Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Bis(tetrelocenes) – fusing tetrelocenes into close proximity

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NMR spectra

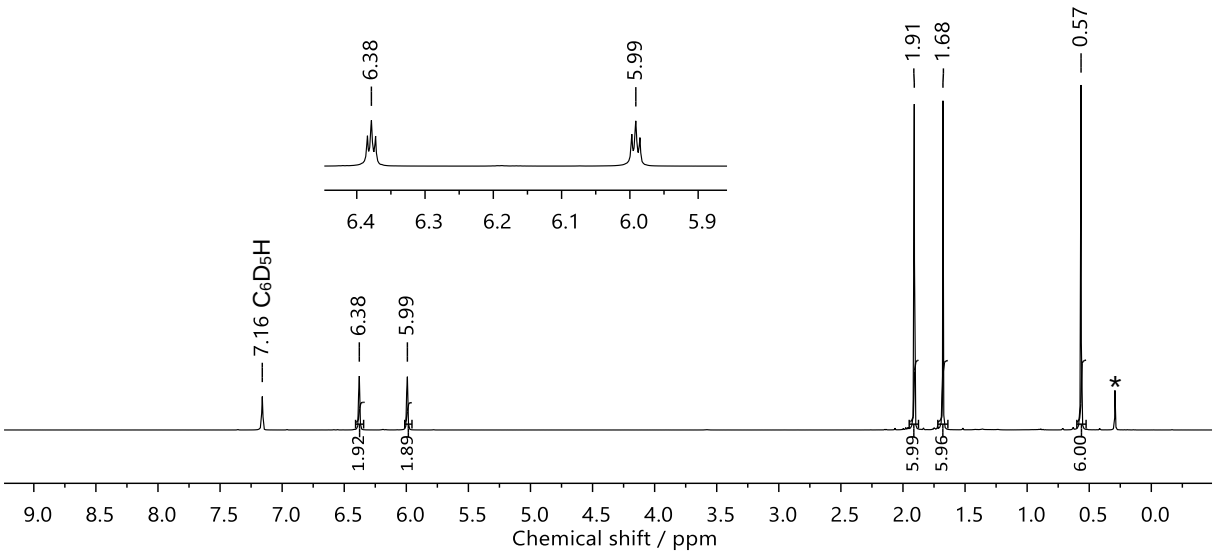

Figure S1: ^{1}H NMR spectrum of **2a** (400.13 MHz, C_6D_6, 296 K) (* silicone grease).

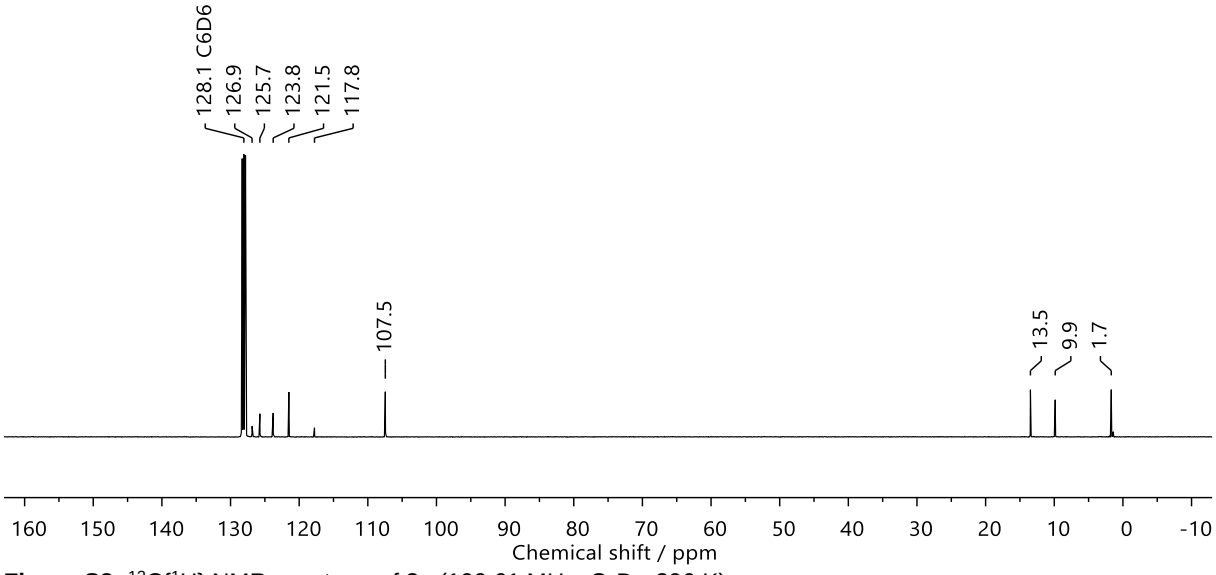

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **2a** (100.61 MHz, C_6D_6, 296 K).

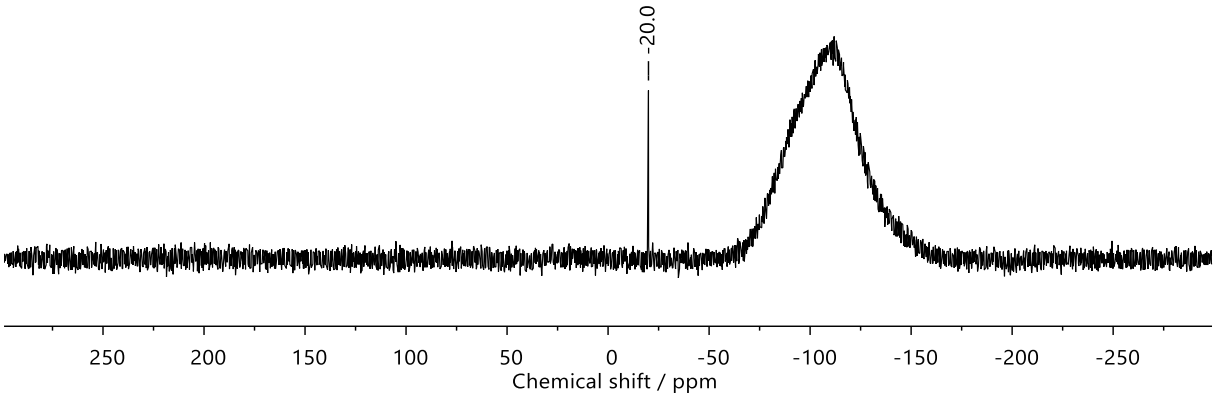

Figure S3: $^{29}Si\{^{1}H\}$ NMR spectrum of **2a** (79.49 MHz, C_6D_6, 296 K).

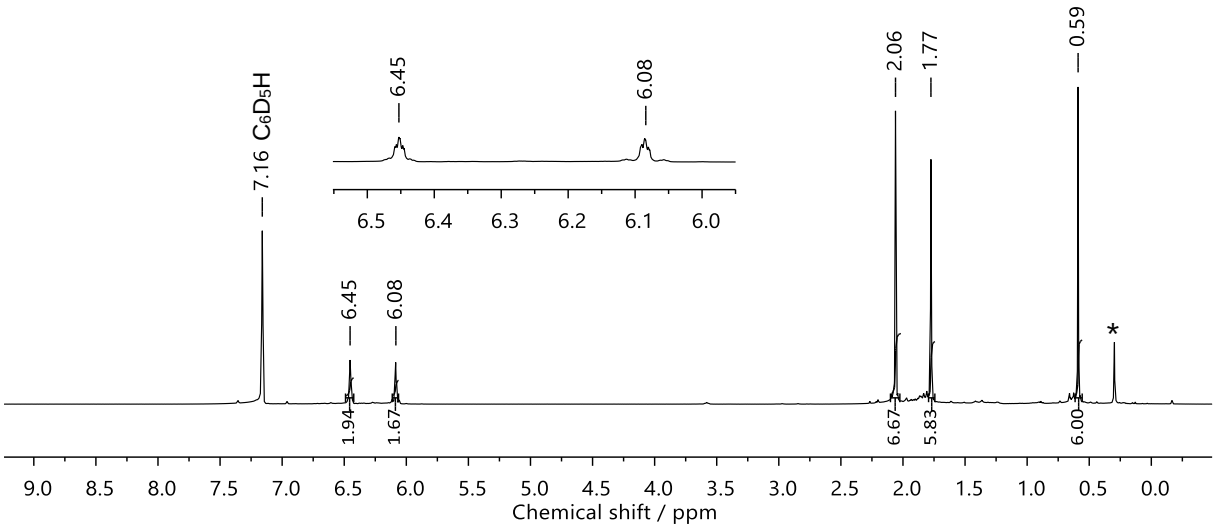

Figure S4: ^{1}H NMR spectrum of **2c** (400.13 MHz, C_6D_6, 296 K) (*silicone grease).

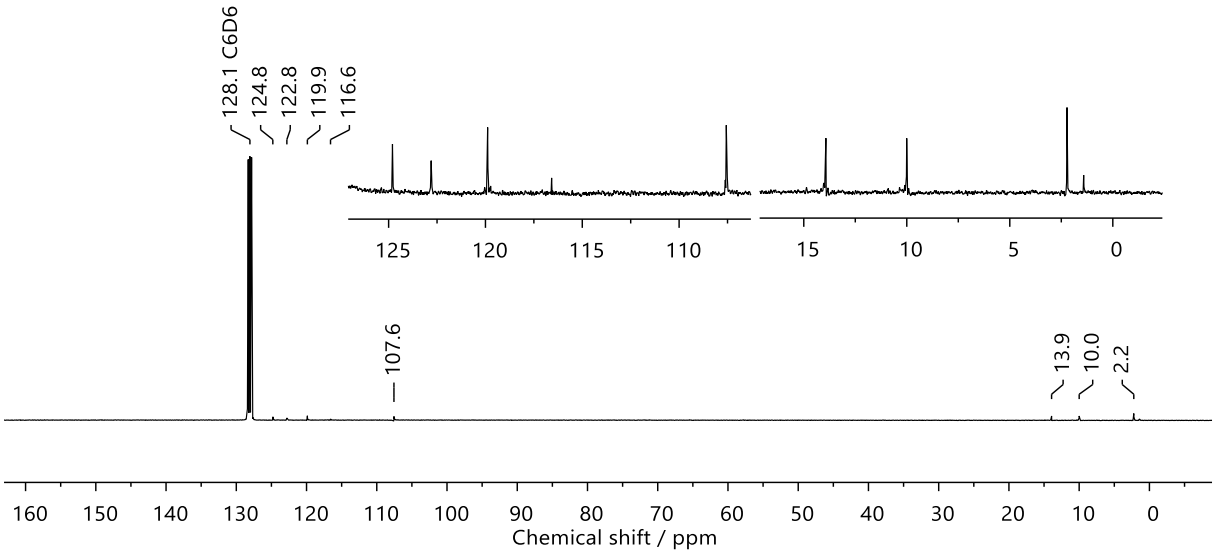

Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of **2c** (100.61 MHz, C_6D_6, 296 K).

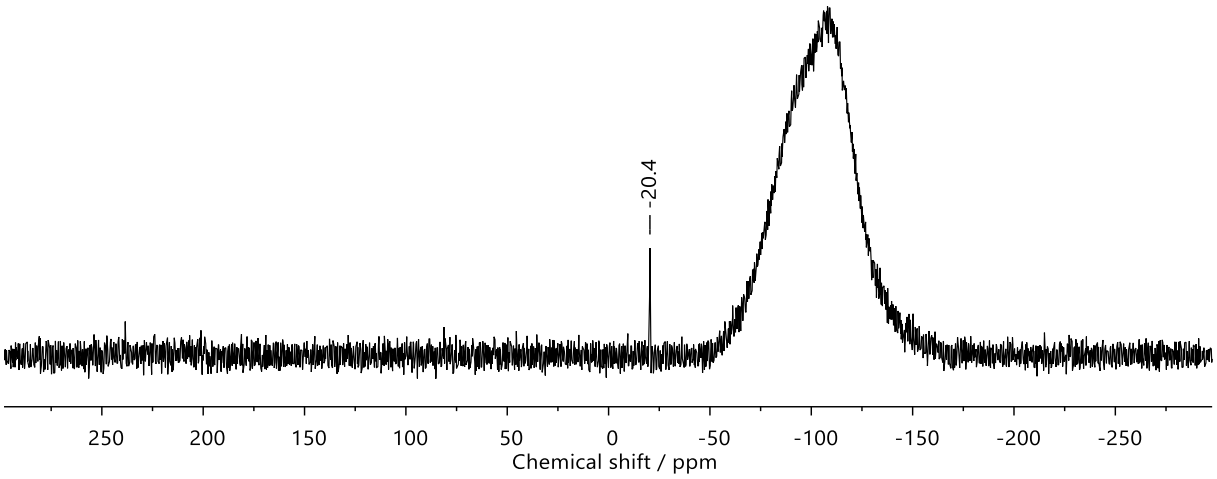

Figure S6: $^{29}Si\{^{1}H\}$ NMR spectrum of **2c** (79.49 MHz, C_6D_6, 296 K).

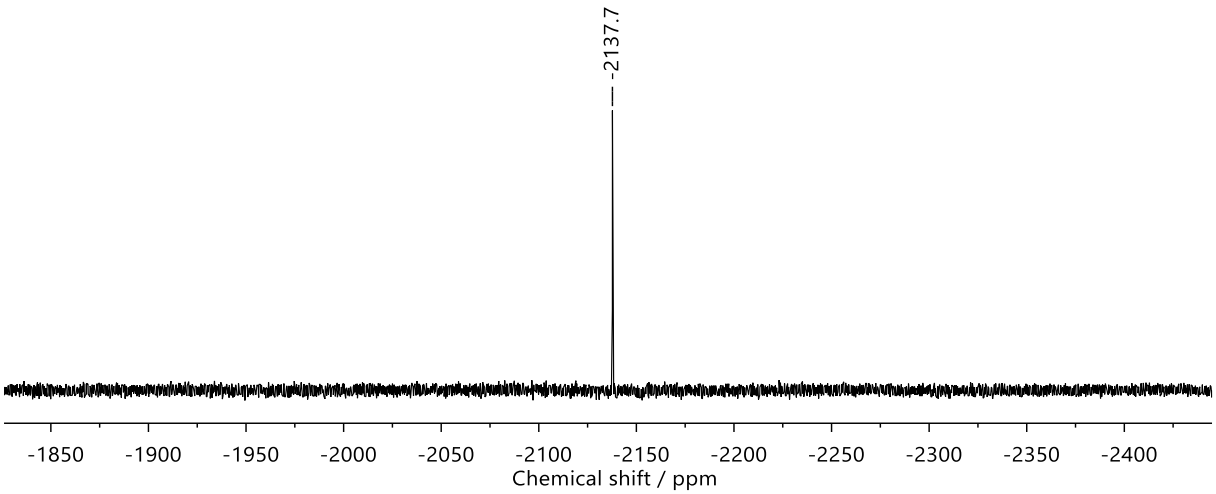

Figure S7: $^{119}Sn\{^{1}H\}$ NMR spectrum of **2c** (149.21 MHz, C_6D_6, 294 K).

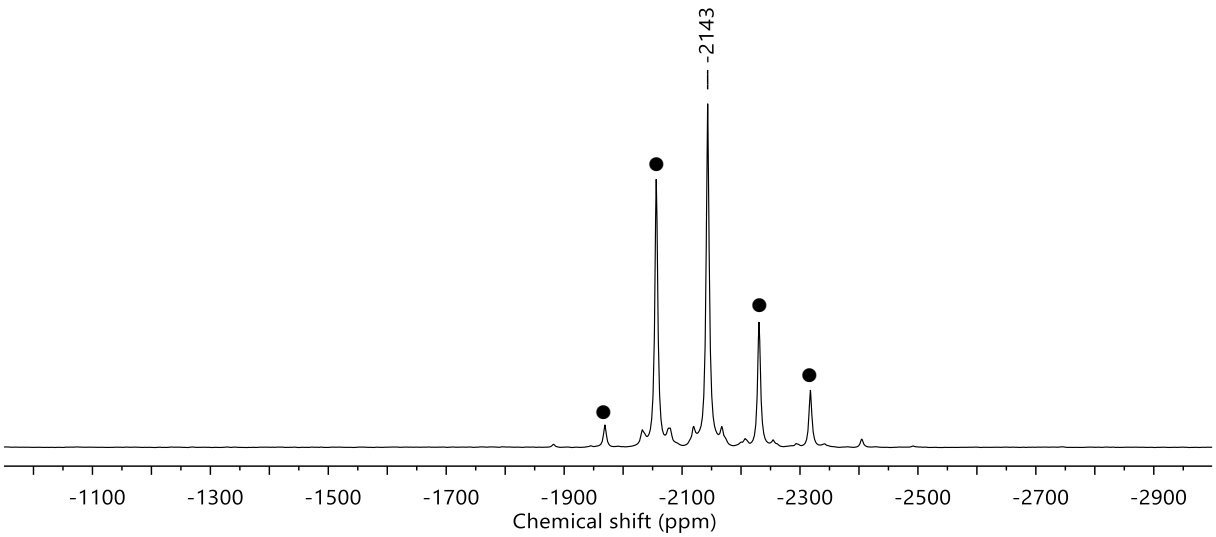

Figure S8: ^{119}Sn CP/MAS NMR spectrum of **2c** (13 kHz, 297 K) (● spinning sideband).

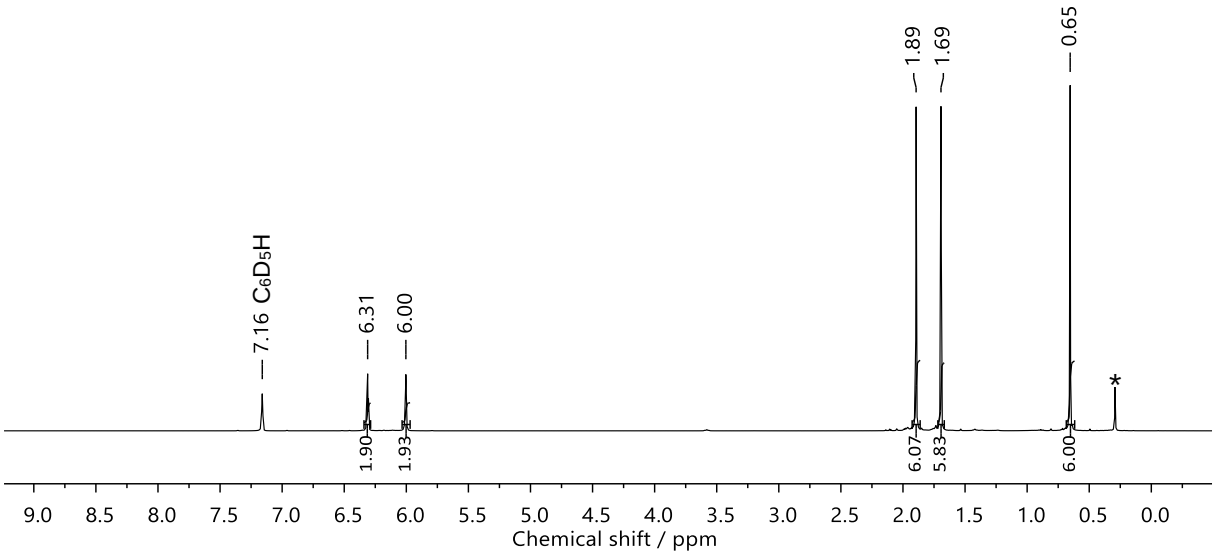

Figure S9: ^{1}H NMR spectrum of **2b** (400.13 MHz, C_6D_6, 296 K) (*silicone grease).

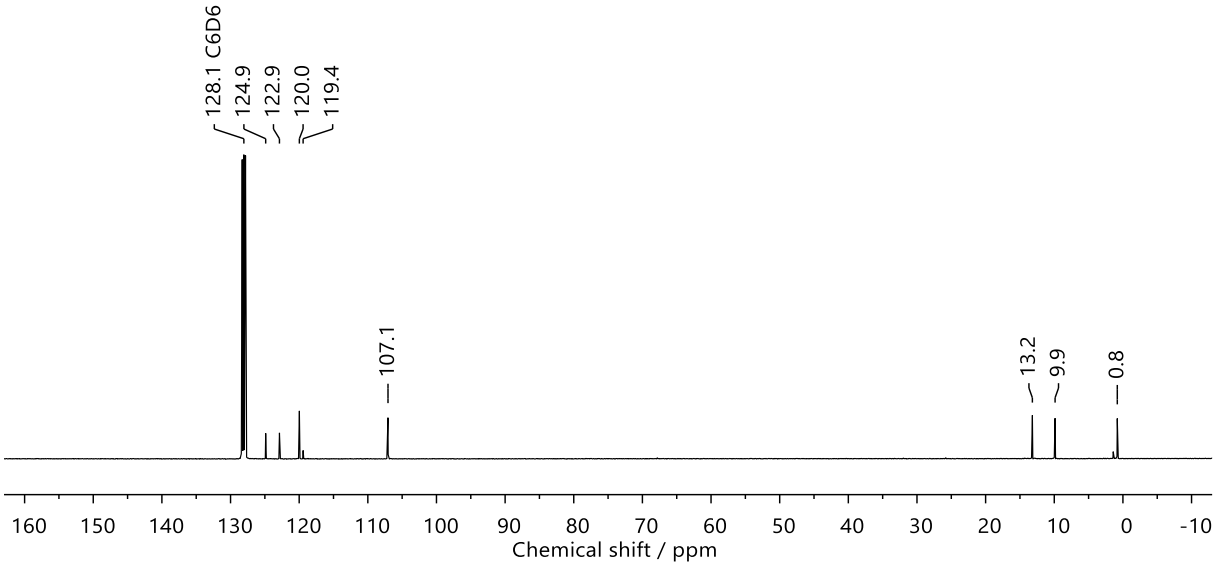

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (100.61 MHz, C_6D_6, 296 K).

Mössbauer spectra

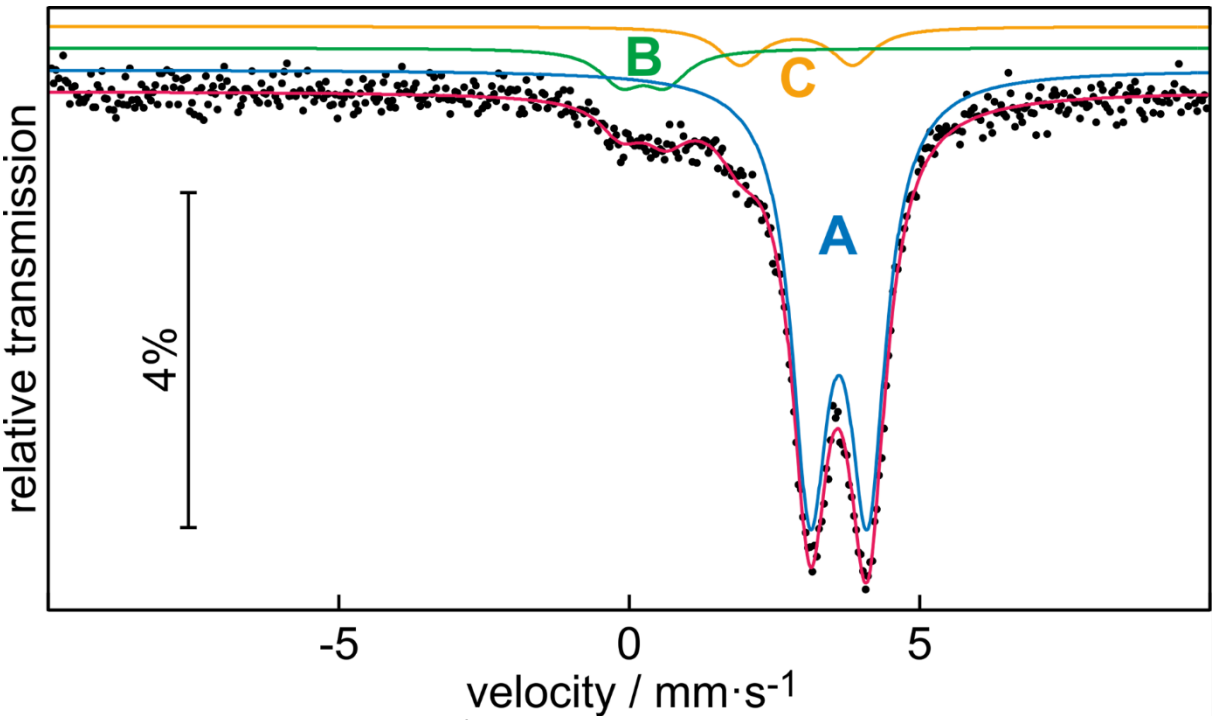

Figure S11: Experimental and simulated ^{119}Sn Mössbauer spectrum of **2c**.

Table S1: Fitting parameters of the ^{119}Sn Mössbauer spectrum recorded at 78 K. δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ = experimental line width.

signal	δ (mm·s^{-1})	ΔE_Q (mm·s^{-1})	Γ (mm·s^{-1})	area
A	3.611(3)	0.991(8)	0.77(1)	83(1)
B	0.25(5)	0.77(7)	0.9(1)	8(1)
C	2.88(4)	1.94(8)	0.9(2)	9(1)

XRD data

Crystal structure data has been deposited with the Cambridge Crystallographic Data Centre (CCDC) and is available free of charge from the Cambridge Crystallographic Database (see reference numbers).

2a:

CCDC	2288212	
Empirical formula	$C_{32}H_{44}Ge_2Si_2$	
Formula weight	630.03	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*C*2	
Unit cell dimensions	a = 17.5006(7) Å	α = 90°
	b = 8.6628(3) Å	β = 130.200(2)°
	c = 13.3527(6) Å	γ = 90°
Volume	1546.17(11) Å^3	
Z	2	
Density (calculated)	1.35 g/cm^3	
Absorption coefficient	2.0 mm^{-1}	
F(000)	656	
Crystal size	0.306 x 0.163 x 0.128 mm^3	
Theta range for data collection	1.997 to 32.052°	
Index ranges	$-26 \le h \le 20$, $-12 \le k \le 12$, $-18 \le l \le 19$	
Reflections collected	36114	
Independent reflections	5375 [R(int) = 0.0249]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.649	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	5375 / 1 / 169	
Goodness-of-fit on F2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0139, wR2 = 0.0371	
R indices (all data)	R1 = 0.0143, wR2 = 0.0372	
Absolute structure parameter	0.0102(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.28 and -0.21 e.Å^{-3}	

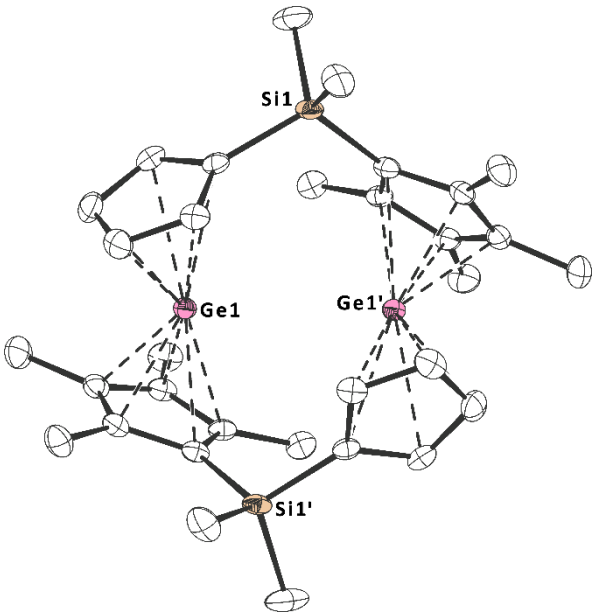

Figure S12: Molecular structure of **2a** in the crystal (displacement ellipsoids at 50% probability level; H atoms omitted for clarity; symmetry label: Ge1$^{\#1}$: #1: *x*, *y*, *z*; Ge1'$^{\#2}$: #2: 1-*x* ,*y*, 1-*z*).

2b:

CCDC	2288213	
Empirical formula	$C_{32}H_{44}Ge_4$	
Formula weight	719.03	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*C*2	
Unit cell dimensions	a = 17.4066(7) Å	α = 90°
	b = 8.7580(4) Å	β = 128.6390(10)°
	c = 13.1177(6) Å	γ = 90°
Volume	1562.00(12) $Å^3$	
Z	2	
Density (calculated)	1.53 g/cm^3	
Absorption coefficient	3.8 mm^{-1}	
F(000)	728	
Crystal size	0.156 x 0.117 x 0.051 mm^3	
Theta range for data collection	1.988 to 31.522°.	
Index ranges	$-25 \le h \le 25$, $-12 \le k \le 12$, $-19 \le l \le 19$	
Reflections collected	21387	
Independent reflections	5215 [R(int) = 0.0322]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.649	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	5215 / 1 / 169	
Goodness-of-fit on F2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0213, wR2 = 0.0434	
R indices (all data)	R1 = 0.0237, wR2 = 0.0443	
Absolute structure parameter	0.019(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.32 and -0.28 e.$Å^{-3}$	

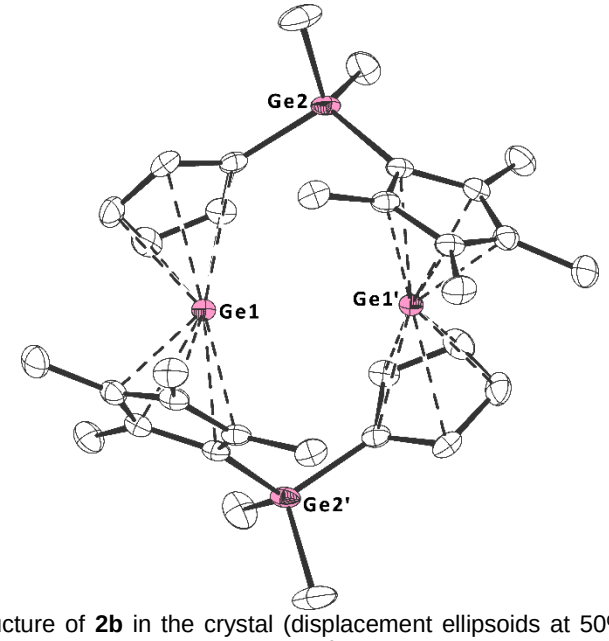

Figure S13: Molecular structure of **2b** in the crystal (displacement ellipsoids at 50% probability level; H atoms omitted for clarity; symmetry label: $Ge1^{\#1}$: #1: *x*, *y*, *z*; $Ge1'^{\#2}$: #2: 1-*x*, *y*, 1-*z*).

2c:

CCDC	2288211	
Empirical formula	$C_{32}H_{44}Si_2Sn_2$	
Formula weight	722.23	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	*Aba*2	
Unit cell dimensions	a = 16.7596(8) Å	α = 90°
	b = 21.3357(10) Å	β = 90°
	c = 8.6837(4) Å	γ = 90°
Volume	3105.1(3) $Å^3$	
Z	4	
Density (calculated)	1.55 g cm^{-3}	
Absorption coefficient	1.7 mm^{-1}	
F(000)	1456	
Crystal size	0.243 x 0.123 x 0.094 mm^3	
Theta range for data collection	2.263 to 26.697°	
Index ranges	$-21 \leq h \leq 21$, $-26 \leq k \leq 26$, $-10 \leq l \leq 10$	
Reflections collected	51606	
Independent reflections	3285 [R(int) = 0.0260]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.691	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	3285 / 1 / 169	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0112, wR2 = 0.0303	
R indices (all data)	R1 = 0.0114, wR2 = 0.0304	
Absolute structure parameter	-0.003(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.19 and -0.32 e.$Å^{-3}$	

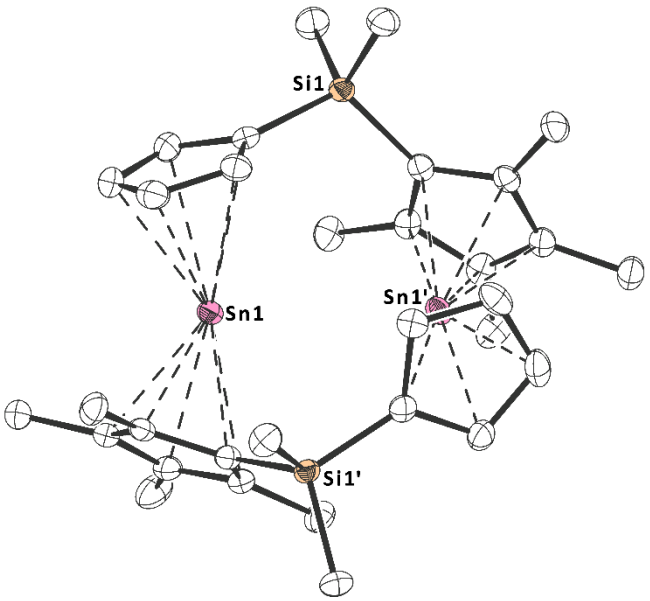

Figure S14: Molecular structure of **2c** in the crystal (displacement ellipsoids at 50% probability level; H atoms omitted for clarity; symmetry label: $Sn1^{\#1}$: #1: *x*, *y*, *z*; $Sn1'^{\#2}$: #2: 1-*x*, 1-*y*, *z*).

Table S2: E–C^{Cp}/$C^{Cp\#}$ bond distances in **2a**-**c** in pm.

	2a (E = Ge)	**2b (E = Ge)**	**2c (E = Sn)**
C^{Cp}	276.9(1); 264.0(1); 246.4(2); 247.7(2); 265.2(1)	277.2(2); 264.5(2); 246.2(4); 245.7(3); 265.0(3)	287.0(2); 272.8(3); 260.5(3); 265.4(2); 281.4(2)
$C^{Cp\#}$	247.0(1); 232.9(1); 237.3(2); 254.6(1); 260.4(1)	247.1(2); 262.0(2); 255.1(3); 237.0(3); 232.9(2)	263.5(2); 252.8(2); 258.5(2); 274.7(2); 276.4(2)

Table S3: Selected E–Cp/Cp# bond distances in **2a**-**c**.

	2a (E = Ge)	**2b (E = Ge)**	**2c (E = Sn)**
E–$Cp^{centroid}$	230.87(2)	230.78(3)	245.71(3)
E–Cp^{plane}	228.21	227.79	243.75
Δ($Cp^{centroid}$-Cp^{plane})	34.95	37.03	30.97
E–$Cp^{\#,centroid}$	214.71(2)	215.34(2)	235.92(4)
E–$Cp^{\#,plane}$	212.64	213.00	234.14
Δ($Cp^{\#,centroid}$-$Cp^{\#,plane}$)	29.74	31.66	28.93

IR spectra

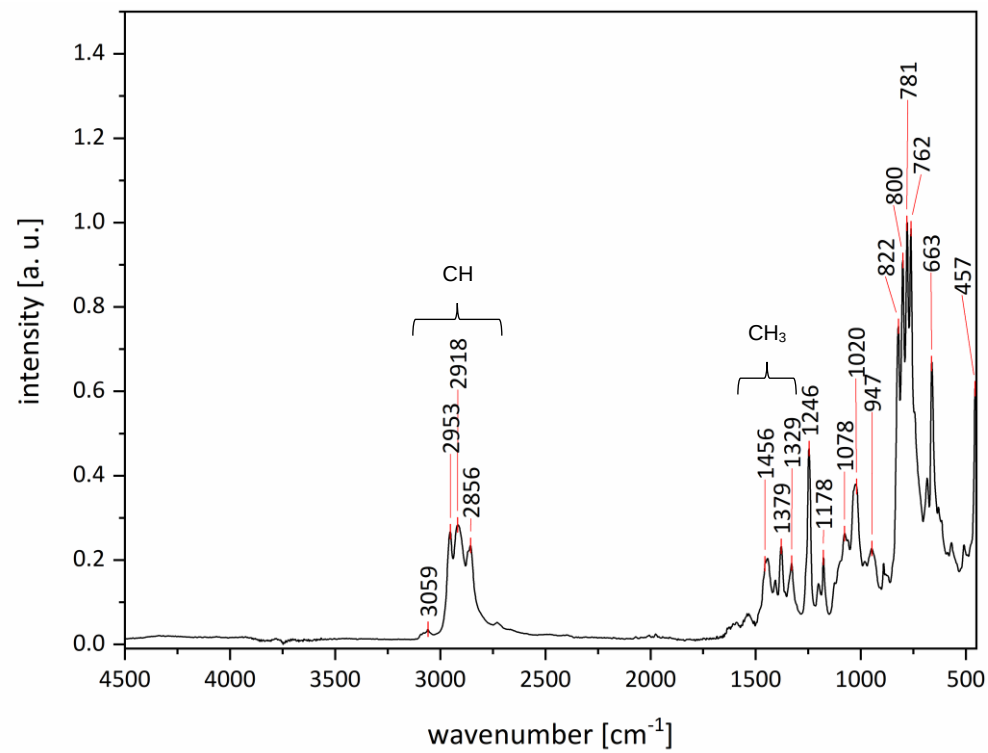

Figure S15: IR spectrum of **2a**.

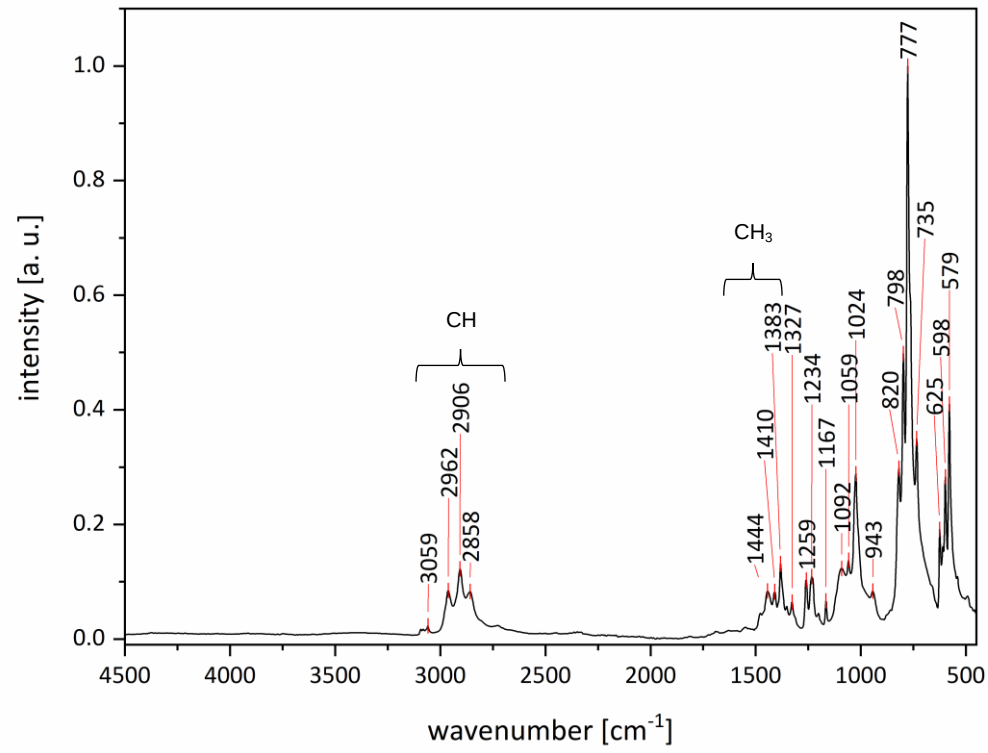

Figure S16: IR spectrum of **2b**.

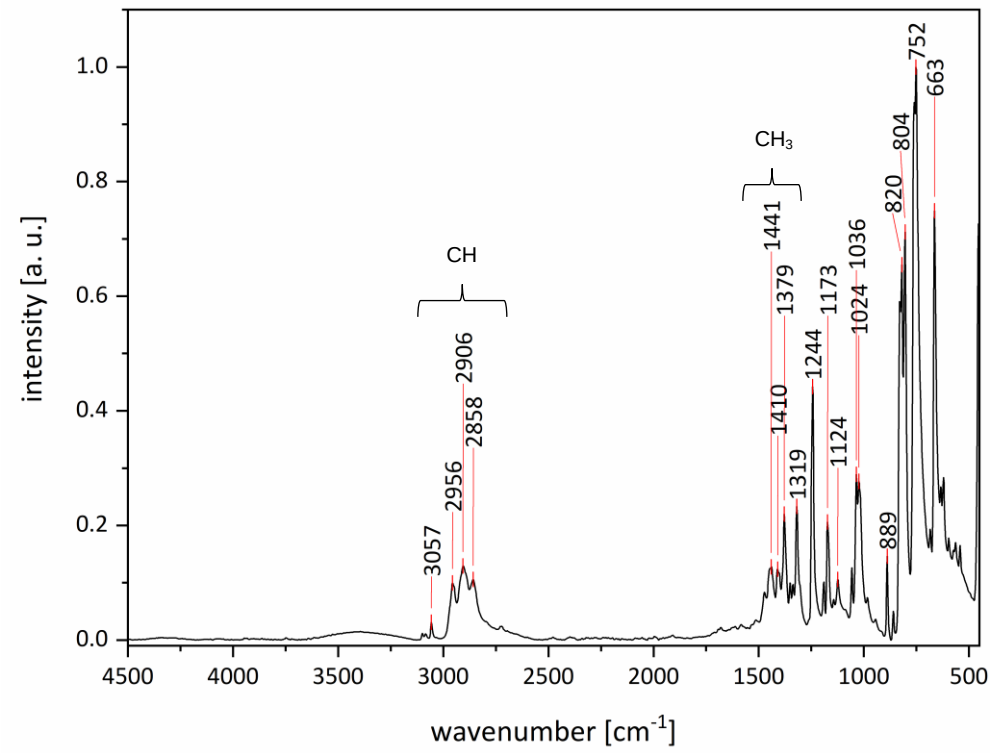

Figure S17: IR spectrum of **2c**.

UV-Vis spectra

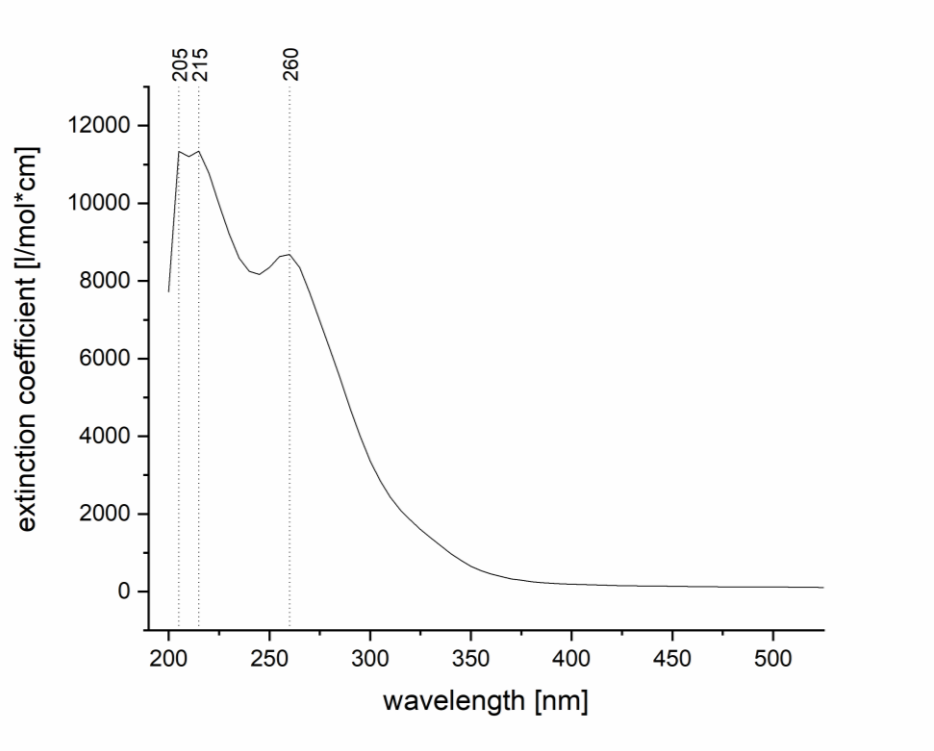

Figure S18: UV-Vis spectrum of **2a** (c = $8.67*10^{-5}$ mol L^{-1} in hexane).

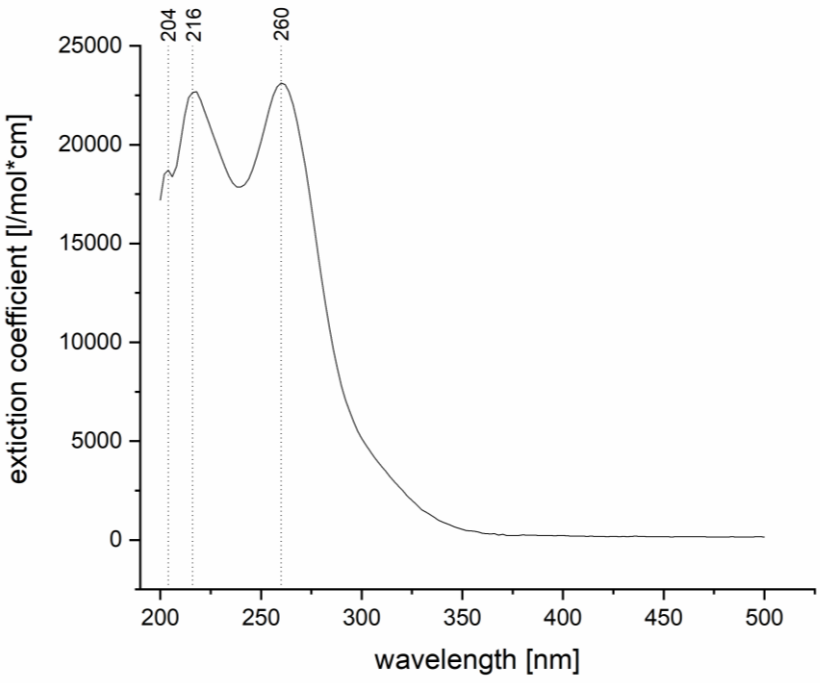

Figure S19: UV-Vis spectrum of **2b** (c = $2.32*10^{-5}$ mol L^{-1} in hexane).

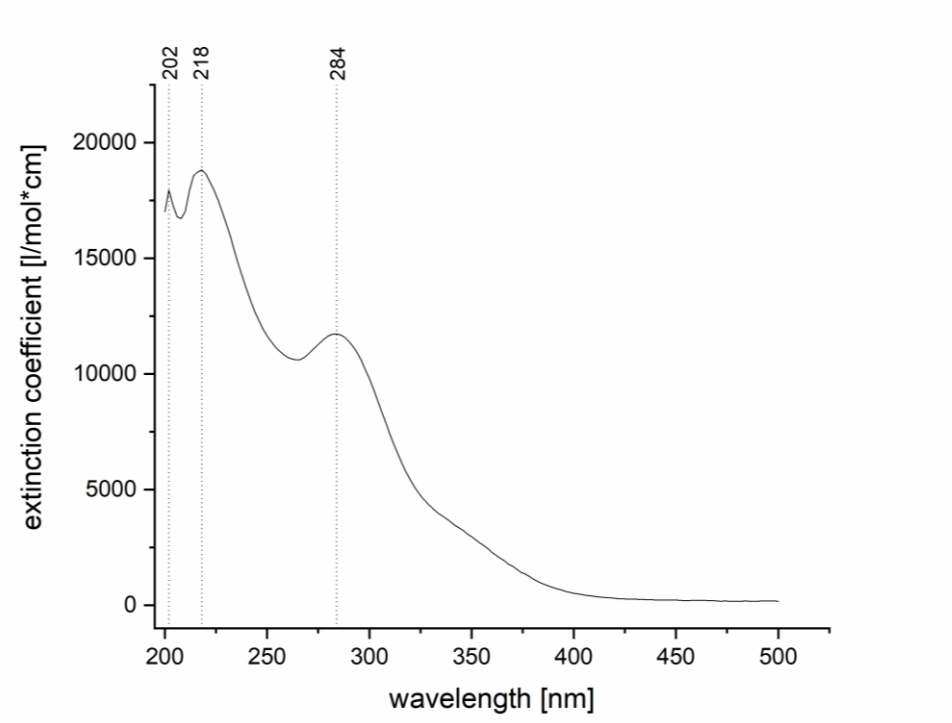

Figure S20: UV-Vis spectrum of **2c** (c = $3.08*10^{-5}$ mol L^{-1} in hexane).

Computational details

All calculations were performed using the Gaussian 16, Revision C.01 package of programs.[1] Geometry optimizations have been carried out at the PBE0-D3/def2-TZVP level of theory and subsequent single-point calculations at the PBE0-D3/def2-TZVPP level of theory.[2] The optimized structures were confirmed to be minima on the potential energy surface by subsequent frequency analysis (all positive eigenvalues). NBO analysis were conducted with the NBO 7.0 software.[3] AIM analysis were carried out with AIMAII.[4]

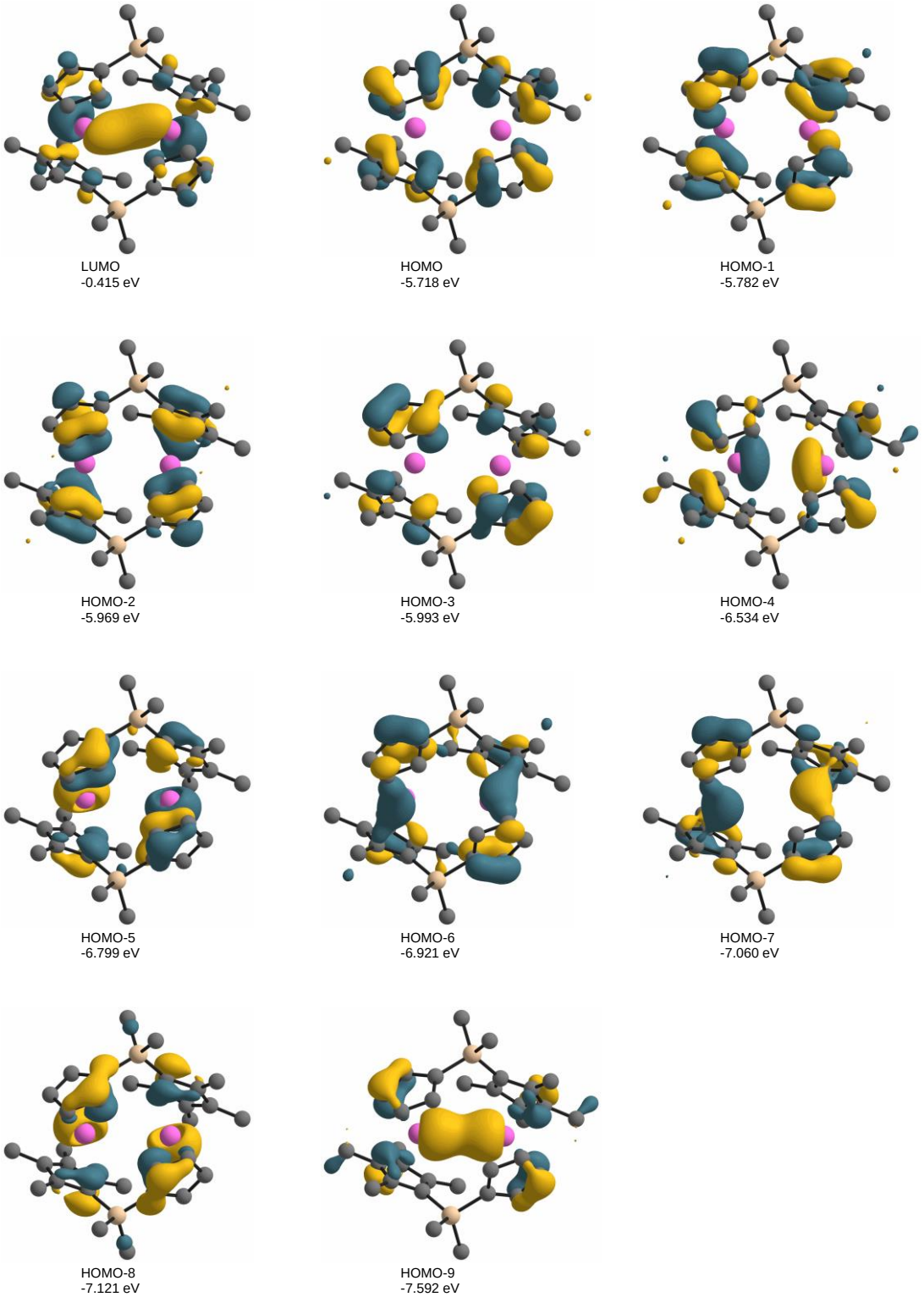

Figure S15: Kohn-Sham molecular orbital contours of **2a** (PBE0-D3/def2-TZVPP//PBE0-D3/def2-TZVP; isovalue = 0.04 a.u.).

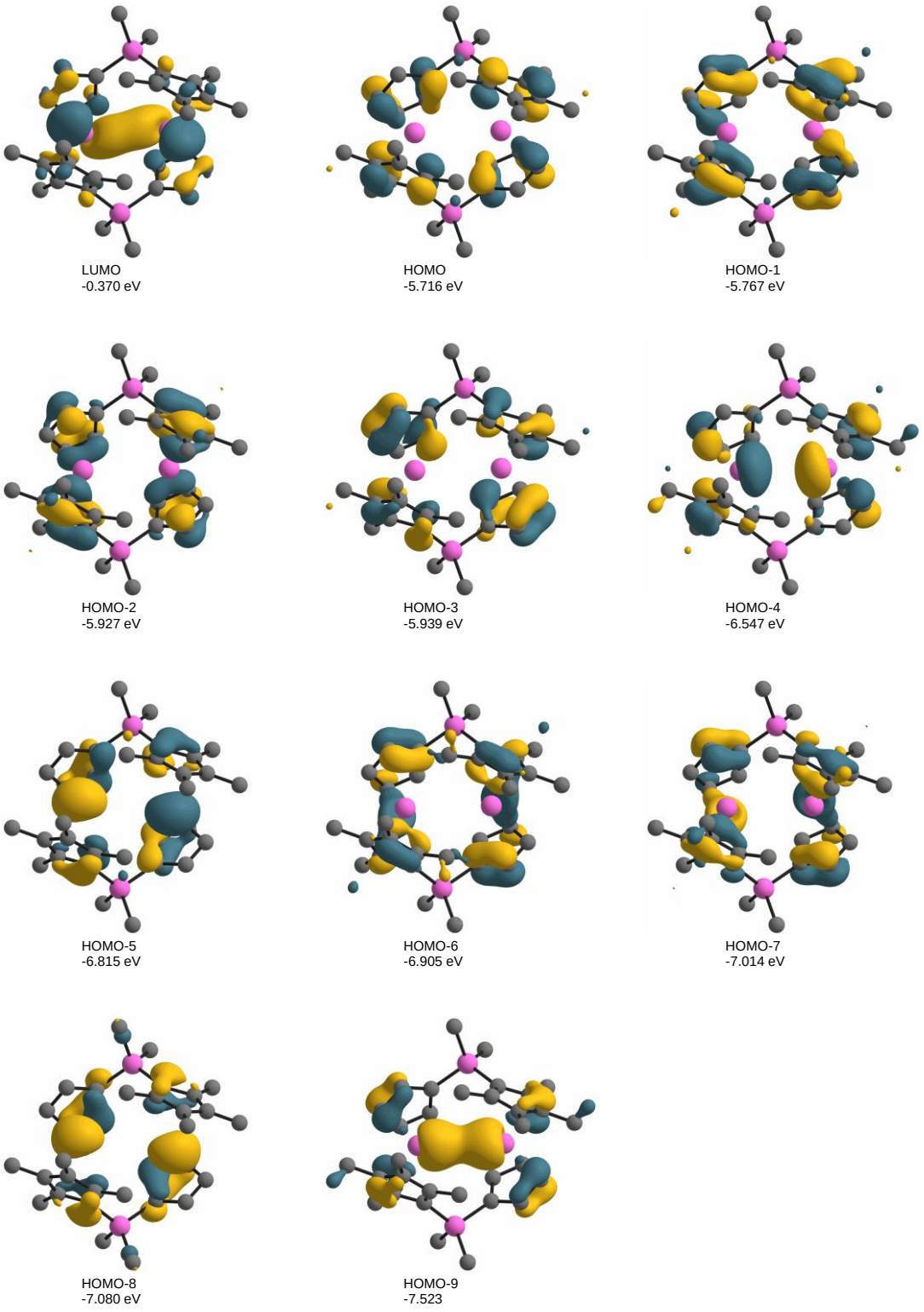

Figure S16: Kohn-Sham molecular orbital contours of **2b** (PBE0-D3/def2-TZVPP//PBE0-D3/def2-TZVP; isovalue = 0.04 a.u.).

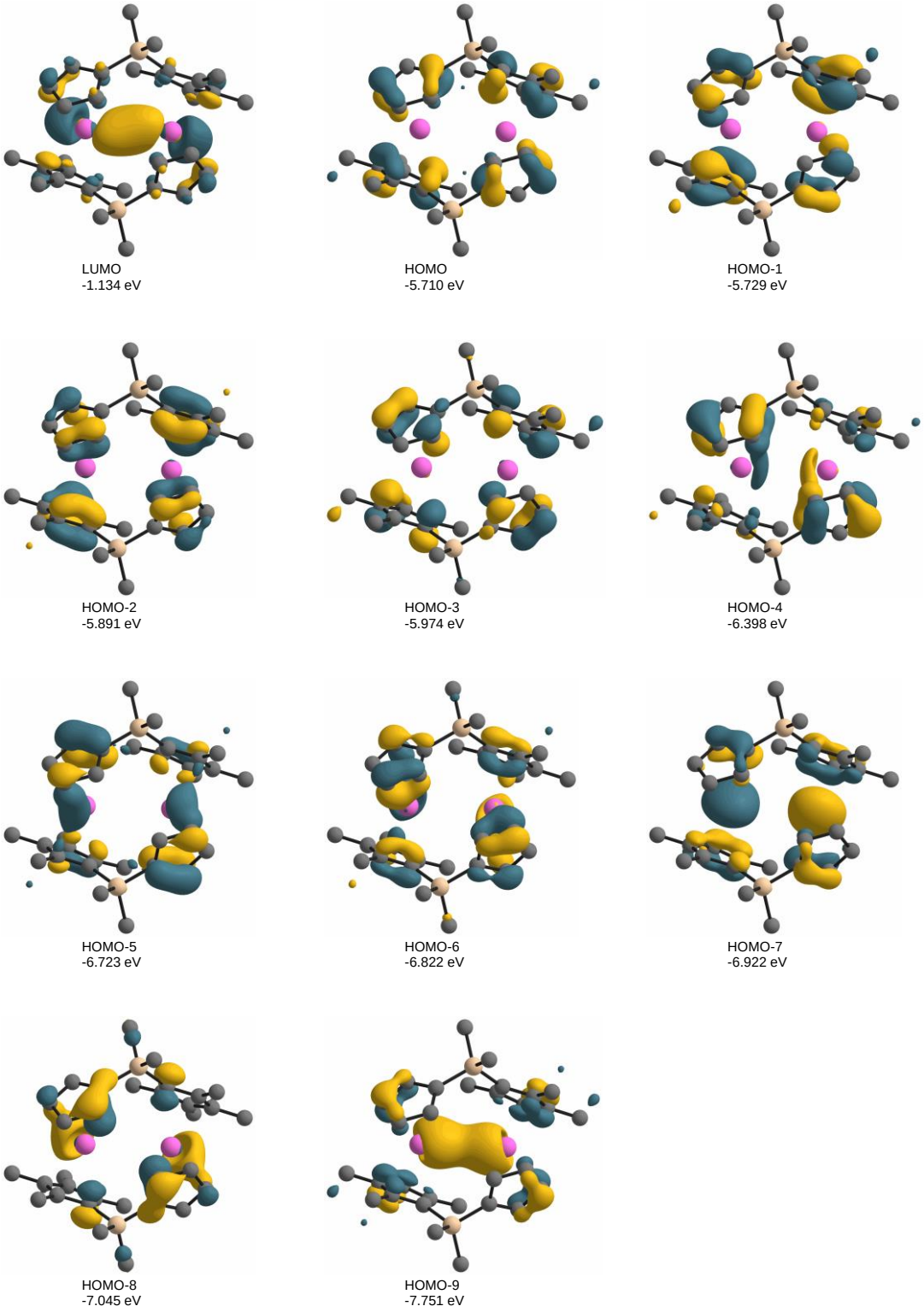

Figure S17: Kohn-Sham molecular orbital contour of **2c** (PBE0-D3/def2-TZVPP//PBE0-D3/def2-TZVP; isovalue = 0.04 a.u.).

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, 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, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

[2] a) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys*., 1992, **97**, 2571; b) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys*., 1994, **100**, 5829; c) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297; d) F. Weigend, *Phys. Chem. Chem. Phys*.,2006, **8**, 1057; e) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865; f) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*.,1997, **78**, 1396; g) C. Adamo and V. Barone, *J. Chem. Phys*.,1999, **110**, 6158; h) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

[3] E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comp. Chem*., 2019, **40**, 25, 2234.

[4] a) R. F. W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon, Oxford, 1990; b) T. A. Keith and T. K. Gristmill, AIMAll, 19.02.13; Overland Park KS, USA (aim.tkgristmill.com), 2019.