Supporting Information

Reactions of neutral scandium/phosphorus Lewis pairs with small molecules

Kejian Chang, Xiaoming Wang, Zhengning Fan, Xin Xu*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China.

*E-mail: xinxu@suda.edu.cn

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. 2,6-di-*t*ert-butylphenol and $(Ph_3P)AuCl$ were purchased from ACROS and Strem Chemical, respectively. 1-(Di-*t*ert-butylphosphanyl)-2-methylpropan-2-ol[1], 1,3-diphenyl-2-propyn-1-one[2], 1,5-diphenylpenta-2,4-dien-1-one[3], $Sc[CH_2SiMe_3][O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3]_2[THF]$[4] and complex **6**[4] were synthesized by following the literature procedures.

X-ray structure analyses: For the complexes **10** and **17** one toluene molecule was found disordered over two positions in asymmetric unit. Several restraints (FLAT, EADP, DANG and DFIX) were used to improve refinement stability. For the complex **14** two hexane molecules were found badly disordered over two positions in asymmetric unit. The program SQUEEZE was therefore used to remove mathematically the effect of the solvent. For the complex **16** one toluene molecule and one hexane molecule were found badly disordered over two positions in asymmetric unit. The program SQUEEZE was therefore used to remove mathematically the effect of the solvent.

References:

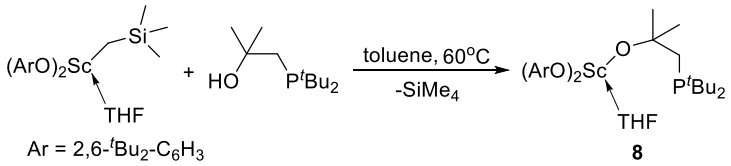
[1] Chapman, A. M.; Haddow, M. F.; Orton, J. P. H.; Wass, D. F. Facile dihydrogen release from phosphino-borinate ester Lewis pairs. *Dalton Trans*. **2010**, *39*, 6184-6186.

[2] Palimkar, S. S.; Kumar, P. H.; Jogdand, N. R.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. Copper-, ligand- and solvent-free synthesis of ynones by coupling acid chlorides with terminal alkynes. *Tetrahedron Lett*. **2006**, *47*, 5527-5530.

[3] Ma, Z.; Xie, F.; Yu, H.; Zhang, Y.; Wu, X.; Zhang, W. Copper-catalyzed asymmetric1,4-conjugate addition of Grignard reagents to linear α, β, γ, δ -unsaturated ketones. *Chem. Commun*., **2013**, *49*, 5292-5294.

[4] Chang, K.; Xu, X. Frustrated Lewis pair behavior of a neutral scandium complex. *Dalton Trans*. **2017**, *46*, 4514-4517.

Characterization of complex 8:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.33 / 6.85 (*m*-O*Ar* / *p*-O*Ar*), 3.93 / 1.17 (*α*-CH_2^{THF} / *β*-CH_2^{THF}).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.33 / 125.6 (*m*-O*Ar*), 6.85 / 118.0 (*p*-O*Ar*), 3.93 / 73.5 (*α*-CH_2^{THF}), 1.94 / 38.5 (P*C*H_2), 1.63 / 32.1 (C(*C*H_3)$_3$), 1.49 / 33.1 (OC(*C*H_3)$_2$), 1.19 / 30.8 (P(C(*C*H_3)$_3$)$_2$), 1.17 / 24.8 (*β*-CH_2^{THF}).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.33 / 161.6, 125.6, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.85 / 138.1 (*p*-O*Ar* / *o*-O*Ar*), 1.94 / 78.6, 33.1 (P*C*H_2 / O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.63 / 138.1, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.49 / 78.6, 38.5 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$), 1.19 / 31.8 (P(C(C*H*$_3$)$_3$)$_2$ / P(*C*(CH$_3$)$_3$)$_2$).

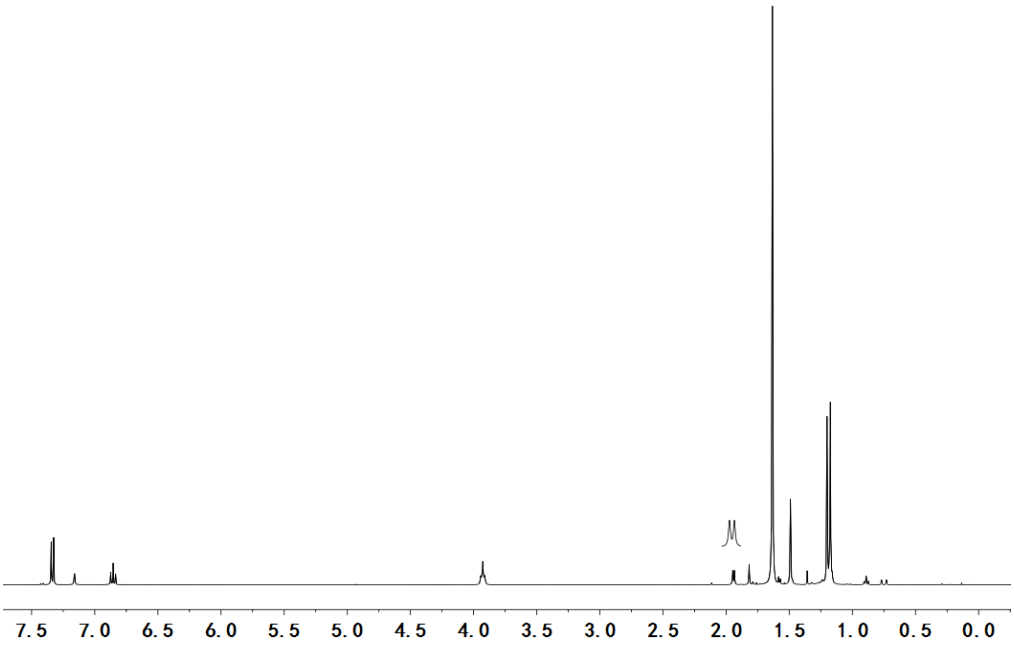


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

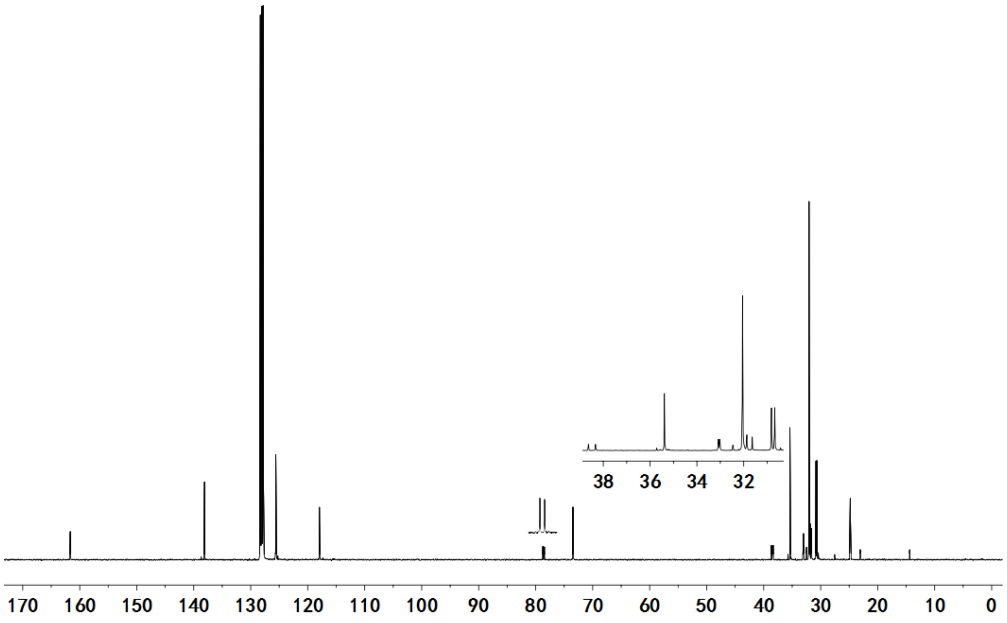


Fig. S2. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K).

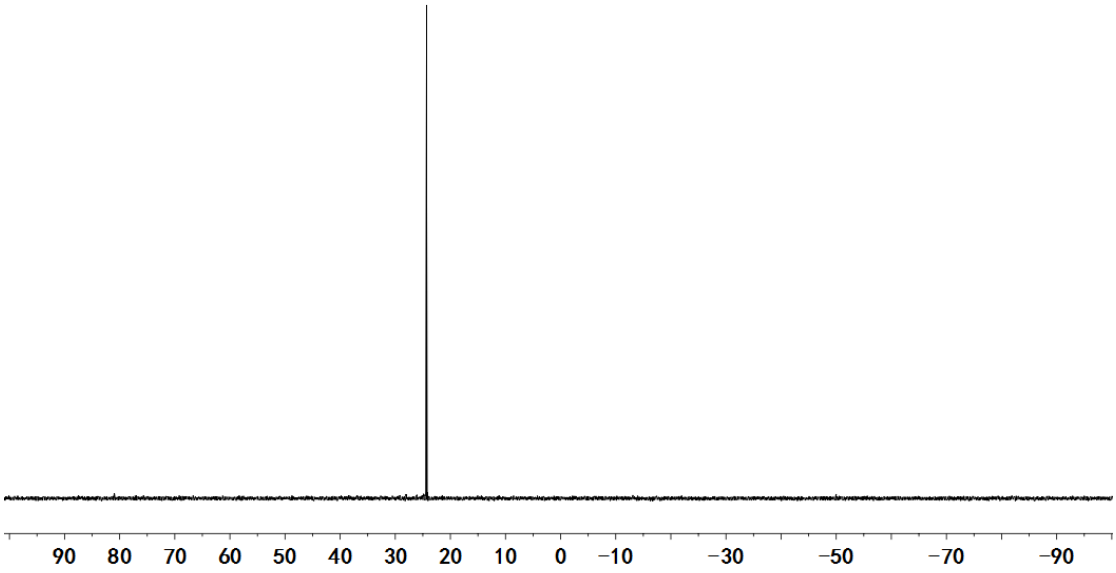


Fig. S3. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K).

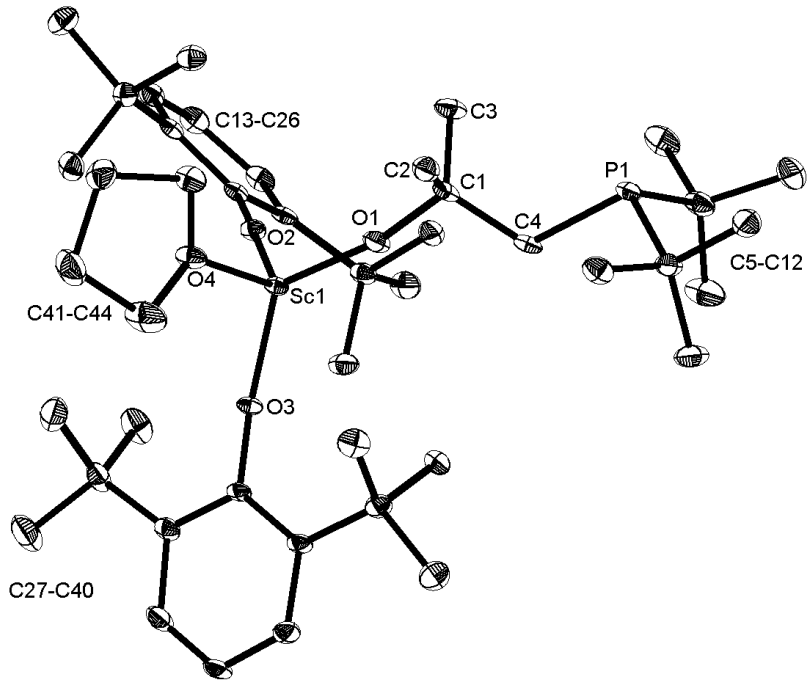
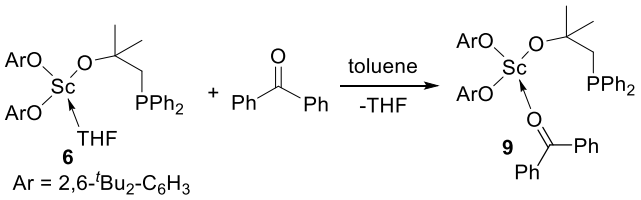


Fig. S4. Crystal structure of complex **8**.

X-ray crystal structure analysis of complex 8: formula $C_{44}H_{76}O_4PSc$, M = 744.98, colourless crystal, 0.30 x 0.20 x 0.15 mm, a = 11.4066(9), b = 28.786(2), c = 13.6171(11) Å, β = 102.315(3)°, V = 4368.3(6) Å^3, ρ_{calc} = 1.133 gcm^{-3}, μ = 0.243 mm^{-1}, empirical absorption correction (0.930 ≤ T ≤ 0.964), Z = 4, monoclinic, space group P 21/n, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 62342 reflections collected (±h, ±k, ±l), 8218 independent (R(int) = 0.0898) and 6237 observed reflections [I>2σ(I)], 471 refined parameters, R = 0.0583, wR^2 = 0.1611, max. (min.) residual electron density 1.307 (-0.611) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 9:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.74 / 6.92 (*o*-Ph_2C / *m*-Ph_2C), 7.37 / 6.88 (*m*-O*Ar* / *p*-O*Ar*), 7.33 / 7.00 (*o*-Ph_2P / *m*-Ph_2P).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.74 / 133.1 (*o*-Ph_2C), 7.37 / 125.4 (*m*-O*Ar*), 7.33 / 133.3 (*o*-Ph_2P), 7.08 / 135.7 (*p*-Ph_2C), 7.00 / 128.5 (*m*-Ph_2P), 6.99 / 128.4 (*p*-Ph_2P), 6.92 / 128.8 (*m*-Ph_2C), 6.88 / 117.7 (*p*-O*Ar*), 2.56 / 47.4 (P*C*H_2), 1.66 / 32.1 (C(*C*H_3)$_3$), 1.40 / 33.0 (OC(*C*H_3)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.74 / 207.8, 133.1 (*o*-Ph_2C / *C*=O, *o*-Ph_2C), 7.37 / 162.5, 125.4, 35.5 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.33 / 133.3, 128.4 (*o*-Ph_2P / *o*-Ph_2P, *p*-Ph_2P), 7.08 / 133.1 (*p*-Ph_2C / *o*-Ph_2C), 7.00 / 141.1, 128.5 (*m*-Ph_2P / *i*-Ph_2P, *m*-Ph_2P), 6.92 / 138.4, 128.8 (*m*-Ph_2C / *i*-Ph_2C, *m*-Ph_2C), 6.88 / 138.6 (*p*-O*Ar* / *o*-O*Ar*), 2.56 / 141.1, 77.7, 33.0 (PCH_2 / *i*-Ph_2P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.66 / 138.6, 35.5 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.40 / 77.7, 47.4 (OC(CH_3)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

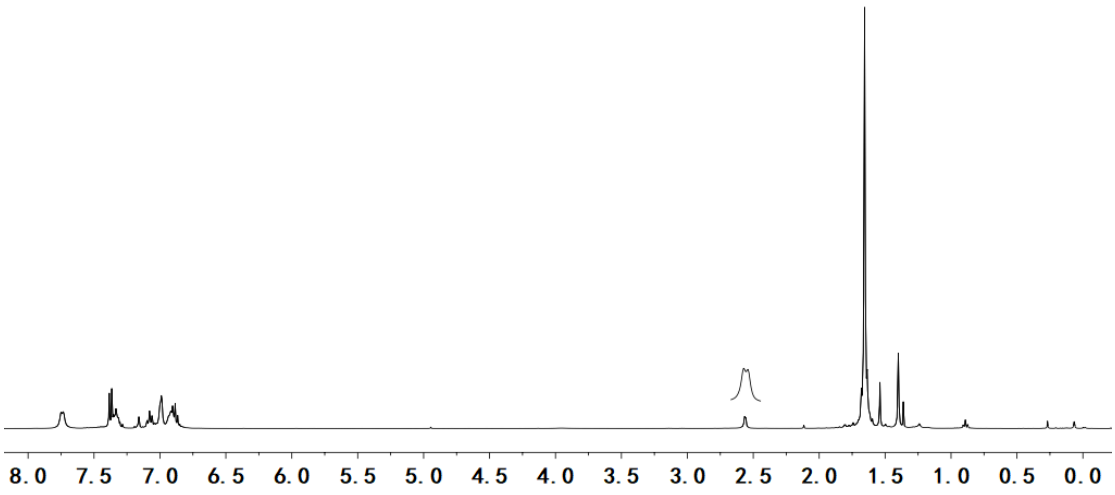


Fig. S5. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

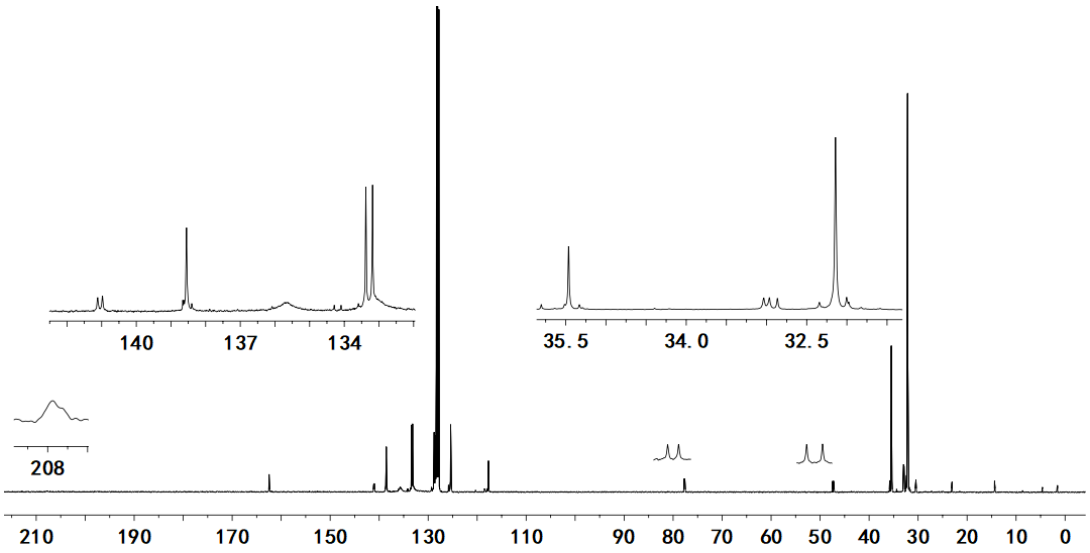


Fig. S6. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

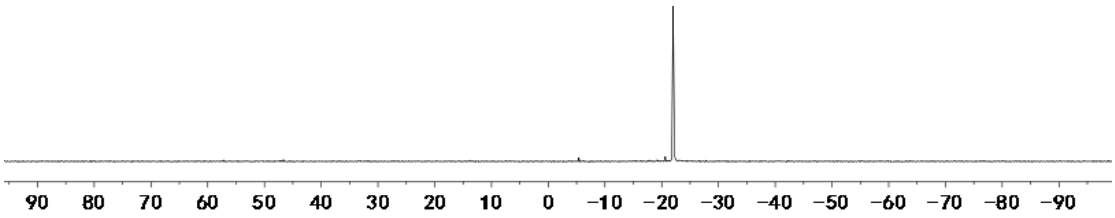
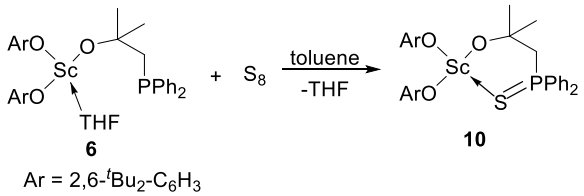


Fig. S7. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

Characterization of complex 10:



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

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.48 / 6.91 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.35 / 6.86 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.48 / 131.6 (*o*-*Ph*$_2$P), 7.35 / 125.2 (*m*-O*Ar*), 6.98 / 132.6 (*p*-*Ph*$_2$P), 6.91 / 129.1 (*m*-*Ph*$_2$P), 6.86 / 117.8 (*p*-O*Ar*), 2.75 / 46.3 (P*C*H$_2$), 1.70 / 31.9 (C(*C*H$_3$)$_3$), 1.09 / 34.0 (OC(*C*H$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.48 / 132.6 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.35 / 162.4, 125.2, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.98 / 131.6 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P), 6.91 / 129.7 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 6.86 / 138.4 (*p*-O*Ar* / *o*-O*Ar*), 2.75 / 129.7, 75.5, 34.0 (P*C*H$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.70 / 138.4, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.09 / 75.5, 46.3 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

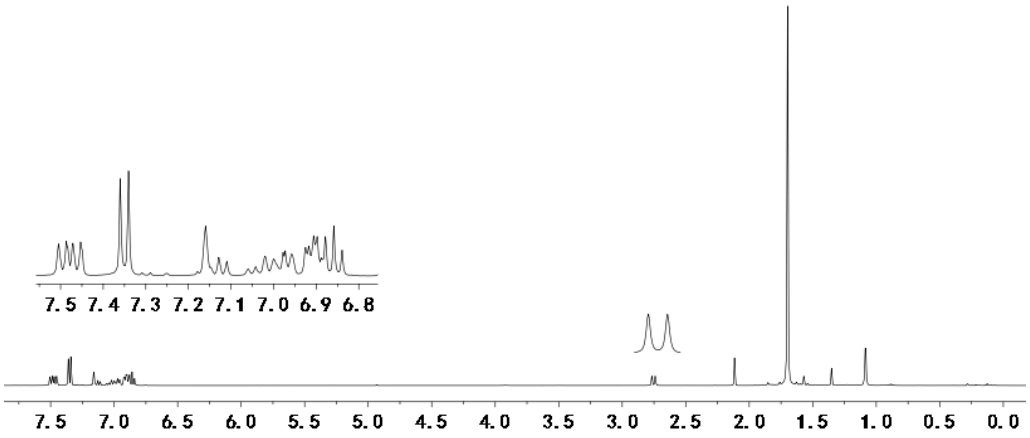


Fig. S8. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

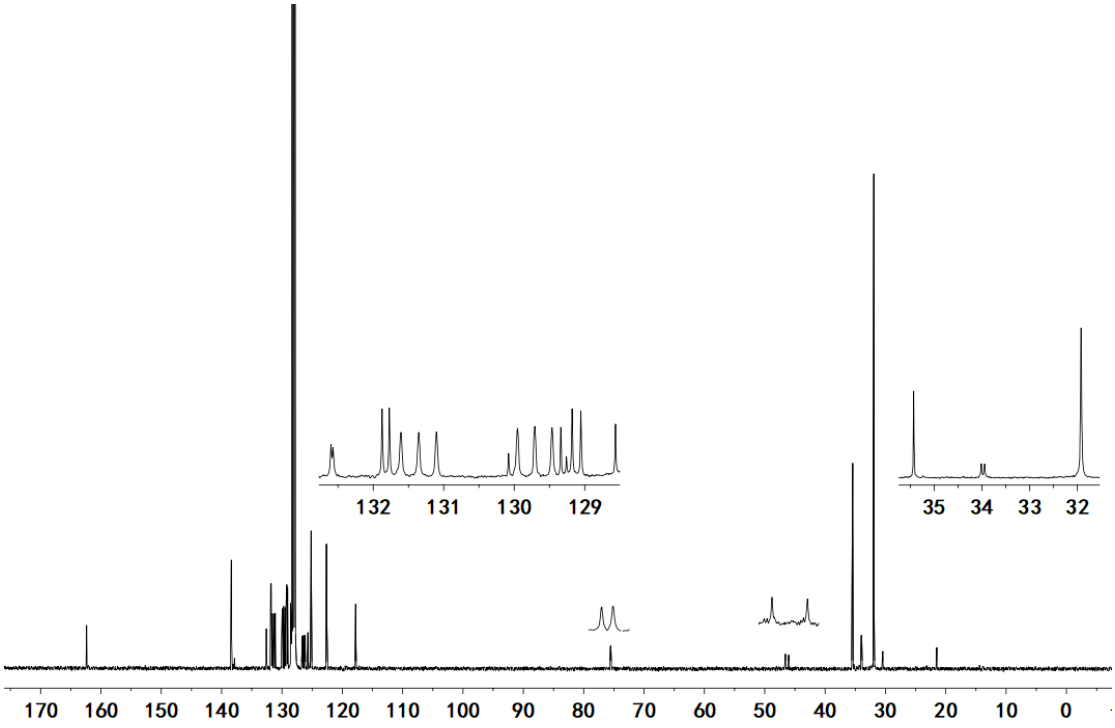


Fig. S9. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

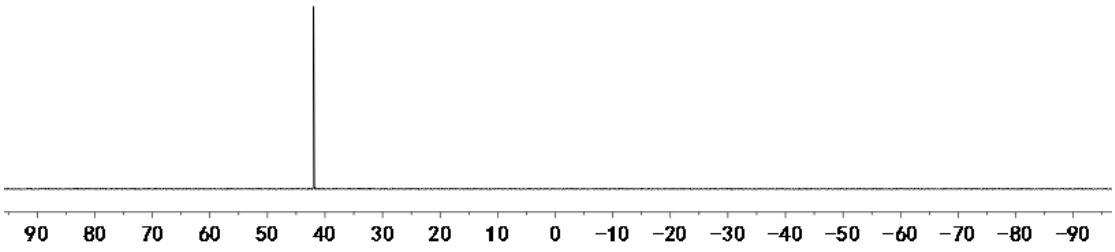


Fig. S10. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

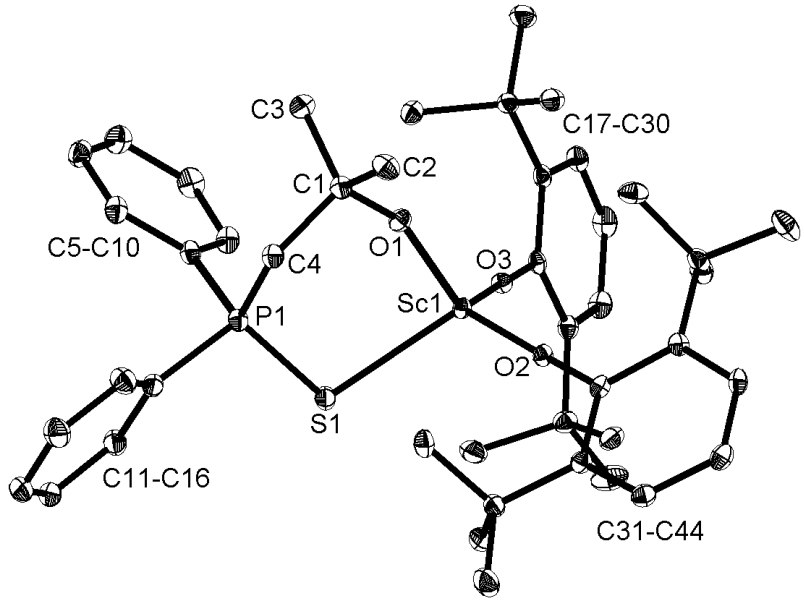
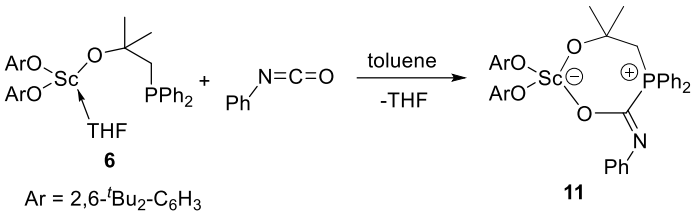


Fig. S11. Crystal structure of complex **10**.

X-ray crystal structure analysis of complex 10: formula $C_{44}H_{60}O_3PSSc$, M = 744.91, colourless crystal, 0.15 x 0.13 x 0.10 mm, a = 11.0399(6), b = 11.7385(6), c = 17.7361(10) Å, β = 91.6395(19) °, V = 2085.3(2) Å^3, ρ_{calc} = 1.186 gcm^{-3}, μ = 0.301 mm^{-1}, empirical absorption correction ($0.956 \leq T \leq 0.970$), Z = 2, triclinic, space group P -1, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 79005 reflections collected ($\pm h$, $\pm k$, $\pm l$), 9618 independent (R(int) = 0.0617) and 7426 observed reflections [$I>2\sigma(I)$], 465 refined parameters, R = 0.0357, wR^2 = 0.1004, max. (min.) residual electron density 0.321 (-0.353) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 11:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.49 / 7.13 (*o*-N*Ph* / *m*-N*Ph*), 7.38 / 6.88 (*m*-O*Ar* / *p*-O*Ar*), 7.36 / 6.89 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.49 / 124.8 (*o*-N*Ph*), 7.38 / 125.1 (*m*-O*Ar*), 7.36 / 133.5 (*o*-*Ph*$_2$P), 7.13 / 128.9 (*m*-N*Ph*), 6.99 / 133.4 (*p*-*Ph*$_2$P), 6.90 / 125.6 (*p*-N*Ph*), 6.89 / 129.4 (*m*-*Ph*$_2$P), 6.88 / 117.4 (*p*-O*Ar*), 2.92 / 43.8 (P*C*H$_2$), 1.67 / 31.8 (C(*C*H$_3$)$_3$), 1.09 / 34.3 (OC(*C*H$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.49 / 125.6 (*o*-N*Ph* / *p*-N*Ph*), 7.38 / 162.4, 125.1, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.36 / 133.5, 133.4 (*o*-*Ph*$_2$P / *o*-*Ph*$_2$P, *p*-*Ph*$_2$P), 7.13 / 146.3, 128.9 (*m*-N*Ph* / *i*-N*Ph*, *m*-N*Ph*), 6.99 / 133.5 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P), 6.89 / 129.4, 123.8 (*m*-*Ph*$_2$P / *m*-*Ph*$_2$P, *i*-*Ph*$_2$P), 6.88 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 2.92 / 152.8, 123.8, 74.3, 34.3 (PC*H*$_2$ / *C*=N, *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.67 / 138.5, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.09 / 74.3, 43.8 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

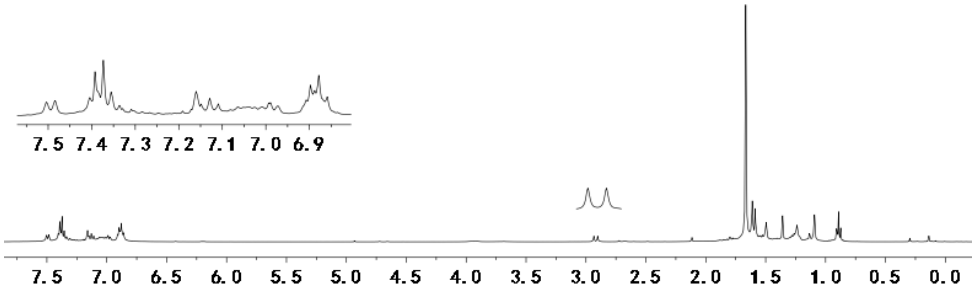


Fig. S12. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

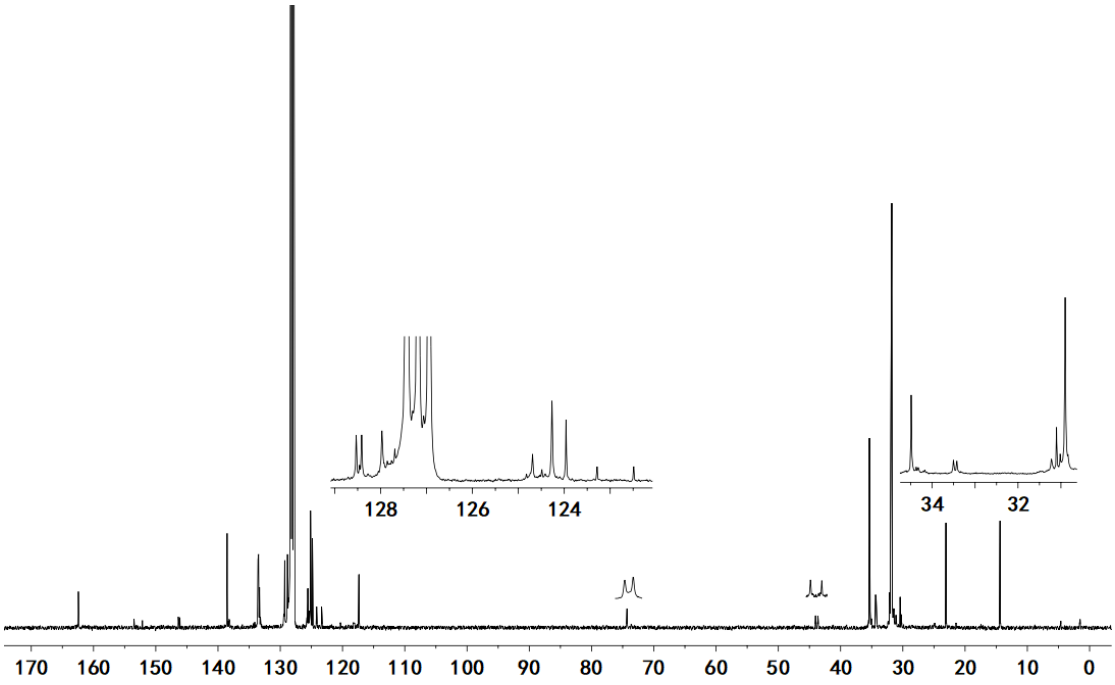


Fig. S13. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

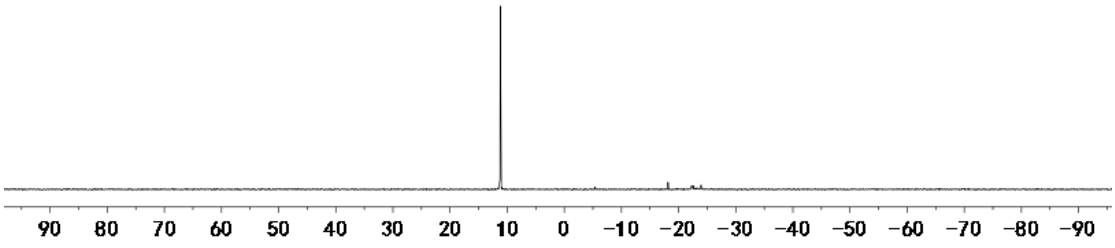
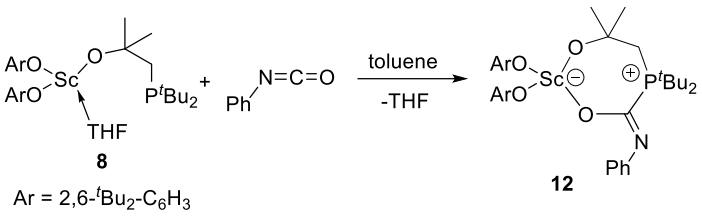


Fig. S14. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

Characterization of complex 12:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.34 / 6.82 (*m*-O*Ar* / *p*-O*Ar*), 7.23 / 7.02 (*o*-N*Ph* / *m*-N*Ph*),

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.34 / 125.0 (*m*-O*Ar*), 7.23 / 129.3 (*o*-N*Ph*), 7.02 / 129.1 (*m*-N*Ph*), 6.98 / 125.4 (*p*-N*Ph*), 6.82 / 117.2 (*p*-O*Ar*), 2.31 / 36.3 (P*C*H$_2$), 1.61 / 31.8 (C(*C*H$_3$)$_3$), 1.39 / 35.7 (OC(*C*H$_3$)$_2$), 1.07 / 28.4 (P(C(*C*H$_3$)$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.34 / 162.5, 125.0, 35.3 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.23 / 146.2 (*o*-N*Ph* / *i*-N*Ph*), 6.98 / 129.3 (*p*-N*Ph* / *o*-N*Ph*), 6.82 / 138.6 (p-O*Ar* / o-O*Ar*), 2.31 / 152.6, 73.5 (PC*H*$_2$ / *C*=N, O*C*(CH$_3$)$_2$), 1.61 / 138.6, 35.3 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.39 / 73.5, 36.3 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$), 1.07 / 37.0 (P(C(C*H*$_3$)$_3$)$_2$ / P(*C*(CH$_3$)$_3$)$_2$).

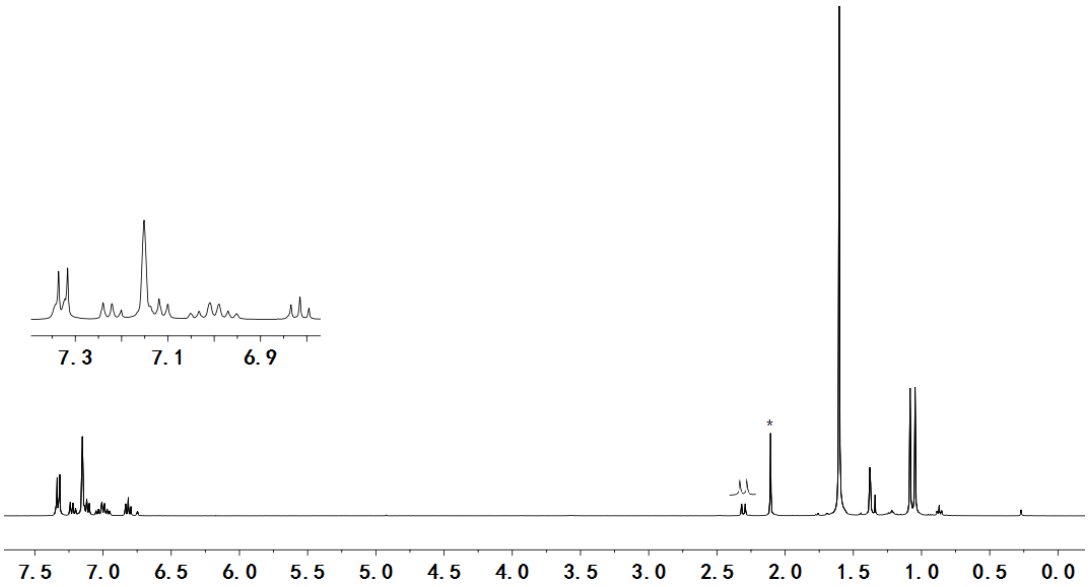


Fig. S15. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [*: Toluene].

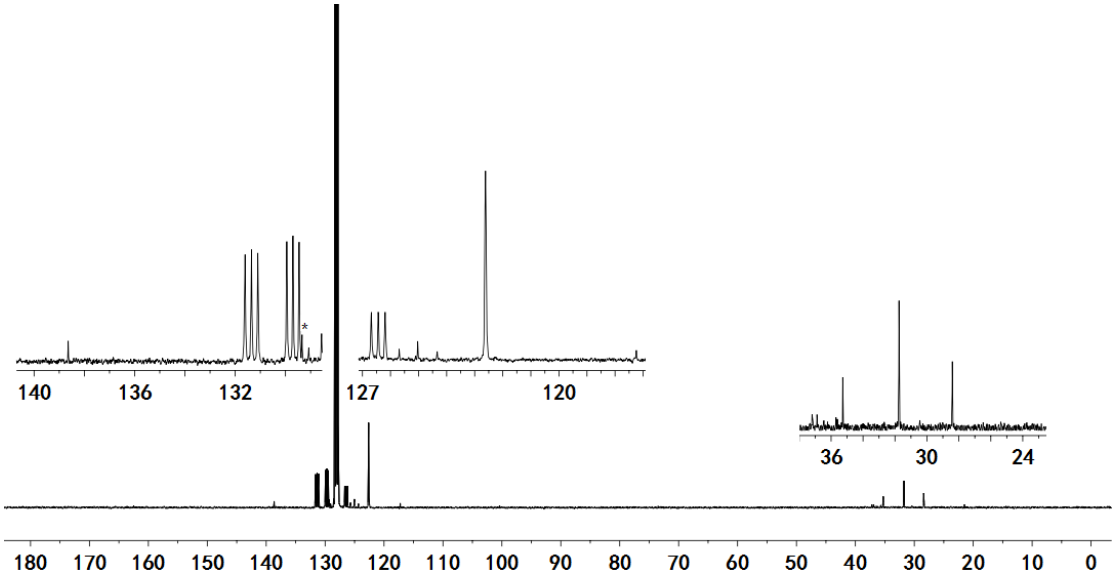


Fig. S16. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [*: Toluene].

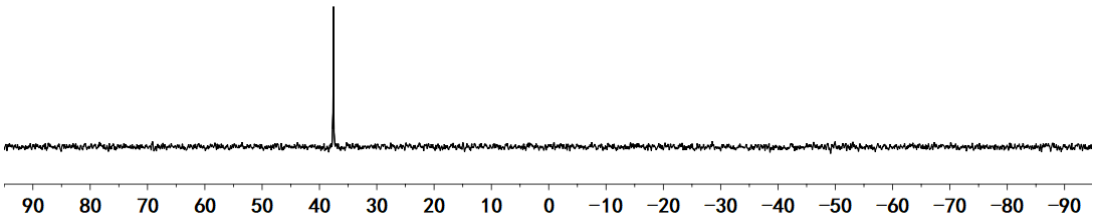


Fig. S17. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

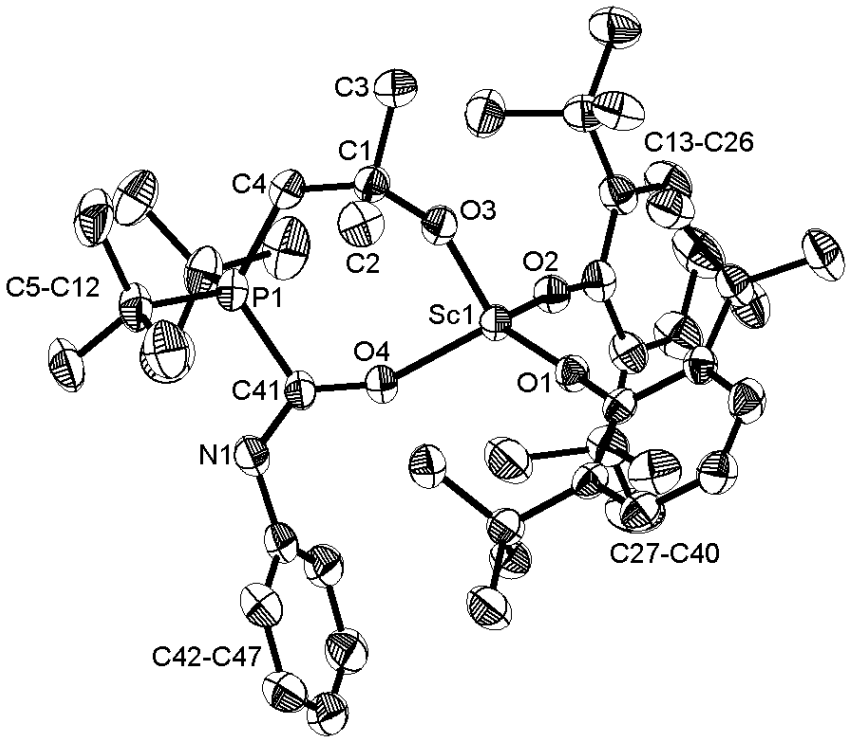
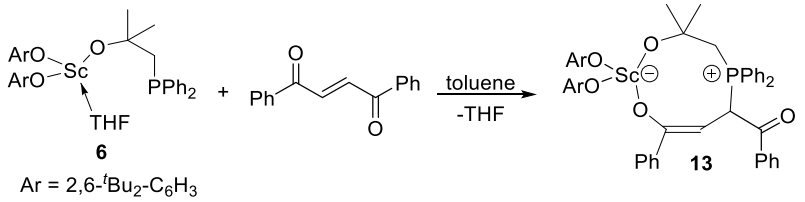


Fig. S18. Crystal structure of complex **12**.

X-ray crystal structure analysis of complex 12: formula $C_{54}H_{73}NO_4PSc$, M = 876.06, colourless crystal, 0.40 x 0.30 x 0.25 mm, a = 14.146(4), b = 14.536(4), c = 15.261(6) Å, β = 83.19(3) °, V = 2647.3(16) Å^3, ρ_{calc} = 1.099 gcm^{-3}, μ = 0.210 mm^{-1}, empirical absorption correction ($0.919 \leq T \leq 0.949$), Z = 2, triclinic, space group P -1, λ = 0.71073 Å, T = 293(2) K, Multi-scan, 24605 reflections collected ($\pm h$, $\pm k$, $\pm l$), 11938 independent (R(int) = 0.0372) and 6631 observed reflections [$I>2\sigma(I)$], 538 refined parameters, R = 0.0837, wR^2 = 0.2592, max. (min.) residual electron density 0.618 (-0.340) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 13:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 8.39 /6.78 (*o-Ph*C=O / *m-Ph*C=O), 7.87 / 7.25 (*o-Ph*C(O) / *m-Ph*C(O)), 7.69 / 6.99 (*o-Ph*'P / *m-Ph*'P), 7.67 / 4.08 (PC*H* / C*H*=), 7.56 / 6.97 (*m*-O*Ar* / *p*-O*Ar*), 7.40 / 6.84 (*m*-O*Ar*'/ *p*-O*Ar*'), 7.08 / 6.82 (*o-Ph*P / *m-Ph*P), 3.22 / 1.76 (PCH_2 / PCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 8.39 / 129.8 (*o-Ph*C=O), 7.87 / 127.5 (*o-Ph*C(O)), 7.69 / 135.2 (*o-Ph*'P), 7.67 / 44.4 (P*CH*), 7.56 / 125.0 (*m*-O*Ar*), 7.40 / 124.4 (*m*-O*Ar*'), 7.25 / 128.1 (*m-Ph*C(O)), 7.15 / 128.6 (*p-Ph*C(O)), 7.08 / 134.2 (*o-Ph*P), 6.99 / 129.2 (*m-Ph*'P), 6.97 / 116.0 (*p*-O*Ar*), 6.95 / 129.5 (*m-Ph*C=O), 6.94 / 133.9 (*p-Ph*'P), 6.84 / 116.1 (*p*-O*Ar*'), 6.83 / 133.7 (*p-Ph*P), 6.82 / 128.5 (*m-Ph*P), 6.78 / 134.9 (*p-Ph*C=O), 4.08 / 82.7 (*CH*=), 3.22, 1.76 / 38.2 (P*C*H_2), 2.03 / 32.6, 1.78 / 32.8, 1.71 / 31.8 (C(*C*H_3)$_3$), 1.43 / 38.5, 0.54 / 30.2 (OC(*C*H_3)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 8.39 / 195.0, 134.9, 129.8 (*o-Ph*C=O / Ph*C*=O, *p-Ph*C=O, *o-Ph*C=O), 7.87 / 168.3, 127.5 (*o-Ph*C(O) / Ph*C*(O), *o-Ph*C(O)), 7.69 / 133.9 (*o-Ph*'P / *p-Ph*'P), 7.67 / 195.0, 168.3 (PC*H* / Ph*C*=O, Ph*C*(O)), 7.56 / 162.8, 125.0, 35.7 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH_3)$_3$), 7.40 / 162.2, 124.4, 35.8 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*', *C*(CH_3)$_3$'), 7.25 / 141.4, 128.1 (*m-Ph*C(O) / *i-Ph*C(O), *m-Ph*C(O)), 6.99 / 129.2, 121.6 (*m-Ph*'P / *m-Ph*'P, *i-Ph*'P), 6.97 / 139.1 (*p*-O*Ar* / *o*-O*Ar*), 6.84 / 138.4 (*p*-O*Ar*' / *o*-O*Ar*'), 6.82 / 128.5, 120.8 (*m-Ph*P / *m-Ph*P, *i-Ph*P), 4.08 / 195.0, 168.3 (C*H*= / Ph*C*=O, Ph*C*(O),), 3.22 / 121.6, 75.9, 38.5 (PCH_2 / *i-Ph*'P, O*C*(CH_3)$_2$, OC(*C*H_3)$_2$), 1.43 / 75.9, 38.2 (OC(C*H*$_3$)$_2$ / O*C*(CH_3)$_2$, P*C*H_2).

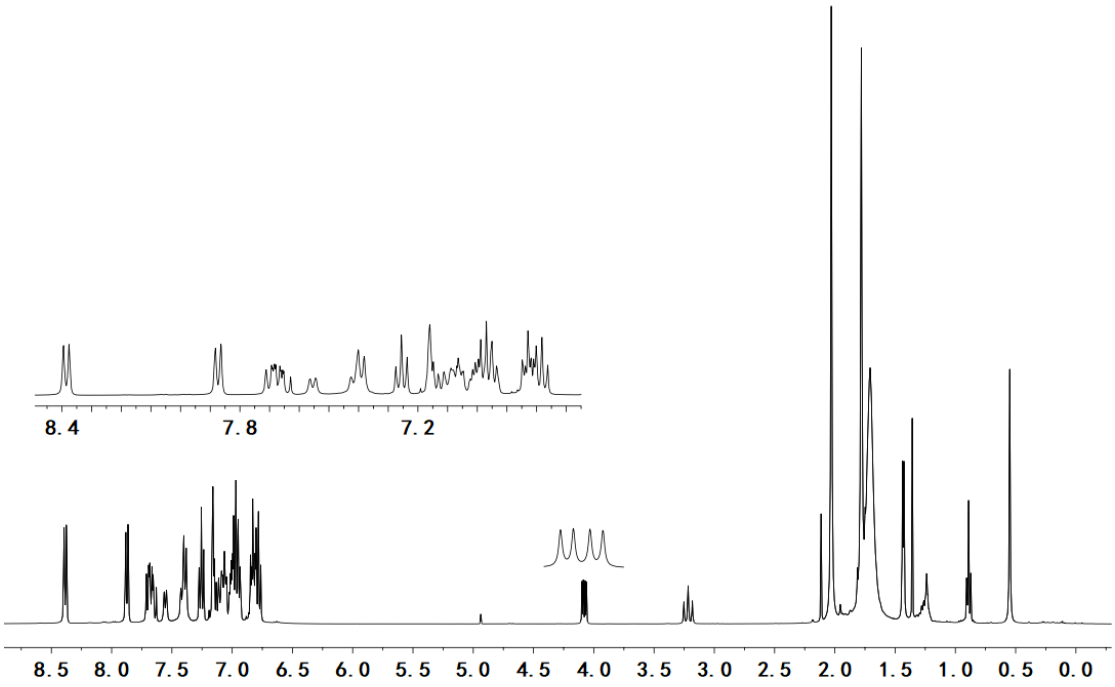


Fig. S19. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

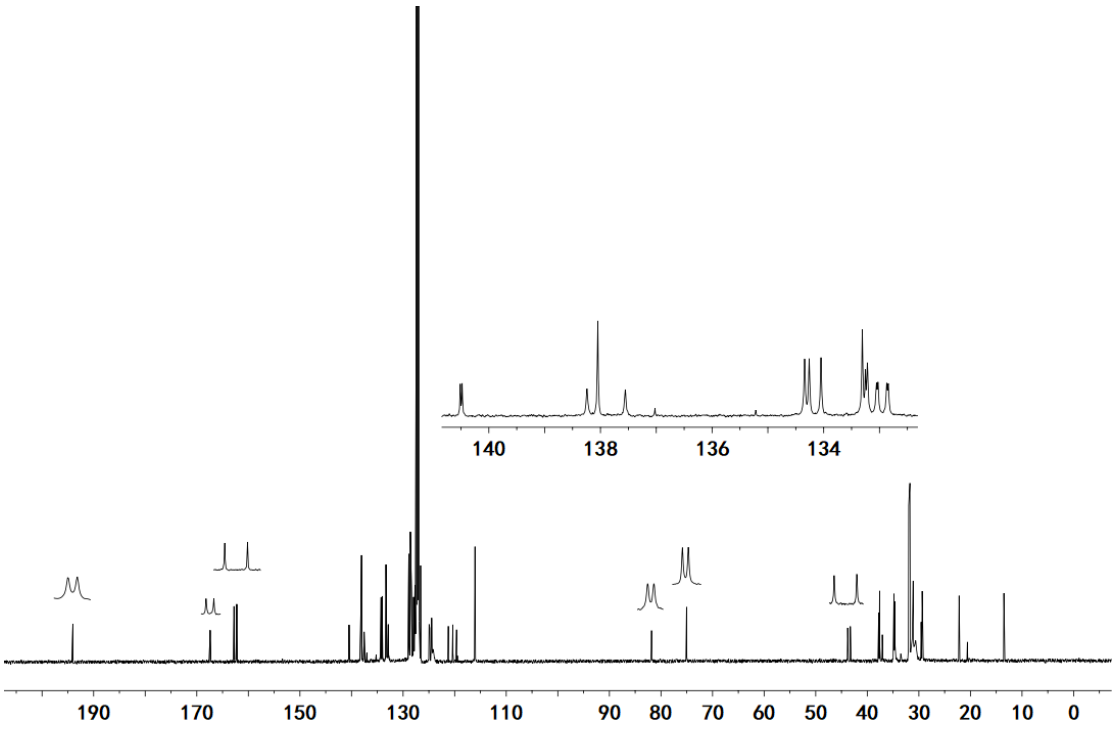


Fig. S20. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K).

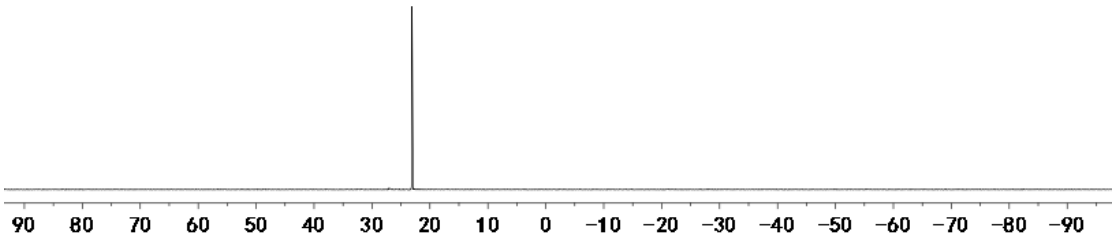


Fig. S21. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6, 298 K).

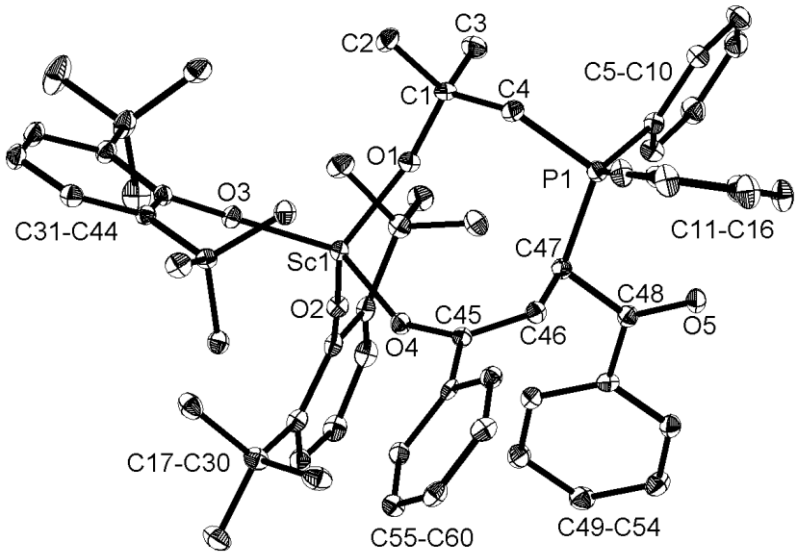
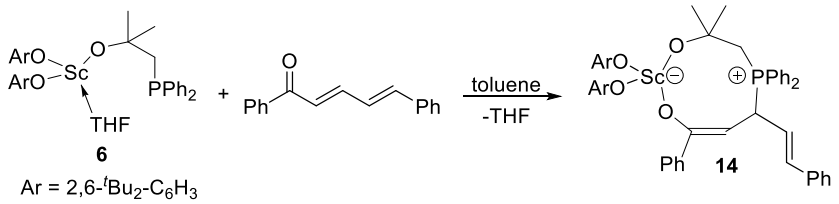


Fig. S22. Crystal structure of complex **13**.

X-ray crystal structure analysis of complex 13: formula $C_{60}H_{72}O_5PSc$, M = 949.11, colourless crystal, 0.20 x 0.15 x 0.10 mm, a = 28.0307(7), b = 28.0307(7), c = 13.4862(7) Å, β = 90 °, V = 10596.4(8) Å^3, ρ_{calc} = 1.190 gcm^{-3}, μ = 0.216 mm^{-1}, empirical absorption correction (0.958 ≤ T ≤ 0.979), Z = 8, tetragonal, space group I -4, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 28629 reflections collected (±h, ±k, ±l), 12179 independent (R(int) = 0.0591) and 8946 observed reflections [I>2σ(I)], 619 refined parameters, R = 0.0491, wR^2 = 0.1171, max. (min.) residual electron density 0.239 (-0.318) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 14:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 243 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.59 / 7.32 (*o-Ph*C(O) / *m-Ph*C(O), 7.16 / 6.60 (*m*-O*Ar* / *p*-O*Ar*), 7.00 / 6.47 (*m*-O*Ar*'/ *p*-O*Ar*'), 6.54 / 6.03 (PhC*H*= / PhCH=C*H*), 6.16 / 3.85 (PC*H* / PhC(O)=C*H*), 3.42 / 2.49 (PCH_2 / PCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 243 K): δ ^{1}H / δ ^{13}C = 7.83 / 134.5 (*p-Ph*'P), 7.74 / 134.6 (*o-Ph*P), 7.71 / 134.3 (*p-Ph*P), 7.70 / 129.4 (*m-Ph*P), 7.63 / 133.6 (*o-Ph*'P), 7.62 / 129.8 (*m-Ph*'P), 7.59 / 126.8 (*o-Ph*C(O)), 7.37 / 127.9 (*p-Ph*CH=), 7.32 / 127.6 (*m-Ph*C(O)), 7.19 / 128.5 (*m-Ph*CH=), 7.16 / 124.6 (*m*-O*Ar*), 7.07 / 126.5 (*o-Ph*CH=), 7.00 / 124.5 (*m*-O*Ar*'), 6.60 / 115.4 (*p*-O*Ar*), 6.54 / 135.5 (Ph*CH*=), 6.47 / 115.4 (*p*-O*Ar*'), 6.16 / 36.5 (P*CH*), 6.03 / 121.3 (PhCH=*CH*), 3.85 / 87.2 (PhC(O)=C*H*), 3.42, 2.49 / 36.9 (PCH_2), 1.63 / 31.3 (C(CH_3)$_3$), 1.37 / 37.7, 0.65 / 30.2 (OC(CH_3)$_2$), 1.25 / 30.6 (C(CH_3)$_3$').

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 243 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.74 / 134.6 (*o-Ph*P / *o-Ph*P), 7.70 / 129.4, 120.5 (*m-Ph*P / *m-Ph*P, *i-Ph*P), 7.62 / 129.8, 120.6 (*m-Ph*'P / *m-Ph*'P, *i-Ph*'P), 7.59 / 164.8, 126.8 (*o-Ph*C(O) / Ph*C*(O), *o-Ph*C(O)), 7.32 / 141.8, 127.6 (*m-Ph*C(O) / *i-Ph*C(O), *m-Ph*C(O)), 7.19 / 135.8, 128.5 (*m-Ph*CH= / *i-Ph*CH=, *m-Ph*CH=), 7.16 / 162.8, 124.6, 35.1 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH_3)$_3$), 7.07 / 135.5, 126.5 (*o-Ph*CH= / Ph*C*H=, *o-Ph*CH=), 7.00 / 162.4, 124.5, 34.9 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*', *C*(CH_3)$_3$'), 6.60 / 138.2 (*p*-O*Ar* / *o*-O*Ar*), 6.54 / 126.5, 36.5 (PhC*H*= / *o-Ph*CH=, P*C*H), 6.47 / 138.6 (*p*-O*Ar*' / *o*-O*Ar*'), 6.16 / 164.8, 135.5 (PC*H* / Ph*C*(O), Ph*C*H=), 6.03 / 135.8, 87.2 (PhCH=C*H* / *i-Ph*CH=, PhC(O)=*C*H), 3.85 / 164.8, 141.8, 121.3, 36.5 (PhC(O)=C*H* / Ph*C*(O), *i-Ph*C(O), PhCH=*C*H, P*C*H), 3.42 / 120.5, 75.8, 37.7 (PCH_2 / *i-Ph*P, O*C*(CH_3)$_2$, OC(CH_3)$_2$), 2.49 / 75.8 (PCH_2 / O*C*(CH_3)$_2$), 1.37 / 75.8, 36.9, 30.2 (OC(CH_3)$_2$ / O*C*(CH_3)$_2$, P*C*H$_2$, OC(CH_3)$_2$).

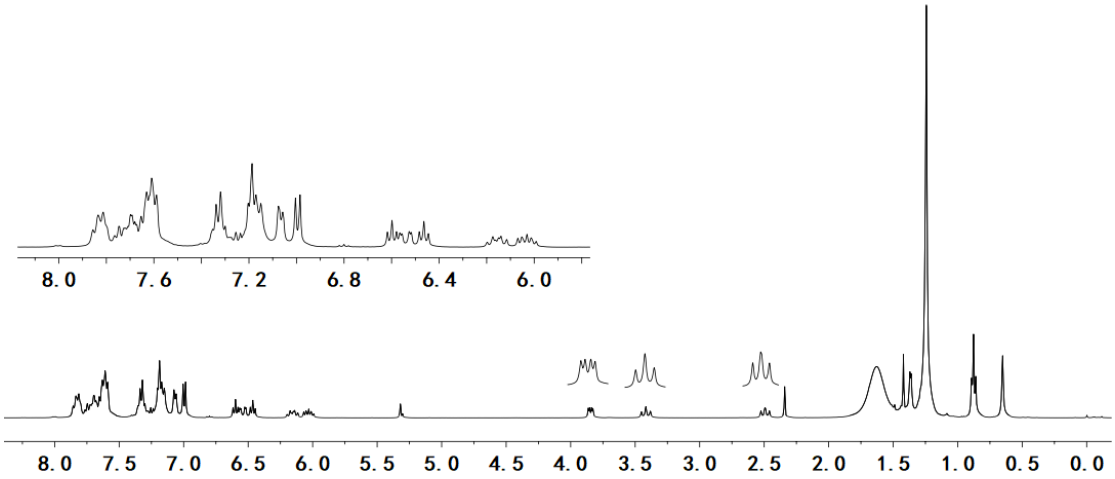


Fig. S23. ^{1}H NMR (400 MHz, CD_2Cl_2, 243 K).

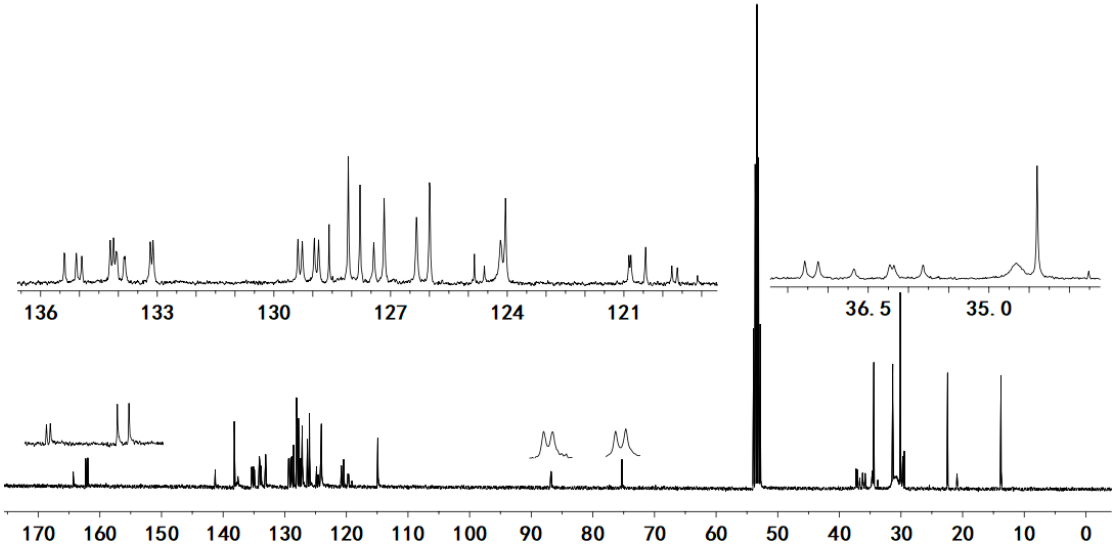


Fig. S24. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 243 K).

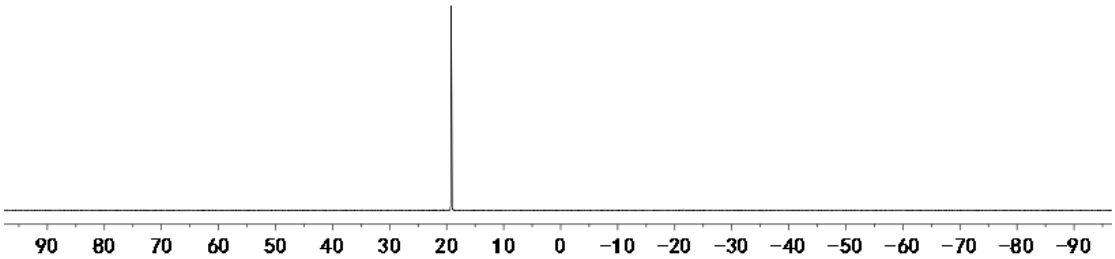


Fig. S25. ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 243 K).

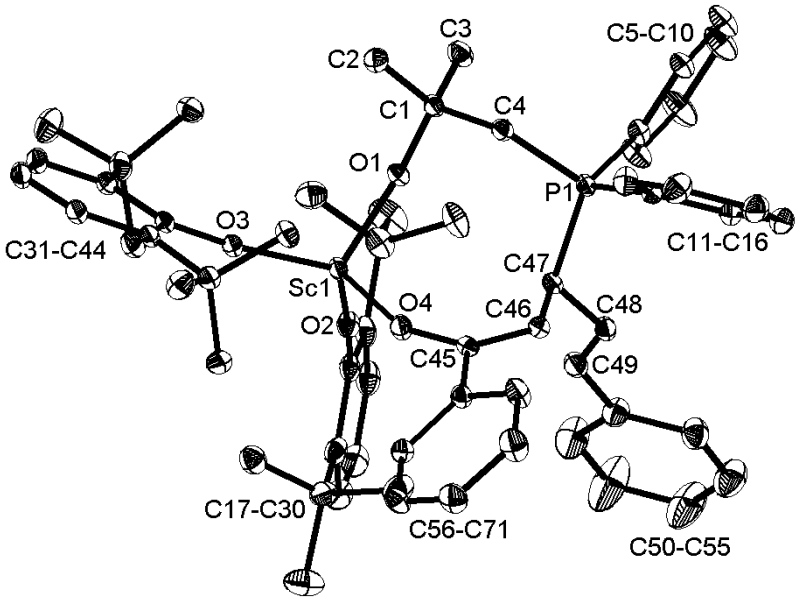
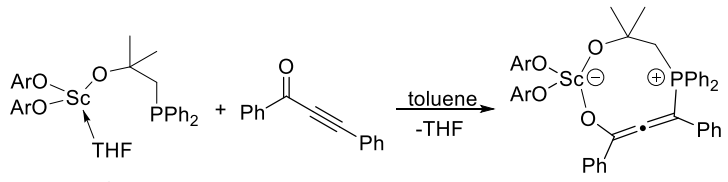


Fig. S26. Crystal structure of complex **14**.

X-ray crystal structure analysis of complex 14: formula $C_{61}H_{74}O_4PSc$, M = 947.13, yellow crystal, 0.20 x 0.15 x 0.10 mm, a = 27.7682(13), b = 18.9225(13), c = 27.1058(17) Å, β = 113.337(3)°, V = 13077.4(14) Å^3, ρ_{calc} = 0.962 gcm^{-3}, μ = 0.174 mm^{-1}, empirical absorption correction ($0.966 \leq T \leq 0.983$), Z = 8, monoclinic, space group C 2/c, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 248622 reflections collected ($\pm h$, $\pm k$, $\pm l$), 15020 independent (R(int) = 0.0832) and 10689 observed reflections [$I>2\sigma(I)$], 618 refined parameters, R = 0.0418, wR^2 = 0.1336, max. (min.) residual electron density 0.296 (-0.340) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 15:



6 **15**

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

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.71 / 6.73 (*o-Ph*P / *m-Ph*P), 7.50 / 7.08 (*o-Ph*C(O)= / *m-Ph*C(O)=), 7.46 / 6.91 (*m*-O*Ar* / *p*-O*Ar*), 7.29 / 6.75 (*m*-O*Ar*'/ *p*-O*Ar*'), 7.21 / 6.97 (*o-Ph*C(P)= / *m-Ph*C(P)=), 7.07 / 6.81 (*o-Ph*'P / *m-Ph*'P).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.71 / 133.6 (*o-Ph*P), 7.50 / 125.9 (*o-Ph*C(O)), 7.46 / 125.2 (*m*-O*Ar*), 7.29 / 125.0 (*m*-O*Ar*'), 7.21 / 129.0 (*o-Ph*C(P)=), 7.08 / 128.3 (*m-Ph*C(O)), 7.07 / 128.2 (*o-Ph*'P), 7.06 / 127.9 (*p-Ph*C(O)), 7.01 / 133.2 (*p-Ph*'P), 6.97 / 128.4 (*m-Ph*C(P)=), 6.97 / 133.3 (*p-Ph*C(P)=), 6.91 / 116.8 (*p*-O*Ar*), 6.81 / 129.4 (*m-Ph*'P), 6.75 / 116.9 (*p*-O*Ar*'), 6.73 / 128.8 (*m-Ph*P), 6.72 / 133.10 (*p-Ph*P), 3.04, 2.34 / 40.6 (P*C*H_2), 1.91 / 32.5 (C(*C*H_3)$_3$), 1.65 / 32.0 (C(*C*H_3)$_3$'), 1.59 / 38.0, 1.34 / 33.8 (OC(CH_3)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.71 / 133.1 (*o-Ph*P / *p-Ph*P), 7.50 / 149.5 (*o-Ph*C(O)= / O*C*=), 7.46 / 163.4, 125.2 35.7 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.29 / 162.8, 125.0, 35.3 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*' *C*(CH$_3$)$_3$'), 7.21 / 129.0, 96.4 (*o-Ph*C(P)= / *o-Ph*C(P)=, P*C*=), 6.97 / 134.3, 128.4 (*m-Ph*C(P)= / *i-Ph*C(P)=, *m-Ph*C(P)), 6.91 / 138.9 (*p*-O*Ar* / *o*-O*Ar*), 6.81 / 129.4, 123.1 (*m-Ph*'P / *m-Ph*'P, *i-Ph*'P), 6.75 / 139.0 (*p*-O*Ar*' / *o*-O*Ar*'), 3.04 / 96.4, 75.5, 38.0 (PCH_2 / P*C*=, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 2.34 / 124.7, 75.5 (PCH_2 / *i-Ph*P, O*C*(CH$_3$)$_2$), 1.91 / 138.9, 35.7 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.65 / 139.0, 35.3 (C(CH_3)$_3$' / *o*-O*Ar*', *C*(CH$_3$)$_3$'), 1.59 / 75.5, 40.6 (OC(CH_3)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$), 1.34 / 75.5 (OC(CH_3)$_2$ / O*C*(CH$_3$)$_2$).

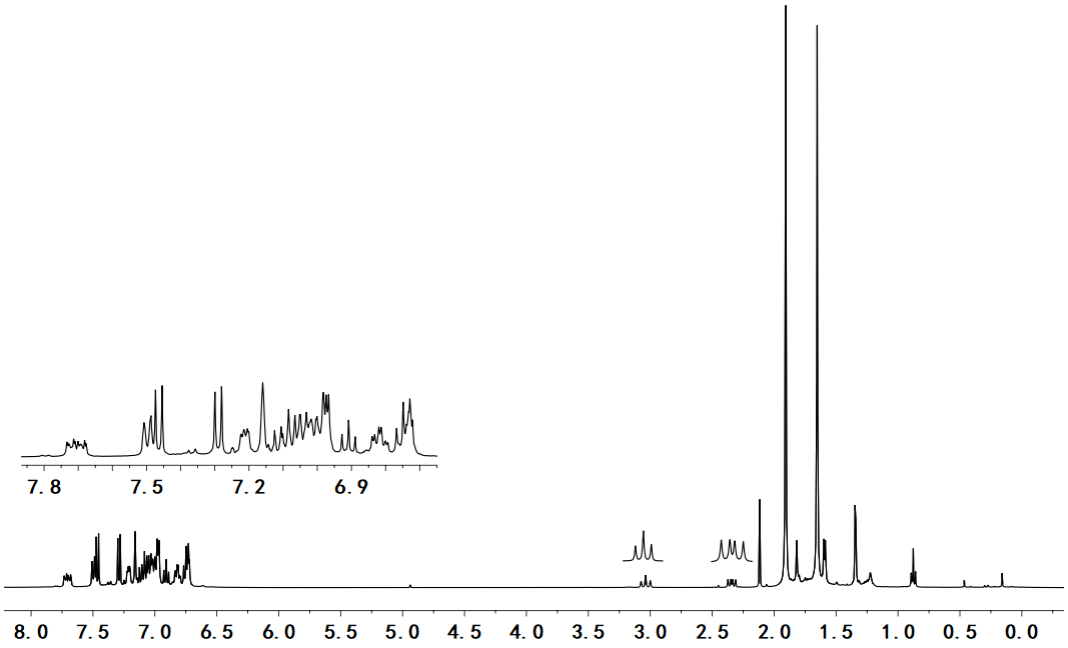


Fig. S27. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

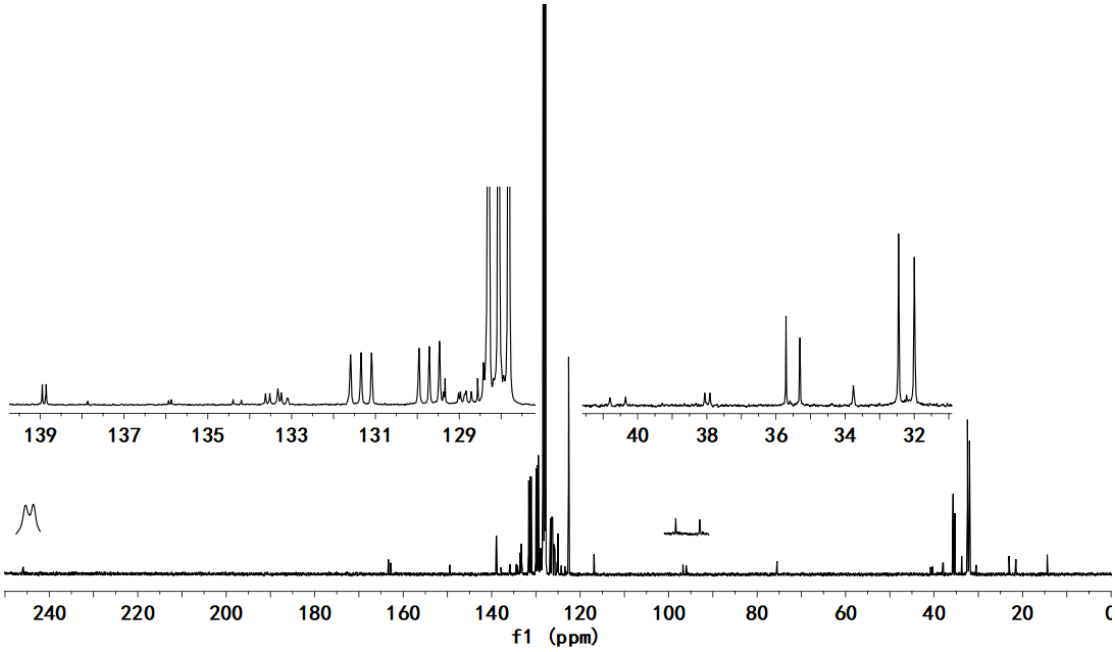


Fig. S28. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

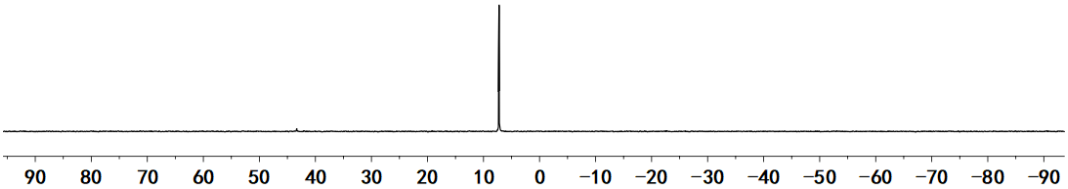


Fig. S29. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

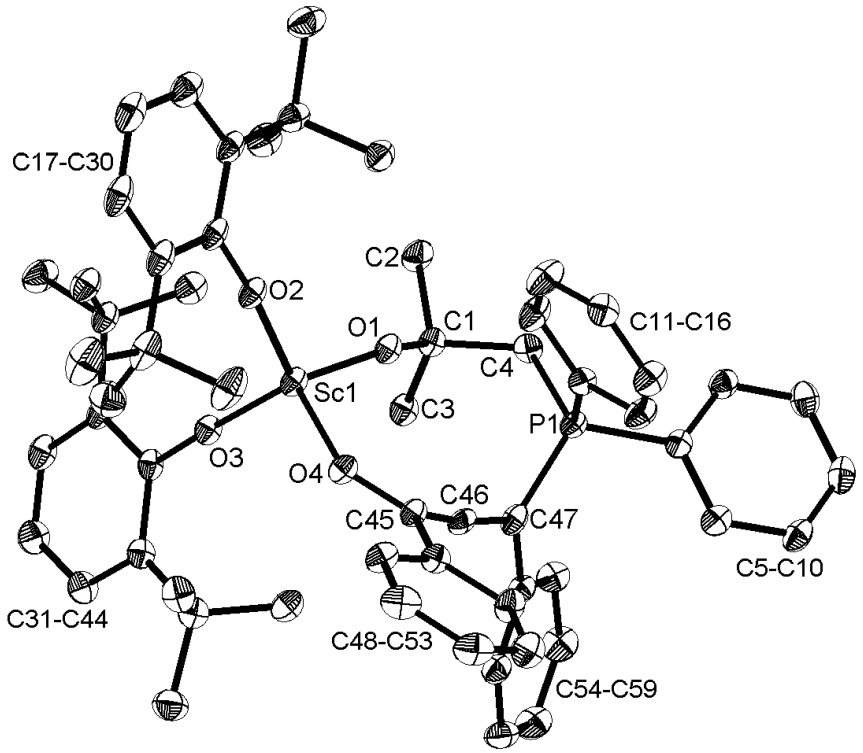
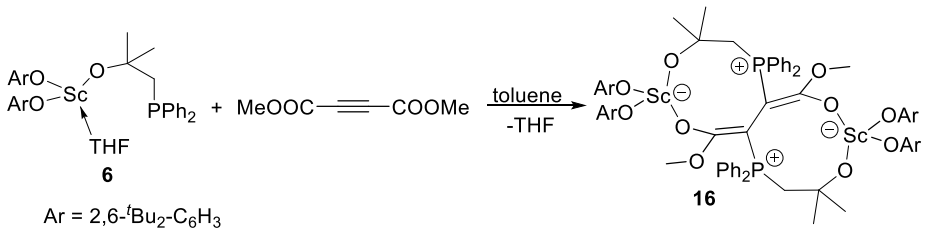


Fig. S30. Crystal structure of complex **15**.

X-ray crystal structure analysis of complex 15: formula $C_{66}H_{78}O_4PSc$, M = 1011.21, colourless crystal, 0.12 x 0.08 x 0.02 mm, a = 16.161(3), b = 22.688(4), c = 16.441(3) Å, β = 109.393(3) °, V = 5686.2(19) Å^3, ρ_{calc} = 1.181 gcm^{-3}, μ = 0.205 mm^{-1}, empirical absorption correction (0.981 ≤ T ≤ 0.996), Z = 4, monoclinic, space group P 2(1)/n, λ = 0.71073 Å, T = 273(2) K, Multi-scan, 43955 reflections collected ($\pm h$, $\pm k$, $\pm l$), 12785 independent (R(int) = 0.0832) and 5292 observed reflections [$I>2\sigma(I)$], 664 refined parameters, R = 0.0666, wR^2 = 0.2122, max. (min.) residual electron density 0.402 (-0.704) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 16:



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

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 8.65 / 6.26 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.32 / 6.77 (*m*-O*Ar* / *p*-O*Ar*), 7.28 / 6.56 (*o*-*Ph*$_2$'P / *m*-*Ph*$_2$'P), 7.19 / 6.62 (*m*-O*Ar*' / *p*-O*Ar*'), 2.48 / 1.50 (PC*H*$_2$ / PC*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 8.65 / 135.5 (*o*-*Ph*$_2$P), 7.32 / 126.2 (*m*-O*Ar*), 7.28 / 132.4 (*o*-*Ph*$_2$'P), 7.19 / 126.5 (*m*-O*Ar*'), 6.91 / 128.3 (*p*-*Ph*$_2$P), 6.77 / 117.3 (*p*-O*Ar*), 6.76 / 128.2 (*p*-*Ph*$_2$'P), 6.62 / 117.2 (*p*-O*Ar*'), 6.56 / 131.8 (*m*-*Ph*$_2$'P), 6.26 / 130.6 (*m*-*Ph*$_2$P), 2.97 / 52.8 (COO*CH*$_3$), 2.48, 1.50 / 38.0 (P*CH*$_2$), 1.84 / 34.0, 1.56 / 32.3 (C(*CH*$_3$)$_3$), 1.58 / 32.2, 1.45 / 33.6 (C(*CH*$_3$)$_3$'), 1.10 / 40.2, 0.28 / 30.8 (OC(*CH*$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.32 / 162.2, 126.2, 36.5 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.19 / 162.6, 126.5, 35.7 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*', *C*(CH$_3$)$_3$'), 6.91 / 135.5 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P), 6.77 / 138.9, 139.1 (*p*-O*Ar* / *o*-O*Ar*, *o*-O*Ar*), 6.76 / 132.4 (*p*-*Ph*$_2$'P / *o*-*Ph*$_2$'P), 6.62 / 140.0, 138.7 (*p*-O*Ar*' / *o*-O*Ar*', *o*-O*Ar*'), 2.97 / 174.9 (COOC*H*$_3$ / C=*C*O), 2.48 / 125.0, 76.2, 40.2 (PC*H*$_2$ / *i*-*Ph*$_2$'P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.84 / 138.9, 36.5 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.50 / 130.6, 76.2 (PC*H*$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$), 1.45 / 138.7, 35.5 (C(C*H*$_3$)$_3$' / *o*-O*Ar*', *C*(CH$_3$)$_3$'), 1.10 / 76.2, 38.0 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

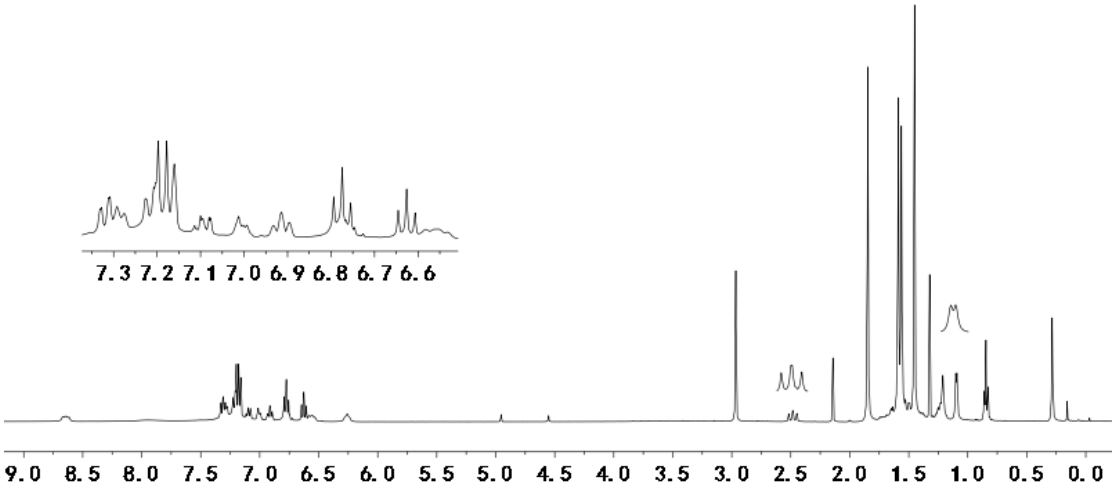


Fig. S31. ^{1}H NMR (400 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

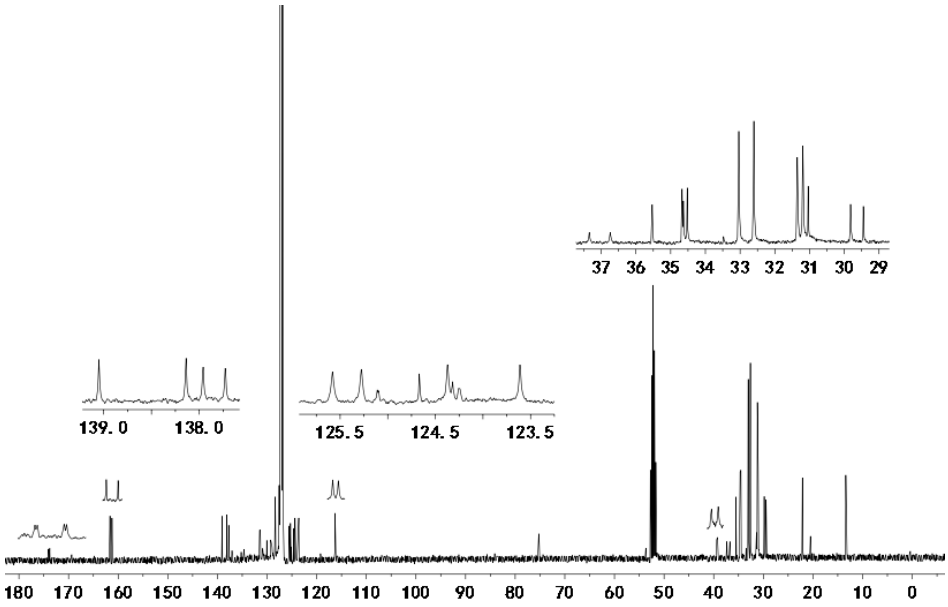


Fig. S32. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

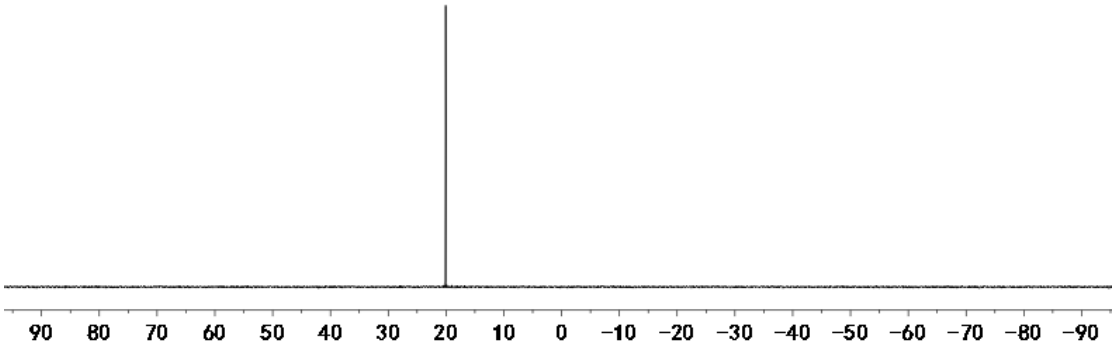


Fig. S33. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

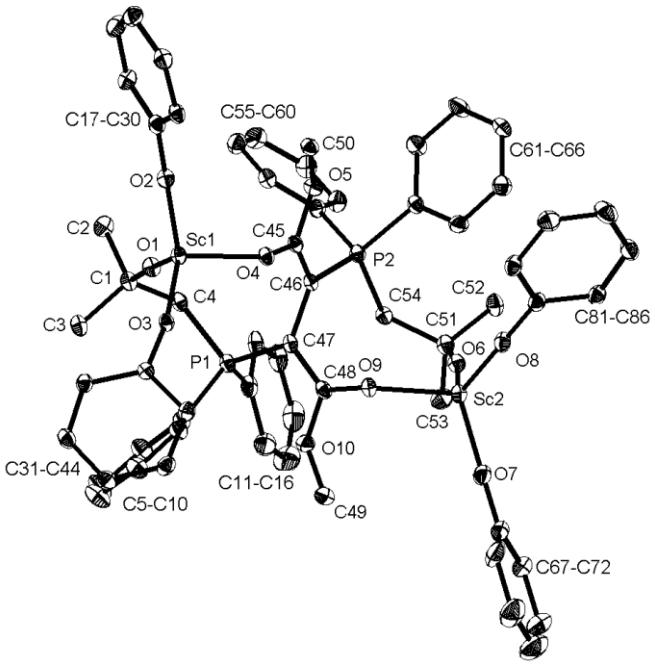
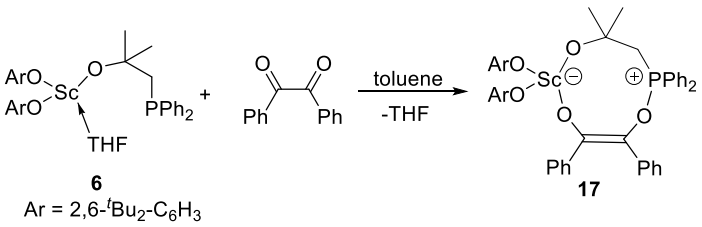


Fig. S34. Crystal structure of complex **16**.

X-ray crystal structure analysis of complex 16: formula $C_{94}H_{126}O_{10}P_2Sc_2$, M = 1567.82, yellow crystal, 0.25 x 0.23 x 0.18 mm, a = 18.1076(10), b = 22.6312(13), c = 26.0981(15) Å, β = 109.032(2) °, V = 10110.3(10) Å^3, ρ_{calc} = 1.030 gcm^{-3}, μ = 0.215 mm^{-1}, empirical absorption correction ($0.948 \leq T \leq 0.962$), Z = 4, monoclinic, space group P 2(1)/n, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 201959 reflections collected ($\pm h$, $\pm k$, $\pm l$), 23314 independent (R(int) = 0.1399) and 12557 observed reflections [$I>2\sigma(I)$], 1003 refined parameters, R = 0.0574, wR^2 = 0.2154, max. (min.) residual electron density 0.402 (-0.704) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 17:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.31 / 6.73 (*m*-O*Ar* / *p*-O*Ar*), 7.29 / 6.95 (*o*-*Ph*P / *m*-*Ph*P), 7.27 / 6.89 (*o*-*Ph*C(O)P / *m*-*Ph*C(O)P), 6.60 / 6.44 (*m*-*Ph*C(O)Sc / *o*-*Ph*C(O)Sc).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.31 / 125.1 (*m*-O*Ar*), 7.29 / 133.1 (*o*-*Ph*$_2$P), 7.27 / 129.8 (*o*-*Ph*C(O)P), 7.04 / 134.9 (*p*-*Ph*$_2$P), 6.95 / 129.2 (*m*-*Ph*$_2$P), 6.89 / 127.7 (*m*-*Ph*C(O)P), 6.73 / 116.2 (*p*-O*Ar*), 6.66 / 127.1 (*p*-*Ph*C(O)Sc), 6.60 / 128.0 (*m*-*Ph*C(O)Sc), 6.44 / 130.5 (*o*-*Ph*C(O)Sc, 2.71 / 44.4 (P*C*H$_2$), 1.71 / 32.1 (C(*C*H$_3$)$_3$), 1.27 / 34.7 (OC(*C*H$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.31 / 163.1, 125.1, 35.6 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.29 / 134.9 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.27 / 153.2, 129.8 (*o*-*Ph*C(O)P / Ph*C*(O)P, *o*-*Ph*C(O)P), 6.95 / 129.2, 122.3 (*m*-*Ph*$_2$P / *m*-*Ph*$_2$P, *i*-*Ph*$_2$P), 6.89 / 138.7, 127.7 (*m*-*Ph*C(O)P / *i*-*Ph*C(O)P, *m*-*Ph*C(O)P), 6.73 / 138.9 (*p*-O*Ar* / *o*-O*Ar*), 6.60 / 135.7, 128.0 (*m*-*Ph*C(O)Sc / *i*-*Ph*C(O)Sc, *m*-*Ph*C(O)Sc), 6.44 / 130.5, 127.1 (*o*-*Ph*C(O)Sc / *o*-*Ph*C(O)Sc, *p*-*Ph*C(O)Sc), 2.71 / 122.3, 75.2, 34.7 (PC*H*$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.71 / 138.9, 35.6 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.27 / 75.2, 44.4, 34.7 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$, OC(*C*H$_3$)$_2$).

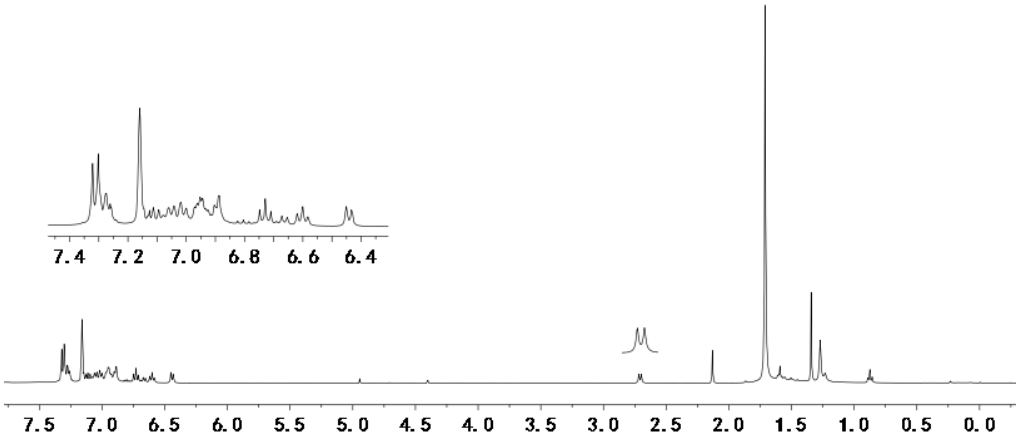


Fig. S35. ^{1}H NMR (400 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

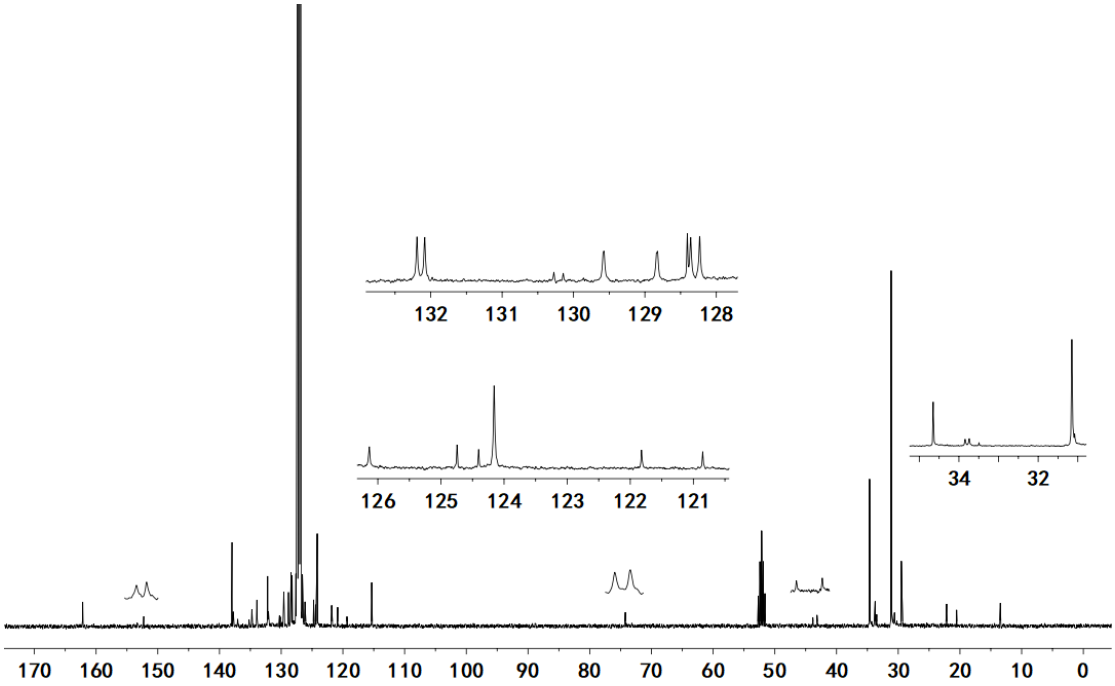


Fig. S36. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

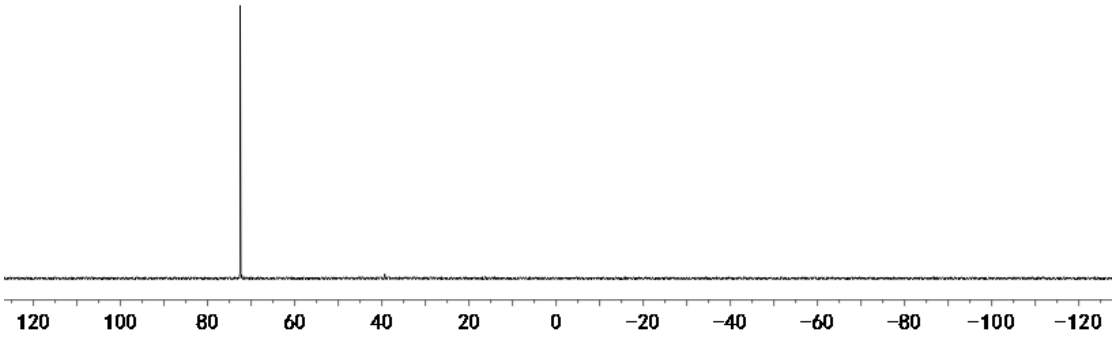


Fig. S37. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / CD_2Cl_2 (5: 1), 298 K).

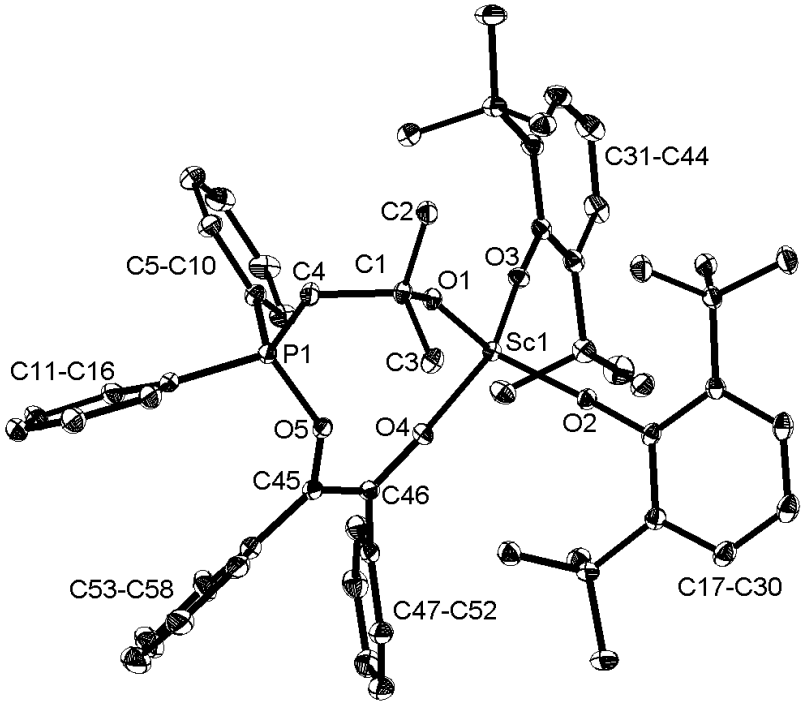
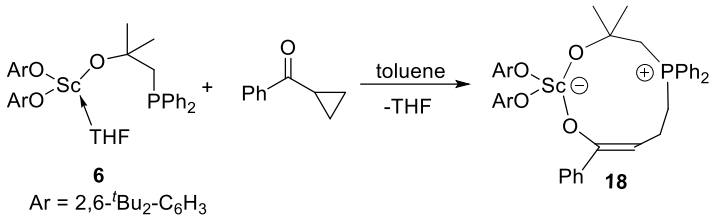


Fig. S38. Crystal structure of complex **17**.

X-ray crystal structure analysis of complex 17: formula $C_{121}H_{140}O_{10}P_2Sc_2$, M = 1906.19, colourless crystal, 0.20 x 0.10 x 0.08 mm, a = 35.395(2), b = 13.1093(8), c = 23.2289(13) Å, β = 99.291(2) °, V = 10636.8(11) Å^3, ρ_{calc} = 1.190 gcm^{-3}, μ = 0.216 mm^{-1}, empirical absorption correction ($0.958 \leq T \leq 0.983$), Z = 4, monoclinic, space group C 2/c, λ = 0.71073 Å, T = 100(2) K, Multi-scan, 85533 reflections collected ($\pm h$, $\pm k$, $\pm l$), 12255 independent (R(int) = 0.0500) and 9867 observed reflections [$I>2\sigma(I)$], 1003 refined parameters, R = 0.0497, wR^2 = 0.1474, max. (min.) residual electron density 1.282 (-0.669) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 18:



6

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

18

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.97 / 7.23 (*o*-OC*Ph* / *m*-OC*Ph*), 7.40 / 6.84 (*m*-O*Ar* / *p*-O*Ar*), 4.96 / 2.57 (=C*H* / PCH_2CH_2), 2.87 / 2.57 (PCH_2CH_2 / PCH_2CH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.97 / 127.1 (*o*-OC*Ph*), 7.40 / 125.3 (*m*-O*Ar*), 7.23 / 127.8 (*m*-OC*Ph*), 7.10 / 127.3 (*p*-OC*Ph*), 7.00 / 133.9 (*p*-Ph_2P), 6.87 / 129.9 (*m*-Ph_2P), 6.84 / 116.3 (*p*-O*Ar*), 6.79 /131.8 (*o*-Ph_2P), 4.96 / 95.4 (=*CH*), 2.87 / 20.5 (PCH_2CH_2), 2.57 / 19.8 (PCH_2CH_2), 2.50 / 35.3 (PCH_2), 1.78 / 32.6 ($C(CH_3)_3$), 1.22 / 35.6 ($OC(CH_3)_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.97 / 163.3, 127.3 (*o*-OC*Ph* / O*C*Ph, *p*-OC*Ph*), 7.40 / 163.2, 125.3, 35.7 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*$(CH_3)_3$), 7.23 / 141.9, 127.8 (*m*-OC*Ph* / *i*-OC*Ph*, *m*-OC*Ph*), 7.10 / 127.1 (*p*-OC*Ph* / *o*-OC*Ph*), 7.00 / 131.8 (*p*-Ph_2P / *o*-Ph_2P), 6.87 / 129.9, 122.3 (*m*-Ph_2P / *m*-Ph_2P, *i*-Ph_2P), 6.84 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 4.96 / 163.3, 141.9 (=C*H* / O*C*Ph, *i*-OC*Ph*), 2.50 / 122.3, 75.3, 35.6 (PCH_2 / *i*-Ph_2P, $OC(CH_3)_2$, $OC(CH_3)_2$), 1.78 / 138.5, 35.7 ($C(CH_3)_3$ / *o*-O*Ar*, *C*$(CH_3)_3$), 1.22 / 75.3, 35.3 ($OC(CH_3)_2$ / $OC(CH_3)_2$, PCH_2).

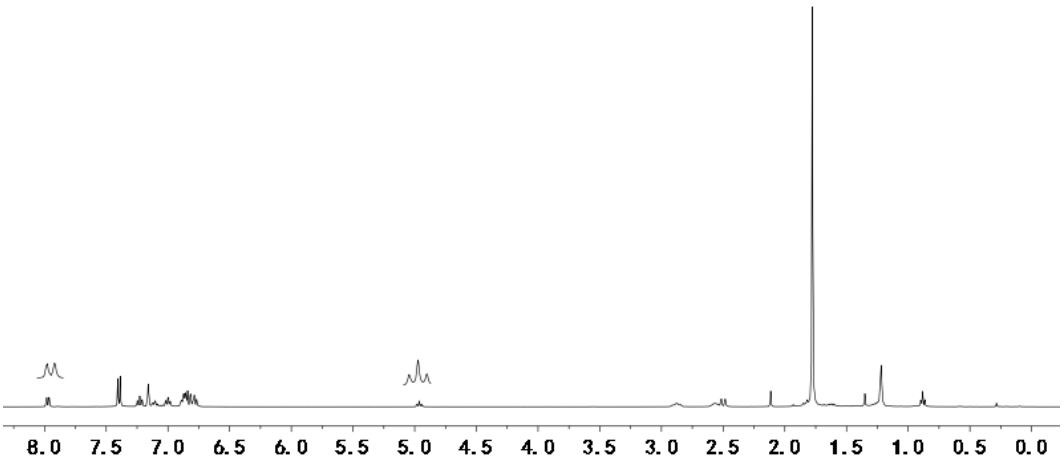


Fig. S39. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

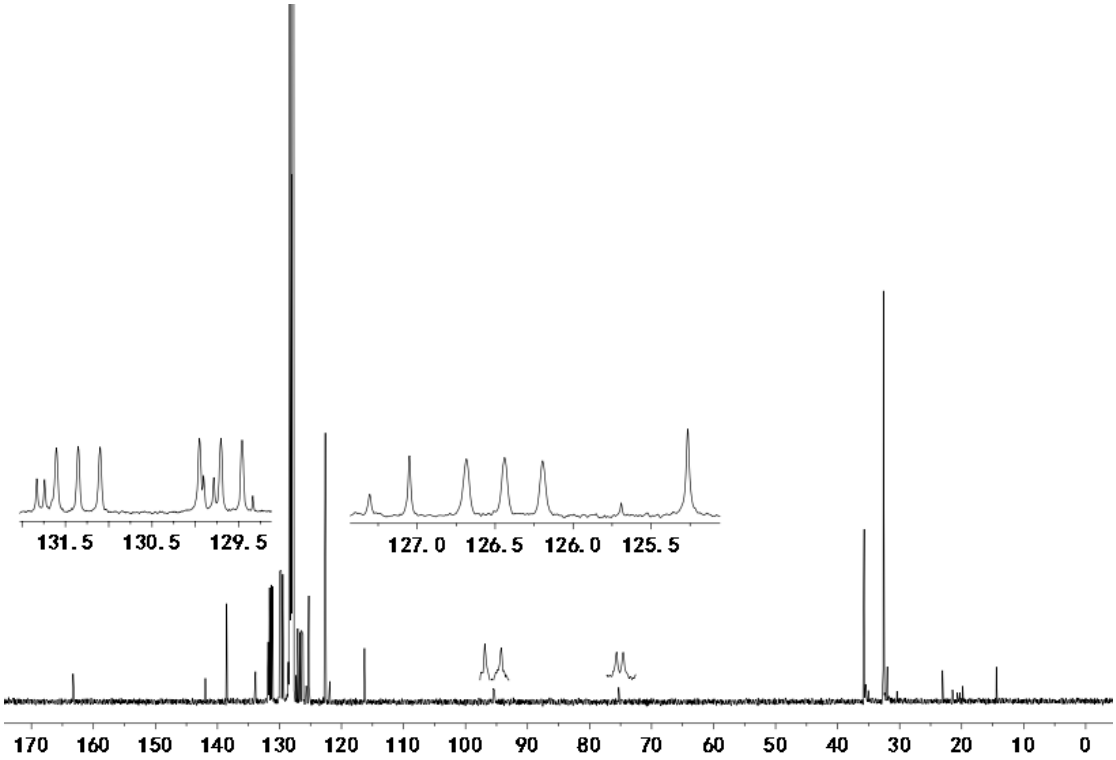


Fig. S40. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

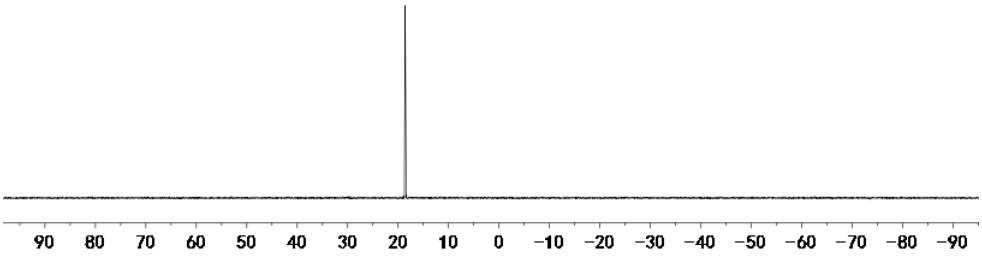


Fig. S41. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

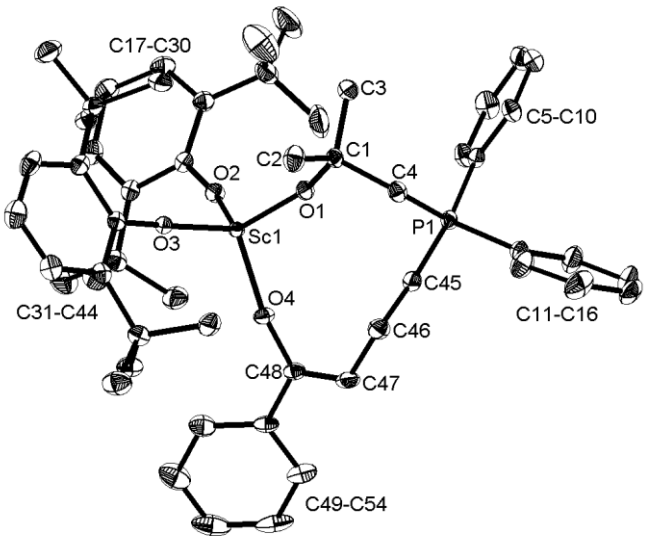
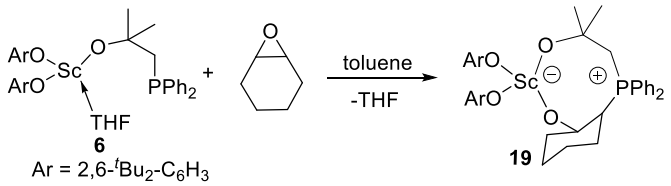


Fig. S42. Crystal structure of complex **18**.

X-ray crystal structure analysis of complex 18: formula $C_{54}H_{70}O_4PSc$, M = 859.03, colourless crystal, 0.50 x 0.20 x 0.20 mm, a = 14.071(7), b = 19.237(9), c = 18.583(9) Å, β = 95.019(16) °, V = 5011(4) Å^3, ρ_{calc} = 1.139 gcm^{-3}, μ = 0.221 mm^{-1}, empirical absorption correction (0.895 ≤ T ≤ 0.957), Z = 4, monoclinic, space group P 21/n, λ = 0.71073 Å, T = 296(2) K, Multi-scan, 109415 reflections collected (±h, ±k, ±l), 9315 independent (R(int) = 0.1167) and 6944 observed reflections [I>2σ(I)], 555 refined parameters, R = 0.0642, wR^2 = 0.1189, max. (min.) residual electron density 0.295 (-0.345) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 19:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.46 / 6.87 (*m*-O*Ar* / *p*-O*Ar*), 7.45 / 6.91 (*o*-*Ph*P / *m*-*Ph*P), 7.43 / 6.82 (*m*-O*Ar*'/ *p*-O*Ar*'), 7.42 / 7.04 (*o*-*Ph*'P / *m*-*Ph*'P), 3.87 / 2.18 (PCH_2 / PCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K): δ ^{1}H / δ ^{13}C = 7.46 / 125.3 (*m*-O*Ar*), 7.45 / 133.9 (*o*-*Ph*P), 7.43 / 125.3 (*m*-O*Ar*'), 7.42 / 133.6 (*o*-*Ph*'P), 7.06 / 133.5 (*p*-*Ph*'P), 7.04 / 129.2 (*m*-*Ph*'P), 6.92 / 133.7 (*p*-*Ph*P), 6.91 / 129.7 (*m*-*Ph*P), 6.87 / 116.3 (*p*-O*Ar*), 6.82 / 116.3 (*p*-O*Ar*'), 3.87, 2.18 / 46.3 (P*C*H_2), 3.57 / 75.3, 3.26 / 42.4, 2.32, 1.77 / 40.5, 1.75, 0.45 / 27.1, 1.17, 0.95 / 25.7, 1.23, 0.57 / 24.7 (*C*$_6$*H*$_{10}$), 1.90 / 32.4 (C(*C*H_3)$_3$), 1.84 / 32.4 (C(*C*H_3)$_3$'), 1.32 / 38.6, 0.74 / 32.0 (OC(*C*H_3)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.46 / 163.0, 125.3, 35.7 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.45 / 133.9, 133.7 (*o*-*Ph*$_2$P / *o*-*Ph*$_2$P, *p*-*Ph*$_2$P), 7.43 / 163.2, 125.3, 35.8 (*m*-O*Ar*' / *i*-O*Ar*', *m*-O*Ar*', *C*(CH$_3$)$_3$'), 7.42 / 133.6, 133.5 (*o*-*Ph*$_2$'P / *o*-*Ph*$_2$'P, *p*-*Ph*$_2$'P), 7.04 / 129.2, 119.6 (*m*-*Ph*$_2$'P / *m*-*Ph*$_2$'P, *i*-*Ph*$_2$'P), 6.91 / 129.7, 121.2 (*m*-*Ph*$_2$P / *m*-*Ph*$_2$P, *i*-*Ph*$_2$P), 6.87 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 6.82 / 138.7 (*p*-O*Ar*' / *o*-O*Ar*'), 3.87 / 121.2, 74.2, 38.6 (PCH_2 / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.90 / 138.5, 35.7, 32.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$, (C(*C*H$_3$)$_3$), 1.84 / 138.7, 35.8, 32.4 (C(C*H*$_3$)$_3$' / *o*-O*Ar*', *C*(CH$_3$)$_3$', (C(*C*H$_3$)$_3$'), 1.32 / 74.2, 46.3, 32.0 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$, OC(*C*H$_3$)$_2$).

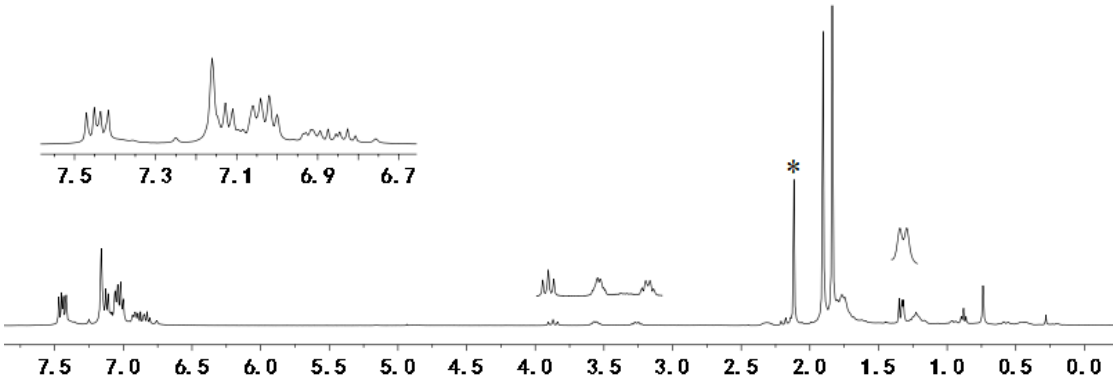


Fig. S43. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [:* Toluene].

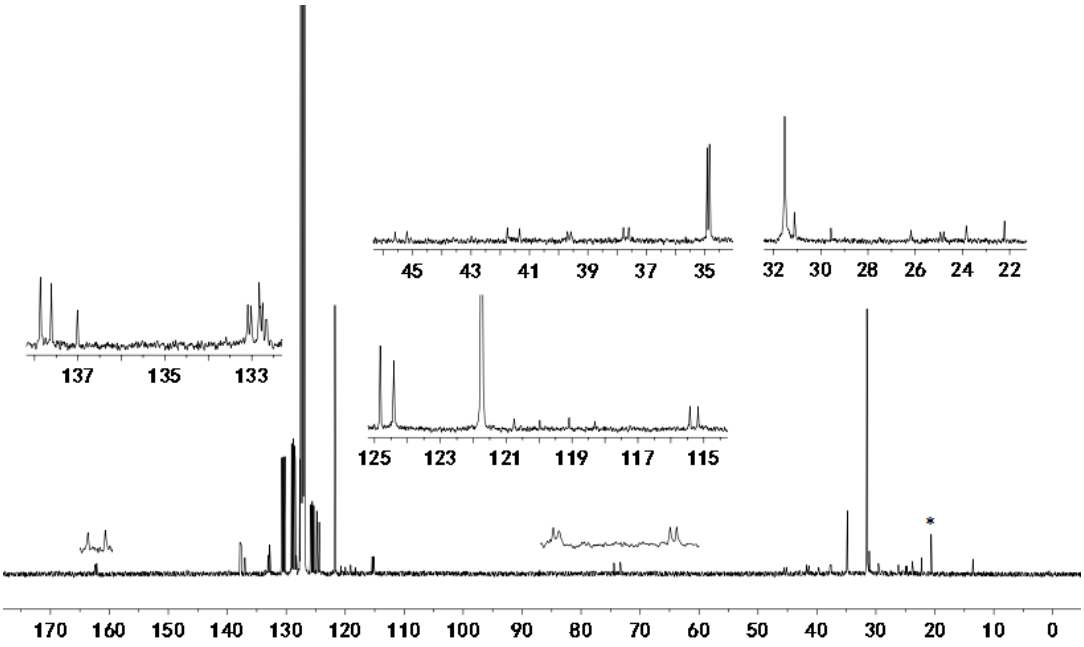


Fig. S44. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K) [:* Toluene].

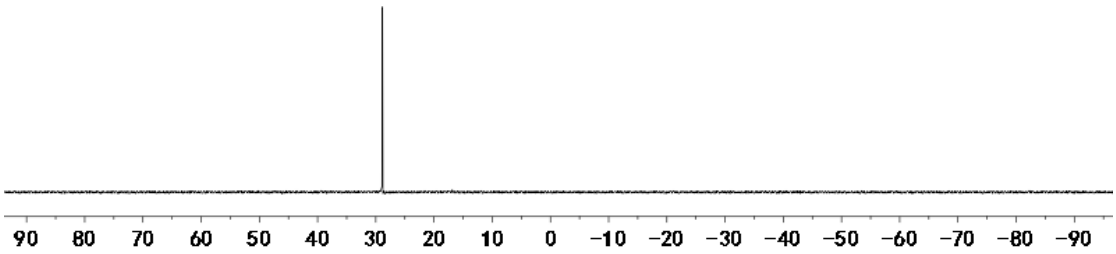


Fig. S45. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 / C_6D_5Br (5: 1), 298 K).

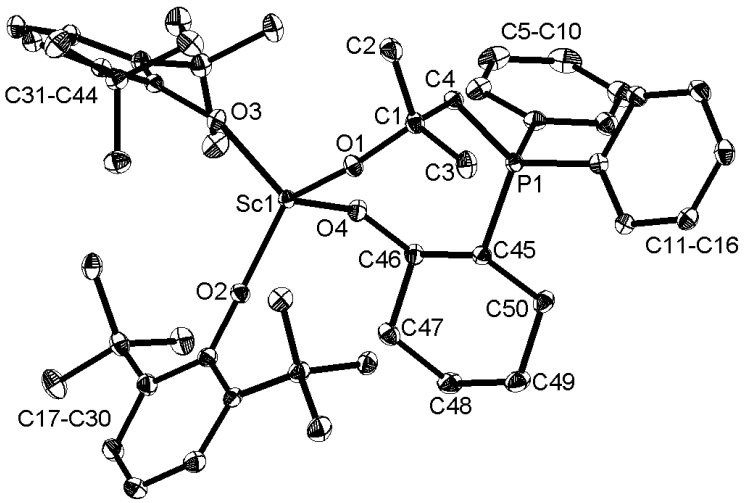
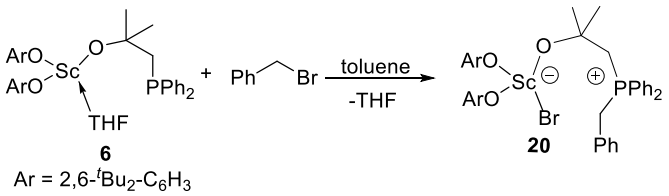


Fig. S46. Crystal structure of complex **19**.

X-ray crystal structure analysis of complex 19: formula $C_{57}H_{70}O_4PSc$, M = 895.06, colourless crystal, 0.25 x 0.18 x 0.14 mm, a = 15.1423(14), b = 19.8402(17), c = 17.7799(16) Å, β = 104.955(3)°, V = 5160.6(8) Å^3, ρ_{calc} = 1.152 gcm^{-3}, μ = 0.217 mm^{-1}, empirical absorption correction (0.947 ≤ T ≤ 0.970), Z = 4, monoclinic, space group P 21/n, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 83250 reflections collected (±h, ±k, ±l), 11933 independent (R(int) = 0.0657) and 8899 observed reflections [I>2σ(I)], 551 refined parameters, R = 0.0607, wR^2 = 0.1932, max. (min.) residual electron density 1.908 (-0.511) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 20:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.78 / 7.61 (*p*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.09 / 6.82 (*m*-*Ph*CH_2 / *o*-*Ph*CH_2), 7.08 / 6.54 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.78 / 135.4 (*p*-*Ph*$_2$P), 7.63 / 133.7 (*o*-*Ph*$_2$P), 7.61 / 130.5 (*m*-*Ph*$_2$P), 7.20 / 129.6 (*p*-*Ph*CH_2), 7.09 / 129.0 (*m*-*Ph*CH_2), 7.08 / 124.9 (*m*-O*Ar*), 6.82 / 130.7 (*o*-*Ph*CH_2), 6.54 / 116.3 (*p*-O*Ar*), 4.35 / 31.9 (Ph*C*H_2), 3.38 / 38.1 (P*C*H_2), 1.49 / 31.8 (C(*C*H_3)$_3$), 1.17 / 33.5 (OC(*C*H_3)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.78 / 133.7 (*p*-*Ph*$_2$P / *o*- *Ph*$_2$P), 7.63 / 135.4 (*o*-*Ph*$_2$P / *p*- *Ph*$_2$P), 7.61 / 118.8 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 7.20 / 130.7 (*p*-*Ph*CH_2 / *o*-*Ph*CH_2), 7.09 / 127.1 (*m*-*Ph*CH_2 / *i*-*Ph*CH_2), 7.08 / 162.9, 124.9, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.82 / 129.6, 31.9 (*o*-*Ph*CH_2 / *p*-*Ph*CH_2, Ph*C*H_2), 6.54 / 138.9 (*p*-O*Ar* / *o*-O*Ar*), 4.35 / 130.7, 127.1, 118.8 (PhCH_2 / *o*-*Ph*CH_2, *i*-*Ph*CH_2, *i*-*Ph*$_2$P), 3.38 / 118.8, 75.6, 33.5 (PCH_2 / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.49 / 138.9, 35.4 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.17 / 75.6, 38.1, 33.5 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$, OC(*C*H$_3$)$_2$).

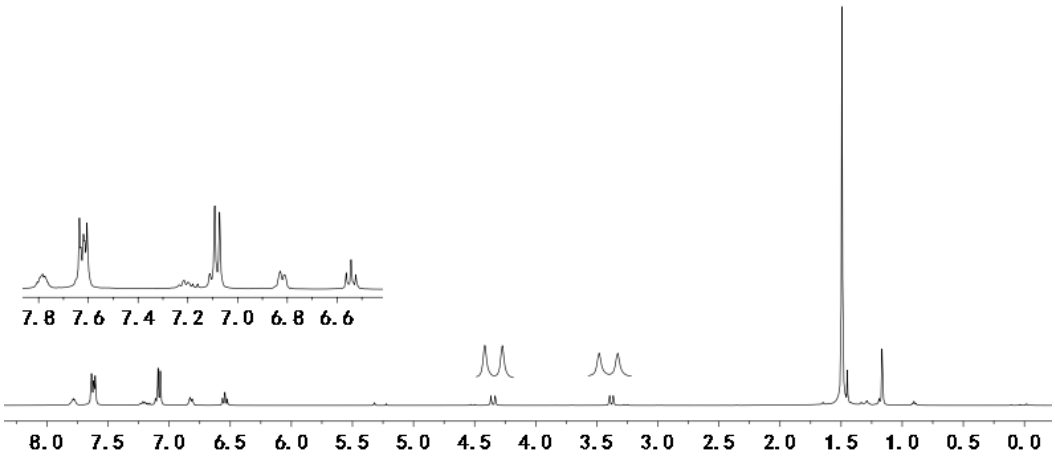


Fig. S47. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K).

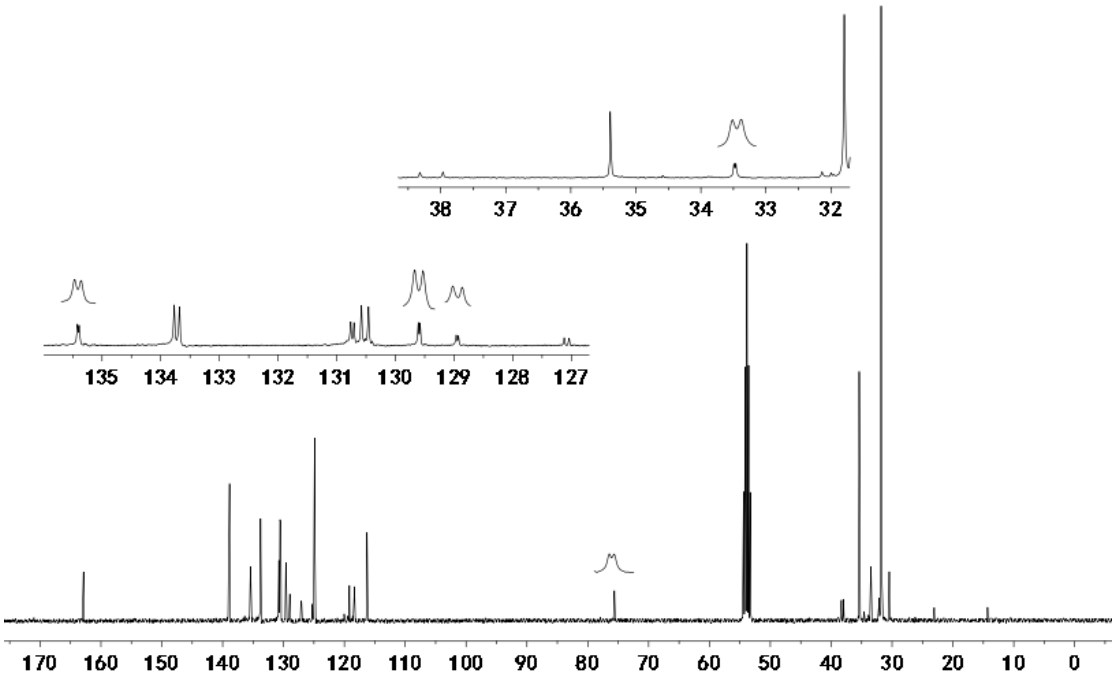


Fig. S48. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, CD_2Cl_2, 298 K).

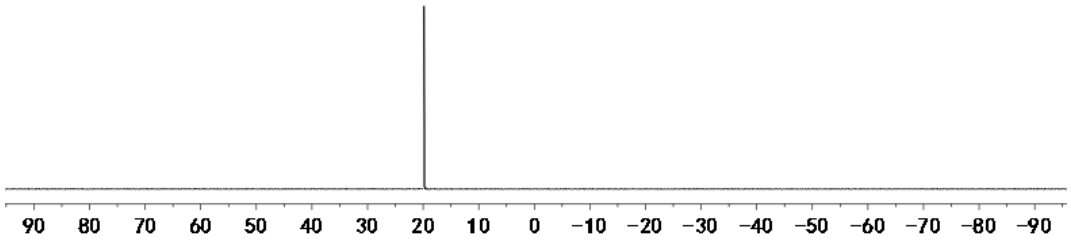


Fig. S49. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, CD_2Cl_2, 298 K).

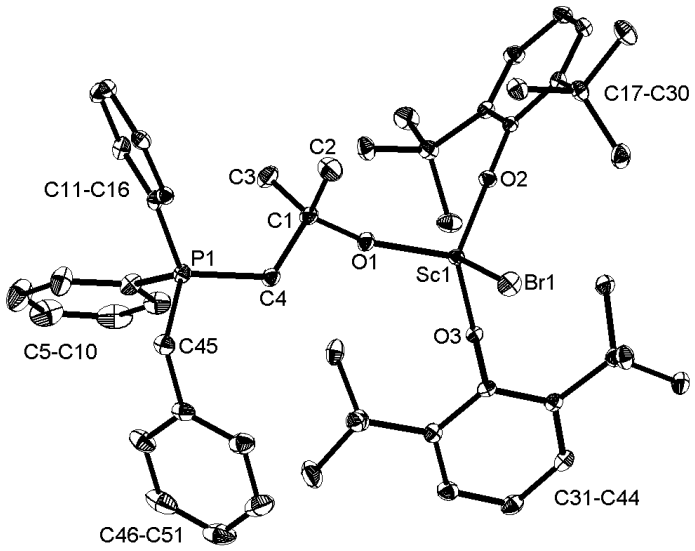
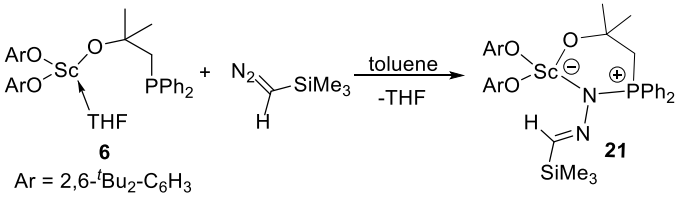


Fig. S50. Crystal structure of complex **20**.

X-ray crystal structure analysis of complex 20: formula $C_{51}H_{67}BrO_3PSc$, M = 883.88, colourless crystal, 0.21 x 0.18 x 0.15 mm, a = 11.9126(6), b = 13.2665(7), c = 16.5748(8) Å, β = 91.156(2) °, V = 2430.0(2) Å^3, ρ_{calc} = 1.208 gcm^{-3}, μ = 1.045 mm^{-1}, empirical absorption correction ($0.803 \leq T \leq 0.855$), Z = 2, triclinic, space group P -1, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 94004 reflections collected ($\pm h$, $\pm k$, $\pm l$), 11220 independent (R(int) = 0.0654) and 8296 observed reflections [$I>2\sigma(I)$], 528 refined parameters, R = 0.0358, wR^2 = 0.0987, max. (min.) residual electron density 0.393 (-0.564) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 21:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.46 / 7.00 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.38 / 6.89 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.46 / 133.1 (*o*-*Ph*$_2$P), 7.38 / 125.2 (*m*-O*Ar*), 7.03 / 132.6 (*p*-*Ph*$_2$P), 7.00 / 128.6 (*m*-*Ph*$_2$P), 6.89 / 117.4 (*p*-O*Ar*), 2.72 / 43.2 (P*CH*$_2$), 1.68 / 32.3 (C(*CH*$_3$)$_3$), 1.16 / 33.9 (OC(*CH*$_3$)$_2$), -0.04 / -1.8 (Si*Me*$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 8.65 / -1.8 (C*H*SiMe$_3$ / CHSi*Me*$_3$), 7.46 / 132.6 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.38 / 162.7, 125.2, 35.5 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 7.03 / 133.1 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P), 7.00 / 128.7 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 6.89 / 138.5 (*p*-O*Ar* / *o*-O*Ar*), 2.72 / 128.7, 74.7, 33.9 (PC*H*$_2$ / *i*-*Ph*$_2$P, O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.68 / 138.5, 35.5 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.16 / 74.7, 43.2 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$), -0.04 / 163.0 (Si*Me*$_3$ / *C*HSiMe$_3$).

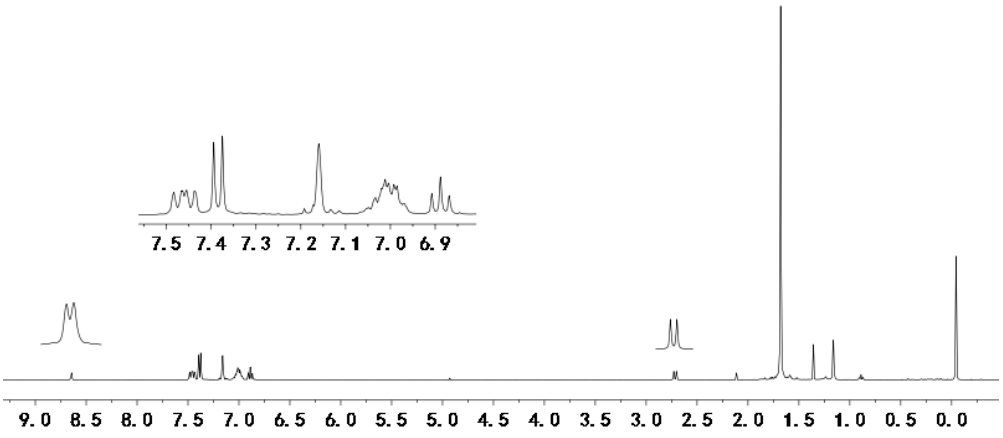


Fig. S51. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

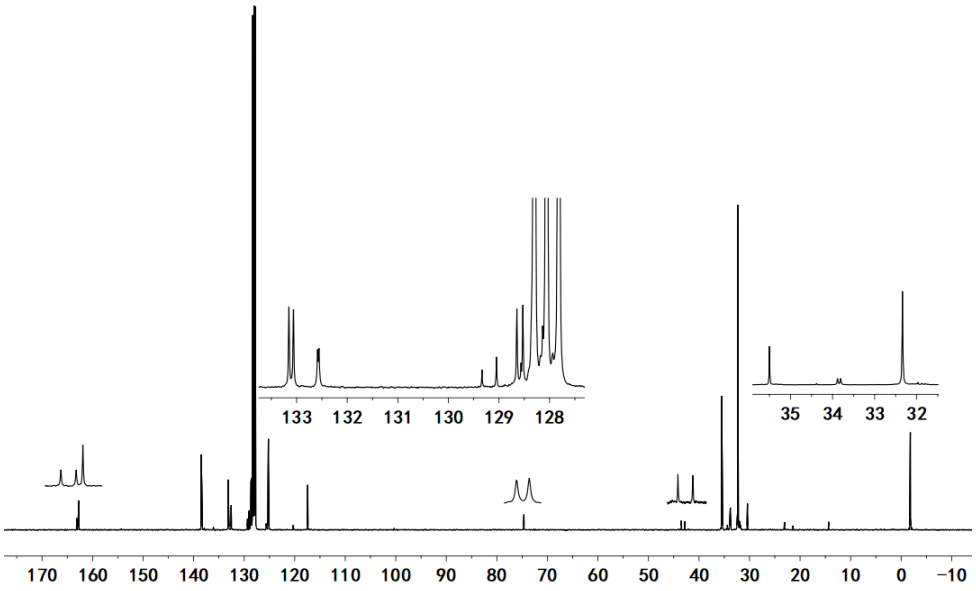


Fig. S52. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K).

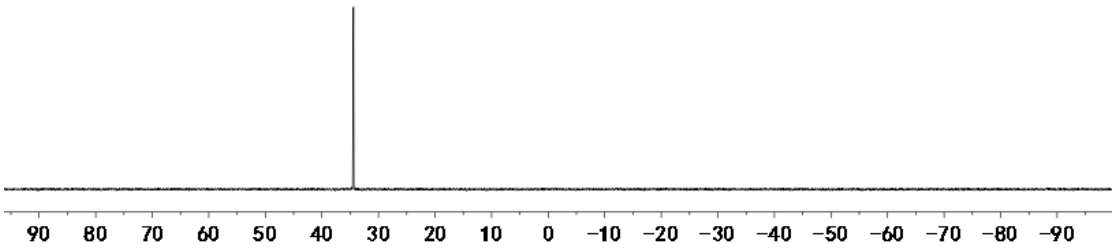


Fig. S53. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

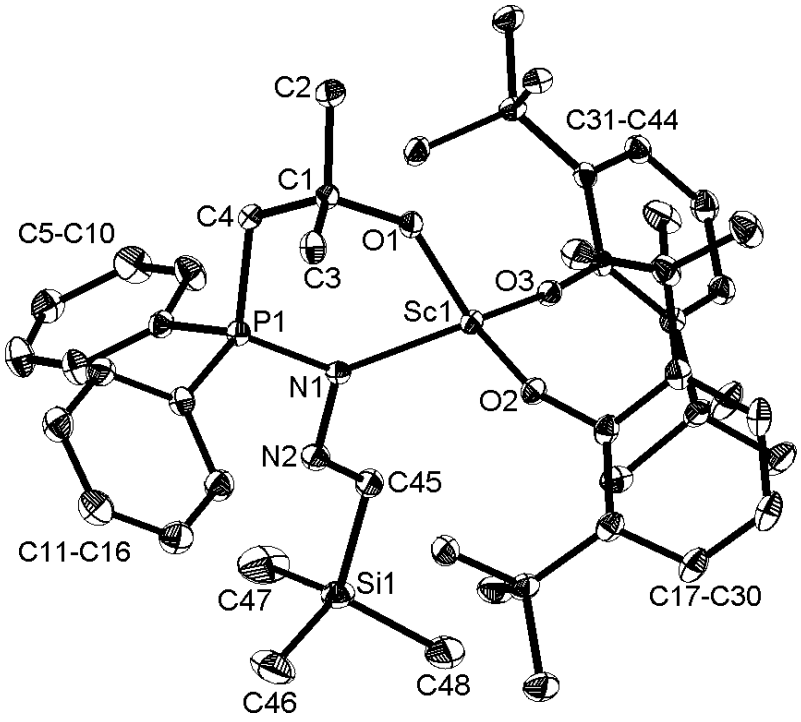
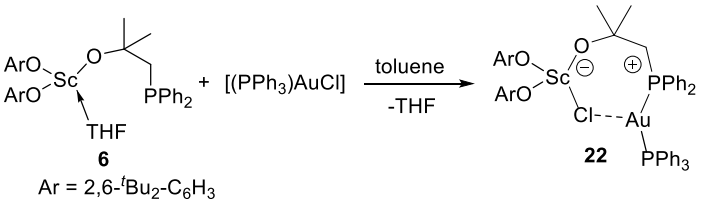


Fig. S54. Crystal structure of complex **21**.

X-ray crystal structure analysis of complex 21: formula $C_{57}H_{91}N_2O_3PScSi$, M = 956.34, colourless crystal, 0.25 x 0.15 x 0.10 mm, a = 12.597(2), b = 13.050(2), c = 19.355(3) Å, β = 76.139(5) °, V = 2950.1(9) Å^3, ρ_{calc} = 1.077 gcm^{-3}, μ = 0.212 mm^{-1}, empirical absorption correction ($0.948 \leq T \leq 0.979$), Z = 2, triclinic, space group P -1, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 112134 reflections collected ($\pm h$, $\pm k$, $\pm l$), 13581 independent (R(int) = 0.1207) and 8633 observed reflections [$I>2\sigma(I)$], 561 refined parameters, R = 0.0615, wR^2 = 0.1997, max. (min.) residual electron density 1.399 (-0.620) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 22:



^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_5Br, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.69 / 7.20 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.39 / 7.08 (*o*-*Ph*$_3$P / *m*-*Ph*$_3$P), 7.25 / 6.73 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_5Br, 298 K): δ ^{1}H / δ ^{13}C = 7.69 / 133.6 (*o*-*Ph*$_2$P), 7.39 / 134.3 (*o*-*Ph*$_3$P), 7.25 / 125.0 (*m*-O*Ar*), 7.20 / 129.4 (*m*-*Ph*$_2$P), 7.19 / 132.2 (*p*-*Ph*$_2$P), 7.08 / 129.6 (*m*-*Ph*$_3$P), 7.07 / 131.9 (*p*-*Ph*$_3$P), 6.73 / 116.5 (*p*-O*Ar*), 3.19 / 46.1 (P*C*H$_2$), 1.64 / 32.3 (C(*C*H$_3$)$_3$), 1.39 / 34.8 (OC(*C*H$_3$)$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_5Br, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.25 / 163.1, 125.0, 35.5 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.73 / 138.7 (*p*-O*Ar* / *o*-O*Ar*), 1.64 / 138.7, 35.5 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.39 / 74.5, 46.1 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$).

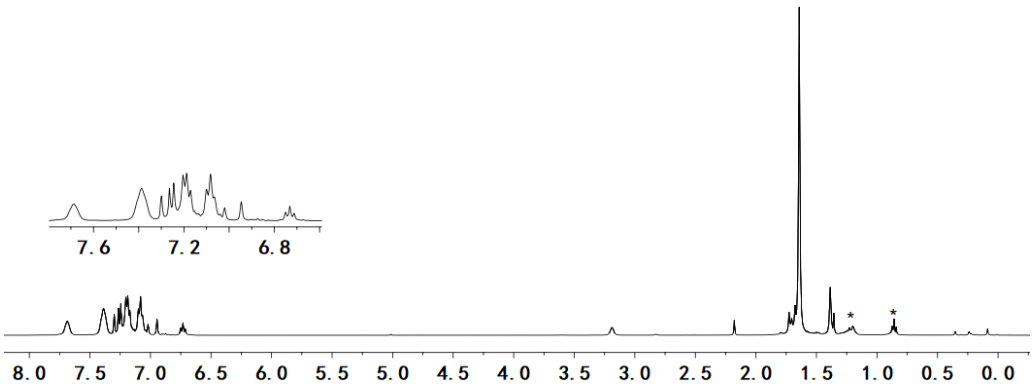


Fig. S55. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K) [*: Hexane].

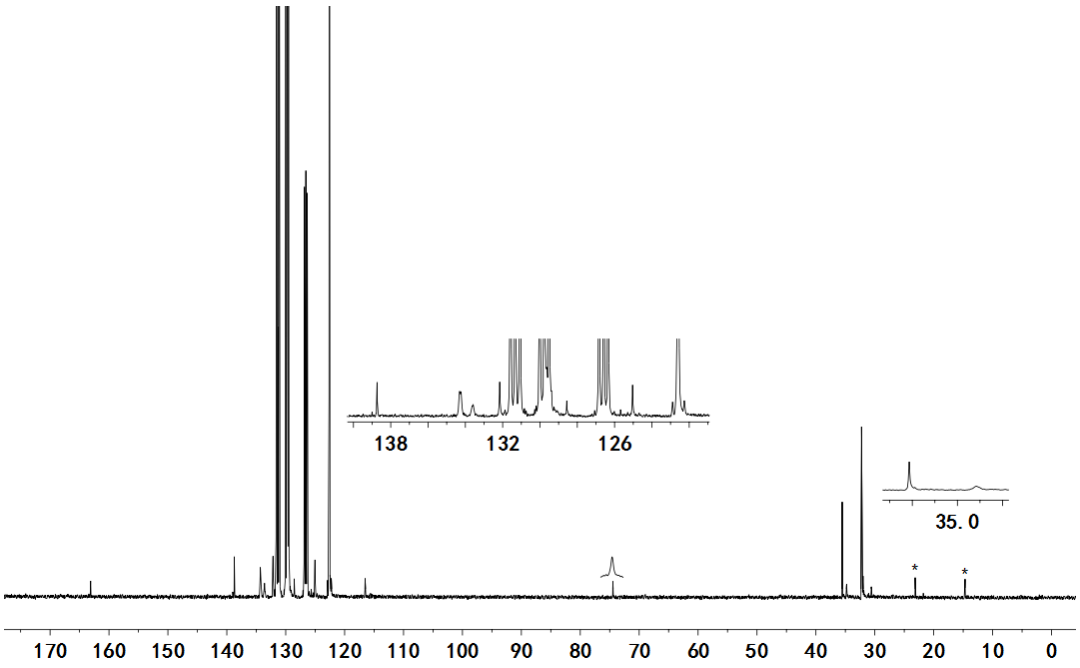


Fig. S56. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_5Br, 298 K) [*: Hexane].

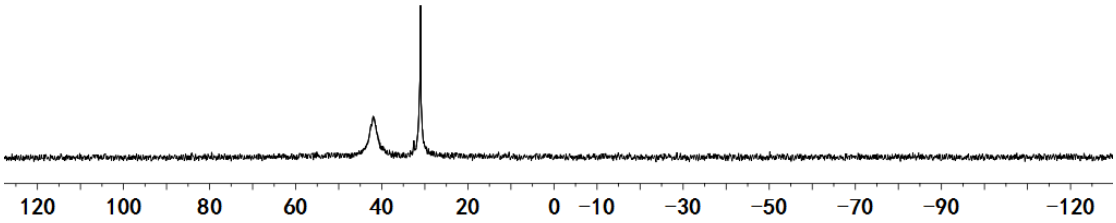


Fig. S57. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_5Br, 298 K).

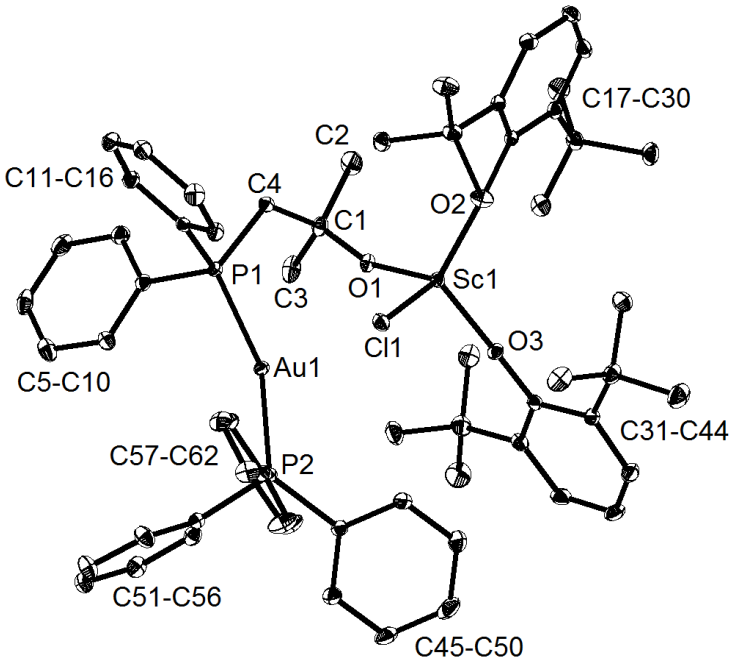
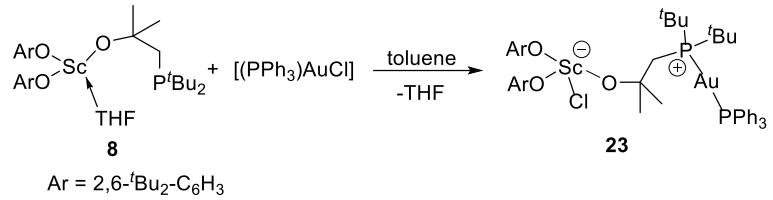


Fig. S58. Crystal structure of complex **22**.

X-ray crystal structure analysis of complex 22: formula $C_{135}H_{150}Au_2Cl_2O_6P_4Sc_2$, *M* = 2547.17, colourless crystal, 0.25 x 0.09 x 0.08 mm, *a* = 9.8155(5), *b* = 13.3604(7), *c* = 25.1505(13) Å, *β* = 87.393(2) °, *V* = 3094.7(3) Å^3, ρ_{calc} = 1.367 gcm^{-3}, μ = 2.616 mm^{-1}, empirical absorption correction (0.520 ≤ T ≤ 0.811), *Z* = 1, triclinic, space group *P* -1, λ = 0.71073 Å, *T* = 120(2) K, Multi-scan, 119409 reflections collected (±*h*, ±*k*, ±*l*), 14222 independent (*R*(int) = 0.0722) and 13239 observed reflections [*I*>2*σ*(*I*)], 690 refined parameters, *R* = 0.0238, *wR*^{2} = 0.0661, max. (min.) residual electron density 1.050 (-0.568) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

Characterization of complex 23:



8 **23**

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

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.42 / 7.54 (*o*-*Ph*$_3$P / *m*-*Ph*$_3$P), 7.10 / 6.55 (*m*-O*Ar* / *p*-O*Ar*).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, $CDCl_3$, 298 K): δ ^{1}H / δ ^{13}C = 7.62 / 132.8 (*p*-*Ph*$_3$P), 7.54 / 130.0 (*m*-*Ph*$_3$P), 7.42 / 133.9 (*o*-*Ph*$_3$P), 7.10 / 124.2 (*m*-O*Ar*), 6.55 / 115.2 (*p*-O*Ar*), 2.67 / 36.4 (P*C*H$_2$), 1.58 / 34.0 (OC(*C*H$_3$)$_2$), 1.50 / 31.5 (C(*C*H$_3$)$_3$), 1.43 / 30.6 (PC(C*H*$_3$)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, $CDCl_3$, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.10 / 162.9, 124.2, 35.2 (*m*-O*Ar* / *i*-O*Ar*, *m*-O*Ar*, *C*(CH$_3$)$_3$), 6.55 / 138.8 (*p*-O*Ar* / *o*-O*Ar*), 2.67 / 75.0, 34.0 (PC*H*$_2$ / O*C*(CH$_3$)$_2$, OC(*C*H$_3$)$_2$), 1.58 / 74.9, 36.4 (OC(C*H*$_3$)$_2$ / O*C*(CH$_3$)$_2$, P*C*H$_2$), 1.50 / 138.8, 35.2 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.43 / 36.9 (PC(C*H*$_3$)$_3$, / P*C*(CH$_3$)$_3$).

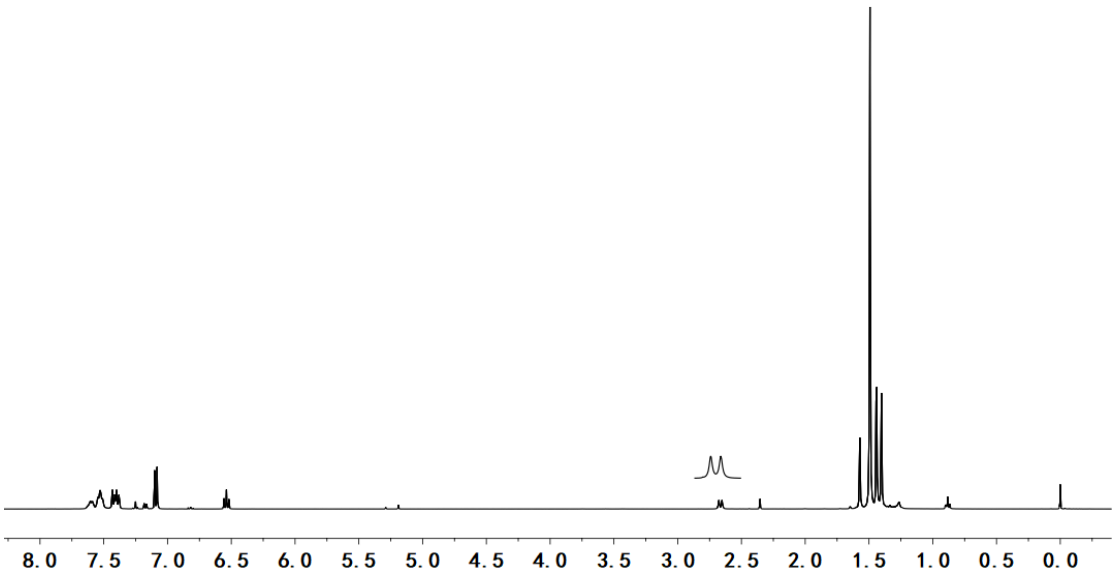


Fig. S59. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

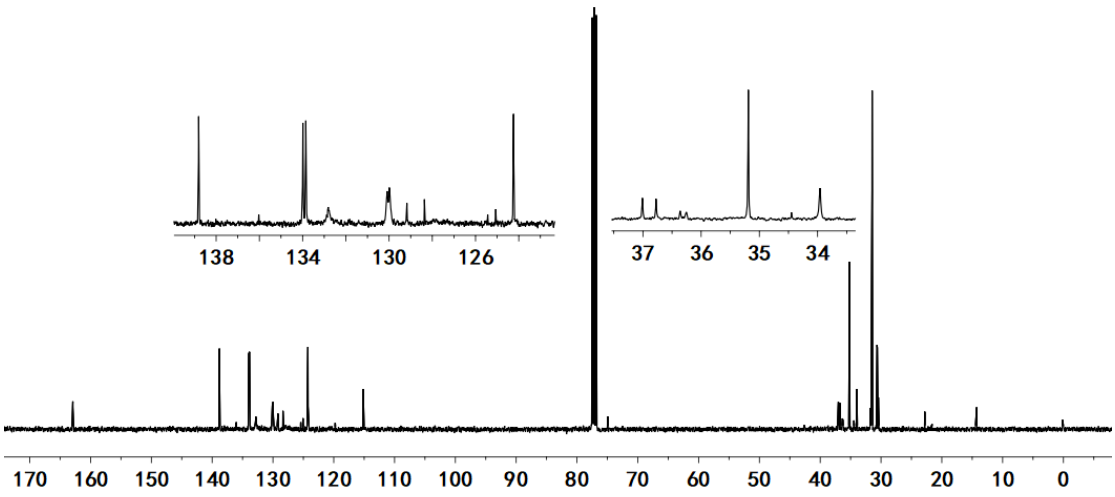


Fig. S60. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$, 298 K).

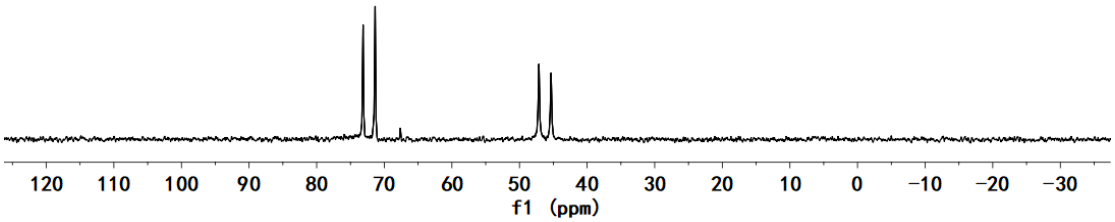


Fig. S61. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, $CDCl_3$, 298 K).

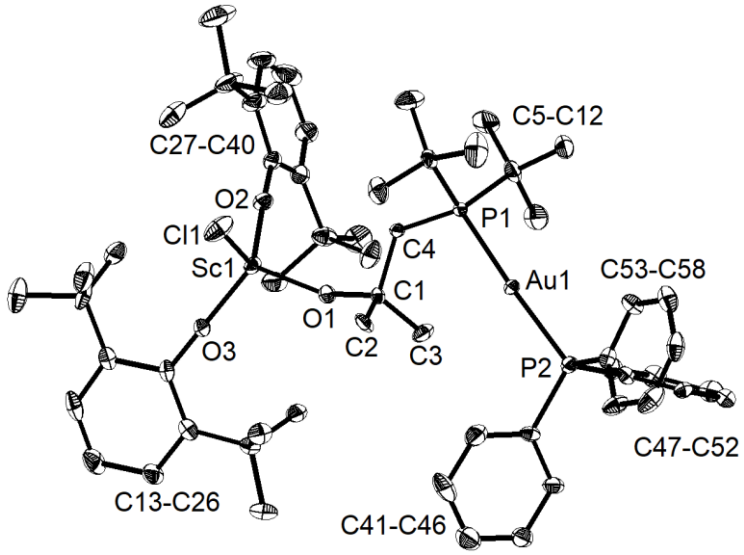


Fig. S62. Crystal structure of complex **23.**

X-ray crystal structure analysis of complex 23: formula $C_{58}H_{83}AuClO_3P_2Sc$, M = 1167.57, colourless crystal, 0.20 x 0.15 x 0.10 mm, a = 13.830(3), b = 14.691(3), c = 16.094(3) Å, β = 102.67(3) (5)°, V = 2848.6(12) Å^3, ρ_{calc} = 1.361 gcm^{-3}, μ = 2.835 mm^{-1}, empirical absorption correction (0.562 ≤ T ≤ 0.753), Z = 2, triclinic, space

group *P* -1, λ = 0.71073 Å, *T* = 293 K, Multi-scan, 27711 reflections collected (±*h*, ±*k*, ±*l*), 13055 independent (*R*(int) = 0.0250) and 12278 observed reflections [*I*>2σ(*I*)], 690 refined parameters, *R* = 0.0262, wR^2 = 0.0515, max. (min.) residual electron density 0.999 (-0.635) e.$Å^{-3}$, hydrogen atoms were calculated and refined as riding atoms.