ELECTRONIC SUPPLEMENTARY INFORMATION

An Iridium–SPO Complex as Bifunctional Catalyst for the Highly Selective Hydrogenation of Aldehydes†

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Contents

1. General procedures

All oxygen and moisture sensitive operations were carried out under an argon atmosphere using standard vacuum-line and Schlenk techniques. Solvents were purchased from Sigma-Aldrich as HPLC grade and dried by means of an MBraun MB SPS800 purification system. Bis(1,5-cyclooctadiene)di-μ-methoxydiiridium(I) and chloro(*tert*-butyl)phenylphosphine were purchased from Sigma-Aldrich. THF-d_8 was dried by distillation over Na/benzophenone under Ar and degassed by three freeze, pump, and thaw cycles. Chemical shifts of ^{1}H, ^{13}C and ^{31}P-NMR are reported in ppm, the solvent was used as internal standard. Signals are quoted as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets).

Nuclear Magnetic Resonance (NMR)

^{1}H, ^{13}C and ^{31}P spectra were recorded at the LCC-Toulouse on Bruker Avance 400 and 300 spectrometers.

X-ray Crystal Structure Determinations (CCDC: 1574554)

Crystals of **7** were obtained by slow evaporation of the resulting solution after the iridium complex **2** was treated with 5 bar of H_2 in acetonitrile at R.T. for 30 min. The measured crystal was prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data were collected at the LCC-Toulouse at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a Mo-Kα radiation (λ = 0.71073 Å) micro-source and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods using SHELXS97,[1] and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97[1] include in the softwares package WinGX.[2] The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography.[3] All hydrogens atoms were placed geometrically, and refined by using a riding model, excepted for the hydrogen Hy1 and Hy2 which were located by Fourier differences.

All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ where $P=(Fo^2+2Fc^2)/3$.

Drawing of molecules was performed with the program ORTEP32[4] with 40% probability displacement ellipsoids for non-hydrogen atoms.

2. Synthetic procedures

tert-Butyl(phenyl)phosphine oxide (1)

A rapidly stirred solution of chloro(*tert*-butyl)phenylphosphine (200.6 mg, 1 mmol) in THF (5 mL) was treated with degassed water (*ca*. 0.5 mL) at room temperature and the progress of the reaction was followed by $^{31}P\{^1H\}$ NMR (*ca*. 5 h, no solvent, 162 MHz, > 99 % s, 55 ppm). The solvent was removed completely and the residue left under vacuum overnight and then dried by azeotropic distillation with toluene (2 x 10 mL). The residue was washed with hexane (2 x 2 mL) and then dried under high vacuum giving the product as a free flowing white powder. Yield: 161 mg, 0.88 mmol, 88 %.

^1H NMR (500 MHz, $CDCl_3$): δ 7.71 – 7.61 (m, 2H, $\underline{H}_{Ar}$), 7.57 – 7.63 (m, 1H, $\underline{H}_{Ar}$), 7.51 – 7.40 (m, 2H, $\underline{H}_{Ar}$), 7.01 (d, $^1J_{HP}$ = 453.1 Hz, 1H), 1.14 (d, $^3J_{PH}$= 16.6 Hz, 9H, $C(C\underline{H}_3)_3$).

^{31}P NMR (202 MHz, $CDCl_3$): δ 50.59 (d, $^1J_{PH}$ = 453.0)

^1H, ^{31}P, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data were consistent with those previously reported.[5]

[(1,2,5,6-η)-1,5-Cyclooctadiene][*tert*-butyl(phenyl)phosphinito-*tert*-butyl(phenyl)phosphinous acid]iridium (2)

tert-butyl(phenyl)phosphine oxide (72.9 mg, 0.4 mmol) and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer ($[Ir(OMe)(COD)]_2$) (66.3 mg, 0.1 mmol) were dissolved in THF (16 mL). 16 μL of H_2O were then added and the solution was stirred overnight. The solvent was removed under vacuum and the residue was dissolved in a mixture ether-pentane 1:2. The resulting solution was concentrated under vacuum and kept overnight in the freezer at -30 ºC, obtaining red crystals of **2**. 76 mg, 0.114 mmol, 57 %.

^{1}H NMR (400 MHz, THF-d^8): δ 7.74 – 7.64 (m, 4H, H_{Ar}), 7.38 (td, J = 7.8, 7.3, 1.7 Hz, 4H, H_{Ar}), 7.34 – 7.27 (m, 2H, H_{Ar}), 4.38 (t, J = 7.0 Hz, 2H, CH_{COD}), 4.03 (dd, J = 8.7, 4.7 Hz, 2H, CH_{COD}), 2.15 – 1.99 (m, 2H, $CH_{2(COD)}$), 1.96 – 1.83 (m, 2H, $CH_{2(COD)}$), 1.64 – 1.49 (m, 2H, $CH_{2(COD)}$), 1.32 (d, $^3J_{PH}$= 13.3 Hz, 18H, $C(C\underline{H}_3)_3$).

^{31}P{^{1}H} NMR (162 MHz, THF-d^8): δ 88.72 (s).

^{13}C{^{1}H} NMR (100 MHz, THF-d^8): δ 142.0 (m, virtual, J_{PP} (approx.) = 23 Hz, Δδ (approx.) = 0.008 ppm, J_{PC} (approx.) = 45.6 Hz, C_{Ar}), 131.0 (t, J_{PC}= 4.2 Hz, C_{Ar}), 129.5 (s, C_{Ar}), 128.3 (t, J_{PC}= 4.3 Hz, C_{Ar}), 88.3 (t, J_{PC} = 3.3 Hz, CH_{COD}), 71.3 (t, J_{PC} = 8.6 Hz, CH_{COD}), 40.8 (m, virtual, J_{PP} (approx.) = 23 Hz, Δδ (approx.) = 0.008 ppm, J_{PC} (approx.) = 35.0 Hz, $\underline{C}(CH_3)_3$), 37.0 (t, J_{PC} = 1.9 Hz, $CH_{2(COD)}$), 28.2 (t, J_{PC} = 2.5 Hz, $CH_{2(COD)}$), 27.0 (br s, $C(\underline{C}H_3)_3$).

^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR data were consistent with those previously reported.[6]

3. Catalytic hydrogenation

Catalytic experiments were performed in a HEL 24–multireactor (volume of the tubes 1.5 mL). In a typical experiment, 0.00125 mmol of **1** in 0.75 mL of THF (as a standard solution, freshly prepared

prior to use) was mixed with 3.75 mmol of substrate in 1.5 mL vials and the reactor was sealed under argon atmosphere in a glove box. The reactor was then pressurized with 5 bar of hydrogen and depressurized three times to purge and finally pressurized to the required pressure (5 or 10 bar). The reactor was stirred the required time for each substrate at room temperature. The reactor was slowly depressurized and samples from each reaction were evaporated to dryness at 150 mbar using a rotary evaporator at room temperature. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR to determine the conversion and selectivity.

4. Reaction times for each substrate

Table S1 Hydrogenation of cinnamaldehyde.[a]

Entry	Time (h)	P (bar)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})
1	1	5	25	>99	750
2	**2.5**	**5**	**97**	**99:1 (UA:A)**	**2040[d]**
3	3	5	99	99:1 (UA:Al+A)	990
4	4.5	5	>99	>99	667
5	5	5	>99	99:1 (UA:A)	600

[a] Reagents and conditions: **2** (0.00125 mmol), substrate (3.75 mmol), THF (0.75 mL), 295 K.[b] Conversions and product identities were determined by ^1H NMR spectroscopy (average of two runs).[c] *UA = Unsaturated Alcohol, A = Saturated Alcohol, Al = Saturated Aldehyde.*[d] *Maximal* TOF.

Table S2 Hydrogenation of prenal (3-methyl-2-butenal).[a]

Entry	Time (h)	P (bar)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})
1	**5**	**5**	**38**	**99:1 (UA:A)**	**228**
2	18	5	60	96:4 (UA:A)	100
3	18	10	99	99:1 (UA:A)	165

[a] Reagents and conditions: **2** (0.00125 mmol), substrate (3.75 mmol), 10 bar H_2, THF (0.75 mL), 295 K.[b] Conversions and product identities were determined by ^1H NMR spectroscopy (average of two runs).[c] *UA = Unsaturated Alcohol, A = Saturated Alcohol, Al = Saturated Aldehyde.*

Table S3 Hydrogenation of *trans*-2-hexen-1-al.[a]

Entry	Time (h)	P (bar)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})
1	**5**	**5**	**94**	**97:3 (UA:A)**	**564**
2	18	5	>99	89:11 (UA:A)	167

[a] Reagents and conditions: **2** (0.00125 mmol), substrate (3.75 mmol), 5 bar H_2, THF (0.75 mL), 295 K.[b] Conversions and product identities were determined by ^{1}H NMR spectroscopy (average of two runs).[c] *UA = Unsaturated Alcohol, A = Saturated Alcohol, Al = Saturated Aldehyde.*

Table S4 Hydrogenation of *p*-nitrobenzaldehyde.[a]

Entry	Time (h)	P (bar)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})
1	4	5	48	>99	360
2	**5**	**5**	**>99**	**>99**	**600**

[a] Reagents and conditions: **2** (0.00125 mmol), substrate (3.75 mmol), 5 bar H_2, THF (0.75 mL), 295 K.[b] Conversions and product identities were determined by ^{1}H NMR spectroscopy (average of two runs).[c] *UA = Unsaturated Alcohol, A = Saturated Alcohol, Al = Saturated Aldehyde.*

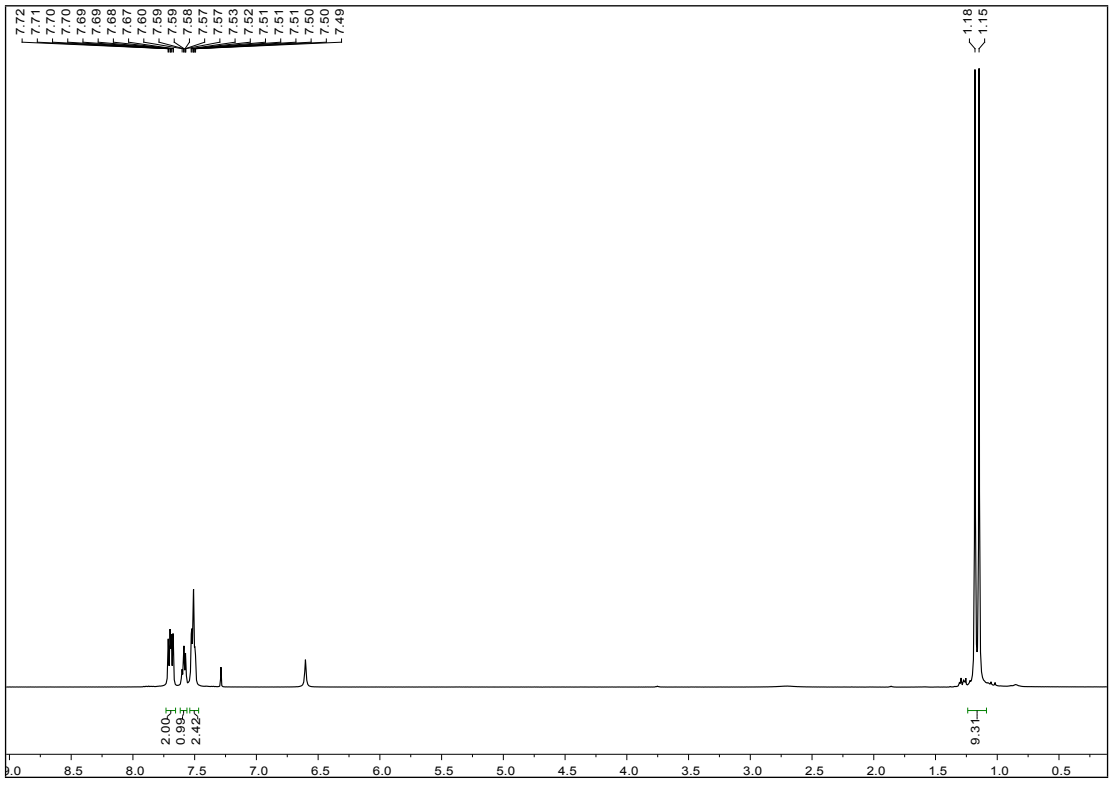
Table S5 Hydrogenation of furfural.[a]

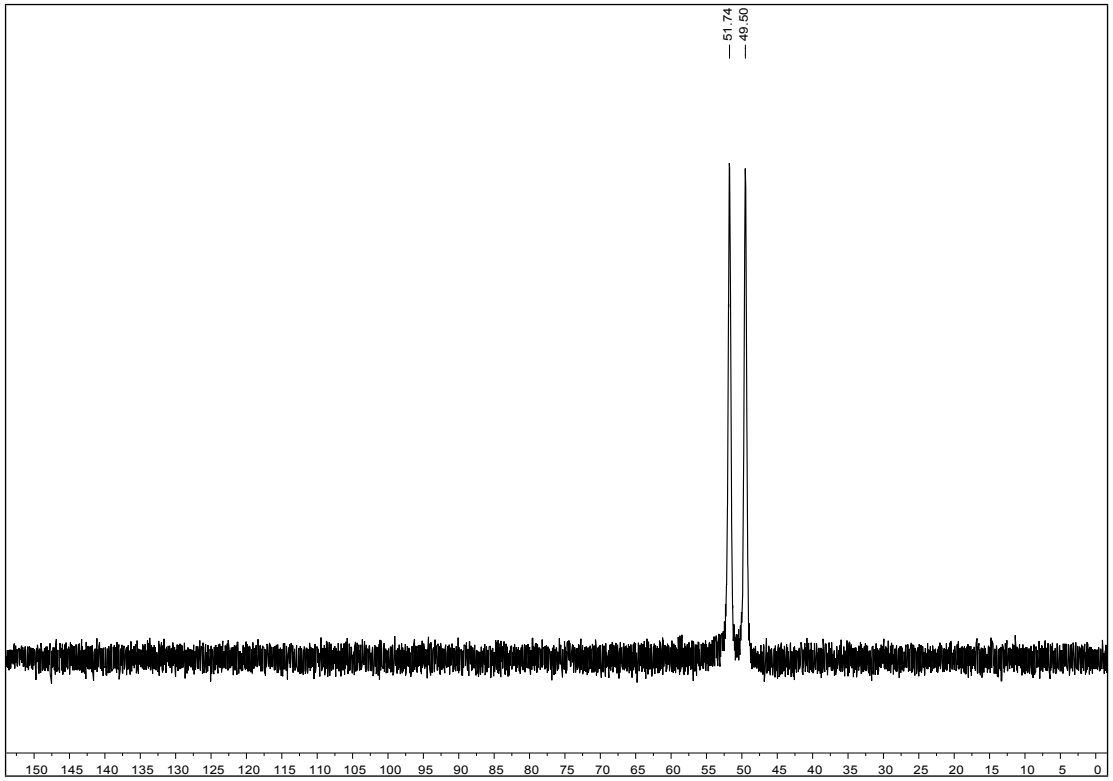
Entry	Time (h)	P (bar)	Conversion (%)[b]	Selectivity (%)[c]	TOF (h^{-1})
1	**3.5**	**5**	**85**	**>99**	**729**
2	4	5	96	>99	720
3	5	5	>99	>99	600

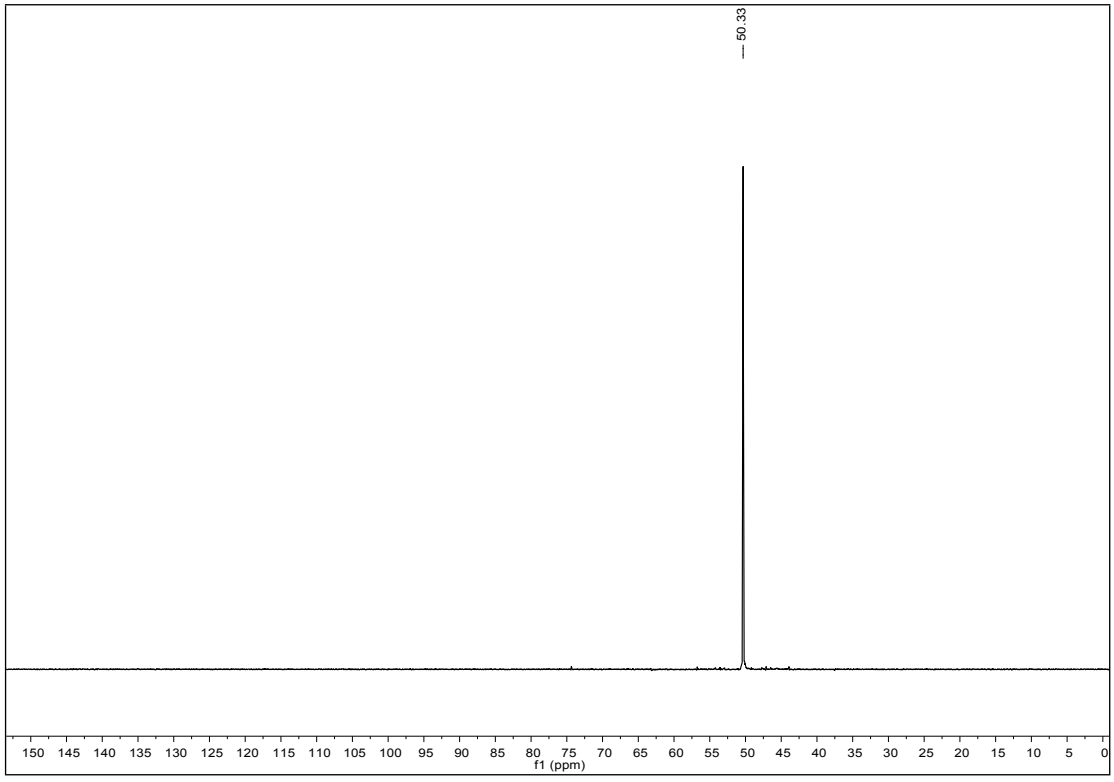
[a] Reagents and conditions: **2** (0.00125 mmol), substrate (3.75 mmol), 5 bar H_2, THF (0.75 mL), 295 K.[b] Conversions and product identities were determined by ^{1}H NMR spectroscopy (average of two runs).[c] *UA = Unsaturated Alcohol, A = Saturated Alcohol, Al = Saturated Aldehyde.*

5. NMR spectra of 1 and 2

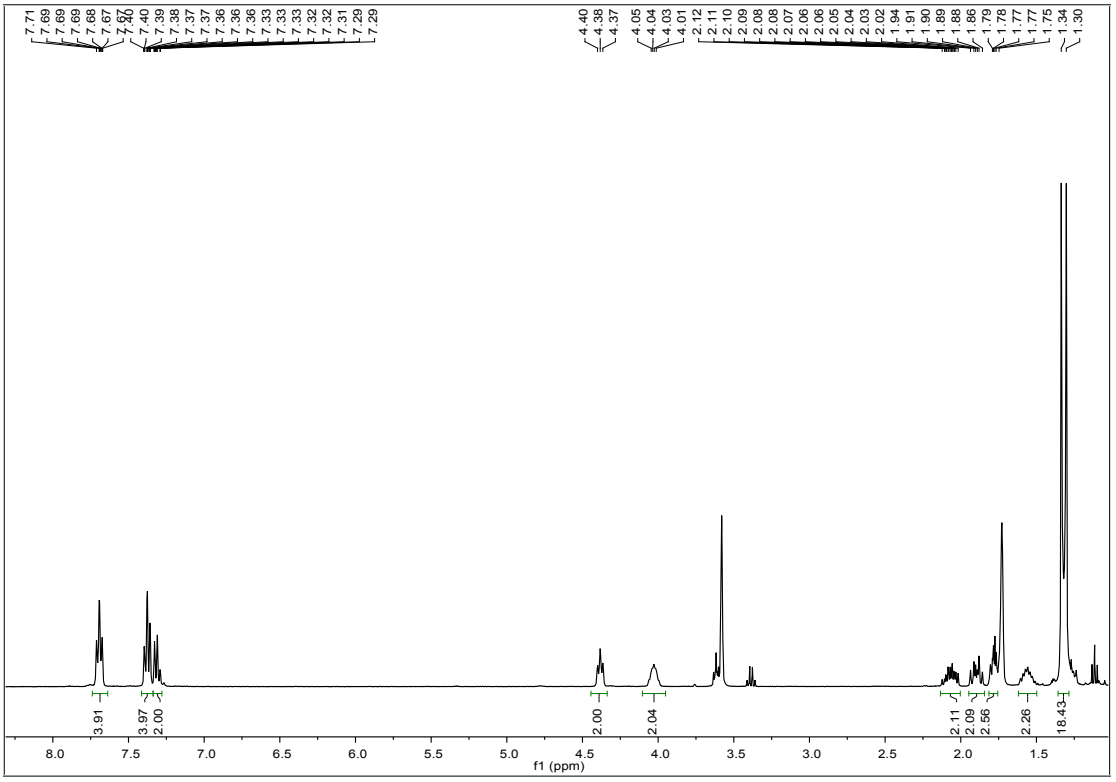
tert-Butyl(phenyl)phosphine oxide oxide (1)

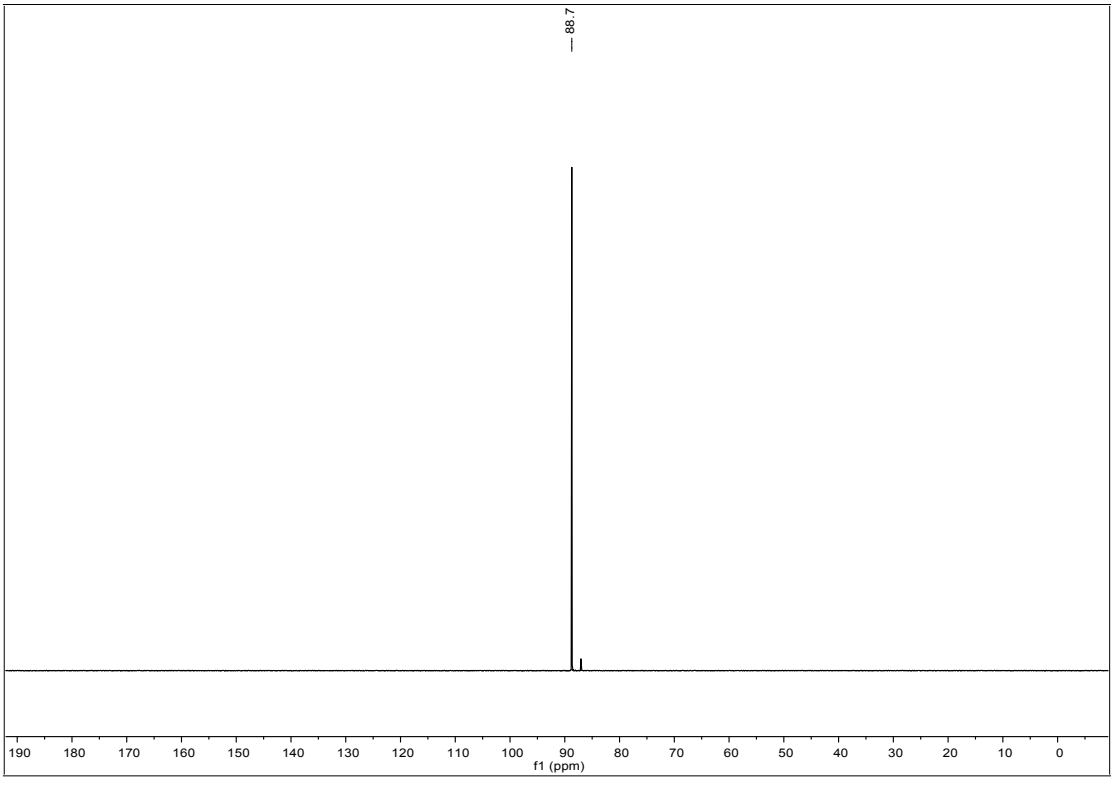





50.33
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

[(1,2,5,6-η)-1,5-Cyclooctadiene][*tert*-butyl(phenyl)phosphinito-*tert*-butyl(phenyl)phosphinous acid]iridium (2)





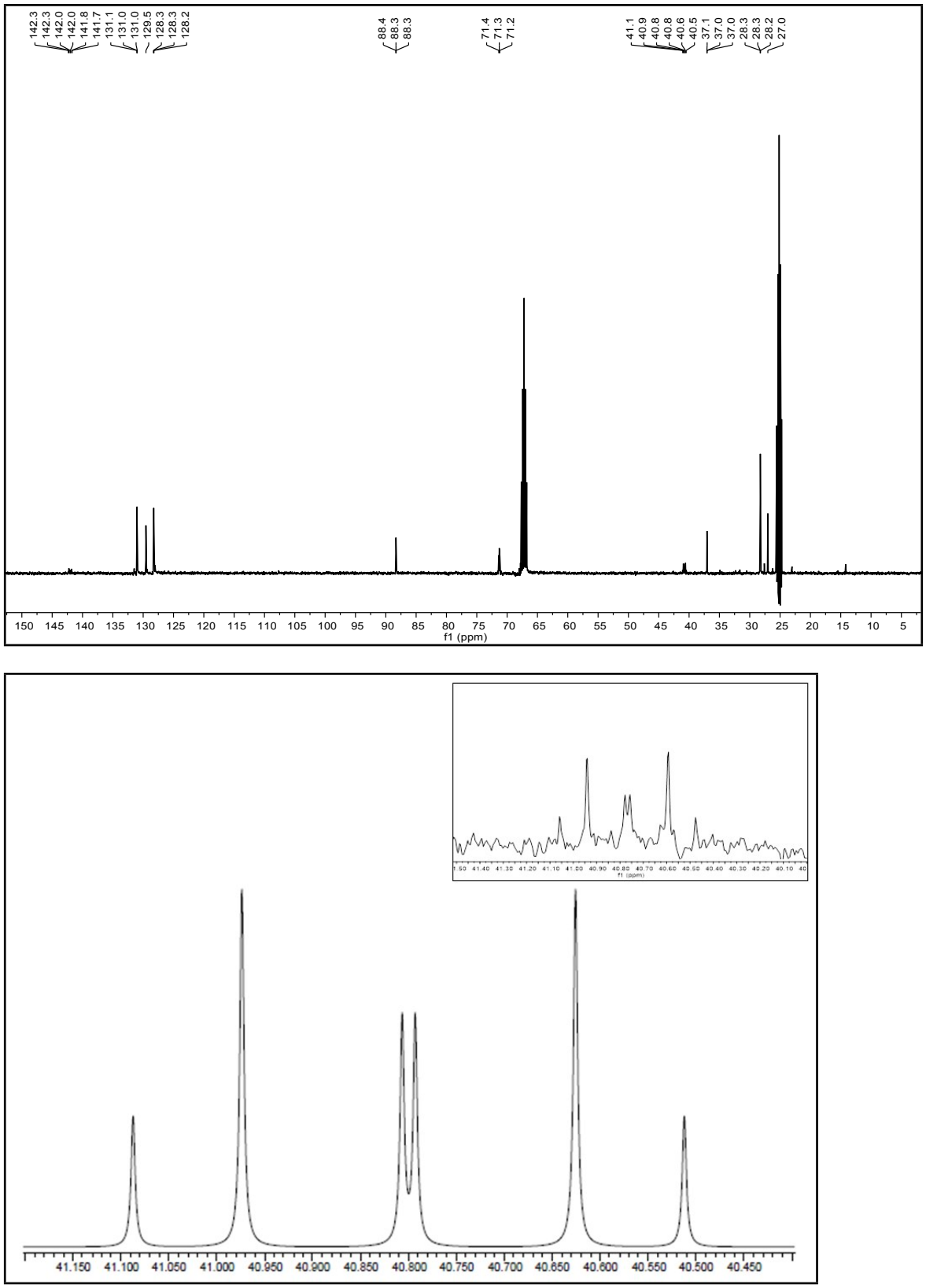


Figure S1. Simulation (software gnmr 5.1) of signal at 40.8 ppm. J_{PP} = 23 Hz, $\Delta\delta$ = 0.008 ppm, J_{PC} = 35 Hz.

6. NMR spectra for the study of hydrides

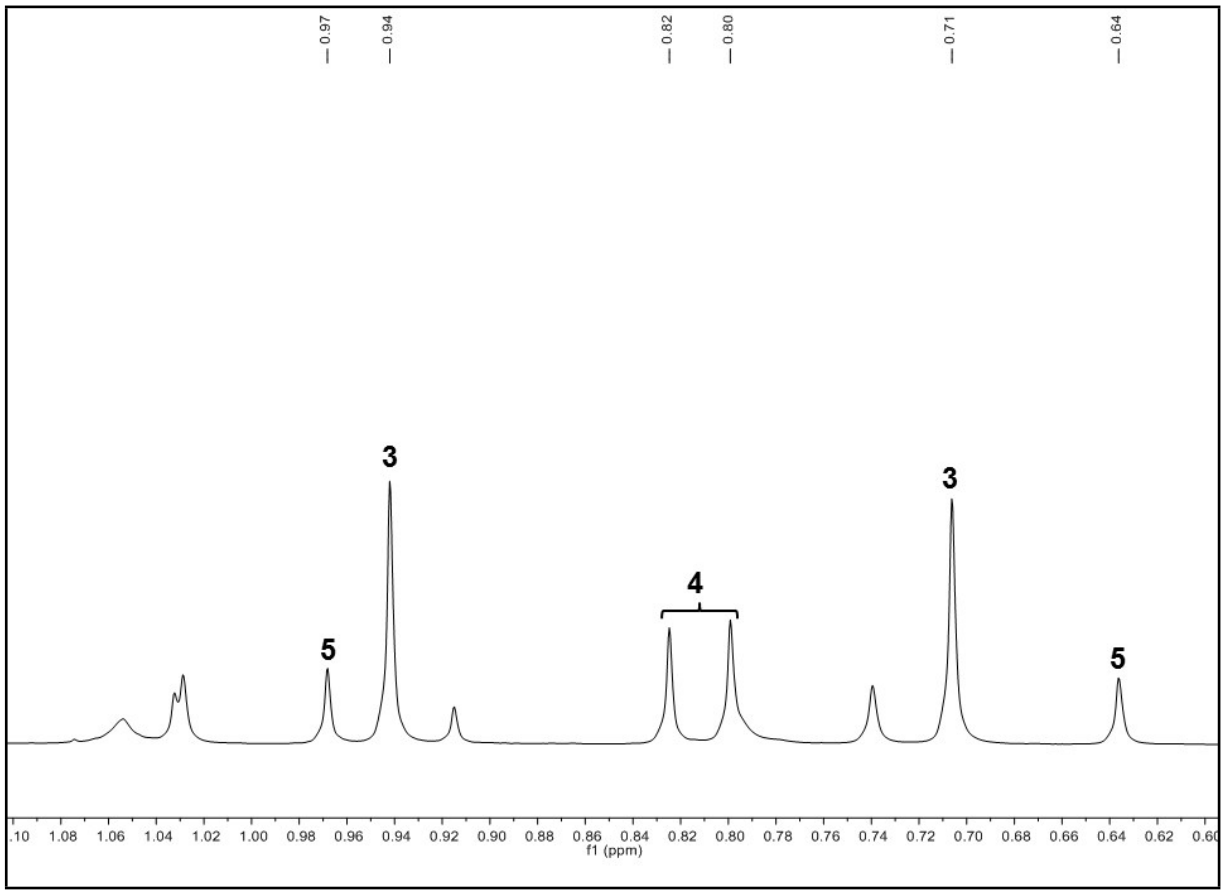


Figure S2. ^{1}H NMR spectrum (500 MHz) in the *tert*-butyl region after reaction of **2** with H_2 (5 bar) in CD_3CN.

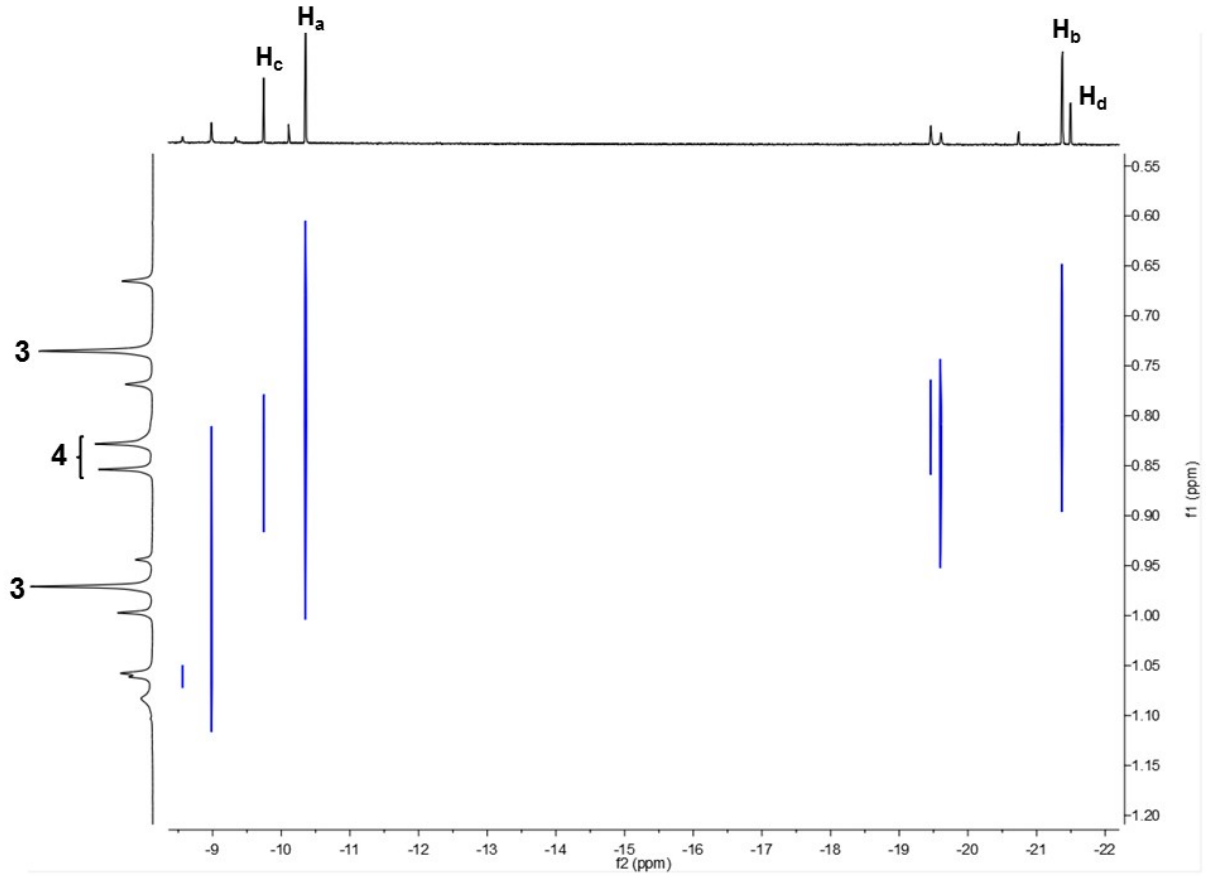


Figure S3. 2D NOESY NMR spectrum (500 MHz) in the *tert*-butyl and hydride regions after reaction of **2** with H_2 (5 bar) in CD_3CN.

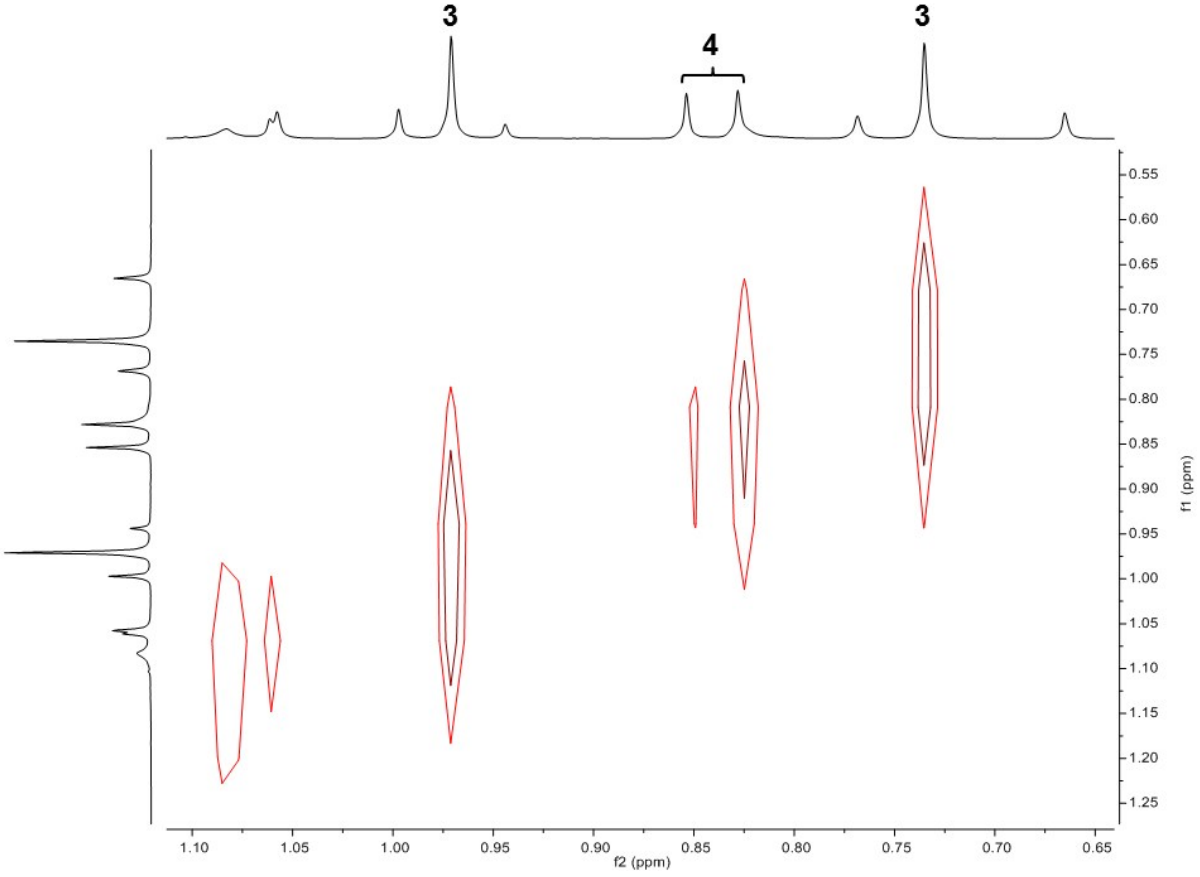


Figure S4. 2D NOESY NMR spectrum (500 MHz) in the *tert*-butyl region after reaction of **2** with H_2 (5 bar) in CD_3CN.

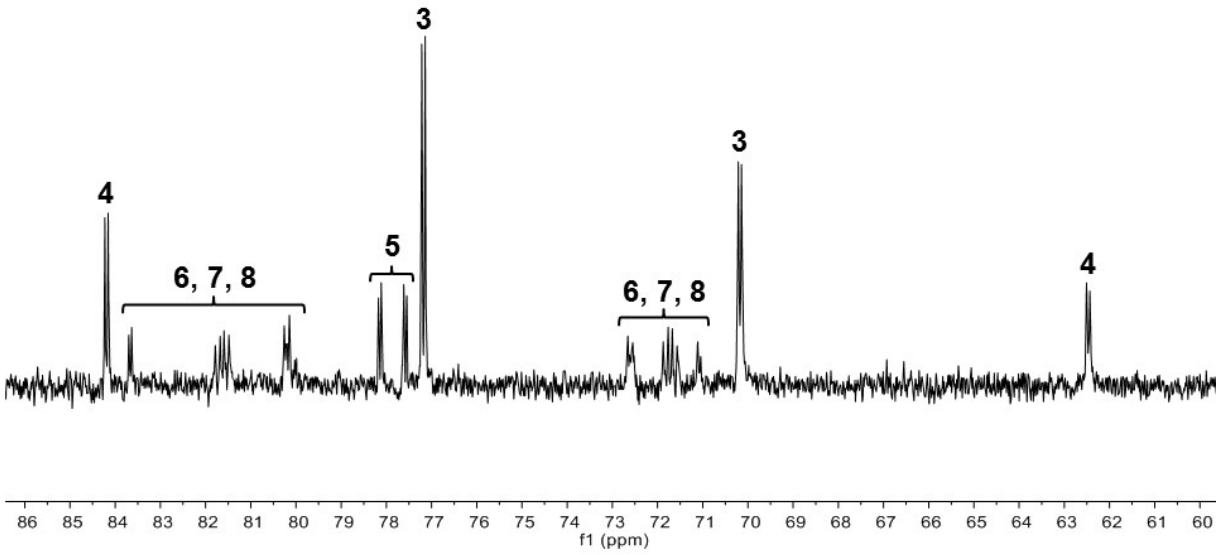


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (203 MHz) in the hydride region after reaction of **2** with H_2 (5 bar) in CD_3CN.

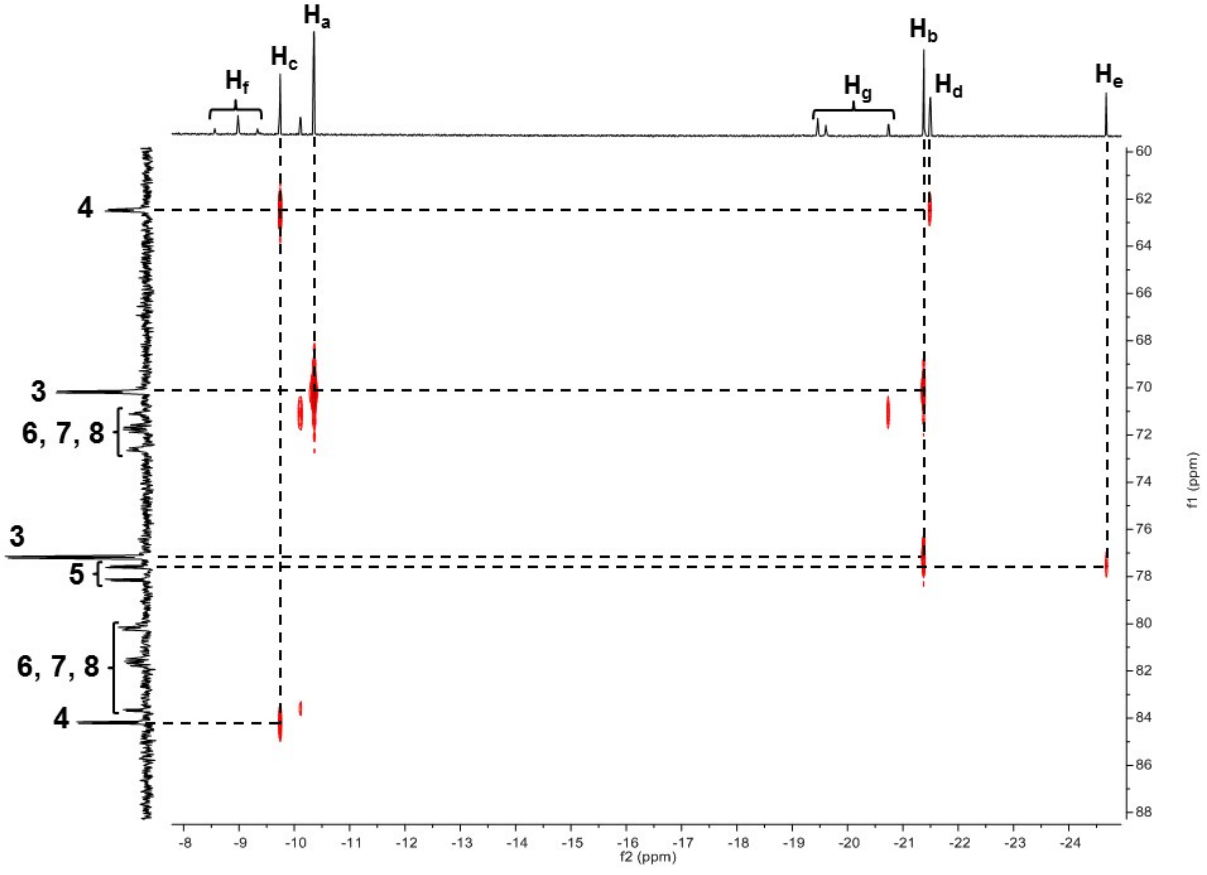


Figure S6. $^{1}H–^{31}P$ HMBC 2D NMR spectrum (500 MHz) in the hydride region after reaction of **2** with H_2 (5 bar) in CD_3CN. Lines are given as guide to the eyes.

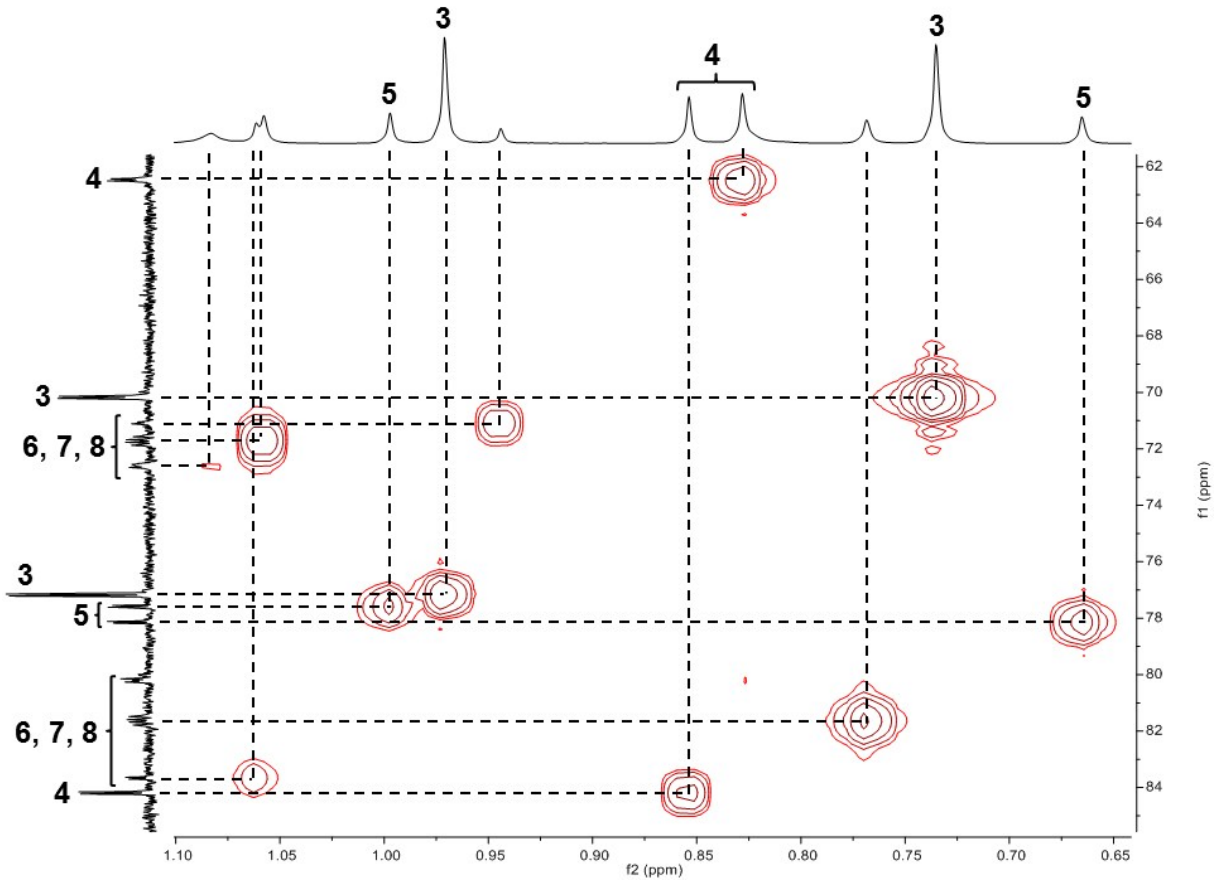
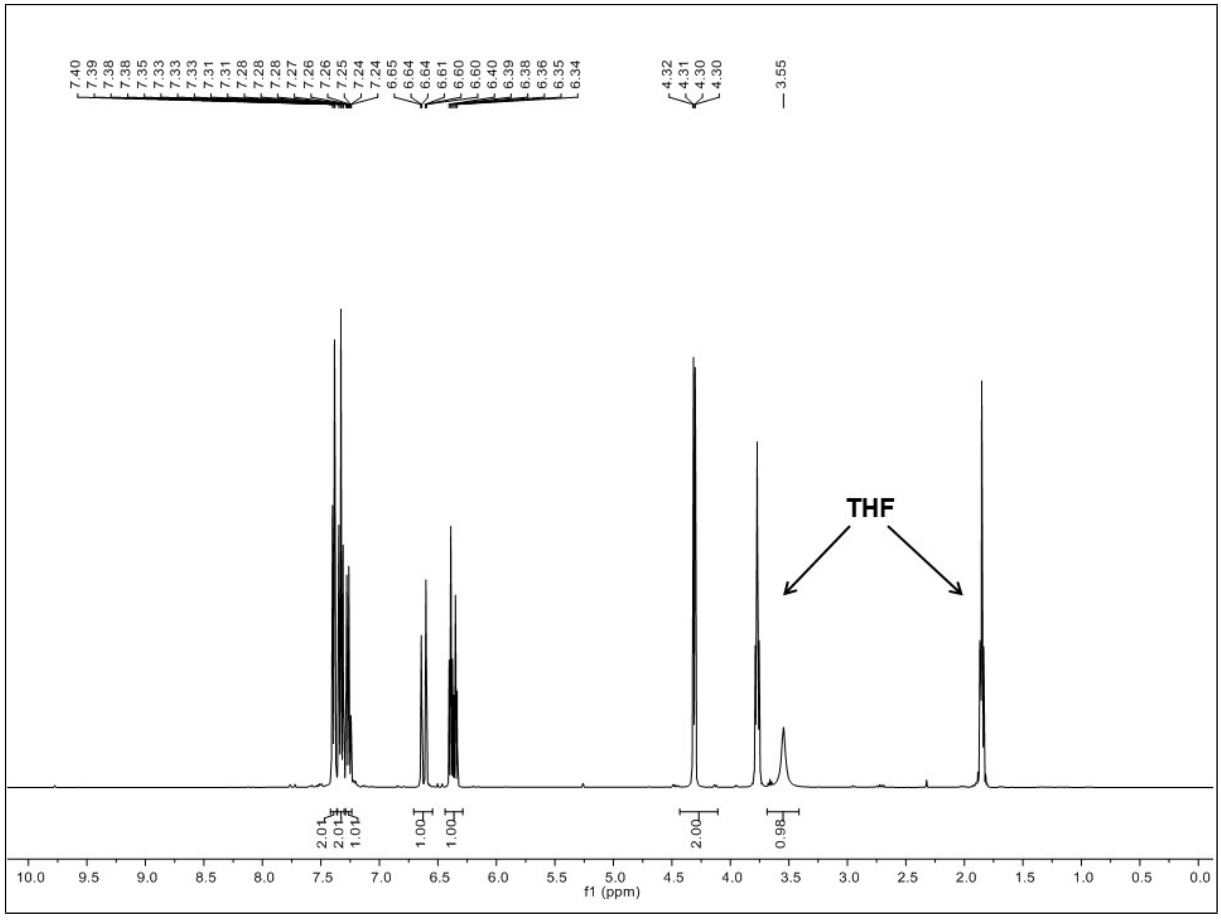


Figure S7. ^{1}H–^{31}P HMBC 2D NMR spectrum (500 MHz) in the *tert*-butyl region after reaction of **2** with H_2 (5 bar) in CD_3CN. Lines are given as guide to the eyes.

7. NMR spectra of reaction products

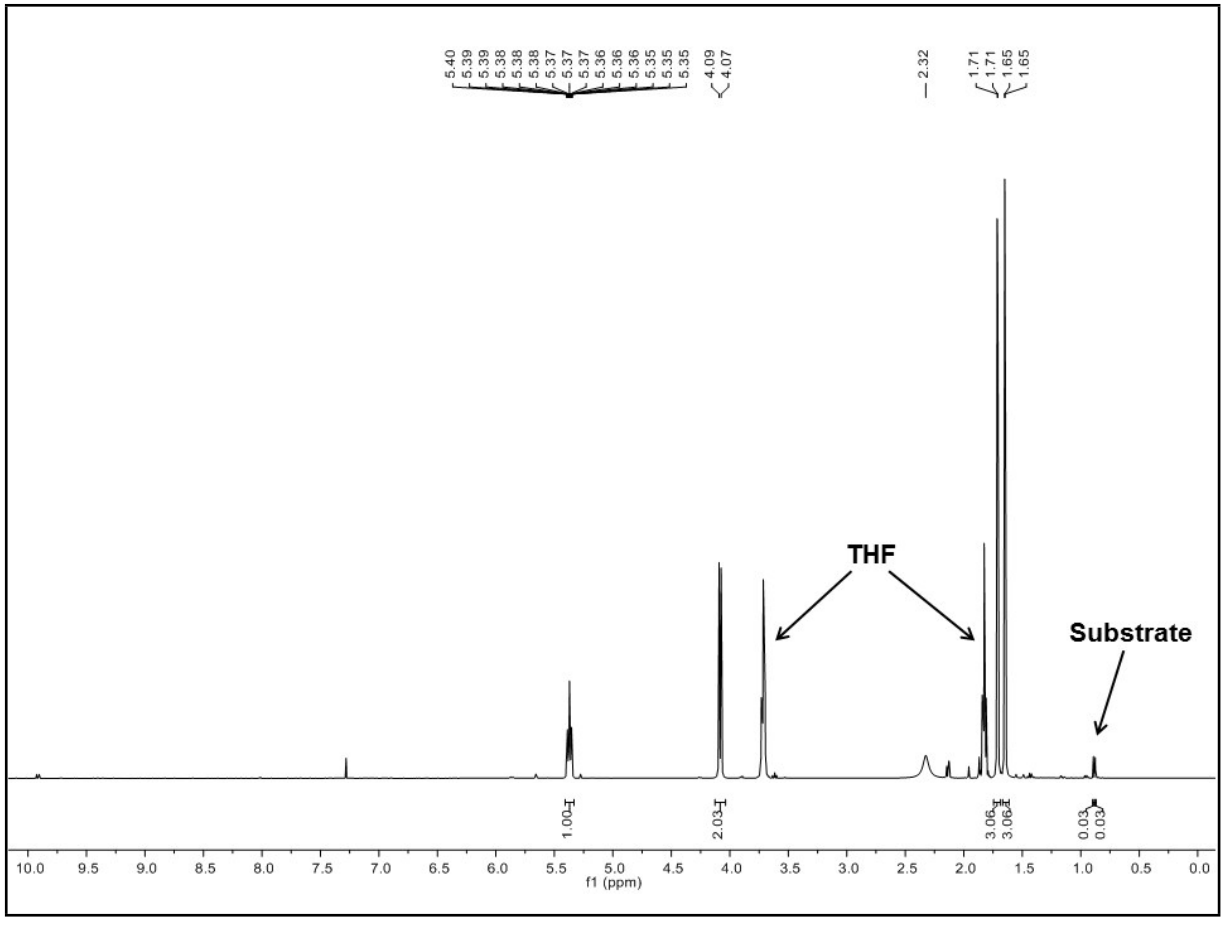
Cinnamyl alcohol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, H), 6.62 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.37 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.31 (dd, *J* = 5.6, 1.6 Hz, 2H), 3.55 (br s, 1H). ^{1}H NMR data were consistent with those previously reported.[7]



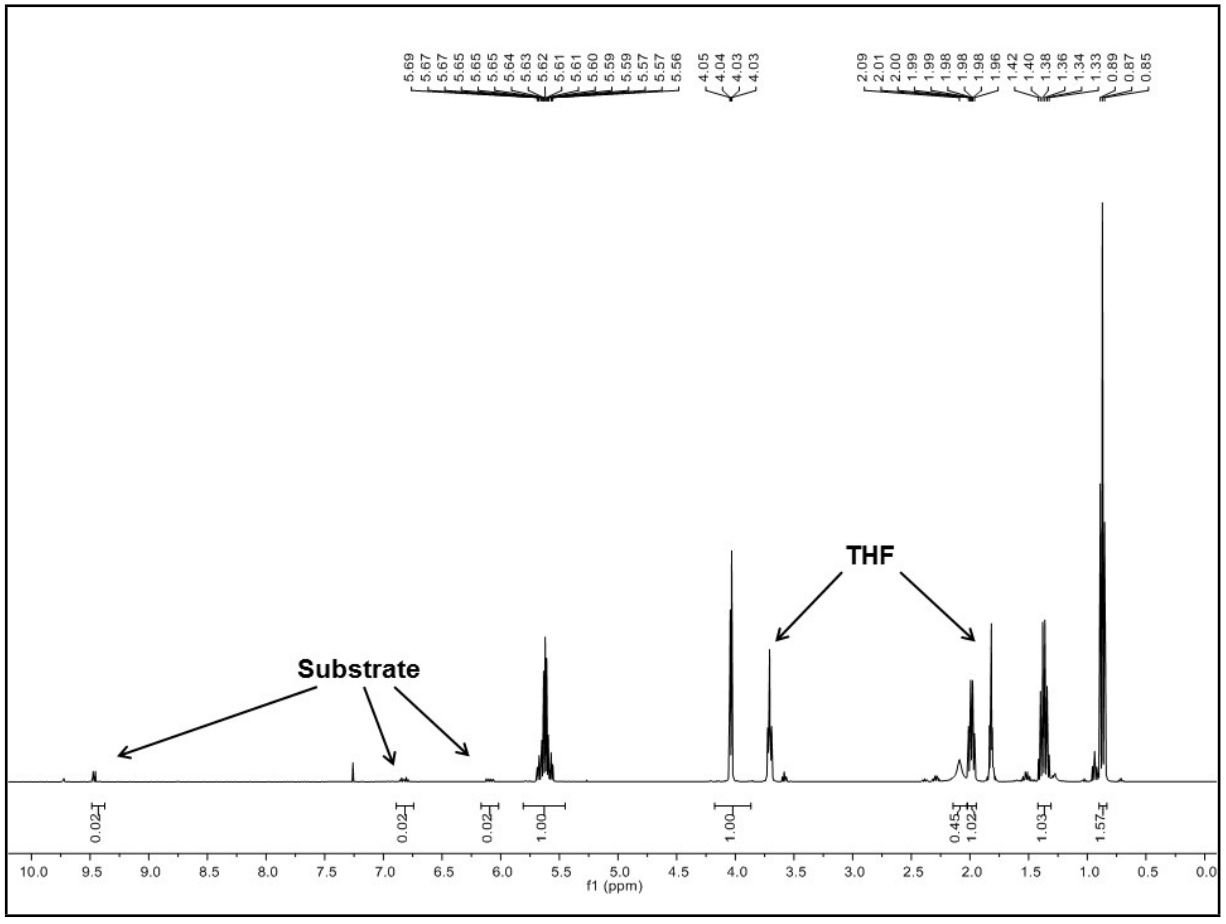
3-Methyl-2-buten-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.34 (m, 1H), 4.08 (d, *J* = 7.0 Hz, 2H), 2.32 (br s, 1H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.65 (d, *J* = 1.4 Hz, 3H). ^{1}H NMR data were consistent with those previously reported.[7]



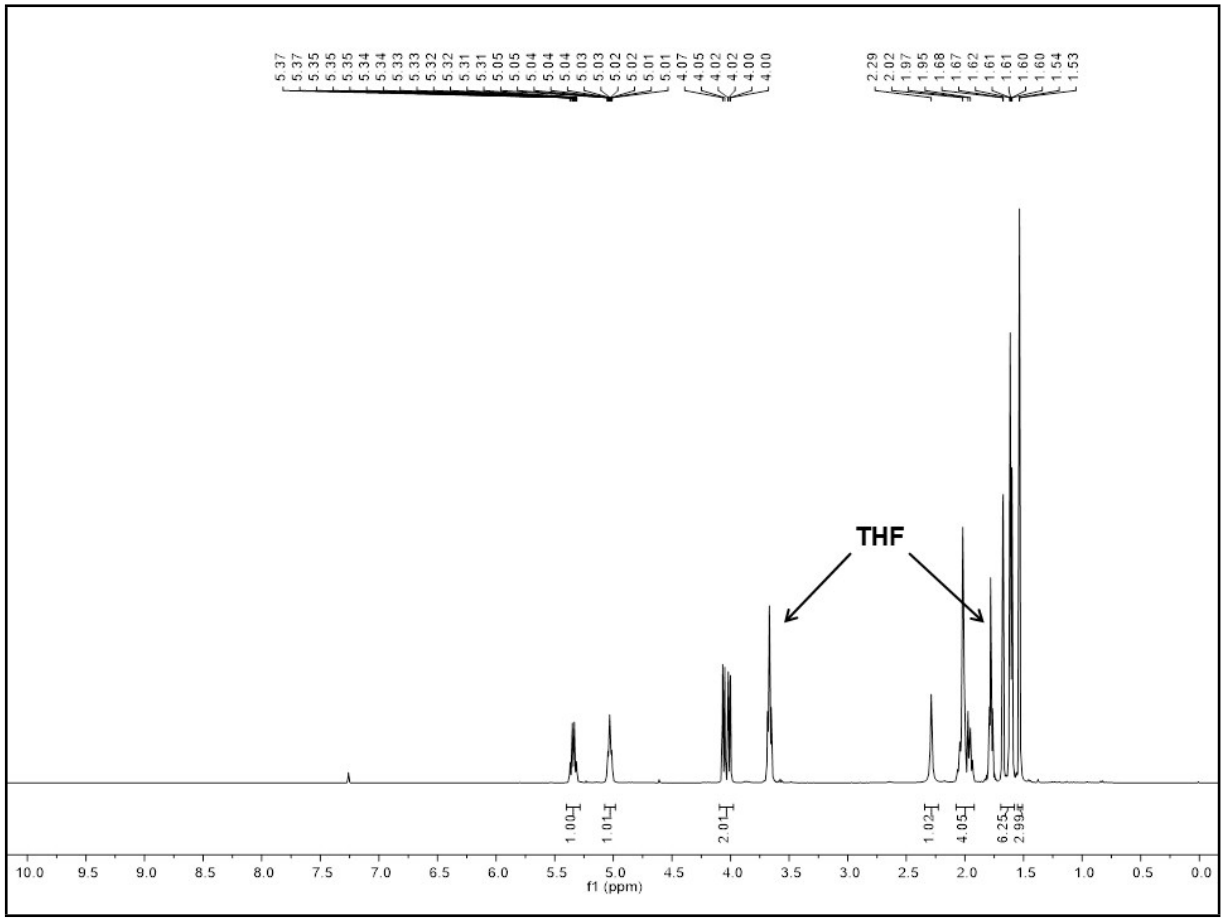
***trans*-2-Hexen-1-ol**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.46 (m, 2H), 4.25 – 3.99 (m, 2H), 2.09 (br s, 1H), 2.04 – 1.94 (m, 2H), 1.42 – 1.32 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{1}H NMR data were consistent with those previously reported.[7]



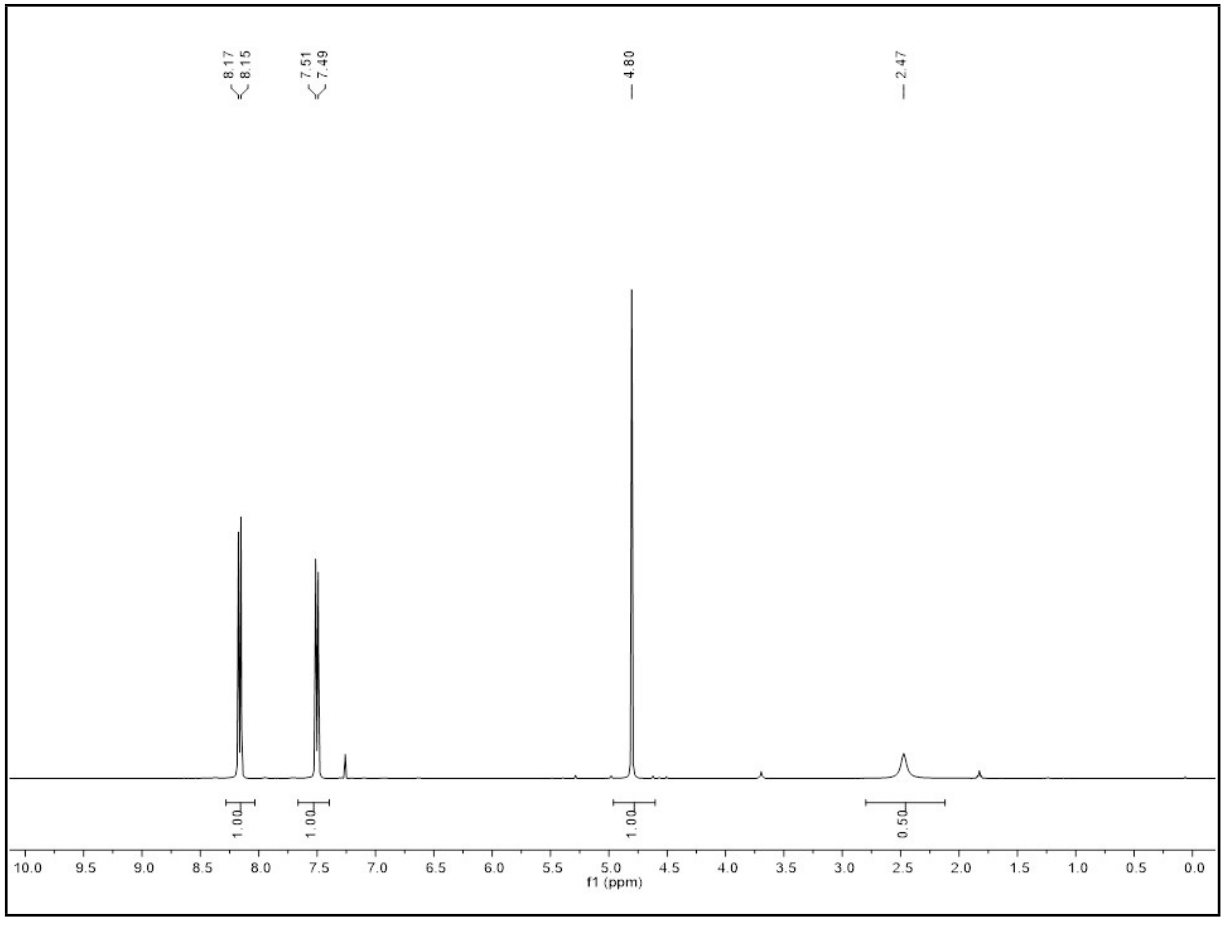
3,7-Dimethyl-2,6-octadien-1-ol (mixture *cis* and *trans*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 – 5.24 (m, 1H), 5.06 – 5.00 (m, 1H), 4.06 (d, J = 6.8 Hz, 1H), 4.01 (d, J = 7.0 Hz, 1H), 2.29 (br s, 1H), 2.10 – 1.90 (m, 4H), 1.72 – 1.57 (m, 6H), 1.53 (s, 3H). ^{1}H NMR data were consistent with those previously reported.[7]



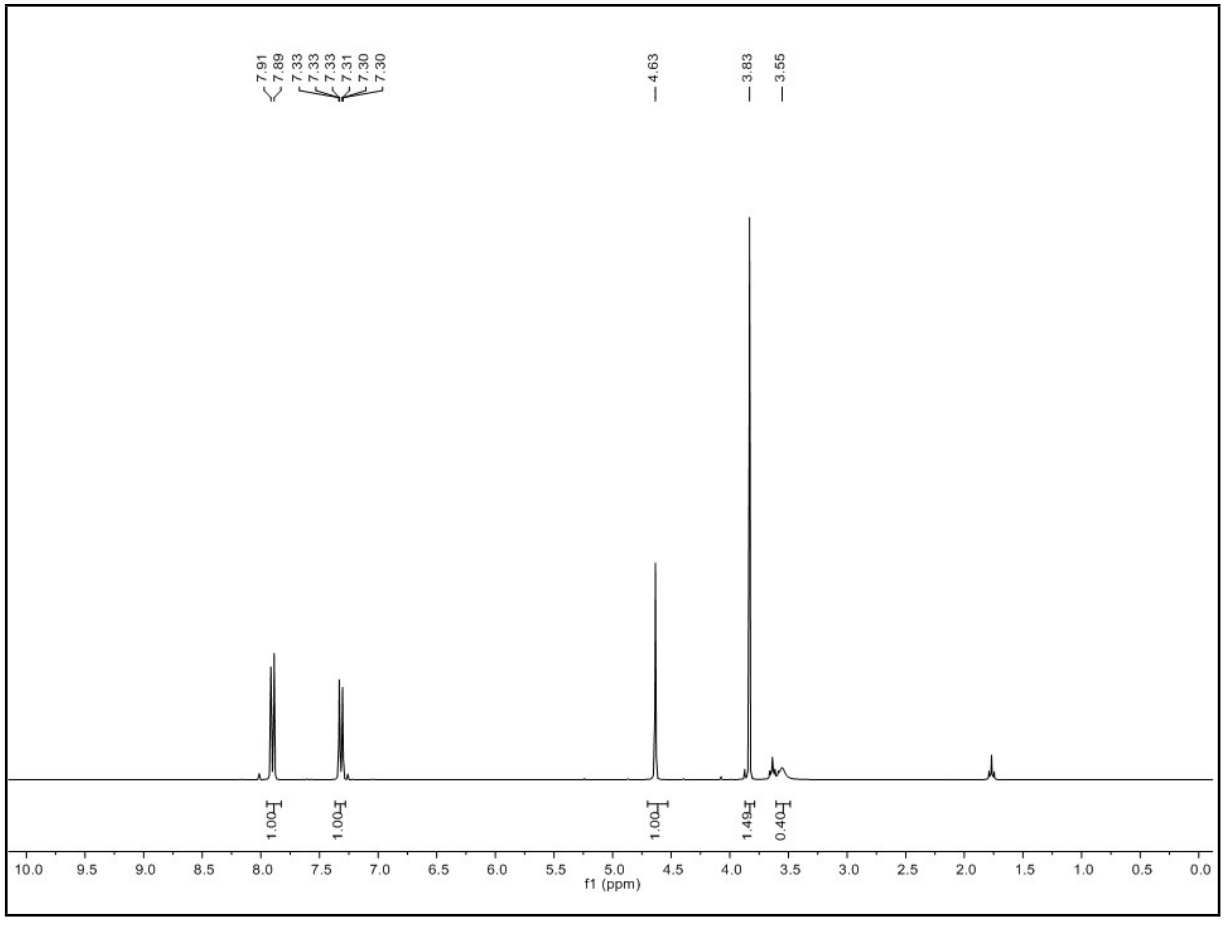
***p*-Nitrobenzyl alcohol**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 4.80 (s, 2H), 2.47 (br s, 1H). ^{1}H NMR data were consistent with those previously reported.[7]



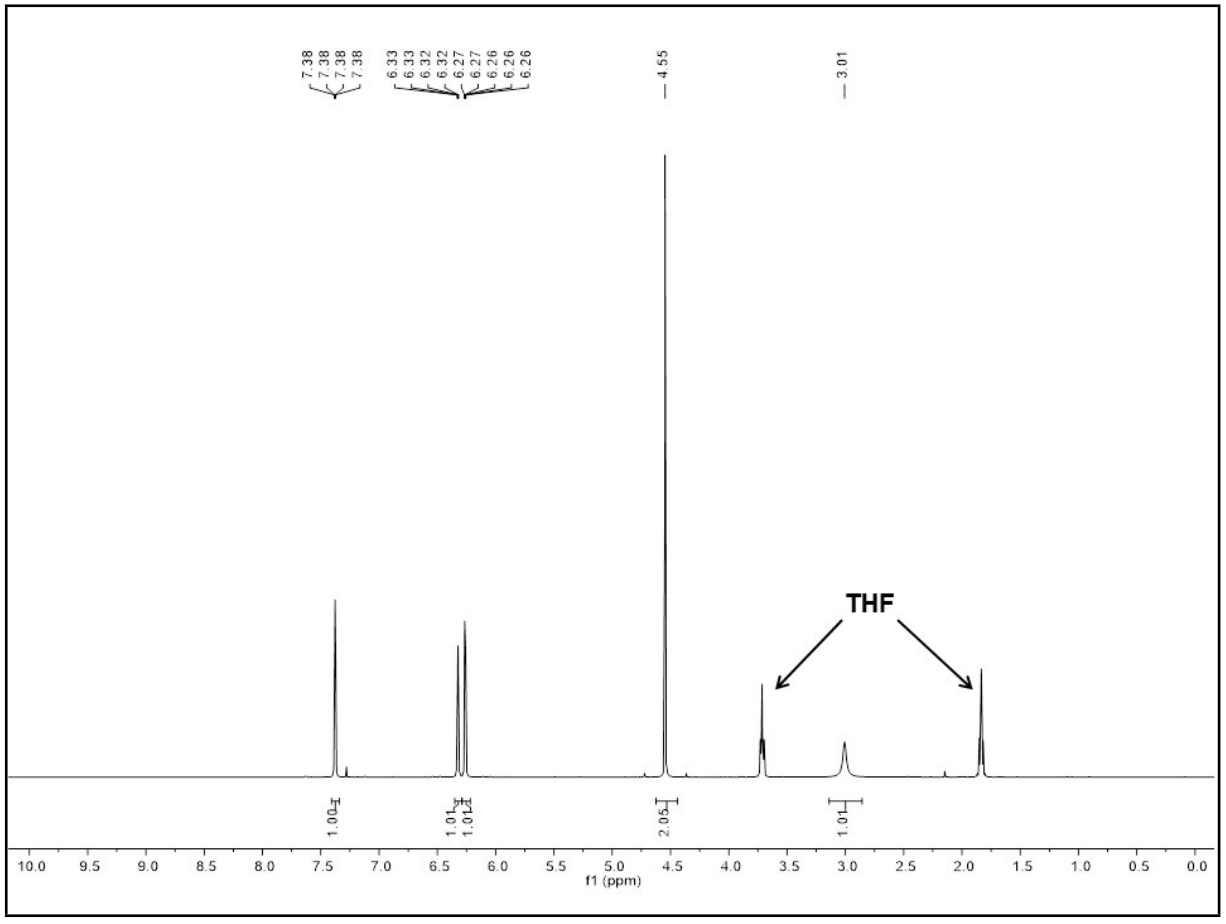
Methyl 4-(hydroxymethyl)benzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.63 (s, 2H), 3.83 (s, 3H), 3.55 (br s, 1H). ^{1}H NMR data were consistent with those previously reported.[7]



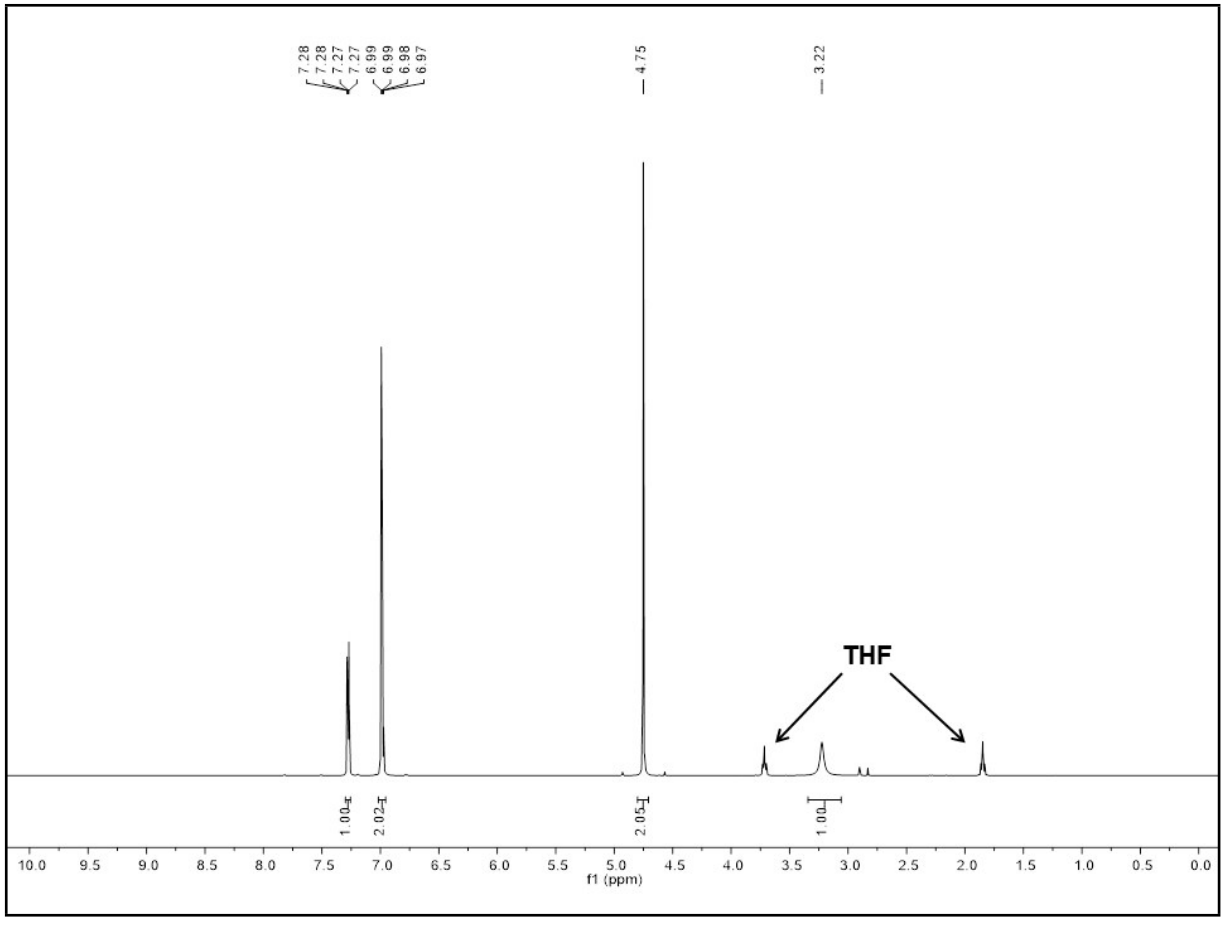
Furfuryl alcohol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 1.9, 0.8 Hz, 1H), 6.32 (dd, J = 3.2, 1.9 Hz, 1H), 6.26 (dd, J = 3.2, 0.8 Hz, 1H), 4.55 (s, 2H), 3.01 (br s, 1H). ^{1}H NMR data were consistent with those previously reported.[7]



2-Thiophenemethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 4.8, 1.5 Hz, 1H), 7.08 – 6.84 (m, 2H), 4.75 (d, J = 0.8 Hz, 2H), 3.22 (br s, 1H). ^{1}H NMR data were consistent with those previously reported.[7]



8. X-ray Crystal Structure of 7

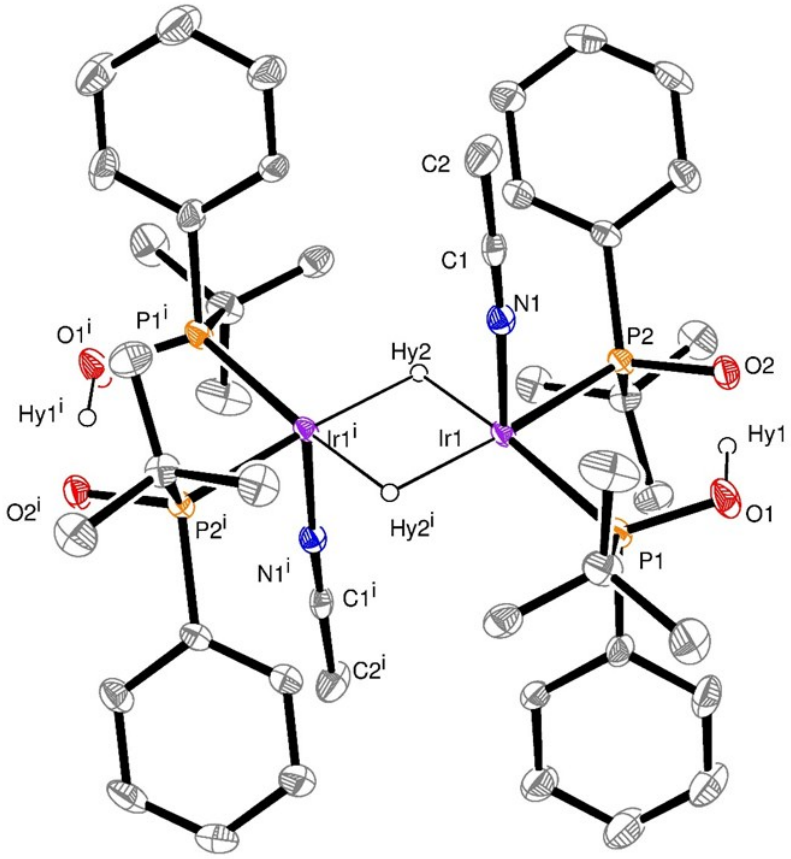


Figure S8. X-ray structure of **7** showing thermal ellipsoids set at 40% probability level. Hydrogen atoms have been removed for clarity.

Empirical formula	$C_{22}H_{33}IrNO_2P_2$
Formula weight	597.63
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 14.6367(7) Å $\alpha = 90^o$
	b = 11.0939(6) Å $\beta = 93.785(2)^o$
	c = 14.9574(7) Å $\gamma = 90^o$

Volume	2423.5(2) $Å^3$
Z	4
Calculated density	1.638 Mg/m^3
Absorption coefficient	5.658 mm^{-1}
F(000)	1180
Crystal size	0.22 x 0.12 x 0.05 mm^3
Theta range for data collection	1.89 to 25.35º .
Limiting indices	-17<=h<=17, -13<=k<=13, -18<=l<=18
Reflections collected / unique	71770
Independent reflections	4435 [R(int) = 0.0333]
Completeness to theta = 25.35º	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9751 and 0.8974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4435 / 0 / 268
Goodness-of-fit on F^2	1.293
Final R indices [I>2sigma(I)]	R1 = 0.0243, wR2 = 0.0734
R indices (all data)	R1 = 0.0285, wR2 = 0.0856
Largest diff. peak and hole	1.299 and -1.067 $e.Å^{-3}$

9. References

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7 The products are commercially available through the web of Sigma-Aldrich in which the corresponding ^{1}H NMR spectra can be found.