Electronic Supporting Information for

Hydroboration of terminal olefins with pinacolborane catalyzed by new 2-iminopyrrolyl iron(II) complexes

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^{1}H NMR spectra of complexes 1a-d and mixtures I and II

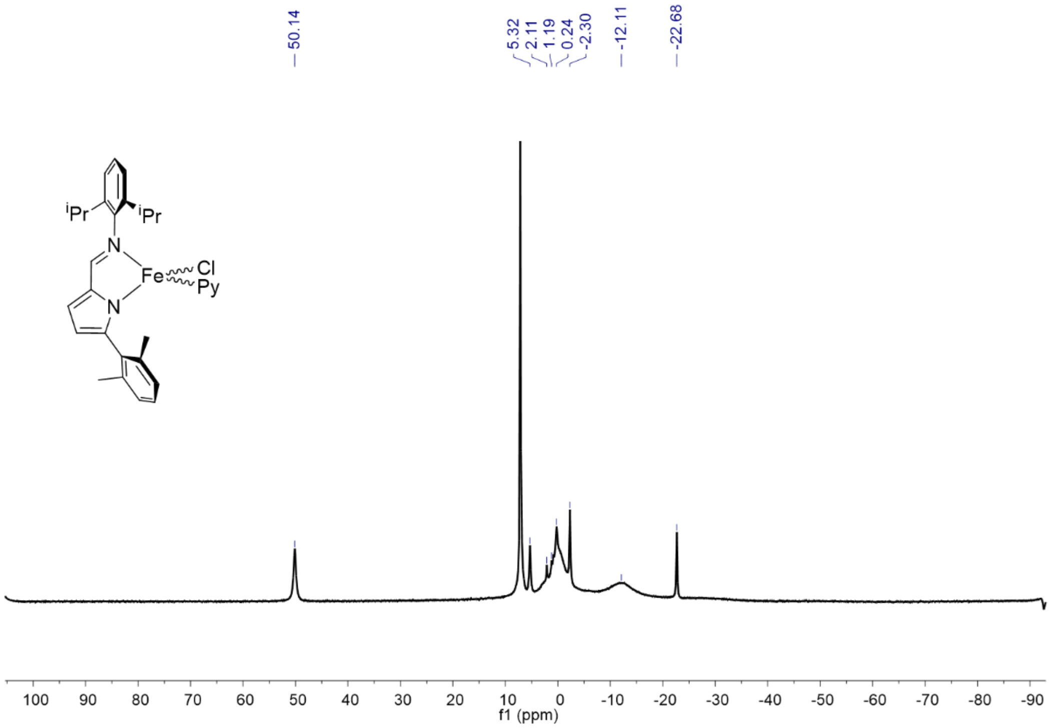

Figure S1 ^{1}H NMR spectrum (300 MHz, C_6D_6) of complex **1a**.

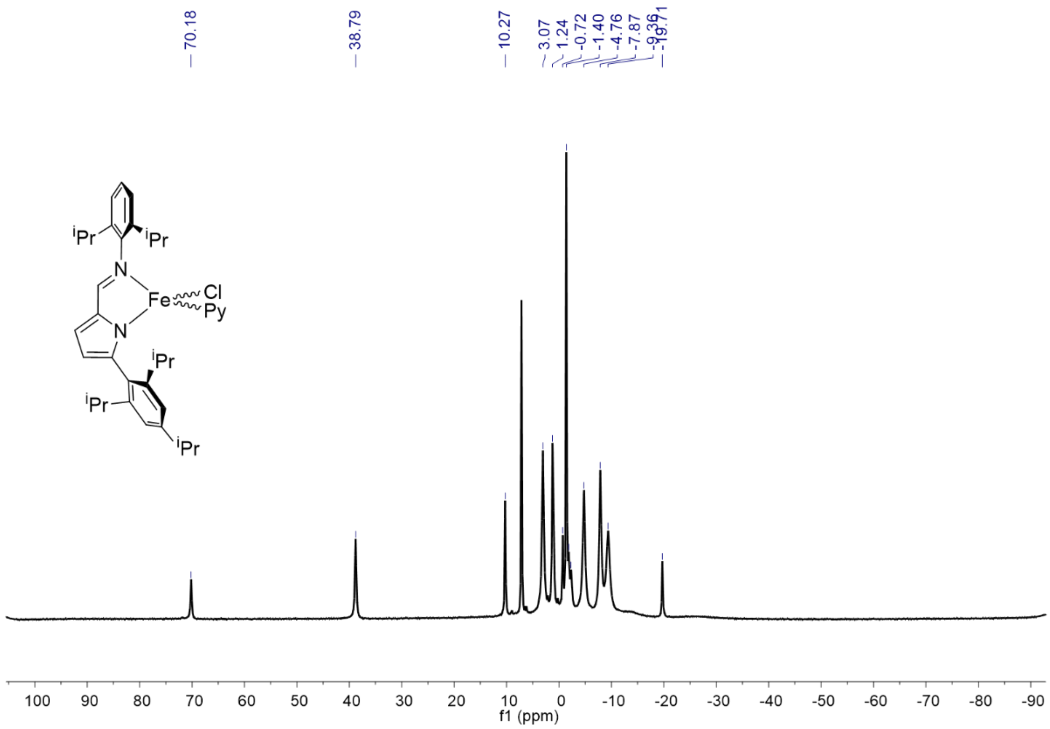

Figure S2 ^{1}H NMR spectrum (300 MHz, C_6D_6) of complex **1b**.

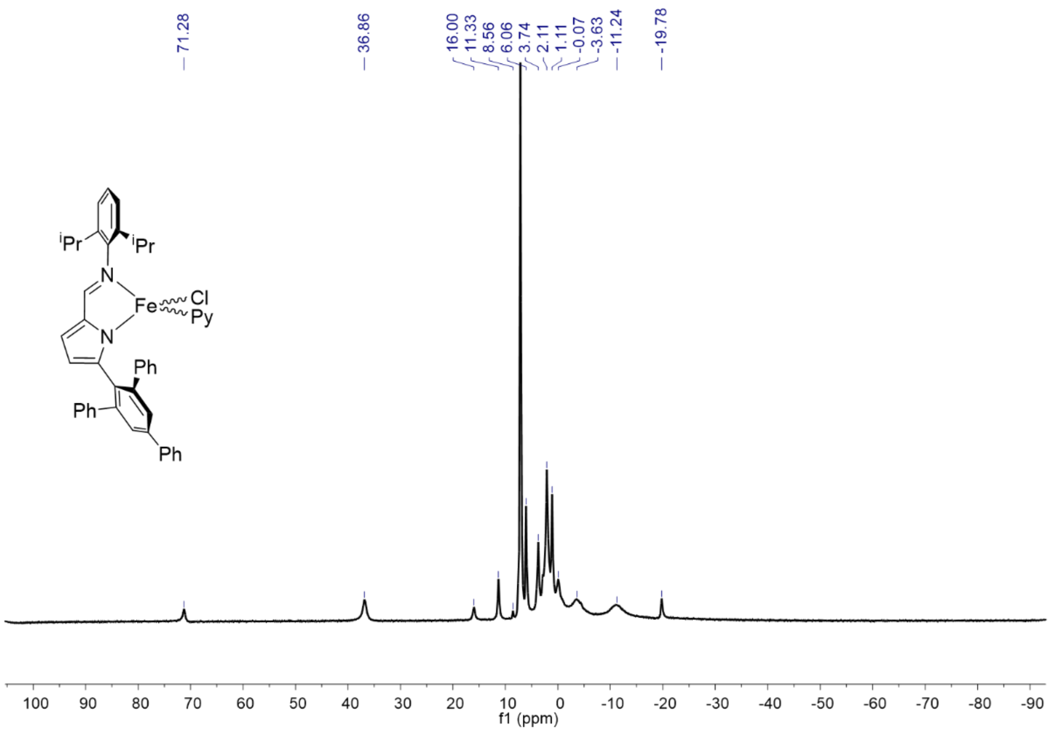

Figure S3 ^{1}H NMR spectrum (300 MHz, C_6D_6) of complex **1c**.

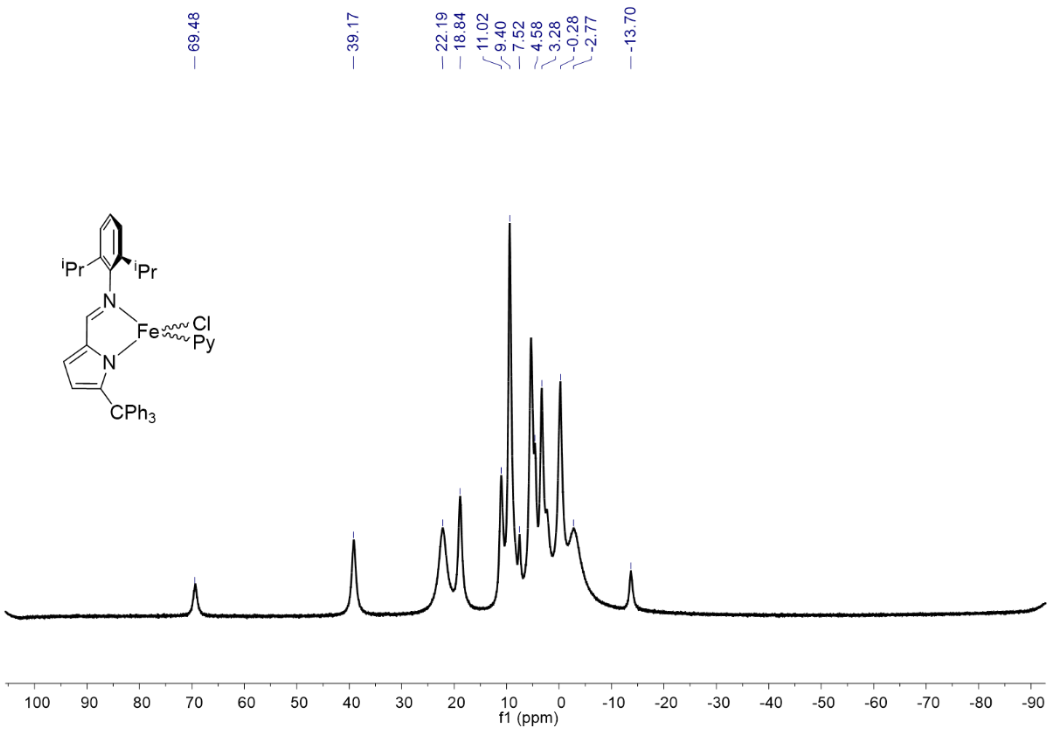

Figure S4 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of complex **1d**.

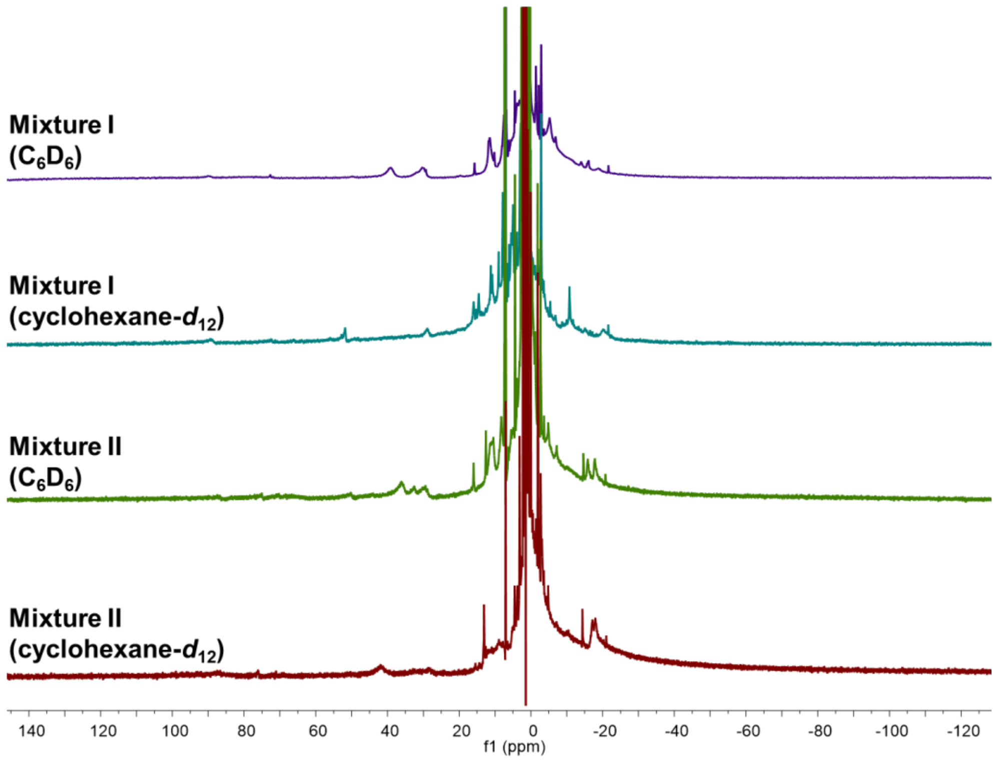

Figure S5 [1]H NMR spectra (300 MHz, C_6D_6 or cyclohexane-d_{12}) of fairly concentrated mixtures I and II, demonstrating their rather uninformative nature. The intense resonances observed correspond to the protio-residual resonance(s) of the respective deuterated solvents.

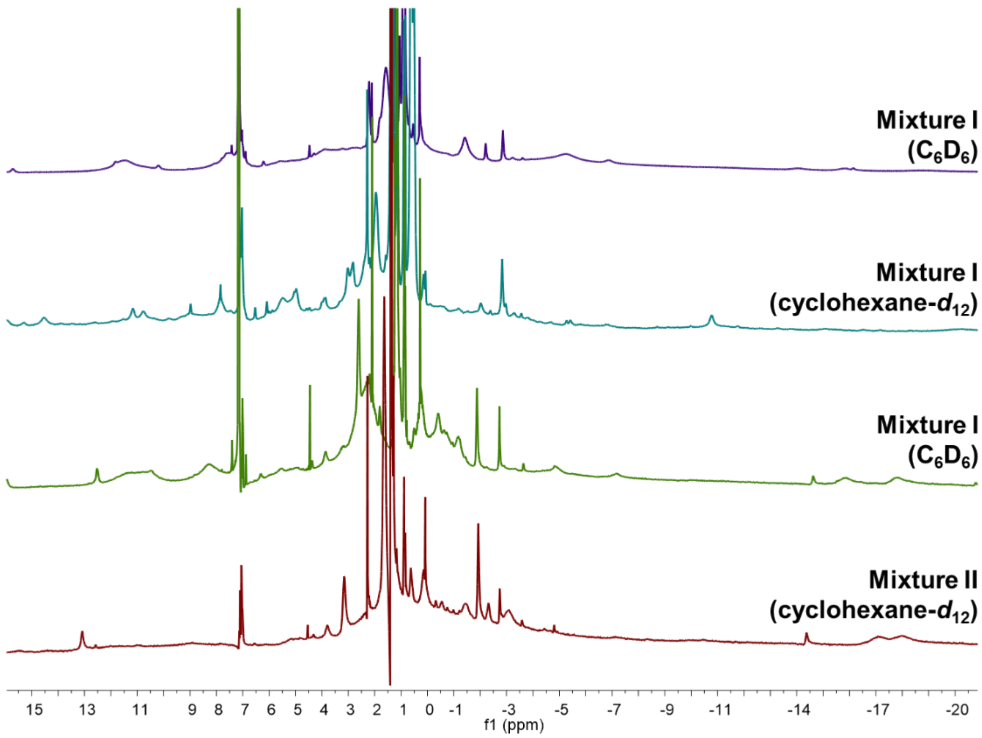

Figure S6 Magnification of the diamagnetic region of the [1]H NMR spectra (300 MHz, C_6D_6 or cyclohexane-d_{12}) of fairly concentrated mixtures I and II, demonstrating their rather uninformative nature. The intense resonances observed correspond to the protio-residual resonance(s) of the respective deuterated solvents.

FTIR spectra of complexes 1a-d and mixtures I and II

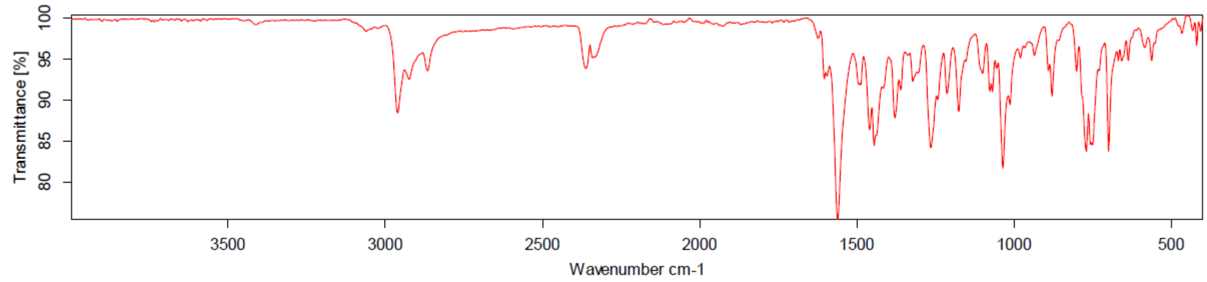

Figure S7 ATR-FTIR spectrum of complex **1a**.

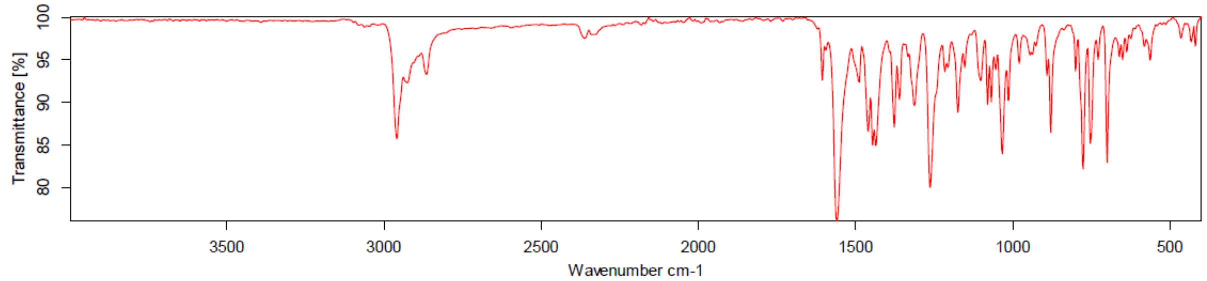

Figure S8 ATR-FTIR spectrum of complex **1b**.

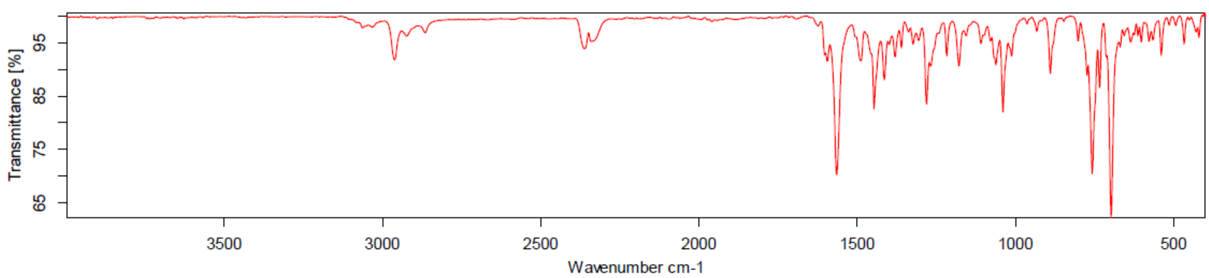

Figure S9 ATR-FTIR spectrum of complex **1c**.

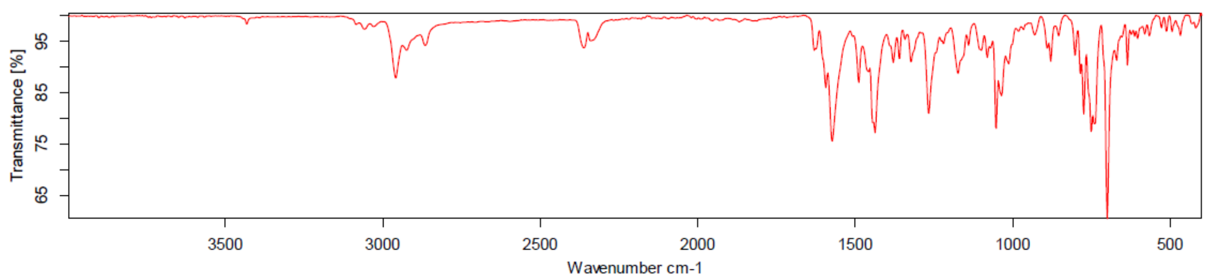

Figure S10 ATR-FTIR spectrum of complex **1d**.

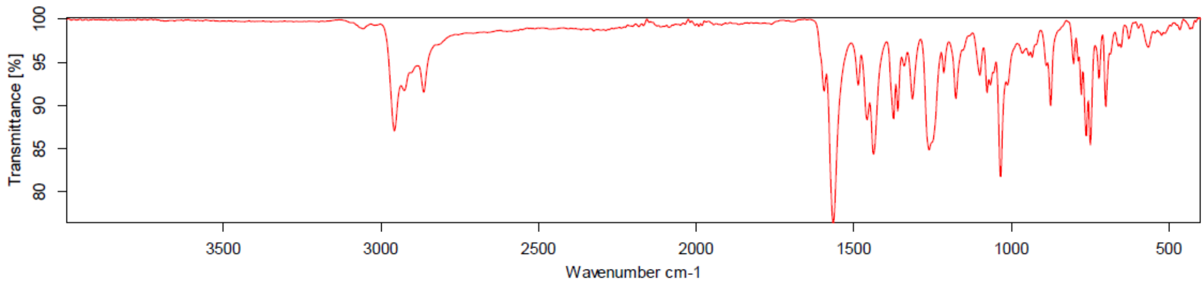

Figure S11 ATR-FTIR spectrum of the mixture of complexes isolated from the 30 min reaction of complex **1b** with $K(HBEt_3)$ in toluene (mixture I).

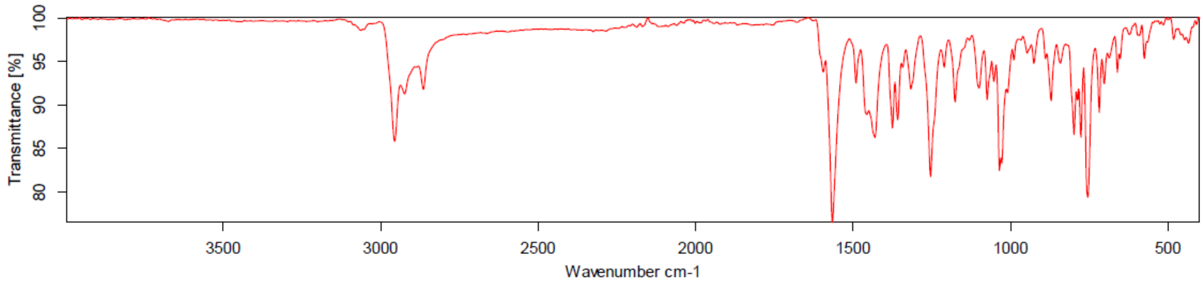

Figure S12 ATR-FTIR spectrum of the mixture of complexes isolated from the 16 h reaction of complex **1b** with $K(HBEt_3)$ in toluene (mixture II).

X-ray diffraction structure of complex 1c

Even though we obtained crystals of complex **1c** suitable for X-ray diffraction, they revealed to be of poor quality, presenting a relatively low ratio of observed/unique reflections. Although the structure of complex **1c** was refined to a perfect convergence, it is only presented in this section (Figure S6) as a proof of its connectivity (selected bond lengths and angles presented in Table S1).

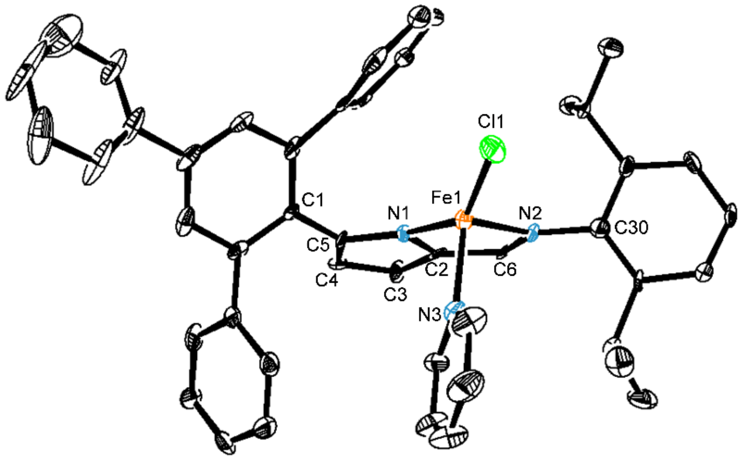

Figure S13 ORTEP-3 diagram for complex **1c** showing 30% probability ellipsoids. All hydrogen atoms were omitted for clarity.

Single crystal X-ray diffraction data

Table S1 Selected bond lengths (Å) and angles (º) for complexes **1a** and **1c**.

Bond lengths	**1a**	**1c**	*Bond angles*	**1a**	**1c**
Fe1−N1	2.0308(19)	2.001(6)	N1−Fe1−N3	103.96(7)	98.3(3)
Fe1−N2	2.112(2)	2.111(8)	N1−Fe1−N2	81.12(8)	82.2(3)
Fe1−N3	2.0917(18)	2.097(6)	N3−Fe1−N2	119.72(8)	105.1(3)
Fe1−Cl1	2.2345(7)	2.231(3)	N1−Fe1−Cl1	136.05(6)	144.00(19)
N1−C5	1.354(3)	1.374(9)	N3−Fe1−Cl1	104.85(5)	106.3(2)
N1−C2	1.378(3)	1.372(10)	N2−Fe1−Cl1	111.43(5)	115.17(19)
N2−C6	1.289(3)	1.309(9)	C5−N1−C2	107.64(18)	104.1(6)
N2−C_{ipso}	1.438(3)	1.446(9)	C6−N2−C_{ipso}	118.9(2)	118.3(7)
C4−C5	1.405(4)	1.375(11)	N1−C5−C4	109.1(2)	111.4(7)
C1−C5	1.479(3)	1.471(10)	N1−C5−C1	121.2(2)	119.9(7)
C2−C6	1.419(3)	1.435(10)	C4−C5−C1	129.6(2)	127.7(7)
C2−C3	1.401(3)	1.400(10)	N2−C6−C2	119.2(2)	118.5(8)
C3−C4	1.387(4)	1.388(10)	N1−C2−C3	109.3(2)	111.8(7)
			N1−C2−C6	117.9(2)	117.7(7)
			C3−C2−C6	132.8(2)	129.7(8)
			C4−C3−C2	106.4(2)	105.0(8)
			C3−C4−C5	107.5(2)	107.5(7)

Table S2 Selected bond lengths (Å) and angles (º) for complex **2_2**.

Bond lengths		*Bond angles*	
Fe1−N1	2.059(2)	N1−Fe1−N2	81.45(9)
Fe1−N2	2.155(2)	N1−Fe1−N3	93.81(9)
Fe1−N3	2.180(3)	N2−Fe1−N3	94.54(9)
Fe1−Fe2	2.4874(5)	N1−Fe1−H1A	174.1(11)
Fe1−H1A	1.69(3)	N2−Fe1−H1A	104.3(11)
Fe1−H1B	1.68(4)	N3−Fe1−H1A	86.9(11)
Fe2−N4	1.990(2)	N1−Fe1−H1B	100.2(13)
Fe2−N5	2.025(2)	N2−Fe2−H1B	126.2(13)
Fe2−H1A	1.55(3)	N3−Fe1−H1B	138.3(13)
Fe2−H1B	1.55(4)	H1A−Fe1−H1B	75.6(16)
N1−C5	1.354(4)	N4−Fe2−N5	82.13(9)
N1−C2	1.399(3)	N4−Fe2−H1A	96.7(12)
N2−C6	1.303(4)	N5−Fe2−H1A	171.7(12)
N2−C_{ipso}	1.435(4)	N4−Fe2−H1B	178.4(14)
C1−C5	1.484(4)	N5−Fe2−H1B	97.9(13)
C2−C3	1.382(4)	H1A−Fe2−H1B	83.5(17)
C2−C6	1.400(4)	C5−N1−C2	105.9(2)
C3−C4	1.377(4)	C6−N2−C_{ipso}	116.0(2)
C4−C5	1.402(4)	C3−C2−N1	109.8(2)
		C3−C2−C6	131.6(3)
		N1−C2−C6	118.6(2)
		C4−C3−C2	107.0(3)
		C3−C4−C5	107.2(3)
		N1−C5−C4	110.1(3)
		N1−C5−C1	126.1(3)
		C4−C5−C1	123.4(3)

Table S3 Selected bond lengths (Å) and angles (º) for complex **3**

Bond lengths		*Bond angles*	
Fe1−N1	1.971(7)	N1−Fe1−N2	82.7(3)
Fe1−N2	1.977(8)	N1−Fe1−C33	129.8(3)
Fe1−C33	2.110(11)	N2−Fe1−C36	125.5(3)
Fe1−C38	2.060(11)	C33−Fe1−C36	85.6(4)
Fe1−C37	2.110(11)	N2−Fe1−C33	99.8(4)
Fe1−C34	2.091(8)	N1−Fe1−C36	119.1(4)
Fe1−C36	2.149(10)	C5−N1−C2	108.2(7)
Fe1−C35	2.062(8)	N1−C2−C3	109.3(8)
N1−C5	1.383(11)	N1−C2−C6	115.1(8)
N1−C2	1.369(12)	C3−C2−C6	135.6(10)
N2−C6	1.293(11)	C4−C3−C2	107.6(9)
N2−C_{ipso}	1.443(11)	C3−C4−C5	107.2(8)
C1−C5	1.456(13)	N1−C5−C1	125.2(8)
C2−C3	1.368(12)	N1−C5−C4	107.7(9)
C2−C6	1.423(12)	N2−C6−C2	117.9(10)
C3−C4	1.401(15)		
C4−C5	1.398(12)		

Table S4 Crystallographic data for compounds **1a**, **1c, $\mathbf{2_2}$** and **3**.

	1a	**1c**	$\mathbf{2_2}$	**3**
Formula	$C_{30}H_{34}ClFeN_3$	$C_{46}H_{42}ClFeN_3$	$C_{69}H_{93}Fe_2N_5$	$C_{39}H_{51}FeN_2$
M	527.90	728.12	1104.18	603.66
λ (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	150	150	150	150
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1$	$P2_1/c$	P-1	P-1
a (Å)	8.9968(3)	20.583(4)	14.0411(13)	9.606(6)
b (Å)	18.4440(8)	11.705(3)	16.3354(14)	10.504(6)
c (Å)	9.3737(4)	19.314(4)	17.4433(18)	17.317(10)
α (Å)	90	90	107.001(4)	103.90(2)
β (Å)	117.856(2)	116.648(6)	92.917(4)	93.89(3)
γ (Å)	90	90	100.939(4)	91.43(3)
V ($Å^3$)	1375.21	4158.8(16)	3732.4(6)	1690.7(18)
Z	2	4	2	2
ρ_{calc} ($g.cm^{-3}$)	1.275	1.163	0.983	1.186
μ (mm^{-1})	0.668	0.460	0.425	0.474
Crystal size	0.20×0.10×0.10	0.20×0.20×0.20	0.30×0.20×0.20	0.05×0.05×0.1
θ_{max} (º)	35.804	25.706	25.61	25.91
Total data	26240	11858	14088	9187
Unique data	12266	7745	9548	5568
R_{int}	0.0398	0.1008	0.0483	0.0724
R [$I > 2\sigma(I)$]	0.0452	0.1008	0.0562	0.1314
R_w	0.0805	0.2386	0.1530	0.3289
Goodness of fit	0.980	0.854	1.015	1.122
ρ_{min}	-0.445	-0.494	-0.496	-0.770
ρ_{max}	0.431	0.515	0.637	1.443

SQUID Magnetometry data for complex 1a

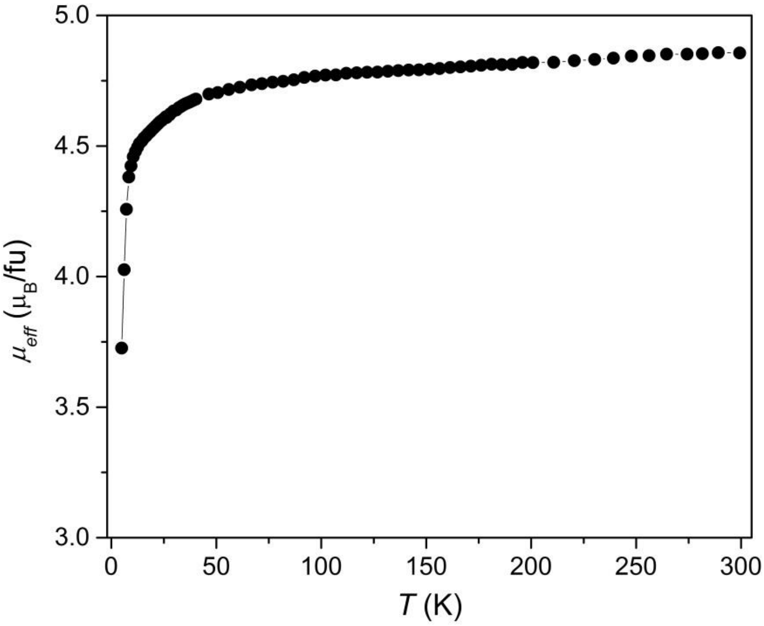

Figure S14 Temperature dependence of the effective magnetic moment, μ_{eff}, of complex **1a** taken at 500 Oe.

^{57}Fe Mössbauer spectroscopy data of complex 1a and mixtures I and II

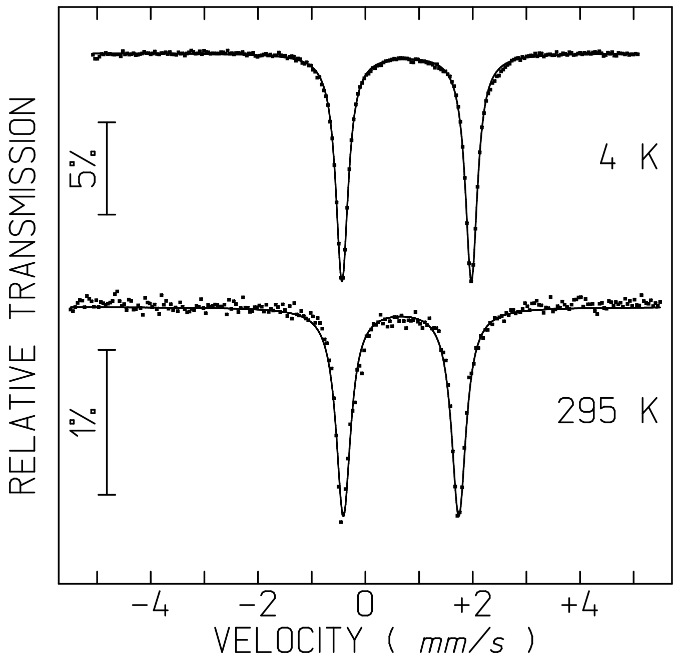

Figure S15 Mössbauer spectra of complex **1a** at 4 and 295 K. Lines over the experimental points are the calculated doublets by the refinement procedure (Table S2).

Table S5 Estimated parameters from the Mössbauer spectra of complex **1a** taken at 4 and 230 K.[d]

T	IS [a]	QS [b]	Fe species, S [c]
4 K	0.88	2.41	Fe(II) (S=2)
295 K	0.77	2.16	Fe(II) (S=2)

[a] IS, Isomer shift (mm s^{-1}) relative to metallic α-Fe at 295 K. [b] QS, Quadrupole splitting (mm s^{-1}). [c] S, spin quantum number. [d] Estimated errors are ≤ 0.02 mm s^{-1} for IS and QS.

Table S3 Estimated parameters from the Mössbauer spectra of the isolated mixtures of complexes, taken at different temperatures (T), from the reaction of complex **1b** with $K(HBEt_3)$ in toluene at different reaction times.

Catalyst	Reaction time	T	IS [a]	QS (ε) [b]	I [c]	Fe species [d]
Mixture I	30 min	4 K	0.69	3.08	33%	Fe(II), CN=4, dimer (**2**$_2$)
			0.96	1.92	32%	Fe(II), CN=5, dimer (**2**$_2$)
			0.63	1.93	35%	Fe(II), CN=4, monomer (**2**)
		150 K	0.65	2.84	32%	Fe(II), CN=4, dimer (**2**$_2$)
			0.88	1.80	31%	Fe(II), CN=5, dimer (**2**$_2$)
			0.65	1.90	37%	Fe(II), CN=4, monomer (**2**)
		230 K	0.57	2.64	30%	Fe(II), CN=4, dimer (**2**$_2$)
			0.81	1.70	31%	Fe(II), CN=5, dimer (**2**$_2$)
			0.62	1.78	39%	Fe(II), CN=4, monomer (**2**)
Mixture II	16 h	4 K	0.69	3.10	28%	Fe(II), CN=4, dimer (**2**$_2$)
			1.06	2.08	29%	Fe(II), CN=5, dimer (**2**$_2$)
			0.60	1.99	34%	Fe(II), CN=4, monomer (**2**)
			0.34	1.66	10%	Fe(I) (**3**)
		150 K	0.68	2.89	28%	Fe(II), CN=4, dimer (**2**$_2$)
			0.96	1.82	28%	Fe(II), CN=5, dimer (**2**$_2$)
			0.59	1.89	38%	Fe(II), CN=4, monomer (**2**)
			0.34	1.48	6%	Fe(I) (**3**)

[a] IS, Isomer shift (mm s^{-1}) relative to metallic α-Fe at 295 K. [b] QS, Quadrupole splitting (mm s^{-1}). [c] I, relative areas. [d] CN, coordination number. [e] Estimated errors are ≤ 0.02 mm s^{-1} for IS and QS and ≤ 2% for *I*.

Atomic coordinates for the DFT optimized complexes

1a (*S* = 2)

Fe	3.023344000	9.420131000	2.770009000
Cl	1.189648000	8.748725000	3.882604000
N	3.970792000	8.979333000	1.034637000
N	4.572156000	9.395279000	4.291862000
N	2.864989000	11.364702000	1.825650000
C	2.156543000	12.550039000	2.180754000
C	4.541387000	7.941822000	0.360825000
C	4.592092000	6.562917000	0.909026000
C	3.467350000	11.305007000	0.659066000
H	3.491718000	12.179105000	-0.001128000
C	2.778564000	13.521404000	3.007249000
C	4.072375000	10.095673000	0.223621000
C	3.402998000	5.792746000	0.992869000
C	0.823740000	12.726196000	1.720974000
C	4.278037000	9.037879000	5.559385000
H	3.227134000	8.832250000	5.758221000
C	0.112176000	11.695187000	0.852198000
H	0.748329000	10.802731000	0.812204000
C	2.056690000	14.678272000	3.333672000
H	2.524874000	15.442364000	3.953447000
C	4.723889000	9.759954000	-0.978258000
H	4.935277000	10.429808000	-1.806983000
C	5.247395000	8.929848000	6.555092000
H	4.952087000	8.638402000	7.561713000
C	0.756312000	14.876713000	2.875026000
H	0.213622000	15.784851000	3.138640000
C	5.023401000	8.395411000	-0.887938000
H	5.514123000	7.780195000	-1.635411000
C	5.830503000	6.009410000	1.323710000
C	0.152804000	13.904283000	2.081233000
H	-0.866199000	14.062665000	1.729971000
C	5.861570000	9.647968000	3.989191000
H	6.062325000	9.928141000	2.956602000
C	4.680451000	3.963069000	1.972218000
H	4.712880000	2.957362000	2.392564000
C	5.177307000	14.295220000	2.783494000
H	6.210379000	14.119305000	3.114095000
H	5.141869000	14.149501000	1.696809000
H	4.939428000	15.348363000	2.982367000
C	5.850246000	4.713016000	1.859548000
H	6.799384000	4.289116000	2.190498000
C	4.205357000	13.351772000	3.510214000
H	4.505959000	12.325448000	3.268143000
C	6.580907000	9.194993000	6.235945000
H	7.361888000	9.117112000	6.992117000
C	2.076943000	6.315984000	0.504170000
H	2.191425000	6.943247000	-0.386996000
H	1.403440000	5.487185000	0.256776000
H	1.577995000	6.923334000	1.270362000
C	3.471415000	4.498936000	1.531474000
H	2.559325000	3.904717000	1.598263000
C	4.315463000	13.503330000	5.034214000
H	5.334498000	13.265792000	5.368104000
H	4.096000000	14.525675000	5.367544000
H	3.622714000	12.828286000	5.551094000
C	7.131781000	6.758796000	1.185201000
H	7.005666000	7.839081000	1.304272000
H	7.864669000	6.410266000	1.922850000
H	7.573175000	6.600720000	0.190595000
C	6.891080000	9.559949000	4.923769000
H	7.914603000	9.774923000	4.620735000
C	-1.230269000	11.249798000	1.451558000
H	-1.103049000	10.882933000	2.475751000
H	-1.968868000	12.061594000	1.466284000
H	-1.655234000	10.433500000	0.852581000
C	-0.062436000	12.195344000	-0.591043000
H	-0.528458000	11.418911000	-1.212564000
H	-0.703252000	13.085912000	-0.634869000
H	0.898899000	12.458971000	-1.048986000

1b (*S* = 2)

Fe	3.341023000	9.453877000	2.978572000
Cl	1.741551000	8.644358000	4.328396000

N	4.176488000	9.018595000	1.186382000
N	4.982718000	9.827182000	4.351808000
N	2.990339000	11.366362000	2.003103000
C	2.203994000	12.502965000	2.352061000
C	4.732104000	7.999763000	0.468052000
C	4.701707000	6.573972000	0.899420000
C	3.621781000	11.345324000	0.851799000
H	3.612074000	12.220673000	0.192610000
C	2.798679000	13.640766000	2.956959000
C	4.281402000	10.164614000	0.413142000
C	3.517062000	5.812876000	0.701219000
C	0.805896000	12.457219000	2.099465000
C	4.808293000	9.680311000	5.682293000
H	3.810136000	9.376670000	5.994649000
C	0.149549000	11.259416000	1.424541000
H	0.873353000	10.434970000	1.453777000
C	1.972882000	14.727847000	3.281450000
H	2.414278000	15.613022000	3.738486000
C	4.936568000	9.871178000	-0.796837000
H	5.151143000	10.570168000	-1.600336000
C	5.830341000	9.895738000	6.605022000
H	5.630208000	9.762701000	7.666995000
C	0.603560000	14.703098000	3.031062000
H	-0.017894000	15.560381000	3.290974000
C	5.223140000	8.501485000	-0.758717000
H	5.703270000	7.910619000	-1.531878000
C	5.855290000	5.947791000	1.435799000
C	0.033178000	13.574040000	2.446557000
H	-1.037912000	13.561542000	2.249425000
C	6.204792000	10.191359000	3.912616000
H	6.314213000	10.292088000	2.834205000
C	4.624706000	3.830435000	1.637173000
C	4.994428000	14.752744000	2.351084000
H	6.077343000	14.753524000	2.537000000
H	4.835606000	14.534443000	1.287882000
H	4.626128000	15.770172000	2.535925000
C	5.786492000	4.592739000	1.791855000
H	6.672015000	4.109358000	2.205955000
C	4.290463000	13.723983000	3.250590000
H	4.719661000	12.742814000	3.019101000
C	7.092476000	10.277140000	6.144165000
H	7.911899000	10.452945000	6.840816000
C	2.285034000	6.395926000	0.014200000
H	2.441278000	7.477739000	-0.074210000
C	3.506731000	4.464649000	1.081741000
H	2.594174000	3.890294000	0.928797000
C	4.573889000	13.999852000	4.735162000
H	5.652983000	13.954528000	4.934139000
H	4.227346000	14.994384000	5.043434000
H	4.078437000	13.261653000	5.376861000
C	7.175953000	6.690565000	1.608271000
H	6.975318000	7.752942000	1.415282000
C	7.279633000	10.425679000	4.767992000
H	8.243733000	10.716987000	4.354141000
C	-1.106384000	10.768541000	2.157201000
H	-0.893846000	10.565750000	3.212504000
H	-1.931874000	11.490030000	2.103309000
H	-1.462567000	9.834682000	1.702964000
C	-0.146021000	11.551215000	-0.056143000
H	-0.568365000	10.663834000	-0.546744000
H	-0.868680000	12.370689000	-0.165585000
H	0.761491000	11.836002000	-0.602357000
C	8.214213000	6.234856000	0.570138000
H	9.142857000	6.813652000	0.669705000
H	8.467566000	5.173939000	0.694942000
H	7.841904000	6.368644000	-0.452319000
C	7.739129000	6.579882000	3.032596000
H	6.997293000	6.880998000	3.781365000
H	8.055928000	5.557080000	3.272770000
H	8.620987000	7.224872000	3.146297000
C	2.150312000	5.846310000	-1.415653000
H	3.052776000	6.046714000	-2.005907000
H	1.984243000	4.760979000	-1.417366000
H	1.299997000	6.315206000	-1.929441000
C	0.990443000	6.195754000	0.814554000
H	0.699981000	5.139205000	0.880557000
H	1.085562000	6.584358000	1.834324000
H	0.161631000	6.726234000	0.326381000
C	4.597795000	2.366684000	2.053560000
H	5.601723000	2.132504000	2.441828000

C	3.603621000	2.111566000	3.196229000
H	2.569124000	2.303704000	2.884226000
H	3.659872000	1.067804000	3.533764000
H	3.815172000	2.758873000	4.056359000
C	4.348215000	1.427279000	0.864364000
H	5.083224000	1.593339000	0.066847000
H	4.420203000	0.377257000	1.178639000
H	3.349844000	1.573731000	0.432681000

1c (*S* = 2)

Fe	8.573410000	2.325109000	14.275878000
Cl	8.057435000	2.481468000	12.094188000
N	9.290436000	0.938489000	15.567984000
N	10.274061000	3.464038000	15.028041000
C	10.811318000	2.766631000	16.001785000
H	11.679393000	3.149816000	16.549600000
N	6.851068000	3.252704000	15.213863000
C	8.186749000	-1.282878000	15.291996000
C	9.124856000	-0.350637000	15.977728000
C	10.882277000	4.693693000	14.637209000
C	6.630506000	3.157331000	16.540751000
H	7.355435000	2.575374000	17.106895000
C	10.030195000	-0.635373000	17.022595000
H	10.140000000	-1.590551000	17.524795000
C	8.580481000	-1.877606000	14.062369000
C	10.579789000	5.900973000	15.319894000
C	11.214128000	7.079228000	14.897318000
H	11.002673000	8.013244000	15.417058000
C	6.377977000	-2.930134000	13.813244000
C	11.788848000	4.681573000	13.543044000
C	6.353316000	-1.056524000	17.091663000
C	6.886063000	-1.561623000	15.792371000
C	9.610445000	5.955742000	16.493690000
H	9.137844000	4.969896000	16.568134000
C	9.945039000	-1.730507000	13.473310000
C	10.314660000	1.475666000	16.330291000
C	6.013541000	-2.371701000	15.045871000
H	5.036921000	-2.604493000	15.467857000
C	11.071673000	-2.272130000	14.117053000
H	10.955028000	-2.752244000	15.086603000
C	10.114030000	-1.147672000	12.204673000
H	9.253912000	-0.716321000	11.694886000
C	5.960005000	3.944842000	14.472459000
H	6.166911000	3.983720000	13.404003000
C	12.158407000	3.396100000	12.814117000
H	11.446330000	2.623823000	13.130338000
C	12.330798000	-2.224397000	13.514493000
H	13.190040000	-2.657510000	14.027642000
C	12.389898000	5.891058000	13.166951000
H	13.098191000	5.896822000	12.339416000
C	12.112489000	7.082482000	13.833557000
H	12.594947000	8.010265000	13.524917000
C	12.030396000	3.516741000	11.289476000
H	11.026610000	3.849076000	11.003012000
H	12.204657000	2.538943000	10.822674000
H	12.760452000	4.215753000	10.861444000
C	10.785552000	0.520653000	17.248047000
H	11.589525000	0.655290000	17.965855000
C	8.485996000	6.978062000	16.270925000
H	8.861813000	8.008877000	16.255720000
H	7.745429000	6.914129000	17.079259000
H	7.968805000	6.798195000	15.321110000
C	12.488347000	-1.636285000	12.255774000
H	13.471005000	-1.603013000	11.784329000
C	5.538984000	3.752476000	17.171088000
H	5.413444000	3.637613000	18.246079000
C	4.557177000	0.050711000	18.323964000
H	3.614391000	0.598719000	18.313858000
C	7.674755000	-2.674940000	13.347040000
H	7.997775000	-3.098926000	12.397415000
C	4.083852000	-3.409672000	12.901260000
H	3.734776000	-2.476831000	13.343502000
C	10.337362000	6.214008000	17.823368000
H	11.106658000	5.456396000	18.016313000
H	9.628459000	6.195470000	18.662567000
H	10.832642000	7.193686000	17.828915000
C	11.375097000	-1.097202000	11.604455000
H	11.483577000	-0.634830000	10.623025000
C	4.625148000	4.475156000	16.401590000
H	3.761657000	4.953533000	16.863707000

C	13.559966000	2.913203000	13.222219000
H	14.335039000	3.630340000	12.920401000
H	13.786837000	1.949814000	12.747127000
H	13.639728000	2.777364000	14.307767000
C	5.866639000	-4.970148000	12.430628000
H	6.901975000	-5.289053000	12.548508000
C	6.381149000	-0.970020000	19.529901000
H	6.867092000	-1.232458000	20.470107000
C	4.842346000	4.567213000	15.024610000
H	4.158693000	5.113996000	14.377052000
C	5.177520000	-0.258858000	19.537846000
H	4.722522000	0.041895000	20.481987000
C	5.139877000	-0.342267000	17.116319000
H	4.653535000	-0.090450000	16.173881000
C	5.435440000	-3.778019000	13.043304000
C	6.958870000	-1.368897000	18.322063000
H	7.872819000	-1.956627000	18.334824000
C	4.978652000	-5.763999000	11.702021000
H	5.333359000	-6.687334000	11.243167000
C	3.639626000	-5.384431000	11.568729000
H	2.947010000	-6.003691000	10.998514000
C	3.196508000	-4.203400000	12.171784000
H	2.156816000	-3.892247000	12.065986000

1d (*S* = 2)

Fe	3.851317000	5.323730000	2.110273000
Cl	2.534339000	6.252710000	0.525599000
C	3.806101000	1.482026000	4.344982000
C	6.529037000	5.051103000	1.249736000
H	7.532633000	5.174084000	0.826895000
C	3.490533000	1.485251000	2.823744000
C	5.684159000	1.520529000	1.350441000
H	5.790462000	0.456288000	1.183316000
C	6.010909000	3.733967000	1.363921000
C	4.628104000	2.155741000	2.041242000
C	4.894155000	2.173467000	4.900613000
H	5.546492000	2.756951000	4.255675000
C	3.019757000	0.701233000	5.217201000
H	2.200986000	0.107831000	4.812950000
C	6.564644000	2.518499000	0.927389000
H	7.488327000	2.392189000	0.370140000
C	6.491332000	8.138033000	0.444813000
C	1.859369000	2.508982000	1.159716000
H	2.593010000	2.287135000	0.386034000
C	1.205373000	2.557197000	3.473393000
H	1.405629000	2.378380000	4.526577000
C	2.164189000	2.217513000	2.505101000
C	7.049060000	7.874473000	2.839557000
C	4.400156000	-0.907169000	2.840110000
H	5.213871000	-0.538911000	3.462544000
C	7.660843000	9.135014000	2.808495000
H	8.125680000	9.526390000	3.712552000
C	5.170629000	2.110856000	6.272968000
H	6.033447000	2.649124000	6.667982000
C	2.348009000	-0.545429000	1.642871000
H	1.536415000	0.097124000	1.311678000
C	6.466115000	7.375291000	1.643131000
C	3.397538000	-0.015273000	2.407437000
C	6.973794000	7.232336000	-1.869827000
H	7.593900000	8.089753000	-2.163794000
H	6.516857000	6.823671000	-2.781143000
H	7.645256000	6.467324000	-1.461185000
C	7.120946000	9.392391000	0.477436000
H	7.158527000	9.988951000	-0.433295000
C	7.075115000	7.046791000	4.118792000
H	6.327668000	6.252388000	3.997600000
C	4.370693000	-2.259313000	2.496062000
H	5.166379000	-2.918530000	2.844888000
C	-0.319974000	3.374127000	1.771401000
H	-1.275293000	3.816555000	1.489255000
C	5.885780000	7.639709000	-0.862157000
H	5.293238000	6.747073000	-0.632452000
C	3.284290000	0.648950000	6.587007000
H	2.652957000	0.036656000	7.231892000
C	-0.020643000	3.127704000	3.111653000
H	-0.742378000	3.378416000	3.890037000
C	4.363269000	1.357311000	7.126240000
H	4.580794000	1.305639000	8.193352000
C	0.632782000	3.067863000	0.796334000
H	0.433110000	3.282542000	-0.252756000

C	3.324006000	-2.767846000	1.720722000
H	3.294632000	-3.824943000	1.455652000
C	7.700913000	9.893240000	1.639920000
H	8.185097000	10.870219000	1.635280000
C	2.312076000	-1.903410000	1.302978000
H	1.478423000	-2.281078000	0.709961000
C	6.687558000	7.848898000	5.368755000
H	7.446396000	8.595164000	5.636376000
H	6.581243000	7.177547000	6.231317000
H	5.735680000	8.374483000	5.229688000
C	8.438991000	6.362136000	4.309782000
H	8.697354000	5.729429000	3.452596000
H	8.433324000	5.726799000	5.206369000
H	9.241470000	7.102078000	4.428484000
C	4.916772000	8.654681000	-1.485791000
H	4.139783000	8.948204000	-0.771827000
H	4.416411000	8.207728000	-2.354401000
H	5.427403000	9.562261000	-1.833230000
N	4.816556000	3.509749000	2.031785000
N	5.850311000	6.089686000	1.675898000
N	3.112365000	6.215724000	3.904997000
C	2.502453000	7.418497000	3.818169000
C	3.150151000	5.614948000	5.112822000
C	1.923724000	8.050977000	4.915733000
C	2.593356000	6.179867000	6.258473000
C	1.967078000	7.424204000	6.164012000
H	2.476748000	7.864072000	2.825277000
H	3.640356000	4.645106000	5.154817000
H	1.446341000	9.020567000	4.783605000
H	2.654514000	5.642688000	7.203596000
H	1.522179000	7.894072000	7.040930000

2 (*S* = 2)

Fe	3.179530000	9.418875000	2.811365000
H	1.869852000	8.726472000	3.508130000
N	4.157406000	9.014592000	1.057755000
N	4.508303000	9.698656000	4.450871000
N	2.996086000	11.367524000	1.897978000
C	2.308293000	12.545312000	2.302902000
C	4.705189000	8.000126000	0.332060000
C	4.742294000	6.584603000	0.795785000
C	3.610060000	11.343601000	0.734235000
H	3.617389000	12.229656000	0.089515000
C	3.019249000	13.669603000	2.802875000
C	4.234793000	10.155328000	0.273854000
C	3.583667000	5.771008000	0.668190000
C	0.889173000	12.561880000	2.217520000
C	3.977841000	9.602215000	5.690817000
H	2.907835000	9.395464000	5.724332000
C	0.104900000	11.380786000	1.659735000
H	0.801668000	10.535472000	1.586064000
C	2.284801000	14.804602000	3.180000000
H	2.814916000	15.680583000	3.553303000
C	4.857472000	9.859882000	-0.954576000
H	5.047014000	10.556107000	-1.766765000
C	4.733742000	9.742279000	6.850912000
H	4.247339000	9.659622000	7.821689000
C	0.896006000	14.841345000	3.085943000
H	0.348849000	15.737009000	3.381329000
C	5.155669000	8.494736000	-0.915372000
H	5.625103000	7.902560000	-1.694236000
C	5.940993000	6.021136000	1.303467000
C	0.211593000	13.723849000	2.611728000
H	-0.874585000	13.757636000	2.534489000
C	5.835918000	9.929281000	4.353153000
H	6.234279000	10.003415000	3.342637000
C	4.806506000	3.864270000	1.617834000
C	5.200325000	14.670636000	1.973719000
H	6.294536000	14.619915000	2.057569000
H	4.933149000	14.451725000	0.932816000
H	4.900099000	15.706384000	2.179222000
C	5.941878000	4.676256000	1.702231000
H	6.862517000	4.241271000	2.092906000
C	4.536335000	13.685193000	2.948763000
H	4.898647000	12.682149000	2.694450000
C	6.108755000	9.975583000	6.742591000
H	6.730135000	10.080579000	7.631413000
C	2.305042000	6.285787000	0.012830000
H	2.416768000	7.369840000	-0.110937000
C	3.642583000	4.435825000	1.089055000

H	2.749199000	3.820865000	0.988892000
C	4.971896000	13.964150000	4.395639000
H	6.061035000	13.861127000	4.494089000
H	4.711031000	14.980704000	4.716748000
H	4.500574000	13.263326000	5.094385000
C	7.236333000	6.821912000	1.393140000
H	6.980969000	7.870260000	1.187460000
C	6.665096000	10.066809000	5.464149000
H	7.729809000	10.244981000	5.320887000
C	-1.034285000	10.929686000	2.583345000
H	-0.660772000	10.703061000	3.588687000
H	-1.825456000	11.685058000	2.675288000
H	-1.498966000	10.017384000	2.186930000
C	-0.405749000	11.673149000	0.239469000
H	-0.914185000	10.792208000	-0.175364000
H	-1.121261000	12.506281000	0.232940000
H	0.416218000	11.936544000	-0.437491000
C	8.237765000	6.384271000	0.311900000
H	9.142442000	7.006990000	0.345142000
H	8.546057000	5.339574000	0.450225000
H	7.805169000	6.472319000	-0.691423000
C	7.879672000	6.770153000	2.786478000
H	7.165544000	7.050532000	3.569364000
H	8.261720000	5.770395000	3.029717000
H	8.733031000	7.460497000	2.838030000
C	2.138473000	5.688915000	-1.394373000
H	3.010988000	5.904678000	-2.022947000
H	2.013210000	4.598615000	-1.358516000
H	1.253152000	6.111294000	-1.889110000
C	1.049877000	6.062540000	0.867597000
H	0.807922000	4.998274000	0.986197000
H	1.167051000	6.499347000	1.865696000
H	0.181972000	6.538539000	0.391241000
C	4.854704000	2.414368000	2.078959000
H	5.882293000	2.230503000	2.430752000
C	3.919896000	2.158541000	3.270610000
H	2.866945000	2.304106000	2.997322000
H	4.028723000	1.128365000	3.636039000
H	4.143599000	2.839258000	4.101485000
C	4.591846000	1.428213000	0.931203000
H	5.286478000	1.595570000	0.098587000
H	4.716512000	0.392022000	1.273809000
H	3.571864000	1.524622000	0.537686000

2_2 (S = 2)

Fe	2.290535000	-2.632547000	13.745192000
Fe	1.552129000	-0.172643000	13.884551000
N	2.288862000	1.686174000	13.714380000
N	1.472431000	-4.598048000	13.927172000
N	3.769774000	-3.492695000	15.221690000
N	-0.085986000	0.794735000	14.526919000
C	2.406583000	-5.370975000	14.603104000
C	5.733422000	1.920690000	12.744485000
C	1.475856000	2.544339000	14.456061000
C	4.902392000	-3.059258000	15.974901000
C	3.327615000	2.453130000	13.277329000
C	7.288581000	-3.039898000	16.428559000
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3 (*S* = 3/2)

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NMR data for the catalytic hydroboration experiments

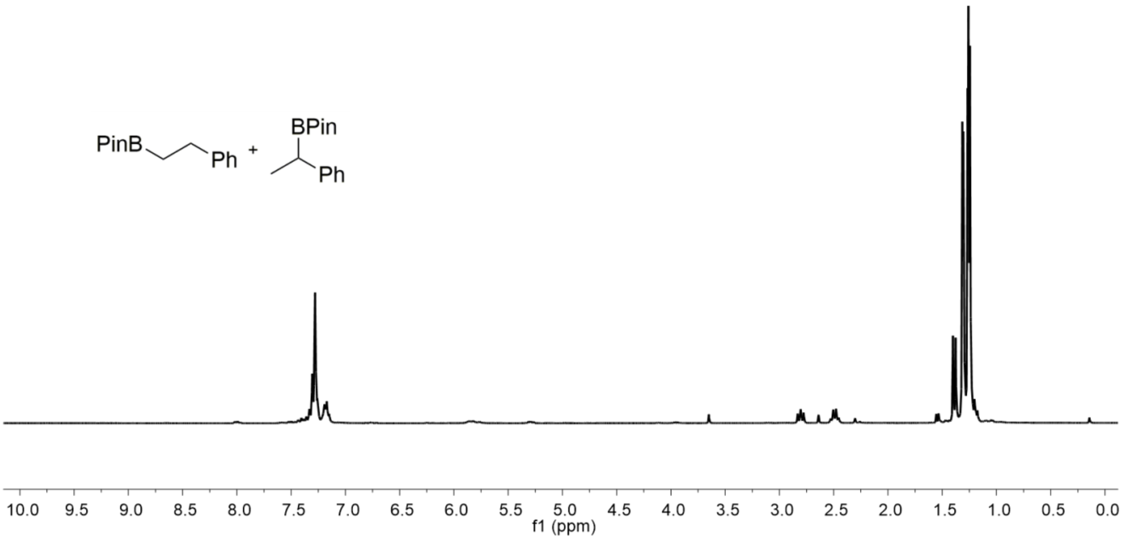

Figure S16 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of styrene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of styrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

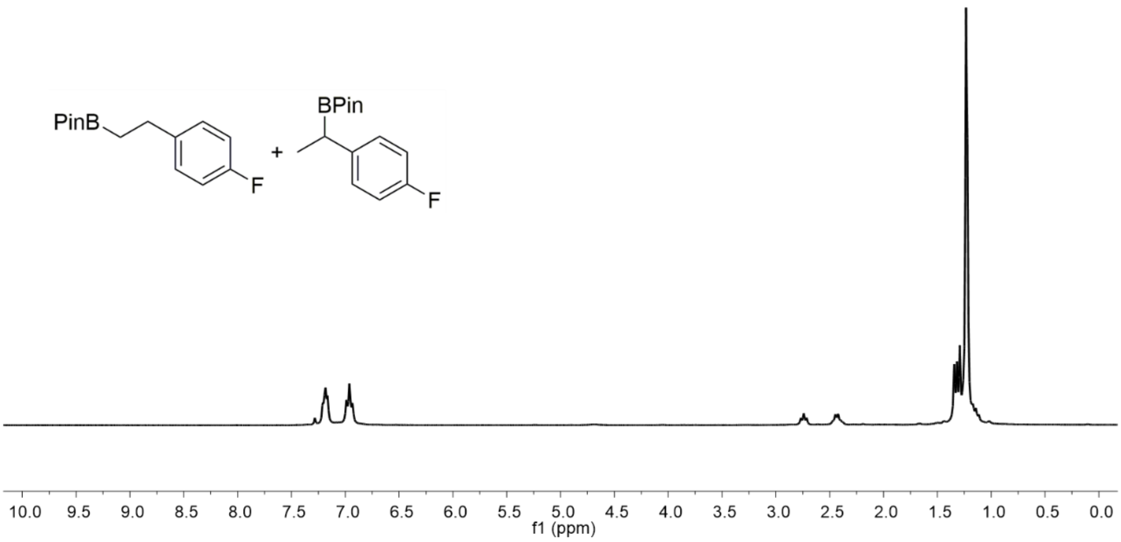

Figure S17 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of 1-fluoro-4-vinylbenzene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of 4-fluorostyrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

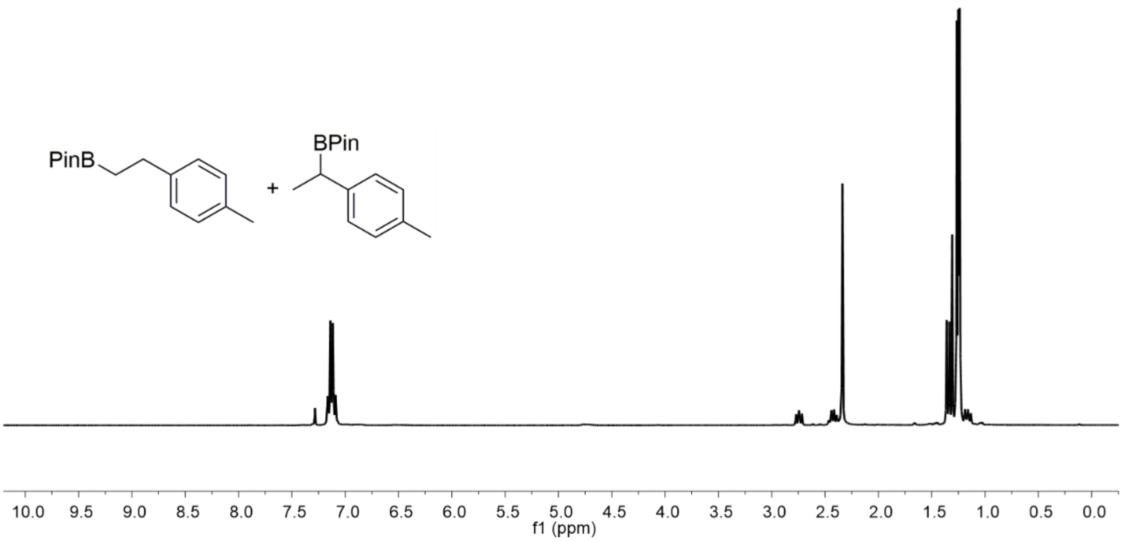

Figure S18 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of 1-methyl-4-vinylbenzene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of 4-methylstyrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

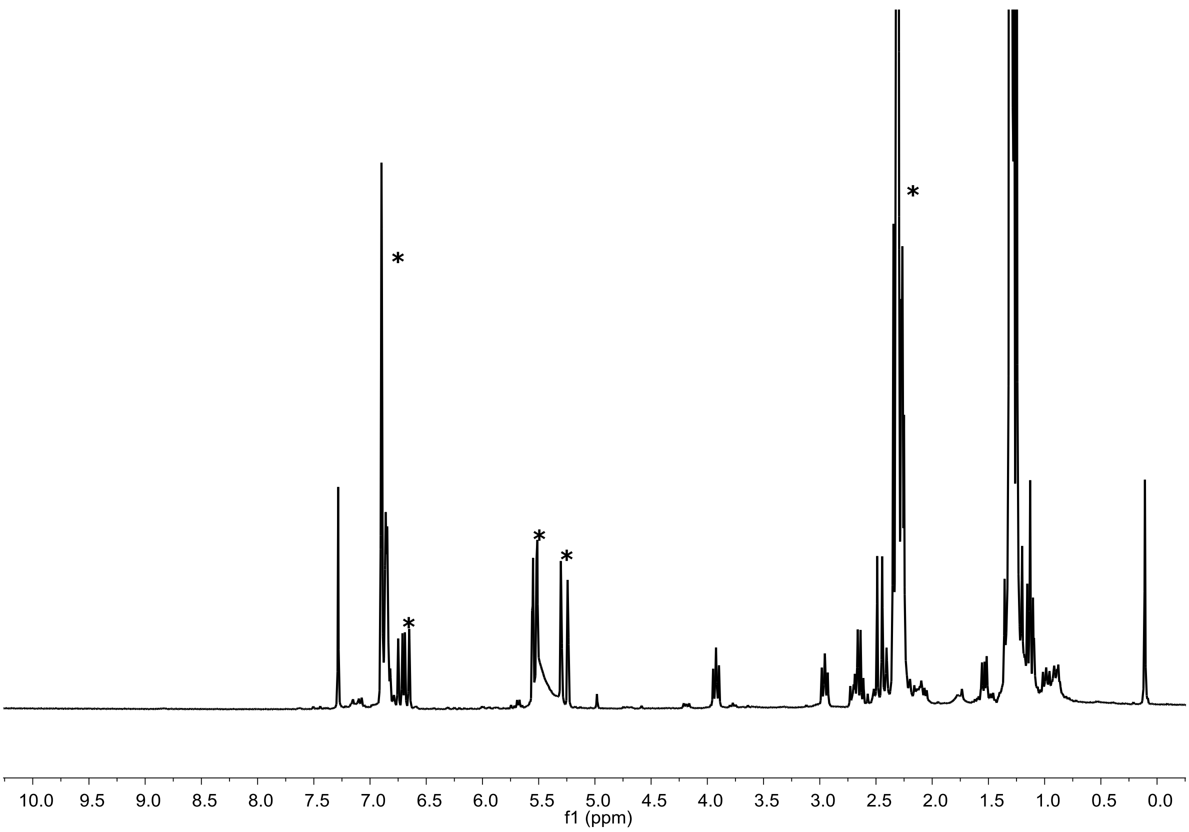

Figure S19 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the isolated mixture of products formed by the catalytic reaction using complex **1a** (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of 1,3,5-trimethyl-2-vinylbenzene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC). Asterisks denote unreacted 1,3,5-trimethyl-2-vinylbenzene.

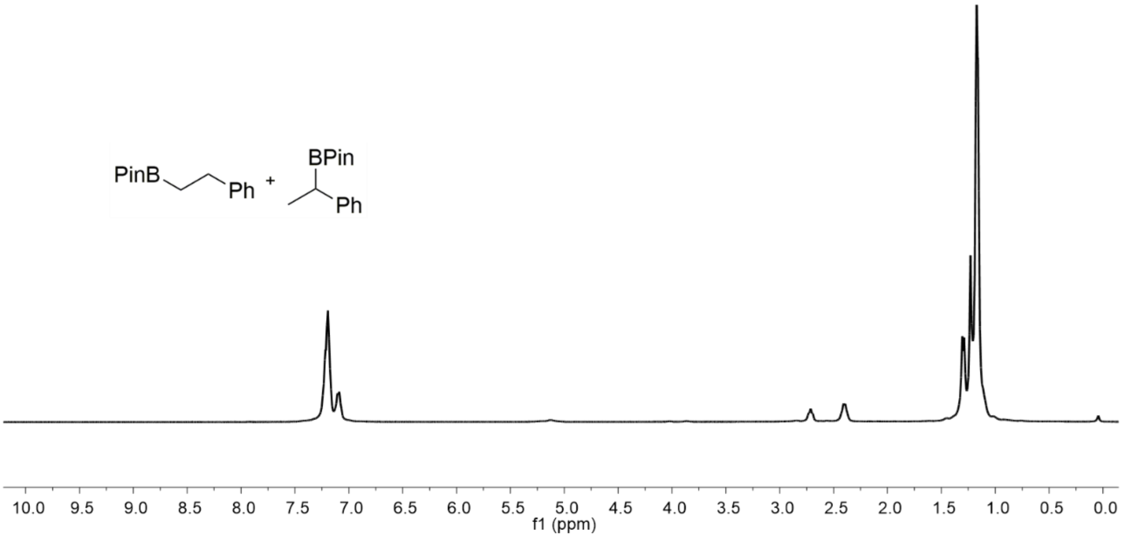

Figure S20 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of styrene (1 mol% of **1b**, 3 mol% of $K(HBEt_3)$), 2 mmol of styrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

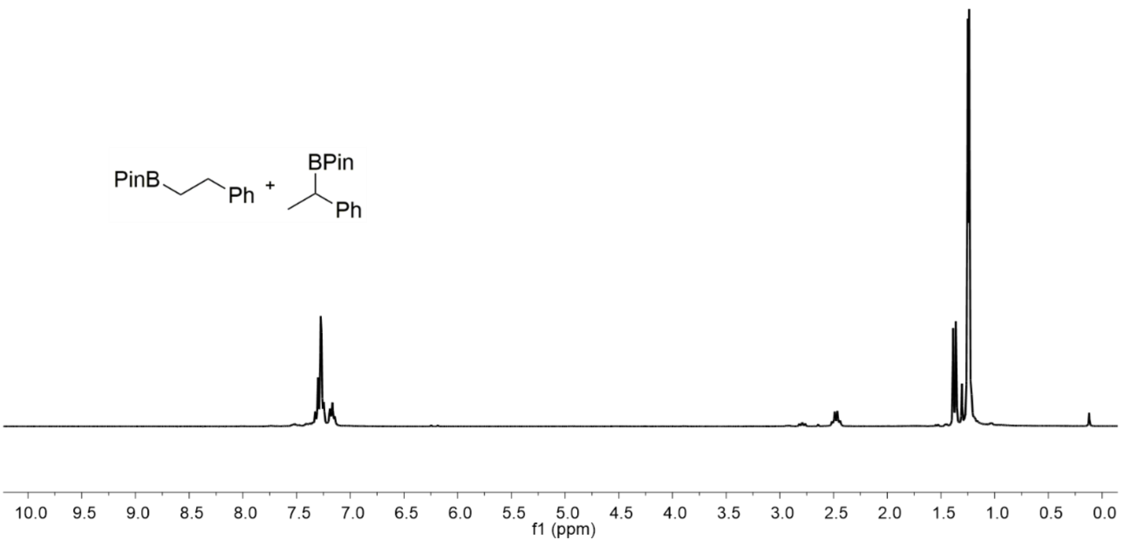

Figure S21 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of styrene (1 mol% of **1c**, 3 mol% of $K(HBEt_3)$), 2 mmol of styrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

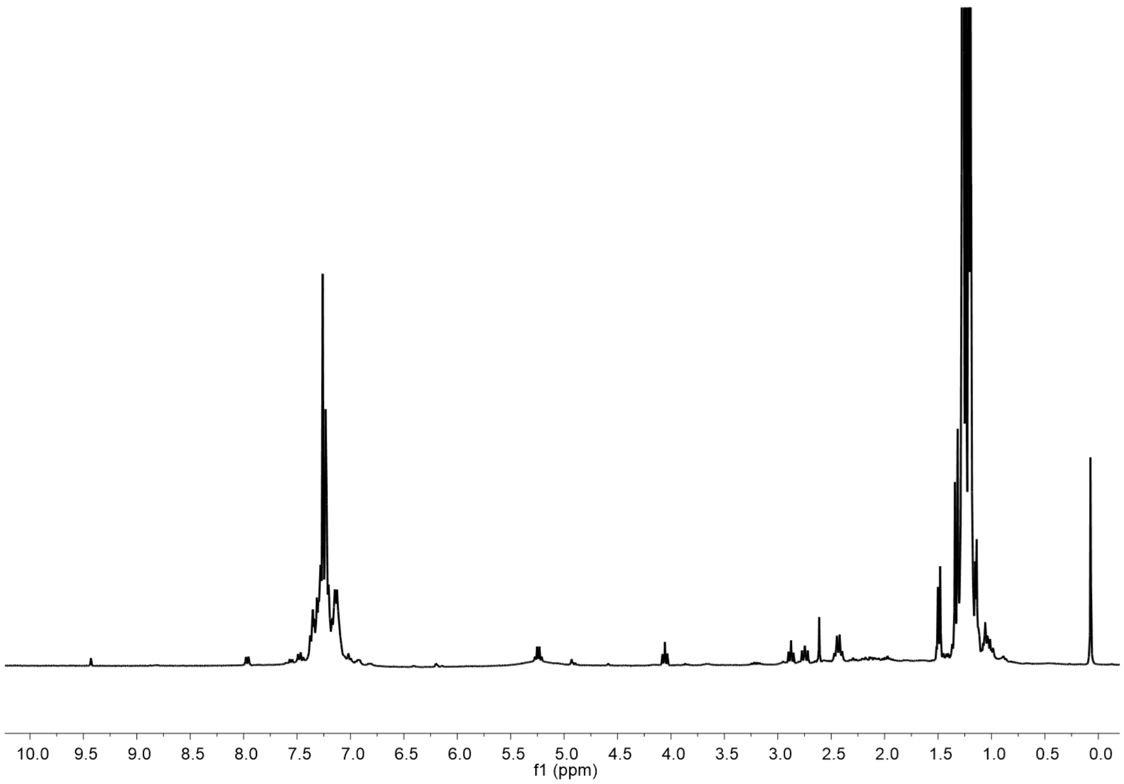

Figure S22 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the isolated mixture of products formed by the catalytic reaction using complex **1d** (1 mol% of **1d**, 3 mol% of $K(HBEt_3)$), 2 mmol of styrene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

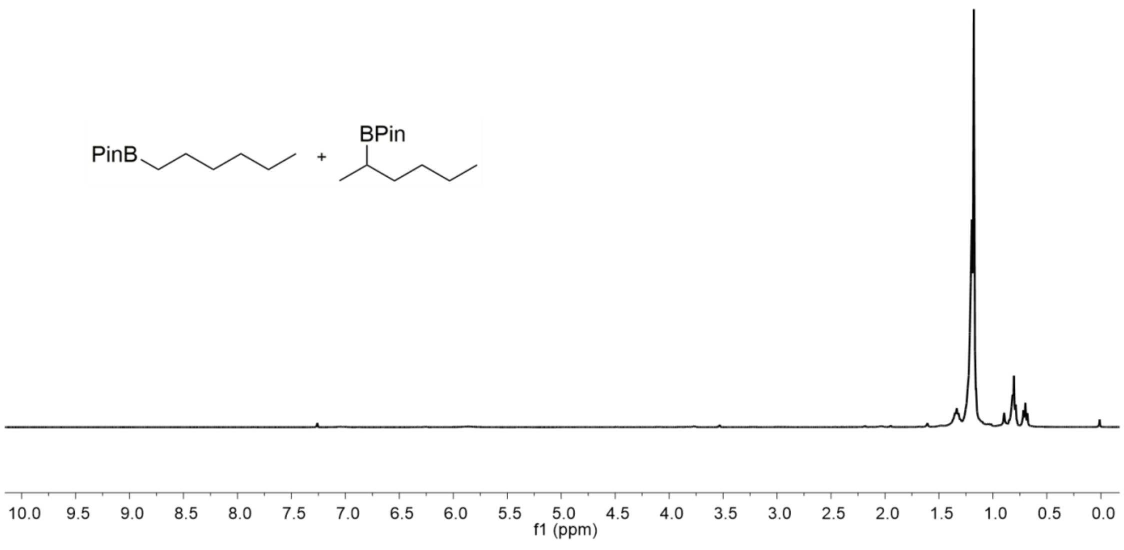

Figure S23 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of 1-hexene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of 1-hexene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

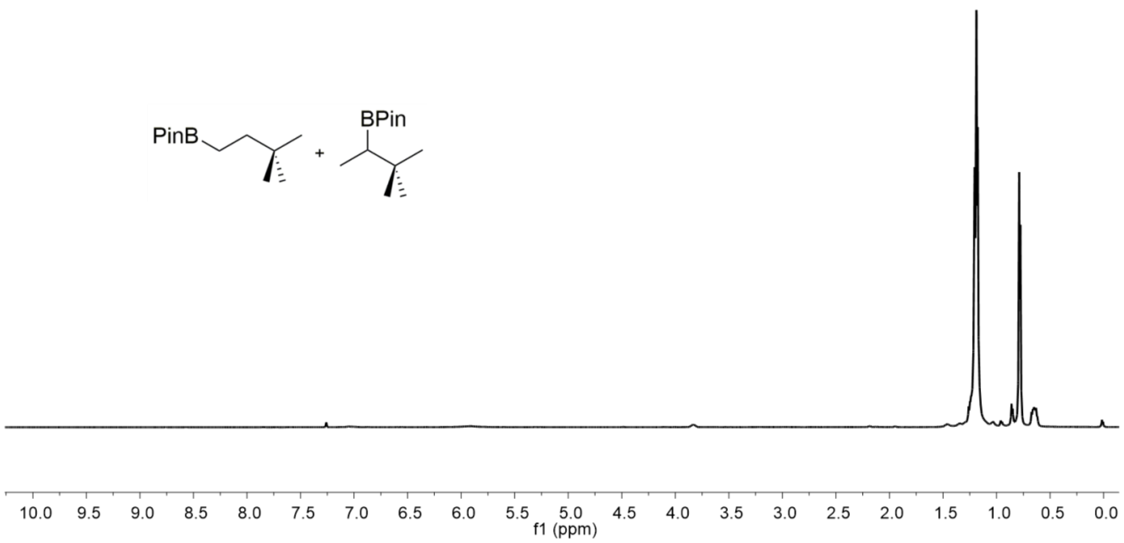

Figure S24 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of 3,3-dimethylbut-1-ene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of 3,3-dimethylbut-1-ene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

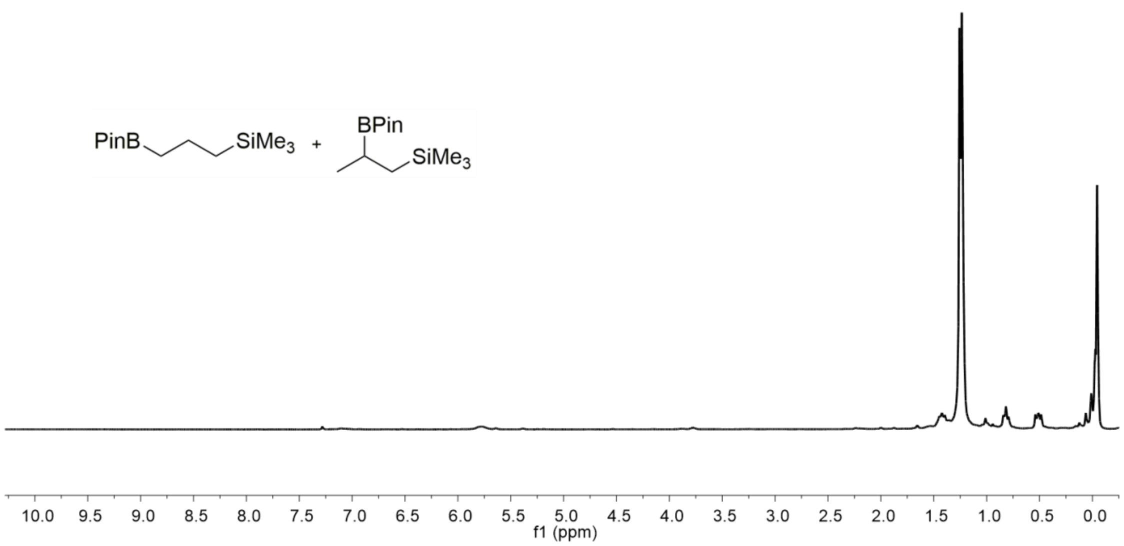

Figure S25 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration products of allyltrimethylsilane (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of allyltrimethylsilane, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

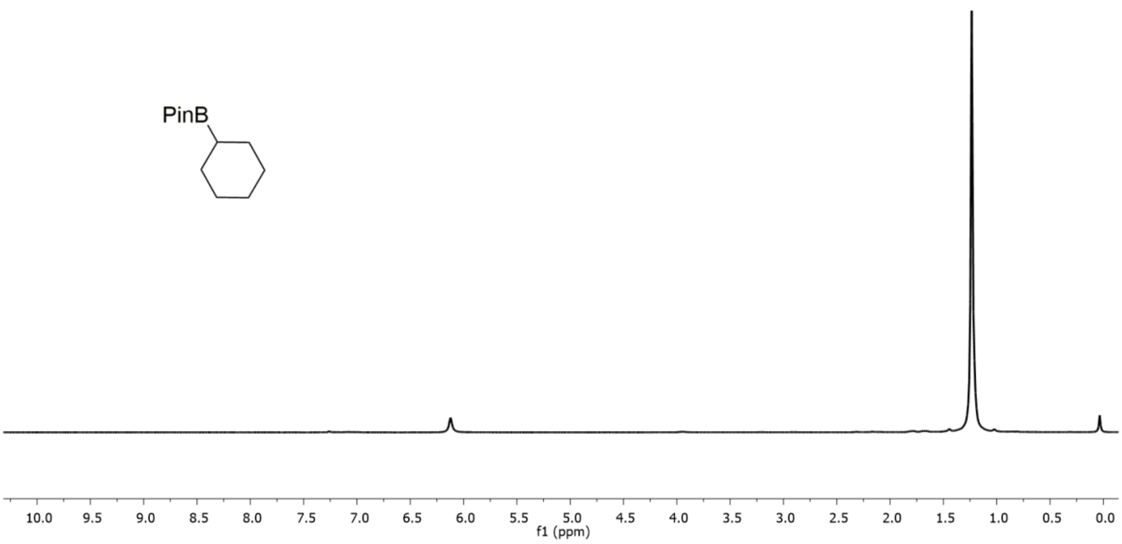

Figure S26 [1]H NMR spectrum (300 MHz, $CDCl_3$) of the hydroboration product of cyclohexene (1 mol% of **1a**, 3 mol% of $K(HBEt_3)$), 2 mmol of cyclohexene, 2.5 mmol of HBPin, Reaction time: 16 h, Temperature: 25 ºC).

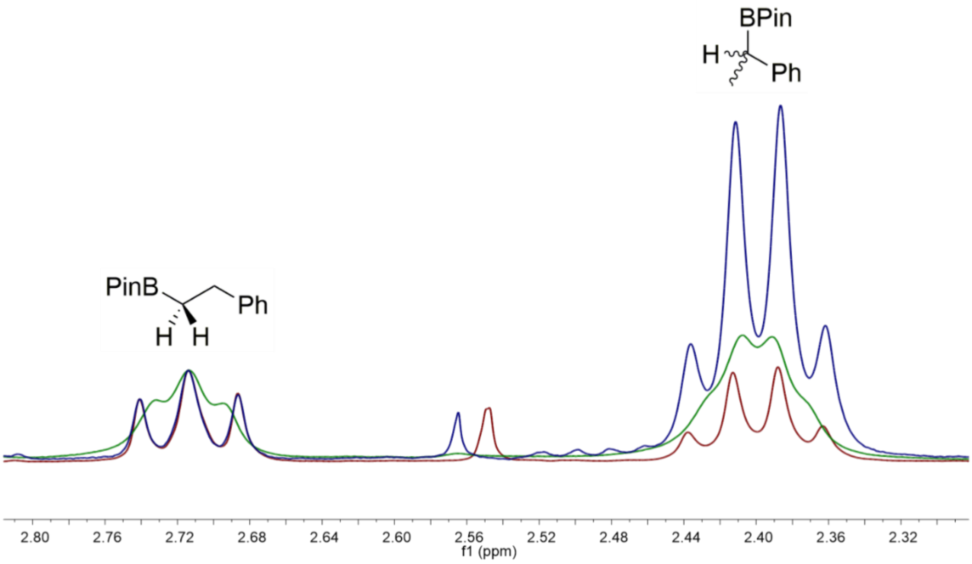

Figure S27 Detail of the superimposition of the [1]H NMR spectra of the products of the hydroboration of styrene, highlighting the zone corresponding to the α-protons catalyzed by different complexes activated by $K(HBEt_3)$ (red – **1a**; green – **1b**; blue – **1c**), showing the increase in the selectivity of the Mk product in the order: **1a** < **1b** < **1c**.

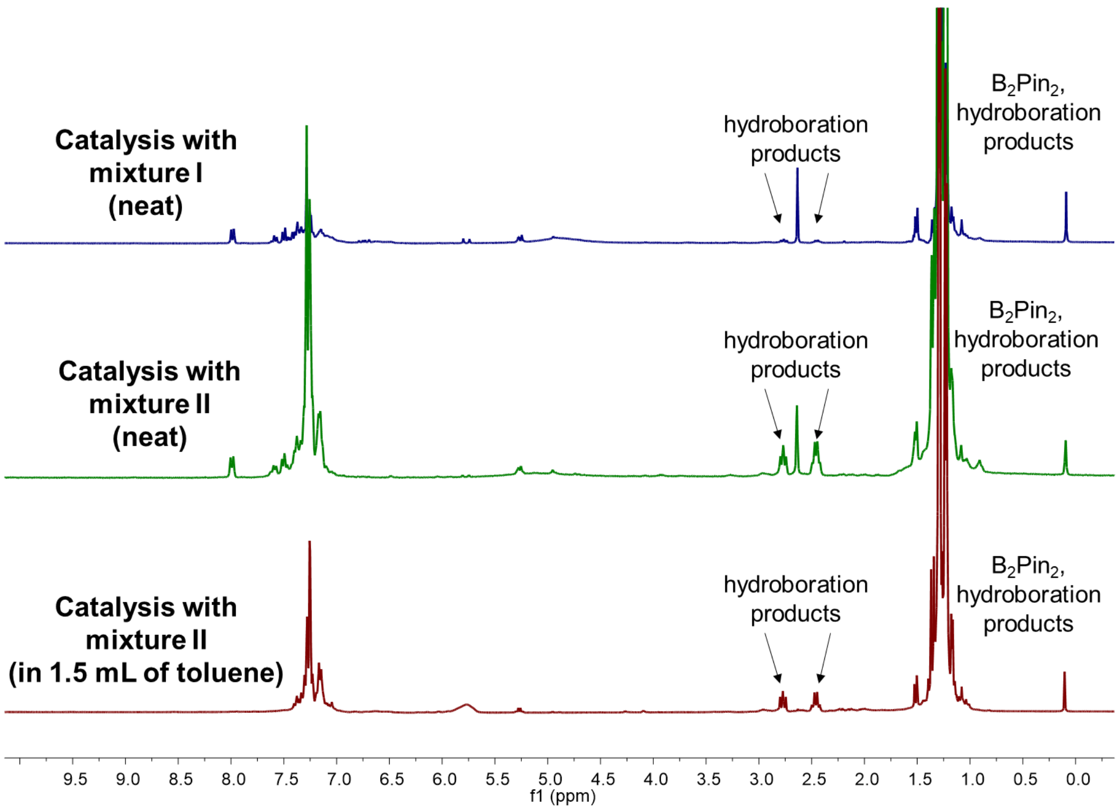

Figure S28 Stacking of the ^{1}H NMR spectra (300 MHz, $CDCl_3$) obtained from the catalytic reactions (reaction time: 16 h, temperature: 25 ºC) using the mixture I (**2** + **2**$_2$; isolated from the reaction of complex **1b** with K(HBEt$_3$) in toluene over 30 min; 1 mol%), in neat conditions (top spectrum) or in 1.5 mL of toluene (middle spectrum) or with mixture II (**2** + **2**$_2$ + **3**; isolated from the reaction of complex **1b** with K(HBEt$_3$) in toluene over 16 h; 1 mol%), in neat conditions (bottom spectrum), with styrene (2 mmol) and HBPin (2.5 mmol). Note that the spectra were normalized in relation to the resonance of the methyl protons of B_2Pin_2, highlighting the much higher selectivity in hydroboration products when the reaction is carried either using mixture II as catalyst in neat conditions or using mixture I with toluene as solvent.