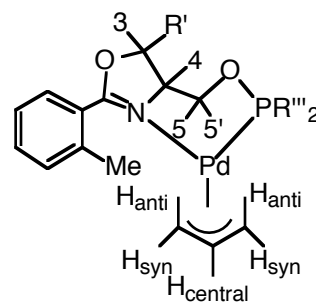
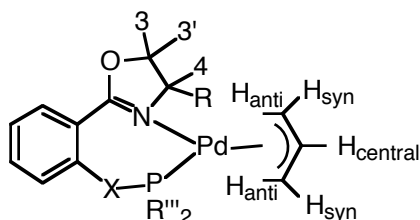


**Table S1. Selected NMR  $^1\text{H}$  (273 K, 500 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  (308 K, 100.56 MHz,  $\text{CDCl}_3$ ) and  $^{31}\text{P}$ -{ $^1\text{H}$ } (273 K, 101.2 MHz,  $\text{CDCl}_3$ ) data<sup>[a]</sup> ( $\delta$  in ppm) for allylic complexes 16-22.**

Complex	central <sup>[b]</sup> [ <i>C</i> <sub>central</sub> ]	syn [ <i>C</i> <sub>terminal</sub> ]	anti	3,3'	4	5,5'
<b>16</b> <sup>[d]</sup> Major	5.63(m) [121.2]	5.08(t; 6.0) 3.52(bs) [81.9] [55.4]	3.62(bs) 2.65(d; 12.5)	4.38(dd; 9,7) 4.94(t; 9)	4.52(m)	-
<b>16</b> <sup>[d]</sup> Minor	5.69(bs) [121.1]	5.02(bs) 3.55(d; 3) [81.4] [55.4]	3.84(bt; 9.5) 2.45(d; 11.5)	4.30(t; 8) 4.94(t; 9)	4.52(m)	-
<b>17</b> Major	5.66(m) [121.6]	5.15(m) 4-3.4 [82.8] [55.7]	4-3.4 2.68(d; 11.5)	4.39(pt; 7.5) 4.93(pt; 9.5)	4.53(m)	-
<b>17</b> Minor	5.55(m) [121.6]	5.04(m) 4-3.4 [82.3] [53.9]	4-3.4 2.41(d; 11.5)	4.93(pt; 9.5) 4.31(m)	4.53(m)	-
<b>18</b> <sup>[d]</sup> Major	5.82(m) [122.7]	5.22(m) 3.65(d,5) [82.6(d; 30)] [55.4]	3.81(t,12.5) 2.83(d,12)	4.93(m) 4.31(pt,7)	4.59(m)	-
<b>18</b> <sup>[d]</sup> Minor	5.82(m) [120.1]	5.17(m) 3.72(bs) [85.4] [53.4]	4.08(t; 12.5) 2.74(d; 12)	4.93(m) 4.26(pt; 7)	4.59(m)	-
<b>19</b> Major	5.83(m) [123.0]	5.19(m) 3.59(pd; 4.5) [83.1(d; 32)] [55.4]	3.74(m) 2.84(d; 12)	4.82(t; 3.6) 4.36(m)	4.49(bm)	-
<b>19</b> Minor	5.83(m) [120.4]	5.07(m) 3.74(m) [86.2(d; 32)] [53.2]	4.10(m) 2.68(d; 12)	4.82(t; 3.6) 4.30(m)	4.49(bm)	-

<b>20</b> <sup>[e]</sup>						
Major	5.52(bs) [121.7]	4.98(bs) 3.43(bs) [82] [50]	3.72(bt) 2.62(d, 5.2)	4.82(bs) 4.22(bs)	4.46(bs)	-
<b>20</b> <sup>[e]</sup>						
Minor	5.67(bs) [118.8]	4.98(bs) 3.62(bs) [85] [48]	3.85(bt) 2.42(bd; 5.2)	4.82(bs) 4.22(bs)	4.46(bs)	-
<b>21</b> <sup>[e]</sup>						
Major	5.64(bs) [124.7]	5.01(bd; 15) 3.54(bs) [82.6(d; 32) [47.6]	3.78(bs) 2.60(bs)	4.71(bs) 4.41(bs)	4.56(bs)	-
<b>21</b> <sup>[e]</sup>						
Minor	5.64(bs) [123.1]	5.01(bd,15) 3.58(bs) [85.5(d; 30)] [46.4]	4.03(bs) 2.50(bs)	4.71(bt) 4.41(bs)	4.56(bs)	-
<b>22</b>						
Major	5.09(m) [137.9]	3.42(d, 6) 3.05(pt; 5.5) [84(d; 28)] [47.77]	3.30(m) 2.30(t; 11)	5.04(t; 10) 4.87(pq; 10)	4.3-4.17	4.45-4.3 4.12(m)
<b>22</b>						
Minor	5.28(m) [137.5]	3.50(pt) 3.32(d, 4.5) [83.25(d; 27.8)] [47.14]	2.70(pq) 2.30(t; 6)	4.90(t; 6) 4.50(pq)	4.3-4.17	4.45-4.3 4.01(m)

[a] Multiplicity (d, doublet; q, quartet; s, singlet; t, triplet; bs, broad signal; m, multiplet), coupling constants in Hz In brackets, <sup>13</sup>C chemical shifts. [b] See figure below for atom labels. [c] In brackets, <sup>31</sup>P chemical shift for free ligand. [d] Spectrum registered at 308 K. [e] The spectrum presents broad signals even at low temperature. [f] Signals overlapped with cyclohexyl group protons. [g] Unique signal at 308 K



**Table S2. Selected NMR  $^1\text{H}$  (273 K, 500 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  (308 K, 100.56 MHz,  $\text{CDCl}_3$ ) and  $^{31}\text{P}$ - $\{^1\text{H}\}$  (273 K, 101.2 MHz,  $\text{CDCl}_3$ ) data<sup>[a]</sup> ( $\delta$  in ppm) for allylic complexes **23**, **24**, **25** and **26**.**

Complex <sup>[b]</sup>	central <sup>[c]</sup> [C <sub>central</sub> ]	anti [C <sub>terminal</sub> ]	3, 3'	4	5, 5'	
<b>23</b>						
Major (70)	6.7 <sup>[e]</sup> [109.3]	5.63(dd; 13.9) 4.23(d; 11) [99.5 (d; 12.6)] [71.7]	4.08(dd; 8.5,7) 3.95(t; 9.5)	2.50(dt; 9.5,3.5)	-	R=C CH <sub>3</sub> = 0.50 CH=
<b>23</b>						
Minor (30)	6.2 <sup>[e]</sup> [110.4]	5.46(t; 11.5) 5.37(d; 12.5) [92.8] [77.8]	4.03(dd; 9, 5.5) 3.24(t; 9.5)	3.86(pq; 5)	-	R=C CH <sub>3</sub> =C 0.62 CH=
<b>24</b>						
Major (80)	6.59(dd; 14,11) [112.6(d; 7.0)]	5.74(dd; 29,10) 4.47(d; 11) [104.4(d; 23)] [62.2]	4.05(m) 3.80(t; 9.5)	2.8(m)	-	R=C CH <sub>3</sub> = 0.61 (
<b>24</b>						
Minor (20)	6.37(t; 12.5) [112.1(d; 5)]	5.58(t; 11.5) 5.23(d; 12) [95.7(d; 25)] [79.9]	4.05(m) 3.00(t; 8.5)	3.99(m)	-	R=C CH <sub>3</sub> = 0.6 (
<b>25</b>						
Major (55)	6.28-6.12(m) [109.8]	6.39(t; 11) 4.66(d; 10) [103.4] [71.9]	5.05(d; 5)	4.4(m)	4.37(bdd; 26,13) 3.92-3.74(bm)	
<b>25</b>						
Minor (45)	6.28-6.12(m) [11.3]	5.25(d; 10) 4.71(t; 12.5) [95.6] [72.21]	5.40(d; 10)	4.57(m)	4.85(bm) 3.92-3.74(bm)	
<b>26</b>						
Major (75)	6.36 (t; 2.5) [111.41(d; 6.1)]	5.03 (d; 2) 151.5 4.77(t; 12.5) [96.46(d; 26.7)] [73.67]	5.16 (d; 5)	4.08 (ddd; 0.5,5,2.5)	4.35(ddd; 4.03(d; 3.5)	
<b>26</b>						
Minor (25)	non observed	4.47(d; 10) Only one proton observed [85.7] [104.5]	5.35(d; 9.5)	4.47(bs)	4.01-3.98(m)	

[a] Multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal) coupling constants (in Hz). In brackets,  $^{13}\text{C}$  chemical shifts. [b] In parentheses ratio of isomers. [c] See Table S1 for labelling. [d] In brackets,  $^{31}\text{P}$  chemical shift for free ligand. [e] Signal overlapped with aromatic protons. [f] Signal overlapped with cyclohexenyl protons.