

Supplementary Information for

The Structures and Reactivity of NHC-supported Copper(I) Triphenylgermyls

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Experimental	4
General Considerations and Starting Materials	4
Synthesis of (6-Dipp)CuOMe	4
Synthesis of Ph ₃ SnOtBu	5
Synthesis of compound 1 , (SiMes)CuGePh ₃	5
Synthesis of compound 2 , (IPr)CuGePh ₃	5
Synthesis of compound 3 , (6-Mes)CuGePh ₃	6
Synthesis of compound 4 , (6-Dipp)CuGePh ₃	6
Synthesis of compound 5 , (IPr)CuSC(=NtBu)GePh ₃	7
Synthesis of compound 6 , (IPr)CuSC(S)GePh ₃	7
Synthesis of compound 7 , (IPr)CuN(Ph)C(O)Ph	7
Synthesis of compound 8 , (IPr)CuN(Ph)C(O)GePh ₃	8
Synthesis of compound 9 , (IPr)CuC(Ph)C(H)GePh ₃	8
Synthesis of compound 10 , (IPr)CuC(H)=C(Ph)GePh ₃	8
Reaction of compound 2 and Ph ₃ SnCl	9
Reaction of compound 2 and Ph ₂ PCl	9
Reaction of compound 2 and carbon dioxide	9
¹ HVT-NMR study of the reaction of compound 2 and carbon dioxide	9
Reaction of compound 2 and di-iso-propyl carbodiimide	9
Thermolysis of compound 5	10
Reaction of compound 2 and phenyl isocyanate	10
Thermolysis of compound 8	10
Reaction of compound 1 and phenyl isocyanate	10
Reaction of compound 2 and phenyl acetylene at -40 °C	10
Reaction of compound 2 and of phenyl acetylene at room temperature	10
Reaction of 10 mol% compound 2 with Ph ₃ GeH and phenyl acetylene	11
Reaction of 10 mol% (SiMes)CuOtBu with Ph ₃ GeH and Ph ₃ SnCl	11
Reaction of (SiMes)CuOtBu with Ph ₃ GeH and Bu ₃ SnOMe	11
General Procedure for the Catalytic Cross Coupling Reactions	11
Catalytic Cross Coupling Reactions	11
General Procedure for the Catalytic Hydrogermylation of Activated Alkenes	12
Catalytic Hydrogermylation of Activated Alkenes	12
X-ray Crystallography	15
X-ray data discussion	15
Figure S1. Molecular structure of (SiMes)CuN(Ph)C(O)N(Ph)C(O)GePh ₃	16
Table S1. Crystal data and structure refinement details (compounds 1-4)	17
Table S2. Crystal data and structure refinement details (compounds 5-8)	18
Table S3. Crystal data and structure refinement details (compounds 9-10 and (SiMes)CuN(Ph)C(O)N(Ph)C(O)GePh ₃)	19
In situ reaction monitoring by NMR spectroscopy	20
Figures S2: Reaction of (SiMes)CuOtBu and Ph ₃ GeH	20

Figure S3: Reaction of (IPr)CuOMe and Ph ₃ GeH	20
Figure S4: Reaction of (6-Mes)CuMes and Ph ₃ GeH	21
Figure S5: Reaction of (6-Dipp)CuOMe and Ph ₃ GeH	21
Figure S6: Reaction of (IPr)CuGePh ₃ and tBuNCS	22
Figure S7: Reaction of (IPr)CuGePh ₃ and CS ₂	22
Figure S8: Reaction of (IPr)CuPh and PhNCO	23
Figure S9-10: Reaction of compound 2 and Ph ₃ SnCl	23
Figures S11-12: Reaction of compound 2 and Ph ₂ PCI	24
Figure S13: Reaction of compound 2 and carbon dioxide	25
Figure S14: ¹ H VT-NMR spectra of the reaction of compound 2 and carbon dioxide	26
Figure S15: Reaction of compound 2 and di-iso-propyl carbodiimide	26
Figure S16: Thermolysis of compound 5	27
Figure S17: Reaction of compound 2 and phenyl isocyanate	27
Figure S18: Thermolysis of compound 8	28
Figure S19: Reaction of compound 1 and phenyl isocyanate	28
Figure S20: Reaction of compound 2 and phenyl acetylene at -40 °C	29
Figure S21: Reaction of compound 2 and phenyl acetylene at room temperature	29
Figure S22: The ¹ H– ¹³ C HSQC NMR spectrum of the reaction of compound 2 and two equivalents of phenyl acetylene at room temperature	30
Figure S23: Reaction of 10 mol% compound 2 with phenyl acetylene and Ph ₃ GeH	30
Figures S24-25: Reaction of 10 mol% (SIMes)CuOtBu with Ph ₃ GeH and Ph ₃ SnCl	31
Figures S26-27: Reaction of (SIMes)CuOtBu with Ph ₃ GeH and Bu ₃ SnOMe	32
Figures S28-29: Reaction of 10 mol% (SIMes)CuOtBu with Ph ₃ GeH and Bu ₃ SnOMe	33
Figures S30-31: Reaction of 10 mol% (SIMes)CuOtBu with Ph ₃ GeH and Ph ₃ SnOtBu	34
Figure S32: Reaction of 10 mol% (SIMes)CuOtBu with Ph ₃ GeH and methyl vinyl ketone	35
Figure S33: Reaction of 5 mol% (SIMes)CuOtBu with Ph ₃ GeH and acrylonitrile	35
Figure S34: Reaction of 10 mol% (SIMes)CuOtBu with Ph ₃ GeH and 4-vinyl pyridine	36
NMR Spectra of Compounds	37
Figures S35-36: NMR spectra of (6-Dipp)CuOMe	37
Figures S37-39: NMR spectra of Ph ₃ SnOtBu	38
Figures S40-42: NMR spectra of Ph ₃ GeSnBu ₃	39
Figures S43-44: NMR spectra of compound 1 , (SIMes)CuGePh ₃	41
Figures S45-46: NMR spectra of compound 2 , (IPr)CuGePh ₃	42
Figures S47-48: NMR spectra of compound 3 , (6-Mes)CuGePh ₃	43
Figures S49-50: NMR spectra of compound 4 , (6-Dipp)CuGePh ₃	44
Figures S51-52: NMR spectra of compound 5 , (IPr)CuSC(=NtBu)GePh ₃	45
Figures S53-54: NMR spectra of compound 6 , (IPr)CuSC(S)GePh ₃	46
Figures S55-56: NMR spectra of compound 7 , (IPr)CuN(Ph)C(O)Ph	47
Figures S57-58: NMR spectra of compound 8 , (IPr)CuN(Ph)C(O)GePh ₃	48
Figures S59-60: NMR spectra of compound 9 , (IPr)CuC(Ph)C(H)GePh ₃	49
Figures S61-62: NMR spectra of compound 11a , Ph ₃ GeCH ₂ CH ₂ C(O)OCH ₃	50
Figures S63-64: NMR spectra of compound 11b , Ph ₃ GeCH ₂ CH ₂ C(O)OCH ₂ CH ₂	51

Figures S65-66: NMR spectra of compound 11c , $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$	52
Figures S67-68: NMR spectra of compound 11d , $\text{Ph}_3\text{GeCH}_2(\text{CH}_3)\text{CHC}(\text{O})\text{OCH}_3$	53
Figures S69-70: NMR spectra of compound 11g , $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}_2$	54
Figures S71-72: NMR spectra of compound 11h , $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C}(\text{O})\text{NMe}_2$	55
Figures S73-74: NMR spectra of compound 11k , $\text{Ph}_3\text{GeCH}_2\text{CH}_2(2\text{-C}_5\text{H}_5\text{N})$	56
Computational details	57
References	68

Experimental

General Considerations and Starting Materials

All reactions dealing with air- and moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line and glovebox techniques. NMR experiments using air sensitive compounds were conducted in J. Young's tap NMR tubes prepared and sealed in a glovebox under argon. Hexane, toluene, and pentane were purified using an MBraun Solvent Purification System and stored over 4Å molecular sieves. Benzene, diethyl ether, and THF were dried with a sodium benzophenone suspension and distilled. C₆D₆ and toluene-d₈ was dried over a potassium mirror prior to vacuum transfer into a sealed ampoule and stored in a glove box under argon. Methanol was dried over magnesium turnings and distilled. All NMR data, unless otherwise stated, were acquired at 298 K on an Agilent ProPulse or Bruker Avance instrument for ¹H (500 MHz), ¹³C{¹H} (126 MHz), and ¹¹⁹Sn (186 MHz) and a Bruker Avance 400 for ¹H (400 MHz), ¹³C{¹H} (101 MHz) and ³¹P{¹H} (162 MHz). ¹H and ¹³C NMR spectra were referenced using residual solvent resonances. Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K. Ph₃GeH and Ph₃SnCl were purchased from Merck and was used as received. Dibutyldimethoxytin was purchased from TCI and was used as received. Sodium methoxide and tributyltin methoxide were purchased from Fisher and were used as received. Phenyl isocyanate, *tert*-butyl isothiocyanate, Ph₂POEt, and Ph₂PCl were purchased from Merck and distilled before use. Carbon disulfide was purchased from Merck and dried over calcium hydride prior to vacuum transfer into reactions. Carbon dioxide was purchased from Boc and atmospheres were applied through an Agilent 1/4 inch OT3-4 oxygen/moisture trap. Phenylacetylene was purchased from Fluorochem and was used as received. Diphenyltin oxide was purchased from Strem and was used as received. Methyl acrylate, ethyl acrylate, *tert*butyl acrylate, methyl methacrylate, methyl crotonate, acrylonitrile, and 4-vinyl pyridine were purchased from Fisher and were distilled before use. Acrylamide, N,N-dimethylacrylamide, styrene, methyl vinyl ketone, and 2-vinyl pyridine were purchased from Merck and were distilled before use. (SiMes)CuOtBu, (IPr)CuPh, (IPr)CuOMe, (IPr)CuOtBu, (6-Mes)CuMes, (6-Dipp)CuCl, Ph₃GeLi, Me₃GeOMe, Ph₃GeOMe, and Ph₃SiOMe were prepared according to literature procedures.¹

Synthesis of (6-Dipp)CuOMe

In a glovebox, (6-Dipp)CuCl (1.254 g, 2.49 mmol) and NaOMe (0.135 g, 2.50 mmol) were added to a Schlenk flask. Methanol (40 mL) was added forming a yellow suspension which was left stirring overnight at room temperature. Volatiles were removed *in vacuo* precipitating a beige powder. Benzene (20 mL) was added and resulting suspension was filtered forming a pale yellow solution. Volatiles were removed *in vacuo* precipitating an off-white powder which was washed with hexane (3 x 10 mL) yielding the product, (6-Dipp)CuOMe (0.475 g, 0.95 mmol, 38 %).

¹H NMR (500 MHz, C₆D₆) δ 7.19 – 7.17 (m, 2H, *para*-H), 7.08 (d, *J* = 7.8 Hz, 4H, *meta*-H), 3.92 (s, 3H, OCH₃), 3.03 (hept, *J* = 6.8 Hz, 4H, CH(CH₃)₂), 2.73 (t, *J* = 5.9 Hz, 4H, NCH₂), 1.52 – 1.47 (m, 14H, CH(CH₃)₂ and NCH₂CH₂), 1.19 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂). ¹³C NMR (126 MHz, C₆D₆) δ 203.2 (CCu), 145.7 (Ar-C), 142.5 (Ar-C), 129.3 (Ar-C), 124.8 (Ar-C), 46.1 (NCH₂), 28.9 (CH(CH₃)₂), 25.0 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 20.4 (NCH₂CH₂). Analysis calculated for C₂₉H₄₃CuN₂O (MW = 499.21 g/mol): Expected: C, 69.77; H, 8.68; N, 5.61. Found: C, 69.37; H, 8.88; N, 5.26. See figures S35-36 for full NMR spectra of (6-Dipp)CuOMe.

Synthesis of Ph₃SnOtBu

In a glovebox, Ph₃SnCl (0.900 g, 2.33 mmol) and KOtBu (0.262 g, 2.33 mmol) were added to a Schlenk flask. Hexane (30 mL) was added forming a colourless suspension which was left stirring overnight at room temperature. The resulting suspension was filtered, and volatiles were removed *in vacuo* precipitating a colourless powder of the product, Ph₃SnOtBu (0.814 g, 1.92 mmol, 82 %). ¹H NMR (500 MHz, C₆D₆) δ 7.78 – 7.63 (m, 6H, Ar-H), 7.19 – 7.07 (m, 11H, Ar-H and residual C₆H₆), 1.37 (s, 9H, SnOtBu). ¹³C NMR (126 MHz, C₆D₆) δ 140.3 (Ar-C), 136.9 (Ar-C), 129.9 (Ar-C), 129.0 (Ar-C), 72.4 (OC(CH₃)₃), 34.1 (OC(CH₃)₃). ¹¹⁹Sn NMR (186 MHz, C₆D₆) δ -114.3. See figures S37-39 for full NMR spectra of Ph₃SnOtBu.

Synthesis of compound 1, (SIMes)CuGePh₃

In a glovebox, (SIMes)CuOtBu (0.300 g, 0.68 mmol) and Ph₃GeH (0.206 g, 0.68 mmol) were added to a Schlenk flask. Diethyl ether (30 mL) was added forming a white suspension which was left stirring overnight at room temperature. Volatiles were removed *in vacuo* precipitating a white powder which was washed with cold hexane (3 x 10 mL) yielding the product, compound 1 (0.355 g, 0.53 mmol, 78 %). Single crystals of compound 1 that were suitable for characterisation by SC-XRD were grown from the slow cooling of a saturated toluene solution overnight.

¹H NMR (500 MHz, C₆D₆) δ 7.57 – 7.54 (m, 6H, Ar-H), 7.20 – 7.17 (m, 4H, Ar-H), 7.17 – 7.12 (m, 9H, Ar-H and residual benzene), 6.73 – 6.72 (m, 4H, *meta*-H), 2.97 (s, 4H, NCH₂), 2.11 (s, 6H, *para*-CH₃), 2.10 (s, 12H, *ortho*-CH₃). ¹³C NMR (126 MHz, C₆D₆) δ 204.5 (CCu), 150.3 (Ar-C), 138.5 (Ar-C), 136.8 (Ar-C), 135.7 (Ar-C), 135.5 (Ar-C), 130.0 (Ar-C), 127.5 (Ar-C), 126.3 (Ar-C), 50.5 (NCH₂), 21.1 (*para*-CH₃), 18.1 (*ortho*-CH₃). Analysis calculated for C₃₉H₄₁CuGeN₂ (MW = 673.95 g/mol): Expected: C, 69.51; H, 6.13; N, 4.16. Found: C, 69.04; H, 6.15; N, 4.02. See figure S2 for the in-situ reaction ¹H NMR spectrum and figures S43-44 for full NMR spectra of 1.

Synthesis of compound 2, (IPr)CuGePh₃

In a glovebox, (IPr)CuOMe (0.780 g, 1.61 mmol) and Ph₃GeH (0.492 g, 1.61 mmol) were added to a Schlenk flask. Toluene (30 mL) was added forming a colourless solution which was stirred overnight at room temperature. Volatiles were removed *in vacuo* precipitating a white powder which was washed with hexane (3 x 10 mL). The white powder was dissolved in the minimum amount of toluene and filtered forming a colourless solution. The solution was cooled to -5 °C overnight precipitating a colourless crystalline material of the product, compound 2 (0.440 g, 0.58 mmol, 36 %). Single crystals of compound 2 were that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane into a saturated toluene solution.

¹H NMR (500 MHz, C₆D₆) δ 7.51 – 7.49 (m, 6H, Ar-H), 7.26 – 7.21 (m, 2H, Ar-H), 7.20 – 7.13 (m, 11H, Ar-H and residual benzene), 7.05 (d, *J* = 7.9 Hz, 4H, *meta*-H), 6.21 (s, 2H, NCH), 2.53 (hept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.27 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 1.05 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂). ¹³C NMR (126 MHz, C₆D₆) δ 183.6 (CCu), 150.3 (Ar-C), 145.9 (Ar-C), 136.8 (Ar-C), 134.8 (Ar-C), 130.7 (Ar-C), 127.5 (Ar-C), 126.2 (Ar-C), 124.3 (Ar-C), 122.2 (NCH), 29.0 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 23.6 (CH(CH₃)₂). Analysis calculated for C₄₅H₅₁CuGeN₂ (MW = 756.09 g/mol): Expected: C, 71.49; H, 6.80; N, 3.71. Found: C, 70.96; H, 6.82; N, 3.69. See figure S3 for the in-situ reaction ¹H NMR spectrum and figures S45-46 for full NMR spectra of 2.

Synthesis of compound 3, (6-Mes)CuGePh₃

In a glovebox, (6-Mes)CuMes (111 mg, 0.220 mmol) and Ph₃GeH (67.2 mg, 0.220 mmol) were added to a Schlenk flask. Toluene (10 mL) was added forming a colourless solution which was stirred for 3 days at 60 °C. Volatiles were removed *in vacuo* forming a white powder which was washed with hexane (3 x 10 mL) yielding the product, compound **3** (75.5 mg, 0.110 mmol, 50 %). Single crystals of compound **3** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane into a saturated toluene solution.

¹H NMR (500 MHz, C₆D₆) δ 7.45 – 7.44 (m, 6H, Ar-H), 7.23 – 7.12 (m, 11H, Ar-H and residual benzene), 6.75 (s, 4H, *meta*-H), 2.46 (t, *J* = 5.9 Hz, 4H, NCH₂), 2.18 (s, 6H, *para*-CH₃), 2.06 (s, 12H, *ortho*-CH₃), 1.32 – 1.27 (m, 2H, NCH₂CH₂). ¹³C NMR (126 MHz, C₆D₆) δ 202.2 (CCu), 150.8 (Ar-C), 141.8 (Ar-C), 138.1 (Ar-C), 136.8 (Ar-C), 134.9 (Ar-C), 130.0 (Ar-C), 127.3 (Ar-C), 126.1 (Ar-C), 43.4 (NC), 21.2 (*para*-CH₃), 20.6 (NCH₂CH₂), 18.1 (*ortho*-CH₃). MS (ESI) [M⁺] C₄₀H₄₃CuGeN₂: 685.1998, found: 685.2069 (err [ppm] = 4.63). Despite repeated attempts, we were unable to obtain satisfactory elemental analysis for this compound. This is most likely due to the compound's high sensitivity towards air and moisture. Analysis calculated for C₄₀H₄₃CuGeN₂ (MW = 687.97 g/mol): Expected: C, 69.83; H, 6.3; N, 4.07. Found: C, 68.22; H, 6.17; N, 3.88. See figure S4 for the in-situ reaction ¹H NMR spectrum and figures S47-48 for full NMR spectra of **3**.

Synthesis of compound 4, (6-Dipp)CuGePh₃

(6-Dipp)CuOMe route:

In a vial in a glovebox, (6-Dipp)CuOMe (30 mg, 0.060 mmol) and Ph₃GeH (27 mg, 0.089 mmol) were combined. Benzene (0.5 mL) was added forming a yellow solution which was transferred into a J Young's NMR tube. The reaction was heated to 40 °C for 4 days and volatiles were removed *in vacuo* precipitating a yellow oil. The oil was triturated with hexane (0.5 mL) precipitating a beige powder. The powder was redissolved in toluene (0.5 mL) and filtered forming a colourless solution. Crystals of compound **4** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane. Despite repeated attempts at purification, this route yielded material that was impure by NMR spectroscopy. Crystalline yield: (6-Dipp)CuGePh₃ (8.5 mg, 0.011 mmol, 18 %). See figure S5 for the in-situ reaction ¹H NMR spectrum and figures S49-50 for full NMR spectra of **4**.

(6-Dipp)CuCl route:

In a vial in a glovebox, (6-Dipp)CuCl (30 mg, 0.060 mmol) and Ph₃GeLi (19 mg, 0.060 mmol) were combined. Diethyl ether (0.5 mL) was added forming a white suspension which was transferred into a J Young's NMR tube. The reaction was heated to 40 °C overnight and volatiles were removed *in vacuo* precipitating a white powder. The powder was redissolved in toluene (0.5 mL) and filtered forming a colourless solution. Crystals of compound **4** were grown from the slow diffusion of hexane with a 5% impurity of (6-Dipp)CuCl, (6-Dipp)CuGePh₃ (4.4 mg, 0.006 mmol, 10 %).

¹H NMR (500 MHz, C₆D₆) δ 7.36 – 7.32 (m, 6H, Ar-H), 7.29-7.26 (m, 2H, Ar-H), 7.22 – 7.17 (m, 8H, Ar-H), 7.09 (d, *J* = 7.8 Hz, 4H, *meta*-H), 2.99 – 2.90 (m, 4H, CH(CH₃)₂), 2.66 (t, *J* = 5.9 Hz, 4H, NCH₂), 1.47 – 1.41 (m, 2H, NCH₂CH₂), 1.29 – 1.24 (m, 14H, NCH₂CH₂ and CH(CH₃)₂), 1.14 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂). ¹³C NMR (126 MHz, C₆D₆) δ 202.3 (CCu), 150.5 (Ar-C), 145.9 (Ar-C), 141.4 (Ar-C), 136.8 (Ar-C), 129.5 (Ar-C), 127.2 (Ar-C), 126.0 (Ar-C), 125.0 (Ar-C), 45.9 (NCH₂), 28.9 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 20.2 (NCH₂CH₂). MS (ESI) [M+K] C₄₆H₅₅CuGeN₂K: 811.2544, found: 811.2502 (err [ppm] = -1.19).

Analysis calculated for $C_{46}H_{55}CuGeN_2$ (MW = 772.14 g/mol): Expected: C, 71.56; H, 7.18; N, 3.63. Found: C, 71.20; H, 7.09; N, 3.55. No in-situ NMR spectra were collected for **4** via this synthetic pathway.

Synthesis of compound **5**, (IPr)CuSC(=NtBu)GePh₃

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in benzene (0.5 mL). *tert*-Butyl isothiocyanate (5.0 μ L, 0.040 mmol) was added forming a pale yellow solution. The reaction mixture was transferred into a J Young's NMR tube and placed at 40 °C for 10 days. Volatiles were removed *in vacuo* precipitating a beige powder. The powder was dissolved in the minimum amount of toluene and single crystals of compound **5** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane, (IPr)CuSC(=NtBu)GePh₃ (8 mg, 0.009 mmol, 20 %).

¹H NMR (500 MHz, C₆D₆) δ 7.85 – 7.81 (m, 6H, Ar-*H*), 7.27 – 7.23 (m, 2H, Ar-*H*), 7.15 – 7.09 (m, 13H, Ar-*H*), 6.37 (s, 2H, NCH), 2.77 (hept, *J* = 6.8 Hz, 4H, CH(CH₃)₂), 1.36 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.08 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 0.60 (s, 9H, NC(CH₃)₃). ¹³C NMR (126 MHz, C₆D₆) δ 187.0 (CCu), 146.0 (Ar-C), 144.4 (Ar-C), 135.8 (Ar-C), 135.3 (Ar-C), 130.4 (Ar-C), 127.7 (Ar-C), 124.2 (Ar-C), 122.5 (Ar-C), 29.7 (NC(CH₃)₃), 29.0 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂). MS (ESI) [M-H]⁻ C₅₀H₅₉CuGeN₃S: 869.2984, found: 869.3023 (err [ppm] = 0.75). Analysis calculated for C₅₀H₆₀CuGeN₃S (MW = 871.29 g/mol): Expected: C, 68.93; H, 6.94; N, 4.82. Found: C, 69.22; H, 6.90; N, 3.98. See figure S6 for the in-situ reaction ¹H NMR spectrum and figures S51-52 for full NMR spectra of **5**.

Synthesis of compound **6**, (IPr)CuSC(S)GePh₃

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in benzene (0.5 mL) and was transferred into a J Young's NMR tube. CS₂ (4.7 μ L, 0.079 mmol) was added via vacuum transfer forming a pale green solution. Volatiles were removed *in vacuo* yielding the product, (IPr)CuSC(S)GePh₃ (19.7 mg, 0.024 mmol, 60 %). Single crystals of compound **6** were that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane into a saturated toluene solution.

¹H NMR (500 MHz, C₆D₆) δ 7.83 – 7.78 (m, 6H, Ar-*H*), 7.21 – 7.18 (m, 2H, Ar-*H*), 7.14 – 7.08 (m, 9H, Ar-*H*), 7.06 (d, *J* = 7.8 Hz, 4H, *meta*-*H*), 6.32 (s, 2H, NCH), 2.62 (hept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.37 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.07 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C NMR (126 MHz, C₆D₆) δ 192.7 (CS₂), 184.4 (CCu), 145.8 (Ar-C), 138.0 (Ar-C), 136.1 (Ar-C), 135.3 (Ar-C), 130.6 (Ar-C), 128.9 (Ar-C), 128.1 (Ar-C), 124.2 (Ar-C), 122.4 (NCH), 29.0 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 24.1 (CH(CH₃)₂). Analysis calculated for C₄₆H₅₁CuGeN₂S₂ (MW = 832.22 g/mol): Expected: C, 66.39; H, 6.18; N, 3.37. Found: C, 66.26; H, 6.11; N, 3.25. See figure S7 for the in-situ reaction ¹H NMR spectrum and figures S53-54 for full NMR spectra of **6**.

Synthesis of compound **7**, (IPr)CuN(Ph)C(O)Ph

In a vial in a glovebox, (IPr)CuPh (30 mg, 0.057 mmol) was dissolved in benzene (0.5 mL) and PhNCO (9.2 μ L, 0.085 mmol) was added forming a colourless suspension. The reaction was left overnight at room temperature before the suspension was transferred into a J Young's NMR tube. Volatiles were removed *in vacuo* precipitating a colourless powder which was washed with hexane (3 x 1 mL) yielding compound **7**, (IPr)CuN(Ph)C(O)Ph (14.6 mg, 0.023 mmol, 40 %).

¹H NMR (400 MHz, C₆D₆) δ 7.98 – 7.96 (m, 2H, Ar-*H*), 7.23 – 7.19 (m, 2H, Ar-*H*), 7.16 – 7.11 (m, 16H, Ar-*H* and residual benzene), 7.05 – 7.00 (m, 2H, Ar-*H*), 6.99 – 6.97 (m, 4H, *meta*-*H*), 6.94 – 6.88 (m, 2H, Ar-*H*), 6.75 – 6.71 (m, 2H, Ar-*H*), 6.16 (s, 2H, NCH), 2.41 (hept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 1.06 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.99 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂).

^{13}C NMR (101 MHz, C_6D_6) δ 182.0 (C(O)), 173.5 (CCu), 151.4 (Ar-C), 145.4 (Ar-C), 144.4 (Ar-C), 135.1 (Ar-C), 130.8 (Ar-C), 128.4 (Ar-C), 128.2 (Ar-C), 127.9 (Ar-C), 127.7 (Ar-C), 126.3 (Ar-C), 124.6 (*meta*-C), 123.0 (NCH), 121.0 (Ar-C), 28.9 ($\text{CH}(\text{CH}_3)_2$), 24.4 ($\text{CH}(\text{CH}_3)_2$), 23.8 ($\text{CH}(\text{CH}_3)_2$). Analysis calculated for $\text{C}_{40}\text{H}_{46}\text{CuN}_3\text{O}$ (MW = 648.37 g/mol): Expected: C, 74.10; H, 7.15; N, 6.48. Found: C, 73.72; H, 6.82; N, 6.12. See figure S8 for the in-situ reaction ^1H NMR spectrum and figures S55-56 for full NMR spectra of **7**.

Synthesis of compound **8**, (IPr)CuN(Ph)C(O)GePh₃

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in benzene (0.5 mL) and PhNCO (5.4 μL , 0.050 mmol) was added forming a colourless solution. The reaction was left for 7 days at room temperature and was then transferred into a J Young's NMR tube. Volatiles were removed *in vacuo* precipitating a beige powder which was dissolved in the toluene (0.5 mL). Single crystals of compound **8** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane, (IPr)CuN(Ph)C(O)GePh₃ (4.4 mg, 0.005 mmol, 13 %).

^1H NMR (400 MHz, C_6D_6) δ 7.68 – 7.64 (m, 6H, Ar-H), 7.24 – 7.20 (m, 2H, Ar-H), 7.09 – 7.05 (m, 13H, Ar-H), 6.59 – 6.52 (m, 3H, Ar-H), 6.42 – 6.39 (m, 2H, Ar-H), 6.28 (s, 2H, NCH), 2.59 (hept, $J = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.35 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (101 MHz, C_6D_6) δ 184.6 (C(O)), 183.0 (CCu), 148.9 (Ar-C), 145.9 (Ar-C), 140.1 (Ar-C), 135.9 (Ar-C), 135.2 (Ar-C), 130.6 (Ar-C), 128.2 (Ar-C), 127.9 (Ar-C), 127.8 (Ar-C), 126.2 (Ar-C), 124.4 (Ar-C), 122.6 (NCH), 122.3 (Ar-C), 29.1 ($\text{CH}(\text{CH}_3)_2$), , 24.8 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$). MS (ESI) $[\text{M}+\text{H}]^+$ $\text{C}_{52}\text{H}_{57}\text{CuGeN}_3\text{S}$: 876.3000, found: 876.2999 (err [ppm] = -2.20). Despite repeated attempts, we were unable to obtain satisfactory yield of this compound for suitable elemental analysis. See figure S16 for the in-situ reaction ^1H NMR spectrum and figures S57-58 for full NMR spectra of **8**.

Synthesis of compound **9**, (IPr)CuC(Ph)C(H)GePh₃

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in cold toluene (0.5 mL) and the solution was cooled to -40 °C. Phenyl acetylene (3.5 μL , 0.032 mmol) was then added and the reaction mixture was left at -40 °C for three days. The reaction mixture was then transferred into J Young's NMR tube and volatiles were removed *in vacuo* precipitating a white powder. The powder was redissolved in toluene (0.5 mL) and filtered forming a colourless solution. Single crystals of compound **8** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of hexane, (IPr)CuC(Ph)C(H)GePh₃ (11.4 mg, 0.013 mmol, 33 %).

^1H NMR (500 MHz, C_6D_6) δ 7.96 – 7.62 (m, 7H, Ar-H), 7.22 – 7.19 (m, 3H, Ar-H), 7.18 – 7.13 (m, 10H, Ar-H and residual benzene), 7.09 – 7.03 (m, 4H, Ar-H), 6.99 – 6.97 (m, 5H, Ar-H), 6.88 (s, 1H, CHGePh_3), 6.74 – 6.70 (m, 2H, Ar-H), 6.16 (s, 2H, NCH), 2.47 (hept, $J = 7.0$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 198.9 (CuCPh), 184.7 (CCu), 159.6 (Ar-C), 145.7 (Ar-C), 145.3 (Ar-C), 141.5 (Ar-C), 135.9 (Ar-C), 135.3 (Ar-C), 132.5 (CHGePh_3), 132.3 (Ar-C), 130.6 (Ar-C), 128.4 (Ar-C), 128.2 (Ar-C), 128.1 (Ar-C), 128.0 (Ar-C), 128.0 (Ar-C), 125.9 (Ar-C), 124.4 (*meta*-C), 122.9 (NCH), 122.7 (Ar-H), 28.9 ($\text{CH}(\text{CH}_3)_2$), 24.4 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$). MS (ESI) $[\text{M}^+]$ $\text{C}_{53}\text{H}_{57}\text{CuGeN}_2$: 859.3054, found: 859.3057 (err [ppm] = -0.37). Analysis calculated for $\text{C}_{53}\text{H}_{57}\text{CuGeN}_2$ (MW = 858.23 g/mol): Expected: C, 74.17; H, 6.69; N, 3.26. Found: C, 74.76; H, 7.05; N, 3.58. See figures S59-60 for full NMR spectra of **9**.

Synthesis of compound **10**, (IPr)CuC(H)=C(Ph)GePh₃

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.04 mmol) was dissolved in toluene (0.5 mL) and phenyl acetylene (3.5 μL , 0.03 mmol) was then added forming a colourless solution.

The reaction was left overnight at room temperature and was then transferred into J Young's NMR tube. Volatiles were removed *in vacuo* precipitating a white powder. The powder was redissolved in toluene (0.5 mL) and filtered forming a colourless solution. Single crystals of compound **10** that were suitable for characterisation by SC-XRD were grown from the slow diffusion of pentane into a saturated THF solution at -40 °C. Despite repeated attempts at purification, we were unable to isolate compound **10** from a mixture containing compound **9**, (IPr)CuCCPh, and PhC(GePh₃)=CH₂. See figures S19-S20 for the in-situ reaction ¹H NMR spectrum.

Reaction of compound **2** and Ph₃SnCl

In a vial in a glovebox, (IPr)CuGePh₃ (20 mg, 0.026 mmol) was dissolved in C₆D₆ (0.5 mL) and Ph₃SnCl (11 mg, 0.03 mmol) was then added forming a colourless solution. The reaction was then transferred into a J Young's NMR tube and was interrogated by ¹H and ¹¹⁹Sn NMR spectroscopy. An aliquot of the reaction mixture was dissolved in THF (1 mL) for investigation by mass spectrometry. MS (ESI) expected for Ph₃GeSnPh₃ [M+K]⁺ C₃₆H₃₀CuGeSnK: 693.0212, found: 693.0217 (err [ppm] = -1.52).

¹H NMR (500 MHz, C₆D₆) δ 7.71 – 7.50 (m, 15H, Ar-H), 7.11 – 7.06 (m, 15H, Ar-H); ¹¹⁹Sn NMR (186 MHz, C₆D₆) δ 160.3 (s, Ph₃GeSnPh₃). Resonances correspond to known literature data for Ph₃GeSnPh₃.⁵ See figures S8-S9 for the in-situ reaction NMR spectra.

Reaction of compound **2** and Ph₂PCI

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in C₆D₆ (0.5 mL) and Ph₂PCI (7.7 μL, 0.042 mmol) was then added forming a colourless suspension. The reaction was then transferred into a J Young's NMR tube and was interrogated by ¹H and ³¹P NMR spectroscopy. A second equivalent of Ph₂PCI (7.7 μL, 0.042 mmol) was then added and the reaction was interrogated by ¹H and ³¹P NMR spectroscopy. See figures S10-S11 for the in-situ reaction NMR spectra.

Reaction of compound **2** and carbon dioxide

In a vial in a glovebox, (IPr)CuGePh₃ (20 mg, 0.026 mmol) was dissolved in C₆D₆ (0.5 mL) and the resulting solution was transferred into a J Young's NMR tube. The solution was degassed, and an atmosphere of CO₂ was applied. The reaction was then interrogated by ¹H NMR spectroscopy at room temperature showing no reaction. See figure S12 for the in-situ reaction ¹H NMR spectrum.

¹H VT-NMR study of the reaction of compound **2** and carbon dioxide

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in toluene-d₈ (0.5 mL) and the resulting solution was transferred into a J Young's NMR tube. The solution was degassed, and an atmosphere of CO₂ was applied. The reaction was then and was interrogated by ¹H NMR spectroscopy at room temperature. The resulting reaction mixture was monitored at different temperatures (298 K, 273K, and 248 K) within an NMR spectrometer showing no reaction. See figure S13 for the in-situ reaction ¹H NMR spectra.

Reaction of compound **2** and di-iso-propyl carbodiimide

In a vial in a glovebox, (IPr)CuGePh₃ (19.5 mg, 0.026 mmol) was dissolved in C₆D₆ (0.5 mL) and di-iso-propyl carbodiimide (4.0 μL, 0.026 mmol) was then added. The reaction was then transferred into a J Young's NMR tube and was interrogated by ¹H NMR spectroscopy.

The reaction displayed no evidence of a reaction even after heating at 80 °C overnight. See figure S14 for the in-situ reaction ¹H NMR spectrum.

Thermolysis of compound 5

In a vial in a glovebox, (IPr)CuSC(=NtBu)GePh₃ (35 mg, 0.040 mmol) was dissolved in C₆D₆ (0.5 mL) and the solution was transferred into a J Young's NMR tube. The solution was heated at 120 °C for overnight and was monitored by ¹H NMR spectroscopy. No evidence of decomposition was observed. See figure S15 for the in-situ reaction ¹H NMR spectrum.

Reaction of compound 2 and phenyl isocyanate

In a vial in a glovebox, (IPr)CuGePh₃ (15.5 mg, 0.021 mmol) was dissolved in C₆D₆ (0.5 mL) and phenyl isocyanate (2.0 μL, 0.019 mmol) was then added forming a colourless solution. The reaction was then transferred into a J Young's NMR tube and was interrogated by ¹H NMR spectroscopy. The reaction mixture was left for 2 days at room temperature and a grey material precipitated out during the course of the reaction. An aliquot of the reaction mixture was dissolved in THF (1 mL) for investigation by mass spectrometry. MS (ESI) expected for Ph₄Ge [M+K]⁺ C₂₄H₂₀GeK: 420.0437, found: 420.0408 (err [ppm] = -4.00). See figure S16 for the in-situ reaction ¹H NMR spectrum.

Thermolysis study of compound 8

In a vial in a glovebox, (IPr)CuN(Ph)C(O)GePh₃ (4.4 mg, 0.005 mmol) was dissolved in C₆D₆ (0.5 mL) and was then transferred into a J Young's NMR tube. The resulting solution was heated at 120 °C for 4 days and was monitored by ¹H NMR spectroscopy. An aliquot of the reaction mixture was dissolved in THF (1 mL) for investigation by mass spectrometry. MS (ESI) expected for [PhNC(O)]₃ [M+H]⁺ C₂₁H₁₆N₃O₃: 358.1192, found: 358.1187 (err [ppm] = 0.31). See figure S17 for the in-situ reaction ¹H NMR spectrum.

Reaction of compound 1 and phenyl isocyanate

In a vial in a glovebox, (SIMes)CuGePh₃ (12 mg, 0.018 mmol) was dissolved in C₆D₆ (0.5 mL) and phenyl isocyanate (2.0 μL, 0.018 mmol) was then added forming a colourless solution. The reaction was then transferred into a J Young's NMR tube and was interrogated by ¹H NMR spectroscopy. Colourless crystals of (SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh₃, crystallised out of solution that were suitably single for characterisation by SC-XRD.

¹H NMR (500 MHz, C₆D₆) δ 8.09 – 8.03 (m, 6H, Ar-H), 7.27 – 7.19 (m, 9H, Ar-H), 6.98 – 6.86 (m, 6H, Ar-H), 6.72 – 6.59 (m, 4H, Ar-H), 6.56 – 6.42 (m, 2H, Ar-H), 6.42 – 6.39 (m, 2H, Ar-H), 2.84 (s, 4H, NCH₂), 2.03 (s, 6H, *para*-CH₃), 1.87 (s, 12H, *ortho*-CH₃). See figure S18 for the in-situ reaction ¹H NMR spectrum.

Reaction of compound 2 and phenyl acetylene at -40 °C

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in cold toluene-d₈ (0.5 mL) and the solution was cooled to -40 °C. Phenyl acetylene (3.5 μL, 0.032 mmol) was then added and the reaction mixture was left at -40 °C for three days. The reaction mixture was then transferred into a J Young's NMR tube and was monitored by ¹H NMR spectroscopy. For corresponding ¹H NMR spectrum, see Figure S13. See figure S19 for the in-situ reaction ¹H NMR spectrum.

Reaction of compound 2 and of phenyl acetylene at room temperature

In a vial in a glovebox, (IPr)CuGePh₃ (30 mg, 0.040 mmol) was dissolved in toluene-d₈ (0.5 mL) and phenyl acetylene (3.5 μL, 0.032 mmol) was added. The reaction was then transferred into a J Young's NMR tube and was monitored by ¹H NMR spectroscopy. Another equivalent of phenyl acetylene (3.5 μL, 0.032 mmol) was then added and the reaction mixture was interrogated by ¹H and ¹H-¹³C HSQC NMR spectroscopy.

An aliquot of the reaction mixture was dissolved in THF (1 mL) for investigation by mass spectrometry. MS (ESI) expected for $\text{PhC}(\text{GePh}_3)=\text{CH}_2$ $[\text{M}+\text{H}]^+$ $\text{C}_{26}\text{H}_{23}\text{Ge}$: 409.1012, found: 409.1018 (err [ppm] = 2.75). Selected ^1H NMR resonances (400 MHz, Toluene- d_8) δ 6.18 (m, 1H, CH), 5.65 (m, 1H, CH). For corresponding ^1H - ^{13}C HSQC NMR spectrum and full ^1H NMR spectral data, see Figures S20-S21.

Reaction of 10 mol% compound 2 with Ph_3GeH and phenyl acetylene

In a vial in a glovebox, $(\text{IPr})\text{CuGePh}_3$ (5.0 mg, 0.007 mmol) was dissolved in C_6D_6 (0.5 mL) and Ph_3GeH (20.0 mg, 0.070 mmol) was added. Phenyl acetylene (7.3 μL , 0.070 mmol) was then added and the reaction mixture was transferred into a J Young's NMR tube. The reaction was heated at 60 °C overnight and was monitored by ^1H NMR spectroscopy showing generation of *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene(phenylacetylido)copper(I) and no catalytic turnover. See figure S22 for the in-situ reaction ^1H NMR spectrum.

Reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and Ph_3SnCl

In a vial in a glovebox, (SIMes)CuOtBu (5 mg, 0.007 mmol) was dissolved in C_6D_6 (0.5 mL) forming a colourless solution. Ph_3GeH (22.6 mg, 0.074 mmol) and Ph_3SnCl (28.6 mg, 0.074 mmol) was then added. The reaction mixture was transferred into a J Young's NMR tube and was monitored by ^1H and ^{119}Sn NMR spectroscopy overnight at 60 °C showing no reaction. See figures S23-S24 for the in-situ reaction NMR spectra.

Reaction of (SIMes)CuOtBu with Ph_3GeH and Bu_3SnOMe

In a vial in a glovebox, (SIMes)CuOtBu (30 mg, 0.068 mmol) was dissolved in C_6D_6 (0.5 mL) forming a colourless solution. Ph_3GeH (21 mg, 0.068 mmol) and Bu_3SnOMe (19 μL , 0.068 mmol) was then added. The reaction mixture was transferred into a J Young's NMR tube and was interrogated by ^1H and ^{119}Sn NMR spectroscopy. See figures S25-S26 for the in-situ reaction NMR spectra.

$\text{Ph}_3\text{GeSnBu}_3$:

^1H NMR (500 MHz, C_6D_6) δ 7.66 – 7.61 (m, 6H, Ar-H), 7.22 – 7.18 (m, 6H, Ar-H), 7.15 – 7.11 (m, 3H, Ar-H), 1.59 – 1.50 (m, 6H, CH_2), 1.30 (s, 6H, CH_2), 1.20 (m, 15H, CH_2 with overlapped tBuOH), 0.81 (t, J = 7.3 Hz, 9H, CH_3). ^{119}Sn NMR spectrum (186 MHz, C_6D_6) δ -86.3 (m, $\text{Ph}_3\text{GeSnBu}_3$).

(SIMes)CuOMe:

^1H NMR (500 MHz, C_6D_6) δ 6.74 (s, 4H, *meta*-H), 3.45 (s, 3H, CuOCH_3), 3.08 (s, 4H, NCH_2), 2.14 – 2.10 (m, 18H, *ortho*- CH_3 and *para*- CH_3).

General Procedure for the Catalytic Cross Coupling Reactions

In a vial in a glovebox, Ph_3GeH (20.6 mg, 0.068 mmol) and the corresponding alkoxide (0.068 mmol) were combined in C_6D_6 (0.5 mL). (SIMes)CuOtBu (3 mg, 0.007 mmol) was then added, and the reaction mixture was transferred into a J Young's NMR tube. The reaction was monitored by ^1H (and ^{119}Sn NMR spectroscopy where relevant) until full conversion was reached. Spectroscopic yields were measured using 50 μL of a 1,3,5-trimethoxybenzene stock solution.

$\text{Ph}_3\text{GeSnBu}_3$

The reaction was conducted on a 2.33 mmol scale. Reaction was allowed to proceed at room temperature overnight before volatiles were removed *in vacuo* in order to push the reaction to completion.

^1H NMR (500 MHz, C_6D_6) δ 7.68 – 7.60 (m, 6H, Ar-H), 7.21 – 7.17 (m, 6H, Ar-H), 7.15 – 7.12 (m, 3H, Ar-H), 1.60 – 1.51 (m, 6H, CH_2), 1.31 – 1.25 (s, 6H, CH_2), 1.24 – 1.18 (, 6H, CH_2), 0.83 – 0.80 (t, $J = 7.3$ Hz, 9H, CH_3). ^{119}Sn NMR (186 MHz, C_6D_6) δ -86.3. ^{13}C NMR (126 MHz, C_6D_6) δ 140.0 (Ar-C), 135.7 (Ar-C), 128.8 (Ar-C), 128.7 (Ar-C), 30.43 (SnBu_3), 27.77 (SnBu_3), 13.82 (SnBu_3), 10.22 (SnBu_3). MS (ESI) $[\text{M}+\text{Cl}]^-$ $\text{C}_{30}\text{H}_{42}\text{GeSnCl}$: Expected: 627.1204, found: 627.1237 (err [ppm] = -1.31). Yield (79 mg, 0.13 mmol, 59 %). See figures S27-S28 for the in-situ reaction NMR spectra and figures S40-S42 for full NMR spectra $\text{Ph}_3\text{GeSnBu}_3$.

$\text{Ph}_3\text{GeSnPh}_3$

NMR data matched those in literature (see figures S29-S30 for the in-situ reaction NMR spectra). Yield (29.3 mg, 0.045 mmol, 66 %).

$\text{Bu}_2\text{Sn}(\text{OMe})_2$

0.034 mmol used. No conversion was observed even after heating at 60 °C overnight.

Ph_2SnO

0.034 mmol used. No conversion was observed at room temperature.

Ph_3GeOMe

5 mol% (SiMe_3) CuOtBu was used in this reaction. No conversion was observed even after heating to 60 °C overnight.

Me_3GeOMe

No conversion was observed even after heating at 80 °C overnight.

Ph_3SiOMe

No conversion was observed even after heating at 100 °C overnight.

Ph_2POEt

No conversion was observed even after heating at 80 °C overnight.

General Procedure for the Catalytic Hydrogermylation of Activated Alkenes

In the glovebox, HGePh_3 (20.6 mg, 0.068 mmol) and 1,3,5-trimethoxybenzene (~2 eq) were dissolved in 400 μL C_6D_6 (unless otherwise stated) and the corresponding alkene (0.068 mmol) was then added. The solution was transferred to a J. Young's NMR tube and a ^1H NMR spectroscopy experiment (using a delay of 25 seconds) was performed to obtain initial ratios of HGePh_3 , 1,3,5-trimethoxybenzene, and the unsaturated substrate. The sample was then returned to the glovebox where 10 mol% of (SiMe_3) CuOtBu (100 μL of a stock solution) was added. The reaction was then heated at 60 °C overnight unless otherwise stated. ^1H NMR spectroscopy was then taken (using a delay of 25 seconds) which provided a spectroscopic conversion and yield of the reaction.

$\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_3$, **11a**

Compound was contaminated with *ca.* 15 mol% **11c** caused by competing transesterification of **11a**.

^1H NMR (500 MHz, C_6D_6) δ 7.47 – 7.44 (m, 6H, Ar-H), 7.19 – 7.11 (m, 18H, Ar-H, and residual C_6H_6 solvent), 3.24 (s, 3H, OCH_3), 2.45 – 2.42 (m, 2H, CH_2), 1.85 – 1.80 (m, 2H, CH_2).

^{13}C NMR (126 MHz, C_6D_6) δ 174.0 (CO), 135.6 (Ar-C), 135.3 (Ar-C), 129.3 (Ar-C), 128.6 (Ar-C), 51.0 (OCH₃), 29.9 (CH₂), 9.3 (CH₂). MS (ESI) expected for $\text{C}_{22}\text{H}_{22}\text{GeO}_2\text{Na}$ [M+Na]⁺: 415.0729, found: 415.0725 (err [ppm] = 0.7). Conversion, >99 %; Yield, 91 %. See figures S61-62 for NMR spectra of **11a**.

Ph₃GeCH₂CH₂C(O)OCH₂CH₂, 11b

Compound was contaminated with *ca.* 11 mol% **11c** caused by competing transesterification of **11b**.

^1H NMR (400 MHz, C_6D_6) δ 7.49 – 7.45 (m, 6H, Ar-H), 7.19 – 7.10 (m, 18H, Ar-H and residual C_6H_6 solvent), 3.86 (q, 2H, $J = 7.1$ Hz, OCH₂), 2.50 – 2.46 (m, 2H, CH₂), 1.89 – 1.85 (m, 2H, CH₂), 0.89 (t, $J = 7.1$ Hz, 3H, CH₃). ^{13}C NMR (101 MHz, C_6D_6) δ 173.7 (CO), 136.8 (Ar-C), 135.3 (Ar-C), 129.3 (Ar-C), 128.6 (Ar-C), 60.2 (OCH₂), 30.2 (CH₂), 14.2 (CH₃), 9.3 (CH₂). MS (ESI) expected for $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C(O)OCH}_3$ [M+Na]⁺ $\text{C}_{23}\text{H}_{24}\text{GeO}_2\text{Na}$: 429.0886, found: 429.0910 (err [ppm] = -5.8). Conversion, >99 %; Yield, 77 %. See figures S63-64 for NMR spectra of **11b**.

Ph₃GeCH₂CH₂C(O)OC(CH₃)₃, 11c

^1H NMR (500 MHz, C_6D_6) δ 7.51 – 7.48 (m, 6H), 7.19 – 7.12 (m, 10H, Ar-H and residual C_6H_6 solvent), 2.54 – 2.51 (m, 2H, CH₂), 1.94 – 1.90 (m, 2H, CH₂), 1.33 (s, 9H, OC(CH₃)₃). ^{13}C NMR (126 MHz, C_6D_6) δ 173.3 (CO), 136.9 (Ar-C), 135.4 (Ar-C), 129.2 (Ar-C), 128.6 (Ar-C), 79.7 (OC(CH₃)₃), 31.3 (CH₂), 28.1 (OC(CH₃)₃), 9.3 (CH₂). MS (ESI) expected for $\text{Ph}_3\text{GeCH}_2\text{CH}_2\text{C(O)OC(CH}_3)_3$ [M+Na]⁺ $\text{C}_{25}\text{H}_{28}\text{GeO}_2\text{Na}$: 457.1199, found: 457.1192 (err [ppm] = 1.5). Conversion, >99 %; Yield, >99 %. See figures S65-66 for NMR spectra of **11c**.

Ph₃GeCH₂(CH₃)CHC(O)OCH₃, 11d

Reaction was heated at 100 °C for two days when full conversion was reached. Compound was contaminated with *ca.* 8 mol% $\text{Ph}_3\text{GeCH}_2(\text{CH}_3)\text{CHC(O)OC(CH}_3)_3$ from competing transesterification of **11d**. MS (ESI) expected for $\text{Ph}_3\text{GeCH}_2(\text{CH}_3)\text{CHC(O)OC(CH}_3)_3$ [M+Na]⁺ $\text{C}_{26}\text{H}_{30}\text{GeO}_2\text{Na}$: 471.1355, found: 471.1353 (err [ppm] = -0.16).

^1H NMR (500 MHz, C_6D_6) δ 7.56 – 7.52 (m, 6H, Ar-H), 7.17 – 7.13 (m, 12H, Ar-H and residual C_6H_6 solvent), 3.06 (s, 3H, OCH₃), 2.80 – 2.73 (m, 1H, CH), 2.12 – 2.02 (m, 1H, CH₂), 1.61 – 1.54 (m, 1H, CH₂), 1.13 – 1.11 (m, 3H, CHCH₃). ^{13}C NMR (126 MHz, C_6D_6) δ 176.6 (CO), 137.2 (Ar-C), 135.5 (Ar-C), 129.2 (Ar-C), 128.6 (Ar-C), 50.9 (OCH₃), 36.6 (CH), 21.1 (CHCH₃), 19.4 (CH₂). MS (ESI) expected for $\text{Ph}_3\text{GeCH}_2(\text{CH}_3)\text{CHC(O)OCH}_3$ [M+Na]⁺ $\text{C}_{23}\text{H}_{24}\text{GeO}_2\text{Na}$: 429.0886, found: 429.0899 (err [ppm] = -3.4). Conversion, >99 %; Yield, 82 %. See figures S67-68 for NMR spectra of **11d**.

Ph₃Ge(H₃C)CHCH₂C(O)OCH₃, 11e

No conversion was observed even after heating to 100 °C overnight.

Ph₃GeCH₂CH₂C(O)CH₃, 11f

Complete consumption of $\text{CH}_2\text{CH}_2\text{C(O)CH}_3$ was observed after heating to 80 °C for three days resulting in an intractable mixture. No consumption of Ph_3GeH was observed (see figure S31).

Ph₃GeCH₂CH₂C(O)NH₂, 11g

Reaction was conducted in THF-*d*₈ and was heated at 100 °C for seven days when full conversion was reached. ^1H NMR (500 MHz, THF) δ 7.52 – 7.46 (m, 6H, m Ar-H), 7.36 – 7.29 (m, 9H, Ar-H), 6.42 (s, 1H, NH), 5.98 (s, 1H, N-H), 2.27 – 2.23 (m, 2H, CH₂), 1.84 – 1.79 (m, 2H, CH₂).

^{13}C NMR (126 MHz, THF- d_8) δ 175.2 (CO), 138.0 (Ar-C), 135.9 (Ar-C), 129.8 (Ar-C), 129.1 (Ar-C), 31.6 (CH₂), 10.0 (CH₂). MS (ESI) expected for Ph₃GeCH₂CH₂C(O)NH₂ [M+Na]⁺ C₂₁H₂₁GeNONa: 400.0733, found: 400.0730 (err [ppm] = -0.2). Conversion, 99 %; Yield, 77 %. See figures S69-70 for NMR spectra of **11g**.

Ph₃GeCH₂CH₂C(O)NMe₂, 11h

^1H NMR (500 MHz, C₆D₆) δ 7.59 – 7.56 (m, 6H, Ar-H), 7.21 – 7.13 (m, 11H, Ar-H and residual C₆H₆ solvent), 2.56 (s, 3H, NCH₃), 2.27 – 2.24 (m, 2H, CH₂), 2.04 – 2.00 (m, 2H, CH₂), 1.96 (s, 3H, NCH₃). ^{13}C NMR (126 MHz, C₆D₆) δ 172.1 (CO), 137.5 (Ar-C), 135.5 (Ar-C), 129.2 (Ar-C), 128.6 (Ar-C), 35.9 (NCH₃), 35.0 (NCH₃), 28.9 (CH₂), 9.3 (CH₂). MS (ESI) expected for Ph₃GeCH₂CH₂C(O)NMe₂ [M+Na]⁺ C₂₃H₂₅GeNONa: 428.1046, found: 428.1045 (err [ppm] = 0.33). Conversion, >99 %; Yield, 97 %. See figures S71-72 for NMR spectra of **11h**.

Ph₃GeCH₂CH₂CN, 11i

Minimal conversion of CH₂CH₂CN was observed even after heating to 100 °C for three days (see figure S32).

4-(Ph₃GeCH₂CH₂)-C₅H₅N, 11j

Complete consumption of CH₂CH₂(4-C₅H₅N) was observed after heating to 60 °C for three days resulting in an intractable mixture (see figure S33).

2-(Ph₃GeCH₂CH₂)-C₅H₅N, 11k

Reaction was heated at 40 °C overnight when full conversion was reached.

^1H NMR (500 MHz, C₆D₆) δ 8.50 – 8.48 (m, 1H, Ar-H), 7.57 – 7.54 (m, 6H, Ar-H), 7.19 – 7.14 (m, 13H, Ar-H and residual C₆H₆ solvent), 7.00 – 6.96 (m, 1H, Ar-H), 6.61 – 6.56 (m, 2H, Ar-H), 3.09 – 3.05 (m, CH₂), 2.10 – 2.07 (m, 2H, CH₂). ^{13}C NMR (126 MHz, C₆D₆) δ 163.9 (CO), 149.7 (Ar-C), 137.5 (Ar-C), 135.7 (Ar-C), 135.4 (Ar-C), 129.2 (Ar-C), 128.6 (Ar-C), 128.4 (Ar-C), 122.2 (Ar-C), 120.9 (Ar-C), 34.1 (CH₂), 14.4 (CH₂). MS (ESI) expected for Ph₃GeCH₂CH₂(2-C₅H₅N) [M+Na]⁺ C₂₅H₂₃GeNNa: 434.0940, found: 434.0955 (err [ppm] = -3.6). Conversion, >99 %; Yield, 97 %. See figures S73-74 for NMR spectra of **11k**.

Ph₃GeCH₂CH₂Ph, 11l

No conversion was observed even after heating to 100 °C overnight.

X-ray crystallography

Data for compounds **2**, **3-8**, and (SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh₃ were obtained using an Agilent SuperNova instrument and a Cu-K α source while those for compounds **1** and **9-10** were obtained garnered with Mo-K α radiation on an Agilent Xcalibur diffractometer. All experiments were conducted at 150 K, solved using SHELXT² and refined using SHELXL² via the Olex2³ interface. Multiscan absorption corrections were employed throughout, *via* the CrysAlisPro (Rigaku) diffractometer software. While the majority of refinements were straightforward there are some points of particular note that merit special mention herein.

In the structure of compound **2**, it was noted that there are two molecules of the copper complex in the asymmetric unit. C11 and C12 were treated for 55:45 disorder with the inclusion of minimal distance and ADP restraints.

For compound **4**, premium sample quality and a routine data collection readily afforded the solution of the structure. The conundrum lay, therefore, with the maximum residual electron density peak located at a chemically insignificant distance (0.84 Å) from the germanium centre. Initial strategies were to consider some minor disorder with the (6-Dipp)HBr adduct (a synthetic precursor) or some by-product. Spectroscopically, the dissolved crystals did not evidence either scenario. Scrutiny of the frames indicated the presence of a second diffracting component that contributed so weakly to the pattern that it was only evident at low Bragg angles. Nonetheless, a twin integration was performed (followed by refinement) until convergence. However, this approach offered no significant change in the intensity or position of the residual electron-density maximum which was unsurprising given the paucity and intensity of the data from the second component. As a test, the data were integrated with triclinic symmetry and this illustrated that the residual electron-density maximum observed herein was also present for all four molecules in the *P1* asymmetric unit. There was no evidence for any twinning.

The asymmetric unit in compound **6** was seen to contain two independent molecules, with S4 (in the complex based on Cu2) necessitating treatment for 60:40 disorder. Distance and ADP restraints were employed, on merit, in this disordered region to assist convergence. The largest residual electron density peak lies at a chemically insignificant distance (0.90 Å) from Cu1. Attempts to model same as a being disordered with Cu1 indicated that any putative disorder was in the region of 4%. As such, a two-component treatment of this copper centre was abandoned as it would have been artificial rather than credible.

The structural solution of compound **7** proved unexpectedly problematic beyond the fact that C23 and C24 were treated for 50:50 disorder. The primary issue relates to smearing of the electron density in the region of the amide ligand, which may be indicative of some disorder or slight rockling/pendulous behaviour of this ligand. This is very evident in the bond precision observed for this region of the molecule wherein the phenyl ring based on C35 was refined as a rigid hexagon. The C34-C35 bond distance is long relative to what one might expect for the *sp*²-hybridised C34 and imposition of a bond-distance restraint had little impact on same. Efforts to model any disorder of the amide were not credible (< 10% occupancy of any putative second component) and, therefore, abandoned. The raw data were textbook in quality and there was no evidence of twinning. Integration in lower symmetries did nothing to improve the movement in the region of the amide, whatsoever. As such, incorrect space group assignment could be excluded. Ultimately, while this structure affords a chemical characterisation of compound **7**, no claims will be made with respect to the metrics withing the amide moiety for the aforementioned reasons.

There were two molecules present in the asymmetric unit of compound **8**, and, in the structure of compound **9**, the hydrogen atoms attached to C29 was located, and refined without restraints.

Refinement was straightforward in the structure of compound **10** with the only notable quirk being the residual electron density maximum. The location of said peak is chemically insignificant, but the location of same may point to some crystallographic disorder. Efforts to model this suggested that it would be in the region of 3% and, as such, disorder modelling was abandoned.

Finally, the asymmetric unit in (SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh₃ comprises one molecule of the copper complex and one molecule of deuterated benzene.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as the following supplementary CCDC publications: 2221285–2221292 for compound **1** (2221285), compound **2** (2221286), compound **3** (2221288), compound **4** (2221287), compound **5** (2221289), compound **6** (2221290), compound **7** (2221291), compound **8** (2249130), compound **9** (2221292), compound **10** (2249131) and (SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh₃ (2249132). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

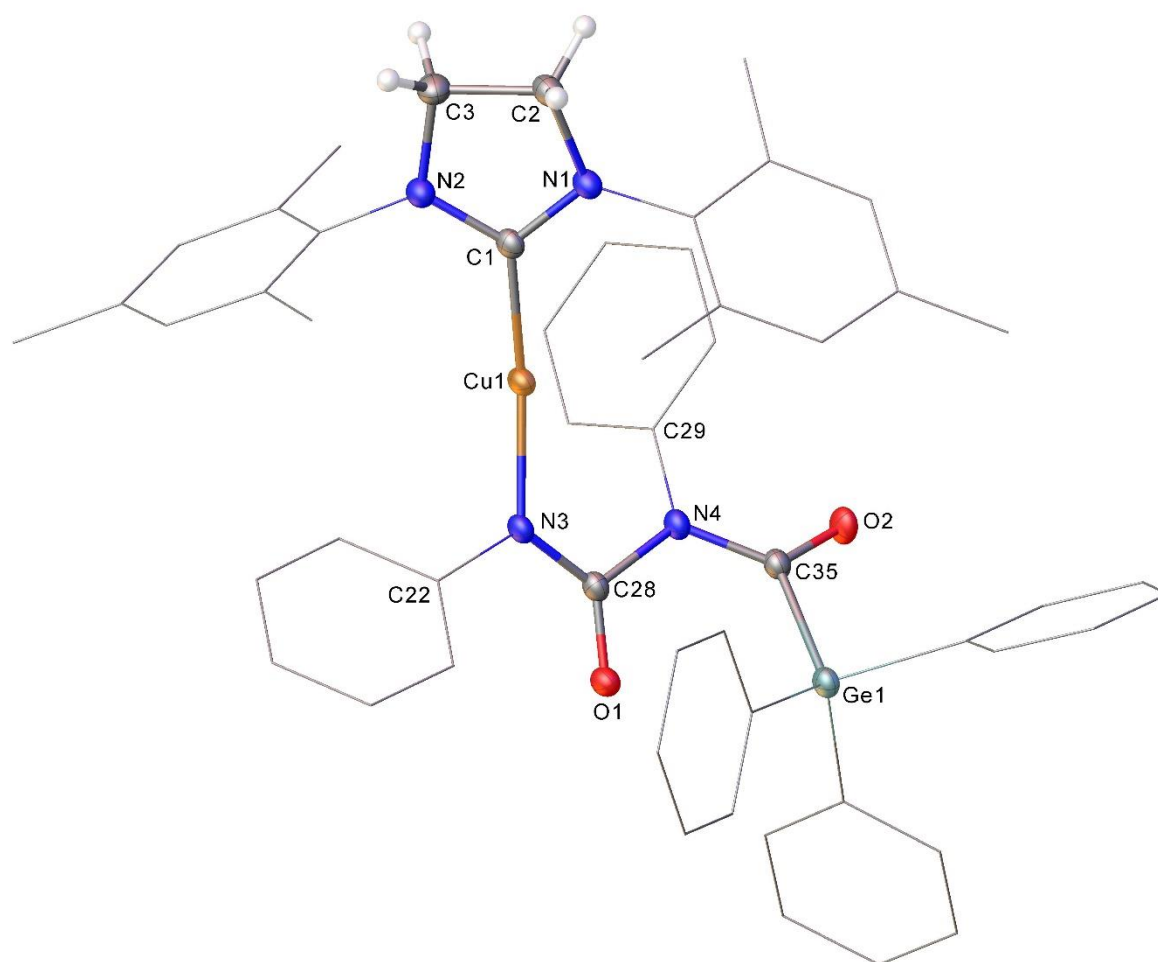


Figure S1. Molecular structure of (SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh₃. Hydrogen atoms have been omitted for clarity. The phenyl and carbene substituents are represented in wireframe view, for clarity. Ellipsoids are represented at 30% probability. Selected bond length (Å) and angle (°) data: C1-Cu1, 1.891(3); Cu1-N3, 1.903(2); N3-C28, 1.332(4); C28-O1, 1.229(4); C28-N4, 1.458(3); N4-C35, 1.384(4); C35-O2, 1.224(4); C35-Ge1, 2.002(3); C1-Cu1-N3, 165.69(11); N4-C35-Ge1, 123.5(2).

Table S1. Crystal data and structure refinement details

Identification code	1	2	3	4
Empirical formula	C ₃₉ H ₄₁ CuGeN ₂	C ₉₀ H ₁₀₂ Cu ₂ Ge ₂ N ₄	C ₄₀ H ₄₃ CuGeN ₂	C ₄₆ H ₅₅ CuGeN ₂
Formula weight	673.87	1512.01	687.89	772.05
Crystal system	triclinic	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i>/ Å	10.6500(4)	11.0264(1)	8.9616(1)	12.0126(1)
<i>b</i>/ Å	11.2963(4)	19.2655(3)	19.7494(1)	17.1438(1)
<i>c</i>/ Å	15.0976(5)	20.3965(3)	20.0400(2)	19.7933(1)
α/ °	111.368(3)	86.283(1)	90	90
β/ °	93.137(3)	77.281(1)	100.990(1)	90
γ/ °	92.330(3)	73.472(1)	90	90
<i>V</i>/ Å³	1685.35(11)	4051.84(10)	3481.76(6)	4076.26(5)
<i>Z</i>	2	2	4	4
ρ_{calc}/ g cm⁻³	1.328	1.239	1.312	1.258
μ/ mm⁻¹	1.551	1.785	2.025	1.784
<i>F</i>(000)	700.0	1584.0	1432.0	1624.0
Crystal size/ mm³	0.423 × 0.267 × 0.166	0.255 × 0.213 × 0.114	0.248 × 0.167 × 0.073	0.212 × 0.157 × 0.09
Radiation	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2θ range for data collection/°	5.812 to 60.584	8.558 to 146.696	8.956 to 145.086	6.822 to 145.22
Index ranges	-14 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -19 ≤ <i>l</i> ≤ 21	-9 ≤ <i>h</i> ≤ 13, -23 ≤ <i>k</i> ≤ 23, -25 ≤ <i>l</i> ≤ 24	-11 ≤ <i>h</i> ≤ 11, -24 ≤ <i>k</i> ≤ 16, -24 ≤ <i>l</i> ≤ 24	-14 ≤ <i>h</i> ≤ 14, -21 ≤ <i>k</i> ≤ 21, -24 ≤ <i>l</i> ≤ 21
Reflections collected	15653	48122	46335	45377
Independent reflections, <i>R</i>_{int}	8491, 0.0241	16059, 0.0274	6896, 0.0212	8021, 0.0368
Data/restraints/parameters	8491/0/394	16059/14/919	6896/0/403	8021/0/459
Goodness-of-fit on <i>F</i>²	1.040	1.065	1.081	1.121
Final <i>R</i>₁, <i>wR</i>₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0328, 0.0795	0.0348, 0.0924	0.0270, 0.0722	0.0564, 0.1432
Final <i>R</i>₁, <i>wR</i>₂ [all data]	0.0437, 0.0853	0.0372, 0.0943	0.0284, 0.0733	0.0566, 0.1433
Largest diff. peak/hole/ e Å⁻³	0.78/-0.41	0.78/-0.44	0.45/-0.23	2.86/-0.77
Flack Parameter	-	-	-	-0.01(2)
CCDC number	2221285	2221286	2221288	2221287

Table S2. Crystal data and structure refinement details

Identification code	5	6	7	8
Empirical formula	C ₅₀ H ₆₀ CuGeN ₃ S	C ₉₂ H ₁₀₂ Cu ₂ Ge ₂ N ₄ S ₄	C ₄₀ H ₄₆ CuN ₃ O	C ₁₀₄ H ₁₁₂ Cu ₂ Ge ₂ N ₆ O ₂
Formula weight	871.20	1664.27	648.34	1750.25
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	<i>P2₁/c</i>	<i>P</i> -1	<i>Pca2₁</i>	<i>P2/c</i>
<i>a</i>/ Å	10.22373(4)	13.1905(5)	16.2264(3)	13.3558(2)
<i>b</i>/ Å	20.07164(9)	18.6418(7)	10.8168(3)	18.1417(3)
<i>c</i>/ Å	22.27774(11)	20.1369(10)	20.4792(7)	38.4583(7)
α/ °	90	66.024(4)	90	90
β/ °	98.8634(4)	81.401(3)	90	99.0988(15)
γ/ °	90	69.363(4)	90	90
<i>V</i>/ Å³	4516.96(4)	4233.9(3)	3594.46(17)	9201.1(3)
<i>Z</i>	4	2	4	4
ρ_{calc}/ g cm⁻³	1.281	1.305	1.198	1.263
μ/ mm⁻¹	2.097	2.656	1.104	1.669
<i>F</i>(000)	1832.0	1736.0	1376.0	3664.0
Crystal size/ mm³	0.212 × 0.186 × 0.114	0.098 × 0.056 × 0.044	0.098 × 0.05 × 0.018	0.099 × 0.082 × 0.016
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2θ range for data collection/°	8.034 to 145.16	7.162 to 145.254	8.174 to 145.636	7.532 to 148.838
Index ranges	-12 ≤ <i>h</i> ≤ 10, -24 ≤ <i>k</i> ≤ 24, -26 ≤ <i>l</i> ≤ 27	-13 ≤ <i>h</i> ≤ 16, -18 ≤ <i>k</i> ≤ 22, -24 ≤ <i>l</i> ≤ 24	-12 ≤ <i>h</i> ≤ 20, -13 ≤ <i>k</i> ≤ 12, -25 ≤ <i>l</i> ≤ 23	-16 ≤ <i>h</i> ≤ 13, -20 ≤ <i>k</i> ≤ 22, -30 ≤ <i>l</i> ≤ 47
Reflections collected	64057	31199	23418	41435
Independent reflections, <i>R</i>_{int}	8941, 0.0194	16439, 0.0251	6888, 0.0370	17933, 0.0395
Data/restraints/parameters	8941/0/516	16439/7/962	6888/91/421	17933/0/1061
Goodness-of-fit on <i>F</i>²	1.056	1.015	1.045	1.014
Final <i>R</i>₁, <i>wR</i>₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0288, 0.0738	0.0383, 0.0923	0.0522, 0.1377	0.0476, 0.1123
Final <i>R</i>₁, <i>wR</i>₂ [all data]	0.0294, 0.0743	0.0469, 0.0978	0.0615, 0.1468	0.0748, 0.1257
Largest diff. peak/hole/ e Å⁻³	0.48/-0.33	1.60/-0.84	0.70/-0.36	0.42/-0.45
Flack Parameter	-	-	0.01(2)	-
CCDC number	2221289	2221290	2221291	2249130

Table S3. Crystal data and structure refinement details

Identification code	9	10	(SIMes)CuN(Ph)C(O)N(Ph)C(O)GePh ₃
Empirical formula	C ₅₃ H ₅₇ CuGeN ₂	C ₅₃ H ₅₇ CuGeN ₂	C ₅₉ H ₅₇ CuGeN ₄ O ₂
Formula weight	858.13	858.13	990.21
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> / Å	14.9501(3)	12.3095(2)	11.4816(1)
<i>b</i> / Å	19.7103(3)	19.8911(3)	30.4535(2)
<i>c</i> / Å	16.1176(3)	18.5854(4)	14.2528(1)
α / °	90	90	90
β / °	105.269(2)	91.1959(18)	94.8925(7)
γ / °	90	90	90
<i>V</i> / Å ³	4581.73(15)	4549.62(15)	4965.40(6)
<i>Z</i>	4	4	4
ρ_{calc} / g cm ⁻³	1.244	1.253	1.325
μ / mm ⁻¹	1.156	1.164	1.635
<i>F</i> (000)	1800.0	1800.0	2064.0
Crystal size/ mm ³	0.429 × 0.274 × 0.261	0.302 × 0.288 × 0.129	0.241 × 0.087 × 0.053
Radiation	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)
2 θ range for data collection/°	5.938 to 60.668	5.916 to 58.26	6.868 to 147.15
Index ranges	-21 ≤ <i>h</i> ≤ 21, -25 ≤ <i>k</i> ≤ 26, -21 ≤ <i>l</i> ≤ 22	-16 ≤ <i>h</i> ≤ 16, -25 ≤ <i>k</i> ≤ 26, -25 ≤ <i>l</i> ≤ 22	-14 ≤ <i>h</i> ≤ 11, -37 ≤ <i>k</i> ≤ 37, -17 ≤ <i>l</i> ≤ 17
Reflections collected	41691	44765	78090
Independent reflections, <i>R</i> _{int}	12097, 0.0261	11791, 0.0440	9988, 0.0490
Data/restraints/parameters	12097/0/526	11791/0/526	9988/0/610
Goodness-of-fit on <i>F</i> ²	1.023	1.099	1.163
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0323, 0.0711	0.0531, 0.1142	0.0512, 0.1262
Final <i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0510, 0.0798	0.0950, 0.1290	0.0545, 0.1281
Largest diff. peak/hole/ e Å ⁻³	0.43/-0.36	1.33/-0.39	1.17/-0.47
Flack Parameter	-	-	-
CCDC number	2221292	2249131	2249132

In situ reaction monitoring by NMR spectroscopy

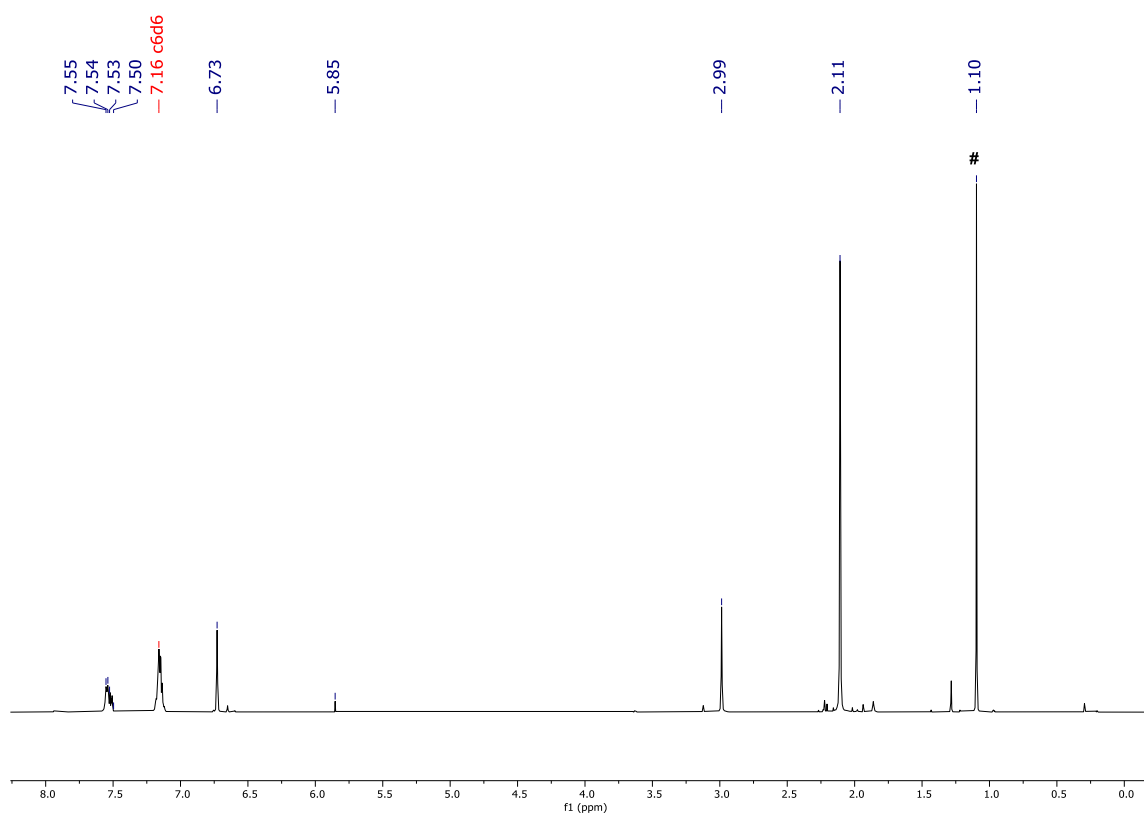


Figure S2. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $(\text{SIMes})\text{CuOtBu}$ and Ph_3GeH after heating for 3 days at 40°C . # = HOtBu .

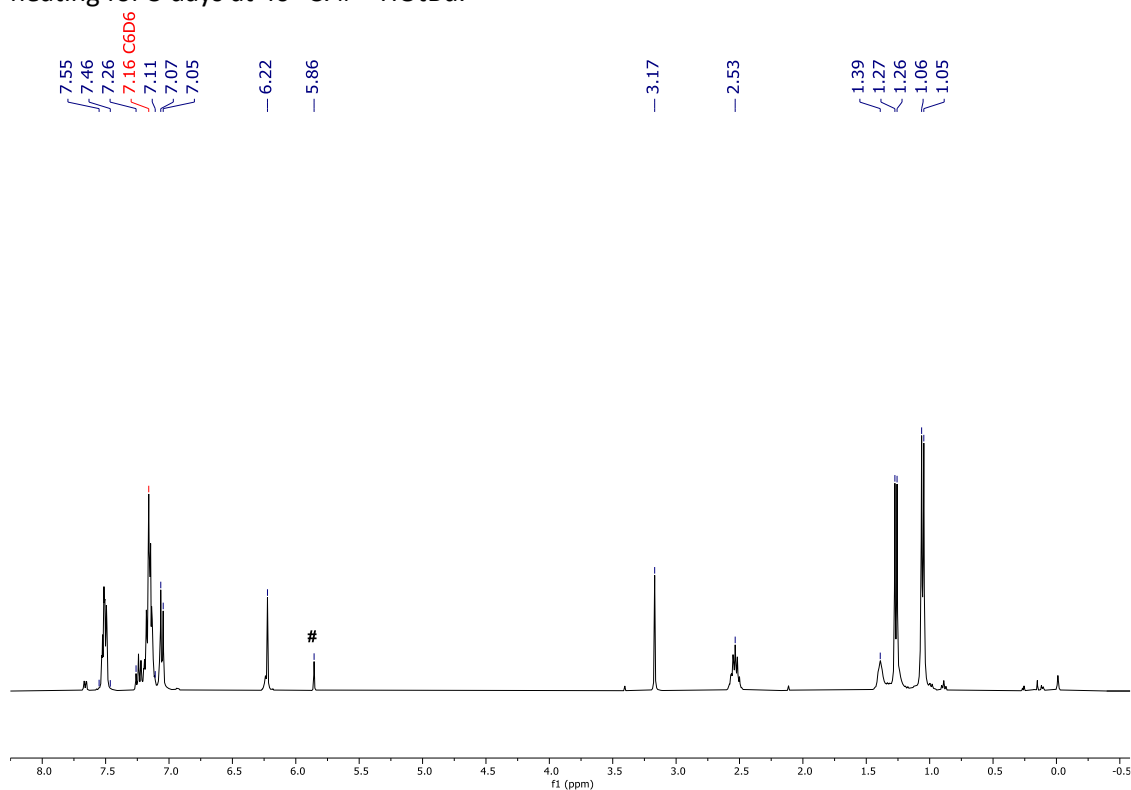


Figure S3. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $(\text{IPr})\text{CuOMe}$ and Ph_3GeH after 3 days at room temperature. # = residual Ph_3GeH .

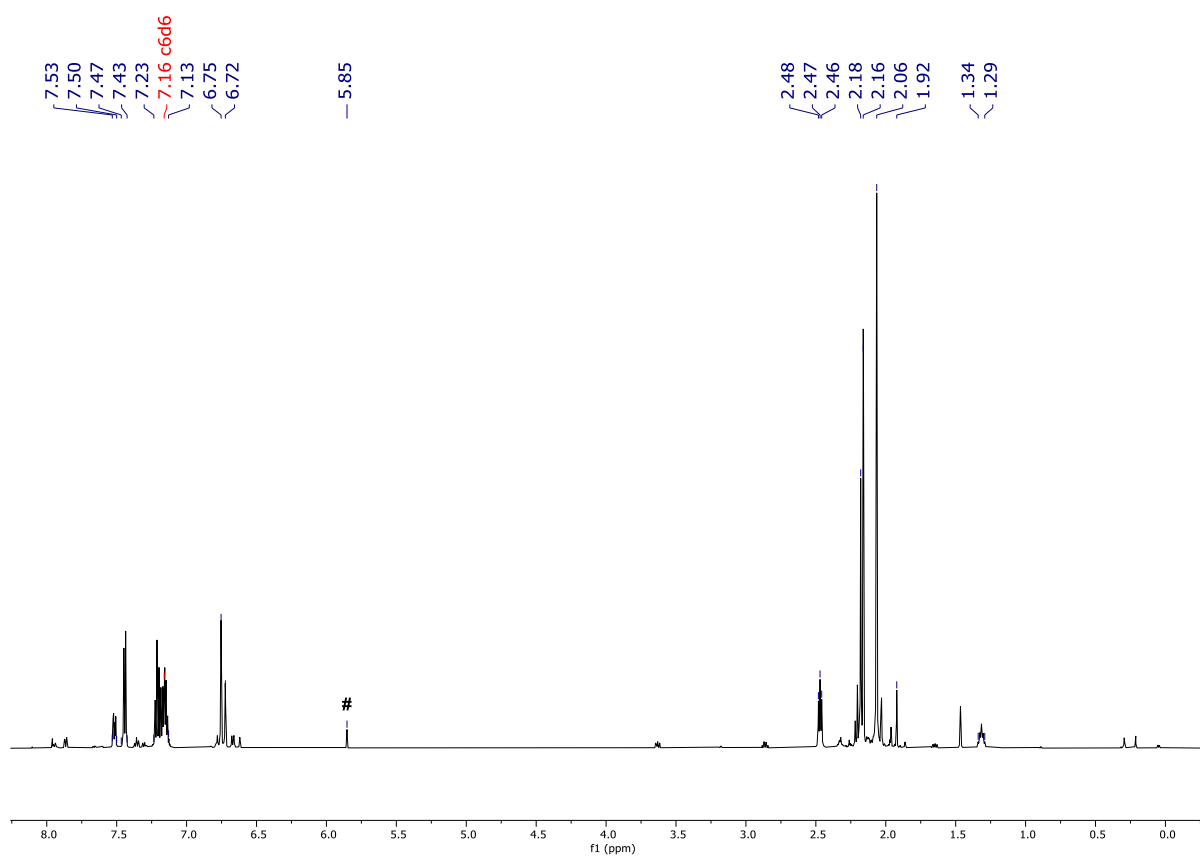


Figure S4. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of (6-Mes)CuMes and Ph_3GeH after heating for 2 days at 40 °C. # = residual Ph_3GeH .

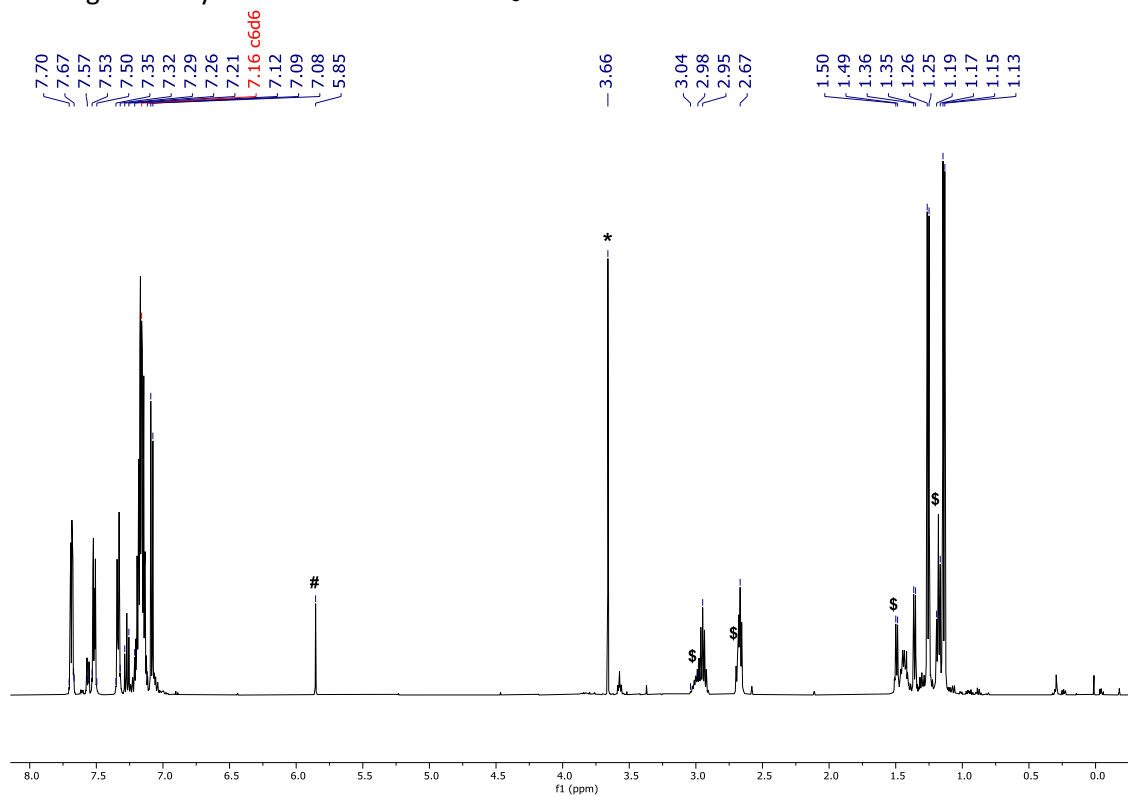


Figure S5. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of (6-Dipp)CuOMe and Ph_3GeH after heating for 3 days at 60 °C. # = residual Ph_3GeH ; * = methanol; § = residual (6-Dipp)CuOMe.

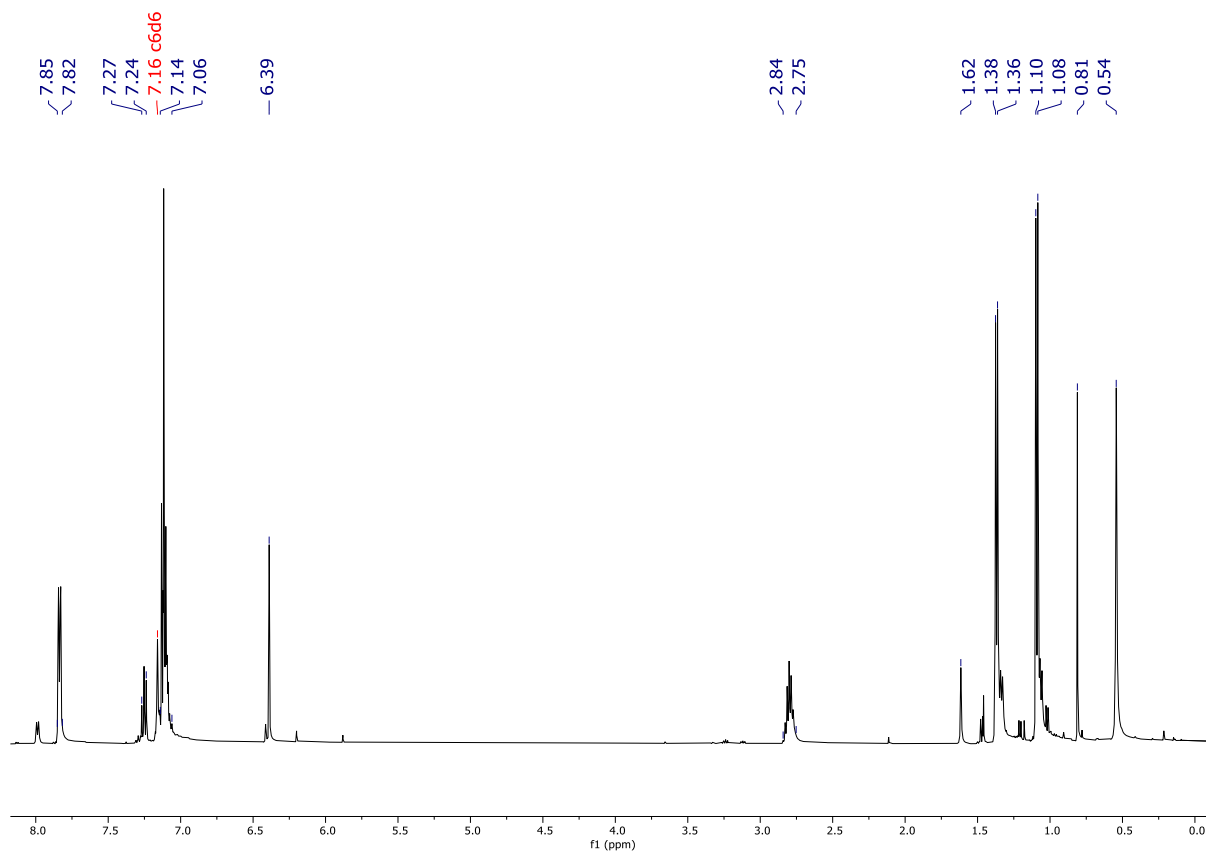


Figure S6. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $(\text{IPr})\text{CuGePh}_3$ and tBuNCS after heating for 10 days at $40\text{ }^\circ\text{C}$.

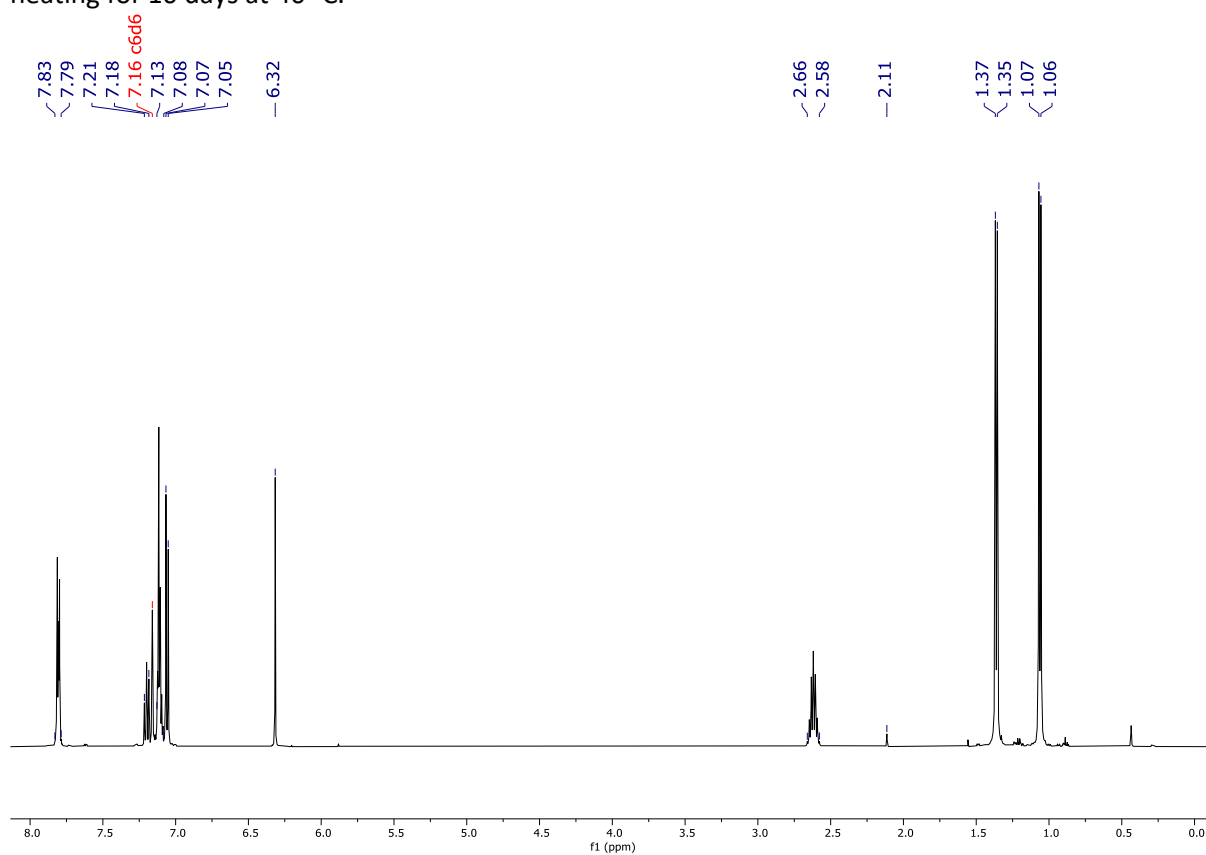


Figure S7. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of $(\text{IPr})\text{CuGePh}_3$ and CS_2 at room temperature.

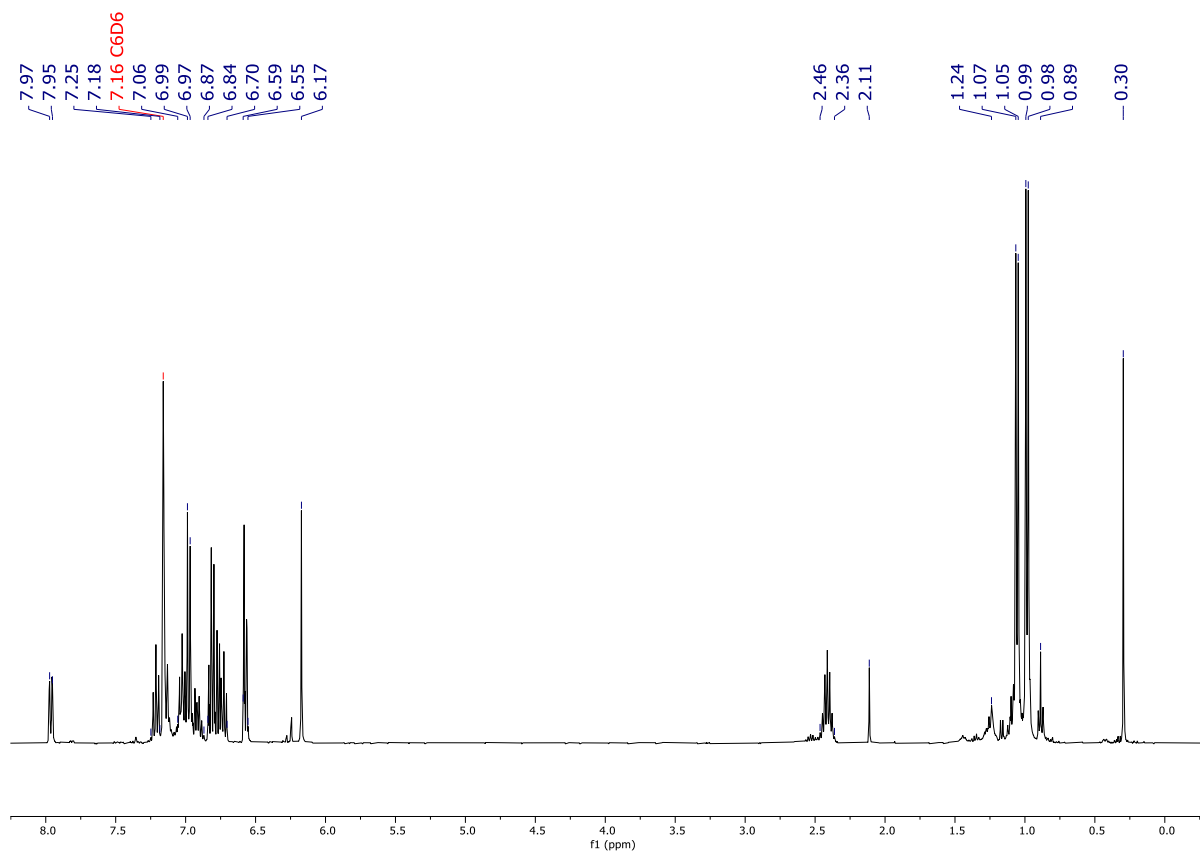


Figure S8. The ^1H NMR spectra (400 MHz, C_6D_6) of the reaction of (IPr)CuPh and PhNCO at room temperature.

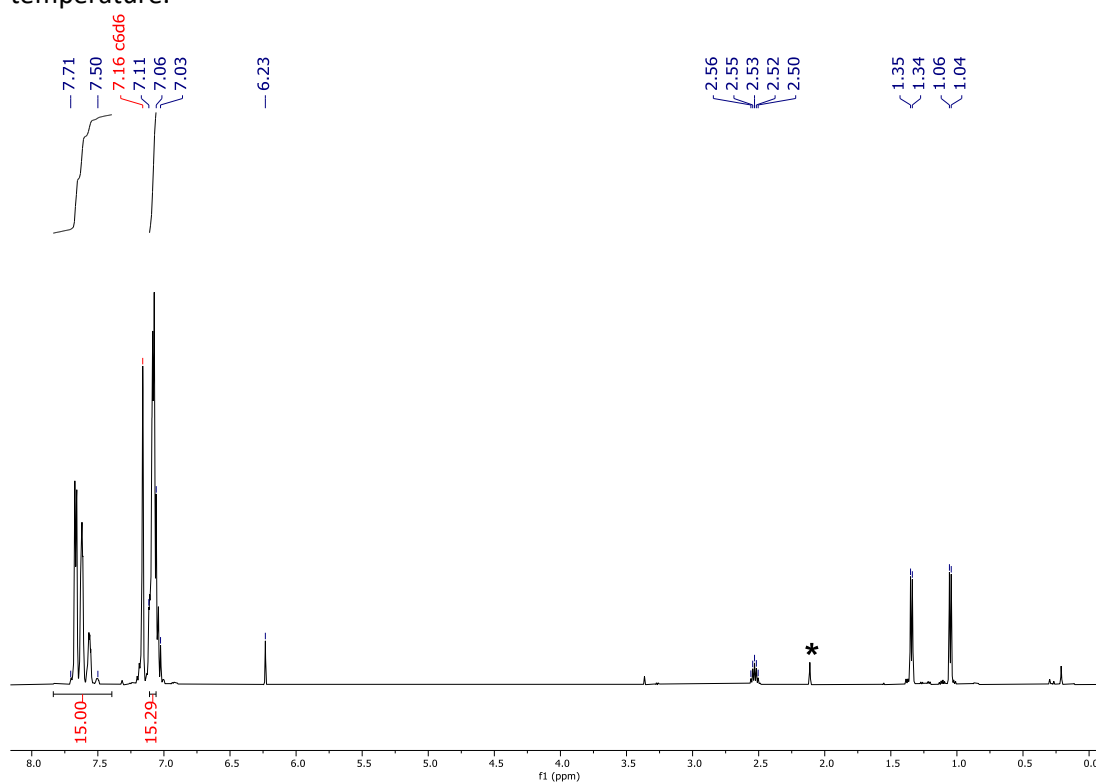


Figure S9. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **2** and Ph_3SnCl . Integrated resonances correspond to $\text{Ph}_3\text{GeSnPh}_3$.⁵ Non-integrated resonances correspond to (IPr)CuCl.⁶ * = residual toluene.⁴

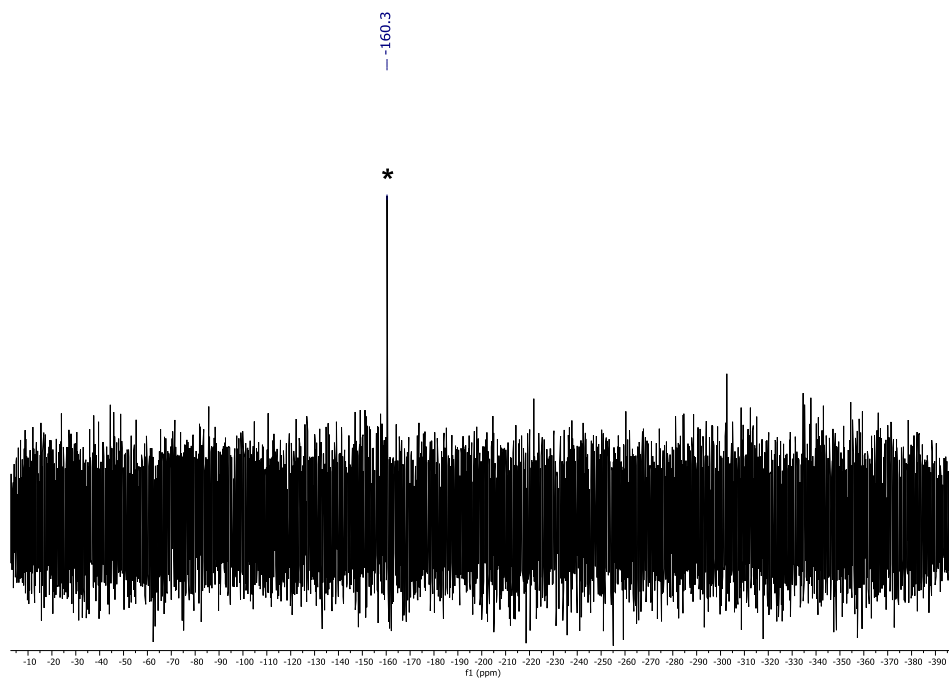


Figure 10. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of the reaction of compound **2** and Ph_3SnCl . * = $\text{Ph}_3\text{GeSnPh}_3$.⁵

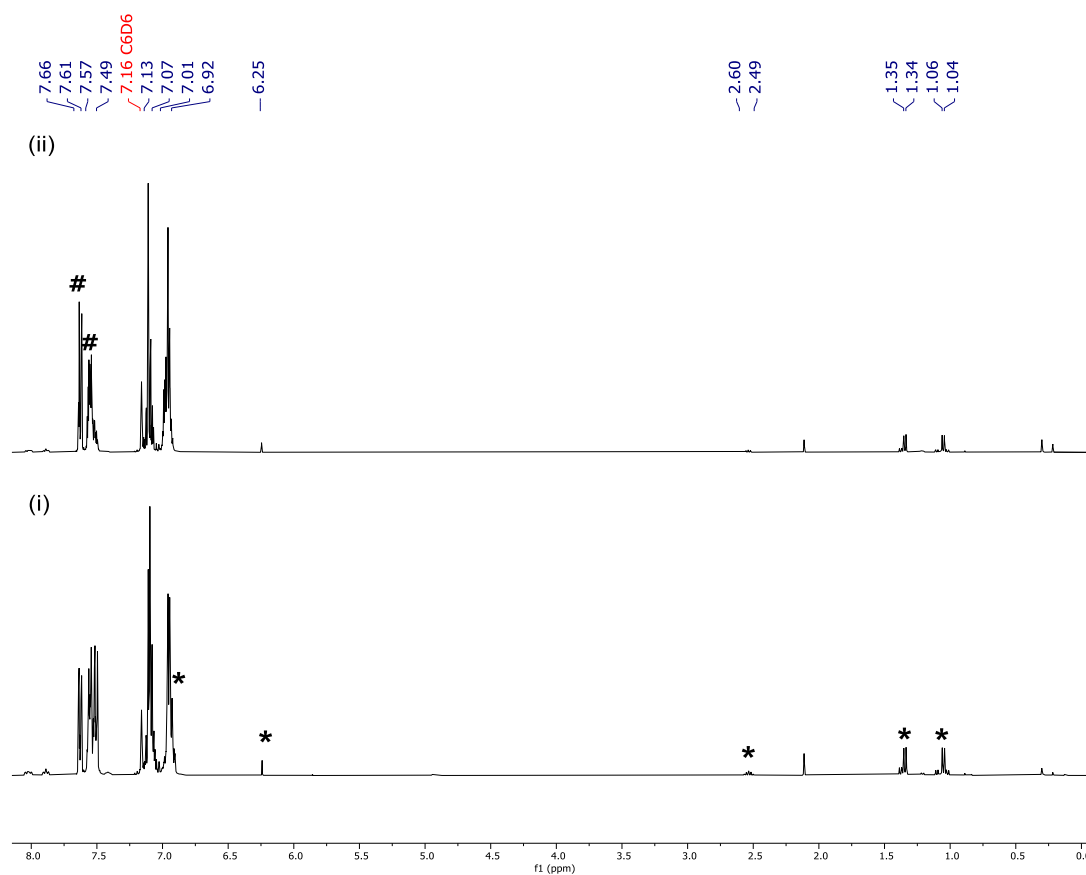


Figure S11. The ^1H NMR spectra (400 MHz, C_6D_6) of the reaction of compound **2** and Ph_2PCl . (i) = After one equivalent of Ph_2PCl . (ii) = After a second equivalent of Ph_2PCl . * = $(\text{IPr})\text{CuCl}$.⁶ # = Ph_3GeCl .⁷

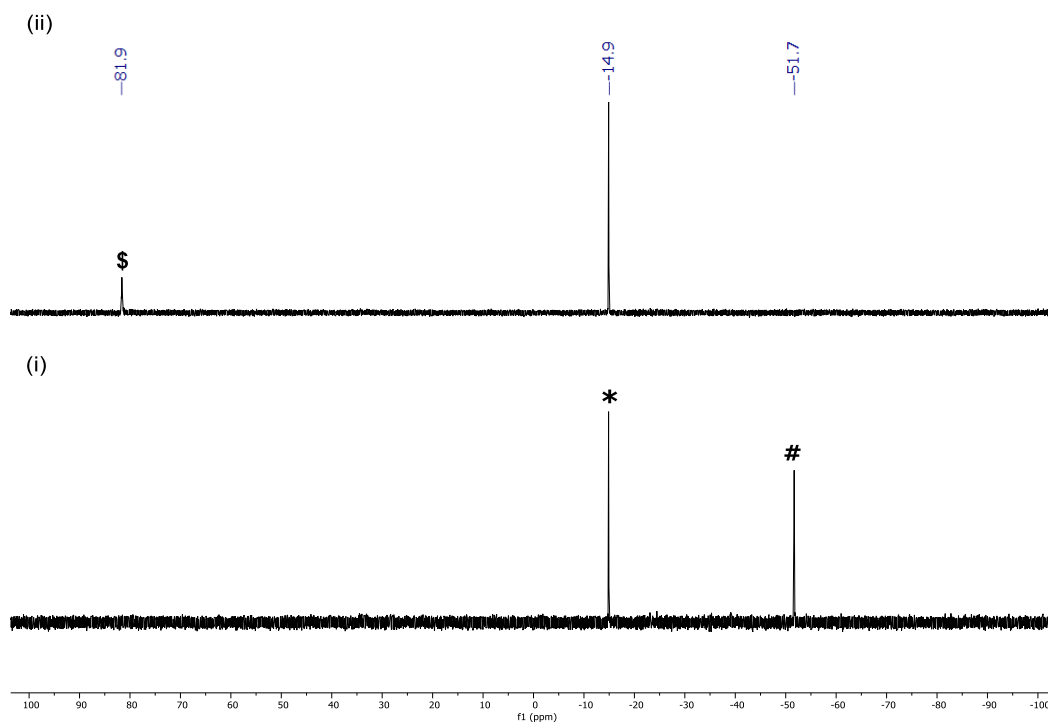


Figure S12. The ^{31}P NMR spectra (162 MHz, C_6D_6) of the reaction of compound **2** and Ph_2PCl . (i) = Addition of one equivalent of Ph_2PCl ; (ii) = Addition of a second equivalent of Ph_2PCl . \$ = Excess Ph_2PCl . * = Ph_2PPPh_2 . # = $\text{Ph}_2\text{PGePh}_3$.

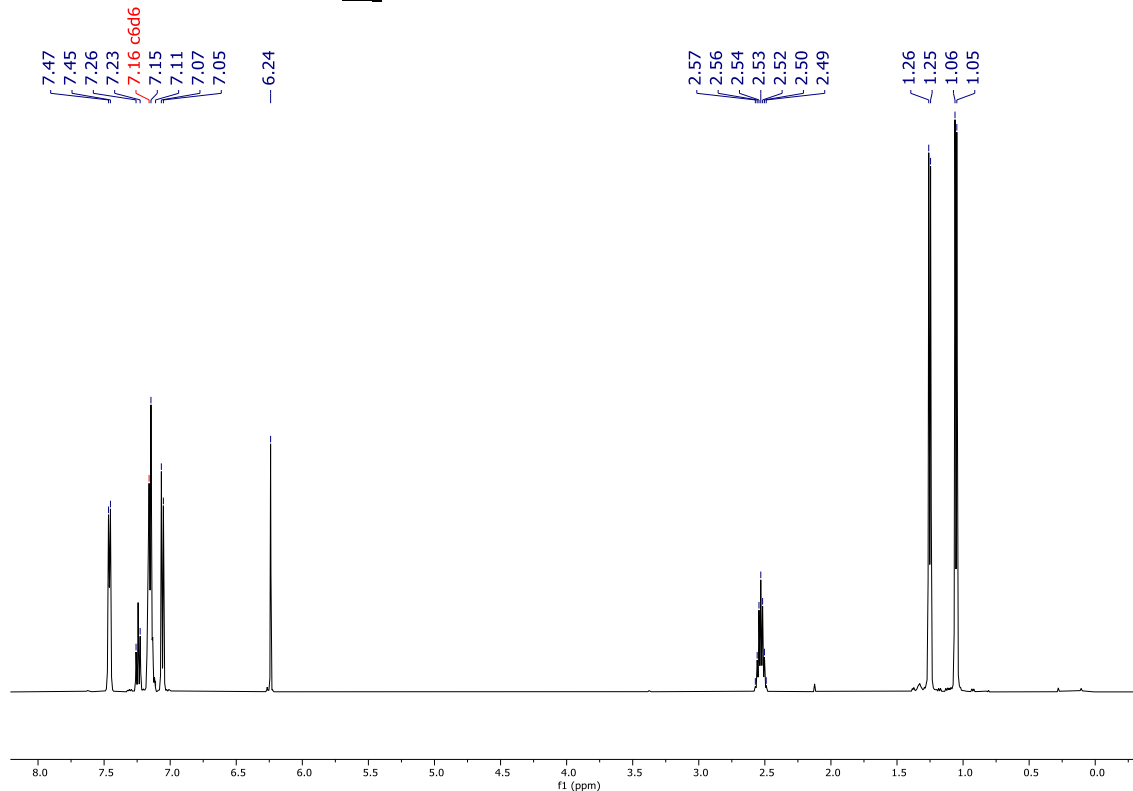


Figure S13. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **2** and carbon dioxide.

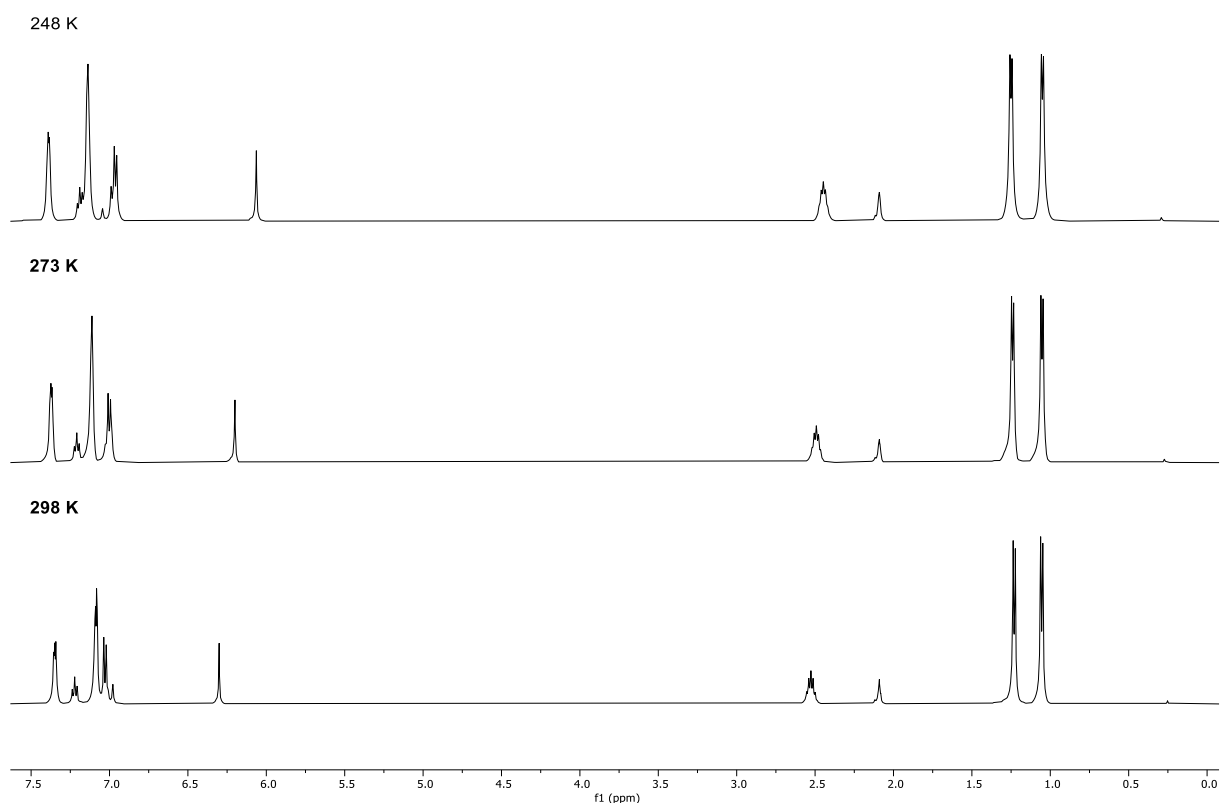


Figure S14. The ^1H VT-NMR spectrum (500 MHz, toluene- d_8) of the reaction of compound **2** and carbon dioxide.

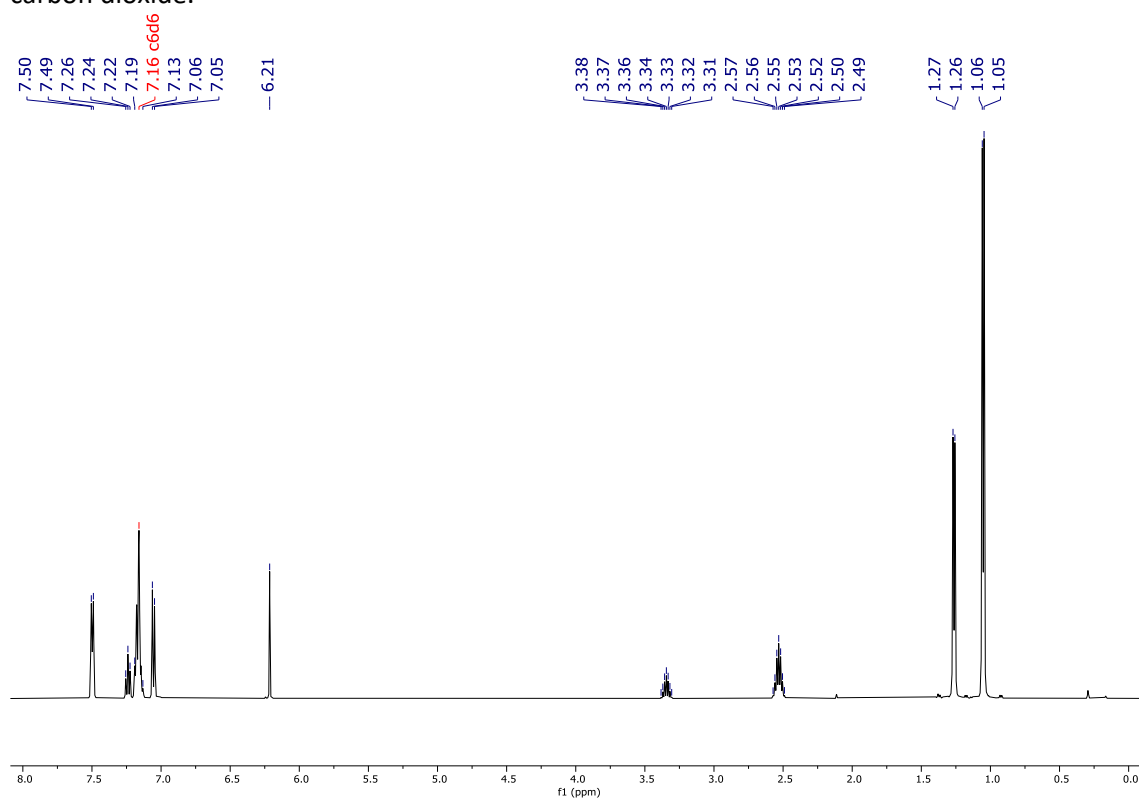


Figure S15. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **2** and di-iso-propyl carbodiimide at room temperature.

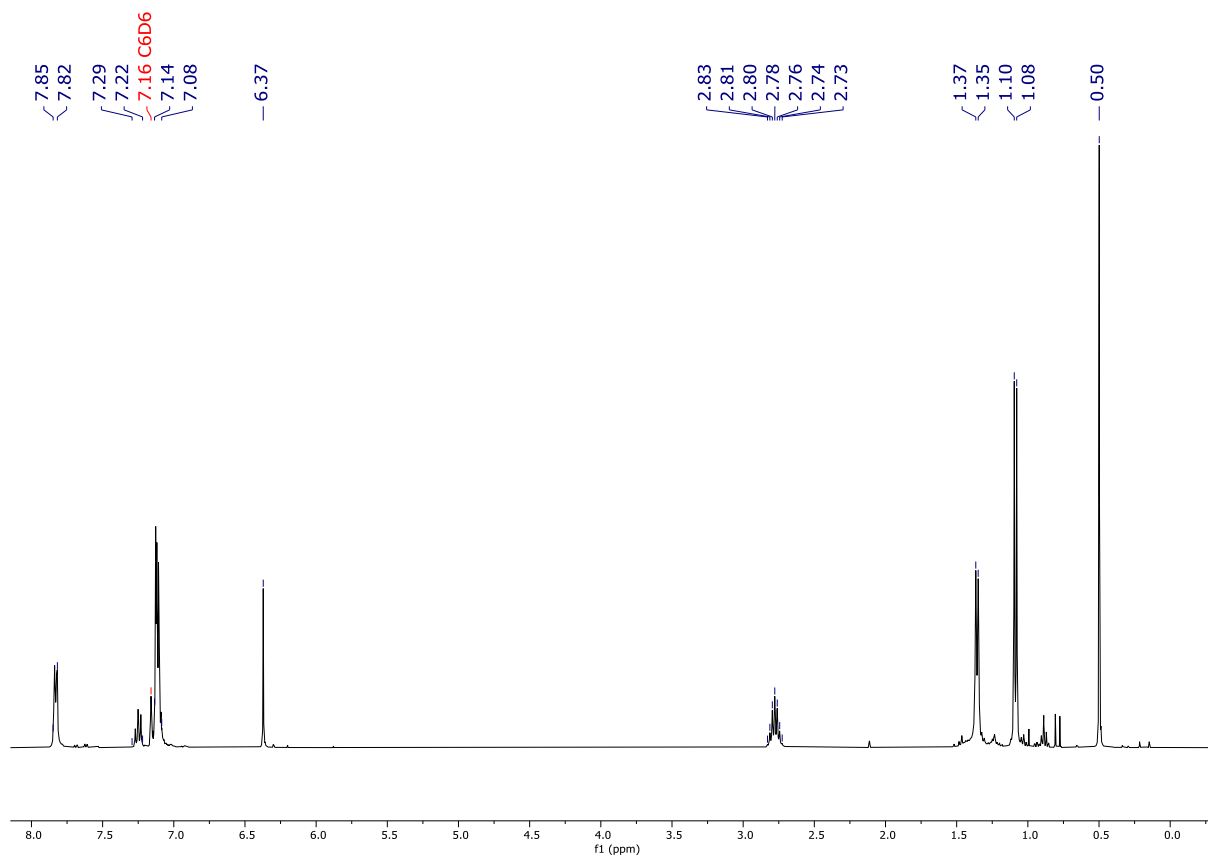


Figure S16. The ^1H NMR spectrum (400 MHz, C_6D_6) of compound **5** after heating at 120 °C overnight.

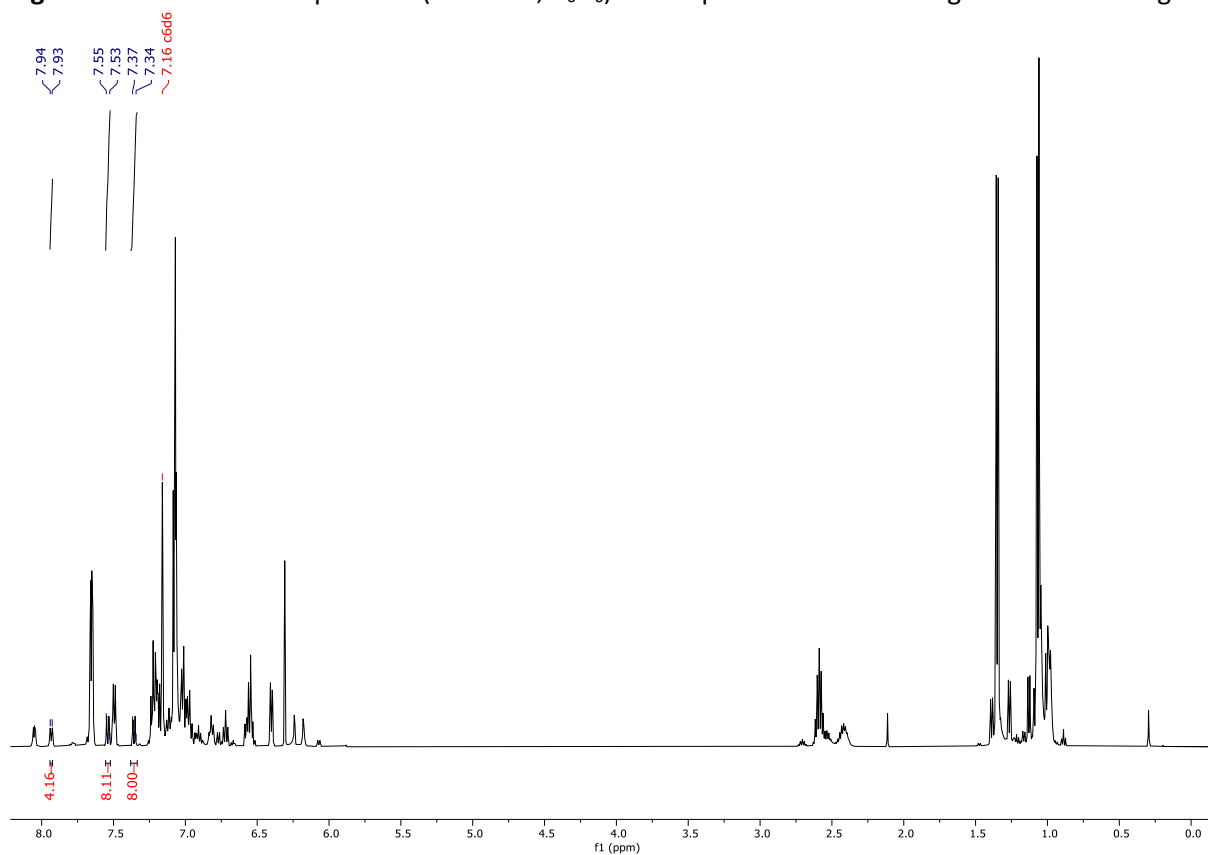


Figure S17. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **2** and phenyl isocyanate. Integrated resonances correspond to Ph_4Ge .⁹

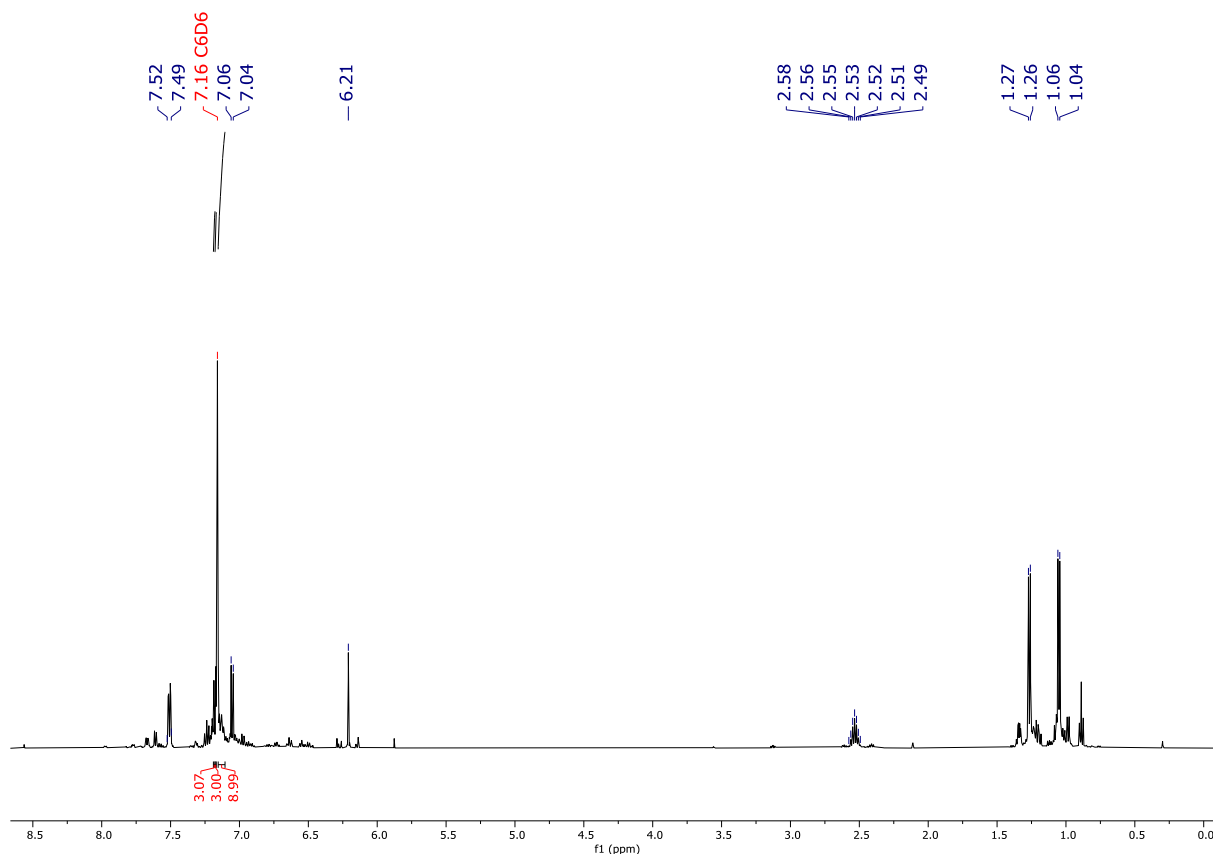


Figure S18. The ^1H NMR spectrum (500 MHz, C_6D_6) of compound **8** after heating at 120 $^\circ\text{C}$ for 4 days. Integrated resonances correspond to $[\text{PhNCO}]_3$.¹⁰

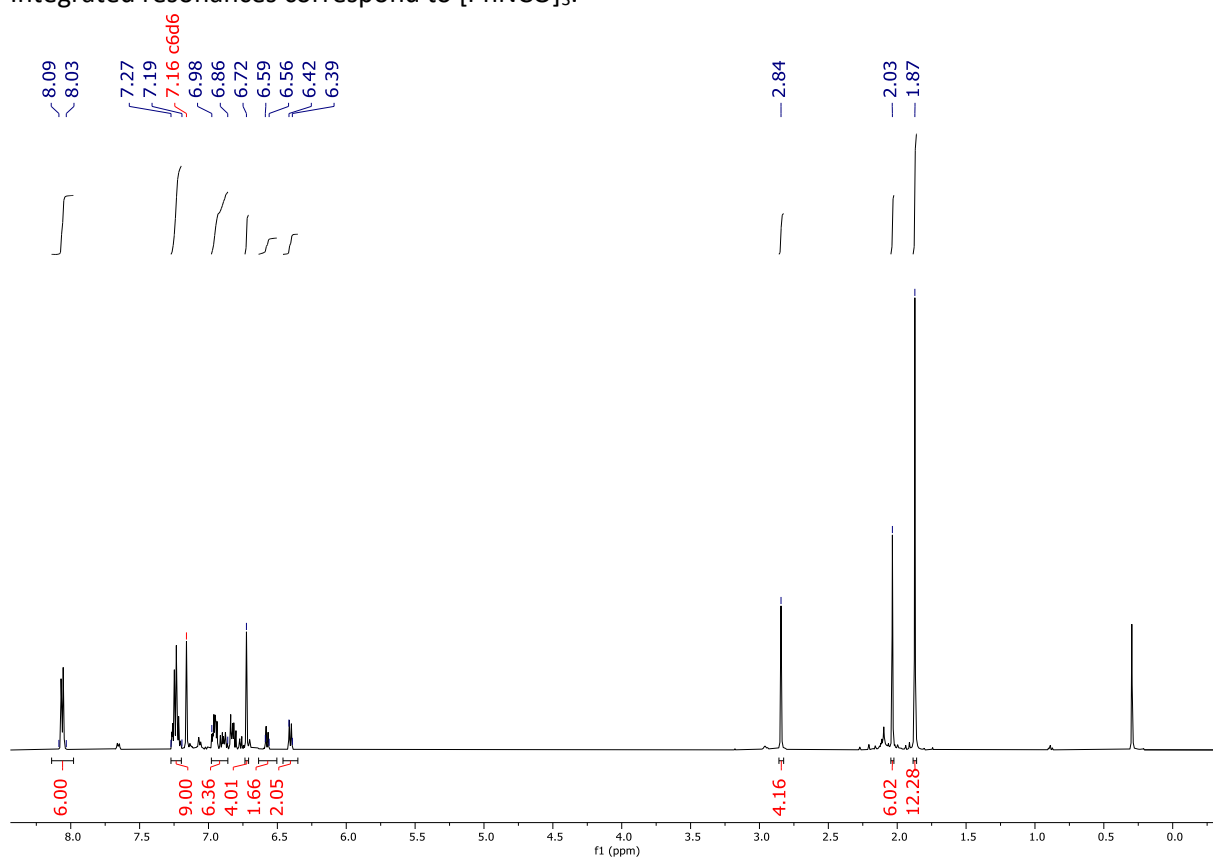


Figure S19. The ^1H NMR spectrum (500 MHz, C_6D_6) of compound **1** and PhNCO. Integrated resonances correspond to $(\text{SiMe}_3)\text{CuN}(\text{Ph})\text{C}(\text{O})\text{N}(\text{Ph})\text{C}(\text{O})\text{GePh}_3$.

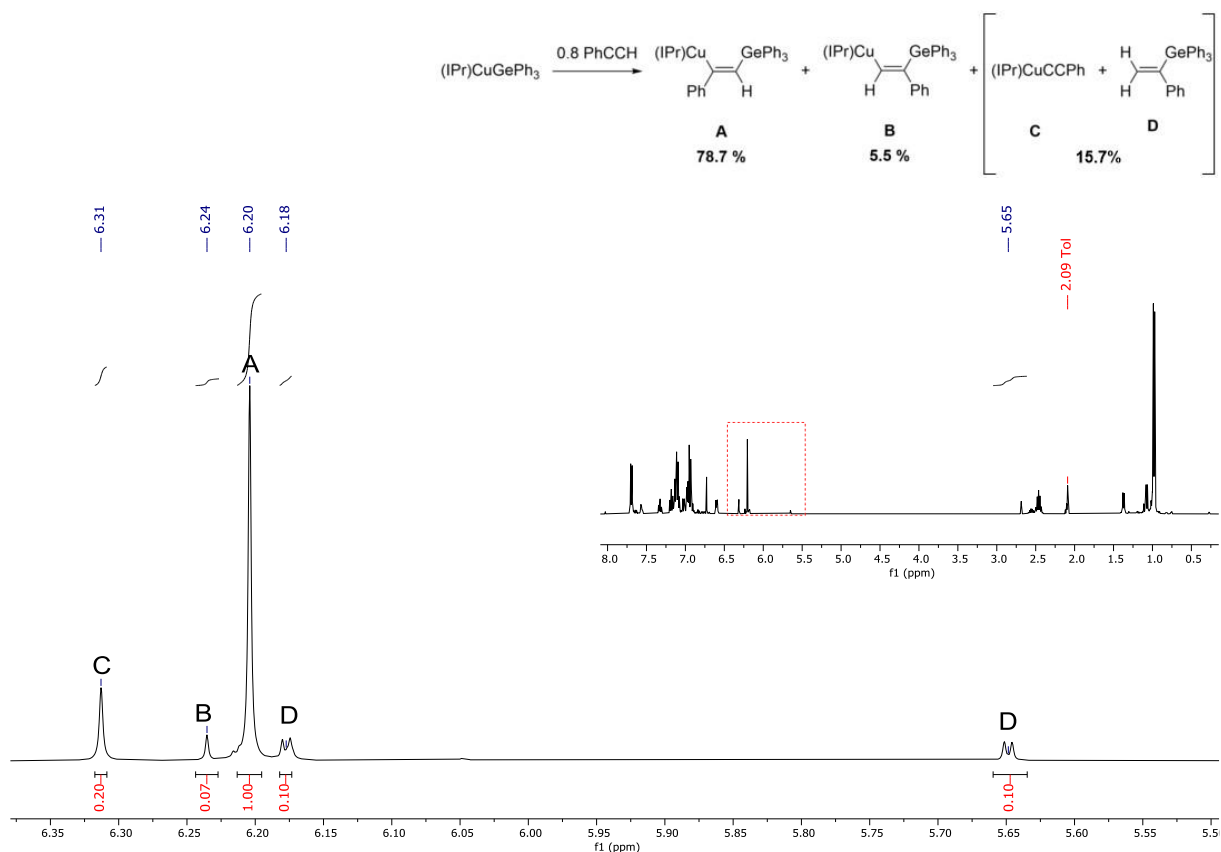


Figure S20. The ^1H NMR spectrum (400 MHz, Toluene- d_8) of the reaction of compound **2** and 0.8 equivalents of phenyl acetylene at -40°C . Ratio of product yields are illustrated A-D.¹¹

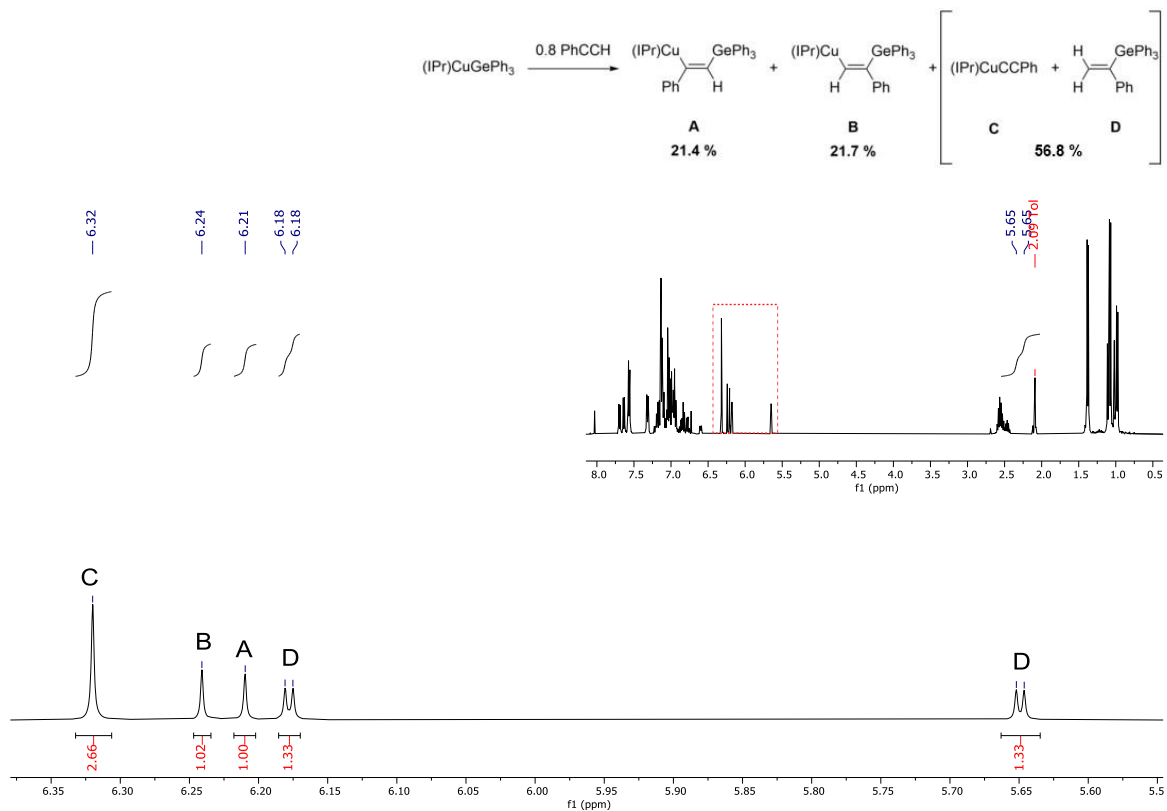


Figure S21. The ^1H NMR spectrum (400 MHz, Toluene- d_8) of the reaction of compound **2** and 0.8 equivalents of phenyl acetylene at room temperature. Ratio of product yields are illustrated A-D.¹

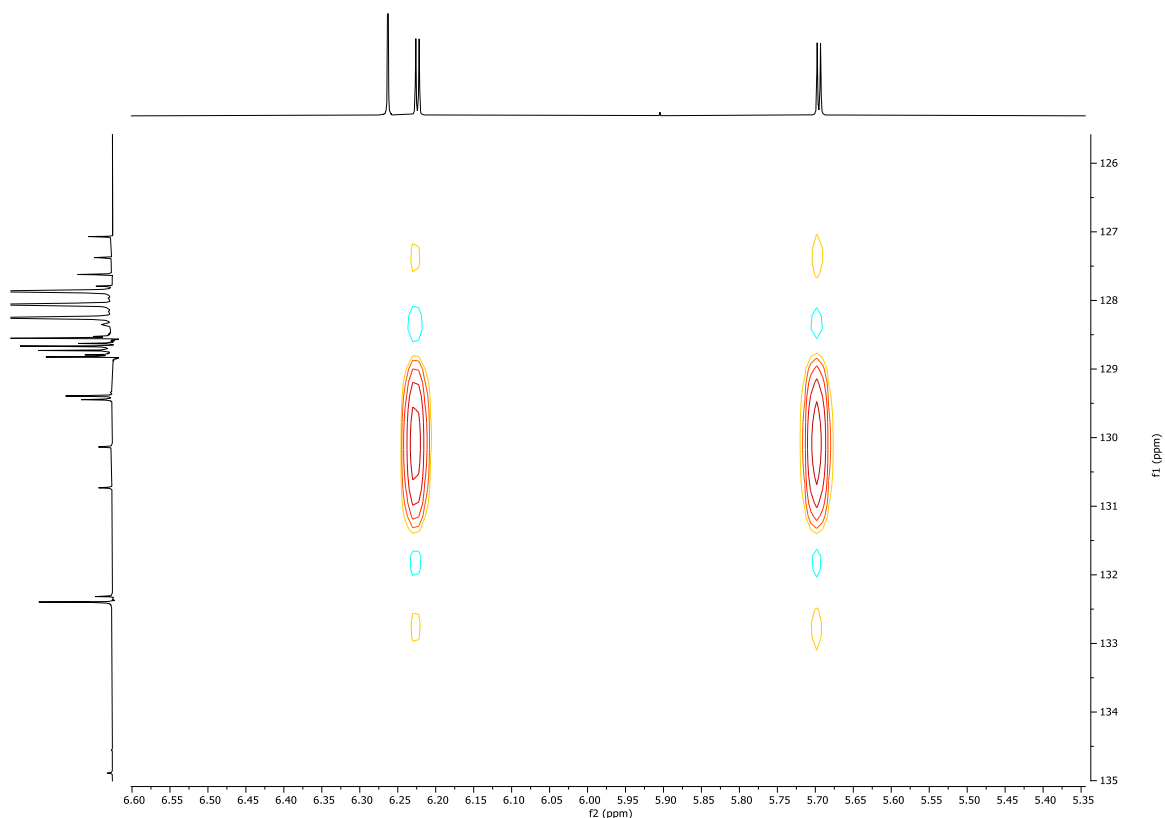


Figure S22. The ^1H - ^{13}C HSQC NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **2** and two equivalents of phenyl acetylene after 3 days at room temperature for confirmation of the geometry of compound **D**, $\text{PhC}(\text{GePh}_3)=\text{CH}_2$, figure S14.

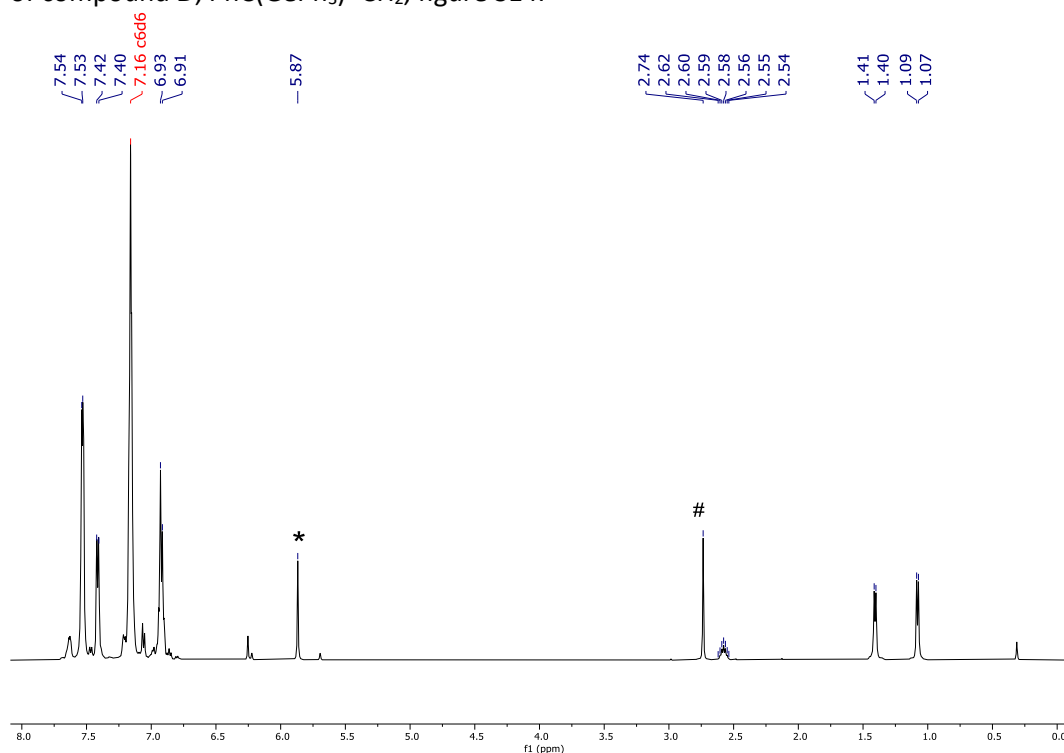


Figure S23. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of 10 mol% compound **2** with an equivalent of phenyl acetylene and Ph_3GeH after overnight at 60°C . # = PhCCH ,¹⁴ * = Ph_3GeH .¹² Remaining labelled resonances in spectrum correspond to $\text{N,N}'$ -bis(2,6-diisopropylphenyl)imidazol-2-ylidene(phenylacetylido)copper(I).¹¹

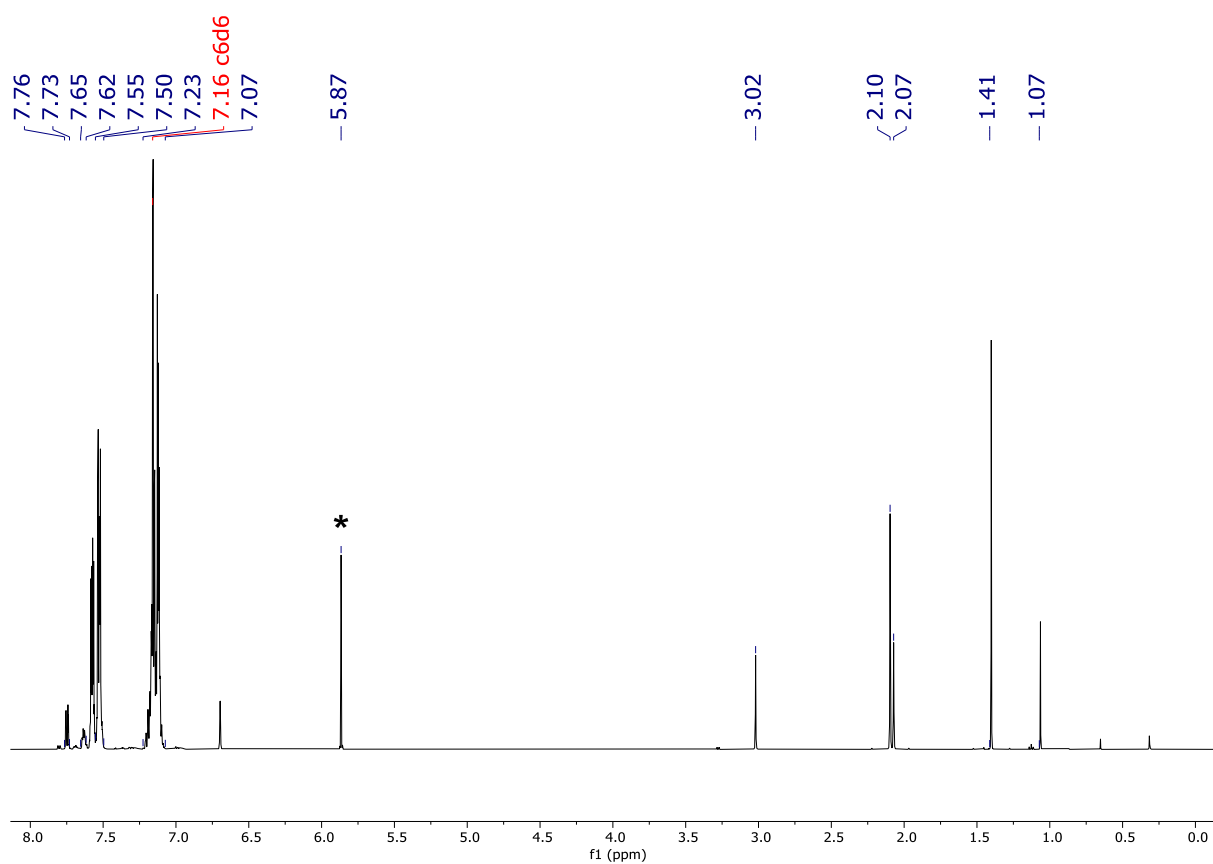


Figure S24. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and Ph_3SnCl at 60 °C overnight. * = Ph_3GeH .¹²

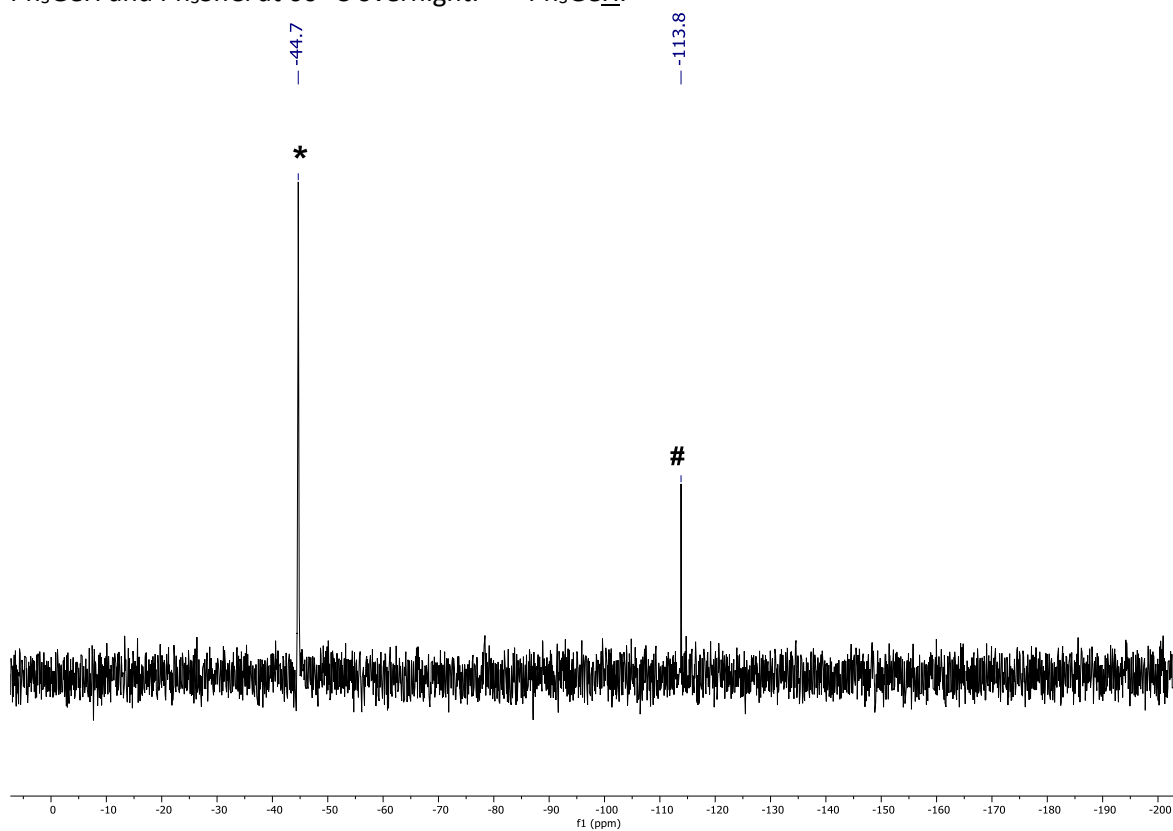


Figure S25. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and Ph_3SnCl at 60 °C overnight. * = Ph_3SnCl .¹³ # = Ph_3SnOtBu .

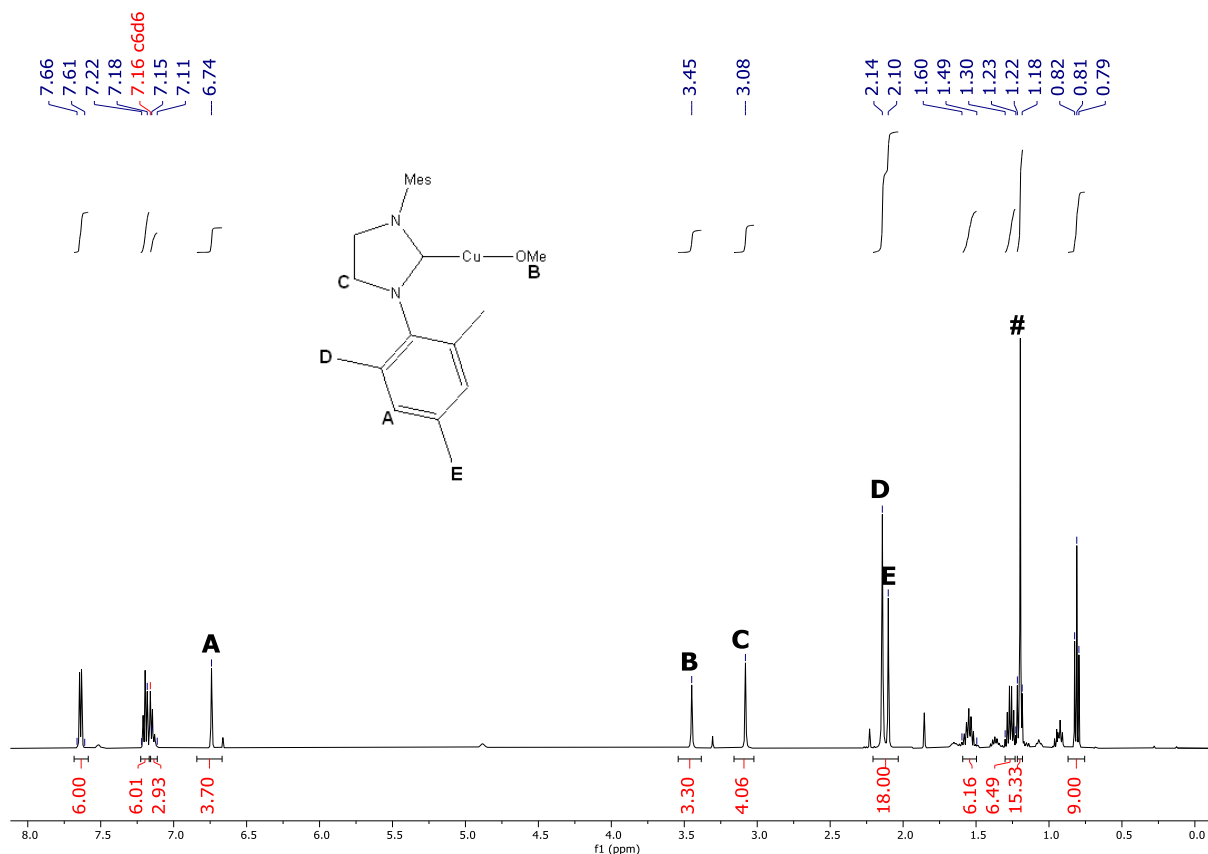


Figure S26. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of (SIMes)CuOtBu with Ph_3GeH and Bu_3SnOMe at room temperature. Unlabelled integrated resonances correspond to $\text{Ph}_3\text{GeSnBu}_3$. Labelled integrated resonances (A-E) correspond to (SIMes)CuOMe. # = tBuOH.⁴

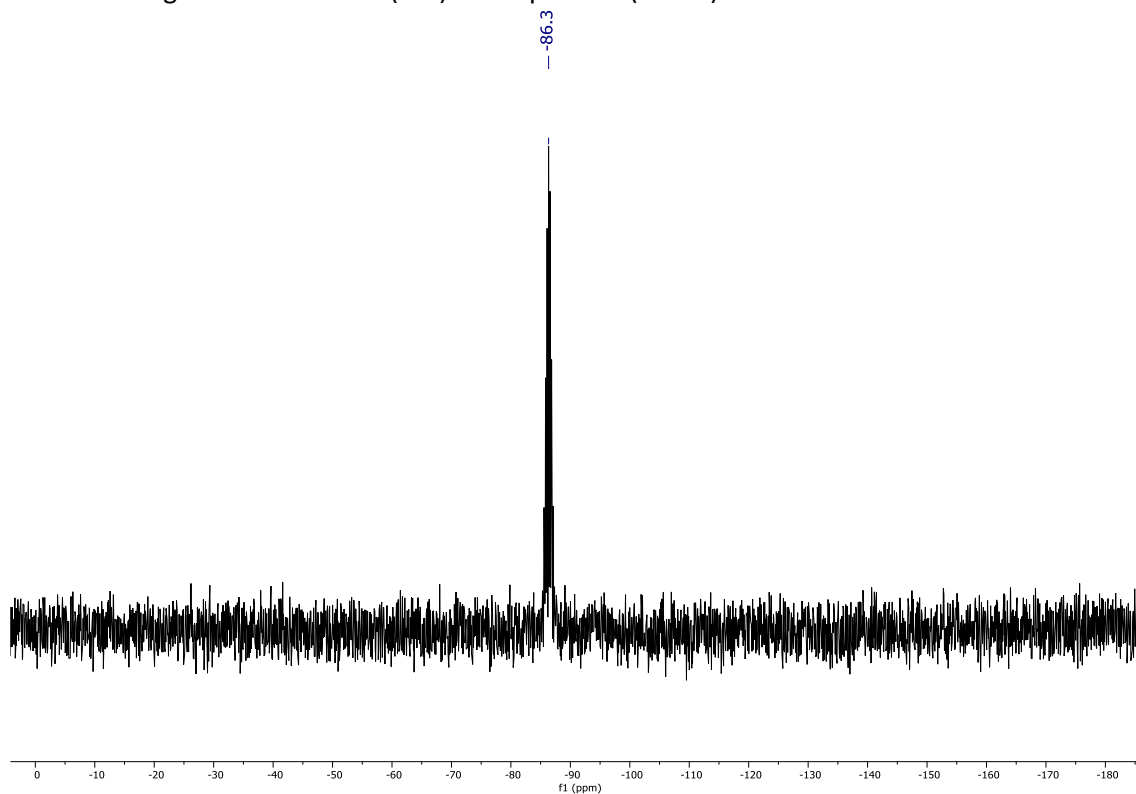


Figure S27. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of reaction of (SIMes)CuOtBu with Ph_3GeH and Bu_3SnOMe at room temperature.

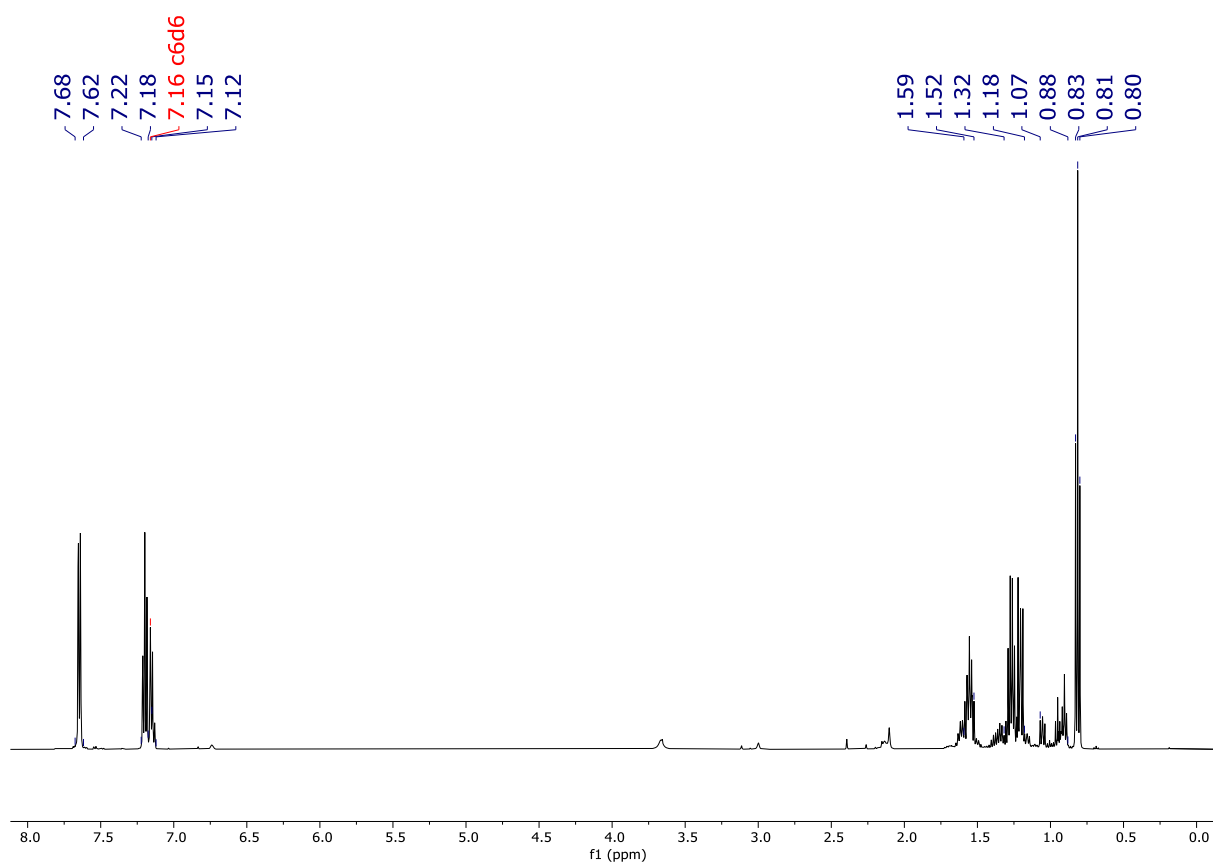


Figure S28. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and Bu_3SnOMe after volatiles were removed *in vacuo*.

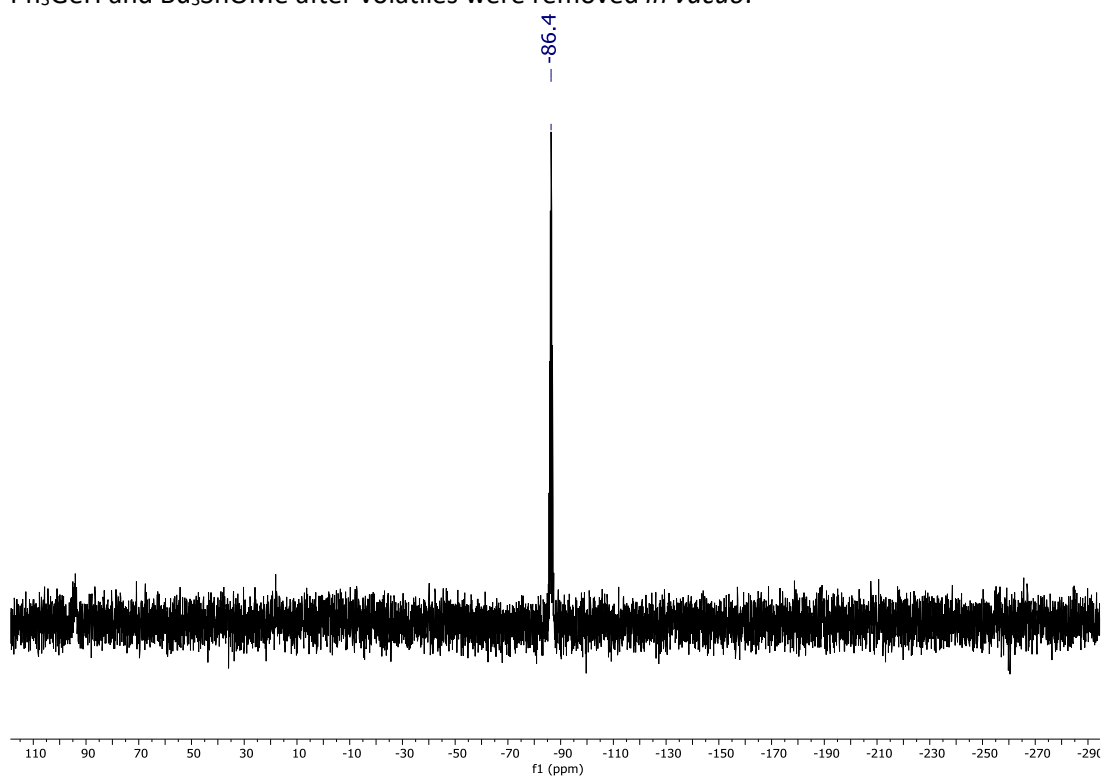


Figure S29. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and Bu_3SnOMe after volatiles were removed *in vacuo*.

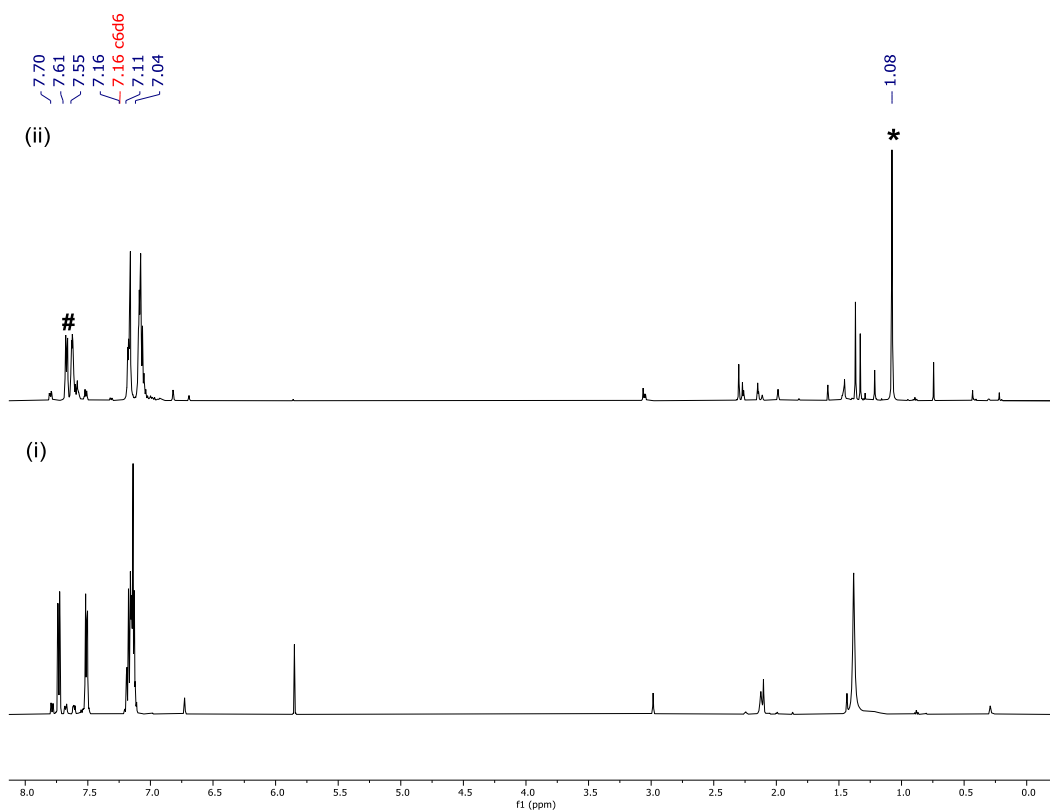


Figure S30. The ^1H NMR spectra (500 MHz, C_6D_6) of the reaction of 10 mol% (SiMes)CuOtBu with Ph_3GeH and Ph_3SnOtBu . (i) = After addition at room temperature. (ii) = After heating at 100 °C overnight. # = $\text{Ph}_3\text{GeSnPh}_3$,⁵ * = tBuOH .⁴

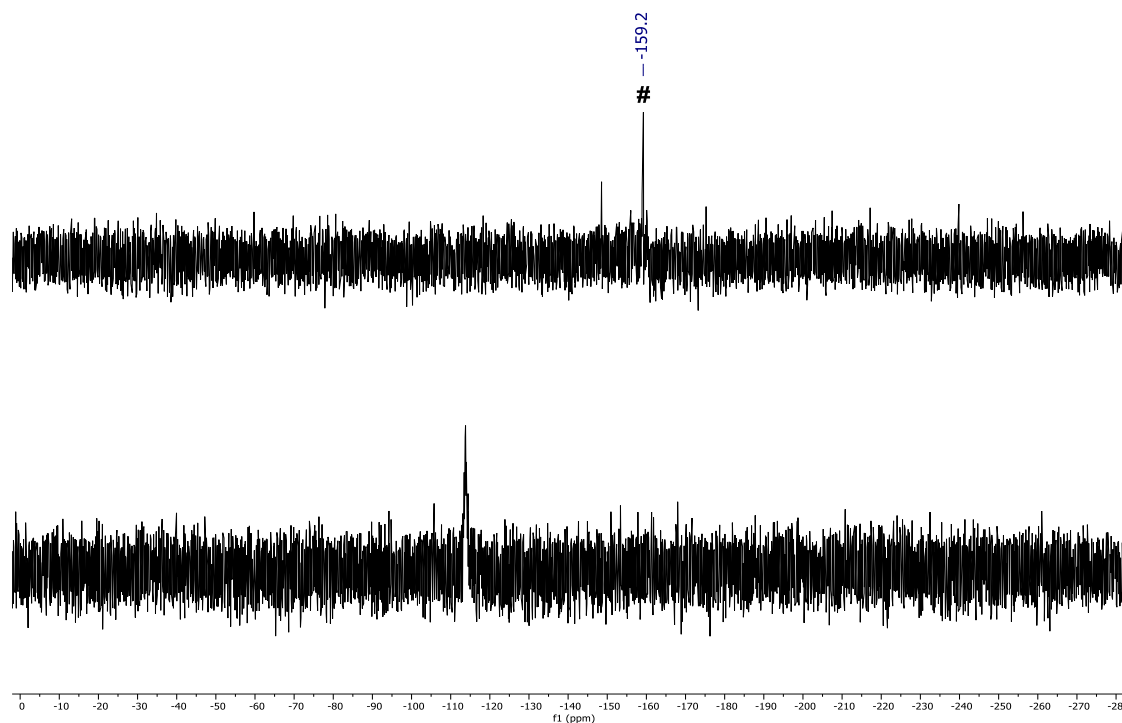


Figure S31. The ^{119}Sn NMR spectra (186 MHz, C_6D_6) of reaction of 10 mol% (SiMes)CuOtBu with Ph_3GeH and Ph_3SnOtBu . # = $\text{Ph}_3\text{GeSnPh}_3$.⁵

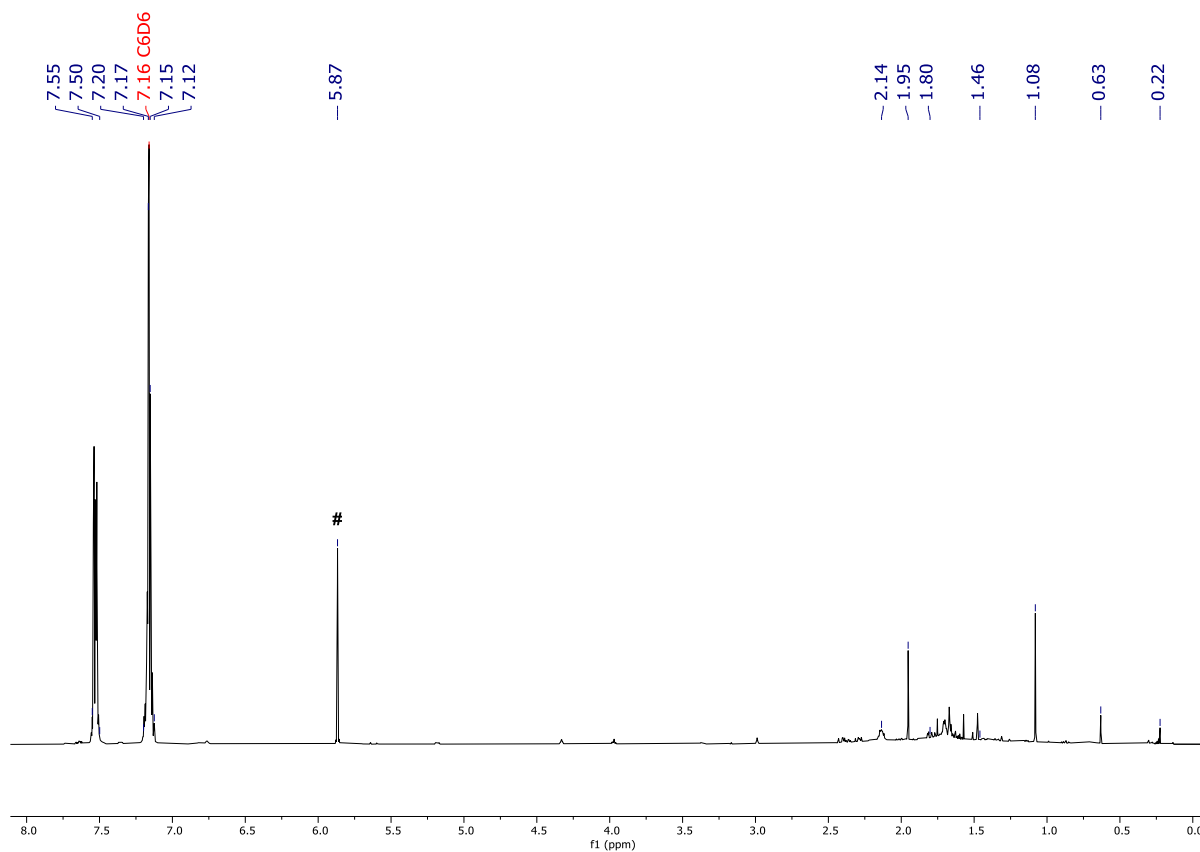


Figure S32. The ^1H NMR spectrum (400 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and methyl vinyl ketone after heating at 80 °C for 3 days. # = HGePh_3 .

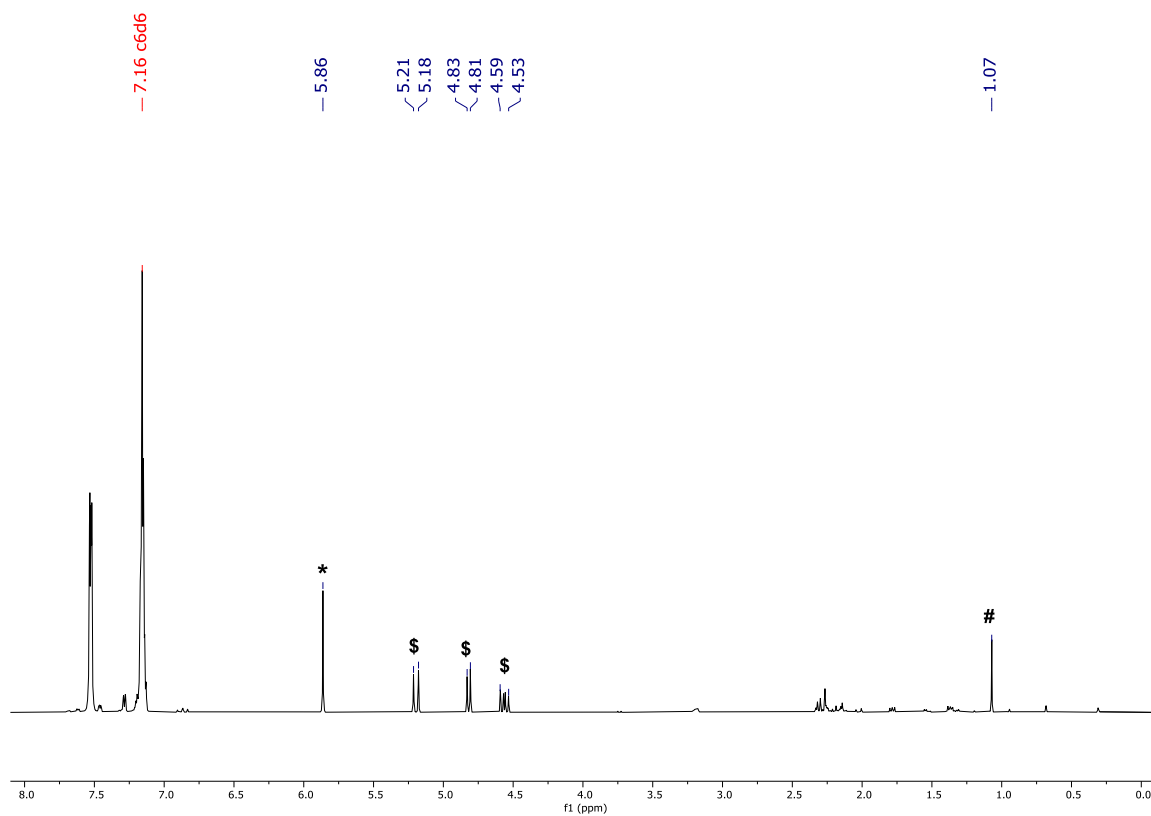


Figure S33. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of 5 mol% (SIMes)CuOtBu with Ph_3GeH and acrylonitrile after heating at 100 °C for 3 days. * = HGePh_3 ; # = $t\text{BuOH}$; \$ = acrylonitrile.

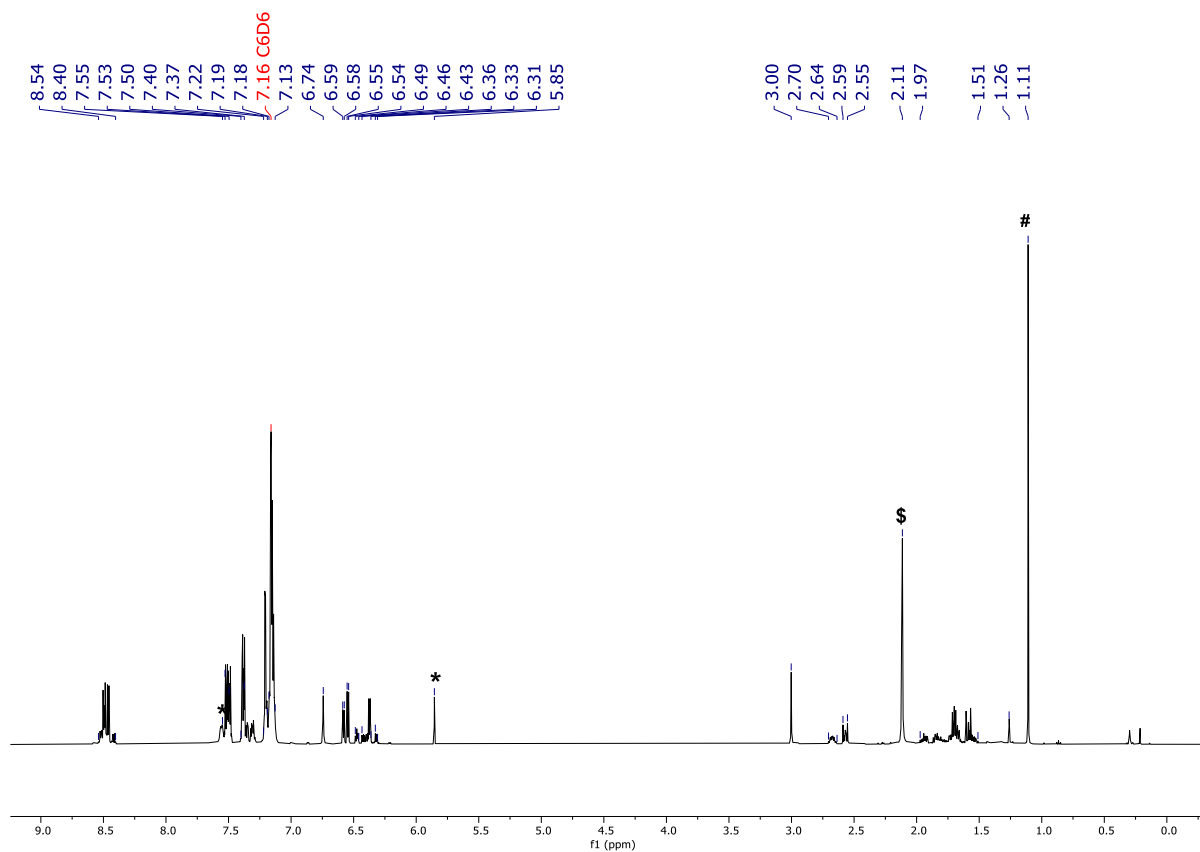


Figure S34. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of 10 mol% (SIMes)CuOtBu with Ph_3GeH and 4-vinyl pyridine after heating at 60 °C for 3 days. * = HGePh_3 ; # = $t\text{BuOH}$; \$ = toluene.

NMR spectra of Compounds

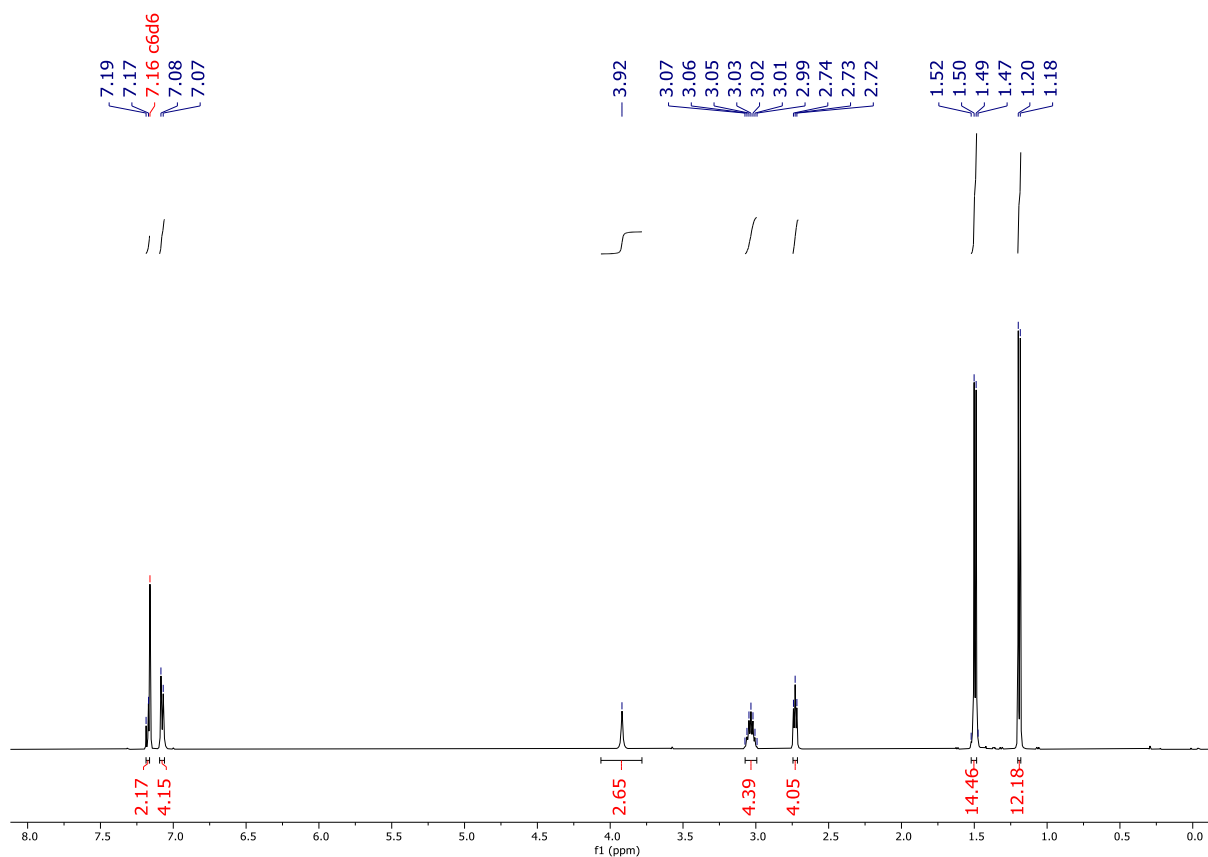


Figure S35. ^1H NMR spectrum (500 MHz, C_6D_6) of (6-Dipp)CuOMe.

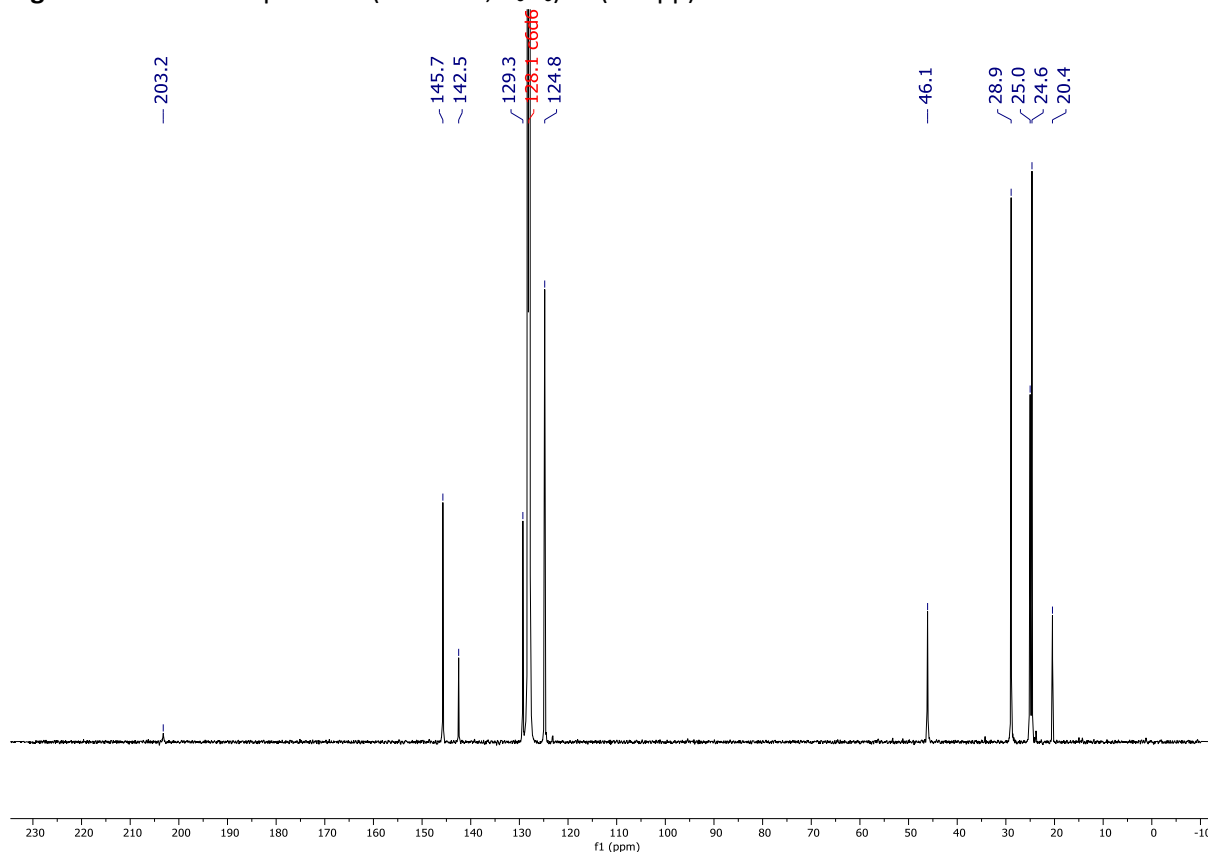


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of (6-Dipp)CuOMe.

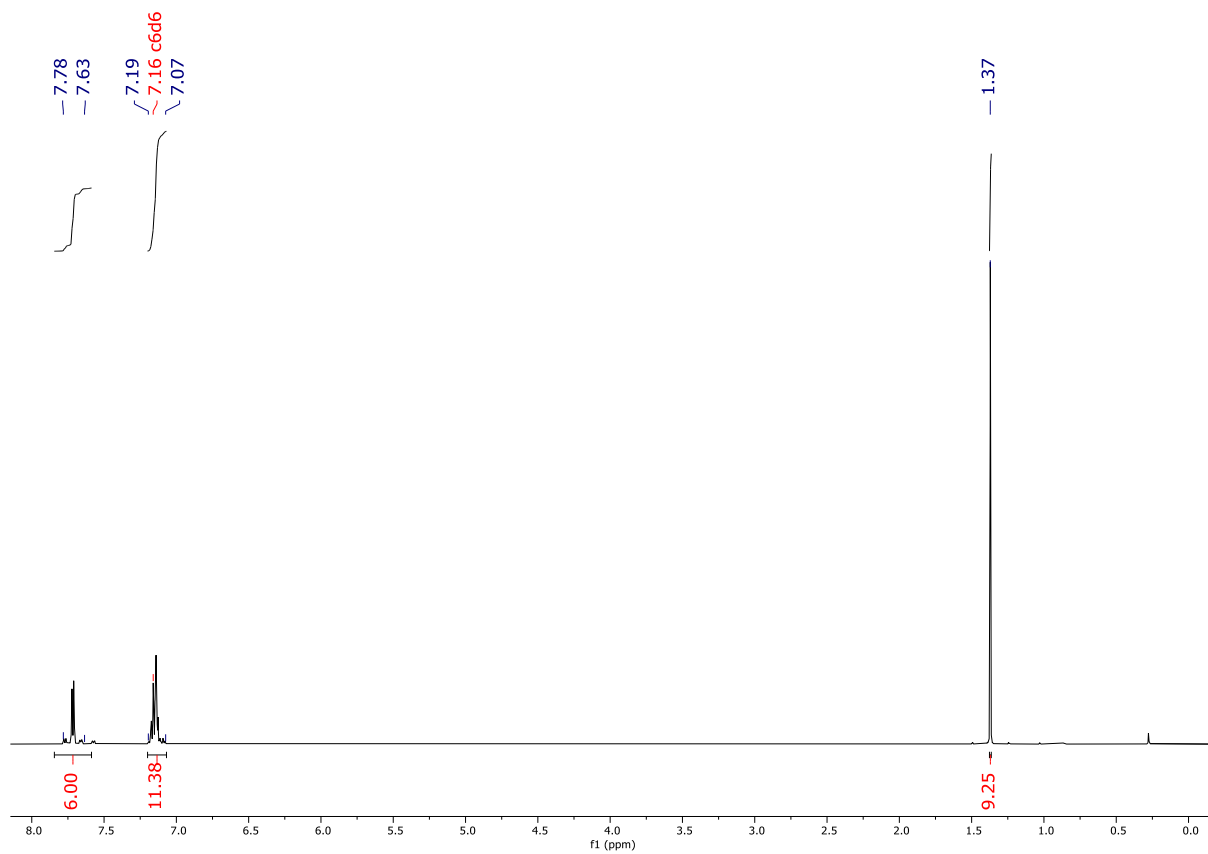


Figure S37. ^1H NMR spectrum (500 MHz, C_6D_6) of Ph_3SnOtBu .

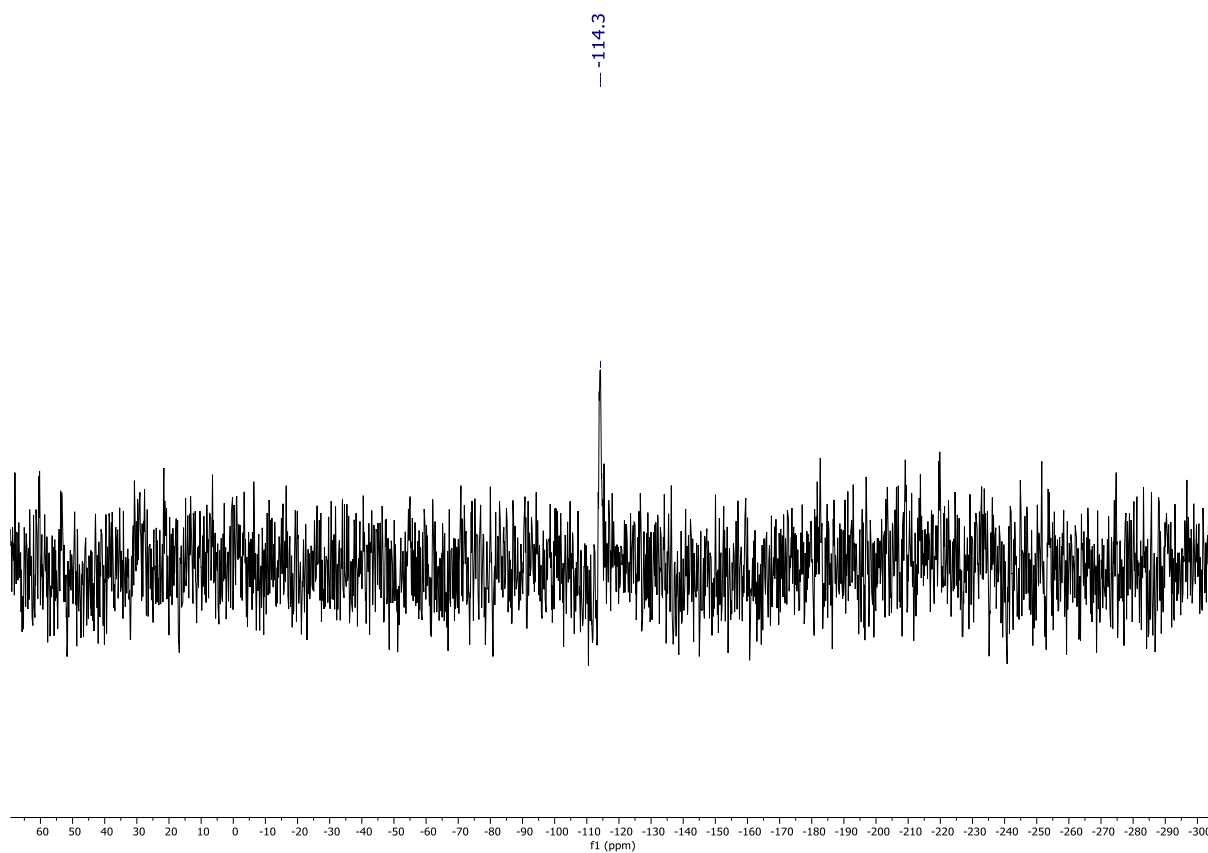


Figure S38. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of Ph_3SnOtBu .

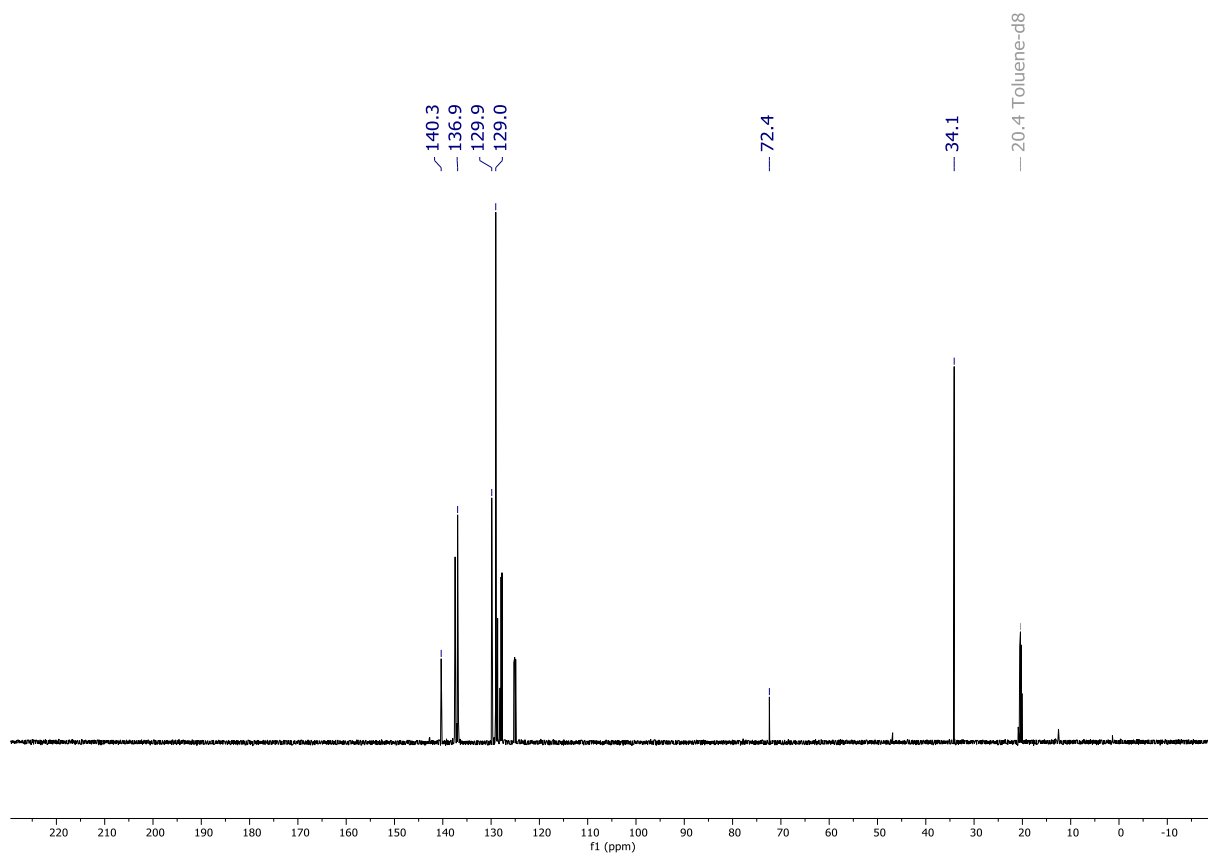


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of Ph_3SnOtBu .

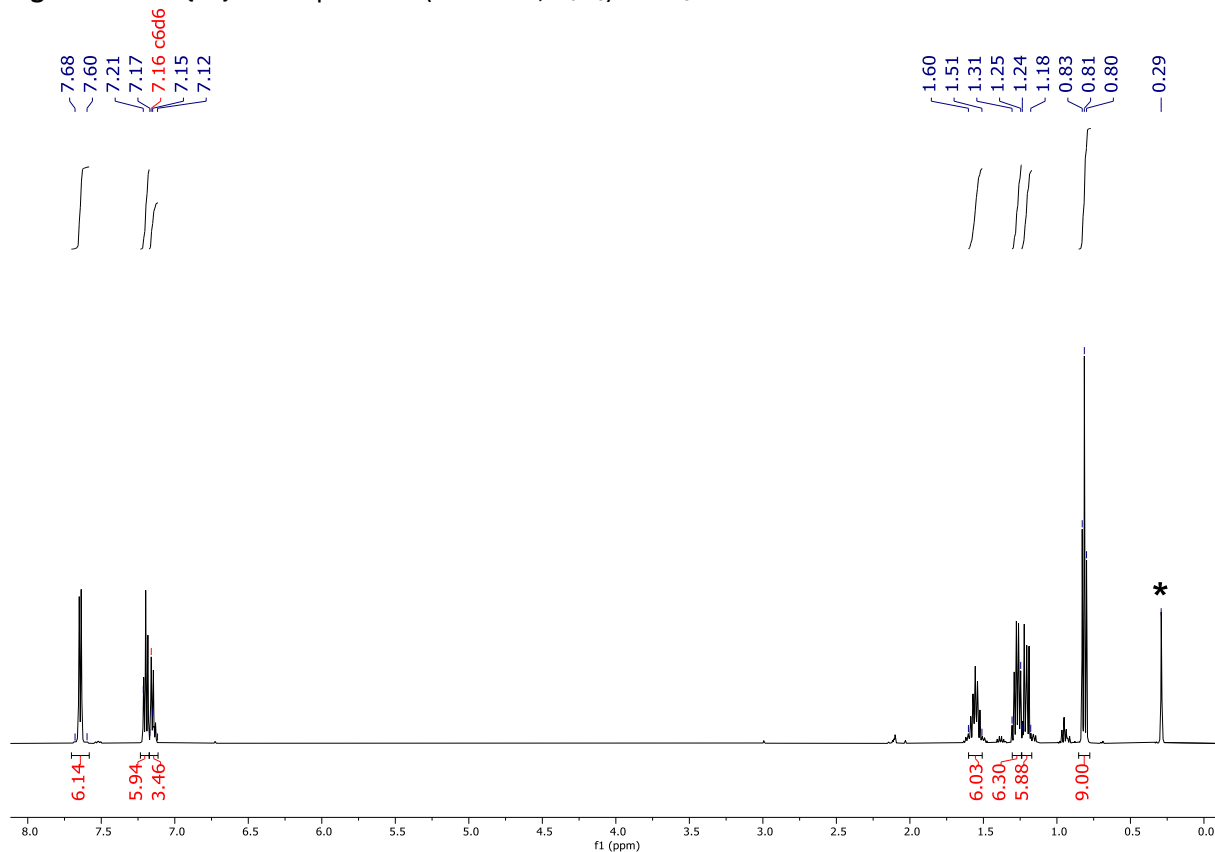


Figure S40. ^1H NMR spectrum (500 MHz, C_6D_6) of $\text{Ph}_3\text{GeSnBu}_3$. * = residual grease.⁴

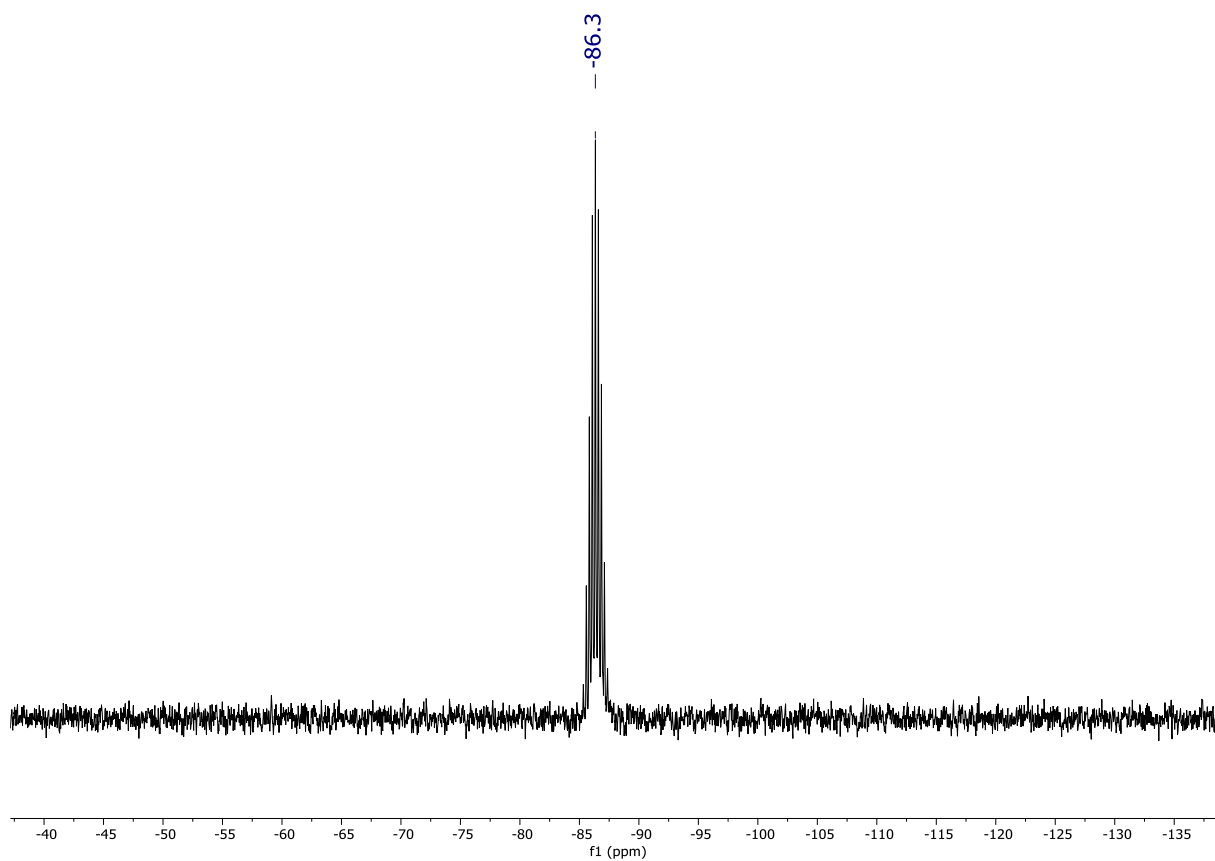


Figure S41. The ^{119}Sn NMR spectrum (186 MHz, C_6D_6) of $\text{Ph}_3\text{GeSnBu}_3$.

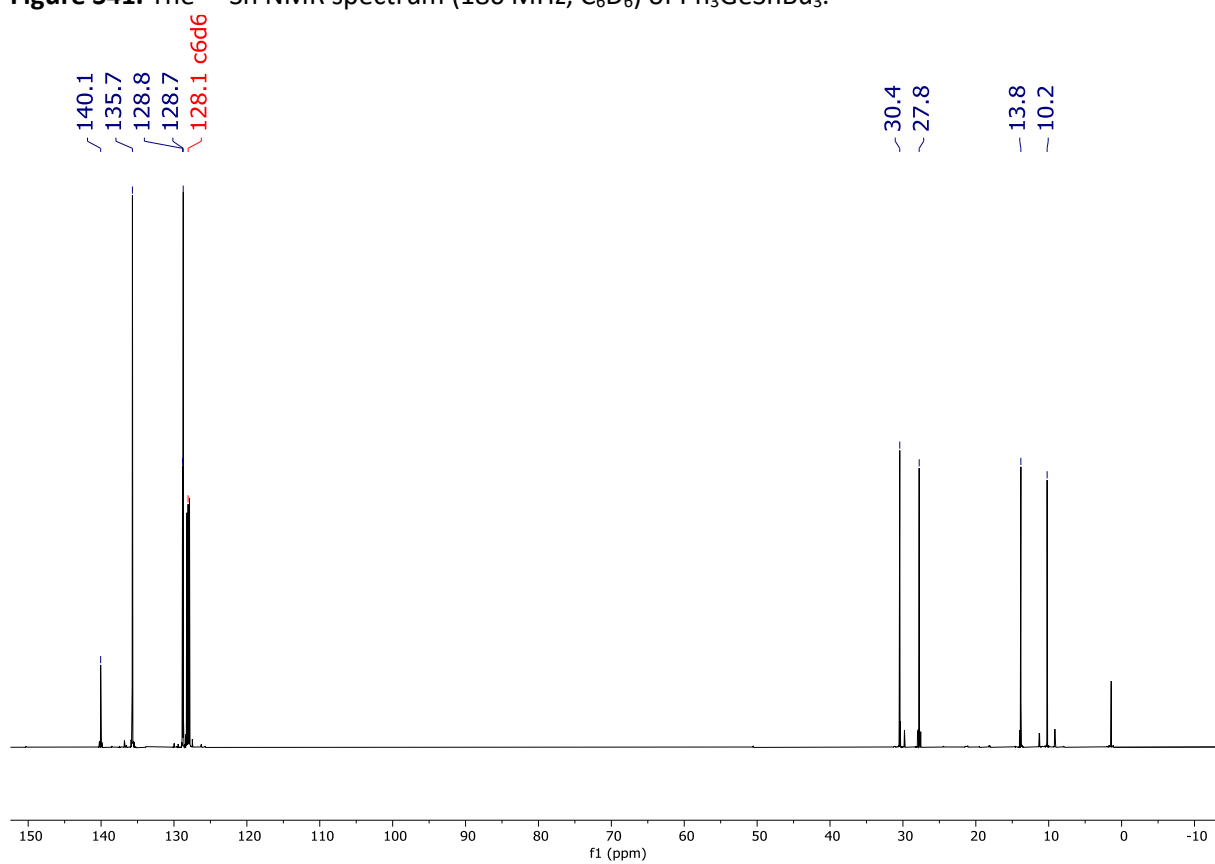


Figure S42. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of $\text{Ph}_3\text{GeSnBu}_3$.

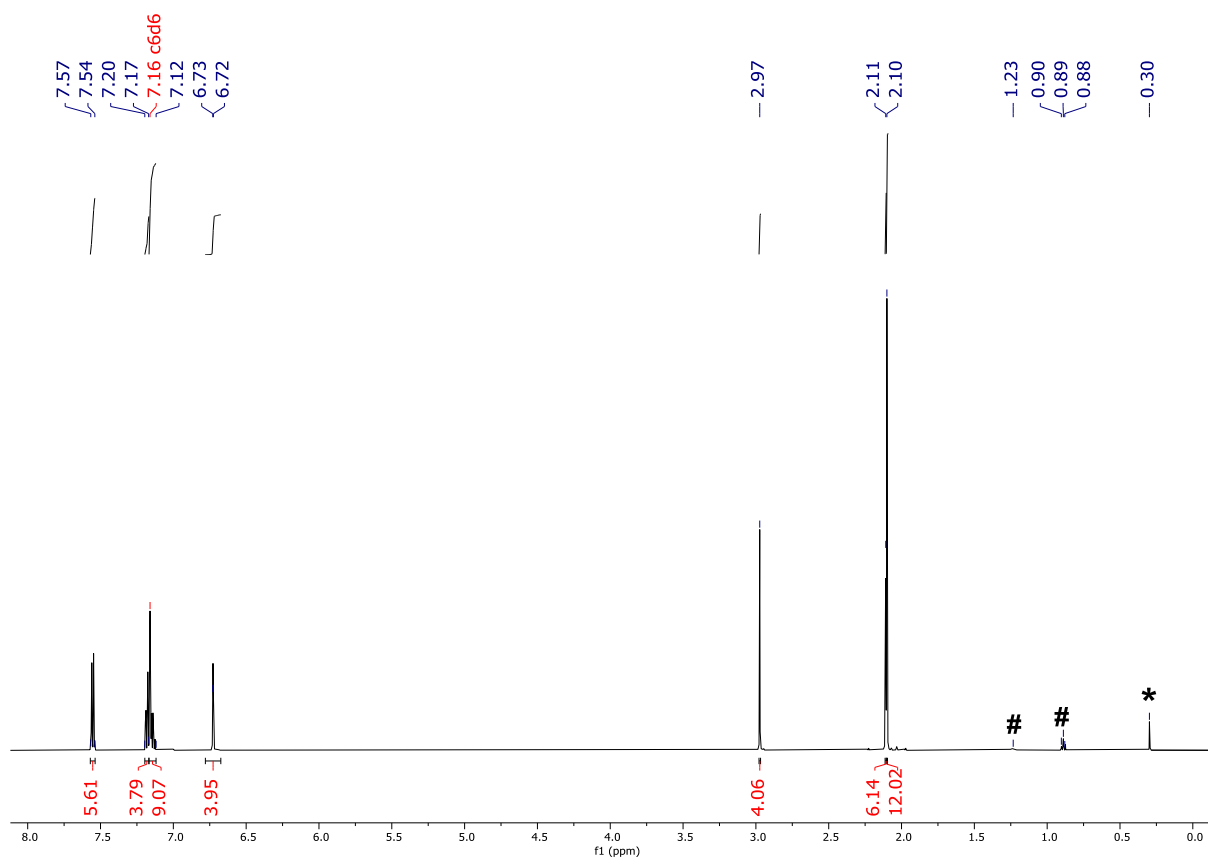


Figure S43. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **1**, $(\text{SiMe}_3)\text{CuGePh}_3$. # = residual hexane.⁴ * = residual grease.⁴

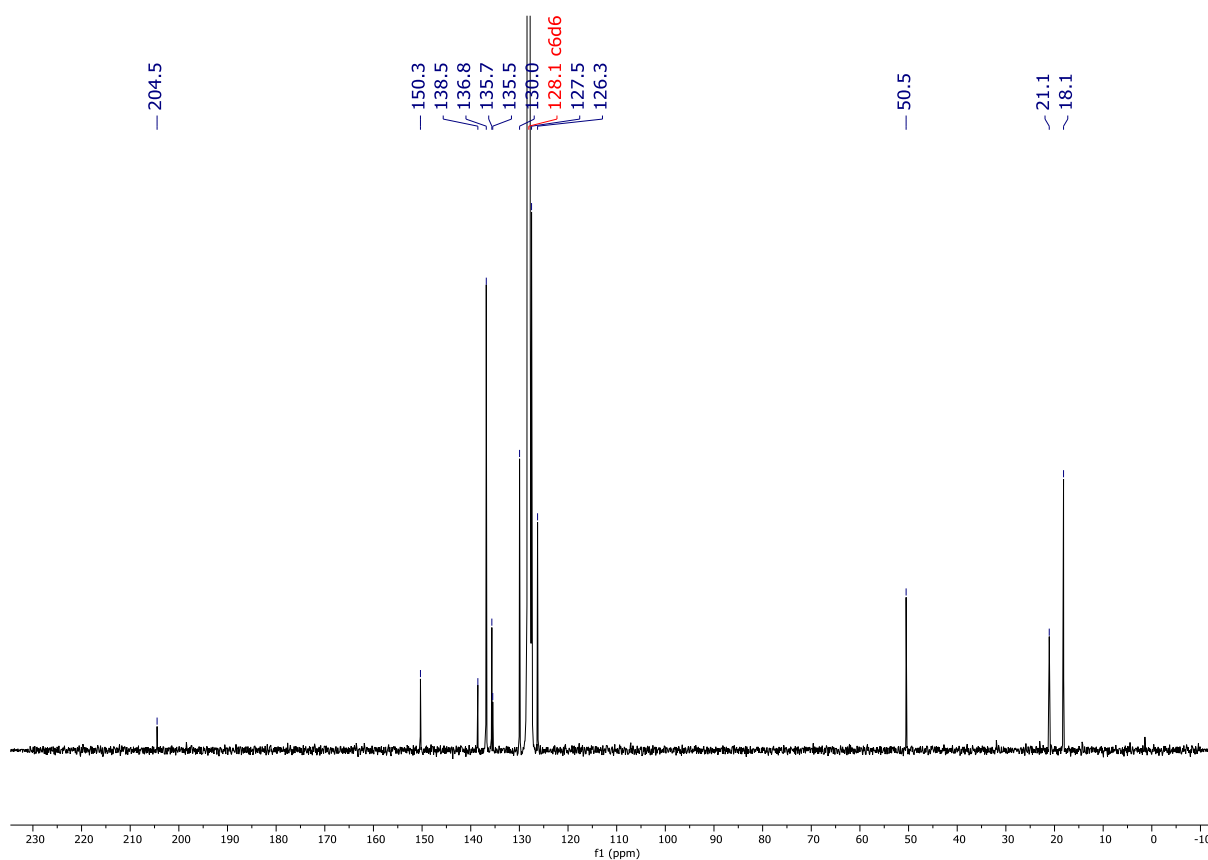


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **1**, $(\text{SiMe}_3)\text{CuGePh}_3$.

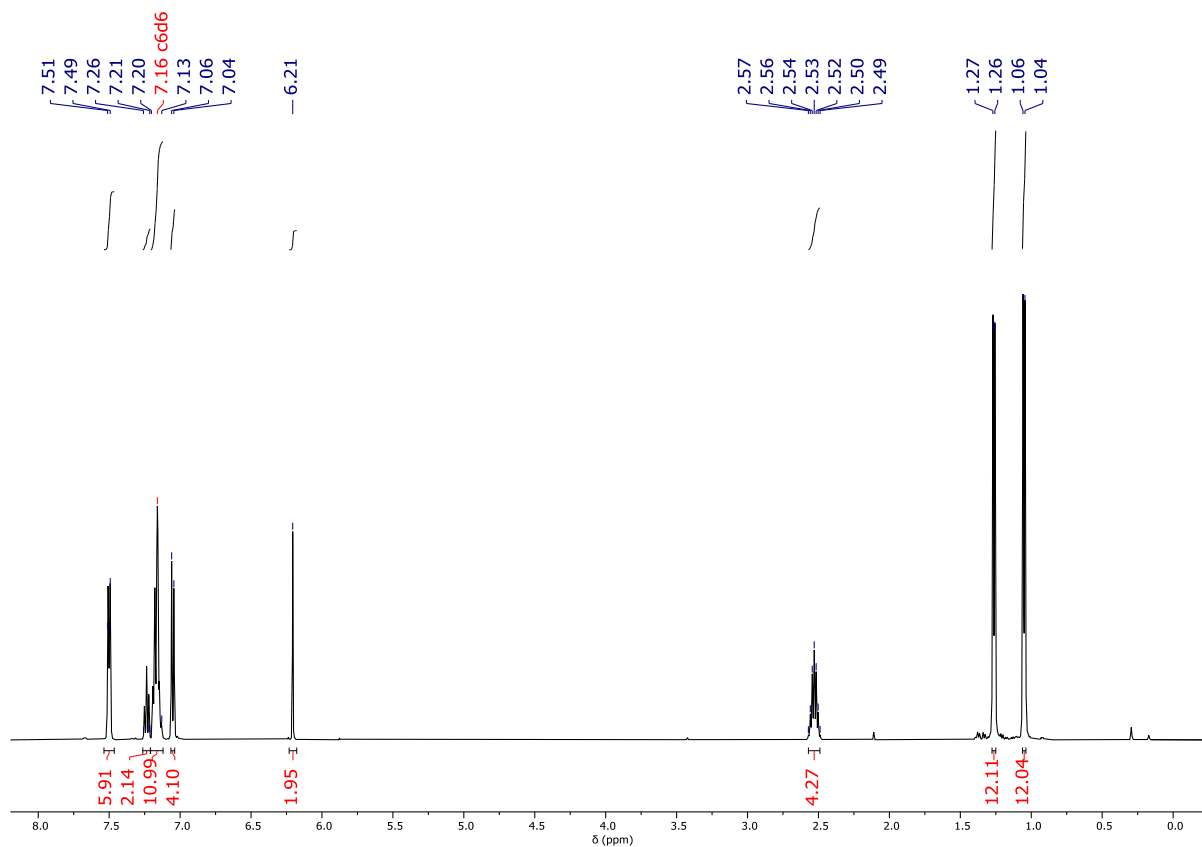


Figure S45. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **2**, $(\text{IPr})\text{CuGePh}_3$.

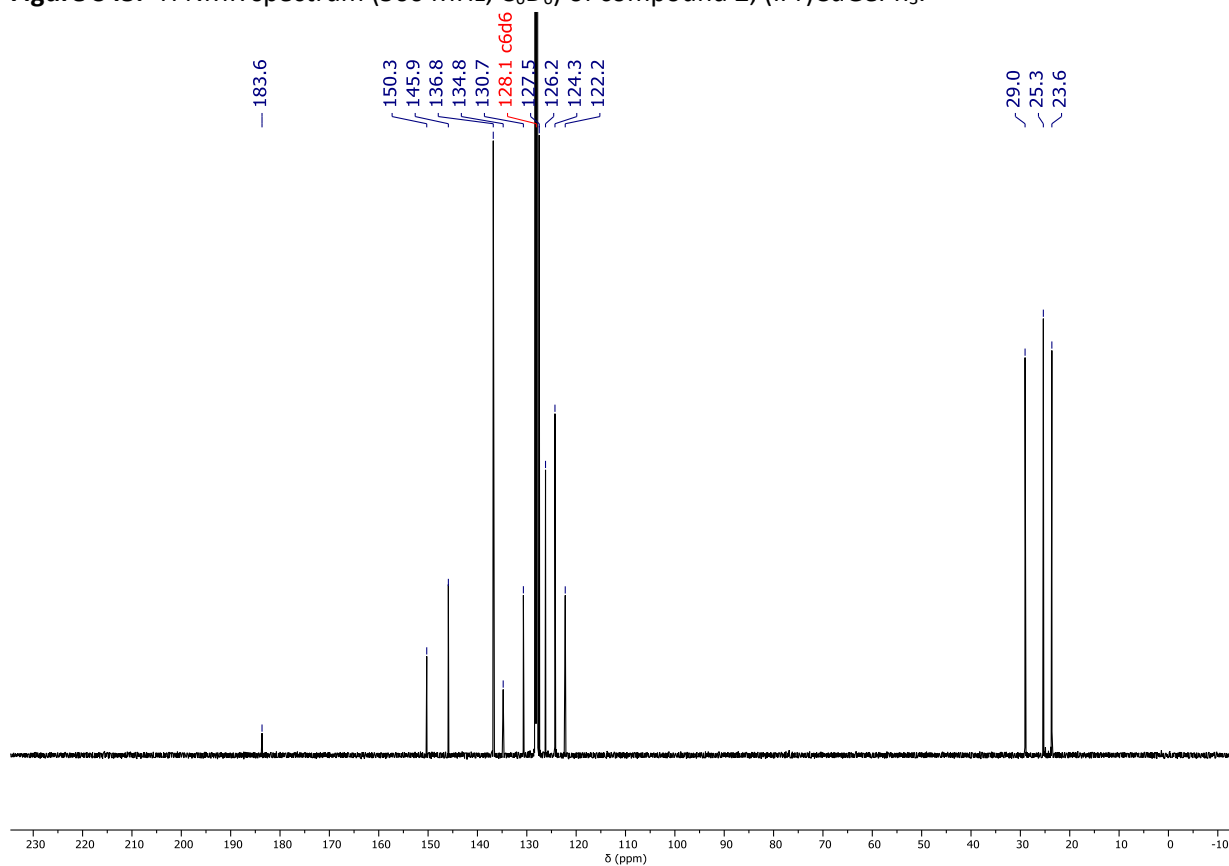


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **2**, $(\text{IPr})\text{CuGePh}_3$.

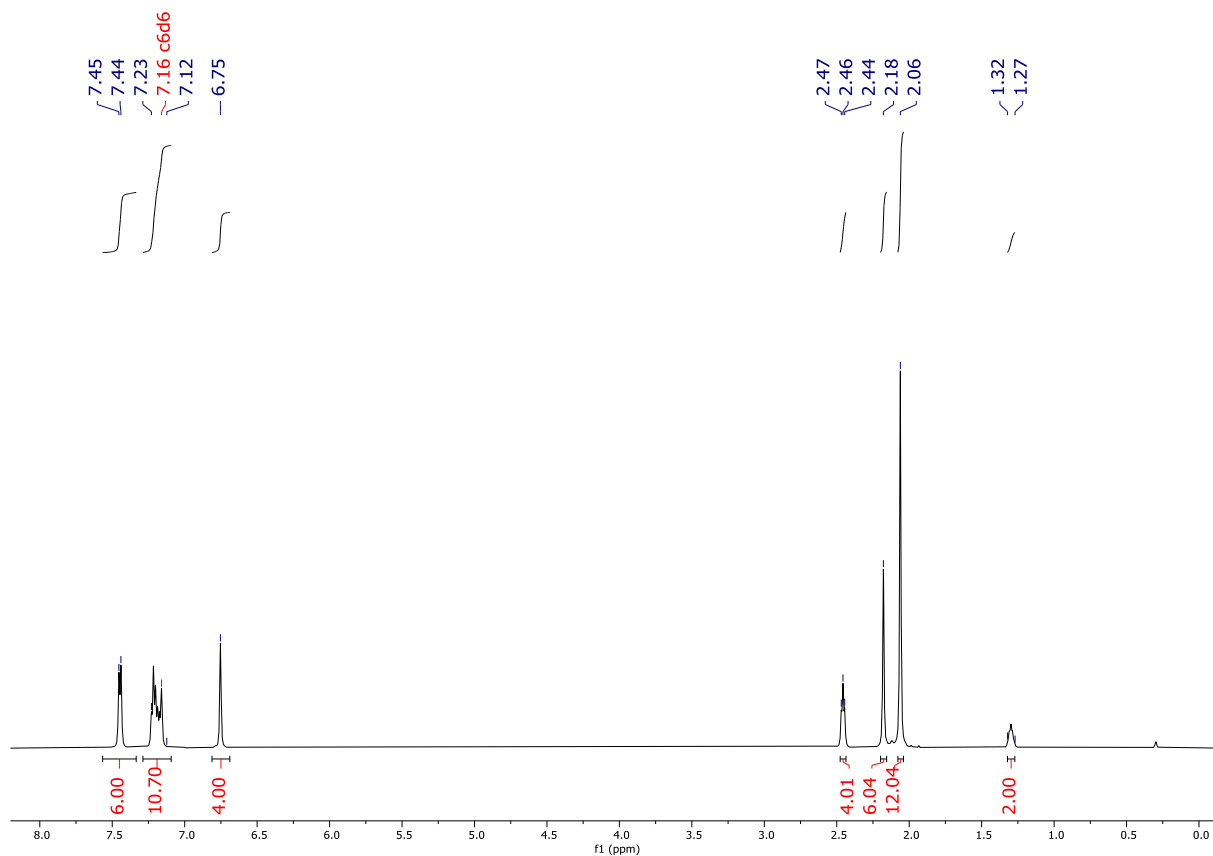


Figure S47. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **3**, (6-Mes) CuGePh_3 .

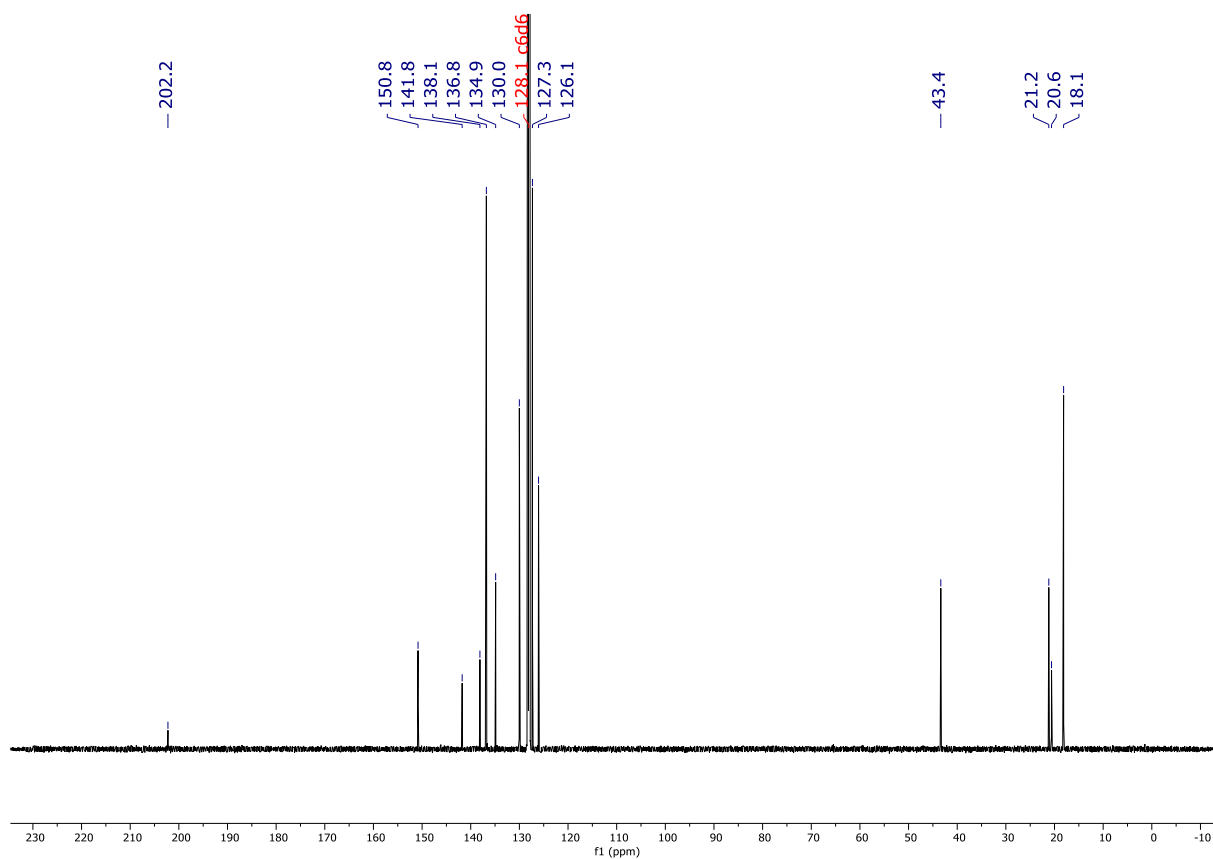


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **3**, (6-Mes) CuGePh_3 .

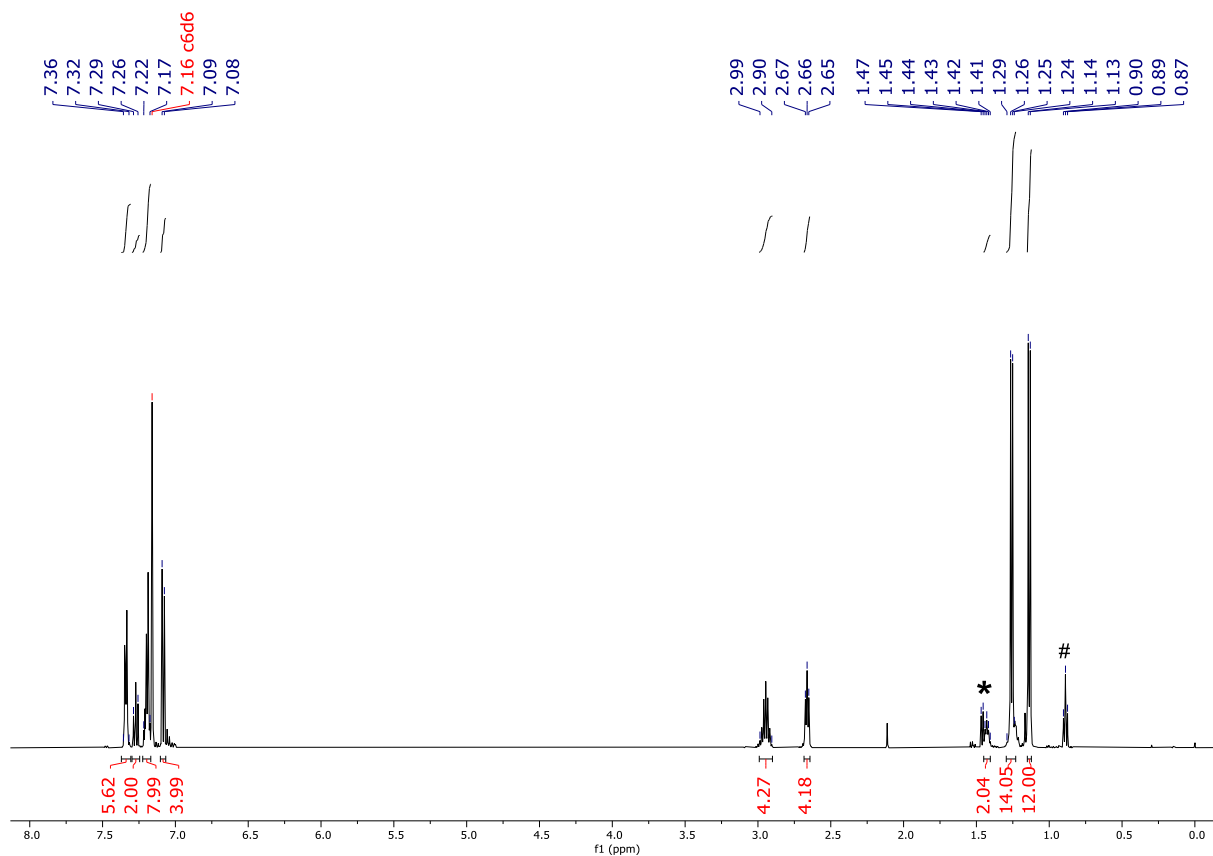


Figure S49. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **4**, (6-Dipp)CuGePh₃. * = 5 % impurity of (6-Dipp)CuCl.¹⁵ # = residual hexane.⁴

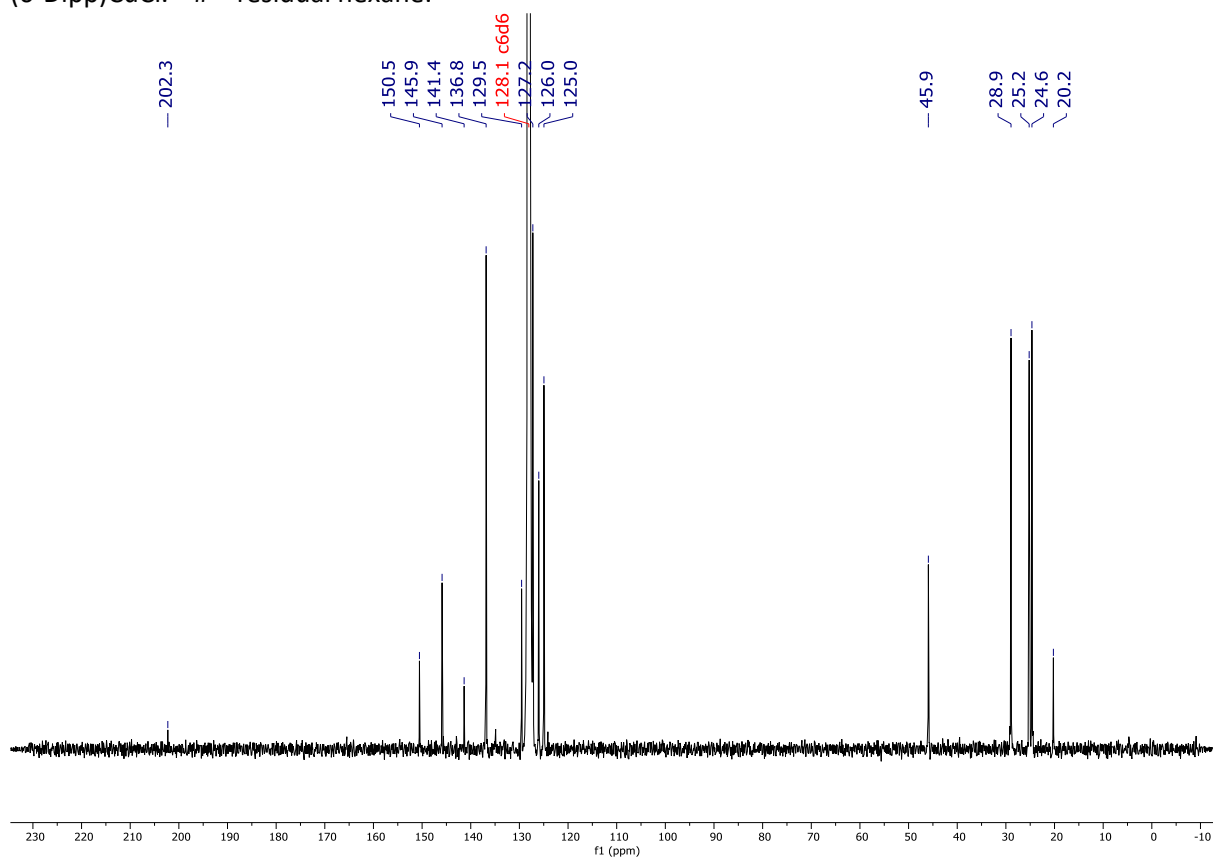


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **4**, (6-Dipp)CuGePh₃.

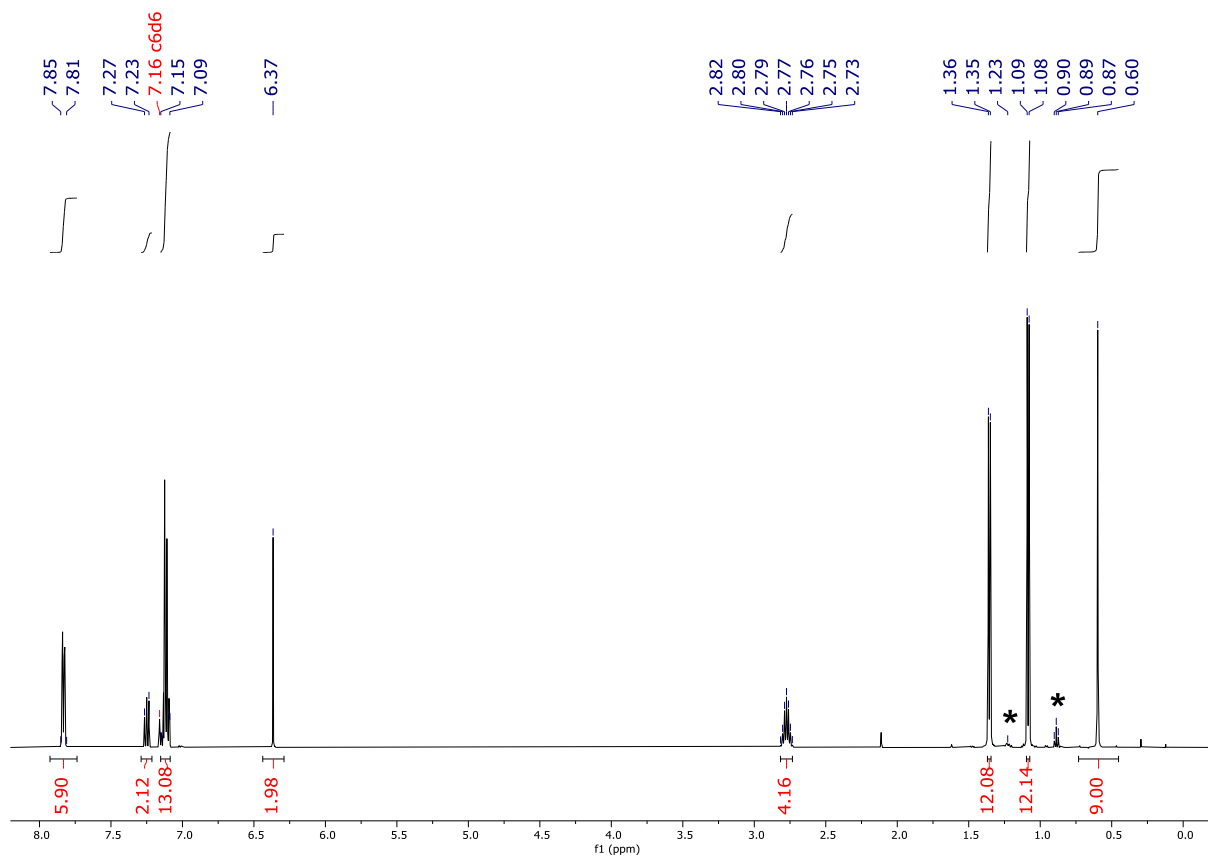


Figure S51. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **5**, $(\text{IPr})\text{CuSC}(\text{=NtBu})\text{GePh}_3$. * = residual hexane.⁴

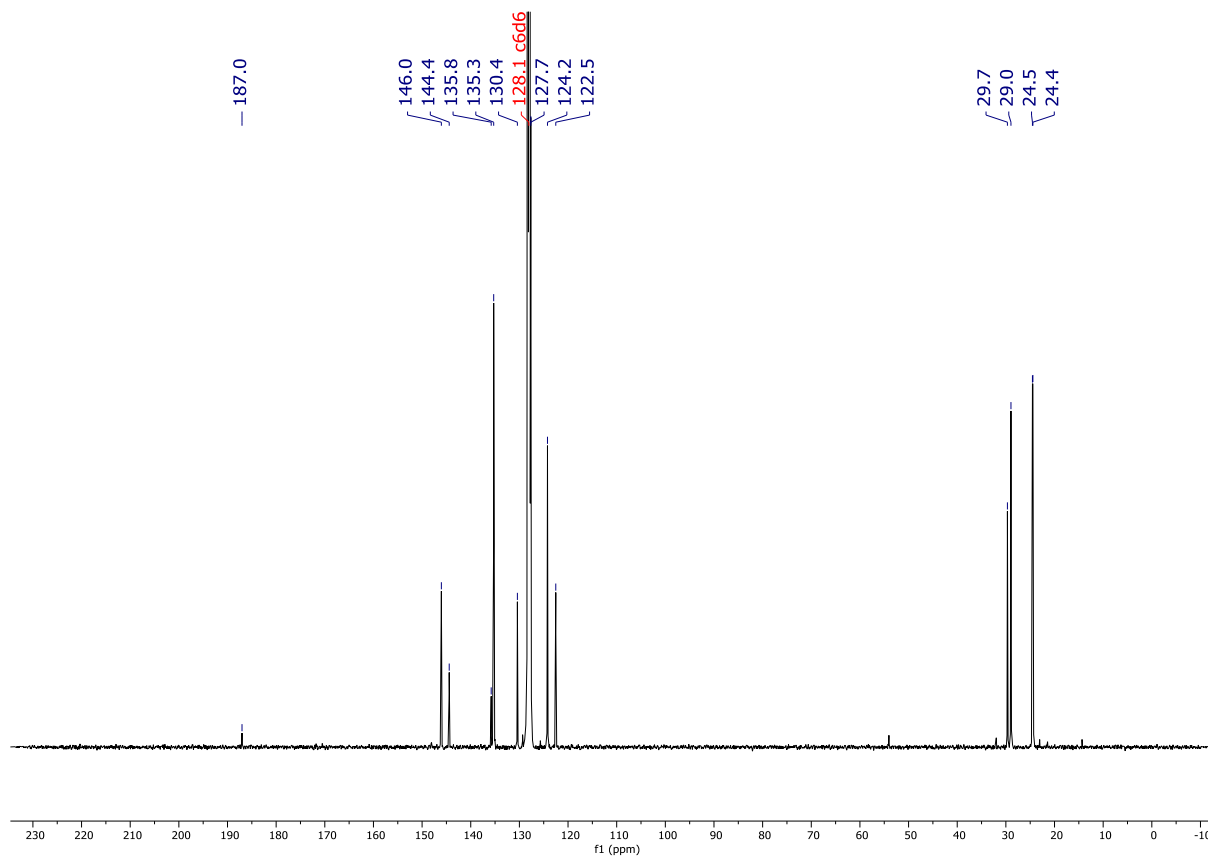


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **5**, $(\text{IPr})\text{CuSC}(\text{=NtBu})\text{GePh}_3$.

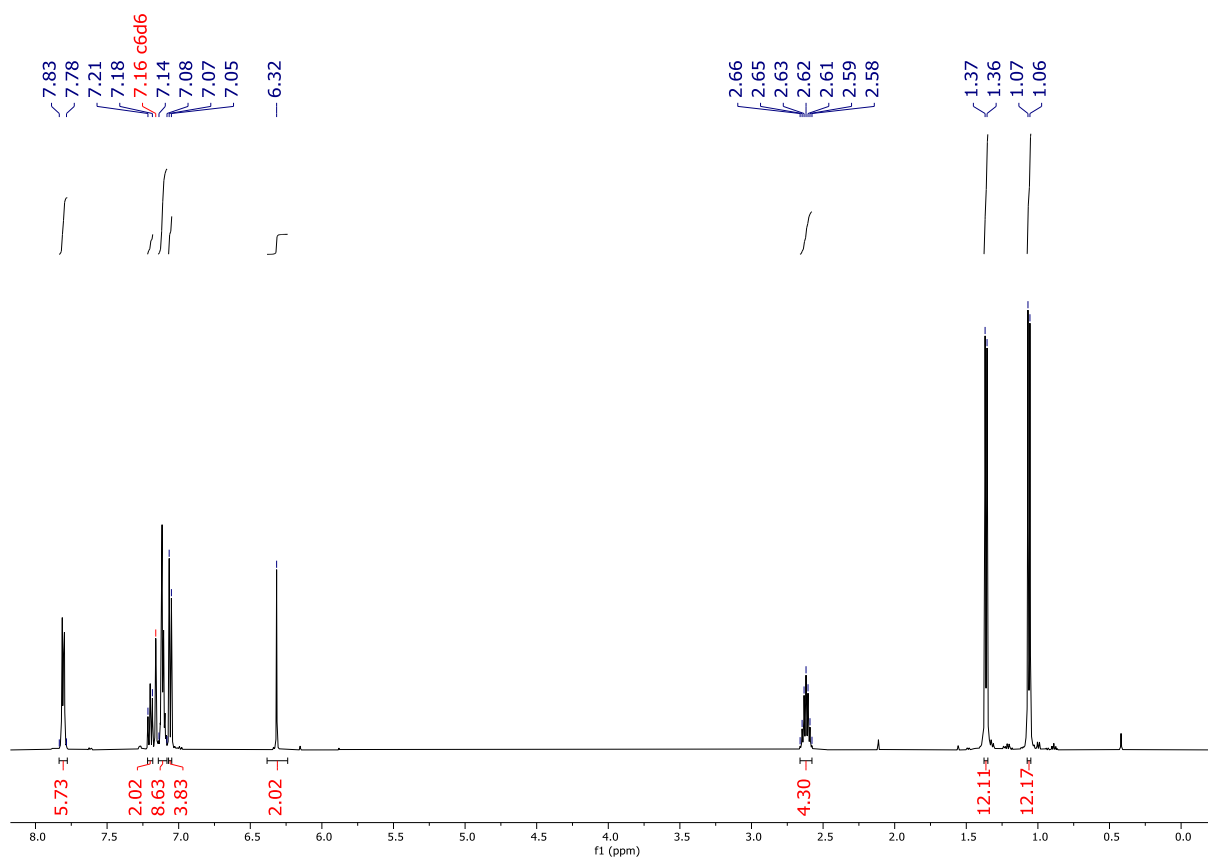


Figure S53. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **6**, $(\text{IPr})\text{CuSC}(\text{S})\text{GePh}_3$.

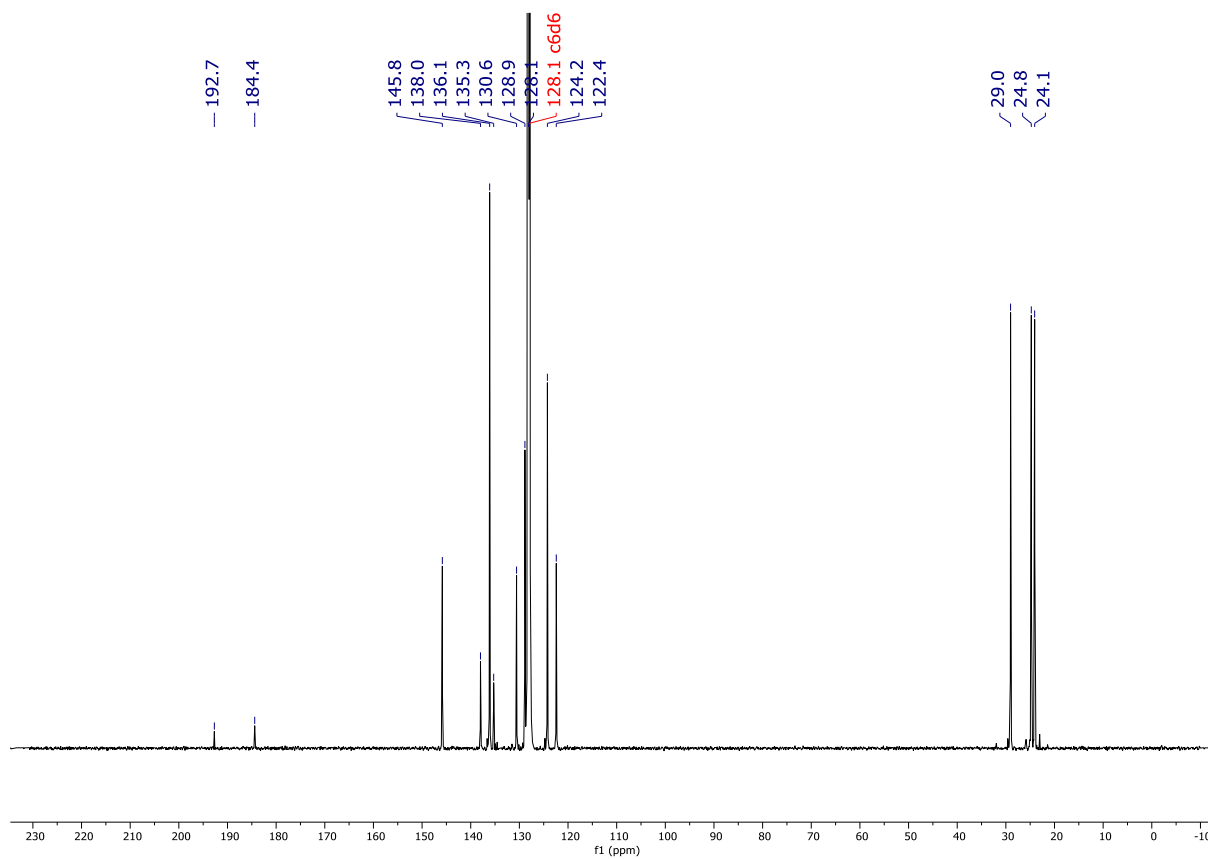


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **6**, $(\text{IPr})\text{CuSC}(\text{S})\text{GePh}_3$.

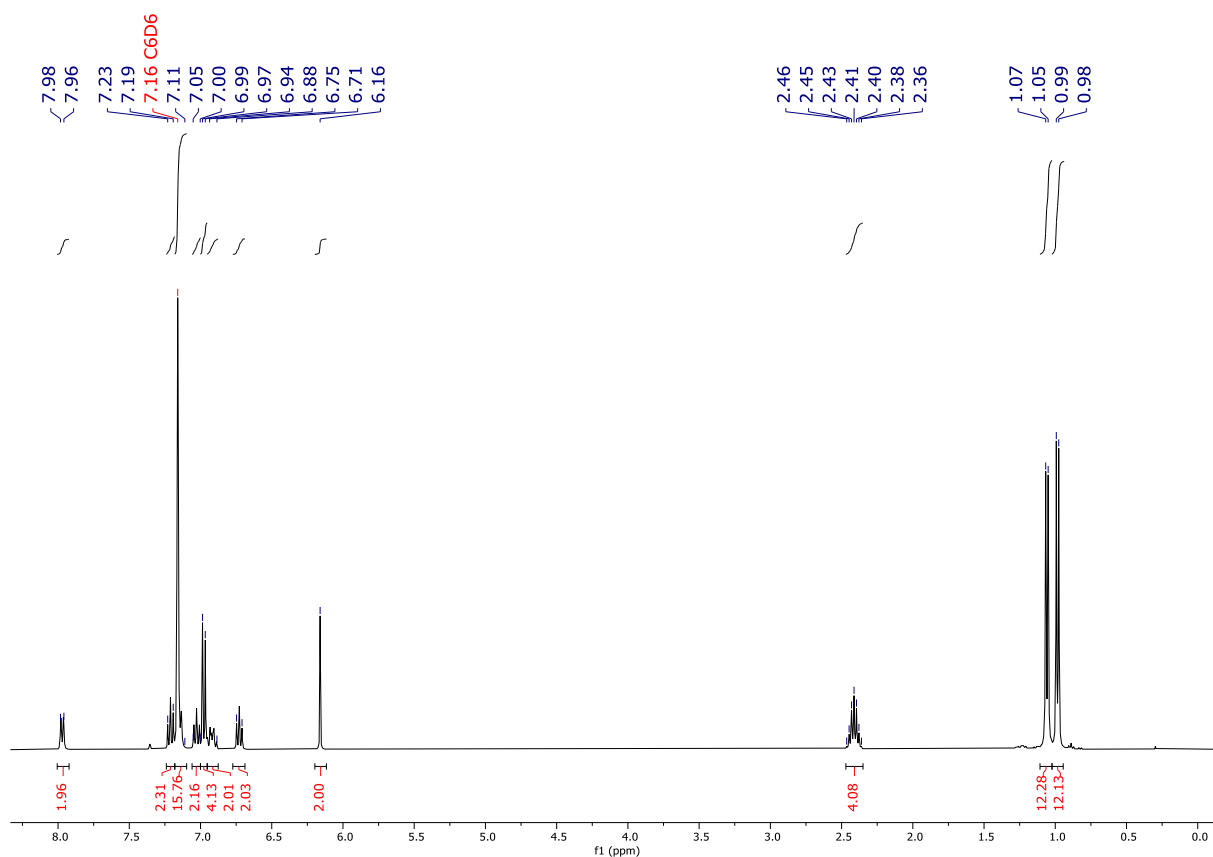


Figure S55. ^1H NMR spectrum (400 MHz, C_6D_6) of compound **7**, $(\text{IPr})\text{CuN}(\text{Ph})\text{C}(\text{O})\text{Ph}$.

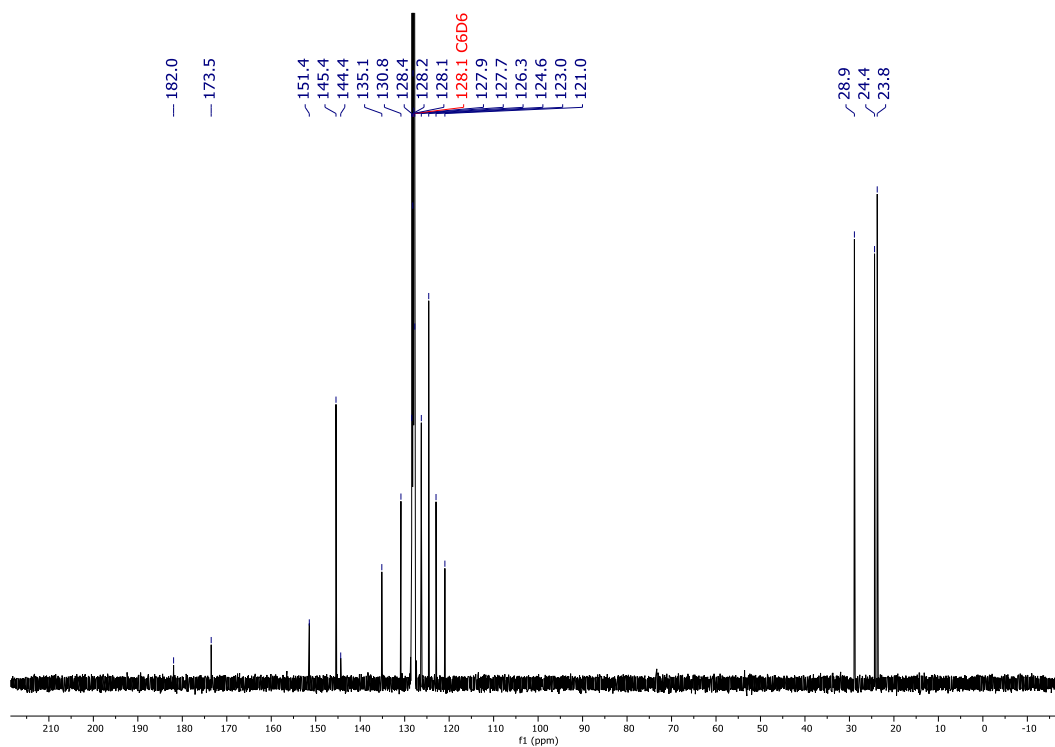


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, C_6D_6) of compound **7**, $(\text{IPr})\text{CuN}(\text{Ph})\text{C}(\text{O})\text{Ph}$.

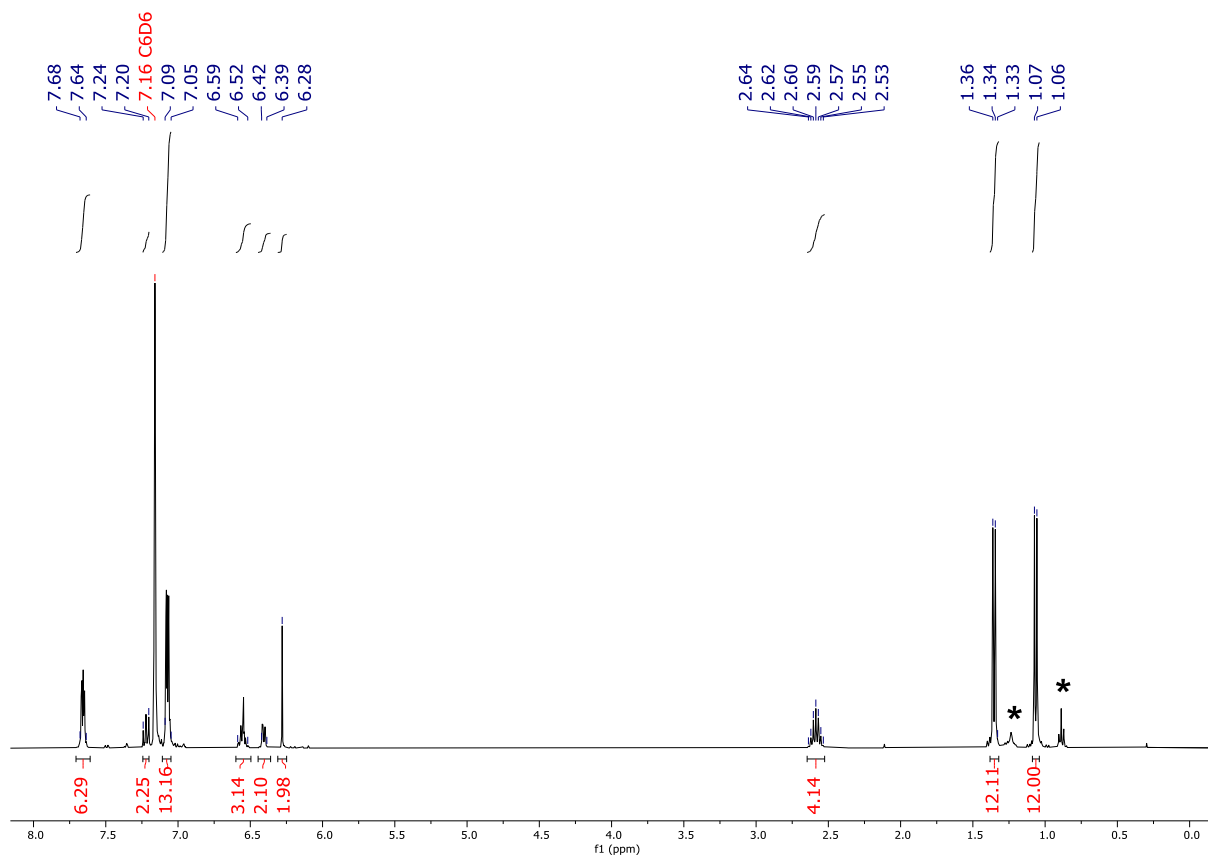


Figure S57. ^1H NMR spectrum (400 MHz, C_6D_6) of compound **8**, $(\text{IPr})\text{CuN}(\text{Ph})\text{C}(\text{O})\text{GePh}_3$. * = residual hexane.⁴

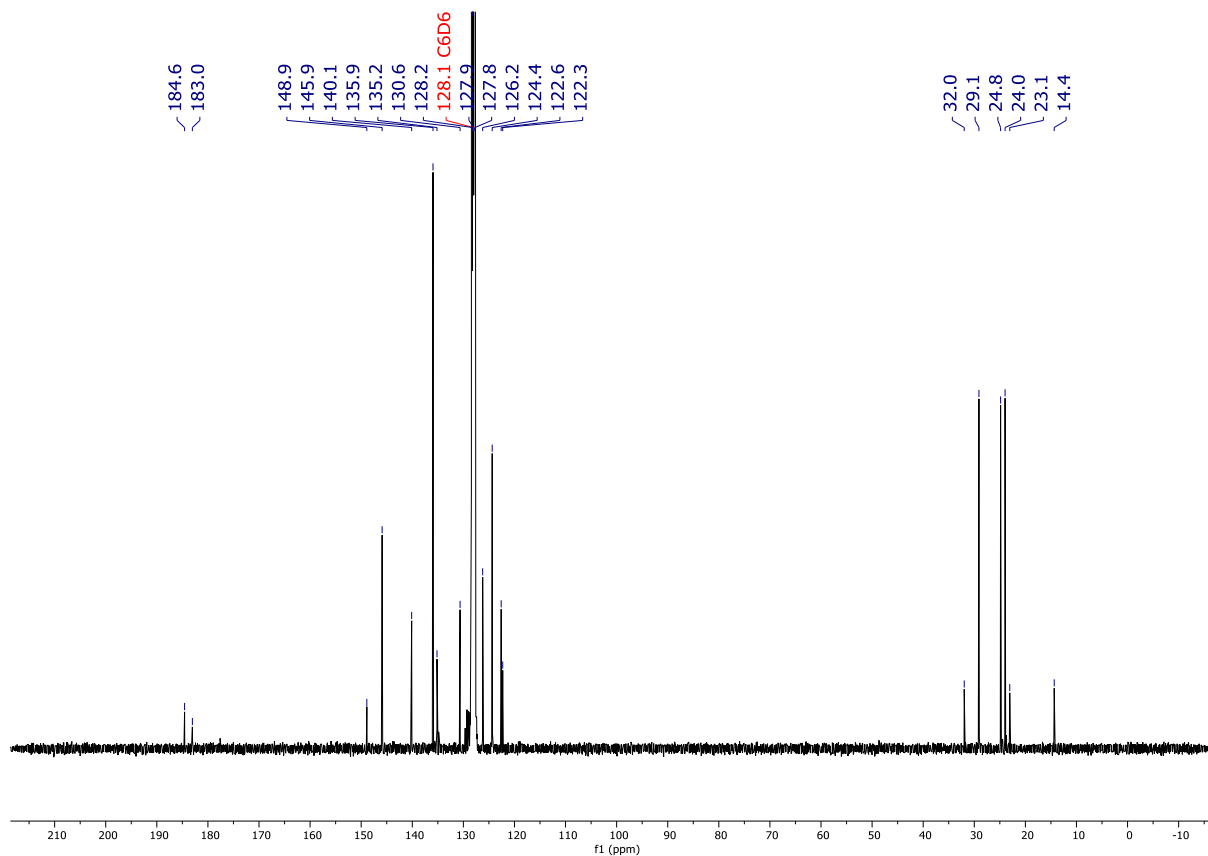


Figure S58. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, C_6D_6) of compound **8**, $(\text{IPr})\text{CuN}(\text{Ph})\text{C}(\text{O})\text{GePh}_3$.

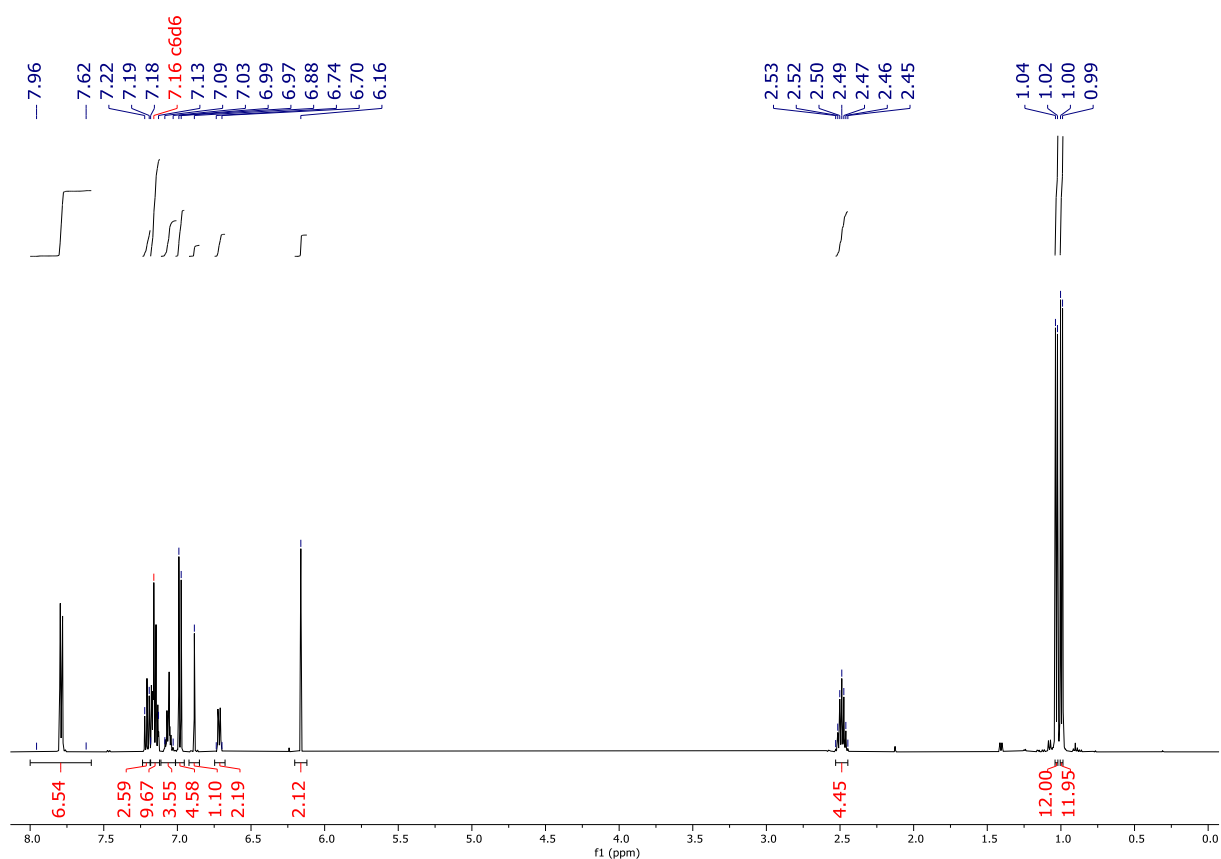


Figure S59. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **9**, $(\text{IPr})\text{CuC}(\text{Ph})\text{C}(\text{H})\text{GePh}_3$.

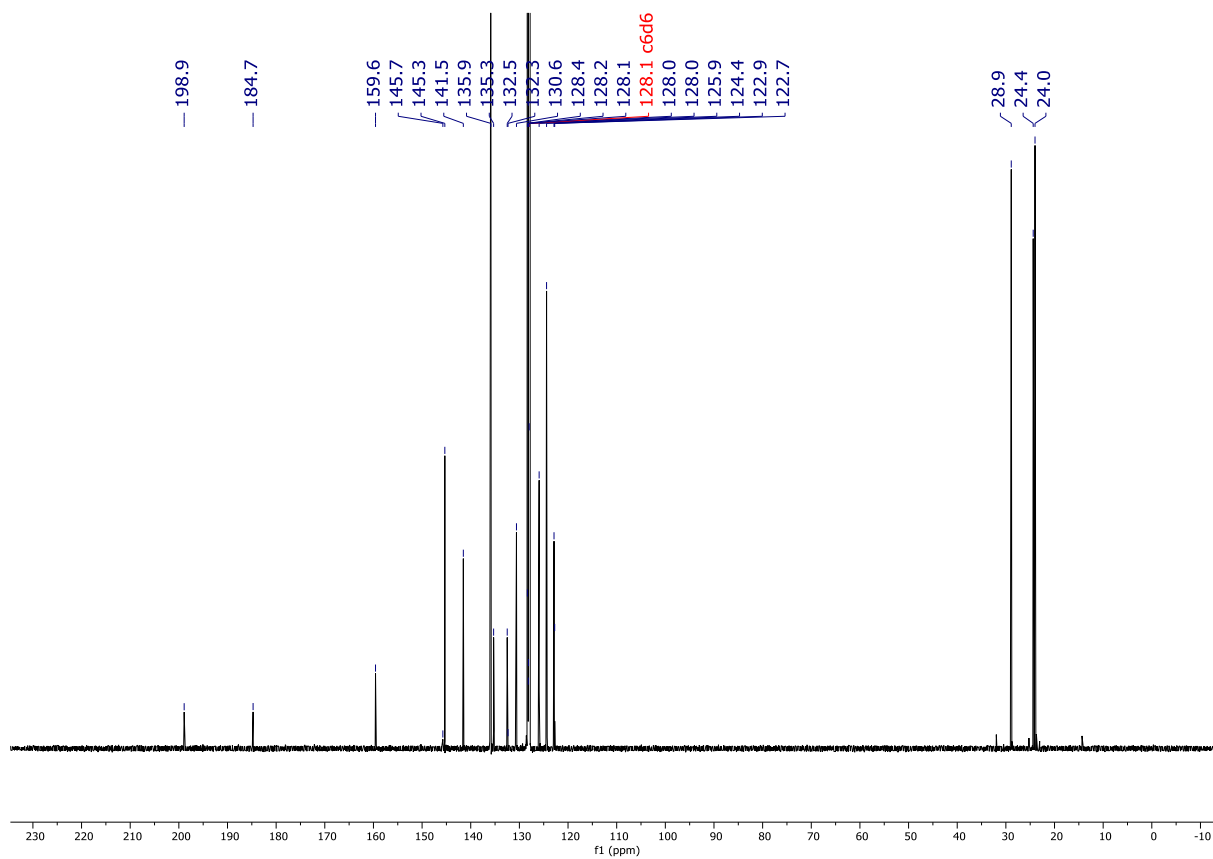


Figure S60. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **9**, $(\text{IPr})\text{CuC}(\text{Ph})\text{C}(\text{H})\text{GePh}_3$.

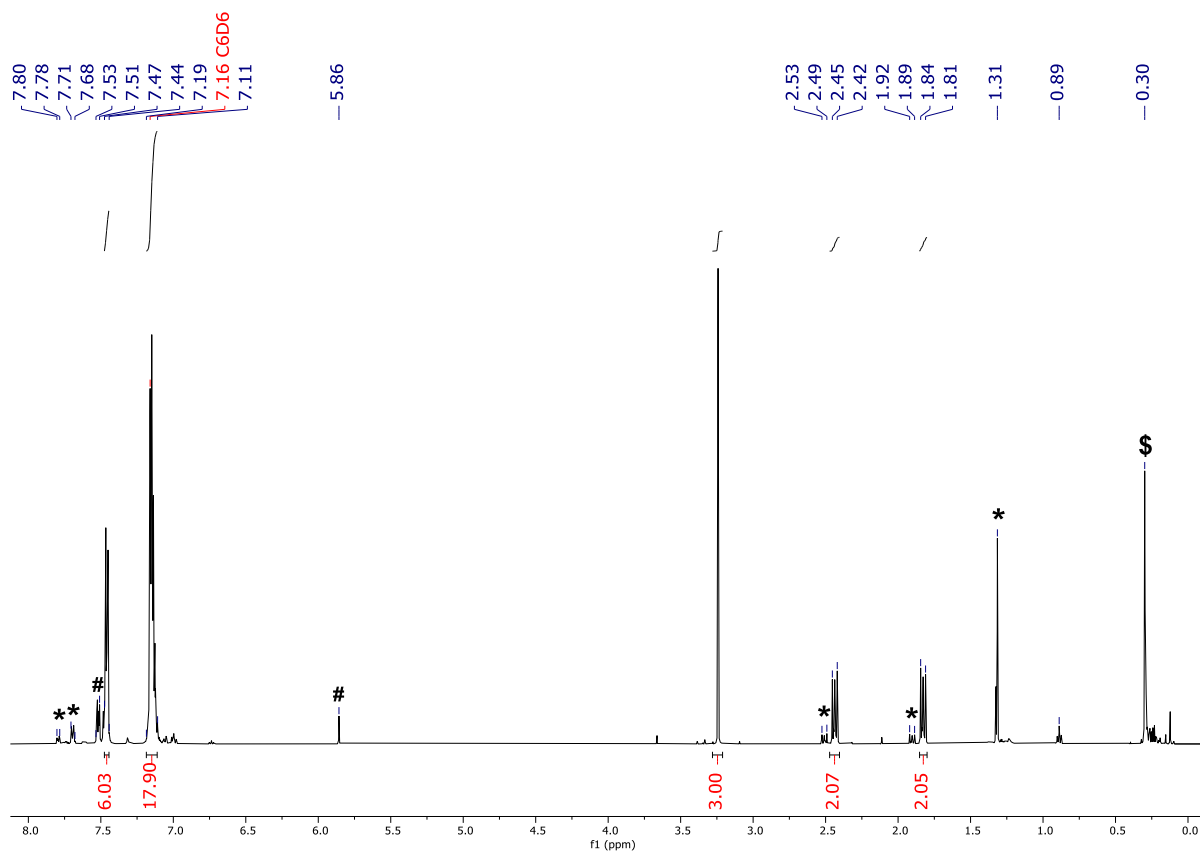


Figure S61. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11a**. # = Triphenylgermane; * = ca. 15 mol % contaminated with **11c** from competing transesterification reaction of **11a**; \$ = grease.

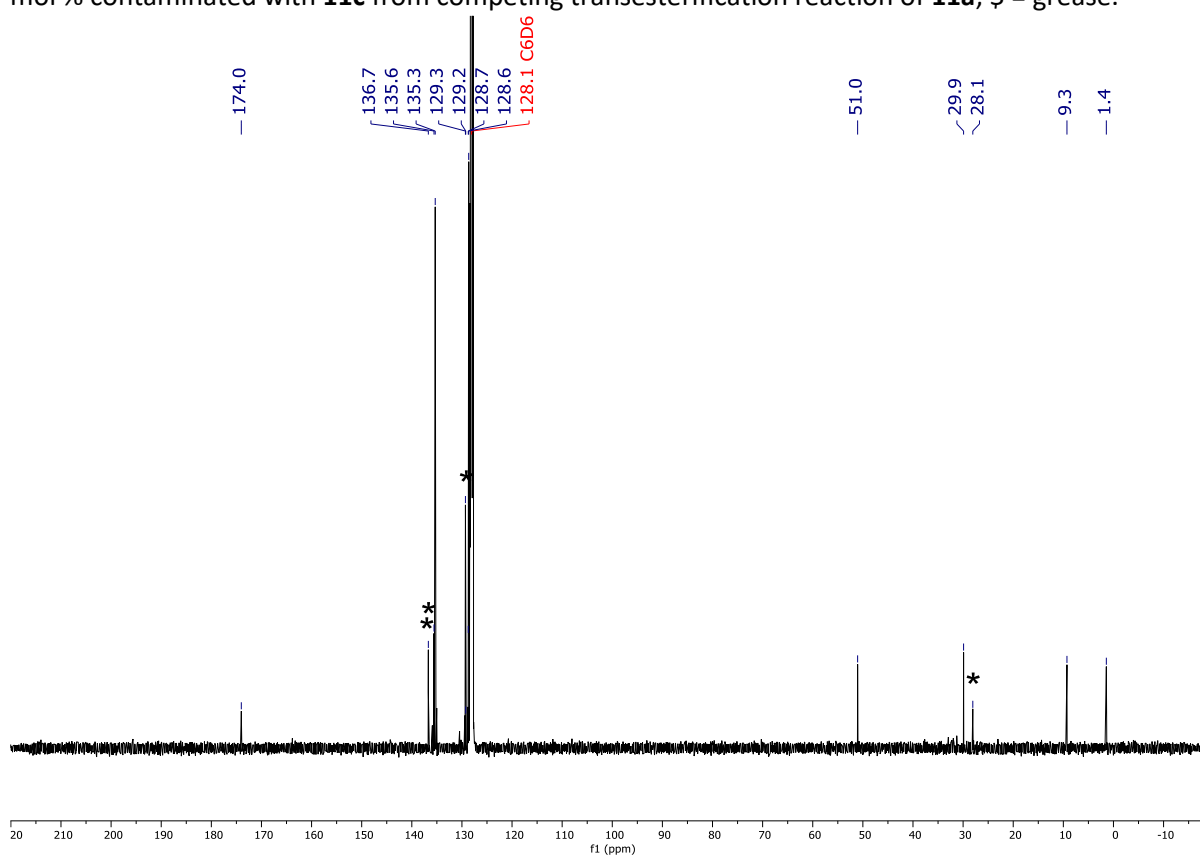


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11a**, * = ca. 15 mol % contaminated with **11c** from competing transesterification reaction of **11a**.

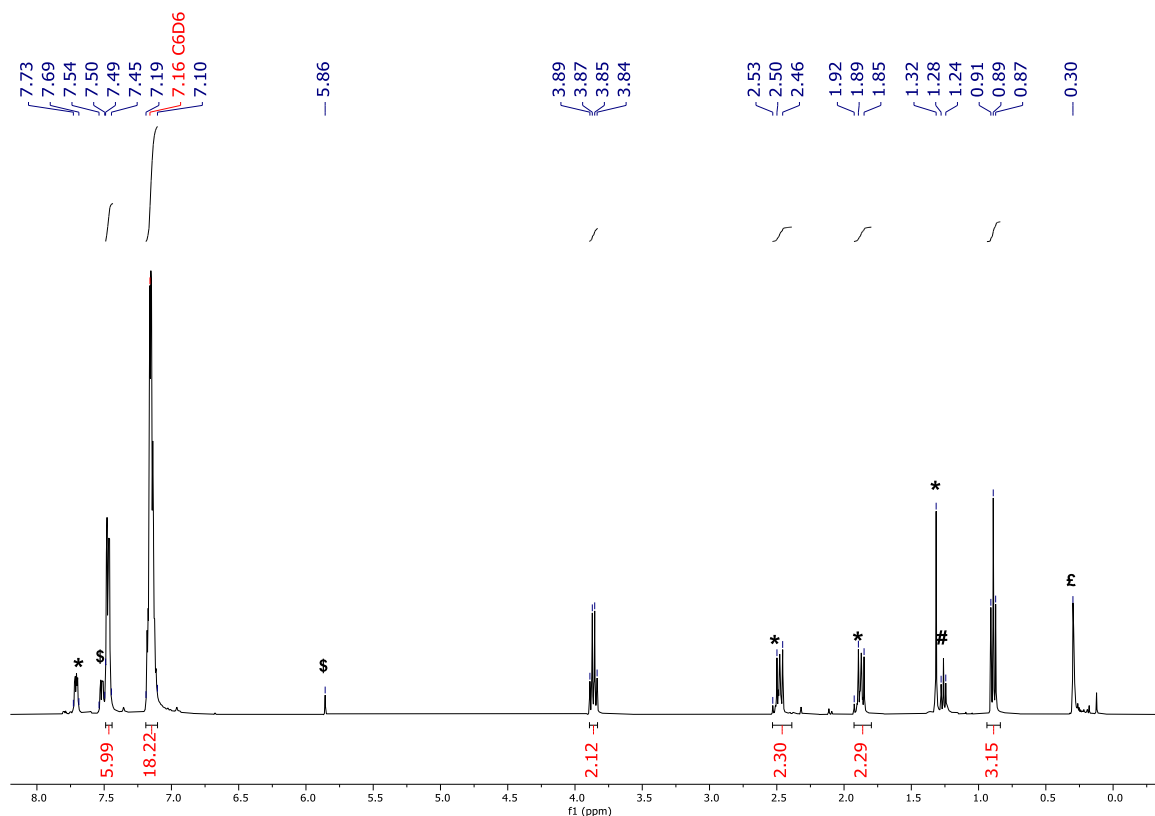


Figure S63. ^1H NMR spectrum (400 MHz, C_6D_6) of compound **11b**. $\$$ = Triphenylgermane; * *ca.* 11 mol % contaminated with **11c** from competing transesterification reaction of **11b**; # = unknown; $\$$ = HGePh_3 ; F = grease.

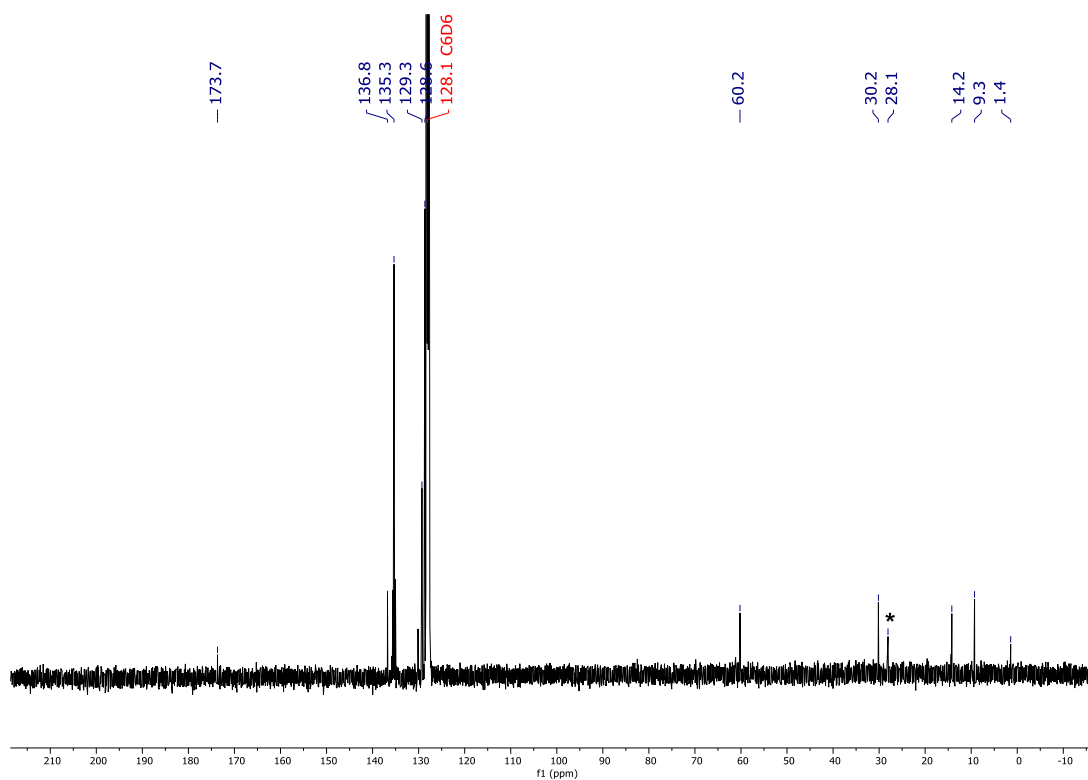


Figure S64. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, C_6D_6) of compound **11b**, * = *ca.* 11 mol % contaminated with **11c** from competing transesterification reaction of **11b**.

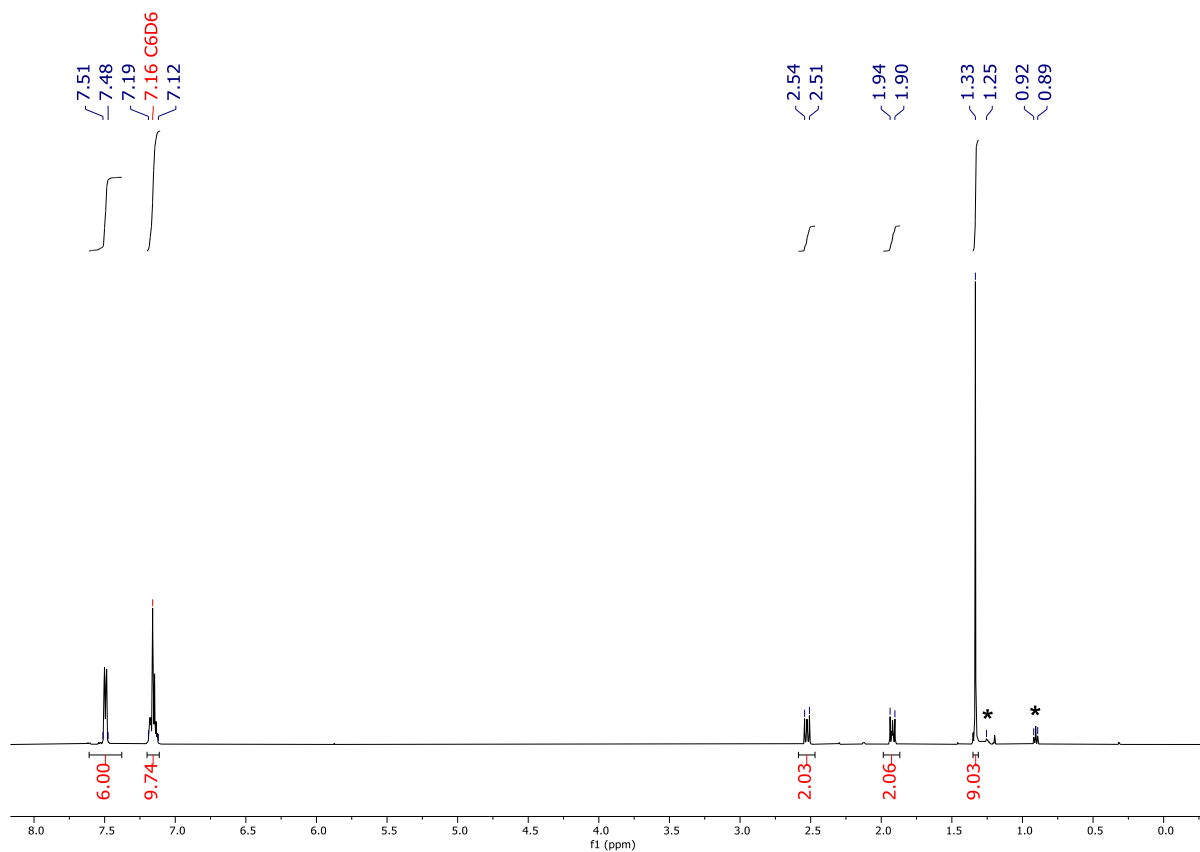


Figure S65. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11c**. * = hexane.

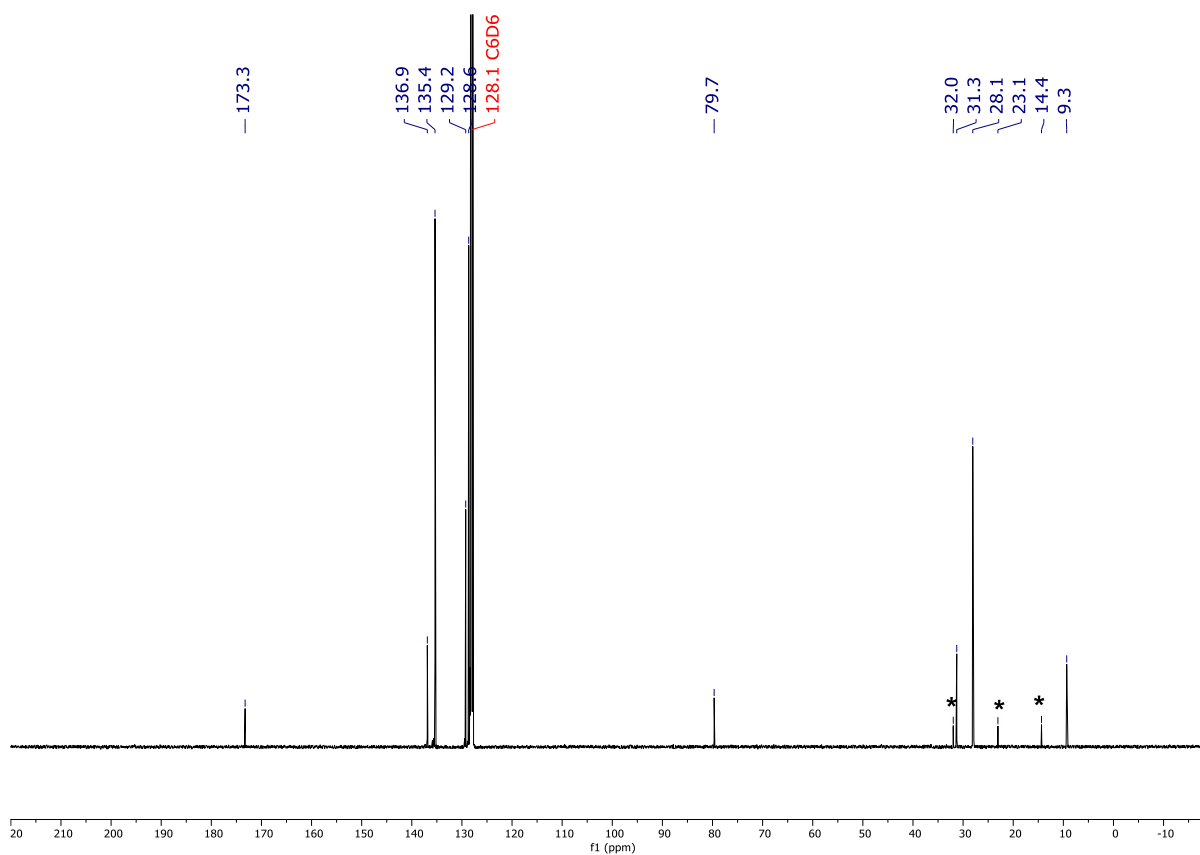


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11c**, * = hexane.

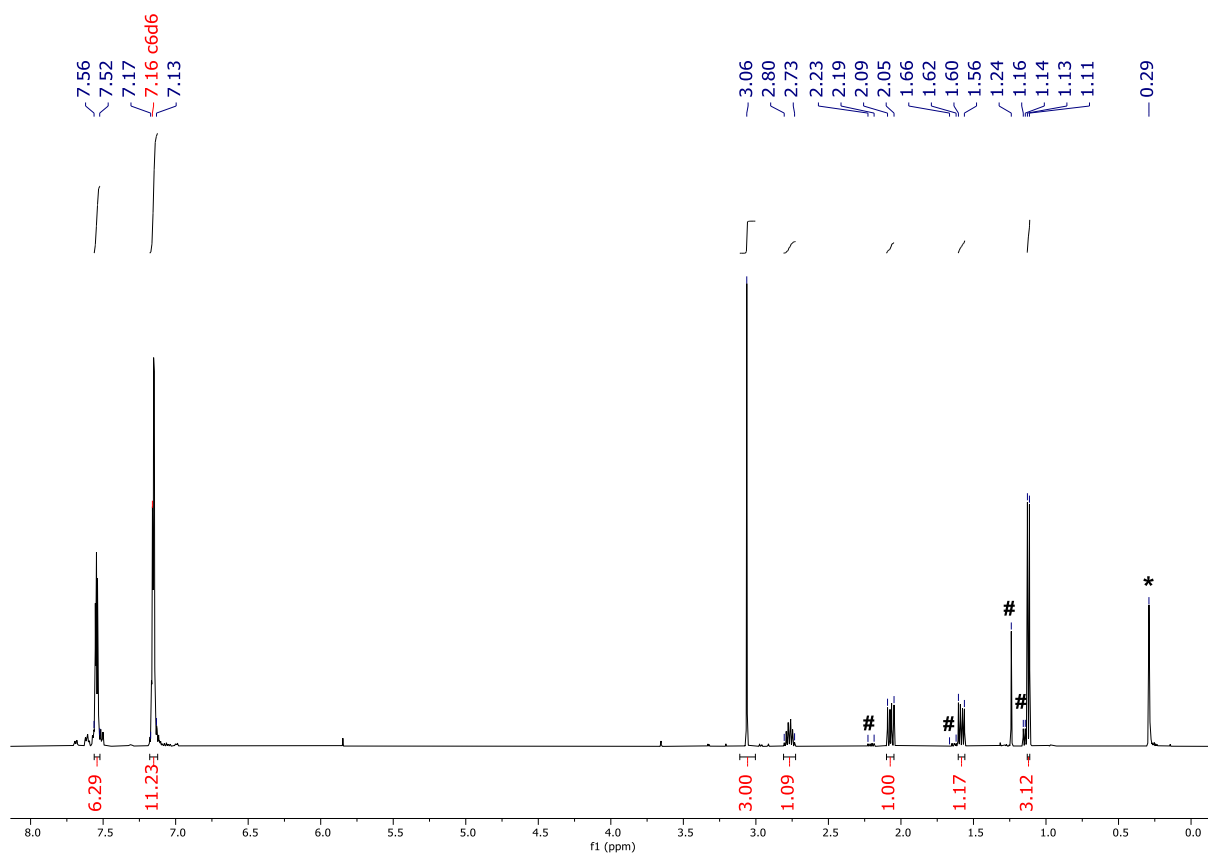


Figure S67. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11d**. * = grease; # = *ca.* 8 mol% contaminated with $\text{Ph}_3\text{GeCH}_2(\text{CH}_3)\text{CHC}(\text{O})\text{OC}(\text{CH}_3)_3$ from competing transesterification of **11d**.

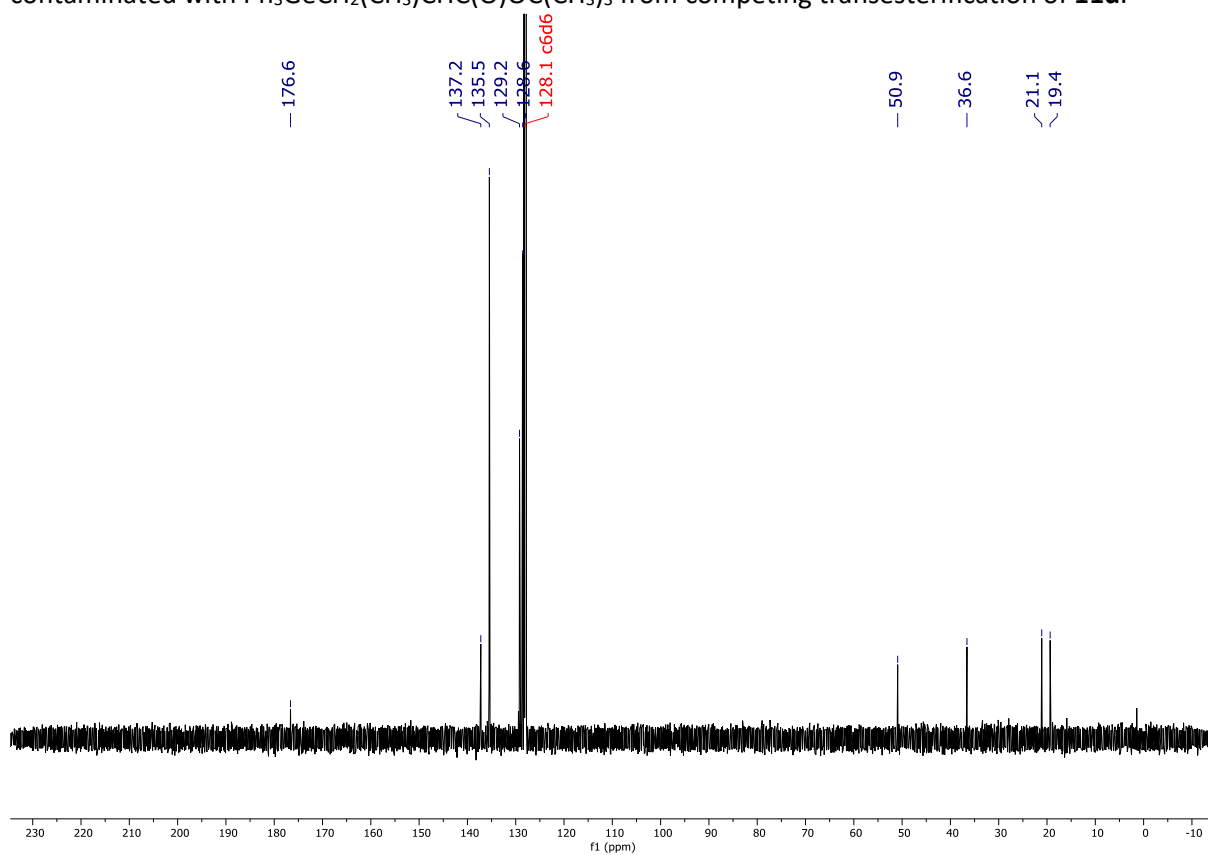


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11d**.

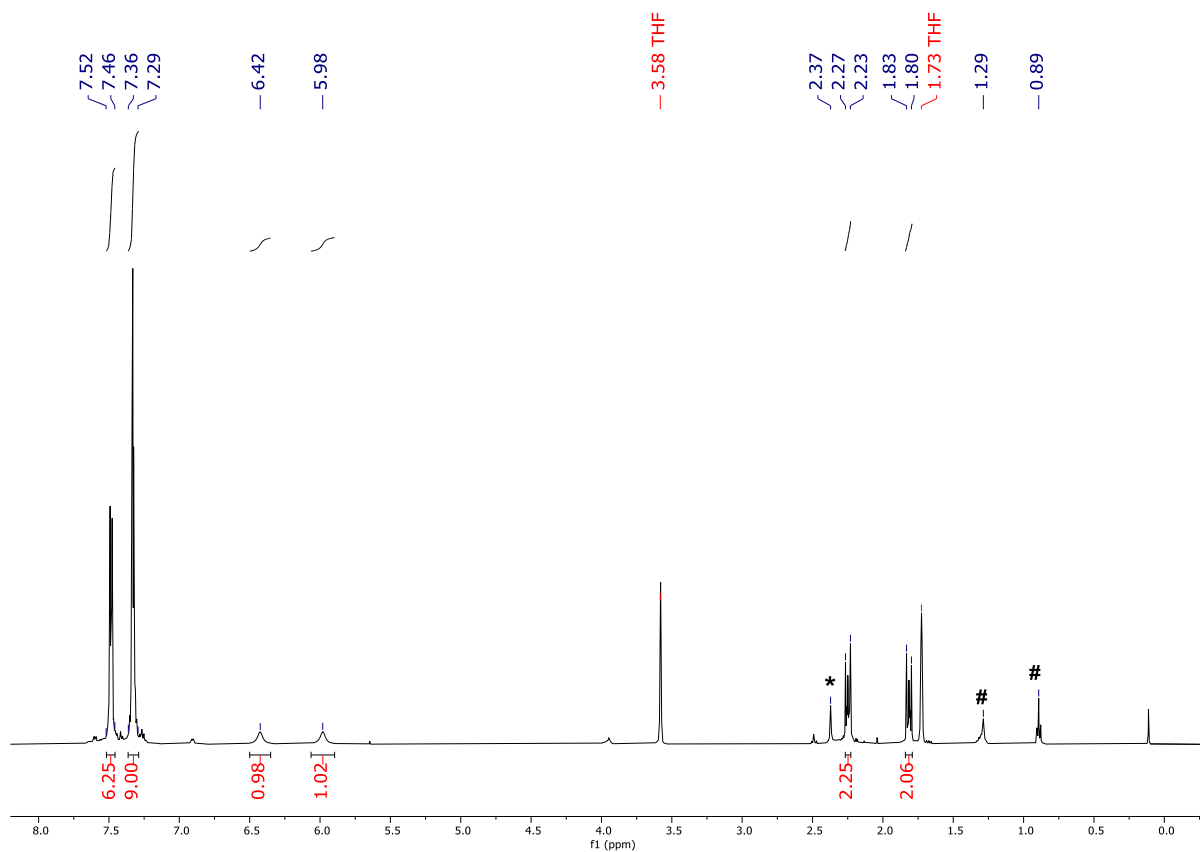


Figure S69. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11g**. * = toluene; # = hexane.

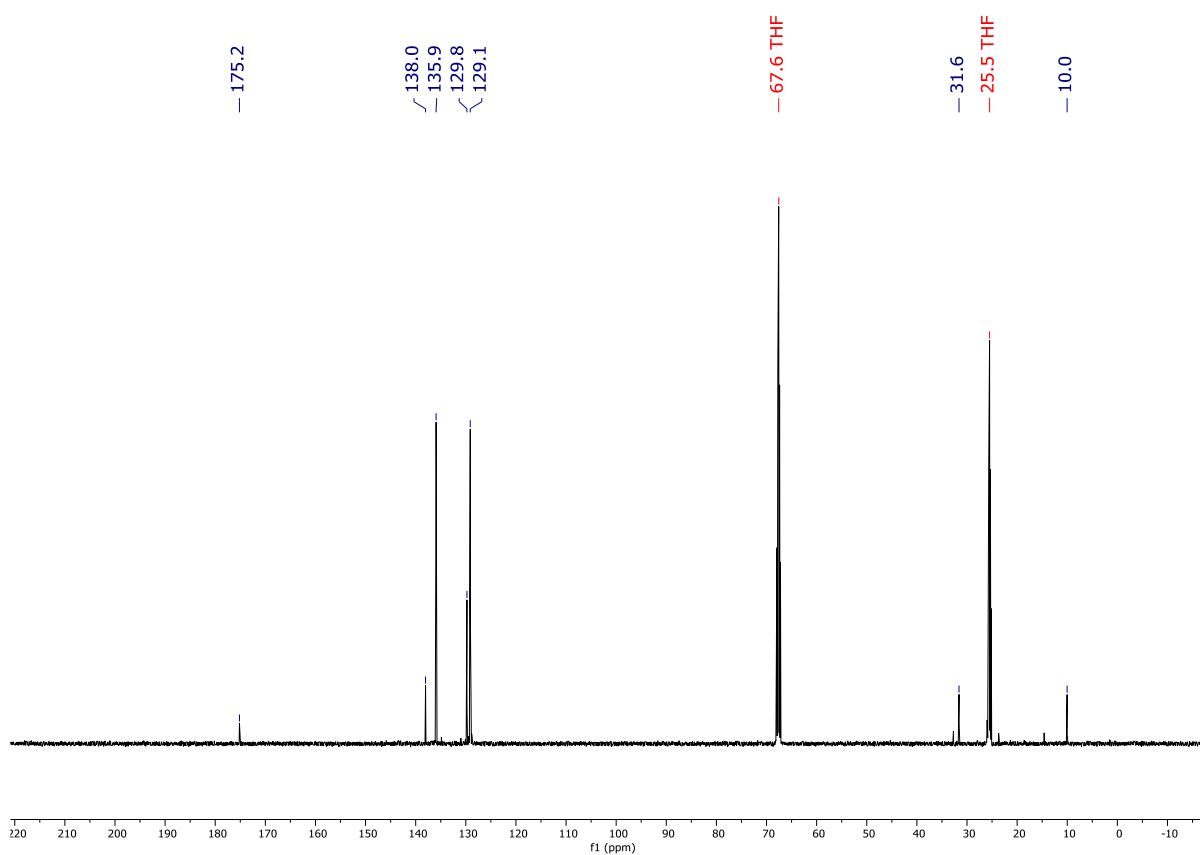


Figure S70. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11g**.

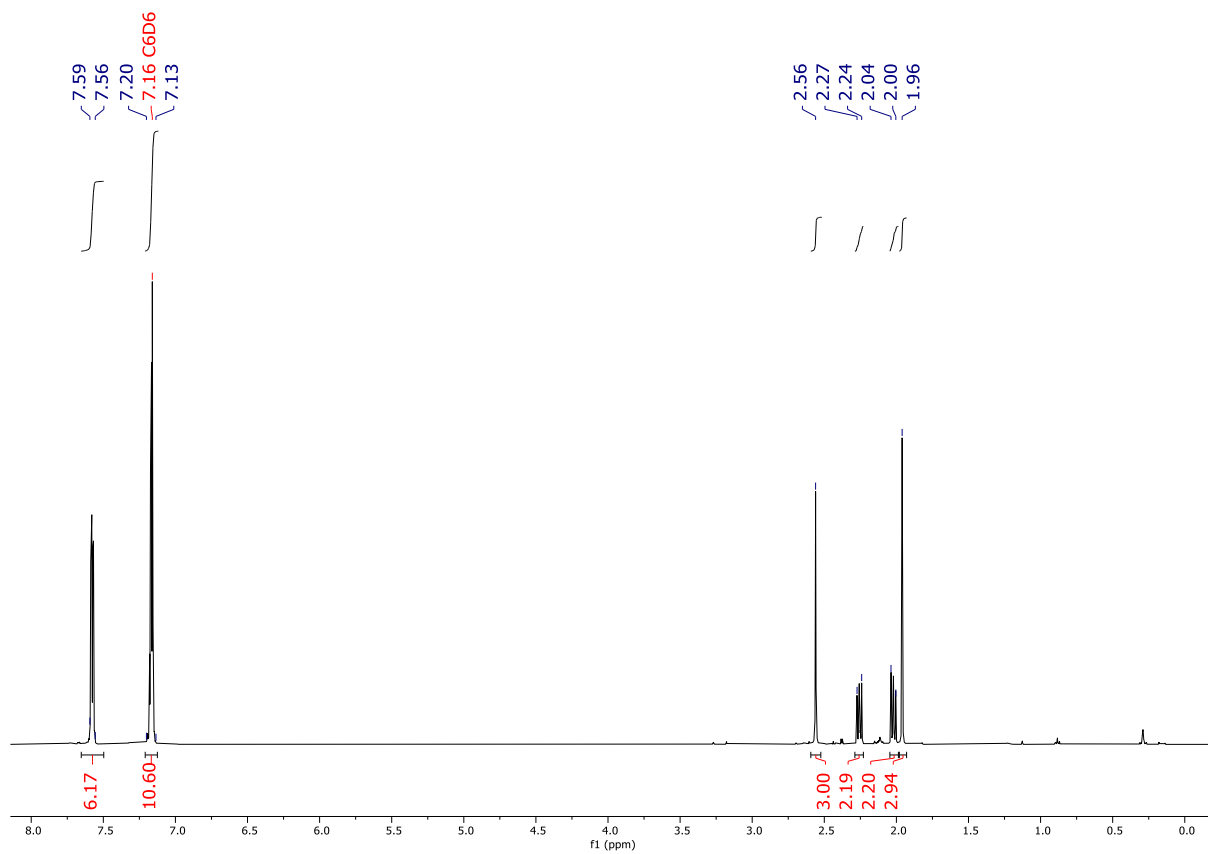


Figure S71. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11h**.

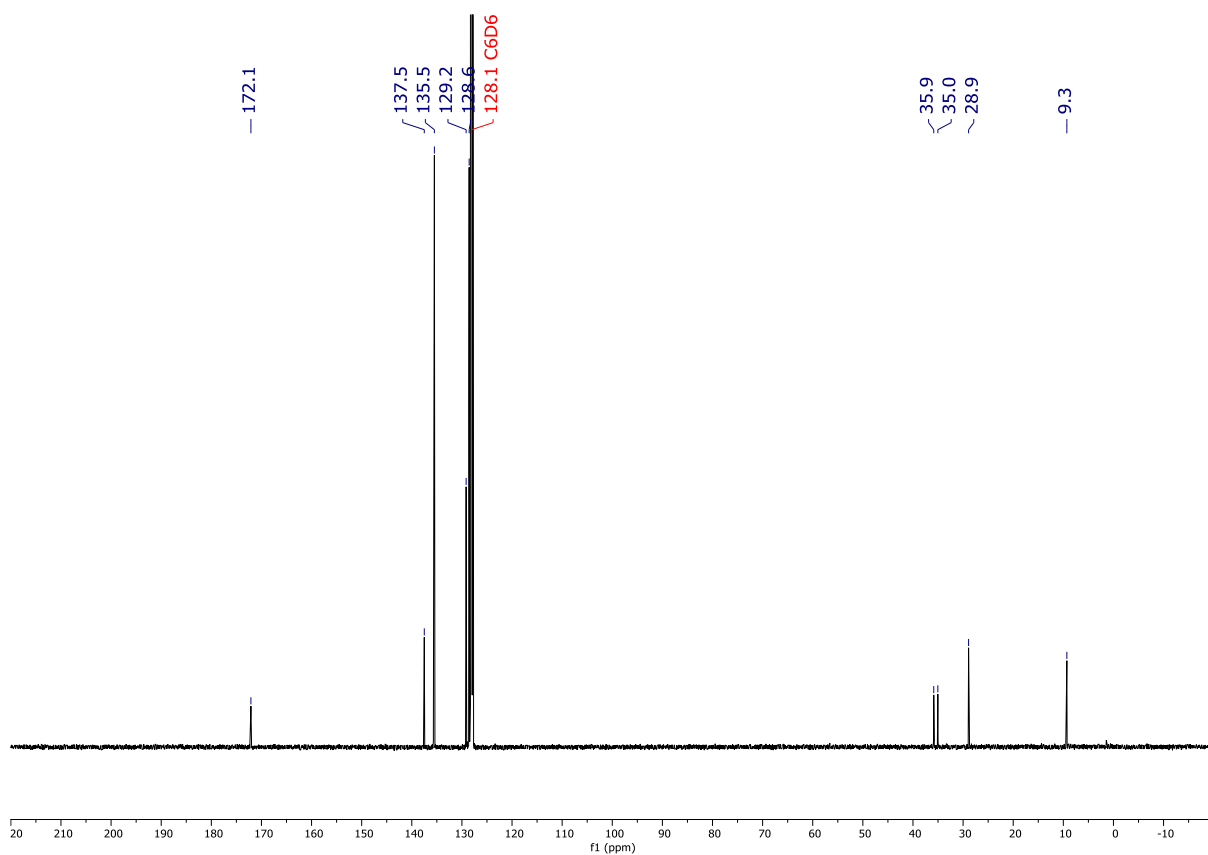


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11h**.

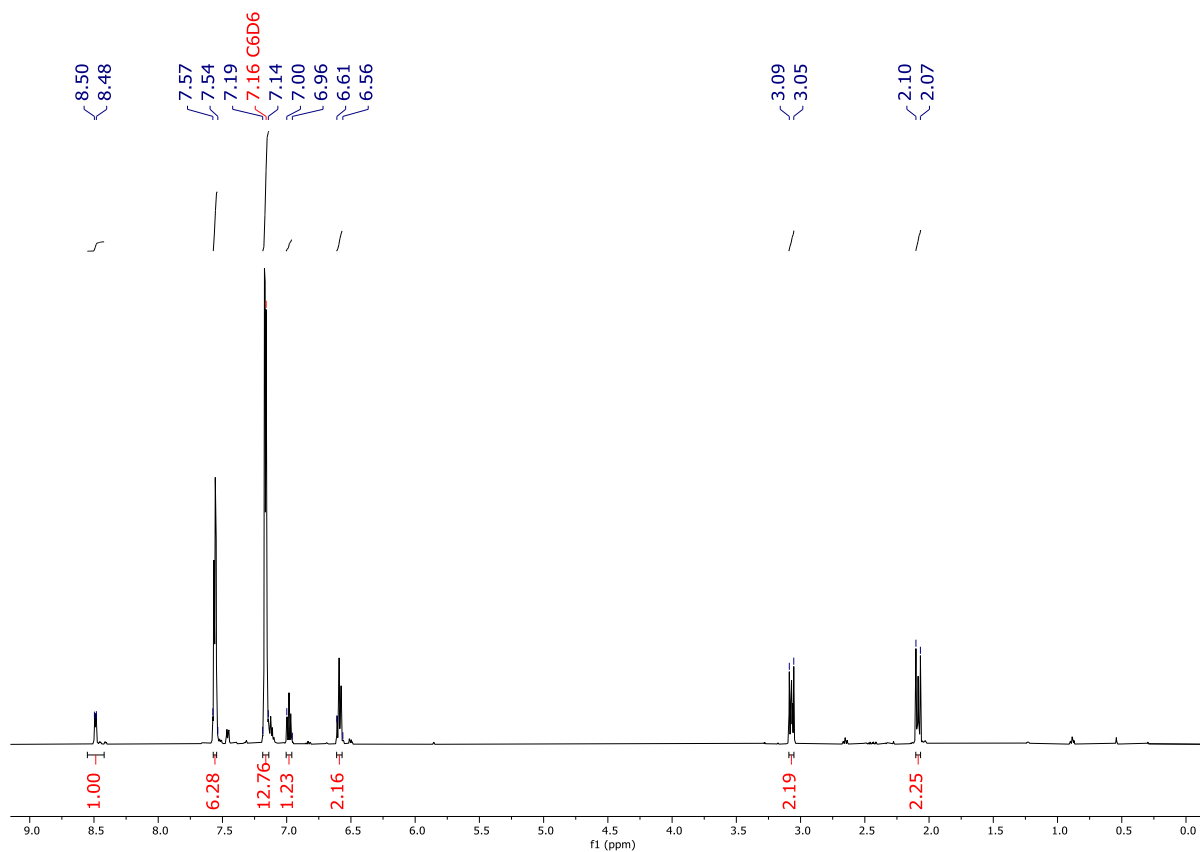


Figure S73. ^1H NMR spectrum (500 MHz, C_6D_6) of compound **11k**.

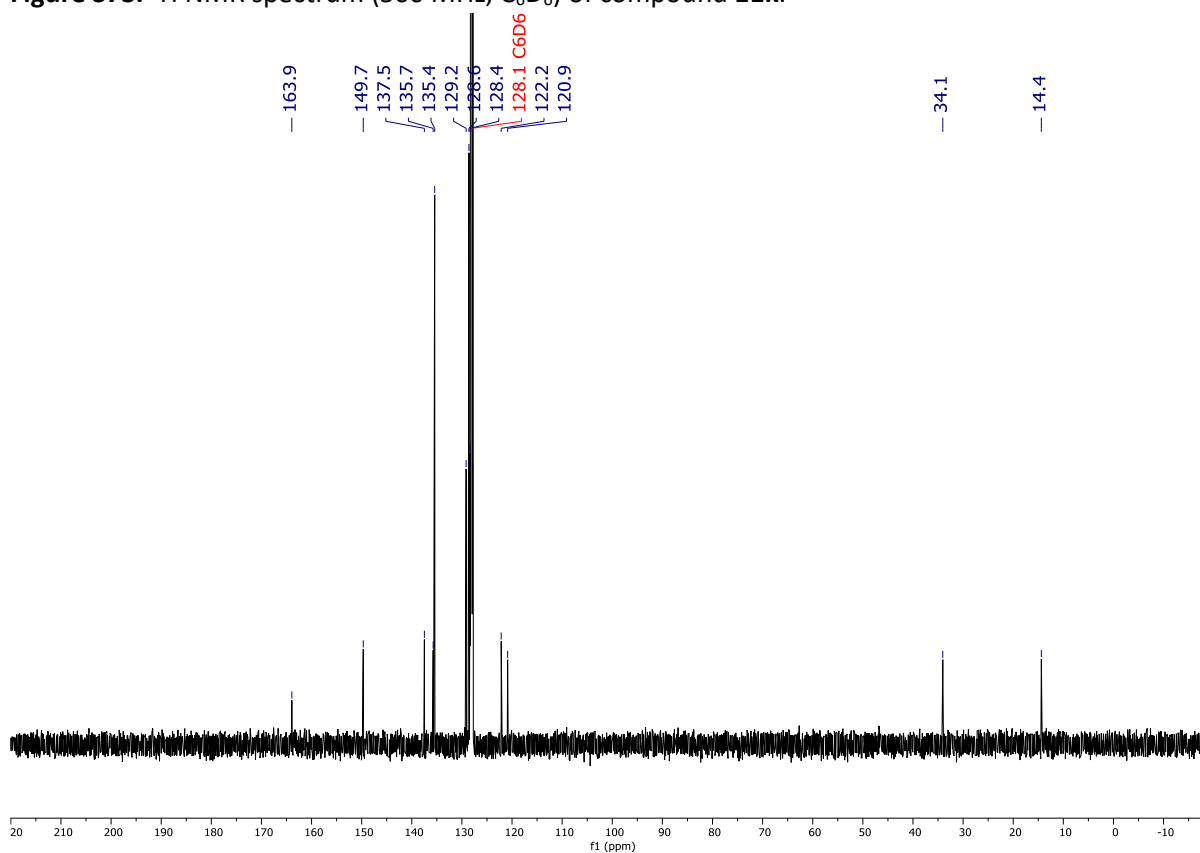


Figure S74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of compound **11k**.

Computational details

DFT calculations were run with Gaussian 16 (C.01).¹⁶ The Cu and Ge centres were described with the Stuttgart RECPs and associated basis sets,¹⁷ and 6-31G** basis sets were used for all other atoms (BS1).¹⁸ Initial BP86^{19,20} optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues). All energies were recomputed with 6-311++G** basis sets for all atoms except copper and germanium, for which the cc-pvtz-pp basis set and corresponding ECP was used (BS2).^{21,22} Corrections for the effect of benzene ($\epsilon = 2.2706$) solvent were run using the polarizable continuum model (PCM) and BS1.²³ Single-point dispersion corrections to the BP86 results employed Grimme's D3 parameter set with Becke-Johnson damping as implemented in Gaussian.²⁴ Bond analyses were performed on compound **2** using NBO7 as implemented in Gaussian16 and EDA-NOCV²⁵ analysis was performed as implemented in the ADF program package (2022.103).²⁶ All EDA-NOCV calculations were performed at the PBE0-d3bj/tz2p//BP86-d3bj/BS1 level of theory (numerical quality very good, nosym).

EDA-NOCV

	$\text{IPrCu}^\bullet + \bullet\text{GePh}_3$	$\text{IPrCu}^+ + \bar{\text{GePh}}_3$	$\text{IPrCu}^- + ^+\text{GePh}_3$
Pauli repulsion	138.73 kcal/mol	82.59 kcal/mol	220.50 kcal/mol
Electrostatic attraction	-144.14 kcal/mol	-162.25 kcal/mol	-241.06 kcal/mol
Orbital Interaction	-74.96 kcal/mol	-55.28 kcal/mol	-243.50 kcal/mol
Dispersion	-8.42 kcal/mol	-8.42 kcal/mol	-8.42 kcal/mol
Overall Bonding Energy	-88.79 kcal/mol	-146.36 kcal/mol	-272.47 kcal/mol

Orbital interaction for $\text{IPrCu}^+ + \bar{\text{GePh}}_3$ fragmentation broken down as follows:

$$\Delta E_{\text{orb1}} = -36.87 \text{ kcal/mol (66.6 \%)}$$

$$\Delta E_{\text{orb2}} = -2.03 \text{ kcal/mol (3.6 \%)}$$

$$\Delta E_{\text{orb3}} = -2.52 \text{ kcal/mol (4.5 \%)}$$

$$\Delta E_{\text{orb4}} = -2.00 \text{ kcal/mol (3.5 \%)}$$

$$\Delta E_{\text{orb(rest)}} = -12.10 \text{ kcal/mol (21.8 \%)}$$

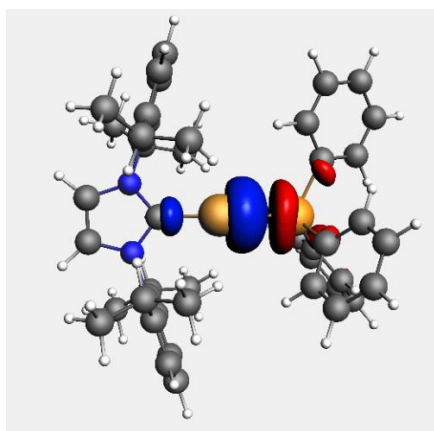


Figure S75. Plot of deformation density $\Delta\rho(1)$ of the pairwise orbital interaction between $[\text{IPrCu}]^+$ and $[\text{GePh}_3]^-$ in compound **2** associated with energy term ΔE_{orb1} . Charge flow from red to blue.

Cartesian Coordinates and Computed Energies [in Hartrees]

Phenylacetylene

SCF (BP86) Energy = -308.376233126

Enthalpy 0K = -308.271436

Enthalpy 298K = -308.270492

Free Energy 298K = -308.308773

Lowest Frequency = 139.6291 cm⁻¹

Second Frequency = 150.8098 cm⁻¹

SCF (BP86-D3BJ) Energy = -
308.406625354

SCF (C₆H₆) Energy = -308.386067339

SCF (BS2) Energy = -308.463935992

C -1.52035 -1.21574 0.00003
C -0.12008 -1.22150 -0.00003
C 0.59980 -0.00001 -0.00006
C -0.12006 1.22149 -0.00003
C -1.52033 1.21575 0.00003
C -2.22513 0.00001 0.00005
H -2.06507 -2.16563 0.00004
H 0.43374 -2.16498 -0.00005
H 0.43378 2.16495 -0.00005
H -2.06504 2.16565 0.00004
H -3.32000 0.00002 0.00010
C 2.02971 -0.00001 -0.00014
C 3.25258 0.00000 -0.00003
H 4.32572 0.00001 0.00096

Compound 2

SCF (BP86) Energy = -2056.32851158

Enthalpy 0K = -2055.456950

Enthalpy 298K = -2055.456005

Free Energy 298K = -2055.609058

Lowest Frequency = 6.1777 cm⁻¹

Second Frequency = 11.3824 cm⁻¹

SCF (BP86-D3BJ) Energy = -
2056.59078181

SCF (C₆H₆) Energy = -2056.34486638

SCF (BS2) Energy = -2347.69568896

Ge 2.21017 0.14177 0.04930
Cu -0.15028 0.06281 -0.03342
N -3.00439 0.93417 -0.10199
N -2.82589 -1.22245 -0.11965
C -2.06457 -0.07381 -0.08224
C -4.30449 0.42790 -0.15131
H -5.17537 1.07738 -0.17311
C -4.19106 -0.93618 -0.16276
H -4.94330 -1.71944 -0.19790
C -2.28057 -2.56647 -0.09788
C -2.12432 -3.21135 1.15484
C -1.62222 -4.52716 1.14550
H -1.48949 -5.05452 2.09588
C -1.28575 -5.16686 -0.05386
H -0.89314 -6.18896 -0.03672
C -1.44504 -4.50016 -1.27442
H -1.17176 -5.00511 -2.20671

C -1.94663 -3.18494 -1.32819
C -2.48946 -2.54271 2.48028
H -2.73690 -1.48741 2.27108
C -1.30577 -2.54566 3.47255
H -1.57858 -1.99642 4.39017
H -0.41136 -2.06914 3.03904
H -1.03034 -3.57148 3.77372
C -3.74072 -3.20291 3.10536
H -3.55391 -4.26546 3.34025
H -4.60775 -3.15916 2.42423
H -4.01773 -2.69446 4.04512
C -2.11630 -2.48971 -2.67848
H -2.46474 -1.45950 -2.48930
C -0.77395 -2.38772 -3.43638
H -0.37288 -3.38506 -3.68720
H -0.01115 -1.85992 -2.84045
H -0.91336 -1.83885 -4.38390
C -3.19141 -3.19602 -3.53674
H -3.33309 -2.66198 -4.49228
H -4.16485 -3.23538 -3.01858
H -2.89665 -4.23320 -3.77401
C -2.68641 2.34851 -0.06016
C -2.59888 2.98482 1.20300
C -2.29606 4.36037 1.21347
H -2.21304 4.88162 2.17285
C -2.09281 5.06734 0.02213
H -1.85495 6.13572 0.05437
C -2.18714 4.40989 -1.21034
H -2.01726 4.96943 -2.13594
C -2.48768 3.03582 -1.28299
C -2.78582 2.23351 2.52097
H -3.11700 1.20719 2.28428
C -1.44350 2.12056 3.28013
H -0.68154 1.60955 2.66683
H -1.57473 1.54794 4.21462
H -1.05174 3.11761 3.54737
C -3.87758 2.87738 3.40441
H -3.59697 3.89678 3.72134
H -4.03011 2.27876 4.31890
H -4.84245 2.94495 2.87373
C -2.54945 2.33665 -2.64049
H -2.91986 1.30923 -2.47779
C -1.13527 2.22537 -3.25590
H -1.17409 1.68671 -4.21872
H -0.45222 1.68219 -2.57976
H -0.70215 3.22365 -3.44171
C -3.53104 3.03198 -3.60960
H -3.20093 4.05471 -3.86126
H -4.54493 3.10251 -3.18041
H -3.59728 2.46640 -4.55490
C 2.97430 -0.68803 1.73710
C 2.57321 -1.98555 2.13182
H 1.85878 -2.54439 1.51304
C 3.07575 -2.58159 3.30161
H 2.75617 -3.59216 3.58266
C 3.98543 -1.88137 4.11168
H 4.37596 -2.34064 5.02679

C	4.39060	-0.58933	3.73982
H	5.10188	-0.03730	4.36555
C	3.89201	-0.00308	2.56280
H	4.22424	1.00330	2.28167
C	3.14177	-0.85878	-1.45330
C	4.07425	-1.89179	-1.21586
H	4.32309	-2.16917	-0.18469
C	4.69246	-2.57352	-2.27954
H	5.41409	-3.37195	-2.06966
C	4.39388	-2.22942	-3.60760
H	4.87728	-2.75763	-4.43720
C	3.47191	-1.20082	-3.86537
H	3.23558	-0.92204	-4.89920
C	2.85271	-0.52922	-2.79766
H	2.13534	0.27236	-3.01696
C	3.04713	1.98695	-0.01755
C	4.28411	2.22364	-0.65712
H	4.80663	1.39406	-1.14802
C	4.85602	3.50777	-0.68254
H	5.81674	3.66811	-1.18591
C	4.19993	4.58414	-0.06322
H	4.64452	5.58565	-0.08212
C	2.96894	4.36919	0.57837
H	2.44937	5.20466	1.06245
C	2.40087	3.08368	0.59544
H	1.43426	2.93207	1.09287

Compound 9

SCF (BP86) Energy = -2364.73457030
 Enthalpy 0K = -2363.754089
 Enthalpy 298K = -2363.753145
 Free Energy 298K = -2363.918566
 Lowest Frequency = 6.0553 cm⁻¹
 Second Frequency = 11.0659 cm⁻¹
 SCF (BP86-D3BJ) Energy = -
 2365.05974322
 SCF (C₆H₆) Energy = -2364.76057947
 SCF (BS2) Energy = -2656.185385

Ge	-3.10468	-0.62661	-0.09000
Cu	0.76610	-0.39675	-0.34167
N	2.37600	2.06004	0.32166
N	3.24805	0.23178	1.09723
C	2.16136	0.69623	0.37916
C	3.55560	2.42258	0.97577
H	3.89706	3.45283	1.01507
C	4.10179	1.27126	1.46964
H	5.01164	1.09292	2.03589
C	3.58196	-1.16665	1.30725
C	4.54827	-1.75093	0.44874
C	4.91773	-3.08725	0.70047
H	5.66298	-3.56476	0.05586
C	4.34231	-3.81158	1.74942
H	4.63987	-4.85062	1.92589
C	3.37811	-3.21246	2.57021
H	2.92547	-3.79256	3.37909
C	2.97488	-1.87742	2.37476
C	5.19420	-0.99888	-0.71616
H	4.68494	-0.02508	-0.81980

C	5.01607	-1.75174	-2.05355
H	5.40752	-1.14218	-2.88638
H	3.95580	-1.97765	-2.25140
H	5.56989	-2.70688	-2.05810
C	6.68876	-0.71601	-0.43655
H	7.25594	-1.65646	-0.32294
H	6.82887	-0.12916	0.48730
H	7.13823	-0.15094	-1.27144
C	1.95392	-1.22796	3.30890
H	1.41863	-0.45427	2.72939
C	0.89147	-2.21841	3.82483
H	1.31796	-2.95313	4.53085
H	0.41694	-2.76637	2.99462
H	0.09909	-1.66880	4.35787
C	2.66903	-0.52830	4.49068
H	1.93196	-0.04003	5.15169
H	3.37832	0.24254	4.14447
H	3.23330	-1.26091	5.09455
C	1.57979	3.01179	-0.43192
C	0.72880	3.90278	0.27159
C	0.02519	4.85932	-0.48471
H	-0.64381	5.55736	0.02727
C	0.15269	4.92223	-1.87686
H	-0.41220	5.66901	-2.44401
C	0.99736	4.02869	-2.54322
H	1.09197	4.08318	-3.63280
C	1.73842	3.05829	-1.84091
C	0.57447	3.87249	1.79317
H	0.96505	2.90289	2.15163
C	1.40712	4.99530	2.45843
H	2.48069	4.91592	2.21856
H	1.30157	4.95682	3.55660
H	1.06261	5.98808	2.11946
C	-0.90156	3.97444	2.23590
H	-1.32087	4.97339	2.02366
H	-0.98216	3.81237	3.32413
H	-1.53211	3.22596	1.73127
C	2.67527	2.13039	-2.61455
H	3.19425	1.48111	-1.88874
C	3.75688	2.92999	-3.37663
H	4.45429	2.24104	-3.88368
H	4.34196	3.57231	-2.69657
H	3.31191	3.57922	-4.15067
C	1.88549	1.20415	-3.56623
H	1.32985	1.78518	-4.32319
H	1.16107	0.58775	-3.00608
H	2.57280	0.52499	-4.09931
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C	-4.97712	-2.93553	-0.06791
H	-4.08363	-3.51316	0.19937
C	-6.20771	-3.60162	-0.19812
H	-6.26449	-4.68311	-0.03030
C	-7.36225	-2.88191	-0.54682
H	-8.32228	-3.39952	-0.65117
C	-7.28006	-1.49712	-0.76490
H	-8.17707	-0.93154	-1.04180
C	-6.04738	-0.83514	-0.63286
H	-5.99524	0.24502	-0.81375
C	-2.81739	-0.35057	1.87796
C	-3.77776	-0.79900	2.81009

H	-4.66755	-1.33226	2.45633
C	-3.61325	-0.56988	4.18741
H	-4.37159	-0.92536	4.89417
C	-2.48326	0.11870	4.65623
H	-2.35721	0.30640	5.72838
C	-1.51636	0.56886	3.74101
H	-0.63227	1.10905	4.09960
C	-1.68270	0.33370	2.36497
H	-0.91485	0.68405	1.66235
C	-3.27715	1.18657	-0.91958
C	-3.92795	2.23920	-0.23884
H	-4.27874	2.08962	0.78960
C	-4.13607	3.48168	-0.86297
H	-4.64907	4.28599	-0.32321
C	-3.68985	3.68987	-2.17838
H	-3.85698	4.65552	-2.66870
C	-3.03107	2.65567	-2.86346
H	-2.67840	2.81489	-3.88874
C	-2.82736	1.41416	-2.23750
H	-2.30939	0.61120	-2.77479
C	0.40448	-3.97567	-4.05791
C	-0.23467	-3.00749	-3.26866
C	0.23718	-2.68558	-1.97066
C	1.38772	-3.37114	-1.50586
C	2.01342	-4.35586	-2.28490
C	1.52905	-4.66063	-3.56904
H	0.02133	-4.19707	-5.06090
H	-1.10959	-2.47413	-3.65641
H	1.77400	-3.13564	-0.50687
H	2.88736	-4.88451	-1.88759
H	2.02661	-5.41881	-4.18347
C	-0.44725	-1.66168	-1.11985
C	-1.80613	-1.77092	-1.02988
H	-2.30944	-2.61212	-1.54537

TS1,

SCF (BP86) Energy = -2364.70355765
 Enthalpy 0K = -2363.717708
 Enthalpy 298K = -2363.716763
 Free Energy 298K = -2363.881402
 Lowest Frequency = -66.6942 cm⁻¹
 Second Frequency = 10.6310 cm⁻¹
 SCF (BP86-D3BJ) Energy = -
 2365.02205855
 SCF (C₆H₆) Energy = -2364.71897370
 SCF (BS2) Energy = -2656.145007

Ge	-2.29469	-0.98064	-0.30089
Cu	-0.06403	-0.11793	-0.11072
N	0.85971	2.53170	0.75121
N	2.02961	1.01404	1.76828
C	1.11981	1.17127	0.73448
C	1.56918	3.18539	1.75996
H	1.49863	4.25856	1.91137
C	2.29776	2.22905	2.40709
H	2.98424	2.29661	3.24631
C	2.78460	-0.18926	2.06965
C	4.16846	-0.19532	1.75110
C	4.91009	-1.34454	2.09183

H	5.97979	-1.37503	1.85980
C	4.30316	-2.44185	2.70961
H	4.89665	-3.32666	2.96395
C	2.93452	-2.40904	3.00787
H	2.46992	-3.27200	3.49214
C	2.14258	-1.28436	2.70712
C	4.89044	0.98188	1.08718
H	4.13852	1.74185	0.81485
C	5.61120	0.57151	-0.21495
H	6.07786	1.45700	-0.68088
H	4.91453	0.12374	-0.94048
H	6.41286	-0.16248	-0.02580
C	5.88516	1.64345	2.07059
H	6.67933	0.93602	2.36687
H	5.38825	1.98587	2.99441
H	6.37092	2.51615	1.60054
C	0.66874	-1.23765	3.11217
H	0.11701	-0.71274	2.30575
C	0.02044	-2.62717	3.25513
H	0.40714	-3.17832	4.13142
H	0.18617	-3.24563	2.35696
H	-1.06650	-2.50960	3.39152
C	0.48835	-0.42463	4.41716
H	-0.58096	-0.37314	4.68411
H	0.86699	0.60655	4.31805
H	1.02723	-0.90588	5.25288
C	0.03895	3.24104	-0.21169
C	-1.23400	3.72147	0.19102
C	-1.97058	4.47014	-0.74671
H	-2.95885	4.84818	-0.46859
C	-1.47222	4.72208	-2.02994
H	-2.06779	5.30091	-2.74350
C	-0.21629	4.23046	-2.40150
H	0.16852	4.43182	-3.40698
C	0.57371	3.48734	-1.50245
C	-1.81021	3.47087	1.58512
H	-1.22129	2.65932	2.04975
C	-1.67582	4.72905	2.47673
H	-0.62687	5.05157	2.58903
H	-2.07981	4.53250	3.48502
H	-2.23991	5.57468	2.04530
C	-3.28273	3.00869	1.53332
H	-3.95118	3.81857	1.19237
H	-3.62066	2.70864	2.53954
H	-3.41687	2.15097	0.85577
C	1.95753	3.00969	-1.94197
H	2.41985	2.46897	-1.09891
C	2.87724	4.20153	-2.29386
H	3.88615	3.84152	-2.56008
H	2.97502	4.90107	-1.44638
H	2.48945	4.77231	-3.15567
C	1.85909	2.01235	-3.11735
H	1.39624	2.47810	-4.00524
H	1.25844	1.13068	-2.83768
H	2.86605	1.66382	-3.40535
C	-2.47598	-2.77150	-1.25761
C	-2.06248	-3.96914	-0.62647
H	-1.68609	-3.93727	0.40404
C	-2.13505	-5.20782	-1.28667
H	-1.81483	-6.12163	-0.77260

C -2.61722 -5.27405 -2.60436
H -2.67279 -6.23749 -3.12317
C -3.02559 -4.09695 -3.25243
H -3.40493 -4.14072 -4.28006
C -2.95500 -2.86195 -2.58451
H -3.28783 -1.95362 -3.10110
C -3.28074 -1.31088 1.44687
C -4.25193 -2.32850 1.58389
H -4.46924 -2.98693 0.73483
C -4.94131 -2.52281 2.79461
H -5.68922 -3.32040 2.87449
C -4.67468 -1.69826 3.89937
H -5.21087 -1.84831 4.84304
C -3.71357 -0.67975 3.78554
H -3.49986 -0.02963 4.64250
C -3.02598 -0.49571 2.57281
H -2.27271 0.29926 2.50121
C -3.56973 0.20084 -1.35533
C -4.95109 0.26064 -1.06476
H -5.35292 -0.31566 -0.22271
C -5.82277 1.04946 -1.83539

Int₉

SCF (BP86) Energy = -2364.71053565
Enthalpy 0K = -2363.727499
Enthalpy 298K = -2363.726555
Free Energy 298K = -2363.887526
Lowest Frequency = 10.8972 cm⁻¹
Second Frequency = 15.8715 cm⁻¹
SCF (BP86-D3BJ) Energy = -
2365.04688703
SCF (C₆H₆) Energy = -2364.72927162
SCF (BS2) Energy = -2656.157705

Ge -2.09679 -0.89372 -0.37841
Cu 0.30295 -0.34547 -0.58873
N 0.71412 2.14986 1.05354
N 1.89580 0.49078 1.81392
C 1.04145 0.83116 0.77611
C 1.32837 2.59354 2.22959
H 1.19192 3.60503 2.59989
C 2.05944 1.54907 2.71301
H 2.68822 1.45995 3.59412
C 2.73903 -0.69150 1.87536
C 4.11846 -0.53341 1.57547
C 4.94152 -1.67214 1.68584
H 6.00924 -1.57947 1.46187
C 4.41859 -2.91278 2.06431
H 5.07584 -3.78591 2.13779
C 3.05425 -3.03776 2.35684
H 2.65477 -4.00916 2.66181
C 2.18487 -1.93214 2.28295
C 4.75038 0.80589 1.18397
H 3.94182 1.54258 1.04180
C 5.53104 0.72956 -0.14550
H 5.93642 1.72518 -0.39788
H 4.88956 0.39366 -0.97456
H 6.38562 0.03445 -0.08040
C 5.66459 1.32925 2.31792

H -6.89115 1.08124 -1.59110
C -5.32820 1.79261 -2.92013
H -6.00746 2.40451 -3.52448
C -3.95770 1.74840 -3.22338
H -3.56252 2.32836 -4.06554
C -3.08989 0.96464 -2.44261
H -2.01855 0.95343 -2.68094
C 5.30909 -1.48296 -3.73402
C 3.95335 -1.38229 -3.39895
C 3.45021 -2.02890 -2.23807
C 4.34723 -2.77672 -1.42907
C 5.69878 -2.87582 -1.77936
C 6.18641 -2.23129 -2.92980
H 5.68233 -0.98192 -4.63345
H 3.26276 -0.81775 -4.03203
H 3.96453 -3.27226 -0.53263
H 6.37749 -3.46255 -1.15126
H 7.24407 -2.31426 -3.20041
C 2.05974 -1.99456 -1.93080
C 0.85199 -1.99552 -1.67780
H -0.17586 -2.32850 -1.66746
H 6.50931 0.64063 2.49493
H 5.12071 1.43646 3.27190
H 6.08425 2.31488 2.05168
C 0.72708 -2.05734 2.71848
H 0.13703 -1.32469 2.14036
C 0.11232 -3.44158 2.43902
H 0.54180 -4.22843 3.08476
H 0.25440 -3.74161 1.38739
H -0.97059 -3.40542 2.64250
C 0.59256 -1.69872 4.21862
H -0.46554 -1.74885 4.52609
H 0.96211 -0.68070 4.43015
H 1.17038 -2.40447 4.84178
C -0.05079 3.04818 0.20507
C -1.28639 3.56048 0.67927
C -1.96671 4.48413 -0.13939
H -2.92673 4.88574 0.19871
C -1.44843 4.88261 -1.37341
H -2.00104 5.59304 -1.99693
C -0.21683 4.37869 -1.80844
H 0.19056 4.71206 -2.76700
C 0.51882 3.46465 -1.03108
C -1.88814 3.19800 2.03811
H -1.33277 2.33187 2.43856
C -1.73195 4.36880 3.03951
H -0.67932 4.66825 3.18113
H -2.14126 4.08924 4.02575
H -2.28115 5.25926 2.68653
C -3.37399 2.79107 1.93350
H -4.00991 3.65134 1.66037
H -3.73039 2.41096 2.90548
H -3.52767 2.00316 1.18072
C 1.92416 3.04584 -1.47121
H 2.11306 2.02647 -1.09227
C 2.97601 3.99364 -0.84251
H 3.99602 3.68310 -1.12880
H 2.91735 3.99758 0.25902
H 2.82390 5.03049 -1.19177
C 2.10147 2.99412 -3.00107

H	2.06827	3.99810	-3.46024
H	1.32527	2.37237	-3.47786
H	3.08562	2.55994	-3.24297
C	-2.58521	-2.60167	-1.37472
C	-2.37090	-3.87441	-0.79646
H	-2.00422	-3.94767	0.23454
C	-2.63317	-5.05661	-1.50912
H	-2.46726	-6.03017	-1.03298
C	-3.10733	-4.99247	-2.83033
H	-3.30995	-5.91274	-3.38931
C	-3.31972	-3.74007	-3.42744
H	-3.69279	-3.67905	-4.45650
C	-3.06205	-2.56023	-2.70493
H	-3.24989	-1.59034	-3.18174
C	-2.98251	-1.19453	1.43205
C	-4.09682	-2.05544	1.56785
H	-4.46896	-2.60085	0.69308
C	-4.73379	-2.23730	2.80867
H	-5.59651	-2.90929	2.88502
C	-4.26705	-1.56203	3.94782
H	-4.76136	-1.70310	4.91536
C	-3.15872	-0.70619	3.83725
H	-2.78570	-0.17431	4.72055
C	-2.52749	-0.53124	2.59239
H	-1.65957	0.13631	2.52504
C	-3.28928	0.46326	-1.31420
C	-4.66030	0.59345	-0.99822
H	-5.09052	-0.00620	-0.18688
C	-5.48780	1.48160	-1.70692
H	-6.54891	1.56695	-1.44467
C	-4.95864	2.25434	-2.75410
H	-5.60392	2.94283	-3.31132
C	-3.59805	2.13950	-3.08141
H	-3.17640	2.74113	-3.89493
C	-2.77356	1.25595	-2.36238
H	-1.70902	1.18619	-2.61935
C	4.83094	-0.64405	-3.90320
C	3.49795	-0.48938	-3.49999
C	2.97366	-1.26358	-2.43120
C	3.83286	-2.18520	-1.77672
C	5.15875	-2.34106	-2.19926
C	5.66787	-1.57300	-3.26098
H	5.21440	-0.04389	-4.73563
H	2.84033	0.21347	-4.01936
H	3.44196	-2.77744	-0.94438
H	5.80100	-3.06880	-1.69172
H	6.70604	-1.69730	-3.58551
C	1.58232	-1.18211	-2.06716
C	0.34562	-1.46721	-2.17351
H	-0.43594	-2.03938	-2.66849

TS2,

SCF (BP86) Energy = -2364.69212453
 Enthalpy 0K = -2363.706178
 Enthalpy 298K = -2363.705233
 Free Energy 298K = -2363.866949
 Lowest Frequency = -128.9081 cm⁻¹
 Second Frequency = 10.9417 cm⁻¹

SCF (BP86-D3BJ) Energy = -
 2365.01978327
 SCF (C₆H₆) Energy = -2364.70851773
 SCF (BS2) Energy = -2656.135861

Ge	2.16078	-0.90209	0.01565
Cu	-0.48335	-0.46215	0.19593
N	-1.32021	2.39298	-0.22041
N	-2.24405	0.98176	-1.60157
C	-1.31929	1.04731	-0.56542
C	-2.20575	3.12240	-1.02254
H	-2.34854	4.19044	-0.88861
C	-2.77693	2.23996	-1.89186
H	-3.51515	2.38156	-2.67601
C	-2.81500	-0.24509	-2.13004
C	-4.07360	-0.66176	-1.61909
C	-4.63251	-1.84017	-2.15242
H	-5.60208	-2.18597	-1.77906
C	-3.97182	-2.57292	-3.14478
H	-4.42242	-3.48953	-3.54009
C	-2.73784	-2.13132	-3.63699
H	-2.23210	-2.70534	-4.41900
C	-2.13240	-0.95720	-3.14829
C	-4.85584	0.13082	-0.56851
H	-4.19890	0.92591	-0.17687
C	-5.28678	-0.73465	0.63458
H	-5.80414	-0.10748	1.38141
H	-4.42256	-1.21185	1.12290
H	-5.99019	-1.53166	0.33585
C	-6.08553	0.81610	-1.21218
H	-6.78951	0.06670	-1.61470
H	-5.79798	1.48116	-2.04422
H	-6.62715	1.42015	-0.46371
C	-0.82551	-0.44914	-3.75016
H	-0.33026	0.18097	-2.99311
C	0.16145	-1.57680	-4.10935
H	-0.19178	-2.18339	-4.96247
H	0.32661	-2.25096	-3.25277
H	1.13417	-1.14183	-4.39136
C	-1.11033	0.44034	-4.98436
H	-0.16542	0.84241	-5.38870
H	-1.76411	1.29259	-4.73132
H	-1.60681	-0.14005	-5.78237
C	-0.65934	2.98768	0.92734
C	0.39065	3.91921	0.71320
C	0.96649	4.52551	1.84668
H	1.78189	5.24258	1.71000
C	0.52100	4.22546	3.13740
H	0.98928	4.70368	4.00397
C	-0.53180	3.32253	3.31860
H	-0.89255	3.11015	4.32984
C	-1.15654	2.69081	2.22609
C	0.88282	4.32704	-0.67701
H	0.46286	3.61594	-1.41042
C	0.37476	5.74164	-1.04862
H	-0.72601	5.81095	-1.02472
H	0.71076	6.01976	-2.06275
H	0.76754	6.49515	-0.34366
C	2.42141	4.27045	-0.79516
H	2.90306	5.04395	-0.17184

H	2.72979	4.45017	-1.83905
H	2.81418	3.29014	-0.48463
C	-2.38869	1.81846	2.47513
H	-2.58556	1.22920	1.56414
C	-3.62086	2.71723	2.74145
H	-4.52417	2.09902	2.88537
H	-3.80890	3.40968	1.90288
H	-3.47850	3.32518	3.65252
C	-2.18679	0.80060	3.61553
H	-2.02259	1.29202	4.59081
H	-1.33282	0.13866	3.40139
H	-3.08275	0.16518	3.71342
C	3.36982	-2.52249	0.07034
C	3.08348	-3.66031	-0.71824
H	2.19937	-3.66892	-1.36868
C	3.91707	-4.79146	-0.68994
H	3.67727	-5.66294	-1.30956
C	5.05506	-4.80354	0.13322
H	5.70559	-5.68458	0.15923
C	5.35273	-3.68238	0.92398
H	6.23791	-3.68675	1.57014
C	4.51542	-2.55307	0.89275
H	4.75798	-1.68668	1.51874
C	2.66165	-0.07666	-1.77766
C	3.70956	-0.63011	-2.54661
H	4.23449	-1.52241	-2.18984
C	4.09184	-0.05089	-3.77012
H	4.90641	-0.49760	-4.35154
C	3.43608	1.09630	-4.24498
H	3.73412	1.54843	-5.19730
C	2.39478	1.66068	-3.48849
H	1.87731	2.55697	-3.84975
C	2.01208	1.07330	-2.27023
H	1.18599	1.50779	-1.69511
C	2.87212	0.31912	1.44542
C	3.94174	1.20092	1.17355
H	4.34788	1.26876	0.15705
C	4.50485	1.98572	2.19482
H	5.33938	2.65927	1.96862
C	4.00289	1.90181	3.50398
H	4.44336	2.51053	4.30144
C	2.93740	1.03210	3.78734
H	2.54289	0.96196	4.80723
C	2.37725	0.24662	2.76534
H	1.55052	-0.43513	2.99550
C	-2.18847	-4.02617	4.24312
C	-1.33175	-3.19624	3.50717
C	-1.63455	-2.84199	2.16609
C	-2.82476	-3.36273	1.59431
C	-3.66451	-4.20919	2.33071
C	-3.35995	-4.54094	3.66249
H	-1.93165	-4.28114	5.27775
H	-0.41486	-2.80883	3.96412
H	-3.06817	-3.10805	0.55730
H	-4.56860	-4.61182	1.85953
H	-4.02504	-5.19270	4.23841
C	-0.74795	-1.96853	1.40899
C	0.45111	-2.18894	0.88784
H	1.04996	-3.10765	0.81815

Compound 10

SCF (BP86) Energy = -2364.74086034
 Enthalpy 0K = -2363.752780
 Enthalpy 298K = -2363.751836
 Free Energy 298K = -2363.916458
 Lowest Frequency = 7.4664 cm⁻¹
 Second Frequency = 8.5196 cm⁻¹
 SCF (BP86-D3BJ) Energy = -
 2365.05573728
 SCF (C₆H₆) Energy = -2364.75936950
 SCF (BS2) Energy = -2656.184351

Ge	-2.81625	-0.29478	0.46065
Cu	0.82510	0.01217	-0.68485
N	3.29555	1.46534	-0.04298
N	3.71492	-0.64972	-0.23512
C	2.66266	0.24713	-0.19944
C	4.68327	1.32997	0.00765
H	5.34109	2.18598	0.12979
C	4.94818	-0.00535	-0.11697
H	5.88628	-0.55287	-0.13279
C	3.58916	-2.09021	-0.34148
C	3.34315	-2.66945	-1.61168
C	3.25783	-4.07447	-1.67526
H	3.06634	-4.55243	-2.64164
C	3.42385	-4.86636	-0.53317
H	3.35749	-5.95690	-0.60908
C	3.68192	-4.26556	0.70497
H	3.81638	-4.89192	1.59282
C	3.76873	-2.86597	0.83314
C	3.22518	-1.84743	-2.89519
H	3.22223	-0.77945	-2.61730
C	1.90193	-2.12482	-3.64101
H	1.83536	-1.49147	-4.54247
H	1.03362	-1.89976	-2.99901
H	1.82976	-3.17672	-3.96901
C	4.44702	-2.09206	-3.81207
H	4.49857	-3.14623	-4.13661
H	5.39436	-1.85329	-3.29921
H	4.37984	-1.46482	-4.71789
C	4.08550	-2.24443	2.19500
H	3.92990	-1.15441	2.11559
C	3.15165	-2.75811	3.31127
H	3.30508	-3.83395	3.50760
H	2.09116	-2.60867	3.05465
H	3.36141	-2.22221	4.25323
C	5.56697	-2.48277	2.57401
H	5.80051	-2.00583	3.54175
H	6.25804	-2.07397	1.81729
H	5.77999	-3.56203	2.66910
C	2.62321	2.74567	0.06351
C	2.26578	3.21469	1.35207
C	1.65755	4.48259	1.43216
H	1.36136	4.87085	2.41193
C	1.42409	5.24934	0.28390
H	0.95624	6.23588	0.37070
C	1.78702	4.75703	-0.97569
H	1.59562	5.36092	-1.86891
C	2.39460	3.49441	-1.11799

C	2.49813	2.39792	2.62292
H	3.07840	1.49966	2.34841
C	3.32794	3.18044	3.66552
H	4.29424	3.51414	3.25028
H	3.53313	2.54425	4.54369
H	2.79063	4.07482	4.02589
C	1.15673	1.91545	3.22049
H	0.51219	2.76620	3.50065
H	1.33712	1.31093	4.12639
H	0.59634	1.29846	2.49947
C	2.78319	2.98960	-2.50719
H	3.18765	1.96847	-2.39637
C	3.89228	3.86728	-3.13176
H	4.18925	3.46896	-4.11740
H	4.79090	3.90377	-2.49242
H	3.54581	4.90493	-3.28099
C	1.55261	2.89558	-3.43682
H	1.10495	3.88833	-3.61856
H	0.77606	2.24557	-3.00076
H	1.84525	2.47900	-4.41632
C	-4.68264	-1.03478	0.55200
C	-4.89173	-2.42838	0.46779
H	-4.03275	-3.10382	0.37632
C	-6.18709	-2.97025	0.51189
H	-6.32774	-4.05494	0.44308
C	-7.29928	-2.12418	0.65002
H	-8.31020	-2.54500	0.68742
C	-7.10880	-0.73633	0.74396
H	-7.97174	-0.07005	0.85641
C	-5.81136	-0.19893	0.69365
H	-5.68078	0.88653	0.77629
C	-1.70781	-1.64319	1.44035
C	-1.09190	-2.70708	0.74522
H	-1.10332	-2.71265	-0.35038
C	-0.46136	-3.75329	1.44137
H	0.01147	-4.57090	0.88619
C	-0.43578	-3.74836	2.84608
H	0.04318	-4.56964	3.39071
C	-1.02707	-2.68600	3.55061
H	-1.00428	-2.67389	4.64637
C	-1.65658	-1.64276	2.85058
H	-2.11743	-0.82223	3.41333
C	-2.83151	1.44232	1.45733
C	-3.55209	1.59237	2.66407
H	-4.13551	0.75316	3.06153
C	-3.55430	2.81545	3.35686
H	-4.12043	2.91405	4.29011
C	-2.84003	3.91234	2.84727
H	-2.84804	4.86893	3.38192
C	-2.12466	3.78007	1.64559
H	-1.56794	4.63146	1.23915
C	-2.11983	2.55399	0.95812
H	-1.55947	2.45734	0.02057
C	-0.80214	-0.00909	-1.65936
C	-2.14669	-0.06435	-1.40823
C	-3.15873	0.05418	-2.49655
C	-4.28926	0.89588	-2.37025
C	-2.99996	-0.65320	-3.71342
C	-5.20860	1.04162	-3.41891
H	-4.43086	1.46375	-1.44393

C	-3.92166	-0.51445	-4.76072
H	-2.14449	-1.32930	-3.81953
C	-5.03127	0.33571	-4.62019
H	-6.06832	1.70989	-3.29678
H	-3.77886	-1.08118	-5.68800
H	-5.75455	0.44144	-5.43590
H	-0.60980	0.14736	-2.74688

TS1₁₀

SCF (BP86) Energy = -2364.70835249
 Enthalpy 0K = -2363.722375
 Enthalpy 298K = -2363.721431
 Free Energy 298K = -2363.888799
 Lowest Frequency = -55.4787 cm⁻¹
 Second Frequency = 6.7245 cm⁻¹
 SCF (BP86-D3BJ) Energy = -
 2365.02164114
 SCF (C₆H₆) Energy = -2364.72464322
 SCF (BS2) Energy = -2656.150453

Ge	1.69718	-1.18586	-0.27751
Cu	-0.35550	-0.03495	0.07335
N	-2.75132	1.45266	-0.94064
N	-3.33963	-0.24134	0.27476
C	-2.22086	0.45259	-0.14784
C	-4.14407	1.37529	-1.01034
H	-4.73169	2.08057	-1.59145
C	-4.51573	0.30841	-0.24037
H	-5.49368	-0.10630	-0.01283
C	-3.32086	-1.39728	1.15238
C	-3.42954	-1.18834	2.55094
C	-3.45440	-2.32889	3.37709
H	-3.53785	-2.20373	4.46127
C	-3.37283	-3.61665	2.83472
H	-3.38948	-4.48967	3.49565
C	-3.26732	-3.79158	1.44970
H	-3.19821	-4.80231	1.03721
C	-3.24128	-2.68970	0.57284
C	-3.56759	0.20582	3.16504
H	-3.25005	0.94205	2.40381
C	-2.67292	0.40361	4.40830
H	-2.72006	1.45276	4.74674
H	-1.61887	0.15654	4.19958
H	-3.00295	-0.22486	5.25344
C	-5.04639	0.50626	3.50979
H	-5.42692	-0.21299	4.25606
H	-5.69344	0.43976	2.61919
H	-5.14948	1.52110	3.93179
C	-3.18135	-2.90296	-0.93998
H	-2.77917	-1.97780	-1.39003
C	-2.24611	-4.05730	-1.35184
H	-2.64710	-5.03966	-1.04526
H	-1.23761	-3.94406	-0.92431
H	-2.14373	-4.08029	-2.44931
C	-4.60374	-3.13182	-1.50867
H	-4.56277	-3.26537	-2.60358
H	-5.27735	-2.28478	-1.29543
H	-5.05580	-4.04027	-1.07272
C	-1.97977	2.49132	-1.59723

C	-1.32044	2.18855	-2.81731
C	-0.60924	3.23191	-3.44017
H	-0.08065	3.03207	-4.37643
C	-0.56580	4.51694	-2.88447
H	-0.00737	5.31153	-3.39062
C	-1.23333	4.78664	-1.68504
H	-1.19525	5.79451	-1.25850
C	-1.95239	3.78093	-1.00910
C	-1.42345	0.81274	-3.47752
H	-1.58570	0.06999	-2.67591
C	-2.64600	0.76696	-4.42711
H	-3.58716	0.98992	-3.89642
H	-2.74207	-0.23338	-4.88381
H	-2.53479	1.50390	-5.24222
C	-0.13972	0.39483	-4.22133
H	0.04063	1.01202	-5.11940
H	-0.23615	-0.64938	-4.56399
H	0.74726	0.46208	-3.57042
C	-2.68530	4.11836	0.29076
H	-3.06270	3.17532	0.72405
C	-3.90682	5.02658	0.01375
H	-4.45206	5.23959	0.94965
H	-4.61270	4.55947	-0.69401
H	-3.59179	5.99176	-0.42005
C	-1.75023	4.76197	1.33801
H	-1.36141	5.73592	0.99290
H	-0.89258	4.10692	1.56209
H	-2.30112	4.94441	2.27722
C	2.79052	-1.54615	1.40029
C	2.14315	-1.77125	2.63583
H	1.04718	-1.73433	2.68437
C	2.87378	-2.03265	3.80932
H	2.34837	-2.20515	4.75622
C	4.27789	-2.06673	3.76831
H	4.85164	-2.26646	4.68041
C	4.94071	-1.84329	2.54926
H	6.03618	-1.87022	2.50879
C	4.20222	-1.58713	1.38058
H	4.73520	-1.40718	0.43935
C	1.55766	-3.04621	-1.09601
C	1.64643	-4.21126	-0.30137
H	1.84004	-4.11795	0.77423
C	1.50676	-5.49278	-0.86367
H	1.58427	-6.38065	-0.22479
C	1.28097	-5.63798	-2.24238
H	1.17904	-6.63570	-2.68398
C	1.19461	-4.49272	-3.05197
H	1.02798	-4.59555	-4.13105
C	1.32725	-3.21521	-2.48102
H	1.26553	-2.33372	-3.13135
C	3.00477	-0.24914	-1.52023
C	3.93740	-0.95425	-2.31455
H	3.94984	-2.05044	-2.29120
C	4.84546	-0.27707	-3.14816
H	5.55942	-0.84669	-3.75491
C	4.83921	1.12617	-3.20393
H	5.54596	1.65560	-3.85305
C	3.92041	1.84601	-2.42250
H	3.91008	2.94174	-2.45734
C	3.01422	1.16248	-1.59320

H	2.30405	1.73827	-0.98687
C	0.16098	1.54471	2.01698
C	1.27083	2.07678	2.09745
C	2.58058	2.63583	2.13855
C	2.81610	3.95437	1.66731
C	3.66183	1.88810	2.67525
C	4.09953	4.50788	1.73628
H	1.98264	4.52848	1.25138
C	4.93992	2.45525	2.73643
H	3.48556	0.86708	3.02500
C	5.16448	3.76249	2.27157
H	4.27117	5.52553	1.36984
H	5.76779	1.86674	3.14448
H	6.16772	4.19844	2.32184
H	-0.85296	1.26842	2.24256

Int₁₀

SCF (BP86) Energy = -2364.71162620

Enthalpy 0K = -2363.724440

Enthalpy 298K = -2363.723495

Free Energy 298K = -2363.884592

Lowest Frequency = 7.2788 cm⁻¹

Second Frequency = 14.7040 cm⁻¹

SCF (BP86-D3BJ) Energy = -

2365.03611263

SCF (C₆H₆) Energy = -2364.72709140

SCF (BS2) Energy = -2656.155666

Ge	-1.74286	-0.37495	0.56134
Cu	0.21412	0.46111	-0.63074
N	2.95380	0.81450	0.52107
N	2.83389	-1.08019	-0.52803
C	2.05098	-0.01274	-0.12509
C	4.24639	0.28001	0.50746
H	5.08386	0.79100	0.97351
C	4.17149	-0.90873	-0.15718
H	4.93133	-1.64671	-0.39634
C	2.36658	-2.28547	-1.19025
C	2.19891	-2.28147	-2.59860
C	1.75653	-3.47473	-3.20270
H	1.61212	-3.50284	-4.28721
C	1.51303	-4.62546	-2.44414
H	1.16483	-5.54055	-2.93479
C	1.73039	-4.61262	-1.06185
H	1.55608	-5.52188	-0.47866
C	2.16804	-3.44846	-0.40062
C	2.57911	-1.08219	-3.46681
H	2.63096	-0.19800	-2.80949
C	1.54172	-0.77805	-4.56677
H	1.83326	0.13259	-5.11863
H	0.54156	-0.61133	-4.13640
H	1.47220	-1.59459	-5.30646
C	3.98397	-1.29852	-4.08099
H	3.99295	-2.18325	-4.74161
H	4.74891	-1.45500	-3.30153
H	4.28387	-0.42260	-4.68278
C	2.48000	-3.49539	1.09639
H	2.53098	-2.45614	1.46594
C	1.39790	-4.22416	1.91650

H	1.36590	-5.30301	1.68289
H	0.39753	-3.80317	1.73873
H	1.62085	-4.13401	2.99289
C	3.86082	-4.15599	1.33533
H	4.10063	-4.16572	2.41276
H	4.67590	-3.62955	0.81096
H	3.85744	-5.20150	0.97985
C	2.64993	2.09109	1.14322
C	2.12711	2.09918	2.46433
C	1.88531	3.35459	3.05466
H	1.46970	3.39782	4.06475
C	2.16770	4.54639	2.37580
H	1.97238	5.50964	2.85891
C	2.70263	4.50789	1.08449
H	2.92737	5.44445	0.56463
C	2.95555	3.28256	0.43616
C	1.89691	0.80957	3.25599
H	1.57820	0.03032	2.54004
C	3.21562	0.34139	3.92225
H	4.01211	0.15394	3.18379
H	3.04877	-0.59453	4.48314
H	3.58195	1.10305	4.63326
C	0.79164	0.93539	4.32242
H	1.09287	1.60034	5.15166
H	0.59466	-0.05523	4.76503
H	-0.15004	1.31667	3.89497
C	3.58562	3.28165	-0.95761
H	3.45468	2.27096	-1.38361
C	5.10526	3.56477	-0.87470
H	5.55921	3.54497	-1.88086
H	5.62955	2.82160	-0.25145
H	5.29352	4.56075	-0.43693
C	2.91006	4.28904	-1.91442
H	3.10880	5.33259	-1.61471
H	1.81790	4.14766	-1.94709
H	3.30931	4.16742	-2.93664
C	-3.25315	-0.84858	-0.72296
C	-2.94018	-1.51387	-1.92932
H	-1.88960	-1.70870	-2.18278
C	-3.94623	-1.93089	-2.81893
H	-3.67688	-2.44846	-3.74736
C	-5.29481	-1.67884	-2.52036
H	-6.08245	-1.99743	-3.21241
C	-5.62613	-1.01132	-1.32989
H	-6.67669	-0.80722	-1.09095
C	-4.61483	-0.60586	-0.44196
H	-4.89534	-0.08583	0.48180
C	-1.78849	-2.05704	1.72241
C	-2.23200	-3.29393	1.20097
H	-2.52110	-3.36385	0.14578
C	-2.34228	-4.43451	2.01609
H	-2.69933	-5.37826	1.58702
C	-2.01026	-4.36399	3.37918
H	-2.10432	-5.24918	4.01819
C	-1.56485	-3.14522	3.91727
H	-1.31213	-3.07581	4.98218
C	-1.45549	-2.00994	3.09524
H	-1.13508	-1.06174	3.54155
C	-2.51916	0.98850	1.86504
C	-3.56642	0.66508	2.75964

H	-3.96728	-0.35519	2.77920
C	-4.09556	1.62171	3.64359
H	-4.91025	1.34564	4.32336
C	-3.57978	2.92848	3.66052
H	-3.99058	3.67478	4.34978
C	-2.52954	3.26881	2.79305
H	-2.11336	4.28294	2.80453
C	-2.00766	2.30566	1.90968
H	-1.18083	2.58468	1.24334
C	0.61201	1.58292	-2.20836
C	-0.65169	1.64791	-2.04059
C	-1.94418	2.12022	-2.50627
C	-3.00562	2.43641	-1.63047
C	-2.12149	2.32231	-3.89963
C	-4.20459	2.95906	-2.13387
H	-2.88143	2.27916	-0.55640
C	-3.32685	2.83160	-4.39559
H	-1.30163	2.07295	-4.58078
C	-4.37233	3.15611	-3.51357
H	-5.01618	3.20331	-1.44102
H	-3.45034	2.97821	-5.47407
H	-5.31496	3.55574	-3.90225
H	1.51989	1.89223	-2.70889

TS2₁₀

SCF (BP86) Energy = -2364.68229854

Enthalpy 0K = -2363.696731

Enthalpy 298K = -2363.695787

Free Energy 298K = -2363.855156

Lowest Frequency = -151.3886 cm⁻¹

Second Frequency = 9.5605 cm⁻¹

SCF (BP86-D3BJ) Energy = -
2365.01392607

SCF (C₆H₆) Energy = -2364.69799211

SCF (BS2) Energy = -2656.125325

Ge	1.82440	-0.89928	-0.50624
Cu	-0.22951	0.10807	0.80968
N	-2.40245	1.96496	0.17300
N	-3.20407	-0.01922	0.53080
C	-2.00118	0.64672	0.34881
C	-3.78988	2.10269	0.25649
H	-4.27938	3.06585	0.14544
C	-4.29339	0.85384	0.47668
H	-5.31397	0.50017	0.59134
C	-3.39789	-1.44889	0.68226
C	-3.29826	-2.02774	1.97395
C	-3.57883	-3.40342	2.08391
H	-3.50969	-3.88546	3.06349
C	-3.95699	-4.16190	0.96814
H	-4.17819	-5.22861	1.08312
C	-4.05833	-3.55882	-0.28995
H	-4.35585	-4.15765	-1.15692
C	-3.78126	-2.18871	-0.46429
C	-2.98507	-1.19139	3.21544
H	-2.37965	-0.32845	2.88660
C	-2.14088	-1.94798	4.25864
H	-1.87710	-1.26640	5.08562
H	-1.20422	-2.31467	3.80977

H	-2.68631	-2.79880	4.70443	C	-0.45906	-4.87555	-2.07788
C	-4.29514	-0.66558	3.85203	H	-0.91078	-5.81167	-2.42447
H	-4.93466	-1.50289	4.18396	C	0.20766	-4.03552	-2.98571
H	-4.88048	-0.05441	3.14444	H	0.27440	-4.31360	-4.04392
H	-4.07094	-0.03975	4.73360	C	0.79776	-2.84058	-2.53880
C	-3.94313	-1.55219	-1.84570	H	1.32399	-2.20046	-3.25665
H	-3.57690	-0.51259	-1.78665	C	2.38615	0.22603	-2.08856
C	-3.10191	-2.27001	-2.92156	C	3.38122	-0.23763	-2.97919
H	-3.43478	-3.31169	-3.07157	H	3.85780	-1.20960	-2.80804
H	-2.03542	-2.29492	-2.64972	C	3.78828	0.54108	-4.07695
H	-3.20346	-1.74865	-3.88956	H	4.55938	0.16242	-4.75761
C	-5.43437	-1.50109	-2.25457	C	3.21720	1.80543	-4.29434
H	-5.54925	-1.01080	-3.23699	H	3.54242	2.41806	-5.14249
H	-6.04248	-0.94356	-1.52174	C	2.23209	2.28225	-3.41461
H	-5.85856	-2.51740	-2.33456	H	1.78485	3.27026	-3.57041
C	-1.53114	3.07464	-0.15408	C	1.81788	1.49430	-2.32620
C	-1.48494	3.51035	-1.50406	H	1.04455	1.87681	-1.64721
C	-0.65567	4.61074	-1.80151	C	0.56063	-0.40595	2.56177
H	-0.60125	4.97498	-2.83279	C	1.54662	0.00124	1.77048
C	0.09516	5.24175	-0.80312	C	2.82869	0.70263	1.96303
H	0.74026	6.08945	-1.05755	C	3.22641	1.78783	1.14855
C	0.01618	4.79903	0.52394	C	3.66174	0.32817	3.04498
H	0.59958	5.30771	1.29649	C	4.41440	2.48496	1.41615
C	-0.80675	3.71483	0.88576	H	2.59346	2.08308	0.30571
C	-2.33166	2.87299	-2.60896	C	4.85088	1.02167	3.30366
H	-2.75560	1.93414	-2.21246	H	3.36758	-0.52232	3.66808
C	-3.51175	3.80040	-2.98837	C	5.23311	2.10407	2.49207
H	-4.14951	4.03429	-2.11923	H	4.70152	3.32818	0.77835
H	-4.14483	3.32545	-3.75785	H	5.48834	0.70990	4.13832
H	-3.14365	4.75783	-3.39723	H	6.16470	2.64311	2.69451
C	-1.51145	2.50836	-3.86447	H	0.54036	-0.20786	3.64413
H	-1.10633	3.40598	-4.36403				
H	-2.15617	1.99220	-4.59660				
H	-0.66636	1.84579	-3.62116				
C	-0.97364	3.30942	2.35203				
H	-1.18732	2.22527	2.37638				
C	-2.18524	4.04989	2.97174				
H	-2.32565	3.74314	4.02281				
H	-3.12100	3.83539	2.42919				
H	-2.02499	5.14262	2.95434				
C	0.28870	3.54120	3.20469				
H	0.50420	4.61611	3.34145				
H	1.17564	3.06132	2.76108				
H	0.13839	3.11385	4.21045				
C	3.53424	-1.83794	0.04569				
C	3.50236	-3.16492	0.52574				
H	2.54860	-3.70113	0.58688				
C	4.68163	-3.82427	0.91220				
H	4.63274	-4.85592	1.27945				
C	5.91941	-3.16814	0.81904				
H	6.84038	-3.68226	1.11599				
C	5.96869	-1.84904	0.34048				
H	6.92960	-1.32752	0.26395				
C	4.78667	-1.19050	-0.03825				
H	4.84641	-0.15860	-0.40066				
C	0.74185	-2.47129	-1.17657				
C	0.04879	-3.31393	-0.27761				
H	-0.02473	-3.04003	0.78115				
C	-0.54533	-4.50768	-0.72571				
H	-1.07659	-5.14839	-0.01395				

References

1. J. W. Hall, D. M. L. Unson, P. Brunel, L. R. Collins, M. K. Cybulski, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2018, **37**, 3102–3110; A. J. Jordan, C. M. Wyss, J. Bacsá, and J. P. Sadighi, *Organometallics*, 2016, **35**, 613–616; A. Bonet, V. Lillo, J. Ramírez, M. M. Díaz-Requejo, and E. Fernandez, *Org. Biomol. Chem.*, 2009, **7**, 1533–1535; L. R. Collins, I. M. Riddlestone, M. F. Mahon and M. K. Whittlesey, *Chem. Eur. J.*, 2015, **21**, 14075–14084; L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, A. W. Pierpont, J. L. Petersen, and P. D. Boyle, *Inorg. Chem.*, 2006, **45**, 9032–9045; E. Colomer, R. J. P. Corriu, C. Marzin, and A. Vioux, *Inorg. Chem.*, 1982, **21**, 368–373; M. Suzuki, H. Son, Ryoji Noyori, and H. Masuda, *Organometallics*, 1990, **9**, 12, 3043–3053; J. E. Griffiths and M. Onyszchuk, *Can. J. Chem.*, 1961, **39**, 339–347; A. Harinath, J. Bhattacharjee, S. Anga and T. K. Panda, *Aust. J. Chem.*, 2017, **70**, 724.
2. G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–80.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
4. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
5. H. Koglin, K. Behrends, and M. Draeger, *Organometallics*, 1994, **13**, 2733–2742.
6. O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.*, 2013, **49**, 10483–10485.
7. K. V. Zaitsev, A. A. Kapranov, Y. F. Oprunenko, A. V. Churakov, J. A.K. Howard, B. N. Tarasevich, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.*, 2012, **700**, 207–213.
8. I. Elser, R. J. Andrews, and D. W. Stephan, *Chem. Commun.*, 2022, **58**, 1740–1743.
9. S. Pelzer, B. Neumann, H. Stammer, N. Ignat'ev, and B. Hoge, *Chem. Eur. J.*, 2016, **22**, 4758–4763.
10. S. R. Foley, G. P. A. Yap, and D. S. Richeson, *Organometallics*, 1999, **18**, 4700–4705.
11. L. A. Goj, E. D. Blue, C. Munro-Leighton, T. B. Gunnoe, and J. L. Petersen, *Inorg. Chem.*, 2005, **44**, 8647–8649.
12. K. V. Zaitsev, A. V. Kharcheva, K. Lam, Z. Zhanabil, G. Issabayeva, Y. F. Oprunenko, A. V. Churakov, G. S. Zaitseva, S. S. Karlov, *J. Organomet. Chem.*, 2018, **867**, 228–237.
13. A. G. Medvedev, M. Yu. Sharipov, D. A. Grishanov, A. V. Eshtukov, A. V. Churakov, I. A. Buldashov, P. A. Egorov, O. Levb and P. V. Prikhodchenko, *Mendeleev Commun.*, 2022, **32**, 57–59.
14. F. Wech, M. Hasenbeck, U. Gellrich, *Chem. Eur. J.*, 2020, **26**, 13445–13450.
15. A. J. Jordan, C. M. Wyss, J. Bacsá, and J. P. Sadighi, *Organometallics*, 2016, **35**, 613–616.
16. Gaussian 16, Revision C.01, 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, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, 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.
17. D. Andrae, U. Häßermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.

18. (a) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222. (b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
19. (a) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098. (b) J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, **33**, 8822–8824.
20. M. Bühl, H. Kabrede, *J. Chem. Theory Comput.*, 2006, **2**, 1282–1290.
21. D. Figgen, G. Rauhut, M. Dolg, H. Stoll, *J. Chem. Phys.*, 2005, **311**, 227–244.
22. K. A. Peterson, C. Puzzarini, *Theor. Chem. Acc.*, 2005, **114**, 283–296.
23. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.
24. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.*, 2011 **32**, 1456–1465.
25. M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.*, 2009, **5**, 962–975.
26. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.