Supporting Information

Cyclopropyl vs. Isopropyl in Zirconocenes: Unexpected Catalytic Performance in Propylene Polymerization

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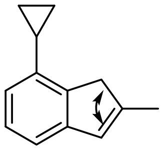
Synthesis of Metallocenes

General details. Reactions involving air or moisture sensitive compounds were carried out under inert atmosphere (argon or nitrogen) using standard Schlenk techniques or a glove box environment (Vacuum Atmospheres Co. and M. Braun Inertgas-Systeme GmbH). Where applicable, all solvents were dried over 4 Å molecular sieves prior to use. The amount of residual water present in dried solvents was quantified, using Karl Fischer Coulometer C20 (Mettler Toledo) and found to be below 10 ppm. All new compounds were characterized by means of GC-MS, ^{1}H-NMR, ^{13}C-NMR, and HRMS. Nuclear magnetic resonance spectra were recorded on Bruker AVANCE 400 (400 MHz) and Bruker AVANCE-II (600 MHz) spectrometers at ambient temperature (unless otherwise stated). Chemical shifts are given in parts per million (ppm) and were referenced to residual solvent peaks using values provided by the MestReNova processing software. Coupling constants (*J*) are quoted in Hertz. Coupling patterns are written using the following abbreviations: br. s (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). GC-MS analysis was performed on an Agilent Technologies 8890/5977C GC-MSD system. GC-MS runs were performed with the following method: GC; HP-5MSI column; inlet temperature 300 °C; column temperature 70 °C for 5 min, then 50 °C/min to 240 °C, then 240 °C for 15 min. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6530 Q-TOF LC/MS system paired Agilent 1260 HPLC and using Agilent JetStream ion source. C, H, N microanalyses were done using a Perkin Elmer 2400 Series II CHNS/O elemental analyzer. 4/7-Bromo-2-methylindene[1] and 7-chloroindene[2] were synthesized according to published procedures. Cyclopropylmagnesium bromide was prepared from bromocyclopropane in THF. All other starting materials were purchased from commercial sourses. Cyanide salts are highly toxic; all manipulations with CuCN were carried out in a well-ventilated fume hood. Procedures for decomposition of cyanide wastes can be found in ref.[3]

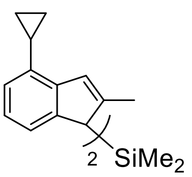
General method A: synthesis of arylsubstituted indenes *via* Suzuki-Miyaura coupling. A mixture of 4/7-chloro-2-cyclopropylindene (1.0 equiv), arylboronic acid (1.2 equiv), K_2CO_3 (3.0 equiv), Pd(*o*Tol)(PCy_3)$_2$Cl (0.01 equiv), toluene (3 mL/mmol) and water (1.5 mL/mmol) was stirred vigorously at 100°C for 12 h under an inert atmosphere. After cooling to room temperature, the organic layer was separated, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and the volatiles were distilled off under reduced pressure. The crude product was purified by short-path distillation using a Kugelrohr apparatus (100–120°C, 0.20 mbar).

General method B: synthesis of dimethylsilylene-bridged bis(indenyl) ligands. To a solution of a substituted indene (1.0 equiv) in diethyl ether under inert atmosphere, a solution of *n*BuLi (2.5 M in hexanes, 1.0 equiv) was added in one portion at 0°C. The mixture was stirred overnight at room temperature, then cooled to -60°C, CuCN (0.05 equiv) was added, and the resulting mixture was stirred at -60°C for 30 minutes before warming to -30°C. Dichlorodimethylsilane (0.5 equiv) was then added in one portion. After stirring overnight at room temperature, the reaction mixture was filtered through a short pad of silica gel, which was washed with dichloromethane. The combined filtrate was concentrated under reduced pressure, and the crude product was isolated by column chromatography (hexane/dichloromethane, 10:1 v/v) as a mixture of *rac* and *meso* diastereomers.

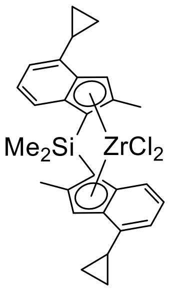
General Method C: synthesis of *ansa*-zirconocene dichlorides. To a solution of dimethylsilylene-bridged bis(indenyl) ligand (1.0 equiv) in diethyl ether at 0°C, a solution of *n*BuLi (2.5 M in hexanes, 2.0 equiv) was added in one portion at 0°C. The mixture was stirred overnight at room temperature, then cooled to -80°C. $ZrCl_4(THF)_2$ (1.0 equiv) was added, and the reaction mixture was stirred for 24 h at room temperature. The volatiles were removed under reduced pressure, and the residue was treated with hot toluene (350 mL). The resulting suspension was filtered hot through a short pad of Celite to remove LiCl. The filtrate was concentrated under reduced pressure, and the product was recrystallized from toluene or a toluene/hexane mixture to afford the pure *rac*-isomer of the *ansa*-zirconocene dichloride complex.



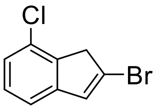
4/7-Cyclopropyl-2-methylindene. To a solution of 4/7-bromo-2-methylindene (5.00 g, 23.9 mmol) and (IPr)Ni(Ph_3P)Cl_2 (186 mg, 0.24 mmol) in THF (100 mL) a solution of cyclopropylmagnesium bromide (0.53 M in THF, 95.0 mL, 50.2 mmol) was added dropwise for 1 h at room temperature. The mixture was stirred for 12 h at 65°C, quenched with water (150 mL), acidified to pH 4 with aqueous HCl and concentrated under reduced pressure. The residue was extracted with dichloromethane (3 × 100 mL). The combined organic extract was dried over Na_2SO_4 and evaporated under reduced pressure to dryness. The crude product was purified by column chromatography (eluent: hexane). Yield: 1.33 g (33%) of a mixture of 4/7-cyclopropyl-substituted indenes (isomers A and B) in ~1:1.2 molar ratio. ^{1}H NMR ($CDCl_3$): δ 7.29-7.19 (m, 2H in A and B), 7.18-7.12 (m, 1H in A or B), 7.12-7.06 (m, 1H in B or A), 6.92-6.87 (m, 1H in B or A), 6.85 (br.s., 1H in B or A), 6.72 (d, *J* = 7.6 Hz, 1H in A or B), 6.60-6.51 (m, 1H in A or B), 3.42 (br.s., 2H in A or B), 3.37 (br.s., 2H in B or A), 2.25 (s, 6H in A and B), 2.19-2.08 (m, 1H in B or A), 2.06-1.96 (m, 1H in A or B), 1.06-0.97 (m, 4H in A and B), 0.85-0.74 (m, 4H in A and B). ^{1}H NMR ($CDCl_3$): δ 145.7, 145.4, 145.4, 145.2, 143.0, 142.3, 137.9, 134.4, 127.3, 126.7, 125.3, 123.7, 122.3, 120.7, 118.8, 117.2, 42.9, 41.5, 16.9, 16.8, 12.6, 12.6, 7.4, 7.4. HRMS (ESI): $[M+H]^+$ calcd. for $C_{13}H_{15}^+$: 171.1168; Found: 171.1169.



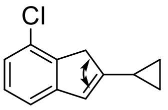
***Rac/meso*-bis(4-cyclopropyl-2-methylinden-1-yl)dimethylsilane.** General Method B was applied using 4/7-cyclopropyl-2-methylindene (3.54 g, 20.8 mmol), diethyl ether (100 mL), *n*BuLi (2.5 M in hexanes, 8.32 mL, 20.8 mmol), CuCN (93 mg, 1.04 mmol) and dichlorodimethylsilane (1.34 g, 1.27 mL, 10.4 mmol). Yield: 3.75 g (91%) of a yellowish solid (*rac/meso* ≈ 1:1.2). ^{1}H NMR ($CDCl_3$): δ 7.38-7.33 (m, 2H in *rac* and *meso*), 7.24-7.20 (m, 2H in *rac* and *meso*), 7.07-7.00 (m, 4H in *rac* and *meso*), 6.95-6.91 (m, 4H in *rac* and *meso*), 6.89-6.82 (m, 4H in *rac* and *meso*), 3.77 (br.s., 2H in *rac*), 3.75 (s, 2H in *meso*), 2.30 (d, *J* = 0.8 Hz, 6H in *meso*), 2.24 (d, *J* = 0.9 Hz, 6H in *rac*), 2.20-2.10 (m, 4H in *rac* and *meso*), 1.03-0.95 (m, 8H in *rac* and *meso*), 0.85-0.66 (m, 8H in *rac* and *meso*), -0.24 (s, 3H in *meso*), -0.29 (s, 6H in *rac*), -0.30 (s, 3H in *meso*). ^{1}H NMR ($CDCl_3$): δ 146.7, 146.5, 144.8, 144.7, 144.5, 144.4, 134.7, 134.6, 125.0, 124.9, 122.9, 122.8, 121.1, 121.1, 120.6, 120.6, 47.4, 47.3, 18.0, 12.9, 12.9, 7.8, 7.2, -5.8, -6.0, -6.1. HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{33}Si^+$: 397.2346; Found: 397.2349.



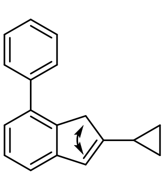
Complex *c*Pr-1. General Method C was applied using *rac/meso*-bis(4-cyclopropyl-2-methylinden-1-yl)dimethylsilane (2.00 g, 5.00 mmol), *n*BuLi (2.5 M in hexanes, 4.00 mL, 10.0 mmol) and $ZrCl_4(THF)_2$ (1.89 g, 5.00 mmol). Yield: 0.36 g (13%) of pure *rac*-isomer as red crystals. Anal. calcd. for $C_{28}H_{30}C_{12}SiZr$: C, 60.40; H, 5.43. Found: C, 60.64; H, 5.69. ^{1}H NMR (CD_2Cl_2): δ 7.53-7.48 (m, 2H), 7.00-6.89 (m, 6H), 2.22 (d, *J* = 0.5 Hz, 6H), 1.99-1.87 (m, 2H), 1.29 (s, 6H), 0.97-0.82 (m, 6H), 0.76-0.67 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 140.5, 135.4, 134.8, 127.6, 126.3, 123.4, 122.9, 121.4, 84.3, 19.0, 14.1, 6.7, 6.2, 2.7.



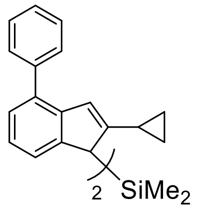
2-Bromo-7-chloroindene. To a solution of 7-chloroindene (130 g, 0.86 mol) in a mixture of DMSO (1000 mL) and water (31 g, 1.72 mol), *N*-bromosuccinimide (161 g, 0.91 mol) was added portionwise over 2 h at 20 °C. The resulting orange solution was stirred overnight at room temperature. The reaction mixture was then poured into water (1000 mL), and the resulting suspension was extracted with dichloromethane (3 × 300 mL). The combined organic extracts were washed with water (5 × 500 mL), dried over Na_2SO_4, and evaporated under reduced pressure to dryness. The residue was washed with hexane (300 mL) and dried *in vacuo* to afford 2-bromo-4-chloro-2,3-dihydroinden-1-ol as a white powder (199 g, 93% yield), which was used as is. A mixture of 2-bromo-4-chloro-2,3-dihydro-1H-inden-1-ol (199 g, 0.80 mol) and $TsOH{\cdot}H_2O$ (10 g, 0.0526 mol) in toluene (1200 mL) was refluxed under a Dean-Stark apparatus for 12 h. After cooling to room temperature in a water bath, the solution was washed with 10% Na_2CO_3(aq). The organic layer was separated, and the aqueous phase was further extracted with dichloromethane (3 × 200 mL). The combined organic extracts were dried over Na_2SO_4 and filtered through a short pad of silica gel 60 (40–63 µm), which was additionally washed with dichloromethane (100 mL). The filtrate was concentrated under reduced pressure, and the crude product was purified by vacuum distillation (b.p. 104-120°C/1 mbar). Yield: 116 g (64%) of a yellowish liquid which crystallized upon standing. ^{1}H NMR ($CDCl_3$): δ 7.24-7.18 (m, 2 H), 7.17-7.14 (m, 1 H), 6.92 (t, J = 1.6 Hz, 1 H), 3.63-3.59 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 145.5, 140.3, 132.7, 129.1, 128.4, 125.7, 125.0, 118.6, 45.0. HRMS (ESI): $[M+H]^+$ calcd. for $C_9H_7BrCl^+$: 228.9414; Found: 228.9412.



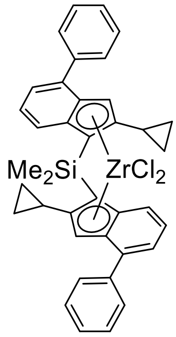
4/7-Chloro-2-cyclopropylindene. To a solution of 2-bromo-4/7-chloroindene (10.0 g, 43.6 mmol) and $(IPr)Ni(PPh_3)Cl_2$ (1.02 g, 1.31 mmol) in THF (200 mL), a solution of cyclopropylmagnesium bromide (0.53 M in THF, 94.0 mL, 49.8 mmol) was added dropwise over 1 h at room temperature. The resulting mixture was stirred at 65 °C for 12 h, then quenched with water (150 mL) and acidified to pH 4 with aqueous HCl. The mixture was concentrated under reduced pressure, and the residue was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated to dryness. The crude product was purified by column chromatography (eluent: hexane). Yield: 5.90 g (71%) of ~4:1 mixture of isomeric 4/7-chloro-2-cyclopropylindenes (A and B) as a yellowish oil. ^{1}H NMR ($CDCl_3$): δ 7.26-6.99 (m, 6H in A and B), 6.69-6.66 (m, 1H in B), 6.54-6.50 (m, 1H in A),3.29-3.26 (m, 2H in B), 3.26-3.20 (m, 2H in A), 1.93-1.80 (m, 2H in A and B), 1.02-0.92 (m, 4H in A and B), 0.76-0.68 (m, 4H in A and B). ^{13}C NMR ($CDCl_3$): δ 154.0, 153.5, 147.3, 143.8, 143.7, 139.8, 129.3, 128.1, 126.4, 124.7, 124.5, 124.2, 123.5, 121.9, 121.6, 117.9, 39.7, 38.3, 12.6, 12.6, 8.9, 8.7. HRMS (ESI): $[M+H]^+$ calcd. for $C_{12}H_{12}Cl^+$: 191.0622; Found: 191.0625.



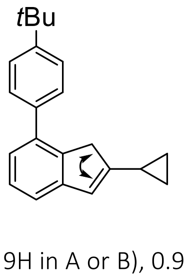
2-Cyclopropyl-4/7-phenylindene. General Method A was applied using 4/7-chloro-2-cyclopropylindene (4.00 g, 21.0 mmol), phenylboronic acid (3.07 g, 25.2 mmol), K_2CO_3 (8.69 g, 62.9 mmol), $Pd(oTol)(PCy_3)_2Cl$ (167 mg, 0.21 mmol), toluene (65 mL), and water (35 mL). The crude product was purified by Kugelrohr distillation at 100°C / 0.20 mbar, yielding 4.73 g (97%) of a clear, yellowish oil (~1:1 mixture of 4/7-phenyl-substituted indenes, isomers A and B). ^{1}H NMR ($CDCl_3$): δ 7.67-7.59 (m, 4H in A and B), 7.59-7.50 (m, 4H in A and B), 7.48-7.38 (m, 4H), 7.38-7.31 (m, 2H in A and B), 7.29-7.19 (m, 2H in A and B), 6.81 (br.s., 1H in A or B), 6.66 (br.s., 1H in A or B), 3.37 (s, 2H in A or B), 3.36 (s, 2H in A or B), 1.97-1.84 (m, 2H in A and B), 1.02-0.92 (m, 4H in A and B), 0.78-0.68 (m, 4H in A and B). ^{13}C NMR ($CDCl_3$): δ 153.0, 152.8, 146.2, 143.3, 142.8, 141.3, 141.1, 139.7, 137.4, 133.7, 128.8, 128.4, 128.4, 128.4, 128.3, 127.1, 127.0, 126.7, 126.7, 124.4, 124.1, 123.7, 123.4, 122.3, 118.7, 39.0, 38.7, 12.7, 12.5, 8.5, 8.5. HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{17}^+$: 233.1325; Found: 233.1329.



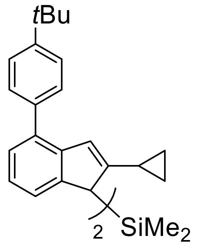
***Rac/meso*-bis(2-cyclopropyl-4-phenylinden-1-yl)dimethylsilane.** General Method B was applied using a 2-cyclopropyl-4/7-phenylindene (4.64 g, 20.0 mmol), diethyl ether (100 ml), *n*BuLi (2.5 M in hexanes, 8.00 ml, 20.0 mmol), CuCN (90 mg, 1.00 mmol) and dichlorodimethylsilane (1.29 g, 1.22 ml, 10.0 mmol). Yield 3.84 g (74%) of a yellowish solid (*rac/meso*≈1:1.3). ^{1}H NMR (CDCl$_3$): δ 7.60-7.46 (m, 20H in *rac* and *meso*), 7.43-7.37 (m, 4H in *rac* and *meso*), 7.33-7.28 (m, 4H in *rac* and *meso*), 7.25-7.19 (m, 4H in *rac* and *meso*), 6.58 (br.s., 4H in *rac* and *meso*), 4.26 (s, 2H in *rac*), 4.25 (s, 2H in *meso*), 1.82-1.67 (m, 4H in *rac* and *meso*), 1.05-0.97 (m, 8H in *rac* and *meso*), 0.83-0.74 (m, 8H in *rac* and *meso*), -0.14 (s, 3H in *meso*), -0.19 (s, 6H in *rac*), -0.24 (s, 3H in *meso*). ^{13}C NMR (CDCl$_3$): δ 155.5, 155.4, 145.0, 144.9, 142.7, 141.4, 141.4, 134.2, 134.2, 128.9, 128.4, 126.7, 125.6, 125.6, 123.0, 122.9, 122.0, 119.2, 119.2, 48.2, 48.1, 12.7, 12.7, 11.8, 11.7, 10.0, 9.8, -5.9, -6.3, -6.5. HRMS (ESI): [M+H]$^+$ Calcd. for $C_{38}H_{37}Si^+$: 521.2659; Found: 521.2651.



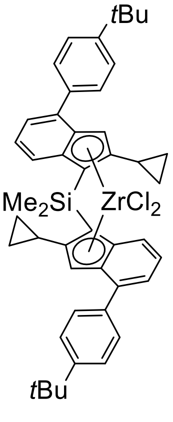
Complex *c*Pr-2. General Method C was applied using *rac*/*meso*-bis(2-cyclopropyl-4-(3,5-di-*tert*-butylphenyl)inden-1-yl)dimethylsilane (1.68 g, 3.23 mmol), of *n*BuLi (2.5 M in hexanes, 2.6 mL, 6.5 mmol) and ZrCl$_4$(THF)$_2$ (1.22 g, 3.23 mmol). Yield: 0.45 g (19%) of pure *rac*-isomer (·0.6PhMe) as orange crystals. Anal. calcd. for $C_{38}H_{34}Cl_2SiZr\cdot 0.6C_7H_8$: C, 68.85; H, 5.31. Found: C, 68.61; H, 5.24. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 -7.57 (m, 4H), 7.47-7.39 (m, 4H), 7.39-7.31 (m, 4H), 7.07 (dd, *J* = 7.0, 8.7 Hz, 2H), 6.61 (s, 2H), 2.06-1.94 (m, 2H), 1.44 (s, 6H), 1.12-0.98 (m, 2H), 0.96-0.84 (m, 2H), 0.80-0.68 (m, 2H), 0.49-0.39 (m, 2H). ^{13}C NMR (CD$_2$Cl$_2$): δ 144.4, 140.2, 139.0, 132.3, 129.1, 129.1, 128.7, 128.2, 127.0, 126.3, 125.1, 115.0, 85.2, 14.6, 13.9, 9.9, 3.5.



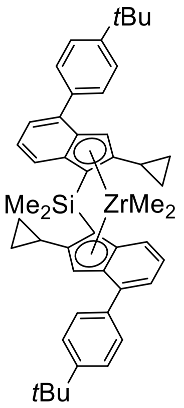
2-Cyclopropyl-4/7-(4-di-*tert*-butylphenyl)indene. General Method A was applied using 4/7-chloro-2-cyclopropylindene (5.10 g, 26.7 mmol), (4-(*tert*-butyl)phenyl)boronic acid (5.71 g, 32.1 mmol), K$_2$CO$_3$ (11.1 g, 80.2 mmol), Pd(oTol)(PCy$_3$)$_2$Cl (212 mg, 0.27 mmol), toluene (80 mL), and water (40 mL). The crude product was purified by Kugelrohr distillation at 110°C / 0.20 mbar, yielding 7.32 g (95%) of a clear, yellowish oil (~1:1 mixture of 4/7-(4-(*tert*-butyl)phenyl)-substituted indenes, isomers A and B). ^{1}H NMR (CDCl$_3$): δ 7.56 - 7.46 (m, 8H in A and B), 7.40 - 7.23 (m, 4H in A and B), 7.23 - 7.13 (m, 2H in A and B), 6.78 (br.s., 1H in A or B), 6.60 (br.s., 1H in A or B), 3.34 (br.s., 2H in A or B), 3.31 (br.s., 2H in A or B), 1.92 - 1.79 (m, 2H in A and B), 1.43 (s, 9H in A or B), 1.43 (s, 9H in A or B), 0.98 - 0.85 (m, 4H A and B), 0.74 - 0.64 (m, 4H A and B). ^{13}C NMR (CDCl$_3$): δ 152.8, 152.8, 149.8, 149.5, 146.2, 143.3, 142.9, 139.7, 138.3, 138.1, 137.3, 133.6, 128.4, 128.0, 127.0, 126.8, 125.3, 124.5, 124.2, 123.7, 123.6, 122.1, 118.5, 39.1, 38.9, 34.5, 34.5, 31.4, 31.4, 12.6, 12.5, 8.5, 8.5. HRMS (ESI): [M+H]$^+$ Calcd. for $C_{22}H_{25}^+$: 289.1951; Found: 289.1954.



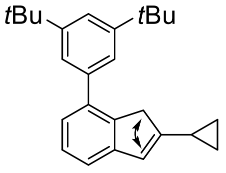
***Rac/meso*-bis(4-(4-*tert*-butylphenyl)-2-cyclopropylinden-1-yl)dimethylsilane.** General Method B was applied using 4/7-(4-*tert*-butylphenyl)-2-cyclopropylindene (5.00 g, 17.4 mmol), diethyl ether (100 mL), *n*BuLi (2.5 M in hexanes, 6.96 mL, 17.4 mmol), CuCN (78 mg, 1.17 mmol) and dichlorodimethylsilane (1.12 g, 1.05 mL, 8.70 mmol). Yield: 4.50 g (82%) of a yellowish solid (*rac/meso* ≈ 1:1.5). ^{1}H NMR (CDCl$_3$): δ 7.60-7.52 (m, 16H in *rac* and *meso*), 7.51-7.47 (m, 4H in *rac* and *meso*), 7.36-7.30 (m, 4H in *rac* and *meso*), 7.26-7.19 (m, 4H in *rac* and *meso*), 6.67 (br.s., 2H in *rac*), 6.66 (br.s., 2H in *meso*), 4.30 (br.s., 2H in *rac*), 4.27 (br.s., 2H in *meso*), 1.86-1.72 (m, 4H), 1.46 (s, 18H in *rac*), 1.46 (s, 18H in *meso*), 1.07-0.98 (m, 8H in *rac* and *meso*), 0.88-0.77 (m, 8H in *rac* and *meso*), -0.13 (s, 3H in *meso*), -0.19 (s, 6H in *rac*), -0.23 (s, 3H in *meso*). ^{1}H NMR (CDCl$_3$): δ 155.1, 155.0, 149.5, 145.0, 144.9, 142.6, 138.5, 138.4, 134.0, 134.0, 128.5, 125.6, 125.6, 125.3, 122.9, 122.9, 121.8, 119.4, 119.4, 48.1, 34.5, 31.4, 12.7, 12.7, 11.8, 11.7, 10.0, 9.7, -5.9, -6.4, -6.5. HRMS (ESI): [M+H]$^+$ Calcd. for $C_{46}H_{53}Si^+$: 633.3911; Found: 633.3917.



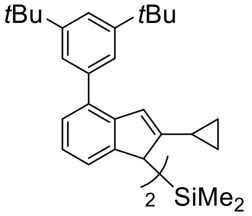
Complex *c*Pr-3. General Method C was applied using *rac/meso*-bis(4-(4-*tert*-butylphenyl)-2-cyclopropylinden-1-yl)dimethylsilane (2.10 g, 3.32 mmol), *n*BuLi (2.5 M in hexanes, 2.66 mL, 6.64 mmol) and ZrCl$_4$(THF)$_2$ (1.25 g, 3.32 mmol). The product has very low solubility, therefore, after filtration, the LiCl formed was washed out with large volume of THF, which also led to the enrichment of the *rac*-isomer in the undissolved solid. The product was used without further purification. Due to its exceptionally low solubility in common deuterated solvents obtaining a ^{13}C NMR spectrum at room temparature in an acceptable amount of time proved unfeasible. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.69 7.65 (m, H), 7.58 7.53 (m, 4 H), 7.36 7.31 (m, 4 H), 7.34 (d, *J* = 7.1 Hz, H), 7.06 (dd, *J* = 7.0, 8.7 Hz, H), 6.65 (br. s., H), 2.07 1.92 (m, H), 1.43 (s, 6 H), 1.34 (s, 18 H), 1.09 0.99 (m, H), 0.95 0.88 (m, H), 0.79 0.67 (m, H), 0.53 0.38 (m, H).



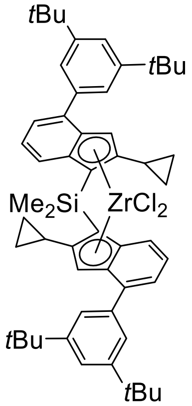
Complex *c*Pr-3^{Me}. Complex ***c*Pr-3** was suspended in toluene (60 mL), and the obtained suspension was refluxed for 3 h. Further on, MeMgBr (3.1 M in diethyl ether, 6.40 mL, 19.9 mmol) was added, and the reaction mixture was stirred for 12 h at 75°C in a glass pressure vessel. The obtained mixture was filtered through glass frit (G4), and the volatiles were removed under reduced pressure. The residue was extracted with toluene (3 × 100 mL) and the combined extracts were evaporated under reduced pressure to dryness. The residue was washed with toluene (50 mL) and dried in vacuo. Yield: 0.18 g (7%) of a 11 to 1 mixture of *rac*- and *meso*-complexes as yellow crystalline solid. Due to its exceptionally low solubility in common deuterated solvents obtaining a ^{13}C NMR spectrum at room temparature in an acceptable amount of time proved unfeasible. Anal. cacld. for $C_{48}H_{56}SiZr$: C, 76.64; H, 7.50. Found: C, 76.38; H, 7.47. ^{1}H NMR (CD_2Cl_2): *δ* 7.58-7.43 (m, 10H), 7.28 (d, J = 6.4 Hz, 2H), 6.98 (dd, *J* = 7.0, 8.7 Hz, 2H), 6.78 (s, 2H), 1.83-1.73 (m, 2H), 1.34 (s, 18H), 1.22 (s, 6H), 0.98-0.89 (m, 2H), 0.76-0.67 (m, 2H), 0.65-0.55 (m, 2H), 0.45-0.34 (m, 2H), -1.16 (s, 6H).



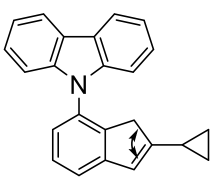
2-Cyclopropyl-4/7-(3,5-di-*tert*-butylphenyl)indene. General Method A was applied using 4/7-chloro-2-cyclopropylindene (4.00 g, 21.0 mmol), (3,5-di-*tert*-butylphenyl)boronic acid (5.89 g, 25.2 mmol), K_2CO_3 (8.69 g, 62.9 mmol), Pd(oTol)$(PCy_3)_2$Cl (167 mg, 0.21 mmol), toluene (65 mL), and water (35 mL). The crude product was purified by Kugelrohr distillation at 120°C / 0.20 mbar, yielding 7.11 g (98%) of a clear, yellowish oil (~3.6:1 mixture of 4/7-(3,5-di-*tert*-butylphenyl)-substituted indenes, isomers A and B). ^{1}H NMR ($CDCl_3$): *δ* 7.48-7.43 (m, 2H in A and B), 7.42-7.37 (m, 4H in A and B), 7.37-7.31 (m, 2H in A and B), 7.29-7.23 (m, 2H in A and B), 7.23-7.14 (m, 2H in A and B), 6.73 (s, 1H in B), 6.60 (s, 1H in A), 3.33 (br. s., 4H in A and B), 1.91-1.79 (m, 2H in A and B), 1.42 (s, 18H in B), 1.41 (s, 18H in A), 0.96-0.87 (m, 4H in A and B), 0.72-0.60 (m, 4H in A and B). ^{13}C NMR ($CDCl_3$): *δ* 152.9 (two resonances), 150.6, 150.6, 146.2, 143.4, 142.9, 140.4, 140.1, 139.8, 138.6, 134.8, 127.0, 126.8, 124.4, 124.3, 123.7, 123.6, 123.3, 122.9, 122.1, 120.9, 120.6, 118.5, 39.2, 39.0, 34.9, 34.9, 31.5, 12.7, 12.5, 8.6, 8.5. HRMS (ESI): $[M+H]^+$ Calcd. for $C_{26}H_{33}^+$: 345.2577; Found: 345.2571.



***Rac/meso*-bis(2-cyclopropyl-4-(3,5-di-*tert*-butylphenyl)-inden-1-yl)dimethylsilane)**. General Method B was applied using 2-cyclopropyl-4/7-(3,5-di-*tert*-butylphenyl)-indene (8.07 g, 23.4 mmol), diethyl ether (250 mL), *n*BuLi (2.5 M in hexanes, 9.37 mL, 23.4 mmol), CuCN (105 mg, 1.17 mmol), and dichlorodimethylsilane (1.51 g, 1.43 mL, 11.7 mmol). The reaction yielded 2.86 g (33%) of a yellowish (*rac/meso* ≈1:1). ^{1}H NMR ($CDCl_3$): *δ* 7.62-7.42 (m, 16H in *rac* and *meso*), 7.40-7.35 (m, 4H in *rac* and *meso*), 7.28-7.21 (m, 4H in *rac* and *meso*), 6.68 (br.s., 2H in *rac*), 6.66 (br.s., 2H in *meso*), 4.32 (br.s., 2H in *rac*), 4.28 (br.s., 2H in *meso*), 1.85-1.72 (m, 4H in *rac* and *meso*), 1.46 (s, 36H in *rac*), 1.46 (s, 36H in *meso*), 1.10-0.96 (m, 8H in *rac* and *meso*), 0.86-0.74 (m, 8H in *rac* and *meso*), -0.12 (s, 3H in *meso*), -0.19 (s, 6H in *rac*), -0.20 (s, 3H in *meso*). ^{13}C NMR ($CDCl_3$): *δ* 155.1, 154.9, 150.6, 145.0, 144.9, 142.7, 140.4, 140.4, 135.1, 135.1, 125.6, 125.6, 123.4, 122.9, 122.9, 121.8, 120.6, 119.5, 119.4, 48.1, 34.9, 31.6, 12.7, 12.6, 12.0, 11.8, 10.2, 9.9, -5.8, -6.3, -6.4. HRMS (ESI): $[M+H]^+$ Calcd. for $C_{54}H_{69}Si^+$: 745.5163; Found: 745.5172.

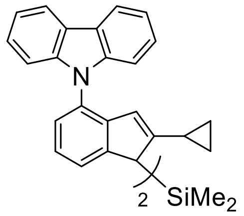


Complex *c*Pr-4. General Method C was applied using *rac*/*meso*-bis(2-cyclopropyl-4-(3,5-di-*tert*-butylphenyl)inden-1-yl)dimethylsilane (2.86 g, 3.84 mmol), *n*BuLi (2.5 M in hexanes, 3.1 mL, 7.7 mmol) and $ZrCl_4(THF)_2$ (1.45 g, 3.84 mmol). Yield: 0.10 g (3%) of pure *rac*-isomer as orange crystals. Anal. calcd. for $C_{54}H_{66}Cl_2SiZr$: C, 71.64; H, 7.35. Found: C, 71.86; H, 7.40. ^{1}H NMR (CD_2Cl_2): *δ* 7.70-7.65 (m, 2H), 7.53 (d, *J* = 1.8 Hz, 4H), 7.42-7.40 (m, 2H), 7.39-7.35 (m, 2H), 7.07 (dd, *J* = 7.0, 8.7 Hz, 2H), 6.66 (br. s., 2H), 2.07-1.96 (m, 2H), 1.44 (s, 6H), 1.31 (s, 36H), 1.08-0.97 (m, 2H), 0.93-0.82 (m, 2H), 0.80-0.69 (m, 2H), 0.45-0.36 (m, 2H). ^{13}C NMR (CD_2Cl_2): *δ* 151.7, 144.0, 140.1, 139.2, 132.1, 127.8, 126.8, 126.3, 124.8, 123.9, 121.9, 115.9, 84.8, 35.5, 31.8, 14.3, 13.8, 9.6, 3.5.

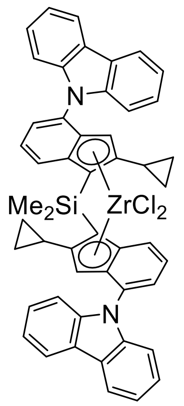


2-Cyclopropyl-4/7-(*N*-carbazolyl)indene. To a suspension of carbazole (10.0 g, 59.8 mmol) in anhydrous toluene (200 mL), a solution of *n*BuLi (2.5 M in hexanes, 29 mL, 73 mmol) was added dropwise over 30 minutes at room temperature. After complete addition, 4/7-chloro-2-cyclopropylindene (10.0 g, 60.8 mmol), $Pd(dba)_2$ (0.70 g, 1.22 mmol), and *t*BuMePhos (0.76 g, 2.43 mmol) were added sequentially to the mixture. The resulting suspension was stirred at 95°C for 12 h under an inert atmosphere. After cooling to room temperature, the reaction mixture was poured into water (500 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and the volatiles were distilled off under reduced pressure. The crude product was purified by flash column chromatography (eluent: hexane/dichloromethane = 5:1, v/v). Yield: 10.3 g (53%) of a ~1:1 mixture of isomeric 2-cyclopropyl-4/7-

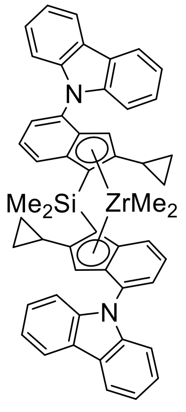
(*N*-carbazolyl)indenes A and B as a yellowish solid. ^{1}H NMR (CDCl$_3$): δ 8.25 (d, *J* = 7.7 Hz, 4H in A and B), 7.55-7.20 (m, 18H in A and B), 6.67 (s, 1H in A), 6.14 (s, 1H in B), 3.40 (s, 2H in B), 2.99 (s, 2H in A), 1.85-1.72 (m, 2H in A and B), 0.94-0.83 (m, 4H in A and B), 0.68-0.54 (m, 4H in A and B). ^{13}C NMR (CDCl$_3$): δ 154.0, 153.6, 148.0, 144.4, 143.3, 141.1, 140.6, 139.8, 132.5, 128.3, 128.2, 125.8, 125.6, 124.5, 124.1, 123.3, 123.1, 123.1, 122.9, 122.1, 120.3, 120.1, 119.6, 119.5, 110.2, 109.9, 39.1, 37.4, 12.7, 12.5, 8.9, 8.7. HRMS (ESI): [M+H]$^+$ Calcd. for $C_{24}H_{20}N^+$: 322.1590; Found: 322.1587.



***Rac/meso*-bis(4-(*N*-carbazol)-2-cyclopropylinden-1-yl)dimethylsilane**. General Method B was applied using 2-cyclopropyl-4/7-(*N*-carbazolyl)indene (5.00 g, 15.6 mmol), diethyl ether (250 mL), *n*BuLi (2.5 M in hexanes, 6.23 mL, 15.6 mmol), CuCN (70 mg, 0.78 mmol), dichlorodimethylsilane (0.95 mL, 1.00 g, 7.79 mmol). Yield: 7.56 g (79%) as yellowish solid (*rac*/*meso* ≈1.1:1). ^{1}H NMR (CDCl$_3$): δ 8.31-8.21 (m, 8H in *rac* and *meso*), 7.77 (d, *J* = 7.3 Hz, 2H in *rac*), 7.69 (d, *J* = 7.3 Hz, 2H in *meso*), 7.56-7.29 (m, 28H in *rac* and *meso*), 7.21 (br.s., 2H in *rac*), 7.19 (br.s., 2H in *meso*), 5.99 (br.s., 4H in *rac* and *meso*), 4.44 (s, 2H in *meso*), 4.43 (s, 2H in *rac*), 1.88-1.76 (m, 2H in *meso*), 1.76-1.66 (m, 2H in *rac*), 1.10-0.89 (m, 8H), 0.75-0.59 (m, 8H), 0.01 (s, 3H in *meso*), -0.04 (s, 6H in rac-), -0.09 (s, 3H in *meso*-). ^{13}C NMR (CDCl$_3$): δ 156.5, 156.4, 146.4, 146.3, 142.7, 142.7, 141.2, 141.2, 129.0, 129.0, 125.8, 125.7, 124.8, 124.7, 123.8, 123.7, 123.2, 123.1, 122.5, 120.3, 120.2, 119.6, 119.5, 117.6, 117.6, 110.2, 110.1, 48.6, 12.8, 12.7, 12.5, 12.5, 10.5, 10.3, -5.8, -6.3, -6.7. HRMS (ESI): [M+H]$^+$ Calcd. for $C_{50}H_{43}N_2Si^+$: 699.3190; Found: 699.3197.



Complex *c*Pr-5. General Method C was applied using *rac*/*meso*-bis(4-(*N*-carbazol)-2-cyclopropylinden-1-yl)dimethylsilane (4.10 g, 5.90 mmol), *n*BuLi (2.5 M in hexanes, 4.90 mL, 11.8 mmol), and $ZrCl_4(THF)_2$ (2.22 g, 5.90 mmol). The reaction yielded 0.31 g (6%) of the *rac*-isomer (96% purity) as orange crystals. Anal. calcd. for $C_{50}H_{40}Cl_2N_2SiZr$: C, 69.61; H, 4.67. Found: C, 70.12; H, 4.74. ^{1}H NMR (CDCl$_3$): δ 8.18-8.02 (m, 4H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.36-7.18 (m, 8H), 7.15 (dd, *J* = 7.4, 8.5 Hz, 2H), 6.83-6.68 (m, 2H), 6.29 (s, 2H), 2.18-2.03 (m, 2H), 1.51 (s, 6H), 1.23-1.10 (m, 2H), 1.00-0.88 (m, 2H), 0.88-0.77 (m, 2H), 0.60-0.43 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 144.3, 140.8, 140.3, 134.4, 131.2, 127.3, 126.2, 126.0, 125.7, 125.1, 124.7, 124.0, 123.6, 120.3, 120.2, 119.8, 119.8, 112.8, 112.5, 110.6, 85.1, 15.6, 13.6, 10.2, 3.3.



Complex *c*Pr-5^{Me}. To a mixture of *rac*- and *meso*-isomers of complex XXX (1.3/2, 2.30 g, 2.68 mmol) in toluene (50 mL), a solution of MeMgBr (2.9 M in diethyl ether, 9.20 mL, 26.7 mmol) was added at room temperature. The mixture was stirred for 24 h at 100 °C, after which the volatiles were evaporated to dryness under vacuum. The residue was taken up in toluene (100 mL), the mixture heated to 100 °C and filtered through a short pad of Celite to remove magnesium salts and excess MeMgBr. The filtrate was concentrated under vacuum. To the residue, THF (50 mL) and LiCl (4.2 mg, 0.1 mmol) were added. The reaction mixture was stirred at 50 °C for 16 h, followed by the addition of toluene (20 mL). The volatiles were evaporated to dryness under vacuum. The residue was taken up in toluene (50 mL) and filtered through a short Celite pad to remove LiCl. The filtrate was concentrated under vacuum, and the residue was recrystallized from toluene. Yield: 0.90 g (41%) of pure *rac*-isomer (·PhMe) as orange crystals. Anal. calcd. for $C_{52}H_{46}N_2SiZr\cdot C_7H_8$: C, 91.25; H, 8.75. Found: C, 91.18, H, 8.64. ^{1}H NMR (CDCl$_3$): δ 8.25-8.10 (m, 4H), 7.78-7.62 (m, 4H), 7.60-7.45 (m, 2H), 7.45-7.17 (m, 8H), 7.16-7.06 (m, 2H), 7.06-6.95 (m, 2H), 6.36 (s, 2H), 2.00-1.80 (m, 2H), 1.35 (s, 6H), 1.18-1.04 (m, 2H), 0.80-0.65 (m, 4H), 0.64-0.48 (m, 2H), -1.00 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 143.1, 140.4, 140.3, 134.0, 129.0, 128.2, 126.9, 125.7, 125.2, 124.8, 123.8, 123.7, 123.6, 123.0, 120.2, 120.1, 120.0, 119.8, 111.4 (two resonances), 107.8, 80.8, 39.6, 14.1, 13.0, 8.8, 3.3.

Crystal Structure Determination

X-ray experiments were carried out using SMART 1000 CCD diffractometer (λ(Mo-*K*α)=0.71073 Å, graphite monochromator, ω-scans) at 100–120 °K. All structures were solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement using riding approximation. The details of data collection and crystal structures refinement for which we used SAINT Plus,14 SADABS15 and SHELXTL-9716 program packages, are summarized in Tables S2 and S3. Crystallographic data for ***c*****Pr-1** have been deposited with the Cambridge Crystallographic Data Center, CCDC #2542331. Crystallographic data for ***c*****Pr-2** have been deposited with the Cambridge Crystallographic Data Center, CCDC #2542342. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

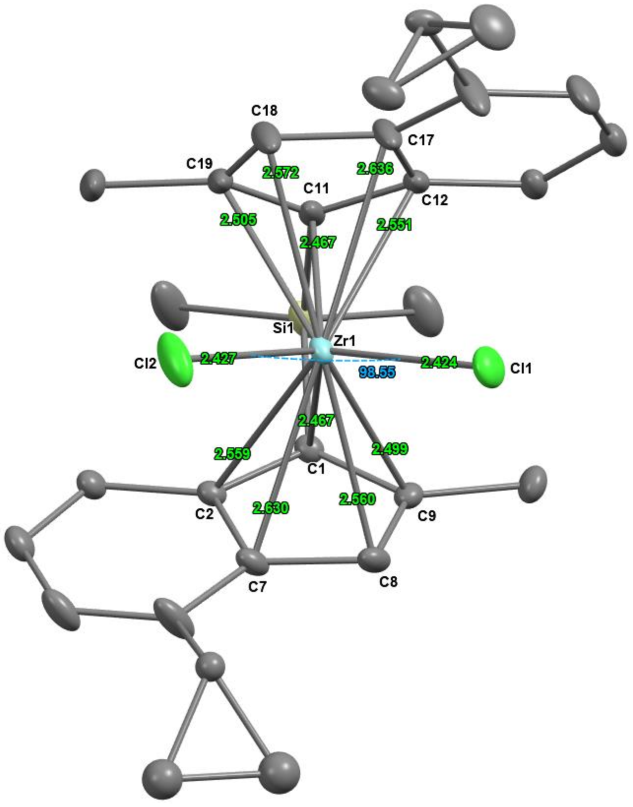


Figure S1. Solid state molecular structure of ***c*****Pr-1.** Image generated with CCDC's Mercury[4] software. Thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. The two cyclopropyl moieties are disordered; for each, one of the two local minima is shown. Green, bond lengths. Blue, angles.

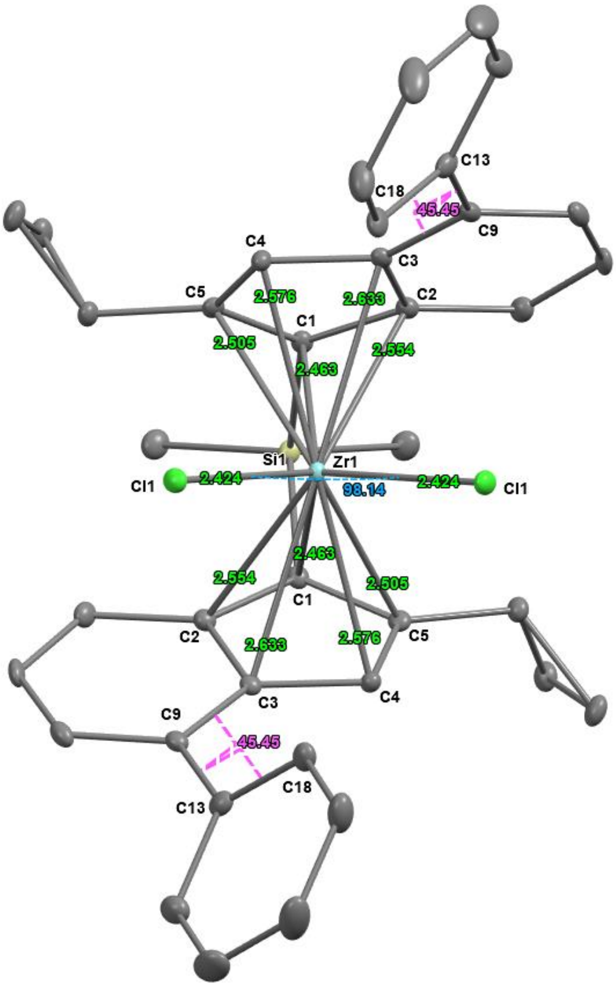


Figure S2. Solid state molecular structure of ***c*****Pr-2.** Image generated with CCDC's Mercury[4] software. Thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and cocrystallized dichloromethane molecule are omitted for clarity. Green, bond lengths. Blue, angles. Purple, torsions.

Table S1. Comparison of the selected bond distances, angles and torsions for ***c*****Pr-2** with literature data for **Me-2**

Metric		in ***c*****Pr-2**	corresponding metric in **Me-2**[5]
bond length, Å	Zr-C1	2.463	2.478
	Zr-C2	2.554	2.568
	Zr-C3	2.633	2.640
	Zr-C4	2.576	2.577
	Zr-C5	2.505	2.517
	Zr-Cl	2.424	2.419
angle, deg	Cl-Zr-Cl	98.14	96.8
torsion, deg	C3-C9-C13-C18	45.45	45.5

Table S2. Crystal data and structure refinement for ***c*Pr-1**.

Empirical formula	$C_{28} H_{30} Cl_2 Si Zr$	
Formula weight	556.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.7981(5) Å	α = 90°.
	b = 19.7102(12) Å	β = 91.1560(10)°.
	c = 14.1522(9) Å	γ = 90°.
Volume	2453.7(3) Å^3	
Z	4	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	1144	
Crystal size	0.27 x 0.20 x 0.11 mm^3	
Theta range for data collection	1.77 to 29.00°.	
Index ranges	$-12 \le h \le 12$, $-26 \le k \le 26$, $-19 \le l \le 19$	
Reflections collected	29835	
Independent reflections	6509 [R(int) = 0.0239]	
Completeness to theta = 29.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.924 and 0.827	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	6509 / 0 / 317	
Goodness-of-fit on F2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0882	
R indices (all data)	R1 = 0.0407, wR2 = 0.0919	
Largest diff. peak and hole	1.739 and -1.008 e.Å^{-3}	

Table S3. Crystal data and structure refinement for ***c*Pr-2**.

Empirical formula	$C_{38} H_{34} Cl_2 Si Zr, CH_2 Cl_2$	
Formula weight	765.79	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	C 2 -2c	
Unit cell dimensions	a = 23.8232(5) Å	α = 90°.
	b = 14.6364(4) Å	β = 90°.
	c = 9.6812(3) Å	γ = 90°.
Volume	3375.70(16) Å^3	
Z	4	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.707 mm^{-1}	
F(000)	1568	
Crystal size	0.34 x 0.30 x 0.29 mm^3	
Theta range for data collection	1.633 to 28.988°.	
Index ranges	$-32 \le h \le 32$, $-19 \le k \le 19$, $-13 \le l \le 13$	
Reflections collected	4476	
Independent reflections	3927	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4476 / 1 / 207	
Goodness-of-fit on F2	1.034	
Extinction coefficient	n/a	

Computational Details

All calculations were performed using Gaussian 16[1] software.[6] All pre-catalysts were optimized at the TPSSTPSS[7]/cc-pVDZ(-PP)[8-10] level of theory, using a small core pseudo potential on the metal.[11, 12] Standard Gaussian 16 quality settings [Scf=Tight and Int(Grid=UltraFine)] were used at the optimization stage. All structures represent true minima (as indicated by the absence of imaginary frequencies). Calculated structures of ***c*Pr-2** and ***c*Pr-2**^{TS} can be found as .xyz file at the journal website. SambVca 2.0 software[13] was used for calculation of the buried volume (%V_{bur}) and generation of the maps of steric bulk.

Polymerization Screening on PPR Setup

Solutions of the precatalysts were made using toluene (ExxonMobil Chemical — anhydrous, dried over 3 Å molecular sieves, stored under N2) (98%). Precatalyst solutions were typically 0.5 mmol/L. Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and are purified by passing through a series of columns: two 500 cc Oxyclear cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company). 1-Octene (98%) (Aldrich Chemical Company) was dried by stirring over Na/K overnight followed by filtration through basic alumina (Aldrich Chemical Company, Brockman Basic 1). Polymerization grade ethylene was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, Calif.) followed by a 500 cc column packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and a 500 cc column packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company). Polymerization grade propylene was used and further purified by passing it through a series of columns: 2250 cc Oxiclear cylinder from Labclear followed by a 2250 cc column packed with 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with Selexsorb CD (BASF), and finally a 500 cc column packed with Selexsorb COS (BASF).

Reactor Description and Preparation

Polymerization experiments were conducted on Freeslate (former Symyx) Parallel Pressure Reactor (PPR) setup. Polymerizations were conducted in an inert atmosphere (N2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor=23.5 mL for ethylene polymerization and ethylene/1-octene copolymerization runs; 22.5 mL for propylene polymerization runs), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with 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.

Polymer Characterization

For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99% from Aldrich) at 165 °C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was between 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. Molecular weights (weight average molecular weight (Mw) and number average molecular weight (Mn) and molecular weight distribution (Mw/Mn) were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with an infrared dector, and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 5000 and 3390000). 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/minute (135 °C sample temperatures, 165 °C oven/columns) using three Polymer Laboratories: PLgel 10mm Mixed-B 300 x 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. The molecular weights obtained are relative to linear polystyrene standards.

Differential Scanning Calorimetry (DSC) measurements were performed on a TAQ100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220 °C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/minute and then cooled at a rate of 50°C/minute. Melting points were collected during the heating period. The results are reported in Tables S4, S5 as T_m (°C).

Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number S10860, Symyx). By this method, approximately between 0.12 and 0.24 mg of polymer is deposited on the wafer cell. The samples were subsequently analyzed on a Brucker Equinox 55 FTIR spectrometer equipped with Pikes' MappIR specular reflectance sample accessory. Spectra, covering a spectral 10 range of 5000 cm-1 to 500 cm-1, were collected at a 2 cm-1 resolution with 32 scans. For ethylene/1-octene copolymers, the wt% comonomer (octene) was determined via measurement of the methyl deformation band at ~1375 cm^{-1}. The peak height of this band was normalized by the combination and overtone band at ~4321 cm^{-1}, which corrects for path length differences. The normalized peak height was correlated to individual calibration curves from 1H NMR data to predict the wt% comonomer content within a concentration range of ~2 to 35 wt% for octene. Typically, R2 correlations of 0.98 or greater are achieved. These numbers are reported in Tables S4 under the heading Octene, wt.%. Reported values below 4.1 wt.% are outside the calibration range.

The polymers were also characterized by quantitative 13C NMR at a frequency of 150 MHz with a Bruker 600 MHz spectrometer at 120 °C equipped with a high-temperature cryoprobe (for 10 mm O.D. tubes) and a preheated robotic sample changer. Samples were dissolved in deuterated tetrachloroethane at a concentration of 67 mg/mL at 140 °C. Polymer resonance peaks are referenced to mmmm=21.8 ppm. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, Carbon-13 NMR Method", Academic Press, New York, 1977. Methods for measuring relative contents of 2,1-regioerrors and 1,3- regioerrors follow standard methods. Additional references include Grassi, A. et. al. *Macromolecules*, **1988**, *21*, 617-622 and Busico et.al. *Macromolecules*, **1994**, *27*, 7538-7543. The intensities used in the calculations are normalized to the total number of monomers in the sample.

Ethylene/1-octene Copolymerization

The reactor was prepared as described above, and then purged with ethylene. Toluene and 1-octene (100 µL when used), were added via syringe at room temperature and atmospheric pressure. The reactor was then heated to process temperature (80 °C) and charged with ethylene to process pressure (75 psig) while stirring at 800 RPM. Then scavenger solution (tri-*n*-octylaluminum in isohexane), solution of activator AB in toluene (typically 0.2 mM), followed by a pre-catalyst solution in toluene (typically 0.2 mM) were added via syringe (three separate injections) to the reactor at process conditions. Total amount of the liquids added was 5.0 mL. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/−2 psig). Reactor temperature was monitored and typically maintained within +/−1°C. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or for a maximum of 30 minutes polymerization time. If a polymerization quench time is 30 minutes or less, then the polymerization ran until the set maximum value of ethylene uptake was reached. The quench time (s) are reported for each run. Polymerizations were halted by addition of approximately 50 psi ultra-pure air gas mixture to the autoclaves for approximately 30 seconds. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in vacuo. Yields reported include total weight of polymer and residual catalyst. The results are presented in Table S4.

Table S4[a]

Precat.	$n_{precat.}$, µmol[b]	Cocatalyst	Polymer yield, g	Quench time, s[c]	Activity, $g_{polym.}$× ×$(mmol_{cat}·h)^{-1}$	M_n, Da	M_w, Da	PDI[d]	Octene, wt.%[e]	Polymer T_m, °C[f]
*c*Pr-1	0,030	AB	0.0876	55	230611	240377	359379	1.50	11.8	109.2
*c*Pr-1	0,030	AB	0.0889	52	245241	234708	349009	1.49	13.5	107.6
*c*Pr-1	0,030	AB	0.0898	52	250120	240113	359917	1.50	10.9	109.4
*c*Pr-1	0,030	MAO	0.1064	53	289087	233122	392566	1.68	19.6	110.5
*c*Pr-1	0,030	MAO	0.1059	56	271345	261858	412980	1.58	24.9	110.2
*c*Pr-1	0,030	MAO	0.1120	60	270604	250450	426123	1.70	17.9	111.7
*c*Pr-2	0,030	MAO	0.1310	56	335062	135518	310786	2.29	30.8	93.3
*c*Pr-2	0,030	MAO	0.1286	51	360280	142708	303204	2.12	32.5	90.3
*c*Pr-2	0,030	MAO	0.1259	51	357586	138581	311049	2.24	32.9	90.9
*c*Pr-2	0,020	MAO	0.1062	49	391721	202123	331653	1.64	28.3	88.5
*c*Pr-2	0,020	MAO	0.1094	53	373662	207178	328872	1.59	27.9	85.7
*c*Pr-2	0,020	MAO	0.1134	54	376605	171274	291700	1.70	30.7	90.0
*c*Pr-2	0,030	AB	0.0981	52	269588	212086	335082	1.58	24.5	87.4
*c*Pr-2	0,030	AB	0.0995	55	259096	216320	337422	1.56	24.8	87.7
*c*Pr-2	0,030	AB	0.1013	58	251503	206669	329670	1.60	29.7	87.9

[a] Polymerization conditions: 0.02–0.03 µmol precatalyst; 500 equiv. MAO or 1.1 equiv AB + 0.5 mmol *n*Oct$_3$Al as scavenger; 3.8 mL isohexane; ethylene pressure 75 psi, 0.1 mL 1-octene; temperature 80 °C; 800 rpm stirring speed. [b] Precatalyst amount. [c] Polymerization time. [d] Polydispersity index, M_w/M_n, determined by GPC. [e] 1-Octene incorporation, wt.%. [f] Polymer melting temperature, determined by DSC

Propylene Polymerization

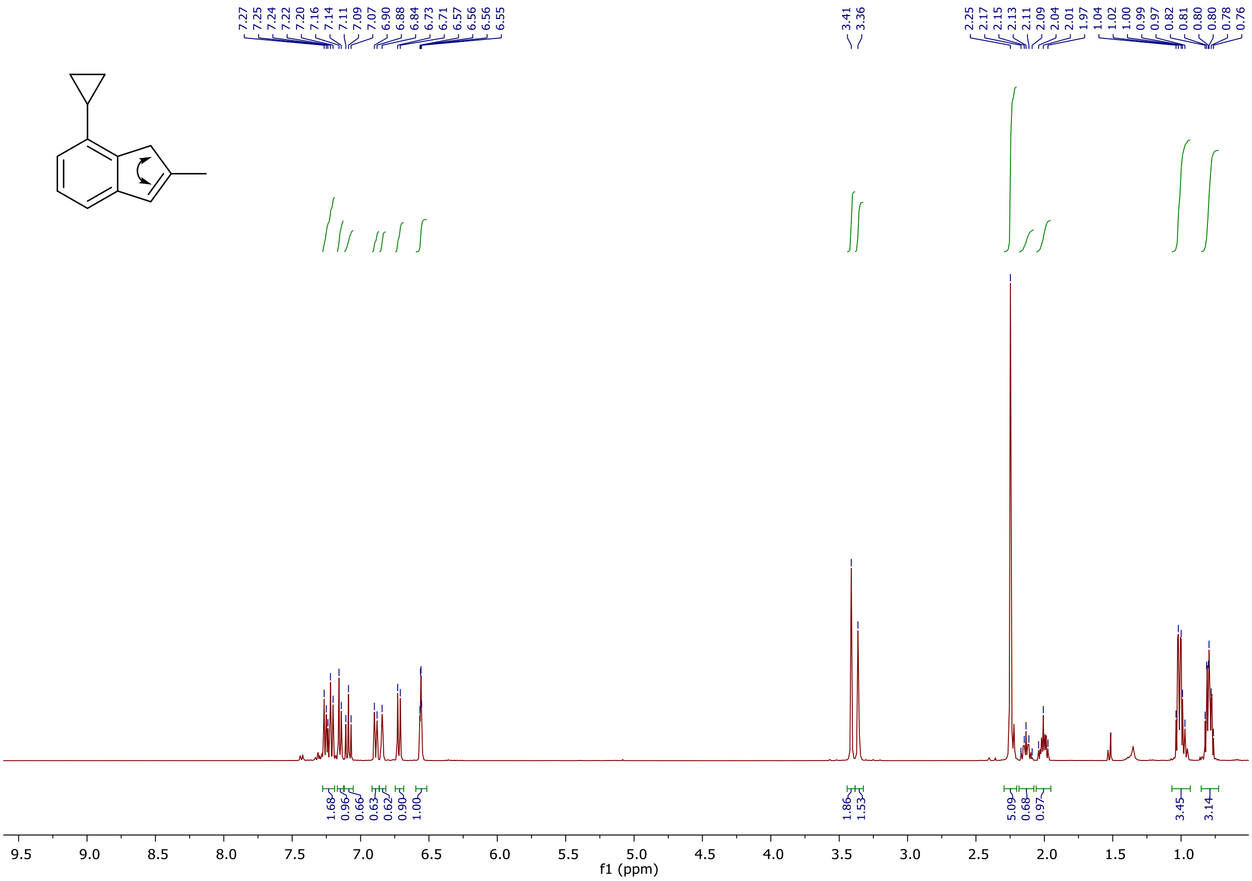
Propylene homopolymerizations were performed in a parallel pressure reactor setup with 48 reaction cells (PPR48), fully contained in glovebox under nitrogen. A pre-weighed glass vial (5.0 mL working volume) feature insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. For experiments with activation by MAO, toluene (solvent unless stated otherwise), a solution of MAO in toluene (500 equiv), and liquid propylene (1.0 mL) were added via syringe. The reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. A precatalyst solution (in toluene) was then added via syringe to the reactor at process conditions. The total amount of solvent added to the reactor, including that used for MAO and precatalysts solutions was 4.1 ml. For experiments with activation by AB, isohexane and liquid propylene (1.0 mL) were added via syringe, and the reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. Solutions of scavenger ((n-octyl)3Al in isohexane), AB (1.1. equiv , in toluene), and, finally, precatalyst (in toluene) were then added via syringe to the reactor at process conditions. The total amount of isohexane added to the reactor including that used for the scavenger solution was 3.8 ml. The total amount of toluene added to the reactor from precatalyst and AB solutions was 0.2 ml. Reactor temperature was monitored and typically maintained within ±1°C. Polymerizations were halted by addition of approximately 50 psi O2/Ar (5 mol% O2) gas mixture to the reactors for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8 psi or for a maximum of 30 minutes polymerization time. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in vacuo. Yields reported include total weight of polymer and residual catalyst. The results are presented in Table S5.

Table S5[a]

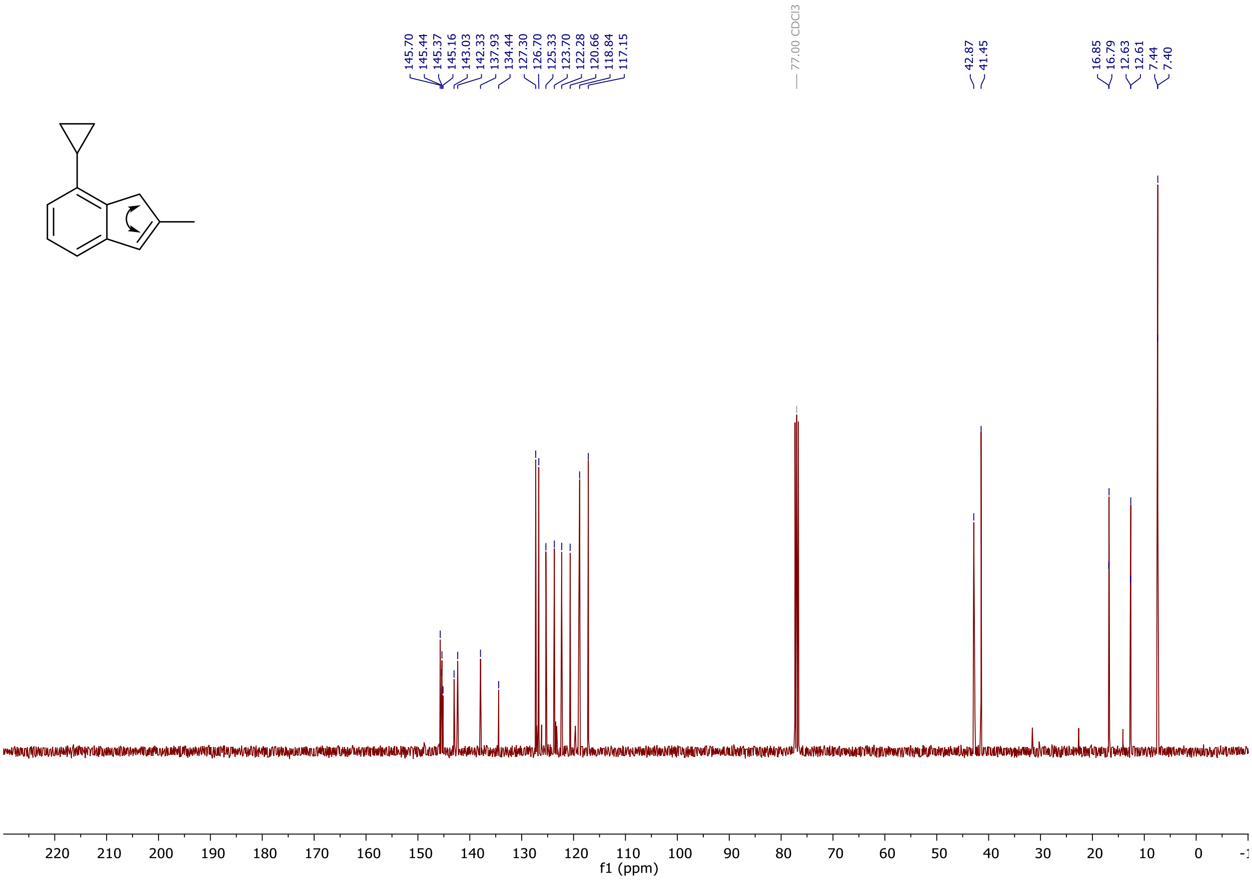
Precat.	$n_{precat.}$, µmol[b]	Co-cat.	T_p, °C[c]	Quench time, s[d]	Polymer yield, g	Activity, $g_{polym.}$× ×$(mmol_{cat}\cdot h)^{-1}$	M_n, Da	M_w, Da	PDI[e]	Polymer T_m, °C[f]
*c*Pr-1	0,030	MAO	70	107	0.1105	149268	103751	142605	1.37	148.4
*c*Pr-1	0,030	MAO	70	120	0.1194	143042	100530	138955	1.38	148.2
*c*Pr-1	0,030	MAO	70	114	0.1016	128112	101645	139548	1.37	148.0
*c*Pr-2	0,025	MAO	70	83	0.215	374365	60925	93818	1.54	153.0
*c*Pr-2	0,025	MAO	70	78	0.2081	383693	65097	99138	1.52	148.2
*c*Pr-2	0,025	MAO	70	77	0.2016	375555	62795	96529	1.54	147.5
Me-2	0,030	MAO	70	61	0.2641	518691	109439	190416	1.74	153.7
Me-2	0,030	MAO	70	70	0.2331	399600	103033	184966	1.80	153.5
Me-2	0,030	MAO	70	71	0.2912	490787	107858	193519	1.79	153.0
*i*Pr-2	0,040	MAO	70	505	0.085	15149	15931	26922	1.69	132.6
*i*Pr-2	0,040	MAO	70	506	0.0886	15759	18486	32001	1.73	134.6
*i*Pr-2	0,040	MAO	70	513	0.0872	15298	21507	33929	1.58	135.4
*c*Pr-3^{Me}	0,025	MAO	70	60	0.2262	544696	42131	67261	1.60	146.5
*c*Pr-3^{Me}	0,025	MAO	70	67	0.2106	453309	51899	80507	1.55	147.3
*c*Pr-3^{Me}	0,025	MAO	70	70	0.2332	482483	48460	76365	1.58	147.0
Me-3	0,080	MAO	70	70	0.1826	117621	152525	291081	1.91	154.2
Me-3	0,100	MAO	70	90	0.1950	77896	155932	302223	1.94	153.7
Me-3	0,100	MAO	70	66	0.2230	121086	121686	254795	2.09	159.1
Me-5	0,040	MAO	70	188	0.3404	162957	298482	630605	2.11	159.6
Me-5	0,040	MAO	70	256	0.449	157852	224554	560175	2.49	159.5
Me-5	0,040	MAO	70	234	0.4033	155115	203125	534216	2.63	158.1
Me-5	0,040	MAO	100	123	0.1486	108732	166877	308565	1.85	157.7
Me-5	0,040	MAO	100	114	0.1373	108395	166844	307246	1.84	156.3
Me-5	0,040	MAO	100	115	0.1392	108939	163385	298673	1.83	156.3
*c*Pr-5	0,040	MAO	70	211	0.1863	79464	179283	382833	2.14	160.5
*c*Pr-5	0,040	MAO	70	205	0.1935	84951	178166	367868	2.06	159.9
*c*Pr-5	0,040	MAO	70	213	0.1983	83789	182887	373725	2.04	159.7
*c*Pr-5	0,040	MAO	100	146	0.1158	71384	70356	148132	2.11	156.2
*c*Pr-5	0,040	MAO	100	135	0.1215	81000	72228	140756	1.95	155.7
*c*Pr-5	0,040	MAO	100	136	0.1187	78551	75711	144062	1.90	156.2
*i*Pr-5	0,080	MAO	70	1803	0.1148	2865	33617	47351	1.41	137.8
*i*Pr-5	0,080	MAO	70	1800	0.1007	2517	32463	47856	1.47	137.6
*i*Pr-5	0,080	MAO	70	1801	0.1219	3046	28737	47792	1.66	137.8
*i*Pr-5	0,080	MAO	100	1801	0.1070	2673	6951	9624	1.38	—
*i*Pr-5	0,080	MAO	100	1531	0.1339	3936	8588	12282	1.43	106.5

*i*Pr-5	0,080	MAO	100	1714	0.1287	3380	7998	11347	1.42	104.0
*c*Pr-3	0,025	AB	70	32	0.3328	1483690	23401	54985	2.35	149.8
*c*Pr-3	0,025	AB	70	32	0.3375	1504644	19354	50984	2.63	148.4
*c*Pr-3	0,025	AB	70	29	0.3244	1594321	23683	55186	2.33	149.6
*c*Pr-5	0,025	AB	70	459	0.1274	39969	380195	658180	1.73	161.7
*c*Pr-5	0,025	AB	70	262	0.1103	60623	371656	630046	1.70	160.6
*c*Pr-5	0,025	AB	70	283	0.0992	50476	369073	660398	1.79	160.7
*c*Pr-5	0,025	AB	100	203	0.0716	50790	89977	169582	1.88	154.9
*c*Pr-5	0,025	AB	100	230	0.0905	56661	99274	179959	1.81	155.8
*c*Pr-5	0,025	AB	100	270	0.0739	39413	98764	165830	1.68	154.1
Me-5	0,025	AB	70	268	0.3633	195206	251696	665814	2.65	161.7
Me-5	0,025	AB	70	323	0.2909	129689	516715	963614	1.86	162.4
Me-5	0,025	AB	70	417	0.1074	37088	723734	1269304	1.75	163.6
Me-5	0,025	AB	100	97	0.1505	223423	125019	215082	1.72	155.8
Me-5	0,025	AB	100	120	0.1669	200280	105326	208174	1.98	155.5
Me-5	0,025	AB	100	254	0.0678	38438	140442	243853	1.74	154.8

[a] Polymerization conditions: 0.025–0.100 µmol precatalyst; 4.1 mL toluene; 1.0 mL propylene; reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes; 500 equiv. MAO, or 1.1 equiv AB + 0.5 mmol *n*Oct$_3$Al as scavenger. [b] Precatalyst amount. [c] Polymerization temperature. [d] Polymerization time. [e] Polydispersity index, M_w/M_n, determined by GPC. [f]Polymer melting temperature, determined by DSC



^{1}H NMR-spectrum of 4/7-cyclopropyl-2-methylindene.



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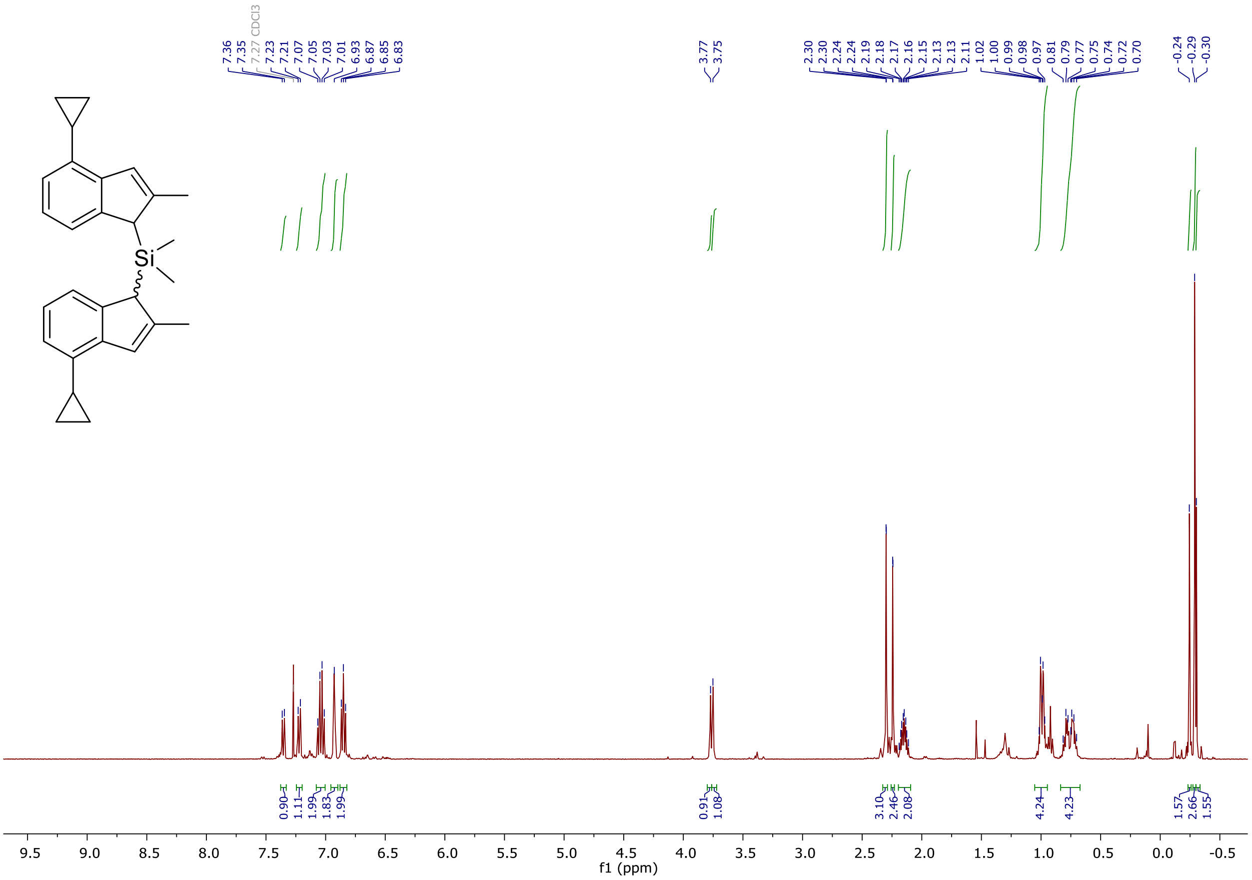

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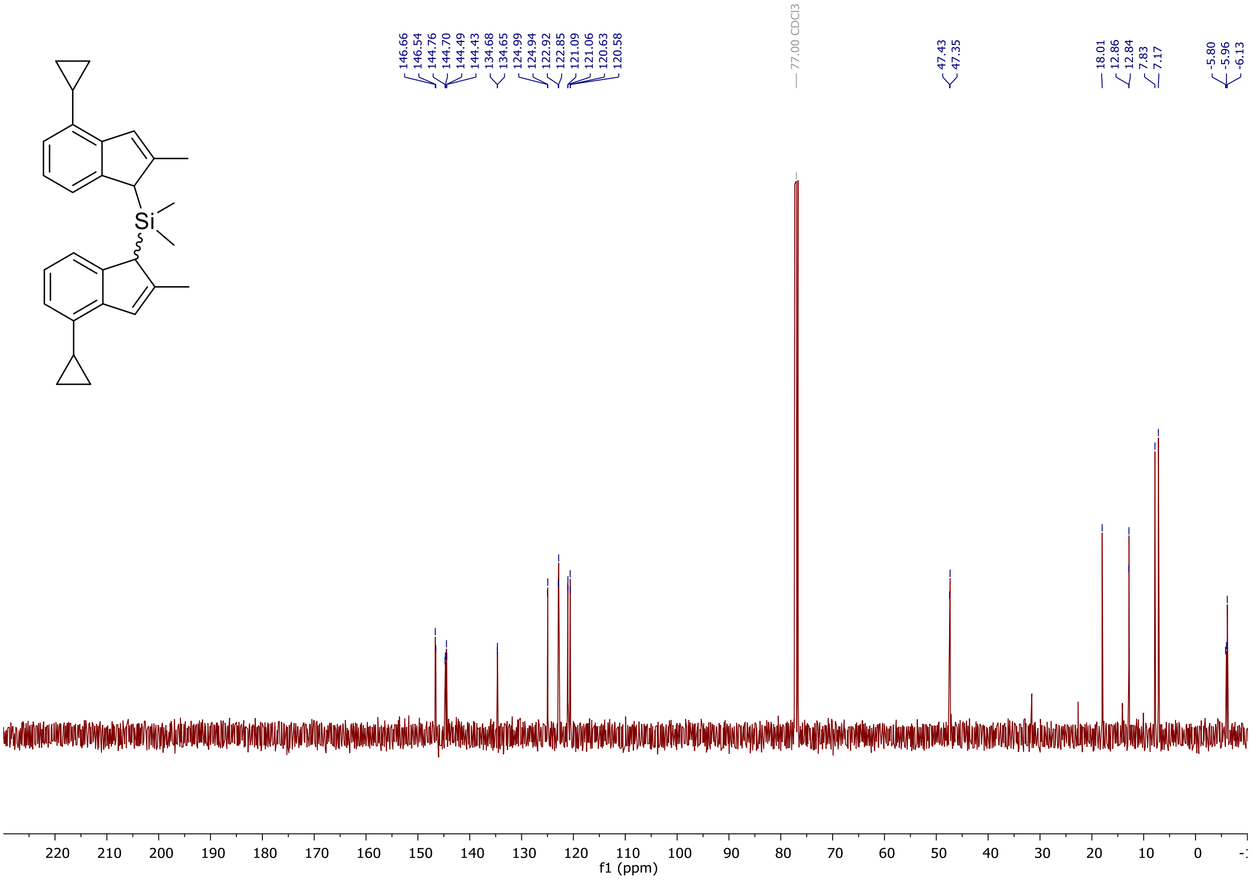

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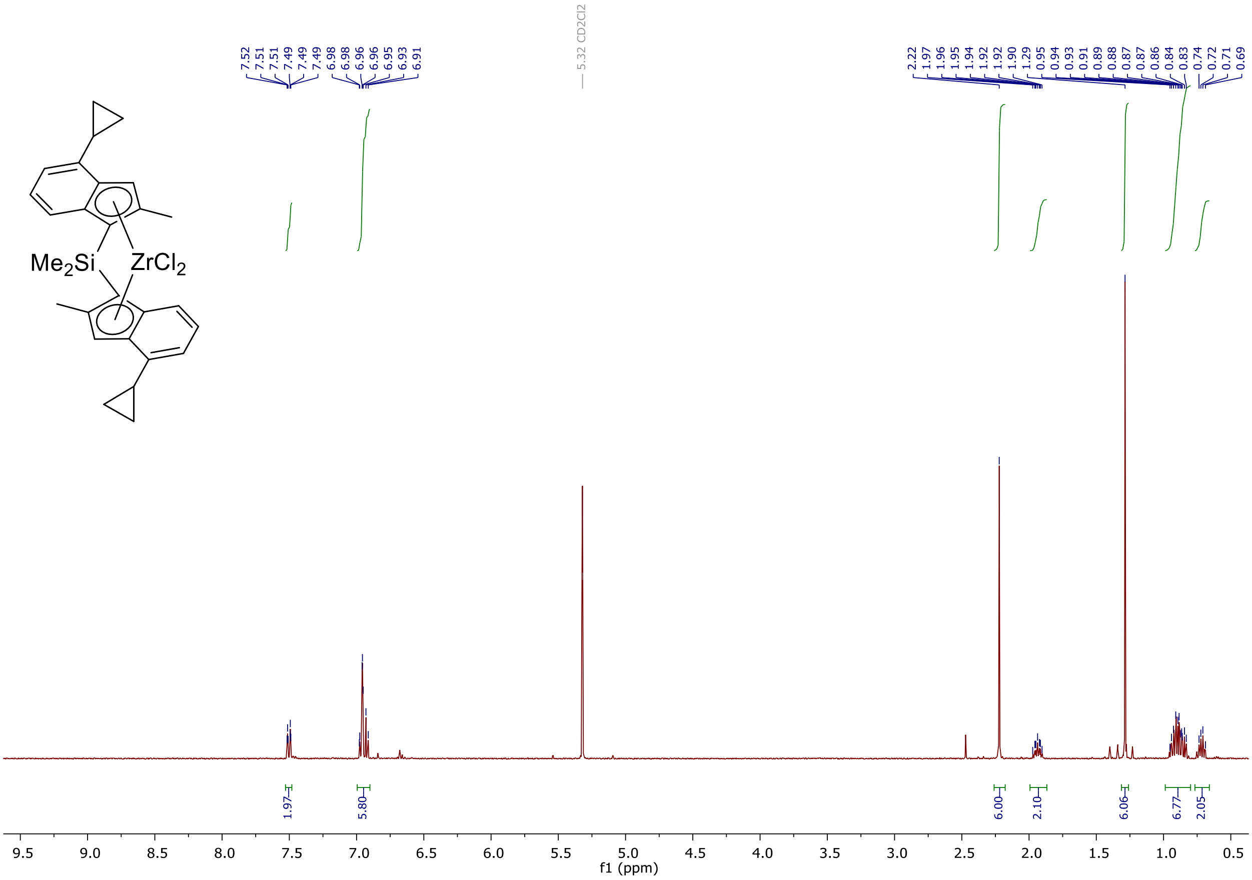

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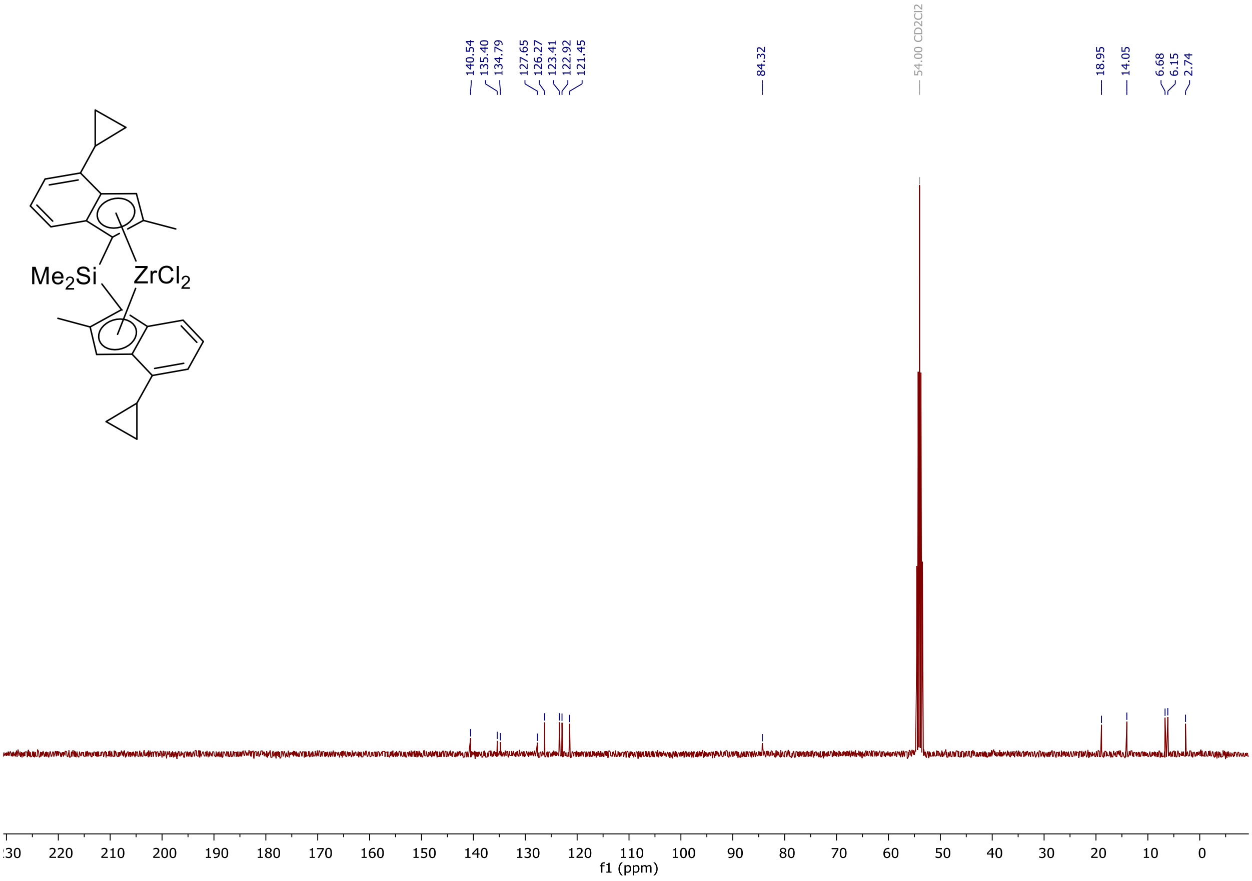

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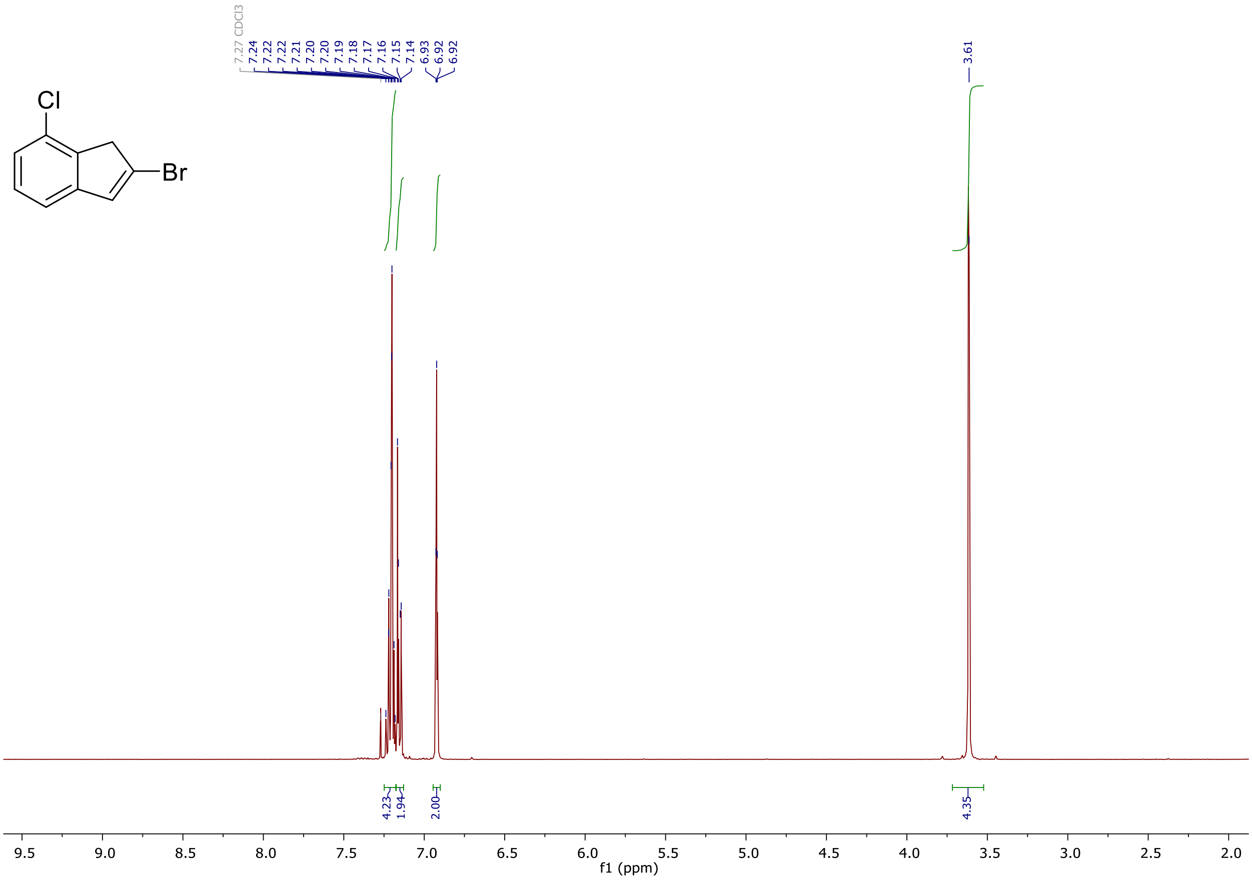
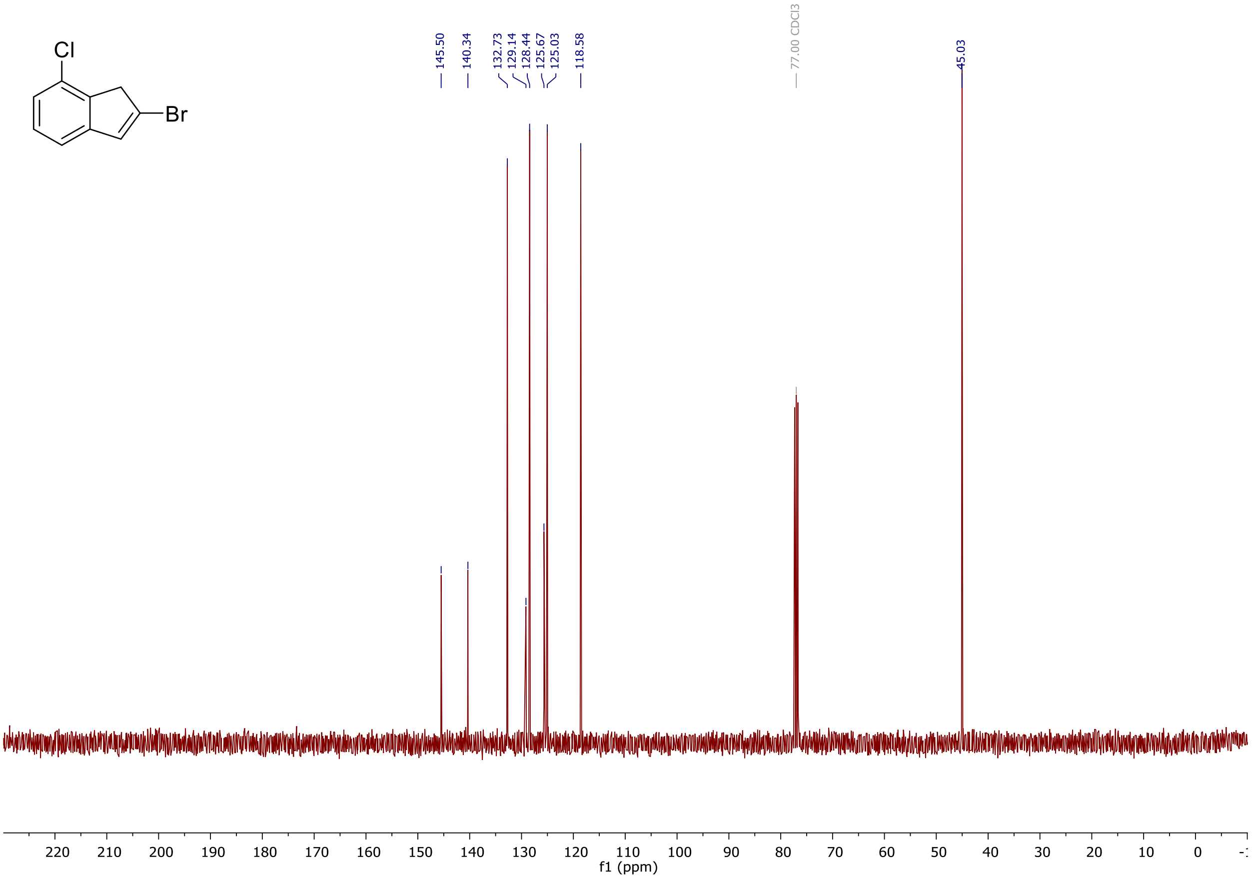


^{1}H NMR-spectrum of 2-bromo-7-chloroindene.



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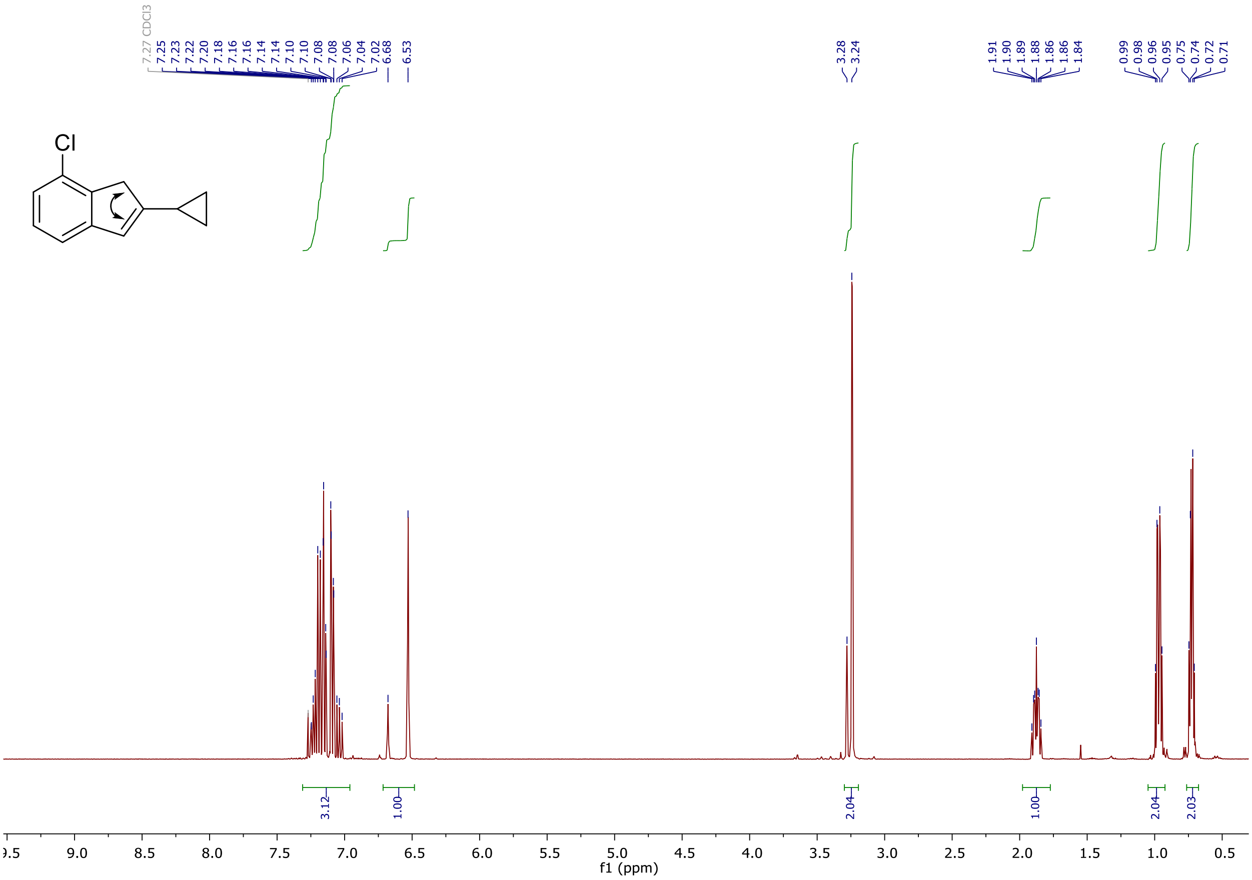

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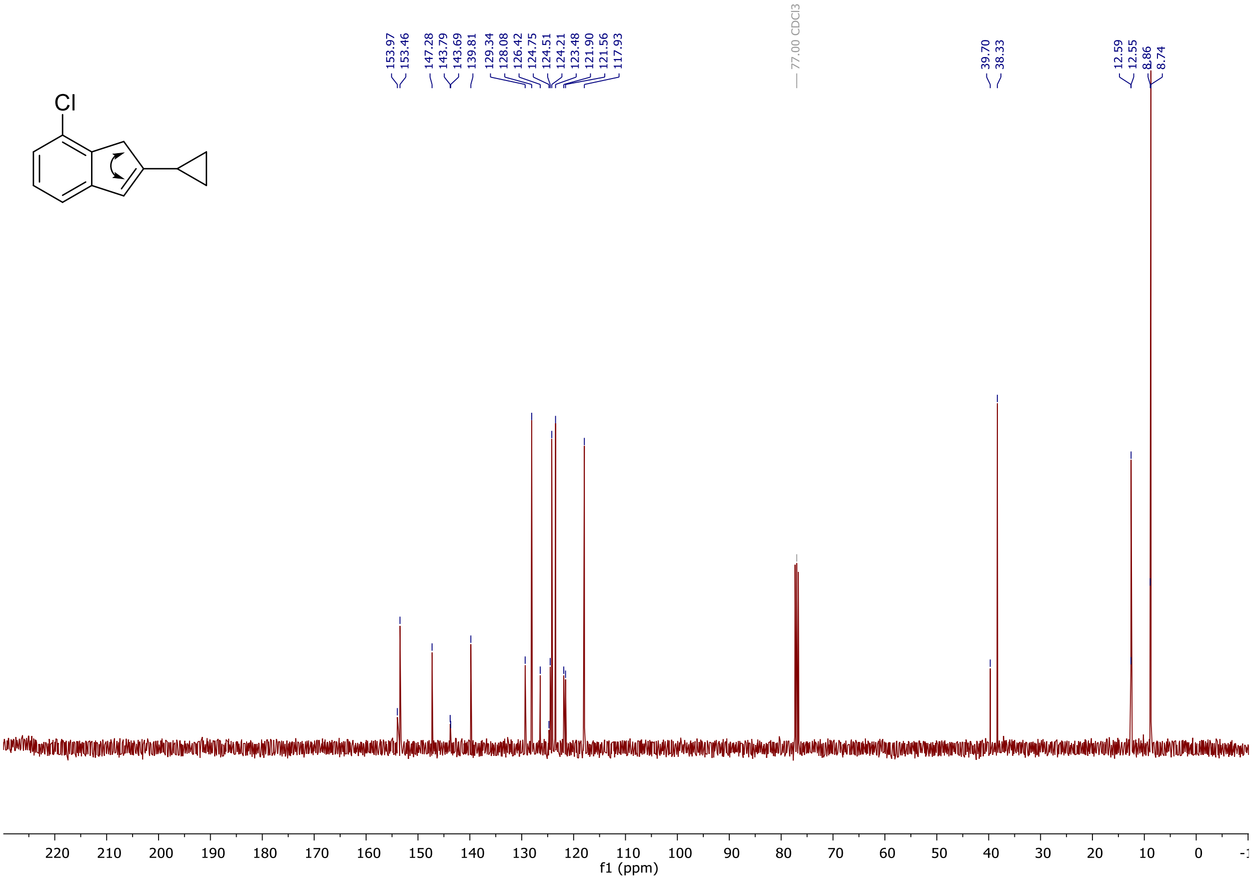

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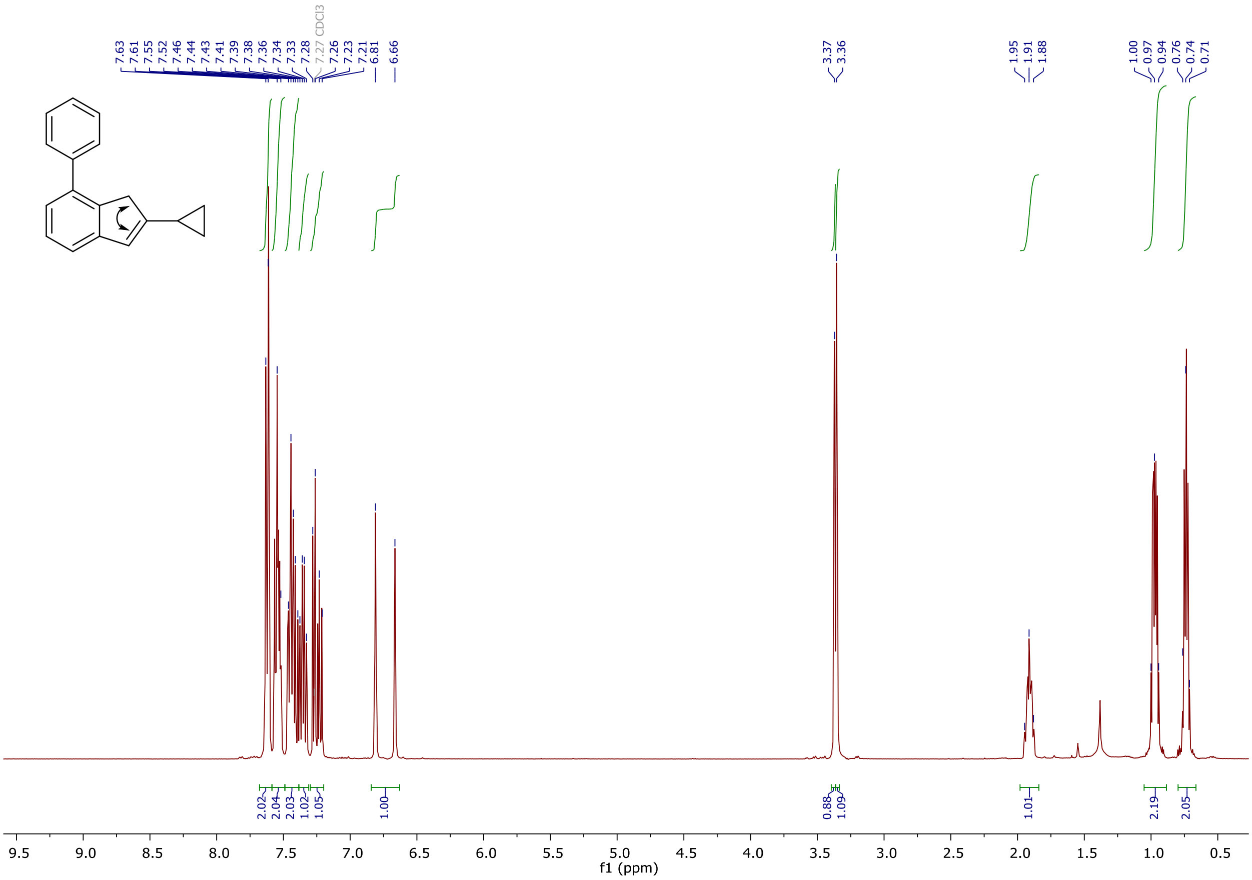

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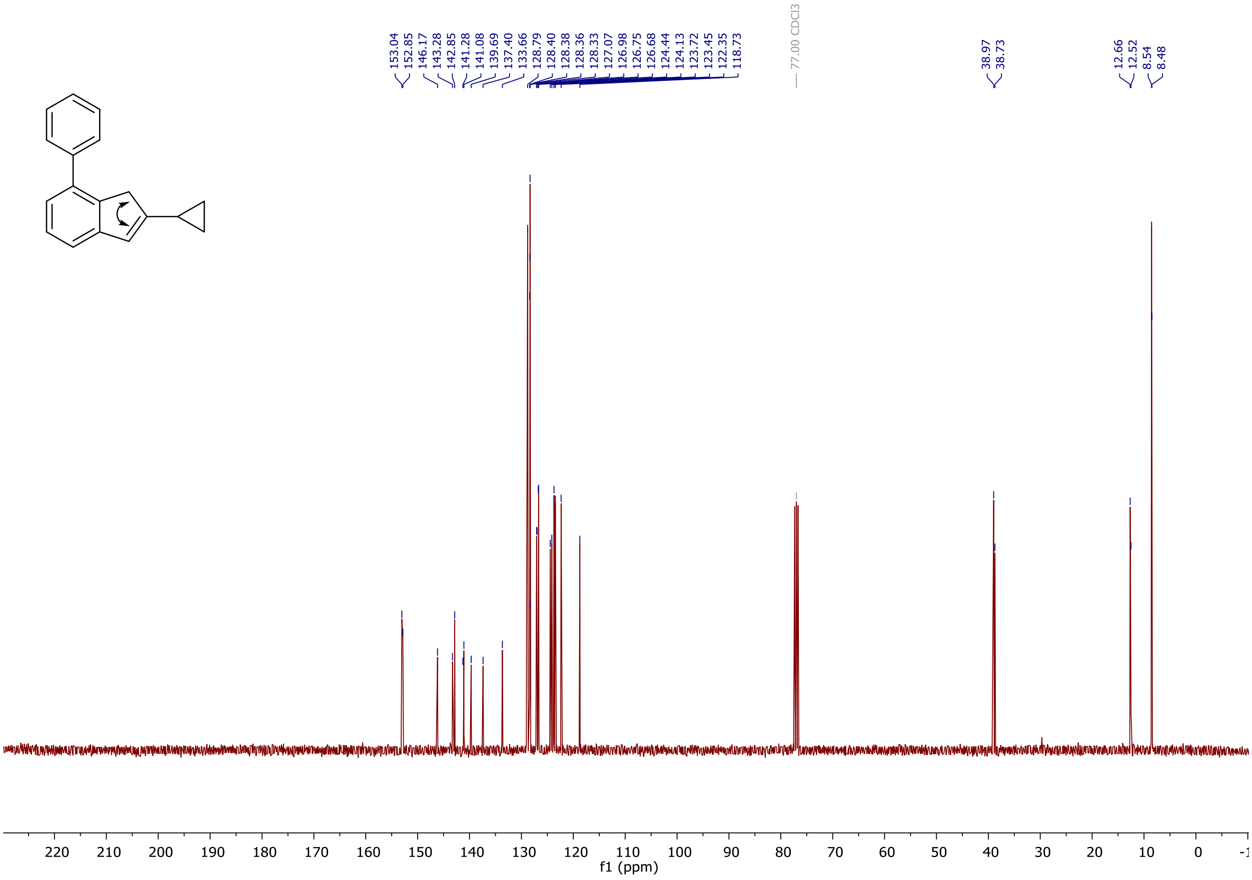

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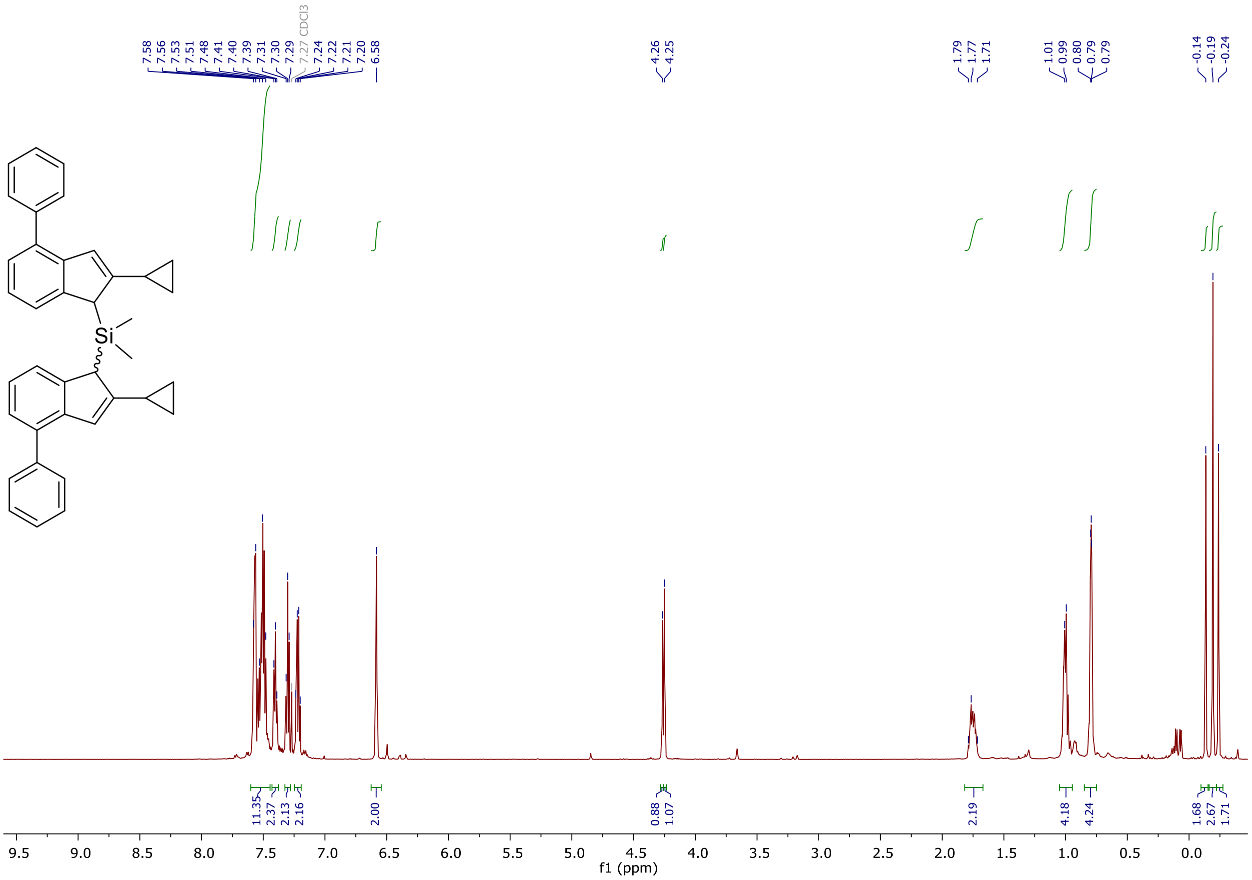

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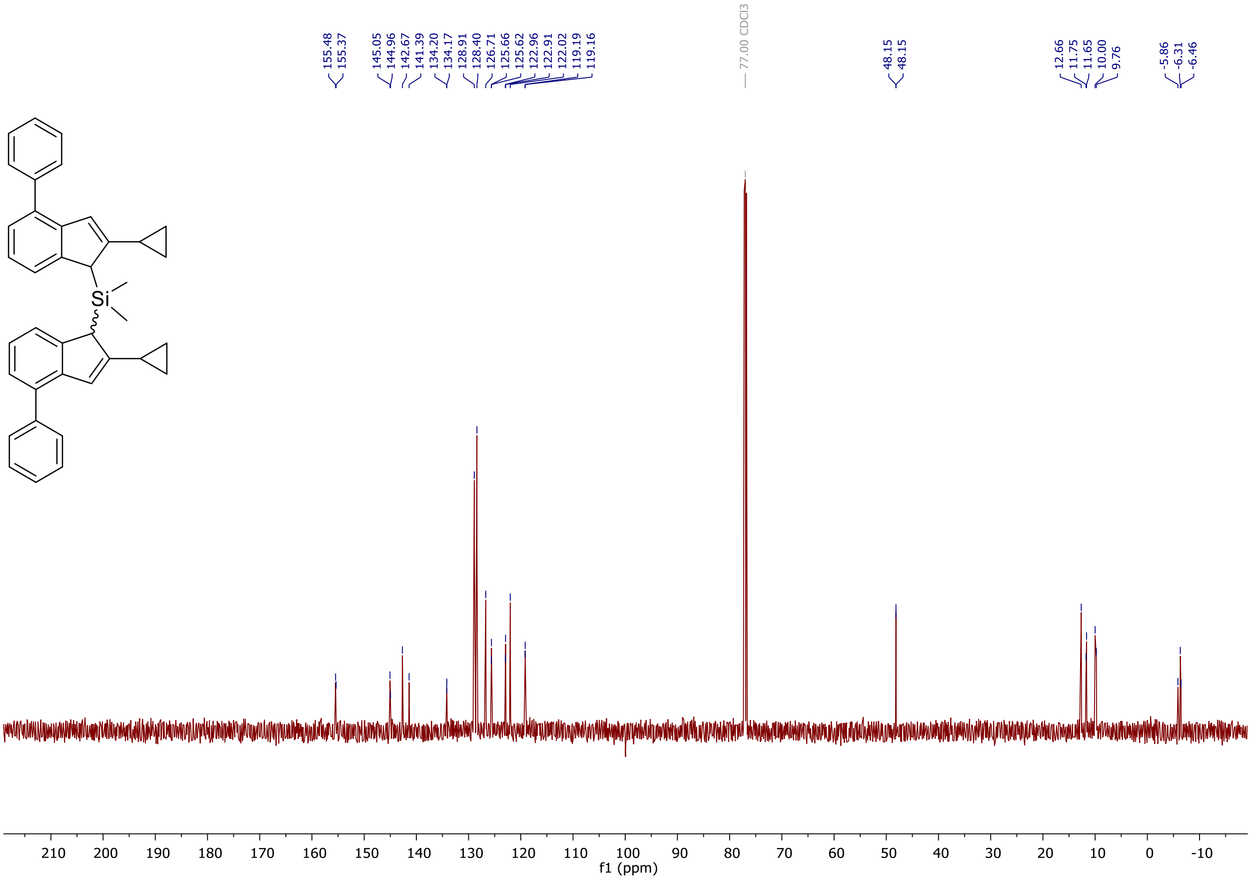

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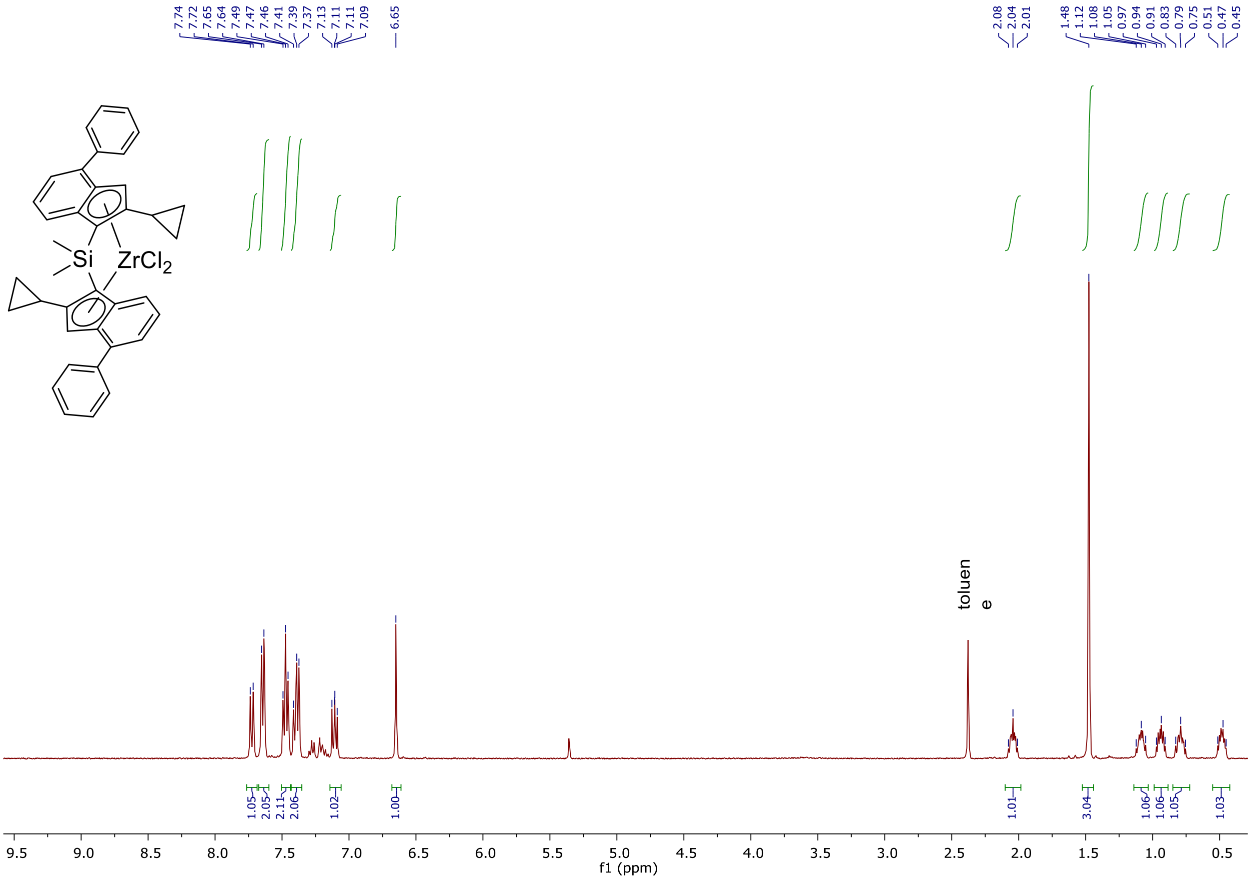

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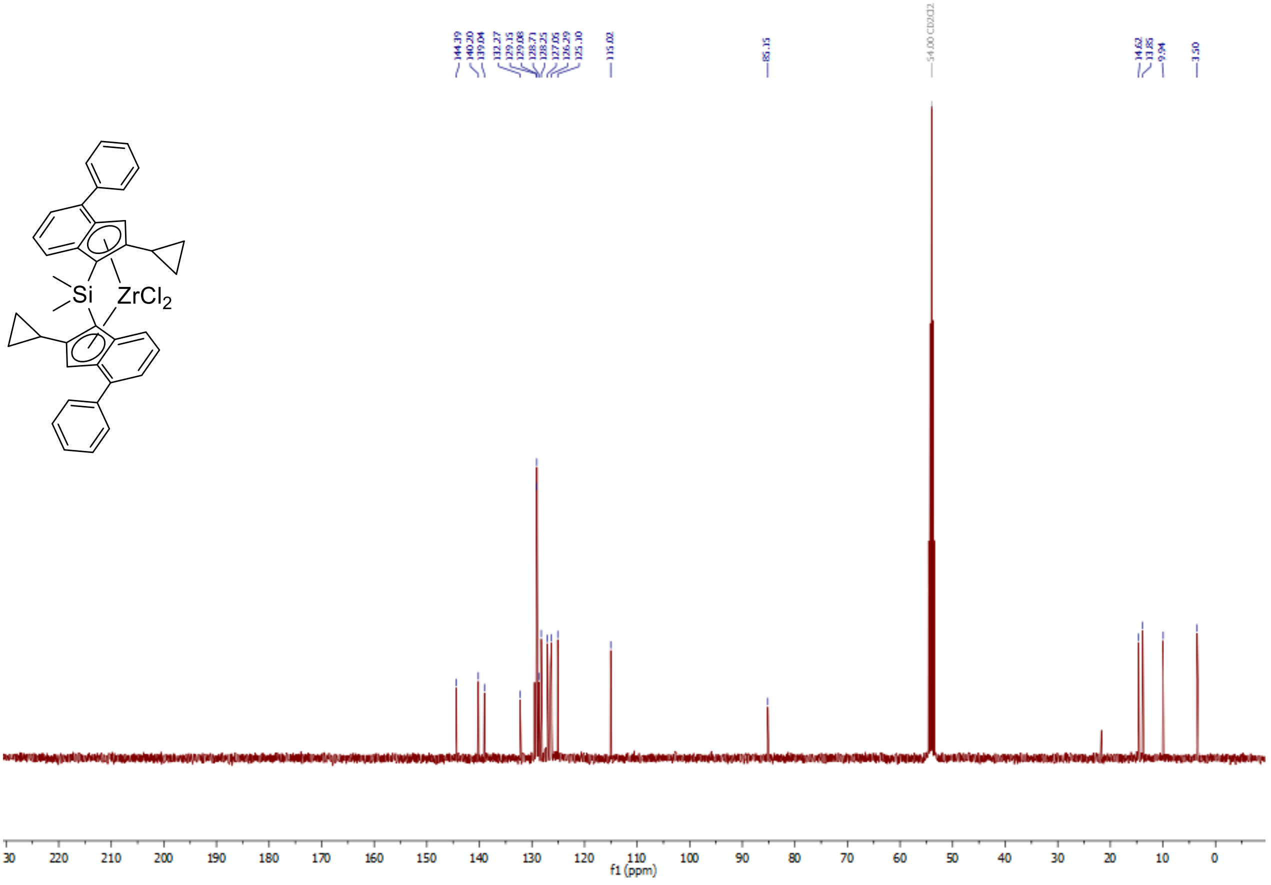
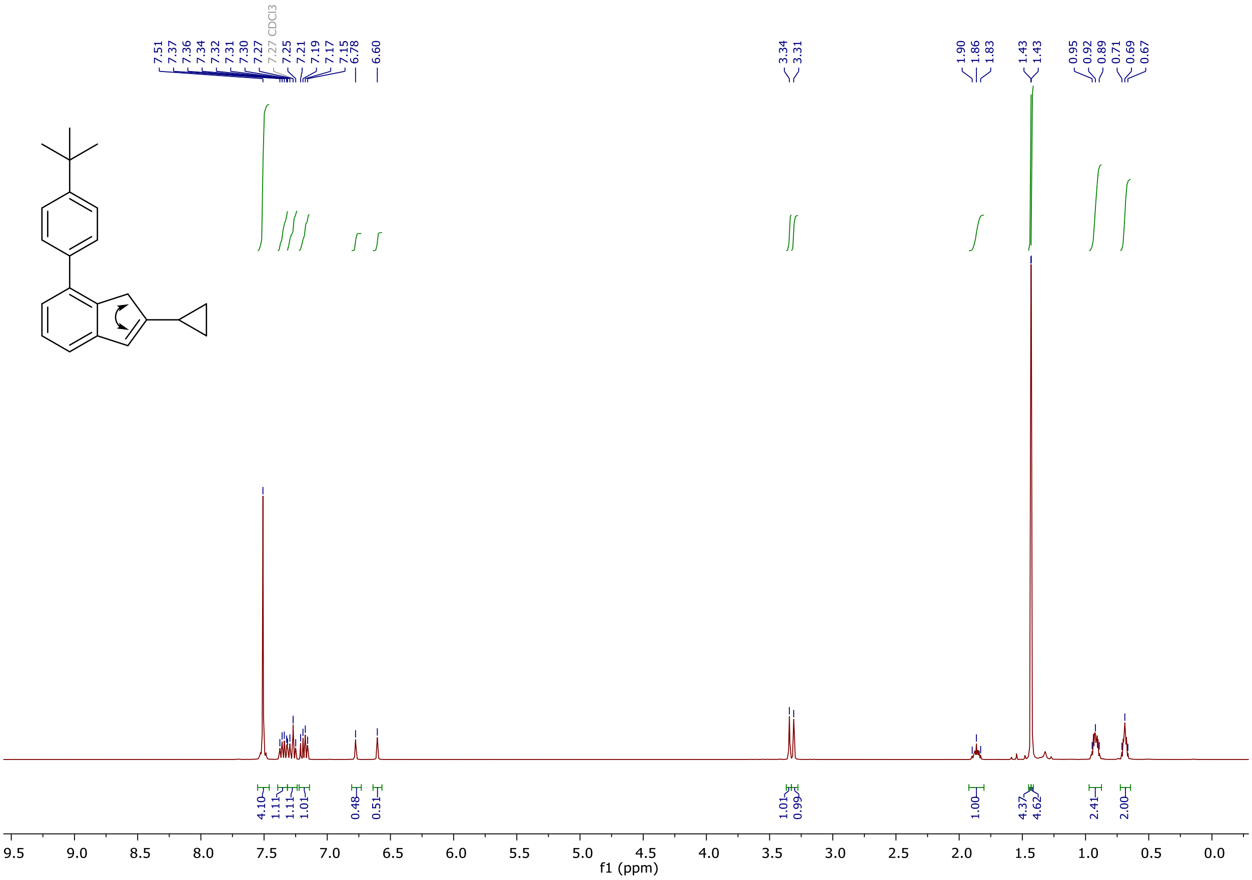
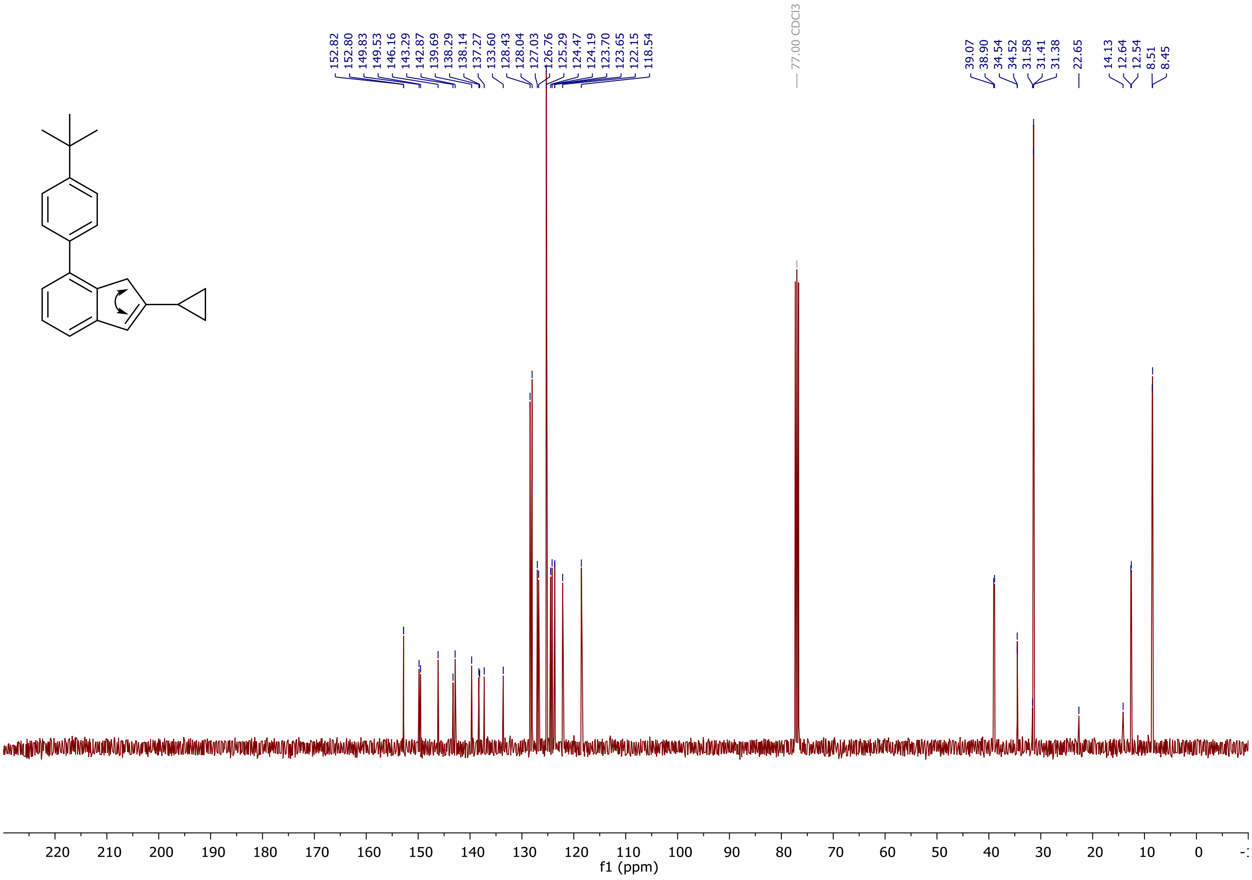


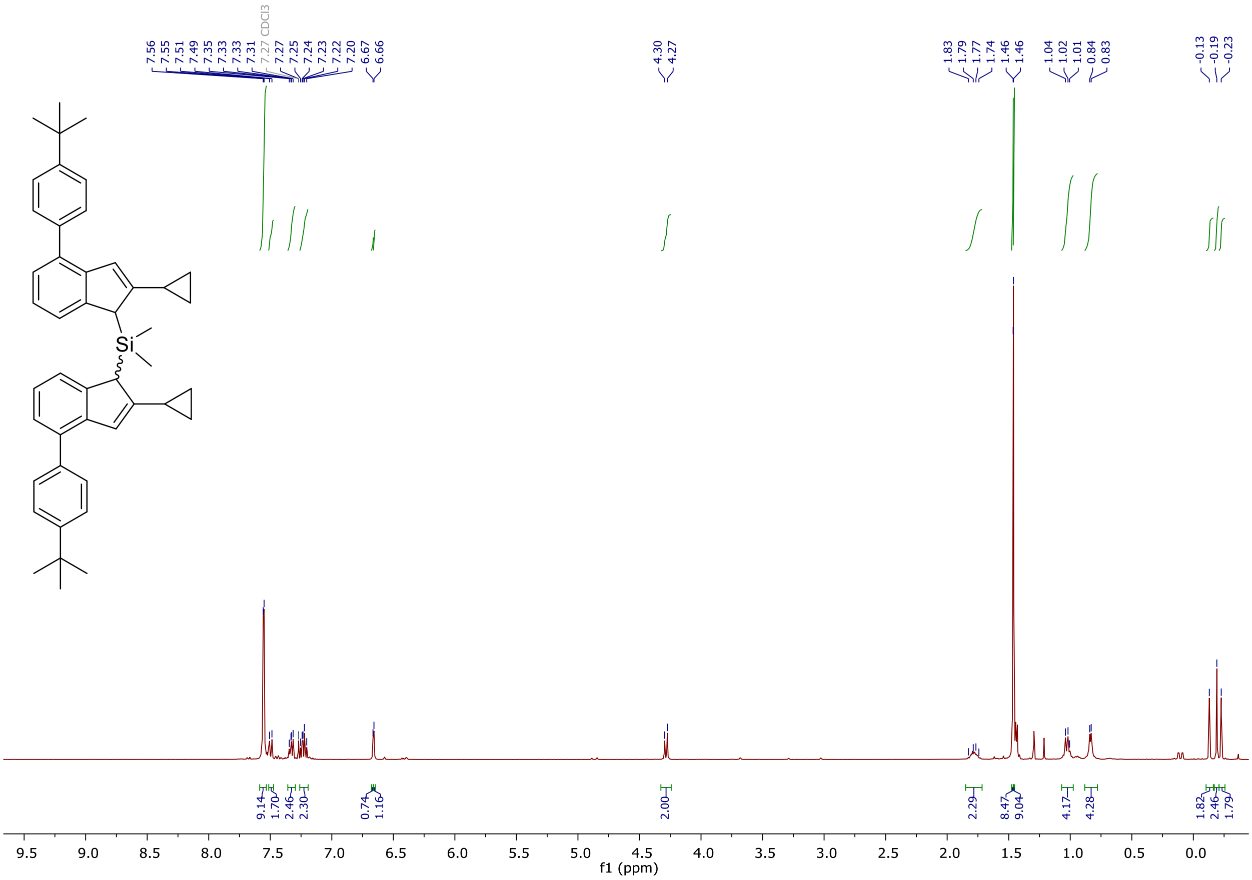
^{13}C NMR-spectrum of complex ***c*Pr-2**.



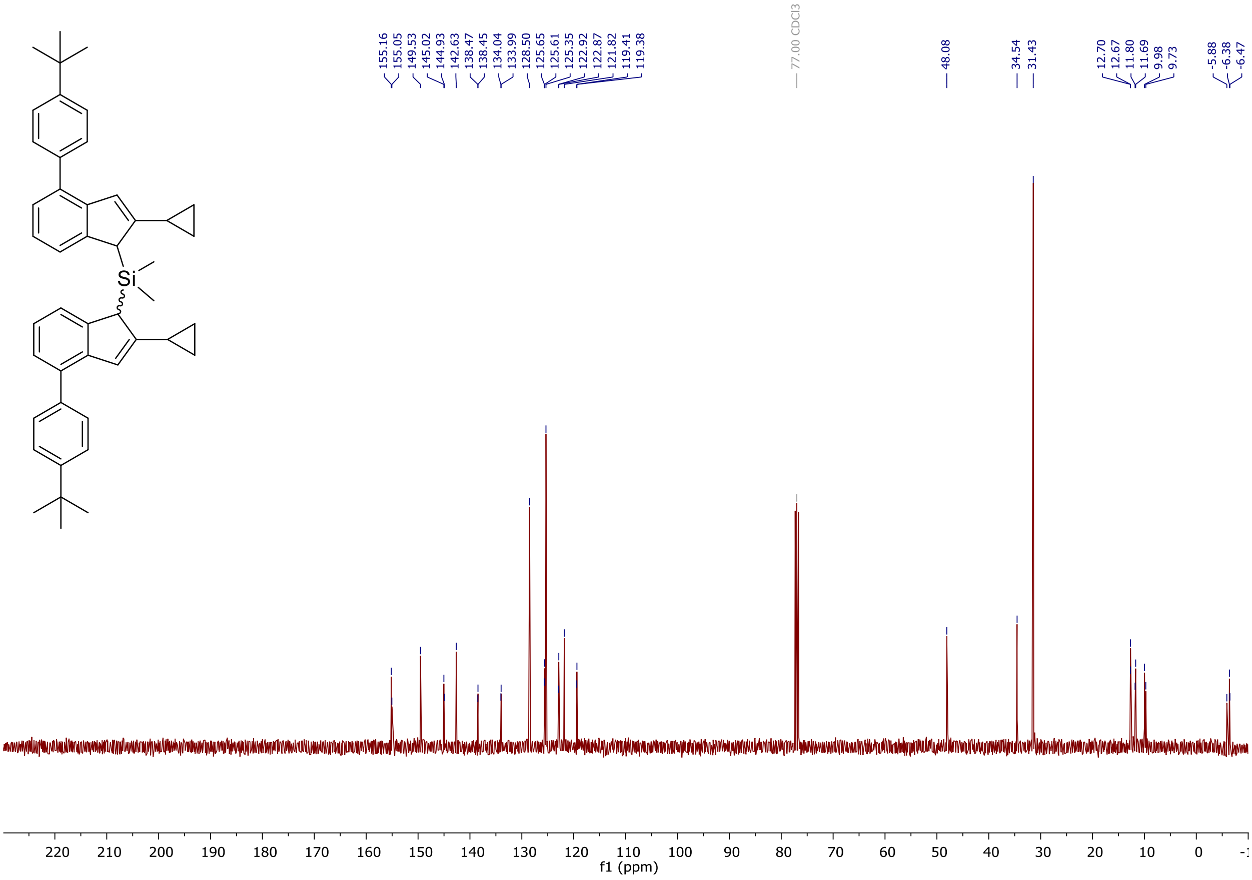
^{1}H NMR-spectrum of 2-cyclopropyl-4/7-(4-di-*tert*-butylphenyl)indene.



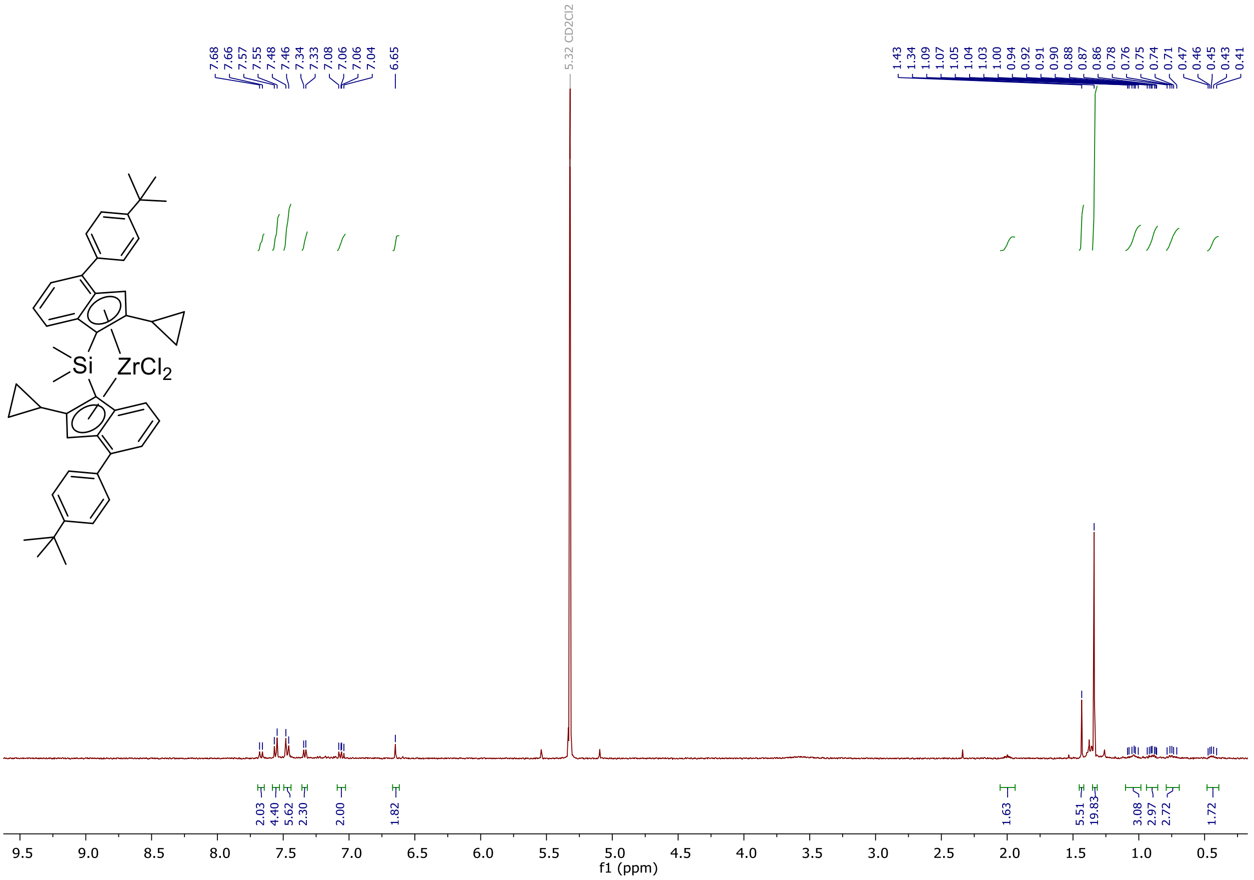
^{13}C NMR-spectrum of 2-cyclopropyl-4/7-(4-di-*tert*-butylphenyl)indene.



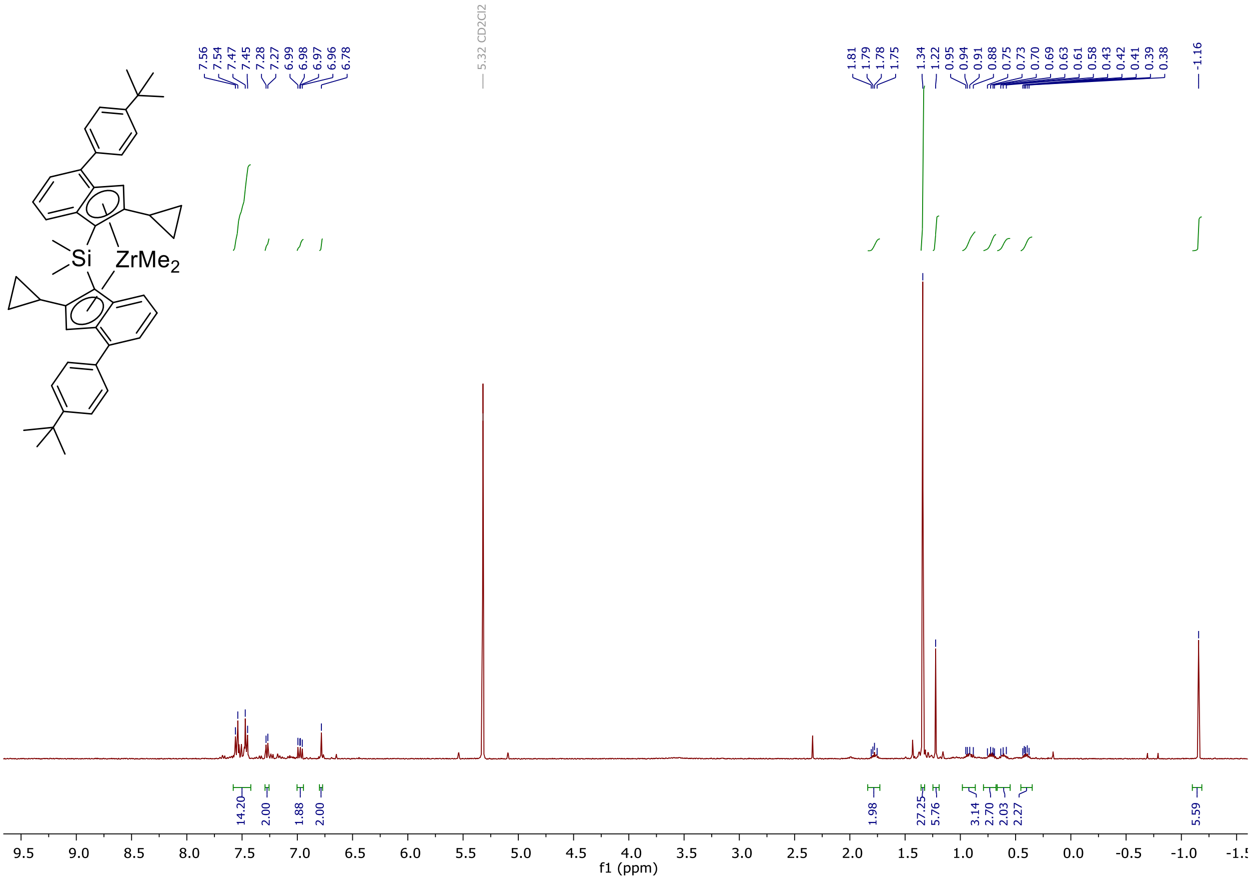
^{1}H NMR-spectrum of *rac*/*meso*-bis(4-(4-*tert*-butylphenyl)-2-cyclopropylinden-1-yl)dimethylsilane.



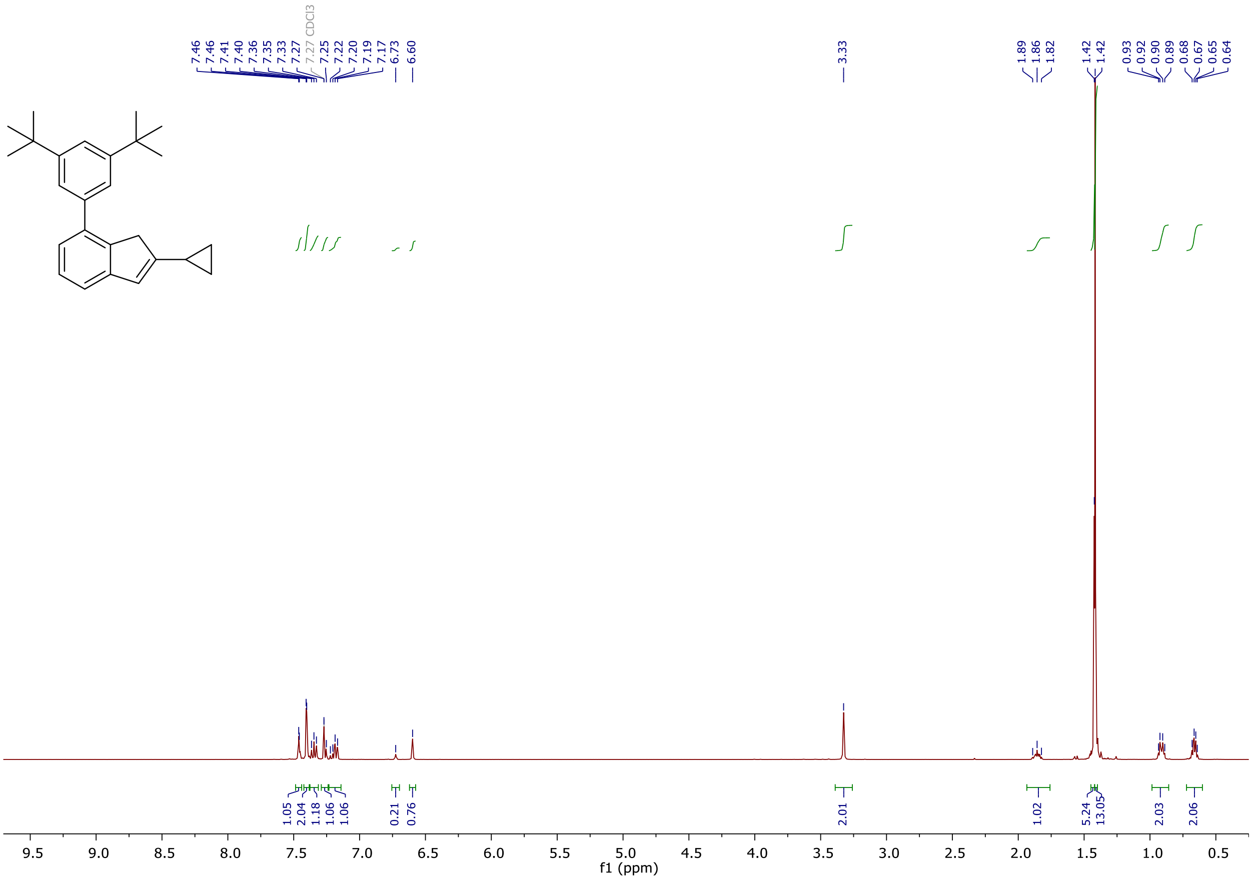
^{13}C NMR-spectrum of *rac*/*meso*-bis(4-(4-*tert*-butylphenyl)-2-cyclopropylinden-1-yl)dimethylsilane.



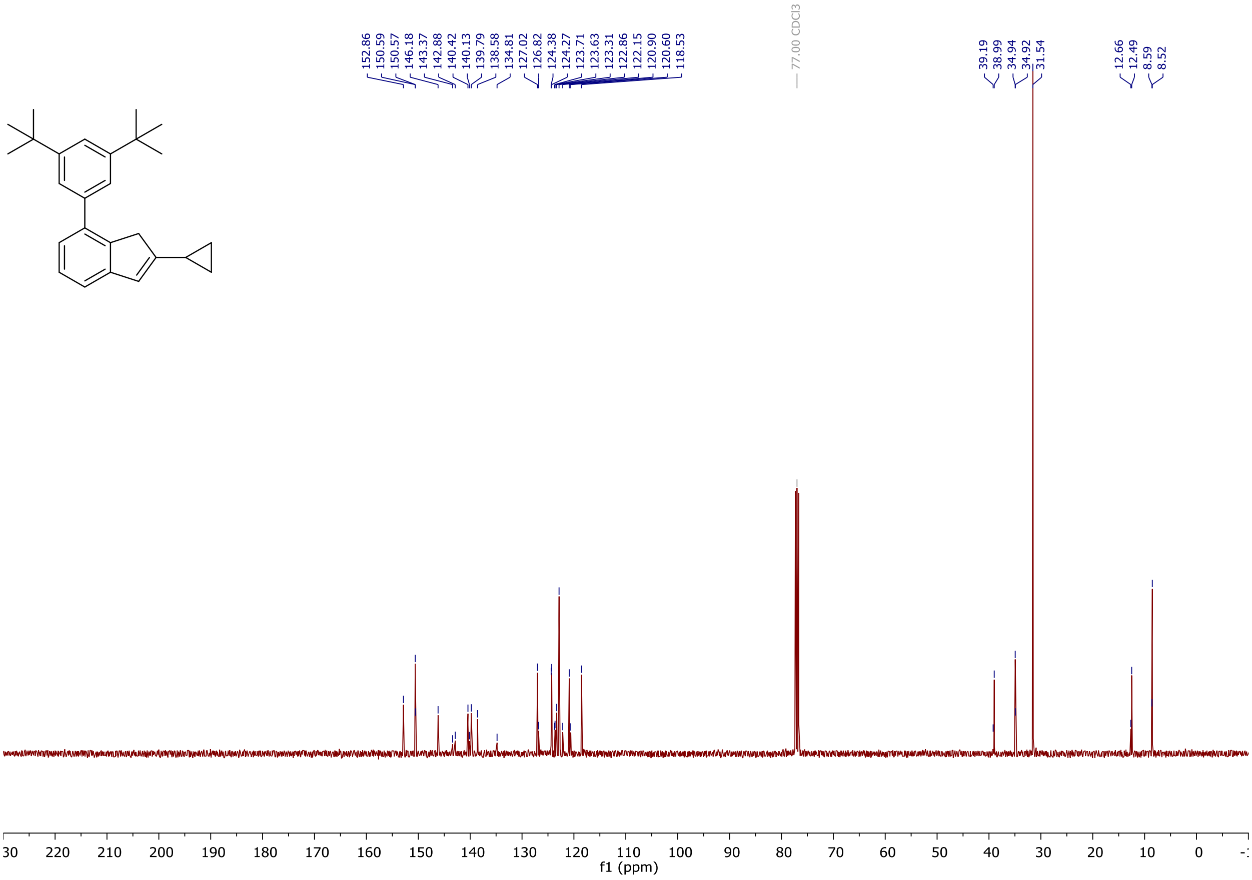
^{1}H NMR-spectrum of complex ***c*Pr-3**.



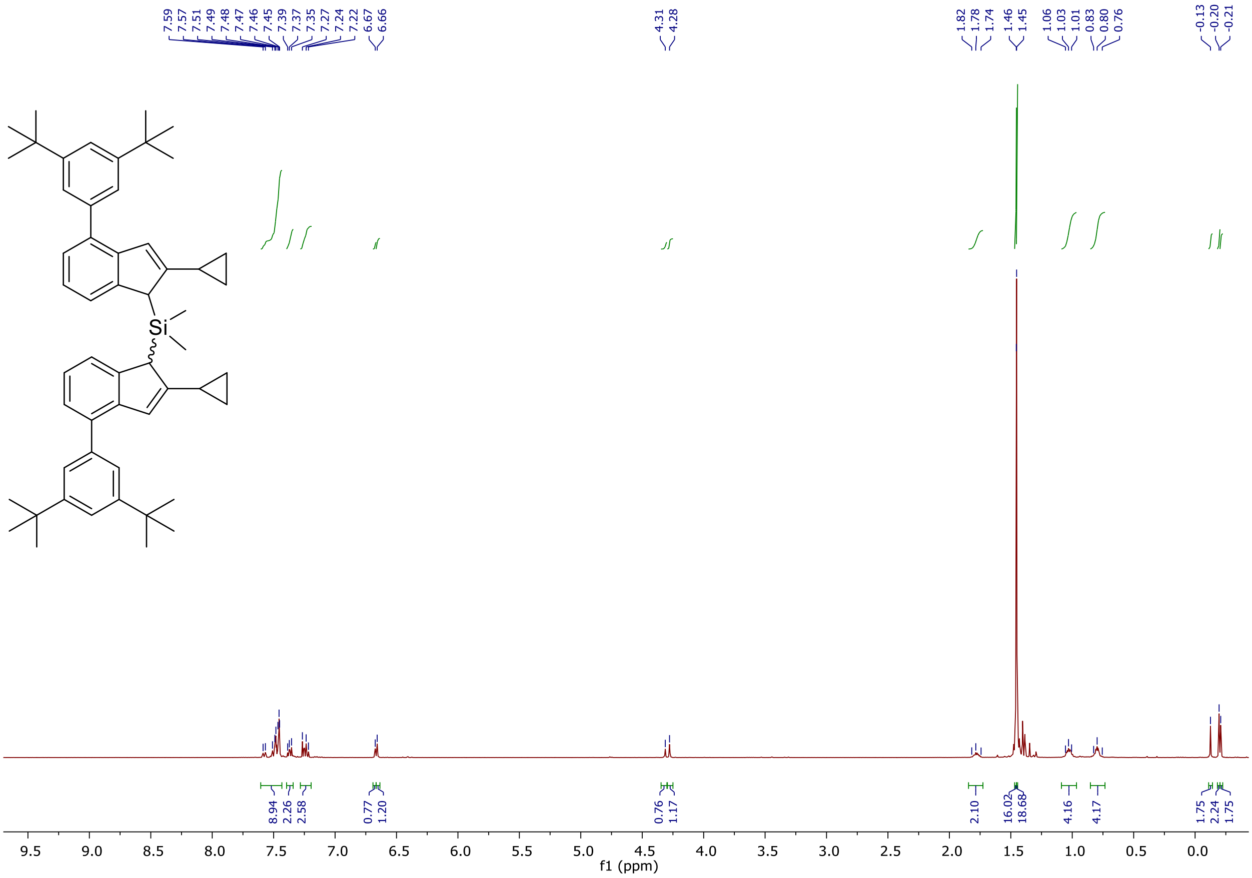
^{1}H NMR-spectrum of complex ***c*Pr-3**$^{\mathrm{Me}}$.



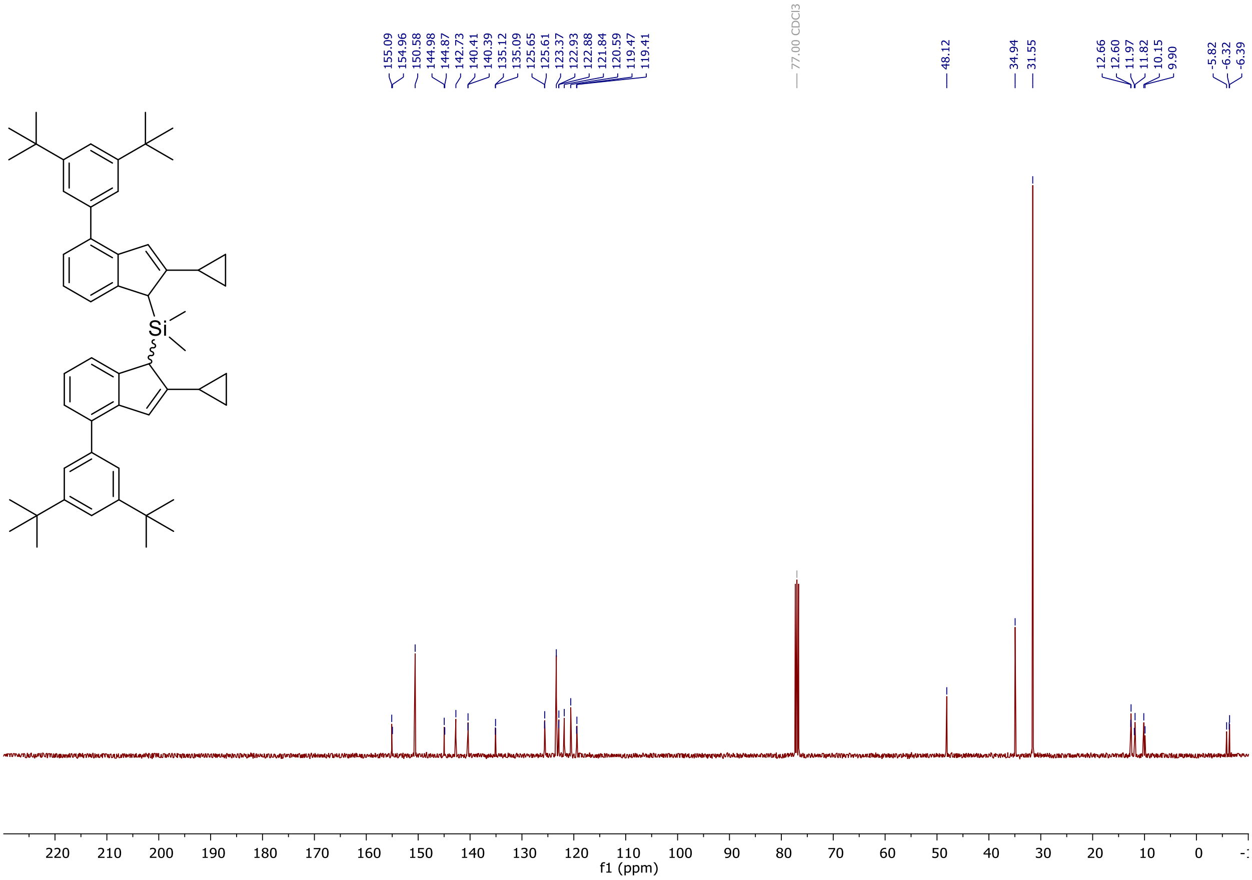
^{1}H NMR-spectrum of 2-cyclopropyl-4/7-(3,5-di-*tert*-butylphenyl)indene.



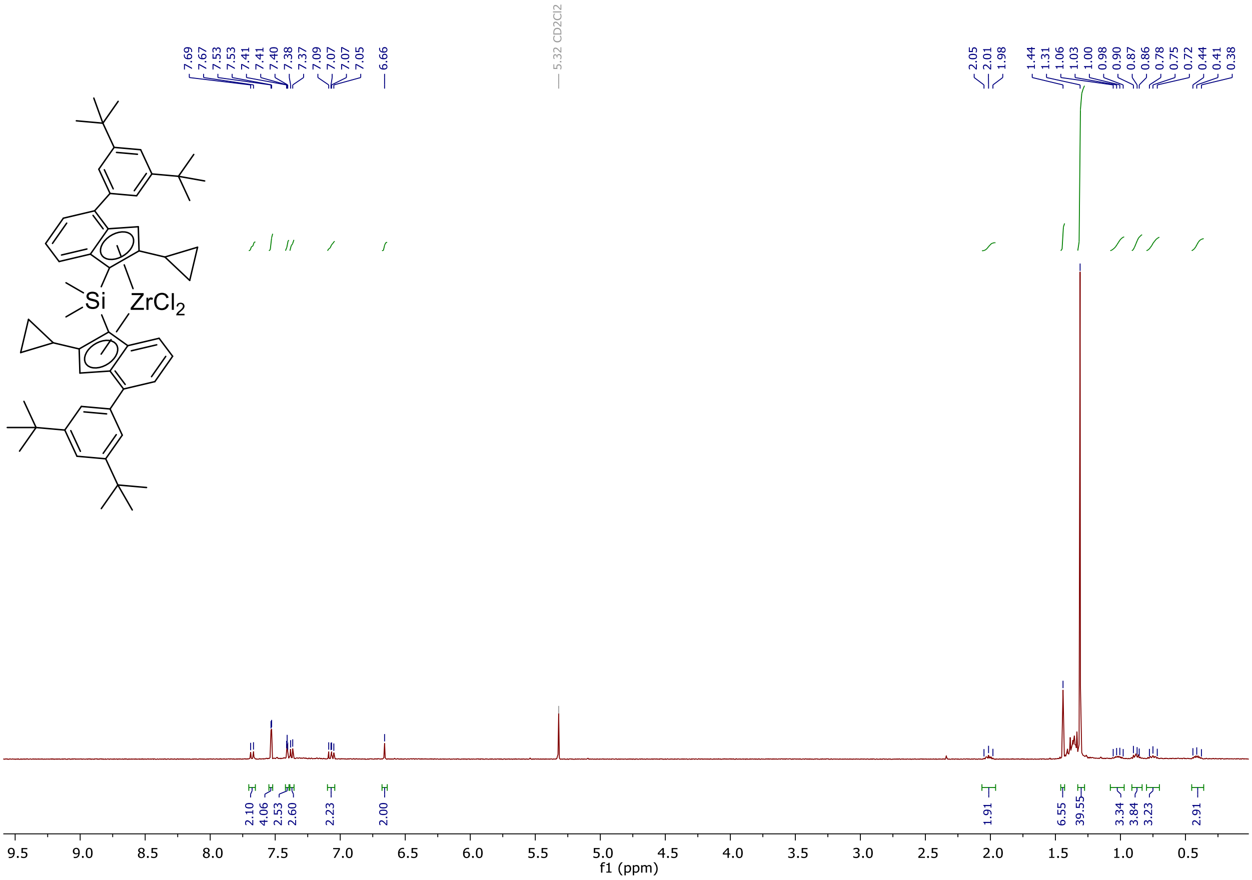
^{13}C NMR-spectrum of 2-cyclopropyl-4/7-(3,5-di-*tert*-butylphenyl)indene.



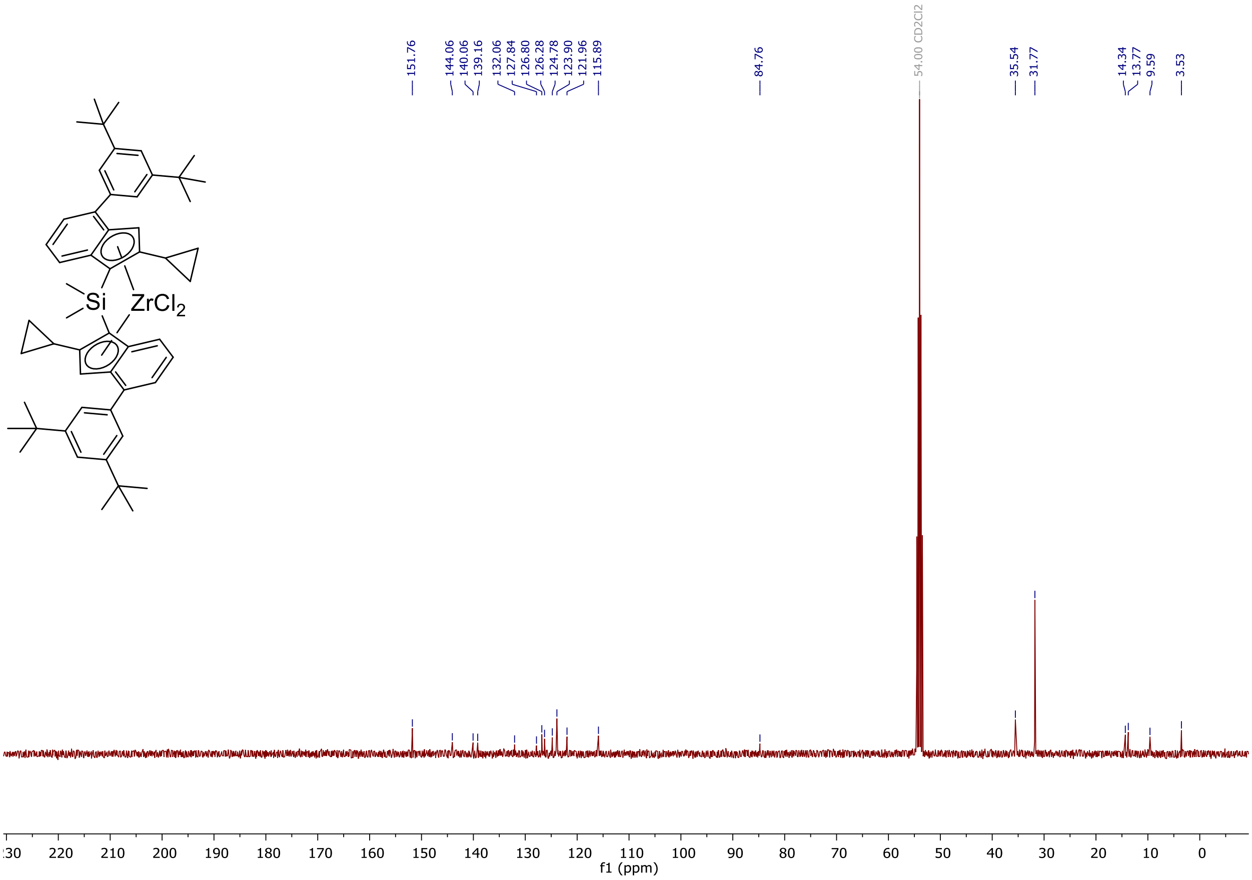
^{1}H NMR-spectrum of *rac/meso*-bis(2-cyclopropyl-4-(3,5-di-*tert*-butylphenyl)-inden-1-yl)dimethylsilane).



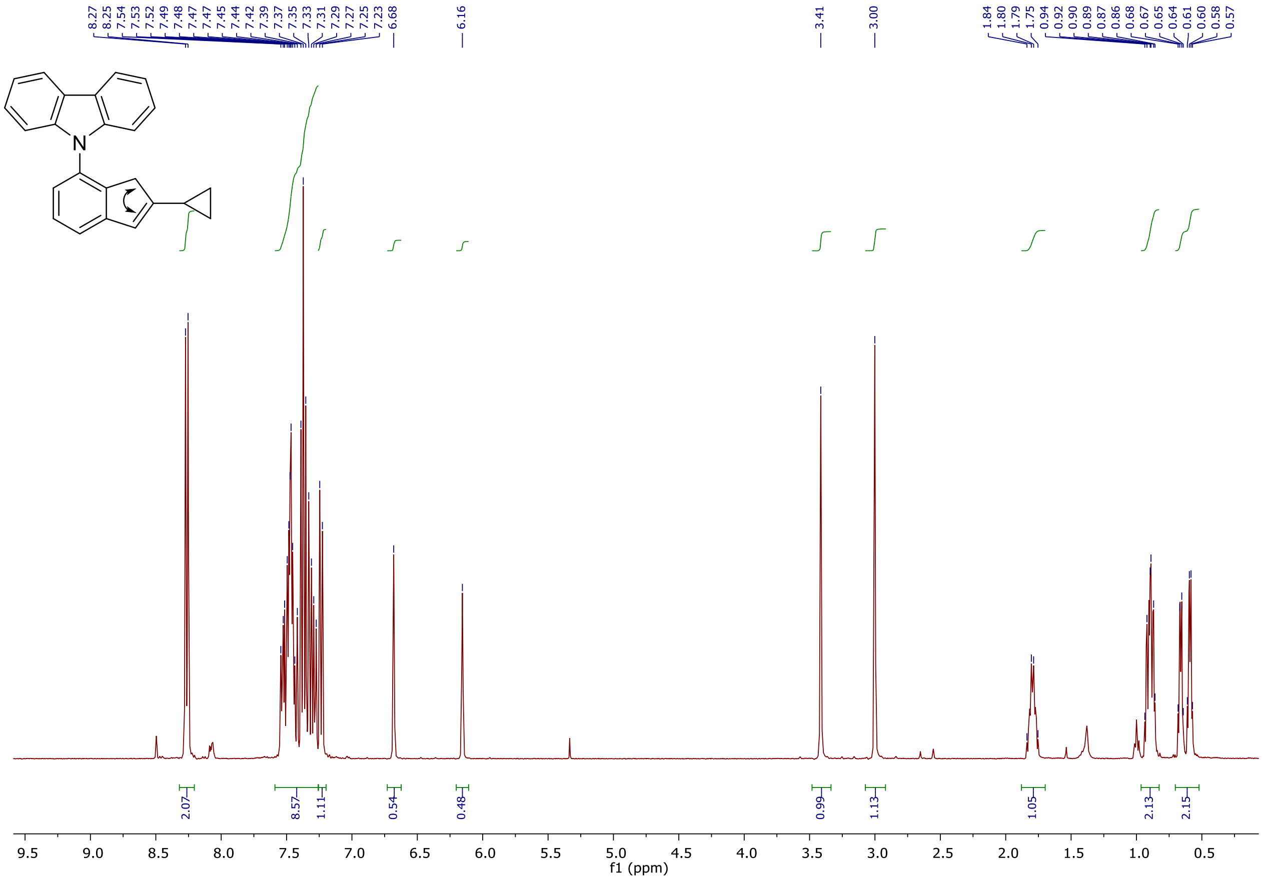
^{13}C NMR-spectrum of *rac/meso*-bis(2-cyclopropyl-4-(3,5-di-*tert*-butylphenyl)-inden-1-yl)dimethylsilane).



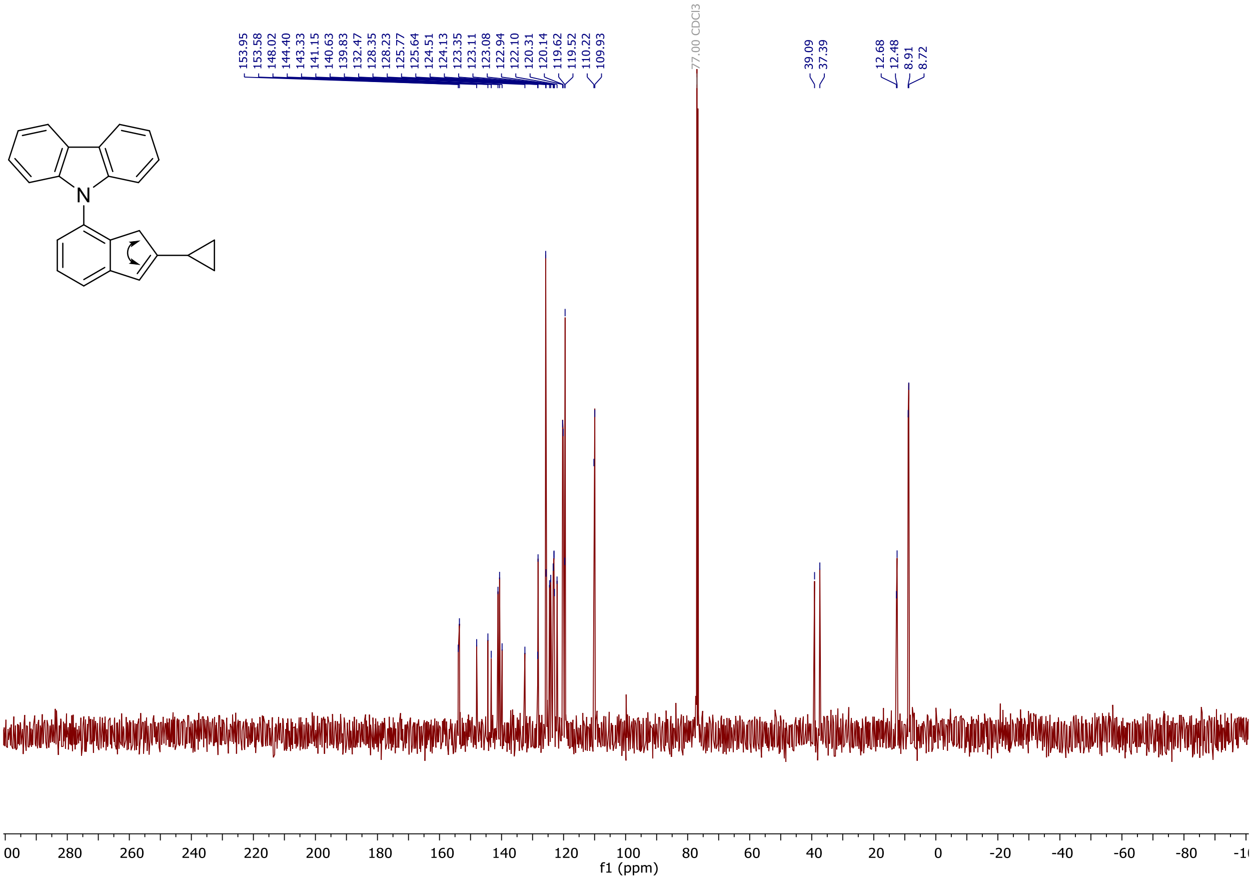
^{1}H NMR-spectrum of complex **_c_Pr-4**.



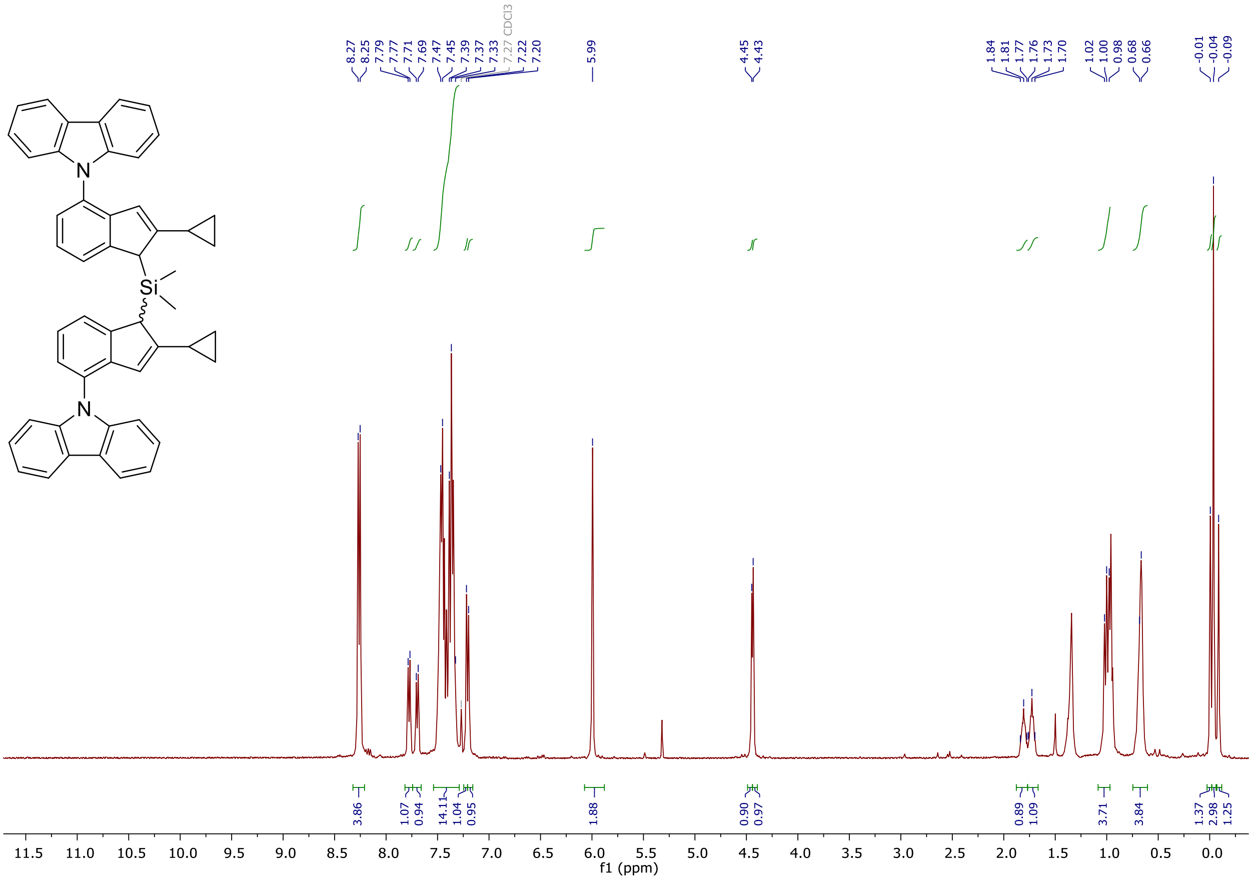
^{13}C NMR-spectrum of complex **_c_Pr-4**.



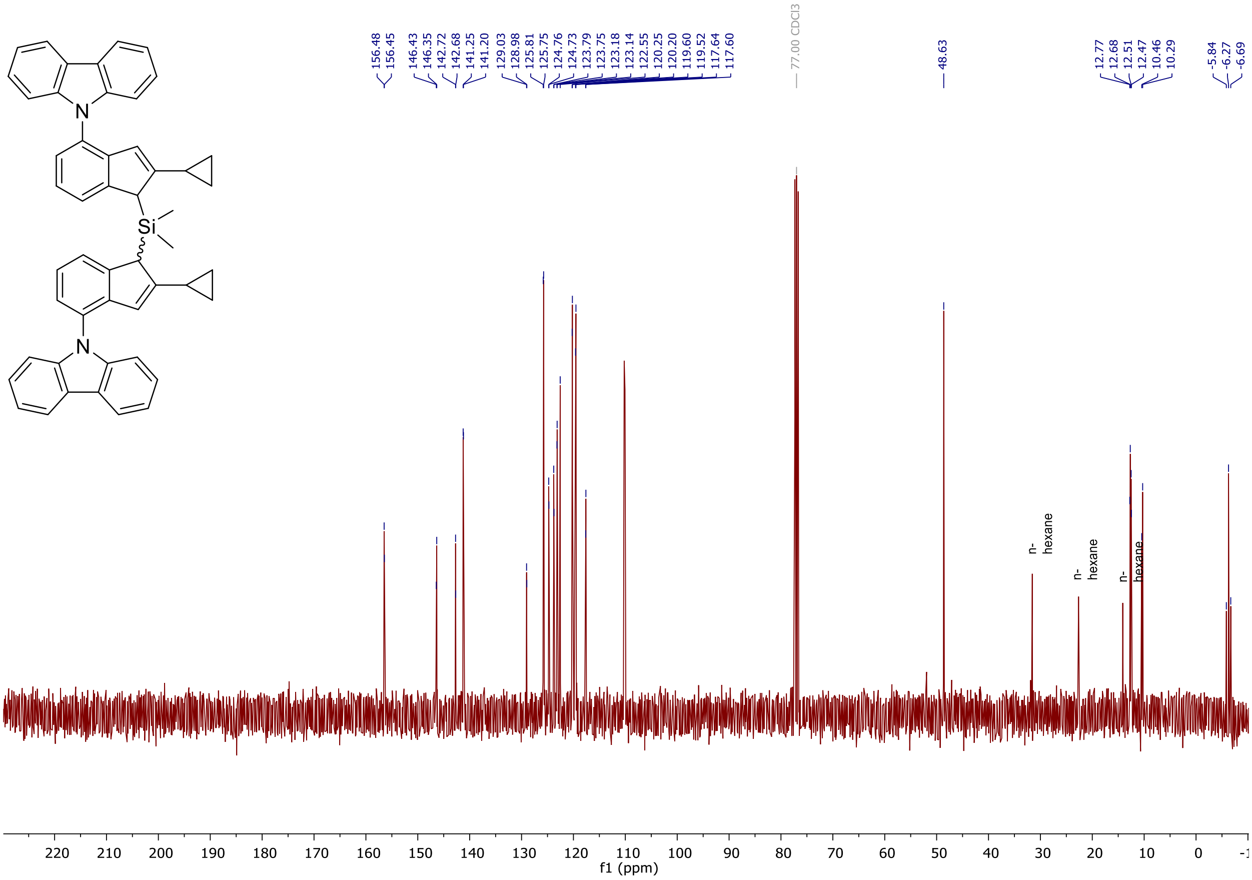
^{1}H NMR-spectrum of 2-cyclopropyl-4/7-(*N*-carbazolyl)indene.



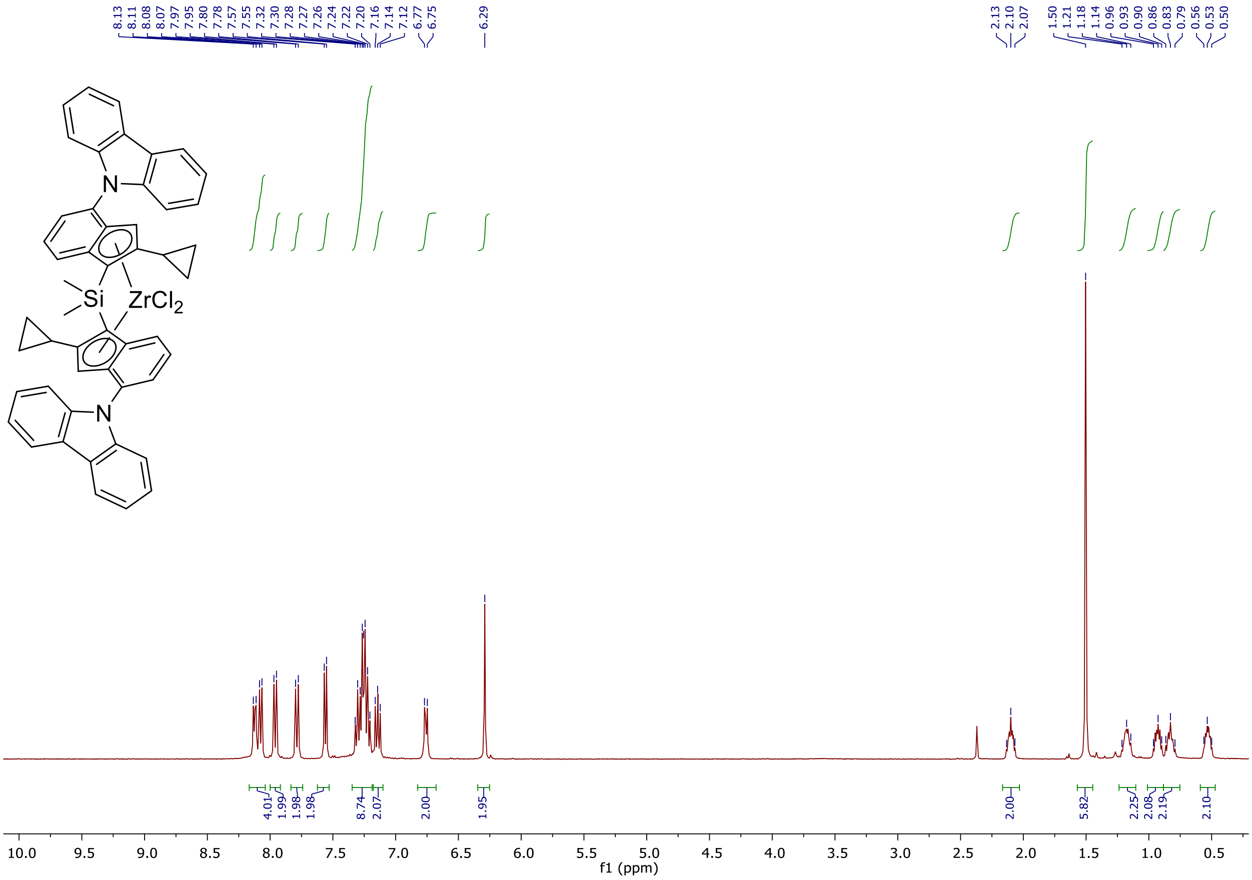
^{13}C NMR-spectrum of 2-cyclopropyl-4/7-(*N*-carbazolyl)indene.



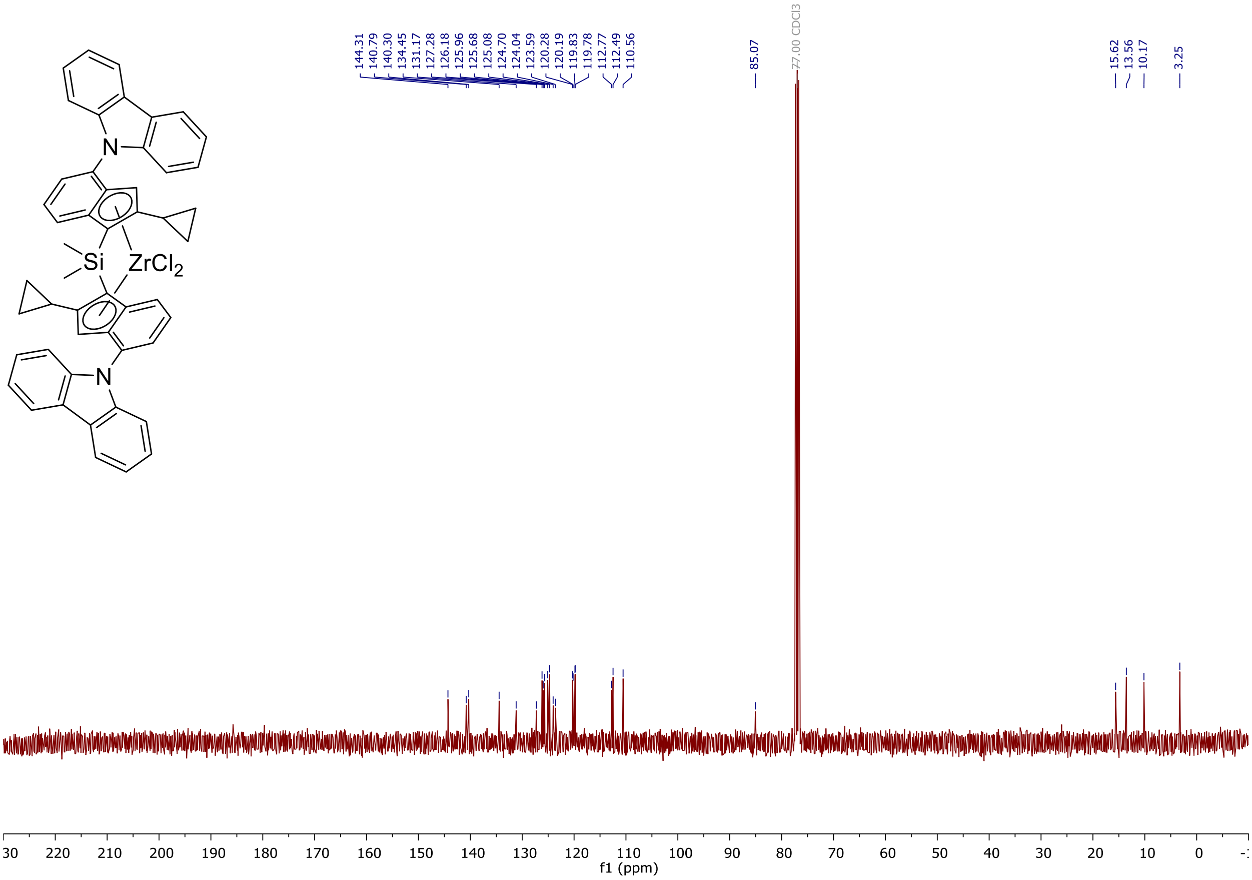
^{1}H NMR-spectrum of *rac*/*meso*-bis(4-(*N*-carbazol)-2-cyclopropylinden-1-yl)dimethylsilane.



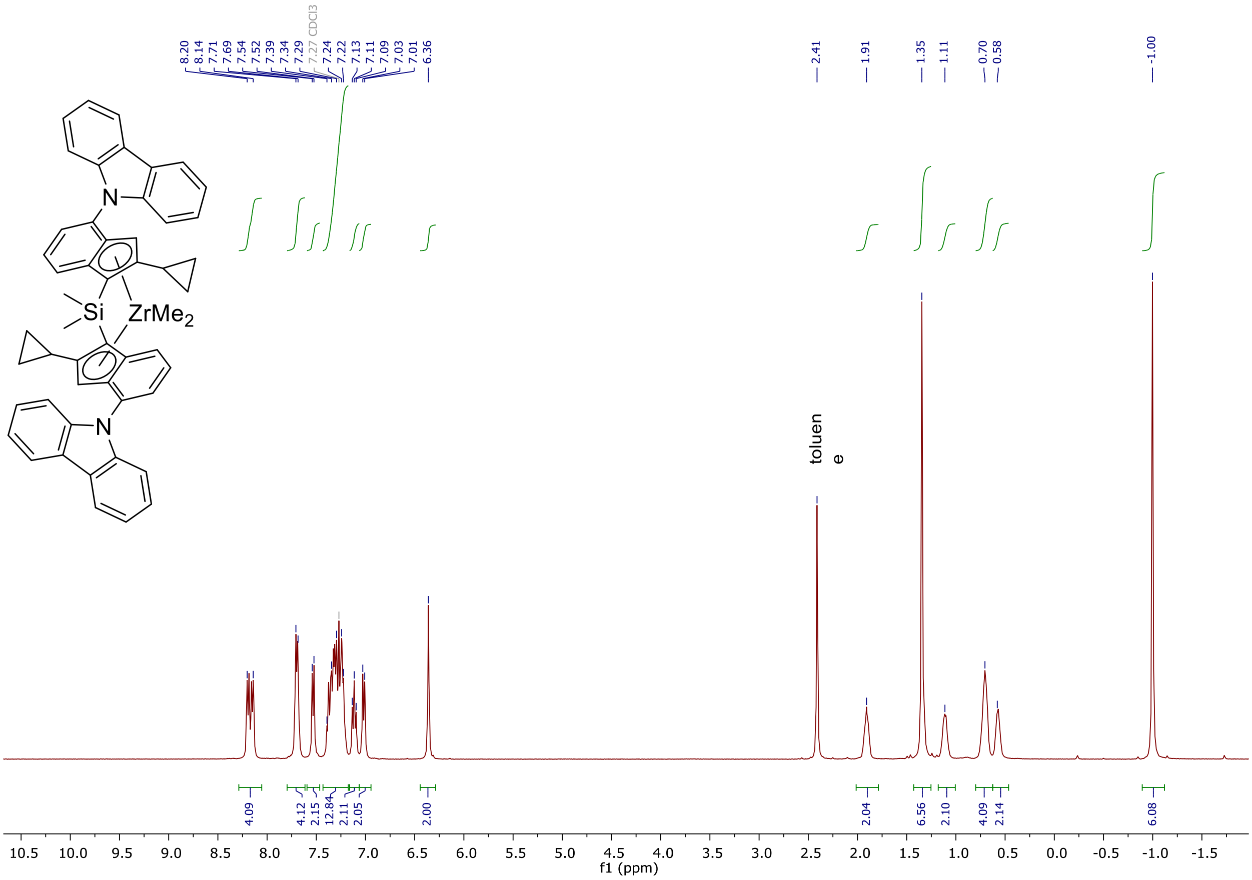
^{13}C NMR-spectrum of *rac*/*meso*-bis(4-(*N*-carbazol)-2-cyclopropylinden-1-yl)dimethylsilane.



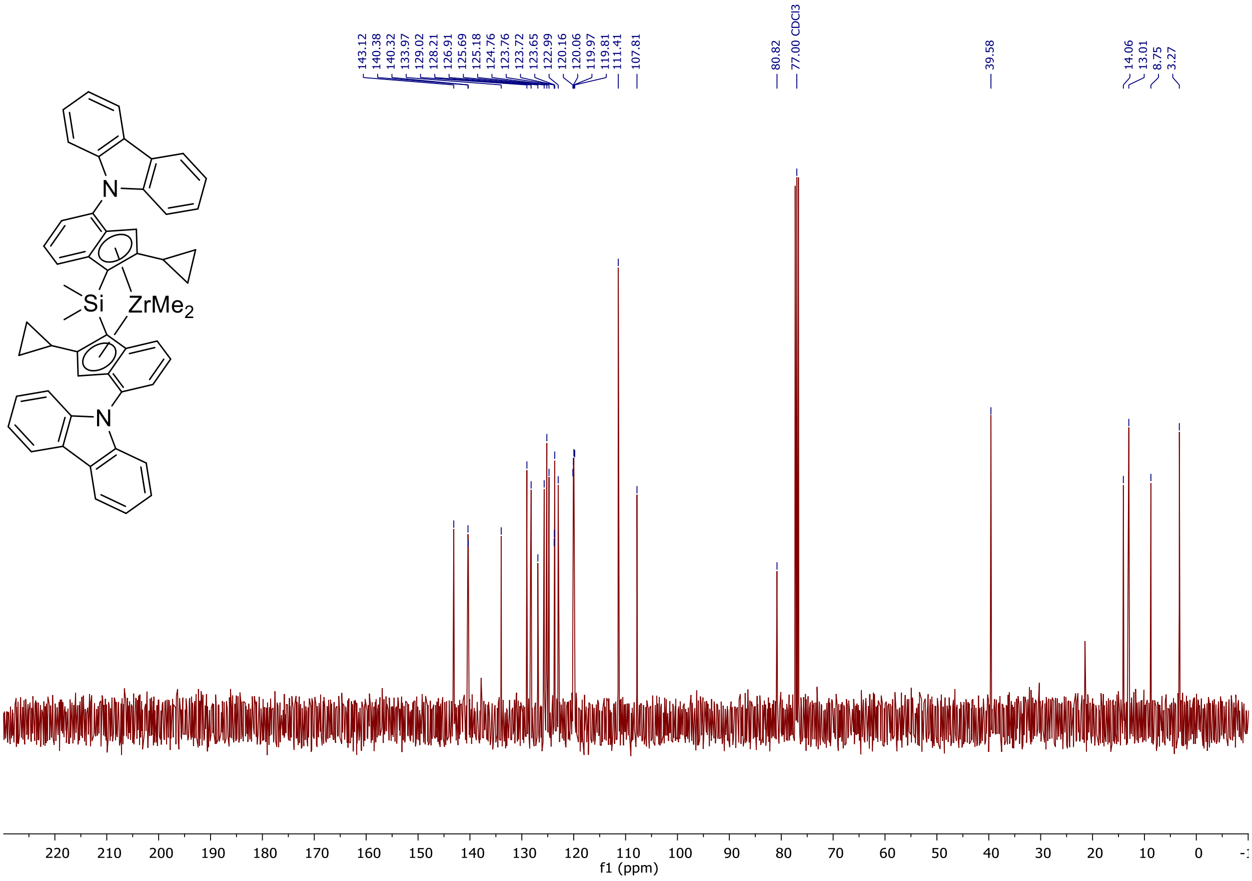
^{1}H NMR spectrum of complex ***c*Pr-5.**



^{13}C NMR spectrum of complex ***c*Pr-5.**



^{1}H NMR spectrum of complex ***c*Pr-5^{Me}**.



^{13}C NMR spectrum of complex ***c*Pr-5^{Me}**.

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