Electronic Supplementary Material (ESI) for ChemComm.

N-heterocyclic carbene phosphaketene adducts as precursors to carbene-phosphinidene adducts and a rearranged π-system

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Supporting Information

S1: Synthetic Details

General: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk techniques. Dry, oxygen-free solvents were employed unless otherwise mentioned. The sodium phosphaethynolate[1], and triphenyl tetrel substituted phosphaketenes RE-P=C=O (E = Sn and Ge),[2] 1,3-Bis(2,6-diisopropylphenyl)imidazolylidene (**IPr**),[3] 1,3-Bis(2,6-diisopropylphenyl)imidazolinylidene (**IPr^{H}**), [3] 1,3-bis(2,4,6-trimethylphenyl)imidazolylidene (**IMes**), [3] were prepared following literature procedures while all other starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 400 MHz spectrometers (^{1}H, 400.1 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.9 MHz). All spectra were obtained in the solvent indicated at 25 °C. The chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to $SiMe_4$ (^{1}H, ^{13}C), and 85% H_3PO_4 (^{31}P). Coupling constants *J* are reported in Hertz [Hz] as absolute values. The elemental analyses were acquired on Vario EL cube elemental analyzer. IR spectra were obtained on a Perkin-Elmer-Spectrum ATR 2000 FT-IR-Raman spectrometer. The ATR technique was used for the analysis of solid compounds. Melting point (M. P.) were measured on Buchi M-560 apparatus.

Preparation of 2aa-2cb: NHC (0.25 mmol) was added to a stirred solution of **Ph$_3$E-PCO** (0.25 mmol) in toluene (3 mL). After stirring for 0.5 hour, the solvent was removed under reduced pressure. The remaining solid was washed with hexane and dried *in vacuo* to afford **2aa-2cb** as yellow powder.

2aa (NHC = **IPr**, E = Sn): 183.7 mg, 0.23 mmol, 92 % yield. Yellow crystals of **2aa** were obtained from a toluene solution layered with hexane on top and stored at –30 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.68 (m, 6 H, C_{ar}*H*), 7.22 (m, 2 H, C_{ar}*H*), 7.11 (m, 13 H, C_{ar}*H*), 6.12 (s, 2 H, NC*H*), 2.70 (m, 4 H, C*H*Me$_2$), 1.31 (d, *J* = 6.8 Hz, 12 H, C*H*$_3$), 1.00 (d, *J* = 6.8 Hz, 12 H, C*H*$_3$); ^{13}C{^{1}H} NMR (C_6D_6,, 100.5 MHz): δ = 198.2 (d, $^{1}J_{PC}$ = 76.4 Hz, *PC*O), 151.2 (d, $^{2}J_{PC}$ = 53.3 Hz, *PC*C), 145.5 (C_{ar}), 144.9 (C_{ar}), 137.8 (t, $^{1}J_{CSn}$ = 19.1 Hz, Sn*C*), 132.0 (C_{ar}), 130.8 (C_{ar}), 127.5 (C_{ar}), 127.1 (C_{ar}), 124.2 (C_{ar}), 120.9 (NCH), 29.2 (CH_3), 25.0 (CH_3), 22.9 (*C*HMe$_2$); ^{31}P{^{1}H} NMR (C_6D_6,, 161.9 MHz) δ = 32.1 (t, $J_{P\text{-}Sn}$ = 390.2 Hz). M. P. = 120 °C (decomposition). Elemental analysis (%): calcd for $C_{46}H_{51}N_2OPSn$; C 69.27, H 6.44, N 3.51; found: C 69.94, H 6.83, N 3.30. IR (solid): 3152, 3062, 2967, 2930, 2870, 1598, 1551, 1475, 1428, 1408, 1107, 918, 800, 726, 699, 655 cm^{-1}.

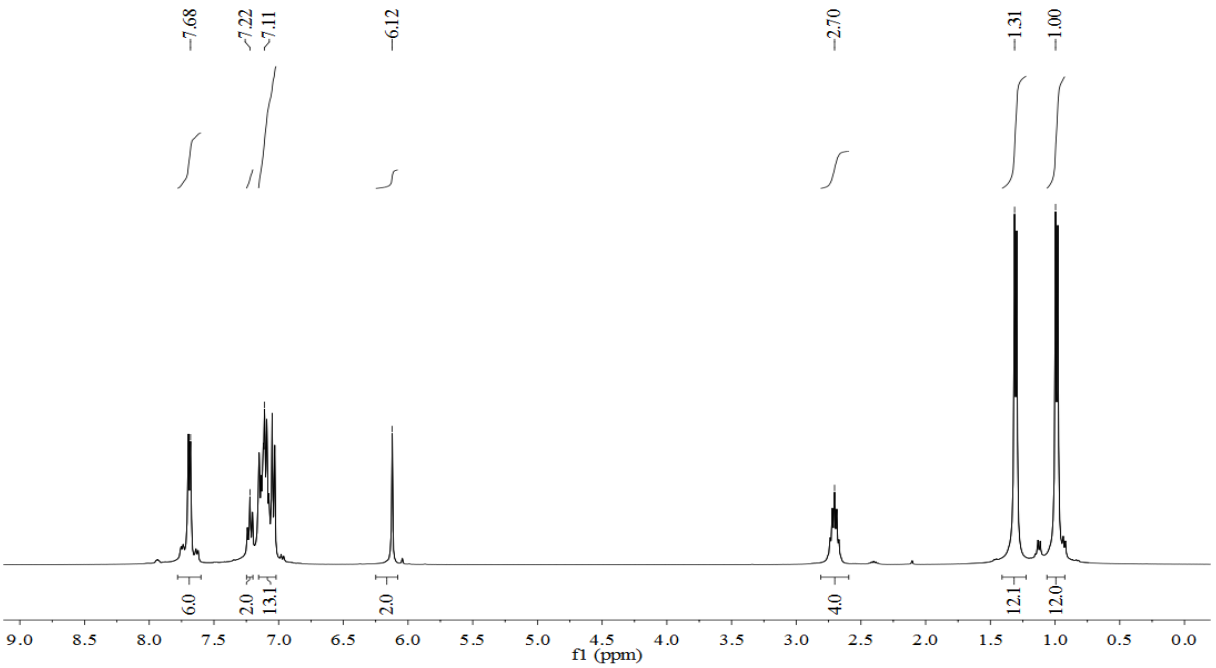


Figure S1. ^{1}H NMR spectrum of **2aa** in C_6D_6.

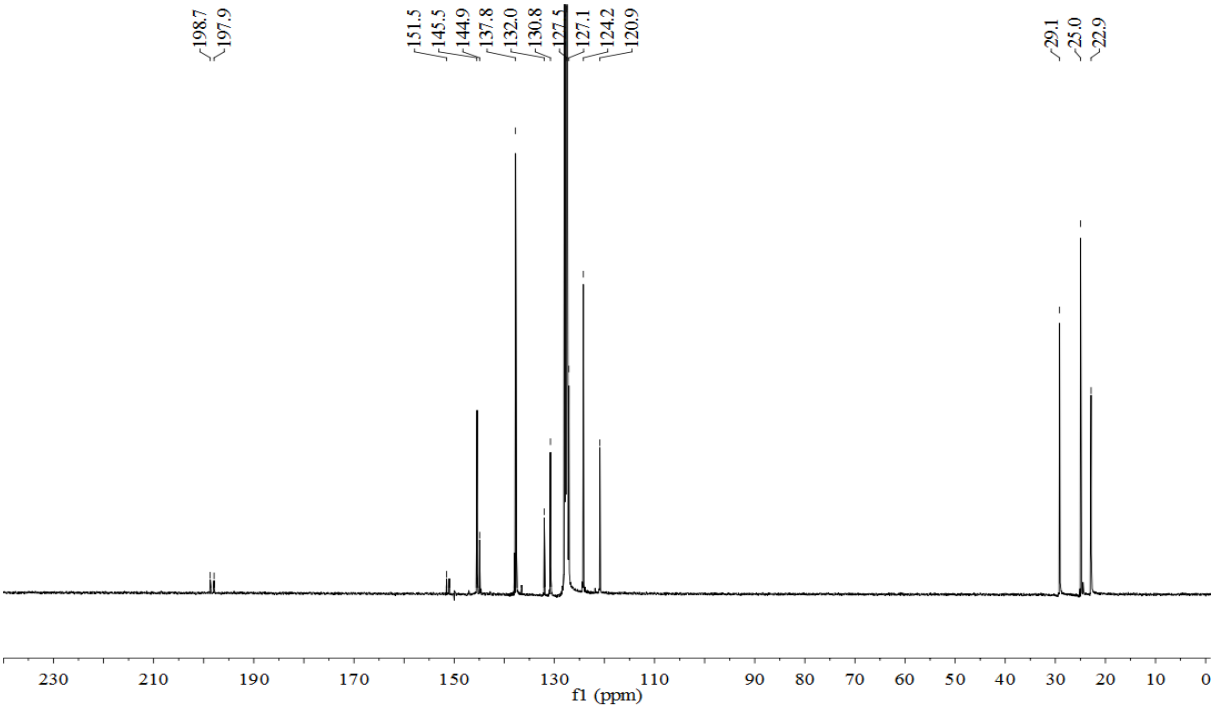


Figure S2. ^{13}C{^{1}H} NMR spectrum of **2aa** in C_6D_6.

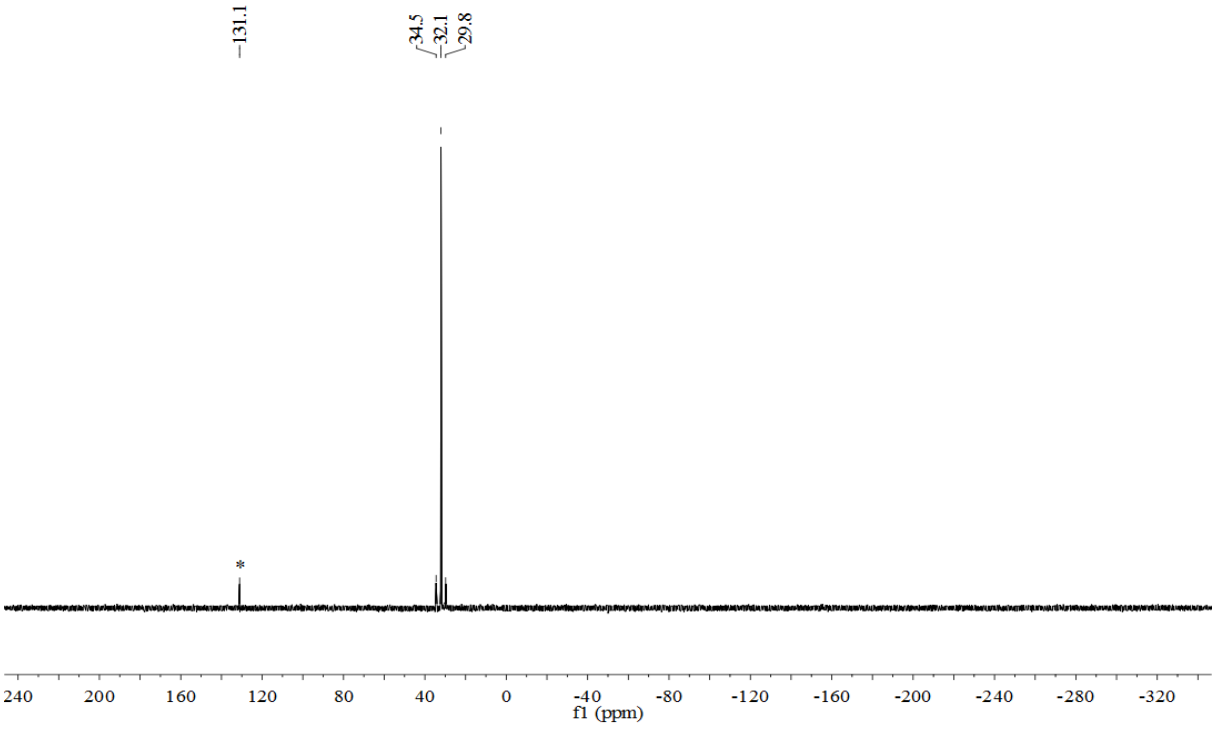


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **2aa** in C_6D_6. *Small impurity.

2ba (NHC = **IMes**, E = Sn): 168.6 mg, 0.24 mmol, 95 % yield. This compound is not soluble in most of the common organic solvent including THF, toluene, dichloromethane, and DMSO. M. P. = 187 °C. Elemental analysis (%): calcd for $C_{40}H_{39}N_2OPSn$; C 67.34, H 5.51, N 3.93; found: C 68.58, H 5.76, N 3.47. IR (solid): 3160, 3061, 3008, 1607, 1552, 1489, 1463, 1426, 1378, 1232, 1070, 906, 860, 763, 731, 700cm^{-1}.

2ab (NHC = **IPr**, E = Ge): 180.6 mg, 0.24 mmol, 96 % yield. Yellow crystals of **2ab** were obtained from a toluene solution layered with hexane on top and stored at –30 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.61 (d, *J* = 6.8 Hz, 6 H, $C_{ar}H$), 7.24 (t, *J* = 7.6 Hz, 2 H, $C_{ar}H$), 7.06 (m, 13 H, $C_{ar}H$), 6.17 (s, 2 H, NC*H*), 2.80 (m, 4 H, C*H*Me$_2$), 1.34 (d, *J* = 6.4 Hz, 12 H, CH_3), 1.00 (d, *J* = 7.2 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.5 MHz): δ = 196.3 (d, $^{1}J_{PC}$ = 70.4 Hz, P*C*O), 151.8 (d, $^{2}J_{PC}$ = 58.3 Hz, PC*C*), 145.9 (C_{ar}), 142.4 (C_{ar}), 135.5 (Car), 131.6 (C_{ar}), 130.8 (C_{ar}), 127.3 (C_{ar}), 127.2 (C_{ar}), 124.2 (C_{ar}), 120.7 (NCH), 29.2 (CH_3), 25.3 (CH_3), 22.8 (*C*HMe$_2$); $^{31}P\{^{1}H\}$ NMR (C_6D_6,, 161.9 MHz) δ = 9.1 (s). M. P. = 130 °C (decomposition). Elemental analysis (%): calcd for $C_{46}H_{51}N_2OPGe$; C 73.52, H 6.84, N 3.73; found: C 73.63, H 6.98, N 3.10. IR (solid): 3153, 3067, 2967, 2930, 2870, 1598, 1553, 1465, 1428, 1384, 1326, 1209, 1185, 1060, 912, 802, 735, 699, 669 cm^{-1}.

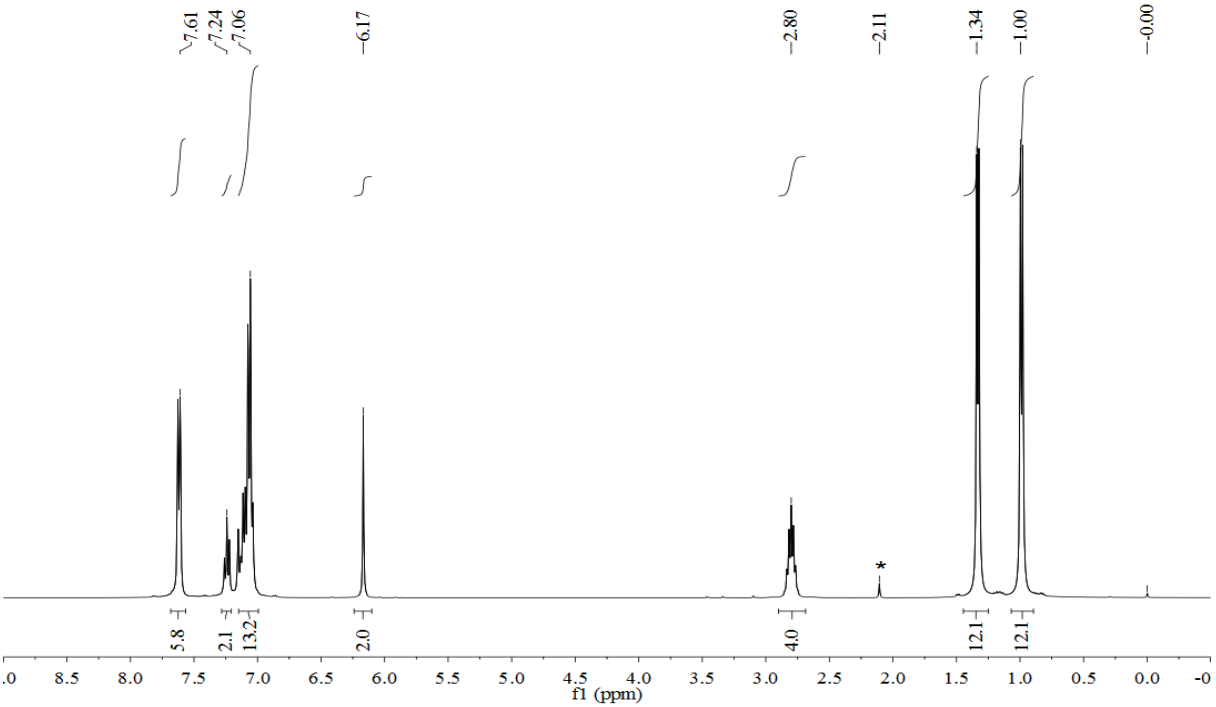


Figure S4. ^{1}H NMR spectrum of **2ab** in C_6D_6. *Toluene.

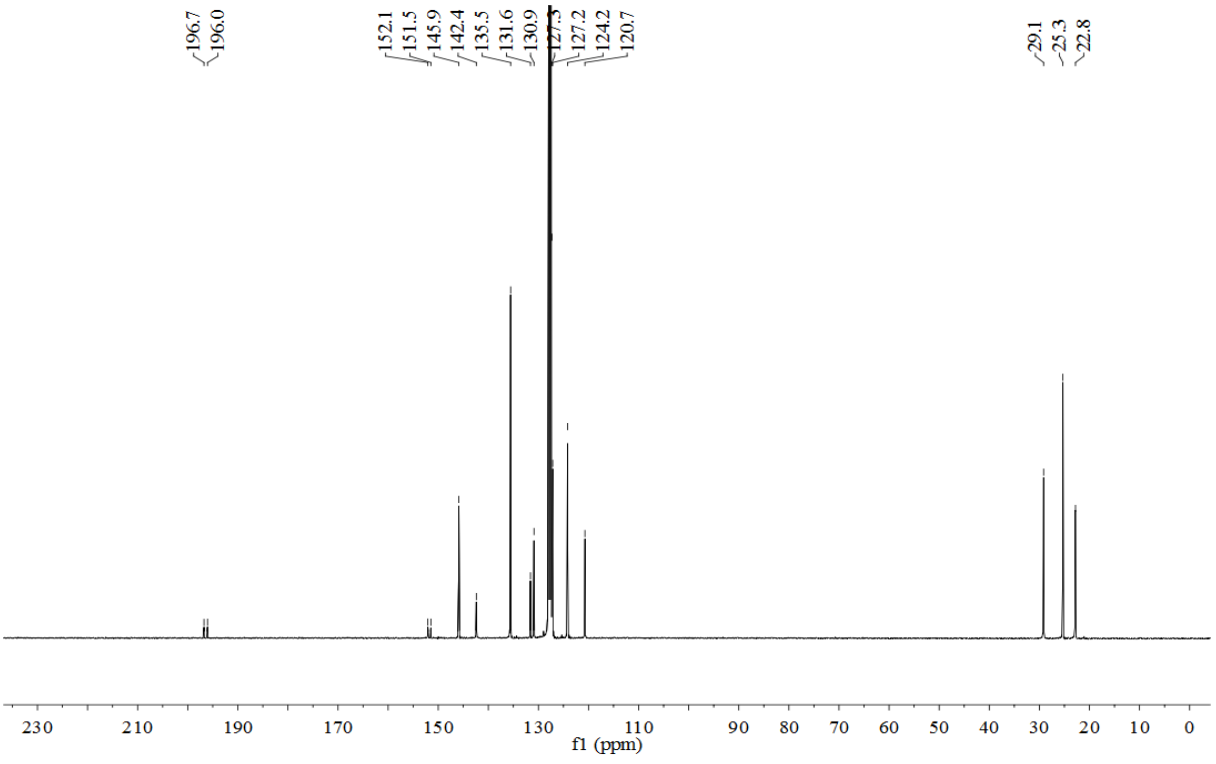


Figure S5. ^{13}C{^{1}H} NMR spectrum of **2ab** in C_6D_6.

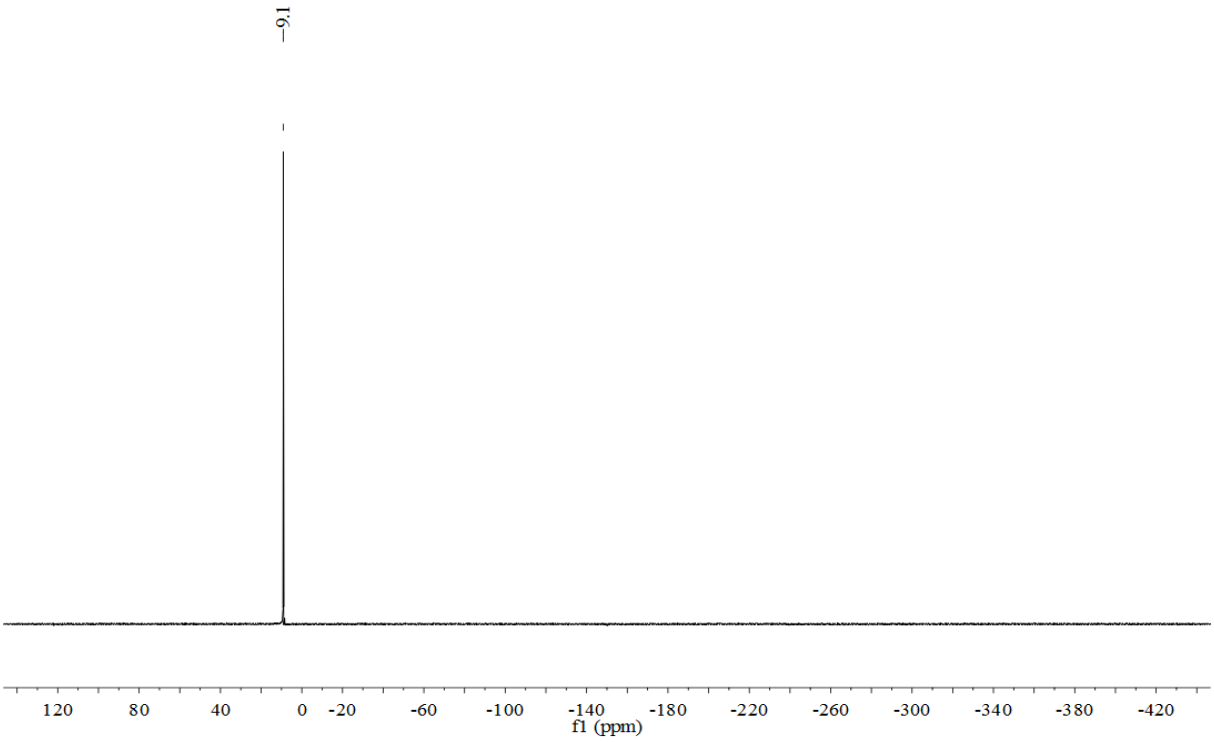


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **2ab** in C_6D_6.

2bb (NHC = **IMes**, E = Ge): 164.1 mg, 0.25 mmol, 98 % yield. This compound is not soluble in most of the common organic solvent including THF, toluene, dichloromethane, and DMSO. M. P. = 190 °C (decomposition). Elemental analysis (%): calcd for $C_{40}H_{39}N_2OPGe$; C 71.99, H 5.89, N 4.20; found: C 72.41, H 6.13, N 4.03. IR (solid): 3162, 3049, 2921, 1606, 1474, 1428, 1378, 1232, 1151, 1083, 1041, 906, 861, 764, 732, 699, 669 cm^{-1}.

2ca (NHC = **IPr^{H}**, E = Sn): 183.6 mg, 0.23 mmol, 92 % yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.49 (t, *J* = 7.6 Hz, 2 H, $C_{ar}H$), 7.29 (d, *J* = 7.6 Hz, 4 H, $C_{ar}H$), 7.11 (m, 15 H, $C_{ar}H$), 4.25 (s, 4 H, NCH_2), 3.28 (m, 4 H, $CHMe_2$), 1.34 (dd, *J* = 6.4 Hz, *J* = 6.8 Hz, 24 H, CH_3); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 200.4 (d, $^{1}J_{PC}$ = 77.9 Hz, *PC*O), 169.0 (d, $^{2}J_{PC}$ = 53.1 Hz, *PCC*), 147.4 (C_{ar}), 144.5 (C_{ar}), 137.4 (t, $^{1}J_{CSn}$ = 19.1 Hz, Sn*C*), 131.9 (C_{ar}), 130.7 (C_{ar}), 127.9 (C_{ar}), 127.7 (C_{ar}), 125.1 (C_{ar}), 52.4 (NCH_2), 29.7 (CH_3), 26.3 (CH_3), 23.9 ($CHMe_2$); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = 6.68 (t, $J_{P\text{-}Sn}$ = 427.4 Hz). M. P. = 105 °C. Elemental analysis

(%): calcd for $C_{46}H_{53}N_2OPSn$; C 69.10, H 6.68, N 3.50; found: C 69.79, H 6.98, N 3.24. IR (solid): 3061, 2964, 2929, 2869, 1591, 1574, 1463, 1428, 1405, 1324, 1281, 1256, 1189, 1105, 1071, 1057, 801, 755, 732, 700, 654 cm^{-1}.

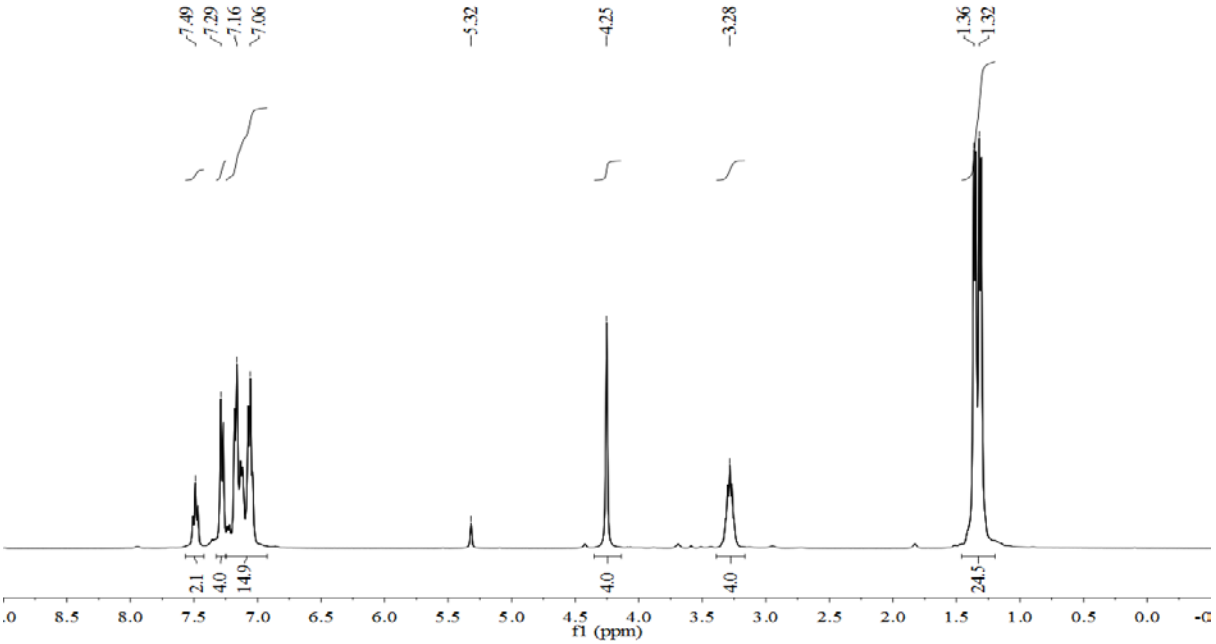


Figure S7. ^{1}H NMR spectrum of **2ca** in CD_2Cl_2.

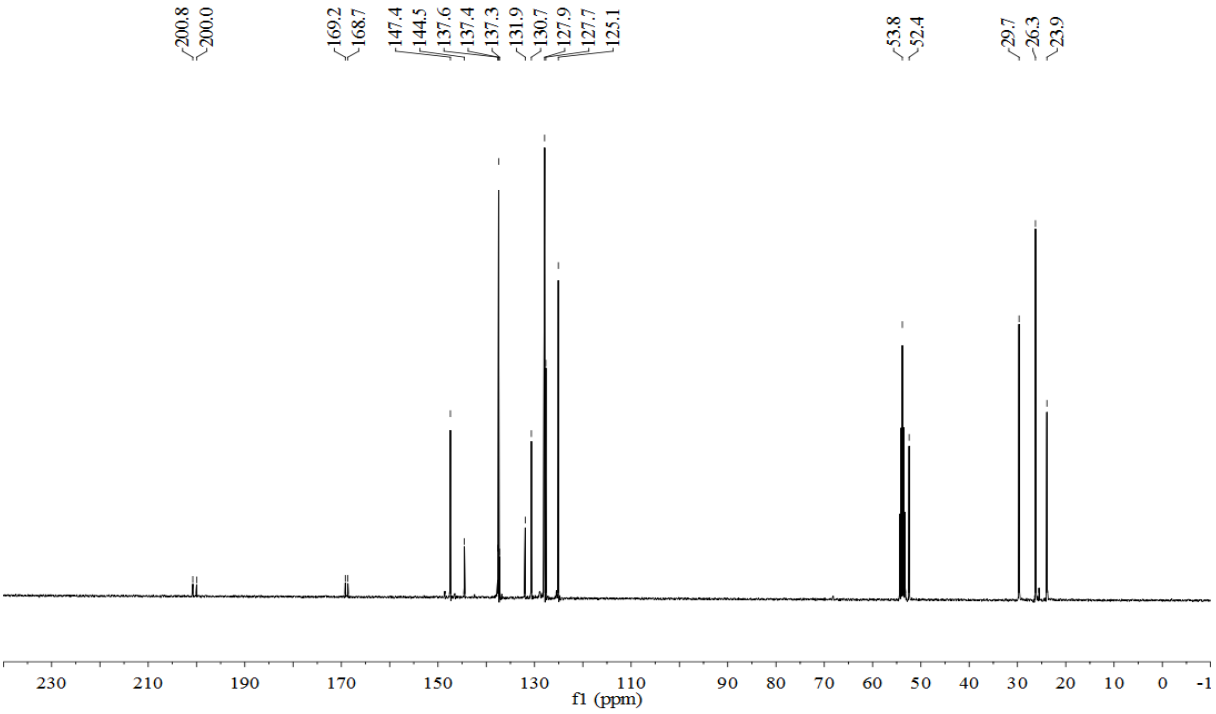


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2ca** in CD_2Cl_2.

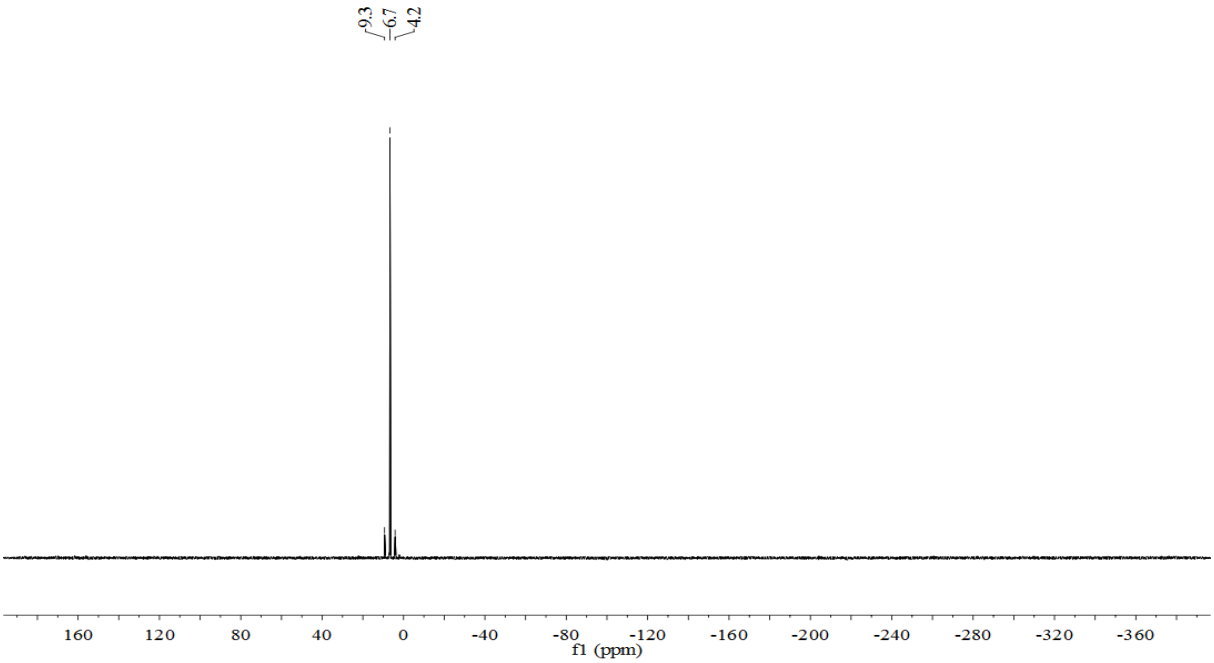


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **2ca** in CD_2Cl_2.

2cb (NHC = **IPr^{H}**, E = Ge): 165.3 mg, 0.23 mmol, 91 % yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.52 (t, *J* = 8.0 Hz, 2 H, $C_{ar}H$), 7.32 (d, *J* = 7.6 Hz, 4 H, $C_{ar}H$), 7.06 (m, 15 H, $C_{ar}H$), 4.27 (s, 4 H, NCH_2), 3.32 (m, 4 H, $CHMe_2$), 1.34 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 24 H, CH_3); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 198.5 (d, $^{1}J_{PC}$ = 73.0 Hz, P*C*O), 151.8 (d, $^{2}J_{PC}$ = 58.2 Hz, PC*C*), 147.7 (C_{ar}), 142.1 (C_{ar}), 135.3 (Car), 131.7 (C_{ar}), 130.7 (C_{ar}), 127.7 (C_{ar}), 125.0 (C_{ar}), 52.3 (NCH_2), 29.7 (CH_3), 26.4 (CH_3), 23.8 ($CHMe_2$); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = – 8.5 (s). M. P. = 115 °C. Elemental analysis (%): calcd for $C_{46}H_{53}N_2OPGe$; C 73.32, H 7.09, N 3.72; found: C 72.28, H 7.17, N 3.43. IR (solid): 3066, 3023, 2963, 2928, 2867, 1590, 1537, 1502, 1431, 1361, 1323, 1280, 1255, 1188, 1086, 1057, 1028, 937, 803, 735, 699, 670 cm^{-1}.

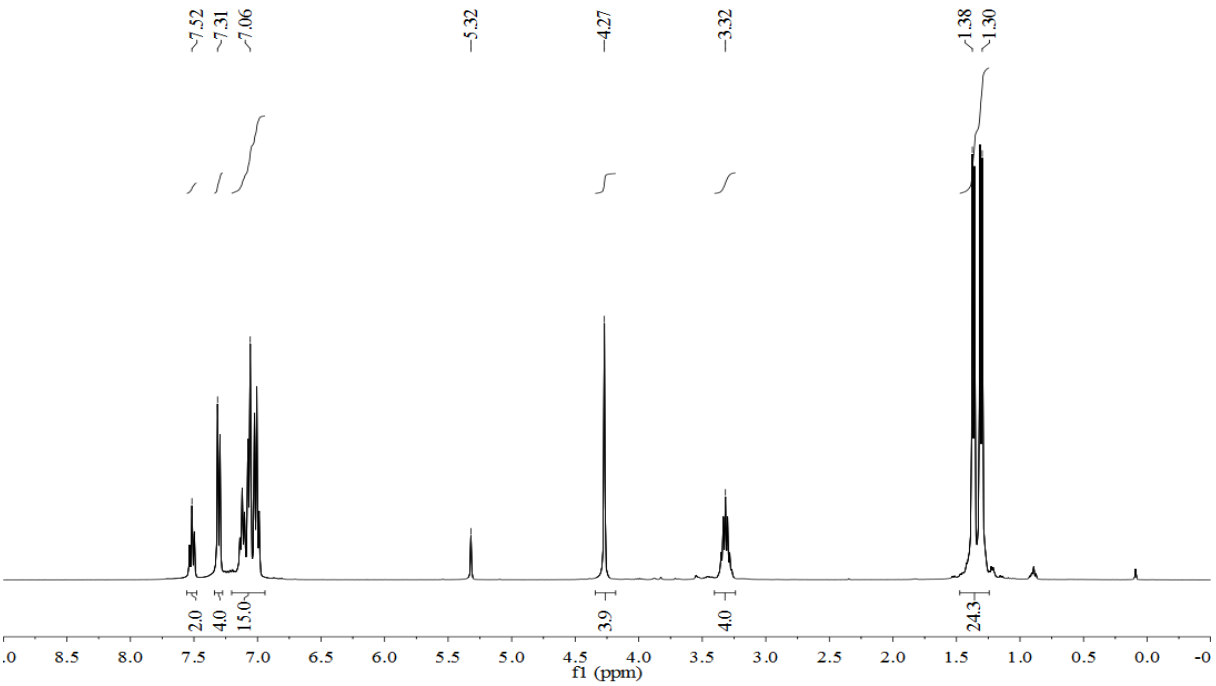


Figure S10. ^{1}H NMR spectrum of **2cb** in CD_2Cl_2.

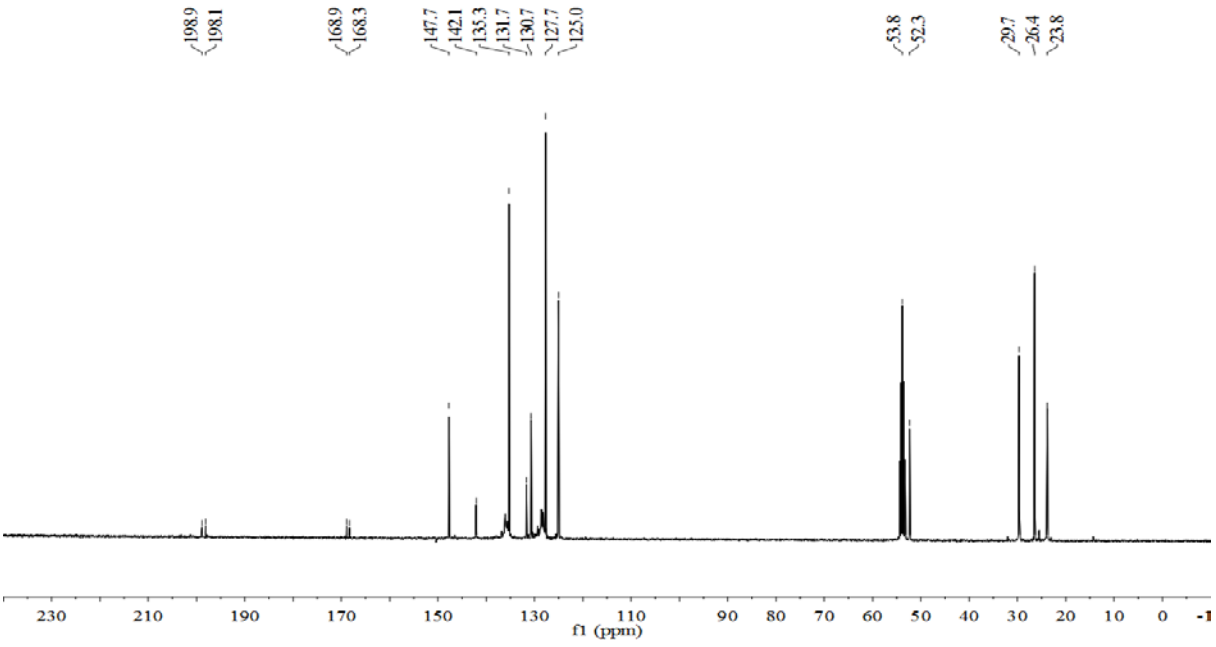


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **2cb** in CD_2Cl_2.

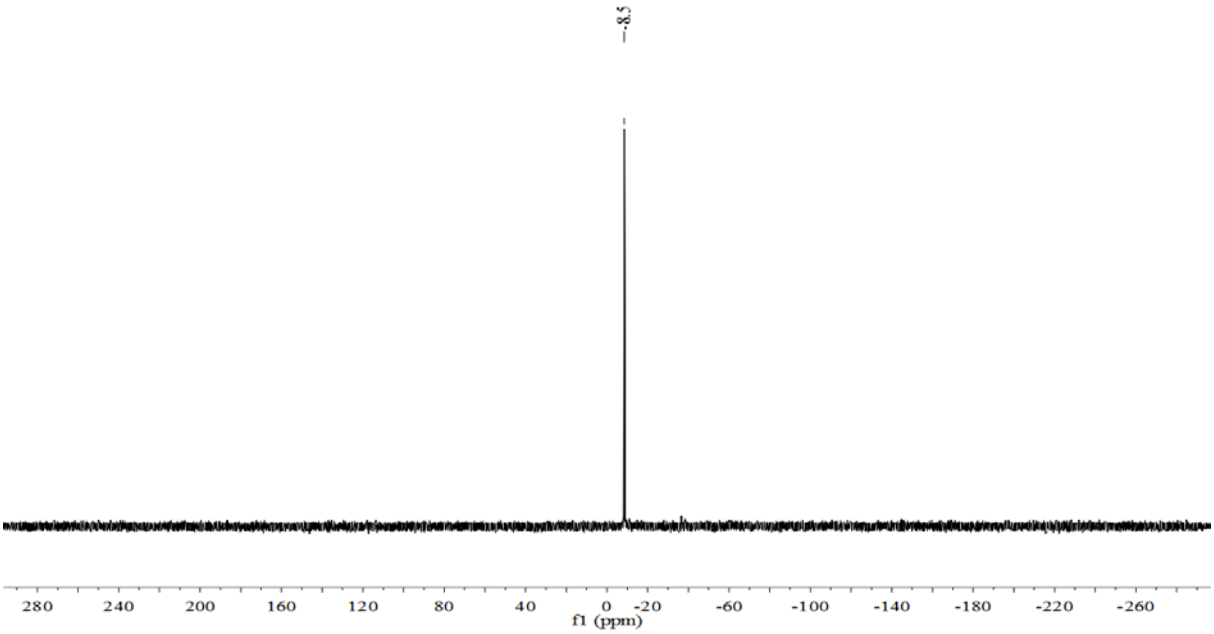


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **2cb** in CD_2Cl_2.

Preparation of 3aa – 3cb: Compound class **2** (0.1 mmol) in toluene (5 mL) was stirred for several hours at elevated temperature. The solvent was removed under reduced pressure, then the remaining solid was washed with hexane and dried *in vacuo* to afford **3aa – 3cb** as orange - yellow powder.

3aa: The decarbonylation reaction was completed after stirring for 12 hours at 90 °C. 69.3 mg, 0.09 mmol, 90 % yield. Crystals of **3aa** were obtained via slow evaporation of solvent from a hexane and diethyl ether solution. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.65 (m, 6 H, $C_{ar}H$), 7.07 (m, 9 H, $C_{ar}H$), 6.88 (m, 6 H, $C_{ar}H$), 6.20 (s, 2 H, NC*H*), 3.09 (m, 4 H, C*H*Me_2), 1.31 (d, *J* = 6.4 Hz, 12 H, CH_3), 1.04 (d, *J* = 7.2 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6,, 100.5 MHz): δ = 174.8 (d, $^{1}J_{PC}$ = 129.6 Hz, *PC*), 145.8 (C_{ar}), 143.7 (d, $^{3}J_{PC}$ = 7.0 Hz, P*C* C_{ar}), 137.5 (C_{ar}), 137.2 (t, $^{1}J_{CSn}$ = 18.1 Hz, Sn*C*), 134.4 (C_{ar}), 130.2 (C_{ar}), 127.6 (C_{ar}), 124.7 (C_{ar}), 120.9 (NCH), 28.9 (CH_3), 24.9 (CH_3), 22.8 (*C*HMe_2); $^{31}P\{^{1}H\}$ NMR (C_6D_6,, 161.9 MHz) δ = –161.5 (t, $J_{P\text{-}Sn}$ = 705.7 Hz). M. P. = 153 °C. Elemental analysis (%): calcd for $C_{45}H_{51}N_2PSn$; C 70.23, H 6.68, N 3.64; found: C 69.40, H 6.77, N 2.97. IR (solid): 3060, 2964, 2928, 2866, 1464, 1428, 1312, 1120, 1070, 803, 728, 700 cm^{-1}.

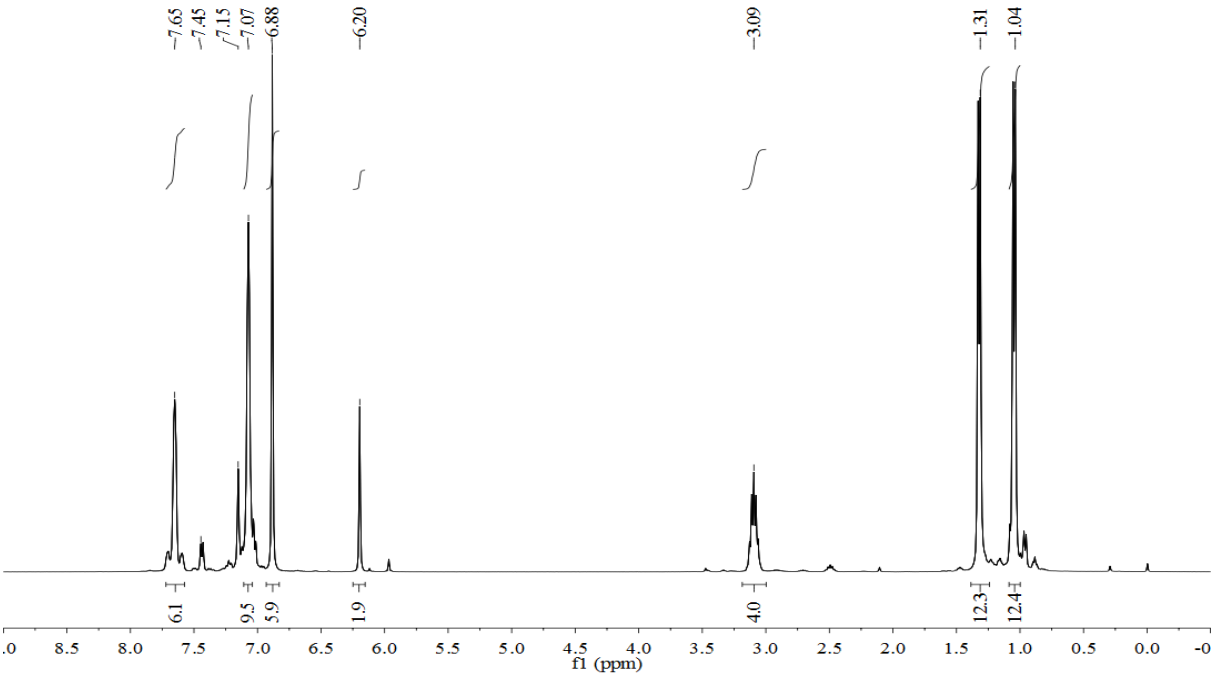


Figure S13. ^{1}H NMR spectrum of **3aa** in C_6D_6.

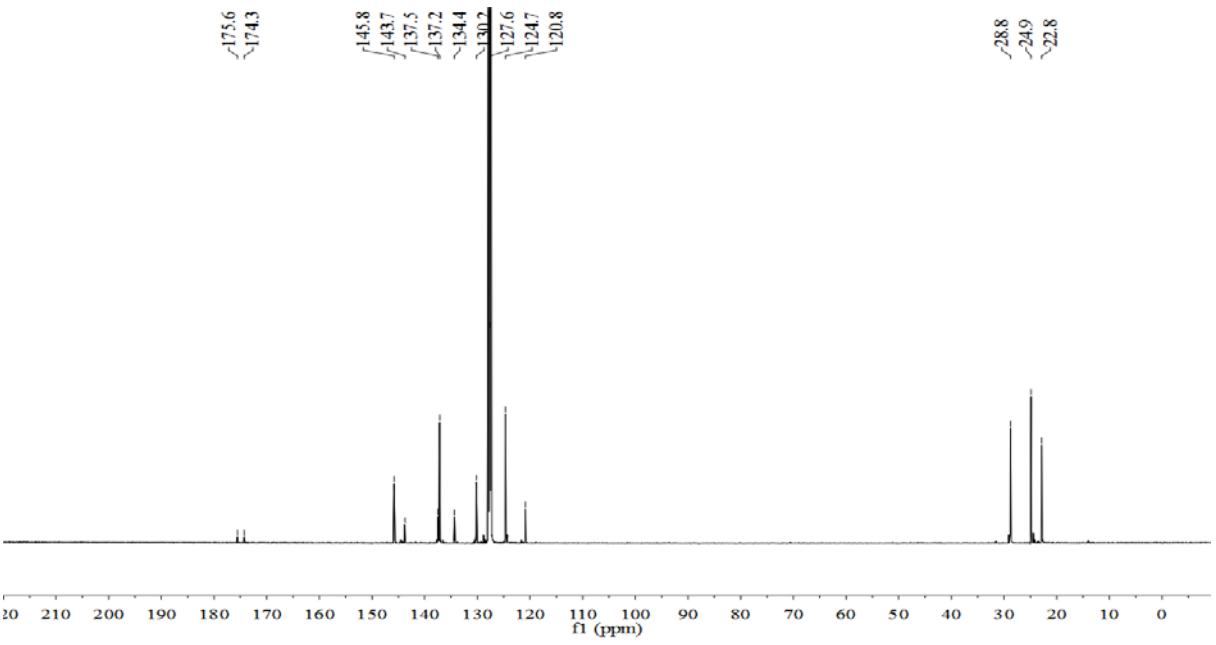


Figure S14. ^{13}C{^{1}H} NMR spectrum of **3aa** in C_6D_6.

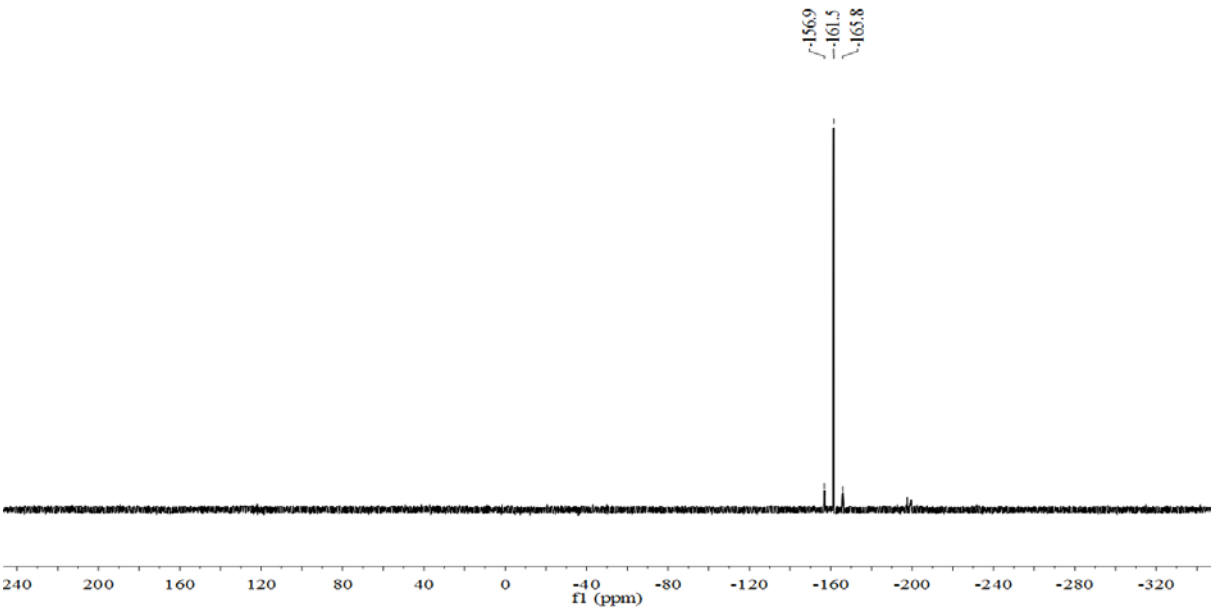


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **3aa** in C_6D_6.

3ba: The decarbonylation reaction was completed after stirring for 16 hours at 90 °C. 64.5 mg, 0.094 mmol, 94 % yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.49 (m, 6 H, $C_{ar}H$), 7.26 (m, 9 H, $C_{ar}H$), 6.72 (m, 6 H, $C_{ar}H$), 6.66 (s, 2 H, NC*H*), 2.24 (s, 6 H, CH_3), 2.01 (s, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 169.4 (d, $^{1}J_{PC}$ = 123.6 Hz, *PC*), 145.8 (C_{ar}), 144.5 (d, $^{3}J_{PC}$ = 8.0 Hz, P*C* C_{ar}), 139.0 (C_{ar}), 136.6 (t, $^{1}J_{CSn}$ = 16.1 Hz, Sn*C*), 135.8 (C_{ar}), 133.8 (C_{ar}), 129.7 (C_{ar}), 127.6 (C_{ar}), 127.5 (C_{ar}), 119.6 (NCH), 20.9 (CH_3), 18.0 (CH_3); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = –179.5 (t, $J_{P\text{-}Sn}$ = 689.7 Hz). M. P. = 140 °C (decomposition). Elemental analysis (%): calcd for $C_{39}H_{39}N_2PSn$; C 68.34, H 5.74, N 4.09; found: C 68.78, H 5.66, N 3.94. IR (solid): 3065, 3046, 2964, 2929, 2867, 1464, 1430, 1398, 1312, 1267, 1120, 1084, 1061, 1042, 934, 803, 736, 699 cm^{-1}.

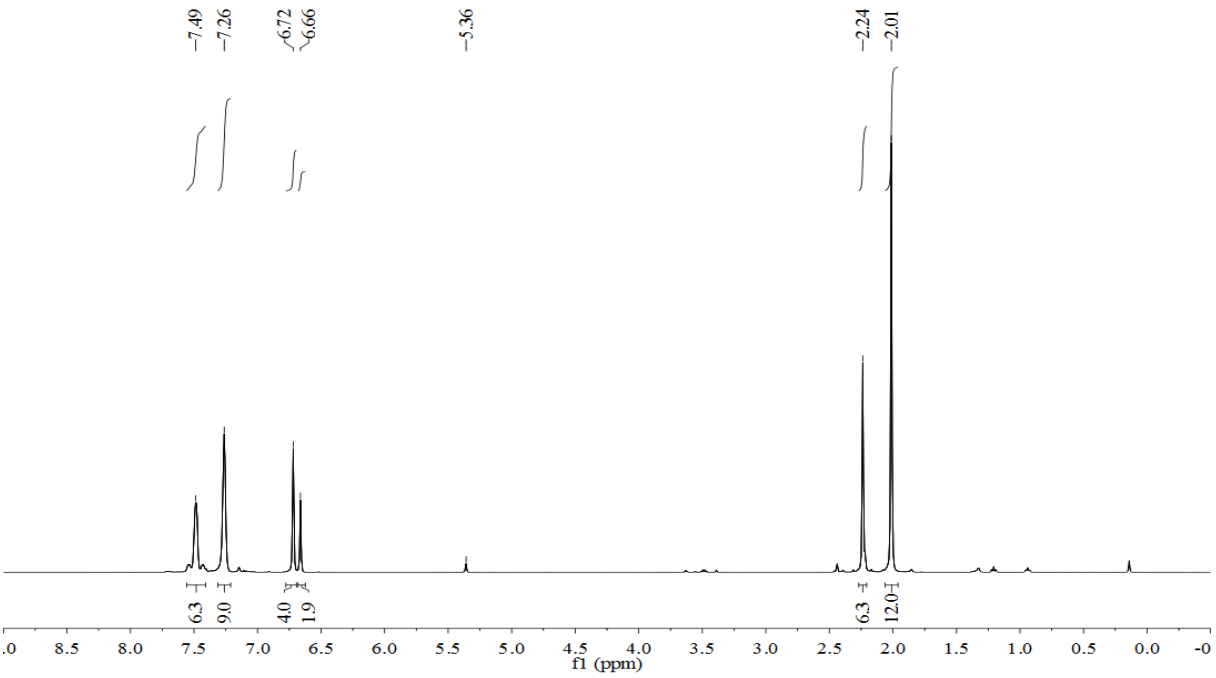


Figure S16. ^{1}H NMR spectrum of **3ba** in CD_2Cl_2.

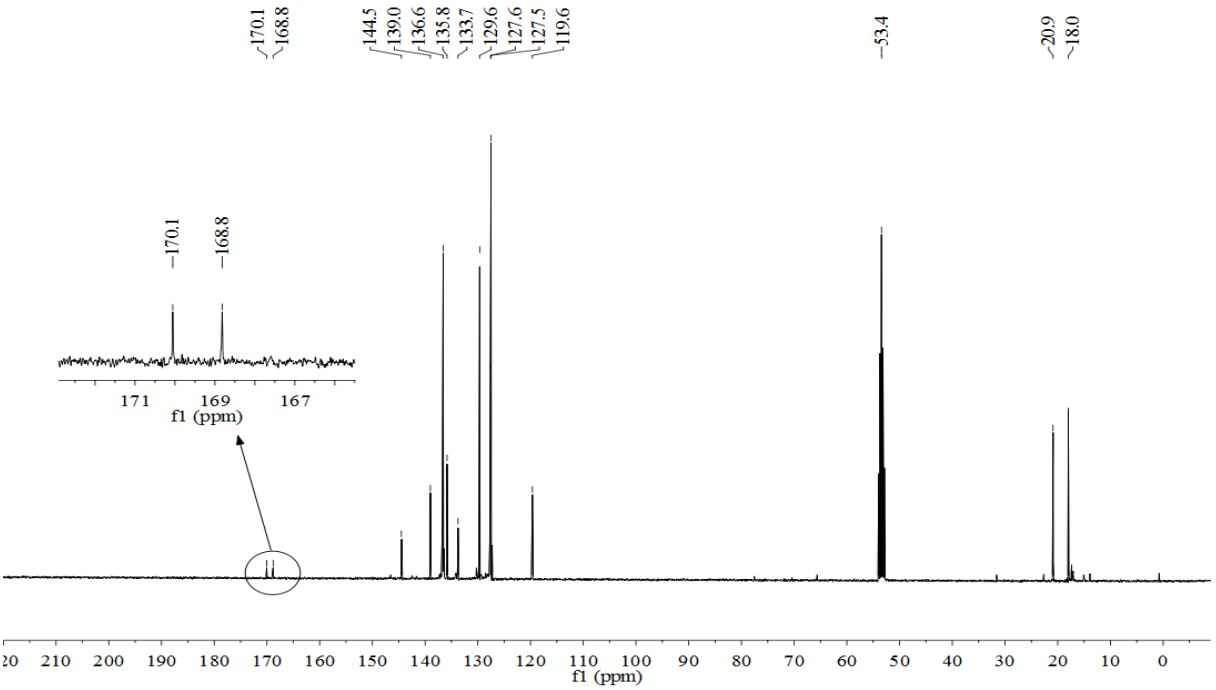


Figure S17. ^{13}C{^{1}H} NMR spectrum of **3ba** in CD_2Cl_2.

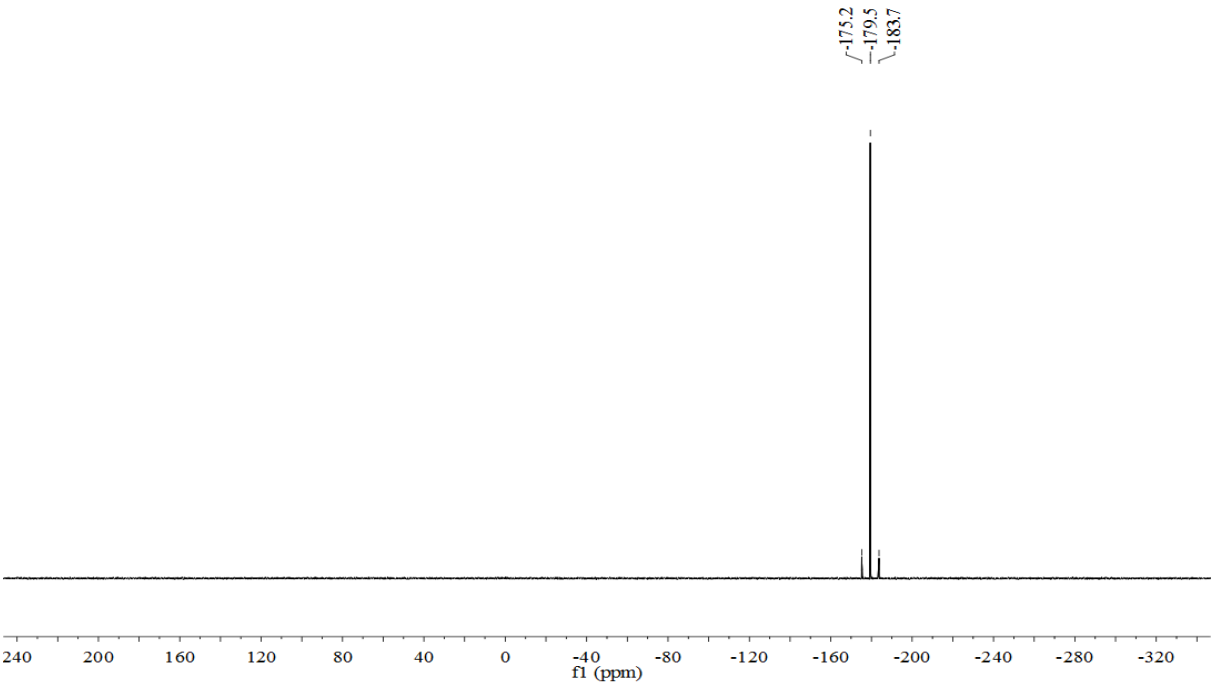


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **3ba** in CD_2Cl_2.

3ab: The decarbonylation reaction was completed after stirring for 12 hours at 90 °C. 63.7 mg, 0.088 mmol, 88 % yield. Crystals of **3ab** were obtained via slow evaporation of solvent from a hexane and diethyl ether solution. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.63 (m, 6 H, $C_{ar}H$), 7.04 (m, 9 H, $C_{ar}H$), 6.87 (m, 6 H, $C_{ar}H$), 6.23 (s, 2 H, NC*H*), 3.14 (m, 4 H, C*H*Me_2), 1.25 (d, *J* = 6.4 Hz, 12 H, CH_3), 1.03 (d, *J* = 6.8 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.5 MHz): δ = 174.4 (d, $^{1}J_{PC}$ = 124.6 Hz, *PC*), 145.8 (C_{ar}), 142.4 (d, $^{3}J_{PC}$ = 9.0 Hz, P*C* C_{ar}), 135.2 (C_{ar}), 134.5, 130.3 (C_{ar}), 127.3 (C_{ar}), 124.5 (C_{ar}), 121.3 (d, $^{3}J_{PC}$ = 4.0 Hz, P*C* NCH), 28.8 (CH_3), 25.2 (CH_3), 22.6 (*C*HMe_2); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz) δ = –145.1. M. P. = 140 °C (decomposition). Elemental analysis (%): calcd for $C_{45}H_{51}N_2PGe$; C 74.70, H 7.10, N 3.87; found: C 75.28, H 7.73, N 3.50. IR (solid): 3064, 2964, 2929, 2866, 1466, 1430, 1397, 1313, 1297, 1118, 1085, 933, 800, 737, 699 cm^{-1}.

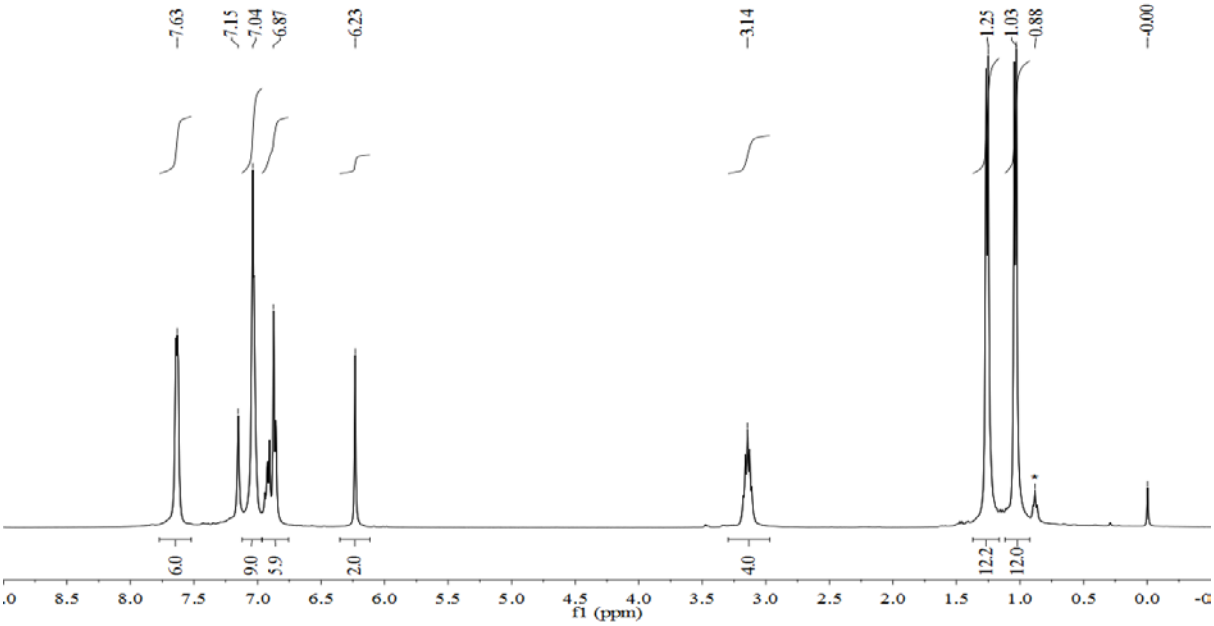


Figure S19. ^{1}H NMR spectrum of **3ab** in C_6D_6. *Hexane.

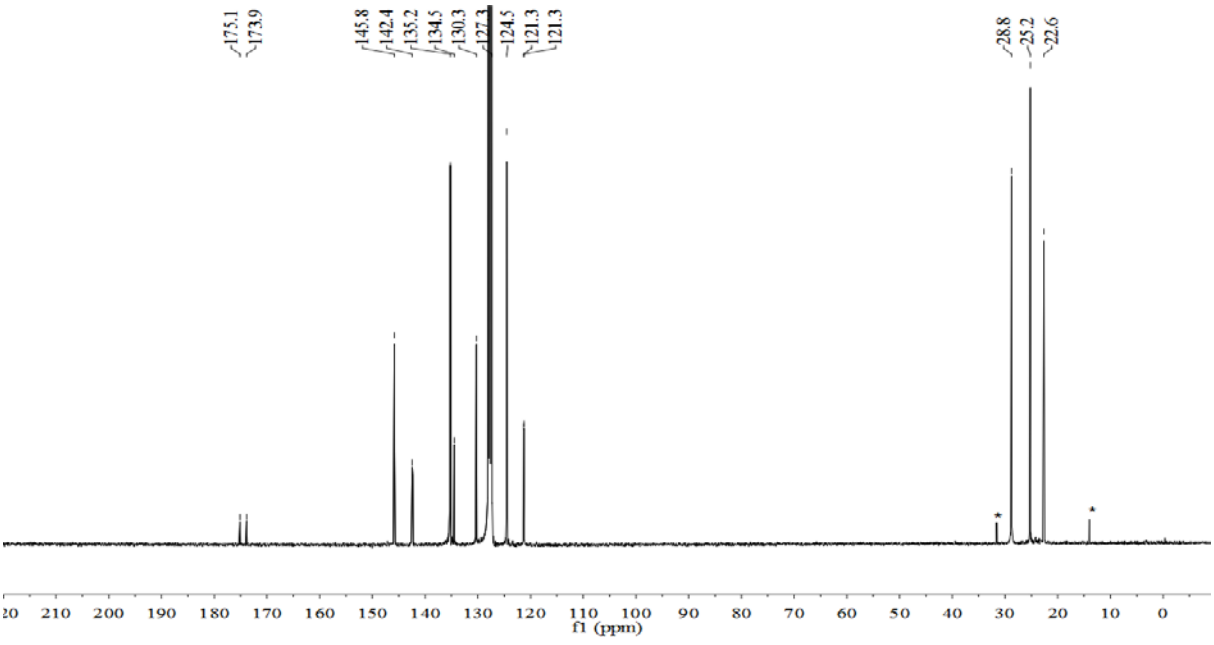


Figure S20. ^{13}C{^{1}H} NMR spectrum of **3ab** in C_6D_6. *Hexane.

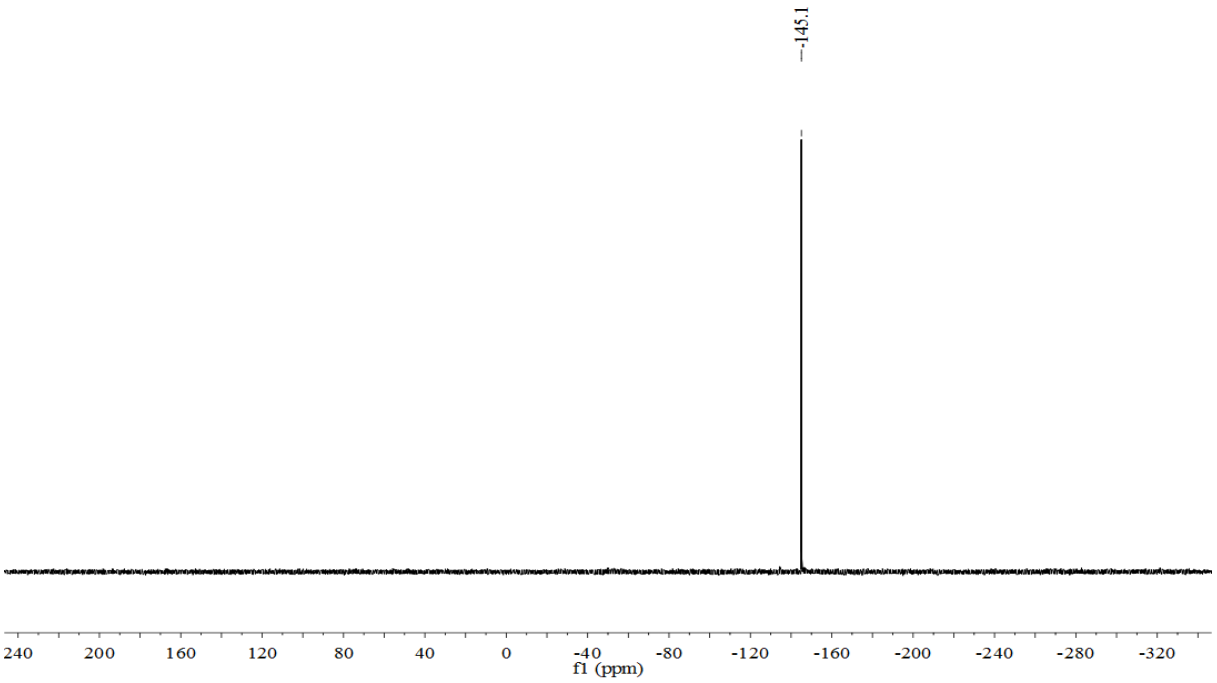


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **3ab** in C_6D_6.

3bb: The decarbonylation reaction was completed after stirring for 80 hours at 90 °C. 58.7 mg, 0.092 mmol, 92 % yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.52 (m, 6 H, $C_{ar}H$), 7.24 (m, 9 H, $C_{ar}H$), 6.70 (m, 4 H, $C_{ar}H$), 6.64 (s, 2 H, NC*H*), 1.23 (s, 6 H, CH_3), 2.01 (s, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 168.7 (d, $^{1}J_{PC}$ = 119.6 Hz, *PC*), 142.7 (d, $^{3}J_{PC}$ = 10.1 Hz, P*C* C_{ar}), 142.6 (C_{ar}), 138.8 (C_{ar}), 135.8 (C_{ar}), 134.7 (C_{ar}), 134.0 (C_{ar}), 133.8 (C_{ar}), 129.3 (C_{ar}), 127.4 (C_{ar}), 127.2 (C_{ar}), 120.0 (d, $^{3}J_{PC}$ = 3.0 Hz, P*C* NCH), 20.8 (CH_3), 18.0 (CH_3); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = –155.2. M. P. = 75 °C. Elemental analysis (%): calcd for $C_{39}H_{39}N_2PGe$; C 73.26, H 6.15, N 4.38; found: C 74.78, H 6.92, N 4.06. IR (solid): 3066, 3047, 2974, 2931, 1457, 1433, 1397, 1315, 1296, 1122, 1085, 936, 804, 737, 700 cm^{-1}.

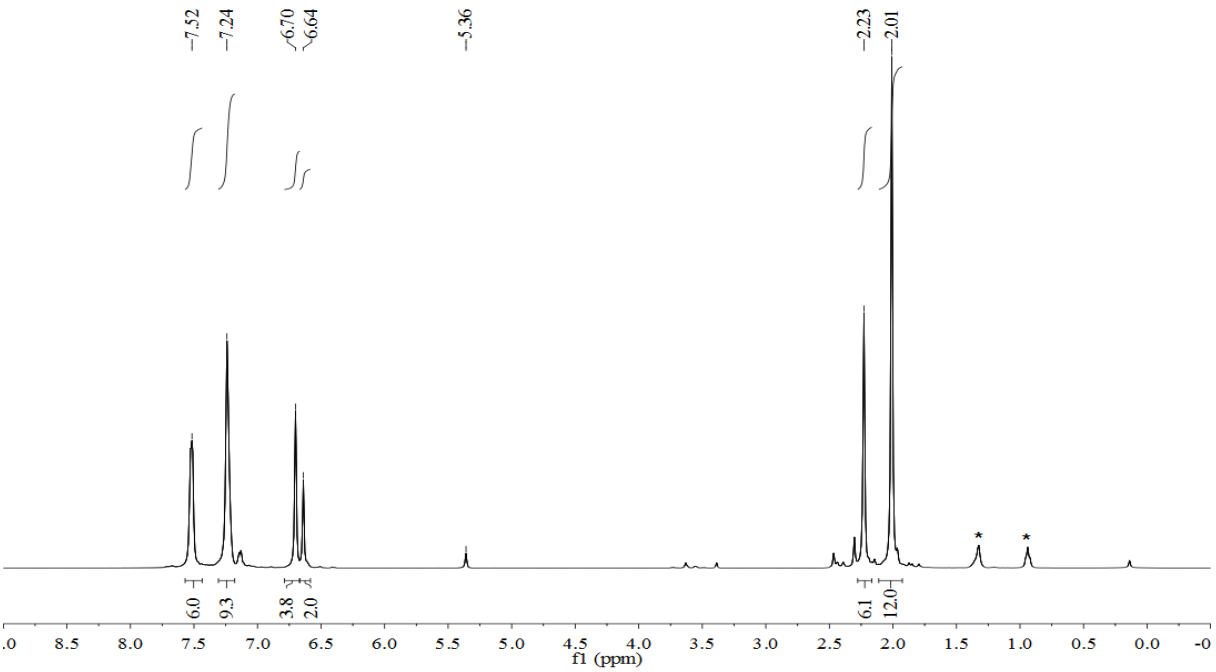


Figure S22. ^{1}H NMR spectrum of **3bb** in CD_2Cl_2. *Hexane.

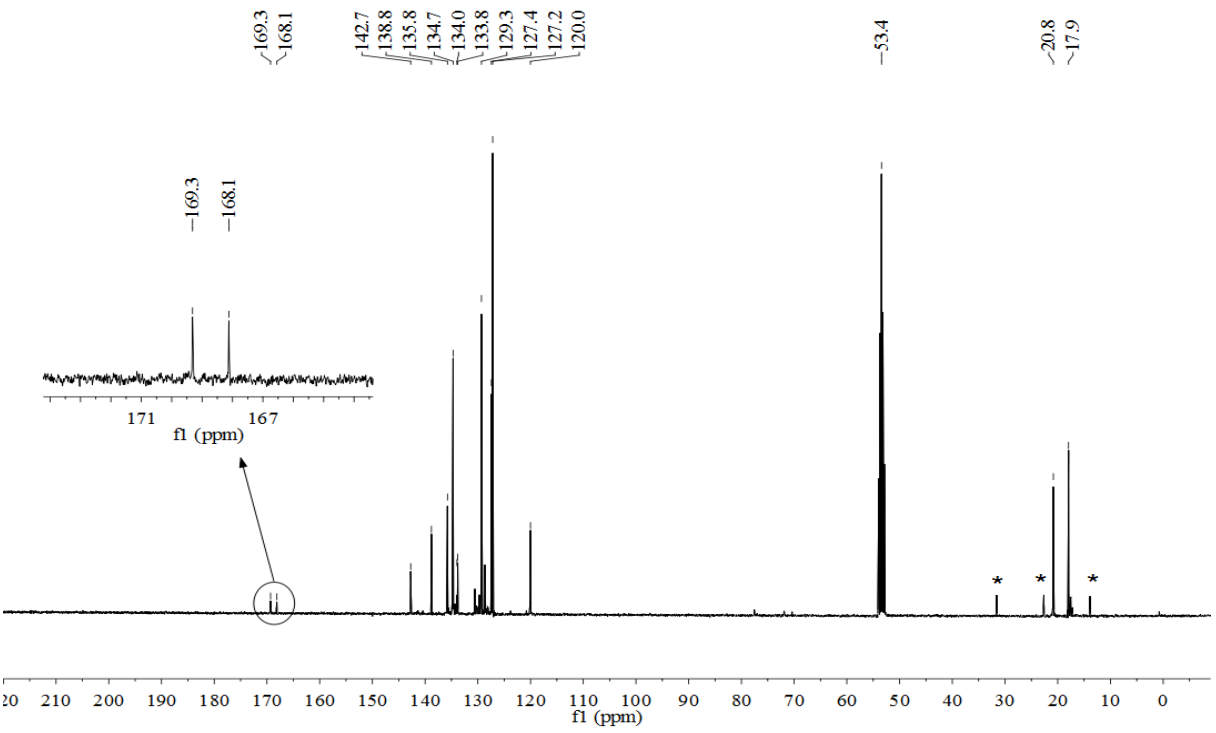


Figure S23. ^{13}C{^{1}H} NMR spectrum of **3bb** in CD_2Cl_2. *Hexane.

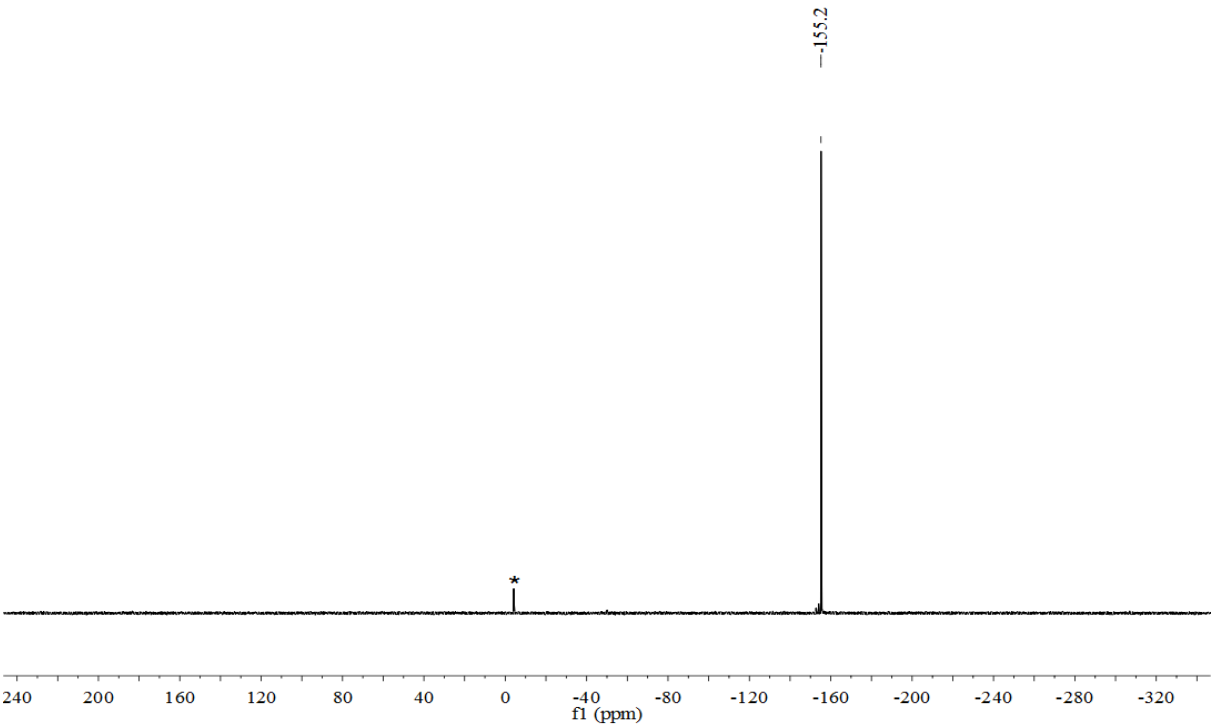


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **3bb** in CD_2Cl_2. *Small impurity.

3ca: The decarbonylation reaction was completed after stirring for 48 hours at 90 °C. 72.5 mg, 0.094 mmol, 94 % yield. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.62 (m, 6 H, $C_{ar}H$), 7.08 (m, 10 H, $C_{ar}H$), 6.85 (m, 5 H, $C_{ar}H$), 3.48 (s, 4 H, NCH_2), 3.39 (m, 4 H, $CHMe_2$), 1.38 (d, J = 6.8 Hz, 12 H, CH_3), 1.15 (d, J = 6.8 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100.5 MHz): δ = 193.1 (d, $^{1}J_{PC}$ = 112.5 Hz, *PC*), 146.6 (C_{ar}), 143.2 (d, $^{3}J_{PC}$ = 6.5 Hz, PCN*C* C_{ar}), 136.6 (t, $^{1}J_{CSn}$ = 18.0 Hz, Sn*C*), 136.2 (C_{ar}), 129.2 (C_{ar}),127.6 (C_{ar}), 125.0 (C_{ar}), 52.4 (NCH_2), 28.7 (CH_3), 25.5 (CH_3), 23.6 ($CHMe_2$); $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz) δ = –124.6 (t, $J_{P\text{-}Sn}$ = 708.5 Hz). M. P. = 101 °C. Elemental analysis (%): calcd for $C_{45}H_{53}N_2PSn$; C 70.05, H 6.92, N 3.63; found: C 68.60, H 6.87, N 3.23. IR (solid): 3070, 2967, 2930, 2869, 1545, 1456, 1430, 1403, 1384, 1325, 1256, 1191, 1092, 1057, 1000, 938, 802, 729, 700, 655 cm^{-1}.

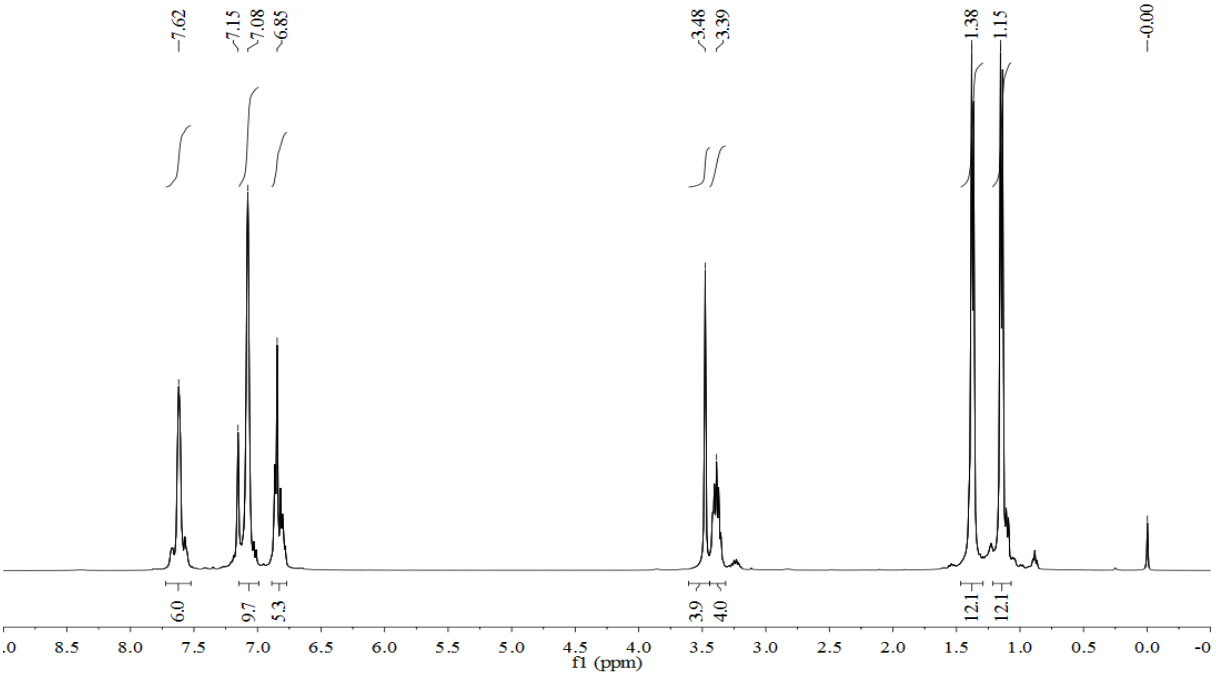


Figure S25. ^{1}H NMR spectrum of **3ca** in C_6D_6.

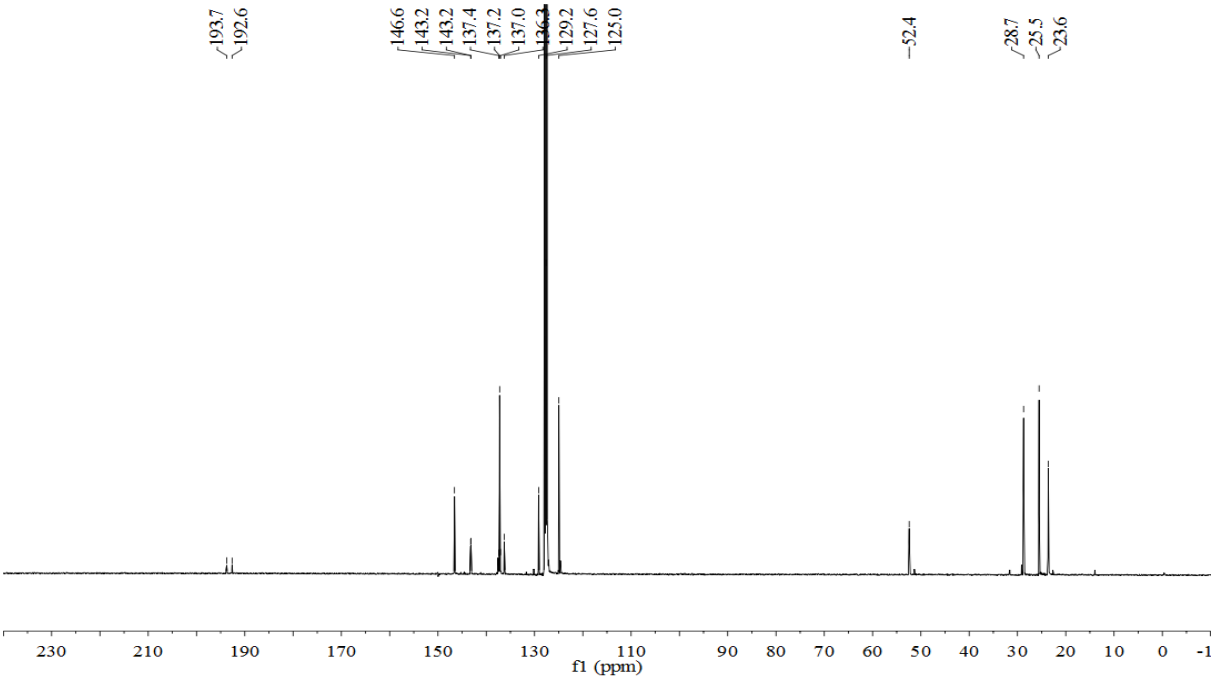


Figure S26. ^{13}C{^{1}H} NMR spectrum of **3ca** in C_6D_6.

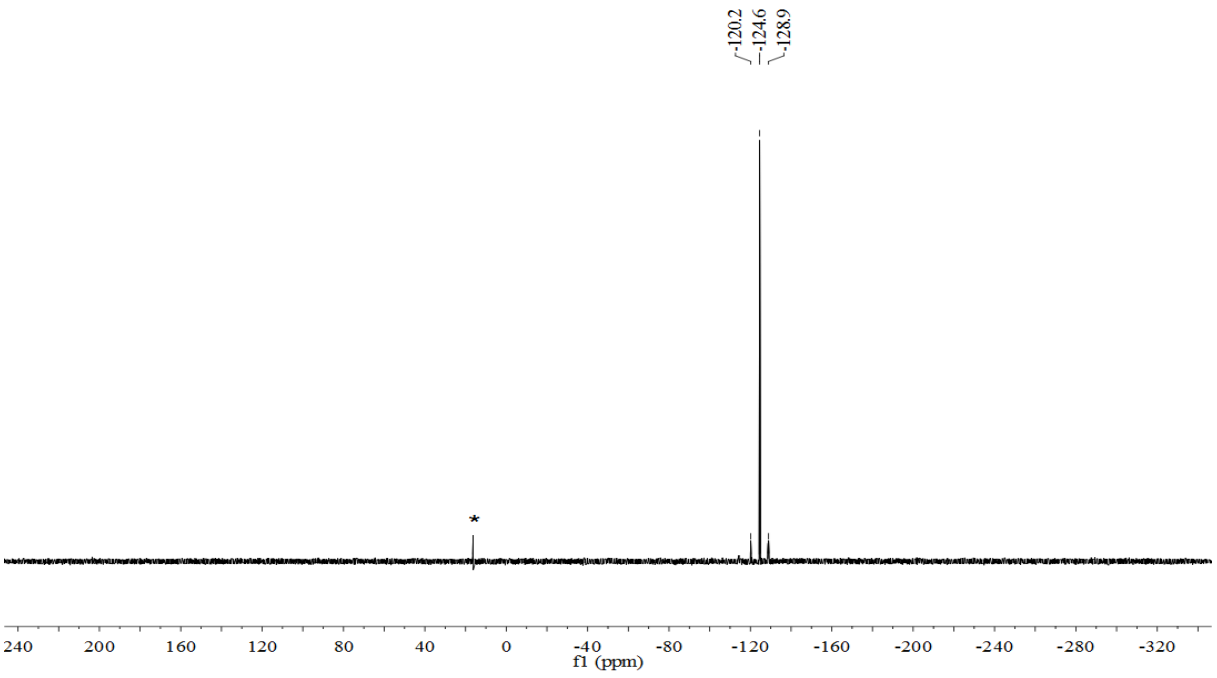


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **3ca** in C_6D_6. *Small impurity

3cb: The decarbonylation reaction was completed after stirring for 192 hours at 106 °C. 65.9 mg, 0.091 mmol, 91 % yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.33 (d, *J* = 6.8 Hz, 6 H, $C_{ar}H$), 7.20 (m, 9 H, $C_{ar}H$), 6.98 (m, 6 H, $C_{ar}H$), 3.99 (s, 4 H, NCH_2), 3.37 (m, 4 H, $CHMe_2$), 1.23 (m, 24 H, CH_3); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 192.5 (d, $^{1}J_{PC}$ = 105.4 Hz, *PC*), 146.6 (C_{ar}), 141.1 (d, $^{3}J_{PC}$ = 9.3 Hz, PCN*C* C_{ar}), 135.0 (C_{ar}), 129.0 (C_{ar}), 127.6 (C_{ar}), 127.3 (C_{ar}), 124.7 (C_{ar}), 52.9 (NCH_2), 28.8 (CH_3), 25.8 (CH_3), 23.0 ($CHMe_2$); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = –114.7 (s). M. P. = 120 °C. Elemental analysis (%): calcd for $C_{45}H_{53}N_2PGe$; C 74.49, H 7.36, N 3.86; found: C 74.84, H 7.53, N 3.69. IR (solid): 3064, 3021, 2961, 2927, 2866, 1584, 1481, 1430, 1362, 1253, 1188, 1085, 1056, 1026, 804, 734, 697, 670 cm^{-1}.

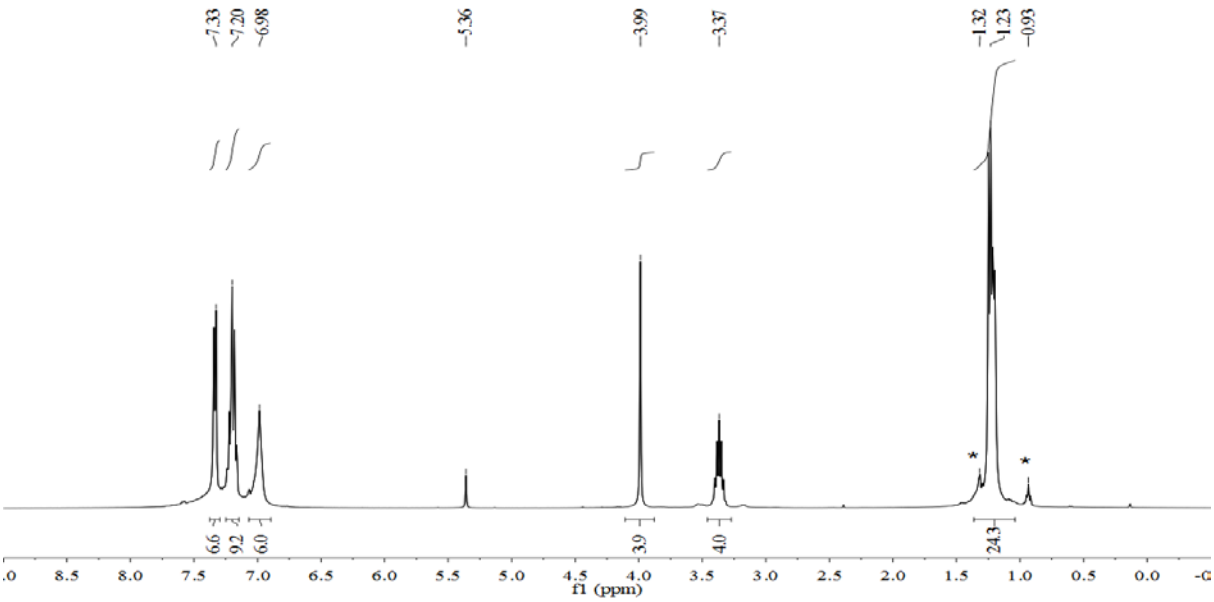


Figure S28. ^{1}H NMR spectrum of **3cb** in CD_2Cl_2. *Hexane.

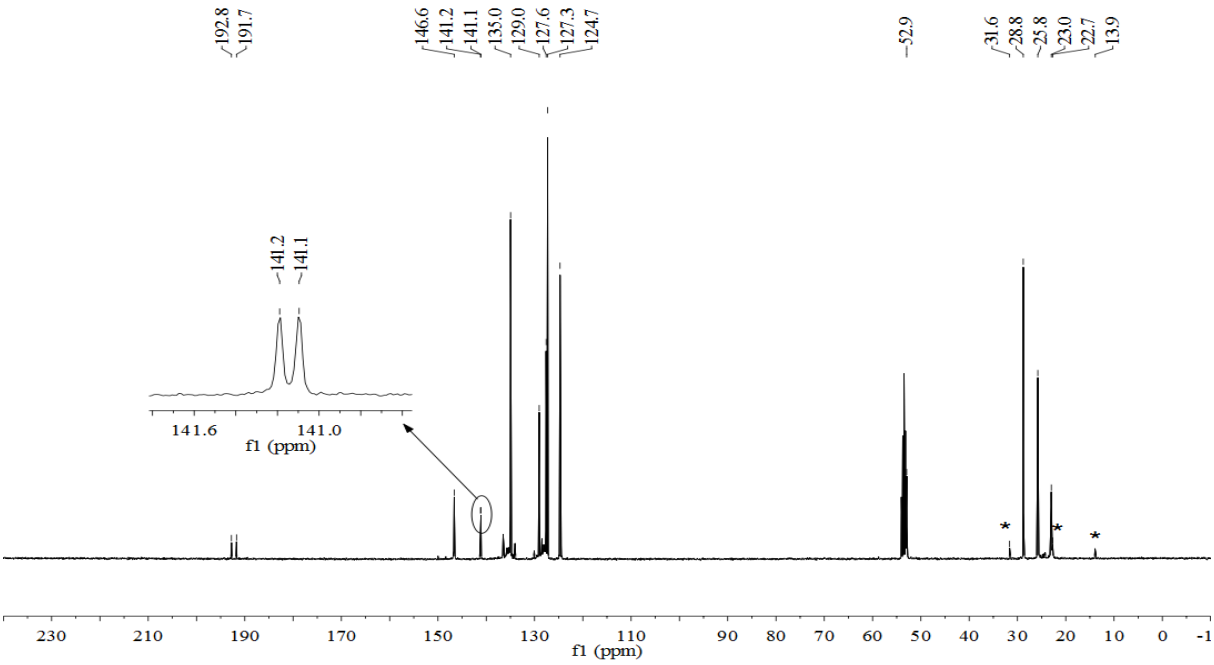


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **3cb** in CD_2Cl_2. *Hexane.

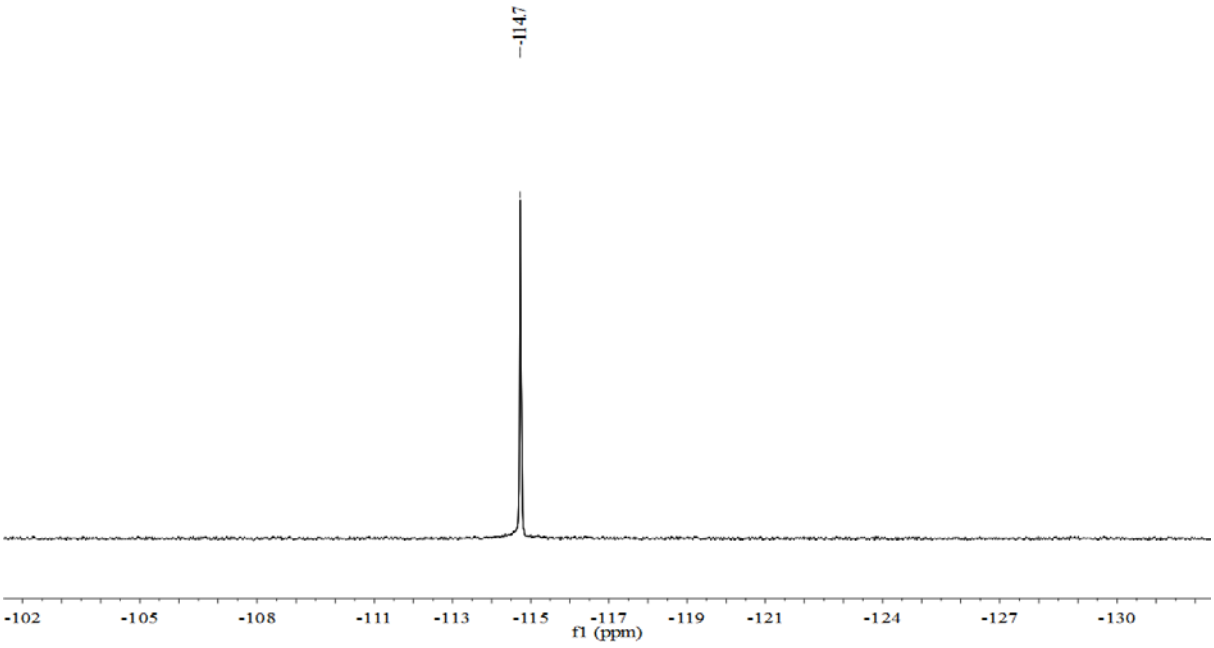


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **3cb** in CD_2Cl_2.

Preparation of 4: **IPr** (97.1 mg. 0.25 mmol) was added to a stirred solution of Sodium phosphaethynolate ([Na(OCP) • $(dioxane)_{2.5}$], 75.5 mg, 0.25 mmol) and chlorotriphenylsilane (73.7 mg, 0.25 mmol) in toluene (3 mL). After stirring for 5 mins, THF (1 ml) was added dropwise and the solution was allowed to stir for further 1 hour. Afterwards, the precipitate of sodium chloride was removed by filtration, and the the solvent was removed under reduced pressure. The remaining solid was washed with hexane and dried *in vacuo* to afford **4** as yellow powder (113.2 mg, 0.16 mmol, 64 % yield). Yellow crystals of **4** were obtained via slow evaporation of solvent from a hexane and ethyl ether solution. ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.56 (d, *J* = 7.6 Hz, 6 H, $C_{ar}H$), 7.22 (t, *J* = 7.2 Hz, 2 H, $C_{ar}H$), 7.12 (m, 13 H, $C_{ar}H$), 6.00 (s, 2 H, NC*H*), 3.12 (m, 4 H, C*H*Me_2), 1.33 (d, *J* = 6.8 Hz, 12 H, CH_3), 1.16 (d, *J* = 6.8 Hz, 12 H, CH_3); $^{13}C\{^{1}H\}$ NMR (C_6D_6,, 100.5 MHz): δ = 194.84 (d, $^{2}J_{PC}$ = 3.0 Hz, *PC*C), 147.5 (C_{ar}), 147.5 (C_{ar}),146.6 (d, $^{1}J_{PC}$ = 11.1 Hz, *PCC*), 136.1 (C_{ar}), 135.5 (C_{ar}), 133.7 (C_{ar}), 129.5 (C_{ar}), 129.2 (C_{ar}), 123.9 (C_{ar}),116.5 (NCH), 28.7 (CH_3), 24.0 (CH_3), 23.6 (*C*HMe_2); $^{31}P\{^{1}H\}$ NMR (C_6D_6,, 161.9 MHz) δ = 170.3 (s). M. P. = 93 °C. Elemental analysis (%): calcd for $C_{46}H_{51}N_2OPSi$; C 78.15, H 7.27, N 3.96; found: C 78.54, H 7.73, N 3.71. IR (solid): 3136, 3068, 2964, 2867, 1679, 1465, 1426, 1405, 1118, 895, 803, 762, 743, 700, 670 cm^{-1}.

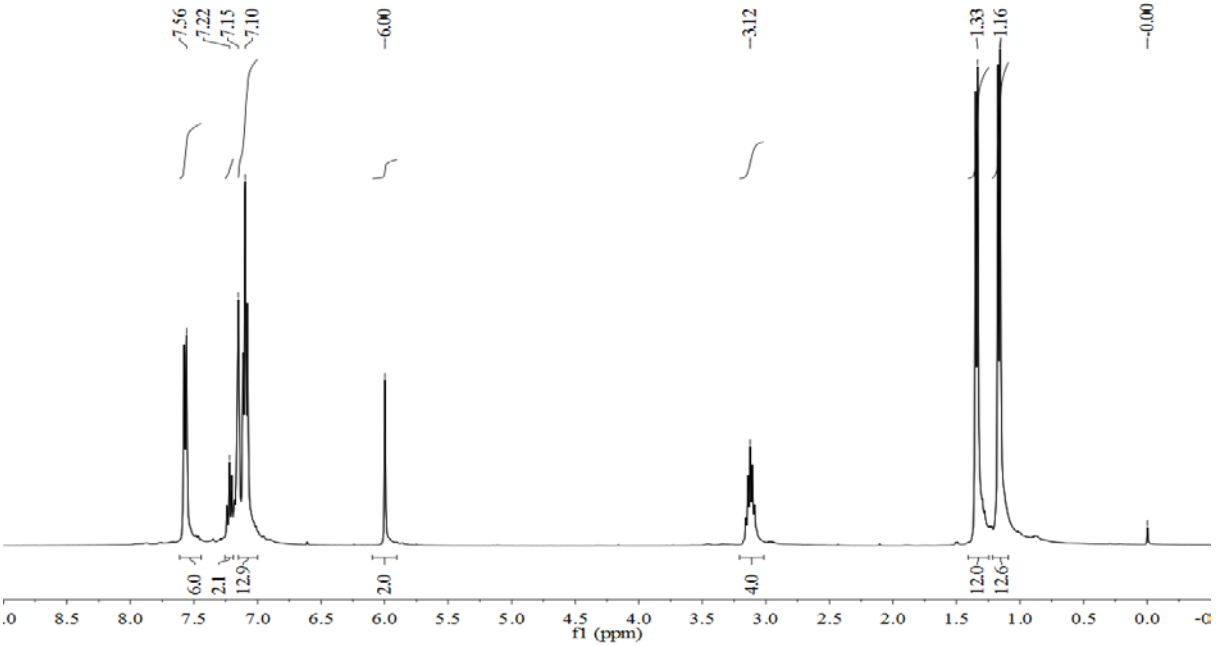


Figure S31. ^{1}H NMR spectrum of **4** in C_6D_6.

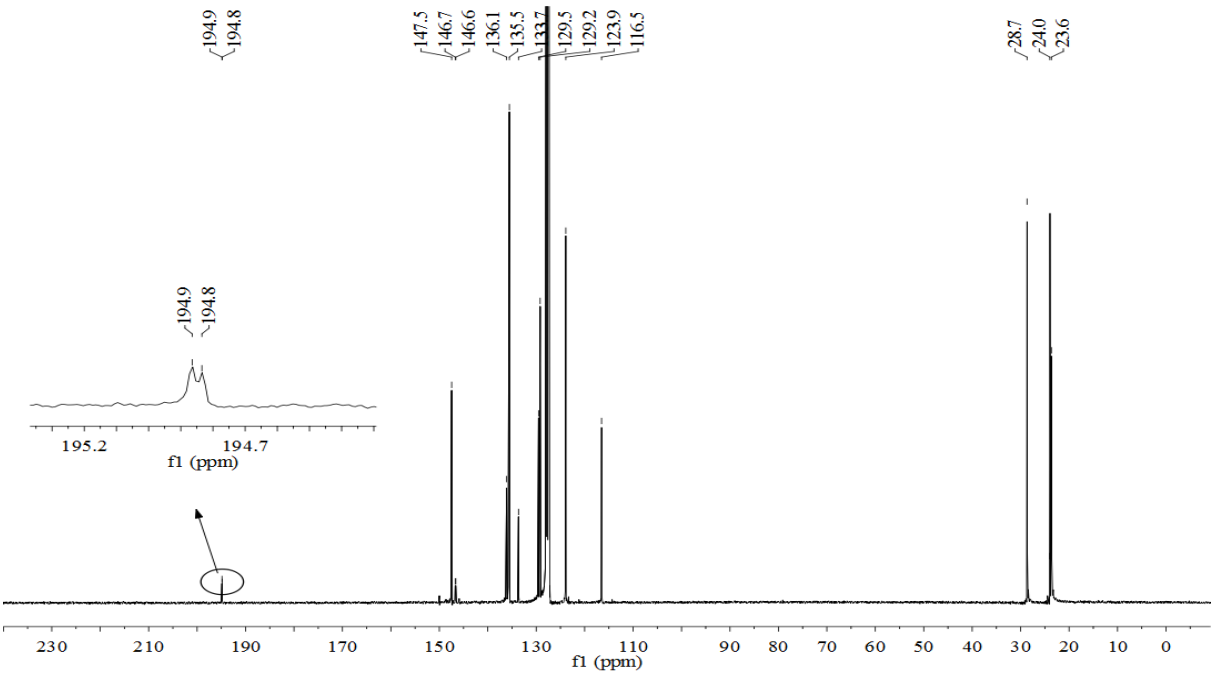


Figure S32. ^{13}C{^{1}H} NMR spectrum of **4** in C_6D_6.

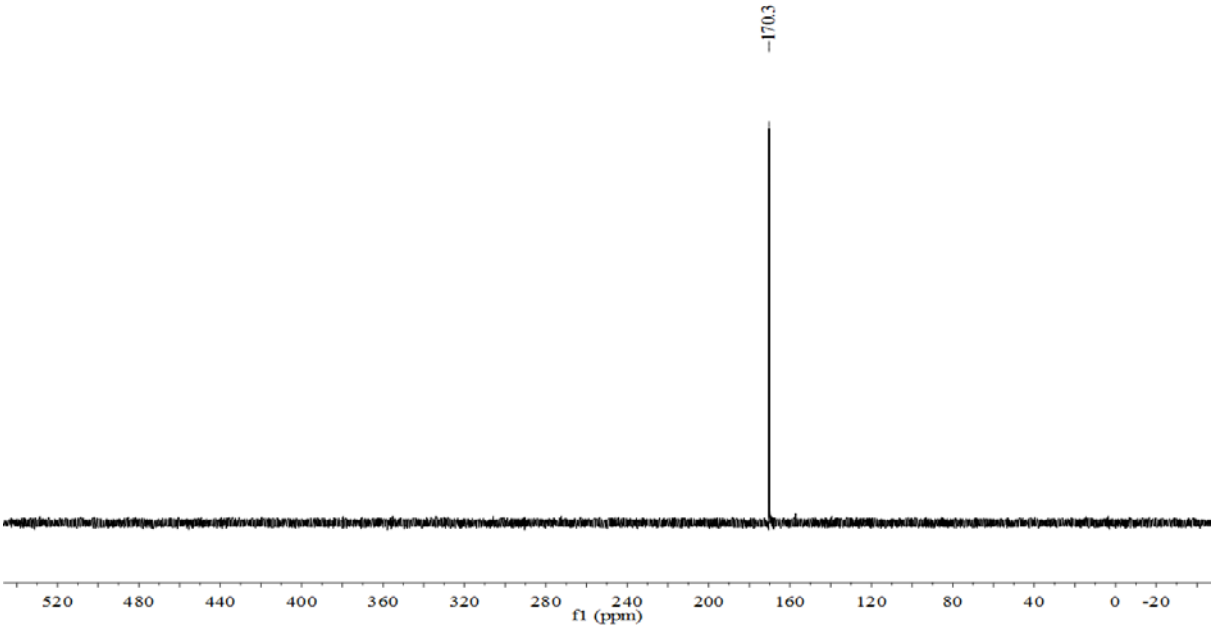


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

S2: X-Ray Diffraction Studies

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers are 1410343, 1410347–1410348, 1425914-1425916.

Table S1. Crystal data and structure refinement for **2aa**

Empirical formula	C10H10NOPSn
Formula weight	309.85
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	14.0166(3)
b/Å	19.8309(6)
c/Å	14.9450(4)
α/°	90
β/°	94.185(2)
γ/°	90
Volume/Å3	4143.07(19)
Z	17

ρcalcg/cm3	2.111
μ/mm-1	2.746
F(000)	2550.0
Crystal size/mm3	0.21 × 0.20 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.628 to 65.308
Index ranges	-21 ≤ h ≤ 21, -29 ≤ k ≤ 29, -22 ≤ l ≤ 18
Reflections collected	40641
Independent reflections	13762 [Rint = 0.0403, Rsigma = 0.0492]
Data/restraints/parameters	13762/0/664
Goodness-of-fit on F2	1.086
Final R indexes [I>=2σ (I)]	R1 = 0.0442, wR2 = 0.0798
Final R indexes [all data]	R1 = 0.0594, wR2 = 0.0853
Largest diff. peak/hole / e Å-3	1.36/-0.77

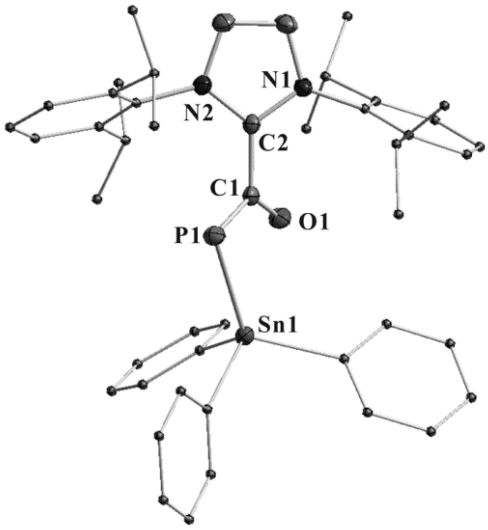


Figure S34. Molecular structure of **2aa** in the solid state (H atoms were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-Sn1 2.4761(5), P1-C1 1.747(2), C1-O1 1.259(2), C1-C2 1.502(3), C2-N1 1.345(2), C2-N2 1.345(2), Sn1-P1-C1 86.59(7), P1-C1-O1 129.63(15), P1-C1-C2 115.75(14), O1-C1-C2 114.54(16), C1-C2-N2 128.07(17), C1-C2-N1 124.85(17), N1-C2-N2 107.07(17).

Table S2. Crystal data and structure refinement for **2ab**

Empirical formula	C46H51N2OPGe
Formula weight	751.44
Temperature/K	100.01(10)

Crystal system	monoclinic
Space group	P21/n
a/Å	13.91699(11)
b/Å	19.62321(16)
c/Å	14.94628(11)
α/°	90
β/°	94.7717(7)
γ/°	90
Volume/Å3	4067.62(5)
Z	4
ρcalcg/cm3	1.227
μ/mm-1	1.661
F(000)	1584.0
Crystal size/mm3	0.16 × 0.14 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.452 to 130.738
Index ranges	-8 ≤ h ≤ 16, -22 ≤ k ≤ 22, -17 ≤ l ≤ 17
Reflections collected	20983
Independent reflections	6846 [Rint = 0.0159, Rsigma = 0.0147]
Data/restraints/parameters	6846/0/664
Goodness-of-fit on F2	1.040
Final R indexes [I>=2σ (I)]	R1 = 0.0251, wR2 = 0.0664
Final R indexes [all data]	R1 = 0.0269, wR2 = 0.0678
Largest diff. peak/hole / e Å-3	0.44/-0.33

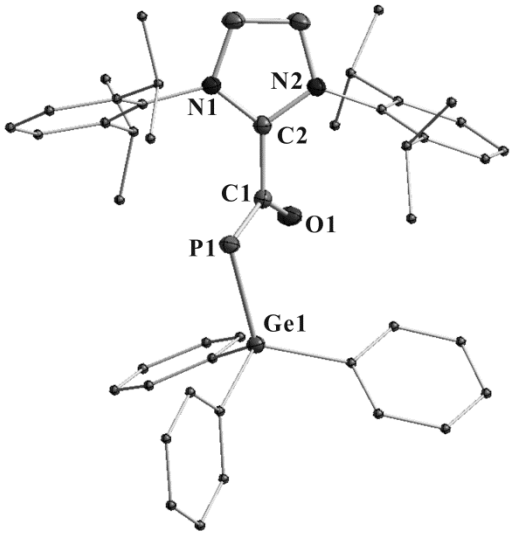


Figure S35. Molecular structure of **2ab** in the solid state (H atoms were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: P1-Ge1 2.2987(4), P1-C1 1.7486(15), C1-O1 1.2519(18), C1-C2 1.5088(19), C2-N1 1.3419(18), C2-N2

1.3444(18), Ge1-P1-C1 93.51(5), P1-C1-O1 132.11(11), P1-C1-C2 114.11(10), O1-C1-C2 113.69(12), C1-C2-N1 128.97(12), C1-C2-N2 123.56(12), N1-C2-N2 107.40(12).

Table S3. Crystal data and structure refinement for **3aa**

Empirical formula	C49H61N2OPSn
Formula weight	843.65
Temperature/K	292.34(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.64809(19)
b/Å	11.6076(2)
c/Å	19.4163(3)
α/°	91.4216(14)
β/°	92.8956(14)
γ/°	110.2887(17)
Volume/Å3	2245.77(7)
Z	2
ρcalcg/cm3	1.248
μ/mm-1	5.127
F(000)	884.0
Crystal size/mm3	0.16 × 0.15 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.13 to 130.776
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	35617
Independent reflections	7579 [Rint = 0.0229, Rsigma = 0.0161]
Data/restraints/parameters	7579/0/464
Goodness-of-fit on F2	1.034
Final R indexes [I>=2σ (I)]	R1 = 0.0341, wR2 = 0.0940
Final R indexes [all data]	R1 = 0.0352, wR2 = 0.0952
Largest diff. peak/hole / e Å-3	1.58/-1.50

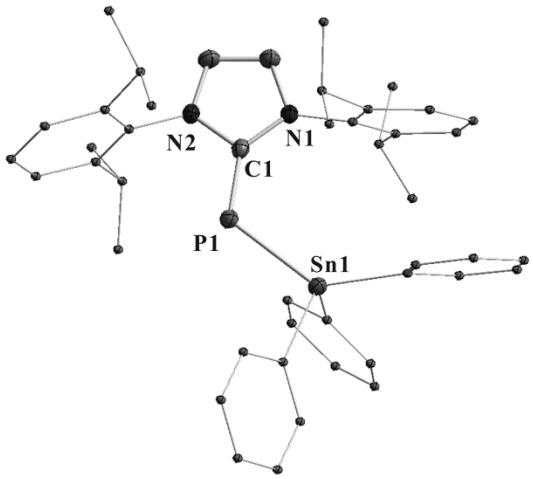


Figure S36. Molecular structure of **3aa** in the solid state (H atoms and solvent were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: Sn1-P1 2.4608(7), P1-C1 1.774(3), C1-N1 1.373(4), C1-N2 1.373(4), Sn1-P1-C1 110.99(9), P1-C1-N1 136.5(2), P1-C1-N2 119.2(2), N1-C1-N2 104.2(2).

Table S4. Crystal data and structure refinement for **3ba**

Empirical formula	C160H164N8O1.5P4Sn4
Formula weight	2821.62
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.0114(3)
b/Å	17.0048(5)
c/Å	18.7117(5)
α/°	111.389(3)
β/°	94.838(2)
γ/°	110.638(3)
Volume/Å3	3498.22(18)
Z	1
ρcalcg/cm3	1.339
μ/mm-1	0.807
F(000)	1452.0
Crystal size/mm3	0.32 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.616 to 59.962

Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 22, -25 ≤ l ≤ 26
Reflections collected	25463
Independent reflections	16210 [Rint = 0.0173, Rsigma = 0.0344]
Data/restraints/parameters	16210/0/774
Goodness-of-fit on F2	1.150
Final R indexes [I>=2σ (I)]	R1 = 0.0326, wR2 = 0.0704
Final R indexes [all data]	R1 = 0.0425, wR2 = 0.0761
Largest diff. peak/hole / e Å-3	1.23/-0.84

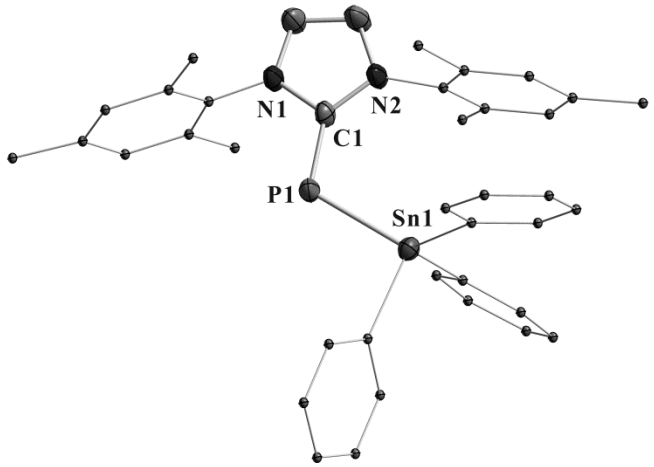


Figure S37.Molecular structure of **3ba** in the solid state (H atoms and solvent were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: Sn1-P1 2.4518(7), P1-C1 1.778(3), C1-N1 1.378(3), C1-N2 1.383(4), Sn1-P1-C1 111.51(9), P1-C1-N1 117.67(18), P1-C1-N2 138.1(2), N1-C1-N2 104.3(2).

Table S5. Crystal data and structure refinement for **3ab**

Empirical formula	C45H51N2PGe
Formula weight	723.43
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	24.06280(20)
b/Å	12.81520(9)
c/Å	25.4632(2)
α/°	90
β/°	94.7933(7)
γ/°	90

Volume/Å3	7824.60(11)
Z	8
ρcalcg/cm3	1.228
μ/mm-1	1.686
F(000)	3056.0
Crystal size/mm3	0.2 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.374 to 130.81
Index ranges	-28 ≤ h ≤ 25, -14 ≤ k ≤ 14, -21 ≤ l ≤ 29
Reflections collected	42736
Independent reflections	13144 [Rint = 0.0199, Rsigma = 0.0179]
Data/restraints/parameters	13144/0/899
Goodness-of-fit on F2	1.008
Final R indexes [I>=2σ (I)]	R1 = 0.0275, wR2 = 0.0729
Final R indexes [all data]	R1 = 0.0328, wR2 = 0.0770
Largest diff. peak/hole / e Å-3	0.27/-0.38

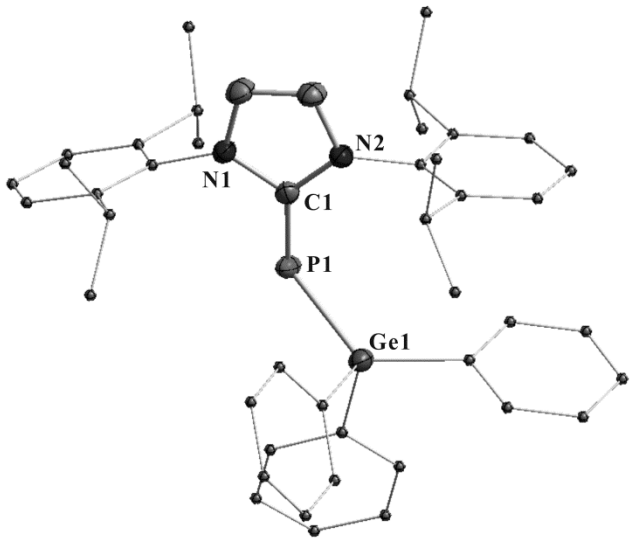


Figure S38. Molecular structure of **3ab** in the solid state (H atoms were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: Ge1-P1 2.2837(4), P1-C1 1.7748(16), C1-N1 1.3833(19), C1-N2 1.384(2), Ge1-P1-C1 110.07(5), P1-C1-N1 121.41(11), P1-C1-N2 133.94(12).

Table S6. Crystal data and structure refinement for **4.**

Empirical formula	C46H51N2OSiP
Formula weight	706.95
Temperature/K	150.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.4352(3)
b/Å	12.6209(7)
c/Å	17.8147(8)
α/°	85.360(4)
β/°	78.369(3)
γ/°	76.089(3)
Volume/Å3	2015.71(16)
Z	2
ρcalcg/cm3	1.165
μ/mm-1	1.158
F(000)	756.0
Crystal size/mm3	0.12 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.22 to 130.742
Index ranges	-5 ≤ h ≤ 11, -14 ≤ k ≤ 14, -20 ≤ l ≤ 21
Reflections collected	10387
Independent reflections	6580 [Rint = 0.0622, Rsigma = 0.0395]
Data/restraints/parameters	6580/0/468
Goodness-of-fit on F2	1.027
Final R indexes [I>=2σ (I)]	R1 = 0.0510, wR2 = 0.1406
Final R indexes [all data]	R1 = 0.0534, wR2 = 0.1445
Largest diff. peak/hole / e Å-3	0.28/-0.49

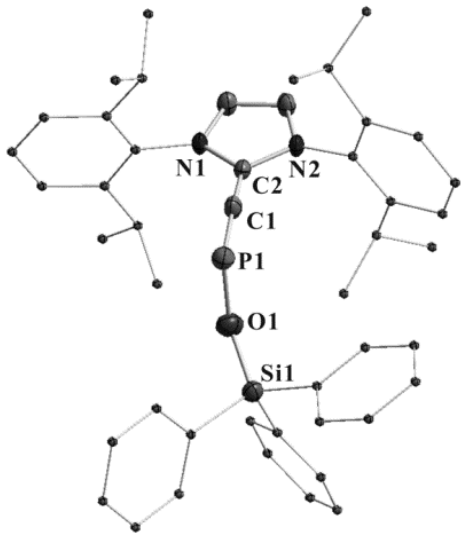
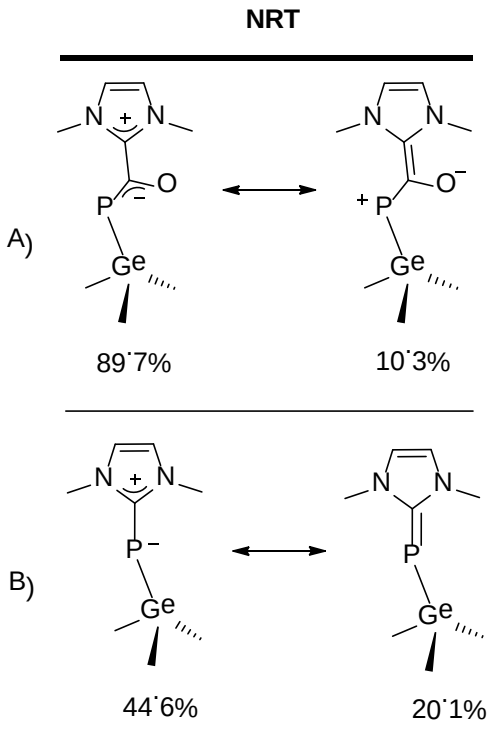


Figure S39. Molecular structure of **4** in the solid state (H atoms were omitted for clarity; 50% probability thermal ellipsoids). Selected distances [Å] and angles [°]: Si1-O1 1.6347(13), P1-

O1 1.6778(14), P1-C1 1.5832(18), C1-C2 1.355(2), C2-N1 1.379(2), C2-N2 1.384(2), Si1-O1-P1 134.51(9), O1-P1-C1 108.44(8), P1-C1-C2 172.67(16), C1-C2-N1 127.57(14), C1-C2-N2 127.77(14), N1-C2-N2 104.57(13).

S3: Theoretical Details

All calculations were carried out using the Gaussian 09 quantum mechanical package.[4] Geometry optimizations of the model compound in which the phenyl groups were replaced by methyl groups were carried out using density functional theory (DFT) at the B3LYP/6–31+G(d,p) level of theory. At each of the optimized structures vibrational analysis was performed to ensure that the geometry corresponds to an energy minimum. For transition states first order saddle points were located with one imaginary vibration frequency, which indicates the movement of the atoms corresponding to the expected transformations along the reaction coordinates. For NBO analysis the NBO 6.0 program was used. [5]



Scheme S1. Main resonance structures (NRT) of NHC-phosphaketene adduct (A) and NHC-phosphanide adduct (B).

^{Me}IPr, E = –304.820213236, ZPE = 0.126496

C	0.00004500	-0.98288400	0.00021800
N	1.06520000	-0.12210700	0.00039300
N	-1.06522700	-0.12205900	0.00008700
C	-0.67967600	1.21490900	-0.00017200
C	0.67958400	1.21491600	0.00003500
H	1.38252900	2.03446300	0.00002100
H	-1.38255100	2.03451800	0.00016900
C	-2.44911400	-0.57207100	-0.00014100
H	-2.44131400	-1.66183900	0.00060000
H	-2.97423300	-0.21282400	0.89127600
H	-2.97353900	-0.21399400	-0.89242400
C	2.44916700	-0.57200900	-0.00023500
H	2.97466900	-0.21215400	0.89069800
H	2.44149000	-1.66178000	0.00106200
H	2.97311300	-0.21439600	-0.89299700

$^{Me}Ph_3SiPCO$, E = –863.974948529, ZPE =0.121009

Si	-0.85435200	-0.12629000	0.00006400
P	0.93714200	1.33938300	0.00009700
O	2.87181100	-0.73984500	-0.00020200
C	2.04665800	0.08966100	-0.00004500
C	-0.84730000	-1.20263400	-1.55147100
H	-0.84876500	-0.58972500	-2.45862500
H	0.03165000	-1.85500600	-1.58694200
H	-1.73934000	-1.84138700	-1.57124100
C	-2.34463000	1.03624500	-0.00272600
H	-2.35299000	1.67779700	-0.89020800
H	-3.27217900	0.45080700	-0.00275200
H	-2.35459400	1.68022200	0.88298200
C	-0.84967900	-1.19891900	1.55417800
H	-0.85206100	-0.58392600	2.45991300
H	-1.74184000	-1.83748300	1.57436100
H	0.02913500	-1.85134000	1.59216100

Si_TS1, E = –1168.79101811, ZPE =0.248442

Si	-3.05568400	-0.04608100	-0.08240700
P	-0.90805600	-0.65650200	-0.62490900
O	-0.14077500	1.37949100	1.20154600
C	2.09879700	-0.00849600	0.06220000
N	3.02900200	0.95821600	-0.17416700
N	2.83279700	-1.15505600	0.10245900
C	-0.20365200	0.48829200	0.43008600
C	4.18587600	-0.91172500	-0.10519900
C	4.31019900	0.42964700	-0.28425000

H	5.18083100	1.03804300	-0.47613600
H	4.92873900	-1.69470700	-0.10269500
C	2.27475900	-2.47675700	0.37063600
H	1.18872900	-2.39132900	0.38245300
H	2.57192500	-3.17587400	-0.41638600
H	2.62574800	-2.84943600	1.33808300
C	2.71325000	2.37348300	-0.34276400
H	2.77494400	2.65806500	-1.39785100
H	1.70342400	2.54946600	0.02327800
H	3.41492900	2.98048200	0.23598100
C	-3.43222800	-0.32415700	1.75429000
H	-3.26992500	-1.37067700	2.03388600
H	-2.79126900	0.29741400	2.38852400
H	-4.47635900	-0.07002400	1.97744300
C	-4.14168300	-1.19747100	-1.12937200
H	-3.95951300	-2.25000900	-0.88534200
H	-5.20320000	-0.98997800	-0.94603000
H	-3.95387600	-1.06276600	-2.20033000
C	-3.42601700	1.75698600	-0.53309300
H	-3.26106900	1.93895000	-1.60047700
H	-4.47019600	2.00380800	-0.30240700
H	-2.78564800	2.44438800	0.02971800

Si_II, E = –1168.81998813, ZPE =0.251344

Si	-2.77057100	-0.00298400	-0.06499000
P	-0.75156700	-0.91134900	-0.59364700
O	0.02292500	1.15552400	1.09770300
C	1.76725100	0.00221600	0.07841900
N	2.62325900	1.03298400	-0.13312400
N	2.51673300	-1.12890200	0.09081200
C	0.28335500	0.19087900	0.33183600
C	3.84296400	-0.80510700	-0.14208100
C	3.90714400	0.54625100	-0.28439700
H	4.74653900	1.19600700	-0.47349800
H	4.61649600	-1.55536800	-0.17355500
C	2.04077200	-2.49820300	0.30523200
H	1.17552100	-2.47866400	0.96663000
H	1.73535000	-2.94405300	-0.64325100
H	2.85454400	-3.07182500	0.75368900
C	2.23575500	2.44229100	-0.26185900
H	1.62222000	2.57435600	-1.15652300
H	1.65474800	2.73287100	0.61196000
H	3.14729700	3.03447800	-0.35008900
C	-3.14874200	-0.12228200	1.79053100
H	-3.15192600	-1.16458900	2.12876300
H	-2.39262200	0.42325100	2.36323100
H	-4.13342800	0.30904100	2.01335100

C	-4.06201300	-1.02362900	-1.01813200
H	-4.03882800	-2.07776900	-0.71851300
H	-5.07310600	-0.64321100	-0.82543500
H	-3.88854400	-0.98065100	-2.09952900
C	-2.89953500	1.80907300	-0.61548000
H	-2.75934400	1.90601100	-1.69795200
H	-3.88427900	2.22338000	-0.36322300
H	-2.13420100	2.40704400	-0.11133800

Si_TS2, E = –1168.78678551, ZPE =0.251121

Si	-2.39437100	0.09311600	0.07350300
P	-0.59700100	-1.66417400	-0.57524500
O	-0.59481400	0.71128800	0.51609300
C	1.61122500	0.01282100	0.05885500
N	2.19158200	1.24463000	-0.05286800
N	2.63447800	-0.88258400	0.17795500
C	0.17911900	-0.27457800	0.05501600
C	3.84214400	-0.21359600	0.11221900
C	3.56654800	1.10940700	-0.03670500
H	4.22368600	1.95945500	-0.12623700
H	4.78399200	-0.73214000	0.18905100
C	2.51045700	-2.32915700	0.35072100
H	1.76561600	-2.54570000	1.11805300
H	2.18065400	-2.79462500	-0.58022400
H	3.48698800	-2.71322200	0.65112300
C	1.49859400	2.51399800	-0.29750000
H	1.28259400	2.62033600	-1.36469000
H	0.56370800	2.51329900	0.25979100
H	2.15300000	3.32480200	0.02691500
C	-3.00181500	1.21283500	1.50976900
H	-2.78920400	0.75034700	2.48255500
H	-2.51071500	2.19223200	1.50415800
H	-4.08706500	1.36314800	1.45170600
C	-3.75722700	-1.27201400	0.17677200
H	-3.61349700	-1.91058300	1.05713800
H	-4.75450600	-0.81659800	0.25958700
H	-3.73386000	-1.91964100	-0.70691700
C	-2.66469200	1.00058200	-1.57793600
H	-2.68214300	0.31116900	-2.42768300
H	-3.63279100	1.51742500	-1.54506700
H	-1.89028100	1.75286800	-1.76125900

Si_III, E = –1168.81093623, ZPE =0.251165

Si	2.48244500	0.14247900	-0.28981600

P	-0.04187100	-1.64819400	1.48370900
O	0.78578200	0.31106300	-0.37355000
C	-1.50888300	0.04415700	-0.02084600
N	-1.96474800	1.31081600	0.21357900
N	-2.55691600	-0.64277400	-0.55956500
C	-0.17165400	-0.45137000	0.30629200
C	-3.67608000	0.17310700	-0.59420600
C	-3.30731800	1.39181200	-0.11726200
H	-3.87594200	2.29898700	0.01021100
H	-4.62678200	-0.17936400	-0.96015900
C	-2.53914200	-2.05985900	-0.89677200
H	-1.66693100	-2.28232900	-1.51389000
H	-2.47160400	-2.64974900	0.02272900
H	-3.45149600	-2.29132300	-1.44892900
C	-1.16239700	2.36919400	0.81394600
H	-0.69425700	1.99331300	1.72756700
H	-0.38094200	2.69097500	0.12265700
H	-1.81835400	3.20595000	1.05727100
C	3.06012500	1.42215000	-1.55150600
H	2.66058800	1.20343300	-2.54812400
H	2.73422000	2.43124900	-1.27434300
H	4.15456700	1.43353100	-1.62306900
C	3.04152900	-1.57454700	-0.82669300
H	2.59457300	-1.84964200	-1.78905600
H	4.13233100	-1.59482800	-0.94668000
H	2.76003200	-2.33211400	-0.09030000
C	3.14941000	0.59010700	1.41572200
H	2.82145600	-0.13384400	2.16665100
H	4.24686800	0.60605800	1.40200500
H	2.80736500	1.58461200	1.72549900

Si_TS3, E = –1168.77769555, ZPE =0.248259

Si	-2.33176800	-0.20649600	0.12373200
P	0.85578400	2.94539100	-0.33140300
O	-1.16487100	0.45922200	-0.76913400
C	1.73401000	0.14128800	-0.15731300
N	2.22620400	-0.52373500	0.92598900
N	1.65404200	-0.74865000	-1.17886400
C	1.39932400	1.49987800	-0.20636800
C	2.05604500	-1.98103300	-0.72398600
C	2.41289200	-1.84586800	0.58858800
H	2.77903300	-2.57151000	1.29679900
H	2.05103500	-2.85081100	-1.36084200
C	0.95705600	-0.46663700	-2.43835700
H	-0.07040800	-0.15880800	-2.13289300
H	1.46984000	0.33947100	-2.96762800
H	0.96904600	-1.37459600	-3.04195800

C	2.37562700	0.05540100	2.25908700
H	2.74950600	1.07595600	2.16785300
H	1.40867200	0.06484400	2.76945400
H	3.08937800	-0.54612700	2.82296600
C	-3.01615900	-1.84309500	-0.59905400
H	-3.42690600	-1.67718100	-1.60322200
H	-2.22280100	-2.59749800	-0.68990200
H	-3.81355900	-2.27389000	0.02121500
C	-3.83322300	0.94921900	0.36193300
H	-4.26806400	1.21634400	-0.60922900
H	-4.62295700	0.49057100	0.97154000
H	-3.52759600	1.88284100	0.85105400
C	-1.72362400	-0.65152800	1.89612000
H	-1.34611600	0.24433600	2.40821700
H	-2.51751200	-1.08010800	2.52200400
H	-0.90705000	-1.38659200	1.85265700

Si_IV, E = –1168.83995301, ZPE =0.249204

P	-0.52286800	-0.00005300	-1.37569000
Si	-3.10545700	-0.00000600	0.32093800
N	2.93118500	1.09920800	0.14023100
N	2.93123700	-1.09918800	0.14024900
C	2.19776000	-0.00000900	-0.26682400
O	-1.44094000	-0.00001600	0.06681500
C	4.09896100	-0.67763600	0.77190100
H	4.81811900	-1.37842000	1.16452800
C	4.09893100	0.67771500	0.77189000
H	4.81805500	1.37853700	1.16450900
C	1.04073700	-0.00004500	-0.99063900
C	2.51280000	2.46427800	-0.10949600
H	2.33084600	2.60922800	-1.17947300
H	1.58849300	2.69137200	0.43191600
H	3.30212200	3.14133200	0.22156900
C	2.51286300	-2.46427600	-0.10939100
H	1.58855100	-2.69133400	0.43202600
H	2.33091400	-2.60929000	-1.17936200
H	3.30218100	-3.14131000	0.22172400
C	-3.87938200	1.54515900	-0.44226900
H	-3.44005900	2.45553600	-0.01847200
H	-3.72370200	1.57337200	-1.52681300
H	-4.96035400	1.57779500	-0.25870400
C	-3.87941000	-1.54519700	-0.44217600
H	-3.72384100	-1.57334200	-1.52674100
H	-3.44002000	-2.45558800	-0.01848500
H	-4.96036200	-1.57787000	-0.25850700
C	-3.34447400	0.00009500	2.18965900
H	-4.40863100	0.00000800	2.45537800

H	-2.88243800	-0.88464200	2.64170900
H	-2.88260800	0.88497200	2.64160700

^{Me}Ph$_3$GePCO, E = –2649.49642565, ZPE =0.11953

Ge	-0.68931400	-0.09792000	0.00003800
P	1.18487400	1.40793700	-0.00001000
O	2.96596800	-0.80410100	-0.00015400
C	2.20510600	0.08687400	-0.00008800
C	-0.65678800	-1.19610300	-1.60988200
H	-0.65144300	-0.56318600	-2.50076300
H	0.23213400	-1.83214100	-1.62399500
H	-1.54477400	-1.83669300	-1.63686100
C	-2.21743800	1.11569300	-0.00109300
H	-2.20373200	1.75079200	-0.89070300
H	-3.14383600	0.53204200	-0.00189000
H	-2.20524400	1.75081700	0.88851800
C	-0.65747100	-1.19450800	1.61106400
H	-0.65189900	-0.56063000	2.50126500
H	-1.54570200	-1.83472200	1.63871000
H	0.23123900	-1.83082600	1.62590100

Ge_TS1, E = –2954.3142907, ZPE =0.247133

Ge	-2.67231000	-0.02659000	-0.02857900
P	-0.52066600	-0.86264200	-0.60477200
O	0.20405100	1.45169700	0.85520800
C	2.50088400	-0.01758200	0.03111400
N	3.42391200	0.97314000	-0.12237500
N	3.25653300	-1.14976400	0.09388100
C	0.17818000	0.44266700	0.23754000
C	4.61398200	-0.87427500	-0.02267200
C	4.72017500	0.47303200	-0.16209000
H	5.58746800	1.10422100	-0.28185900
H	5.37181800	-1.64201500	0.01121800
C	2.71685500	-2.49253900	0.28415300
H	1.63089500	-2.42104700	0.33173900
H	2.99838500	-3.13513700	-0.55546300
H	3.09791300	-2.92413700	1.21478000
C	3.09687300	2.38708800	-0.28872100
H	3.21305400	2.68547300	-1.33545300
H	2.06731600	2.54673000	0.02425100
H	3.76075100	2.99323500	0.33381500
C	-2.93177100	0.01468800	1.91193800
H	-2.91749800	-1.00287400	2.31190800
H	-2.14711700	0.59905400	2.39898100

H	-3.90239800	0.46792300	2.14180700
C	-3.94254900	-1.28895500	-0.82138800
H	-3.79072300	-2.29191700	-0.41193400
H	-4.96821800	-0.97491000	-0.60007800
H	-3.81890500	-1.33097200	-1.90740800
C	-2.97512800	1.76068000	-0.76946300
H	-2.96174900	1.72172500	-1.86212800
H	-3.95294900	2.13203400	-0.44344800
H	-2.20464200	2.45710800	-0.42928200

Ge_II, E = –2954.34477131, ZPE =0.250784

Ge	-2.38761300	0.00092600	-0.01570100
P	-0.39332400	-1.04677600	-0.68241200
O	0.28449400	1.20591100	0.75653900
C	2.11108200	-0.00038500	0.03442400
N	2.96781300	1.04617600	-0.08951300
N	2.87705700	-1.12113800	0.09505900
C	0.61354700	0.16229100	0.12285100
C	4.21173000	-0.77358100	-0.01444100
C	4.26632100	0.58048800	-0.13048400
H	5.10890100	1.24509600	-0.23428100
H	4.99751500	-1.51116500	0.01323700
C	2.41645900	-2.50412200	0.24794400
H	1.50825100	-2.51750800	0.84973600
H	2.18414800	-2.93549900	-0.72761300
H	3.21237000	-3.07084500	0.73550000
C	2.58775400	2.45738600	-0.23406800
H	1.92365900	2.57325100	-1.09233800
H	2.06018700	2.78731200	0.65870800
H	3.50264100	3.02982900	-0.39468700
C	-2.59389400	0.02451300	1.93630900
H	-2.78654300	-0.98742000	2.30465000
H	-1.69885600	0.42781600	2.41355200
H	-3.45326400	0.65492200	2.19231200
C	-3.86361700	-1.07362800	-0.73897600
H	-3.81169800	-2.10282800	-0.36963000
H	-4.82504900	-0.64634600	-0.43230400
H	-3.83133700	-1.09692100	-1.83290700
C	-2.59179800	1.82533700	-0.71054200
H	-2.71585100	1.80547100	-1.79736000
H	-3.48693200	2.27628200	-0.26710400
H	-1.72020700	2.42821900	-0.45009100

Ge_TS2, E = –2954.31179947, ZPE =0.249688

P	-0.21040600	1.56885000	0.79782300
O	-0.24445400	-0.73490700	-0.51301800
C	1.94994500	-0.02507100	-0.04637200
N	2.56077700	-1.24205700	0.05581500
N	2.94734800	0.88902200	-0.21893500
C	0.50815200	0.22002200	0.02902400
C	4.17194000	0.24679800	-0.18956800
C	3.93095300	-1.07971400	-0.01455200
H	4.60940300	-1.91445700	0.05904700
H	5.09855200	0.78386400	-0.31116500
C	2.78371300	2.32998600	-0.40561200
H	1.99535700	2.51879800	-1.13551300
H	2.49279900	2.80178600	0.53498300
H	3.73460500	2.72944300	-0.76336000
C	1.89103400	-2.51507900	0.33506600
H	1.70219000	-2.60955700	1.40866500
H	0.94290700	-2.53160800	-0.20090900
H	2.54502400	-3.32395700	0.00511300
C	-2.75386900	-1.37342600	-1.42096300
H	-2.47867500	-1.04759100	-2.42919000
H	-2.31577000	-2.35945600	-1.24093500
H	-3.84644700	-1.45402200	-1.37302600
C	-3.30275800	1.48741000	-0.52555700
H	-2.88342900	2.04874200	-1.36603200
H	-4.30184000	1.13256700	-0.80667500
H	-3.37429600	2.15629900	0.33677000
C	-2.62361500	-0.83172600	1.67491500
H	-2.93087900	-0.04413000	2.36793100
H	-3.45018100	-1.53891700	1.54476400
H	-1.77239400	-1.36339900	2.10973800
Ge	-2.14203300	-0.06005800	-0.06499600

Ge_III, E = –2954.32086509, ZPE =0.249536

Ge	-2.21394600	0.08051000	-0.17951200
P	0.29831900	-1.58237300	1.42704000
O	-0.40771200	0.36688000	-0.45788400
C	1.87105800	0.04859600	-0.04426600
N	2.34195000	1.31620300	0.15471800
N	2.93058100	-0.68332400	-0.49502200
C	0.50702400	-0.40168100	0.23672300
C	4.06707400	0.10890600	-0.50975400
C	3.70109200	1.35534100	-0.10859500
H	4.28186500	2.25654200	0.00586600
H	5.02679000	-0.27800700	-0.81172600
C	2.90247600	-2.11362800	-0.77111400
H	2.76249900	-2.66047500	0.16652600
H	2.06650400	-2.34709700	-1.43282400

H	3.84315300	-2.38616800	-1.25286500
C	1.53411300	2.41616100	0.66675700
H	0.75862600	2.67962400	-0.05474500
H	1.05756100	2.11193100	1.60286600
H	2.18821200	3.26949100	0.85028600
C	-2.88222900	1.36268300	-1.49049500
H	-3.97718600	1.36335200	-1.50514700
H	-2.53755600	2.37040800	-1.24146500
H	-2.51931800	1.10317300	-2.48883900
C	-2.77931900	0.63980800	1.59835700
H	-2.36913600	1.62999600	1.81787700
H	-3.87291000	0.71009300	1.61449600
H	-2.44428400	-0.06923900	2.35528300
C	-2.75015300	-1.71619600	-0.70755200
H	-3.81108800	-1.70414700	-0.98212500
H	-2.16893600	-2.02599800	-1.58067400
H	-2.58616300	-2.42933200	0.10081400

Ge_TS3, E = –2954.2710528, ZPE =0.24632

P	1.45683600	2.95665700	-0.26817800
O	-0.77866000	0.80755800	-0.76659700
C	1.98988300	0.06283300	-0.16122000
N	2.39106900	-0.67488400	0.91513700
N	1.82473000	-0.79556100	-1.20175000
C	1.82131900	1.45094900	-0.18331900
C	2.06965300	-2.07594400	-0.76223500
C	2.42364900	-2.00546200	0.55529700
H	2.69527900	-2.78100300	1.25315800
H	1.97351200	-2.92814800	-1.41540900
C	1.15435900	-0.41348400	-2.44583200
H	0.17139000	0.01174300	-2.11476800
H	1.74514700	0.34444900	-2.96487500
H	1.05771400	-1.30300500	-3.06922300
C	2.59984200	-0.13517200	2.25556100
H	1.63694400	0.01309800	2.75205100
H	3.20822600	-0.83886500	2.82485500
H	3.12033300	0.82076600	2.18076100
C	-2.39598800	-1.82727300	-0.72652900
H	-2.71880400	-1.67077200	-1.76120600
H	-1.50038800	-2.45950800	-0.73428200
H	-3.19046300	-2.36416800	-0.19545000
C	-3.69259700	0.93714100	0.19777000
H	-4.05034100	1.13534200	-0.81732900
H	-4.47079500	0.39731700	0.74910200
H	-3.51014300	1.89717000	0.69101600
C	-1.44732000	-0.44857500	1.97431500
H	-1.20393100	0.49497600	2.47519400

H	-2.23792300	-0.94776100	2.54639600
H	-0.56143700	-1.09504700	1.98494900
Ge	-2.01359300	-0.07855800	0.11106100

Ge_IV, E = –2954.34346096, ZPE =0.24781

P	-0.09909200	0.00044000	-1.31593900
Ge	-2.79812400	-0.00001000	0.22856400
N	3.38117500	1.09940000	0.13737700
N	3.38121400	-1.09954700	0.13685800
C	2.64093900	0.00000500	-0.26308200
O	-0.97484000	0.00031800	0.13162000
C	4.55565500	-0.67794000	0.75561300
H	5.27955300	-1.37840800	1.14013500
C	4.55566400	0.67752600	0.75586300
H	5.27954600	1.37783400	1.14070500
C	1.47826900	0.00017000	-0.97491000
C	2.96042800	2.46376000	-0.10739300
H	2.76184200	2.60721600	-1.17475400
H	2.04417300	2.69277600	0.44715700
H	3.75521200	3.14097100	0.21052300
C	2.96017100	-2.46379500	-0.10799900
H	2.04491100	-2.69335400	0.44799300
H	2.75975400	-2.60649100	-1.17510800
H	3.75560800	-3.14111800	0.20804100
C	-3.44797900	1.61732000	-0.64030700
H	-2.99817400	2.49477200	-0.16752700
H	-3.17610800	1.60907700	-1.69918300
H	-4.53694200	1.69249500	-0.55675500
C	-3.44769300	-1.61720400	-0.64079200
H	-3.17611800	-1.60881000	-1.69972900
H	-2.99784700	-2.49472300	-0.16817400
H	-4.53664800	-1.69241000	-0.55695900
C	-3.12617700	-0.00069100	2.14232600
H	-4.19915100	-0.00294100	2.35868300
H	-2.67162000	-0.88805100	2.59064400
H	-2.67530600	0.88846300	2.59082000

^{Me}**3b**, E = –2841.01492193, ZPE =0.240432

Ge	-1.75546300	-0.08021000	0.09631900
P	0.10596300	-1.10006200	-0.89125300
C	1.48003700	-0.15053000	-0.26079700
N	1.68396200	1.20712900	-0.10844800
N	2.69611900	-0.71639400	0.07101400
C	3.61787100	0.26376000	0.40228400

C	2.98674600	1.46016200	0.30218000
H	3.34411400	2.46025900	0.48898000
H	4.62832600	0.02523800	0.69366200
C	2.96380600	-2.14524500	0.06197300
H	2.07258500	-2.66783400	0.41996700
H	3.18595900	-2.49954700	-0.94990900
H	3.81508500	-2.34960200	0.71510700
C	0.74973000	2.23141300	-0.54100000
H	0.23178400	1.87564700	-1.43620800
H	0.00730800	2.45251900	0.22951800
H	1.30743200	3.14118400	-0.77338200
C	-1.43393300	0.50035600	1.94728700
H	-1.18132200	-0.37374300	2.55432800
H	-0.61445600	1.21946900	2.03028100
H	-2.34116000	0.95771200	2.35745600
C	-3.06389600	-1.53995200	0.15621600
H	-2.67525000	-2.37187100	0.74968700
H	-4.00273700	-1.19209200	0.60072500
H	-3.27240900	-1.90384700	-0.85446500
C	-2.64584200	1.36947100	-0.89968100
H	-2.72535900	1.09090800	-1.95450900
H	-3.65836500	1.50459500	-0.50318800
H	-2.12384500	2.32688500	-0.83020100

CO, E = –113.317323135, ZPE =0.005017

O	0.00000000	0.00000000	0.48739600
C	0.00000000	0.00000000	-0.64986100

S4: References

[1] F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H. F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420–8423; *Angew. Chem.*, **2011,** 123, 8570–8574.

[2] D. Heift, Z. Benko, H. Grützmacher, *Dalton T* **2014**, *43*, 5920–5928.

[3] a) A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt, *Tetrahedron* **1999**, *55*, 14523–14534; b) X. Bantreil, S. P. Nolan, *Nat. Protoc.* **2011**, *6*, 69–77.

[4] M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.;

Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision A.1 ed., Gaussian, Inc., Wallingford CT, **2009**.

[5] E. D. Glendening, J. K. Badenhoop. A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2013**.