

Supporting Information

Cyclodiphosphazane based pincer ligand, 2,6- $\{\mu\text{-}(\text{tBuN})\text{P}(\text{tBuHN})\text{PO}\}_2\text{C}_6\text{H}_3$: **Ni^{II}, Pd^{II}, Pt^{II} and Cu^I complexes, and catalytic studies**

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The isolated yields of compounds **a** – **i** are shown in Chart 1 in main text. The $^{31}\text{P}\{^1\text{H}\}$, ^1H and mass spectral data of all the compounds are given below.

- a. Triphenylphosphine oxide.**¹ $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 29.3. ^1H NMR (500 MHz, CDCl_3): δ 7.69-7.65 (m, 6H), 7.56 (t, $J = 7.5$ Hz, 3H), 7.48-7.45 (m, 6H). HRMS (Calcd. for $\text{M}+\text{H}$ $\text{C}_{18}\text{H}_{16}\text{OP}$): 279.0933. Found: 279.0936.
- b. Diphenyl(o-tolyl)phosphine oxide.**¹ $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 31.2. ^1H NMR (500 MHz, CDCl_3): δ 7.69-7.63 (m, 4H), 7.55 (d, $J = 7.5$ Hz, 2H), 7.49-7.46 (m, 4H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.29 (m, 1H), 7.13 (t, $J = 7.0$ Hz, 1H), 7.02 (m, 1H), 2.45 (s, 3H). HRMS (Calcd. for $\text{M}+\text{H}$ $\text{C}_{19}\text{H}_{18}\text{OP}$): 293.1090. Found: 293.1087.
- c. Diphenyl(p-tolyl)phosphine oxide.**² $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 29.2. ^1H NMR (500 MHz, CDCl_3): δ 7.68-7.64 (m, 4H), 7.57-7.51 (m, 4H), 7.47-7.43 (m, 4H), 7.28-7.27 (m, 2H), 2.40 (s, 3H). HRMS (Calcd. for $\text{M}+\text{H}$ $\text{C}_{19}\text{H}_{18}\text{OP}$): 293.1090. Found: 293.1090.
- d. (3-methoxyphenyl)diphenylphosphine oxide.**³ $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 29.5. ^1H NMR (500 MHz, CDCl_3): δ 7.70-7.64 (m, 4H), 7.50-7.29 (m, 8H), 7.19-7.13 (m, 1H), 7.03 (d, $J = 9$ Hz, 1H), 3.75 (s, 3H). HRMS (Calcd. for $\text{M}+\text{H}$ $\text{C}_{19}\text{H}_{18}\text{O}_2\text{P}$): 309.1039. Found: 309.1038.
- e. (4-methoxyphenyl)diphenylphosphine oxide.**¹ $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 29.2. ^1H NMR (500 MHz, CDCl_3): δ 7.69-7.64 (m, 4H), 7.60-7.53 (m, 4H), 7.52-7.46 (m, 4H), 6.97-6.96 (m, 2H), 3.84 (s, 3H). HRMS (Calcd. for $\text{M}+\text{H}$ $\text{C}_{19}\text{H}_{18}\text{O}_2\text{P}$): 309.1039. Found: 309.1034.
- f. 4-(diphenylphosphoryl)benzotrile.**⁴ $^{31}\text{P}\{^1\text{H}\}$ (202.5 MHz, CDCl_3): δ 28.0. ^1H NMR (500 MHz, CDCl_3): δ 7.79 (t, $J = 10.5$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 2H), 7.62 (t, $J = 10.0$ Hz, 4H),

7.57 (t, $J = 7.0$ Hz, 2H), 7.48 (m, 4H). HRMS (Calcd. for M+H C₁₉H₁₅NOP): 304.0883. Found: 304.0886.

g. Benzo[d][1,3]dioxol-5-ylidiphenylphosphine oxide.⁵ ³¹P{¹H} (202.5 MHz, CDCl₃): δ 29.7. ¹H NMR (500 MHz, CDCl₃): δ 7.66-7.62 (m, 4H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.46-7.43 (m, 4H), 7.16 (m, 1H), 7.05 (d, $J = 11$ Hz, 1H), 6.86 (m, 1H), 6.00 (s, 2H). HRMS (Calcd. for M+H C₁₉H₁₆O₃P): 323.0832. Found: 323.0837.

h. (2-(diphenylphosphoryl)phenyl)methanol.⁶ ³¹P{¹H} (202.5 MHz, CDCl₃): δ 35.0. ¹H NMR (500 MHz, CDCl₃): δ 7.64-7.46 (m, 13H), 7.03 (m, 1H), 4.59 (s, 2H). HRMS (Calcd. for M+Na C₁₉H₁₇O₂PNa): 331.0864. Found: 331.0852.

i. Naphthalen-2-ylidiphenylphosphine oxide.⁷ ³¹P{¹H} (202.5 MHz, CDCl₃): δ 32.3. ¹H NMR (500 MHz, CDCl₃): δ 8.59 (d, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.71-7.67 (m, 4H), 7.56-7.28 (m, 10H). HRMS (Calcd. for M+H C₂₂H₁₈OP): 329.1090. Found: 329.1084.

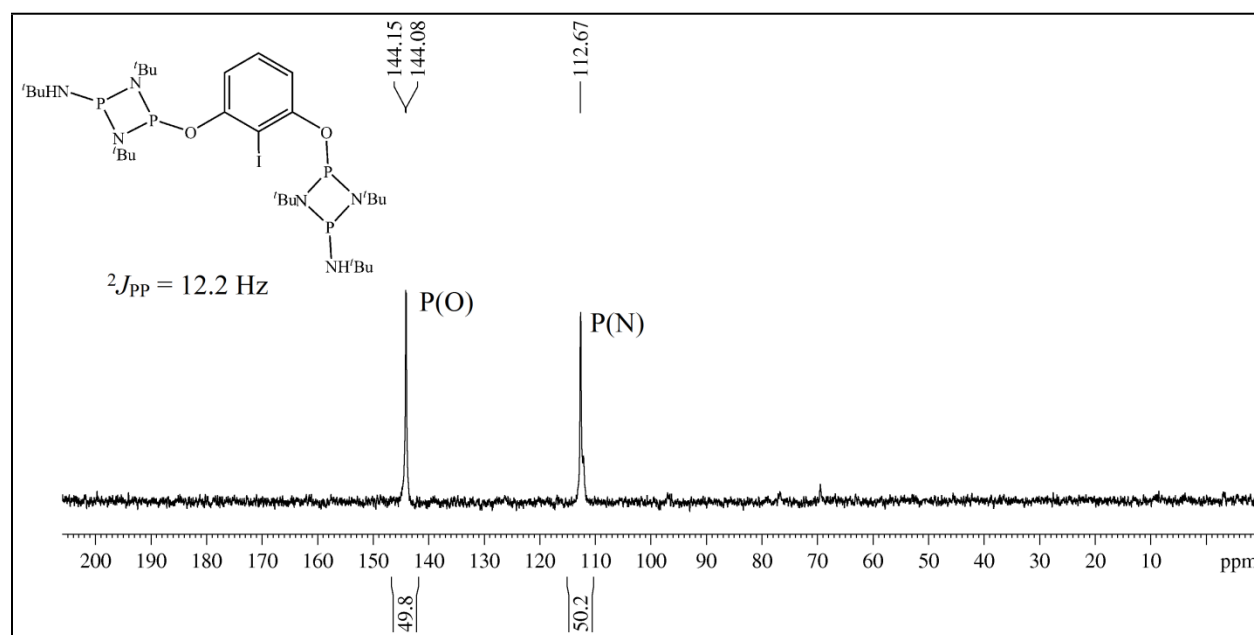


Figure S1. ³¹P{¹H} NMR spectrum of **1**

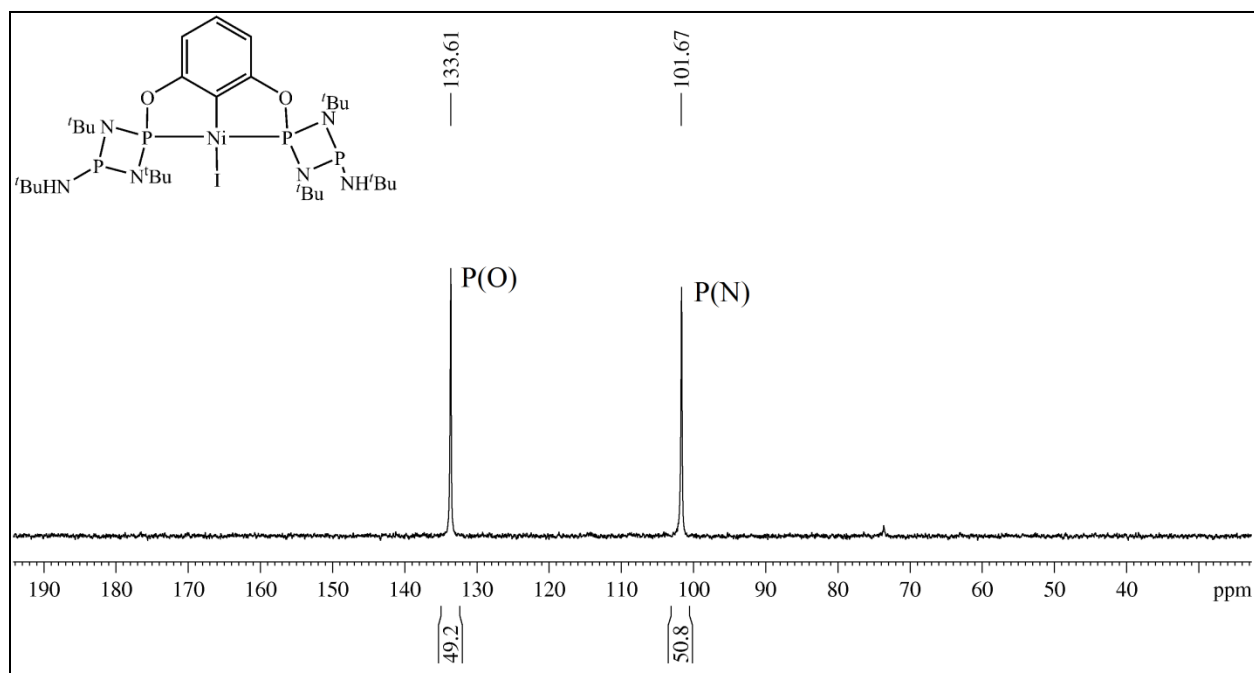


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2**

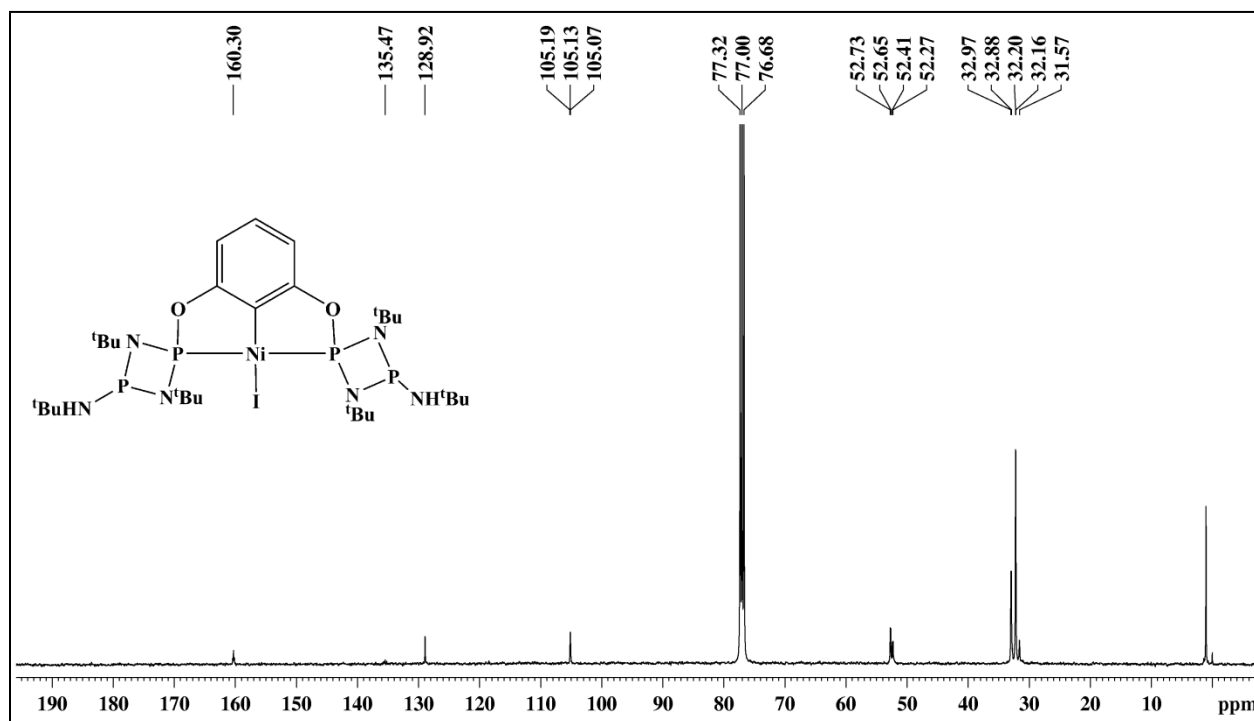


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2**

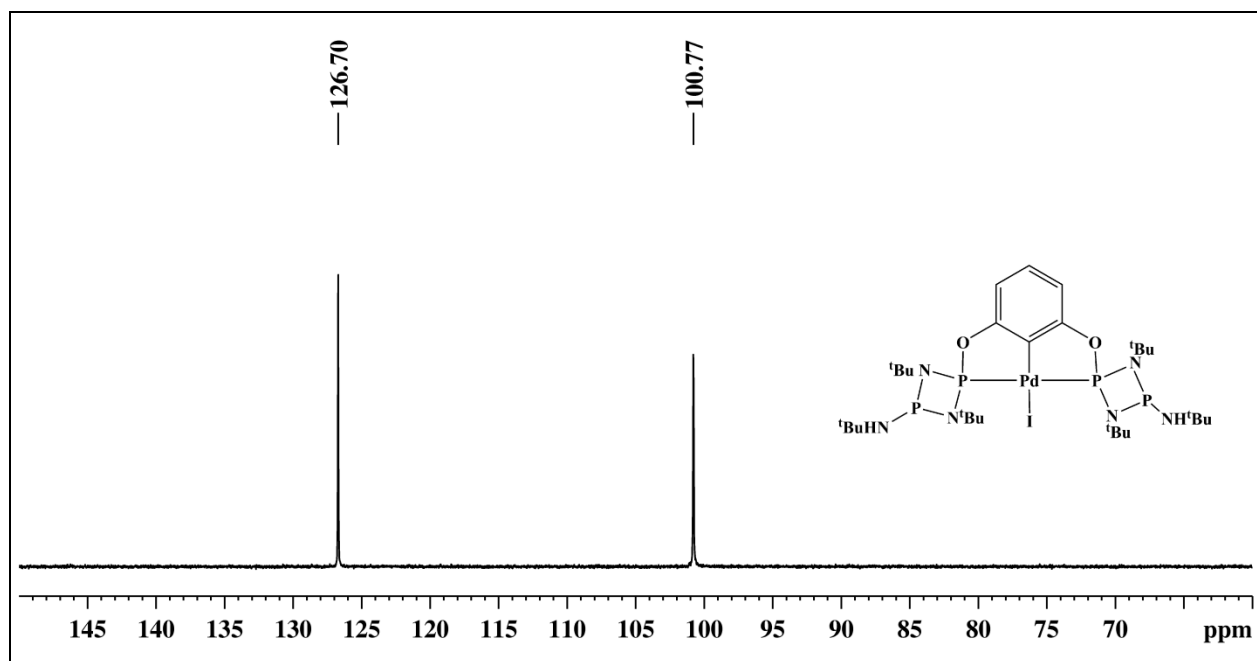


Figure S4. $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum of **3**

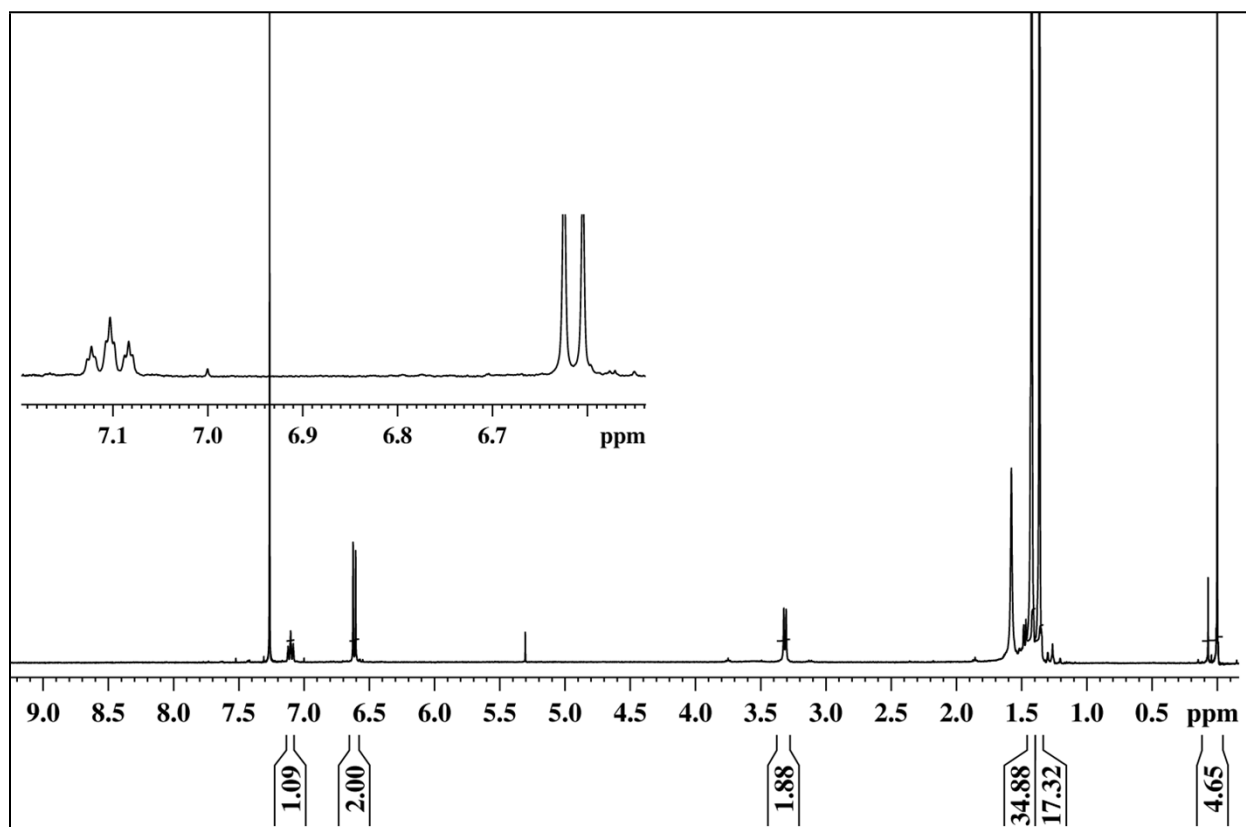


Figure S5. Partial ^1H NMR spectrum of **3**

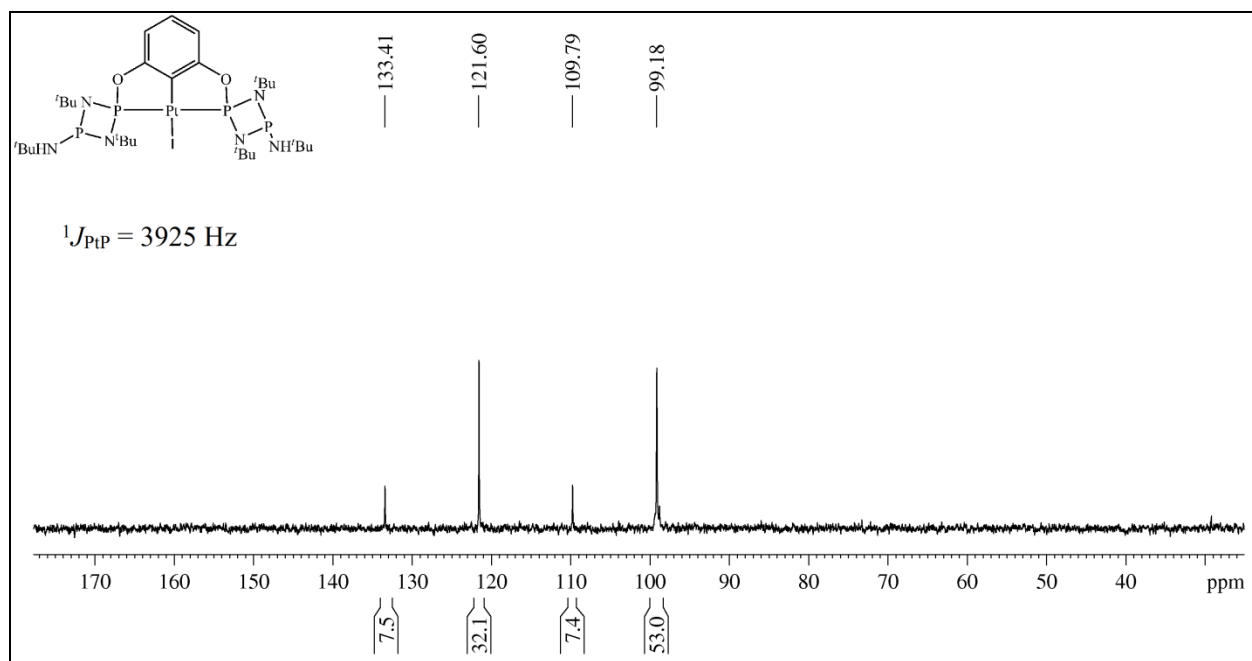


Figure S6. $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**

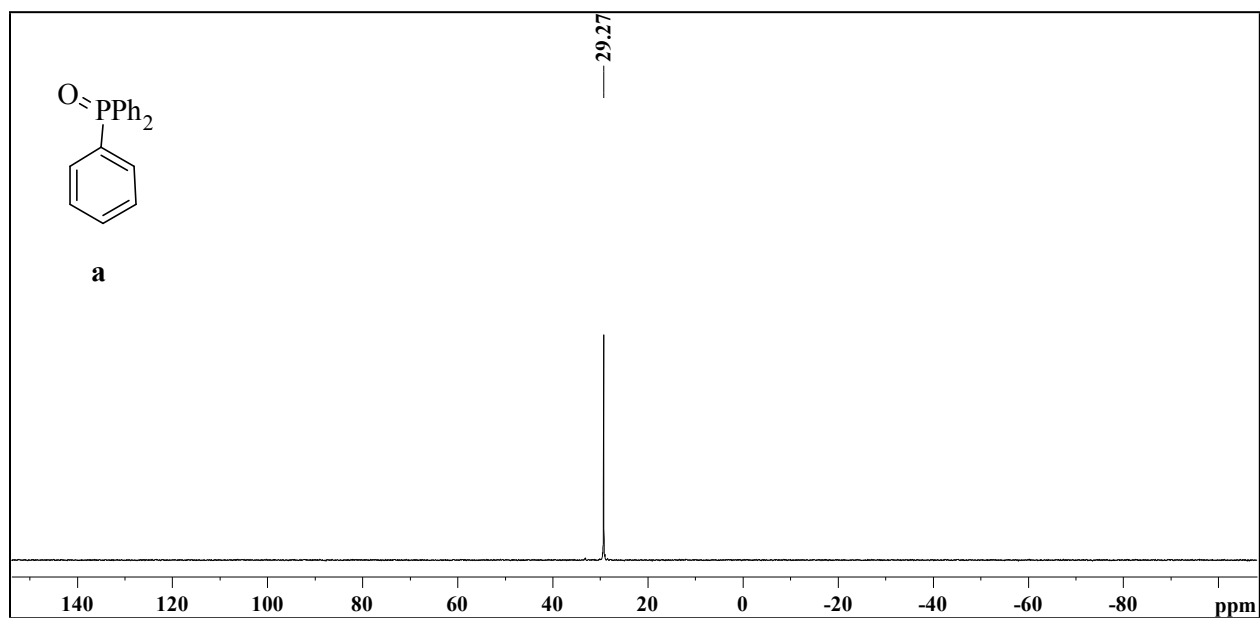


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **a**

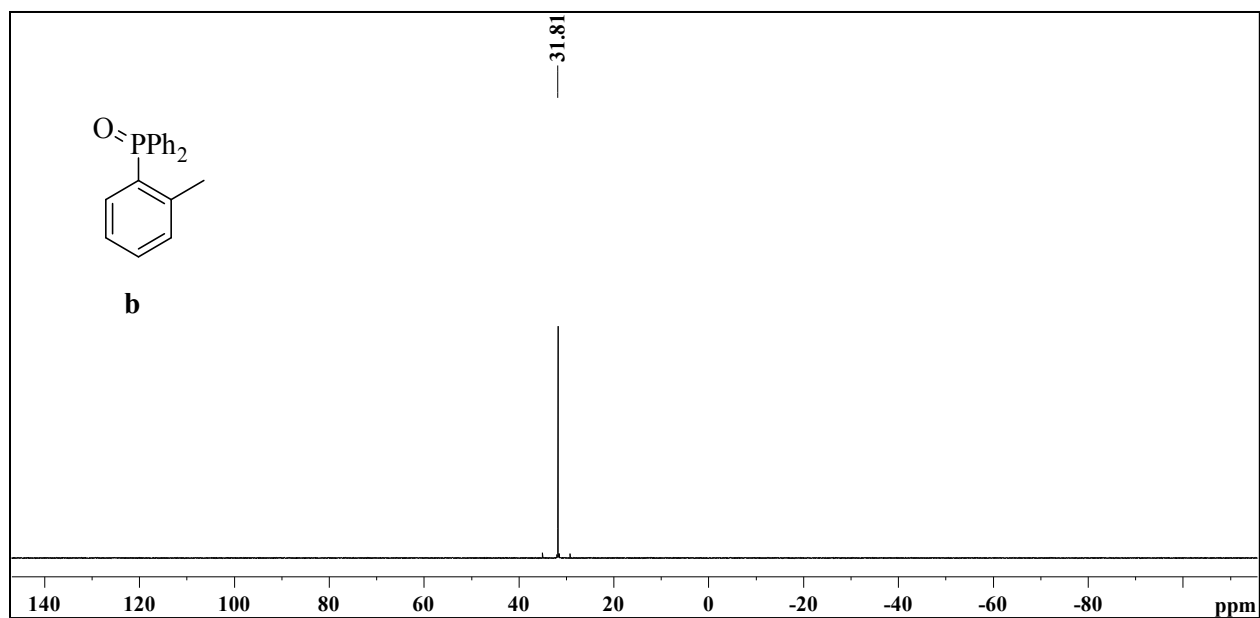


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **b**

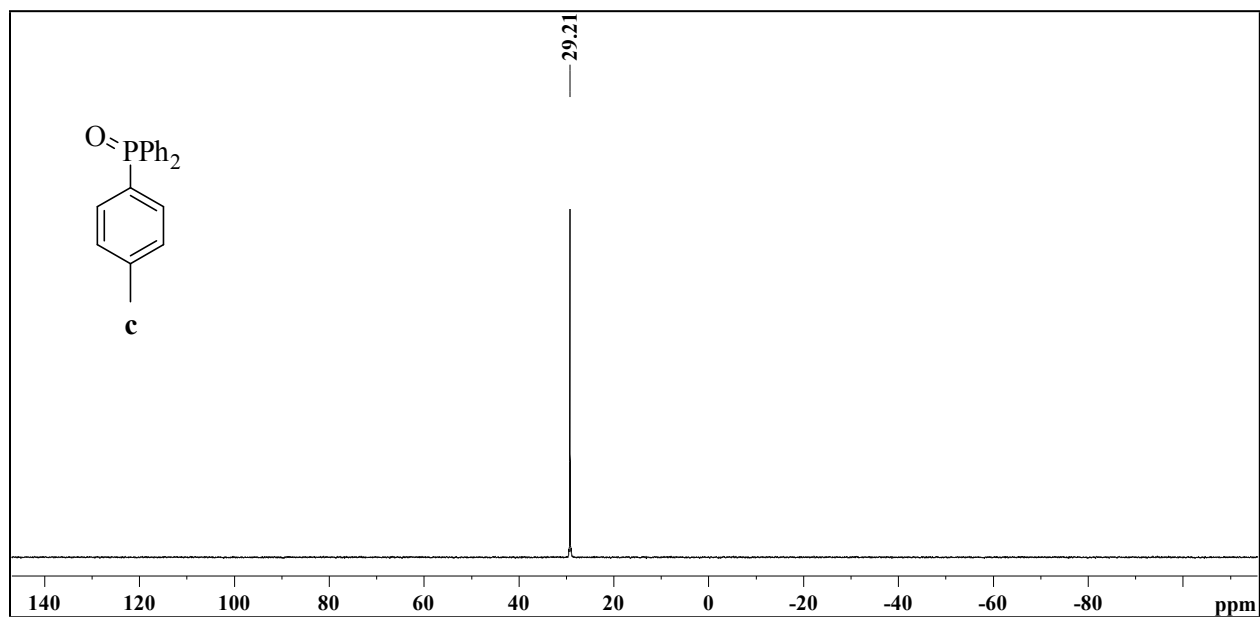


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **c**

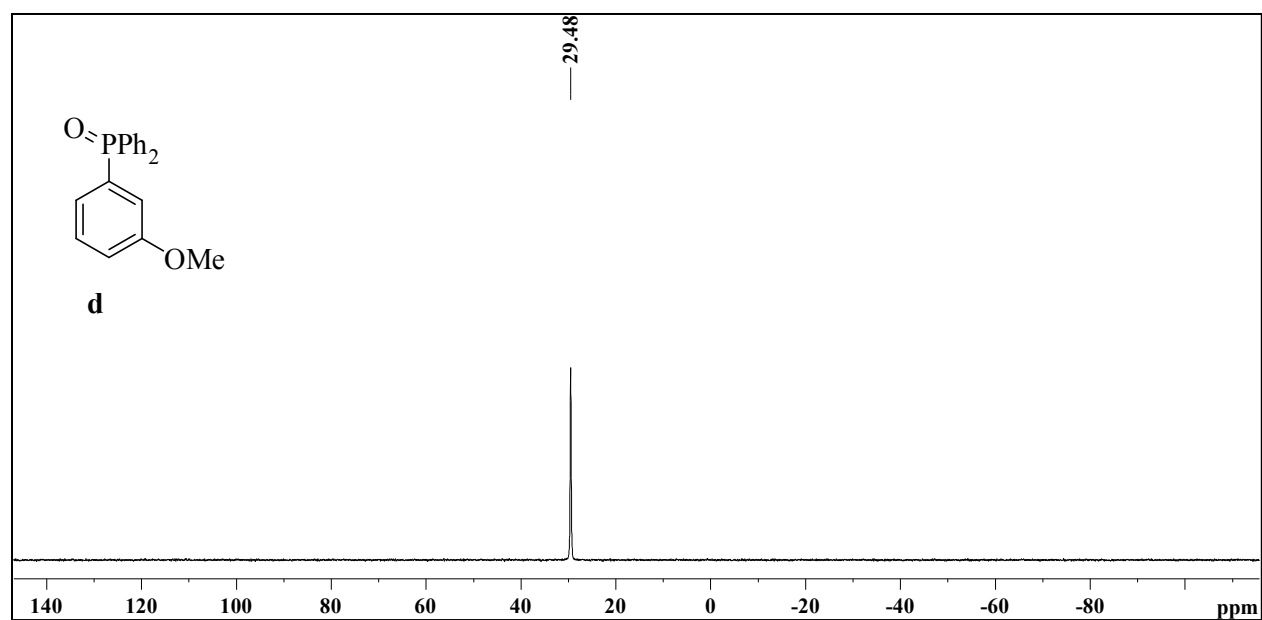


Figure S10. ³¹P{¹H} NMR spectrum of **d**

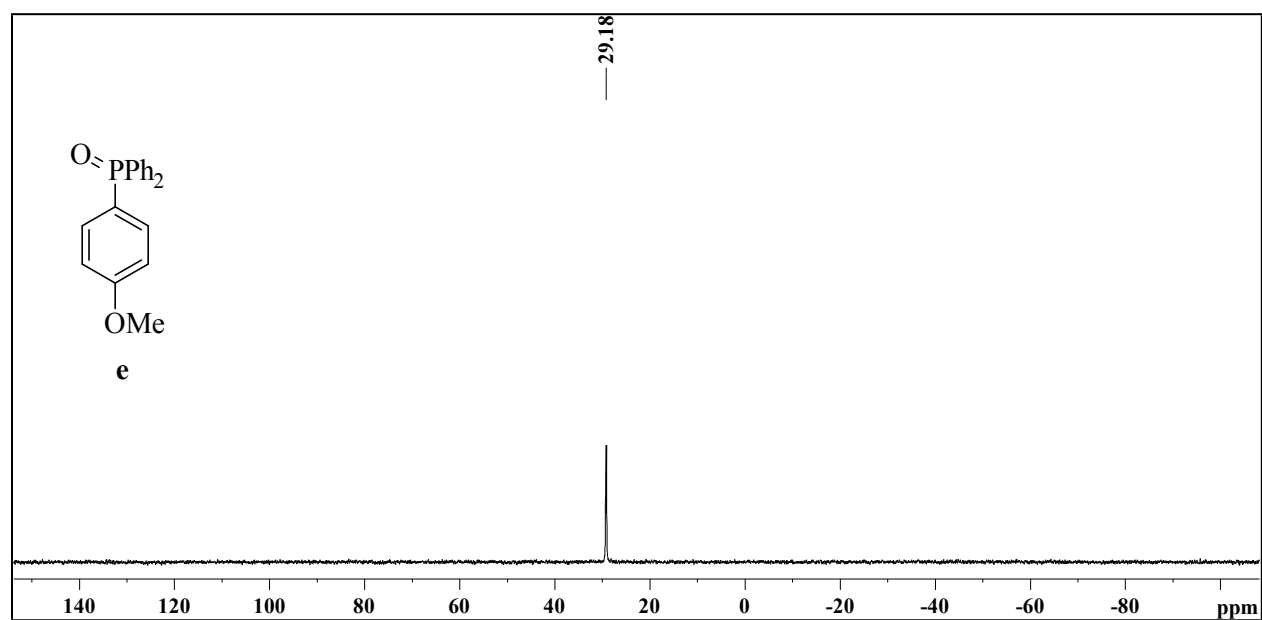


Figure S11. ³¹P{¹H} NMR spectrum of **e**

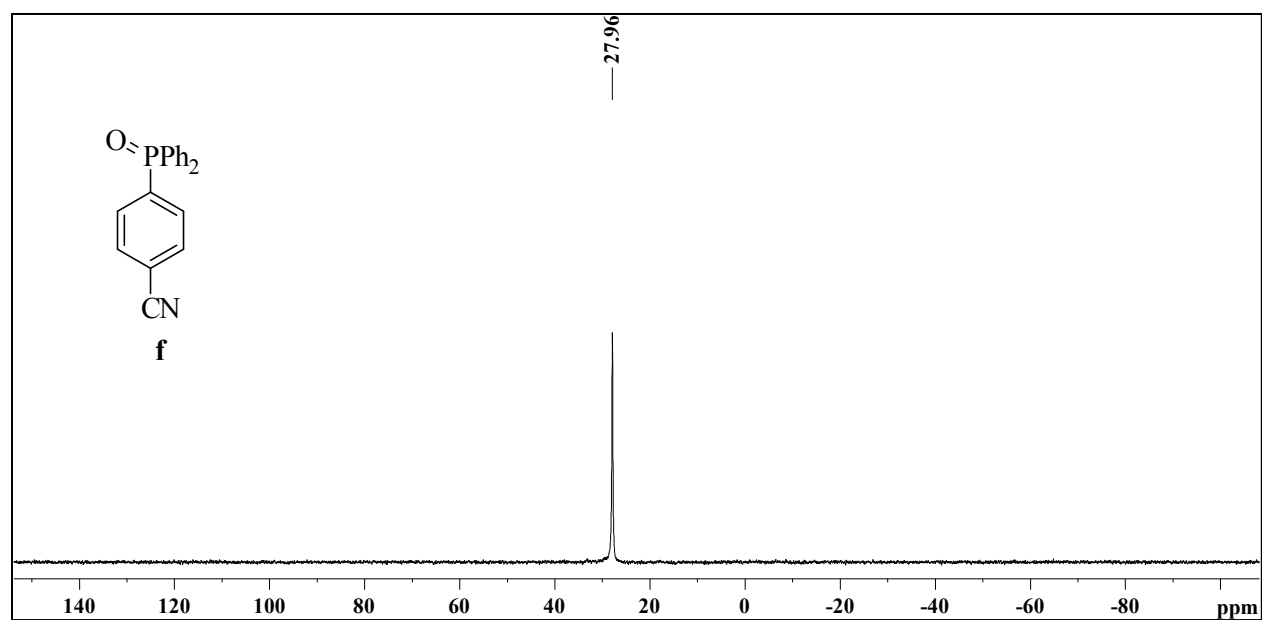


Figure S12. ³¹P{¹H} NMR spectrum of **f**

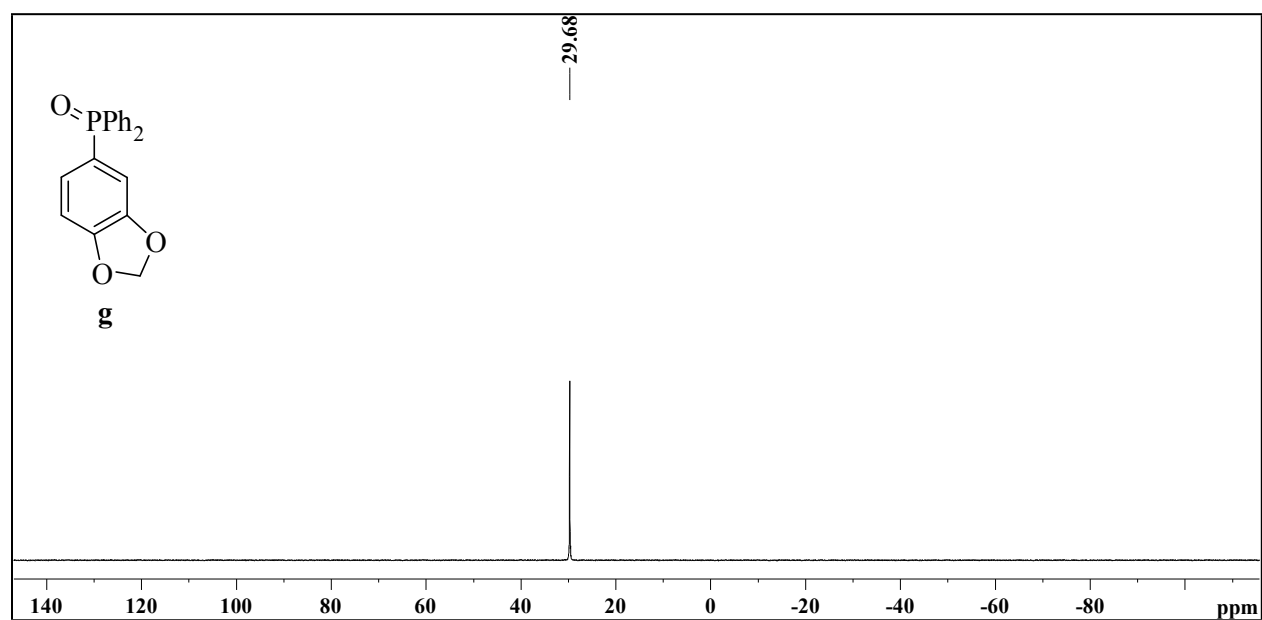


Figure S13. ³¹P{¹H} NMR spectrum of **g**

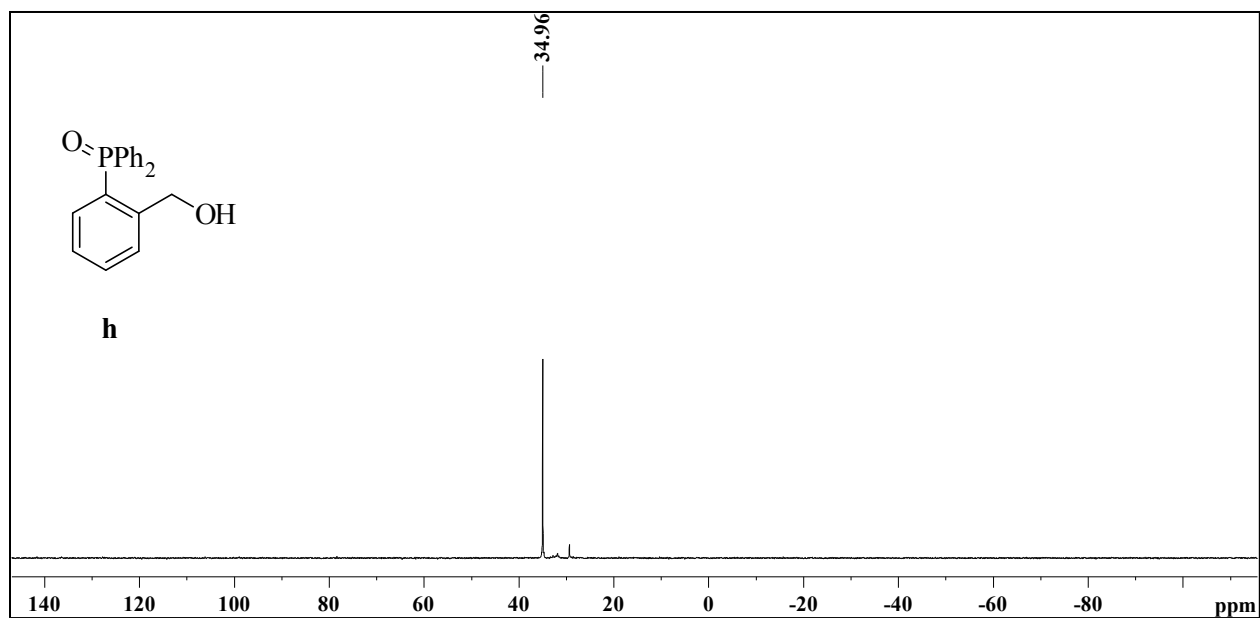


Figure S14. ³¹P{¹H} NMR spectrum of **h**

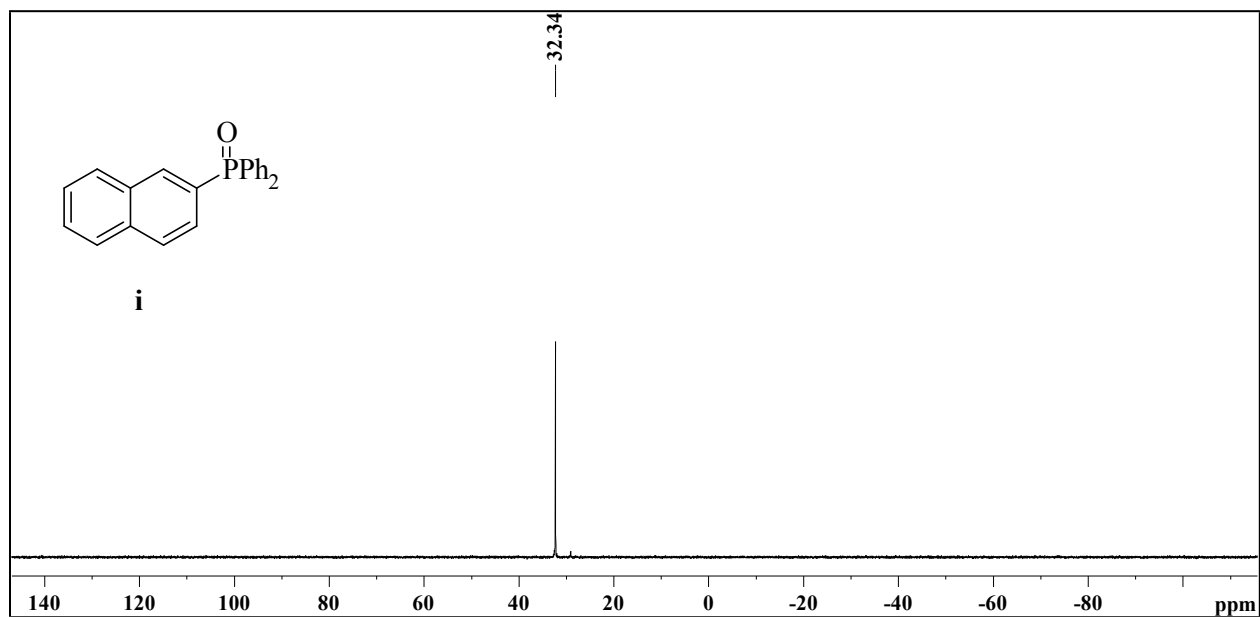


Figure S15. ³¹P{¹H} NMR spectrum of **i**

References

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