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Sn(II)–Carbon Bond Reactivity: Radical Generation and Consumption via Reactions of a Stannylene with Alkynes

Supporting information

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General Information

All manipulations were carried out under anaerobic and anhydrous conditions by using Schlenk techniques or in a Vacuum Atmospheres OMNI-Lab drybox under an atmosphere of dry argon or nitrogen. Solvents were dried by the method of Grubbs[1] and co-workers, stored over potassium or sodium, and then degassed by the freeze-pump-thaw method. All physical measurements were made under strictly anaerobic and anhydrous conditions. The NMR spectra were recorded on a Varian Inova 600 MHz spectrometer, and the ^{1}H NMR and ^{13}C NMR spectra were referenced to the residual solvent signals in deuterated benzene. The $^{119}Sn\{^{1}H\}$ NMR spectra were referenced to an external standard of $SnMe_4$ (δ = 0). IR spectra were recorded as Nujol mulls between CsI plates on a PerkinElmer 1430 spectrometer. UV−vis spectra were recorded as dilute hexane solutions in 3.5 mL quartz cuvettes using an Olis 17 modernized Cary 14 UV−vis−near-IR spectrophotometer or an HP 8452 diode-array spectrophotometer. The stannylene reagent $Sn(Ar^{iPr4})_2$ was prepared according to the literature.[2] Unless otherwise stated, all materials were obtained from commercial sources and used as received. Temperatures reported throughout the experimental reflect the oil bath temperature recorded using a thermometer and usually indicate refluxing conditions within the Schlenk glassware.

Synthesis of complexes 1-4

Synthesis of complex, 1 $\{Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(Ar^{iPr4})\}$:

$Sn(Ar^{iPr4})_2$ (0.914 g, 1 mmol) and phenylacetylene (0.216 g, 2 mmol) were dissolved in ca. 30 mL of benzene. The reaction solution was then heated to 60 °C and stirred for 3 days. The color of solution turned from blue to dark red which indicated the reaction is completed. Solvent was removed under reduced pressure; ca. 50 mL ether was then added into the reaction residue and the resulting red solution was filtered through celite. The filtrate was concentrated under reduced pressure until the formation of small red crystals was observed. The solution was storage in -30 °C freezer for 4 days to afford red crystals which were suitable for SCXRD analysis. Yield = 0.47 g (46%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 8.36 (s, 1H), 7.24 - 7.21 (m, 5H), 7.11 – 6.88 (m, 15H), 3.50 (s br, 2H), 3.02 (s br, 1H), 2.86 (s br, 6H), 1.48 (s, 8H), 1.05 - 0.98 (m, 24H), 0.87 (m, 12H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 149.1, 147.5, 145.7, 144.4, 140.9, 138.6, 138.5, 137.2, 132.8, 130.4, 129.2, 129.1, 126.5, 126.26, 125.7, 125.6, 124.5, 123.4, 123.1, 30.8, 30.4, 26.1, 25.9, 25.7, 25.4, 24.1, 23.2, 22.9. ^{119}Sn NMR (125 MHz, Benzene-d_6) *δ*: 1596.3 (distannene $[Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(Ar^{iPr4})]_2$ present at more upfield (shielded) chemical shift, observed at *δ* = 389.6). UV/vis: λ/nm (ε/ M^{-1} cm^{-1}): 472 (3800).

Synthesis of complex 2, $\{Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(C_6H_5)\}$:

$Sn(Ar^{iPr4})_2$ (Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-$^{i}Pr_2)_2$) (0.914 g, 1 mmol) was mixed with diphenylacetylene (0.213 g, 1.2 mmol), followed by addition of ca. 40 mL of benzene, the reaction mixture was stirred for 4 hours at 120 °C, the color of solution became dark red after 2 h. Solvent was removed under reduced pressure; ca. 50 mL hexane was added to the reaction residue then the resulting red solution was filtered through celite. The filtrate was concentrated under reduced pressure until the formation of small red crystals was observed. Storage of the reaction mixture in -30 °C freezer for 3 days resulted in the product as red crystals. Yield = 0.38 g (55%). ^{1}H NMR (599 MHz, Benzene-d_6) *δ*: 7.61 (s, 1H), 7.45-7.44 (m, 2H), 7.40-7.37 (m, 1H), 7.18-7.17 (m, 1H), 7.13-7.12 (m, 4H), 7.08-7.06 (m, 4H), 6.91-6.84 (m, 4H), 6.77-6.75 (m, 2H), 3.33 (hept, $^{3}J_{HH}$ = 7.2 Hz, 4H), 1.27-1.26 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H), 1.14-1.13 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, Benzene-d_6) *δ*: 193.9, 181.8, 147.3, 147.1, 145.4, 139.2, 137.1, 136.8, 130.7, 129.3, 129.1, 127.2, 126.1, 125.4, 123.9, 123.6, 31.4, 26.9, 23.4. $^{119}Sn\{^{1}H\}$ NMR (149 MHz, Benzene-d_6) *δ*: 1607.19. UV/vis: λ/nm (ε/ M^{-1} cm^{-1}): 518 (3300).

Synthesis of complex 3, $\{Ar^{iPr4}Sn\{C(C_4H_9)\text{-}C(H)(Ar^{iPr4})\}$:

$Sn(Ar^{iPr4})_2$ (0.914 g, 1 mmol) and 1-hexyne (0.247 g, 3 mmol) were combined in ca. 40 mL of benzene. The reaction solution turned purple after heating and stirring at 80 °C for 2 days. Removal of benzene under reduced pressure resulted in dark purple powder, which was then re-dissolved in ca. 50 mL ether and was filtered through celite. The filtrate was concentrated under reduced pressure until the formation of powder was observed. The solution was storage in -38 °C freezer for 4 days to afford purple powder of pure complex **4**. Yield = 0.68 g (68%). ^{1}H NMR (500 MHz, Toluene-d_8) δ 7.59 (s, 1H), 6.94 (br s, 2H), 6.92 (br s, 2H), 6.91-6.89 (m, 3H), 6.87-6.86 (m, 3H), 6.86 (s, 1H), 6.84-6.81(m, 6H), 2.78-2.58 (m, 8H), 0.95-0.94 (m, 9H), 0.86-0.84 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H), 0.71-0.69 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H). ^{13}C NMR (126 MHz, Toluene-d_8) δ 194.0, 188.1, 148.1, 146.3, 144.9, 141.6, 140.1, 139.9, 139.7, 132.5, 130.7, 129.8, 123.4, 42.5, 31.3, 26.5, 23.7, 23.6, 15.7. UV/vis: λ/nm (ε/ M^{-1} cm^{-1}): 558 (4300).

Synthesis of complex 4, {Sn(CCSiMe$_3$)Ar^{iPr4}}$_2$:

Sn(Ar^{iPr4})$_2$ (500 mg, 0.54 mmol) and trimethylsilylacetylene (54 mg, 78.0 µL, 0.54 mmol) were combined in ca. 40 mL of benzene. The reaction solution turned from blue to red after heating and stirring at 80 °C for 12 hours. Removal of benzene under reduced pressure resulted in pink-orange powder, which was then re-dissolved in ca. 50 mL of hexane, which was filtered via cannula. The filtrate was concentrated under reduced pressure to ca. 30 mL and left at room temperature which afforded pure complex **3** as pink-orange crystals with a yield of 84% (0.56 g). All spectroscopic (^{1}H, ^{13}C and ^{119}Sn NMR) and single crystal X-ray analysis and melting point of this sample matched those previously reported.[3]

NMR Spectra

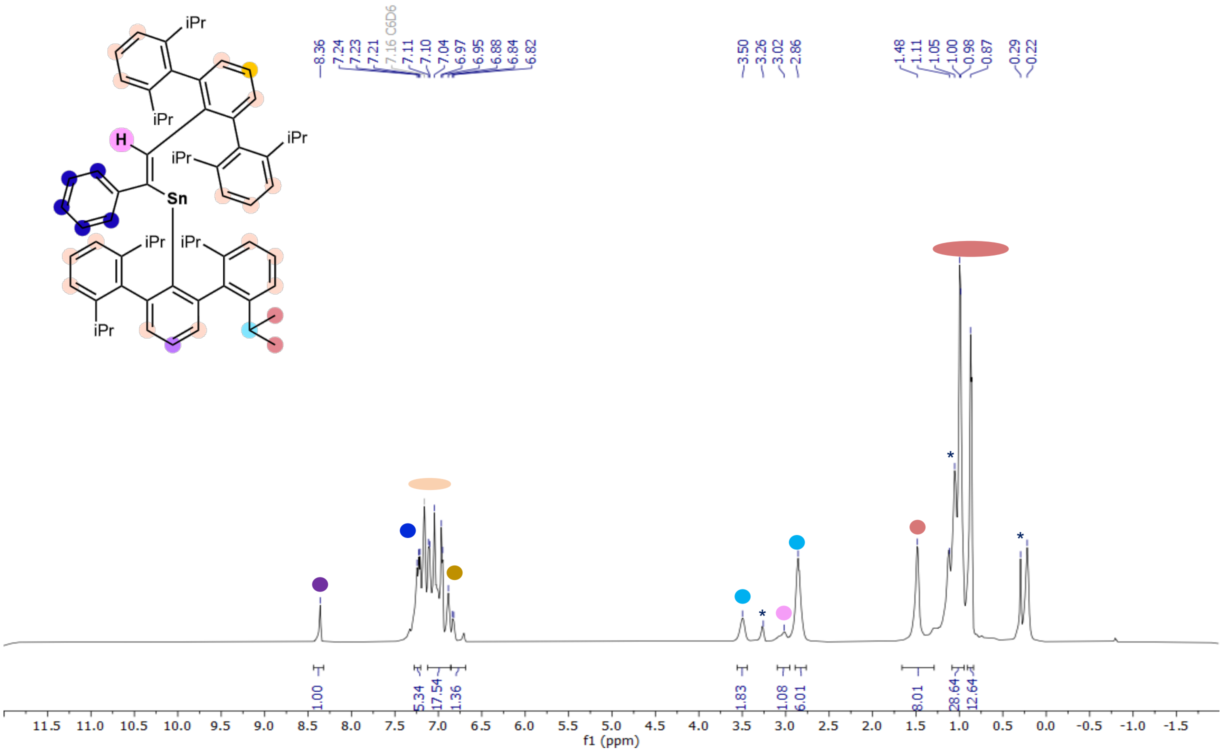

Figure S1 ^{1}H NMR spectrum of **1** in C_6D_6 (600 MHz, 298 K). Asterisks indicate diethyl ether and grease impurities.

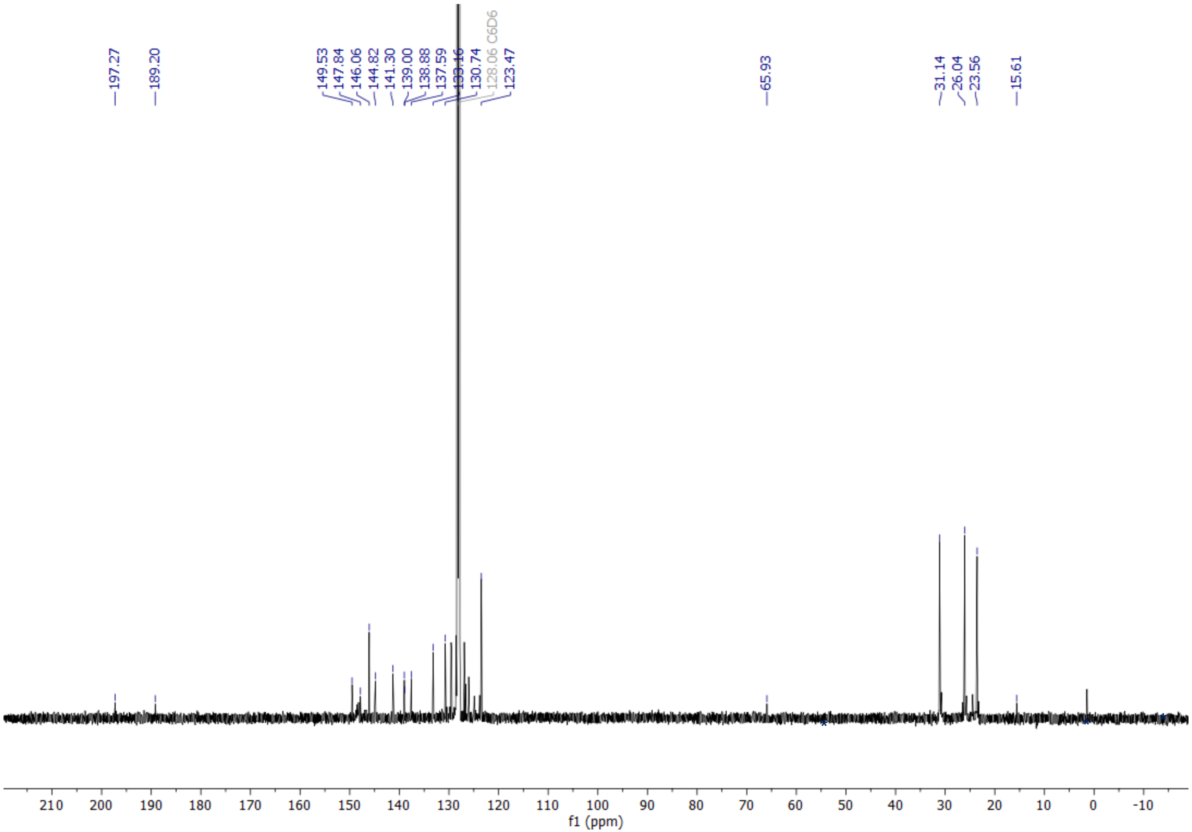

Figure S2 $^{13}C\{^1H\}$ NMR spectrum of **1** in C_6D_6 (600 MHz, 298 K). Asterisks indicate diethyl ether and grease impurities.

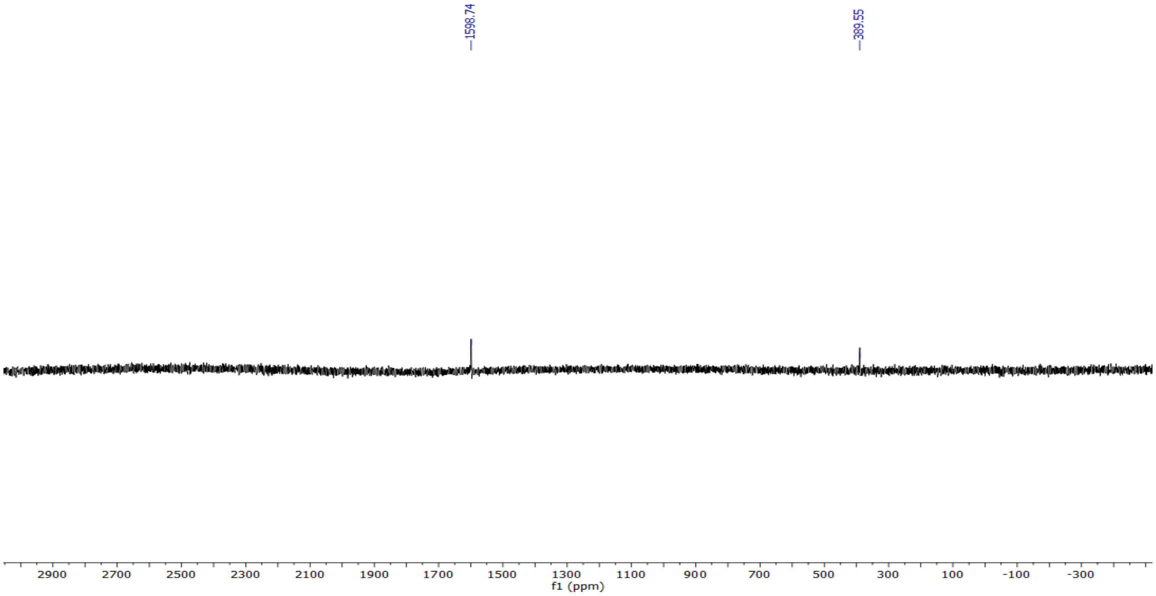

Figure S3 $^{119}Sn\{^1H\}$ NMR spectrum of **1** in C_6D_6 (500 MHz, 298 K). Signal at 389.55 ppm indicates distannene species $[Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(Ar^{iPr4})\}]_2$ associating in solution.

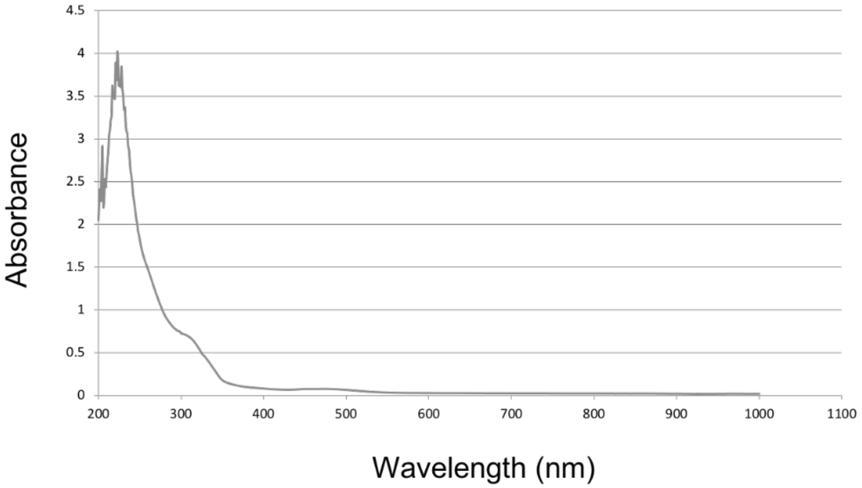

Figure S4 UV-Vis spectrum of **1** at 25 °C (39 μM in hexanes).

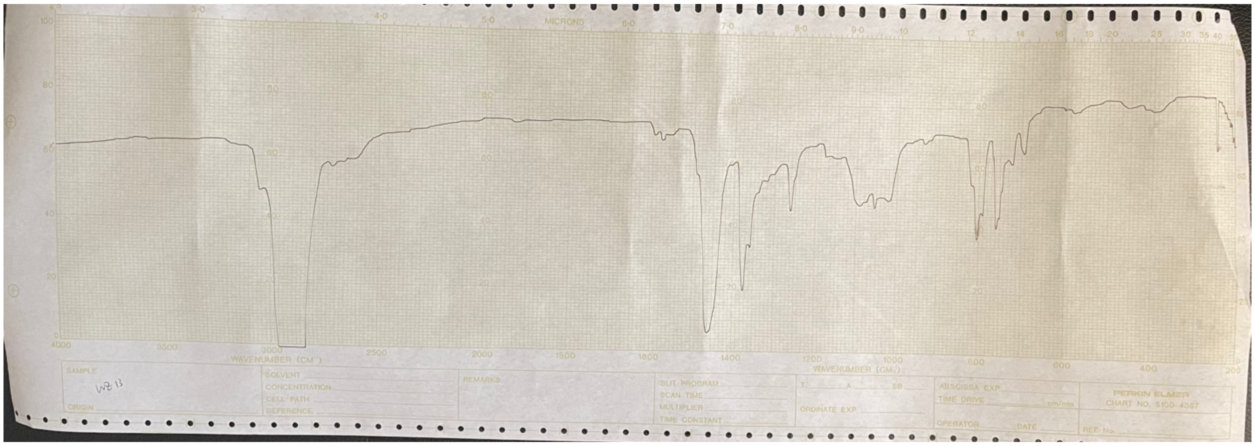

Figure S5 Infrared spectrum of a Nujol mull of **1** at 25 °C.

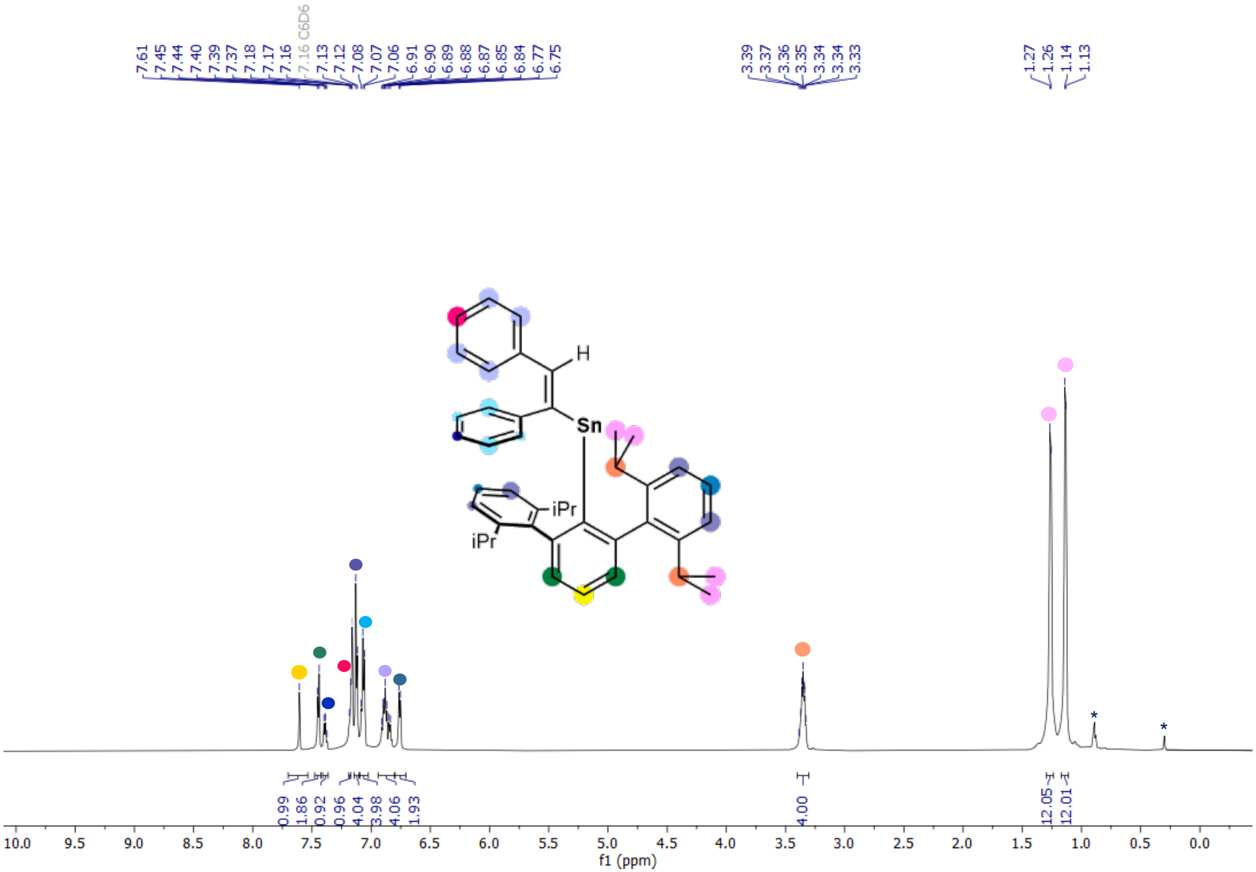

Figure S6: ^{1}H NMR spectrum of complex **2** in C_6D_6 (600 MHz, 298 K). Asterisks indicate diethyl ether and grease impurities.

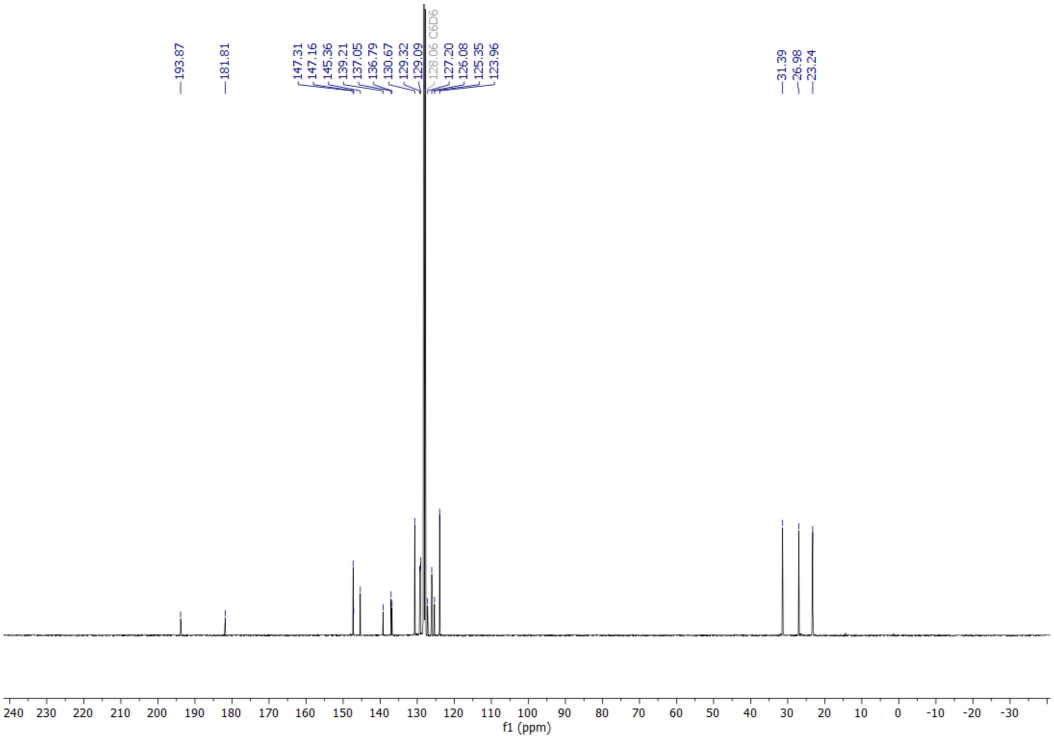

Figure S7: ^{13}C{^{1}H} NMR spectrum of **2** in C_6D_6 (600 MHz, 298 K).

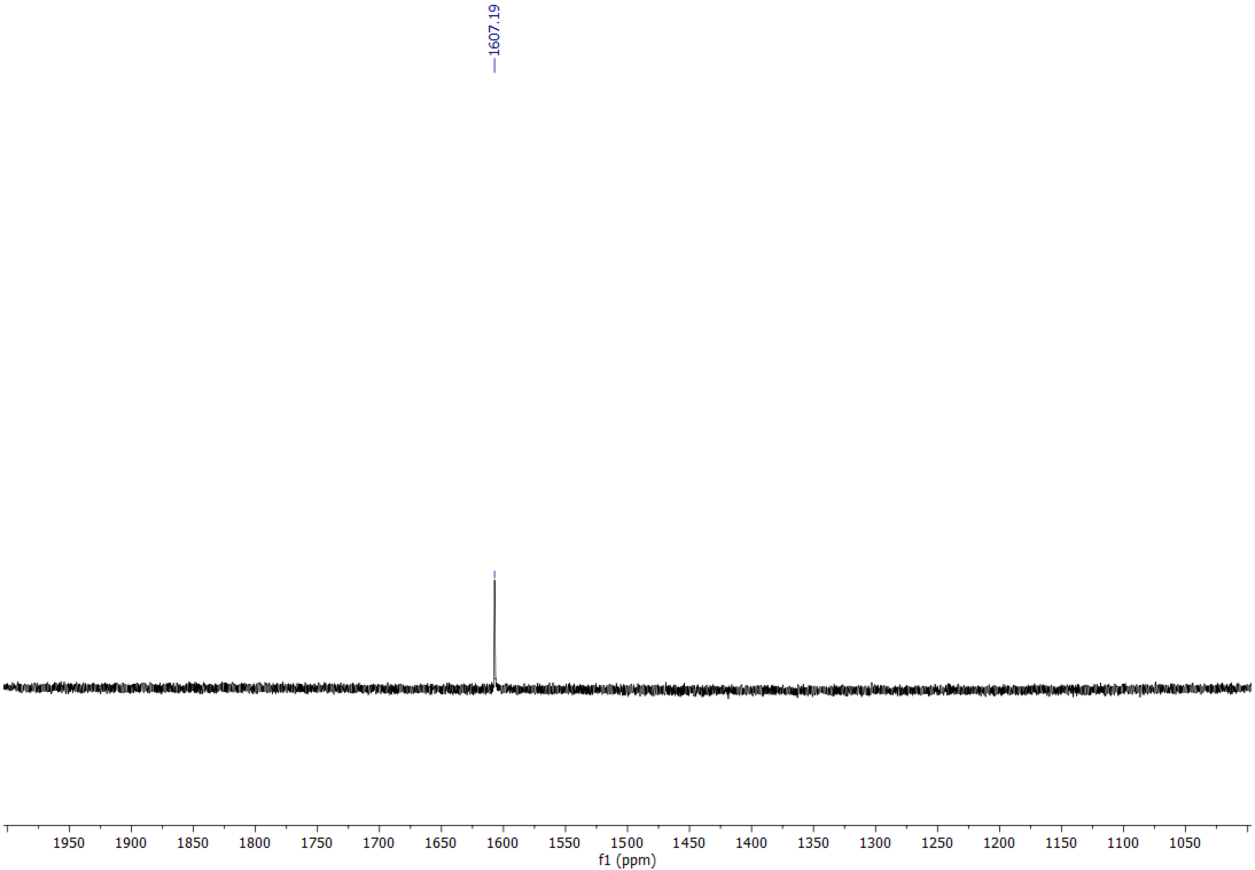

Figure S8: ^{119}Sn{^{1}H} NMR spectrum of **2** in C_6D_6 (500 MHz, 298 K).

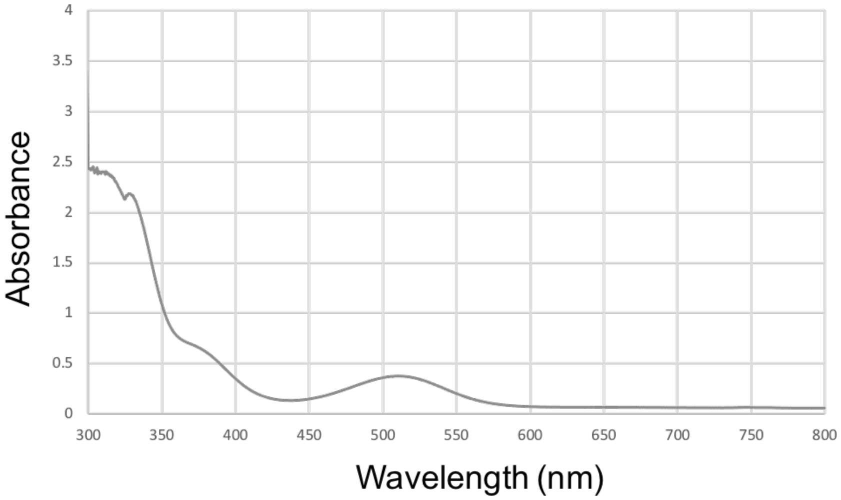

Figure S9: UV-Vis spectrum of **2** at 25 °C (42 μM in hexanes).

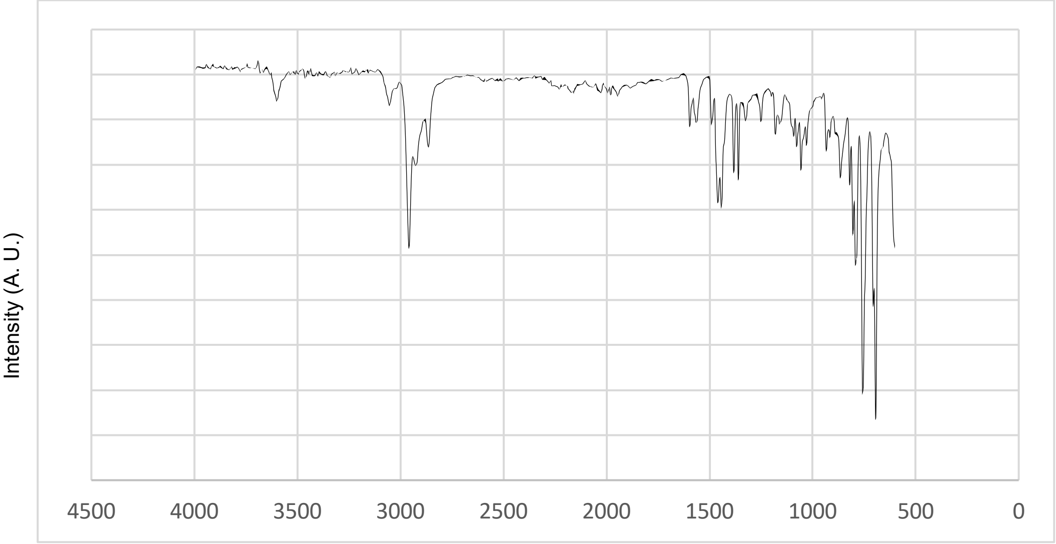

Figure S10: FTIR spectrum of **2**.

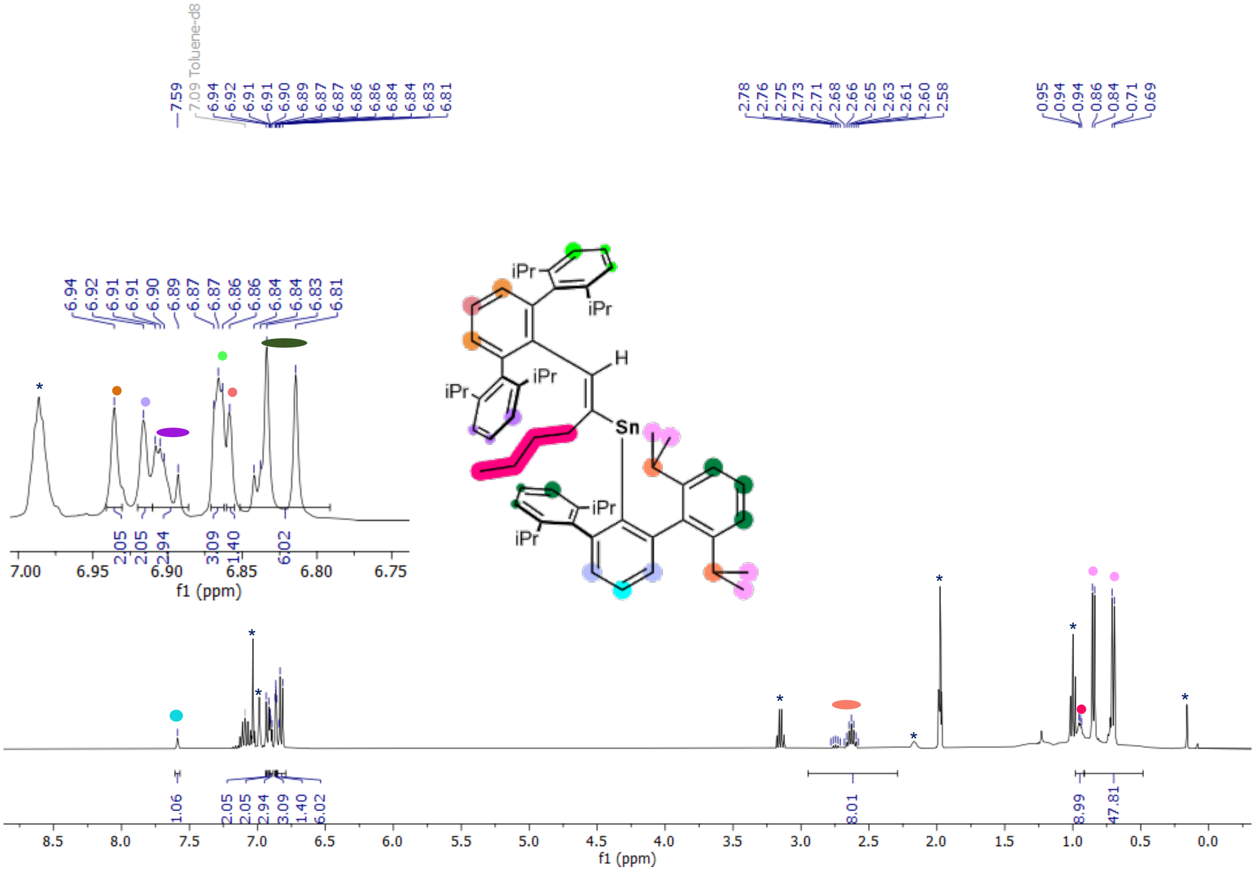

Figure S11: ^{1}H NMR spectrum of **3** in C_7D_8 (500 MHz, 298 K). Asterisks indicate diethyl ether, toluene and grease impurities.

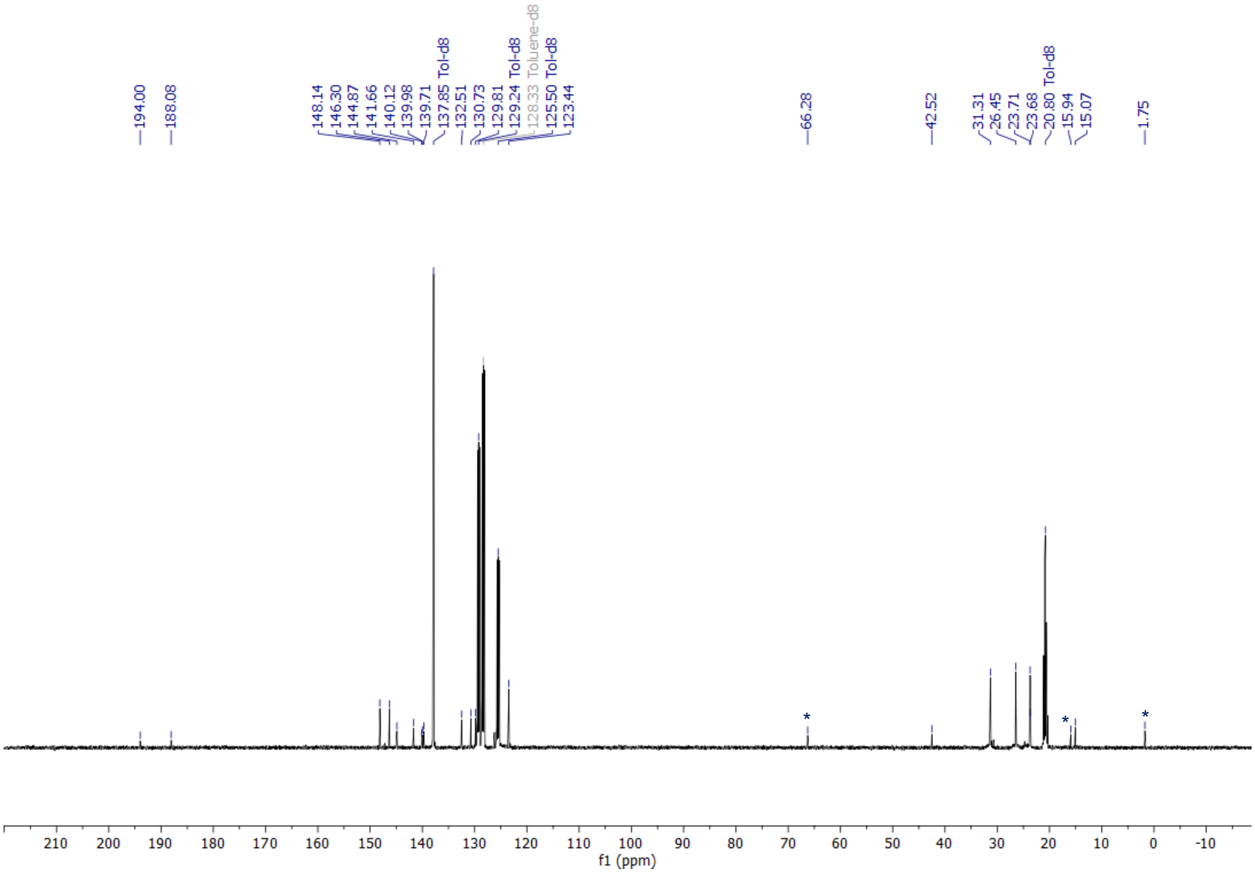

Figure S12: $^{13}C\{^1H\}$ NMR spectrum of **3** in C_7D_8 (500 MHz, 298 K). Asterisks indicate diethyl ether and grease impurities.

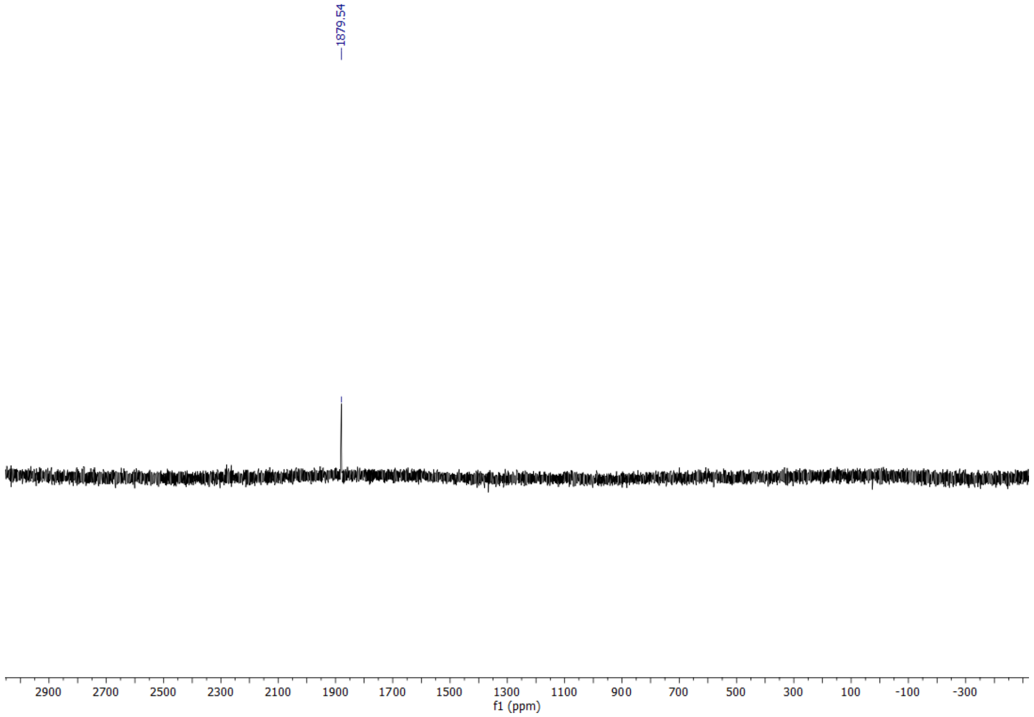

Figure S13: $^{119}Sn\{^1H\}$ NMR spectrum of **3** in C_7D_8 (500 MHz, 298 K).

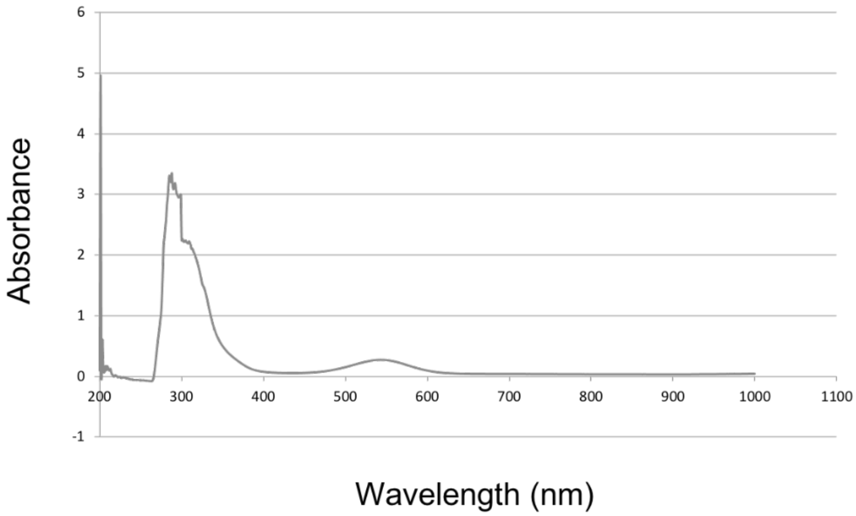

Figure S14: UV-Vis spectrum of **3** at 25 °C (42 μM in hexanes).

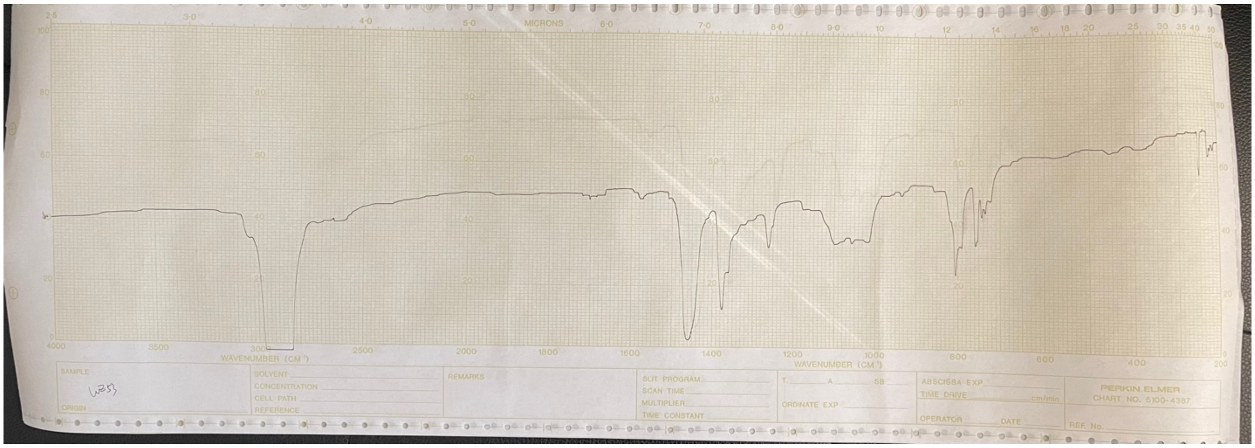

Figure S15: Infrared spectrum of a Nujol mull of **3** at 25 °C.

Crystallographic Data

	1	**2**
formula	$C_{72}H_{90}OSn$	$C_{44}H_{49}Sn$
fw	1090.12	696.59
color	red	red
cyst syst	Triclinic	Triclinic
space group	P-1	P-1
a, Å	17.8418(9)	9.6848(11)
b, Å	17.8598(9)	11.7885(13)
c, Å	19.2380(10)	18.193(2)
α, deg	88.9389(8)	90.359(2)
β, deg	81.5494(8)	100.783(2)
γ, deg	89.9199(8)	107.774(2)
V, Å^3	6062.6(5)	1938.6(4)
Z	4	2
Density (calculated), Mg/m^3	1.194	1.193
Absorption coefficient, mm^{-1}	0.464	0.686
Temperature of collection (K)	90.15	90.15
F(000)	2320	725
Crystal size, mm^3	0.288 x 0.218 x 0.188	0.381 x 0.33 x 0.266
Crystal color and habit	red block	red block
Theta range for data collection, deg	1.837 to 25.250	4.16 to 61.4
Index ranges	-21<=h<=21, -21<=k<=21, -23<=l<=23	-13<=h<=13, -16<=k<=16, -26<=l<=26
Reflections collected	43731	31833
Independent reflections	21950 [R(int) = 0.0589]	11908 [R(int) = 0.0211]
Data / restraints / parameters	21950 / 149 / 1434	11908 / 0 / 193
Goodness-of-fit on F^2	1.135	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1091	R1 = 0.0992, wR2 = 0.2606
R indices (all data)	R1 = 0.0931, wR2 = 0.1183	R1 = 0.1042, wR2 = 0.2673
Largest diff. peak and hole, e.Å^{-3}	0.678/-0.842	12.56/-5.26
CCDC No.	2271751	2271752

References:

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification, *Organometallics*, **1996**, *15*, 1518-1520.

[2] McCrea-Hendrick, M. L.; Bursch, M.; Gullett, K. L.; Maurer, L. R.; Fettinger, J. C.; Grimme, S.; Power, P. P. Counterintuitive Interligand Angles in the Diaryls E{C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)$_2$}$_2$ (E = Ge, Sn, or Pb) and Related Species: The Role of London Dispersion Forces, *Organometallics*, **2018**, *37*, 2075-2085.

[3] Lei, H.; Fettinger, J. C.; Power, P. P.; Synthesis and Structures of Low-Valent Alkynyl Tin and Germanium Complexes Supported by Terphenyl Ligands: Heavier Group 14 Element Enediyne Analogues, *Organometallics* **2010**, *29*, 5585-5590.