Supporting Information

Reactions of a Geminal Sc/P Lewis Pair with Pyridotetrazole and Beyond

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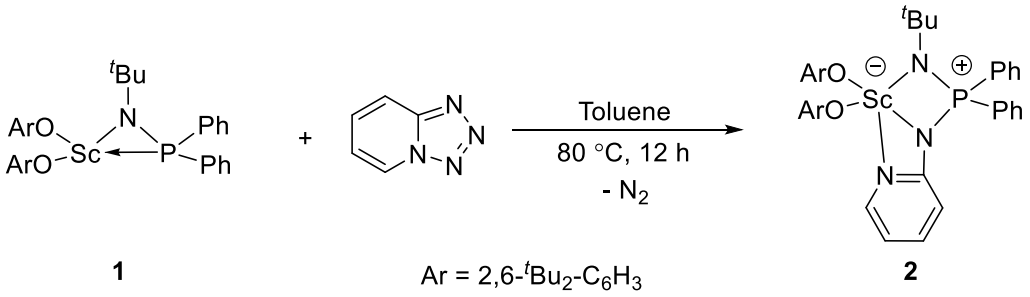
Preparation of complex 2



Scheme S1.

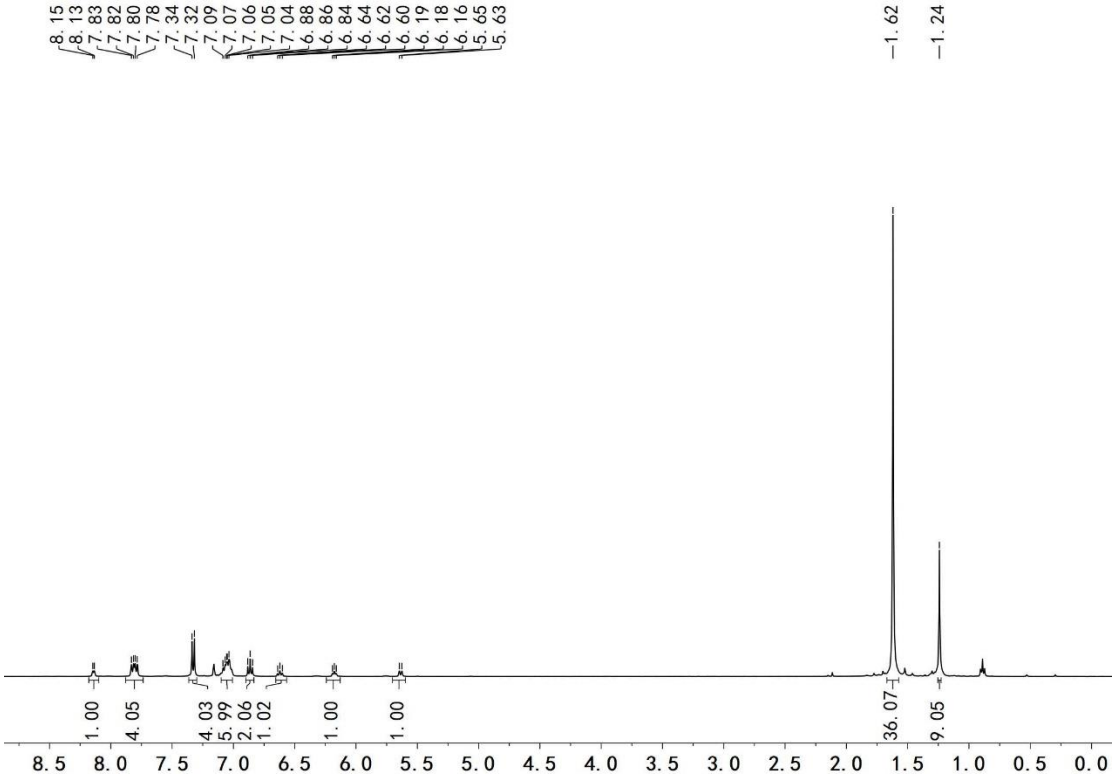


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

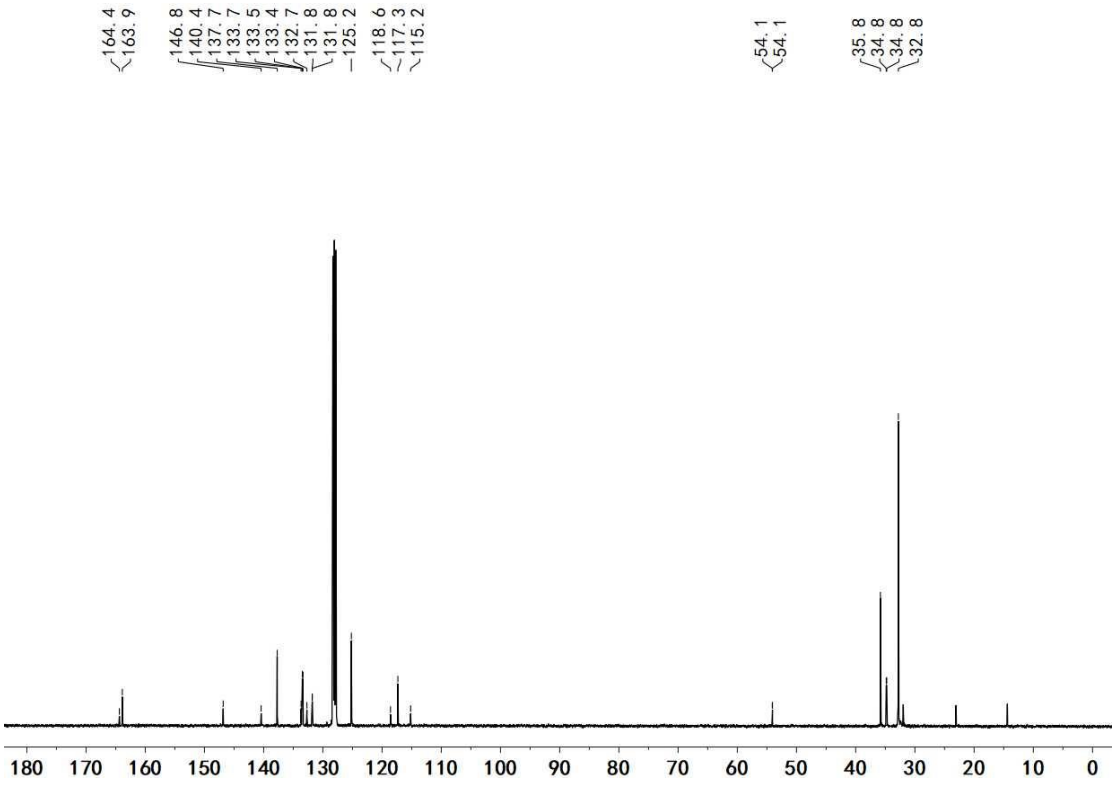


Fig. S2. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K).

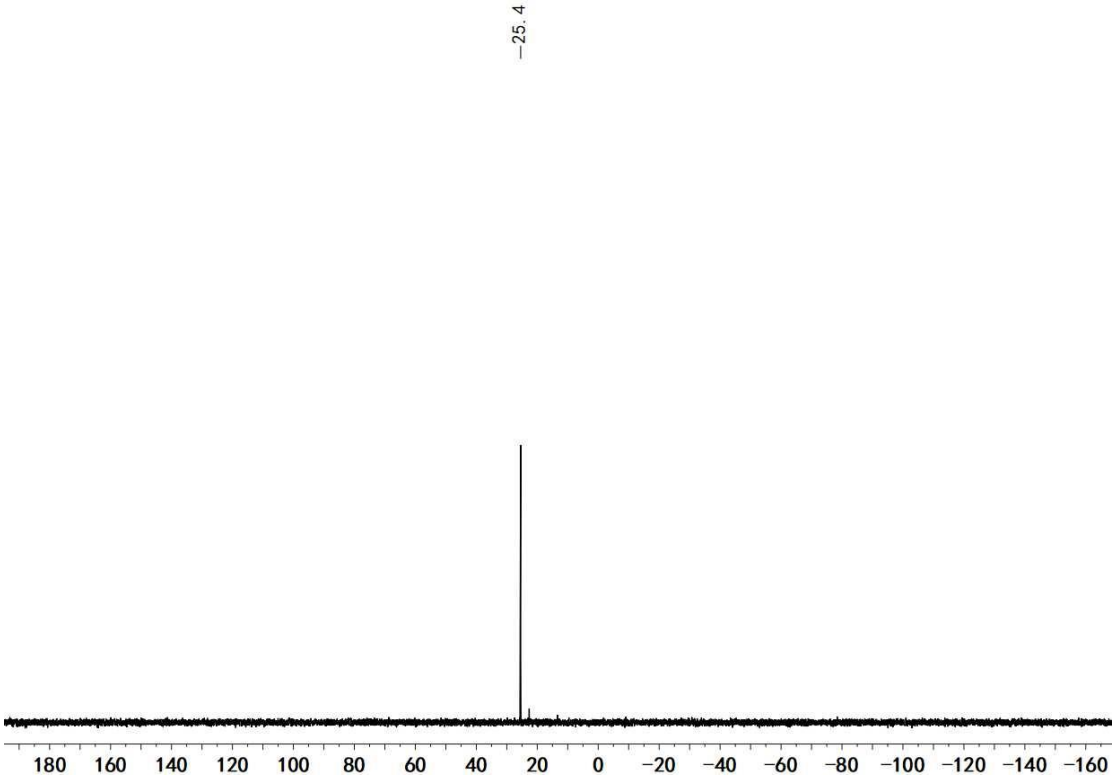


Fig. S3. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 2: formula $C_{49}H_{65}N_3O_2PSc$, M = 803.97 gmol^{-1}, colorless, 0.08 × 0.06 × 0.05 mm, orthorhombic, space group *Pbca*, a =

22.0487(8), b = 18.0563(8), c = 22.8495(9) Å, α = 90°, β = 90°, γ = 90°, V = 9096.8(6) Å^3, ρ_{calc} = 1.174 gcm^{-3}, μ = 0.237 mm^{-1}, empirical absorption correction (0.5132 ≤ T ≤ 0.7456), Z = 8, λ = 0.71073 Å, T = 273.15 K, 86418 reflections collected (-26 ≤ h ≤ 26, -21 ≤ k ≤ 21, -26 ≤ l ≤ 27), 8024 independent (R_{int} = 0.1527) and 5350 observed reflections [I>2σ(I)], 520 refined parameters, the final R_1 was 0.0835 [I>2σ(I)] and wR_2 was 0.1483 (all data), max. (min.) residual electron density 0.47 (-0.30) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

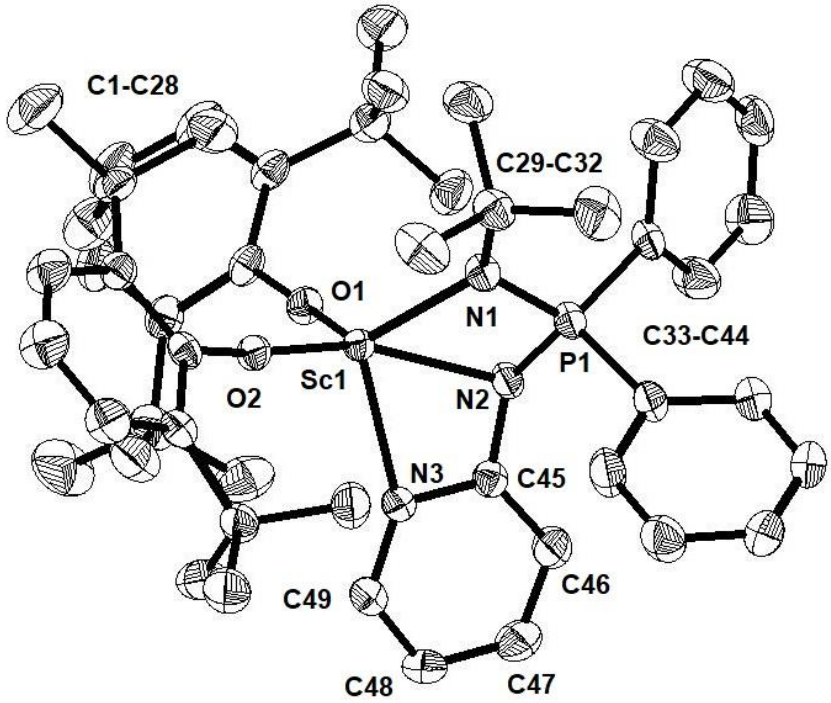
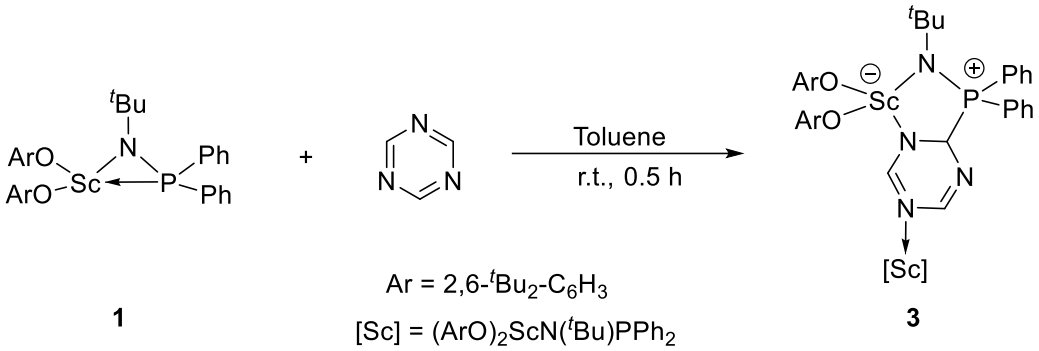


Fig. S4. Molecular structure of complex **2**.

Preparation of complex 3



Scheme S2.

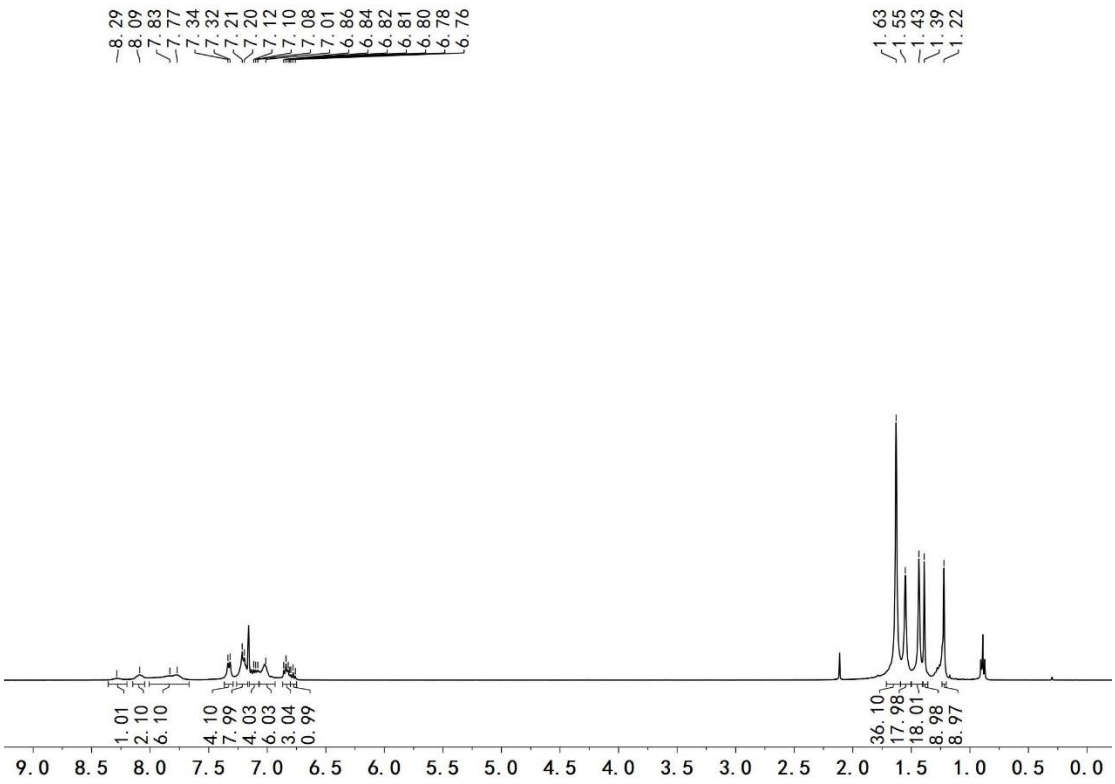


Fig. S5. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

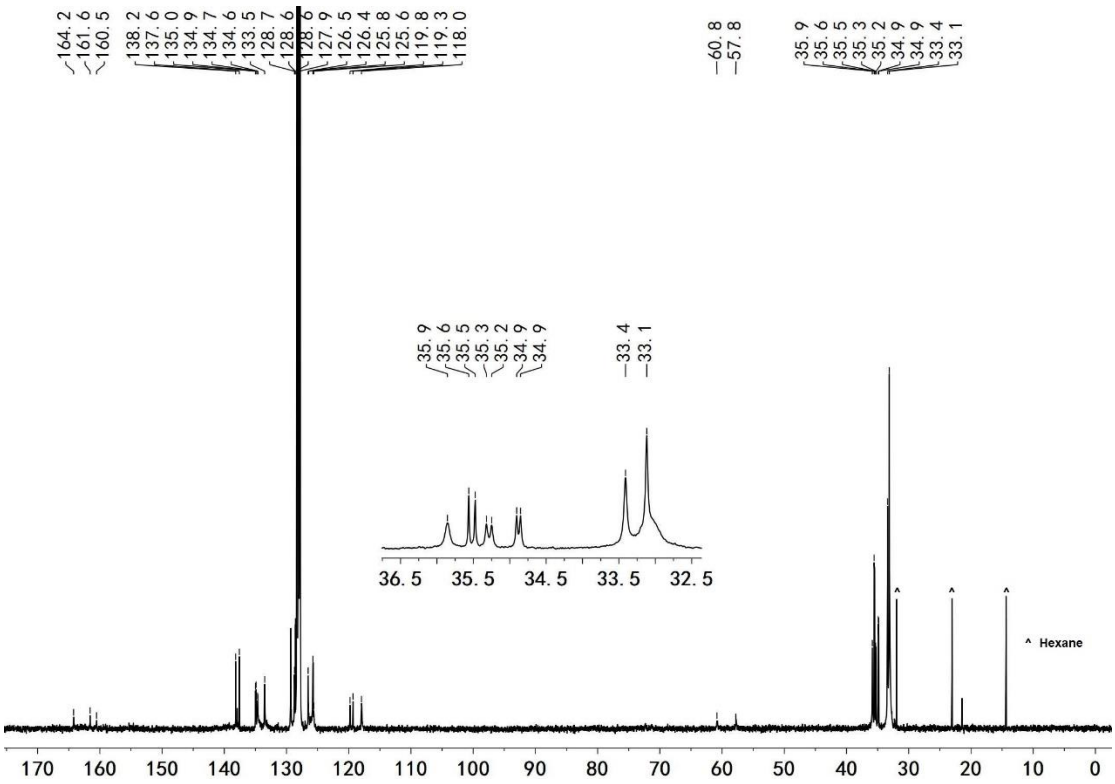


Fig. S6. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K).

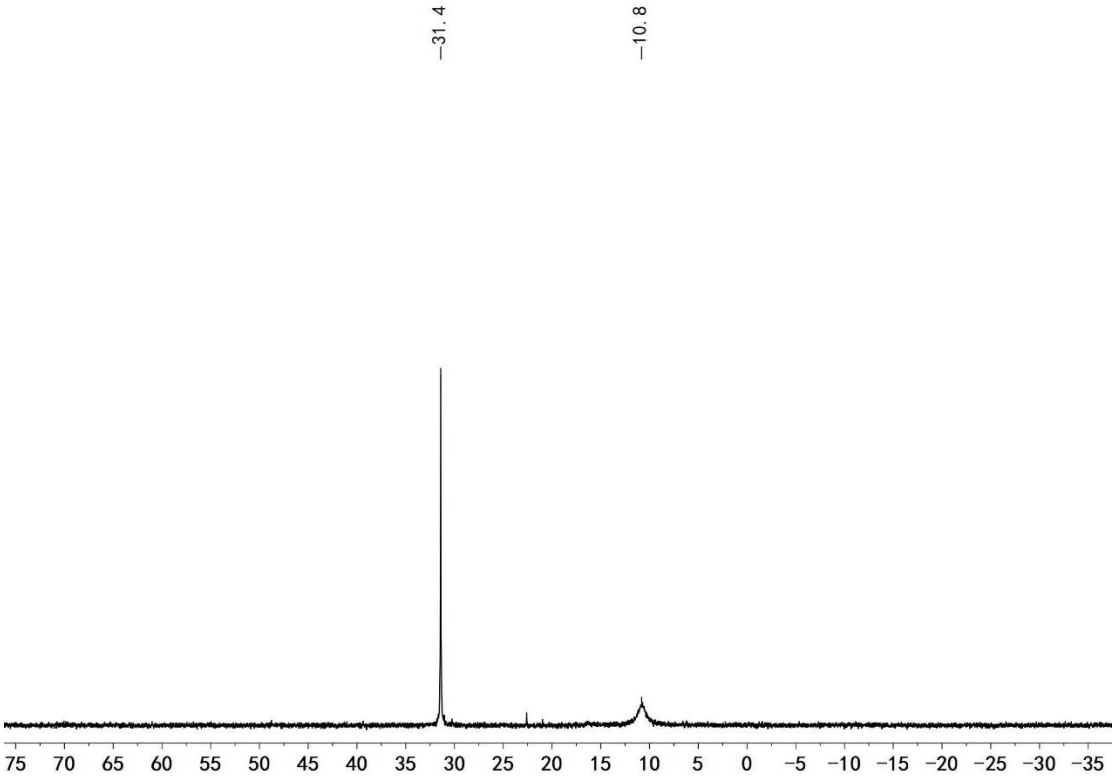


Fig. S7. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 3: formula $C_{91}H_{125}N_5O_4P_2Sc_2$, M = 1504.81 gmol^{-1}, colorless, 0.1 × 0.06 × 0.04 mm, monoclinic, space group $P2_1/c$, a =

25.380(7), b = 12.984(3), c = 29.626(7) Å, α = 90°, β = 113.566(9)°, γ = 90°, V = 8949(4) Å^3, ρ_{calc} = 1.117 gcm^{-3}, μ = 1.345 mm^{-1}, empirical absorption correction (0.4742 ≤ T ≤ 0.7518), Z = 4, λ = 1.34139 Å, T = 150.15 K, 115653 reflections collected (-30 ≤ h ≤ 30, -15 ≤ k ≤ 13, -35 ≤ l ≤ 35), 15791 independent (R_{int} = 0.1543) and 11936 observed reflections [I>2σ(I)], 969 refined parameters, the final R_1 was 0.0786 [I>2σ(I)] and wR_2 was 0.2258 (all data), max. (min.) residual electron density 0.65 (-0.78) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

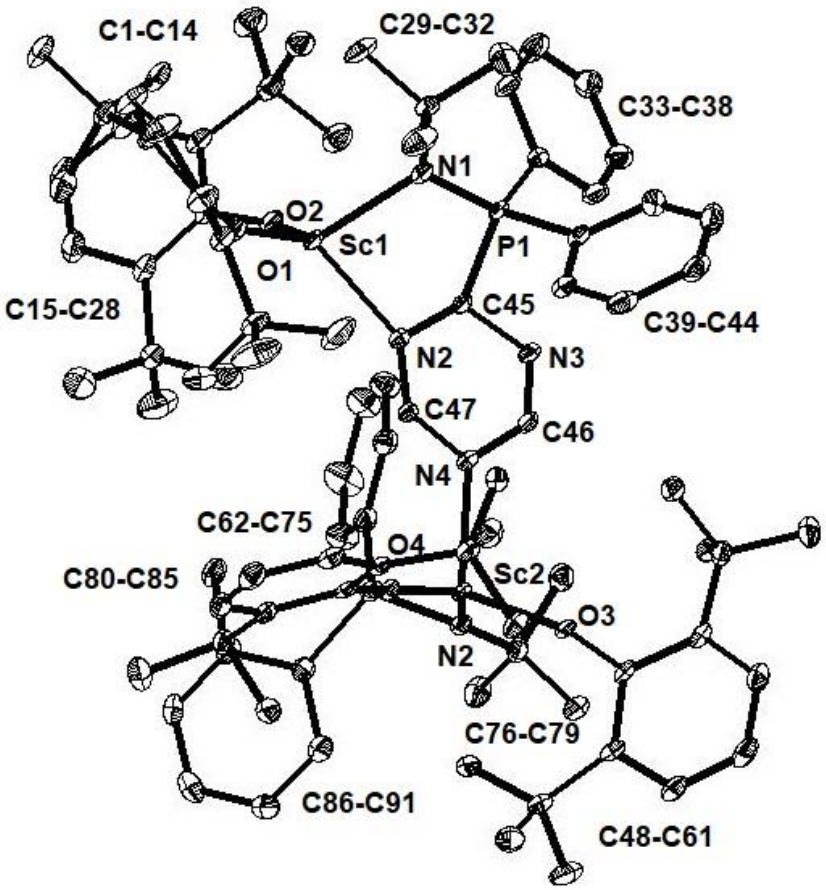
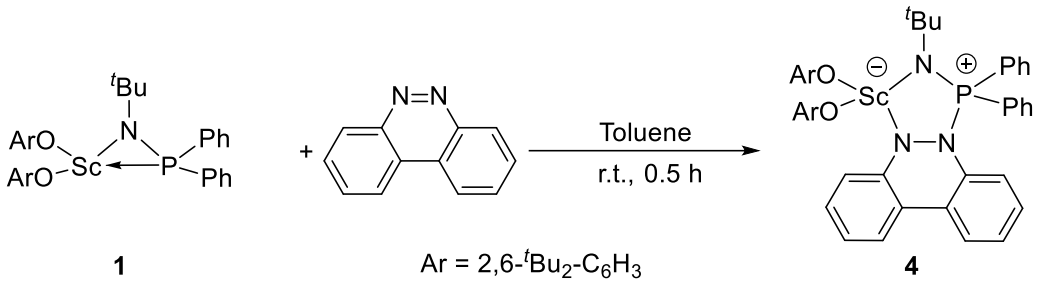


Fig. S8. Molecular structure of complex **3**.

Preparation of complex 4



Scheme S3.

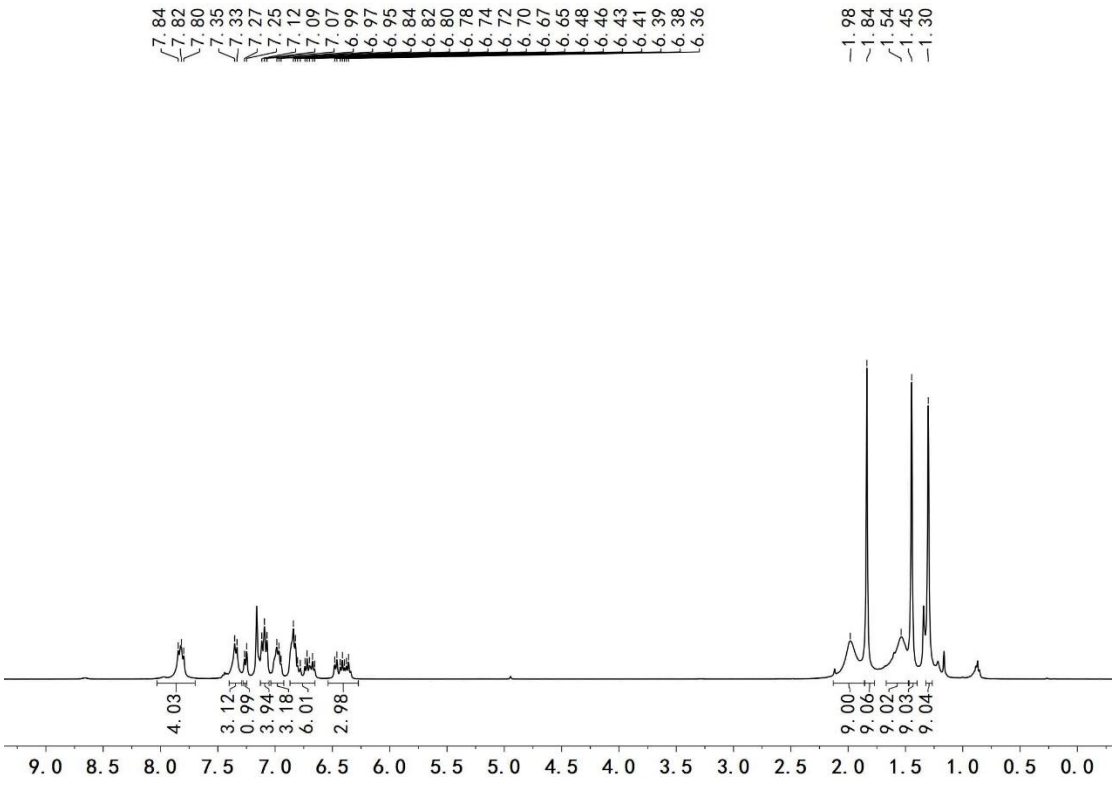


Fig. S9. ^{1}H NMR (400 MHz, C_6D_6/Bromobenzene-d_5 = 5:1, 298 K).

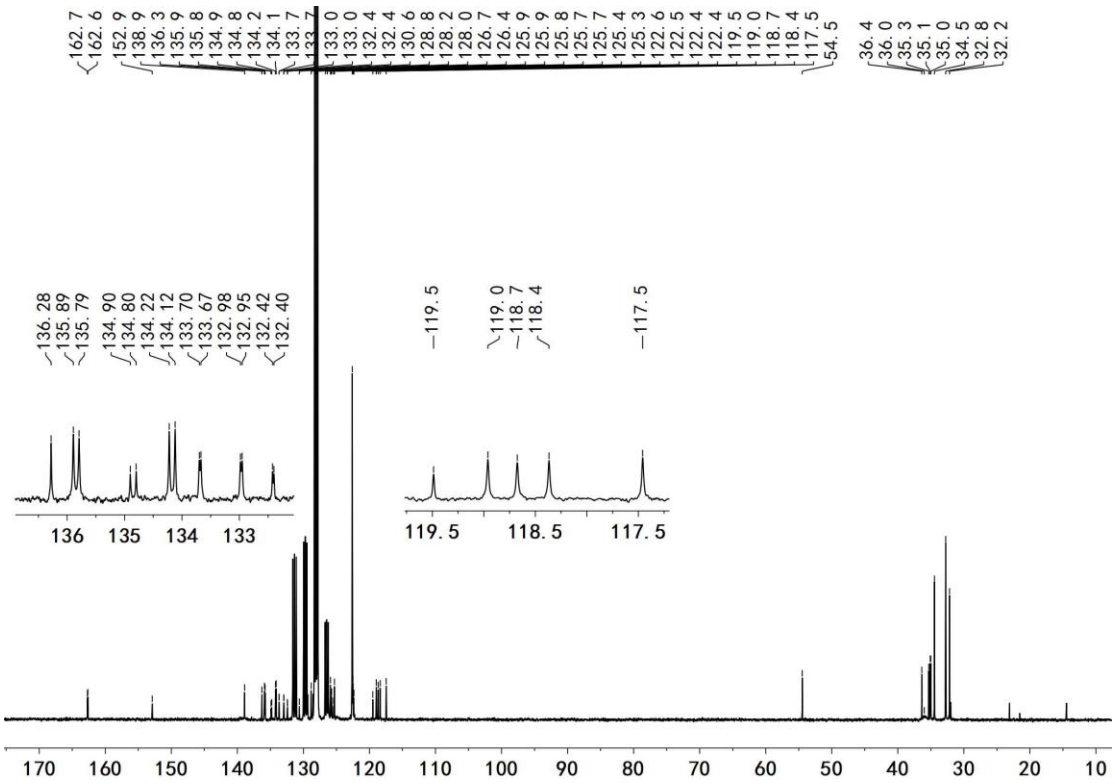


Fig. S10. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6/Bromobenzene-d_5 = 5:1, 298 K).

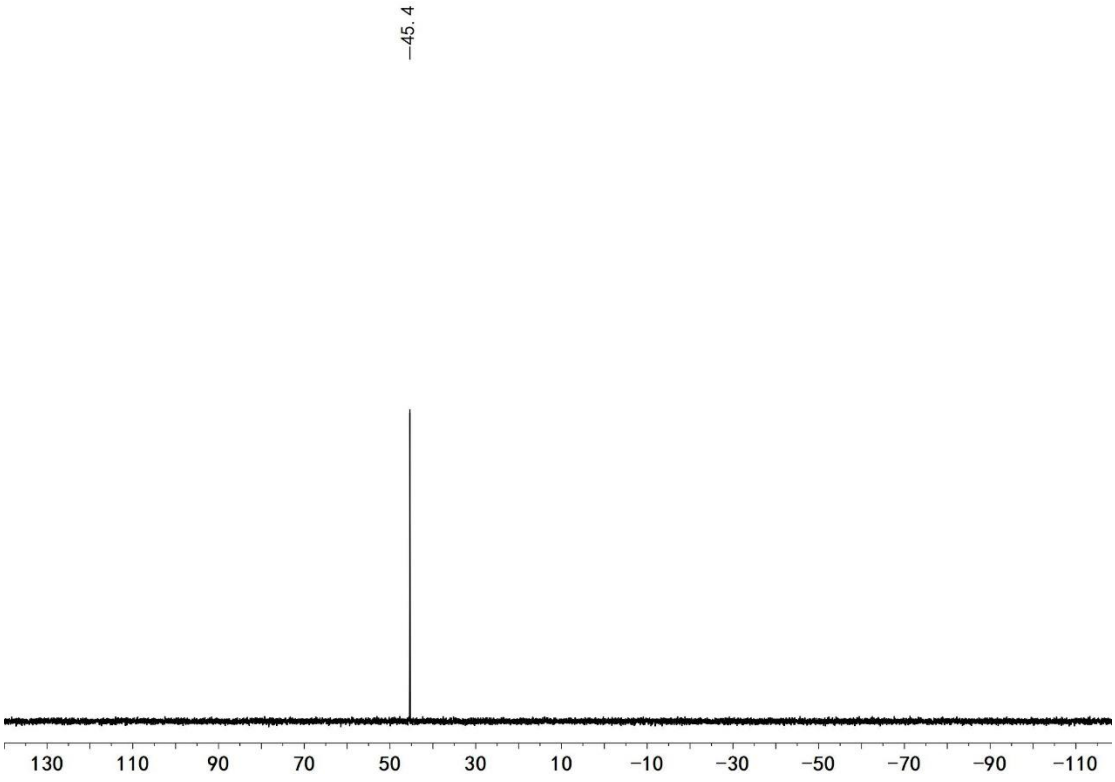


Fig. S11. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6/Bromobenzene-d_5 = 5:1, 298 K).

X-ray crystal structure analysis of complex 4: formula $C_{56}H_{69}N_3O_2PSc$, M = 892.07 gmol^{-1}, colorless, 0.16 × 0.14 × 0.13 mm, monoclinic, space group $P2_1/n$, a =

11.2105(4), b = 23.0554(9), c = 19.3556(7) Å, α = 90°, β = 97.0520(10)°, γ = 90°, V = 4964.9(3) Å^3, ρ_{calc} = 1.193 gcm^{-3}, μ = 0.224 mm^{-1}, empirical absorption correction (0.4657 ≤ T ≤ 0.7456), Z = 4, λ = 0.71073 Å, T = 119.99 K, 83669 reflections collected (-14 ≤ h ≤ 14, -29 ≤ k ≤ 29, -25 ≤ l ≤ 25), 11378 independent (R_{int} = 0.1215) and 7350 observed reflections [I>2σ(I)], 583 refined parameters, the final R_1 was 0.0497 [I>2σ(I)] and wR_2 was 0.1405 (all data), max. (min.) residual electron density 0.37 (-0.51) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

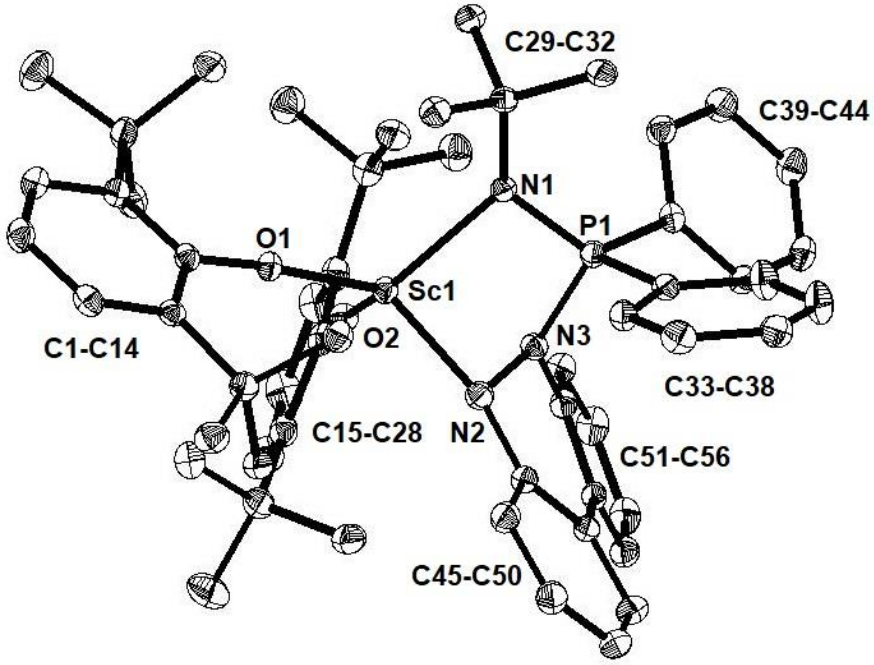
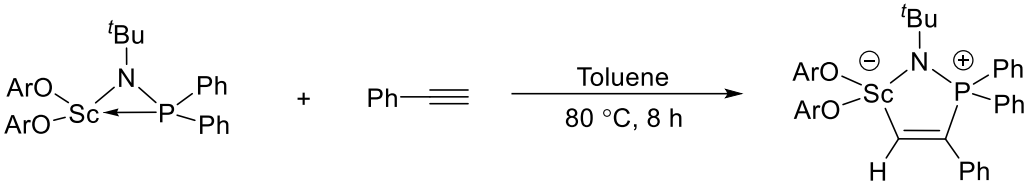


Fig. S12. Molecular structure of complex **4**.

Preparation of complex 5



1 Ar = 2,6-^{t}Bu$_2$-C$_6$H$_3$ **5**

Scheme S4.

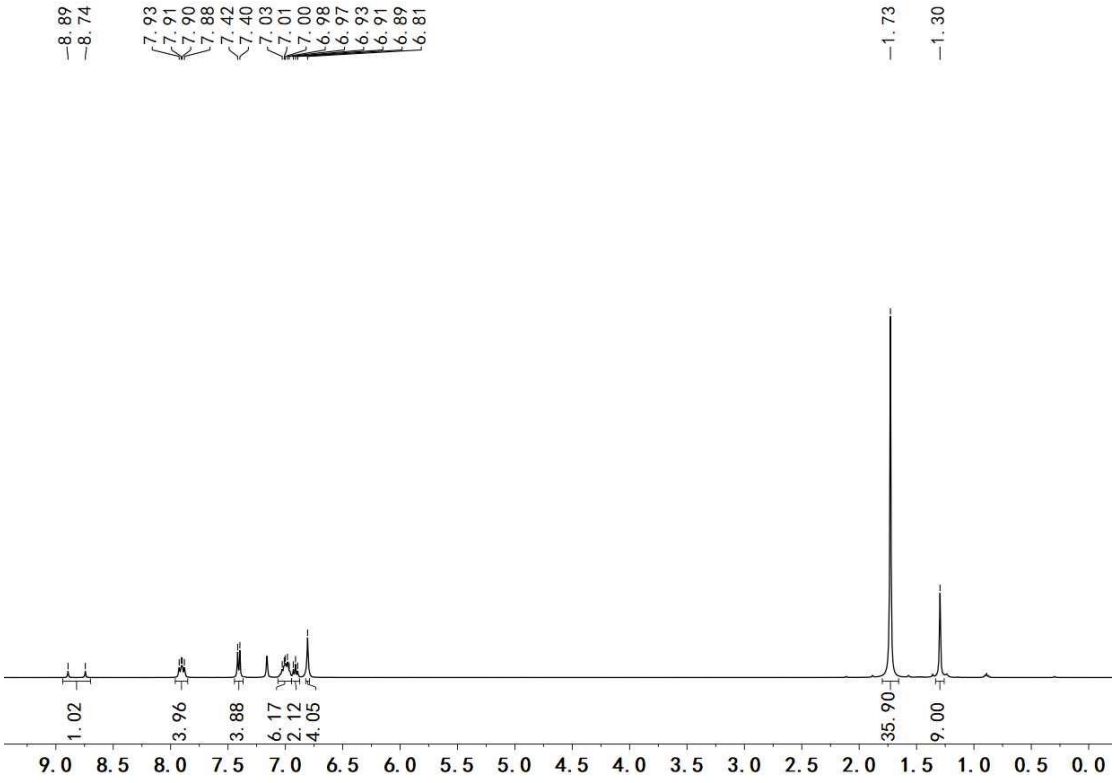


Fig. S13. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

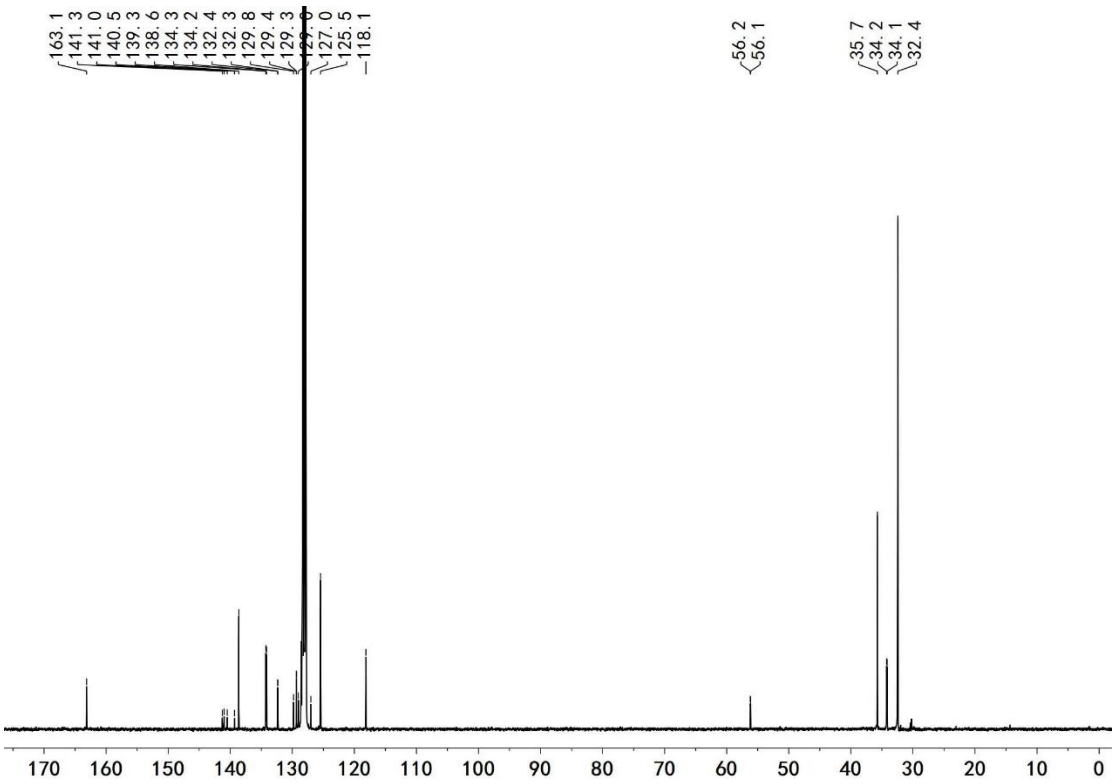


Fig. S14. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

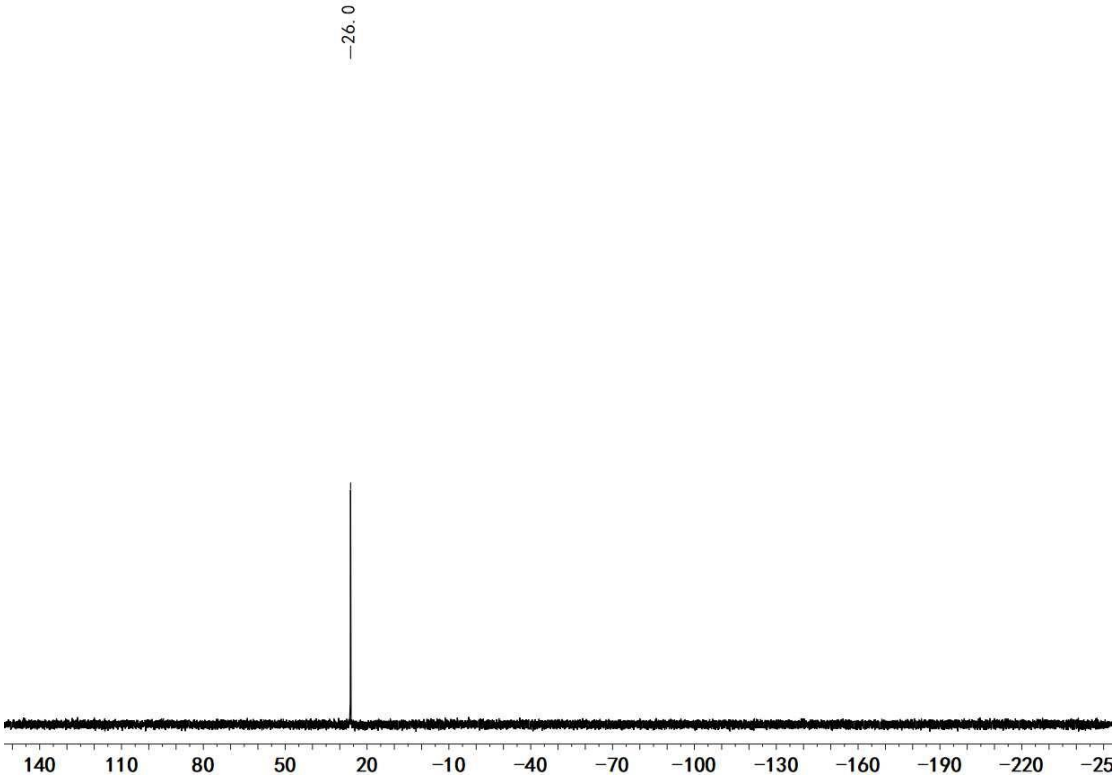


Fig. S15. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 5: formula $C_{52}H_{67}NO_2PSc$, M = 813.99 $gmol^{-1}$, colorless, 0.20 × 0.17 × 0.15 mm, monoclinic, space group *C2/c*, a = 41.923(3),

b = 10.2466(5), c = 22.4660(12) Å, α = 90°, β = 98.649(5)°, γ = 90°, V = 9541.0(9) Å^3, ρ_{calc} = 1.133 gcm^{-3}, μ = 1.279 mm^{-1}, Z = 8, λ = 1.34138 Å, T = 120.0 K, 60208 reflections collected (-49 ≤ h ≤ 50, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27), 8780 independent (R_{int} = 0.1128) and 5507 observed reflections [I>2σ(I)], 533 refined parameters, the final R_1 was 0.0569 [I>2σ(I)] and wR_2 was 0.1493 (all data), max. (min.) residual electron density 0.32 (-0.46) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

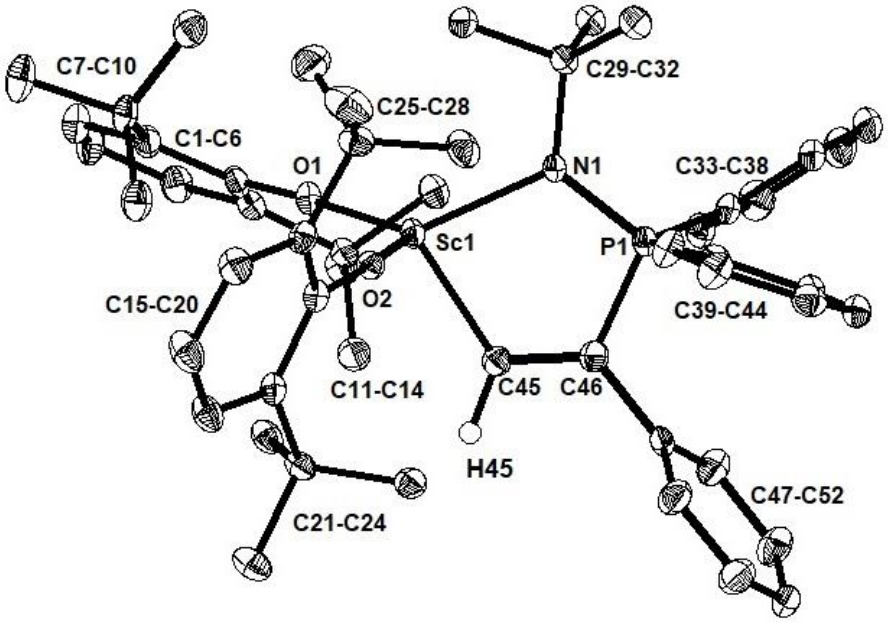
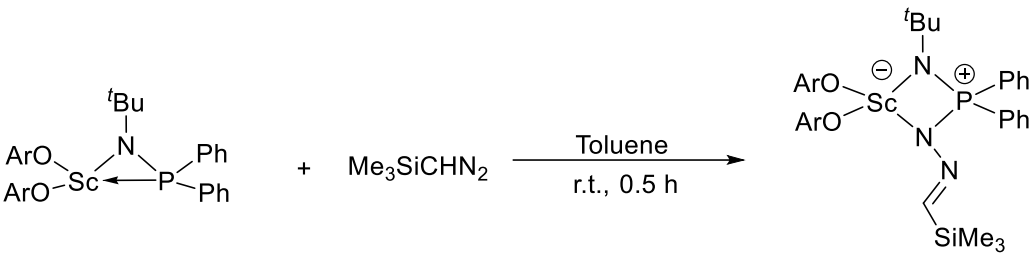


Fig. S16. Molecular structure of complex **5**.

Preparation of complex 6



1 Ar = 2,6-^{t}Bu$_2$-C$_6$H$_3$ **6**

Scheme S5.

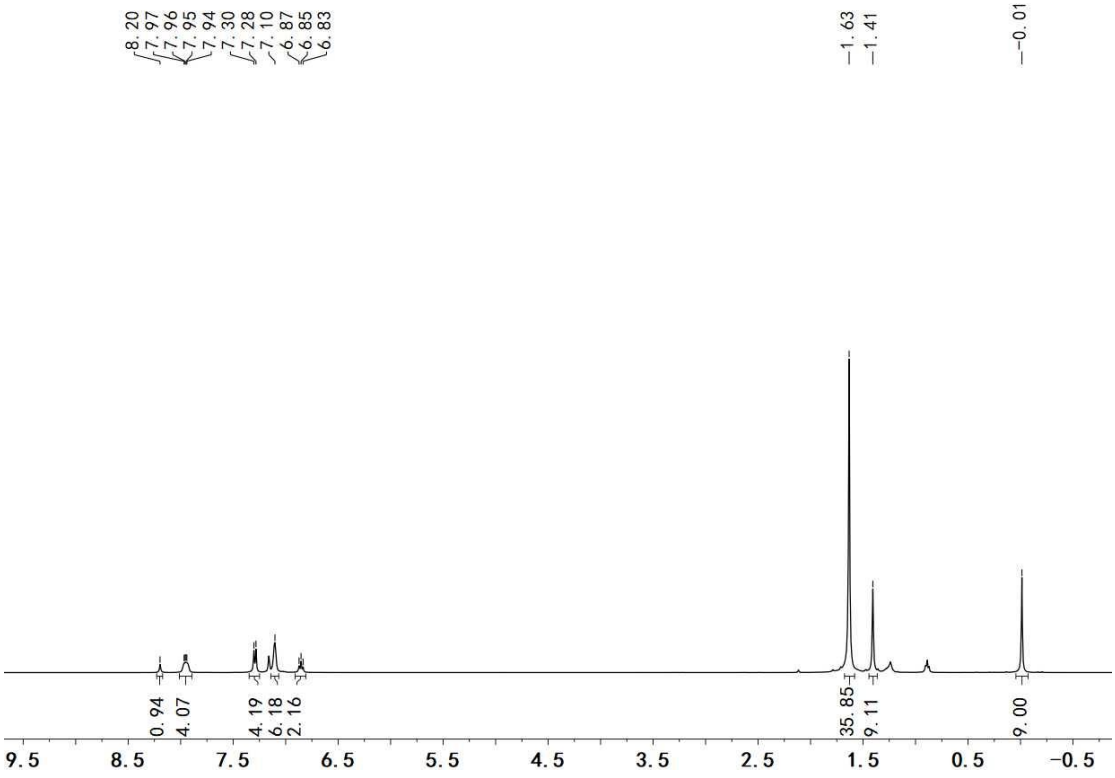


Fig. S17. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

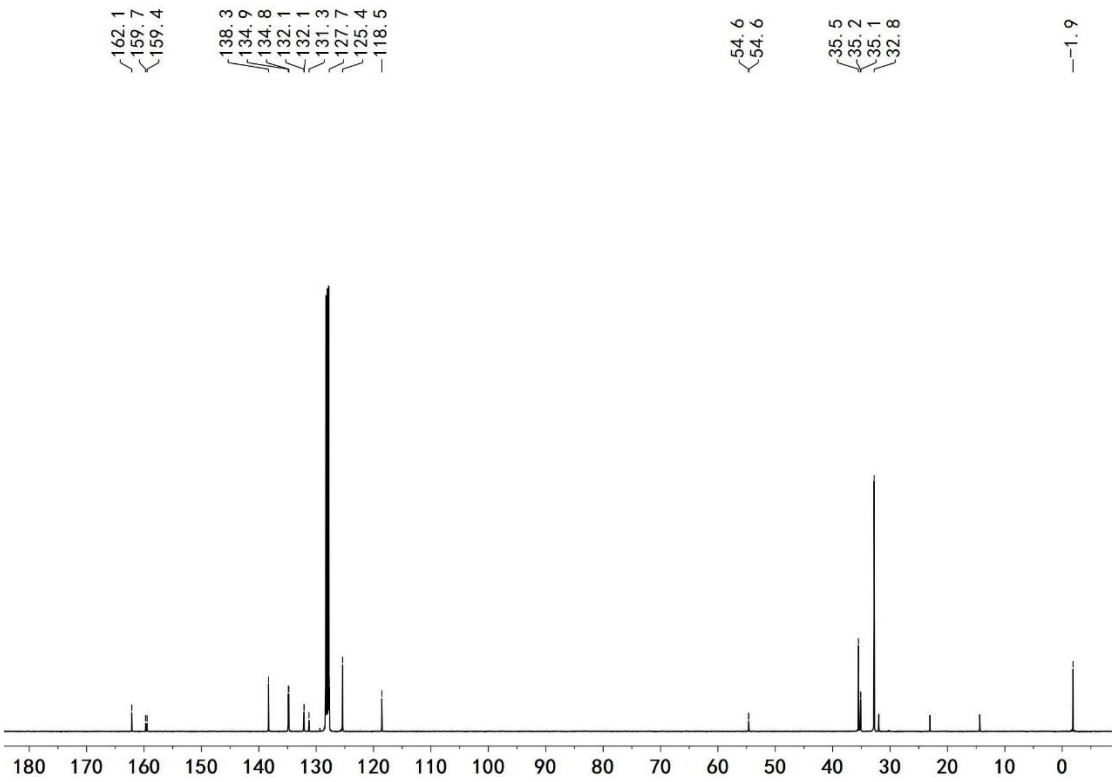


Fig. S18. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

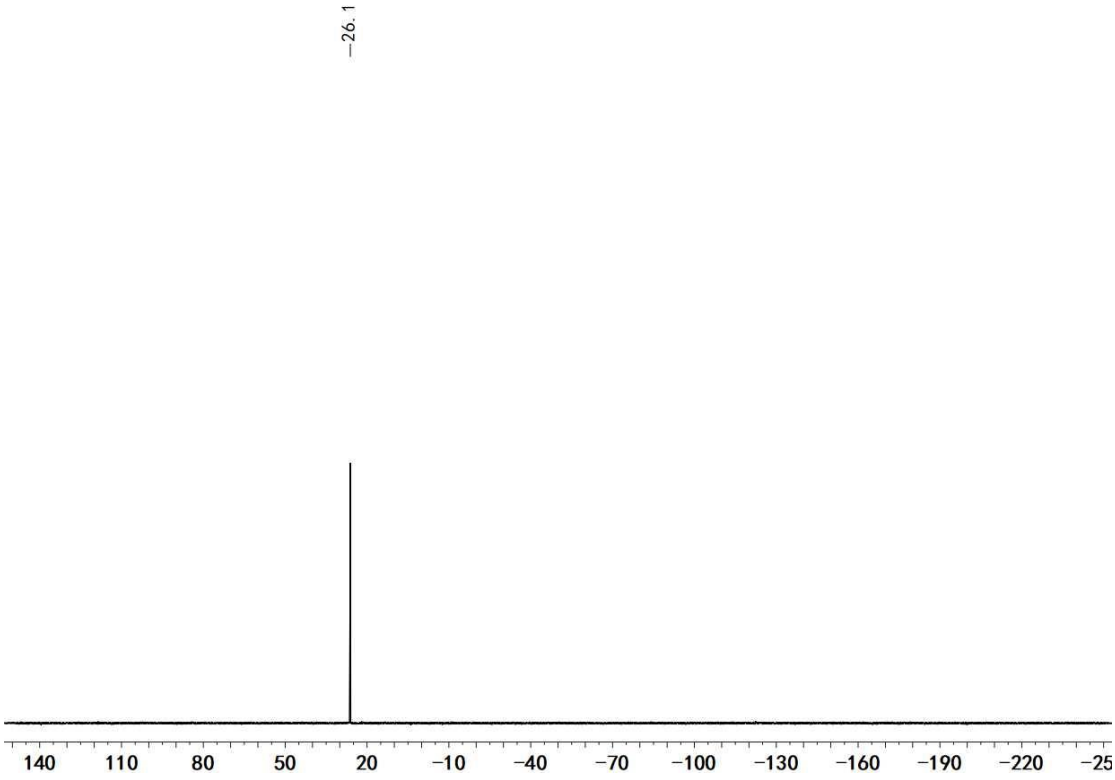


Fig. S19. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 6: formula $C_{48}H_{71}N_3O_2PScSi \cdot 0.5C_7H_8$, M = 872.16 gmol^{-1}, colorless, 0.17 × 0.16 × 0.15 mm, triclinic, space group P_{-1}, a =

11.2343(5), b = 11.7686(6), c = 21.1672(10) Å, α = 78.026(2)°, β = 78.416(2)°, γ = 68.270(2)°, V = 2519.3(2) Å^3, ρ_{calc} = 1.150 gcm^{-3}, μ = 1.381 mm^{-1}, empirical absorption correction (0.6409 ≤ T ≤ 0.7506, Z = 2, λ = 1.34138 Å, T = 120.0 K, 85193 reflections collected (-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25), 9302 independent (R_{int} = 0.0881) and 6625 observed reflections [I>2σ(I)], 588 refined parameters, the final R_1 was 0.0490 [I>2σ(I)] and wR_2 was 0.1287 (all data), max. (min.) residual electron density 0.33 (-0.41) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

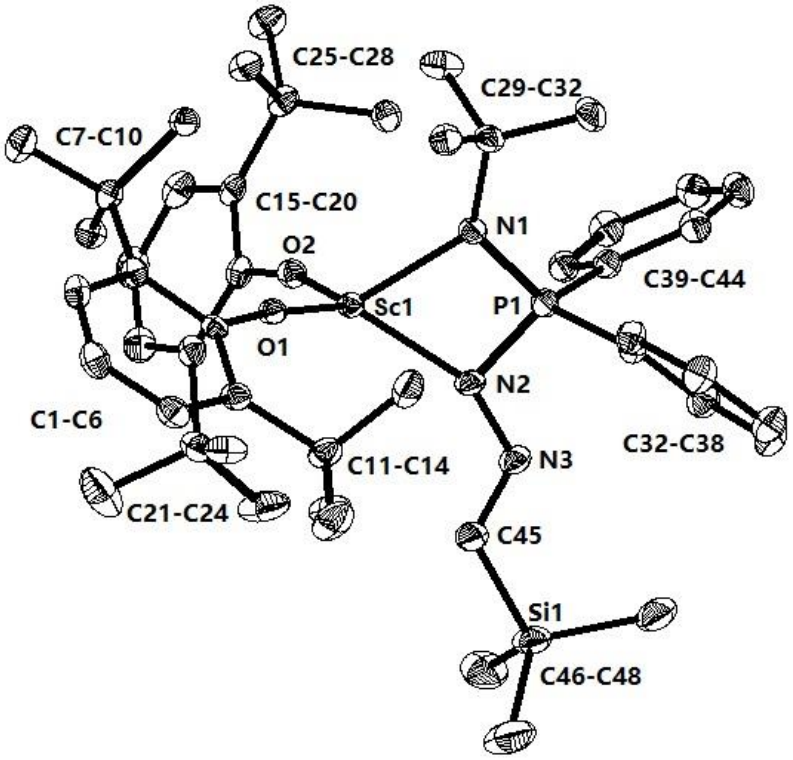
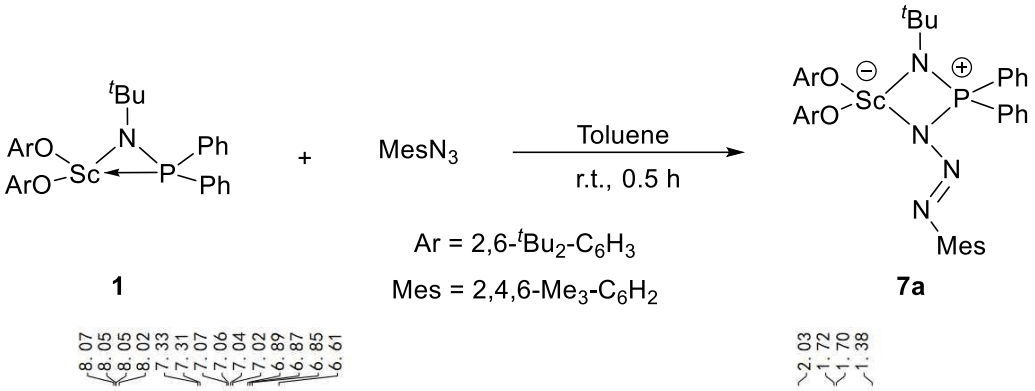


Fig. S20. Molecular structure of complex **6**.

Preparation of complex 7a



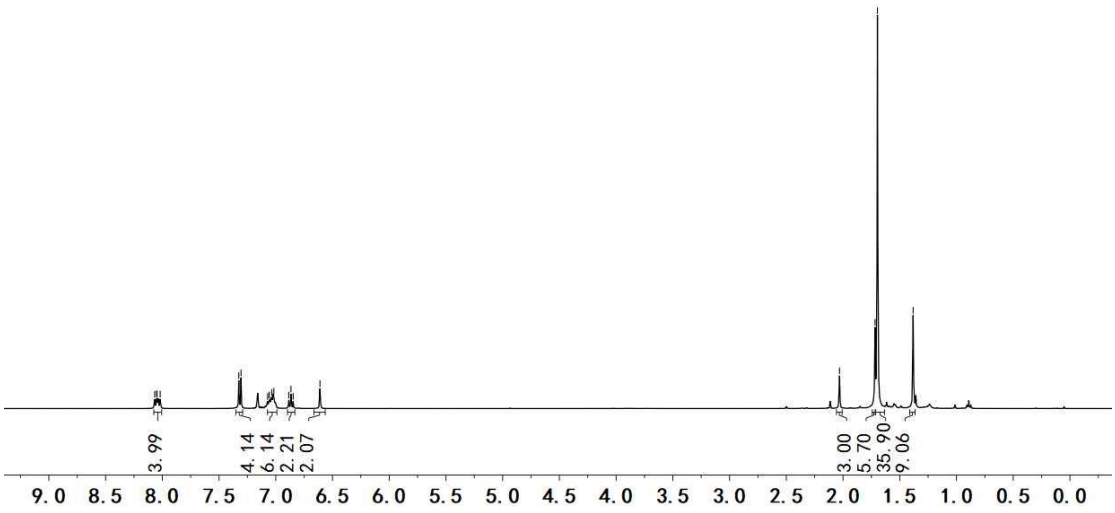


Fig. S21. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

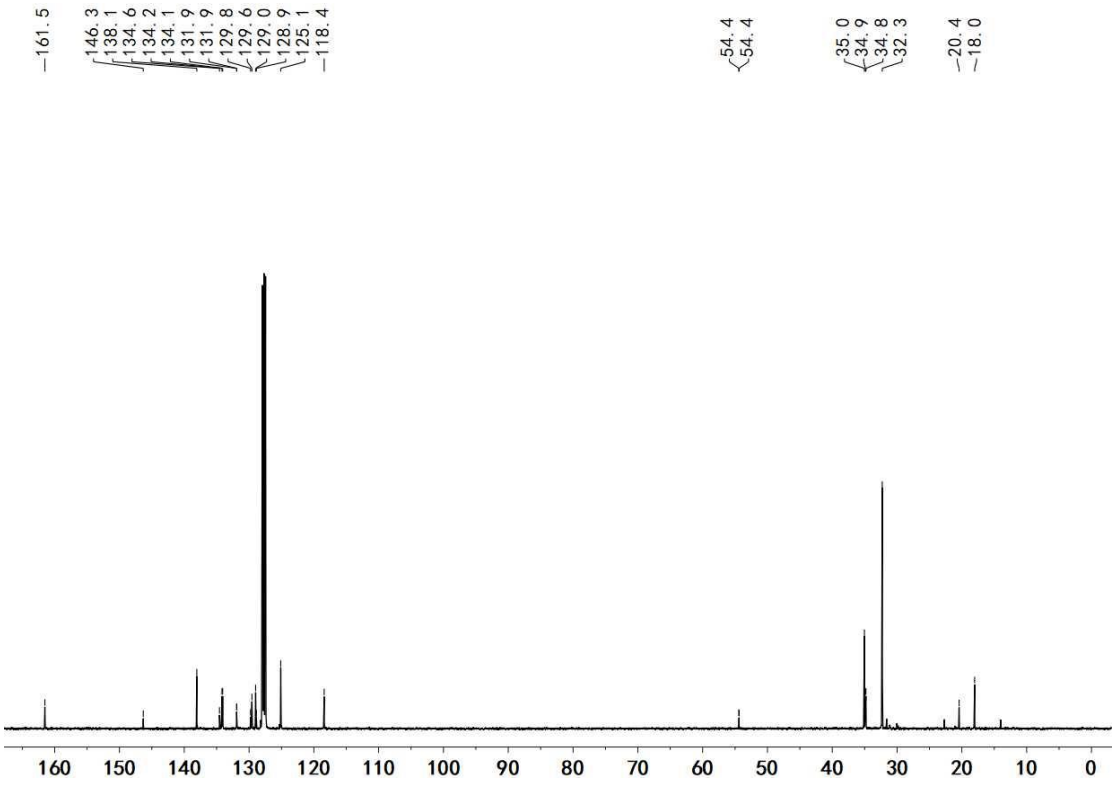


Fig. S22. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

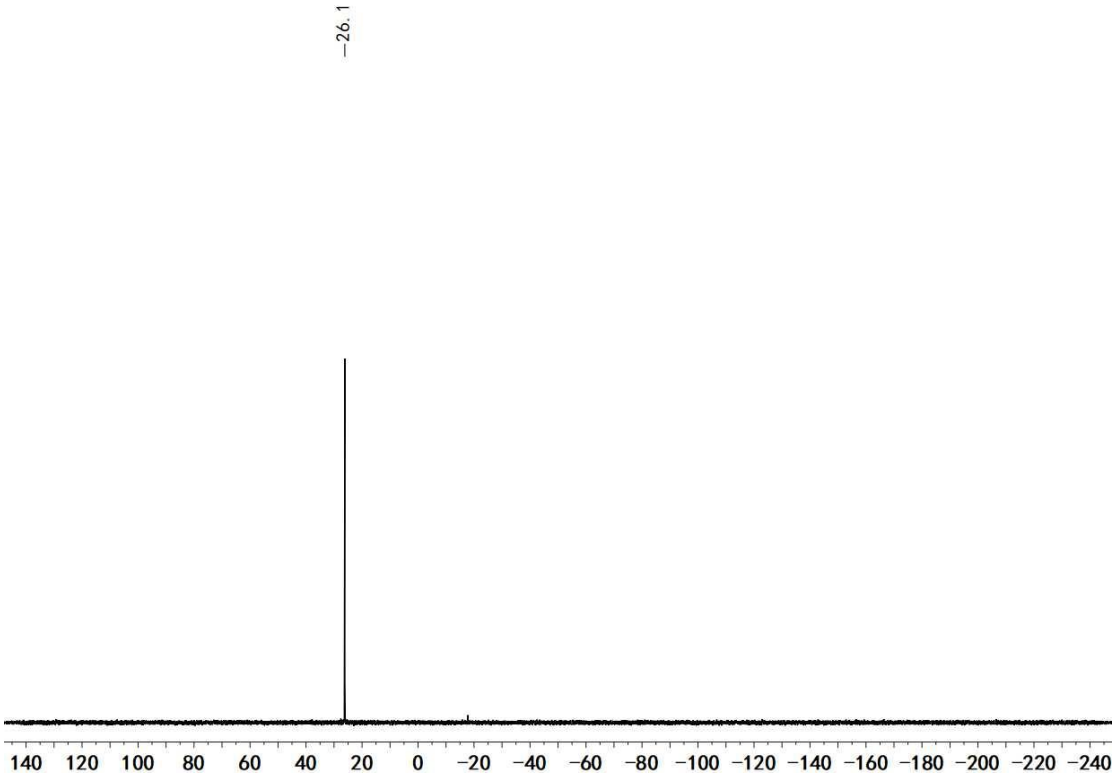


Fig. S23. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 7a: formula $C_{53}H_{72}N_4O_2PSc$, $M = 873.07$ gmol^{-1}, colorless, 0.18 × 0.16 × 0.15 mm, monoclinic, space group $P2_1$, $a = 10.1260(5)$,

b = 22.6532(11), c = 21.7871(11) Å, α = 90°, β = 101.164(2)°, γ = 90°, V = 4903.1(4) Å^3, ρ_{calc} = 1.183 gcm^{-3}, μ = 1.276 mm^{-1}, empirical absorption correction (0.6366 ⩽ T ⩽ 0.7506), Z = 4, λ = 1.34138 Å, T = 120.0 K, 127635 reflections collected (-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -26 ≤ l ≤ 26), 18016 independent (R_{int} = 0.0900) and 13778 observed reflections [I>2σ(I)], 1136 refined parameters, the final R_1 was 0.0500 [I>2σ(I)] and wR_2 was 0.1257 (all data), max. (min.) residual electron density 0.31 (-0.60) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

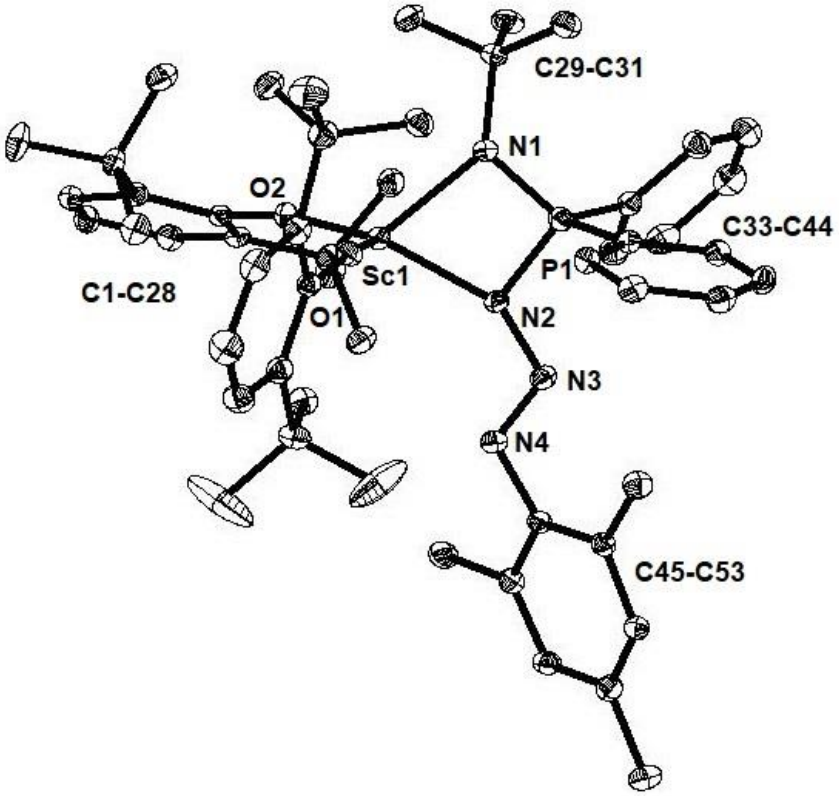
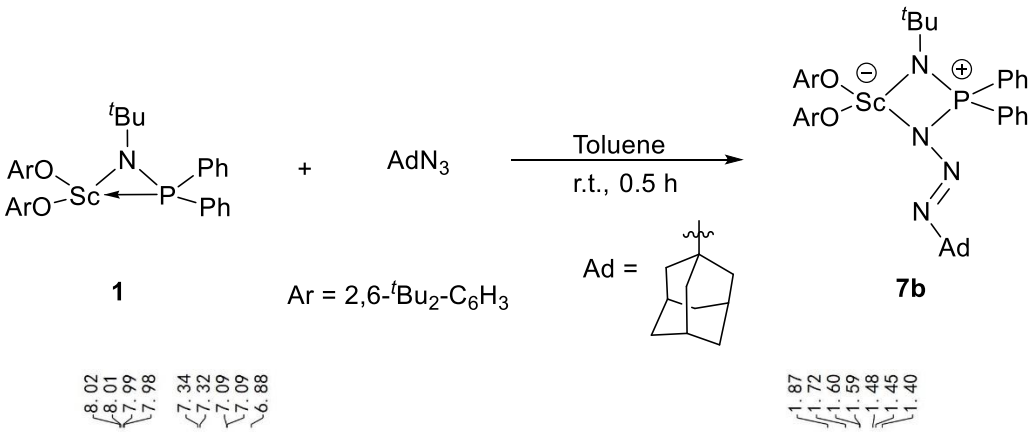


Fig. S24. Molecular structure of complex **7a**.

Preparation of complex 7b



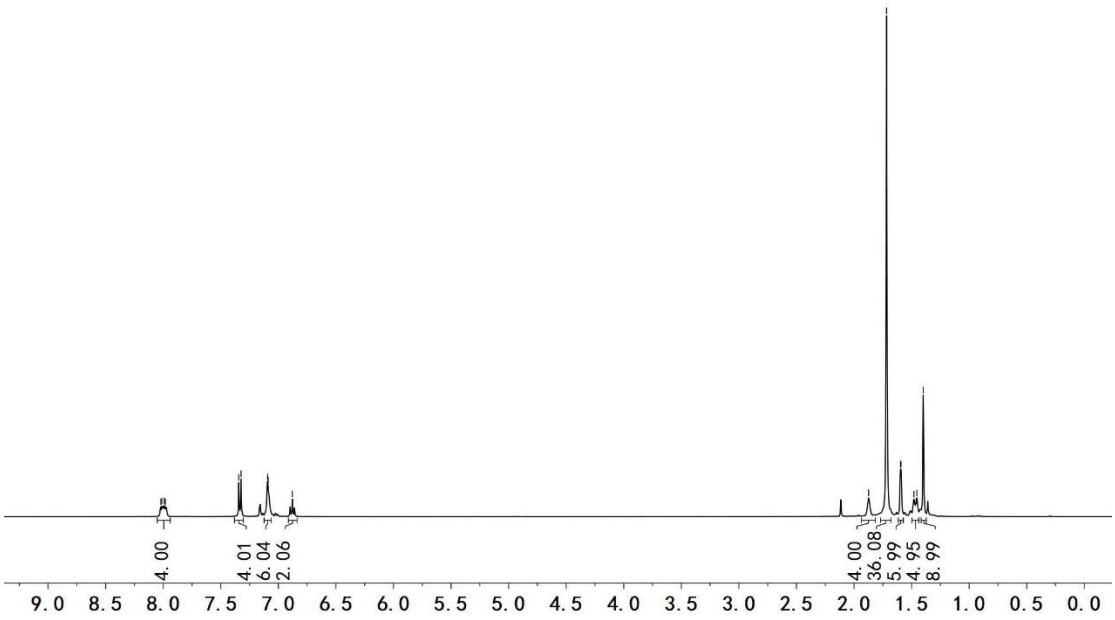


Fig. S25. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

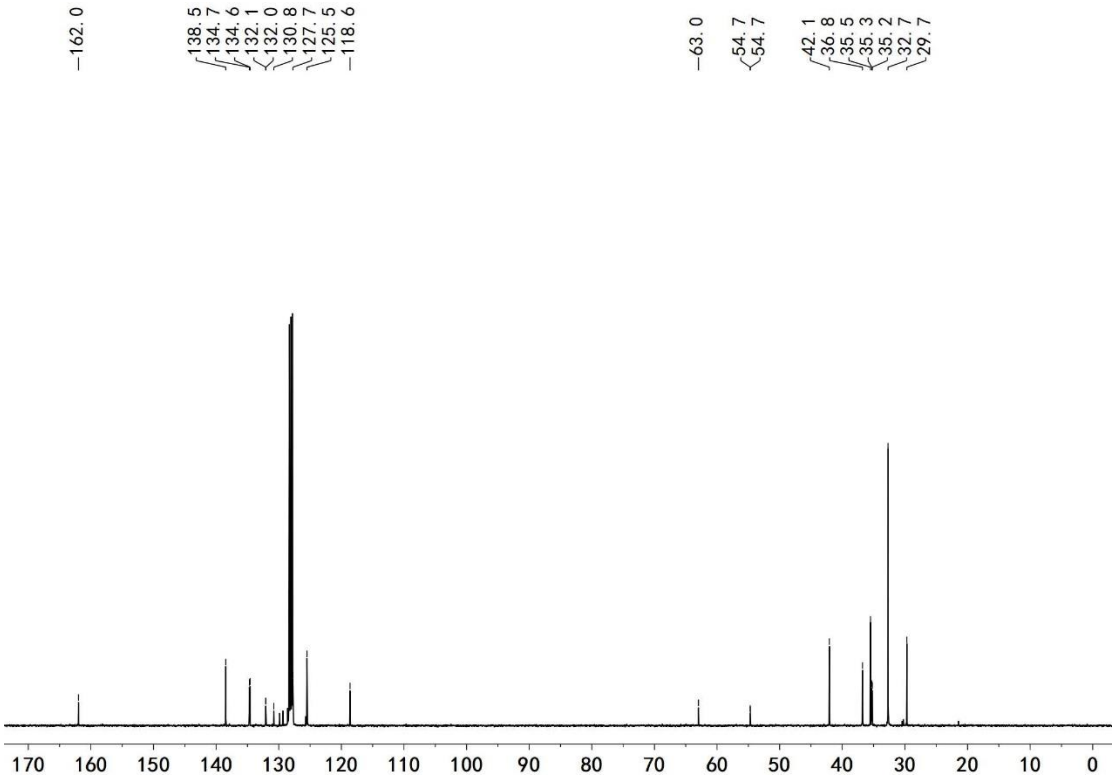


Fig. S26. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

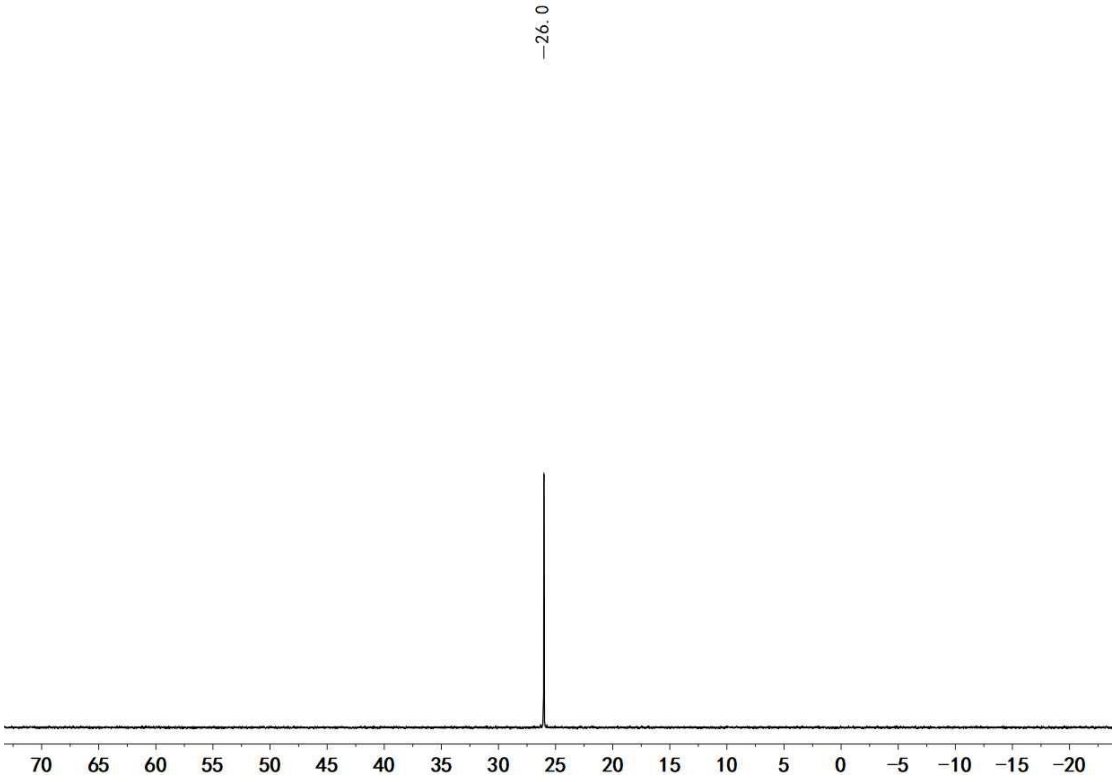


Fig. S27. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 7b: formula $C_{54}H_{76}N_4O_2PSc \cdot 0.5C_7H_8$, M = 935.18 gmol^{-1}, colorless, 0.16 × 0.15 × 0.14 mm, triclinic, space group $P\text{-}1$, a =

11.2256(5), b = 12.2433(6), c = 22.3628(9) Å, α = 92.103(2)°, β = 103.575(2)°, γ = 116.889(2)°, V = 2628.2(2) Å^3, ρ_{calc} = 1.182 gcm^{-3}, μ = 1.210 mm^{-1}, empirical absorption correction (0.6060 ≤ T ≤ 0.7506), Z = 2, λ = 1.34138 Å, T = 120.0 K, 51906 reflections collected (-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26), 9651 independent (R_{int} = 0.1029) and 6064 observed reflections [I>2σ(I)], 639 refined parameters, the final R_1 was 0.0648 [I>2σ(I)] and wR_2 was 0.1736 (all data), max. (min.) residual electron density 0.47 (-0.58) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

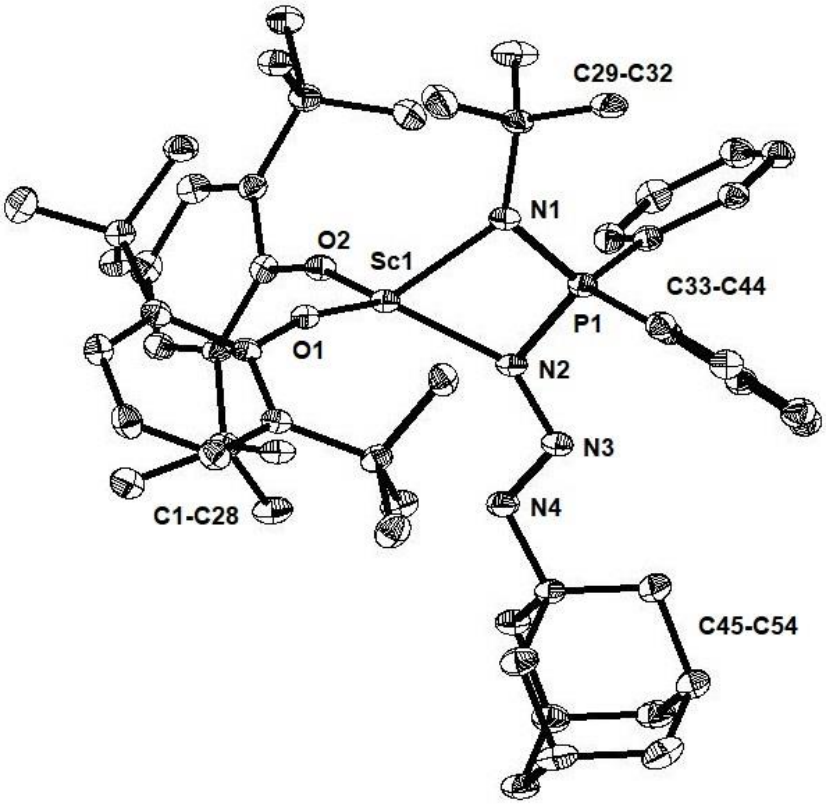
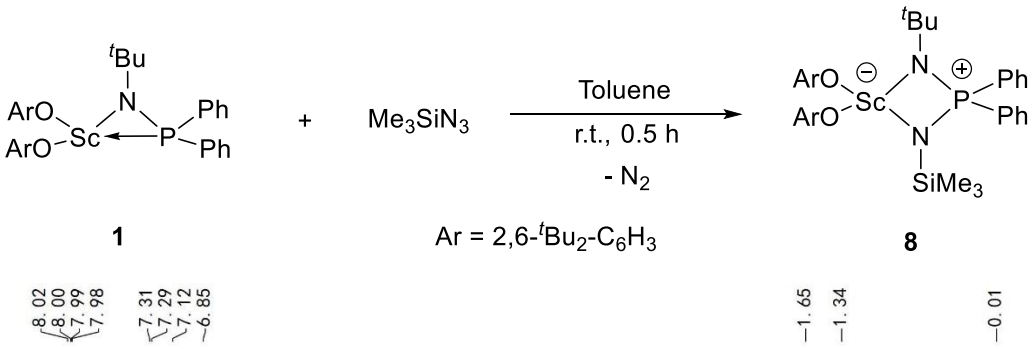


Fig. S28. Molecular structure of complex **7b**.

Preparation of complex 8



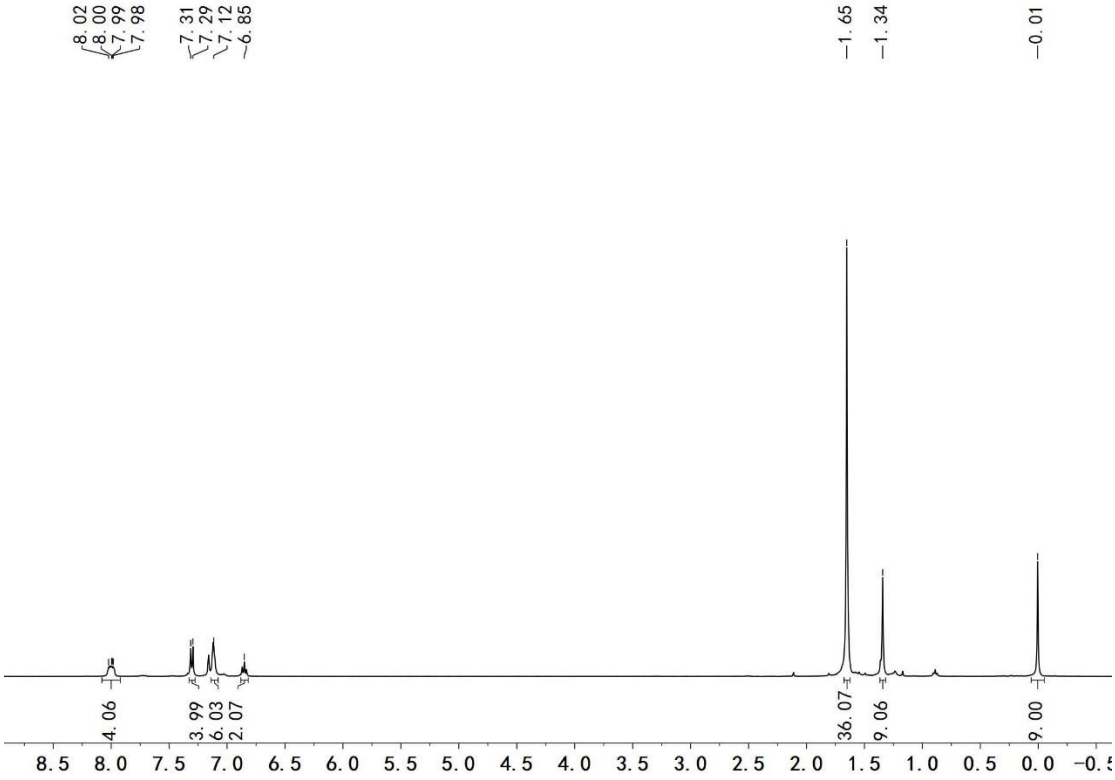


Fig. S29. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

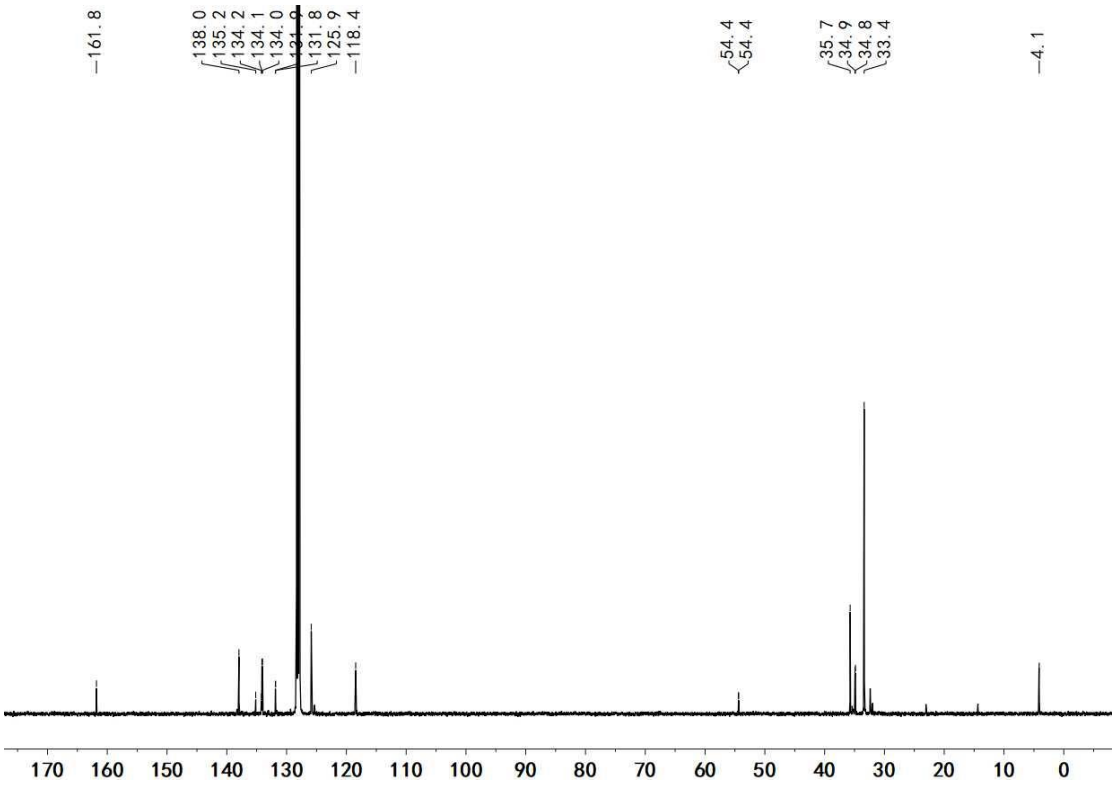


Fig. S30. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

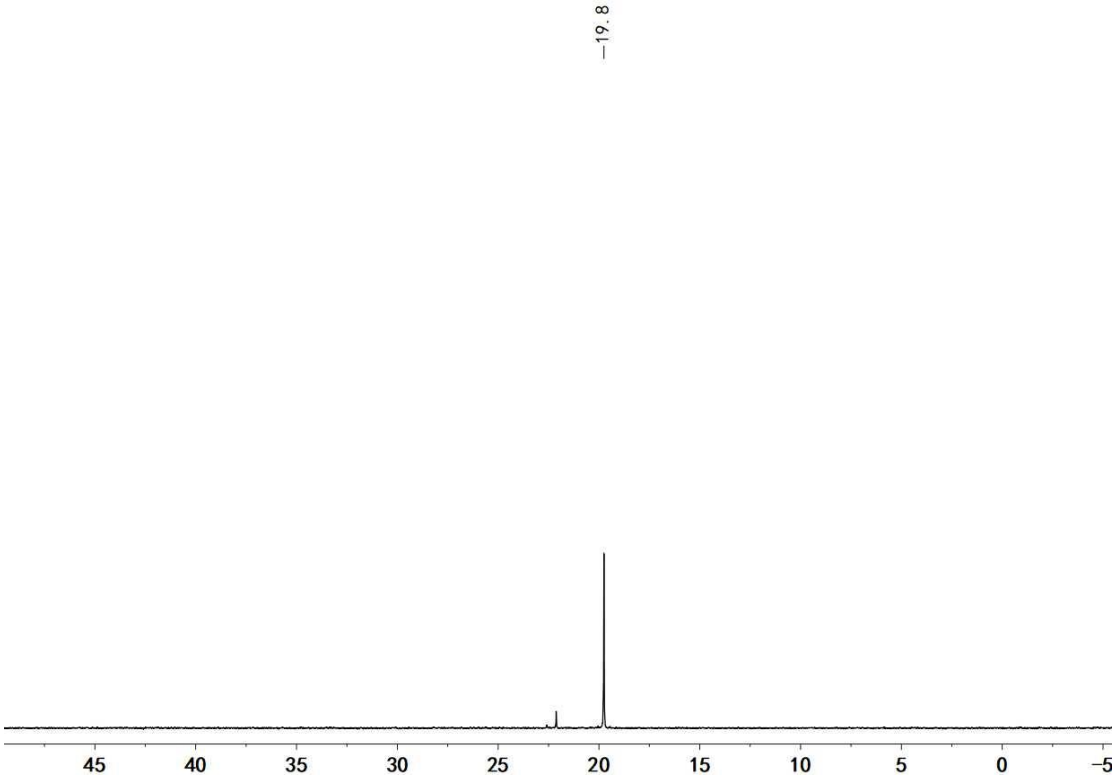


Fig. S31. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 8: formula $C_{47}H_{70}N_2O_2PScSi$, M = 799.07 gmol^{-1}, colorless, 0.18 × 0.16 × 0.15 mm, monoclinic, space group *C*2/*c*, a =

41.237(4), b = 10.5045(10), c = 21.735(2) Å, α = 90°, β = 102.852(4)°, γ = 90°, V = 9179.1(15) Å^3, ρ_{calc} = 1.156 gcm^{-3}, μ = 0.259 mm^{-1}, empirical absorption correction (0.6941 ≤ T ≤ 0.7455), Z = 8, λ = 0.71073 Å, T = 153 K, 66916 reflections collected (-53 ≤ h ≤ 53, -13 ≤ k ≤ 12, -28 ≤ l ≤ 28), 10545 independent (R_{int} = 0.1396) and 5811 observed reflections [I>2σ(I)], 505 refined parameters, the final R_1 was 0.0627 [I>2σ(I)] and wR_2 was 0.1349 (all data), max. (min.) residual electron density 0.54 (-0.42) e Å^{-3}, hydrogen atoms were placed in calculated positions and refined using a riding model.

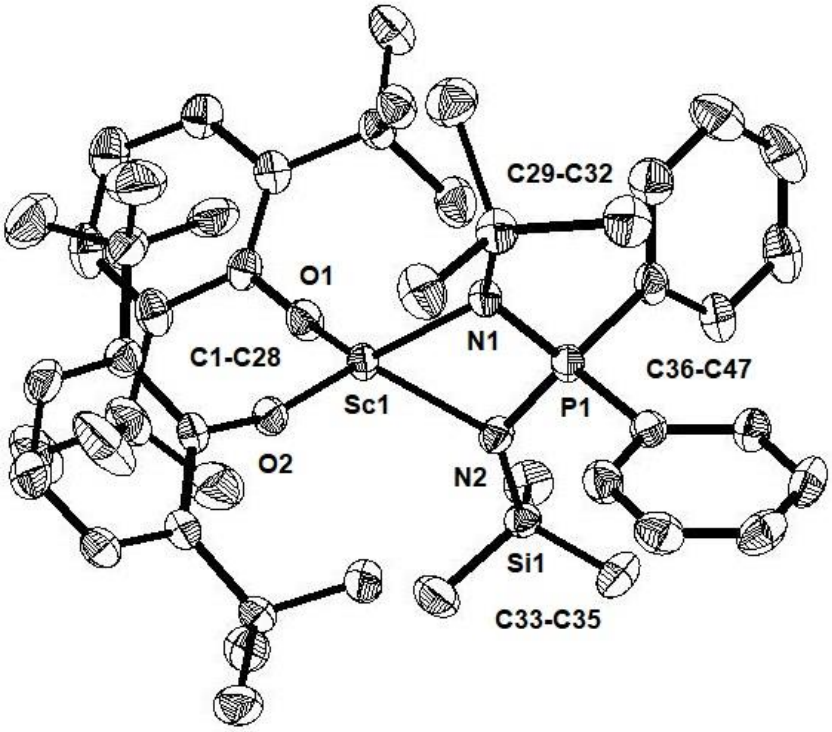


Fig. S32. Molecular structure of complex **8**.