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Supporting Information

69451 Weinheim, Germany

A d^{10} Ni–(H_2) Adduct as an Intermediate in H–H Oxidative Addition across a Ni–B Bond**

*W. Hill Harman, Tzu-Pin Lin, and Jonas C. Peters**

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Supporting Information

Contents

Experimental Part

General considerations. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Solvents were dried and deoxygenated by sparging with dinitrogen and passage through activated alumina in a solvent purification system from SG Waters USA, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. [MesDPBPh]Ni (**1**)[1] and ^{Ph}DPB^{iPr} (**3**)[2] were synthesized by previously reported procedures. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3Å molecular sieves prior to use. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent ^{1}H and ^{13}C resonances as internal standards. ^{31}P and ^{11}B chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4 and $BF_3{\cdot}Et_2O$, respectively. Solution effective magnetic moments (μ_{eff}) were determined by Evans' method.[3] Optical spectroscopy measurements were taken on a Cary 50 UV-vis spectrophotometer using a 1 cm two-window quartz cell. IR spectra were obtained on KBR pellet samples using a Bio-Rad Excalibur FTS 3000 spectrometer or as a thin film on a Bruker Alpha FT-IR spectrometer with a diamond ATR attachment.

X-ray crystallography. Single crystal X-ray diffraction studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystals were mounted on glass fibers. Structures were solved using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL. Relevant details for individual data collections are reported in Tables S1 and S2.

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[1] Harman, W. H.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 5080–5082.
[2] Bontemps, S.; Bouhadir, G.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Inorg. Chem.* **2007**, *46*, 5149–5151.
[3] a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003; b) Bain, G. A.; Berry, J. F. *J. Chem. Ed.* **2008**, *85*, 1–5.

[^{Ph}DPB^{iPr}]NiBr (4). **3** (500 mg, 1.05 mmol) and Ni(cod)$_2$ (145 mg, 0.527 mmol) were dissolved in THF (15 mL). $NiBr_2$ (115 mg, 0.527 mmol) was added to this solution as a solid, and the resulting suspension was stirred rapidly. After 5 hours the deep red/orange mixture was filtered over celite and concentrated to 1 mL. Layering with pentane (15 mL) gave the title complex as deep red crystals (510 mg, 79%). Single crystals suitable for X-ray diffraction were grown by the slow diffusion of pentane vapor into a saturated benzene solution. μ_{eff} (Evan's method): 1.70 B.M. Anal. Calcd for $C_{30}H_{41}BBrNiP_2$: C, 58.78; H, 6.74; N, 0. Found: C, 58.52; H, 6.81; N, 0.

[^{Ph}DPB^{iPr}]Ni(N_2) (5). **4** (319 mg, 0.521 mmol) was dissolved in THF (10 mL) and stirred vigorously over Na/Hg amalgam (3 g, 1% wt, 1.30 mmol) resulting in a gradual color change to dark red-brown. After 16 hours, the supernatant was decanted from the remaining Hg and filtered. The volatiles were removed from the filtrate *in vacuo*. (The solution turns blue-green when exposed to vacuum.) The resulting brown residue was dissolved in benzene and filtered to give a red-brown solution that was lyophilized. The resulting residue was dissolved in pentane and concentrated to dryness three times to give a deep red powder. ^{1}H NMR (400 MHz, C_6D_6) δ 8.11 (d, J = 7.8 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.20 (m, 3H), 6.98 (d, J = 7.4 Hz, 2H), 6.84 (t, J = 7.3 Hz, 2H), 2.54 (h, J = 7.1 Hz, 2H), 2.03 (h, J = 7.3 Hz, 2H), 1.13 (p, J = 7.1 Hz, 18H), 0.76 (q, J = 6.7 Hz, 6H). ^{11}B NMR (128 MHz, C_6D_6) δ 19.97. ^{31}P NMR (162 MHz, C_6D_6) δ 46.61. ^{13}C NMR (75 MHz, C_6D_6) δ 137.6, 132.4, 131.7, 129.4, 129.3, 125.3, 124.5, 27.6, 24.0, 20.3, 19.8, 12.4, 12.1 (assignments of the ^{13}C resonances are provided in Figure S8). IR (KBr): 2152 cm^{-1} (ν_{NN}). UV-vis (THF, nm {$M^{-1}cm^{-1}$}): 479 {2400}. Anal. Calcd for $C_{30}H_{41}BBrNiP_2$: C, 64.22; H, 7.36; N, 4.99. Found: C, 63.83; H, 7.30; N, 4.45.

[^{Ph}DPB^{iPr}]Ni(H_2) (7). In J. Young NMR tube, **5** was dissolved in toluene-d_8 and subjected to four freeze-pump-thaw cycles on a high vacuum line. Hydrogen was introduced while the solution remained frozen in liquid nitrogen. After allowing the solution to thaw, the tube was shaken vigorously and inserted into a precooled NMR probe. ^{31}P and ^{1}H NMR spectra and T_1 measurements were recorded from 193–303 K in 10 K intervals. Formation of the dihydride species **8** was detected at temperatures above 273 K. The partially deuterated analog was prepared in an analogous fashion by substituting HD for H_2. ^{1}H NMR (500 MHz, toluene-d_8, 273 K) δ 8.08 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.25–7.21 (m, 2H), 7.18 (t, J = 7.3 Hz, 2H), 7.09–7.04 (m, 1H), 6.80 (d, J = 5.2 Hz, 4H), 2.45 (h, J = 7.2 Hz, 2H), 1.94 (p, J = 7.2 Hz, 2H), 1.09 (dq, J = 14.4, 7.0 Hz, 12H), 1.05–0.99 (m, 6H), 0.73 (q, J = 6.6 Hz, 6H). ^{11}B NMR (128 MHz, C_6D_6, 273 K) δ 19.99. ^{31}P NMR (202 MHz, toluene-d_8, 273 K) δ 51.41. ^{13}C NMR (100 MHz, toluene-d_8, 233 K) δ 162.4, 161.5, 132.5, 131.7, 129.3, 124.22, 117.6, 116.6, 27.3, 27.0, 23.7, 22.1, 19.9, 19.5, 19.1 (three of the aromatic ^{13}C resonances overlapped with the solvent peaks and were not observed, see Figure S10 for details).

[^{Ph}DPB^{iPr}](μ-H)NiH (8). In a typical preparation, **5** (~7 mg) was dissolved in C_6D_6 (0.7 mL) and the solution transferred to a J. Young resealable NMR tube. The tube was subjected to three freeze-pump-thaw cycles on a high vacuum line and refilled with H_2. Higher pressures (up to 3.8 atm) were achieved by cooling the tube during gas addition. The tube was inverted constantly for 16 h, at which point the reaction was complete by NMR. Although the rate of H_2 loss from **5** is slow, exposure to vacuum or N_2 result in H_2 loss, precluding the isolation of this material as a pure solid. The deuterated analog [^{Ph}DPB^{iPr}](μ-D)NiD was prepared in an analogous fashion by substituting D_2 for H_2. ^{1}H NMR (400 MHz, C_6D_6) δ 7.67 (d, J = 7.5 Hz, 2H), 7.31 (d, J = 7.4 Hz,

2H), 7.27–7.14 (m, 4H), 7.08 (t, J = 7.2 Hz, 1H), 7.03 (s, 4H), 2.09–1.93 (m, 1H), 1.08–0.94 (m, 18H), 0.74 (q, J = 7.4 Hz, 6H), –6.65 (s, 1H), –16.11 (td, $^2J_{PH}$ = 58.9 Hz, $^2J_{HH}$ = 12.5 Hz, 1H). ^{11}B NMR (128 MHz, C_6D_6) δ –2.28. ^{31}P NMR (162 MHz, C_6D_6) δ 64.32. IR (ATR film): 1814 cm^{-1} (ν_{NiH}). UV-vis (THF, nm {$M^{-1}cm^{-1}$}): 500 {500}.

Kinetics experiments on the formation of 8 from 7. In a typical experiment, **5** (~7 mg) was dissolved in C_6D_6 (0.7 mL) and the solution transferred to a J. Young resealable NMR tube. The tube was subjected to three freeze-pump-thaw cycles on a high vacuum line and refilled with H_2. Higher pressures were achieved by cooling the tube during gas addition. The tube was allowed to reach room temperature, shaken vigorously and inserted into a temperature controlled NMR probe. Automated single transient scans were collected at fixed intervals. Integration data was processed using MestreNova and fit to a three parameter exponential expression of the form $y = a + be^{ct}$ where $c = -k$.

Kinetics experiments on the equilibrium between 1 and 2. A J. Young NMR tube was charged with **1** (~10 mg), C_6D_6 (0.7 mL) and placed under H_2 (1 atm). ^{1}H 2D-EXSY spectra were recorded with mixing times of 0 and 500 ms at 298 K. Data workup was performed with EXSYCalc.[4] Resonances corresponding to the mesityl aryl protons used for kinetic analysis.

[4] Lu, J.; Ma, D.; Hu, J.; Tang, W.; Zhu, D. *J. Chem. Soc., Dalton Trans.* **1998**, 2267–2274.

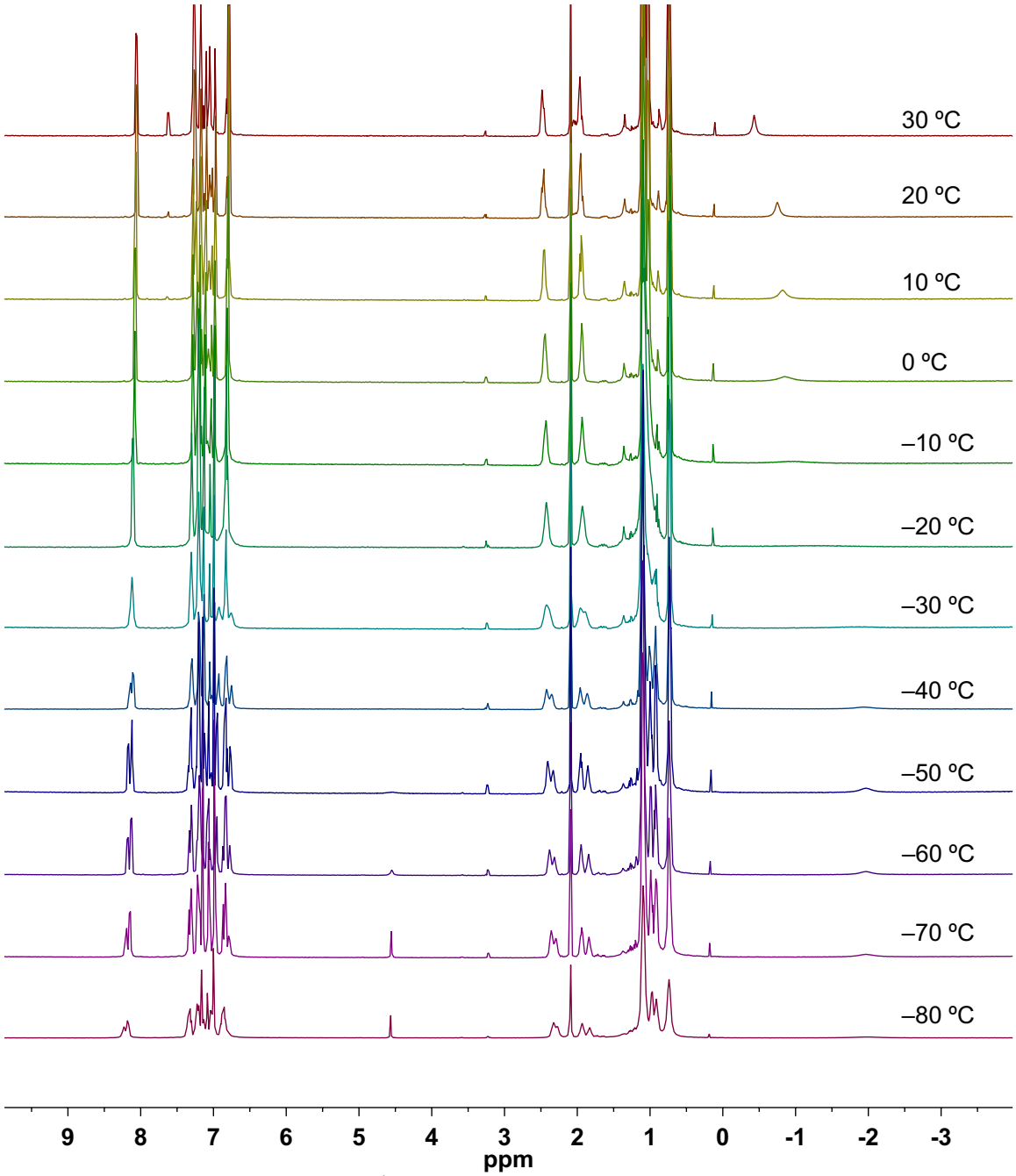

Figure S1. Variable temperature ^{1}H NMR spectra of **7** under H_2 in toluene-d_8.

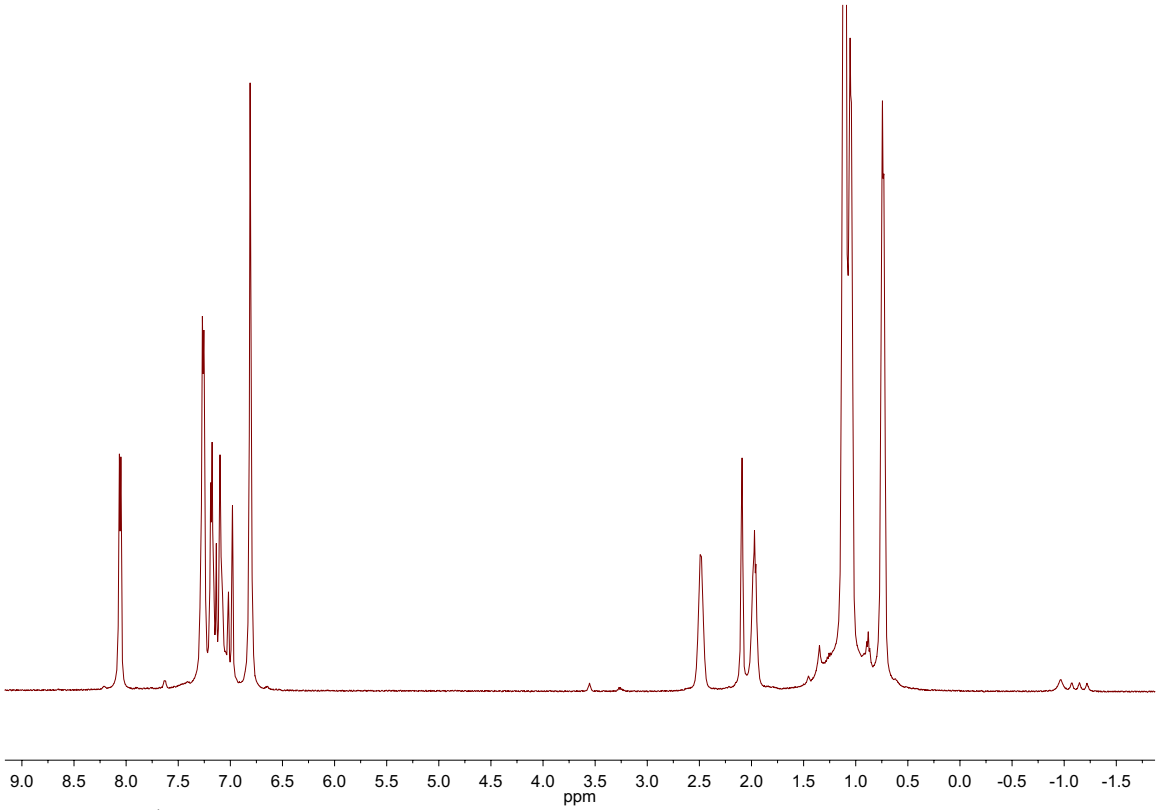

Figure S2. ^{1}H NMR spectrum of **7** under a mixture of H_2 and HD.

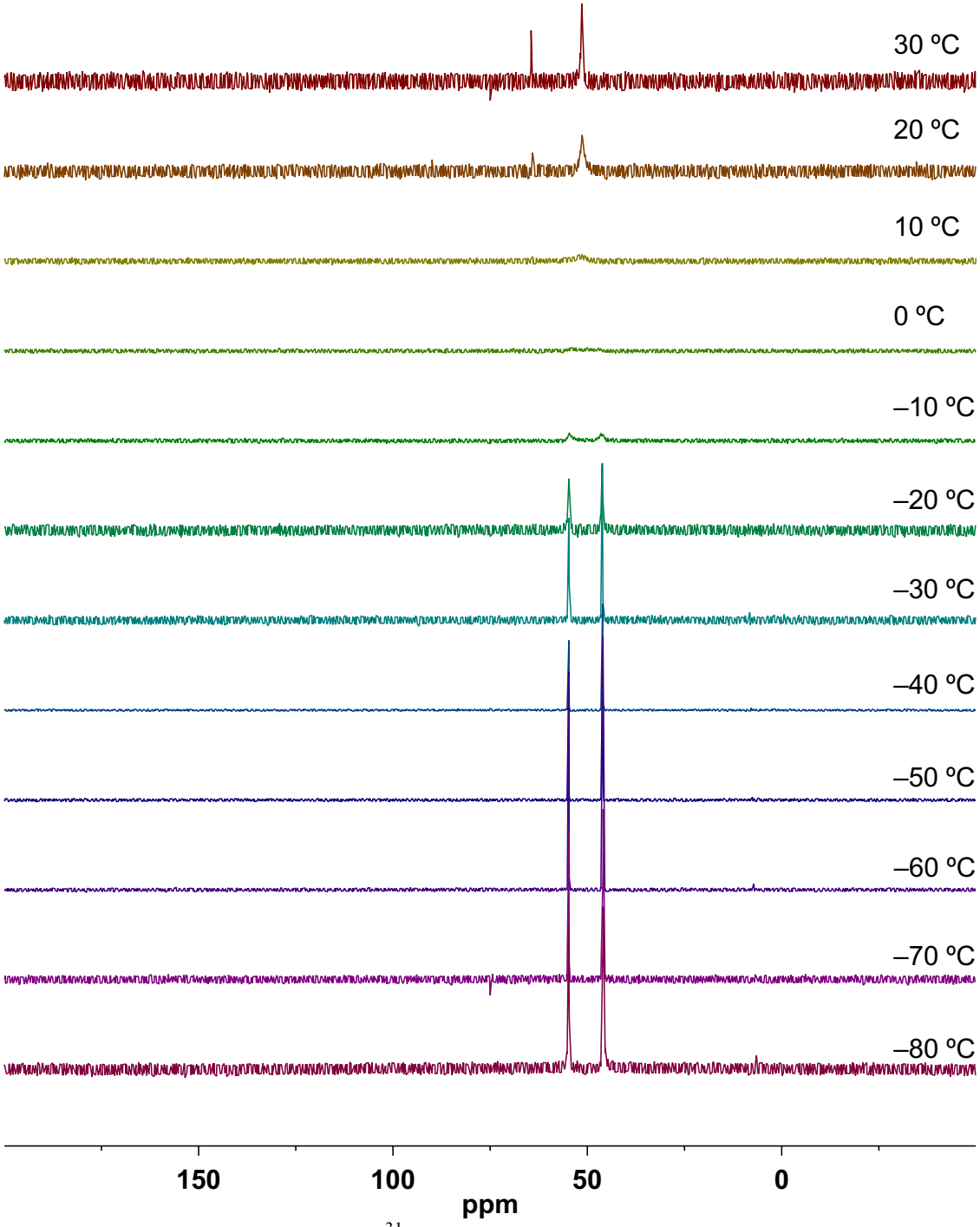

Figure S3. Variable temperature ^{31}P spectra of **7** in toluene-d_8 under H_2. The dynamic process observed here corresponds to the helical inversion of the complex between enantiomeric C_1 structures, rendering the two ^{31}P nuclei distinct at low temperature.

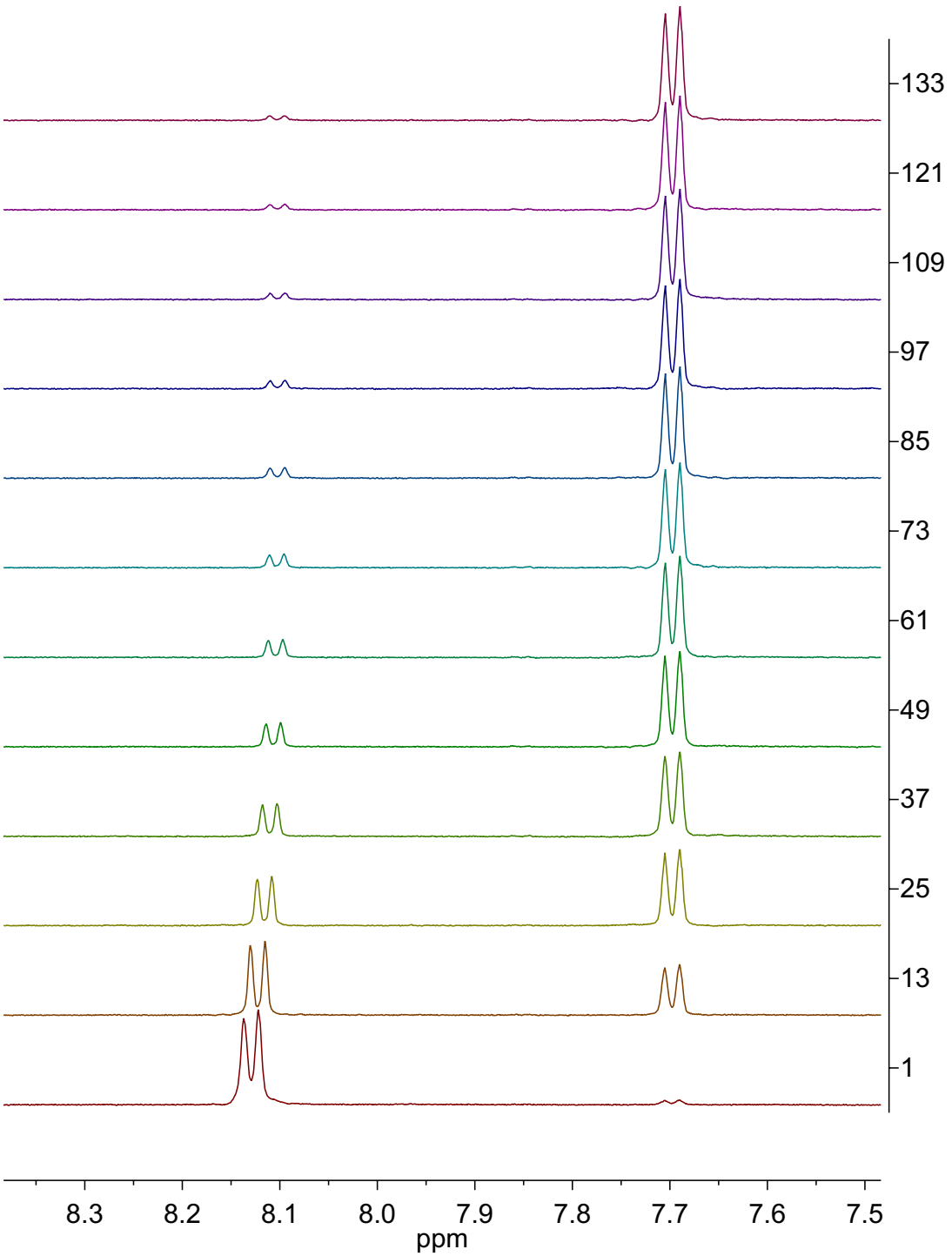

Figure S4. Sample kinetic data for the conversion of **7** to **8** at 25 ºC. Spectra collected every 300 s. Every 12th spectrum shown.

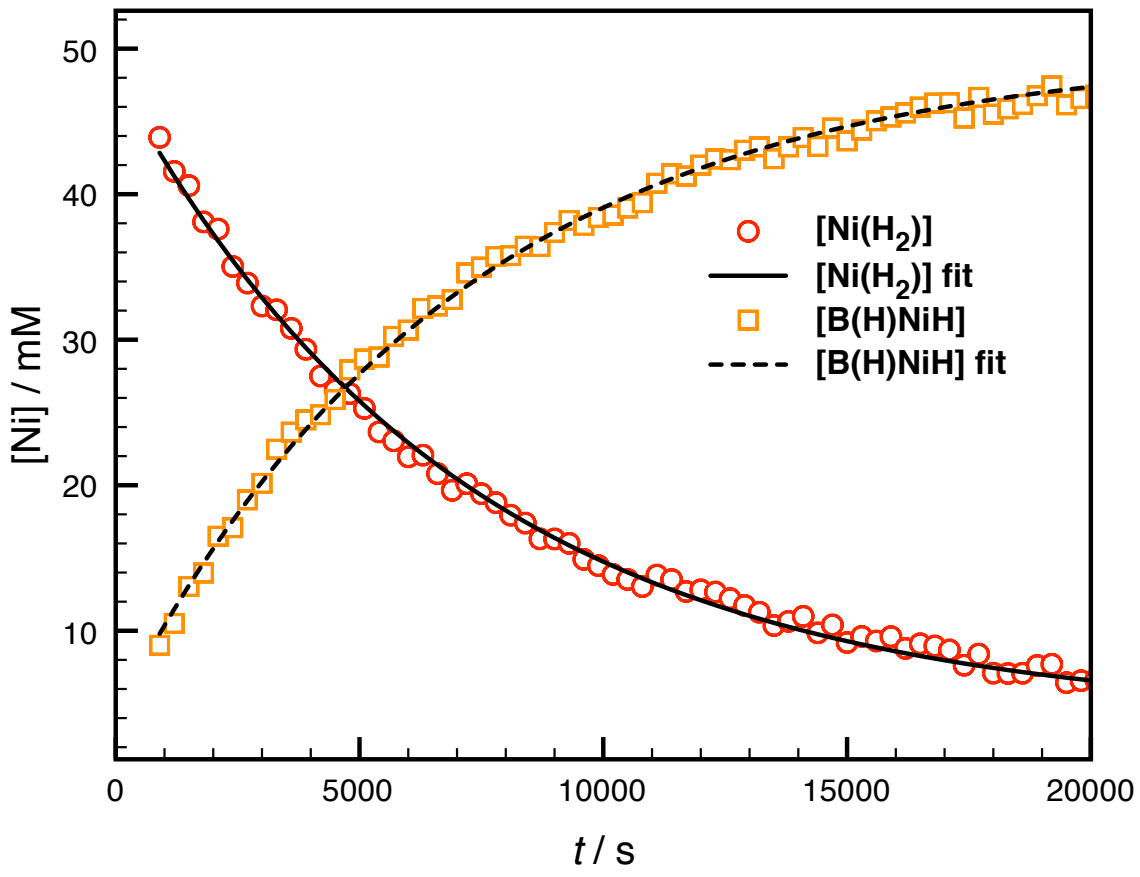

Figure S5. Kinetic data for the conversion of **7** to **8** at 298 K in C_6D_6. Black lines represent three-parameter exponential fits to the data.

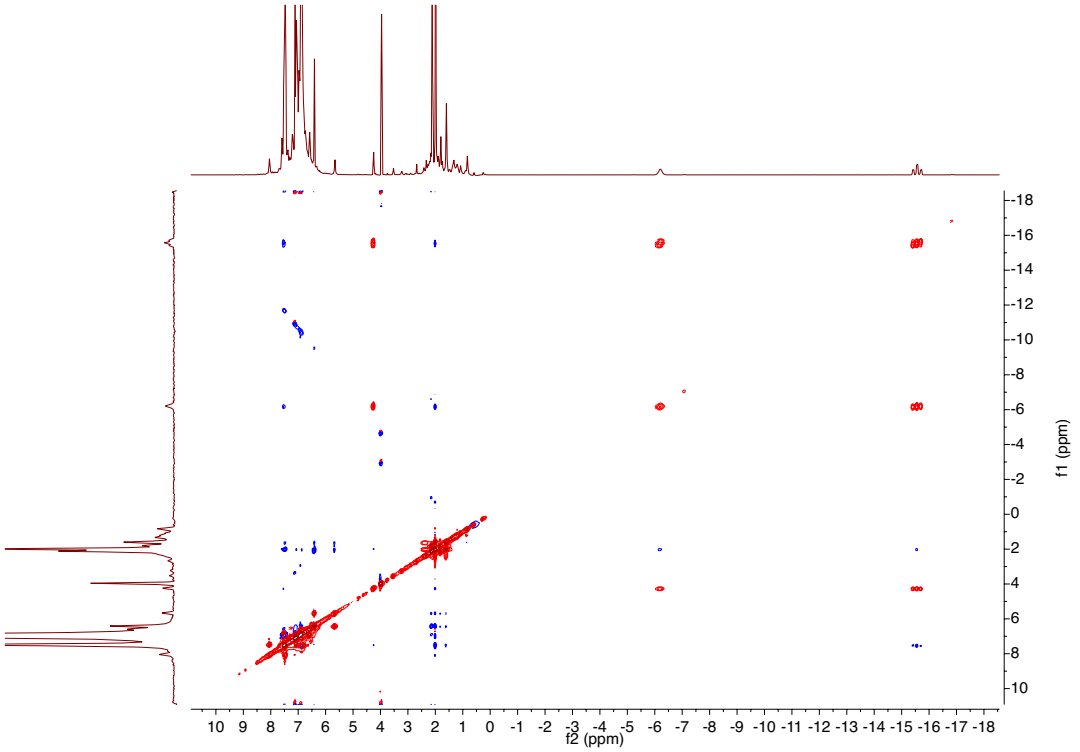

Figure S6. 2D-EXSY spectrum of an equilibrium mixture of **1** and **2** under H_2 in C_6D_6 at 298 K.

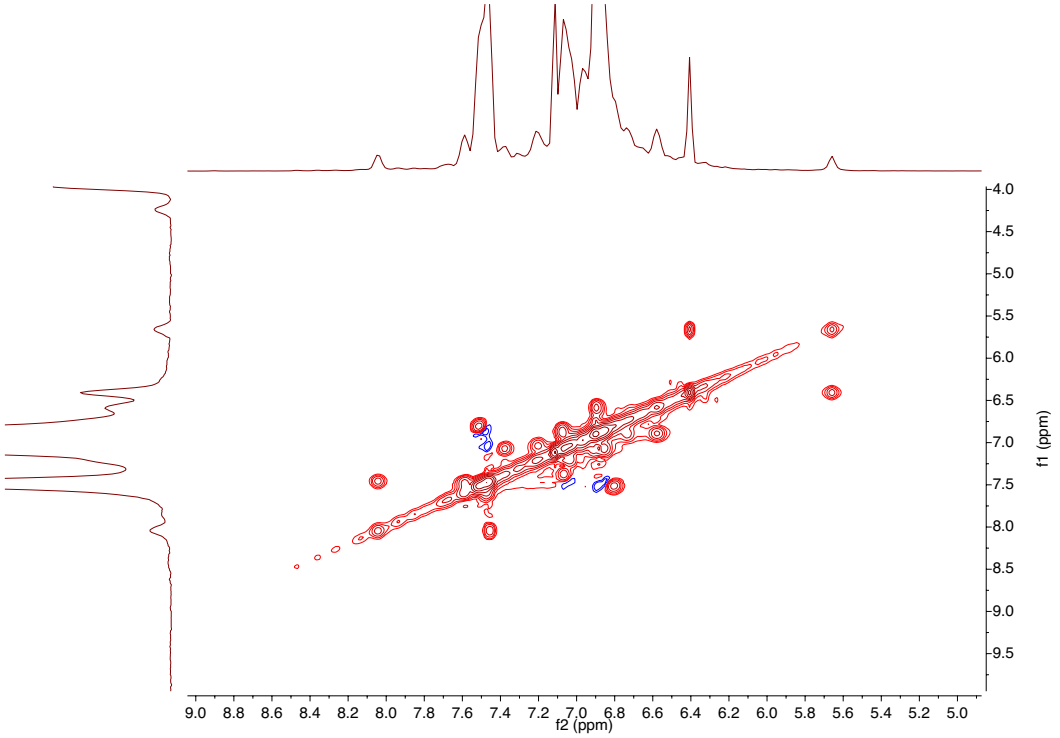

Figure S7. Excerpt of the aromatic region of the 2D-EXSY spectrum of an equilibrium mixture of **1** and **2** under H_2 in C_6D_6 at 298 K.

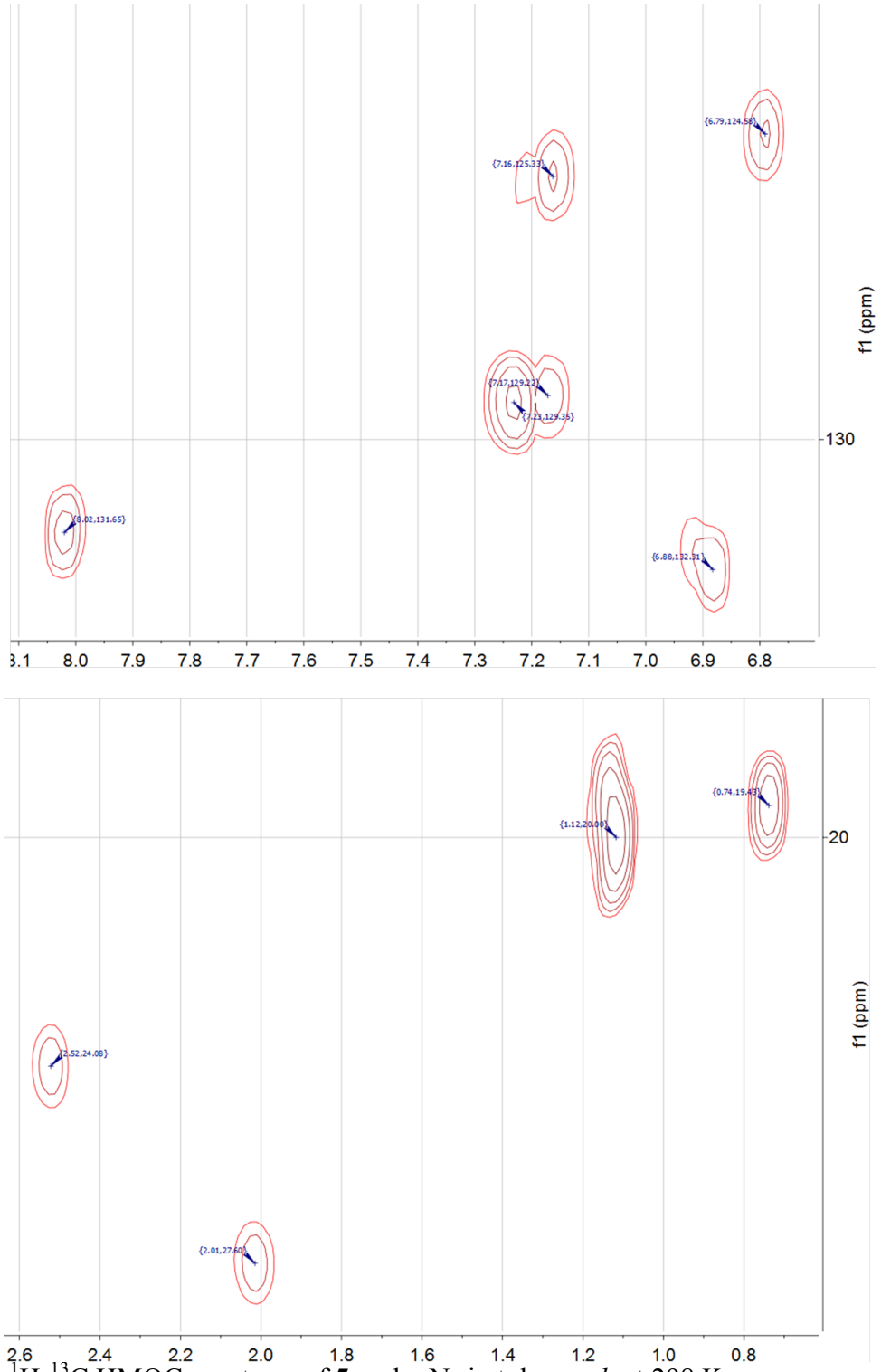

Figure S8. ^{1}H-^{13}C HMQC spectrum of **5** under N_2 in toluene-d_8 at 298 K.

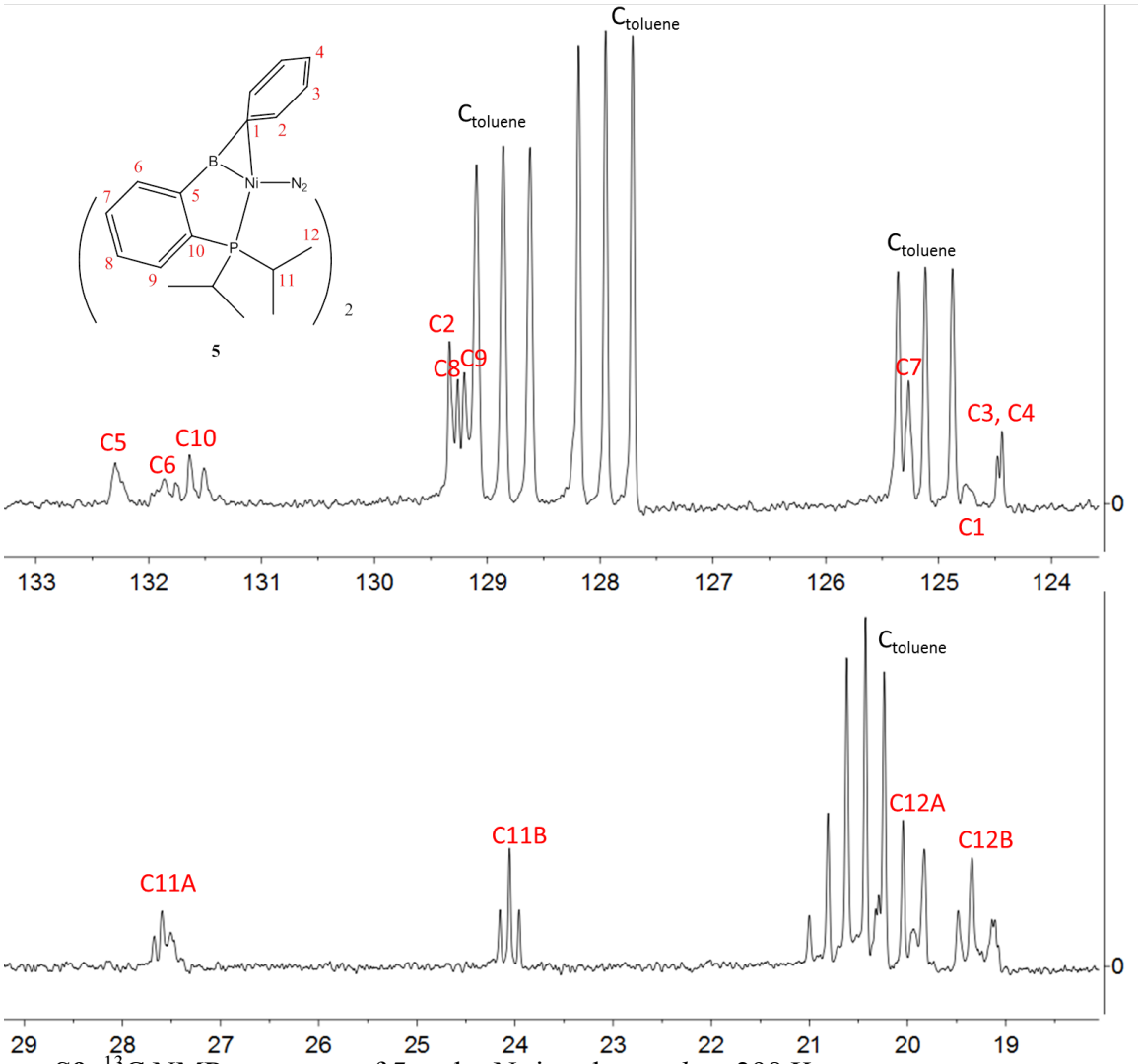

Figure S9. ^{13}C NMR spectrum of **5** under N_2 in toluene-d_8 at 298 K.

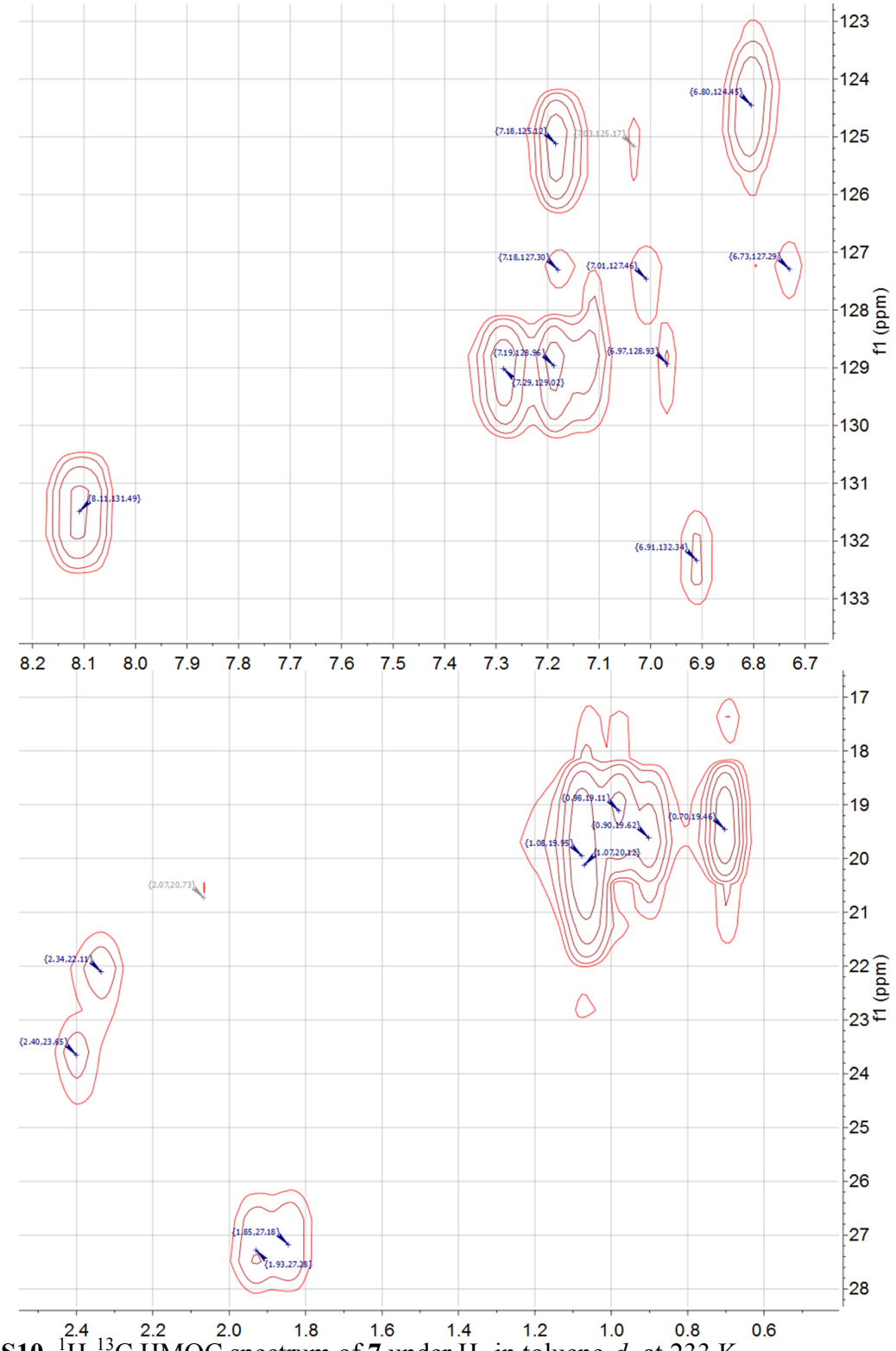

Figure S10. ^{1}H-^{13}C HMQC spectrum of **7** under H_2 in toluene-d_8 at 233 K.

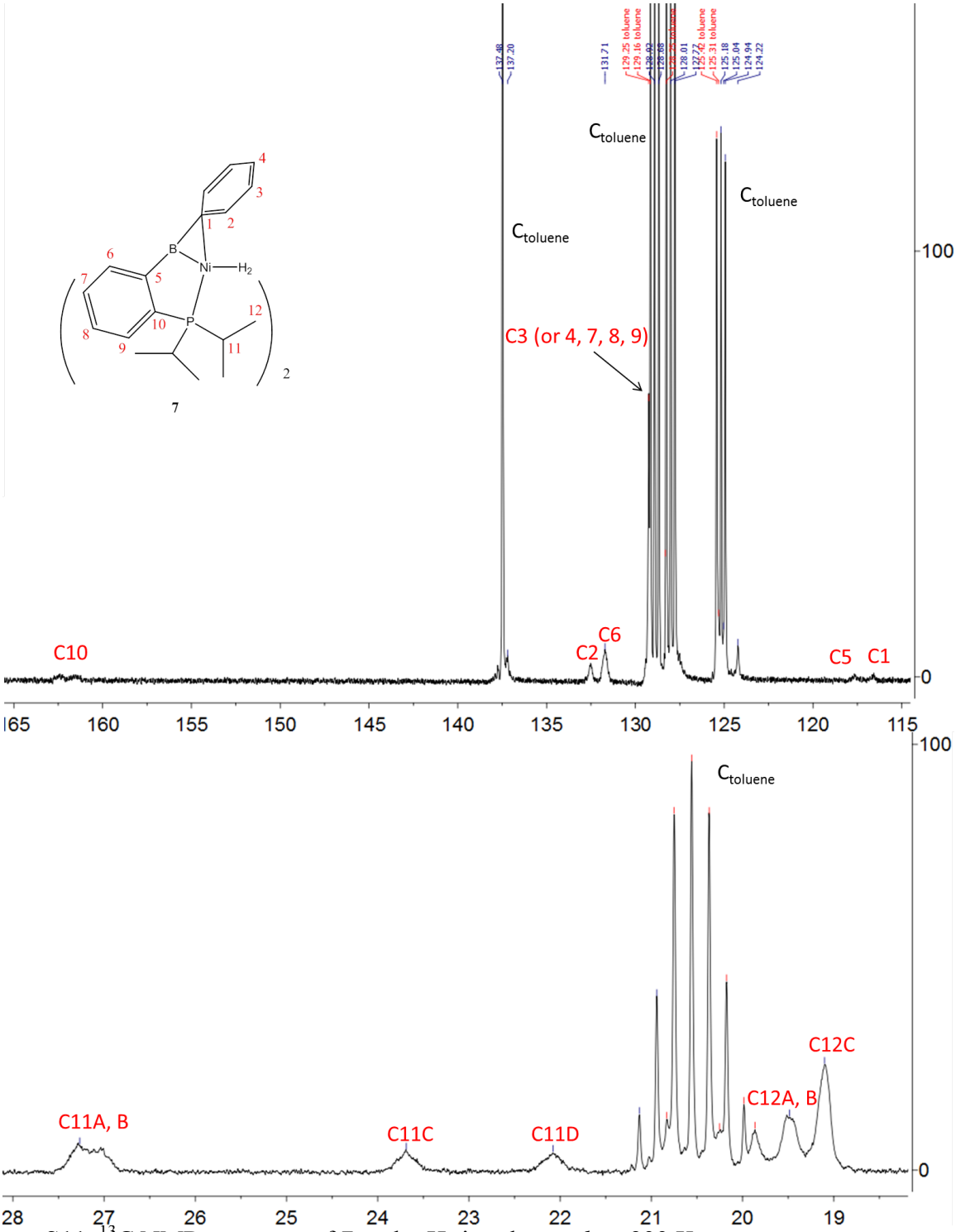

Figure S11. ^{13}C NMR spectrum of **7** under H_2 in toluene-d_8 at 233 K.

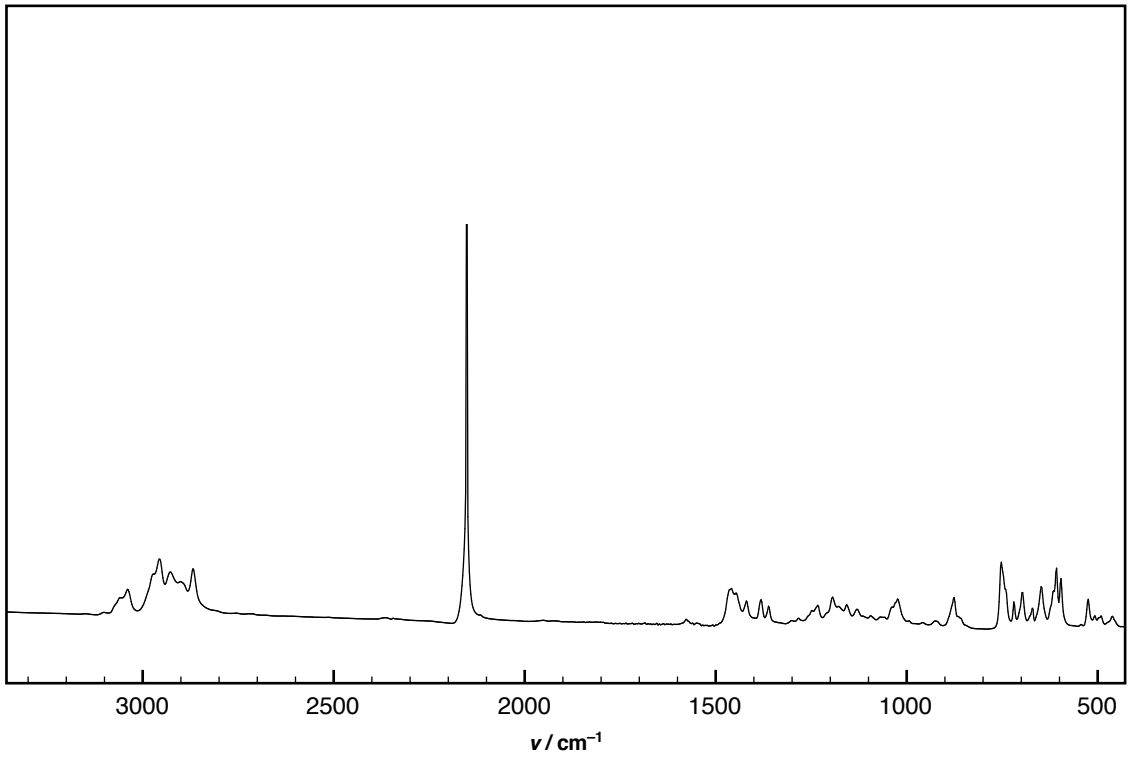

Figure S12. Infrared spectrum of **5** as a KBr pellet.

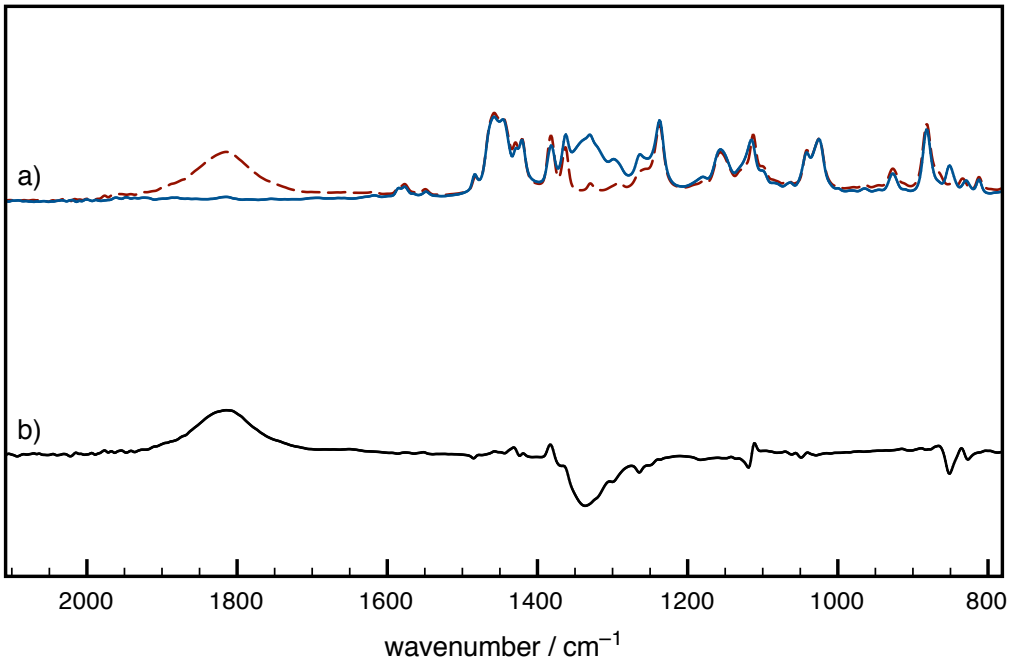

Figure S13. Infrared spectra of (a) **8** (solid blue) and **8**-d_2 (dashed red) as thin films on a diamond ATR plate and (b) the corresponding spectral subtraction.

Table S1. Crystal data and structure refinement for [^{Ph}DPB^{iPr}]NiBr (**4**).

Empirical formula	$C_{30}H_{41}BBrNiP_2$	
Formula weight	613.00	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 12.9449(10) Å	a= 90°
	b = 13.6196(11) Å	b= 90°
	c = 33.276(2) Å	g = 90°
Volume	5866.7(7) Å^3	
Z	8	
Density (calculated)	1.388 Mg/m^3	
Absorption coefficient	2.150 mm^{-1}	
F(000)	2552	
Crystal size	0.38 x 0.31 x 0.24 mm^3	
Theta range for data collection	1.93 to 35.68°.	
Index ranges	-21<=h<=21, -22<=k<=22, -54<=l<=54	
Reflections collected	224981	
Independent reflections	27096 [R_{int} = 0.0527]	
Completeness to theta = 35.68°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6264 and 0.4955	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27096 / 0 / 647	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R_1 = 0.0229, wR_2 = 0.0486	
R indices (all data)	R_1 = 0.0279, wR_2 = 0.0498	
Absolute structure parameter	0.0069(19)	
Largest diff. peak and hole	0.375 and -0.286 e.Å^{-3}	

Table S2. Crystal data and structure refinement for 2 [^{Ph}DPB^{iPr}]Ni(N_2) 0.5 {[^{Ph}DPB^{iPr}]Ni}$_2$(N_2) (**5** and **6**).

Empirical formula	$C_{30}H_{41}BN_{1.67}NiP_2$	
Formula weight	556.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	*P*–1	
Unit cell dimensions	a = 10.8095(9) Å	a= 70.162(2)°
	b = 18.0174(14) Å	b= 81.012(2)°
	c = 24.613(2) Å	g = 74.536(2)°
Volume	4334.4(6) Å^3	
Z	6	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.803 mm^{-1}	
F(000)	1774	
Crystal size	0.30 x 0.15 x 0.13 mm^3	
Theta range for data collection	1.76 to 33.04°.	
Index ranges	-16<=h<=16, -27<=k<=27, -37<=l<=37	
Reflections collected	155107	
Independent reflections	32473 [R_{int} = 0.0580]	
Completeness to theta = 33.04°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9028 and 0.7947	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32473 / 0 / 988	
Goodness-of-fit on F^2	1.013	
Final R indices [I > 2sigma(I)]	R_1 = 0.0437, wR_2 = 0.0968	
R indices (all data)	R_1 = 0.0695, wR_2 = 0.1079	
Largest diff. peak and hole	2.795 and –1.355 e.Å^{-3}	

Computational methods. Electronic structure calculations were performed using the Gaussian03[5] or Gaussian09[6] packages. The relative energies of reasonable isomers of the postulated structure were first compared using the B3LYP or M06L functional as indicated with a 6-31G(d) basis set. After locating an unambiguous global minimum, the resulting structure was further optimized with the 6-31+G* or 6-311++G** basis set, as indicated. Table S3 shows selected metrical parameters for **5** as determined by X-ray diffraction and various computational methods. Overestimation of the Ni–(B,C) distance by B3LYP calculations is a general trend in these systems, hence our use of the M06L functional. Transition state searches were begun from guesses and optimized via the quadratic synchronous transit method. Frequency calculations were performed to confirm the optimization to a true saddle point. Intrinsic reaction coordinate calculations were used to insure that the identified transition state went on to the desired product. In the case of the pathway containing TS2, there is a very shallow minimum approaching the transition state corresponding to rotation of the H_2 ligand. The coordinates for this structure and the transition state preceding it are given in Tables S14 and S15 below. See Figure S9 for a graphical explanation. Preliminary transition state calculations with B3LYP gave energies that were dramatically lower (10–20 kcal/mol) than the corresponding calculations with M06L, consistent with the tendency for B3LYP to underestimate transition state energies. Free energies were computed from frequency calculations. The NBO analysis is performed at the same level of

[5] Gaussian 03, Revision C.02, 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.

[6] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

theory using NBO 3.0 program.[7] The electron density of the optimized structures of complexes **7** and **7'** were subjected to an Atoms-In Molecules[8] analysis using AIM2000.[9]

Table S3. Selected distances [Å] and angles [º] for [^{Ph}DPB^{iPr}]Ni(N_2) (**5**) from X-ray diffraction and DFT calculations, as indicated.

			B3LYP		M06L	
	X-ray		6-31+G*	6-311++G**	6-31+G*	6-311++G**
Ni–B	2.2006(17)	2.1806(19)	2.193	2.199	2.195	2.208
Ni–P1	2.2283(5)	2.1972(5)	2.243	2.249	2.199	2.218
Ni–P2	2.2077(5)	2.2360(5)	2.265	2.271	2.221	2.238
Ni–C_{ipso}	2.1702(16)	2.1492(16)	2.282	2.297	2.164	2.174
Ni–C_{ortho}	2.4842(16)	2.6595(17)	2.779	2.782	2.567	2.543
Ni–N	1.8612(14)	1.8510(15)	1.854	1.871	1.843	1.861
Σ(∠C–B–C)	352.6º	352.5º	351.0º	350.7º	352.5º	352.7º
N–N	1.102(2)	1.101(2)	1.120	1.111	1.129	1.121

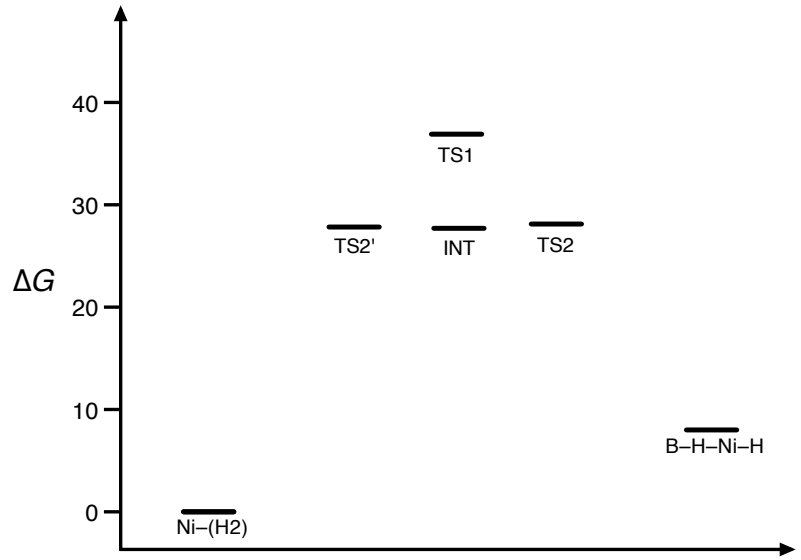

Figure S14. Energy diagram for H_2 cleavage by [^{Ph}DPB^{Me}]Ni.

[7] Weinhold, F.; Landis, C. R. *Valency and Bonding*; Cambridge University Press, 2005.
[8] R. F. W. Bader *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1994.
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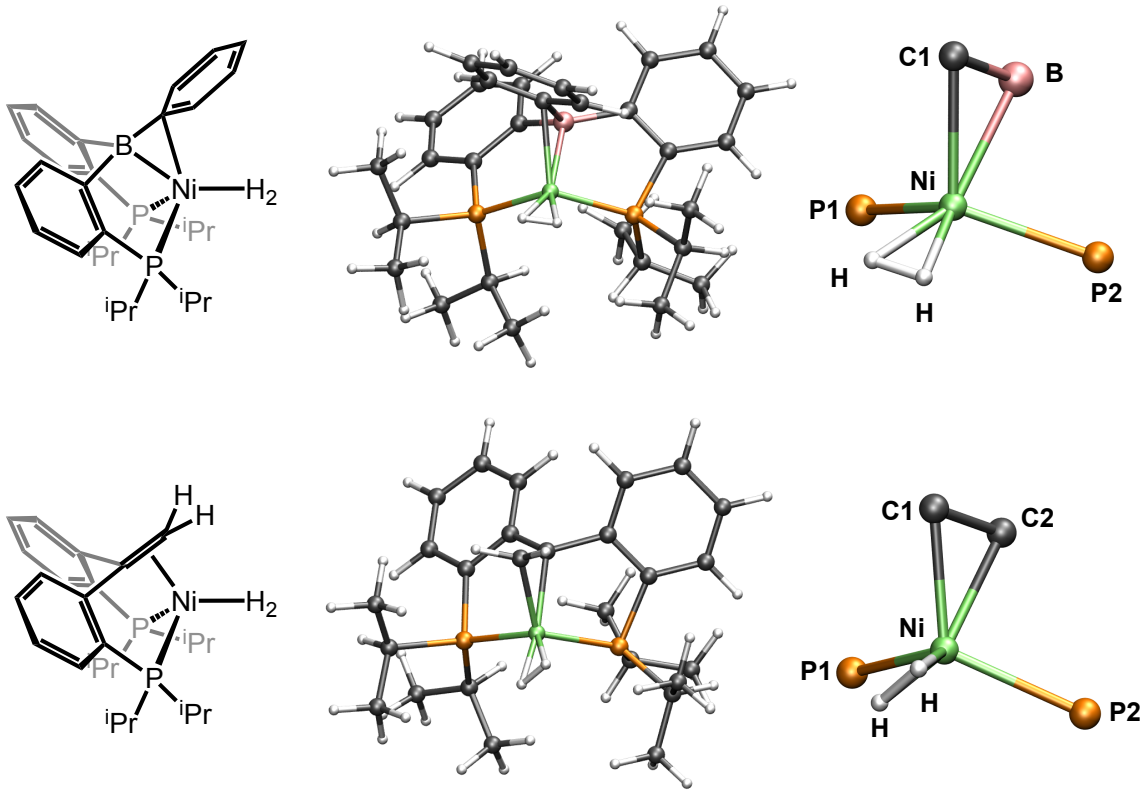

Figure S15. Comparison of the calculated structures (M06L/6-31+G*) of **7** (top) and an analogous hypothetical alkene complex **7'** (bottom) showing the homology between the B–Ph donor and an alkene donor.

Table S4. Selected distances [Å] and angles [º] calculated for **7** and **7'** (M06L/6-31+G*).

	7	**7'**
Ni–B	2.193	—
Ni–C1	2.168	2.012
Ni–C2	—	2.009
Ni–P1	2.194	2.192
Ni–P2	2.178	2.185
∠P–Ni–P	119.6º	116.0º
H–H	0.829	0.834

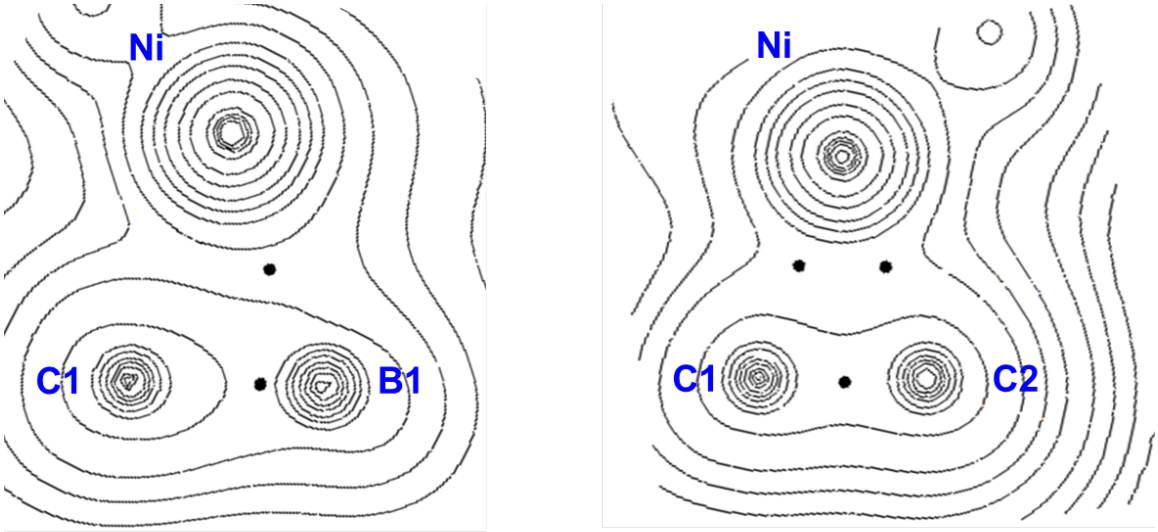

Figure S16. Calculated electron density contour plots for **7** (left) and **7'** (right) with (3, -1) bond critical points. The maps are drawn in the plane containing Ni, B1, and C1 for **7** and Ni, C1, and C2 for **7'**.

Table S5. Bond critical points associated with the Ni-B and Ni-C interactions in complexes **7** and **7'**.

	Critical Point	**7**	**7'**
Ni–B1 (or C2)	dNi (Å)	1.160	0.992
	dB1 (or dC1) (Å)	1.041	1.017
	$\rho(r)$ (e bohr^{-3})	0.067	0.099
	$L = -1/4\ \nabla^2 \rho(r)$	-0.011	-0.042
Ni–C1	dNi (Å)	-[a]	0.997
	dC (Å)		1.015
	$\rho(r)$ (e bohr^{-3})		0.097
	$L = -1/4\ \nabla^2 \rho(r)$		-0.047
B1 (or C2)–C1	dB1 (or C1) (Å)	0.516	0.725
	dC2 (Å)	1.065	0.696
	$\rho(r)$ (e bohr^{-3})	0.167	0.287
	$L = -1/4\ \nabla^2 \rho(r)$	0.005	0.170

[a]A bond critical point could not be found.

Table S6. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(N_2) (**5**) (B3LYP/6-31+G*).

C	2.66800000	0.61200000	-0.65900000
C	-0.03500000	1.72500000	1.31700000
C	-1.27000000	2.22400000	1.80800000

H	-2.08700000	2.36800000	1.10900000
C	1.74000000	1.67300000	-0.68900000
C	-0.99400000	1.66900000	-1.26400000
C	1.01100000	1.61400000	2.27300000
H	1.99900000	1.31400000	1.94300000
C	-0.98900000	2.77400000	-2.14200000
H	-0.11400000	3.41300000	-2.19100000
C	-2.15100000	0.84700000	-1.28600000
C	-3.23500000	2.30100000	-2.91000000
H	-4.09700000	2.54700000	-3.52500000
C	-1.45500000	2.57500000	3.14200000
H	-2.41200000	2.97400000	3.47100000
C	-3.26100000	1.18000000	-2.08000000
H	-4.15700000	0.56400000	-2.05700000
C	-3.77200000	-0.83000000	0.53600000
H	-4.47900000	-0.94300000	-0.29700000
C	3.17200000	-1.96200000	0.74000000
H	4.06300000	-2.03700000	0.10400000
C	-2.01000000	-2.09800000	-1.50700000
H	-1.23600000	-1.75100000	-2.20000000
C	-0.40800000	2.41700000	4.06200000
H	-0.55300000	2.68400000	5.10600000
C	0.82500000	1.93600000	3.62200000
H	1.65000000	1.82700000	4.32200000
C	2.24200000	2.95000000	-1.01400000
H	1.58000000	3.81300000	-0.99800000
C	1.81700000	-1.88600000	-1.90400000
H	1.10500000	-2.70600000	-1.75000000
C	-2.08300000	3.09000000	-2.95100000
H	-2.03800000	3.95700000	-3.60600000
C	4.02700000	0.81100000	-0.95000000
H	4.73000000	-0.01800000	-0.90800000
C	-1.51000000	-3.41700000	-0.88500000
H	-2.28600000	-3.90900000	-0.28800000
H	-0.64200000	-3.26100000	-0.23700000
H	-1.22500000	-4.11800000	-1.68000000
C	3.59100000	3.15500000	-1.31100000
H	3.94700000	4.15600000	-1.54800000
C	1.26200000	-0.95700000	-2.99900000
H	2.01000000	-0.21200000	-3.29000000
H	0.36800000	-0.41100000	-2.68800000
H	1.01100000	-1.54600000	-3.89200000
C	-4.18500000	0.41700000	1.33300000
H	-5.21100000	0.28800000	1.70300000
H	-4.16400000	1.32500000	0.72300000
H	-3.53400000	0.57000000	2.19900000

C	-3.28600000	-2.34300000	-2.32600000
H	-3.09300000	-3.11700000	-3.08100000
H	-3.62000000	-1.44700000	-2.85700000
H	-4.11300000	-2.70400000	-1.70200000
C	3.14900000	-2.48800000	-2.38400000
H	3.00200000	-2.95400000	-3.36800000
H	3.54100000	-3.26100000	-1.71500000
H	3.91700000	-1.71500000	-2.50500000
C	4.49100000	2.08400000	-1.28200000
H	5.54300000	2.24300000	-1.50400000
C	2.67000000	-3.38500000	1.04300000
H	3.45500000	-3.95800000	1.55200000
H	2.39300000	-3.93800000	0.13800000
H	1.79600000	-3.36400000	1.70200000
C	3.57300000	-1.24300000	2.03700000
H	2.71700000	-1.12600000	2.71000000
H	3.99000000	-0.24900000	1.84300000
H	4.33700000	-1.82900000	2.56500000
C	-3.88200000	-2.07700000	1.43100000
H	-3.15200000	-2.04800000	2.24700000
H	-3.73500000	-3.01000000	0.88000000
H	-4.88200000	-2.12000000	1.88300000
Ni	-0.05200000	-0.50200000	0.81800000
P	-2.04700000	-0.67100000	-0.24300000
P	1.87500000	-0.98300000	-0.22300000
N	-0.19600000	-1.49200000	2.37900000
N	-0.31900000	-2.03300000	3.35200000
B	0.21400000	1.40700000	-0.22800000

Total Energy (a.u.): -3493.29464398

Table S7. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(N_2) (**5**) (B3LYP/6-311++G**).

C	2.66353600	0.61611600	-0.67085400
C	-0.03928100	1.73627900	1.29751900
C	-1.26811000	2.25018400	1.78152800
H	-2.08345400	2.39149400	1.08380200
C	1.72701100	1.66614600	-0.70969200
C	-1.00641000	1.64868000	-1.27526400
C	1.00519500	1.63066000	2.25036300
H	1.99018800	1.32558400	1.92329500
C	-1.00442000	2.74384500	-2.16078000
H	-0.12935900	3.37845200	-2.22350100
C	-2.16372800	0.83283900	-1.28093400
C	-3.25308600	2.27335500	-2.90287700
H	-4.11725400	2.51843200	-3.51074800

C	-1.44672800	2.61692500	3.10863200
H	-2.39715800	3.02741800	3.43378600
C	-3.27667500	1.16118500	-2.06711400
H	-4.17120200	0.54979900	-2.03339100
C	-3.76642900	-0.83749200	0.56228500
H	-4.47703400	-0.94539700	-0.26396400
C	3.19700100	-1.93827400	0.74736000
H	4.08339400	-2.00287500	0.10875300
C	-2.03099700	-2.10795100	-1.49716300
H	-1.26673800	-1.75905100	-2.19575900
C	-0.40337500	2.46211100	4.02682500
H	-0.54395800	2.74234300	5.06529000
C	0.82237800	1.96823400	3.59262200
H	1.64554500	1.86437900	4.29168600
C	2.21566400	2.94222300	-1.04589000
H	1.54794200	3.79690700	-1.03635600
C	1.83621300	-1.90161900	-1.88844700
H	1.14413800	-2.73076300	-1.71409500
C	-2.10111700	3.05597100	-2.95971800
H	-2.06046600	3.91568900	-3.62061800
C	4.01719800	0.82518200	-0.96477600
H	4.72653200	0.00588900	-0.91724800
C	-1.52429400	-3.42396100	-0.88111700
H	-2.28535300	-3.90814600	-0.26550800
H	-0.64253000	-3.26794200	-0.25735700
H	-1.26105300	-4.12809600	-1.67776200
C	3.55918400	3.15608800	-1.34499300
H	3.90475100	4.15499800	-1.59063300
C	1.25002700	-0.99670300	-2.98437600
H	1.97428600	-0.23587200	-3.28442200
H	0.34676900	-0.47460500	-2.66918700
H	1.00854000	-1.59562000	-3.86862200
C	-4.16425900	0.40788600	1.36492500
H	-5.18219900	0.28127300	1.74877900
H	-4.14975300	1.31383700	0.75686900
H	-3.50210900	0.55848700	2.21976100
C	-3.31670600	-2.34804800	-2.29998700
H	-3.13748300	-3.12700300	-3.04925300
H	-3.64619800	-1.45596800	-2.83414400
H	-4.13741200	-2.69640100	-1.66700100
C	3.17489100	-2.48112100	-2.37126700
H	3.02710400	-2.96999000	-3.34032500
H	3.59203700	-3.22689300	-1.69314500
H	3.91955500	-1.69442000	-2.51955200
C	4.46667700	2.09666200	-1.30777700
H	5.51459600	2.26375500	-1.53190600

C	2.71496500	-3.36523500	1.05463500
H	3.50198100	-3.92154300	1.57393200
H	2.45649400	-3.92628200	0.15354000
H	1.83712400	-3.35417500	1.70467400
C	3.59175400	-1.20743100	2.03808700
H	2.73805600	-1.09761100	2.71071200
H	3.99677000	-0.21342000	1.83751900
H	4.36095600	-1.78004700	2.56684900
C	-3.87027700	-2.08714100	1.45131100
H	-3.12985700	-2.06604700	2.25488100
H	-3.73732000	-3.01518100	0.89464000
H	-4.86051600	-2.12552200	1.91695400
Ni	-0.04893700	-0.51066800	0.82078900
P	-2.05248200	-0.68152600	-0.23452900
P	1.88888900	-0.98268900	-0.21935800
N	-0.18262100	-1.49217000	2.40780200
N	-0.27938100	-2.00317400	3.38931300
B	0.20499700	1.39718000	-0.24264300

Total Energy (a.u.): -3493.75798897

Table S8. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(N_2) (**5**) (M06L/6-31+G*).

C	2.68086700	0.80585200	-0.05883900
C	0.00343500	0.43069500	2.07830300
C	-1.23481800	0.43527100	2.76728000
H	-2.03509600	1.07011500	2.38495600
C	1.79405900	1.69900900	0.57277100
C	-0.91836900	2.14523500	0.16153500
C	1.02208900	-0.39214700	2.62787400
H	2.01783100	-0.36411400	2.18600600
C	-0.89051100	3.55040500	0.21025400
H	0.00177200	4.05506700	0.58018600
C	-2.08555100	1.55172400	-0.37632000
C	-3.14209100	3.71614900	-0.64941400
H	-4.00088200	4.31731500	-0.94494800
C	-1.44621700	-0.31990600	3.91099100
H	-2.40913000	-0.27841500	4.42032800
C	-3.18950600	2.32885300	-0.74863700
H	-4.09633600	1.85054600	-1.12248700
C	-3.71910900	-0.84714100	-0.15841600
H	-4.40691100	-0.29628800	-0.82125600
C	2.97795200	-2.02381000	-0.79086900
H	3.89479800	-1.69409200	-1.30499700
C	-1.90218400	-0.52376800	-2.43774800
H	-1.12329800	0.19507500	-2.73101700

C	-0.42775500	-1.14592100	4.40444700
H	-0.59869400	-1.74996800	5.29475700
C	0.80433100	-1.17997000	3.76250300
H	1.60599800	-1.81201500	4.14446800
C	2.35152100	2.86533300	1.12137000
H	1.71713700	3.56926900	1.66178100
C	1.71543400	-0.08438500	-2.59425000
H	0.97891300	-0.75784400	-3.05856800
C	-1.97731900	4.32609300	-0.18484800
H	-1.92053300	5.41247000	-0.12076800
C	4.05559100	1.05146900	-0.13234400
H	4.72219400	0.33034700	-0.60977200
C	-1.39147700	-1.92184200	-2.78640100
H	-2.16275300	-2.68951500	-2.65287000
H	-0.53381400	-2.20894300	-2.16291500
H	-1.07795300	-1.96272000	-3.83899200
C	3.71880100	3.12541100	1.04182400
H	4.12345000	4.03318400	1.48878100
C	1.21296800	1.35279500	-2.71222200
H	1.99314700	2.06225800	-2.40721700
H	0.33793100	1.55529500	-2.08263100
H	0.94386200	1.57857400	-3.75270900
C	-4.08460700	-0.52507800	1.28402200
H	-5.11740400	-0.83732700	1.48882200
H	-4.01069000	0.54714900	1.50208000
H	-3.42864800	-1.05801100	1.98426900
C	-3.16499600	-0.18518700	-3.21817400
H	-2.97558400	-0.26152600	-4.29750400
H	-3.51515700	0.83462200	-3.02056500
H	-3.98568700	-0.87770400	-2.98892100
C	3.04115000	-0.22585500	-3.33347500
H	2.93961900	0.15664200	-4.35806700
H	3.38869100	-1.26263500	-3.40545800
H	3.82950700	0.36567200	-2.84791900
C	4.57746600	2.21846500	0.41937500
H	5.64724400	2.41756800	0.37281600
C	2.37459200	-3.19551000	-1.55845700
H	3.07730200	-4.03786900	-1.59987200
H	2.11142700	-2.93289400	-2.59174400
H	1.46055200	-3.55485600	-1.06762300
C	3.33844800	-2.42207300	0.63525200
H	2.44562000	-2.72122600	1.20082500
H	3.81740500	-1.59923400	1.18131800
H	4.03321900	-3.27230500	0.63377600
C	-3.88809600	-2.33966700	-0.42370900
H	-3.13275400	-2.93116900	0.10959900

H	-3.81995900	-2.59137900	-1.48724900
H	-4.87311200	-2.67587900	-0.07378800
Ni	-0.07383100	-0.87900400	0.35774100
P	-1.99077000	-0.25898700	-0.57675700
P	1.78485200	-0.59450100	-0.78180500
N	-0.29132100	-2.64422400	0.84063200
N	-0.46261700	-3.69855200	1.20621800
B	0.26675600	1.25352700	0.74935400

Total Energy (a.u.): -3493.02357691

Table S9. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(N_2) (**5**) (M06L/6-311++G**).

C	2.67908300	0.81851100	-0.04430800
C	-0.01316900	0.43002600	2.08133800
C	-1.24719500	0.44016700	2.77541600
H	-2.03987700	1.08555200	2.40611300
C	1.78252700	1.69858000	0.58762000
C	-0.92797300	2.13912100	0.16100400
C	0.99926500	-0.40944100	2.61370200
H	1.99253400	-0.37785900	2.17637900
C	-0.89752600	3.54292100	0.20568800
H	-0.00605400	4.04576700	0.56806500
C	-2.09609200	1.54679700	-0.37121200
C	-3.15014400	3.70857300	-0.64011800
H	-4.00692000	4.30869100	-0.93018200
C	-1.45816500	-0.32319900	3.91019300
H	-2.41299900	-0.27623000	4.42624200
C	-3.19967400	2.32374100	-0.73842000
H	-4.10575300	1.84879200	-1.10599000
C	-3.72783400	-0.85852600	-0.16655100
H	-4.41124400	-0.30395000	-0.82464800
C	3.01200700	-2.00408300	-0.79748700
H	3.92295900	-1.65838100	-1.30370600
C	-1.90896500	-0.51257700	-2.44572800
H	-1.13246000	0.20952400	-2.72365000
C	-0.44773600	-1.16596100	4.38718200
H	-0.61940900	-1.77434300	5.26995800
C	0.77733100	-1.20708600	3.73946200
H	1.57102300	-1.84903200	4.11106200
C	2.32751000	2.86167500	1.15182700
H	1.68700500	3.55297600	1.69349500
C	1.73999600	-0.06159700	-2.59556300
H	1.01311400	-0.73882800	-3.06094300
C	-1.98394500	4.31696300	-0.18478800
H	-1.92656700	5.39991400	-0.12378300

C	4.05099900	1.07462000	-0.10405900
H	4.72468300	0.36554700	-0.57998000
C	-1.39197500	-1.90554200	-2.80473900
H	-2.15516000	-2.67610300	-2.67131700
H	-0.53131800	-2.18878000	-2.19087600
H	-1.08672500	-1.93893600	-3.85636200
C	3.69097600	3.13118700	1.08520900
H	4.08524700	4.03395300	1.54280000
C	1.22086400	1.37047200	-2.70189500
H	1.98969000	2.08444700	-2.39076800
H	0.34566700	1.55477200	-2.07398600
H	0.95217200	1.60235300	-3.73741500
C	-4.09100400	-0.54615100	1.27832500
H	-5.11848700	-0.86336000	1.48378600
H	-4.02247600	0.52158700	1.50097200
H	-3.43332700	-1.07792600	1.97213500
C	-3.16987100	-0.16852200	-3.22666200
H	-2.97782900	-0.23564100	-4.30271900
H	-3.52038600	0.84579100	-3.02339500
H	-3.98759800	-0.86187900	-3.00734500
C	3.06931100	-0.18492500	-3.33121700
H	2.96789700	0.20366200	-4.34990000
H	3.42503600	-1.21418600	-3.41108700
H	3.84800100	0.40836900	-2.84070400
C	4.55900500	2.23803800	0.46152200
H	5.62408100	2.44456400	0.42574700
C	2.42474300	-3.17619900	-1.57667700
H	3.13129900	-4.01094200	-1.61476800
H	2.17188200	-2.91124400	-2.60766100
H	1.51120300	-3.54332100	-1.09845500
C	3.36842100	-2.40696800	0.62813500
H	2.47823900	-2.71657700	1.18529200
H	3.83666000	-1.58645700	1.17936500
H	4.06830900	-3.24849200	0.62584500
C	-3.89294800	-2.34897400	-0.44496600
H	-3.13514500	-2.94080900	0.07743500
H	-3.83034700	-2.58950700	-1.50738700
H	-4.87125900	-2.69144200	-0.09326100
Ni	-0.07066000	-0.89394500	0.35851200
P	-2.00120500	-0.26355200	-0.58206200
P	1.80397700	-0.58626400	-0.78686300
N	-0.28061500	-2.68173200	0.82878700
N	-0.42553000	-3.73251800	1.19214600
B	0.25552600	1.25311200	0.75624800

Total Energy (a.u.): -3493.49816431

Table S10. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(H_2) (**7**) (M06L/6-31+G*).

C	2.64544300	-0.42084100	0.60053700
C	-0.06897900	-1.93406500	-0.94039400
C	-1.29796600	-2.53906000	-1.30501400
H	-2.08209400	-2.61228000	-0.54971100
C	1.73280000	-1.43064800	0.96276400
C	-0.97970100	-1.26827300	1.54066300
C	0.93061600	-1.88444300	-1.94769200
H	1.93214600	-1.54593800	-1.68308700
C	-0.98942300	-2.08413800	2.68575300
H	-0.11653100	-2.69634900	2.91308500
C	-2.12091600	-0.45861700	1.32607000
C	-3.22901600	-1.39144400	3.26968100
H	-4.09836800	-1.45109400	3.92317600
C	-1.51967700	-3.05065300	-2.57341900
H	-2.47209300	-3.52569300	-2.80995900
C	-3.23804000	-0.54340700	2.16595400
H	-4.12609600	0.05680700	1.96096000
C	-3.68678700	0.70684500	-0.83118200
H	-4.38429200	0.99857100	-0.02892300
C	3.03835700	1.76389100	-1.32013700
H	3.94277200	1.99172700	-0.73470400
C	-1.88510300	2.40364500	0.73513900
H	-1.13523000	2.23852200	1.52250000
C	-0.52611800	-2.94579000	-3.55752100
H	-0.70597900	-3.33681300	-4.55841400
C	0.69425700	-2.36248900	-3.24383900
H	1.48120900	-2.29700900	-3.99567700
C	2.25638000	-2.55176700	1.62729400
H	1.59928200	-3.38174000	1.89136100
C	1.72855000	2.20646300	1.26391200
H	1.01425200	2.98319800	0.94989700
C	-2.08947000	-2.14949600	3.53725900
H	-2.06303600	-2.80268400	4.40922100
C	4.01268400	-0.52407200	0.87619700
H	4.70113800	0.26507700	0.56659100
C	-1.32251400	3.45534000	-0.22050800
H	-2.06562000	3.78284500	-0.95751000
H	-0.45415000	3.07449100	-0.77570500
H	-1.00797800	4.34977100	0.33556500
C	3.61601700	-2.65844000	1.91573600
H	3.99417400	-3.54692300	2.42101300
C	1.18264700	1.51287700	2.50982100
H	1.93478800	0.83860600	2.93972700

H	0.29227600	0.90546900	2.30659000
H	0.92154900	2.25474500	3.27638100
C	-4.08275900	-0.67577500	-1.32996400
H	-5.11139500	-0.65716200	-1.71469200
H	-4.03547200	-1.43223800	-0.53748100
H	-3.42549900	-1.00288800	-2.14518400
C	-3.16207700	2.89598600	1.40226500
H	-2.97131500	3.83435500	1.94071300
H	-3.55624500	2.17777700	2.13043400
H	-3.95184800	3.10515600	0.66830400
C	3.06114800	2.87111100	1.58909800
H	2.95450300	3.50652100	2.47873700
H	3.43756000	3.50628300	0.77915400
H	3.83086400	2.12225700	1.82151800
C	4.50088000	-1.64764500	1.53817100
H	5.56494300	-1.74026400	1.75165700
C	2.47325300	3.06166800	-1.88587100
H	3.19720200	3.54842200	-2.55232000
H	2.20368900	3.78349400	-1.10336100
H	1.56582700	2.86278800	-2.47451000
C	3.41368700	0.79763400	-2.43603700
H	2.52976200	0.52009700	-3.02828200
H	3.85581700	-0.12847800	-2.04710800
H	4.14124300	1.25756200	-3.11783900
C	-3.79634600	1.72642800	-1.95914600
H	-3.01704200	1.56481400	-2.71767800
H	-3.70915100	2.76005300	-1.60711200
H	-4.76740400	1.63480500	-2.46357700
Ni	-0.05758900	0.23203600	-1.03431800
P	-1.97264600	0.70387300	-0.07424400
P	1.79460100	0.98522800	-0.17079400
B	0.21203200	-1.29699800	0.48072200
H	-0.58949600	0.71825400	-2.55754300
H	0.22338300	0.88160500	-2.56687900

Total Energy (a.u.): -3384.65743889

Table S11. Optimized coordinates (Å) for [^{Ph}DPB^{iPr}]Ni(H_2) (**7**) (M06L/6-311++G**).

C	2.64521200	-0.42285000	0.60726700
C	-0.07713000	-1.94691700	-0.91381200
C	-1.30164000	-2.56463700	-1.26699500
H	-2.08077700	-2.63466000	-0.51190100
C	1.72421400	-1.41961800	0.97626900
C	-0.98829700	-1.24201200	1.55157100

C	0.91999500	-1.90305800	-1.92211300
H	1.91758700	-1.56080600	-1.66385300
C	-0.99627500	-2.04249600	2.70570700
H	-0.12301700	-2.64229800	2.94472700
C	-2.13288500	-0.44431100	1.32348300
C	-3.24209900	-1.36478200	3.26718900
H	-4.11152900	-1.42570600	3.91435400
C	-1.51957500	-3.09511900	-2.52524100
H	-2.46423200	-3.58104600	-2.75335300
C	-3.25274200	-0.52969700	2.15674000
H	-4.14161400	0.05814300	1.94211300
C	-3.69045700	0.70962600	-0.85202700
H	-4.38909000	0.99331100	-0.05286300
C	3.06821600	1.74547100	-1.32728900
H	3.96456300	1.96856500	-0.73451600
C	-1.89531800	2.41350600	0.72243800
H	-1.14656000	2.24502500	1.50514400
C	-0.53031700	-2.99546500	-3.51149300
H	-0.70824100	-3.40086900	-4.50299900
C	0.68349600	-2.39971600	-3.20945400
H	1.46500400	-2.33998600	-3.96206200
C	2.23685600	-2.53986900	1.64780200
H	1.57542800	-3.36029800	1.91464000
C	1.74713400	2.21717700	1.24947000
H	1.03969700	2.98939700	0.92246400
C	-2.09879300	-2.10685200	3.54996800
H	-2.07225500	-2.74706600	4.42709400
C	4.00981500	-0.53740000	0.88378200
H	4.70417900	0.23842900	0.56872000
C	-1.33238900	3.46399500	-0.23438300
H	-2.07284200	3.78977600	-0.96917200
H	-0.46680500	3.08521400	-0.78699700
H	-1.02077400	4.35651500	0.31941100
C	3.59274900	-2.65625500	1.93732400
H	3.96181600	-3.54165000	2.44702800
C	1.18985400	1.53368400	2.49585900
H	1.93593100	0.86540500	2.93689900
H	0.30460900	0.92727900	2.28931500
H	0.92352500	2.27884800	3.25231400
C	-4.07283300	-0.67372400	-1.35851100
H	-5.09367500	-0.66006700	-1.75415000
H	-4.03128900	-1.42926600	-0.57011300
H	-3.40693800	-0.99419400	-2.16456900
C	-3.17195700	2.90395700	1.39166200
H	-2.98285100	3.84207400	1.92422000
H	-3.55986500	2.19041400	2.12180300

H	-3.96185700	3.10834000	0.66209000
C	3.08109100	2.87831100	1.57601200
H	2.97288700	3.51864200	2.45772700
H	3.46261600	3.50454300	0.76683700
H	3.84387000	2.13087400	1.81801000
C	4.48554500	-1.65821700	1.55394000
H	5.54492300	-1.75947100	1.76816200
C	2.51877900	3.04350800	-1.90739500
H	3.24858500	3.51472200	-2.57289700
H	2.25560700	3.77275200	-1.13530000
H	1.61497900	2.85001800	-2.49656200
C	3.44459800	0.76520600	-2.43050500
H	2.56734400	0.49047800	-3.02703600
H	3.87522800	-0.15703500	-2.03028300
H	4.17982600	1.21111500	-3.10780500
C	-3.79721400	1.73509700	-1.97486800
H	-3.00894800	1.58847100	-2.72190700
H	-3.72822100	2.76352000	-1.61616500
H	-4.75708900	1.63473400	-2.49121600
Ni	-0.05735000	0.23319300	-1.06046200
P	-1.98241400	0.71141400	-0.08239200
P	1.81165200	0.98660100	-0.17766800
B	0.20420300	-1.28840300	0.49523600
H	-0.59354700	0.69127500	-2.56318700
H	0.22426000	0.86965100	-2.57089800

Total Energy (a.u.): -3385.11489345

Table S12. Optimized coordinates (Å) for [^{Ph}DPB^{Me}]Ni(H_2) (M06L/6-31+G*).

C	2.54509000	-0.58485100	0.21022400
C	-0.16903600	1.09255300	-1.35374800
C	-1.43740400	1.46476800	-1.87784100
H	-2.20548700	0.69361000	-1.97241300
C	1.69175300	-0.81474600	-0.88413900
C	-0.97441800	-1.44462800	-0.77090500
C	0.80501800	2.12329000	-1.26048800
H	1.82646100	1.86080000	-0.98232700
C	-0.93819900	-2.60602700	-1.56261200
H	-0.06025600	-2.80843700	-2.17700600
C	-2.11845200	-1.25948000	0.03315400
C	-3.13270700	-3.28697500	-0.80758400
H	-3.96028700	-3.99494400	-0.82375500
C	-1.71189900	2.75780600	-2.28769600
H	-2.68811900	3.00275400	-2.70614600

C	-3.18667300	-2.16087300	0.00865200
H	-4.06094000	-1.99575700	0.64240200
C	-3.64276800	1.03258100	0.91040400
H	-4.49255100	0.34026600	0.97040800
C	2.98109900	1.16839800	2.46888000
H	3.81652500	0.53281900	2.78961100
C	-2.33961000	-0.58548100	2.80612400
H	-1.54395300	-1.29949900	3.04067700
C	-0.73376900	3.75800600	-2.16160000
H	-0.95297300	4.77677000	-2.47938200
C	0.51538600	3.44169500	-1.64937900
H	1.28306200	4.21078900	-1.56679700
C	2.25496400	-1.42261300	-2.01824300
H	1.64009000	-1.58682400	-2.90494600
C	1.42276300	-1.17313200	2.76743100
H	0.93772700	-0.81750800	3.68427400
C	-1.99754700	-3.50970600	-1.58805400
H	-1.93820900	-4.39722100	-2.21765000
C	3.89497900	-0.94796400	0.18321500
H	4.53828500	-0.75712000	1.04419300
C	3.60069700	-1.78303100	-2.05596000
H	4.01516800	-2.23769700	-2.95548100
C	4.42518200	-1.55085300	-0.95415200
H	5.47730000	-1.83084400	-0.98694500
Ni	-0.11117200	1.14630400	0.78956500
P	-2.03296600	0.17481900	1.15557700
P	1.67350000	0.22033500	1.58859600
B	0.17074500	-0.33922700	-0.79102300
H	-0.66065600	2.64675500	1.32040500
H	0.14737900	2.64892000	1.49715600
H	-3.30105300	-1.11410600	2.84046700
H	-2.34110800	0.19000300	3.58079600
H	-3.65528300	1.52237200	-0.06924200
H	-3.77148900	1.80618600	1.67624600
H	3.37078500	1.95646200	1.81524600
H	2.55607200	1.64669400	3.35815400
H	2.37408500	-1.65243000	3.03217800
H	0.77382500	-1.92290200	2.30048700

Total Energy (a.u.): -3070.20473325

Table S13. Optimized coordinates (Å) for [^{Ph}DPB^{Me}](μ-H)NiH (M06L/6-31+G*).

C	-2.56738100	0.58043800	-0.02108200
C	1.20368300	1.84351400	-0.27476900

C	2.22669600	2.12264200	0.64513800
H	2.28733500	1.53994200	1.56716000
C	-1.39485600	1.31593100	0.24808500
C	0.54944100	-0.34627100	1.12391700
C	1.18028800	2.62364500	-1.44431900
H	0.39691700	2.43963500	-2.18412200
C	0.10335700	-0.18185200	2.44709600
H	-0.65360700	0.57773800	2.65224000
C	1.52768800	-1.36008800	0.91301000
C	1.57000800	-1.91709200	3.27091100
H	1.96498500	-2.51270100	4.09270900
C	3.17797000	3.11778500	0.41256600
H	3.95875400	3.30567200	1.14997600
C	2.01694800	-2.13568500	1.97011100
H	2.74805100	-2.92224100	1.77959300
C	3.21292900	-0.73101000	-1.47015900
H	3.46803800	-1.05044200	-2.48696800
C	-3.49523400	-1.11777300	-2.19472100
H	-4.52582000	-0.89108800	-1.89512500
C	2.57944300	-3.43691400	-0.84328700
H	1.90494000	-4.14059400	-0.34666200
C	3.13472400	3.86599100	-0.76167100
H	3.87892600	4.63889700	-0.95073500
C	2.12516400	3.61612900	-1.69255200
H	2.07836200	4.19606700	-2.61452400
C	-1.57044000	2.58498500	0.82368200
H	-0.68670300	3.18981400	1.03606300
C	-3.16563900	-2.21316400	0.41895200
H	-3.17125800	-3.22891500	0.01038700
C	0.60258100	-0.94139900	3.50360900
H	0.23471400	-0.77147100	4.51539300
C	-3.83890600	1.08287800	0.28244000
H	-4.73246000	0.49372900	0.06273100
C	-2.83138600	3.09342900	1.12706900
H	-2.92532500	4.08347000	1.57296200
C	-3.97539800	2.34243700	0.85711200
H	-4.96432700	2.73747300	1.08541100
Ni	-0.26793900	-1.37619900	-1.08515700
P	1.84707400	-1.76655500	-0.83177600
P	-2.36004800	-1.07122900	-0.76071800
B	0.08187900	0.70476800	-0.02411000
H	0.02844700	0.20844500	-1.23721900
H	-0.57013900	-2.81078000	-1.29660100
H	-4.19665000	-1.90455100	0.63093500
H	-2.60075600	-2.22195900	1.35675900
H	-3.47086600	-2.11221500	-2.65222900

H	-3.17903500	-0.38577600	-2.94353700
H	2.71306500	-3.76796800	-1.87830800
H	3.55740100	-3.45975500	-0.34718900
H	2.91338100	0.32074800	-1.49978600
H	4.10104200	-0.82603300	-0.83379700

Total Energy (a.u.): -3070.20062763

Table S14. Optimized coordinates (Å) for **TS1** (M06L/6-31+G*).

C	-2.62346000	0.52903600	-0.09439400
C	1.07070000	1.79685400	0.11547500
C	2.05541900	2.01634900	1.09571500
H	2.07155900	1.37692400	1.98152000
C	-1.53424400	1.27071900	0.39867600
C	0.27763500	-0.58330800	1.15628100
C	1.08255100	2.66163900	-0.99507800
H	0.32421200	2.52999200	-1.77044100
C	-0.56091300	-1.06449000	2.20393300
H	-1.46758500	-0.49975500	2.43125700
C	1.43063800	-1.39418200	0.85056900
C	0.94658800	-2.88724900	2.70081800
H	1.20999800	-3.74734900	3.31484000
C	3.01743600	3.01792000	0.96432000
H	3.76769700	3.15866100	1.74293900
C	1.74851800	-2.52593100	1.63982100
H	2.63181100	-3.11836500	1.40295100
C	3.56035800	0.09474800	-0.93228000
H	4.17365600	-0.23166600	-1.78025300
C	-2.72884900	-0.63759000	-2.73320300
H	-3.81881300	-0.51631500	-2.73525600
C	3.06747900	-2.65825000	-1.16849500
H	2.39996500	-3.50996100	-1.01386200
C	3.02373100	3.83544900	-0.16405800
H	3.77814600	4.61321000	-0.27686400
C	2.04412700	3.65648000	-1.14441800
H	2.03459200	4.29715100	-2.02633400
C	-1.83679900	2.48133200	1.04791700
H	-1.02033800	3.09888200	1.42689400
C	-3.13339800	-2.30862500	-0.46407400
H	-2.93570800	-3.19170300	-1.07995400
C	-0.23095600	-2.16310500	2.96988500
H	-0.87460500	-2.46704200	3.79505300
C	-3.94875400	0.93322900	0.09091400
H	-4.77343700	0.33591700	-0.30425000
C	-3.15220600	2.90108000	1.22733600

H	-3.35652800	3.84177200	1.73868800
C	-4.21515400	2.12539400	0.75780500
H	-5.24266100	2.46033400	0.89414200
Ni	0.03392700	-1.21945700	-0.89723400
P	2.17925500	-1.10961900	-0.77921300
P	-2.09452400	-0.91849200	-1.04200400
B	-0.04959400	0.69788300	0.29884900
H	0.07180600	-1.13174200	-2.33453000
H	-0.03890000	-2.75132100	-1.20571500
H	-2.27023500	0.26488000	-3.14882600
H	-2.46208100	-1.48728800	-3.37070700
H	-4.20206400	-2.06348300	-0.51607600
H	-2.87319800	-2.55300000	0.57104200
H	3.97461800	-2.77594200	-0.56141900
H	3.36694700	-2.64523300	-2.22207600
H	3.21307500	1.11278400	-1.11639700
H	4.18245200	0.09170400	-0.03060800

Total Energy (a.u.): -3070.14643563

Table S15. Optimized coordinates (Å) for **TS2** (M06L/6-31+G*).

C	-2.46708700	0.74987000	-0.15206900
C	1.41393000	1.82610200	0.05721700
C	2.47317600	1.72646600	0.97711500
H	2.43844200	0.94611300	1.74000200
C	-1.29980300	1.48821600	0.17785300
C	0.31745500	-0.48968500	1.00203800
C	1.50419800	2.85608800	-0.89781600
H	0.69739100	2.97279400	-1.62578100
C	-0.44904100	-0.55249100	2.19817600
H	-1.10042000	0.29129100	2.42948000
C	1.15257800	-1.63536100	0.71382900
C	0.45541700	-2.69608700	2.80489200
H	0.53570600	-3.52613200	3.50602800
C	3.56664800	2.59078500	0.93980900
H	4.36897400	2.48445200	1.66997500
C	1.16550500	-2.72533400	1.61973800
H	1.78038800	-3.59628900	1.40193200
C	3.36911800	-0.79062400	-1.15404200
H	3.89420700	-1.09726400	-2.06652700
C	-3.45626800	-0.97426100	-2.23271200
H	-4.47775100	-0.70815300	-1.93316000
C	2.67886300	-3.51024200	-0.90374600
H	1.93244500	-4.29548500	-0.75274800

C	3.63470100	3.58904800	-0.02967600
H	4.48880400	4.26414400	-0.06634900
C	2.59343800	3.72103700	-0.95023700
H	2.63361700	4.50107700	-1.71032000
C	-1.48711500	2.80708100	0.62585700
H	-0.60837000	3.40154800	0.88135500
C	-3.20412900	-1.98278400	0.39628100
H	-3.30548600	-3.00603600	0.01765400
C	-0.36203300	-1.59705100	3.09876900
H	-0.92651500	-1.56579000	4.03015700
C	-3.73514600	1.32193000	-0.00748000
H	-4.62634900	0.74402400	-0.26166100
C	-2.75197500	3.37336500	0.76769500
H	-2.85350300	4.39791800	1.12474600
C	-3.88587800	2.62735900	0.45440200
H	-4.88025500	3.05900000	0.56247700
Ni	-0.09864200	-1.00776800	-1.03226900
P	1.88519100	-1.85298900	-0.95892700
P	-2.27869100	-0.96322200	-0.82125200
B	0.16781000	0.84284200	0.13209500
H	0.23158300	0.48256000	-1.46937300
H	-0.04798600	-0.09797700	-2.25611000
H	-4.20574000	-1.57684900	0.58922500
H	-2.65178400	-2.02229500	1.34106600
H	-3.47671700	-1.97421200	-2.67972300
H	-3.12193300	-0.26845500	-2.99975600
H	3.15585000	-3.68934600	-1.87363400
H	3.44986000	-3.58774200	-0.12532700
H	3.08525400	0.25965700	-1.25820800
H	4.05639800	-0.88667800	-0.30503600

Total Energy (a.u.): -3070.15723383 a.u.

Table S16. Optimized coordinates (Å) for **INT** (M06L/6-31+G*).

C	-2.49845500	0.65331400	-0.12706400
C	1.32426900	1.85214900	0.12592100
C	2.43386000	1.76169000	0.98691200
H	2.46006900	0.96269000	1.73052800
C	-1.36959500	1.43006600	0.24695800
C	0.31321600	-0.50947200	1.04696700
C	1.33387300	2.90886900	-0.80521200
H	0.48446300	3.02119500	-1.48382300
C	-0.47398100	-0.66653400	2.21890000
H	-1.17656300	0.12913400	2.47030400

C	1.20965800	-1.59383700	0.71582800
C	0.53367700	-2.77961900	2.75020400
H	0.65200800	-3.63438300	3.41553500
C	3.49824700	2.65878900	0.91483700
H	4.34060600	2.55981400	1.59942500
C	1.26341600	-2.71735400	1.57510400
H	1.92355800	-3.54719100	1.33332500
C	3.45175200	-0.64372600	-1.08792700
H	4.02895700	-0.96203900	-1.96452100
C	-3.39192600	-1.03717700	-2.26979300
H	-4.42997500	-0.86369200	-1.95898700
C	2.79708400	-3.36699800	-0.94520100
H	2.06620400	-4.17274400	-0.83016300
C	3.48729100	3.67952000	-0.03353600
H	4.31960200	4.37922900	-0.09848700
C	2.39564700	3.80322700	-0.89567700
H	2.37499500	4.60127100	-1.63746200
C	-1.61752200	2.73672000	0.70546400
H	-0.76901400	3.35975400	0.99284500
C	-3.08612700	-2.13961900	0.30851000
H	-3.14096900	-3.14616200	-0.12121500
C	-0.34867500	-1.74546300	3.07690900
H	-0.93229000	-1.78669600	3.99590500
C	-3.78982600	1.17558300	-0.00791100
H	-4.65136000	0.57027700	-0.29711800
C	-2.90615900	3.25239600	0.82182700
H	-3.05639700	4.26734800	1.18873600
C	-4.00158700	2.46717500	0.46976800
H	-5.01420200	2.85922900	0.55776400
Ni	-0.03688400	-0.92434000	-1.07403600
P	1.96870800	-1.72388200	-0.96149800
P	-2.21055000	-1.01990700	-0.85806100
B	0.11371700	0.84796300	0.26079500
H	0.27255800	0.57328900	-1.72633100
H	-0.02812900	0.09541700	-2.35016800
H	4.09405800	-0.71782300	-0.20206300
H	3.16604500	0.40164800	-1.22793100
H	3.28830000	-3.50231600	-1.91516600
H	3.56140400	-3.45617200	-0.16112700
H	-3.34082300	-2.01049700	-2.77003600
H	-3.11306100	-0.26875400	-2.99820200
H	-4.10549100	-1.79031300	0.51945600
H	-2.53158500	-2.20118000	1.25067700

Total Energy (a.u.): -3070.15945381

Table S17. Optimized coordinates (Å) for **TS2'** (M06L/6-31+G*).

C	-2.51129800	0.60549500	-0.11671700
C	1.28530100	1.86797500	0.12616100
C	2.40822000	1.79804100	0.97170000
H	2.46173600	0.99679800	1.71147600
C	-1.39698100	1.39982300	0.26187200
C	0.32361300	-0.50970500	1.06006800
C	1.25951500	2.92850300	-0.80062800
H	0.39841600	3.02514800	-1.46673400
C	-0.45334100	-0.67482100	2.23560200
H	-1.17215100	0.10650700	2.48604800
C	1.23978000	-1.57465200	0.73094700
C	0.59906400	-2.76389100	2.77390200
H	0.73813200	-3.61351200	3.44178600
C	3.45191500	2.71841300	0.88894200
H	4.30535800	2.63505000	1.56176500
C	1.32336600	-2.69040500	1.59378900
H	1.99885800	-3.50777000	1.35193800
C	3.48802800	-0.63279000	-1.05275600
H	4.06473000	-0.94014400	-1.93360300
C	-3.37253400	-1.08546100	-2.27345200
H	-4.41285600	-0.95372400	-1.95018500
C	2.79974300	-3.34677500	-0.95208900
H	2.06132300	-4.14460400	-0.82940200
C	3.40622700	3.74195800	-0.05531900
H	4.22243900	4.45958500	-0.12853300
C	2.30064400	3.84527200	-0.90241200
H	2.25296200	4.64546400	-1.64060600
C	-1.66844200	2.69699700	0.73359900
H	-0.83156600	3.33385100	1.02485900
C	-3.00601300	-2.21241000	0.28648400
H	-3.03815700	-3.21222900	-0.16094900
C	-0.30263200	-1.74847100	3.09898600
H	-0.88301500	-1.79783500	4.01961900
C	-3.81251800	1.09981400	0.01037200
H	-4.66254700	0.48085000	-0.28385800
C	-2.96697000	3.18584100	0.85793900
H	-3.13639800	4.19428000	1.23432500
C	-4.04777400	2.38265200	0.50110100
H	-5.06747200	2.75449000	0.59476900
Ni	-0.02112200	-0.88273100	-1.11509000
P	1.98898600	-1.69466100	-0.95290600
P	-2.18023700	-1.04682600	-0.87180600
B	0.09492400	0.84235700	0.27194500
H	0.38901400	0.56950600	-1.81034400

H	-0.09065200	0.17085300	-2.36748500
H	4.12595700	-0.73424600	-0.16619600
H	3.21698900	0.41916400	-1.17202200
H	3.27640200	-3.48411200	-1.92902000
H	3.57401000	-3.44770600	-0.17922000
H	-3.29208900	-2.04899500	-2.78845600
H	-3.12803000	-0.29701100	-2.99266800
H	-4.03171100	-1.89658100	0.51844100
H	-2.43559800	-2.27447100	1.21921000

Total Energy (a.u.): -3070.15940235

Table S18. Optimized coordinates (Å) for **7'** (M06L/6-31+G*).

C	-2.53404885	0.55008429	-0.07217188
C	0.08180252	1.10664294	-2.24382474
C	-1.75655220	1.59291899	-0.60729527
C	0.72014724	1.97217298	0.01893777
C	0.51226685	3.24371193	0.57260243
H	-0.43015320	3.75806330	0.39296491
C	1.93105368	1.30284624	0.31929129
C	2.70860215	3.23903824	1.57338797
H	3.48422169	3.73069319	2.15863927
C	2.91957383	1.96311171	1.05874654
H	3.87133183	1.46567811	1.24654754
C	3.70695509	-0.49755752	-1.07836826
H	4.47186759	-0.14567608	-0.36549295
C	-2.85307453	-2.33604240	-0.26172920
H	-3.73146900	-2.19062318	0.38665258
C	2.36421583	-1.40421322	1.38715232
H	1.67017472	-0.91981845	2.09205505
C	-2.37861940	2.80897777	-0.91473089
H	-1.79418165	3.60604894	-1.37510888
C	-1.47159284	-1.14912463	2.02248579
H	-0.74824004	-1.96476668	2.18971776
C	1.48660762	3.86772429	1.34564328
H	1.29339344	4.85634080	1.76027366
C	-3.90046778	0.74205659	0.15931924
H	-4.50798089	-0.07729739	0.54680537
C	1.91003634	-2.85372513	1.22278850
H	2.58821232	-3.42190305	0.57218938
H	0.90839298	-2.91065251	0.77619952
H	1.88797817	-3.36518021	2.19518198
C	-3.74030389	2.99435591	-0.68035052
H	-4.21043917	3.94160442	-0.94137463

C	-0.87817112	0.13925345	2.58332910
H	-1.59334946	0.96903757	2.49942019
H	0.03271710	0.44745663	2.05678255
H	-0.63029856	0.02079917	3.64665225
C	3.69017955	0.43916991	-2.27978724
H	4.66675205	0.43944111	-2.78215886
H	3.45784157	1.47311541	-1.99592209
H	2.93868703	0.11498825	-3.01239928
C	3.76495537	-1.34101913	1.98345847
H	3.79865651	-1.89593887	2.93114979
H	4.08945545	-0.31738220	2.19898019
H	4.51275003	-1.79694144	1.32164745
C	-2.76650511	-1.48572478	2.75099802
H	-2.59579515	-1.50354650	3.83622547
H	-3.17818280	-2.46242808	2.47123274
H	-3.53692170	-0.72565883	2.56178828
C	-4.50399185	1.96219812	-0.13837766
H	-5.57073648	2.10046126	0.03212857
C	-2.24802961	-3.70625970	0.02684799
H	-2.96625763	-4.50648962	-0.19547119
H	-1.94042799	-3.81939767	1.07485515
H	-1.35868827	-3.87617686	-0.59599790
C	-3.30398455	-2.22878118	-1.71220414
H	-2.46071558	-2.37790981	-2.39909469
H	-3.74148347	-1.24834429	-1.93680017
H	-4.05729848	-2.99516304	-1.93875777
C	4.05345456	-1.91573423	-1.51746175
H	3.26753710	-2.32468712	-2.16787785
H	4.17440766	-2.60519467	-0.67382427
H	4.99279175	-1.92577952	-2.08656368
Ni	0.08793615	-0.59967954	-1.17707069
P	2.05003310	-0.45395392	-0.21170007
P	-1.60127231	-1.01415325	0.14624766
H	0.38162905	-1.88196412	-2.18236047
H	-0.30897068	-1.51175806	-2.48436049
C	-0.29783109	1.35221551	-0.89728414
H	-0.69145326	1.09767944	-3.01375632
H	1.07055447	1.41212373	-2.58942083

Total Energy (a.u.): -3205.53962386

Table S19. Optimized coordinates (Å) for (dmpe)Ni(PPh_3)(C_2H_4) (M06L/6-31+G*).

Ni	1.06856204	-0.05857975	-1.02310495
P	-0.87372358	0.02098044	-0.05593275
P	2.26093429	-1.64505591	-0.15203348

P	2.41575620	1.45433356	-0.13334915
C	1.41309599	-0.44498844	-2.97354034
C	0.56435860	0.66686320	-2.84246805
C	3.40615564	-0.83964261	1.07407399
C	3.88228703	0.49426122	0.50753201
C	3.47346772	-2.49182926	-1.25085332
C	1.65487015	-3.08839250	0.81564215
C	3.25221594	2.72625678	-1.17405060
C	2.04848554	2.49429582	1.35175773
C	-1.05302556	-0.93056757	1.50492808
C	-1.80470350	-2.10743197	1.60504724
C	-1.76650737	-2.88047540	2.76599945
C	-0.98756889	-2.48612717	3.85140304
C	-0.24420339	-1.30647592	3.77031338
C	-0.27164878	-0.54574869	2.60678480
C	-2.32244640	-0.58227216	-1.02287481
C	-3.63755140	-0.15375578	-0.80702196
C	-4.68549348	-0.68204323	-1.55767823
C	-4.43266186	-1.64814018	-2.53158050
C	-3.12650871	-2.07911057	-2.75774130
C	-2.07872701	-1.54286738	-2.01195774
C	-1.43821419	1.70394650	0.44719005
C	-2.13388503	1.98795504	1.62863615
C	-2.48752665	3.29887749	1.94873322
C	-2.16972450	4.34304721	1.08284793
C	-1.49183371	4.07045672	-0.10598794
C	-1.11974103	2.76501296	-0.41312572
H	1.01072133	-1.41378757	-3.27799229
H	2.46888036	-0.30623105	-3.21824008
H	0.95807917	1.67401083	-2.99675602
H	-0.50284332	0.56708696	-3.05457925
H	4.24677418	-1.49786115	1.34125109
H	2.82021603	-0.67827018	1.99312788
H	4.45352188	1.07432622	1.24782872
H	4.55405822	0.32140679	-0.34696014
H	2.94319878	-3.07796728	-2.00974540
H	4.07820687	-1.74781975	-1.78172536
H	4.14305773	-3.16088307	-0.69395393
H	1.06268566	-2.75334405	1.67442363
H	1.00343745	-3.70935721	0.18961265
H	2.48481295	-3.70848272	1.18029368
H	3.63179054	2.26606347	-2.09412987
H	2.52601565	3.49515170	-1.46537593
H	4.08545342	3.21912120	-0.65496222
H	1.18600394	3.14492156	1.16547973
H	1.79179712	1.85071640	2.20203618

H	2.90605511	3.11758813	1.64114223
H	-2.42105343	-2.42972571	0.76570651
H	-2.35336871	-3.79664573	2.82049757
H	-0.95986382	-3.09049269	4.75662141
H	0.36405631	-0.98369058	4.61477646
H	0.32280576	0.36779433	2.54198384
H	-3.84308163	0.60006895	-0.04593787
H	-5.70436453	-0.33909326	-1.38143969
H	-5.25309782	-2.05895144	-3.11830221
H	-2.92206124	-2.82689281	-3.52291418
H	-1.04710123	-1.85916481	-2.18763865
H	-2.39694881	1.17907512	2.31071245
H	-3.01846747	3.50249584	2.87803353
H	-2.44740505	5.36581804	1.33340618
H	-1.24029007	4.88072045	-0.78960685
H	-0.55371310	2.55203200	-1.32205652

Total Energy (a.u.): -3543.90319933