

# Supplementary Information

## Pd Complexes Based on Phosphine-Linked Cyclophosphazenes: Synthesis, Characterization and Application in Suzuki Coupling Reactions

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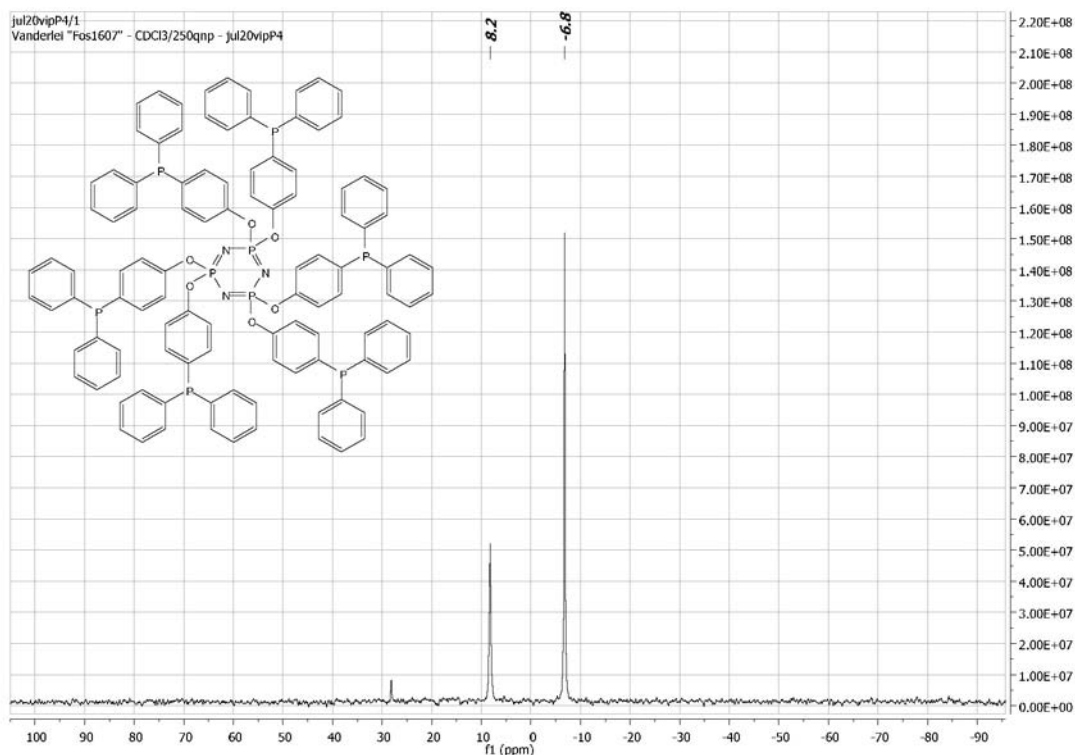


Figure S1.  $^{31}\text{P}$  NMR spectrum of ligand **1a**.



Figure S2.  $^1\text{H}$  NMR spectrum of ligand **1a**.

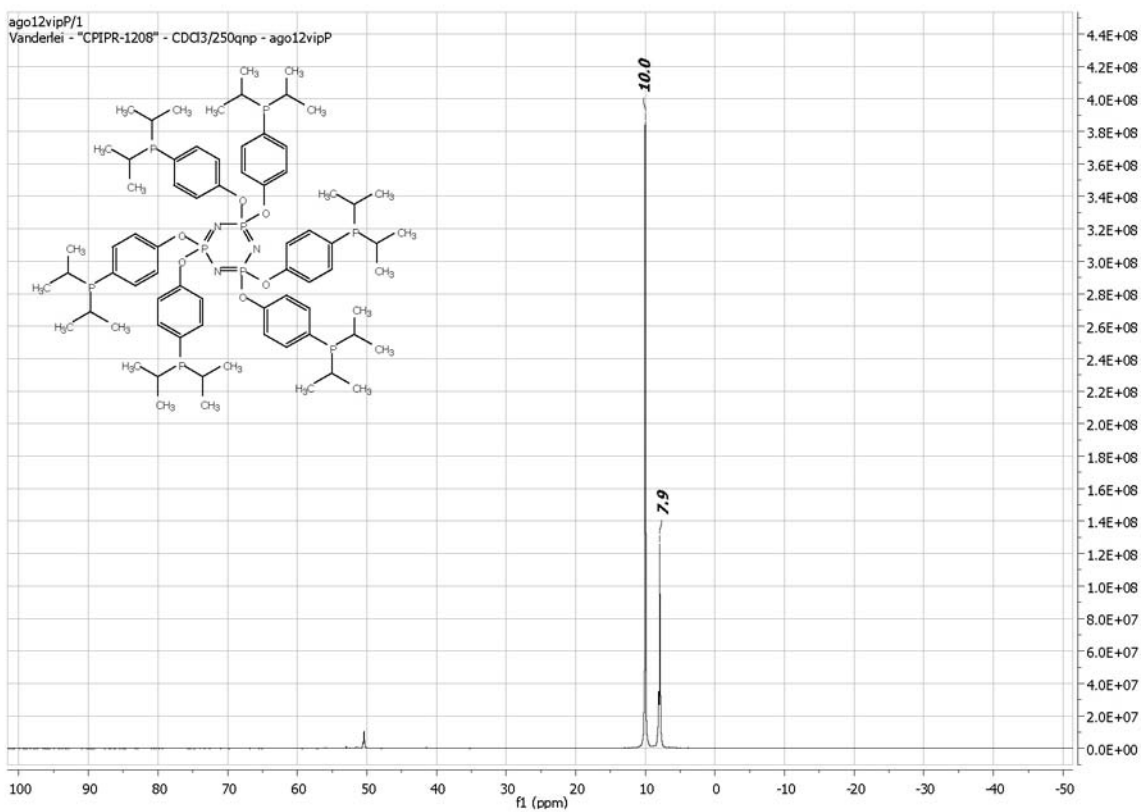
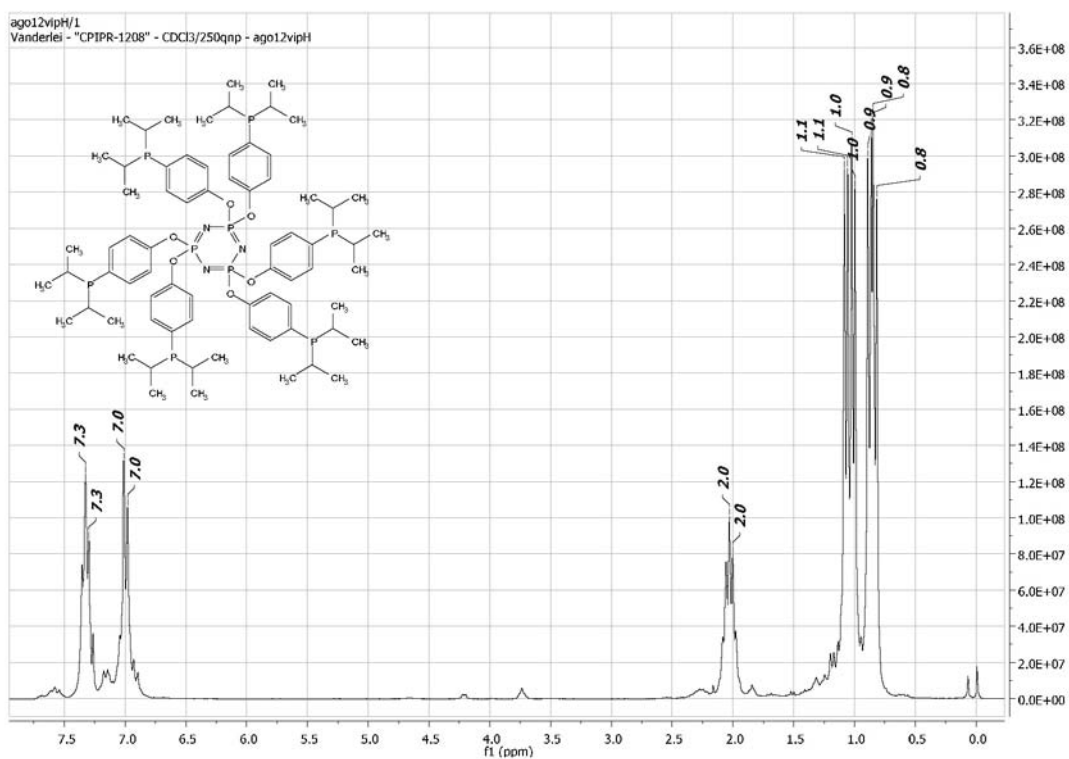
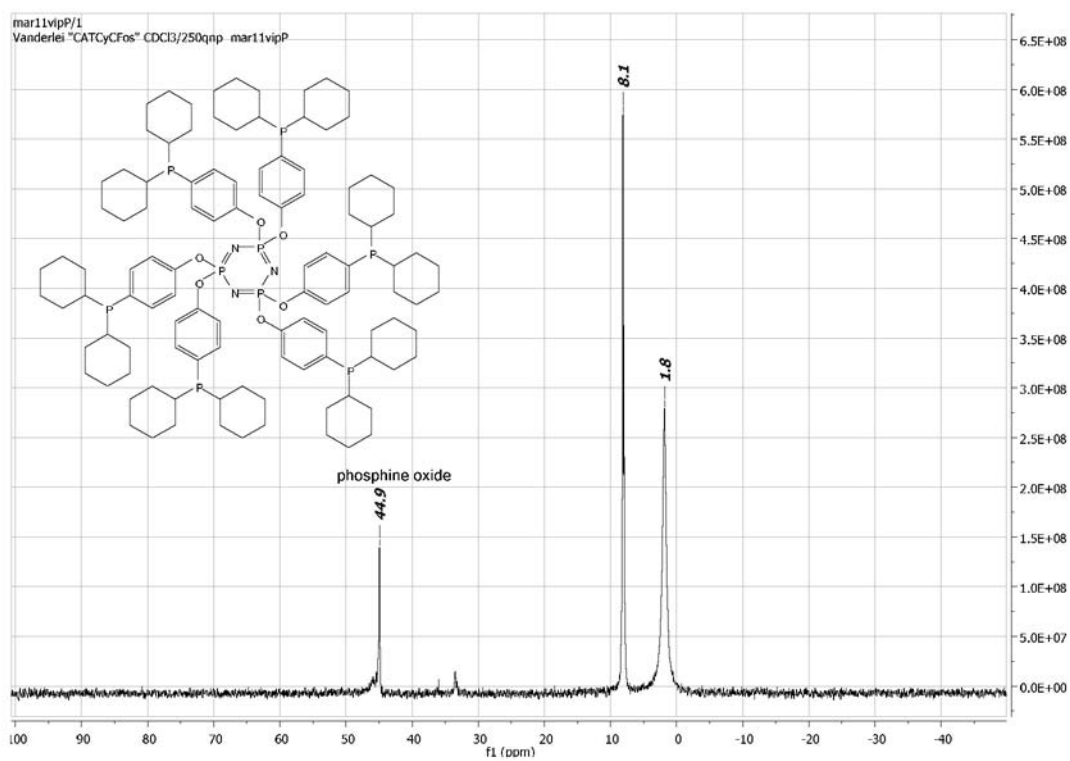


Figure S3.  $^{31}\text{P}$  NMR spectrum of ligand **1b**.

Figure S4. <sup>1</sup>H NMR spectrum of ligand **1b**.Figure S5. <sup>31</sup>P NMR spectrum of ligand **1c**.

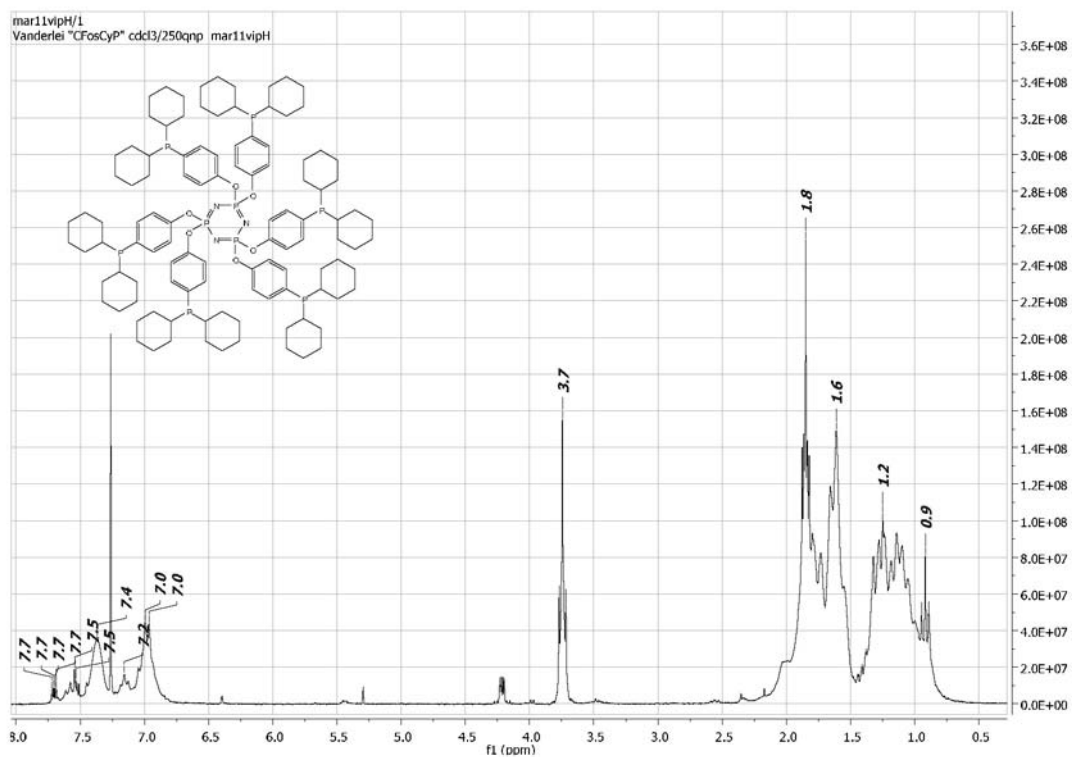


Figure S6. <sup>1</sup>H NMR spectrum of ligand **1c**.

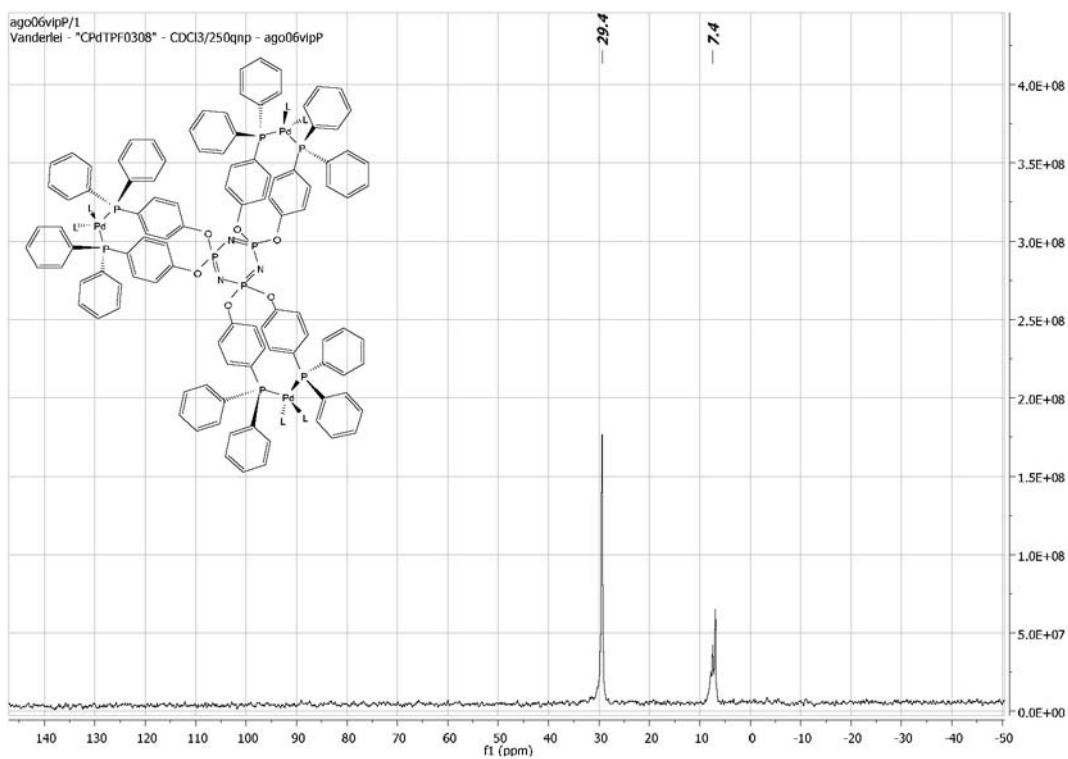


Figure S7. <sup>31</sup>P NMR spectrum of complex **1aPd<sub>3</sub>(dba)**.

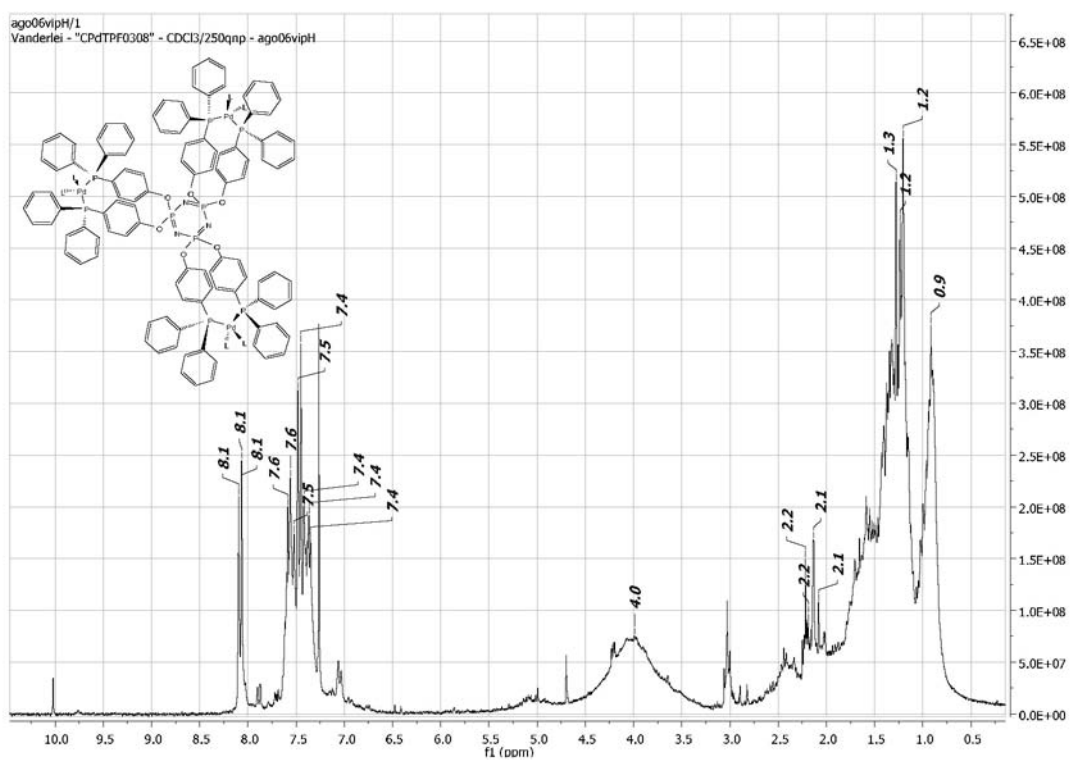


Figure S8. <sup>1</sup>H NMR spectrum of complex **1aPd<sub>3</sub>(dba)<sub>3</sub>**.

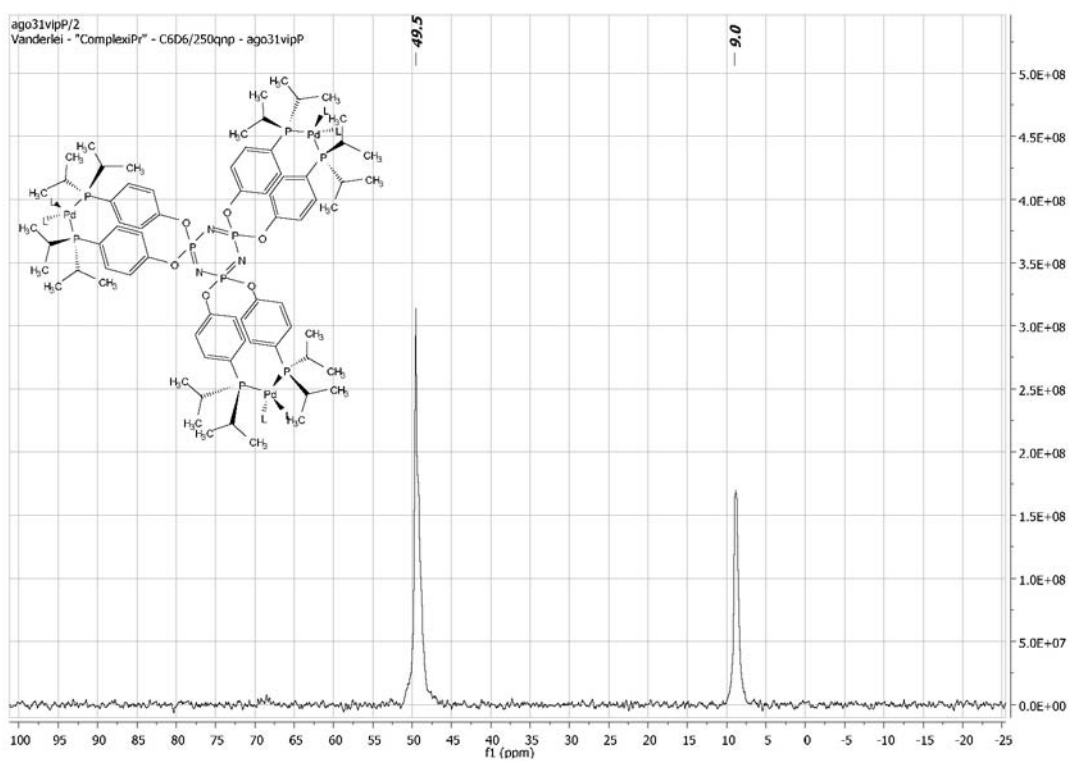


Figure S9. <sup>31</sup>P NMR spectrum of complex **1bPd<sub>3</sub>(dba)<sub>3</sub>**.

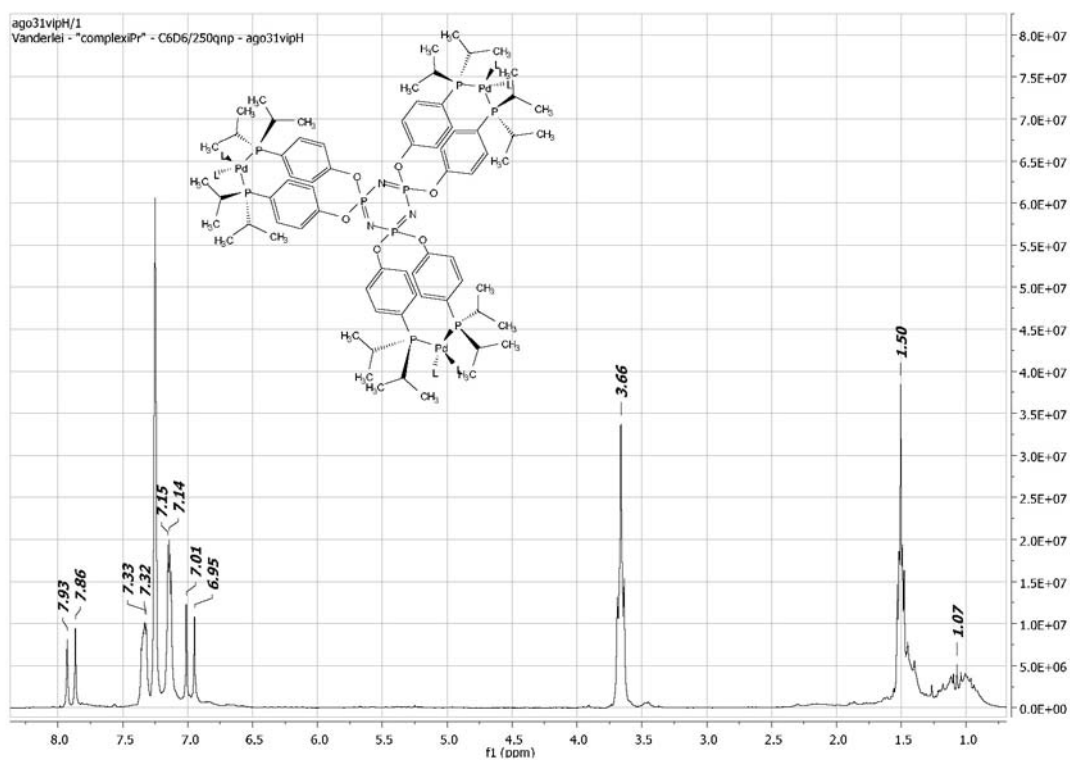


Figure S10.  $^1\text{H}$  NMR spectrum of complex  $1\text{bPd}_3(\text{dba})_3$ .

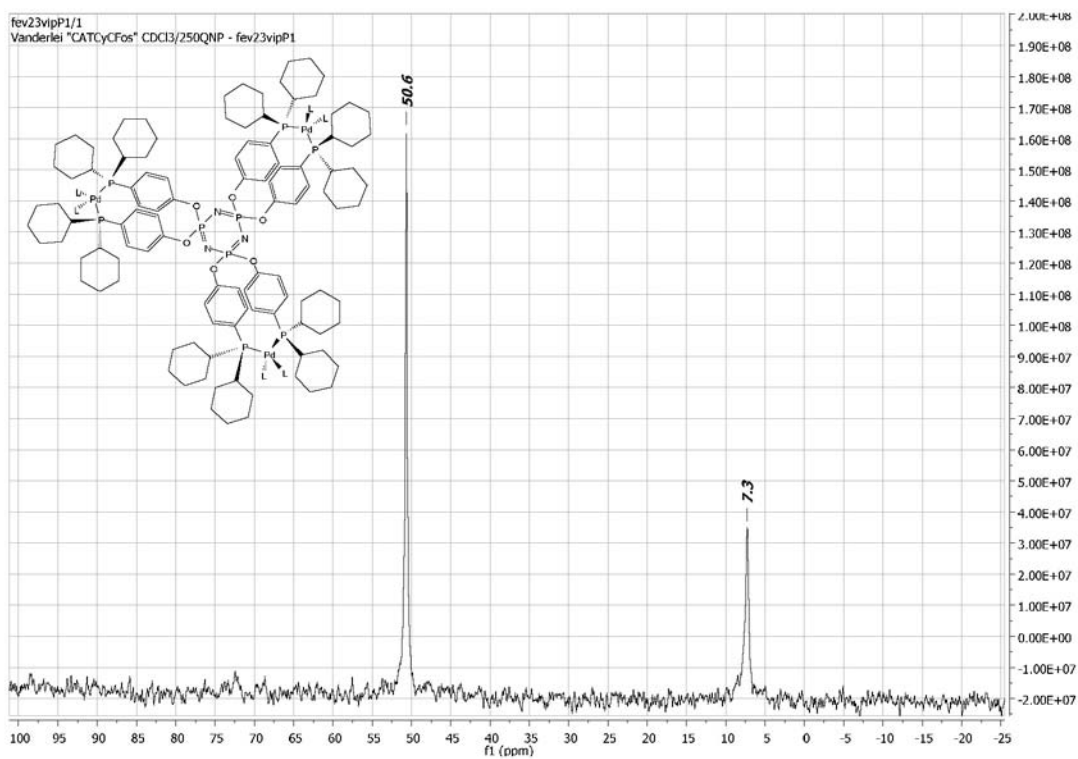


Figure S11.  $^{31}\text{P}$  NMR spectrum of complex  $1\text{cPd}_3(\text{dba})_3$ .

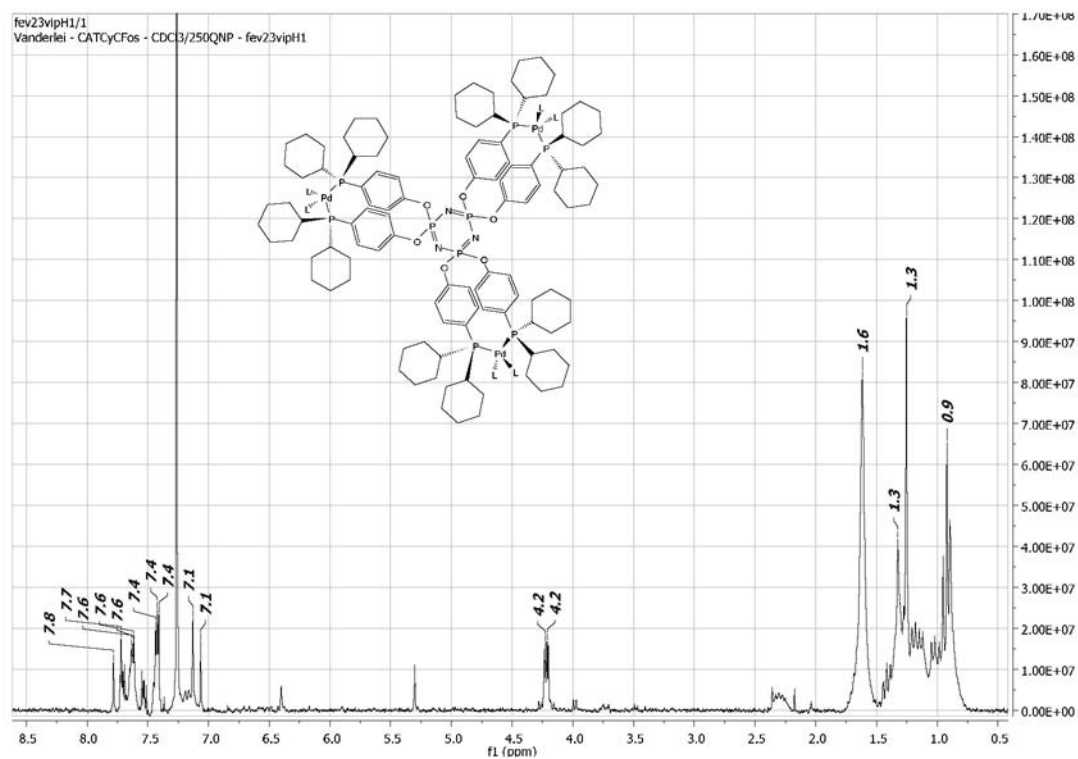


Figure S12.  $^1\text{H}$  NMR spectrum of complex  $1c\text{Pd}_3(\text{dba})$ .

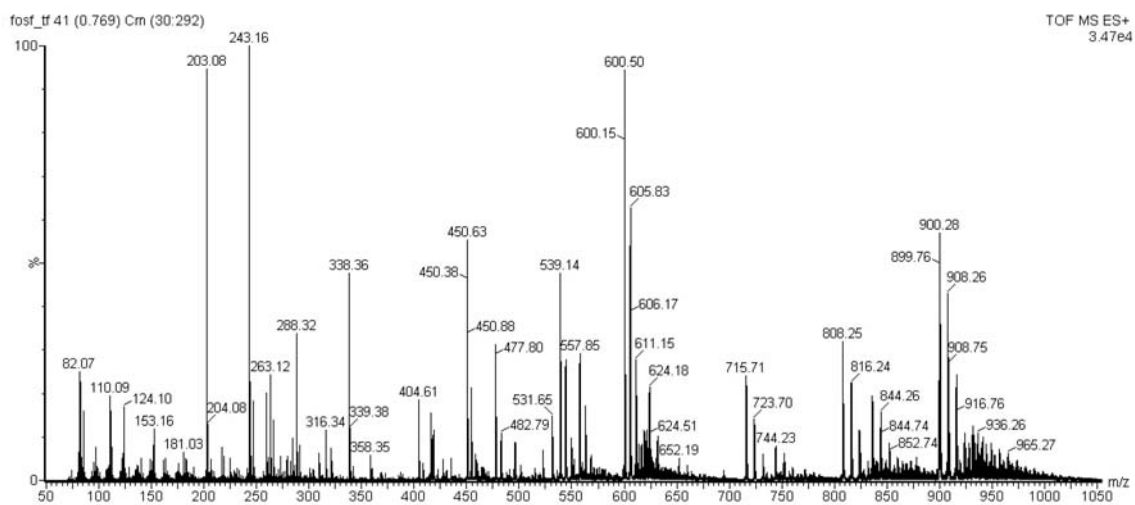


Figure S13. Mass spectrum of ligand  $1a$ .

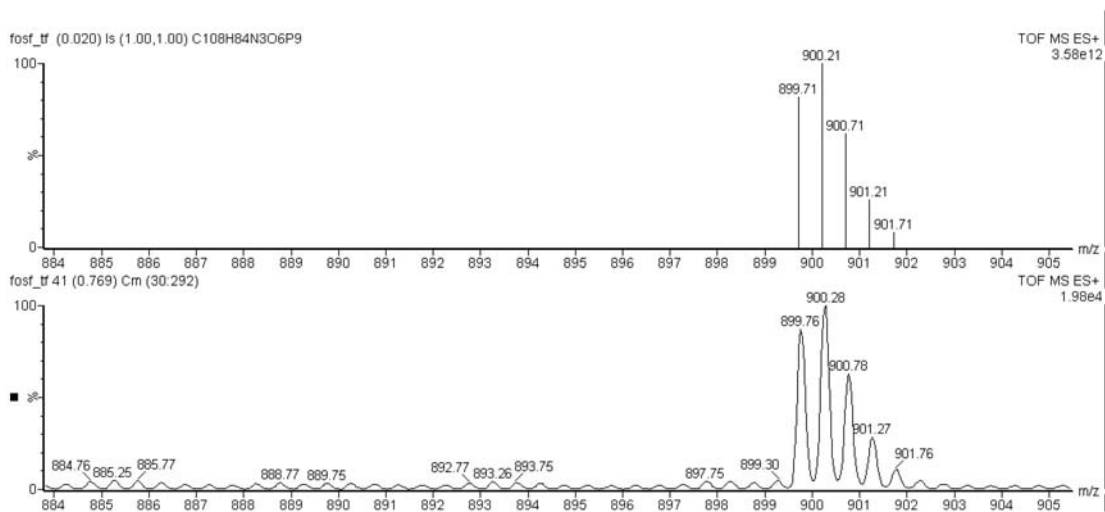


Figure S14. Mass spectrum of the ligand **1a** and isotopic pattern around 900.2.

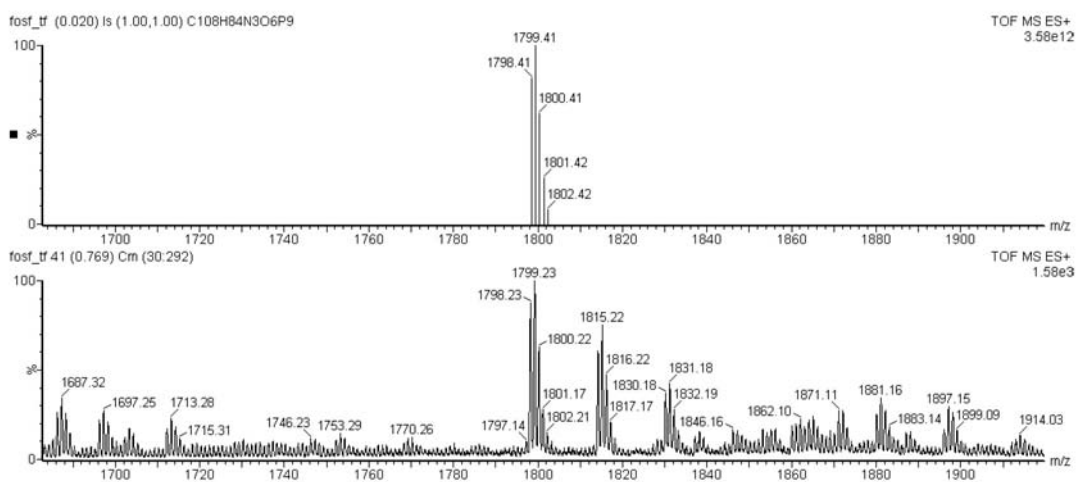


Figure S15. Mass spectrum of ligand **1a** and isotopic pattern around 1799.2.

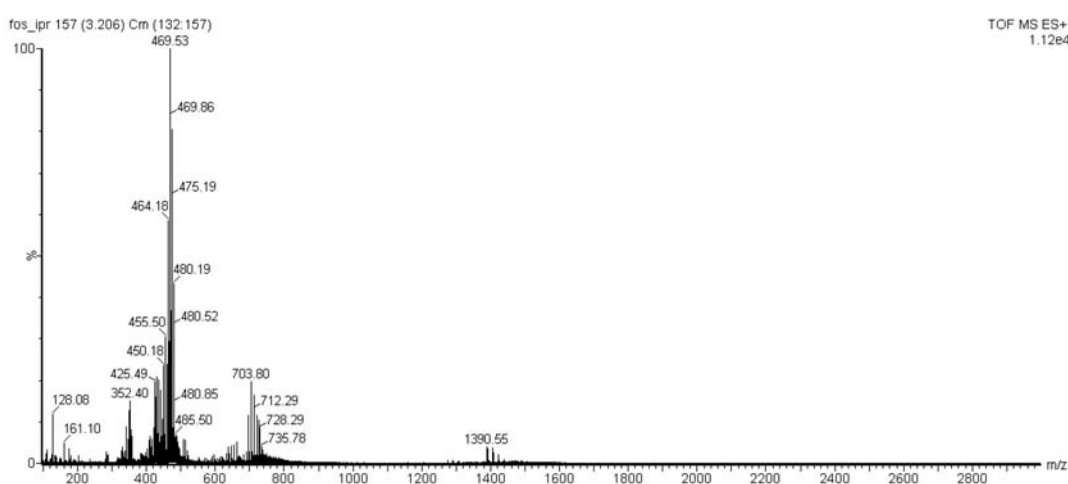


Figure S16. Mass spectrum of ligand **1b**.



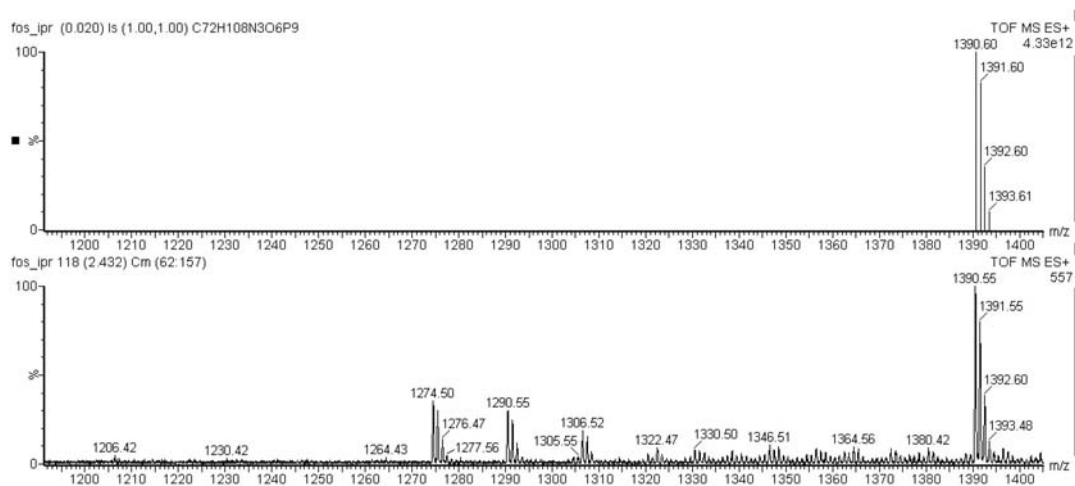


Figure S17. Mass spectrum of ligand **1b** and isotopic pattern around 1390.6.

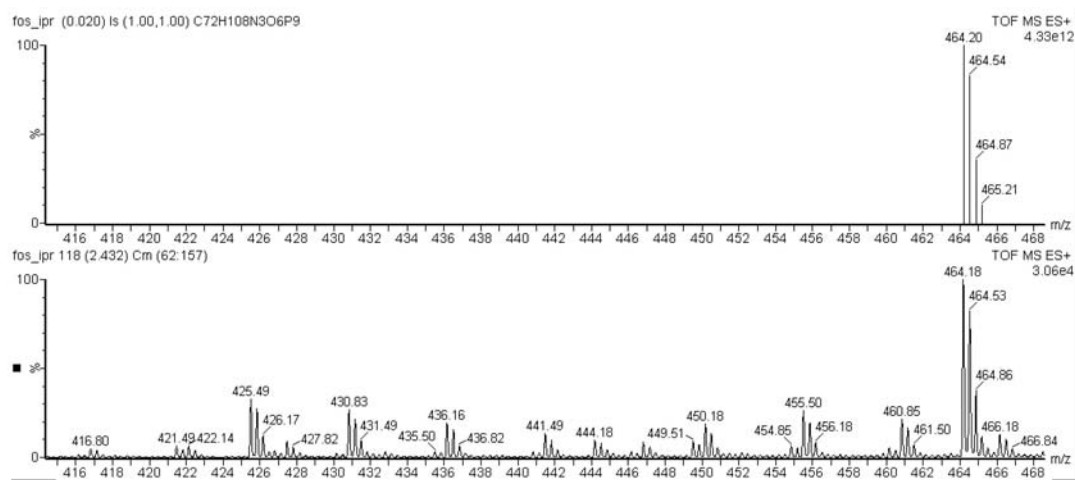


Figure S18. Mass spectrum of ligand **1b** and the isotopic pattern around 464.2.

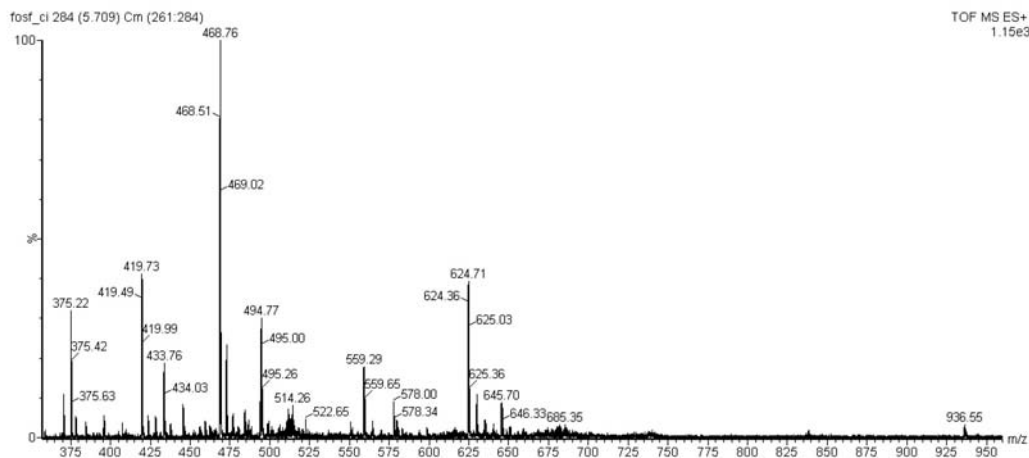


Figure S19. Mass spectrum of ligand **1c**.

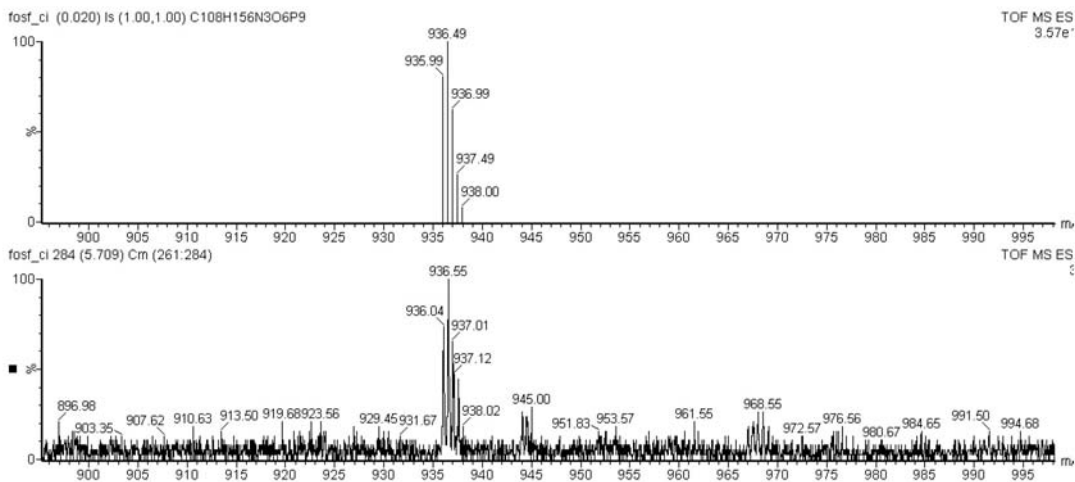


Figure S20. Mass spectrum of ligand **1c** and isotopic pattern around 936.5.

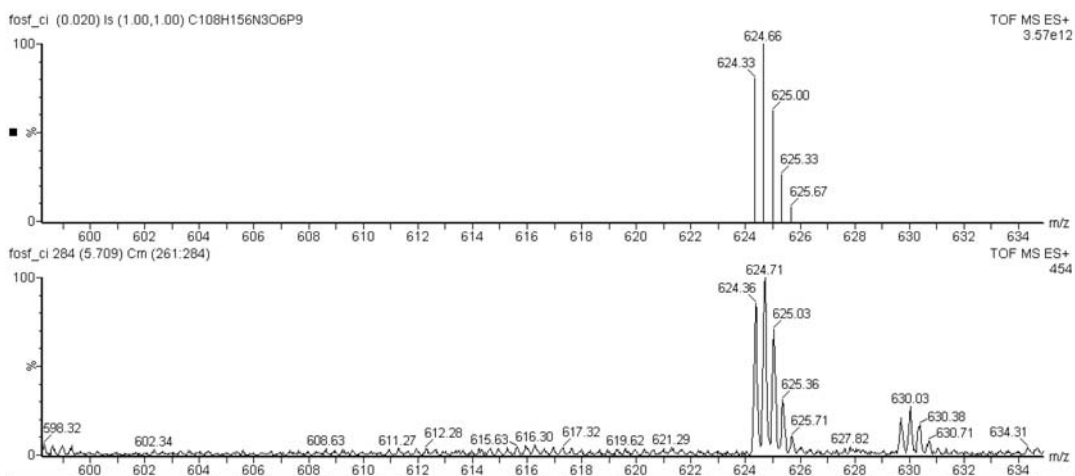


Figure S21. Mass spectrum of ligand **1c** and isotopic pattern around 624.7.

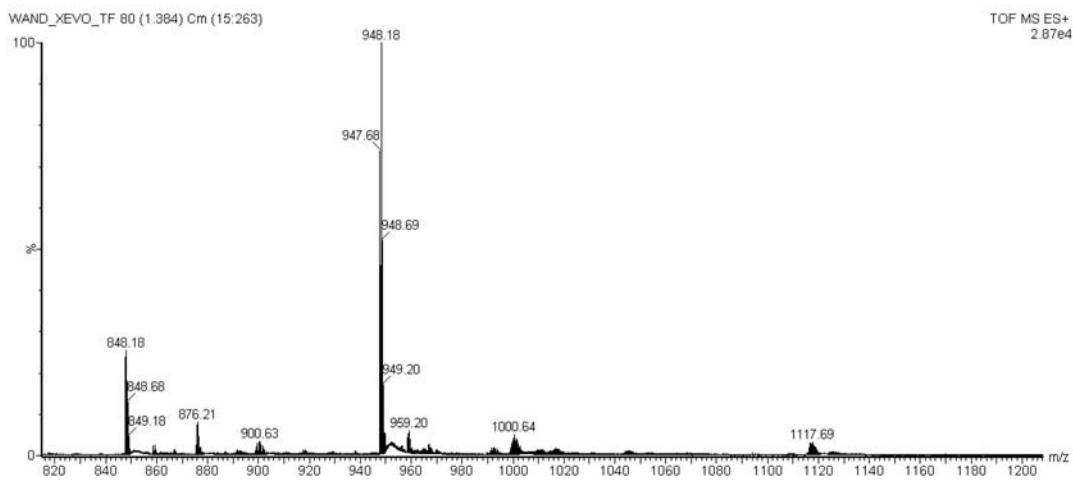


Figure S22. Mass spectrum of complex **1aPd<sub>3</sub>(dba)**.

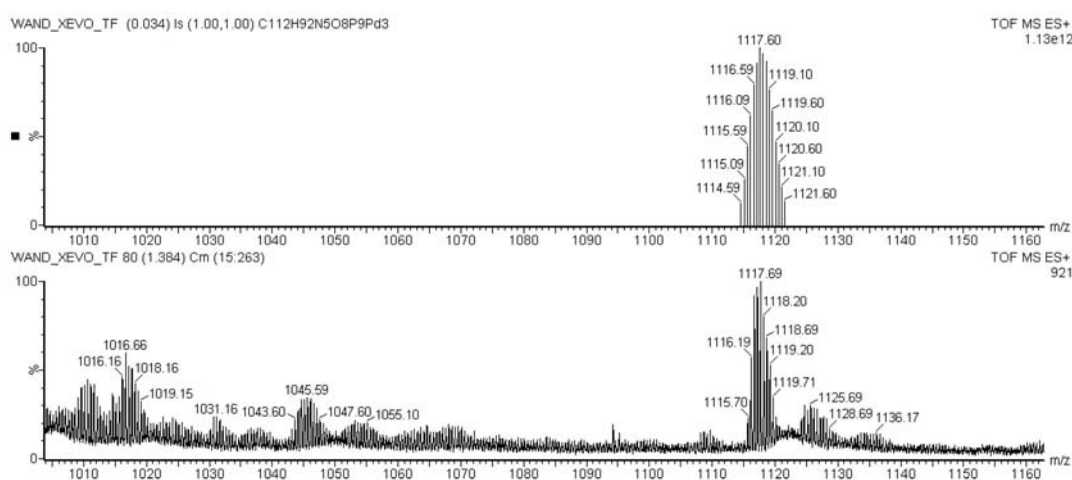


Figure S23. Mass spectrum of complex **1aPd<sub>3</sub>(dba)** and isotopic pattern around 1117.6.

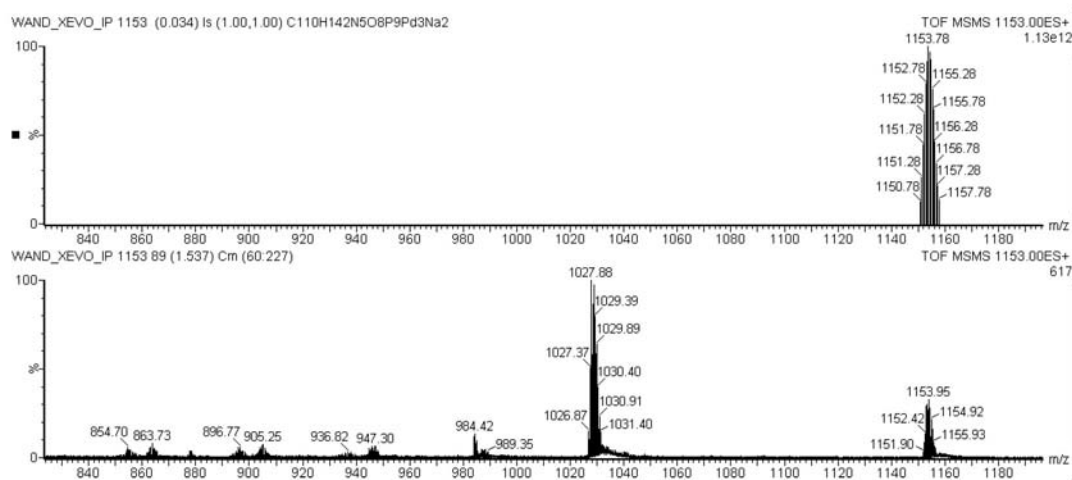


Figure S24. Mass spectrum of complex **1bPd<sub>3</sub>(dba)<sub>3</sub>** and isotopic pattern around 1153.

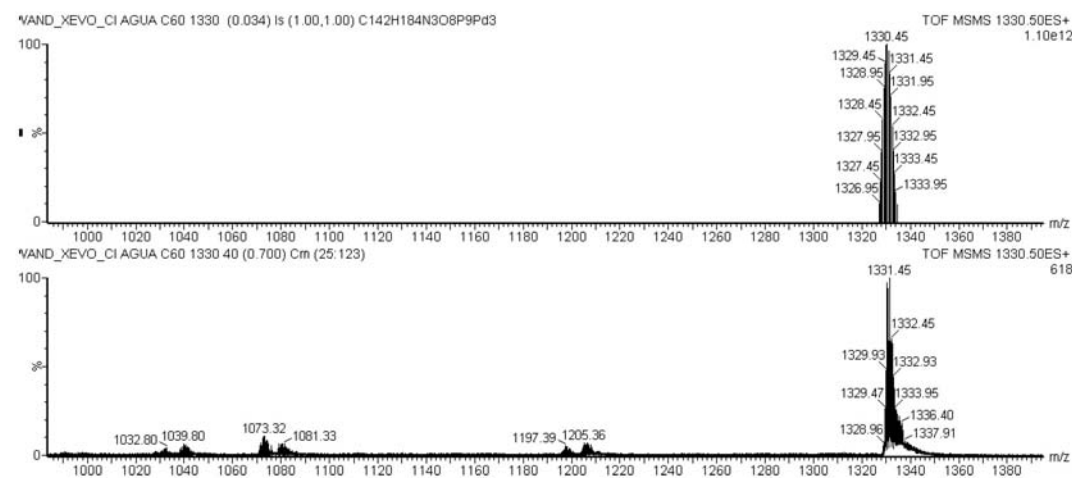


Figure S25. Mass spectrum of complex **1cPd<sub>3</sub>(dba)** and isotopic pattern around 1330.4.

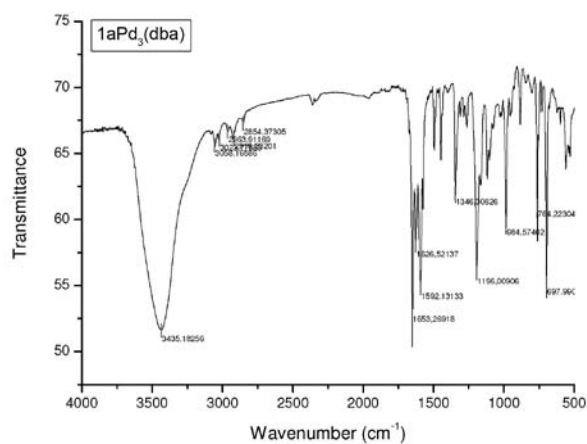


Figure S26. Infrared spectrum of complex **1aPd<sub>3</sub>(dba)**.

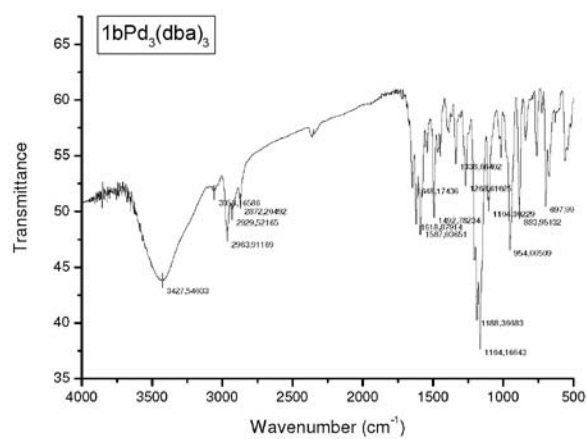


Figure S27. Infrared spectrum of complex **1bPd<sub>3</sub>(dba)<sub>3</sub>**.

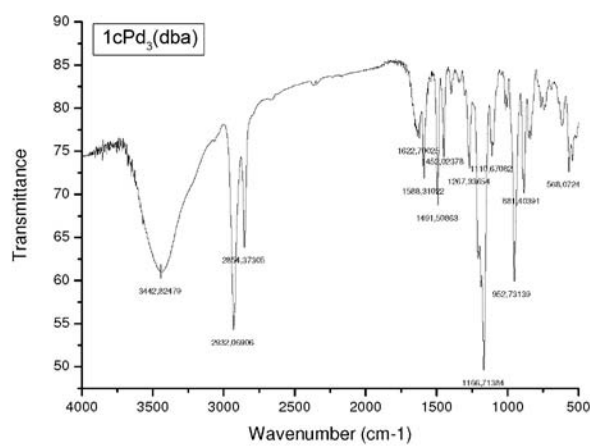
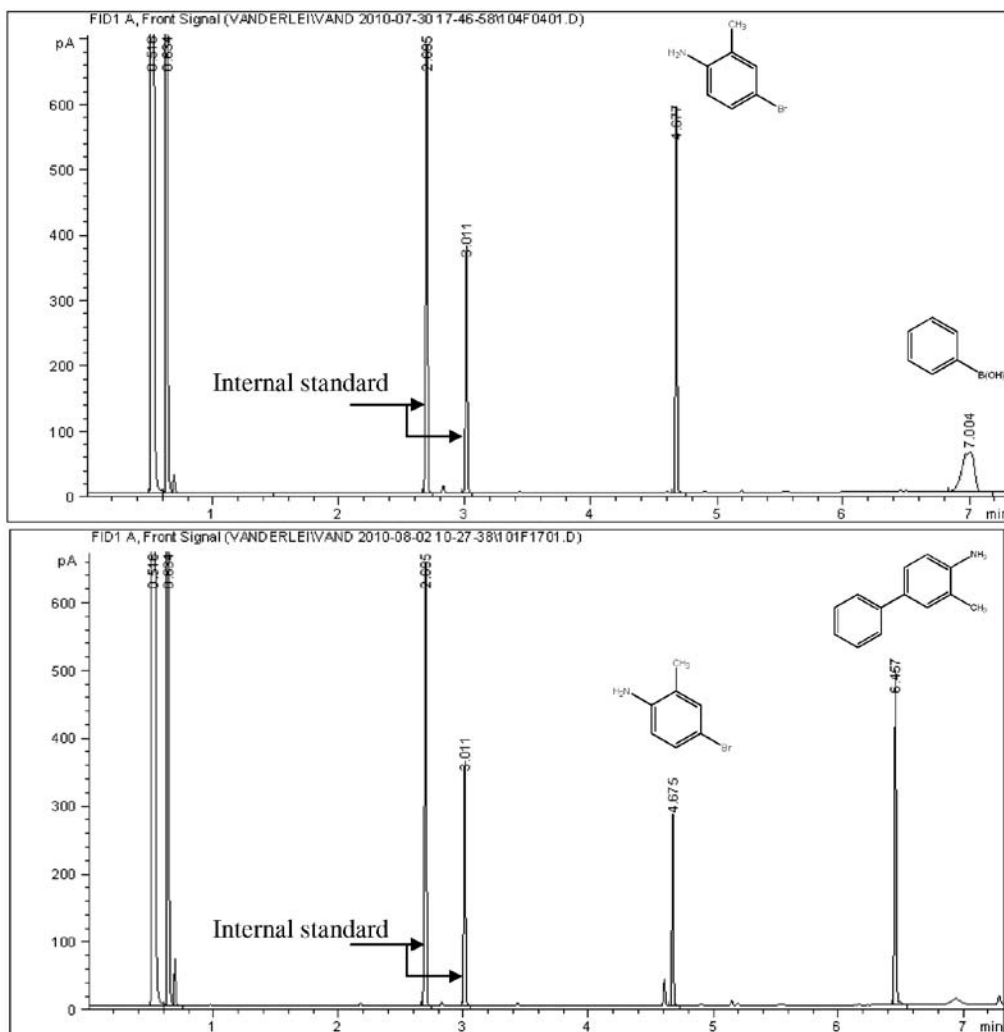
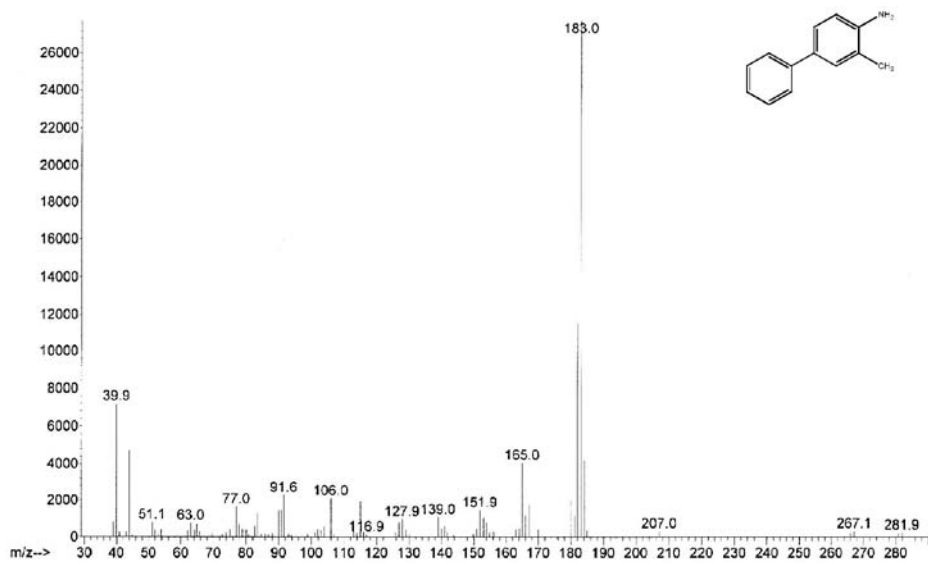


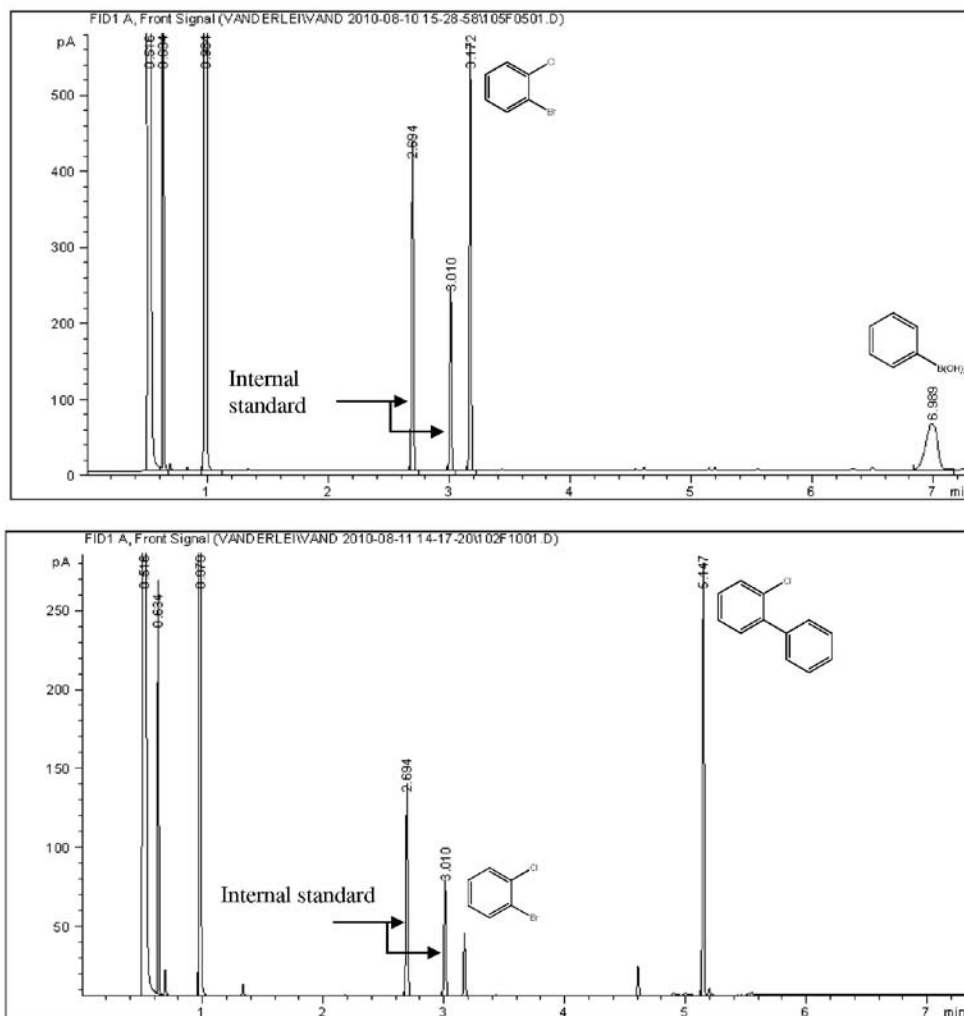
Figure S28. Infrared spectrum of complex **1cPd<sub>3</sub>(dba)**.



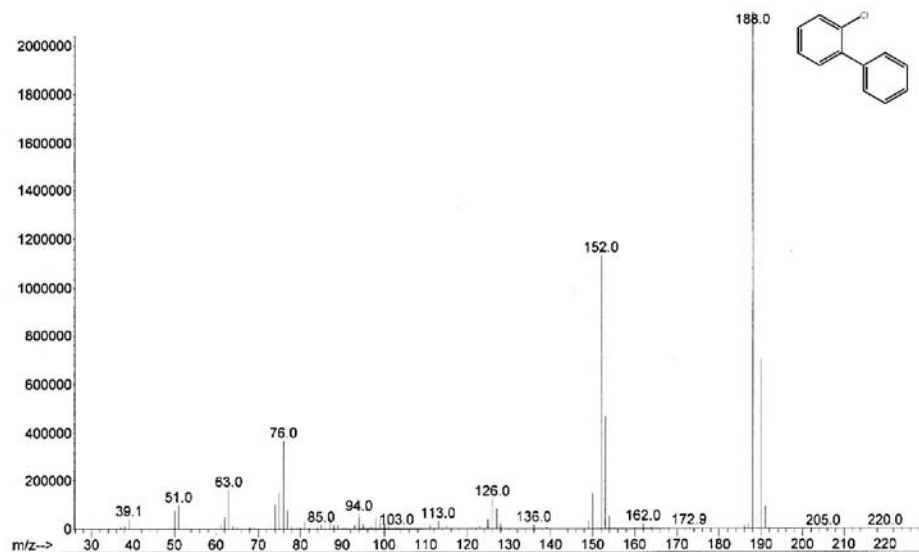
**Figure S29.** Gas phase chromatograms of the reaction described in Table 2, entry 24 (top: t = 0; bottom: t = 24 h). Peak at 4.60: biphenyl. The peak at 6.457 was assigned to 3-methyl-[1,1'-biphenyl]-4-amine based on its mass spectrum:  $m/z$  183.0, 165.0, 151.9, 139.0, 127.9, 16.0, 91.6, 77.0, 63.0, 51.1, 39.9.



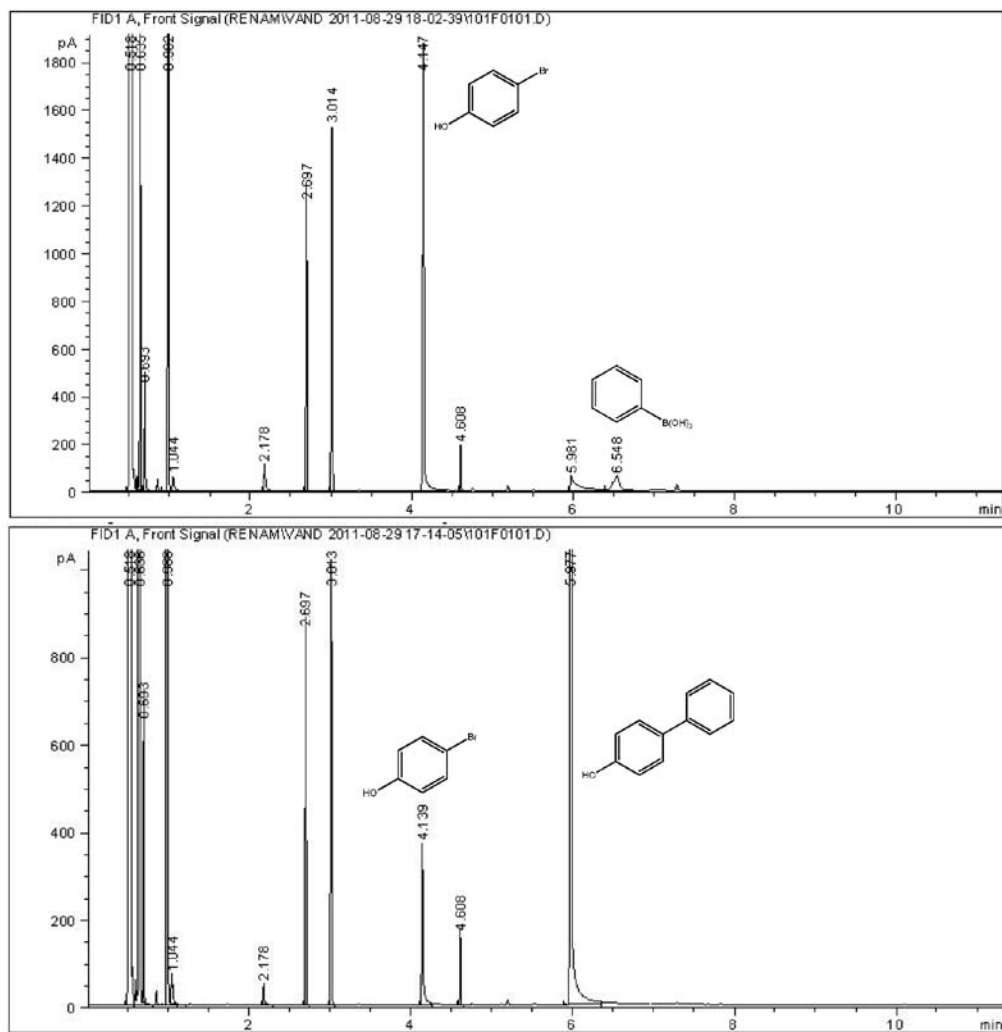
**Figure S30.** MS spectrum of the product of the reaction described in Table 2, entry 24.



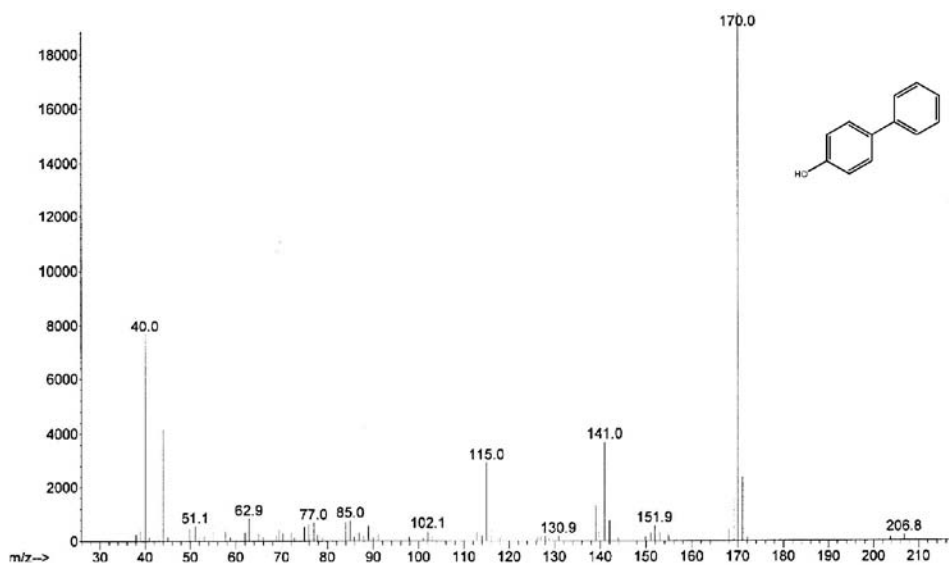
**Figure S31.** Gas phase chromatograms of the reaction described in Table 3, entry 5 (top:  $t = 0$ ; bottom:  $t = 24$  h). Peak at 4.60: biphenyl. The peak at 5.147 was assigned to 2-chloro-1,1'-biphenyl based on its mass spectrum (Figure S32).  $m/z$  188.0, 152.0, 126.0, 113.0, 103.0, 94.0, 76.0, 63.0, 51.0, 39.1.



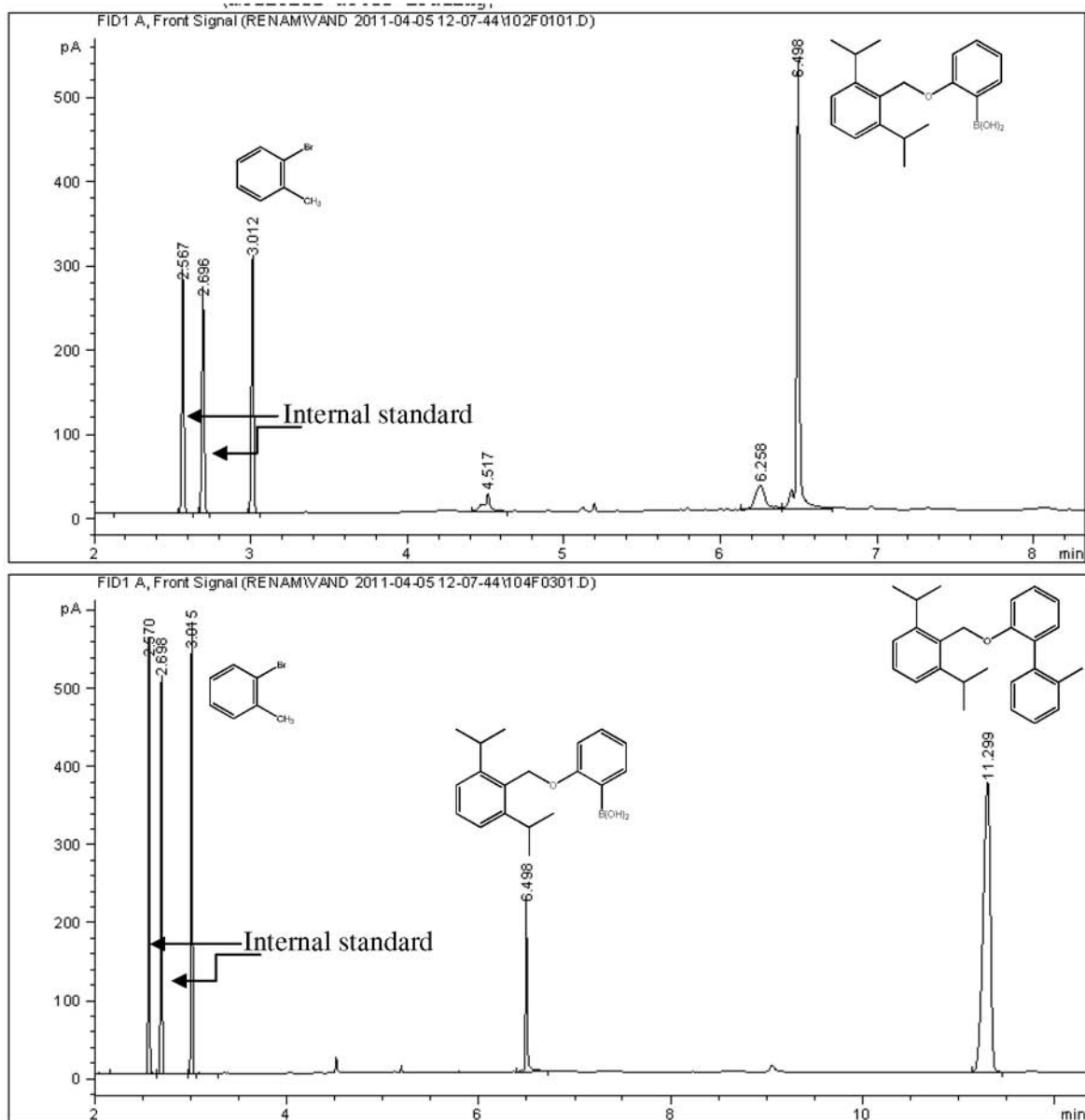
**Figure S32.** MS spectrum of the product of the reaction described in Table 3, entry 5



**Figure S33.** Gas phase chromatograms of the reaction described in Table 3, entry 1 (top:  $t = 0$ ; bottom:  $t = 24$  h). Peak at 4.60: biphenyl. The peak at 4.610 was assigned to [1,1'-biphenyl]-4-ol based on its mass spectrum (Figure S34):  $m/z$  170.0, 151.9, 141.0, 130.9, 115.0, 102.1, 85.0, 77.0, 62.9, 51.1, 40.0.



**Figure S34.** MS spectrum of the product of the reaction described in Table 3, entry 1.



**Figure S35.** Gas phase chromatograms of the reaction described in Table 4, entry 4 (top: t = 0; bottom: t = 2 h).

The peak at 11.299 was assigned to 2-((2,6-diisopropylbenzyl)oxy)-2'-methyl-1,1'-biphenyl (tr = 11.299), based on its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure S36).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J$  7.5 Hz, 1H), 7.45 (dtd,  $J$  20.4, 7.5, 1.5 Hz, 3H), 7.31-7.09 (m, 5H), 7.06 (s, 2H), 4.51 (s, 2H), 3.10 (p,  $J$  6.9 Hz, 2H), 2.08 (s, 3H), 1.11 (d,  $J$  6.9 Hz, 12H).  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ )  $\delta$  152.97(s, Ar-O, 1C), 141.93 (s, Ar-Ar, 2C), 140.83(s, Ar-Ar, 1C), 140.08 (s, Ar, 1C), 135.94(s, Ar, 1C), 135.46(s, Ar, 1C), 129.88(s, Ar, 1C), 129.54(s, Ar, 1C), 129.35(s, Ar, 1C), 128.37(s, Ar, 1C), 127.7-127.58(m, Ar, 3C), 125.51(s, Ar, 1C), 124.56(s, Ar, 1C), 123.95(s, Ar, 2C), 73.96(s,  $\text{CH}_2$ , 1C), 26.25(s, CH, 2C), 24.1(s,  $\text{CH}_3$ , 4C), 19.98(s,  $\text{CH}_3$ , 1C).



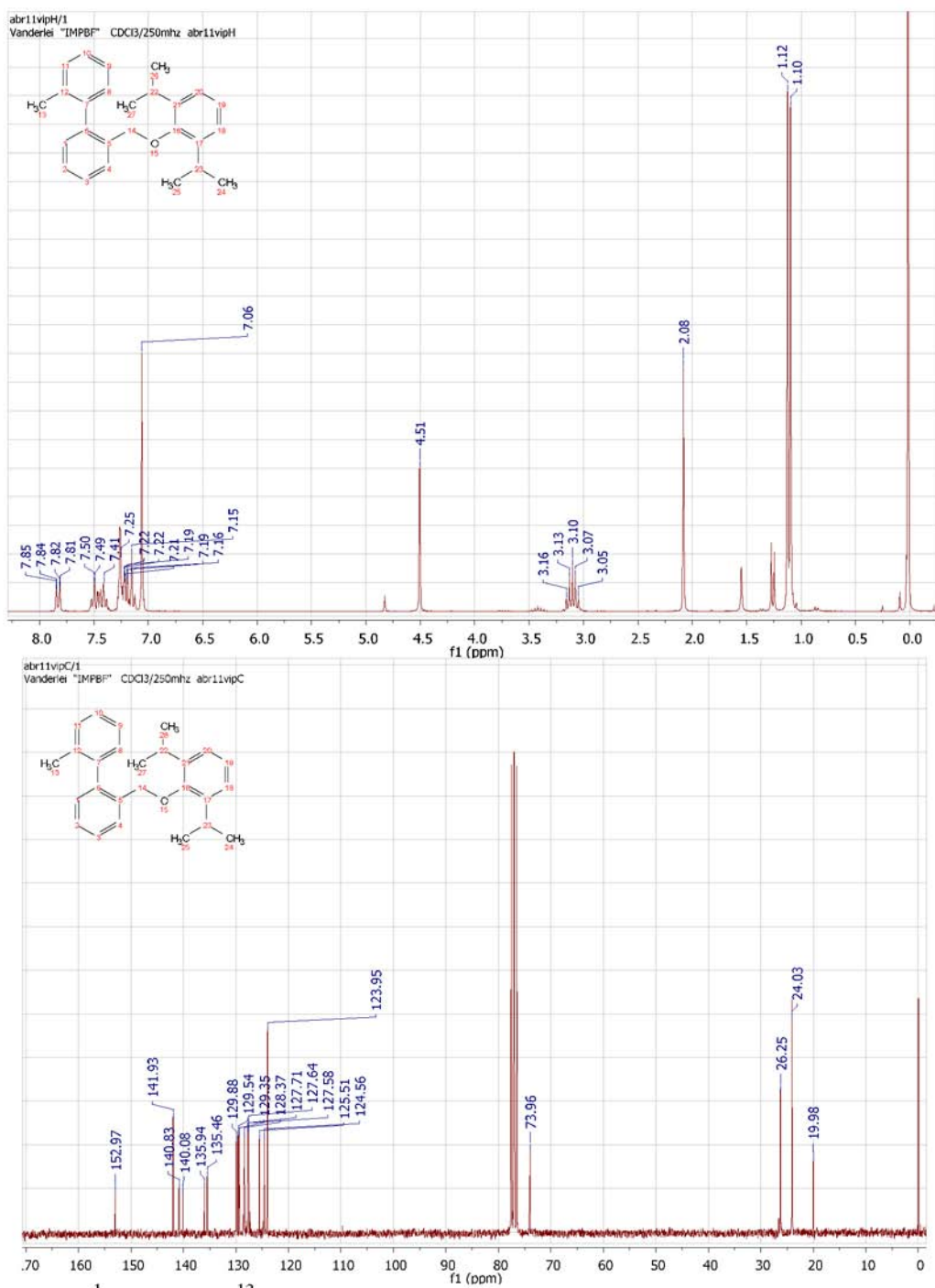


Figure S36.  $^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) NMR spectra of the product of the reaction described in Table 4, entry 4.