Supporting Information for:

One-electron Ni(II)/(I) Redox Couple: Potential Role in Hydrogen Activation and Production

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SI Table of Contents:

Page		
2	Experimental Section	
4	Figure 1S:	UV-vis spectra of **4**-**6**
5	Figure 2S:	IR spectrum of **5**
5	Figure 3S:	IR spectrum of **6**
6	Table 1S:	Redox Potentials for Complexes **1** – **6** and free ligand
6	Figure 4S:	Cyclic voltammograms of **5** and **6**.
7	Figure 5S:	^{1}H NMR Spectrum of the photolysis of **5**
8	Figure 6S:	^{1}H NMR Spectrum of the photolysis of **6**
9	Figure 7S:	^{1}H NMR spectrum highlighting H_2 and HD in the photolysis of **5**

Experimental Section

Synthetic Considerations. Unless otherwise stated, all manipulations were performed under a dinitrogen atmosphere in a MBraun glovebox or using standard Schlenk techniques. Standard solvents were deoxygenated by sparging with dinitrogen and dried by passing through activated alumina columns of a SG Water solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., dried over CaH_2, distilled, and stored over activated 4 Å molecular sieves. Elemental analyses were performed by Columbia Analytical Services. The syntheses of 4,6-bis(3-diisopropylphosphinophenyl)dibenzofuran, referred to as ^{iPr}DPDBFphos, $Ni(Cl)_2$(^{iPr}DPDBFphos), $Ni(Br)_2$(^{iPr}DPDBFphos), and Ni(Cl)(^{iPr}DPDBFphos) was previously reported.[1,2] Other reagents were purchased commercially and used without further purification.

Synthesis of Ni(Br)(^{iPr}DPDBFphos) 4: A solution of **2** (200 mg, 0.259 mmol) in 7 mL THF was cooled to −27°C, then added to KC_8 (34.8 mg, 0.257 mmol). The solution was warmed to rt after an hour. After stirring overnight, the reaction mixture was filtered through Celite, and the filtrate was pumped down. Several recrystallizations from THF/Et_2O gave a tan powder (126 mg, 70%). UV−vis λ_{max}(THF)/ nm (ε/L mol^{-1} cm^{-1}): 296 (19 200), 313 sh (12 900), 323 (11 400), 341 sh (3 600), 369 sh (3 300). ^{1}H NMR (300 MHz, d_8-THF): δ 13.90, 9.00, 8.57, 7.94, 3.20. Found: C, 61.97; H, 6.37; N, <0.05. Calc. for $C_{36}H_{42}P_2ONiBr$: C, 62.55; H, 6.12; N, 0%.

Synthesis of Ni(H)(Cl)(^{iPr}DPDBFphos) 5: To a stirring solution of $Ni(Cl)_2$(^{iPr}DPDBFphos) (239 mg, 0.350 mmol) in THF was added a THF solution of $NaHBEt_3$ (360 μL, 0.360 mmol) at −27°C. After 2.5 h, the solution was warmed to rt and stirred overnight. Then, the solution was filtered through Celite, and the filtrate dried *in vacuo*. Repeated layering of pentane on a THF solution of **5** provided an orange-yellow powder (155 mg, 70%). UV−vis λ_{max}(THF)/nm (ε/L mol^{-1} cm^{-1}): 295 (19 300), 309 sh (14 900), 319 (12 900), 382 (1 900), 500 sh (150). ^{1}H NMR (300 MHz, d_8-THF): δ 8.66 (2H, m, CH), 8.11 (2H, dd, J = 1.5 & 7.5 Hz, CH), 7.69 (2H, m, CH), 7.59 (2H, dd, J = 1.2 Hz & 7.5 Hz, CH), 7.50 (6H, m, CH), 2.78 (4H, m, $P(CH(CH_3)(C'H_3))$), 1.34 (12H, m, $P(CH(CH_3)(C'H_3))$), 1.08 (12H, m, $P(CH(CH_3)(C'H_3))$), −23.21 (1H, t, J_{HP} = 74 Hz, Ni*H*). ^{31}P NMR (121 MHz, d_8-THF): δ 36.8. IR ν_{max}/cm^{-1}: 1944 (NiH). Found: C, 66.63; H, 7.23; N, <0.05. Calc. for $C_{36}H_{43}P_2ONiCl{\bullet}C_4H_8O$: C, 66.73; H, 7.14; N, 0%.

Synthesis of Ni(H)(Br)(^{iPr}DPDBFphos) 6: To a stirring solution of $Ni(Br)_2$(^{iPr}DPDBFphos) (212 mg, 0.275 mmol) in 4 mL THF was added a THF solution of $NaHBEt_3$ (280 μL, 0.280 mmol) at −49°C. The reaction was warmed to rt after an hour. After overnight stirring, the reaction was filtered through Celite, and the filtrate was dried *in vacuo*. Repeated layering of pentane on a THF solution of **6** provided an orange-yellow powder (90 mg, 50%). A yellow needle suitable for diffraction was grown by vapor diffusion of pentane into a benzene solution. UV−vis λ_{max}(THF)/nm (ε/L mol^{-1} cm^{-1}): 296 sh (20 800), 308 (16 600), 319 sh (14 300), 388 (1 240), 500 sh (150). ^{1}H

NMR (300 MHz, d_8-THF): δ 8.61 (2H, m, CH), 8.10 (2H, dd, J = 1.5 & 7.5 Hz, CH), 7.68 (2H, m, CH), 7.58 (2H, dd, J = 1.2 Hz & 7.5 Hz, CH), 7.50 (6H, m, CH), 2.86 (4H, m, $P(CH(CH_3)(C'H_3))$), 1.33 (12H, m, $P(CH(CH_3)(C'H_3))$), 1.08 (12H, m, $P(CH(CH_3)(C'H_3))$), −21.68 (1H, t, J_{HP} = 74 Hz, NiH). ^{31}P NMR (121 MHz, d_8-THF): δ 36.6. IR ν_{max}/cm^{-1}: 1943 (NiH). Found: C, 62.49; H, 6.51; N, <0.05. Calc. for $C_{36}H_{43}P_2ONiBr$: C, 62.46; H, 6.26; N, 0%.

General Procedure for Photolysis Experiments. Photolysis experiments were conducted in a J Young NMR tube at a concentration of 0.0126 M (700 μL d_8-THF, 0.00880 mmol) with a standard of 0.108 M triphenylphosphine oxide (50 μL C_6D_5Cl, 0.0054 mmol, sealed in a capillary tube). The light source consisted of four Pyrex-filtered medium pressure 175 W Hg vapor lamps ($\lambda > 313$ nm). The reactions were monitored by proton NMR spectroscopy.

X-Ray Crystallographic Data Collection and Refinement of the Structures. A yellow needle of **6** was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for data collection at 173(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator). The data intensity was corrected for absorption and decay (SADABS). Final cell constants were obtained from least squares fits of all measured reflections. The structure was solved using SHELXS-97 and refined using SHELXL-97. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, except for the hydride, which was located in the difference map and refined isotropically.

Physical Measurements. ^{1}H and ^{31}P NMR spectra were acquired on Varian Inova 300 and 500 MHz spectrometers at ambient temperature unless otherwise stated. Chemical shifts were referenced to residual d_8-THF in ^{1}H NMR spectra, while ^{31}P NMR spectra were referenced to an external reference of 85% H_3PO_4 set to 0 ppm. Electronic spectra of complexes were recorded on a Cary 300 Bio UV-Visible spectrophotometer. Cyclic voltammetry experiments were performed inside a glovebox with a CHInstruments Model 600D potentiostat/galvanostat. A single-chamber cell was set up with a glassy carbon working electrode (3 mm diameter), a Pt wire as the auxiliary electrode, and a reference electrode consisting of a silver wire in 10 mM $AgNO_3$ solution (0.1 M $[^{n}Bu_4N]PF_6$ in CH_3CN). All measurements were conducted in THF with 0.1 M $[^{n}Bu_4N]PF_6$ as a supporting electrolyte and were calibrated to an internal ferrocene standard. Infrared spectra were recorded on a Bruker TENSOR 37 FT-IR spectrometer.

References

1. Ding, K.; Miller, D. L.; Young, V. G., Jr.; Lu, C. C. *Inorg. Chem.* **2011**, *50*, 2545-2552.
2. Marlier, E. E.; Tereniak, S. J.; Ding, K.; Milliken, J. E.; Lu, C. C. *Inorg. Chem.* **2011**, *50*, 9290-9299.

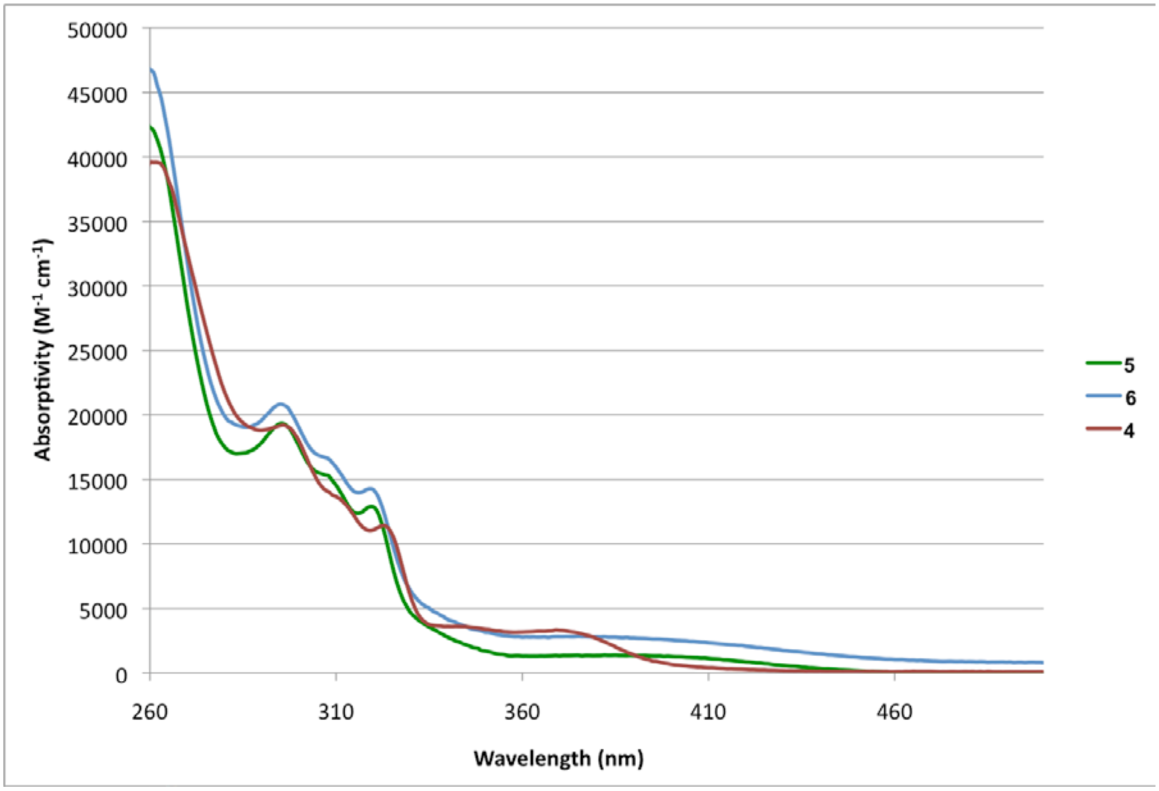

Figure 1S. UV-vis spectra of Ni(Br)(^{iPr}DPDBFphos) **4**, Ni(H)(Cl)(^{iPr}DPDBFphos) **5**, and Ni(H)(Br)(^{iPr}DPDBFphos) **6**, all in THF.

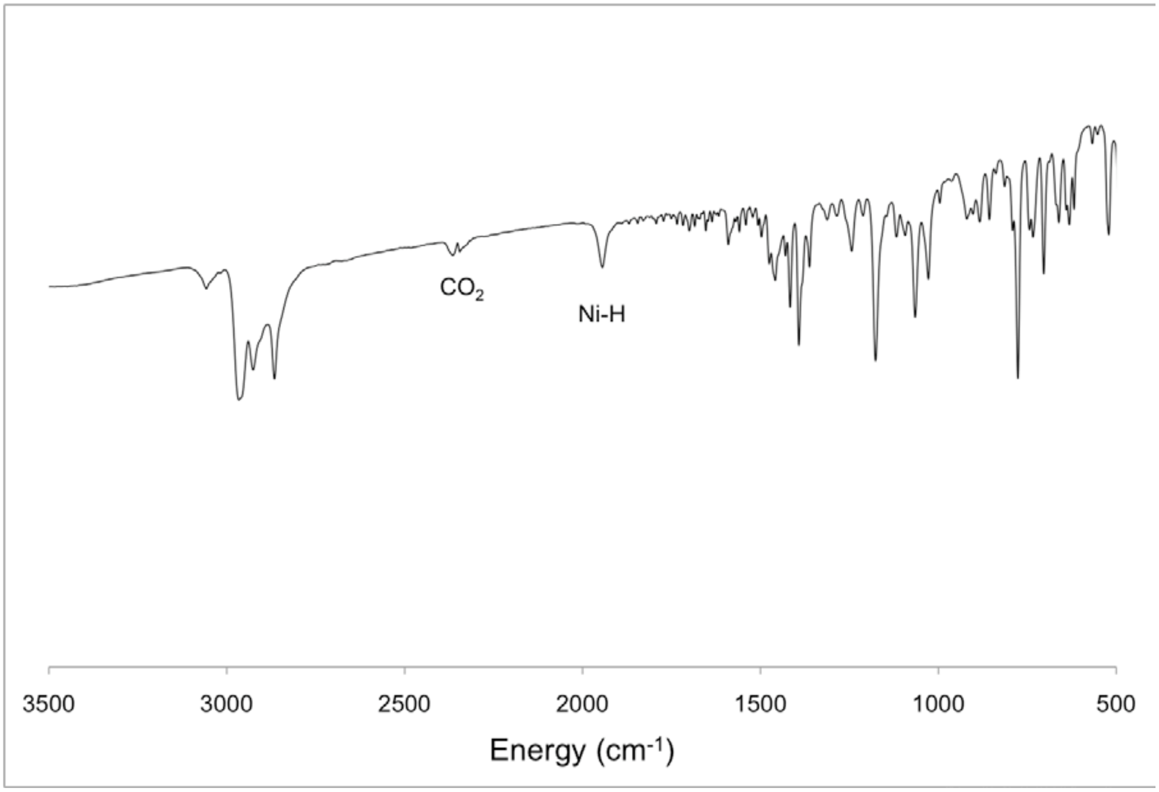

Figure 2S. IR spectrum of Ni(H)(Cl)(^{iPr}DPDBFphos) **5** (KBr pellet).

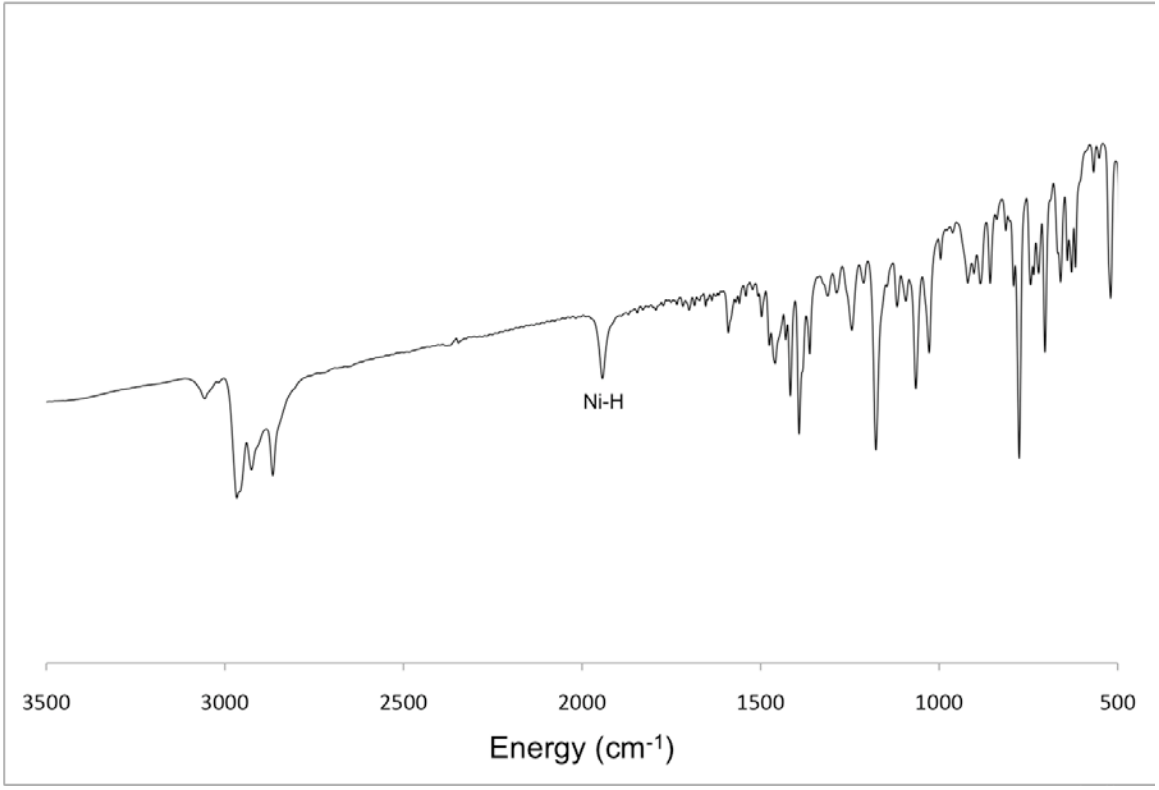

Figure 3S. IR spectrum of Ni(H)(Br)(^{iPr}DPDBFphos) **6** (KBr pellet).

Table 1S. Redox Potentials (V) for Complexes 1 to 6 and Free ligand (iPrDPDBFphos).

Compound	Ni(H)(X)(L) Oxidation	Ni(II/I)	Ni(I/0)	Ligand Reduction
iPrDPDBFphos	N/A	N/A	N/A	-2.89
1	N/A	-1.85	-2.50	-2.97
2	N/A	-1.46	-2.38	-2.97
3	N/A	N/A	-2.32	-2.89
4	N/A	N/A	-2.28	-2.93
5	0.50	N/A	N/A	-2.97
6	0.74	N/A	N/A	-3.02

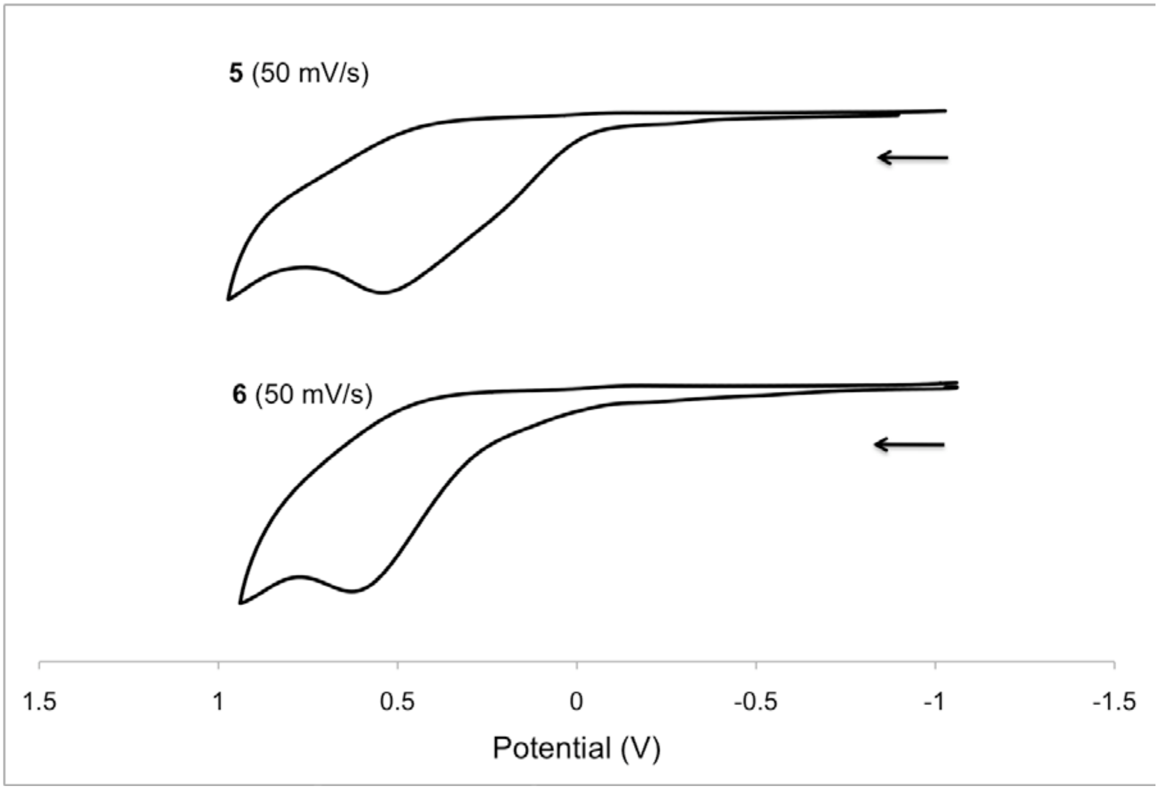

Figure 4S. Cyclic voltammograms of Ni(H)(Cl)(iPrDPDBFphos) **5** and Ni(H)(Br)(iPrDPDBFphos) **6**. Both CVs were conducted in THF with 0.1 M [^{n}Bu$_4$N]PF$_6$ as a supporting electrolyte and are referenced against ferrocene.

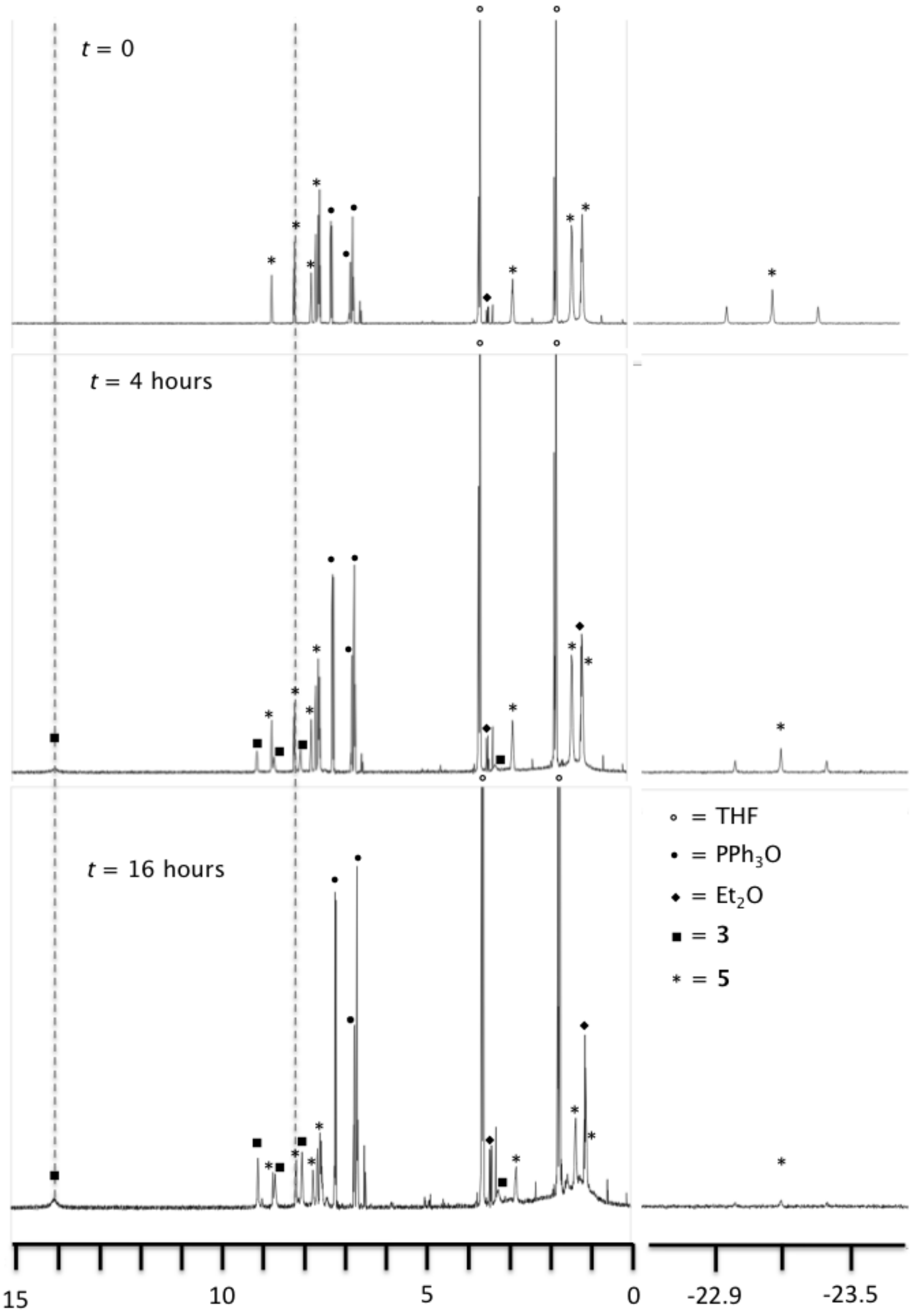

Figure 5S. Stacked ^{1}H NMR spectra (300 MHz, d$_8$-THF) of the photolysis of **5** after 0 hours, 4 hours, and 16 hours (from top to bottom).

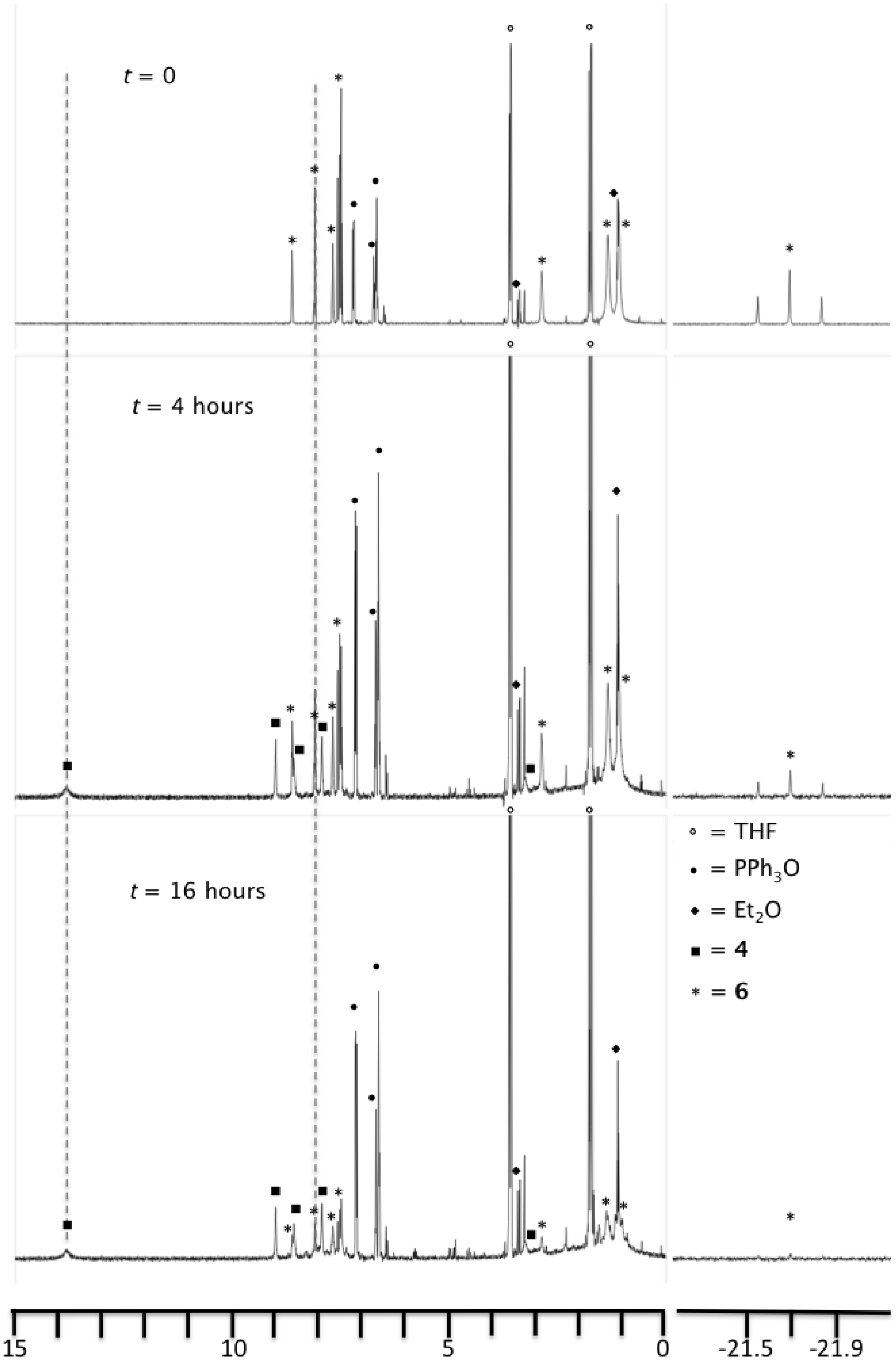

Figure 6S. Stacked ^{1}H NMR spectra (300 MHz, d_8-THF) of the photolysis of **6** after 0 hours, 4 hours, and 16 hours (from top to bottom).

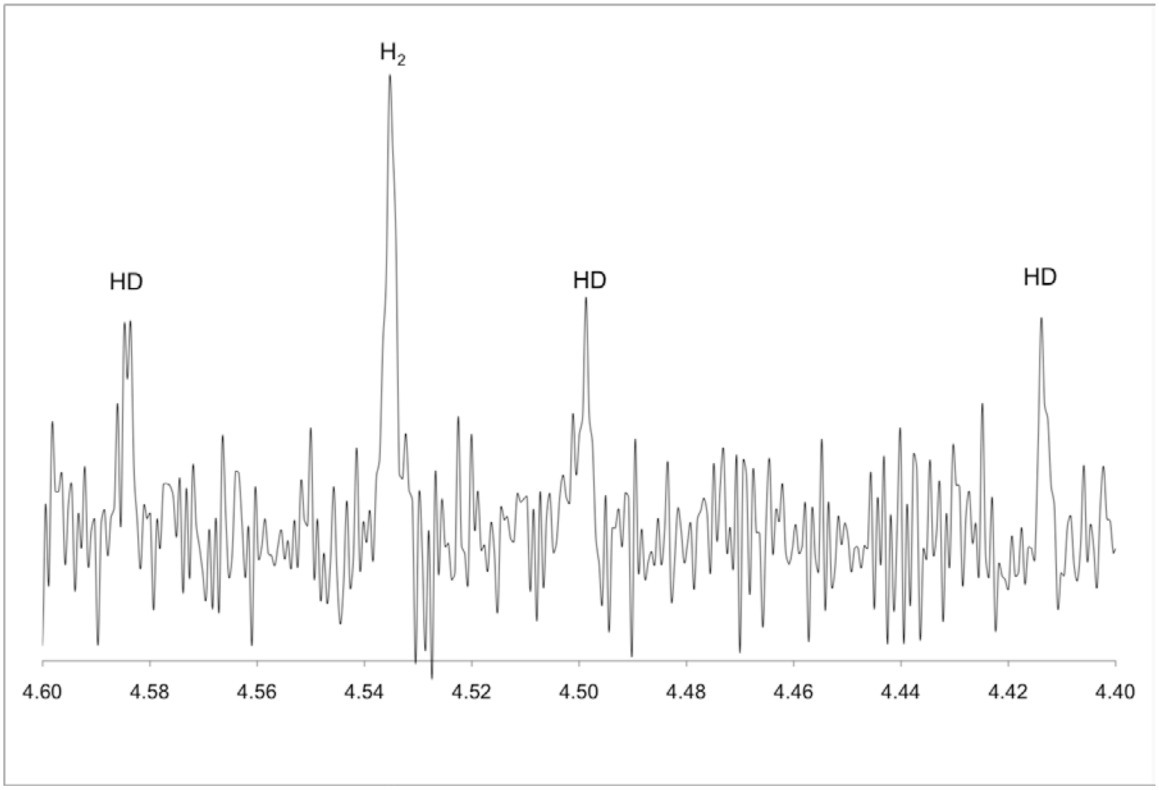

Figure 7S. ^{1}H NMR spectrum of the photolysis of **5** after 16 hours, highlighting the presence of both H_2 and HD in the products.