Pyridyl and pyridiniumyl *β*-diketones as building blocks for palladium(II) and allyl-palladium(II) isomers. Multinuclear NMR structural elucidation and liquid crystal behaviour

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

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Table S1. Analytical data of the compounds [$HL^{R(n)py}$] (**1**-**4**).

COMPOUND		MOLECULAR FORMULA	YIELD (%)	MOLECULAR WEIGHT ($gmol^{-1}$)	ELEMENTAL ANALYSIS					
					REQUIRES (%)			FOUND (%)		
n					C	H	N	C	H	N
12	**1**	$C_{26}H_{35}NO_3$	68	409.6	76.2	8.6	3.4	75.9	8.6	3.5
14	**2**	$C_{28}H_{39}NO_3$	66	437.6	76.8	9.0	3.2	76.4	8.9	3.3
16	**3**	$C_{30}H_{43}NO_3$	65	465.7	77.4	9.3	3.0	77.0	9.3	2.9
18	**4**	$C_{32}H_{47}NO_3$	65	493.7	77.9	9.6	2.8	77.4	9.5	2.8

Table S2. NMR data of **1**. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz)

Atom	**^{1}H**	**^{1}H**	**^{13}C**	**^{13}C**	**^{13}C**	**^{15}N**	**^{15}N**	**^{15}N**
Ratio	**Enol, 94%**	**Keto, 6%**	**Enol**	**Keto**		**Enol**	**Keto**	
Phase Conc.	**$CDCl_3$ 0.05 M**	**$CDCl_3$ 0.05 M**	**$CDCl_3$ 0.19 M**	**$CDCl_3$ 0.19 M**	**CPMAS**	**$CDCl_3$ 0.19 M**	**$CDCl_3$ 0.19 M**	**CPMAS**
7			181.2	196.8	180.7			
8	7.52	4.8	92.9	48.0 ^{1}J= 129.3	91.1			
9			187.1	193.6	187.0			
OH	16.64							
2			152.6 ^{3}J= ^{3}J= 8.6	152.7	151.2			
3	8.15 ^{3}J= 7.8	8.17	122.0 ^{1}J= 166.4 ^{3}J= 6.4	122.1	118.5			
4	7.87 ^{3}J= ^{3}J= 7.7 ^{4}J= 1.7	7.89	137.1 ^{1}J= 163.4 ^{3}J= 6.1	137.0 ^{1}J= 163.7 ^{3}J= 6.8	135.4			
5	7.43 ^{3}J= 7.5 ^{3}J= 4.8 ^{4}J= 1.1	7.47	126.1 ^{1}J= 164.3 ^{3}J= ^{2}J= 7.5	126.1	122.7			
6	8.71 ^{3}J= 4.8 ^{4}J= 1.7 ^{5}J= 0.8	8.62	149.1 ^{1}J= 179.6 ^{3}J= 6.8 ^{4}J= 2.8	149.0 ^{1}J= 179.6	151.2			
o	8.06	7.96	129.7 ^{1}J= 160.3 ^{3}J= 7.0	130.9 ^{1}J= 160.7 ^{3}J= 7.0	129.8			
m	6.96	6.93	114.4 ^{1}J=161.0 ^{3}J= 4.5	114.3 ^{1}J=161.1 ^{3}J= 4.5	112.4			
p			163.1	163.4	163.6			

			^3J= ^3J= 10.3 ^3J= ^3J= 7.8					
ipso			127.8 ^3J= ^3J= 7.4	127.3	126.2 127.3			

Table S2 (Continue). NMR data of **1**. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz)

Atom	**^{1}H**	**^{1}H**	**^{13}C**	**^{13}C**	**^{13}C**	**^{15}N**	**^{15}N**	**^{15}N**
Ratio	**Enol, 94%**	**Keto, 6%**	**Enol**	**Keto**		**Enol**	**Keto**	
Phase Conc.	**$CDCl_3$ 0.05 M**	**$CDCl_3$ 0.05 M**	**$CDCl_3$ 0.19 M**	**$CDCl_3$ 0.19 M**	**CPMAS**	**$CDCl_3$ 0.19 M**	**$CDCl_3$ 0.19 M**	**CPMAS**
N1						-73.5 ^2J (H6)= 13.1 ^3J (H3)= 8.1 ^3J (H5)= 9.9	-66.3	-68.3
CH_3	0.88 ^3J= ^3J= 6.9		14.1 ^1J= 124.4		15.0			
$(CH_2)_x$	1.27-1.81		22.7-31.9		24.6-33.8			
OCH_2	4.03 ^{3}J= ^{3}J= 6.6		68.3 ^1J= 143.2		69.1			

Table S3. NMR data of **8** at 323 K. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz)

Atom	**^{1}H**	**^{1}H**	**^{13}C**	**^{13}C**	**^{13}C**	**^{15}N**
Ratio	**Enol, 93%**	**Keto, 7%**	**Enol**	**Keto**		
Phase	**$CDCl_3$**	**$CDCl_3$**	**$CDCl_3$**	**$CDCl_3$**	**CPMAS**	**CPMAS**
Conc.	**0.033 M**	**0.033 M**	**0.033 M**	**0.033 M**		
7			174.1		170.5[a]	
8	8.11	4.82	96.0		94.8[a]	
9			189.9		188.6[a]	
OH	16.48					
2			149.9		142.6[a] 144.4[a]	
3	8.39 ^{3}J=7.9		123.8		118.2[a]	
4	8.25 ^{3}J= ^{3}J= 7.6	7.96	141.7		134.1[a]	
5	7.59 ^{3}J= ^{3}J= 6.3	6.92	126.8		127.1[a]	
6	8.89 ^{3}J= 4.9	8.64	145.6		150.1[a] 153.0[a]	
o	8.26	7.91	130.8		130.0[a] 130.6[b]	
m	7.00	6.91	114.8	114.3	113.5[a]	
p			164.0		165.6[a]	
ipso			127.6		124.2[a]	
N1						−181.6
CH_3	0.87 ^{3}J= ^{3}J= 6.8		14.0		16.4[a] 14.6[b]	
$(CH_2)_x$	1.22-1.82		22.7-32.2		24.8-35.5	
OCH_2	4.06	4.01	68.5	71.3	69.1[a]	

	^3J= ^3J= 6.6			68.0[b]	

Table S4. Analytical data of the complexes [Pd(κ^2-$L^{R(n)py}$)$_2$] (**9-12**).

COMPOUND		MOLECULAR FORMULA	YIELD (%)	MOLECULAR WEIGHT ($gmol^{-1}$)	ELEMENTAL ANALISYS					
					REQUIRES (%)			FOUND (%)		
n					C	H	N	C	H	N
12	**9**	$C_{52}H_{68}N_2O_6Pd$	70	923.5	67.6	7.4	3.0	67.4	7.3	3.1
14	**10**	$C_{56}H_{76}N_2O_6Pd$	68	979.6	68.7	7.8	2.9	68.2	7.6	2.9
16	**11**	$C_{60}H_{84}N_2O_6Pd$	72	1035.7	69.6	8.2	2.7	69.6	8.2	2.5
18	**12**	$C_{64}H_{92}N_2O_6Pd$	70	1091.9	70.4	8.5	2.6	70.0	8.3	2.6

Table S5. Analytical data of the organometallic compounds [Pd(η^3-C_3H_5)($HL^{R(n)py}$)][PF_6] (**13-16**).

COMPOUND		MOLECULAR FORMULA	YIELD (%)	MOLECULAR WEIGHT ($gmol^{-1}$)	ELEMENTAL ANALISYS					
					REQUIRED (%)			FOUND (%)		
n					C	H	N	C	H	N
12	**13**	$C_{29}H_{39}NO_3PdPF_6$	65	701.0	49.7	5.6	2.0	49.5	5.4	2.0
14	**14**	$C_{31}H_{43}NO_3PdPF_6$	66	729.1	51.1	6.0	1.9	51.5	5.9	2.1
16	**15**	$C_{33}H_{47}NO_3PdPF_6$	60	757.1	52.4	6.3	1.9	52.5	6.2	2.1
18	**16**	$C_{35}H_{51}NO_3PdPF_6$	60	785.2	53.5	6.6	1.8	53.7	6.8	1.8

Table S6. NMR data of **14** at 323 K. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz)

Atom **Phase** **Concentration**	**^{1}H** **$CDCl_3$** **0.042 M**	**^{13}C** **$CDCl_3$** **0.042 M**	**^{13}C** **CPMAS**	**^{15}N** **CPMAS**
7		185.3	189.8	
8	7.23	94.1 ^{1}J= 167.2	92.1	
9		185.3	180.7	
OH	14.80			
2		152.8	149.6	
3	8.58 ^{3}J= 7.9	126.6 ^{1}J= 173.6	127.1	
4	8.11	141.3	139.0	
5	7.64 ^{3}J= ^{3}J= 5.8	129.7	131.7	
6	8.70 ^{3}J= 4.2	151.9	151.6	
o	8.16	131.6	131.7	
m	7.01	115.5 ^{1}J= 162.7	119.7	
p		165.8	163.0	

ipso		123.7	122.0	
CH_2-allyl (H_s)	4.38 ^{s}J= 6.5	61.0	66.6 / 68.3	
CH_2-allyl (H_a)	3.39 ^{a}J= 12.2	61.0	66.6 / 68.3	
CH_2-allyl (H_{meso})	5.80 ^{s}J= 6.5 ^{a}J= 12.2	115.8	113.1 / 116.3	
N1				-130.0
CH_3	0.89 ^{3}J= ^{3}J= 6.9	14.0	15.2	
CH_2	1.29-1.85	22.7-31.9	25.6-34.6	
OCH_2	4.07 ^{3}J= ^{3}J= 6.5	68.9	56.1	

Table S7. Analytical data of the organometallic compounds $[Pd(\eta^3\text{-}C_3H_5)(L^{R(n)pyH})][PF_6]$ (**17-20**).

COMPOUND		MOLECULAR FORMULA	YIELD (%)	MOLECULAR WEIGHT ($gmol^{-1}$)	ELEMENTAL ANALISYS					
					REQUIRED (%)			FOUND (%)		
n					C	H	N	C	H	N
12	**17**	$C_{29}H_{39}NO_3PdPF_6$	65	701.0	49.7	5.6	2.0	49.6	5.5	2.0
14	**18**	$C_{31}H_{43}NO_3PdPF_6$	68	729.1	51.1	6.0	1.9	51.0	5.9	2.0
16	**19**	$C_{33}H_{47}NO_3PdPF_6$	70	757.1	52.4	6.3	1.9	52.4	6.3	2.1
18	**20**	$C_{35}H_{51}NO_3PdPF_6$	70	785.2	53.5	6.6	1.8	53.7	6.6	1.9

Table S8. NMR data of **18** at 323 K. Chemical shifts (δ in ppm) and coupling constants (*J* in Hz)

Atom	**^{1}H**	**^{13}C**	**^{15}N**
Phase	**$CDCl_3$**	**$CDCl_3$**	**CPMAS**
Concentration	**0.042 M**	**0.042 M**	
7		185.4	
8	7.53	94.6 ^{1}J= 167.2	
9		185.4	
NH	14.60		
2		152.7	
3	8.52 ^{3}J= 7.9	126.0 ^{1}J= 173.6	
4	8.16	140.7	
5	7.67 ^{3}J= ^{3}J= 5.8	128.9	
6	8.78 ^{3}J= 4.2	152.2	

o	8.20	131.3	
m	7.02	115.2 ^{1}J= 162.7	
p		165.2	
ipso		124.2	
CH_2-allyl (H_s)	4.23 ^{s}J= 6.5	61.0	
CH_2-allyl (H_a)	3.19 ^{a}J= 12.2	61.0	
CH_2-allyl (H_{meso})	5.68 ^{s}J= 6.5 ^{a}J= 12.2	115.2	
N1			-185.6
CH_3	0.88 ^{3}J= ^{3}J= 6.9	14.1	
$(CH_2)_X$	1.29-1.85	22.7-31.9	
OCH_2	4.08 ^{3}J= ^{3}J= 6.5	68.7	

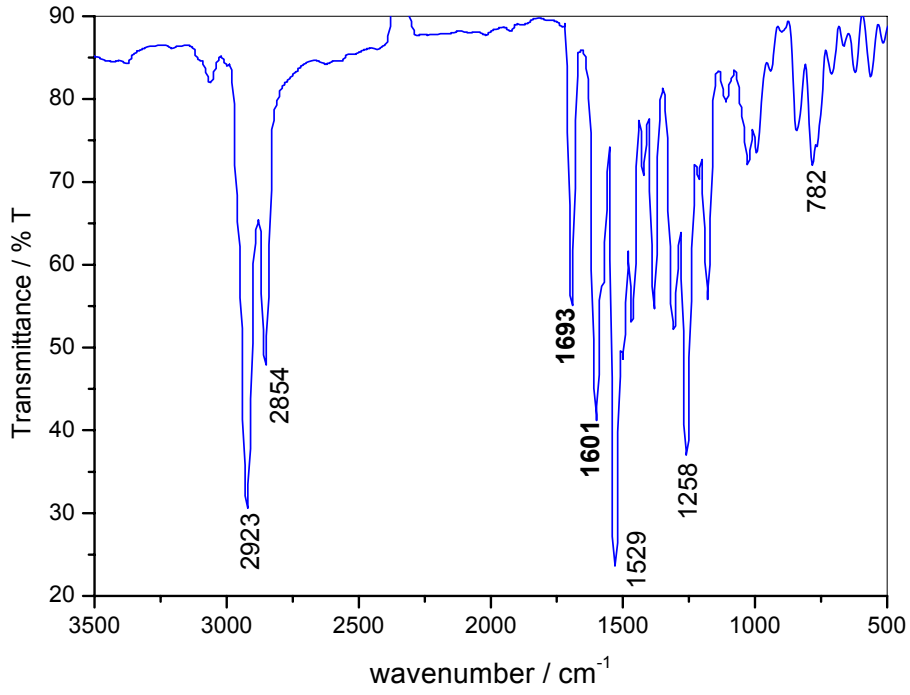

Fig. S1 IR spectrum of the complex $[Pd(\kappa^2\text{-}L^{R(12)py})_2]$ (**9**).

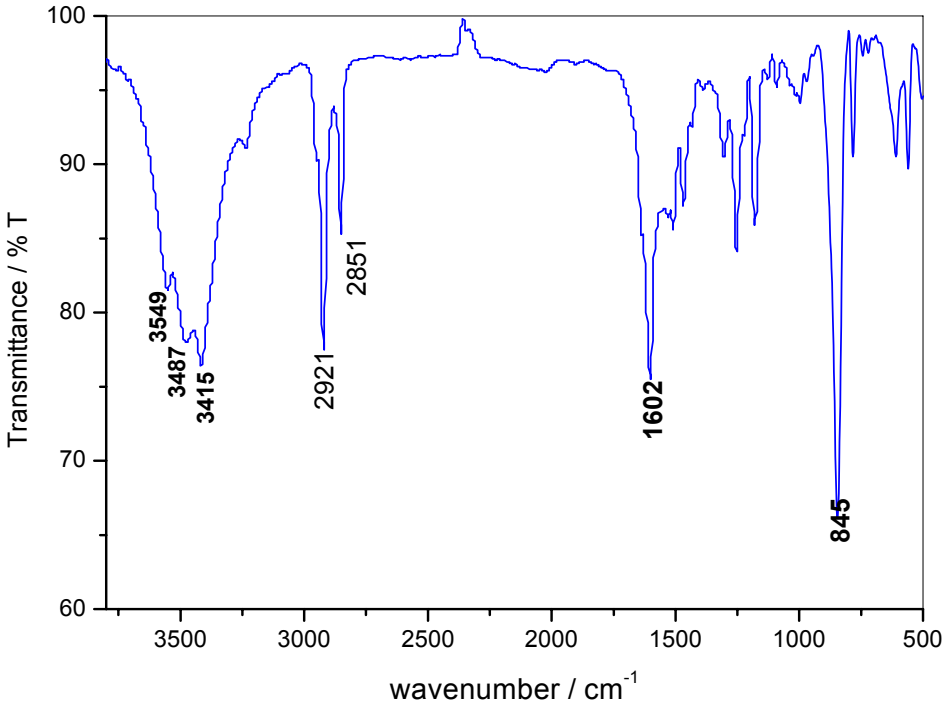

Fig. S2 IR spectrum of the complex $[Pd(\eta^3\text{-}C_3H_5)(L^{R(14)pyH})][PF_6]$ (**18**).

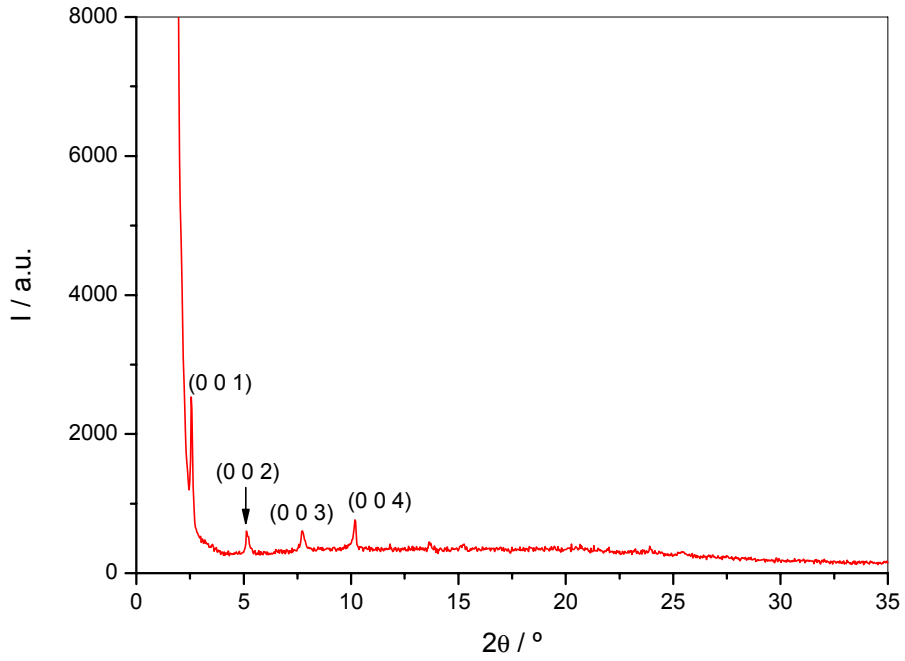

Fig. S3 X-Ray diffraction pattern of $[Pd(\eta^3\text{-}C_3H_5)(HL^{R(16)py})][PF_6]$ (**15**) at 160 ºC on heating