

**Amide and phosphide complexes of Ca^{II} with tris(pyrazolylmethyl)amine.
Synthesis, structure, and catalytic activity in the intermolecular
hydrophosphination of alkenes and alkynols**

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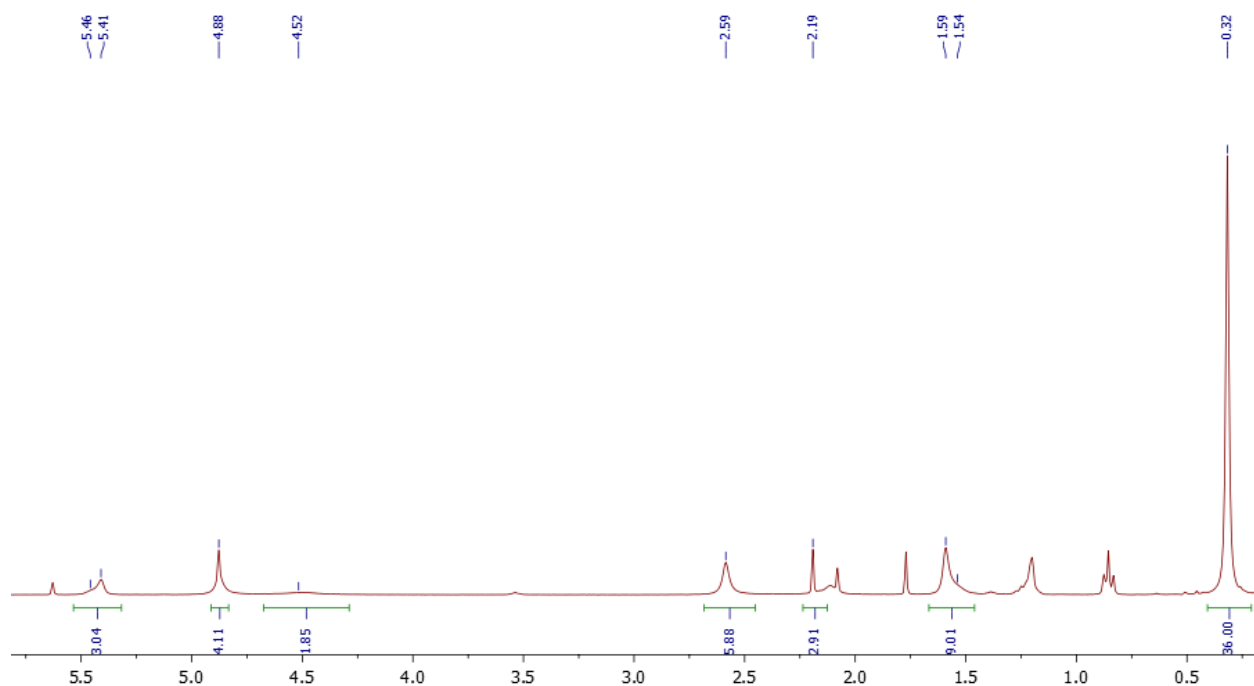


Figure S1. ^1H NMR spectrum of $(\text{TPMA})\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ (**1**) (300 MHz, 293 K, C_6D_6).

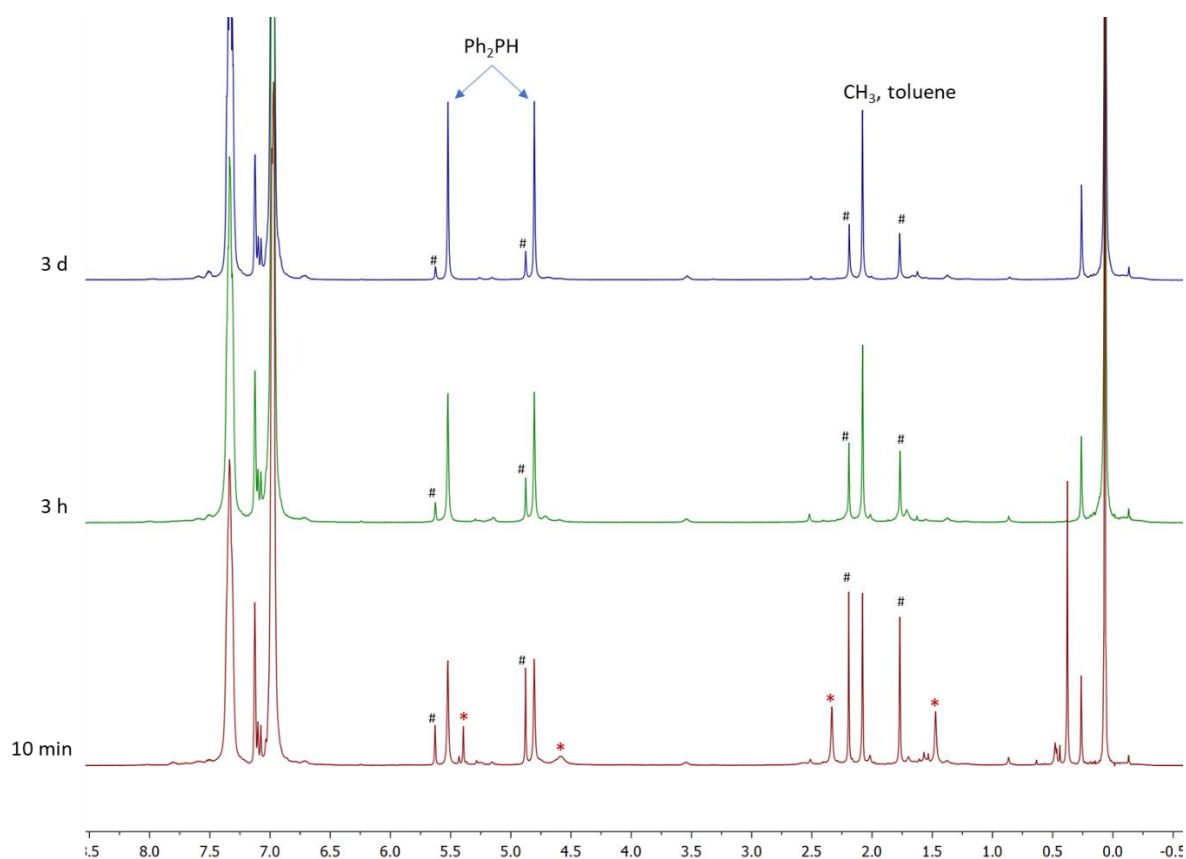


Figure S2. ^1H NMR spectrum of reaction mixture of complex **1** with excess Ph_2PH (300 MHz, 293 K, C_6D_6). TPMA ligand signals of bis(phosphide) intermediate $(\text{TPMA})\text{Ca}(\text{PPh}_2)_2$ are marked (*); signals of uncoordinated TPMA ligand are marked (#).

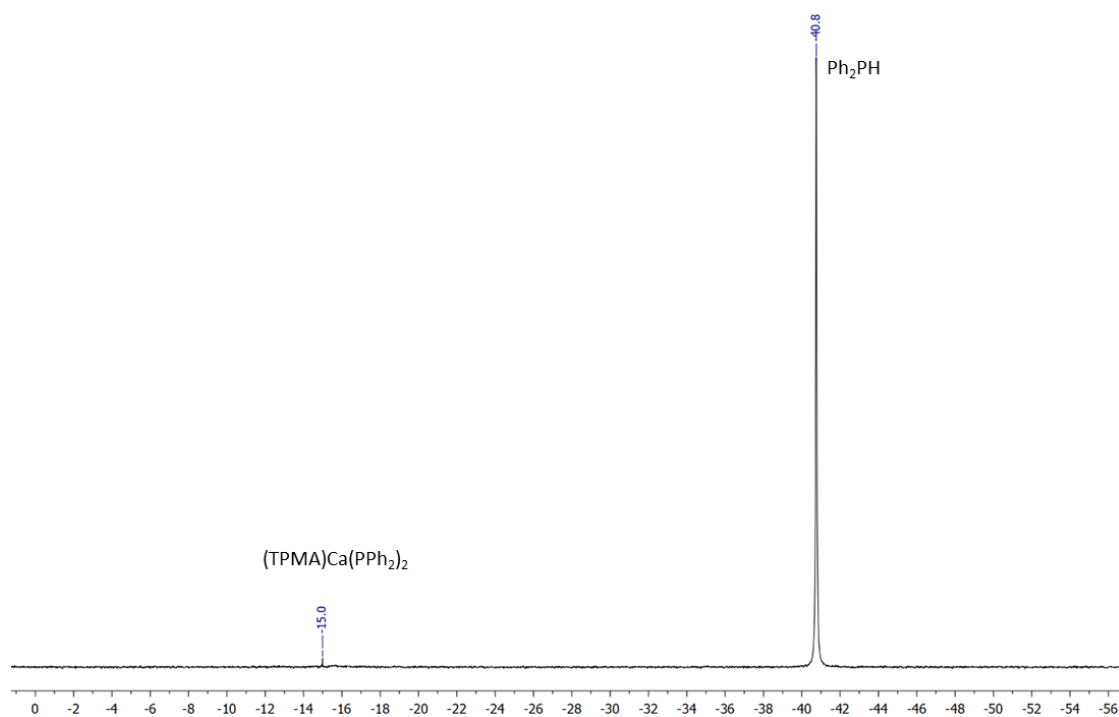


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture of complex **1** with excess Ph_2PH (121.5 MHz, 293 K, C_6D_6).

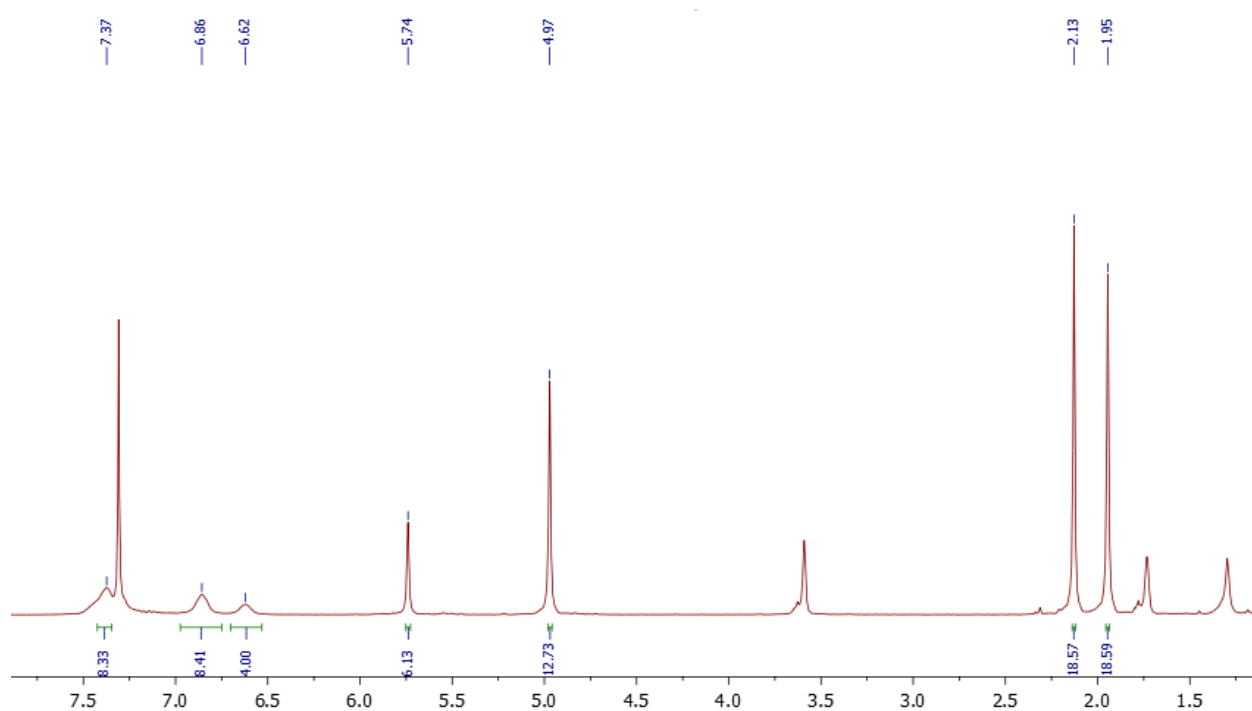


Figure S4. ^1H NMR spectrum of $[(\text{TPMA})_2\text{Ca}][\text{PPh}_2]_2$ (**2**) (300 MHz, 293 K, THF-d_8).

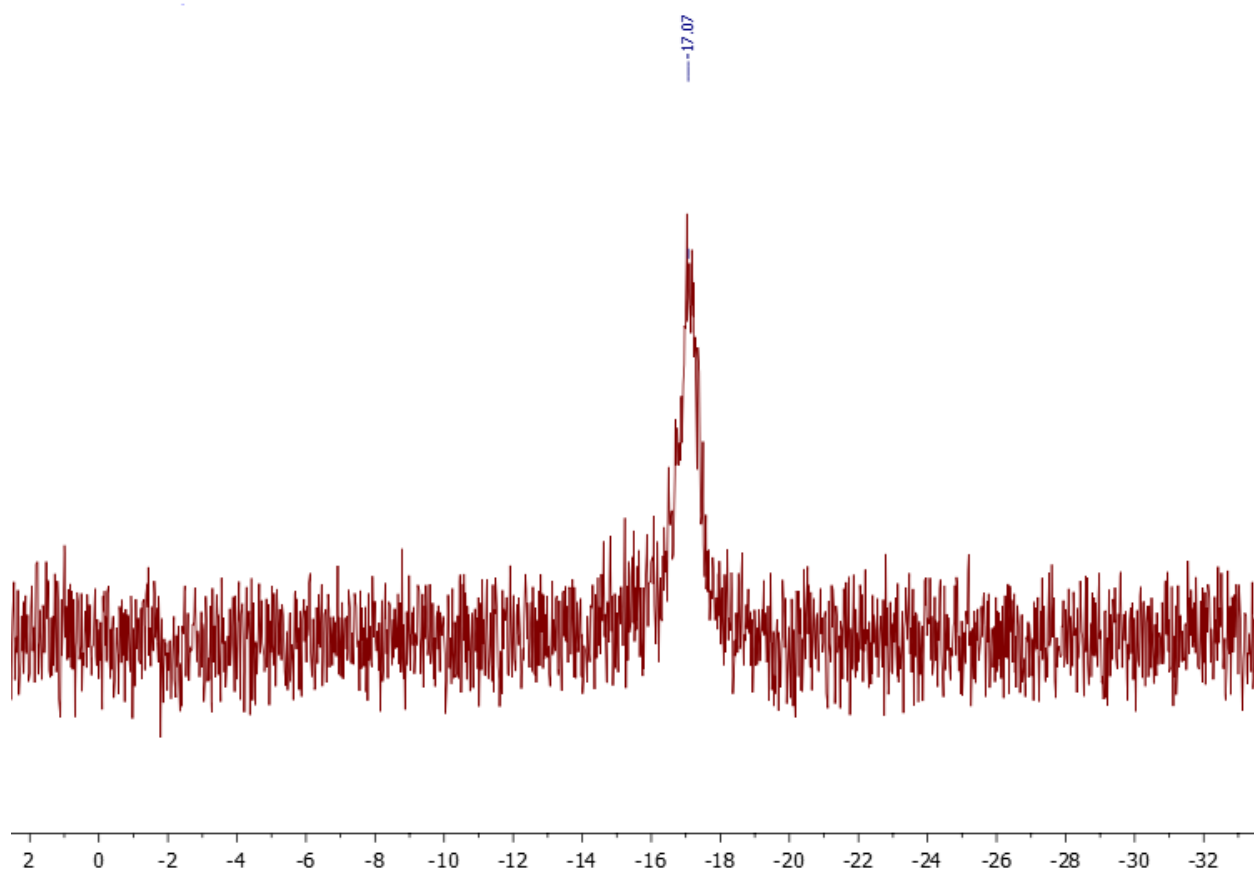


Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\text{TPMA})_2\text{Ca}][\text{PPh}_2]_2$ (**2**) (121.5 MHz, 293 K, THF-d_8).

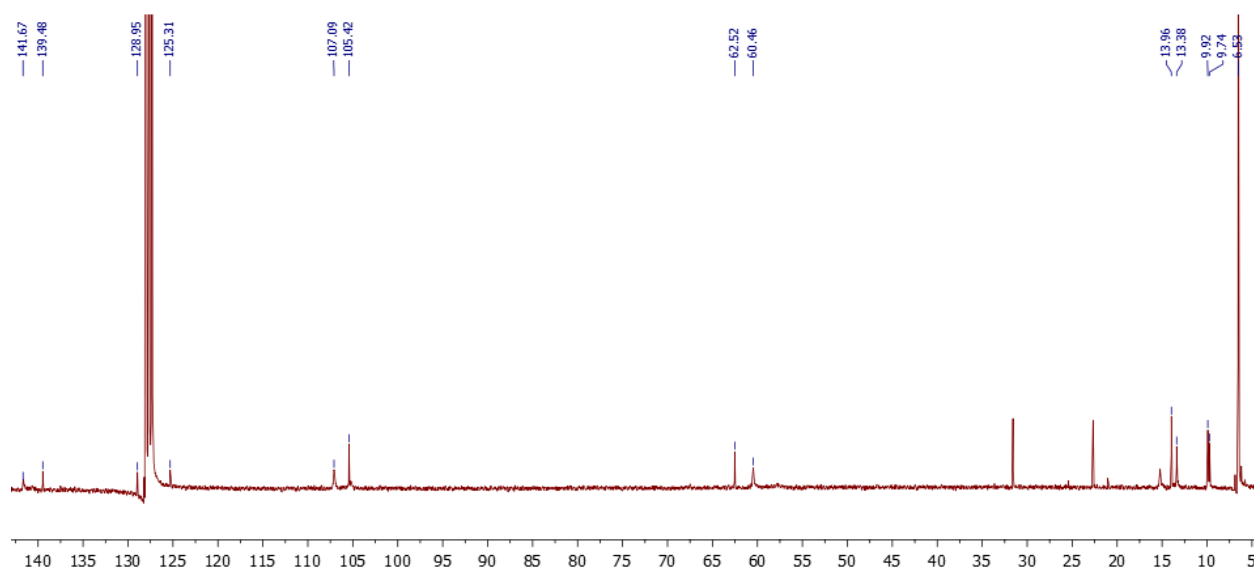


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $(\text{TPMA})\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2$ (**1**) (75 MHz, 293 K, THF-d_8).

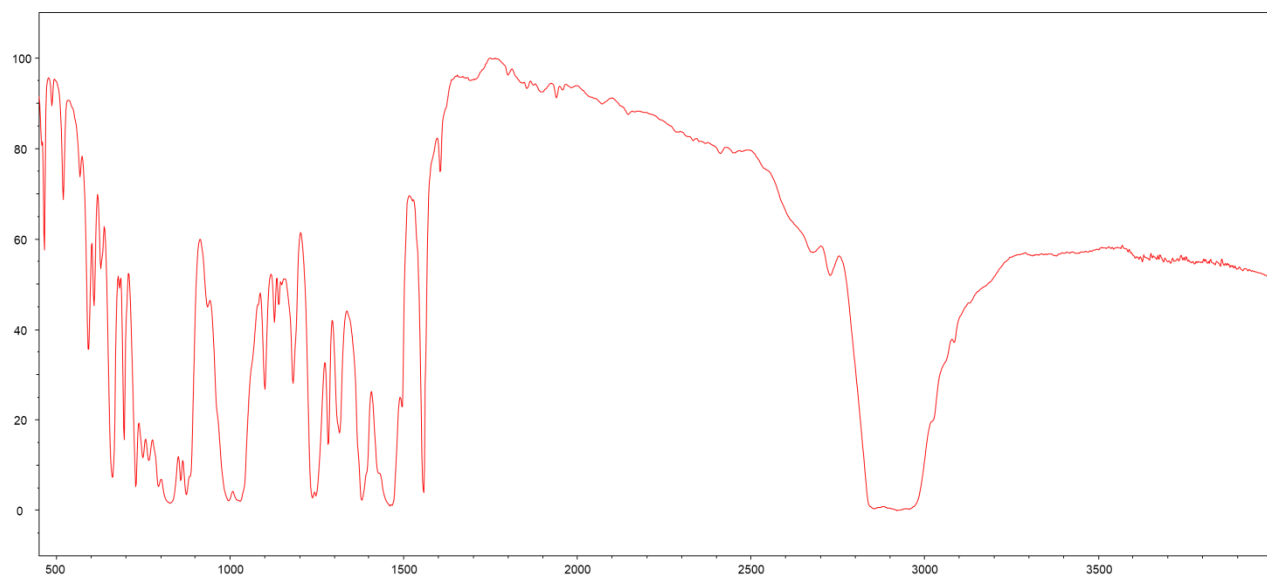


Figure S7. IR spectrum of (TPMA)Ca[N(SiMe₃)₂]₂ (**1**) (KBr, Nujol).

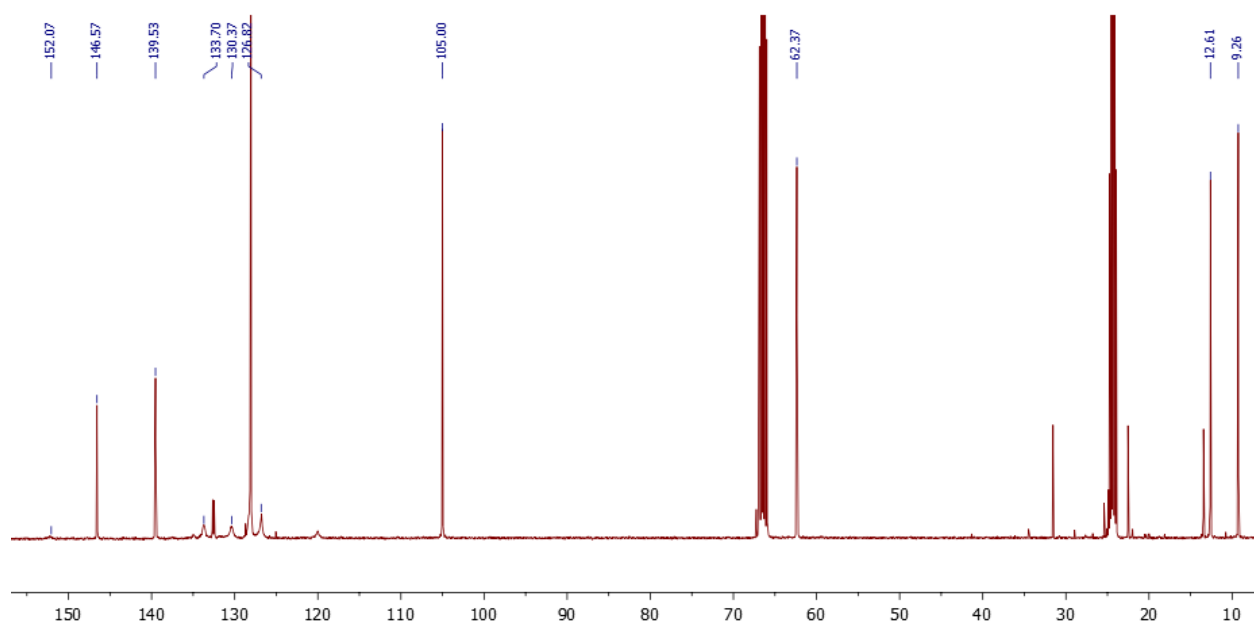


Figure S8. ¹³C{¹H} NMR spectrum of [(TPMA)₂Ca][PPh₂]₂ (**2**) (75 MHz, 293 K, THF-d₈).

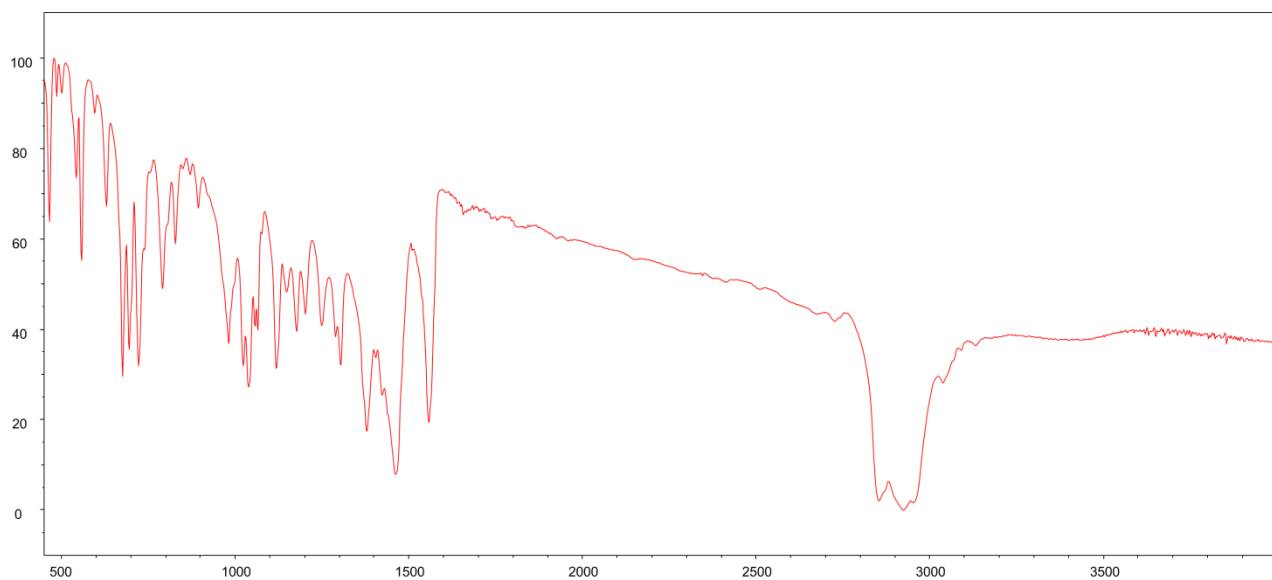


Figure S9. IR spectrum of [(TPMA)₂Ca][PPh₂]₂ (**2**) (KBr, Nujol).

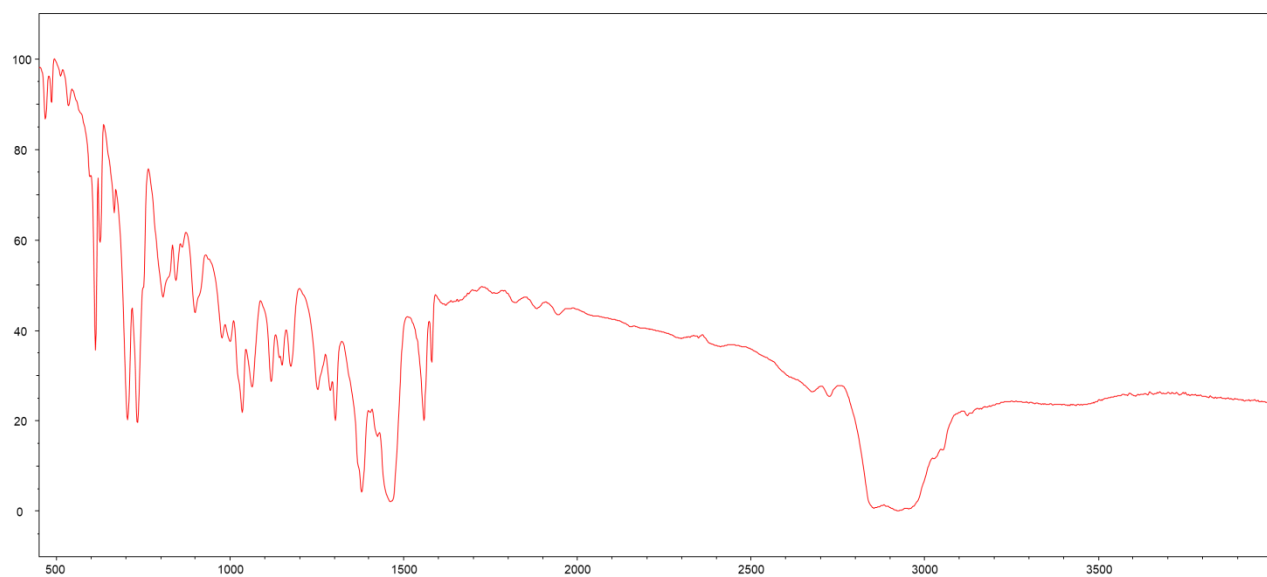


Figure S10. IR spectrum of [(TPMA)₂Ca][BPh₄]₂ (**4**) (KBr, Nujol).