Supporting Information

Synthesis and characterization of heterotrimetallic Mg-Ni-Mg complexes with amidinato ligands

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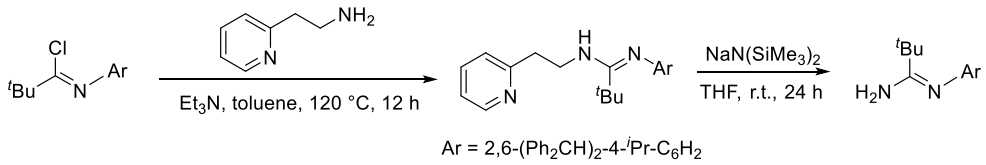


Scheme S1. Synthesis of (2,6-(Ph$_2$CH)$_2$-4-^{i}Pr-(C$_6$H$_2$))NC(NH$_2$)^{t}Bu

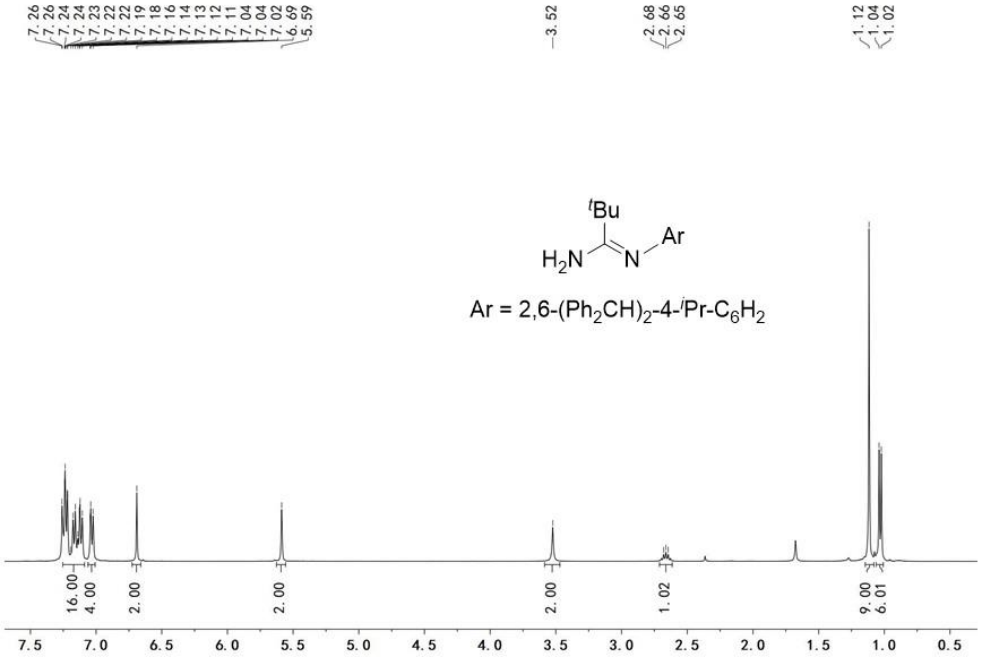


Fig. S1. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K)

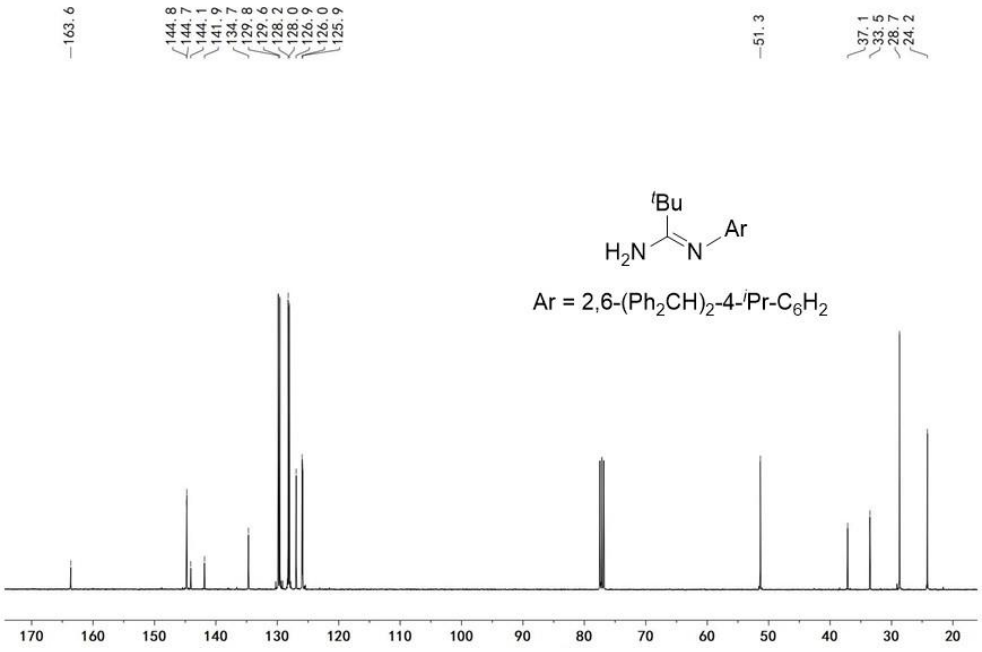
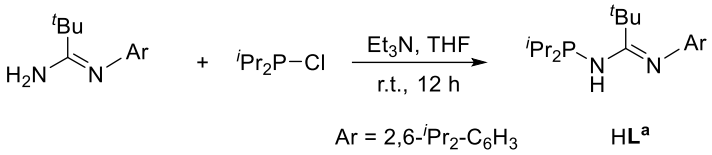


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K)

Synthesis and NMR spectra of HL[a]



Scheme S2. Synthesis of H**L**[a]

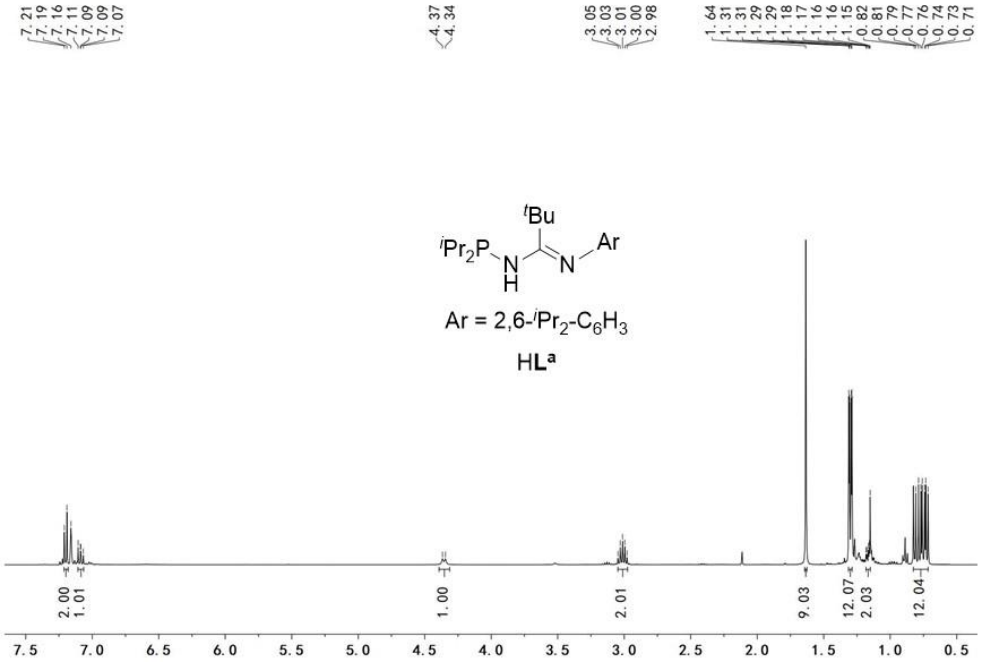


Fig. S3. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

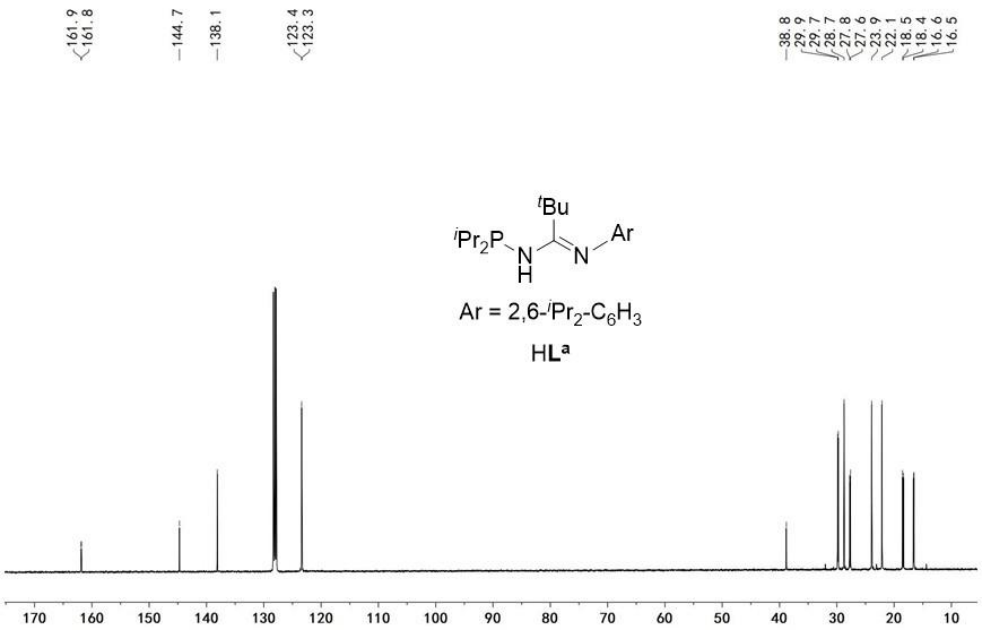


Fig. S4. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

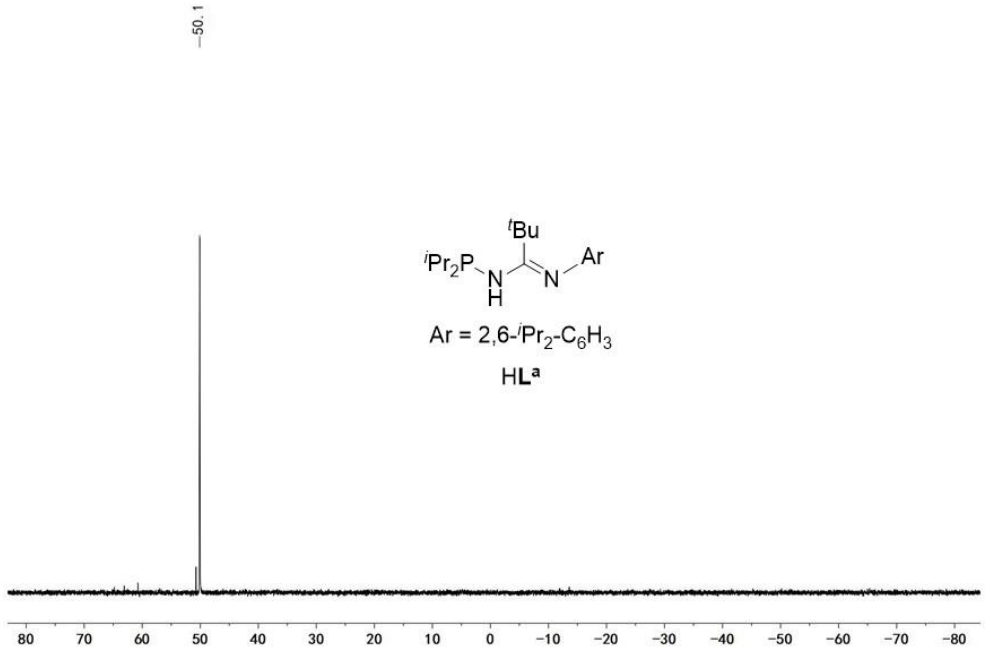
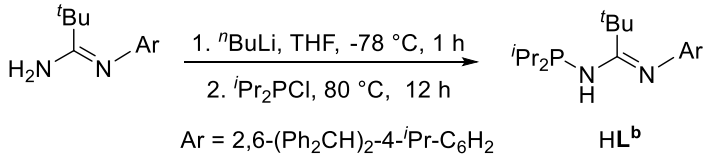


Fig. S5. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

Synthesis and NMR spectra of HL^{b}



Scheme S3. Synthesis of H**L^{b}**

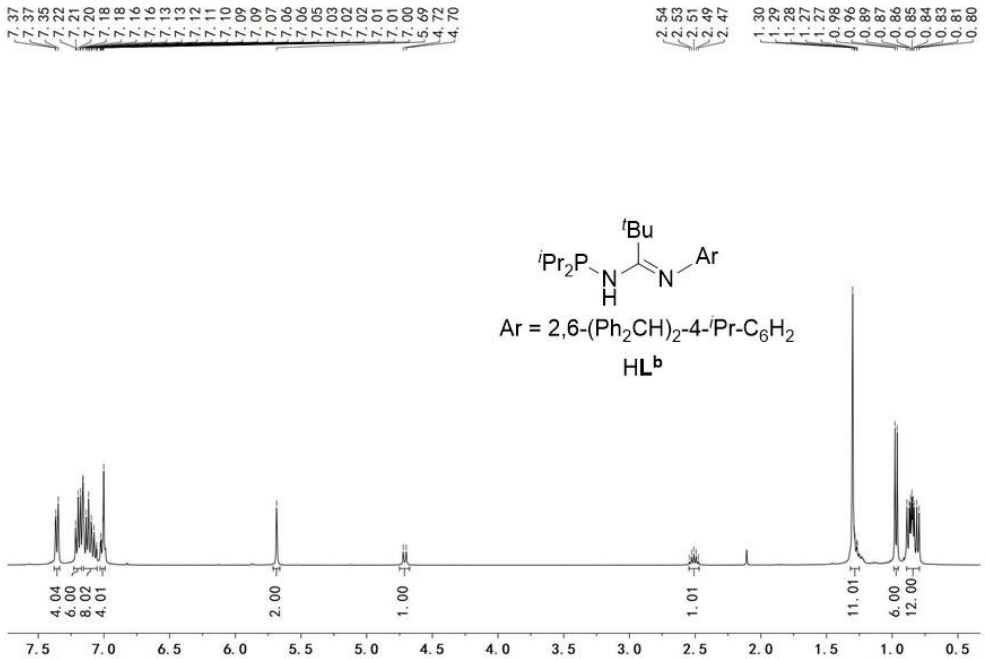


Fig. S6. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

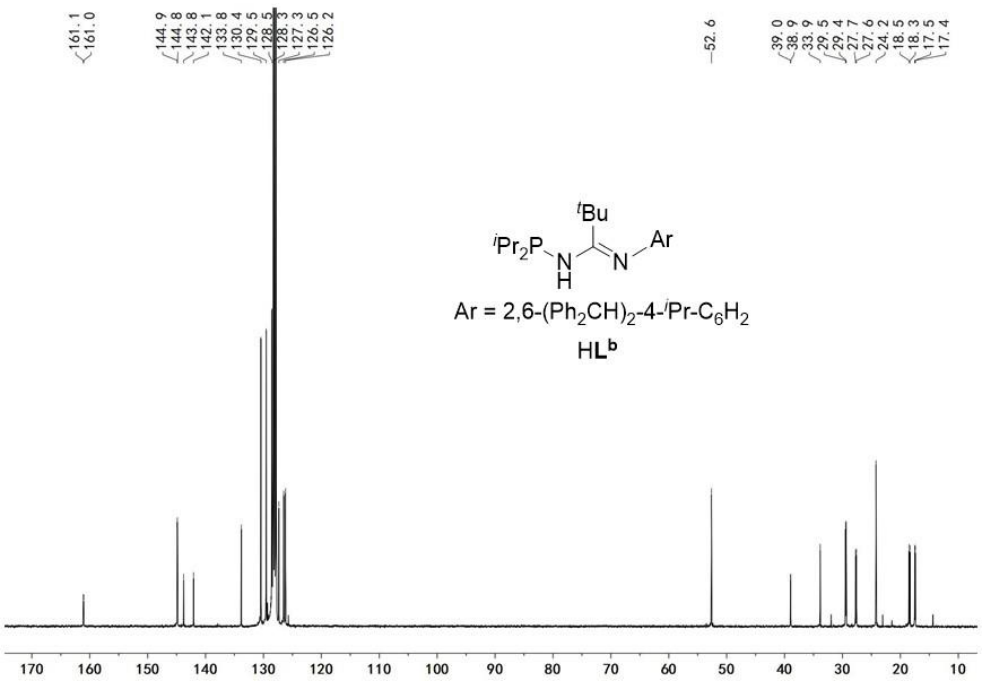


Fig. S7. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K)

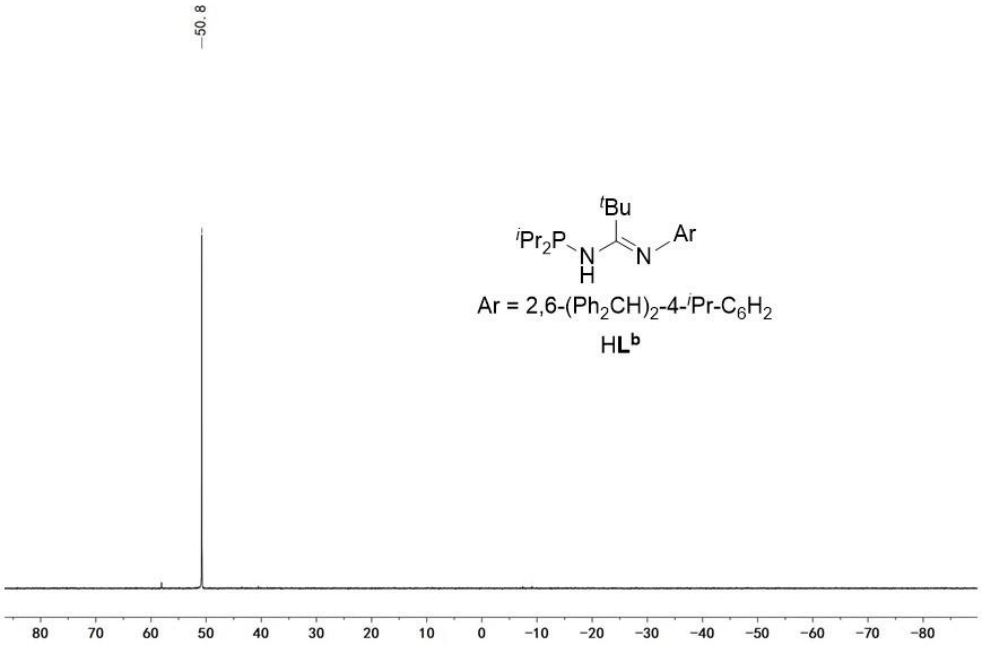
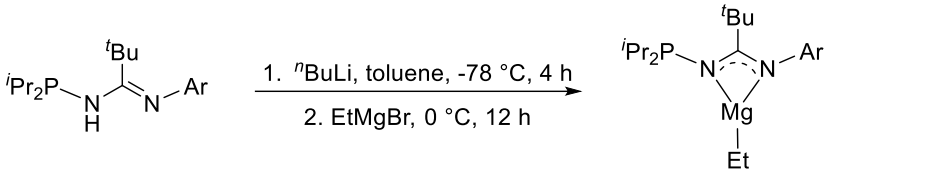


Fig. S8. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

2. Synthesis and NMR spectra of compounds 1



HL

1a (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$)
1b (Ar = 2,6-(Ph$_2$CH)$_2$-4-^{i}Pr-C$_6$H$_2$)

Scheme S4. Synthesis of compounds **1**

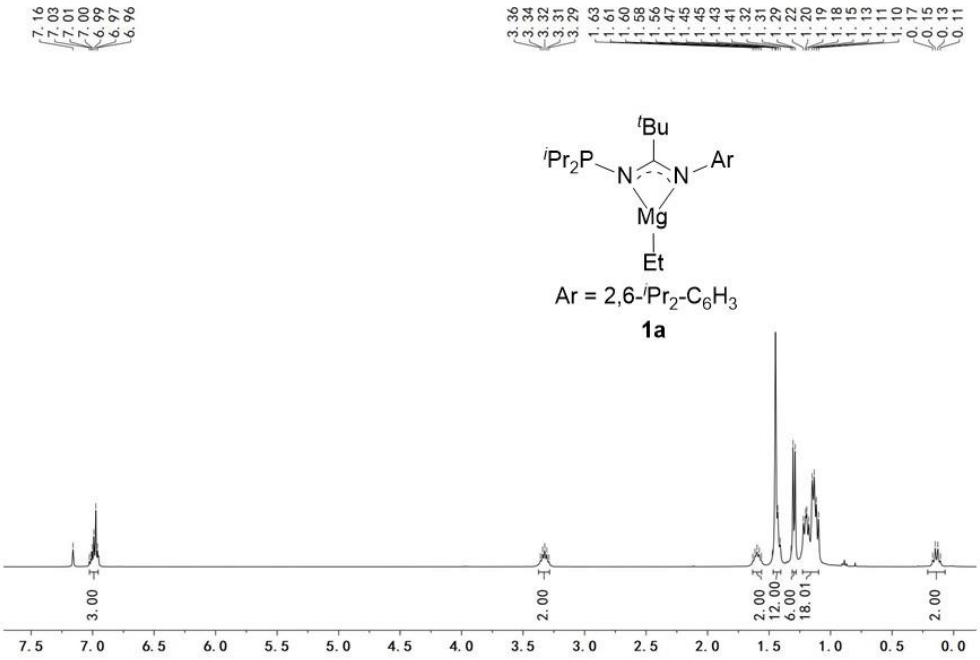


Fig. S9. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

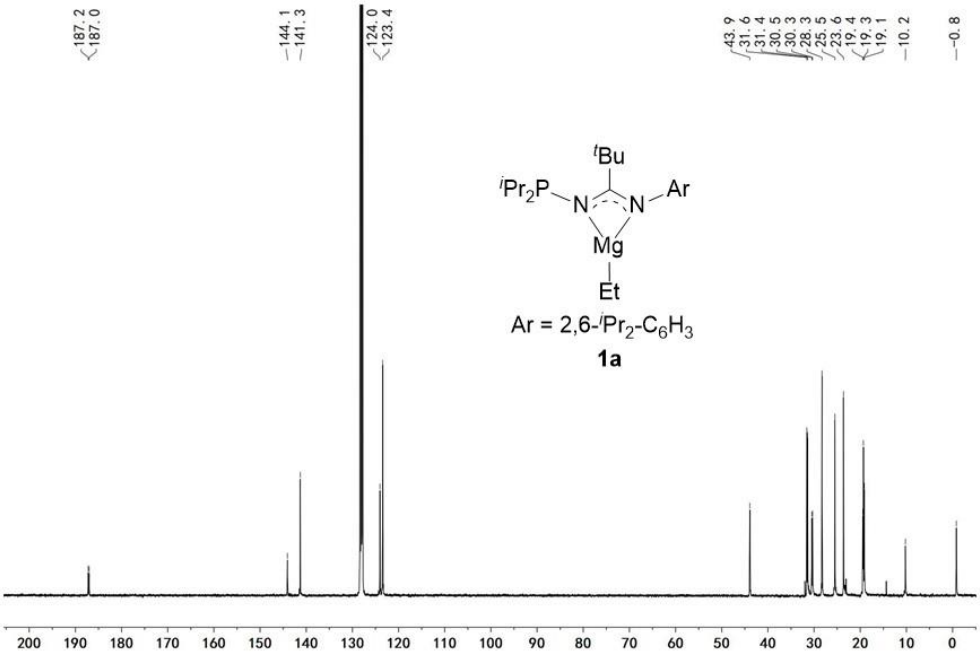


Fig. S10. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

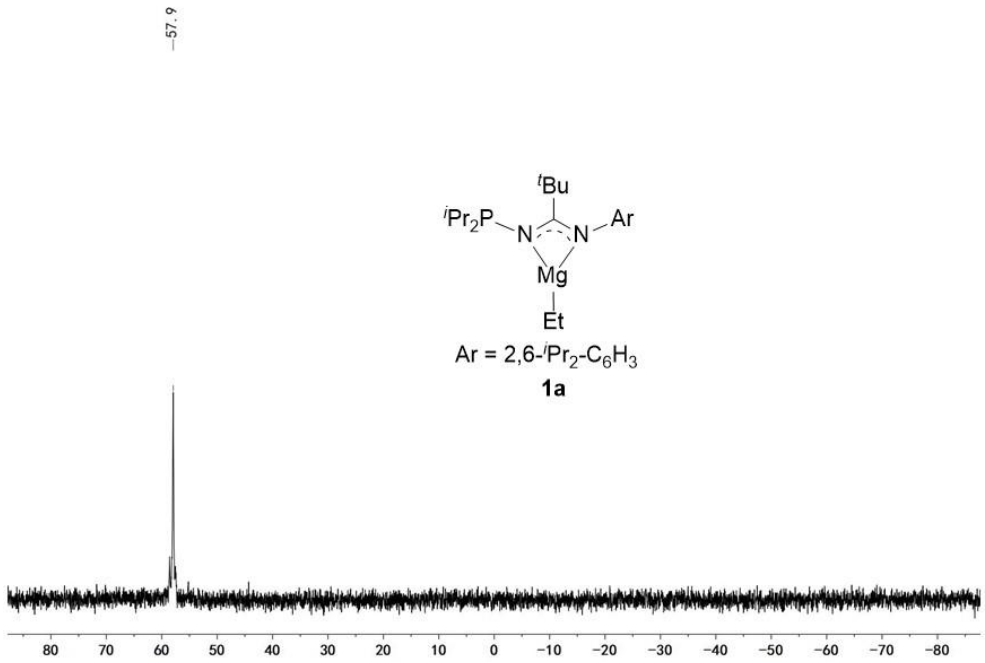


Fig. S11. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K)

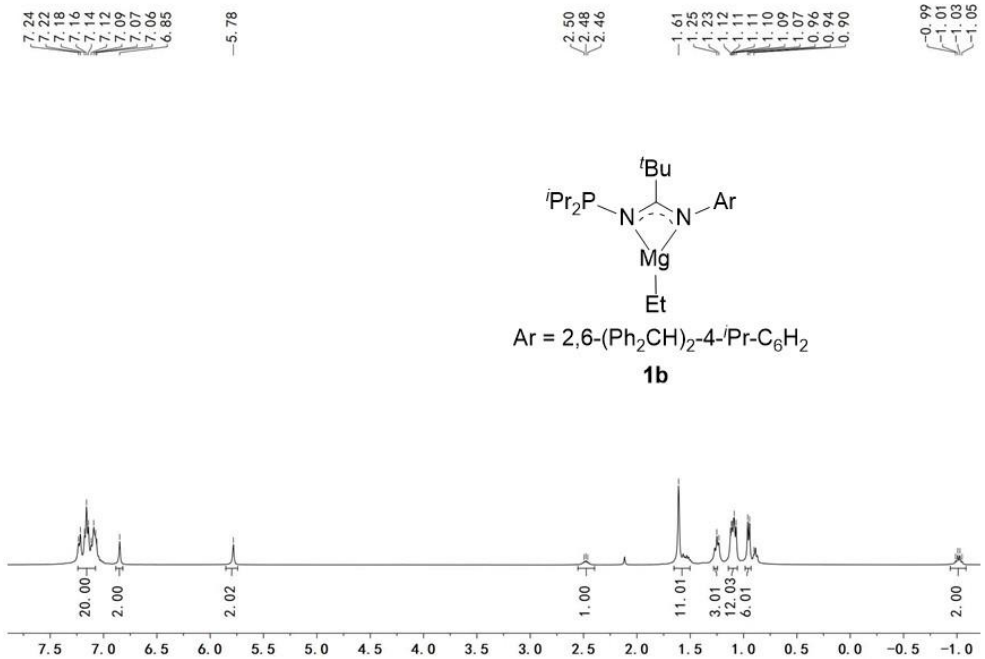


Fig. S12. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

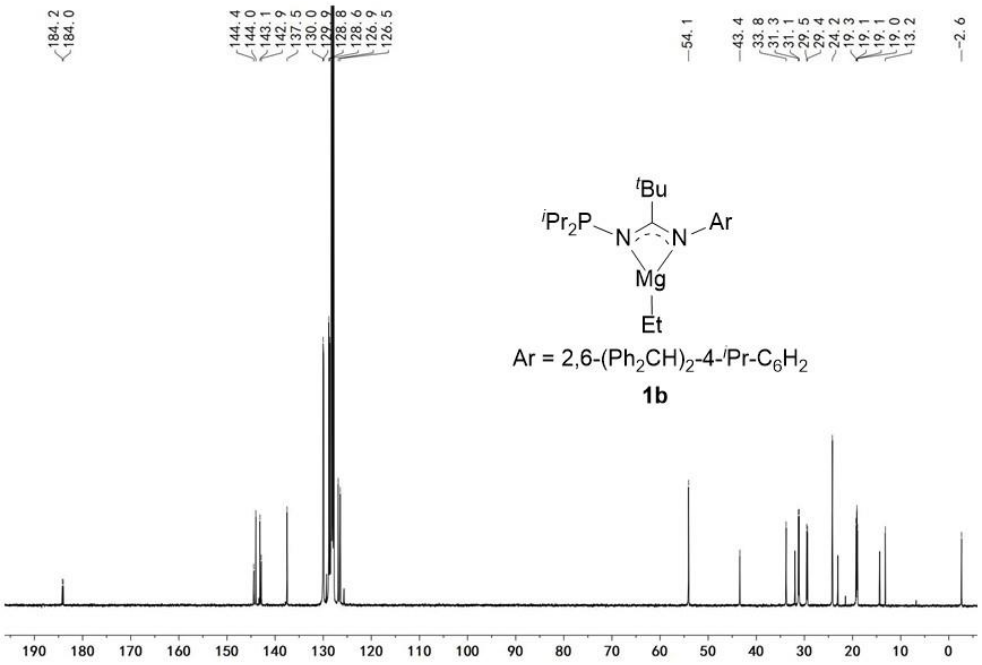


Fig. S13. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K)

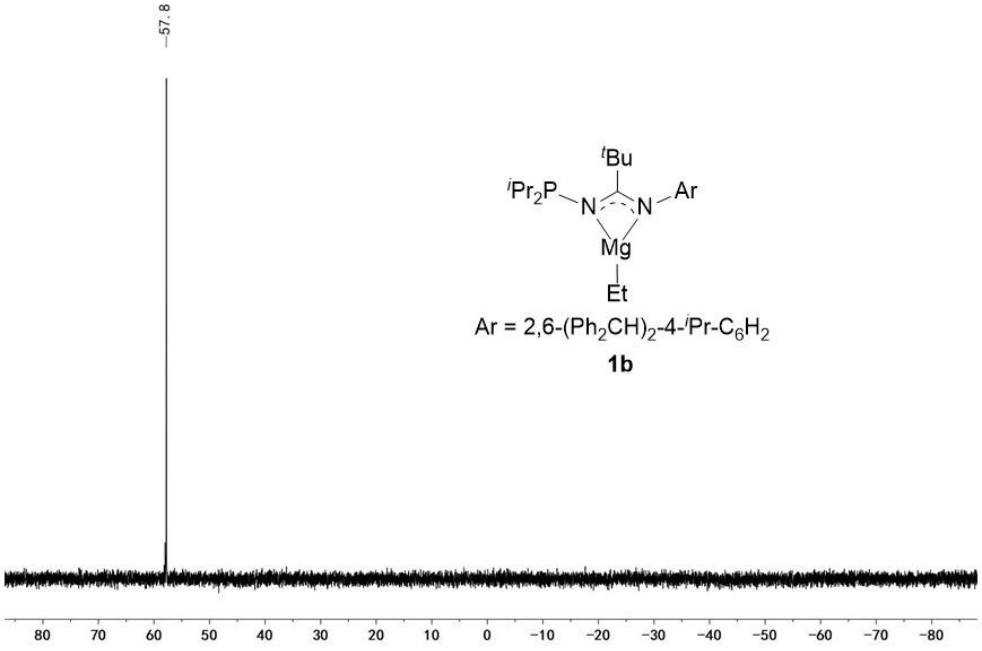
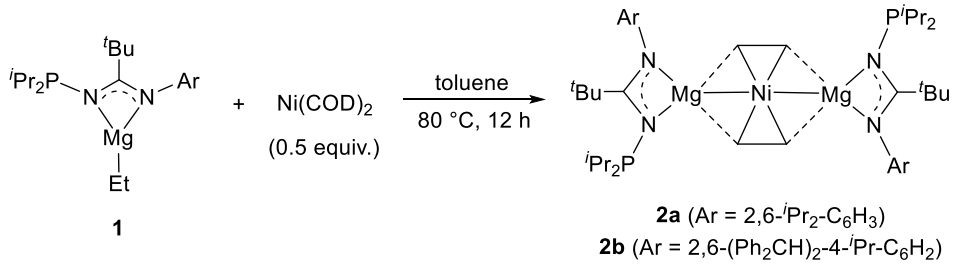


Fig. S14. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K)

3. Synthesis and NMR spectra of complexes 2



Scheme S5. Synthesis of complexes **2**

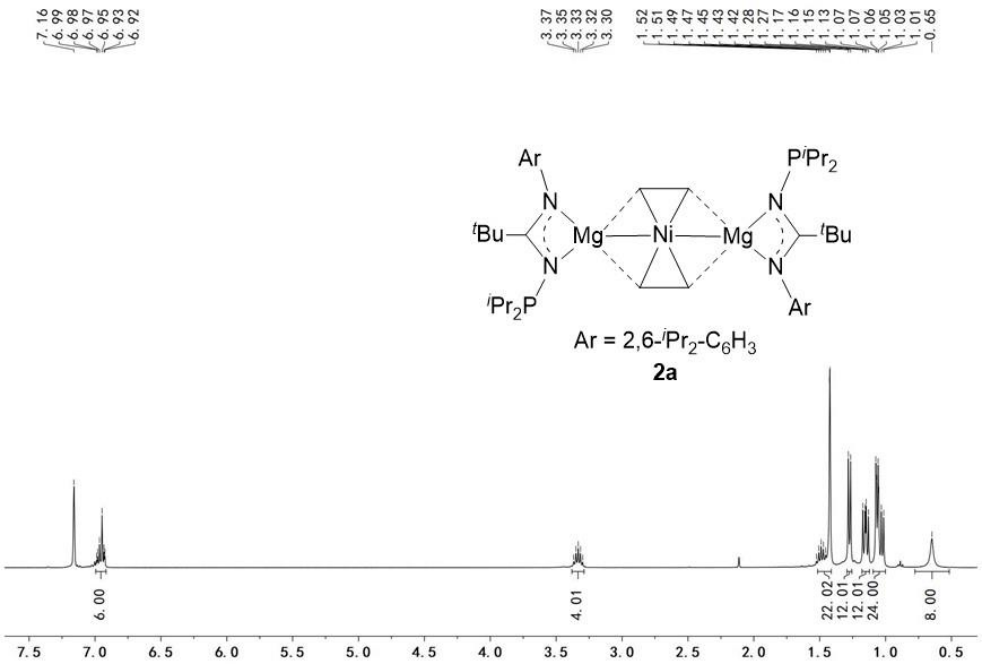


Fig. S15. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

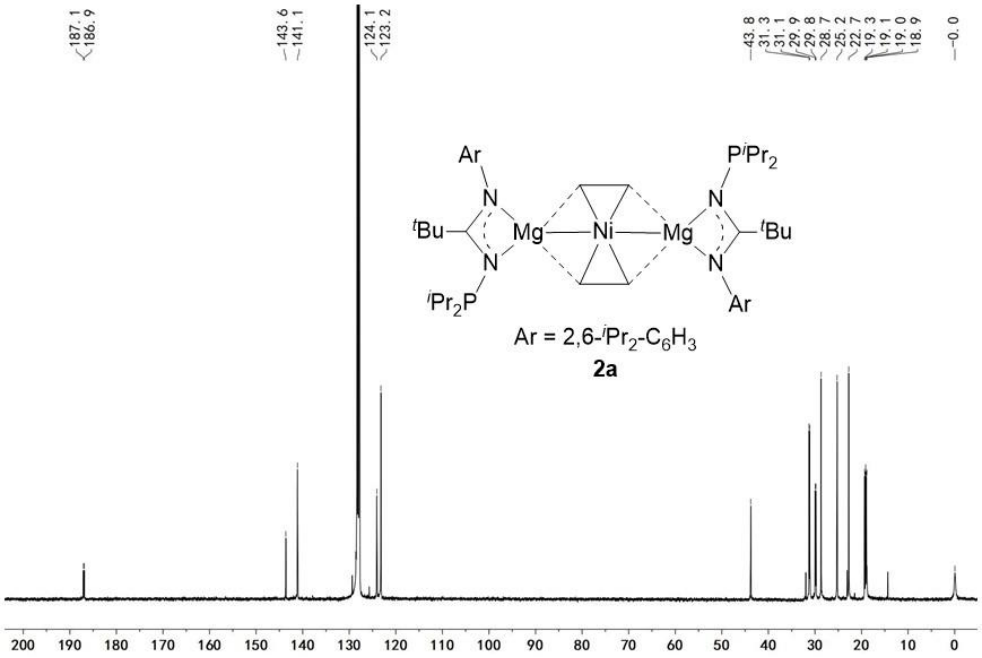


Fig. S16. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

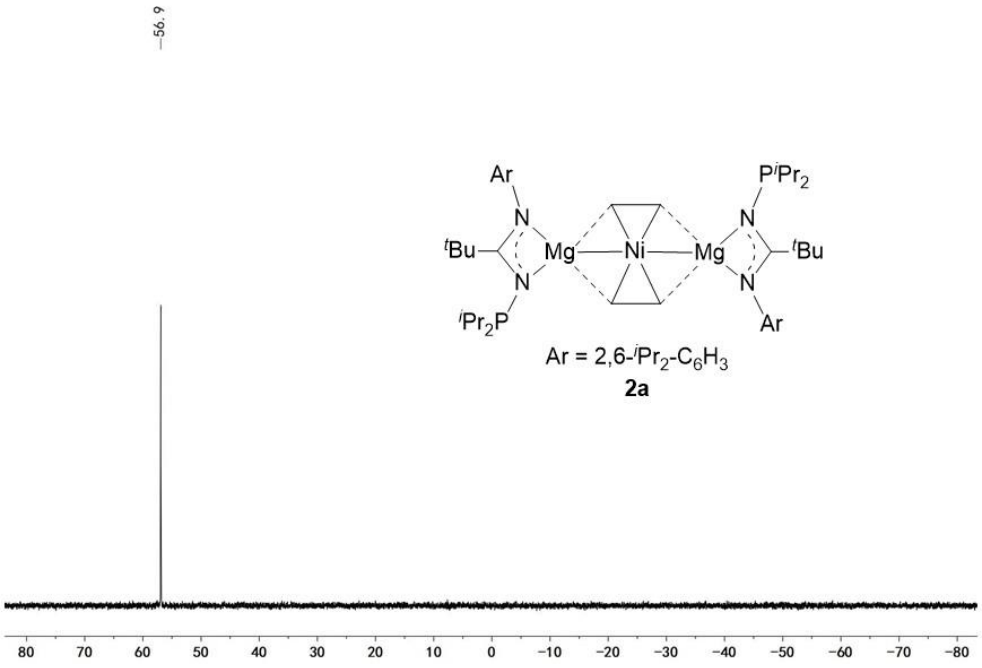


Fig. S17. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K)

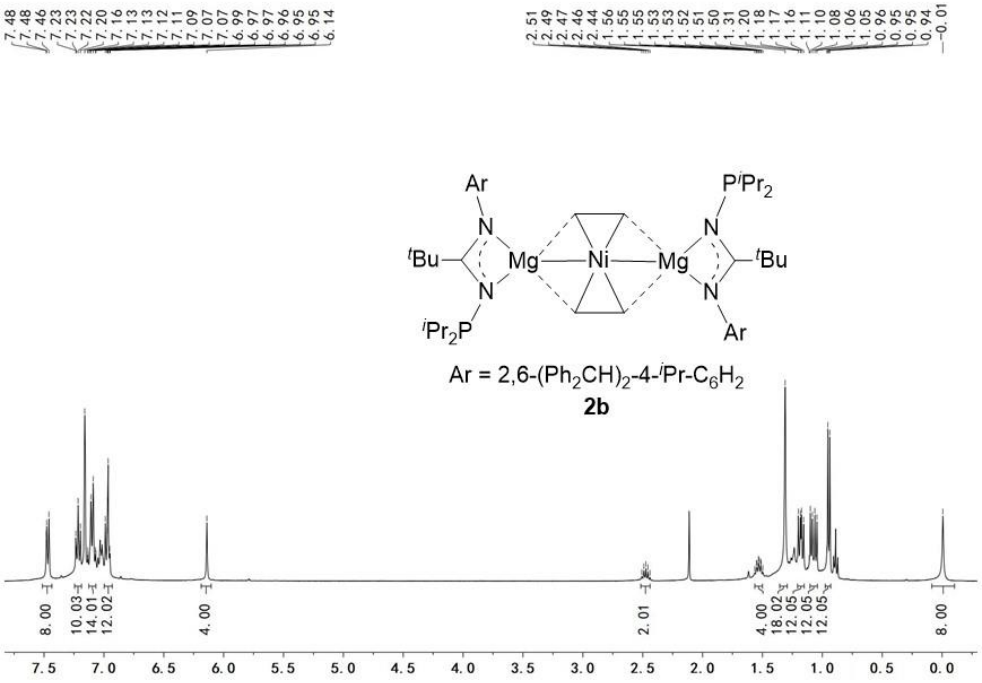


Fig. S18. ^1H NMR (400 MHz, C_6D_6, 298 K)

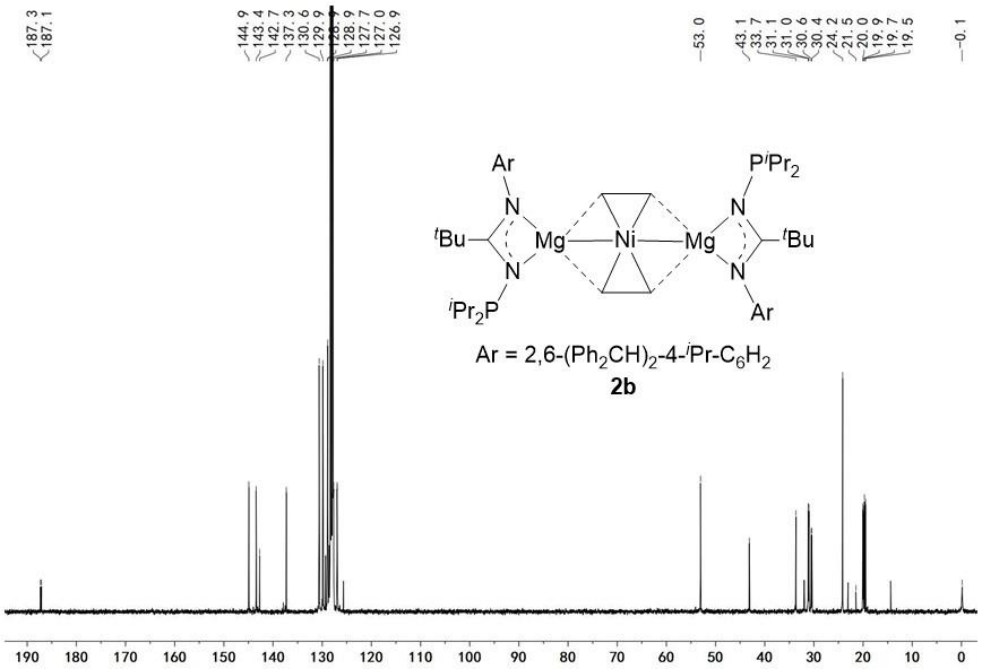


Fig. S19. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K)

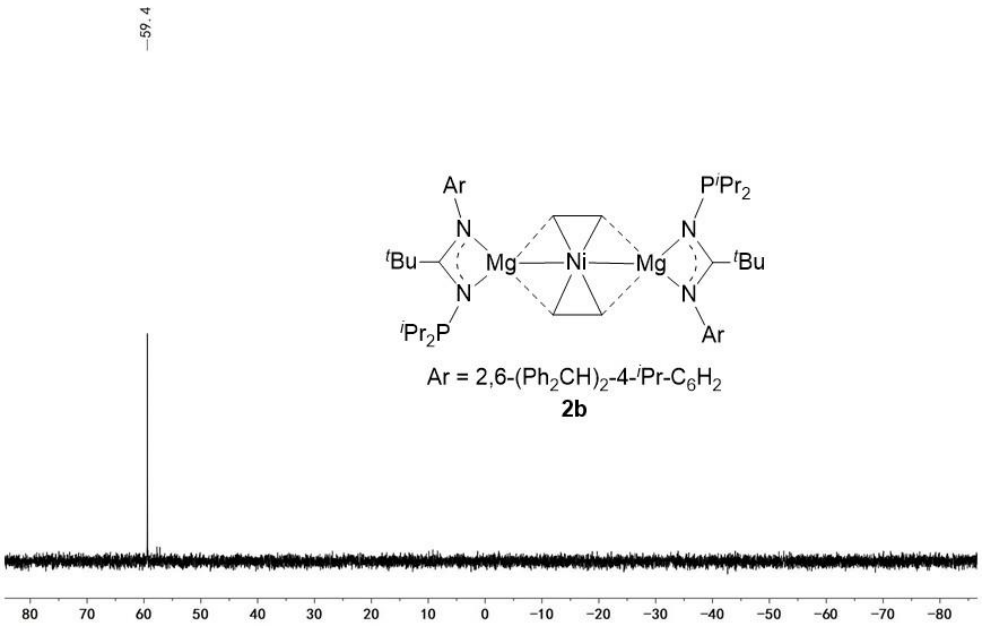
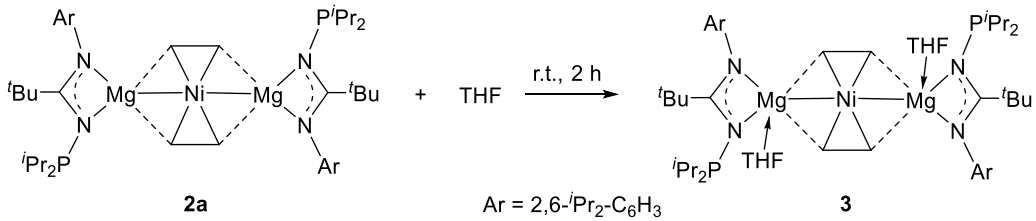


Fig. S20. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K)

4. Synthesis and NMR spectra of complex 3



Scheme S6. Synthesis of complex **3**

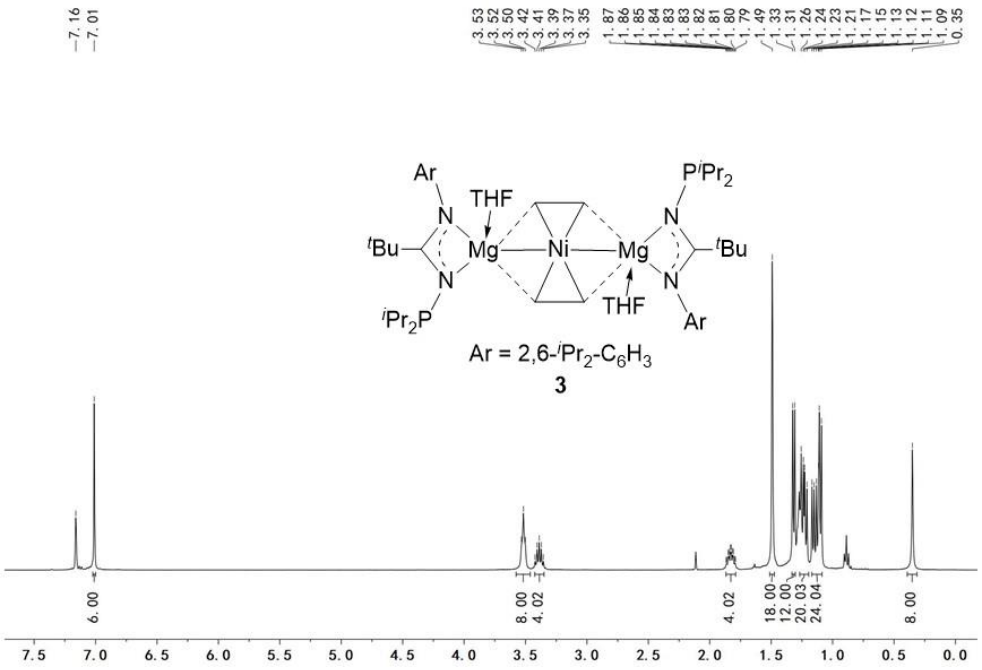


Fig. S21. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

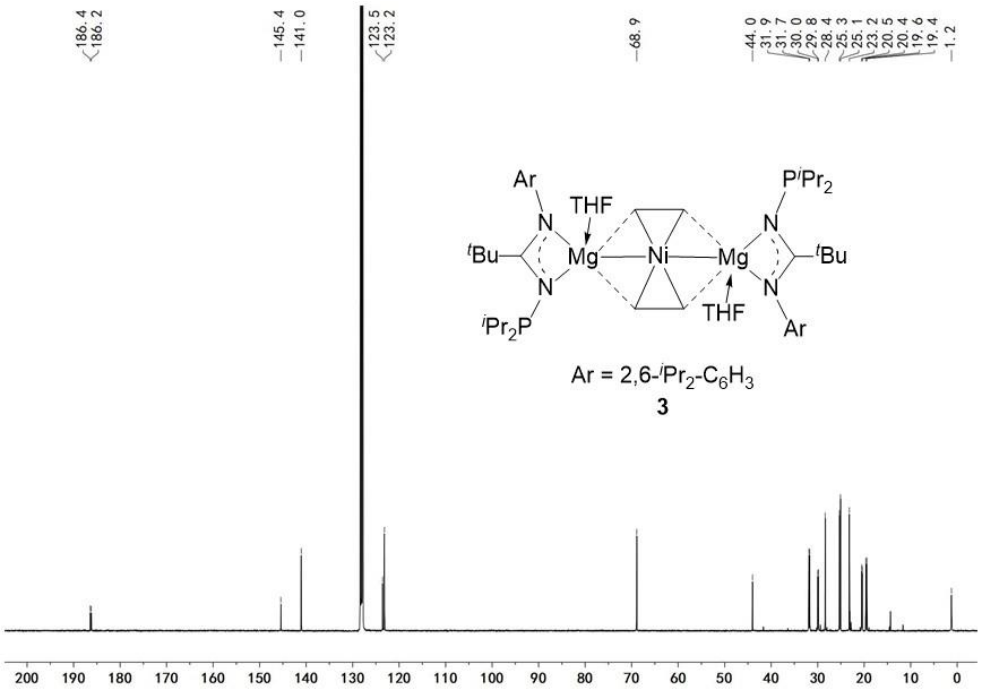


Fig. S22. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

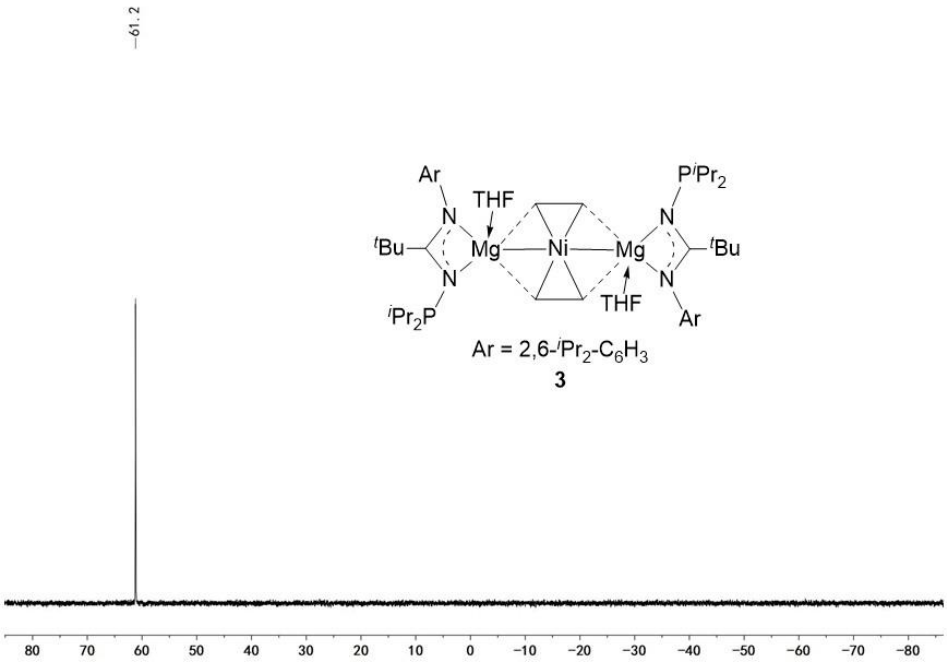
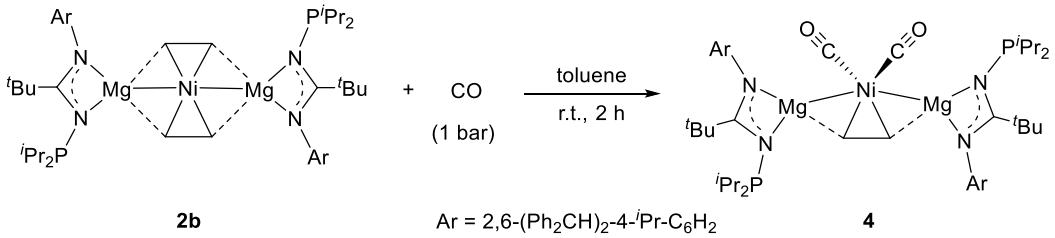


Fig. S23. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

5. Synthesis and NMR spectra of complex 4



Scheme S7. Synthesis of complex **4**

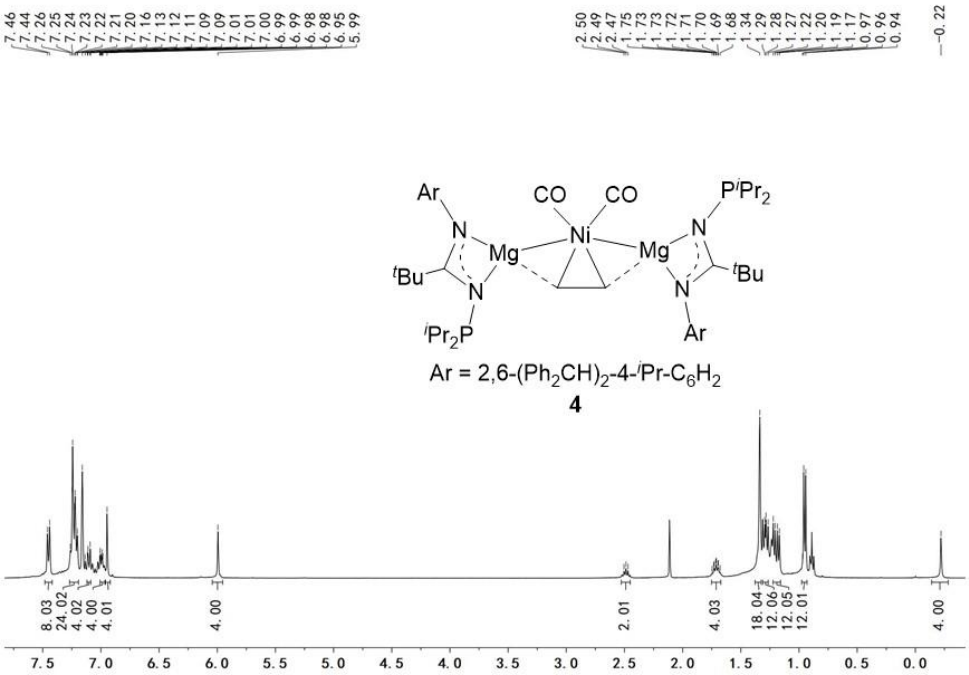


Fig. S24. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

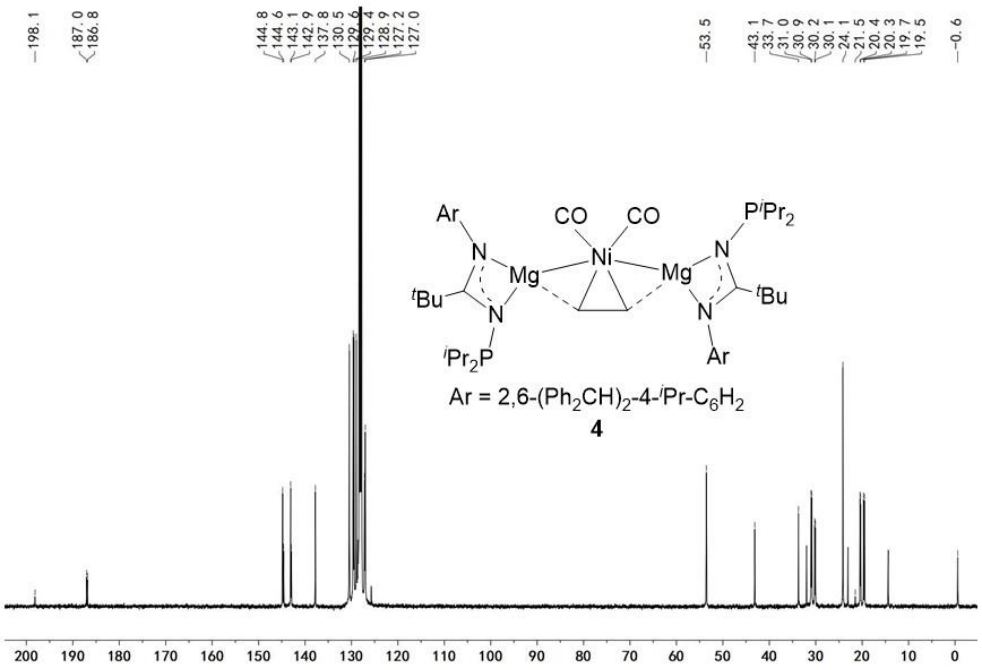


Fig. S25. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K)

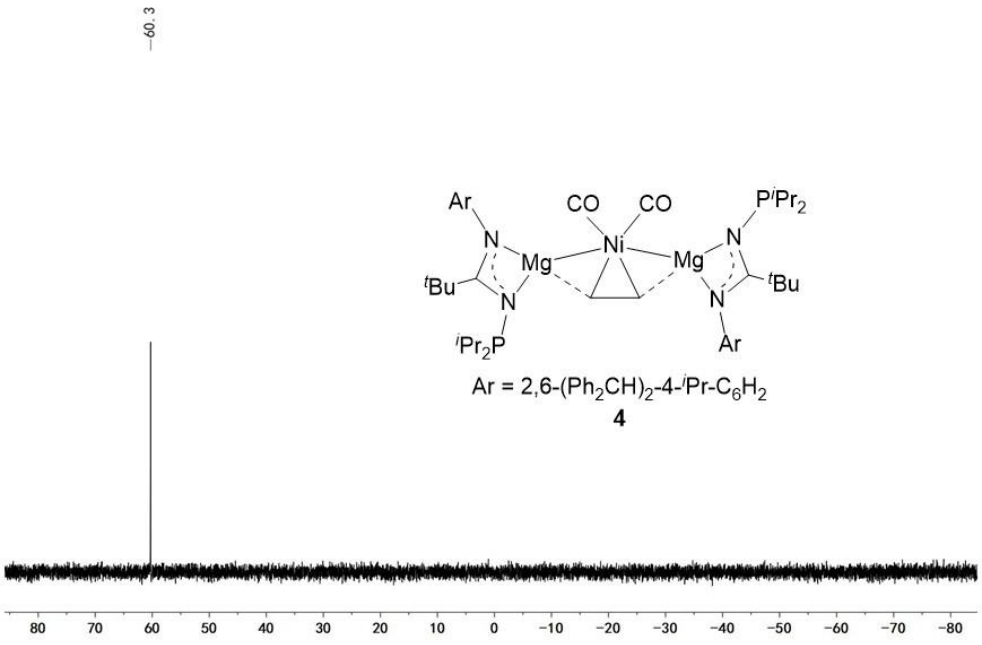


Fig. S26. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K)

6. FT-IR spectrum of complex 4

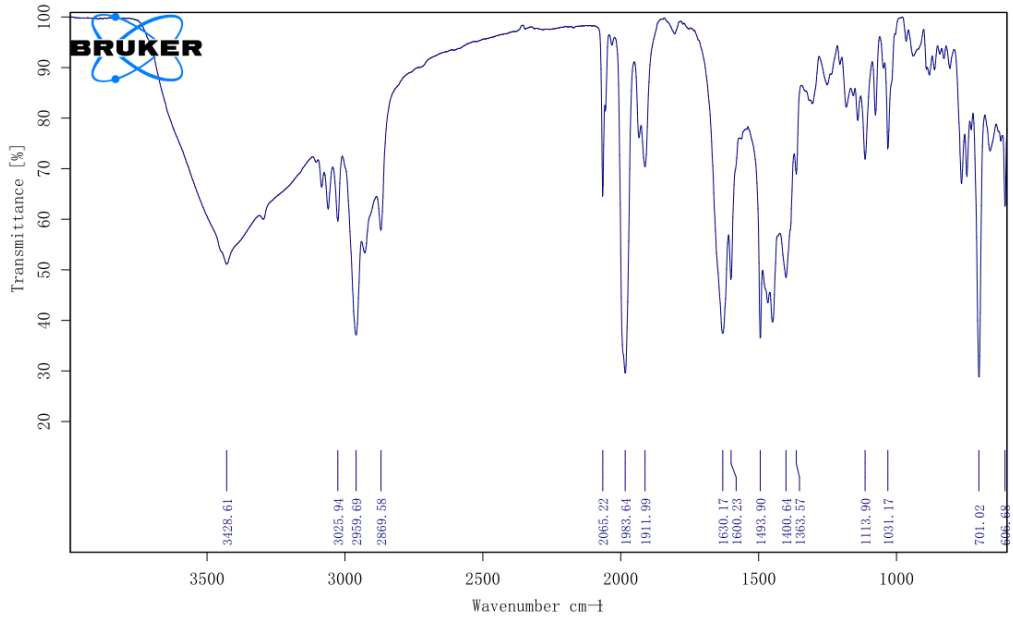


Fig. S27. FT-IR spectrum of complex 4

7. NMR reaction of complex 2b with CO

In a glove box, complex **2b** (0.01 mmol, 14.9 mg) and ferrocene (0.008 mmol, 1.5 mg) were dissolved in 0.5 mL of C_6D_6 and transferred to a sealed J. Young NMR tube. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar of CO at room temperature. The reaction was monitored by ^{1}H NMR spectrum after 2 h.

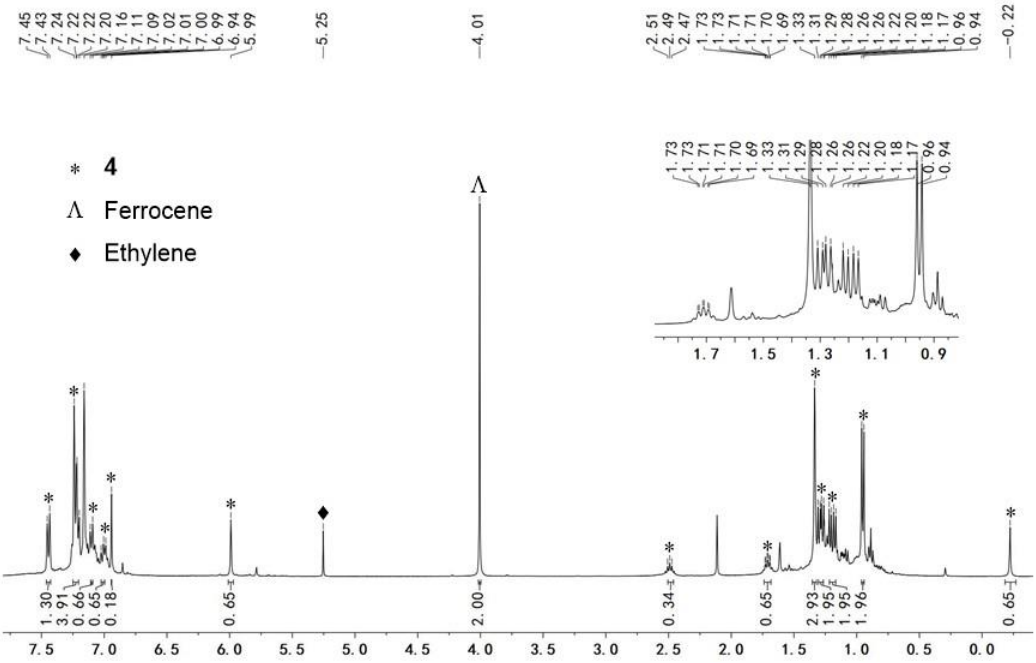


Fig. S28. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

8. Crystallographic information

X-ray crystal structure analysis of compound 1b: formula $C_{48}H_{59}MgN_2P \cdot 0.5C_6H_{14}$, M = 762.33 gmol^{-1}, colorless, 0.04 x 0.03 x 0.02 mm, Triclinic, space group P-1, a = 10.5976(7), b = 19.2049(13), c = 23.4676(17) Å, α = 76.930(3)°, β = 89.321(3)°, γ = 78.848(3)°, V = 4562.1(5) Å^3, ρ_{calc} = 1.110 gcm^{-3}, μ = 0.594 mm^{-1}, empirical absorption correction (0.5888 ⩽ T ⩽ 0.7512), Z = 4, λ = 1.34138 Å, T = 120.00 K, 63230 reflections collected (-13 ⩽ h ⩽ 11, -23 ⩽ k ⩽ 24, -29 ⩽ l ⩽ 29), 18697 independent (R_{int} = 0.0871) and 9965 observed reflections (I > 2σ(I)), 1013 refined parameters, the final R_1 was 0.0753 (I > 2σ(I)) and wR_2 was 0.2347 (all data). max. (min.) residual electron density 0.52 (-0.42) e.Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

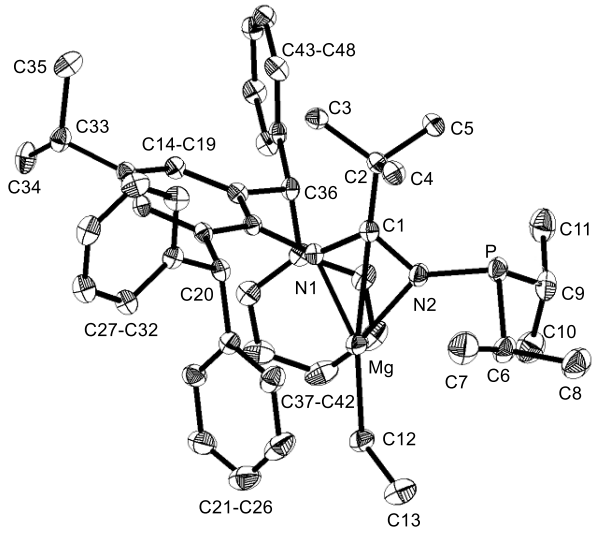


Fig. S29. Molecular structure of compound **1b**

X-ray crystal structure analysis of complex 2a: formula $C_{50}H_{88}Mg_2N_4NiP_2$, M = 914.51 gmol^{-1}, colorless, 0.24 × 0.22 × 0.2 mm, Triclinic, space group P-1, a = 9.0128(4), b = 10.6971(4), c = 15.9172(6) Å, α = 107.9280(10)°, β = 93.3990(10)°, γ = 105.3290(10)°, V = 1391.49(10) Å^3, ρ_{calc} = 1.091 gcm^{-3}, μ = 0.462 mm^{-1}, empirical absorption correction (0.5308 ⩽ T ⩽ 0.7456), Z = 1, λ = 0.71073 Å, T = 120 K, 30580 reflections collected (-11 ⩽ h ⩽ 11, -13 ⩽ k ⩽ 13, -20 ⩽ l ⩽ 20), 6378 independent (R_{int} = 0.0720) and 4899 observed reflections (I > 2σ(I)), 295 refined parameters, the final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1228 (all data). max. (min.) residual electron density 0.34 (-0.33) e.Å^{-3}, hydrogen atoms except for those in

Ni-C_2H_4 moieties were placed in calculated positions and refined using a riding model, hydrogen atoms in Ni-C_2H_4 moieties were located in a Fourier difference map and was refined with isotropic displacement parameters.

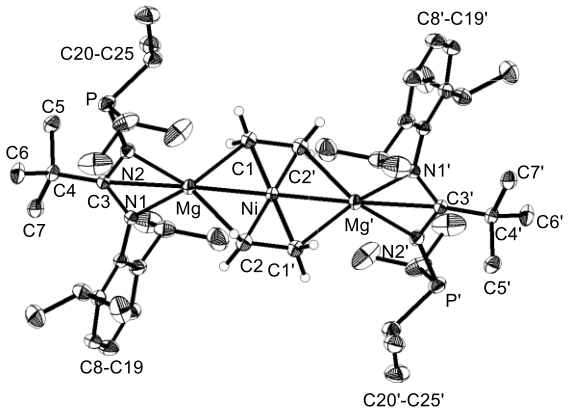


Fig. S30. Molecular structure of complex **2a**

X-ray crystal structure analysis of complex 2b: formula $C_{96}H_{116}Mg_2N_4NiP_2 \cdot 4C_6H_6$, M = 1807.62 gmol^{-1}, colorless, 0.2 × 0.2 × 0.15 mm, Monoclinic, space group $P2/c$, a = 18.2558(11), b = 15.2714(9), c = 18.9886(12) Å, β = 104.001(2)°, V = 5136.6(5) Å^3, ρ_{calc} = 1.169 gcm^{-3}, μ = 1.543 mm^{-1}, empirical absorption correction (0.5860 ⩽ T ⩽ 0.7518, Z = 2, λ = 1.34139 Å, T = 150.00 K, 113318 reflections collected (-22 ⩽ h ⩽ 22, -19 ⩽ k ⩽ 19, -23 ⩽ l ⩽ 23), 10130 independent (R_{int} = 0.1040) and 8774 observed reflections (I > 2σ(I)), 648 refined parameters, the final R_1 was 0.0549 (I > 2σ(I)) and wR_2 was 0.1551 (all data). max. (min.) residual electron density 0.84 (-0.48) e.Å^{-3}, hydrogen atoms except for those in Ni-C_2H_4 moieties were placed in calculated positions and refined using a riding model, hydrogen atoms in Ni-C_2H_4 moieties were located in a Fourier difference map and was refined with isotropic displacement parameters.

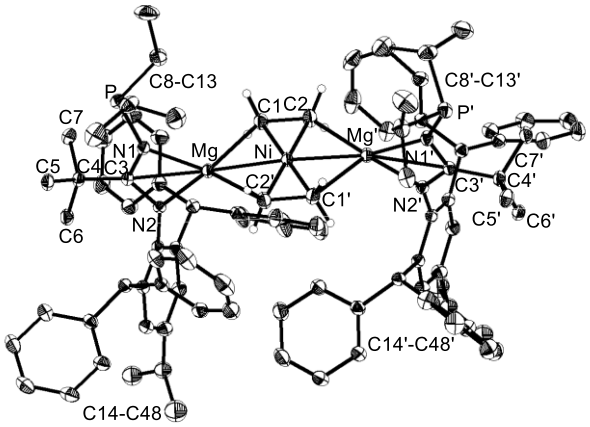


Fig. S31. Molecular structure of complex **2b**

X-ray crystal structure analysis of complex 3: formula $C_{58}H_{104}Mg_2N_4NiO_2P_2$, M = 1058.72 gmol^{-1}, colorless, 0.3 × 0.25 × 0.2 mm, Monoclinic, space group *C*2/*c*, a = 19.0876(12), b = 11.5755(8), c = 28.1191(18) Å, β = 95.476(2)°, V = 6184.5(7) Å^3, ρ_{calc} = 1.137 gcm^{-3}, μ = 0.427 mm^{-1}, empirical absorption correction (0.6646 ⩽ T ⩽ 0.7456, Z = 4, λ = 0.71073 Å, T = 296.15 K, 64867 reflections collected (-24 ⩽ h ⩽ 24, -15 ⩽ k ⩽ 15, -36 ⩽ l ⩽ 36), 7154 independent (R_{int} = 0.1517) and 3961 observed reflections (I > 2σ(I)), 340 refined parameters, the final R_1 was 0.0585 (I > 2σ(I)) and wR_2 was 0.1375 (all data). max. (min.) residual electron density 0.89 (-0.43) e.Å^{-3}, hydrogen atoms except for those in Ni-C_2H_4 moieties were placed in calculated positions and refined using a riding model, hydrogen atoms in Ni-C_2H_4 moieties were located in a Fourier difference map and was refined with isotropic displacement parameters.

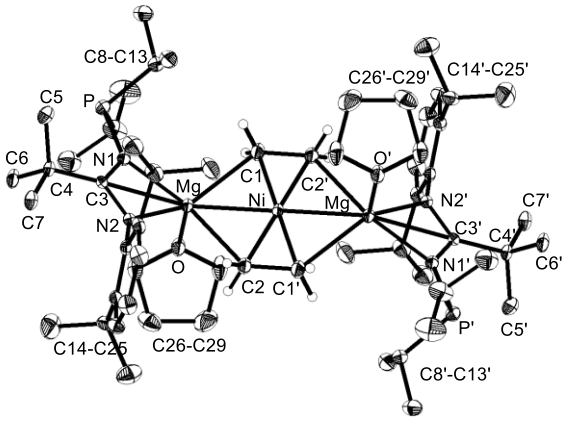


Fig. S32. Molecular structure of complex **3**

X-ray crystal structure analysis of complex 4: formula $C_{96}H_{112}Mg_2N_4NiO_2P_2$, M = 1523.16 gmol^{-1}, colorless, 0.2 × 0.2 × 0.2 mm, Triclinic, space group P-1, a = 15.0759(14), b = 18.5965(17), c = 20.2198(16) Å, α = 110.227(3)°, β = 101.922(4)°, γ = 108.780(4)°, V = 4702.6(7) Å^3, ρ_{calc} = 1.076 gcm^{-3}, μ = 1.643 mm^{-1}, empirical absorption correction (0.6199 ⩽ T ⩽ 0.7512), Z = 2, λ = 1.34138 Å, T = 120.00 K, 108711 reflections collected (-18 ⩽ h ⩽ 18, -23 ⩽ k ⩽ 23, -25 ⩽ l ⩽ 24), 19250 independent (R_{int} = 0.0741) and 13971 observed reflections (I > 2σ(I)), 998 refined parameters, the final R_1 was 0.0573 (I > 2σ(I)) and wR_2 was 0.1692 (all data). max. (min.) residual electron density 1.02 (-0.45) e.Å^{-3}, hydrogen atoms except for those in Ni-C_2H_4 moieties were placed in calculated positions and refined using a riding model, hydrogen atoms in Ni-C_2H_4 moieties were located in a Fourier difference map and was refined with isotropic displacement parameters.

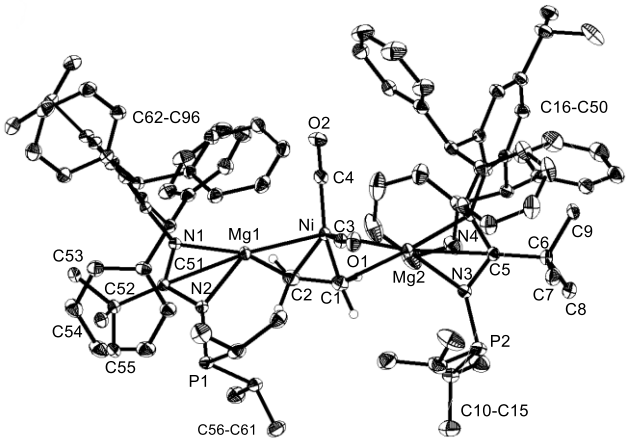


Fig. S33. Molecular structure of complex **4**