

Supporting Information for:

Nickel(0) Complexes of N-Alkyl Substituted N-
Heterocyclic Carbenes and their Use in the
Catalytic Carbon-Carbon Bond Activation of
Biphenylene

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A. Preparation and characterization of imidazolium salts and N heterocyclic carbenes

Synthesis of 1,3-di(methyl)imidazolium iodide. Methylimidazole (20.8 g, 0.253 mol) and iodomethane (35.9 g, 0.253 mol) were dissolved in 100 ml toluene and stirred at reflux over night. After cooling to room temperature a white solid was formed, which was filtered off, washed with 40 ml hexane, and dried *in vacuo* to yield 56.0 g (99 %) of a white powder. – ^1H -NMR (D_2O): δ = 3.85 (s, 6 H, CH_3), 7.38 (s, 2 H, CHCH), 8.62 (s, 1 H, NCHN). – ^{13}C -NMR (D_2O): δ = 35.95 (CH_3), 123.48 (CHCH), 136.64 (NCN).

Synthesis of 1,3-di(methyl)imidazol-2-ylidene (Me_2Im). 1,3-Di(methyl)imidazolium iodide (32.0 g, 0.143 mol) and NaH (3.43 g, 0.143 mol) were dissolved in 200 ml liquid NH_3 at -78°C and stirred for 1 hour at this temperature. Afterwards, the temperature was raised to room temperature in order to remove ammonia. Last traces of ammonia were eliminated *in vacuo* at room temperature. The remaining yellow precipitate was distilled at 150°C and 10^{-2} mbar into a flask which was cooled with liquid nitrogen to give 11.9 g (77 %) of a red, crystalline solid (at -30°C). – ^1H -NMR (C_6D_6): δ = 3.43 (s, 6 H, CH_3), 6.70 (s, 2 H, NCHCHN). – ^{13}C -NMR (C_6D_6): δ = 37.35 (CH_3), 120.24 (NCCN), 214.55 (NCN).

Synthesis of 1,3-di(*n*propyl)imidazolium chloride. *N*propyl amine (29.7 ml, 0.36 mol) was added dropwise to a suspension of 10.8 g (0.36 mol) formaldehyde in 60 ml toluene. The temperature was kept below 40°C during addition. Afterwards the reaction mixture was stirred for ten minutes and then cooled to 0°C . Another equivalent *n*propyl amine (29.7 ml, 0.36 mol) and 6 N HCl (60 ml, 0.36 mol) were added slowly. The temperature of the solution was raised to room temperature and glyoxal (41.4 ml, 0.36 mol; 40 % in H_2O) was added dropwise. The mixture was stirred over night to give a dark brown solution. All volatile material was removed *in vacuo* and the brown residue was vigorously dried *in vacuo* at 150°C for 6 hours to yield 56.5 g (83 %) of a brown solid. – ^1H -NMR (D_2O): 0.82 (t, 6 H, $^3J_{\text{HH}} = 7.4$ Hz, CH_3), 1.80 (sext, 4 H, $^3J_{\text{HH}} = 7.2$ Hz, NCH_2CH_2), 4.08 (t, 4 H, $^3J_{\text{HH}} = 7.0$, NCH_2), 7.41

(s, 2 H, NCHCHN), 8.71 (s, 1 H, NCHN). – ^{13}C -NMR (D_2O): 9.79 (CH_3), 22.79 ($\text{NCH}_2\text{-CH}_2$), 51.08 (N-CH_2), 122.29 (NCCN), 135.16 (NCN).

Synthesis of 1,3-di-*n*propylimidazol-2-ylidene ($^n\text{Pr}_2\text{Im}$). THF (300 ml) was added at room temperature to a mixture of 1,3-di(*n*propyl)imidazolium chloride (56.5 g, 0.30 mol), sodium hydride (8.40 g, 0.35 mol) and potassium *tert*.butanolate (1.70 g, 15.1 mmol). The mixture was stirred over night to give a dark suspension, all volatiles were removed *in vacuo* and the resulting brown oil was distilled at 170 °C into a trap cooled with liquid nitrogen to afford 1,3-di(*n*propyl)imidazol-2-ylidene (41.1 g, 90 %) as a yellow liquid (at -30°C). The carbene is thermally labile and forms a dark oil at room temperature, but it can be stored for a longer period of time at -40°C without decomposition. – ^1H -NMR (400 MHz, C_6D_6): δ = 0.72 (t, 6 H, $^3J_{\text{HH}} = 7.8$ Hz, CH_3), 1.63 (sext, 4 H, $^3J_{\text{HH}} = 7.6$ Hz, CH_2CH_3), 3.80 (t, 4 H, $^3J_{\text{HH}} = 7.1$ Hz, NCH_2), 6.8 (s, 2 H, NCHCHN). – ^{13}C -NMR (400 MHz, C_6D_6): δ = 11.71 (CH_3), 26.14 (NCH_2CH_2), 53.66 (NCH_2), 119.67 (NCCN), 214.91 (NCN).

Synthesis of 1-methyl-3-isopropyl-imidazolium iodide: Methylimidazole (12.3 g, 0.150 mol) and 2-iodopropane (25.5 g, 0.150 mol) were dissolved in 80 ml toluene and stirred at reflux over night. After cooling to room temperature a white solid was formed, which was filtered off, washed twice with 40 ml hexane and dried in vacuum to yield 34.2 g (90 %) of a white powder. – ^1H -NMR (400 MHz, CDCl_3): δ = 1.61 (d, 6 H, $^3J_{\text{HH}} = 6.7$ Hz, $^i\text{Pr-CH}_3$), 4.10 (s, 3 H, N- CH_3), 4.81 (sept, 1 H, $^3J_{\text{HH}} = 6.7$ Hz, $^i\text{Pr-CH}$), 7.60 (m, 2 H, NCHCHN), 9.95 (s, 1 H, NCHN). – ^{13}C -NMR (400 MHz, CDCl_3): δ = 23.27 ($^i\text{Pr-CH}_3$), 37.13 (N- CH_3), 53.45 ($^i\text{Pr-CH}$), 120.53 (NCCN), 125.25 (NCCN), 135.54 (NCN).

Synthesis of 1-methyl-3-isopropyl-imidazol-2-ylidene (Me^iPrIm): 1-Methyl-3-isopropyl-imidazolium iodide (34.2 g, 0.135 mol) and NaH (3.45 g, 0.143 mol) were dissolved in 200 ml liquid NH_3 at -78°C and stirred for 1 hour at this temperature. Afterwards, the temperature was raised to room temperature in order to remove ammonia. Traces of ammonia were removed *in vacuo* at room temperature. The remaining brown precipitate was distilled at 170

°C and 10^{-2} mbar into a flask which was cooled with liquid nitrogen to give 14.9 g (79%) of a red liquid (at -30 °C). – ^1H -NMR (400 MHz, C_6D_6): δ = 1.26 (d, 6 H, $^3J_{\text{HH}}$ = 6.7 Hz, $^i\text{Pr-CH}_3$), 3.44 (s, 3 H, N- CH_3), 4.36 (sept, 1 H, $^3J_{\text{HH}}$ = 6.7 Hz, $^i\text{Pr-CH}$), 6.59 (d, 1 H, $^3J_{\text{HH}}$ = 1.6 Hz, NCHCHN), 6.71 (d, 1 H, $^3J_{\text{HH}}$ = 1.6 Hz, NCHCHN). – ^{13}C -NMR (400 MHz, C_6D_6): δ = 25.04 ($^i\text{Pr-CH}_3$), 38.44 (N- CH_3), 52.69 ($^i\text{Pr-CH}$), 117.35 (NCCN), 120.83 (NCCN), 214.35 (NCN).

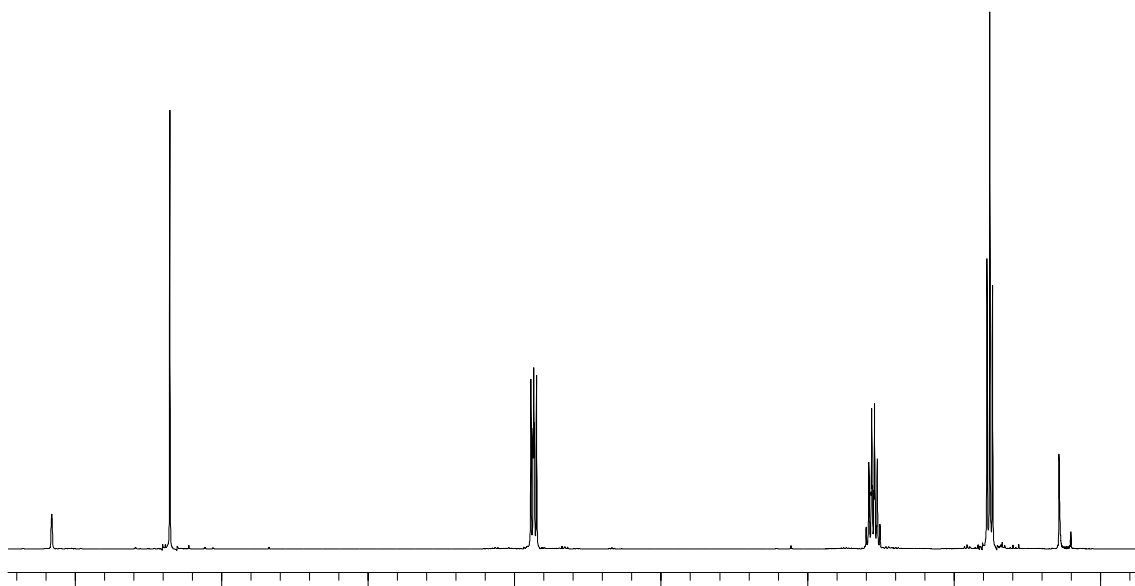
Synthesis of 1,3-Di(isopropyl)imidazolium chloride. Isopropyl amine (61.8 ml, 0.72 mol) was added dropwise to a suspension of 21.6 g (0.71 mol) formaldehyde in 120 ml toluene. The temperature of the reaction mixture was kept below 40 °C during addition. Afterwards, the reaction mixture was stirred for ten minutes and then cooled to 0 °C. Another equivalent of isopropyl amine (61.8 ml, 0.72 mol) and 6 N HCl (120 ml, 0.72 mol) were slowly added. The solution was warmed to room temperature and glyoxal (82.8 ml, 0.72 mol; 40 % in H_2O) was added dropwise. The mixture was stirred over night to give a dark solution. All volatile material was removed *in vacuo*. The brown residue was vigorously dried *in vacuo* at 150 °C for 6 hours to yield 113.0 g (83 %) of a brown solid: – ^1H -NMR (400 MHz, D_2O): δ = 1.43 (d, 12 H, CH_3), 4.52 (m, 2 H, $^i\text{Pr-CH}$), 7.47 (s, 2 H, NCHCHN), 8.76 (s, 1 H, NCHN). – ^{13}C -NMR (400 MHz, D_2O): δ = 22.07 (CH_3), 53.04 ($^i\text{Pr-CH}$), 120.47 (NCCN), 132.47 (NCN).

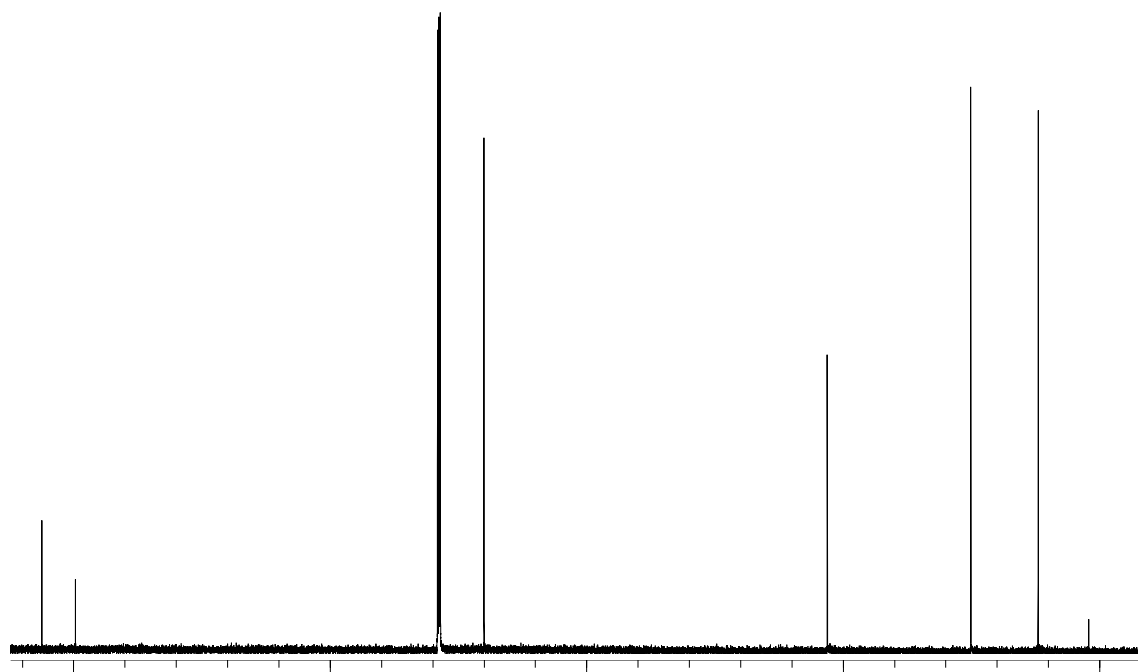
1,3-Di(isopropyl)imidazol-2-ylidene ($^i\text{Pr}_2\text{Im}$). THF (600 ml) was added at room temperature to a mixture of 1,3-di(isopropyl)imidazolium chloride (113.0 g, 0.60 mol), sodium hydride (15.7 g, 0.65 mol) and potassium *tert*.butanolate (3.30 g, 29.4 mmol). The mixture was stirred over night to give a dark suspension. All volatiles were removed *in vacuo* and the resulting brown oil was distilled at 150 °C into a trap cooled with liquid nitrogen to afford 1,3-di(isopropyl)imidazol-2-ylidene (73.0 g, 80 %) as a colorless liquid (melting point approximately 20°C). The carbene is thermally labile and forms a dark oil at room temperature, but it can be stored for a longer period of time at -40°C without recognizable decomposition. – ^1H -NMR (400 MHz, C_6D_6): δ = 1.27 (d, 12 H, CH_3), 4.40 (m, 2 H, $^i\text{Pr-CH}$),

6.63 (s, 2 H, NCHCHN). – ^{13}C -NMR (100 MHz, C_6D_6): δ = 24.27 ($i\text{Pr-CH}_3$), 52.12 ($i\text{Pr-CH}$), 115.74 (NCCN), 211.86 (NCN). – IR ($[\text{cm}^{-1}]$): 407 (m), 496 (w), 555 (m), 640 (w), 669 (m), 682 (m), 710 (s), 879 (m), 928 (w), 981 (m), 1089 (m), 1131 (s), 1215 (vs), 1242 (s), 1267 (s), 1328 (m), 1388 (vs), 1459 (s), 1669 (m), 2642 (w), 2874 (s), 2963 (vs), 3055 (m), 3103 (m) cm^{-1} .

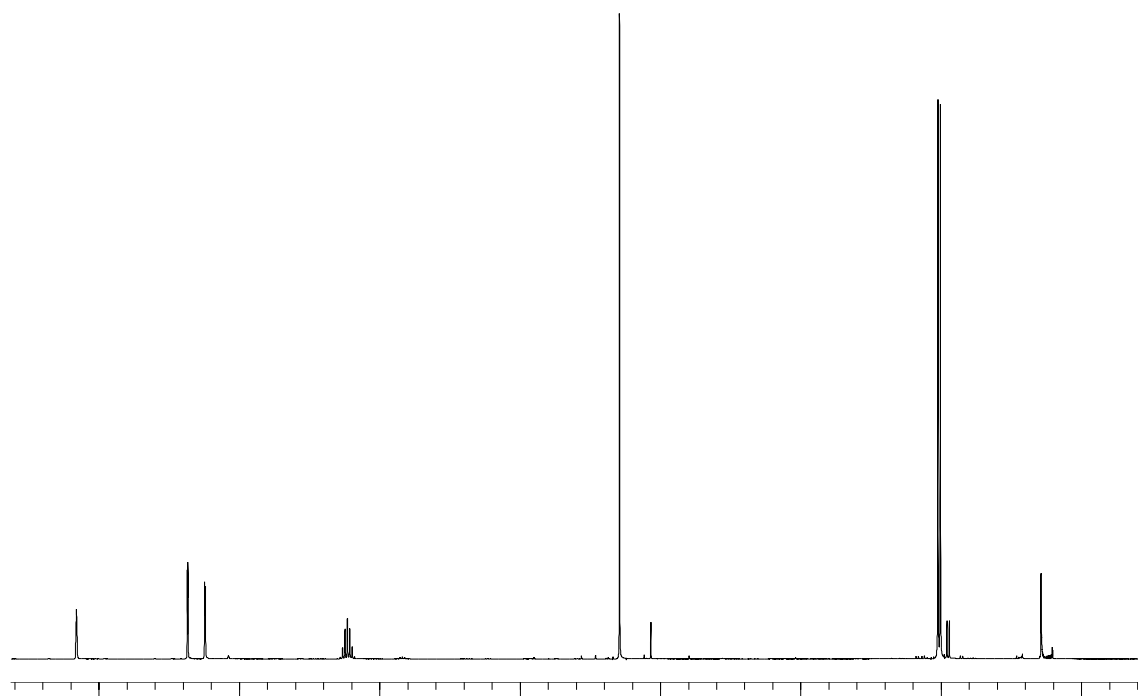
B NMR Spectra of compounds

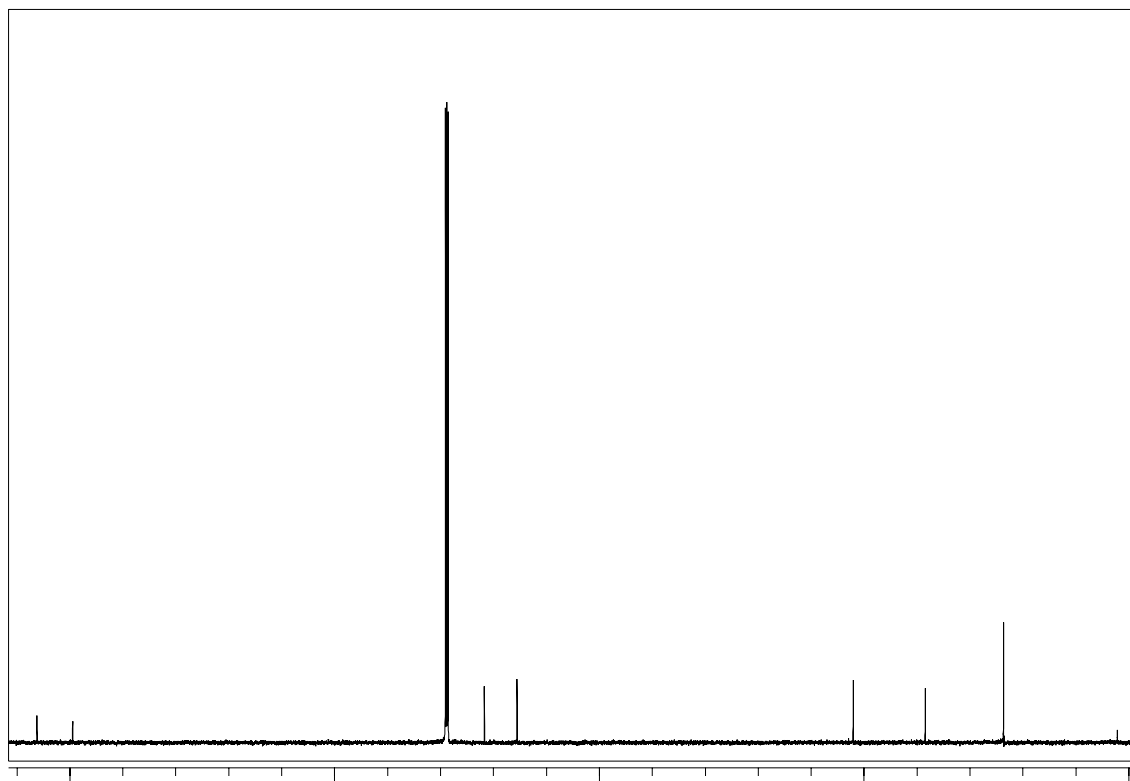
$[\text{Ni}(\text{}^{\text{a}}\text{Pr}_2\text{Im})_2(\text{CO})_2]$ (**6**):



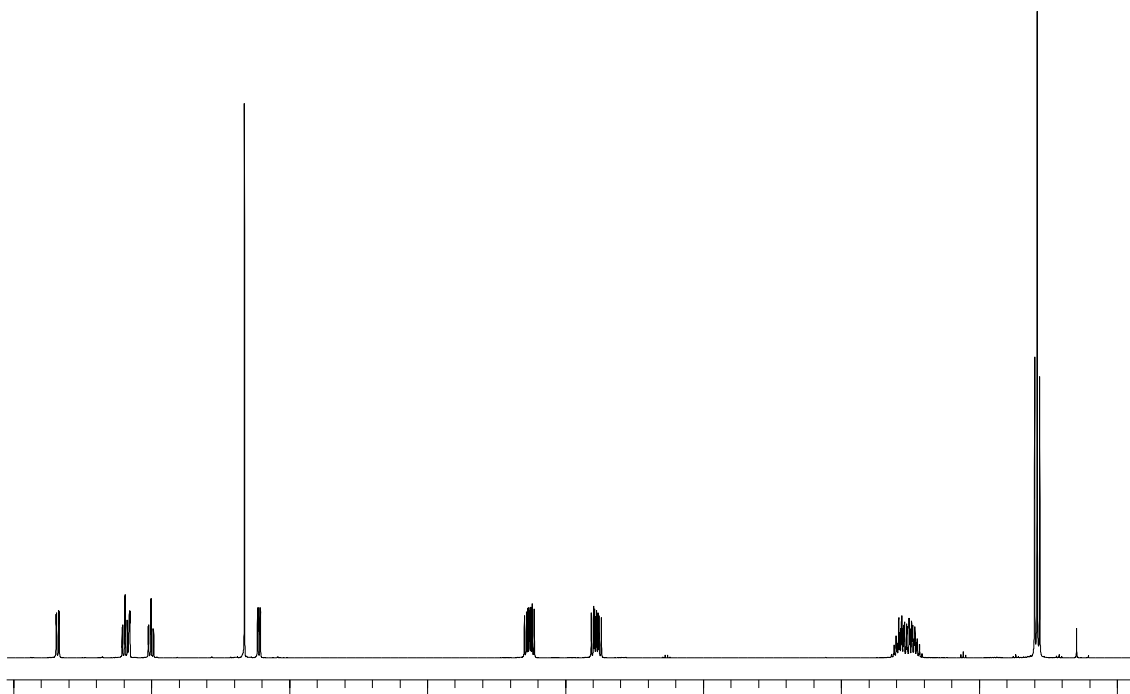


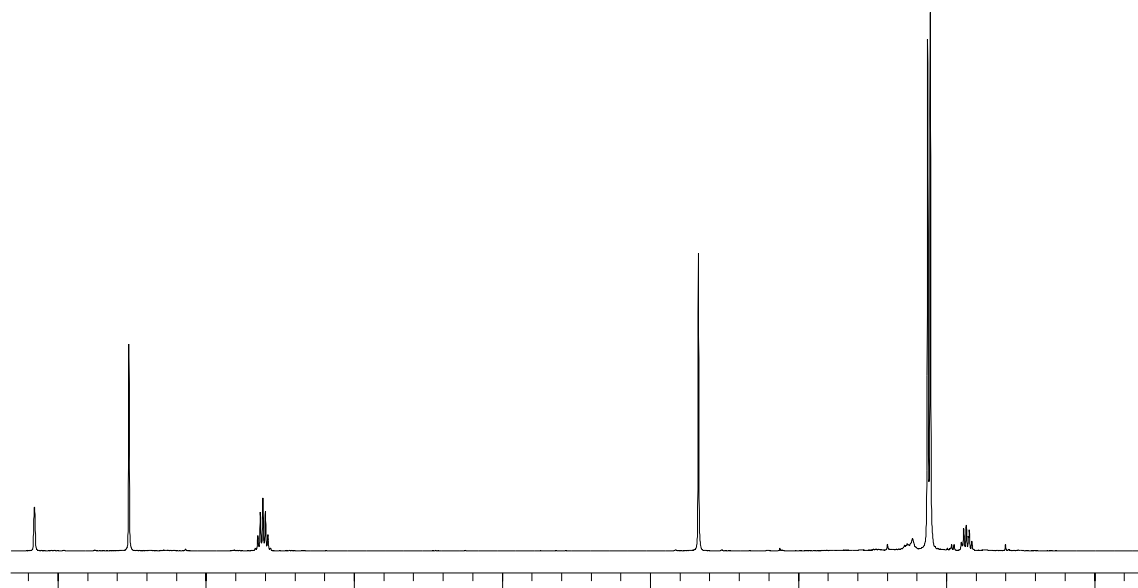
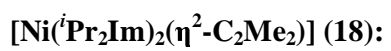
$[\text{Ni}(\text{Me}^i\text{PrIm})_2(\text{CO})_2]$ (7):

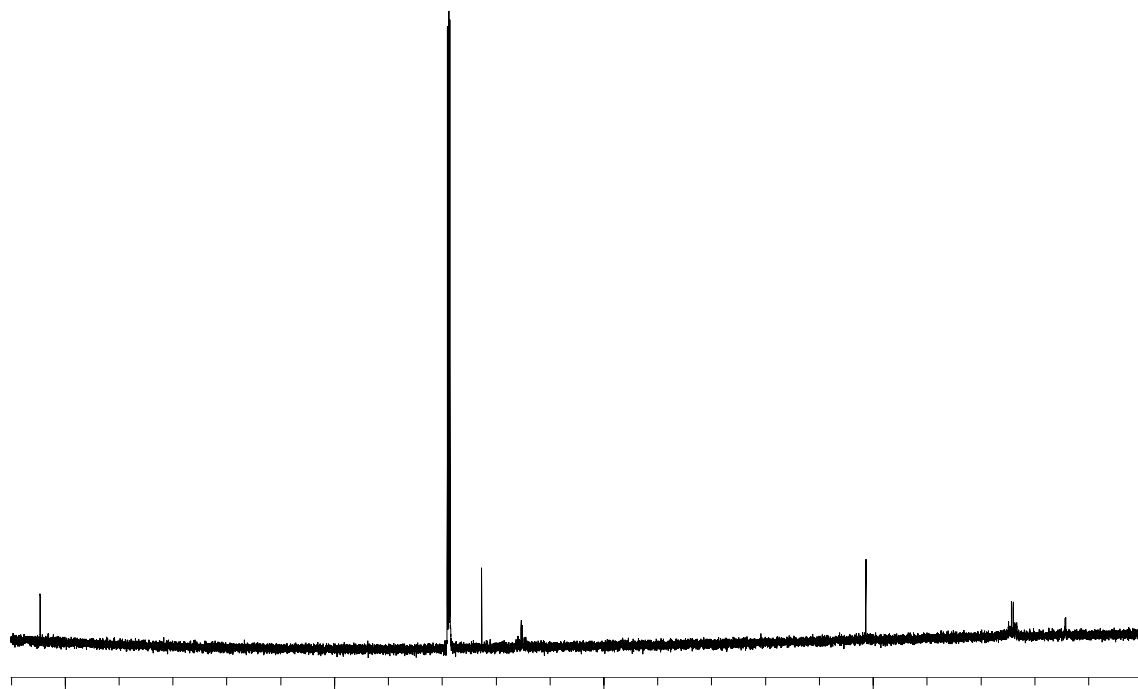




[Ni(ⁿPr₂Im)₂(2,2'-biphenylene)] (14):







$[\text{Ni}(\text{Pr}_2\text{Im})_2(\eta^2\text{-C}_2\text{Et}_2)]$ (19):

