## Supporting Information for:

# A Strongly Bent Nickel Imide Supported By a New Chelating Bis(*N*-Heterocyclic Carbene) Ligand

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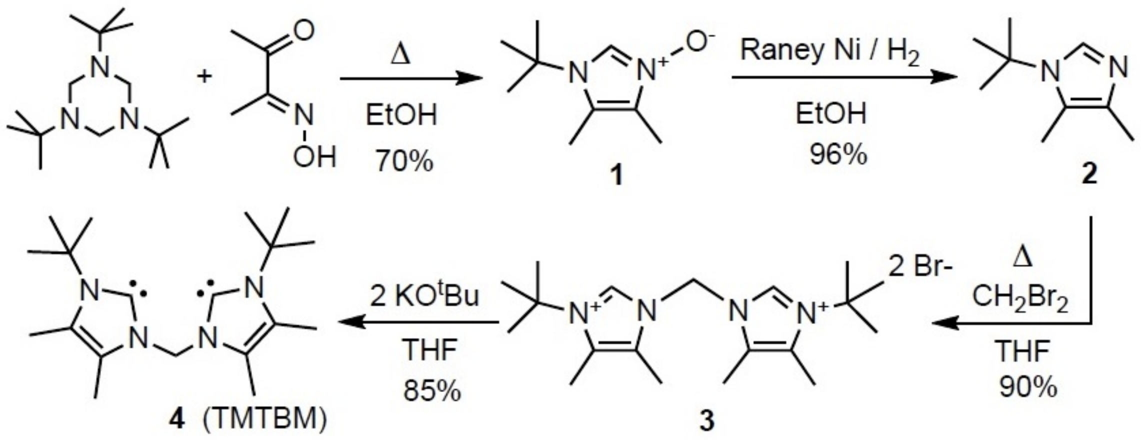
# 1. Experimental Section

**General Considerations.** Unless stated otherwise, all operations were performed in an MBraun *Lab Master* dry box under an atmosphere of purified nitrogen. Anhydrous diethyl ether and tetrahydrofuran were purchased from Fischer, stirred over sodium metal, and filtered through activated alumina.[1] Pentane was purchased from Sigma Aldrich and dried by passage through activated alumina and Q-5 columns. $C_6D_6$ was purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over $CaH_2$ or activated 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated by evacuation overnight at 180°C. $N_3$(dmp) (dmp = 2,6-dimesitylphenyl, $N_3$dippp (dippp = 2,6-bis(2,6-diisopropylphenyl)phenyl), $N_3$Ar (Ar = 2,6-di-*iso*-propylphenyl) were prepared according to the literature.[2,3] All other chemicals were used as received. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). $^1$H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer and reported with reference to solvent resonance (for example, residual $C_6D_5H$ in $C_6D_6$ at 7.16 ppm). X-ray diffraction data were collected on a Siemens Platform goniometer with a Charged Coupled Device (CCD) detector. Structures were solved by direct or Patterson methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).[4]



**Synthesis of 1-*tert*-butyl-4,5-dimethyl-1*H*-imidazole-3-oxide (1).** A solution of 2,3-butanedione monoxime (47.9 g, 0.474 mol) and 1,3,5-tri-*tert*-butyl-hexahydro-[1,3,5]triazine (40.33 g , 0.158 mol) in EtOH (200 mL) was heated at reflux for 12 h. Evaporation of the solvent under reduced pressure yielded a red oil, which was washed twice with $Et_2O$ (2 x 200 mL). The viscous oily crude product **1** was used in the next step without further purification. Yield: 79.59 g (70%). Dark red oil. IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 3358, 3139, 2958, 2931, 2873, 1626, 1450 (br), 1396, 1381, 1339, 1255, 1194, 1150, 1080. $^1H$ NMR (22°C, 400 MHz, $CDCl_3$): δ 7.87 (s, 1H, $HC$), 2.25 (s, 3H, $CCH_3$), 2.08 (s, 3H, $CCH_3$), 1.52 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (22°C, 125.75 MHz, $CDCl_3$): δ 127.89, 122.94, 120.86, 57.87, 29.78, 11.95, 6.98. GC-MS (m/z): 168 (M+), 112, 97, 42.

**Synthesis of 1-*tert*-butyl-4,5-dimethyl-1*H*-imidazole (2).** To a stirring solution of the imidazole N-oxide **1** (55.71 g, 0.332 mol) in EtOH (500 mL), a water suspension of Raney-nickel was added in small portions (~20 g Ni total). The reaction was stirred at room temperature under an atmosphere of hydrogen gas until gas consumption ceased. After reduction of **2** was completed, the solution was filtered through Celite and the filtrate was reduced to dryness under reduced pressure. The product was extracted with $Et_2O$ (3 x 100 mL) and reduced to dryness. Pure **2** was obtained after distillation of the product resulting in a pale yellow oil (48.46 g, 96%) *****NOTE: it is very important to extract 2 from precursor 1 before distillation. N-oxides are known to be violently explosive under standard distillation conditions.**[5] IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 2959, 2932, 2873, 1500, 1451, 1388, 1366, 1202. $^1H$ NMR (22°C, 400 MHz, $CDCl_3$): δ 7.432 (s, 1H, $HC(2)$), 2.260 (s, 3H, $CCH_3$), 2.094 (s, 3H, $CCH_3$), 1.539 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (22°C, 125.75 MHz, $CDCl_3$): δ 138.84, 132.63, 122.66, 55.61, 30.10, 12.70, 11.92. GC-MS (m/z): 152 (M+)

**Synthesis of 3,3'-methylenebis(1-*tert*-butyl-4,5-dimethyl-1*H*-imidazol-3-ium dibromide (3).** Dibromomethane (41.50 g, 0.239 mol) was added to a stirring solution of **2** (48.46 g, 0.318 mol) in 100 mL of benzene. The solution was refluxed for 2 days after which the solvent was removed under reduced pressure. Acetone (200 mL) was added to the flask and the resulting white suspension was allowed to stir at room temperature for 1 hour. The white solids were filtered and dried under reduced pressure for 2 hours.

Yield: 68.5 g (90%). IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 3026, 2919, 2308, 1782, 1720, 1620, 1541, 1458. $^1H$ NMR (22$^o$C, 400 MHz, $CDCl_3$): δ 10.632 (s, 2H, NC*H*N) 7.532 (s, 2H, NC$H_2$N), 2.438 (s, 6H, CC$H_3$), 2.389 (s, 6H, CC$H_3$), 1.6912 (s, 18H, C(C$H_3$)$_3$); $^{13}C\{^1H\}$ NMR (22$^o$C, 125.75 MHz, $CDCl_3$): δ 135.89, 129.50, 127.76, 62.44, 56.02, 29.63, 11.86, 9.81. Anal. Calcd. for $C_{19}H_{34}N_4Br_2$: C, 47.71; H, 7.16; N, 11.71. Found: C, 47.54; H, 6.94; N, 11.45.

**Synthesis of 1-*tert*-butyl-4,5-dimethyldimethylimidazoliylidene (4).** A suspension of **3** (8 g, 0.017 mol) was stirred in THF (100 mL) for 20 min after which time freshly sublimed KO$^t$Bu (3.75 g, 0.033 mol) was added. After the solution was allowed to stir for 3 hours, the solvent was removed under reduced pressure. Pentane (100 mL) was added to the flask and the suspension was filtered through Celite. The filtrate was reduced to ½ volume and stored overnight at -35°C. The resulting white power was filtered, washed with cold pentane, and dried under reduced pressure for 2 hours. Yield: 4.50 g (85%). IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 2971, 2930, 2883, 1510, 1462, 1389. $^1H$ NMR (22$^o$C, 400 MHz, $C_6D_6$): δ 6.197 (s, 2H, NC$H_2$N), 2.414 (s, 6H, CC$H_3$), 2.199 (s, 6H, CC$H_3$), 1.527 (s, 18H, C(C$H_3$)$_3$). $^{13}C\{^1H\}$ NMR (22$^o$C, 125.75 MHz, $CDCl_3$): δ 214.12, 126.07, 122.89, 63.20, 56.82, 31.71, 12.56, 10.23.

**Synthesis of (TMTBM)Ni($\eta^2$-cod) (5).** The ligand **4** (1.00 g, 3.160 mmol) was added to a stirring solution of Ni(cod)$_2$ (0.870 g, 3.160 mol) in THF (40 mL). The solution was stirred for 8 hours at room temperature and then reduced to dryness under vacuum. The resulting orange powder was washed with pentane (3 x 20 mL) and then dried under vacuum for 3 hours. Yield: 1.20 g (94%). IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 3002, 2830, 2823, 1525, 1475, 1390; $^1H$ NMR (22$^o$C, 400 MHz, $C_6D_6$): δ 6.106 (s, 2H, cod), 5.908 (d, 1H, NC$H_2$N), 4.996 (d, 1H, NC$H_2$N), 2.759 – 2.259 (m, 8H, cod), 2.201 – 2.168 (m, 2H, cod), 1.758 (s, 18H, C(C$H_3$)$_3$), 1.758 (s, 6H, CC$H_3$), 1.535 (s, 6H, CC$H_3$). $^{13}C\{^1H\}$ NMR (22$^o$C, 125.75 MHz, $CDCl_3$): δ 203.50, 132.26, 122.15, 57.98, 55.88, 52.88, 35.85, 33.20, 32.16, 13.42, 8.36 (s, cod); Anal. Calcd. for $C_{29}H_{50}N_4Ni$: C, 67.84; H, 9.82; N, 10.91. Found: C, 67.09; H, 9.29; N, 10.85.

**Synthesis of (TMTBM)Ni($\eta^2$-N$_3$Ar) (6).** 2,6-di-iso-propylphenylazide (0.150 g, 0.740 mmol) was added to a cold (-35°C) stirring solution of **5** (0.300 g, 0.740 mmol) in

$Et_2O$ (15 mL). The resulting yellow suspension was stirred for 1 hour and then filtered. The resulting yellow powder was washed with pentane (2 x 10 mL) and then dried under vacuum for 3 hours. Yield: 0.427 g (94%). IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 2725, 1641, 1485, 1419, 1402, 1376, 1327; $^1H$ NMR (22°C, 400 MHz, $C_6D_6$): δ 7.356 (d, 2H, *m*-$C_6H_3$), 7.084 (t, *p*-$C_6H_3$), 5.908 (d, 1H, NC$H_2$N), 4.996 (d, H, NC$H_2$N), 4.597 (sept, 1H, C$H$($CH_3$)$_2$), 4.157 (sept, 1H, C$H$($CH_3$)$_2$); 2.026 (s, 3H, CC$H_3$), 1.821 (s, 3H, CC$H_3$), 1.579 (s, 3H, CC$H_3$), 1.456 (s, 3H, CC$H_3$), 1.857 (s, 9H, C(C$H_3$)$_3$), 1.387 (s, 9H, C(C$H_3$)$_3$); 1.542 (d, 6H, CH(C$H_3$)$_2$), 1.387 (d, 6H, CH(C$H_3$)$_2$); $^{13}C\{^1H\}$ NMR (22°C, 125.75 MHz, $CDCl_3$): δ 190.01, 187.23, 161.09, 123.09, 115.98, 59.88, 58.98, 56.88, 55.23, 54.99, 32.18, 30.72, 31.08, 24.52, 22.10, 21.98, 28.79, 23.17. Anal. Calcd. for $C_{31}H_{49}N_7Ni$: C, 64.37; H, 8.54; N, 16.95. Found: C, 64.23; H, 8.40; N, 16.73.

**Synthesis of (TMTBM)Ni=N(dmp) (7a).** 2,6-dimesitylphenylazide (0.263 g, 0.740 mmol) was added to a cold (-35 °C) stirring solution of **5** (0.300 g, 0.740 mmol) in $Et_2O$ (15 mL). Gas evolution was immediately observed, and the resulting red solution was stirred for 1 hour and then filtered and reduced to dryness. The resulting red powder was washed with pentane (2 x 10 mL) and then dried under vacuum for 3 hours. Yield: 520 mg (86%). IR ($CaF_2$, fluorolube): ν ($cm^{-1}$) 3349, 3047, 1641, 1574, 1457, 1365, 1334, 1303, 1266, 1218; $^1H$ NMR (22°C, 400 MHz, $C_6D_6$): δ 6.704 (s, 4H, *H*-mesityl); 6.592 (d, 2H, *H*-phenyl) 6.574 (t, 1H, *H*-phenyl); 6.331 (d, 1H, NC$H_2$N), 4.814 (d, 1H, 1 NC$H_2$N); 2.614 (s, 12H, *o*-C$H_3$); 2.165 (s, 6H, CC$H_3$), 1.617 (1s, 6H, CC$H_3$); 1.584 (s, 18H, C(C$H_3$)$_3$); 1.353 (s, 6H, *p*-C$H_3$); $^{13}C\{^1H\}$ NMR (22°C, 125.75 MHz, $CDCl_3$): δ 183.12, 163.18, 143.36, 137.80, 133.25, 124.45, 124.24, 111.03, 87.76, 58.14, 55.51, 52.88, 32.80, 22.08, 21.92, 13.62, 8.68. Anal. Calcd. for $C_{43}H_{57}N_5Ni$: C, 73.50; H, 8.18; N, 9.97. Found: C, 72.96; H, 8.08; N, 9.95.

**Synthesis of (TMTBM)Ni=N(dippp) (7b).** $N_3$dippp (0.325 g, 0.740 mmol) was added to a cold (-35 °C) stirring solution of **5** (0.300 g, 0.740 mmol) in diethyl ether (15 mL). Gas evolution was immediately observed, and the resulting red solution was stirred for 1 hour and then filtered and reduced to dryness. The resulting red powder was washed with pentane (2 x 10 mL) and then dried under vacuum for 3 hours. Yield: 518 mg (89 %). Crystals suitable for X-ray diffraction were grown from a concentrated diethyl ether solution at -35 °C; IR ($CaF_2$, Fluorolube): ν ($cm^{-1}$) 3035 (s), 1637 (m), 1572 (m), 1450 (w), 1368 (w), 1334 (w), 1266 (w), 1217 (w); $^1$H NMR (22°C, 400 MHz, $C_6D_6$): δ 7.24 (d, 4H, $C_6H_3$), 7.15 (t, 2H, $C_6H_3$), 6.85 (d, 2H, $C_6H_3$), 6.70 (t, 1H, $C_6H_3$), 3.76 (m, 4H, C*H*($CH_3$)$_2$), 1.64 (s, 6H, C*H*$_3$), 1.54 (s, 6H, C*H*$_3$), 1.54 (s, 18H, $^t$*Bu*), 1.45 (d, 12H, CH(C*H*$_3$)$_2$), 1.25 (d, 12H, CH(C*H*$_3$)$_2$; $^{13}$C{$^1$H} NMR (22°C, 125.75 MHz, $CDCl_3$): δ 182.5, 148.8, 144.7, 130.2, 126.8, 124.8, 124.4, 122.6, 58.0, 55.6, 32.9, 31.2, 26.1, 24.7, 13.6, 8.8.

**Synthesis of [(TMTBM)Ni=N(dippp)]$_2$[B($C_6F_5$)$_4$]$_2$ (9).** In a scintillation vial, **7b** (100 mg, 0.125 mmol) was dissolved in 10 mL thf and cooled to -45 °C. Subsequently, 108 mg [$FeCp_2$][B($C_6F_5$)$_4$], was added via spatula and the solution was stirred for 2 hours. The deep purple solution was filtered through Celite and reduced to dryness. The powder was washed with *n*-pentane (3 x 10 mL) and then dried under vacuum for 3 hours. Yield: 163 mg (89 %). Crystals suitable for X-ray diffraction were grown from a concentrated thf solution at -35 °C. Anal. Calcd. for $C_{146}H_{136}N_{10}Ni_2B_2F_{20}$: C, 59.86; H, 4.68; N, 4.78. Found: C, 62.21; H, 4.81; N, 4.64. **Complex **9** is not sufficiently thermally stable to give accurate elemental analyses. IR ($CaF_2$, Fluorolube): ν 1359(m), 1242 (m), 1210 (w), 1170 (s), 1095 (s), 940 (w), 849 (w), 680 (s), 659 (m), 592 (s), 455 (m) cm$^{-1}$. $^1$H NMR (22°C, 400 MHz, thf-$d_8$): δ 7.844 (d, 2H, NC*H*$_2$N), 7.19 (t, 4H, $C_6H_4$), 7.15 (s, 4H, $C_6H_2$), 6.94 (d, 8H, $C_6H_4$), 6.28 (d, 2H, NC*H*$_2$N), 2.83-2.93 (m, 8H, C*H*($CH_3$)$_2$), 2.29 (s, 12H, CC*H*$_3$), 2.24 (s, 12H, CC*H*$_3$), 2.01 (s, 36H, $^t$*Bu)*, 1.15 – 1.10 (d, 48H, CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H} NMR (22°C, 125.75 MHz, thf-$d_8$) δ 149.1, 139.8, 139.7, 137.6, 137.5, 130.4, 129.4, 124.3, 32.4, 31.8, 26.2, 26.0, 25.8, 28.9, 13.3, 8.6;

## 2. DFT calculations

Gaussian 03 (revision E.01) was used for all reported calculations.[6] The B3LYP (DFT) method was used to carry out the geometry optimizations on the model compounds specified in text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian. For the optimization of (TMTBM)Ni=N(dmp) the initial structure used was derived from the crystal structure of **7a**.

### Table 1. Select metrical data for (TMTBM)Ni=N(dmp) (7a) DFT & Experimental Solid-State Structure

| Bond | DFT (Å) | Structure (Å) | Angle (°) | DFT (°) | Structure (°) |
|---|---|---|---|---|---|
| Ni(1)-N(1) | 1.706 | 1.732(3) | C(1)-Ni(1)-C(18) | 89.02 | 89.79(16) |
| N(1)-C(25) | 1.345 | 1.344(5) | C(18)-Ni(1)-N(1) | 134.24 | 137.51(16) |
| C(1)-Ni(1) | 1.930 | 1.872(4) | C(1)-Ni(1)-N(1) | 134.17 | 128.70(16) |
| C(18)-N(1) | 1.929 | 1.885(4) | Ni(1)-N(1)-C(25) | 145.67 | 127.3(3) |

### Table 2. Optimized geometry for (TMTBM)Ni=N(dmp) (7a)

| Atom Number | Atom Type | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| | | X | Y | Z |
| 1 | Ni | 0.107866 | -0.192120 | -0.395978 |
| 2 | C | -1.470238 | -1.153574 | -0.091856 |
| 3 | N | -1.603019 | -1.662259 | 1.177383 |
| 4 | C | -2.818025 | -2.322470 | 1.347778 |
| 5 | C | -3.457156 | -2.233842 | 0.173722 |
| 6 | C | -4.852380 | -2.704016 | -0.116202 |
| 7 | H | -5.205003 | -3.176820 | 0.665755 |
| 8 | H | -4.842349 | -3.309902 | -0.885798 |
| 9 | H | -5.423044 | -1.932581 | -0.315238 |
| 10 | N | -2.625400 | -1.519911 | -0.717663 |
| 11 | C | -2.727656 | -1.550332 | -2.224910 |
| 12 | C | -2.382772 | -2.980905 | -2.648156 |
| 13 | H | -3.030630 | -3.604208 | -2.257003 |
| 14 | H | -1.482049 | -3.207405 | -2.333499 |
| 15 | H | -2.413744 | -3.049614 | -3.625281 |
| 16 | C | -4.121969 | -1.163439 | -2.705191 |
| 17 | H | -4.318535 | -0.242907 | -2.432070 |
| 18 | H | -4.786155 | -1.767456 | -2.313009 |
| 19 | H | -4.159532 | -1.228739 | -3.682526 |
| 20 | C | -1.759940 | -0.574600 | -2.836277 |
| 21 | H | -1.996611 | 0.336948 | -2.563604 |
| 22 | H | -1.801699 | -0.644267 | -3.812920 |
| 23 | H | -0.850876 | -0.778185 | -2.532992 |
| 24 | C | -3.197506 | -2.952728 | 2.644610 |
| 25 | H | -4.080220 | -3.370559 | 2.558953 |

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| Atom | Atom | Coordinates (Angstroms) | | |
|---|---|---|---|---|
| Number | Type | X | Y | Z |
| 26 | H | -3.228685 | -2.267674 | 3.345219 |
| 27 | H | -2.535873 | -3.635855 | 2.884194 |
| 28 | C | -0.484831 | -1.610202 | 2.107523 |
| 29 | H | -0.696754 | -2.137029 | 2.915818 |
| 30 | H | -0.318271 | -0.675002 | 2.379756 |
| 31 | N | 0.701076 | -2.156398 | 1.456997 |
| 32 | C | 1.460400 | -3.249539 | 1.870940 |
| 33 | C | 2.402566 | -3.426472 | 0.916467 |
| 34 | C | 3.463931 | -4.483336 | 0.917116 |
| 35 | H | 3.365067 | -5.043629 | 1.714213 |
| 36 | H | 4.348248 | -4.061363 | 0.923069 |
| 37 | H | 3.374118 | -5.040088 | 0.115527 |
| 38 | N | 2.200095 | -2.412927 | -0.061001 |
| 39 | C | 1.112529 | -1.648282 | 0.265957 |
| 40 | C | 2.871029 | -2.349096 | -1.399229 |
| 41 | C | 2.580657 | -1.008629 | -2.070678 |
| 42 | H | 2.952653 | -0.282132 | -1.528199 |
| 43 | H | 1.612395 | -0.886968 | -2.157264 |
| 44 | H | 2.992791 | -0.996920 | -2.959625 |
| 45 | C | 4.386241 | -2.490353 | -1.253659 |
| 46 | H | 4.733472 | -1.753288 | -0.709662 |
| 47 | H | 4.801958 | -2.464704 | -2.140667 |
| 48 | H | 4.598329 | -3.342840 | -0.820647 |
| 49 | C | 2.281740 | -3.484533 | -2.256028 |
| 50 | H | 1.311098 | -3.366668 | -2.331974 |
| 51 | H | 2.473697 | -4.348482 | -1.835591 |
| 52 | H | 2.684166 | -3.460635 | -3.150705 |
| 53 | C | 1.202340 | -3.993783 | 3.130257 |
| 54 | H | 1.857689 | -4.717725 | 3.223443 |
| 55 | H | 0.299055 | -4.373640 | 3.109160 |
| 56 | H | 1.280648 | -3.384540 | 3.894847 |
| 57 | N | 0.318981 | 1.514975 | -0.593426 |
| 58 | C | 0.309901 | 2.470531 | 0.351165 |
| 59 | C | -0.904656 | 3.025803 | 0.879881 |
| 60 | C | -2.237042 | 2.554264 | 0.432814 |
| 61 | C | -2.714886 | 2.871751 | -0.860748 |
| 62 | C | -3.994316 | 2.493024 | -1.229796 |
| 63 | H | -4.318654 | 2.736336 | -2.093821 |
| 64 | C | -4.819213 | 1.772238 | -0.382759 |
| 65 | C | -4.336587 | 1.422245 | 0.860768 |
| 66 | H | -4.886392 | 0.902910 | 1.444161 |
| 67 | C | -3.058512 | 1.807641 | 1.289878 |
| 68 | C | -2.601743 | 1.410030 | 2.667124 |
| 69 | H | -1.695440 | 1.748987 | 2.822145 |
| 70 | H | -2.601380 | 0.432714 | 2.742185 |
| 71 | H | -3.210599 | 1.787430 | 3.335582 |
| 72 | C | -6.231132 | 1.396190 | -0.791826 |
| 73 | H | -6.407502 | 1.724863 | -1.698484 |
| 74 | H | -6.871574 | 1.798182 | -0.169289 |
| 75 | H | -6.329263 | 0.420754 | -0.775475 |
| 76 | C | -1.842345 | 3.623668 | -1.820209 |
| 77 | H | -2.323358 | 3.759930 | -2.662652 |
| 78 | H | -1.025131 | 3.110567 | -1.988916 |
| 79 | H | -1.606059 | 4.493887 | -1.434664 |

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| Atom Number | Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 80 | C | -0.833927 | 3.980804 | 1.904563 |
| 81 | H | -1.648040 | 4.342753 | 2.249348 |
| 82 | C | 0.352958 | 4.414803 | 2.427452 |
| 83 | H | 0.367333 | 5.049881 | 3.139791 |
| 84 | C | 1.540887 | 3.913250 | 1.900395 |
| 85 | H | 2.373737 | 4.211220 | 2.261198 |
| 86 | C | 1.544482 | 2.992485 | 0.861938 |
| 87 | C | 2.831806 | 2.472632 | 0.321543 |
| 88 | C | 3.379984 | 3.002580 | -0.851244 |
| 89 | C | 4.571011 | 2.495992 | -1.353705 |
| 90 | H | 4.927379 | 2.850481 | -2.166045 |
| 91 | C | 5.257948 | 1.469799 | -0.687433 |
| 92 | C | 4.714292 | 0.962749 | 0.467723 |
| 93 | H | 5.177004 | 0.265906 | 0.930270 |
| 94 | C | 3.508483 | 1.432466 | 0.990560 |
| 95 | C | 2.927104 | 0.794893 | 2.218170 |
| 96 | H | 2.087439 | 1.242083 | 2.451351 |
| 97 | H | 3.559048 | 0.879249 | 2.962175 |
| 98 | H | 2.753619 | -0.153765 | 2.042257 |
| 99 | C | 6.529967 | 0.880463 | -1.273781 |
| 100 | H | 6.872146 | 0.181243 | -0.677332 |
| 101 | H | 7.204553 | 1.585568 | -1.369238 |
| 102 | H | 6.336395 | 0.493152 | -2.153151 |
| 103 | C | 2.661223 | 4.109711 | -1.596495 |
| 104 | H | 1.843115 | 4.351244 | -1.114508 |
| 105 | H | 2.429878 | 3.800738 | -2.496804 |
| 106 | H | 3.246161 | 4.894245 | -1.659374 |

## Table 3. Geometry for (TMTBM)Ni=N(dippp)+ (7b+)

**Symbolic Z-matrix:**
**Charge = 1 Multiplicity = 2**

| Atom Number | Atom Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|
| 1 | Ni | 9.08417 | 15.05299 | 4.01871 |
| 2 | N | 10.3082 | 15.90372 | 3.16454 |
| 3 | N | 6.02979 | 15.40263 | 4.01958 |
| 4 | N | 7.09335 | 15.54878 | 5.87349 |
| 5 | C | 13.06753 | 15.19065 | 3.94351 |
| 6 | C | 5.7148 | 15.10201 | 2.591 |
| 7 | C | 9.27184 | 18.13069 | 0.88113 |
| 8 | N | 9.42887 | 12.33679 | 5.37954 |
| 9 | C | 5.75482 | 15.67759 | 6.20674 |
| 10 | C | 5.06581 | 15.59514 | 5.05046 |
| 11 | C | 7.28168 | 15.35698 | 4.54357 |
| 12 | C | 8.20789 | 15.33185 | 6.77699 |
| 13 | H | 8.90759 | 16.01413 | 6.61935 |
| 14 | H | 7.90175 | 15.4113 | 7.71513 |
| 15 | C | 7.41256 | 19.49826 | 2.43578 |
| 16 | H | 6.76872 | 19.95529 | 2.96393 |

| | | | | |
|---|---|---|---|---|
| 17 | C | 9.14083 | 13.66667 | 5.29009 |
| 18 | C | 12.59314 | 16.59184 | 3.60785 |
| 19 | C | 13.55355 | 13.43718 | 5.51942 |
| 20 | H | 13.52529 | 13.09657 | 6.40581 |
| 21 | N | 8.74607 | 14.01206 | 6.54503 |
| 22 | C | 9.16658 | 11.86913 | 6.69192 |
| 23 | C | 10.28033 | 17.404 | 0. |
| 24 | H | 10.95256 | 16.97403 | 0.6027 |
| 25 | C | 9.59211 | 18.48722 | 2.20579 |
| 26 | C | 8.9624 | 19.57186 | 4.42606 |
| 27 | H | 9.86087 | 19.20418 | 4.66547 |
| 28 | C | 13.51855 | 17.61509 | 3.62407 |
| 29 | H | 14.40474 | 17.4247 | 3.90865 |
| 30 | C | 8.64979 | 19.17127 | 3.00055 |
| 31 | C | 9.77305 | 11.49738 | 4.18818 |
| 32 | C | 11.23836 | 16.84681 | 3.20247 |
| 33 | C | 11.91562 | 19.16915 | 2.79095 |
| 34 | H | 11.68846 | 20.04713 | 2.50769 |
| 35 | C | 13.01286 | 14.70124 | 5.25282 |
| 36 | C | 12.37417 | 15.5118 | 6.36021 |
| 37 | H | 11.58928 | 15.99361 | 5.97062 |
| 38 | C | 10.95151 | 18.17811 | 2.74469 |
| 39 | C | 4.8644 | 16.21938 | 2.00124 |
| 40 | H | 5.3524 | 17.0671 | 2.06022 |
| 41 | H | 4.02496 | 16.28998 | 2.50221 |
| 42 | H | 4.66854 | 16.01979 | 1.06201 |
| 43 | C | 13.61351 | 14.87305 | 1.46936 |
| 44 | H | 13.5797 | 15.8724 | 1.4709 |
| 45 | C | 7.10405 | 19.17375 | 1.13151 |
| 46 | H | 6.26025 | 19.41474 | 0.76735 |
| 47 | C | 8.38711 | 13.07781 | 8.85343 |
| 48 | H | 8.43993 | 12.20479 | 9.29564 |
| 49 | H | 7.47529 | 13.42851 | 8.9306 |
| 50 | H | 9.01338 | 13.69887 | 9.28051 |
| 51 | C | 10.30886 | 12.37165 | 3.06281 |
| 52 | H | 9.63239 | 13.03605 | 2.81507 |
| 53 | H | 10.51739 | 11.81251 | 2.2856 |
| 54 | H | 11.12148 | 12.82939 | 3.36339 |
| 55 | C | 8.74118 | 12.92706 | 7.41279 |
| 56 | C | 8.0284 | 18.49554 | 0.35408 |
| 57 | H | 7.8159 | 18.27613 | -0.54547 |
| 58 | C | 14.16319 | 13.15531 | 3.23974 |
| 59 | H | 14.55227 | 12.62025 | 2.55812 |
| 60 | C | 13.20343 | 18.91878 | 3.23864 |
| 61 | H | 13.85097 | 19.61274 | 3.28161 |
| 62 | C | 3.58174 | 15.65848 | 4.90335 |
| 63 | H | 3.17179 | 15.79526 | 5.78295 |
| 64 | H | 3.25553 | 14.81855 | 4.51792 |
| 65 | H | 3.34348 | 16.40322 | 4.31249 |
| 66 | C | 7.01199 | 15.03282 | 1.77893 |
| 67 | H | 7.46579 | 15.90071 | 1.81335 |
| 68 | H | 6.80306 | 14.81041 | 0.84759 |
| 69 | H | 7.5972 | 14.34311 | 2.15603 |
| 70 | C | 13.64415 | 14.40734 | 2.91438 |
| 71 | C | 9.3182 | 10.47096 | 7.20298 |
| 72 | H | 9.05802 | 10.43822 | 8.14725 |
| 73 | H | 10.25233 | 10.18909 | 7.11155 |
| 74 | H | 8.74343 | 9.86971 | 6.68469 |
| 75 | C | 5.29244 | 15.87877 | 7.61011 |

| | | | | |
|---|---|---|---|---|
| 76 | H | 4.31565 | 15.95751 | 7.62414 |
| 77 | H | 5.69129 | 16.69783 | 7.97142 |
| 78 | H | 5.56635 | 15.11315 | 8.15734 |
| 79 | C | 13.33973 | 16.56937 | 6.92454 |
| 80 | H | 13.67215 | 17.13133 | 6.19381 |
| 81 | H | 14.09425 | 16.12242 | 7.36215 |
| 82 | H | 12.86758 | 17.12761 | 7.57722 |
| 83 | C | 14.12264 | 12.68147 | 4.52801 |
| 84 | H | 14.48927 | 11.82915 | 4.73212 |
| 85 | C | 12.3492 | 14.36505 | 0.78642 |
| 86 | H | 12.33587 | 14.67009 | -0.1447 |
| 87 | H | 11.5622 | 14.71274 | 1.2556 |
| 88 | H | 12.33666 | 13.38533 | 0.80944 |
| 89 | C | 5.01892 | 13.74169 | 2.52545 |
| 90 | H | 4.18543 | 13.77602 | 3.03979 |
| 91 | H | 5.60756 | 13.05499 | 2.90276 |
| 92 | H | 4.81778 | 13.52229 | 1.5917 |
| 93 | C | 14.84863 | 14.44538 | 0.65816 |
| 94 | H | 15.65862 | 14.78564 | 1.09248 |
| 95 | H | 14.78629 | 14.81094 | -0.24906 |
| 96 | H | 14.88799 | 13.46726 | 0.61432 |
| 97 | C | 11.8657 | 14.66178 | 7.53184 |
| 98 | H | 11.23823 | 13.98693 | 7.19772 |
| 99 | H | 11.41045 | 15.23843 | 8.18036 |
| 100 | H | 12.62338 | 14.21678 | 7.96572 |
| 101 | C | 7.93252 | 18.98549 | 5.38941 |
| 102 | H | 8.14912 | 19.25868 | 6.30518 |
| 103 | H | 7.94758 | 18.00754 | 5.32802 |
| 104 | H | 7.03986 | 19.31389 | 5.15306 |
| 105 | C | 8.50531 | 10.79405 | 3.72624 |
| 106 | H | 7.81868 | 11.46182 | 3.5184 |
| 107 | H | 8.1816 | 10.20342 | 4.43812 |
| 108 | H | 8.69905 | 10.26429 | 2.92491 |
| 109 | C | 8.99133 | 21.02985 | 4.62842 |
| 110 | H | 9.68073 | 21.42566 | 4.05554 |
| 111 | H | 9.19471 | 21.22537 | 5.56699 |
| 112 | H | 8.11755 | 21.40903 | 4.39778 |
| 113 | C | 10.87398 | 10.48299 | 4.5291 |
| 114 | H | 10.56335 | 9.89289 | 5.24734 |
| 115 | H | 11.67789 | 10.96019 | 4.82332 |
| 116 | H | 11.08331 | 9.94881 | 3.73479 |
| 117 | C | 9.66105 | 16.31051 | -0.84825 |
| 118 | H | 9.19154 | 15.67441 | -0.26923 |
| 119 | H | 10.36551 | 15.84303 | -1.34373 |
| 120 | H | 9.0258 | 16.70756 | -1.4801 |
| 121 | C | 11.02349 | 18.40158 | -0.8796 |
| 122 | H | 11.42234 | 19.09873 | -0.3179 |
| 123 | H | 10.39615 | 18.81049 | -1.51167 |
| 124 | H | 11.73019 | 17.93729 | -1.37509 |

## 3. Crystallographic Experimental Section and Tables

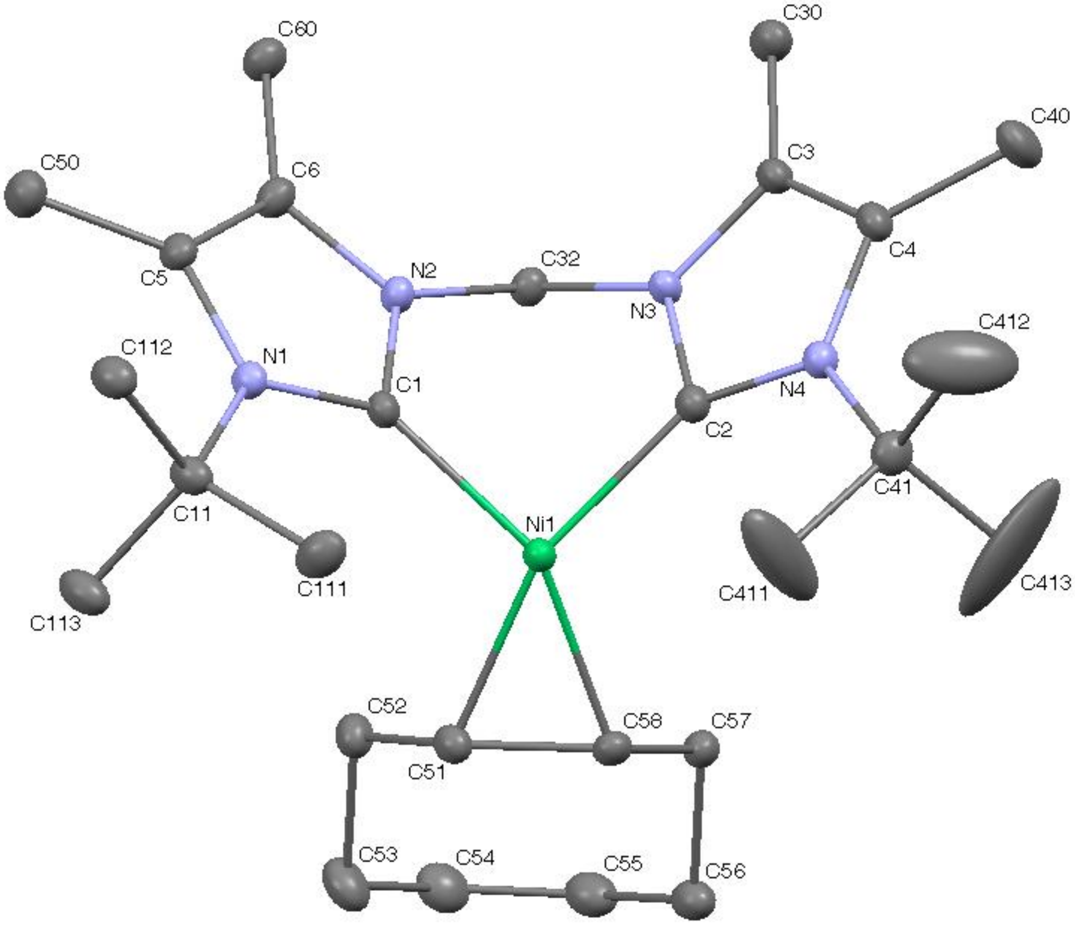
**Data collection**: Suitable crystals of **5**, **6**, **7a**, or **7b** were selected under a stereomicroscope while they were immersed in mineral oil to minimize contact with air or water. The crystal was removed from the oil using a tapered fiber that also served to hold the crystal for data collection. The crystal was mounted on a Bruker SMART APEX system. Rotation and still images showed diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and the initial cell parameters. Final cell parameters were obtained from the full data set. A hemisphere data set was obtained of reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using 10 (2) second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT. Absorption corrections were applied using psi- scan. Observation during and after data collection showed that crystal was still clear suggesting no decomposition.

**Table 4. Crystal data and structure refinement for (TMTBM)Ni($\eta^2$-cod) (5)**

| | | |
|---|---|---|
| **Identification code** | Nicole40 | |
| **Empirical formula** | $C_{27}H_{44}N_4Ni$ | |
| **Formula weight** | 483.37 | |
| **Temperature** | 100(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal system** | Orthorhombic | |
| **Space group** | Fdd2 | |
| **Unit cell dimensions** | *a* = 17.8294(19) Å | a = 90° |
| | *b* = 42.047(5) Å | b = 90° |
| | *c* = 17.6823(19) Å | c = 90° |
| **Volume** | 13256(3) $Å^3$ | |
| **Z** | 16 | |
| **Density (calculated)** | 0.969 g/$cm^3$ | |
| **Absorption coefficient** | 0.602 $mm^{-1}$ | |
| **F(000)** | 3487 | |
| **Crystal size** | 0.6 x 0.2 x 0.2 $mm^3$ | |
| **Theta range for data collection** | 2.18 to 28.28° | |
| **Index ranges** | -23<=h<=17, -56<=k<=51, -23<=l<=23 | |
| **Reflections collected** | 20306 | |
| **Independent reflections** | 7756 [R(int) = 0.0847] | |
| **Completeness to theta = 25.00°** | 99.9% | |
| **Absorption correction** | Empirical | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Data / restraints / parameters** | 7756 / 1 / 289 | |
| **Goodness-of-fit on $F^2$** | 1.065 | |
| **Final R indices ]I>2sigma(I)]** | R1 = 0.0576, wR2 = 0.1542 | |
| **R indices (all data)** | R1 = 0.0604, wR2 = 0.1566 | |
| **Largest diff. peak and hole** | 0.756 and -0.546 e.Å-3 | |

**(TMTBM)Ni($\eta^2$-cod) (5)**. The space group was determined to be Fdd2 based on systematic absences and intensity statistics. Direct methods were used to locate C, Ni, and N atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. See Table 3 (SI-10) for crystal and refinement data. The solvent molecules ($Et_2O$) were disordered and could not be modeled properly, thus the SQUEEZE/PLATON3 program was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. One of the *tert*-butyl groups of the TMTBM ligand also presents some degree of rotational disorder.

**Figure 1: Fully labeled ORTEP for (TMTBM)Ni($\eta^2$-cod) (5)**

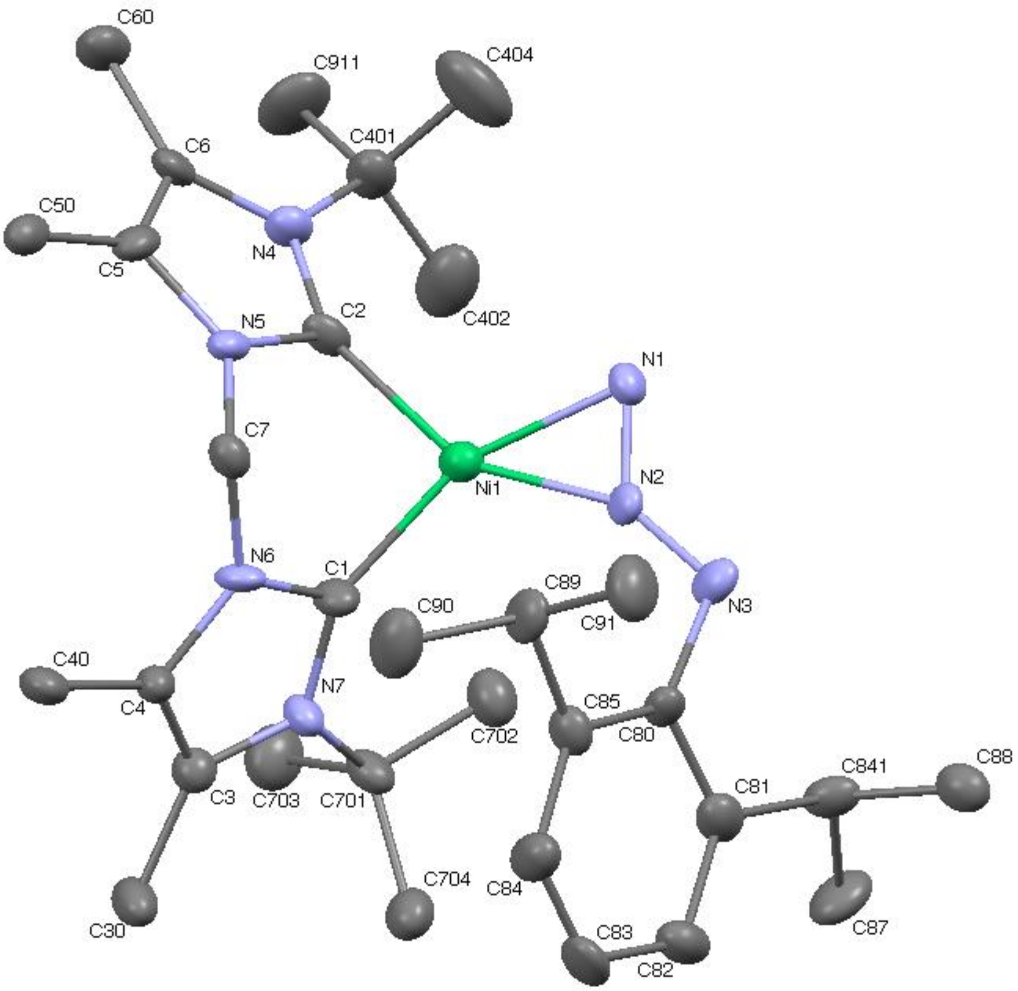


## Table 5. Crystal data and structure refinement for (TMTBM)Ni($\eta^2$-$N_3$Ar) (6)

| | | |
|---|---|---|
| **Identification code** | Nicole712 | |
| **Empirical formula** | $C_{31}H_{49}N_7Ni$ | |
| **Formula weight** | 578.46 | |
| **Temperature** | 100(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal system** | Triclinic | |
| **Space group** | P-1 | |
| **Unit cell dimensions** | *a* = 12.1740(13) Å | a = 112.359(2)° |
| | *b* = 26.324(3) Å | b = 99.666(2)° |
| | *c* = 31.697(3) Å | c = 92.719(2)° |
| **Volume** | 9191.5(17)Å$^3$ | |
| **Z** | 10 | |
| **Density (calculated)** | 1.041 g/cm$^3$ | |
| **Absorption coefficient** | 0.550 mm$^{-1}$ | |
| **F(000)** | 3119 | |
| **Crystal size** | 0.6 x 0.2 x 0.2 mm$^3$ | |
| **Theta range for data collection** | 1.33 to 28.33° | |
| **Index ranges** | -16<=h<=15, -30<=k<=34, -41<=l<=40 | |
| **Reflections collected** | 45871 | |
| **Independent reflections** | 45871 [R(int) = 0.0960] | |
| **Completeness to theta = 25.00°** | 98.6% | |
| **Absorption correction** | Empirical | |
| **Refinement method** | Full-matrix least-squares on F$^2$ | |
| **Data / restraints / parameters** | 42427 / 0 / 1756 | |
| **Goodness-of-fit on F$^2$** | 1.032 | |
| **Final R indices ]I>2sigma(I)]** | R1 = 0.0854, wR2 = 0.2299 | |
| **R indices (all data)** | R1 = 0.1602, wR2 = 0.1781 | |
| **Largest diff. peak and hole** | 0.837 and -0.605 e.Å-3 | |

**(TMTBM)Ni($\eta^2$-$N_3$Ar) (6).** The space group was determined to be Fdd2 based on systematic absences and intensity statistics. Direct methods were used to locate C, Ni, and N atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. See Table 4 (SI-12) for crystal and refinement data. There were five independent molecules in the unit cell, one of which is shown below. The solvent molecules ($Et_2O$) were disordered and could not be modeled properly, thus the SQUEEZE/PLATON3 program was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

**Figure 2: Fully labeled ORTEP for (TMTBM)Ni($\eta^2$-$N_3$Ar) (6)**

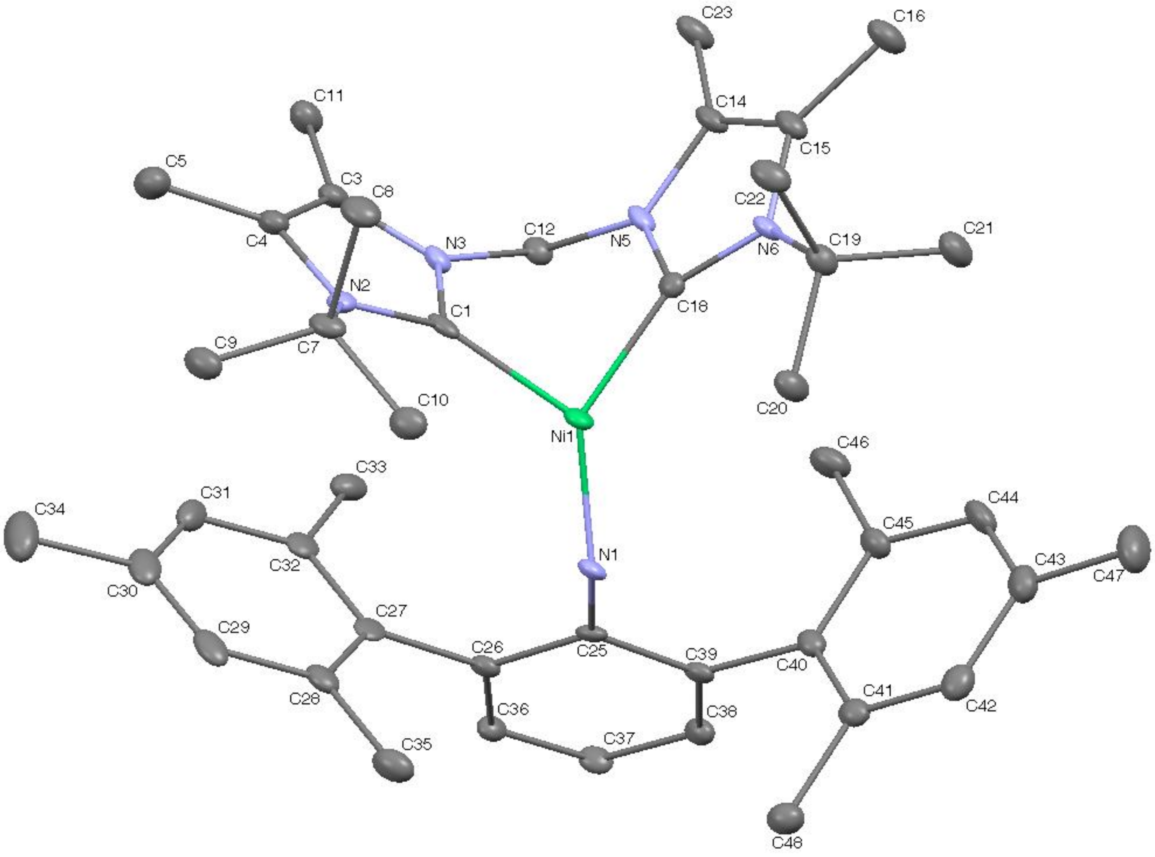


### Table 6. Crystal data and structure refinement for (TMTBM)Ni=N(dmp) (7a)

| | | |
|---|---|---|
| **Identification code** | Nicole84 | |
| **Empirical formula** | $C_{43}H_{57}N_5Ni$ | |
| **Formula weight** | 702.64 | |
| **Temperature** | 100(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal system** | Triclinic | |
| **Space group** | P-1 | |
| **Unit cell dimensions** | *a* = 10.911(2) Å | a = 103.994(4)° |
| | *b* = 12.339(2) Å | b = 97.621(4)° |
| | *c* = 15.869(5) Å | c = 107.921(3)° |
| **Volume** | 1922.2(7) Å$^3$ | |
| **Z** | 2 | |
| **Density (calculated)** | 1.214 g/cm$^3$ | |
| **Absorption coefficient** | 0.541 mm$^{-1}$ | |
| **F(000)** | 1584 | |
| **Crystal size** | 0.6 x 0.2 x 0.2 mm$^3$ | |
| **Theta range for data collection** | 1.59 to 25.00° | |
| **Index ranges** | -13<=h<=13, -27<=k<=26, -9<=l<=18 | |
| **Reflections collected** | 21583 | |
| **Independent reflections** | 7264 [R(int) = 0.0418] | |
| **Completeness to theta = 25.00°** | 98.6% | |
| **Absorption correction** | Empirical | |
| **Refinement method** | Full-matrix least-squares on F$^2$ | |
| **Data / restraints / parameters** | 7264 / 0 / 502 | |
| **Goodness-of-fit on F$^2$** | 1.002 | |
| **Final R indices ]I>2sigma(I)]** | R1 = 0.0637, wR2 = 0.1006 | |
| **R indices (all data)** | R1 = 0.0455, wR2 = 0.0956 | |
| **Largest diff. peak and hole** | 0.810 and -0.461 e.Å-3 | |

**(TMTBM)Ni=N(dmp)** (**7a**). The space group was determined to be P-1 based on systematic absences and intensity statistics. Direct methods were used to locate C, Ni, and N atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined isotropically using a riding model. See Table 5 (SI-14) for crystal and refinement data.

**Figure 3: Fully labeled ORTEP for (TMTBM)Ni=N(dmp) (7a)**

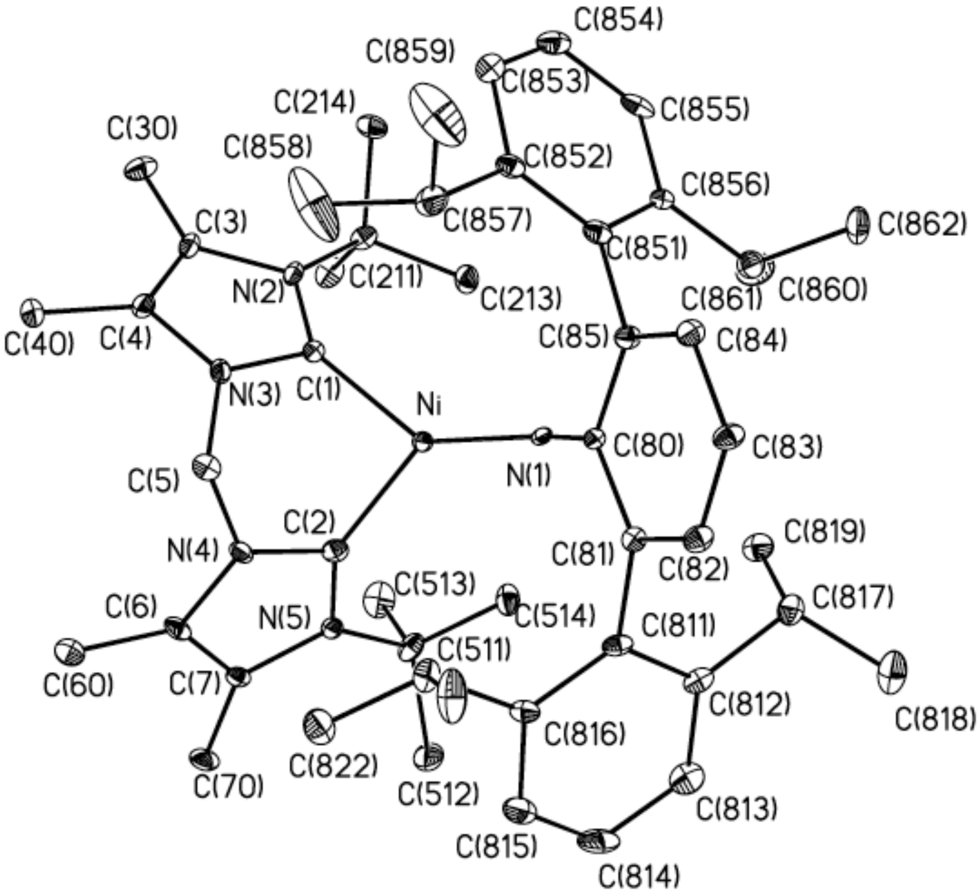


## Table 7. Crystal data and structure refinement for (TMTBM)Ni=N(dippp)

| | | | |
|---|---|---|---|
| Identification code | Nicole740a | Crystal size | 0.6 x 0.2 x 0.2 mm$^2$ |
| Empirical formula | $C_{49} H_{69} N_5 Ni$ | Theta range for data collection | 1.48 to 28.33 ° |
| Formula weight | 786.8 | Index ranges | -17 ≤ h ≤ 17 |
| Temperature | 100(2) | | -23 ≤ k ≤ 23 |
| Wavelength | 0.71073 Å | | -19 ≤ l ≤ 29 |
| Crystal system | Orthorhombic | Reflections collected | 32704 |
| Space group | P2(1)2(1)2(1) | Independent reflections | 12325 |
| Unit cell dimensions | a = 13.2070(10) Å | Completeness to theta = 25.00° | 98.1 % |
| | b = 17.6940(14) Å | Absorption correction | psi-scan |
| | c = 21.9242(17) Å | Max. and min. transmission | 0.9204 and 0.7860 |
| | α = 90.00 ° | Refinement method: Full-matrix least-squares on F$^2$ | |
| | β = 90.00 ° | Data / restraints / parameters | 12325 / 0 / 496 |
| | γ = 90.00 ° | Goodness-of-fit on F$^2$ | 1.045 |
| Volume | 5123.3(7) | Final R indices [I>2sigma(I)] | R1 = 0.0574 |
| Z | 4 | | wR2 = 0.0854 |
| Density (calculated) | 1.020 mg/m$^3$ | R indices (all data) | R1 = 0.0833 |
| Absorptions coefficient | 0.412 mm$^{-1}$ | | wR2 = 0.0905 |
| F(000) | 1704.0 | Largest diff. peak hole | 1.316 & -0.644 e.Å$^{-3}$ |

**(TMTBM)Ni=N(dippp)** (**7b**). The space group was determined to be P2(1)2(1)2(1) based on systematic absences and intensity statistics. Direct methods were used to locate Ni, C, and N atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions and refined isotropically. Contributions of disordered solvent molecules were removed from the diffraction data with SQUEEZE.

**Figure 4: Fully labeled ORTEP for (TMTBM)Ni=N(dippp) (7b)**



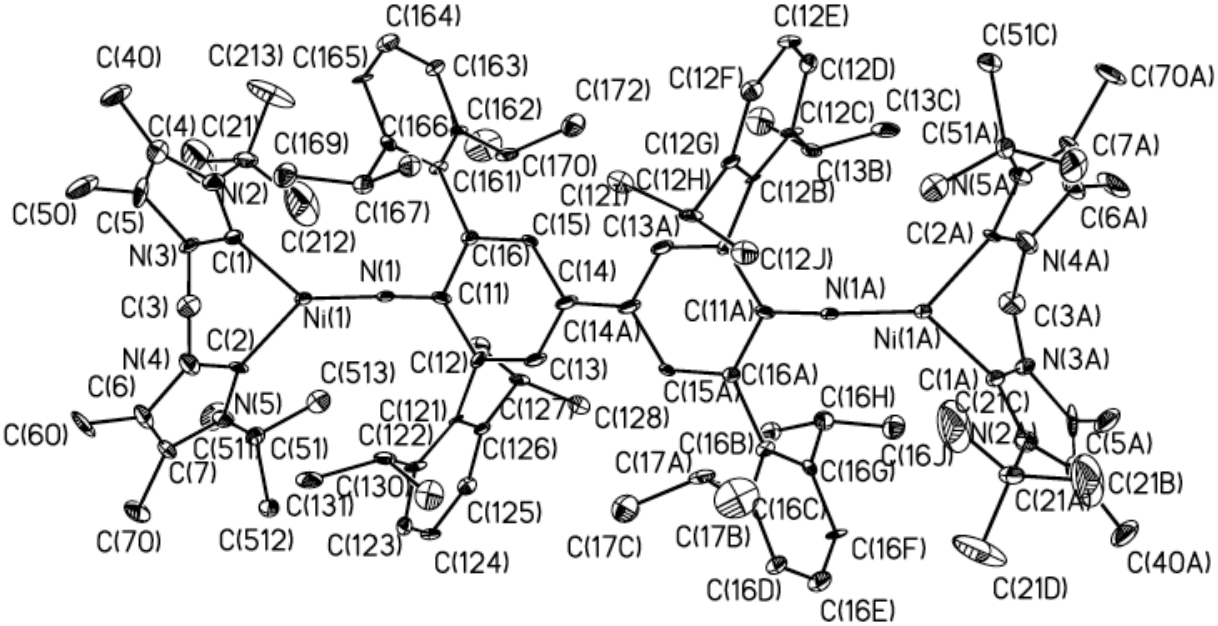
### Table 8. Crystal data and structure refinement for [(TMTBM)Ni=N(dippp)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (9)

| | | | |
|---|---|---|---|
| Identification code | Nicole867a | Crystal size | 0.6 x 0.2 x 0.2 mm$^2$ |
| Empirical formula | $C_{146}$ $H_{136}$ $N_{10}$ $Ni_2$ $B_2$ $F_{20}$ | Theta range for data collection | 1.75 to 25.00 ° |
| Formula weight | 2929.65 | Index ranges | $-17 \leq h \leq 17$<br>$-18 \leq k \leq 18$<br>$-19 \leq l \leq 19$ |
| Temperature | 100(2) | | |
| Wavelength | 0.71073 Å | | |
| Crystal system | Triclinic | Reflections collected | 23669 |
| Space group | P-1 | Independent reflections | 13101 |
| Unit cell dimensions | a = 14.779(2) Å | Completeness to theta = 25.00° | 98.9 % |
| | b = 15.500(2) Å | Absorption correction | psi-scan |
| | c = 16.733(3) Å | Max. and min. transmission | 0.9242 and 0.7952 |
| | α = 92.778(4) ° | Refinement method: Full-matrix least-squares on F$^2$ | |
| | β = 98.247(3) ° | Data / restraints / parameters | 6295 / 0 / 448 |
| | γ = 100.522(4) ° | Goodness-of-fit on F$^2$ | 0.982 |
| Volume | 3718.6(10) | Final R indices [I>2sigma(I)] | R1 = 0.0879<br>wR2 = 0.2298 |
| Z | 1 | | |
| Density (calculated) | 1.308 mg/m$^3$ | R indices (all data) | R1 = 0.1879<br>wR2 = 0.2298 |
| Absorptions coefficient | 0.354 mm$^{-1}$ | | |
| F(000) | 1508 | Largest diff. peak hole | 0.517 & -0.223 e.Å$^{-3}$ |

### [(TMTBM)Ni=N(dippp)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (9)

The space group was determined to be P-1 based on systematic absences and intensity statistics. Direct methods were used to locate Ni, C, N, B, and F atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions and refined isotropically.

**Figure 5: Fully labeled ORTEP for [(TMTBM)Ni=N(dippp)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (9)**



## 4. References

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4. All software and sources of scattering factors are contained in the SHELXTL (version 1.5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).
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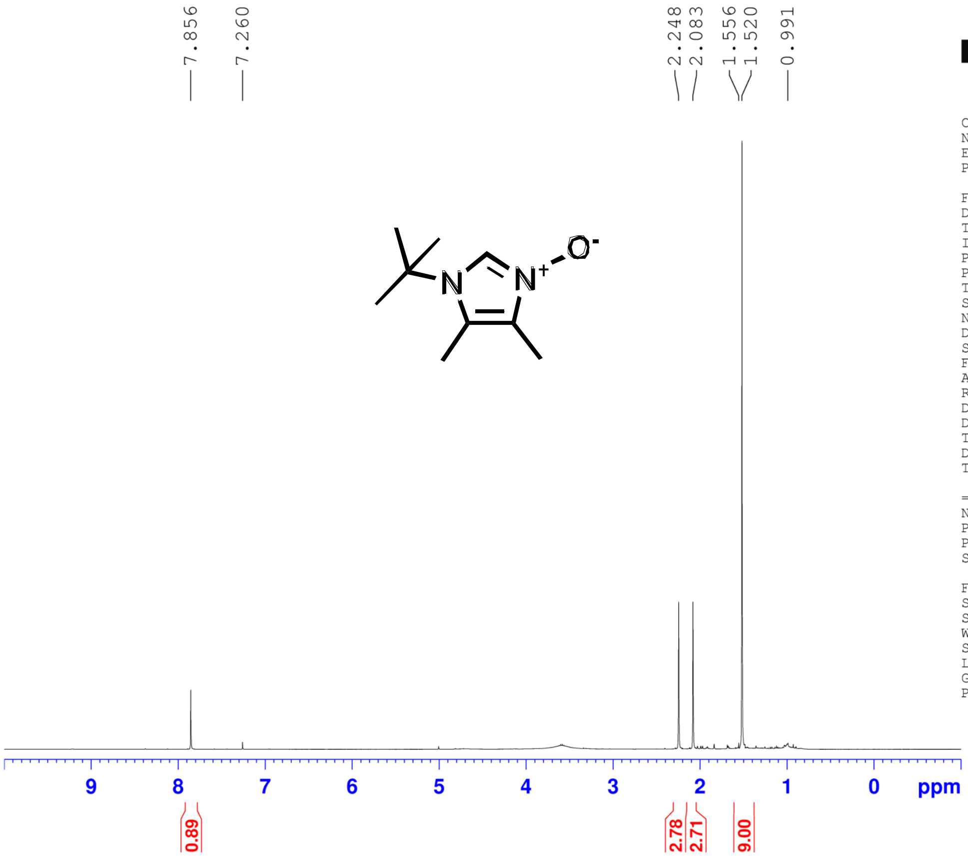
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.



```
Current Data Parameters
NAME             nh-4-157
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091006
Time                 4.01
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH             10000.000 Hz
FIDRES           0.260010 Hz
AQ              1.9230500 sec
RG                   71.8
DW                 50.000 usec
DE                 111.43 usec
TE                  295.4 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -6.00 dB
SFO1          400.1300000 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300087 MHz
WDW                    EM
SSB      0
LB       0 Hz
GB       0
PC                   1.00
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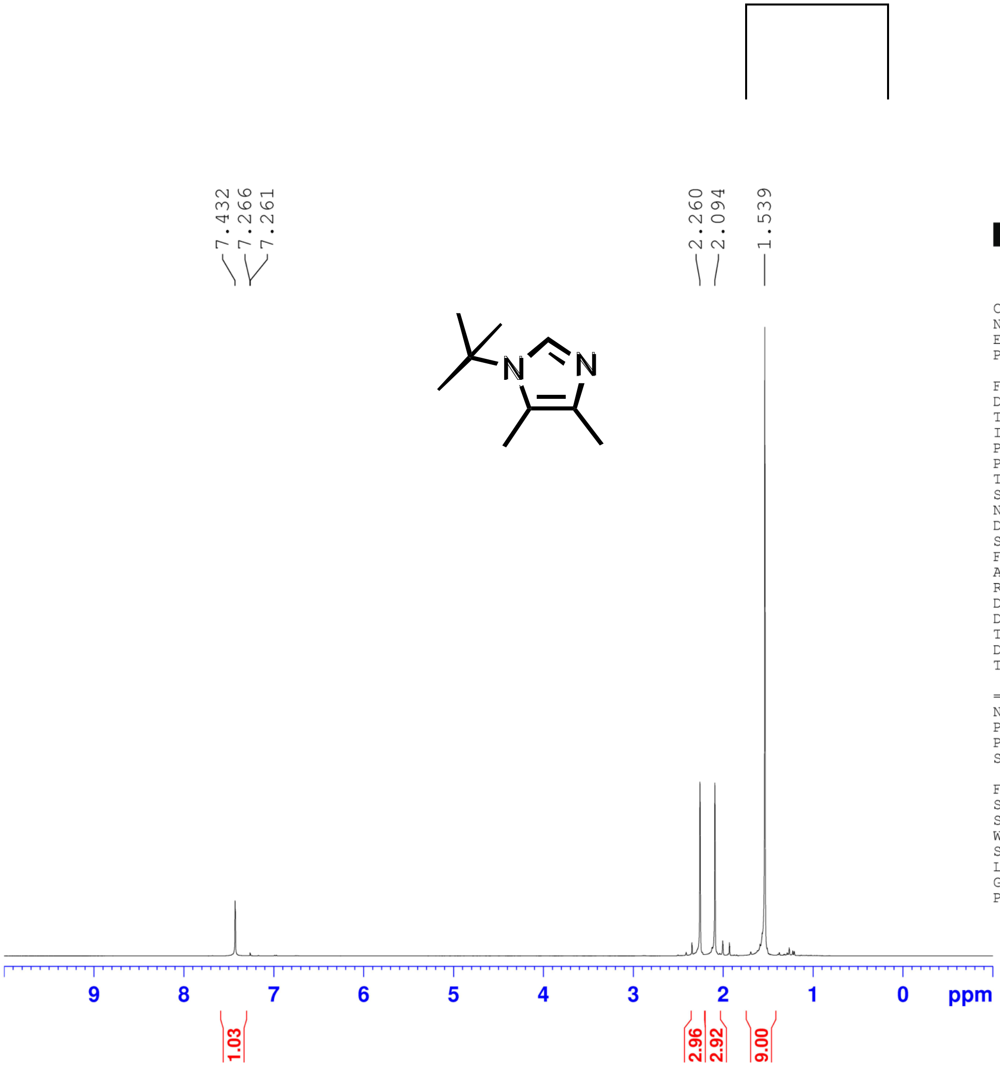

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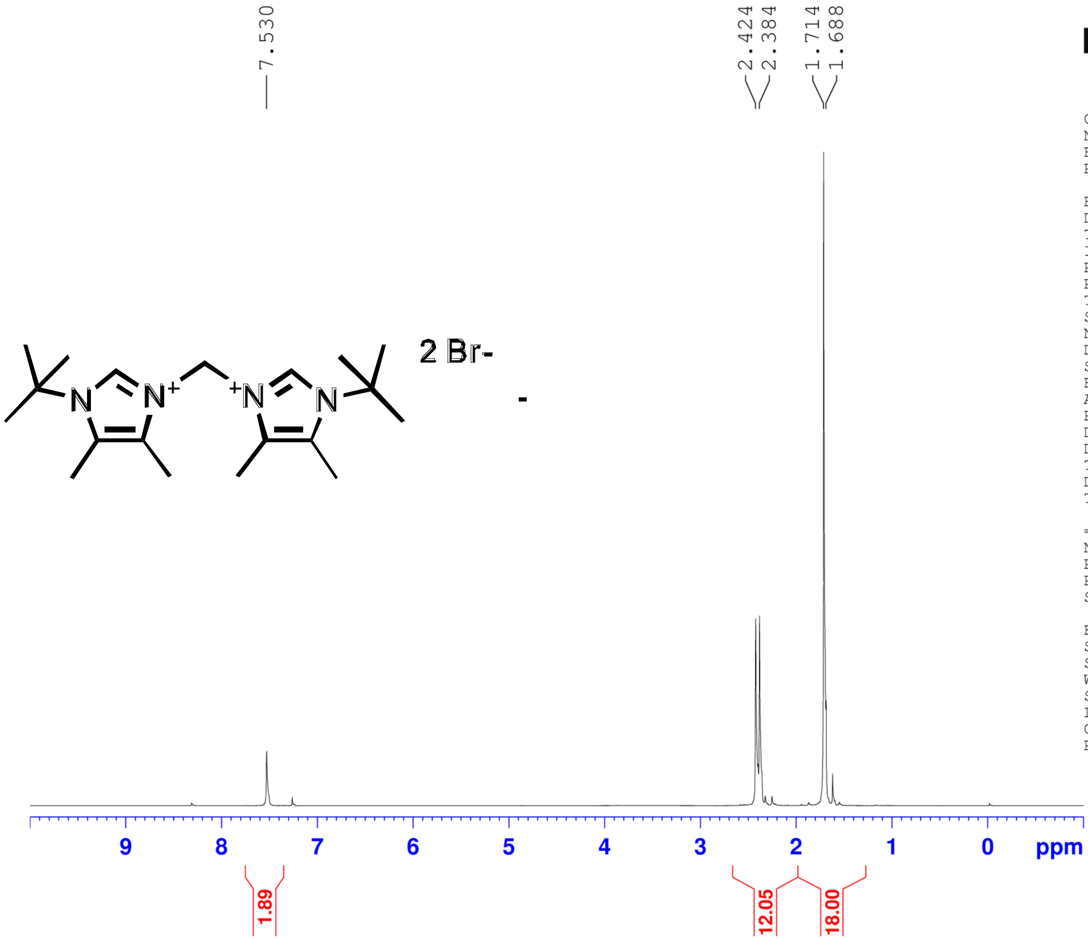
Current Data Parameters
NAME             nh-4-159
EXPNO                  22
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091031
Time                 5.00
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT             CDCl3
NS                      4
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ              2.9999299 sec
RG                   45.3
DW                 78.000 usec
DE                 111.43 usec
TE                  295.2 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -6.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300067 MHz
WDW                    EM
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



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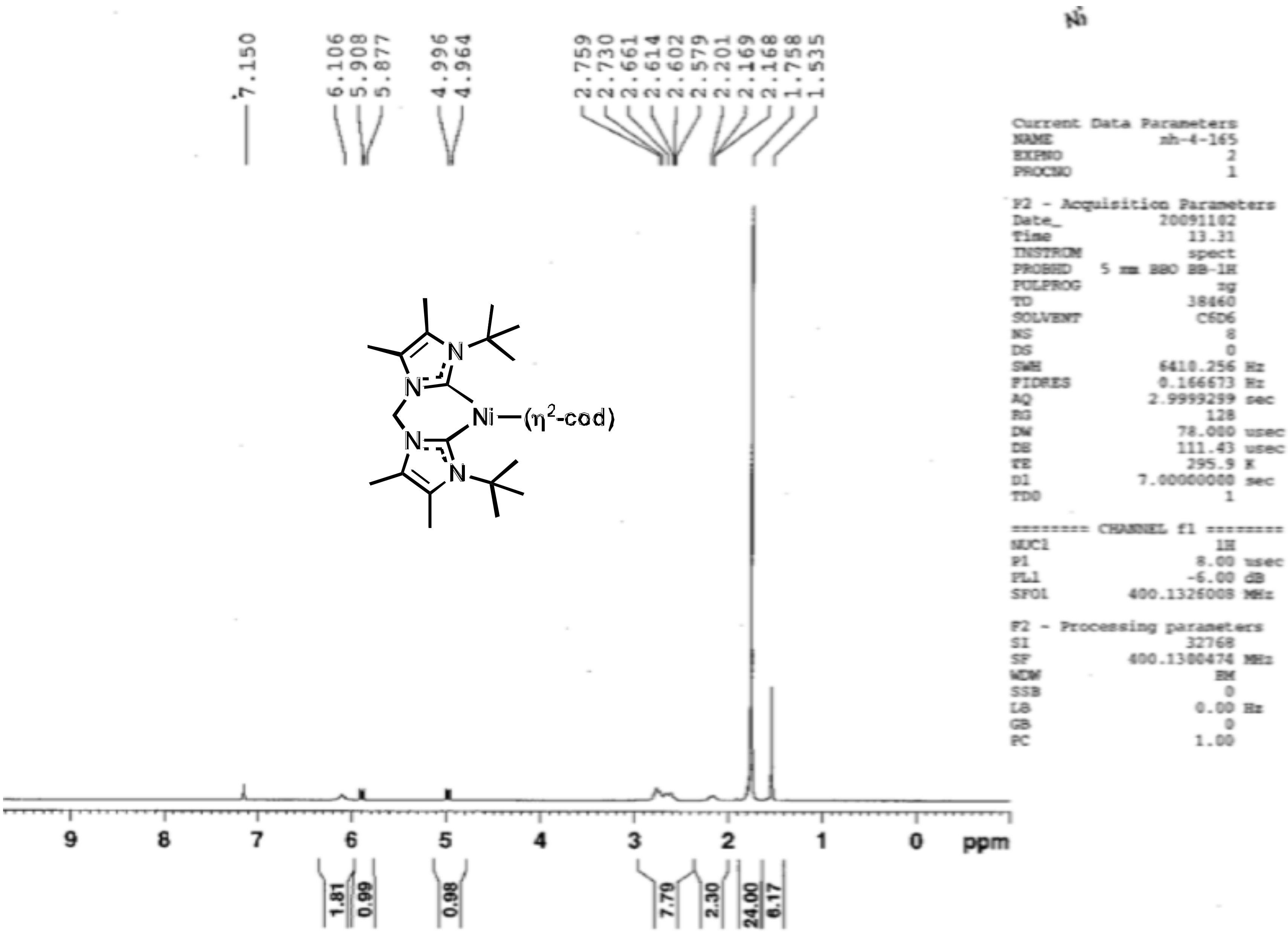
Current Data Parameters
NAME        TMTBMBr2salt
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100829
Time               13.41
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10416.667 Hz
FIDRES         0.270844 Hz
AQ            1.8461300 sec
RG                  80.6
DW                48.000 usec
DE                111.43 usec
TE                 296.3 K
D1           7.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                -6.00 dB
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300091 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

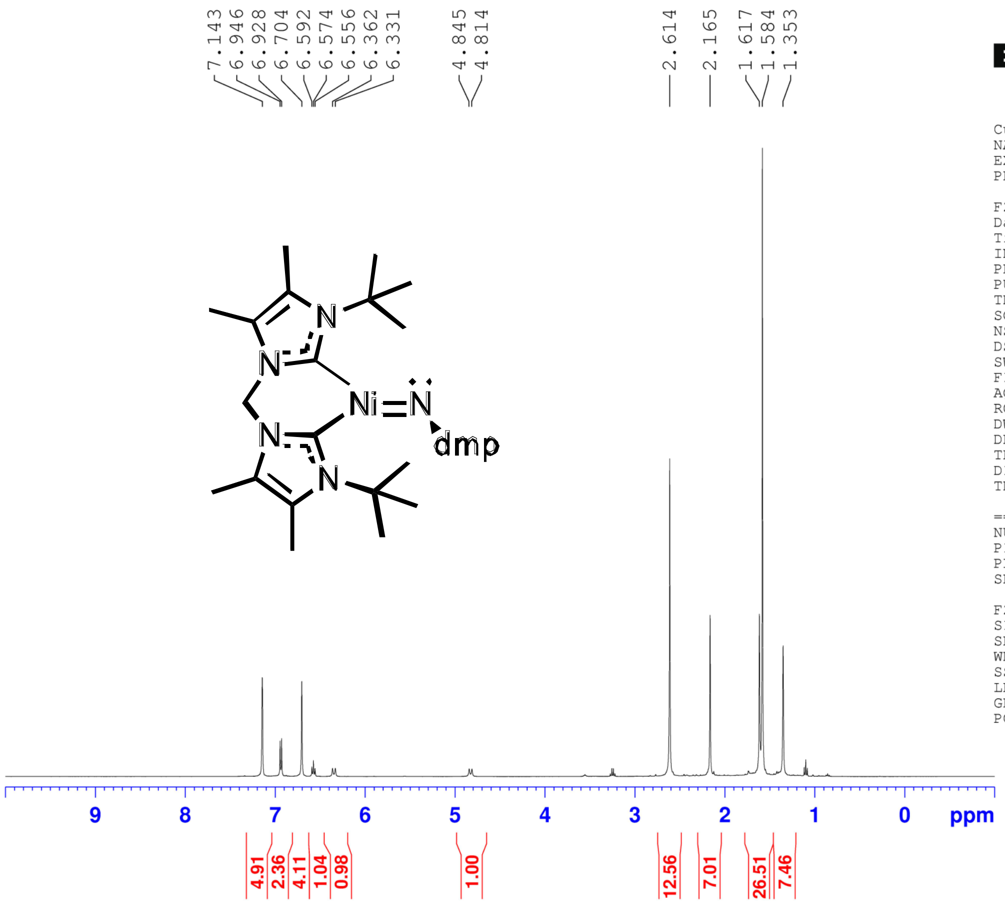


```
Current Data Parameters
NAME             nh-4-165
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091102
Time                13.31
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT              C6D6
NS                      8
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ              2.9999299 sec
RG                    128
DW                 78.000 usec
DE                 111.43 usec
TE                  295.9 K
D1             7.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -6.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300474 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

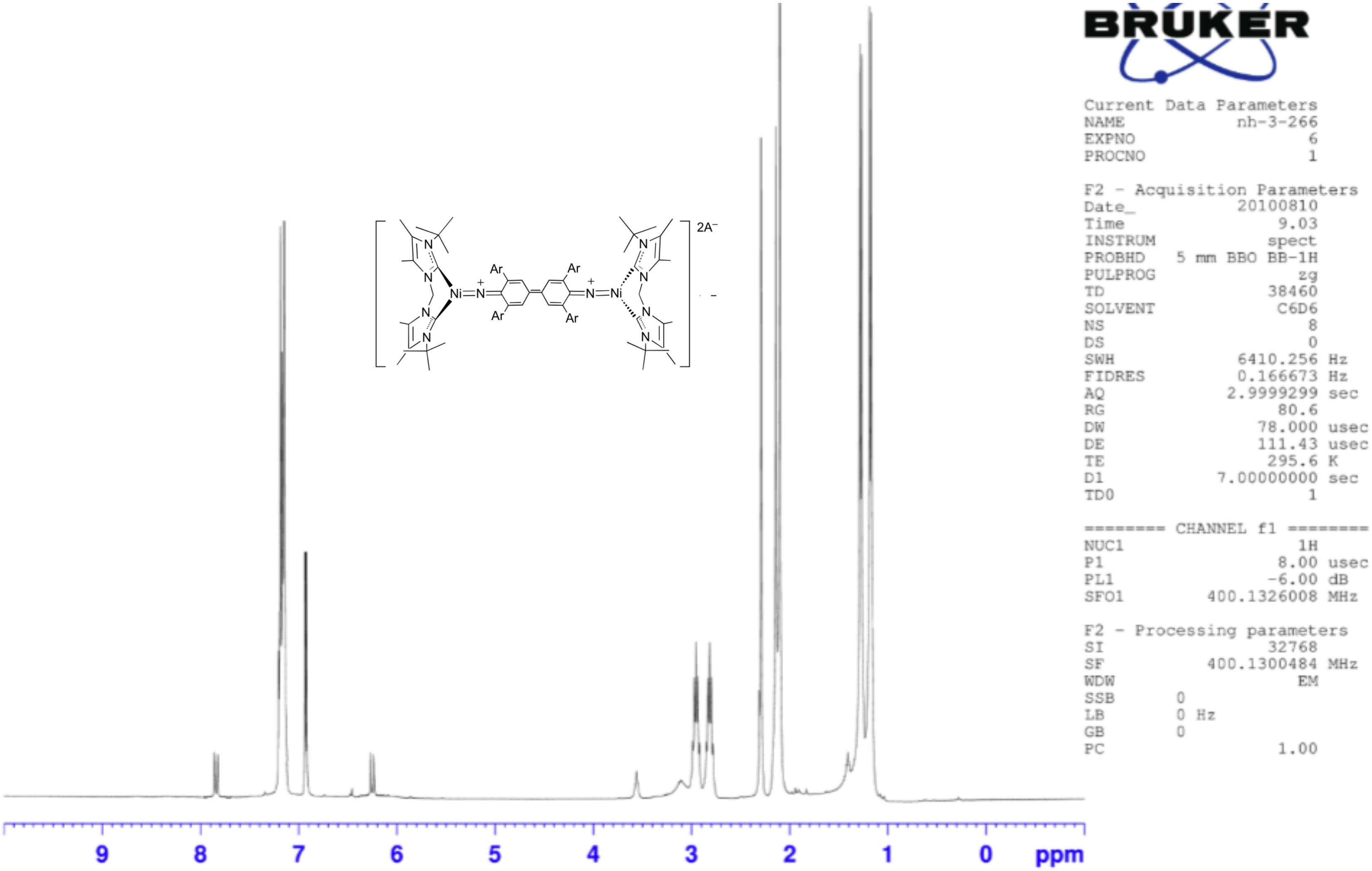


```
Current Data Parameters
NAME              nh-4-176
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20100126
Time                  5.23
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG                 zg
TD                   38460
SOLVENT               C6D6
NS                       8
DS                       0
SWH               6410.256 Hz
FIDRES            0.166673 Hz
AQ               2.9999299 sec
RG                     128
DW                  78.000 usec
DE                  111.43 usec
TE                   295.5 K
D1              7.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.00 usec
PL1                  -6.00 dB
SFO1           400.1326008 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300502 MHz
WDW                     EM
SSB      0
LB       0 Hz
GB       0
PC                    1.00
```



```
Current Data Parameters
NAME             nh-3-266
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100810
Time                 9.03
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg
TD                  38460
SOLVENT              C6D6
NS                      8
DS                      0
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ              2.9999299 sec
RG                   80.6
DW                 78.000 usec
DE                 111.43 usec
TE                  295.6 K
D1            7.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -6.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300484 MHz
WDW                    EM
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```