(Phosphino)(stannyl)carbene

Rui Wei, Xin-Feng Wang, Chaopeng Hu, Liu Leo Liu*

Department of Chemistry and Research Center for Chemical Biology and Omics Analysis, College of Science, Southern University of Science and Technology, Shenzhen 518055 China

Table of Contents

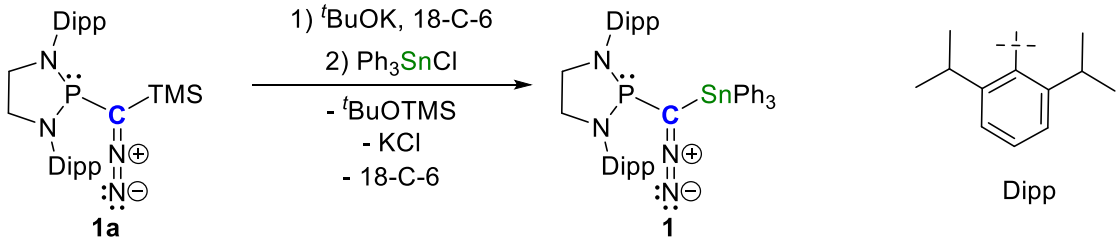
I. General Information

All reactions were carried out under an inert gas atmosphere by using either standard Schlenk or in a N_2-filled glove box. Solvents were dried by distillation over sodium/potassium alloy or $LiAlH_4$ and stored with 4Å molecular sieves before use. NMR spectra were recorded with Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) or 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) spectrometer at 298 K. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal), integration, coupling constants J in hertz (Hz).

High resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q-Exactive MS System with electrospray ionization (ESI) method. Infrared spectra were recorded on a FT-IR spectrometer (Bruker ALPHA II) using a DLaTGS detector. Crystal data were collected on a Bruker D8 Venture diffractometer with graphite monochromated Cu Kα (λ =1.54178). Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS). The model was refined with the ShelXL program using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. A photoreaction instrument (300W, PL-DY1600, Beijing Precise Technology Co., Ltd.) equipped with a broad band LED lamp with the central wavenumber of 365 nm was used for the irradiation.

Commercial reagents were purchased from Energy Chemical, J&K, or TCI Chemical Co. and used as received. The abbreviation for the ligand is as follows: Dipp = 2,6-diisopropylphenyl. Compound **1a** was synthesized according to literature procedure[S1]. Note: Although we have not experienced any problems, cautions should be exercised when handling diazo reagents due to their potentially explosive nature, especially for large scale reactions.

II. Experimental Details



Scheme 1. Synthesis of **1**.

A solution of ^{t}BuOK (51 mg, 0.45 mmol) and 18-C-6 (143 mg, 0.55 mmol) in THF (4 mL) was added dropwise into a THF solution of **1a** (236 mg, 0.45 mmol) (3 mL) at -50 °C. After stirring for 4 h, a THF solution of Ph_3SnCl (176 mg, 0.45 mmol) (5 mL) was added dropwise into the solution at -50 °C. After stirring for 30 min, all the volatiles were removed under vacuum, and the residue was extracted with 5 mL of toluene. The solvent was removed under vacuum; the residue was washed with 3 x 2 mL of *n*-hexane, affording **1** as a gray solid. (200 mg, 56%). Colorless crystals suitable for single-crystal X-ray analysis were obtained from a concentrated Et_2O/*n*-pentane solution at -30 °C.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.27 (m, 7H, ^{Ph}Ar-H), 7.19 (m, 5H, ^{Ph}Ar-H), 6.99 (m, 9H, ^{Ph}Ar-H), 4.20 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 2H, ^{Dipp}CH), 4.06 (m, 2H, CH_2), 3.56 (m, 2H, ^{Dipp}CH), 3.22 (m, 2H, CH_2), 1.40 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.34 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.24 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.13 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$).

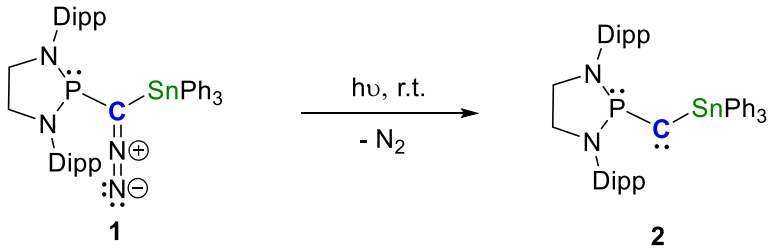
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 149.7 (Ar-*C*), 148.2 (Ar-*C*), 138.4 (d, $^{2}J_{P\text{-}C}$ = 13.5 Hz, P-N-C_{Ar}), 137.1 (Ar-*C*), 129.4 (Ar-*C*), 129.1 (Ar-*C*), 124.8 (Ar-*C*), 124.9 (Ar-*C*), 54.9 (d, $^{2}J_{P\text{-}C}$ = 7.3 Hz, NCH_2), 29.8 (d, $^{1}J_{P\text{-}C}$ = 154.3 Hz, CN_2), 29.0 (d, $^{4}J_{P\text{-}C}$ = 9.4 Hz, $CHMe_2$), 28.1 (CH_3), 25.8 (CH_3), 25.7 (CH_3), 24.2 (d, $^{5}J_{P\text{-}C}$ = 2.7 Hz, , $^{Dipp}CH_3$), 23.0 (CH_3).

^{31}P NMR (162 MHz, C_6D_6) δ (ppm) = 121.1 ($^{2}J^{119}_{Sn\text{-}P}$ = 301.4 Hz, $^{2}J^{117}_{Sn\text{-}P}$ = 287.6 Hz).

^{119}Sn NMR (149 MHz, C_6D_6) δ (ppm) = -97.3 (d, $^{2}J_{P\text{-}Sn}$ = 301.4 Hz).

HRMS (ESI) $[M+H]^+$ $C_{45}H_{54}N_4PSn^+$: calc. 801.31026, found. 801.31462 m/z.

IR (ATR, neat): 3055, 2960, 2867, 1975 (N=N stretching), 1455, 1426, 1321, 1257, 1072, 800, 726, 697, 650, 555, 446 cm^{-1}.



Scheme 2. Synthesis of **2**.

1 (18 mg, 0.02 mmol) was placed in a J-Young tube, and then dry C_6D_6 (0.6 mL) was added at room temperature. The NMR tube was subjected to 352 nm broadband irradiation by LED lamp and monitored by ^{1}H NMR spectroscopy. After 2 h, the reaction was completed, and the volatiles were removed under vacuum. The residue was washed with 0.5 mL of *n*-pentane and dried under vacuum to afford **2** as a white powder

(88%, 15 mg). Colorless crystals of **2** suitable for single-crystal X-ray diffraction were grown by evaporation of a C_6D_6/*n*-pentane mixture solution (C_6D_6: 0.2 mL/*n*-pentane: 0.4 mL) at -30 °C.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.46 (m, 6H, ^{Ph}Ar-H), 7.18 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, ^{Dipp}Ar-H), 7.10 (m, 13H, Ar-H), 3.56 (sept, $^3J_{H-H}$ = 7.1 Hz, 4H, ^{Dipp}CH), 3.27 (d, $^3J_{H-H}$ = 6.9, 4H, CH_2), 1.29 (d, $^3J_{H-H}$ = 6.9 Hz, $^{Dipp}CH_3$), 1.24 (d, $^3J_{H-H}$ = 7.0 Hz, $^{Dipp}CH_3$).

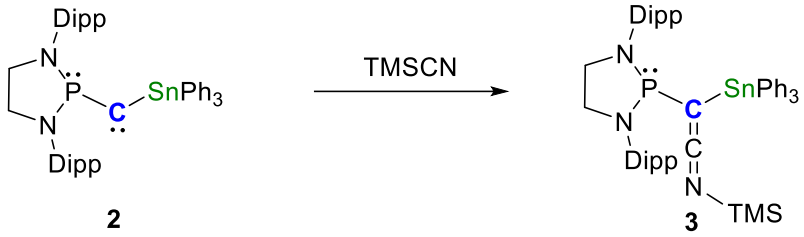
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) 148.3 (d, $^3J_{P-C}$ = 2.1 Hz, Sn-*o*-C_{Ar}), 142.2 (d, $^2J_{P-C}$ = 11.5 Hz, P-N-C_{Ar}), 136.8 (Ar-*C*), 134.5 (d, $^3J_{P-C}$ = 4.4 Hz, P-N-C-C_{Ar}), 124.3 (Ar-*C*), 49.6 (d, $^1J_{P-C}$ = 44.6 Hz, P*C*Sn), 47.5 (d, $^2J_{P-C}$ = 9.9 Hz, NCH_2), 29.1 (CH_3), 24.4 (CH_3), 24.3 (CH_3).

^{31}P NMR (162 MHz, C_6D_6) δ (ppm) = 10.2 ($^2J^{119}_{Sn-P}$ = 317.5 Hz, $^2J^{117}_{Sn-P}$ = 303.5 Hz).

^{119}Sn NMR (149 MHz, C_6D_6) δ (ppm) = -102.2 (d, $^2J_{P-Sn}$ = 317.5 Hz).

HRMS (ESI) $[M+H]^+$ $C_{45}H_{54}N_2PSn^+$: calc. 773.30411, found. 773.30408 m/z.

IR (ATR, neat): 3059, 2957, 2923, 2865, 1460, 1427, 1320, 1255, 1073, 964, 854, 801, 726, 697, 445 cm^{-1}.



Scheme 3. Synthesis of **3**.

2 (15 mg, 0.02 mmol) in 1 mL of THF was added in TMSCN (2 mg, 0.02 mmol). After stirring for 5 min at room temperature, the solvent was removed under reduced pressure. The residue was washed with 0.5 mL of *n*-pentane and then dried under vacuum to afford **3** as a slightly yellow solid (15 mg, 88%). Colorless single crystals of **3** suitable for X-ray diffraction were obtained from a saturated solution of **3** in Et_2O at -30 °C.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.36 (m, 8H, $^{Dipp/Ph}$Ar-H), 7.26 (m, 4H, $^{Dipp/Ph}$Ar-H), 7.07 ($^{Dipp/Ph}$Ar-H), 6.99 ($^{Dipp/Ph}$Ar-H), 4.22 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, ^{Dipp}CH), 4.03 (m, 2H, CH_2), 3.76 (m, 2H, ^{Dipp}CH), 3.36 (m, 2H, CH_2), 1.39 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.38 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.30 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 0.05 (s, 9H, TMS-H).

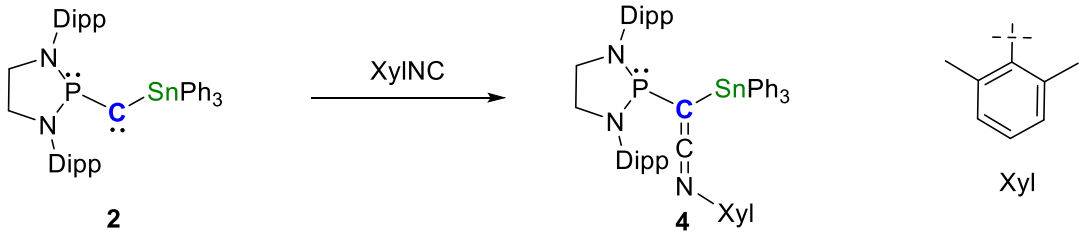
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) = 150.0 (d, $^3J_{P-C}$ = 2.0 Hz, Sn-*o*-C_{Ar}), 149.7 (d, $^2J_{P-C}$ = 5.4 Hz, P-N-C_{Ar}), 140.0 (d, $^2J_{P-C}$ = 13.8 Hz, P-N-C_{Ar}, P-C-*C*), 139.2 (d, $^3J_{P-C}$ = 2.8 Hz, P-N-C-C_{Ar}), 137.4 (Ar-*C*), 128.9 (Ar-*C*), 128.7 (Ar-*C*), 124.8 (d, $^3J_{P-C}$ = 6.2 Hz, P-N-C-C_A), 55.5 (d, $^2J_{P-C}$ = 8.0 Hz, NCH_2), 28.9 (d, $^4J_{P-C}$ = 9.2 Hz, $CHMe_2$), 28.2 (CH_3), 26.1 (CH_3), 25.9 (CH_3), 24.7 (CH_3), 24.3 (d, $^5J_{P-C}$ = 3.2 Hz, $^{Dipp}CH_3$), 23.2 (d, $^1J_{P-C}$ = 133.1 Hz, P-*C*), 0.4 (TMS-*C*).

^{31}P NMR (162 MHz, C_6D_6) δ (ppm) = 112.6 ($^2J^{119}_{Sn-P}$ = 352.7 Hz, $^2J^{117}_{Sn-P}$ = 339.6 Hz).

^{119}Sn NMR (149 MHz, C_6D_6), δ (ppm) = -91.6 ($^2J_{P-Sn}$ = 352.7 Hz).

HRMS (ESI) $[M+H]^+$ $C_{49}H_{63}N_3PSiSn^+$: calc. 872.35454, found. 872.35419 m/z.

IR (ATR, neat): 3055, 2960, 2867, 2056 (CCN stretching), 1428, 1252, 1105, 1071, 837, 803, 726, 696, 659, 599, 568, 552, 506, 446 cm^{-1}.



Scheme 4. Synthesis of **4**.

A mixture of **2** (15 mg, 0.02 mmol) and 2,6-xylyl isocyanide (2.6 mg, 0.02 mmol) were dissolved in C_6D_6 and stirred for 5 min at room temperature. All volatiles were removed under vacuum, and the residue was washed with 0.5 mL of cooled *n*-pentane and then dried under vacuum, affording **4** as a white solid (16 mg, 91%). Single crystals (colorless) suitable for X-ray diffraction of **4** were obtained from a concentrated Et_2O solution at -30 °C.

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) = 7.41 (m, 5H, ^{Ph}Ar-H), 7.28 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, ^{Dipp}Ar-H), 7.21 (m, 4H, Ar-H), 7.04 (m, 4H, Ar-H), 6.96 (m, 6H, Ar-H), 6.78 (s, 3H, ^{Ph}Ar-H,), 4.15 (m, 2H, CH_2,), 4.11 (m, 2H, ^{Dipp}CH), 3.61 (m, 2H, ^{Dipp}CH), 3.32 (m, 2H, NCH_2), 2.01 (s, 6H, $^{Xyl}CH_3$), 1.29 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $^{Dipp}CH_3$), 1.26 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.16 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.08 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $^{Dipp}CH_3$).

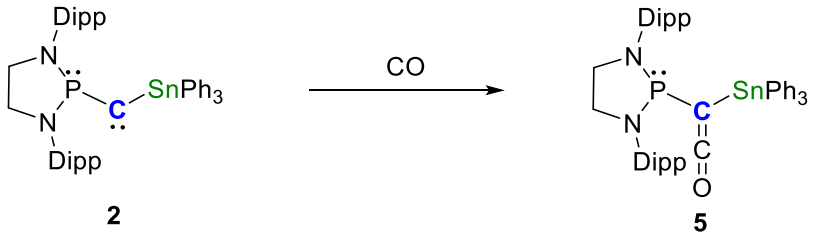
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ (ppm) 160.0 (d, $^3J_{P-C}$ = 4.5 Hz, Sn-*o*-C_{Ar}), 150.0 (d, $^2J_{P-C}$ = 2.5 Hz, P-N-C_{Ar}), 149.1 (Ar-*C*), 139.4 (d, $^2J_{P-C}$ = 13.5 Hz, P-C-*C*), 138.9 (d, $^3J_{P-C}$ = 3.7 Hz, P-N-C-C_{Ar}), 138.1 (Ar-*C*), 137.5 (Ar-*C*), 137.4 (Ar-*C*), 137.2 (Ar-*C*), 137.1 (Ar-*C*), 131.0 (Ar-*C*), 129.1 (Ar-*C*), 128.9 (Ar-*C*), 127.5 (Ar-*C*), 124.5 (Ar-*C*), 55.6 (d, $^2J_{P-C}$ = 8.0 Hz, NCH_2), 40.8 (d, $^1J_{P-C}$ = 138.6 Hz, P*C*), 28.9 (d, $^4J_{P-C}$ = 9.1 Hz, *C*HMe$_2$), 28.7 (*C*H$_3$), 25.9 (*C*H$_3$), 24.4 (*C*H$_3$), 24.1 (d, $^5J_{P-C}$ = 2.8 Hz, ^{Dipp}*C*H$_3$), 19.1(*C*H$_3$).

^{31}P NMR (162 MHz, C_6D_6) δ (ppm) = 114.7 ($^2J^{119}_{Sn-P}$ = 362.9 Hz, $^2J^{117}_{Sn-P}$ = 350.1).

^{119}Sn NMR (149 MHz, C_6D_6) δ (ppm) = -106.5 (d, $^2J_{P-Sn}$ = 362.9 Hz).

HRMS (ESI) $[M+H]^+$ $C_{54}H_{63}N_3PSn^+$: calc. 904.37761, found. 904.37836 m/z.

IR (ATR, neat): 3046, 2960, 2865, 1985 (CCN stretching), 1428, 1253, 1073, 765, 725, 697, 564, 505, 456, 444 cm^{-1}.



Scheme 5. Synthesis of **5**.

2 (15 mg, 0.02 mmol) was charged into a 5 mL Schlenk flask, and then 1 mL of C_6D_6 was added. The flask was freeze-pumped and backfilled with CO gas (3 atm) 3 times. After stirring for 10 min, the solvents were removed under vacuum, and the residue was washed with 0.5 mL of *n*-pentane and dried under vacuum, affording **5** as a white solid (12 mg, 77%). Colorless single crystals of **5** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **5** in Et_2O at -30 °C.

^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.30 (m, 11H, Ar-H), 7.06 (m, 4H, Ar-H), 6.96 (m, 6H, Ar-H), 4.12 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, ^{Dipp}CH), 3.98 (m, 2H, NCH_2), 3.52 (m, 2H, DippCH), 3.22 (m, 2H, NCH_2), 1.40

(d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.33 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.22 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$), 1.10 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $^{Dipp}CH_3$).

$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6) δ (ppm) = 169.4 (d, $^{2}J_{P\text{-}C}$ =6.5 Hz, C*C*O), 150.1 (d, $^{2}J_{P\text{-}C}$ = 3.0 Hz, P-N-C_{Ar}), 149.1 (Ar-*C*), 138.4 (Ar-*C*), 137.4 (d, $^{3}J_{P\text{-}C}$ = 2.9 Hz, P-N-C-C_{Ar}), 137.0 (Ar-*C*), 124.9 (Ar-*C*), 124.6 (Ar-*C*), 55.2 (d, $^{2}J_{P\text{-}C}$ = 8.2 Hz, N*C*H_2), 31.0 (d, $^{1}J_{P\text{-}C}$ = 175.0 Hz, P*C*), 29.0 (d, $^{4}J_{P\text{-}C}$ = 9.6 Hz, *C*HMe_2), 28.8 (*C*H_3).

^{31}P NMR (162 MHz, C_6D_6) δ (ppm) = 117.4 ($^{2}J^{119}_{Sn\text{-}P}$ = 302.6 Hz, $^{2}J^{117}_{Sn\text{-}P}$ = 288.4).

^{119}Sn NMR (149 MHz, C_6D_6), δ (ppm) = 100.1 (d, $^{2}J_{P\text{-}Sn}$ = 302.6 Hz)

HRMS (ESI) $[M+H]^+$ $C_{46}H_{54}ON_2PSn^+$: calc. 801.29902, found. 801.29961 m/z.

IR (ATR, neat): 3064, 2960, 2923, 2866, 2049 (CCO stretching), 1428, 1253, 1069, 799, 727, 697, 580, 509, 438 cm^{-1}.

III. NMR Spectra

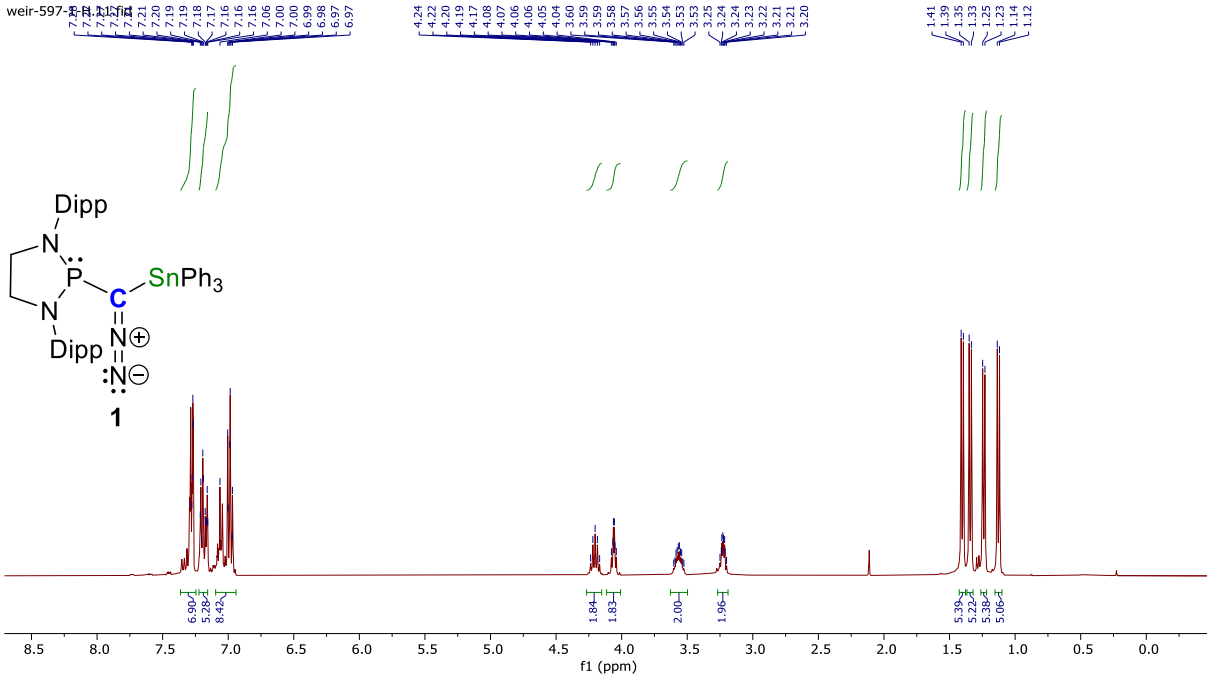


Figure S1. ^{1}H NMR spectrum of **1** (400 MHz, C_6D_6).

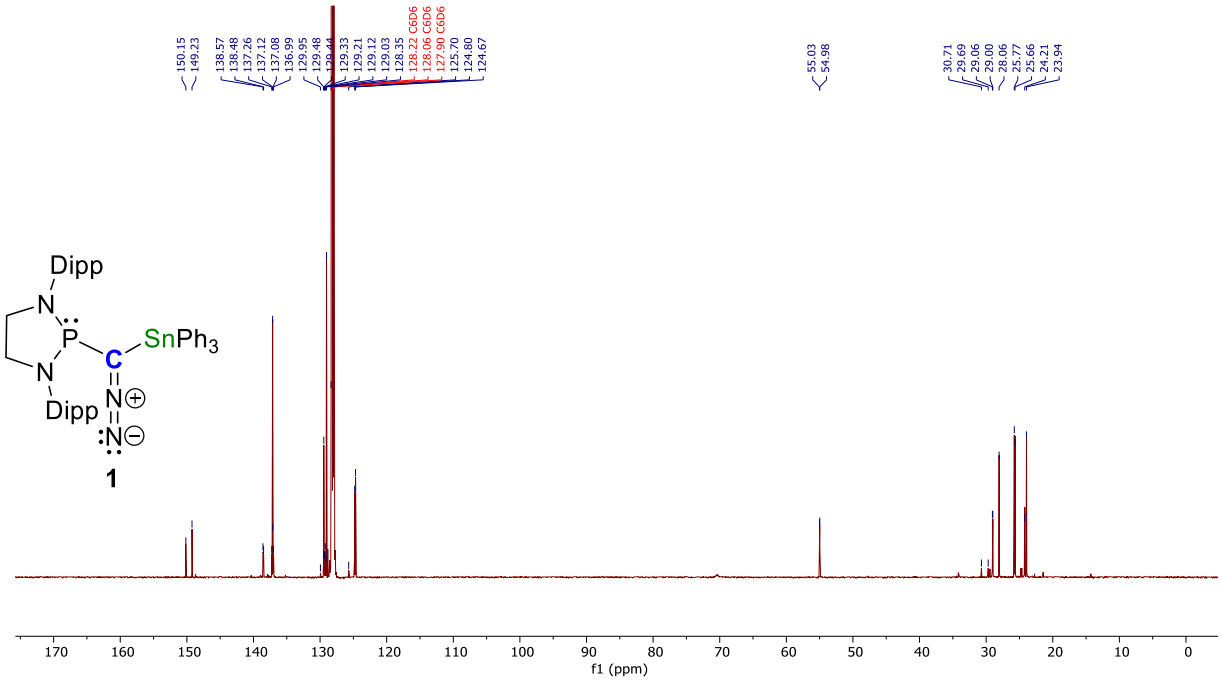


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (101 MHz, C_6D_6).

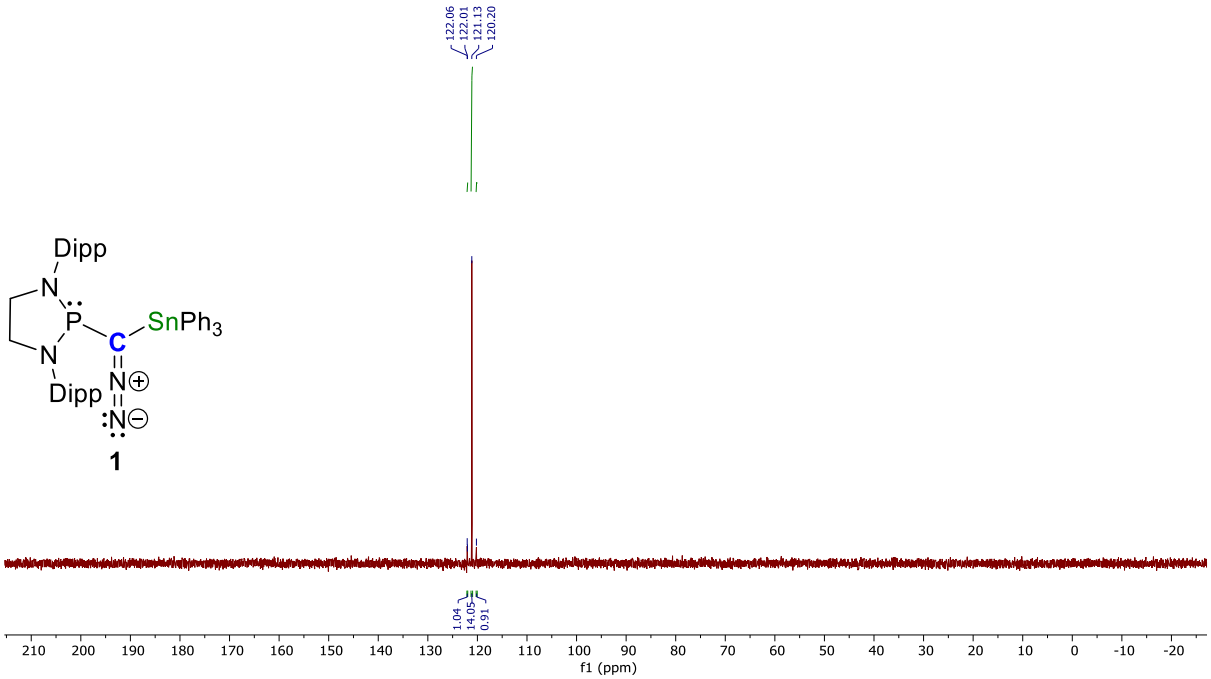


Figure S3. ^{31}P NMR spectrum of **1** (162 MHz, C_6D_6).

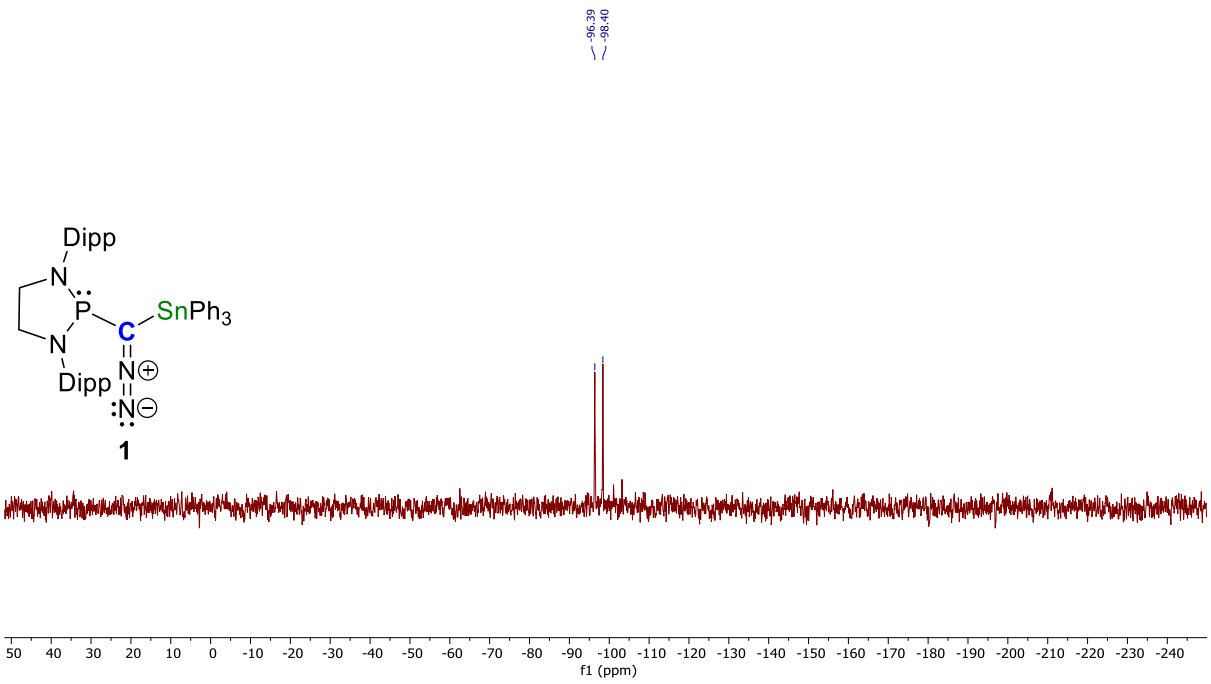


Figure S4. ^{119}Sn NMR spectrum of **1** (149 MHz, C_6D_6).

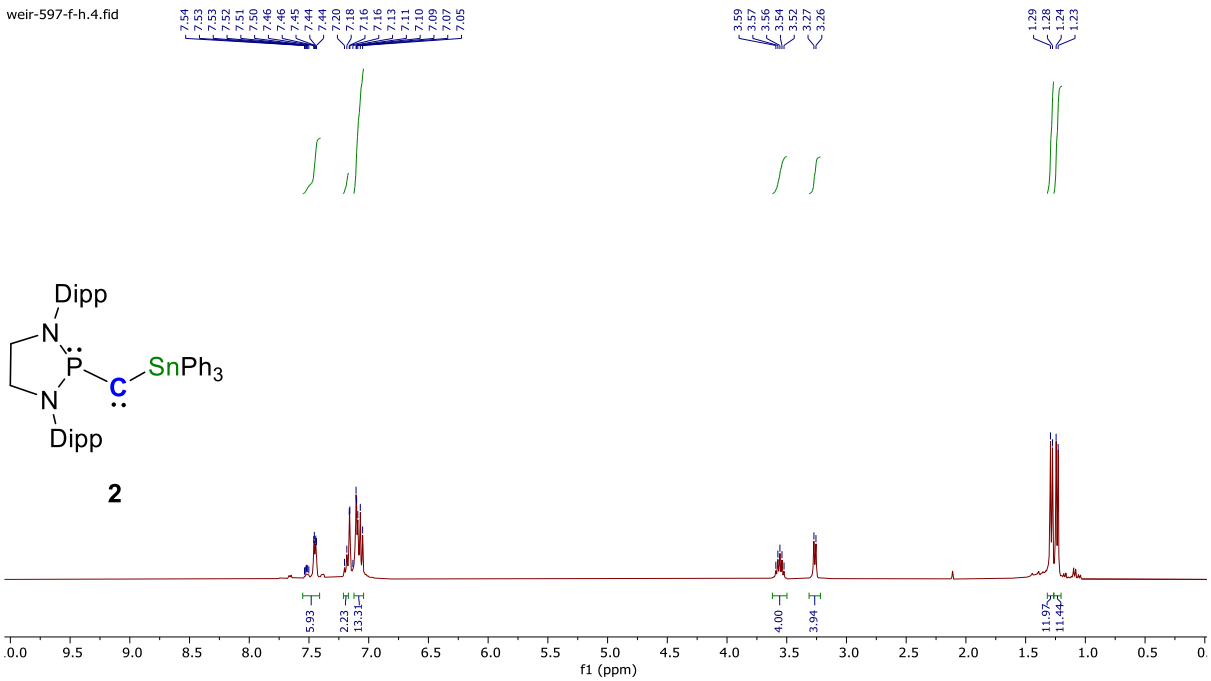


Figure S5. ^{1}H NMR spectrum of **2** (400 MHz, C_6D_6).

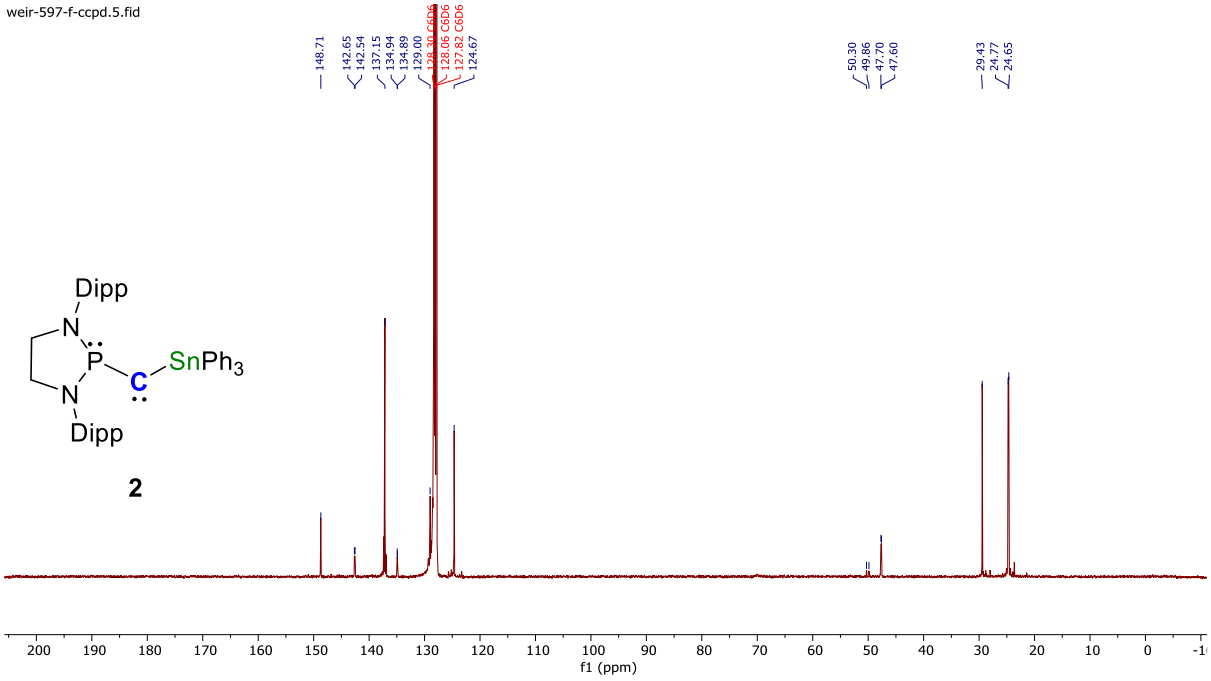


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (101 MHz, C_6D_6).

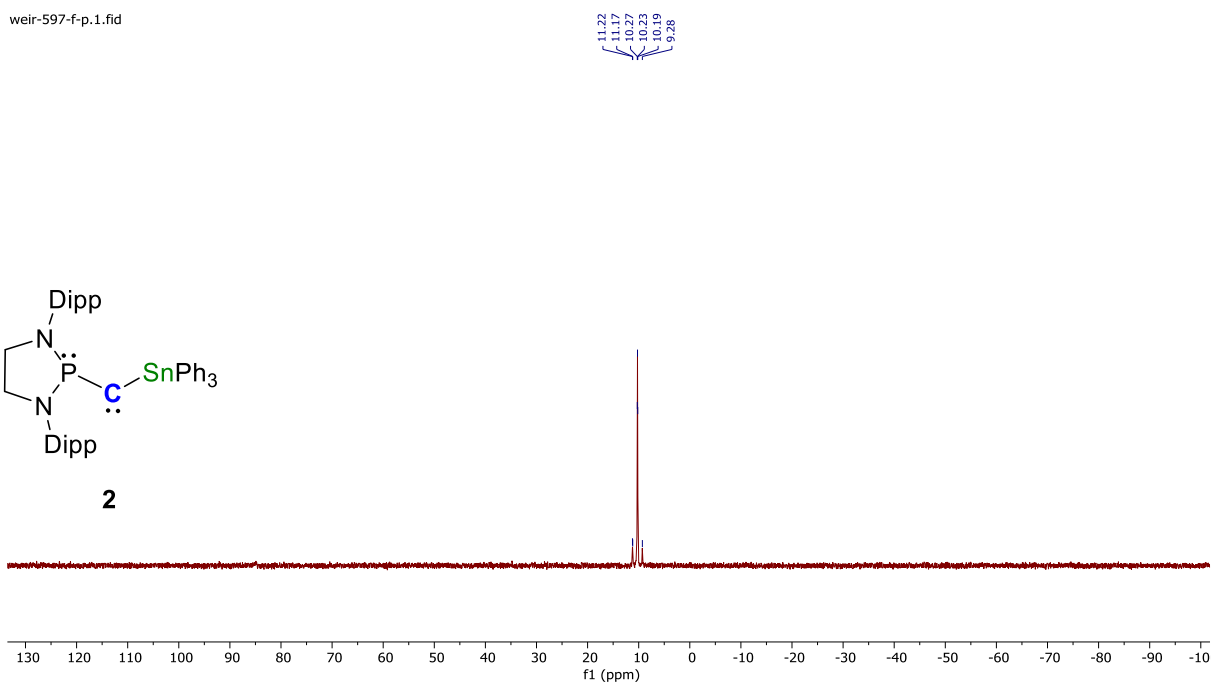


Figure S7. ^{31}P NMR spectrum of **2** (162 MHz, C_6D_6).

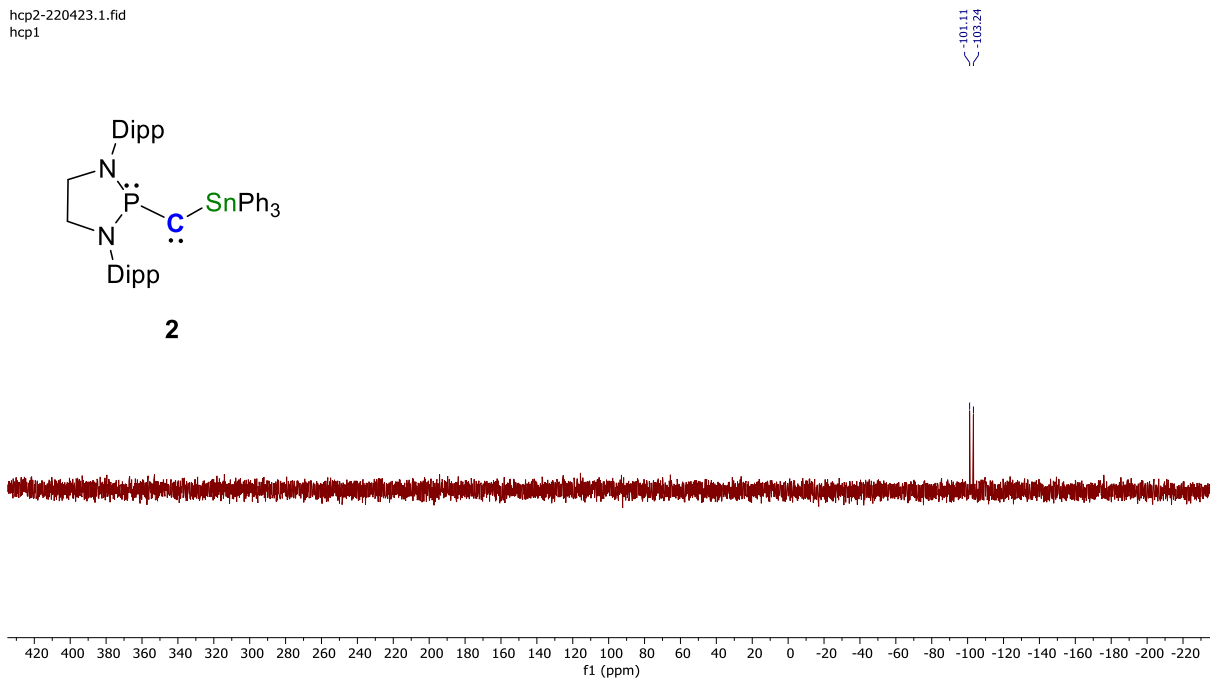


Figure S8. ^{119}Sn NMR spectrum of **2** (149 MHz, C_6D_6).

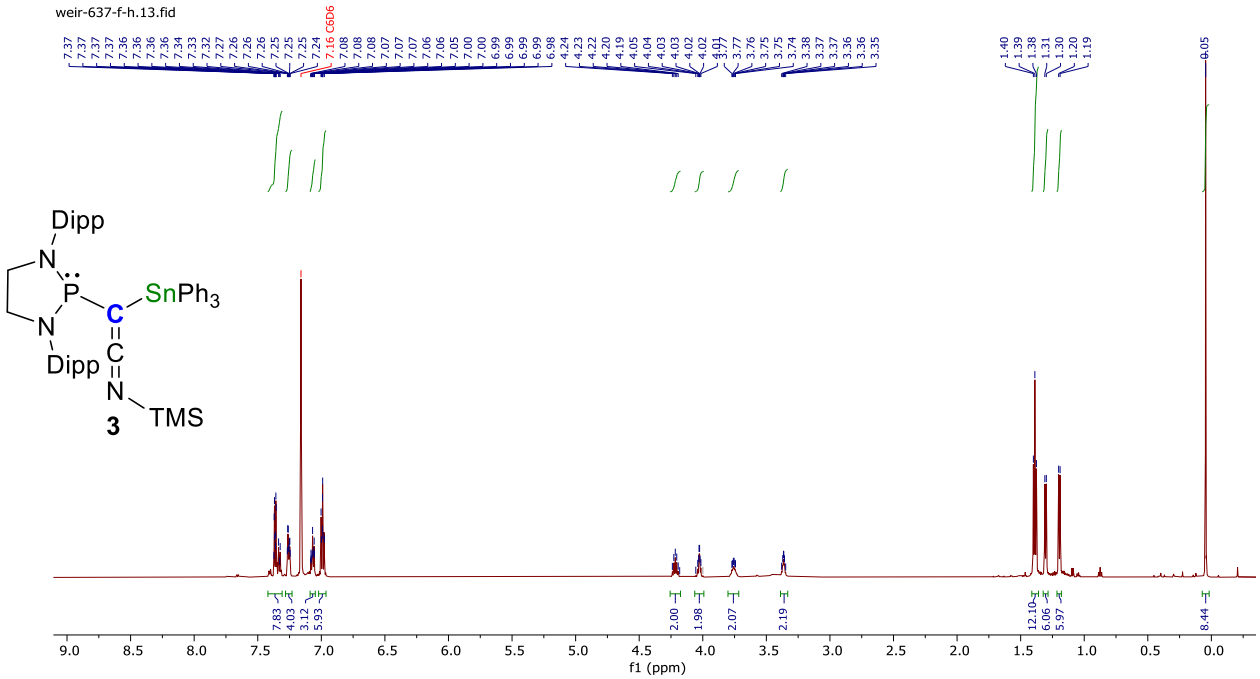


Figure S9. ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6).

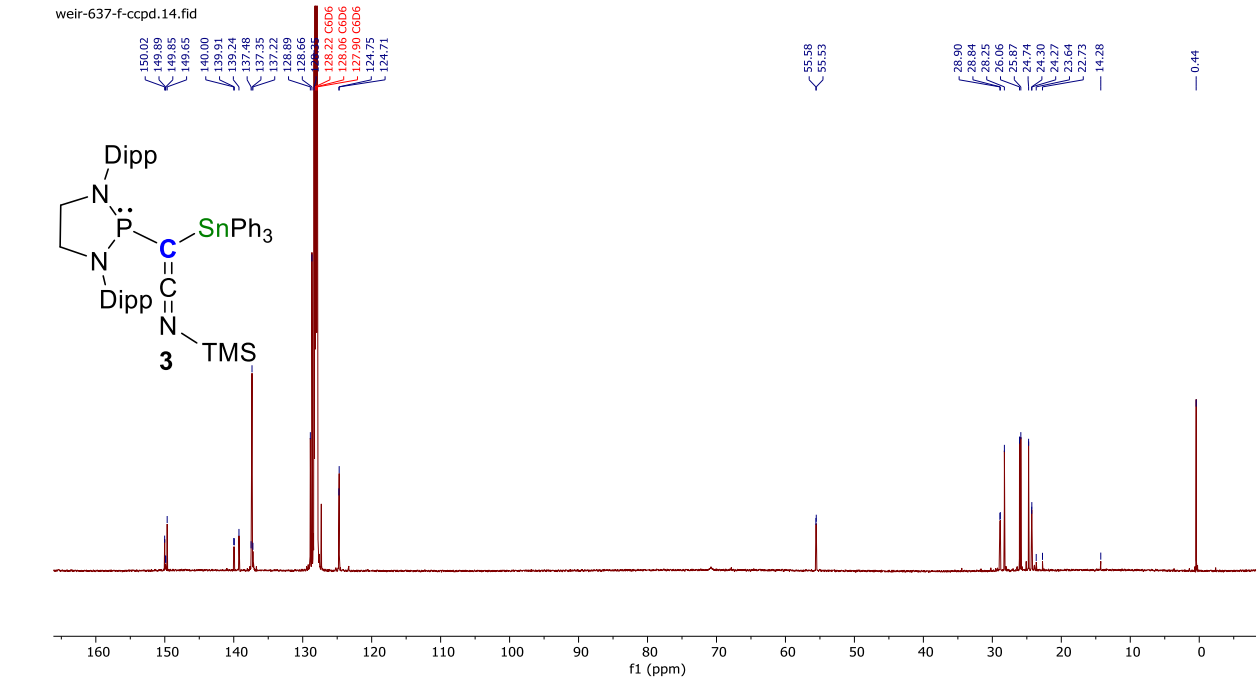


Figure S10. ^{13}C{^{1}H} NMR spectrum of **3** (101 MHz, C_6D_6).

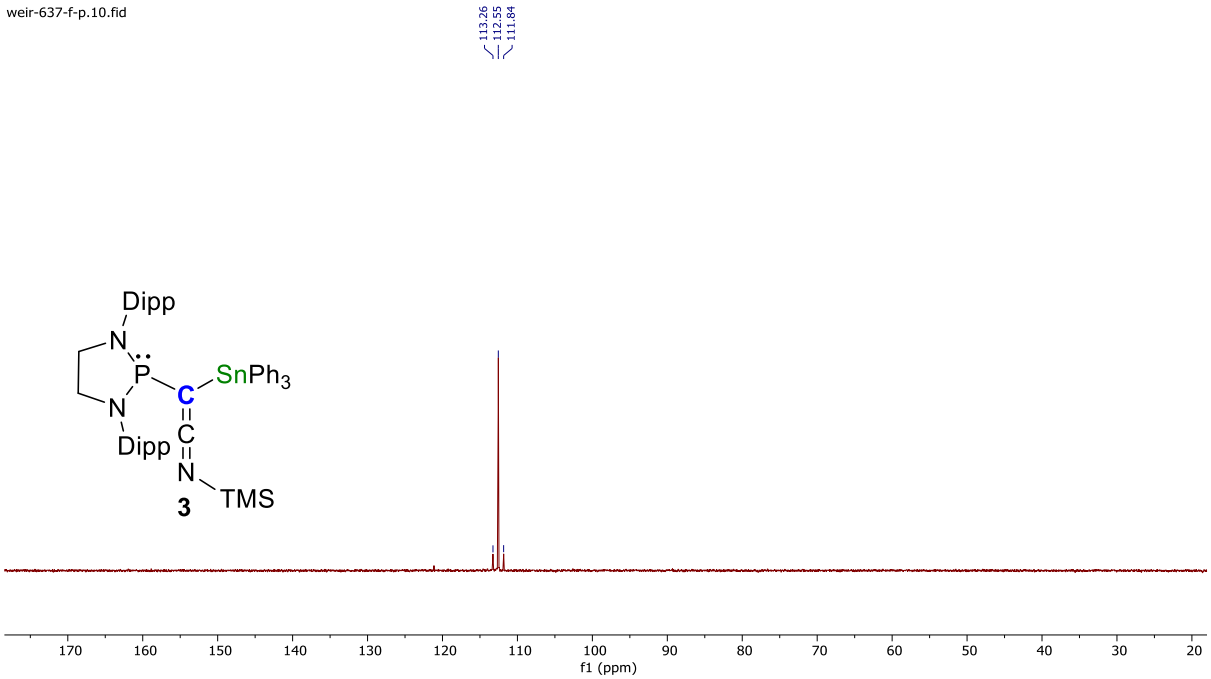


Figure S11. ^{31}P NMR spectrum of **3** (162 MHz, C_6D_6).

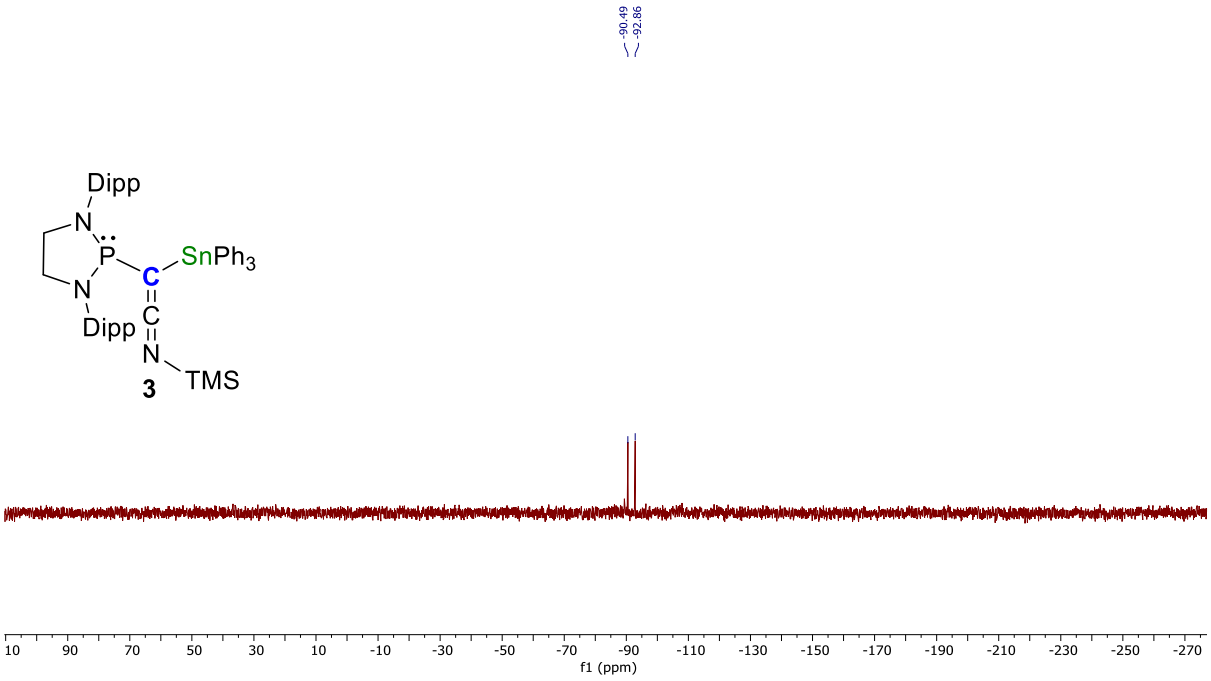


Figure S12. ^{119}Sn NMR spectrum of **3** (149 MHz, C_6D_6).

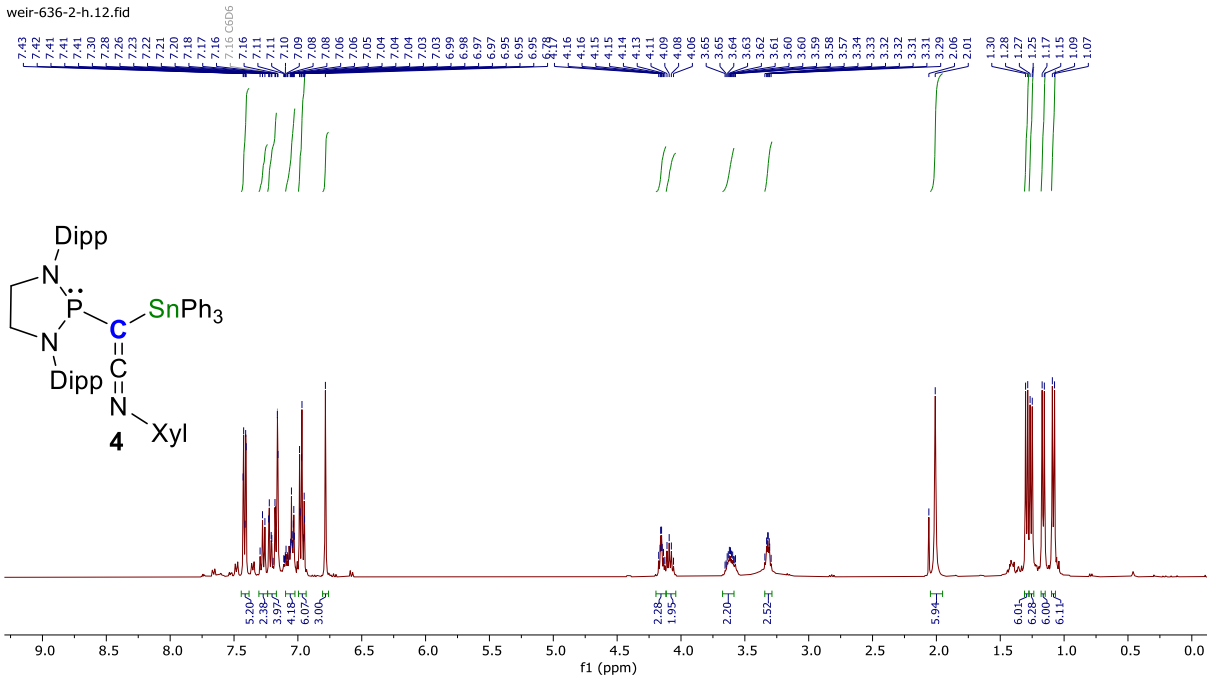


Figure S13 ^{1}H NMR spectrum of **4** (400 MHz, C_6D_6).

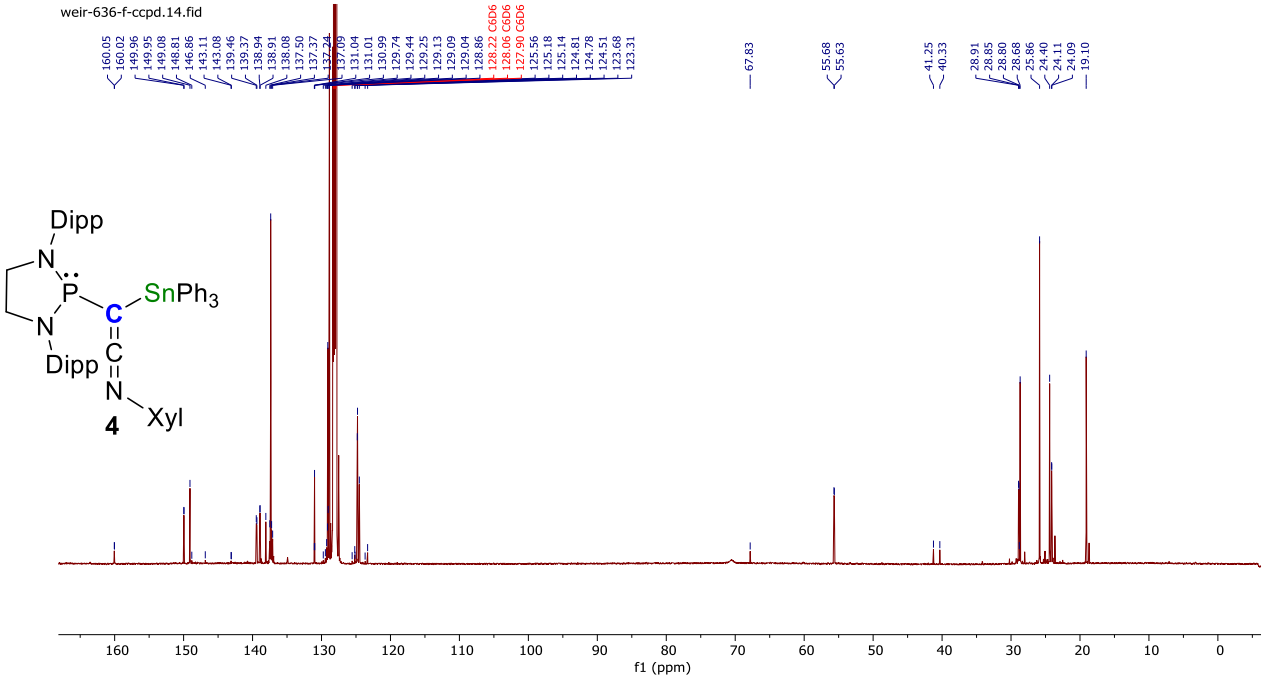


Figure S14. ^{13}C{^{1}H} NMR spectrum of **4** (101 MHz, C_6D_6).

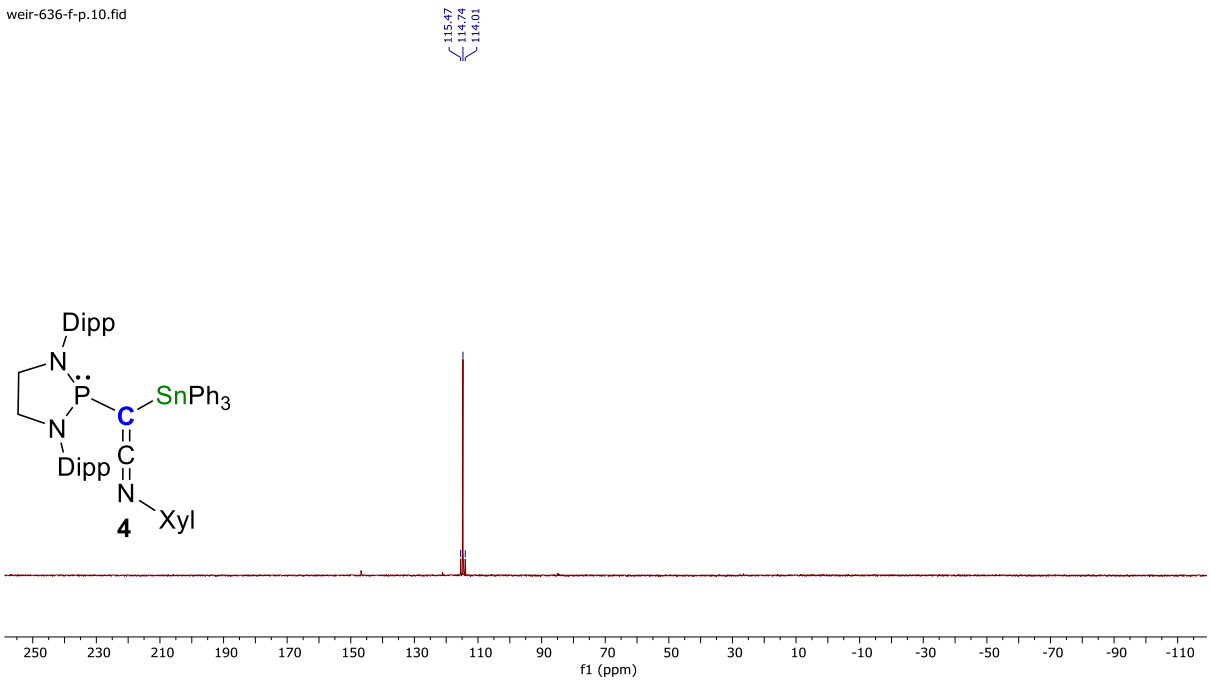


Figure S15. ^{31}P NMR spectrum of **4** (162 MHz, C_6D_6).

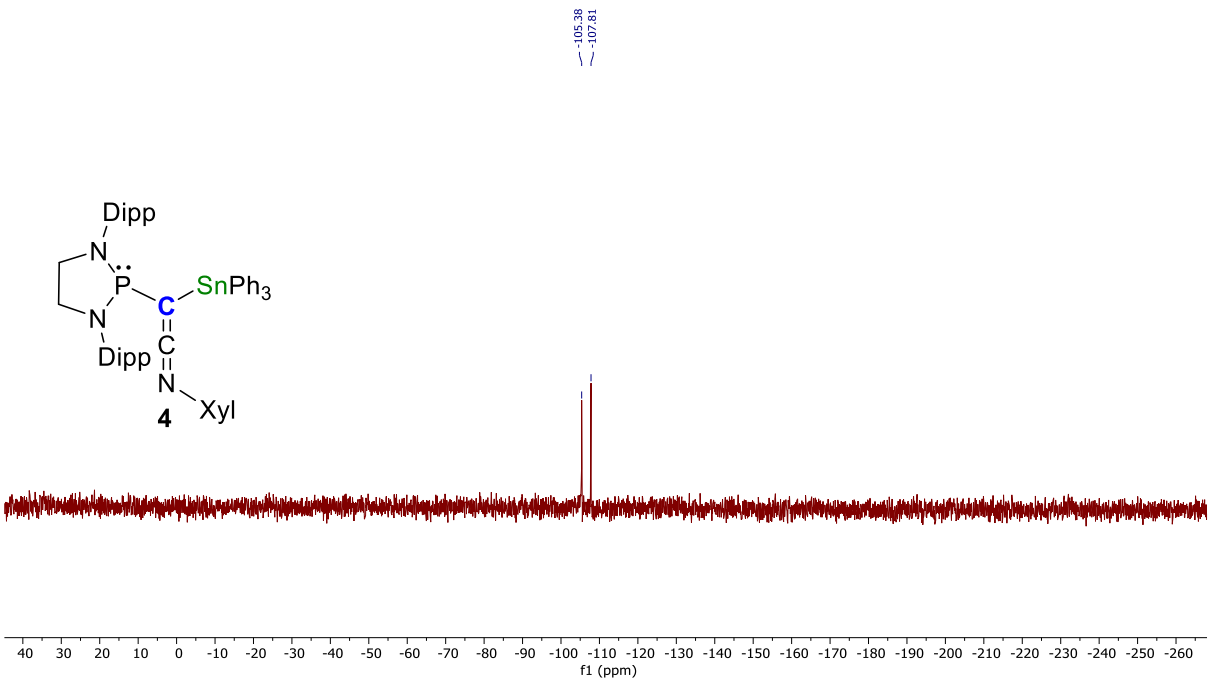


Figure S16. ^{119}Sn NMR spectrum of **4** (149 MHz, C_6D_6).

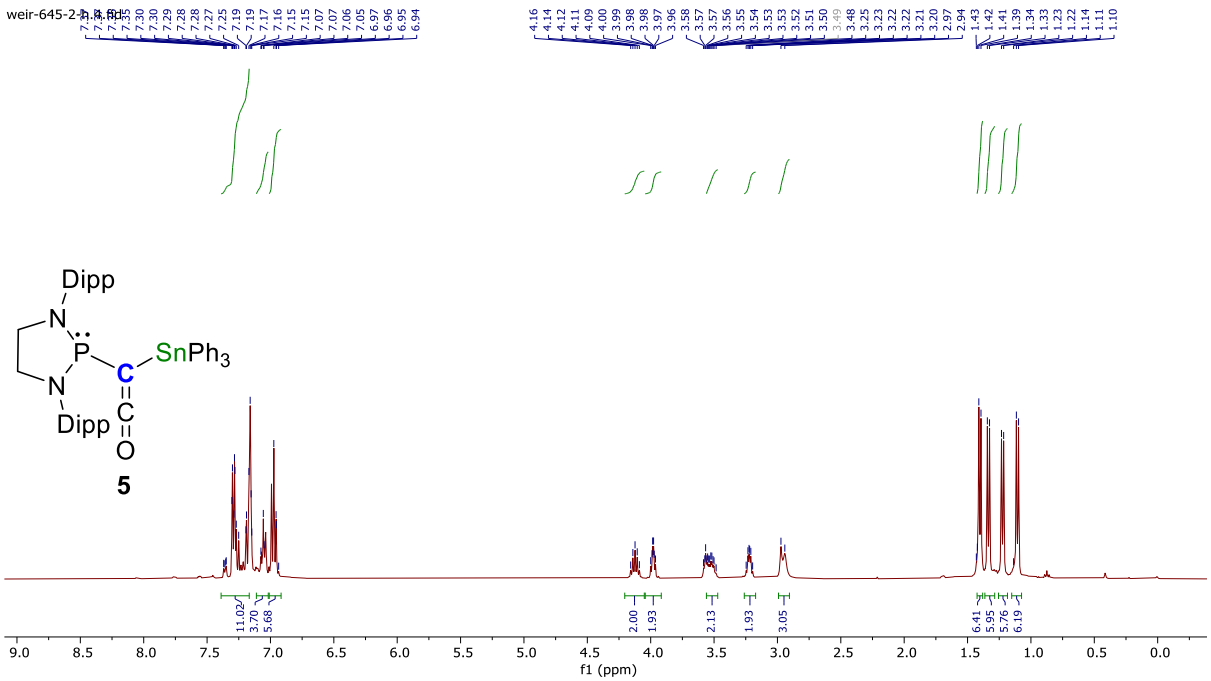


Figure S17. ^{1}H NMR spectrum of **5** (400 MHz, C_6D_6).

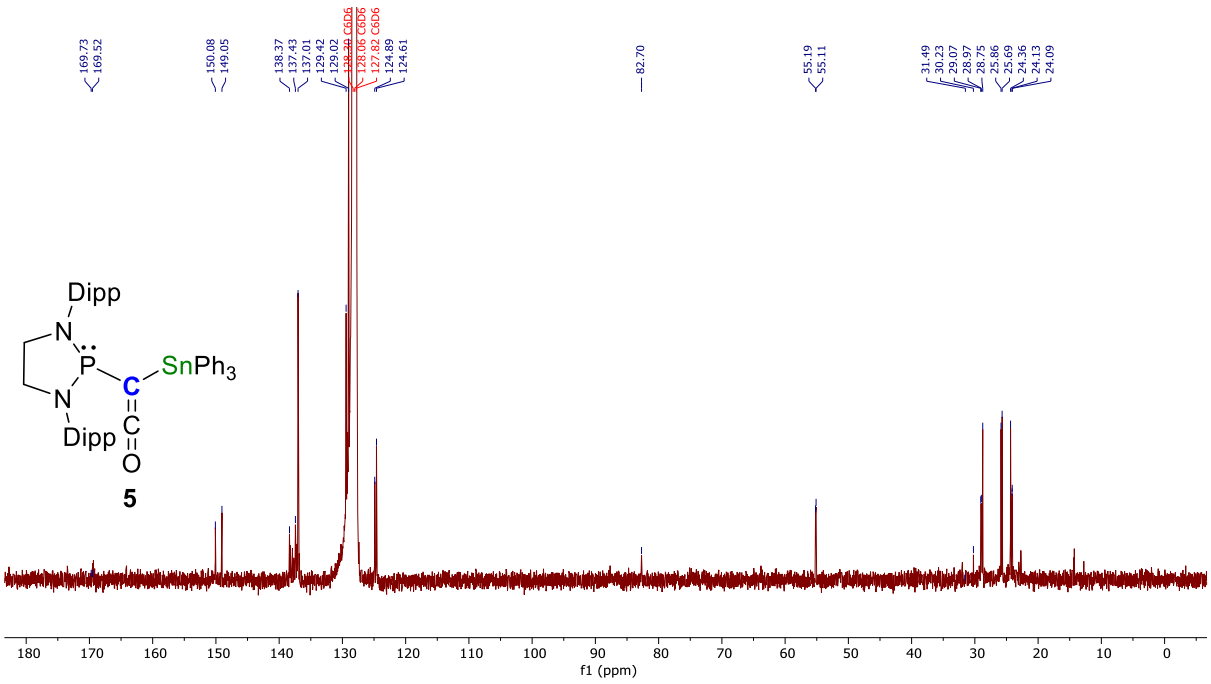


Figure S18. ^{13}C{^{1}H} NMR spectrum of **5** (101 MHz, C_6D_6).

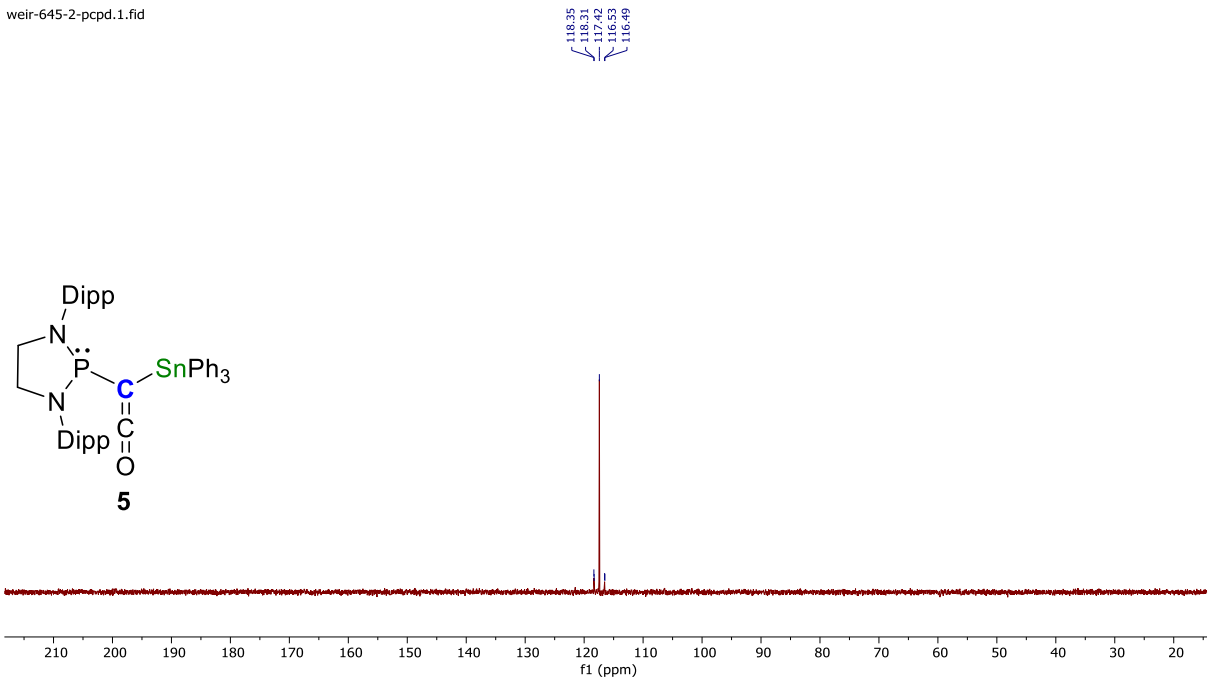


Figure S19. ^{31}P NMR spectrum of **5** (162 MHz, C_6D_6).

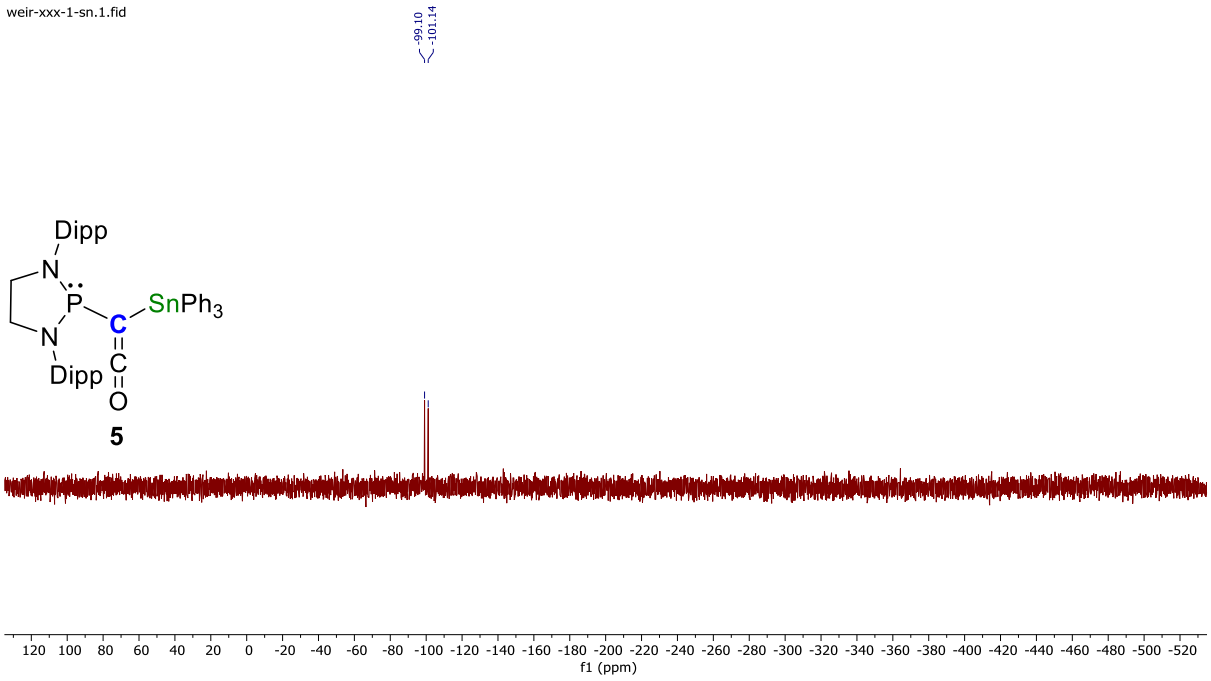


Figure S20. ^{119}Sn NMR spectrum of **5** (149 MHz, C_6D_6).

IV. X-ray Crystallographic Data

Table S1 Crystal data and structure refinement for 1.

Identification code	2189531
Empirical formula	$C_{45}H_{53}N_4PSn$
Formula weight	799.57
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9707(5)
b/Å	10.4091(5)
c/Å	20.4298(11)
α /°	89.295(3)
β /°	76.839(3)
γ /°	77.221(3)
Volume/Å^3	2011.88(18)
Z	2
ρ_{calc}g/cm^3	1.320
μ /mm^{-1}	5.691
F(000)	832.0
Crystal size/mm^3	0.2×0.1×0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.446 to 136.878
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -23 ≤ l ≤ 24
Reflections collected	28065
Independent reflections	7217 [R_{int} =0.0515, R_{sigma} = 0.0456]
Data/restraints/parameters	7217/0/468
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0695
Final R indexes [all data]	R_1 = 0.0328, wR_2 = 0.0707
Largest diff. peak/hole / e Å^{-3}	1.23/-0.64

Table S2 Crystal data and structure refinement for 2.

Identification code	2178246
Empirical formula	$C_{45}H_{53}N_2PSn$
Formula weight	771.55
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.1795(4)
b/Å	10.3793(2)
c/Å	38.5800(9)
α/°	90
β/°	91.604(2)
γ/°	90
Volume/Å^3	4074.6(2)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	5.586
F(000)	1608.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.582 to 136.644
Index ranges	$-10 \leq h \leq 12$, $-10 \leq k \leq 12$, $-45 \leq l \leq 46$
Reflections collected	35056
Independent reflections	7314 [R_{int} = 0.0688, R_{sigma} = 0.0560]
Data/restraints/parameters	7314/72/450
Goodness-of-fit on F^2	1.166
Final R indexes [I>=2σ (I)]	R_1 = 0.0799, wR_2 = 0.1486
Final R indexes [all data]	R_1 = 0.0983, wR_2 = 0.1556
Largest diff. peak/hole / e Å^{-3}	1.44/-1.00

Table S3 Crystal data and structure refinement for 3.

Identification code	2178248
Empirical formula	$C_{49}H_{62}N_3PSiSn$
Formula weight	870.76
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.0214(5)
b/Å	12.3053(4)
c/Å	20.7838(6)
α/°	90
β/°	93.7730(10)
γ/°	90
Volume/Å^3	4599.0(2)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	5.255
F(000)	1824.0
Crystal size/mm^3	0.42 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.914 to 136.562
Index ranges	$-21 \leq h \leq 21$, $-14 \leq k \leq 14$, $-14 \leq l \leq 25$
Reflections collected	55163
Independent reflections	8416 [R_{int} = 0.0306, R_{sigma} = 0.0193]
Data/restraints/parameters	8416/0/507
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0220, wR_2 = 0.0510
Final R indexes [all data]	R_1 = 0.0237, wR_2 = 0.0518
Largest diff. peak/hole / e Å^{-3}	0.36/-0.45

Table S4 Crystal data and structure refinement for 4.

Identification code	2178247
Empirical formula	$C_{54}H_{62}N_3PSn$
Formula weight	902.72
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.5741(4)
b/Å	18.2905(4)
c/Å	12.3909(3)
α/°	90
β/°	90.5410(10)
γ/°	90
Volume/Å^3	4662.62(18)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	4.967
F(000)	1888.0
Crystal size/mm^3	0.74 × 0.19 × 0.17
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.294 to 137.474
Index ranges	$-24 \leq h \leq 24$, $-21 \leq k \leq 20$, $-14 \leq l \leq 14$
Reflections collected	73801
Independent reflections	8553 [R_{int} = 0.0526, R_{sigma} = 0.0247]
Data/restraints/parameters	8553/0/542
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0226, wR_2 = 0.0493
Final R indexes [all data]	R_1 = 0.0273, wR_2 = 0.0509
Largest diff. peak/hole / e Å^{-3}	0.36/-0.38

Table S5 Crystal data and structure refinement for 5.

Identification code	2178249
Empirical formula	$C_{46}H_{53}N_2OPSn$
Formula weight	799.56
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.9668(4)
b/Å	10.3764(4)
c/Å	20.4573(8)
α/°	89.474(2)
β/°	76.827(2)
γ/°	77.353(2)
Volume/Å^3	2008.19(14)
Z	2
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	5.707
F(000)	832.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.44 to 144.47
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 12, -24 ≤ l ≤ 25
Reflections collected	35235
Independent reflections	7653 [R_{int} = 0.0268, R_{sigma} = 0.0212]
Data/restraints/parameters	7653/0/468
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0193, wR_2 = 0.0499
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0501
Largest diff. peak/hole / e Å^{-3}	0.45/-0.35

V. Computational Details

Density functional theory (DFT) calculations were carried out using the Gaussian 16 package[S2]. Geometry optimizations were performed with the M06-2X [S3]or BP86 [S4]functional augmented with the D3 version of Grimme's empirical dispersion correction. The def2-SVP basis set was employed for all the atoms[S5]. Analytical frequency calculations were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. For the mechanistic study, the single-point energy calculations were performed at the BP86-D3(BJ)/def2-TZVP level of theory based on the structures optimized at the BP86-D3(BJ)/def2-SVP level of theory. SMD method was used with tetrahydrofuran as the solvent, while Bondi radii were chosen as the atomic radii to define the molecular cavity[S6]. Natural bond orbital (NBO) calculations were carried out using NBO 7.0 program[S7] at the M06-2X/def2-SVP level of theory. Energy decomposition analyses based on extended transition state–natural orbitals for chemical valence (ETS-NOCV) calculations were carried out using Multiwfn package[S8] with the wave function obtained at the M06-2X/ def2-SVP level of theory using the Gaussian 16 package.

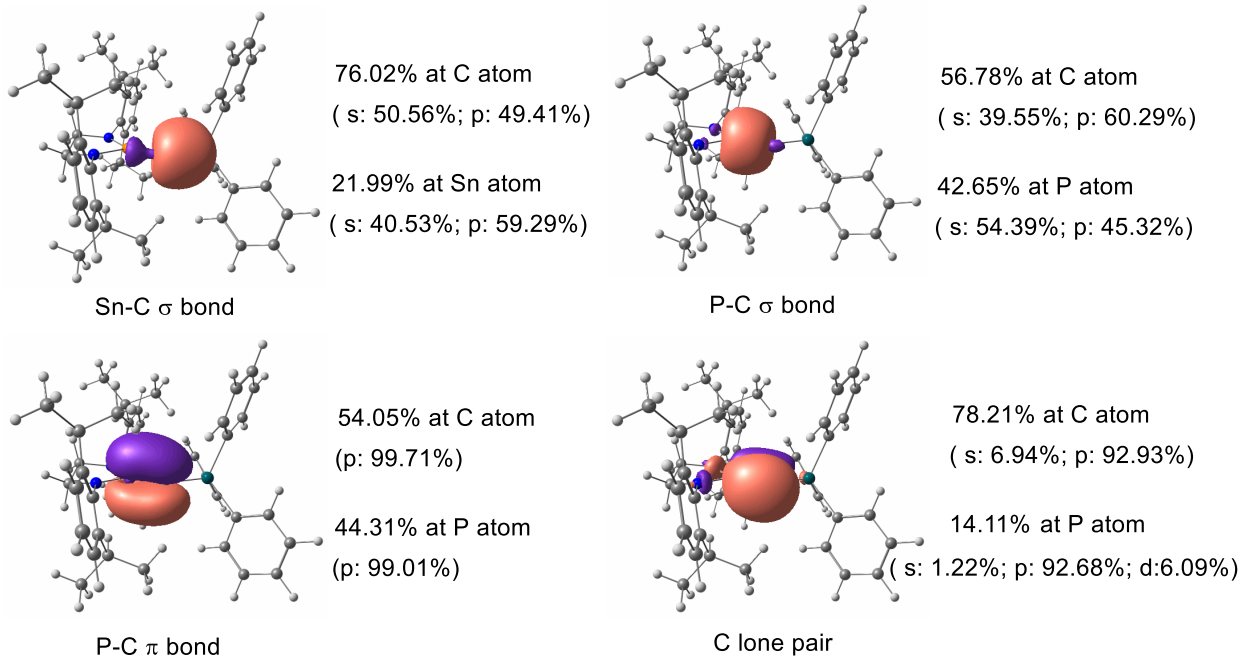


Figure S21. Selected NLMOs and orbital composition analysis of **2**.

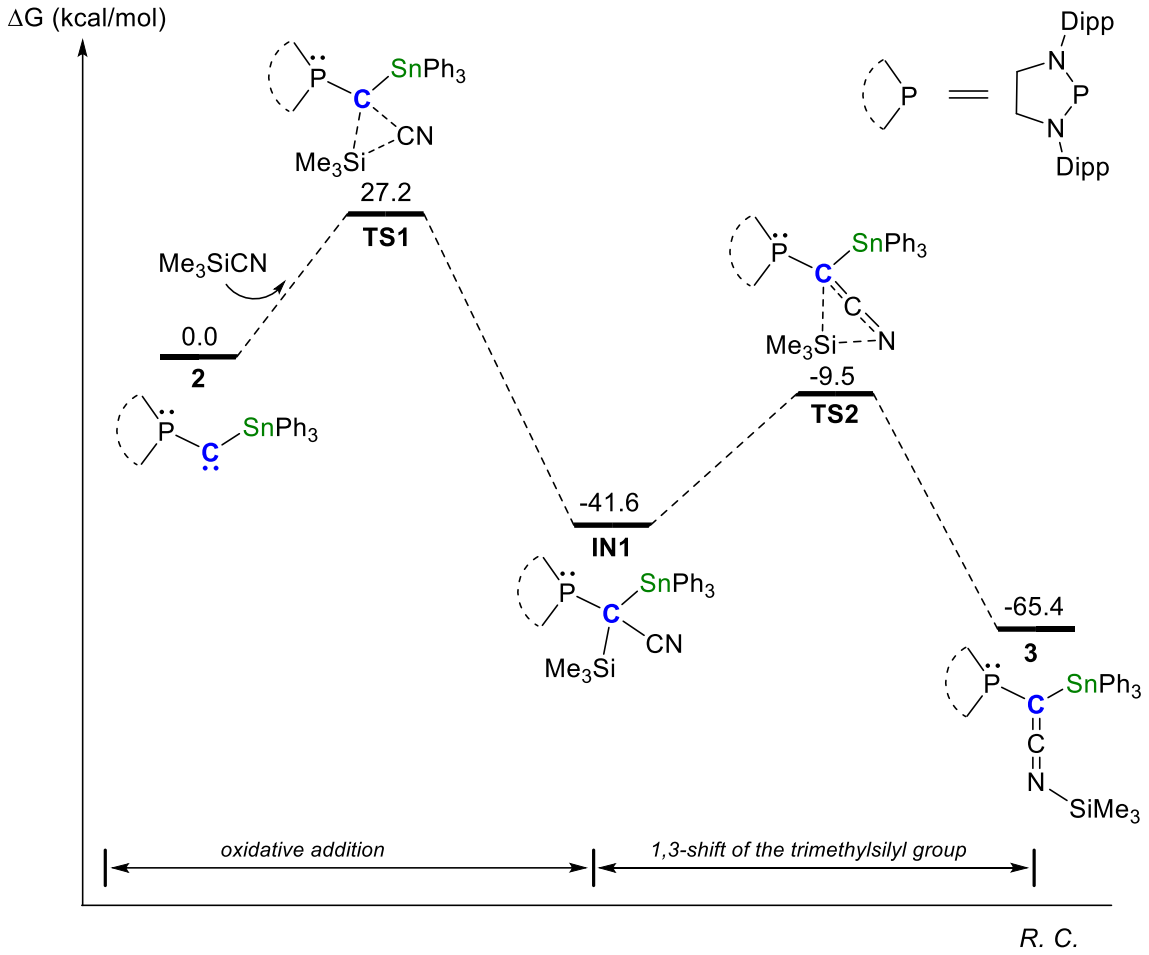


Figure S22. Computed free energy profile for the reaction of **2** and trimethylsilyl cyanide. Energies are given in kcal/mol.

```
      --------------- Pair and NOCV orbital information --------------
There are totally  576 NOCV pairs and  1152 NOCV orbitals
NOCV orbitals with absolute eigenvalues smaller than 1.0E-03 are not shown
Note: All energies are given in kcal/mol

 Pair  Energy | Orbital  Eigenvalue    Energy  | Orbital  Eigenvalue    Energy
    1 -597.38       1      1.65250    -153.84     1152     -1.65250     207.66
    2  -72.30       2      0.58619    -147.50     1151     -0.58619     -24.17
    3  -38.84       3      0.50975    -131.33     1150     -0.50975     -55.14
    4  -17.99       4      0.27184    -101.79     1149     -0.27184     -35.60
    5   -3.46       5      0.12440     -20.57     1148     -0.12440       7.21
    6   -2.82       6      0.10344      -7.35     1147     -0.10344      19.93
```

```
Sum of NOCV eigenvalues:  -0.00000
Sum of pair energies:    -741.39 kcal/mol
```

Figure S23. Selected ETS-NOCV analysis results of **4**.

Cartesian Coordinates:

2

0 1

Sn	-1.20128300	1.48076100	0.13353000
P	1.14610300	-0.86610600	0.30420700
N	0.60568000	-2.48532600	0.17348900
N	2.78363300	-1.33490000	0.30051400
C	-1.64456300	-2.84444200	1.15000400
C	-2.42201000	0.63857100	-1.44175700
C	-0.75970600	-2.89354700	0.03750500
C	-1.18459200	-3.35912200	-1.23844200
C	-0.70621300	3.48218300	-0.52446600
C	-2.48983200	-3.86852900	-1.36036600
H	-2.83970300	-4.24193800	-2.33347700
C	-3.14106600	0.66861900	-3.78109200
H	-3.08472200	1.11206000	-4.78842600
C	-2.36583600	1.20097900	-2.73561800
H	-1.70959900	2.06531800	-2.93219600
C	-2.95081600	-3.34656200	0.96809900
H	-3.65833800	-3.32536000	1.80888400
C	-3.36103800	-3.87717700	-0.26203400
H	-4.38075600	-4.27887800	-0.37239400
C	-0.27200800	-3.21479600	-2.45361500
H	0.77184500	-3.38389700	-2.11590500
C	-2.33790500	1.48313900	1.97019900
C	1.69711100	-3.46472900	0.26795000
H	1.50148700	-4.32743500	-0.40168600
H	1.78198700	-3.85861800	1.30709600
C	-3.27119400	-0.46292900	-1.21136000
H	-3.31833300	-0.93244300	-0.21560400
C	-1.20319700	-2.28092400	2.50003500
H	-0.57911900	-1.38326200	2.28704500
C	-4.05514900	-0.98978900	-2.25320600
H	-4.71431900	-1.84967700	-2.05761800
C	-1.66130300	1.57147900	3.20549600
H	-0.55911300	1.61167800	3.22535000
C	-3.98992900	-0.42685800	-3.53969800
H	-4.60166200	-0.84219700	-4.35651800
C	2.97878200	-2.71859600	-0.13637700
H	3.87252200	-3.15719600	0.35459400
H	3.13855800	-2.76975700	-1.24099000
C	-1.68146600	4.37004700	-1.02658700
H	-2.74010400	4.06312700	-1.07557200
C	-3.74718500	1.41480600	1.96511100

H	-4.29383600	1.34066400	1.00997400
C	-4.46765700	1.43009300	3.17384300
H	-5.56799100	1.36987500	3.15914800
C	3.80751600	-0.35593400	0.06267500
C	-0.34559400	-1.76850100	-2.98684500
H	-1.36589400	-1.53469500	-3.35149200
H	0.36840500	-1.62191000	-3.82404600
H	-0.10652500	-1.02799200	-2.19770100
C	0.02824000	6.05856200	-1.42723900
H	0.31404000	7.06235700	-1.78063200
C	-0.55945100	-4.22692200	-3.57212500
H	-0.55447400	-5.27130400	-3.19718200
H	0.20782600	-4.14326500	-4.36894600
H	-1.54326600	-4.03983900	-4.05140100
C	0.70706800	0.66450000	0.45925100
C	-3.78436200	1.52350600	4.39893600
H	-4.34784200	1.53743800	5.34546100
C	4.38926300	-0.58691600	2.53219900
H	3.93618600	-1.58927900	2.37699900
C	-2.37995200	1.59740900	4.41333600
H	-1.84180400	1.66972900	5.37245000
C	0.64105400	3.89951100	-0.47866700
H	1.40757200	3.20616000	-0.09058600
C	-1.31739300	5.65220100	-1.47617600
H	-2.08677400	6.33771800	-1.86731700
C	-2.37510000	-1.81947200	3.37732900
H	-3.04010600	-1.11212800	2.84442700
H	-1.99100900	-1.29541500	4.27399400
H	-2.98522900	-2.67681200	3.73351900
C	4.65360800	-0.00637200	1.14782700
C	-0.33121700	-3.28805600	3.27770800
H	-0.90657300	-4.21094500	3.50306700
H	0.00349900	-2.84852400	4.24024900
H	0.57199200	-3.58486100	2.71192500
C	1.00700600	5.18138800	-0.92741700
H	2.06246900	5.49667800	-0.88820500
C	3.94309400	0.24370900	-1.21680100
C	4.97178100	1.19099000	-1.39499500
H	5.09554400	1.67439300	-2.37715800
C	3.00374400	-0.08082200	-2.37413100
H	2.26945100	-0.83303200	-2.01695400
C	5.66953400	0.94093100	0.92093400
H	6.33916000	1.22965100	1.74500400
C	5.83068200	1.53200900	-0.34185300

H	6.62922300	2.27357400	-0.50263300
C	2.19014500	1.15547400	-2.79846800
H	1.63001400	1.56284900	-1.93391800
H	1.46004900	0.88880900	-3.59069900
H	2.84590000	1.95780700	-3.19703000
C	3.75603200	-0.71271100	-3.56039100
H	4.48804700	-0.00304500	-4.00046700
H	3.04602100	-1.00117600	-4.36373100
H	4.31613200	-1.61967700	-3.25082000
C	3.33397700	0.27584700	3.25930600
H	3.73537300	1.29270000	3.45612500
H	3.05379800	-0.17895500	4.23307800
H	2.41745300	0.39514200	2.64565500
C	5.65565600	-0.76262400	3.38301100
H	6.43136700	-1.35027000	2.84966900
H	5.41348700	-1.29026500	4.32870700
H	6.10376900	0.21368900	3.66505500

TMSCN

0 1

Si	-2.30648700	0.19050800	0.06116800
C	-1.63810900	1.13596300	1.54880000
H	-1.99546000	2.18606000	1.54731400
H	-1.97728900	0.65689600	2.49150200
H	-0.52895300	1.14883400	1.54780800
C	-4.18962200	0.23406400	-0.01391700
H	-4.56423700	1.27805800	-0.02581600
H	-4.56447600	-0.27752800	-0.92394900
H	-4.62061900	-0.27761700	0.87245800
C	-1.63821500	-1.57056700	-0.01373400
H	-1.99606700	-2.09463100	-0.92351200
H	-0.52906000	-1.57614300	-0.02598500
H	-1.97690000	-2.14710300	0.87290200
C	-1.67910900	1.07756500	-1.47528900
N	-1.28761500	1.63126600	-2.43428700

IN1

0 1

P	1.77239500	-0.17205500	-0.44427300
C	1.97768700	3.52550100	0.66419900
N	2.09135900	1.04125700	0.75005700
N	1.33045700	-1.34184700	0.81398800
C	1.48309100	-2.75115100	0.54626400
C	3.96145000	4.79102200	-0.01839000

H	4.44947600	5.75821100	-0.21663000
C	4.66145600	3.59379200	-0.21776100
H	5.70423000	3.63051800	-0.56448400
C	0.45930300	-3.67028600	0.95320300
C	2.70188800	2.31298000	0.47709800
C	3.92272100	-2.46129700	-0.31006100
H	3.77103900	-1.46302000	0.14581700
C	2.62946500	-3.25343300	-0.14209800
C	2.63746900	4.74837400	0.42747800
H	2.08434100	5.68881800	0.57091900
C	0.50709100	-4.99336000	0.47376600
H	-0.29479200	-5.69129700	0.75435700
C	0.10225400	0.32881800	-1.28920100
C	1.59790400	0.69196400	2.08409300
H	0.56260500	1.04479300	2.26559200
H	2.25102600	1.15176000	2.85482400
C	-0.33560400	4.57357800	0.32782600
H	-0.05953700	5.62266700	0.56390000
H	-1.40585200	4.44754800	0.58882000
H	-0.22310900	4.41156100	-0.76041500
C	-0.02597300	-3.52713600	3.41100400
H	-0.70178400	-3.08877100	4.17523900
H	0.98310500	-3.09380200	3.54777200
H	0.06002100	-4.61670900	3.60867000
C	5.06215100	-3.13618700	0.48131600
H	4.79644000	-3.24593000	1.55254000
H	5.99106000	-2.53194000	0.41409700
H	5.29225900	-4.14776100	0.08634400
C	2.61861500	-4.58273100	-0.61381200
H	3.48442600	-4.95248800	-1.18586900
C	1.63736300	-0.83112400	2.16553200
H	2.64224700	-1.19168200	2.49285200
H	0.88887600	-1.18159900	2.90280700
C	4.06124600	2.34777100	0.03909000
C	1.54967800	-5.44154300	-0.34844300
H	1.54716100	-6.47050000	-0.74049100
C	-0.59325600	-3.29115400	1.98845500
H	-0.80052000	-2.20671300	1.87038500
C	0.52236100	3.57216900	1.12342400
H	0.09116700	2.56167800	0.94817100
C	-1.91879900	-4.06077400	1.87549800
H	-1.77512700	-5.14716900	2.05118600
H	-2.40711300	-3.93246100	0.89143400
H	-2.62250000	-3.70849100	2.65491700

C	0.44528700	3.90043700	2.63075100
H	0.97108800	3.15360000	3.25854400
H	-0.60978800	3.96615700	2.97176900
H	0.91636500	4.88621700	2.82660100
C	4.31053100	-2.24843800	-1.78202600
H	4.47539300	-3.21524500	-2.30223900
H	5.24773000	-1.66055100	-1.86242800
H	3.51577600	-1.69578100	-2.31978000
C	4.87616800	1.06457100	-0.07571500
H	4.20725300	0.29810900	-0.52131700
C	5.29082200	0.57636900	1.32703000
H	5.84662200	-0.38235000	1.27036000
H	4.40670800	0.41992300	1.97548200
H	5.94545400	1.32492500	1.82113300
C	6.09646100	1.16833200	-1.00017200
H	6.87601400	1.84644900	-0.59268400
H	5.81562400	1.53513900	-2.00846700
H	6.56881700	0.17101600	-1.11771700
C	0.32269800	1.67317700	-1.75088000
N	0.53689800	2.74241500	-2.20163400
Si	0.08674500	-0.67231600	-2.98790000
C	1.53315100	-0.01020600	-4.01371600
H	1.60574700	-0.59153400	-4.95771100
H	1.39514100	1.05994600	-4.26587900
H	2.49492700	-0.11111300	-3.47090300
C	-1.50120700	-0.29736700	-3.94014200
H	-1.40380100	-0.71965700	-4.96316000
H	-2.40614000	-0.73095000	-3.47434700
H	-1.64581700	0.79746500	-4.04640700
C	0.34201300	-2.53267500	-2.72514000
H	1.33643900	-2.83247500	-3.11276500
H	0.30316900	-2.85141000	-1.66722700
H	-0.43258600	-3.10263100	-3.27755600
C	-3.06248500	-1.24969400	-1.05143500
C	-4.36457300	-0.95389700	-1.50990000
C	-2.57400600	-2.56428600	-1.18734300
C	-5.15656600	-1.95429600	-2.10158200
H	-4.76105800	0.07124100	-1.41947700
C	-3.36090800	-3.56517100	-1.78388700
H	-1.56352500	-2.81889500	-0.83604000
C	-4.65344500	-3.26001900	-2.24431300
H	-6.17000600	-1.71165400	-2.45957000
H	-2.95949100	-4.58602200	-1.88820800
H	-5.27089600	-4.04098900	-2.71573800

C	-2.86333500	2.20804900	-0.62983500
C	-3.65930100	2.77685200	0.38922100
C	-2.76125900	2.87833500	-1.86703800
C	-4.33103200	3.99449100	0.17925700
H	-3.75300800	2.27223300	1.36463600
C	-3.42946500	4.09670800	-2.07669900
H	-2.13528700	2.47056800	-2.67376600
C	-4.21231300	4.65878800	-1.05355800
H	-4.94497400	4.42808300	0.98503100
H	-3.32831300	4.61463000	-3.04361900
H	-4.72964400	5.61752200	-1.21707400
C	-2.14918800	0.12157400	1.92313300
C	-1.73389600	1.07853900	2.87179500
C	-2.96665500	-0.94334400	2.35469900
C	-2.07128900	0.94218700	4.23000700
H	-1.16400200	1.96194000	2.55592700
C	-3.31137700	-1.08163900	3.71146600
H	-3.34746500	-1.67288500	1.62325700
C	-2.85122400	-0.14722100	4.65515600
H	-1.73047400	1.69841500	4.95519000
H	-3.94943200	-1.92127100	4.03106600
H	-3.11717600	-0.25670500	5.71840200
Sn	-1.85635400	0.33835700	-0.21777700

TS1

0 1

P	1.18973500	-0.67619200	-0.12006800
C	-1.21013100	-3.28553800	-1.32682900
N	0.82421900	-2.33469000	-0.30101600
N	2.88584800	-0.92493700	-0.38024200
C	3.86818000	-0.01211100	0.15124500
C	-3.05178200	-3.98733700	0.11871500
H	-4.06712900	-4.39603100	0.22982500
C	-2.32256700	-3.60902100	1.25470900
H	-2.77502700	-3.74577600	2.24609800
C	4.94135200	0.40857200	-0.68906100
C	-0.48985900	-2.89301200	-0.16572800
C	2.86218200	-0.22576700	2.53168000
H	2.23476000	-0.97970900	2.00772700
C	3.79583500	0.41425100	1.50733200
C	-2.49233900	-3.84278900	-1.15277700
H	-3.06928900	-4.14972400	-2.03704000
C	5.82094700	1.39199200	-0.19953900
H	6.63949200	1.74724600	-0.84360000

C	0.29153700	0.63930600	-0.55905400
C	1.97173600	-3.10887500	-0.78988600
H	1.97424700	-3.17480400	-1.90029800
H	1.93429000	-4.13901000	-0.38091600
C	-1.52971200	-2.74960400	-3.83861400
H	-2.46972100	-3.33792000	-3.87931200
H	-1.02598900	-2.87077100	-4.81990800
H	-1.76686700	-1.67554900	-3.73309200
C	6.30248400	-1.38324800	-1.78436100
H	6.45527100	-1.98739900	-2.70330900
H	6.02992800	-2.06952400	-0.95736000
H	7.27661300	-0.92478100	-1.51251200
C	3.67242300	-0.99627500	3.59272400
H	4.32661600	-1.76256000	3.12807700
H	2.99053800	-1.50554500	4.30537300
H	4.32132500	-0.31221700	4.17874200
C	4.69319800	1.41052000	1.94364000
H	4.62441600	1.77760300	2.97969500
C	3.20960900	-2.36132400	-0.30570100
H	3.47201500	-2.64174900	0.74211300
H	4.08295100	-2.59037100	-0.94584900
C	-1.02579900	-3.07341600	1.14669000
C	5.67719200	1.92191700	1.09062500
H	6.36012300	2.71043700	1.44326700
C	5.23982700	-0.28150300	-2.01826000
H	4.29718400	-0.76363800	-2.35576300
C	-0.58887600	-3.23059300	-2.72153200
H	0.24879500	-2.50345500	-2.68365400
C	5.72382900	0.65417400	-3.13891000
H	6.71165600	1.10118000	-2.90002700
H	5.00786800	1.47455200	-3.32894000
H	5.84899900	0.08202000	-4.08124800
C	-0.03137000	-4.63083100	-3.07347200
H	0.62664700	-5.03964700	-2.28070500
H	0.54220700	-4.60152700	-4.02367400
H	-0.86665000	-5.35118600	-3.20381500
C	1.89680600	0.78289500	3.16408400
H	2.43456700	1.54572100	3.76504900
H	1.16891300	0.27854500	3.83251200
H	1.32314300	1.31058900	2.38180900
C	-0.20709400	-2.75208400	2.40171500
H	0.12828700	-1.69056800	2.32067000
C	1.04875900	-3.64301500	2.51573700
H	1.61382900	-3.39730300	3.43811800

H	1.73639200	-3.51970900	1.66300100
H	0.75658500	-4.71267100	2.56891100
C	-0.99509300	-2.89260800	3.71341900
H	-1.21963100	-3.95857600	3.92957800
H	-1.95334900	-2.34278600	3.70409400
H	-0.39412200	-2.49870100	4.55752500
Si	1.01847100	2.34632100	-1.59925000
C	2.56543100	1.82938000	-2.56113300
H	2.77472600	0.75035300	-2.44008600
H	2.42674500	2.03277600	-3.64232600
H	3.44152900	2.39916400	-2.19240400
C	1.63901400	3.16122100	0.03612100
H	2.20578300	4.09400300	-0.17510700
H	0.77558800	3.43867800	0.67767100
H	2.28874400	2.47008500	0.60940400
C	0.30206700	3.92462900	-2.42878400
H	-0.07194100	3.74242500	-3.45585300
H	-0.51863200	4.37456100	-1.83649900
H	1.12775900	4.66921900	-2.47167300
C	-0.21646000	1.15727800	-2.73473900
N	-0.92745900	0.53044200	-3.44084500
C	-2.41210500	2.82830800	-0.61822000
C	-2.40727000	4.02648900	0.12689400
C	-2.94900800	2.84296800	-1.92384000
C	-2.89948200	5.22076500	-0.42972600
H	-2.02353800	4.04233900	1.15799400
C	-3.44341500	4.03471000	-2.47955600
H	-2.96314000	1.92622400	-2.53094200
C	-3.41353300	5.22774800	-1.73733700
H	-2.88112100	6.14921900	0.16336800
H	-3.84747400	4.03051200	-3.50438600
H	-3.79376700	6.16349200	-2.17710100
C	-3.28228100	-0.42475600	-0.29977200
C	-4.29289600	-0.78711900	0.61595900
C	-3.43323100	-0.77745700	-1.65624500
C	-5.42475600	-1.50182000	0.18475200
H	-4.22140900	-0.49669700	1.67556700
C	-4.57177100	-1.47872400	-2.08937900
H	-2.66093100	-0.48925000	-2.38690900
C	-5.56834900	-1.84560900	-1.17035500
H	-6.20426500	-1.78062800	0.91209100
H	-4.67531800	-1.73854600	-3.15491100
H	-6.46129800	-2.39468900	-1.50951400
C	-1.55209200	1.24390300	2.37393100

C	-0.94393100	2.39770000	2.91623200
C	-2.06773400	0.28214300	3.26524800
C	-0.86203400	2.58702200	4.30602400
H	-0.49370200	3.15296000	2.25368600
C	-1.98089800	0.46011700	4.65800500
H	-2.53884700	-0.62980200	2.86931600
C	-1.38028200	1.61701900	5.18154800
H	-0.38011200	3.49301200	4.70661200
H	-2.38534300	-0.30850700	5.33595800
H	-1.31376000	1.76218900	6.27139900
Sn	-1.71213200	0.96034700	0.23226900

TS2

0 1

P	1.67747500	-0.11589500	-0.35342300
C	2.06916400	3.46395200	0.63821200
N	2.22902800	0.98920500	0.87426200
N	1.28974500	-1.32017700	0.89782100
C	1.38788600	-2.71431100	0.56102700
C	4.08964300	4.72717400	0.06890500
H	4.58686700	5.69270200	-0.11499800
C	4.80867500	3.52917400	-0.05804900
H	5.86992500	3.56453700	-0.34473500
C	0.36544900	-3.63172000	0.97220200
C	2.81878500	2.25734500	0.56361700
C	3.80054100	-2.44121300	-0.35612100
H	3.67662700	-1.46173900	0.14695000
C	2.48473100	-3.20406500	-0.21351100
C	2.73482100	4.68769100	0.41111100
H	2.16606600	5.62804600	0.48148300
C	0.35394600	-4.92626500	0.41735900
H	-0.44878600	-5.62167300	0.70278900
C	0.00838400	0.44283000	-0.88827900
C	1.70253400	0.67427700	2.19844600
H	0.68790800	1.09299100	2.37424900
H	2.37255400	1.08148100	2.98506000
C	-0.20243900	4.30413700	-0.12425600
H	0.06734600	5.38046400	-0.08775200
H	-1.29277700	4.22942100	0.05574700
H	0.00026400	3.93361800	-1.14835100
C	0.03243200	-3.58227000	3.45826700
H	-0.59495400	-3.18026700	4.28156900
H	1.04826900	-3.15378000	3.55292000
H	0.12788700	-4.67978000	3.59995100

C	4.91580600	-3.18704300	0.40675300
H	4.63751200	-3.34468500	1.46874800
H	5.86122400	-2.60544200	0.37773400
H	5.11987900	-4.18334900	-0.03873900
C	2.41405200	-4.50098600	-0.76313300
H	3.24111000	-4.85865800	-1.39740900
C	1.64431800	-0.85377600	2.25307300
H	2.63128600	-1.27540700	2.56152000
H	0.88593900	-1.16851500	2.99791200
C	4.19793300	2.28730900	0.19022700
C	1.33706400	-5.34836900	-0.48867700
H	1.28636400	-6.35286300	-0.93719300
C	-0.61760700	-3.28171900	2.08448500
H	-0.81379400	-2.18997300	2.02272000
C	0.57236800	3.49357600	0.93249400
H	0.20607100	2.44741500	0.87268100
C	-1.96110300	-4.02557800	2.02202900
H	-1.82606100	-5.12035500	2.14625100
H	-2.50385200	-3.85164800	1.07352800
H	-2.61027200	-3.69201500	2.85520600
C	0.29125100	4.03338500	2.34864400
H	0.78636500	3.42211700	3.13118200
H	-0.80001000	4.05234000	2.55385800
H	0.66663500	5.07302800	2.45482300
C	4.20865300	-2.16919500	-1.81297400
H	4.31405400	-3.11152400	-2.39059900
H	5.18357300	-1.64138700	-1.85447600
H	3.45890300	-1.52999000	-2.31918500
C	4.99496800	0.99120000	0.10560400
H	4.31538000	0.24101900	-0.34847100
C	5.36975400	0.49171200	1.51501200
H	5.89946600	-0.48238400	1.46494700
H	4.46821000	0.35681000	2.14314200
H	6.03580900	1.22036500	2.02369800
C	6.23636100	1.07279300	-0.79285900
H	7.01815400	1.73887700	-0.36967400
H	5.98443400	1.44319900	-1.80764100
H	6.69461800	0.06758500	-0.89929300
C	0.04480000	1.34985500	-1.93330900
N	0.04481300	2.07926600	-2.90263000
Si	0.11548100	-0.22087700	-3.46372000
C	1.59912900	0.26508700	-4.51030300
H	1.85363500	-0.56076800	-5.20866800
H	1.42321500	1.20312800	-5.06983700

H	2.47084300	0.42198100	-3.84025600
C	-1.60448500	-0.09151700	-4.19765000
H	-1.74032600	-0.92556900	-4.91914200
H	-2.37501700	-0.22218800	-3.41035300
H	-1.76233600	0.87499000	-4.71226300
C	0.41435000	-2.00122800	-2.92862700
H	0.46703100	-2.61544000	-3.85651000
H	1.36679700	-2.12933800	-2.38114400
H	-0.40754100	-2.38782900	-2.30192900
C	-3.01394600	-1.27831500	-0.95365200
C	-4.27173600	-1.04283200	-1.54950100
C	-2.43683100	-2.56003000	-1.06474900
C	-4.93405500	-2.06898000	-2.24850400
H	-4.73659100	-0.04499200	-1.47875000
C	-3.09647100	-3.58810100	-1.76075400
H	-1.45499400	-2.76662800	-0.60964200
C	-4.34567900	-3.34170700	-2.35696500
H	-5.91329500	-1.87267700	-2.71408700
H	-2.62679800	-4.58183900	-1.83863900
H	-4.86271700	-4.14339100	-2.90794700
C	-3.01646800	2.16297700	-0.43096400
C	-3.60314900	2.89668500	0.62356800
C	-3.10122600	2.67298000	-1.74503300
C	-4.24872100	4.12069900	0.37372400
H	-3.55157500	2.51495500	1.65669300
C	-3.74528100	3.89725900	-1.99548900
H	-2.64515300	2.13070200	-2.58612800
C	-4.31550000	4.62519000	-0.93678500
H	-4.69810400	4.68471600	1.20691200
H	-3.79314800	4.28879900	-3.02412500
H	-4.81367300	5.58780300	-1.13365800
C	-2.20479900	0.09554600	2.15315000
C	-1.67863800	0.99879500	3.10029600
C	-3.05259800	-0.93834100	2.60203000
C	-1.94745100	0.84010100	4.47166400
H	-1.06824500	1.85278600	2.77509800
C	-3.32770600	-1.09752800	3.97187900
H	-3.50462800	-1.63133300	1.87479700
C	-2.76405600	-0.21631300	4.91099400
H	-1.52237200	1.55140500	5.19777700
H	-3.98925500	-1.91253500	4.30699900
H	-2.97474000	-0.34305600	5.98466900
Sn	-1.95440600	0.33432900	0.01918900

4

0 1

Sn	16.85386300	9.45493800	2.07871300
C	15.73662500	9.44311200	3.92069000
C	17.49526100	11.44698000	1.58746800
C	15.36568000	8.62058000	0.76718100
C	18.58689100	8.19891700	2.29476900
P	15.06430200	7.74253900	4.25977300
C	16.87109800	12.18201100	0.57064100
C	18.51659600	12.06030500	2.32905800
C	15.66916700	7.70464800	-0.24835600
C	14.01822900	8.91686300	1.02408100
C	18.46922500	6.89272500	2.79481300
C	19.86664300	8.69550500	2.00954600
N	13.49380300	8.02502800	4.93488000
N	15.63355300	7.27701200	5.81545600
H	16.07208800	11.72784700	-0.02283400
C	17.25025600	13.49914400	0.30643800
H	19.02014300	11.51336400	3.13218700
C	18.90054900	13.37585500	2.06478200
H	16.70893700	7.43823300	-0.45778700
C	14.65077500	7.10608900	-0.99344900
H	13.74763500	9.60096200	1.83547100
C	12.99804500	8.32261300	0.28094000
H	17.48420200	6.47121100	3.02021800
C	19.60270400	6.10976100	3.01382500
H	19.98836500	9.70712200	1.61157300
C	21.00200200	7.91348400	2.22957900
C	12.31787700	7.96206000	4.13025900
C	13.38389400	7.72081800	6.35705700
C	16.93115600	6.72634400	6.03880400
C	14.80884800	7.79546800	6.90078400
H	16.75289800	14.06019000	-0.48682100
C	18.26403300	14.09725000	1.05472100
H	19.69509400	13.84010500	2.65156200
H	14.90105600	6.38964800	-1.77801100
C	13.31633800	7.41523300	-0.72994600
H	11.95672200	8.55804000	0.50961800
C	20.87030900	6.62171500	2.73645500
H	19.49258400	5.09947000	3.41089100
H	21.99149000	8.31558500	2.00458900
C	11.50775700	9.11447700	4.01774100
C	11.95176700	6.76398100	3.47327500
H	12.95891200	6.70858800	6.50804300

H	12.72000300	8.44198600	6.86349200
C	17.13721600	5.34770800	5.78000700
C	17.98917000	7.53010200	6.50676700
H	15.05823300	8.84037600	7.16495300
H	14.93831400	7.17571200	7.80129500
H	18.56059900	15.12709900	0.84879900
H	12.52157100	6.94050400	-1.30821000
H	21.75704600	6.01049300	2.91324000
C	11.82447800	10.39365300	4.77442200
C	10.35696700	9.05501600	3.22462700
C	12.75995500	5.48321700	3.60450000
C	10.80469800	6.75803300	2.67398800
C	15.99980100	4.48695600	5.25304000
C	18.39284400	4.79750700	6.04068400
C	19.22967200	6.93292900	6.76503200
C	17.83441800	9.02549200	6.71575600
H	12.83244100	10.27852600	5.20130500
C	11.83737400	11.62271000	3.86329000
C	10.83418300	10.59809100	5.92793100
H	9.71997400	9.93778600	3.13849700
C	10.00856300	7.89095700	2.54784200
H	13.50245400	5.63637100	4.40107000
C	13.50554800	5.16407600	2.30318600
C	11.88923600	4.30025600	4.03986600
H	10.52520400	5.84269900	2.14779500
H	15.47922900	5.08140500	4.48648400
C	14.99791500	4.17254400	6.36980800
C	16.46133900	3.19799800	4.57606700
C	19.43277500	5.57931700	6.54181900
H	18.56840100	3.73815700	5.85045200
H	20.05168300	7.55015900	7.13464200
H	16.83936100	9.30770400	6.36173100
C	18.84003500	9.81345200	5.87041200
C	17.92991400	9.40633800	8.19560000
H	10.87338600	11.75345800	3.34865200
H	12.62244500	11.54163400	3.09538400
H	12.02531400	12.53110800	4.45358300
H	11.11034400	11.48785200	6.51479100
H	10.80685300	9.72717000	6.59974600
H	9.81398400	10.74967400	5.54129800
H	9.11094500	7.86489000	1.92752700
H	14.14028900	4.27270000	2.42986200
H	14.14318400	6.00349900	1.98931200
H	12.79064100	4.95909400	1.49018500

H	11.12870100	4.05551100	3.28341500
H	11.37055800	4.51190800	4.98640800
H	12.51190300	3.40326900	4.17862600
H	15.47922500	3.56623800	7.15275800
H	14.13799800	3.60844000	5.97738800
H	14.62029100	5.09332700	6.83391600
H	17.20709600	3.39535200	3.79158300
H	15.60159300	2.69516000	4.10931300
H	16.89902500	2.49092400	5.29720600
H	20.40626600	5.12933000	6.74381200
H	19.86848300	9.69191600	6.24487100
H	18.59304700	10.88635300	5.89497800
H	18.82411200	9.46801100	4.82514600
H	17.16845800	8.88176000	8.79207300
H	17.78387900	10.48987000	8.32256000
H	18.91666300	9.14644000	8.60962900
C	15.51319500	10.48808000	4.68251600
N	15.37769300	11.39008800	5.48491700
C	14.55849400	12.50668300	5.67925300
C	14.52876800	13.54359000	4.72787700
C	13.81582600	12.57346200	6.87091400
C	13.73182000	14.65757000	4.99925000
C	15.30591800	13.42389900	3.44917300
C	13.01514300	13.69645700	7.09017600
C	13.88085700	11.43690600	7.85084200
H	13.69974100	15.46950800	4.26993900
C	12.97341500	14.73735200	6.16528100
H	16.37171900	13.22386000	3.63676700
H	15.22539100	14.33965000	2.85019600
H	14.93121600	12.58713500	2.83761400
H	12.42455600	13.75323100	8.00712300
H	13.35736000	11.68652100	8.78232600
H	14.92627800	11.18127300	8.08239000
H	13.41575400	10.53079100	7.42796600
H	12.35118600	15.61291400	6.35438800

VI. Reference.

S1. C. Y. Hu, X. F. Wang, R. Wei, C. P. Hu, D. A. Ruiz, X. Y. Chang and L. L. Liu, *Chem*, 2022, **8**, 2278-2289.

S2. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, F. Goings, J. B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S3 Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

S4. (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100; (b), J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.

S5. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

S6. A. v. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.

S7. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, *NBO 7.0, University of Wisconsin: Madison, WI*, 2018.

S8. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592