^{1}H and ^{2}H NMR spectroscopic characterization of heterobinuclear ion pairs formed upon the activation of bis(imino)pyridine vanadium(III) pre-catalysts with $AlMe_3/[Ph_3C]^+[B(C_6F_5)_4]^-$ and MAO

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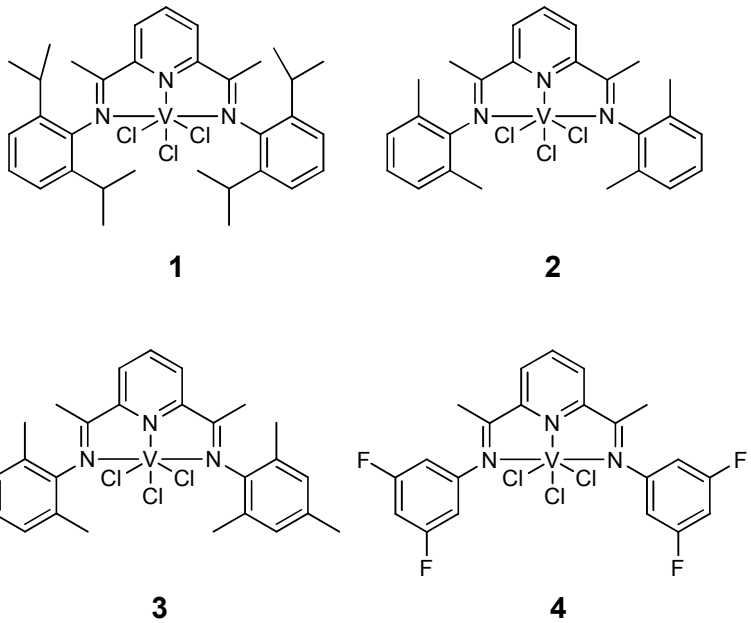
Supporting information



1 **2**

3 **4**

Chart S1.

^{1}H NMR spectra of the complexes 1-4 in $CDCl_3$ at 25 °C.

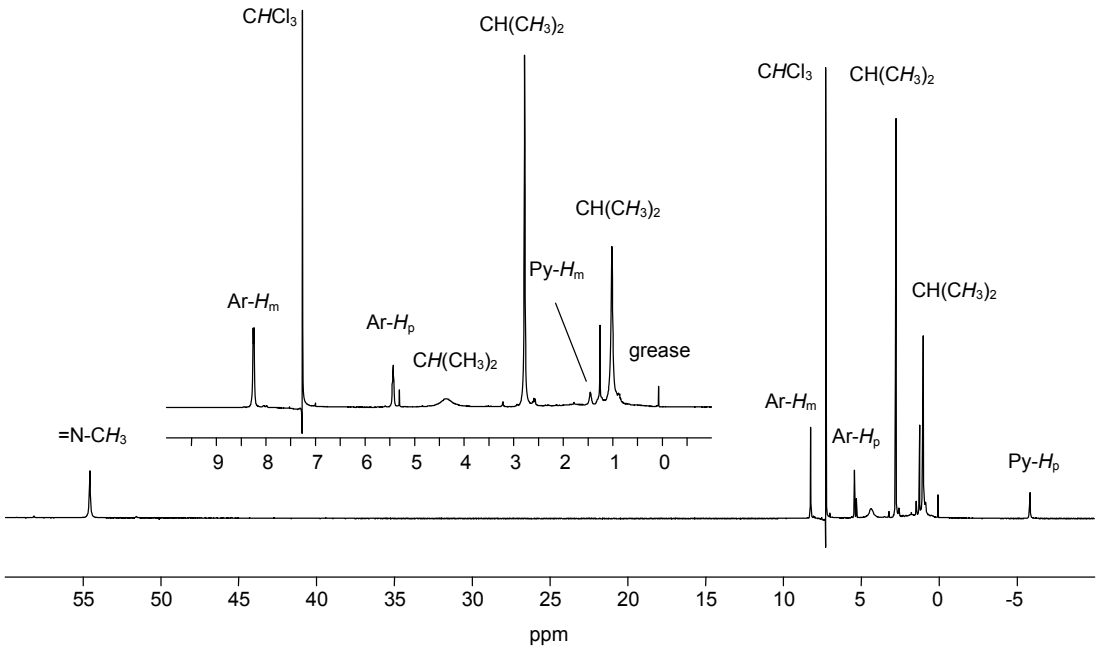


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 °C.

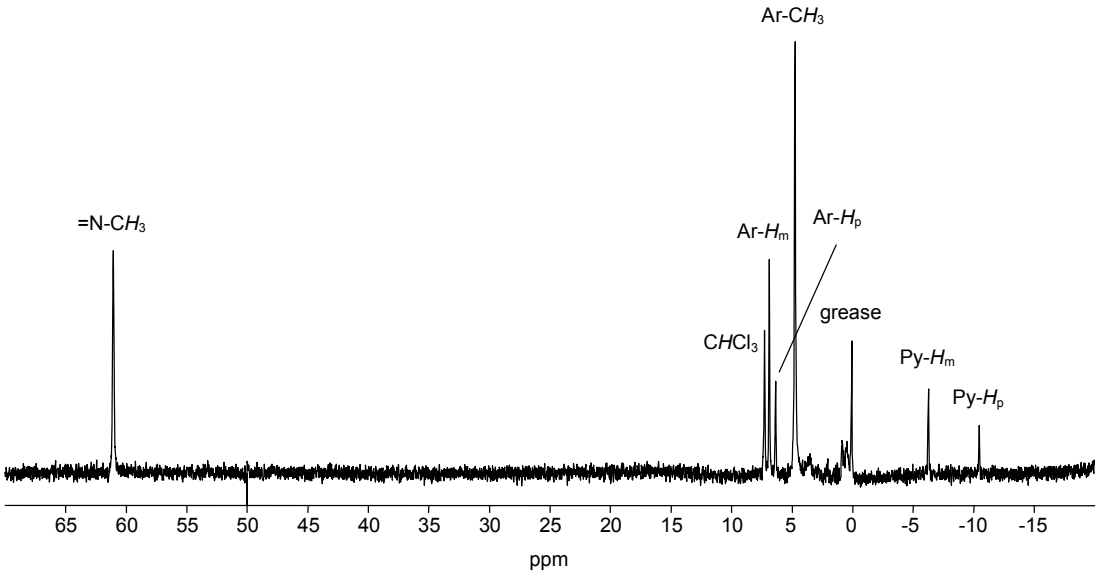


Figure S2. ^{1}H NMR spectrum of **2** in $CDCl_3$ at 25 °C.

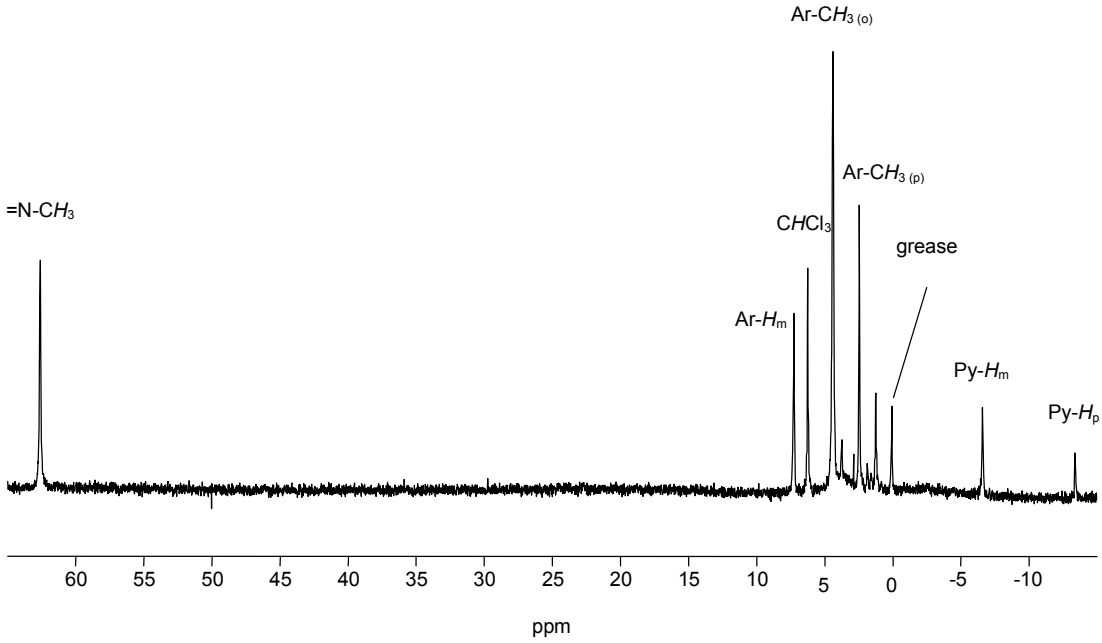


Figure S3. ^{1}H NMR spectrum of **3** in $CDCl_3$ at 25 °C.

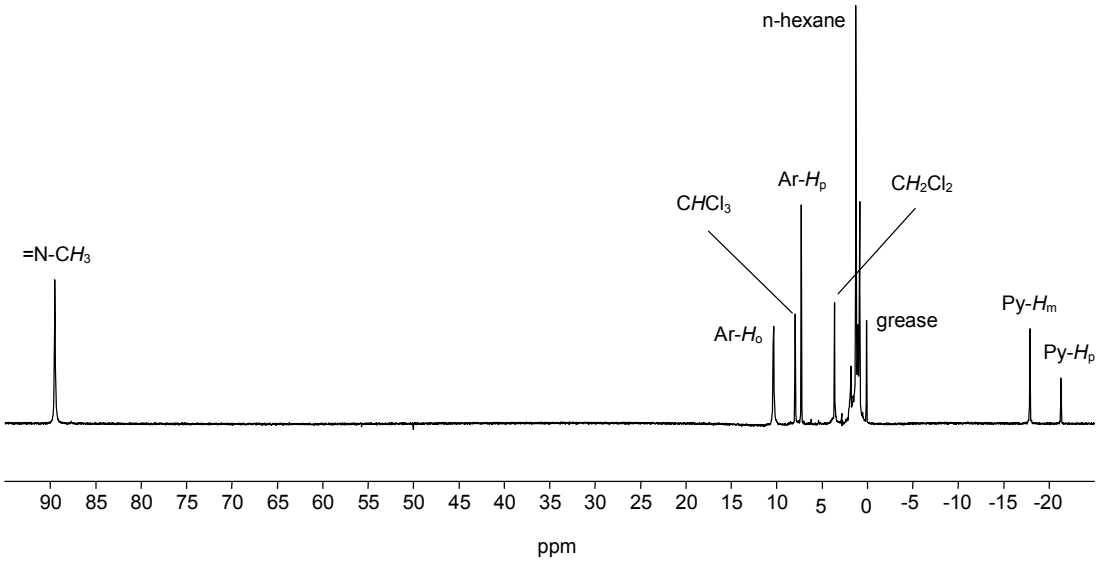


Figure S4. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 25 °C.

^{1}H NMR spectra of the samples 1-4/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$ in toluene-d_8 at −20 °C.

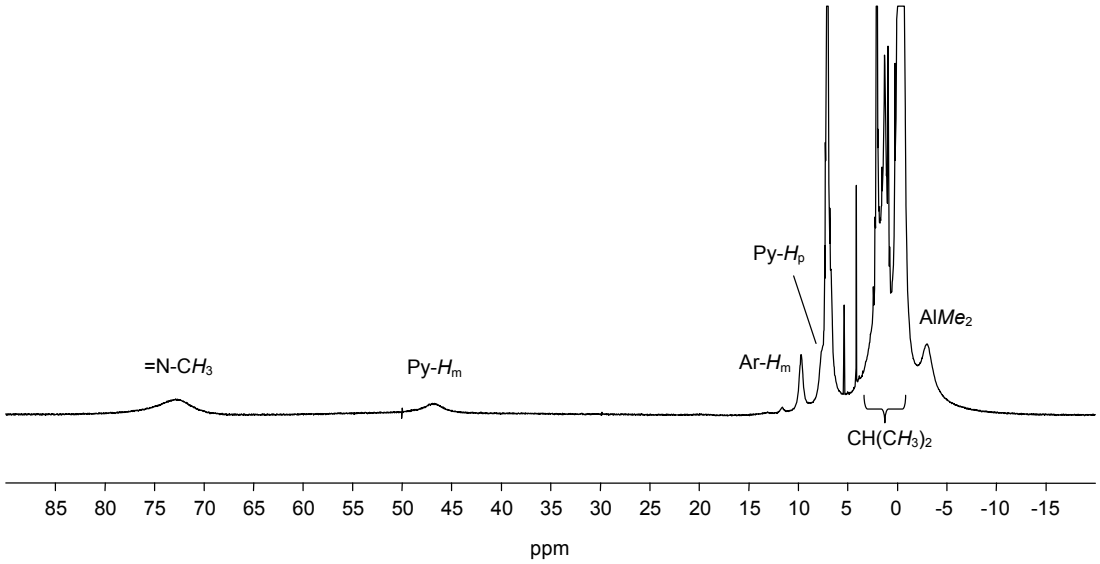


Figure S5. ^{1}H NMR spectrum (−20 °C, toluene-d_8) of the sample **1**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([V]:[Al]:[B] = 1:10:1.2).

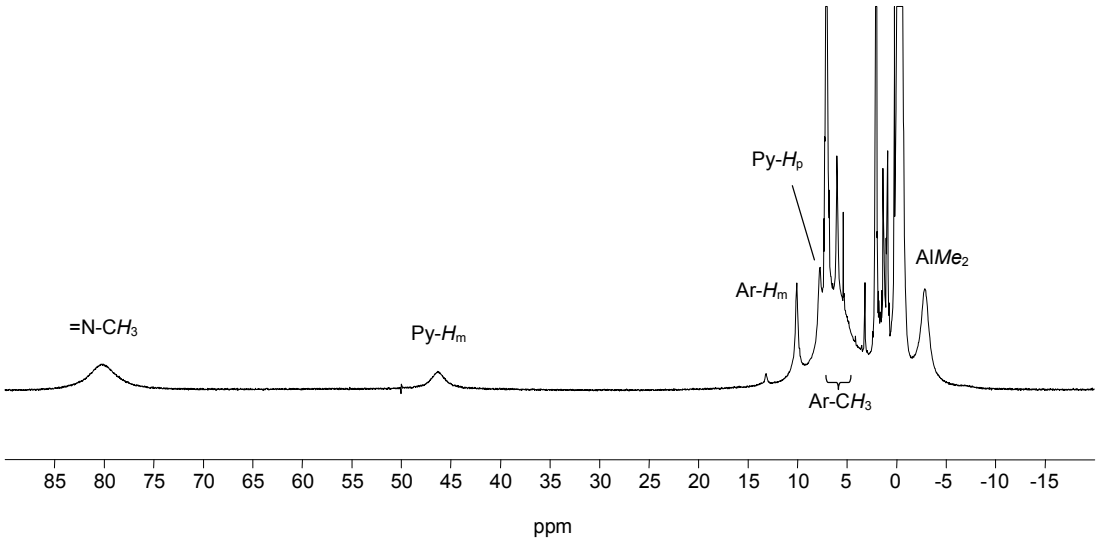


Figure S6. ^{1}H NMR spectrum (−20 °C, toluene-d_8) of the sample **2**/AlMe$_3$/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ([V]:[Al]:[B] = 1:10:1.2).

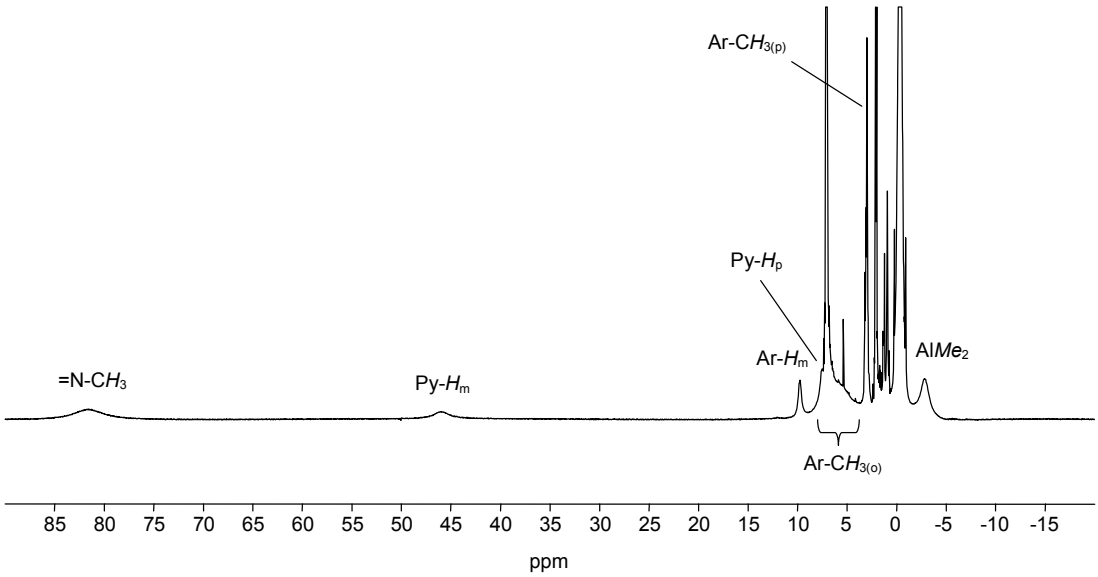


Figure S7. ^{1}H NMR spectrum (−20 °C, toluene-d_8) of the sample **3**/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$ ([V]:[Al]:[B] = 1:10:1.2).

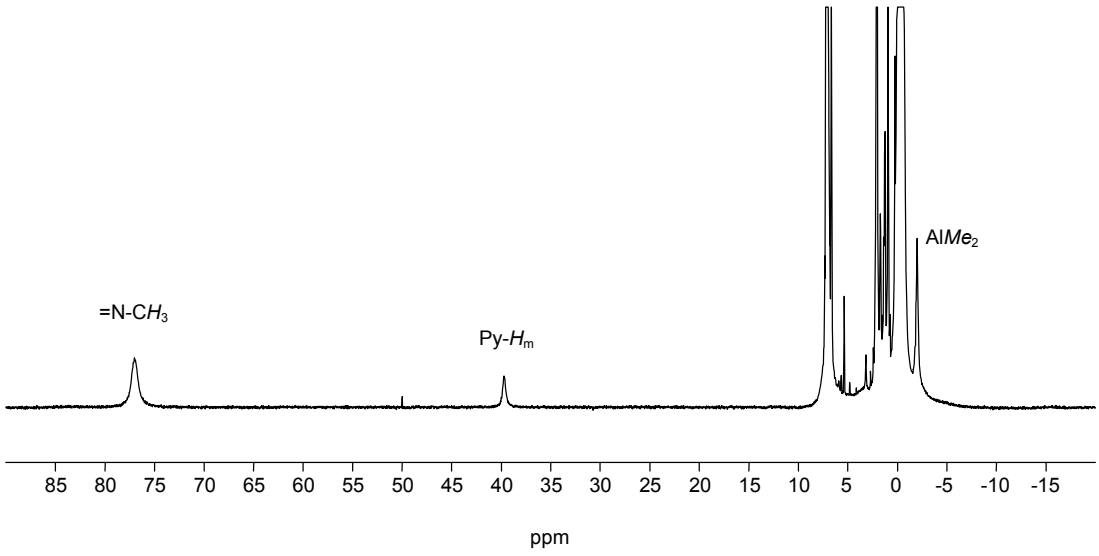


Figure S8. ^{1}H NMR spectrum (−20 °C, toluene-d_8) of the sample **4**/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$ ([V]:[Al]:[B] = 1:10:1.2).

^{1}H NMR data (δ, ppm and $\Delta\nu_{1/2}$, Hz) for the complexes 1b-4b observed in the systems 1-4/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$ ([V]:[Al]:[B] = 1:10:1.2) at −20 °C.

Table S1. ^{1}H NMR data for the complex 1b (toluene-d_8, −20 °C).

		=N-CH_3	Py-H_m	Py-H_p	Ar-H_m	Ar-H_p	$(CH_3)_2$CH-		$(CH_3)_2$CH-	AlMe_2
1	δ	65.2	−8.3	−2.5	8.6	5.5	3.4	1.1	5.9	-
	$\Delta\nu_{1/2}$	(80)	(30)	(40)	(20)	(20)	(15)	(25)	(120)	-
1b	δ	72.9	47.0	7.7	9.7	N/O[a]	~2[b]		N/O[a]	−3.0
	$\Delta\nu_{1/2}$	(1370)	(800)	(~200)	(170)	-	(~700)		-	(530)

[a] N/O – not observed.
[b] The signal was observed using inversion-recovery ^{1}H NMR experiment with 10 ms delay between 180° and 90° pulses.

Table S2. ^{1}H NMR data for the complex 2b (toluene-d_8, −20 °C).

		=N-CH_3	Py-H_m	Py-H_p	Ar-H_m	Ar-H_p	Ar-CH_3	AlMe_2
2	δ	72.6	−8.3	−19.8	6.5	7.1	5.7	-
	$\Delta\nu_{1/2}$	(100)	(90)	(100)	(60)	(70)	(80)	-
2b	δ	80.2	47.0	7.7	10.1	6.0	~6[a]	−2.9
	$\Delta\nu_{1/2}$	(1100)	(580)	(140)	(100)	(65)	(~1000)	(290)

[a] The signal was observed using inversion-recovery ^{1}H NMR experiment with 10 ms delay between 180° and 90° pulses.

Table S3. ^{1}H NMR data for the complex 3b (toluene-d_8, −20 °C).

		=N-CH_3	Py-H_m	Py-H_p	Ar-H_m	Ar-C$H_{3(p)}$	Ar-C$H_{3(o)}$	AlMe_2
3	δ	74.9	−8.8	−23.9	5.8	1.6	5.1	-
	$\Delta\nu_{1/2}$	(90)	(40)	(60)	(20)	(20)	(40)	-
3b	δ	81.5	45.9	7.5	9.7	3.0	~5.8[a]	−2.8
	$\Delta\nu_{1/2}$	(1400)	(740)	(180)	(130)	(40)	(~800)	(400)

[a] The signal was observed using inversion-recovery ^{1}H NMR experiment with 10 ms delay between 180° and 90° pulses.

Table S4. ^{1}H NMR data for the complex 4b (toluene-d_8, −20 °C).

		=N-CH_3	Py-H_m	Py-H_p	Ar-H_o	Ar-H_p	AlMe_2
4	δ	109.9	−24.8	−32.0	12.5	9.7	-
	$\Delta\nu_{1/2}$	(140)	(50)	(70)	(60)	(20)	-
4b	δ	77.0	39.7	N/O[a]	N/O[a]	N/O[a]	−2.0
	$\Delta\nu_{1/2}$	(290)	(160)	-	-	-	(80)

[a] N/O – not observed.

^{1}H NMR spectra of the complex $[LAlMe_2]^+[B(C_6F_5)_4]^-$ in toluene-d_8 at 25 °C.

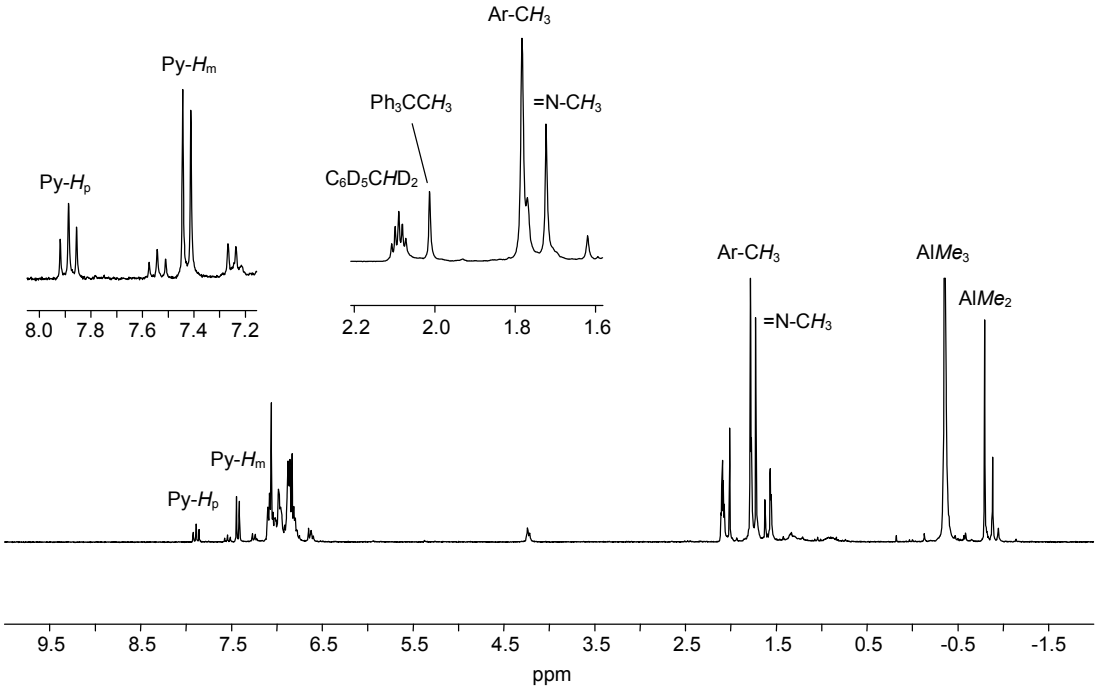


Figure S9. ^{1}H NMR spectrum (25 °C, toluene-d_8) of the complex $[LAlMe_2]^+[B(C_6F_5)_4]^-$ {L = [2,6-(ArN=CMe)$_2$C$_5$H$_3$N], Ar = 2,6-Me$_2$C$_6$H$_3$} independently prepared by the reaction of L with $AlMe_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$.

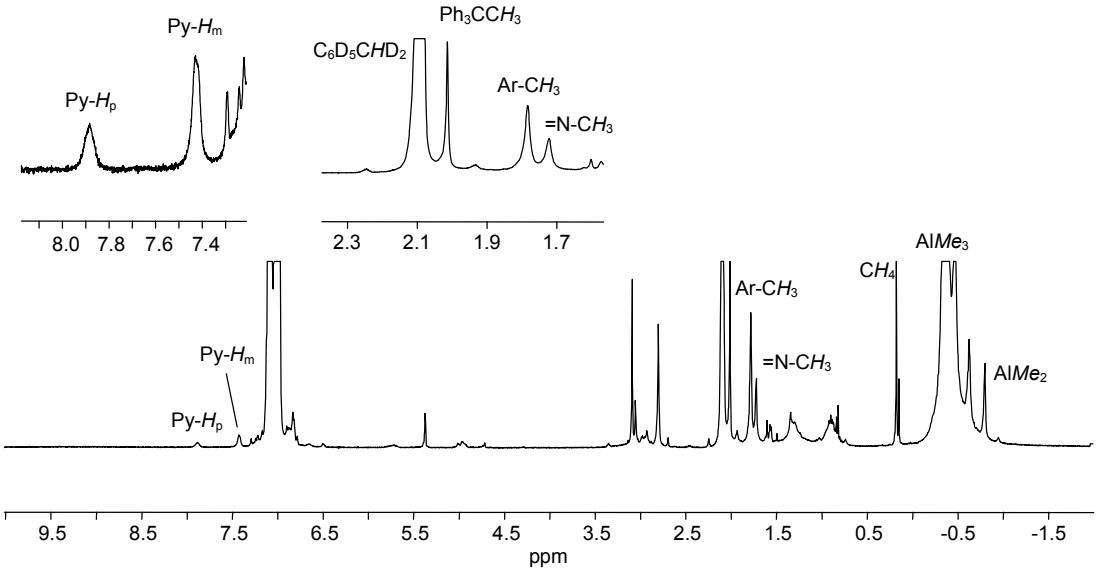


Figure S10. ^{1}H NMR spectrum (25 °C, toluene-d_8) of the complex $[LAlMe_2]^+[B(C_6F_5)_4]^-$ {L = [2,6-(ArN=CMe)$_2$C$_5$H$_3$N], Ar = 2,6-Me$_2$C$_6$H$_3$} observed in the catalyst system **2**/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$/C_2H_4 ([V]:[Al]:[B] = 1:10:1.2; N(V):N(C_2H_4) = 1:50).