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Supplementary Information

for

Deoxygenative hydroboration of primary and secondary amides: A catalyst-free and solvent-free approach

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Contents:

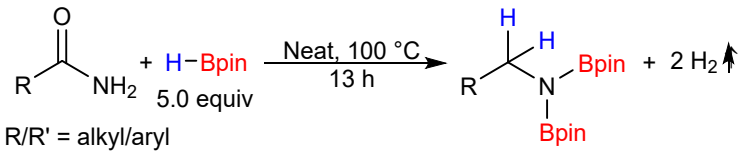
General experimental information

All reactions were performed under argon atmosphere using Schlenk techniques or inside a MBraun glove box. Pinacolborane (HBpin), amides were purchased from Sigma–Aldrich, TCI and used without further purification. C_6D_6, DMSO-d_6, $CDCl_3$ were purchased from Sigma-Aldrich, were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. ^1H and $^{13}C\{^1H\}$ spectra were recorded on Bruker AV-200 MHz, AV-400 MHz and AV-500 MHz and referenced to the resonances of the solvent used.

Table S1. Optimization table of catalyst and solvent free for the hydroboration of benzamide

Entry	Catalyst	Equiv. of HBpin	Solvent	Temperature (ºC)	Time (h)	NMR Yield (%)
1.	-	4.5	Neat	60	20	55
2.	-	4.5	Neat	70	20	60
3.	-	5.0	Neat	80	12	56
4.	-	5.0	Neat	80	16	73
5.	-	5.0	Neat	90	12	72
6.	-	5.0	Neat	90	16	85
7.	-	5.0	Neat	95	12	91
8.	-	5.0	Neat	100	13	98

General procedure for the hydroboration of primary amides



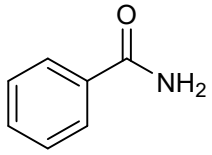
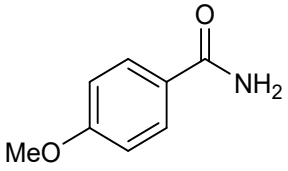
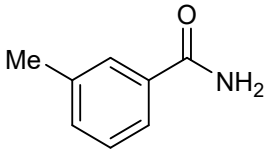
Scheme S1. General procedure for the hydroboration of primary amides.

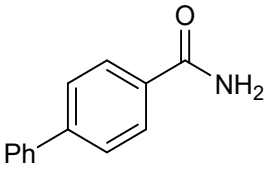
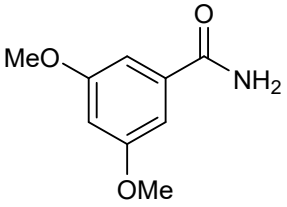
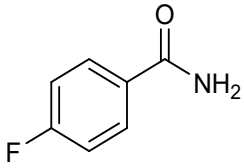
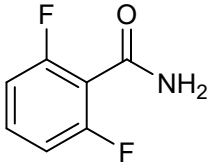
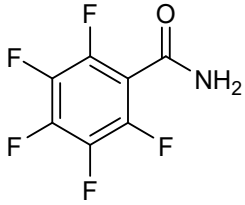
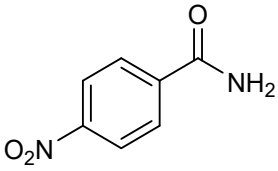
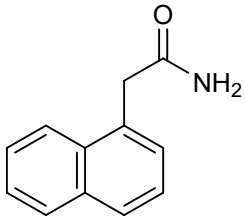
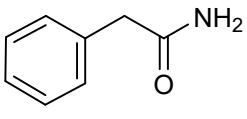
Primary amide (0.127 mmol), pinacolborane (5.0 equiv, 0.635 mmol) were mixed together in a Schlenk tube or in a screw cap NMR tube inside the glove box. The reaction mixture was allowed

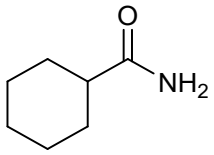
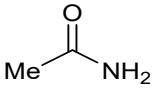
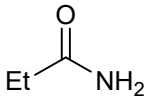
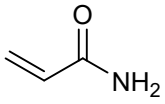
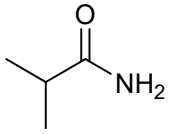
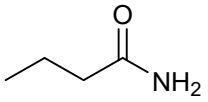
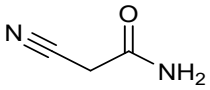
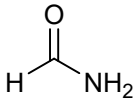
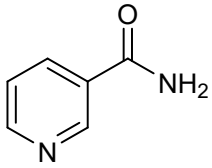
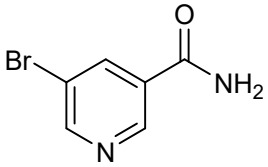
to heat at 100 °C for 13 h without adding any solvent. Upon completion of the reaction, mesitylene (0.127 mmol) as an internal standard, was added while making the NMR in an appropriate deuterated solvent. The progress of the reaction was monitored by ^{1}H NMR, which indicates the completion of the reaction by the appearance of a new R-CH_2-N(Bpin)$_2$ resonance (Scheme S1). Upon completion, the reaction mixture was stirred with 1.0 mL 2.0 (M) NaOH solutions and 1.0 mL Et_2O for 1 h to complete the hydrolysis. Next, the reaction mixture was worked up with Et_2O: H_2O mixture (1:1) and the Et_2O part were concentrated in vacuum to get corresponding reduced amines. Consequently, 1.0 mL 1.0 (M) methanolic HCl solution was added to the concentrated amines followed by addition of 1.0 mL Et_2O and the corresponding amine hydrochloride salt was purified by washing with Et_2O. Isolated amine hydrochlorides were characterized through NMR spectroscopy in DMSO-d_6.

Hydroboration product of primary amides, **1a**, **1e** were isolated and in both the cases little discrepancy was observed with the NMR yield.

Table S2. Substrates scope for the primary amide hydroboration.

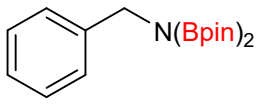
Entry	Amide Precursor	Temperature (°C)	Time (h)	NMR yield (%)	Product
1.		100	13	97	**1a**
2.		100	13	98	**1b**
3.		100	13	98	**1c**

4.		100	13	95	**1d**
5.		100	13	95	**1e**
6.		100	13	96	**1f**
7.		100	13	22	**1g**
8.		100	13	28	**1h**
9.		100	13	>99	**1i**
10.		100	13	70	**1j**
11.		100	13	90	**1k**

12.		100	13	66	**1l**
13.		100	13	99	**1m**
14.		100	13	87	**1n**
15.		100	13	85(reduction of both C=C and C=O bond)	**1o**
16.		100	13	69	**1p**
17.		100	13	94	**1q**
18.		100	13	76	**1r**
19.		100	13	70	**1s**
20.		100	13	n. r.	**1t**
21.		100	13	n. r.	**1u**

Analytical data (^{1}H and ^{13}C NMR) of the borylamines of corresponding primary amides:

For every reaction, along with the *N*-borylated amine Bpin-O-Bpin formed as second product which show a singlet at δ 1.17-1.18 ppm in ^{1}H NMR and peak at δ 24.1-24.4 and 82.4-82.9 ppm in ^{13}C NMR.

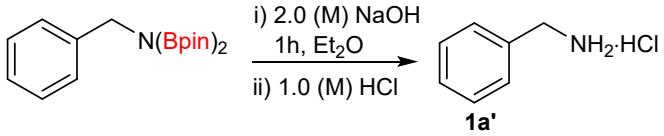


1. **1a:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36-7.32 (m, 2H, *Ph*), 7.22-7.20 (t, 2H, *Ph*), 7.17-7.14 (t, 1H, *Ph*), 4.26(s, 2H, PhCH_2N(Bpin)$_2$), 1.29 (s, 24H,N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 142.9 (*Ph*), 137.5(*Ph*), 127.6 (*Ph*), 127.4 (*Ph*), 126.8 (*Ph*), 125.9(*Ph*),82.95(PhCH$_2$N(B*pin*)$_2$), 82.19(PhCH$_2$N(B*pin*)$_2$), 81.78(PhCH$_2$N(B*pin*)$_2$),47.1(Ph*C*H$_2$N(Bpin)$_2$), 24.4 (Ph*C*H$_2$N(B*pin*)$_2$) ppm.

The spectroscopic data is consistent with literature data.[1]

Phenylmethanamine hydrochloride (1a′).

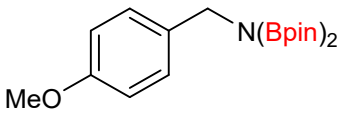
The general procedure was followed to isolate phenylmethanamine hydrochloride salt, **1a′** (15.15 mg, 85.2% yield) as a colorless solid.



^{1}H NMR (200 MHz, DMSO-d$_6$): δ 8.47(br, 3H, NH_2·*H*Cl), 7.52-7.49 (d, $^3J_{H\text{-}H}$ = 6.50 Hz, 2H, *Ph*), 7.39-7.41 (m, 3H, *Ph*), 4.00 (br,2H, CH_2) ppm.

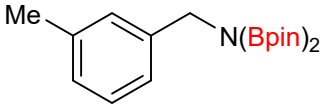
^{13}C{^{1}H} (100.6 MHz, DMSO-d$_6$): δ 134.18 (*Ph*),129.0 (*Ph*), 128.6 (*Ph*), 128.6 (*Ph*), 42.2 (*C*H$_2$) ppm.

The spectroscopic data is consistent with literature data.[2]



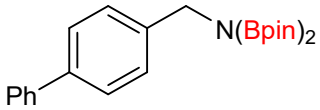
2. **1b:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.27-7.23 (m, 2H, *Ph*), 6.77 (m, 2H, Ph),4.17(s, 2H, PhCH_2N(Bpin)$_2$), 3.78 (s, 3H, OCH_3), 1.21 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 157.9 (*ArC*-OMe), 137.4 (*Ph*), 135.3 (*Ph*), 133.8 (*Ph*), 128.6 (*Ph*),127.7 (*Ph*), 126.7 (*Ph*),82.8 (PhCH$_2$N(B*pin*)$_2$), 54.9 (O*Me*), 46.4 (Ph*C*H$_2$N(Bpin)$_2$), 24.39(Ph*C*H$_2$N(B*pin*)$_2$) ppm.

The spectroscopic data is consistent with literature data.[1]



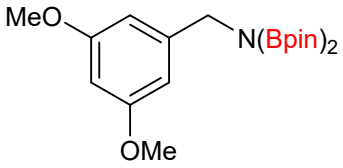
3. **1c:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.16-7.00 (m, 5H, *Ph*), 4.23(s, 2H, PhC*H*$_2$N(Bpin)$_2$), 2.32 (s, 3H, C*H*$_3$), 1.22 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 142.8 (*ArC*-Me), 137.5 (*Ph*), 128.1 (*Ph*), 127.3 (*Ph*), 126.7 (*Ph*), 124.3 (*Ph*), 123.6 (*Ph*), 82.9 (PhCH$_2$N(B*pin*)$_2$), 82.1 (PhCH$_2$N(B*pin*)$_2$),46.9 (Ph*C*H$_2$N(Bpin)$_2$), 24.4(Ph*C*H$_2$N(B*pin*)$_2$), 21.2 (Ar-*C*H$_3$)ppm.

The spectroscopic data is consistent with literature data.[3]



4. **1d:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.63-7.61 (m, 2H, *Ph*), 7.54-7.52 (d, 2H, *Ph*), 7.46-7.41 (m, 4H, *Ph*), 7.35-7.33 (m, 1H, *Ph*), 4.32(s, 2H, PhC*H*$_2$N(Bpin)$_2$), 1.24 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 142.1 (CH$_2$Ar*C*-Ph), 141.1 (CH$_2$Ar-*C*Ar), 138.8(*Ph*), 137.5 (*Ph*), 128.5 (*Ph*), 127.8 (*Ph*),126.7 (*Ph*), 126.4 (*Ph*), 82.2 (PhPhCH$_2$N(B*pin*)$_2$), 46.8 (PhPh*C*H$_2$N(Bpin)$_2$), 24.4(Ph*C*H$_2$N(B*pin*)$_2$) ppm.

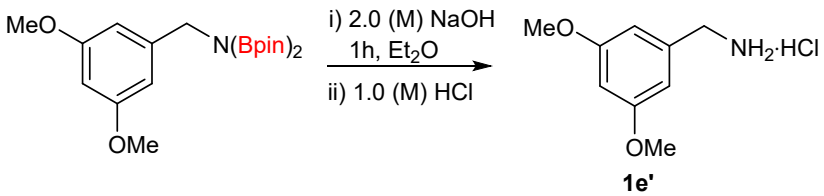
5. **1e:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 6.52-6.51 (m, 2H, *Ph*), 6.29 (s, 1H, *Ph*), 4.18 (s, 2H,



PhC*H*$_2$N(Bpin)$_2$), 3.76 (s, 6H, OC*H*$_3$), 1.22 (s, 24H, N(B*pin*)$_2$) ppm;^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 160.6(Ar*C*-OMe), 160.2(Ar*C*-OMe), 145.3(*Ph*), 137.4 (*Ph*), 126.7 (*Ph*), 104.3(*Ph*), 98.4 (*Ph*), 82.8 (PhCH$_2$N(B*pin*)$_2$), 55.0 (-O*Me*), 45.1 (Ph*C*H$_2$N(Bpin)$_2$), 24.3 (Ph*C*H$_2$N(B*pin*)$_2$) ppm.

(3,5-dimethoxyphenyl)methanamine hydrochloride (1e′).

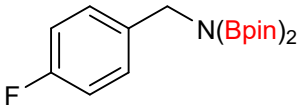
The general procedure was followed for the isolation of (3,5-dimethoxyphenyl)methanamine hydrochloride salt, **1e′** (22.58 mg, 87.6% yield) as a colorless solid.



1e'

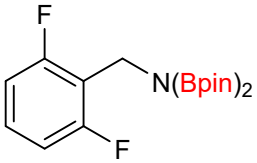
^{1}H NMR (200MHz, DMSO-d_6): δ 8.59 (br, 3H, NH_2·HCl), 6.74-6.73 (d, 2H, *Ph*), 6.46 (t, 1H, *Ph*), 3.90 (q, 2H, CH_2), 3.73 (s, 6H, O*Me*) ppm.
^{13}C{^{1}H} (100.6 MHz, DMSO-d_6): δ 160.4 (*Ph*), 136.2 (*Ph*), 106.8 (*Ph*), 99.9 (*Ph*), 55.3 (O*Me*),42.1 (*C*H_2) ppm.

The spectroscopic data is consistent with literature data.[2]

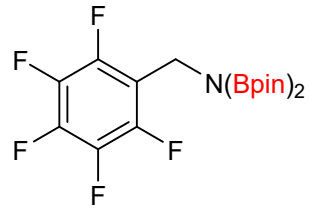


6. **1f:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.33-7.30 (m, 2H, *Ph*), 6.98-6.89 (t, 2H, *Ph*), 4.20(s, 2H, PhCH_2N(Bpin)$_2$), 1.21 (s, 24H, N(B*pin*)$_2$) ppm;^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 162.5-160.2 (Ar*C*-F), 138.6-137.4 (*Ph*), 129.8 (*Ph*), 128.7 (*Ph*), 114.7-114.1 (*Ph*), 82.8 (PhCH$_2$N(B*pin*)$_2$), 46.3 (Ph*C*H$_2$N(Bpin)$_2$), 24.3 (Ph*C*H$_2$N(B*pin*)$_2$) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$, 128 MHz, 298 K): -117.45 ppm.

The spectroscopic data is consistent with literature data.[1]

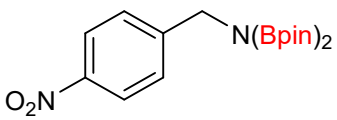


7. **1g:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.05-7.00 (m, 1H, *Ph*), 6.75-6.71 (t, 2H, *Ph*), 4.33(s, 2H, PhCH_2N(Bpin)$_2$), 1.27 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 163.0 (Ar*C*-F), 160.6-160.5(Ar*C*-F), 128.0-127.9 (*Ph*), 112.0-111.7 (*Ph*), 110.5-110.2 (*Ph*), 81.5 (PhCH$_2$N(B*pin*)$_2$),35.7 (Ph*C*H$_2$N(Bpin)$_2$), 24.1 (Ph*C*H$_2$N(B*pin*)$_2$) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$, 128 MHz, 298 K): -103.58 (*product*), -113.38 (*starting material*) ppm.



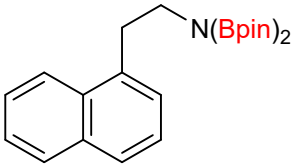
8. **1h:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 4.35(s, 2H, PhCH_2N(Bpin)$_2$), 1.28 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 137.6-126.6 (Ph), 83.0 (PhCH$_2$N(Bpin)$_2$), 36.0 (PhCH$_2$N(Bpin)$_2$), 24.4 (PhCH$_2$N(Bpin)$_2$) ppm; ^{19}F{^{1}H} NMR ($CDCl_3$, 128 MHz, 298 K): δ - 131.34 (*product*), -140.57 (product), -141.87 (*starting material*), -152.89(*product*), -157.90 (*starting material*), -162.37 (*starting material*), -164.33 (*starting material*) ppm.

9. **1i:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.15-8.11 (m, 2H, *Ph*), 7.47-7.43 (m, 2H, *Ph*), 4.31 (s, 2H, PhCH_2N(Bpin)$_2$), 1.20 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 150.6 (*ArC*-NO$_2$), 146.4 (*Ph*), 137.5

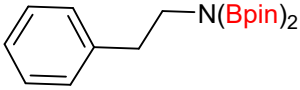


(*Ph*), 127.9 (*Ph*), 126.7 (*Ph*), 123.4 (*Ph*), 82.9 ($NO_2PhCH_2N(Bpin)_2$), 46.8 ($NO_2PhCH_2N(Bpin)_2$), 24.4 ($NO_2PhCH_2N(Bpin)_2$) ppm.

The spectroscopic data is consistent with literature data.[4]



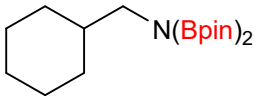
10. **1j:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.42-8.40 (d,1H, *Ar*), 7.86-7.84 (d,1H, *Ar*), 7.73-7.71 (d,1H, *Ar*), 7.53-7.48 (m, 2H, *Ar*), 7.40-7.36 (m, 2H, *Ar*), 3.46-3.42 (t, 2H, $ArCH_2CH_2N(Bpin)_2$), 3.24-3.20 (t, 2H,$ArCH_2CH_2N(Bpin)_2$), 1.25 (s, 24H, $N(Bpin)_2$) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 137.5 (*Ar*), 136.4(*Ar*), 133.7(*Ar*), 132.4(*Ar*), 128.3 (*Ar*), 126.8 (*Ar*), 126.4 (*Ar*), 125.3 (*Ar*), 125.1 (*Ar*), 124.6 (*Ar*),82.9 ($ArCH_2CH_2N(Bpin)_2$), 44.8 ($ArCH_2CH_2N(Bpin)_2$), 37.1 ($ArCH_2CH_2N(Bpin)_2$), 24.4 ($ArCH_2CH_2N(Bpin)_2$) ppm.



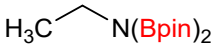
11. **1k:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.29-7.24 (m, 5H, *Ph*), 3.36-3.33 (t, 2H, $PhCH_2CH_2N(Bpin)_2$), 2.77-2.74 (t, 2H, $PhCH_2CH_2N(Bpin)_2$), 1.22 (s, 24H, $N(Bpin)_2$) ppm;$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.53 MHz, 298 K): δ 139.7(Ar*C*-R), 137.5 (*Ph*), 128.8 (*Ph*), 126.7(*Ph*), 82.9 ($PhCH_2CH_2N(Bpin)_2$), 42.2 ($PhCH_2CH_2N(Bpin)_2$), 39.7 ($PhCH_2CH_2N(Bpin)_2$), 24.4 ($PhCH_2CH_2N(Bpin)_2$) ppm.

The spectroscopic data is consistent with literature data.[3]

12. **1l:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 2.90-2.87 (d, 2H, $CyCH_2N(Bpin)_2$), 1.71-1.66 (m, 4H, *Cy*), 1.59 (br, 1H, Cy), 1.22 (s, 24H, $N(Bpin)_2$), 0.88-0.83 (m, 2H, *Cy*) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 81.8 ($CyCH_2N(Bpin)_2$), 49.5 ($CyCH_2N(Bpin)_2$), 40.4 ($CyCH_2N(Bpin)_2$), 30.4 ($CyCH_2N(Bpin)_2$), 26.6 ($CyCH_2N(Bpin)_2$), 26.0 ($CyCH_2N(Bpin)_2$), 24.77 ($CyCH_2N(Bpin)_2$), 24.4 ($CyCH_2N(Bpin)_2$) ppm.



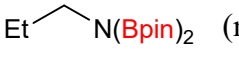
The spectroscopic data is consistent with literature data.[3]



13. **1m:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.08-3.03 (q, 2H, CH_2), 1.22 (s, 24H, $N(Bpin)_2$),1.04-1.00 (t, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 81.8 ($CH_3CH_2N(Bpin)_2$), 38.4 ($CH_3CH_2N(Bpin)_2$), 24.4 ($CH_3CH_2N(Bpin)_2$), 18.5 ($CH_3CH_2N(Bpin)_2$) ppm.

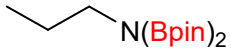
The spectroscopic data is consistent with literature data.[3]

14. **1n:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.03-2.96 (t, 2H, CH_2), 1.47-1.39 (m, 2H, CH_2), 1.22 (s, 24H, N(B*pin*)$_2$), 0.87-0.80 (t, 3H, CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 81.8 ($CH_3CH_2CH_2N(Bpin)_2$), 45.2 ($CH_3CH_2CH_2N(Bpin)_2$), 26.5 ($CH_3CH_2CH_2N(Bpin)_2$), 24.4 ($CH_3CH_2CH_2N(Bpin)_2$), 10.9 ($CH_3CH_2CH_2N(Bpin)_2$) ppm.

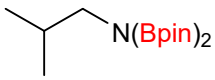


The spectroscopic data is consistent with literature data.[6]

15. **1o:** NMR data is same as entry 14 **1n**.

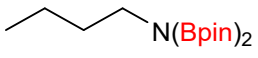


16. **1p:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 2.88-2.84 (d, 2H, CH_2), 1.67-1.60 (m, 1H, CH), 1.22 (s, 24H, N(B*pin*)$_2$), 0.85-0.82 (d, 6H, CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 81.8 ($(CH_3)_2CHCH_2N(Bpin)_2$), 50.8 ($(CH_3)_2CHCH_2N(Bpin)_2$),30.6 ($(CH_3)_2CHCH_2N(Bpin)_2$), 24.7 ($(CH_3)_2CHCH_2N(Bpin)_2$), 19.7 ($(CH_3)_2CHCH_2N(Bpin)_2$) ppm.

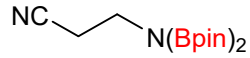


The spectroscopic data is consistent with literature data.[3]

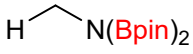
17. **1q:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.06-3.00(t, 2H, CH_2), 1.40-1.38 (t, 3H, CH), 1.22 (s, 24H, N(B*pin*)$_2$), 0.92-0.85 (m, 4H, CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 81.5 ($CH_3CH_2CH_2CH_2N(Bpin)_2$), 46.7 ($CH_3CH_2CH_2CH_2N(Bpin)_2$), 30.9 ($CH_3CH_2CH_2CH_2N(Bpin)_2$), 24.5($CH_3CH_2CH_2CH_2N(Bpin)_2$), 21.0 ($CH_3CH_2CH_2CH_2N(Bpin)_2$) ppm.



18. **1r:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.15-3.11 (t,2H, CH_2), 2.41-2.38 (t, 2H, CH_2), 1.19 (s, 24H, N(B*pin*)$_2$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ81.7 (N(B*pin*)$_2$), 79.2 (-N*C*), 37.2 ($CH_2N(Bpin)_2$), 20.96 ($CH2CH_2N(Bpin)_2$ppm.



19. **1s:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 2.66 (s, 3H, CH_3), 1.22 (s, 24H, N(B*pin*)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 82.95 ($CH_3N(Bpin)_2$), 30.5 ($CH_3N(Bpin)_2$), 24.4($CH_3CH_2N(Bpin)_2$) ppm.



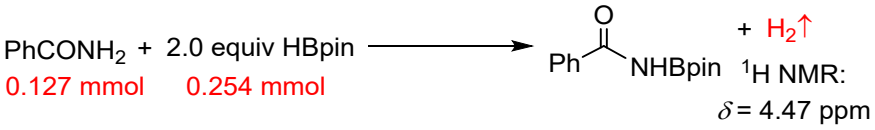
Note: In case of **1t** (nicotinamide) and **1u** (5-bromo nicotinamide), no reduction product was observed even after using 6 equivalents of HBpin.

Control experiments for the mechanistic investigation

To understand the mechanism associated with hydroboration of primary amide, we have carried out a series of experimental studies as mentioned below.

- **Detection of molecular hydrogen in hydroboration of benzamide.**

An oven dried screw-cap NMR tube was charged with benzamide (15.37 mg, 0.127 mmol, 1.0 qeuiv), HBpin (32.48 mg, 0.254 mmol, 2.0 equiv), and benzene-d_6 (500 µL) and immediate evolution of molecular hydrogen was observed which was characterized through ^{1}H NMR spectroscopy. A sharp resonance at δ 4.48 ppm in ^{1}H NMR spectrum indicates the formation of molecular hydrogen (Scheme S2 and Figure S1).



Scheme S2. Detection of molecular hydrogen in hydroboration of benzamide.

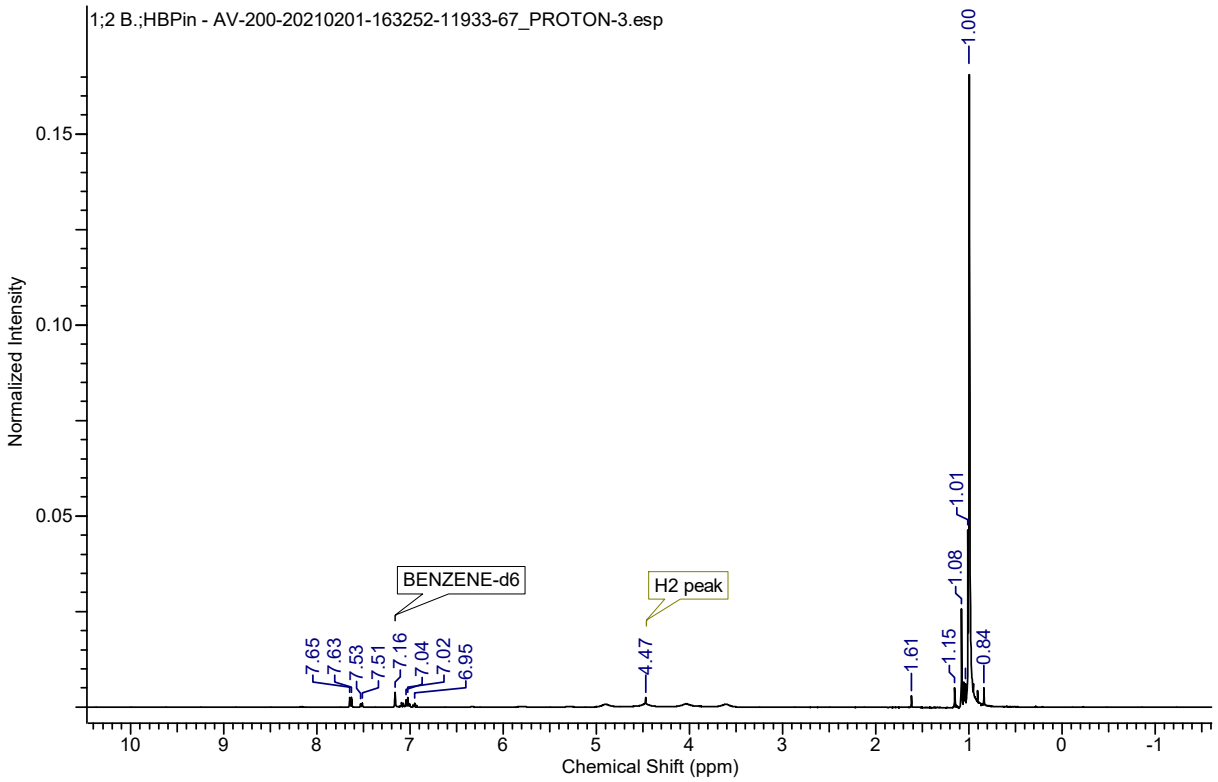
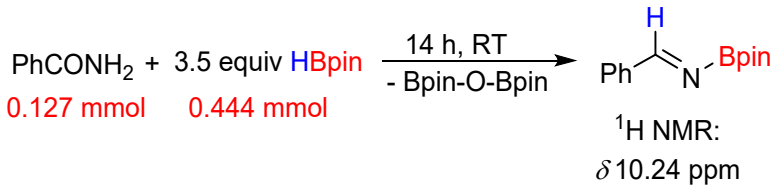


Figure S1. ^{1}H NMR spectrum of molecular hydrogen recorded in C_6D_6 for hydroboration of benzamide.

➢ **Characterization of in situ generated imine intermediate.**

A Screw cap tube was charged with benzamide (15.37 mg, 0.127 mmol), HBpin (56.88 mg, 0.444 mmol) in an argon filled glovebox and after the reaction time of 14 h, at room temperature, ^{1}H NMR of the reaction mixture was recorded in $CDCl_3$. A sharp resonance at δ 10.24 ppm for benzamide was observed in ^{1}H NMR spectrum, indicating an imine intermediate formation (Scheme S3 and Figure S3).



Scheme S3. Synthetic scheme for the formation of intermediate imine.

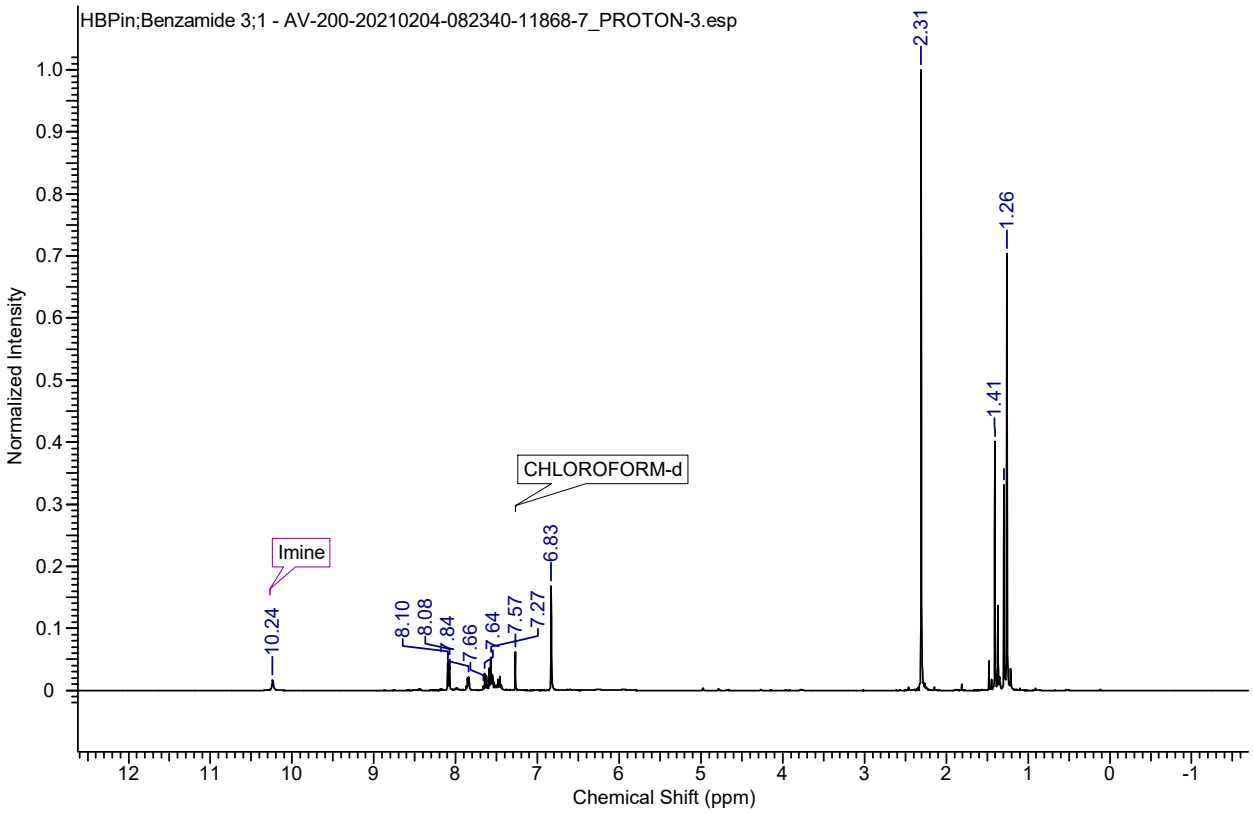
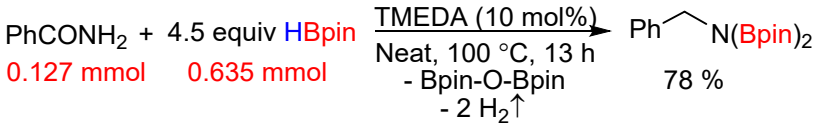


Figure S2. ^{1}H NMR spectrum of in situ generated *N*-borylated imine recorded in $CDCl_3$.

➢

➢ **Reaction in presence of TMEDA.**



Scheme S4. Synthetic scheme for the hydroboration of benzamide in presence of TMEDA.

To identify whether the $BH_3$is behaving as hidden catalyst in the hydroboration of benzamide or not, we performed the reaction in presence of *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) as a BH_3 scavenger. A screw cap NMR tube was charged with HBpin (81.22 mg, 0.635 mmol, 5.0 equiv), and TEMDA (0.15 mg, 10 mol%) inside the argon-filled glovebox. Subsequently benzamide (15.37 mg, 0.127 mmol, 1.0 equiv), was added to the reaction mixture and heated at 100 °C for 13h in an oil bath. After completion of the reaction 0.127 mmol mesitylene was added as an internal standard prior to the NMR measurement in $CDCl_3$ solvent. For the mentioned

reaction, 78% NMR yield (98% for without TMEDA) for the corresponding N-borylated product was observed (Scheme S4) suggesting for the non-involvement or very less influence of BH_3 as an active catalyst for the hydroboration of benzamide.

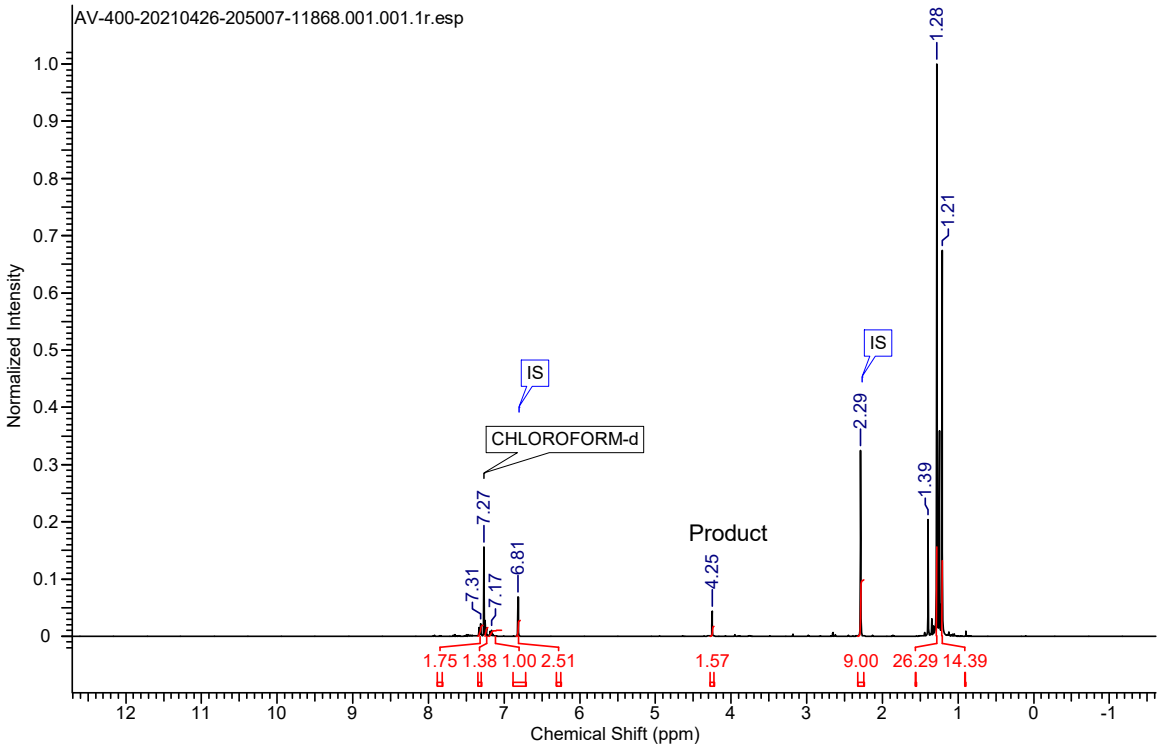


Figure S3. ^{1}H NMR for the hydroboration of benzamide in presence of TMEDA.

➢ **Effect of heating on HBpin**

In another experiment, to identify whether HBpin is decomposing into BH_3, HBpin was heated at 100 °C for 13 h in benzene-d_6. ^{11}B NMR shows a doublet at 27.78-29.18 ppm similar to HBpin which clearly indicates that only HBpin is doing the reduction not the BH_3(figure S4).

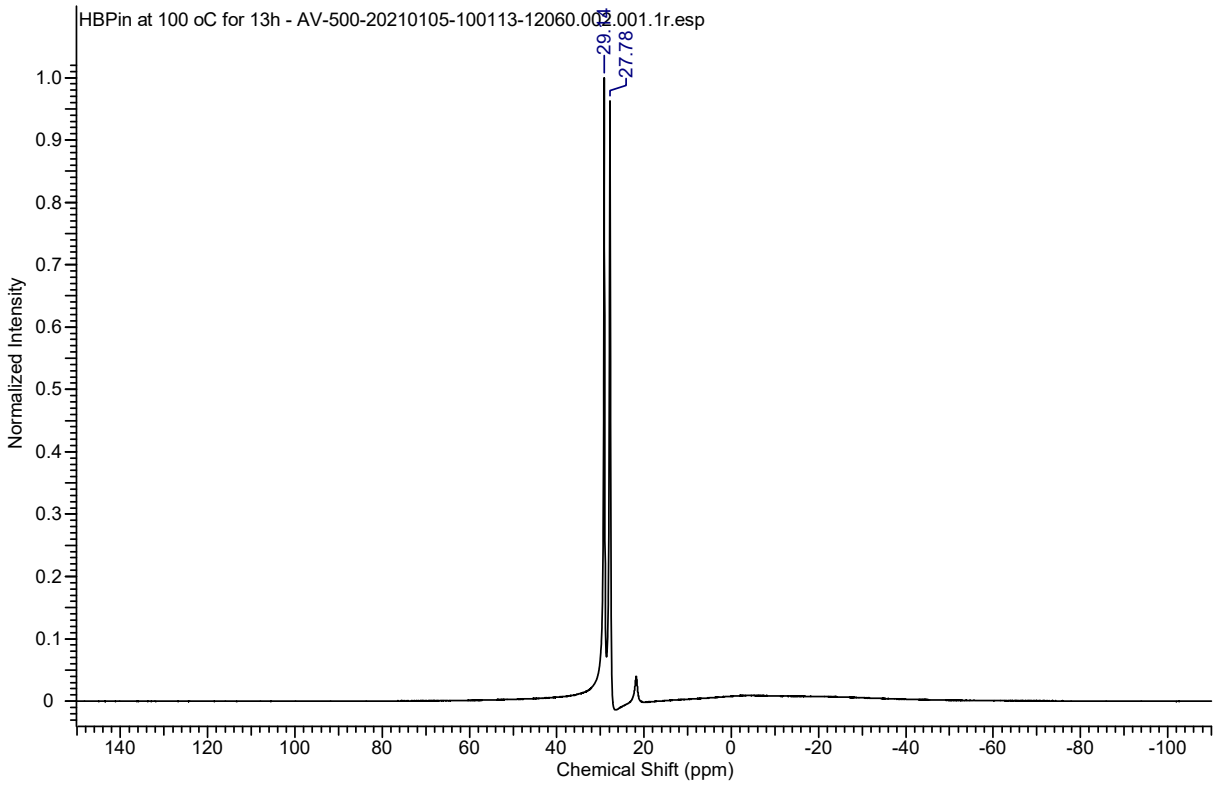


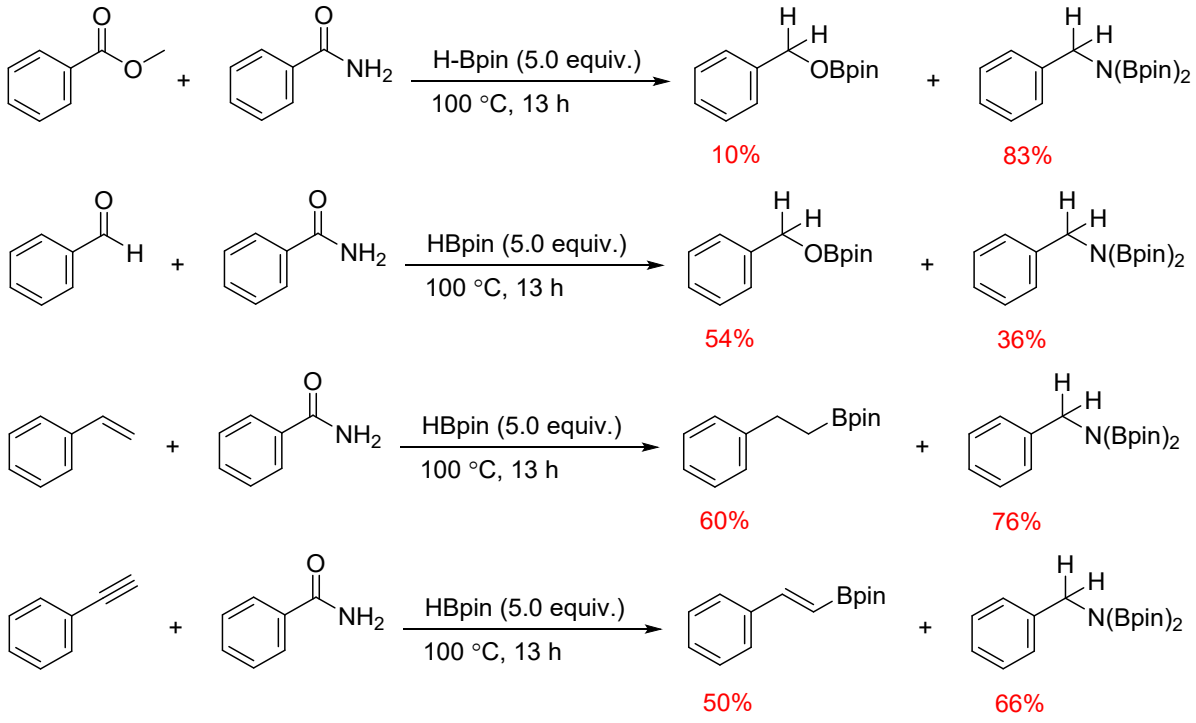
Figure S4. ^{11}B NMR spectrum of heating of HBpin at 100 °C for 13 h (C_6D_6, 200 MHz, 298 K).

- **Competitive experiment for chemo selective hydroboration in case of ester, aldehyde, alkene and alkyne with amide functionality**

Selective hydroboration of benzamide over methyl benzoate, benzaldehyde, styrene and phenyl acetylene in presence of 5 equiv. of HBpin has been performed and only negligible conversion was found in case of ester which is confirmed by ^1H NMR spectra and in other cases significant conversion was observed (Scheme S5).

Methyl benzoate (17.28 mg, 0.127 mmol), benzaldehyde (13.46 mg, 0.127 mmol), styrene (13.26 mg, 0.127 mmol) and phenyl acetylene (12.96 mg, 0.127 mmol) were charged for separate reactions with benzamide (15.37 mg, 0.127 mmol), pinacolborane (82 mg, 0.635 mmol) in a Schlenk tube/ screw cap nmr tube inside the glove box. The reaction mixture was heated at 100 ºC for 13 h. The progress of the reaction was monitored by ^1H NMR after addition of mesitylene (0.127 mmol) as an internal standard in $CDCl_3$. A sharp resonance at δ= 4.26 ppm indicates for the formation of hydroboration product from benzamide and resonance at δ= 4.95 ppm (figure S5)

indicates for the formation of hydroboration product from ester. Similarly, hydroborated product of benzaldehyde shows singlet resonance at δ= 4.96 ppm (figure S6), while hydroborated product of styrene shows triplet resonance at δ= 2.77-2.81 ppm (figure S7) and hydroborated product of phenyl acetylene shows doublet resonance at δ= 6.19-6.23 ppm (figure S8).



Scheme S5. Chemo selective experiments for hydroboration of benzamide vs methyl benzoate, benzaldehyde, styrene and phenyl acetylene, respectively in presence of 5 equiv. of HBpin.

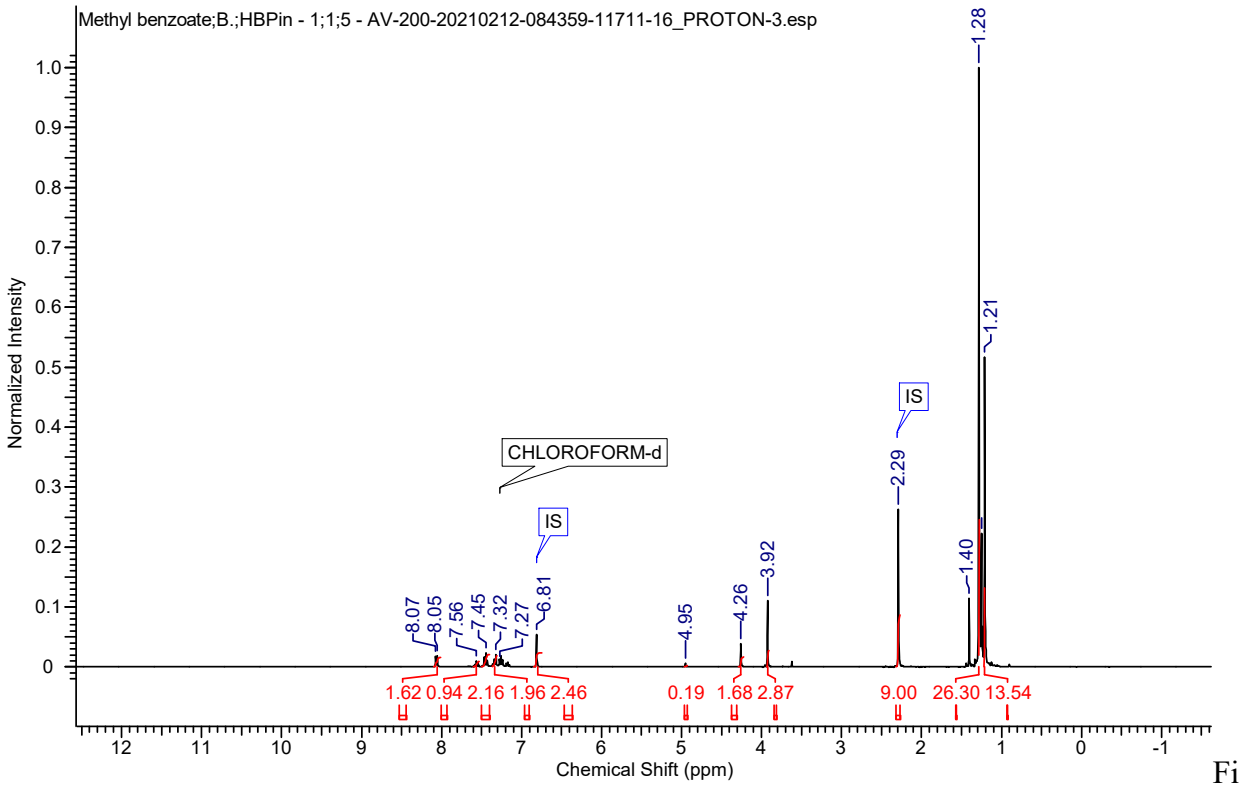


Figure S5. ^{1}H NMR for competitive experiments for hydroboration for ester and amide.

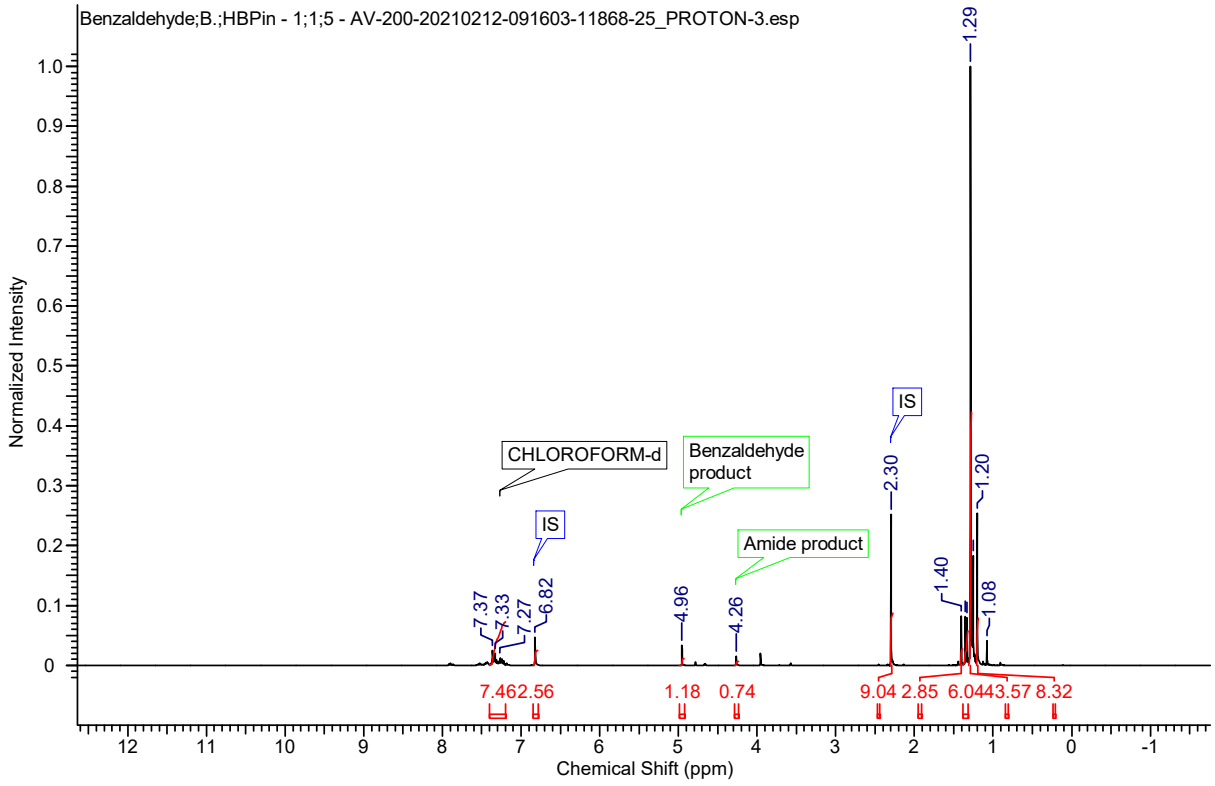
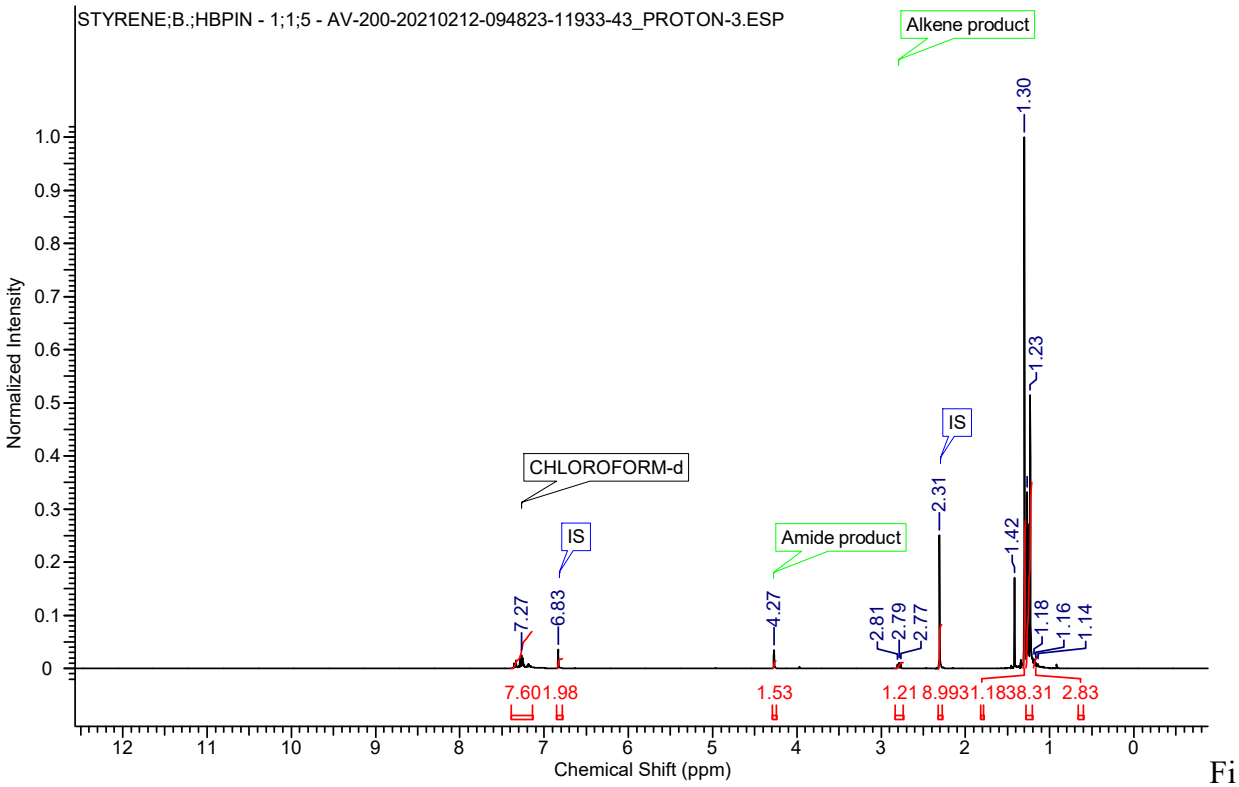


Figure S6. ^{1}H NMR for competitive experiments for hydroboration of aldehyde and amide.



Fi

gure S7. ^{1}H NMR for competitive experiments for hydroboration of alkene and amide.

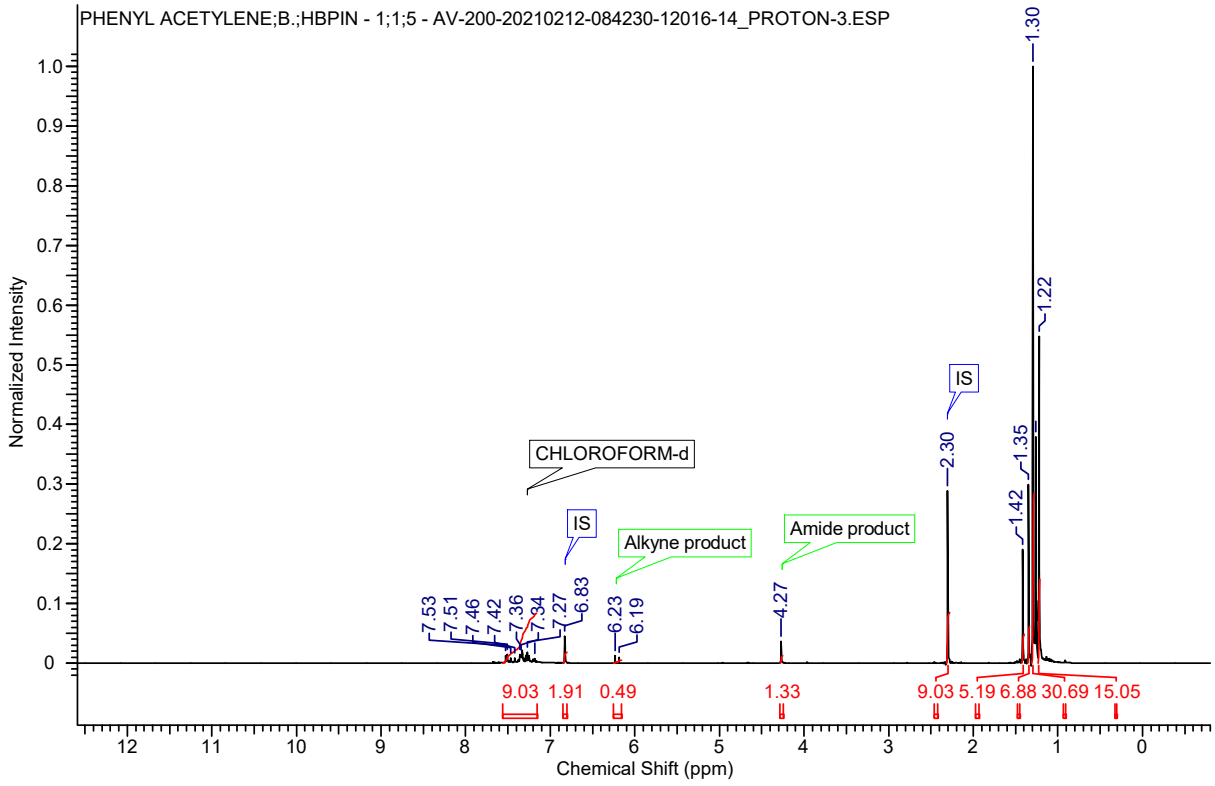
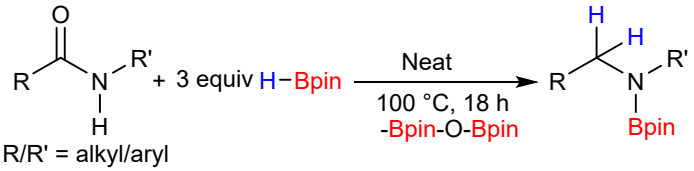


Figure S8. ^{1}H NMR for competitive experiments for hydroboration of alkyne and amide.

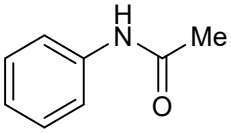
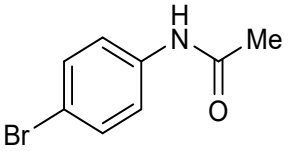
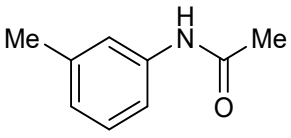
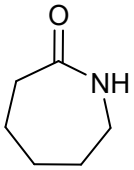
General procedure for the hydroboration of secondary amides

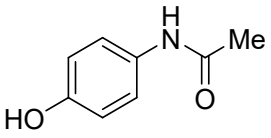


Scheme S6. General procedure for the hydroboration of secondary amides.

Secondary amide (0.127 mmol), pinacolborane (3.0 equiv., 0.381mmol) were mixed together in a Schlenk tube or in a screw cap NMR tube inside the glove box. The reaction mixture was allowed to heat at 100 °C for 18 h without adding any solvent. Volatiles of the mixture were removed under reduced pressure and mesitylene (0.127 mmol) as an internal standard, was added while making the NMR in appropriate deuterated solvent. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the appearance of a new R-CH_2-NR′(Bpin) resonance (Scheme S5).

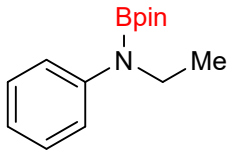
Table S4. Substrate scope for the secondary amide hydroboration:

Entry	Substrate	Temperature (°C)	Time (h)	NMR yield (%)	Product
1.		100	18	73	**2a**
2.		100	18	72	**2b**
3.		100	18	81	**2c**
4.		100	18	70	**2d**

5.		100	18	95	**2e**

- **Analytical data (^{1}H and ^{13}C NMR) of the borylamines of the corresponding secondary amides:**

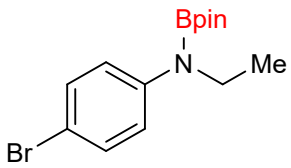
1. **2a:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.28-7.27 (m, 4H, *Ph*), 6.97-6.90 (m, 1H, *Ph*), 3.59-



3.54 (q, 2H, CH_2), 1.31 (s, 12H, PhN(B*pin*)CH_2CH_3), 1.19-1.15 (t,3H, PhN(Bpin)CH_2CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 148.3 (*Ph*), 129.0 (*Ph*), 119.8(*Ph*), 117.1(*Ph*), 112.7 (*Ph*), 83.0 (PhN(B*pin*)CH_2Me), 38.3 (PhN(Bpin)CH_2Me), 24.4 (PhN(B*pin*)CH_2Ph), 14.7 (PhN(Bpin)CH_2*Me*)ppm.

The spectroscopic data is consistent with literature data.[11]

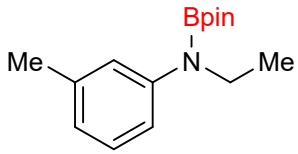
2. **2b:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.34-7.32 (d, 2H, *Ph*), 7.15-7.13 (d, 2H, *Ph*), 3.54-



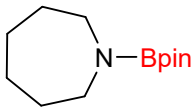
3.48 (q, 2H, CH_2), 1.28 (s, 12H, PhN(B*pin*)CH_2CH_3), 1.14-1.11(t, 3H, PhN(Bpin)CH_2CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 147.1 (*Ar*), 131.6 (*Ar*), 121.1 (*Ar*), 114.5 (*Ar*), 114.2 (*Ar*), 82.9 (ArN(B*pin*)CH_2Me), 38.3 (ArN(Bpin)CH_2Me), 24.6 (ArN(B*pin*)CH_2Ph), 14.4 (ArN(Bpin)CH_2*Me*)ppm.

The spectroscopic data is consistent with literature data.[7]

3. **2c:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.15-7.08 (m, 3H, *Ph*), 6.80 (s, 1H, *Ph*), 3.58-3.53



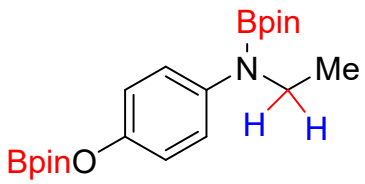
(q, 2H, CH_2), 2.35 (s, 3H, *Me*),1.31 (s, 12H, PhN(B*pin*)CH_2CH_3), 1.18-1.15 (t, 3H, PhN(Bpin)CH_2CH_3) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, 298 K): δ 148.3 (*Ar*), 138.6 (*Ar*), 128.9 (*Ar*), 117.8 (*Ar*), 113.3 (*Ar*), 109.7 (*Ar*), 82.9 (PhN(B*pin*)CH_2Me), 38.2 (*Ar*N(Bpin)CH_2Me), 24.3 (*Ar*N(B*pin*)CH_2Ph), 21.0 (Ar-*Me*), 14.7 (*Ar*N(Bpin)CH_2*Me*)ppm.



4. **2d:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.02-2.99 (t, 4H, RC*H*$_2$N(Bpin)C*H*$_2$R), 1.60 (br, 4H, RC*H*$_2$CH$_2$N(Bpin)CH$_2$C*H*$_2$R), 1.49 (br, 4H, -C*H*$_2$CH$_2$CH$_2$N(Bpin)CH$_2$CH$_2$C*H*$_2$), 1.19 (s, 12H, -C*H*$_2$CH$_2$CH$_2$N(B*pin*)CH$_2$CH$_2$C*H*$_2$-) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 82.0 (PhCH$_2$N(Me)B*pin*), 47.3 (-C*H*$_2$CH$_2$*C*H$_2$N(Bpin)*C*H$_2$CH$_2$C*H*$_2$-), 28.7 (-CH$_2$*C*H$_2$CH$_2$N(Bpin)CH$_2$*C*H$_2$CH$_2$-), 26.6 (-C*H*$_2$CH$_2$CH$_2$N(Bpin)CH$_2$CH$_2$C*H*$_2$-), 24.5(-CH$_2$CH$_2$CH$_2$N(B*pin*)CH$_2$CH$_2$CH$_2$-) ppm.

The spectroscopic data is consistent with literature data.[8]

5. **2e:** ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.14-7.12 (d, 2H, *Ph*), 7.00-6.98 (d, 2H, *Ph*), 3.51-3.46 (q, 2H, C*H*$_2$), 1.33 (s, 12H, PhN(B*pin*)CH$_2$CH$_3$), 1.28 (s, 12H, *pin*BO-PhN(Bpin)CH$_2$CH$_3$), 1.13-1.09(t, 3H, PhN(Bpin)C*H*$_2$CH$_3$) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 148.0 (*Ar*), 141.0 (*Ar*), 128.8 (*Ar*), 122.2 (*Ar*), 119.2 (*Ar*), 82.9 (ArN(B*pin*)CH$_2$Me), 42.2 (ArN(Bpin)*C*H$_2$Me), 24.4 (ArN(B*pin*)CH$_2$Ph), 14.4 (ArN(Bpin)CH$_2$*Me*)ppm.



Representative NMR Spectra:

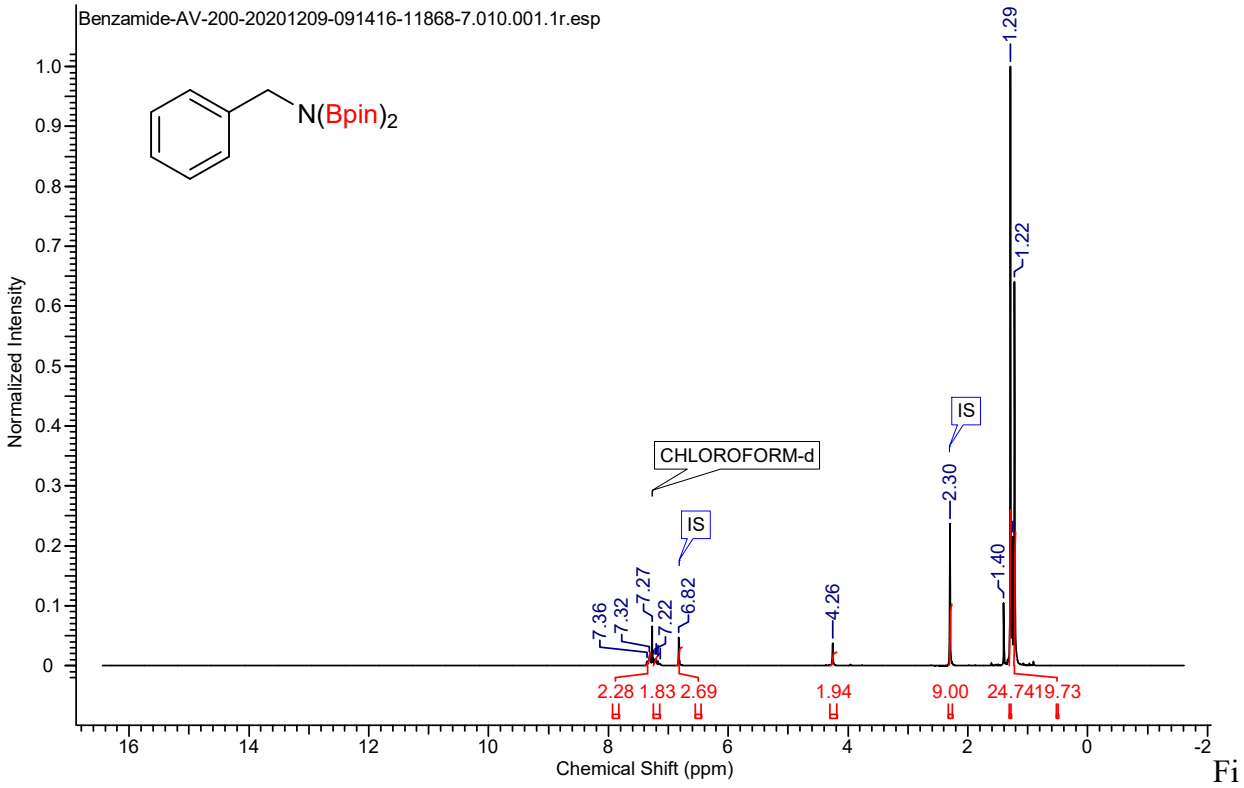


Figure S9. ^{1}H NMR Spectrum of **1a** ($CDCl_3$, 200 MHz, 298 K).

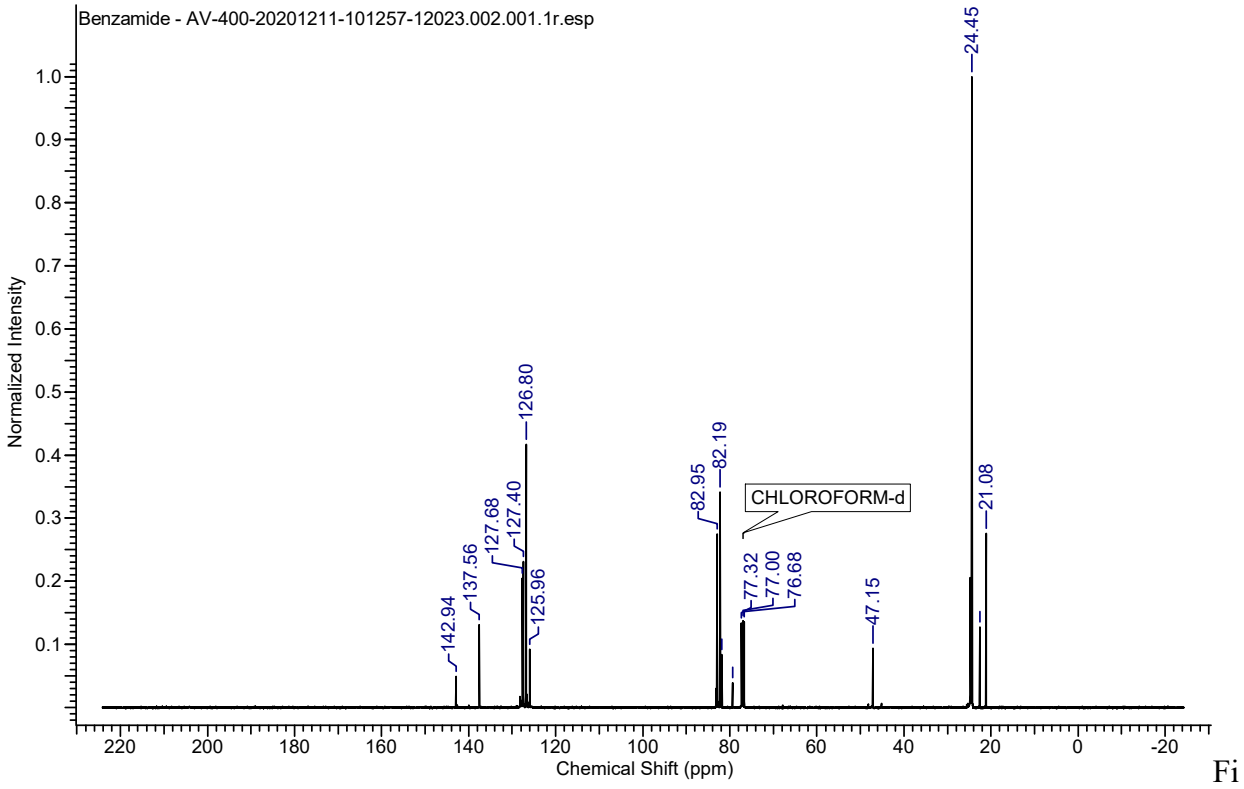
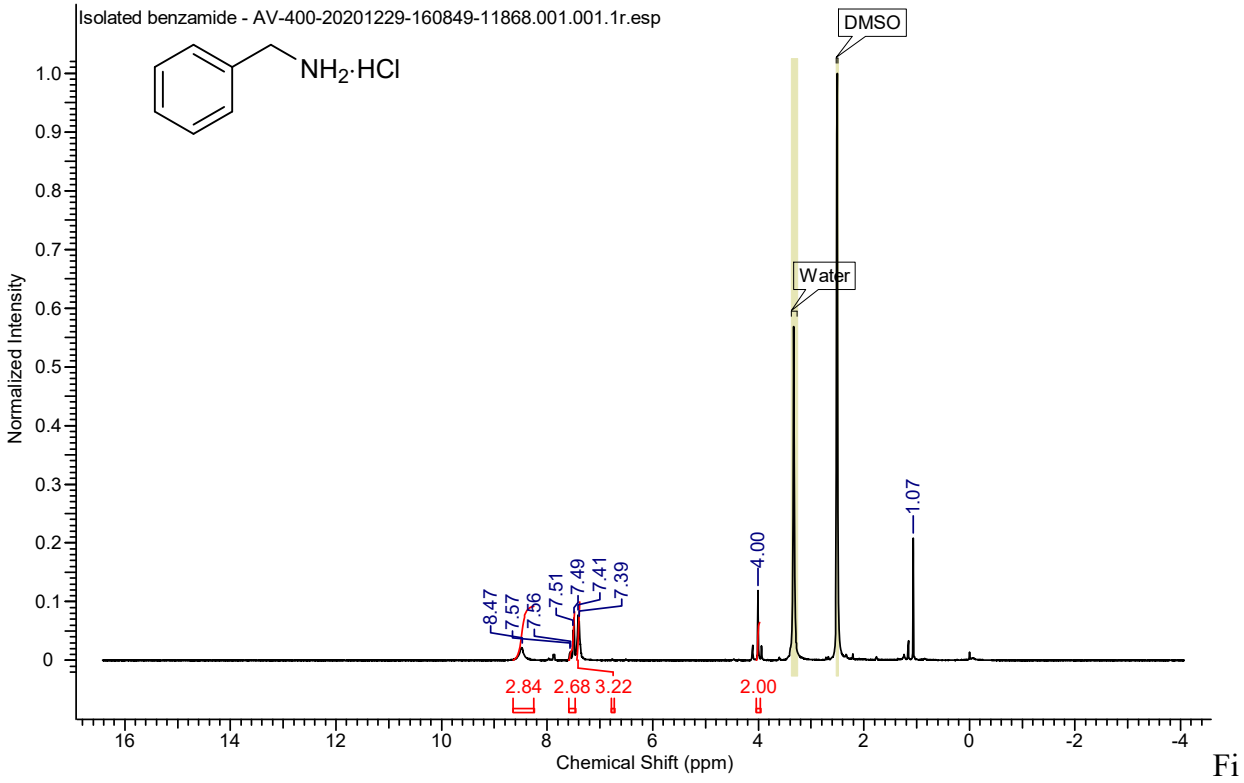


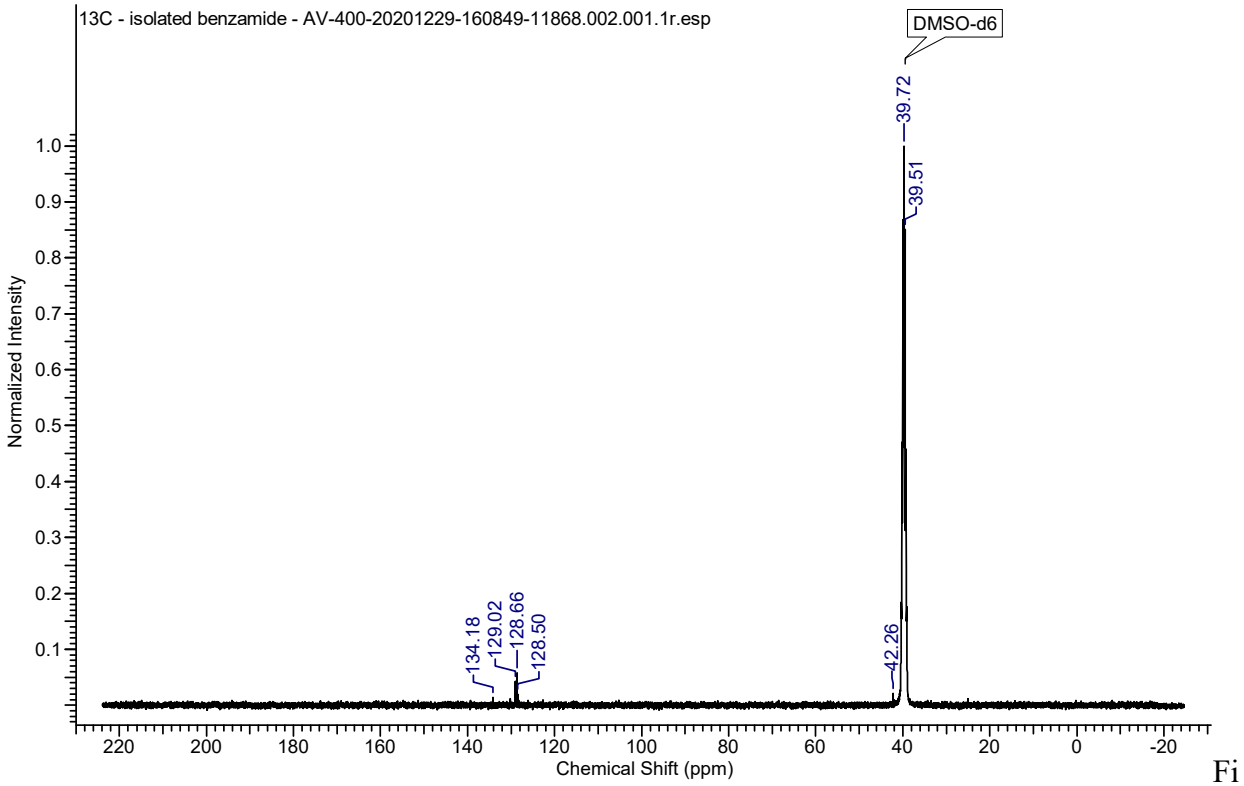
Figure S10. ^{13}C NMR Spectrum of **1a** ($CDCl_3$, 400 MHz, 298 K).

gure S10. ^{13}C NMR spectrum of **1a** ($CDCl_3$, 100.5 MHz, 298 K).



Fi

gure S11. ^{1}H NMR spectrum of **1a′** (DMSO-d_6, 200 MHz, 298 K).



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gure S12. ^{13}C NMR spectrum of **1a′** (DMSO-d_6,100.6 MHz, 298 K).

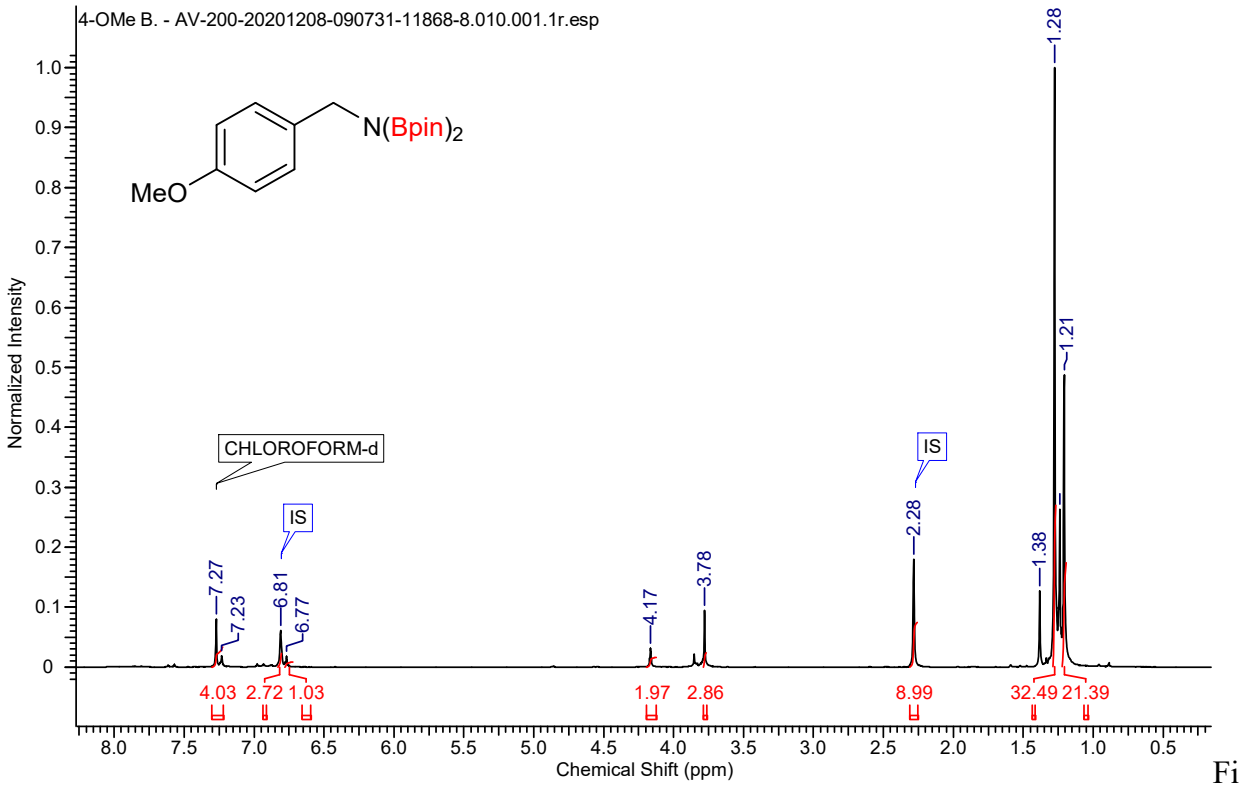

Figure S13. ^{1}H NMR Spectrum of **1b** ($CDCl_3$, 200 MHz, 298 K).

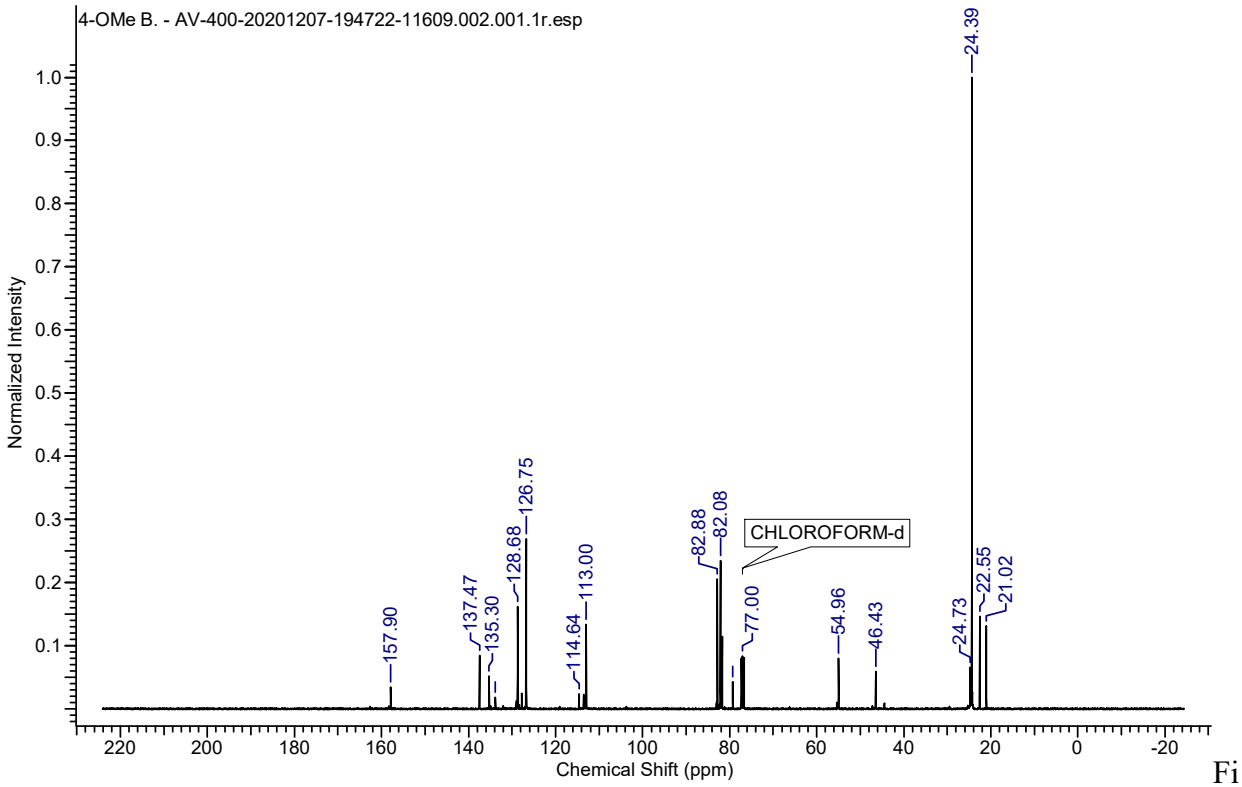

Figure S14. ^{13}C NMR spectrum of **1b** ($CDCl_3$, 100.5 MHz, 298 K).

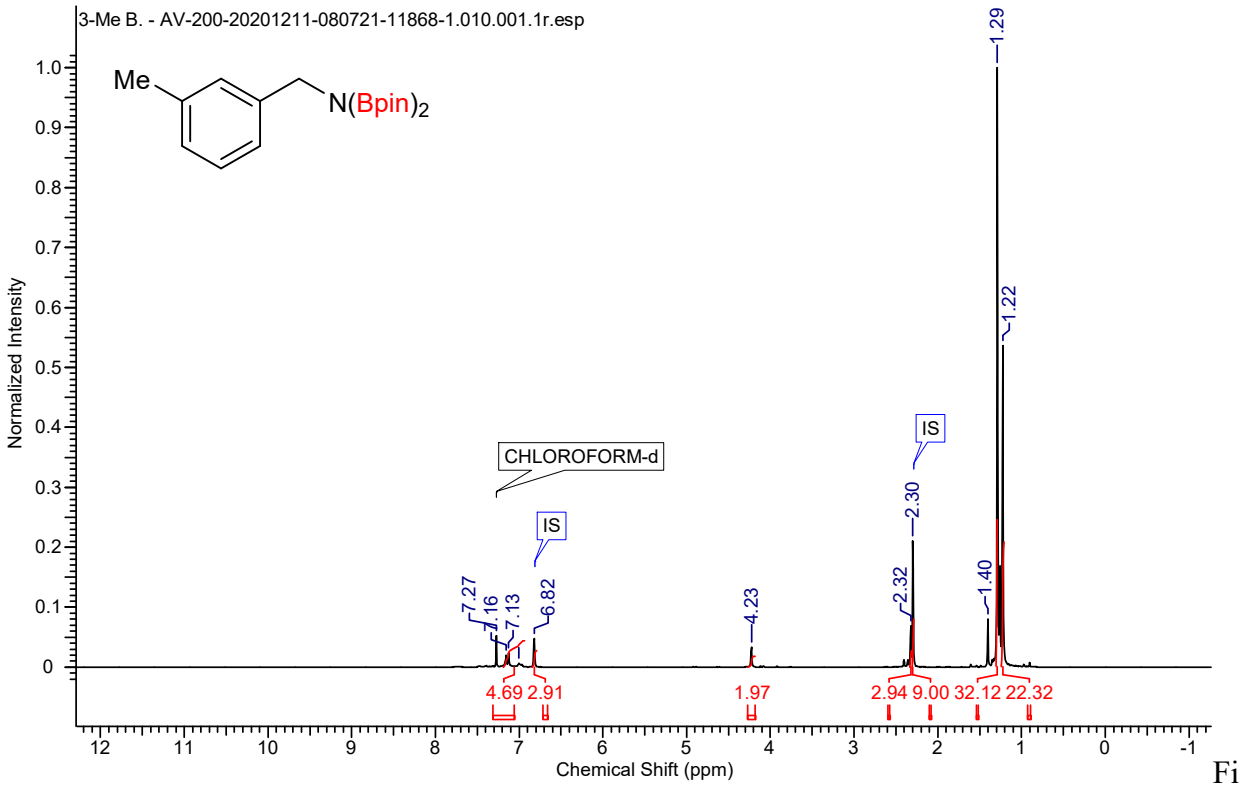

Figure S15. ^{1}H NMR Spectrum of **1c** ($CDCl_3$, 200 MHz, 298 K).

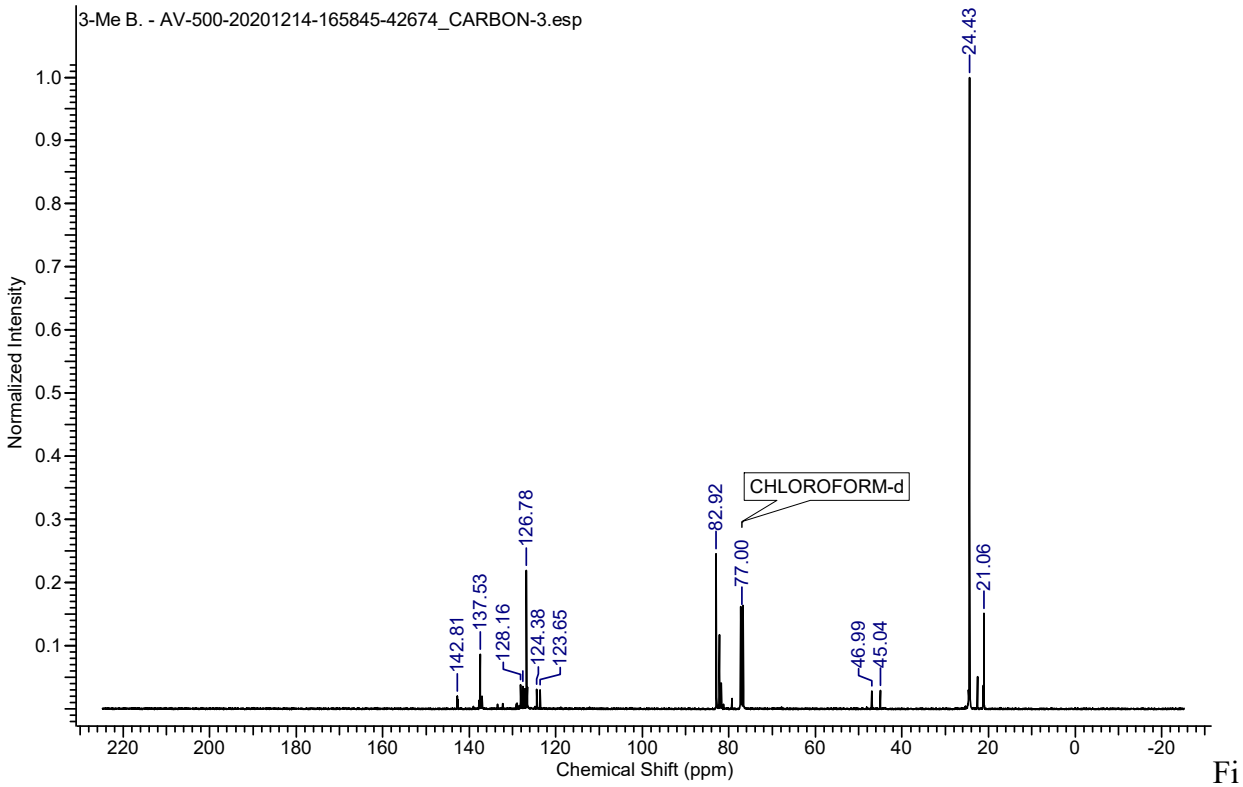

Figure S16. ^{13}C NMR Spectrum of **1c** ($CDCl_3$, 200 MHz, 298 K).

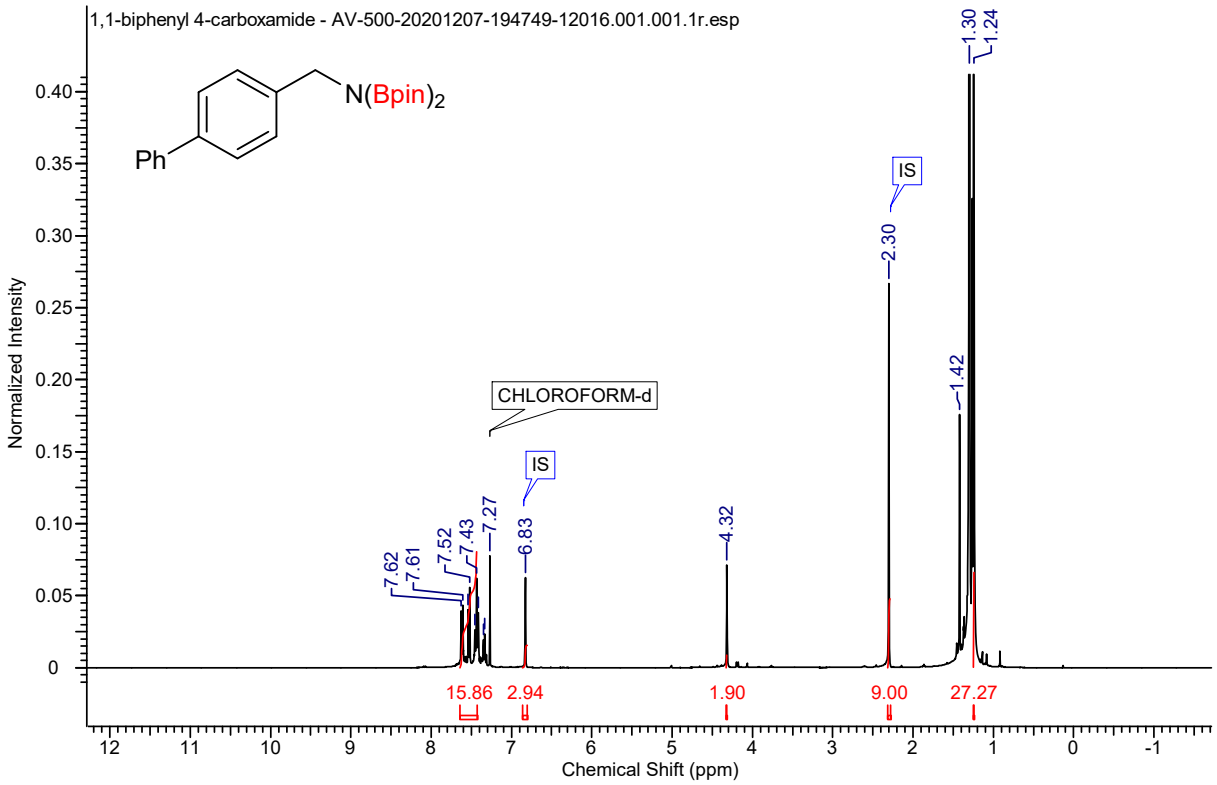

Figure S17. ^{1}H NMR spectrum of **1d** ($CDCl_3$, 200 MHz, 298 K).

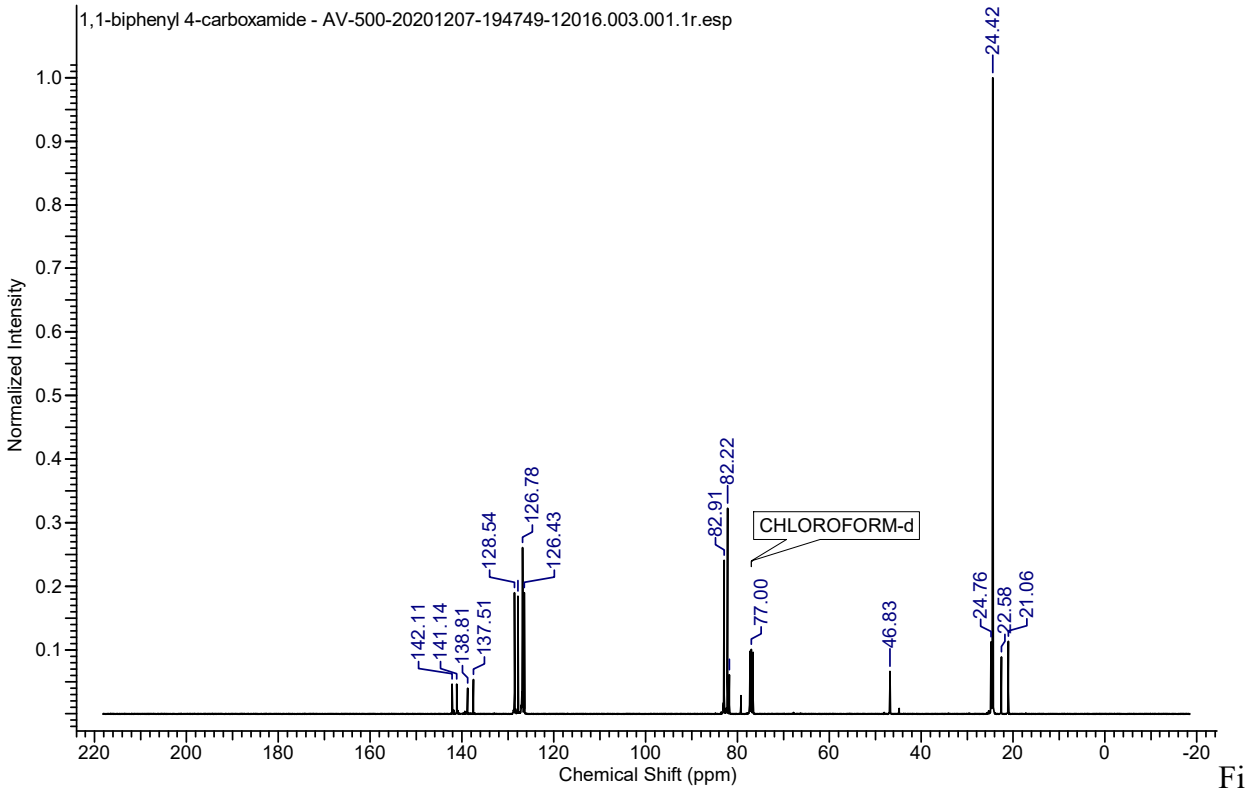

Figure S18. ^{13}C NMR spectrum of **1d** ($CDCl_3$, 100.6 MHz, 298 K).

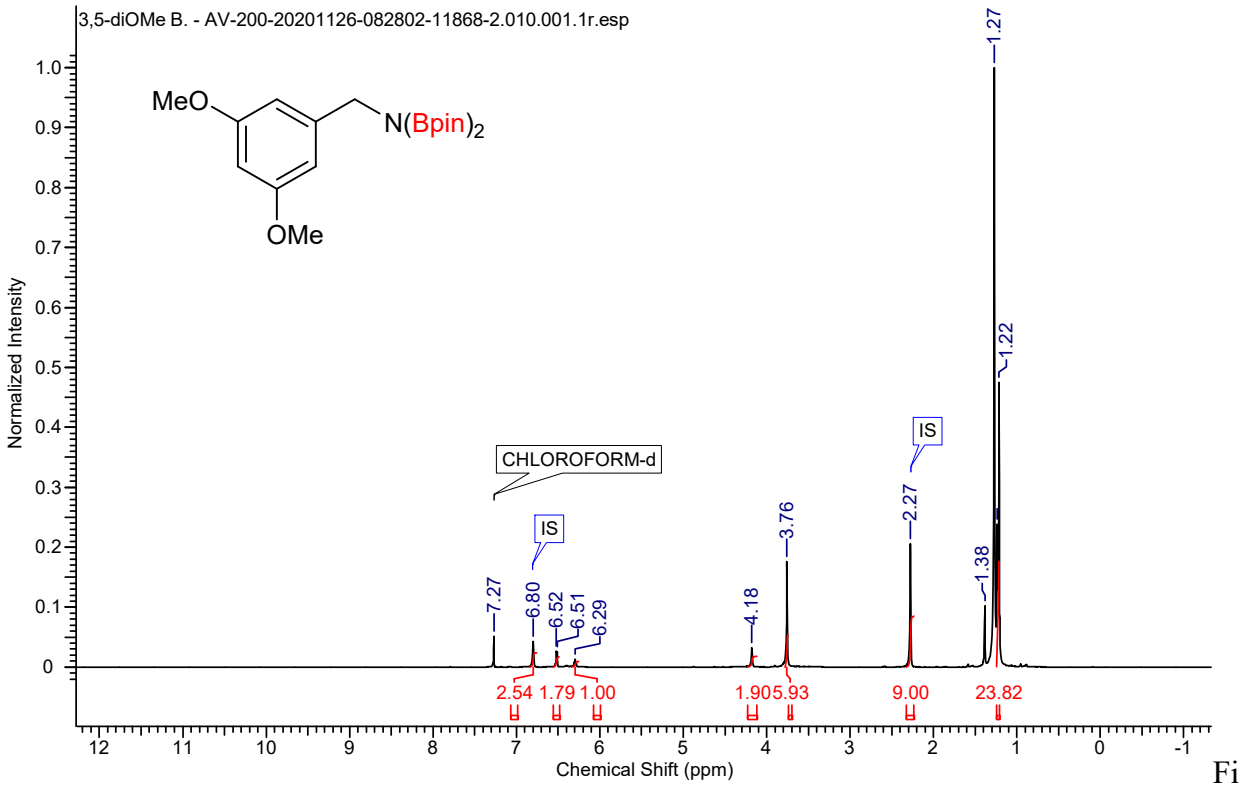

Figure S19. ^{1}H NMR Spectrum of **2e** ($CDCl_3$, 200 MHz, 298 K).

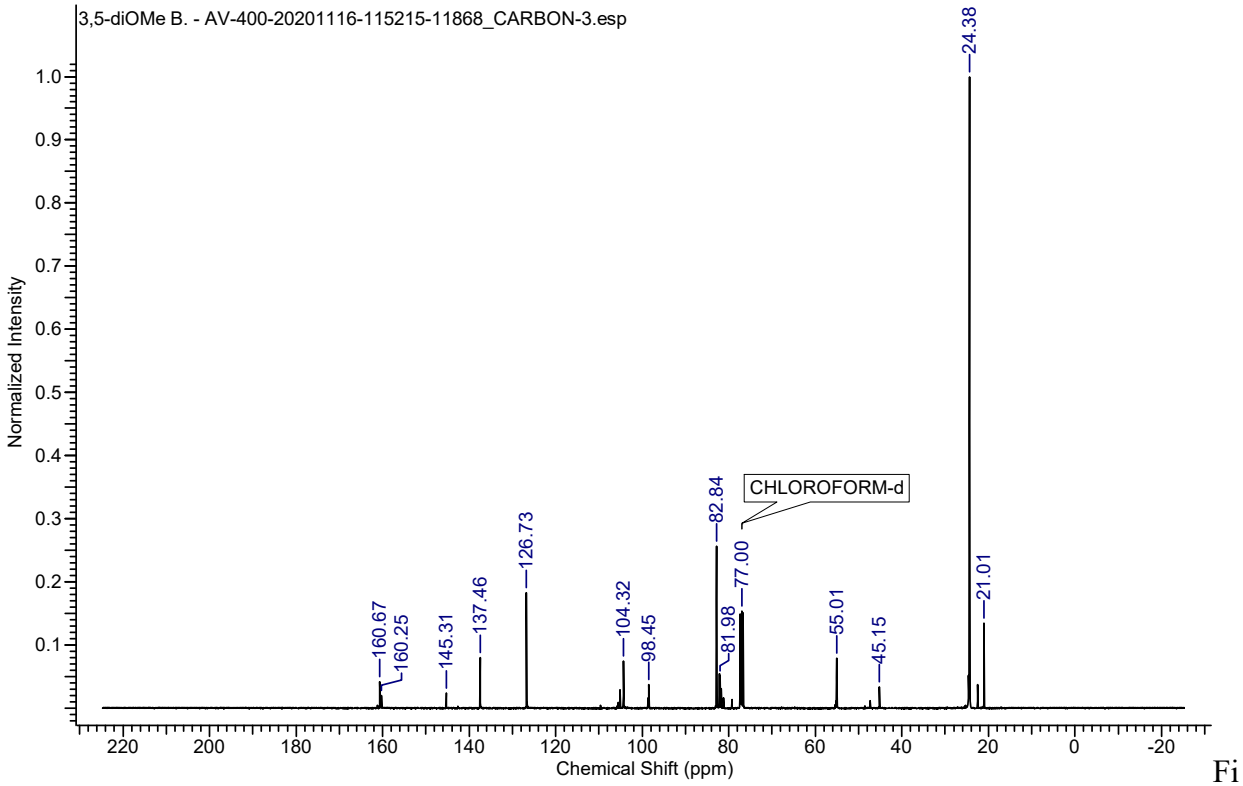

Figure S20. ^{13}C NMR spectrum of **1e** ($CDCl_3$, 100.6 MHz, 298 K).

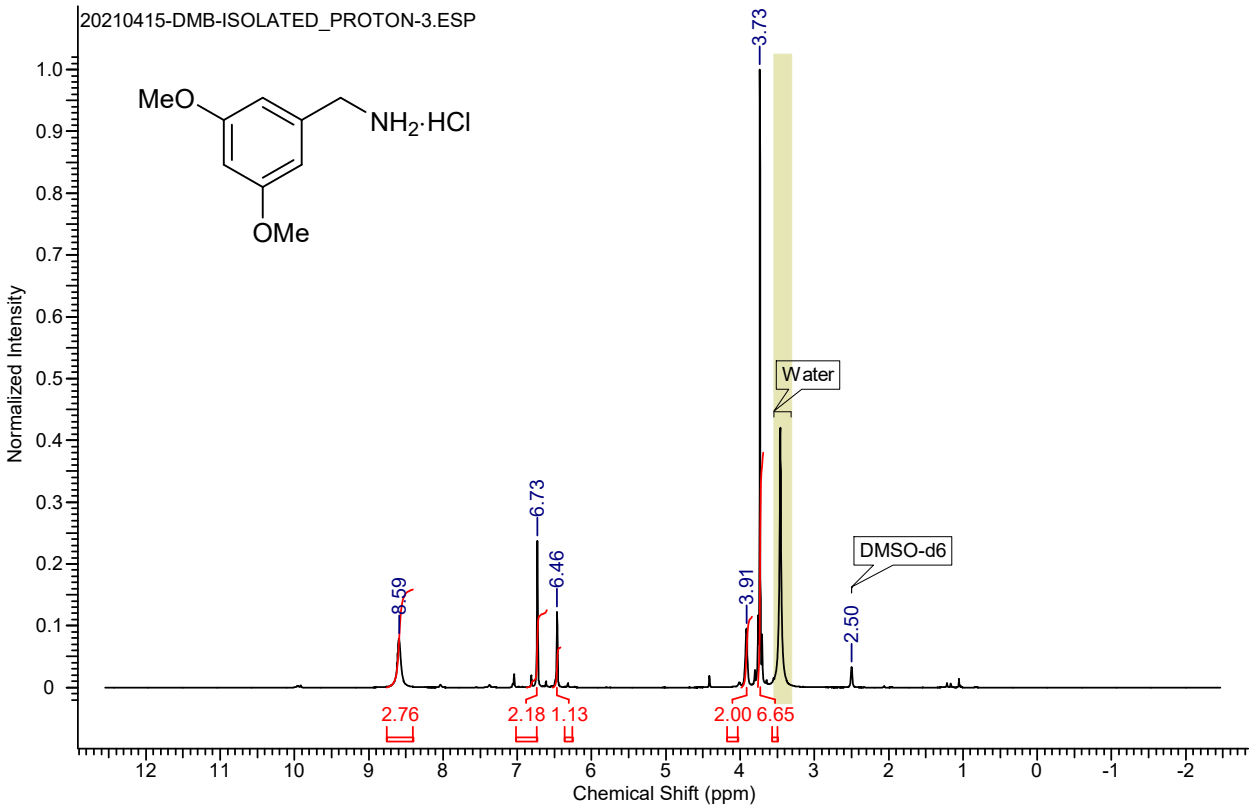

Figure S21. ^{1}H NMR Spectrum of **1e′** (DMSO-d_6, 200 MHz, 298 K).

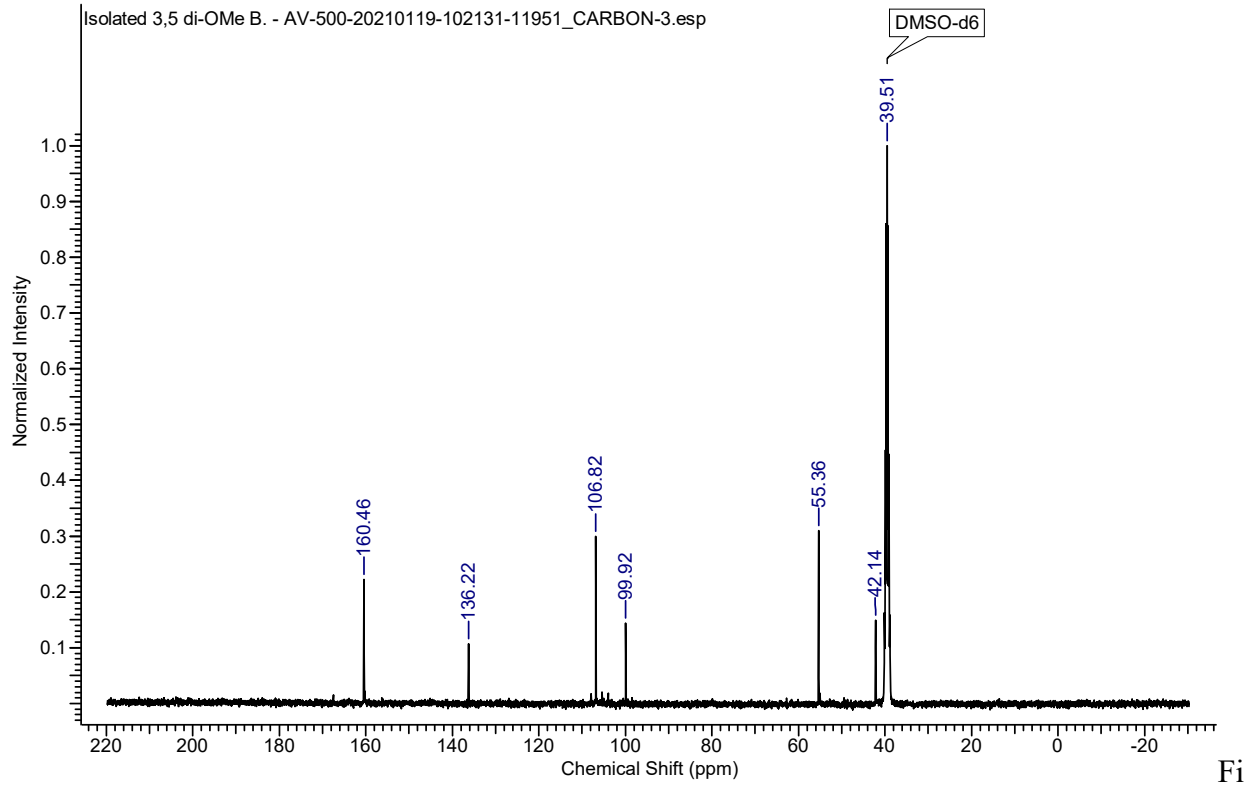

Figure S22. ^{13}C NMR spectrum of **1e′** (DMSO-d_6, 100.6 MHz, 298 K).

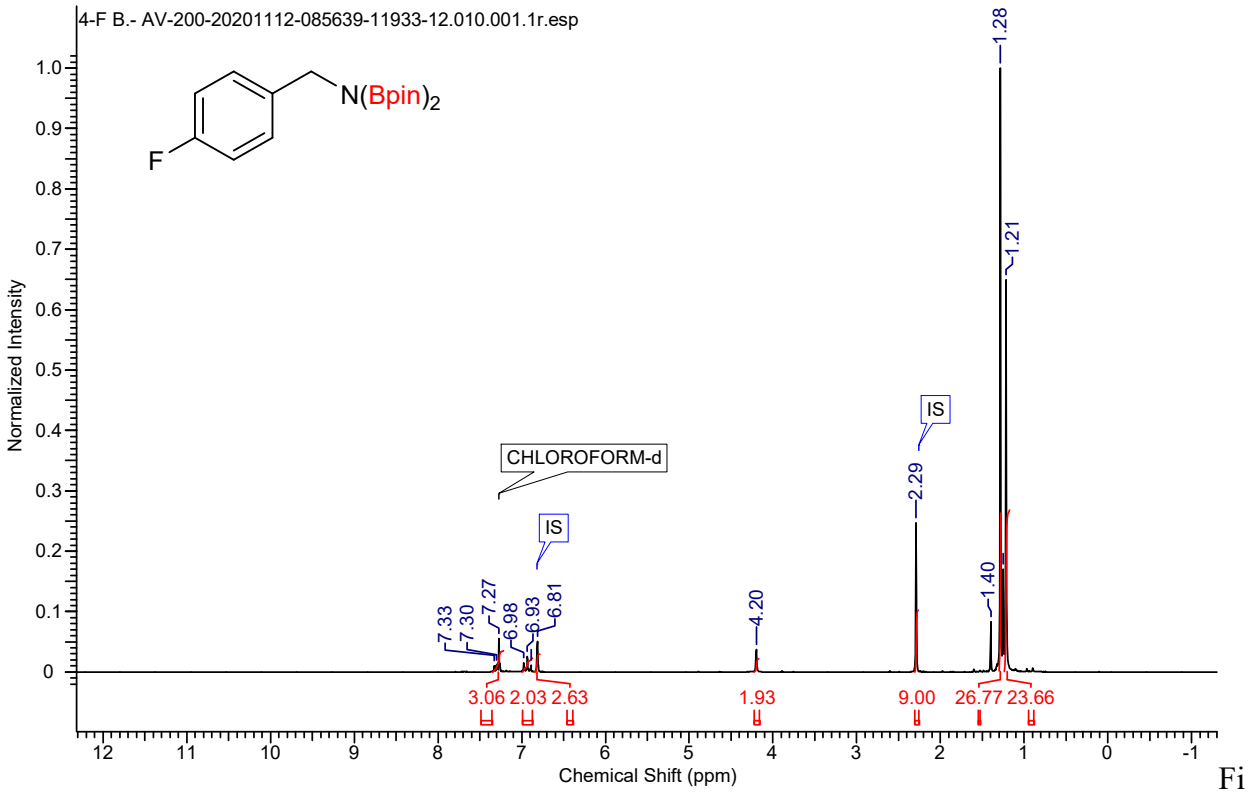

Figure S23. ^{1}H NMR spectrum of **1f** ($CDCl_3$, 200 MHz, 298 K).

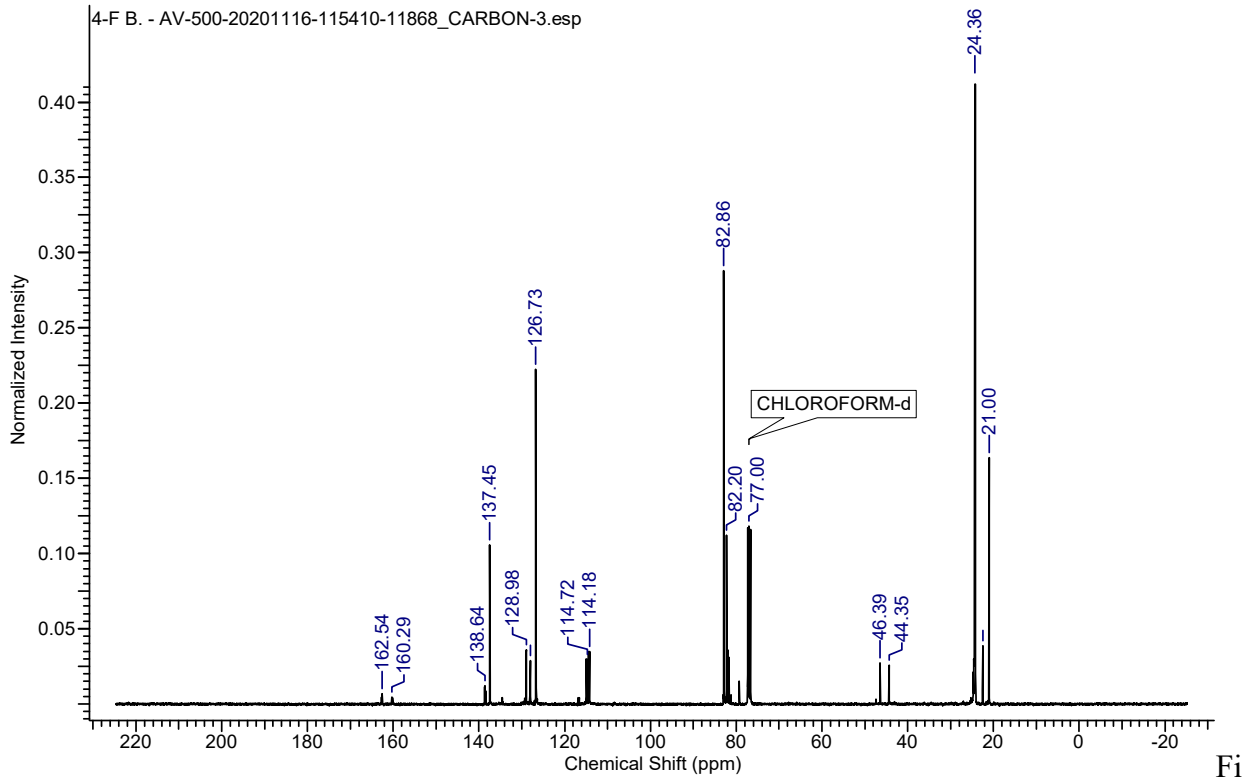

Figure S24. ^{13}C NMR Spectrum of **1f** ($CDCl_3$, 100.6 MHz, 298 K).

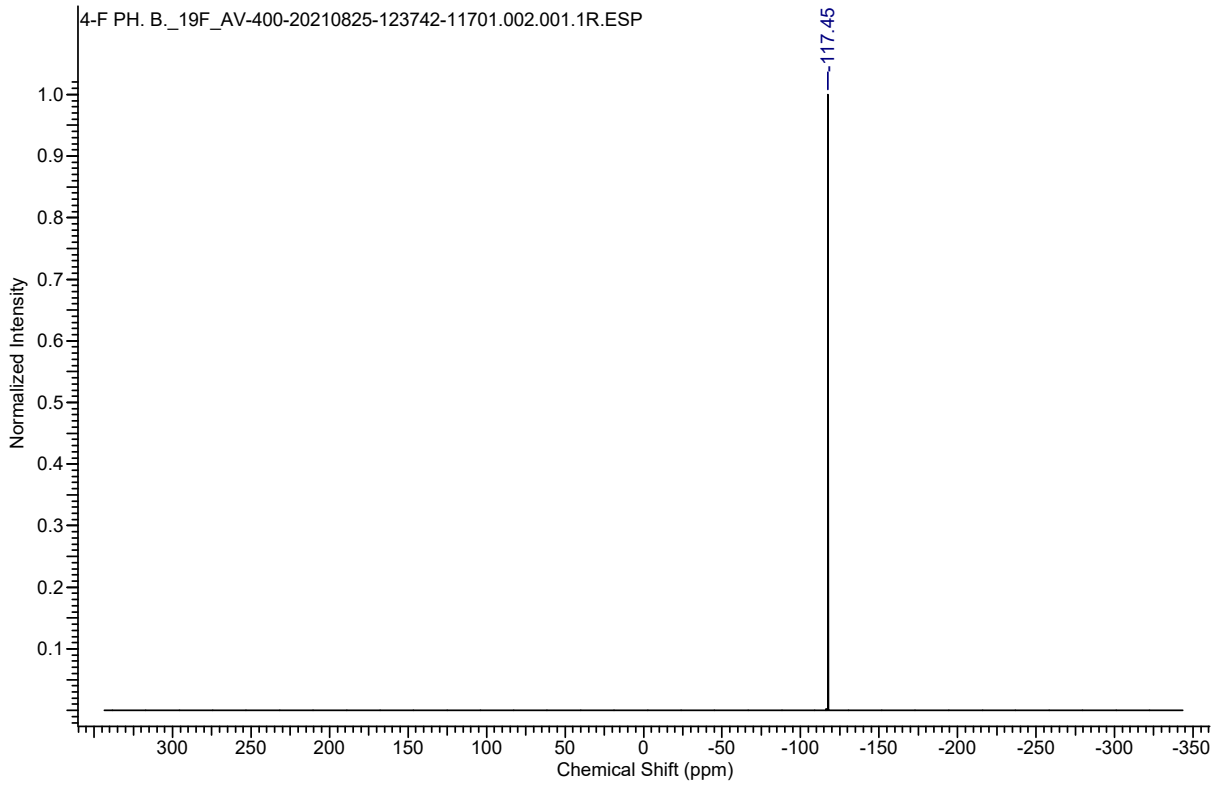

Figure S25. ^{19}F NMR Spectrum of **1f** ($CDCl_3$, 400 MHz, 298 K).

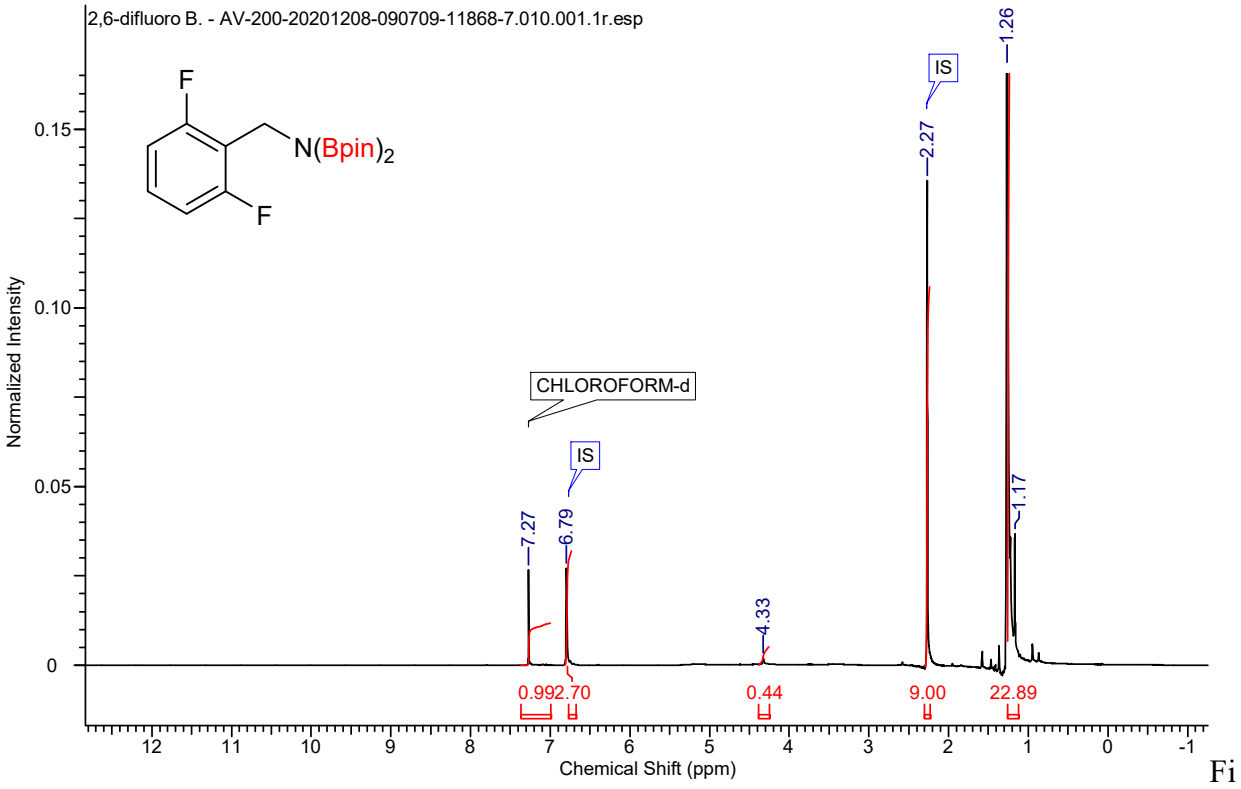

Figure S26. ^{1}H NMR Spectrum of **1g** ($CDCl_3$, 200 MHz, 298 K).

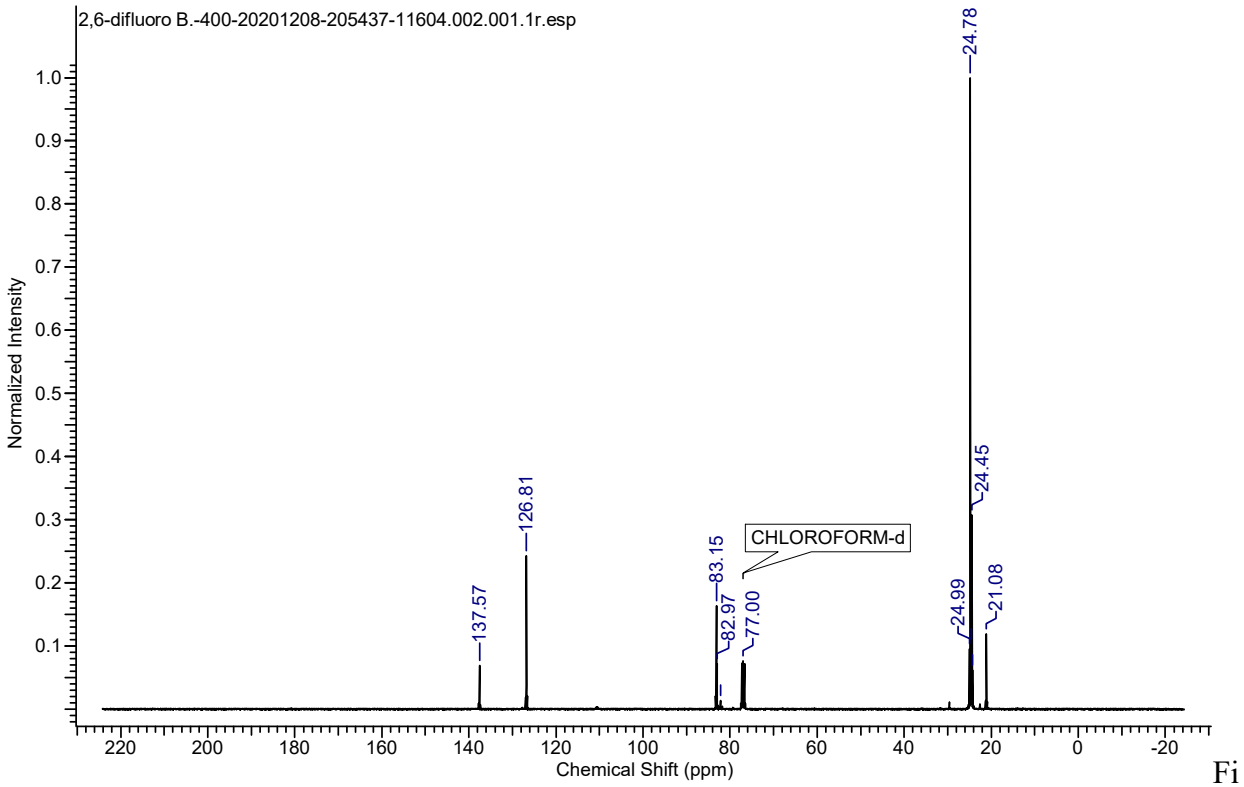

Figure S27. ^{13}C NMR spectrum of **1g** ($CDCl_3$, 100.6 MHz, 298 K).

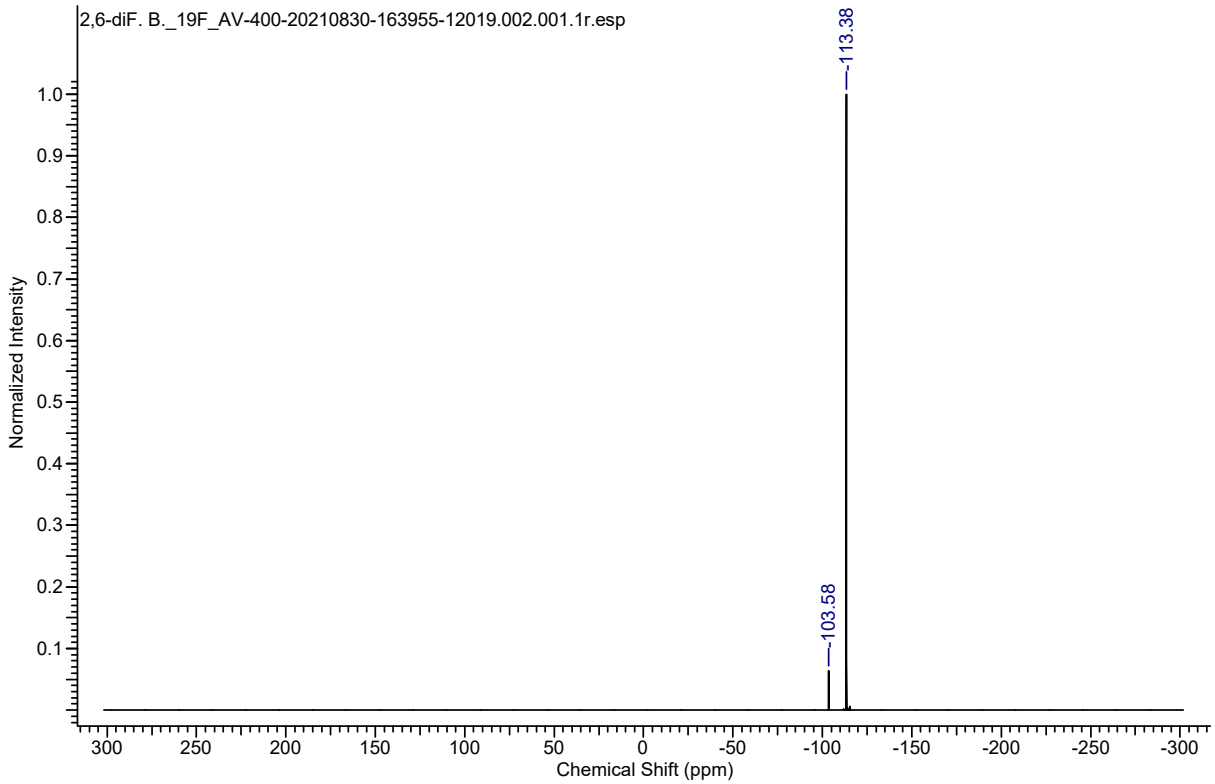

Figure S28. ^{19}F NMR Spectrum of **1g** ($CDCl_3$, 400 MHz, 298 K).

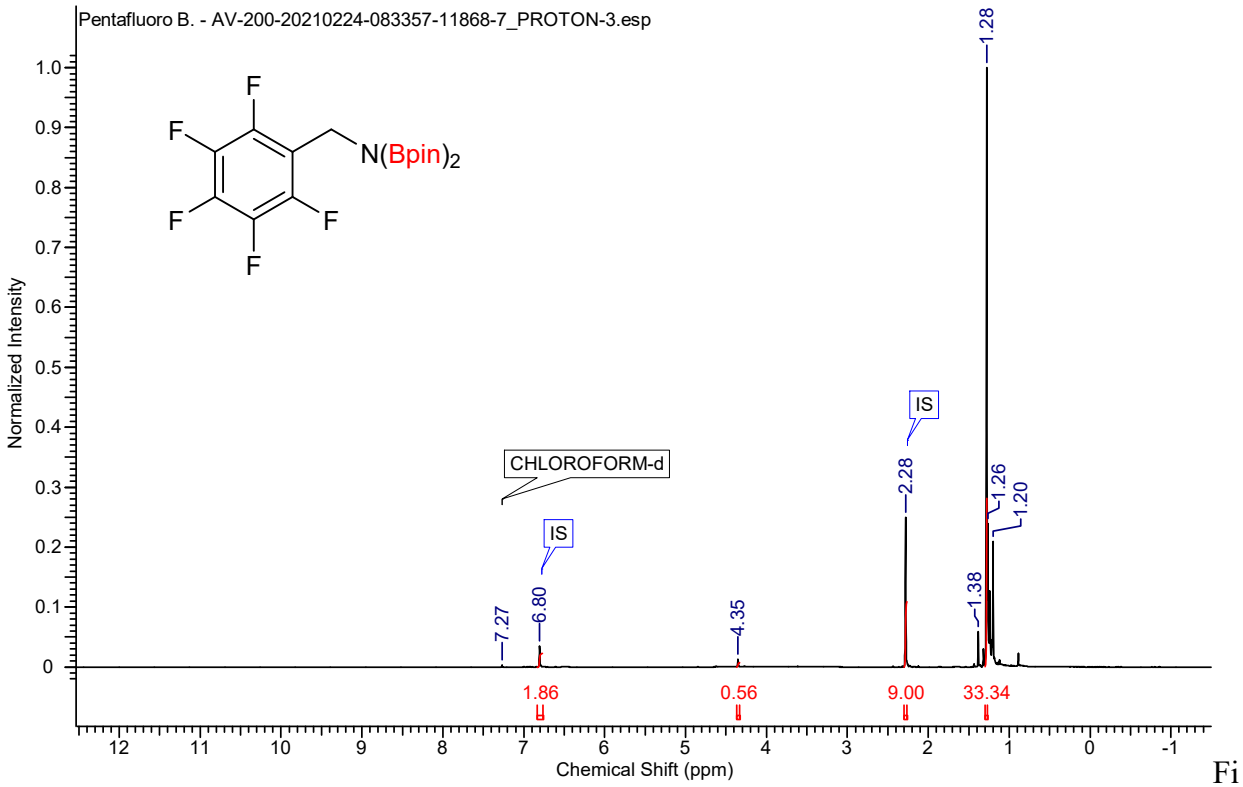

Figure S29. ^{1}H NMR spectrum of **1h** ($CDCl_3$, 200 MHz, 298 K).

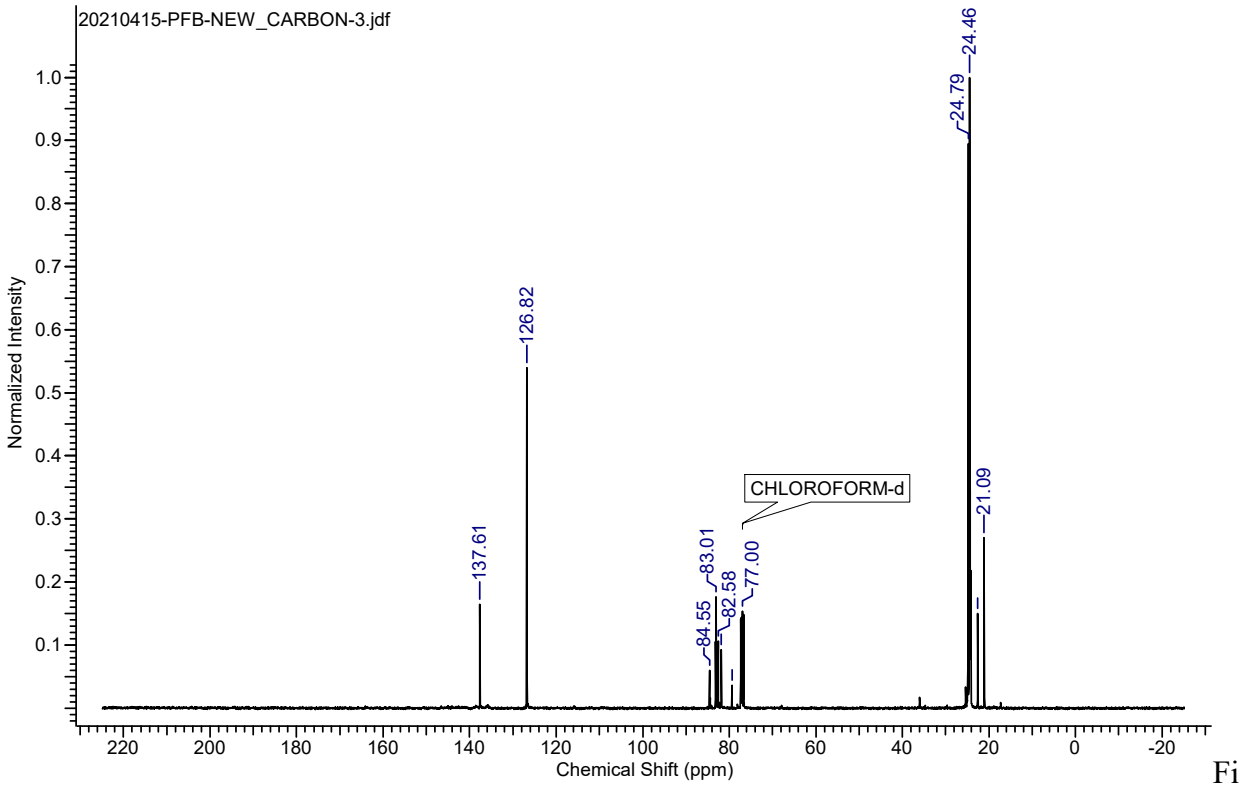

Figure S30. ^{13}C NMR spectrum of **1h** ($CDCl_3$, 100.6 MHz, 298 K).

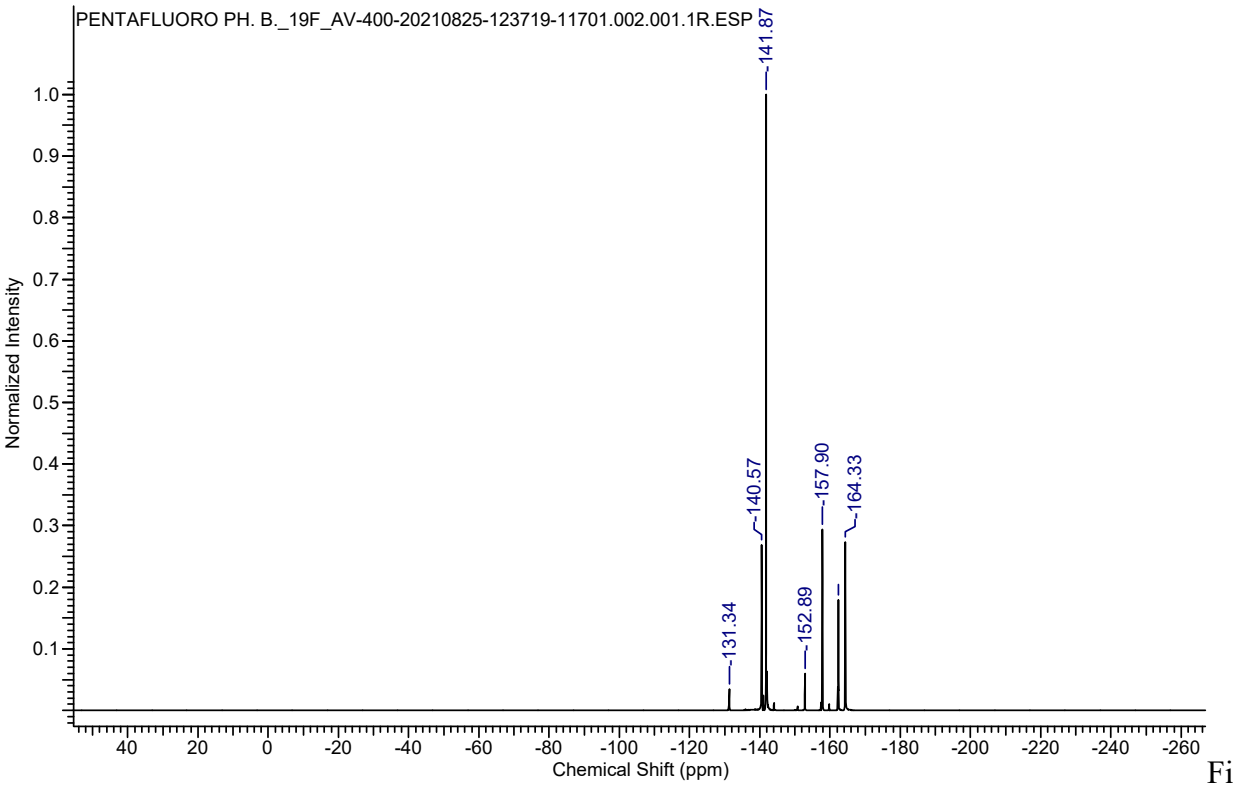

Figure S31. ^{19}F NMR Spectrum of **1h** ($CDCl_3$, 400 MHz, 298 K).

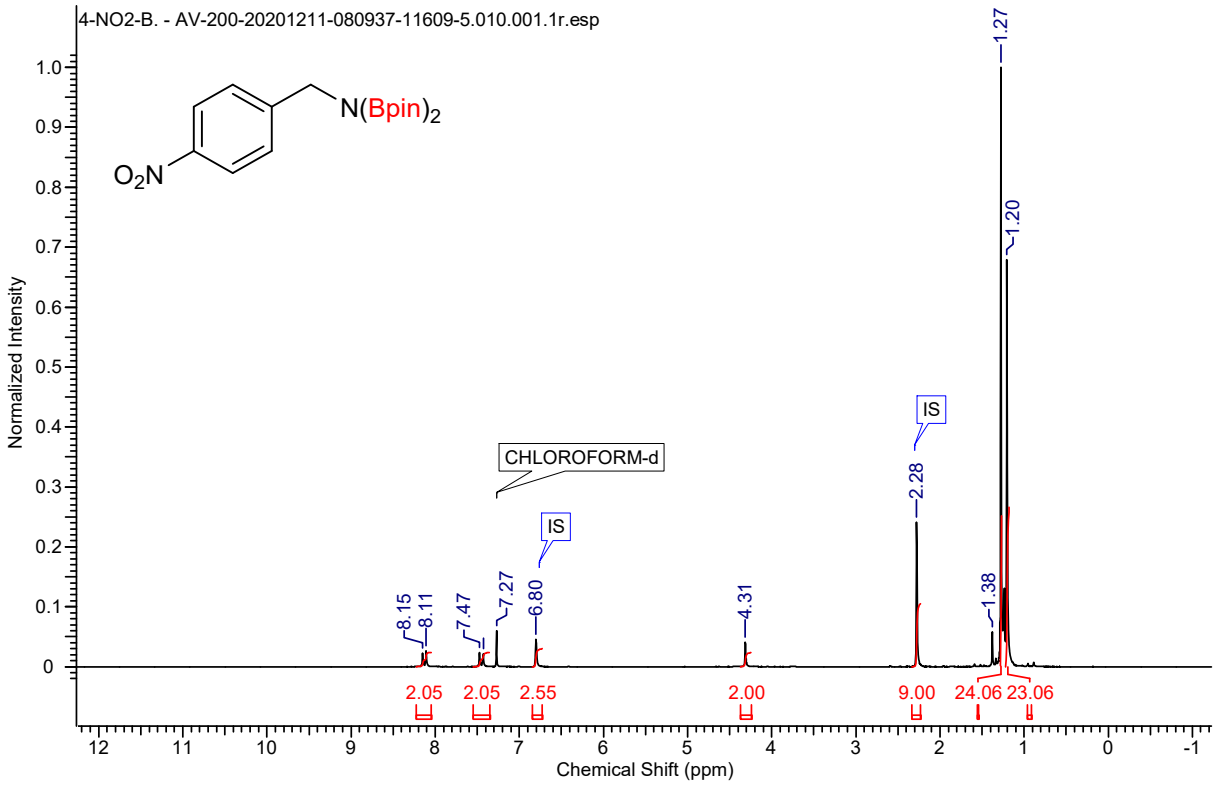

Figure S32. ^{1}H NMR spectrum of **1i** ($CDCl_3$, 200 MHz, 298 K).

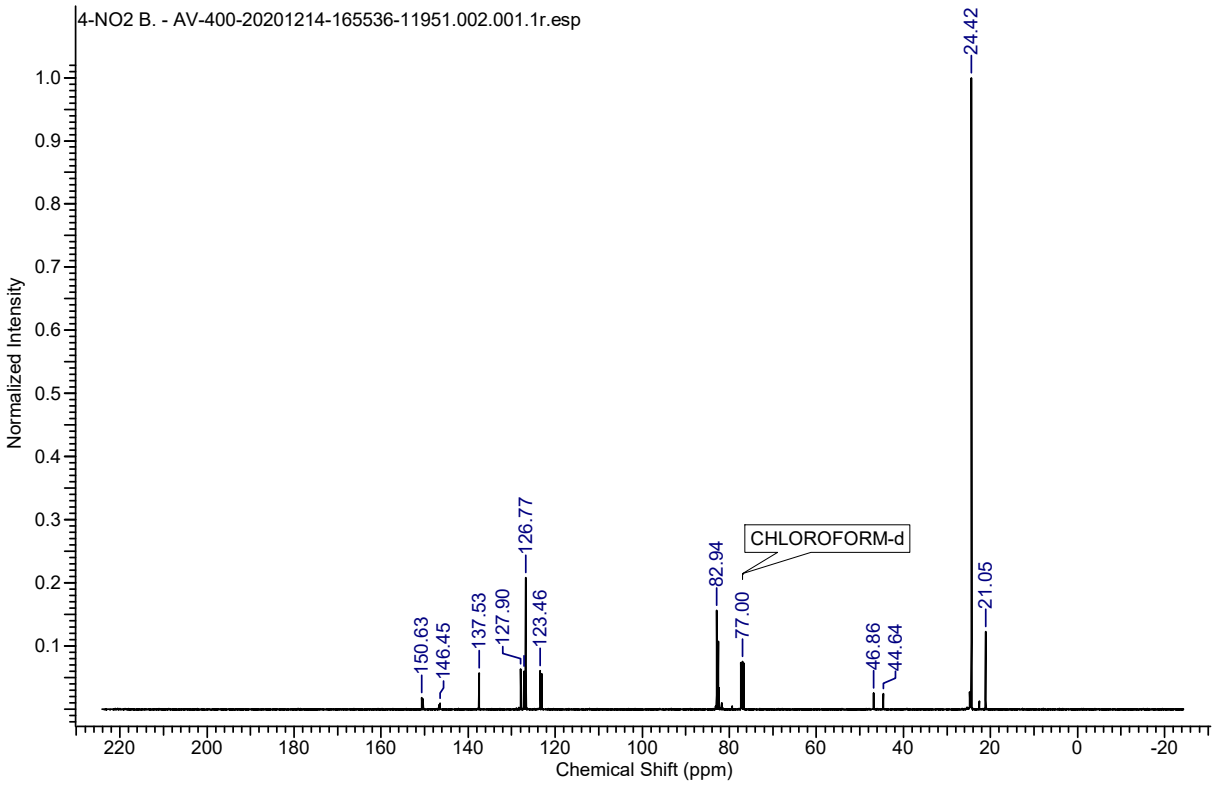

Figure S33. ^{13}C NMR spectrum of **1i** ($CDCl_3$, 100.6 MHz, 298 K).

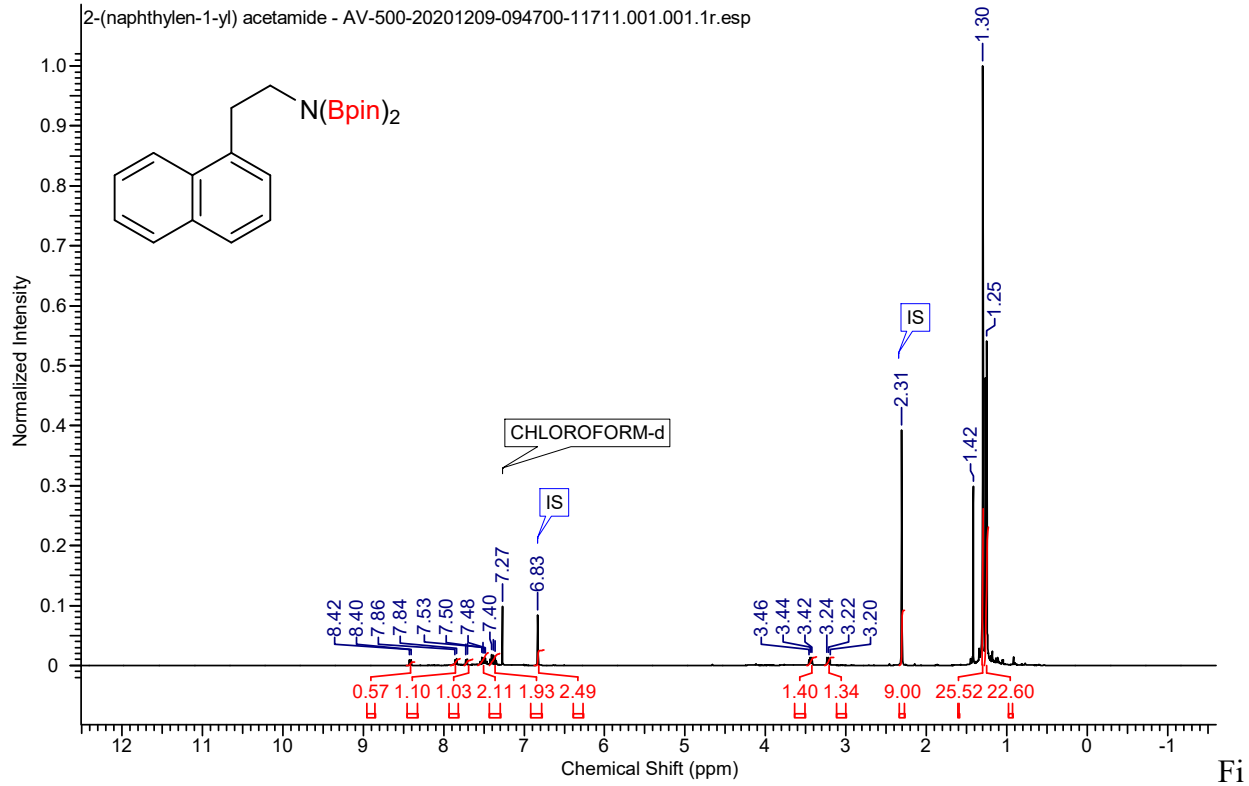

Figure S34. ^{1}H NMR Spectrum of **1j** ($CDCl_3$, 200 MHz, 298 K).

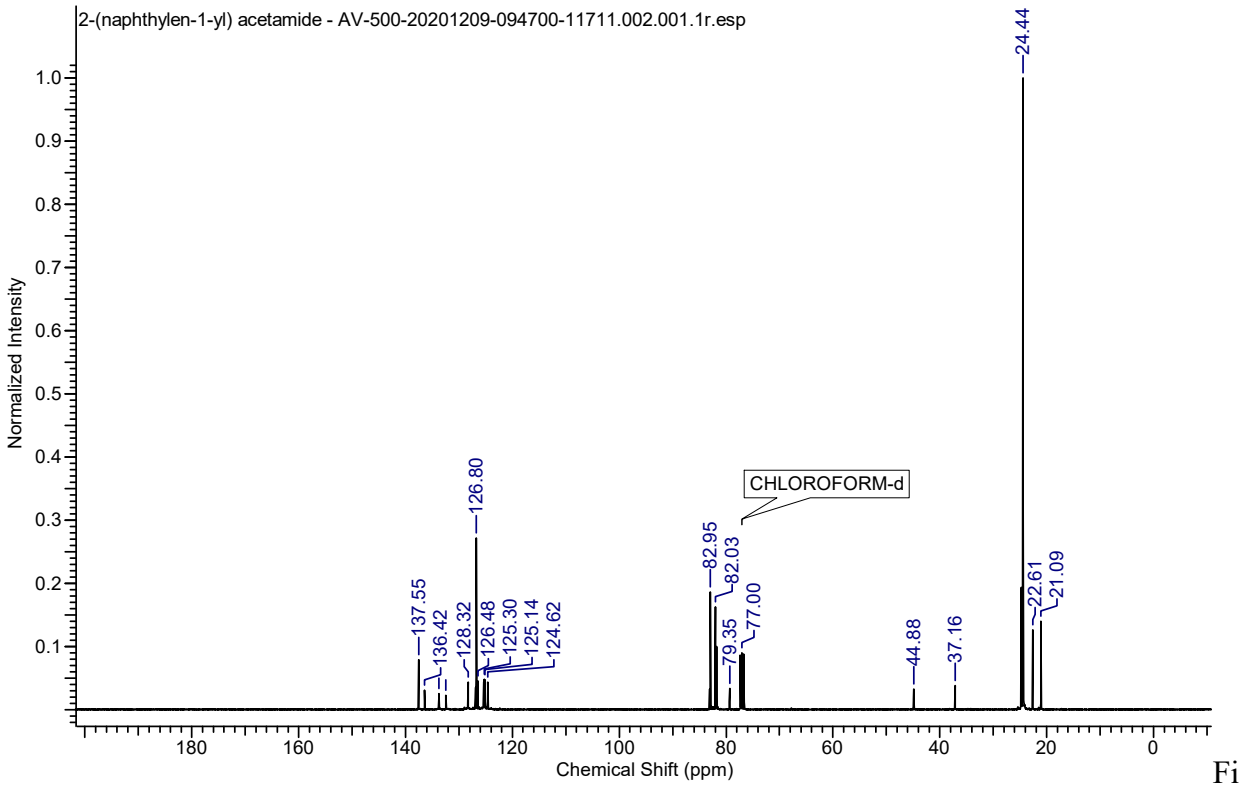

Figure S35. ^{13}C NMR spectrum of **1j** ($CDCl_3$, 100.5 MHz, 298 K).

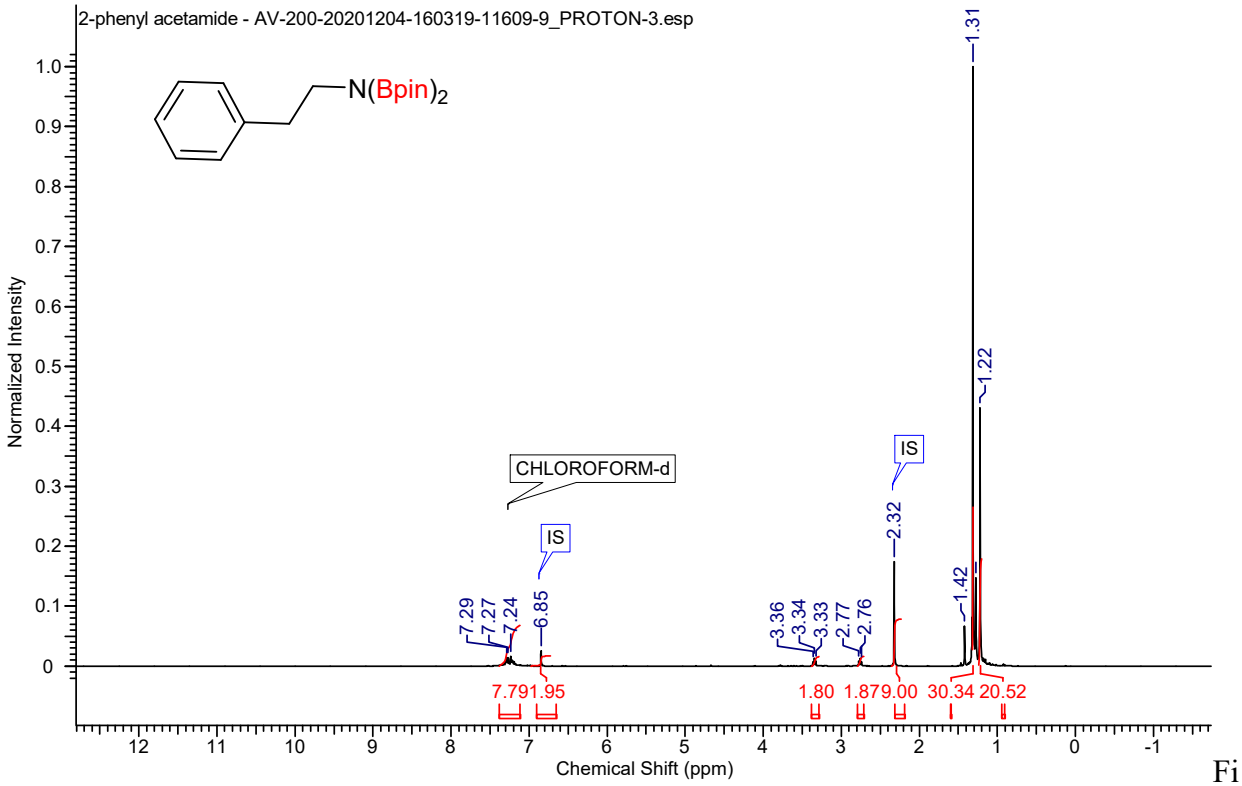

Figure S36. ^{1}H NMR Spectrum of **1k** ($CDCl_3$, 200 MHz, 298 K).

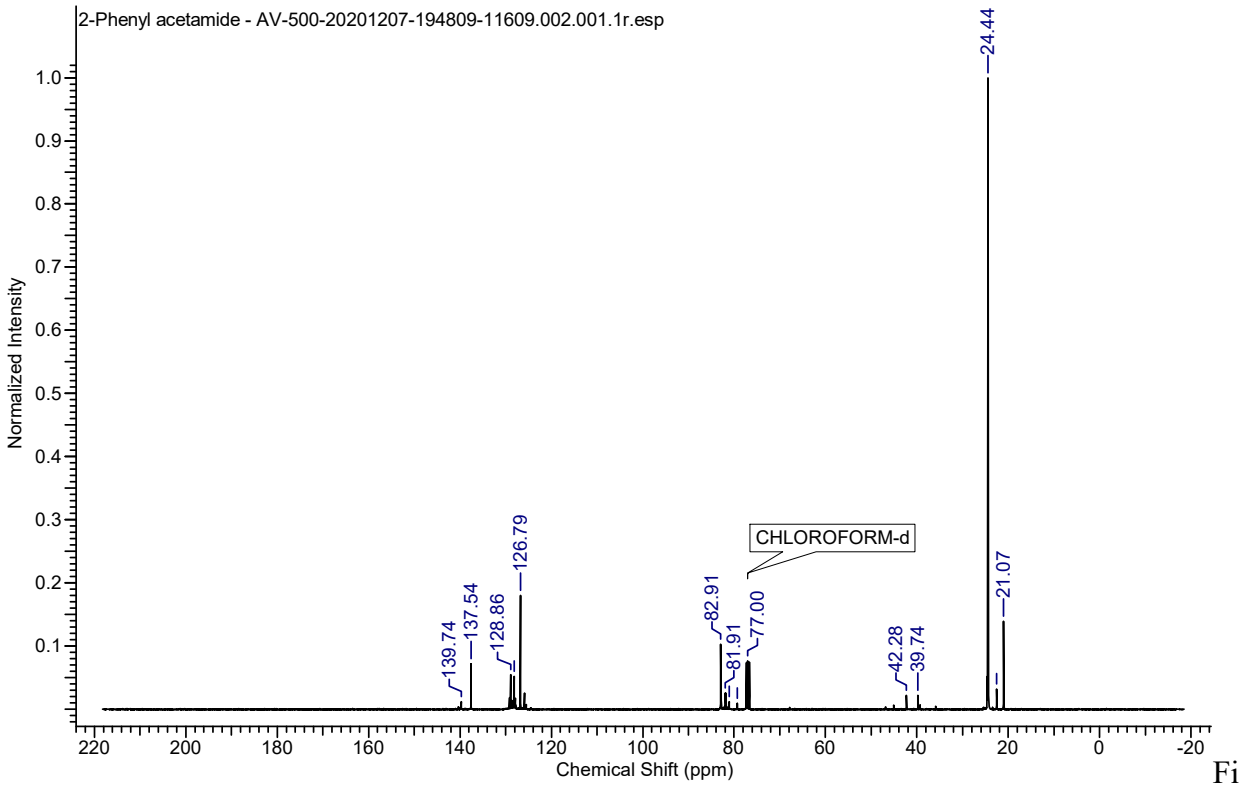

Figure S37. ^{13}C NMR spectrum of **1k** ($CDCl_3$, 100.5 MHz, 298 K).

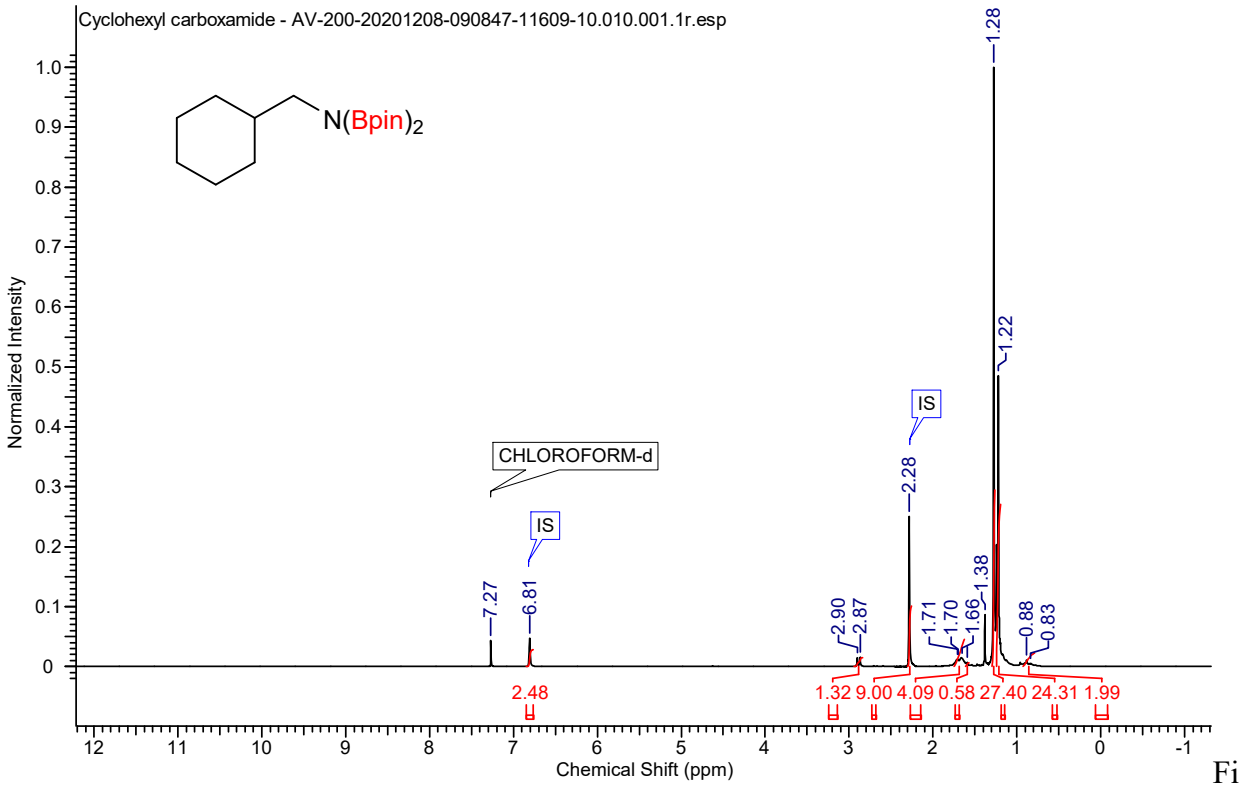

Figure S38. ^{1}H NMR Spectrum of **1l** ($CDCl_3$, 200 MHz, 298 K).

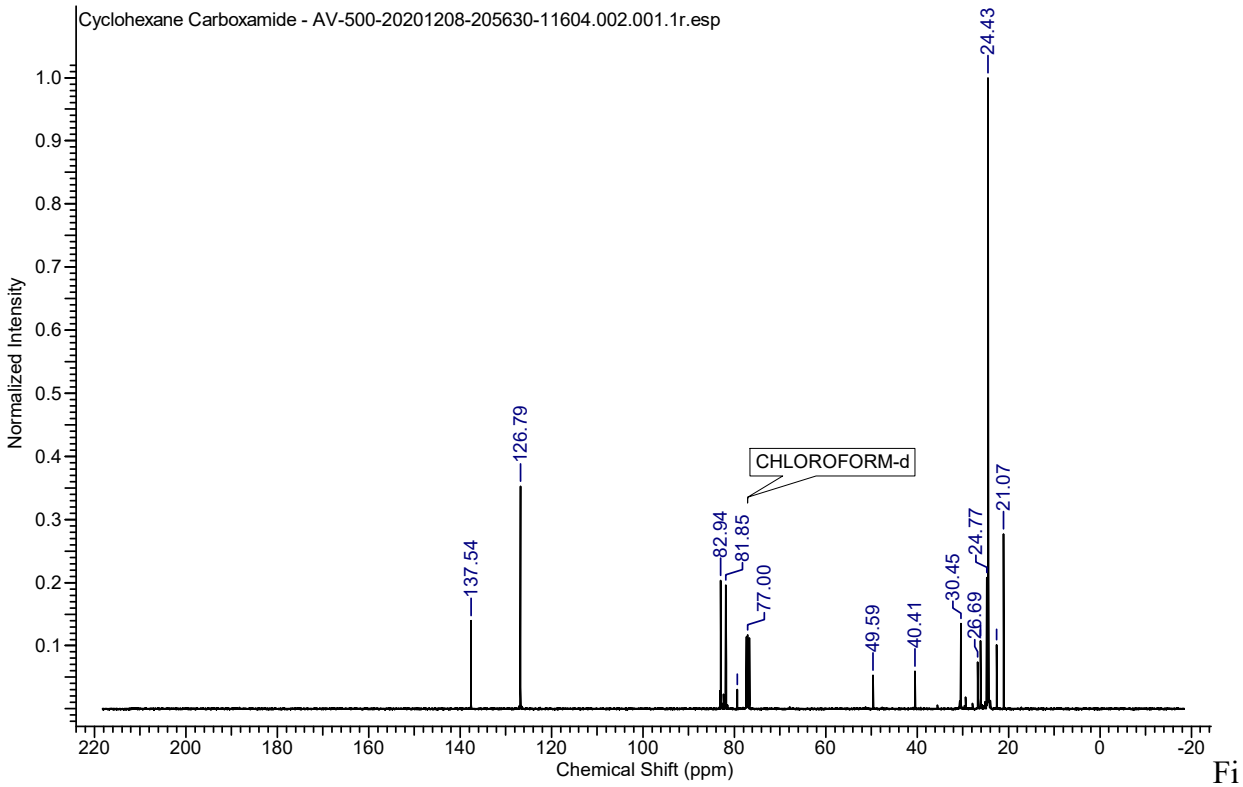

Figure S39. ^{13}C NMR spectrum of **1l** ($CDCl_3$, 100.5 MHz, 298 K).

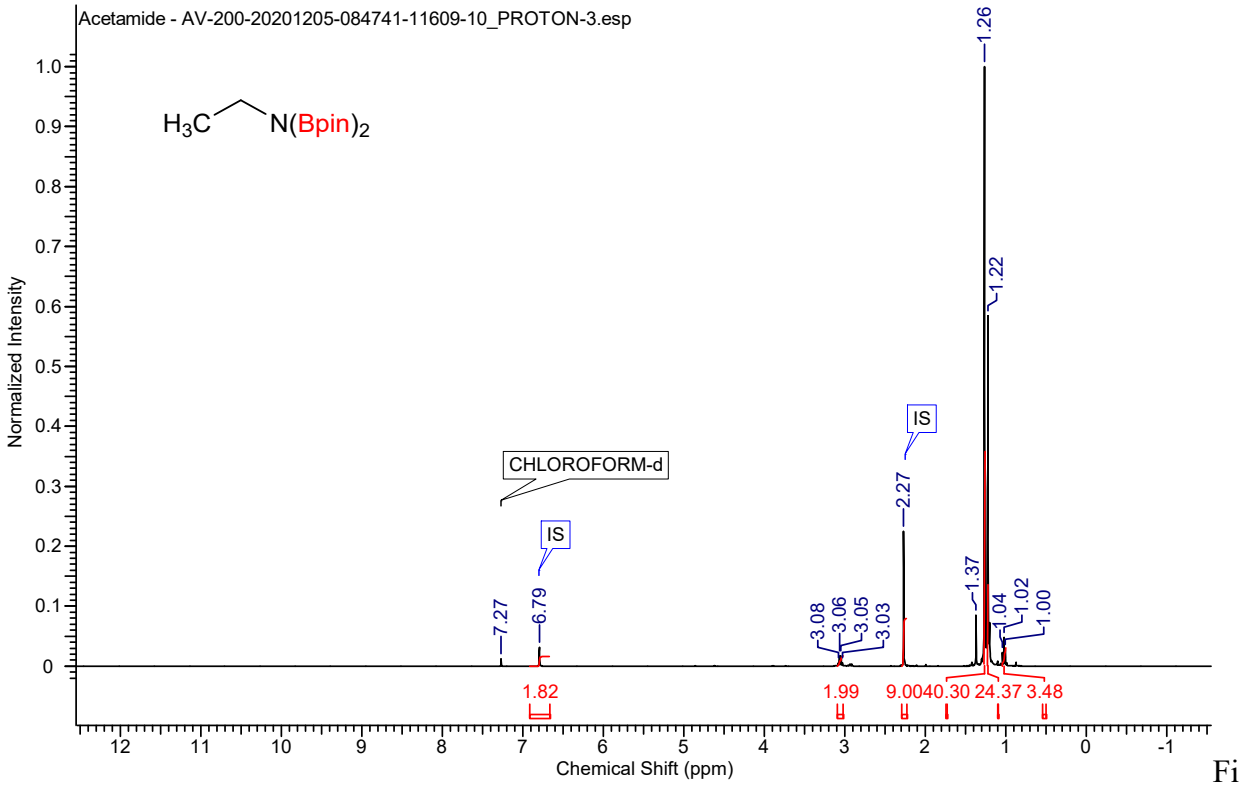

Figure S40. ^{1}H NMR Spectrum of **1m** ($CDCl_3$, 200 MHz, 298 K).

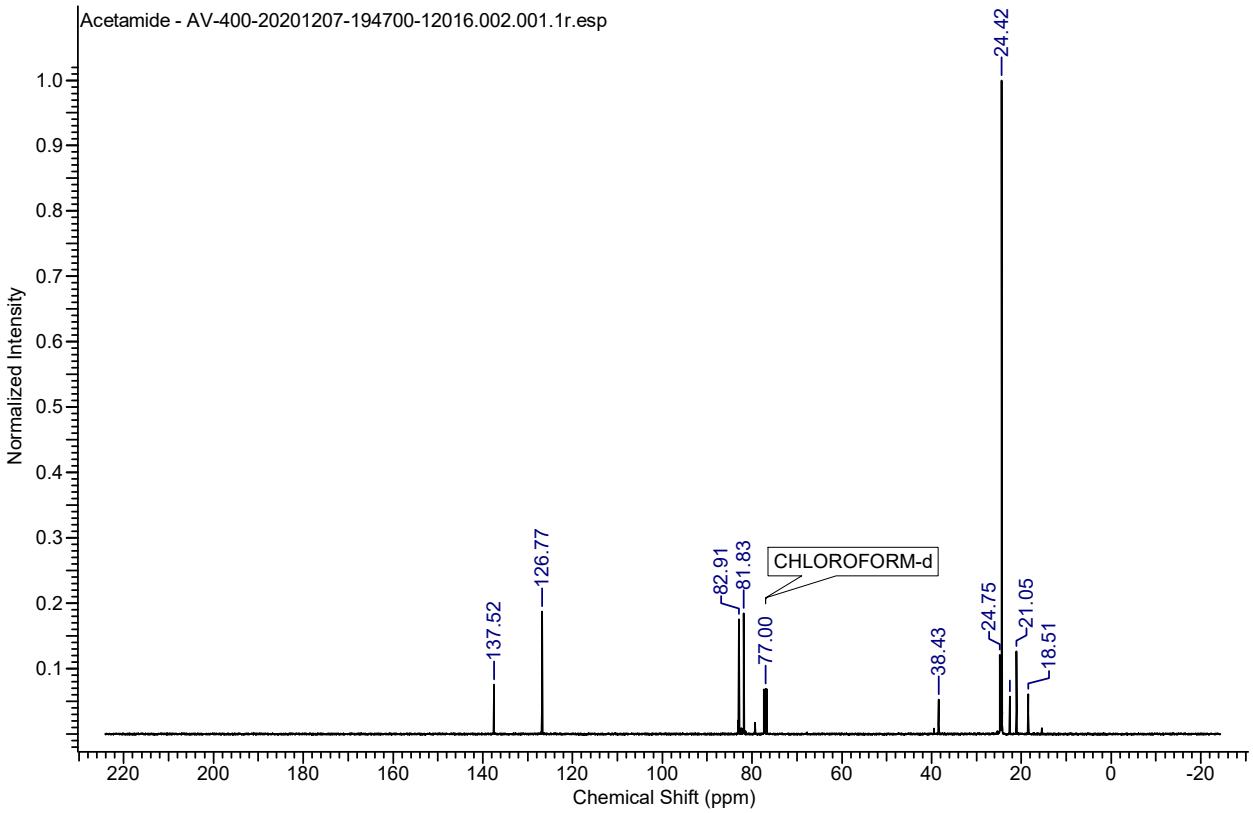

Figure S41. ^{13}C NMR spectrum of **1m** ($CDCl_3$, 100.5 MHz, 298 K).

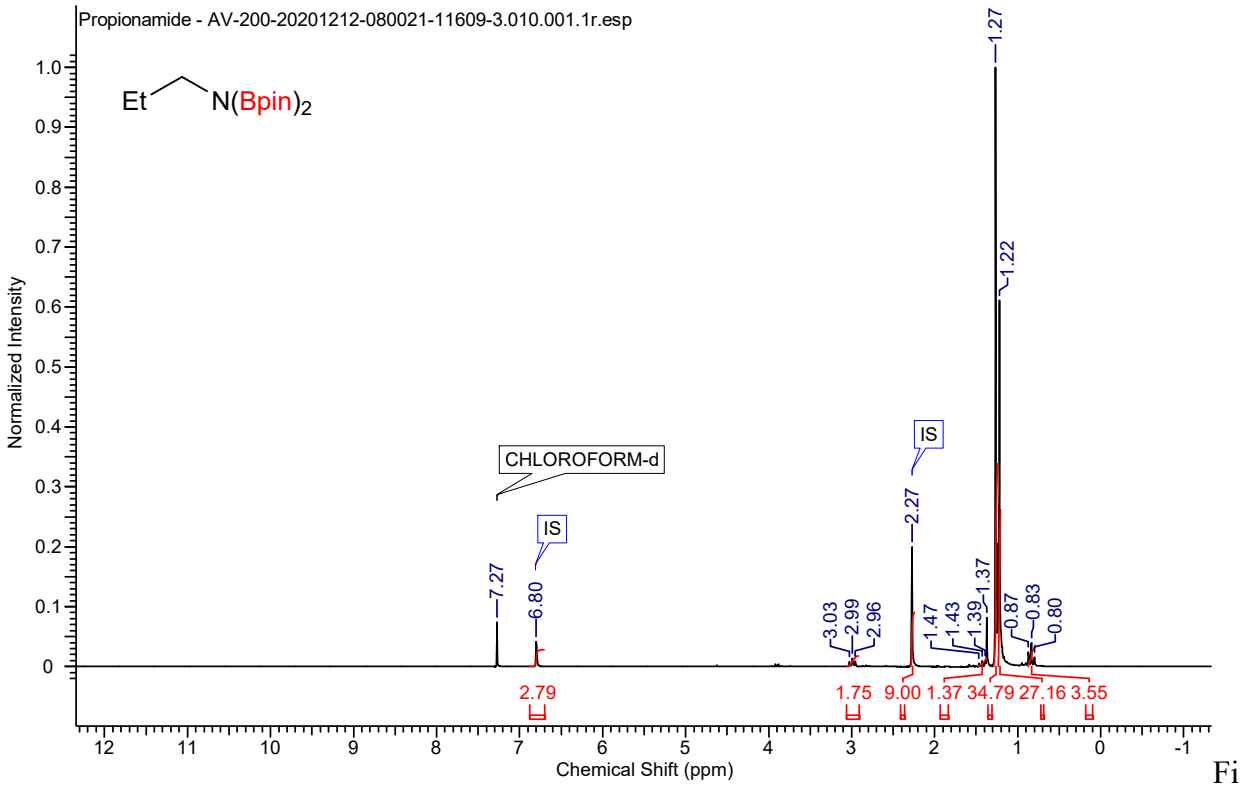

Figure S42. ^{1}H NMR Spectrum of **1n** ($CDCl_3$, 200 MHz, 298 K).

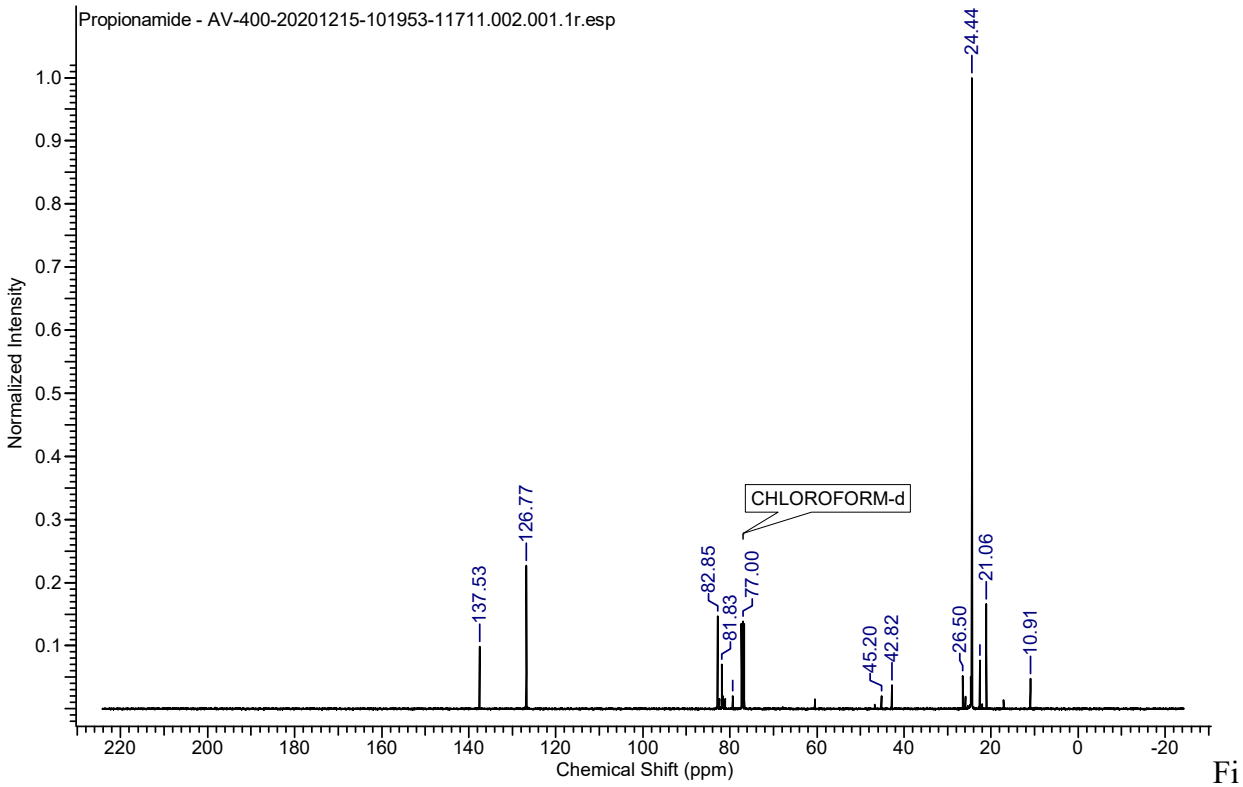

Figure S43. ^{13}C NMR spectrum of **1n** ($CDCl_3$, 100.5 MHz, 298 K).

Note: ^{1}H NMR spectra of **1o** is same as **1n**.

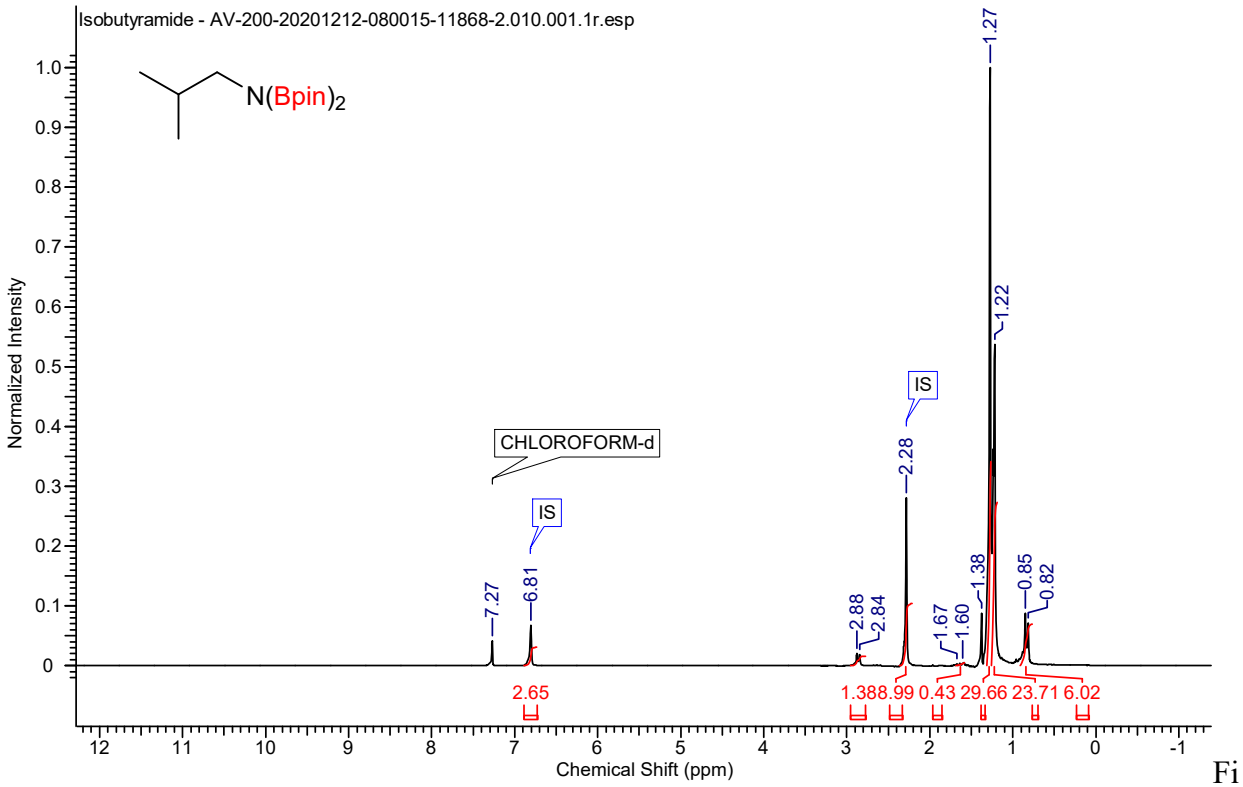

Figure S44. ^{1}H NMR Spectrum of **1p** ($CDCl_3$, 200 MHz, 298 K).

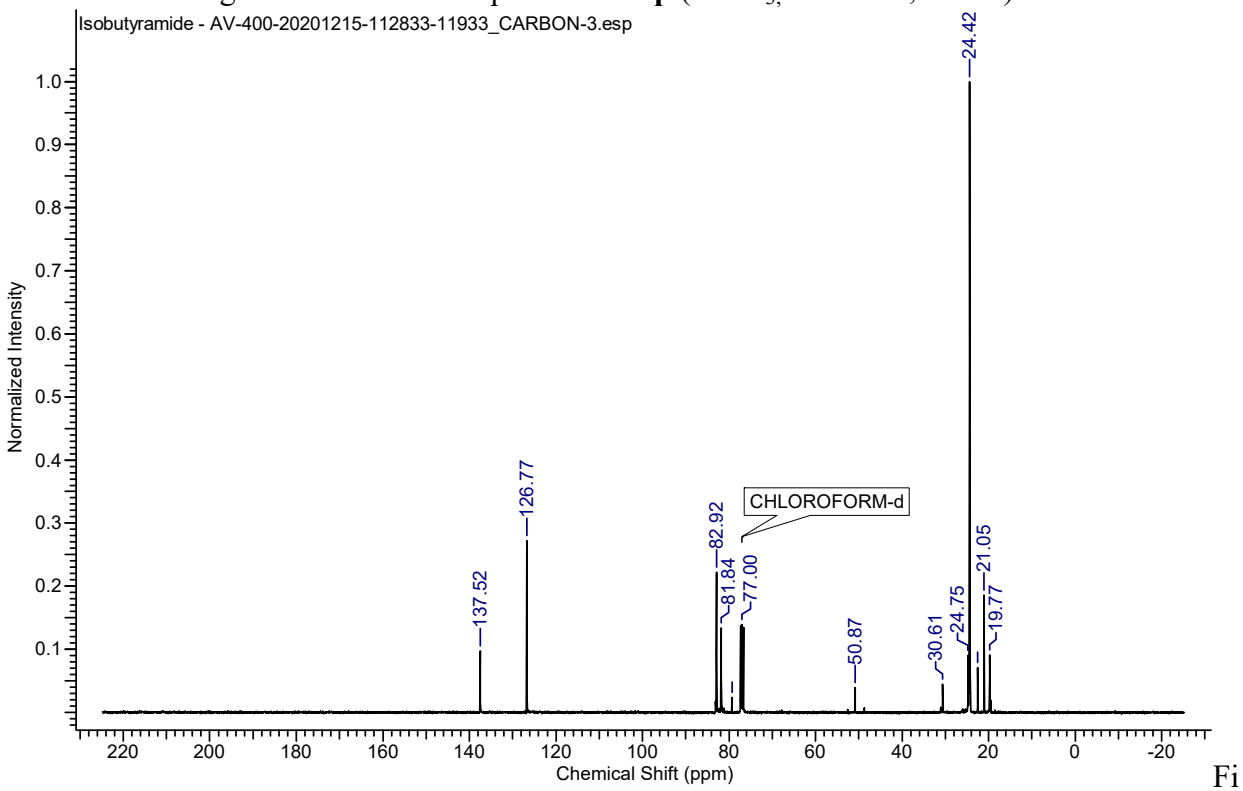

Figure S45. ^{13}C NMR spectrum of **1p** ($CDCl_3$, 100.5 MHz, 298 K).

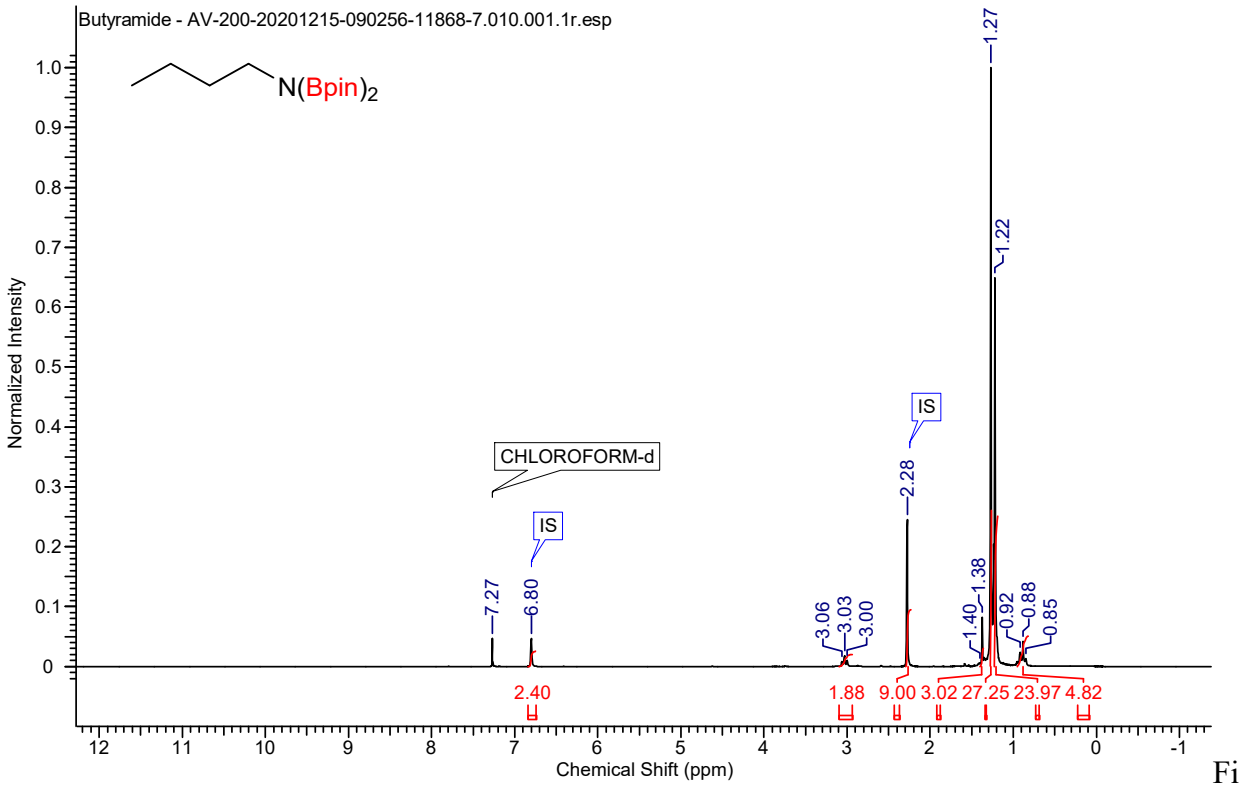

Figure S46. ^{1}H NMR Spectrum of **1q** ($CDCl_3$, 200 MHz, 298 K).

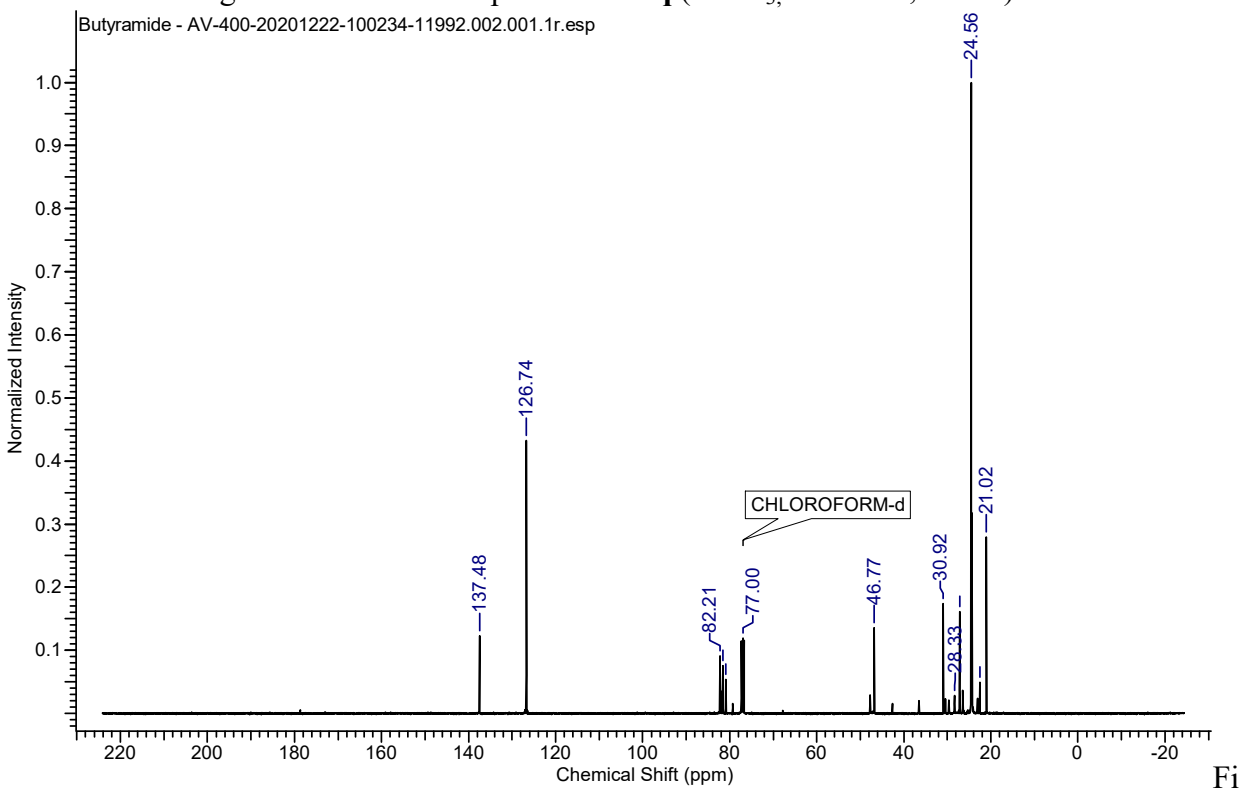

Figure S47. ^{13}C NMR spectrum of **1q** ($CDCl_3$, 100.5 MHz, 298 K).

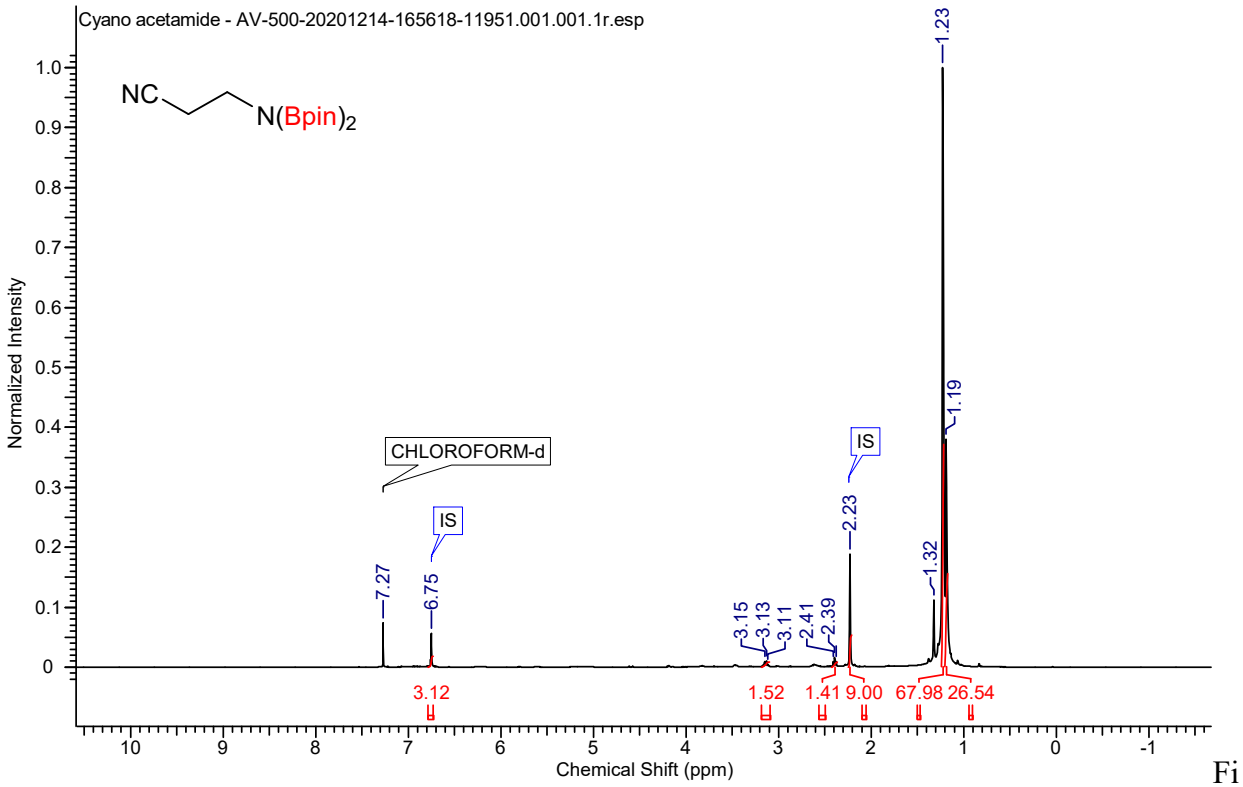

Figure S48. ^{1}H NMR Spectrum of **1r** ($CDCl_3$, 200 MHz, 298 K).

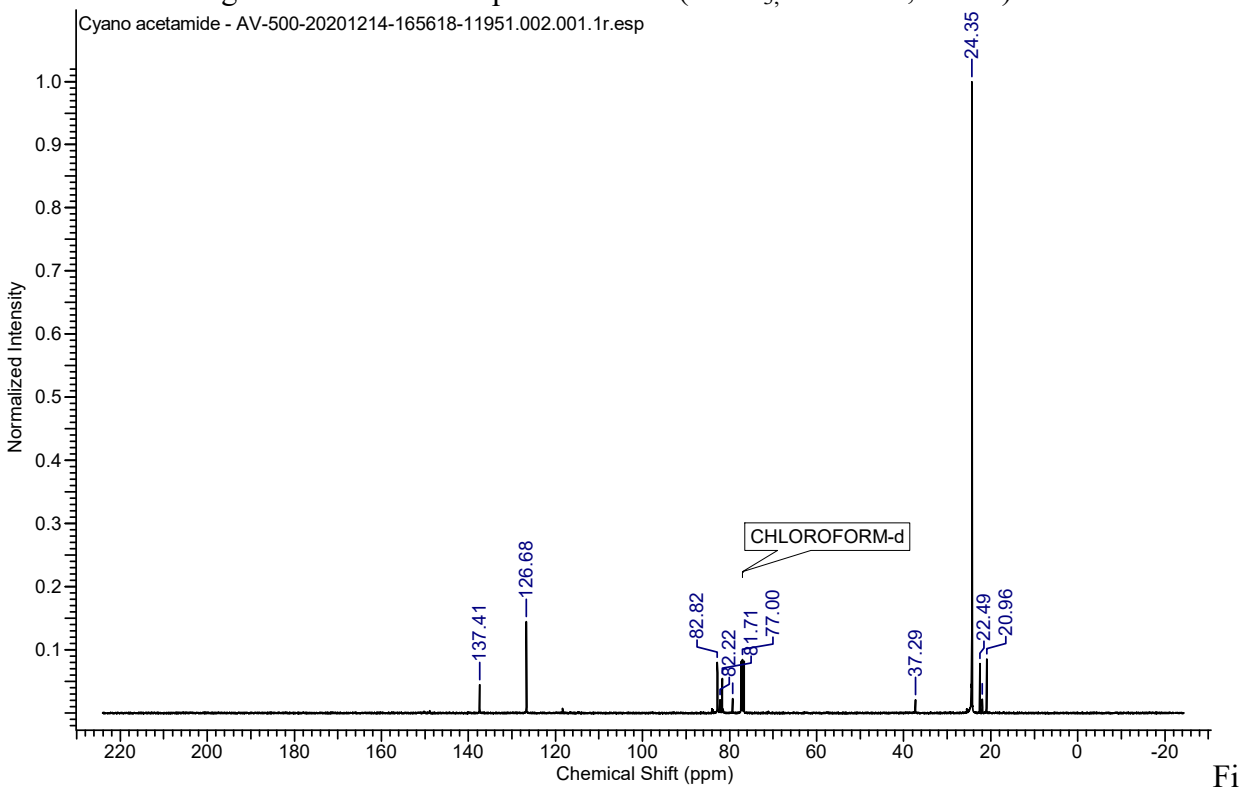

Figure S49. ^{13}C NMR spectrum of **1r** ($CDCl_3$, 100.6 MHz, 298 K).

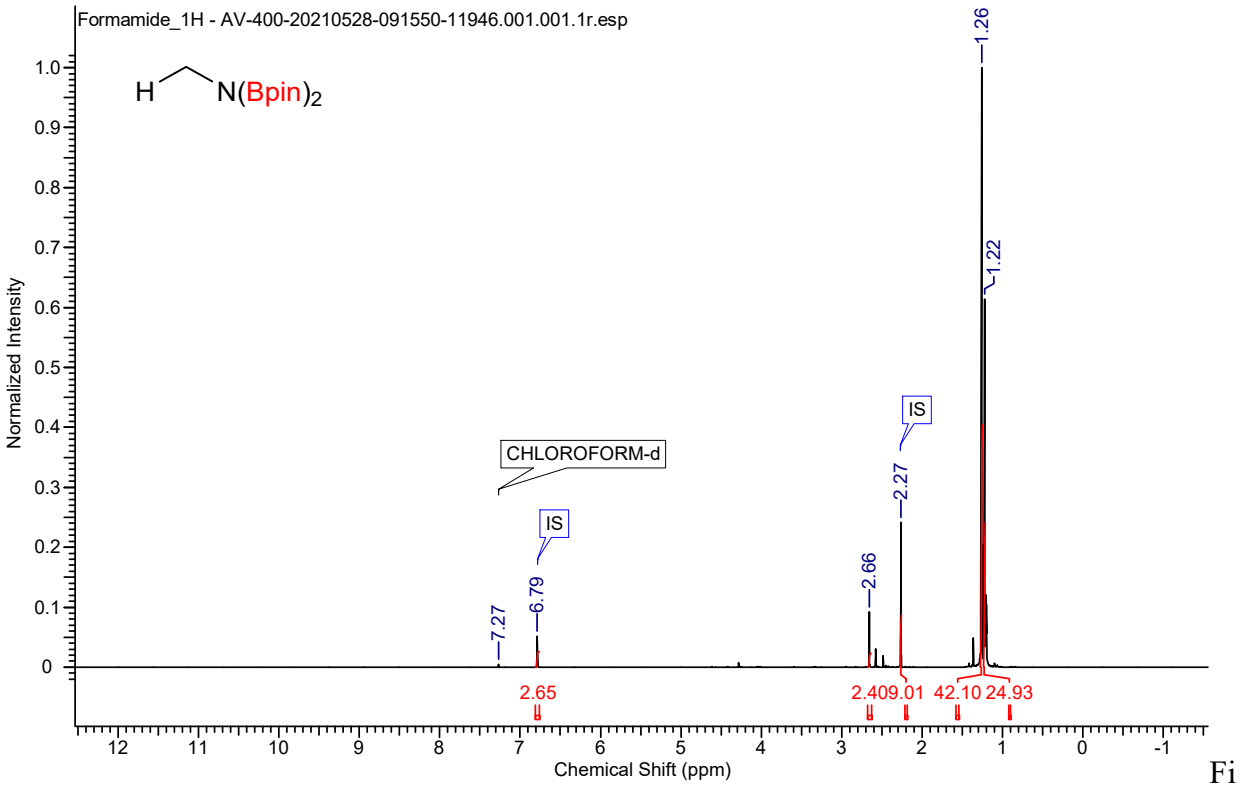

Figure S50. ^{1}H NMR Spectrum of **1s** ($CDCl_3$, 200 MHz, 298 K).

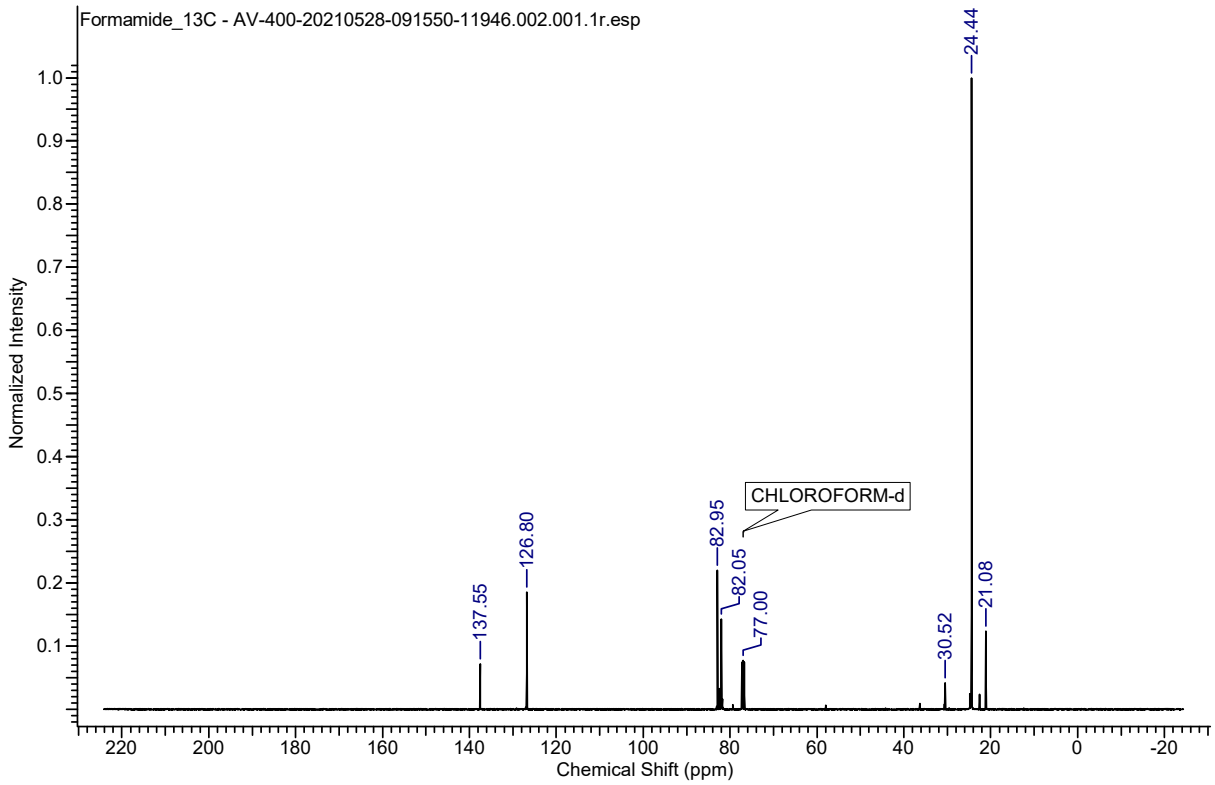

Figure S51. ^{13}C NMR spectrum of **1s** ($CDCl_3$, 100.6 MHz, 298 K).

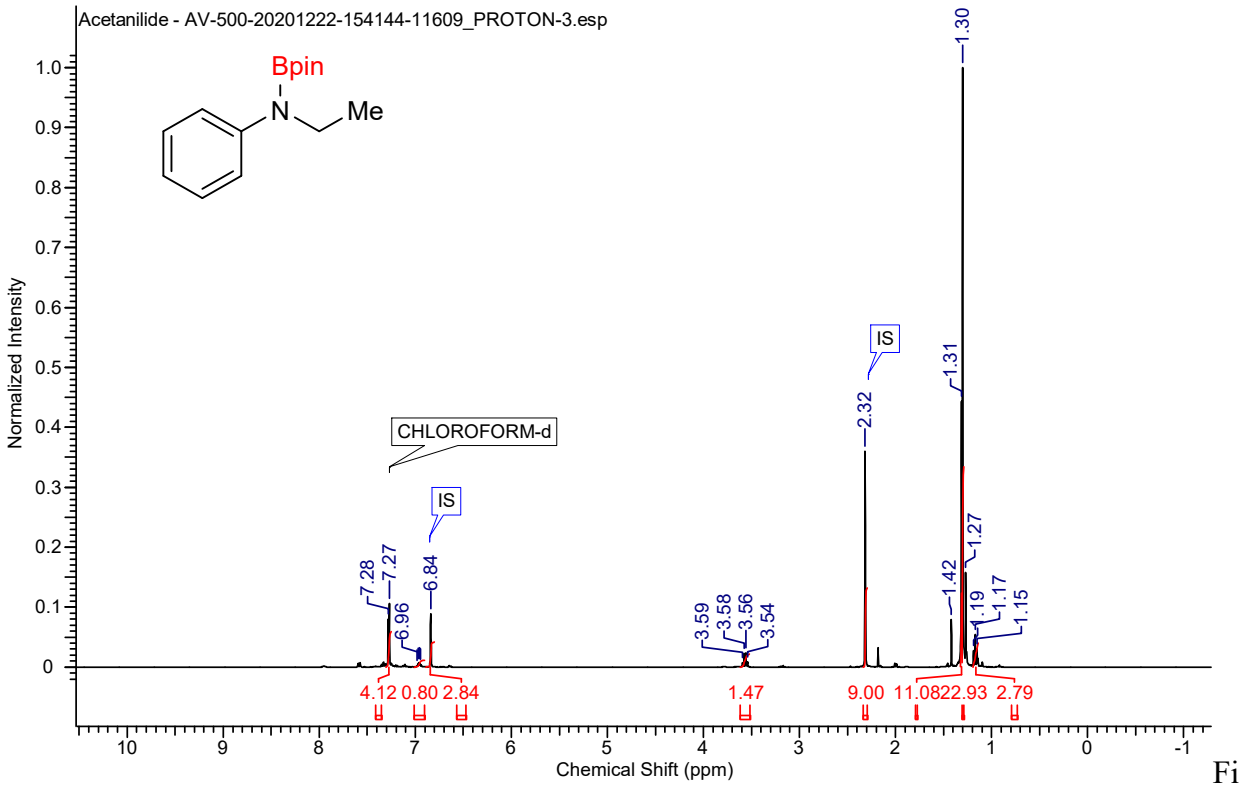

Figure S52. ^{1}H NMR Spectrum of **2a** ($CDCl_3$, 500 MHz, 298 K).

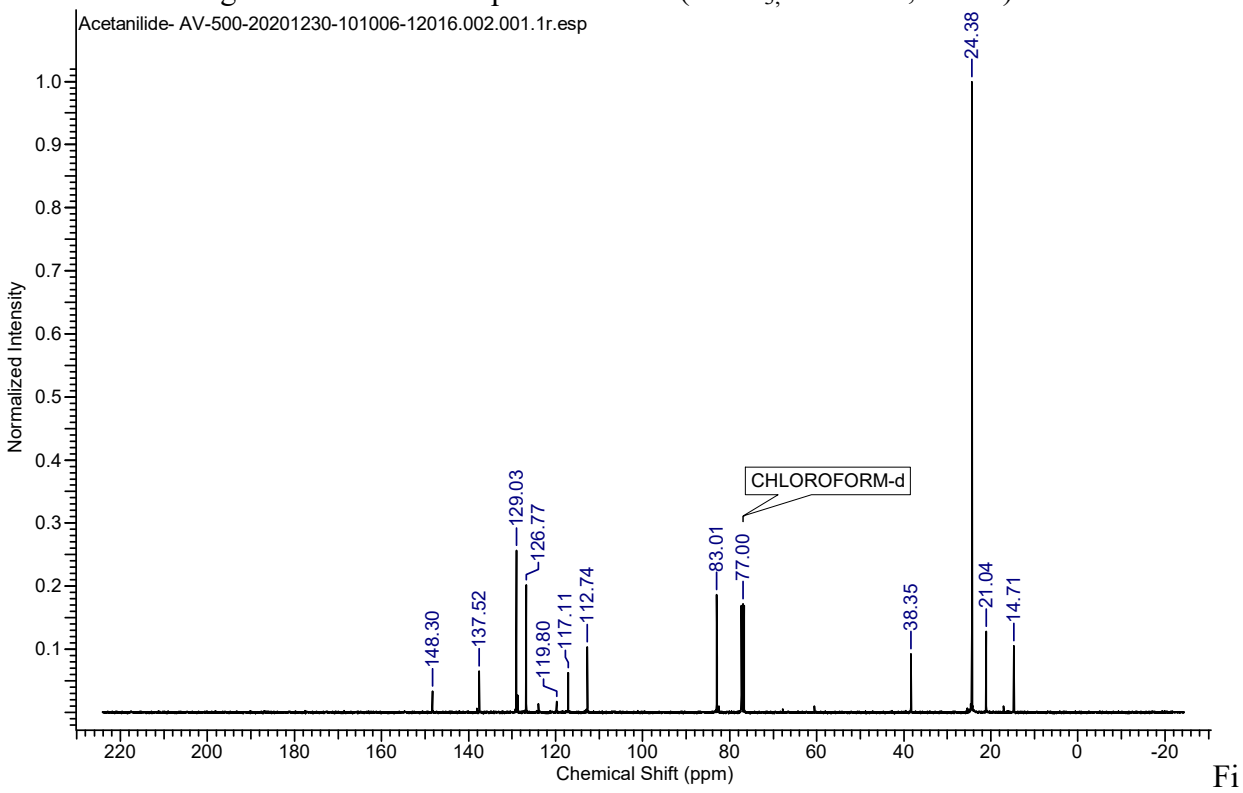

Figure S53. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 100.6 MHz, 298 K).

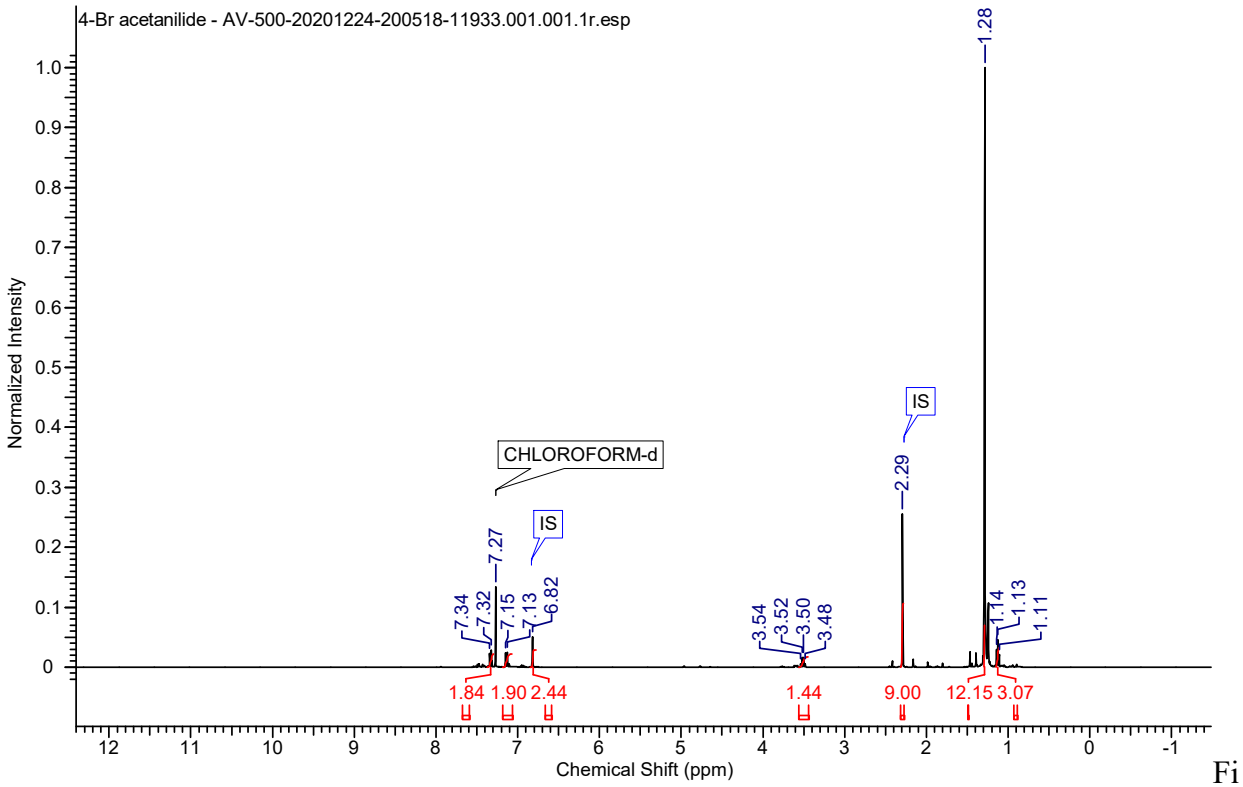

Figure S54. ^{1}H NMR Spectrum of **2b** ($CDCl_3$, 200 MHz, 298 K).

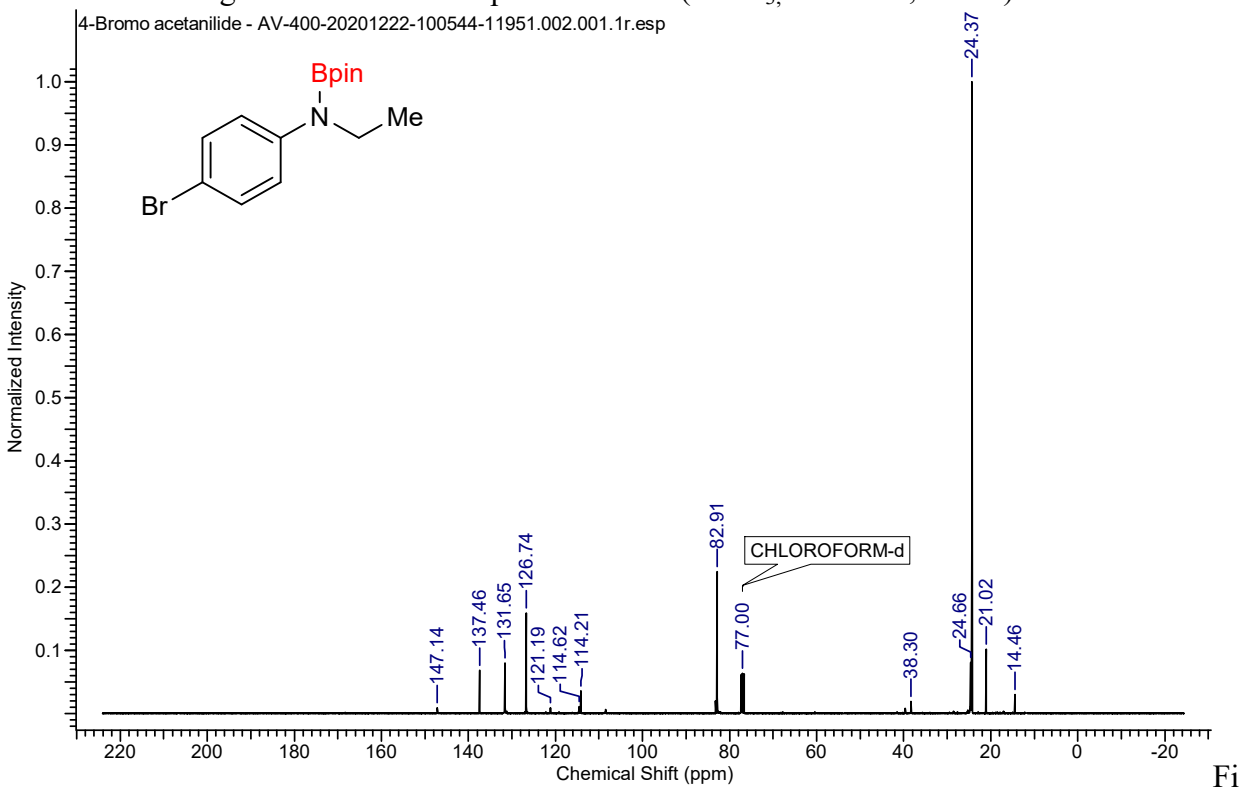

Figure S55. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 100.6 MHz, 298 K).

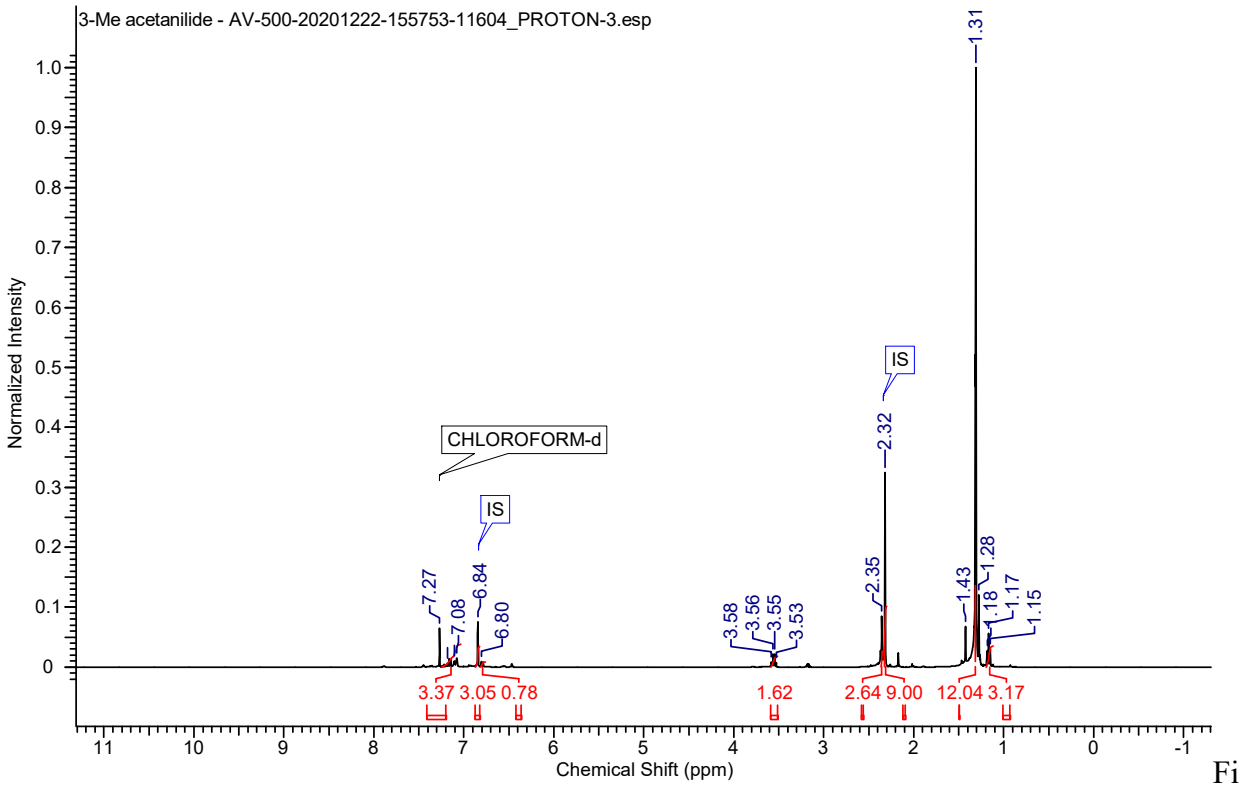

Figure S56. ^{1}H NMR Spectrum of **2c** ($CDCl_3$, 500 MHz, 298 K).

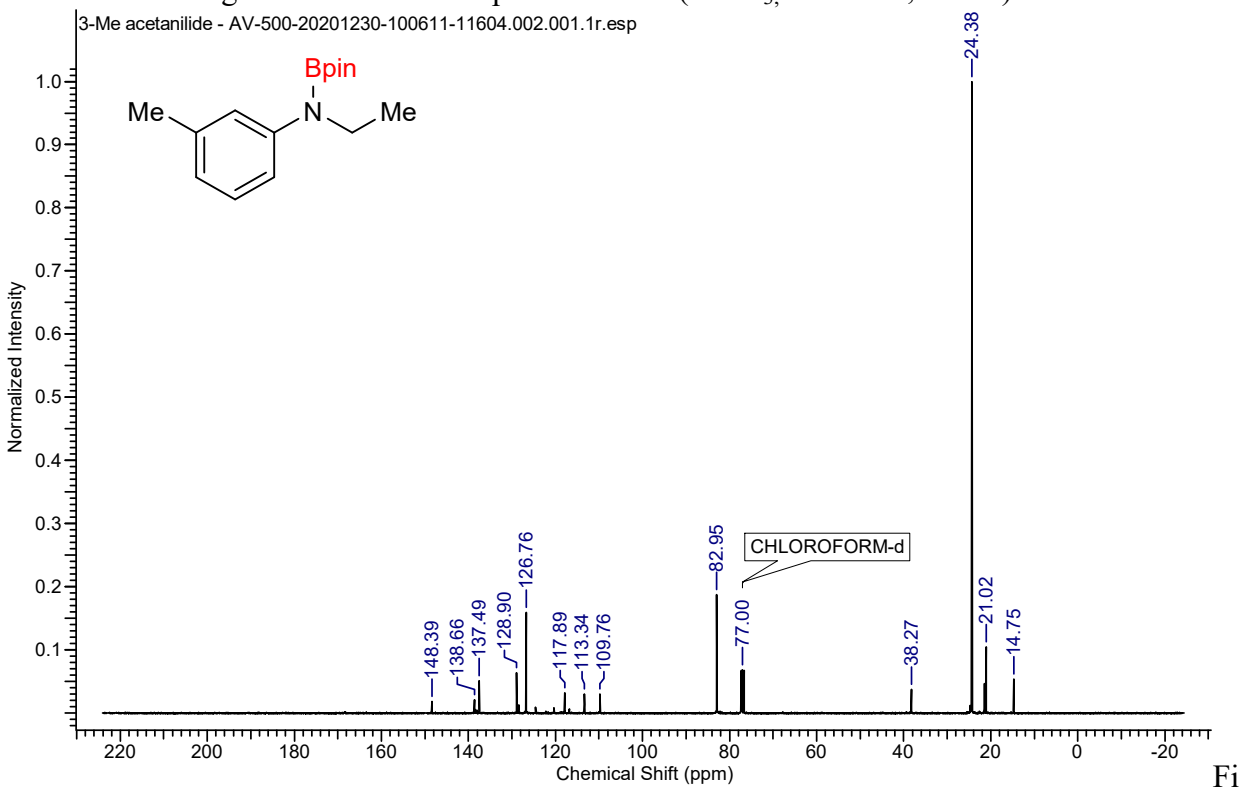

Figure S57. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 100.5 MHz, 298 K).

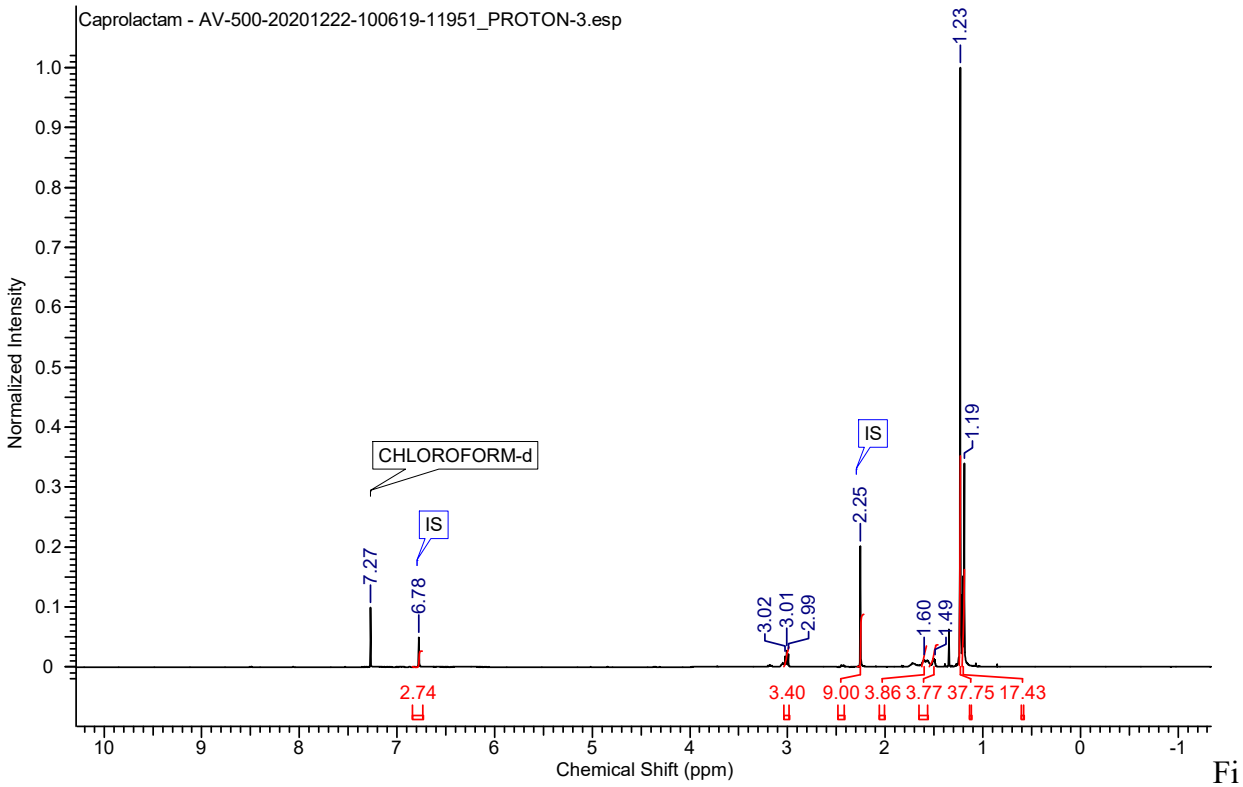

Figure S58. ^{1}H NMR Spectrum of **2d** ($CDCl_3$, 500 MHz, 298 K).

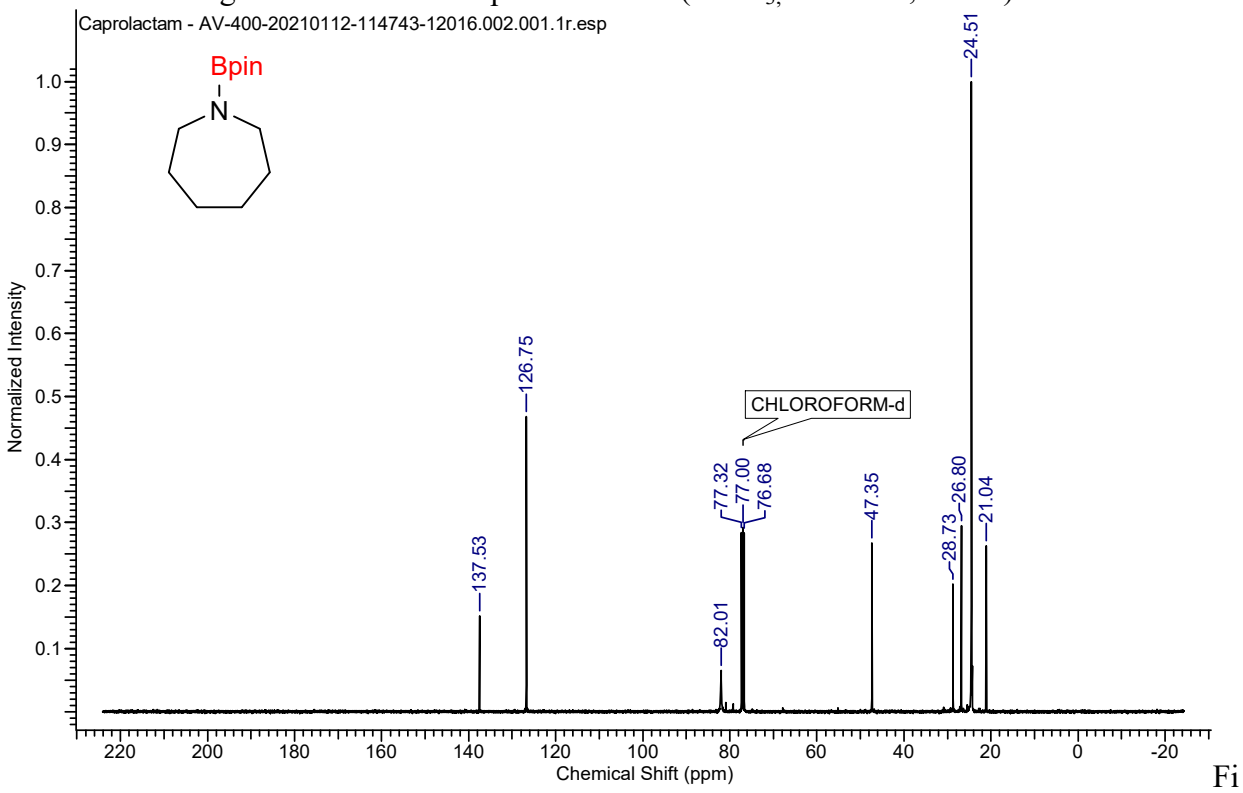

Figure S59. ^{13}C NMR spectrum of **2d** ($CDCl_3$, 100.6 MHz, 298 K).

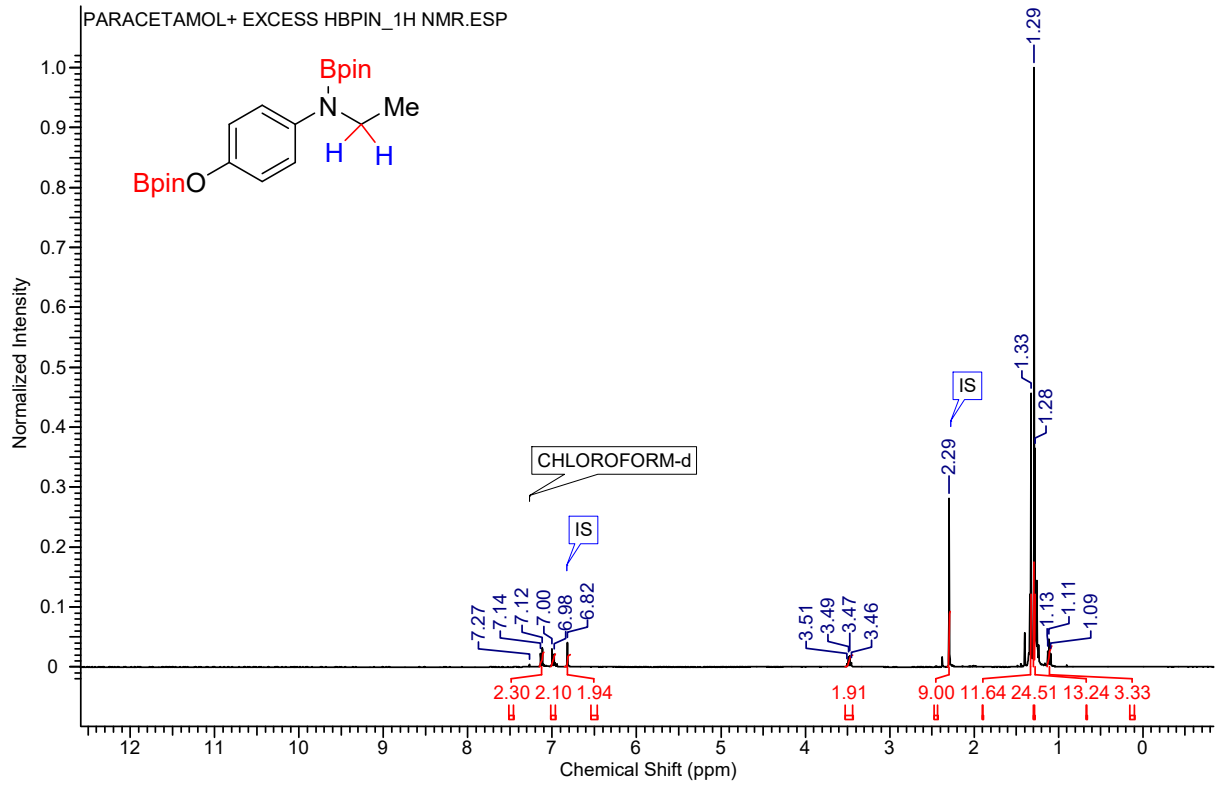

Figure S60. ^{1}H NMR Spectrum of **2e** ($CDCl_3$, 500 MHz, 298 K).

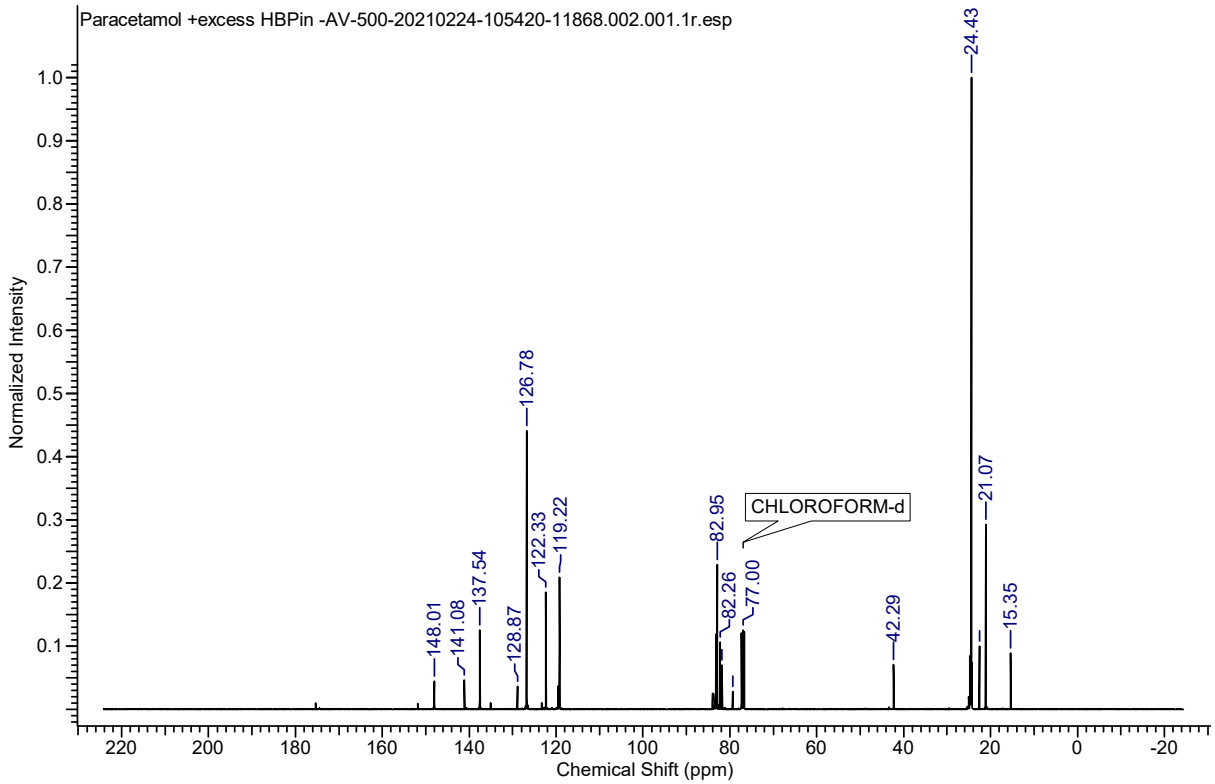

Figure S61. ^{13}C NMR spectrum of **2e** ($CDCl_3$, 100.6 MHz, 298 K).

Kinetic study

Kinetics for hydroboration of amides was studied by performing NMR scale reactions. Benzamide is used as substrate for the kinetic study because it is the simplest compound of aromatic amides. The reaction was monitored by ^{1}H NMR analysis at time interval of 10 min and the reaction was performed at 100 ºC. The kinetic data was obtained by the proton integral of -CH_2 peak relative to CH_3 protons of mesitylene (internal standard).

- **General procedure for the rate determination**

In argon atmosphere, required amount of HBpin and benzamide were taken along with mesitylene. NMR was recorded at room temperature considering it at T= 0 min (no product was observed). Then NMR tube was kept in oil bath, 100 ºC temperature and spectra was recorded at the interval of 10 min up to 1 hour.

- **HBpin rate order assessment**

Varying concentration of HBpin while keeping benzamide concentration constant.

HBpin [M]	Benzamide [M]	Rate (M/min)	R^2
0.635	0.127	$8.06\times 10^{-4}\pm 2.41\times 10^{-5}$	0.99555
0.508	0.127	$7.29\times 10^{-4}\pm 2.61\times 10^{-5}$	0.99360
0.381	0.127	$5.17\times 10^{-4}\pm 1.70\times 10^{-5}$	0.99463

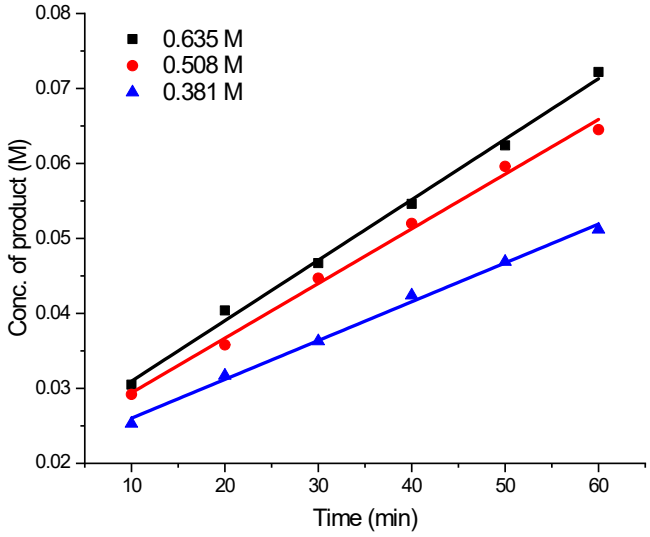

Figure S62. Plot of conc. of product vs. time at different HBpin concentrations.

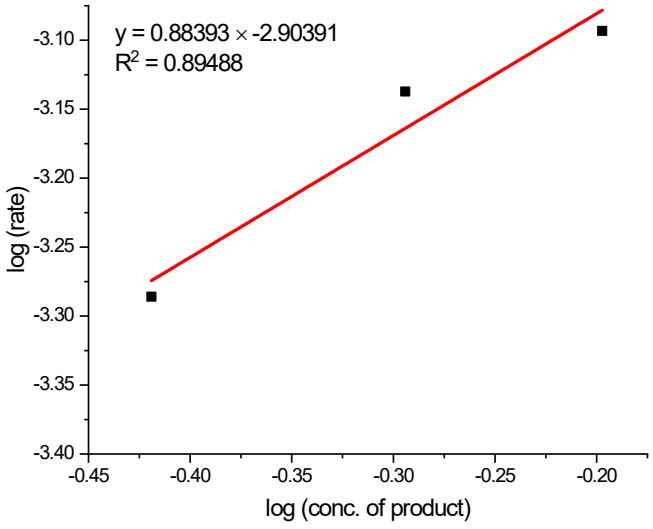

Figure S63. Plot of log (rate) vs. log (conc. of product). This shows first order dependence over HBpin.

➢ **Benzamide rate order assessment**

Varying concentration of HBpin while keeping benzamide concentration constant.

HBpin [M]	Benzamide [M]	Rate (M/min)	R^2
0.635	0.381	$1.85 \times 10^{-4} \pm 1.73 \times 10^{-5}$	0.95804
0.635	0.254	$5.60 \times 10^{-4} \pm 2.50 \times 10^{-5}$	0.99006
0.635	0.063	$4.68 \times 10^{-4} \pm 3.08 \times 10^{-5}$	0.97824

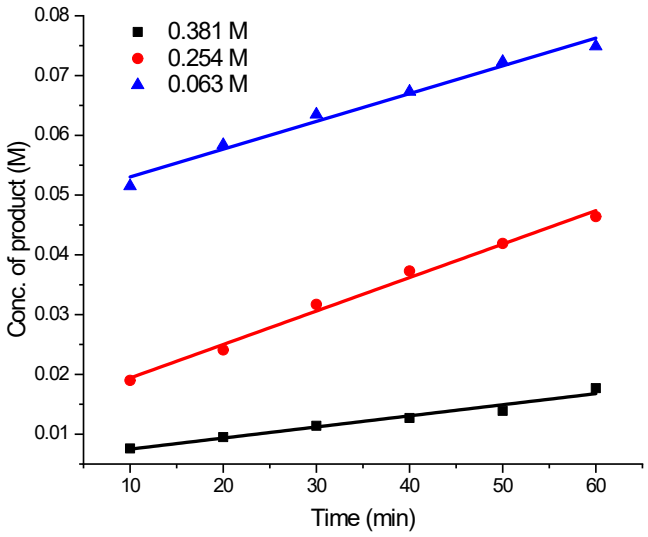

Figure S64. Plot of conc. of product vs. time at different benzamide concentrations. The reaction follows first order dependence over benzamide.

Details of DFT calculations:

The quantum chemical calculations have been performed using density functional theory (DFT), as a tool with the aid of the Turbomole 7.0 suite of programs.[9] The PBE functional,[10] and the TZVP[11] basis set has been employed. The resolution of identity (RI),[12] along with the multipole accelerated resolution of identity (marij)[13] approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. The option "disp" provided in the Turbomole package (DFT-D3) was employed for dispersion-corrected DFT calculations.[14] The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures. Furthermore, intrinsic reaction coordinate (IRC) calculations were carried out with all transition states to further confirm that they were the correct transition state, yielding the correct reactant and product structures.[15]

References:

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PBE/TZVP optimized geometries for all the compounds and transition states

HBpin

B	-0.002940	-0.022707	1.379727
O	-1.256412	-0.097901	1.943236
O	-0.001661	0.004803	0.003578
C	-1.379910	-0.283326	-0.424518
C	-2.222148	0.103121	0.851007
C	-1.684023	0.542131	-1.667273
C	-1.431267	-1.778098	-0.750980
H	-1.208299	-2.387917	0.135810
H	-0.675978	-2.001305	-1.516525
H	-2.417030	-2.070548	-1.138994
H	-1.041854	0.211961	-2.495326
H	-1.500296	1.609691	-1.498585
H	-2.732217	0.408439	-1.973182
C	-3.436256	-0.778575	1.108553
H	-3.947403	-0.445026	2.022164
H	-3.153306	-1.829682	1.241207
H	-4.148906	-0.707921	0.273440
H	-3.392159	1.807092	0.138702
H	-1.754037	2.232777	0.706883
C	-2.620143	1.580999	0.887438
H	-3.021576	1.816207	1.882447
H	0.999625	0.015650	2.030356

Benzamide

C	0.356516	-0.715766	0.220395
C	0.268498	-0.364556	1.575127
C	1.345287	0.247878	2.215627
C	2.516203	0.532016	1.504578
C	2.604010	0.204573	0.148382
C	1.530769	-0.420291	-0.490719
H	-0.660776	-0.578258	2.105859
H	1.270789	0.510327	3.272270
H	3.356410	1.017981	2.004985
H	3.507848	0.442702	-0.415342
H	1.599648	-0.637610	-1.558988
C	-0.845229	-1.369835	-0.406817
O	-1.978075	-1.237213	0.054261
N	-0.604610	-2.112137	-1.539039
H	0.327987	-2.435955	-1.768650
H	-1.392050	-2.626593	-1.920267

TS_1

C	-0.282842	0.141009	1.362687
C	-0.979020	-1.182874	1.648392
C	-2.332095	-1.242089	0.930576
O	-0.139141	-2.258243	1.124186
B	-0.432286	-3.371719	1.931314
N	0.789539	-4.449663	2.127348
C	2.112316	-4.386587	1.602434

O	3.062418	-4.591871	2.347148
O	-1.087369	-3.023922	3.133514
C	-1.080748	-1.560809	3.174658
C	0.151687	-1.122695	3.972983
C	-2.356870	-1.093483	3.862696
C	2.277066	-4.102568	0.146792
H	-2.859584	-2.181313	1.149688
H	-2.157586	-1.190565	-0.152678
H	-2.979612	-0.401863	1.218799
H	-0.253855	0.316897	0.278290
H	0.748252	0.137837	1.735003
H	-0.827677	0.974612	1.830669
H	-2.344616	-1.404621	4.916569
H	-3.247270	-1.525287	3.390228
H	-2.434975	0.003702	3.831432
H	0.171902	-0.033451	4.121985
H	1.079480	-1.426202	3.468059
H	0.123911	-1.605647	4.959123
H	0.822714	-4.754309	3.105266
H	-0.305603	-4.805832	1.517608
H	-1.245520	-4.331504	1.263596
C	3.564277	-3.752487	-0.295179
C	3.801839	-3.500062	-1.644211
C	2.759119	-3.610715	-2.570741
C	1.479201	-3.971535	-2.140394
C	1.236360	-4.210892	-0.787889
H	4.365489	-3.686234	0.442322
H	4.802856	-3.219818	-1.977057
H	2.944505	-3.417267	-3.629290
H	0.664136	-4.062341	-2.860482
H	0.226344	-4.480474	-0.476601

RC

C	-1.005759	1.162060	-1.108986
C	-1.893400	-0.060065	-0.917235
C	-2.378932	-0.589226	-2.268524
O	-1.087764	-1.143456	-0.320285
B	-1.908495	-1.804658	0.562690
N	1.207297	-1.277412	2.180628
C	1.274494	-0.035108	1.616793
O	0.699496	0.939199	2.111552
O	-3.120234	-1.199285	0.782000
C	-3.051655	0.127074	0.138156
C	-2.711134	1.130421	1.241721
C	-4.417304	0.435625	-0.462017
C	2.110496	0.086543	0.373383
H	-3.012480	-1.478919	-2.146041
H	-1.505571	-0.871905	-2.872249
H	-2.946904	0.174629	-2.817804
H	-0.207575	0.929279	-1.827308
H	-0.537296	1.477916	-0.169475

H	-1.595327	1.999716	-1.511033
H	-5.158253	0.532820	0.343432
H	-4.752434	-0.357999	-1.140865
H	-4.388929	1.385832	-1.015210
H	-2.725029	2.159908	0.856804
H	-1.721487	0.941511	1.681055
H	-3.465904	1.049039	2.036389
H	0.566506	-1.416495	2.954803
H	1.644242	-2.087259	1.757893
H	-1.590677	-2.830271	1.094113
C	2.753183	1.310026	0.135302
C	3.508168	1.495129	-1.022430
C	3.610324	0.465958	-1.964599
C	2.952606	-0.747581	-1.743965
C	2.209112	-0.939997	-0.577771
H	2.639250	2.108799	0.870031
H	4.014240	2.446964	-1.195177
H	4.193303	0.613626	-2.875919
H	3.009178	-1.544108	-2.488568
H	1.647247	-1.866423	-0.445564

Int_1

C	-2.041572	1.966144	-1.599950
C	-1.848856	0.722590	-0.980924
C	-1.707453	-0.427345	-1.771157
C	-1.717743	-0.328833	-3.162093
C	-1.904005	0.915003	-3.774926
C	-2.079117	2.059676	-2.991503
C	-1.889347	0.560759	0.508204
O	-2.447415	-0.398442	1.035233
N	-1.312429	1.568435	1.283883
B	-0.230045	2.483898	1.010249
O	0.114280	3.448920	1.941858
C	1.393656	4.008728	1.488121
C	1.425826	5.488008	1.844881
O	0.561345	2.475550	-0.119240
C	1.364582	3.701046	-0.059297
C	0.616062	4.762788	-0.870501
C	2.723695	3.415863	-0.682489
C	2.498102	3.250052	2.227607
H	-0.360891	4.994694	-0.422347
H	0.443991	4.375029	-1.883912
H	1.194603	5.693912	-0.945327
H	2.599892	3.199615	-1.752590
H	3.207446	2.551032	-0.213576
H	3.384882	4.289285	-0.583024
H	1.430962	5.605381	2.937345
H	0.550069	6.016495	1.449859
H	2.334756	5.961659	1.446051
H	3.491771	3.656805	1.993689
H	2.487427	2.181358	1.970976

H	2.329997	3.344136	3.309020
H	-1.571930	1.467562	2.265997
H	-1.591631	-1.392578	-1.275712
H	-1.588846	-1.225193	-3.771567
H	-1.923188	0.990309	-4.864005
H	-2.245371	3.028517	-3.466945
H	-2.185037	2.859005	-0.989572

TS_2

C	-3.123723	2.747780	6.956289
C	-3.986080	1.641515	6.957966
C	-5.142263	1.657864	6.185118
C	-5.450362	2.781815	5.408388
C	-4.586246	3.879345	5.395316
C	-3.416724	3.861026	6.157801
C	-1.846852	2.729524	7.723397
N	-1.852667	2.316029	9.034311
B	-2.908176	1.993113	9.978315
O	-2.576477	1.376975	11.169521
C	-3.772691	1.475673	12.020097
C	-3.859513	0.221833	12.878182
O	-0.863523	3.599563	7.399738
B	-0.172039	2.588222	6.545532
O	1.113482	2.202308	7.055064
C	1.900505	1.817598	5.899605
C	3.372634	2.062367	6.217490
O	-0.098596	2.823614	5.134233
C	1.307128	2.748142	4.773321
C	1.879148	4.172797	4.834467
C	1.429748	2.194638	3.358031
C	1.662762	0.329285	5.614568
O	-4.241378	2.302731	9.842507
C	-4.927639	1.631952	10.956042
C	-5.436576	0.292750	10.416196
C	-6.091501	2.508426	11.395939
C	-3.589913	2.717973	12.894632
H	1.830760	4.570827	5.857879
H	1.274466	4.821736	4.186067
H	2.922665	4.209006	4.488064
H	0.990778	2.905224	2.643172
H	0.898664	1.240367	3.256653
H	2.485709	2.044876	3.085785
H	3.702095	1.370515	7.006027
H	3.537446	3.086665	6.573016
H	3.997164	1.889791	5.328156
H	2.300800	-0.038221	4.797664
H	0.611928	0.143505	5.349961
H	1.895651	-0.244655	6.522372
H	-1.105333	1.603169	6.822370
H	-0.908259	2.323433	9.425624
H	-3.527459	3.629818	12.284429

H	-4.416139	2.830955	13.610509
H	-2.653190	2.619026	13.459529
H	-3.834656	-0.688486	12.267505
H	-4.786215	0.224817	13.470536
H	-3.009208	0.189514	13.573297
H	-5.761202	3.525863	11.636045
H	-6.831168	2.573133	10.585874
H	-6.033581	-0.242938	11.167546
H	-6.585594	2.078286	12.279258
H	-4.605183	-0.355557	10.104284
H	-6.070414	0.484493	9.539849
H	-5.802625	0.788389	6.176992
H	-4.815132	4.749079	4.776872
H	-3.727546	0.753665	7.537310
H	-2.711488	4.692412	6.134257
H	-6.355956	2.790937	4.798588

Int_2

C	-0.535254	-1.547233	-2.211336
C	-1.468631	-2.592770	-2.232454
C	-2.346344	-2.737245	-3.306677
C	-2.297974	-1.836856	-4.376122
C	-1.361384	-0.801194	-4.362630
C	-0.479722	-0.657755	-3.287137
C	0.394479	-1.427471	-1.013681
N	-0.322833	-1.368448	0.231360
B	-1.489763	-0.595436	0.506754
O	-2.100449	-0.624797	1.758503
C	-3.121113	0.424190	1.730449
C	-4.304188	-0.025732	2.576726
O	1.266258	-0.279570	-1.214055
B	2.300409	-0.102120	-0.340513
O	2.577363	-0.946818	0.733177
C	3.884108	-0.531274	1.250627
C	3.892396	-0.728043	2.760360
O	3.181824	0.958982	-0.458039
C	3.965867	0.972084	0.776880
C	3.266949	1.937532	1.739238
C	5.371383	1.462323	0.455366
C	4.932592	-1.426346	0.584645
O	-2.132722	0.222468	-0.408434
C	-3.423813	0.557264	0.188984
C	-4.431541	-0.479968	-0.316652
C	-3.819261	1.954328	-0.270448
C	-2.484542	1.686310	2.320732
H	2.255151	1.586766	1.988578
H	3.176457	2.917379	1.251306
H	3.835179	2.062992	2.671570
H	5.329719	2.510963	0.130476
H	5.827156	0.874710	-0.350560
H	6.015700	1.404327	1.344934

H	3.821497	-1.799435	2.994657
H	3.047138	-0.217111	3.237071
H	4.827531	-0.345284	3.195462
H	5.941128	-1.224446	0.972282
H	4.941146	-1.284346	-0.505371
H	4.685484	-2.476813	0.791609
H	1.042654	-2.320510	-0.977799
H	0.209312	-1.712113	1.026349
H	-1.635710	2.023151	1.707956
H	-3.209916	2.508479	2.398002
H	-2.111242	1.456060	3.327963
H	-4.673606	-1.007435	2.257437
H	-5.128112	0.700587	2.509601
H	-4.000040	-0.100593	3.630190
H	-3.029042	2.684510	-0.058630
H	-3.994055	1.946493	-1.355185
H	-5.453901	-0.249150	0.015424
H	-4.746344	2.279560	0.224737
H	-4.167774	-1.489622	0.029053
H	-4.408987	-0.484105	-1.414958
H	-3.072928	-3.552634	-3.308264
H	-1.317100	-0.094164	-5.193887
H	-1.519112	-3.282876	-1.386878
H	0.244941	0.155392	-3.264991
H	-2.986181	-1.945733	-5.217007

TS_3

C	-0.257642	-1.372297	-2.170406
C	-1.510142	-0.745224	-2.274756
C	-2.079956	-0.538872	-3.531065
C	-1.423697	-0.978809	-4.686403
C	-0.191450	-1.630621	-4.583576
C	0.390559	-1.821092	-3.329847
C	0.422572	-1.547008	-0.851251
N	-0.357026	-1.503517	0.315392
B	-0.125531	-0.048272	0.728038
O	-0.940209	1.017158	0.280501
C	-1.286724	1.790452	1.458208
C	-1.418542	3.254527	1.055554
O	1.239272	-0.125213	-0.492572
B	1.756732	0.832840	-1.344699
O	1.684881	2.198647	-1.105914
C	2.559988	2.830607	-2.102118
C	1.951348	4.168083	-2.504253
O	2.430303	0.499183	-2.502846
C	2.588266	1.749254	-3.249784
C	1.389653	1.854052	-4.196053
C	3.890987	1.676251	-4.032111
C	3.922855	3.039679	-1.437629
O	0.320093	0.151116	2.039338
C	-0.088583	1.487302	2.445250

C	1.102735	2.431672	2.255710
C	-0.479717	1.427403	3.917994
C	-2.628902	1.250989	1.969732
H	0.443861	1.900812	-3.637787
H	1.357582	0.957878	-4.829709
H	1.464095	2.739323	-4.843016
H	3.819098	0.885495	-4.792063
H	4.740085	1.445261	-3.377521
H	4.088596	2.627730	-4.547548
H	1.968849	4.855599	-1.646983
H	0.910538	4.053377	-2.829336
H	2.530654	4.624505	-3.320348
H	4.375607	2.081014	-1.147875
H	3.786440	3.640688	-0.528119
H	4.617995	3.570600	-2.103192
H	1.218861	-2.301983	-0.887383
H	0.042323	-2.102941	1.040146
H	-2.544484	0.192678	2.253607
H	-3.001818	1.821081	2.833046
H	-3.367084	1.326744	1.159029
H	-0.519065	3.596724	0.529511
H	-1.586349	3.890583	1.937789
H	-2.277560	3.374819	0.379817
H	-1.228075	0.647293	4.103058
H	0.408941	1.197097	4.522719
H	1.389433	2.506982	1.199587
H	-0.882904	2.393287	4.257242
H	1.957325	2.032527	2.820063
H	0.878259	3.439215	2.636389
H	-3.046994	-0.037984	-3.609691
H	0.319825	-1.983394	-5.481568
H	-2.011109	-0.403288	-1.369018
H	1.368668	-2.300888	-3.247378
H	-1.876495	-0.819294	-5.667000

Int_3

C	0.372349	0.182340	-2.628593
C	-0.553722	-0.771229	-2.174999
C	-1.137099	-1.655859	-3.100601
C	-0.795779	-1.583408	-4.448201
C	0.130845	-0.629961	-4.892320
C	0.714461	0.253368	-3.980529
C	-0.892275	-0.829668	-0.742429
N	-1.714761	-1.689925	-0.264192
H	-0.376106	-0.073643	-0.118503
H	-1.814688	-1.568578	0.752123
H	-1.250237	-2.273346	-5.162206
H	1.436685	0.997004	-4.322671
H	-1.855171	-2.391705	-2.734414
H	0.827840	0.871576	-1.911855
H	0.396546	-0.577775	-5.950127

Bpin_o_Bpin

C	-3.392037	12.545958	-3.656193
C	-2.036295	12.952081	-3.094497
C	-1.990224	14.460392	-2.835550
O	-1.849539	12.295254	-1.798507
B	-0.494229	12.024429	-1.699716
O	0.107787	11.561737	-0.557625
O	0.208181	12.209785	-2.874634
C	-0.795318	12.427549	-3.918738
C	-1.048073	11.070558	-4.581442
C	-0.236021	13.419832	-4.928968
H	-1.012913	14.766052	-2.435921
H	-2.755063	14.713759	-2.089214
H	-2.193303	15.033514	-3.751166
H	-4.191922	12.946238	-3.018015
H	-3.500723	11.455429	-3.694878
H	-3.528854	12.951412	-4.669777
H	0.627774	12.975694	-5.442592
H	0.097226	14.344257	-4.441950
H	-0.993211	13.671497	-5.685922
H	-1.741833	11.158420	-5.429547
H	-1.459940	10.347495	-3.862905
H	-0.093169	10.674987	-4.952325
B	-0.208773	11.884352	0.737454
O	-0.595225	13.152145	1.141173
O	-0.115326	10.965245	1.763720
C	-0.260303	11.725806	3.006829
C	-1.039809	13.014694	2.529810
C	-0.686413	14.289414	3.283300
H	-0.934303	14.189312	4.349986
H	-1.264107	15.131202	2.876732
H	0.379264	14.529051	3.189565
C	-2.557829	12.817240	2.489043
H	-2.824993	11.899386	1.945978
H	-2.987225	12.767741	3.499827
H	-3.009091	13.666928	1.959406
C	-1.008109	10.865404	4.016138
H	-1.961571	10.507888	3.609632
H	-1.205342	11.432044	4.938340
H	-0.398348	9.989260	4.276786
H	1.135958	12.547674	4.477210
C	1.153972	12.033674	3.505892
H	1.701572	12.660709	2.787951
H	1.702106	11.088716	3.620773

TS_4

C	0.837319	1.131194	-2.873286
C	-0.224541	2.042128	-2.702784
C	-0.579644	2.900791	-3.740327
C	0.116135	2.876312	-4.955667
C	1.168790	1.974046	-5.137904

C	1.520938	1.105034	-4.106607
C	1.307130	0.208672	-1.833132
N	0.988373	0.119823	-0.590112
B	-0.149453	0.556134	0.369874
O	-1.438297	0.922767	-0.069080
C	-2.074302	1.573687	1.073899
C	-3.094262	2.576885	0.549037
O	0.240914	1.284092	1.513349
C	-0.838776	2.211090	1.818600
C	-0.436435	3.575553	1.244846
C	-0.991173	2.302998	3.333331
C	-2.775899	0.488282	1.898621
H	2.087794	-0.487873	-2.181187
H	0.728385	-0.858339	0.173771
H	-2.052753	-0.238202	2.294120
H	-3.340287	0.920477	2.737215
H	-3.477120	-0.051551	1.247533
H	-2.639893	3.285015	-0.155725
H	-3.540000	3.145767	1.378181
H	-3.901300	2.044242	0.026633
H	-1.131720	1.312040	3.781369
H	-0.084524	2.746897	3.767545
H	-0.334186	3.531887	0.151167
H	-1.847119	2.940343	3.602593
H	0.539615	3.856946	1.662804
H	-1.164648	4.358844	1.501033
H	-1.409369	3.596943	-3.602470
H	1.710374	1.945771	-6.085064
H	-0.784404	2.039732	-1.766904
H	2.341357	0.396312	-4.247746
H	-0.165512	3.557226	-5.761273
H	-0.155139	-0.952006	0.793707

Int_4

C	0.635679	-0.170026	-2.549489
C	-0.689569	0.069590	-2.146731
C	-1.615524	0.541654	-3.094100
C	-1.215806	0.786061	-4.405909
C	0.112514	0.564140	-4.791921
C	1.038585	0.084263	-3.861216
C	-1.058995	-0.193419	-0.736697
N	-2.113064	0.150983	-0.121823
B	-3.310512	0.870750	-0.391387
O	-3.496541	2.188267	0.012579
C	-4.807784	2.595041	-0.491225
C	-5.439319	3.542597	0.521034
O	-4.449443	0.297916	-0.954040
C	-5.552104	1.214968	-0.657242
C	-6.201320	0.726458	0.640955
C	-6.549367	1.158562	-1.806513
C	-4.576800	3.317061	-1.822221

H	-0.287564	-0.754499	-0.174276
H	-5.491896	0.768078	1.479605
H	-7.087336	1.323248	0.900514
H	-6.511546	-0.319057	0.509467
H	-6.064591	1.356896	-2.770130
H	-7.354459	1.893577	-1.658141
H	-7.003671	0.159201	-1.852358
H	-5.473356	3.095597	1.521715
H	-4.847131	4.466103	0.580121
H	-4.130557	2.645738	-2.569581
H	-6.462278	3.810318	0.217143
H	-3.879417	4.149180	-1.656261
H	-5.513066	3.722165	-2.231212
H	-1.942748	1.144674	-5.137501
H	2.072794	-0.096159	-4.160090
H	-2.657086	0.688116	-2.801144
H	1.354181	-0.549560	-1.817921
H	0.421684	0.757833	-5.820792

TS_5

C	4.432458	1.235133	2.998441
C	3.725174	0.445848	2.081999
C	3.411237	0.948357	0.824241
C	3.795048	2.259530	0.469868
C	4.536336	3.033042	1.390252
C	4.840566	2.529069	2.650843
C	3.500777	2.817465	-0.833305
N	2.523753	2.399127	-1.680193
B	1.208441	1.888066	-1.406669
O	0.352753	1.533981	-2.434744
C	-0.784532	0.862199	-1.809418
C	-0.482896	-0.639009	-1.840372
B	3.345846	2.309236	-2.993807
O	3.127732	3.290662	-4.025599
C	3.026922	2.573439	-5.280546
C	1.532938	2.455832	-5.615023
O	3.306642	0.979321	-3.563017
C	3.680455	1.171915	-4.945332
C	3.114351	0.003279	-5.747827
C	5.211639	1.191063	-5.058407
O	0.654897	1.734595	-0.141465
C	-0.771112	1.463913	-0.352841
C	-1.248362	0.515853	0.738532
C	-1.497161	2.808148	-0.255488
C	-2.035703	1.173247	-2.620468
C	3.749204	3.364411	-6.367352
H	3.992837	3.767134	-1.059815
H	-2.295588	0.224807	0.568363
H	-1.187444	1.016464	1.714901
H	-0.633757	-0.391155	0.779377
H	-1.268404	3.265612	0.717059

H	-1.163032	3.496766	-1.044498
H	-2.586137	2.684405	-0.334587
H	-2.178181	2.253867	-2.740892
H	-2.928109	0.748679	-2.137095
H	-1.944109	0.728784	-3.620979
H	-1.326016	-1.229549	-1.454641
H	0.414131	-0.876247	-1.250639
H	-0.289119	-0.938808	-2.878951
H	3.265351	0.158546	-6.826910
H	3.627173	-0.925297	-5.458821
H	2.042191	-0.122994	-5.552969
H	1.007947	1.877738	-4.843035
H	5.607427	0.263352	-4.621702
H	5.542444	1.252245	-6.105544
H	5.640279	2.037869	-4.504624
H	4.783539	3.587676	-6.077913
H	3.758869	2.808598	-7.317779
H	3.229558	4.318846	-6.535728
H	1.371511	1.988357	-6.598462
H	1.100209	3.466120	-5.636450
H	4.551305	2.494161	-2.438570
H	5.401398	3.136337	3.363245
H	2.885548	0.332649	0.095118
H	4.679997	0.834389	3.983444
H	3.429283	-0.569236	2.352204
H	4.856134	4.038270	1.105052

Prod

C	3.468873	-0.579069	3.309841
C	2.754202	-1.255724	2.318783
C	1.900960	-0.555085	1.460212
C	1.748346	0.830860	1.578441
C	2.468131	1.501441	2.578904
C	3.322501	0.806419	3.436453
C	0.845818	1.632349	0.652934
N	-0.090075	0.821338	-0.142467
B	-1.285309	0.367953	0.518307
O	-2.236502	-0.471791	-0.037841
C	-3.097817	-0.891596	1.066582
C	-2.528335	-2.212589	1.595207
B	0.299832	0.454362	-1.475229
O	1.524291	0.844433	-2.010748
C	1.481916	0.496361	-3.430159
C	1.024079	1.747245	-4.185814
O	-0.467590	-0.301699	-2.346769
C	0.413064	-0.661532	-3.456035
C	-0.418123	-0.738813	-4.729461
C	1.011839	-2.032082	-3.122749
O	-1.577232	0.752425	1.822492
C	-2.939474	0.294233	2.091126
C	-3.035514	-0.106724	3.557119

C	-3.874900	1.469227	1.791741
C	-4.508883	-1.094517	0.531247
C	2.881180	0.087583	-3.871281
H	0.272823	2.350299	1.258331
H	-4.021593	-0.542590	3.776506
H	-2.904871	0.780730	4.191919
H	-2.258925	-0.832880	3.825045
H	-3.566761	2.331175	2.399286
H	-3.819952	1.758614	0.732692
H	-4.918997	1.227567	2.036235
H	-4.871924	-0.200923	0.009529
H	-5.204305	-1.335813	1.348742
H	-4.514806	-1.930769	-0.181810
H	-3.161746	-2.641128	2.384910
H	-1.513072	-2.074183	1.994655
H	-2.473221	-2.928806	0.764020
H	0.224132	-0.931300	-5.601576
H	-1.141149	-1.562323	-4.647044
H	-0.978238	0.188462	-4.899993
H	0.010200	2.043134	-3.882263
H	0.191415	-2.739458	-2.940859
H	1.629519	-2.416756	-3.946849
H	1.629048	-1.984005	-2.214149
H	3.288110	-0.704816	-3.231458
H	2.871219	-0.266937	-4.912510
H	3.555281	0.953429	-3.810906
H	1.033179	1.588603	-5.273681
H	1.708182	2.573894	-3.950176
H	1.475305	2.213496	-0.037664
H	3.871352	1.346354	4.211045
H	1.339495	-1.092000	0.693365
H	4.133153	-1.126233	3.981480
H	2.858654	-2.337872	2.212293
H	2.351923	2.583556	2.689782

H_2

H	0.000000	0.000000	0.128127
H	0.000000	0.000000	0.879873