Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 815–818

Sulfur-bridged bis(2-indenyl) zirconocenes and their performance in olefin polymerization

Oleg V. Samsonov, Georgy P. Goryunov, Dmitry V. Uborsky, Andrey F. Asachenko,
Jo Ann M. Canich, Jian Yang and Alexander Z. Voskoboynikov

Table of contents

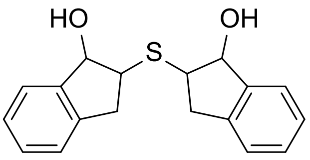
Synthesis of the Ligands and Complexes

General Information

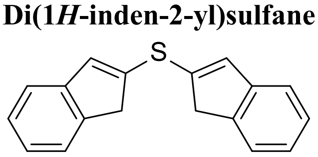
All manipulations with air- or moisture-sensitive compounds were performed in a glovebox under controlled atmosphere of purified argon (≤1 ppm O_2, ≤ 1 ppm water). Toluene, diethyl ether and THF were distilled from sodium/benzophenone. Commercial reagents were purchased from Sigma-Aldrich, Merck, Abcr and Acros and we used as received. Sodium sulfide was used in two forms: sodium sulfide nonahydrate and sodium sulfide hydrate, ≥60% purity, scales. All new compounds were characterized by means of ^{1}H-NMR and ^{13}C-NMR. NMR spectra were recorded on Bruker AVANCE (400 MHz) or Agilent Technologies 400-MR (400 MHz) NMR spectrometers and can be found at the end of the document. All ^{1}H-NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to residual resonances of the deuterated solvents (7.27 ppm for $CDCl_3$, 2.50 ppm for DMSO-d$_6$, 5.32 ppm for CD_2Cl_2). All ^{13}C-NMR data are reported in ppm relative to residual resonances of the deuterated solvents (77.00 ppm for $CDCl_3$, 54.00 ppm for CD_2Cl_2, 39.51 ppm for DMSO-d$_6$) and were obtained with ^{1}H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, br.s = broad signal, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Elemental analysis was done using a Carlo Erba 1106 analyzer.

4,7-Dimethyl-1*H*-indene[S1] (**1b**), 5,6-dimethyl-1*H*-indene[S2] (**1c**), $ZrCl_2(NMe_2)_2(THF)_2$[S3] and 2-bromoindan-1-ol (**2a**)[S4] were synthesized according to the reported procedures.

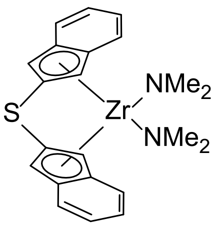
Experimental Procedures and Characterization Data



2,2'-Thiodiindan-1-ol (3a). A mixture of 55.1 g (259 mmol) 2-bromoindan-1-ol **2a** (synthesized from indene **1a**[S4]), 37.5 g (156 mmol) of sodium sulfide nonahydrate, and 1.88 g (5.00 mmol) of trioctyl methylammonium chloride in 1000 ml of water was refluxed for 4 h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane (3 x 500 ml). The combined organic extract was washed with water (2 x 200 ml), dried over Na_2SO_4, and then evaporated to dryness. The residue was washed with 30 ml of ethanol and then dried in vacuo. Yield: 19.3 g (50%) of a white crystalline solid as ~ 1:1 mixture of two diastereomers. ^{1}H NMR (DMSO-*d*$_6$) for both isomers: δ 7.30-7.39 (m, 2H), 7.12-7.27 (m, 6H), 5.42 (d, J = 4.1 Hz, 1H), 5.33 (d, J = 4.4 Hz, 1H), 4.46-4.54 (m, 1H), 4.37-4.45 (m, 1H), 4.27 (d, J = 3.1 Hz, 1H), 4.17 (d, J = 3.1 Hz, 1H), 3.19-3.32 (m, 2H), 2.76 (dd, J = 6.4, 3.6 Hz, 1H), 2.71 (dd, J = 6.4, 3.6 Hz, 1H). ^{13}C NMR (DMSO-*d*$_6$) for both isomers: δ 141.8, 141.4, 141.4, 141.2, 127.6, 126.7, 126.5, 125.3, 125.3, 125.0, 124.9, 78.8, 78.1, 56.1, 56.0, 39.9, 39.8.

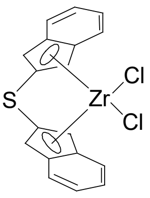


Di(1*H*-inden-2-yl)sulfane (4a). To a solution of 19.3 g (64.7 mmol) of **3a** in 1000 ml of toluene, 9.41 g (49.5 mmol) of TsOH monohydrate was added. The obtained mixture was refluxed with a Dean–Stark head for 90 min and then cooled to room temperature using a water bath. The formed solution was washed by 10% Na_2CO_3, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 x 150 ml). The combined organic extract was dried over Na_2SO_4 and then passed through a short pad of silica gel 60 (40-63 µm) which was additionally washed by 100 ml of dichloromethane. The combined organic elute was evaporated to dryness. The crude product was purified by flash chromatography on silica gel 60 (40-63 µm, eluent: hexane-ethyl acetate = 5:1, vol.). Yield: 13.4 g (79%) of a white solid. ^{1}H NMR ($CDCl_3$): δ 7.43 (d, J = 7.4 Hz, 2H), 7.28-7.38 (m, 4H), 7.17-7.25 (m, 2H), 6.95 (s, 2H), 3.63 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 144.3, 143.4, 139.8, 133.1, 126.6, 124.7, 123.4, 120.3, 42.5.

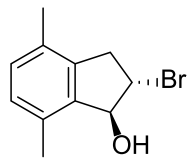


Complex 5a. A solution of 2.04 g (7.62 mmol) of $Zr(NMe_2)_4$ and 2.00 g (7.62 mmol) of **4a** in 50 ml of toluene was stirred for 48 h at 110 °C. The obtained hot solution passed through a short pad of Celite 503 which was additionally washed by 50 ml of hot toluene and evaporated to dryness. Yield: 1.20 g (36%) of a powdery product. EA calcd. for $C_{22}H_{24}N_2SZr$: C, 60.09; H, 5.50; N, 6.37. Found: C, 60.32; H, 5.71, N, 6.15. ^{1}H NMR ($CDCl_3$): δ 7.49-7.56 (m, 4H), 6.92-7.00 (m, 4H), 6.19 (s, 4H), 2.44 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 129.2, 123.6, 122.7, 111.5, 101.7, 46.5.

Complex 6a. To a solution of 0.70 g (1.59 mmol) of **5a**, 1.03 g (7.95 mmol) of dimethyldichlorosilane was added and the resulting solution was stirred at 50 °C for overnight. The solution was passed through a short pad of Celite 503 which was additionally washed by 50 ml of hot toluene. The obtained filtrate was evaporated to dryness. The residue was washed with 50 ml of hot hexane and then dried in vacuo. Yield: 0.55 g (82%) of a yellow solid. EA calcd. for $C_{18}H_{12}Cl_2SZr$: C, 51.17; H, 2.86. Found: C, 51.29; H, 3.00. ^{1}H NMR (CD_2Cl_2): *δ* 7.50-7.57 (m, 4H), 7.25-7.31 (m, 4H), 6.39 (s, 4H). The substance has an extremely low solubility, making it too difficult to record the ^{13}C NMR spectrum in an acceptable amount of time.

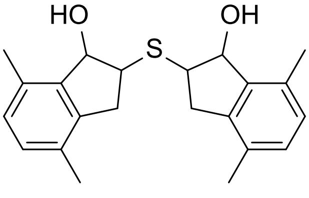


***trans*-2-Bromo-4,7-dimethylindan-1-ol (2b)**. To a solution of 39.6 g (274 mmol) of **1b** in 300 ml of DMSO and 10 ml of water, 51.2 g (288 mmol) of NBS was added portionwise for 30 min at 20 °C. The resulting orange solution was stirred overnight at room temperature. Then, the obtained mixture was poured into 500 ml of water, and thus obtained suspension was extracted with ethyl acetate (3 x 250 ml). The combined organic extract was washed with water (5 × 500 ml), dried over Na_2SO_4, and then evaporated to dryness. The residue was washed with 300 ml of hexane and dried in vacuo. Yield 62.2 g (94%) of a white powder. ^{1}H NMR (DMSO-d_6): *δ* 7.00 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 5.74 (br. s., 1H), 5.19 (d, J = 2.2 Hz, 1H), 4.52 - 4.40 (m, 1H), 3.63 (dd, J = 17.5, 6.3 Hz, 1H), 3.03 (dd, J = 17.4, 3.0 Hz, 1H), 2.28 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (DMSO-d_6): *δ* 140.1, 139.2, 132.2, 130.7, 129.4, 128.4, 81.9, 56.3, 39.7, 18.1, 17.6.

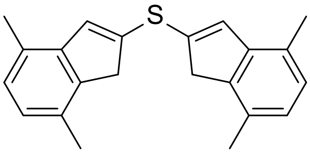


one of two
enantiomers
is shown

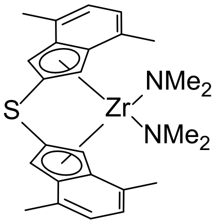
2,2'-Thiobis(4,7-dimethylindan-1-ol) (3b). To a solution of 62.2 g (258 mmol) of **2b** in 1000 ml of ethanol, 16.8 g (129 mmol, ≥60% purity) of sodium sulfide hydrate was added. The obtained mixture was refluxed for 5 h and then evaporated to dryness. To the residue, 500 ml of water was added, and the obtained mixture was extracted with ethyl acetate (3 x 500 ml). The combined extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was washed with 50 ml of ethanol and dried in vacuo. Yield: 35.0 g (77%) of a white crystalline solid as ~ 2:1 mixture of two diastereomers. *Major isomer*. ^{1}H NMR (DMSO-d_6): *δ* 6.86-6.98 (m, 4H), 5.13 (br.s., 2H), 4.69 (t, J = 4.3 Hz, 2H), 4.20 (s, 2H), 3.25-3.34 (m, 2H), 2.71 (d, J = 17.0 Hz, 2H), 2.28 (s, 6H), 2.17 (s, 6H). ^{13}C NMR (DMSO-d_6): *δ* 140.8, 138.8, 131.7, 131.1, 128.7, 127.8, 76.5, 55.8, 38.8, 18.5, 17.8. *Minor isomer*. ^{1}H NMR (DMSO-d_6): *δ* 6.86-6.98 (m, 4H), 5.08 (br. s., 2H), 4.52 (t, J = 4.1 Hz, 2H), 4.30 (s, 2H), 3.16 (dd, J = 16.8, 4.7 Hz, 2H), 2.65 (d, J = 16.8 Hz, 2H), 2.37 (s, 6H), 2.16 (s, 6H). ^{13}C NMR (DMSO-d_6): *δ* 140.5, 139.8, 131.8, 131.0, 128.6, 127.8, 77.2, 57.7, 38.6, 18.5, 18.1.



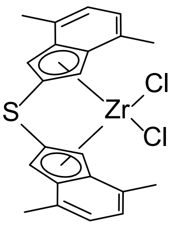
Bis(4,7-dimethyl-1*H*-inden-2-yl)sulfane (4b). This synthesis was carried out similarly to **4a** starting from **3b** (12.6 g, 35.7 mmol) and TsOH monohydrate (4.93 g, 25.9 mmol) in toluene. Yield 7.10 g (62%) of a white crystalline solid. ^{1}H NMR ($CDCl_3$): *δ* 7.00-7.10 (m, 4H), 6.90-6.98 (m, 2H), 3.50 (s, 4H), 2.42 (s, 6H), 2.31 (s, 6H). ^{13}C NMR ($CDCl_3$): *δ* 142.9, 142.1, 139.0, 132.1, 130.0, 128.0, 127.3, 126.1, 41.9, 18.3, 18.2.



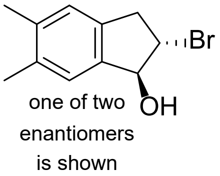
Complex 5b. To a solution of 0.64 g (6.32 mmol) of diisopropylamine in 50 ml of diethyl ether, 2.50 ml (6.32 mmol) of 2.5 M ^{n}BuLi in hexanes was added at −30 °C. The obtained solution was allowed to warm to room temperature, stirred for 1 h, and then 1.00 g (3.16 mmol) of **4b** was added. After that, the resulting mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure, and 50 ml of THF was added to the residue. Then, 1.24 g (3.16 mmol) of $ZrCl_2(NMe_2)_2(THF)_2$ was added at −78 °C. The obtained mixture was allowed to warm to room temperature and stirred overnight. After that the mixture was warmed to 50 °C, passed through a short pad of Celite 503 which was additionally washed by 50 ml of hot toluene. The obtained filtrate was evaporated to dryness. Yield: 0.63 g (40%) of a powdery product. EA calcd. for $C_{26}H_{32}N_2SZr$: C, 62.98; H, 6.51, N, 5.65. Found: C, 63.35; H, 6.73, N, 5.42. ^{1}H NMR (CD_2Cl_2): *δ* 6.73 (s, 4H), 6. 20 (s, 4H), 2.42 (s, 12H), 2.39 (s, 12H). ^{13}C NMR (CD_2Cl_2): *δ* 131.6, 129.6, 124.6, 113.3, 102.8, 46.2, 19.6.



Complex 6b. This synthesis was carried out similarly to **6a** starting from **5b** (0.64 g, 1.26 mmol) and dimethyldichlorosilane (0.81 g, 6.30 mmol). Yield: 0.38 g (63%) of a yellow solid. EA calcd. for $C_{22}H_{20}Cl_2SZr$: C, 55.21; H, 4.21. Found: C, 55.50; H, 4.44. ^{1}H NMR (CD_2Cl_2): δ 6.96 (s, 4H), 6.31 (s, 4H), 2.41 (s, 12H). ^{13}C NMR (CD_2Cl_2): δ 143.2, 132.3, 131.8, 126.8, 107.2, 19.7.

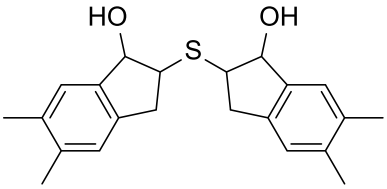


***trans*-2-Bromo-5,6-dimethylindan-1-ol (2c)**. This synthesis was carried out similarly to **2b** starting from **1c** (13.2 g, 91.8 mmol), NBS (17.2 g, 96.3 mmol) and 4 ml of water in DMSO. Yield: 19.7 g (89%) of a white powder. ^{1}H NMR (DMSO-d_6): δ 7.09 (s, 1H), 6.99 (s, 1H), 5.86 (br. s., 1H), 5.00 (d, J = 5.3 Hz, 1H), 4.22-4.29 (m, 1H), 3.47 (dd, J = 16.2, 6.9 Hz, 1H), 3.00 (dd, J = 16.0, 6.6 Hz, 1H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 140.6, 137.0, 136.2, 134.9, 125.2, 125.1, 81.8, 56.4, 39.8, 19.5, 19.5.

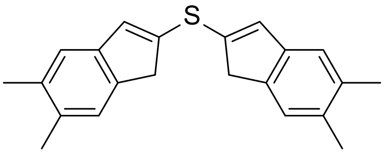


one of two enantiomers is shown

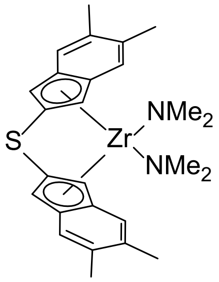
2,2'-Thiobis(5,6-dimethylindan-1-ol) (3c). This synthesis was carried out similarly to **3b** starting from **2c** (19.7 g, 81.7 mmol), and sodium sulfide hydrate (5.32 g, 40.9 mmol, ≥60% purity) in ethanol. Yield: 11.2 g (77%) of a white crystalline solid as ~3:1 mixture of two isomeric compounds. *Major isomer*. ^{1}H NMR (DMSO-d_6): δ 7.12 (s, 2H), 7.00 (s, 2H), 5.34 (d, J = 4.3 Hz, 2H), 4.36-4.44 (m, 2H), 4.20-4.24 (m, 2H), 3.1-3.25 (m, 2H), 2.61-2.72 (m, 2H), 2.17 (s, 12H). ^{13}C NMR (DMSO-d_6): δ 139.2, 138.5, 135.3, 134.1, 126.2, 125.8, 78.6, 56.1, 19.4. *Minor isomer*. ^{1}H NMR (DMSO-d_6): δ 7.09 (s, 2H), 6.98 (s, 2H), 5.22 (d, J = 4.5 Hz, 2H), 4.45-4.52 (m, 2H), 4.09-4.13 (m, 2H), 3.13-3.25 (m, 2H), 2.61-2.72 (m, 2H), 2.18 (s, 12H). ^{13}C NMR (DMSO-d_6): δ 138.7, 138.7, 135.4, 134.2, 126.1, 125.7, 79.2, 55.9, 19.3.



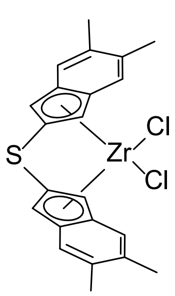
Bis(5,6-dimethyl-1*H*-inden-2-yl)sulfane (4c). This synthesis was carried out similarly to **4a** starting from **3c** (11.2 g, 31.6 mmol) and TsOH monohydrate (4.20 g, 22.1 mmol) in toluene Yield: 7.55 g (75%) of **4c** as a white crystalline solid. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 2H), 7.13 (s, 2H), 6.86 (s, 2H), 3.55 (s, 4H), 2.34 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 142.3, 141.2, 138.7, 134.7, 132.9, 124.7, 121.4, 42.1, 19.9.



Complex 5c. This synthesis was carried out similarly to **5a** starting from $Zr(NMe_2)_4$ (1.10 g, 4.14 mmol) and **4c** (1.32 g, 4.14 mmol) in toluene. Yield 0.87 g (43%) of a yellow solid. EA calcd. for $C_{26}H_{32}N_2SZr$: C, 62.98; H, 6.51; N, 5.65. Found: C, 63.29; H, 6.82; N, 5.51. ^{1}H NMR (CD_2Cl_2): δ 7.22 (s, 4H), 5.99 (s, 4H), 2.38 (s, 12H), 2.18 (s, 12H). ^{13}C NMR (CD_2Cl_2): δ 133.7, 128.9, 122.4, 101.2, 47.1, 20.6.



Complex 6c. This synthesis was carried out similarly to **6a** starting from **5c** (0.70 g, 1.41 mmol) and dimethyldichlorosilane (0.91 g, 7.05 mmol) in toluene. Yield: 0.54 g (80%). EA calcd. for $C_{22}H_{20}Cl_2SZr$: C, 55.21; H, 4.21. Found: C, 55.53; H, 4.48. ^{1}H NMR (CD_2Cl_2): δ 7.26 (s, 4H), 6.19 (s, 4H), 2.30 (s, 12H). The substance has an extremely low solubility, making it too difficult to record the ^{13}C NMR spectrum in an acceptable amount of time.



X-ray Crystallography Data

Crystal data for **6b** were collected on a Bruker SMART 1000 CCD area detector with MoKα radiation (λ = 0.71073 Å) using the φ- and ω-scan techniques. The structures were solved and refined by direct methods using SHELXTL. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELXTL. The coordinates of the hydrogen atoms were calculated from geometrical positions.

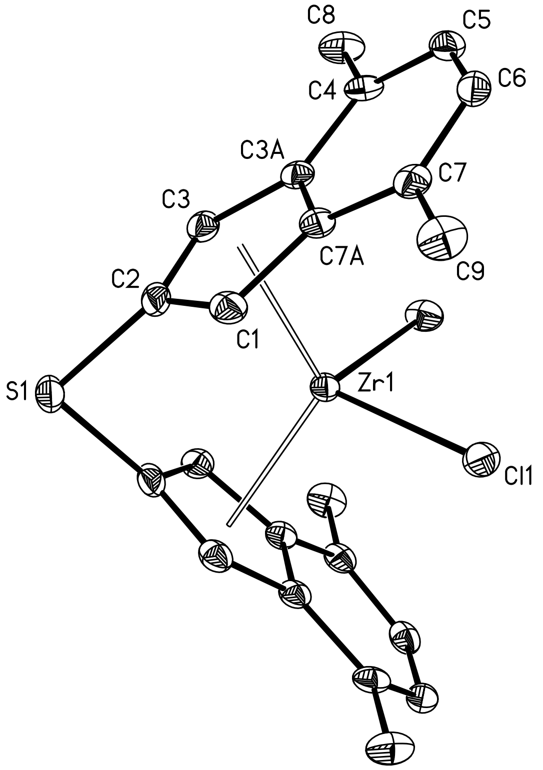


Figure S1. Solid state molecular structure of complex **6b** (CCDC 2350110) with thermal ellipsoids shown at 50% probability level. The hydrogen atoms are removed for clarity

Table S1. Crystal data and structure refinement for **6b**.

Identification code	**6b**	
Empirical formula	$C_{22} H_{20} Cl_2 S Zr$	
Formula weight	478.56	
Temperature	120.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.6854(8) Å	α = 90°.
	b = 9.3958(5) Å	β = 107.727(10)°.
	c = 13.7831(7) Å	γ = 90°.
Volume	1934.86(17) $Å^3$	
Z	4	
Density (calculated)	1.643 Mg/m^3	
Absorption coefficient	0.956 mm^{-1}	
F(000)	968	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	2.56 to 27.99°.	
Index ranges	$-20 \leq h \leq 20, -12 \leq k \leq 12, -18 \leq l \leq 18$	
Reflections collected	9645	
Independent reflections	2323 [R(int) = 0.0268]	
Completeness to theta = 27.99°	100 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.832 and 0.796	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2323 / 0 / 121	
Goodness-of-fit on F^2	1.012	
Final R indices [for 2118 rflns with $I>2\sigma(I)$]	R1 = 0.0290, wR2 = 0.0724	
R indices (all data)	R1 = 0.0312, wR2 = 0.0741	
Largest diff. peak and hole	0.970 and -0.377 e.$Å^{-3}$	

Polymerization Examples

Polymerization Reagents. Pre-catalyst solutions were made using a given metallocene complex dissolved in toluene (ExxonMobil Chemical, anhydrous, stored under N_2), typically at a concentration of 0.5 mmol/L.

Activation of the metallocene complexes was performed using either methylalumoxane (MAO, 10 wt% in toluene, Albemarle Corp.), or borate activator AB ($PhNHMe_2^+[B(C_6F_5)_4]^-$, Boulder Scientific or Albemarle Corp). MAO was typically used as a 0.5 wt% or 1.0 wt% toluene solution. Micromoles of MAO reported are based on the micromoles of aluminum in MAO, which has a formula weight of 58.0 grams/mole. AB was typically used as a 5 mmol/L solution in toluene.

In experiments with activation by AB, the metallocene dichloride complexes were pre-alkylated using triisobutyl aluminum (TIBA, neat, AkzoNobel). Prealkylation was performed by first dissolving the metallocene complex in the appropriate amount of toluene, and then adding 20 equivalents of TIBA to give final pre-catalyst solution concentrations of 0.5 mmol metallocene complex/L and 10 mmol TIBA/L.

For polymerization runs using AB, tri-*n*-octylaluminum (TOA, neat, AkzoNobel) was also used as a scavenger prior to introduction of the activator and metallocene complex into the reactor. TOA was typically used as a 5 mmol/L solution in toluene.

Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and were purified by passage through a series of columns: two 500 mL OXYCLEAR cylinders in series from Labclear (Oakland, Calif.), followed by two 500 mL columns in series packed with dried 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), and two 500 mL columns in series packed with dried 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company).

1-Octene (98%) (Aldrich Chemical Company) and 1-decene (Aldrich Chemical Company) were dried by stirring over NaK for at least two hours to overnight followed by filtration through basic alumina (Aldrich Chemical Company, Brockman Basic 1). 1-Decene can also be purified by mixing 1 L of untreated raw material with 20 grams of activated 13X molecular sieves (activated by calcination at 200°C for at least four hours under a purge stream of dry nitrogen gas), and 10 grams of OXICLEAR catalyst (purchased from Altech Associates, Inc. or Deerfield, Ill. 60115) for at least two days inside a glove box under a dry nitrogen atmosphere. The molecular sieves and deoxygenation catalyst are then removed by filtration in the glove box to provide purified 1-decene. Alternatively, the feeds can be purified by passage through a bed of activated 13X molecular sieve alone under nitrogen atmosphere.

Polymerization grade ethylene was purified by passage through a series of columns: 500 mL OXYCLEAR cylinder from Labclear (Oakland, Calif.) followed by a 500 mL column packed with dried 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), and a 500 mL column packed with dried 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company).

Reactor Description and Preparation: Polymerizations were conducted in an inert atmosphere (N_2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 23.5 mL), septum inlets, a regulated supply of nitrogen and, ethylene, and disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours.

Ethylene Polymerization (PE) or Ethylene/1-octene Copolymerization (EO): The reactor was prepared as described above, and then purged with ethylene. Toluene (4.9 mL), 1-octene (100 µL when used), and activator (MAO at 500:1 molar ratio of Al:Zr) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80°C) and charged with ethylene to process pressure (75 psig = 6.2 bar or 200 psig = 14.8 bar) while stirring at 800 RPM. The pre-catalyst solution containing 0.025 umol of metallocene compound was then added via syringe to the reactor at process conditions. Ethylene was allowed to enter (through the use of computer-controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (±0.2 bar). The reactor temperature was monitored and typically maintained within ±1°C. Polymerizations were halted by addition of approximately 3.5 psi O_2/Ar (5 mol% O_2) gas mixture to the autoclave for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or for a maximum of 30 minutes polymerization time (maximum quench time). Actual quench times are reported in Table 3. Afterward, the reactors were cooled and vented. Polymers were isolated after solvent removal in vacuo. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol metallocene compound per hour of reaction time ($g_P/mmol_{cat}\cdot h$). Ethylene polymerization and ethylene/1-octene copolymerization data are summarized in Table 3 below

1-Decene Polymerizations:

The reactor was prepared as described above. Isohexane (2.79 mL), 1-decene (2.0 mL) and scavenger (TOA, 0.2 or 0.6 umol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (T = 60, 85, or 110°C) while stirring at 800 RPM. The activator solution containing AB at 1:1 molar ratio of AB:Zr, followed by the pre-catalyst solution containing 0.080 mmol of metallocene prealkylated with TIBA at a 20:1 molar ratio of Al:Zr, was injected via syringe to the reactor at process conditions. The reactor temperature was monitored and typically maintained within +/-1°C.The polymerization was halted after 60 min of reaction time. The reactor was then cooled and vented. The polymer was isolated after solvent removal in vacuo. Reported yields include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol metallocene complex per hour of reaction time ($g_P/mmol_{cat}\cdot h$).

1-Decene polymerization was conducted using 0.080 umol of transition metal compound, after prealkylation with (TIBA) at a 20:1 molar ratio of Al:Zr, and sufficient AB to provide a 1:1 molar ratio of activator to transition metal. An additional 0.6 umol TOA was added as a scavenger. Polymerizations were conducted using 2.0 ml 1-decene, 2.79 ml isohexane solvent and 0.21 ml toluene solvent at various reaction temperatures. Quenching was conducted at 60 minutes. 1-Decene homopolymerizations are summarized in Table 4 below.

Polymer Characterization. For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, Sigma-Aldrich, 99%) at 165°C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was from 0.1 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples were cooled to 135°C for testing.

High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in patents US6491816, US6491823, US6475391, US6461515, US6436292, US6406632, US6175409, US6454947, US6260407, US6294388. Molecular weights (weight average molecular weight (M_w) and number average molecular weight (M_n)) and molecular weight distribution referred to as the polydispersity index (PDI = M_w/M_n) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector (ELSD) and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: M_p (peak Mw) between 5000 and 3390000 kDa). Alternatively, samples were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with dual wavelength infrared detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 580 and 3039000 kDa). Samples (250 µL of a polymer solution in TCB were injected into the system) were run at an eluent flow rate of 2.0 mL/min (135°C sample temperatures, 165°C oven/columns) using three Polymer Laboratories: PLgel 10um Mixed-B 300 × 7.5 mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch@ software available from Symyx Technologies or Automation Studio software available from Freeslate.

Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220°C for 15 min and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/min and then cooled at a rate of 50°C/min. Melting points were collected during the heating period.

Samples for infrared analysis are prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number SI 0860, Symyx). By this method, approximately between 0.12 mg and 0.24 mg of polymer is deposited on the wafer cell. The samples are subsequently analyzed on a Bruker Equinox 55 FTIR spectrometer equipped with Pikes' MappIR specular reflectance sample accessory. Spectra, covering a spectral range of 5000 cm^{-1} to 500 cm^{-1}, are collected at a 2 cm^{-1} resolution with 32 scans. For ethylene-/1-octene copolymers, the wt% copolymer is determined via measurement of the methyl deformation band at ~1375 cm^{-1}. The peak height of this band is normalized by the combination and overtone band at ~4321 cm^{-1}, which corrects for path length differences. The normalized peak height is correlated to individual calibration curves from ^{1}H NMR data to predict the wt% copolymer content within a concentration range of -2 wt% to 35 wt% for octene. Typically, R^2 correlations of 0.98 or greater are achieved. Values below 4.1 wt% are outside the calibration range and are not reported.

^{1}H NMR was used to determine the number average molecular weight (M_n) of the unsaturated PAO and the quantitative breakdown of the olefinic structure types therein (e.g., vinyl, vinylene, di-substituted vinylene, tri-substituted vinylene, and vinylidene). Specifically, an NMR instrument of 400 or 500 MHz was run under the following conditions: a ~30° flip angle RF pulse, 128 scans, with a relaxation delay of ~5 seconds between pulses; sample (60-100 mg) dissolved in $CDCl_3$ (deuterated chloroform) in a 5 mm NMR tube; and signal collection temperature at ~25°C. The following approach was taken to determine the concentrations of the various olefins among all of the olefins from an NMR spectrum. First, peaks corresponding to different types of hydrogen atoms in vinyls (T1), vinylidenes (T2), di-substituted vinylenes (i.e., vinylenes, T3), and tri-substituted vinylenes (i.e., trisubstituted or trisubs, T4) were identified at the peak regions specified in Table 2 below.

Second, areas of each of the above peaks (A1, A2, A3, and A4, respectively) were then determined by integration. Third, quantities of each type of olefin (Q1, Q2, Q3, and Q4, respectively) in moles were calculated (as A1/2, A2/2, A3/2, and A4, respectively). Fourth, the total quantity of all olefins (Qt) in moles were calculated as the sum total of all four types (Qt=Q1+Q2+Q3+Q4). Finally, the molar concentrations (C1, C2, C3, and C4, respectively, in mol%) of each type of olefin, on the basis of the total molar quantity of all of the olefins, were then calculated (in each case, Ci=100·Qi/Qt).

The number average molecular weight was determined by: M_n = {[Saturated + (vinylene + vinylidene + vinyl + trisubstituted x 2)]/ (vinylene + vinylidene + vinyl + trisubstituted x 2)} x 14 ("Saturated," "vinylene," "vinyl," and "trisubstituted" in this equation refer to peak area integration).

Table S2. Areas of ^{1}H NMR spectra used for analysis of content of unsaturated chain and groups.

Hydrogen Atoms		Peak Region (ppm)	Peak Area	Number of Hydrogen Atoms	Quantity of Olefin (mol)	Concentration of Olefin (mol%)
Chain End Olefin Type	Chain End Olefin Structure					
Vinyl	CH_2=CHR	4.95-5.10	A1	2	Q_1=A1/2	C1
Vinylidene	$CH_2=CR^1R^2$	4.65-4.84	A2	2	Q_2=A2/2	C2
Di-substituted vinylenes	$CHR^1=CHR^2$	5.31-5.55	A3	2	Q_3=A3/2	C3
Tri-substituted vinylenes	$CR^1R^2=CHR^3$	5.11-5.30	A4	1	Q4=A4	C4

Table S3. Ethylene polymerization and ethylene/1-octene copolymerization data (0.025 umol metallocene, 500 equiv. MAO, 4.9 mL toluene, 80°C).

	C8, uL[1]	C2, bar[2]	Quench time, s	Polymer yield, g	A[3]	M_n	M_w	PDI[4]	Wt.% C8[5]	T_m, °C[6]
6a	0	6,2	81	0,0500	14,37	3 902	7 929	2,0	–	125,9
6a	0	6,2	74	0,0551	17,33	3 820	7 661	2,0	–	126,4
6a	0	6,2	71	0,0577	18,92	3 844	7 218	1,9	–	127,4
6a	100	6,2	66	0,0544	19,19	3 654	6 701	1,8	*	109,9
6a	100	6,2	72	0,0586	18,95	3 966	6 808	1,7	*	120,8
6a	100	6,2	63	0,0581	21,47	3 576	6 562	1,8	*	110,4
6a	100	14,8	27	0,0781	28,13	3 355	6 091	1,8	*	118,0
6a	100	14,8	27	0,0792	28,53	3 662	6 205	1,7	*	117,8
6a	100	14,8	24	0,0777	31,49	3 271	5 857	1,8	*	118,0
6b	0	6,2	194	0,0827	9,92	78 470	219 155	2,8	–	135,2
6b	0	6,2	102	0,0707	16,13	92 881	195 335	2,1	–	134,7
6b	0	6,2	147	0,0764	12,10	89 658	211 976	2,4	–	134,7
6b	100	6,2	77	0,0633	19,14	68 944	145 732	2,1	10,2	111,5
6b	100	6,2	86	0,0677	18,32	71 561	186 671	2,6	7,4	111,9
6b	100	6,2	77	0,0625	18,89	59 824	145 322	2,4	10,0	110,8
6b	100	14,8	66	0,1071	15,78	138 375	287 718	2,1	4,5	120,4
6b	100	14,8	68	0,1186	16,96	143 986	289 864	2,0	5,3	120,3
6b	100	14,8	68	0,1154	16,50	137 005	295 547	2,2	4,5	120,1
6c	0	6,2	16	0,0849	123,5	5 957	10 634	1,8	–	127,5
6c	0	6,2	16	0,0833	121,2	5 692	10 670	1,9	–	126,6
6c	0	6,2	17	0,0828	113,4	5 332	10 661	2,0	–	126,5
6c	100	6,2	17	0,0849	116,3	3 941	8 202	2,1	*	112,7
6c	100	6,2	22	0,0898	95,0	4 551	9 418	2,1	*	110,6
6c	100	6,2	18	0,0948	122,6	4 447	8 780	2,0	*	113,7
6c	100	14,8	5	0,1503	292,3	4 072	7 971	2,0	*	121,4
6c	100	14,8	4	0,1493	363,0	4 761	8 429	1,8	*	121,3
6c	100	14,8	4	0,1443	350,8	4 863	9 612	2,0	*	121,5
7	0	6,2	50	0,0866	40,00	266 637	413 896	1,6	–	134,5
7	0	6,2	55	0,0996	42,08	279 696	426 304	1,5	–	136,4
7	0	6,2	67	0,1040	36,40	285 472	437 006	1,5	–	134,3
7	0	6,2	57	0,0960	39,00	274 249	421 566	1,5	–	136,3
7	100	6,2	46	0,1107	55,78	184 456	277 994	1,5	12,2	116,6
7	100	6,2	41	0,1020	57,35	179 319	267 327	1,5	14,2	117,0
7	100	6,2	44	0,1043	55,18	188 382	280 575	1,5	15,5	116,3
7	100	6,2	39	0,1008	60,32	184 157	274 004	1,5	11,3	115,5
7	100	14,8	64	0,1823	27,53	185 058	275 452	1,5	6,9	125,6
7	100	14,8	67	0,1830	26,56	185 125	273 643	1,5	7,7	125,3
7	100	14,8	60	0,1839	29,91	191 434	282 039	1,5	6,1	125,3
7	100	14,8	60	0,1797	29,27	188 139	277 167	1,5	6,8	125,3

[1] Loading of 1-octene in polymerization reactor

[2] Ethylene partial pressure in polymerization reactor

[3] Polymerization activity in $g_{polymer}/mmol_{catalyst}\cdot h\cdot bar_{ethylene}$

[4] Polydispersity index, PDI = M_w/M_n

[5] Content of incorporated 1-octene in the polymer

[6] Melting temperature of the polymer

Table S4. 1-Decene polymerization data (0.080 umol metallocene prealkylated with 20 equiv of TIBA, 1.1 equiv. AB, 2 mL decene, 2.8 mL isohexane, 0.2 ml toluene, 0.2 (for **8**) or 0.6 umol (for **6a–6c**) scavenger (*n*Oct$_3$Al), 60 min).

Pre-cat.	T_p, °C[1]	Polymer yield, g	A[2]	M_n[3]	Content of unsaturated chain end groups, mol%			
					disubstituted vinylene	trisubstituted vinylene	vinyl	vinylidene
6c	60	0,3514	4391	539	4,3	1,9	0,3	93,6
6c	60	0,3463	4329					
6c	85	0,7325	9154	453	3,0	2,6	0,2	94,2
6c	85	0,7107	8881					
6c	110	0,3582	4478	439	3,1	3,0	0,3	93,6
6c	110	0,3353	4190					
6b	60	0,0226	282					
6b	60	0,0459	573	1971	4,5	22,2	2,0	71,3
6b	85	0,0101	126					
6b	85	0,0104	130					
6b	110	0,0021	26					
6b	110	0,0029	36					
6a	60	0,102	1275	632	7,3	4,1	0,7	87,9
6a	60	0,0989	1236					
6a	85	0,0733	916					
6a	85	0,0903	1128	634	7,3	4,1	0,7	87,9
6a	110	0,014	175					
6a	110	0,0142	178					
8	60	0,5868	7333					
8	60	0,8662	10828	373	23,1	27,3	8,9	40,6
8	85	0,3222	4028	361	21,5	25,3	8,8	44,4
8	85	0,3145	3930					
8	110	0,1112	1390	338	19,7	24,0	8,0	48,3
8	110	0,079	987					

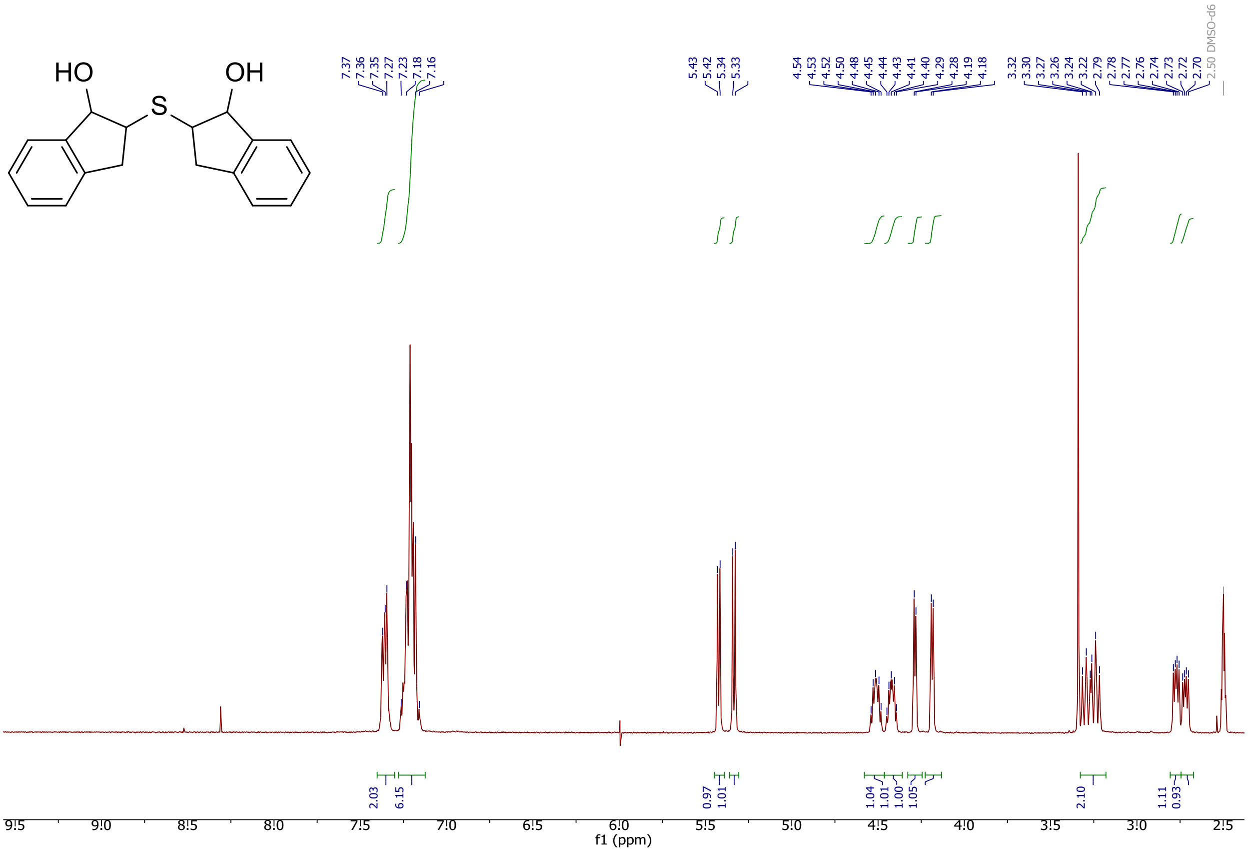
[1] Polymerization temperature

[2] Polymerization activity in $g_{polymer}/mmol_{catalyst}\cdot h$

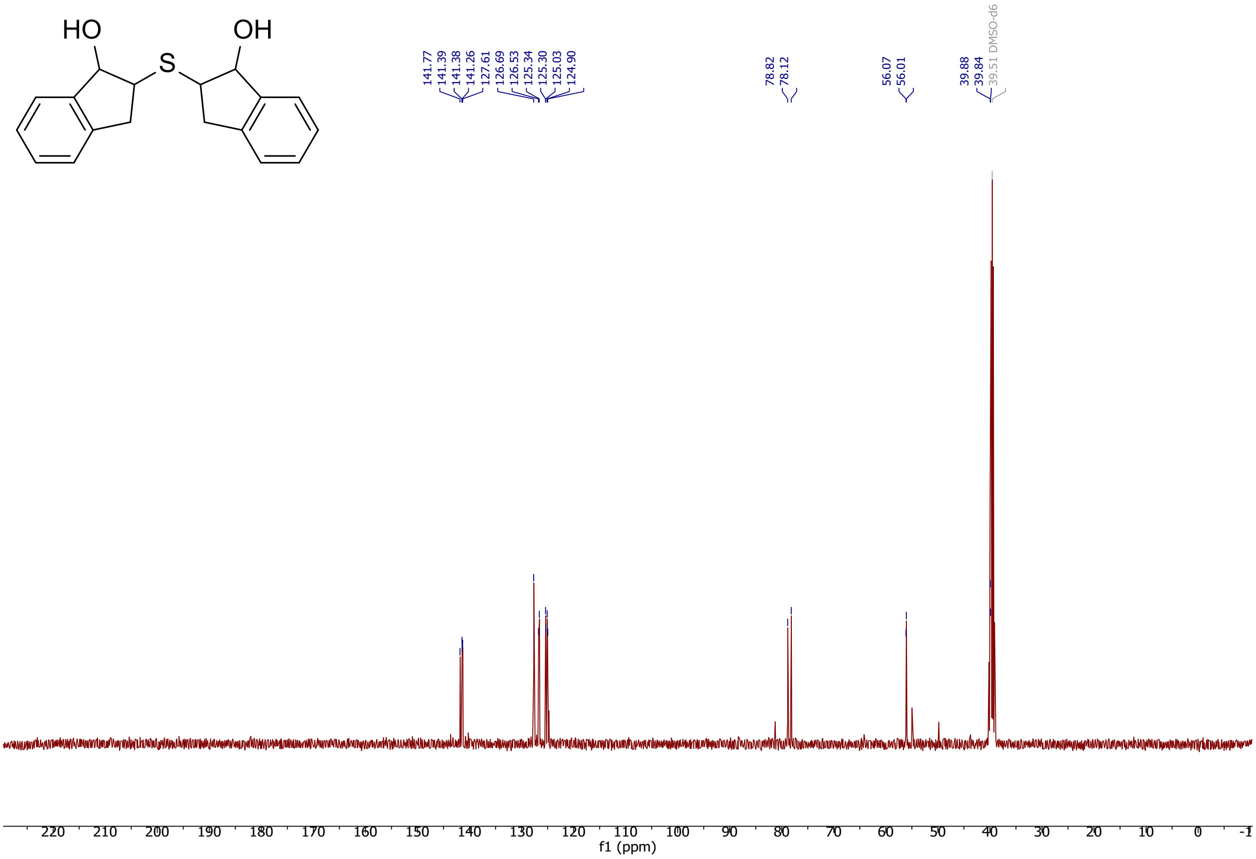
[3] Measured by ^1H NMR

^{1}H and ^{13}C NMR Spectra of Organic Compounds and Complexes

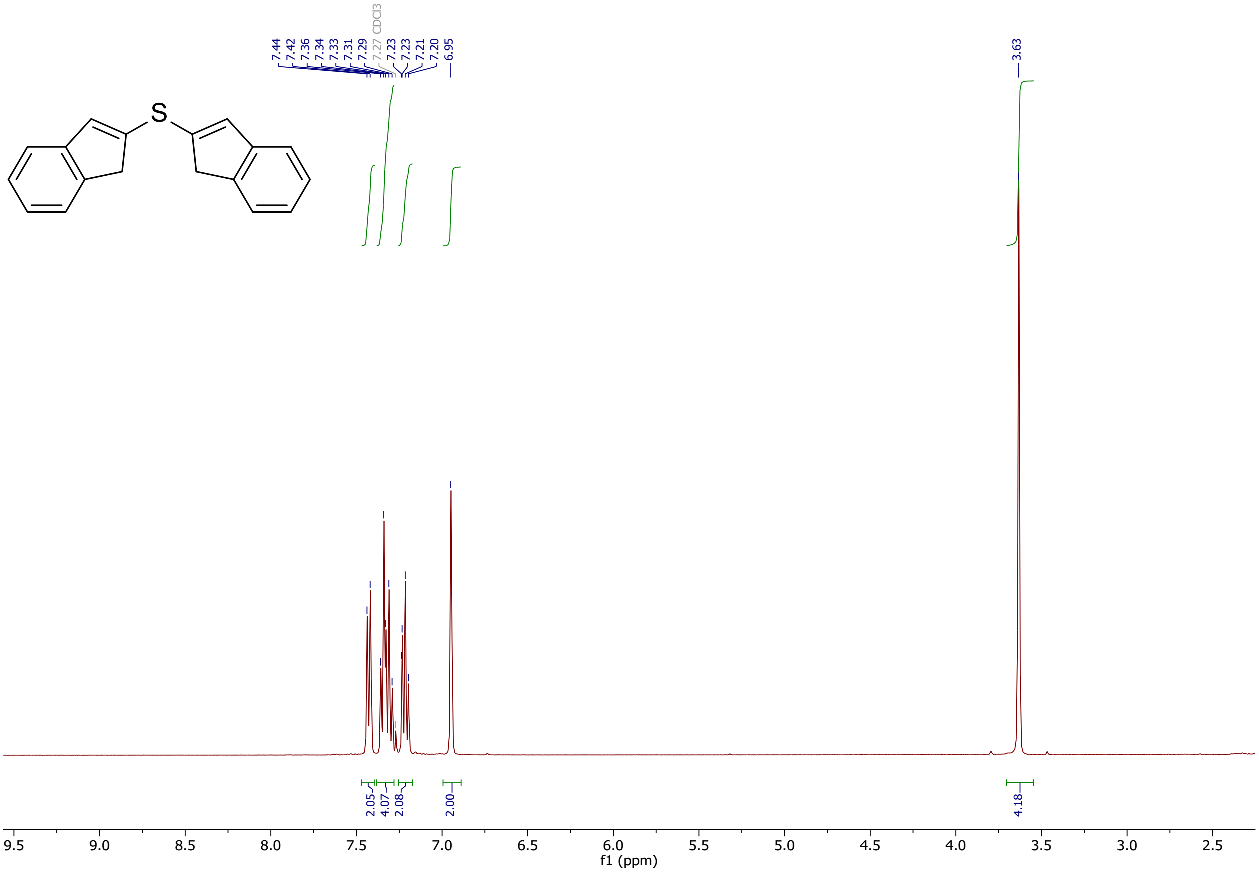
^{1}H NMR-spectrum of **3a** (mixture of two isomers):



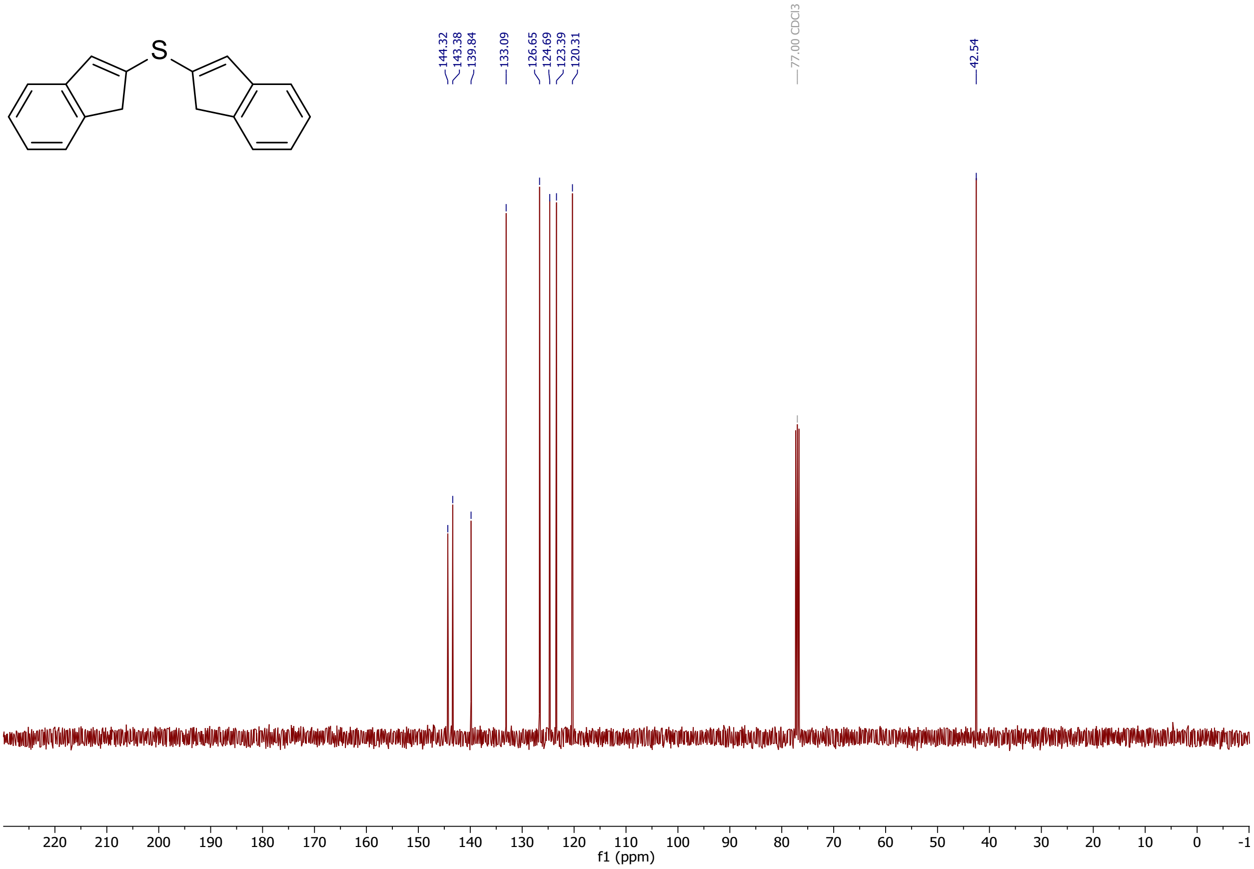
^{13}C NMR-spectrum of **3a** (mixture of two isomers):



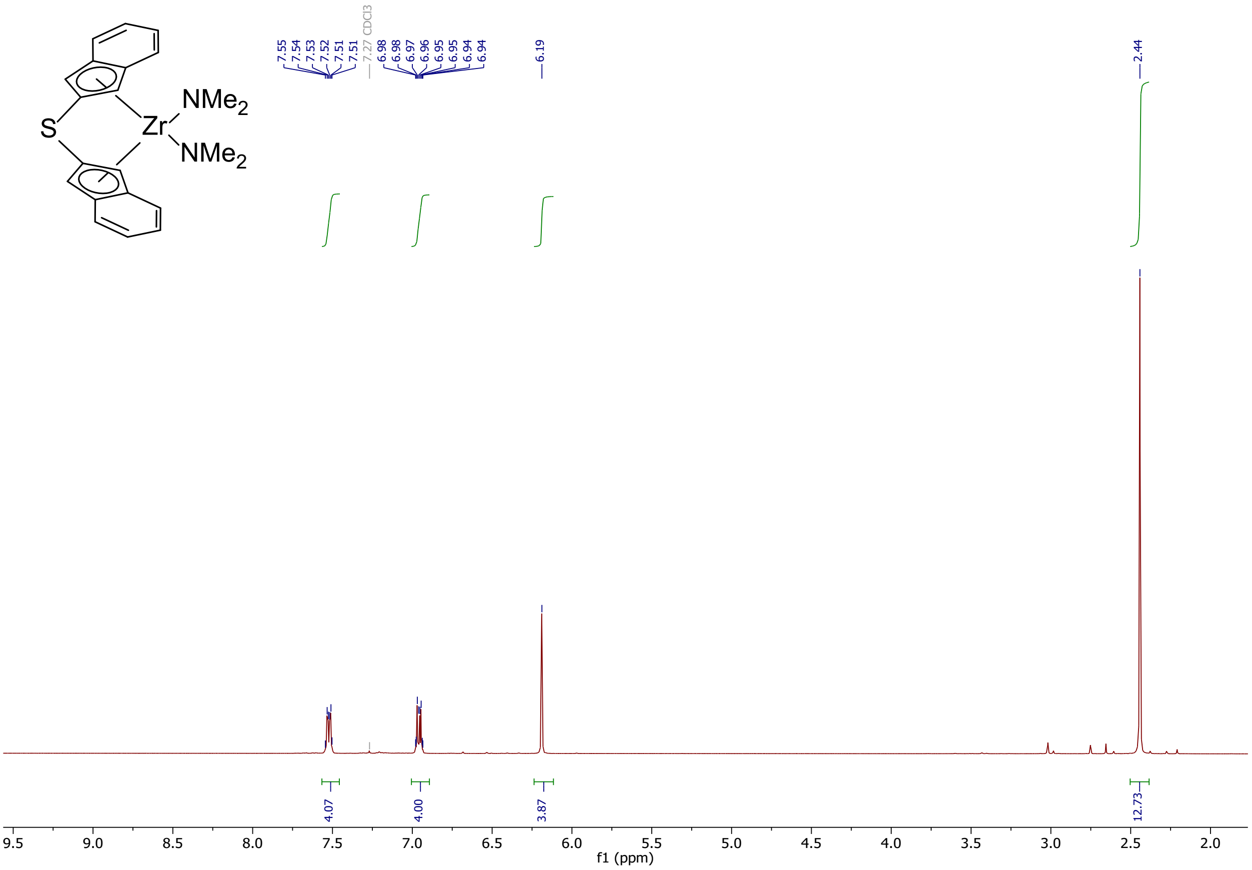
^{1}H NMR-spectrum of **4a**:



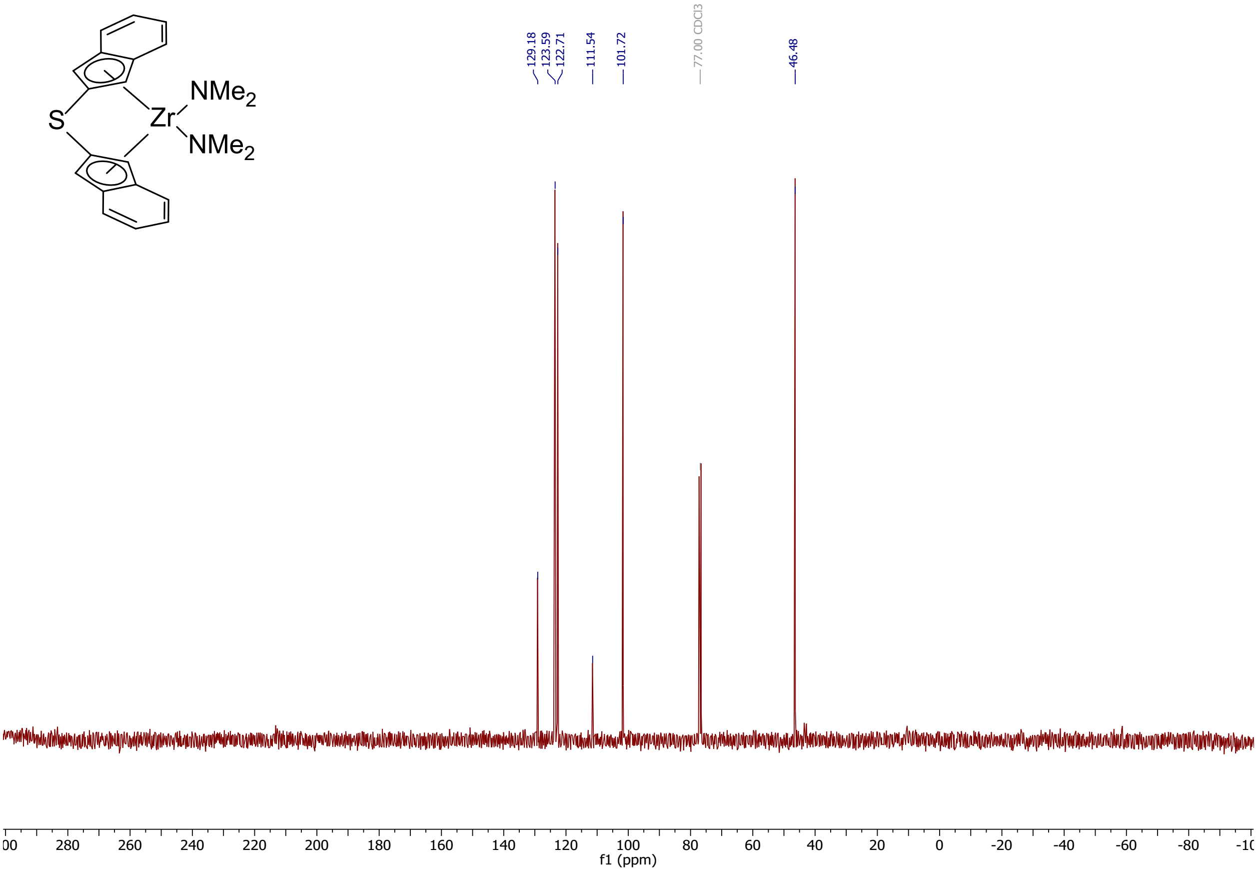
^{13}C NMR-spectrum of **4a**:



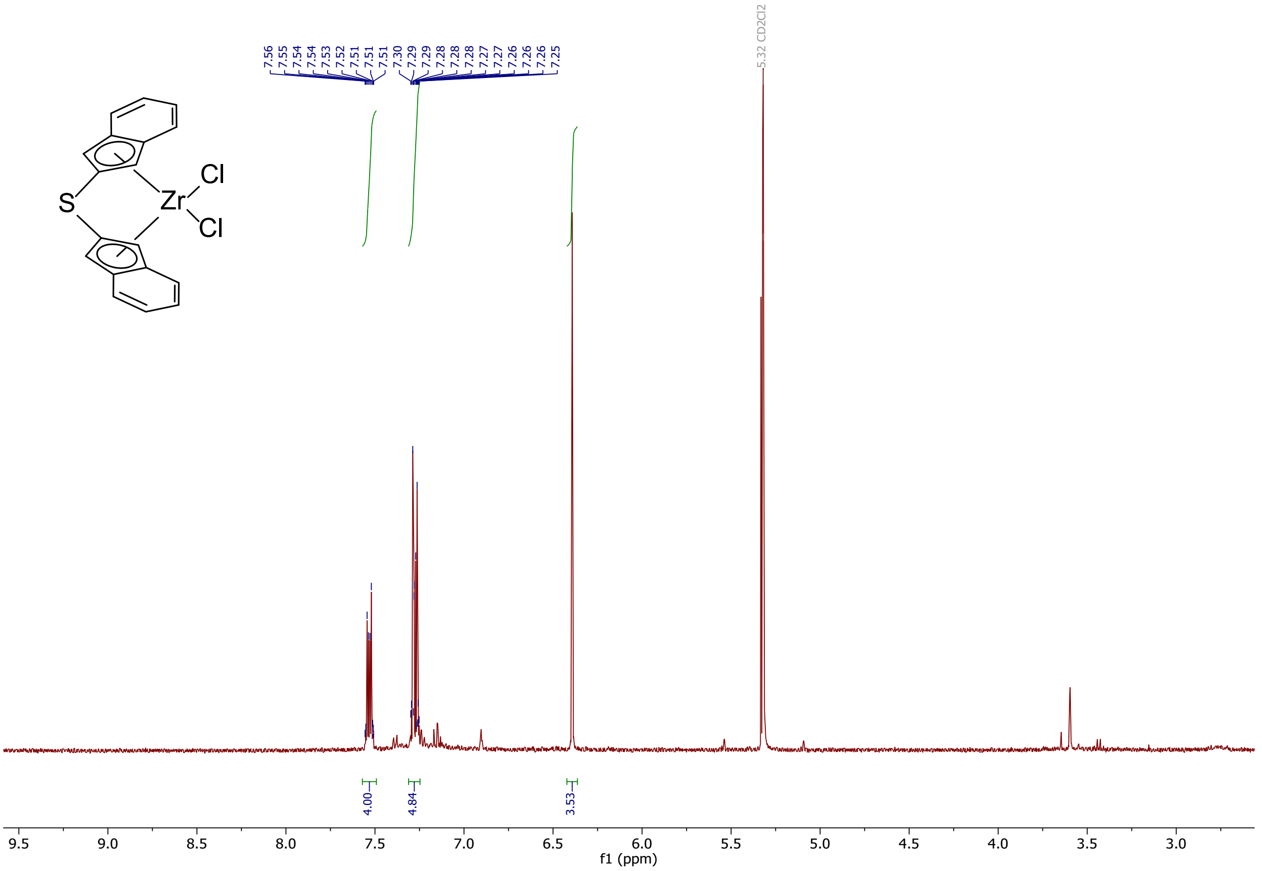
^{1}H NMR-spectrum of **5a**:



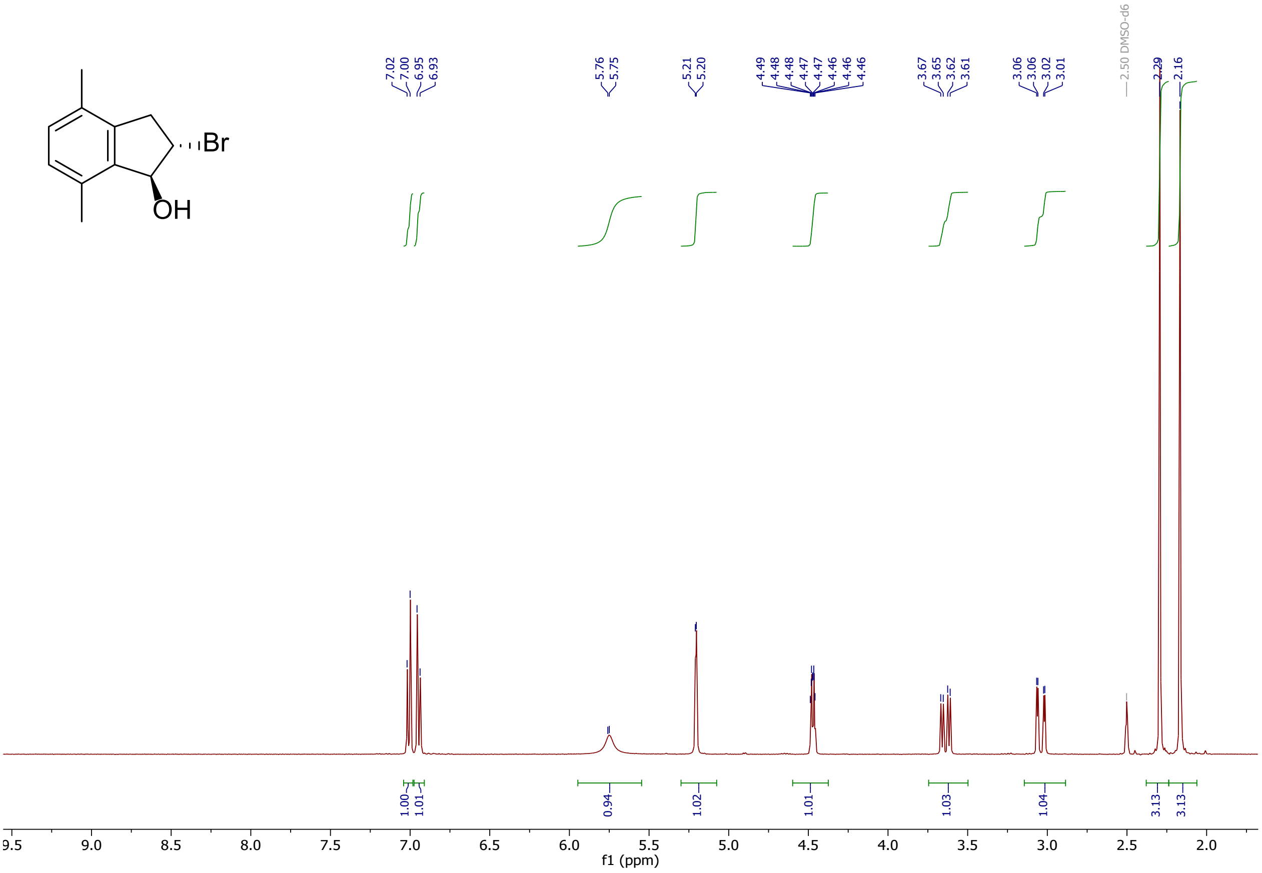
^{13}C NMR-spectrum of **5a**:



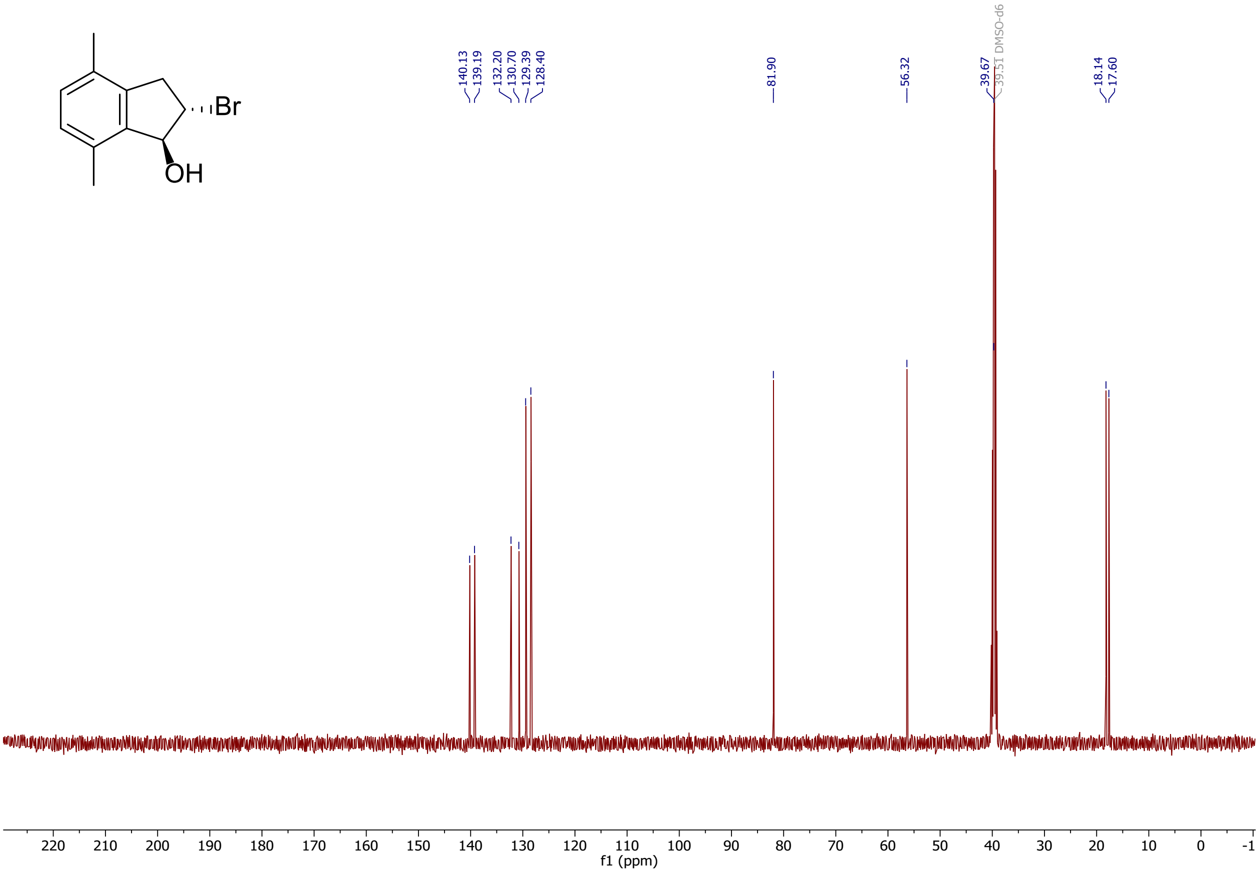
^{1}H NMR-spectrum of **6a**:



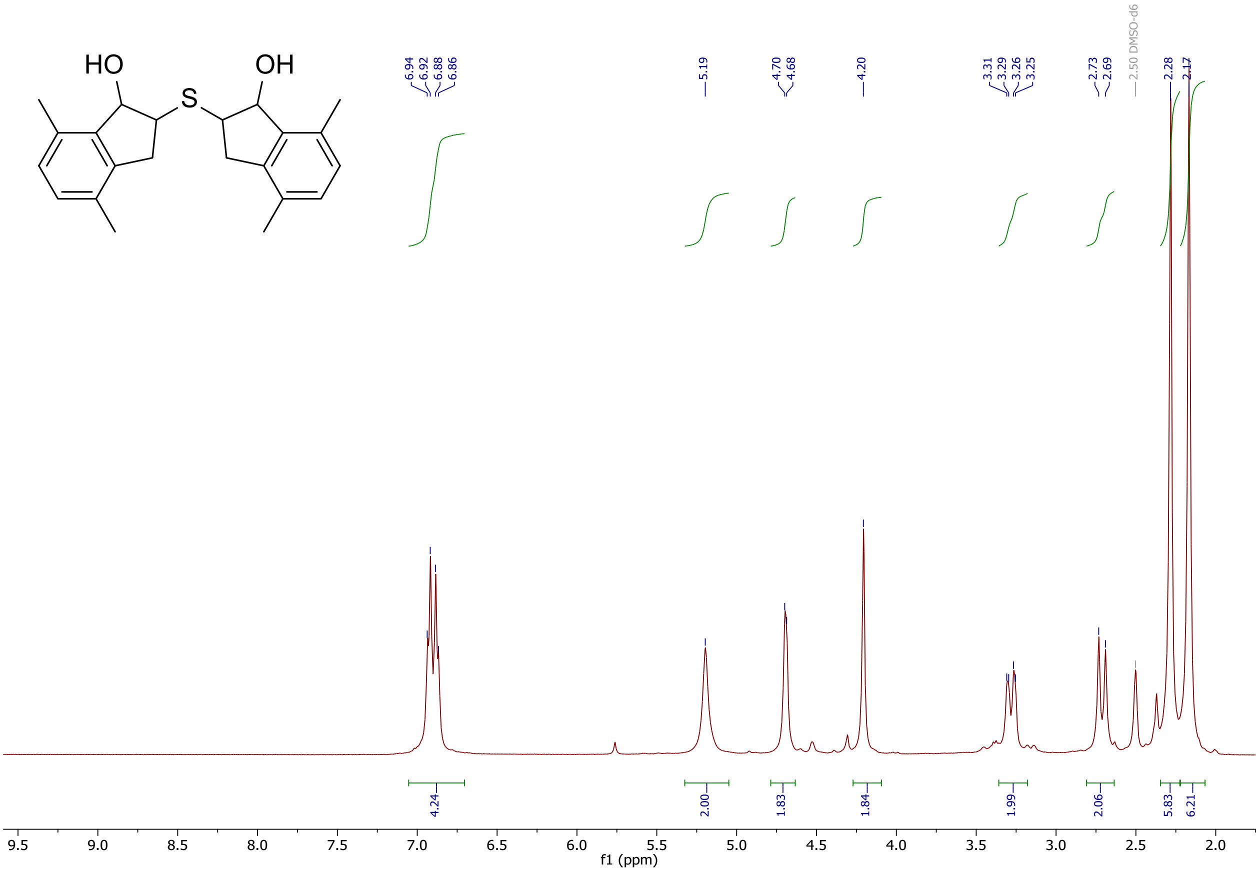
^{1}H NMR-spectrum of **2b**:



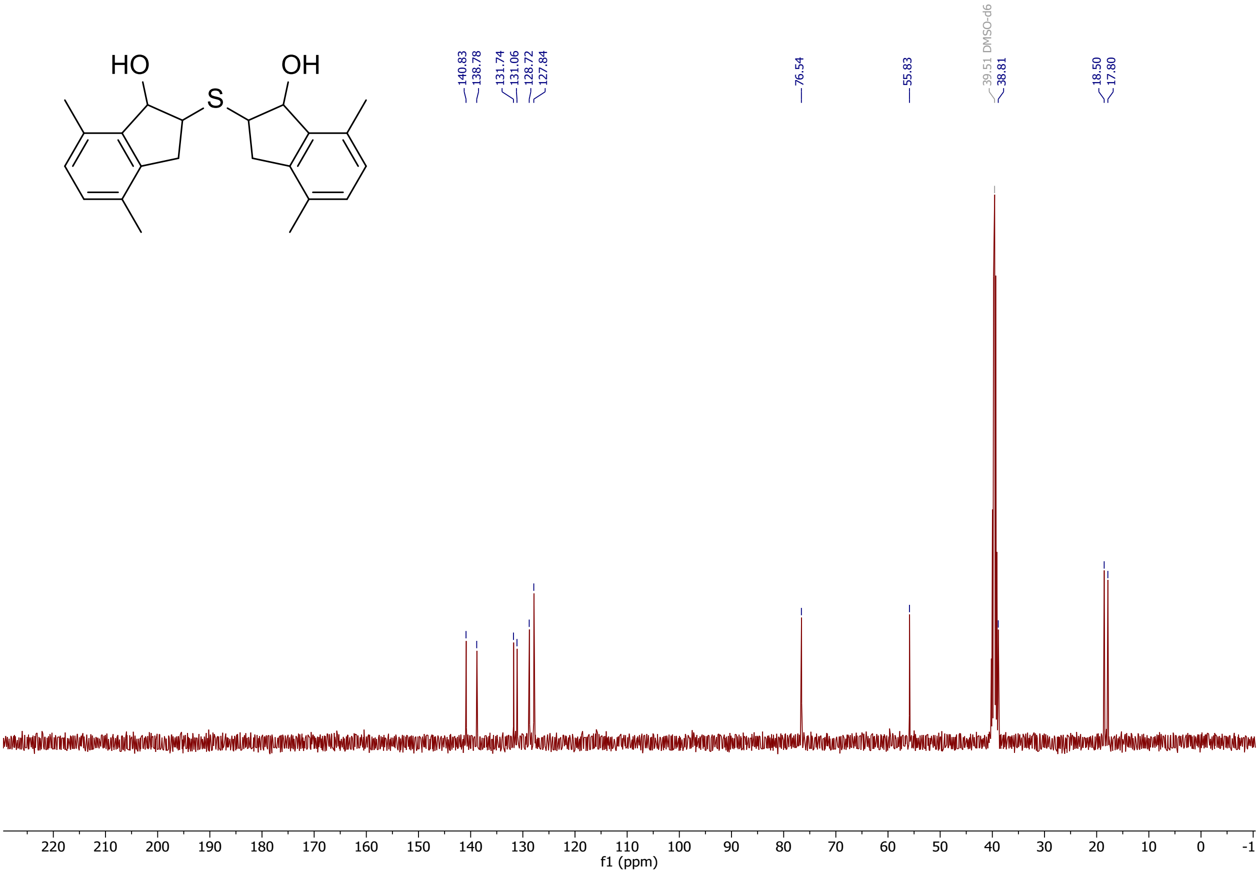
^{13}C NMR-spectrum of **2b**:



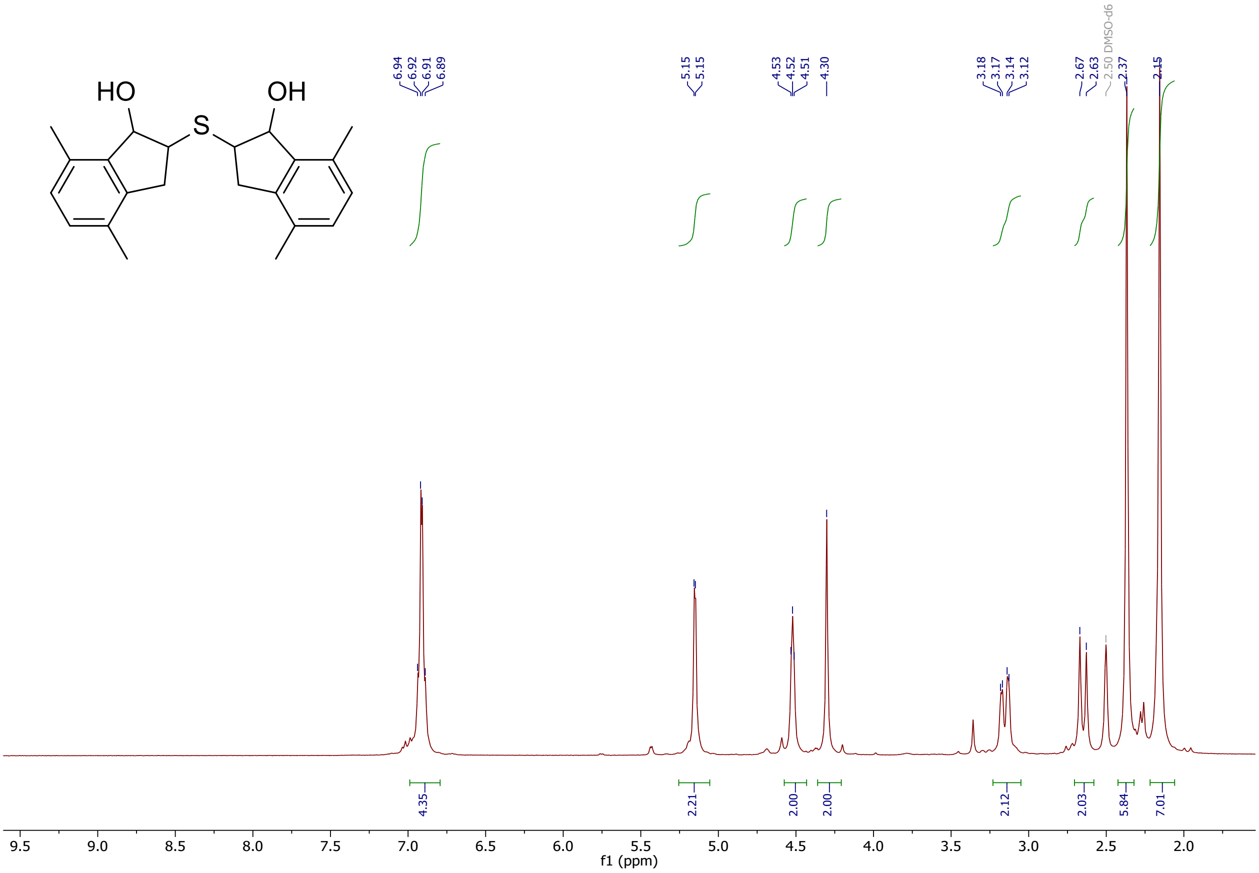
^{1}H NMR-spectrum of **3b** (1st isomer):



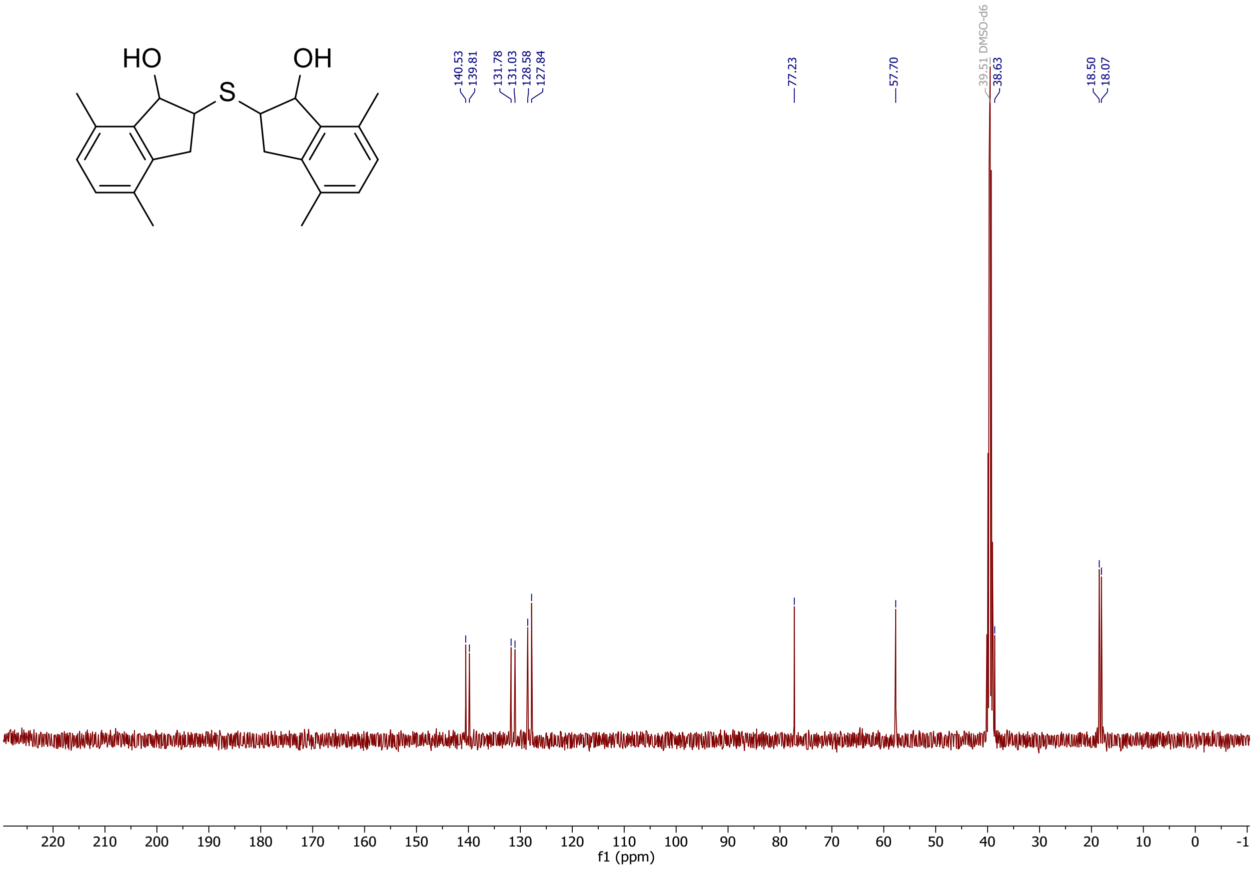
^{13}C NMR-spectrum of **3b** (1st isomer):



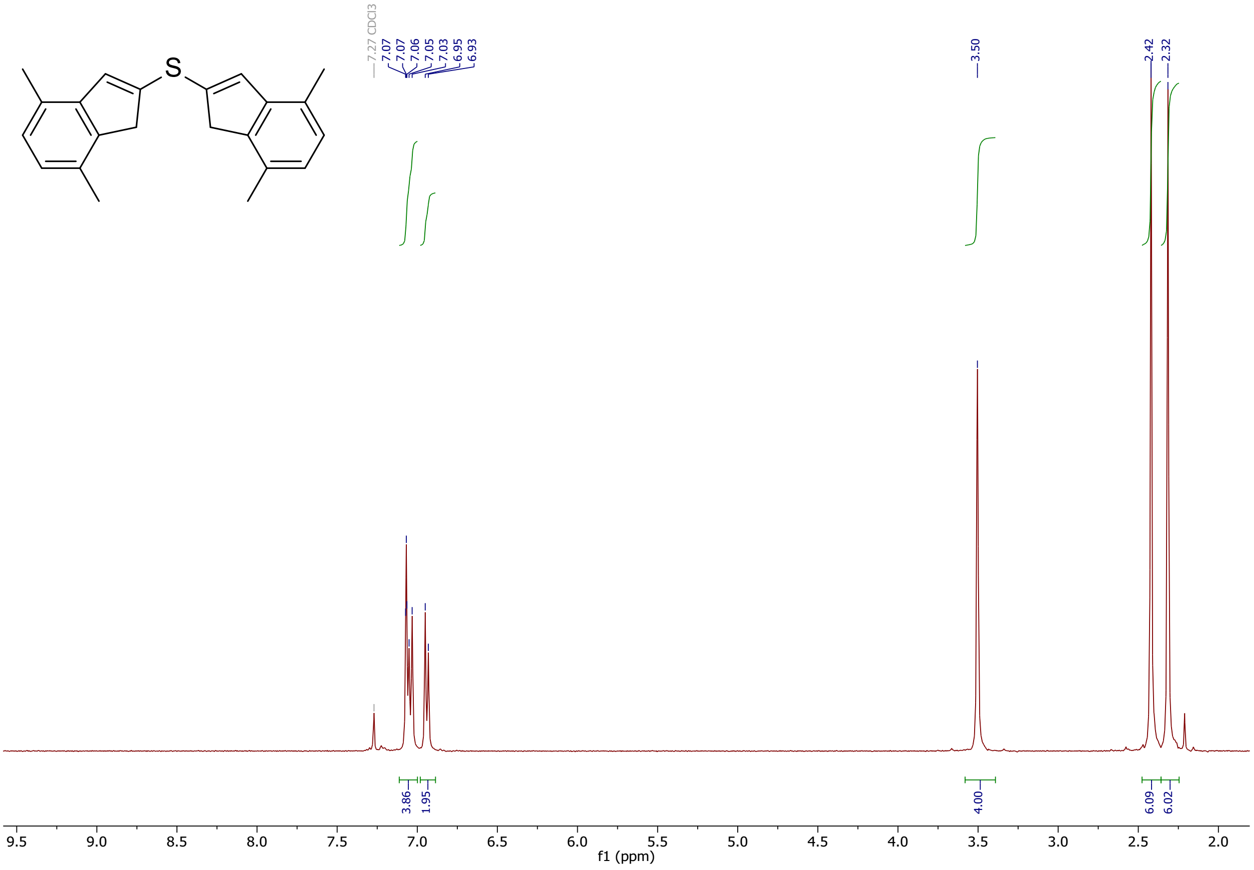
^{1}H NMR-spectrum of **3b** (2nd isomer):



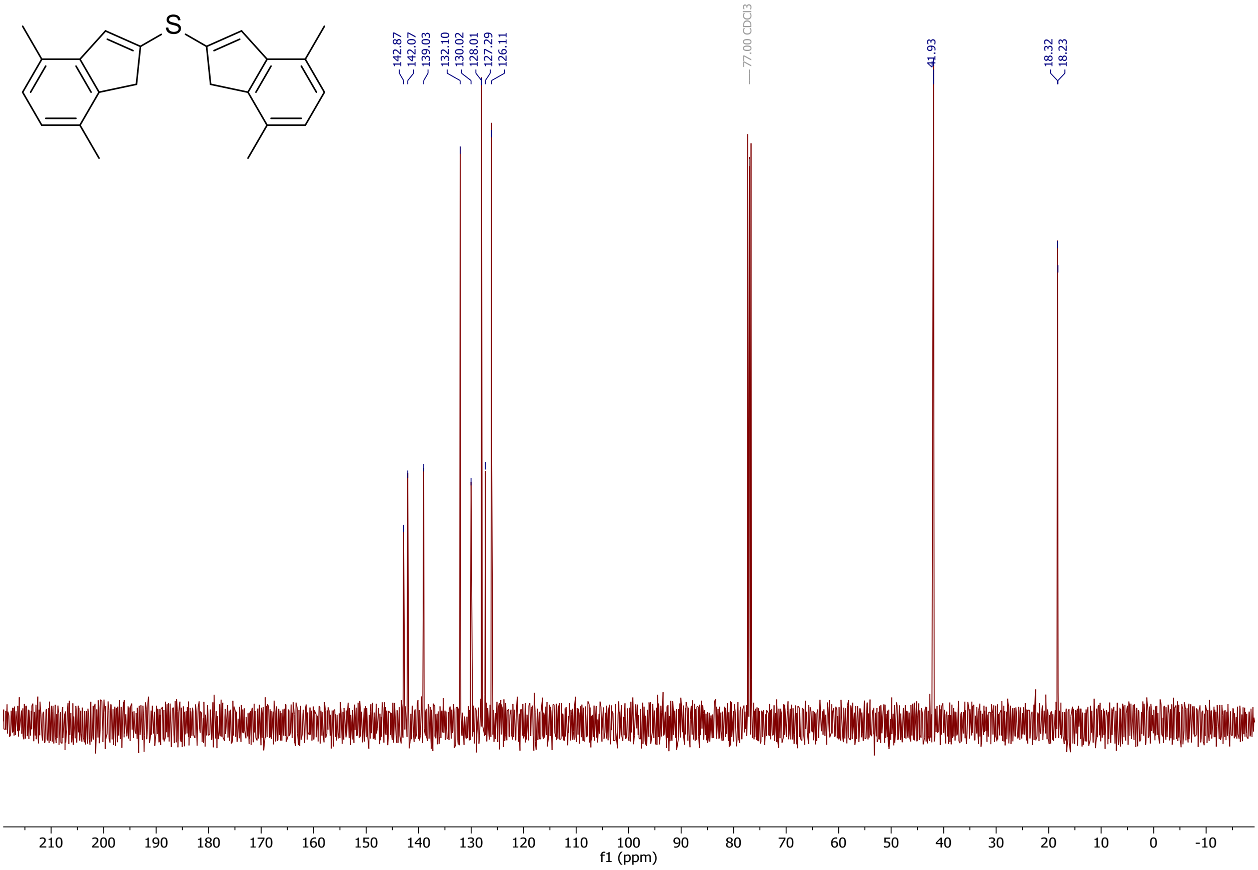
^{13}C NMR-spectrum of **3b** (2nd isomer):



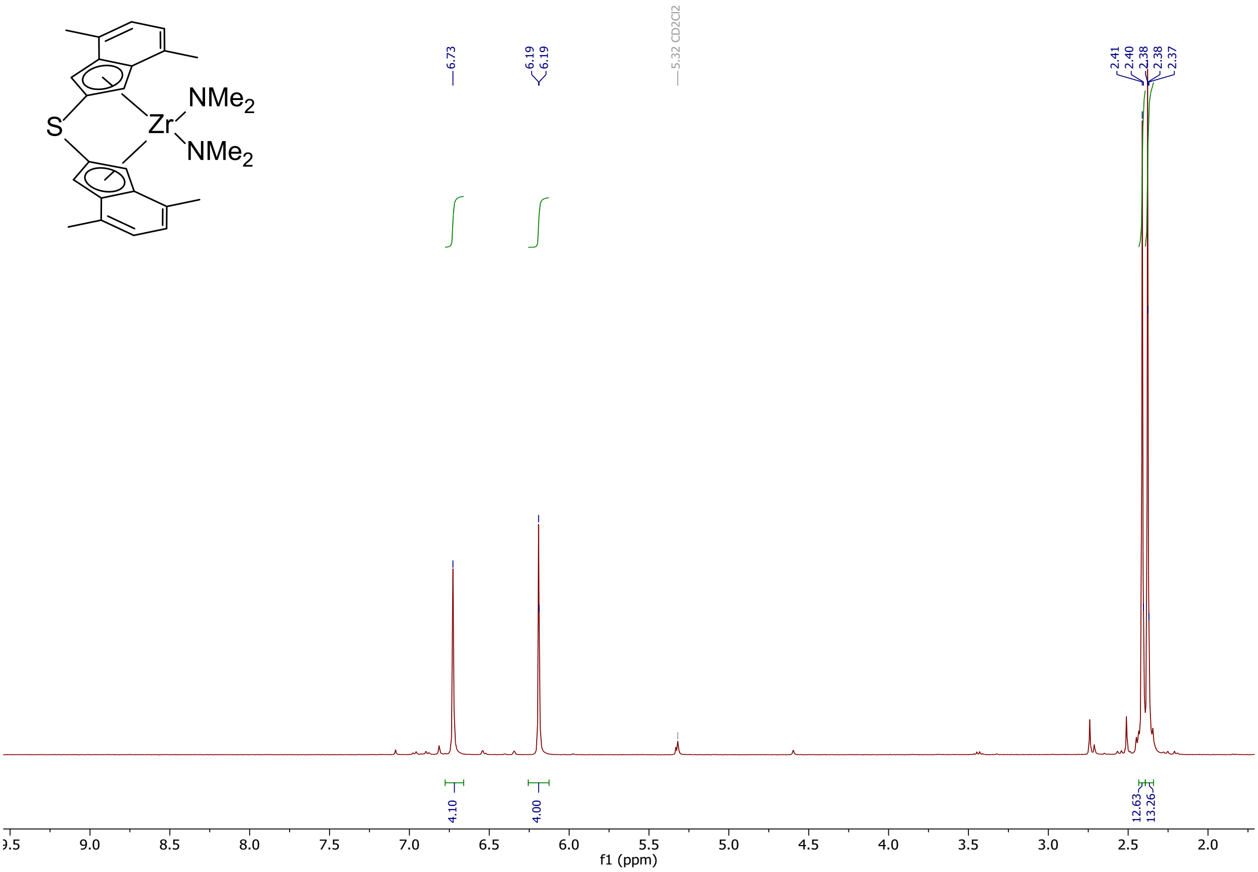
^{1}H NMR-spectrum of **4b**:



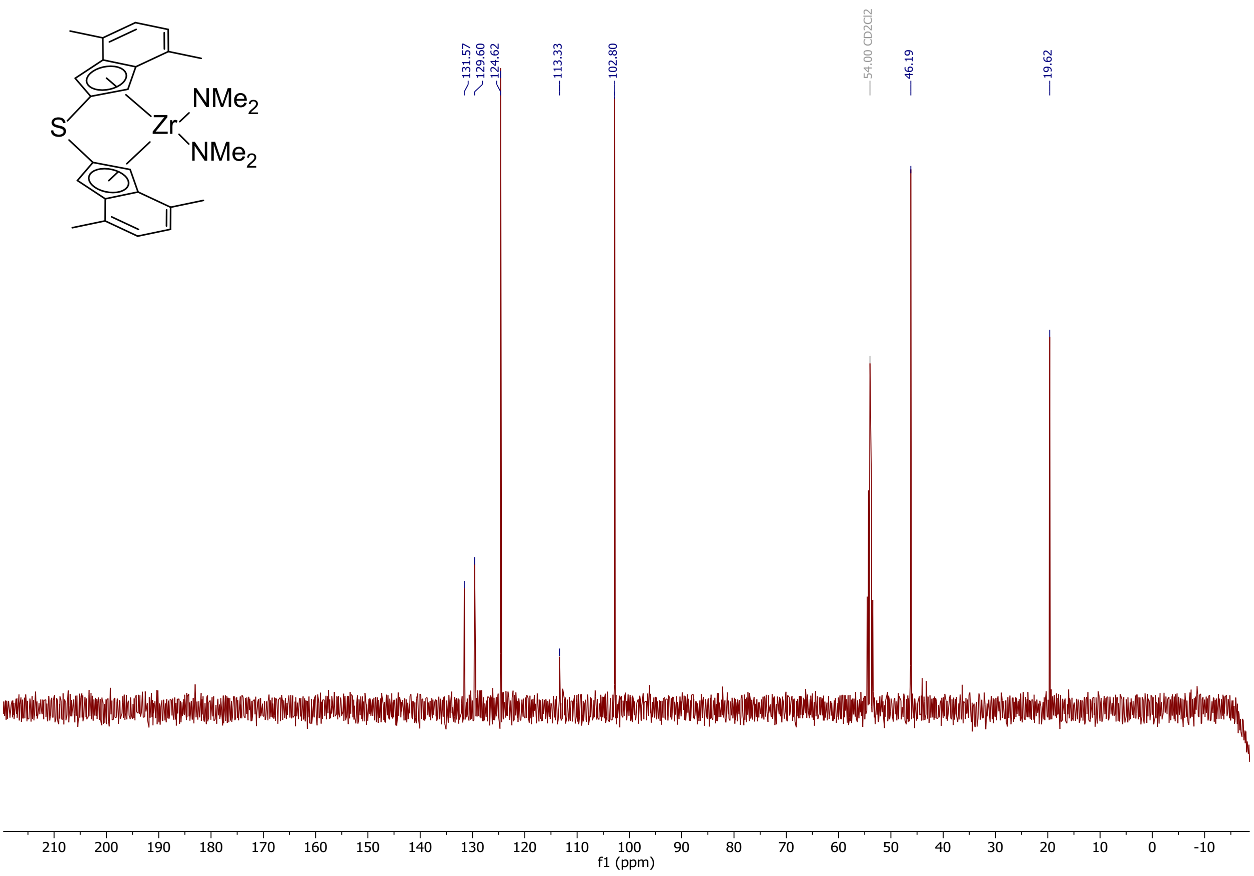
^{13}C NMR-spectrum of **4b**:



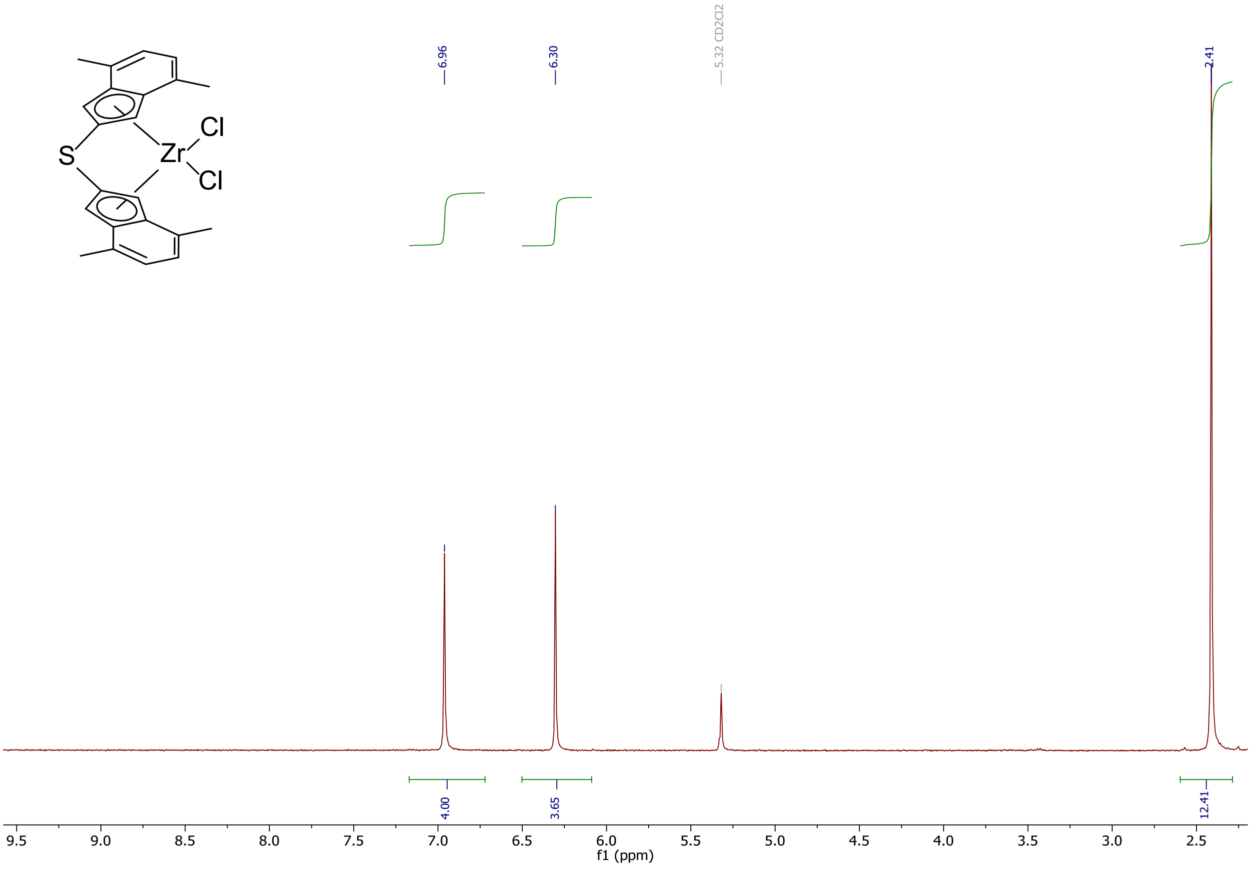
^{1}H NMR-spectrum of **5b**:



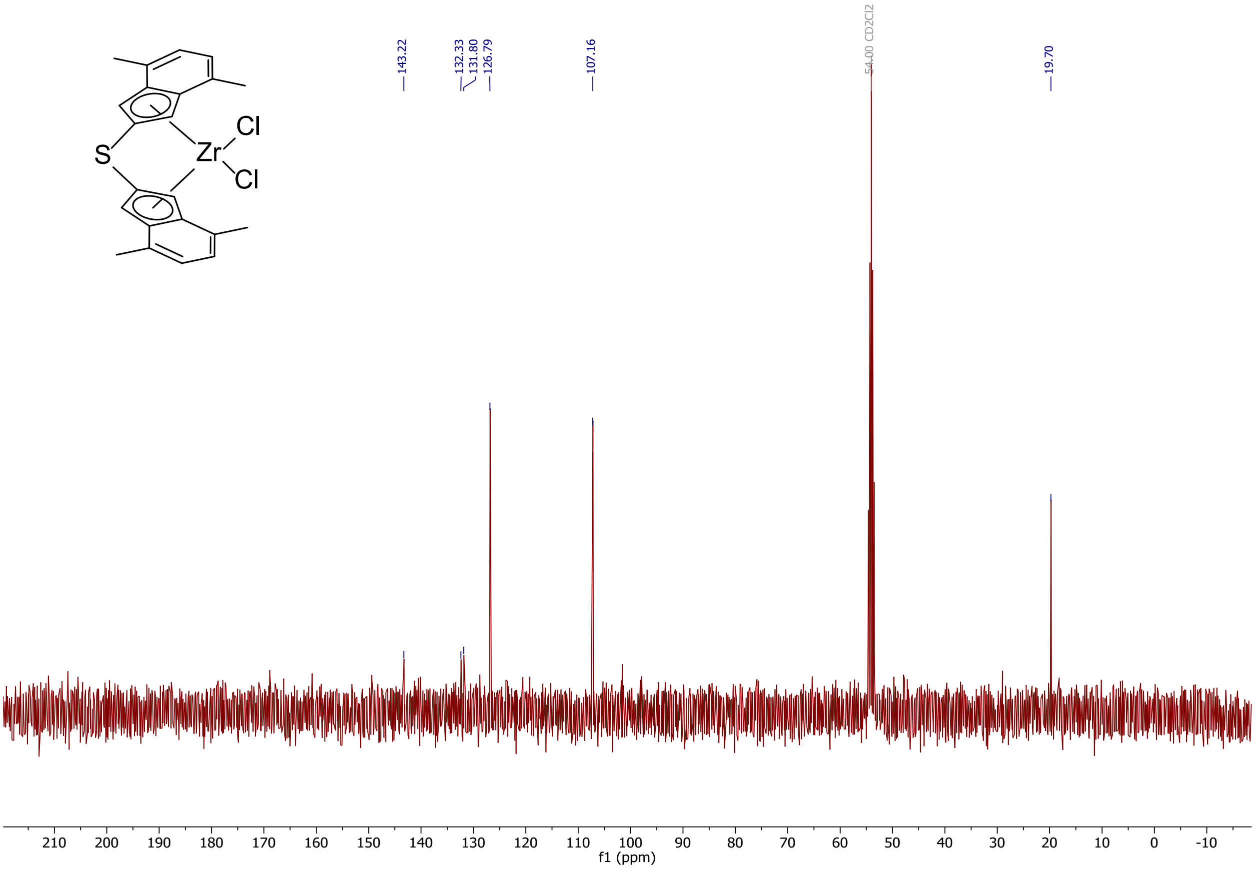
^{13}C NMR-spectrum of **5b**:



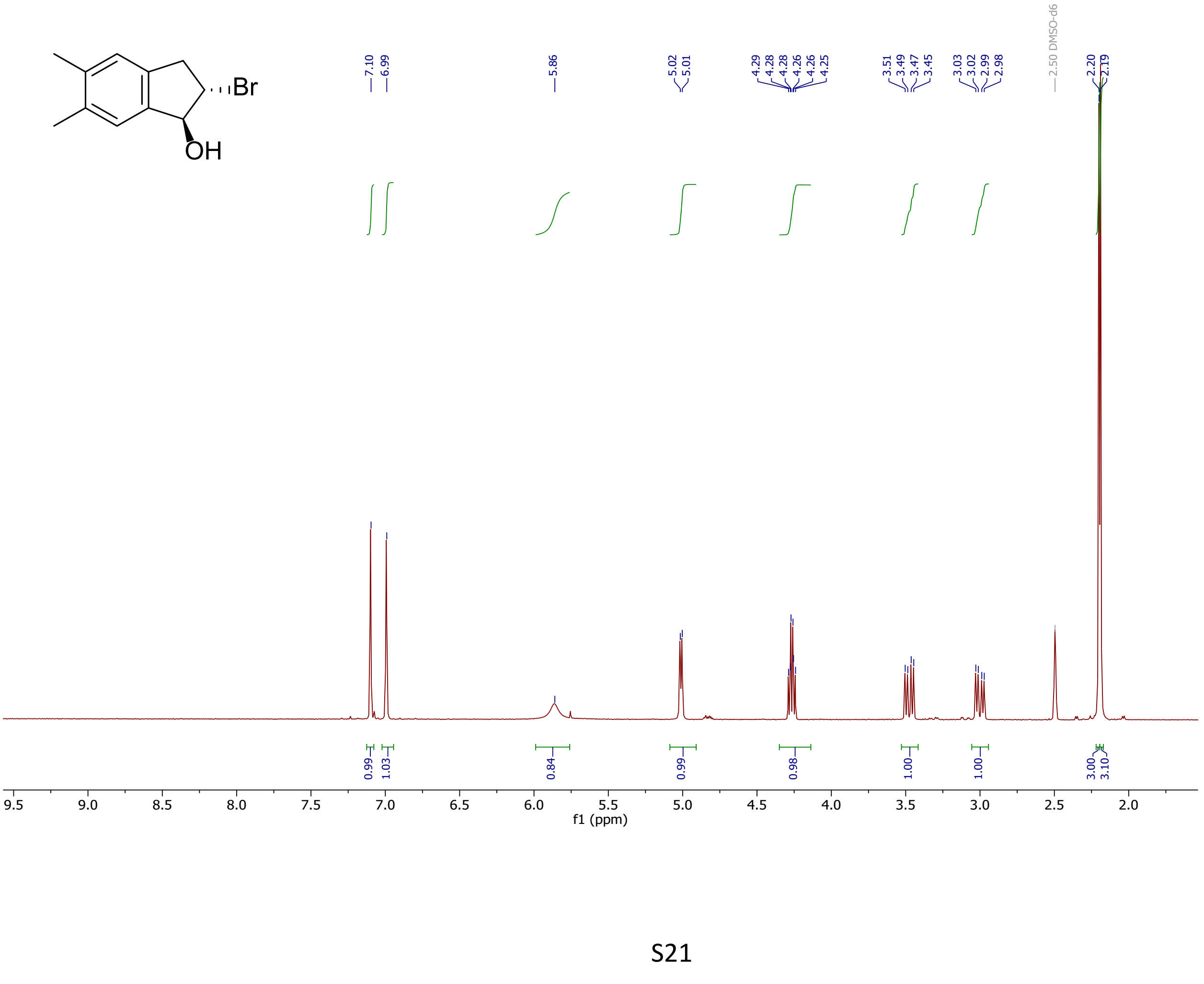
^{1}H NMR-spectrum of **6b**:



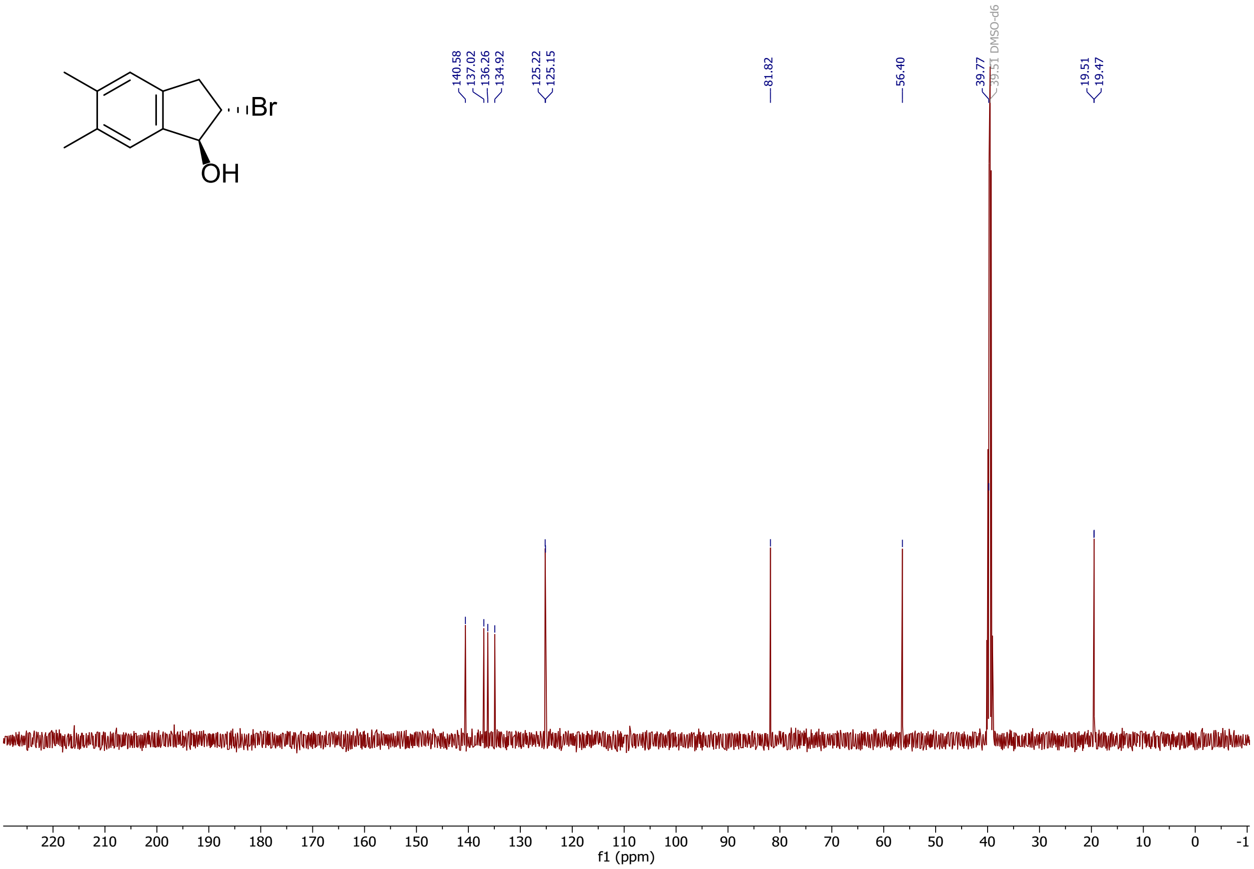
^{13}C NMR-spectrum of **6b**:



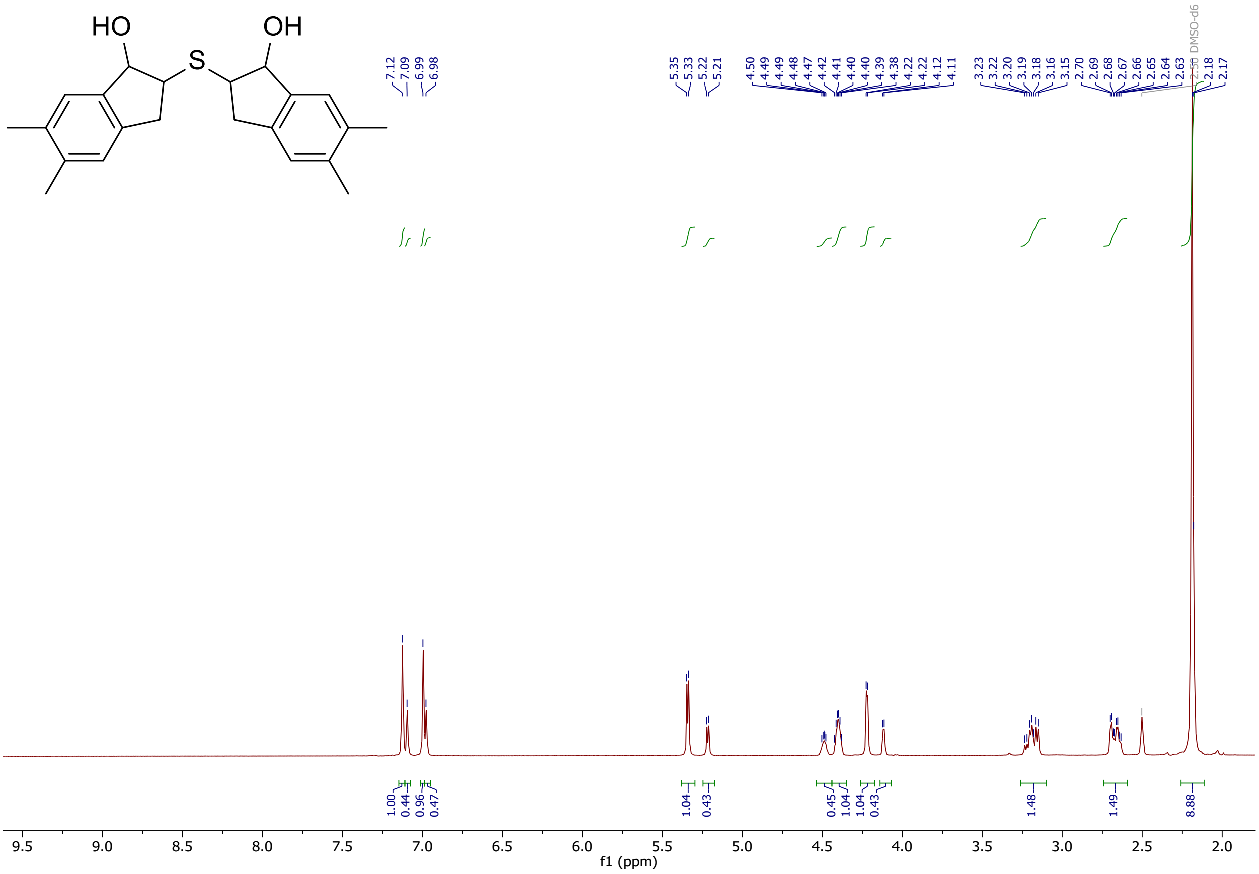
^{1}H NMR-spectrum of **2c**:



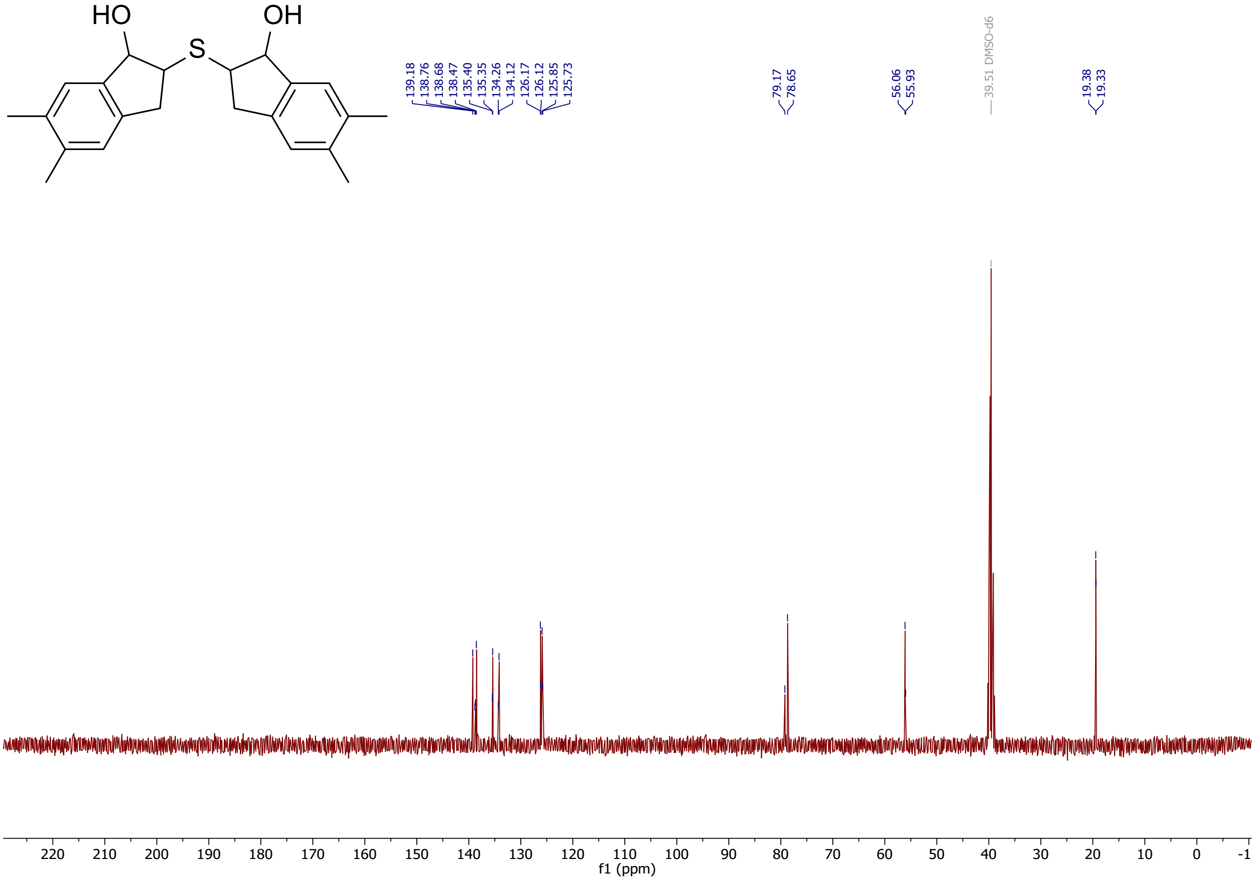
^{13}C NMR-spectrum of **2c**:



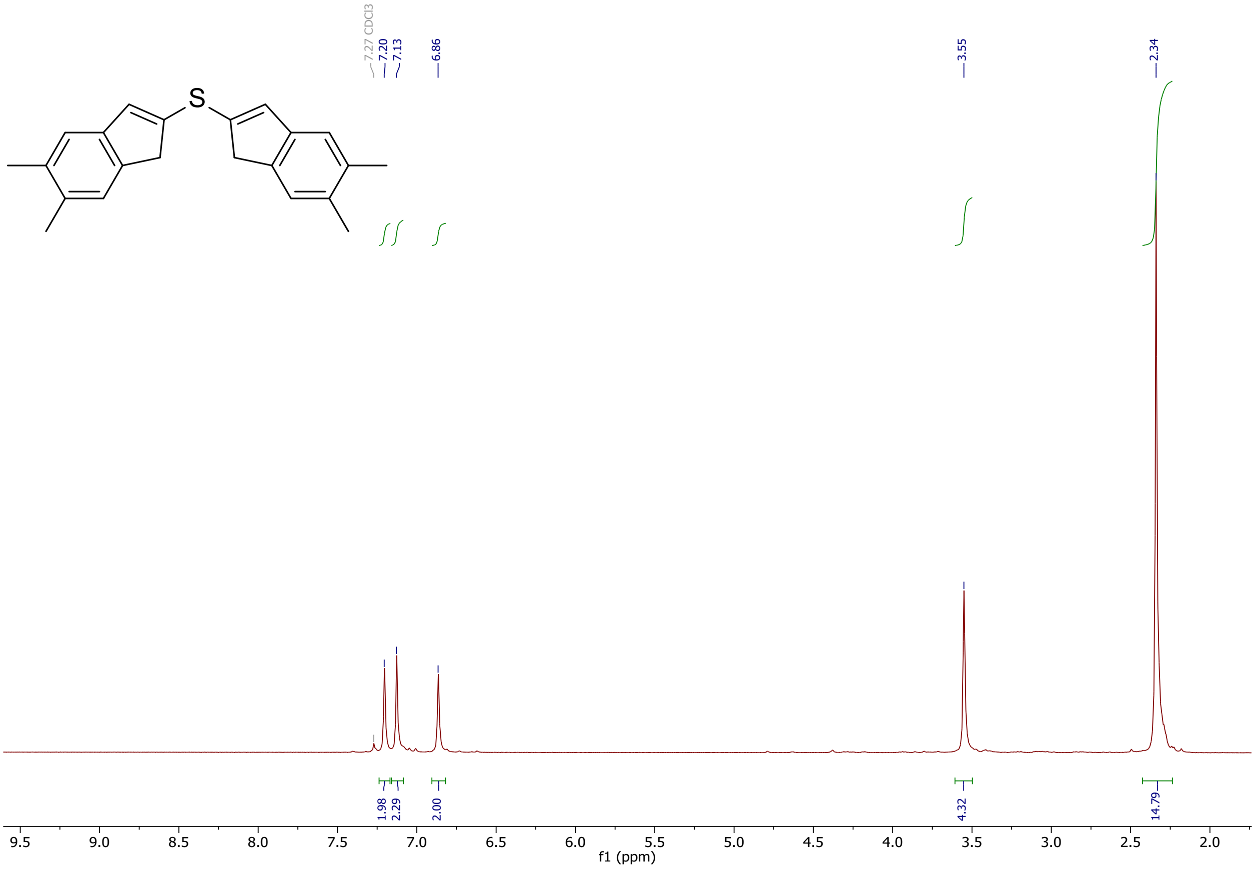
^{1}H NMR-spectrum of **3c** (mixture of two isomers):



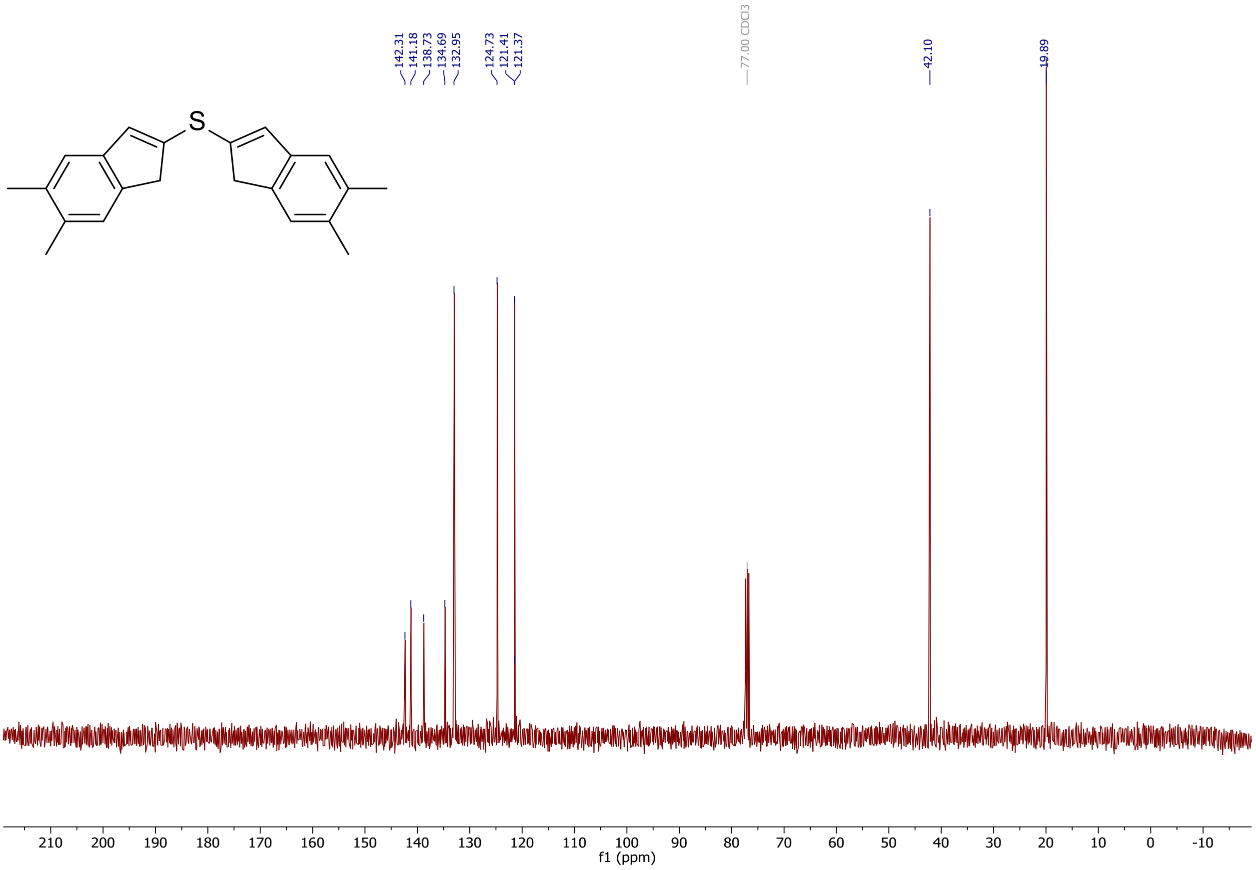
^{13}C NMR-spectrum of **3c** (mixture of two isomers):



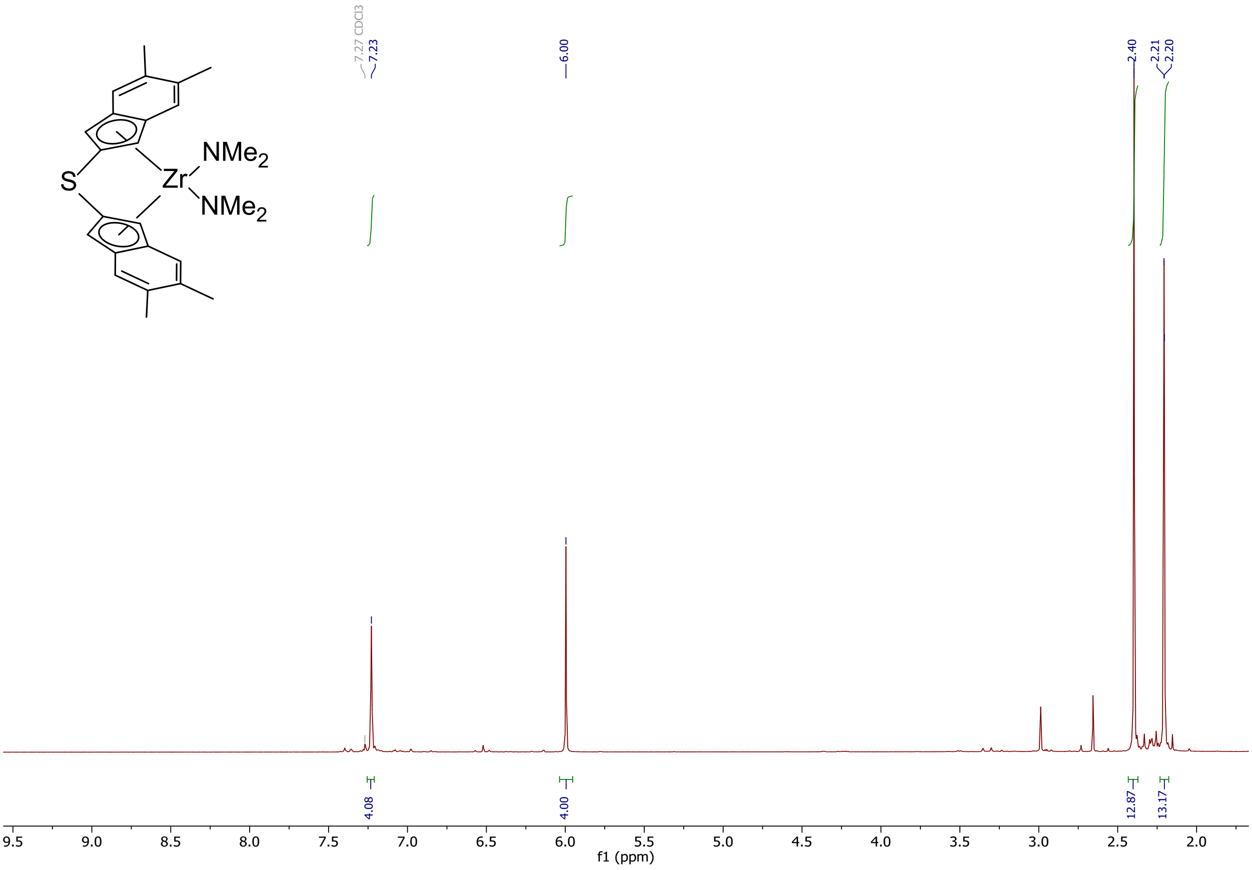
^{1}H NMR-spectrum of **4c**:



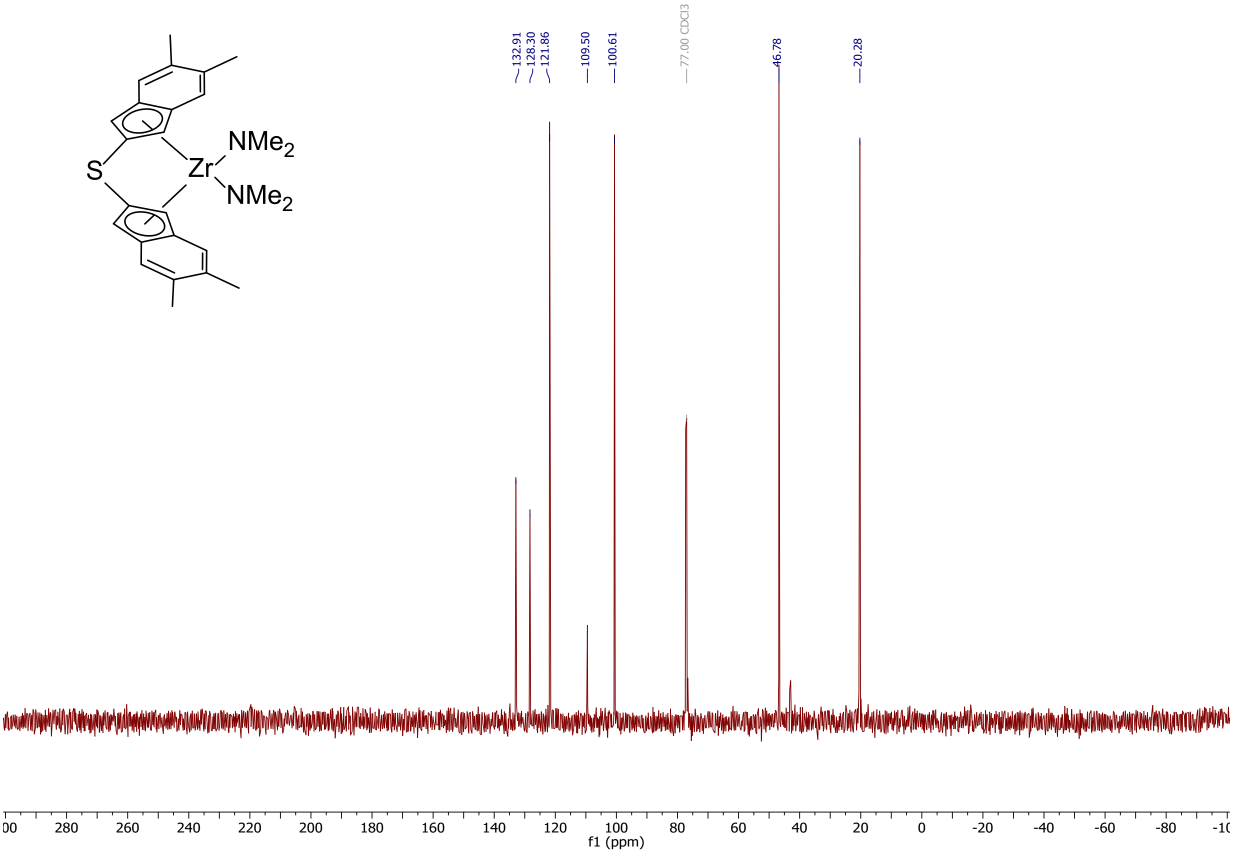
^{13}C NMR-spectrum of **4c**:



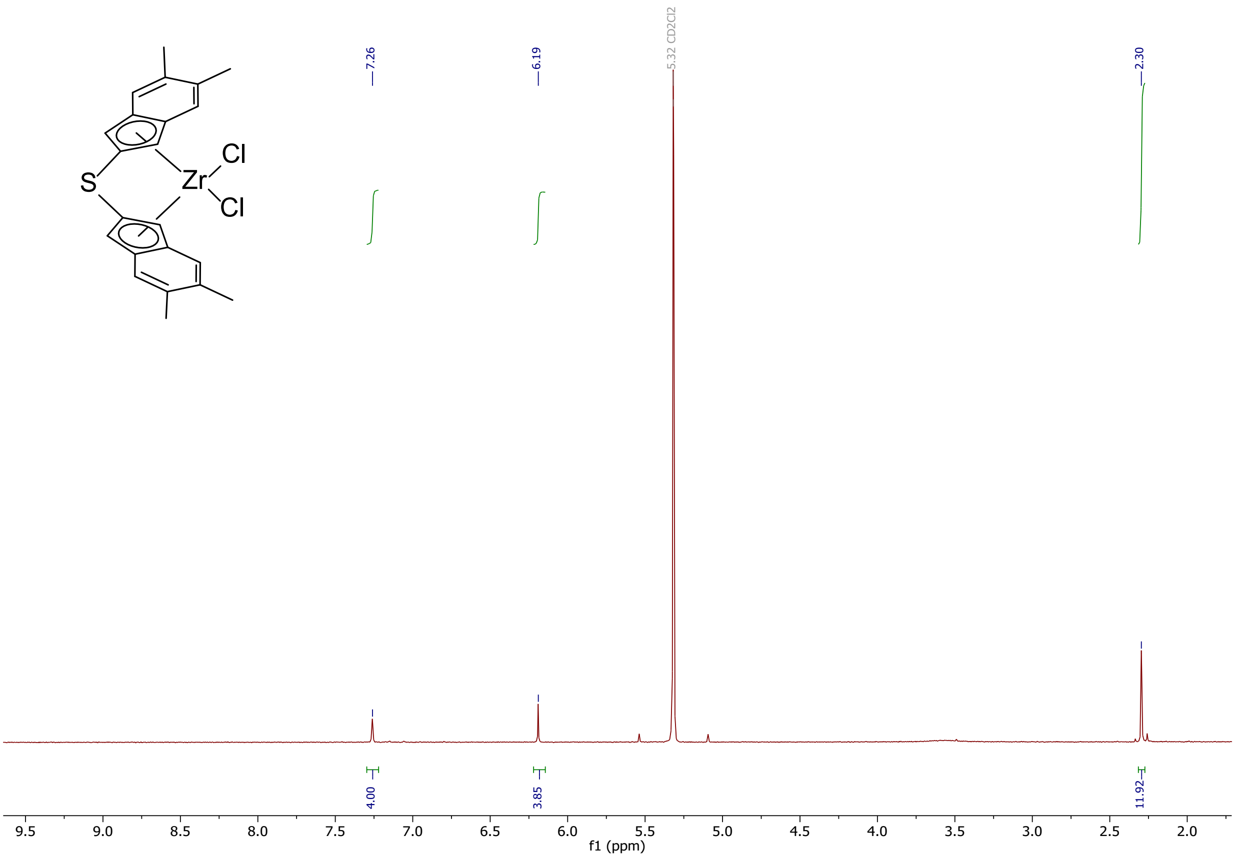
^{1}H NMR-spectrum of **5c**:



^{13}C NMR-spectrum of **5c**:



^{1}H NMR-spectrum of **6c**:



References

S1. J. A. M. Canich, I. S. Borisov, A. K. Golenishchev, G. P. Goryunov, D. V. Uborsky, P. S. Kulyabin, D. S. Kononovich, V. V. Izmer and A. Z. Voskoboynikov, *US Patent 9458254*, 2016.

S2. R. Santi, G. Borsotti, G. Longhini, P. Biagini, A. Proto, F. Masi and V. Banzi, *US Patent 6417418*, 2002.

S3. S. Brenner, R. Kempe and P. Arndt, *Z. Anorg. Allg. Chem.*, 1995, **621**, 2021. DOI: 10.1002/zaac.19956211207

S4. R. L. Halterman, D. R. Fahey, E. F. Bailly, D. W. Dockter, O. Stenzel, J. L. Shipman, M. A. Khan, S. Dechert, and H. Schumann, *Organometallics,* 2000, **19**, 546. DOI: 10.1021/om000551y