Electronic Supplementary Material (ESI) for Dalton Transactions.

Diversity of Transformation of Heteroallenes on Acenaphthene-1,2-diimine Aluminum Oxide

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Table 1S. Crystal data and structure refinement details for compounds **2-7**.

	2	**3**	**4**	**5**	**6**	**7**
Empirical Formula	$C_{94}H_{100}Al_2N_5O_3$	$C_{86}H_{99}Al_2N_5O_3$	$C_{99.38}H_{134.50}Al_2N_6O_2$	$C_{90}H_{117}Al_2BN_4O_7$	$C_{106}H_{128}Al_2BN_5O_5$	$C_{84}H_{88}Al_2B_2N_4O_7$
M	1401.74	1304.66	1499.08	1431.64	1616.90	1341.16
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$Pna2_1$	*P-1*	*P-1*	*Cm*	$P2_1/n$
a/Å	23.6752(2)	28.4173(15)	12.4538(2)	12.4182(2)	14.8161(4)	12.8530(12)
b/Å	13.4747(1)	12.7221(7)	18.3729(3)	12.9986(3)	21.5593(4)	22.1044(18)
c/Å	13.4747(1)	20.6197(10)	21.5379(4)	14.7000(3)	14.4379(4)	13.1216(10)
α/deg	90	90	81.328(2)	66.956(2)	90	90
β/deg	97.428(1)	90	75.143(2)	69.651(2)	92.943(2)	92.077(7)
γ/deg	90	90	73.658(2)	88.084(2)	90	90
V/Å^3	7920.62(13)	7454.6(7)	4554.49(15)	2032.70(8)	4605.7(2)	3725.5(5)
Z	4	4	2	1	2	2
d_{calc}/Mg m^{-3}	1.175	1.162	1.093	1.170	1.166	1.196
μ(Mo Kα)/mm^{-1}	0.091	0.091	0.082	0.092	0.088	0.097
F(000)	2996	2800	1630	772	1740	1424
Crystal Size/mm	0.58 × 0.31 × 0.29	0.28 × 0.23 × 0.18	0.55 × 0.38 × 0.30	0.63 × 0.31 × 0.20	0.62 × 0.47 × 0.23	0.60 × 0.23 × 0.10
θ range/deg	2.228–30.508	2.365–25.025	2.191–28.000	2.249–29.129	2.232–26.733	2.179–26.022
Limiting indices	–13 ≤ h ≤ 33 –19 ≤ k ≤ 19 –35 ≤ l ≤ 35	-33 ≤ h ≤ 32 -15 ≤ k ≤ 15 -24 ≤ l ≤ 24	-16 ≤ h ≤ 16 -24 ≤ k ≤ 24 -28 ≤ l ≤ 28	-17 ≤ h ≤ 17 -17 ≤ k ≤ 17 -20 ≤ l ≤ 20	–18 ≤ h ≤ 18 –27 ≤ k ≤ 27 –18 ≤ l ≤ 17	-15 ≤ h ≤ 15 -27 ≤ k ≤ 27 -16 ≤ l ≤ 16
Reflections Collected/ Unique	156778 / 24148	72003 / 13075	54832 / 7556	37428 / 10903	30266 / 9633	84321 / 7335
R_{int}	0.0581	0.1449	0.0464	0.0414	0.0306	0.0972
Data/Restraints/ Parameters	24148 / 109 / 984	13075 / 3 / 882	21964 / 496 / 1338	10903 / 200 / 582	9633 / 213 / 609	7335 / 253 / 460
S	1.017	1.044	1.063	1.051	1.064	1.015
R_1 / wR_2 (I>2σ(I))	0.0548 / 0.1270	0.0735 / 0.1384	0.0899 / 0.2647	0.0859 / 0.2115	0.0733 / 0.2030	0.0605 / 0.1284
R_1 / wR_2 (all data)	0.0936 / 0.1473	0.1217 / 0.1622	0.1448 / 0.2969	0.1252/ 0.2351	0.0843 / 0.2165	0.1044 / 0.1512
Larg. Diff. Peak and Hole/*e* Å^{-3}	0.629 / -0.371	0.291 / -0.280	0.901 / -0.633	0.941 / -0.684	0.779 / -0.441	0.848 / -0.544

Table 2S. Selected bond lengths [Å] and angles [°] for complexes **2-7**.

Bond	**2**	**Bond**	**3**
Al(1)–N(1)	1.9069(13)	Al(1)–N(1)	1.915(5)
Al(1)–N(2)	1.8898(13)	Al(1)–N(2)	1.892(5)
N(1)–C(1)	1.3389(18)	N(1)–C(1)	1.346(8)
N(2)–C(2)	1.3395(18)	N(2)–C(2)	1.341(8)
C(1)–C(2)	1.4360(19)	C(1)–C(2)	1.430(8)
Al(2)–N(3)	1.9099(13)	Al(2)–N(3)	1.893(5)
Al(2)–N(4)	1.8916(13)	Al(2)–N(4)	1.915(5)
N(3)–C(37)	1.3367(18)	N(3)–C(37)	1.350(7)
N(4)–C(38)	1.3391(19)	N(4)–C(38)	1.349(8)
C(37)–C(38)	1.435(2)	C(37)–C(38)	1.419(8)
Al(1)–O(1)	1.6924(11)	Al(1)–O(1)	1.692(4)
Al(1)–O(3)	1.7571(12)	Al(1)–O(2)	1.747(4)
Al(2)–O(1)	1.6922(12)	Al(2)–O(1)	1.709(4)
Al(2)–O(2)	1.7622(12)	Al(2)–O(3)	1.748(4)
O(2)–C(73)	1.3398(19)	O(2)–C(73)	1.343(7)
O(3)–C(73)	1.3180(19)	O(3)–C(73)	1.354(7)
N(5)–C(73)	1.282(2)	N(5)–C(73)	1.271(8)
Angle		**Angle**	
O(1)–Al(1)–O(3)	109.26(6)	O(1)–Al(1)–O(2)	109.3(2)
N(2)–Al(1)–N(1)	88.73(5)	N(2)–Al(1)–N(1)	87.9(2)
O(1)–Al(2)–O(2)	109.37(6)	O(1)–Al(2)–O(3)	109.7(2)
N(4)–Al(2)–N(3)	88.50(5)	N(4)–Al(2)–N(3)	88.8(2)
Al(2)–O(1)–Al(1)	117.93(7)	Al(2)–O(1)–Al(1)	118.3(2)
O(3)–C(73)–O(2)	115.94(14)	O(3)–C(73)–O(2)	115.8(5)

Bond	**4**	**Bond**	**5**
Al(1)–N(1)	1.914(2)	Al(1)–N(1)	1.928(2)
Al(1)–N(2)	1.930(2)	Al(1)–N(2)	1.932(2)
N(1)–C(1)	1.339(3)	N(1)–C(1)	1.333(3)
N(2)–C(2)	1.341(3)	N(2)–C(2)	1.337(3)
C(1)–C(2)	1.427(4)	C(1)–C(2)	1.434(4)
Al(2)–N(3)	1.919(2)	Al(1)–O(1)	1.6832(8)
Al(2)–N(4)	1.930(2)	Al(1)–H(1)	1.541(3)
N(3)–C(37)	1.341(4)	Al(1)–O(2)	1.670(4)
N(4)–C(38)	1.336(3)		
C(37)–C(38)	1.443(4)		

Al(1)–O(1)	1.6823(19)
Al(1)–O(2)	1.579(4)
Al(2)–N(5)	2.060(5)
Al(2)–O(1)	1.691(2)
O(2)–C(73)	1.343(6)
N(5)–C(73)	1.413(6)
N(6)–C(73)	1.280(6)

Angle		**Angle**	
O(1)–Al(1)–O(2)	111.76(17)	O(1)–Al(1)–O(2)	115.4(3)
N(2)–Al(1)–N(1)	87.45(10)	N(2)–Al(1)–N(1)	86.83(9)
O(1)–Al(2)–N(5)	108.01(15)	Al(1')-O(1)-Al(1)	180.0
N(4)–Al(2)–N(3)	87.68(10)	O(1)–Al(1)–H(1)	111(5)
Al(2)–O(1)–Al(1)	117.34(11)		
N(5)–C(73)–O(2)	116.3(4)		

Bond	**6**	**Bond**	**7**
Al(1)–N(1)	1.921(4)	Al(1)–N(1)	1.921(2)
N(1)–C(1)	1.338(6)	Al(1)–N(2)	1.916(2)
C(1)–C(1)'	1.429(8)	N(1)–C(1)	1.339(3)
Al(2)–N(2)	1.940(4)	N(2)–C(2)	1.338(3)
N(2)–C(20)	1.338(6)	C(1)–C(2)	1.426(4)
C(20)–C(20)'	1.449(8)	Al(1)–O(1)	1.6783(7)
Al(1)–O(1)	1.748(6)	Al(1)–O(2)	1.7324(18)
Al(1)–O(3)	1.683(6)	O(2)–B(1)	1.309(4)
Al(2)–O(2)	1.701(6)		
Al(2)–O(3)	1.683(6)		
O(1)–C(39)	1.282(10)		
N(3)–C(39)	1.246(11)		
O(2)–B(1)	1.396(10))		

Angle		**Angle**	
O(1)–Al(1)–O(3)	113.3(3)	O(1)–Al(1)–O(2)	114.45(7)
N(1)–Al(1)–N(1)'	87.0(2)	N(1)–Al(1)–N(2)	87.11(9)
O(2)–Al(2)–O(3)	114.6(3)	Al(1)–O(1)–Al(1')	180.00(3)
N(2)–Al(2)–N(2)'	86.7(2)		
Al(2)–O(3)–Al(1)	179.9(4)		

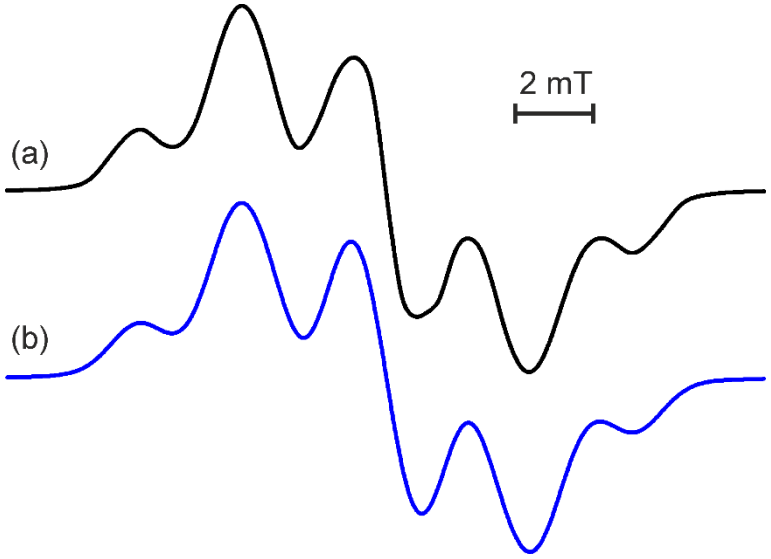


Figure S1.ESR spectrum of compound **2** (2-MeTHF, 130 K): (a) experimental; (b) simulated (g = 2.0068, D = 6.36 mT, E = 0.48 mT).

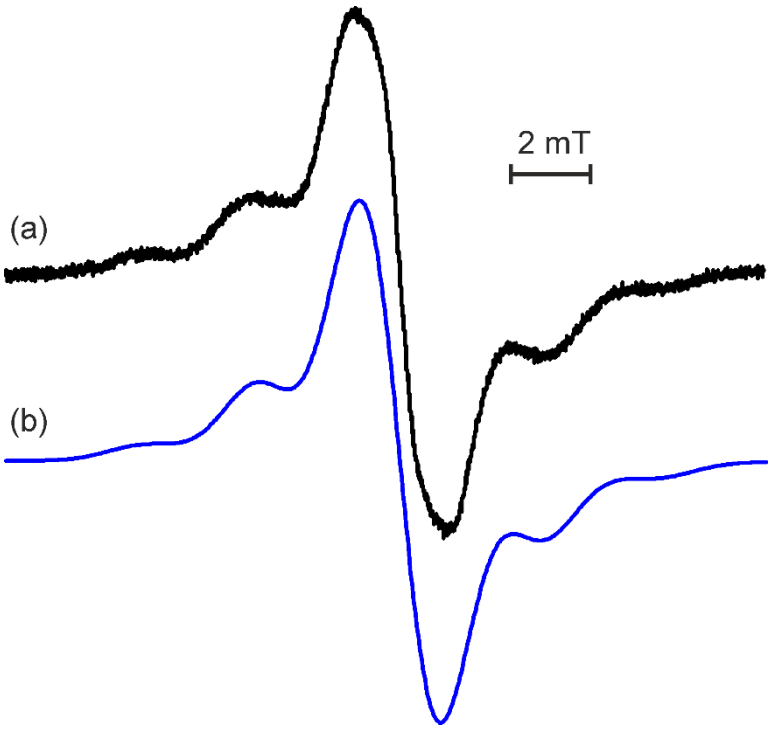


Figure S2. ESR spectrum of compound **3** (toluene, 150 K): (a) experimental; (b) simulated (g = 2.0054, D = 6.53 mT, E = 0 mT).

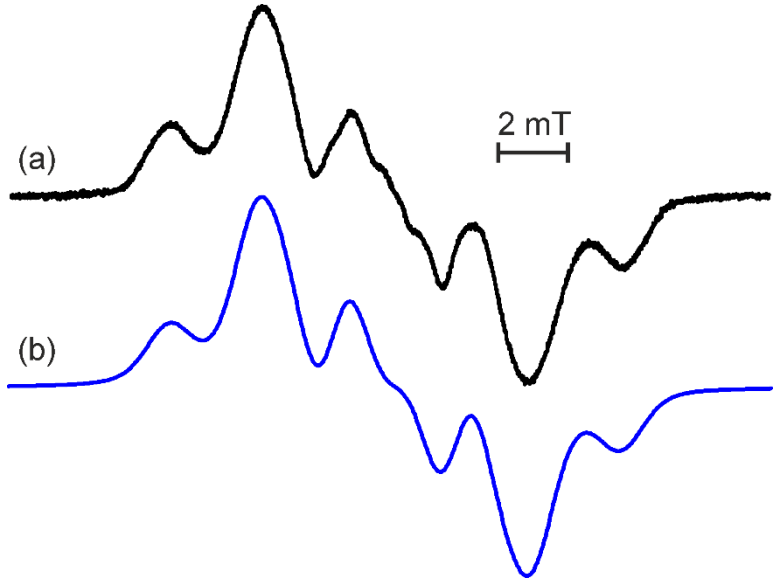


Figure S3. ESR spectrum of compound **4** (2-MeTHF, 130 K): (a) experimental; (b) simulated (g = 2.0047, D = 6.56 mT, E = 0.49 mT).

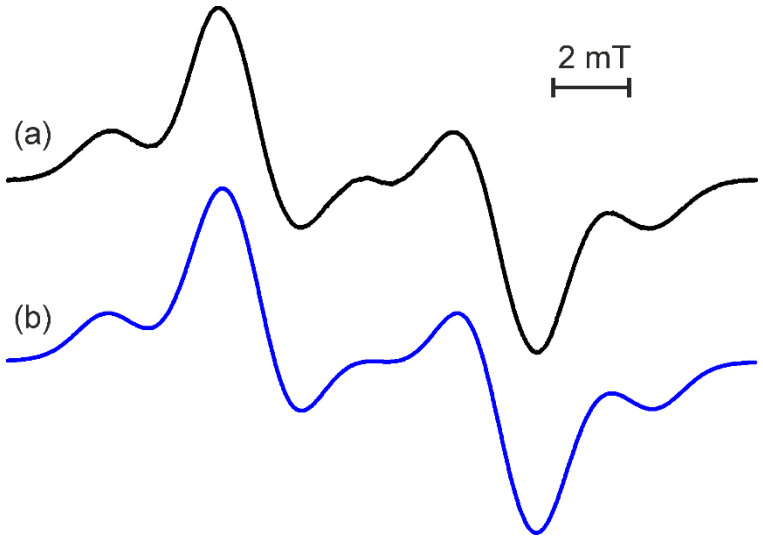


Figure S4. ESR spectrum of compound **5** (2-MeTHF, 130 K): (a) experimental; (b) simulated (g = 2.0055, D = 7.29 mT, E = 0.46 mT).

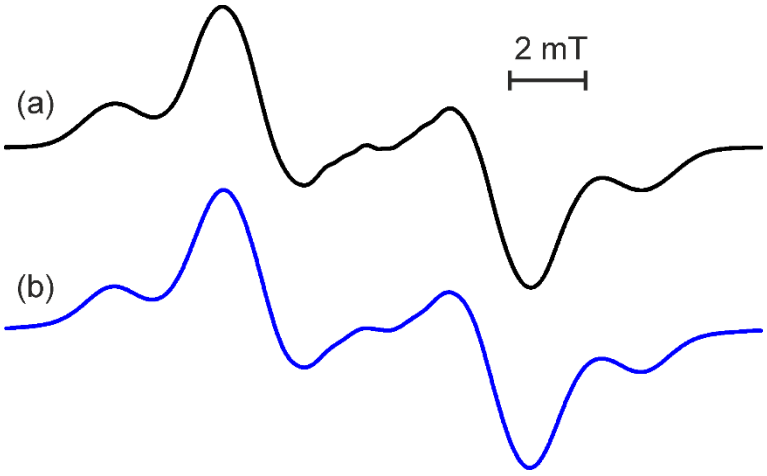


Figure S5. ESR spectrum of compound **6** (2-MeTHF, 130 K): (a) experimental; (b) simulated (g = 2.0055, D = 7.04 mT, E = 0.47 mT).

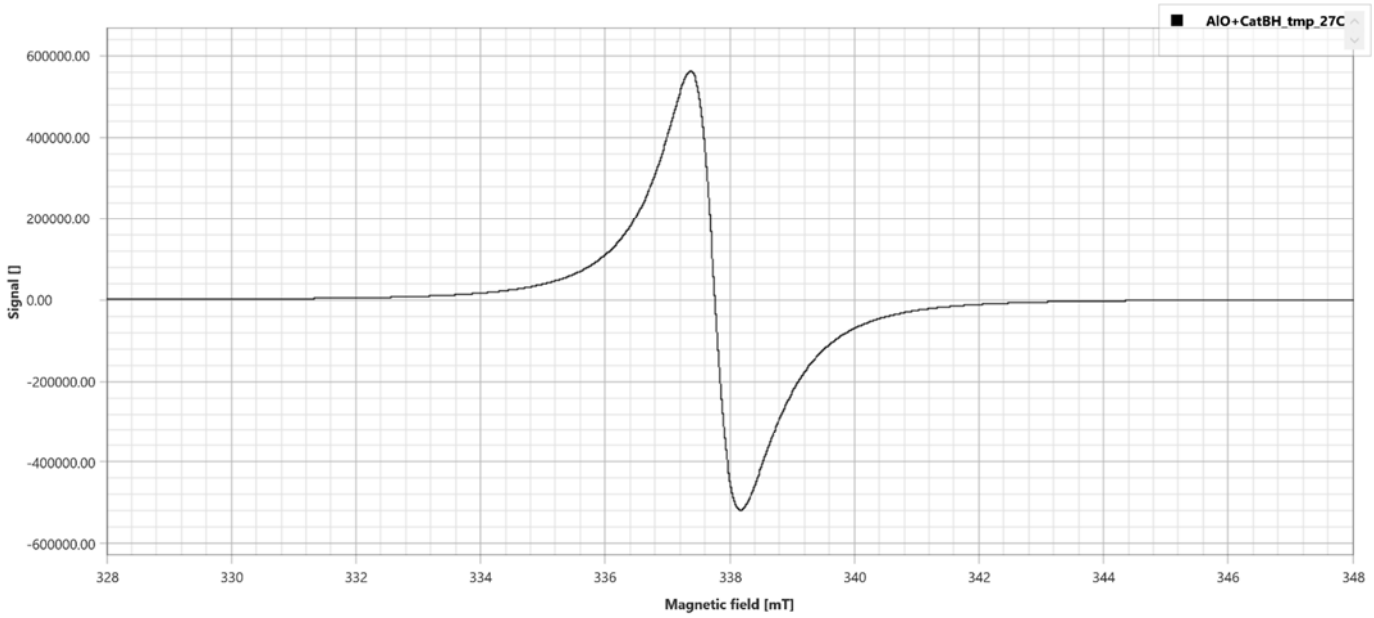


Figure S6. ESR spectrum of compound **7** in the solid state.

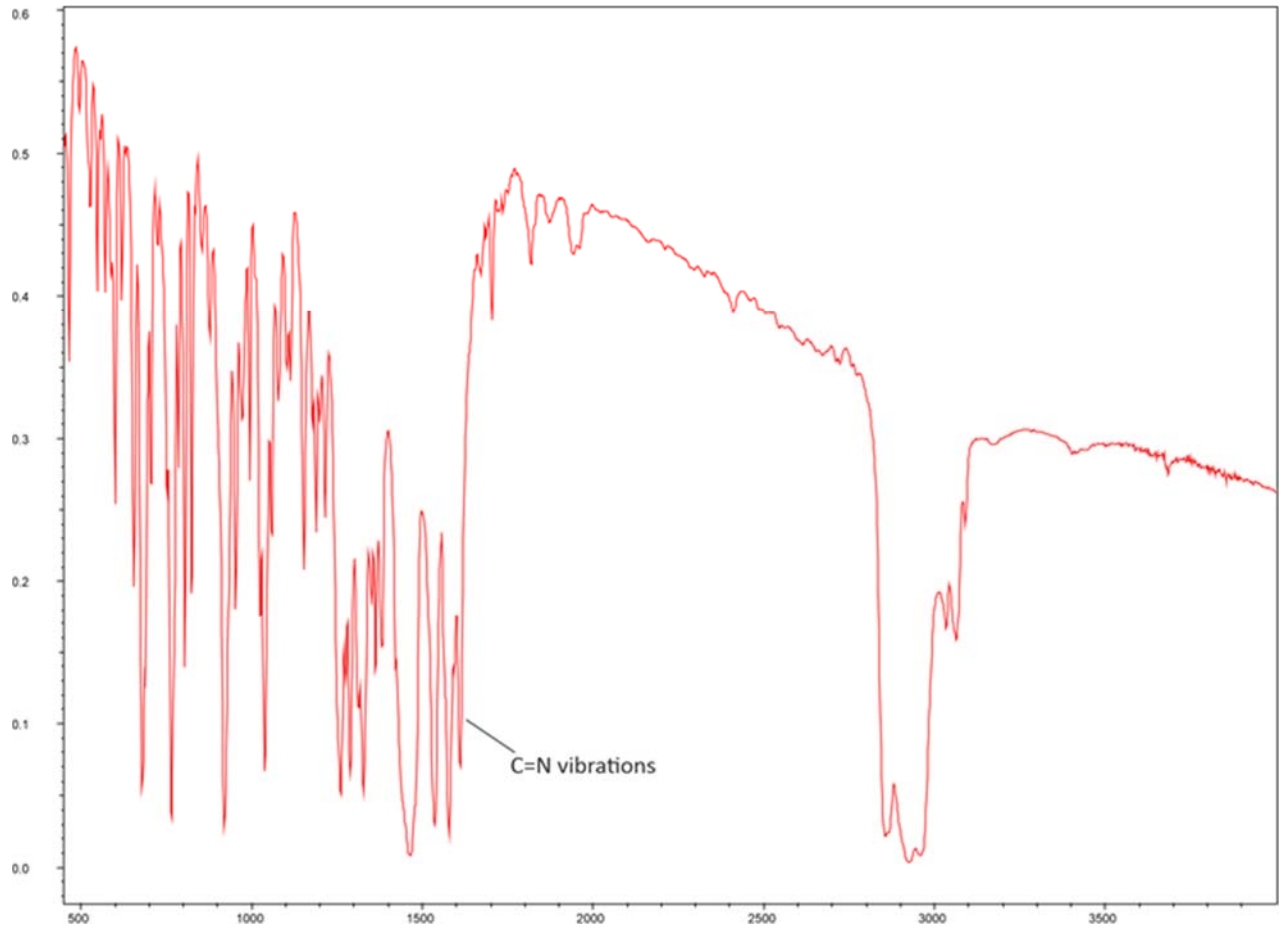


Figure S7. IR spectrum of compound **2**.

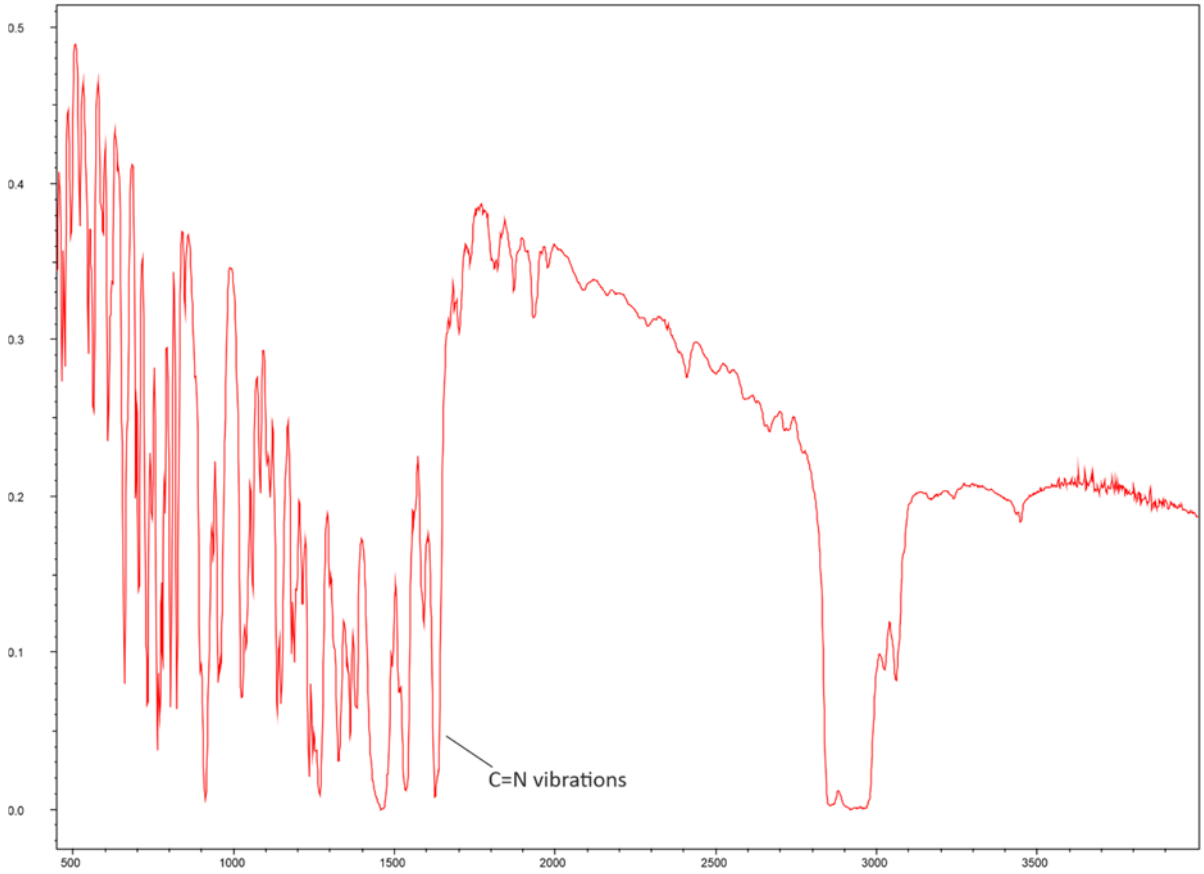


Figure S8. IR spectrum of compound **3**.

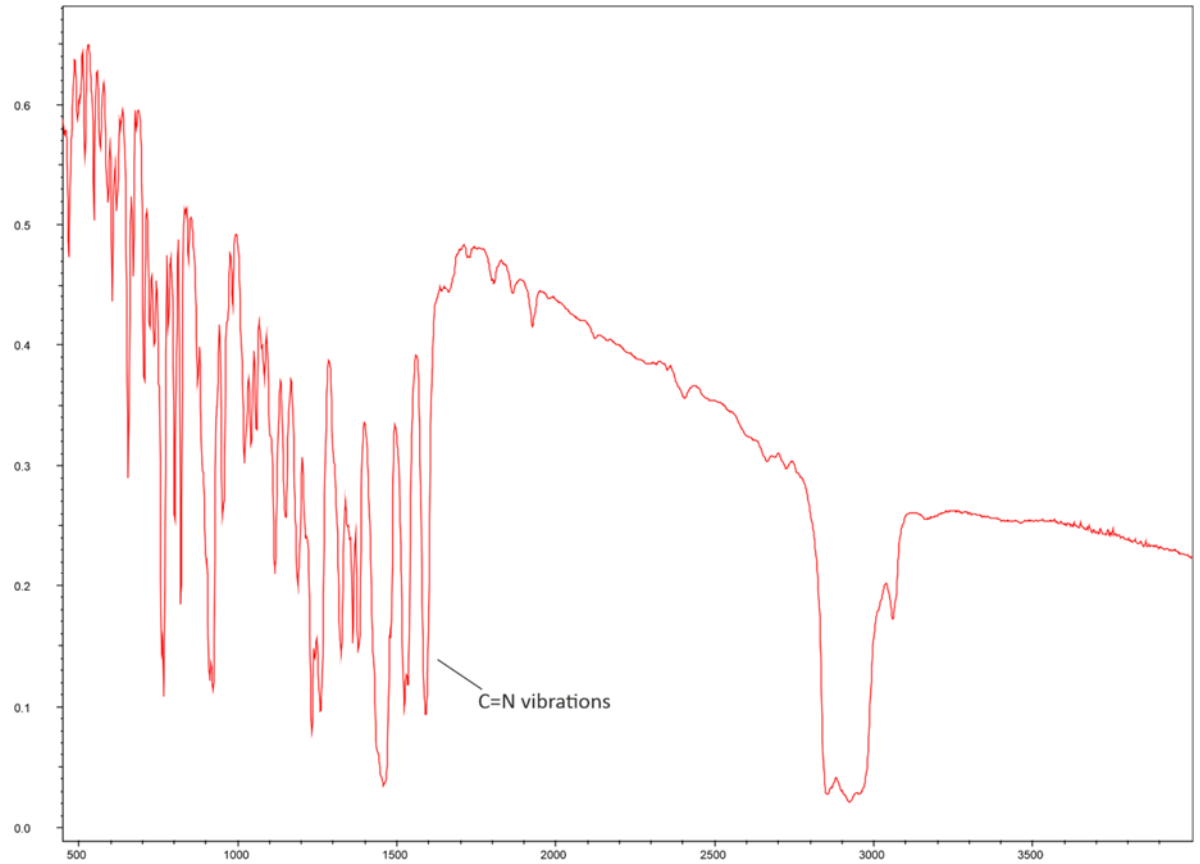


Figure S9. IR spectrum of compound **4**.

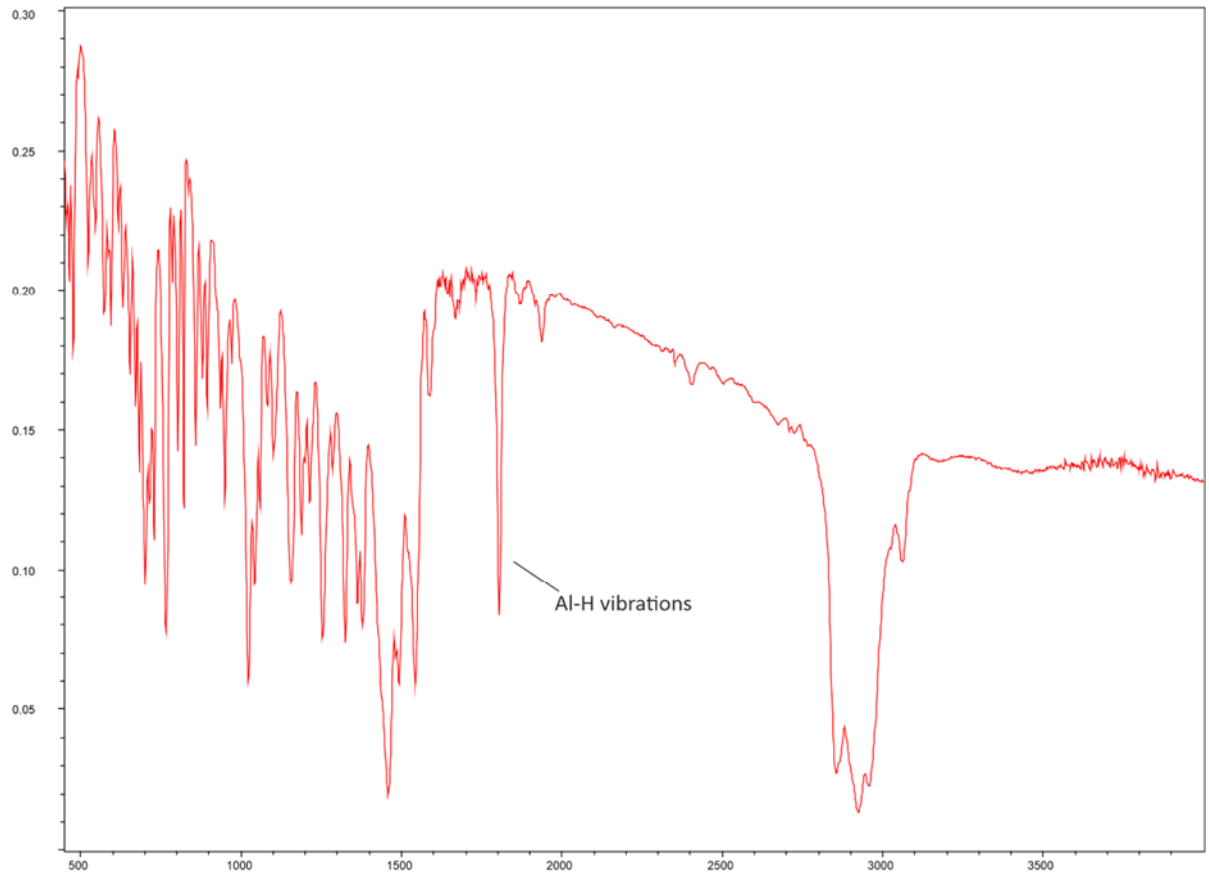


Figure S10. IR spectrum of compound **5**.

Figure S11. IR spectrum of compound **6**.

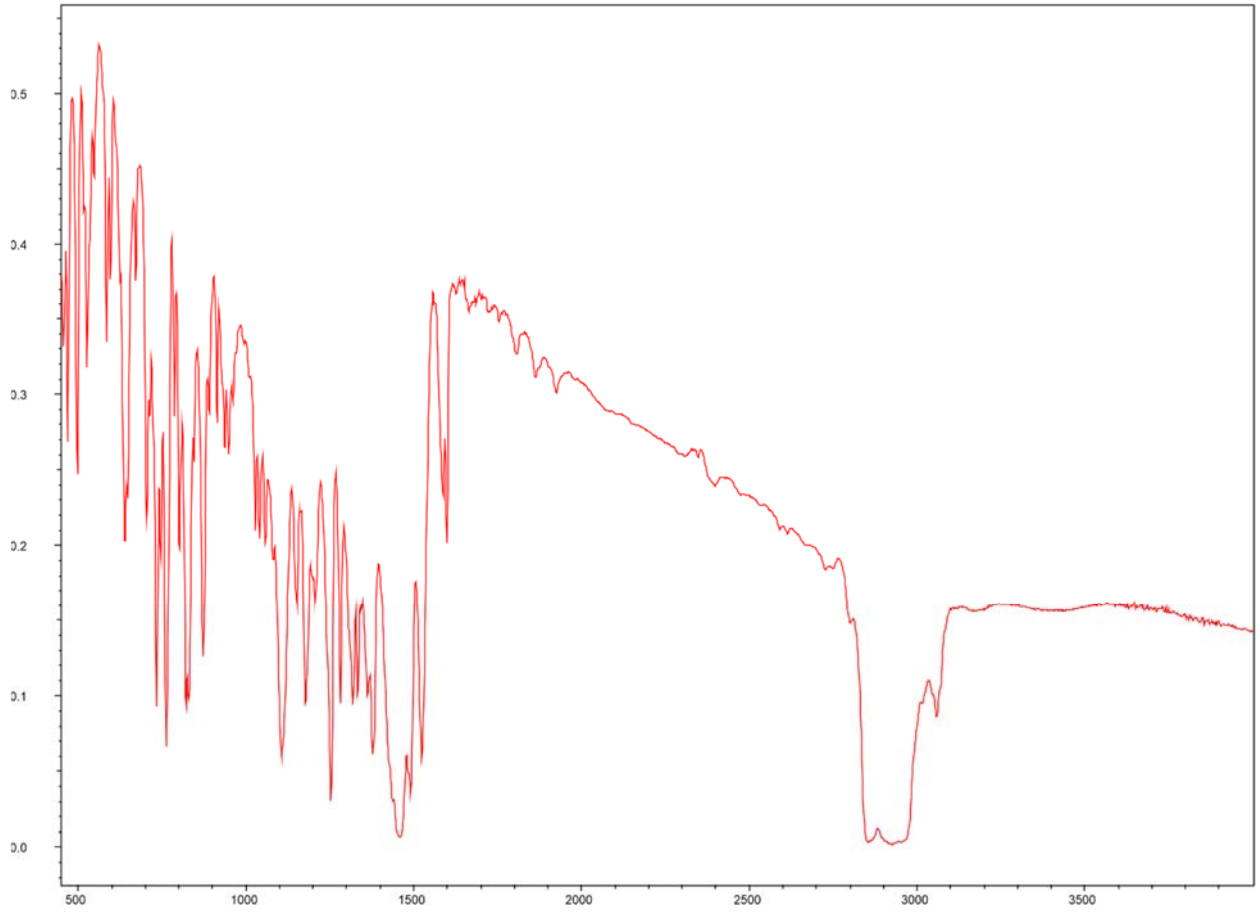


Figure S12. IR spectrum of compound **7**.

General Procedure for Catalytic Hydroboration of Heteroallenes

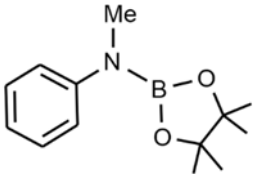
General Procedures

All manipulations were performed under a dinitrogen atmosphere using standard glovebox and Schlenk techniques. NMR spectra were recorded on Bruker NMR spectrometers at 400 MHz (^{1}H) and 300 MHz (^{1}H) and 128.36 MHz (^{11}B). Multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Chemical shifts are reported in ppm. Benzene-d6 (C_6D_6) was dried over Na/ benzophenone and distilled.

General Procedure for Trihydroboration of Isocyanates.

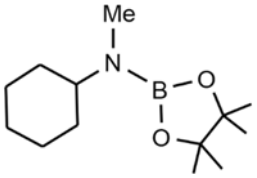
In a NMR tube, 13.0 mg (5 mol%) of catalyst **1**, 96 mg (3.0 equiv., 0.75 mmol) of HBpin was added, followed by 0.25 mmol (1.0 equiv.) of Isocyanates and C_6D_6 (0,5 ml). The NMR tube was sealed. This mixture was then transferred to an oil bath at 100 °C for 24-48 h. The ^{1}H NMR spectrum confirms the appearance of a new NCH_3 peak of N-boryl methylamines. $(Bpin)_2O$ is found as a side-product in all substrates: ^{1}H NMR δ 0.98 ppm; ^{11}B NMR δ 21.68 ppm.

Analytical data of Trihydroboration Products of Isocyanates.



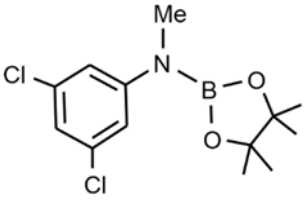
NMR yield 75%.

^{1}H NMR (400 MHz, C_6D_6): δ 7.42 (d, 2H, Ph), 7.17 (t, 2H, Ph), 6.83 (t, 1H, Ph), 2.97 (s, 3H, CH_3), 1.05 (s, 12H, Bpin). ^{11}B NMR (128 MHz, C_6D_6): 24.59.



NMR yield 71%.

^{1}H NMR (400 MHz, C_6D_6): δ 3.25 (t, 1H, Cy), 2.59 (s, 3H, CH_3), 1.66-1.54 (m, 4H, Cy), 1.48-1.37 (m, 3H, Cy), 1.20-1.11 (m, 3H, Cy), 1.09 (s, 12H, Bpin). ^{11}B NMR (128 MHz, C_6D_6): 24.33.



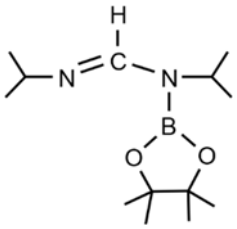
NMR yield 49%.

^{1}H NMR (400 MHz, C_6D_6): δ 7.31 (s, 2H, 3,6-ClPh), 6.84 (s, 2H, 3,6-ClPh), 2.62 (s, 3H, CH_3), 0.96 (s, 12H, Bpin). ^{11}B NMR (128 MHz, C_6D_6): 24.45.

General Procedure for Catalytic Monohydroboration of Carbodiimide.

In a NMR tube, 13.0 mg (5 mol%) of catalyst **1**, 32 mg (1.0 equiv., 0.25 mmol) of HBpin was added, followed by 0.25 mmol (1.0 equiv.) of Carbodiimides and C_6D_6 (0,5 ml). The NMR tube was sealed. This mixture was then transferred to an oil bath at 100 °C for 24-48 h. The ^{1}H NMR spectrum confirms the appearance of a new NC*H*N peak of N-boryl formamidines.

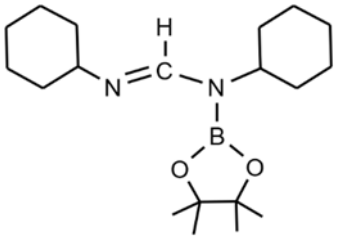
Analytical data of Monohydroboration Products of Carbodiimides.



NMR yield 73%.

^{1}H NMR (400 MHz, C_6D_6): δ 8.20 (s, 1H, CH), 4.92 (sept, 1H, C*H*$(CH_3)_2$), 3.27 (sept, 1H, C*H*$(CH_3)_2$), 1.40 (d, 6H, CH(C*H*$_3)_2$), 1.15 (d, 6H, CH(C*H*$_3)_2$), 1.00 (s, 12H, Bpin).

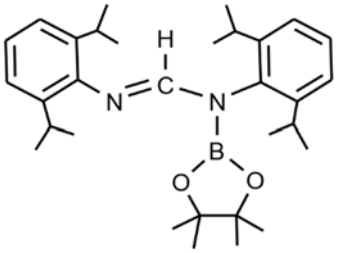
^{11}B NMR (128 MHz, C_6D_6): 25.25.



NMR yield 70%.

^{1}H NMR (400 MHz, C_6D_6): δ 8.27 (s, 1H, CH), 4.60-4.49 (m, 1H, Cy), 3.00-2.89 (m, 1H, Cy), 2.18-2.03 (m, 2H, Cy), 1.91-1.84 (m, 2H, Cy), 1.73-1.62 (m, 6H, Cy), 1.51-1.42 (m, 2H, Cy), 1.33-1.05 (m, 8H, Cy), 1.02 (s, 12H, Bpin).

^{11}B NMR (128 MHz, C_6D_6): 25.33.



NMR yield 45%.

^{1}H NMR (400 MHz, C_6D_6): δ 8.28 (s, 1H, CH), 7.17 (s, 3H, Ph), 7.09 (s, 3H, Ph), 3.32 (sept, 2H, C*H*$(CH_3)_2$), 3.24 (sept, 2H, C*H*$(CH_3)_2$), 1.40-1.32 (m, 12H, CH(C*H*$_3)_2$), 1.16 (d, 12H, CH(C*H*$_3)_2$), 0.95 (s, 12H, Bpin).

^{11}B NMR (128 MHz, C_6D_6): 25.28.

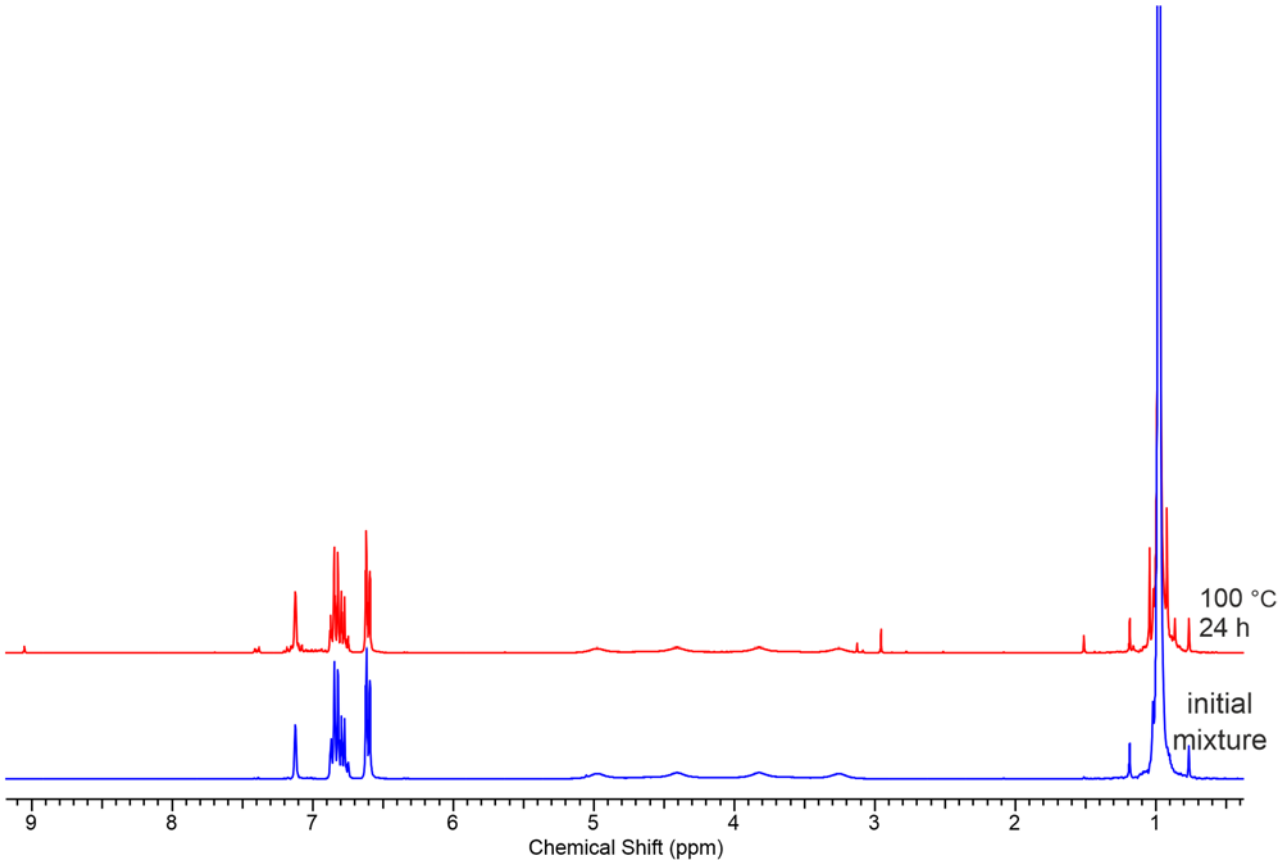


Figure S13. ^{1}H NMR spectrum of phenylisocyanate with 3 equiv. of HBpin in the absence of catalyst (C_6D_6, 300 MHz).

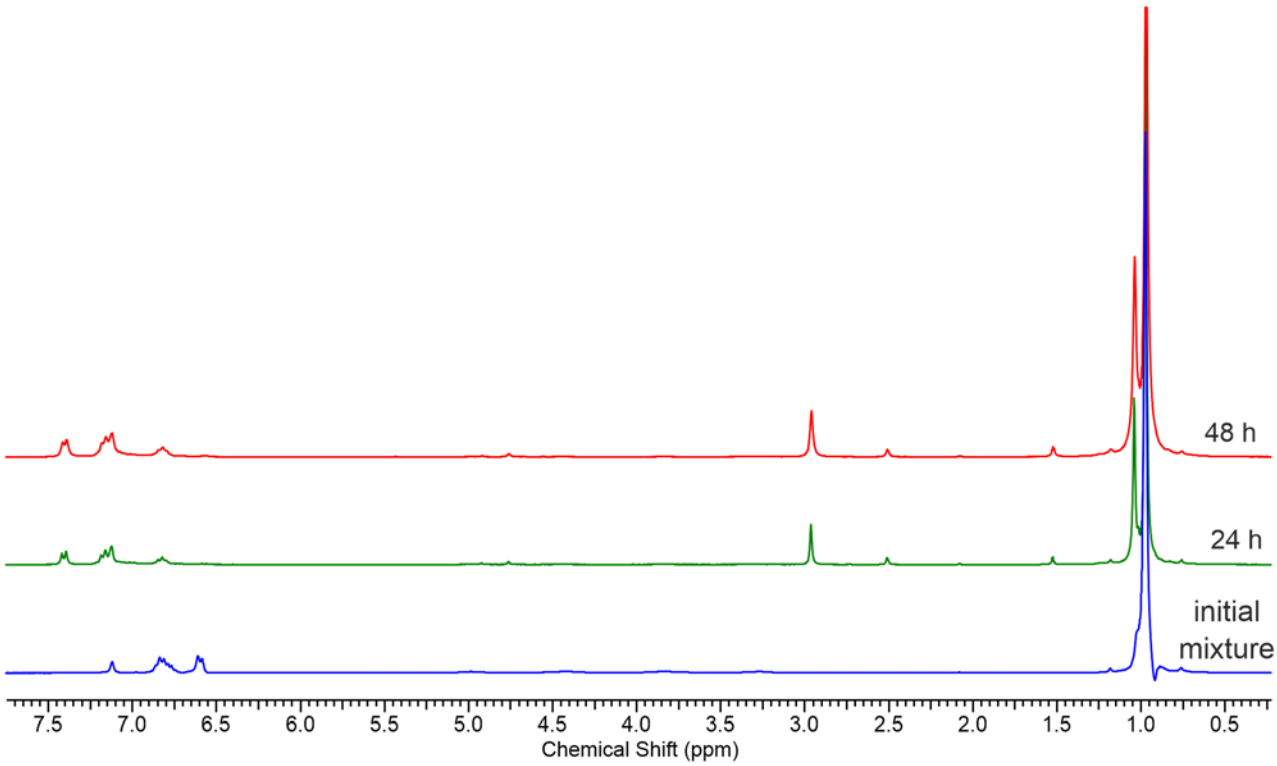


Figure S14. Spectrum of evolution of the reaction mixture (PhNCO + 3HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

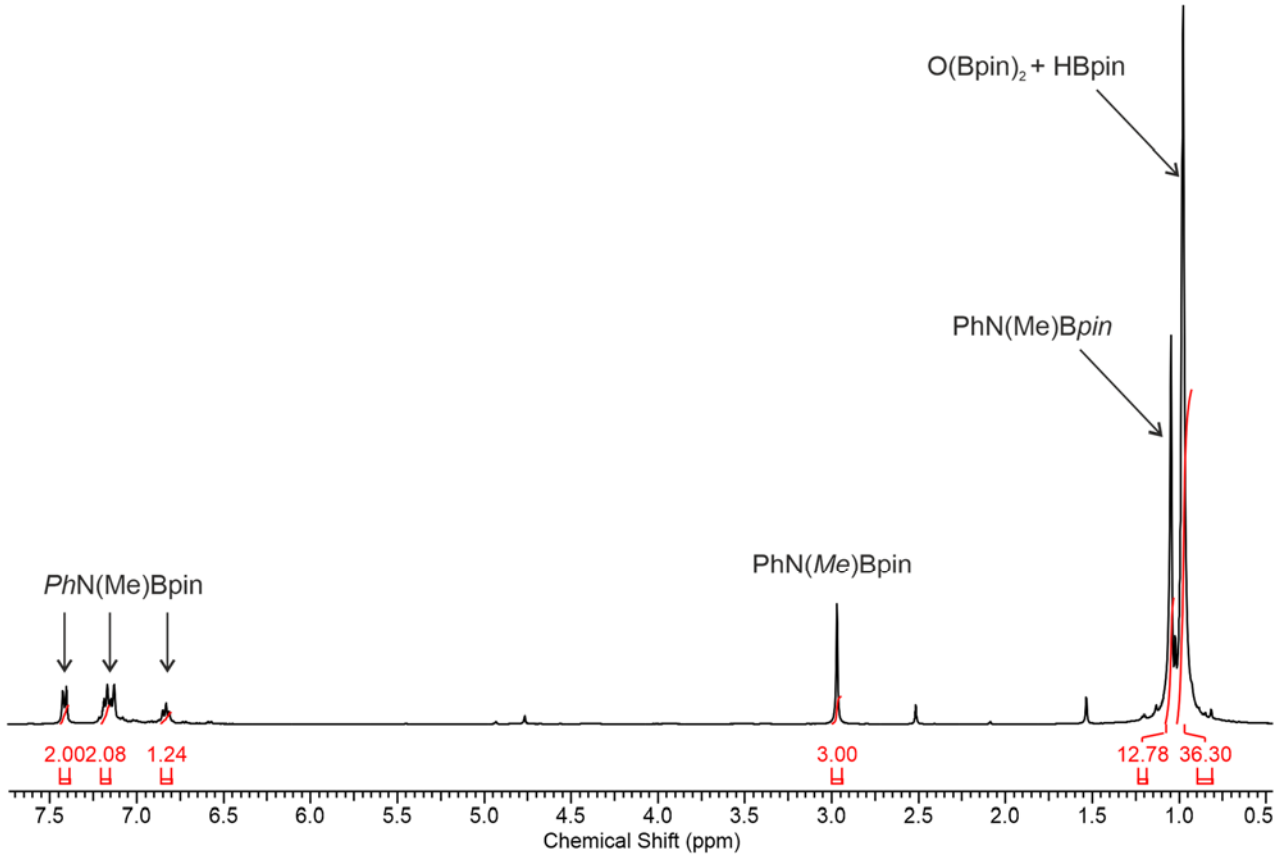


Figure S15. ^{1}H NMR spectrum of compound PhN(Me)Bpin (Cat **1**, C_6D_6, 400 MHz, 21 °C).

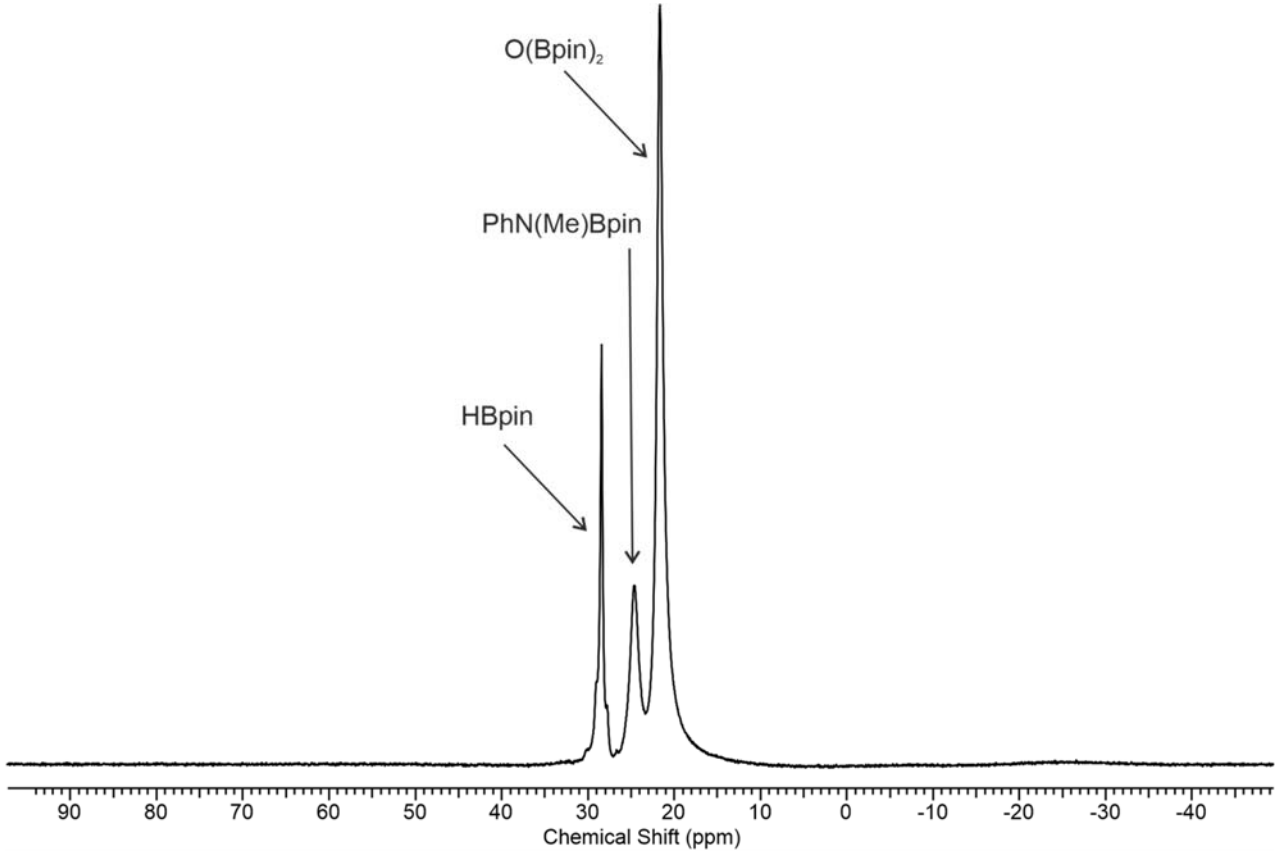


Figure S16. ^{11}B NMR spectrum of compound PhN(Me)Bpin (Cat **1**, 128 MHz, C_6D_6, 21 °C)

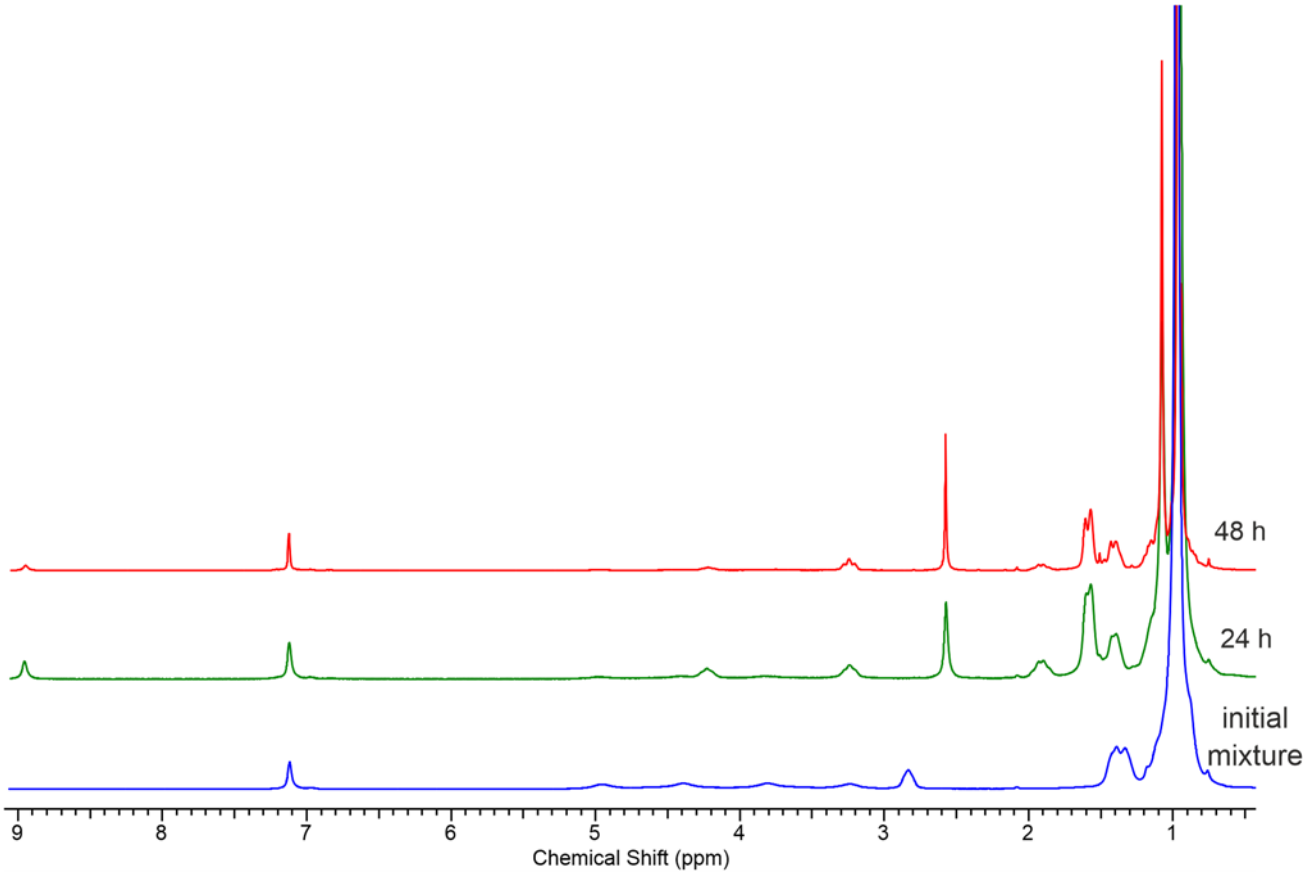


Figure S17. Spectrum of evolution of the reaction mixture (CyNCO + 3HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

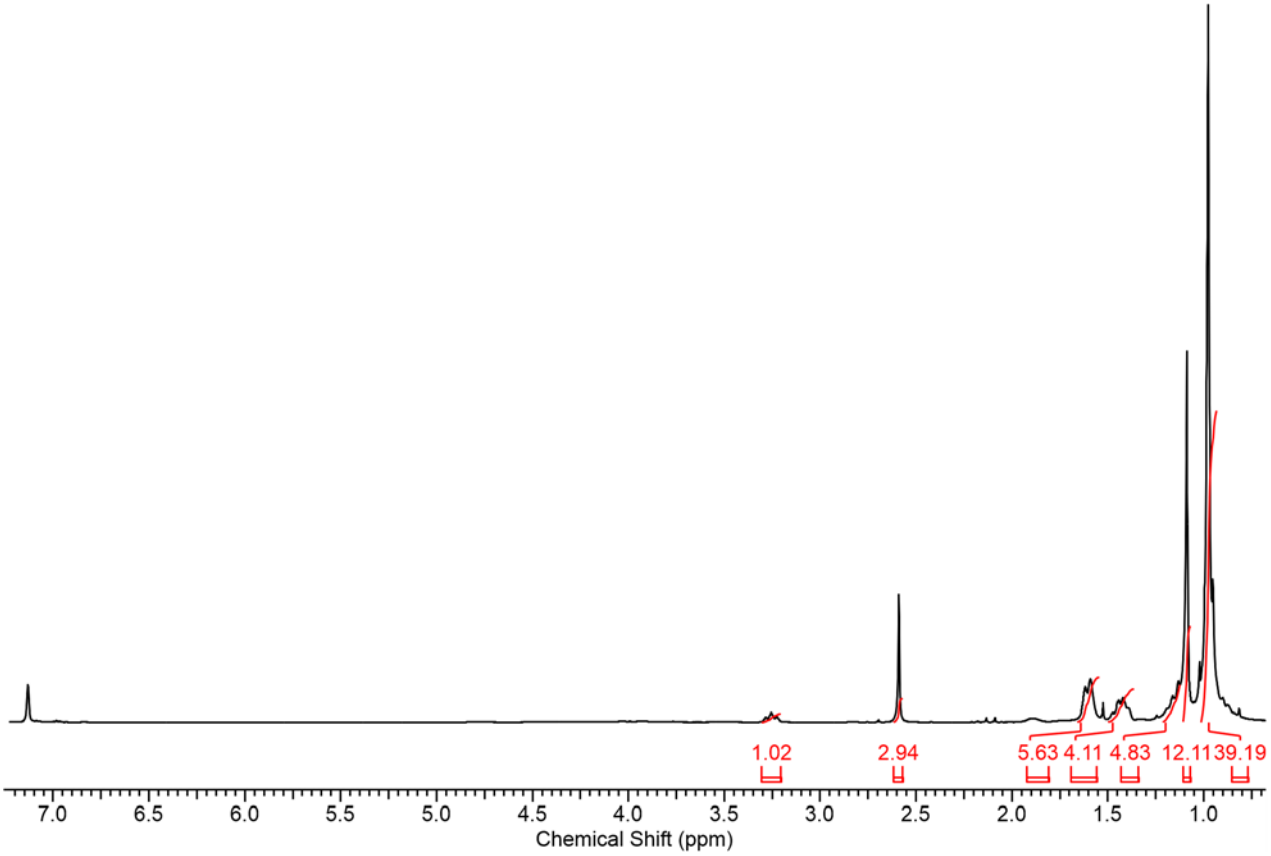


Figure S18. ^{1}H NMR spectrum of compound CyN(Me)Bpin (Cat **1**, C_6D_6, 400 MHz, 21 °C).

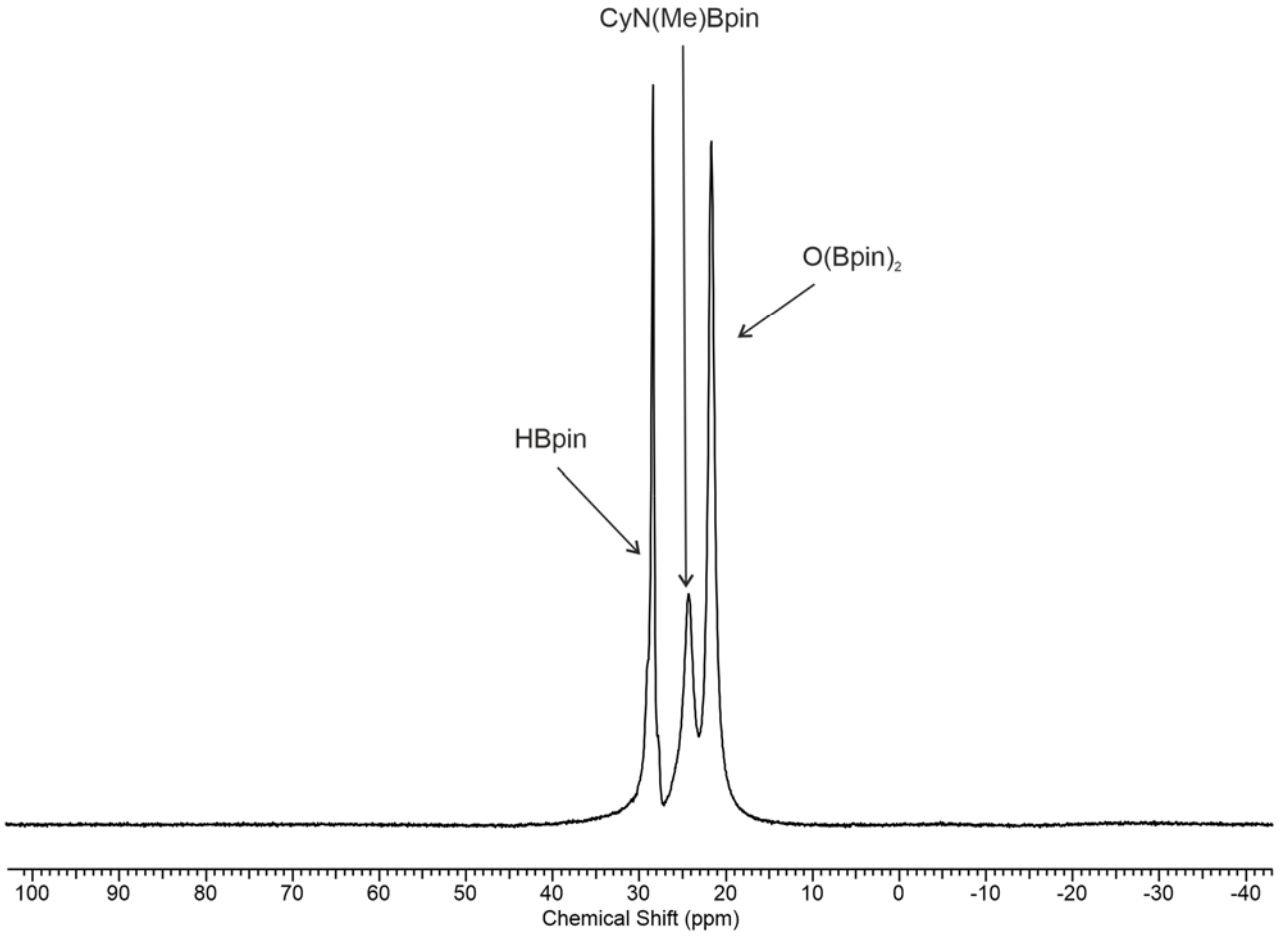


Figure S19. ^{11}B NMR spectrum of compound CyN(Me)Bpin (Cat **1**, 128 MHz, C_6D_6, 21 °C)

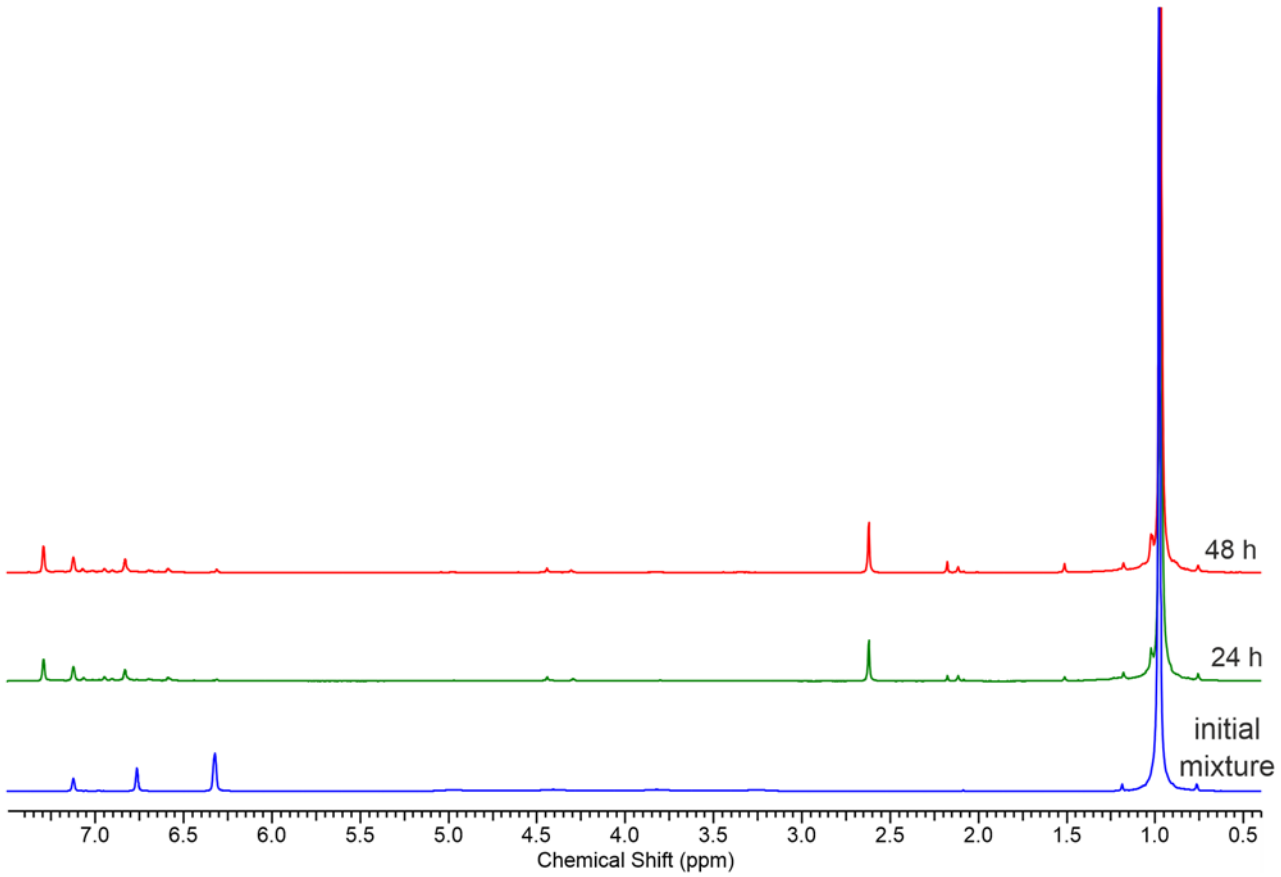


Figure S20. Spectrum of evolution of the reaction mixture (3,5-Cl_2PhNCO + 3HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

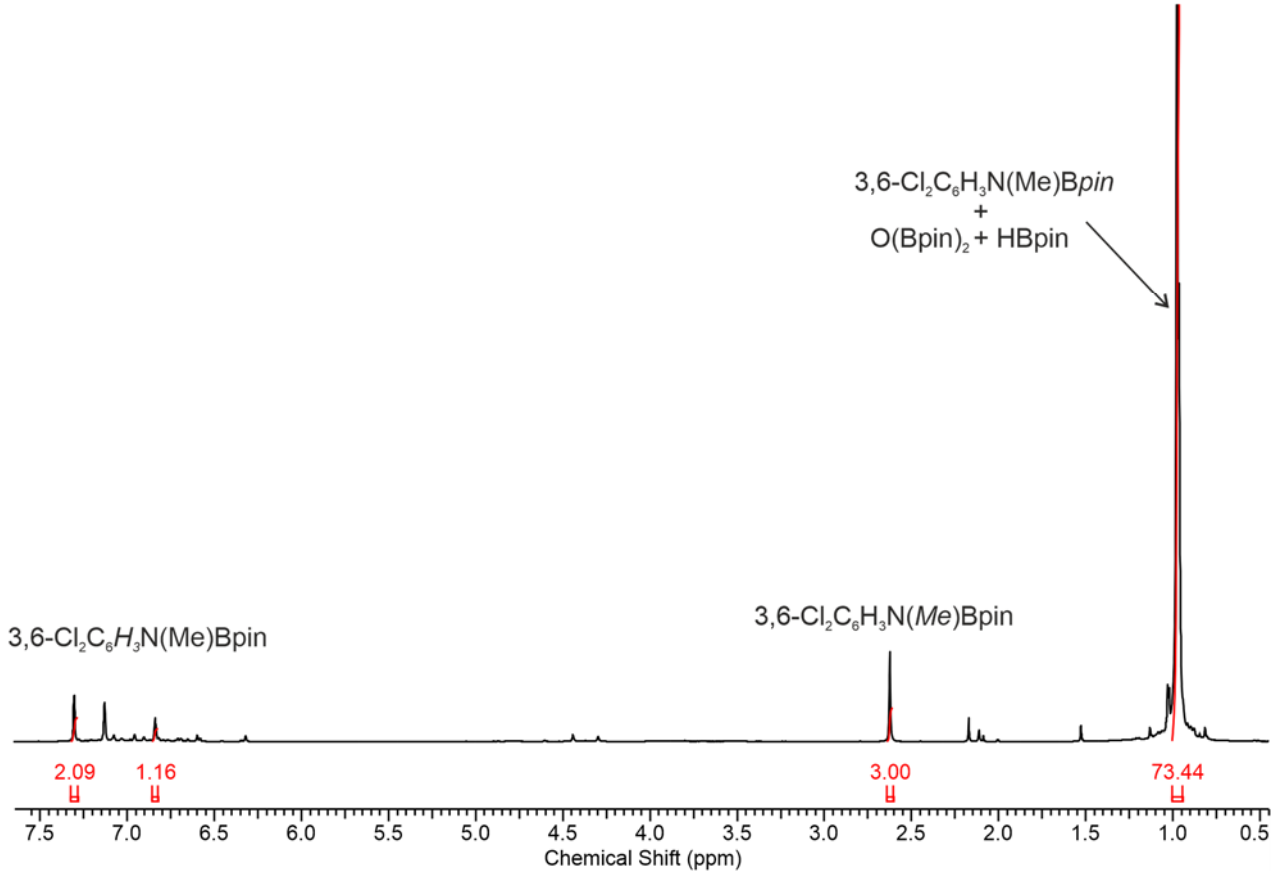


Figure S21. ^{1}H NMR spectrum of compound 3,6-Cl_2PhN(Me)Bpin (Cat **1**, C_6D_6, 400 MHz, 21 °C).

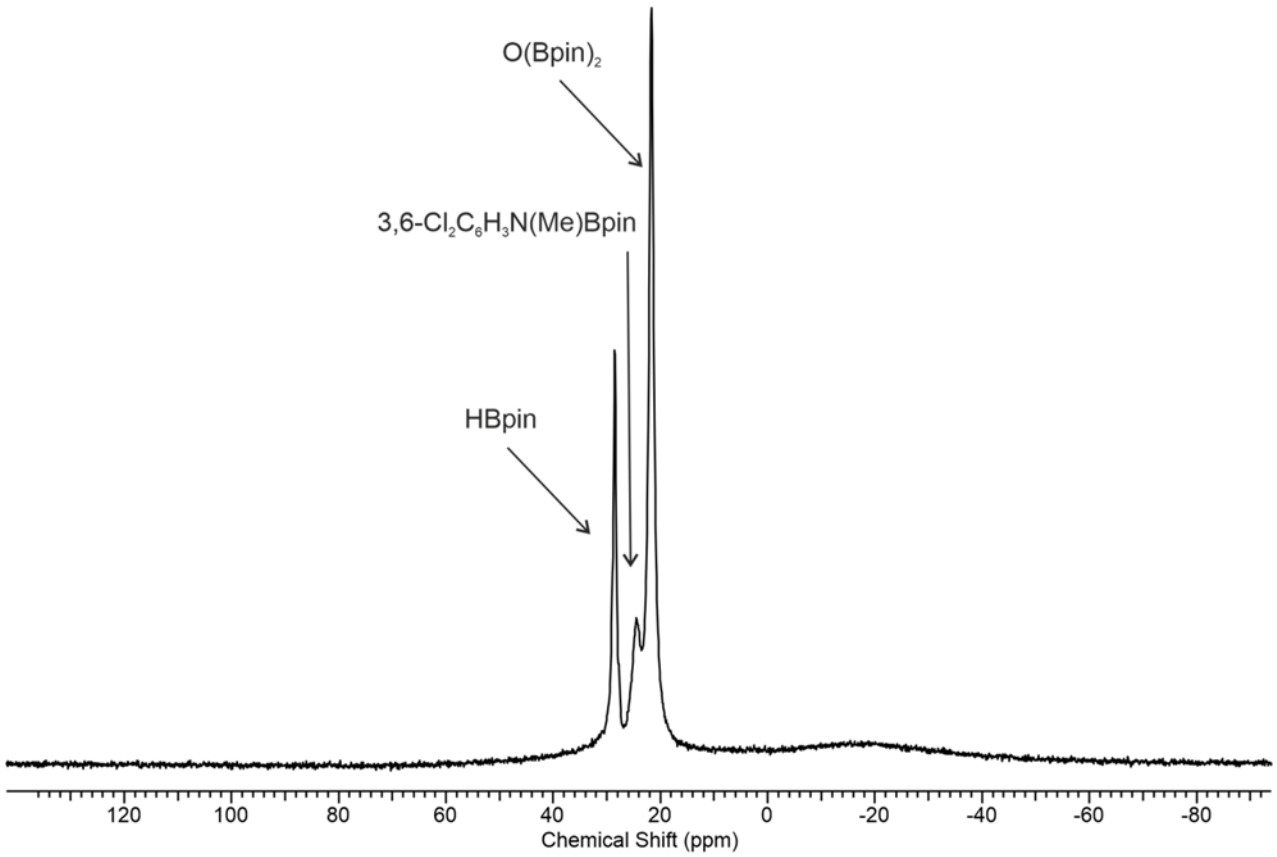


Figure S22. ^{11}B NMR spectrum of compound 3,6-Cl_2PhN(Me)Bpin (Cat **1**, 128 MHz, C_6D_6, 21 °C)

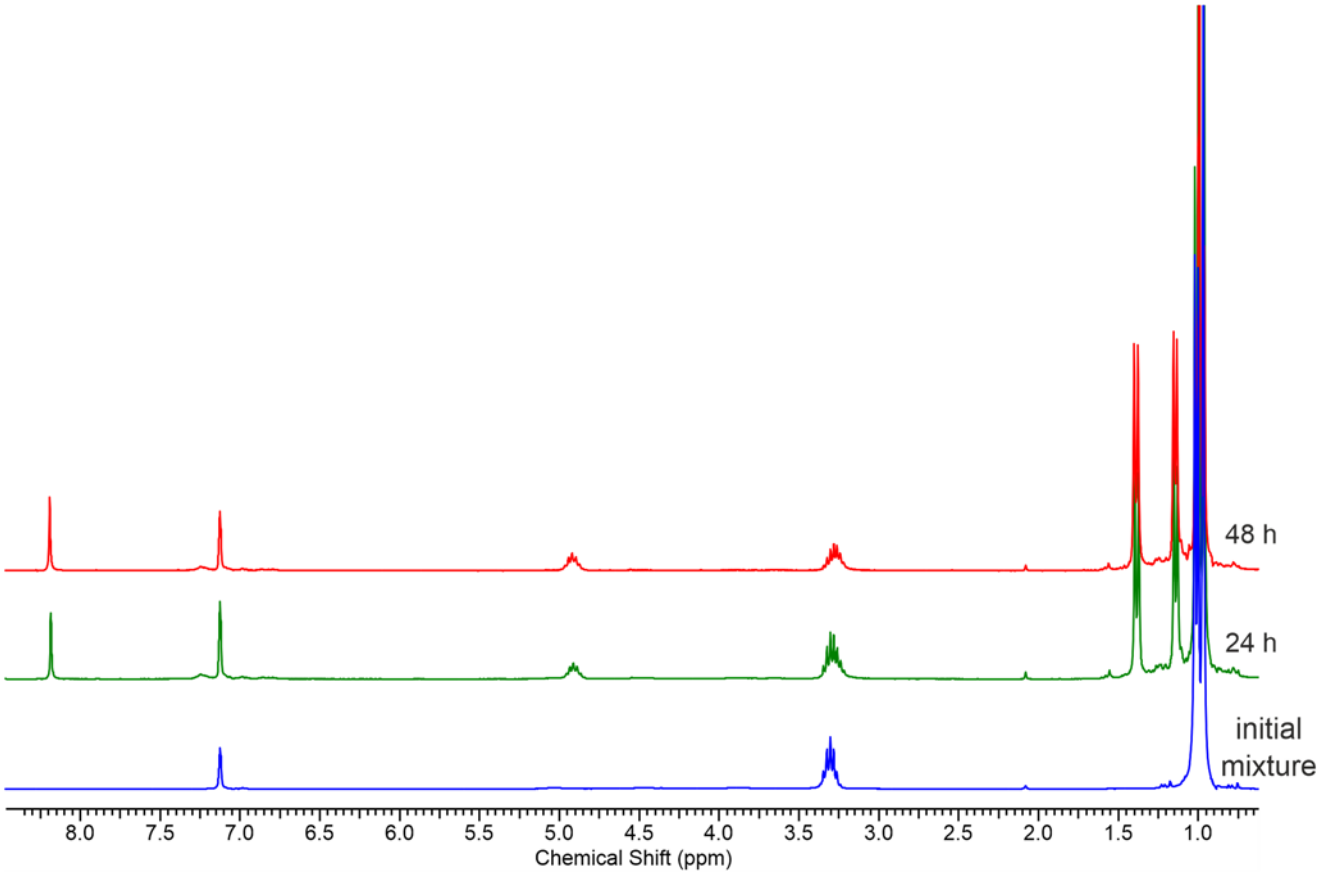


Figure S23. Spectrum of evolution of the reaction mixture (*i*PrNCN*i*Pr + HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

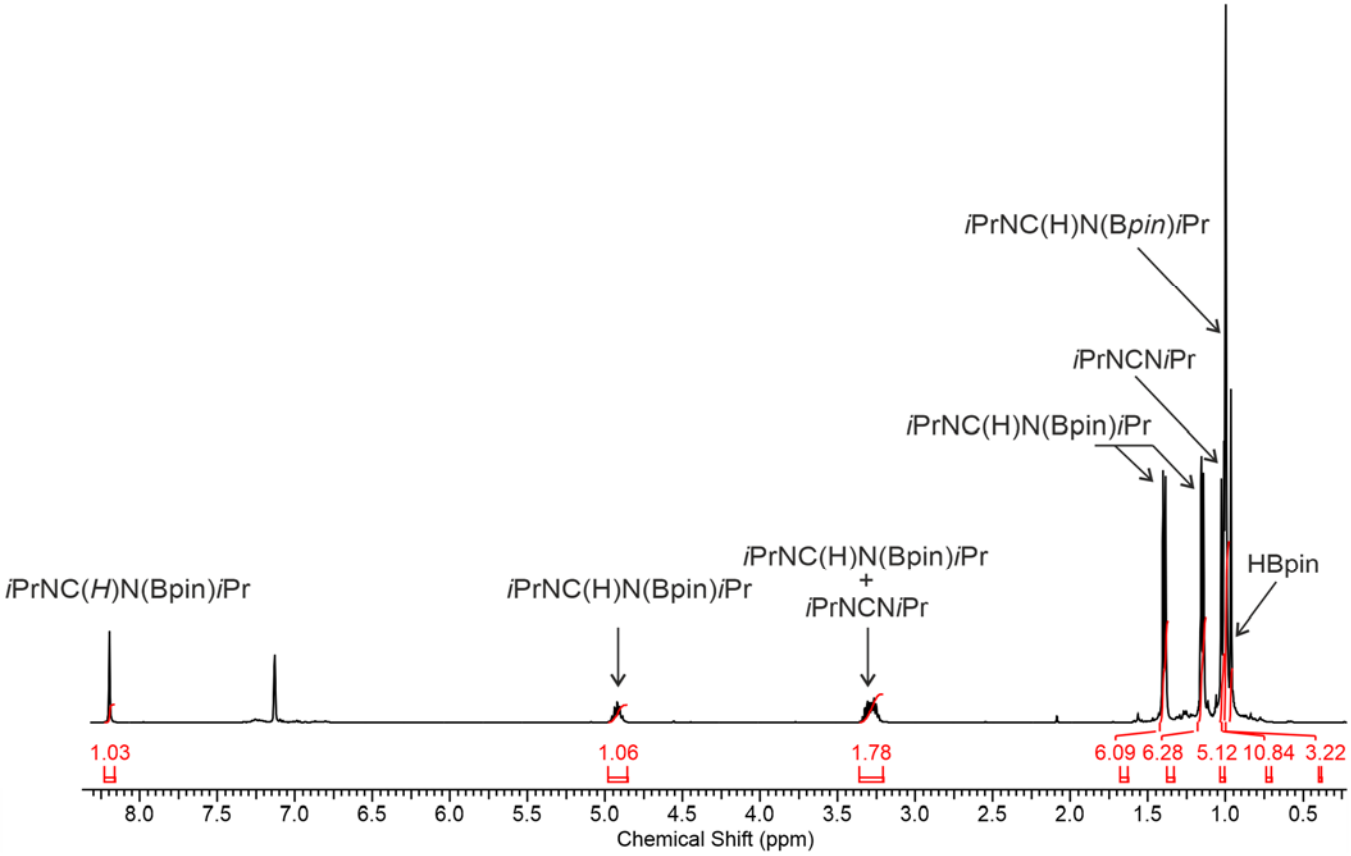


Figure S24. ^{1}H NMR spectrum of compound *i*PrNC(H)N(Bpin)*i*Pr (Cat **1**, C_6D_6, 400 MHz, 21 °C).

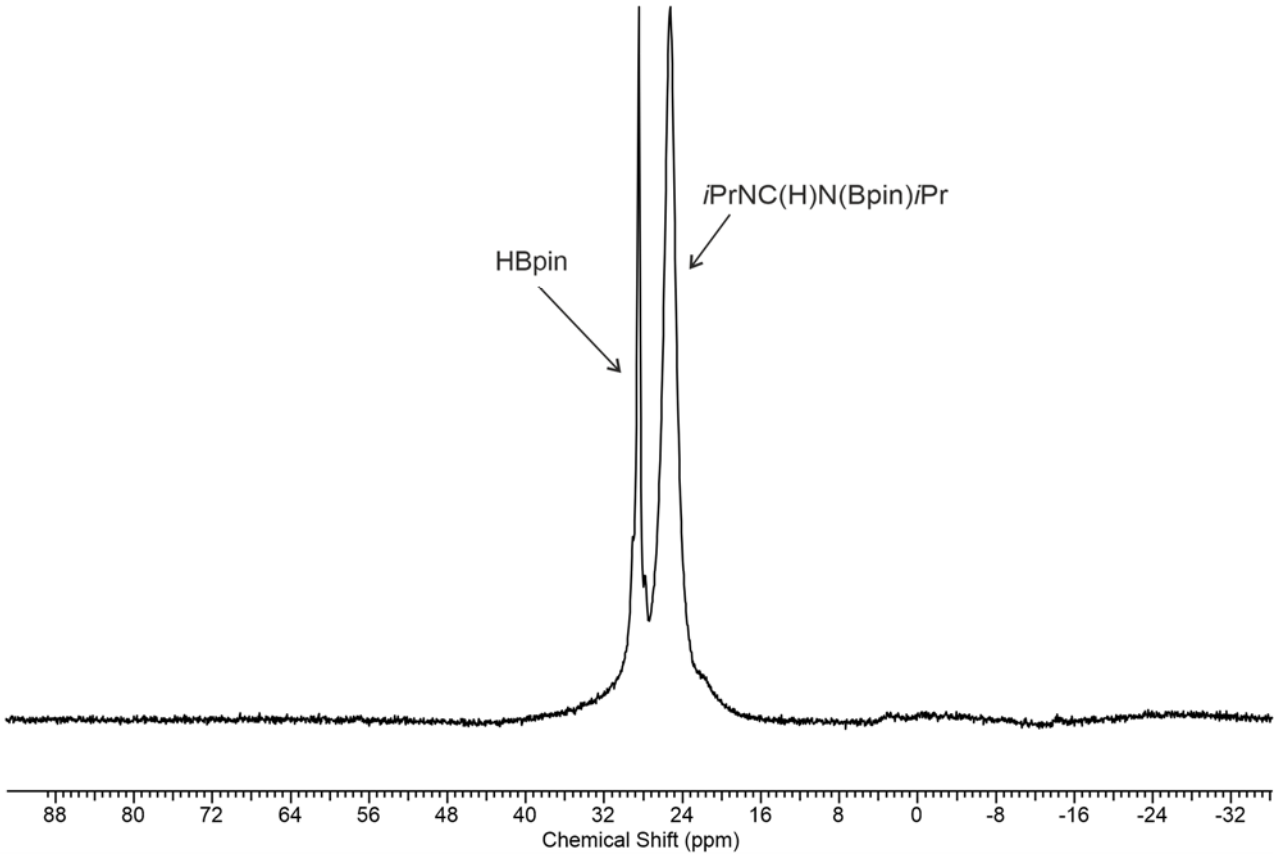


Figure S25. ^{11}B NMR spectrum of compound *i*PrNC(H)N(Bpin)*i*Pr (Cat **1**, 128 MHz, C_6D_6, 21 °C)

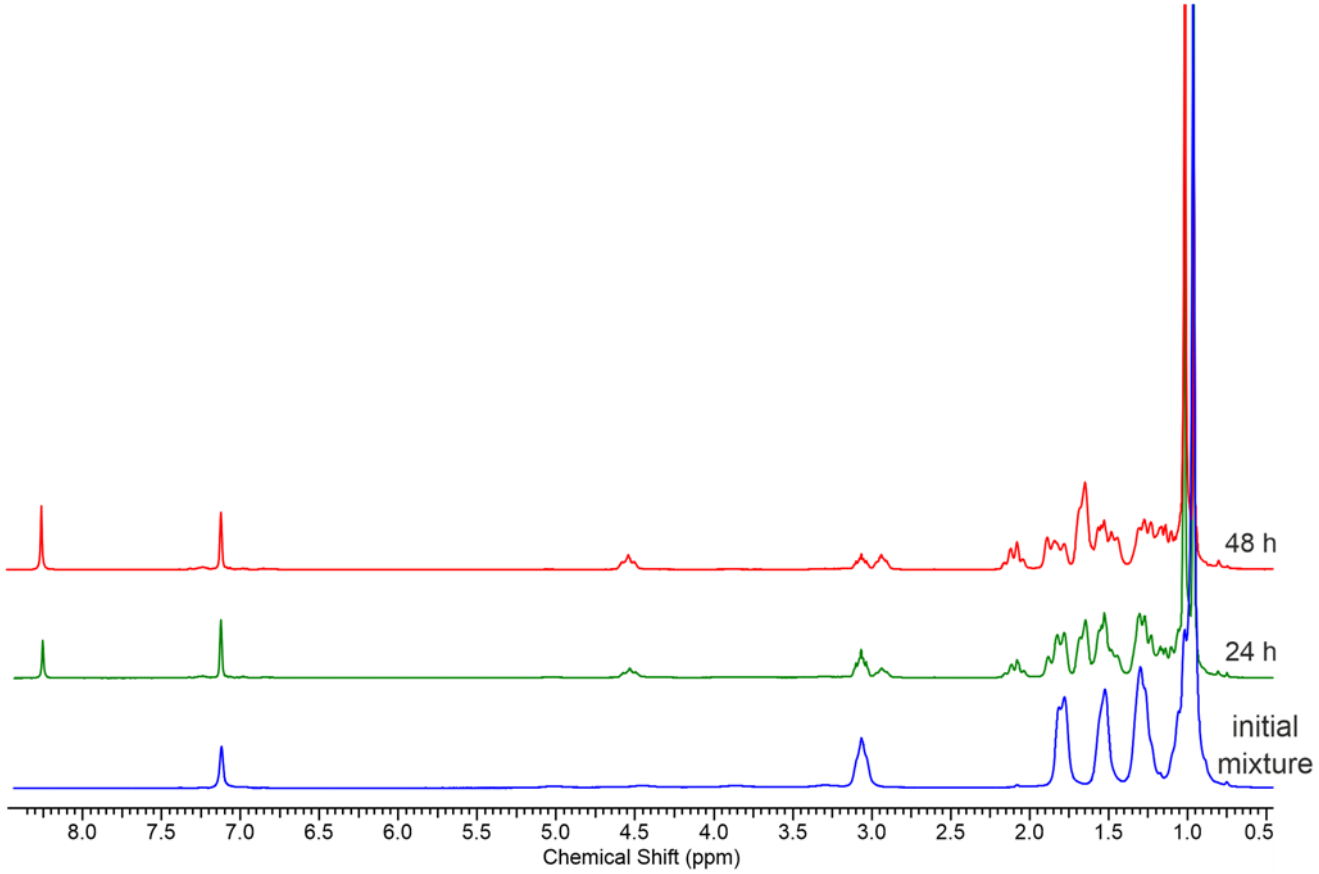


Figure S26. Spectrum of evolution of the reaction mixture (CyNCNCy + HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

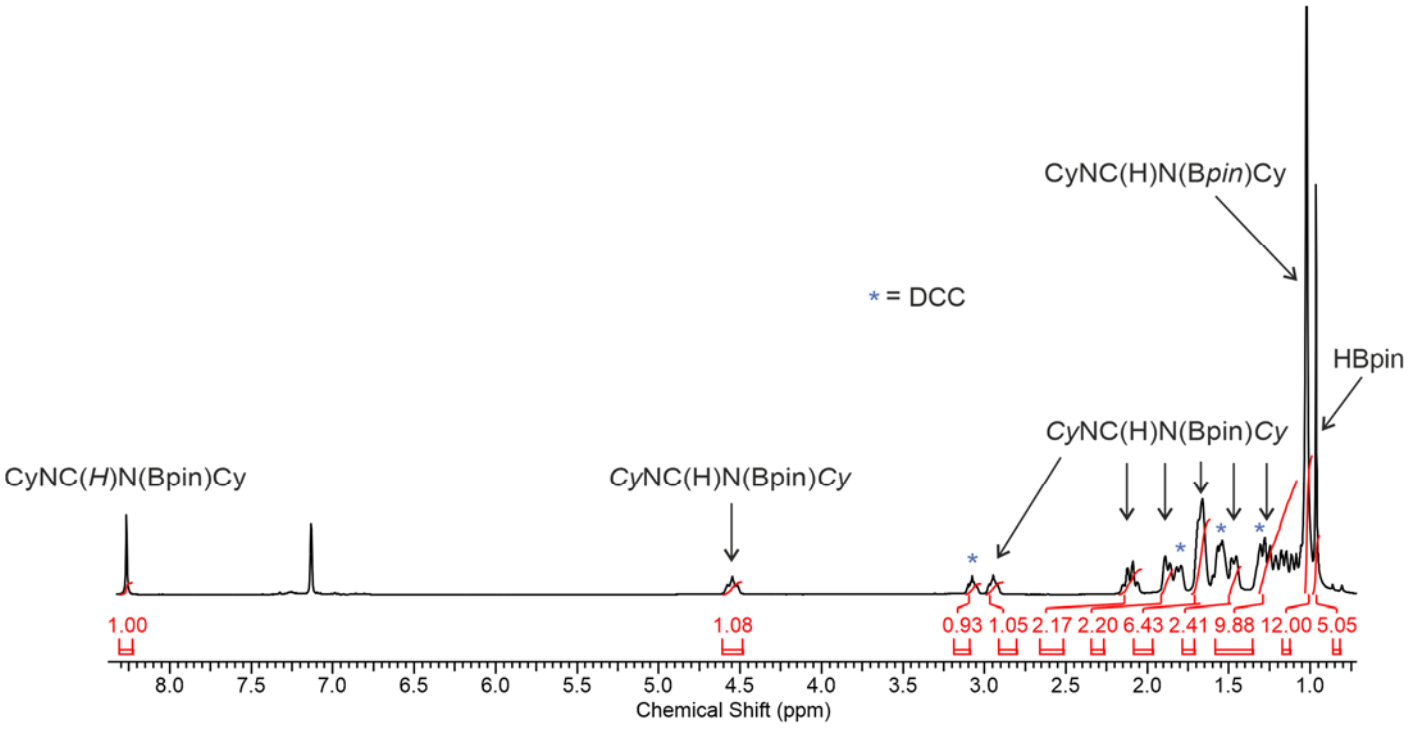


Figure S27. ^{1}H NMR spectrum of compound CyNC(H)N(Bpin)Cy (Cat **1**, C_6D_6, 400 MHz, 21 °C).

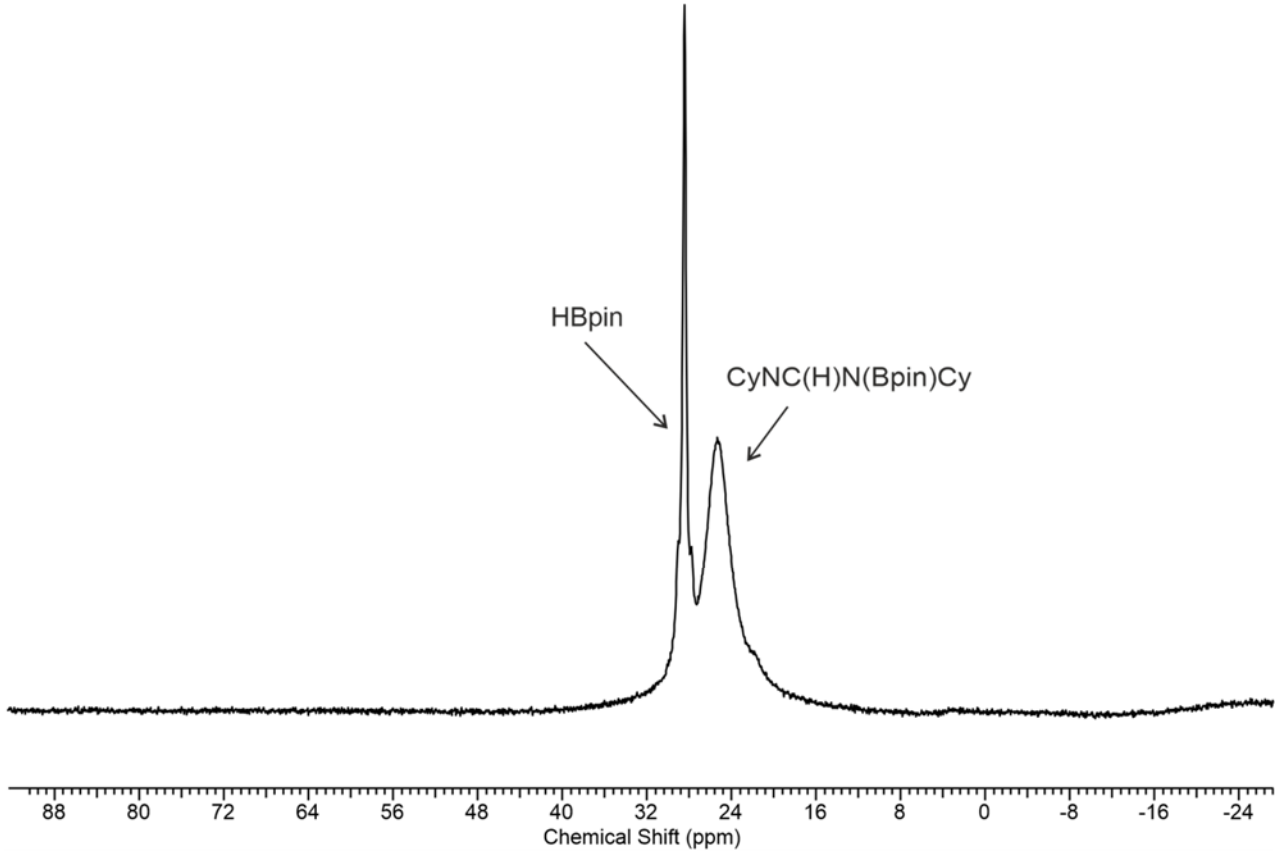


Figure S28. ^{11}B NMR spectrum of compound CyNC(H)N(Bpin)Cy (Cat **1**, 128 MHz, C_6D_6, 21 °C)

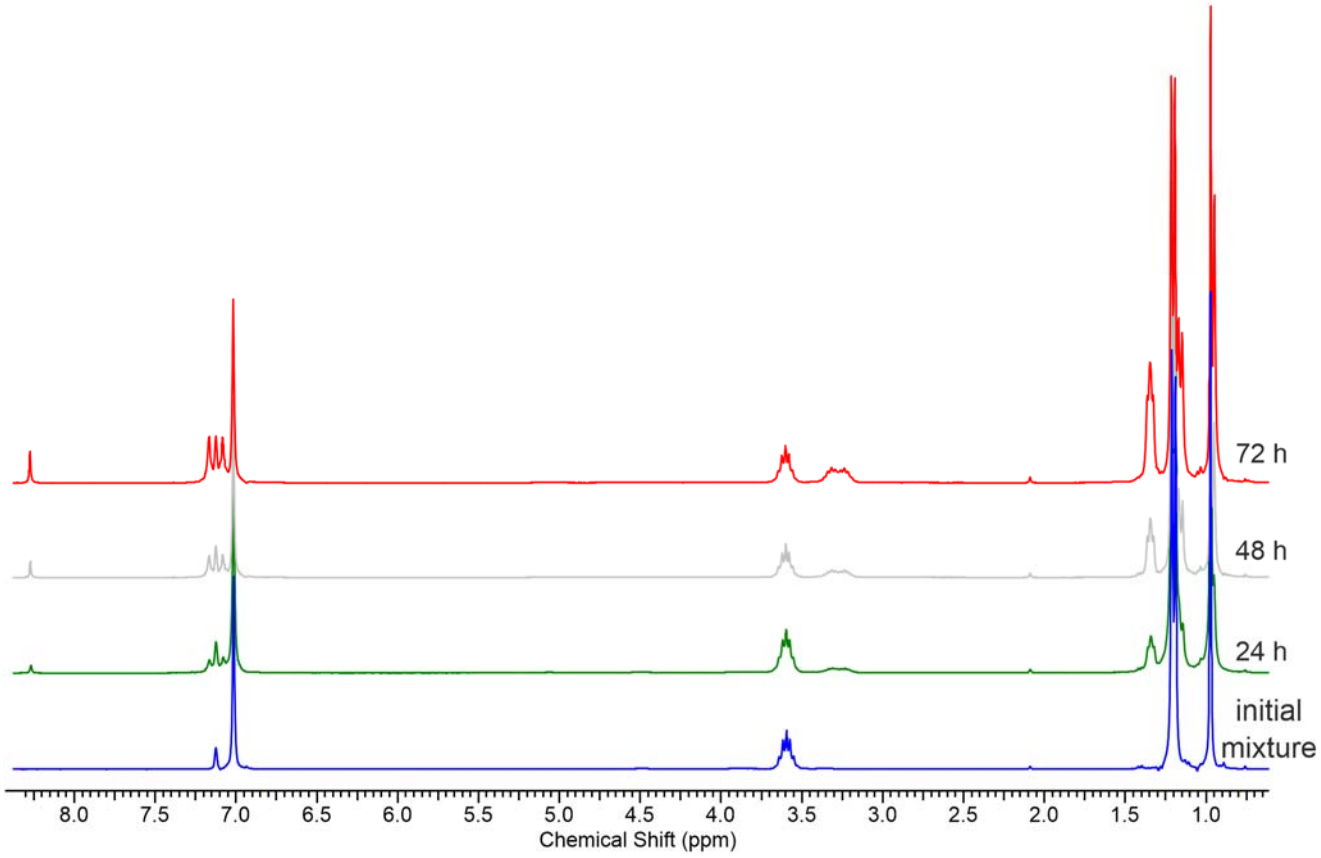


Figure S29. Spectrum of evolution of the reaction mixture (DppNCNDpp + HBpin) over time (Cat **1**, C_6D_6, 300 MHz).

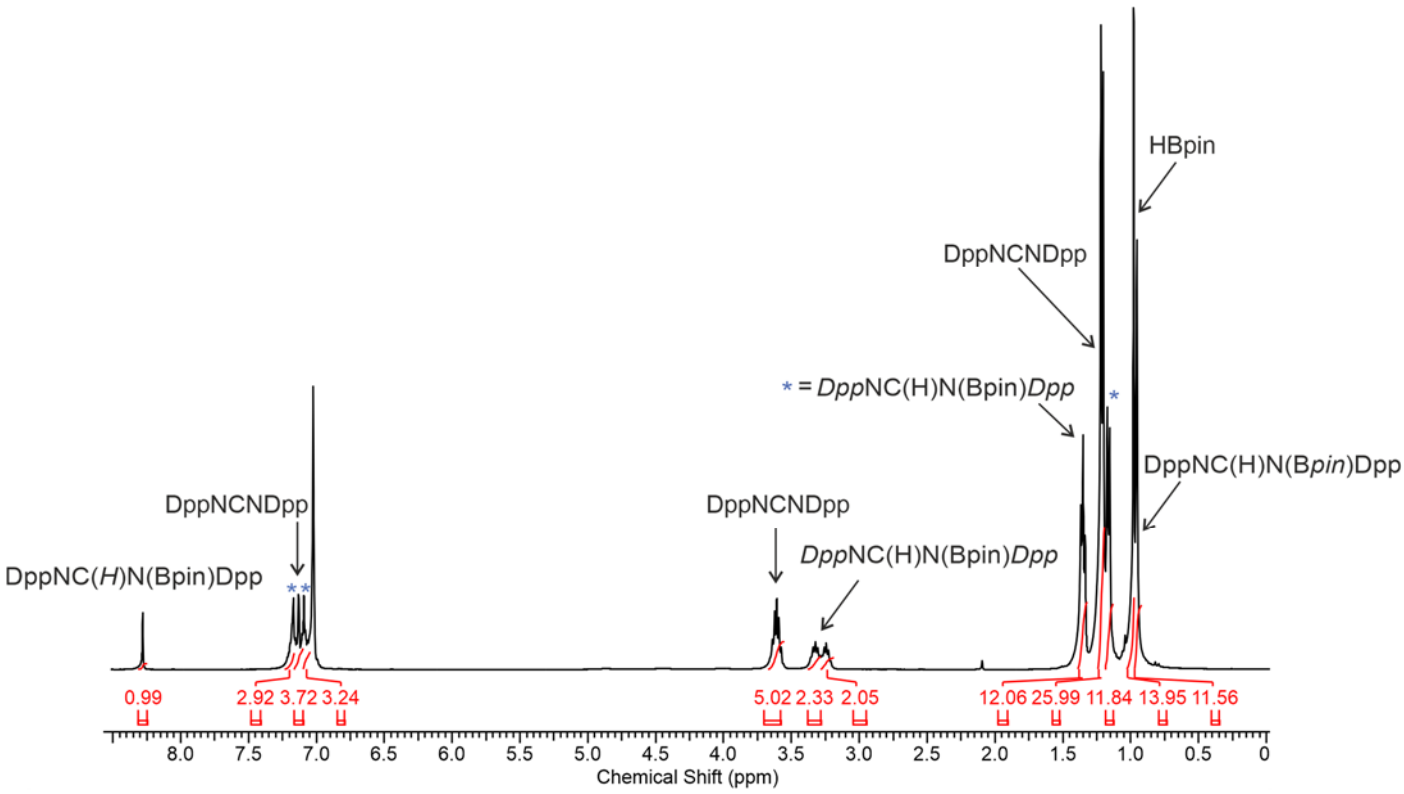


Figure S30. ^{1}H NMR spectrum of compound DppNC(H)N(Bpin)Dpp (Cat **1**, C_6D_6, 400 MHz, 21 °C).

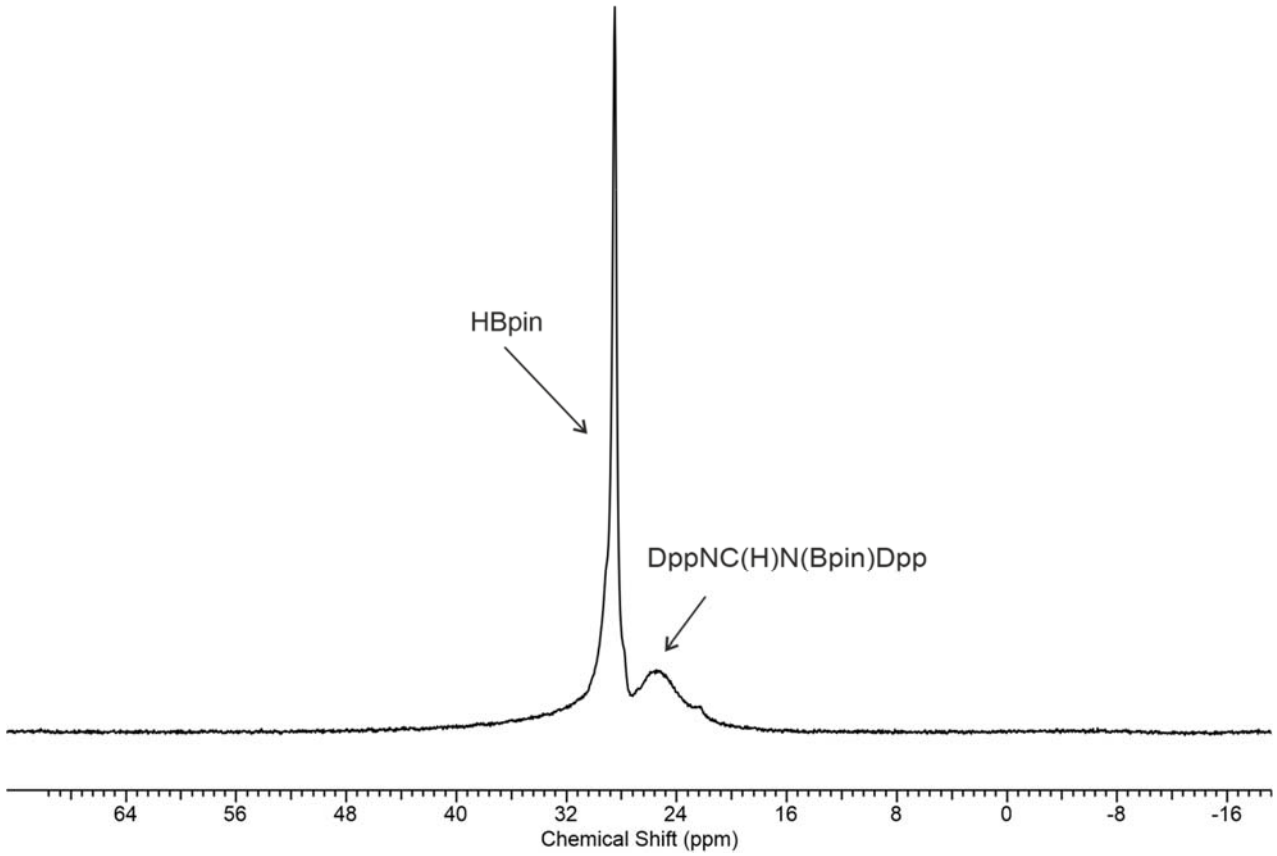


Figure S31. ^{11}B NMR spectrum of compound DppNC(H)N(Bpin)Dpp (Cat **1**, 128 MHz, C_6D_6, 21 °C)

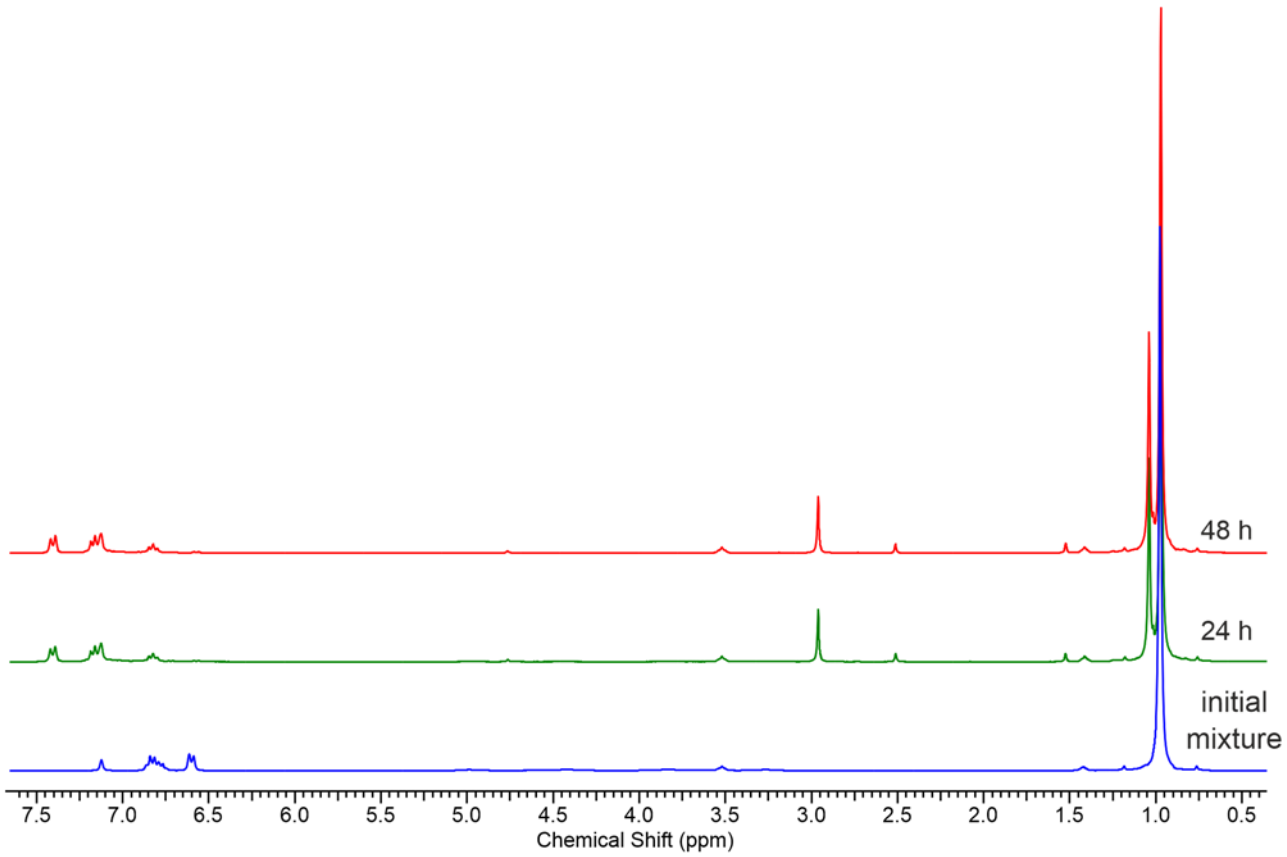


Figure S32. Spectrum of evolution of the reaction mixture (PhNCO + 3HBpin) over time (Cat **5**, C_6D_6, 300 MHz).

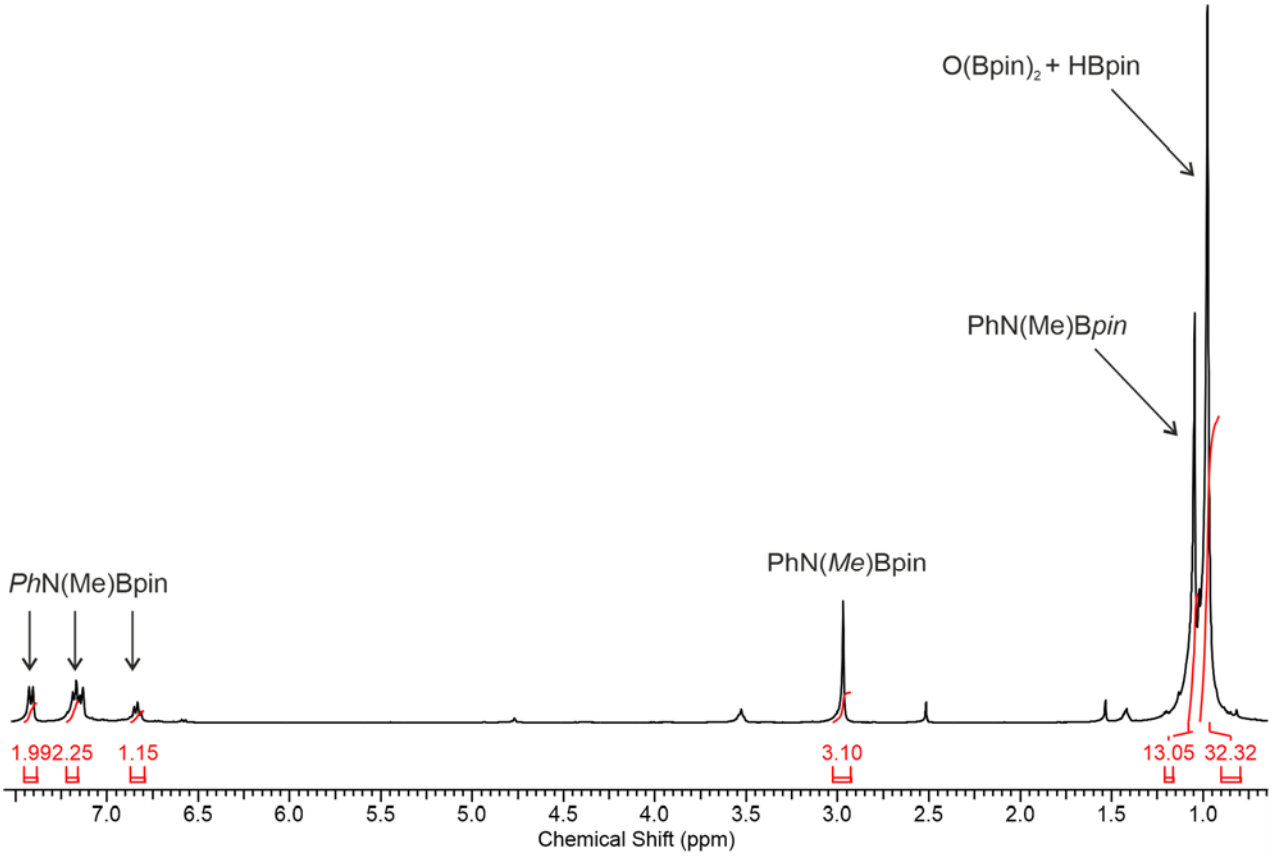


Figure S33. ^{1}H NMR spectrum of compound PhN(Me)Bpin (Cat **5**, C_6D_6, 400 MHz, 21 °C).

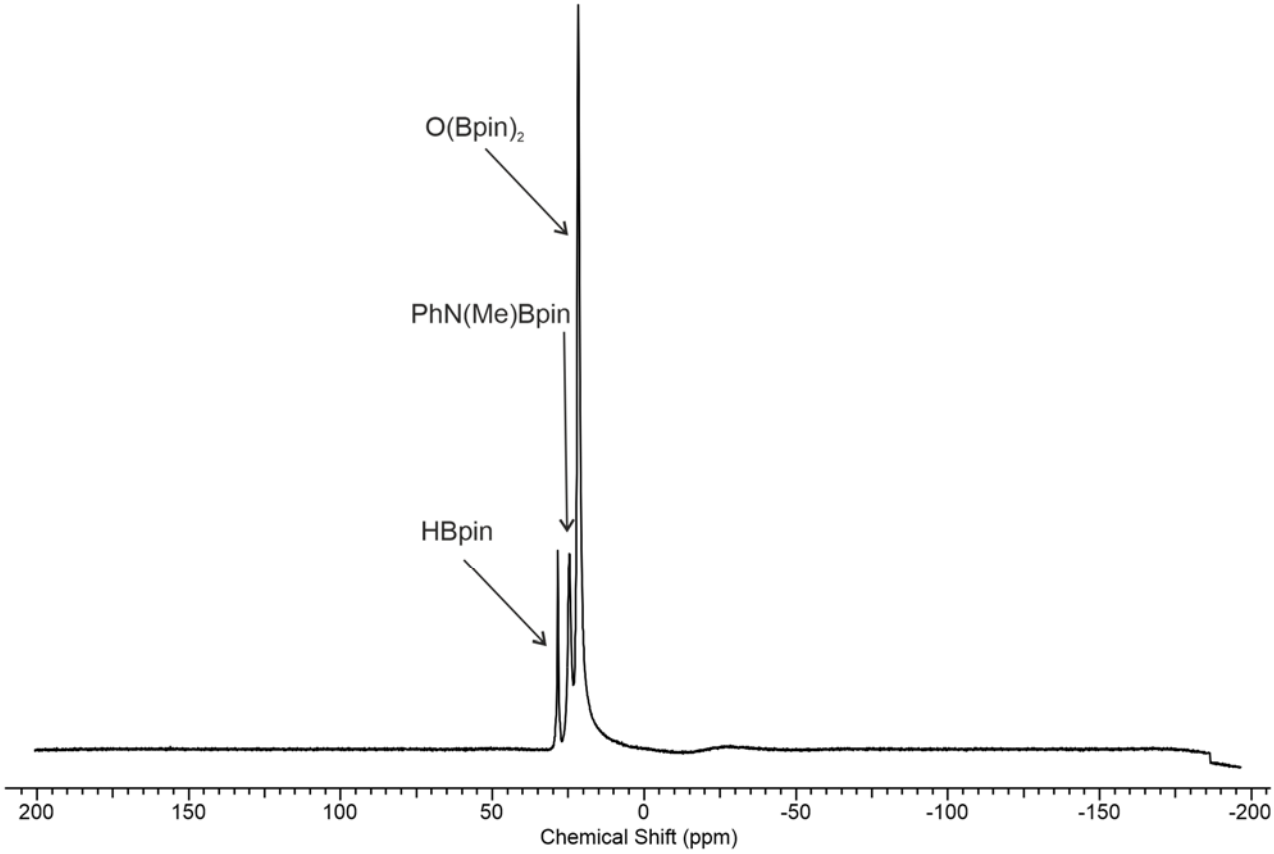


Figure S34. ^{11}B NMR spectrum of compound PhN(Me)Bpin (Cat **5**, 128 MHz, C_6D_6, 21 °C)