Electronic Supplementary Information

Chemoseletive H/D Exchange Catalyzed by Nickel Nanoparticles Stabilized by *N*-Heterocyclic Carbene Ligands

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ESI-1. Experimental Part.

All syntheses of non-commercial compounds were performed under argon atmosphere either by using Schlenk techniques or in a glove box. Tetrahydrofuran was obtained from VWR Prolabo, then purified on alumina desiccant and degassed by bubbling Ar through the solution for 20 minutes. The commercial products, bis(1,5-cyclooctadiene)nickel(0), 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene, 1,3-dicyclohexyl-imidazolium chloride, sodium *tert*-butoxide, 2-phenylpyridine, pyridine, phenanthroline, 1-phenyl-1*H*-1,2,4-triazole, 2-phenylimidazole, 5-(4-methylphenyl)-1,3-oxazole and 2,5-diphenyl-1,3-oxazole were obtained from Sigma-Aldrich. 2,2'-bipyridyl was obtained from Alpha Aesar. All these compounds were used without any additional purification.

The size and the morphology of the NPs were studied by transmission electronic microscopy (TEM). TEM grids were prepared by deposition of one drop of a colloidal solution containing the NPs on a copper grid covered with amorphous carbon. Conventional bright-field images were performed using JEOL microscopes (Model 1400) working at 120 kV. Magnetic measurements were performed on a Vibrating Sample Magnetometer (VSM, Quantum Device PPMS Evercool II). VSM measurements were carried out on compact powder samples that were prepared and sealed under argon atmosphere. WAXS was performed at CEMES-CNRS. Samples were sealed in 1.0 mm diameter Lindemann glass capillaries. The samples were irradiated with graphite monochromatized molybdenum Kα (0.071069 nm) radiation and the X-ray intensity scattered measurements were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier transformation of the reduced intensity functions. Thermogravimetric analyses (TGA) were performed in a TGA/DSC 1 STAR System equipped with an ultra-microbalance UMX5, a gas switch GC200 and sensors DTA and DSC. ICP-MS measurements were performed at Laboratoire de Chimie de Coordination in Toulouse. NMR spectra were recorded in a Bruker Avance 400 MHz or in a Bruker Avance 500 MHz spectrometer. Gas Chromatography–Mass Spectrometry analyses were performed on a PerkinElmer 580 Gas Chromatograph coupled to a Clarus SQ8T Mass Spectrometer. Electrospray mass spectra were recorded using an ESI/TOF Mariner Mass Spectrometer.

Synthesis of Ni@ICy nanoparticles (1)

In the glove box, 48.7 mg of 1,3-dicyclohexylimidazolium chloride (0.181 mmol) and 22.0 mg KO^{t}Bu (0.196 mmol, 1.1 eg.) were dispersed in THF (15 mL) in a Schlenk flask. The mixture was let to stir at room temperature for 15 hours to give a yellowish solution containing the *free* carbene. Then, 200.0 mg of $Ni(COD)_2$ (0.727 mmol) was dispersed in THF (15 mL) in a Fischer Porter bottle. The carbene solution was filtered through celite to remove the KCl formed during the deprotonation of the imidazolium salt and was transferred dropwise into the Fischer Porter containing the $Ni(COD)_2$ solution. The mixture was pressurized with H_2 (3 bar) under stirring and heated at 70 °C for 5 h. At the end of the reaction, the NPs were isolated as a dark-brown solid after evaporation of the solvent under vacuum and washed with pentane (2×20 mL). Yield: 40 mg, 75% in Ni. ICP analysis: Ni, 80 wt%.

Synthesis of Ni@IMes nanoparticles (2)

In the glove box, 55.2 mg of 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (0.181 mmol) was dispersed in THF (15 mL) in a Schlenk flask. In parallel, 200 mg of $Ni(COD)_2$ (0.727 mmol) was dispersed in THF

(15 mL) in a Fischer Porter bottle. Then, the *free* carbene solution was transferred dropwise into the Fischer Porter containing the $Ni(COD)_2$ solution. The mixture was pressurized with H_2 (3 bar) under stirring and heated at 70 °C for 5 h. At the end of the reaction, the NPs were isolated as a dark-brown solid after evaporation of the solvent under vacuum. Yield: 50 mg, 49% in Ni. ICP analysis: Ni, 42 wt%.

General catalytic conditions

In a typical catalytic reaction, 0.15 mmol of the corresponding substrate and 2-3 mg of the NPs (12 mol%) were dissolved in 1 mL of THF in a Fischer-Porter bottle. Then, the reaction mixture was pressurized with D_2 (2 bar) and heated at 55 ºC (or room temperature) for the indicated time. The deuterium incorporation values were determined by ^1H NMR and mass spectrometry.

ESI-2. Characterization of Ni@NHC NPs.

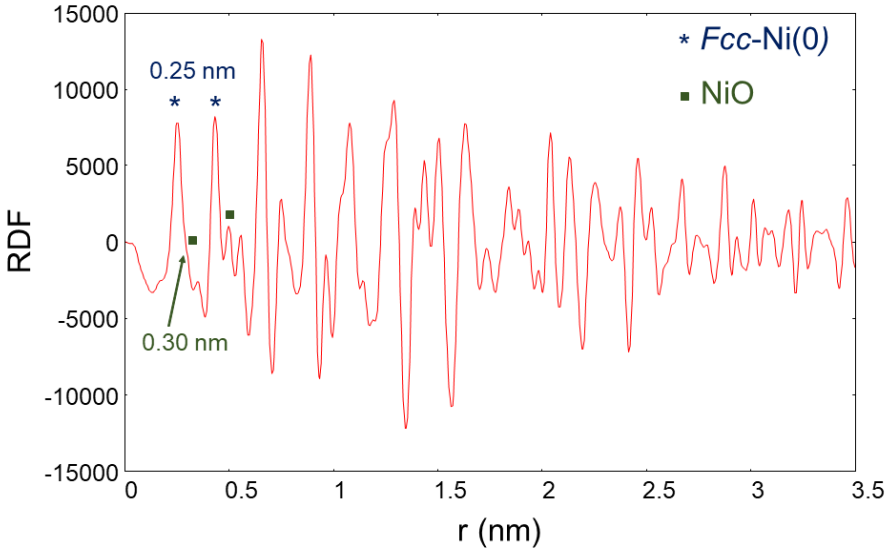

Figure S1. RDF function for NPs Ni@ICy **1**.

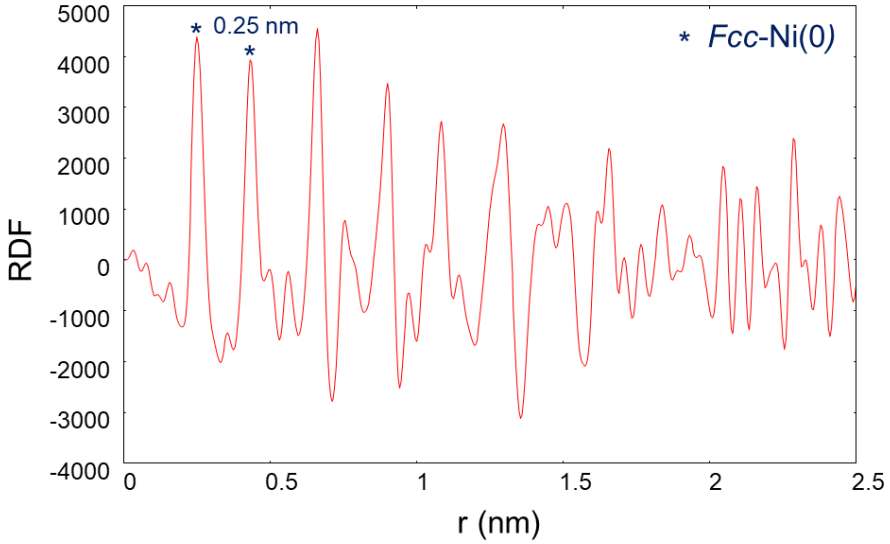

Figure S2. RDF function for NPs Ni@IMes **2**.

ESI-3. Optimization of reaction conditions for 2-phenylpyridine.

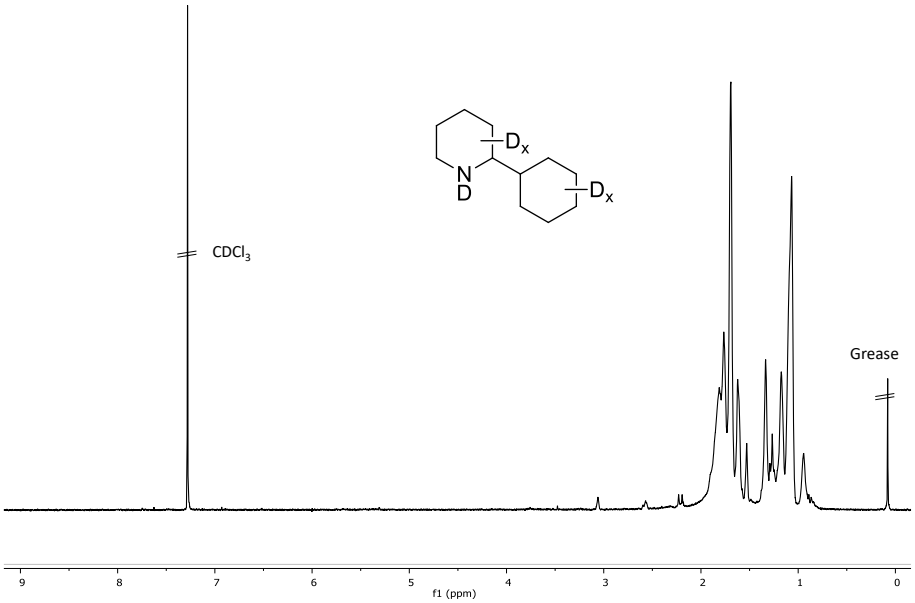

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 7.26 ppm) after 24 h of reaction of 2-phenylpyridine at 55 ºC in THF, under 2 bar of D_2 and using NPs **Ru@ICy** as catalyst. The signals in the 1-2 ppm region correspond to the product derived from the complete reduction of the aromatic rings. No signals can be observed in the aromatic region.

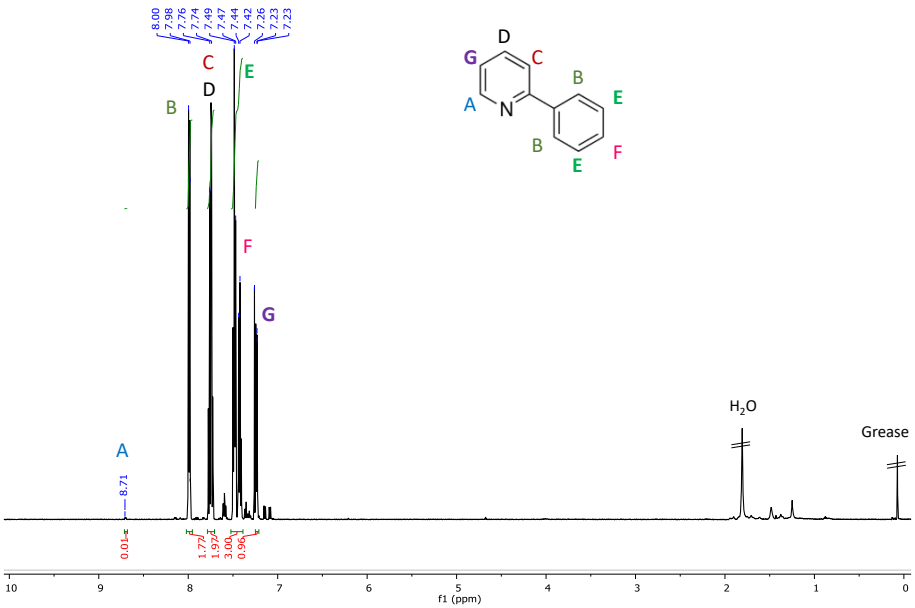

Figure S4. ^{1}H NMR spectrum (400 MHz) of 2-phenylpyridine after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **1** as catalyst. The absence of signals in the 1-2 ppm region indicates that the reduction of the aromatic rings does not take place.

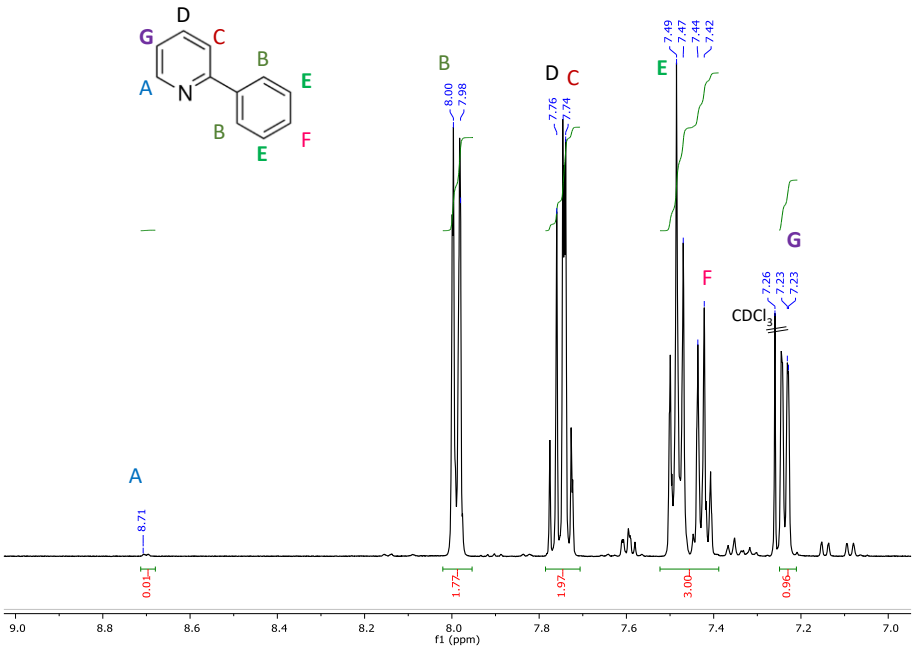

Figure S5. Amplification of the ^{1}H NMR spectrum (400 MHz) of 2-phenylpyridine after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **1** as catalyst.

^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm): δ 8.70 (d, A, 0.01H), 7.99 (d, B, 1.77H), 7.76 (t, D, 1H), 7.73 (d, C, 1H), 7.49 (t, E, 2H), 7.42 (t, F, 1H), 7.23 (d, G, 1H). Deuterium incorporation was expected at *δ* 8.72 and at *δ* 7.98-8.00 ppm. Isotopic enrichment values were determined against the integral at *δ* 7.40 – 7.50.

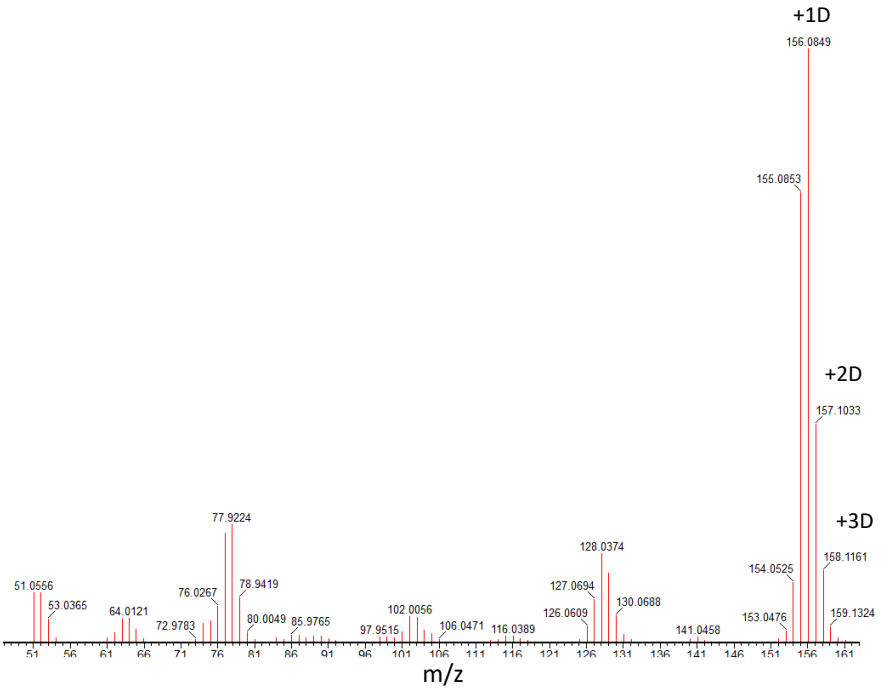

Figure S6. MS spectrum of 2-phenylpyridine after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **1** as catalyst.

MS (EI, positive mode, $CHCl_3$): 154.1 [**2-phenylpyridine** -H -e^{-}]$^{+}$, 9%; 155.1 {[**2-phenylpyridine** -e^{-}]$^{+}$ + [**2-phenylpyridine** -H +H/D -e^{-}]$^{+}$}, 76%; 156.1 {[**2-phenylpyridine** +H/D -e^{-}]$^{+}$+ [**2-phenylpyridine** -H +2H/D -e^{-}]$^{+}$}, 100%; 157.1 {[**2-phenylpyridine** -+2H/D -e^{-}]$^{+}$+ [**2-phenylpyridine** -H +3H/D -e^{-}]$^{+}$}, 38%; 158.1 {[**2-phenylpyridine** +3H/D -e^{-}]$^{+}$+ [**2-phenylpyridine** -H +4H/D -e^{-}]$^{+}$}, 13%.
N. of deuterium incorporated calculated by NMR: 1.3. N. of deuterium incorporated calculated by MS: 1.2.

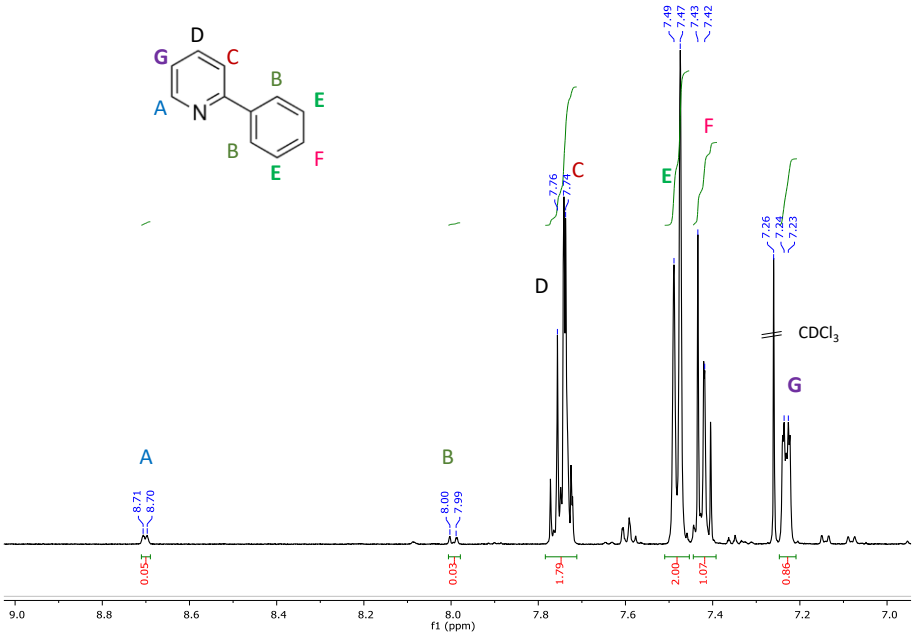

Figure S7. [1]H NMR spectrum of 2-phenylpyridine after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm): δ 8.70 (d, A, 0.05H), 8.00 (d, B, 0.03H), 7.76-7.73 (m, C-D, 1.79H), 7.48 (d, E, 2H), 7.41 (t, F, 1H), 7.23 (m, G, 0.86H). Deuterium incorporation was expected at *δ* 8.72 and at *δ* 7.98-8.00 ppm. Isotopic enrichment values were determined against the integral at *δ* 7.48.

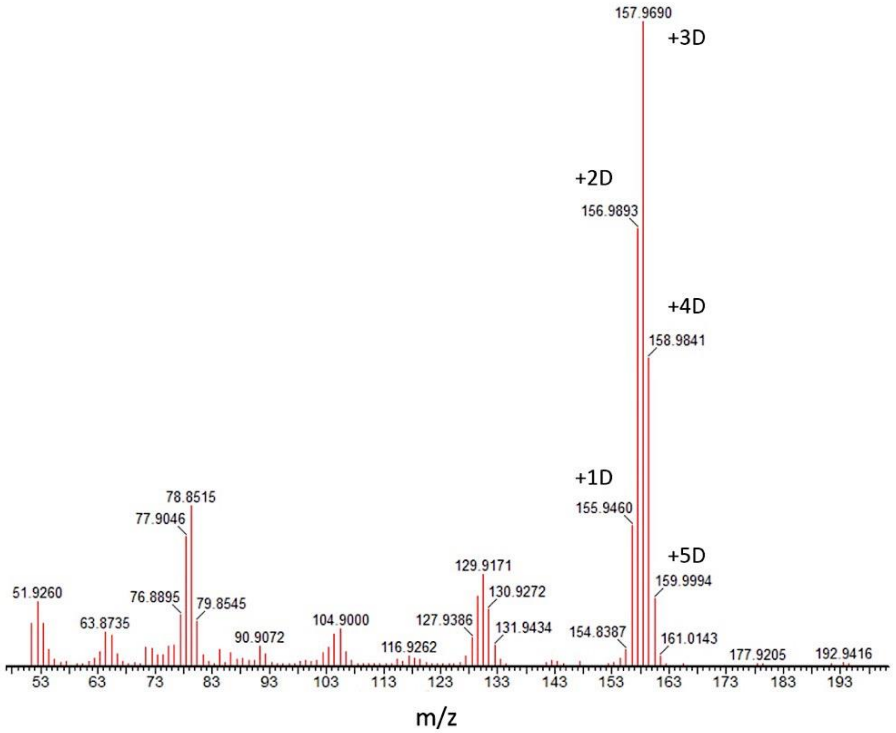

Figure S8. MS spectrum of 2-phenylpyridine after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (EI, positive mode, $CHCl_3$): 154.8 {[**2-phenylpyridine** -e$^-$]$^+$ + [**2-phenylpyridine** -H +H/D -e$^-$]$^+$}, 3%; 155.9 {[**2-phenylpyridine** +H/D -e$^-$]$^+$+ [**2-phenylpyridine** -H +2H/D -e$^-$]$^+$}, 26%; 157.0 {[**2-phenylpyridine** -+2H/D -e$^-$]$^+$+ [**2-phenylpyridine** -H +3H/D -e$^-$]$^+$}, 68%; 158.0 {[**2-phenylpyridine** +3H/D -e$^-$]$^+$+ [**2-phenylpyridine** -H +4H/D -e$^-$]$^+$}, 100%; 159.0 {[**2-phenylpyridine** -+4H/D -e$^-$]$^+$+ [**2-phenylpyridine** -H +5H/D -e$^-$]$^+$}, 48%; 160.0 {[**2-phenylpyridine** -+5H/D -e$^-$]$^+$+ [**2-phenylpyridine** -H +6H/D -e$^-$]$^+$}, 12%.
N. of deuterium incorporated calculated by NMR: 3.3. N. of deuterium incorporated calculated by MS: 3.1.

ESI-4. Scope of substrates.

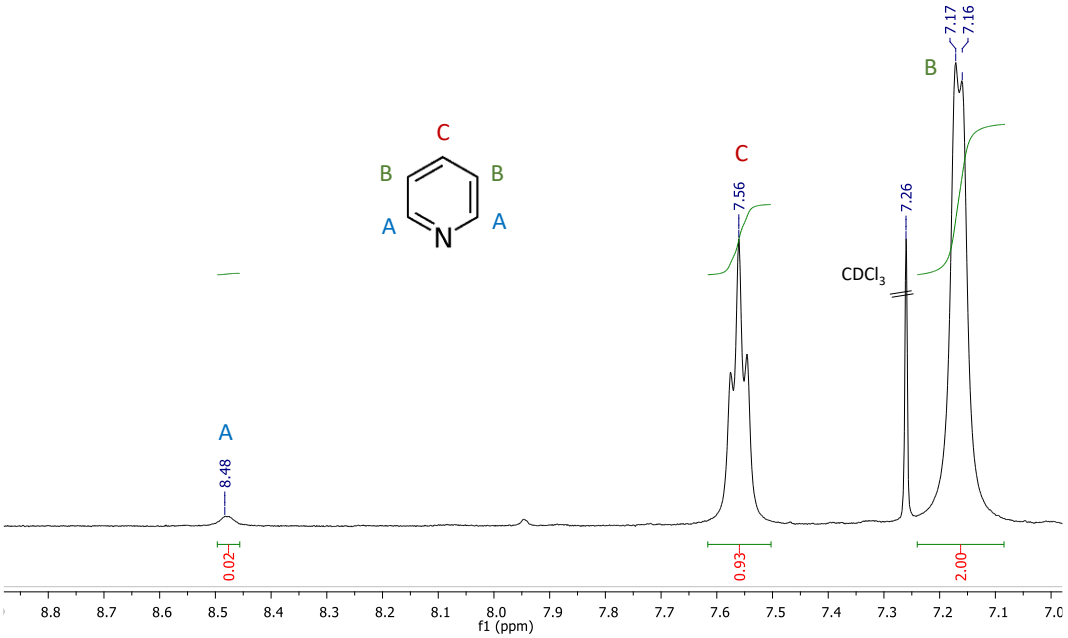

Figure S9. [1]H NMR spectrum of pyridine (**4**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

[1]H NMR (400 MHz, $CDCl_3$, 7.26 ppm): δ 8.48 (broad, A, 0.02H), 7.56 (t, C, 0.93H), 7.17 (d, B, 2H). Deuterium incorporation was expected at *δ* 8.48 ppm. Isotopic enrichment values were determined against the integral at *δ* 7.17.

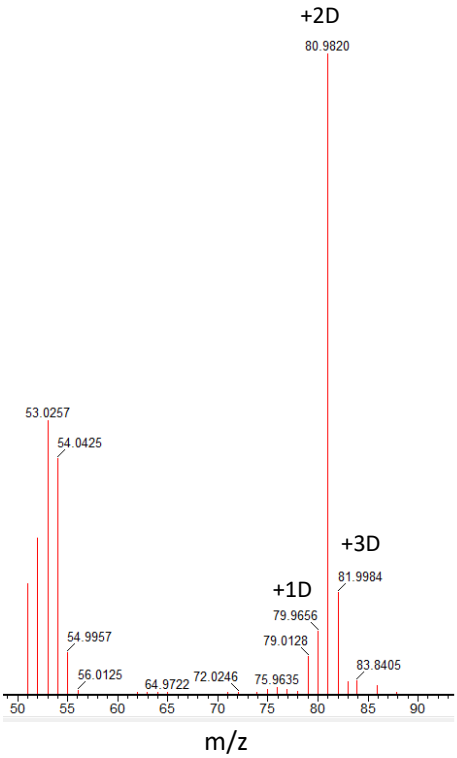

Figure S10. MS spectrum of pyridine (**4**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (EI, positive mode, $CHCl_3$): 80.0 [**4** +H/D – e^-]$^+$, 10%; 81.0 [**4** +2H/D – e^-]$^+$, 100%; 82.0 [**4** +H/D – e^-]$^+$, 16%. N. of deuterium incorporated calculated by NMR: 2.1. N. of deuterium incorporated calculated by MS: 2.1.

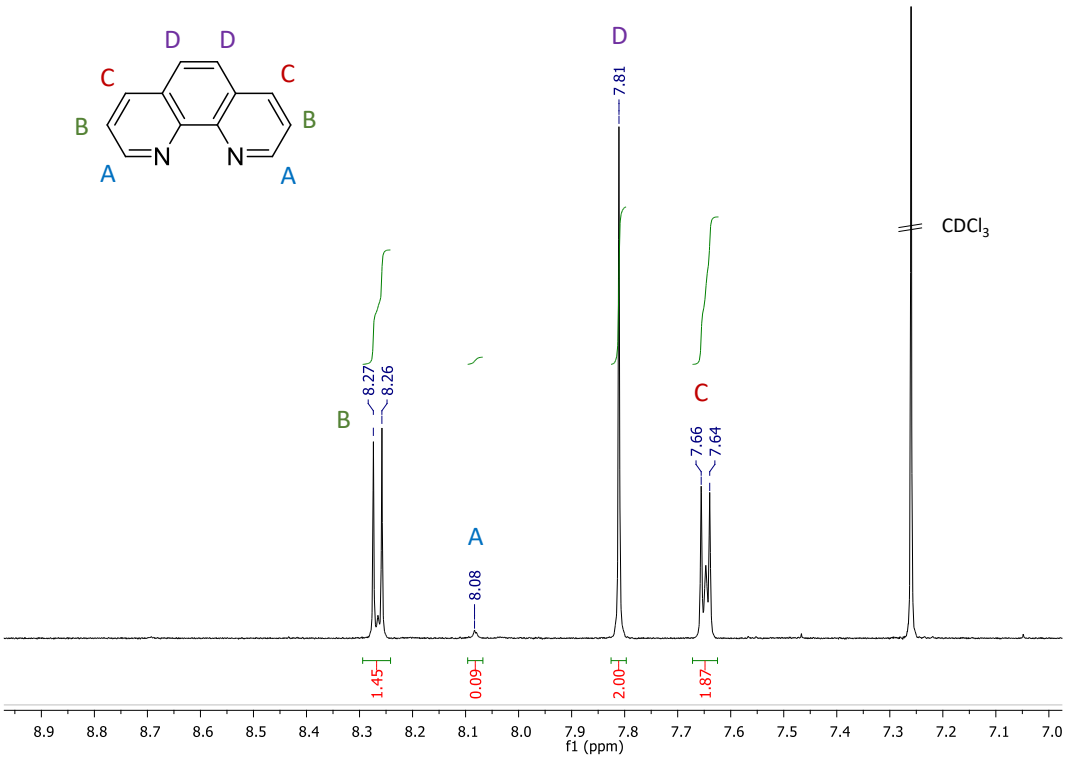

Figure S11. ^{1}H NMR spectrum of phenanthroline (**5**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm): δ 8.27 (d, B, 1.45H), 8.08 (b, A, 0.09H), 7.81 (s, D, 2H), 7.65 (d+s, C, 1.87H). Deuterium incorporation was expected at *δ* 8.08 ppm. Assuming that D uptake was of 3.7 as determined by MS, isotopic enrichment values were determined by the relative values of the NMR integrals.

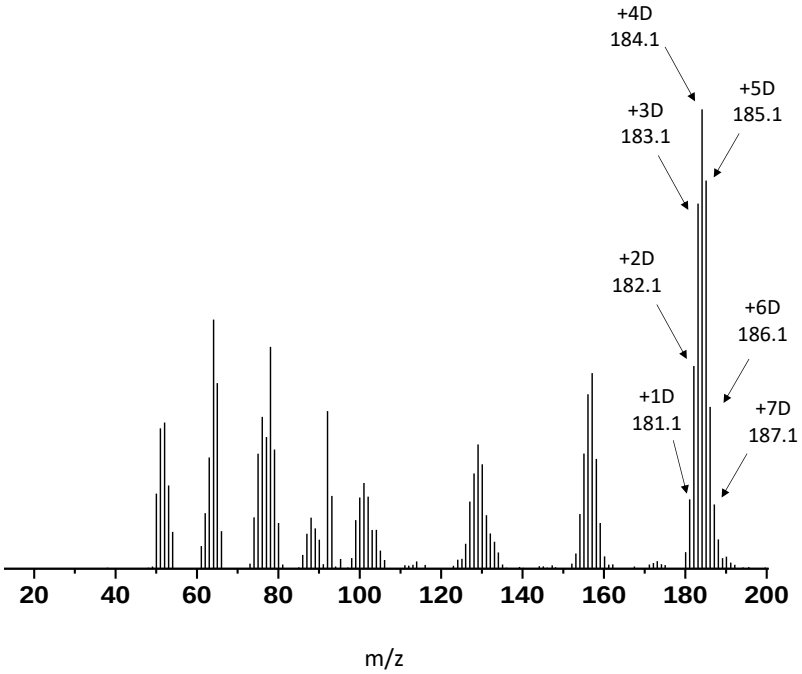

Figure S12. MS spectrum after deuteration of phenanthroline (**5**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (EI, positive mode, $CHCl_3$): 181.1 [**5** +H/D – e^{-}]$^{+}$, 15%; 182.1 [**5** +2H/D – e^{-}]$^{+}$, 45%; 183.1 [**5** +3H/D – e^{-}]$^{+}$, 80%; 184.1 [**5** +4H/D – e^{-}]$^{+}$, 100%; 185.1 [**5** +5H/D – e^{-}]$^{+}$, 84%; 186.1 [**5** +6H/D – e^{-}]$^{+}$, 35%; 187.1 [**5** +7H/D – e^{-}]$^{+}$, 14%.
N. of deuterium incorporated calculated by NMR: 2.7. N. of deuterium incorporated calculated by MS: 3.7.

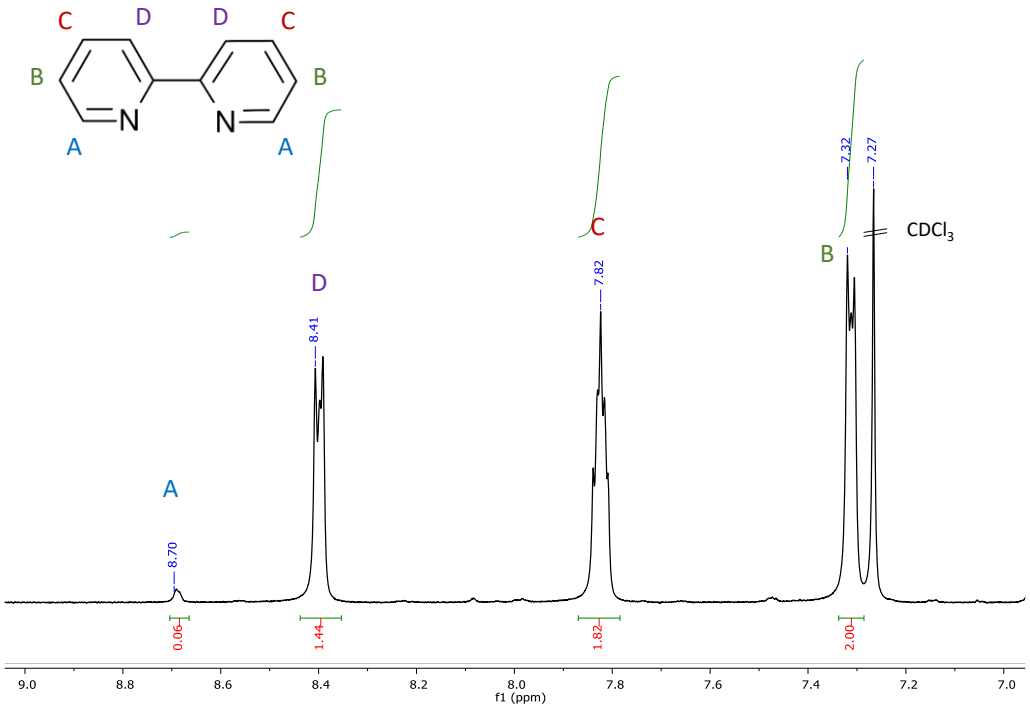

Figure S13. ^{1}H NMR spectrum of 2,2'-bipyridyl (**6**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm): δ 8.69 (broad, A, 0.06H), 8.39 (d+s, D, 1.44H), 7.82 (m, C, 1.82H), 7.31 (s+s, B, 2H). Deuterium incorporation was expected at *δ* 8.70 ppm. Assuming that D uptake was of 3.2 as determined by MS, isotopic enrichment values for **6** were determined by the relative values of the NMR integrals.

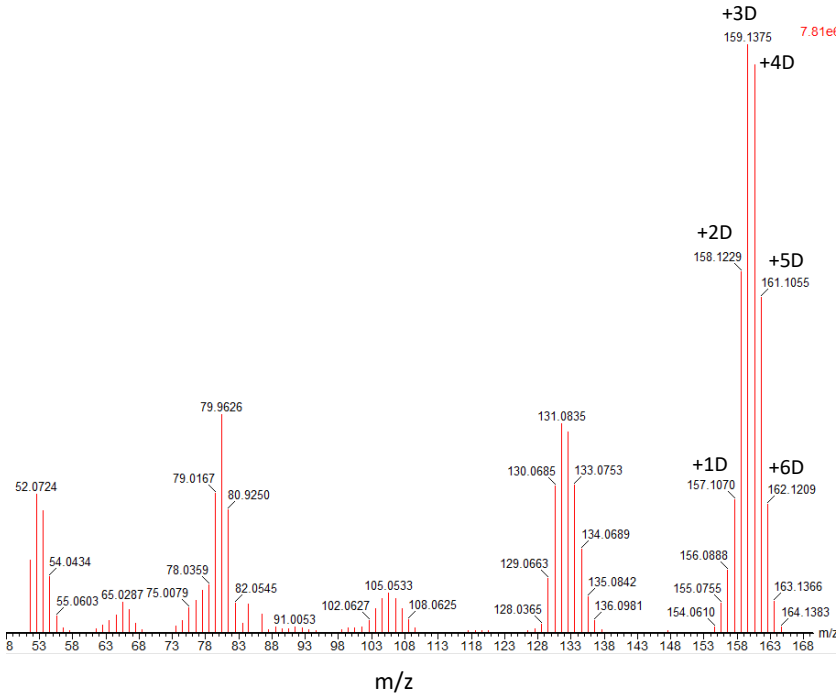

Figure S14. MS spectrum after deuteration of 2,2'-bipyridyl (**6**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (EI, positive mode, $CHCl_3$): 155.1 [**6** -H -e$^-$]$^+$, 5%; 156.1 {[**6** -e$^-$]$^+$ + [**6** -H +H/D -e$^-$]$^+$}, 10%; 157.1 {[**6** +H/D -e$^-$]$^+$ + [**6** -H +2H/D -e$^-$]$^+$}, 22%; 158.1 {[**6** +2H/D -e$^-$]$^+$ + [**6** -H +3H/D -e$^-$]$^+$}, 61%; 159.1 {[**6** +3H/D -e$^-$]$^+$ + [**6** -H +4H/D -e$^-$]$^+$}, 100%; 160.1 {[**6** +4H/D -e$^-$]$^+$ + [**6** -H +5H/D -e$^-$]$^+$}, 97%; 161.1 {[**6** +5H/D -e$^-$]$^+$ + [**6** -H +6H/D -e$^-$]$^+$}, 57%; 162.1 {[**6** +6H/D -e$^-$]$^+$ + [**6** -H +7H/D -e$^-$]$^+$}, 22%.
N. of deuterium incorporated calculated by NMR: 2.8. N. of deuterium incorporated calculated by MS: 3.2.

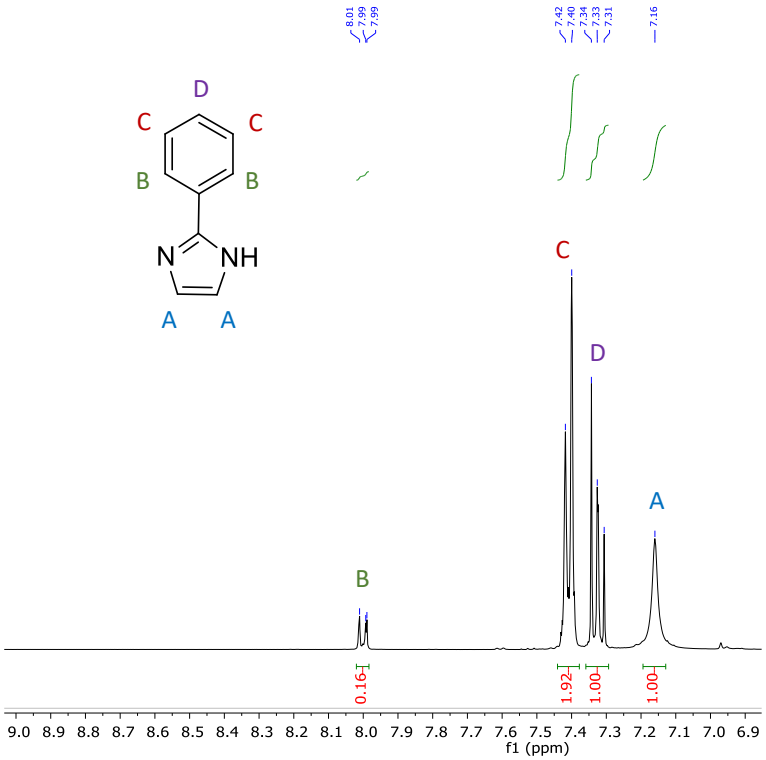

Figure S15. [1]H NMR spectrum of 2-phenylimidazole (**7**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

[1]H NMR (400 MHz, acetone-d_6, 2.05 ppm): δ 7.99 (d, B, 0.16H), 7.41 (d, C, 2H), 7.33 (t, D, 1H), 7.16 (broad, A, 1.00H). Deuterium incorporation was expected at *δ* 7.99 and *δ* 7.16 ppm. Isotopic enrichment values were determined against the integral at *δ* 7.33.

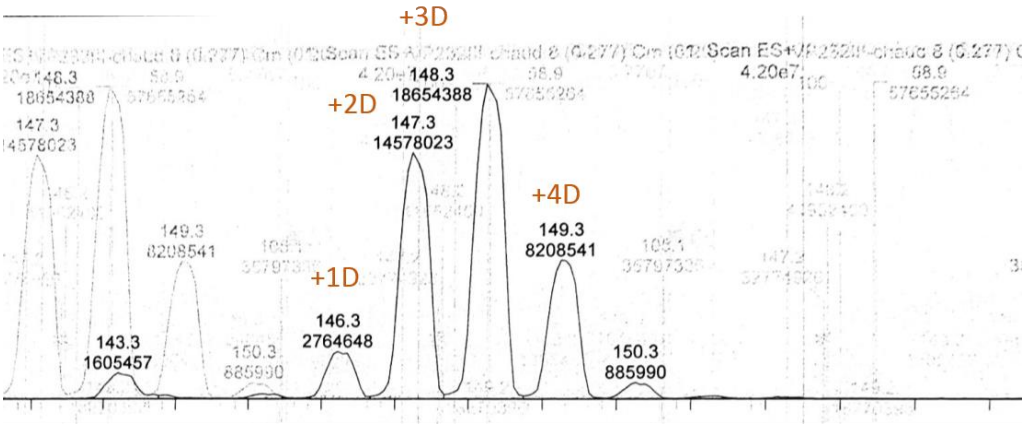

Figure S16. MS spectrum after deuteration of 2-phenylimidazole (**7**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (ESI, positive mode, acetone): 146.3 [**7** +H +H/D]$^+$, 15%; 147.3 [**7** +H +2H/D]$^+$, 78%; 148.3 [**7** +H +3H/D]$^+$, 100%; 149.3 [**7** +H +4H/D]$^+$, 44%; 150.3 [**7** +H +5H/D]$^+$, 5%.
N. of deuterium incorporated calculated by NMR: 2.8. N. of deuterium incorporated calculated by MS: 2.8.

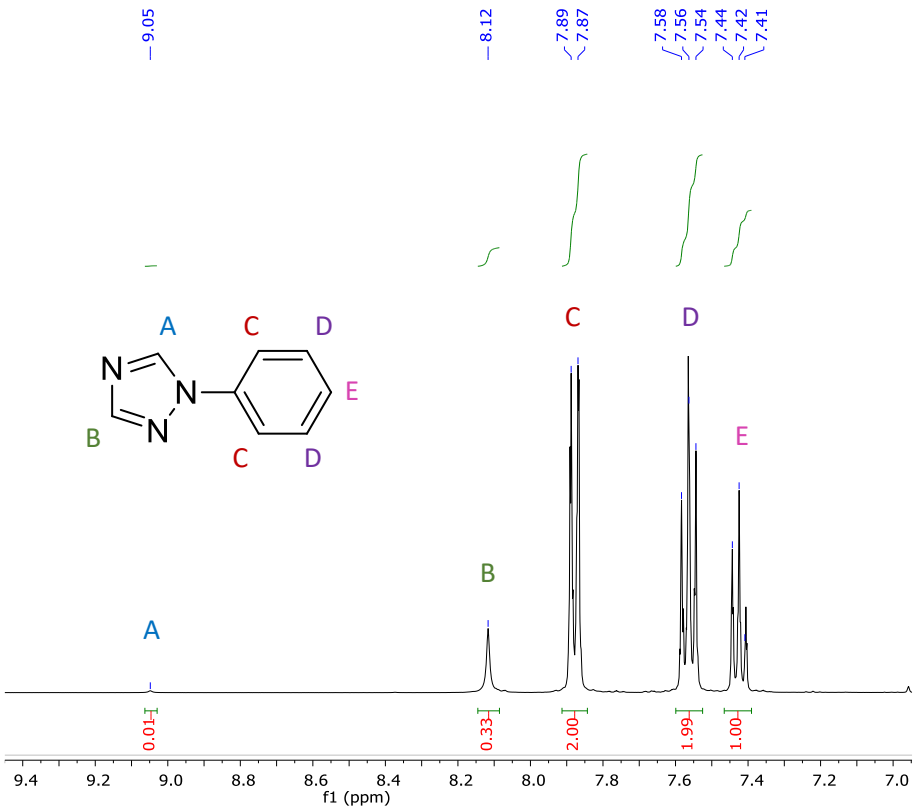

Figure S17. ^{1}H NMR spectrum of 1-phenyl-1*H*-1,2,4-triazole (**8**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

^{1}H NMR (400 MHz, acetone-d$_6$, 2.05 ppm): δ 9.05 (broad, A, 0.01H), 8.12 (broad, B, 0.33H), 7.88 (d, C, 2H), 7.56 (d, D, 2H), 7.42 (t, E, 1H). Deuterium incorporation was expected at *δ* 9.05 and *δ* 8.12 ppm. Isotopic enrichment values were determined against the integral at *δ* 7.42.

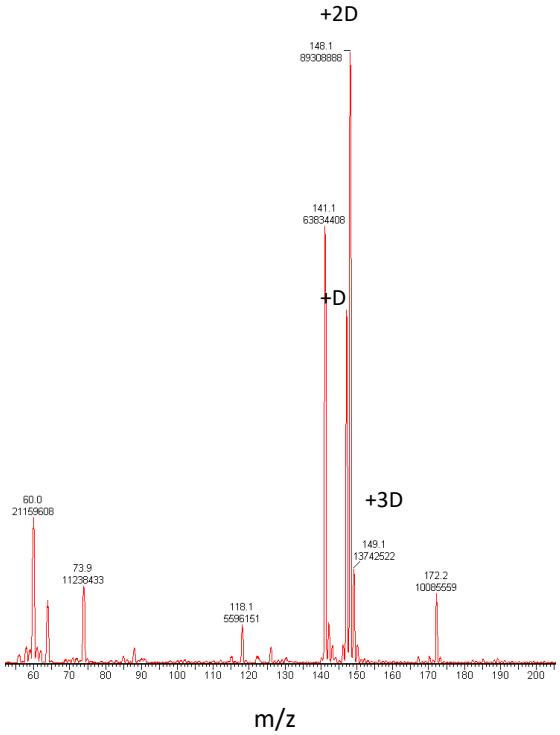

Figure S18. MS spectrum after deuteration of 1-phenyl-1*H*-1,2,4-triazole (**8**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (ESI, positive mode, acetone): 147.1 [**8** +H +H/D]$^{+}$, 57%; 148.1 [**8** +H +2H/D]$^{+}$, 100%; 149.1 [**8** +H +3H/D]$^{+}$, 5%; 150.1 [**8** +H +4H/D]$^{+}$, 2%.
N. of deuterium incorporated calculated by NMR: 1.7. N. of deuterium incorporated calculated by MS: 1.7.

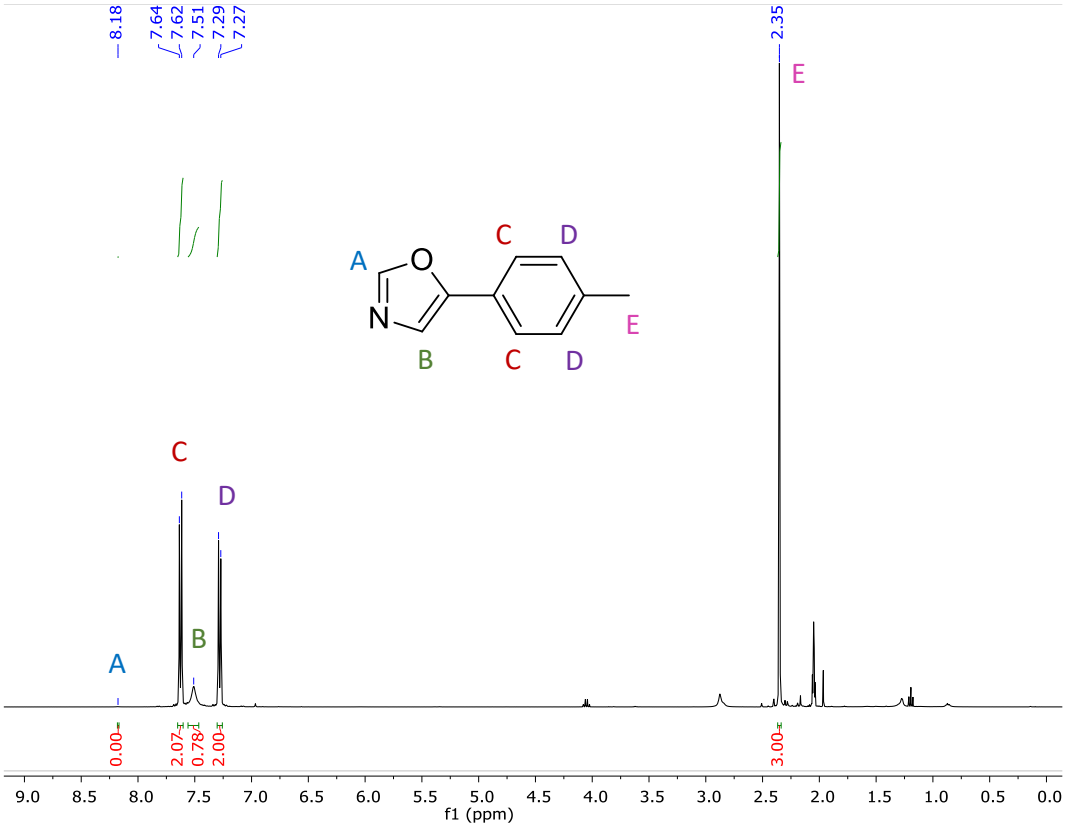

Figure S19. [1]H NMR spectrum of 5-(4-methylphenyl)-1,3-oxazole (**9**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

[1]H NMR (400 MHz, acetone-d_6, 2.05 ppm): δ 7.64 (d, C, 2H), 7.51 (broad, B, 0.78H), 7.28 (d, D, 2H), 2.35 (s, E, 3H). Deuterium incorporation was expected at *δ* 8.18 and *δ* 8.51 ppm. Isotopic enrichment values were determined against the integral at *δ* 2.35.

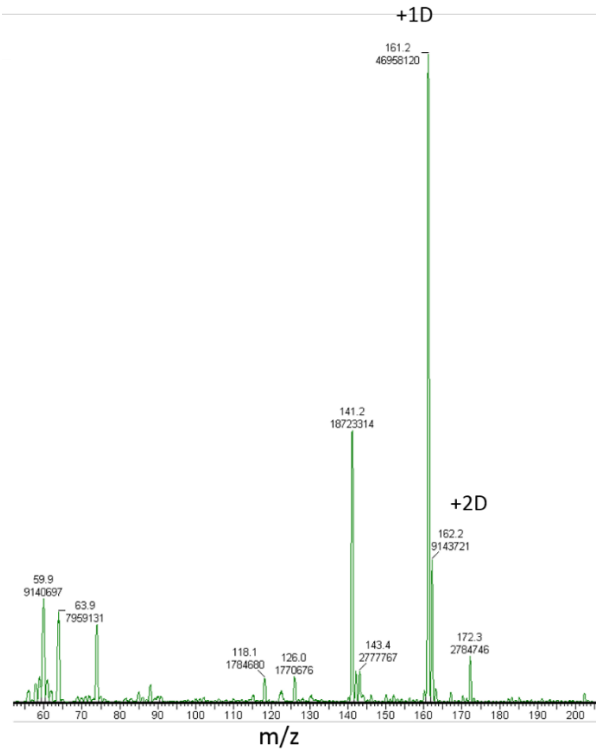

Figure S20. MS spectrum after deuteration of 5-(4-methylphenyl)-1,3-oxazole (**9**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (ESI, positive mode, acetone): 161.2 [**9** +H +H/D]$^+$, 100%; 162.2 [**9** +H +2H/D]$^+$, 8%; 163.2 [**9** +H +3H/D]$^+$, 1%.

N. of deuterium incorporated calculated by NMR: 1.2. N. of deuterium incorporated calculated by MS: 1.1.

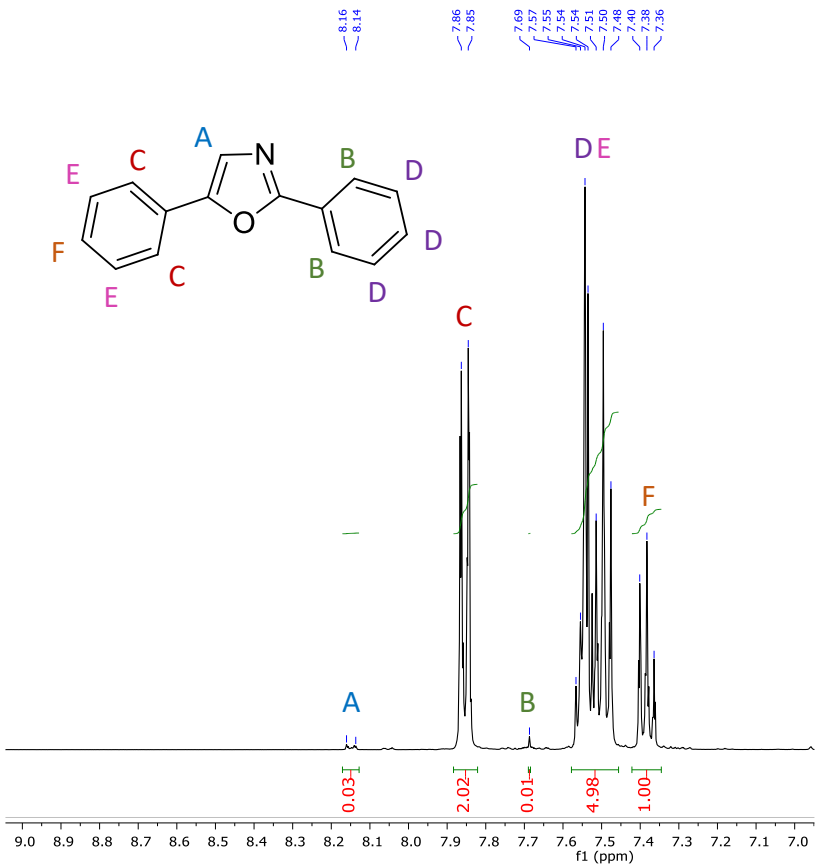

Figure S21. [1]H NMR spectrum of 2,5-diphenyl-1,3-oxazole (**10**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

^{1}H NMR (400 MHz, acetone-d$_6$, 2.05 ppm): δ 8.15 (d, A, 0.03H), 7.86 (d, C, 2H), 7.69 (s, B, 0.01H), 7.55 (m, D, 3H), 7.50 (t, E, 2H), 7.38 (t, F, 1H). Deuterium incorporation was expected at δ 8.15 and δ 8.79 ppm. Isotopic enrichment values were determined against the integral at δ 7.38.

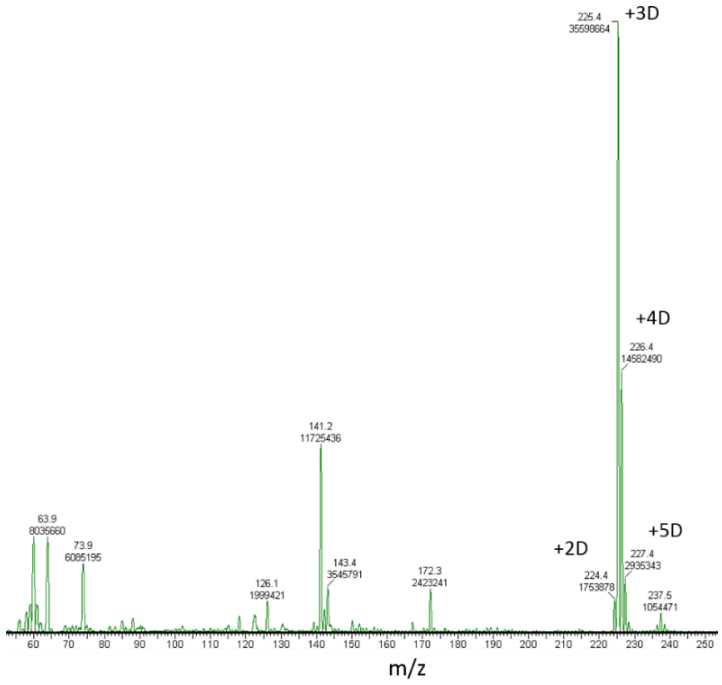

Figure S22. MS spectrum of 2,5-diphenyl-1,3-oxazole (**10**) after 24 h of reaction at 55 ºC in THF, under 2 bar of D_2 and using NPs **2** as catalyst.

MS (ESI, positive mode, acetone): 224.4 [**10** +H +2H/D]$^+$, 5%; 225.4 [**10** +H +3H/D]$^+$, 100%; 226.4 [**10** +H +4H/D]$^+$, 41%; 227.4 [**10** +H +5H/D]$^+$, 8%.
N. of deuterium incorporated calculated by NMR: 3.0. N. of deuterium incorporated calculated by MS: 3.2.