Supplementary Data

The insertion reaction of acetonitrile on aryl nickel complexes stabilized by bidentate *N*, *N*'-chelating ligands.

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Figure 1S. MS (FAB^+) of compounds **7c** and **7c'**

Figure 2S. ^1H NMR spectra of complexes **5a** (500 MHz), **7a** and **7c** (250 MHz).

Figure 3S. MS (CI, NH_3) of imine NH=C(Mes)Me.

Scheme 1S. Altenative mechamisms proposed for the evolution of the Mesityl-nitrile cationic species.

Tables 1 and 2. ^1H NMR spectra of all compounds

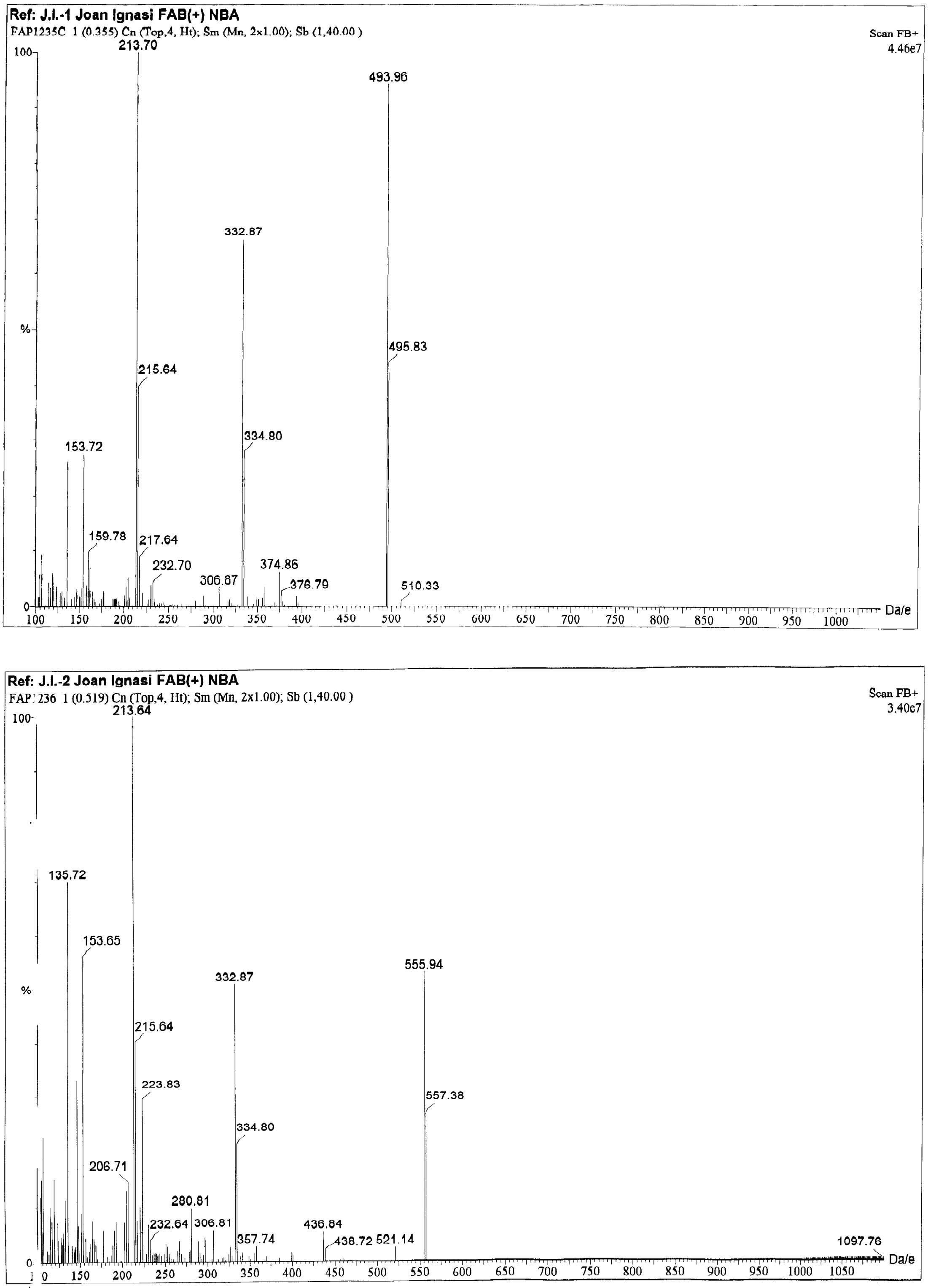
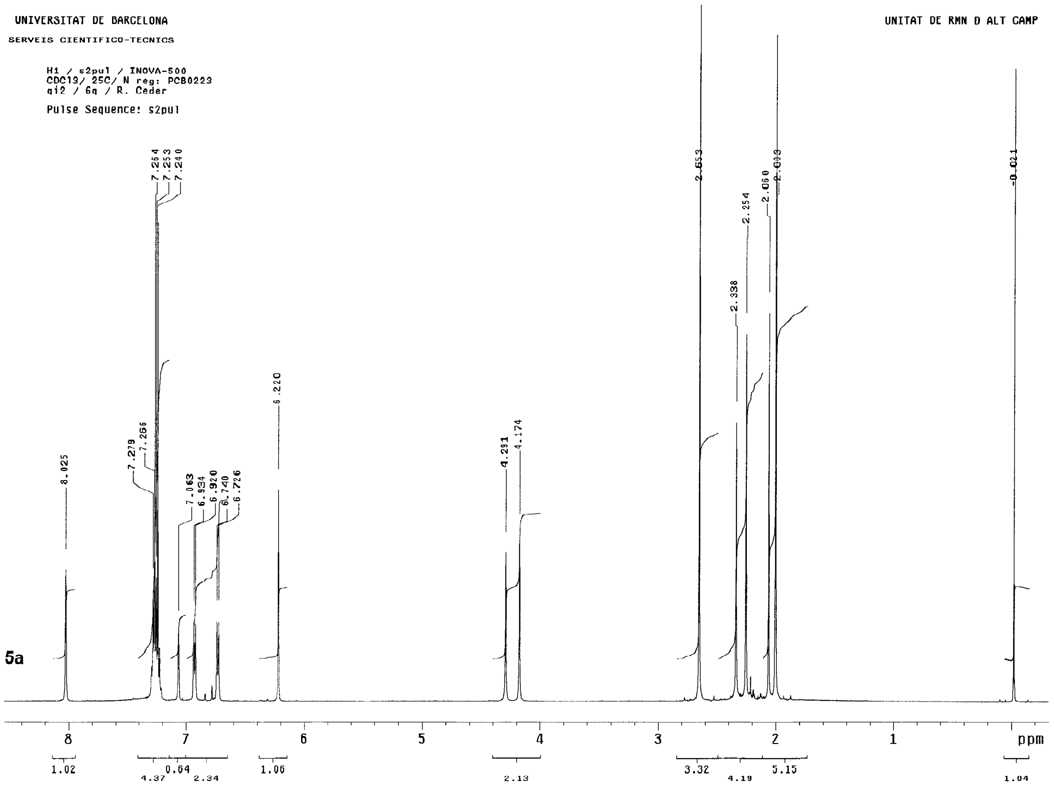


Figure 1S. MS (FAB+) of compounds **7c** and **7c'**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qi2 / 6q / R. Ceder
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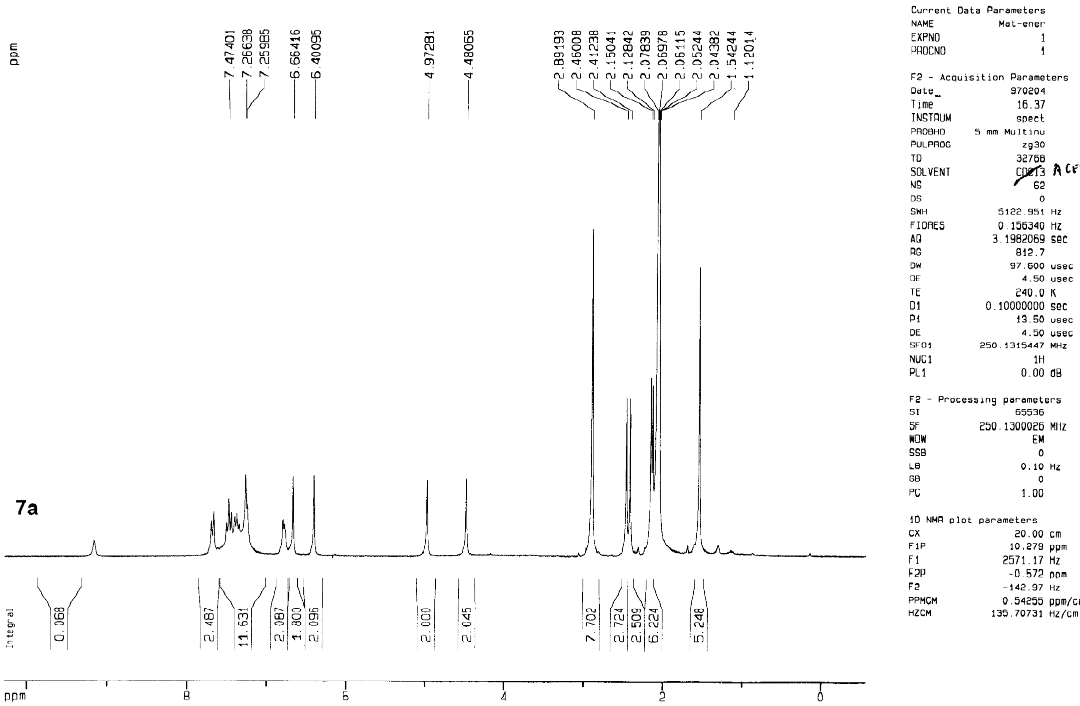
ppm


7a
ppm
Integral
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PROCNO 1
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FIDRES 0.156340 Hz
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DE 4.50 usec
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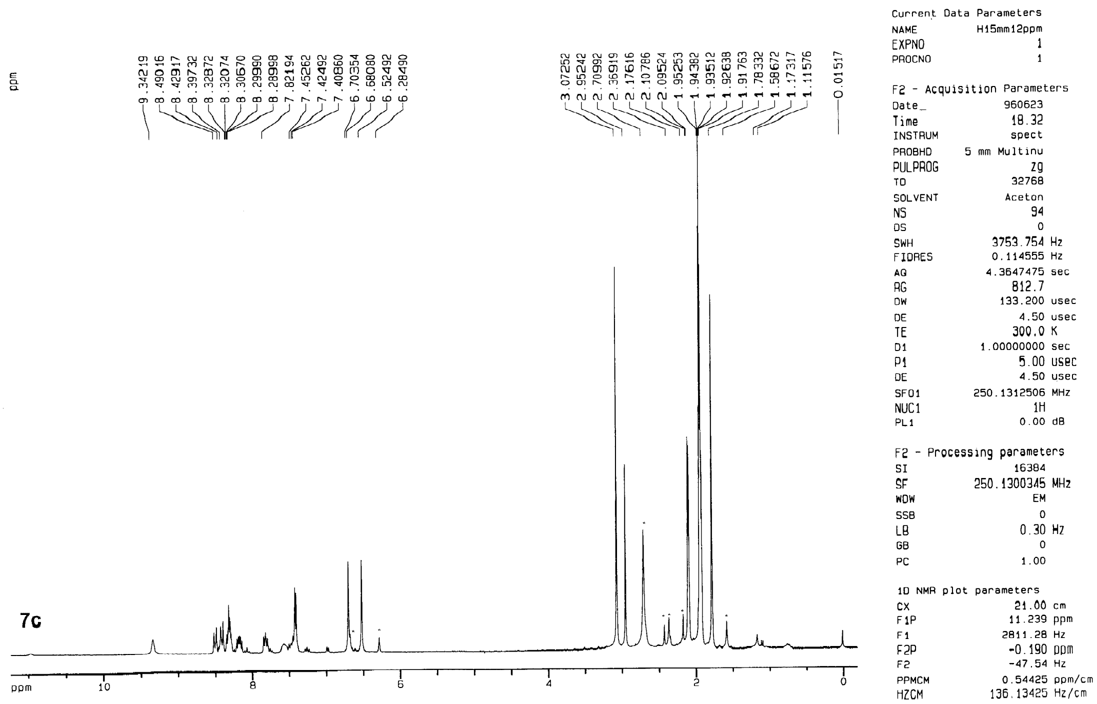


Figure 2S. Proton NMR spectra of complexes **5a** (500 MHz), **7a** and **7c** (250 MHz).

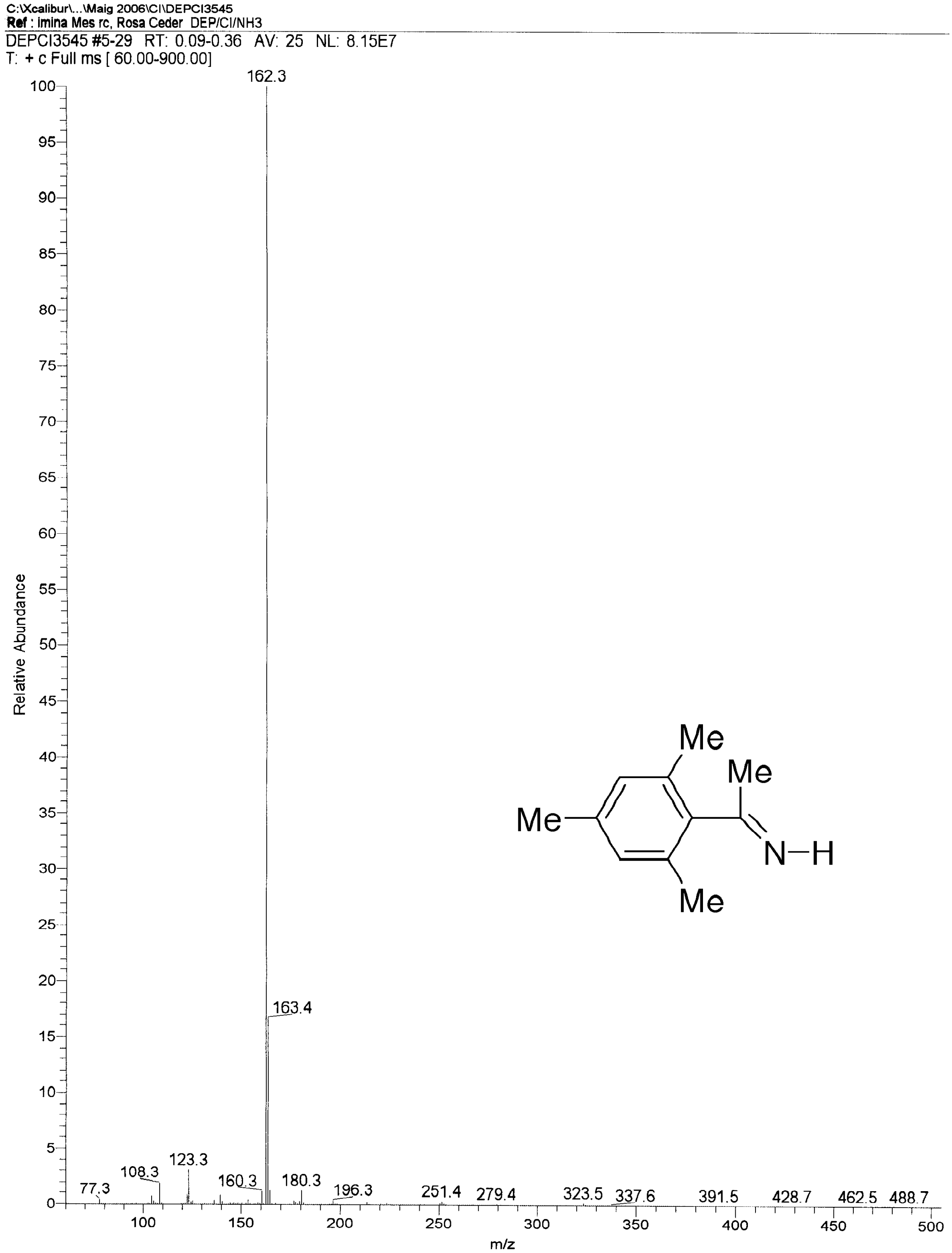
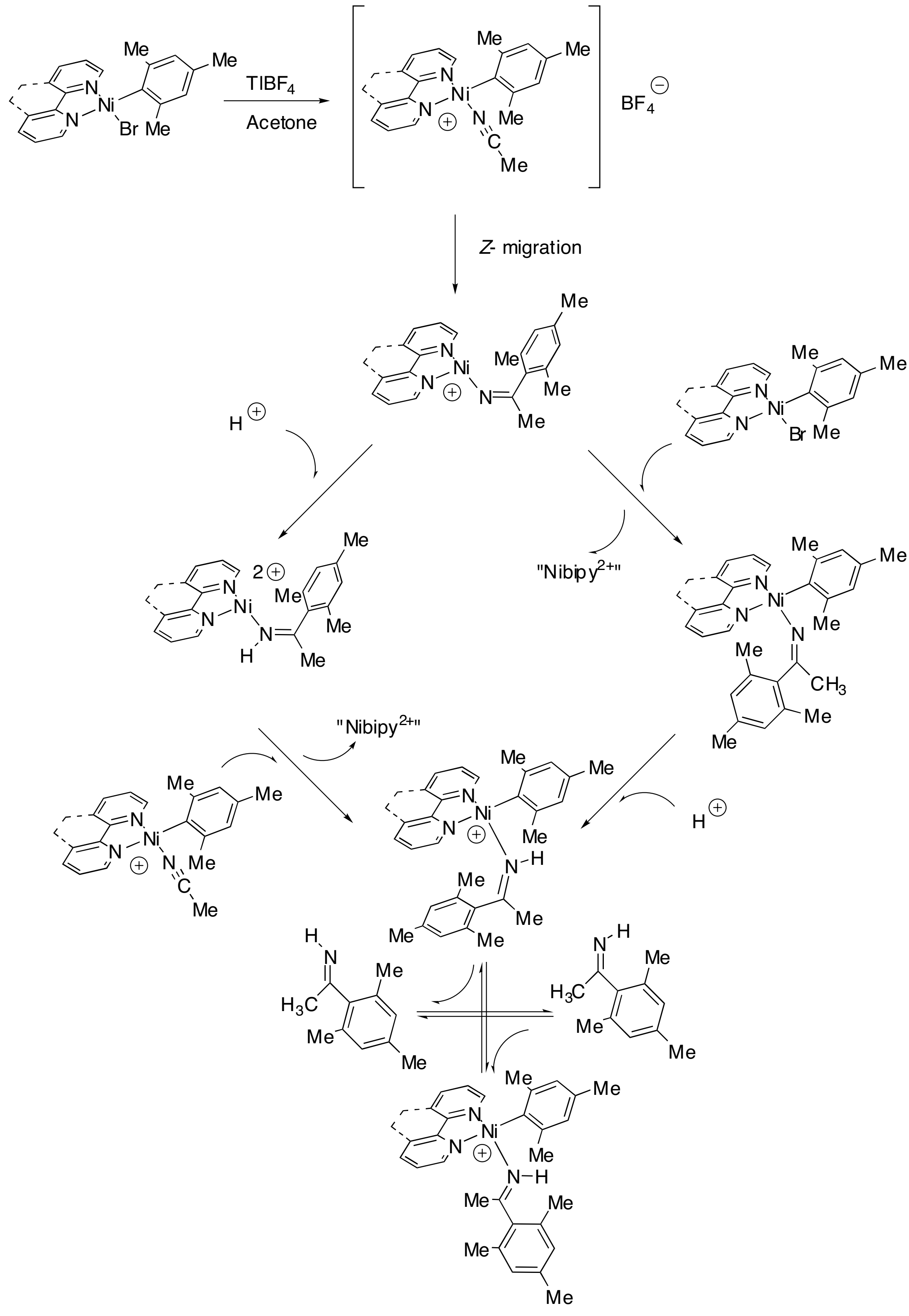


Figure 3S. MS (CI, NH_3) of imine NH=C(Mes)Me.



Scheme 1S. Altenative mechanisms proposed for the evolution of the Mesityl-nitrile cationic species.

Table 1
^{1}H NMR Data of the [MBr(Mes)PIM] and [M(3,5-lut)(Mes)PIM] complexes[a)]

	PIM				Mesityl	L(3,5-Lut or imine)
	Aromatic		H^{5}	H^{6}		
b [b)]	8.65 (d, *J* 4.8, 1H, H^{1})					
	8.06 (d, *J* 8, 1H, H^{4})					
	7.72 (t, *J* 7.8, 1H, H^{3})					
	7.36-7.27 (m, 6H, H$^{2,7,7',8,8',9}$)		8.49s	4.88s		
2b [c)]	9.19 (d, *J* 5.2, 1H, H^{1})		8.75s	5.21s		
	8.32 (t, *J* 7.5, 1H, H^{3})					
	8.13 (d, *J* 7.5, 1H, H^{4})					
	7.86 (t, *J* 5.5, 1H, H^{2})					
	7.50-7.30 (m, 5H, H$^{7,7',8,8',9}$)					
3b(*cis*)	9.31 (d, *J* 5.5, 1H, H^{1})		8.62s	4.13s	6.36 (s, *m*-H)	
	8.18 (td, *J* 7.5, 1.5, 1H, H^{3})				2.87(s, *o*-CH_3)	
	7.96 (d, *J* 7.5, 1H, H^{4})				2.17(s, *p*-CH_3)	
	7.82 (t, *J* 7.5, 1H, H^{2})					
	7.38-7.24*(m, 3H, H$^{8,8',9}$)					
	6.85 (d, *J* 7.5, 2H, H$^{7,7'}$)					
3b(*trans*)	8.12 (td, *J* 7.5, 1.5, 1H, H^{3})		8.58s	5.19s	6.43 (s, *m*-H)	
	7.85 (d, *J* 7.5, 1H, H^{4})				2.96 (s, *o*-CH_3)	
	7.67 (d, *J* 7.5, 2H, H$^{7,7'}$)				2.04 (s, *p*-CH_3)	
	7.44 (t, *J* 7, 1H, H^{2})					
	7.40 (d, *J* 7.5, 2H, H$^{8,8'}$)					
	7.38-7.24*(m, 1H, H^{9})					
	7.15 (d, *J* 5.5, 1H, H^{1})					
4b(*cis*)	9.13 (d, *J* 5.5, 1H, H^{1})		8.88t	4.49s	6.45 (s, *m*-H)	
	8.26 (td, *J* 8.2, 1H, H^{3})				2.42 (s, *o*-CH_3)	
	8.12 (d, *J* 8.0, 1H, H^{4})				2.02* (s, *p*-CH_3)	
	7.87 (dd, *J* 5, 1.5, 1H, H^{2})					
	7.28 (tt, J 7.5, 1.5, 1H, H^{9})					
	7.22 (tt, *J* 7.5, 1.5, 2H, H$^{8,8'}$)					
	6.80 (d, *J* 7.0, 2H, H$^{7,7'}$)					
4b(*trans*)	8.21 (td, *J* 7.5, 2, 1H, H^{3})	8.69t	5.23s		6.55 (s, *m*-H)	
	8.04 (d, 1H, H^{4})				2.57 (s, *o*-CH_3)	
	7.70 (d, *J* 7.5, 2H, H^{7,7})				2.02*(s, *p*-CH_3)	

	7.59 (dd, J 5.5, 1.5, 1H, H^2) 7.46 (dd, J 5.5, 1.5, 1H, H^1) 7.40 (tt, J 7, 1.5, 2H, $H^{8,8'}$) 7.33 (tt, J 7.5, 1.5, 1H, H^9)				
5b(*cis*)	8.30 (d, J 8, 1H, H^3) 8.19 (d, J 7.5, 1H, H^4) 7.74 (dd, J 5.5, 1.5, 1H, H^2) 7.34-7.33*(m, 3H, $H^{8,8',9}$) 7.18 (d, J 5, 1H, H^1) 6.86 (d, J 7.5, 2H, $H^{7,7'}$)	8.68s	4.23s	6.45 (s, *m*-H) 3.01 (s, *o*-CH_3) 2.16*(s, *p*-CH_3)	8.76 (s, *o*-H) 7.65 (s, *p*-H) 2.31(s, *m*-CH_3)
5b(*trans*)	8.30 (d, J 7, 1H, H^3) 8.16 (d, J 7, 1H, H^4) 7.61 (dd, J 5.5, 1.5, 1H, H^2) 7.33-7.34* (m, 3H, $H^{8,8',9}$) 7.26 (d, J 5.5, 1H, H^1) 7.06-7.07 (m, 2H, $H^{7,7'}$)	8.97s	4.67s	6.49 (s, *m*-H) 3.06 (s, *o*-CH_3) 2.12(s, *p*-CH_3)	8.32 (s, *o*-H) 7.46 (s, *p*-H) 2.16* (s, *m*-CH_3)
6b(*cis*)	8.39 (td, J 8.0, 2.0, 1H, H^3) 8.33 (d, J 7.5, 1H, H^4) 7.98 (d, J 5, 1H, H^1) 7.85 (ddd, J 7.5, 5.0, 1.5, 1H, H^2) 7.31 (t, J 7.5, 1H, H^9) 7.24 (t, J 5.0, 2H, $H^{8,8'}$) 6.78 (d, J 7.5, 2H, $H^{7,7'}$)	9.05s	4.60s	6.53 (s, *m*-H) 2.51 (s, *o*-CH_3) 2.20 (s, *p*-CH_3)	8.49 (s, *o*-H) 7.74 (s, *p*-H) 2.33 (s, *m*-CH_3)
6b(*trans*)	8.40 (td, J 8.0, 1.5, 1H, H^3) 8.31 (d, J 6.5, 1H, H^4) 7.73 (ddd, 1H, H^2) 7.64 (d, J 5.5, 1H, H^1) 7.31-7.23*(m, 3H, $H^{8,8',9}$) 7.02 (d, J 7.0, 2H, $H^{7,7'}$)	9.08s	5.01s	6.58 (s, *m*-H) 2.68 (s, *o*-CH_3) 2.15 (s, *p*-CH_3)	8.10 (s, *o*-H) 7.52 (s, *p*-H) 2.20 (s, *m*-CH_3)
7b(*transE*)[d]	7.21-7.80 (m, 7H) 6.77 (bs, 2H, H^1)	8.68s	4.84s	6.55(s, *m*-H) 3.00 (s, *o*-CH_3) 2.20 (s, *p*-CH_3)	10.33 (s, NH) 6.70 (s, *m*-H) 2.89 (s, N=CCH_3) 2.19 (s, *p*-CH_3) 1.64 (s, *o*-CH_3)

a) Recorded at 500 MHz in acetone-d^6, unless noted otherwise, J in Hz, positions and splitting pattern of the peaks with asterisks are not determined precisely due to overlapping with other signals. Numbering is given in the diagram at the top of the table. b) 200 MHz, $CDCl_3$

c) 250 MHz, DMSO-d^6. d) 500MHz, $CDCl_3$

For the Neutral and Ionic complexes, Trans : Trans configuration between the mesityl and the iminic nitrogen, Cis : Cis configuration between the mesityl and the iminic nitrogen.

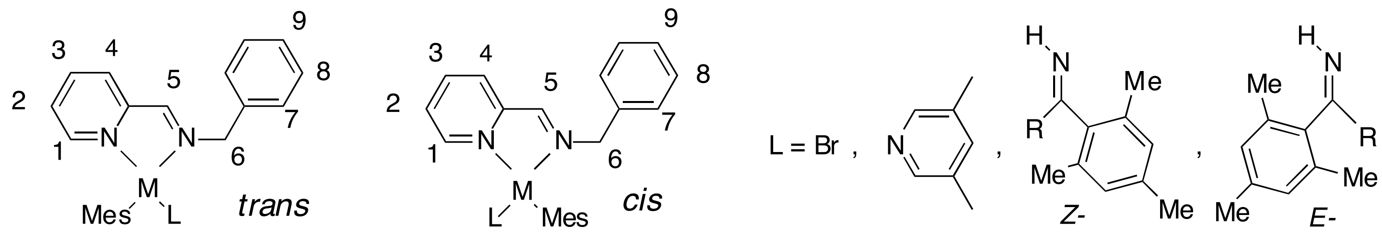


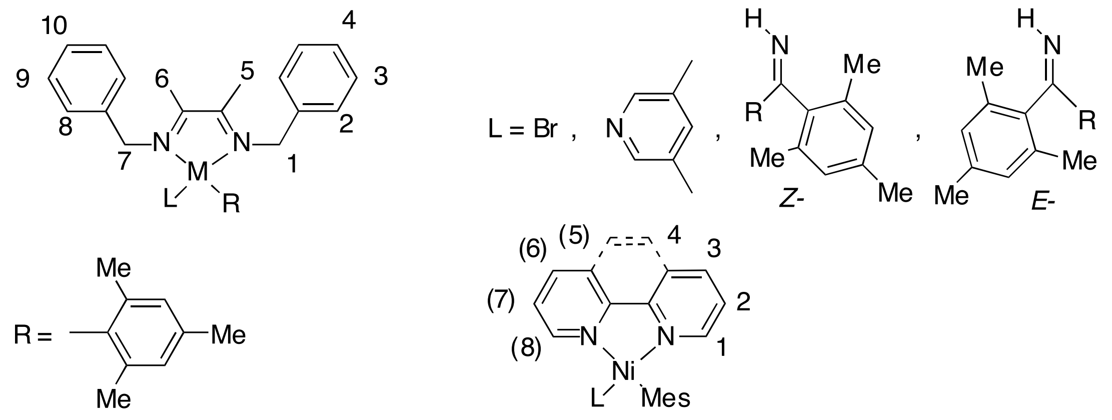
Table 2
^1H NMR Data of the [MBr(R)NN], [M(R)(3,5-lut)NN] and [Ni(Mes){*E*-(NH=C(R)(Mes)}NN]BF_4 complexes where NN = DAD, 2,2'-bipy or *o*-phen and R = Mes[a)]

	NN					R(Mes)	L(3,5-Lutidine or imine)
	Aromatic	H^1	H^7	H^5	H^6		
a [b)]	7.25-7.45 (m, 10H)	4.70s		2.25s			
2a [b)]	7.57 (d, *J* 7,4H, $H^{2,2',8,8'}$)	5.63s		2.27s			
	7.40-7.28 (m, 6H)						
3a [b)]	7.65 (d, *J* 6.8, 2H, $H^{8,8'}$)	4.29s	5.37s	1.91s	2.16s	6.33 (s, *m*-H)	
	7.21-7.38 (m, 6H)					2.75 (s, *o*-CH_3)	
	6.68 (bs, 2H, $H^{2,2'}$)					1.69 (s, *p*-CH_3)	
3 c	9.52 (d, *J* 6, 2H, H^8)					6.53 (s, *m*-H)	
	7.95 (t, *J* 6, 2H, H^6)					3.10 (s, *o*-CH_3)	
	7.9-7.8(m, 4H, $H^{5,4,3}$)					2.23 (s, *p*-CH_3)	
	7.50 (t, *J* 6, 2H, H^7)						
	7.29 (d, *J* 6, 2H, H^1)						
	7.14 (t, 2H, H^2)						
3d	9.71 (d, *J* 8 1H, H^8)					6.59 (s, *m*-H)	
	8.43 (m, 1H, H^6)					3.15 (s, *o*-CH_3)	
	8.36 (t, 1H, H^3)					2.27 (s, *p*-CH_3)	
	7.95-7.85 (m, 2H, $H^{4,5}$)						

	7.82 (m, 1H, H[7])						
	7.46 (m, 1H, H[2])						
4a	7.63 (d, *J* 7.5, 2H, H[8,8'])	4.51s	5.34s	2.10s	2.17s	6.40 (s, *m*-H)	
	7.36-7.17 (several m, 6H)					2.40 (s, *o*-CH_3)	
	6.65 (d, *J* 7.5, 2H, H[2,2'])					2.15 (s, *p*-CH_3)	
5a	7.40-7.22 (m, 6H)	4.17	4.29s	2.25s	2.34s	6.22 (s, *m*-H)	8.02 (s, *o*-H)
	6.93 (d, *J* 7, 2H, H[8,8'])					2.65 (s, *o*-CH_3)	7.06 (s, *p*-H)
	6.73 (d, *J* 7, 2H, H[2,2'])					2.06 (s, *p*-CH_3)	2.03 (s, *m*-
CH_3)							
6a [b)]	7.32-7.16 (m, 6H)	4.51s	4.74s	2.32s		6.34 (s, *m*-H)	7.78 (s, *o*-H)
	6.88 (m, 2H, H[8,8'])					2.47 (s, *o*-CH_3)	7.14 (s, *p*-H)
	6.71 (m, 2H, H[2,2'])					2.11 (s, *p*-CH_3)	2.04 (s, *m*-
CH_3)							
7a(*E*) [c)]	7.70-7.25 (m, 8H)	4.48s	4.97s	2.13s	2.15s	6.40 (s, *m*-H)	9.16 (s, NH)
	6.78 (m, 2H, H[2,2'])					2.89 (s, *o*-CH_3)	6.66 (s, *m*-H)
						1.54 (s, *p*-CH_3)	2.89 (s,
N=CCH_3)							
							2.41 (s, 3H, *o*-
CH_3)							
							2.46 (s, 3H, *o*-
CH_3)							
							1.54 (s, *p*-CH_3)
7c(*E*) [c)]	8.50 (d, 1H)					6.81 (s, *m*-H)	9.45 (s, NH)
	8.41 (d, 1H)					3.18 (s, *o*-CH_3)	6.63 (s, *m*-H)

	8.32(m, 2H)	3.06 (s, *p*-CH_3)	2.22 (s, N=CCH_3)
	8.20 (dd, 1H)		2.21 (s, *p*-CH_3)
	7.82 (dd, 1H)		1.89 (s, *o*-CH_3)
	7.42 (d, 2H)		
7c'(*E*)[c]	8.62-8.22 (m, 5H)	6.88 (s, *m*-H)	9.83 (s, NH)
	7.70-7.40 (m, 3H)	2.81 (s, *o*-CH_3)	7.50 (m, 5H Ph)
		2.60 (s, *p*-CH_3)	6.52 (s, *m*-H)
			2.26 (s, *o*-CH_3)
			2.17 (s, *p*-CH_3)
7d(*E*)[c]	9.00 (dd, 1H)	6.84 (s, *m*-H)	9.57 (s, NH)
	8.88 (dd, 1H)	3.23 (s, *o*-CH_3)	6.67 (s, *m*-H)
	8.79 (dd, 1H)	3.14 (s, *p*-CH_3)	2.24 (s, N=CCH_3)
	8.31 (d, 2H, $H^{5,4}$)		2.22 (s, *p*-CH_3)
	8.25 (dd, 1H)		2.02 (s, *o*-CH_3)
	7.86 (dd, 1H)		
	7.78 (dd, 1H)		

a) Recorded at 500 MHz in $CDCl_3$, unless noted otherwise, J in Hz. b) Recorded at 250MHz in $CDCl_3$. c) Recorded at 250 MHz in acetone-d^6



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