*Electronic Supplementary Information*

# α-Diimine nickel complexes of ethylene and related alkenes

Yanxia Zhao,[a] Zeyi Wang,[ab] Xiaojing Jing,[a] Qingsong Dong,[c] Shida Gong,[d] Qian-Shu Li,[d] Juan Zhang,[b] Biao Wu[a] and Xiao-Juan Yang*[a]

[a] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China*
[b] *Institute of Chemistry in Shaanxi Province, School of Chemical Engineering, Northwest University, Xi'an 710069, China*
[c] *State Key Laboratory for Oxo Synthesis & Selective Oxidation, Lanzhou Institute of Chemical Physics, CAS, Lanzhou 730000, China*
[d] *Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, China*

---

**Table of Contents:**



---

## Experimental Section

**General considerations:** All reactions and manipulations of the compounds described were performed under $N_2$ atmosphere using Schlenk techniques, or under Ar atmosphere in a glove box. The solvents ($Et_2O$ and hexane) were dried by using appropriate methods and were distilled under $N_2$ prior to

use. $LNiBr_2$ and [{Ni(μ-$L^{\bullet-}$)}$_2$] (**1**) were prepared according to published procedures.[1] All the alkenes were purchased from Alfa Aesar and TCI and were used without further purification.

**X-ray crystallography**: Diffraction data for **2**−**6** were collected on a Bruker SMART APEX II diffractometer at room temperature with graphite-monochromated Mo $K_\alpha$ radiation (λ = 0.71073 Å). An empirical absorption correction by using SADABS was applied for all data.[2] The structures were solved by direct methods using the SHELXS program.[3] All non hydrogen atoms were refined anisotropically by full-matrix least squares on $F^2$ by the use of the SHELXL program.[3] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement details for **2**–**6** are given in Table S1. CCDC 1060103–1060107. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

**[LNi($\eta^2$-$H_2C{=}CH_2$)] (2):** Sodium (0.023 g, 1.0 mmol) was added to a suspension of $LNiBr_2$ (0.31 g, 0.50 mmol) in $Et_2O$ (30 mL), and the mixture was stirred for 2 days at room temperature, upon which a color change from purple to green occurred. Then excess dry ethylene was bubbled into the solution for 0.5h. A very quick color change from green to dark blue was observed. The mixture was filtered and the filtrate was concentrated to ca. 8 mL and stored at room temperature for several days to afford dark blue crystals of **2**.

Data for **2**: Yield: 0.19 g (80%). m.p. 152 °C. $^1$H NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ = –1.52 (s, 6H, NCC$H_3$), 1.07 (d, 12H, $J$ = 4.0 Hz, CH(C$H_3$)$_2$), 1.32 (d, 12H, $J$ = 4.0 Hz, CH(C$H_3$)$_2$), 2.13 (s, 4H, C$H_2$=C$H_2$), 3.09 (m, 4H, $J$ = 8.0 Hz, C$H$(CH$_3$)$_2$), 7.41−7.32 (m, 6H, $C_6H_3$); $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ = 22.9 (NC$C$H$_3$), 23.4 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 31.8 (*C*H$_2$=*C*H$_2$), 123.5 (*p*-$C_6H_3$), 125.7 (*m*-$C_6H_3$), 137.2 (*o*-$C_6H_3$), 152.7 (N-$C_6H_3$), 160.7 (N=*C*). IR (KBr, ν/cm$^{-1}$): 2960(s), 2868(s), 1579(w), 1535(w), 1546(m), 1447(m), 1381(s), 1321(s), 1254(m), 1142(s), 976(m), 847(m), 783(m), 733(m), 698(w), 496(w). Anal. Calcd for $C_{30}H_{44}N_2Ni$ (491.38): C, 73.33; H, 9.03; N, 5.70. Found: C, 72.91; H, 8.99; N, 5.45.

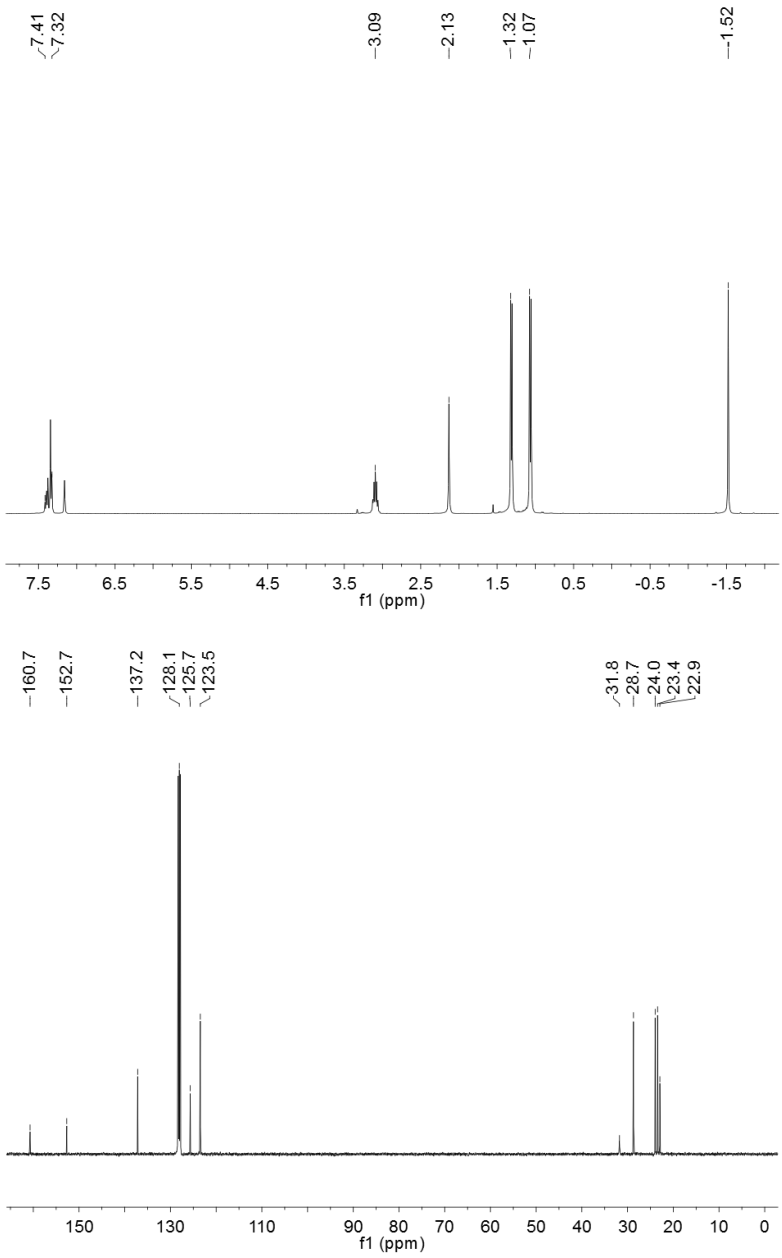



**Fig. S1**. $^{1}$H and $^{13}$C NMR of compound [LNi($\eta^2$-$H_2C$=$CH_2$)] (**2**).

**[LNi($\eta^2$-$H_2C$=C(H)Ph)] (3):** $LNiBr_2$ (0.31 g, 0.50 mmol) and sodium (0.023 g, 1.0 mmol) were suspended in $Et_2O$ (30 mL) and stirred for 2 days at room temperature to generate a green color. Then styrene (52 μL, 0.50 mmol) was added and the mixture stirred for another 2 days with the color change to dark green. The solution was filtered and the filtrate was concentrated to ca. 8 mL and stored at room temperature for several days to yield **3** as dark-green crystals.

Data for **3**: Yield: 0.21 g (73%). m.p. 165 °C. $^{1}$H NMR (400 MHz, $C_6D_6$, 25 ℃): $\delta$ = –0.89 (s, 6H, NCC$H_3$), 0.98 (d, 12H, $J$ = 4.0 Hz, CH(C$H_3$)$_2$), 1.31 (d, 12H, $J$ = 8.0 Hz, CH(C$H_3$)$_2$), 1.64 (d, 1H, C$H_2$CHC$_6$H$_5$), 2.37 (d, 1H, C$H_2$CHC$_6$H$_5$), 2.89 (m, 2H, $J$ = 6.0 Hz, C$H$(CH$_3$)$_2$), 3.09 (m, 2H, $J$ = 6.0 Hz,

C*H*($CH_3$)$_2$), 3.77 (q, 1H, $CH_2CHC_6H_5$), 6.78−6.89 (m, 5H, $C_2H_3C_6H_5$), 7.42−7.29 (m, 6H, $NC_6H_3$). $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ = 22.0 (NC*C*$H_3$), 23.3 (NC*C*$H_3$), 23.6 (CH(*C*$H_3$)$_2$), 23.9 (*C*H($CH_3$)$_2$), 24.6 (*C*H($CH_3$)$_2$), 28.8 (CH(*C*$H_3$)$_2$), 51.0 ($CH_2$=*C*H$C_6H_5$), 122.2 (*C*$H_2$=CH*C*$_6H_5$), 123.6 (*p*-$C_2H_3C_6H_5$), 123.8 (*p*-N-*C*$_6H_3$), 124.6 (*m*-$C_2H_3C_6H_5$), 125.6 (*m*-N-*C*$_6H_3$), 128.8 (*o*-$C_2H_3C_6H_5$), 173.9 (*o*-N-*C*$_6H_3$), 145.9 ($C_2H_3C_6H_5$), 151.0 (N-*C*$_6H_3$), 163.4 (N=*C*). IR (KBr, ν/cm$^{-1}$): 3323(w), 2956(s), 2866(s), 1660(w), 1456(m, C=C), 1381(m), 1321(m), 1138(s), 982(w), 870(w), 785(w), 737(w), 696(w). Anal. Calcd for $C_{36}H_{48}N_2Ni$ (567.47): C, 76.19; H, 8.52; N, 4.94. Found: C, 76.45; H, 8.17; N, 5.10.

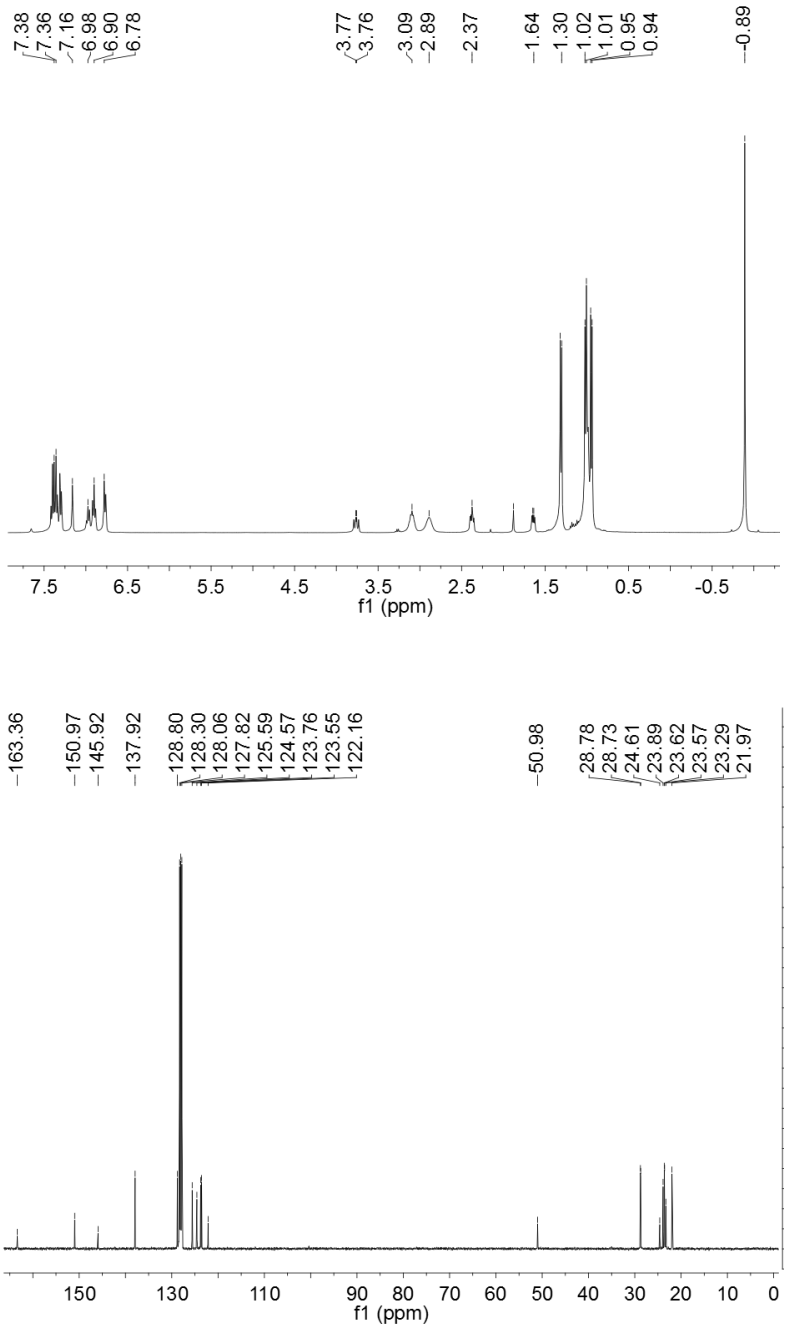
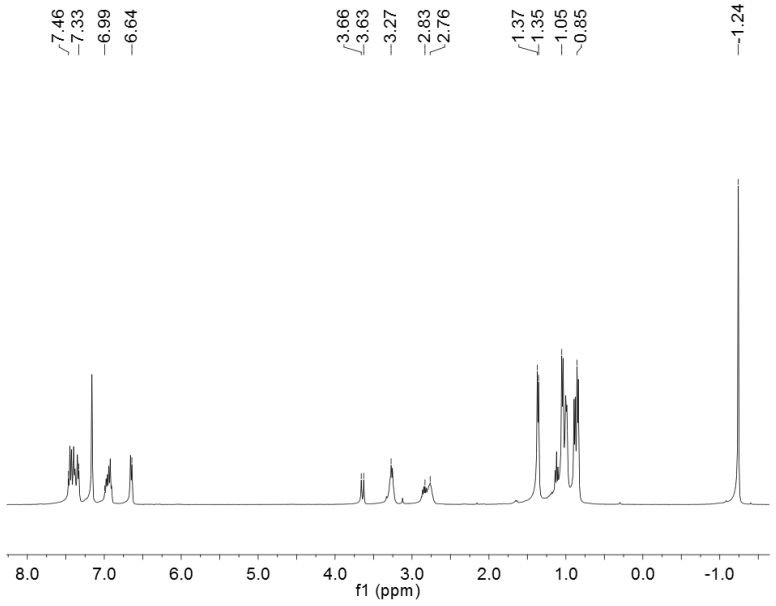



**Fig. S2**. $^1$H and $^{13}$C NMR of compound [LNi($\eta^2$-$H_2$C=C(H)Ph)] (**3**).

**[LNi{$\eta^2$-(CH$_3$)(H)C=C(H)Ph}] (4):** Similar procedures to the preparation of **3** were employed by using *trans*/*cis*-1-phenyl-1-propene (65 μL, 0.50 mmol) or allylbenzene (70 μL, 0.50 mmol) and in situ generated precursor **1** (0.25 mmol in $Et_2O$). Yield for *trans*/*cis*-1-phenyl-1-propene: 0.18 g, 61%; for allylbenzene: 0.16 g, 55%.

Data for **4**: green crystals. m.p. 181 °C. $^1$H NMR (400 MHz, $C_6D_6$, 25 ℃): $\delta$ = −1.24 (s, 6H, NCC$H_3$), 0.87 (d, 12H, $J$ = 5.3Hz, CH(C$H_3$)$_2$), 1.12 (d, 12H, $J$ = 8.0Hz, CH(C$H_3$)$_2$), 1.37 (d, 3H, C$H_3$C$_2$H$_2$C$_6$H$_5$), 2.81 (m, 1H, CH$_3$C$_2$$H_2$C$_6$H$_5$), 3.26 (m, 4H, $J$ = 6.0Hz, C$H$(CH$_3$)$_2$), 3.64 (d, 1H, CH$_3$C$_2$$H_2$C$_6$H$_5$), 6.64−6.94 (m, 5H, CH$_3$C$_2$H$_2$C$_6$$H_5$), 7.33−7.46 (m, 6H, NC$_6$$H_3$). $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ =15.6 (*C*H$_3$C$_2$H$_2$C$_6$H$_5$), 17.6 (NC*C*H$_3$), 23.0 (NC*C*H$_3$), 23.5 (CH(*C*H$_3$)$_2$), 24.3 (*C*H(CH$_3$)$_2$), 28.8 (CH(*C*H$_3$)$_2$), 36.9 (*C*H(CH$_3$)$_2$), 55.0 (CH$_3$*C*$_2$H$_2$C$_6$H$_5$), 121.8 (CH$_3$*C*$_2$H$_2$C$_6$H$_5$), 123.7 (*p*-CH$_3$C$_2$H$_2$*C*$_6$H$_5$), 124.5 (*p*-N-*C*$_6$H$_3$), 125.5 (*m*-CH$_3$C$_2$H$_2$*C*$_6$H$_5$), 128.8 (*m*-N-*C*$_6$H$_3$), 137.2 (*o*-CH$_3$C$_2$H$_2$*C*$_6$H$_5$), 138.2 (*o*-N-*C*$_6$H$_3$), 145.3 (CH$_3$C$_2$H$_2$*C*$_6$H$_5$), 151.8 (N-*C*$_6$H$_3$), 162.9 (N=*C*). IR (KBr, ν/cm$^{-1}$): 3743(w), 2960(s), 2870(m), 1583(w), 1533(w), 1456(m, C=C), 1331(m), 1319(s), 1255(m), 1209(m), 1032(m), 980(m), 868(m), 787(m), 737(m), 692(m), 534(m). Anal. Calcd for $C_{37}H_{50}N_2Ni$ (581.50): C, 76.42; H, 8.67; N, 4.82. Found: C, 76.13; H, 8.40; N, 4.33.



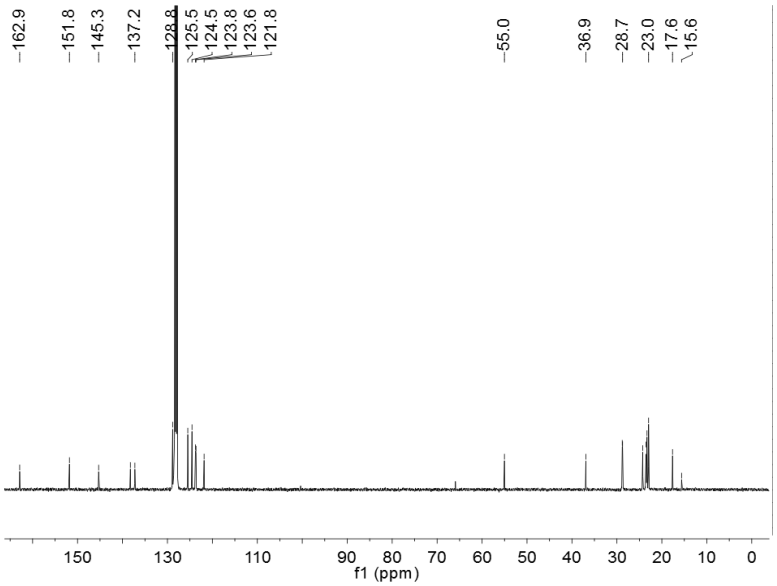



**Fig. S3**. $^{1}$H and $^{13}$C NMR of compound [LNi{$\eta^2$-($CH_3$)(H)C=C(H)Ph}] (**4**).

**[LNi($\eta^2$-PhCH=CHPh)]** (**5**)**:** Similarly to the preparation of above complexes, the reaction of **1** with *cis*/*trans*-stilbene (82 μL, 0.50 mmol) yielded product **5** as dark-blue crystals.

Data for **5**: Yield: 0.196 g (61 %). m.p. 195 °C. $^{1}$H NMR (400 MHz, $C_6D_6$, 25 ℃): $\delta$ = 1.04 (d, 12H, $J$ = 6.8 Hz, CH(C$H_3$)$_2$), 1.11 (d, 12H, $J$ = 6.4 Hz, CH(C$H_3$)$_2$), 2.73 (s, 6H, N-CC$H_3$), 3.01 (m, 4H, C$H$(C$H_3$)$_2$), 3.25 (d, 2H, $J$ = 6.4 Hz, $C_6H_5$(C$H$)$_2$$C_6H_5$)), 6.96−7.45 ppm (m, 16H, (CH-$C_6H_5$)$_2$, N-$C_6H_3$). IR (KBr, ν/cm$^{-1}$): 1581(m), 1431(w), 1378(m), 1320(s), 1249 (m), 1215(w), 1109 (m), 1090(m), 1030(m), 973(m), 887(m), 853(w), 784(m), 733(m), 694(m). Anal. Calcd for $C_{42}H_{52}N_2Ni$ (643.57): C, 78.38; H, 8.14; N, 4.35. Found: C, 77.93; H, 8.51; N, 4.14.

**[LNi{$\eta^2$-PhCH=CH-CH=CHPh)}] (6):** The similar reaction was carried out for precursor **1** (0.25 mmol) and 1,4-diphenyl-1,3-butadiene (0.103 g, 0.50 mmol) to yield complex **6** as dark-green crystals.

Data for **6**: Yield: 0.26 g (78%). m.p. 204 °C. $^{1}$H NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ = −0.54 (s, 6H, NCC$H_3$), 0.91 (d, 12H, $J$ = 4.0 Hz, CH(C$H_3$)$_2$), 1.12 (d, 12H, $J$ = 4.0 Hz, CH(C$H_3$)$_2$), 3.12 (d, 4H, C$H$(C$H_3$)$_2$), 3.33 (d, 1H, PhC$H$CHC$_2$H$_2$Ph), 4.79 (s, 1H, PhCHC$H$C$_2$H$_2$Ph), 6.49 (d, 1H, PhCHCHC$_2$$H_2$Ph), 6.81 (d, 1H, PhCHCHC$_2$$H_2$Ph), 7.0−7.5 (m, 16H, (-CHCH-$C_6H_5$)$_2$, N-$C_6H_3$)). $^{13}$C NMR (100.6 MHz, $C_6D_6$): $\delta$ =15.6 (NC$C$H$_3$), 21.4 (NC$C$H$_3$), 22.8 (CH(C$H_3$)$_2$), 23.7 (CH(C$H_3$)$_2$), 25.0 (C$H$(CH$_3$)$_2$), 26.2 (CH(C$H_3$)$_2$), 27.0 (CH(C$H_3$)$_2$), 29.1 (C$H$(CH$_3$)$_2$), 58.7 (PhC$H$CHC$_2$H$_2$Ph), 72.2 (PhCH$C$HC$_2$H$_2$Ph), 121.0 (*p*-$C_6H_5C_4H_4C_6H_5$), 123.3 (*p*-$C_6H_5C_4H_4C_6H_5$), 123.9 (*p*-N-$C_6H_3$), 124.9 (*m*-$C_6H_5C_4H_4C_6H_5$), 125.5

(*m*-$C_6H_5C_4H_4C_6H_5$), 126.8 (*m*-N-$C_6H_3$), 128.8 (*o*-$C_6H_5C_4H_4C_6H_5$), 129.0 (*o*-$C_6H_5C_4H_4C_6H_5$), 129.7 (*o*-N-$C_6H_3$), 133.2 ($C_6H_5CHCHC_2H_2C_6H_5$), 137.9 ($C_6H_5CHCHC_2H_2C_6H_5$), 138.3 $C_6H_5C_4H_4C_6H_5$), 143.8 ($C_6H_5C_4H_4C_6H_5$), 149.2 (N−$C_6H_3$), 165.2 (N=*C*). IR (KBr, $\nu$/cm$^{-1}$): 2960(s), 2868(m), 1642(w), 1581(m), 1456(s, C=C), 1365(w), 1307(w), 1140(m), 966(w), 733(m), 683(m), 536(w). Anal. Calcd for $C_{44}H_{54}N_2Ni$ (669.60): C, 78.92; H, 8.13; N, 4.18. Found: C, 78.58; H, 7.87; N, 4.49.

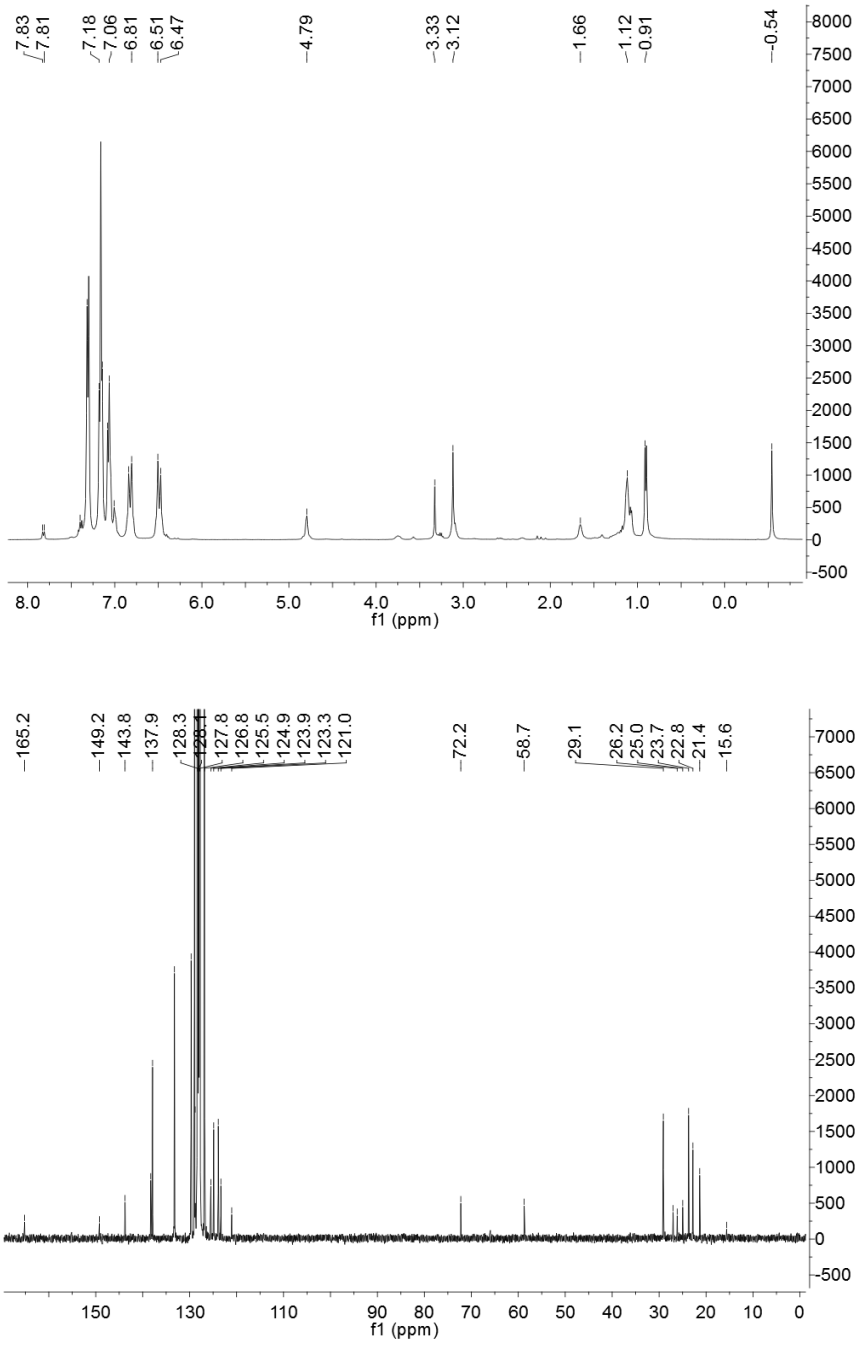



**Fig. S4**. $^1$H and $^{13}$C NMR of compound [LNi{$\eta^2$-PhCH=CH-CH=CHPh)}] (**6**).

**Table S1**. Crystal Data and refinement details for compounds **2**−**6**.

| | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|
| formula | $C_{30}H_{44}N_2Ni$ | $C_{36}H_{48}N_2Ni$ | $C_{37}H_{50}N_2Ni$ | $C_{42}H_{52}N_2Ni$ | $C_{44}H_{54}N_2Ni$ |
| $M_w$ | 491.38 | 567.47 | 581.50 | 643.57 | 669.60 |
| crystal system | Monoclinic | Triclinic | Triclinic | orthorhombic | Monoclinic |
| space group | *C*2/*c* | *P*-1 | *P*-1 | *Fdd*2 | *P*2(1)/*c* |
| *a* (Å) | 16.404(3) | 9.649(2) | 9.7243(18) | 19.024(11) | 19.995(4) |
| *b* (Å) | 9.3422(18) | 10.406(2) | 10.4129(19 | 41.19(2) | 9.4506(17) |
| *c* (Å) | 19.045(4) | 18.470(4) | 18.679(3) | 9.557(6) | 20.667(4) |
| $\alpha$ (°) | 90 | 81.915(3) | 83.031(3) | 90 | 90 |
| $\beta$ (°) | 93.067(2) | 83.476(2) | 87.778(3) | 90 | 92.609(3) |
| $\gamma$ (°) | 90 | 65.495(2) | 63.827(3) | 90 | 90 |
| *V* (Å$^3$) | 2914.5(10) | 1667.6(6) | 1684.7(5) | 7489(7) | 3901.3(12) |
| *Z* | 4 | 2 | 2 | 8 | 4 |
| $\mu$ (mm$^{-1}$) | 0.684 | 0.606 | 0.601 | 0.547 | 0.528 |
| *F*(000) | 1064 | 612 | 628 | 2768 | 1440 |
| $\theta$ range | 2.14−25.00 | 2.16−25.02 | 2.34−25.17 | 1.98−26.72 | 1.97−25.00 |
| total reflns | 2566 | 5702 | 5916 | 12565 | 6839 |
| unique reflns | 2355 | 4889 | 5102 | 2920 | 4434 |
| $R_1$, $wR_2$ [$I>2\sigma(I)$] | 0.0319, 0.0910 | 0.0489, 0.1341 | 0.0564, 0.1746 | 0.0429, 0.0905 | 0.0579, 0.1842 |
| GOF ($F^2$) | 1.068 | 1.074 | 1.065 | 1.036 | 1.086 |

**Table S2**. Selected bond lengths (Å, experimental and calculated) and bond orders.

| compound | Ni−C (experimental) | Ni−C (DFT) | Ni−C (bond order) | C=C (experimental) | C=C (DFT) | C=C (bond order) |
|---|---|---|---|---|---|---|
| **2** | 1.926(2), 1.926(2) | 1.966, 1.966 | 0.50, 0.50 | 1.392(5) | 1.442 | 1.45 |
| **3** | 1.940(4), 1.966(4) | 1.946, 2.013 | 0.52, 0.41 | 1.443(6) | 1.445 | 1.45 |
| **4** | 1.962(5), 1.974(5) | 1.963, 2.018 | 0.48, 0.38 | 1.418(8) | 1.442 | 1.37 |
| **5** | 1.965(3), 1.965(3) | 1.963, 1.954 | 0.41, 0.41 | 1.447(5) | 1.439 | 1.31 |
| **6** | 1.967(4), 1.978(4) | 1.995, 1.991 | 0.40, 0.42 | 1.434(6) | 1.453 | 1.31 |

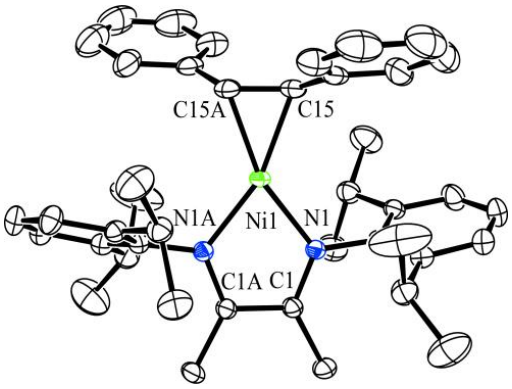



**Fig. S5.** Molecular structure of **5** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−N1, 1.937(2); Ni1−C15, 1.965(3); C15−C15A, 1.447(5); N1−C1, 1.296(4); C1−C1A, 1.487(4); N1−Ni1−N1A, 80.85(12); C15−Ni1−C(15A), 43.19(16).

## DFT Computational Details

The model compounds [**L**′Ni($C_2H_4$)] (**2′**), [**L**′Ni($H_2C$=C(H)Ph)] (**3′**), [**L**′Ni($CH_3$)(H)C=C(H)Ph)] (**4′**), and [**L**′Ni(PhCH=CH-CH=CHPh)] (**6′**), wherein the 2,6-diisopropylphenyl groups on the nitrogen atoms of **L** were replaced by phenyl groups (**L**′ = ($C_6H_5$N=C($CH_3$))$_2$), were used for the products **2**, **3**, **4**, **6**, respectively, in the DFT computations. The structure optimization and NBO bonding analysis were carried out at the DFT (BP86)[4] level with the 6-311G* basis sets using the Gaussian 03 program.[5] Geometry optimizations gave bond distances that were in good agreement with the X-ray structures.

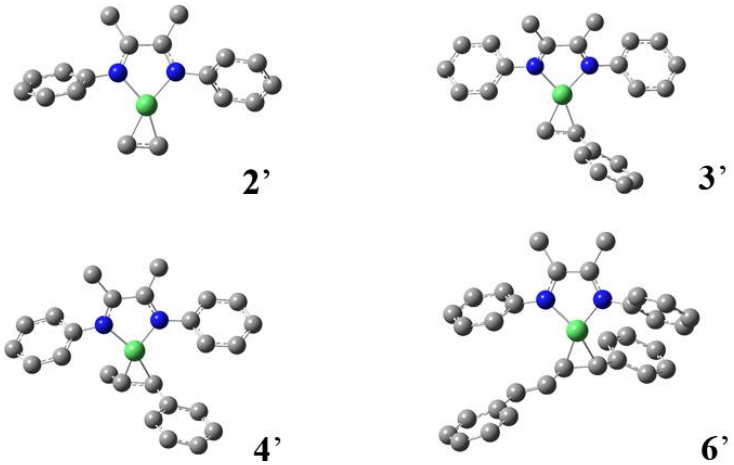



**Fig. S6**. Optimized structure of **2′**, **3′**, **4′**, **6′** (hydrogen atoms have been omitted for clarity)**.**

**Table S3.** The calculated energies (kcal/mol).

| | Singlet state | Triplet state | $\Delta E$ ($E_T$-$E_S$) |
|---|---|---|---|
| **2'** | -1453404.05 | -1453392.60 | 11.46 |
| **3'** | -1598421.70 | -1598411.27 | 10.43 |
| **4'** | -1623095.28 | -1623087.54 | 7.74 |
| **6'** | -1792021.42 | -1792008.66 | 12.77 |

**Table S4.** Cartesian coordinates of the optimized geometry of **2′** in the singlet state.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni | -0.00945100 | -1.02629900 | -0.14890800 | C | 1.53783200 | 2.84666900 | -0.60062100 |
| N | -1.22339100 | 0.41503600 | 0.05848100 | H | 2.57999600 | 2.62624100 | -0.86852000 |
| C | -0.69287700 | 1.59744600 | -0.26137900 | H | 1.55672200 | 3.53582800 | 0.26282600 |
| C | -1.46388500 | 2.87630100 | -0.45937200 | H | 1.07682000 | 3.40116000 | -1.43482600 |
| H | -2.47857600 | 2.80218900 | -0.04503900 | C | 2.68827800 | 0.19286700 | 0.06603300 |
| H | -1.56405100 | 3.14130700 | -1.52797600 | C | 3.40569400 | 0.93405400 | 1.02952000 |
| H | -0.95353800 | 3.72239800 | 0.02857800 | C | 4.76243400 | 0.67475700 | 1.25230400 |
| C | -2.62816000 | 0.23376800 | 0.18456100 | H | 5.30180900 | 1.24366400 | 2.01636500 |
| C | -3.52061800 | 0.49558900 | -0.87370800 | C | 5.42744600 | -0.31006500 | 0.50912200 |
| C | -4.88999600 | 0.24791900 | -0.71751800 | H | 6.48915500 | -0.50859700 | 0.68349400 |
| H | -5.57154800 | 0.44151500 | -1.55196500 | C | 4.71665100 | -1.05188300 | -0.44640600 |
| C | -5.38692200 | -0.24640000 | 0.49536900 | H | 5.22420100 | -1.83028100 | -1.02468500 |
| H | -6.45763600 | -0.43645500 | 0.61540100 | C | 3.35507600 | -0.81752800 | -0.65527700 |
| C | -4.49914600 | -0.51330700 | 1.54903200 | C | 0.49136300 | -2.82198900 | -0.67154200 |
| H | -4.87639700 | -0.91013900 | 2.49674300 | H | 1.17700700 | -3.28870200 | 0.04948400 |
| C | -3.12839200 | -0.29194900 | 1.39146200 | H | 0.80103000 | -2.94683300 | -1.71850700 |
| C | -0.90125900 | -2.71795800 | -0.35082400 | H | 2.78049500 | -1.40204900 | -1.37697100 |
| H | -1.64960600 | -2.75149400 | -1.15438800 | H | 2.88233700 | 1.68229200 | 1.63196800 |
| H | -1.26914100 | -3.11426600 | 0.60654300 | H | -3.12849600 | 0.85827700 | -1.82842100 |
| N | 1.29991400 | 0.37368200 | -0.14634900 | H | -2.42164200 | -0.52075500 | 2.19398400 |
| C | 0.76482000 | 1.58338400 | -0.31902300 | | | | |

**Table S5.** Cartesian coordinates of the optimized geometry of **3′** in the singlet state.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni | -0.31034700 | -0.30289400 | -0.49689400 | H | 0.98529100 | 3.34302600 | 1.86907200 |
| N | 0.38133200 | 1.35461200 | 0.16989900 | H | -0.33025900 | 2.87341500 | 2.97653800 |
| N | -1.95472600 | 0.36458500 | 0.20156300 | H | -0.64797700 | 4.01855300 | 1.66702200 |
| C | -0.44025600 | 1.94399800 | 1.03447700 | C | -2.82361700 | 1.87462100 | 2.02531800 |
| C | -1.77933200 | 1.35746700 | 1.07155200 | H | -3.72483900 | 1.24811400 | 2.01219600 |
| C | -0.08464700 | 3.10455300 | 1.92582800 | H | -3.13017300 | 2.90848600 | 1.78645600 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.43318600 | 1.89487700 | 3.05721100 | H | -0.73753000 | -2.88687000 | -0.57135400 |
| C | 1.62401500 | 1.94951000 | -0.17809900 | H | -0.97085100 | -2.05263900 | -2.18778400 |
| C | 1.68225400 | 3.24730300 | -0.72751100 | C | 0.94581800 | -1.63479700 | -1.21587800 |
| C | 2.91107800 | 3.78985800 | -1.11938700 | H | 1.35267300 | -1.24269000 | -2.16110900 |
| H | 2.94241300 | 4.79081300 | -1.56148200 | C | 1.98099000 | -2.22741900 | -0.33809400 |
| C | 4.09437000 | 3.05756200 | -0.95065300 | C | 3.32665600 | -2.28014400 | -0.76898500 |
| H | 5.05442000 | 3.48551900 | -1.25442300 | H | 3.58032200 | -1.88287000 | -1.75823100 |
| C | 4.03639300 | 1.76739400 | -0.40331100 | C | 4.33146800 | -2.83793900 | 0.03079700 |
| H | 4.95195600 | 1.18261700 | -0.27226600 | H | 5.36235000 | -2.86963700 | -0.33819500 |
| C | 2.81025800 | 1.20686900 | -0.03285700 | C | 4.02154800 | -3.36133400 | 1.29278300 |
| C | -3.25054000 | -0.15402700 | -0.06214500 | H | 4.80390700 | -3.79902400 | 1.92061400 |
| C | -3.51513800 | -1.52326100 | 0.12975400 | C | 2.69245500 | -3.31534100 | 1.74144800 |
| C | -4.77839700 | -2.04376700 | -0.16671100 | H | 2.43519000 | -3.71505700 | 2.72832900 |
| H | -4.97312300 | -3.10807700 | -0.00185600 | C | 1.69172200 | -2.75404400 | 0.94315700 |
| C | -5.78682400 | -1.21647600 | -0.68270300 | H | 0.66485400 | -2.71048700 | 1.32146100 |
| H | -6.76885700 | -1.63128700 | -0.92827800 | H | 2.75495900 | 0.19377200 | 0.37073900 |
| C | -5.52149100 | 0.14336800 | -0.89314500 | H | 0.75482600 | 3.80823800 | -0.87865300 |
| H | -6.29542700 | 0.79632300 | -1.30900300 | H | -4.05068100 | 1.73334100 | -0.76291100 |
| C | -4.26684900 | 0.67673500 | -0.57801100 | H | -2.71869800 | -2.16216800 | 0.51624300 |
| C | -0.42828200 | -2.06562700 | -1.23221400 | | | | |

**Table S6.** Cartesian coordinates of the optimized geometry of **4′** in the singlet state.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni | 0.28871300 | -0.15678800 | 0.35416700 | C | 3.14518300 | 0.05586800 | -0.24341200 |
| C | 0.35321300 | 2.44018800 | -0.56672200 | C | 3.33786700 | -1.07640600 | -1.05848900 |
| C | 1.73609500 | 1.96433300 | -0.63336400 | C | 4.18418800 | 0.47489900 | 0.61102900 |
| C | -1.89133200 | 1.79642200 | -0.01227600 | C | 4.56122900 | -1.75179100 | -1.04559300 |
| C | -2.33277100 | 2.81631600 | 0.85689400 | H | 4.70314200 | -2.62145700 | -1.69476800 |
| C | 2.83828900 | 2.85244600 | -1.14556100 | C | 5.39978500 | -0.22089400 | 0.63318800 |
| H | 3.79623500 | 2.31991700 | -1.19864900 | H | 6.19553400 | 0.10778400 | 1.30917100 |
| H | 2.97788700 | 3.74066700 | -0.50453200 | C | 5.59808100 | -1.32995000 | -0.19894400 |
| H | 2.60270600 | 3.22880000 | -2.15613700 | H | 6.54897700 | -1.87037300 | -0.18026800 |
| C | 0.00731600 | 3.85342700 | -0.95470300 | N | 1.87756600 | 0.69970800 | -0.25185700 |
| H | -1.07153700 | 3.97409300 | -1.11955700 | N | -0.51399900 | 1.50182800 | -0.19615000 |
| H | 0.53245400 | 4.14376700 | -1.87936100 | C | -1.75593400 | -2.18347300 | 0.35504900 |
| H | 0.30847000 | 4.58344300 | -0.18159900 | C | -0.82416200 | -1.48800800 | 1.26861400 |
| C | -2.84200900 | 0.99558000 | -0.67449400 | H | -1.31102700 | -1.07745600 | 2.16640200 |
| C | -4.20670500 | 1.24930600 | -0.51224100 | C | 0.58563900 | -1.77203300 | 1.36103100 |
| H | -4.93258900 | 0.62585400 | -1.04234400 | H | 0.97884200 | -2.57083400 | 0.71089000 |
| C | -4.64419700 | 2.27234400 | 0.34230700 | C | -3.14703300 | -2.15849500 | 0.61446900 |
| H | -5.71405100 | 2.45586600 | 0.47974500 | H | -3.50875600 | -1.62609200 | 1.50079900 |
| C | -3.70176300 | 3.04343600 | 1.03671600 | C | -1.33049200 | -2.88299100 | -0.80216700 |
| H | -4.03263500 | 3.82766800 | 1.72507000 | H | -0.26418200 | -2.92598300 | -1.04624300 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.33234300 | -1.64848200 | 2.67644200 | H | -4.33216100 | -4.00170000 | -2.01791800 |
| H | 0.89082600 | -0.87022500 | 3.32161800 | C | -4.06219000 | -2.80402800 | -0.22450600 |
| H | 2.39389400 | -1.39029700 | 2.52231000 | H | -5.13046600 | -2.77275100 | 0.01621500 |
| H | 1.30666300 | -2.59785900 | 3.24554900 | H | -1.59671800 | 3.40215500 | 1.41541300 |
| C | -2.24408500 | -3.52748800 | -1.64092900 | H | -2.49379200 | 0.17636600 | -1.30779300 |
| H | -1.87940900 | -4.06368700 | -2.52388500 | H | 4.01884200 | 1.32791500 | 1.27594200 |
| C | -3.61903100 | -3.49380000 | -1.36115800 | H | 2.51876800 | -1.40661300 | -1.70377500 |

**Table S7.** Cartesian coordinates of the optimized geometry of **6′** in the singlet state.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni | -0.53077300 | 0.09601400 | -0.02118400 | C | -3.85607600 | -3.01426000 | 2.71166100 |
| N | -1.92501800 | 0.97394600 | -0.99036600 | H | -4.58191100 | -3.82909400 | 2.61846100 |
| N | 0.23290600 | 1.84092700 | 0.02583100 | C | -2.87282000 | -2.84710500 | 1.72923300 |
| C | -1.86481900 | 2.30145100 | -0.90362100 | H | -2.83255700 | -3.53800300 | 0.87957700 |
| C | -0.65069900 | 2.79759100 | -0.26317400 | C | -1.91146300 | -1.81369100 | 1.81480200 |
| C | -2.93710300 | 3.25054400 | -1.37157000 | C | -1.98617300 | -0.94900100 | 2.93266300 |
| H | -3.86824400 | 2.71771300 | -1.60615400 | H | -1.27291100 | -0.12255500 | 3.02011900 |
| H | -2.63721900 | 3.80912600 | -2.27623000 | C | -2.96200200 | -1.11980800 | 3.91821700 |
| H | -3.15437000 | 4.00224500 | -0.59477100 | H | -2.99159000 | -0.43605900 | 4.77334100 |
| C | -0.43739300 | 4.27241500 | -0.04662500 | C | -0.89183100 | -1.65982900 | 0.75512800 |
| H | 0.62184900 | 4.50341900 | 0.12821000 | H | -0.99756800 | -2.38883600 | -0.06499200 |
| H | -1.00529200 | 4.65037400 | 0.82304400 | C | 0.45887200 | -1.21311800 | 1.02609600 |
| H | -0.77824500 | 4.84993500 | -0.92108300 | H | 0.73042000 | -0.90315600 | 2.04434400 |
| C | -2.91506100 | 0.32567000 | -1.77432600 | C | 1.54754400 | -1.56896900 | 0.13823700 |
| C | -3.08174000 | 0.62130500 | -3.14368900 | H | 1.25819500 | -2.03930700 | -0.81206300 |
| C | -4.02334500 | -0.08100500 | -3.90414900 | C | 2.87685600 | -1.38611700 | 0.40384000 |
| H | -4.13207200 | 0.14393100 | -4.96986800 | H | 3.14630400 | -0.97412600 | 1.38516300 |
| C | -4.82031300 | -1.06871500 | -3.30893200 | C | 4.00201500 | -1.70397700 | -0.46940200 |
| H | -5.55822600 | -1.61341600 | -3.90543000 | C | 3.85974800 | -2.09938400 | -1.82445200 |
| C | -4.65609000 | -1.36207600 | -1.94710000 | H | 2.86175000 | -2.16730400 | -2.26894600 |
| H | -5.27092700 | -2.13296300 | -1.47242500 | C | 4.97306100 | -2.39435500 | -2.61303800 |
| C | -3.70071400 | -0.68305000 | -1.18503200 | H | 4.82964500 | -2.69660800 | -3.65590700 |
| C | 1.47035100 | 2.15319500 | 0.65448700 | C | 6.27051500 | -2.30217400 | -2.08384700 |
| C | 1.52118900 | 2.72994400 | 1.94060200 | H | 7.14029500 | -2.53365100 | -2.70625300 |
| C | 2.75483500 | 2.99027900 | 2.54601600 | C | 6.43556900 | -1.90649700 | -0.74930500 |
| H | 2.78260100 | 3.42898100 | 3.54849800 | H | 7.44031900 | -1.82916300 | -0.32051200 |
| C | 3.94965300 | 2.69339300 | 1.87332600 | C | 5.32139400 | -1.61108700 | 0.04147800 |
| H | 4.91355300 | 2.90443700 | 2.34605600 | H | 5.46183200 | -1.30810600 | 1.08511200 |
| C | 3.90125000 | 2.11029000 | 0.59989500 | H | -2.44250100 | 1.37575400 | -3.61206800 |
| H | 4.82602400 | 1.85539100 | 0.07417800 | H | -3.55412800 | -0.91466700 | -0.12745400 |
| C | 2.67062200 | 1.82042600 | -0.00130200 | H | 2.62400900 | 1.34544200 | -0.98358500 |
| C | -3.90693500 | -2.15216900 | 3.81458000 | H | 0.58692200 | 2.94855300 | 2.46694000 |
| H | -4.67293600 | -2.28146000 | 4.58541400 | | | | |

## References


1. (a) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc*., 1995, **117**, 6414; (b) Q. Dong, X.-J. Yang, S. Gong, Q. Luo, Q.-S. Li, J.-H. Su, Y. Zhao and B. Wu, *Chem. – Eur. J.*, 2013, **19**, 15240.
2. G. M. Sheldrick, *Program SADABS: Area-Detector Absorption Correction*; University of Göttingen, Germany, 1996.
3. G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Programs for Crystal Structure Analysis; University of Göttingen, Germany, 1997.
4. (a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098; (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822; *erratum*: J. P. Perdew, *Phys. Rev. B* 1986, **34**, 7406.
5. 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 03, Revision E.01, Gaussian, Inc. , Wallingford CT, 2004.