Scandium complexes containing *β*-diketiminato ligands with pendant phosphanyl groups: competition between Sc/γ-C [4+2] cycloaddition and Sc/P frustrated Lewis pair reactions

Tu Yao, Pengfei Xu and 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

Supporting Information

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 and a Bruker 600 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-tert-butylphenol was purchased from ACROS. Complex **6a**[1], $CH_3C(2,6\text{-}iPr_2C_6H_3N)CHC(CH_3)(NHCH_2CH_2CH_2PPh_2)$[2], 2-(diphenylphosphino)ethanamine[3], $Sc(CH_2SiMe_3)_3(THF)_2$[4], 4-(2,6-diisopropylphenyl)amino-3-methylpent-3-en-2-one[5] were synthesized by following the literature procedures.

References

[1] P. Xu, Y. Yao and X. Xu, *Chem. - Eur. J.*, 2017, **23**, 1263-1267.

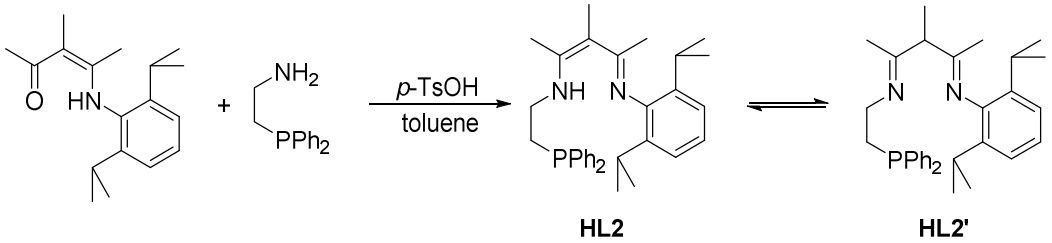
[2] M. Chen, S. Jiang, L. Maron and X. Xu, *Dalton Trans.*, 2019, **48**, 1931-1935.

[3] W. Jia, X. Chen, R. Guo, C. Sui-Seng, D. Amoroso, A. J. Lough and K. Abdur-Rashi, *Dalton Trans.*, 2009, **39**, 8301-8307.

[4] M. F. Lappert and R. Pearce, *J. Chem. Soc*., *Chem. Commun.*, 1973, **4**, 126.

[5] B. Liu, H. Li, C.-S. Ha, I. Kim and W. Yan, *Macromol. Res.*, 2008, **16**, 441-445.

Characterization of HL2:



HL2 **HL2'**

Scheme S1.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: for **HL2**: δ ^{1}H / δ ^{1}H = 12.5 / 3.25 (N*H* / NHCH_2), 7.35 / 7.02 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.22 / 7.12 (*m*-N*Ar* / *p*-N*Ar*), 3.25 / 2.25 (NHCH_2 / PCH_2). 3.17 / 1.23, 1.20 (ArC*H*Me$_2$ / ArCH*Me*$_2$). For **HL2'**: δ ^{1}H / δ ^{1}H = 7.51 / 7.08 (*o*-*Ph*P / *m*-*Ph*P), 7.16 / 7.11 (*m*-N*Ar* / *p*-N*Ar*), 3.41 / 1.41 (γ-C*H*Me / γ-CH*Me*), 3.40 / 2.53 (NCH_2 / PCH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): for **HL2**: δ ^{1}H / δ ^{13}C = 7.35 / 133.0 (*o*-*Ph*$_2$P), 7.22 / 123.4 (*m*-N*Ar*), 7.12 / 123.3 (*p*-N*Ar*), 7.04 / 128.73 (*p*-*Ph*$_2$P), 7.02 / 128.76 (*m*-*Ph*$_2$P), 3.25 / 41.0 (NH*C*H_2), 3.17 / 28.6 (Ar*C*H*C*Me$_2$), 2.25 / 31.4 (P*C*H_2), 1.80 / 15.9 (*Me*C), 1.77 / 20.3 (*Me*C), 1.57 / 15.1 (γ-C*Me*), 1.23 / 24.4 (ArCH*Me*$_2$), 1.20 / 23.2 (ArCH*Me*$_2$). For **HL2'**: δ ^{1}H / δ ^{13}C = 7.51 / 133.3 (*o*-*Ph*P), 7.49 / 133.1 (*o*-*Ph*'P), 7.16 / 123.8 (*m*-N*Ar*), 7.11 / 123.6 (*p*-N*Ar*), 7.08 / 128.82, 128.8 (*m*, *p*-*Ph*P), 7.07 / 128.79, 128.7 (*m*, *p*-*Ph*'P), 7.05 / 123.4 (*m*-N*Ar*), 3.41 / 56.7 (γ-*C*H*C*Me), 3.40 / 48.9 (N*C*H_2), 3.01 / 28.2 (Ar*C*H*C*Me$_2$), 2.89 / 28.4 (Ar*C*H*C*Me$_2$), 2.53 / 30.8 (P*C*H_2), 1.53 / 18.8 (*Me*C), 1.51 / 16.0 (*Me*C), 1.41 / 15.2 (γ-CH*Me*), 1.22 / 23.6, 23.5 (ArCH*Me*$_2$), 1.16 / 24.5, 23.1 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: for **HL2**: δ ^{1}H / δ ^{13}C = 7.35 / 128.73 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.22 / 147.0, 28.6 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.12 / 138.5 (*p*-N*Ar* / *o*-N*Ar*), 3.25 / 153.4, 31.4 (NHCH_2 / Me*C*, PCH_2), 3.17 / 147.0, 138.5, 123.4 (Ar*C*H*C*Me$_2$ / *i*, *o*, *m*-NAr), 2.25 / 139.1 (PCH_2 / *i*-*Ph*$_2$P), 1.80, 1.77 / 95.8 (*Me*C / γ-*C*), 1.57 / 167.9, 153.4 (γ-C*Me* / Me*C*). For **HL2'**: δ ^{1}H / δ ^{13}C = 7.51 / 128.8 (*o*-*Ph*P / *p*-*Ph*P), 7.49 / 128.7 (*o*-*Ph*'P / *p*-*Ph*'P), 7.16 / 147.2, 28.4 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.11 / 136.3 (*p*-N*Ar* / *o*-N*Ar*), 3.41 / 18.8 (γ-C*H* / Me*C*), 3.40 / 171.3 (NCH_2 / Me*C*), 3.01 / 147.2, 136.3, 123.4 (ArC*H*Me$_2$ / *i*, *o*, *m*-NAr), 2.53

/ 139.9 (PCH_2 / *i-Ph*P), 1.53 / 56.7 (*Me*C / γ-*C*), 1.41 / 171.3, 169.1 (γ-C*Me* / Me*C*).

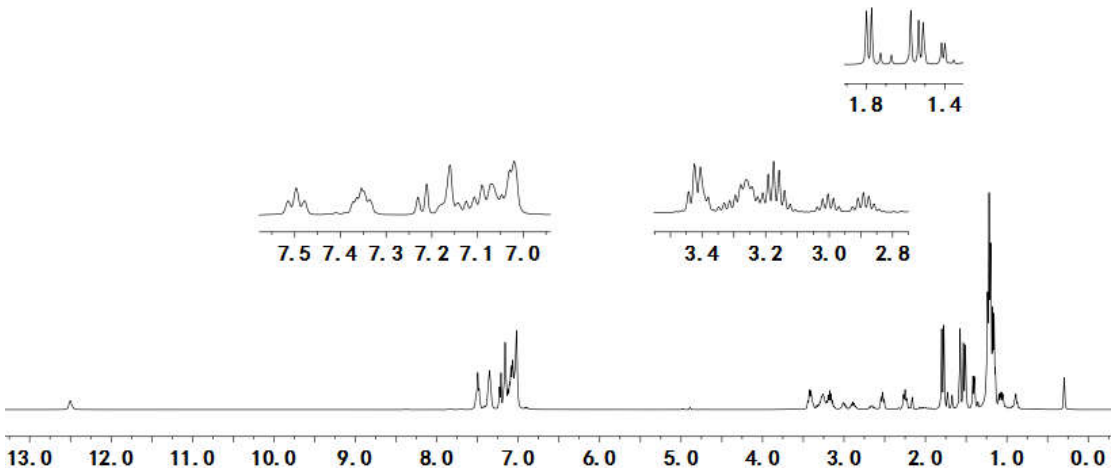


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

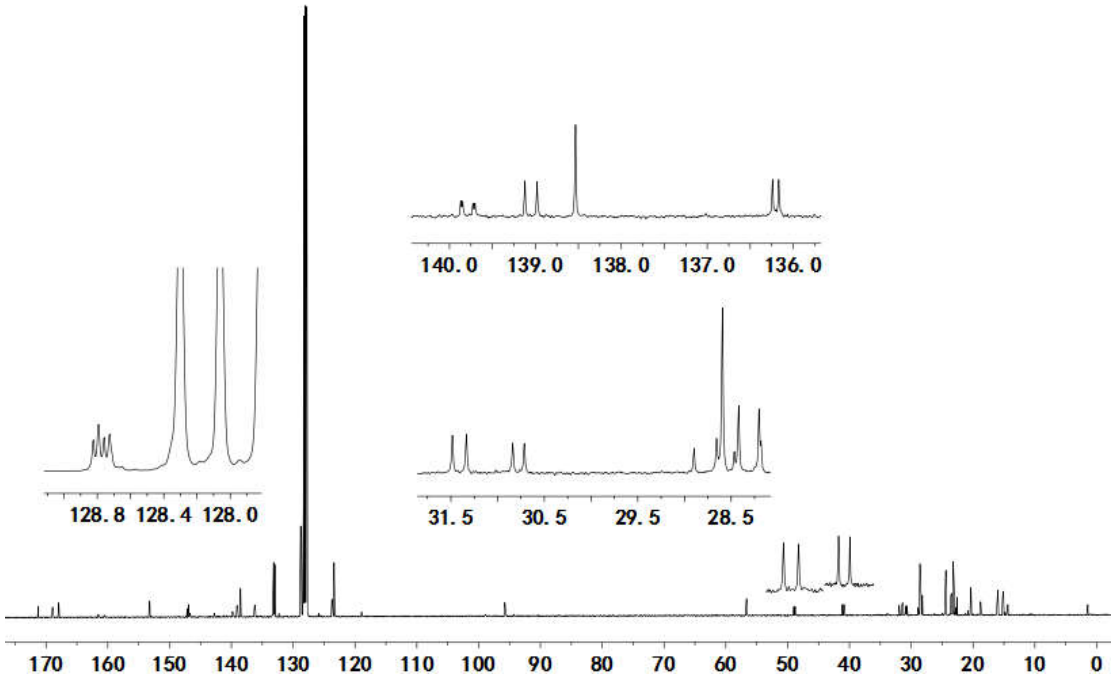


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

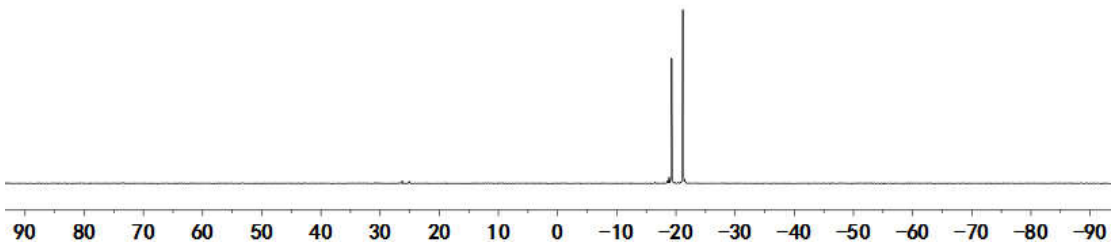
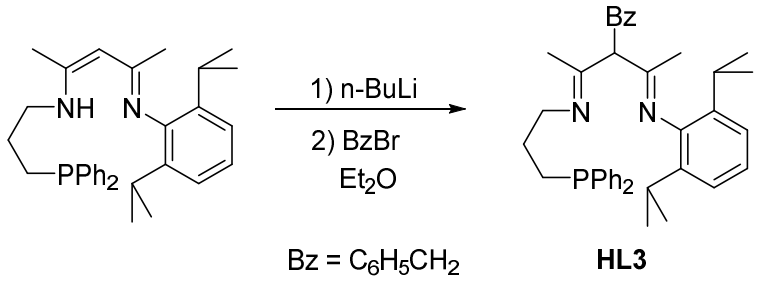


Fig. S3. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

Characterization of HL3:



Scheme S2.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.51 / 7.09 (*o*-*Ph*P / *m*-*Ph*P), 7.49 / 7.07 (*o*-*Ph*'P / *m*-*Ph*'P), 7.11 / 7.03 (*m*-CH_2*Ph* / *p*-CH_2*Ph*), 7.13 / 7.08 (*m*-N*Ar* / *p*-N*Ar*), 3.92 / 3.30, 1.66 (γ-C*H* / C*H*$_2$Ph, *Me*C), 3.16, 2.15 / 1.90 (NC*H*$_2$, PC*H*$_2$ / NCH$_2$C*H*$_2$), 2.75 / 1.17, 1.08 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.56 / 1.12, 1.05 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.51 / 133.2 (*o*-*Ph*P), 7.49 / 133.1 (*o*-*Ph*'P), 7.19 / 129.4 (*o*-CH_2*Ph*), 7.13 / 123.4 (*m*-N*Ar)*, 7.11 / 123.3 (*m*-CH_2*Ph*), 7.10 / 123.9 (*m*-N*Ar*), 7.09 / 128.77, 128.70 (*m*, *p*-*Ph*P), 7.08 / 128.7 (*p*-N*Ar)*, 7.07 / 128.68, 128.63 (*m*, *p*-*Ph*'P), 7.03 / 126.4 (*p*-CH_2*Ph*), 3.92 / 63.5 (γ-*CH*), 3.29 / 36.0 (*CH*$_2$Ph), 3.16 / 52.5 (N*CH*$_2$), 2.75 / 28.2 (ArCH*Me*$_2$), 2.56 / 28.0 (ArCH*Me*$_2$), 2.15 / 26.5 (P*CH*$_2$), 1.90 / 27.8 (NCH$_2$*CH*$_2$), 1.66 / 17.1 (*Me*C), 1.55 / 18.6 (*Me*C), 1.17 / 23.6 (ArCH*Me*$_2$), 1.12 / 23.9 (ArCH*Me*$_2$). 1.08 / 23.2 (ArCH*Me*$_2$), 1.05 / 23.1 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.51 / 128.70 (*o*-*Ph*P / *p*-*Ph*P), 7.49 / 128.63 (*o*-*Ph*'P / *p*-*Ph*'P), 7.19 / 126.4, 36.0 (*o*-CH_2*Ph* / *p*-CH_2*Ph*, *C*H$_2$Ph), 7.13 / 146.9, 28.2 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.11 / 140.5 (*m*-CH_2*Ph* / *i*-CH_2*Ph*), 7.10 / 146.9, 28.0 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.09 / 139.9 (*m*-*Ph*P / *i*-*Ph*P), 7.08 / 136.4 (*p*-N*Ar* / *o*-N*Ar*), 7.07 / 139.8 (*m*-*Ph*'P / *i*-*Ph*'P), 7.03 / 129.4 (*p*-CH_2*Ph* / *o*-CH_2*Ph*), 3.30 / 170.1, 129.4 (C*H*$_2$Ph / Me*C*, *o*-CH_2*Ph*), 3.16 / 167.6, 26.5 (NC*H*$_2$ / Me*C*, P*C*H$_2$), 2.75 / 146.9, 136.2, 123.4 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 2.15 / 139.9 (PC*H*$_2$ / *i*-*Ph*P).

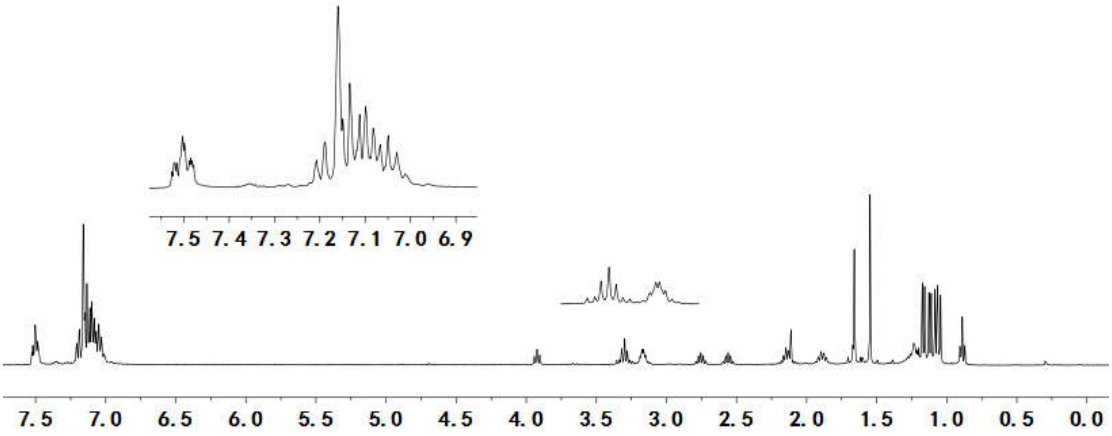


Fig. S4. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

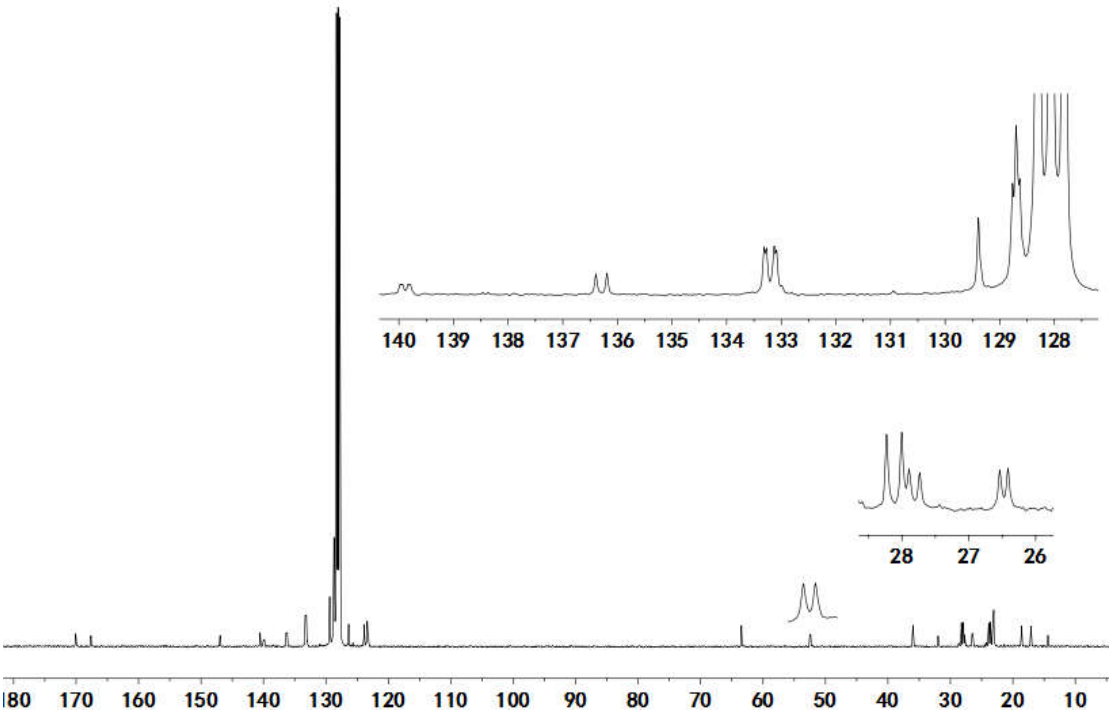


Fig. S5. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

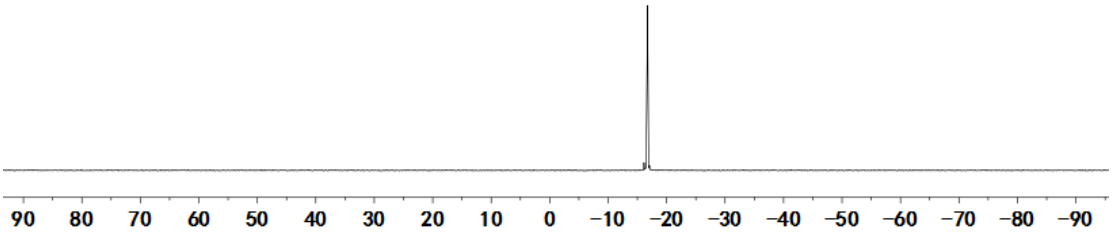
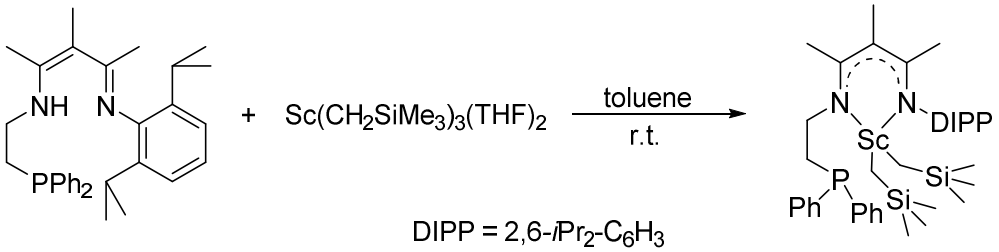


Fig. S6. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

Characterization of complex 4b:



HL2 **4b**

Scheme S3.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.51 / 7.11 (*o*-Ph_2P / *m*-Ph_2P), 7.11 / 7.05 (*m*-Ph_2P / *p*-Ph_2P), 3.49 / 2.41 (NCH_2 / PCH_2), 3.24 / 1.47, 1.12 (ArC*H*Me_2 / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.51 / 133.4 (*o*-Ph_2P), 7.17 / 126.4, 124.4 (*p*-N*Ar*, *m*-N*Ar*), 7.11 / 129.1 (*m*-Ph_2P), 7.05 / 129.9 (*p*-Ph_2P), 3.49 / 47.0 (NCH_2), 3.24 / 28.4 (Ar*CH*Me_2), 2.41 / 29.2 (P*CH*$_2$), 1.81 / 18.8 (γ-C*Me*), 1.73 / 21.2 (*Me*C), 1.66 / 17.3 (*Me*C), 1.47 / 25.1 (ArCH*Me*$_2$), 1.12 / 24.6 (ArCH*Me*$_2$), 0.10, 0.09 / 43.5 (*CH*$_2$SiMe_3), 0.05 / 4.0 (Si*Me*$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.51 / 129.9 (*o*-Ph_2P / *p*-Ph_2P), 7.17 / 144.3 (*m*-N*Ar* / *i*-N*Ar*), 7.17 / 142.7 (*p*-N*Ar* / *o*-N*Ar*), 7.11, 2.41 / 135.4 (*m*-Ph_2P, PCH_2 / *i*-Ph_2P), 7.05 / 133.4 (*p*-Ph_2P / *o*-Ph_2P), 3.49 / 162.6 (NCH_2 / Me*C*), 3.24 / 144.3, 142.7, 124.4 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 1.81 / 164.5, 162.6 (γ-C*Me* / C*Me*), 1.73, 1.66 / 99.4, (*Me*C / γ-*C*), 1.47, 1.12 / 142.7 (ArCH*Me*$_2$ / *o*-N*Ar*), 0.05 / 43.5 (Si*Me*$_3$ / *C*H_2Si*Me*$_3$).

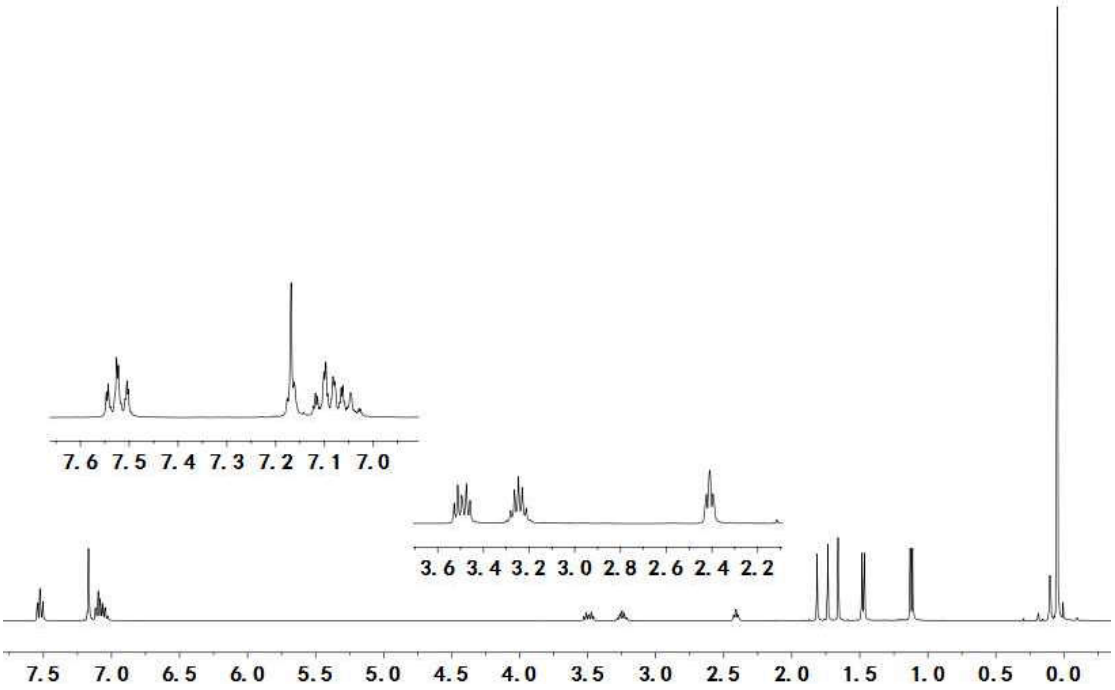


Fig. S7. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

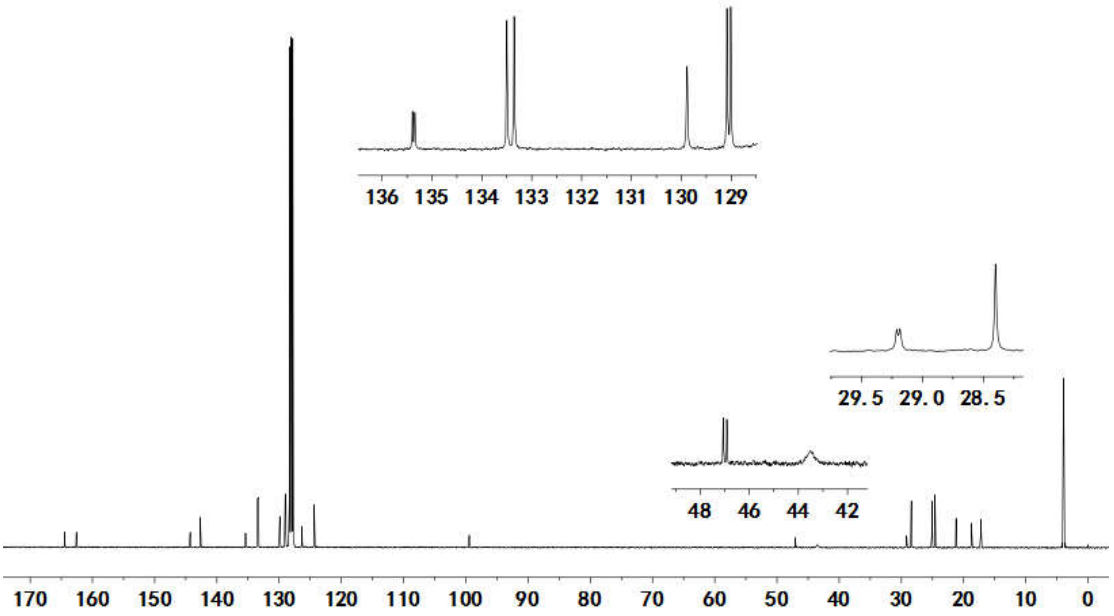


Fig. S8. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

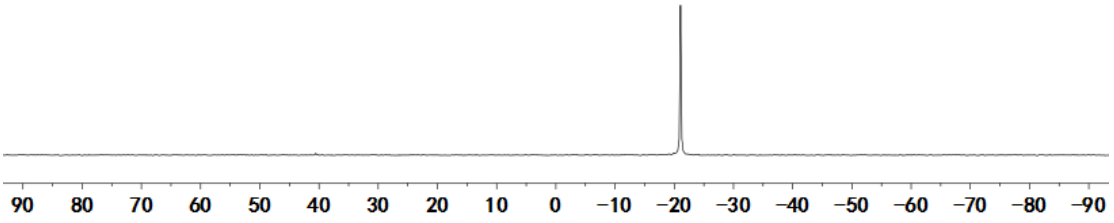
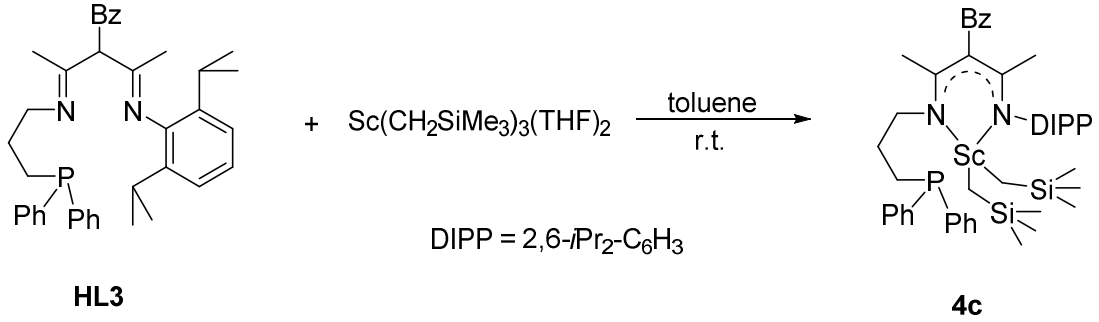


Fig. S9. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

Characterization of complex 4c:



Scheme S4.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.45 / 7.10 (*o*-Ph_2P / *m*-Ph_2P), 7.18 / 7.09 (*m*-CH_2Ph / *o*-CH_2Ph), 7.10 / 7.07 (*m*-Ph_2P / *p*-Ph_2P), 3.85 / 1.72 (NCH_2 / NCH_2CH_2), 3.10 / 1.33, 1.06 (ArC*H*Me_2 / ArCH*Me*$_2$), 2.00 / 1.72 (PCH_2 / NCH_2CH_2).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.45 / 133.2 (*o*-Ph_2P), 7.18 / 126.3 (*m*-CH_2Ph), 7.10 / 129.0 (*m*-Ph_2P), 7.09 / 127.1 (*o*-CH_2Ph), 7.08 / 128.0, 124.5 (*p*-N*Ar*, *m*-N*Ar*), 7.07 / 128.9 (*p*-Ph_2P), 7.06 / 127.7 (*p*-CH_2Ph), 3.85 / 48.5 (NCH_2), 3.64 / 37.5 (CH_2Ph), 3.10 / 28.5 (ArC*H*Me_2), 2.00 / 26.1 (PCH_2), 1.78 / 17.6 (*Me*C), 1.72 / 28.8 (NCH_2CH_2), 1.53 / 20.7 (*Me*C), 1.33 / 25.3 (ArCH*Me*$_2$), 1.06 / 24.3 (ArCH*Me*$_2$), 0.19 / 3.7 (Si*Me*$_3$), 0.06, 0.04 / 41.7 (CH_2SiMe_3).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.45 / 128.9 (*o*-Ph_2P / *p*-Ph_2P), 7.10 / 138.7 (*m*-Ph_2P / *i*-Ph_2P), 7.09 / 37.5 (*o*-CH_2Ph / CH_2Ph), 7.08 / 140.6 (*m*-N*Ar* / *i*-N*Ar*), 7.08 / 143.4 (*p*-N*Ar* / *o*-N*Ar*), 7.07 / 133.2 (*p*-Ph_2P / *o*-Ph_2P), 3.85 / 167.4, 26.1 (NCH_2 / Me*C*, PCH_2), 3.64 / 167.4, 141.3, 127.1 (CH_2Ph / Me*C*, *i*-CH_2Ph, *o*-CH_2Ph), 3.10 / 143.4, 140.6, 124.5 (ArC*H*Me_2 / *o*, *i*, *m*-N*Ar*), 2.00 / 138.7 (PCH_2 / *i*-Ph_2P), 1.78, 1.53 / 102.9 (*Me*C / γ-*C*), 1.33, 1.06 / 143.4 (ArCH*Me*$_2$ / *o*-N*Ar*), 0.19 / 41.7 (Si*Me*$_3$ / CH_2SiMe_3).

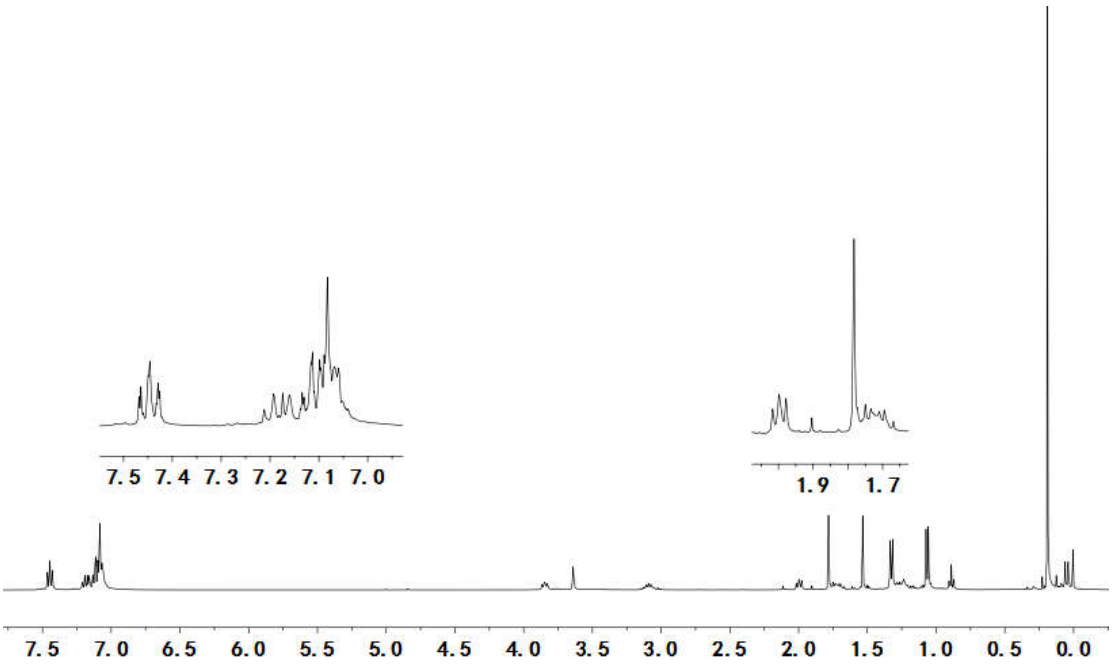


Fig. S10. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

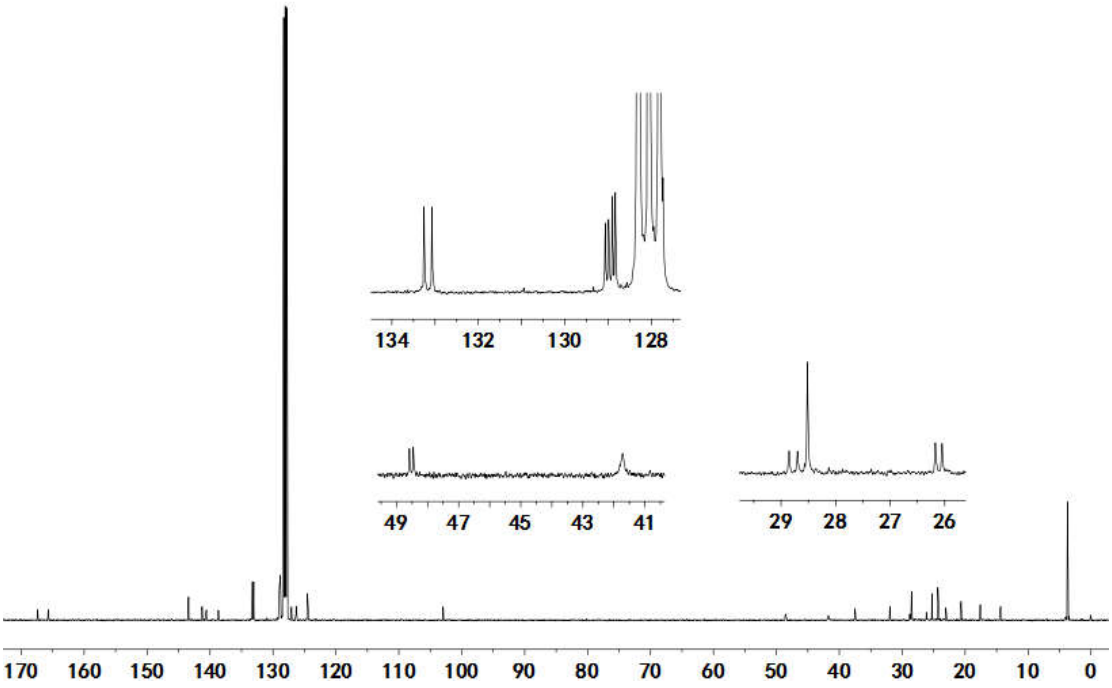


Fig. S11. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

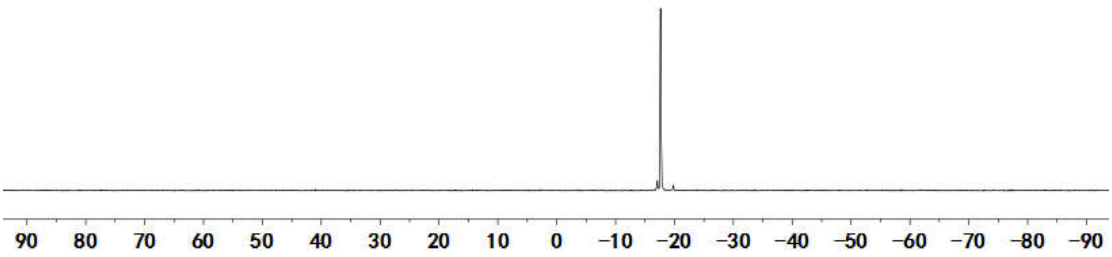
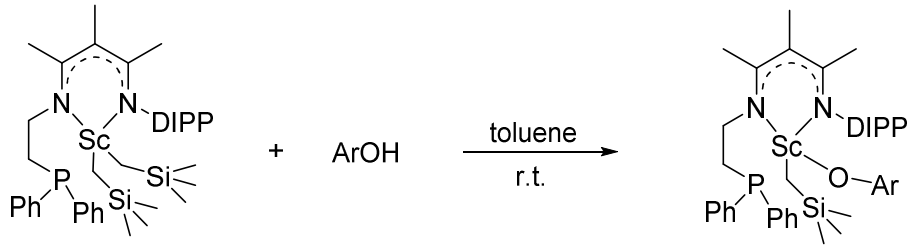


Fig. S12. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

Characterization of complex 5b:



4b **5b**

Ar = 2,6-*t*Bu$_2$-C$_6$H$_3$

Scheme S5.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: 7.51 / 7.11 (*o*-*Ph*P / *m*-*Ph*P), 7.45 / 7.05 (*o*-*Ph*'P / *m*-*Ph*'P), 7.30 / 6.85 (*m*-O*Ar* / *p*-O*Ar*), 3.90 / 2.70 (NCH_2 / PCH_2), 3.31 / 1.38, 1.14 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.71 / 1.23, 0.96 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.51 / 133.3 (*o*-*Ph*P), 7.45 / 133.2 (*o*-*Ph*'P), 7.30 / 125.2 (*m*-O*Ar*), 7.11 / 129.3, 129.0 (*p*, *m*-*Ph*P), 7.10 / 126.3, 124.5, 124.4 (*p*, *m*-N*Ar*), 7.05 /129.2, 128.9 (*p*, *m*-*Ph*'P), 6.85 / 117.9 (*p*-O*Ar*), 3.90, 3.74 / 48.2 (NCH_2), 3.31 / 28.8 (ArC*H*Me$_2$), 2.71 / 28.2 (ArC*H*Me$_2$), 2.70, 2.41 / 30.9 (PCH_2), 1.66 / 17.8 (*Me*C), 1.62 / 21.5 (*Me*C), 1.58 / 18.2 (γ-C*Me*), 1.46 / 31.3 (C(CH_3)$_3$), 1.38 / 24.6 (ArCH*Me*$_2$), 1.23 / 24.8 (ArCH*Me*$_2$), 1.14 / 25.5 (ArCH*Me*$_2$), 0.96 / 24.7 (ArCH*Me*$_2$), 0.31, 0.19 / 42.1 (*C*H_2SiMe$_3$), 0.08 / 4.0 (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 = 7.51 / 129.3 (*o*-*Ph*P / *p*-*Ph*P), 7.45 / 129.2 (*o*-*Ph*'P / *p*-*Ph*'P), 7.30 / 162.6, 35.0 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.10 / 145.0 (*m*-N*Ar* / *i*-N*Ar*), 7.10 / 142.6 (*p*-N*Ar* / *o*-N*Ar*), 6.85 / 138.1 (*p*-O*Ar* / *o*-O*Ar*), 3.90, 3.74 / 166.3 (NCH_2 / Me*C*), 3.31 / 145.0, 142.6, 124.4 (ArC*H*Me$_2$ / *i*, *o*, *m*-NAr), 2.71 / 145.0, 142.7, 124.5 (ArC*H*Me$_2$ / *i*, *o*, *m*-NAr), 2.70, 2.41 / 138.0 (PCH_2 / *i*-*Ph*P), 1.66, 1.62 / 98.1 (*Me*C / γ-*C*), 1.58 / 166.3, 162.4 (γ-C*Me* / Me*C*), 1.46 / 138.1 (C(CH_3)$_3$ / *o*-O*Ar*), 1.38, 1.14 / 142.6 (ArCH*Me*$_2$ / *o*-N*Ar*), 1.23, 0.96 / 142.7 (ArCH*Me*$_2$ / *o*-N*Ar*), 0.31, 0.19 / 4.0 (CH_2SiMe$_3$ / Si*Me*$_3$), 0.08 / 42.1 (CH$_2$Si*Me*$_3$ / *C*H$_2$SiMe$_3$).

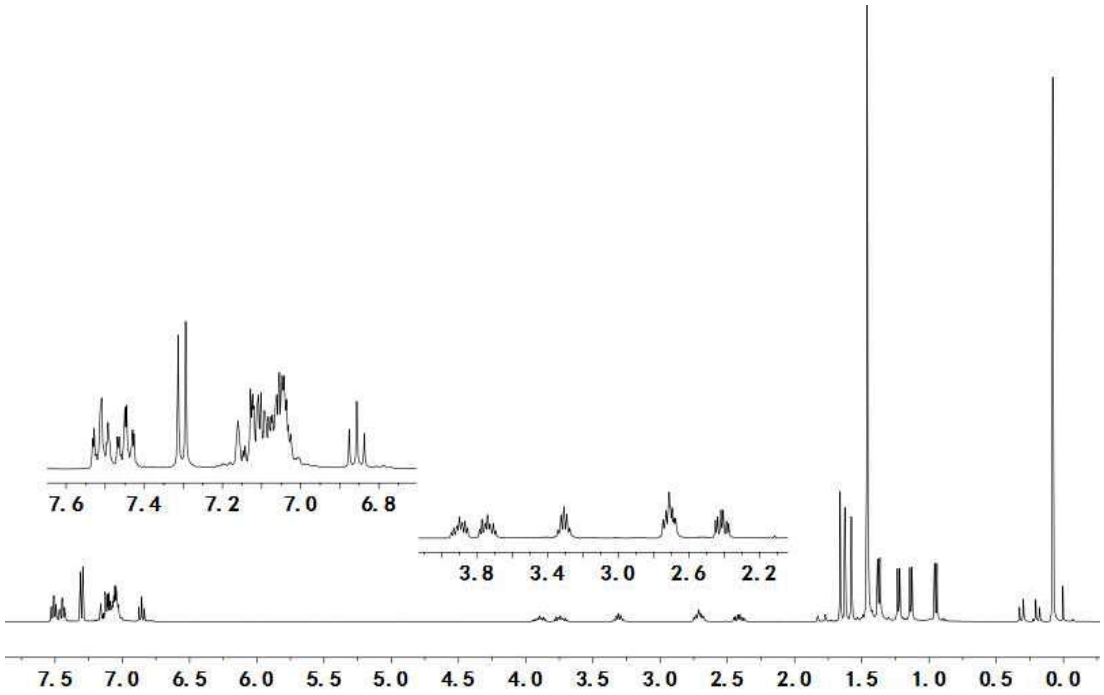


Fig. S13. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

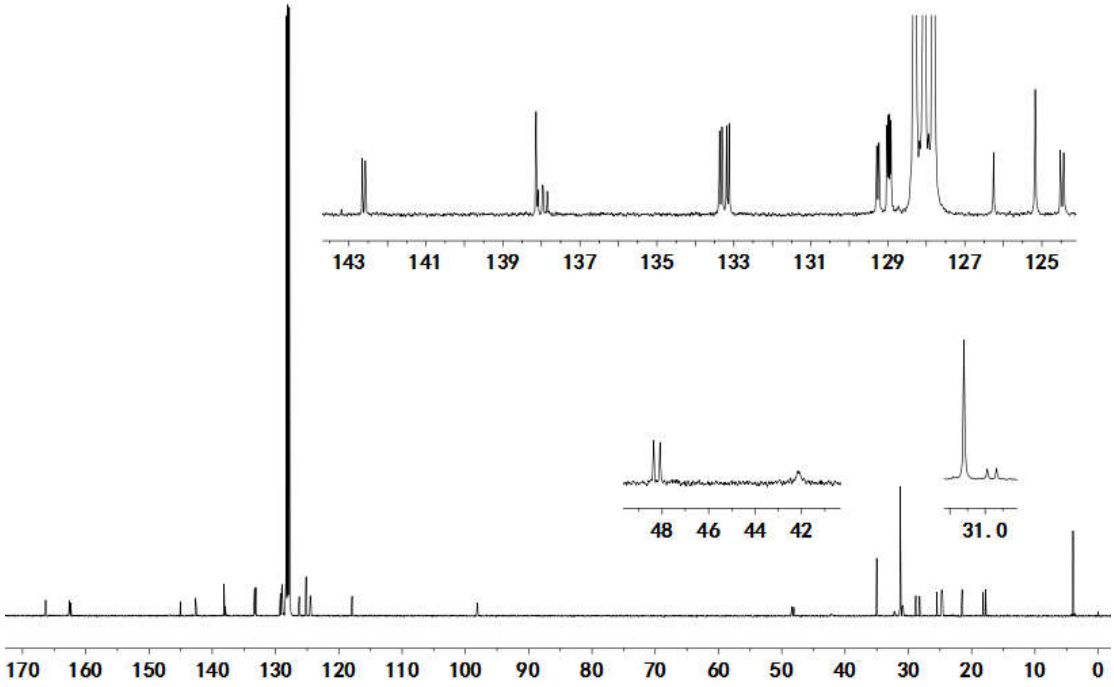


Fig. S14. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

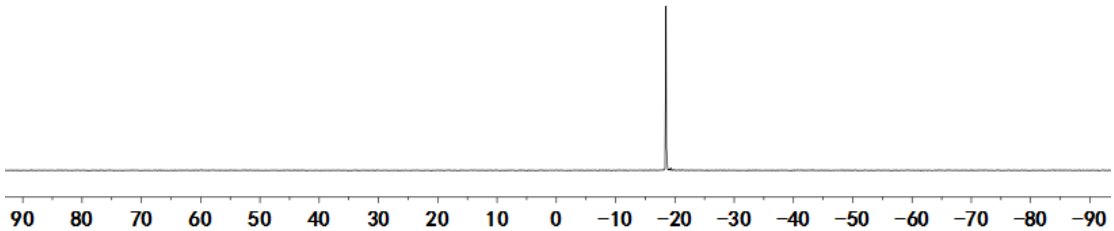


Fig. S15. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 5b: formula $C_{50}H_{72}N_2OPScSi \cdot 0.5C_6H_{14}$, M = 864.20, colorless crystal, 0.20 x 0.15 x 0.10 mm, a = 9.7689(7), b = 13.2332(9), c = 21.5000(12) Å, β = 102.325(5)°, V = 2555.4(3) Å^3, ρ_{calc} = 1.123 gcm^{-3}, μ = 0.236 mm^{-1}, empirical absorption correction (0.8596 ≤ T ≤1.0000), Z = 2, Triclinic, space group P -1, λ = 0.71073 Å, T = 293(2) K, Multi-scan, 28994 reflections collected (±h, ±k, ±l), 13310 independent (R(int) = 0.0808) and 5919 observed reflections [I>2σ(I)], 534 refined parameters, R = 0.0839, wR2 = 0.1969, max. (min.) residual electron density 0.792 (-0.408) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

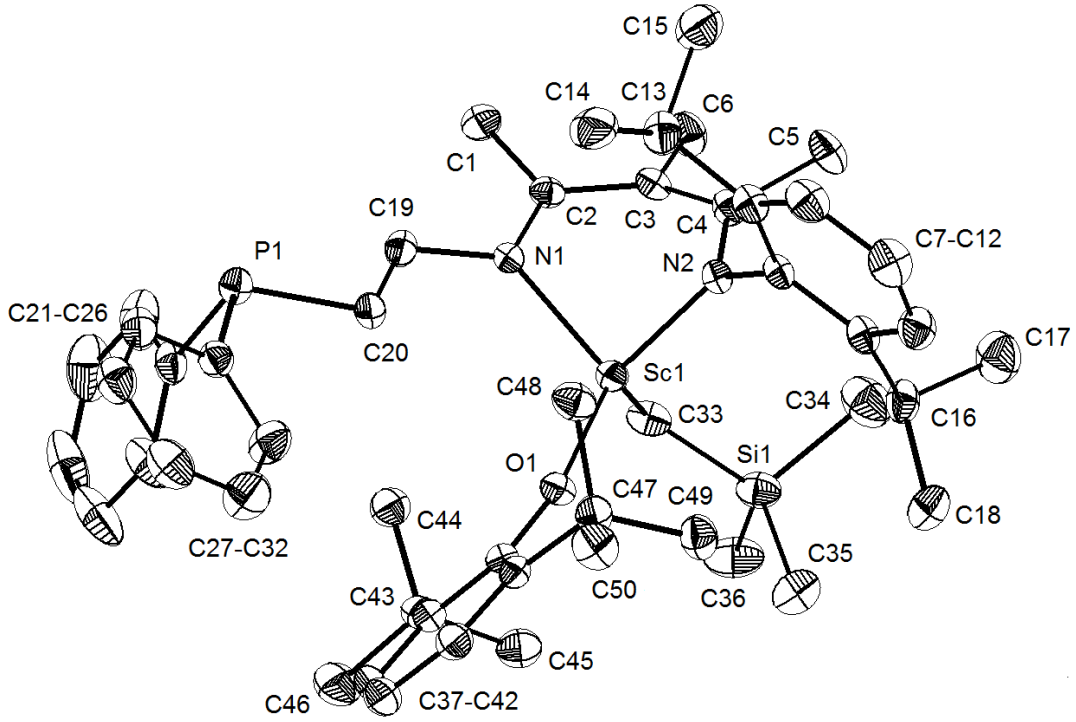
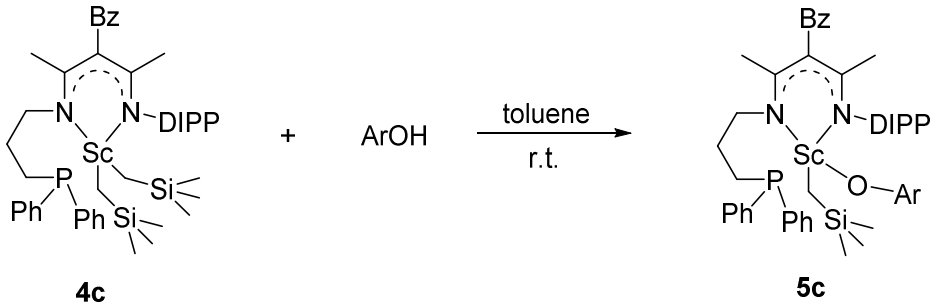


Fig. S16. Molecular structure of complex **5b**.

Characterization complex 5c:



4c **5c**

Ar = 2,6-*t*Bu$_2$-C$_6$H$_3$

Scheme S6.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: 7.39 / 7.08 (*o*-*Ph*P / *m*-*Ph*P), 7.36 / 6.89 (*m*-O*Ar* / *p*-O*Ar*), 7.07 / 7.04 (*p*-NAr / *m*-NAr), 3.89 / 1.93 (NCH_2 / NCH$_2$CH_2), 3.31 / 1.37, 1.13 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.74 / 1.20, 1.05 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.99 / 1.69 (PCH_2 / NCH$_2$CH_2), 0.40 / 0.22 (CH_2SiMe$_3$ / CH_2SiMe$_3$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.39 / 133.2, 133.0 (*o*-*Ph*P, *o*-*Ph*'P), 7.36 / 125.2 (*m*-O*Ar*), 7.10 / 126.3 (*m*-CH$_2$*Ph*), 7.09 / 124.6 (*m*-NAr), 7.08 / 129.0, 128.87 (*p*, *m*-*Ph*P), 7.08 /128.94, 128.8 (*p*, *m*-*Ph*'P), 7.07 / 126.4 (*p*-NAr), 7.06 / 128.92 (*p*-CH$_2$*Ph*), 7.05 / 127.9 (*o*-CH$_2$*Ph*), 7.04 / 124.5 (*m*-N*Ar*), 6.89 / 118.1 (*p*-O*Ar*), 3.89, 3.59 / 51.5 (NCH_2), 3.52 / 37.6 (CH_2Ph), 3.31 / 28.9 (ArC*H*Me$_2$), 2.74 / 28.2 (ArC*H*Me$_2$), 1.99, 1.97 / 26.4 (PCH_2), 1.93, 1.69 / 28.5 (NCH$_2$CH_2), 1.72 / 18.1 (*Me*C), 1.58 / 21.3 (*Me*C), 1.52 / 31.3 (C(CH_3)$_3$), 1.37 / 24.7 (ArCH*Me*$_2$), 1.20 / 25.0 (ArCH*Me*$_2$), 1.13 / 25.8 (ArCH*Me*$_2$), 1.05 / 25.1 (ArCH*Me*$_2$), 0.40, 0.22 / 41.7 (CH_2SiMe$_3$), 0.16 / 4.0 (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 = 7.39 / 129.0 (*o*-*Ph*P / *p*-*Ph*P), 7.36 / 162.4, 35.1 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.10 / 140.7 (*m*-CH$_2$Ph / *i*-CH$_2$*Ph*), 7.09 / 144.3, 28.9 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.06 / 127.9 (*p*-CH$_2$Ph / *o*-CH$_2$*Ph*), 7.05 / 37.6 (*o*-CH$_2$Ph / CH_2Ph), 7.04 / 144.3, 28.2 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 6.89 / 138.3 (*p*-O*Ar* / *o*-O*Ar*), 3.89, 3.59 / 168.1 (NCH_2 / Me*C*), 3.52 / 168.1, 127.9 (CH_2Ph / Me*C*, *o*-CH$_2$*Ph*), 3.31 / 144.3, 142.6, 124.6 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 1.99, 1.97 / 139.3 (PCH_2 / *i*-*Ph*P), 1.72, 1.58 / 101.5 (*Me*C /

γ-*C*), 1.52 / 138.3 (C(CH_3)$_3$ / *o*-O*Ar*), 1.37, 1.13 / 142.6 (ArCH*Me*$_2$ / *o*-N*Ar*), 1.20, 1.05 / 142.5 (ArCH*Me*$_2$ / *o*-N*Ar*), 0.40, 0.22 / 4.0 (CH_2SiMe$_3$ / Si*Me*$_3$).

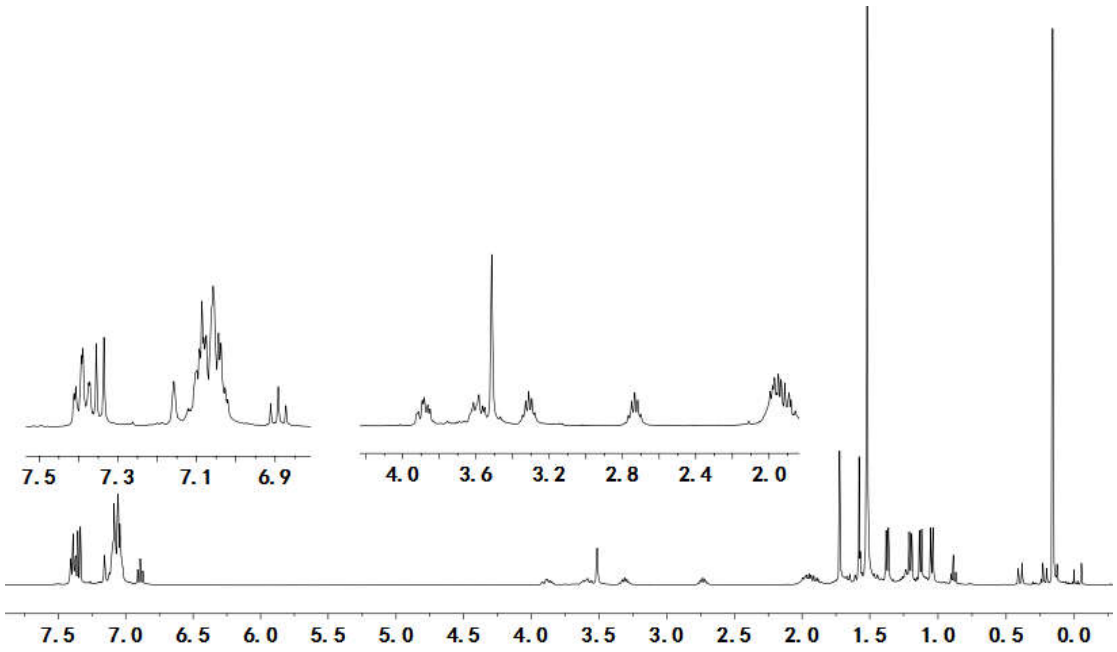


Fig. S17. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

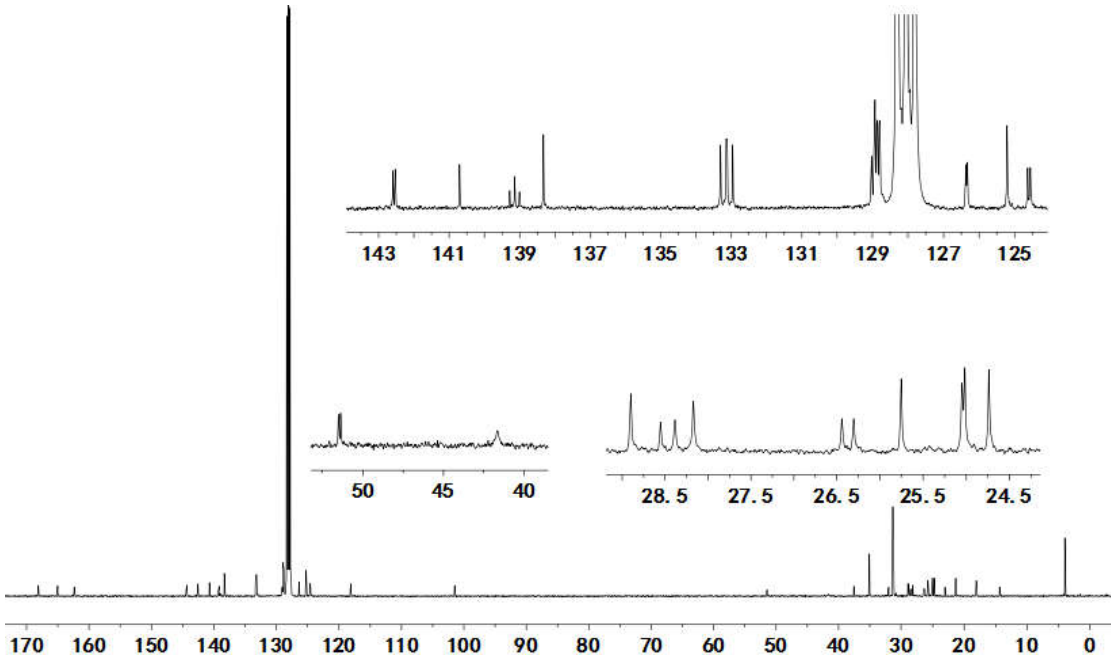


Fig. S18. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

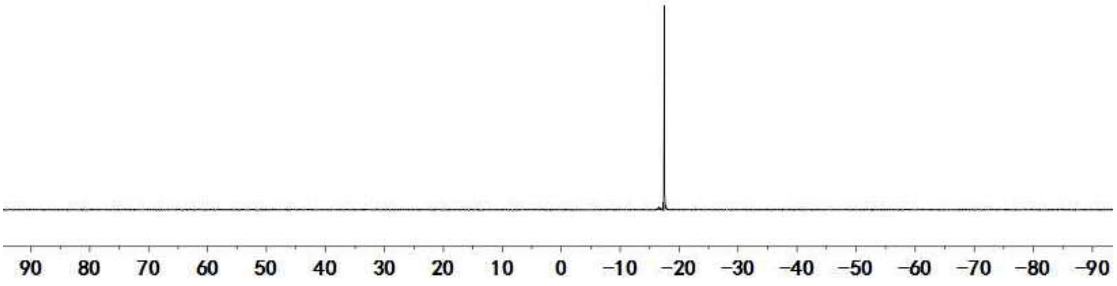


Fig. S19. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6, 298 K)

X-ray crystal structure analysis of complex 5c: formula $C_{57}H_{78}N_2OPScSi$, M = 911.23, clear dark colourless crystal, 0.20 x 0.20 x 0.10 mm, a = 11.2604(8), b = 13.4439(9), c = 19.4751(8) Å, β = 104.788(5)°, V = 2736.8(3) Å^3, ρ_{calc} = 1.106 gcm^{-3}, μ = 0.223 mm^{-1}, empirical absorption correction (0.8125 ≤ T ≤1.0000), Z = 2, Triclinic, space group P -1, λ = 0.71073 Å, T = 223.(10) K, Multi-scan, 30894 reflections collected (±h, ±k, ±l), 16647 independent (R(int) = 0.0611) and 6620 observed reflections [I>2σ(I)], 583 refined parameters, R = 0.0733, wR2 = 0.1873, max. (min.) residual electron density 0.270 (-0.374) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

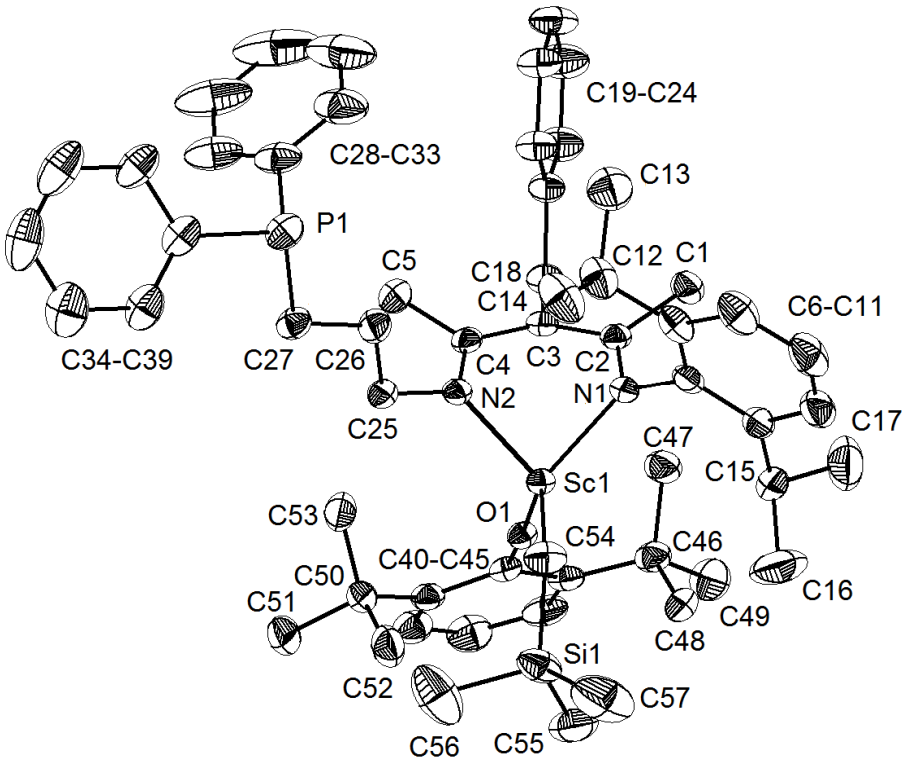
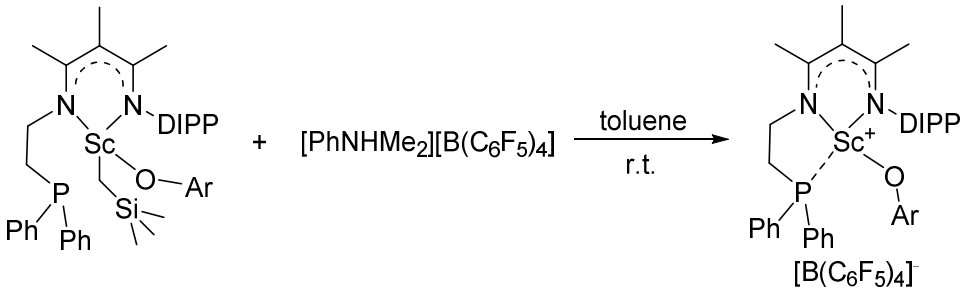


Fig. S20. Crystal structure of complex **5c**.

Characterization of complex 6b:



5b **6b**

Ar = 2,6-*t*Bu$_2$-C$_6$H$_3$

Scheme S7.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: 7.09 / 6.78 (*m*-O*Ar* / *p*-O*Ar*), 7.05 / 7.01 (*p*-N*Ar* / *m*-N*Ar*), 2.45 / 0.92 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.09 / 125.6 (*m*-O*Ar*), 7.05 / 130.0 (*p*-N*Ar*), 7.04 / 132.3 (*m*-*Ph*$_2$P), 7.01 / 128.6 (*m*-N*Ar*), 6.90 / 129.9 (*o*-*Ph*$_2$P), 6.78 / 120.8 (*p*-O*Ar*), 3.43 / 47.9 (N*CH*$_2$), 2.43 / 28.5 (P*CH*$_2$), 1.95 / 18.3 (*Me*C), 1.69 / 17.3 (γ-C*Me*), 1.66 / 21.5 (*Me*C), 1.12/ 31.0 (C(*CH*$_3$)$_3$), 0.92, 0.78 / 24.0 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.09 / 160.4, 34.5 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.01 / 139.1 (*m*-N*Ar* / *i*-N*Ar*), 6.90 / 129.9 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 6.78 / 137.0 (*p*-O*Ar* / *o*-O*Ar*), 1.12 / 137.0, 34.5 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.95, 1.66 / 96.3 (*Me*C / γ-*C*), 1.69 / 166.3, 165.6 (γ-C*Me* / Me*C*).

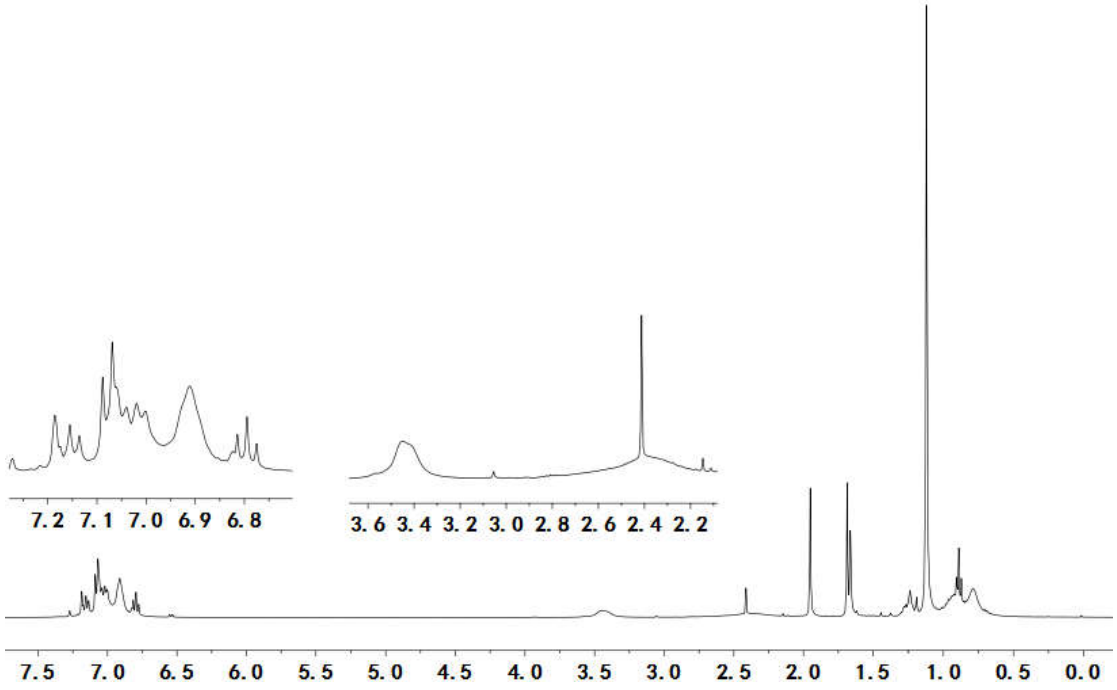


Fig. S21. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K)

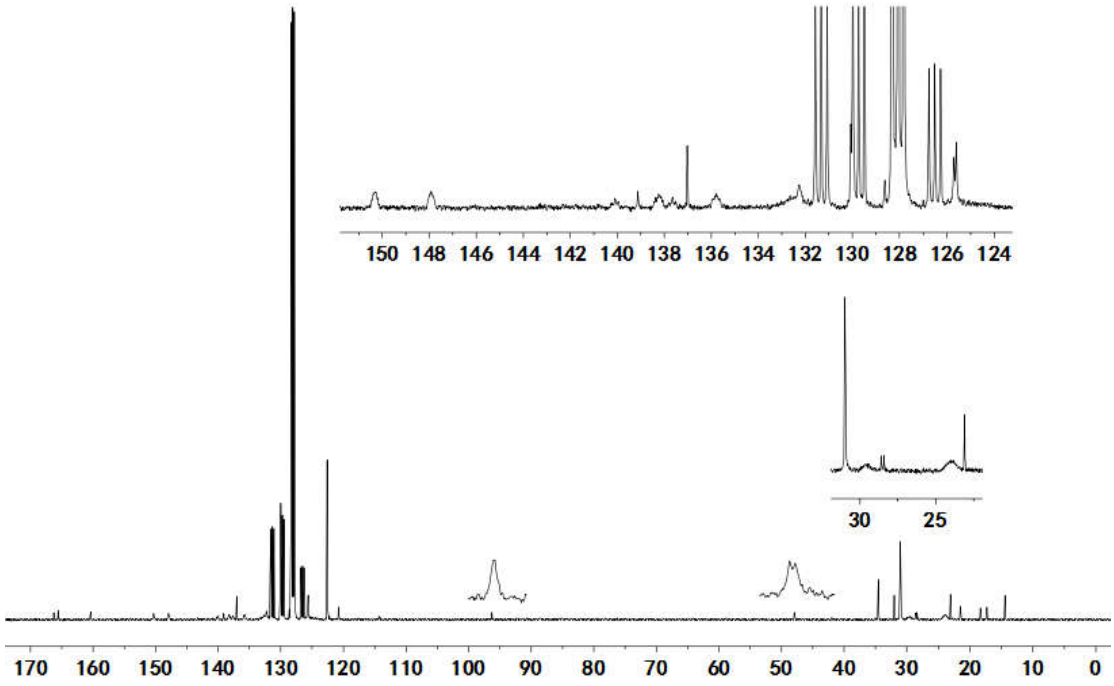
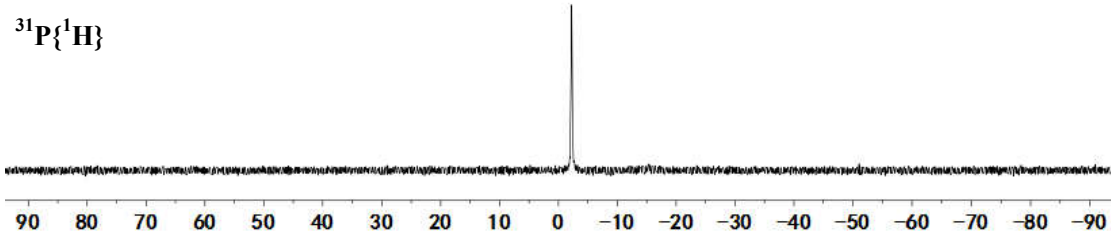


Fig. S22. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K)



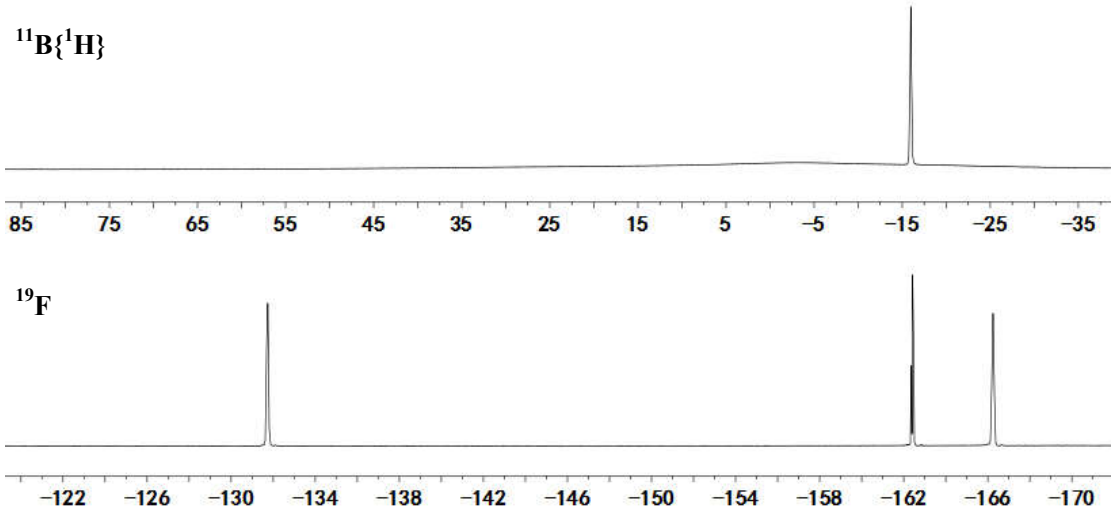
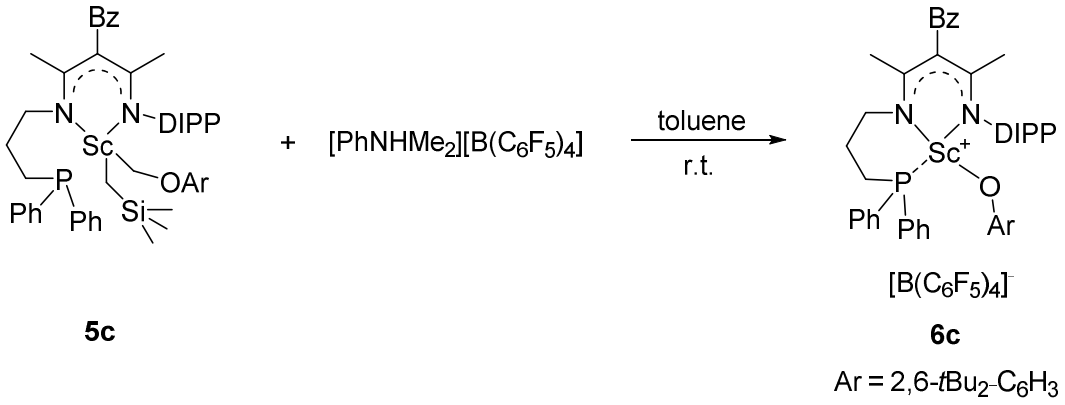


Fig. S23. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

Characterization of complex 6c:



5c **6c**

Ar = 2,6-*t*Bu$_2$-C$_6$H$_3$

Scheme S8.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: 7.19 / 6.98 (*m*-CH_2*Ph* / *o*-CH_2*Ph*), 7.07 / 6.77 (*m*-O*Ar* / *p*-O*Ar*), 3.63 / 3.43 (NC*H*$_2$ / NC*H*$_2$), 2.07 / 1.97 (PC*H*$_2$ / PC*H*$_2$), 1.64 / 1.56 (NCH$_2$C*H*$_2$ / NCH$_2$C*H*$_2$), 2.74, 1.97/ 0.87 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.74, 1.97/ 0.61 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.19 / 129.3, 127.2 (*m*, *p*-CH_2*Ph*), 7.12 / 132.6 (*m*-Ph_2P), 7.07 / 125.9 (*m*-O*Ar*), 7.06 / 129.0, 125.8 (*p*, *m*-N*Ar*), 7.04 / 132.2 (*o*-Ph_2P), 6.98 / 127.4 (*o*-CH_2*Ph*), 6.89 / 129.9. (*p*-Ph_2P), 6.77 / 121.2 (*p*-O*Ar*), 3.63, 3.43 / 50.2 (NC*H*$_2$), 3.55 / 36.7 (*C*H_2Ph), 2.74, 1.97 / 29.6 (Ar*C*HMe$_2$), 2.07, 1.97 / 25.4 (PC*H*$_2$), 1.83 / 18.8 (*Me*C), 1.49 / 21.9 (*Me*C), 1.15 / 31.5 (C(C*H*$_3$)$_3$), 0.87, 0.61 / 23.6 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.19 / 138.8 (*m*-CH_2*Ph* / *i*-CH_2*Ph*), 7.19 / 127.4 (*p*-CH_2*Ph* / *o*-CH_2*Ph*), 7.07 / 160.6 (*m*-O*Ar* / *i*-O*Ar*), 7.06 / 143.8 (*m*-N*Ar* / *i*-N*Ar*), 7.06 / 141.4, 137.9 (*p*-N*Ar* / *o*-N*Ar*), 6.98 / 127.2, 36.7 (*o*-CH_2*Ph* / *p*-CH_2*Ph*, *C*H$_2$Ph), 6.77 / 137.3 (*p*-O*Ar* / *o*-O*Ar*), 3.55 / 167.8, 138.8, 127.4 (C*H*$_2$Ph / Me*C*, *i*, *o*-CH_2*Ph*), 1.15 / 137.3, 34.7 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 0.87 / 143.8, 141.1, 29.6 (ArCH*Me*$_2$ / *i*, *o*-NAr, Ar*C*HMe$_2$).

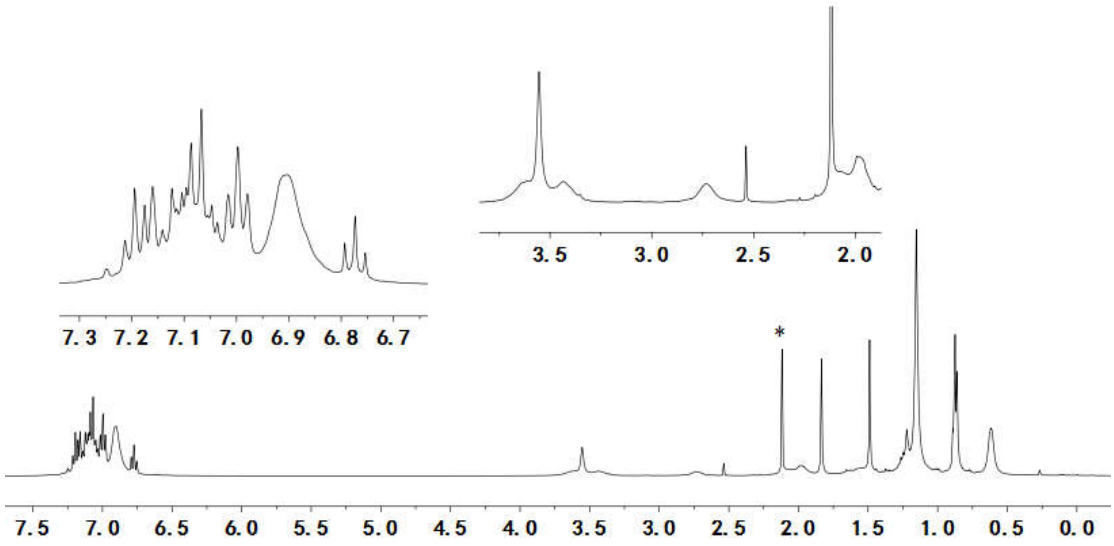


Fig. S24. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*:Toluene]

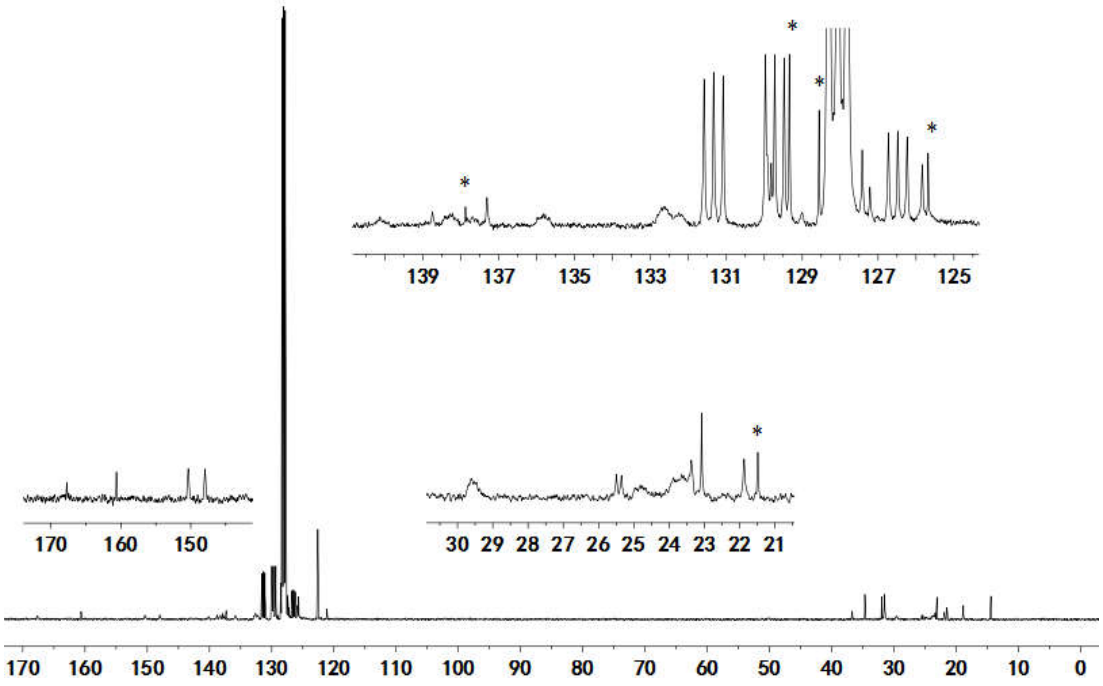
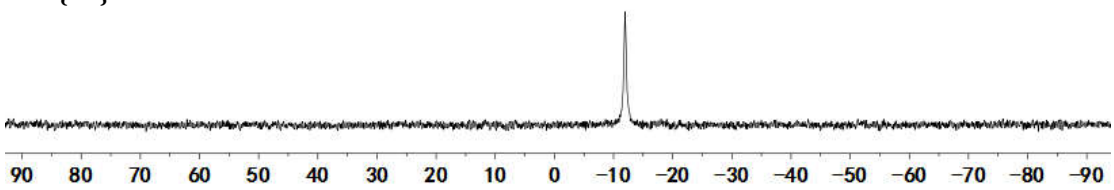


Fig. S25. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*: Toluene]

^{31}P{^{1}H}



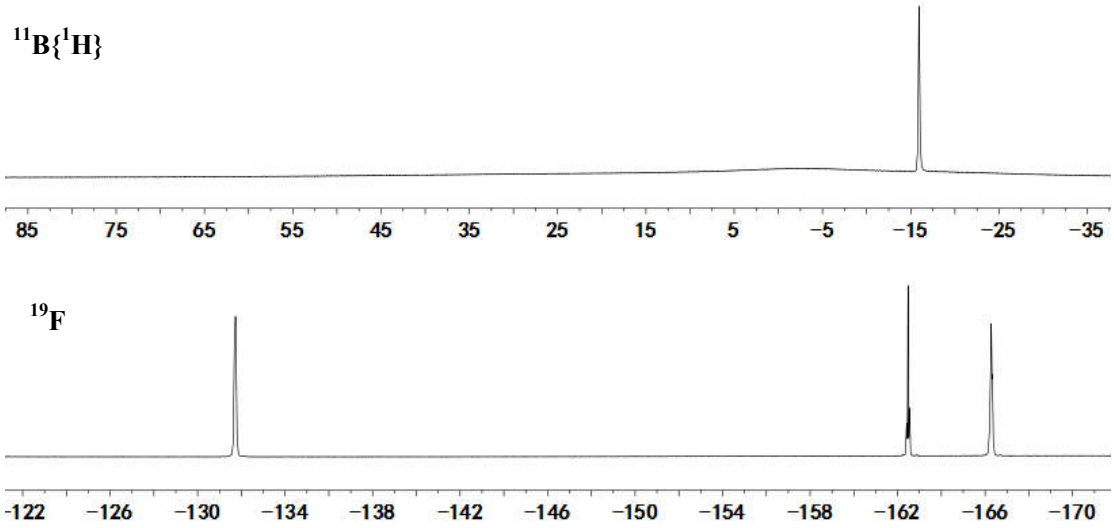
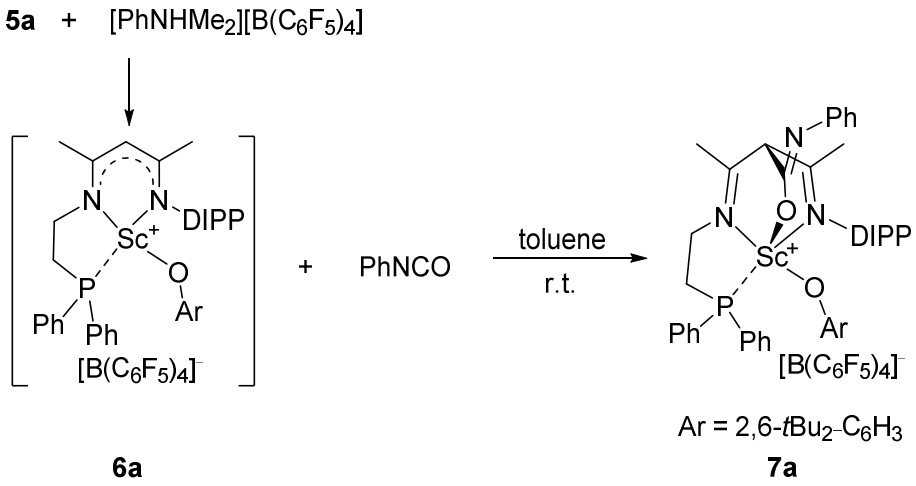


Fig. S26. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

Characterization of complex 7a:



6a **7a**

Scheme S9.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: 7.62 / 7.37 (*o*-OCN*Ph* / *m*-OCN*Ph*), 7.37 / 7.12 (*m*-OCN*Ph* / *p*-OCN*Ph*), 7.10 / 6.83 (*o*-*Ph*P / *m*-*Ph*P), 7.07 / 6.68 (*m*-O*Ar* / *p*-O*Ar*), 6.94 / 6.89 (*o*-*Ph*'P / *m*-*Ph*'P), 6.92 / 6.90 (*m*-N*Ar* / *p*-N*Ar*), 3.49 / 2.56, 1.84 (NCH_2 / PCH_2), 2.88 / 0.92, 0.76 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.90 / 1.06, 0.79 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.62 / 124.6 (*o*-OCN*Ph*), 7.37 / 129.0 (*m*-OCN*Ph*), 7.12 / 125.0 (*p*-OCN*Ph*), 7.10 / 133.0 (*o*-*Ph*P), 7.07 / 126.1 (*m*-O*Ar*), 6.94 / 131.9 (*o*-*Ph*'P), 6.92 / 125.5 (*m*-N*Ar*), 6.90 / 125.6 (*p*-N*Ar*), 6.89 / 131.8, 129.8 (*p*-*Ph*'P, *m*-*Ph*'P), 6.86 / 125.3 (*m*-N*Ar*), 6.83 / 132.1, 130.1 (*p*-*Ph*P, *m*-*Ph*P), 6.76 / 125.7 (*m*-O*Ar*), 6.68 / 120.8 (*p*-O*Ar*), 4.88 / 70.3 (γ-*CH*), 3.55, 3.49 / 49.5 (NCH_2), 2.88 / 30.4 (Ar*CH*Me$_2$), 2.56, 1.84 / 27.5 (PCH_2), 1.90 / 29.1 (Ar*CH*Me$_2$), 1.76 / 21.7 (*Me*C), 1.44 / 26.5 (*Me*C), 1.41 / 31.1 (C(CH_3)$_3$), 1.06 / 23.4 (ArCH*Me*$_2$), 0.92 / 23.3 (ArCH*Me*$_2$), 0.79 / 23.5 (ArCH*Me*$_2$), 0.76 / 24.3 (ArCH*Me*$_2$), 0.72 / 33.3 (C(CH_3)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.62 / 125.0 (*o*-OCN*Ph* / *p*-OCN*Ph*), 7.37 / 147.6 (*m*-OCN*Ph* / *i*-OCN*Ph*), 7.10 / 132.1 (*o*-*Ph*P / *p*-*Ph*P), 7.07 / 159.2, 35.3 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH_3)$_3$), 6.94 / 131.8 (*o*-*Ph*'P / *p*-*Ph*'P), 6.92, 6.86 / 140.6, (*m*-N*Ar* / *i*-N*Ar*), 6.89 / 125.2 (*m*-*Ph*'P / *i*-*Ph*'P), 6.83 / 128.1 (*m*-*Ph*P / *i*-*Ph*P), 6.76 / 159.2, 34.1 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH_3)$_3$), 6.68 /

137.7, 136.6 (*p*-O*Ar* / *o*-O*Ar*), 4.88 / 153.9, 26.5 (γ-C*H* / O*C*NPh, *Me*C), 3.55 / 179.5 (NCH_2 / Me*C*), 2.88 / 140.6, 139.8, 125.3 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 1.90 / 140.6, 138.9, 125.5 (Ar*CH*Me$_2$ / *i*, *o*, *m*-N*Ar*), 1.84 / 128.1, 125.2 (PCH2 / *i*-*Ph*P, *i*-*Ph*'P), 1.76, 1.44 / 70.3 (*Me*C / γ-*C*), 1.41 / 137.7 (C(CH_3)$_3$ / *o*-O*Ar*), 0.72 / 136.6 (C(CH_3)$_3$ / *o*-O*Ar*).

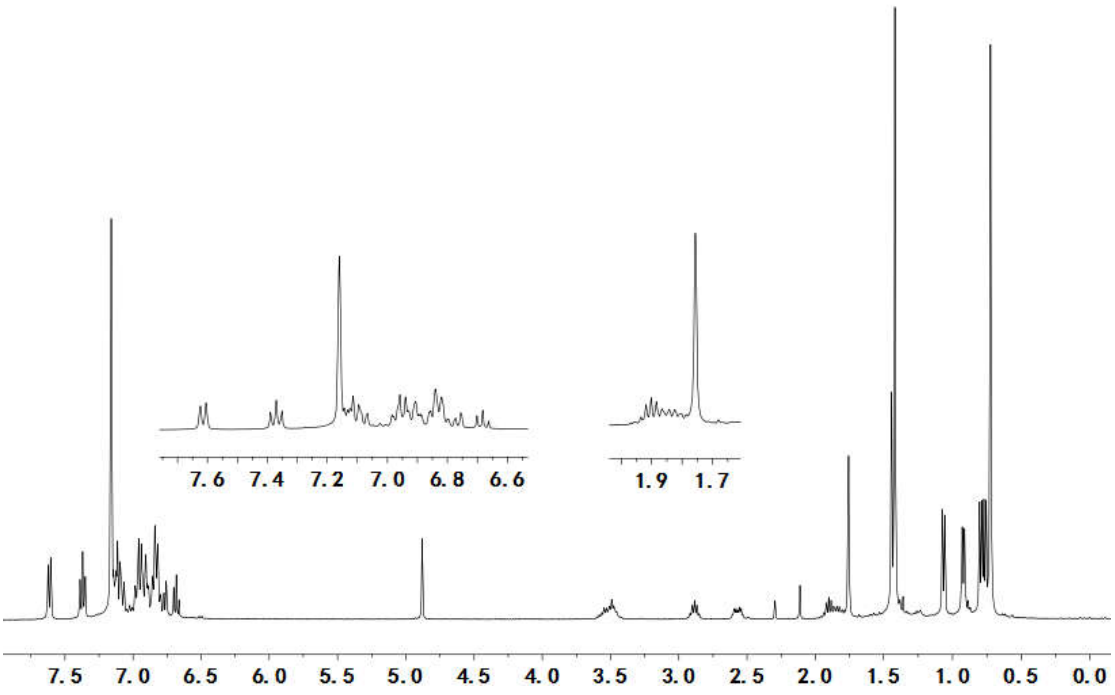


Fig. S27. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

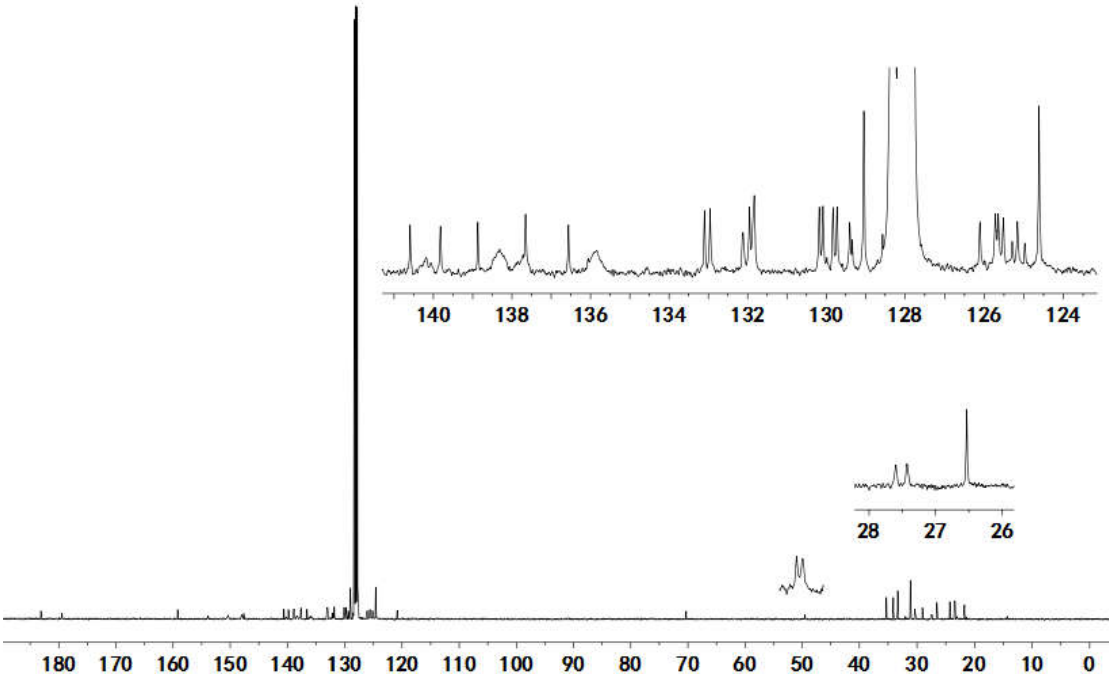


Fig. S28. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

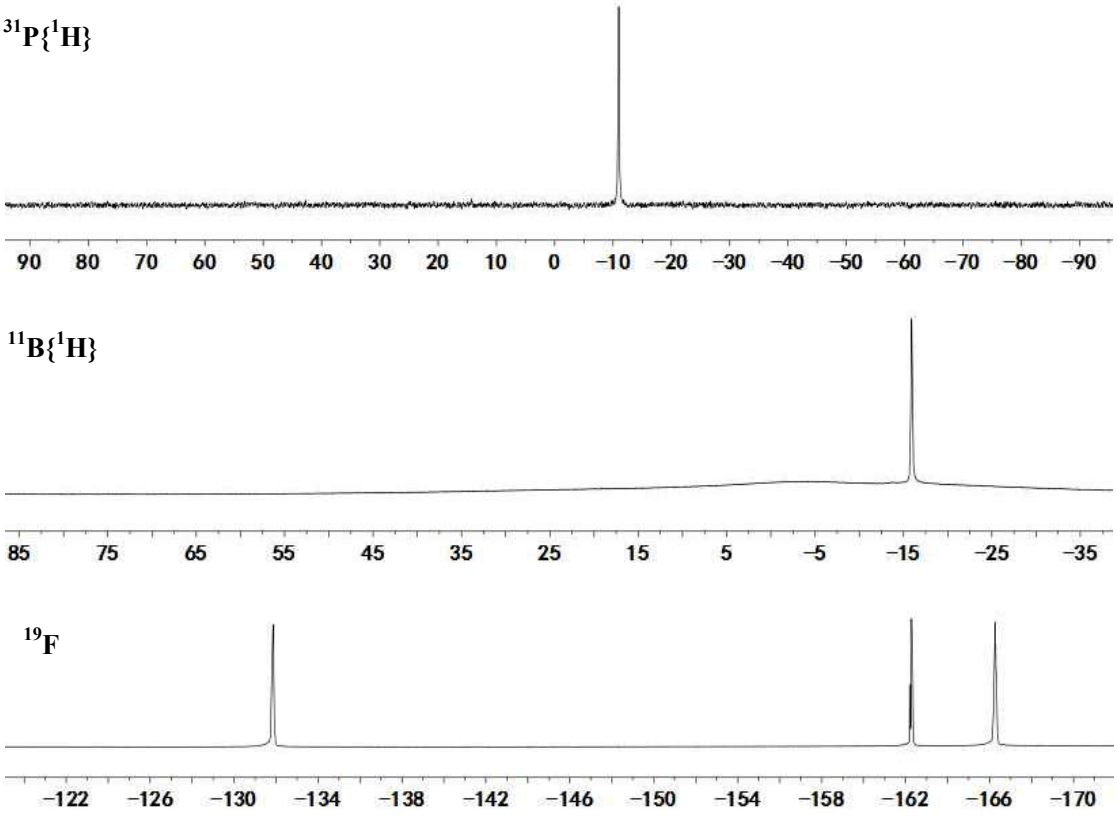
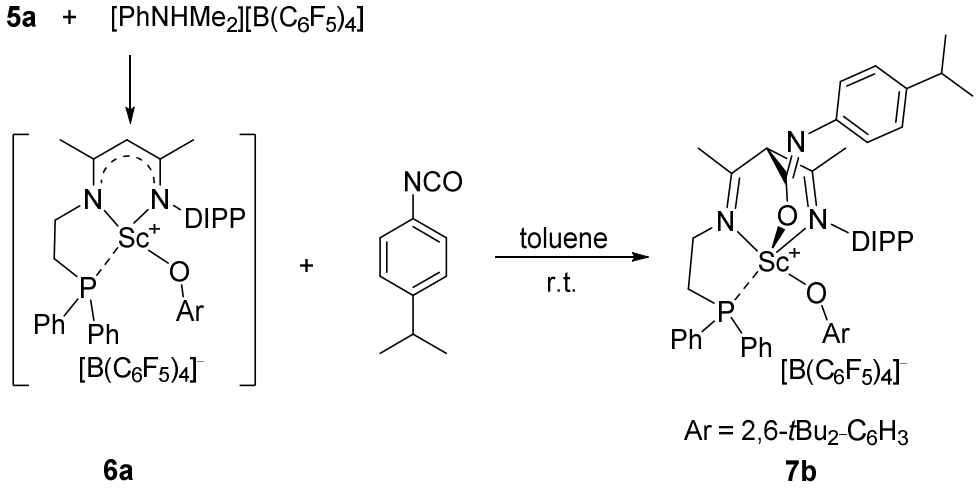


Fig. S29. ^{31}**P{**^{1}**H} NMR** (162 MHz, C_6D_6, 298 K), ^{11}**B{**^{1}**H} NMR** (128 MHz, C_6D_6, 298 K), ^{19}**F NMR** (376 MHz, C_6D_6, 298 K)

Characterization of complex 7b:



6a **7b**

Scheme S10.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: 7.58 / 7.31 (*o*-OCN*Ph* / *m*-OCN*Ph*), 7.13 / 6.86 (*o*-*Ph*P / *m*-*Ph*P), 7.08 / 6.69 (*m*-O*Ar* / *p*-O*Ar*), 6.96 / 6.93 (*o*-*Ph*'P / *m*-*Ph*'P), 6.99 / 6.88 (*p*-N*Ar* / *m*-N*Ar*), 3.42 / 1.83 (NCH_2 / PCH_2), 2.89 / 0.94, 0.81 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.86 / 1.27 (OCNPhC*H*Me$_2$ / OCNPhCH*Me*$_2$), 1.91 / 1.07, 0.81 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.58 / 124.6 (*o*-OCN*Ph*), 7.31 / 126.9 (*m*-OCN*Ph*), 7.13 / 133.1 (*o*-*Ph*P), 7.08 / 125.7 (*m*-O*Ar*), 6.99 / 129.4 (*p*-N*Ar*), 6.96 / 132.0 (*o*-*Ph*'P), 6.94 / 125.5 (*m*-N*Ar*), 6.93 / 129.8 (*m*-*Ph*'P), 6.88 / 125.6 (*m*-N*Ar*), 6.86 / 132.1, 130.1 (*p*-*Ph*P, *m*-*Ph*P), 6.78 / 126.1 (*m*-O*Ar*), 6.69 / 120.8 (*p*-O*Ar*), 4.92 / 70.3 (γ-*CH*), 3.47, 3.42 / 49.5 (NCH_2), 2.89 / 30.4 (Ar*CH*Me$_2$), 2.86 / 34.2 (OCNPh*CH*Me$_2$), 2.52, 1.83 / 27.4 (PCH_2), 1.91 / 29.1 (Ar*CH*Me$_2$), 1.76 / 21.8 (*Me*C), 1.50 / 26.5 (*Me*C), 1.41 / 31.2 (C(CH_3)$_3$), 1.27 / 24.4 (OCNPhCH*Me*$_2$), 1.07 / 23.5 (ArCH*Me*$_2$), 0.94 / 23.4 (ArCH*Me*$_2$), 0.81 / 24.3, 23.3 (ArCH*Me*$_2$), 0.72 / 33.3 (C(CH_3)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.58 / 145.8 (*o*-OCN*Ph* / *p*-OCN*Ph*), 7.31 / 145.6, 34.2 (*m*-OCN*Ph* / *i*-OCN*Ph*, OCNPh*C*HMe$_2$), 7.13 / 132.1 (*o*-*Ph*P / *p*-*Ph*P), 7.08 / 159.3, 35.3 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 6.99 /139.8 (*p*-NAr / *o*-NAr), 6.96 / 131.9 (*o*-*Ph*'P / *p*-*Ph*'P), 6.94, 6.88 / 140.6, (*m*-N*Ar* / *i*-N*Ar*), 6.93 / 125.1 (*m*-*Ph*'P / *i*-*Ph*'P), 6.86 / 128.2 (*m*-*Ph*P / *i*-*Ph*P),

6.78 / 159.3, 34.1 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH_3)$_3$), 6.69 / 137.7, 136.6 (*p*-O*Ar* / *o*-O*Ar*), 4.92 / 153.6, 21.8 (γ-C*H* / O*C*NPh, Me*C*), 3.47 / 179.5 (NCH_2 / Me*C*), 2.89 / 140.6, 139.8, 125.6 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 2.86 / 145.8, 126.9 (OCNPhC*H*Me$_2$ / *p*, *m*-OCN*Ph*), 2.52 / 128.2 (PCH_2 / *i*-*Ph*P), 1.91 / 140.6, 138.9, 125.5 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 1.83 / 125.1 (PCH_2 / *i*-*Ph*'P), 1.76, 1.50 / 70.3 (*Me*C / γ-*C*), 1.43 / 137.7 (C(CH_3)$_3$ / *o*-O*Ar*), 1.27 / 145.8 (OCNPhCH*Me*$_2$ / *p*-OCN*Ph*), 0.72 / 136.6 (C(CH_3)$_3$ / *o*-O*Ar*).

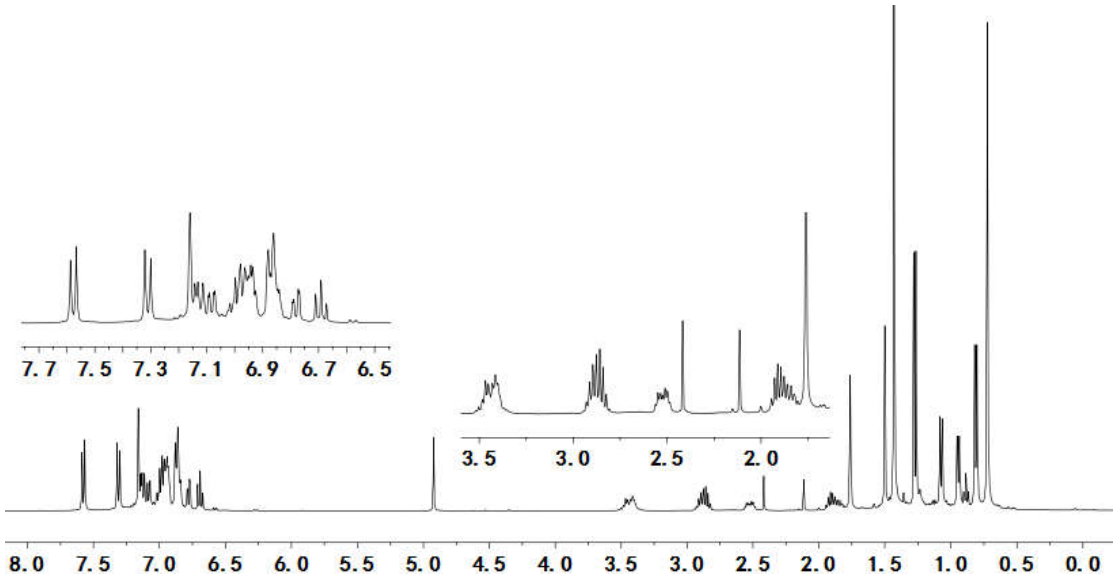


Fig. S30. ^{1}H NMR (400 MHz, C_6D_6, 298 K)

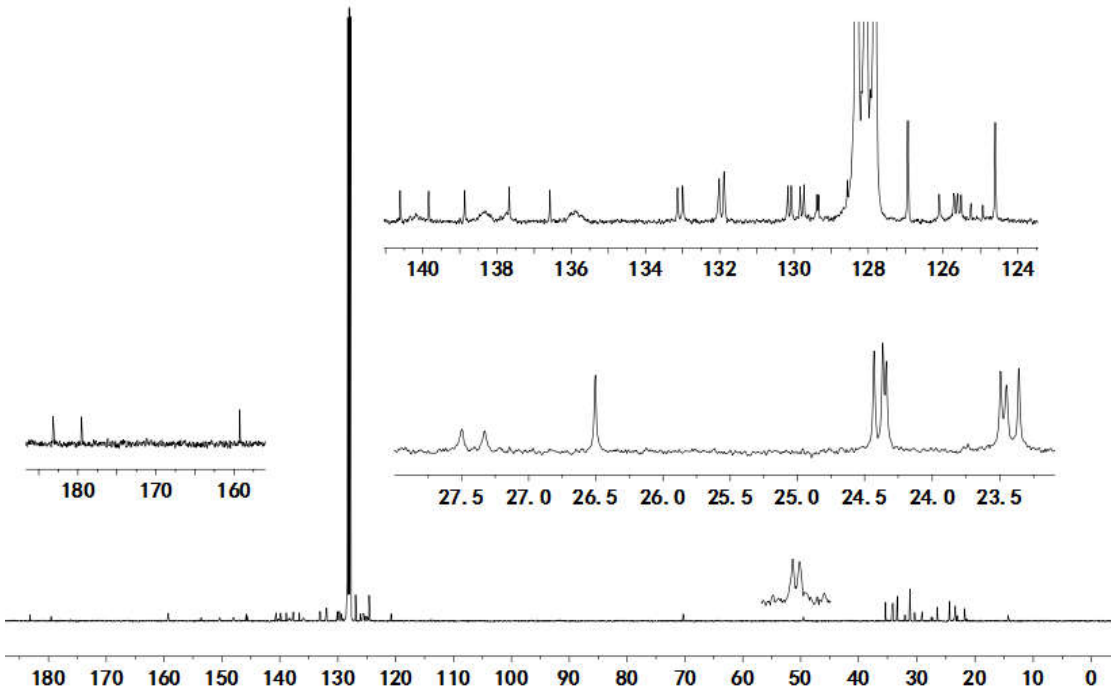


Fig. S31. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K)

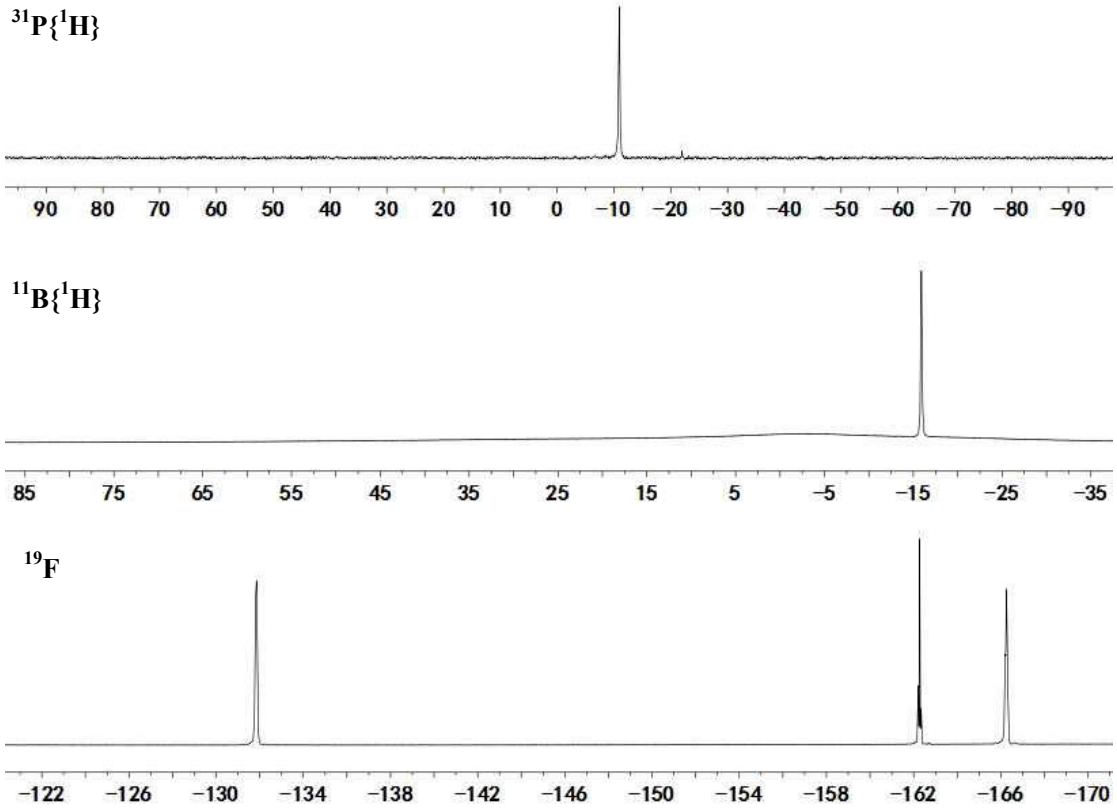


Fig. S32. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6, 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6, 298 K), ^{19}F **NMR** (376 MHz, C_6D_6, 298 K).

X-ray crystal structure analysis of complex 7b: formula $C_{79}H_{70}BF_{20}N_3O_2PSc \cdot 2C_6H_6$, M = 1716.34, colorless crystal, 0.50 x 0.35 x 0.20 mm, a = 12.8116(7), b = 17.3758(9), c = 19.3172(8) Å, β = 98.990(4)°, V = 4171.4(3) Å^3, ρ_{calc} = 1.367 gcm^{-3}, μ = 0.203 mm^{-1}, empirical absorption correction (0.7791 ≤ T ≤ 1.0000), Z = 2, Triclinic, space group P -1, λ = 0.71073 Å, T = 153(2) K, Multi-scan, 40078 reflections collected (±h, ±k, ±l), 14688 independent (R(int) = 0.0807) and 7776 observed reflections [I>2σ(I)], 1050 refined parameters, R = 0.0792, wR2 = 0.2520, max. (min.) residual electron density 0.850 (-0.863) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

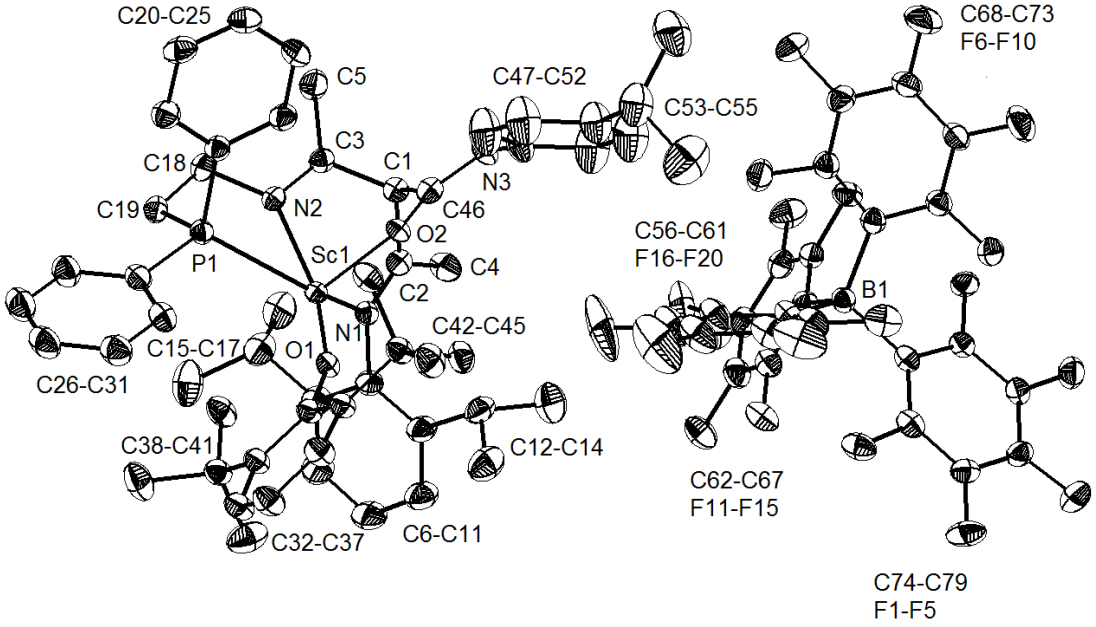
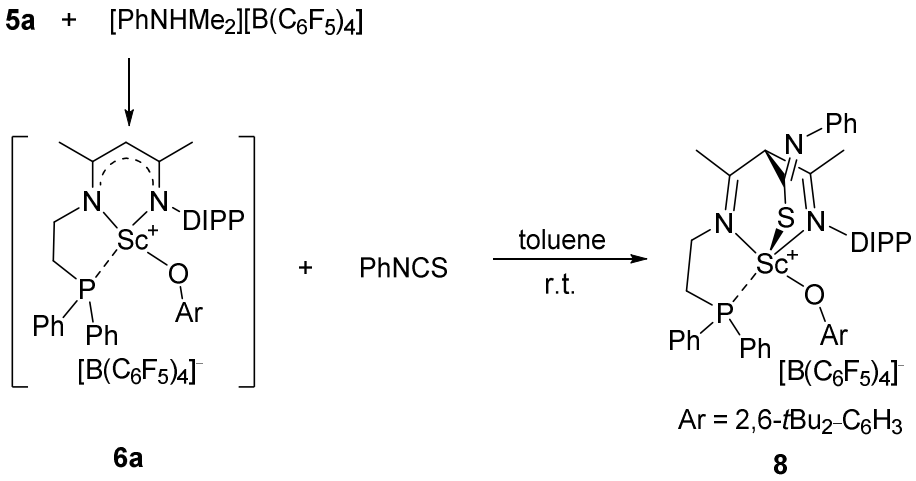


Fig. S33. Crystal structure of complex **7b**.

Characterization of complex 8:



6a **8**

Scheme S11.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K) [selected traces]: 7.30 / 7.03 (*o*-SCN*Ph* / *m*-SCN*Ph*), 7.23 / 7.02 (*o*-*Ph*P / *m*-*Ph*P), 7.05 / 6.94 (*m*-N*Ar* / *p*-N*Ar*), 7.00 / 6.67 (*m*-O*Ar* / *p*-O*Ar*), 3.83 / 2.66 (NCH_2 / PCH_2), 3.20 / 0.95, 0.87 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.03 / 1.06, 0.84 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K): δ ^{1}H / δ ^{13}C = 7.30 / 129.33 (*o*-SCN*Ph*), 7.23 / 132.9 (*o*-*Ph*P), 7.10 / 131.7 (*o*-*Ph*'P), 7.05 / 125.9 (*p*-N*Ar*), 7.03 / 129.37, 120.5 (*m*, *p*-SCN*Ph*), 7.02 / 131.3, 130.3 (*p*, *m*-*Ph*P), 7.00 / 125.5 (*m*-O*Ar*), 6.97 / 125.7 (*m*-N*Ar*), 6.96 / 129.8, 129.6 (*p*, *m*-*Ph*'P), 6.94 / 125.4 (*m*-N*Ar*), 6.72 / 125.8 (*m*-O*Ar*), 6.67 / 121.3 (*p*-O*Ar*), 5.49 / 74.9 (γ-*CH*), 3.83, 3.45 / 50.5 (NCH_2), 3.20 / 30.7 (ArC*H*Me$_2$), 2.66, 1.63 / 28.6 (PCH_2), 2.16 / 21.5 (*Me*C), 2.03 / 28.9 (ArC*H*Me$_2$), 1.76 / 27.4 (*Me*C), 1.20 / 31.4 (C(CH_3)$_3$), 1.06 / 23.6 (ArCH*Me*$_2$), 0.95 / 23.8 (ArCH*Me*$_2$), 0.87 / 24.5 (ArCH*Me*$_2$), 0.84 / 24.2 (ArCH*Me*$_2$), 0.58 / 32.9 (C(CH_3)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K): [selected traces]: δ ^{1}H / δ ^{13}C = 7.30 / 120.5 (*o*-SCN*Ph* / *p*-SCN*Ph*), 7.23 / 131.3 (*o*-*Ph*P / *p*-*Ph*P), 7.10 / 129.8 (*o*-*Ph*'P / *p*-*Ph*'P), 7.03 / 150.5 (*m*-SCN*Ph* / *i*-SCN*Ph*), 7.03 / 129.33 (*p*-SCN*Ph* / *o*-SCN*Ph*), 7.02 / 132.9 (*p*-*Ph*P / *o*-*Ph*P), 7.00 / 159.6, 35.1 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 6.97 / 141.6, 28.9 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 6.96 / 131.7 (*p*-*Ph*'P / *o*-*Ph*'P), 6.94 / 30.7 (*m*-N*Ar* / Ar*C*HMe$_2$), 6.72 / 159.6, 33.5 (*m*-O*Ar* /

i-O*Ar*, *C*(CH_3)$_3$), 6.67 / 137.1, 136.9 (*p*-O*Ar* / *o*-O*Ar*), 5.49 / 161.8, 21.5 (γ-C*H* / S*C*NPh, *Me*C), 3.83 / 180.2, 28.6 (NCH_2 / Me*C*, P*C*H_2), 3.20 / 141.6, 140.3, 125.4 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 2.16, 1.76 / 74.9 (*Me*C / γ-*C*), 2.03 / 141.6, 138.9, 125.7 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 1.63 / 129.6, 125.3 (PCH_2 / *i*-*Ph*P, *i*-*Ph*'P), 1.20 / 137.1, 35.1 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH_3)$_3$), 0.58 / 136.9, 33.5 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH_3)$_3$).

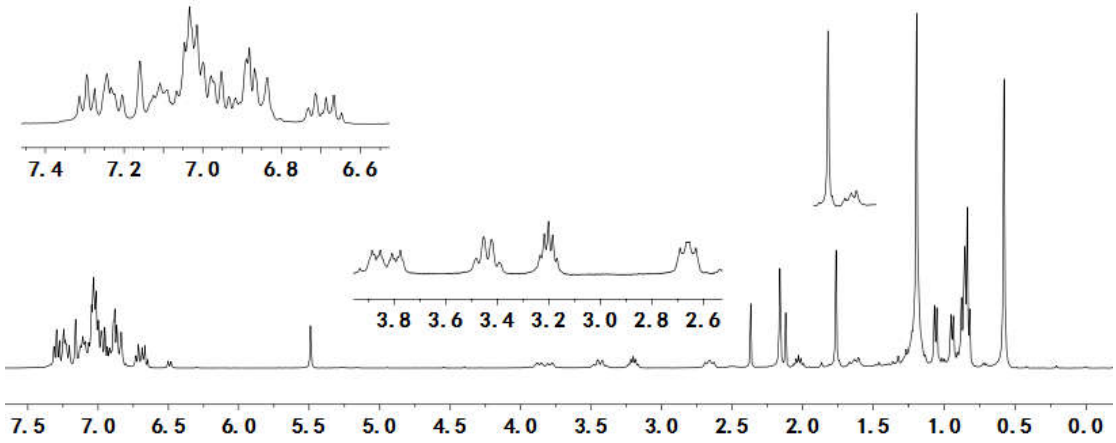


Fig. S34. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K)

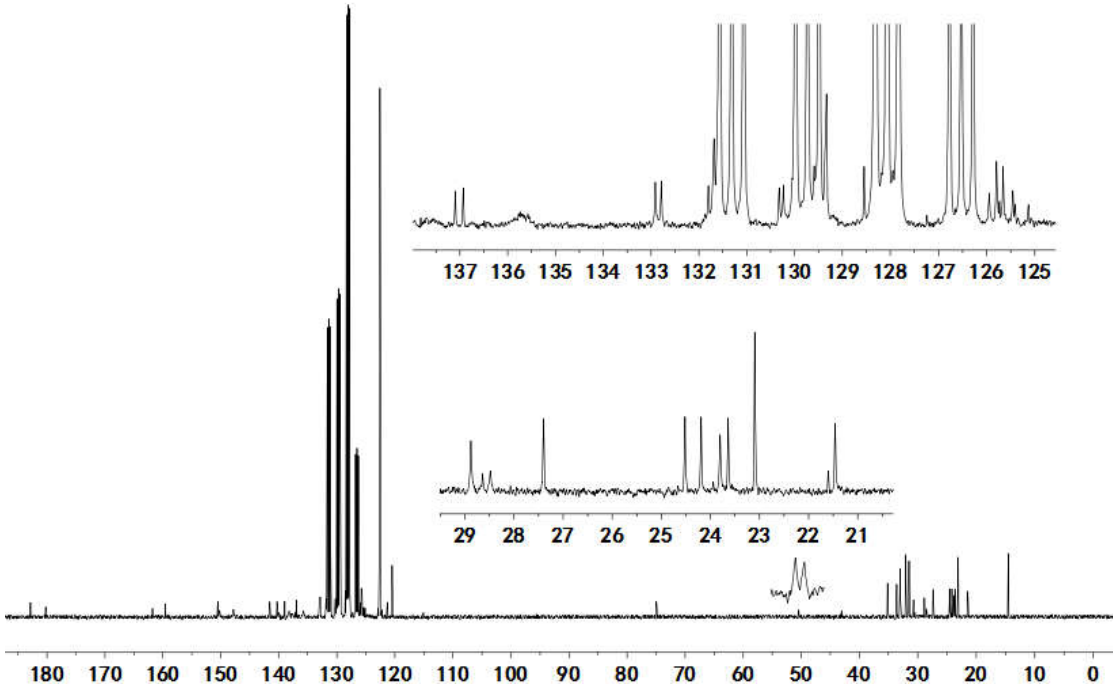


Fig. S35. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K)

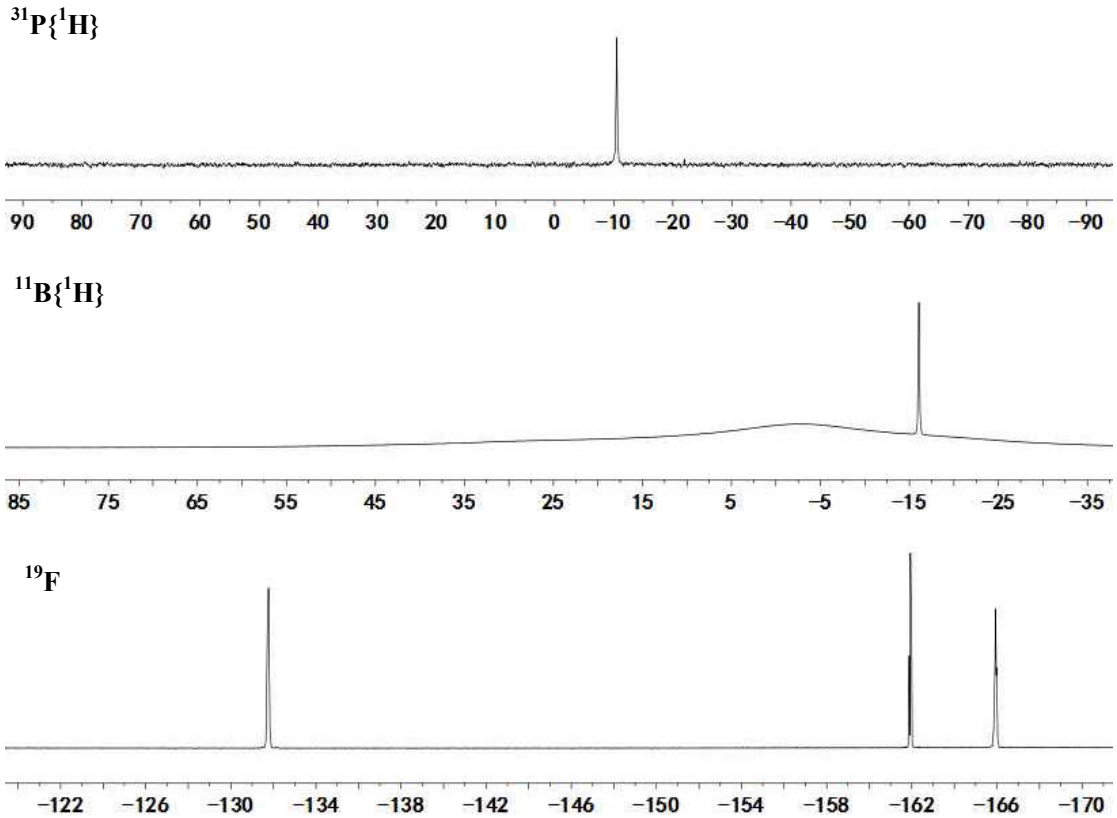


Fig. S36. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K).

X-ray crystal structure analysis of complex 8: formula $C_{76}H_{64}BF_{20}N_3OPSSc \cdot 3C_6H_5Cl$, M = 1871.75, colorless crystal, 0.40 x 0.30 x 0.20 mm, a = 12.5176(6), b = 17.4496(9), c = 20.4570(10) Å, β = 79.057(2)°, V = 4319.0(4) Å^3, ρ_{calc} = 1.439 gcm^{-3}, μ = 0.315 mm^{-1}, empirical absorption correction (0.7456 ≤ T ≤ 0.6800), Z = 2, Triclinic, space group P -1, λ = 0.71073 Å, T = 120(2) K, Multi-scan, 95954 reflections collected (±h, ±k, ±l), 19902 independent (R(int) = 0.0516) and 15174 observed reflections [I>2σ(I)], 1138 refined parameters, R = 0.0581, wR2 = 0.1640, max. (min.) residual electron density 1.733 (-1.318) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

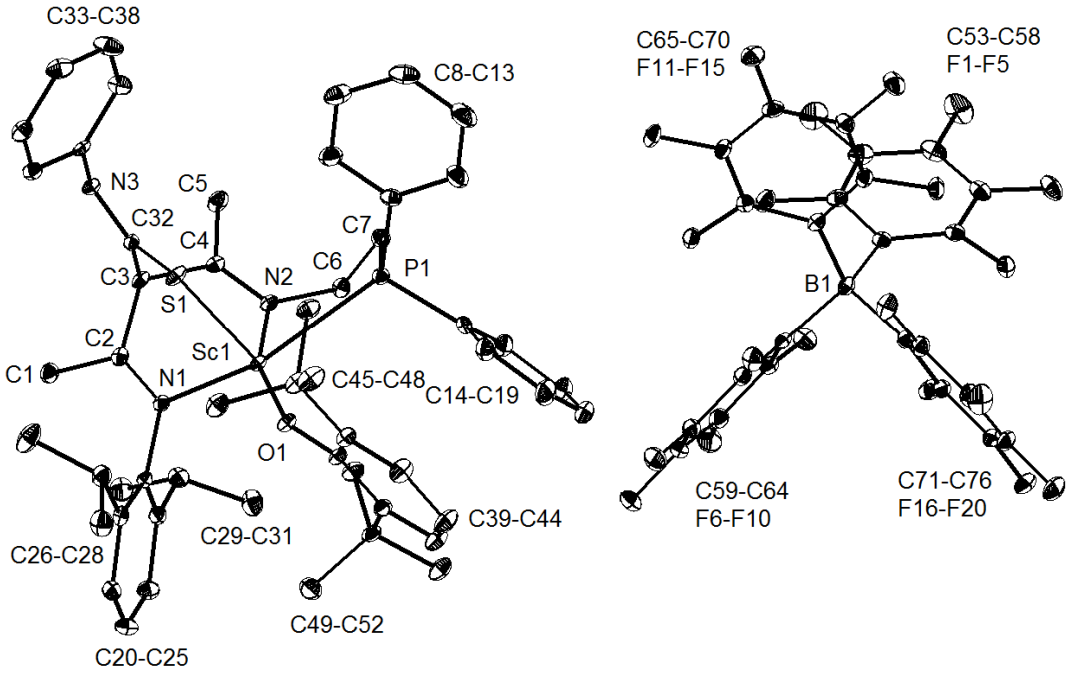
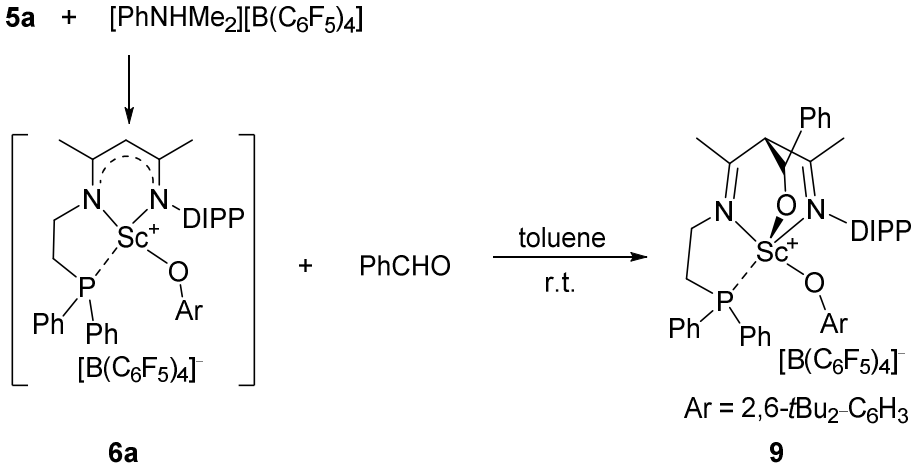


Fig. S37. Crystal structure of complex **8**.

Characterization of complex 9:



Scheme S12.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6, 298 K) [selected traces]: 7.57 / 7.27 (*o*-OCH*Ph* / *m*-OCH*Ph*), 7.27 / 7.12 (*m*-OCH*Ph* / *p*-OCH*Ph*), 7.45 / 7.02 (*o*-*Ph*P / *m*-*Ph*P), 7.17 / 6.73 (*m*-O*Ar* / *p*-O*Ar*), 7.05 / 6.96 (*o*-*Ph*'P / *m*-*Ph*'P), 6.90 / 6.87 (*m*-N*Ar* / *p*-N*Ar*), 5.63 / 4.24 (OCH*Ph* / γ-C*H*), 3.42 / 1.99 (NCH_2 / PCH_2), 2.90 / 1.05, 0.61 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.97 / 1.10, 0.75 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.57 / 125.3 (*o*-OCH*Ph*), 7.45 / 133.2 (*o*-*Ph*P), 7.27 / 129.2 (*m*-OCH*Ph*), 7.17 / 125.65 (*m*-O*Ar*), 7.12 / 128.7 (*p*-OCH*Ph*), 7.05 / 132.2 (*o*-*Ph*'P), 7.02 / 132.1, 129.9 (*p*, *m*-*Ph*P), 6.96 / 131.6, 129.8 (*p*, *m*-*Ph*'P), 6.90 / 125.1 (*m*-N*Ar*), 6.87 / 125.69 (*p*-N*Ar*), 6.86 / 125.6 (*m*-N*Ar*), 6.84 / 126.1 (*m*-O*Ar*), 6.73 / 119.9 (*p*-O*Ar*), 5.63 / 82.4 (O*CH*Ph), 4.24 / 70.2 (γ-*CH*), 3.46, 3.42 / 49.4 (N*CH*$_2$), 2.90 / 29.5 (Ar*CH*Me$_2$), 2.52, 1.99 / 27.2 (P*CH*$_2$), 1.97 / 29.3 (Ar*CH*Me$_2$), 1.82 / 21.7 (*Me*C), 1.68 / 31.5 (C(*CH*$_3$)$_3$), 1.14 / 28.1 (*Me*C), 1.10 / 23.1 (ArCH*Me*$_2$), 1.05 / 24.2 (ArCH*Me*$_2$), 0.75 / 23.3 (ArCH*Me*$_2$), 0.72 / 32.8 (C(*CH*$_3$)$_3$), 0.61 / 25.4 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.57 / 128.7, 82.4 (*o*-OCH*Ph* / *p*-OCH*Ph*, O*C*HPh), 7.45 / 132.1 (*o*-*Ph*P / *p*-*Ph*P), 7.27 / 140.7 (*m*-OCH*Ph* / *i*-OCH*Ph*), 7.17 / 160.0, 35.4 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.12 / 125.3 (*p*-OCH*Ph* / *o*-OCH*Ph*), 7.05 / 131.6 (*o*-*Ph*'P / *p*-*Ph*'P), 7.02 / 133.2 (*p*-*Ph*P / *o*-*Ph*P), 7.02 / 128.9 (*m*-*Ph*P / *i*-*Ph*P), 6.96 / 132.2 (*p*-*Ph*'P/ *o*-*Ph*'P), 6.96 /

126.3 (*m-Ph*'P/ *i-Ph*'P), 6.90 / 141.5, 29.3 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 6.87 / 140.0, 138.5 (*p*-N*Ar* / *o*-N*Ar*), 6.86 / 29.5 (*m*-N*Ar* / Ar*C*HMe$_2$), 6.84 / 160.0, 34.1 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 6.73 / 137.9, 136.7 (*p*-O*Ar* / *o*-O*Ar*), 5.63 / 183.0, 140.7, 125.3, 70.2 (OC*H*Ph / Me*C*, *i*-OCH*Ph*, *o*-OCH*Ph*, γ-*C*), 4.24 / 140.7, 82.4, 21.7 (γ-C*H* / *i*-OCH*Ph*, O*C*HPh, *Me*C), 3.46 / 180.7, 27.2 (NCH_2 / Me*C*, P*C*H$_2$), 2.90 / 141.5, 140.0, 125.6 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 2.52 / 128.9, 126.3 (PCH_2 / *i-Ph*P, *i-Ph*'P), 1.97 / 141.5, 138.5, 125.1 (Ar*CH*Me$_2$ / *i*, *o*, *m*-N*Ar*), 1.82, 1.14 / 70.2 (*Me*C / γ-*C*), 1.68 / 137.9, 35.4 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 1.10, 0.75 / 138.5 (ArCH*Me*$_2$ / *o*-NAr), 1.05, 0.61 / 140.0 (ArCH*Me*$_2$ / *o*-NAr), 0.72 / 136.7, 34.1 (C(CH_3)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$).

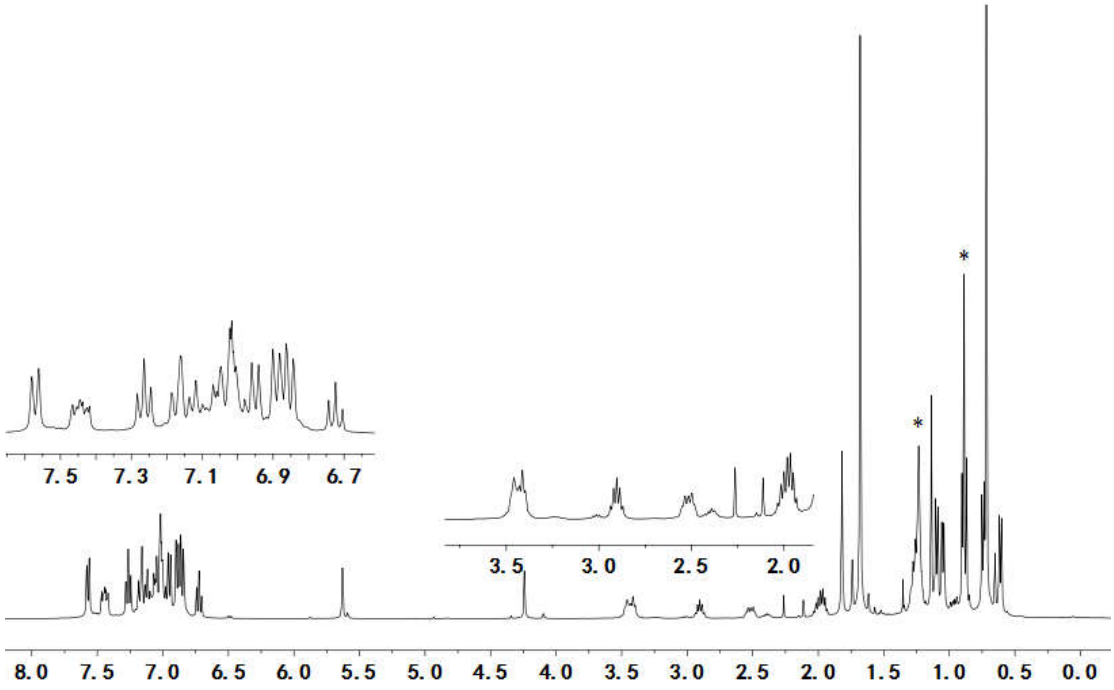


Fig. S38. ^{1}H NMR (400 MHz, C_6D_6, 298 K) [*: Hexane]

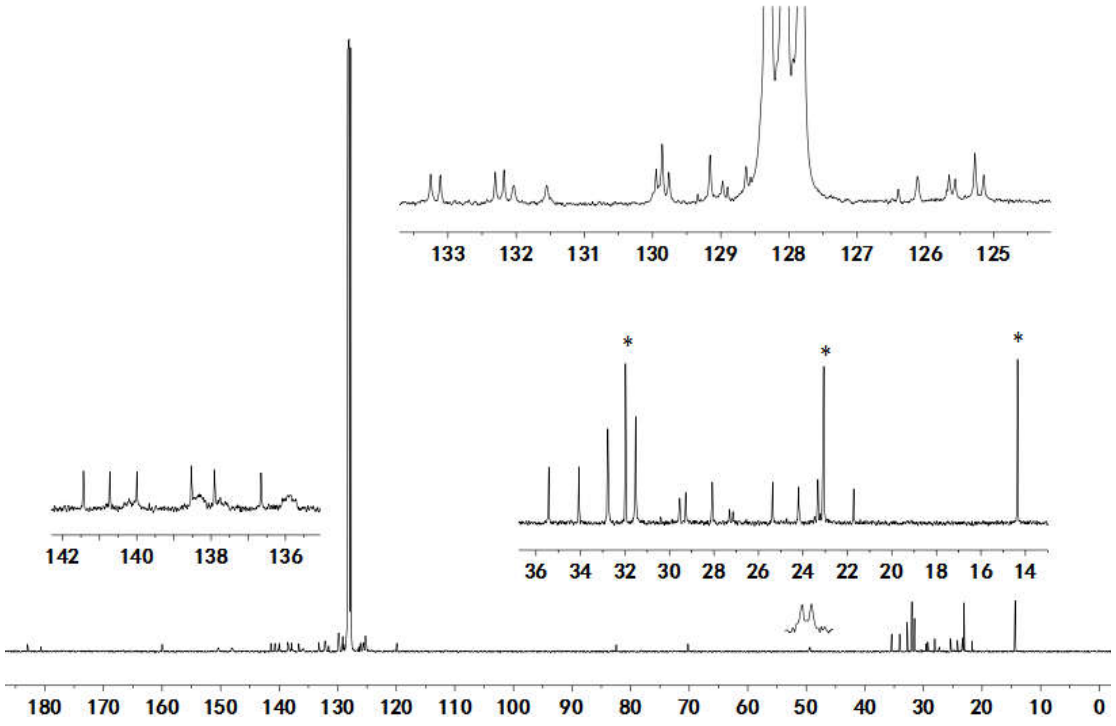


Fig. S39. $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6, 298 K) [*: Hexane]

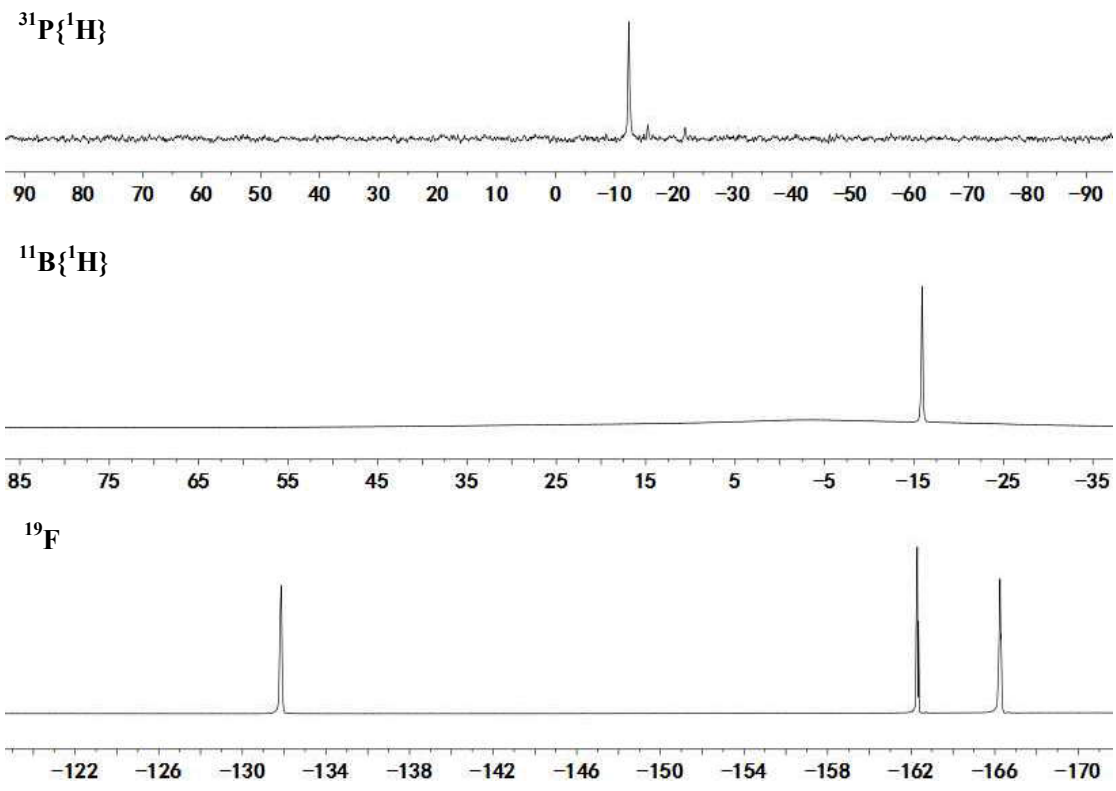
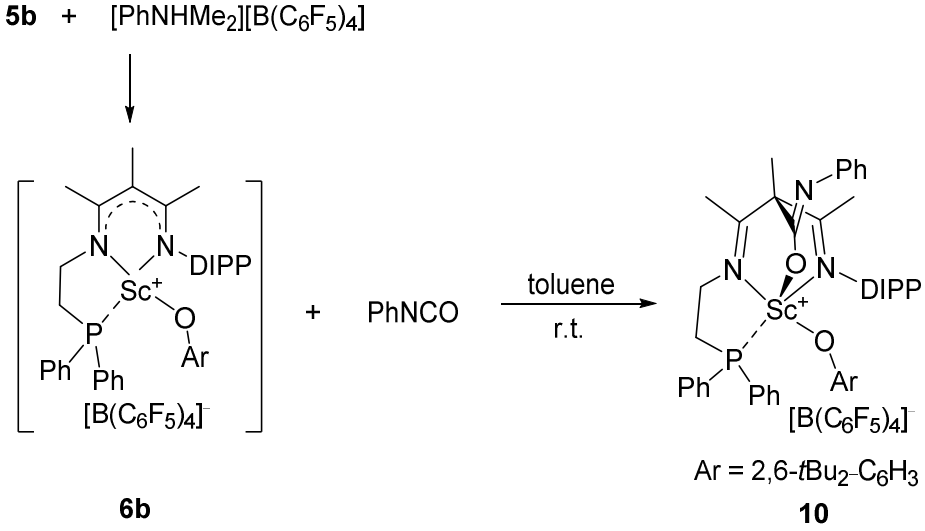


Fig. S40. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K), **$^{11}B\{^{1}H\}$ NMR** (128 MHz, C_6D_6, 298 K), **^{19}F NMR** (376 MHz, C_6D_6, 298 K).

Characterization of complex 10:



Scheme S13.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: 7.38 / 7.36 (*o*-OCN*Ph* / *m*-OCN*Ph*), 7.36 / 7.10 (*m*-OCN*Ph* / *p*-OCN*Ph*), 7.07 / 6.68 (*m*-O*Ar* / *p*-O*Ar*), 7.05 / 6.89 (*o*-*Ph*P / *m*-*Ph*P), 6.95 / 6.92 (*m*-N*Ar* / *p*-N*Ar*), 6.93 / 6.87 (*o*-*Ph*'P / *m*-*Ph*'P), 6.92 / 6.90 (*p*-N*Ar* / *m*-N*Ar*), 3.44 / 1.72 (NCH_2 / PCH_2), 2.85 / 0.96, 0.81 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.86 / 1.07, 0.79 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K): δ ^{1}H / δ ^{13}C = 7.38 / 124.0 (*o*-OCN*Ph*), 7.36 / 129.0 (*m*-OCN*Ph*), 7.10 / 124.6 (*p*-OCN*Ph*), 7.07 / 125.7 (*m*-O*Ar*), 7.05 / 133.0 (*o*-*Ph*P), 6.99 / 132.0 (*p*-*Ph*P), 6.95 / 125.8 (*m*-N*Ar*), 6.93 / 131.9 (*o*-*Ph*'P), 6.92 / 126.3 (*p*-N*Ar*), 6.91 / 131.7 (*p*-*Ph*'P), 6.90 / 125.9 (*m*-N*Ar*), 6.89 / 130.1 (*m*-*Ph*P), 6.87 / 129.7 (*m*-*Ph*'P), 6.77 / 126.0 (*m*-O*Ar*), 6.68 / 120.6 (*p*-O*Ar*), 3.63, 3.44 / 50.6 (N*C*H_2), 2.85 / 30.5 (Ar*CH*Me$_2$), 2.58, 1.72 / 27.4 (P*C*H_2), 1.86 / 29.1 (Ar*CH*Me$_2$), 1.76 / 22.6 (γ-C*Me*), 1.68 /17.3 (*Me*C), 1.54 / 23.1 (*Me*C), 1.33 / 31.2 (C(*C*H_3)$_3$), 1.07 / 23.5 (ArCH*Me*$_2$), 0.96 / 23.7 (ArCH*Me*$_2$), 0.81 / 24.5 (ArCH*Me*$_2$), 0.79 / 23.4 (ArCH*Me*$_2$), 0.68 / 33.4 (C(*C*H_3)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.38 / 124.6 (*o*-OCN*Ph* / *p*-OCN*Ph*), 7.36 / 148.2 (*m*-OCN*Ph* / *i*-OCN*Ph*), 7.10 / 124.0 (*p*-OCN*Ph* / *o*-OCN*Ph*), 7.07 / 159.3, 35.2 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.05 / 132.0 (*o*-*Ph*P / *p*-*Ph*P), 6.99 / 133.0 (*p*-*Ph*P / *o*-*Ph*P), 6.95 / 141.3, 29.1 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 6.93 / 131.7 (*o*-*Ph*'P / *p*-*Ph*'P), 6.92 / 139.7, (*p*-N*Ar*

/ *o*-N*Ar*), 6.91 / 131.9 (*p-Ph*'P / *o-Ph*'P), 6.89 / 125.2 (*m-Ph*P/ *i-Ph*P), 6.87 / 126.4 (*m-Ph*'P/ *i-Ph*'P), 6.77 / 159.3, 34.0 (*m*-O*Ar* / *i*-O*Ar*, *C*$(CH_3)_3$), 6.68 / 137.8, 136.5 (*p*-O*Ar* / *o*-O*Ar*), 3.44 / 184.5, 27.4 (NCH_2 / Me*C*, P*C*H_2), 2.85 / 141.3, 139.7, 125.9 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 2.58 / 126.4, 125.2 (PCH_2 / *i-Ph*'P, *i-Ph*P), 1.86 / 141.3, 138.7, 125.8 (Ar*CH*Me_2 / *i*, *o*, *m*-N*Ar*), 1.76 / 184.5, 156.9 (γ-C*Me* / Me*C*, O*C*NPh), 1.72 / 126.4 (PCH_2 / *i-Ph*'P), 1.68, 1.54 / 67.0 (*Me*C / γ-*C*), 1.33 / 137.8, 35.2 (C(CH_3)$_3$ / *o*-O*Ar*, *C*$(CH_3)_3$), 1.07, 0.79 / 138.7 (ArC*H*Me_2 / *o*-NAr), 0.96, 0.81 / 139.7 (ArC*H*Me_2 / *o*-NAr), 0.68 / 136.5, 34.0 (C(CH_3)$_3$ / *o*-O*Ar*, *C*$(CH_3)_3$).

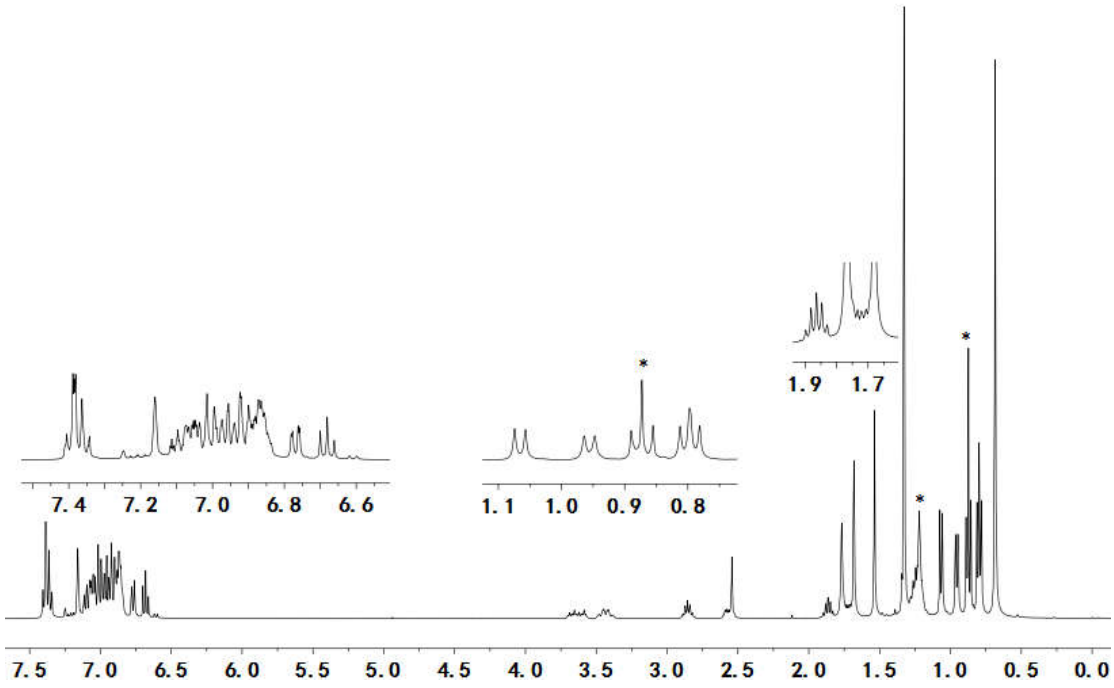


Fig. S41. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*: Hexane]

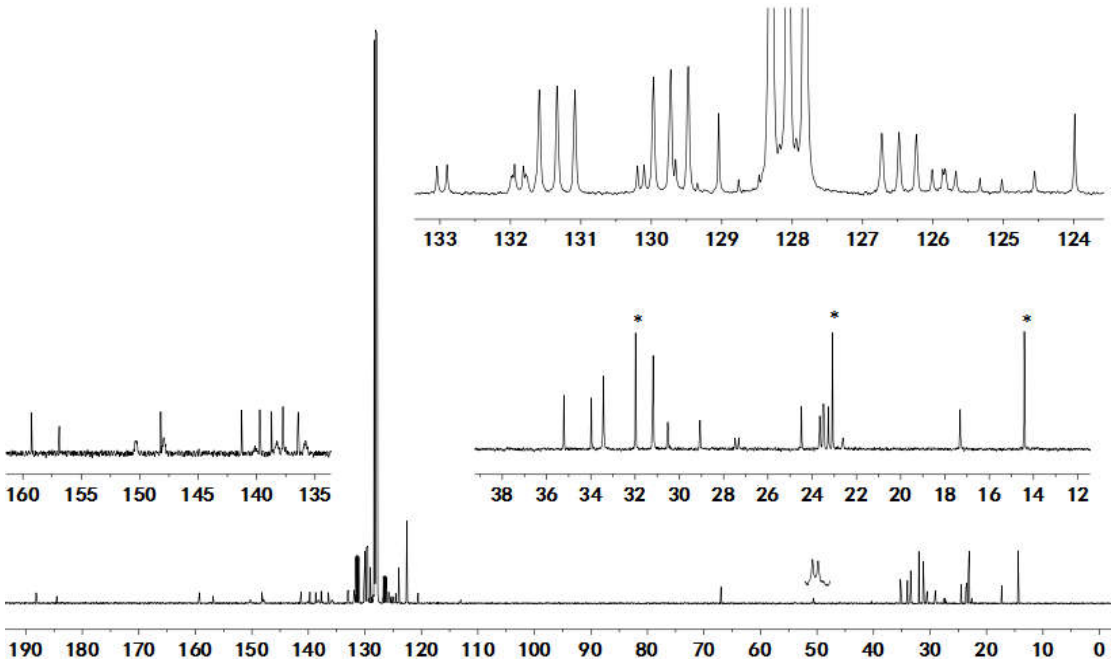


Fig. S42. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*: Hexane]

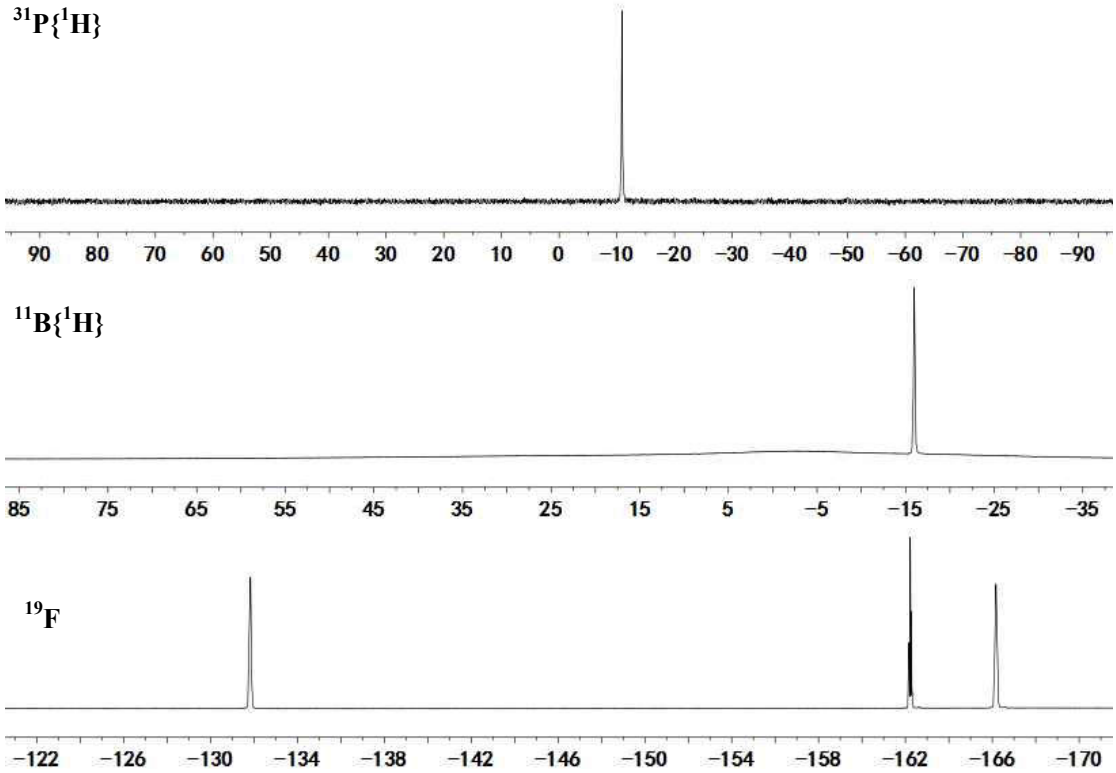
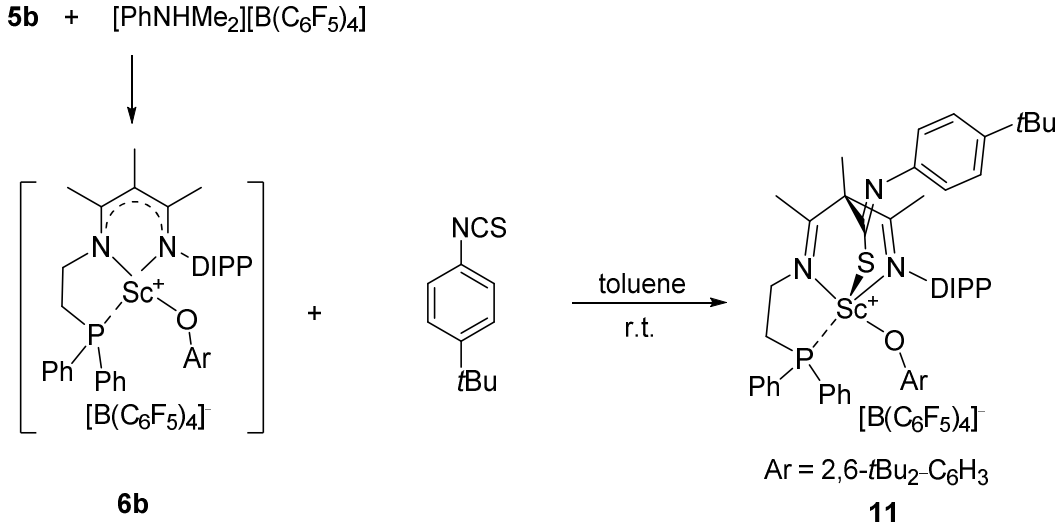


Fig. S43. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

Characterization of complex 11:



Scheme S14.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K) [selected traces]: 7.43 / 7.05 (*o*-SCN*Ph* / *m*-SCN*Ph*), 7.20, 7.13 / 6.96 (*o*, *p*-*Ph*P / *m*-*Ph*P), 7.19 / 7.02 (*p*-N*Ar* / *m*-N*Ar*), 7.11, 7.09 / 6.98 (*o*, *p*-*Ph*'P / *m*-*Ph*'P), 7.04 / 6.75 (*m*-O*Ar* / *p*-O*Ar*), 3.51 / 1.63 (NCH_2 / PCH_2), 3.30 / 1.02, 0.97 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.08 / 1.13, 0.87 (ArC*H*Me$_2$ / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K): δ ^{1}H / δ ^{13}C = 7.43 / 126.12 (*o*-SCN*Ph*), 7.20 / 132.8 (*o*-*Ph*P), 7.19 / 126.07 (*p*-N*Ar*), 7.13 / 131.7 (*p*-*Ph*P), 7.11 / 131.9 (*o*-*Ph*'P), 7.09 / 131.9 (*p*-*Ph*'P), 7.05 / 120.6 (*m*-SCN*Ph*), 7.04 / 125.8 (*m*-O*Ar*), 7.02 / 125.6 (*m*-N*Ar*), 7.01 / 125.5 (*m*-N*Ar*), 6.98 / 129.3 (*m*-*Ph*'P), 6.96 / 130.3 (*m*-*Ph*P), 6.79 / 126.09 (*m*-O*Ar*), 6.75 / 121.1 (*p*-O*Ar*), 4.01, 3.51 / 51.2 (NCH_2), 3.30 / 30.8 (Ar*C*HMe$_2$), 2.74, 1.63 / 28.1 (PCH_2), 2.11 / 18.1 (*Me*C), 2.08 / 29.0 (Ar*C*HMe$_2$), 2.00 / 25.0 (γ-C*Me*), 1.74 / 25.3 (*Me*C), 1.27 / 31.5 (SCNPhC(CH_3)$_3$), 1.26 / 31.2 (C(CH_3)$_3$), 1.13 / 23.4 (ArCH*Me*$_2$), 1.02 / 24.4 (ArCH*Me*$_2$), 0.97 / 24.7 (ArCH*Me*$_2$), 0.87 / 24.1 (ArCH*Me*$_2$), 0.62 / 33.1 (C(CH_3)$_3$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.43 / 147.2 (*o*-SCN*Ph* / *p*-SCN*Ph*), 7.20 / 131.7 (*o*-*Ph*P/ *p*-*Ph*P), 7.19 / 138.9 (*p*-N*Ar* / *o*-N*Ar*), 7.13 / 132.8 (*p*-*Ph*P/ *o*-*Ph*P), 7.11 / 129.6 (*o*-*Ph*'P/ *p*-*Ph*'P), 7.09 / 131.9 (*p*-*Ph*'P/ *o*-*Ph*'P), 7.05 / 148.0, 34.5 (*m*-SCN*Ph* / *i*-SCN*Ph*, SCNPh*C*(CH_3)$_3$), 7.04 / 159.6, 35.2 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH_3)$_3$), 7.02 / 142.5,

29.0 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 7.01 / 142.5, 30.8 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe$_2$), 6.98 / 126.2 (*m*-*Ph*'P/ *i*-*Ph*'P), 6.96 / 125.2 (*m*-*Ph*P/ *i*-*Ph*P), 6.79 / 159.6, 33.7 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 6.75 / 137.2, 136.7 (*p*-O*Ar* / *o*-O*Ar*), 4.01 / 186.1 (NC*H*$_2$ / Me*C*), 3.51 / 28.1 (NC*H*$_2$ / P*C*H$_2$), 3.30 / 142.5, 140.5, 125.5 (ArC*H*Me$_2$ / *i*, *o*, *m*-N*Ar*), 2.74 / 126.2, 125.2 (PC*H*$_2$ / *i*-*Ph*'P, *i*-*Ph*P), 2.11 / 186.1, 71.8, 51.2 (*Me*C / Me*C*, γ-*C*, N*C*H$_2$), 2.08 / 142.5, 138.9, 125.6 (Ar*CH*Me$_2$ / *i*, *o*, *m*-N*Ar*), 2.00 / 186.1, 163.1 (γ-C*Me* / Me*C*, S*C*NPh), 1.63 / 125.3 (PC*H*$_2$ / *i*-*Ph*P), 1.27 / 147.2 (SCNPhC(C*H*$_3$)$_3$ / *p*-SCN*Ph*), 1.26 / 137.2, 35.2 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$), 0.62 / 136.7, 33.7 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH$_3$)$_3$).

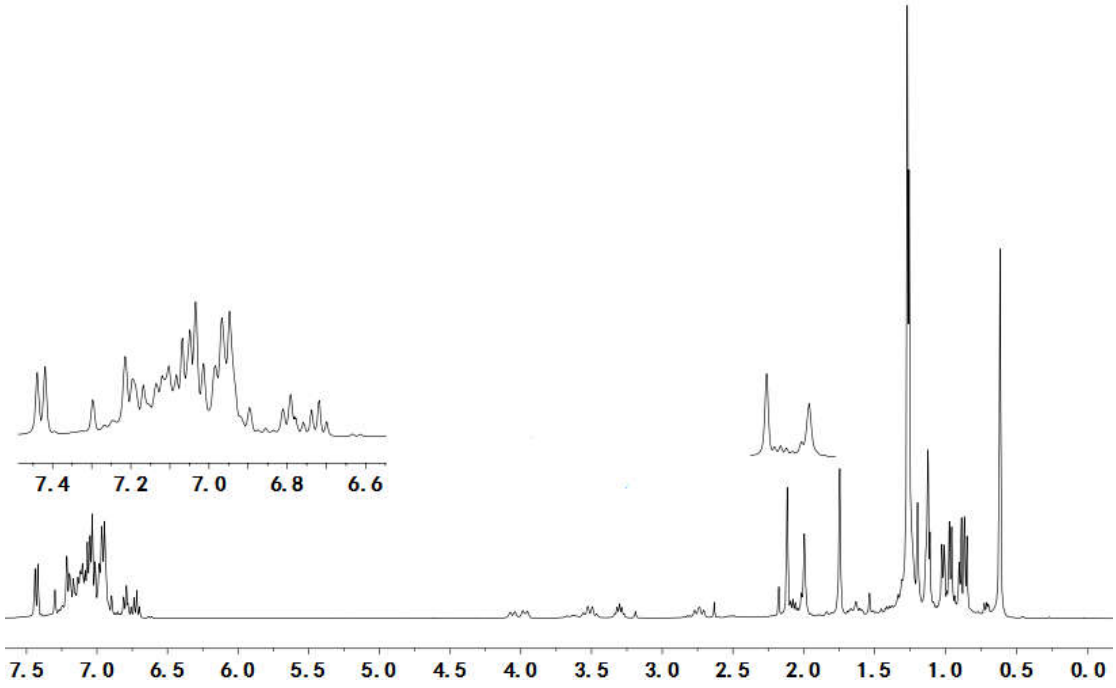


Fig. S44. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K)

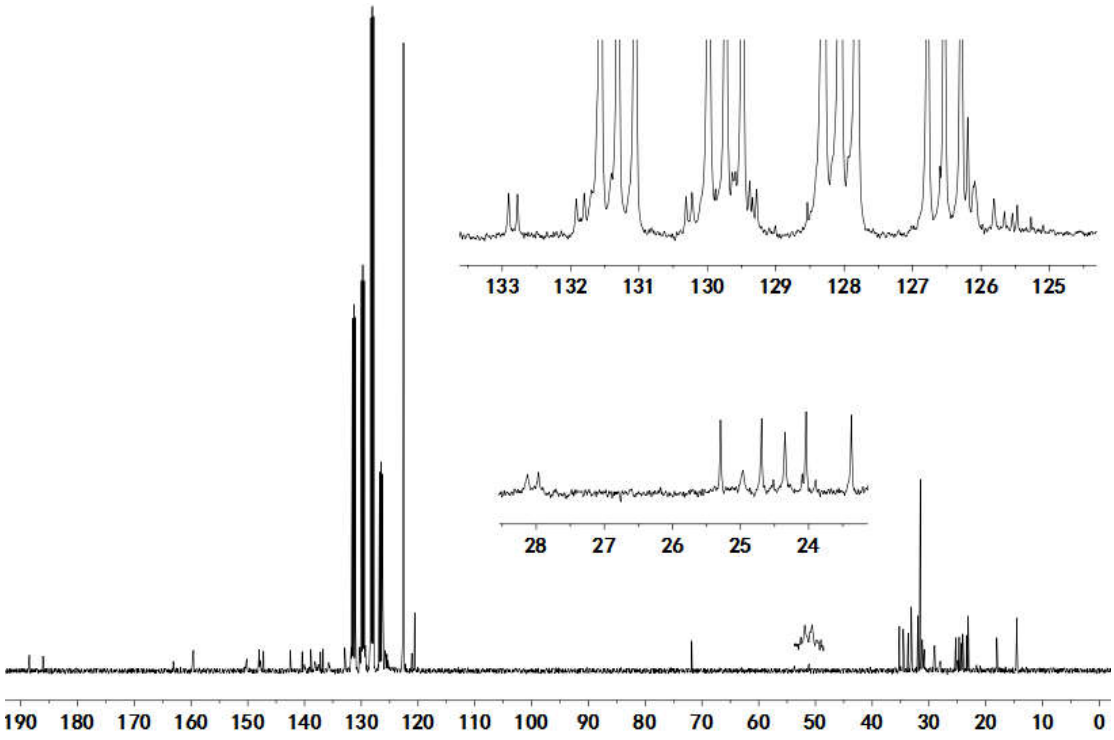


Fig. S45. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K)

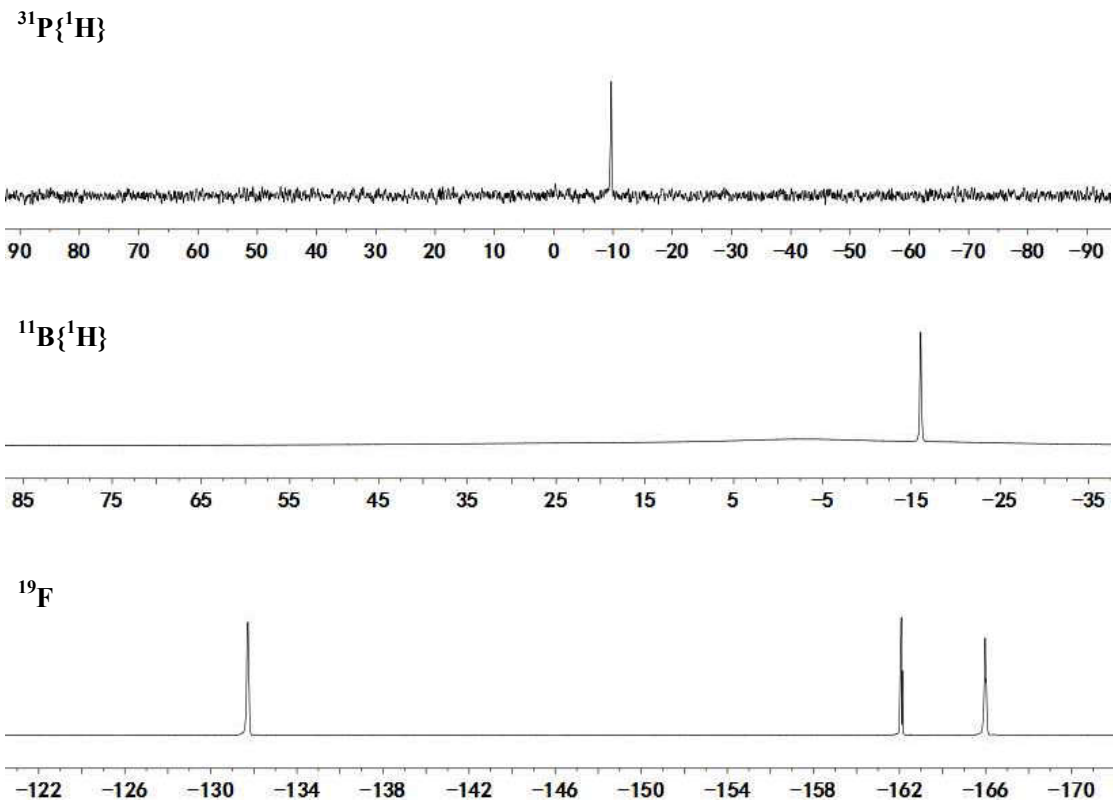
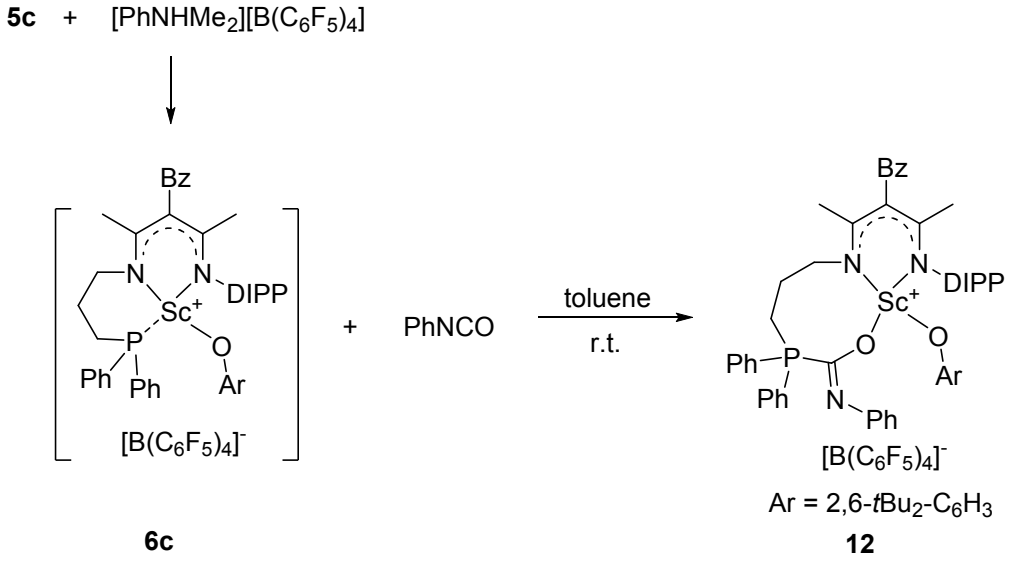


Fig. S46. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K), **$^{11}B\{^1H\}$ NMR** (128 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K), **^{19}F NMR** (376 MHz, C_6D_6 / C_6D_5Br (1:1), 298 K).

Characterization of complex 12:



Scheme S15.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: 7.66, 7.24 / 7.16 (*o*-*Ph*P, *p*-*Ph*P / *m*-*Ph*P), 7.22 / 6.84 (*m*-O*Ar* / *p*-O*Ar*), 7.21, 7.04 / 6.97 (*p*-*Ph*'P, *o*-*Ph*'P / *m*-*Ph*'P), 7.19 / 7.06 (*m*-OCN*Ph* / *o*-OCN*Ph*), 7.10 / 7.07, 7.01 (*m*-CH_2*Ph* / *p*, *o*-CH_2*Ph*), 7.02 / 6.80 (*p*-N*Ar* / *m*-N*Ar*), 3.54 / 3.02, 2.12 (NCH_2 / NCH_2, NCH_2CH_2), 2.82 / 0.97, 0.57 (ArC*H*Me_2 / ArCH*Me*$_2$), 2.78 / 2.28, 1.75 (PH_2 / PH_2, NCH_2CH_2), 1.93 / 1.08, 0.97 (ArC*H*Me_2 / ArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K): δ ^{1}H / δ ^{13}C = 7.66 / 133.7 (*o*-*Ph*P), 7.24 / 135.5 (*p*-*Ph*P), 7.22 / 125.5 (*m*-O*Ar*), 7.19 / 129.3 (*m*-OCN*Ph*), 7.21 / 134.8 (*p*-*Ph*'P), 7.16 / 130.4 (*m*-*Ph*P), 7.15 / 124.8 (*p*-OCN*Ph*), 7.10 / 126.9 (*m*-CH_2*Ph*), 7.07 / 127.4 (*p*-CH_2*Ph*), 7.06 / 127.1 (*o*-OCN*Ph*), 7.02 / 124.5 (*p*-N*Ar*), 7.04 / 131.4 (*o*-*Ph*'P), 7.01 / 127.9 (*o*-CH_2*Ph*), 6.97 / 130.5 (*m*-*Ph*'P), 6.96 / 125.2 (*m*-N*Ar*), 6.84 / 119.5 (*p*-O*Ar*), 6.80 / 125.0 (*m*-N*Ar*), 3.54, 3.02 / 50.4 (NCH_2), 3.50 / 36.5 (*C*H_2Ph), 2.82 / 30.8 (ArC*H*Me_2), 2.78, 2.28 / 18.4 (PCH_2), 2.12, 1.75 / 23.5 (NCH_2CH_2), 1.93 / 27.5 (ArC*H*Me_2), 1.87 /19.5 (*Me*C), 1.59 / 20.7 (*Me*C), 1.28 / 30.9 (C(CH_3)$_3$), 1.08 / 24.6 (ArCH*Me*$_2$), 0.97 / 25.7, 24.7 (ArCH*Me*$_2$) 0.57 / 23.4 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.66 / 135.5 (*o*-*Ph*P / *p*-*Ph*P), 7.22 / 161.4, 34.8 (*m*-O*Ar* / *i*-O*Ar*,

C(CH_3)$_3$), 7.19 / 144.2 (*m*-OCN*Ph* / *i*-OCN*Ph*), 7.10 / 138.7 (*m*-CH_2*Ph* / *i*-CH_2*Ph*), 7.07 / 127.9 (*p*-CH_2*Ph* / *o*-CH_2*Ph*), 7.06 / 124.8 (*o*-OCN*Ph* / *p*-OCN*Ph*), 7.04 / 134.8 (*o*-*Ph*'P/ *p*-*Ph*'P), 7.02 / 141.2 (*p*-N*Ar* / *o*-N*Ar*), 7.01 / 127.4, 36.5 (*o*-CH_2*Ph* / *p*-CH_2*Ph*, *C*H_2Ph), 6.98 / 142.1, 27.5 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe_2), 6.97 / 119.0 (*m*-*Ph*'P/ *i*-*Ph*'P), 6.84 / 137.5 (*p*-O*Ar* / *o*-O*Ar*), 6.80 / 142.1, 30.8 (*m*-N*Ar* / *i*-N*Ar*, Ar*C*HMe_2), 3.54 / 170.5 (N*C*H_2 / Me*C*), 3.50 / 170.5, 127.9, 99.6 (*C*H_2Ph / Me*C*, *o*-CH_2*Ph*, γ-C), 2.82 / 142.1, 141.9, 125.0 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 2.78 / 119.0, 115.7, 50.4 (P*C*H_2 / *i*-*Ph*'P, *i*-*Ph*P, N*C*H_2), 2.28 / 148.4 (P*C*H_2 / O*C*NPh), 1.93 / 142.1, 141.2, 125.2 (ArC*H*Me_2 / *i*, *o*, *m*-N*Ar*), 1.28 / 137.5, 34.8 (C(C*H*$_3$)$_3$ / *o*-O*Ar*, *C*(CH_3)$_3$), 1.08, 0.97 / 141.3 (ArCH*Me*$_2$ / *o*-N*Ar*), 0.97, 0.57 / 141.9 (ArCH*Me*$_2$ / *o*-N*Ar*).

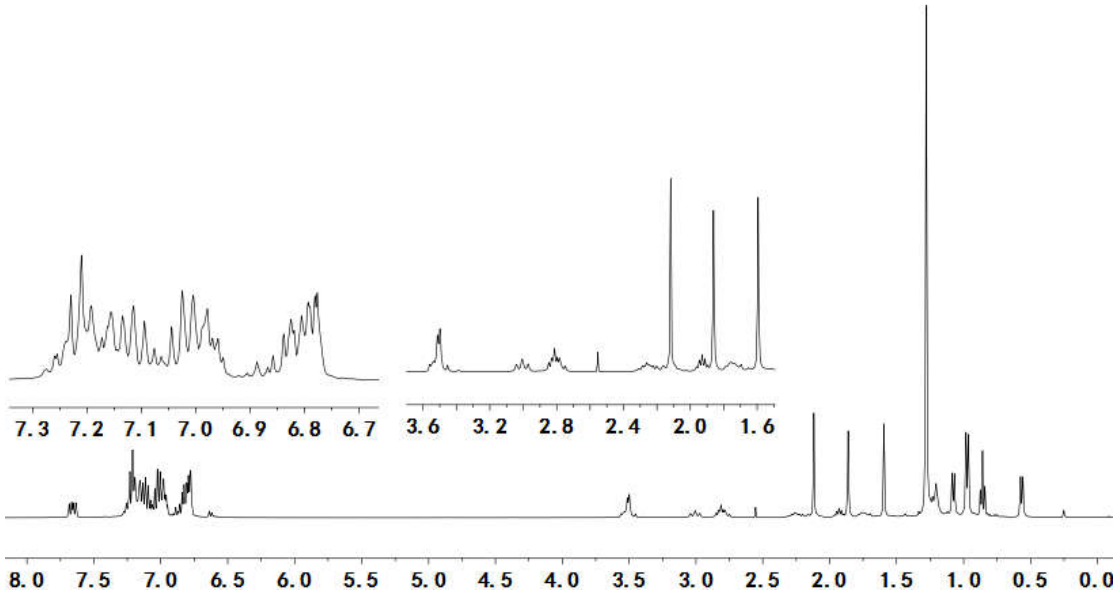


Fig. S47. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

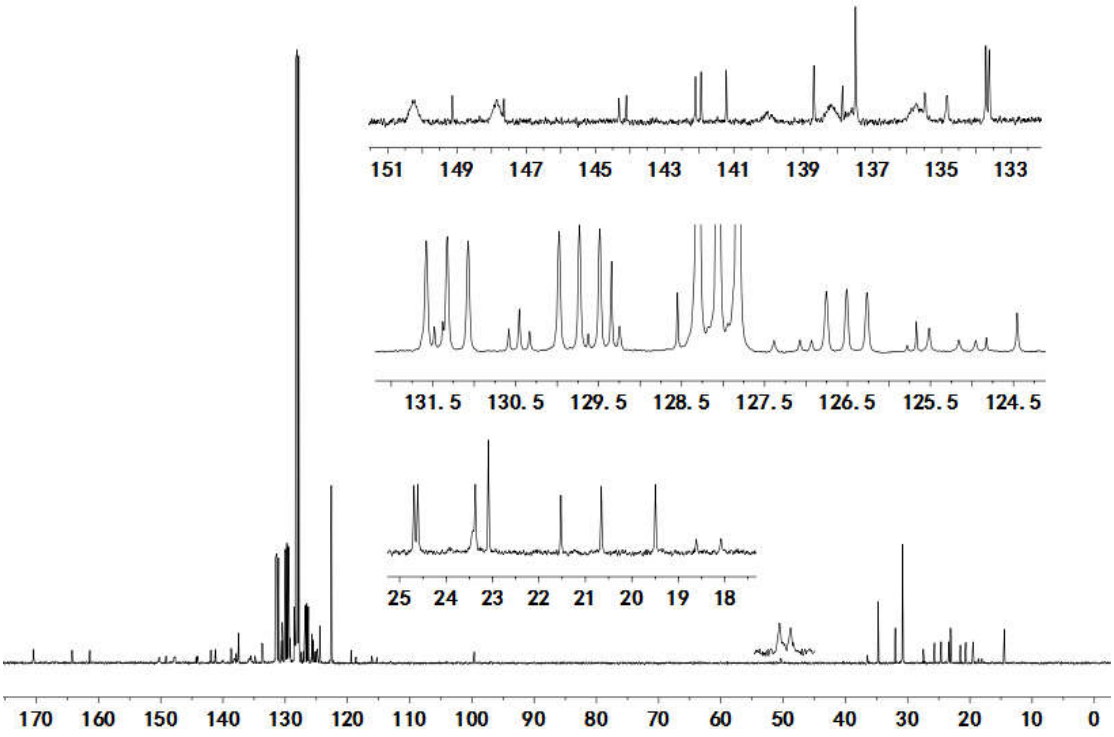


Fig. S48. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

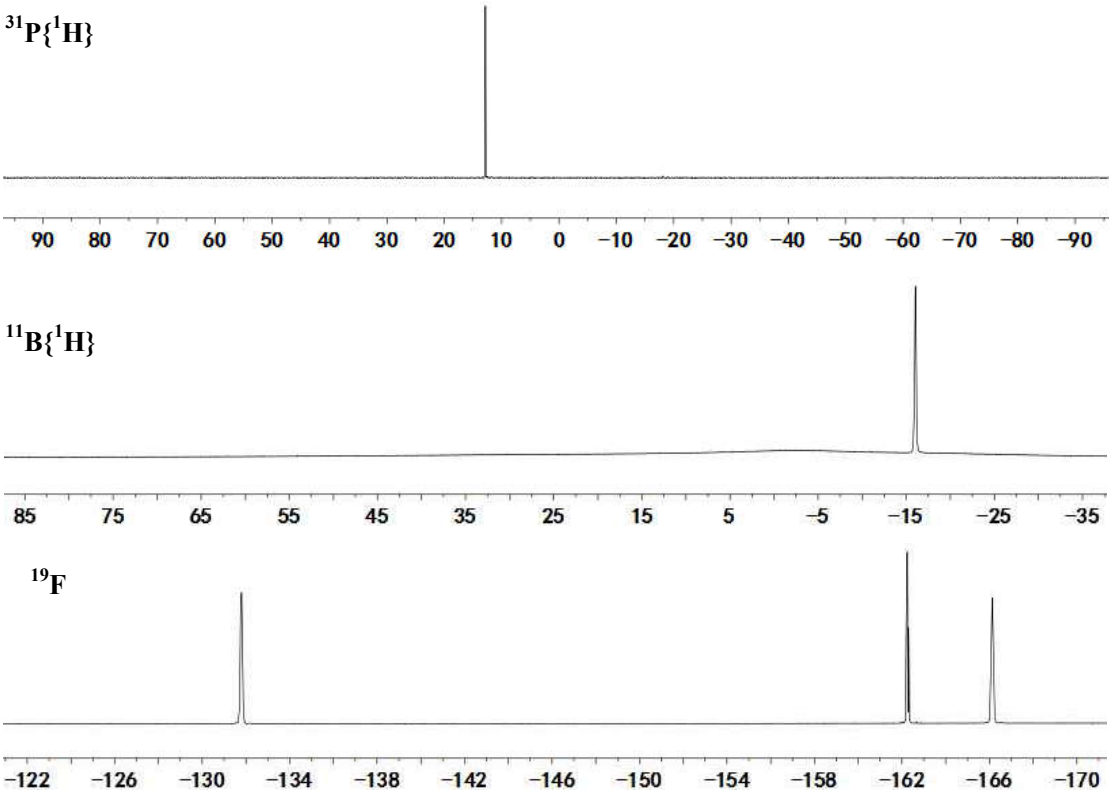
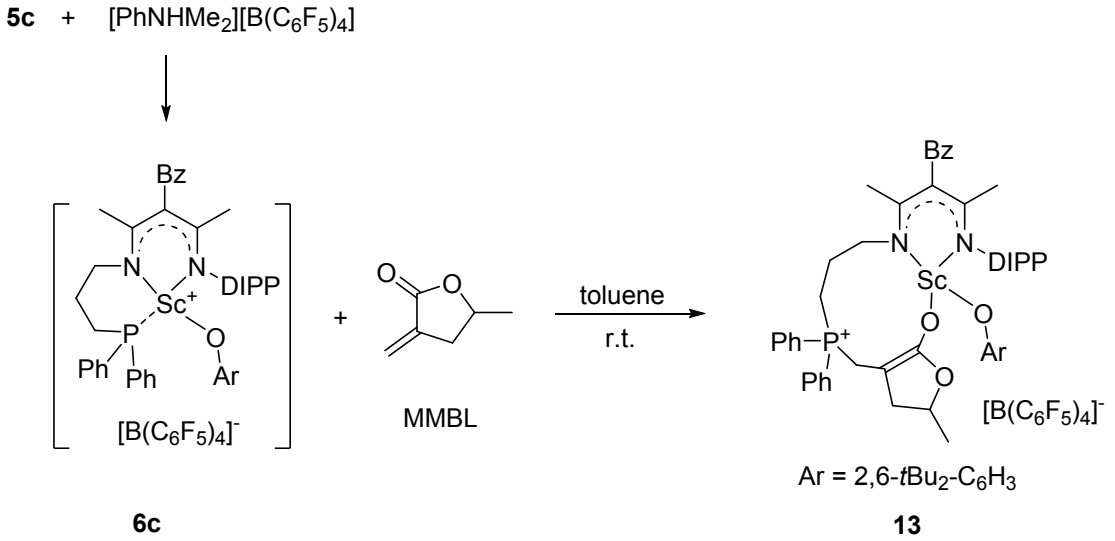


Fig. S49. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

Characterization of complex 13:



Scheme S16.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: 7.28 / 7.04 (*p*-*Ph*$_2$P / *m*-*Ph*$_2$P), 7.25 / 6.83 (*m*-O*Ar* / *p*-O*Ar*), 7.18 / 7.06 (*m*-CH_2*Ph* / *o*-CH_2*Ph*), 7.09 / 7.07 (*p*-N*Ar* / *m*-N*Ar*), 3.94 / 1.70, 1.16, 0.73 (OC*H* / OCHC*H*$_2$, OCHC*H*$_2$, OCH*Me*), 3.82 / 1.63, 1.23, 0.77 (OC*H* / OCHC*H*$_2$, OCHC*H*$_2$, OCHC*H*$_3$), 3.37 / 3.13, 1.72 (NC*H*$_2$ / NC*H*$_2$, NCH$_2$C*H*$_2$), 3.14 / 1.21, 1.08 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 3.12 / 1.17, 1.05 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 2.91 / 2.77 (PC*H*$_2$C= / PC*H*$_2$C=), 2.66 / 1.72, 1.68 (PC*H*$_2$CH$_2$ / PCH$_2$C*H*$_2$, PC*H*$_2$CH$_2$), 2.42, 2.32 / 1.08 (ArC*H*Me$_2$ / ArCH*Me*$_2$), 1.93 / 1.72 (PCH$_2$C*H*$_2$ / NCH$_2$C*H*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K): δ ^{1}H / δ ^{13}C = 7.28 / 135.3, 7.15 / 135.2 (*p*-*Ph*$_2$P), 7.25 / 125.4, 125.3 (*m*-O*Ar*), 7.18 / 129.1 (*m*-CH_2*Ph*), 7.14 / 130.3, 7.04 / 130.0 (*m*-*Ph*$_2$P), 7.09 / 126.8 (*p*-N*Ar*), 7.08 / 127.3 (*p*-CH_2*Ph*), 7.07 / 124.9, 124.8, 7.03 / 124.7, 124.6 (*m*-N*Ar*), 7.06 / 127.8 (*o*-CH_2*Ph*), 7.05 / 132.1, 6.93 / 132.0 (*o*-*Ph*$_2$P), 6.83 / 119.0, 118.9 (*p*-O*Ar*), 3.94 / 73.7, 3.82 / 73.6 (O*CH*), 3.60 / 37.5, 3.56 / 37.4 (*CH*$_2$Ph), 3.37, 3.13 / 50.42, 3.37, 3.13 / 50.40 (N*CH*$_2$), 3.14 / 27.9, 3.12 / 27.8, 2.42 / 30.0, 2.32 / 28.7 (Ar*CH*Me$_2$), 2.91, 2.77 / 19.9, 2.91, 2.77 / 19.7 (P*CH*$_2$C=), 2.66, 1.68 / 20.2, 2.66, 1.68 / 19.8 (P*CH*$_2$CH$_2$), 1.93, 1.72 / 23.1 (PCH$_2$*CH*$_2$), 1.80 / 19.5, 19.4 (*Me*C), 1.59 / 21.5 (*Me*C), 1.57 / 21.3 (*Me*C), 1.70, 1.16 / 39.2, 1.63, 1.23 / 38.9 (OCH*CH*$_2$), 1.45 / 30.9, 30.8 (C(*CH*$_3$)$_3$), 1.21 / 24.2, 24.1

(ArCH*Me*$_2$), 1.17 / 23.9 (ArCH*Me*$_2$), 1.08 / 25.6, 25.5, 24.9, 24.7, 24.0 (ArCH*Me*$_2$), 0.77 / 21.9, 0.73 / 22.0 (OCH*Me*).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.28 / 132.1 (*p*-*Ph*$_2$P / *o*-*Ph*$_2$P), 7.25 / 161.8, 34.9 (*m*-O*Ar* / *i*-O*Ar*, *C*(CH$_3$)$_3$), 7.18 / 139.8 (*m*-CH$_2$*Ph* / *i*-CH$_2$*Ph*), 7.09 / 142.0 (*p*-N*Ar* / *o*-N*Ar*), 7.07 / 143.3 (*m*-N*Ar* / *i*-N*Ar*), 7.06 / 127.3, 37.5 (*o*-CH$_2$*Ph* / *p*-CH$_2$*Ph*, *C*H$_2$Ph), 7.05 / 135.3 (*o*-*Ph*P / *p*-*Ph*P), 7.04 / 119.0 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 7.03 / 143.5 (*m*-N*Ar* / *i*-N*Ar*), 6.93 / 135.2 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 6.83 / 137.9 (*p*-O*Ar* / *o*-O*Ar*), 3.60 / 170.4, 139.8, 127.8, 102.1 (C*H*$_2$Ph / Me*C*, *i*-CH$_2$*Ph*, *o*-CH$_2$*Ph*, γ-C), 3.37 / 170.4 (NC*H*$_2$ / Me*C*), 3.14 / 143.5, 142.0, 124.8 (ArC*H*Me$_2$ / *i*, *o*, *m*-NAr), 3.12 / 143.3, 141.9, 124.9 (ArC*H*Me$_2$ / *i*, *o*, *m*-NAr), 2.91, 2.77 / 163.1 (PC*H*$_2$C= / O*C*=), 2.42 / 142.0, 124.7 (Ar*CH*Me$_2$ / *o*, *m*-NAr), 2.32 / 141.9, 124.6 (ArC*H*Me$_2$ / *o*, *m*-NAr), 1.70 / 56.7, 22.0 (OCHC*H*$_2$ / PCH$_2$*C*=, OCH*Me*), 1.63 / 56.6, 19.4 (OCHC*H*$_2$ / PCH$_2$*C*=, P*C*H$_2$C=), 1.45 / 137.9 (C(C*H*$_3$)$_3$) / *o*-O*Ar*), 1.23 / 162.9, 73.7, 56.6 (OCHC*H*$_2$ / O*C*=, O*C*H, PCH$_2$*C*=), 1.16 / 163.1, 73.6, 56.7 (OCHC*H*$_2$ / O*C*=, O*C*H, PCH$_2$*C*=), 0.77 / 38.9 (OCH*Me* / OCH*C*H$_2$), 0.73 / 39.2 (OCH*Me* / OCH*C*H$_2$).

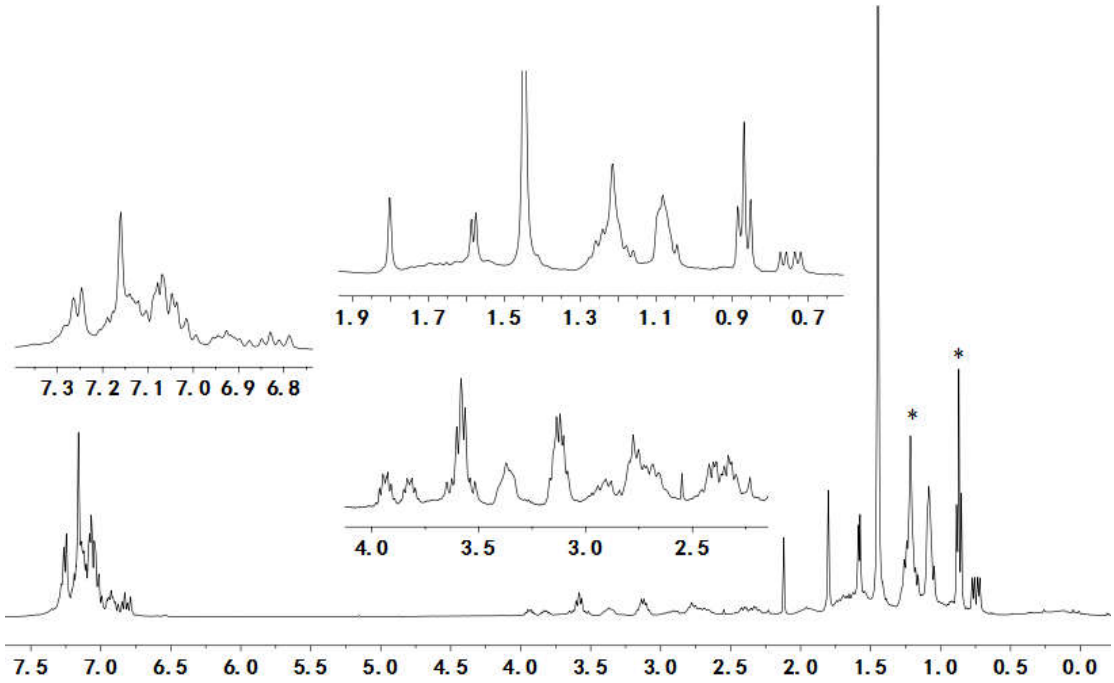


Fig. S50. ^{1}H NMR (400 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*: Hexane]

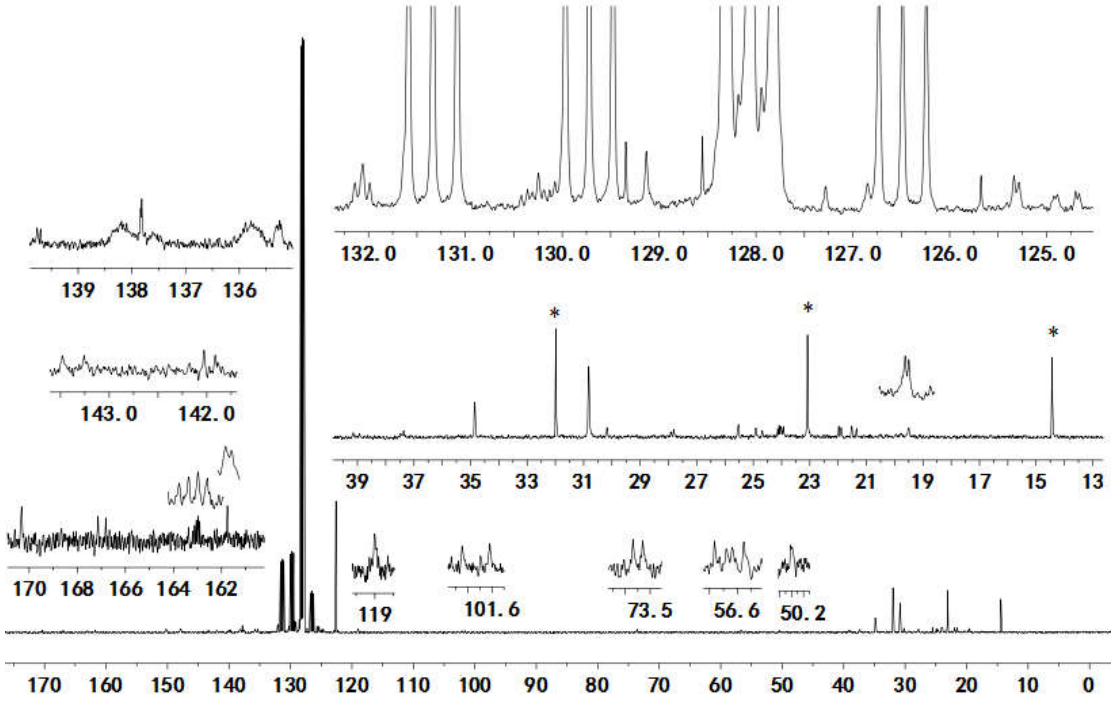


Fig. S51. $^{13}C\{^{1}H\}$ **NMR** (101 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K) [*: Hexane]

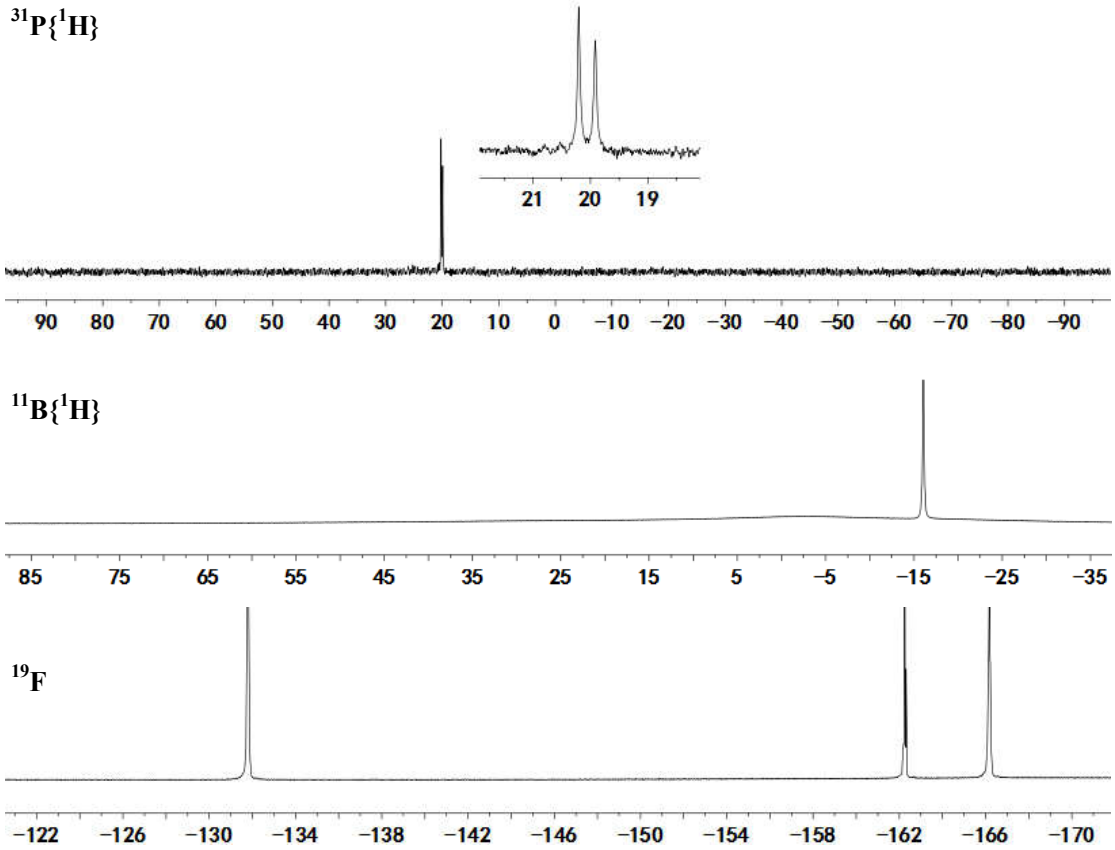


Fig. S52. $^{31}P\{^{1}H\}$ **NMR** (162 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), $^{11}B\{^{1}H\}$ **NMR** (128 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K), ^{19}F **NMR** (376 MHz, C_6D_6 / C_6D_5Br (4:1), 298 K).

X-ray crystal structure analysis of complex 13: formula $C_{181}H_{147}B_2F_{40}N_4O_6P_2Sc_2$, M = 3407.51, colorless crystal, 0.30 x 0.25 x 0.20 mm, a = 17.6536(13), b = 21.5307(15), c = 22.7521(16) Å, β = 97.834(8)°, V = 8567.2(11) Å^3, ρ_{calc} = 1.321 gcm^{-3}, μ = 0.197 mm^{-1}, empirical absorption correction (0.2420 ≤ T ≤1.0000), Z = 2, Monoclinic, space group P 21/n, λ = 0.71073 Å, T = 293(2) K, Multi-scan, 51374 reflections collected (±h, ±k, ±l), 15073 independent (R(int) = 0.1083) and 8268 observed reflections [I>2σ(I)], 1037 refined parameters, R = 0.0980, wR2 = 0.3062, max. (min.) residual electron density 1.142 (-1.066) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

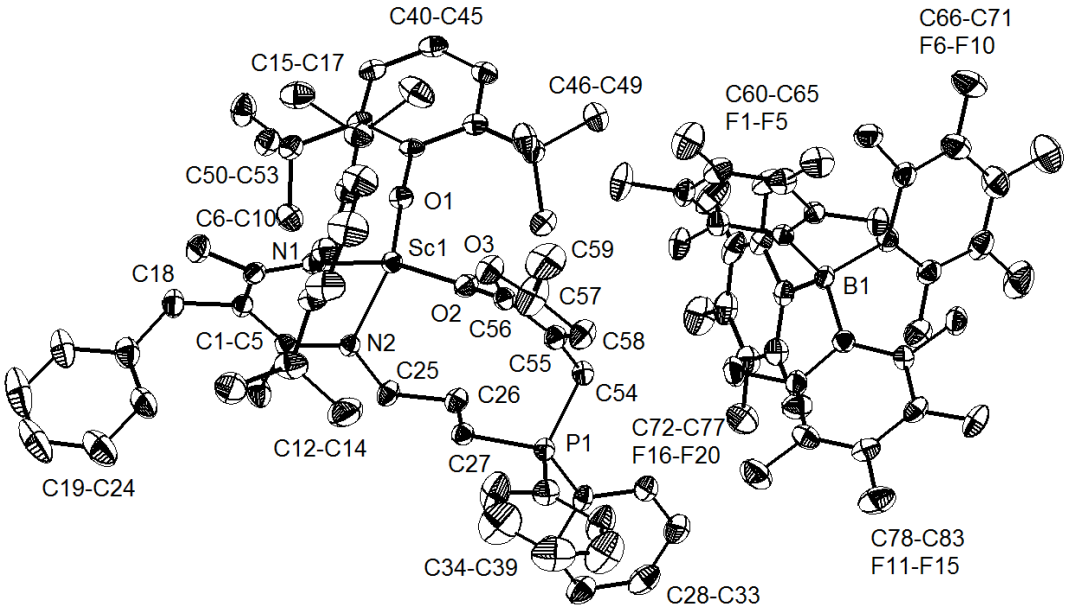


Fig. S53. Molecular structure of complex **13**.

Polymerization of MMBL. A predetermined amount of complex **6c** (30 mg, 20 μmol) was first dissolved in chlorobenzene (1 mL). Then the polymerization was started by rapid addition of MMBL (214 μL, 2 mmol) via a gastight syringe to the above solution under vigorous stirring. After 5 min, a 0.1 mL aliquot was taken from the reaction mixture via a syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried "wet" $CDCl_3$. The quenched aliquots were later analyzed by ^1H NMR to obtain the conversion data of monomer (96%). The polymerization was immediately quenched after the removal of the aliquot by addition of 5 mL 5% HCl-acidified methanol. The quenched mixture was precipitated into methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 ^oC overnight to a constant weight to verify the polymer conversions determined by ^1H NMR.

Polymer characterization. Polymer number (M_n) and weight (M_w) average molecular weights and polydispersity index (PDI = M_w/M_n) were measured by gel permeation chromatography (GPC) analyses carried out at 40 ºC and a flow rate of 0.8 mL/min with DMF as the eluent, on a Waters University 1515 GPC instrument coupled with a Waters RI detector and equipped with four PLgel 5 μm mixed-C columns. The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower software.