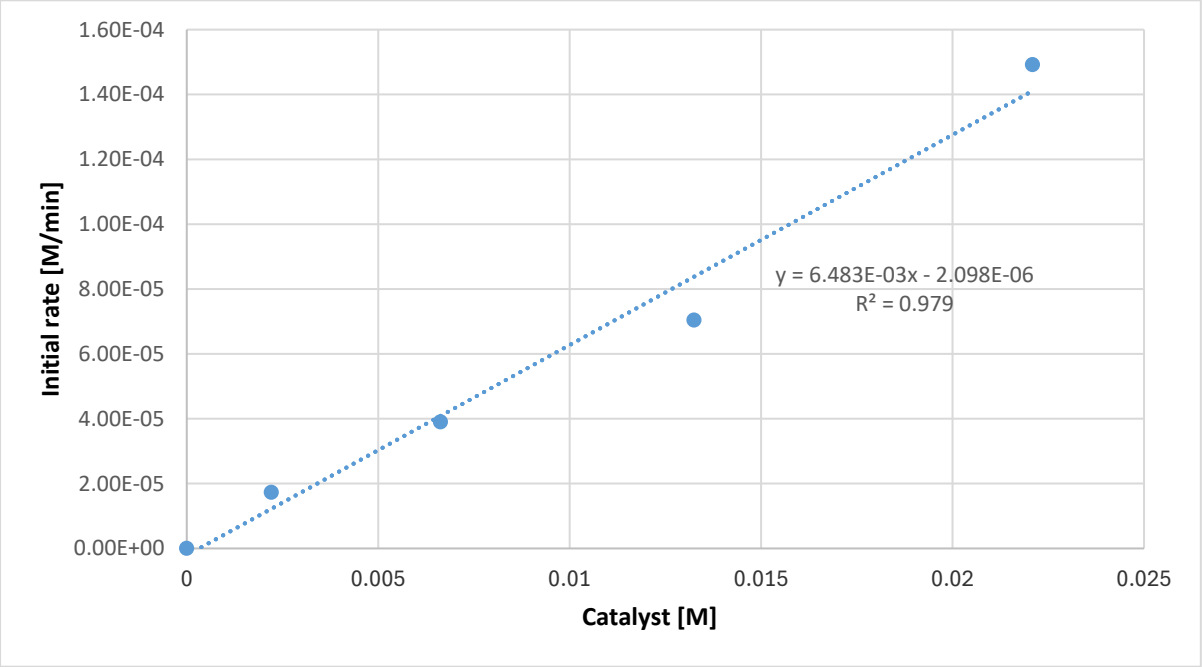



Figure S128. Plot of the initial reaction rate as a function of uranium catalyst **II** concentration.

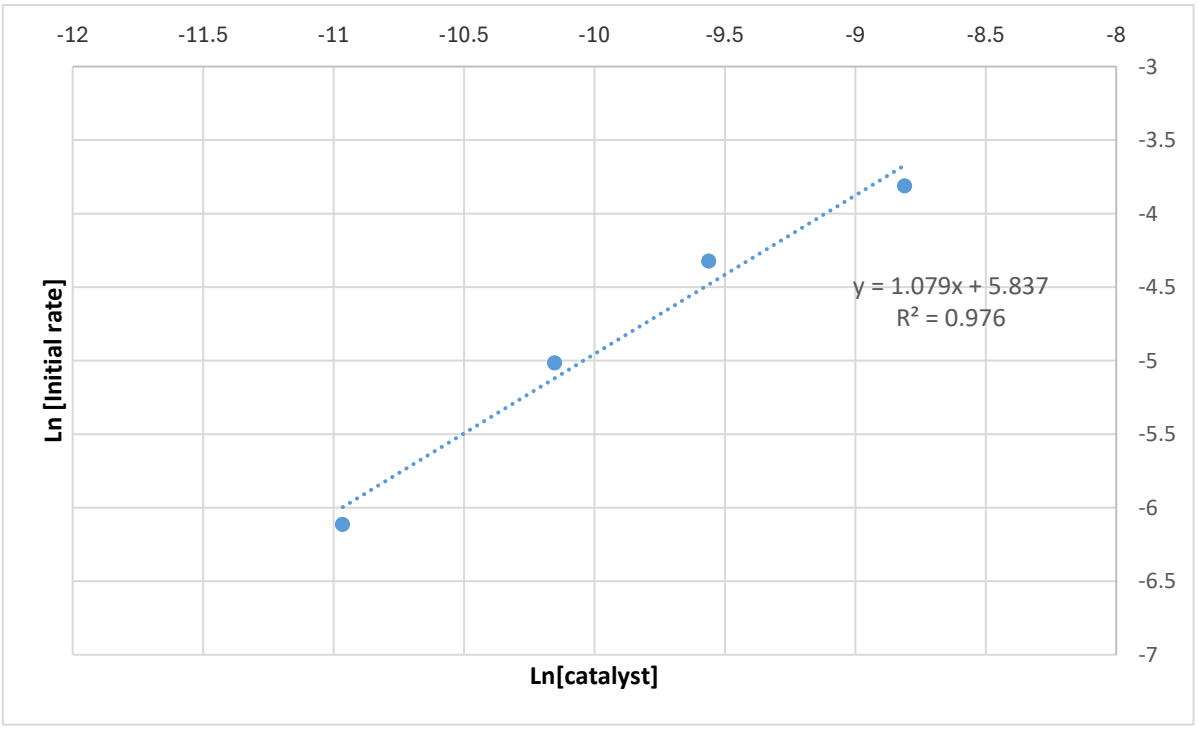



Figure S128. Plot of Ln(reaction rate) as a function of the Ln(catalyst concentration).

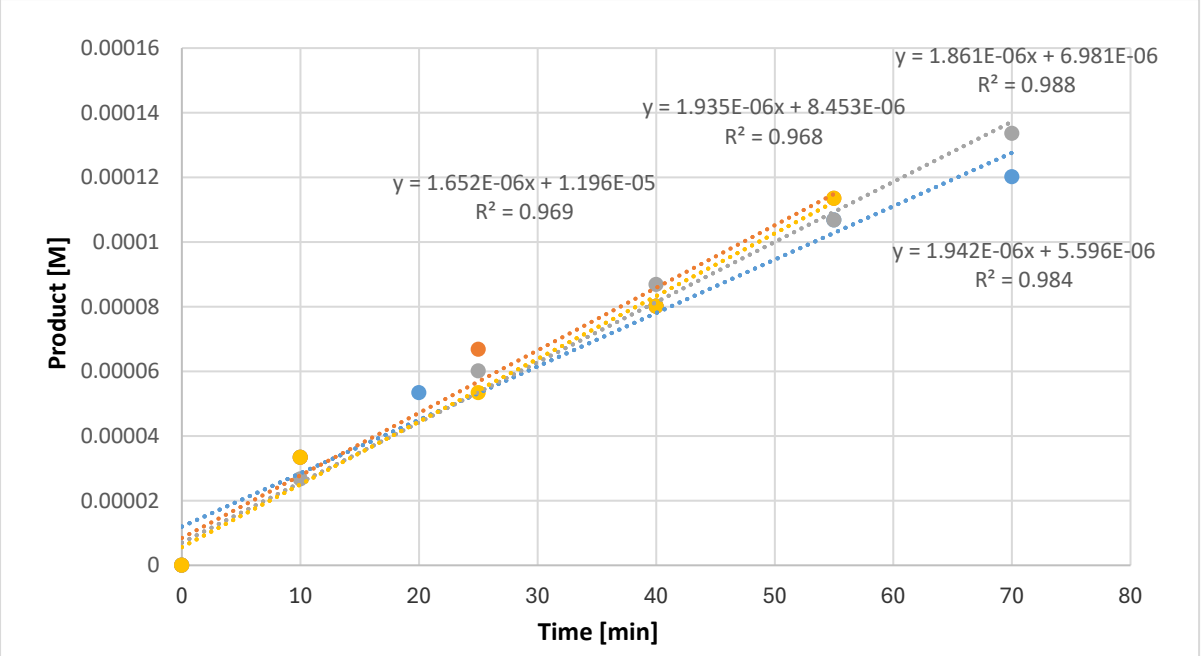



Figure S129. Initial reaction progress at different concentrations of carbamate (3-methyl-2-oxazolidinone). (0.05 M (●), 0.1 M (●), 0.2 M (●), 0.4 M (●)).

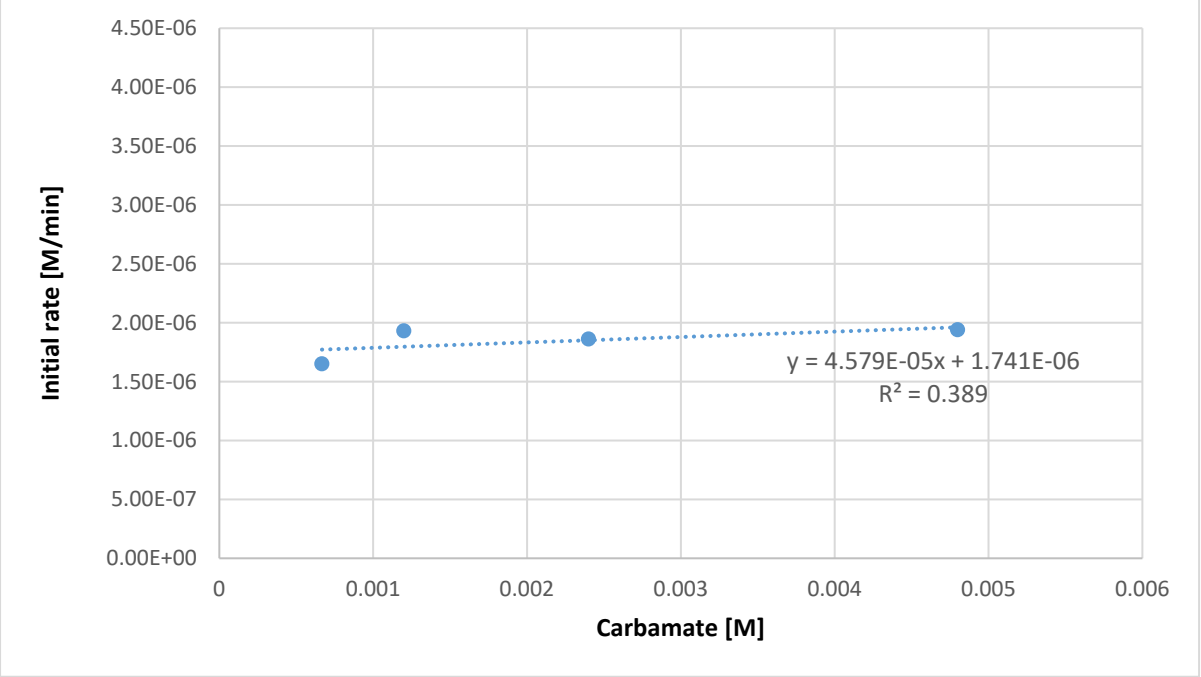



Figure S130. Plot of the initial reaction rate as a function of carbamate **1a** (3-methyl-2-oxazolidinone) concentration.

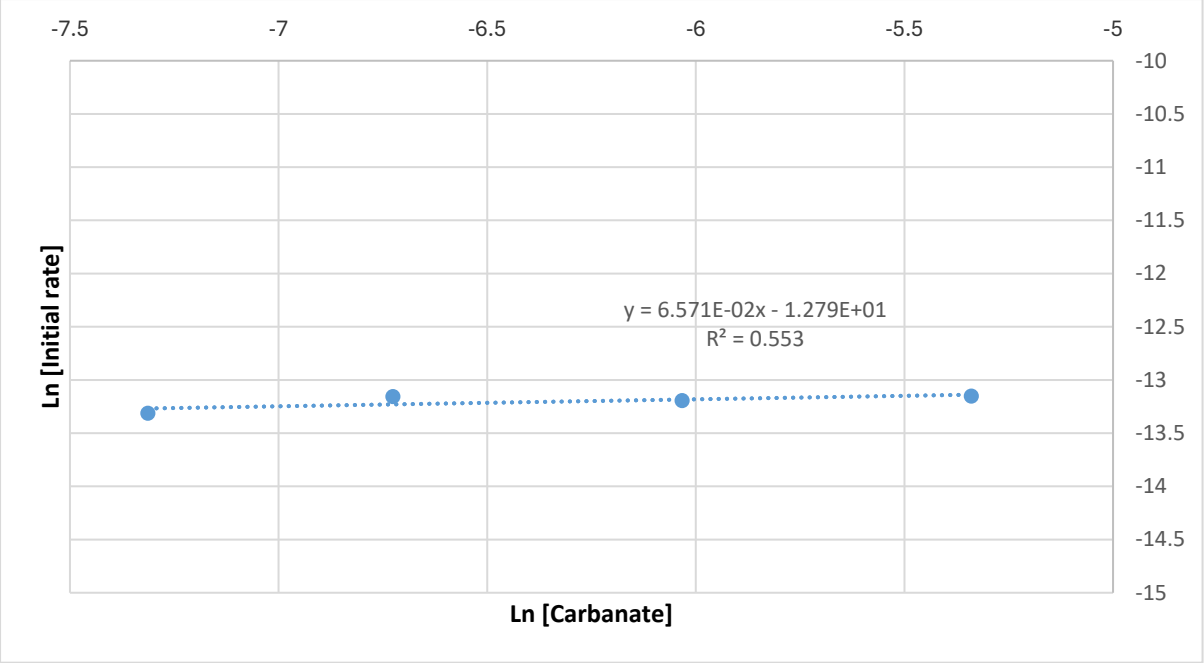



Figure S131. Plot of Ln(initial rate) as a function of Ln(3-methyl-2-oxazolidinone concentration).

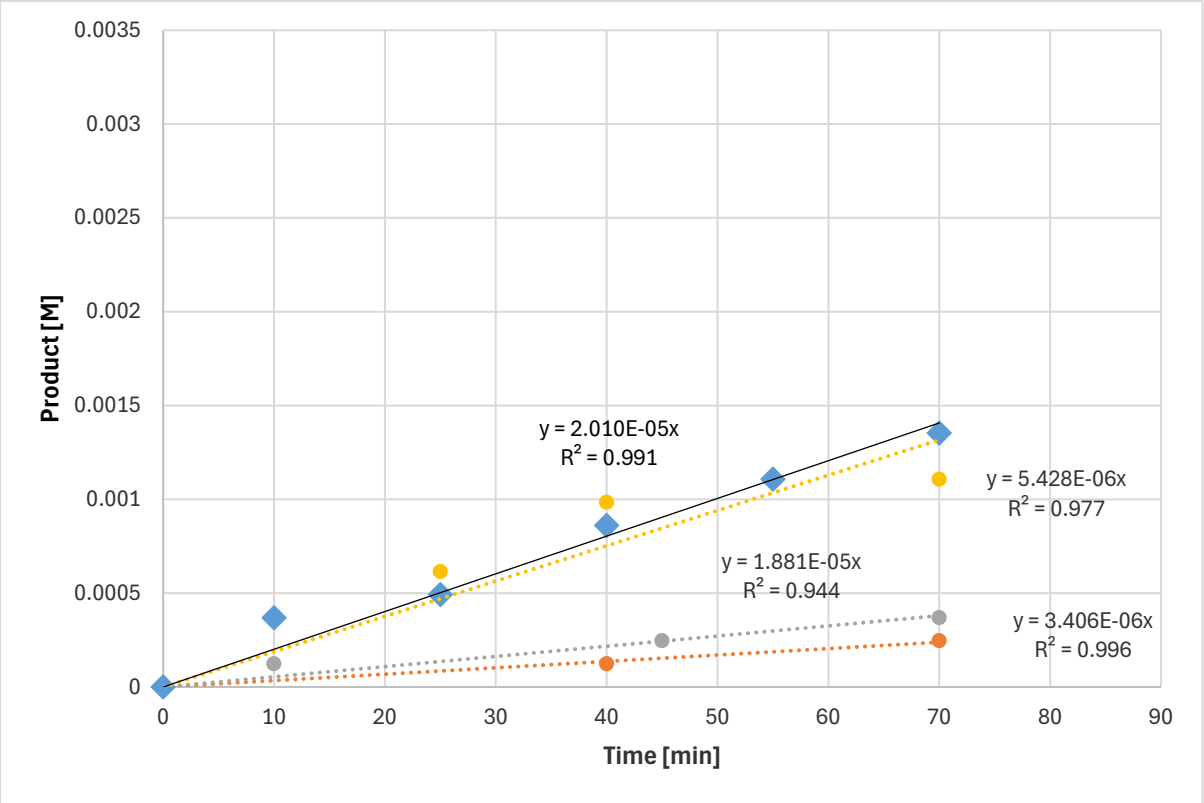



Figure S132. Initial reaction progress at different concentrations of HBpin. (0.07 M (●), 2 M (●), 4 M (●), 6 M (●)).

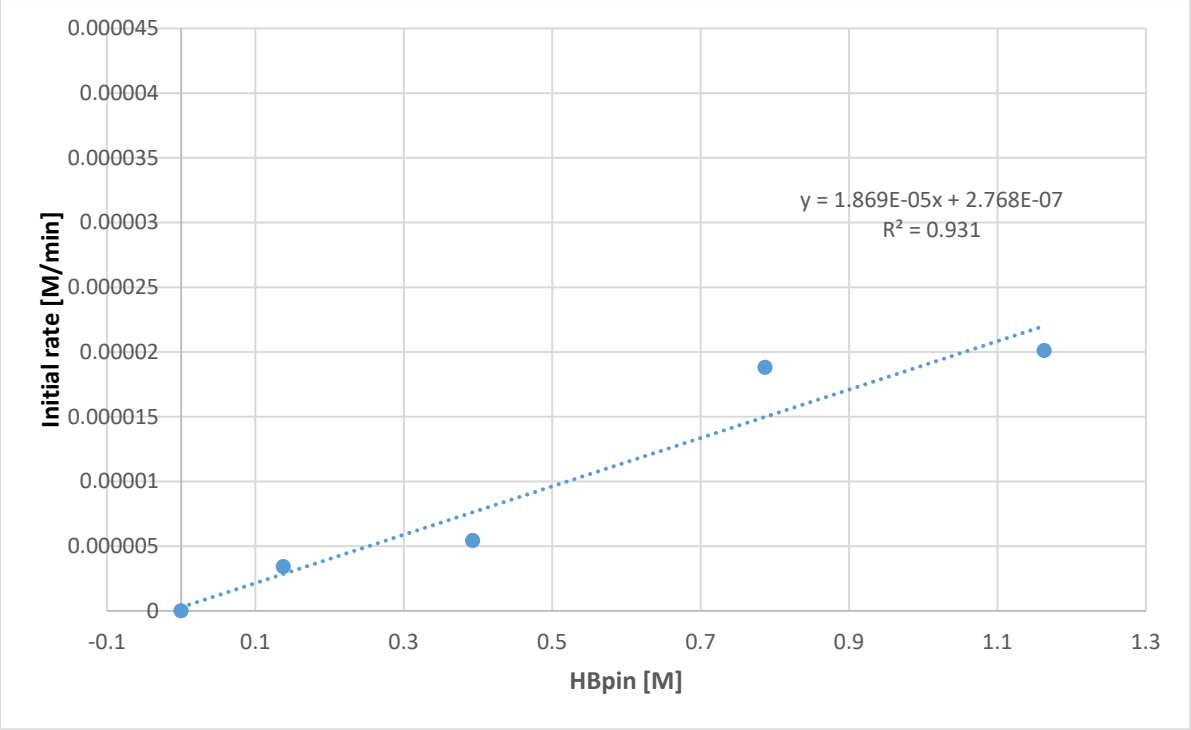



Figure S133. Plot of the initial reaction rate as a function of HBpin concentration.

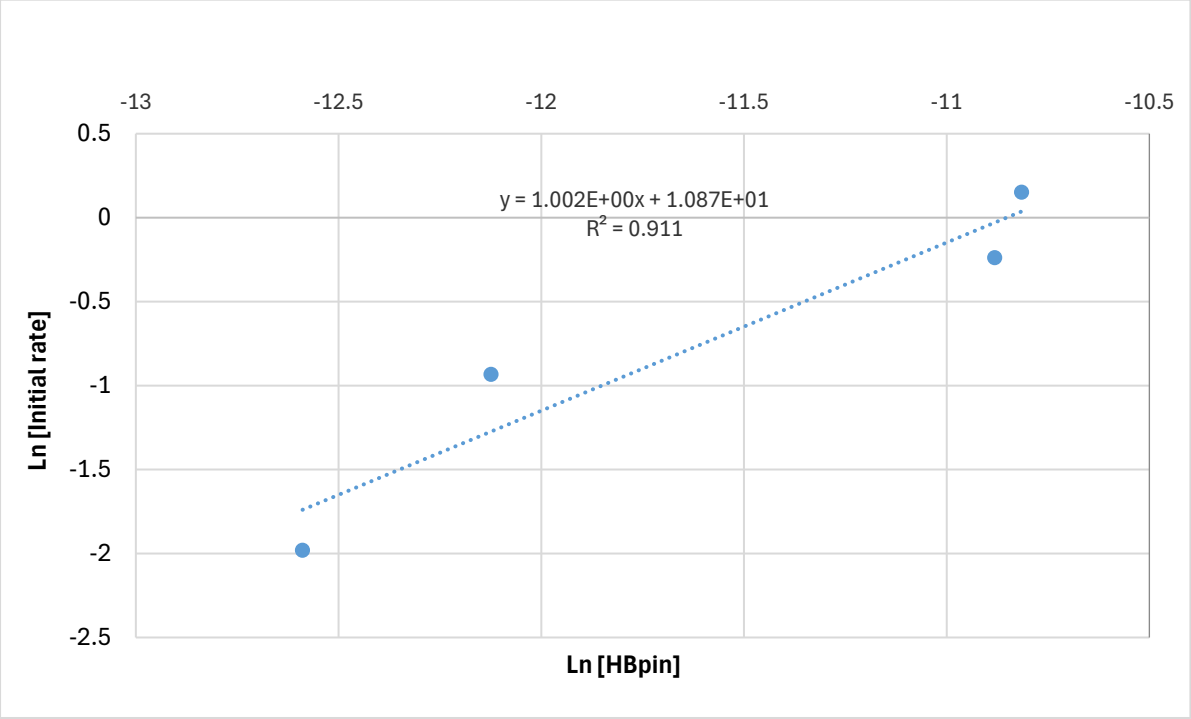



Figure S134. Plot of Ln(initial rate) as a function of Ln(HBpin concentration).

### 4.2 Activation parameters

Activation parameters, including enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and activation energy (Ea) were calculated from the kinetic data using Eyring and Arrhenius plots. Performed similarly to

the kinetic experiments in a typical sample. The J. Young tube was loaded with the desired amount of uranium catalyst **II** (3%mmol) from stock solution, 3-methyl 2-oxazolidinones **1a** (0.2 mmol), HBpin **2** (0.61 mmol), diluted to a final volume of 0.75 mL with Toluene-$d_8$, and sealed. The sample was then inserted into a Bruker Avance 300 spectrometer. The data was collected at appropriate time intervals. Data on the rate dependence on temperature was obtained as shown above. The least square fit of initial product concentration versus time determined reaction rates at each temperature. These data were then plotted as ln(k/T) vs. 1/T from which the enthalpy ($\Delta H^{\ddagger}$), and the entropy ($\Delta S^{\ddagger}$) of the transition state could be derived using the Eyring equation. From a plot of ln(k) vs. 1/T, the activation energy can be obtained using the Arrhenius equation. Enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and activation energy (Ea) were calculated from the slope and intercept of the least-square fit.

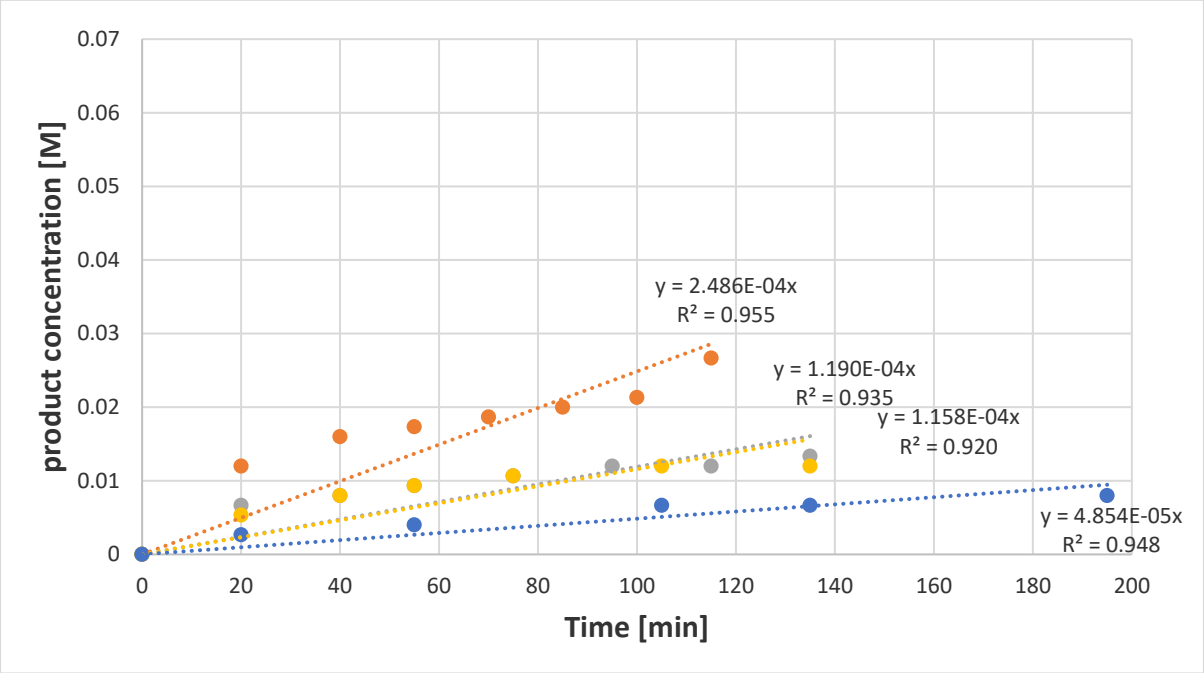



Figure S135. Initial reaction progress at different temperatures (measurements at 120 $^0$C (●), 100 $^0$C (●), 90 0C (●), 70 $^0$C (●))

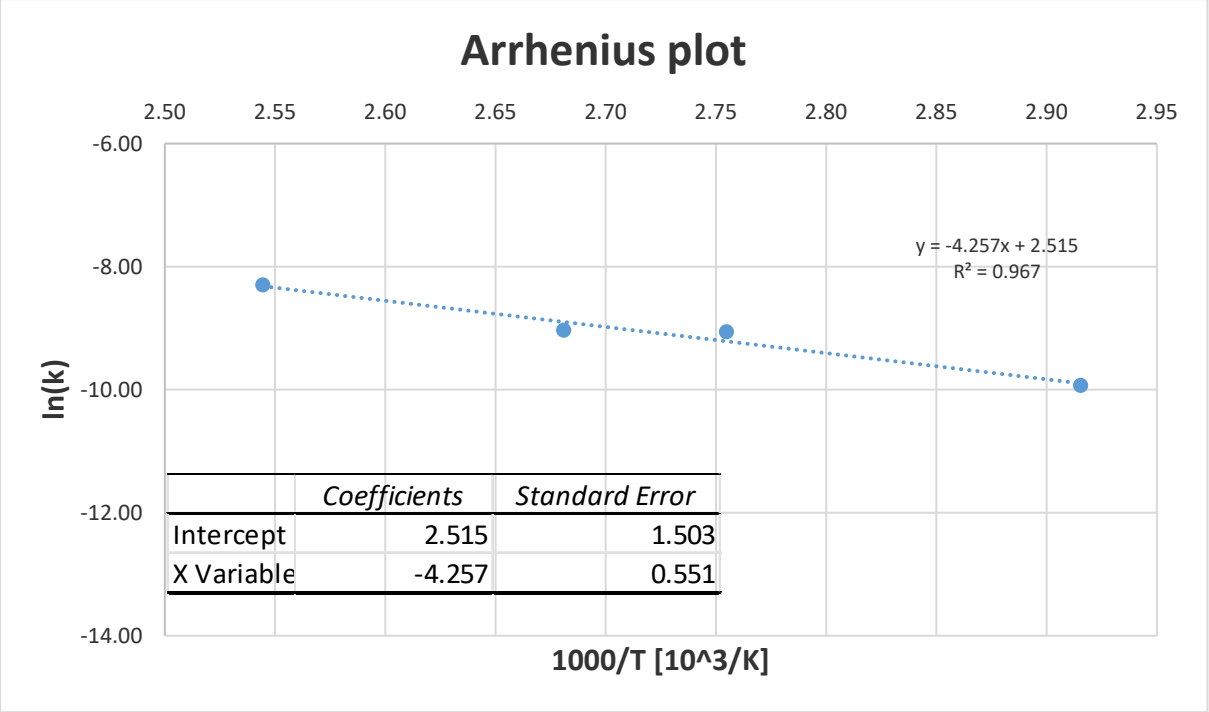



Figure S136. Arrhenius plot for the reaction between 3-methyl 2-oxazolidinones and HBpin using uranium catalyst **II**.

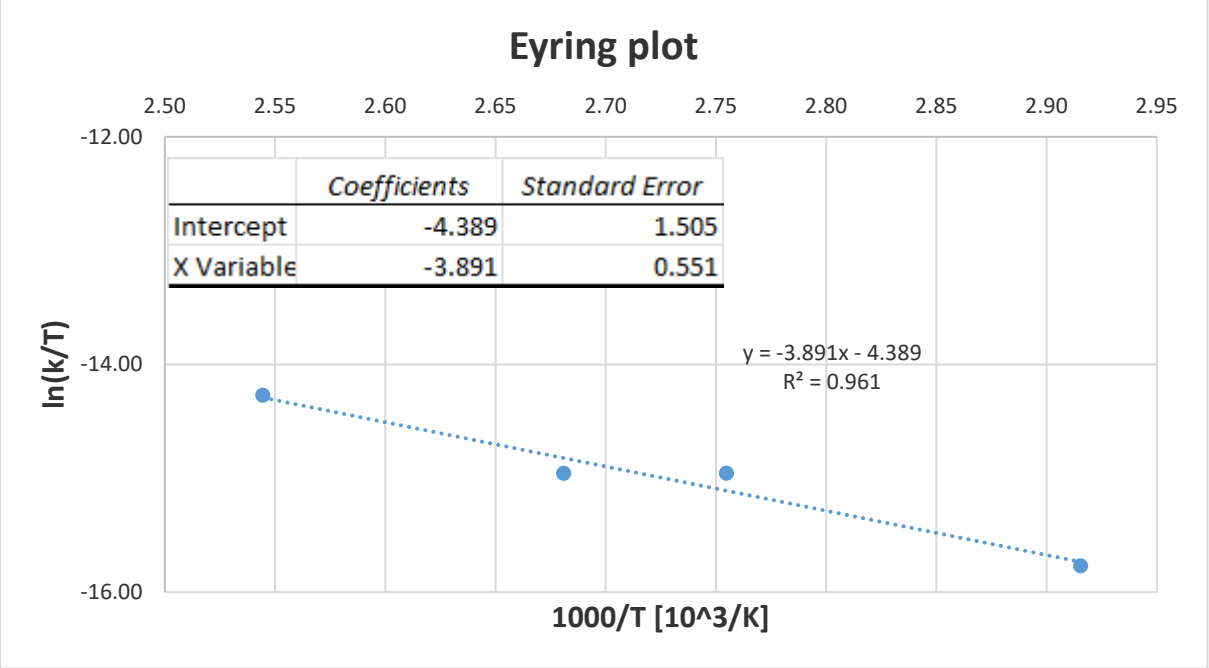



Figure S137. Eyring plot for the reaction between 3-methyl 2-oxazolidinones and HBpin using uranium catalyst **II**.

## 5 Formaldehyde C=O deoxygenation

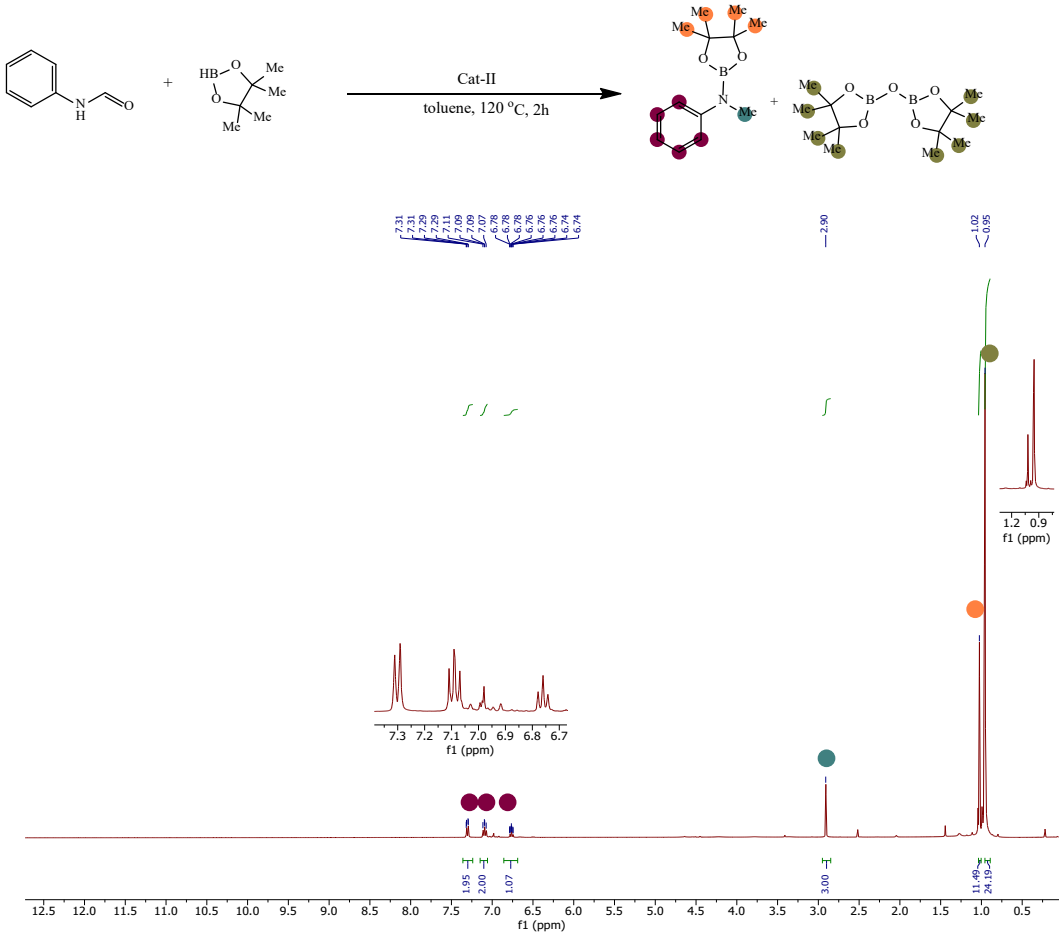



Figure S138: $^{1}$H NMR of formanilide deoxygenation

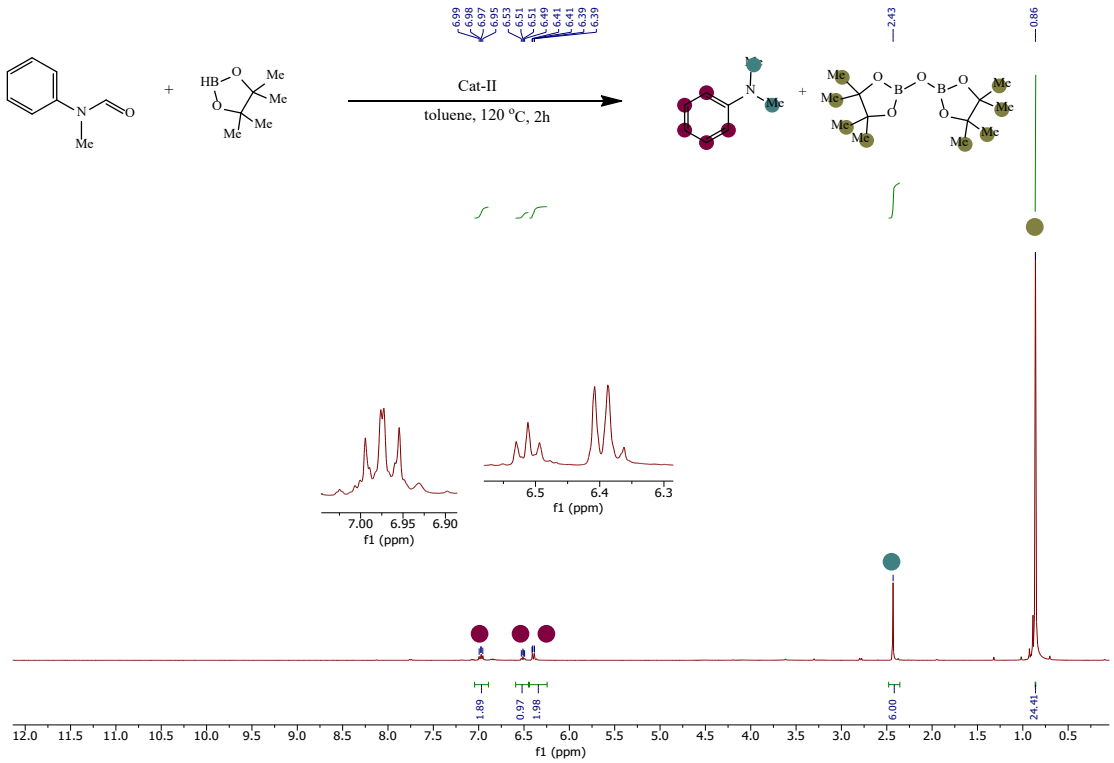



Figure S139: $^{1}$H NMR of N-methylformanilide deoxygenation

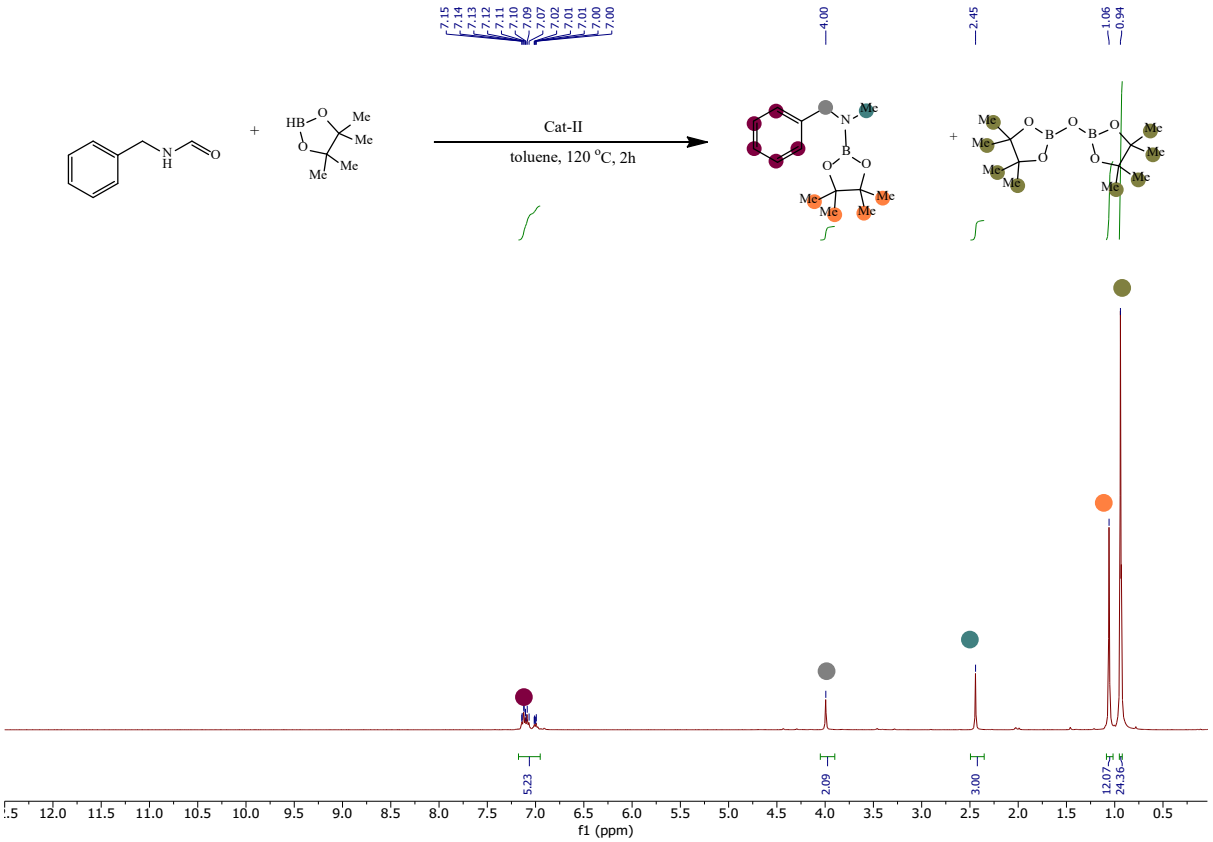



Figure S138: $^{1}$H NMR of N-benzylformamide deoxygenation

## 6 Computational details

All geometries were optimized with Gaussian16 package[5] at the BP86-D3(BJ)[6,7] level of theory, using for Th the SDD ECP78 core potential, adapted to An(IV) oxidation state,[8] and def2SVP[9] for B, C, H, N, Si, and O atoms. The reported free energies were obtained adding thermal corrections in gas-phase to the electronic energy in solvent (SMD model) computed via single point energy calculations in toluene at the B3PW91-D3(BJ) level,[10,6] as basis set 6-311g(d,p) for the atoms of the main groups and SDD ECP78 pseudopotential for Th. The optimized minima and transition states were verified by harmonic vibrational analysis to have no and one proper imaginary frequency, respectively. In addition, the ΔG values reported in the Schemes 1 and 2 of the main text were calculated at a temperature of 298.15 K and a pressure of 1.0 atm.

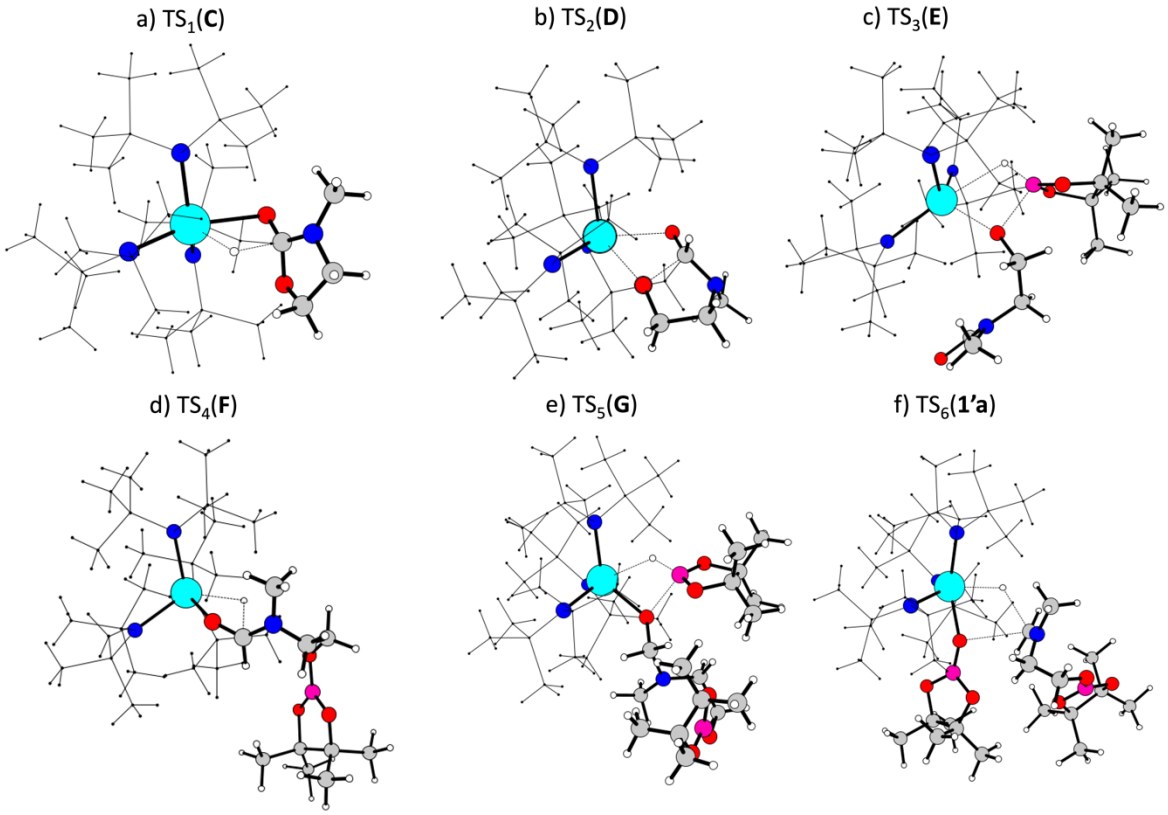



**Figure S13.** Optimized geometries of the transition states involved in the proposed catalytic mechanism: a) $TS_1$(**C**), b) $TS_2$(**D**), c) $TS_3$(**E**), d) $TS_4$(**F**), e) $TS_5$(**G**) and f) $TS_6$(**1'a**). The structures are represented in balls and sticks, and C, H, O, N, B, and Th are depicted in gray, white, red, blue, pink, and cyan, respectively.

## 7 References


1) Simpson, S. J.; Turner, H. W.; Andersen, R. A. Hydrogen-deuterium exchange: perdeuteriohydridotris(hexamethyldisilylamido)thorium(IV) and -uranium(IV) *J. Chem. Soc.* **1979**, *101*, 7728- 7729
2) Dormond, A.; El Bouadili, A.; Aaliti, A.; Moise, C. Insertion of Carbonyl Compounds into Actinide─Carbon σ Bonds: Reactivity of $[(Me_3Si)_2)_2N]_2SiMe_3$, *J. Organomet. Chem*. **1985**, *288*, C1−C5.
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