CHEMISTRY
A European Journal

Supporting Information

Negishi's Reagent Versus Rosenthal's Reagent in the Formation of Zirconacyclopentadienes

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1 General Considerations

1.1 Abbreviations

br	broad
BTMSA	bis(trimethylsilyl)acetylene
calcd.	calculated
Cp	cyclopentadienyl
d	doublet (NMR)
EI	electron impact
GB	glove box
IR	infrared spectroscopy
m	multiplet (NMR)
m	medium (IR)
NMR	nuclear magnetic resonance
Pin	pinacol
$[PdCl_2(dppf)]$	[1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II)
$[Pd(PPh_3)_4]$	tetrakis(triphenylphosphine)palladium(0)
ppm	parts per million
R	resolution (mass spectrometry)
s	singlet (NMR)
s	strong (IR)
SPS	solvent purification system
t	triplet (NMR)
TLC	thin layer chromatography
THF	tetrahydrofuran
TMS	tetramethylsilane
w	weak (IR)

1.2 Chemicals and Solvents

All reactions were carried out using standard Schlenk techniques under a dry, inert nitrogen or argon atmosphere unless noted otherwise. Some reactions were performed inside a nitrogen filled glovebox from Inert, Innovative Technology, Inc. Company (< 0.1 ppm O_2 and < 0.1 ppm H_2O). All dry solvents were taken from the solvent purification system (SPS), degassed by freeze-pump-thaw cycles and stored under a nitrogen atmosphere unless noted otherwise. All chemicals were commercially available and were used without further purification unless noted otherwise.

Table S 1. List of supplier and purity of used chemicals.

Reagent	Supplier	Purity	Comments
Ammonium chloride	Carl Roth	≥ 99.5%	
Bis(trimethylsilyl)acetylene	Sigma Aldrich	99%	stored in a freezer in a GB
1-Bromo-4-iodobenzene	Alfa Aesar	98%	
1-Bromo-2-(2-trimethylsilylethynyl)benzene	Sigma Aldrich	98%	
2-Bromothiophene	Sigma Aldrich	98%	
Copper (II) chloride	Alfa Aesar	99.995%	
Copper (I) iodide	Alfa Aesar	99.998%	stored in a GB
N-Bromosuccinimide	Merck	99%	
n-Butyllithium	Acros Organics	n. a.	Titrated with Lin& Paquette-Method[1]
Diphenylacetylene	Sigma Aldrich	98%	
1,6-Heptadiyne			
Iodine	ABCR	99%.	
Iodobenzene	Alfa Aesar	98%	
n-Iodosuccinimide	MOLEKULA	95%	
2-Iodothiophene	TCI	≥ 98%	
LiCl	Sigma Aldrich	≥ 99%	anhydrous
Magnesium sulfate	Grüssing	99%	
2-Methoxythiophene	Alfa Aesar	99%	
1-(1-Naphthyl)-2-(trimethylsilyl)acetylene	Sigma Aldrich	97%	
1,8-Nonadiyne	Sigma Aldrich	98%	
1,7-Octadiyne	VWR Chemicals	98%	

[PdCl$_2$(dppf)]	Sigma Aldrich	n.a.	
[Pd(PPh$_3$)$_4$]	TCI	> 97%	stored in a freezer in a GB
Sodium carbonate	VWR Chemicals	n.a.	ACS, Reag. Ph. Eur.
Sodium hydrogen carbonate	VWR Chemicals	n.a.	ACS, Reag. Ph. Eur.
Sodium sulfate	Grüssing	99%	
Sodium thiosulfate	Grüssing	97%	
p-Toluenesulfonic acid·H_2O	Acros Organics	97.5 %	
Trimethylstannyl chloride	Sigma Aldrich	99 %	Stored in a GB
Zirconocene dichloride	abcr	99%	stored in a freezer inside a GB

Table S2. List of suppliers and purity of used solvents.

Solvent	**Comments**
Acetic acid	Alfa Aesar, 99+%
Chloroform	VWR Chemicals; ACS, Reag. Ph. Eur.
Dichloromethane	VWR Chemicals; for HPLC; dry from the SPS
Diethyl ether	VWR Chemicals; for HPLC; dry, distilled from sodium / benzophenone
N,*N*-Dimethylformamide	Extra dry from Acros Organics; 99.8%
Ethyl acetate	VWR Chemicals; ACS, Reag. Ph. Eur.
Ethanol	VWR Chemicals, ACS, Reag. Ph. Eur.
n-Hexane	VWR Chemicals; ACS, Reag. Ph. Eur.
n-Pentane	VWR Chemicals; for HPLC; dry from the SPS and degassed
Pyridine	Acros Organics 99.8%; dried over KOH, degassed, stored over 4 Å molecule sieves
Triethylamine	Grüssing; 99%; dry, distilled over CaH_2; degassed
t-Butanol	VWR Chemicals, ACS, Reag. Ph. Eur.
Tetrahydrofuran	VWR Chemicals; for HPLC; dry from the SPS and degassed
Toluene	VWR Chemicals; for HPLC; dry, from the SPS and degassed

1.3 Analytical Instruments

^{1}H , ^{13}C{^{1}H}, ^{19}F, ^{29}Si{^{1}H}, ^{11}B{^{1}H} and ^{119}Sn{^{1}H} NMR spectra were recorded on a Bruker Avance Neo 500, Bruker Avance Neo 600 or Bruker DPX-200 spectrometer at 300 K. All ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced against the solvent residual proton signals (^{1}H), or the solvent itself (^{13}C). The reference for the ^{119}Sn{^{1}H} NMR spectra was calculated based on the ^{1}H NMR spectrum of TMS. ^{19}F and ^{11}B{^{1}H} NMR spectra were referenced against $BF_3{\cdot}Et_2O$ in $CDCl_3$. ^{29}Si{^{1}H} NMR spectra were referenced against TMS in $CDCl_3$. All chemical δ shifts are given in parts per million (ppm) and all coupling constants J in Hz. The exact assignment of the peaks was proved by two-dimensional NMR spectroscopy such as ^{1}H COSY, ^{13}C HSQC or ^{1}H/^{13}C HMBC when possible.

Electron Impact (EI) ionization mass spectra were obtained on the double focusing mass spectrometer MAT 95XL or MAT 8200 from FINNIGAN mat. Samples were measured by direct inlet or indirect inlet method with a source temperature of 200° C. The ionization energy of the electron impact ionization was 70 eV. All signals were reported with the quotient from mass to charge *m/z*. High resolution (HR) mass spectra were recorded on the double focusing mass spectrometer MAT 95XL from FINNIGAN MAT. Precision weights were determined via the peak-matching method. The reference substance was perfluorokerosene (PFK). The resolution (R) of the peak-matching performance was 10000. The calculated isotopic distribution for each ion was in agreement with experimental values.

IR spectra were recorded on a NICOLET Thermo IS10 SCIENTIFIC IR spectrometer with a diamond-ATR-unit. The resolution was 4 cm^{-1}. Relative intensities of the IR bands were described by s = strong, m = medium or w = weak.

All melting points were measured with a BÜCHI Melting Point M-560 apparatus and are uncorrected.

Thin layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60 F_{254} with a layer thickness of 0.2 mm from Fluka or Macherey-Nagel. All bands were detected by using a fluorescent lamp (254 nm and 366 nm). Column chromatography was carried out by using the column machine PuriFlash 4250 from Interchim. Silica gel columns of the type PF-15SiHP-F0012, PF-15SiHP-F0025, PF-50SiHP-JP-F0080, PF-50SiHP-JP-F0120, and PF-50SiHP-JP-F0220 were used. The injection of the sample was made via dry load. The column material of the dry load was Celite 503 from Macherey-Nagel.

1.4 Crystallography

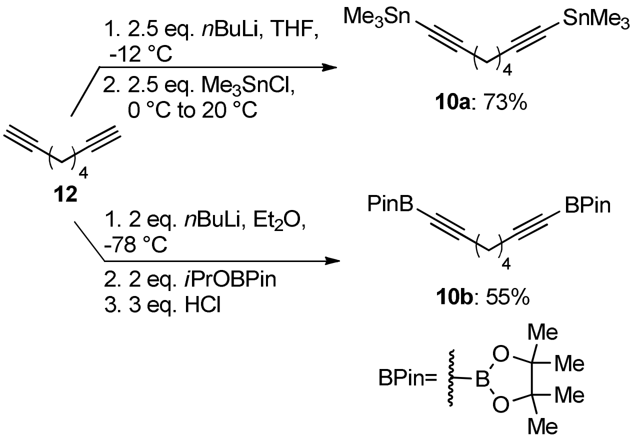
Crystallography. Intensity data of **11d**, **11f**, **11h**, **11i**, **11j**, **11k** and **11l** were collected on a Bruker Venture D8 diffractometers at 100 K with Mo-Kα (0.7107 Å) radiation. All structures were solved by intrinsic phasing and refined based on F^2 by use of the SHELX[2] program package as implemented in OLex2 1.2.[3] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Tables S3-5.

A rotational disorder was resolved for the thiophene groups of compound **11f.** The refinement led to a split atom model for each group with refined occupancies of 76:24 and 53:47, respectively. Compound **11h** comprised two crystallographically independent conformers. The fluorine atoms of the two CF_3-groups of compound **11i** were disordered and were refined with split occupancies of 71:29 and 57:43, respectively. The C-F-distances were restrained to be equal. Compound **11k** crystallized with one molecule of toluene per asymmetric unit. The toluene was disordered over two positions with split occupancies of 65:35. Compound **11l** crystallized with a half molecule in the asymmetric unit. The Zr-atom was located on the Wyckoff-Position 4e of space group C2/c.

Crystallographic data for the structural analyses have been deposited with in Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

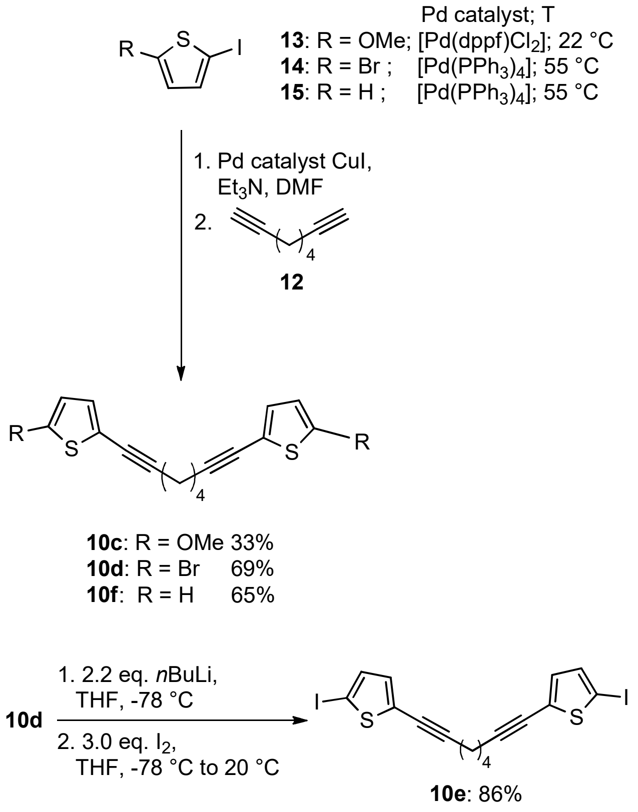
1.5 Results and Discussion of the Precursor Synthesis

The dialkynes **11a-11f** required for the synthesis of the zirconacyclopentadienes were prepared by two methods starting with 1,7-octadiyne (**12**): the first method was based on the deprotonation of **12**, followed by a nucleophilic substitution either with trimethyltin chloride or *iso*propyl pinacol boronic ester to give **10a** and **10b** in yields of 73% and 55%, respectively (Scheme 6).[4]



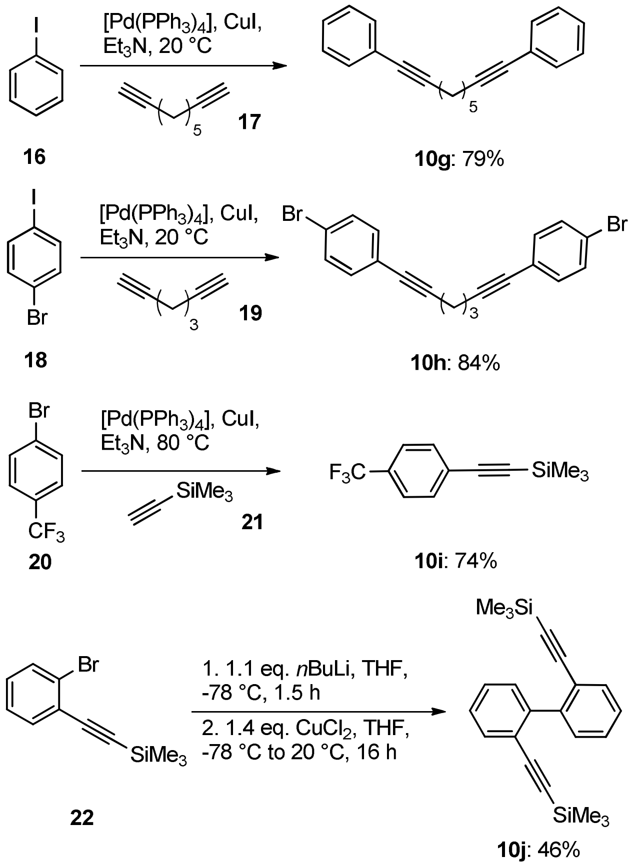
Scheme S1. Synthetic route to form the dialkynes **10a** and **11b** by nucleophilic substitution.

The second route was based on Sonogashira cross coupling reactions of two equivalents of functionalized thiophenes **13**, **14** or **15** with 1,7-octadiyne (**12**) using different Pd sources and temperatures (Scheme 7). The yields ranged from 33% for the electron rich compound **13** up to 69% and 65% for 2-bromo-5-iodothiophene (**14**) and 5-iodothiophene (**15**) respectively. The product of the Sonogashira reaction between the 2-iodo-5-bromothiophene (**14**) and 1,7-octadiyne (**12**) gave the dialkyne **10d**, which contained two bromide groups.[5] The substituents were transformed into iodide groups via bromo-lithium exchange followed by iodination in order to prepare compound **10e**.[6] The diynes **10d** and **10e** are of high interest for this study, because with these compounds it is possible to synthesize functionalized heterocycles, which are useful for further polymerizations (materials science) and other reactions. With these functionalities it can be analyzed a potential difference in the stability aryl iodides vs. aryl bromides under the experimentally more extreme Negishi conditions, which are both prone to halogen metal exchange reactions, but to a different extent.



Scheme S2. Synthetic path to form the dialkynes **10c-10f**.

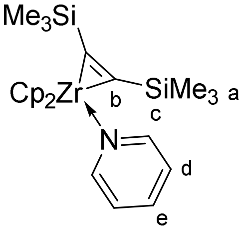
The dialkynes **10g** and **10h** and the monoalkyne **10i** were prepared by a Sonogashira reaction between the benzene derivatives **16**, **18** and **20** and 1,8-nonadiyne (**17**), 1,4-heptadiyne (**19**)[7] and trimethylsilylacetylene (**21**)[8] respectively (Scheme 8). The dialkyne **10j** was prepared by the Ullman reaction between the aryllithium species, formed *in situ* from the bromide-lithium exchange of the starting material **19** with *n*BuLi, and an equivalent of **19**.[9] The monoalkynes **10k** and **10l** were obtained from commercial sources.



Scheme S3. Synthetic path to form the alkynes **10g**-**10j**.

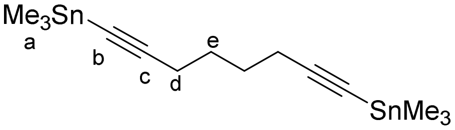
2 Syntheses

Rosenthal´s Zirconocene (9)[6, 10]



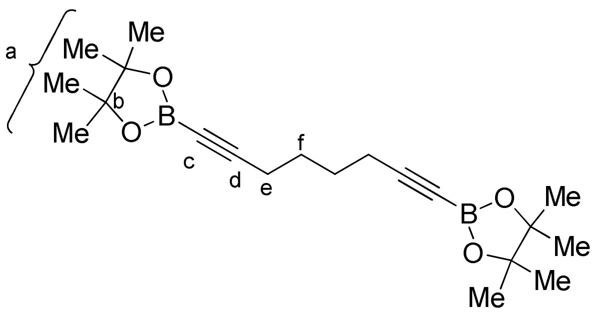
In a GB, zirconocene dichloride (5.00 g, 17.1 mmol) and bis(trimethylsilyl)acetylene (2.91 g, 17.1 mmol) were dissolved in tetrahydrofuran (100 mL). At the Schlenk line, *n*-butyllithium (2.5 M in hexanes, 13.7 mL, 34.2 mmol) was added dropwise over the course of 40 min at -78 °C to the colorless solution. The yellow mixture was stirred for 10 min and the reaction was allowed to warm to 22 °C over 2 h by removing the cooling bath. During that, the color changed from yellow to dark red. The flask was transferred into a GB and pyridine (1.38 mL, 17.1 mmol) was added leading to a color change from dark red to purple. The solvent was removed *in vacuo* under inert conditions until only ca. 1 mL remained. *n*-Pentane (250 mL) was added and the solution was stirred for further 48 h. Then, the crude compound was filtered with PTFE syringe filters (0.45 µm pore size) and placed in a -30 °C freezer in the GB for 72 h. The supernatant was removed by decantation and dried *in vacuo* to afford long black-purple crystals in a yield of 5.06 g (63%). **^{1}H NMR** (500 MHz, C_6D_6): δ 8.89-8.82 (m, 2H, c), 6.86-6.71 (m, 1H, e), 6.46-6.34 (m, 2H, d), 5.47 (s, 10H, Cp), 0.32 (s, 18H, a) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 153.9 (d), 136.5 (f), 123.1 (e), 111.1 (b), 106.4 (Cp), 2.5 (c) ppm. The data are consistent with the literature.[6, 10]

1,8-bis(Trimethylstannyl)octa-1,7-diyne (10a)[4a]



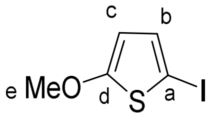
n-Butyllithium (19.6 mL, 2.4 M in hexanes) was added dropwise over the course of 8 min to a solution of 1,7-octadiyne (2.00 g, 18.8 mmol) in THF (47 mL) at -12 °C under nitrogen atmosphere. The slightly yellow slurry was stirred for 80 min at 0 °C and trimethylstannyl chloride (9.38 g, 47.1 mmol) in THF (10 mL) was added. After removal of the cooling bath, the slightly yellow solution was stirred for 2 h at 22 °C and was quenched with a saturated solution of ammonium chloride (1 x 5 mL). The crude product was extracted with diethyl ether (3 x 10 mL) and dried over magnesium sulfate, filtered, and the volatiles were removed *in vacuo*. The yellow oil was purified by sublimation (75 °C, $4.5 \cdot 10^{-2}$ mbar) to afford a slightly yellow solid in a yield of 6.00 g (73%). **M.p**: 70°C; ^{1}**H NMR** (500 MHz, C_6D_6): *δ* 2.16-2.09 (m, 4 H, d), 1.63-1.53 (m, 4 H, e), 0.16 (s, 18H, a) ppm; ^{13}**C{^{1}H} NMR** (126 MHz, $CDCl_3$): *δ* 110.4 (c), 82.2 (b), 28.3 (e), 19.8 (d), -8.3 (a) ppm; ^{119}**Sn{^{1}H} NMR** (187 MHz, C_6D_6): *δ* -73.2 ppm.; **IR** (ATR): ν 3619 (w), 2984 (w), 2942 (m), 2866 (w), 2147 (m), 1548 (m), 1459 (m), 1373 (m),1326 (m), 1307 (m), 1191 (m), 1028 (m), 925 (m), 771 (s), 721 (s), 538 (s), 516 (s) cm^{-1}; **HR-MS** (EI, [M-H]$^{+}$, $C_{13}H_{23}{}^{120}Sn_2$): *m/z* calcd. 418.9843, found 418.9844 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 419 (20) [M]$^{+\cdot}$, 329 (100) [M-OC_4H_9]$^{+}$. The data are consistent with the literature.[4a]

1,8-bis(4,4,5,5-Tetrametyhl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne (10b)[4b]



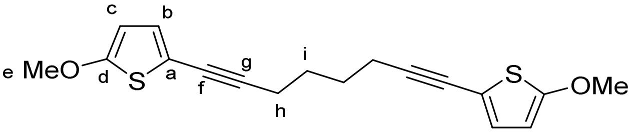
n-Butyllithium (14.5 mL, 2.4 M in hexanes) was added dropwise over the course of 30 min to a solution of 1,7-octadiyne (2.34 mL, 17.6 mmol) in diethyl ether (350 mL) at -78 °C under nitrogen atmosphere. The resulting slurry was mechanically stirred for 15 min and isopropylpinacol borate (6.56 g, 34.9 mmol) was added at once and the slurry was stirred at 22 °C for 3 h. HCl (28 mL, 2 M in diethyl ether) was added at -40 °C and the mixture was stirred until it reached 22 °C. It was stirred for a further 1 h at this temperature. Afterwards the mixture was filtered and concentrated to dryness. The residue was dried via oil pump vacuum ($2.0\cdot10^{-1}$ mBar) at 50 °C for 3h. The crude product was then recrystallized in *n*-hexane (1 x 20 mL) and hot filtered to afford a white solid in a yield of 3.64 g (58%). **M.p**: 129 °C; ^{1}**H NMR** (500 MHz, C_6D_6): 1.82-1.78 (m, 4H, f), 1.29-1.24 (m, 4H, e), 1.00 (s, 24H,a) ppm; ^{13}**C{^{1}H} NMR** (126 MHz, C_6D_6)83.83 (b), 69.2 (d), 27.5 (f) , 24.9 (a), 19.2 (e) ppm; ^{11}B NMR (160 MHz, C_6D_6): δ 24.6 ppm; **IR** (ATR): ν 2975 (w), 2923 (w), 1577 (w), 1430 (m), 1369 (m), 1316 (s), 1265 (m), 1165 (s), 1074 (w), 966 (w), 847 (s), 727 (s), 696 (s), 672 (m) cm^{-1}; **HR-MS** (EI, $C_{20}H_{32}O_4{}^{10}B_2$): *m/z* calcd. 356.25538, found 356.25674 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 358 (9) [M]$^{+\cdot}$, 285 (100) [M-OC_4H_9]$^{+}$. The data are consistent with the literature.[4b]

5-Methoxy-2-iodothiophene (13)[11]



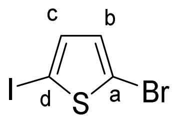
This reaction was not carried out under inert conditions. 2-Methoxythiophene (1.00 g, 8.76 mmol.) was dissolved in ethanol (17.5 mL). *N*-Iodosuccinimide (1.97 g, 8.76 mmol) and *p*-toluenesulfonic acid (170 mg, 870 mmol, 10 mol%) were added and reaction was stirred for 10 min at 22 °C. A saturated solution of sodium thiosulfate (17.5 mL) was added. The mixture was extracted with ethyl acetate (1 x 26 mL) and the organic phase was washed with a solution of sodium carbonate (1 M, 1 x 18 mL), dried over magnesium sulfate and filtered. The volatiles were removed *in vacuo*. The crude product was purified by column chromatography (silica gel, *n*-hexane, $R_f = 0.33$) to afford a yellow oil (1.36 g, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.91 (d, ^3J = 4.0 Hz, 1H, b), 5.93 (d, ^3J = 4.0 Hz, 1H, c), 3.87 (s, 3H, e) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 170.1 (d), 134.6 (b), 106.0 (c), 60.6 (e), 57.4 (a) ppm; **IR** (ATR): ν 2932 (w), 2821 (w), 1541 (m), 1464 (m), 1419 (m), 1367 (w), 1320 (w), 1277 (w), 1232 (w), 1219 (w), 1195 (m), 1179 (m), 1147 (w), 1098 (w), 1074 (w), 1057 (m), 1044 (m), 992 (m), 968 (w), 931 (m), 848 (w), 808 (w), 758 (m), 736 (w), 718 (w) cm^{-1}; **HR-MS** (EI, C_5H_5OSI): *m/z* calcd. 239.91004, found 239.90994 (R = 10000); **MS** (EI, 70 eV, indirect inlet, 200 °C): *m/z* (% relative intensity) = 240 (100) $[M]^{+\cdot}$, 98 (77) $[M-CH_3-I]^+$. The data are consistent with the literature. [11]

1,8-bis(5-Methoxy-thiophen-2-yl)octa-1,7-diyne (10c)[5]



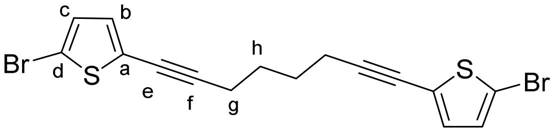
In a GB, a mixture of 5-methoxy-2-iodothiophene (**15**) (2.00 g, 8.33 mmol), [$PdCl_2$(dppf)] (607 mg, 830 µmol) and copper (I) iodide (158 mg, 830 µmol) in triethylamine (4.5 mL) and *N*,*N*-dimethylformamide (14 mL) was stirred at 20 °C. After addition of 1,7-octadiyne (441 mg, 4.16 mmol), the red-brown suspension was stirred under for further 20 h. The reaction was quenched with a saturated solution of ammonium chloride (1 x 50 mL) and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with water (1 x 100 mL), separated and the organic phase was dried over magnesium sulfate. After filtration, the solvents were removed *in vacuo*. The product was purified by column chromatography (silica gel, 1:5 dichloromethane/*n*-hexane, $R_f = 0.14$) to give an orange yellow solid (455 mg, 33%). **M.p.**: 36 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.77 (d, ^3J = 4.0 Hz, 2H, b), 6.02 (d, ^3J = 4.0 Hz, 2H, c), 3.87 (s 6H, e), 2.47-2.41 (m, 4H, g), 1.75-1.65 (m, 4H, h) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 165.9 (d), 129.6 (b), 110.6 (c), 103.8 (a), 91.6 (g), 74.7 (f), 60.3 (e), 27.9 (h), 19.4 (i) ppm; **IR** (ATR): ν 2945 (w), 1542 (m), 1488 (s), 1458 (m), 1449 (m), 1424 (s), 1344 (w), 1329 (w), 1251 (m), 1197 (m), 1154 (w), 1045 (s), 1008 (w), 987 (m), 903 (w), 859 (w), 773 (s), 739 (m), 728 (m), 712 (m) cm^{-1}; **HR-MS** (EI, $C_{18}H_{18}O_2S_2$): *m/z* calcd. 330.07427, found 330.07389 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 330 (16) $[M]^{+\cdot}$, 315 (100) $[M-CH_3]^+$. The data are consistent with the literature.[5]

2-Bromo-5-iodothiophene (14)[11]



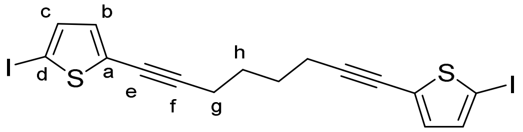
This reaction was not carried out under Schlenk conditions. To a solution of 2-bromothiophene (10.0 g, 61.3 mmol) in ethanol (123 mL), *n*-iodosuccinimide (15.2 g, 67.4 mmol, 1.1 eq) and *p*-toluenesulfonic acid (1.17 g, 6.13 mmol, 10 mol%) were added at 22 °C. The reaction mixture was stirred for 10 min at 50 °C. It was taken out of the heating bath and a saturated solution of sodium thiosulfate (1 x 123 mL) was added. The mixture was extracted with ethyl acetate (3 x 100 mL) and the organic phase was washed with a 1 M solution of sodium carbonate (1 x 200 mL). The organic phase was dried over magnesium sulfate, filtered, and dried *in vacuo*. Purification by Kugelrohrdistillation ($9\cdot10^{-2}$ mbar, 48-50 °C) gave 2-bromo-5-iodo-thiophene as colorless oil (13.6 g, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.04 (d, ^3J = 3.8 Hz, 1H, c), 6.75 (d, ^3J = 3.8 Hz, 1H, b) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 137.6 (c), 131.8 (b), 115.3 (a), 72.4 (d) ppm; **IR** (ATR): ν 3091 (w), 1731 (w), 1567 (w), 1508 (m), 1397 (m), 1202 (m), 968 (s), 929 (m), 780 (s) cm^{-1}; **HR-MS** (EI, $C_4H_2{}^{79}BrIS$): *m/z* calcd. 287.80998, found 287.81052 (R = 10000); **MS** (EI, 70 eV, indirect inlet, 200 °C): *m/z* (% relative intensity) = 288 (92) $[M]^{+\cdot}$, 82 (100). The data are consistent with the literature.[11]

1,8-bis(5-Bromo-thiophen-2-yl)octa-1,7-diyne (10d)



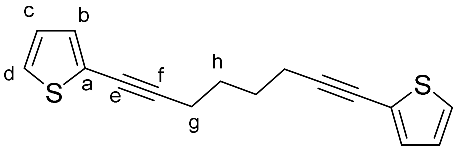
In a GB, a mixture of 2-bromo-5-iodothiophene (5.00 g, 17.3 mmol), $[Pd(PPh_3)_4]$ (404 mg, 2 mol%, 350 µmol) and copper iodide (66.7 mg, 2 mol%, 350 µmol) in dry triethylamine (5.00 mL) and dry *N*,*N*-dimethylformamide (9.00 mL) was stirred at 20 °C. After addition of 1,7-octadiyne (920 mg, 8.65 mmol), the red suspension was stirred under a nitrogen atmosphere at 55 °C for 20 h. Then, the reaction was quenched with a saturated solution of ammonium chloride (1 x 50 mL). The mixture was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were washed with water (1 x 100 mL). They were separated and dried over magnesium sulfate. The volatiles were removed *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-hexane; R_f = 0.24) to obtain a yellow oil, which crystallised at 0-5 °C (2.57 g, 69%).**M.p.**: 53 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.88 (d, ^3J = 3.9 Hz, 2H, b), 6.86 (d, ^3J = 3.9 Hz, 2H, c), 2.51-2.43 (m, 4H, g), 1.79-1.69 (m, 4H, h) ; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 131.5 (b), 129.9 (c), 125.9 (a), 111.7 (d), 95.1 (f), 73.6 (e), 27.7 (g), 19.4 (h) ppm; **IR** (ATR): ν 3091 (w), 3079 (w), 2949 (w), 2926 (m), 2898 (w), 2859 (w), 2823 (w), 2226 (w), 1749 (w), 1587 (w), 1526 (w), 1452 (w), 1428 (m), 1418 (m), 1326 (m), 1305 (w), 1222 (w), 1188 (m), 1111 (w), 1054 (w), 991 (m), 964 (m), 893 (w), 876 (w), 793 (s), 757 (m), 727 (w) cm^{-1}; **HR-MS** (EI, $C_{16}H_{12}{}^{79}Br_2S_2$): *m/z* calcd. 425.87472, found 425.87555 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 428 (100) $[M]^+$.

1,8-bis(5-Iodothiophen-2-yl)octa-1,7-diyne (10e)



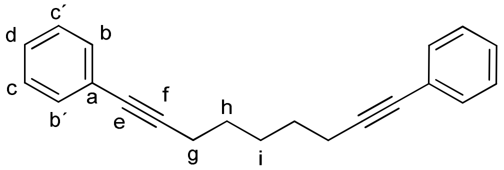
To a solution of 1,8-bis(5-bromo-thiophen-2-yl)octa-1,7-diyne (**11d**) (800 mg, 1.87 mmol) in THF (13 mL) at -78 °C, *n*-butyllithium (2.50 M in hexanes, 1.6 mL, 4.1 mmol) was added dropwise over the course of 15 min. The red solution was stirred for 60 min and iodine (1.42 g, 5.61 mmol) in THF (2.70 mL) was added within 5 min. The brown suspension was warmed to 20 °C over the course of 2 h by removing the cooling bath. The reaction mixture was quenched with a saturated solution of sodium thiosulfate (1 x 25 mL) and it was extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over magnesium sulfate. The solvents were removed *in vacuo*. The crude product was purified by column chromatography (silica gel, *n*-hexane; R_f = 0.14) to obtain a yellow oil (836 mg, 86%), which crystallized at 0-5 °C. **M.p.**: 73 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.07 (d, ^3J = 3.8 Hz, 2H, c), 6.77 (d, ^3J = 3.8 Hz, 2H, b), 2.53-2.43 (m, 4H, g), 1.79-1.68 (m, 4H, h) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 136.9 (c), 132.5 (b), 130.4 (a), 96.0 (f), 73.3 (e), 73.1 (d), 27.7 (g), 19.4 (h) ppm; **IR** (ATR): ν 3072 (w), 2946 (w), 2924 (w), 2896 (w), 2857 (w), 2223 (w), 1752 (w), 1590 (w), 1519 (w), 1451 (w), 1434 (w), 1417 (m), 1325 (w), 1304 (w), 1220 (w), 1185 (m), 1052 (w), 987 (w), 942 (m), 891 (w), 877 (w), 794 (s), 755 (m) cm^{-1}; **HR-MS** (EI, $C_{16}H_{12}I_2S_2$): *m/z* calcd. 521.84700, found 521.84899 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 522 (100) $[M]^+$.

1,8-bis(Thiophen-2-yl)octa-1,7-diyne (10f)[5]



In a GB, a mixture of 2-iodothiophene (5.00 g, 23.8 mmol), $[Pd(PPh_3)_4]$ (555 mg, 480 µmol) and copper (I) iodide (91.4 mg, 480 µmol) in triethylamine (8 mL) and *N*,*N*-dimethylformamide (14 mL) was stirred at 20 °C. After addition of 1,7-octadiyne (0.59 g, 5.65 mmol), the red-brown suspension was stirred under a nitrogen atmosphere at 55 °C for 20 h. The reaction was quenched with a saturated solution of ammonium chloride (1 x 30 mL). The aqueous layer was extracted with diethyl ether (3 x 30 mL) and the combined organic layers were washed with water (1 x 100 mL). The phases were separated and dried over magnesium sulfate. The volatiles were removed *in vacuo*. The residue was purified by column chromatography (silica gel, 1/20 dichloromethane/*n*-hexane, R_f = 0.18) to give the product as a yellow waxy solid (2.09 g, 65%). **M.p.**: 44 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.17 (dd, ^3J = 5.2 Hz, ^4J = 1.0 Hz, 2H, d), 7.12 (dd, ^3J = 3.6 Hz, ^4J = 1.0 Hz, 2H, b), 6.94 (dd, ^3J = 5.2 Hz, ^3J = 3.6 Hz, 2H, c), 2.54-2.43 (m, 4H, g), 1.82-1.72 (m, 4H, h) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 131.2 (b), 126.9 (d), 126.1 (c), 124.2 (a), 94.0 (f), 74.2 (e), 27.9 (g), 19.4 (h) ppm; **IR** (ATR): ν 3107 (w), 2939 (w), 2860 (w), 1516 (w), 1449 (w), 1427 (m), 1355 (w), 1294 (w), 1275 (w), 1237 (w), 1222 (w), 1185 (m), 1141 (w), 1083 (w), 1043 (w), 1015 (w), 897 (w), 846 (m), 829 (s), 741 (w), 691 (s), 662 (m) cm^{-1}; **HR-MS** (EI, $C_{16}H_{14}S_2$): *m/z* calcd. 270.05314, found 270.05306 (R = 12000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 270 (100) $[M]^{+\cdot}$, 242 (70) $[M-C_2H_4]^+$. The data are consistent with the literature.[5]

1,9-Diphenylnona-1,8-diyne (10g)



In a GB, a mixture of iodobenzene (2.00 g, 9.80 mmol), $[Pd(PPh_3)_4]$ (453 mg, 392 µmol, 4 mol%) and copper iodide (74.7 mg, 392 µmol, 4 mol%) in dry triethylamine (20 mL) was stirred at 20 °C. After addition of 1,8-nonadiyne (294 mg, 4.90 mmol), the suspension was stirred under a nitrogen atmosphere at 20 °C for 48 h. The reaction was quenched with a saturated solution of ammonium chloride (1 x 30 mL) and was extracted with dichloromethane (3 x 30 mL). The combined organic layers were washed with water (1 x 90 mL). They were separated and dried over magnesium sulfate. The volatiles were removed *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-pentane, R_f = 0.05) to give a colorless oil (1.06 g, 79%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.45-7.35 (m, 4H, b, b´), 7.30-7.23 (m, 6H, c, c´, d)*, 2.49-2.42 (m, 4H, g), 1.71-1.63 (m, 6H, h, i) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ 131.7 (b, b´), 128.3 (c, c´), 127.6 (d), 124.1 (a), 90.3 (f), 80.9 (e), 28.4 (h), 28.3 (i), 19.5 (g) ppm; **IR** (ATR): ν 3053 (w), 2935 (w), 2858 (w), 2231 (w), 1597 (w), 1570 (w), 1488 (m), 1441 (m), 1330 (w), 1069 (w), 1026 (w), 912 (w), 753 (s), 689 (s) cm^{-1}; **HR-MS** (EI, $C_{21}H_{20}$): *m/z* calcd. 272.15595, found 272.15599 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 272 (46) $[M]^{+\cdot}$, 115 (100).

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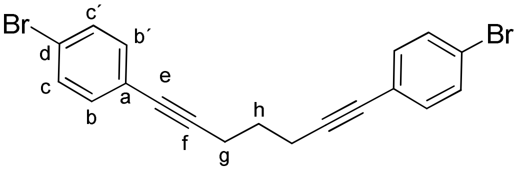
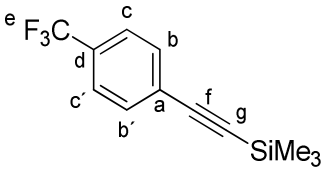
[*] This signal was overlapping with the solvent signal.

1,7-bis(4-Bromophenyl)hepta-1,6-diyne (10h)[7]



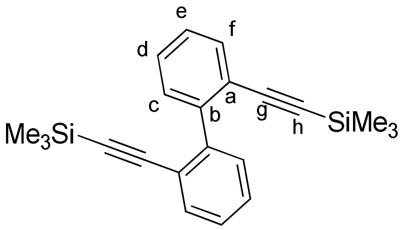
In a GB, a mixture of 1-bromo-4-iodobenzene (2.00 g, 7.07 mmol), [Pd(PPh$_3$)$_4$] (327 mg, 283 µmol, 4 mol%) and copper iodide (54 mg, 283 µmol, 4 mol%) in dry triethylamine (20 mL) was stirred at 20 °C. After addition of 1,6-heptadiyne (326 mg, 3.54 mmol), the suspension was stirred under a nitrogen atmosphere at 20 °C for 24 h. The reaction was quenched with a saturated solution of ammonium chloride (1 x 30 mL). The mixture was extracted with dichloromethane (3 x 30 mL) and the combined organic layers were washed with water (1 x 90 mL) and dried over magnesium sulfate. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (silica gel, *n*-pentane, R_f = 0.15) to give a colorless solid (1.20 g, 84%). **M.p.:** 61 °C; **^{1}H NMR** (600 MHz, CDCl$_3$): δ 7.47-7.41 (m, 4H, c, c´), 7.30-7.26 (m, 4H, b, b´), 2.59 (t, ^3J = 7.0 Hz, 4H, g), 1.92 (p, ^3J = 7.0 Hz, 2H, h) ppm; **^{13}C{^{1}H} NMR** (151 MHz, CDCl$_3$): δ 133.1 (b, b´), 131.5 (c, c´), 122.7 (d), 121.8 (a), 90.4 (f), 80.3 (e), 27.7 (h), 18.7 (g) ppm; **IR** (ATR): ν 3071 (w), 2953 (w), 2903 (w), 2828 (w), 2236 (w), 2146 (w), 1900 (w), 1779 (w), 1651 (w), 1583 (w), 1481 (m), 1454 (w), 1423 (w), 1392 (w), 1351 (w), 1318 (w), 1291 (w), 1253 (w), 1199 (w), 1175 (w), 1096 (w), 1065 (m), 1043 (w), 1009 (m), 907 (w), 857 (w), 821 (s), 761 (m), 736 (w), 703 (w) cm^{-1}; **HR-MS** (EI, $C_{19}H_{14}{}^{79}Br_2$): *m/z* calcd. 399.94568, found 399.94568 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 400 (20) $[M]^{+\cdot}$, 242 (100) $[M-C_6H_4Br]^+$. The data are consistent with the literature.[7]

4-Trifluoromethyl-phenylethynyltrimethylsilane (10i)[8]



1-Bromo-4-(trifluoromethyl)benzene (1.53 g, 6.82 mmol) was dissolved in triethylamine (10 mL). Trimethylsilylacetylene (736 mg, 7.50 mmol), [Pd(PPh$_3$)$_4$] (46.2 mg, 40.0 µmol) and copper iodide (8 mg, 40.0 µmol) were added and the reaction mixture was heated to 80 °C for 12 h in a microwave apparatus. Then, the mixture was filtered to remove insoluble by-products and was diluted with diethyl ether (1 x 40 mL). It was washed with a saturated solution of ammonium chloride (1 x 40 mL). The aqueous layer was extracted with diethyl ether (3 x 40 mL) and the combined organic layers were washed with water (1 x 40 mL). The organic phase was dried using magnesium sulfate and the volatiles were removed *in vacuo* leaving a yellow oil. Purification by column chromatography (silica gel, *n*-pentane, R_f = 0.47) gave 4-(trifluoromethylphenyl)ethynyltrimethylsilane as a colorless oil (1.23 g, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 (s, 4H, b, b´, c, c´), 0.27 (s, 9H, $SiMe_3$) ppm; **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 132.3 (s, b, b´), 130.3 (q, $^2J_{C\text{-}F}$ = 32.7 Hz, d), 127.1 (q, $^5J_{C\text{-}F}$ = 1.5 Hz, a), 125.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, c, c´), 123.0 (s, e), 103.6 (s, f), 97.3 (s, g), -0.1 (s, $SiMe_3$) ppm; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -63.4 ppm; **^{29}Si{^{1}H} NMR** (99 MHz, $CDCl_3$): δ -17.1 ppm; **IR** (ATR): ν 2961 (w), 2162 (w), 1614 (w), 1405 (w), 1320 (s), 1250 (m), 1220 (w), 1166 (m), 1126(s), 1104 (m), 1066 (s), 1014 (w), 861 (s), 838 (s), 759 (m), 699 (w), 656 (m) cm^{-1}; **HR-MS** (EI, $C_{12}H_{13}F_3Si$): *m/z* calcd. 242.07331, found 242.07332 (R = 10000); **MS** (EI, 70 eV, indirect inlet, 200 °C): *m/z* (% relative intensity) = 242 (12) $[M]^{+\cdot}$, 227 (100) $[M-CH_3]^+$. The data are consistent with the literature.[8]

2,2'-bis((Trimethylsilyl)ethynyl)biphenyl (10j)[9]



To a solution of 1-bromo-2-(2-trimethylsilylethynyl)benzene (1.20 g, 4.74 mmol) in tetrahydrofuran (24 mL), *n*-butyllithium (2.5 M in hexanes, 2.10 mL, 5.2 mmol) was added dropwise over the course of 8 min. The reaction mixture was stirred for 1.5 h, then copper(II) chloride (0.88 g, 6.5 mmol) was added. The red-brownish mixture was allowed to warm up by removing the cooling bath and was stirred at 20 °C for further 16 h. The reaction mixture was quenched with a saturated solution of ammonium chloride (1 x 100 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water (1 x 100 mL) and dried over magnesium sulfate. Filtration, removing of the solvents *in vacuo* and purification by column chromatography (silica gel, *n*-pentane, R_f = 0.1) gave the product as a slightly yellow oil (378 mg, 46%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55 (d, ^3J = 7.2 Hz, 2H, c), 7.44 (d, ^3J = 7.5 Hz, 2H, f), 7.37-7.31 (m, 2H, d), 7.29 (t, ^3J = 7.5 Hz, 2H, e), 0.06 (s, 18H, $SiMe_3$) ppm; **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$): δ 143.6 (b), 132.2 (f), 130.2 (d), 127.8 (e), 127.2 (c), 122.7 (a), 104.7 (g), 97.5 (h), -0.2 ($SiMe_3$)ppm; **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_6): δ -18.3 ppm; **IR** (ATR): ν 3061 (w), 2957 (w), 2897 (w), 2158 (w), 1466 (w), 1437 (w), 1247 (m), 1212 (w), 1095 (w), 1062 (w), 1047 (w), 1002 (w), 946 (w), 858 (s), 836 (s), 752 (s), 697 (m) cm^{-1}; **HR-MS** (APCI pos, $C_{22}H_{27}Si_2$): *m/z* calcd. 347.16458, found 347.16410; **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 346 (27) $[M]^{+\cdot}$, 73 (100) $(SiMe_3)^+$. The data are consistent with the literature.[9]

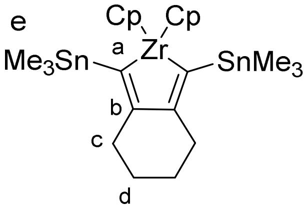
3 Reaction Monitoring Using Rosenthal´s Zirconocene vs. Negishi´s Reagent for the Synthesis of Zirconacyclopentadienes.

General Procedure for the Synthesis of the Zirconacyclopentadienes and Reaction Monitoring.

A mixture of a “Cp_2Zr” species, either from Negishi’s reagent or Rosenthal’s reagent, and a diyne (**10a-l**) was stirred at 22 °C in THF or toluene (amounts see below). A defined sample (0.3 mL) of the reaction was taken after 10 min, 30 min, 1 h, 3 h and 22 h and the solvent was removed immediately *in vacuo* at 22 °C. The reaction monitorings were analyzed by ^1H NMR spectroscopic measurements of each sample. Naphthalene in C_6D_6 was added in an equimolar amount to the sample and used as an internal standard.

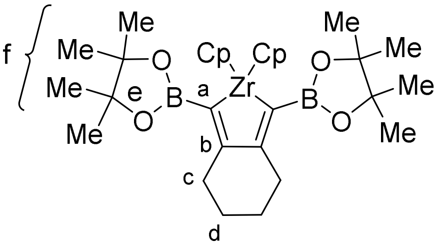
3.1 Reactions with the Negishi´s reagent

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11a[4a]



To a solution of Cp_2ZrCl_2 (67.7 mg, 231 µmol) in THF (2.0 mL) at -78 °C, *n*-butyllithium (0.18 mL, 463 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10a** (100 mg, 231 µmol) in THF (1.0 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. The partial formation of the zirconacyclopentadiene **11a** was observed after 10 min of reaction. Over time, the mixture turned from yellow to bright orange. After 22 h, the reaction mixture was yellowish again.

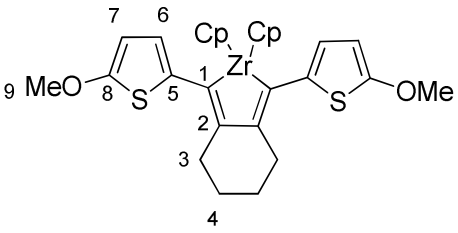
Reaction Monitoring of the Formation of Zirconacyclopentadiene 11b[12]



To a solution of Cp_2ZrCl_2 (81.6 mg, 279 µmol) in THF (2 mL) at -78 °C, *n*-butyllithium (0.22 mL, 558 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10b** (100 mg, 279 µmol) in THF

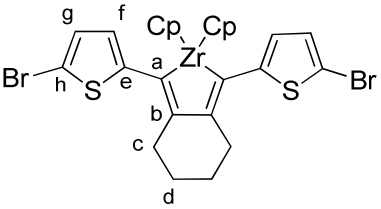
(1.0 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. The partial formation of the zirconacyclopentadiene **11b** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to bright orange. After 22 h, the reaction mixture was yellowish again.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11c[5]



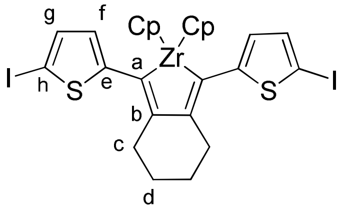
To a solution of Cp_2ZrCl_2 (88.7 mg, 303 µmol) in THF (1.5 mL) at -78 °C, *n*-butyllithium (0.23 mL, 606 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10c** (100 mg, 303 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. A low amount of formation of the zirconacyclopentadiene **11c** was observed after 10 min of reaction. Over time, the mixture turned from yellow to orange-brown. After 22 h, the reaction mixture was yellowish again.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11d



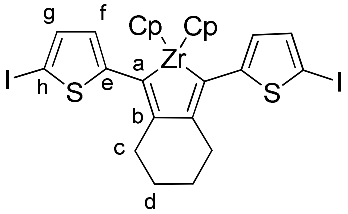
To a solution of zirconocene dichloride (68.7 mg, 235 µmol) in THF (1.5 mL) at -78 °C, *n*-butyllithium (0.18 mL, 470 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10d** (100 mg, 235 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. A low amount of formation of the zirconacyclopentadiene **11d** was observed after 10 min of reaction. Over time, the mixture turned from yellow to orange. After 22 h, the reaction mixture was yellowish again.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11e



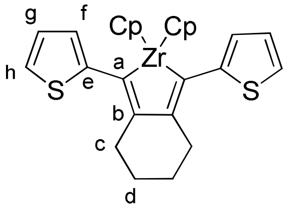
To a solution of zirconocene dichloride (56.1 mg, 192 µmol) in THF (1.5 mL) at -78 °C, *n*-butyllithium (0.15 mL, 384 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10e** (100 mg, 192 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. No formation of the zirconacyclopentadiene **11e** was observed after 10 min of reaction. Over time, the mixture did not change the color.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11e with BTMSA in the Reaction Mixture



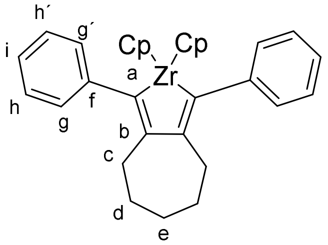
To a solution of zirconocene dichloride (83.9 mg, 287 µmol) in THF (3.0 mL) at -78 °C, *n*-butyllithium (0.23 mL, 574 µmol; 2.50 M in hexanes) was added dropwise over the course of 1-2 min. The reaction mixture was stirred at -78°C for 1 h. Then, a solution of bis(trimethylsilyl)acetylene (48.9 mg, 287 µmol) in THF (0.5 mL) was added and one minute later a solution of diyne **10e** (150 mg, 287 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. A low amount of formation of the zirconacyclopentadiene **11e** was observed after 10 min of reaction. Over time, the mixture turned from yellow to orange-red. After 22 h, the reaction mixture was bright yellow again.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11f[5]



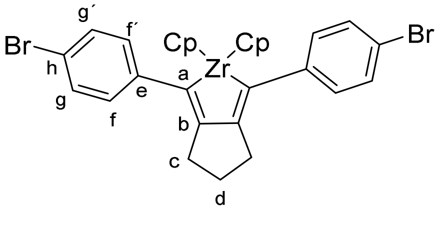
To a solution of zirconocene dichloride (108 mg, 370 µmol) in THF (1.5 mL) at -78 °C, *n*-butyllithium (0.29 mL, 740 µmol; 2.59 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10f** (100 mg, 370 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. High formation of the zirconacyclopentadiene **11f** was observed after 10 min of reaction. Over time, the mixture turned from yellow to orange-red. After 22 h, the reaction mixture was yellowish again.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11g



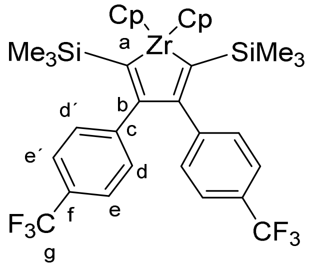
To a solution of Cp_2ZrCl_2 (161 mg, 551 µmol) in THF (5 mL) at -78 °C, *n*-butyllithium (0.44 mL, 1.10 mmol; 2.50 M in hexanes) was added dropwise over the course of 2 min. The reaction mixture was stirred at -78 °C for 1 h and a solution of diyne **10g** (150 mg, 551 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and after 3 h of reaction the solvent was removed *in vacuo*. After removing of the solvent, the sample could not be completely redissolved in deuterated solvents so that the conversion could not be determined by ^{1}H NMR with an internal standard. The reaction was repeated. After filtration of the reaction mixture over celite and removing of the solvent, an orange-pink solid-like film was obtained (239 mg, 88%, purity 90%).

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11h[13]



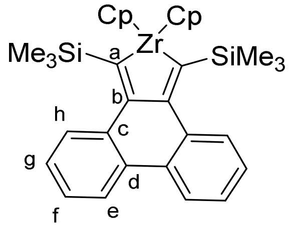
To a solution of Cp_2ZrCl_2 (109 mg, 373 µmol) in THF (3 mL) at -78 °C, *n*-butyllithium (0.30 mL, 746 µmol; 2.50 M in hexanes) was added dropwise over the course of 2 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10h** (150 mg, 373 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. Formation of the zirconacyclopentadiene **11h** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to orange-red.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11i



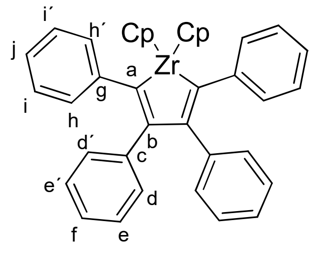
To a solution of Cp_2ZrCl_2 (90 mg, 309 µmol) in THF (3 mL) at -78 °C, *n*-butyllithium (250 µL, 618 µmol; 2.50 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of acetylene **10i** (150 mg, 618 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. Formation of the zirconacyclopentadiene **11i** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to orange. After 22 h the reaction mixture turned ligther in color.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11j[9]



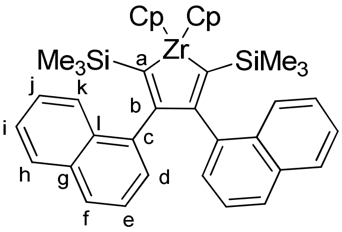
To a solution of Cp_2ZrCl_2 (84 mg, 288 µmol) in THF (5 mL) at -78 °C, *n*-butyllithium (230 µL, 576 µmol; 2.50 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diyne **10j** (100 mg, 288 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. Formation of the zirconacyclopentadiene **11j** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to orange-red. After 22 h the reaction mixture went to bright orange.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11k[13]



To a solution of Cp_2ZrCl_2 (123 mg, 421 µmol) in THF (3 mL) at -78 °C, *n*-butyllithium (330 µL, 842 µmol; 2.50 M in hexanes) was added dropwise over the course of 2 min. The reaction mixture was stirred at -78°C for 1 h and a solution of diphenylacetylene (**10k**) (150 mg, 842 µmol) in THF (2 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. Formation of the zirconacyclopentadiene **11k** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to orange-red. After 22 h the reaction mixture changed to bright orange.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11l

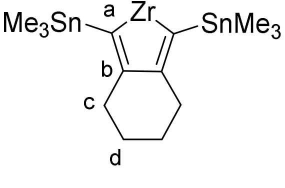


To a solution of Cp_2ZrCl_2 (97 mg, 334 µmol) in THF (3 mL) at -78 °C, *n*-butyllithium (270 µL, 668 µmol; 2.50 M in hexanes) was added dropwise over the course of 1 min. The reaction mixture was stirred at -78°C for 1 h and a solution of 1-(1-naphthyl)-2-(trimethylsilyl)acetylene (**10l**) (150 mg, 668 µmol) in THF (0.5 mL) was added. The reaction was allowed to warm to 22 °C and samples (0.3 mL) were taken for the reaction monitoring after the defined times. Formation of the zirconacyclopentadiene **11l** was observed after 10 min of reaction. Over this time, the mixture turned from yellow to orange. After 22 h the reaction mixture changed to bright orange-yellow.

3.2 Reactions with the Rosenthal's Reagent

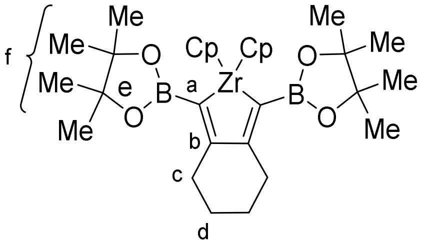
In the case of the reactions with Rosenthal´s zirconocene, two reaction pots with the same amount were made: one for the reaction monitoring and one was stirred for 10 min and was used for further analytics and crystallization purposes. An exception was **11g**, where no reaction monitoring by ^1H NMR measurements could be performed.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11a[4a]



In a GB, a solution of zirconocene **9** (108 mg, 230 µmol) and diyne **10a** (100 mg, 230 µmol) in toluene (5 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11a** was observed after 10 min of reaction. Over this time the mixture turned to bright orange. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a bright orange-yellow solid was obtained for further analysis (141 mg, 94%). **^{1}H NMR** (500 MHz, C_6D_6) δ 6.00 (s, 10H, Cp), 2.22-2.15 (m, 4H, c), 1.57-1.50 (m, 4H, d), 0.20 (d, 18H, e; $^2J_{\text{Sn-H}}$= 24 Hz) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 206.1 (a), 150.7 (b), 111.4 (Cp), 38.7 (c), 23.1(d), -6.7 (e; $^1J_{\text{Sn-C}}$ = 146 Hz) ppm; **^{119}Sn{^{1}H} NMR** (187 MHz, $CDCl_3$): δ -81.3 ppm; **HR-MS** (EI, $C_{24}H_{36}Sn_2Zr$): *m/z* calcd 653.99153, found 653.99188 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 654 (5) $[M]^{+\cdot}$, 155 $[M-C_{12}H_{12}]^{+\cdot}$, (100).

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11b[12]



In a GB, a solution of zirconocene **9** (132 mg, 280 µmol) and diyne **10b** (100 mg, 280 µmol) in toluene (5 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11b** was observed after 10 min of reaction. Over this time the mixture turned to bright orange. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a bright orange-yellow solid was obtained for further analysis (151 mg, 93%). **^{1}H NMR** (500 MHz, C_6D_6): δ= 6.37(s, 10, Cp), 2.59-2.54 (m, 4 m, c), 1.65-1.58 (m, 4H, d), 1.10 (s, 24H, f) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): † δ 147.0 (b), 111.7 (Cp), 81.5(e), 35.4 (c), 24.9 (f), 23.5(d) ppm; **^{11}B{^{1}H} NMR** (160 MHz, C_6D_6): δ 30.9 ppm; **HR-MS** (EI, $C_{30}H_{42}{}^{10/11}B_2O_4{}^{90}Zr$): *m/z* calcd. 577.23471, found 577.23484 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 578 (13) $[M]^{+\cdot}$, 83 (100).

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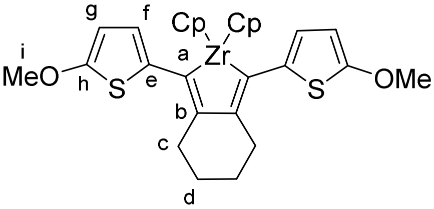
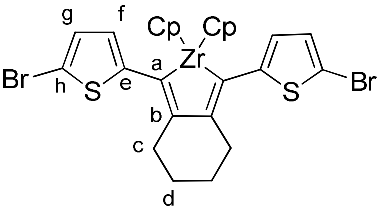
† The signal from the carbon atom bond to boron was not visible due to the high quadrupole moment of the boron nucleus

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11c[5]



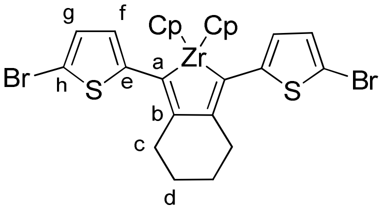
In a GB, a solution of zirconocene **9** (214 mg, 454 µmol) and diyne **10c** (150 mg, 454 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11c** was observed after 10 min of reaction. Over this time the mixture turned to yellowish brown. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a dark greenish-purple solid was obtained for further analysis (233 mg, 93%). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.07 (d, ^3J= 3.8 Hz, 2H, g), 6.05 (s, 10H, Cp), 5.77 (d, ^3J= 3.7 Hz, 2H, f), 3.43 (s, 6H, i), 2.80-2.75 (m, 4H, c), 1.63-1.56 (m, 2H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 177.9 (a), 165.7 (h), 141.3 (b), 136.8 (e), 119.9 (f), 112.1 (Cp), 104.1 (g), 59.7 (i), 30.7 (c), 24.4 (d) ppm; **HR-MS** (EI, $C_{28}H_{28}O_2S_2{}^{90}Zr$): *m/z* calcd. 550.05723, found 550.05796 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 550 (74) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^{+\cdot}$.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11d



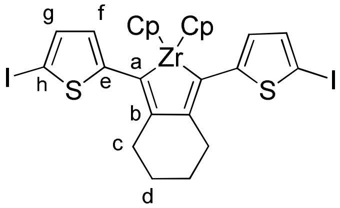
In a GB, a solution of zirconocene **9** (165 mg, 352 µmol) and diyne **10d** (150 mg, 352 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11d** was observed after 10 min of reaction. Over this time the mixture turned to dark red. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a dark red solid was obtained for further analysis (210 mg, 93%). Crystals could be obtained from a saturated toluene solution. **^{1}H NMR** (600 MHz, C_6D_6): δ 6.82 (d, ^3J = 3.8 Hz, 2H, g), 5.84 (s, 10H, Cp), 5.69 (d, ^3J = 3.8 Hz, 1H, f), 2.49 (m, 4H, c), 1.50-1.46 (m, 4H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 177.0 (a), 151.8 (e), 143.0 (b), 130.2 (g), 121.8 (f), 112.3 (Cp), 109.4 (h), 30.1 (c), 23.8 (d) ppm; **HR-MS** (EI, $C_{26}H_{22}{}^{79}Br_2S_2{}^{90}Zr$): *m/z* calcd. 645.85712, found 645.85714 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 646 (38) $[M]^{+\cdot}$, 301 (100).

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11d in THF



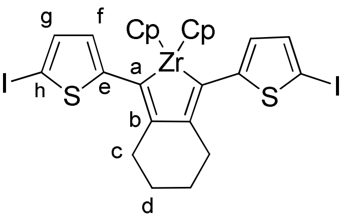
In a GB, a solution of zirconocene **9** (111 mg, 235 µmol) and diyne **10d** (100 mg, 235 µmol) in THF (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11d** was observed after 10 min of reaction. Over this time the mixture turned to dark red. After 22 h, the zirconacyclopentadiene partly decomposed to starting material.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11e



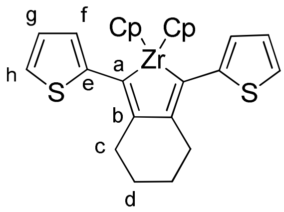
In a GB, a solution of zirconocene **9** (135 mg, 287 µmol) and diyne **10e** (150 mg, 287 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitorings after the defined times. The formation of the zirconacyclopentadiene **11e** was observed after 10 min of reaction. Over this time the mixture turned to dark red. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a dark red solid was obtained for further analysis (194 mg, 91%). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.03 (d, ^3J = 3.7 Hz, 2H, g), 5.85 (s, 10H, Cp), 5.65 (d, ^3J = 3.7 Hz, 2H, f), 2.52-2.45 (m, 4H, c), 1.50-1.44 (m, 4H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 176.9 (a), 156.1 (e), 142.8 (b), 137.1 (g), 129. (f), 112.1 (Cp), 70.0 (h), 29.9 (c), 23.6 (d) ppm; **HR-MS** (EI, $C_{26}H_{22}I_2S_2{}^{90}Zr$): *m/z* calcd. 741.82939, found 741.82934 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 742 (44) $[M]^{+\cdot}$, 347 (100).

Stability Test of Zirconacyclopentadiene 11e in Toluene with LiCl



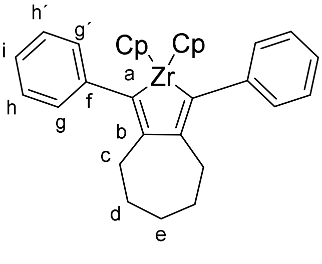
A mixture of zirconacyclopentadiene **11e** (50 mg, 67 µmol) and LiCl (89.5 mg, 134 µmol) in toluene (3 mL) was stirred at 22 °C in a GB. The stability of the zirconacyclopentadiene **11e** was observed by ^{1}H NMR measurements after 10 min, 30 min, 60 min, 3 h and 22 h. The color of the reaction mixture turned over the time of 22 h from dark red to bright yellow and a precipitate was formed.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11f[5, 14]



In a GB, a solution of zirconocene **9** (261 mg, 555 µmol) and diyne **10f** (150 mg, 555 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11f** was observed after 10 min of reaction. Over this time the mixture turned to dark red. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a red solid was obtained for further analysis (259 mg, 95%). Crystals could be obtained from a saturated toluene solution **^{1}H NMR** (500 MHz, C_6D_6): δ 6.96 (dd, ${}^3J$ = 5.2 Hz, ${}^4J$ = 1.0 Hz, 2H, h), 6.90 (dd, ${}^3J$ = 5.2 Hz, 3.5 Hz, 2H, g), 6.21 (dd, ${}^3J$ = 3.5 Hz, ${}^4J$ = 1.0 Hz, 2H, f), 6.00 (s, 10H, Cp), 2.70-2.65(m, 4H, c), 1.59-1.52 (m, 4H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 177.9 (a), 150.3 (e), 142.4 (b), 127.3 (g), 123.0 (h), 121.4 (f), 112.2 (Cp), 30.1 (c), 24.0 (d) ppm; **HR-MS** (EI, $C_{26}H_{24}S_2{}^{90}Zr$): *m/z* calcd. 490.03610, found 490.03669 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 490 (19) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^{+\cdot}$.

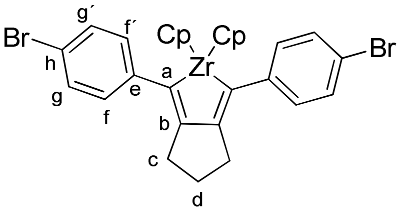
Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11g



A solution of zirconocene **9** (259 mg, 552 µmol) and diyne **10g** (150 mg, 551 µmol) in toluene (6 mL) was stirred at 22 °C for 3 h. The reaction mixture was filtered over celite. The solvent was removed *in vacuo* and an orange-pink solid-like film was obtained (248 mg, 91%, 92% purity). Crystal data could not be received, the compound was just forming gel-like needles. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.42-7.23 (m, 4H, g, g’), 7.09-6.95 (m, 6H, h, h’, i), 5.93 (s, 10H, Cp), 2.38-2.31 (m, 4H, c), 1.61-1.50 (m, 6H, d, e) ppm;

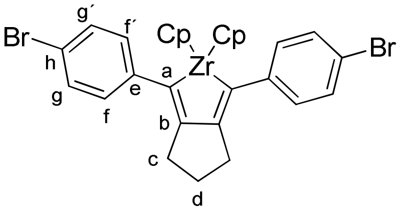
$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 189.3 (a), 149.6 (b), 137.9 (f), 128.6 (g, g'), 126.3 (h, h´), 123.3 (i), 112.2 (Cp), 31.6 (c), 31.1 (d, e) ppm; **HR-MS** (EI, $C_{31}H_{30}{}^{90}Zr$): *m/z* calcd. 492.13891, found 492.13982 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 492 (8) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^{+\cdot}$.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11h[13]



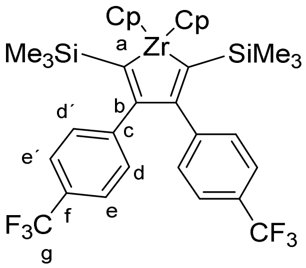
A solution of zirconocene **9** (176 mg, 373 µmol) and diyne **11h** (150 mg, 373 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11h** was observed after 10 min of reaction. Over this time, the mixture turned to orange-red. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a reddish-orange solid was obtained for further analysis (223 mg, 96%). Crystals could be obtained from a saturated toluene solution. **^1H NMR** (600 MHz, C_6D_6): δ 7.49-7.44 (m, 4H, g, g´), 6.80-6.74 (m, 4H, f, f´), 5.70 (s, 10H, Cp), 2.33 (t, ^3J = 7.1 Hz, 4H, c), 1.26 (p, ^3J = 7.1 Hz, 2H, d) ppm; **$^{13}C\{^1H\}$ NMR** (151 MHz, C_6D_6): δ 182.2 (a), 149.0 (b), 131.7 (g, g'), 128.0 (f, f'), 126.2 (e), 117.8 (h), 110.4 (Cp), 35.6 (c), 22.5 (d) ppm; **HR-MS** (EI, $C_{29}H_{24}{}^{79/81}Br_2{}^{90}Zr$): *m/z* calcd. 621.92728, found 621.92652 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 620 (69) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^{+\cdot}$.

Reaction Monitoring of the Formation of Zirconacyclopentadiene 11h in THF[13]



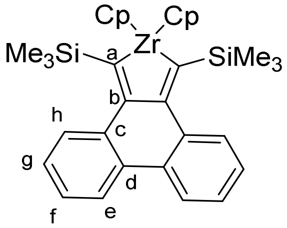
A solution of zirconocene **9** (117 mg, 249 µmol) and diyne **11h** (100 mg, 249 µmol) in THF (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11h** was observed after 10 min of reaction. Over this time, the mixture turned to orange-red. After 22 h, the zirconacyclopentadiene partly decomposed.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11i



A solution of zirconocene **9** (146 mg, 310 µmol) and acetylene **10i** (150 mg, 619 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11i** was observed after 10 min of reaction. Over this time, the mixture turned to orange-yellow. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and a bright yellow solid was obtained for further analysis (206 mg, 94%). Crystals could be obtained from a saturated toluene solution. **^{1}H NMR** (600 MHz, C_6D_6): δ 7.11 (d, ^3J = 7.8 Hz, 4H, e, e´), 6.49 (d, ^3J = 7.8 Hz, 4H, d, d´), 6.09 (s, 10H, Cp), -0.28 (s, 18H, $SiMe_3$) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 206.3 (a), 149.4 (c) 148.2 (b), 130.2 (d, d´), 127.5 (q, ^2J = 32.2 Hz, f)[‡], 125.0 (q, $^1J_{C\text{-}F}$ = 271.7 Hz, g), 124.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, e, e´), 111.7 (Cp), 2.70 ($SiMe_3$) ppm; **^{19}F NMR** (471 MHz, C_6D_6): δ -62.1 ppm; **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_6): δ -15.4 ppm; **MS** (EI, 70 eV, direct inlet, 200 °C): compound shows no molecule ion.

Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11j[9]

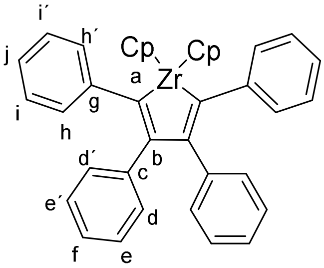


A solution of zirconocene **9** (166 mg, 352 µmol) and diyne **10j** (122 mg, 352 µmol) in toluene (3 mL) was stirred at 25 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11j** was observed after 10 min of reaction. Over this time, the mixture turned to red. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and an orange-red solid was obtained for further analysis (192 mg, 96%). Crystals could be obtained from a saturated toluene solution. **^{1}H NMR** (600 MHz, C_6D_6): δ 7.60 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, e), 7.51 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, h), 7.14 (td, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, f), 7.07 (td, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 2H, g), 5.94 (s, 10H, Cp), 0.21 (s, 18H, $SiMe_3$) ppm;

[‡] This signal is overlapping with the solvent signal.

$^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ 208.9 (a), 137.5 (b), 136.2 (c or d), 133.7 (d or c), 129.7 (h), 128.8 (f), 126.9 (g), 123.7 (e), 110.2 (Cp), 3.8 ($SiMe_3$) ppm; **$^{29}Si\{^1H\}$ NMR** (99 MHz, C_6D_6): δ -12.0 ppm; **HR-MS** (EI, $C_{32}H_{36}{}^{28}Si_2{}^{90}Zr$): *m/z* calcd. 566.13971, found 566.13966 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 566 (5) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^+$.

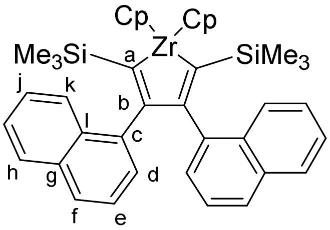
Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11k[13]



A solution of zirconocene **9** (198 mg, 421 µmol) and diphenylacetylene (**10k**) (150 mg, 842 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11k** was observed after 10 min of reaction. Over this time, the mixture turned to orange-pink. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and an orange-pink solid was obtained for further analysis (231 mg, 95%). Single crystals could be obtained from a saturated toluene solution. **^1H NMR** (500 MHz, C_6D_6): δ 7.06-7.01 (m, 4H, i, i´), 7.00-6.93 (m, 4H, d, d´), 6.86-6.82 (m, 4H, e, e´), 6.82-6.79 (m, 2H, j), 6.76-6.71 (m, 2H, f), 6.71-6.66 (m, 4H, h, h´), 6.00 (s, 10H, Cp) ppm;

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): δ 194.8 (a), 148.6 (b), 142.8 (g), 141.7 (c), 131.3 (d, d´), 128.3 (i, i´), 127.2 (h, h´), 127.1 (e, e´), 125.1 (f), 123.4 (j), 112.3 (Cp) ppm; **HR-MS** (EI, $C_{38}H_{30}{}^{90}Zr$): *m/z* calcd. 576.13891, found 576.13987 (R = 10000); **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 576 (18) $[M]^{+\cdot}$, 220 (100) $[Cp_2Zr]^{+\cdot}$.

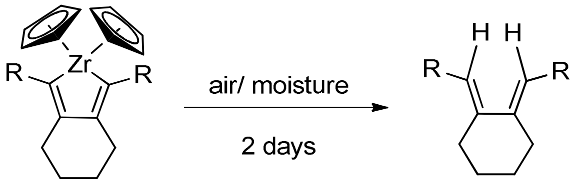
Reaction Monitoring and Synthesis of Zirconacyclopentadiene 11l



A solution of zirconocene **9** (158 mg, 335 µmol) and 1-(1-naphthyl)-2-(trimethylsilyl)acetylene (**10l**) (150 mg, 669 µmol) in toluene (6 mL) was stirred at 22 °C. Samples (0.3 mL) were taken for the reaction monitoring after the defined times. The formation of the zirconacyclopentadiene **11l** was observed after 10 min of reaction. Over this time, the mixture turned to yellow-orange. The second reaction mixture was filtered over celite, the solvent was removed *in vacuo* and an orange-yellow solid was obtained for further analysis (202 mg, 90%). Crystals could be obtained from a saturated toluene solution. **^{1}H NMR** (600 MHz, C_6D_6): δ 8.32 (dq, ^3J = 8.4 Hz, ^4J = 0.9 Hz, 2H, k), 7.46 (ddd, ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 2H, j), 7.38 (ddt, ^3J = 8.1 Hz, ^4J = 1.2 Hz, 0.6 Hz, 2H, h), 7.21 (ddd, ^3J = 8.1 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz, 2H, i), 7.02 (d, ^3J = 8.1 Hz, 2H, f), 6.84 (dd, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 2H, d), 6.59 (dd, ^3J = 8.2 Hz, ^3J = 7.0 Hz, 2H, e), 6.34 (s, 10H, Cp), -0.39 (m, 18H, $SiMe_3$) ppm; **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 207.7 (a), 150.0 (b), 142.6 (c), 133.4 (l), 132.8 (g), 128.0 (h), 126.8 (k), 126.0 (d), 125.8 (f), 124.8 (j), 124.6 (i), 124.0 (e), 111.1 (Cp), 2.1 ppm; **^{29}Si{^{1}H} NMR** (99 MHz, C_6D_6): δ -14.9 ppm; **MS** (EI, 70 eV, direct inlet, 200 °C): compound shows no molecular ion.

4 Air Stability Tests

The zirconacyclopentadienes **11a-f** were exposed to compressed air and normal atmospheric conditions in order to study their stability under such conditions. The samples were then analyzed by ^{1}H NMR spectroscopy. After flushing the zirconacyclopentadienes with compressed air for 10 min and 30 min no change was observed in the spectra. This procedure was repeated with the same sample the next day obtaining the same result. A significant change was observed only when the samples were exposed to normal atmospheric conditions for one further day. Under such conditions new signals were observed presumably arising from the ring-opening of the zirconacyclopentadienes **11a-f**. After 2 days the zirconacyclopentadienes were completely decomposed. Because the main difference between compressed air and atmospheric air is the higher moisture content in the latter, we assume that the decomposition is a protonolysis that forms the dienes **16a-f** (Scheme S4). Those types of decomposition products are already known from the literature, when the zirconacyclopentadienes were exposed to acidic conditions, for example in the formation of **3** (Scheme 1, main manuscript).[9, 15] The structure of the compounds **16a-f** was confirmed by two-dimensional NMR and mass spectrometry.



11a-f **16a-f**

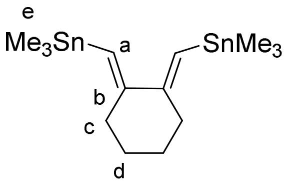
Scheme S4. Decomposition path of the zirconacyclopentadienes **11a-f** to the dienes **16a-f.**

4.1 General procedure for the air stability test

Zirconacyclopentadienes **11a-f** were stirred in toluene under normal atmospheric conditions for 24 h. After normal work up with water and dichloromethane and drying of the organic layer over magnesium sulfate, the solvents were removed *in vacuo*. The main product of decomposition was analyzed by NMR spectroscopy and MS spectrometry.

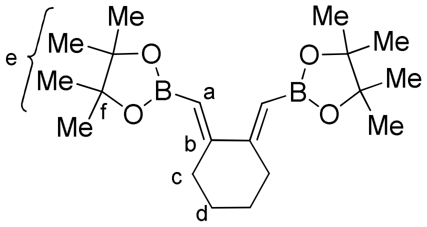
A second by-product was observed in all of the decomposition tests by NMR spectroscopic analysis; however it was not possible to isolate this compound. The chemical shifts were (^{1}H δ (C_6D_6): 6.30 (ddd, 2H), 6.50 (ddd, 2H), 2.68 (m, 2H) ppm. ^{13}C δ (C_6D_6): 132, 133, 41 ppm.

Decomposition of Zirconacyclopentadiene 11a



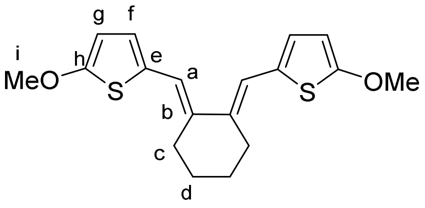
A sample of zirconacyclopentadiene **11**a (50.0 mg, 116 µmol) was exposed to the air under normal atmospheric conditions during 24 h to yield a white-yellowish solid (32 mg, 73 µmol, 63%). **^{1}H NMR** (600 MHz, C_6D_6): δ 6.03 (s, 2H, a), 2.13 (m, 4H, c), 1.57 (m, 4H, d), 0.18 (m, 18H, e) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 111.1 (a), 82.5 (b), 28.5 (c), 20.1(d), -8.04(e) ppm; MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 419 (40) $[M\text{-}CH_3]^+$, 241 (100) $[M\text{-}C_5H_{13}Sn]^+$.

Decomposition of Zirconacyclopentadiene 11b



A sample of zirconacyclopentadiene **11b** (50.0 mg, 140 µmol) was exposed to the air under normal atmospheric conditions during 24 h to yield a pink-yellowish solid (20 mg, 56 µmol, 40%). **^{1}H NMR** (600 MHz, C_6D_6): δ 5.95 (s, 2H, a), 2.99 (m, 4H, c), 1.62 (dt, ^3J = 6.4, 3.0 Hz, 4H, d), 1.05 (s, 24H, e) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 167.5 (b), 82.7 (f), 34.0 (c), 27.4 (d), 25.0 (e) ppm; [§]MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 360(12) $[M]^{+\cdot}$,44 (100) $[M\text{-}C_{20}H_{34}BO]^{+\cdot}$.

Decomposition of Zirconacyclopentadiene 11c

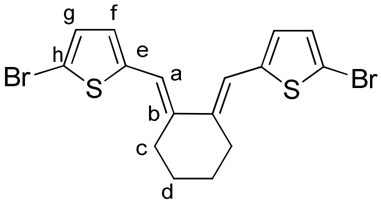


A sample of zirconacyclopentadiene **11c** (50.0 mg, 150 µmol) was exposed to the air under normal atmospheric conditions during 24 h to yield a yellowish solid (41 mg, 123 µmol, 82%).

[§] Carbon *b* was not possible to identify carbon d because the quadrupole moment from the adjacent boron atom.

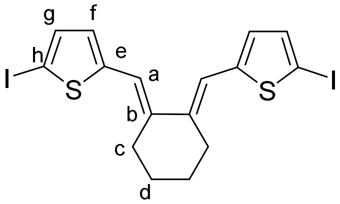
^{1}H NMR (600 MHz, C_6D_6): δ 6.7(s, 2H, a), 6.58 (d, ^{3}J = 3.9 Hz, 4H, g), 5.96 (d,^{3}J = 3.9 Hz, 4H, f), 3.32 (s, 6H, i), 2.66 (d, ^{3}J = 1.7 Hz, 4H, c), 1.44 (m, 4H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 166.8 (h), 139.1 (b) 128.4 (e), 125.9 (g), 118.7(a), 104.0 (f), 59.6 (i), 30.3(c), 25.9 (d) ppm; **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 332 (100) $[M]^{+\cdot}$.

Decomposition of Zirconacyclopentadiene 11d



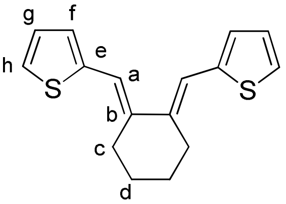
A sample of zirconacyclopentadiene **11d** (50.0 mg, 96.2 µmol) was exposed to air under normal atmospheric conditions during 24 h to yield an orange solid (36.0 mg, 83.7 µmol, 87%). ^{1}H NMR (600 MHz, C_6D_6): δ 6.58 (d, ^{3}J = 3.8 Hz, 2H, g), 6.27 (d, ^{3}J = 3.8 Hz, 2H, f), 6.04 (s, 2H, a), 2.46 (t, ^{3}J = 5.8 Hz, 2H, c), 1.40 (dt, ^{3}J = 10.1, 5.0 Hz, 2H, d) ppm; ^{13}C NMR (126 MHz, C_6D_6): δ 142.8 (e), 139.6 (b), 130.2 (f), 128.75 (g), 117.5 (a), 74.0 (h), 31.4 (c), 24.4 (d) ppm; MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 428 (24) $[M]^{+\cdot}$, 270 (100).

Decomposition of Zirconacyclopentadiene 11e



A sample of zirconacyclopentadiene **11e** (50 mg, 95.8 µmol) was exposed to air under normal atmospheric conditions during 24 h to yield a yellowish solid (49 mg, 93 µmol, 97%). **^{1}H NMR** (600 MHz, C_6D_6): δ 6.92 (d, ^{3}J =3.83 Hz, 2H, g), 6.57 (s, 2H, a), 6.33 (d, ^{3}J =3.83, 4H, f), 2.40 (d, 4H, c), 1.32 (m, 4H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 14.7 (e), 142.1 (b), 137.1 (f), 129.5 (g), 118.0 (a), 73.9 (h), 30.3 (c), 24.4 (d) ppm; **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 524 (30) $[M]^{+}$, 237 (100) $[M-C_6H_3IS]^{+}$.

Decomposition of Zirconacyclopentadiene 11f



A sample of zirconacyclopentadiene **11f** (50 mg, 138 µmol) was exposed to air under normal atmospheric conditions during 24 h to yield a yellowish solid (29.7 mg, 109 µmol, 79%). **^{1}H NMR** (600 MHz, C_6D_6): δ 6.90 (d, ^3J = 5.1 Hz, 2H, g), 6.87 (d, ^3J = 3.4 Hz, 2H, h), 6.84 (s, 2H, a), 6.80 (dd, ^3J = 5.1 Hz, ^4J = 3.6 Hz, 2H, f), 2.69-2.63 (m, 4H, c), 1.41 (m, 2H, d) ppm; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 141.82 (e), 141.79 (b), 128.35 (h), 127.20 (f), 125.27 (g), 118.36 (a), 30.39 (c), 24.78 (d) ppm; **MS** (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 272 (62) $[M]^{+\cdot}$, 111 (100).

5 Literature

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6 Spectra

6.1 Isolated Compounds

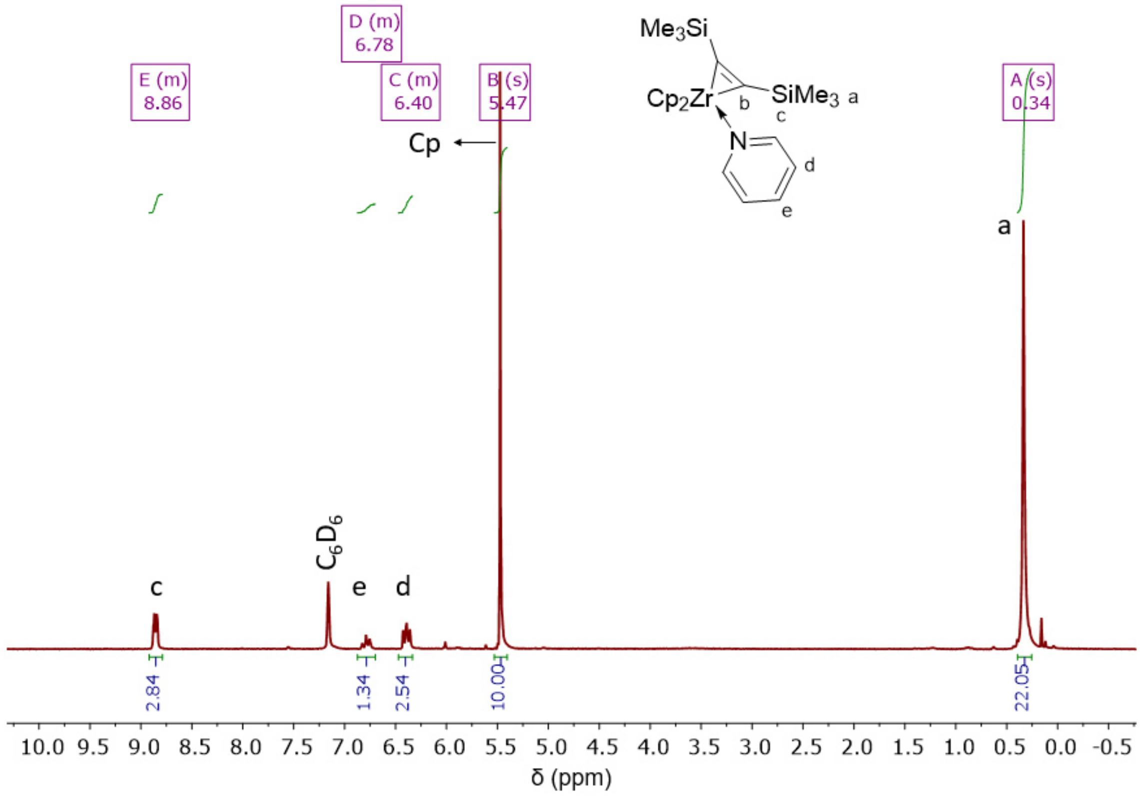

Figure S1. ^{1}H NMR (500 MHz) spectrum of Rosenthal´s zirconocene in C_6D_6.

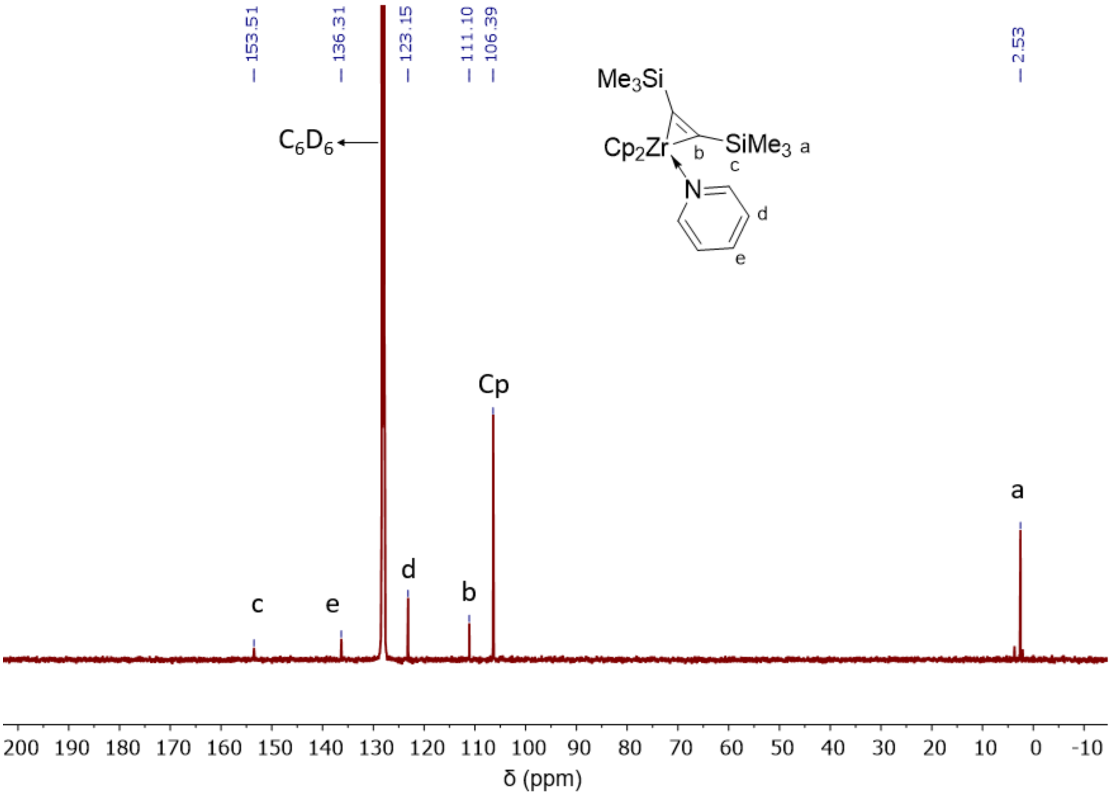

Figure S2. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of Rosenthal´s zirconocene in C_6D_6.

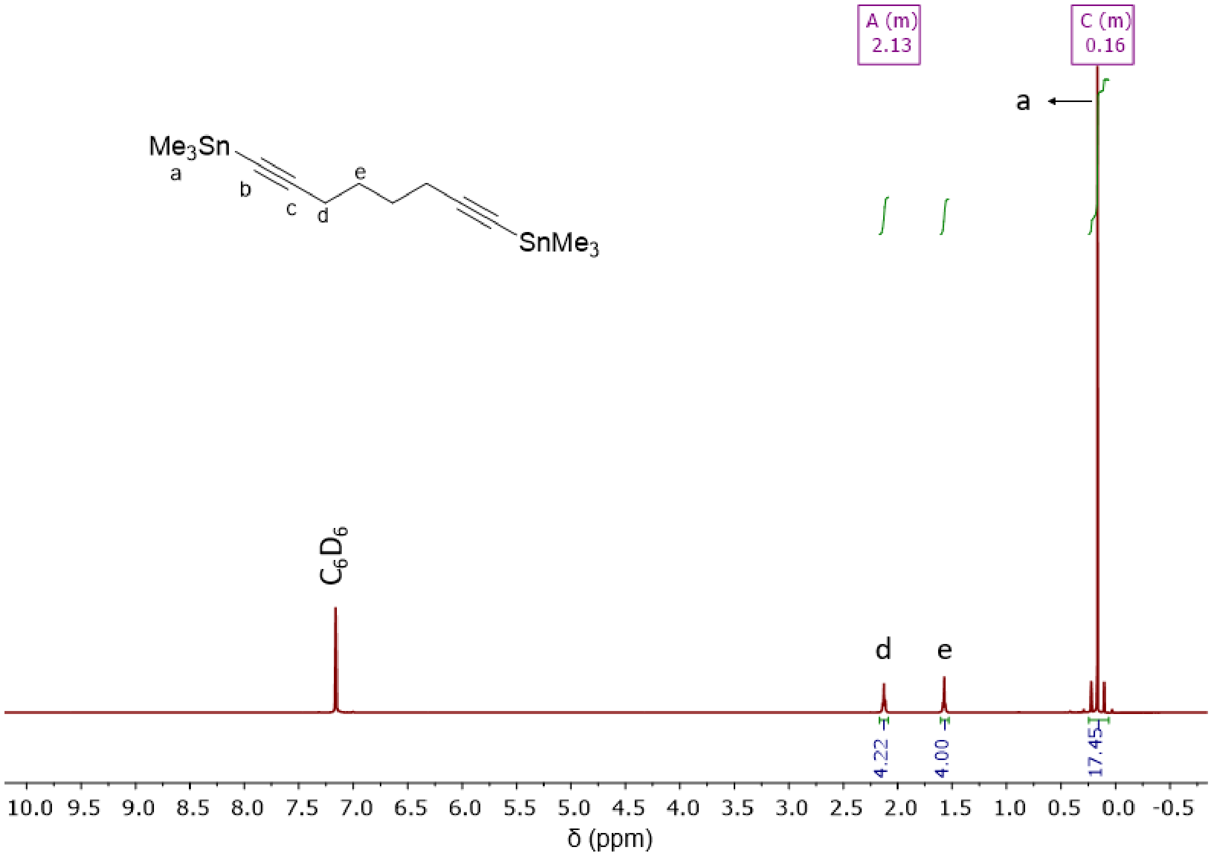

Figure S3. ^{1}H NMR (500 MHz) spectrum of 1,8-bis(trimethylstannyl)octa-1,7-diyne in $CDCl_3$.

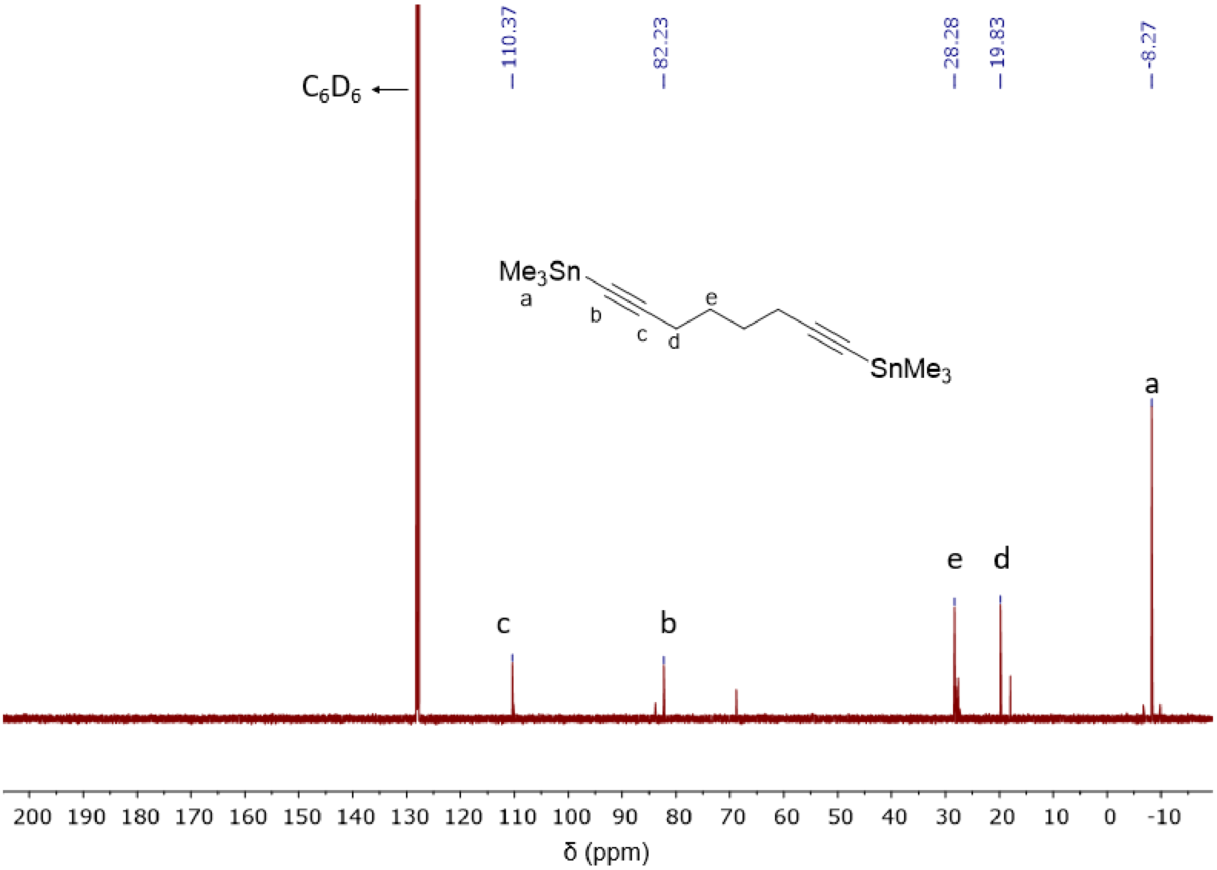

Figure S4. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of 1,8-bis(trimethylstannyl)octa-1,7-diyne in $CDCl_3$.

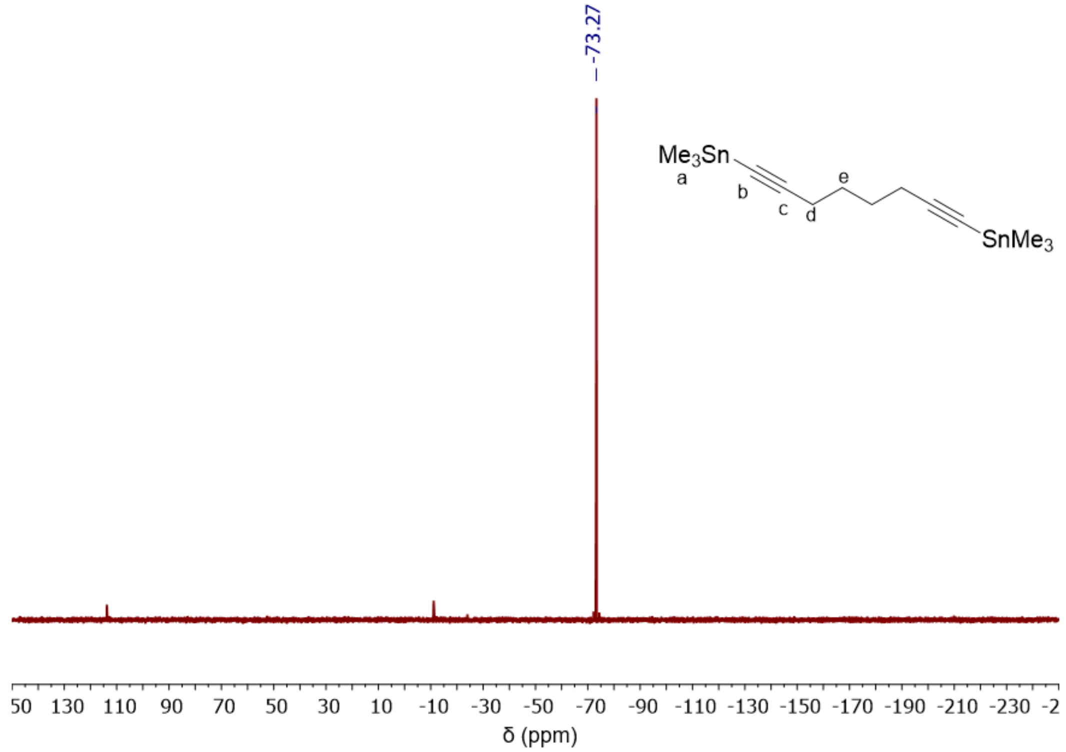

Figure S5. ^{119}Sn{^{1}H} NMR (187 MHz) spectrum of 1,8-bis(trimethylstannyl)octa-1,7-diyine in $CDCl_3$.

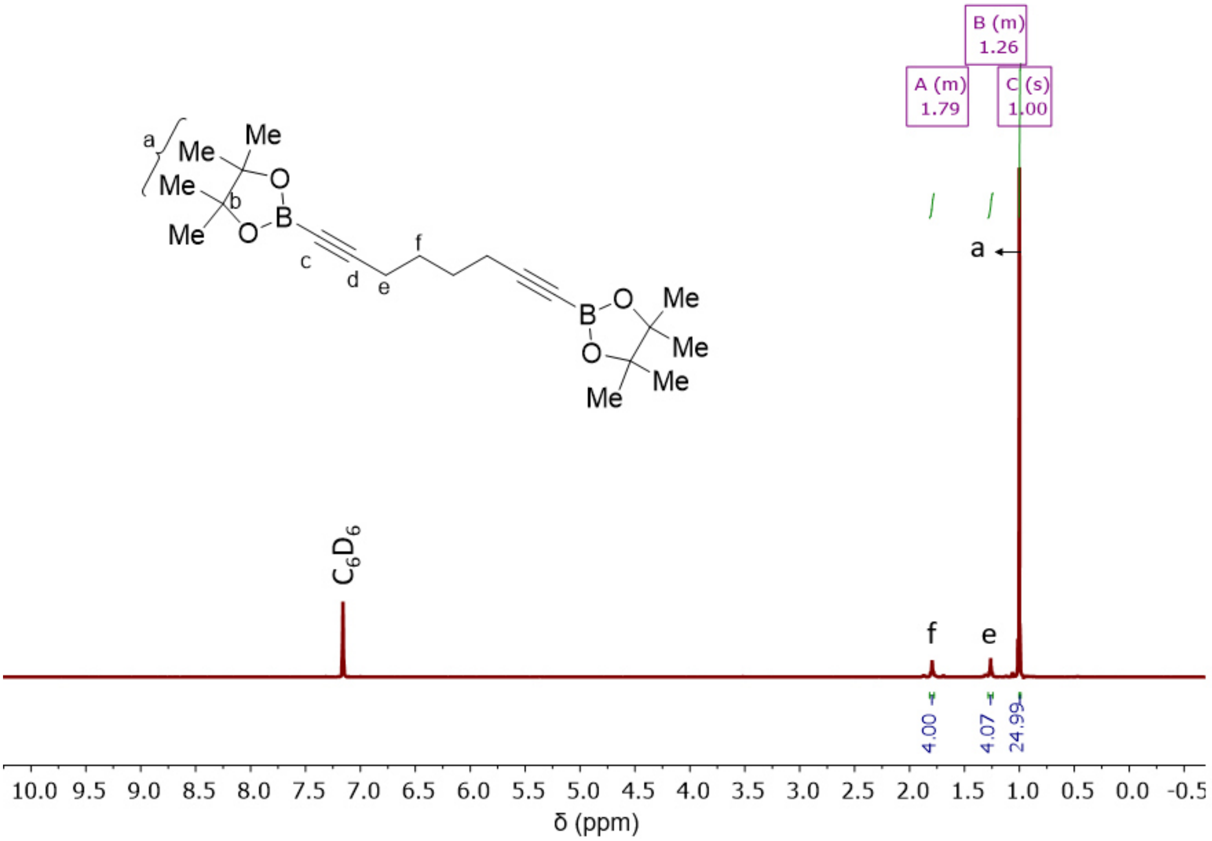

Figure S6. ^{1}H NMR (500 MHz) spectrum of 1,8-bis(4,4,5,5-tetrametyhl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

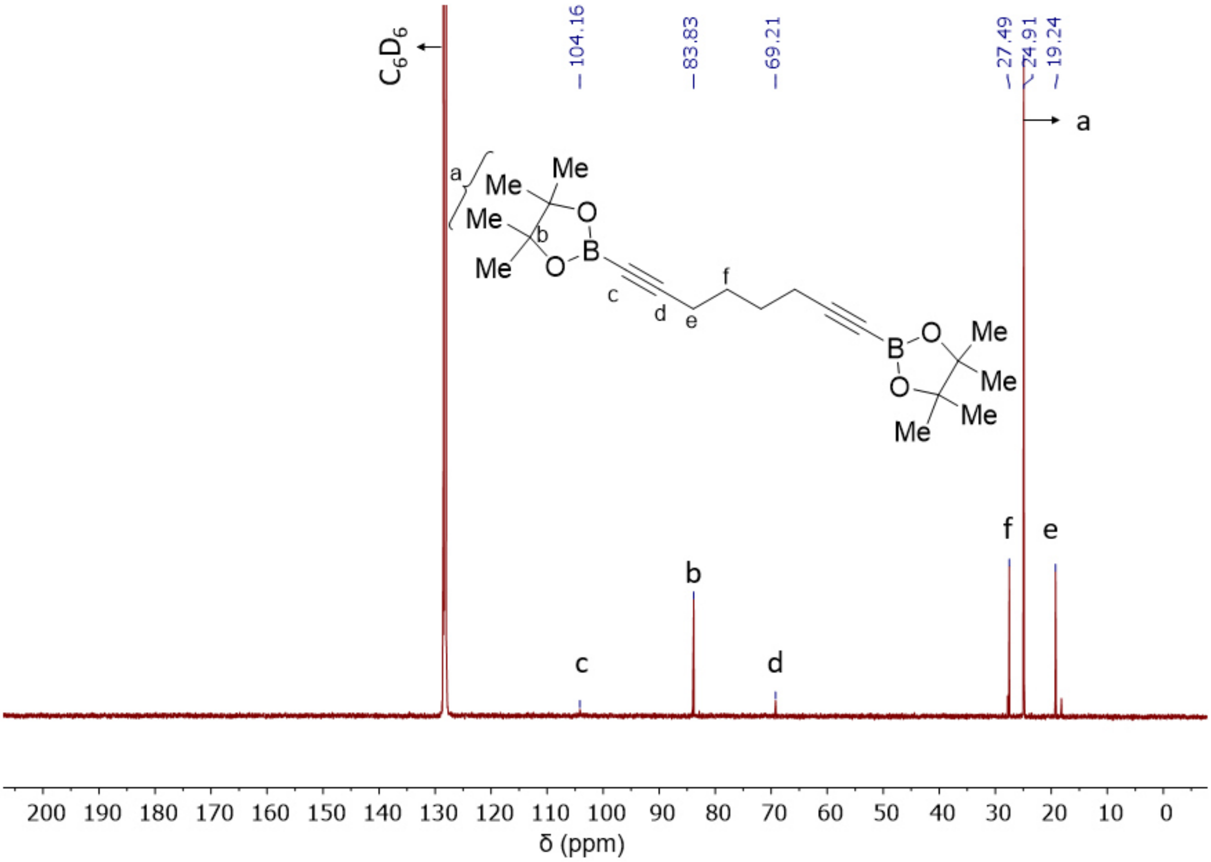

Figure S7. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of 1,8-bis(4,4,5,5-tetrametyhl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

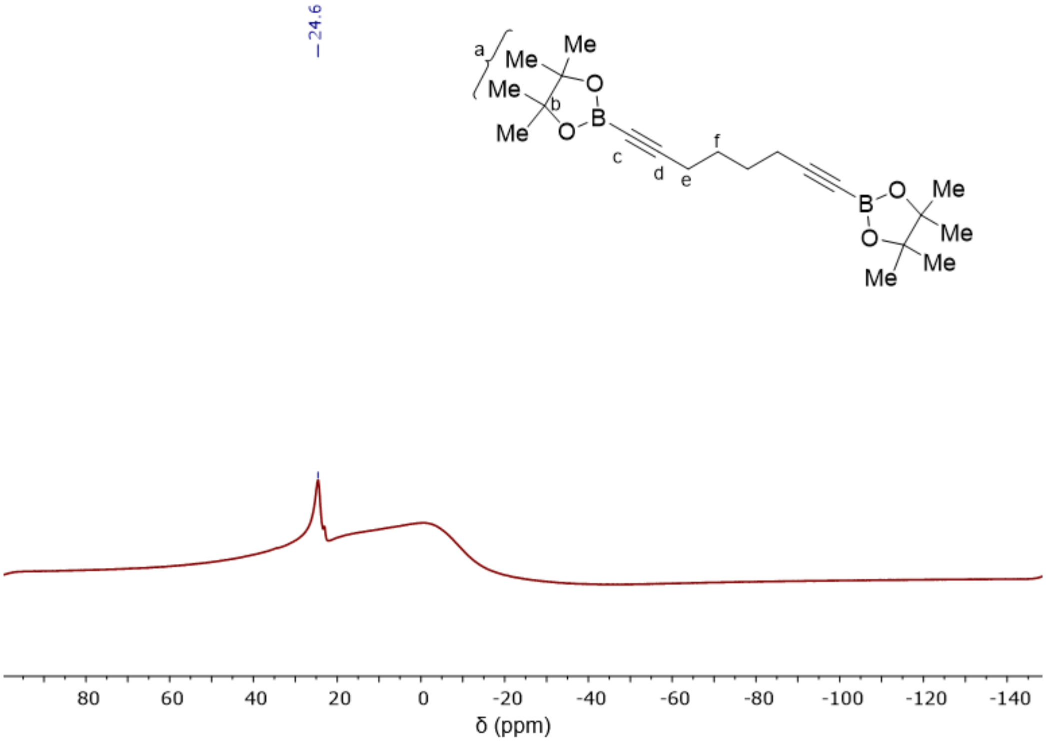

Figure S8. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6): spectrum of 1,8-bis(4,4,5,5-tetrametyhl-1,3,2-dioxaborolan-2-yl)octa-1,7-diyne in C_6D_6.

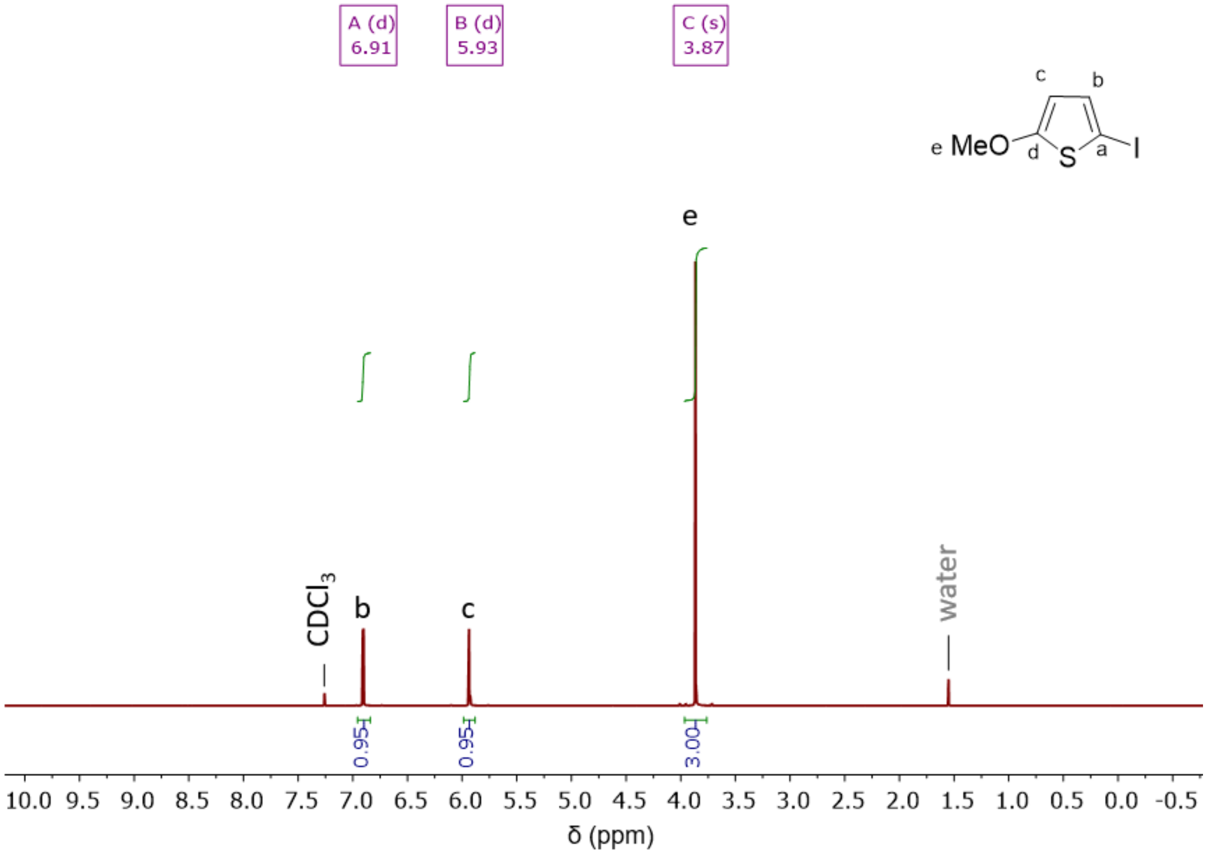

Figure S9. ^1H NMR (500 MHz) spectrum of 5-methoxy-2-iodothiophene in $CDCl_3$.

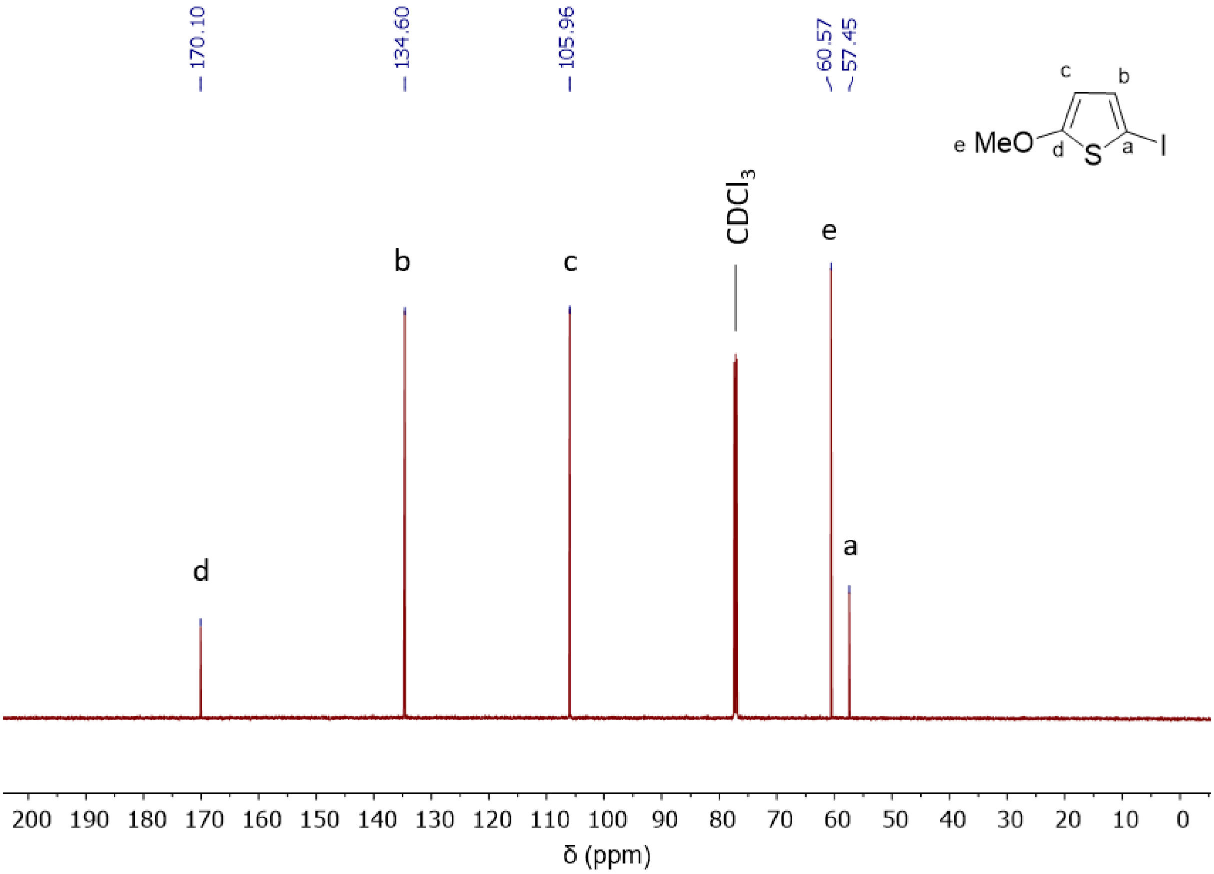

Figure S10. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of 5-methoxy-2-iodothiophene in $CDCl_3$.

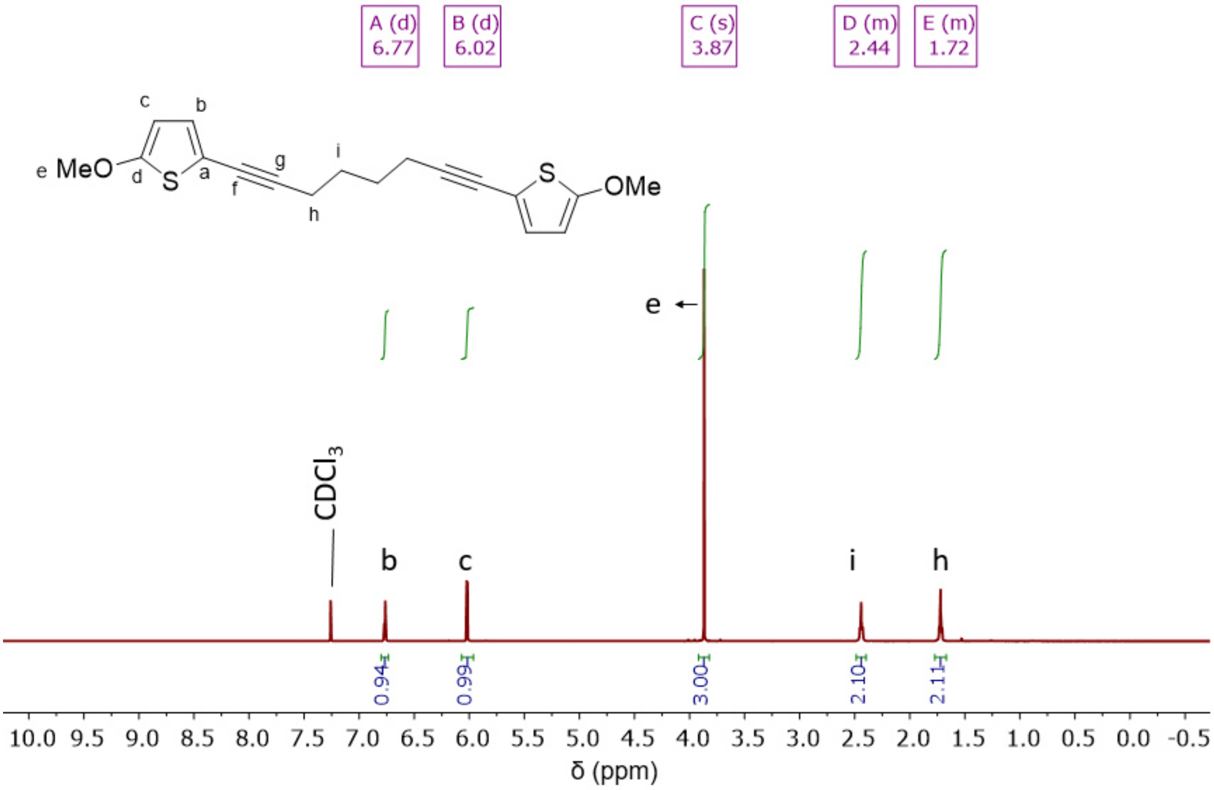

Figure S11. ^{1}H NMR (500 MHz) spectrum of 1,8-bis(5-methoxy-thiophen-2-yl)octa-1,7-diyne in $CDCl_3$.

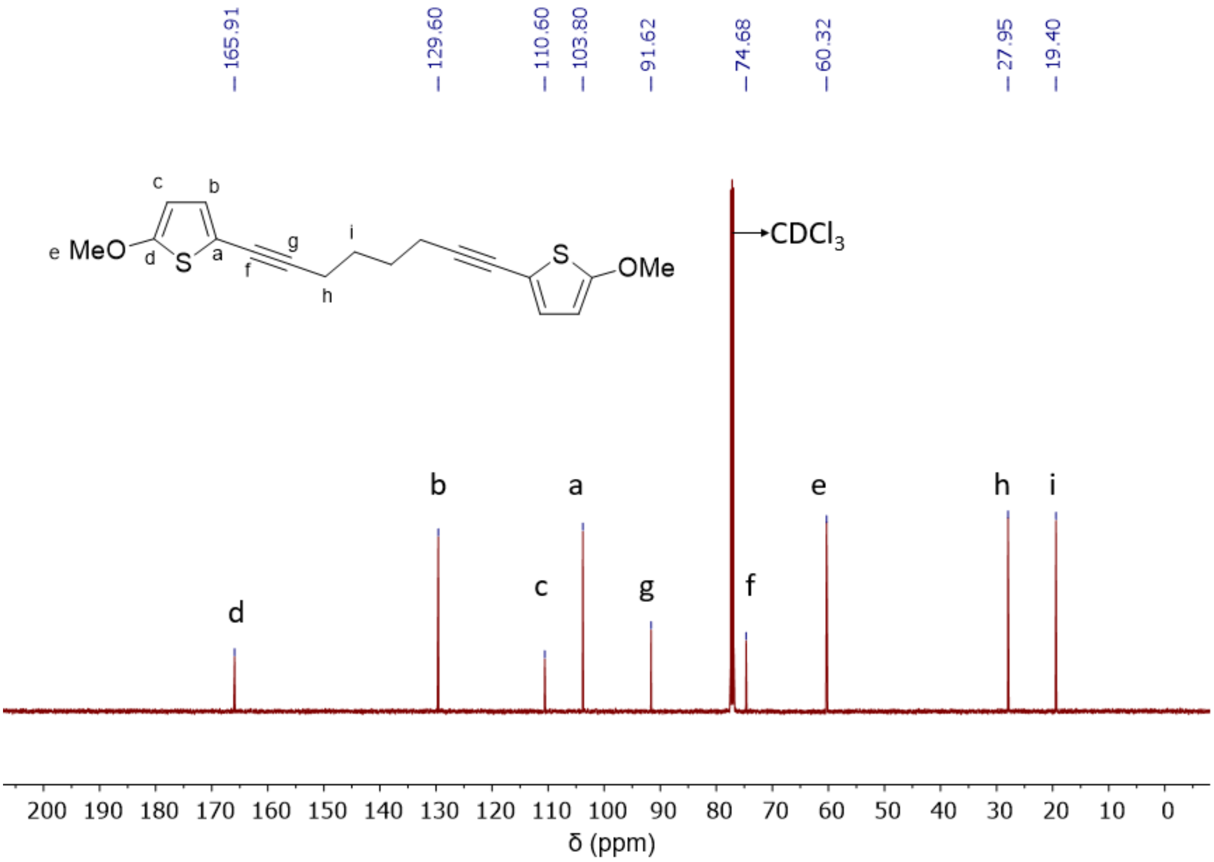

Figure S12. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of 1,8-bis(5-methoxy-thiophen-2-yl)octa-1,7-diyne in $CDCl_3$.

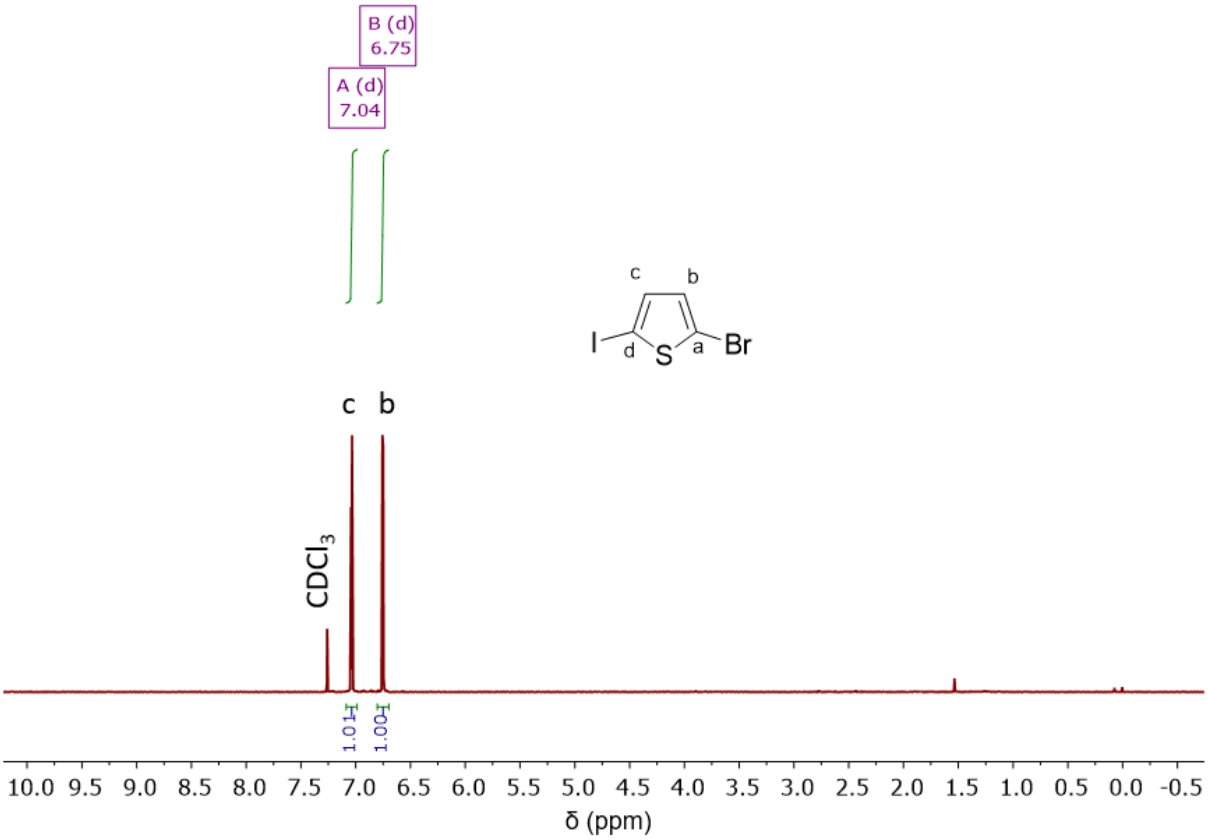

Figure S13. ^{1}H NMR (500 MHz) spectrum of 2-bromo-5-iodothiophene in CDCl$_3$.

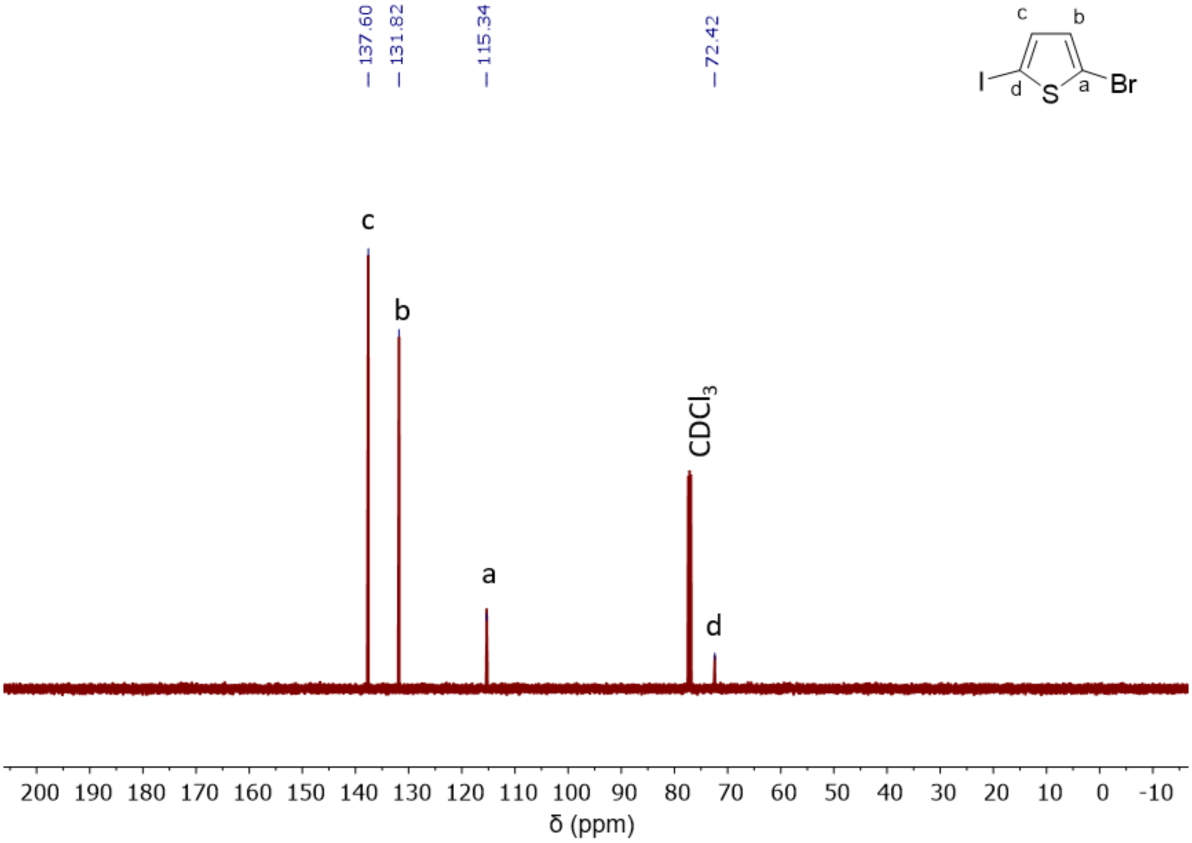

Figure S14. ^{13}C{^{1}H} NMR (126 MHz) spectrum of 2-bromo-5-iodothiophene in CDCl$_3$.

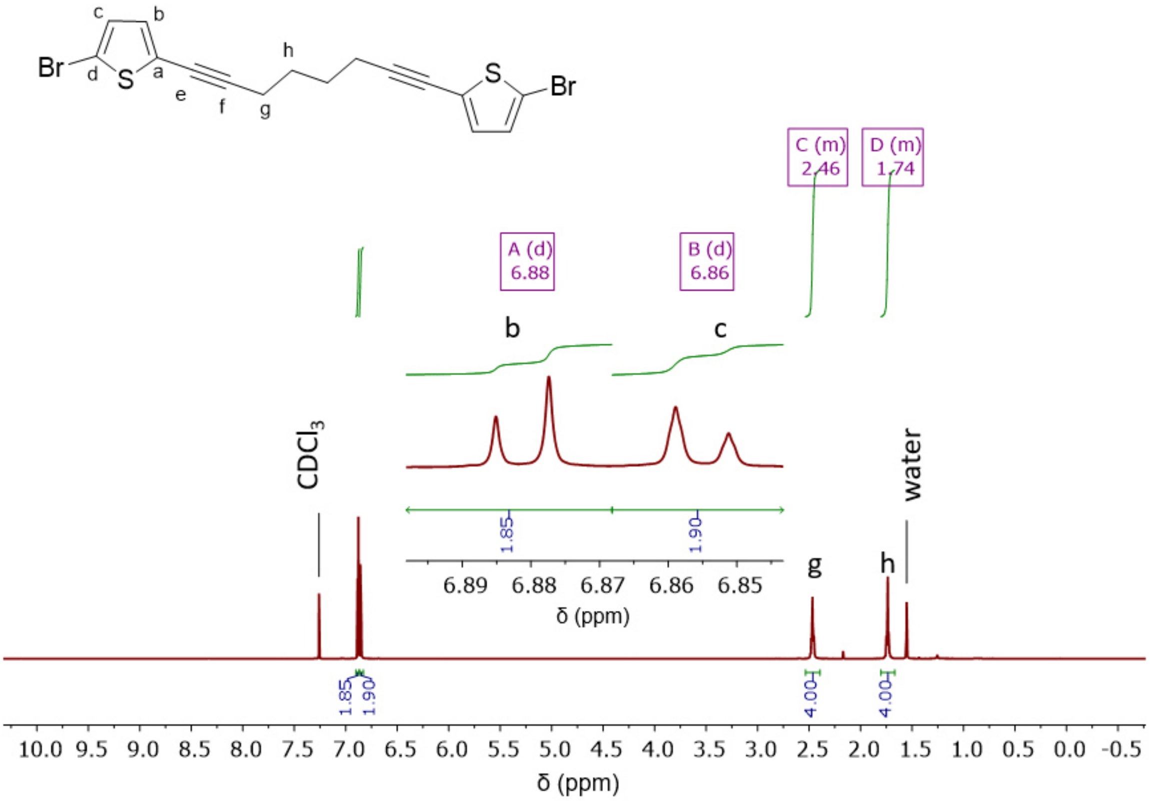

Figure S15.^{1}H NMR (500 MHz) spectrum of 1,8-bis(5-bromo-thiophen-2-yl)octa-1,7-diyne in $CDCl_3$.

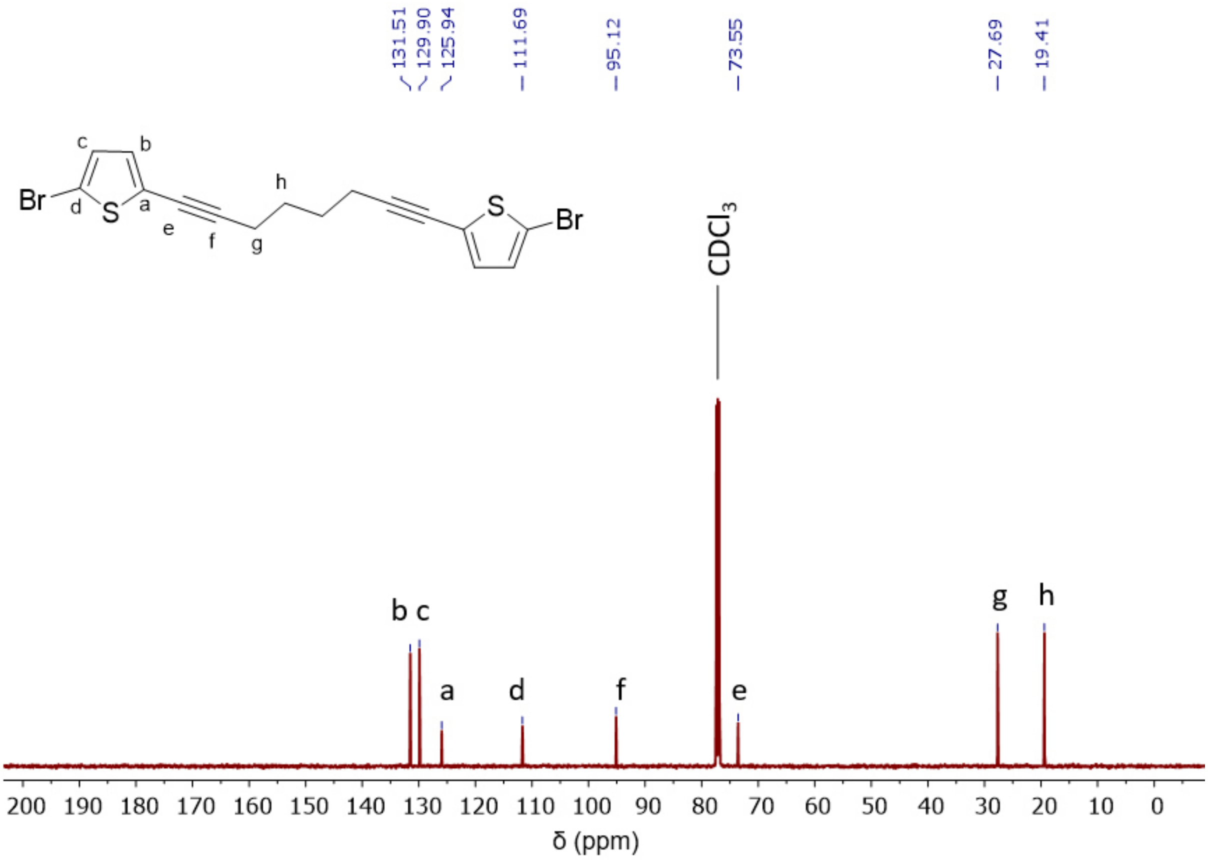

Figure S16.$^{13}C\{^1H\}$ NMR (126 MHz) spectrum of 1,8-bis(5-bromo-thiophen-2-yl)octa-1,7-diyne in $CDCl_3$.

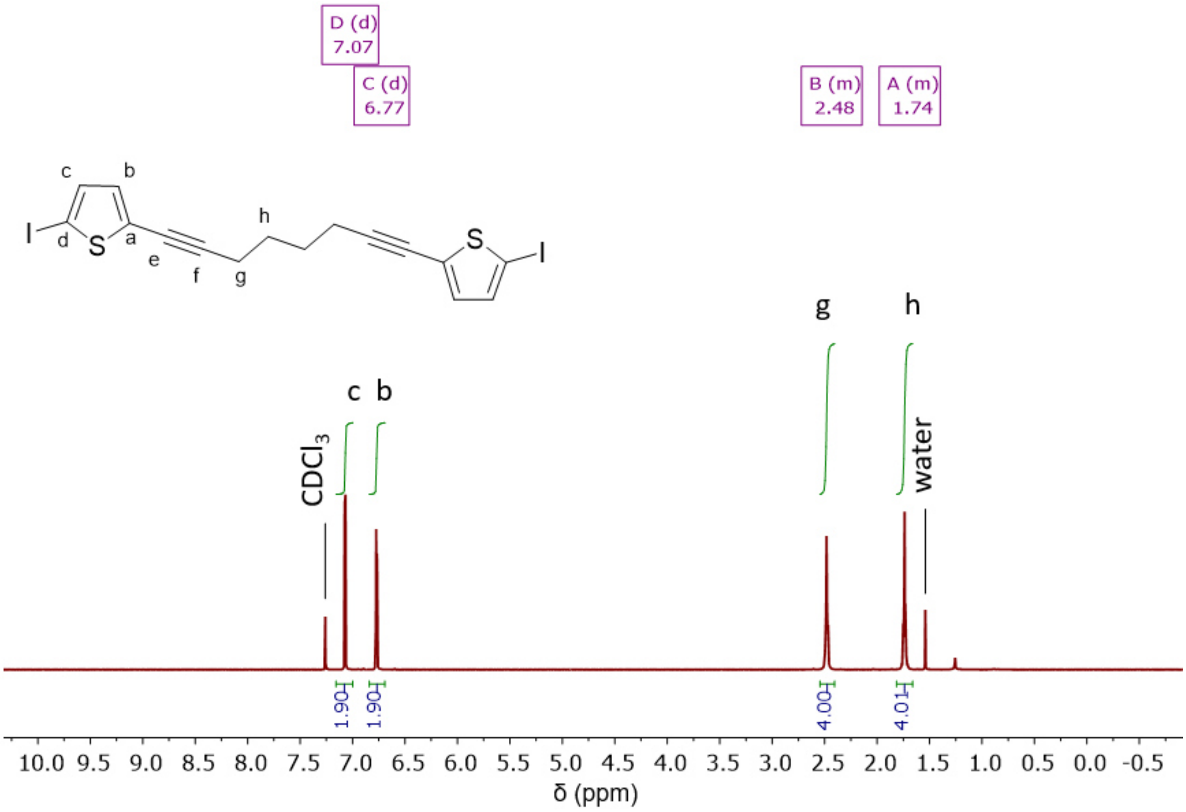

Figure S17. ^{1}H NMR (500 MHz) spectrum of 1,8-bis(5-iodo-thiophen-2-yl)octa-1,7-diyne in CDCl$_3$.

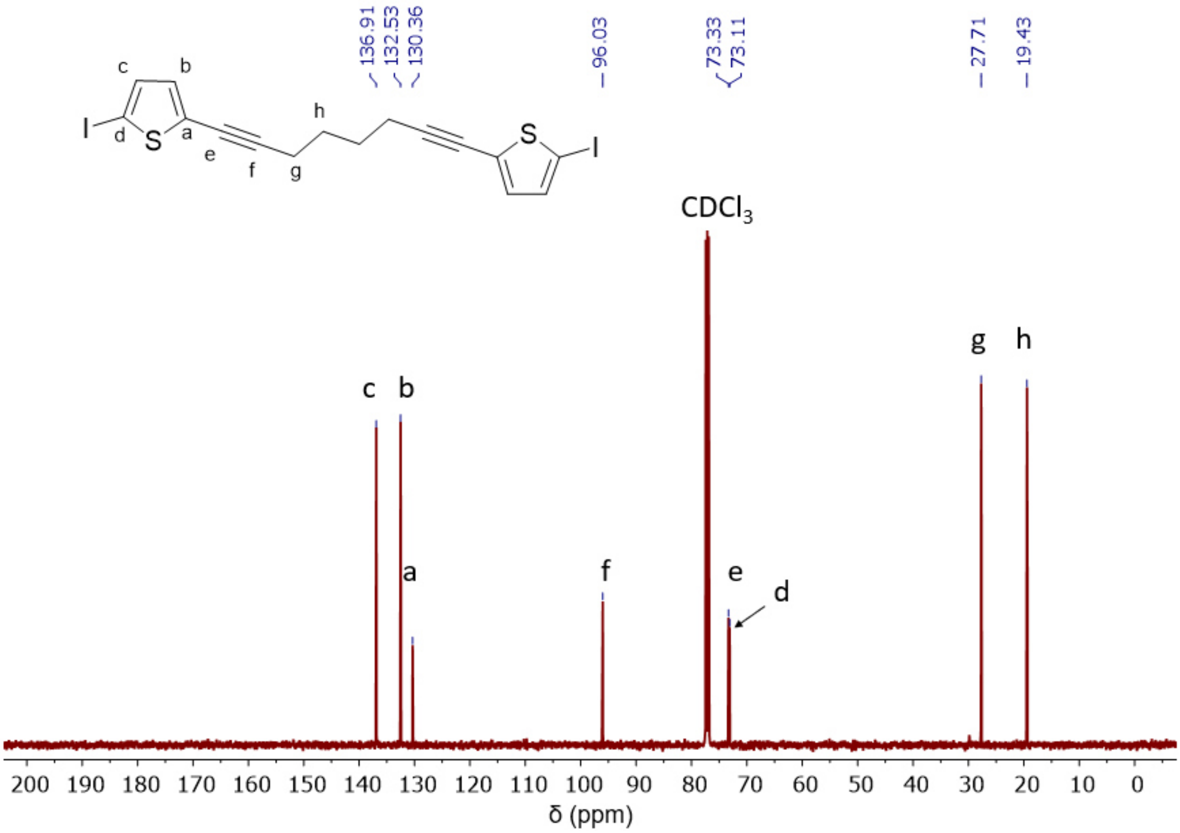

Figure S18. ^{13}C{^{1}H} NMR (126 MHz) spectrum of 1,8-bis(5-iodo-thiophen-2-yl)octa-1,7-diyne in CDCl$_3$.

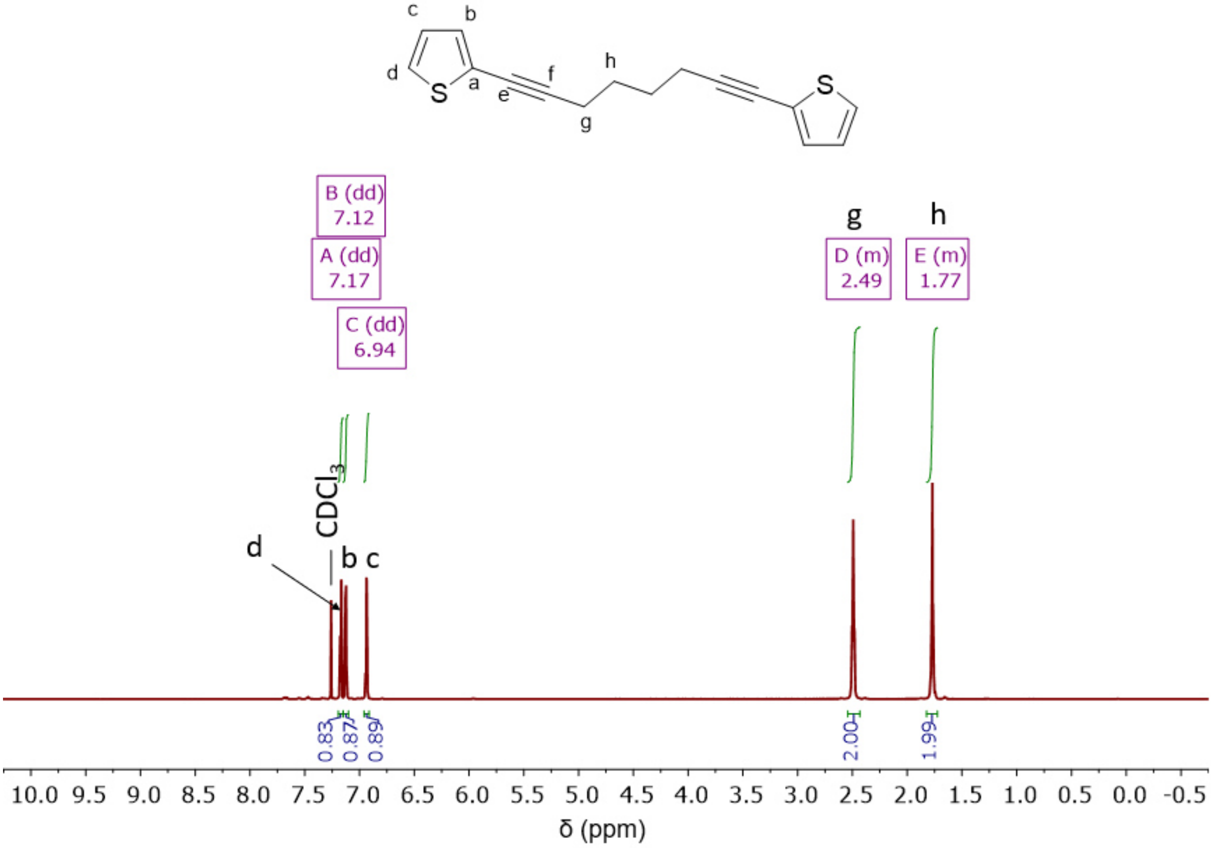

Figure S19. ^{1}H NMR (500 MHz) spectrum of 1,8-bis(thiophen-2-yl)octa-1,7-diyne in CDCl$_3$.

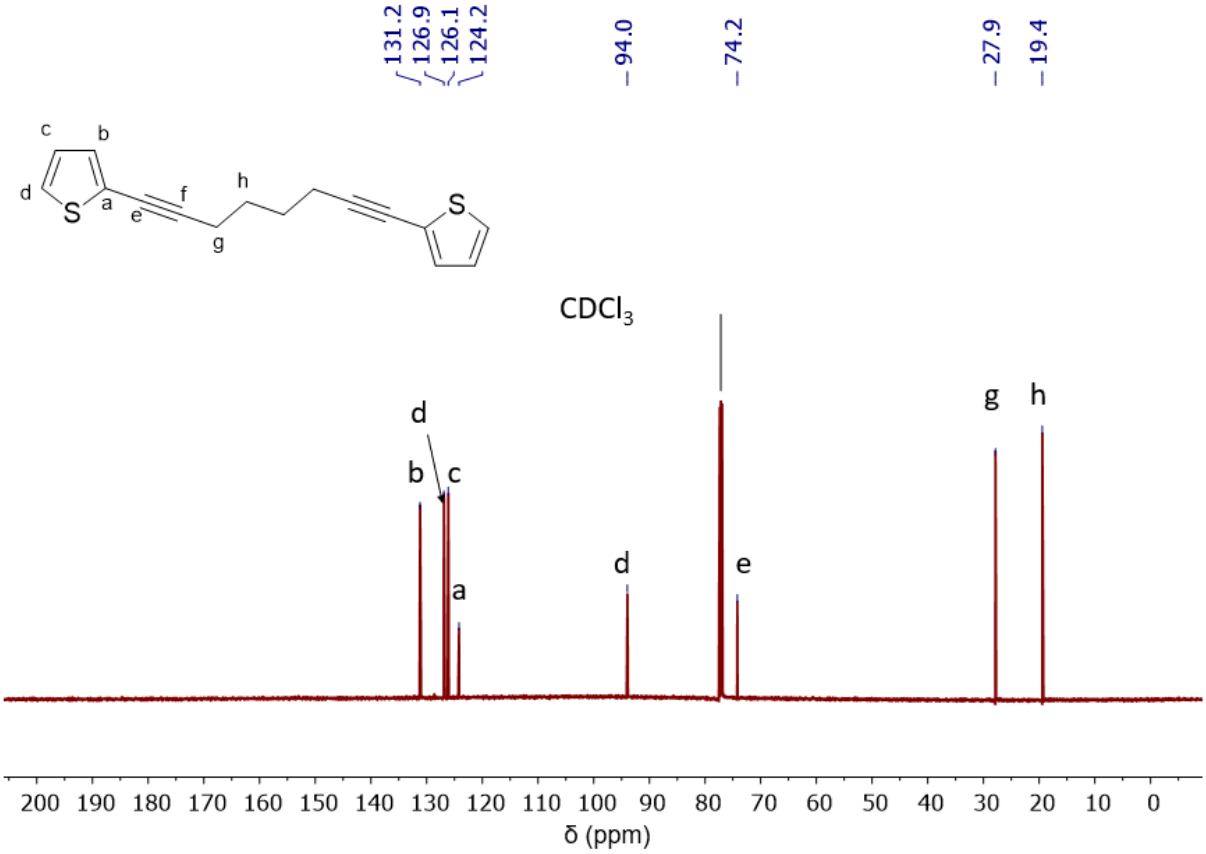

Figure S20. ^{13}C{^{1}H} NMR (126 MHz) spectrum of 1,8-bis(thiophen-2-yl)octa-1,7-diyne in CDCl$_3$.

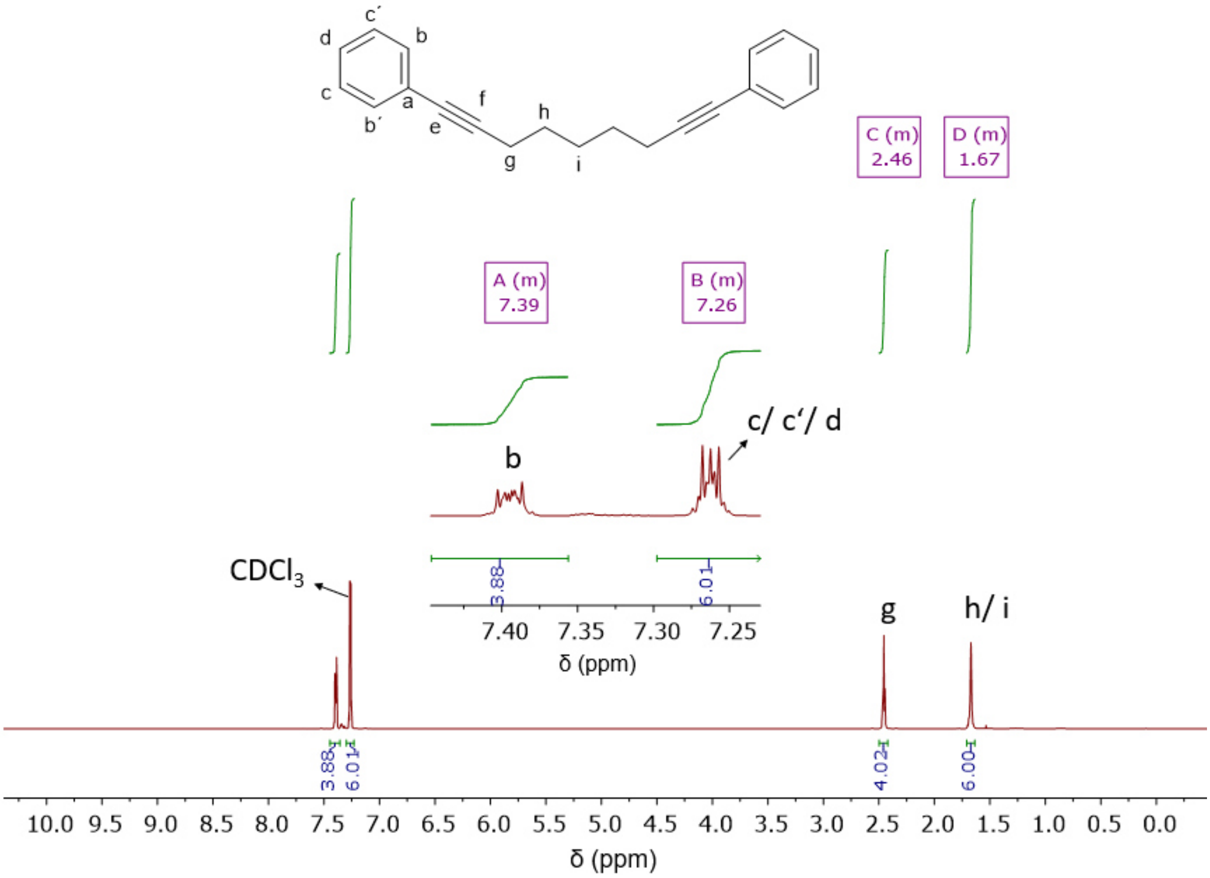

Figure S21. ^{1}H NMR (600 MHz) spectrum of 1,9-diphenylnona-1,8-diyne in $CDCl_3$.

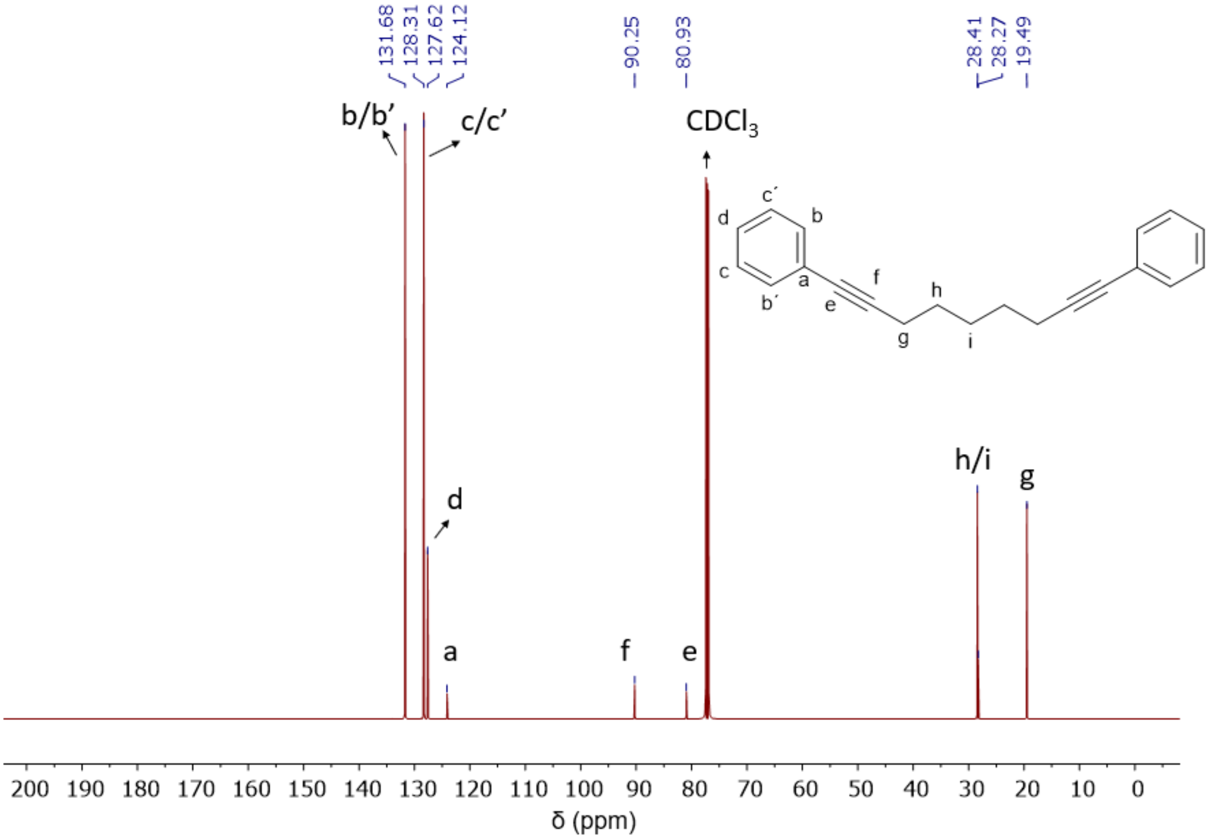

Figure S22. $^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of 1,9-diphenylnona-1,8-diyne in $CDCl_3$.

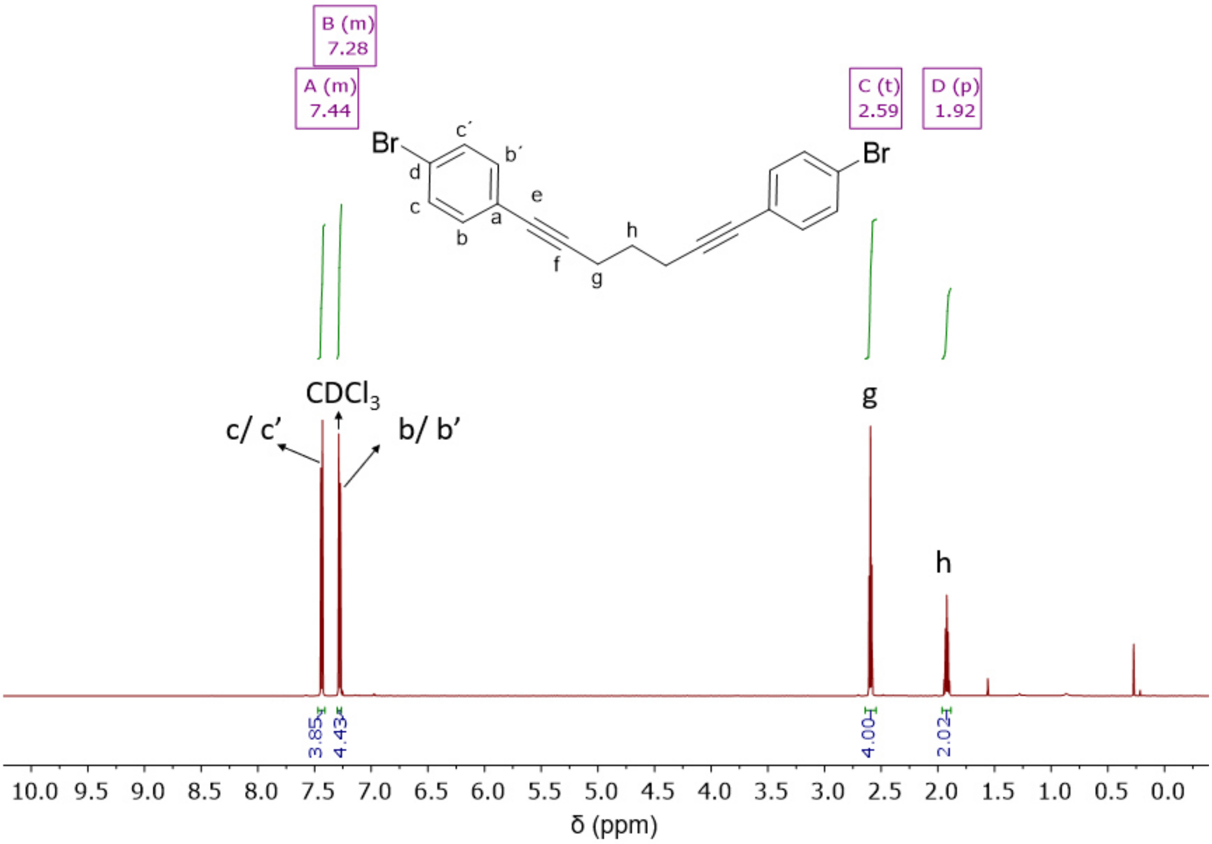

Figure S23.^{1}H NMR (600 MHz) spectrum of 1,7-bis(4-bromophenyl)hepta-1,6-diyne in $CDCl_3$.

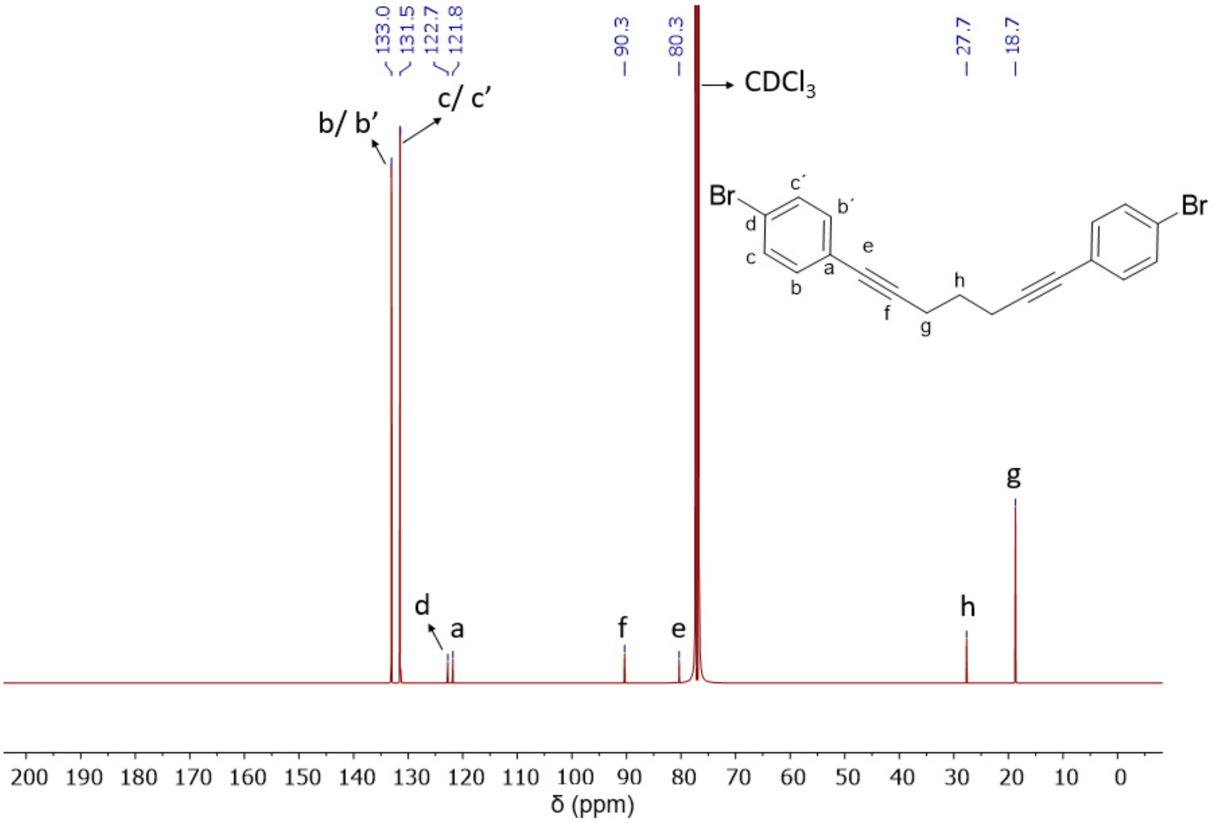

Figure S24.$^{13}C\{^1H\}$ NMR (151 MHz) spectrum of 1,7-bis(4-bromophenyl)hepta-1,6-diyne in $CDCl_3$.

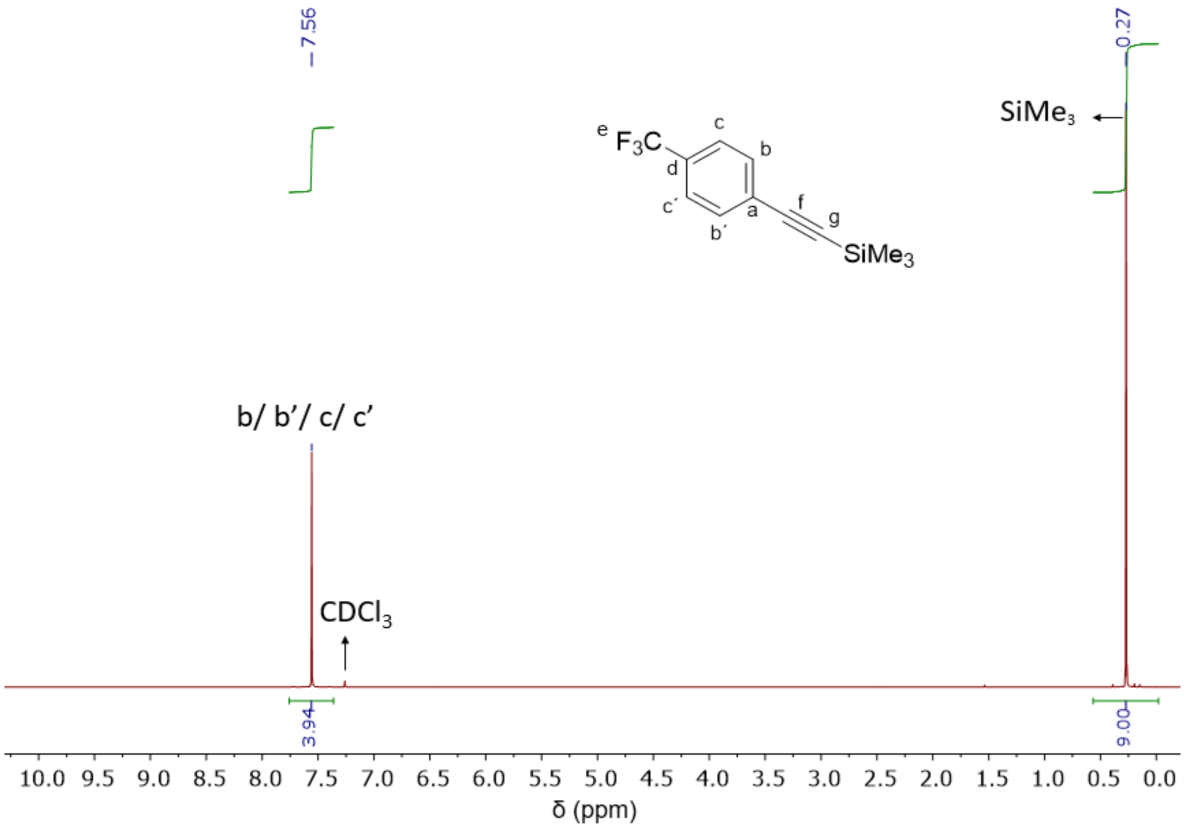

Figure S25.^{1}H NMR (500 MHz) spectrum of 4-trifluoromethyl-phenylethynyltrimethylsilane in CDCl$_3$.

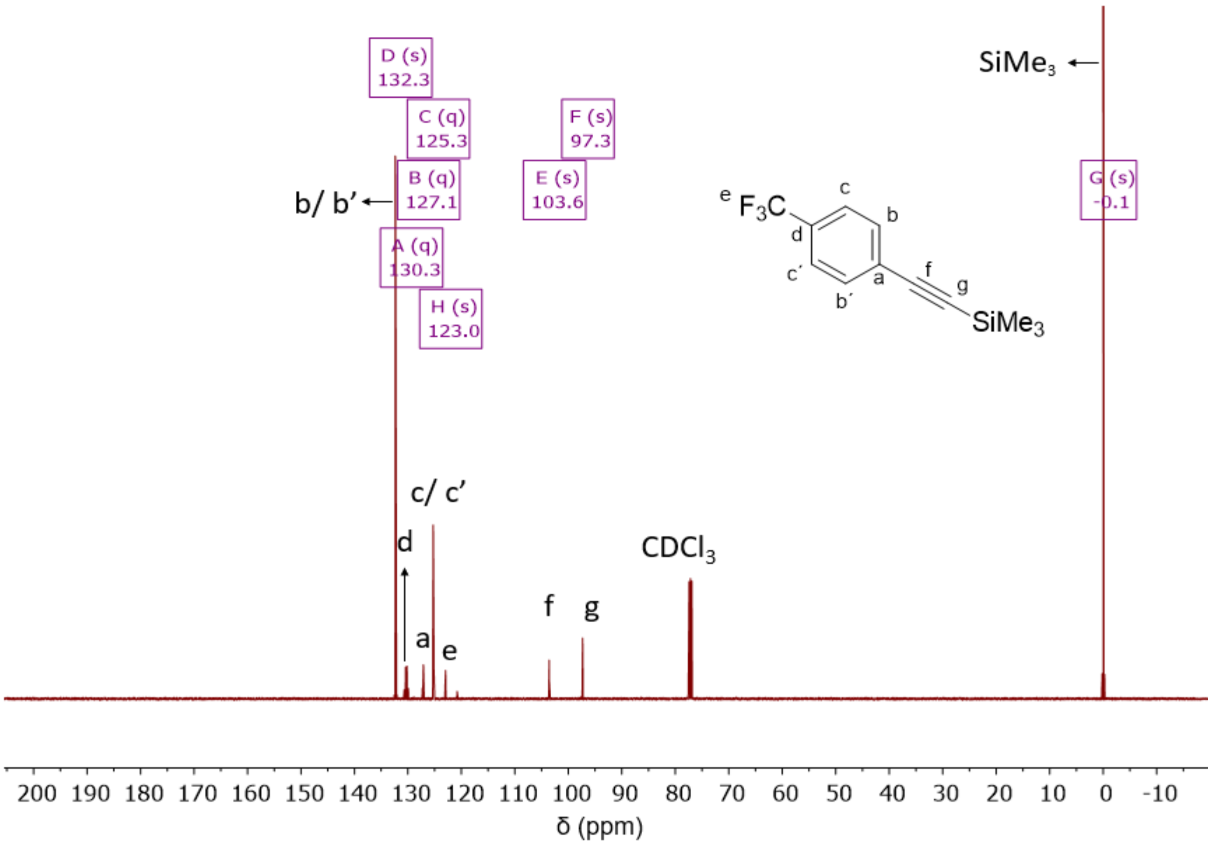

Figure S26.^{13}C{^{1}H} NMR (126 MHz) spectrum of 4-trifluoromethyl-phenylethynyltrimethylsilane in CDCl$_3$.

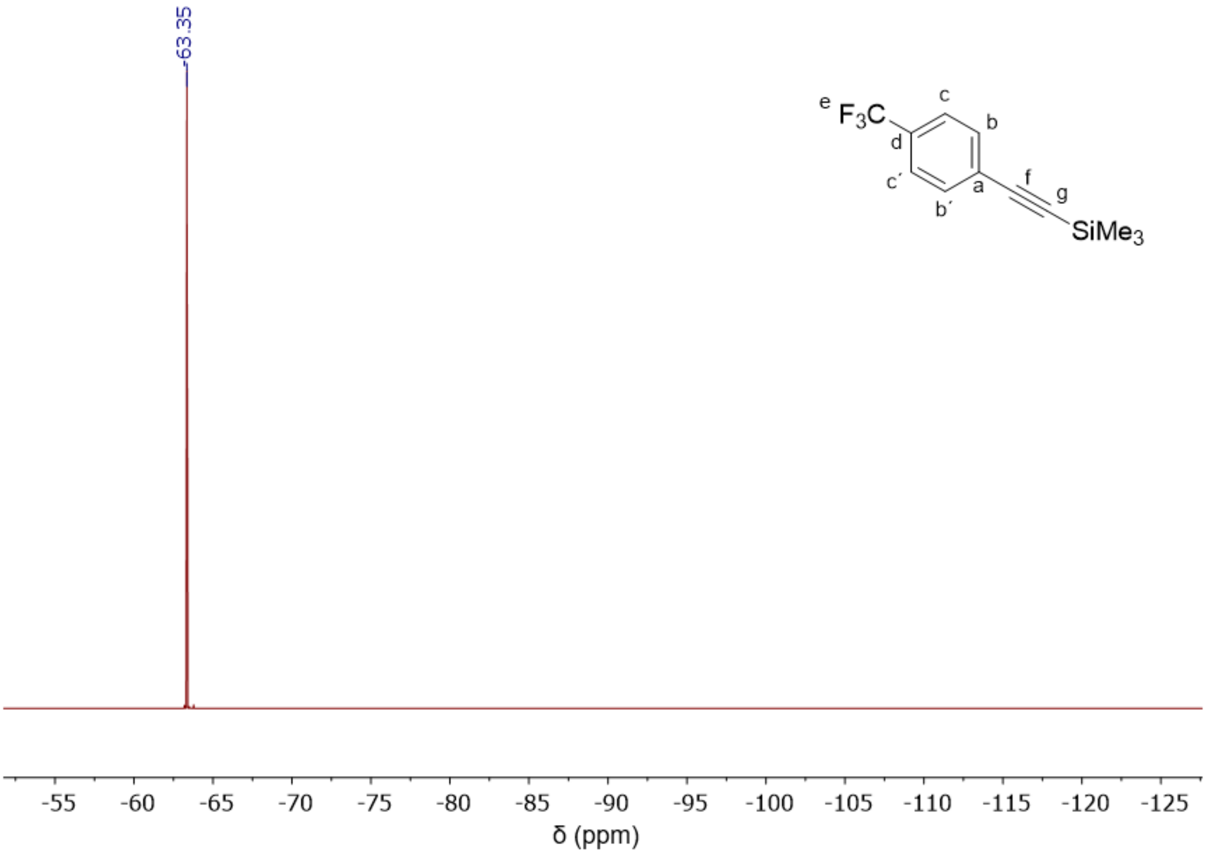

Figure S27. ^{19}F NMR (471 MHz) spectrum of 4-trifluoromethyl-phenylethynyltrimethylsilane in $CDCl_3$.

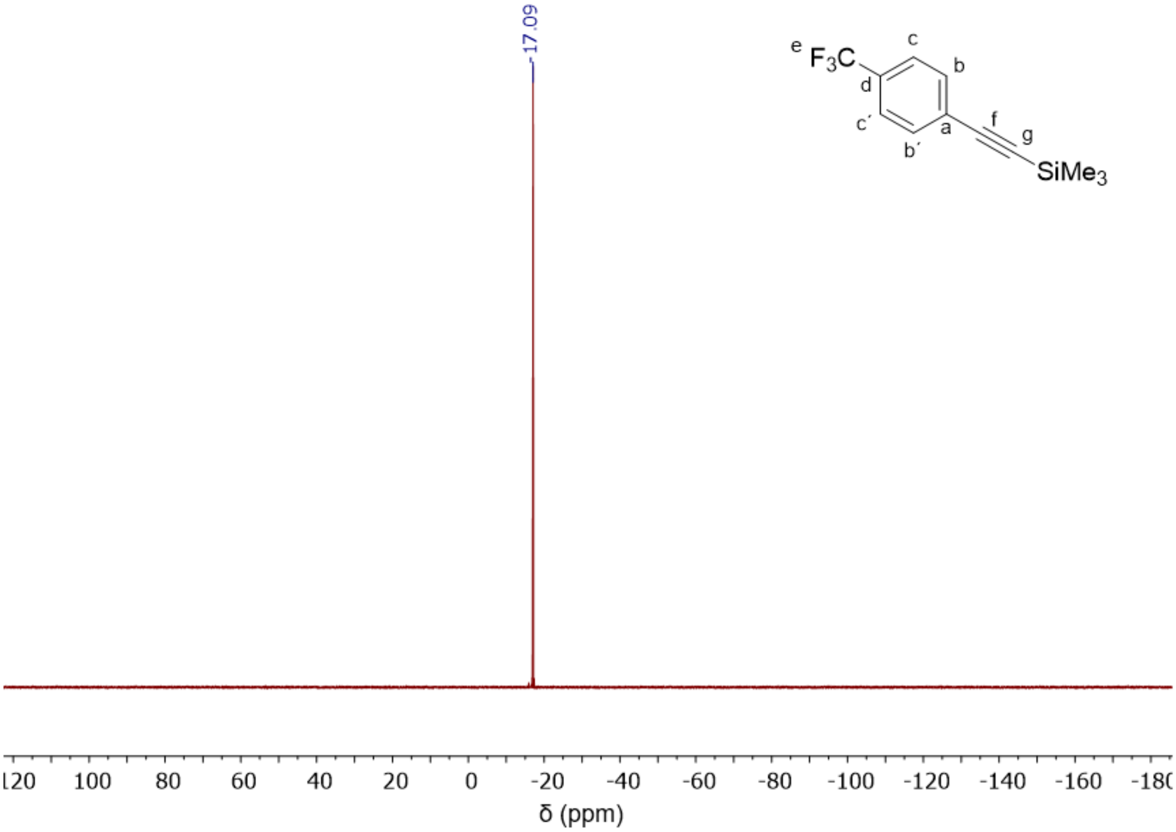

Figure S28. $^{29}Si\{^1H\}$ NMR (99 MHz) spectrum of 4-trifluoromethyl-phenylethynyltrimethylsilane in $CDCl_3$.

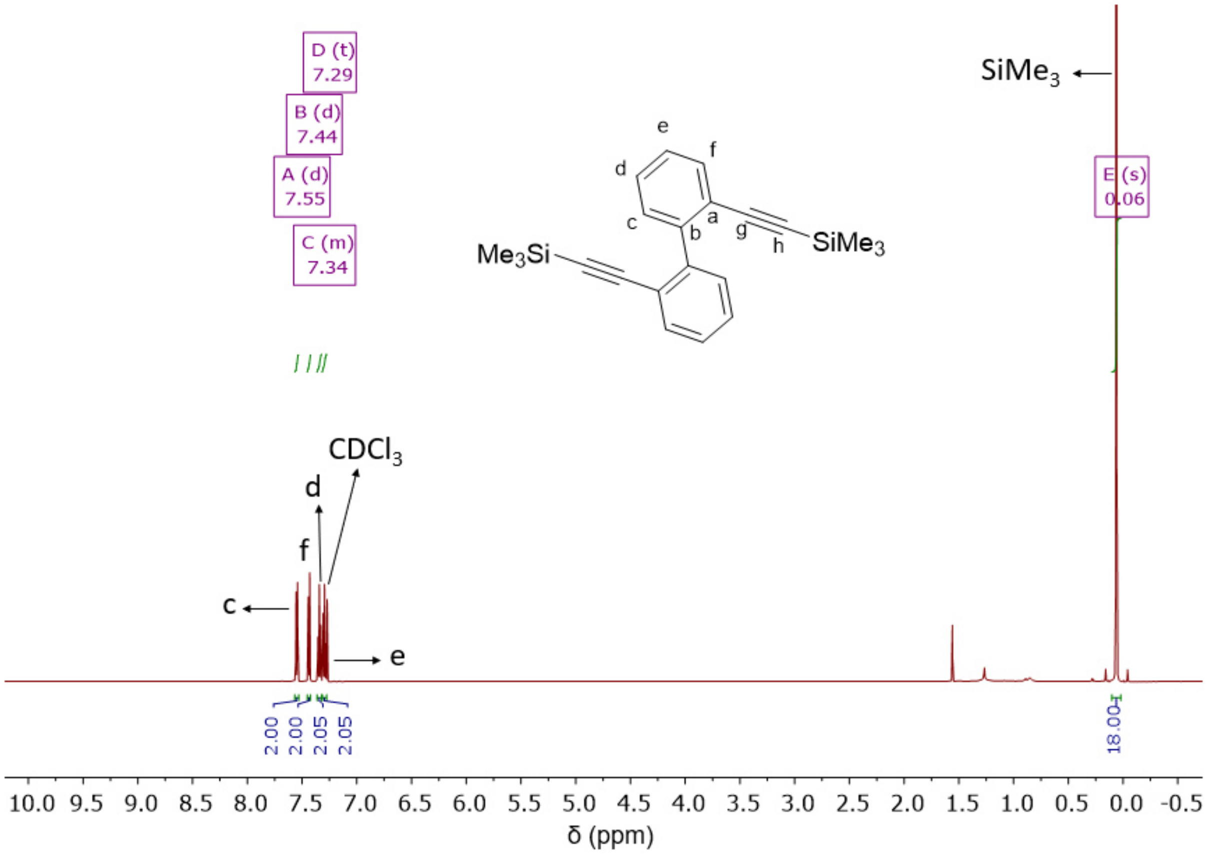

Figure S29. ^{1}H NMR (600 MHz) spectrum of 2,2'-bis((trimethylsilyl)ethynyl)biphenyl in $CDCl_3$.

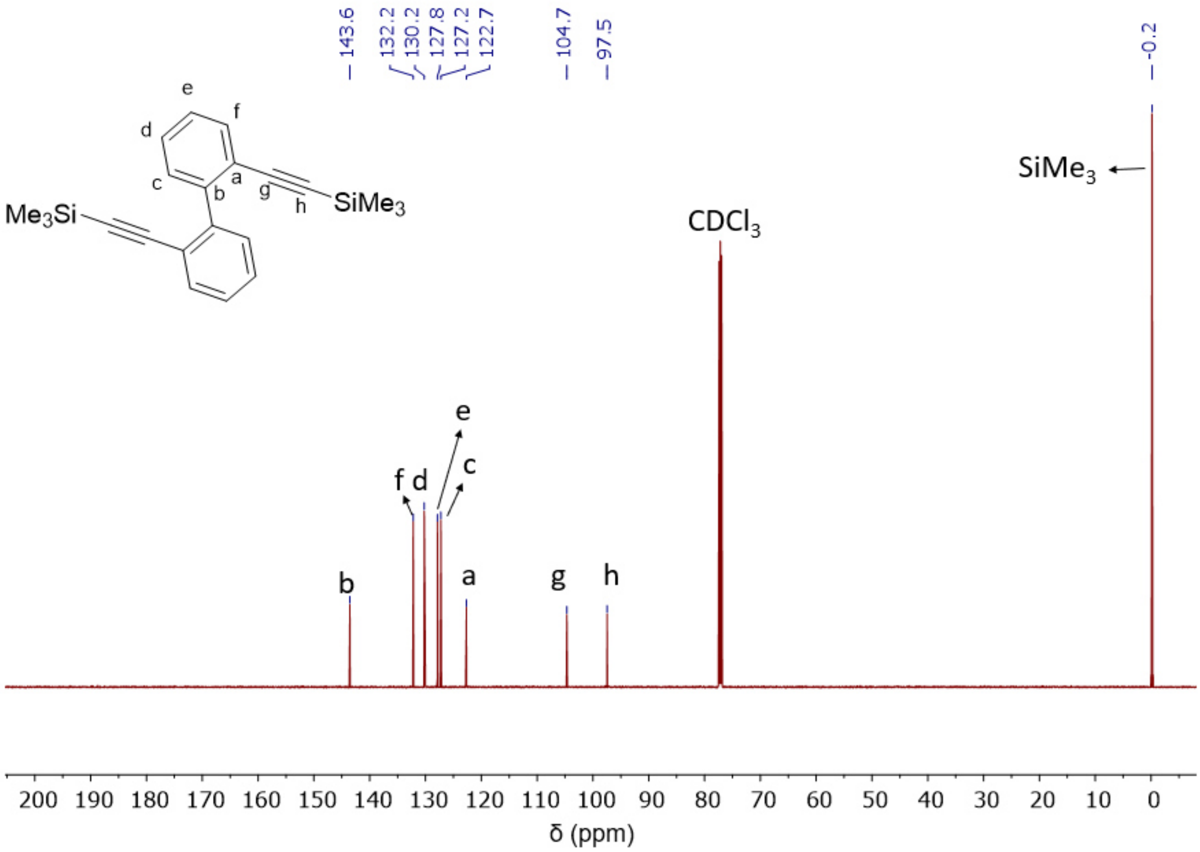

Figure S30. $^{13}C\{^1H\}$ NMR (151 MHz) spectrum of 2,2'-bis((trimethylsilyl)ethynyl)biphenyl in $CDCl_3$.

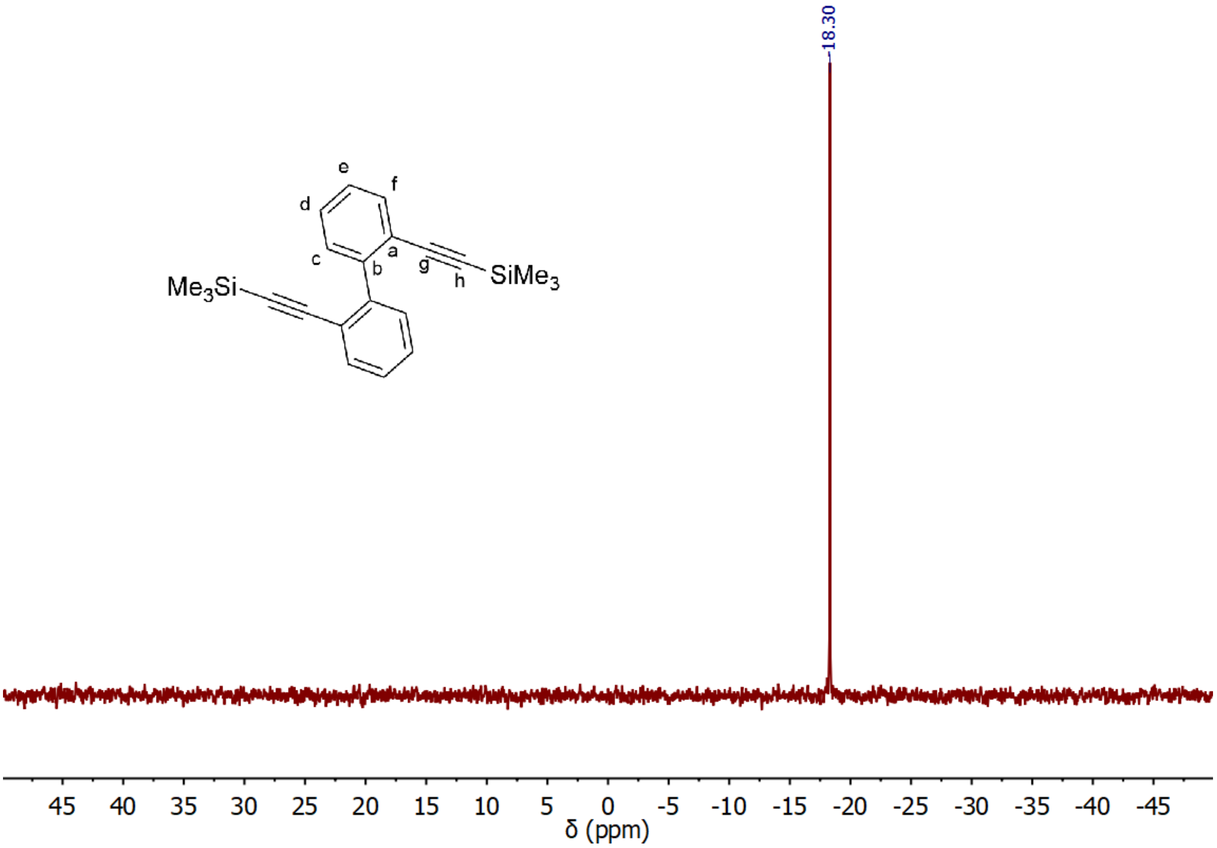

Figure S31. ^{29}Si{^{1}H} NMR (99 MHz) spectrum of 2,2'-bis((trimethylsilyl)ethynyl)biphenyl in C_6D_6.

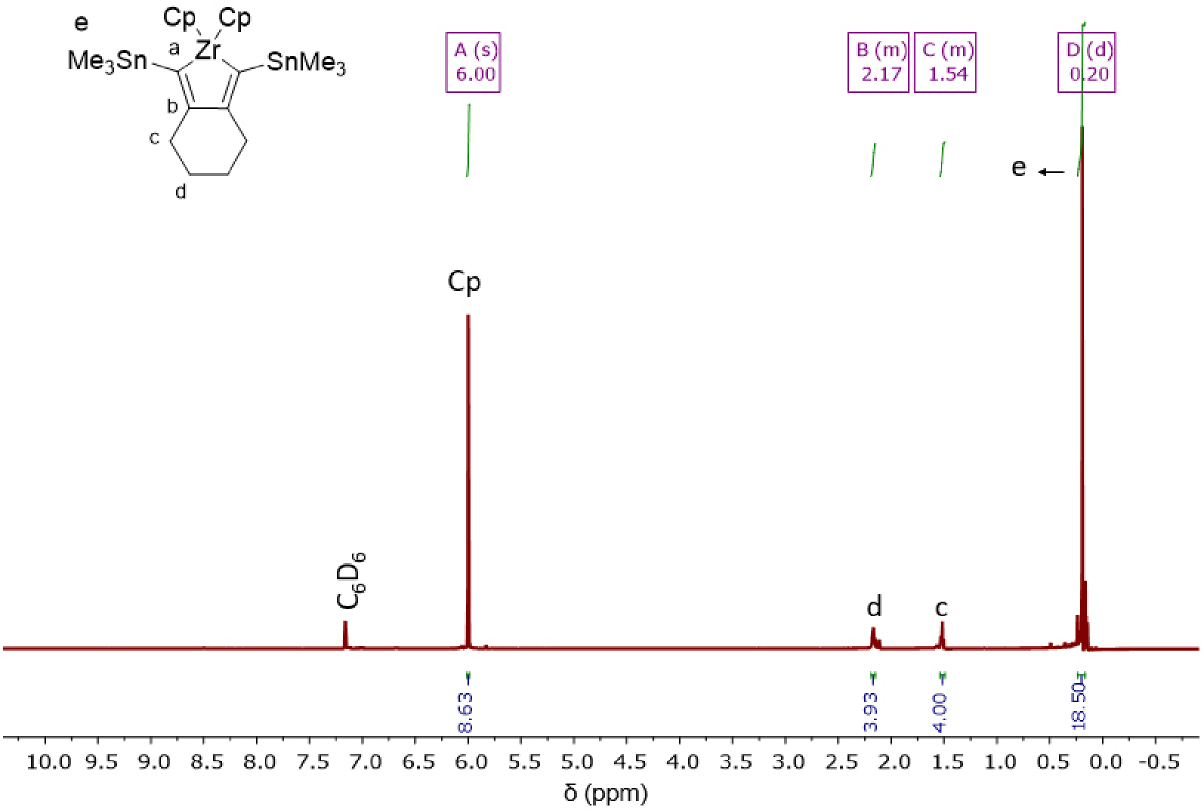

Figure S32. ^{1}H NMR (500 MHz) spectrum of zirconacyclopentadiene **11a** in C_6D_6.

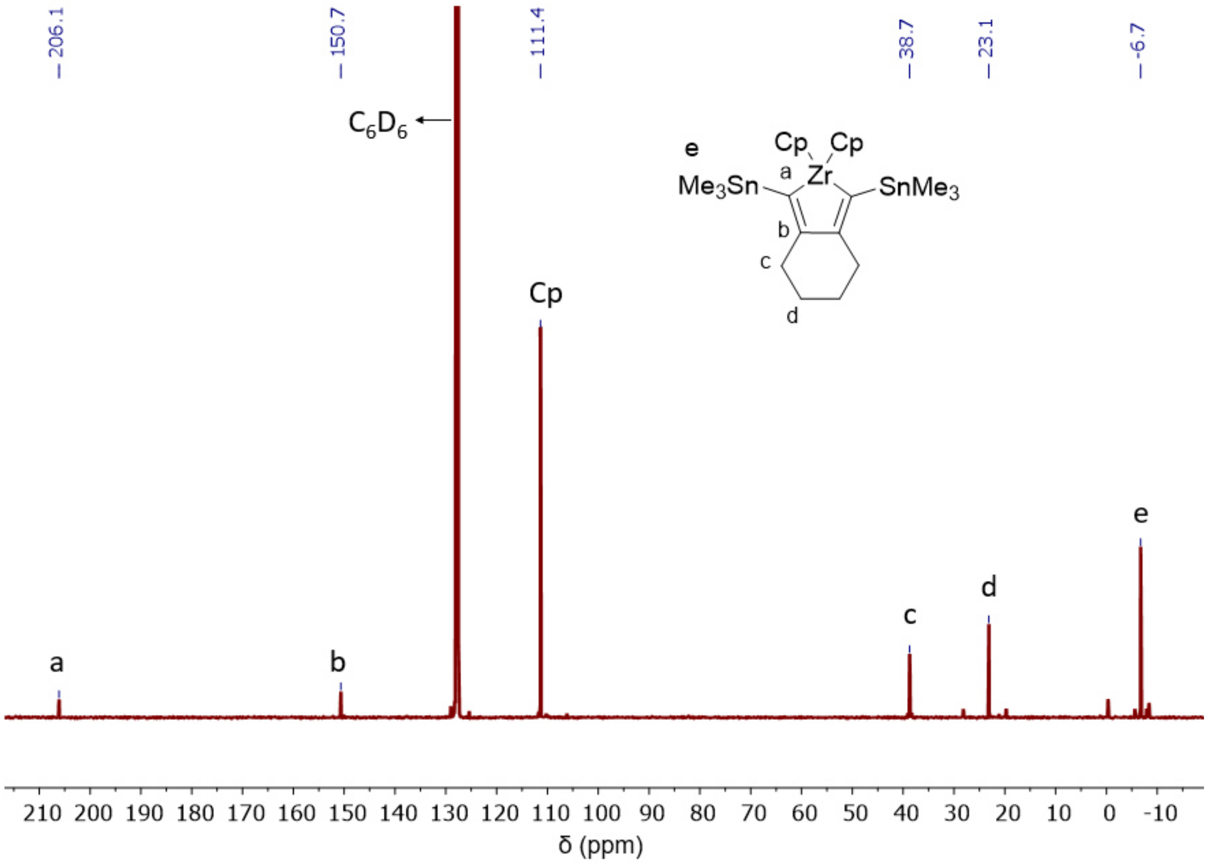

Figure S33. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11a** in C_6D_6.

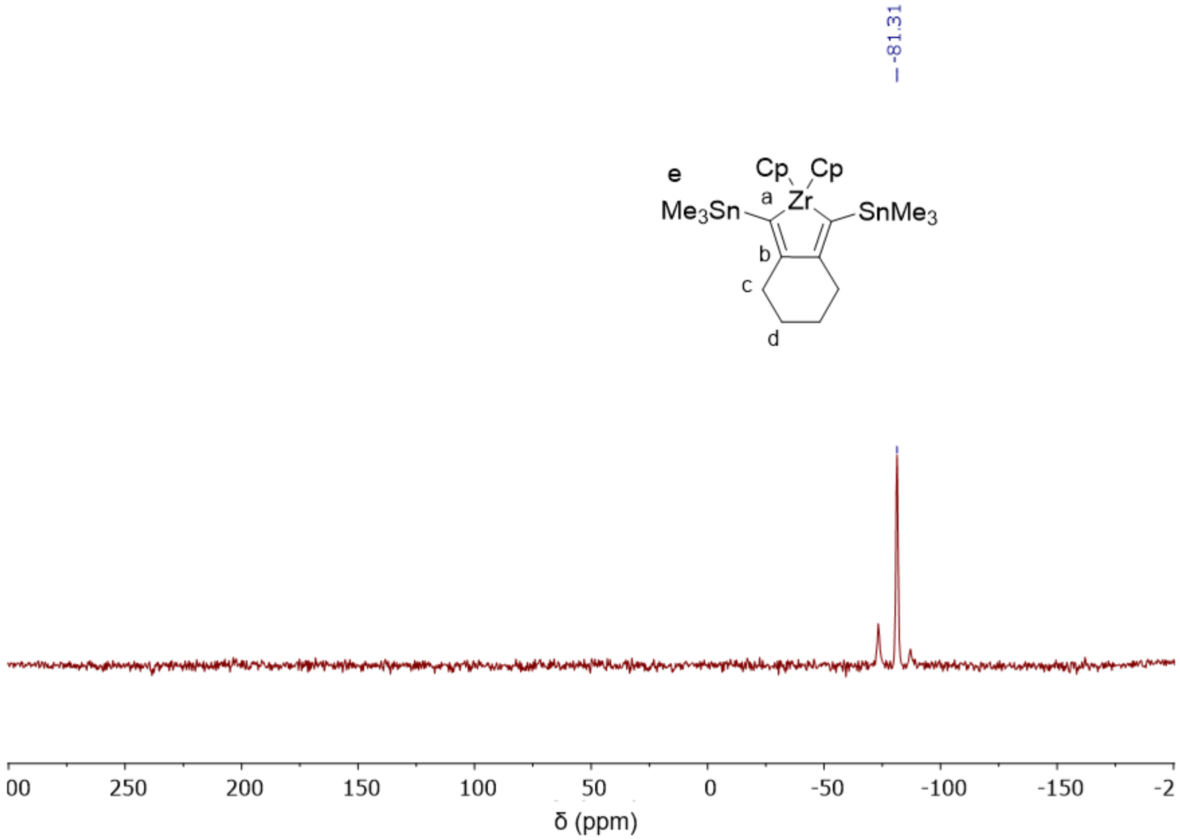

Figure S34. $^{119}Sn\{^1H\}$ NMR (187 MHz spectrum of zirconacyclopentadiene **11a** in C_6D_6.

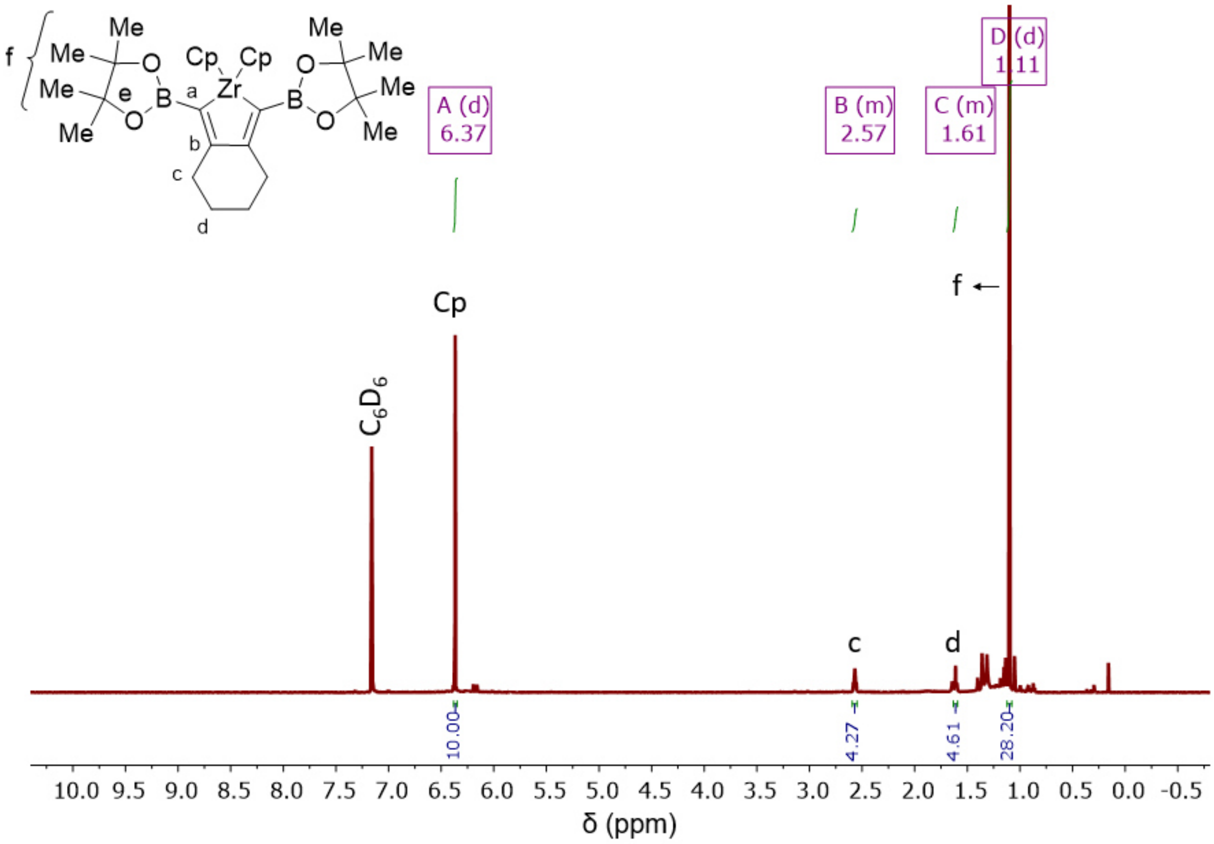

Figure S35. ^1H NMR (500 MHz) spectrum of zirconacyclopentadiene **11b** in C_6D_6.

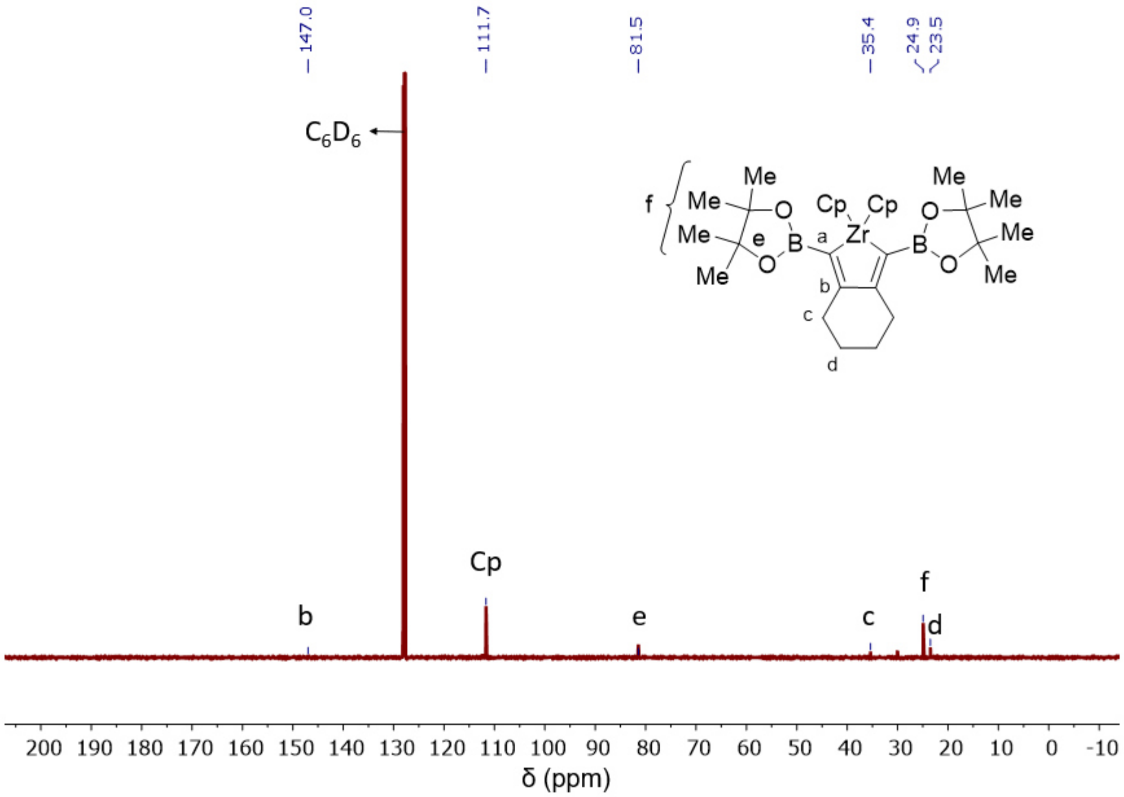

Figure S36. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11b** in C_6D_6.

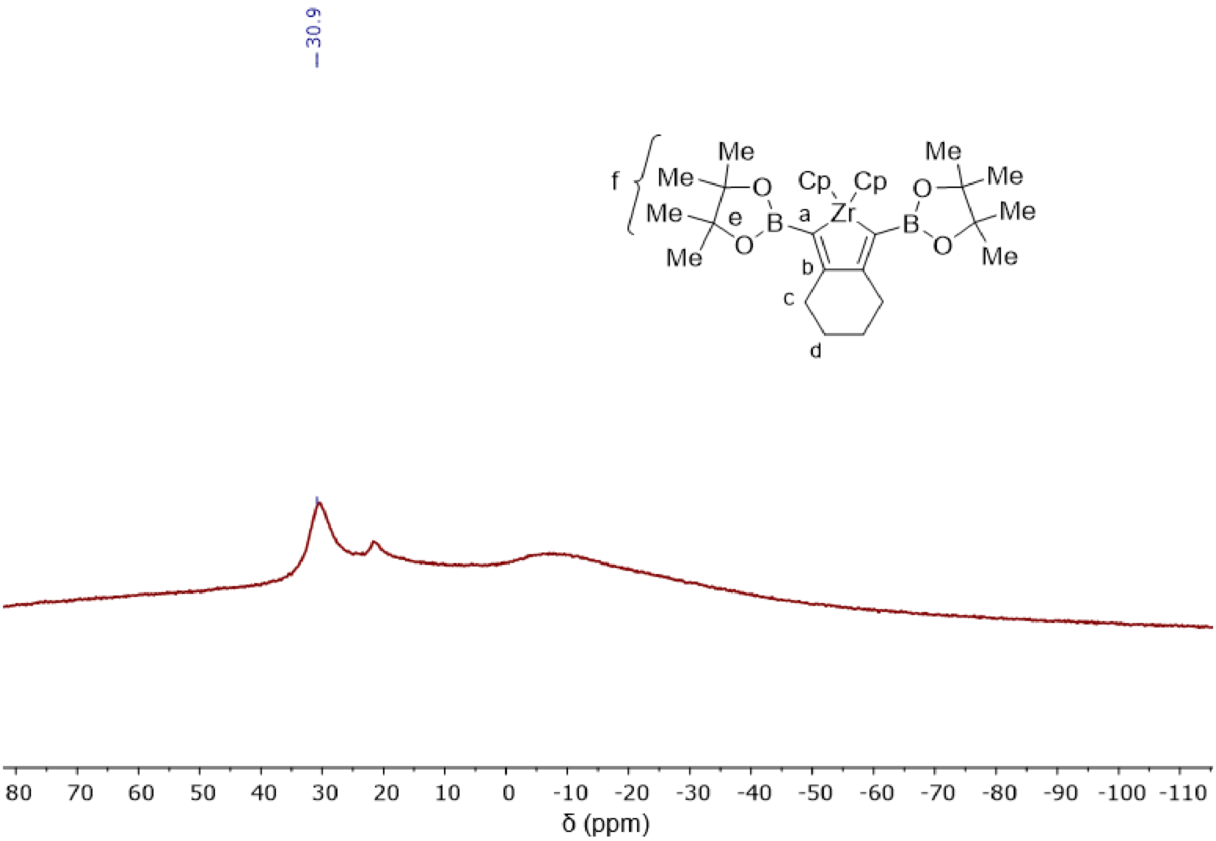

Figure S37. $^{11}B\{^1H\}$ NMR (160 MHz) spectrum of zirconacyclopentadiene **11b** in C_6D_6.

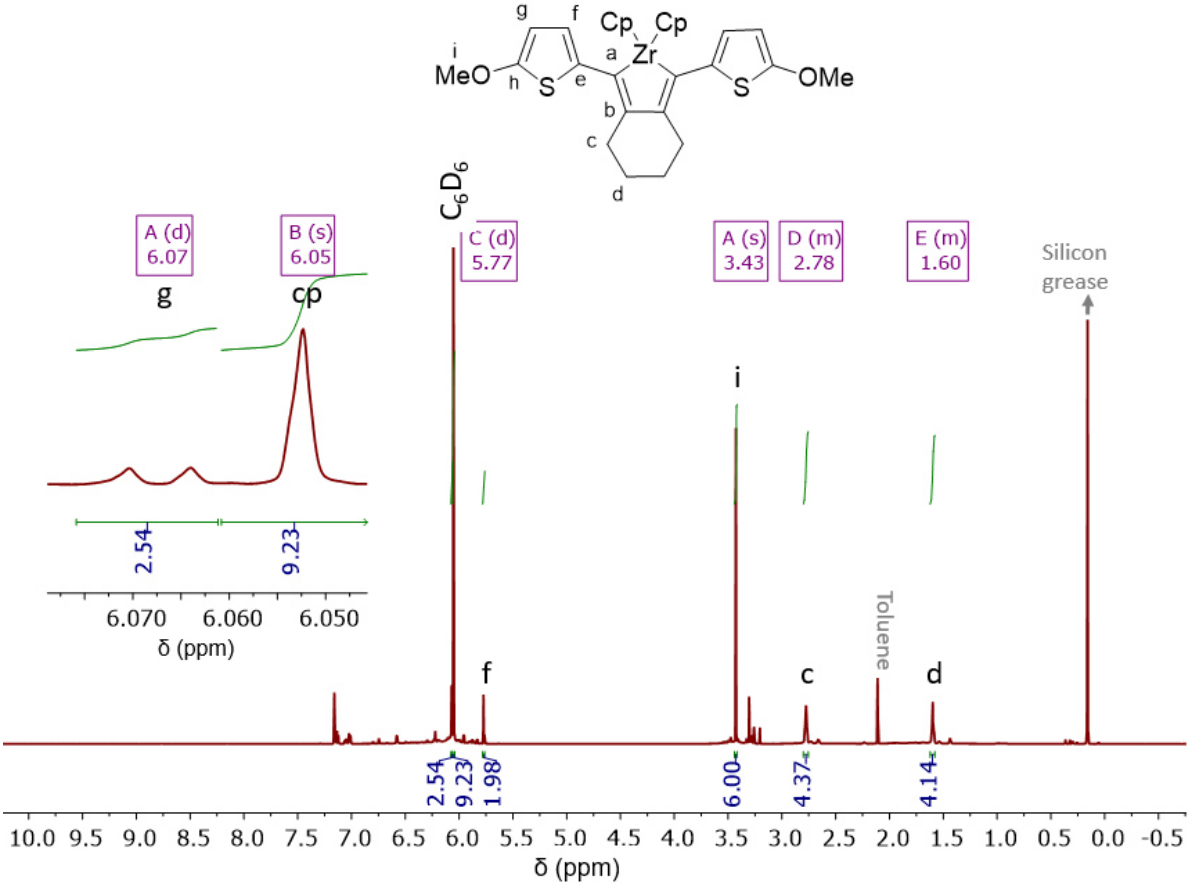

Figure S38. ^1H NMR (500 MHz) spectrum of zirconacyclopentadiene **11c** in C_6D_6.

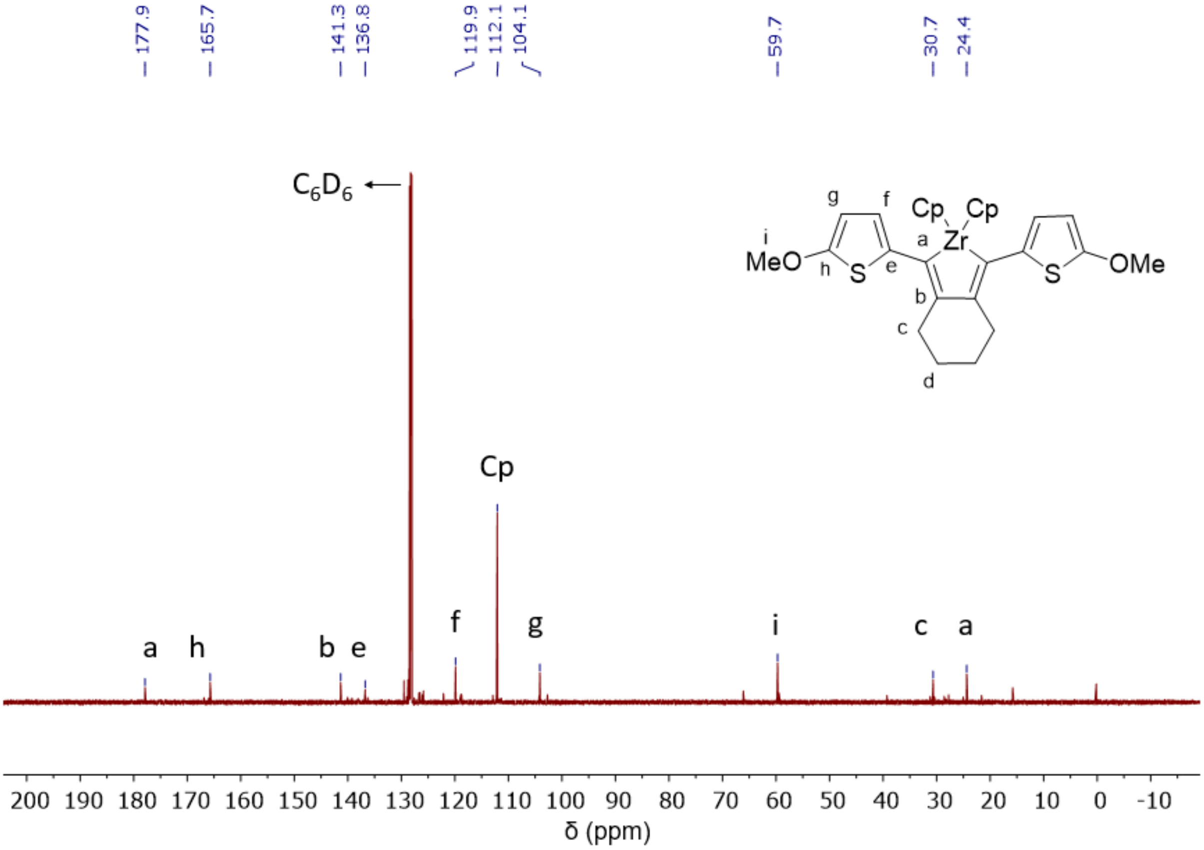

Figure S39. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11c** in C_6D_6.

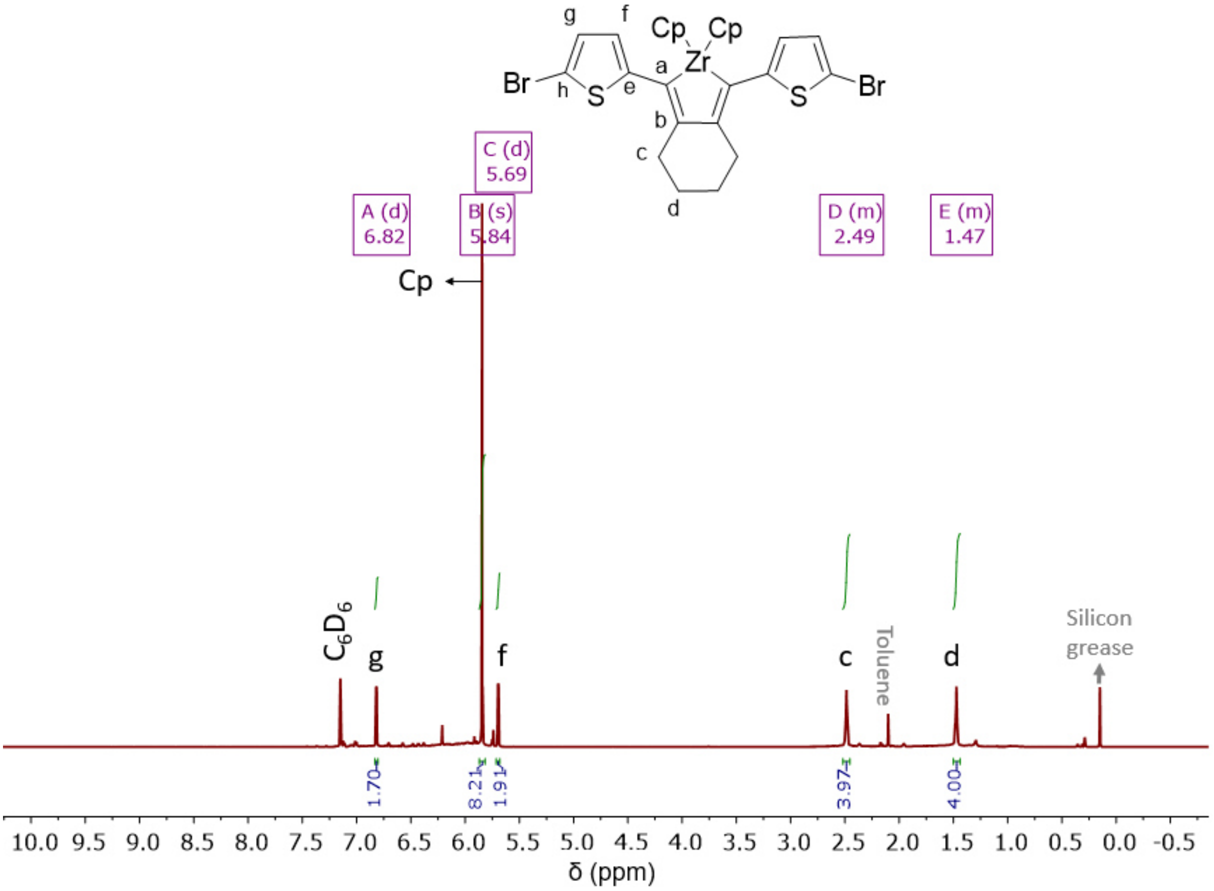

Figure S40. ^1H NMR (500 MHz) spectrum of zirconacyclopentadiene **11d** in C_6D_6.

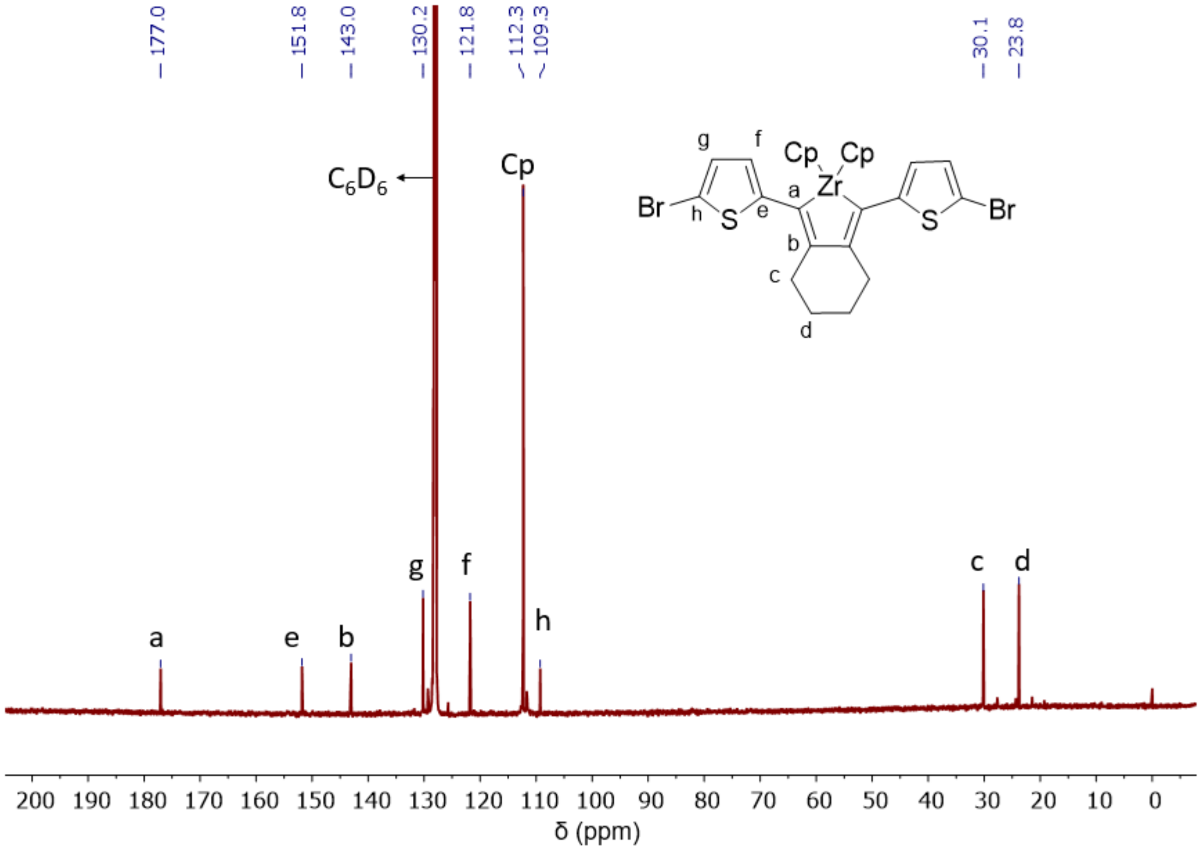

Figure S41. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11d** in C_6D_6.

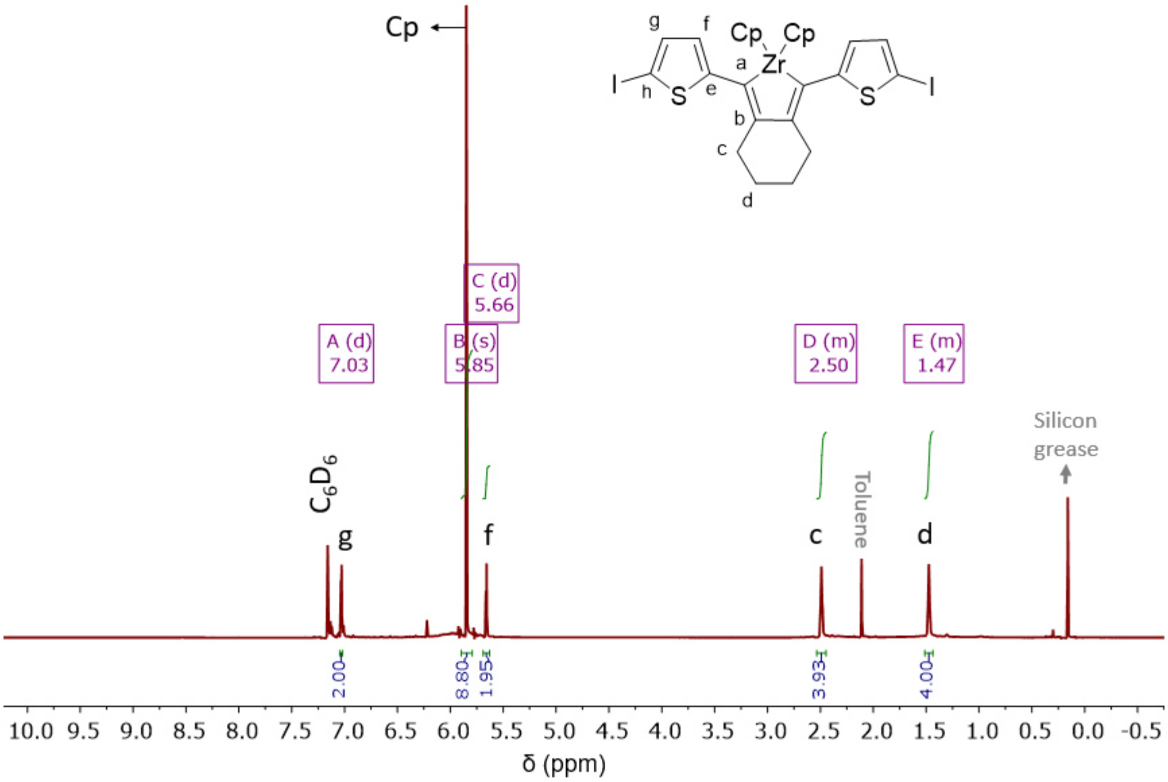

Figure S42. ^1H NMR (500 MHz) spectrum of zirconacyclopentadiene **11e** in C_6D_6.

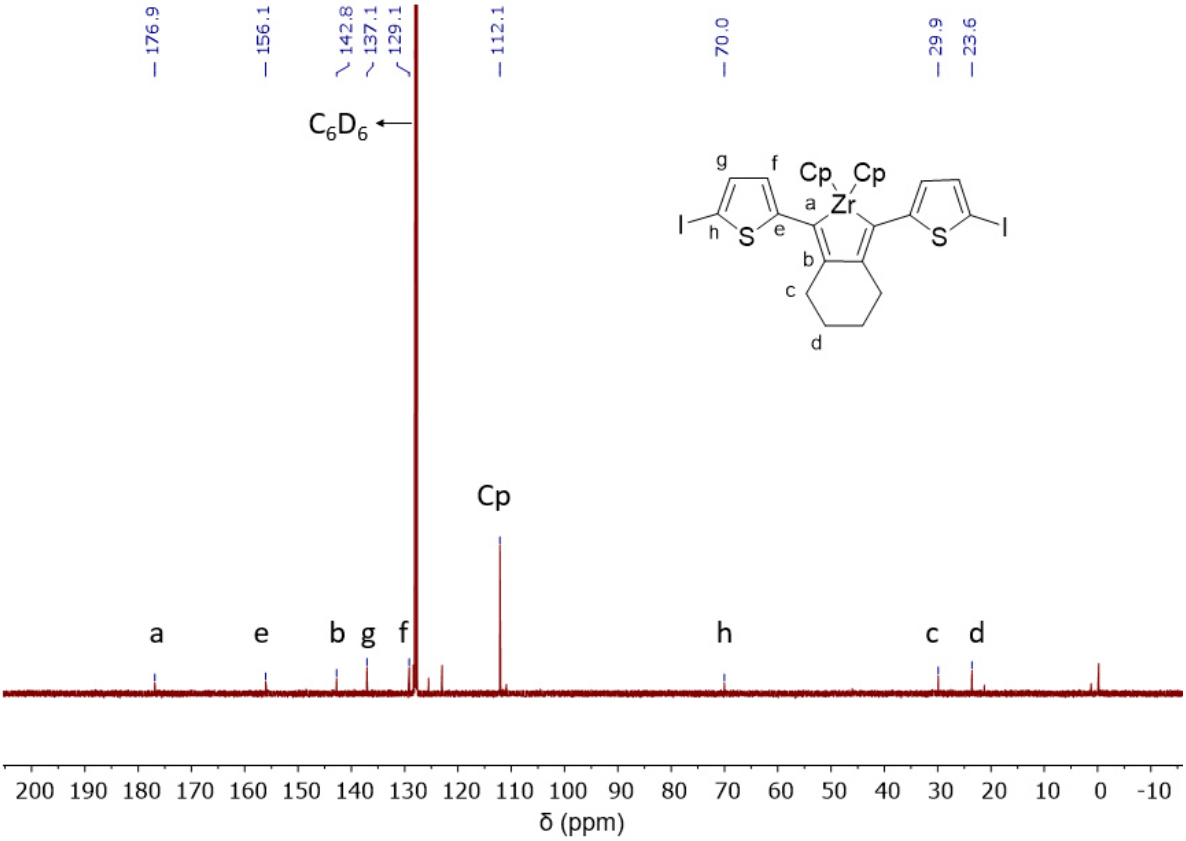

Figure S43. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11e** in C_6D_6.

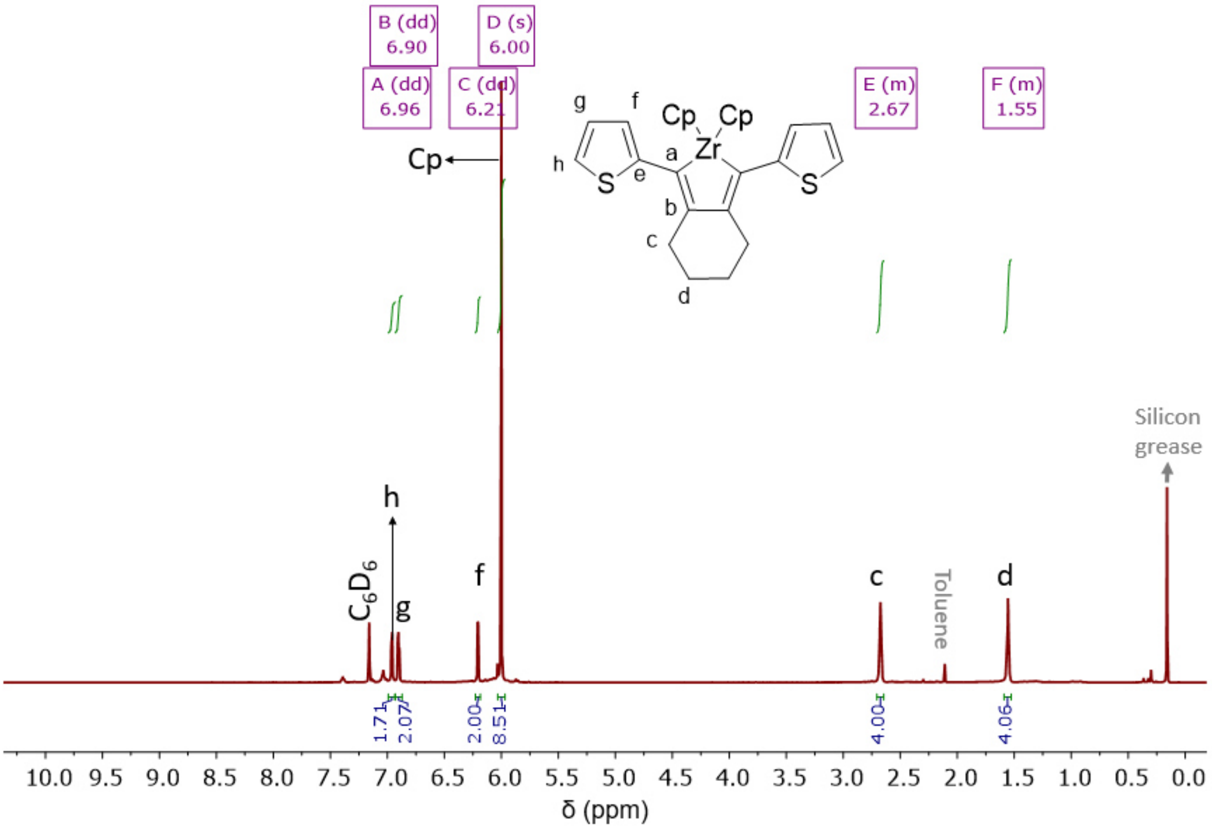

Figure S44. ^{1}H NMR (500 MHz) spectrum of zirconacyclopentadiene **11f** in C_6D_6.

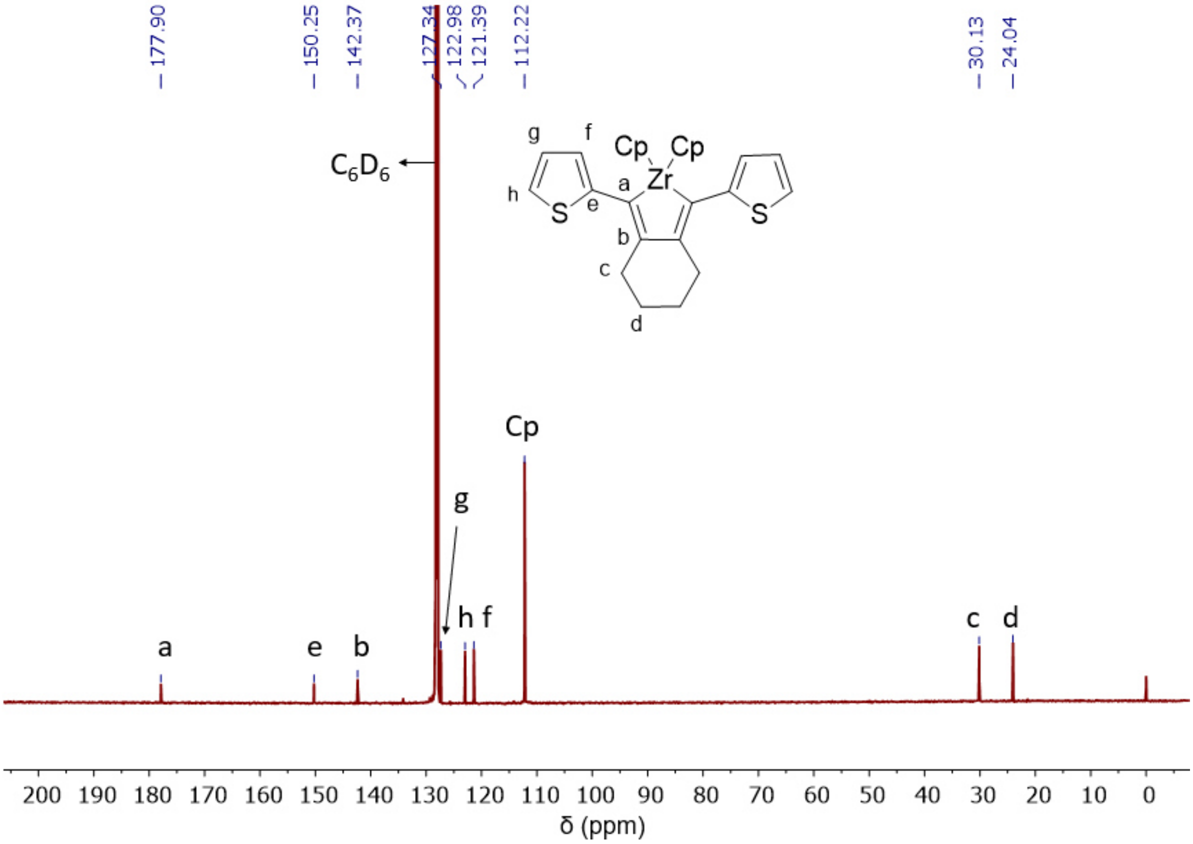

Figure S45. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11f** in C_6D_6.

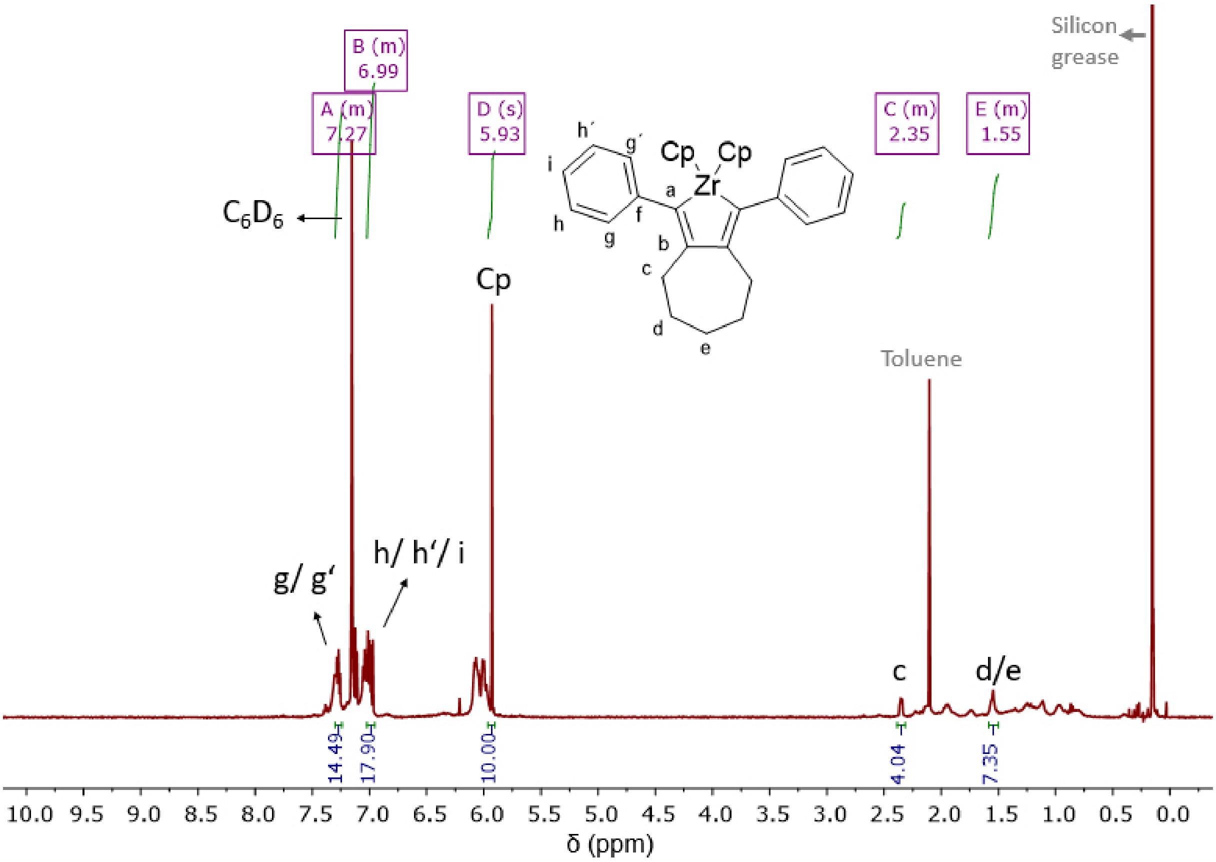

Figure S46. ^1H NMR (500 MHz) spectrum of zirconacyclopentadiene **11g** in C_6D_6.

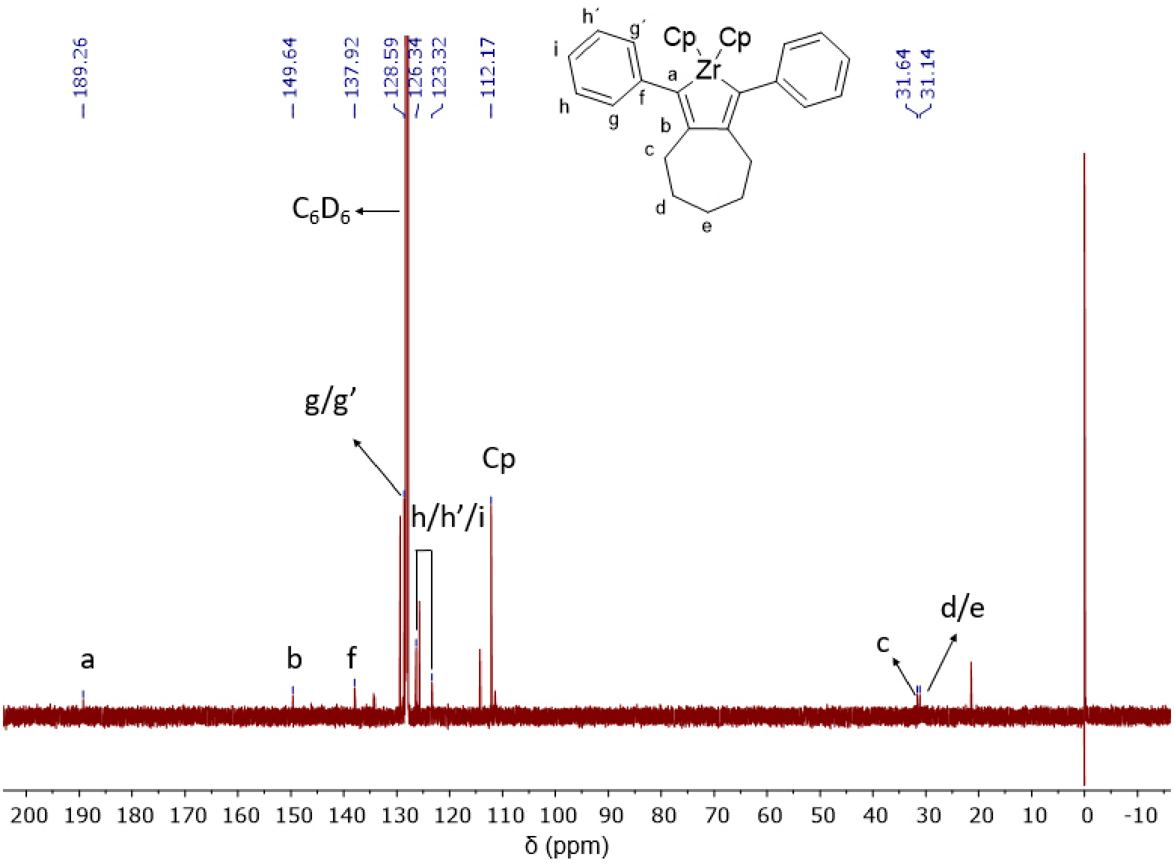

Figure S47. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11g** in C_6D_6.

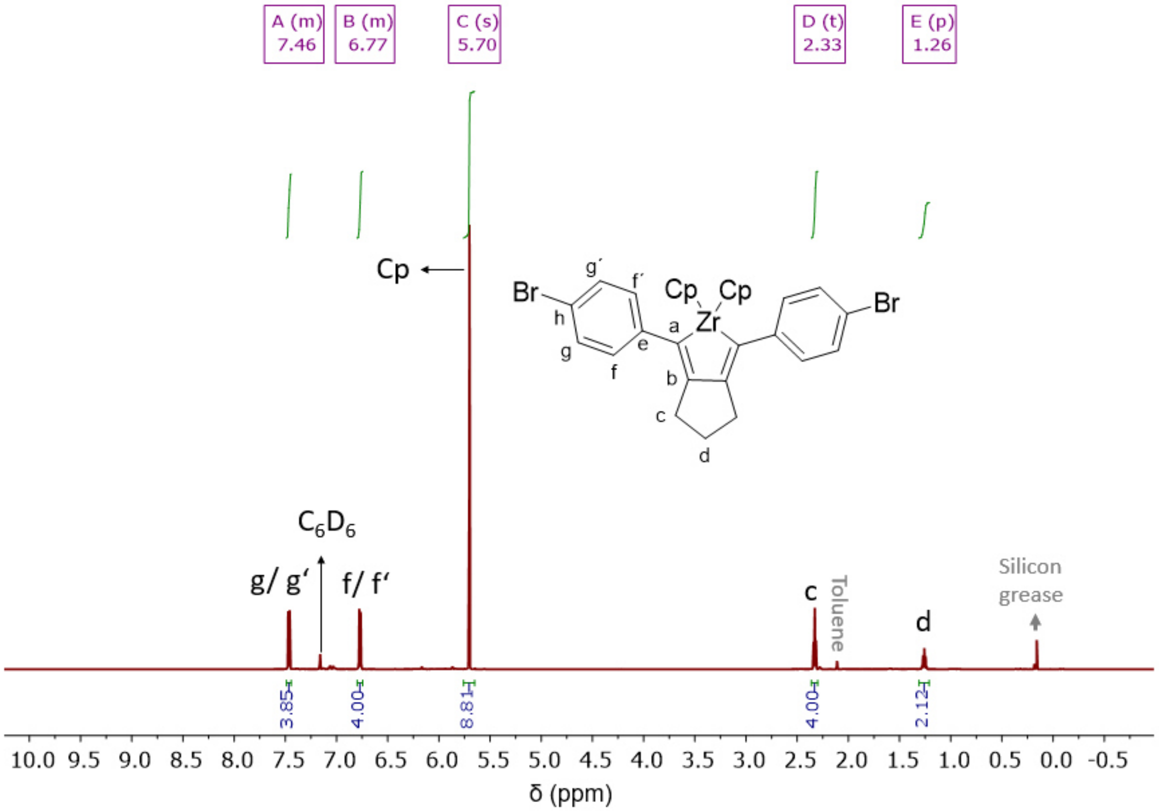

Figure S48. ^{1}H NMR (600 MHz) spectrum of zirconacyclopentadiene **11h** in C_6D_6.

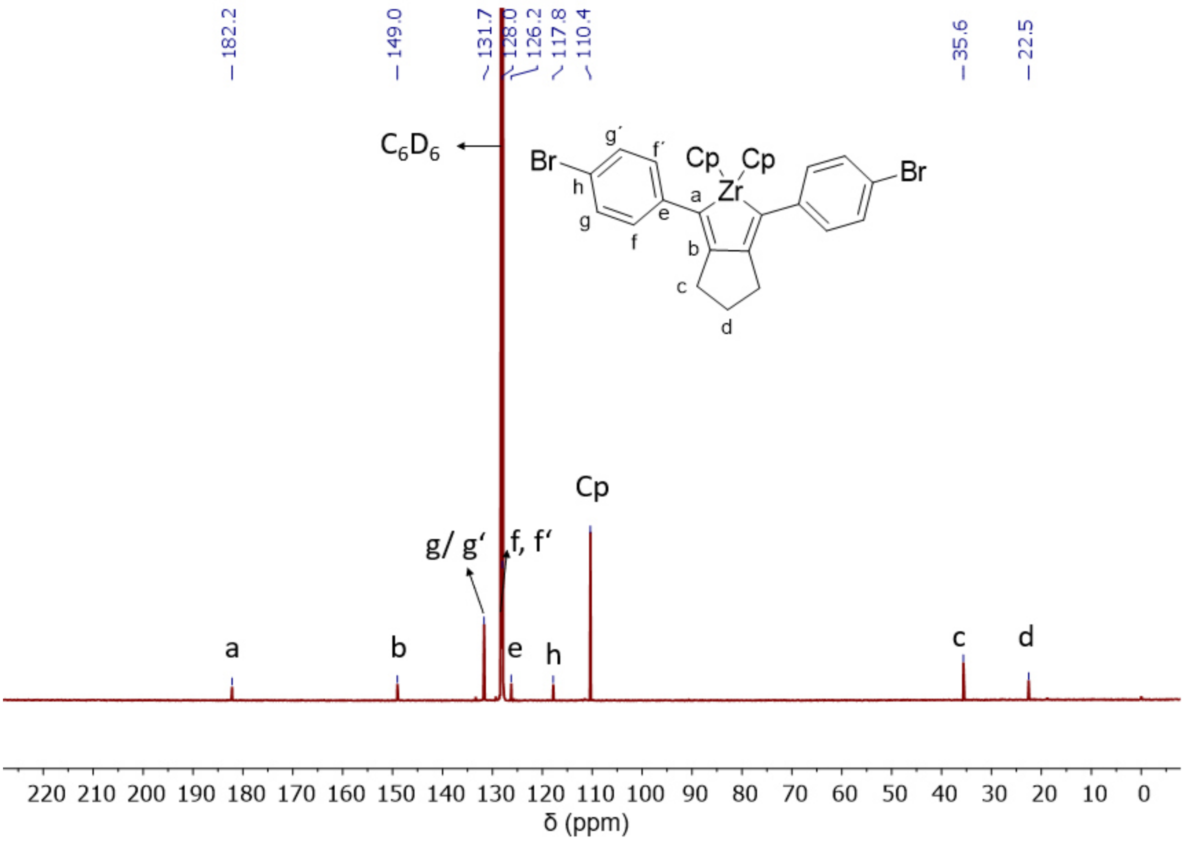

Figure S49. $^{13}C\{^1H\}$ NMR (151 MHz) spectrum of zirconacyclopentadiene **11h** in C_6D_6.

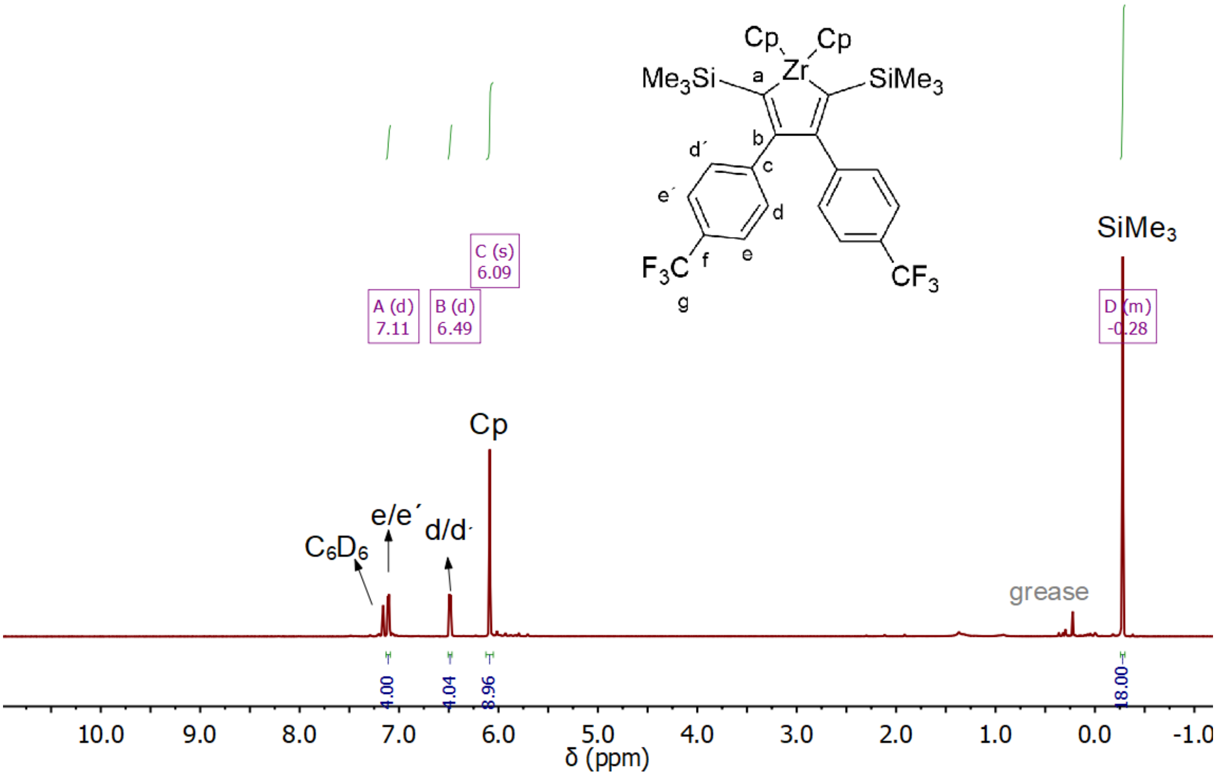

Figure S50. ^1H NMR (600 MHz) spectrum of zirconacyclopentadiene **11i** in C_6D_6.

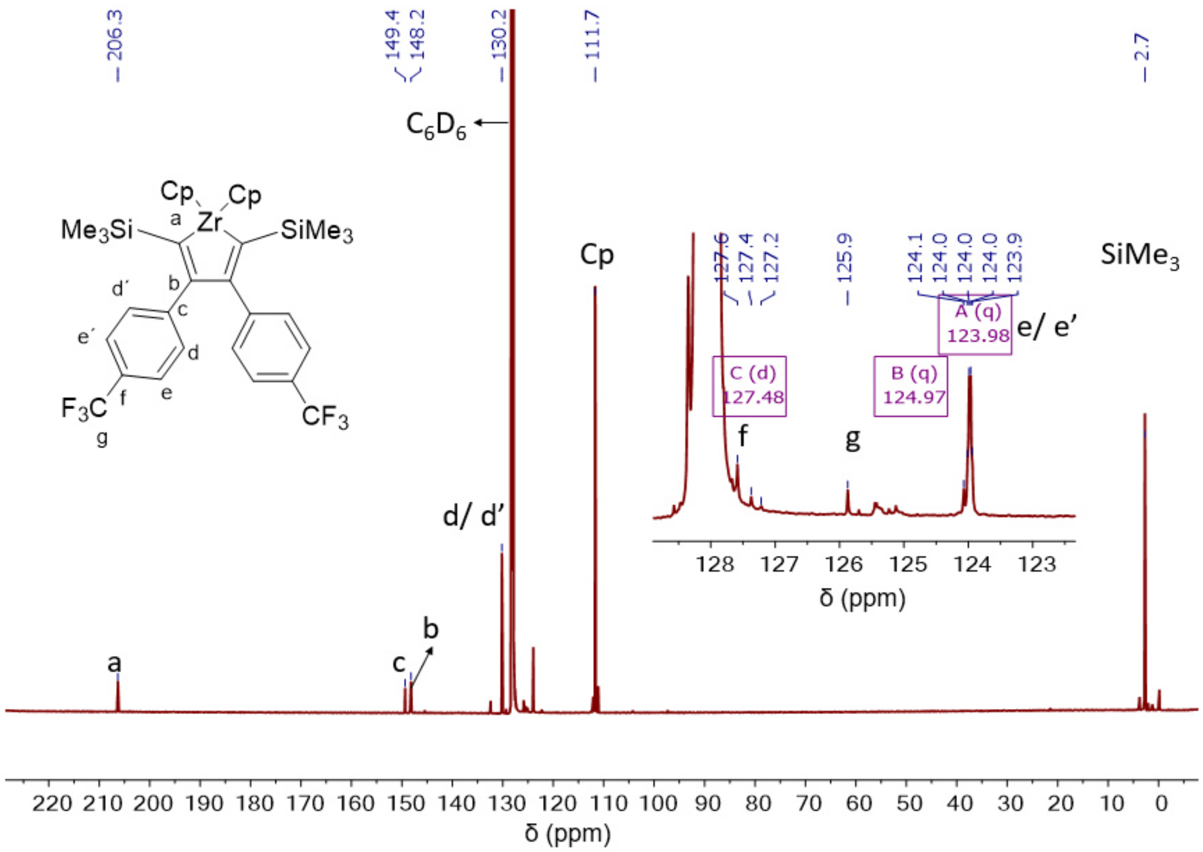

Figure S51. $^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of zirconacyclopentadiene **11i** in C_6D_6.

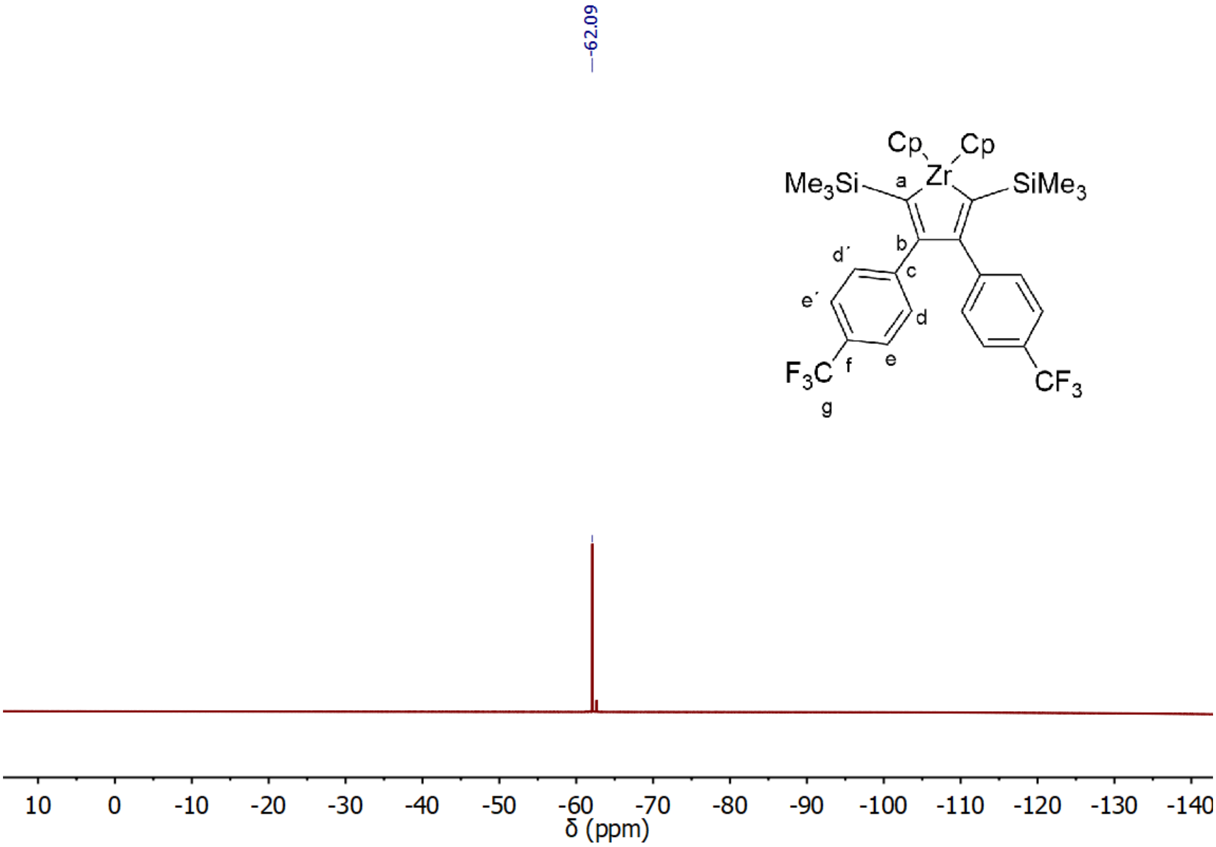

Figure S52. ^{19}F NMR (471 MHz) spectrum of zirconacyclopentadiene **11i** in C_6D_6.

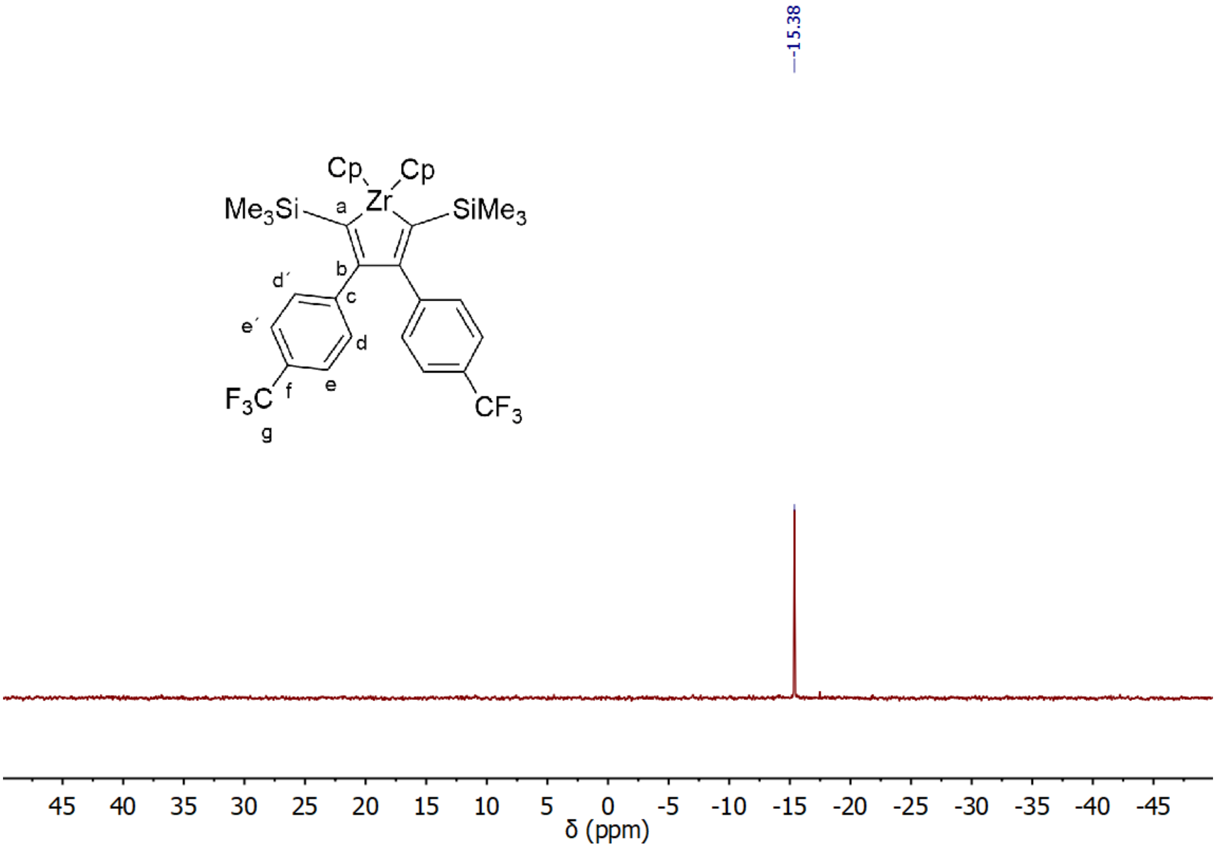

Figure S53. ^{29}Si{^{1}H} NMR (99 MHz) spectrum of zirconacyclopentadiene **11i** in C_6D_6.

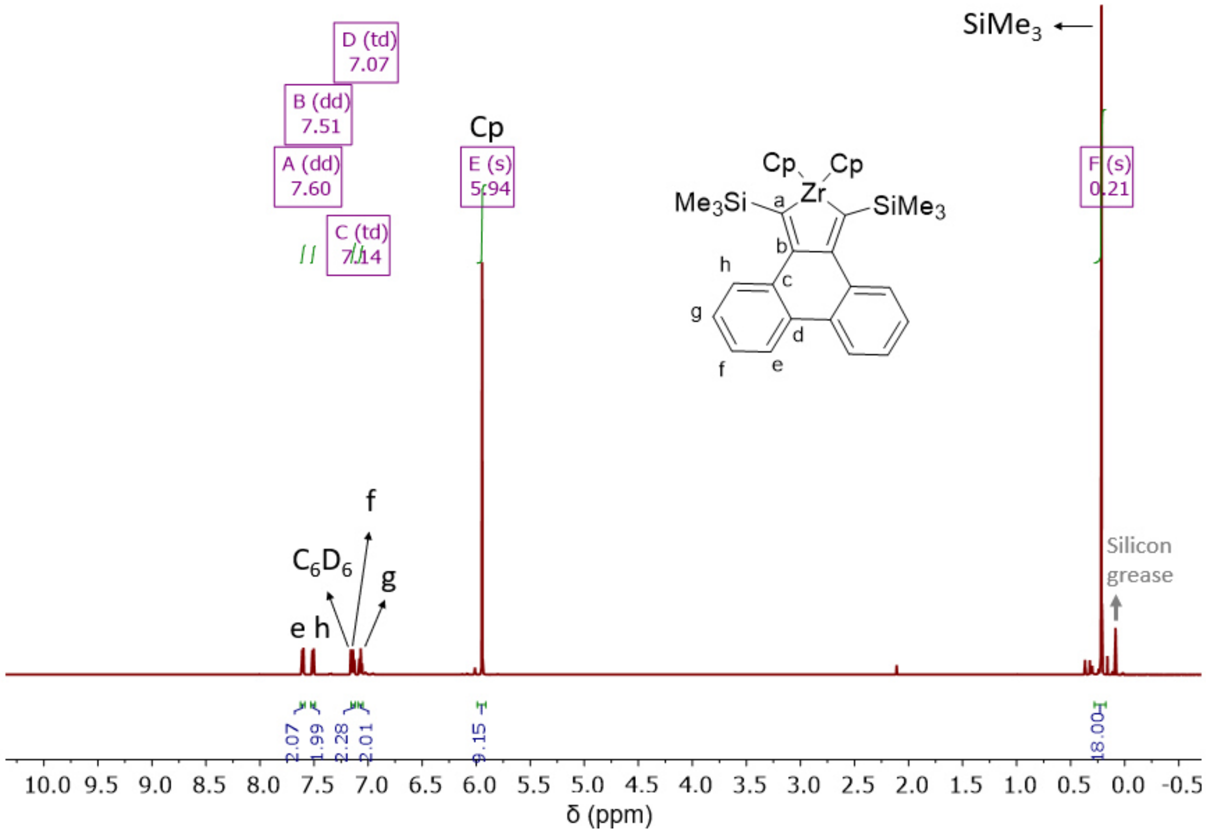

Figure S54. ^{1}H NMR (600 MHz) spectrum of zirconacyclopentadiene **11j** in C_6D_6.

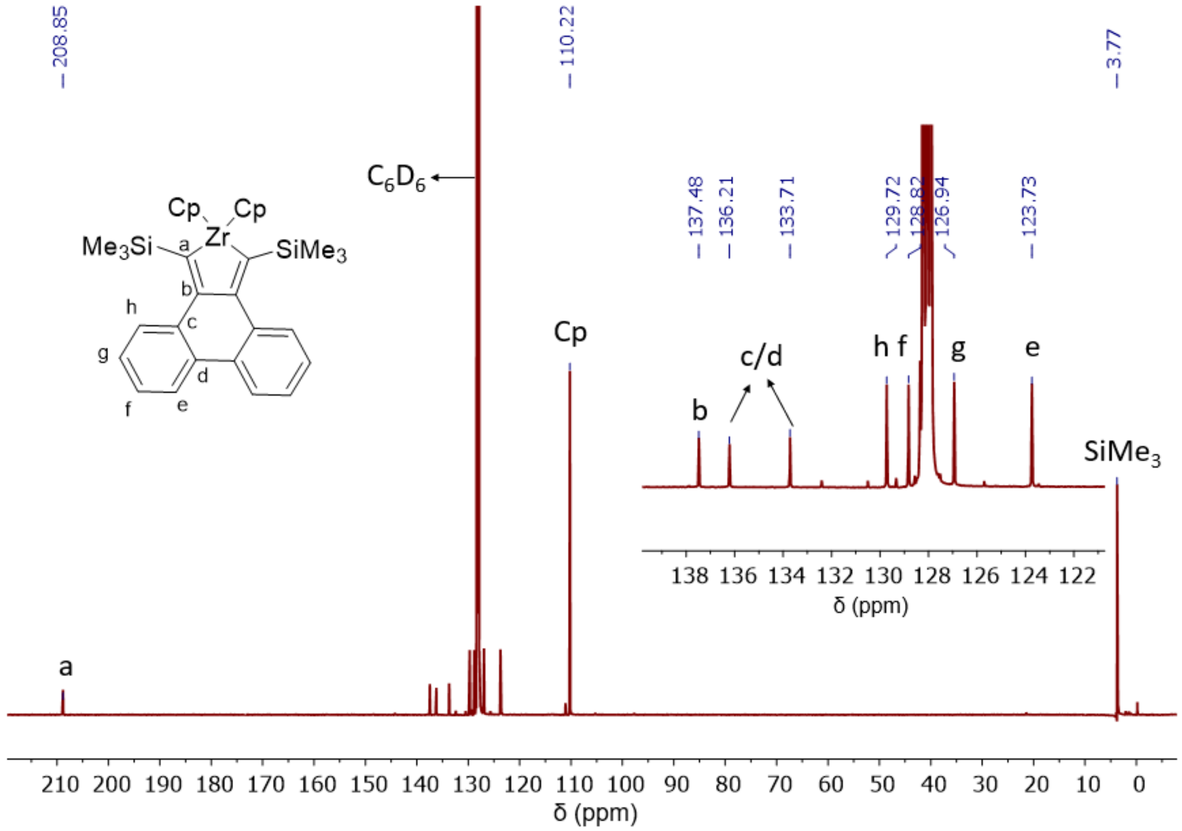

Figure S55. ^{13}C NMR (151 MHz) spectrum of zirconacyclopentadiene **11j** in C_6D_6.

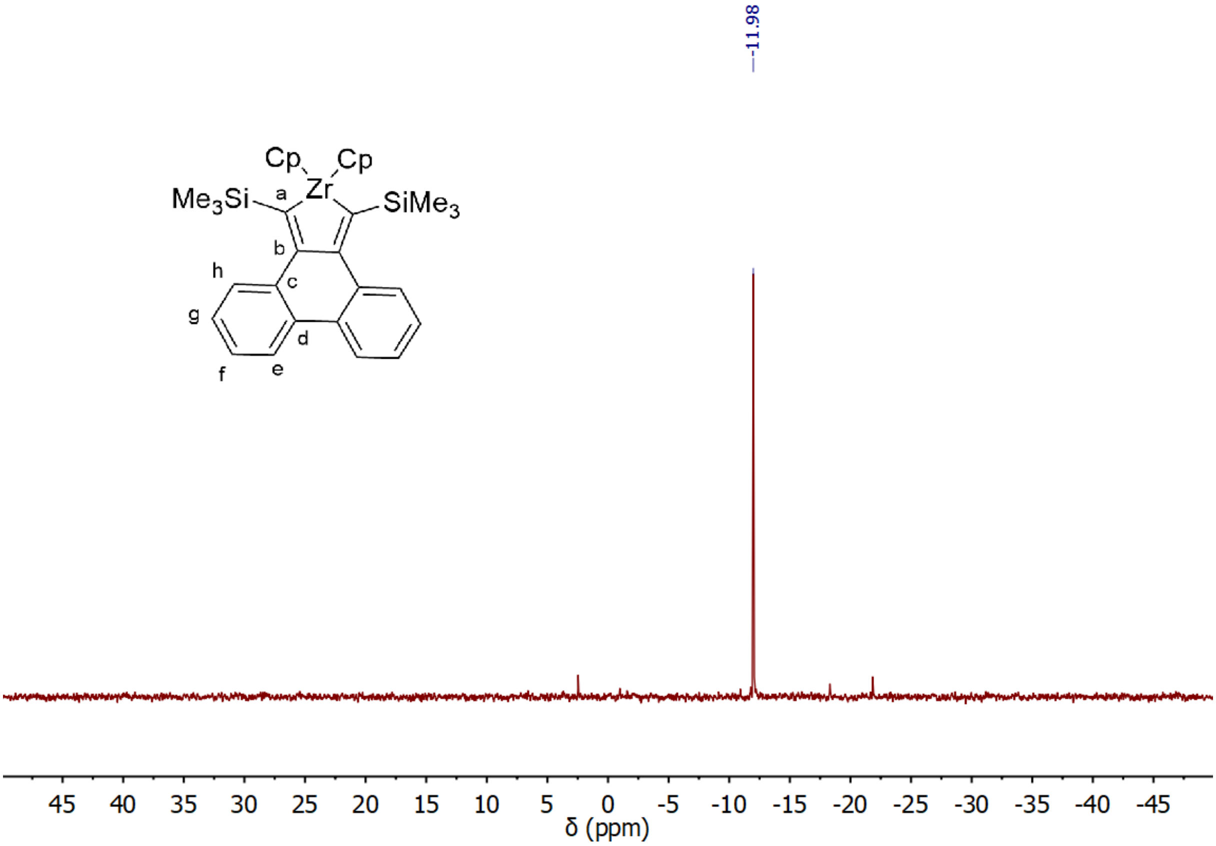

Figure S56. ^{29}Si{^{1}H} NMR (99 MHz) spectrum of zirconacyclopentadiene **11j** in C_6D_6.

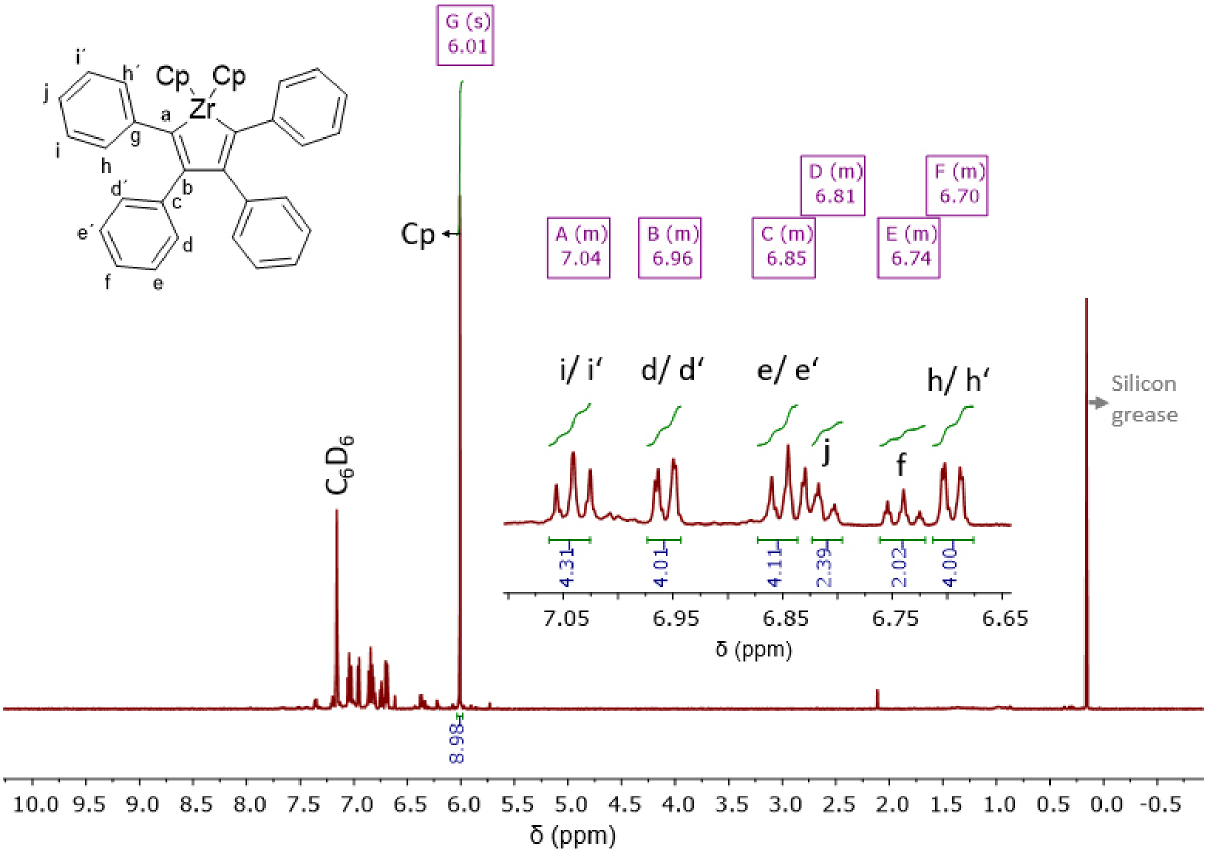

Figure S57. ^{1}H NMR (500 MHz) spectrum of zirconacyclopentadiene **11k** in C_6D_6.

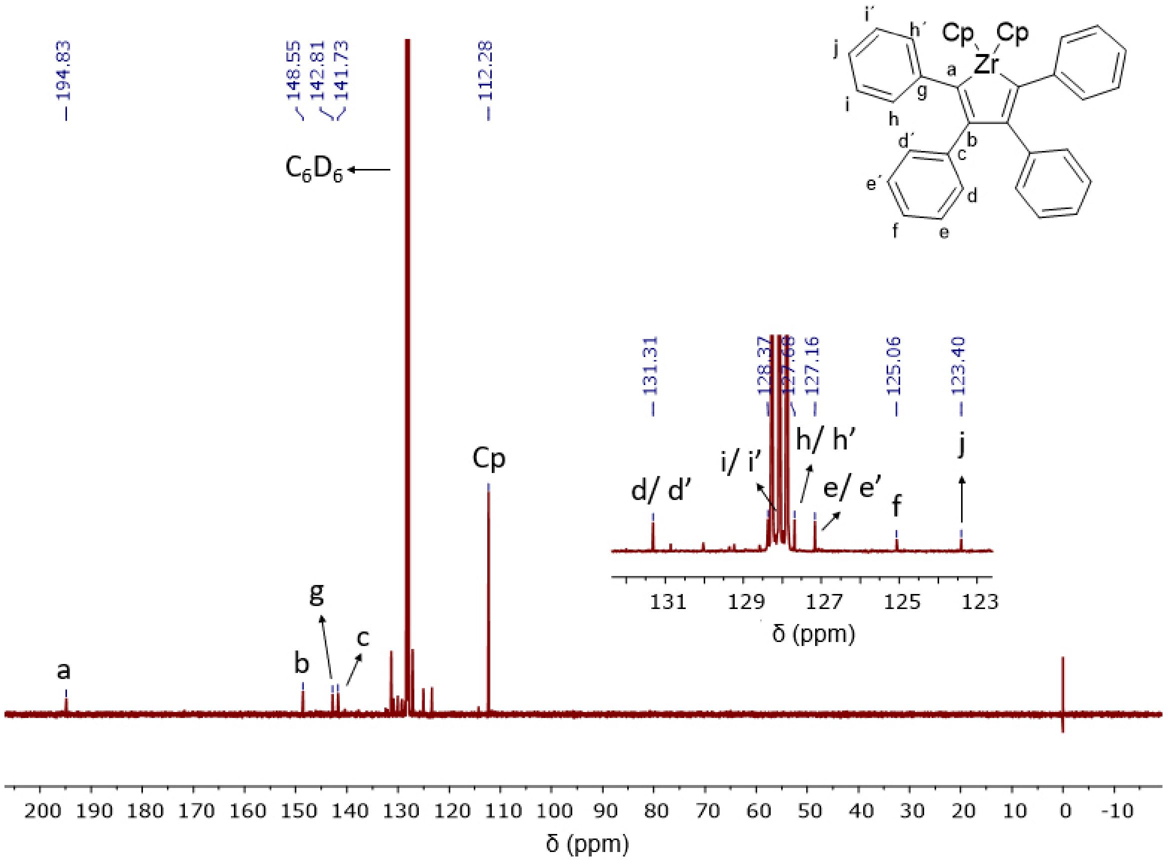

Figure S58. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11k** in C_6D_6.

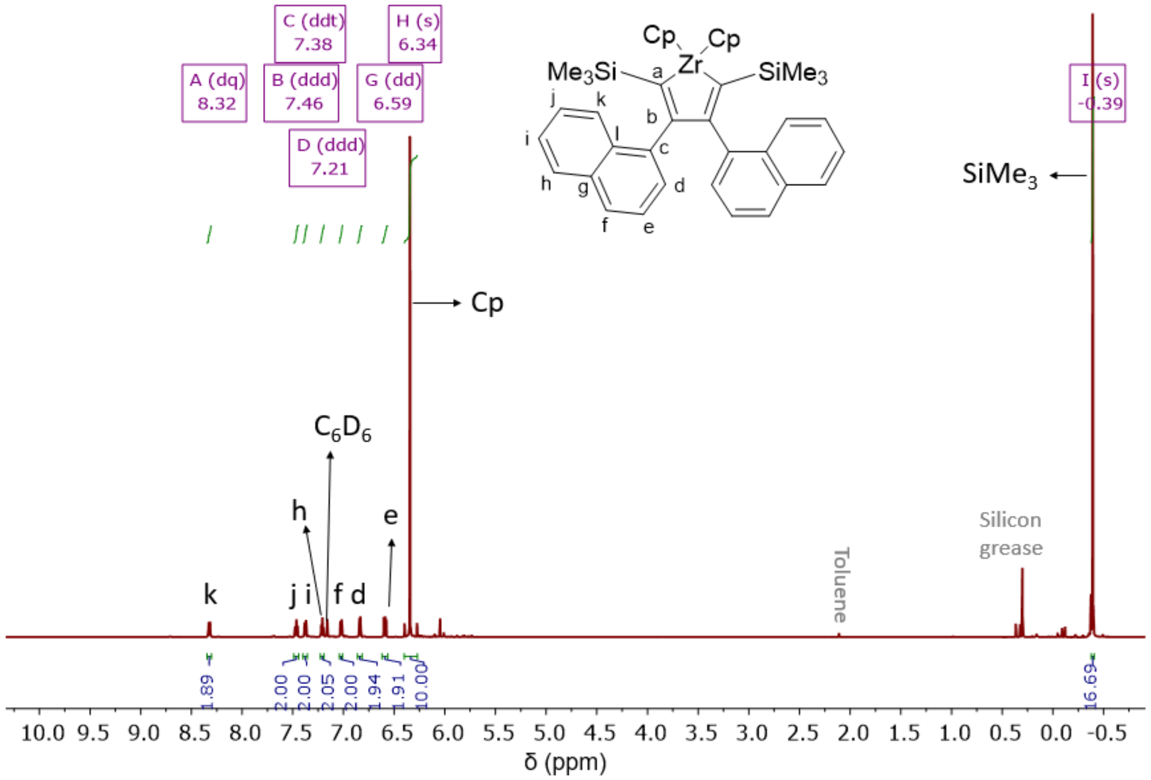

Figure S59. ^{1}H NMR (500 MHz) spectrum of zirconacyclopentadiene **11l** in C_6D_6.

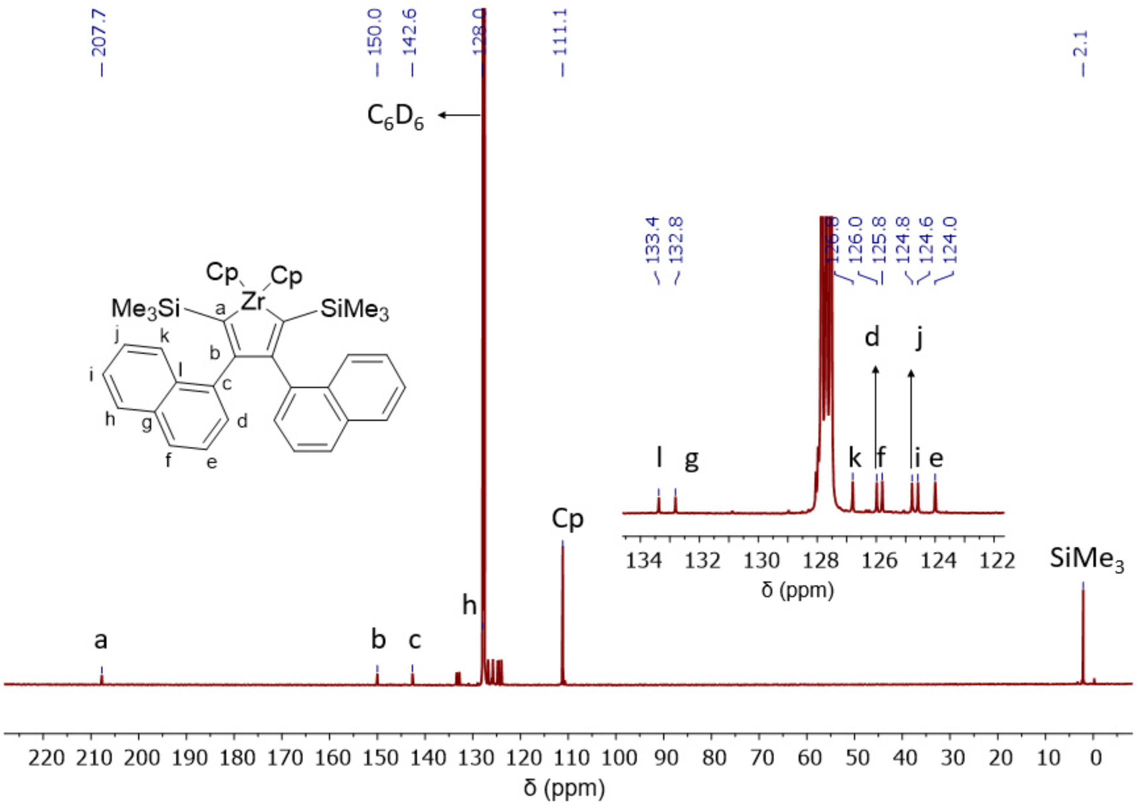

Figure S60. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of zirconacyclopentadiene **11l** in C_6D_6.

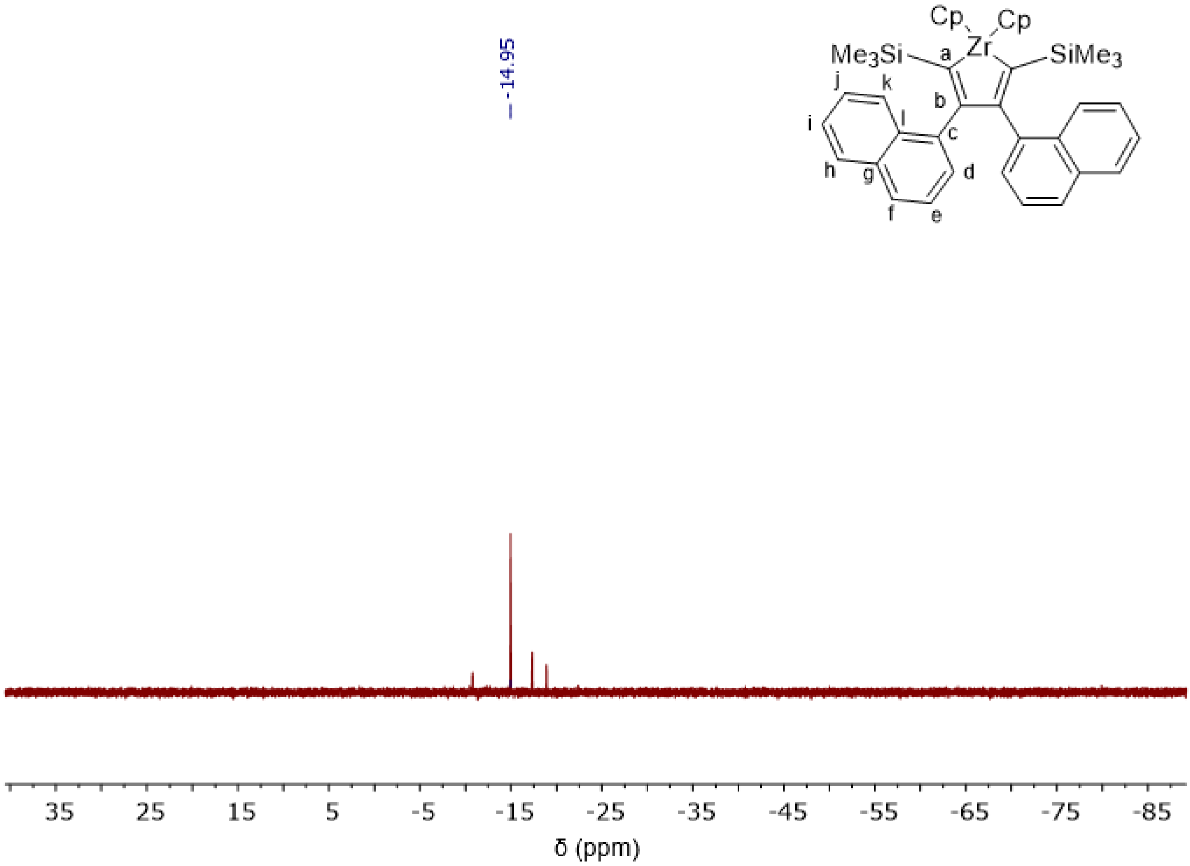

Figure S61. ^{29}Si{^{1}H} NMR (99 MHz) spectrum of zirconacyclopentadiene **11l** in C_6D_6.

6.2 Reaction Monitoring Experiments

Negishi conditions

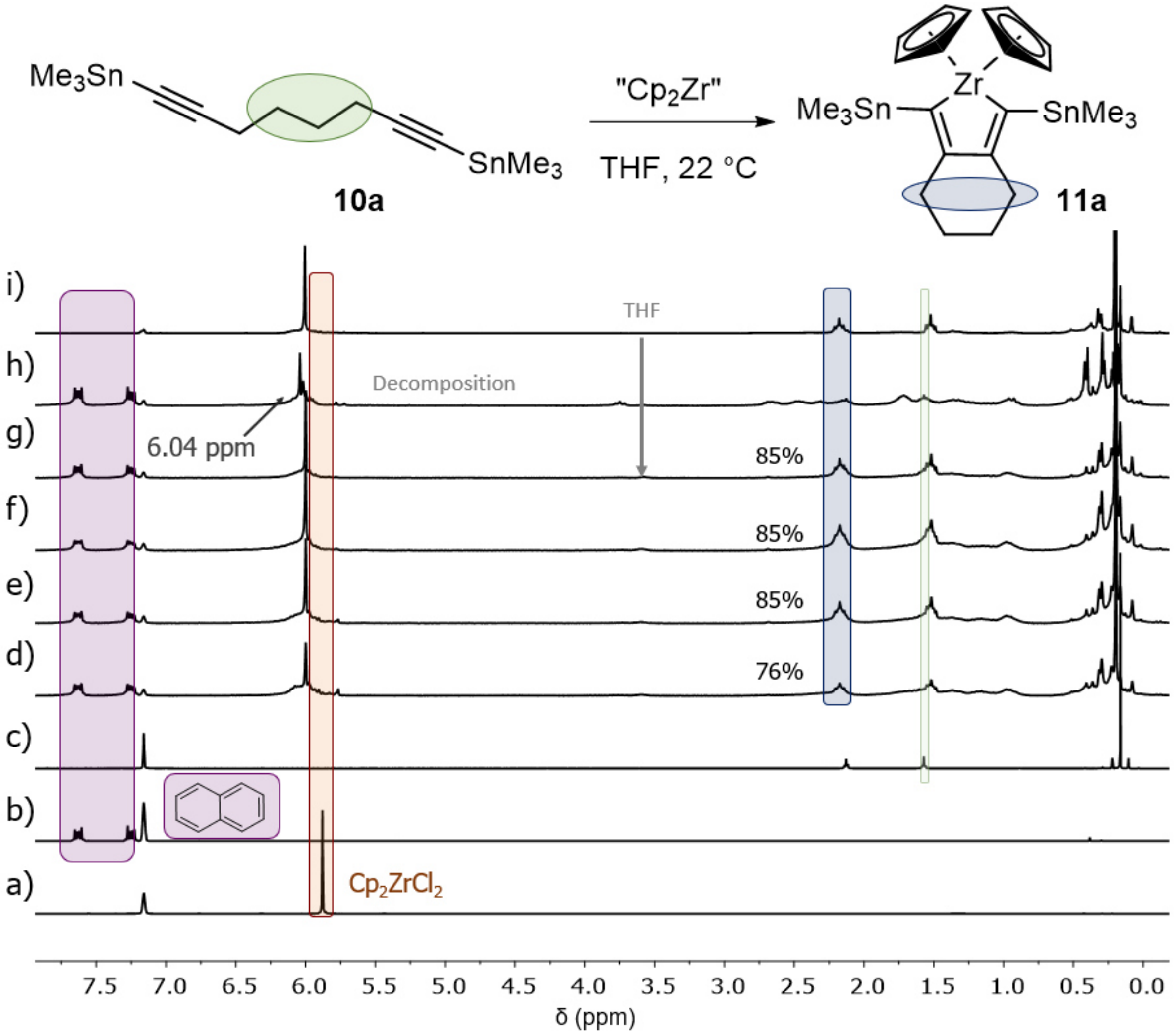

Figure S62. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11a** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10a**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11a** that had been previously isolated.

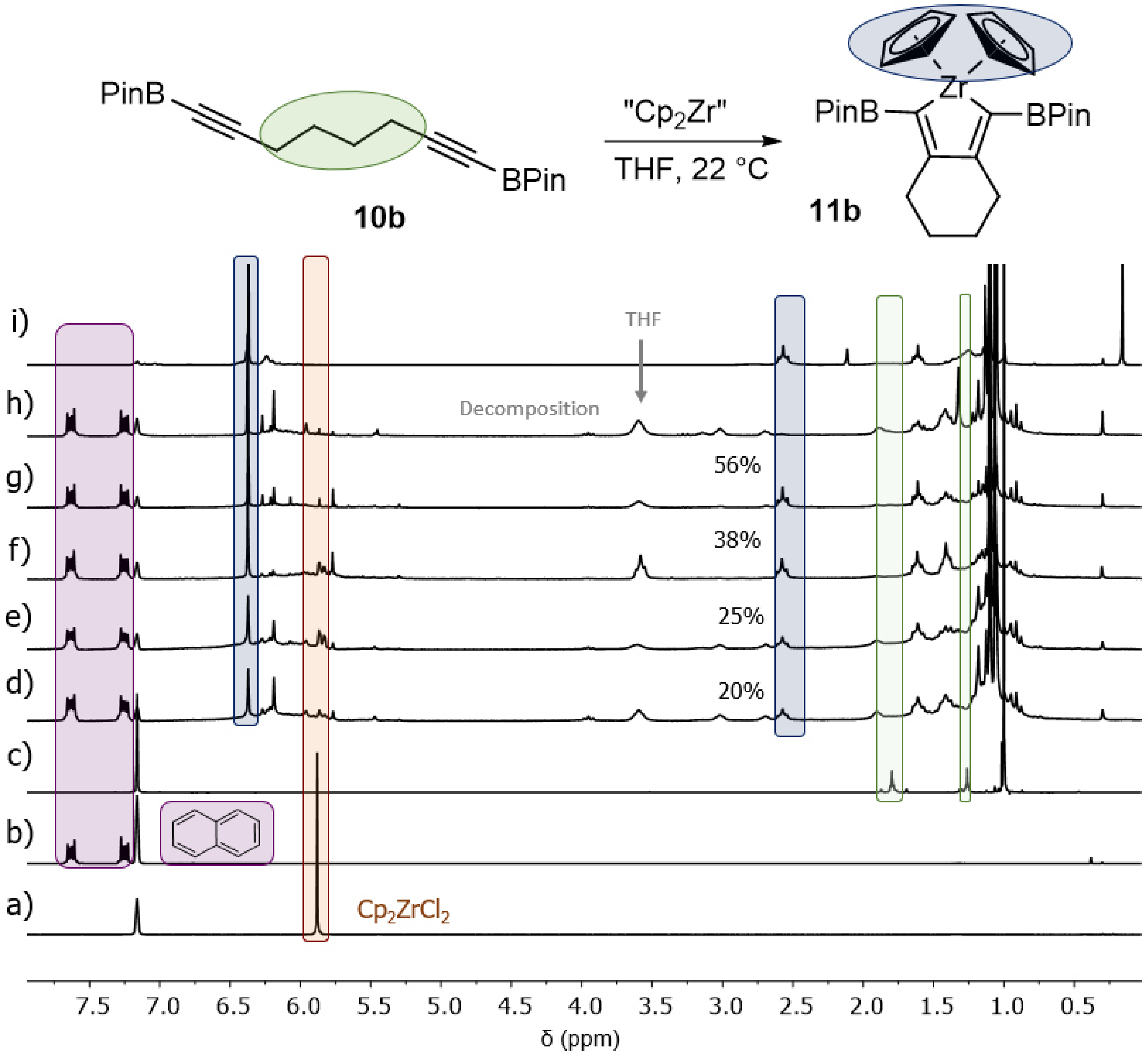

Figure S63. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11b** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10b**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11b** that had been previously isolated.

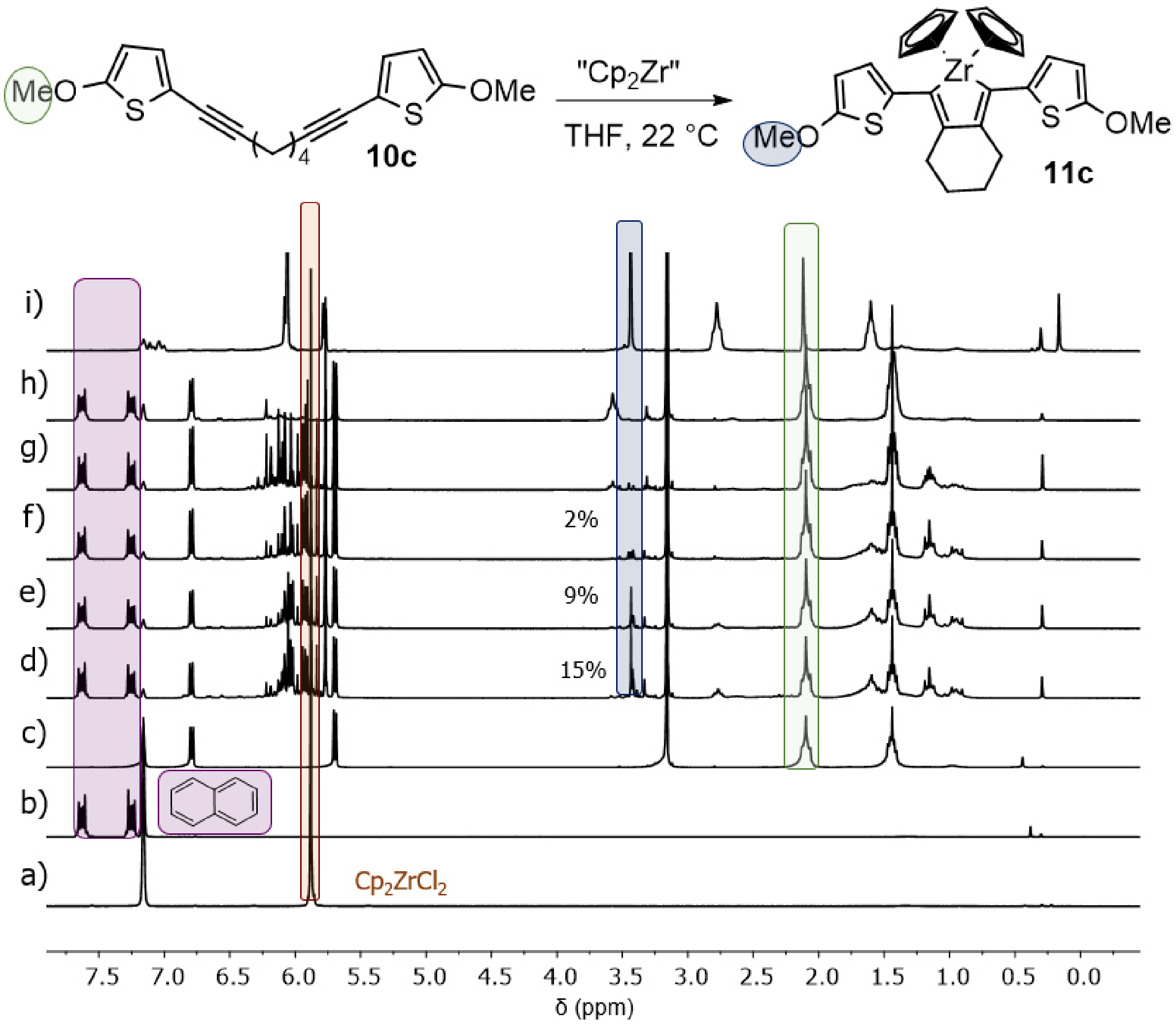

Figure S64.^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11c** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10c**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11c** that had been previously isolated.

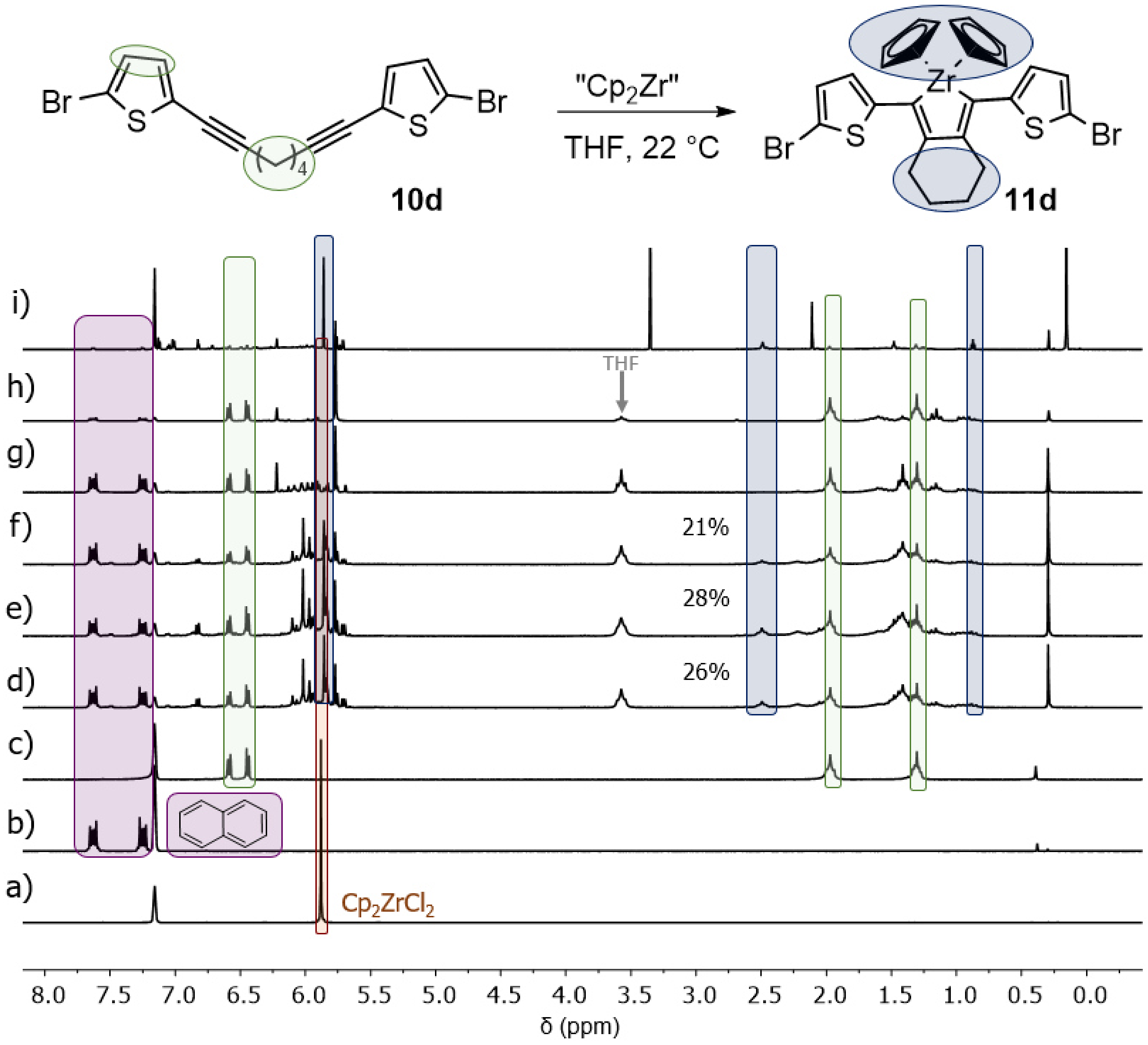

Figure S65. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11d** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10d**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11d** that had been previously isolated.

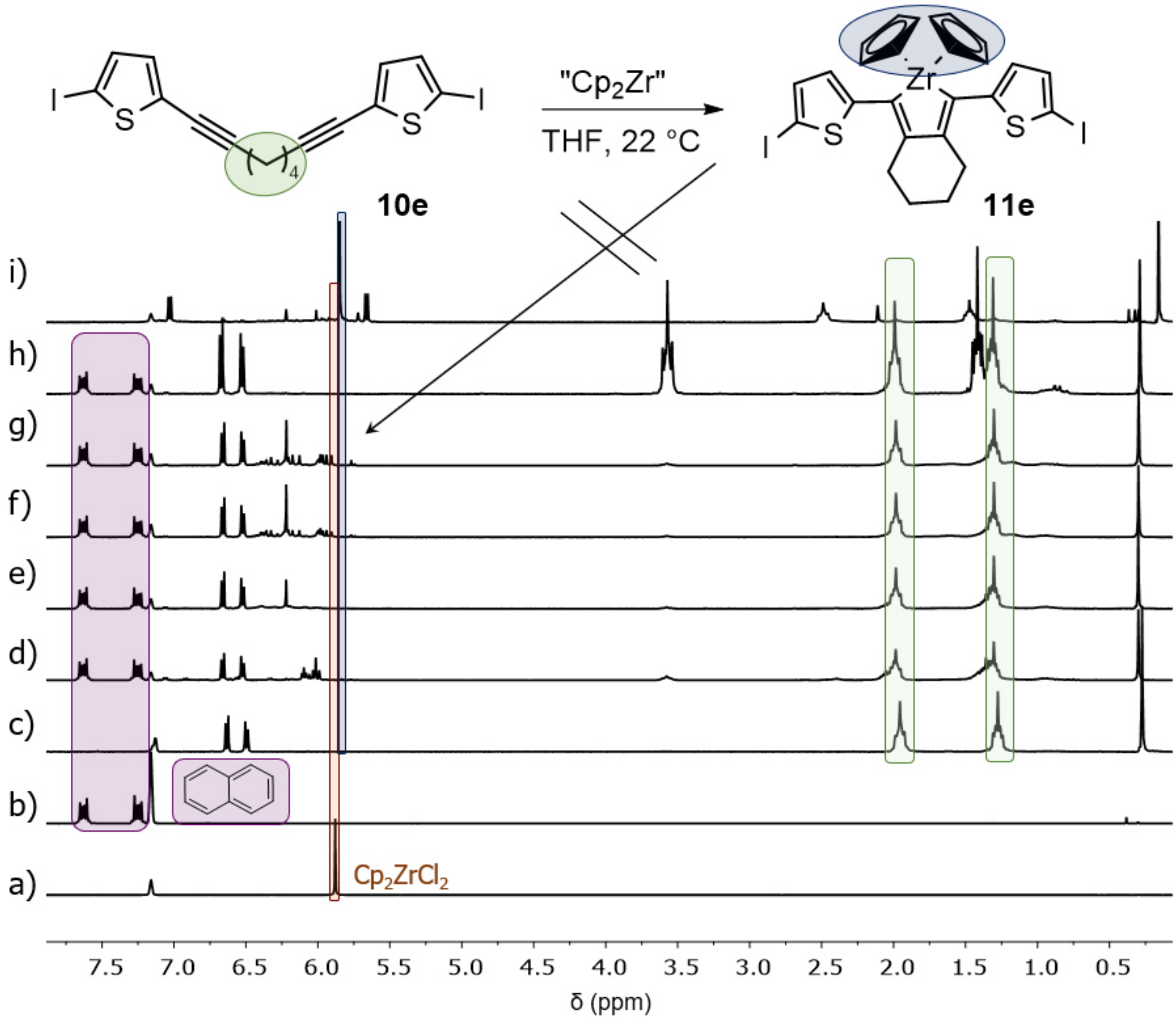

Figure S66. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11e** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10e**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11e** that had been previously isolated.

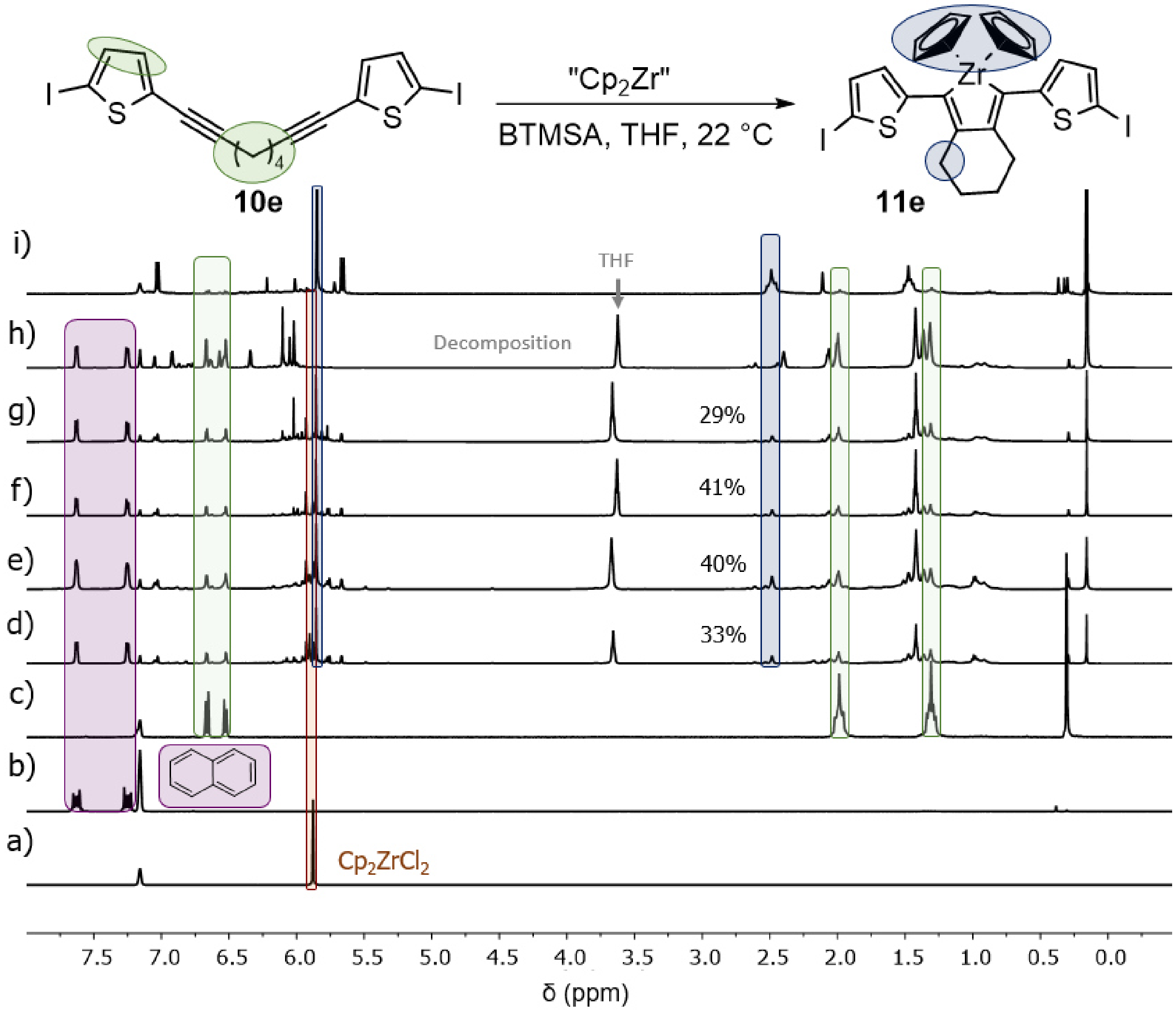

Figure S67. ^{1}H NMR spectra (recorded at 300 K, 600 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11e** using Negishi's reagent and BTMSA as ligand with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10e**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11e** that had been previously isolated.

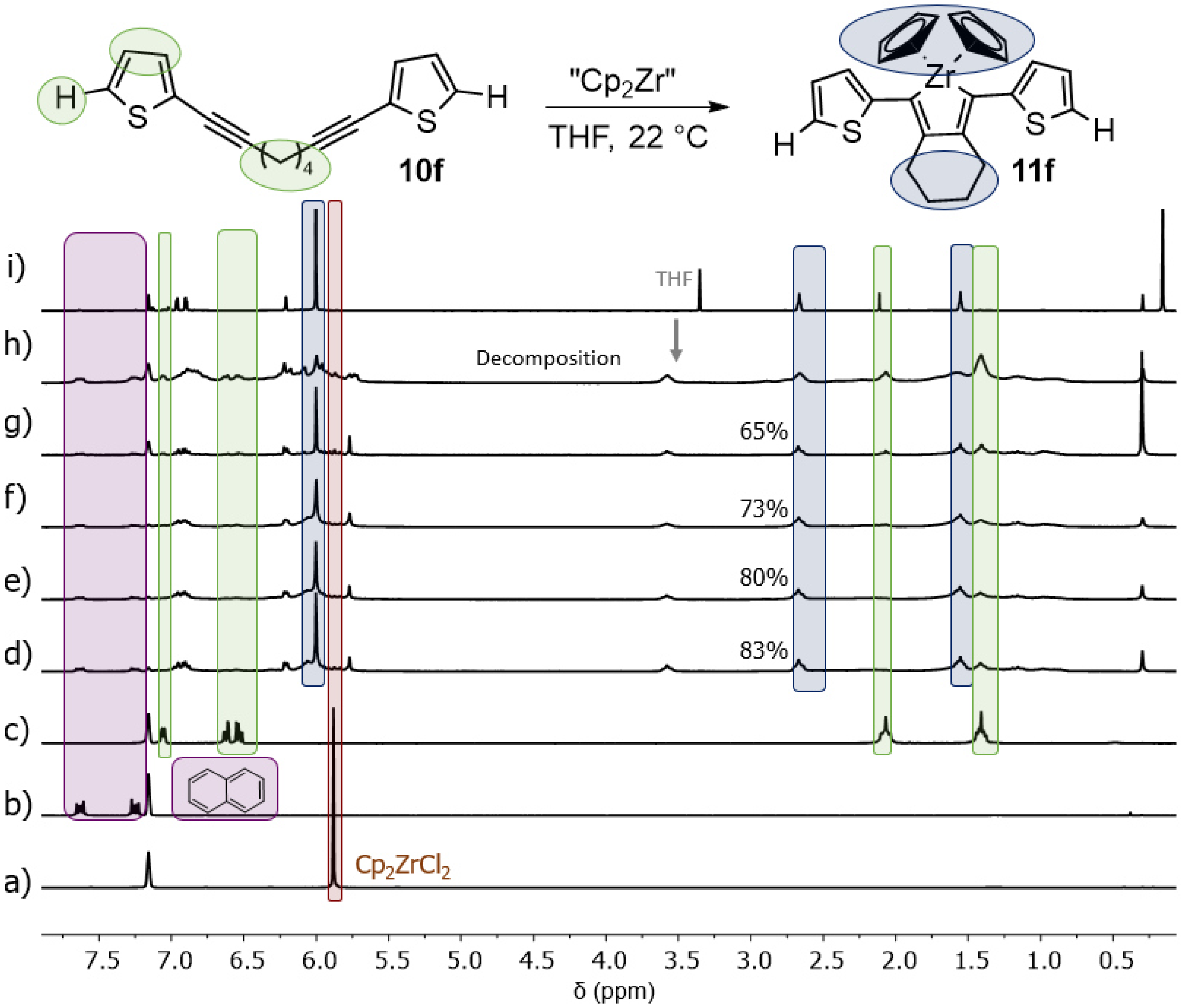

Figure S68. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11f** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10f**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11f** that had been previously isolated.

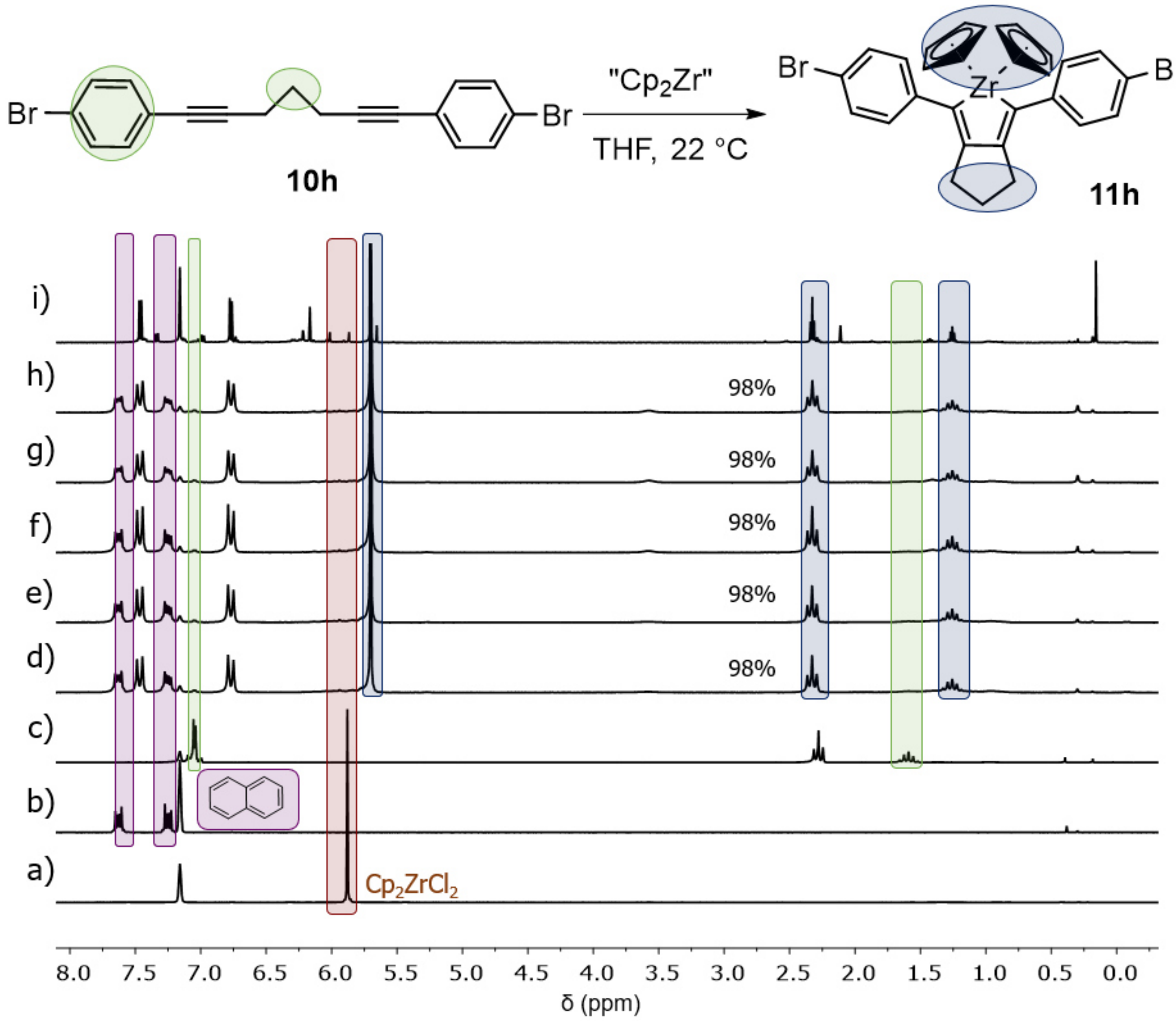

Figure S69. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11h** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10h**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11h** that had been previously isolated.

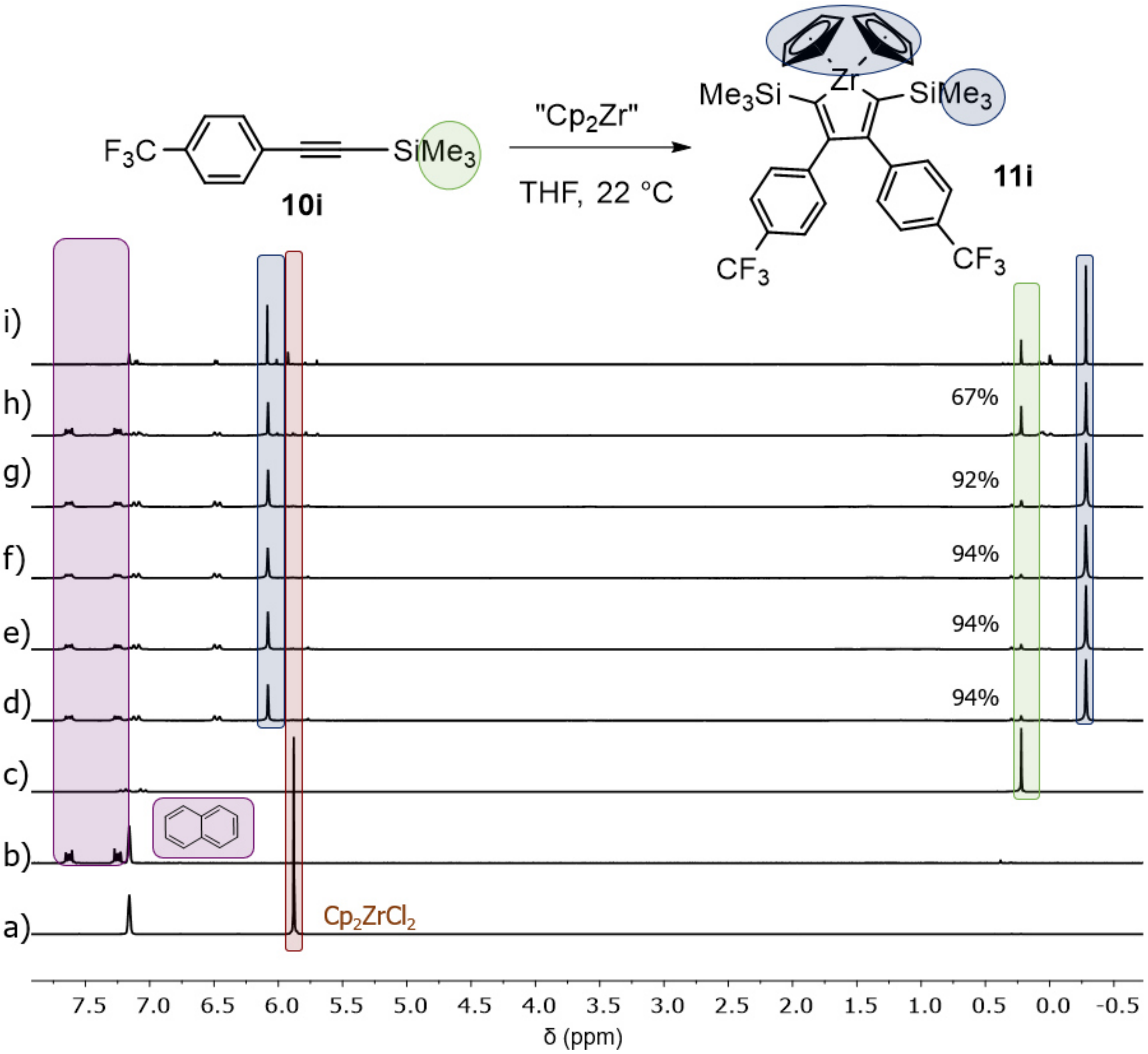

Figure S70. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11i** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10i**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11i** that had been previously isolated.

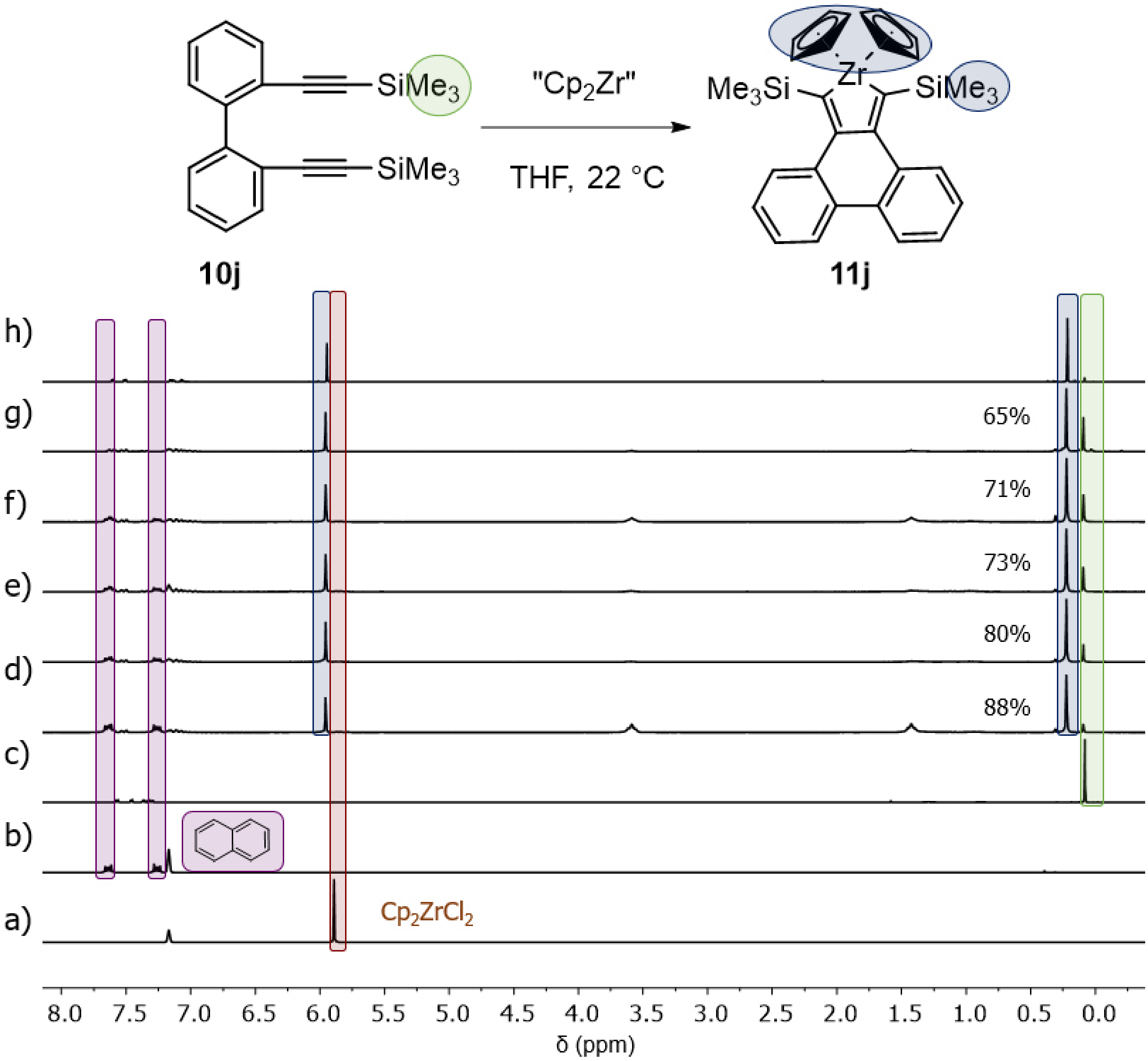

Figure S71. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11j** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10j**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11j** that had been previously isolated.

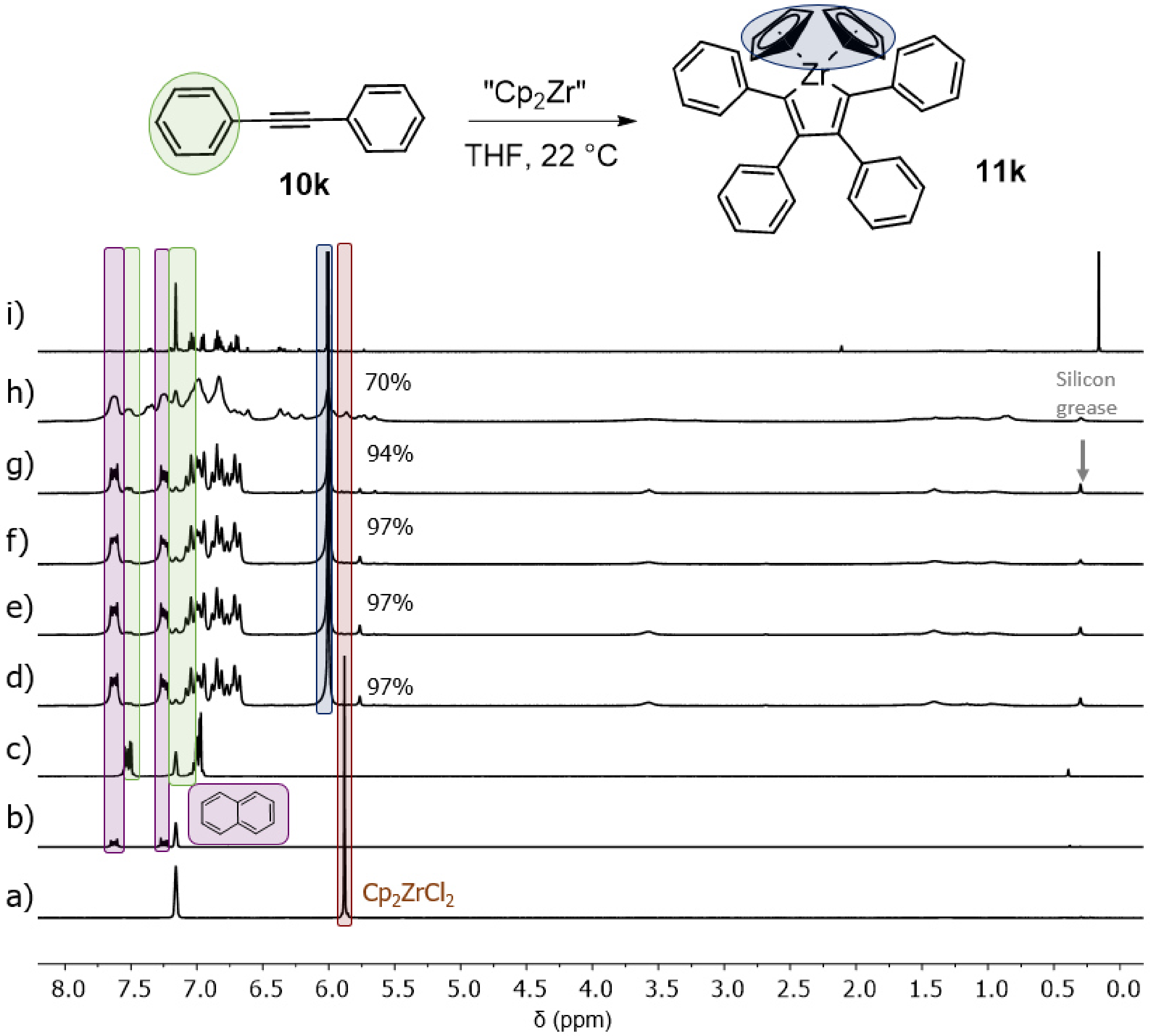

Figure S72. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11k** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10k**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11k** that had been previously isolated.

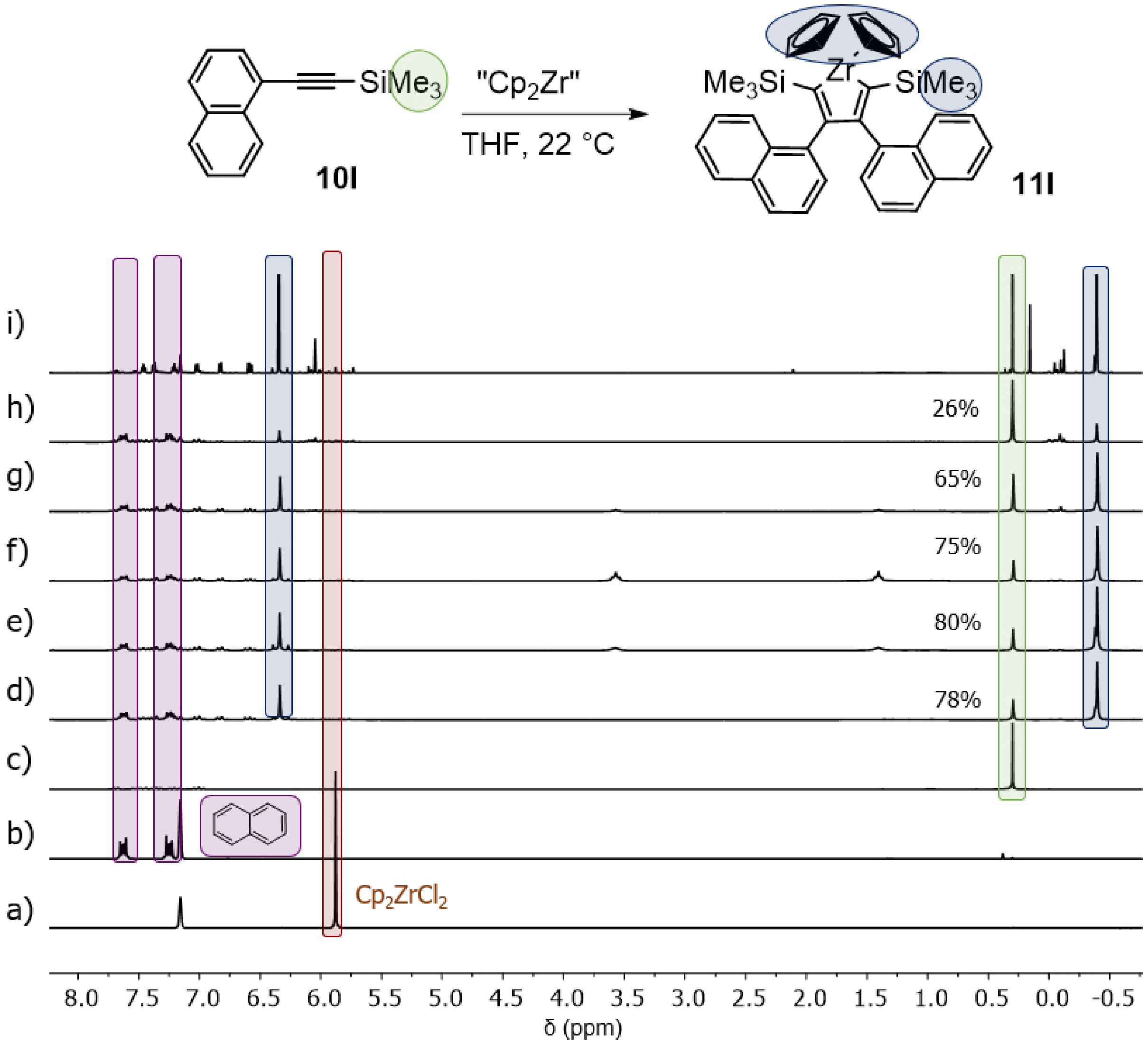

Figure S73. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11l** using Negishi's reagent with naphthalene as standard (1 eq.). a) Starting material Cp_2ZrCl_2. b) Naphthalene. c) Starting material **10l**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h. i) zirconacyclopentadiene **11l** that had been previously isolated.

Rosenthal conditions

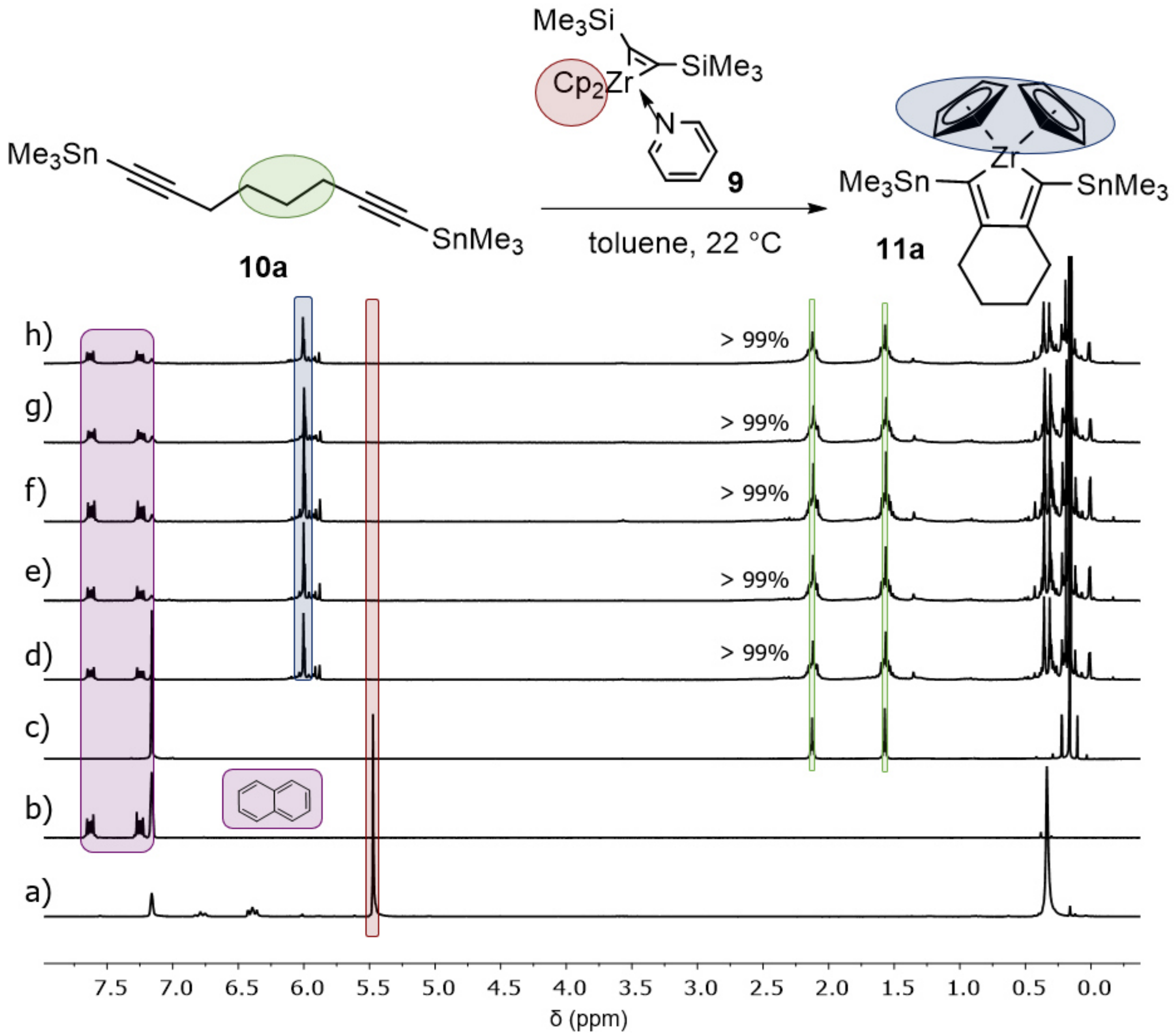

Figure S74.^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11a** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10a**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

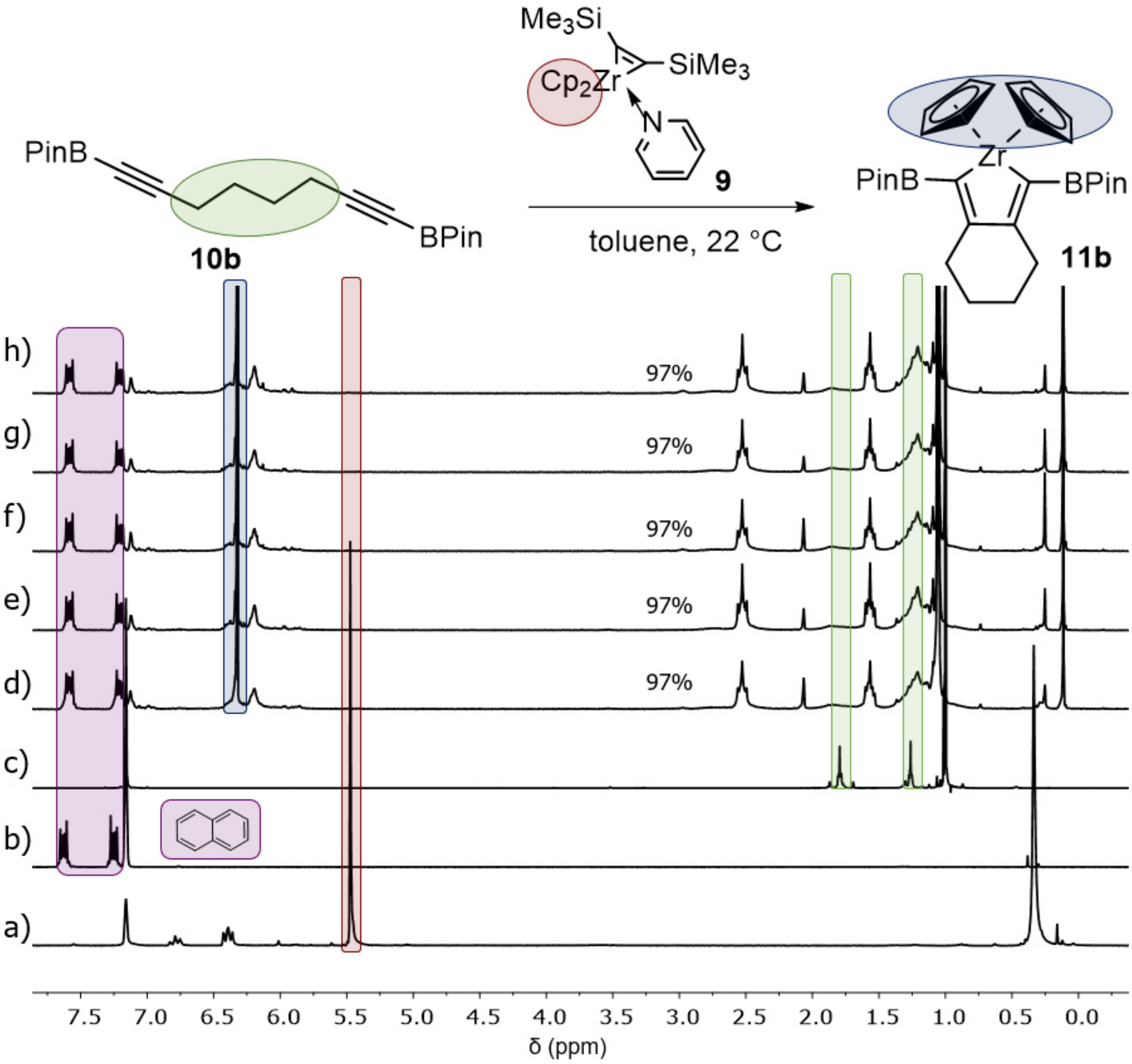

Figure S75. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11b** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10b**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

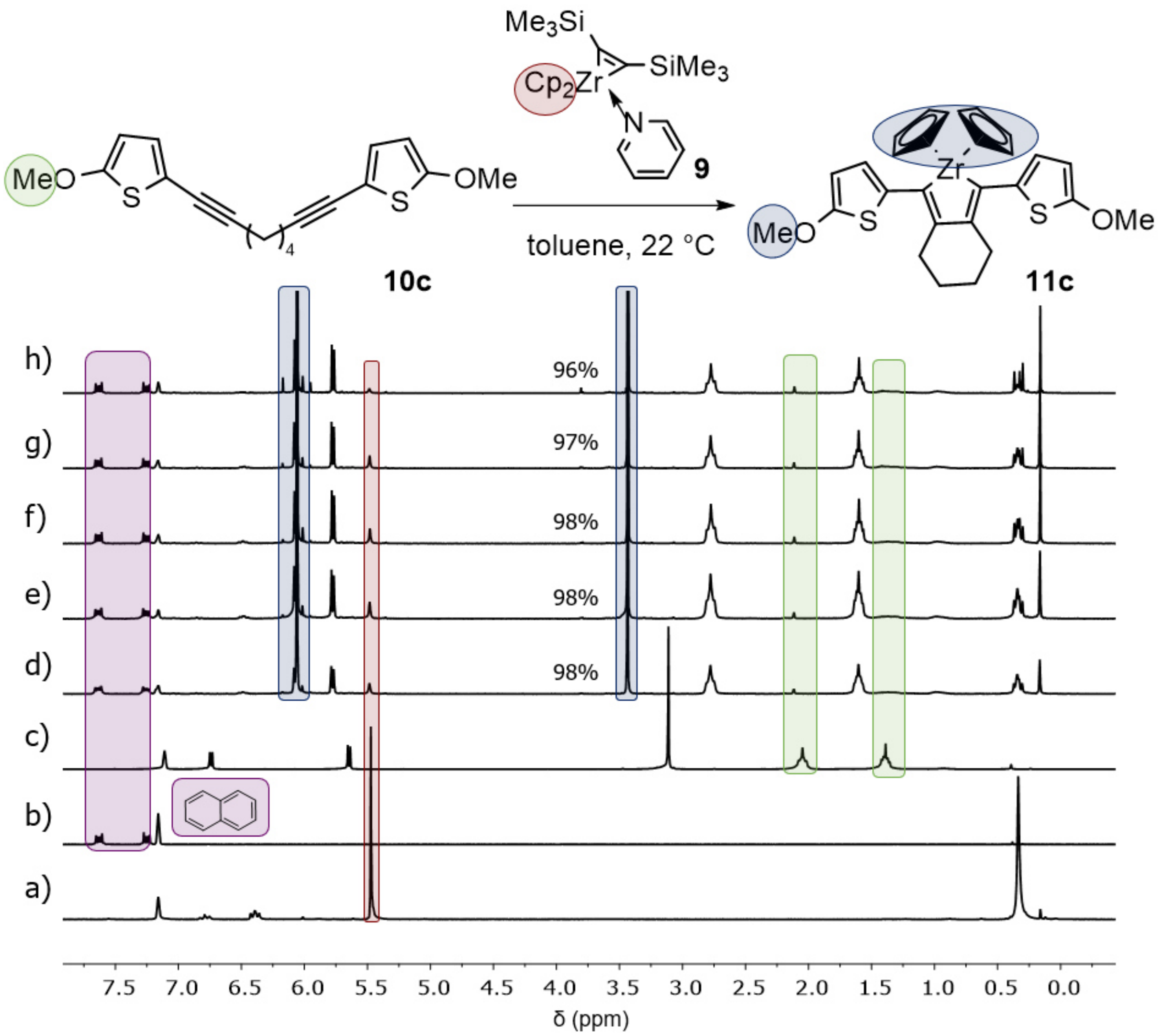

Figure S76. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11c** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10c**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

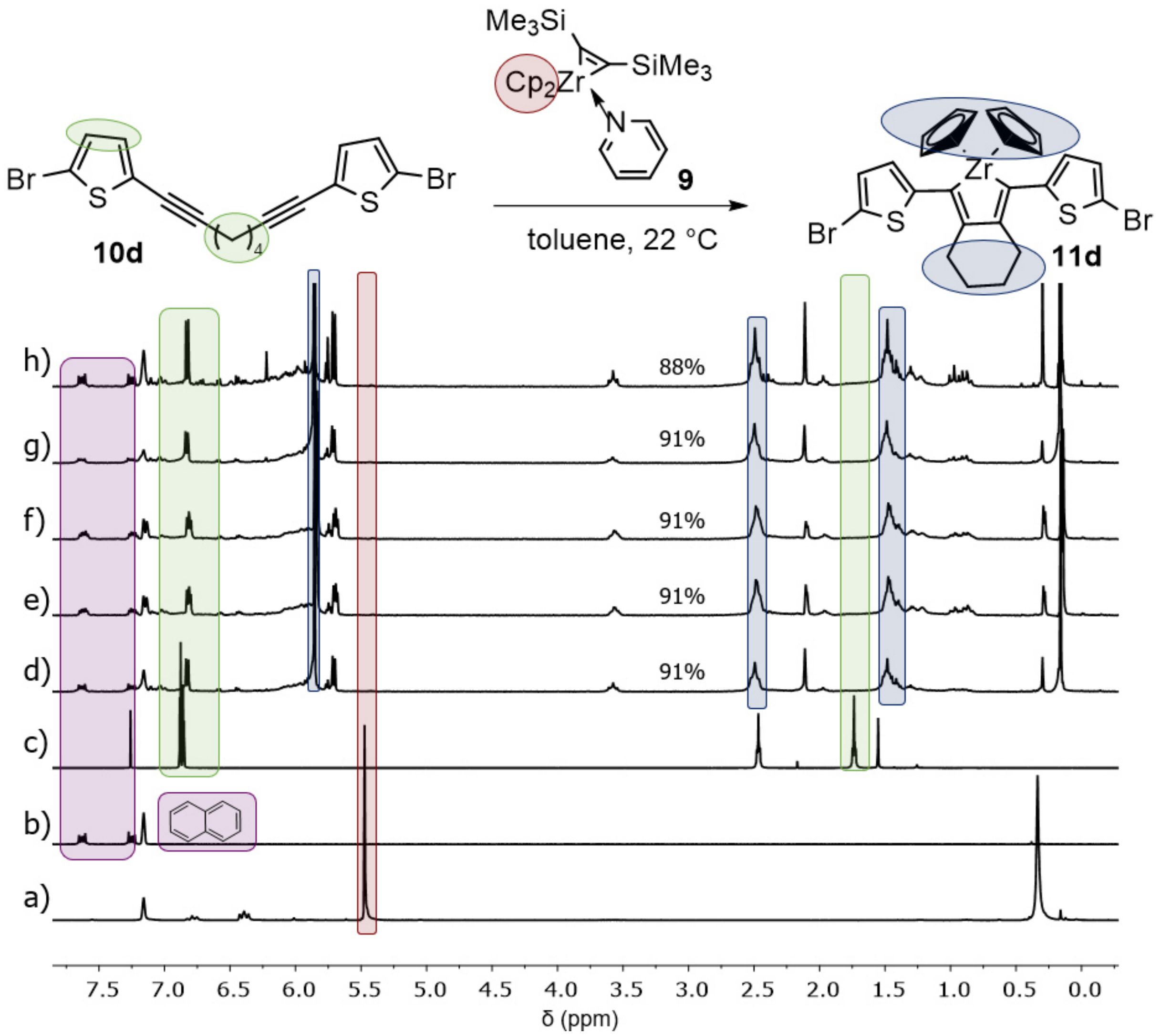

Figure S77.[1]H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11d** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10d**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

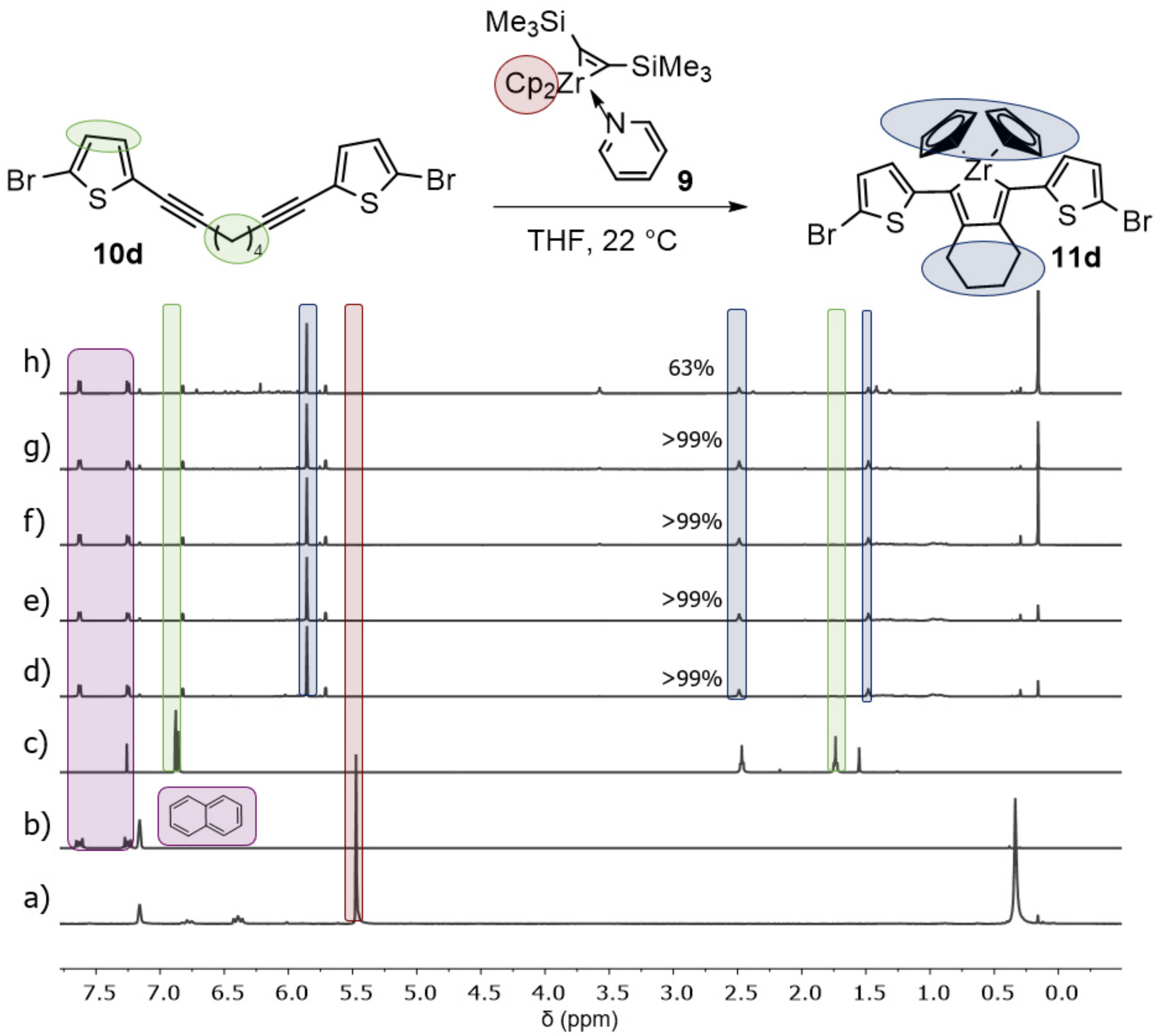

Figure S78. ^{1}H NMR spectra (recorded at 300 K, 600 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11d** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10d**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

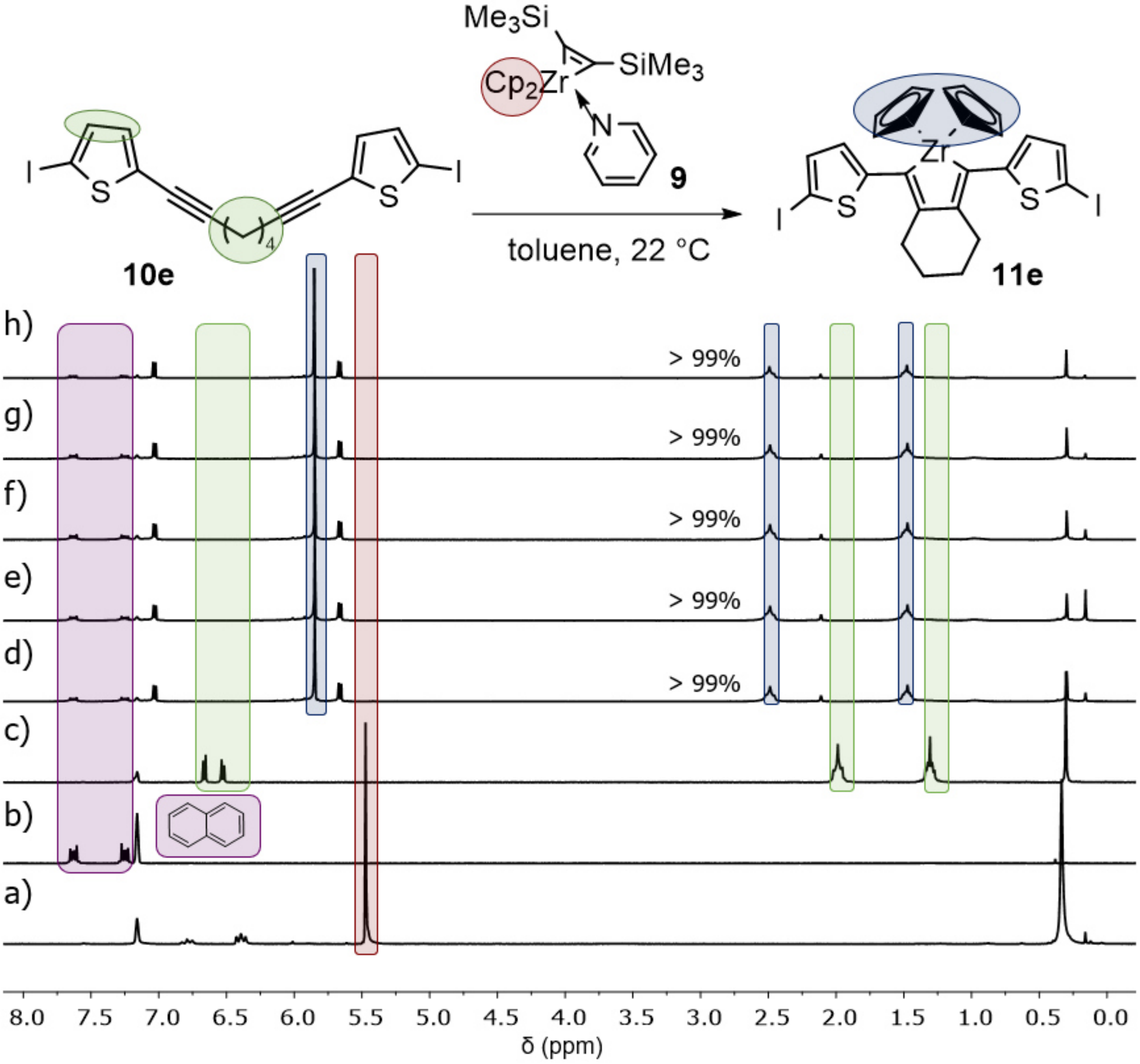

Figure S79. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11e** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10e**. Reaction monitoring after. d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

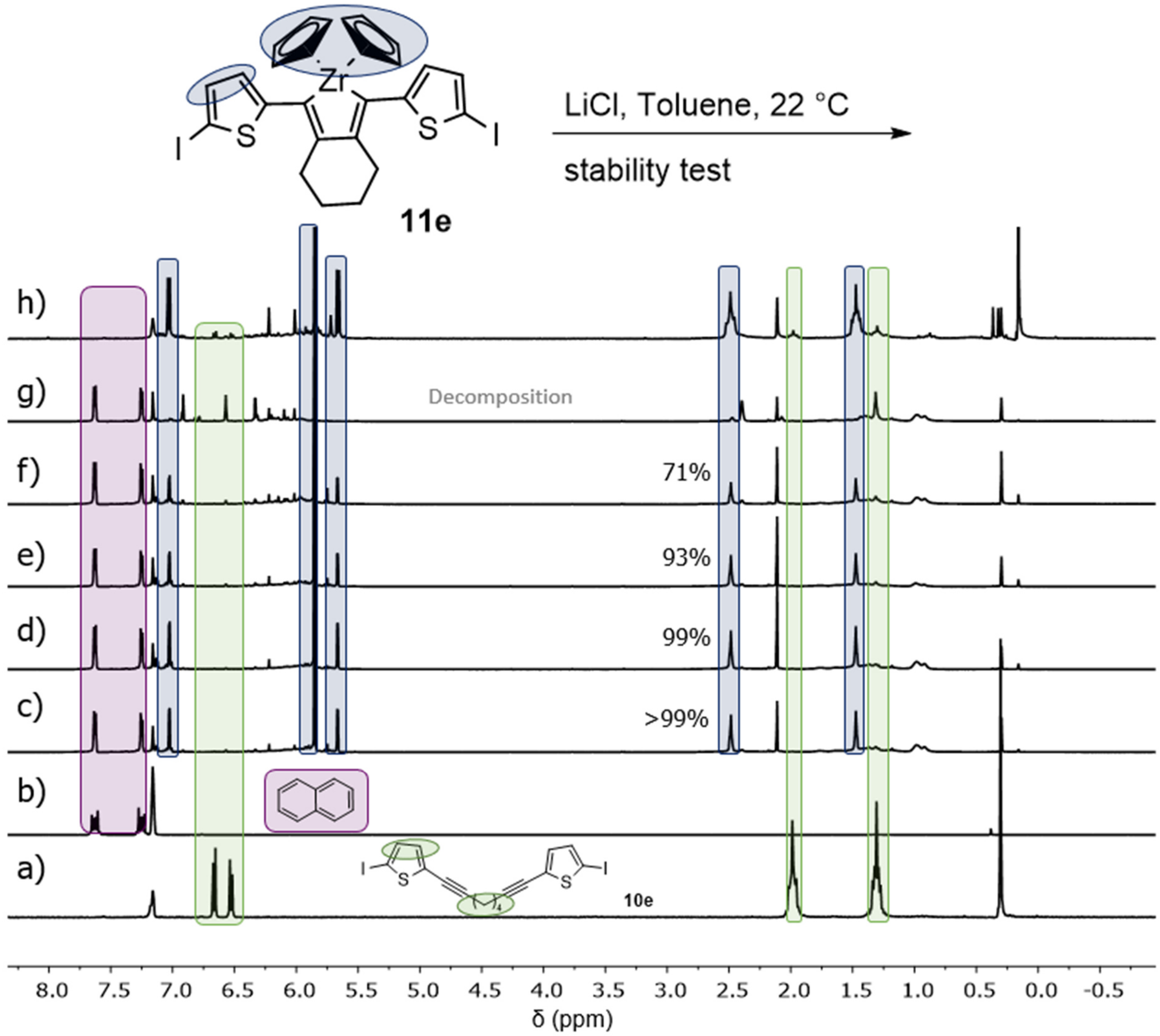

Figure S80. ^{1}H NMR spectra (recorded at 300 K, 600 MHz in C_6D_6) of the reaction monitoring for the stability test of zirconacyclopentadiene **11e** with naphthalene as standard (1 eq.). a) Naphthalene. b) Starting material **10e**. Reaction monitoring after. c) 10 min. d) 30 min. e) 1 h. f) 3 h. g) 22 h. and h) isolated zirconacyclopentadiene **11e**.

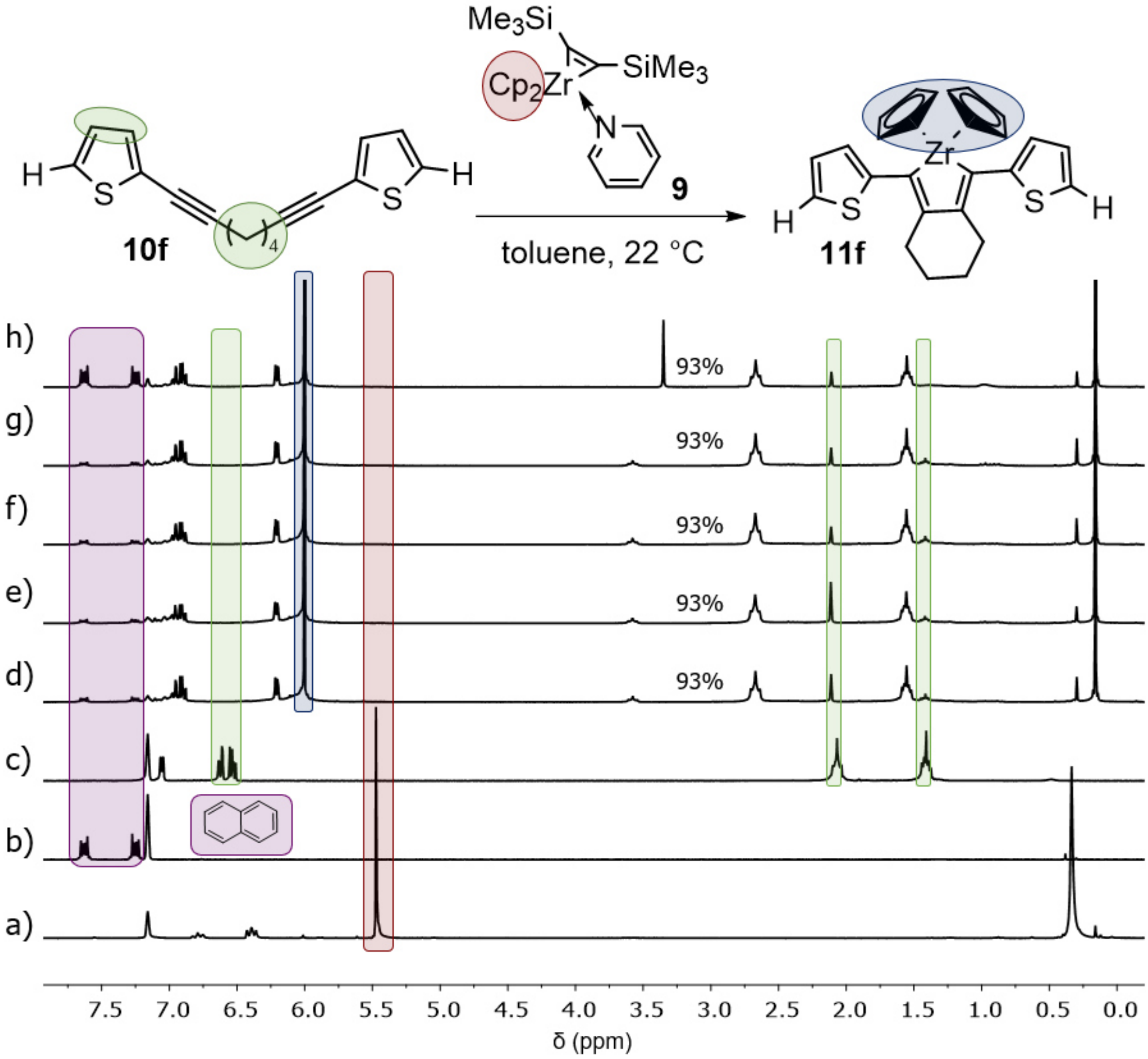

Figure S81. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11f** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10f**. Reaction monitoring after. d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

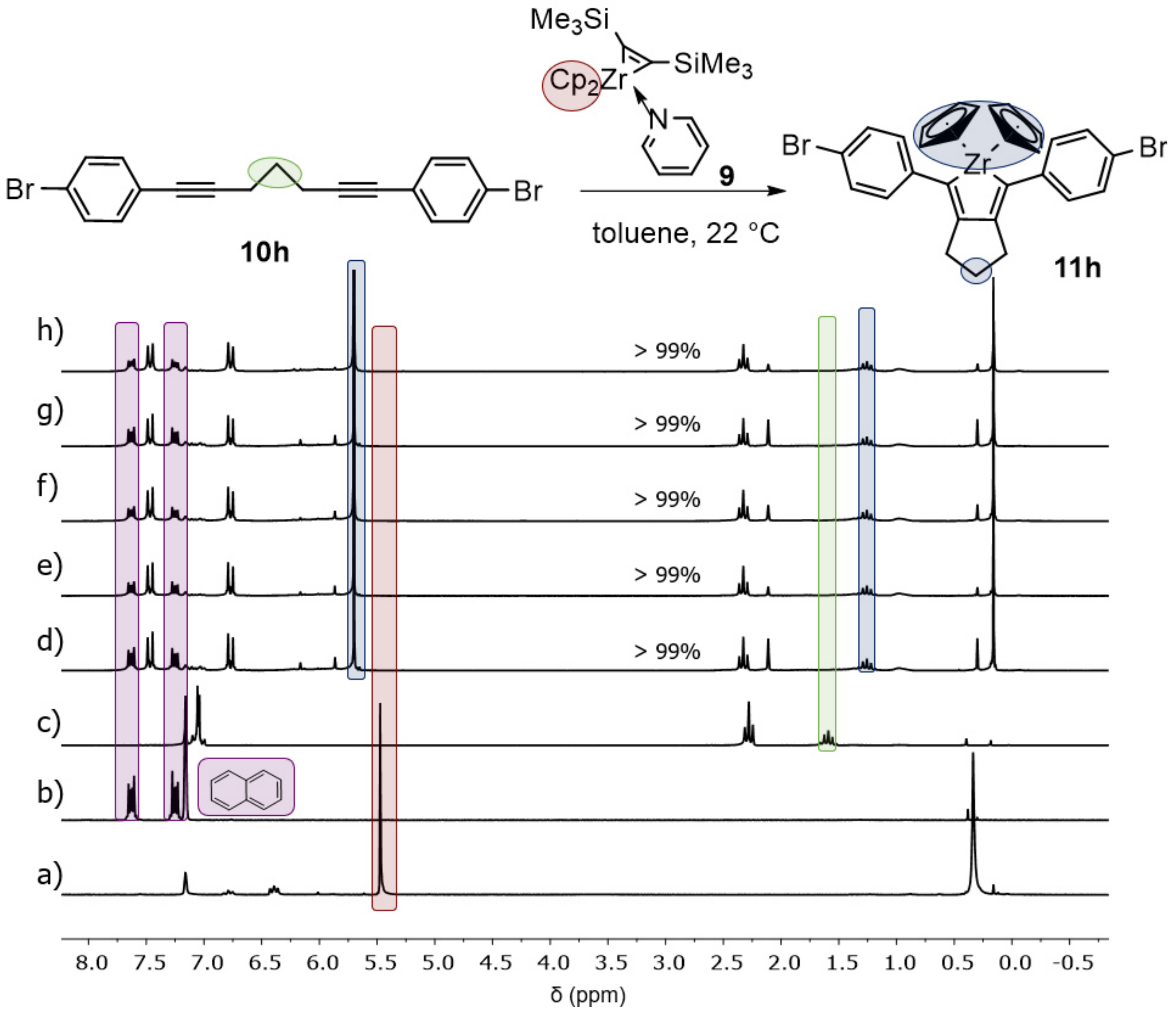

Figure S82. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11h** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10h**. Reaction monitoring after. d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

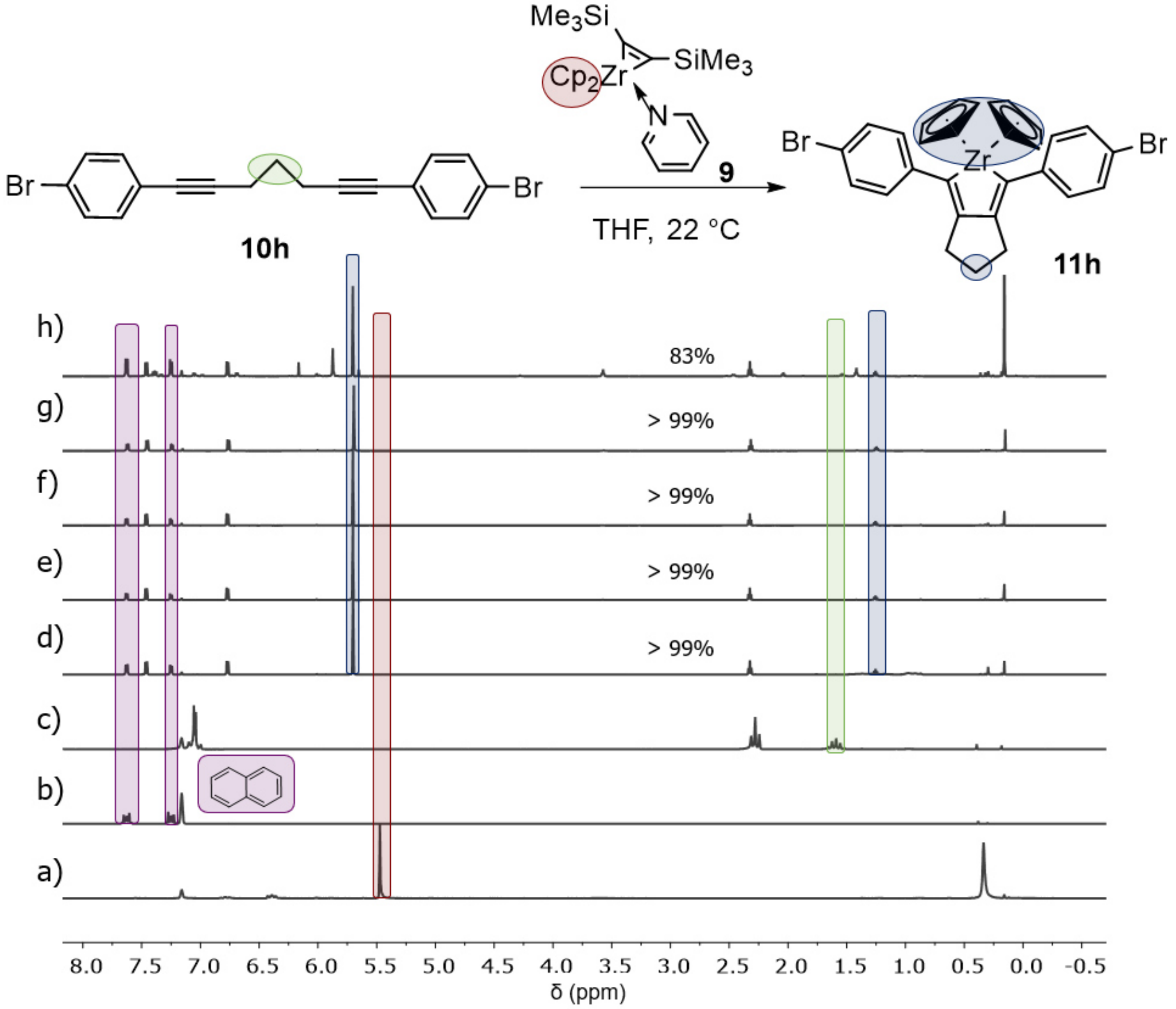

Figure 83. ^{1}H NMR spectra (recorded at 300 K, 600 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11h** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10h**. Reaction monitoring after. d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

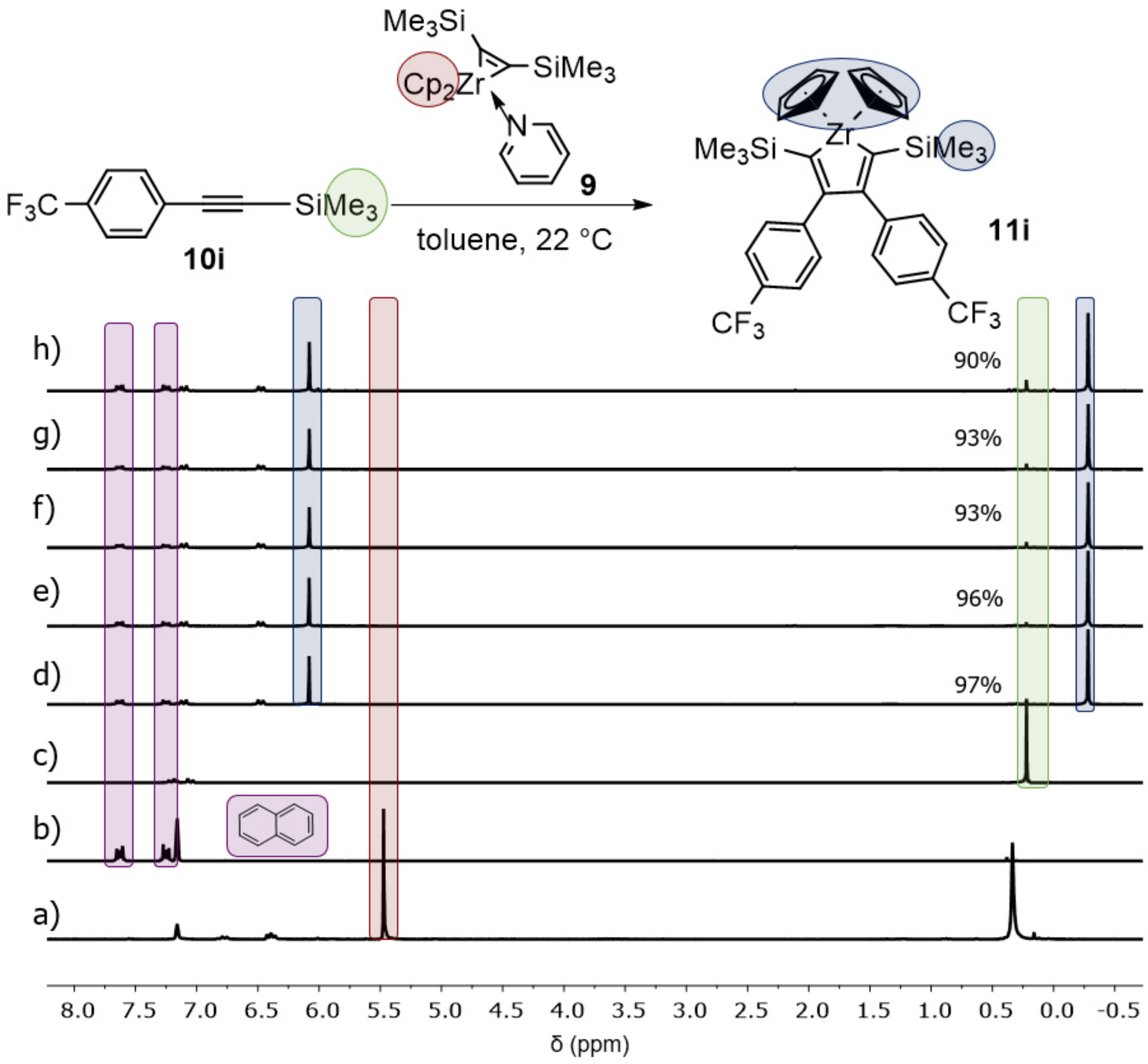

Figure S84. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11i** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10i**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

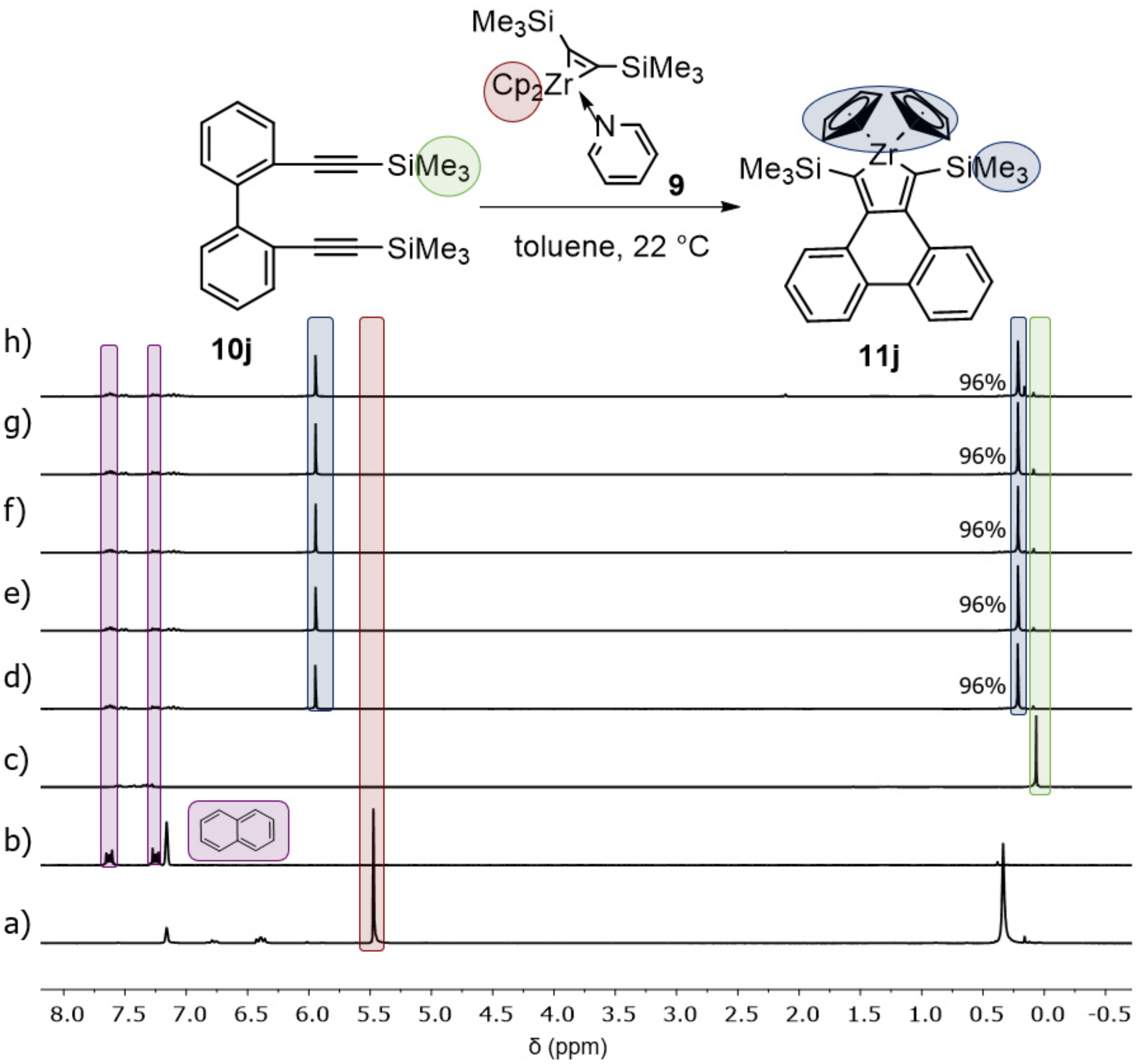

Figure S85. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11j** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10j**. Reaction monitoring after. d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

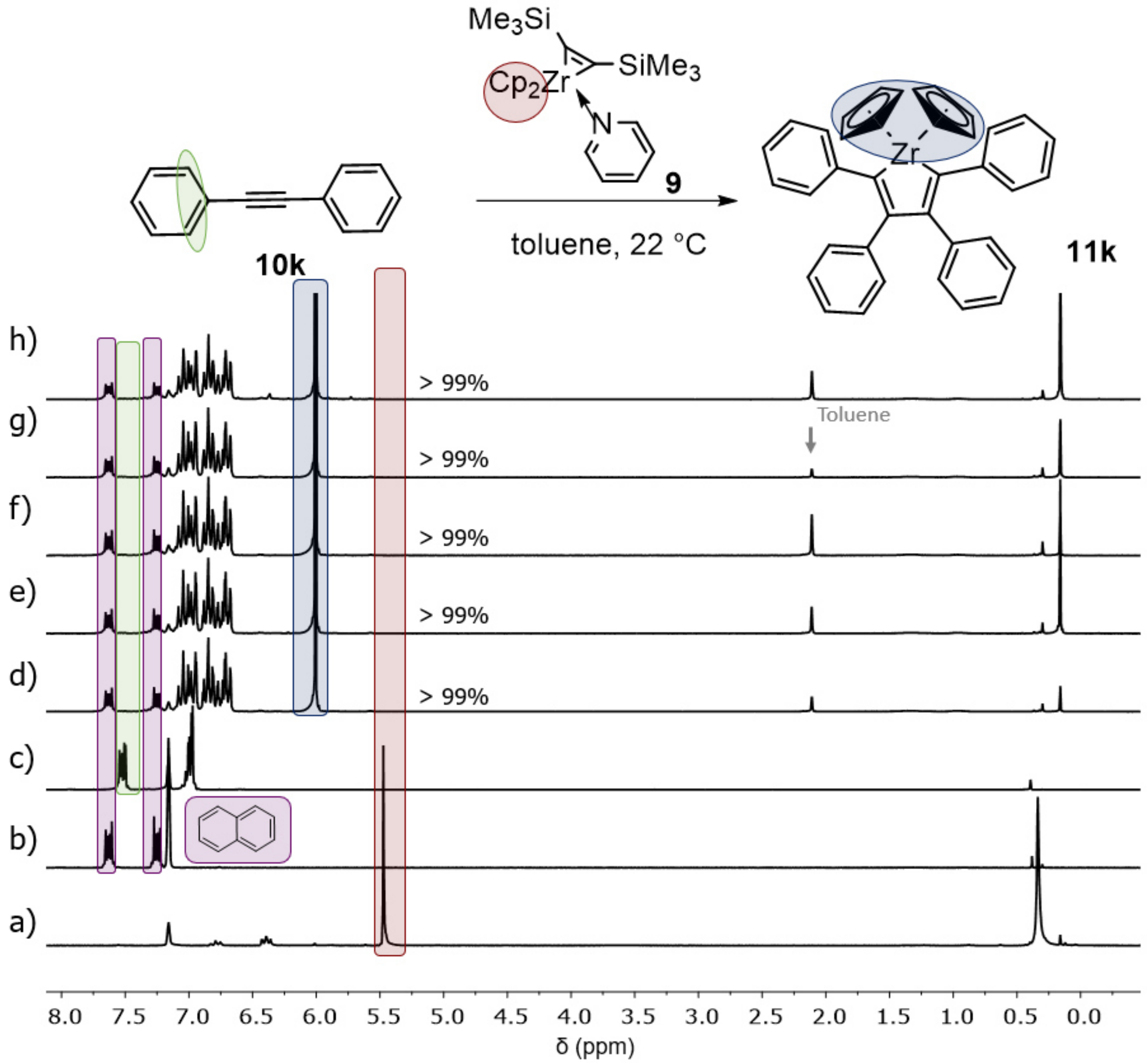

Figure S86. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11k** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (9). b) Naphthalene. c) Starting material **10k**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

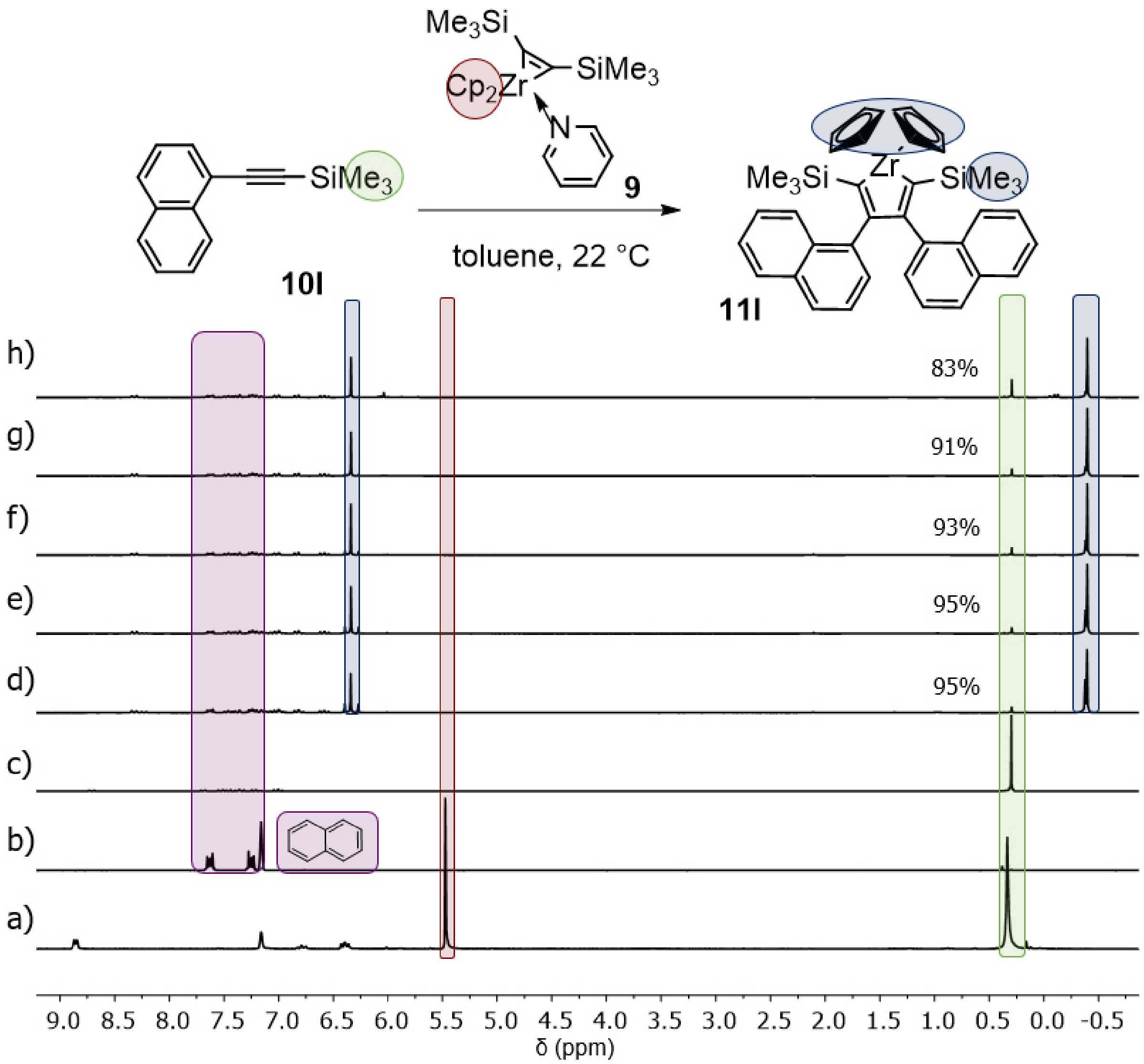

Figure S87. ^{1}H NMR spectra (recorded at 300 K, 200 MHz in C_6D_6) of the reaction monitoring for the synthesis of zirconacyclopentadiene **11l** using Rosenthal's reagent with naphthalene as standard (1 eq.). a) Rosenthal's reagent (**9**). b) Naphthalene. c) Starting material **10l**. Reaction monitoring after d) 10 min. e) 30 min. f) 1 h. g) 3 h and h) 22 h.

6.3 Air Stability Tests

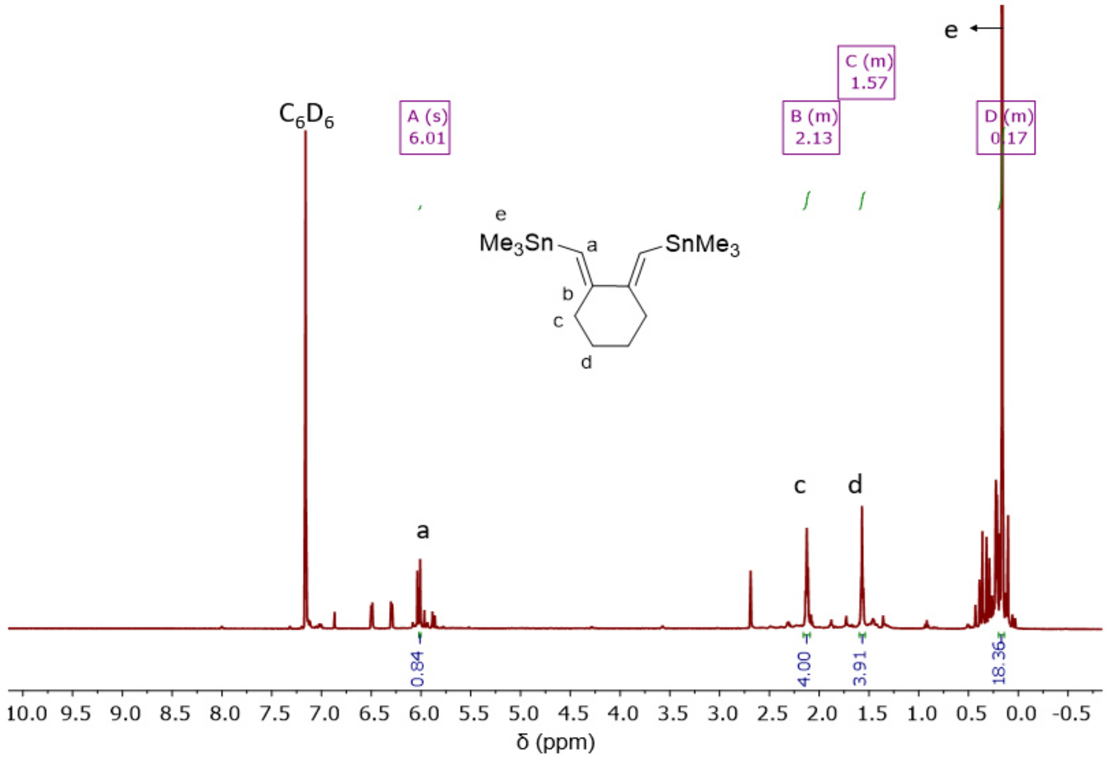

Figure S88. ^{1}H NMR (500 MHz) spectrum of (1*E*,2*E*)-1,2-bis((trimethylstannyl)methylene)cyclohexane main product in the decomposition of zirconacyclopentadiene **11a** under air, in C_6D_6.

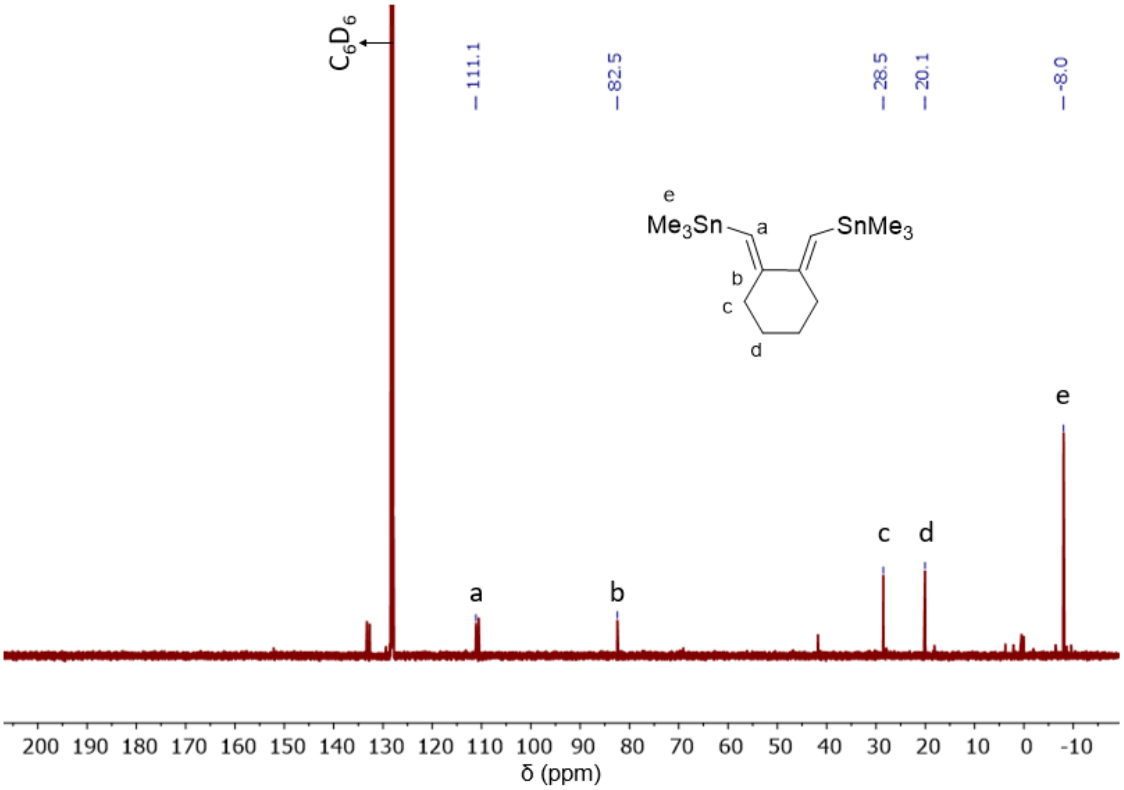

Figure S89. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of (1*E*,2*E*)-1,2-bis((trimethylstannyl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11a** under air, in C_6D_6.

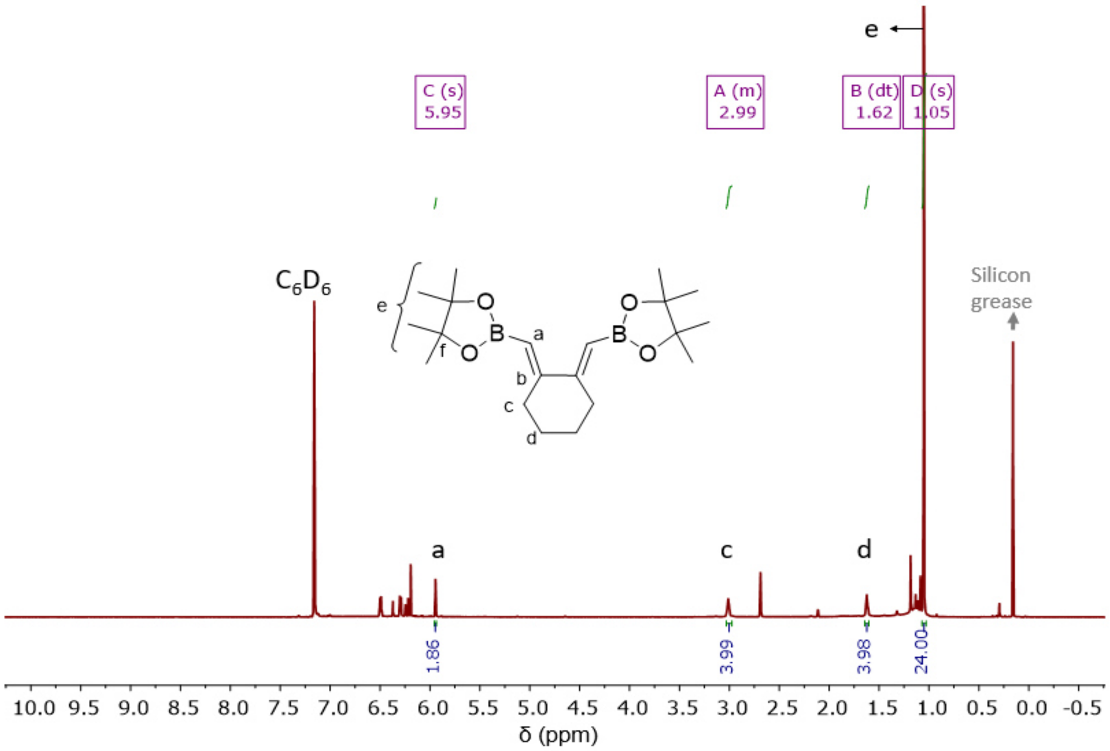

Figure S90. ^{1}H NMR (500 MHz) spectrum of (1*E*,2*E*)-1,2-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11b** under air, in C_6D_6.

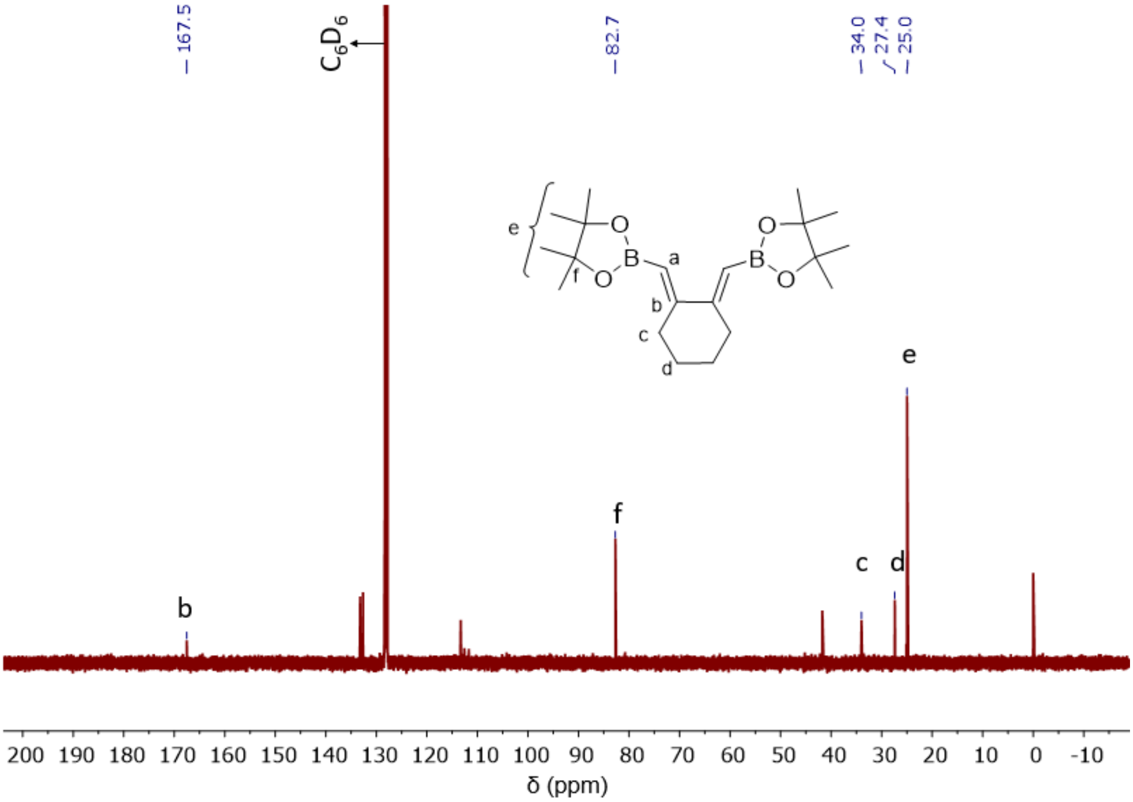

Figure S91. ^{13}C{^{1}H} NMR (126 MHz) spectrum of (1*E*,2*E*)-1,2-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11b** under air, in C_6D_6.

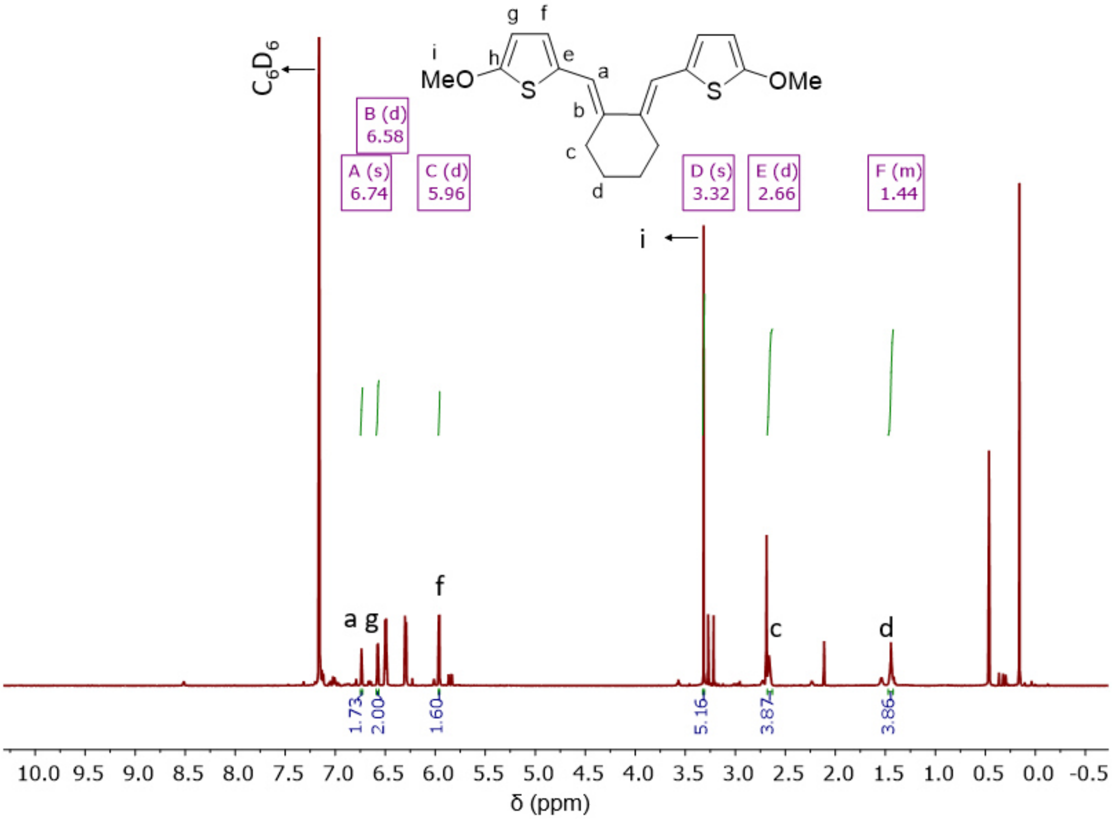

Figure S92. ^{1}H NMR (500 MHz) spectrum of (1*E*, 2*E*)-1, 2-bis ((5-methoxythiophen-2-yl) methylene) cyclohexane main product of the decomposition of zirconacyclopentadiene **11c** under air, in C$_6$D$_6$.

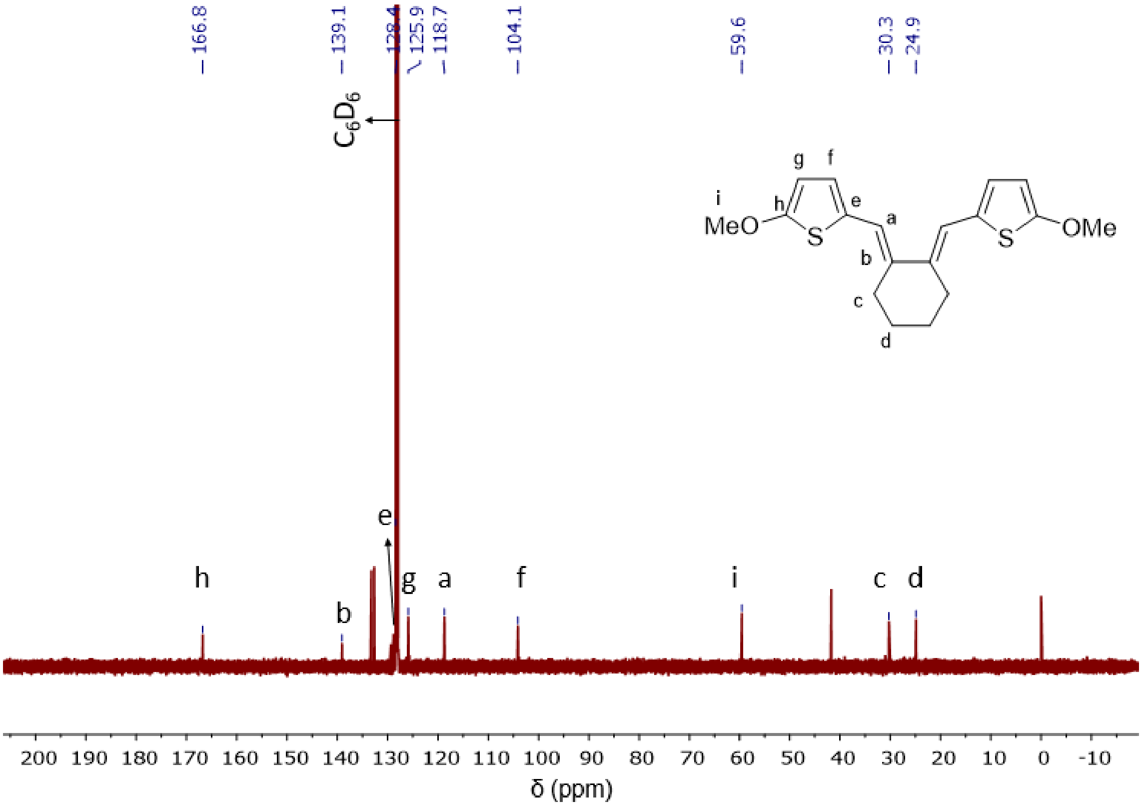

Figure S93. ^{13}C{^{1}H} NMR (126 MHz) spectrum of (1*E*, 2*E*)-1, 2-bis ((5-methoxythiophen-2-yl) methylene) cyclohexane main product of the decomposition of zirconacyclopentadiene **11c** under air, in C$_6$D$_6$.

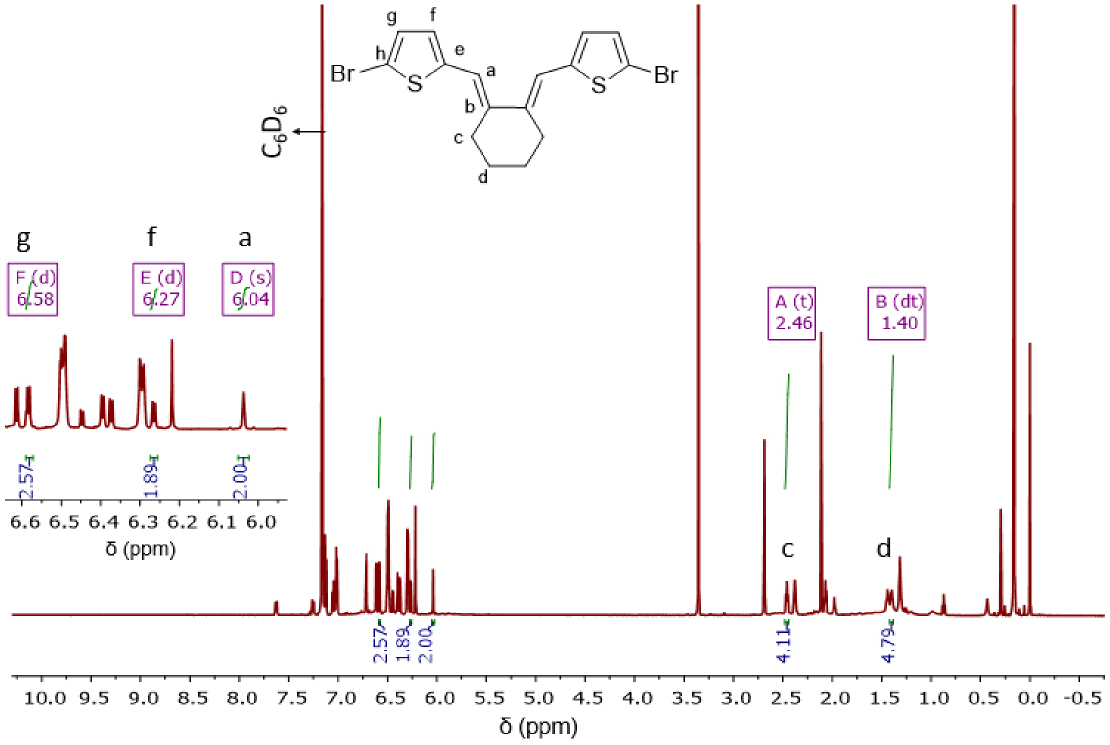

Figure S94. ^{1}H NMR (500 MHz) spectrum of (1*E*,2*E*)-1,2-bis((5-bromothiophen-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11d** under air, in C_6D_6.

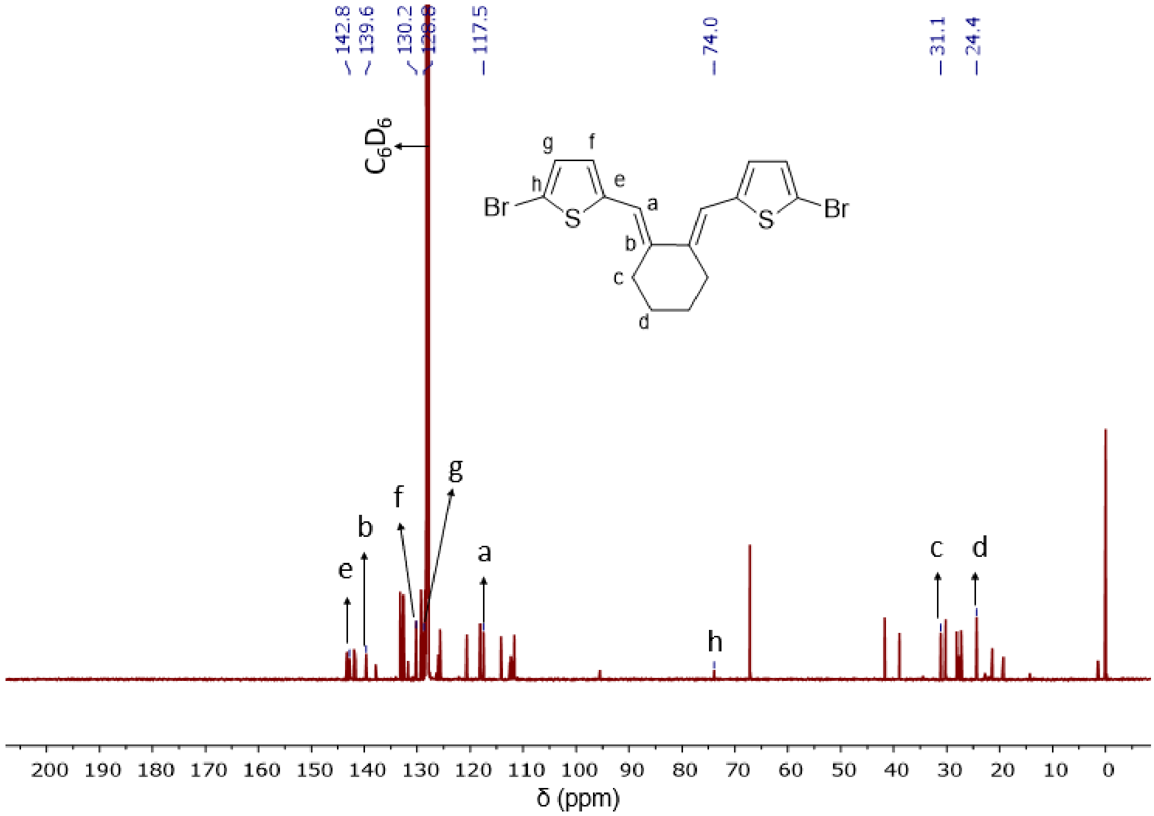

Figure S95. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of (1*E*,2*E*)-1,2-bis((5-bromothiophen-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11d** under air, in C_6D_6.

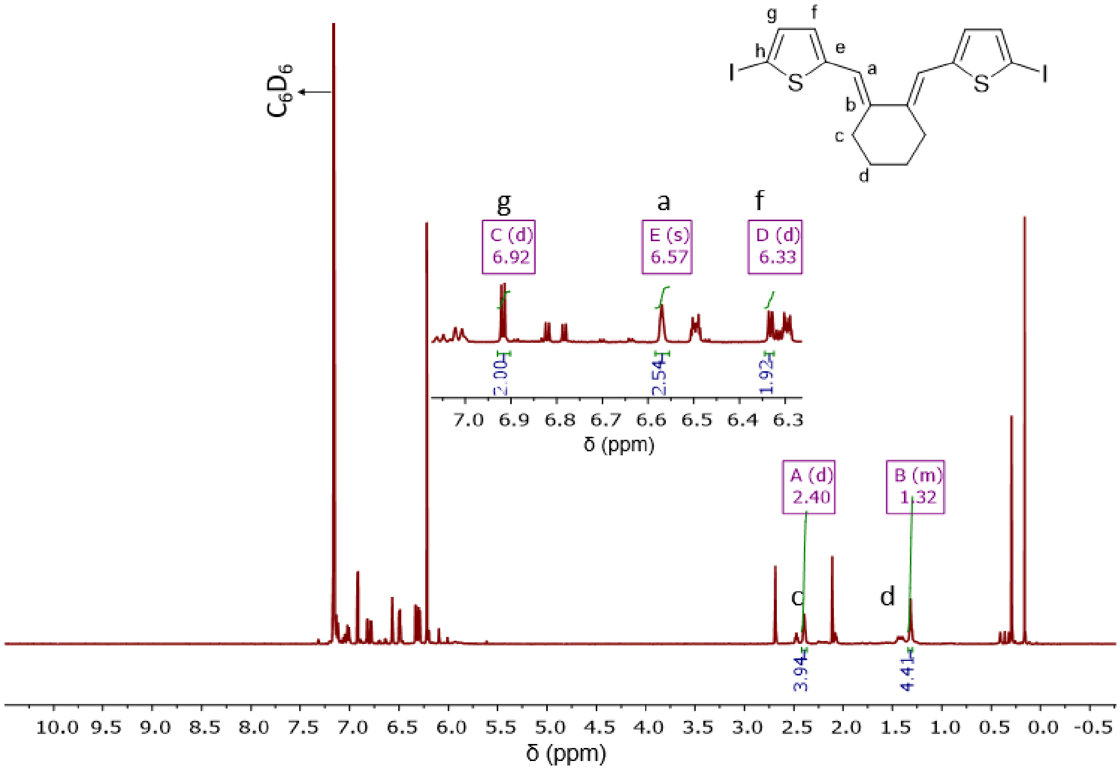

Figure S96. ^{1}H NMR (500 MHz) spectrum of (1*E*,2*E*)-1,2-bis((5-iodothiophen-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11e** under air, in C_6D_6.

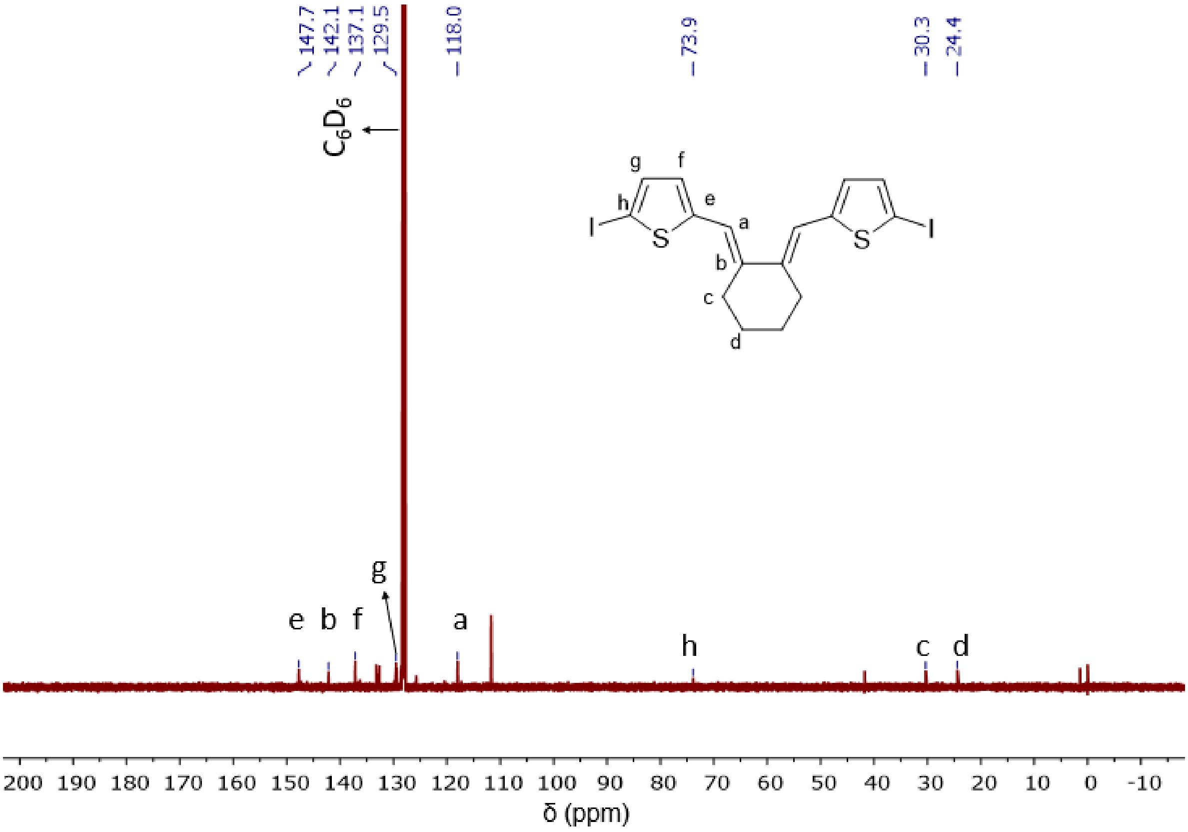

Figure S97. $^{13}C\{^1H\}$ NMR (126 MHz) spectrum of (1*E*,2*E*)-1,2-bis((5-iodothiophen-2-yl)methylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11e** under air, in C_6D_6.

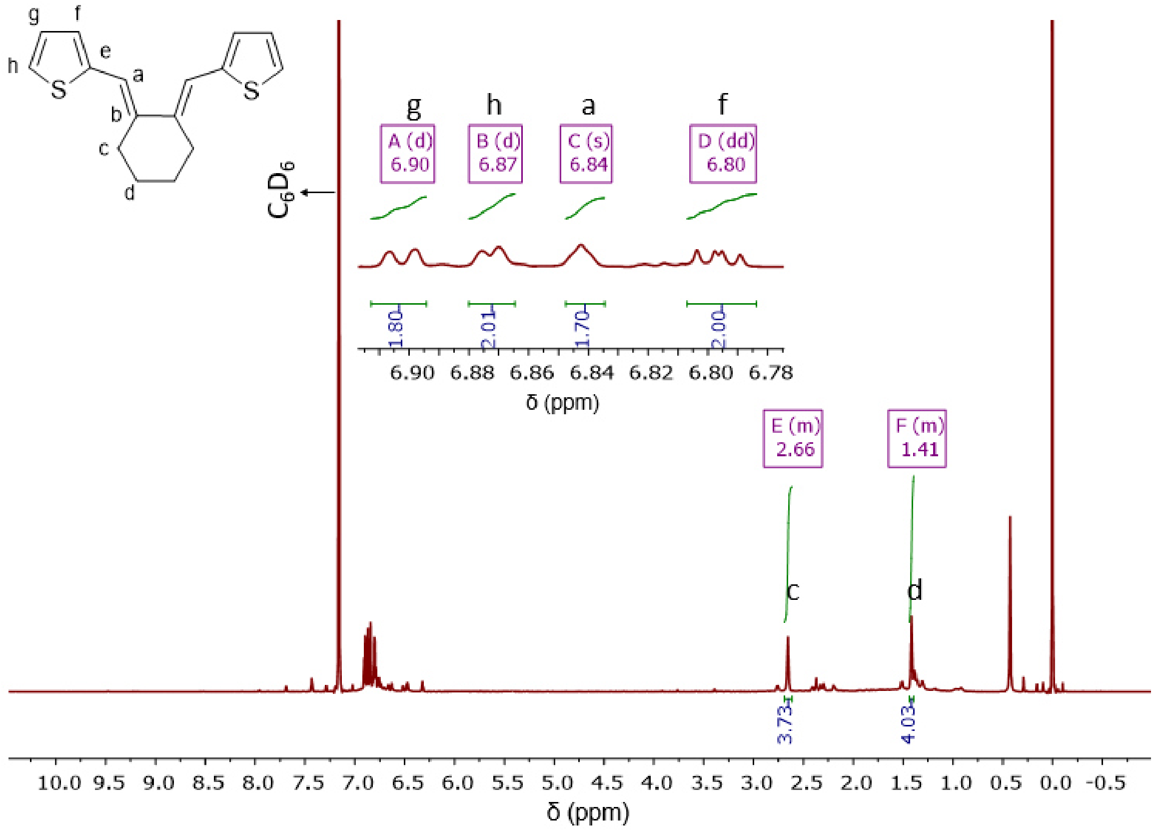

Figure S98. ^{1}H NMR (500 MHz) spectrum of (1*E*,2*E*)-1,2-bis(thiophen-2-ylmethylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11f** under air, in C_6D_6.

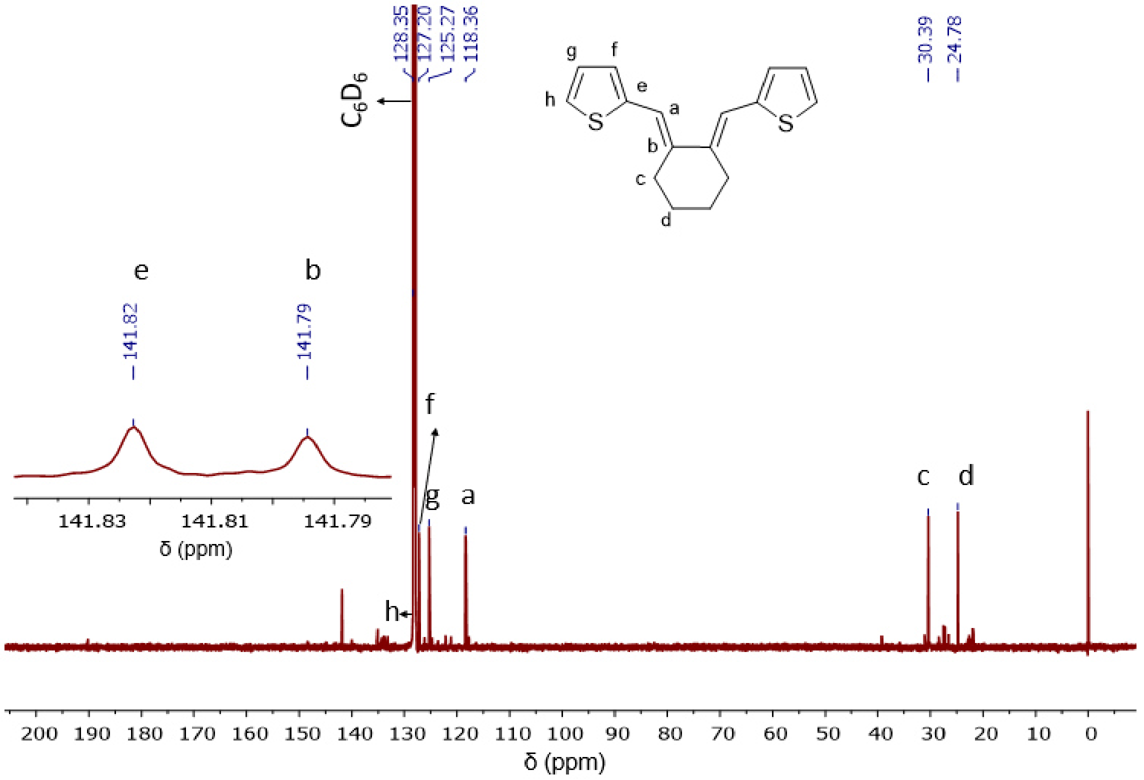

Figure S99. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (1*E*,2*E*)-1,2-bis(thiophen-2-ylmethylene)cyclohexane main product of the decomposition of zirconacyclopentadiene **11f** under air, in C_6D_6.

7 Crystal Structures

Table S3. Crystal data and structure refinement of **11d** and **11f**.

	11d	**11f**
Empirical formula	$C_{26}H_{22}S_2Br_2Zr$	$C_{26}H_{24}S_2Zr$
Formula weight	649.59	491.79
Temperature/K	100.0	100.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	15.0327(11)	9.6714(3)
b/Å	8.6378(6)	12.0118(4)
c/Å	18.2944(17)	18.6458(7)
α/°	90	90
β/°	100.400(4)	99.1990(10)
γ/°	90	90
Volume/Å^3	2336.5(3)	2138.24(13)
Z	4	4
ρ_{calc}g/cm^3	1.847	1.528
μ/mm^{-1}	4.082	0.720
F(000)	1280.0	1008.0
Crystal size/mm^3	0.22 × 0.2 × 0.15	0.3 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.528 to 59.998	5.576 to 57
Index ranges	$-21 \le h \le 21$, $-12 \le k \le 11$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-25 \le l \le 25$
Reflections collected	55126	49315
Independent reflections	6820 [R_{int} = 0.0475, R_{sigma} = 0.0291]	5401 [R_{int} = 0.0225, R_{sigma} = 0.0120]
Data/restraints/parameters	6820/0/281	5401/18/300
Goodness-of-fit on F^2	1.041	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0534	R_1 = 0.0230, wR_2 = 0.0528
Final R indexes [all data]	R_1 = 0.0378, wR_2 = 0.0573	R_1 = 0.0253, wR_2 = 0.0542
Largest diff. peak/hole / e Å^{-3}	0.58/-0.64	0.48/-0.35
CCDC Number	1900225	Our experimental data is in agreement with the literature.[14]

Table S4. Crystal data and structure refinement of **11h** and **11i**.

	11h	**11i**
Empirical formula	$C_{29}H_{24}Br_2Zr$	$C_{34}H_{36}F_6Si_2Zr$
Formula weight	623.52	706.03
Temperature/K	100.0	100.0
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a/Å	9.0975(3)	9.2700(4)
b/Å	13.0160(4)	13.8588(6)
c/Å	22.4469(8)	26.4170(12)
α/°	74.3840(10)	90
β/°	83.3870(10)	93.081(2)
γ/°	70.9900(10)	90
Volume/Å^3	2419.18(14)	3388.9(3)
Z	4	4
ρ_{calc}g/cm^3	1.712	1.384
μ/mm^{-1}	3.773	0.450
F(000)	1232.0	1448.0
Crystal size/mm^3	0.35 × 0.2 × 0.15	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.738 to 59	4.584 to 66.472
Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-31 \le l \le 31$	$-14 \le h \le 14$, $-21 \le k \le 21$, $-40 \le l \le 40$
Reflections collected	81502	81669
Independent reflections	13464 [R_{int} = 0.0704, R_{sigma} = 0.0347]	13006 [R_{int} = 0.0350, R_{sigma} = 0.0259]
Data/restraints/parameters	13464/0/578	13006/78/450
Goodness-of-fit on F^2	1.025	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0570	R_1 = 0.0365, wR_2 = 0.0854
Final R indexes [all data]	R_1 = 0.0297, wR_2 = 0.0585	R_1 = 0.0485, wR_2 = 0.0906
Largest diff. peak/hole / e Å^{-3}	0.75/-0.64	0.92/-0.87
CCDC Number	1900228	1900226

Table S5. Crystal data and structure refinement of **11j**, **11k** and **11l**.

	11j	**11k**	**11l**
Empirical formula	$C_{32}H_{36}Si_2Zr$	$C_{45}H_{38}Zr$	$C_{40}H_{42}Si_2Zr$
Formula weight	568.01	669.97	670.13
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2	P-1	C2/c
a/Å	12.1783(5)	11.0860(4)	21.8814(9)
b/Å	28.7591(12)	11.3088(4)	10.8845(4)
c/Å	24.7926(10)	14.1880(5)	14.3210(6)
α/°	90	90.1010(10)	90
β/°	95.4680(10)	108.9690(10)	98.3850(10)
γ/°	90	90.0260(10)	90
Volume/Å^3	8643.8(6)	1682.14(10)	3374.3(2)
Z	12	2	4
ρ_{calc}g/cm^3	1.309	1.323	1.319
μ/mm^{-1}	0.483	0.358	0.424
F(000)	3552.0	696.0	1400.0
Crystal size/mm^3	0.18 × 0.16 × 0.16	0.2 × 0.15 × 0.15	0.37 × 0.19 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.952 to 54.966	4.706 to 55.994	4.922 to 61.14
Index ranges	$-13 \le h \le 15$, $-37 \le k \le 37$, $-32 \le l \le 32$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-18 \le l \le 17$	$-31 \le h \le 31$, $-15 \le k \le 15$, $-20 \le l \le 20$
Reflections collected	80826	35430	36277
Independent reflections	19556 [R_{int} = 0.0316, R_{sigma} = 0.0316]	8114 [R_{int} = 0.0244, R_{sigma} = 0.0219]	5186 [R_{int} = 0.0359, R_{sigma} = 0.0243]
Data/restraints/parameters	19556/1/966	8114/0/480	5186/0/198
Goodness-of-fit on F^2	1.145	1.060	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.0810	R_1 = 0.0344, wR_2 = 0.0910	R_1 = 0.0282, wR_2 = 0.0656
Final R indexes [all data]	R_1 = 0.0399, wR_2 = 0.0818	R_1 = 0.0384, wR_2 = 0.0939	R_1 = 0.0369, wR_2 = 0.0697
Largest diff. peak/hole / e Å^{-3}	1.04/-0.57	2.02/-0.60	0.45/-0.34
CCDC Number	1915992	1900380	1900227

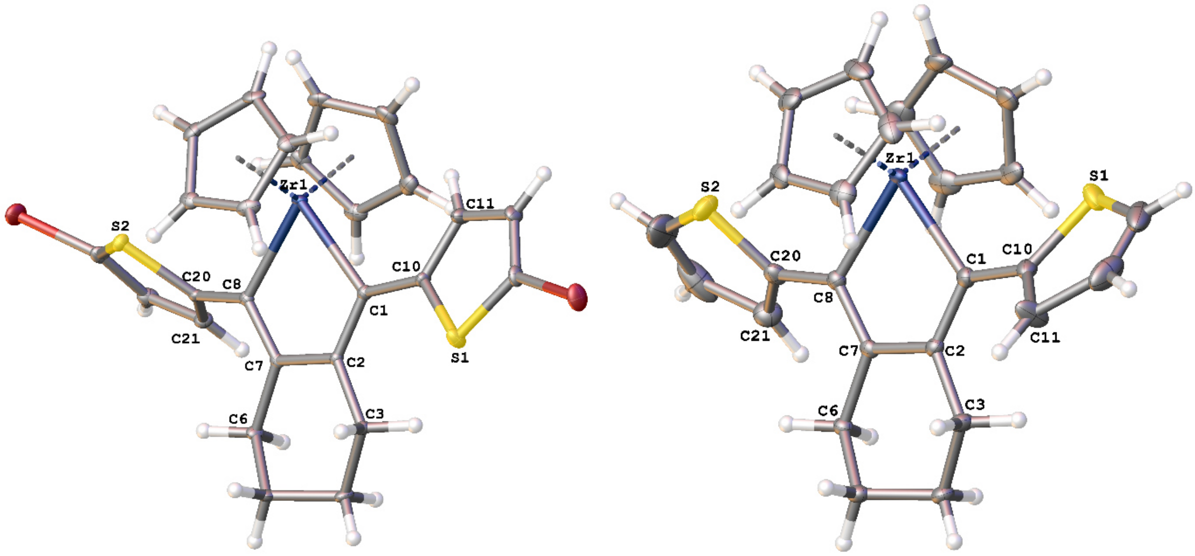

Figure S100. Molecular structures of **11d** and **11f** showing 50% probability ellipsoids and the crystallographic numbering scheme. Only the major parts of the disordered molecule of **11f** is shown for clarity.

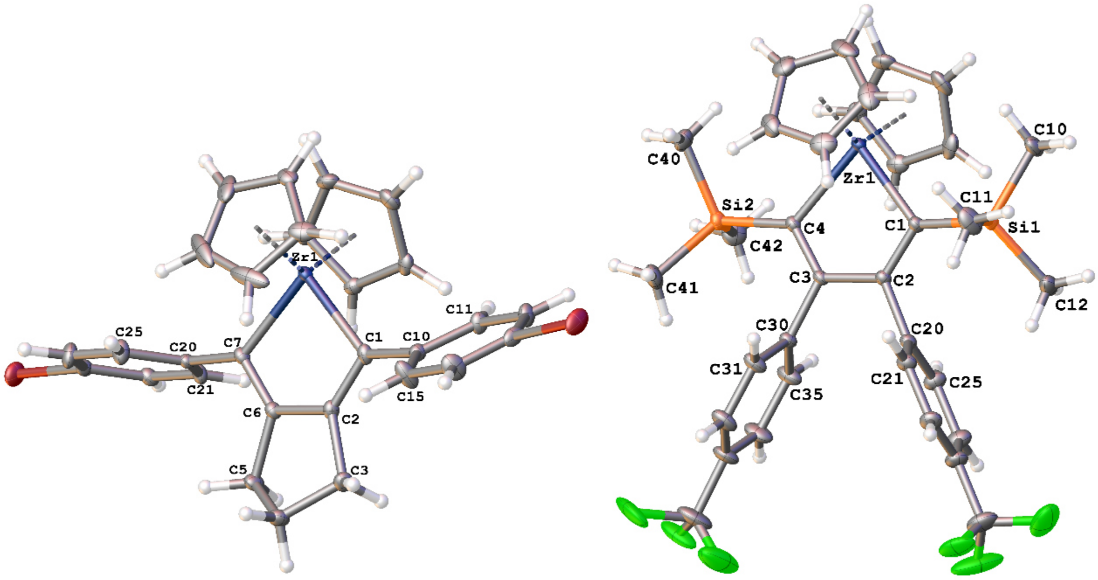

Figure S101. Molecular structures of **11h** (only one independent molecule is shown) and **11i** showing 50% probability ellipsoids and the crystallographic numbering scheme. Only the major parts of the disordered molecule of **11i** is shown for clarity.

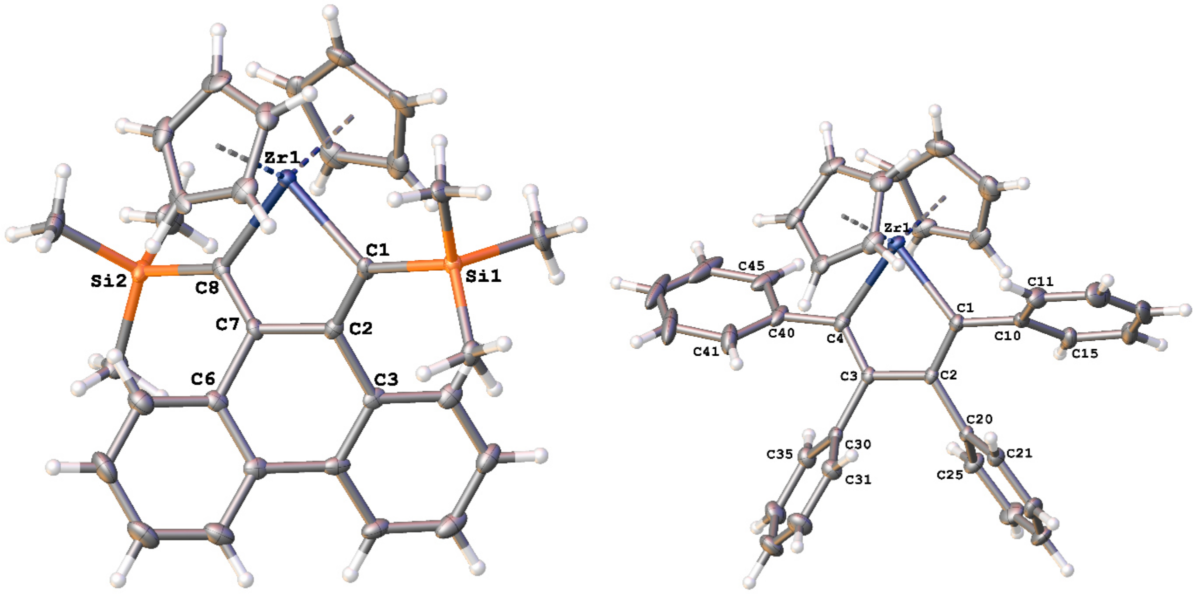

Figure S102. Molecular structures of **11j** and **11k** showing 50% probability ellipsoids and the crystallographic numbering scheme.

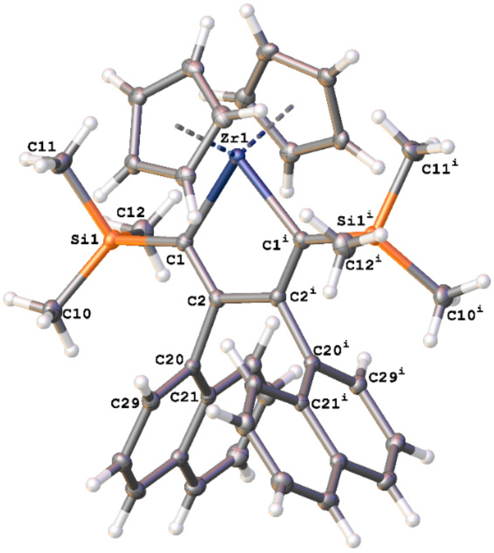

Figure S103. Molecular structure of **11l** showing 50% probability ellipsoids and the crystallographic numbering scheme.

Table S6. Selected Bond Parameters of Molecular Structures **11d**, **11f** and **11h**.

	11d	**11f**	**11h**
Bond lengths [Å] and angles [°]			
Zr(1)-C(1)	2.2878(2)	2.2619(2)	2.2468(2)
C(1)-C(2)	1.369(3)	1.3665(2)	1.361(2)
C(1)-C(10)	1.451(3)	1.460(2)	1.470(2)
C(2)-C(7)	1.481(3)	1.4866(2)	-
C(2)-C(6)	-	-	1.502(2)
C(2)-C(3)	1.525(3)	1.5199(2)	1.529(2)
C(2)-C(1)-Zr(1)	112.23(2)	112.84(2)	101.94(2)
C(8)-Zr(1)-C(1)	76.40(7)	76.52(5)	-
C(7)-Zr(1)-C(1)	-	-	86.12(6)
Zr(1)-C(1)-C(2)-C(7)	8.3(2)	7.58(2)	-
Zr(1)-C(1)-C(2)-C(6)	-	-	5.28(2)
Zr(1)-C(1)-C(10)-C(11)	-23.0(3)	125.5(6)	-65.3(2)

Table S7. Selected Bond Parameters of Molecular Structures **11i** and **11j.**

	11i	**11j**
Bond lengths [Å] and angles [°]		
Zr(1)-C(1)	2.2633(2)	2.250(5)
C(1)-C(2)	1.3660(2)	1.365(7)
C(1)-Si(1)	1.8723(2)	1.875(5)
C(2)-C(3)	1.5056(2)	1.505(7)
C(2)-C(20)	1.5005(2)	-
C(2)-C(1)-Zr(1)	105.71(9)	100.1(3)
C(1)-Zr(1)-C(4)	82.69(5)	-
C(1)-Zr(1)-C(8)	-	87.00(2)
Zr(1)-C(1)-C(2)-C(3)	-2.16(2)	155.5(4)
C(8)-Zr(1)-C(1)-C(2)	-	1.8(3)
C(1)-C(2)-C(20)-C(21)	75.78(2)	-

Table S8. Selected Bond Parameters of Molecular Structures **11k** and **11l**.

	11k	**11l**
Bond lengths [Å] and angles [°]		
Zr(1)-C(1)	2.2588(2)	2.2684(2)
C(1)-C(2)	1.359(2)	1.3667(2)
C(1)-Si(1)	-	1.8752(2)
C(1)-C(10)	1.483(2)	-
C(2)-C(3)	1.498(2)	-
C(2)-C(20)	1.499(2)	1.5079(2)
C(2)-C(1)-Zr(1)	109.09(2)	106.00(9)
C(1)-Zr(1)-C(4)	79.37(6)	-
Zr(1)-C(1)-C(2)-C(3)	-7.40(2)	-
C(1)-C(2)-C(20)-C(21)	54.6(2)	83.36(2)
Zr(1)-C(1)-C(10)-C(11)	71.8(2)	-