SUPPORTING INFORMATION

FOR

Strong π-Acceptor Ligands in Rhodium Catalyzed Hydroformylation of Ethene and 1-Octene: Operando Catalysis

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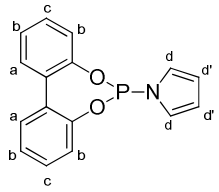
Synthesis of L1:

Triethylamine (0.70 mL, 5.00 mmol) was added to a mixture of chlorodibenzo[*d*,*f*][1,3,2]dioxaphosphepine (1.2. g, 4.8 mmol) and freshly distilled 1H-pyrrole (0.33 mL, 4.8 mmol) in THF (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo afforded pure **L1** as a white solid (1.1 g, 81%).



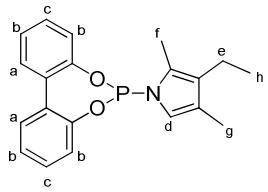
^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 7.56-7.52 (m, 2 H, H_a), 7.41-7.33 (m, 4 H, H_b), 7.10-7.06 (m, 2 H, H_c), 6.88 (bs, 2H, $H_{d'}$), 6.42 (bs, 2H, H_d).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 139.2.

ESI-MS: [M][Na^+] for $C_{16}H_{12}NO_2P$ calculated 304.23, found 304.1 m/z.

Synthesis of L2:

Triethylamine (0.98 mL, 7.00 mmol) was added to a mixture of chlorodibenzo[*d*,*f*][1,3,2]dioxaphosphepine (1.5 g, 6 mmol) and 1H-(2,4-dimethyl-3-ethyl)pyrrole (0.81 mL, 6 mmol) in THF (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo afforded a thick yellow oil that was taken in hexane and filtered through neutral alumina to afford a colorless solution. Removal of the solvent in vacuo gave pure **L2** as a white solid (0.51 g, 25%).



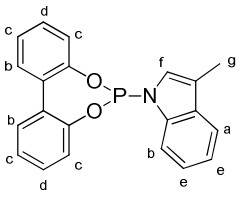
^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 7.55-7.52 (m, 2 H, H_a), 7.39-7.31 (m, 4 H, H_b), 7.11-7.05 (m, 2 H, H_c), 6.25 (bs, 1H, H_d), 2.34 (m, 2 H, H_e), 2.37 (s, 3 H, H_f), 1.88 (s, 3 H, H_g), 1.08 (t, J_{HH} = 7.3 Hz, 3 H, H_h).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 137.7.

ESI-MS: [M][Na^+] for $C_{20}H_{20}NO_2P$ calculated 360.34, found 360.2 m/z.

Synthesis of L3:

Triethylamine (1 mL, 7.2 mmol) was added to a mixture of chlorodibenzo[*d*,*f*][1,3,2]dioxaphosphepine (1.2 g, 4.8 mmol) and 3-methyl-1H-indole (0.628 g, 4.8 mmol) in THF (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo afforded



athick yellow oil. Purification by column chromatography (Al_2O_3/hexanes) afforded pure **L3** as a white solid (0.76 g, 46%). **Warning**: 3-methyl-1H-indole has an obnoxious smell.

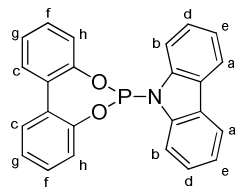
^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 7.71-7.67 (m, 1 H, H_a), 7.60-7.53 (m, 3 H, H_b), 7.38-7.34 (m, 4 H, H_c), 7.24-7.19 (m, 2H, H_d), 7.07-7.03 (m, 2 H, H_e), 6.84-6.81 (m, 1 H, H_f), 2.20 (bs, 3 H, H_g).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 138.1.

ESI-MS: [M][Na^+] for $C_{21}H_{16}NO_2P$ calculated 368.32, found 368.4 m/z.

Synthesis of L4:

Triethylamine (1 mL, 7.2 mmol) was added to a mixture of chlorodibenzo[*d,f*][1,3,2]dioxaphosphepine (1.2 g, 4.8 mmol) and 9H-carbazole (0.628 g, 4.8 mmol) in THF (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Removal of the volatiles in vacuo afforded a thick yellow oil. Purification by column chromatography (Al_2O_3/hexanes) afforded pure **L3** as a white solid (1.3 g, 64%).



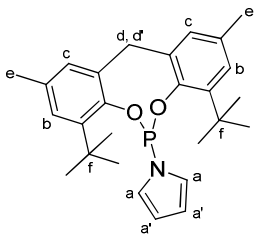
^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 8.03-7.98 (m, 2 H, H_a), 7.66-7.62 (m, 2 H, H_b), 7.53-7.49 (m, 2 H, H_c), 7.41-7.35 (m, 2 H, H_d), 7.33-7.29 (m, 2H, H_e), 7.28-7.24 (m, 2 H, H_f), 7.23-7.17 (m, 2 H, H_g), 7.08-7.04 (m, 2 H, H_h).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 145.6.

ESI-MS: [M][Na^+] for $C_{24}H_{16}NO_2P$ calculated 404.08, found 404.1 m/z.

Synthesis of L6:

Triethylamine (0.70 mL, 5.00 mmol) was added to a mixture of 2,2'-methenebis(4-methyl-6-tert-butylphenyl)chlorophosphite (2.00 g, 4.94 mmol) and freshly distilled 1H-pyrrole (0.35 mL, 4.94 mmol) in toluene (100 mL). The mixture was then heated at reflux for 18 hours, allowed to cool and filtered to remove precipitated triethylamine hydrochloride. Purification by column chromatography (Al_2O_3/hexanes) afforded **L6** as an off-white solid (1.05 g, 49%).



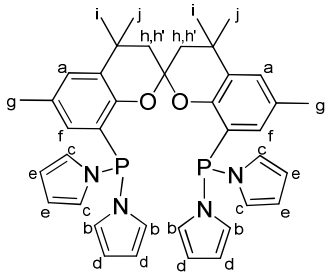
^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 7.42-7.39 (m, 2H, $H_{a'}$), 7.18 (s, 2 H, H_b), 7.07 (s, 2 H, H_c), 6.48 (m, 2H, H_a), 4.48 (dd, J_{HH} = 12.7 Hz, J_{HP} = 1.9 Hz, 1 H, H_d), 3.46 (d, J_{HH} = 12.7 Hz, 1 H, $H_{d'}$), 2.34 (s, 6 H, H_e), 1.56 (s, 18 H, H_f).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 131.7.

ESI-MS: [M][Na^+] for $C_{27}H_{34}NO_2P$ calculated 458.53, found 458.5 m/z.

Synthesis of pySPAN:

8,8'-dibromo-4,4,4,4,6,6'-hexamethylspiro-2,2'-bichroman (0.65 g, 1.32 mmol) was azeotropically dried with toluene (×3) and dissolved in dry and degassed THF under inert atmosphere. The colorless solution was treated with n-BuLi (3.3 mmol) at -78 ºC for 2h and then freshly distilled bis(1-pyrrolyl)chlorophosphine[1] (0.44 mL, 3.3 mmol) was also added while the low temperature was maintained. Mixture was allowed to warm up slowly overnight. The pale yellow solution was filtered through neutral alumina and the solvent removed to give a thick colorless oil. This was dried under reduced pressure to afford a white sticky foam. This foam was dissolved in boiling MeOH and left in the freezer at -30 ºC for 2 hours to give PySPAN (0.65 g, 75%) as a white crystalline solid.



^{1}H-NMR ($CDCl_3$, 25 ºC, 400 MHz): δ = 7.18 (bs, 2 H, H_a), 6.64-6.60 (m, 4H, H_b), 6.51-6.47 (m, 4H, H_c), 6.26-6.23 (m, 4H, H_d), 6.14-6.10 (m, 4H, H_e), 6.06 (m, 2 H, H_f), 2.23 (s, 6 H, H_g), 1.99 (d, J_{HH} = 14.6 Hz, 2H, H_h), 1.94 (d, J_{HH} = 14.6 Hz, 2H, $H_{h'}$), 1.46 (s, 6 H, H_i), 1.29 (s, 6 H, H_j).

^{31}P{^{1}H}-NMR ($CDCl_3$, 25 ºC, 160 MHz): δ = 71.2.

ESI-MS: [M][Na^+] for $C_{39}H_{42}N_4O_2P_2$ calculated 683.27, found 683.3 m/z.

(1) van der Slot, S. C.; Duran, J.; Luten, J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **2002**, *21,* 3873-3883

Hydrolysis of pyrrolylphosphine ligands.

The catalytic results presented here can be very interesting in terms of industrial application. Although the tris(pyrrolyl)phosphine ligand is known for its high reactivity towards air and moisture, the bidentate ligands may not suffer from this. We then decided to perform a stability test with a model ligand, the pyrrolyl-phosphine ligand **L7**. This particular ligand mimics well the ligands pyXANT and pySPAN since the phosphorus centre is also substituted by two pyrroles and an aromatic group.

For this purpose, 0.1 mmol of ligand **L7** was dissolved in 3 mL of acetone/DCM 1:1 and 0.1 mL of water and the mixture was then heated to 60 ºC. Samples were analyzed by inverse gated decoupling $^{31}P\{^{1}H\}$-NMR.[2] No sign of degradation was observed after 48h. Traces of decomposition were however observed after 7 days and the ligand was completely hydrolyzed after 10 days.

The same test was also performed under acidic conditions. In this case, the ligand was totally decomposed within 24 hours.

(2) Following the method reported previously by Pringle *et al.*: Cobbley, C. J.; Ellis, D. D.; Orpen, A. G.; Pringle, P. G. *Dalt. Trans.* **2000***,* 1101-1107.

$^{31}P\{^{1}H\}$ HPNMR spectra with $[Rh(CO)_2(acac)]$ and SPANphos.

When SPANphos was used as ligand, in addition to the expected rhodium hydride species a second product was observed by HPNMR at 21 ppm (See Figure S1). This product appears is the same the one observed as the main product when a CO only atmosphere was applied instead of syngas.

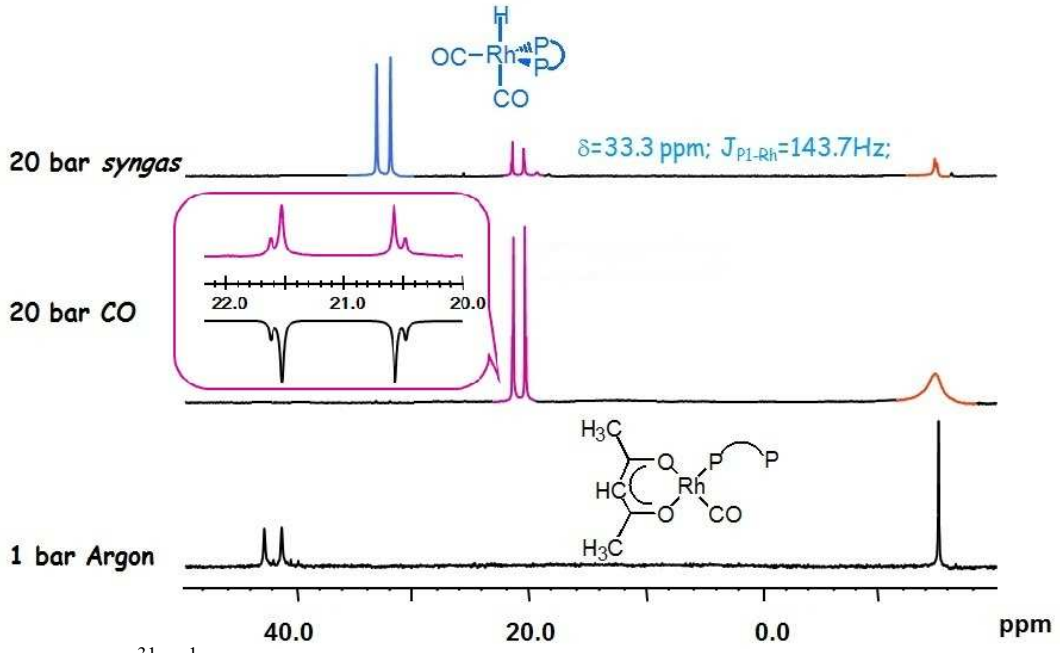


Figure S1. $^{31}P\{^{1}H\}$ HPNMR of $[Rh(CO)_2(acac)]$ and SPANPhos in toluene.

Modeling using gNMR lead us to propose various dimeric structures for the observed complex (See Figure S2). Structure **A** is the most likely one to be formed since it would explain the broad peak observed at –14.8 ppm (close to free ligand). Fitting the coupling constants of the program with the spectrum obtained experimentally, the following coupling constants were obtained. In the case of compound **A**, the broad signal at –14.8 ppm accounts for phosphorus P^1 and P^4, whereas is the case of **B**, this signal accounts for the excess of free ligand.

Proposed structures for the side-product obtained with SPANphos.

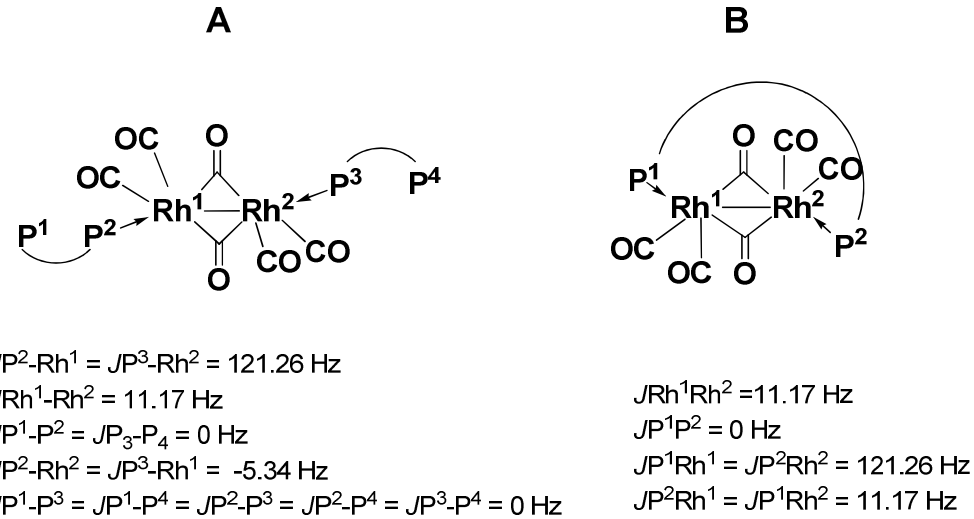


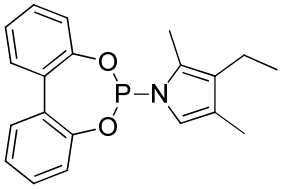
Figure S2. Proposed structures based on gNMR modeling with corresponding coupling constants.

Crystal data and structure refinement for PySPAN.

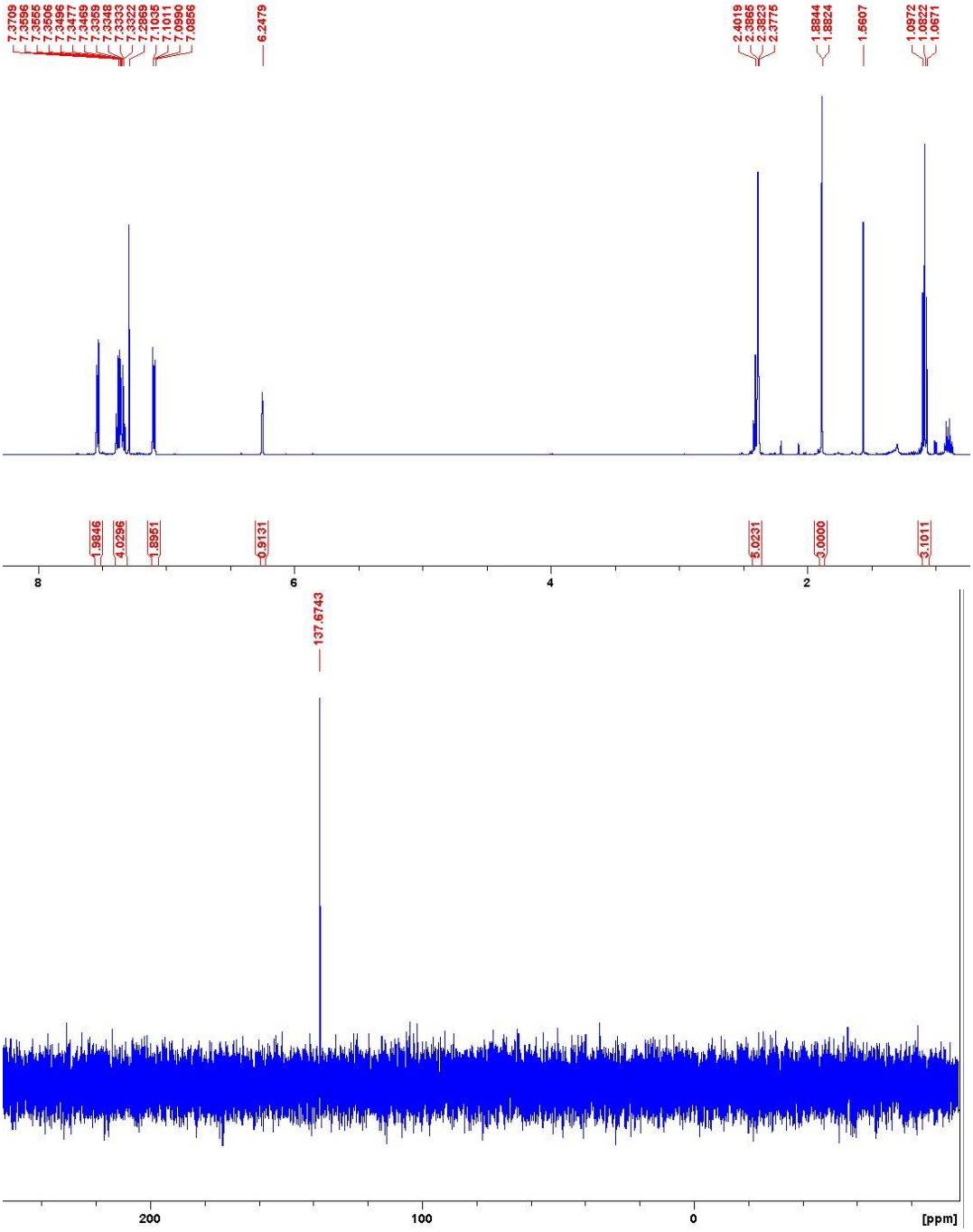
The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 891787

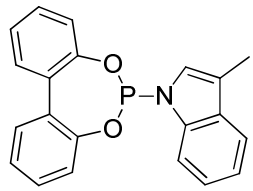
Identification code	mo_PySPAN	
Empirical formula	C39 H42 N4 O2 P2	
Formula weight	660.71	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 23.496(3) Å	α= 90.00 °.
	b = 10.8964(16) Å	β = 90.00 °.
	c = 13.6474(18) Å	γ = 90.00 °.
Volume	3494.0(8) $Å^3$	
Z	4	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	0.165 mm^{-1}	
F(000)	1400	
Crystal size	0.30 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.73 to 30.53 °.	
Index ranges	-31 <=h<=33 ,-15 <=k<=15 ,-11 <=l<=19	
Reflections collected	30764	
Independent reflections	7983 [R(int) = 0.0358]	
Completeness to theta =30.53 °	0.997 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9523 and 0.9523	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7983 / 1501 / 847	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0441 , wR2 = 0.1130	
R indices (all data)	R1 = 0.0510 , wR2 = 0.1180	
Flack parameter	x =0.05(8)	
Largest diff. peak and hole	0.325 and -0.336 $e.Å^{-3}$	

NMR spectra for ligands L2-4, L6 and pySPAN

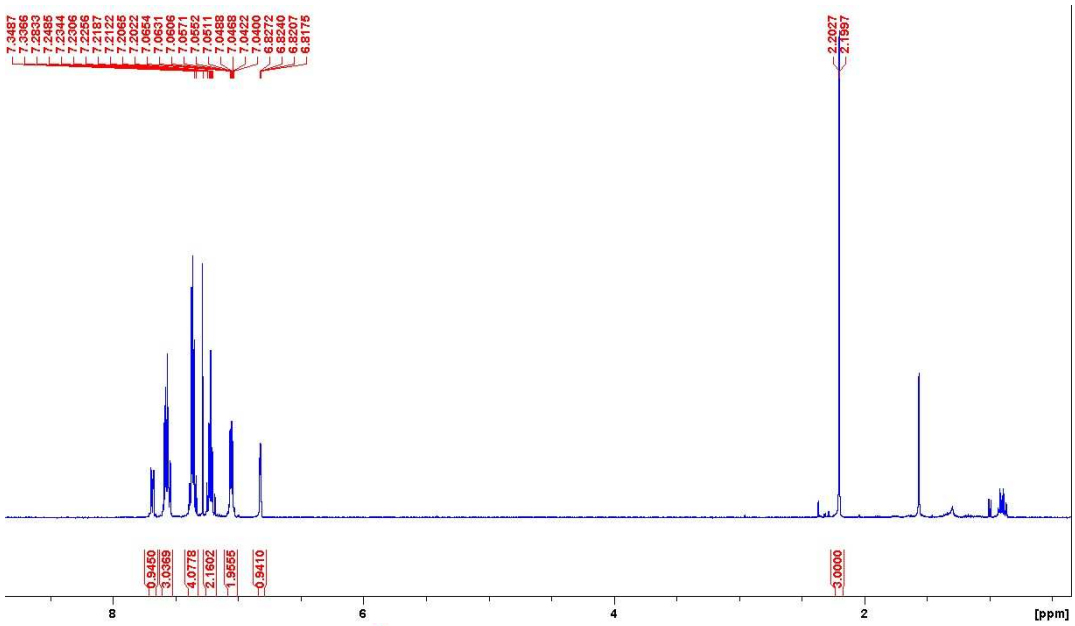


L2





L3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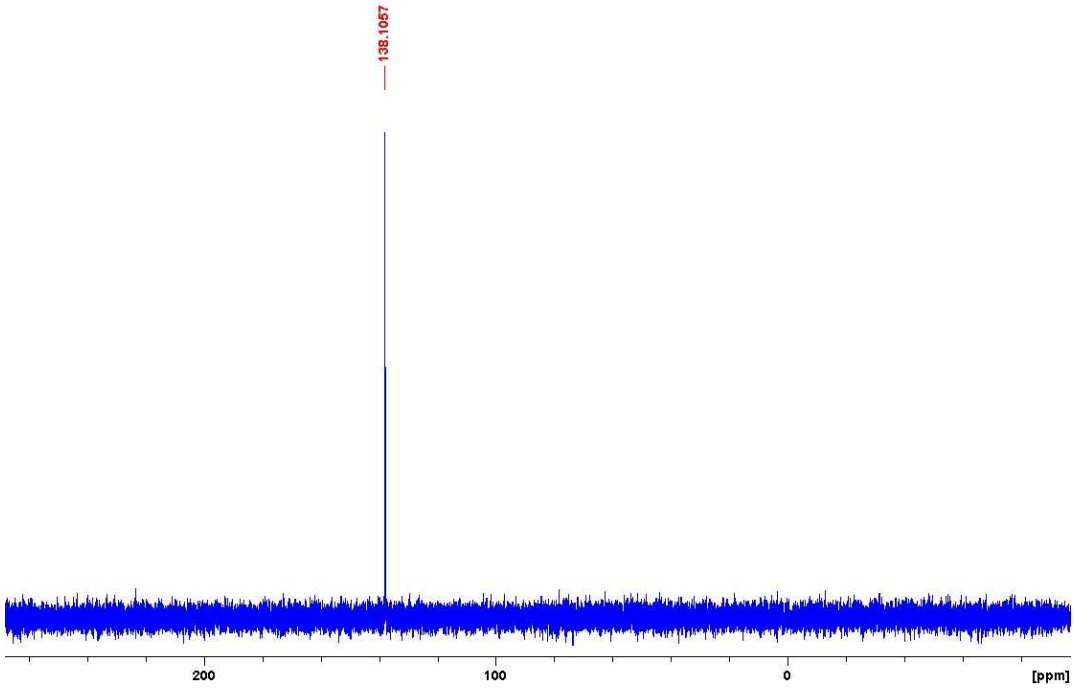
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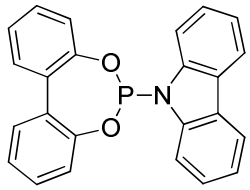
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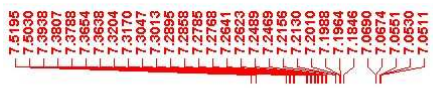
L4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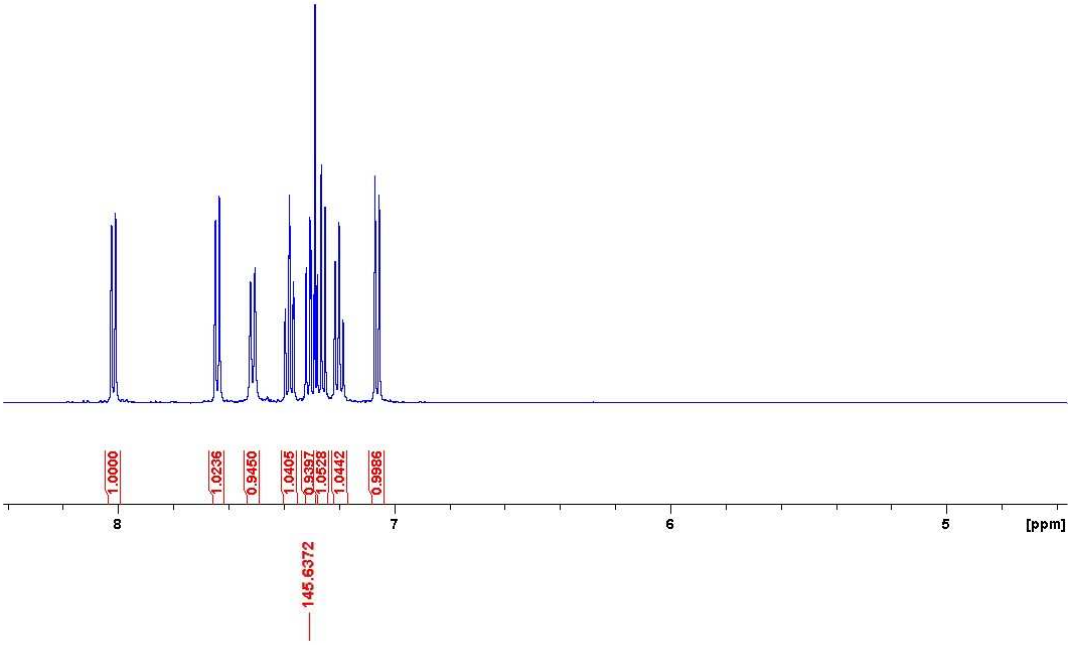
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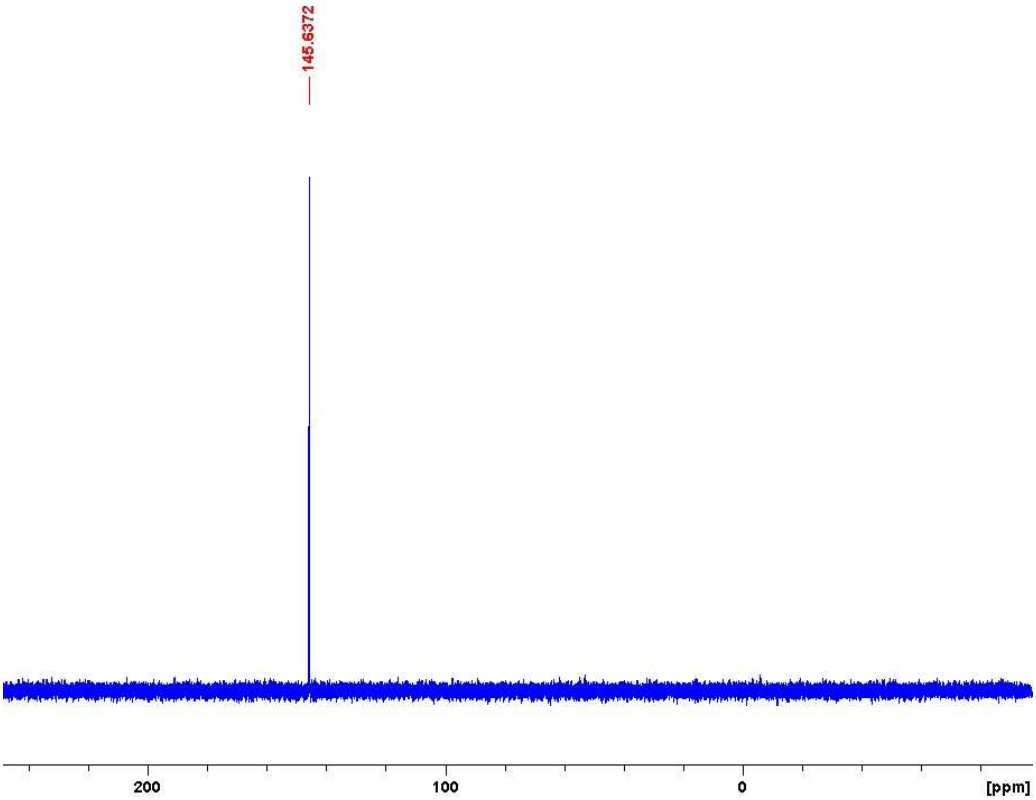
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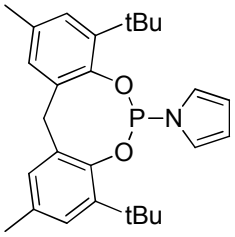
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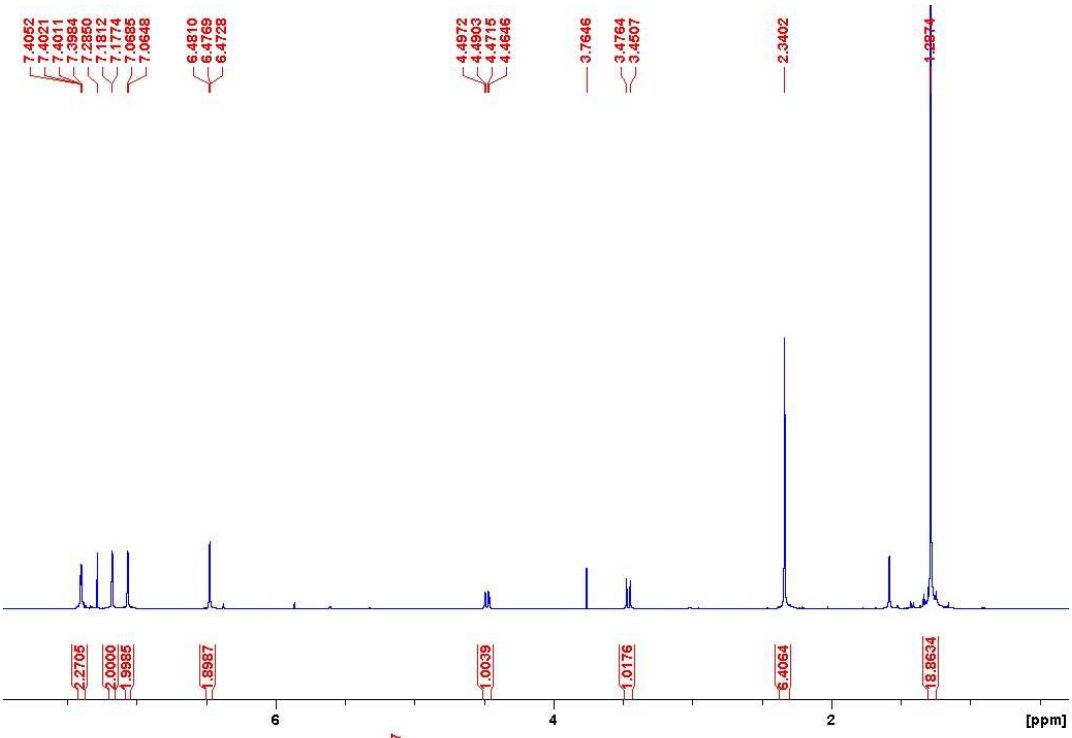
L6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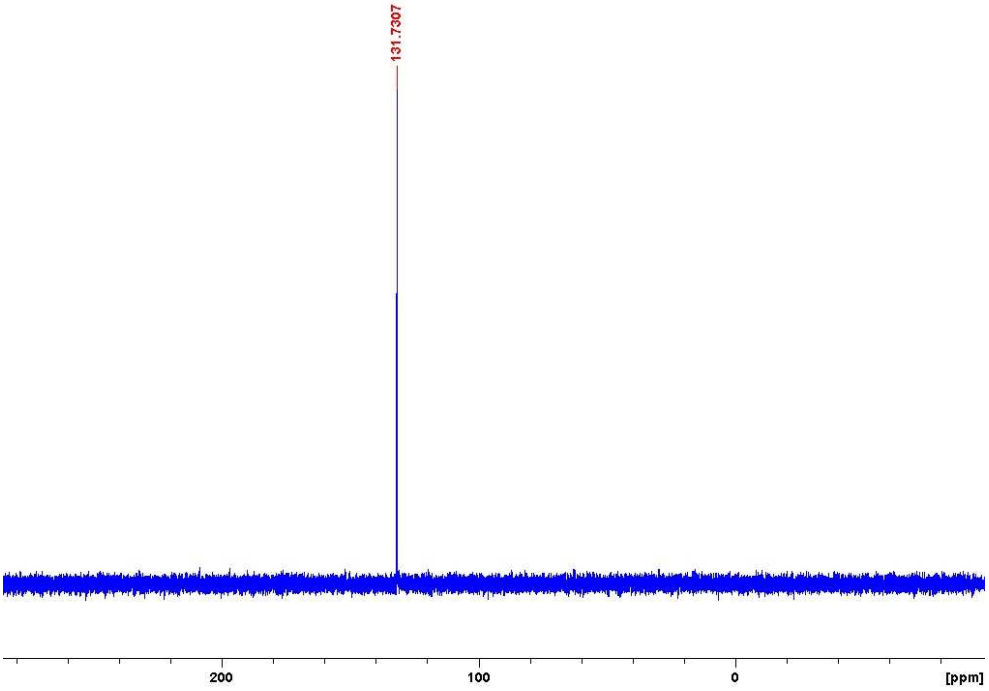
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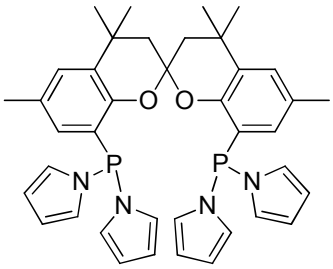
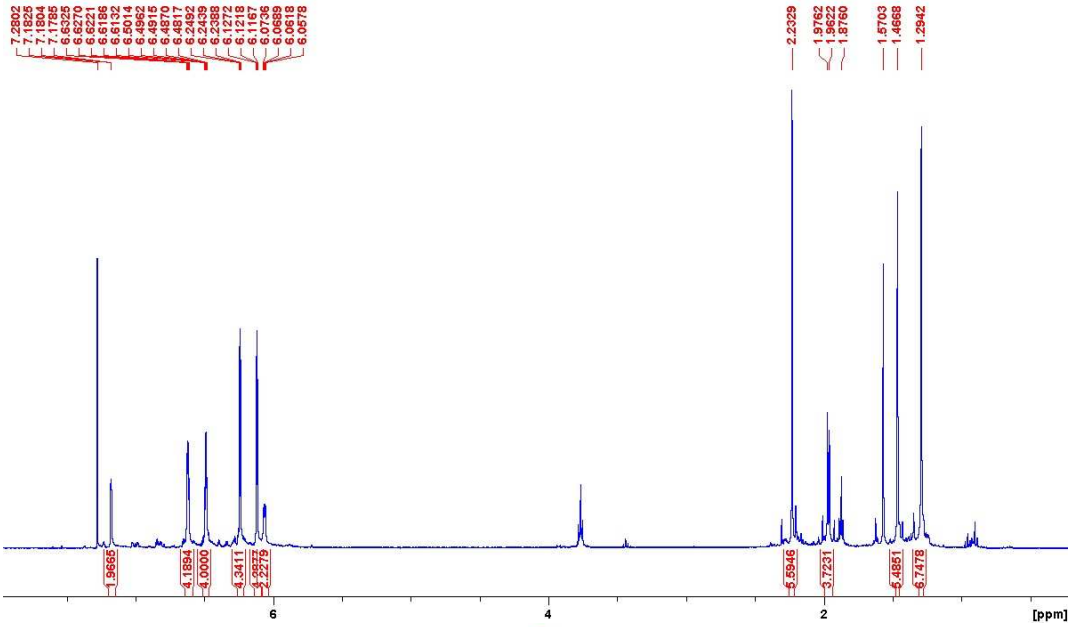


pySPAN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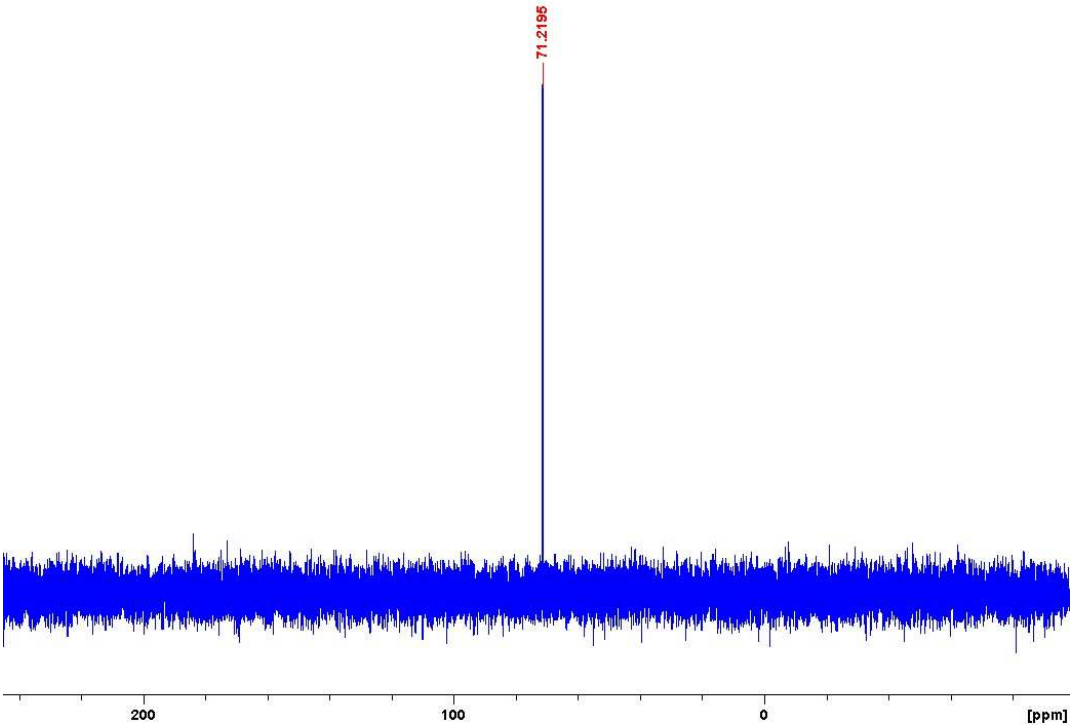
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