Supporting Information

Triptycene as a Scaffold in Metallocene Catalyzed Olefin Polymerization

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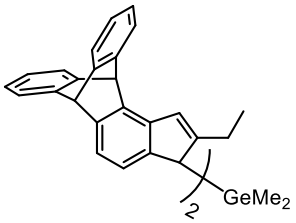
Synthesis

General details

All manipulations with compounds, which are sensitive to moisture and air, were performed either in an atmosphere of argon using a standard Schlenk technique or in an inert atmosphere (Ar) of glove box (MBraun). Ethereal solvents were distilled from sodium/benzophenone. Toluene and hexane were sparged with argon and dried over molecular sieves 4A. 1-(Bromomethyl)triptycene, [1] 2-ethylcyclopenta[*a*]triptycene (**2**), [1] 6-amino-2-methylindanone (**8**), [2] were prepared according to literature procedures. Other reagents were purchased from commercial sources and used as received. GC/MS analysis was performed on Agilent Technologies 7890A paired with Agilent Technologies 5975C MSD GC/MS system and on Agilent Technologies 8890 GC/5977C MSD system. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6530 Q-TOF LC/MS system paired with Agilent 1260 HPLC and using Agilent JetStream ion source. NMR spectra were recorded on Bruker AVANCE (400 MHz) or Agilent Technologies 400-MR (400 MHz) NMR spectrometers and can be found in the respective section of the document. Chemical shifts for ^{1}H and ^{13}C are reported relatively to TMS and referenced to the residual ^{1}H or ^{13}C resonances of the deuterated solvents. 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 (7.26 ppm for $CDCl_3$, 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) and were obtained with ^{1}H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet, br.s = broad signal. C, H, N microanalyses were done using Perkin Elmer 2400 Series II CHNS/O elemental analyzer.

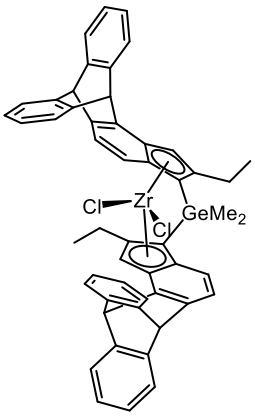
Synthesis of complex Ty4

Proligand **4b**



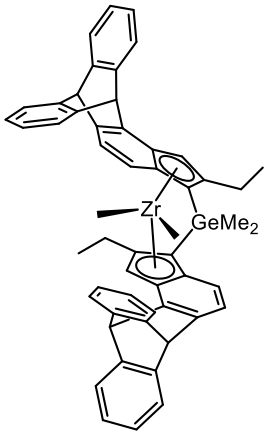
To a solution of 2.76 g (8.61 mmol) of 2-ethyl-6,7-(9,10-dihydroanthracene-9,10-diyl)indene **4a** in 120 mL of tetrahydrofuran, 3.45 mL (8.61 mmol) of 2.5 M *n*BuLi in hexanes was added dropwise at vigorous stirring at –78 °C. This mixture was stirred for 13 h at room temperature and then cooled to –80 °C. At this temperature, 50 µl of *N*-methylimidazole was added. Next, to the mixture, 0.50 mL (0.75 g, 4.31 mmol) of Me_2GeCl_2 was added. The resulting mixture was stirred overnight at ambient temperature. Then 0.5 mL of water was added and the volatiles were evaporated. The residue was purified by column chromatography on silica gel (40–63 µm, eluent: hexane/dichloromethane = 3/1, vol.), to give 2.27 g (71%) of the product (mixture of isomers *rac*/*meso* = 1/1) as a white fluffy powder. HRMS (ESI) m/z calcd for $C_{52}H_{43}Ge$ $[M-H]^-$: 741.2582 found: 741.2573. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 2H in *rac* or 2H in *meso*), 7.39–7.47 (m, 14H in *rac* and *meso*), 7.16 (d, *J* = 7.4 Hz, 2H in *rac* or 2H in *meso*), 6.98–7.08 (m, 18H in *rac* and *meso*), 6.89 (d, *J* = 7.6 Hz, 2H in *meso*), 6.86 (m, 2H in *rac*), 6.85 (s, 2H in *meso*), 6.77 (s, 2H in *rac*), 5.74 (s, 2H in *rac*), 5.70 (s, 2H in *meso*), 5.47 (s, 2H in *meso*), 5.46 (s, 2H in *rac*), 3.62 (s, 2H in *rac*), 3.58 (s, 2H in *meso*), 2.27–2.36 (m, 2H in *meso*), 2.13–2.26 (m, 4H in *rac*), 2.00–2.08 (m, 2H in *meso*), 1.04 (t, *J* = 7.4 Hz, 6H in *rac*), 0.99 (t, *J* = 7.4 Hz, 6H in *rac*), –0.02 (s, 3H in *meso*), –0.08 (s, 6H in *rac*), –0.13 (s, 3H in *meso*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 154.9, 154.4, 146.2, 146.1, 146.0, 145.5, 145.45, 145.41, 145.39, 142.2, 141.9, 139.2, 139.1, 136.4, 136.2, 124.9, 124.80, 124.77, 123.52, 123.46, 123.4, 123.3, 120.1, 119.7, 119.1, 118.9, 118.2, 54.1, 51.1, 51.0, 46.5, 46.2, 24.3, 24.2, 13.0, 12.9, –2.9, –4.3, –4.8.

A mixture of *meso*- and *rac*-**Ty4-Cl$_2$**



To a solution of 2.18 g (2.94 mmol) of proligand **4b** in 120 mL of diethyl ether, 2.41 mL (6.03 mmol) of 2.5 M *n*BuLi in hexanes was added at ambient temperature. This mixture was stirred overnight, then cooled to –80 °C and 1.11 g (2.94 mmol) of $ZrCl_4(THF)_2$ was added in one portion. The resulting mixture was stirred for 24 h at room temperature and then evaporated to dryness. Further on, 100 mL of toluene was added. The resulting mixture was heated to 110 °C and filtered through a short pad of Celite® 503. The filtrate was evaporated to dryness. The residue was recrystallized from toluene to give 320 mg (12% yield) of almost exclusively *meso*-isomer (*meso/rac* = 95/5). The mother liquor was evaporated to dryness. According to ^{1}H NMR spectrum, the residue (2.3 g, ~87%) was a sufficiently pure *rac/meso* = 1/1.5 mixture of isomers of complex **Ty4-Cl$_2$**. This mixture was used in the next step without purification. *Meso*-**Ty4-Cl$_2$**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34–7.42 (m, 6H), 7.29 (m, 2H), 7.24 (m, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.99–7.01 (m, 4H), 6.86–6.93 (m, 6H), 5.58 (s, 2H), 5.38 (s, 2H), 2.90 (m, 2H), 2.82 (m, 2H), 1.56 (s, 3H), 1.37 (s, 3H), 1.31 (t, J = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 146.8, 146.3, 145.9, 145.3, 144.3, 143.8, 140.9, 133.9, 126.5, 125.3, 125.1, 124.9, 124.8, 124.6, 123.60, 123.56, 122.9, 122.6, 121.7, 113.0, 84.8, 54.3, 51.6, 26.7, 17.7, 3.1, 2.9. *Rac*-**Ty4-Cl$_2$**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.23–7.52 (m, 10H), 7.10 (m, 4H), 6.95–7.02 (m, 2H), 6.86–6.94 (m, 6H), 5.66 (s, 2H), 5.61 (s, 2H), 2.69 (m, 2H), 2.38 (m, 2H), 1.40 (s, 6H), 1.15 (t, J = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 146.9, 146.8, 146.4, 145.9, 144.4, 142.8, 141.9, 131.8, 125.6, 125.2, 125.13, 125.10, 125.05, 124.7, 123.78, 123.75, 123.1, 123.0, 122.1, 114.4, 83.7, 54.7, 51.7, 26.3, 17.3, 3.0.

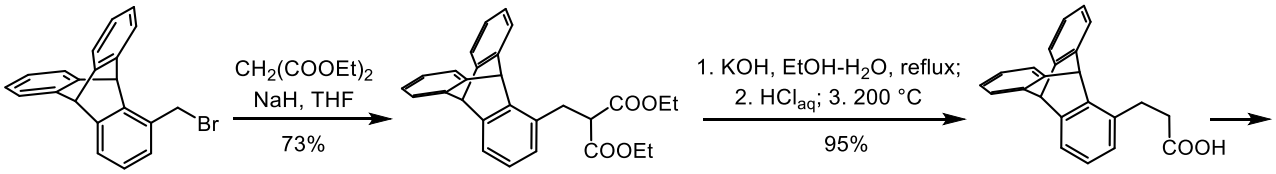
Complex *rac*-**Ty4**

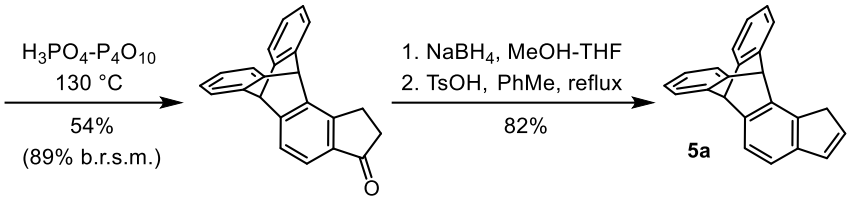


To a suspension of 0.30 g (0.33 mmol) of a mixture *rac/meso*-**Ty4-Cl$_2$** (molar ratio *rac/meso* = 1/1.5) in 50 mL of toluene, 1.15 mL of 2.9 M MeMgBr (3.3 mmol) in diethyl ether was added at room temperature. The mixture was stirred for 14 h at 100 °C and then evaporated to dryness in vacuum. To the residue, 50 mL of toluene was added, the mixture was heated up to 110 °C, and then passed through a short pad of Celite® 503. The solvent was evaporated to dryness. According to ^{1}H NMR analysis, a mixture of zirconium dimethyl complexes was obtained with molar ratio *rac/meso*= 1/1.5. This mixture of complexes was dissolved in 50 mL of THF, 4.2 mg of LiCl (0.10 mmol) was added, and the mixture was stirred in darkness at 50 °C for 58 h. Then, 10 mL of toluene was added, and the mixture was evaporated to dryness in vacuum. After that, 50 mL of toluene was added and the mixture was filtered through a short pad of Celite 503®. The filtrate was evaporated in vacuum, and the residue was recrystallized from toluene/hexane mixture giving 81 mg (28% over two steps from **4b**) of pure *rac*-isomer of **Ty4**. Anal. Calcd for $C_{54}H_{48}GeZr$: C, 75.35; H, 5.62. Found: C, 75.73; H, 5.89. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.38–7.42 (m, 6H), 7.31 (d, J = 7.0 Hz, 2H), 7.16 (d, J = 4.0 Hz, 4H), 6.92–7.01 (m, 8H), 6.86 (s, 2H), 5.63 (s, 2H), 5.51 (s, 2H), 2.48 (dq, J = 14.6 Hz, J = 7.4 Hz, 2H), 2.08 (dq, J = 14.6 Hz, J = 7.4 Hz, 2H), 1.15 (s, 6H), 1.08 (t, J = 7.4 Hz, 6H), –2.02 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 147.4, 147.1, 146.1, 144.5, 143.1, 142.2, 141.2, 127.4, 126.0, 125.2, 125.1, 125.0, 124.9, 124.4, 123.7, 123.6, 123.1, 121.7, 120.9, 108.6, 78.8, 54.6, 51.9, 35.5, 25.5, 17.2, 3.0.

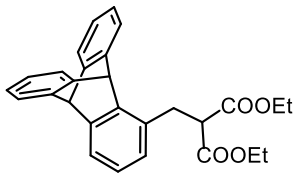
Synthesis of complex Ty5

Synthesis of indene **5a**:



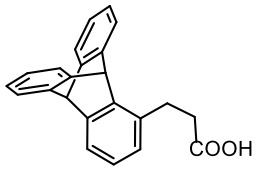


2-((Triptycen-1-yl)methyl)malonate



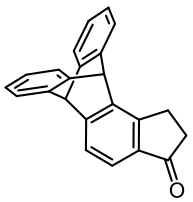
Under argon, a solution of 13.6 g (85 mmol) of diethyl malonate in 20 mL of dry THF was added dropwise to a suspension of 3.4 g (~60 wt.% in paraffin, 85 mmol) of NaH in 200 mL of dry THF at 0 °C. The resulting mixture was stirred for 15 min at 0 °C and 14.7 g (42 mmol) of 1-(bromomethyl)triptycene in 100 mL of dry THF was added slowly. The reaction mixture was further stirred overnight at room temperature. Then the reaction was quenched with 100 mL of aqueous ammonium chloride and the mixture extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with water (50 mL), brine (50 mL), dried over Na_2SO_4, and the solvents were evaporated in vacuum. The product was isolated by column chromatography on silica gel (40–63 μm, eluent: hexane/dichloromethane = 5/1, vol.) to give 13.2 g (73% yield) of the product as a colorless oil. HRMS (ESI) m/z calcd. for $C_{28}H_{26}NaO_4^+$ $[M+Na]^+$: 449.1723 found: 449.1729. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 2H), 7.39 (m, 2H), 7.29 (m, 1H), 7.01 (m, 4H), 6.93 (m, 1H), 6.91 (m, 1H), 5.82 (s, 1H), 5.43 (s, 1H), 4.13 (m, 4H), 3.68 (t, J = 7.5 Hz, 1H), 3.51 (d, J = 7.5 Hz, 2H), 1.13 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.9, 145.6, 145.4, 144.8, 143.7, 132.2, 126.4, 125.12, 125.06, 124.9, 123.8, 123.4, 122.5, 61.5, 54.3, 53.5, 49.9, 31.3, 13.8.

3-(Triptycene-1-yl)propanoic acid



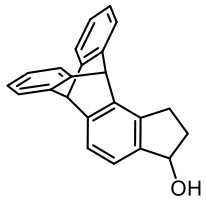
To a solution of 10.3 g (24 mmol) of diethyl 2-((triptycen-1-yl)methyl)malonate in 50 mL of ethanol, a solution of 5.4 g (96 mmol) of KOH in 50 mL of water was added. The mixture was refluxed for 3 h, after that, ethanol was distilled off, and the remaining aqueous solution was washed with 20 mL of diethyl ether. To the aqueous phase, 100 mL of water was added, and the mixture was acidified to pH 1 with 12 M HCl and extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was evaporated. The residue was heated at 200 °C under argon until gas evolution has ceased, and complete decarboxylation has occurred. This gave 7.5 g (95% yield) of the product as a yellowish solid. HRMS (ESI) m/z calcd. for $C_{23}H_{18}NaO_2^+$ $[M+Na]^+$: 349.1199 found: 349.1206. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 4H), 7.28 (d, J = 7.1 Hz, 1H), 7.00 (m, 4H), 6.93 (m, 1H), 6.87 (m, 1H), 5.70 (s, 1H), 5.42 (s, 1H), 3.22 (m, 2H), 2.69 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.4, 145.6, 145.5, 144.8, 143.3, 134.2, 125.7, 125.3, 125.19, 125.18, 123.63, 123.56, 122.3, 54.3, 50.0, 35.5, 27.6.

4,5-(9,10-Dihydroanthracene-9,10-diyl)-indan-1-one



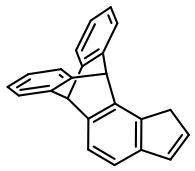
To polyphosphoric acid prepared from 306 g of H_3PO_4 and 367 g of P_4O_{10} via mechanical stirring, a solution of 6.95 g (21 mmol) of 3-(triptycene-1-yl)propanoic acid in 80 mL of CH_2Cl_2 was added dropwise at 130 °C within 15 min. The reaction mixture was vigorously stirred at 130 °C for another 20 min and then poured on 2 kg of ice. The mixture was extracted with diethyl ether (3 × 200 mL), the combined organic extracts were dried over Na_2SO_4, and the solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel (40–63 μm, eluent: dichloromethane) to give 2.5 g (35%) of the starting 3-(triptycene-1-yl)propanoic acid and 3.8 g (54%, or 89% b.r.s.m. yield) of the product as a white solid. HRMS (ESI) m/z calcd. for $C_{23}H_{17}O^+$ $[M+H]^+$: 309.1274 found: 309.1272. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 2H), 7.42 (m, 4H), 7.02 (m, 4H), 5.62 (s, 1H), 5.54 (s, 1H), 3.28 (m, 2H), 2.69 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 206.0, 152.3, 148.2, 144.5, 144.3, 143.0, 134.6, 125.52, 125.47, 124.0, 123.7, 123.4, 121.3, 54.5, 50.0, 36.3, 23.6.

4,5-(9,10-Dihydroanthracene-9,10-diyl)-indan-1-ol



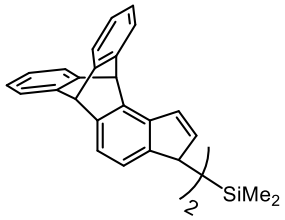
To a solution of 5.46 g (17.7 mmol) of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-one in 50 mL of THF, 0.67 g (17.6 mmol) of $NaBH_4$ was added at 0 °C followed by addition 50 mL of methanol dropwise at 0 °C. The resulting mixture was stirred for additional 3 h at room temperature. Then, the solvents were evaporated, the residue was dissolved in 100 mL of dichloromethane and the solution was washed with 300 mL of water. The organic layer was dried over Na_2SO_4 and evaporated to dryness. This gave 5.5 g (~quant. yield) of the product which was used in the next step without purification. HRMS (ESI) m/z calcd for $C_{23}H_{19}O^+$ $[M+H]^+$: 311.1430 found: 311.1439. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 4H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.99 (m, 4H), 5.50 (s, 1H), 5.45 (s, 1H), 3.23 (ddd, *J* = 15.8 Hz, *J* = 8.5 Hz, *J* = 5.3 Hz, 1H), 2.96 (m, 1H), 2.45 (dddd, *J* = 13.5 Hz, *J* = 8.3 Hz, *J* = 6.7 Hz, *J* = 5.3 Hz, 1H), 1.95 (m, 1H), 1.60 (br.s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.7, 145.5, 145.4, 144.9, 144.8, 142.4, 141.2, 137.5, 125.2, 125.09, 125.08, 123.67, 123.64, 123.62, 123.59, 122.4, 120.7, 76.3, 54.0, 51.0, 35.9, 27.4.

6,7-(9,10-Dihydroanthracene-9,10-diyl)-indene (**5a**)



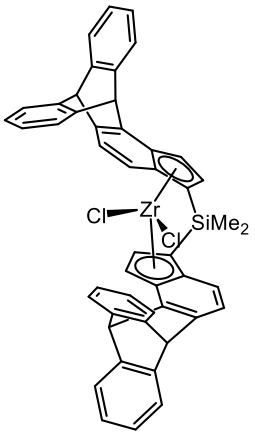
5.4 g (17.4 mmol) of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-ol was dissolved in 100 mL of toluene and 300 mg of *p*-toluenesulfonic acid was added. The mixture was refluxed under a Dean-Stark apparatus for 15 min, cooled to room temperature and passed through a short pad of silica gel. The filtrate was evaporated in vacuum to dryness. The residue was purified by flash chromatography on silica gel (40–63 μm, eluent: hexane), to give 4.12 g of **5a** as a white solid (80% over two steps from 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-one). HRMS (ESI) m/z calcd for $C_{23}H_{17}^+$ $[M+H]^+$: 293.1325 found: 293.1318. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 4H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.04 (m, 4H), 6.87 (m, 1H), 6.53 (m, 1H), 5.62 (s, 1H), 5.52 (s, 1H), 3.58 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.8, 144.8, 142.4, 141.7, 140.1, 137.5, 133.0, 132.5, 125.2, 125.0, 123.52, 123.47, 121.8, 117.2, 53.9, 51.2, 36.6.

Proligand **5b**



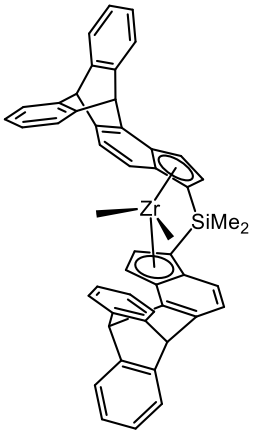
To a solution of 3.99 g (13.7 mmol) of 6,7-(9,10-dihydroanthracene-9,10-diyl)-indene (**5a**) in 50 mL of diethyl ether, 5.75 mL (14.4 mmol) of 2.5 M *n*BuLi in hexanes was added dropwise at –78 °C. This mixture was stirred for 13 h at room temperature and then cooled to –80 °C. At this temperature, 300 mg (3.4 mmol) of CuCN and 0.83 mL (0.88 g, 6.8 mmol) of Me_2SiCl_2 were added. The mixture was stirred overnight at ambient temperature, then quenched with 0.5 mL of water, and the volatiles were evaporated in vacuum. The residue was purified by column chromatography on silica gel (40–63 μm, eluent: hexane/dichloromethane = 3/1, vol.) to give 3.84 g (88%) of the product (mixture of isomers, *rac*/*meso* = 1/1) as a white fluffy powder. HRMS (ESI) m/z calcd. for $C_{48}H_{36}NaSi^+$ $[M+Na]^+$: 663.2478 found: 663.2471. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.56 (m, 8H in *rac* and 8H in *meso*), 7.33–7.40 (m, 2H in *rac* or 2H in *meso*), 7.23 (d, *J* = 7.5 Hz, 2H in *rac*), 7.06–7.16 (m, 20H in *rac* and *meso*), 6.99 (d, *J* = 7.5 Hz, 2H in *meso*), 6.75 (dd, *J* = 5.5 Hz, *J* = 1.8 Hz, 2H in *rac*), 6.57 (dd, *J* = 5.4 Hz, *J* = 1.9 Hz, 2H in *meso*), 5.87 (s, 2H in *rac*), 5.86 (s, 2H in *meso*), 5.61 (s, 2H in *meso*), 5.58 (s, 2H in *rac*), 3.64 (m, 2H in *rac*), 3.61 (s, 2H in *meso*), –0.11 (s, 3H in *meso*), –0.26 (s, 6H in *rac*), –0.48 (s, 3H in *meso*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 146.0, 145.9, 145.4, 145.3, 142.49, 142.45, 142.0, 141.9, 139.2, 137.7, 137.6, 135.72, 135.68, 126.3, 126.2, 124.94, 124.92, 124.89, 124.8, 123.5, 123.4, 119.6, 119.5, 119.2, 54.1, 51.2, 45.08, 45.06, –5.3, –5.8, –6.8.

Complex *rac*-**Ty5-Cl$_2$**



To a solution of 3.8 g (5.9 mmol) of proligand **5b** in 120 mL of diethyl ether, 4.75 mL (11.8 mmol) of 2.5 M *n*BuLi in hexanes was added at ambient temperature. This mixture was stirred overnight, then cooled to –80 °C and 2.23 g (5.9 mmol) of $ZrCl_4(THF)_2$ was added in one portion. The resulting mixture was stirred for 24 h at room temperature and then evaporated to dryness. Further on, 100 mL of toluene was added. The resulting mixture was heated to 100 °C and filtered through a short pad of Celite® 503. The filtrate was evaporated to dryness. The residue was recrystallized from toluene to give 759 mg (16% yield) of *meso*-isomer. The mother liquor was evaporated to dryness, and the residue was recrystallized from toluene to give 300 mg (6% yield) of *rac*/*meso* = 5/1 mixture of isomers. The mother liquor was evaporated to dryness. According to ^{1}H NMR spectrum, the residue consisted of the *rac*-isomer contaminated with some polymeric material. This mixture was used in the next step without purification. *Rac*-**Ty5-Cl$_2$**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40–7.42 (m, 4H), 7.35 (m, 4H), 7.25–7.28 (m, 4H), 7.20 (m, 2H), 7.01 (m, 4H), 6.92–6.97 (m, 4H), 6.09 (d, J = 3.4 Hz, 2H), 5.63 (s, 2H), 5.55 (s, 2H), 1.03 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 146.7, 146.6, 146.4, 145.7, 144.4, 142.5, 131.7, 125.3, 125.21, 125.18, 125.09, 125.08, 124.74, 124.68, 123.82, 123.81, 123.2, 121.7, 119.3, 113.5, 90.3, 54.7, 51.7, –1.5.

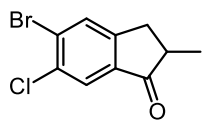
Complex *rac*-**Ty5**



To a suspension of 3.66 g (~4.6 mmol) of *rac*-**Ty5-Cl$_2$** (contaminated with polymeric material) in 200 mL of toluene, 15.7 mL of 2.9 M MeMgBr (45.5 mmol) in diethyl ether was added at room temperature. This mixture was stirred for 14 h at 100 °C and then evaporated to dryness in vacuum. To the residue 100 mL of toluene was added and the mixture was heated to 110 °C and passed through a short pad of Celite® 503. The solvent was evaporated to dryness. The residue was triturated in 50 mL of toluene at 100 °C. The solids were filtered off on a short pad of Celite® 503. The filtrate was evaporated to dryness in vacuum and the residue was recrystallized from toluene to give 190 mg (0.5% over two steps) of pure *rac*-**Ty5**. The mother liquor was concentrated and additional 166 mg (0.5% over two steps) of pure *rac*-**Ty5** were isolated after crystallization. Anal. Calcd for $C_{50}H_{40}SiZr{\cdot}C_7H_8$: C, 80.33; H, 5.68. Found: C, 80.54; H, 5.90. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35–7.40 (m, 6H), 7.19–7.27 (m, 4H), 7.08 (dd, J = 8.6 Hz, J = 0.8 Hz, 2H), 6.88–6.99 (m, 10H), 5.91 (d, J = 3.4 Hz, 2H), 5.66 (s, 2H), 5.50 (s, 2H), 0.82 (s, 6H), –2.12 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 147.2, 146.8, 146.0, 144.6, 143.7, 141.8, 128.2, 125.3, 125.1, 125.0, 124.8, 124.3, 123.2, 122.3, 121.7, 119.0, 107.5, 85.0, 54.6, 52.0, 35.8, –1.5.

Synthesis of complex Ty6

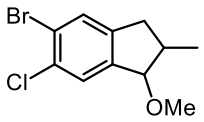
5-Bromo-6-chloro-2-methylindan-1-one (**6b**)



6.5 g (0.29 mol) of sodium metal was dissolved in 160 mL of dry ethanol. To the resulting solution 47.0 g (0.28 mol) of diethylmethylmalonate was added. This mixture was stirred for 15 min, then 76.8 g (0.27 mol) of 2-bromo-4-(bromomethyl)-1-chlorobenzene (**6a**) was added at a rate that allowed the reaction mixture to maintain a gentle reflux. Additionally, this mixture was refluxed for 4 h, then cooled to room temperature and a solution of 56.0 g of KOH in 150 mL of water was added. The mixture was refluxed for 6 h to saponificate the diester formed and, after that, ethanol was distilled off. To the residue 200 mL of water and then 12 M HCl were added to pH 1. The precipitated diacid was collected by filtration, washed with 2 × 100 mL of cold water and dried in air. Next, the diacid was placed in a round bottom flask and decarboxylated by heating at 180 °C for 1.5 h to give crude 3-(3-bromo-4-chlorophenyl)-2-methylpropanoic acid. To the acid, 59 mL (0.81 mol) of $SOCl_2$, and 100 mL of dichloromethane were added, and the mixture was refluxed for 3 h, then, thionyl chloride and dichloromethane were distilled off, the residue was dried in vacuum and then redissolved in 95 mL of dichloromethane. The solution was added dropwise to a suspension of 53.7 g (0.40 mol) of $AlCl_3$ in 330 mL of dichloromethane at 0 °C for

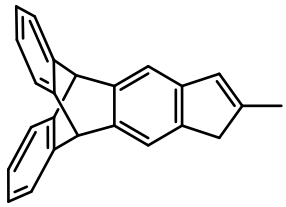
1 h. The mixture was refluxed for 1.5 h, cooled to ambient temperature, and then poured on 500 cm^3 of ice. The organic layer was separated, and the aqueous layer was extracted with 3 × 200 mL of dichloromethane. The combined organic extract was dried over K_2CO_3 and evaporated to dryness. The residue was distilled in vacuum to give 64.2 g of a mixture of 5-bromo-6-chloro-2-methylindan-1-one and 7-bromo-6-chloro-2-methylindan-1-one as a colorless liquid (b.p. 150–190°C/3 mm Hg), which rapidly solidified at room temperature. Crystallization of this mixture from 100 mL of *n*-hexane gave 31.2 g of 5-bromo-6-chloro-2-methylindan-1-one (90% purity, 40% yield) which was used in the next step without purification. HRMS (ESI) m/z calcd. for $C_{10}H_9BrClO^+$ $[M+H]^+$: 258.9520 found: 258.9529. ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.72 (s, 1H), 7.71 (s, 1H), 3.33–3.29 (m, 1H), 2.71–2.67 (m, 2H), 1.28 (d, *J* 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ206.9, 152.1, 135.2, 131.8, 129.6, 126.1, 125.0, 42.4, 34.1, 16.0.

5-Bromo-6-chloro-1-methoxy-2-methylindane (**6c**)



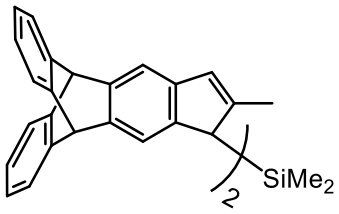
To a mixture of 120 g of 5-bromo-6-chloro-2-methylindan-1-one of 90% purity (0.42 mol) and 28.1 g (0.74 mol) of $NaBH_4$ in 650 mL of THF, 300 mL of methanol was added dropwise for 5 h at 5 °C. This mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was partitioned between 400 mL of dichloromethane and 500 mL of 1 M HCl. The organic layer was separated, and the aqueous layer was additionally extracted with 3 × 200 mL of dichloromethane. The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in 600 mL of DMSO, and 103 g (1.85 mol) of KOH and 65.6 g (0.46 mol) of MeI were added. This mixture was stirred for 1 h at ambient temperature. Additionally, 65.6 g (0.46 mol) of MeI was added and the mixture was stirred for 3 h at ambient temperature. The solution was decanted from excess of KOH, which was additionally washed with 3 × 250 mL of dichloromethane. The combined organic solutions was washed with 3000 mL of water. The organic layer was separated, and the aqueous layer was extracted with 2 × 250 mL of dichloromethane. The combined organic extract was washed with 7 × 1000 mL of water, dried over Na_2SO_4, and then evaporated to dryness. The residue was distilled in vacuum to give 117 g of the title product of 90% purity (91% yield) consisting of two diastereomers, b.p. 130-175 °C/4 mm Hg. HRMS (ESI) m/z calcd. for $C_{11}H_{13}BrClO^+$ $[M+H]^+$: 274.9833 found: 274.9821. Mixture of two diastereomers: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (s), 7.44 (s), 7.42 (s), 7.41 (s), 4.43 (d, *J* = 5.5 Hz), 4.29 (d, *J* = 4.4 Hz), 3.44 (s), 3.39 (s), 3.13 (dd, *J* = 16.1 Hz, *J* = 7.6 Hz), 2.88–2.81 (m), 2.63–2.58 (m), 2.53–2.45 (m), 2.37 (dd, *J* = 16.0 Hz, *J* = 5.5 Hz), 1.13 (d, *J* = 7.0 Hz), 1.04 (d, *J* = 6.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 143.7, 143.44, 143.35, 143.29, 131.9, 131.6, 130.0 (two resonances), 126.8, 126.6, 121.9, 121.6, 90.3, 85.1, 56.9, 56.8, 40.5, 38.9, 37.6, 37.4, 18.9, 13.2.

2-Methyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**6d**)



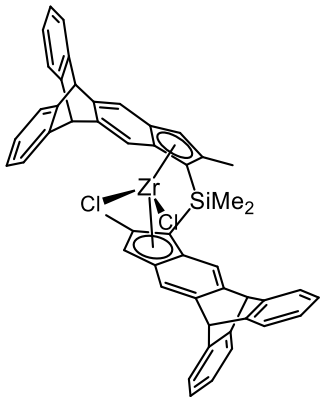
To a solution of 12.0 g of 5-bromo-6-chloro-1-methoxy-2-methylindane of 90% purity (39 mmol) and 15.5 g (87.2 mmol) of anthracene in 1200 mL of toluene a solution of 35 mL (87 mmol) of 2.5 M *n*BuLi in hexane in 200 mL of toluene was added in dropwise over 3 h at room temperature. Then, 600 mL of water was added, the organic layer was separated and evaporated to dryness. The obtained crude material was taken up in 200 mL of hot *n*-hexane, excess of anthracene was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in of 300 mL of methanol, 10 mL of CH_2Cl_2 and 200 mL of conc. HCl were added, and the resulting solution was refluxed for 8 h. After cooling to room temperature, the organic layer was separated, and the aqueous layer was extracted with 2 × 250 mL of dichloromethane. The combined organic extract was washed with 2 × 200 mL of water, aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated to dryness. The product was isolated by column chromatography on silica gel 60 (40–63 μm; eluent: hexanes-dichloromethane = 8:1, vol.) and recrystallized from hot *n*-hexane. HRMS (ESI) m/z calcd. for $C_{24}H_{19}^+$ $[M+H]^+$: 307.1481 found: 307.1492. This procedure gave 3.03 g (25%) of the product as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (s, 1H), 7.36–7.34 (m, 4H), 7.28 (s, 1H), 6.96–6.93 (m, 4H), 6.34 (s, 1H), 5.39 (s, 1H), 5.37 (s, 1H), 3.13 (s, 2H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.0, 145.7, 143.8, 143.1, 141.1, 140.4, 126.7, 125.0, 124.9, 123.4, 123.3, 119.2, 115.5, 54.3, 54.1, 42.3, 16.8.

Proligand **6e**



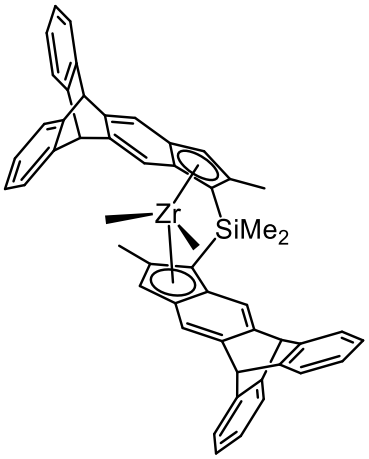
To a suspension of 9.02 g (29.4 mmol) of 2-methyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**6d**) in 200 mL of diethyl ether, 12.2 mL (29.7 mmol) of 2.43 M *n*BuLi in hexanes was added in one portion at –50 °C. The mixture was stirred overnight at room temperature. Then the mixture was cooled to –60 °C and 40 mL of THF was added followed by 200 mg (2.2 mmol) of CuCN. The mixture was stirred for 15 min at –25°C, then 1.90 g (14.7 mmol) of dichlorodimethylsilane was added in one portion. The mixture was stirred overnight at room temperature, then 250 mL of dichloromethane was added and the resulting mixture was filtered through a pad of silica gel, which was additionally washed by 2 × 50 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure and the product was isolated by flash-chromatography on silica gel 60 (40–63 μm; eluent: hexanes-dichloromethane = 3:1 → 2:1). This procedure gave 7.04 g (72%) of the product as a white solid. According to ^{1}H NMR, the product was a ~4/1 mixture of *meso* and *rac* isomers. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.61 (s, 2H in *meso*), 7.46–7.27 (m, 10H in *rac* and *meso*), 7.05–6.91 (m, 8H in *rac* and *meso*), 6.51 (s, 2H in *meso*), 6.33 (s, 2H in *rac*), 5.44 (s, 2H in *rac*), 5.42 (s, 2H in *meso*), 5.40 (s, 2H in *rac*), 5.31 (s, 2H in *meso*) 3.55 (s, 2H in *meso*), 3.54 (s, 2H in *rac*), 2.17 (s, 6H, *meso*), 2 06 (s, 6H in *rac*), –0.33 (s, 3H in *meso*), –0.35 (s, 6H in *rac*), –0.42 (s, 3H in *meso*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 147.1, 145.92, 145.86, 147.78, 142.7, 142.6, 141.8, 140.3, 126.5, 124.9, 123.55, 123.45, 123.34, 123.27, 115.72, 115.66, 54.30, 24.23, 46.85, 46.77, 17.9, 14.1, –5.5, –5.7, –6.1.

Complex *rac*-**Ty6-Cl$_2$**



To a suspension of 7.04 g (10.52 mmol) of **6e** in 200 mL of diethyl ether, 8.7 mL (21.1 mmol) of 2.43 M *n*BuLi in hexanes were added in one portion at –50 °C. The mixture was stirred overnight at room temperature. Then it was cooled to –60 °C and 2.46 g (10.56 mmol) of $ZrCl_4$ was added. The mixture was stirred for 24 h resulting in light yellow solution with a lot of yellow precipitate. The resulting mixture was evaporated to dryness and the residue was taken up in 400 mL of hot toluene. A yellow precipitate isolated by hot filtration of the suspension formed through a glass frit was a mixture of *rac*-**Ty6-Cl$_2$** with lithium chloride (~3.0 g, ~34%). A yellow solid that precipitated from the mother liquor overnight at room temperature was collected and dried in vacuum. This procedure gave 1.25 g (14%) of *meso*-zirconium dichloride complex. The mixture of *rac*-complex and LiCl was used in the next step without further purification. *Rac*-complex: ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.48 (s, 2H), 7.41–7.31 (m, 8H), 7.26 (s, 2H), 7.05–6.94 (m, 8H), 6.45 (s, 2H), 5.39 (s, 2H), 5.20 (s, 2H), 2.02 (s, 6H), 1.27 (s, 6H). *Meso*-complex: Anal. Calcd for $C_{50}H_{38}Cl_2SiZr$: C, 72.44; H, 4.62. Found: C, 72.70; H, 4.85. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.49 (s, 2H), 7.33–7.23 (m, 8H), 6.98–6.90 (m, 6H), 6.81–6.77 (m, 4H), 6.54 (s, 2H), 5.23 (s, 2H), 5.12 (s, 2H), 2.33 (s, 6H), 1.42 (s, 3H), 1.09 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 144.8, 144.7, 144.2, 143.9, 143.0, 141.6, 135.3, 135.0, 126.7, 126.0, 125.6, 125.41, 125.39, 123.6, 123.51, 123.45, 123.3, 121.5, 119.0, 118.2, 85.6, 54.1, 53.6, 18.7, 2.79, 2.75.

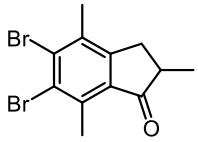
Complex *rac*-**Ty6**



To a suspension of ~3.0 g (~3.6 mmol) of *rac*-**Ty6-Cl$_2$** in 400 mL of diethyl ether, 8.0 mL (21.6 mmol) of 2.7 M MeMgBr in diethyl ether was added in one portion. This mixture was stirred for 3 days at room temperature. Then 50 mL of toluene was added and the suspension was additionally refluxed for 12 h. Then the mixture was evaporated to dryness and extracted with 120 mL of hot toluene, and the toluenic extract was evaporated to ~20 mL. A solid that precipitated form the concentrated solution at room temperature was collected and dried in vacuum. This procedure gave 1.88 g (66%, or 22% from **6e**) of the product as a yellow solid. Anal. Calcd for $C_{52}H_{44}SiZr$: C, 79.24; H, 5.63. Found: C, 79.72; H, 5.91. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (s, 2H), 7.38–7.35 (m, 6H), 7.31–7.26 (m, 2H), 7.23–7.19 (m, 2H), 7.03–6.99 (m, 4H), 6.97–6.93 (m, 4H), 6.39 (s, 2H), 5.34 (s, 2H), 5.19 (s, 2H), 1.88 (s, 6H), 1.06 (s, 6H), –1.93 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 145.5, 144.30, 144.25, 144.1, 142.1, 140.2, 133.5, 126.3, 125.49, 125.45, 125.42, 125.3, 125.0, 123.54, 123.50, 123.2, 123.0, 119.11, 119.07, 115.0, 78.5, 54.0, 53.6, 33.1, 17.5, 2.9.

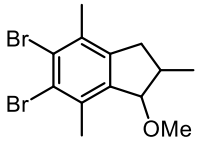
Synthesis of complex Ty7

5,6-Dibromo-2,4,7-trimethylindan-1-one (**7b**)



To a suspension of 325 g (2.44 mol) of $AlCl_3$ in 300 mL of CH_2Cl_2, 211 g (0.92 mol) of 2-bromo-2-methylpropionyl bromide was added dropwise at –30 °C over 15 minutes. The reaction mixture was stirred at –30 °C for 0.5 h, then the temperature was raised to –20 °C and a solution of 97.5 g (0.92 mol) of *p*-xylene in 300 mL of CH_2Cl_2 was added dropwise over 30 minutes. The cooling bath was removed, the temperature was brought to room temperature and the reaction mixture was stirred at this temperature for 3 hours. Further on, 323 g (2.02 mol) of bromine was added dropwise over 3 h. The resulting mixture was stirred overnight at room temperature and then poured onto 2 L of the crushed ice. The organic layer was separated, and the aqueous layer was extracted with 3 × 1000 mL of dichloromethane. The combined organic extract was washed with aqueous K_2CO_3, dried over K_2CO_3, passed through a short pad of silica gel (40–63 μm), and then evaporated to dryness. The crude product was treated with 2000 mL of warm *n*-hexane and filtered. This procedure gave 215 g (70% yield) of pure product as a white powder. HRMS (ESI) m/z calcd. for $C_{12}H_{13}Br_2O^+$ $[M+H]^+$: 330.9328 found: 330.9333. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.24 (dd, J = 17.1 Hz, J = 8.1 Hz, 1H), 2.79 (s, 3H), 2.74-2.65 (m, 1H), 2.54 (dd, J = 17.1 Hz, J = 4.2 Hz, 1H), 2.45 (s, 3H), 1.31 (d, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 208.9, 152.0, 138.0, 135.1, 134.3, 133.1, 128.6, 42.5, 33.9, 20.1, 18.6, 16.4.

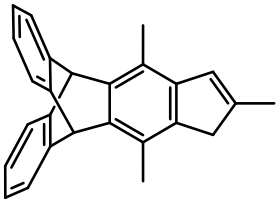
5,6-Dibromo-1-methoxy-2,4,7-trimethylindane (**7c**)



To a mixture of 215 g (646 mmol) of 5,6-dibromo-2,4,7-trimethylindan-1-one (**7b**) and 36.7 g (970 mmol) of $NaBH_4$ in 1050 mL of THF, 520 mL of methanol was added dropwise at 5 °C for 5 h. The mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was partitioned between 1000 mL of dichloromethane and 1000 mL of 2 M HCl. The organic layer was separated, and the aqueous layer was additionally extracted with 3 × 500 mL of dichloromethane. The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in 1300 mL of DMSO, and 145 g (2.59 mol) of KOH and 185 g (1.29 mol) of MeI were added. This mixture was stirred for 5 h at ambient temperature. The solution was decanted from excess of KOH, the latter was additionally washed with 3 × 300 mL of dichloromethane. The combined organic extract was washed with 3000 mL of water. The organic layer was separated, and the aqueous layer was extracted with 2 × 300 mL of dichloromethane. The combined organic extract was washed with 7 × 500 mL of water, dried over Na_2SO_4, and then evaporated to dryness. Crude product was isolated by column chromatography on silica gel (40–63 μm; eluent: hexanes-dichloromethane = 1:1, vol.). The crude product was crystallized from 200 mL of n-hexane at –30 °C to give 198 g (88%) of pure 5,6-dibromo-1-methoxy-2,4,7-trimethylindane as a mixture of two

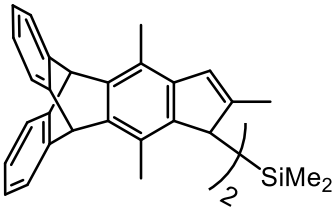
diastereomers. HRMS (ESI) m/z calcd. for $C_{13}H_{17}Br_2O^+$ $[M+H]^+$: 346.9641 found: 346.9636. ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of isomers): δ 4.61 (d, J = 5.8 Hz), 4.42 (s), 3.39 (s), 3.37 (s), 3.21 (dd, J = 16.4 Hz, J = 7.5 Hz), 2.88–2.80 (m), 2.65–2.55 (m), 2.48 (s), 2.45 (s), 2.43-2.38 (m), 2.35 (s), 1.22 (d, J = 6.8 Hz), 1.07 (d, J = 7.3 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, mixture of isomers): δ 143.0, 142.5, 141.6, 139.9, 135.6, 134.8, 133.9, 133.5, 128.1, 127.8, 126.2, 126.0, 91.2, 85.4, 57.8, 55.9, 38.8, 38.7, 36.2, 25.5, 21.4 (two resonances), 21.3, 20.9, 20.3, 13.8.

2,4,7-Trimethyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**7d**)



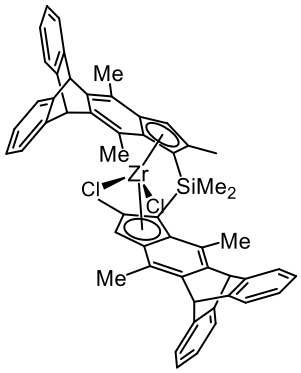
To a solution of 17.4 g (50.0 mmol) of 5,6-dibromo-1-methoxy-2,4,7-trimethylindane (**7c**) and 20.0 g (112.2 mmol) of anthracene in 1400 mL of toluene a solution of 30.0 mL (75.0 mmol) of 2.5 M *n*BuLi in hexanes in 250 mL of toluene was added dropwise over 5 h at room temperature. The resulting mixture was stirred overnight at room temperature. Then, 250 mL of water was added, the organic layer was separated and evaporated to dryness. Thus obtained crude material was treated with a mixture of 200 mL of *n*-hexane and 100 mL of CH_2Cl_2, excess of anthracene was filtered off and the filtrate was evaporated to dryness. The intermediate product 1-methoxy-2,4,7-trimethyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indane was purified by column chromatography on silica gel 60 (40–63 μm; eluent: hexanes-dichloromethane = 2:1, vol.). This procedure gave ~7.5 g of a white solid which was dissolved in 130 mL of toluene, then, 200 mg of *p*TsOH was added, and the mixture was refluxed under Dean-Stark head for 1 h. After cooling to room temperature, the mixture was washed with 400 mL of 10% aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was additionally extracted with 300 mL of dichloromethane. The combined organic extract was evaporated to dryness. The residue was treated with 200 mL of warm *n*-hexane and the solid product was isolated by filtration. This procedure gave 3.04 g (18% yield) of the product. HRMS (ESI) m/z calcd. for $C_{26}H_{23}^+$ $[M+H]^+$: 335.1794 found: 335.1796. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.34 (m, 4H), 6.96–6.91 (m, 4H), 6.46 (s, 1H), 5.68 (s, 1H), 5.65 (s, 1H), 3.04 (s, 2H), 2.50 (s, 3H), 2.42 (s, 3H), 2.07 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 145.9, 144.9, 142.2, 141.4, 139.5, 138.9, 125.7, 124.91, 124.87, 124.5, 123.5, 123.4, 121.1, 50.6, 50.4, 42.0, 16.9, 14.8, 14.6.

Proligand **7e**



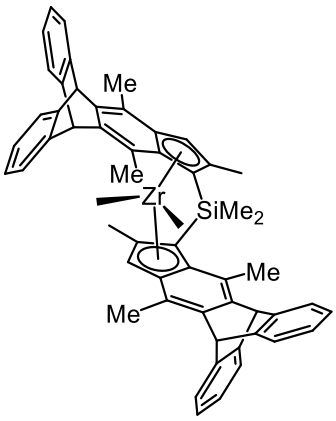
To a suspension of 10.0 g (30.0 mmol) of 2,4,7-trimethyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**7d**) in 200 mL of diethyl ether, 12.3 mL (29.9 mmol) of 2.43 M *n*BuLi in hexanes was added in one portion at –50 °C. This mixture was stirred for 6 h at room temperature. Then the mixture was cooled to –50 °C and 20 mL of THF was added followed by 200 mg of CuCN. The resulting mixture was stirred for 15 min at –25 °C, then 1.94 g (15.03 mmol) of dichlorodimethylsilane was added in one portion. This mixture was stirred overnight at room temperature, then 250 mL of dichloromethane was added and the resulting mixture was filtered through a pad of silica gel which was additionally washed by 2 × 50 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure, and the solid residue was dried in vacuum to give 12.2 g (ca. 100%, containing LiCl and THF) of the product (approx. 1.5/1 mixture of *rac* and *meso* isomers) as a white powder which was used on the next step without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43–7.27 (m, 8H in *rac* and *meso*), 7.10–6.88 (m, 8H in *rac* and *meso*), 6.47 (s, 2H in *rac*), 6.44 (s, 2H in *meso*), 5.65 (s, 2H in *meso*), 5.63 (s, 2H in *rac*), 5.46 (s+s, 1H in *rac* and 1H in *meso*), 3.55 (s, 2H in *meso*), 3.27 (s, 2H in *rac*), 2.50 (s, 6H in *meso*), 2.47 (s, 6H in *rac*), 2.11 (s, 6H in *rac*), 2.02 (s, 6H in *meso*), 1.96 (s, 6H in *meso*), 1.89 (s, 6H in *rac*), –0.29 (s, 3H in *meso*), –0.38 (s, 6H in *rac*), –0.77 (s, 3H in *meso*).

Complex *rac*-**Ty7-Cl_2**



A suspension of 11.35 g (ca. 15.65 mmol) of **7e** in 300 mL of diethyl ether was cooled to –50 °C and 12.9 mL (31.4 mmol) of 2.43 M *n*BuLi in hexanes were added in one portion. The mixture was stirred overnight at room temperature. The mixture was then cooled to –60 °C and 3.65 g (15.66 mmol) of $ZrCl_4$ was added. The reaction mixture was stirred for 24 h at room temperature, then, it was evaporated to dryness and the residue was taken up in 400 mL of toluene. The mixture was filtered while hot through glass frit. The filtrate was evaporated to a volume ca. 120 ml. The yellow solid that precipitated from this solution overnight at room temperature was collected and dried in vacuum. This procedure gave 1.2 g of zirconium dichloride complex *rac*-**Ty7-Cl_2**. Subsequent recrystallization of the evaporated mother liquor from 50 mL, and then from 30 mL of toluene, gave respectively 0.55 g and 0.37 g of *rac*-**Ty7**-Cl_2. Thus, the total yield of *rac*-**Ty7-Cl_2** isolated in this synthesis was 2.12 g (15%). Anal. Calcd for $C_{54}H_{46}Cl_2SiZr$: C, 73.27; H, 5.24. Found: C, 73.48; H, 5.41. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.32 (m, 6H), 7.26–7.24 (m, 2H), 7.04–6.97 (m, 8H), 6.59 (s, 2H), 5.66 (s, 12H), 5.49 (s, 2H), 2.63 (s, 6H), 2.33 (s, 6H), 1.91 (s, 6H), 1.24 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 145.5, 144.6, 143.9, 143.8, 142.5, 141.1, 132.4, 131.4, 129.4, 125.68, 125.65, 125.55, 125.4, 125.3, 123.7, 123.6, 123.53, 123.50, 123.1, 122.8, 82.1, 50.6, 49.7, 20.1, 19.1, 14.6, 8.5.

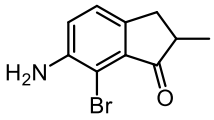
Complex *rac*-**Ty7**



To a suspension of 1.00 g (1.13 mmol) of *rac*-**Ty7-Cl$_2$** in a mixture of 40 mL of toluene and 30 mL of diethyl ether, 2.0 mL (5.4 mmol) of 2.7 M MeMgBr in diethyl ether was added in one portion. This mixture was refluxed for 12 h, and then evaporated to dryness. The residue was extracted with 30 mL of hot toluene, and the toluenic extract was evaporated to ca. 10 mL. The yellow solid that precipitated from this solution at room temperature was collected and dried in vacuum. This procedure gave 0.45 g (47%) of the zirconium dimethyl complex *rac*-**Ty7**. Anal. Calcd for $C_{56}H_{52}SiZr$: C, 79.66; H, 6.21. Found: C, 79.91; H, 6.54. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.38–7.36 (m, 2H), 7.34–7.32 (m, 2H), 7.29–7.27 (m, 2H), 7.25–7.23 (m, 2H), 7.02–6.93 (m, 8H), 6.49 (s, 2H), 5.63 (s, 2H), 5.50 (s, 2H), 2.57 (s, 6H), 2.39 (s, 6H), 1.77 (s, 6H), 1.05 (s, 6H), –1.92 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): *δ* 146.0, 144.8, 144.7, 144.2, 140.4, 138.5, 132.5, 130.3, 126.0, 125.4, 125.3, 125.2, 125.0, 124.2, 123.4, 123.3, 123.1, 115.6, 77.7, 50.6, 49.7, 32.4, 20.1, 18.6, 14.7, 8.6.

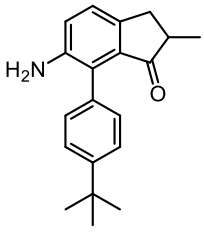
Synthesis of complex Ty8

6-Amino-7-bromo-2-methylindan-1-one



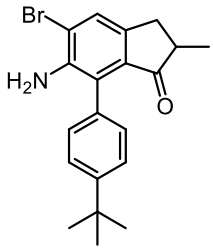
To solution of 23.1 g (0.143 mol) of 6-amino-2-methylindan-1-one (**8**) in 450 mL of DMF, a solution of 25.5 g (0.143 mol) of *N*-bromosuccinimide in 200 mL of DMF was added dropwise at –30 °C. Then the reaction mixture was stirred for 3 h at room temperature and poured into 2.5 L of water. The mixture was extracted with diethyl ether (3 × 300 ml). The organic layer was washed with water (3 × 200 ml), dried over Na_2SO_4 and the solvent was evaporated. The residue was dissolved in 200 mL of dichloromethane and 400 mL of toluene was added. The solvents were evaporated until precipitate started to form. The mixture was cooled to room temperature, the precipitate was filtered and washed with toluene. The resulting pale brown solid was dried in vacuo to give 31.4 g (92% yield) of the product. HRMS (ESI) m/z calcd. for $C_{10}H_{11}BrNO^+$ [M+H]$^+$: 240.0019 found: 240.0016. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 5.62 (br.s., 2H), 3.27 (dd, *J* = 16.5 Hz, *J* = 7.8 Hz, 1H), 2.78 (m, 1H), 2.60 (m, 1H), 1.28 (d, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 207.0, 145.7, 144.1, 133.5, 125.6, 122.4, 103.5, 43.0, 33.0, 16.3.

6-Amino-7-(4-*tert*-butylphenyl)-2-methylindan-1-one



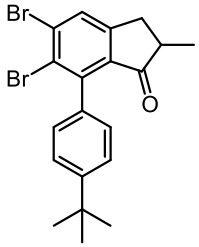
The mixture of 31.4 g (0.131 mol) of 6-amino-7-bromo-2-methylindan-1-one, 30.7 g (0.170 mol) of 4-*tert*-butylphenylboronic acid, 107 g (0.328 mol) of cesium carbonate, 3.0 g (2.62 mmol) of $Pd[PPh_3]_4$, 600 mL of dioxane and 300 mL of water was stirred at 95 °C overnight under inert atmosphere in pressure vessel. Then, dioxane was rotary evaporated, and 500 mL of water was added. The mixture was extracted with dichloromethane (3 × 200 ml). The combined organic extracts were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (40–63 µm, eluent: hexane-ethyl acetate = 10:1, vol.) to give 38.7 g (99%) of the product. HRMS (ESI) m/z calcd. for $C_{20}H_{24}NO^+$ [M+H]$^+$: 294.1852 found: 294.1859. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.46 (m, 2H), 7.15–7.25 (m, 3H), 7.04 (m, 1H), 3.96 (br.s., 2H), 3.27 (m, 1H), 2.60 (m, 2H), 1.35 (s, 9H), 1.22 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 208.6, 150.2, 144.2, 143.8, 133.9, 131.7, 129.0, 125.9, 125.5, 124.3, 122.3, 42.9, 34.6, 33.6, 31.4, 16.0.

6-Amino-5-bromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8a**)



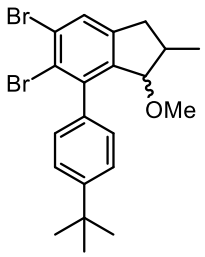
To solution of 38.0 g (0.129 mol) of 6-amino-7-(4-*tert*-butylphenyl)-2-methylindan-1-one in 400 mL of DMF, a solution of 23.0 g (0.129 mol) of *N*-bromosuccinimide in 200 mL of DMF was added dropwise at –30 °C. Then, the reaction mixture was stirred for 3 h at room temperature and poured into 2 L of water. Water was extracted with diethyl ether (3 × 300 mL). The organic layer was washed with water (3 × 200 mL), dried over Na_2SO_4 and the solvent was evaporated. The procedure gave 47.9 g (99%) of crude product which was used in the next step without purification. HRMS (ESI) m/z calcd. for $C_{20}H_{23}BrNO^+$ $[M+H]^+$: 372.0958 found: 372.0962. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.48 (m, 2H), 7.21 (m, 2H), 4.35 (br. s., 2H), 3.25 (m, 1H), 2.60 (m, 2H), 1.36 (s, 9H), 1.21 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 207.8, 150.8, 143.5, 141.8, 133.0, 131.4, 129.2, 128.8, 125.8, 125.7, 124.9, 117.2, 42.9, 34.7, 33.3, 31.4, 16.0.

5,6-Dibromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8b**)



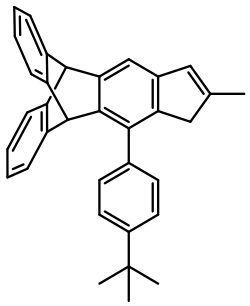
To suspension of 34.6 g (0.155 mol) of $CuBr_2$ in 900 mL of acetonitrile, 26.0 mL (0.193 mol) of amyl nitrite was added dropwise at 50 °C. Then, a solution of 47.9 g (0.129 mol) 6-amino-5-bromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8a**) in 900 mL of acetonitrile was added over an hour at 50 °C. The mixture was stirred at 50 °C for an additional hour and poured into 4 L of water. The resulting mixture was extracted with dichloromethane (3 × 200 ml), the combined organic extracts were dried over Na_2SO_4 and the solvent was evaporated. The residue was suspended in 100 mL of diethyl ether and filtered. The precipitate was collected, dissolved in 300 mL of dichloromethane and the solution was passed through a short pad of silica to get rid of copper-containing byproducts. The solvent was evaporated to give 41.3 g (74%) of the pure product. HRMS (ESI) m/z calcd. for $C_{20}H_{21}Br_2O^+$ $[M+H]^+$: 434.9954 found: 434.9964. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.45 (m, 2H), 7.12 (m, 1H), 7.04 (m, 1H), 3.31 (m, 1H), 2.62–2.69 (m, 2H), 1.38 (s, 9H), 1.23 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 205.8, 153.2, 150.9, 143.4, 134.6, 133.8, 132.3, 130.7, 128.3, 128.0, 126.9, 124.9, 124.8, 42.8, 34.7, 33.6, 31.4, 15.8.

5,6-Dibromo-7-(4-*tert*-butylphenyl)-1-methoxy-2-methylindane (**8c**)



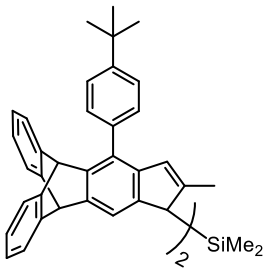
Sodium borohydride (5.30 g, 0.139 mol) was added to a solution of 40.3 g (0.092 mol) of 5,6-dibromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8b**) in 500 mL of THF at 0 °C. Then, 500 mL of methanol was added dropwise at 0 °C. The mixture was stirred for additional 3 hours at room temperature. Then, the solvents were evaporated, and the residue was dissolved in 200 mL of dichloromethane and washed with 500 mL of water. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in 200 mL of dry THF and added to a mixture of 3.3 g (0.138 mmol) of NaH (prepared from 60 wt.% suspension in paraffin) and dry THF under inert atmosphere at 0°C. Then, 11.5 mL (0.184 mol) of methyl iodide was added dropwise at 0 °C and the reaction mixture was stirred overnight at room temperature. Next, the reaction mixture was poured into 1000 mL of water, and the mixture was extracted with diethyl ether (3 × 200 ml). The combined organic layers were dried over Na_2SO_4 and the solvents were evaporated to give 28.3 g (98% yield) of the product (a mixture of *syn*- and *anti*-diastereomers) as a colorless oil. HRMS (ESI) m/z calcd. for $C_{21}H_{25}Br_2O^+$ $[M+H]^+$: 451.0267 found: 451.0258. *Syn*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 1H), 7.43–7.47 (m, 2H), 7.29–7.33 (m, 1H), 7.14 (m, 1H), 3.92 (d, J = 1.3 Hz, 1H), 2.96 (s, 3H), 2.76–2.86 (m, 1H), 2.40 (m, 2H), 1.39 (s, 9H), 0.97 (d, J = 7.0 Hz, 3H). *Anti*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (m, 1H), 7.43–7.47 (m, 2H), 7.29–7.33 (m, 1H), 7.12 (m, 1H), 4.16 (d, J = 5.4 Hz, 1H), 3.28-3.35 (m, 1H), 2.88 (s, 3H), 2.47 (m, 2H), 1.38 (s, 9H), 1.18 (d, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$, mixture of isomers): δ 150.6, 150.5, 144.9, 144.2, 143.8, 143.5, 142.6, 141.8, 137.2, 136.9, 129.8, 129.6, 129.4, 128.8, 128.1, 127.9, 125.8, 125.5, 124.8, 124.7, 124.6, 124.5, 123.8, 123.5, 90.3, 85.1, 67.9, 58.5, 56.8, 39.9, 38.4, 38.3, 38.0, 34.6, 31.4, 25.6, 19.2, 13.6.

2-Methyl-4-(4-*tert*-butylphenyl)-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**8d**)



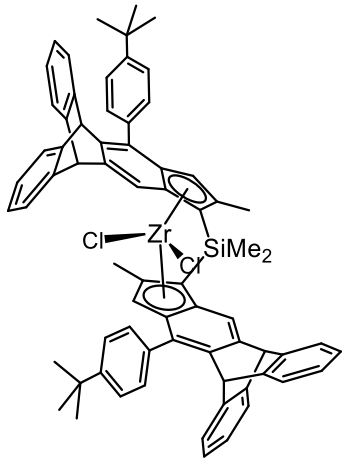
To a solution of 11.0 g (24.3 mmol) of 5,6-dibromo-7-(4-*tert*-butylphenyl)-1-methoxy-2-methylindane (**8c**) and 8.70 g (48.7 mmol) of anthracene in 600 mL of toluene, 19.5 mL (48.7 mmol) of 2.5 M solution of *n*BuLi in hexane were added dropwise at room temperature. Then the reaction mixture was stirred for additional 3 h at room temperature and poured into 1000 mL of water. The organic layer was separated and aqueous layer was extracted with 100 mL of toluene. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. To the residue 70 mL of hexane was added, the mixture was heated to 70 °C and filtered to get rid of the excess of anthracene. The filtrate was evaporated to dryness. The residue was dissolved in 500 mL of toluene and 2.00 g (8.80 mmol) of *p*-toluenesulfonic acid was added. The reaction mixture was refluxed with Dean-Stark apparatus for 1 h. The reaction mixture was cooled down to room temperature and passed through a short pad of silica gel. The filtrate was evaporated to dryness. The residue was purified by flash chromatography on silica gel (40-63 μm, eluent: hexane-ethyl acetate = 20:1, vol.) to give 2.10 g (20%) of the product as a white solid. HRMS (ESI) m/z calcd. for $C_{34}H_{31}^+$ $[M+H]^+$: 439.2420 found: 439.2427. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H), 7.41 (m, 3H), 7.26–7.33 (m, 4H), 6.97 (m, 4H), 6.26 (s, 1H), 5.59 (s, 2H), 5.45 (s, 2H), 3.23 (s, 2H), 2.04 (s, 3H), 1.48 (s, 9H).

Proligand **8e**



To a solution of 2.10 g (4.80 mmol) of 2-methyl-4-(4-*tert*-butylphenyl)-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**8d**) in 100 mL of diethyl ether, 1.93 mL of 2.5M *n*BuLi (4.80 mmol) in hexanes was added dropwise at vigorous stirring at room temperature. The mixture was stirred for 13 h at room temperature and then cooled to –80 °C. At this temperature, 10.0 μl of *N*-methylimidazole was added. Next, to the mixture 293 μL (2.40 mmol) of Me_2SiCl_2 was added. The resulting mixture was stirred overnight at room temperature, and white precipitate was formed. The mixture was poured into water, the organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic phases was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel (40–63 μm, eluent: hexane-dichloromethane = 5:1, vol.) to give 1.45 g (64%) of the product. HRMS (ESI) m/z calcd. for $C_{70}H_{64}NaSi^+$ $[M+Na]^+$: 955.4669 found: 955.4679. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 4H), 7.28–7.37 (m, 14H), 6.98 (m, 8H), 6.36 (s, 2H), 5.57 (s, 2H), 5.33 (s, 2H), 3.61 (s, 2H), 2.09 (s, 6H), 1.48 (s, 18H), –0.27 (s, 3H), –0.37 (s, 3H).

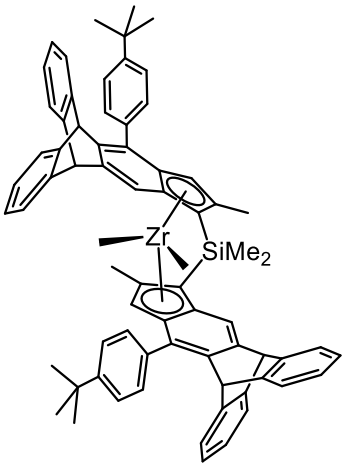
Complex *rac*-**Ty8-Cl$_2$**



To a solution of 3.40 g (3.64 mmol) of proligand **8e** in 120 mL of diethyl ether, 3.00 mL (7.30 mmol) of 2.5 M *n*BuLi in hexanes was added at ambient temperature. This mixture was stirred overnight, and then 1.40 g (3.64 mmol) of $ZrCl_4(THF)_2$ was added at –80 °C in one portion. The resulting mixture was stirred for 24 h at room temperature and then evaporated to dryness. Further on, 100 mL of toluene was added. The resulting mixture was heated to 110 °C and filtered through a short pad of Celite 503. The filtrate was evaporated to dryness. The residue was recrystallized from toluene to give 50 mg of pure *meso*-**Ty8-Cl$_2$** as a first crop. The mother liquor was evaporated to dryness and the residue was recrystallized from toluene to give 300 mg of pure *meso*-**Ty8-Cl$_2$** as orange crystals. The overall yield of the pure meso-complex was 350 mg (9%). The mother liquor was again evaporated and the residue was recrystallized from toluene/hexane mixture to give 1.30 g of a mixture of *rac*- and *meso*-**Ty8-Cl$_2$** with ratio *rac/meso*=5/1. This crop was washed with hot toluene (50 mL) and hot hexane (20 mL) to give 0.50 g (12%) of pure *rac*-**Ty8-Cl$_2$** as a yellow powder. *Meso*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 2H), 7.50 (m, 4H), 7.40 (m, 2H), 7.16–7.29 (m, 6H), 7.14 (m, 2H), 6.92–7.02 (m, 8H), 6.83 (m, 2H), 6.36 (s, 2H), 5.41 (s, 2H), 5.23 (s, 2H), 2.28 (s, 6H), 1.50 (s, 3H), 1.43 (s, 18H), 1.11

(s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 150.3, 145.5, 145.3, 144.1, 143.8, 142.5, 141.1, 135.7, 134.8, 134.6, 131.5, 129.3, 126.7, 126.0, 125.4, 125.3, 123.7, 123.6, 123.5, 123.4, 122.5, 118.1, 86.0, 55.0, 50.2, 34.7, 31.5, 18.5, 2.89, 2.85. *Rac*-isomer: Anal. calc. for $C_{70}H_{62}Cl_2SiZr$: C, 76.89; H, 5.72. Found: C, 77.08; H, 5.95. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.51 (m, 8H), 7.40 (m, 2H), 7.35 (m, 2H), 7.22 (m, 2H), 7.15–7.18 (m, 4H), 7.03 (m, 4H), 6.96 (m, 4H), 6.36 (s, 2H), 5.53 (s, 2H), 5.23 (s, 2H), 6.07 (s, 6H), 1.39 (s, 18H), 1.29 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 150.1, 145.2, 144.3, 143.8, 142.5, 141.9, 134.2, 134.1, 132.1, 131.7, 129.5, 129.1, 125.9, 125.7, 125.6, 125.5, 124.8, 124.4, 123.7, 123.0, 121.9, 117.9, 82.7, 54.5, 50.0, 34.7, 31.5, 17.9, 2.9.

Complex *rac*-**Ty8**



To a suspension of 300 mg (0.27 mmol) of *rac*-**Ty8-Cl$_2$** in 40 mL of toluene, 0.94 mL of 2.9 M MeMgBr (2.70 mmol) in diethyl ether was added at room temperature. This mixture was stirred for 24 h at 100 °C and then evaporated to dryness in vacuum. To the residue 100 mL of toluene was added, and the mixture was heated to 110 °C and then passed through a short pad of Celite® 503. The filtrate was evaporated to dryness. The residue was washed with hot hexane to give 210 mg (73% yield) of pure *rac*-**Ty8** as a pale yellow solid. Anal. calc. for $C_{72}H_{68}SiZr$: C, 82.15; H, 6.51. Found: C, 82.57; H, 6.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.38–7.42 (m, 6H), 7.28–7.33 (m, 6H), 7.19 (m, 2H), 7.14 (m, 2H), 7.02 (m, 4H), 6.92 (m, 4H), 6.36 (s, 2H), 5.53 (s, 2H), 5.22 (s, 2H), 1.90 (s, 6H), 1.40 (s, 18H), 1.09 (s, 6H), –1.81 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 150.0, 145.6, 144.7, 144.6, 144.4, 140.7, 139.1, 134.9, 133.6, 132.0, 129.7, 129.1, 128.7, 128.3, 127.2, 125.5, 125.4, 125.3, 125.2, 124.6, 123.6, 123.3, 123.0, 118.4, 115.6, 78.2, 54.6, 50.0, 34.7, 33.0, 31.5, 17.5, 3.0.

Crystal structure determinations

X-ray experiments were carried out using Bruker D8 Quest with Photon III detector diffractometer (λ(Mo-Kα)=0.71073 Å, graphite monochromator, ω-scans) at 100 K. Structure was 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 model. The details of data collection and crystal structure refinement for which we used SAINT Plus, SADABS and SHELXL-2018/3 program packages, are summarized in Table S1. Crystallographic data for **Ty7-Cl$_2$** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 2308227. 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).

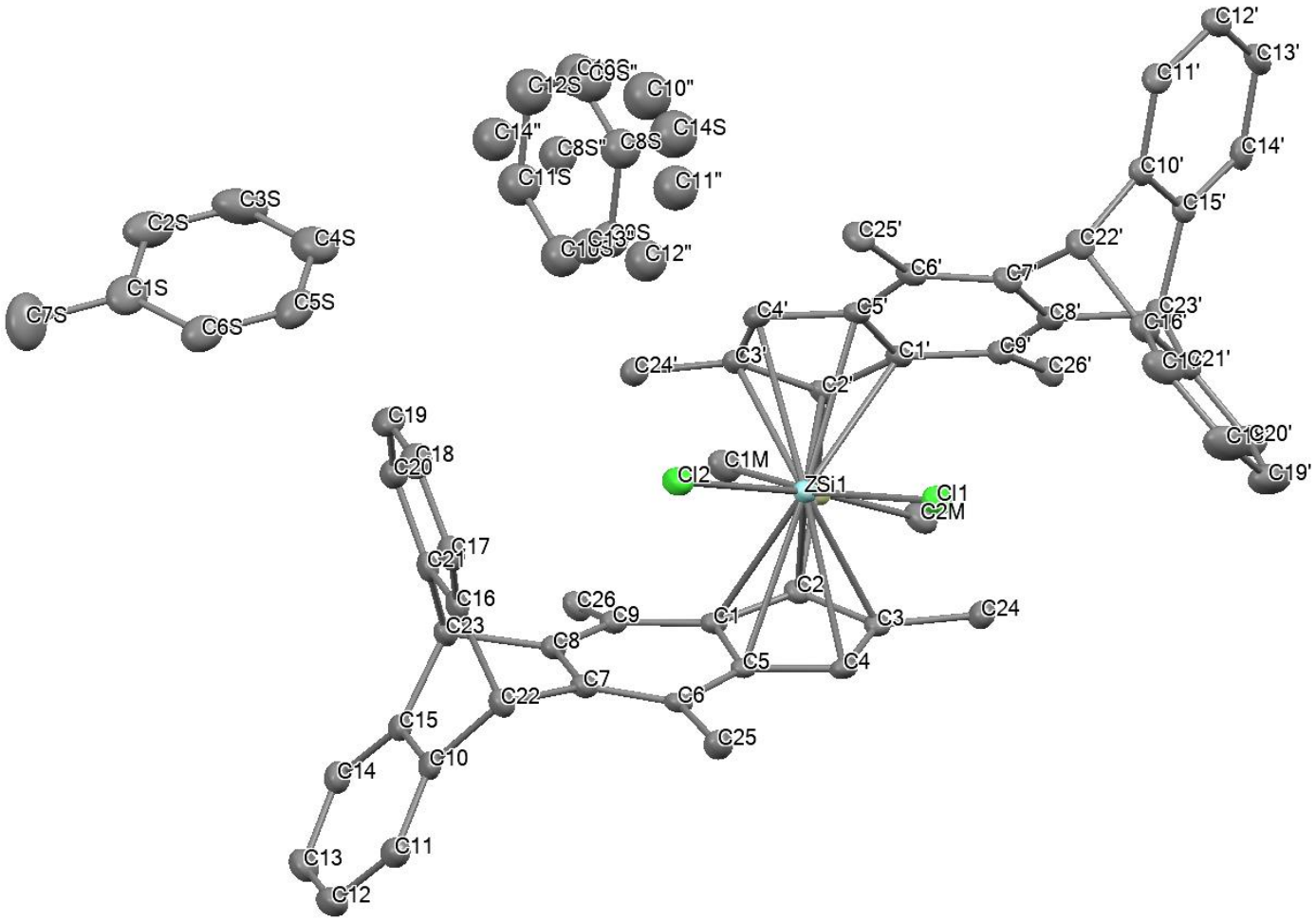


Figure S1. Image of crystal structure of **Ty7-Cl$_2$** generated by CCDC's Mercury software[3] with thermal ellipsoids at 50% probability level; hydrogen atoms omitted for clarity.

Table S1. Crystal data and structure refinement for Ty7-Cl_2.

Identification code	Ty7-Cl2	
Empirical formula	C68 H62 Cl2 Si Zr	
Formula weight	1069.38	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.3784(7) Å	α= 110.9348(10)°.
	b = 14.5841(8) Å	β= 103.3509(11)°.
	c = 15.1837(8) Å	γ = 96.2143(11)°.
Volume	2632.2(2) Å 3	
Z	2	
Density (calculated)	1.349 Mg/m^3	
Absorption coefficient	0.377 mm^{-1}	
F(000)	1116	
Crystal size	0.250 x 0.220 x 0.220 mm^3	
Theta range for data collection	1.600 to 29.000°.	
Index ranges	-18<=h<=18, -19<=k<=19, -20<=l<=20	
Reflections collected	53217	
Independent reflections	14004 [R(int) = 0.0705]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	14004 / 45 / 652	
Goodness-of-fit on F2	1.003	
Final R indices for 10193 refl. With [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.0881	
R indices (all data)	R1 = 0.0729, wR2 = 0.1016	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.551 and -0.590 e. $Å^{-3}$	

NMR spectra

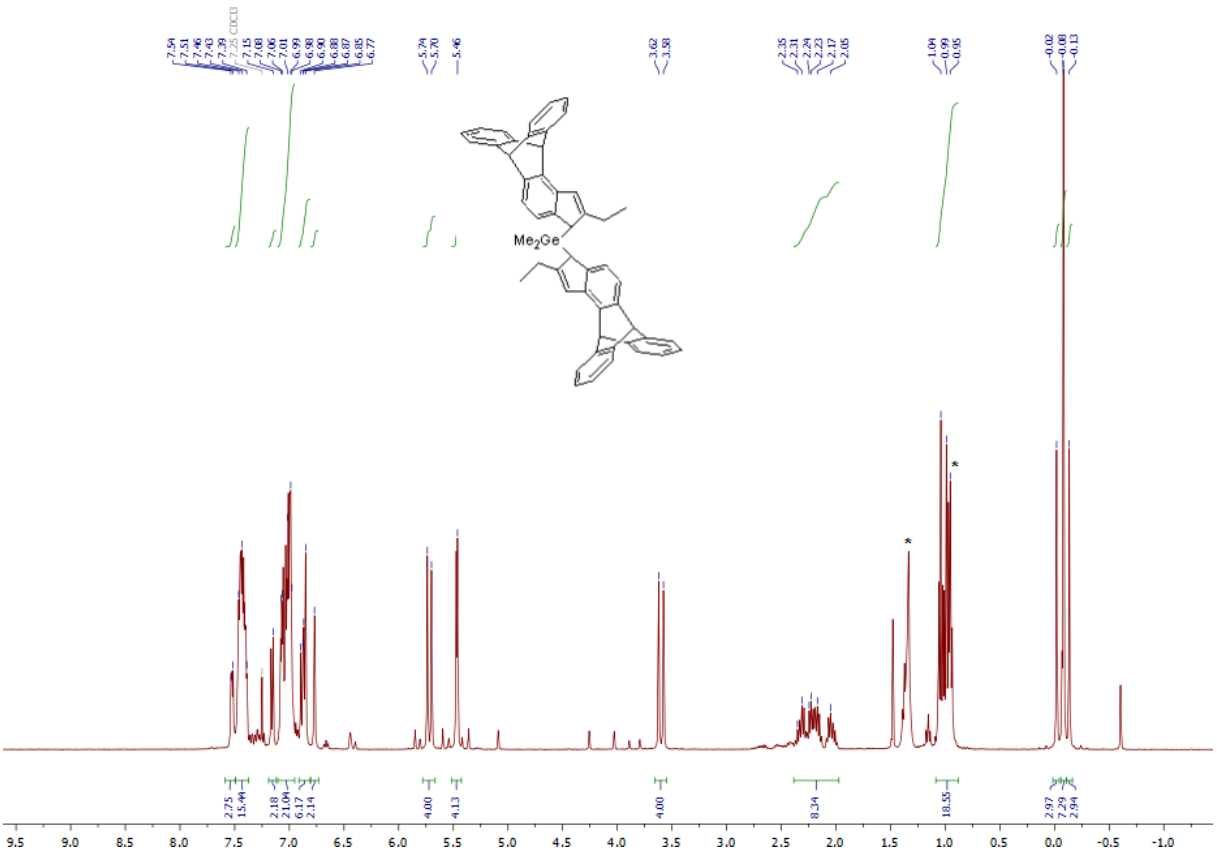


Figure S2. ^{1}H NMR spectrum of proligand **4b** in $CDCl_3$ at room temperature. (*****) – signals of *n*-hexane.

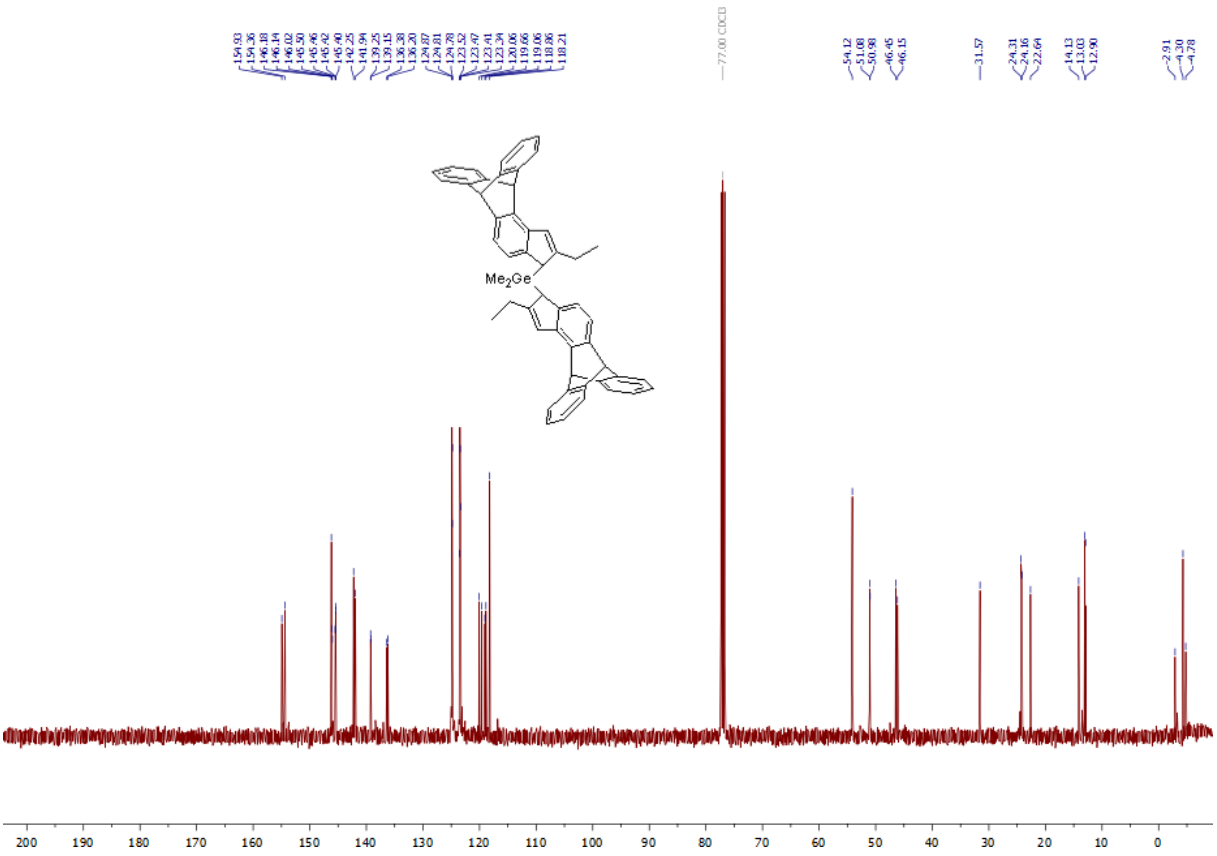


Figure S3. ^{13}C NMR spectrum of proligand **4b** in $CDCl_3$ at room temperature.

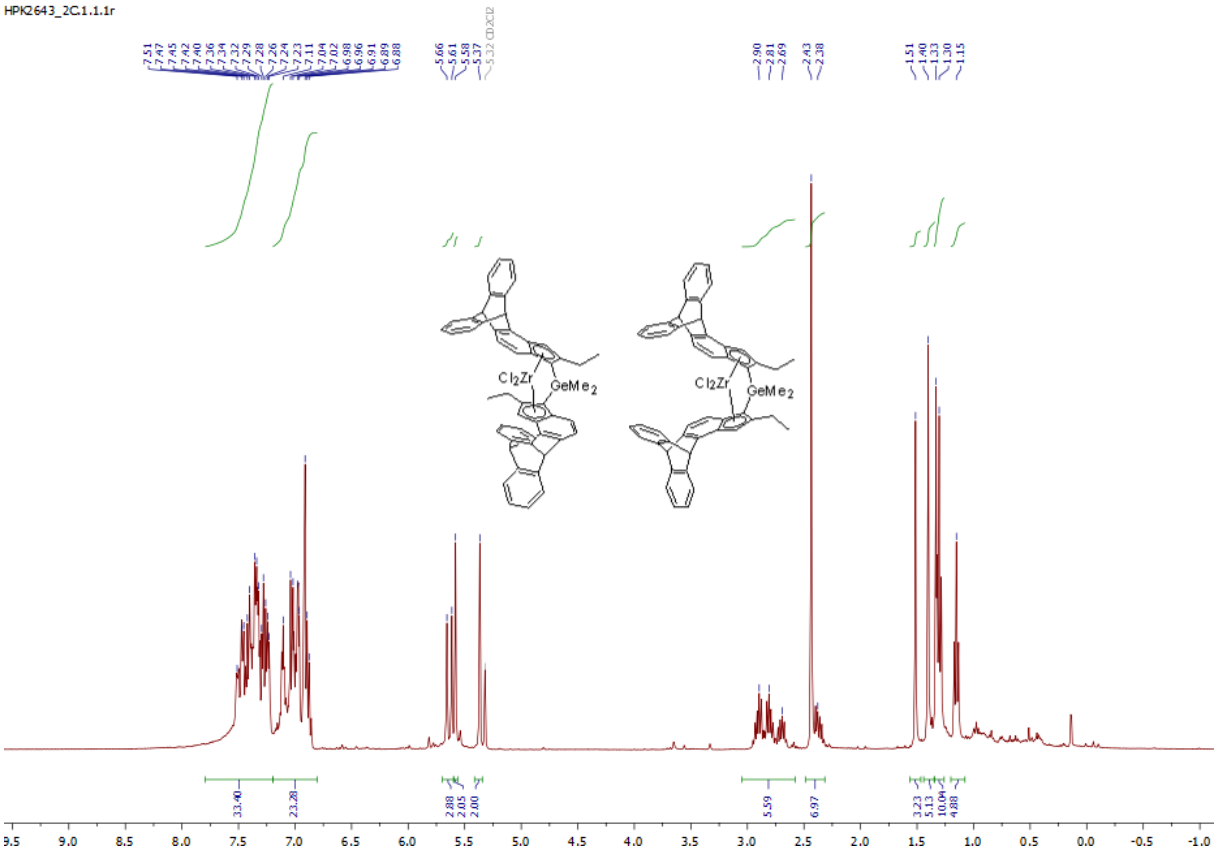


Figure S4. ^{1}H NMR spectrum of crude mixture of *rac*- and *meso*- **Ty4-Cl$_2$** in CD_2Cl_2 at room temperature.

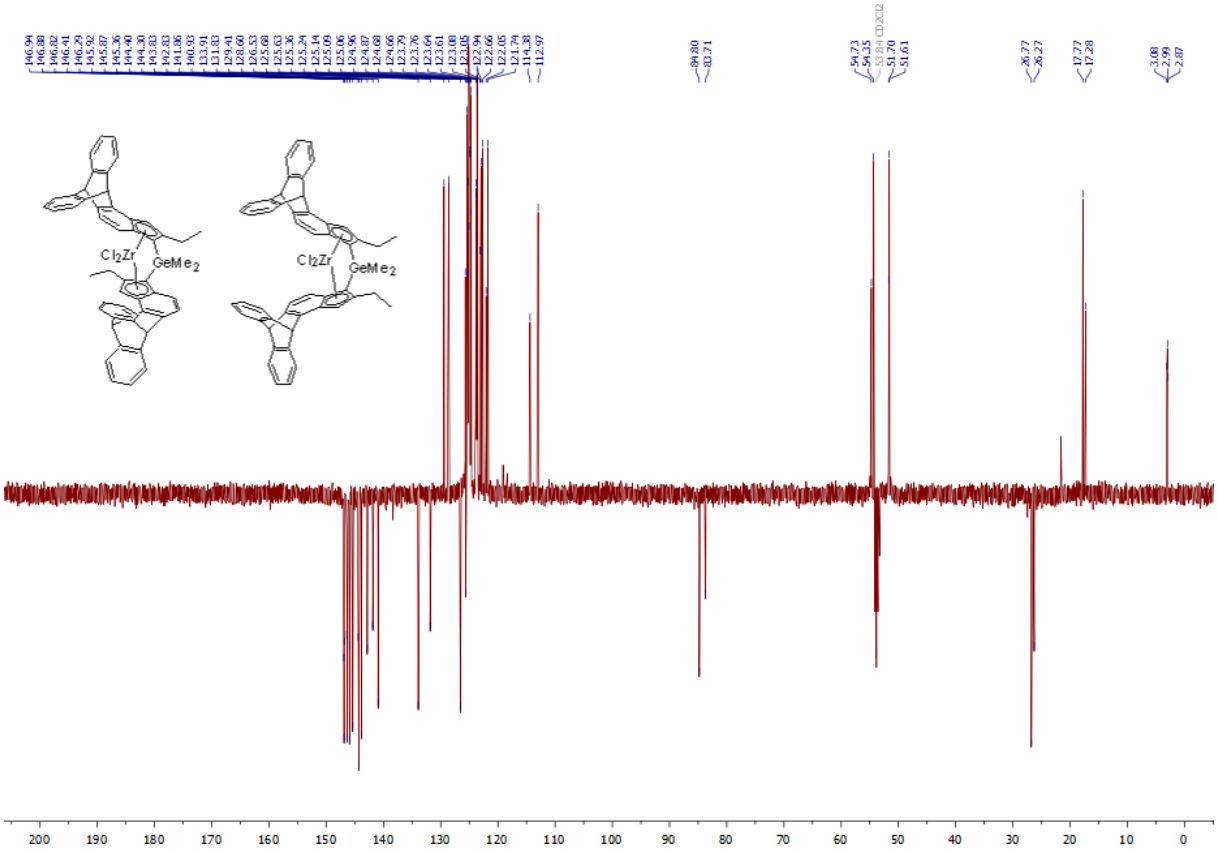


Figure S5. ^{13}C NMR spectrum of crude mixture of *rac*- and *meso*-**Ty4-Cl$_2$** in CD_2Cl_2 at room temperature.

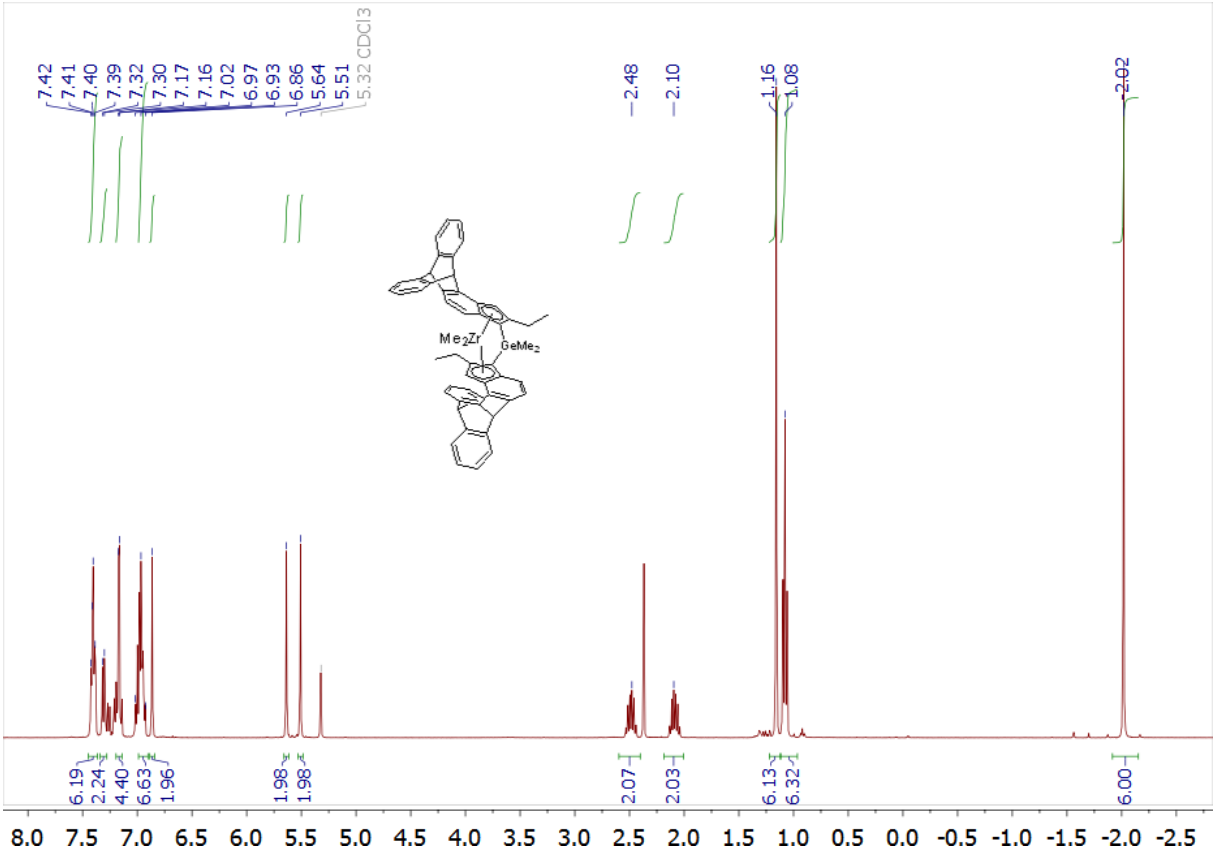


Figure S6. ^{1}H NMR spectrum of *rac*-**Ty4** in CD_2Cl_2 at room temperature.

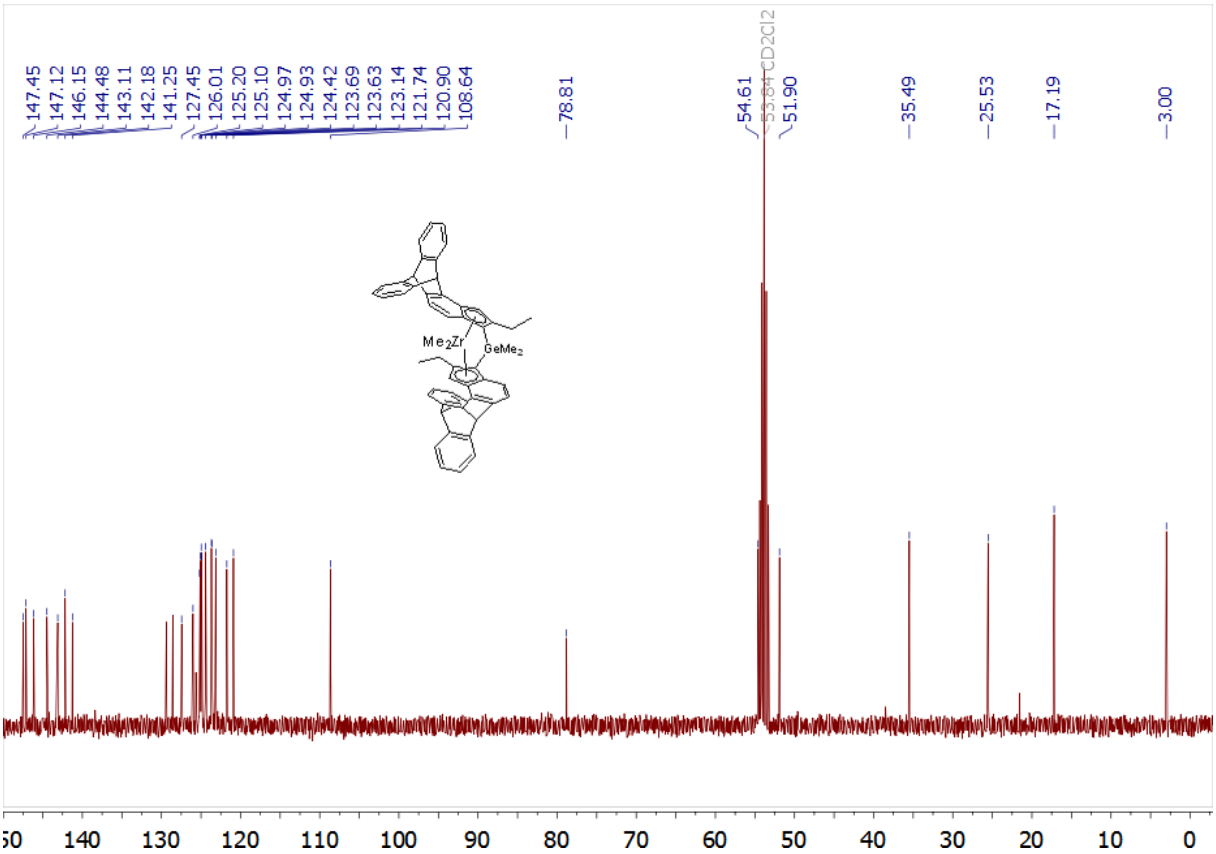


Figure S7. ^{1}H NMR spectrum of *rac*-**Ty4** in CD_2Cl_2 at room temperature.

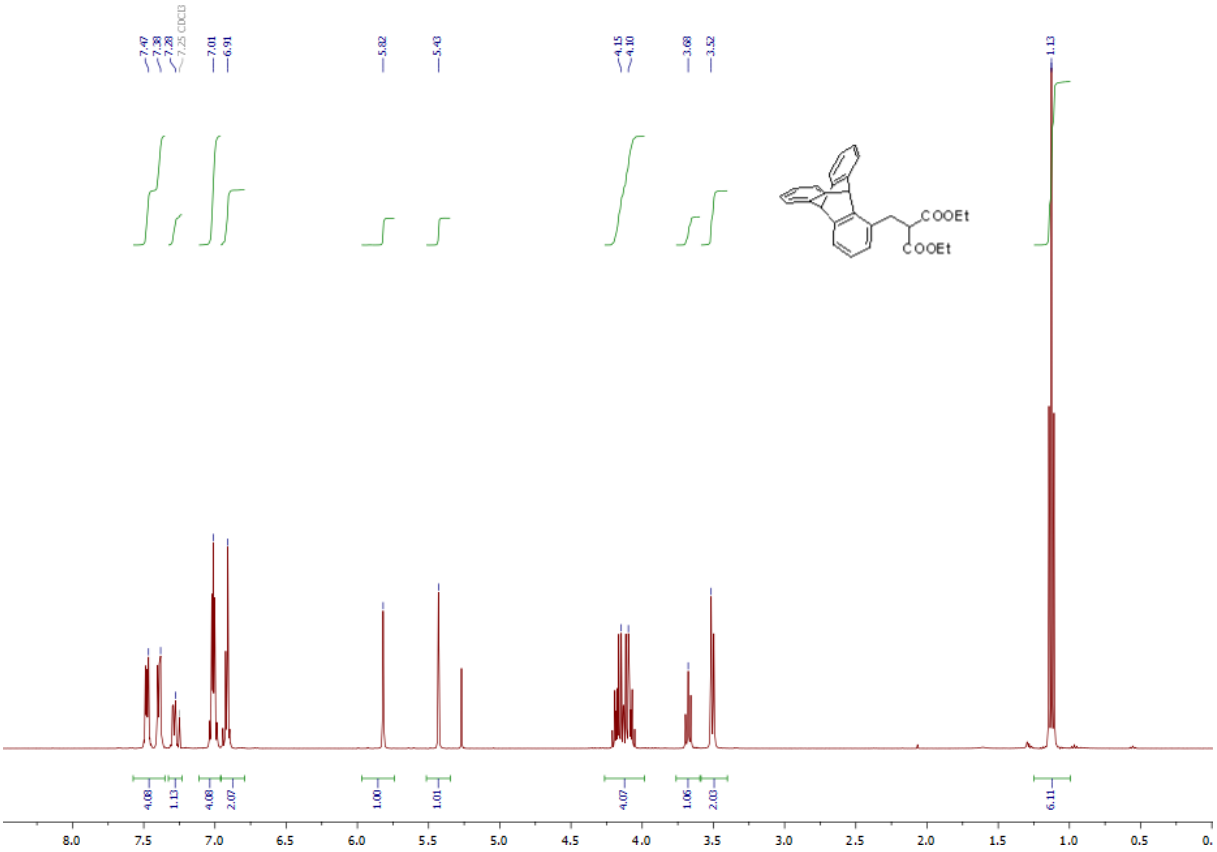


Figure S8. ^{1}H NMR spectrum of 2-((triptycen-1-yl)methyl)malonate in $CDCl_3$ at room temperature.

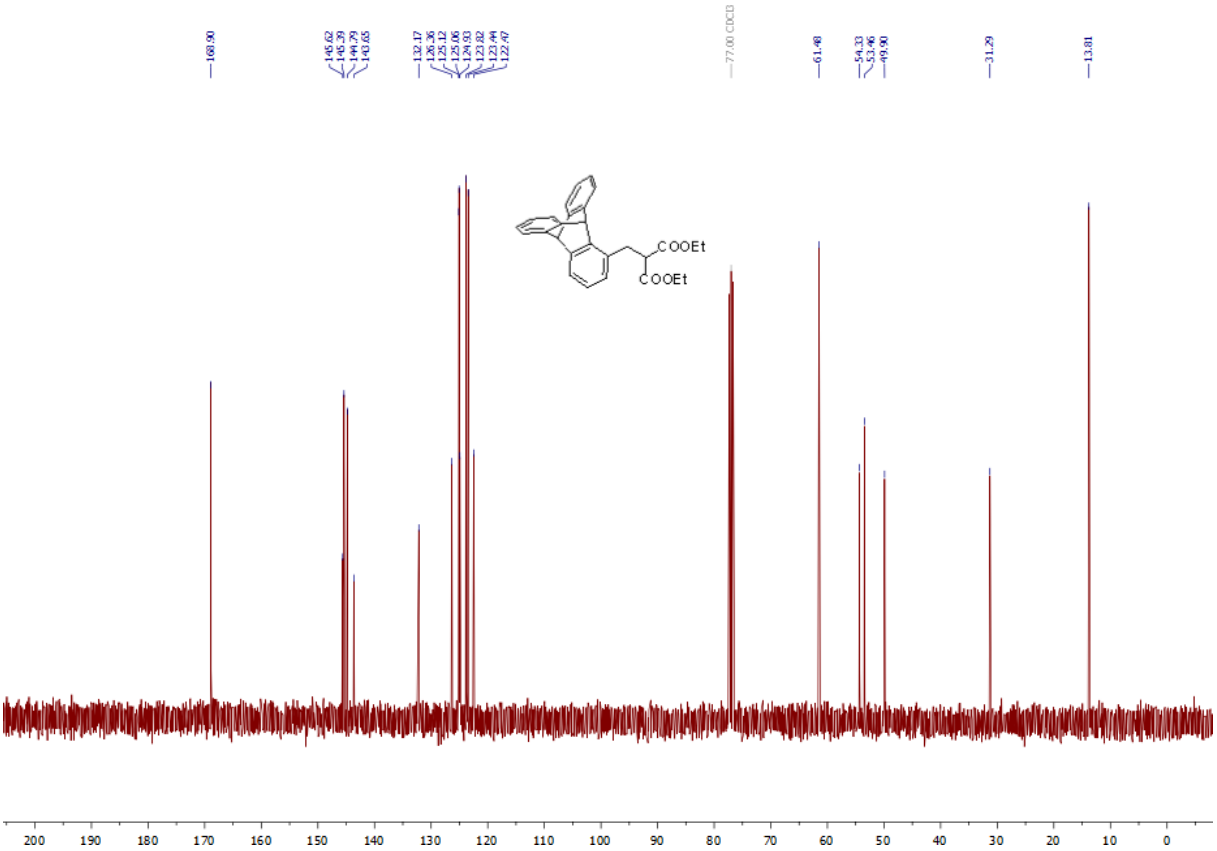


Figure S9. ^{13}C NMR spectrum of 2-((triptycen-1-yl)methyl)malonate in $CDCl_3$ at room temperature.

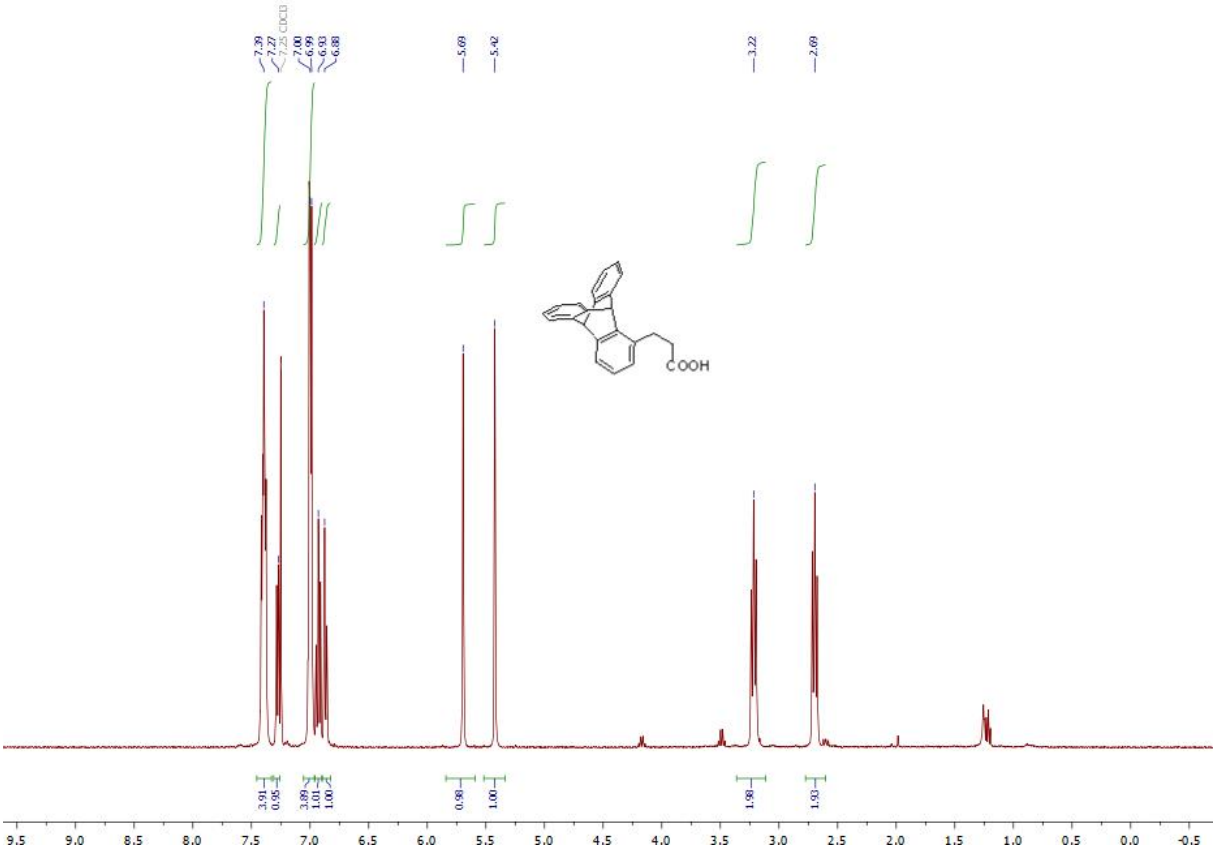


Figure S10. ^{1}H NMR spectrum of 3-(triptycene-1-yl)propanoic acid in $CDCl_3$ at room temperature.

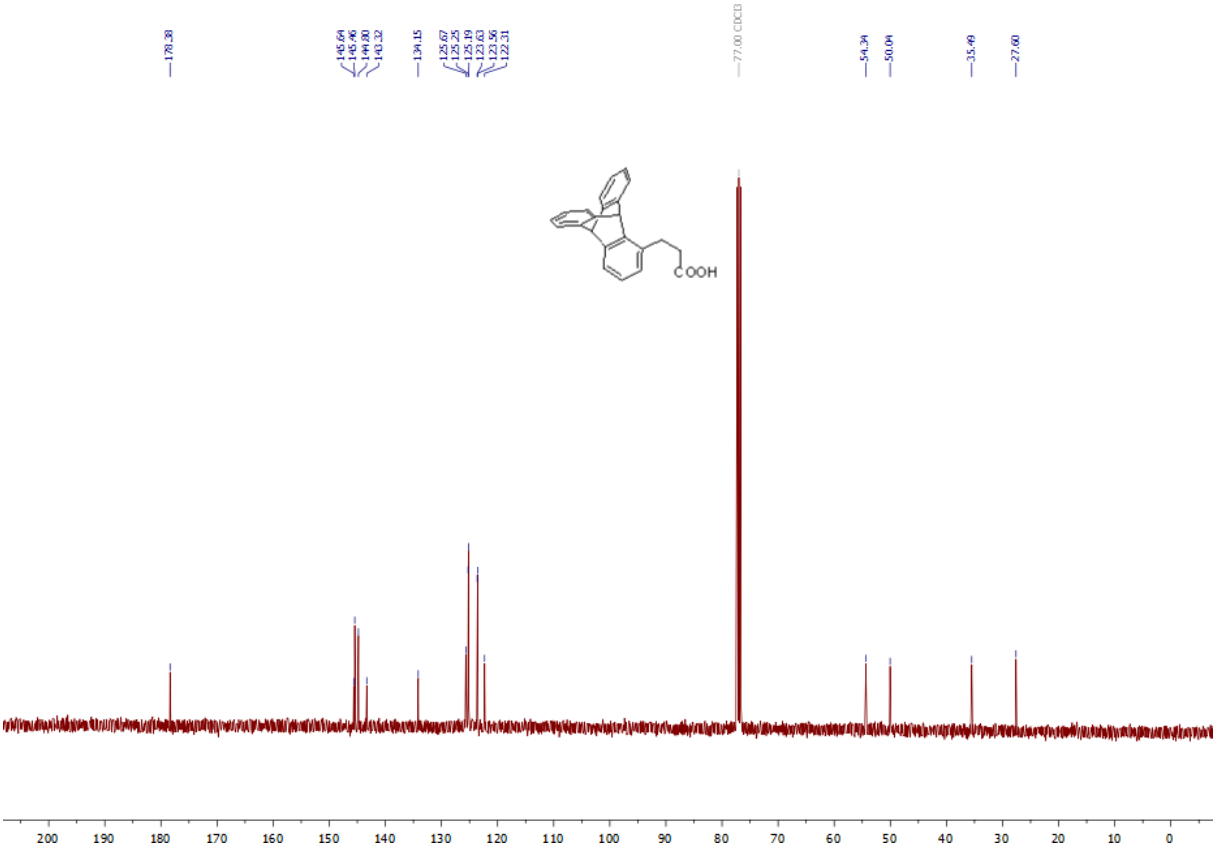


Figure S11. ^{13}C NMR spectrum of 3-(triptycene-1-yl)propanoic acid in $CDCl_3$ at room temperature.

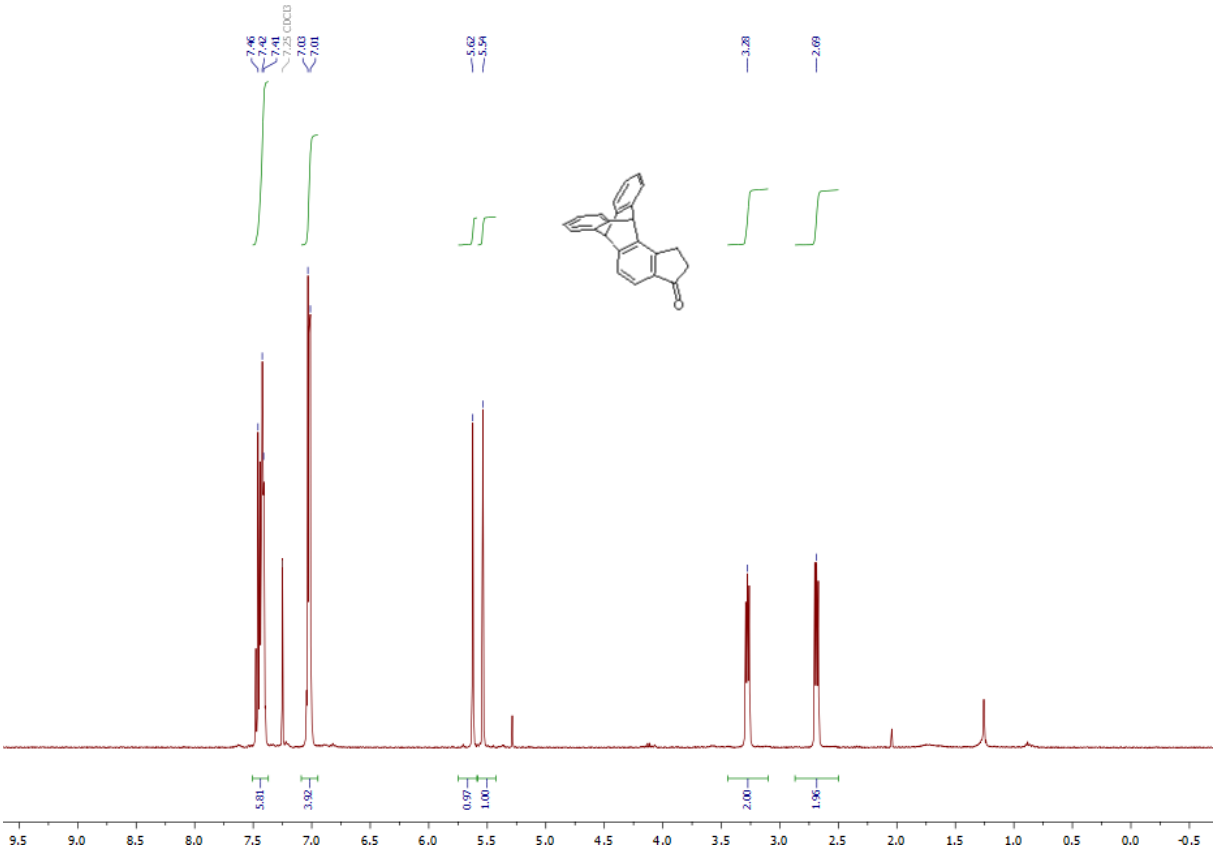


Figure S12. ^{1}H NMR spectrum of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-one in $CDCl_3$ at room temperature.

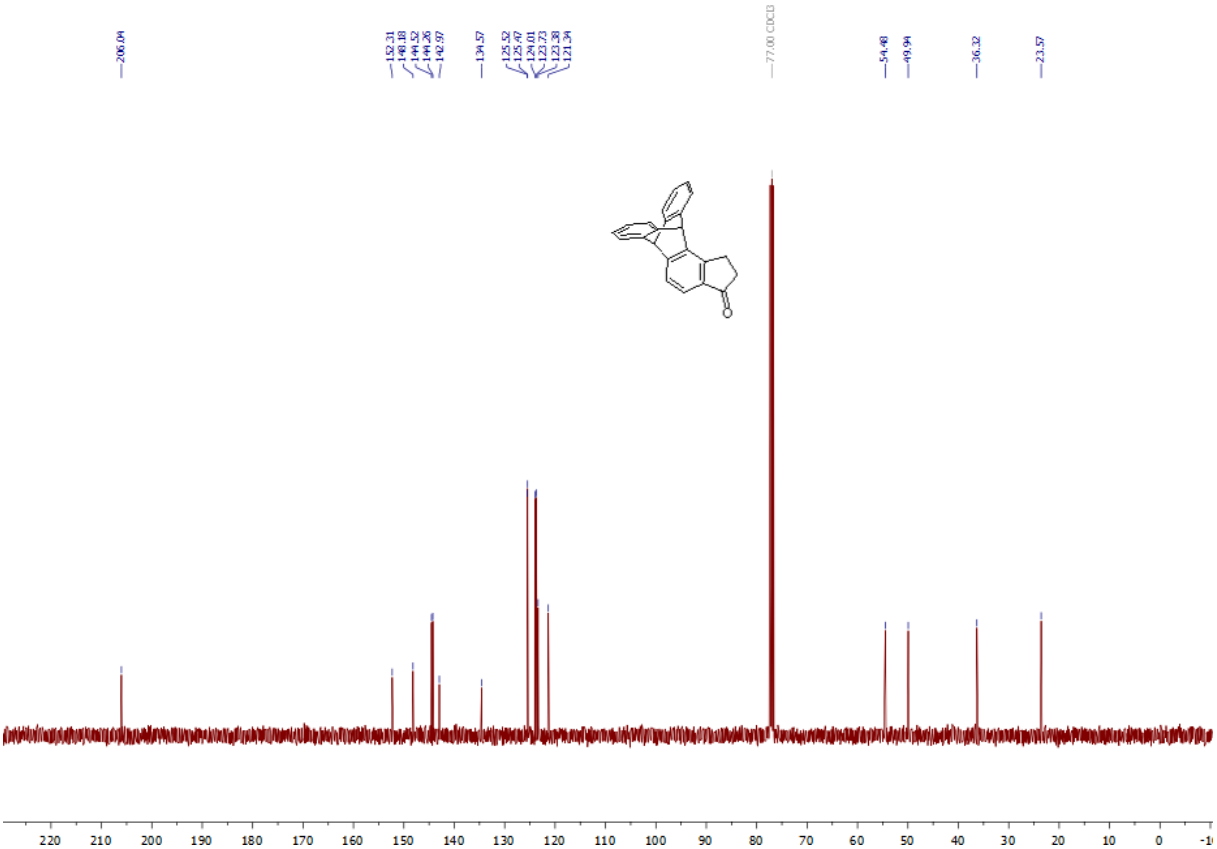


Figure S13. ^{13}C NMR spectrum of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-one in $CDCl_3$ at room temperature.

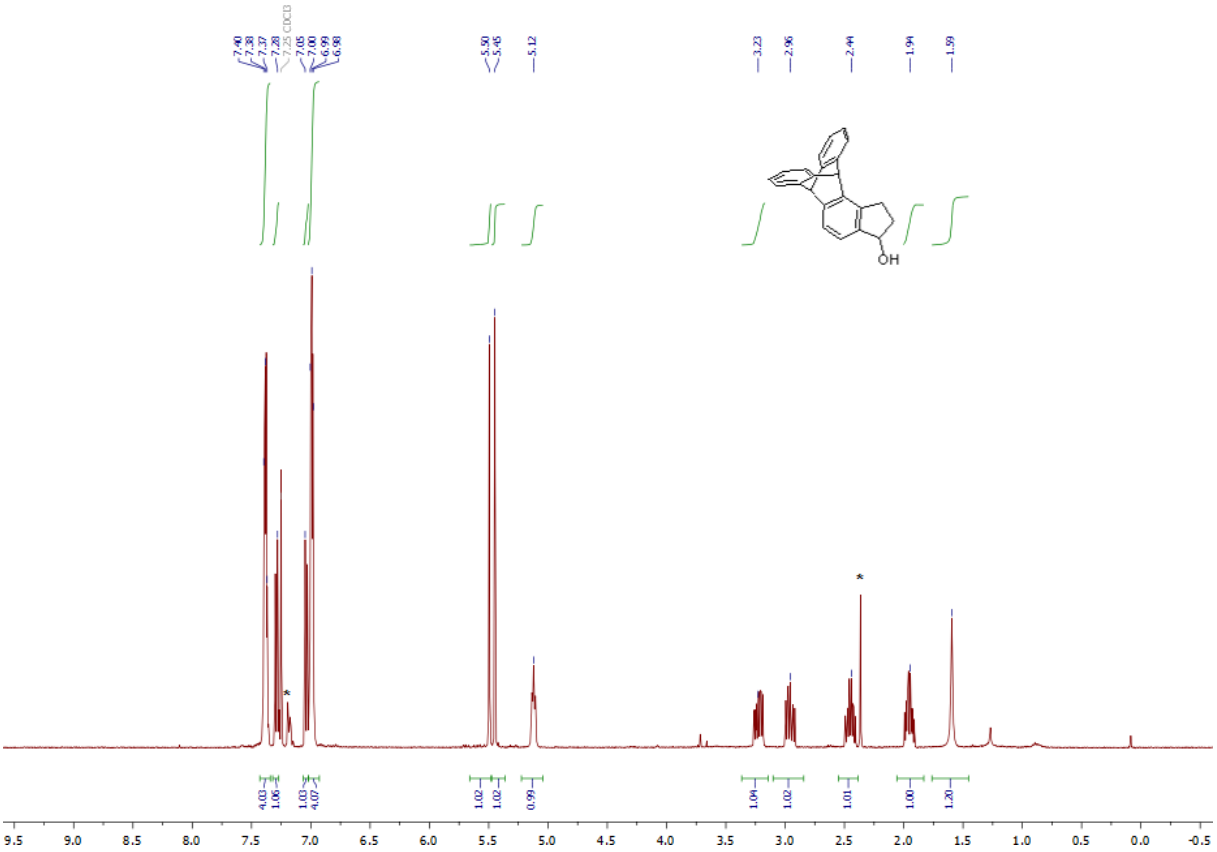


Figure S14. ^{1}H NMR spectrum of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-ol in $CDCl_3$ at room temperature.

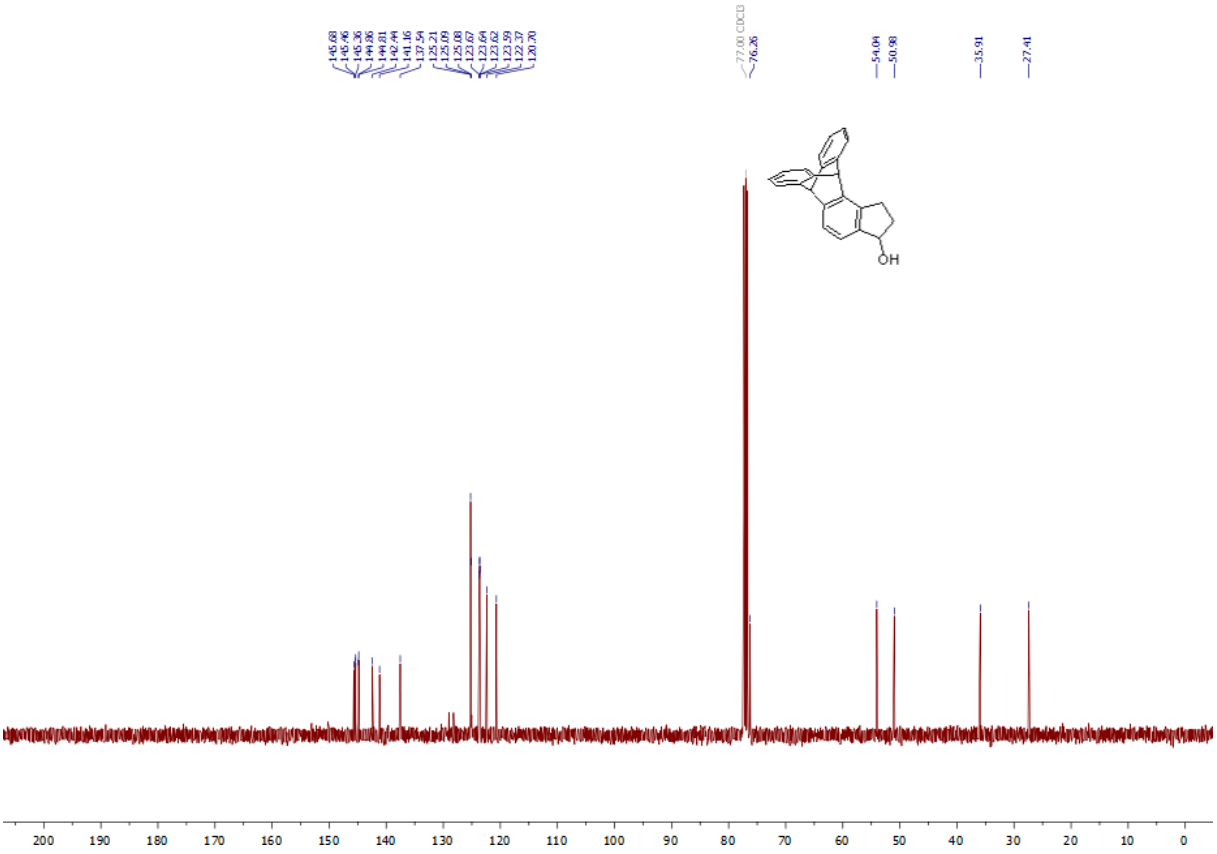


Figure S15. ^{13}C NMR spectrum of 4,5-(9,10-dihydroanthracene-9,10-diyl)-indan-1-ol in $CDCl_3$ at room temperature.

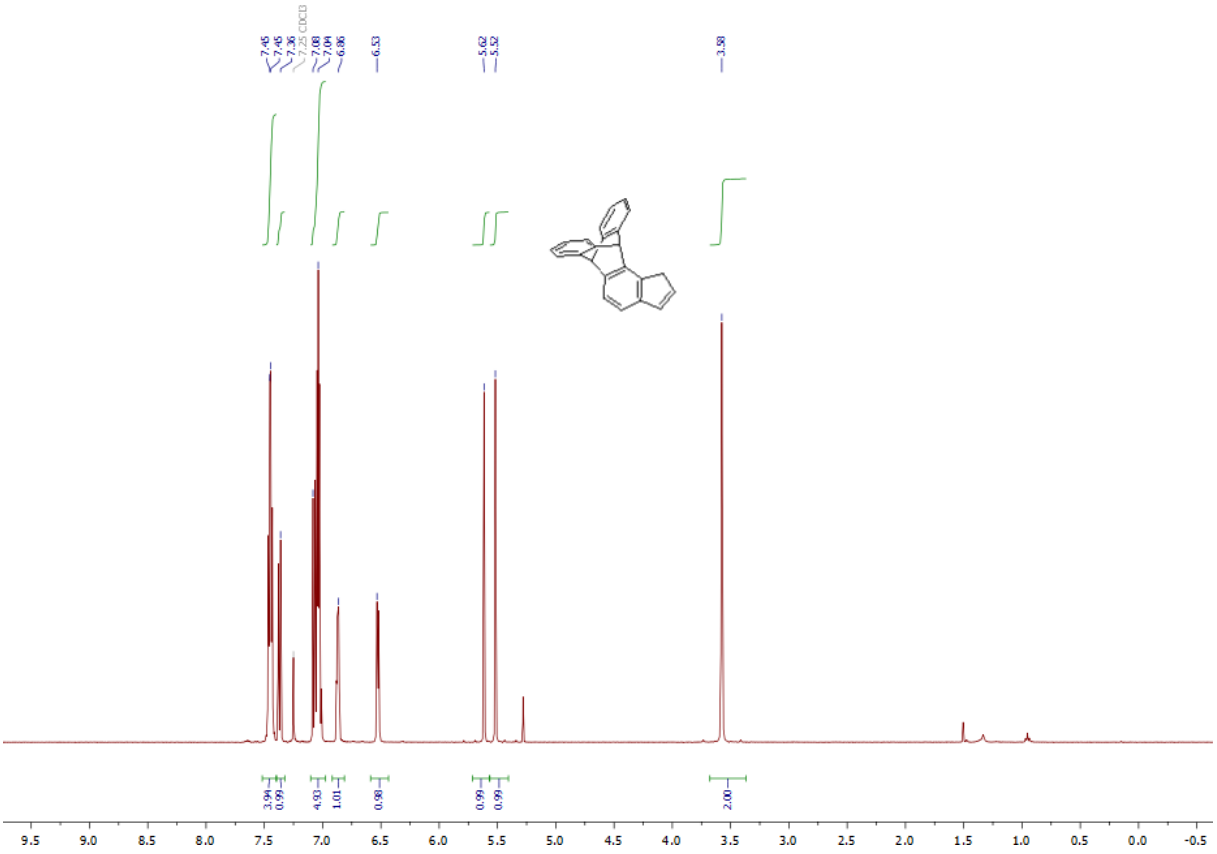


Figure S16. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at room temperature.

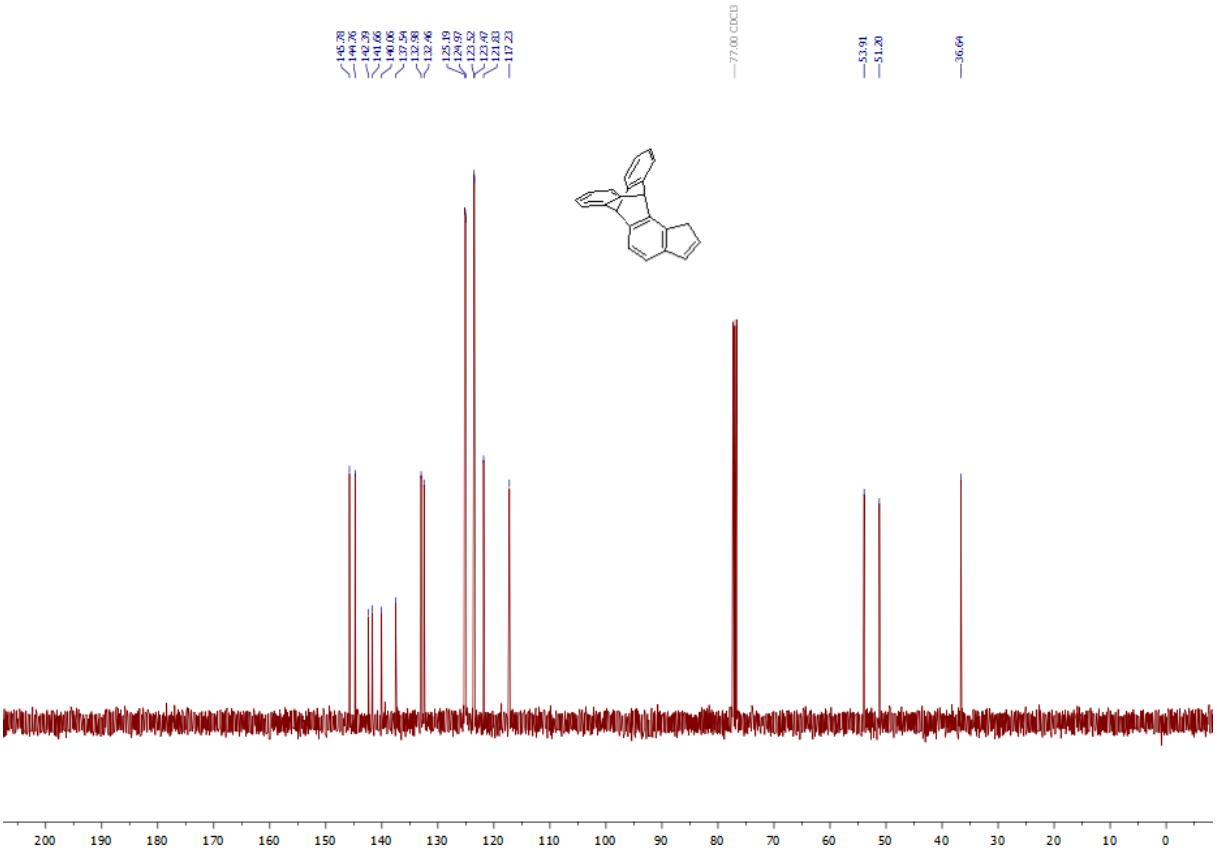


Figure S17. ^{13}C NMR spectrum of **5a** in $CDCl_3$ at room temperature.

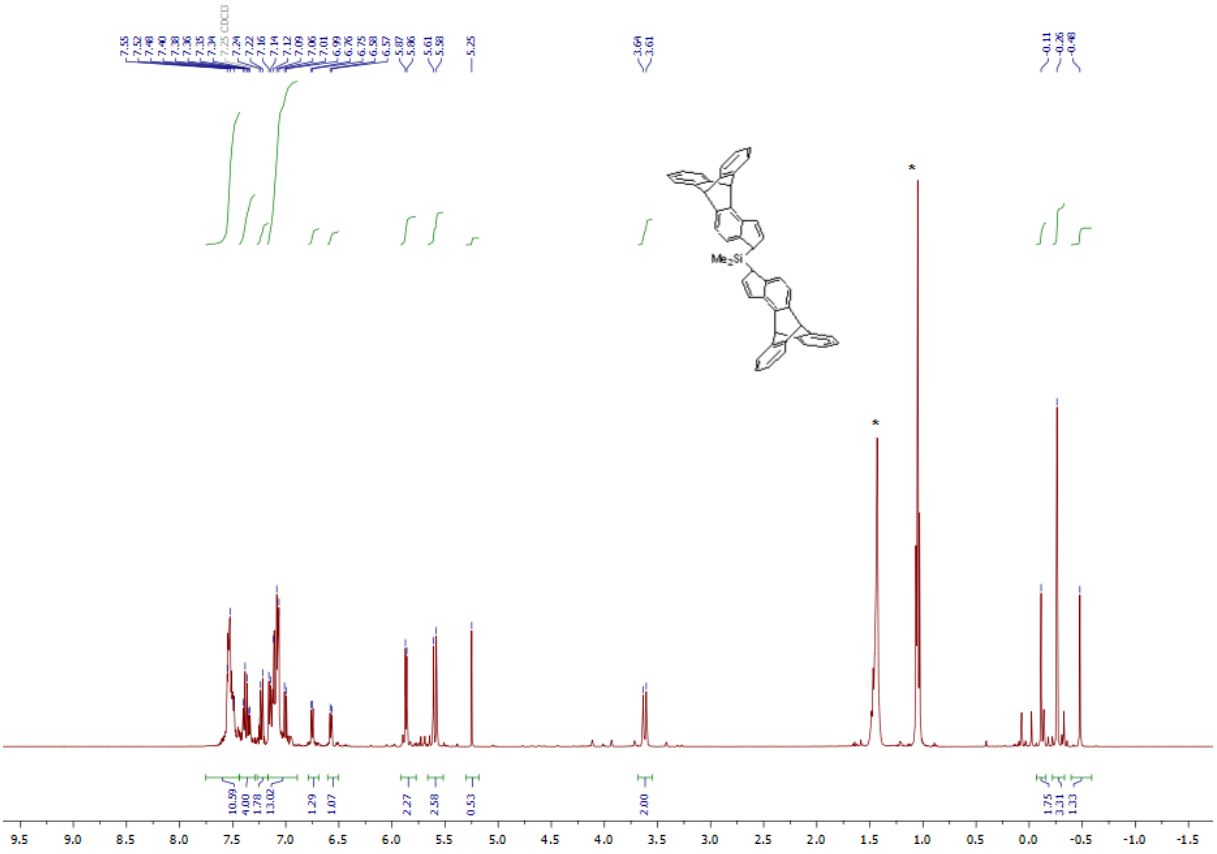


Figure S18. ^{1}H NMR spectrum of proligand **5b** in $CDCl_3$ at room temperature. (*****) – signals of *n*-hexane.

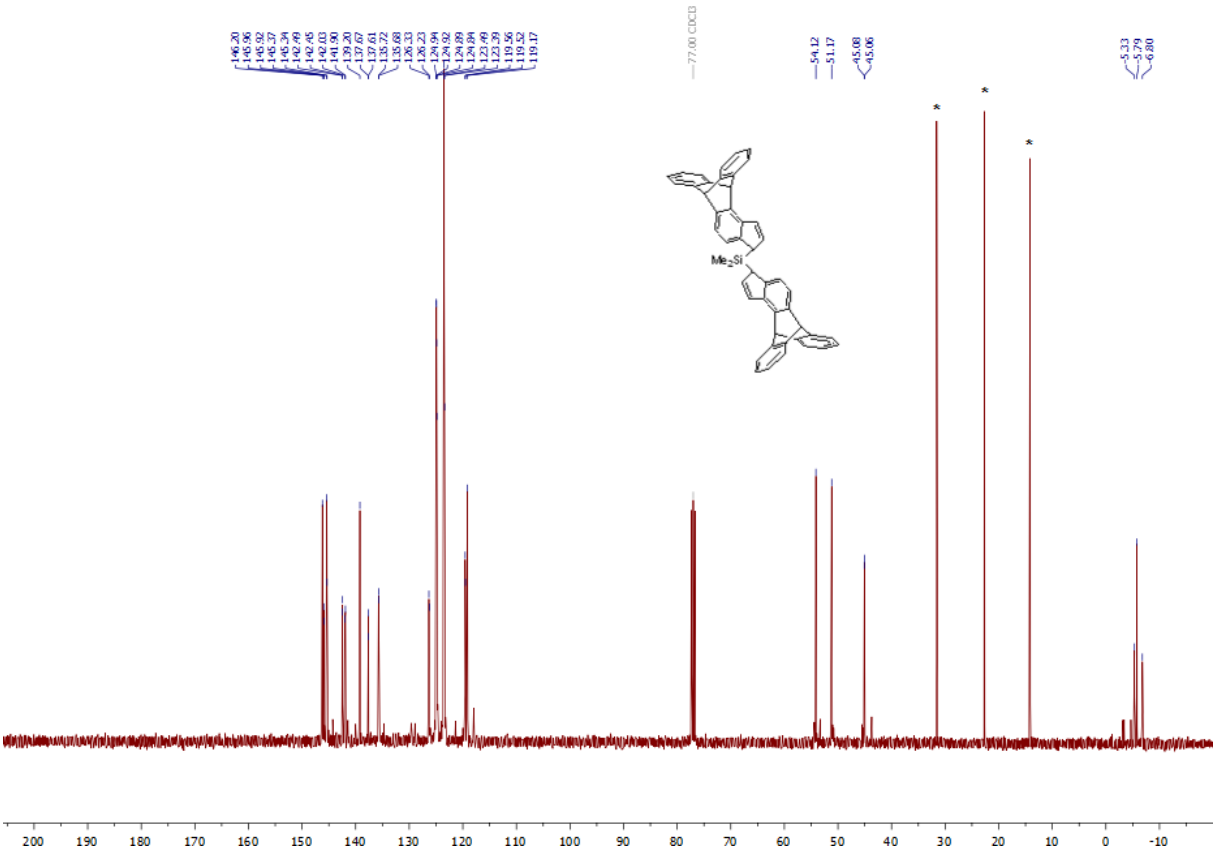


Figure S19. ^{13}C NMR spectrum of proligand **5b** in $CDCl_3$ at room temperature. (*****) – signals of *n*-hexane.

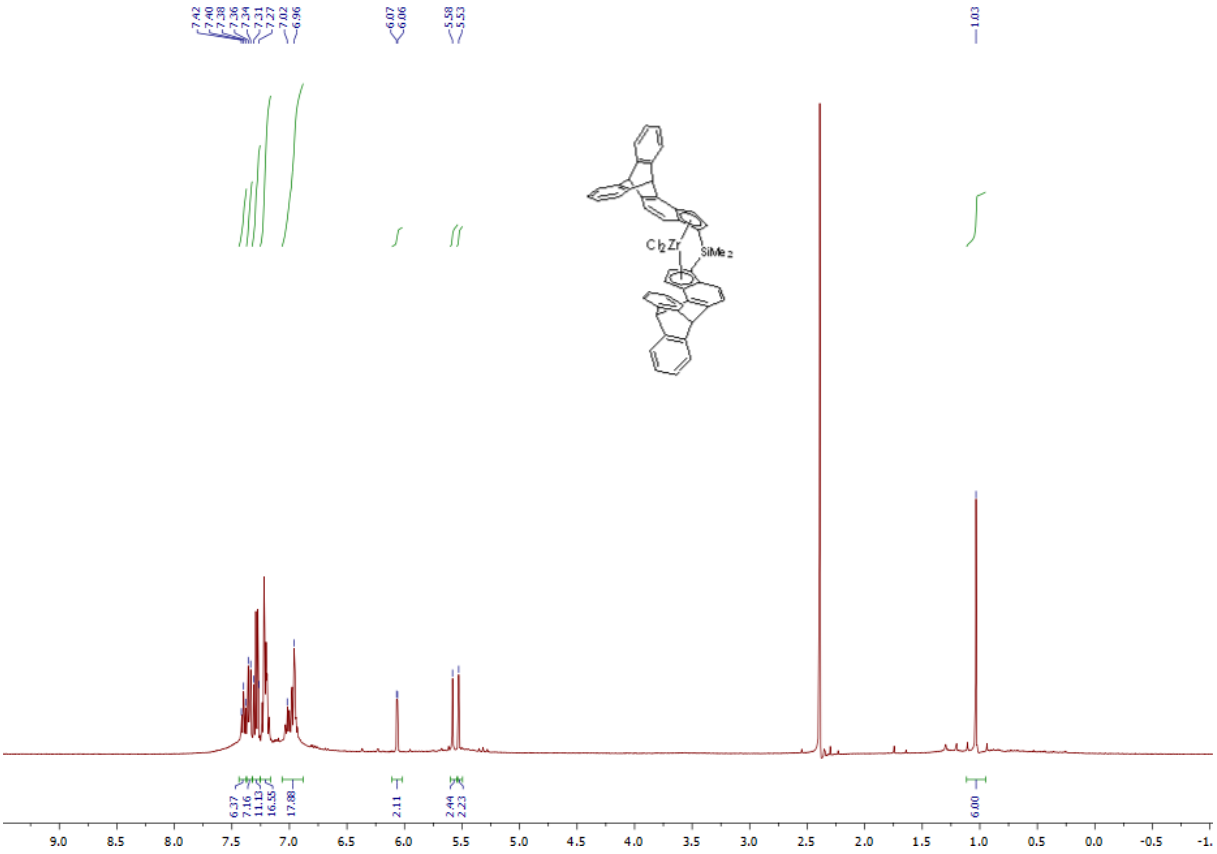


Figure S20. ^{1}H NMR spectrum of crude *rac*-**Ty5-Cl$_2$** in CD_2Cl_2 at room temperature.

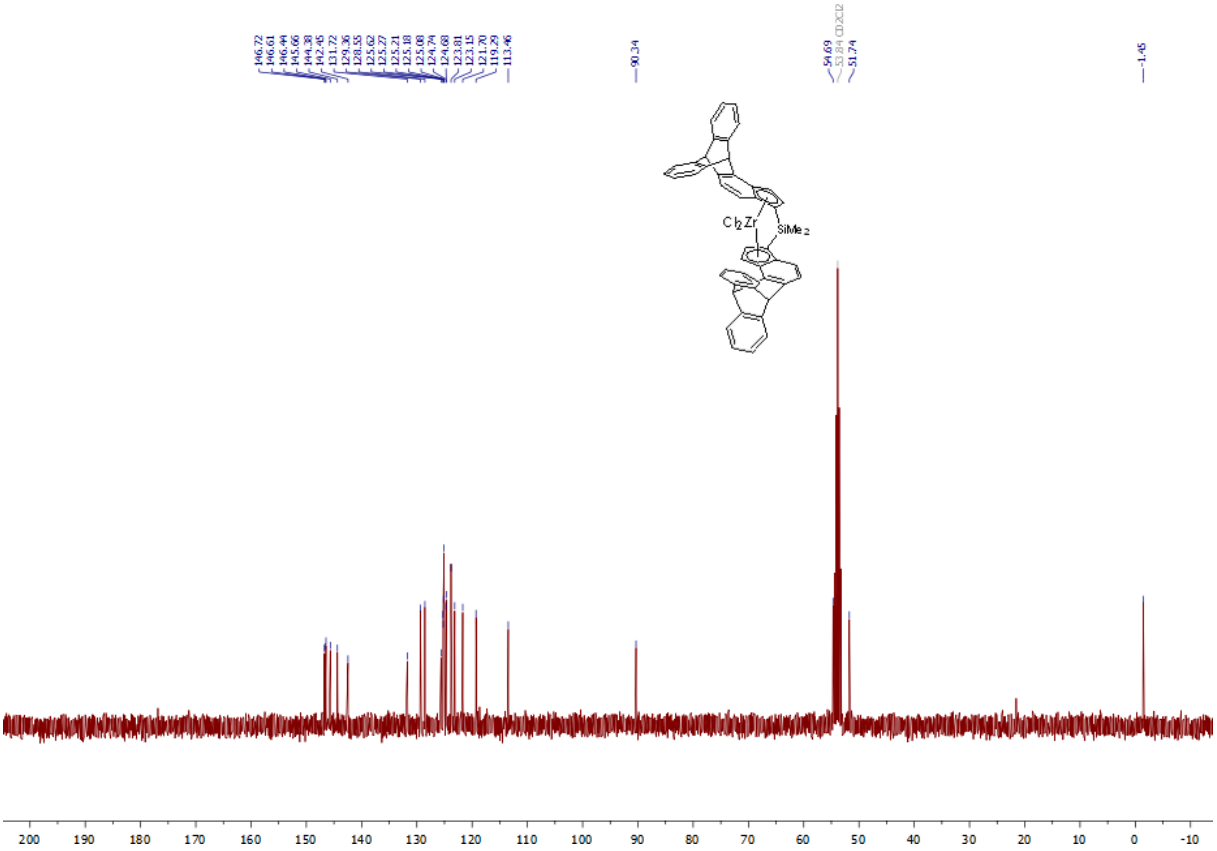


Figure S21. ^{13}C NMR spectrum of crude *rac*-**Ty5-Cl$_2$** in CD_2Cl_2 at room temperature.

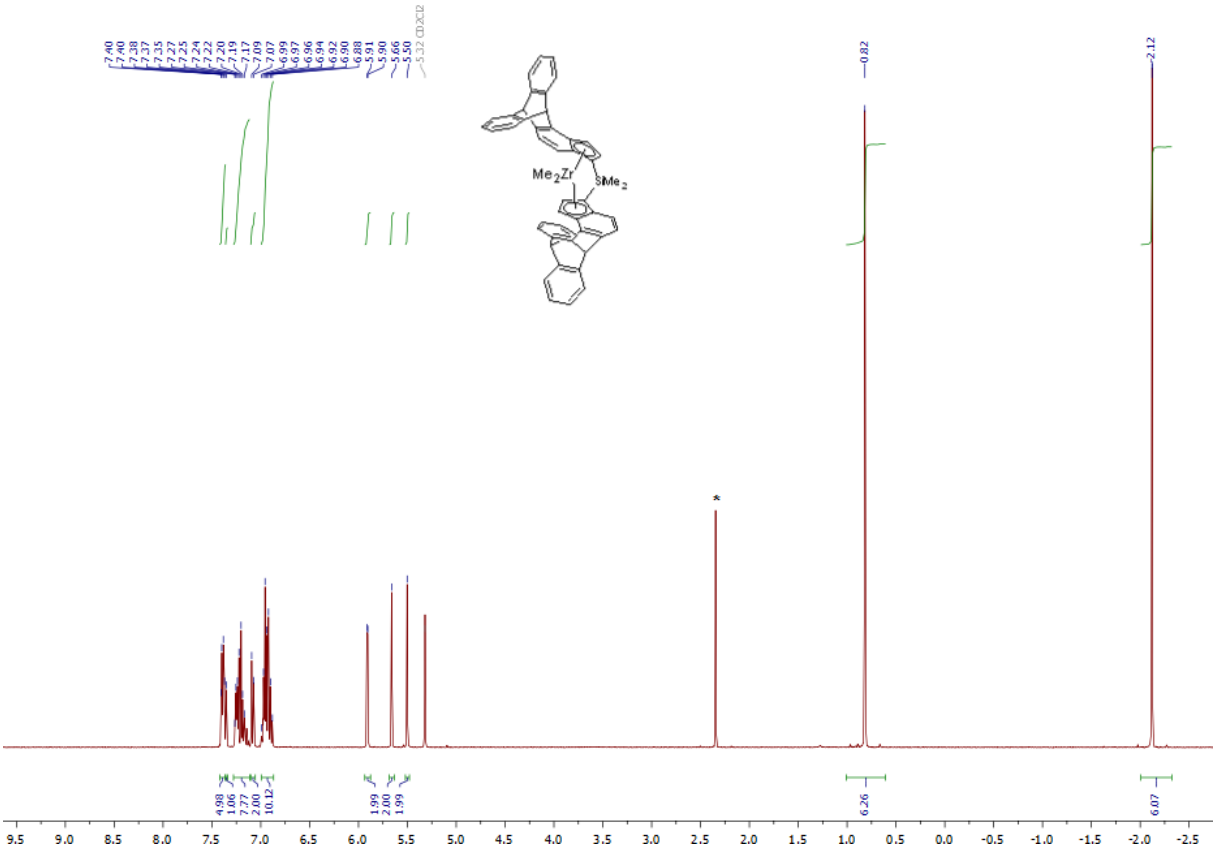


Figure S22. ^{1}H NMR spectrum of *rac*-**Ty5** in CD_2Cl_2 at room temperature. (*****) – signals of toluene.

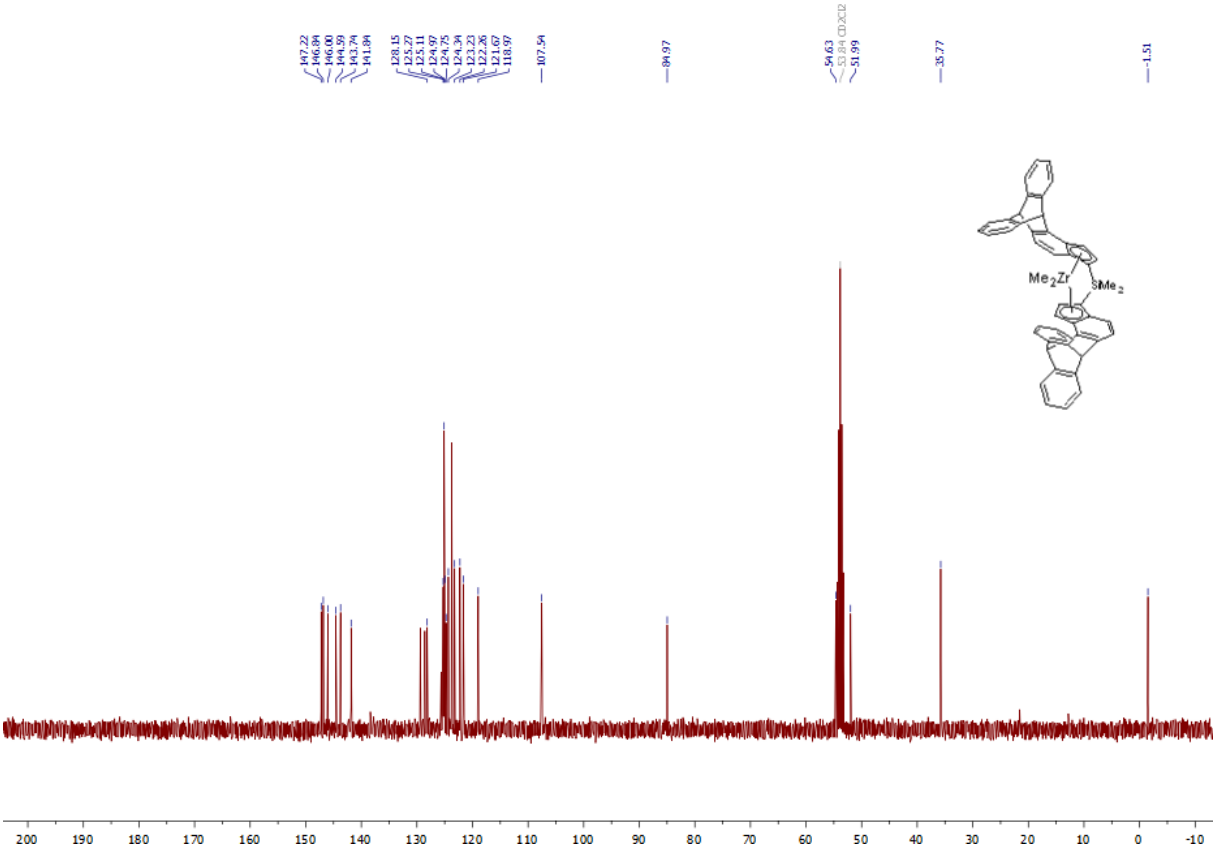


Figure S23. ^{13}C NMR spectrum of *rac*-**Ty5** in CD_2Cl_2 at room temperature.

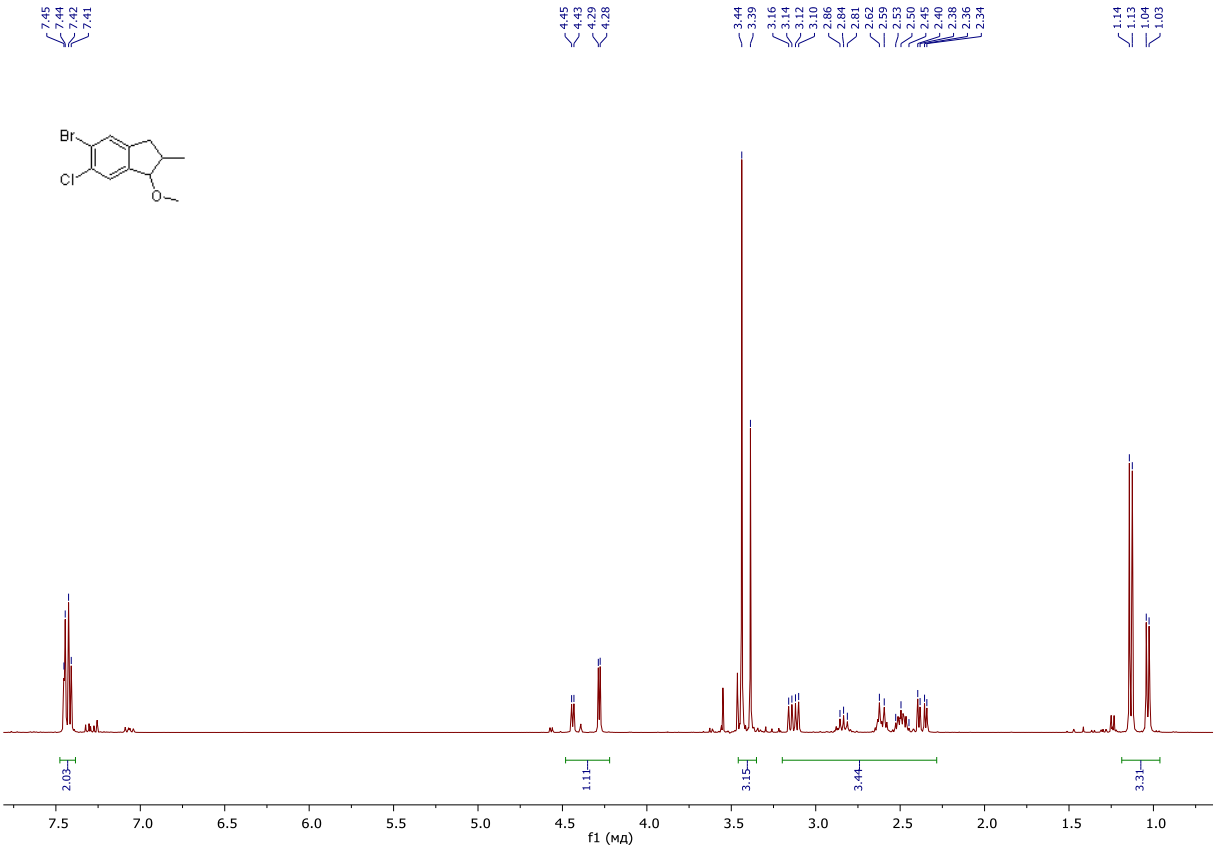


Figure S24. ^{1}H NMR spectrum of 5-bromo-6-chloro-1-methoxy-2-methylindane (**6b**) in $CDCl_3$ at room temperature.

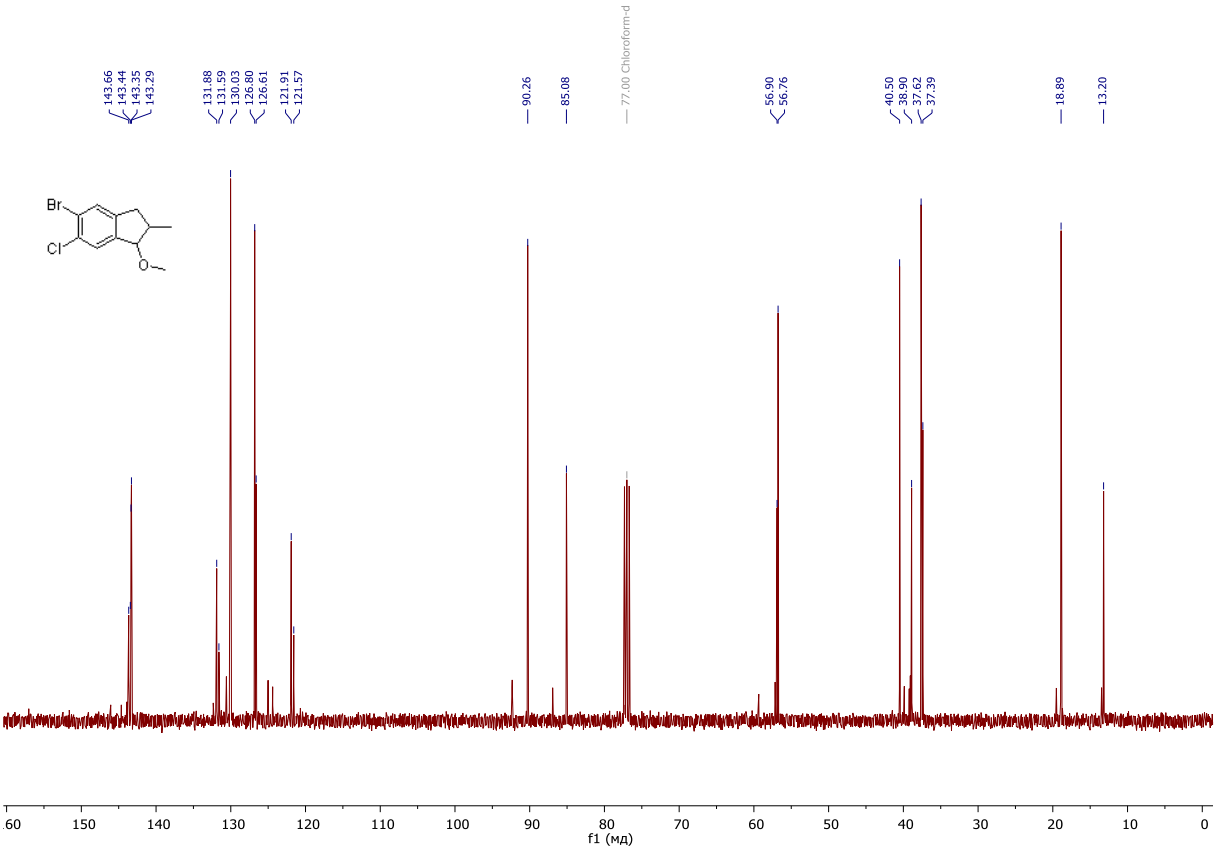


Figure S25. ^{13}C NMR spectrum of 5-bromo-6-chloro-1-methoxy-2-methylindane (**6c**) in $CDCl_3$ at room temperature.

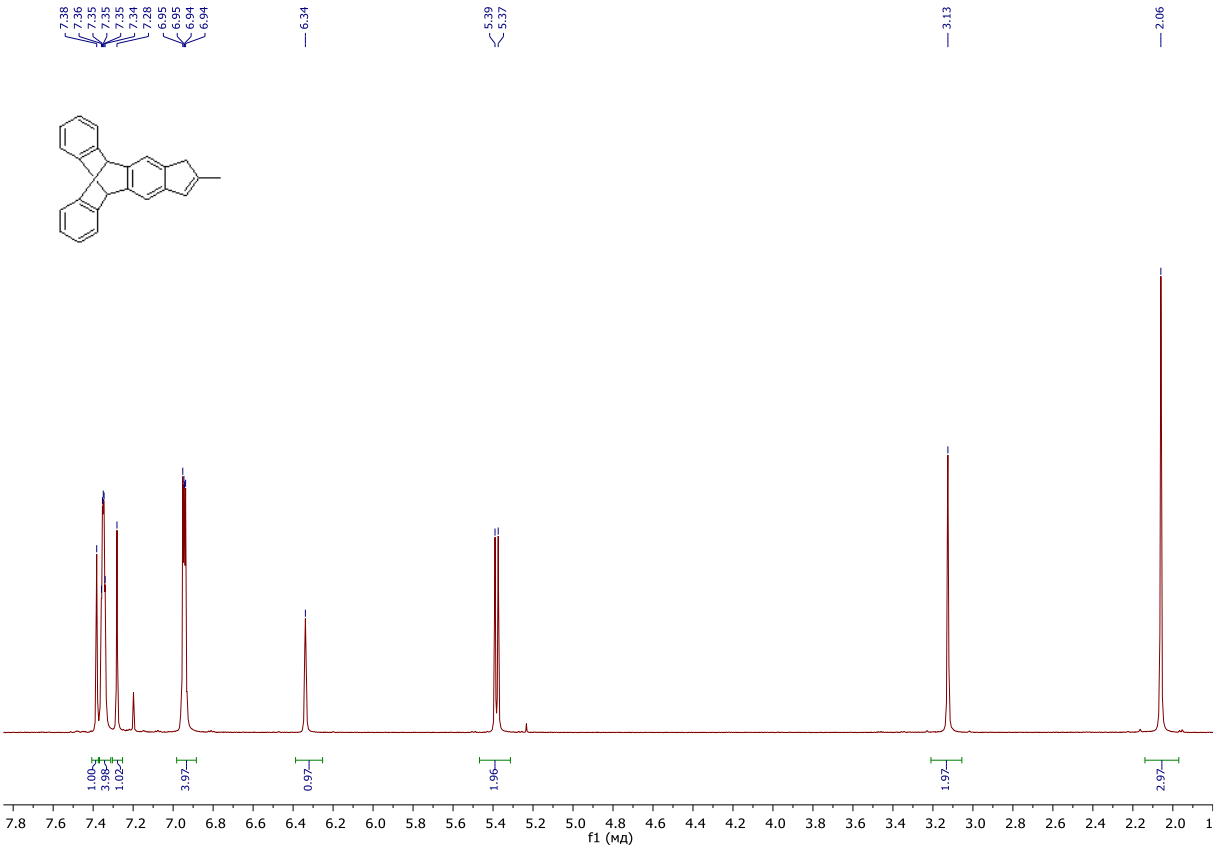


Figure S26. ^{1}H NMR spectrum of 2-methyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**6d**) in $CDCl_3$ at room temperature.

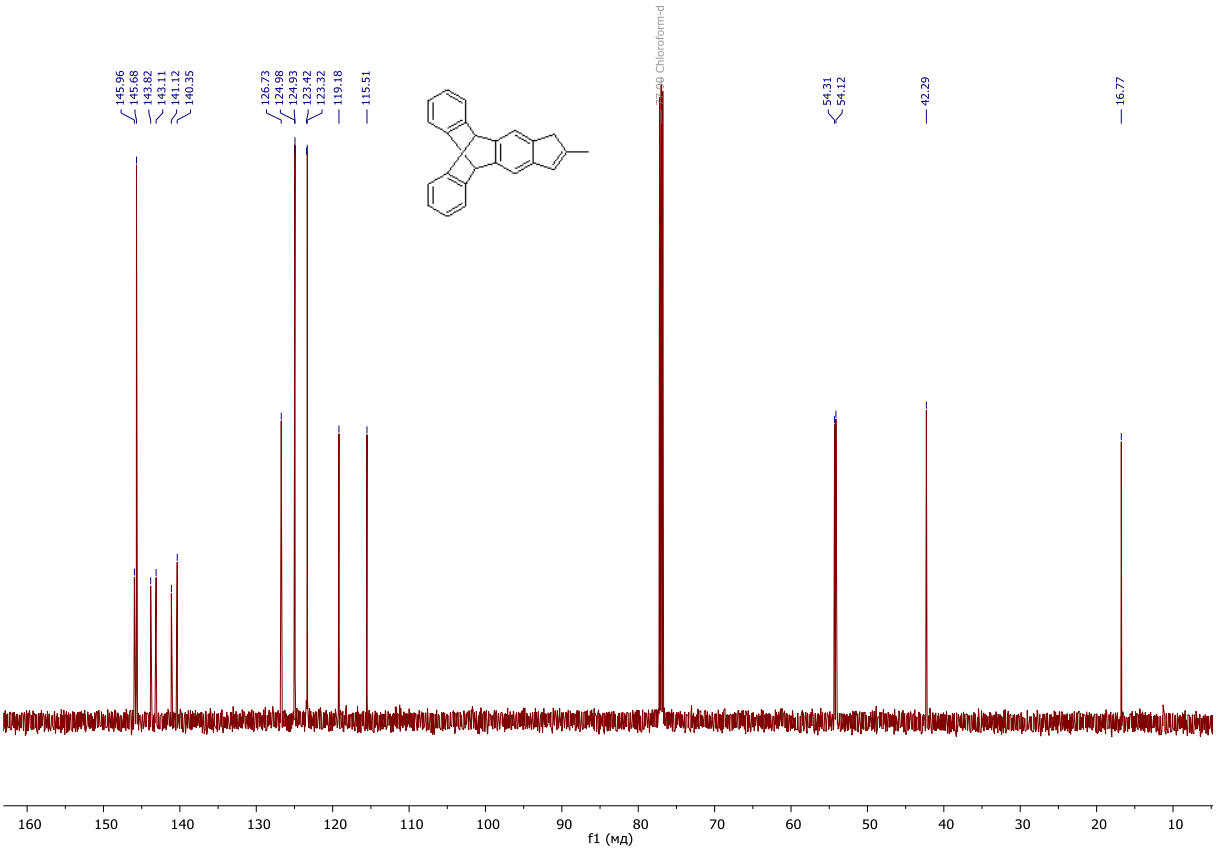


Figure S27. ^{13}C NMR spectrum of 2-methyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**6d**) in $CDCl_3$ at room temperature.

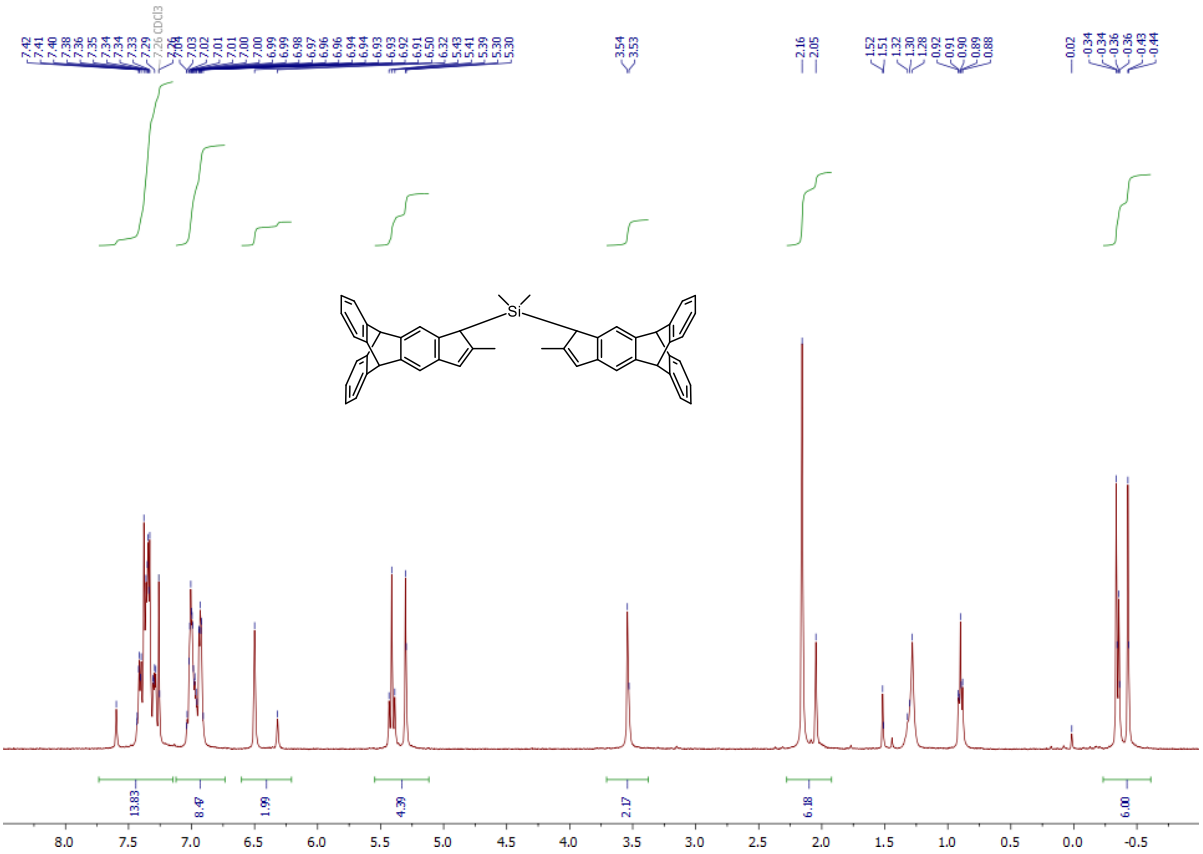


Figure S28. ^{1}H NMR spectrum of proligand **6e** in $CDCl_3$ at room temperature (residual n-hexane).

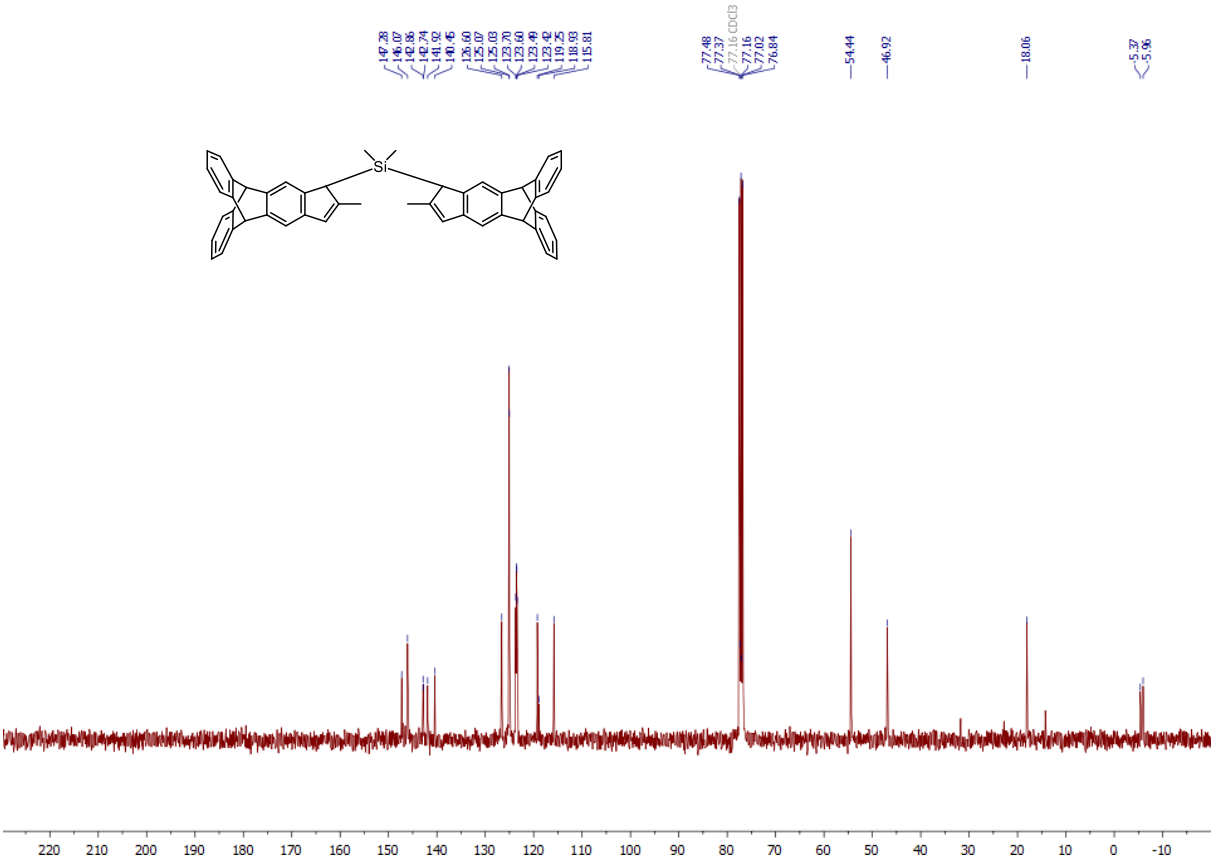


Figure S29. ^{13}C NMR spectrum of proligand **6e** in $CDCl_3$ at room temperature.

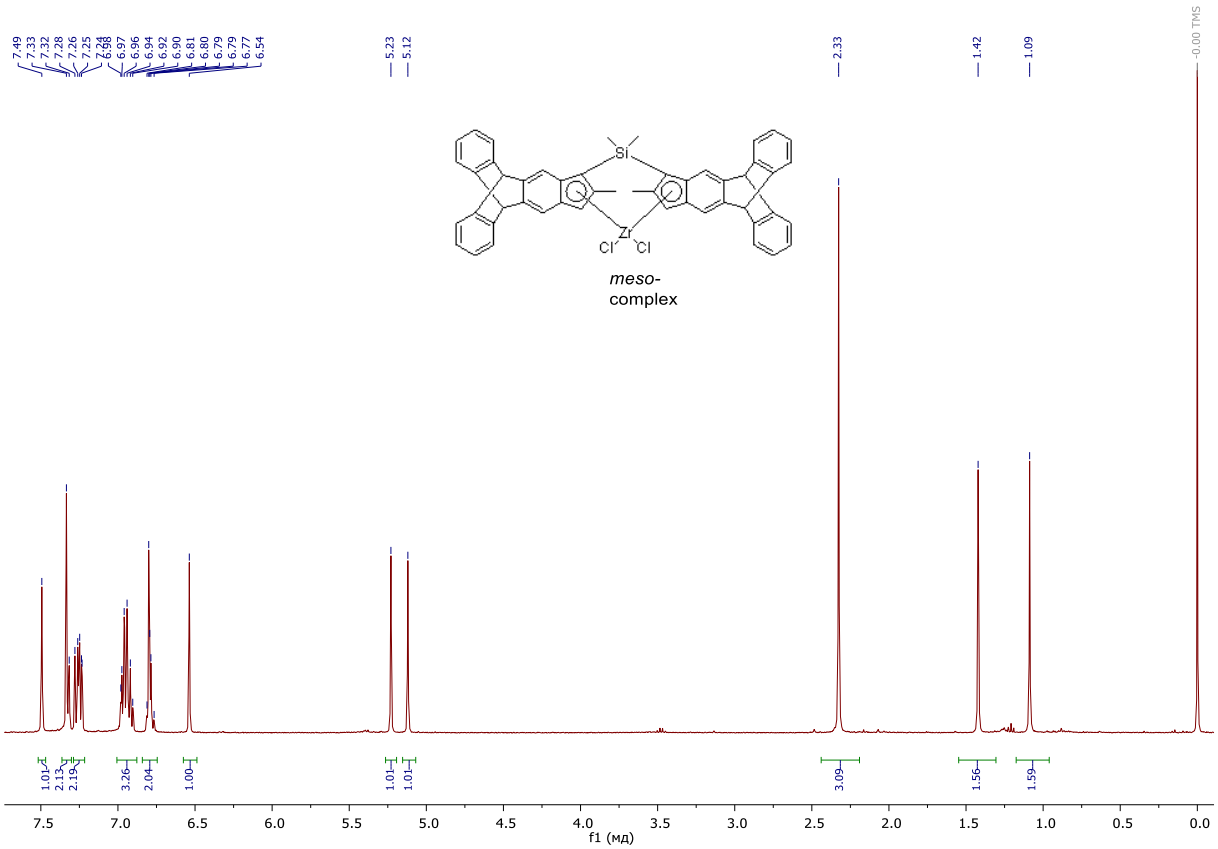


Figure S30. ^{1}H NMR spectrum of *meso*-**Ty6-Cl$_2$** in $CDCl_3$ at room temperature.

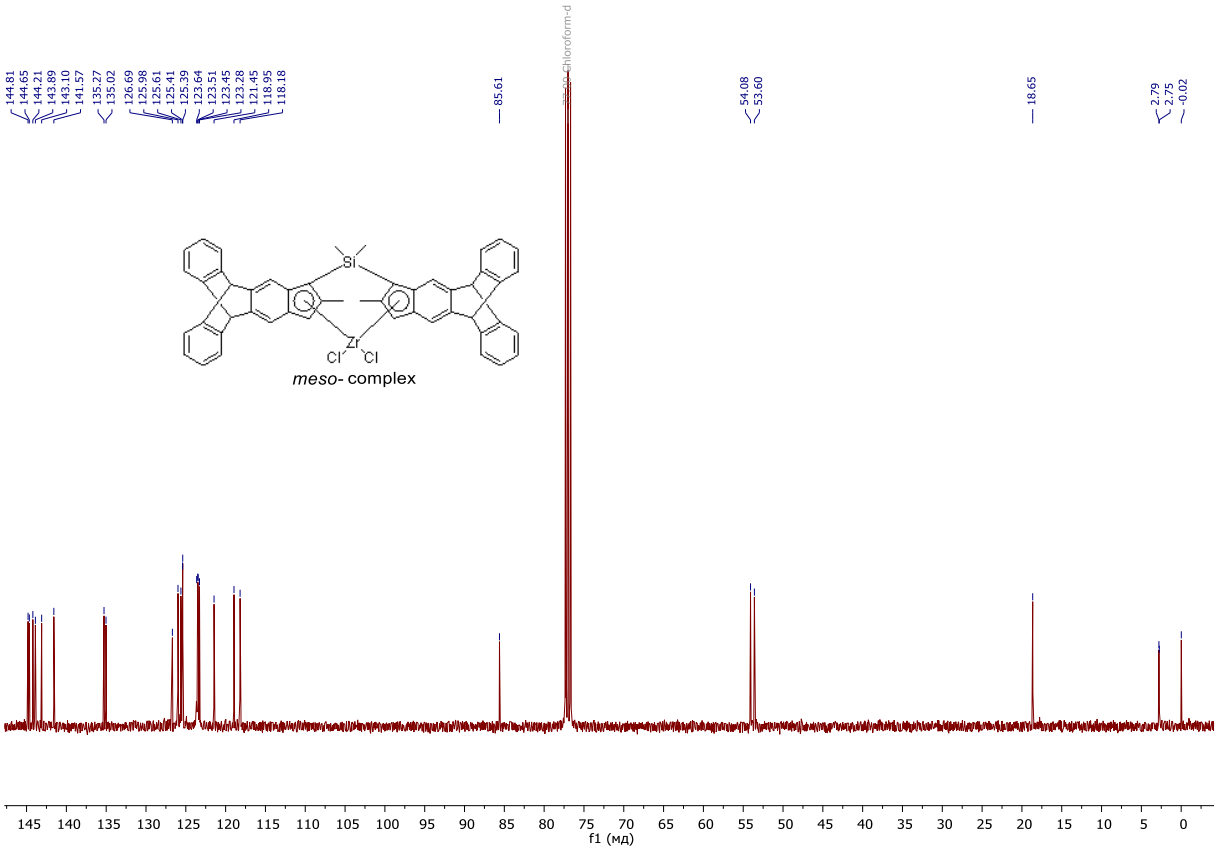


Figure S31. ^{13}C NMR spectrum of *meso*-**Ty6-Cl$_2$** in $CDCl_3$ at room temperature.

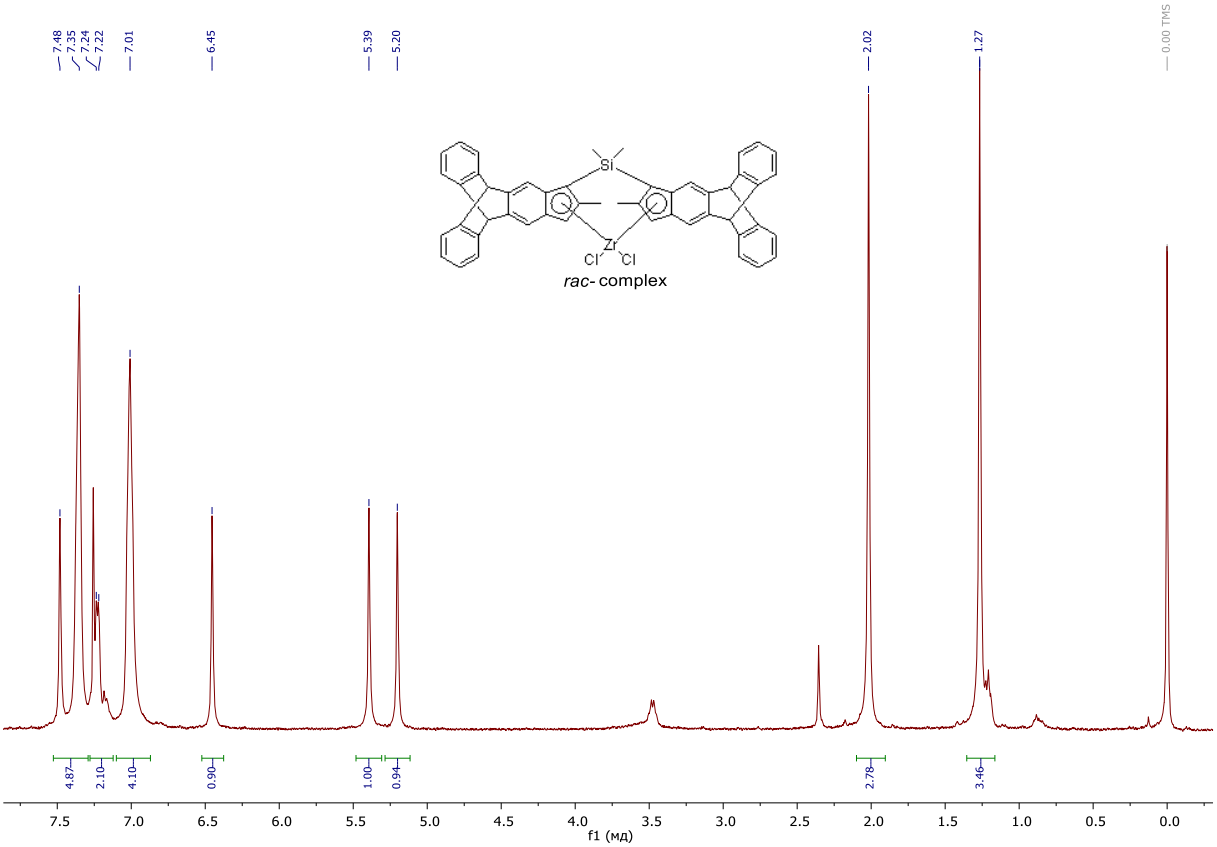


Figure S32. ^{1}H NMR spectrum of *rac*-**Ty6-Cl$_2$** in $CDCl_3$ at room temperature.

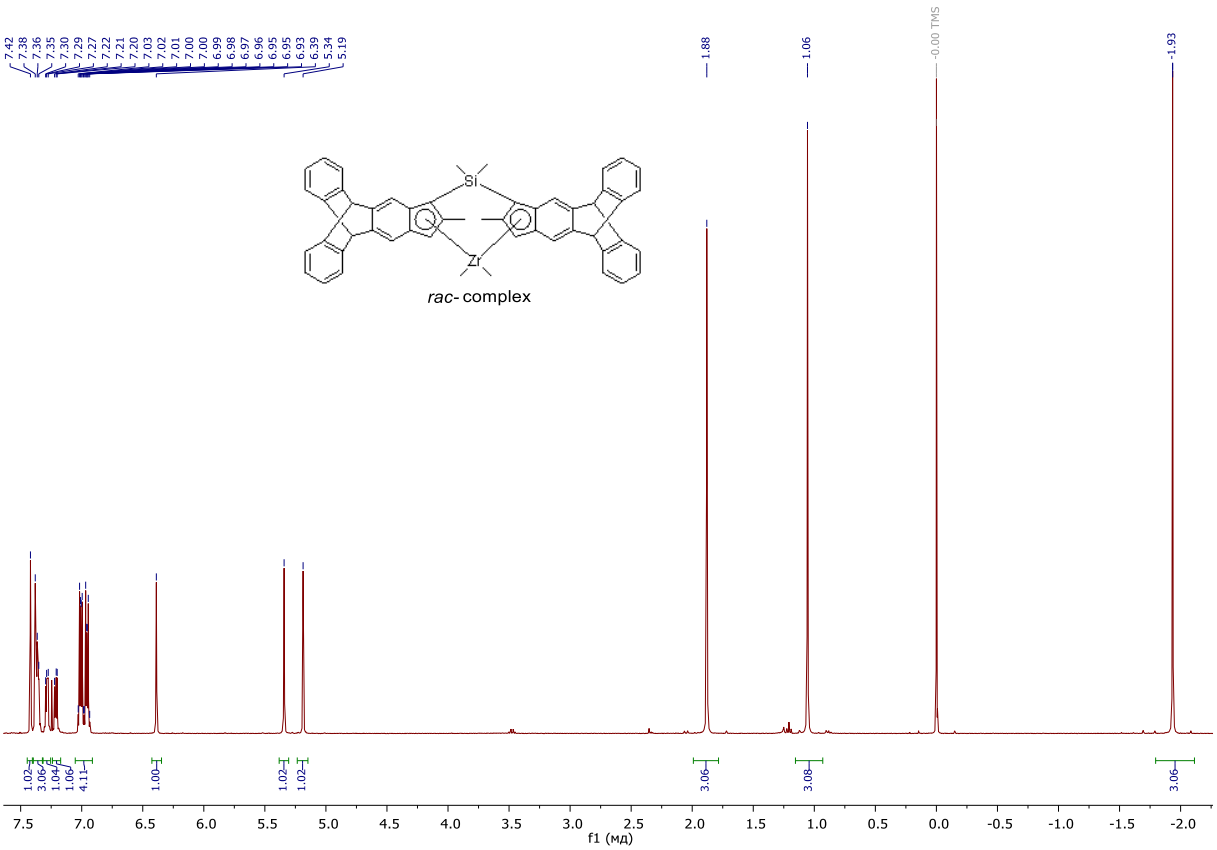


Figure S33. ^{1}H NMR spectrum of *rac*-**Ty6** in $CDCl_3$ at room temperature.

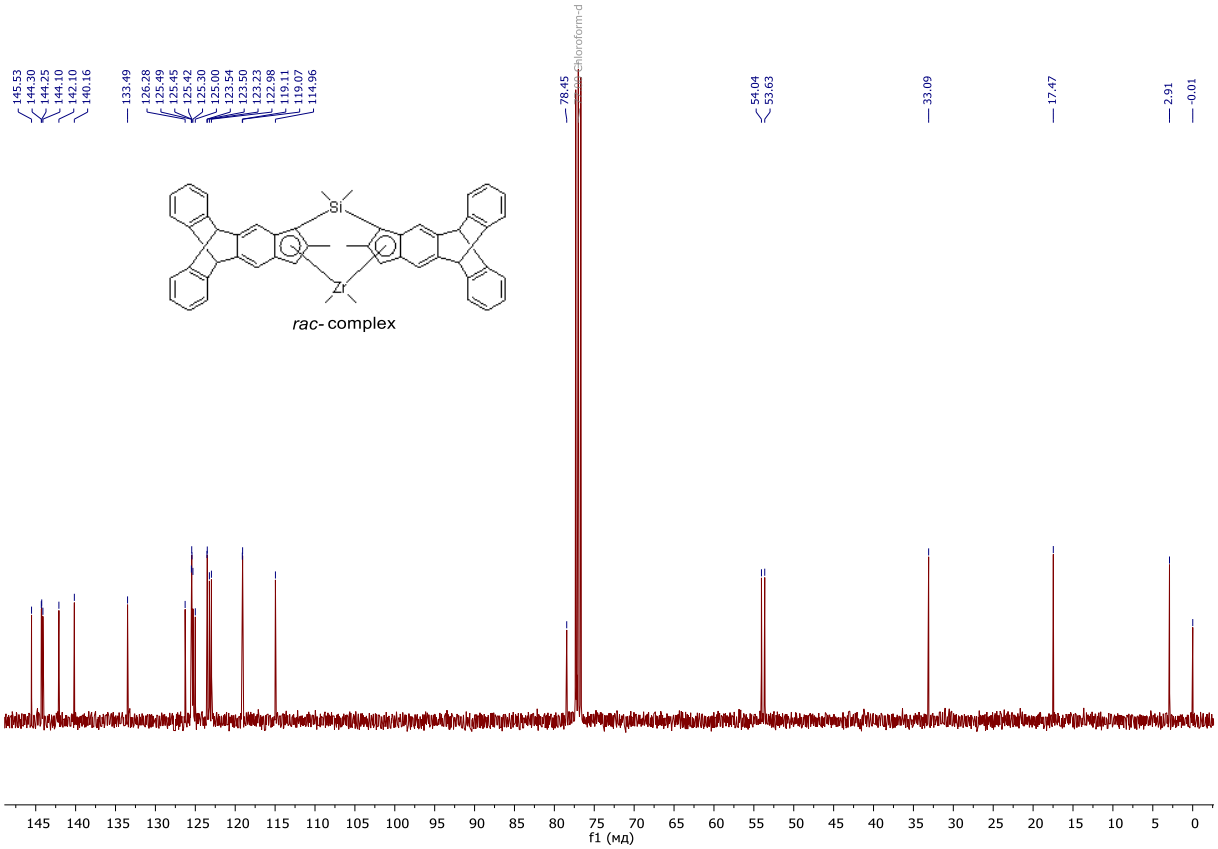


Figure S34. ^{13}C NMR spectrum of *rac*-**Ty6** in $CDCl_3$ at room temperature.

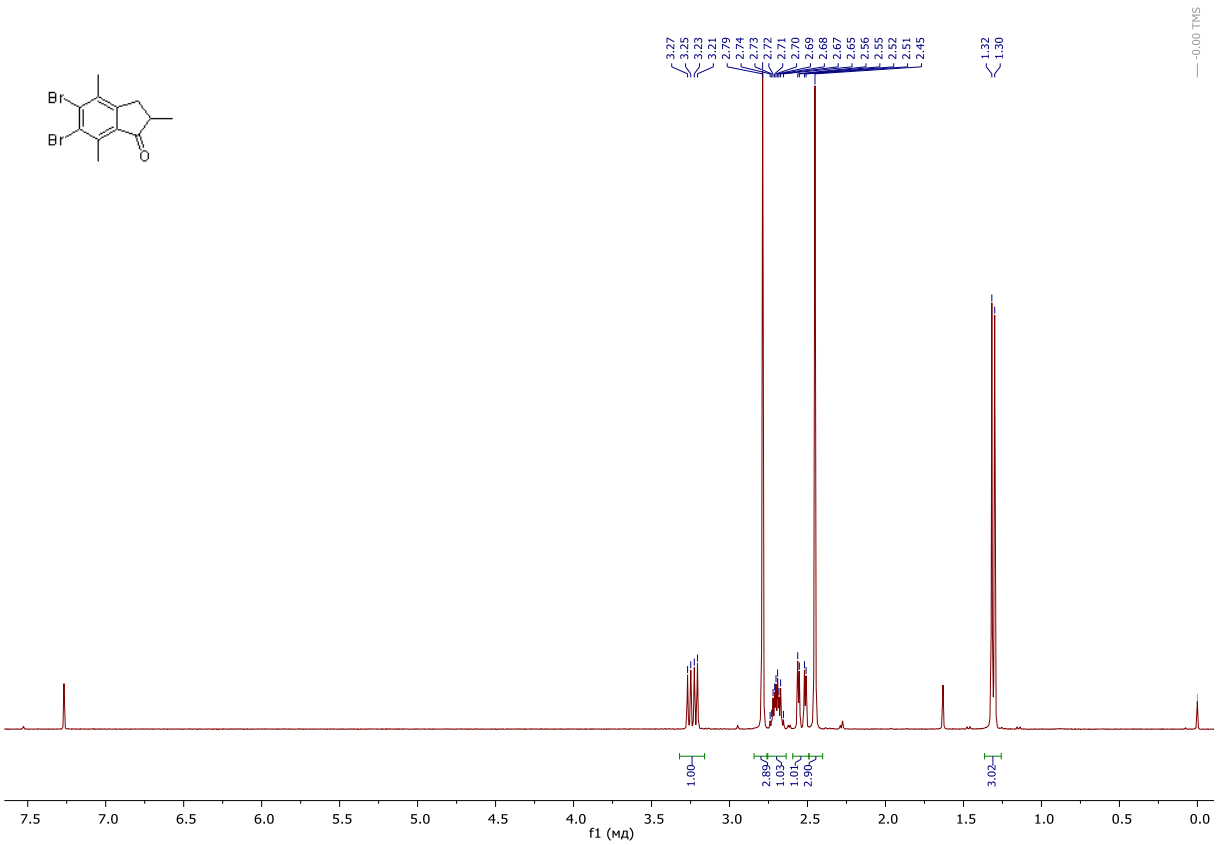


Figure S35. ^{1}H NMR spectrum of dibromo-2,4,7-trimethylindan-1-one (**7b**) in $CDCl_3$ at room temperature.

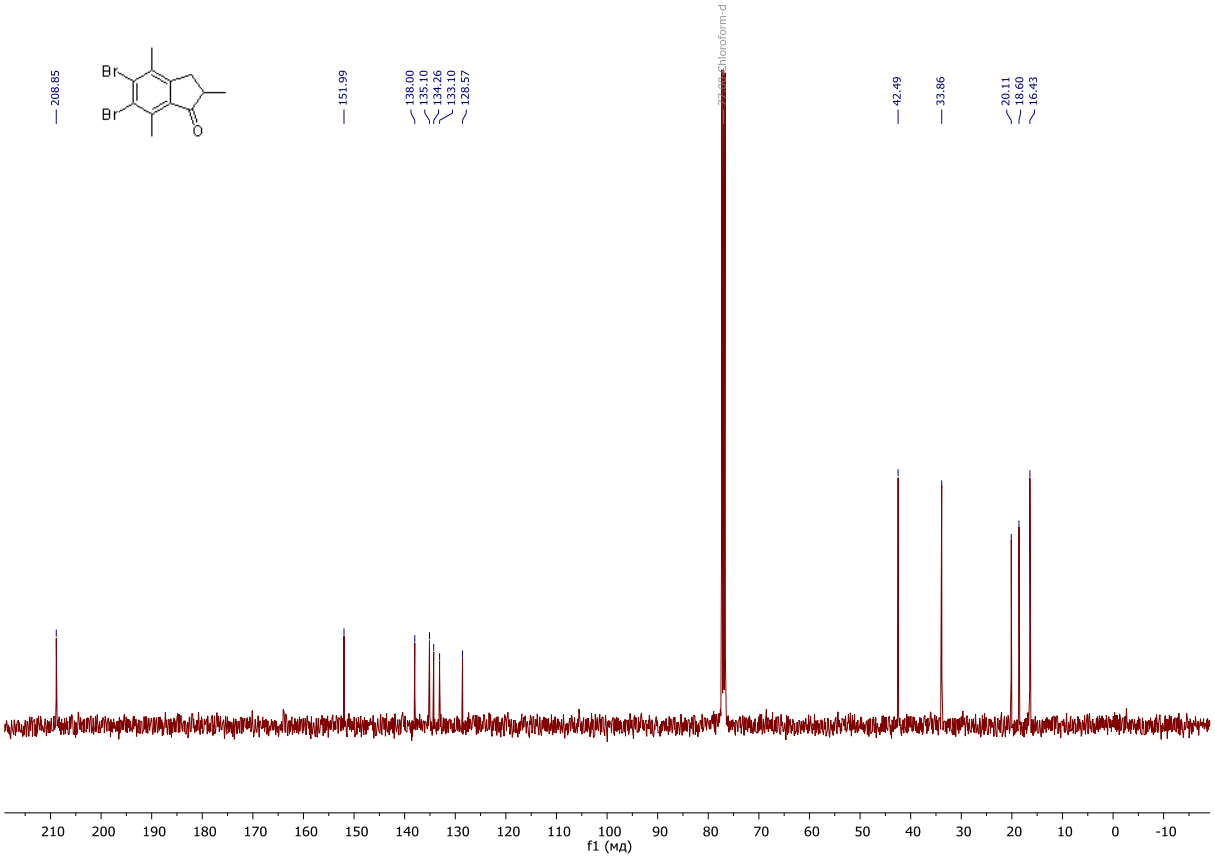


Figure S36. ^{13}C NMR spectrum of dibromo-2,4,7-trimethylindan-1-one (**7b**) in $CDCl_3$ at room temperature.

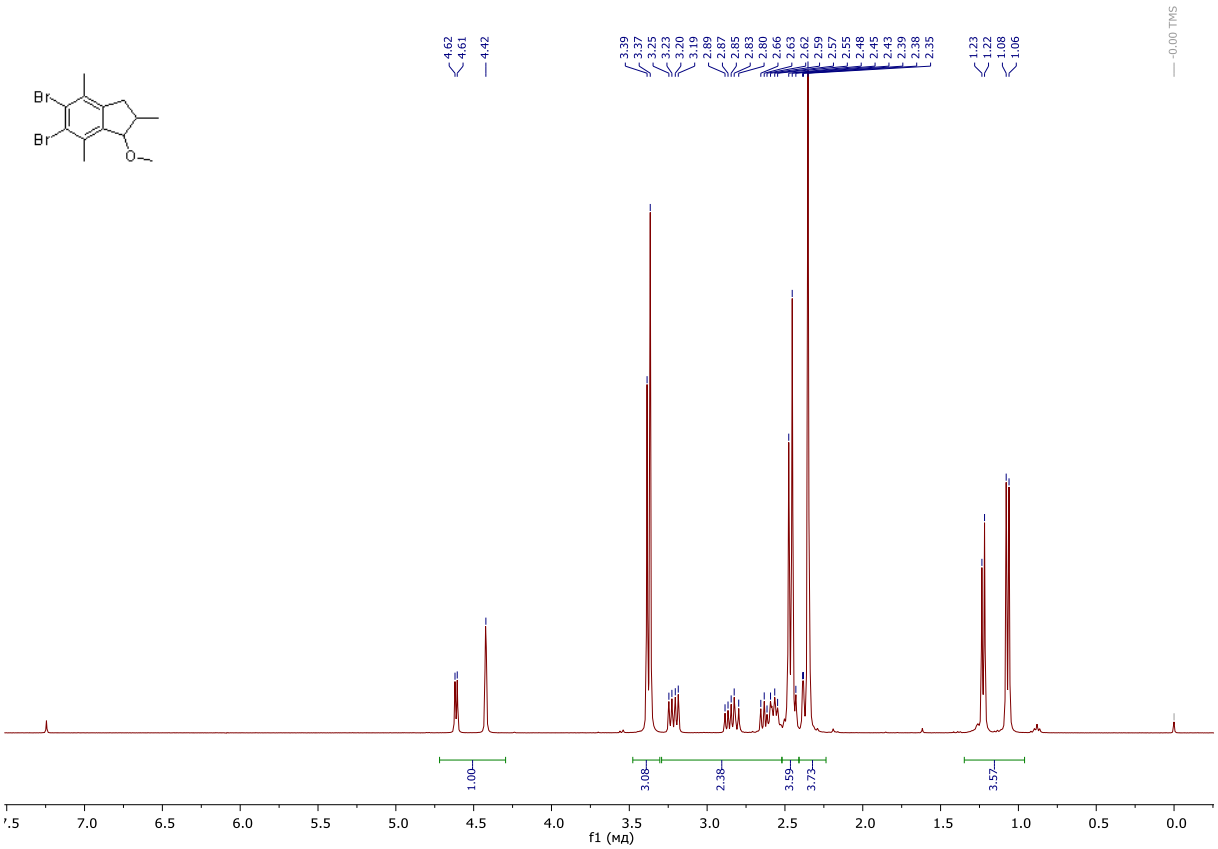


Figure S37. ^{1}H NMR spectrum of 5,6-dibromo-1-methoxy-2,4,7-trimethylindane (**7c**) in $CDCl_3$ at room temperature.

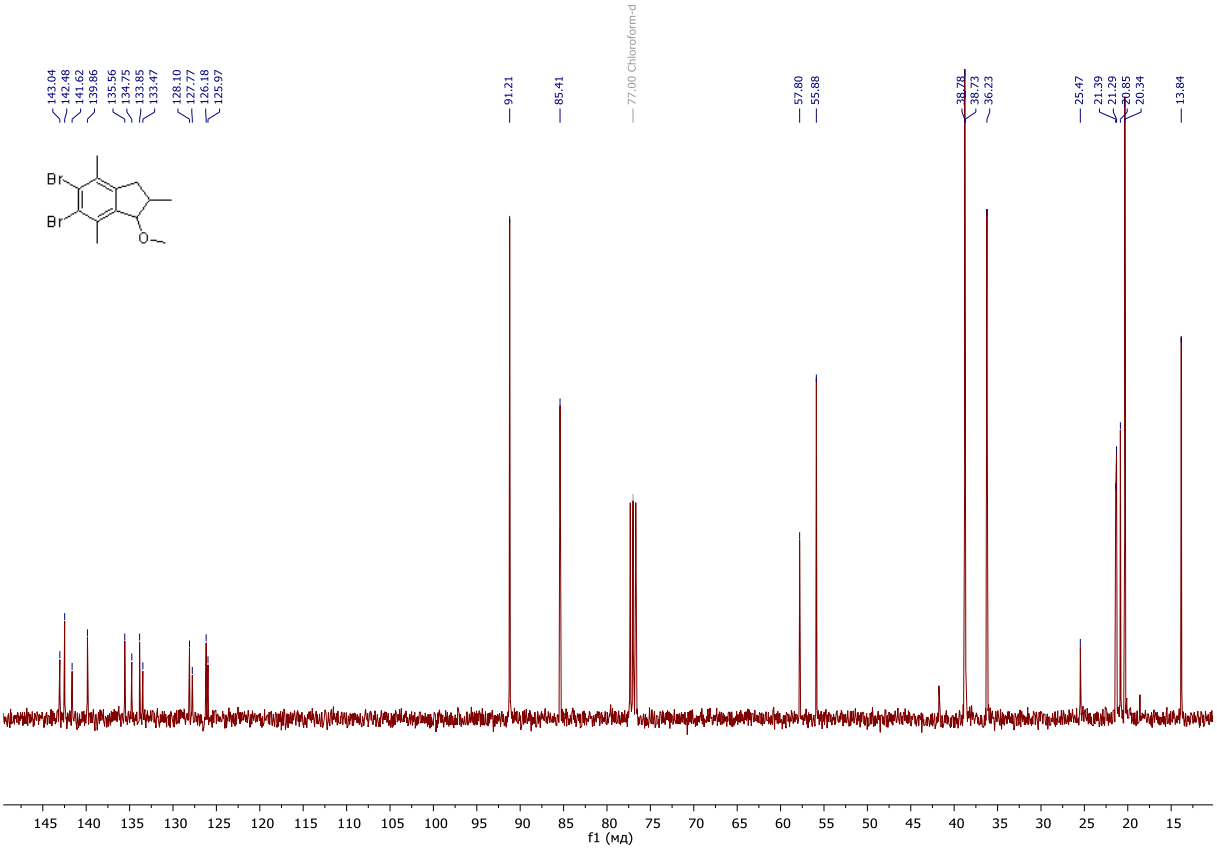


Figure S38. ^{13}C NMR spectrum of 5,6-dibromo-1-methoxy-2,4,7-trimethylindane (**7c**) in $CDCl_3$ at room temperature.

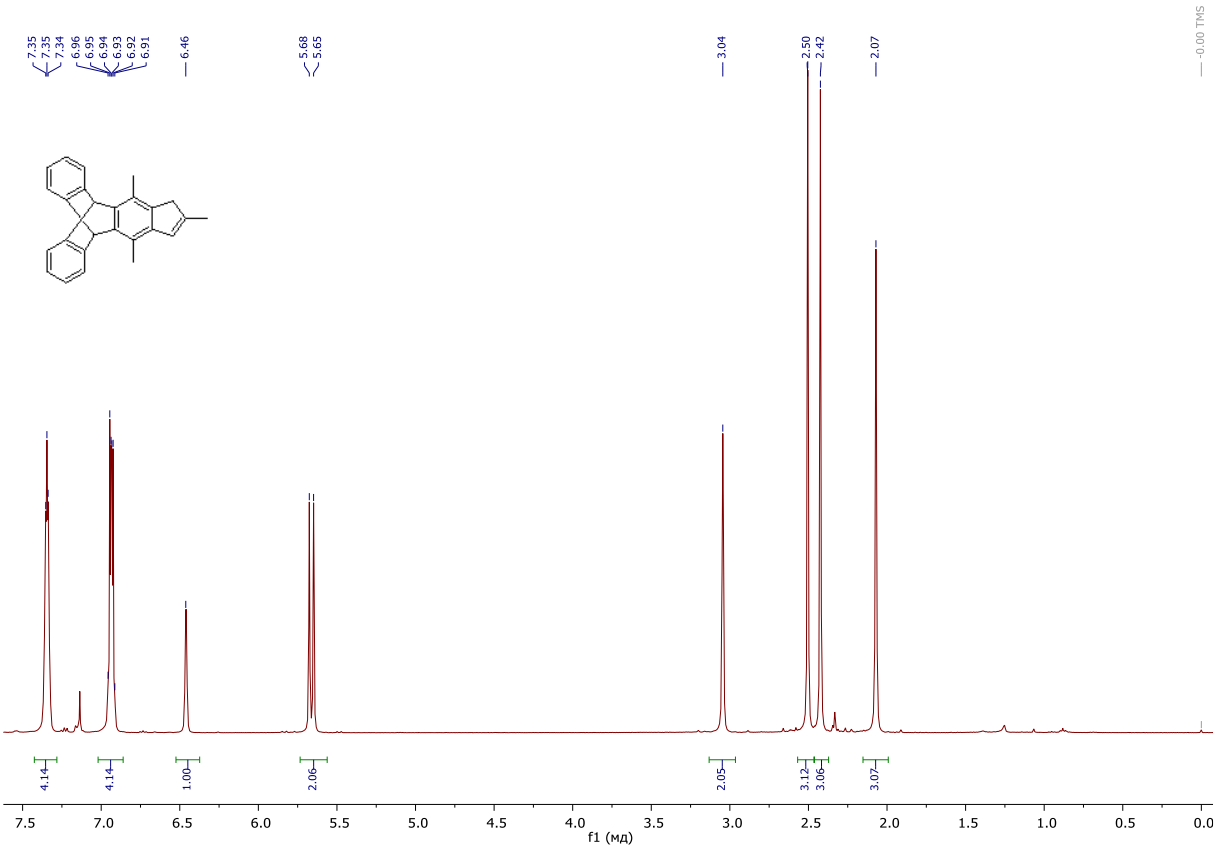


Figure S39. ^{1}H NMR spectrum of 2,4,7-trimethyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**7d**)_n $CDCl_3$ at room temperature.

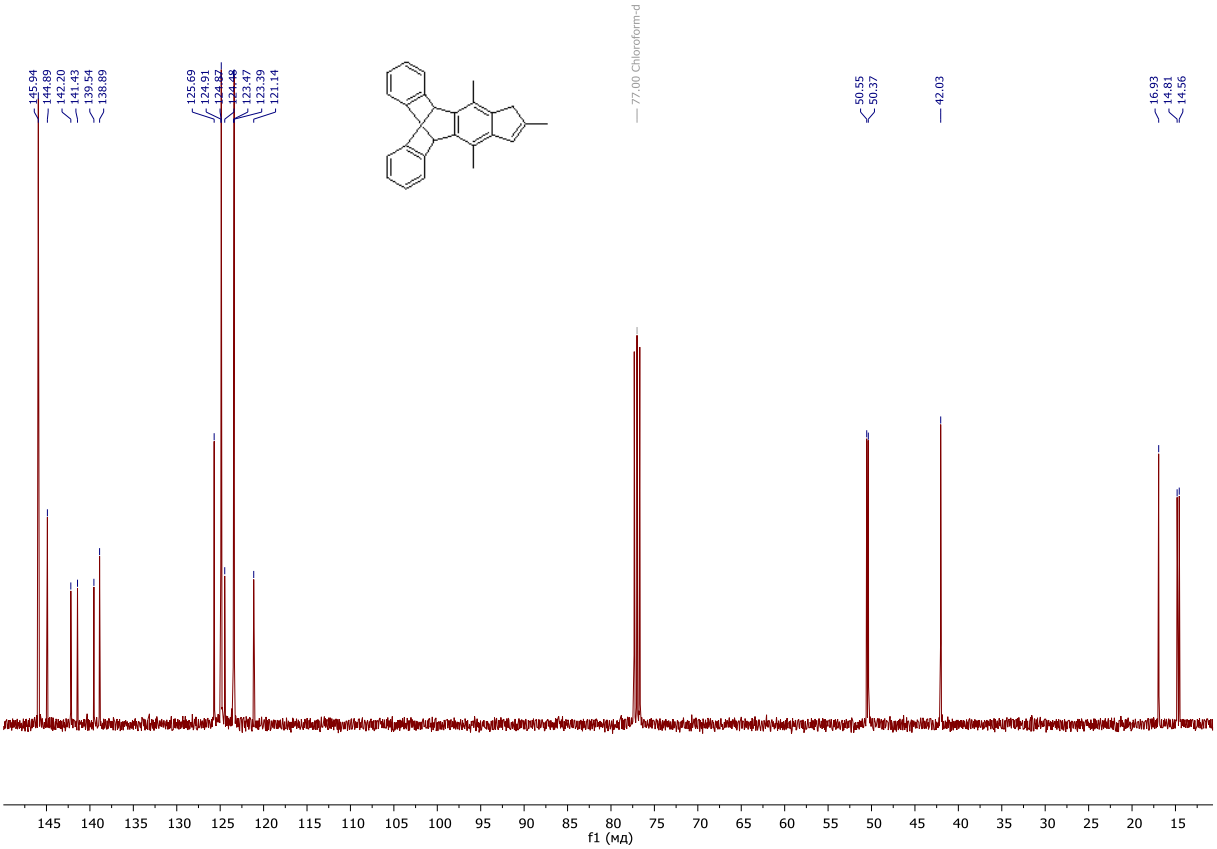


Figure S40. ^{13}C NMR spectrum of 2,4,7-trimethyl-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**7d**) in $CDCl_3$ at room temperature.

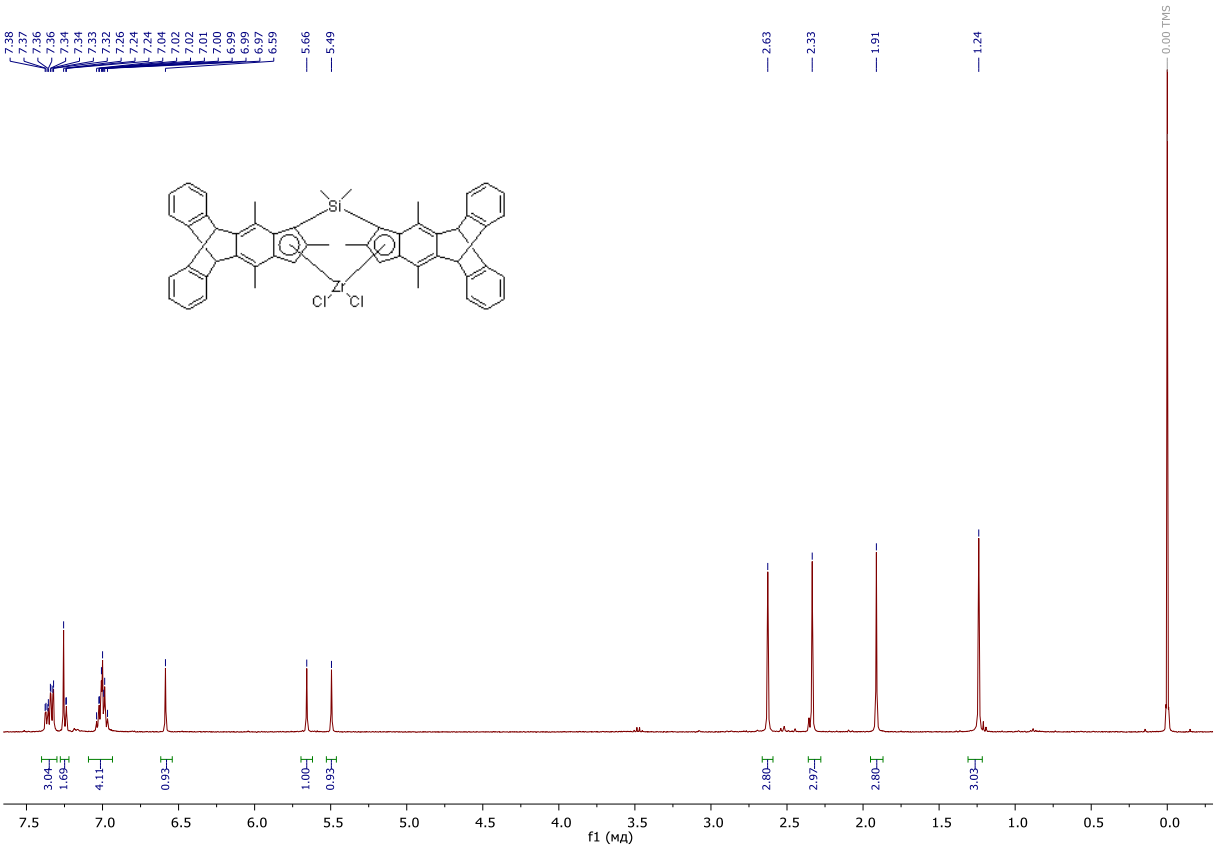


Figure S41. ^{1}H NMR spectrum of *rac*-**Ty7-Cl$_2$** in $CDCl_3$ at room temperature.

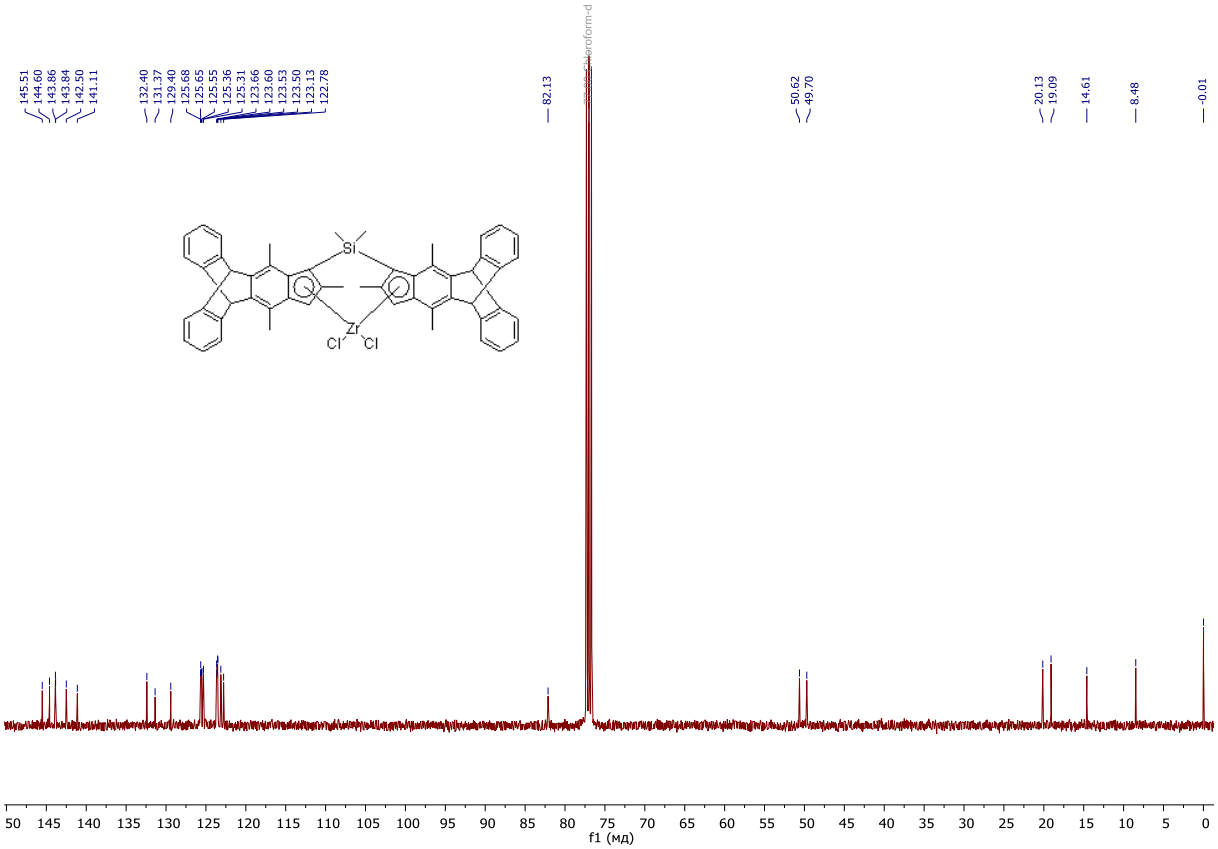


Figure S42. ^{13}C NMR spectrum of *rac*-**Ty7-Cl$_2$** in $CDCl_3$ at room temperature.

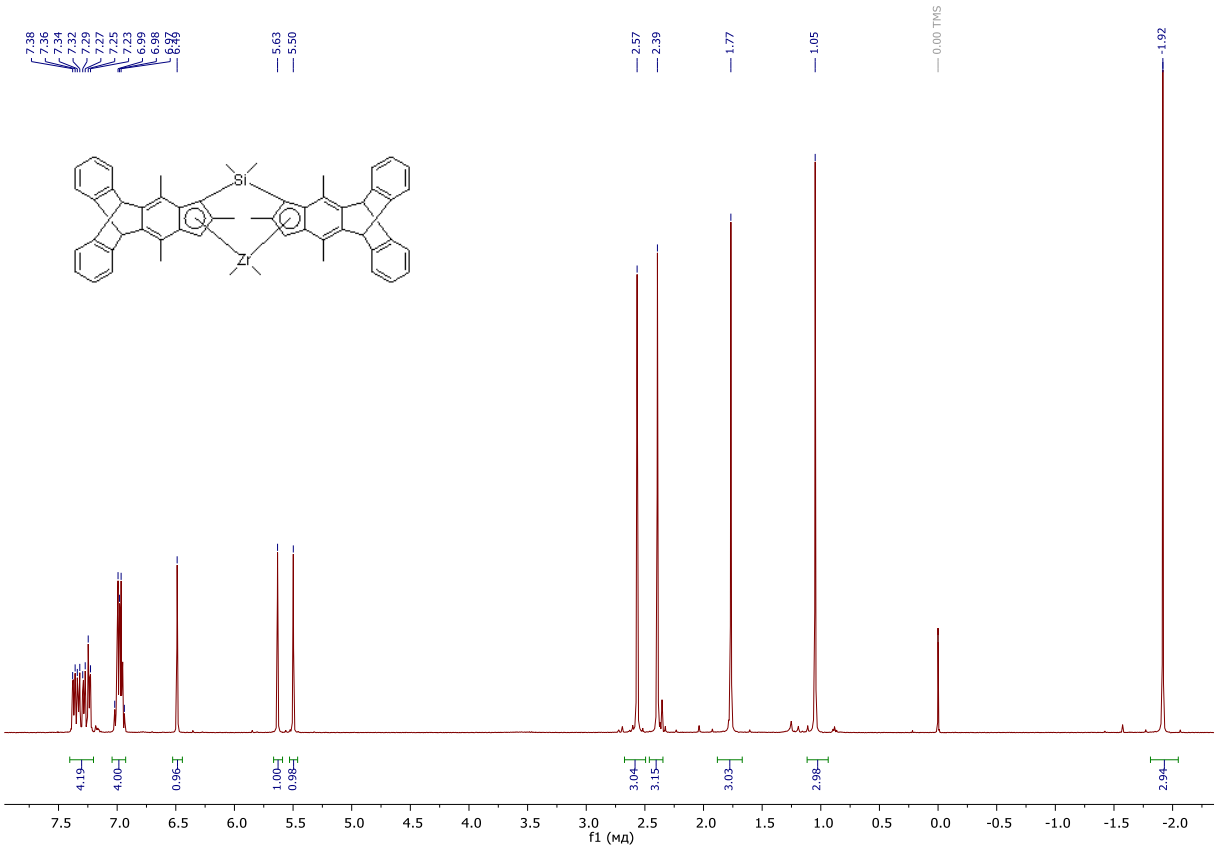


Figure S43. ^{1}H NMR spectrum of *rac*-**Ty7** in $CDCl_3$ at room temperature.

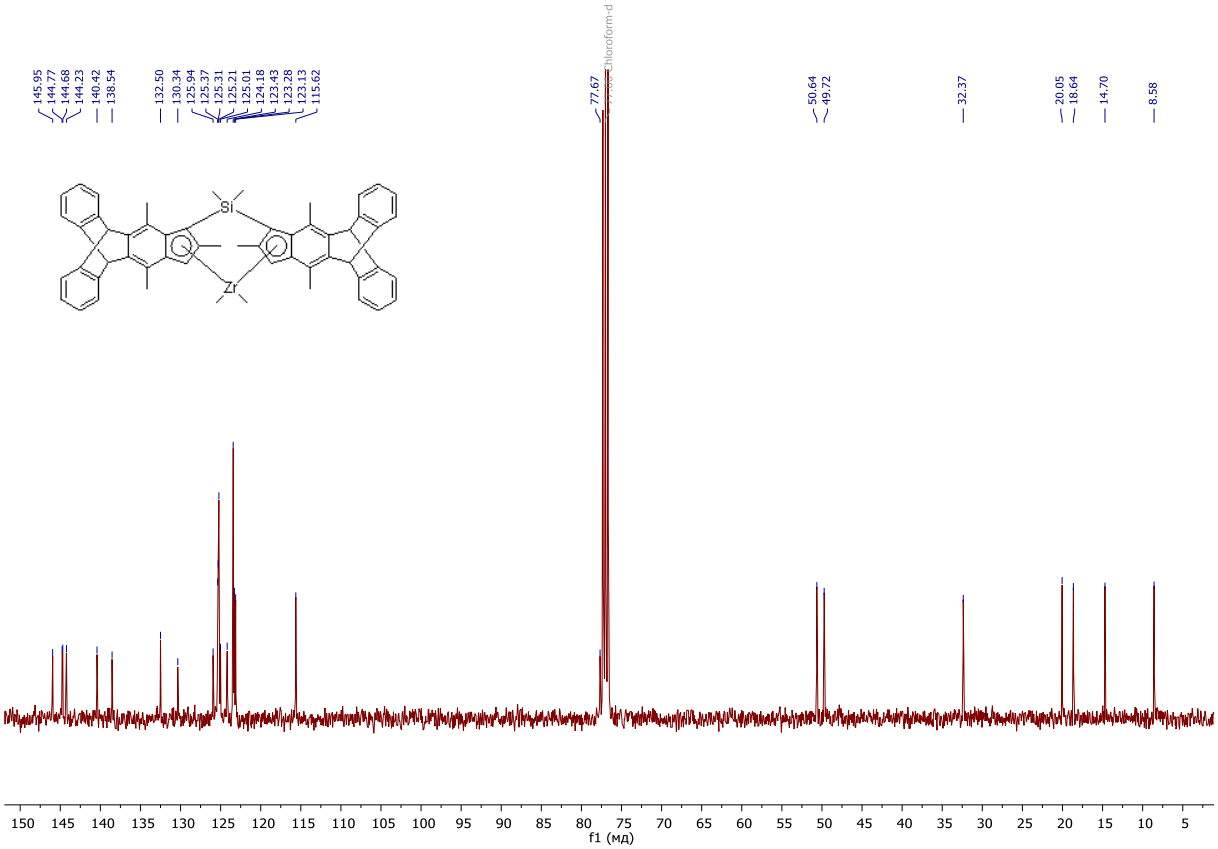


Figure S44. ^{13}C NMR spectrum of *rac*-**Ty7** in $CDCl_3$ at room temperature.

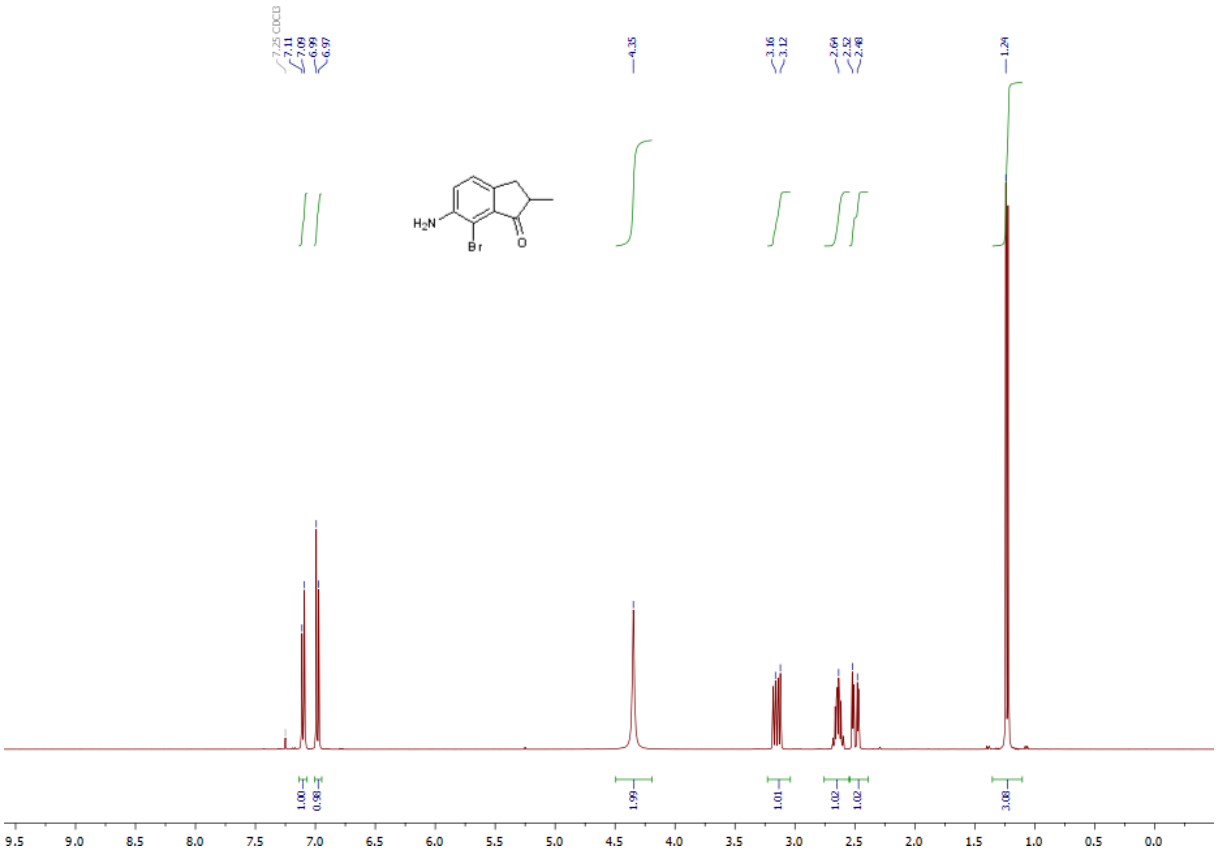


Figure S45. ^{1}H NMR spectrum of 6-amino-7-bromo-2-methylindan-1-one in $CDCl_3$ at room temperature.

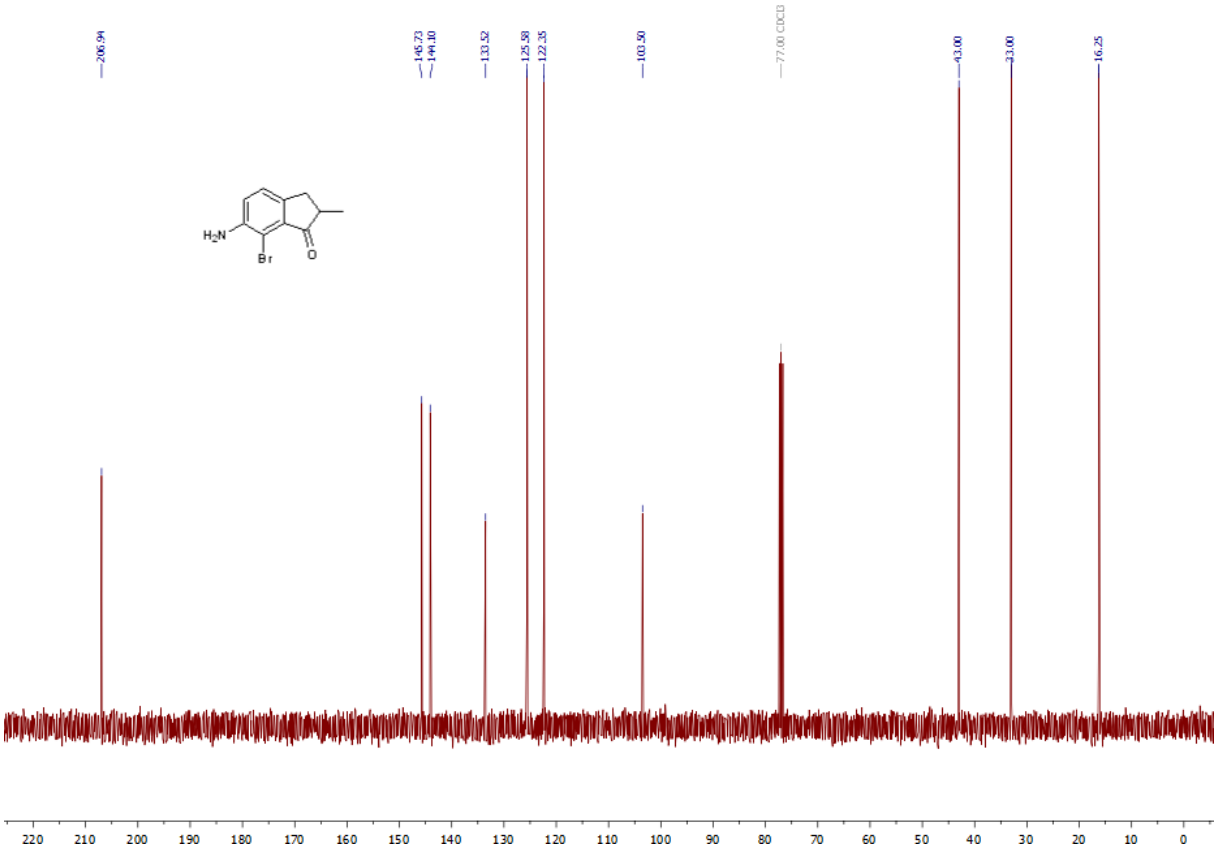


Figure S46. ^{13}C NMR spectrum of 6-amino-7-bromo-2-methylindan-1-one in $CDCl_3$ at room temperature.

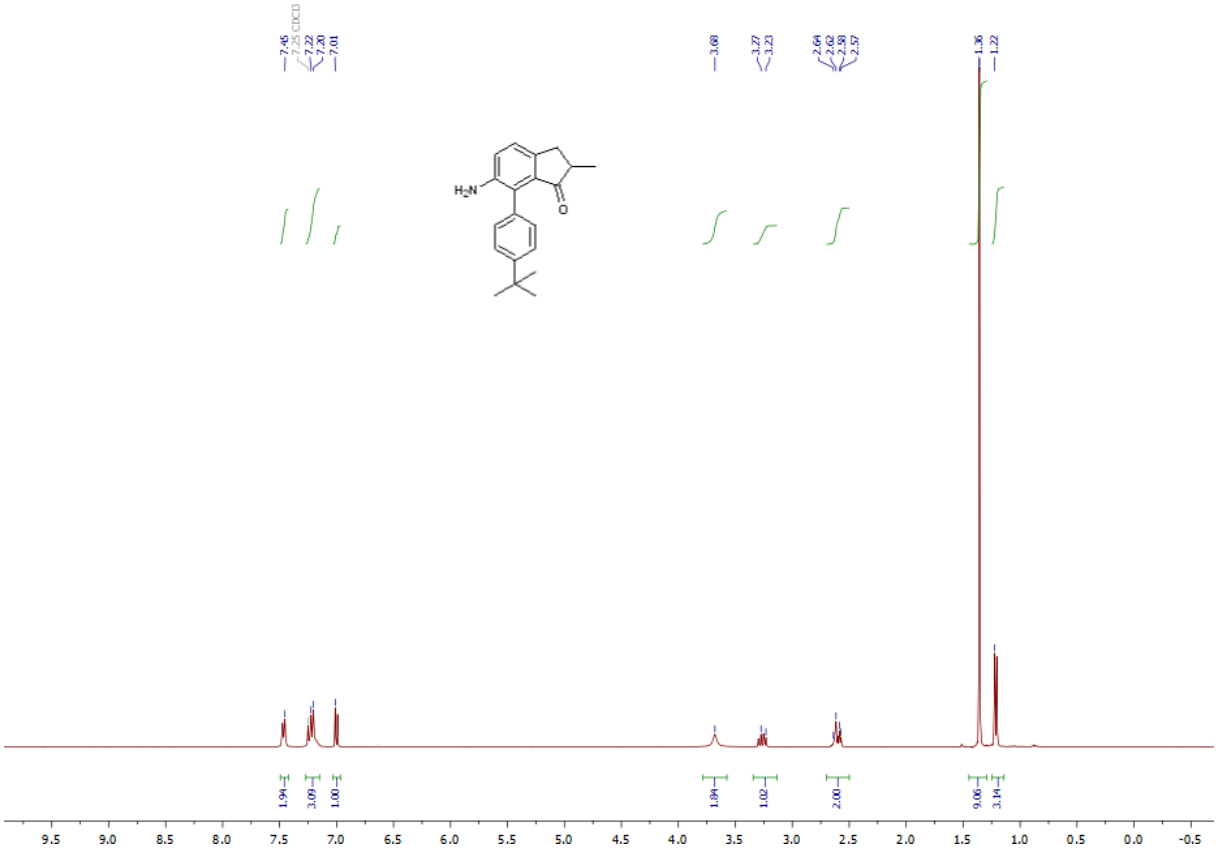


Figure S47. ^{1}H NMR spectrum of 6-amino-7-(4-*tert*-butylphenyl)-2-methylindan-1-one in $CDCl_3$ at room temperature.

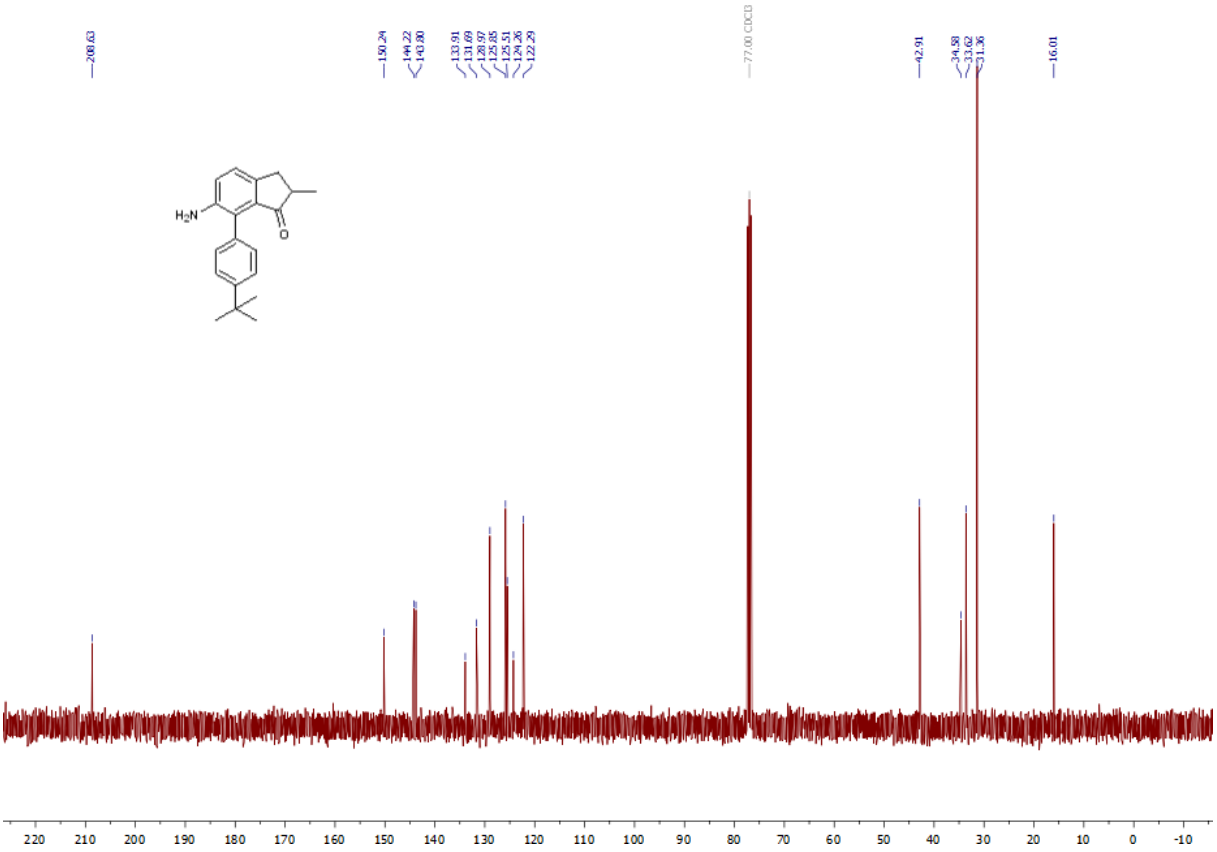


Figure S48. ^{13}C NMR spectrum of 6-amino-7-(4-*tert*-butylphenyl)-2-methylindan-1-one in $CDCl_3$ at room temperature.

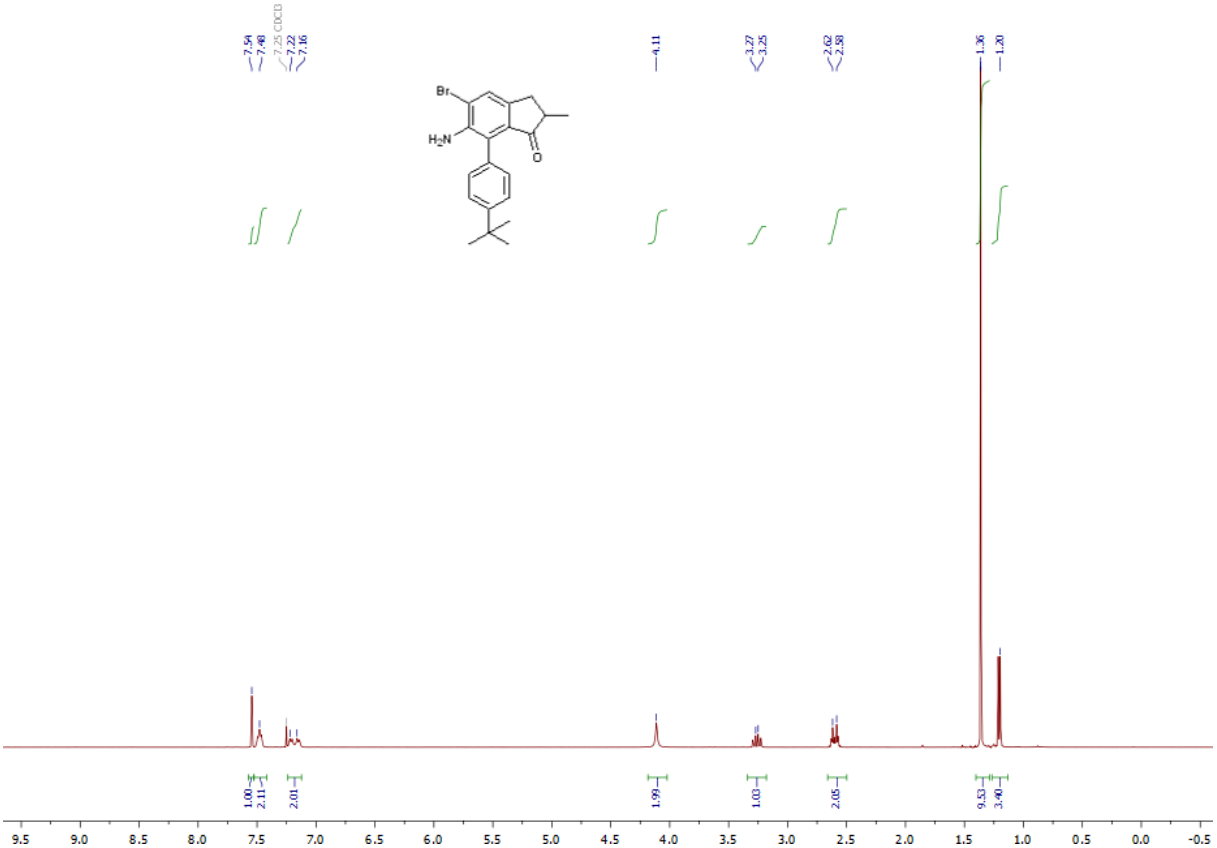


Figure S49. ^{1}H NMR spectrum of 6-amino-5-bromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8a**) in $CDCl_3$ at room temperature.

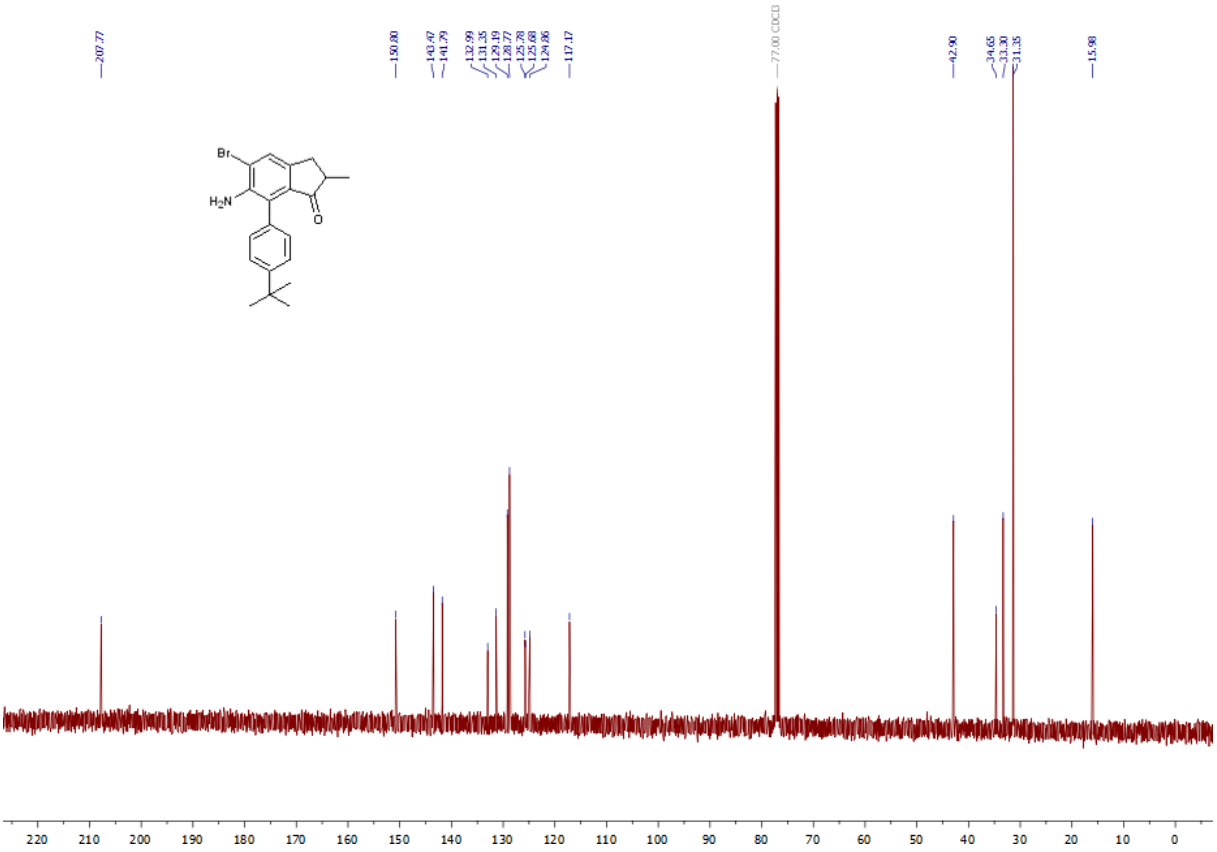


Figure S50. ^{13}C NMR spectrum of 6-amino-5-bromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8a**) in $CDCl_3$ at room temperature.

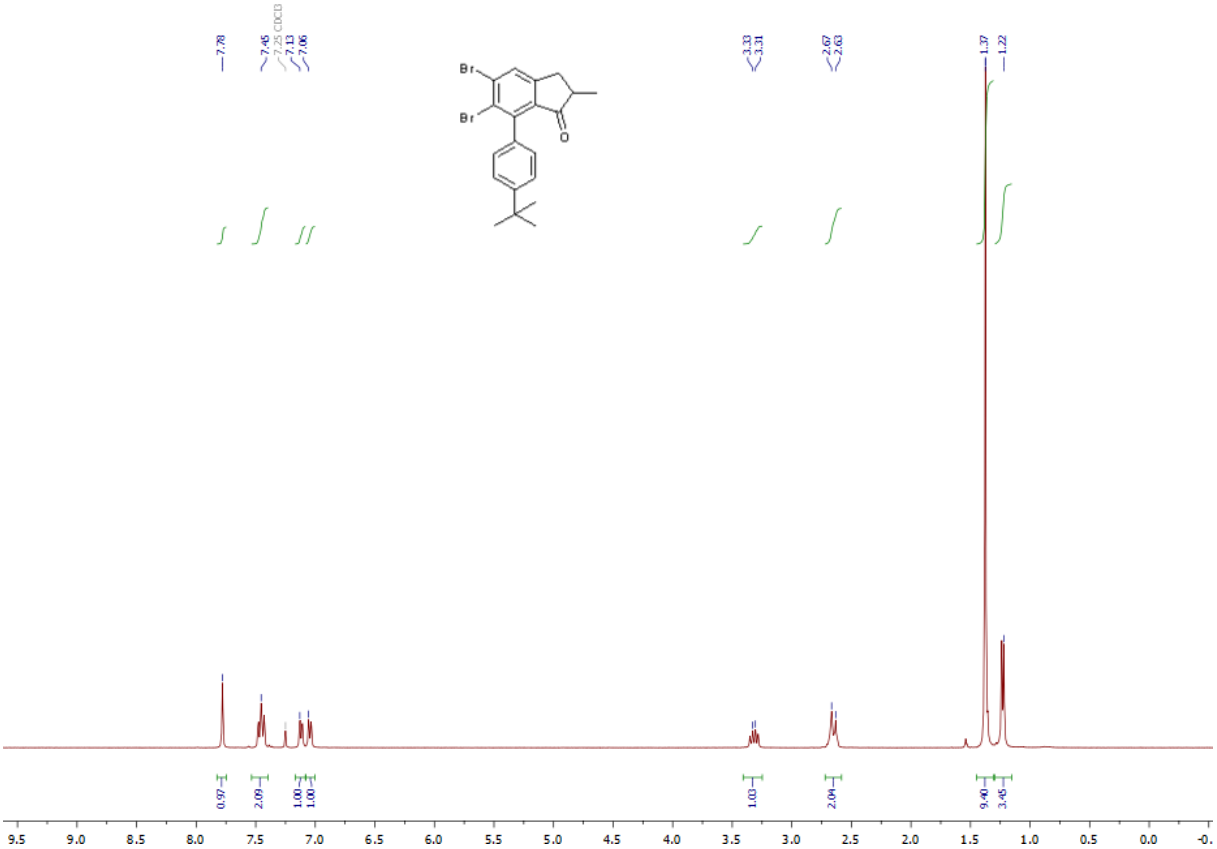


Figure S51. ^{1}H NMR spectrum of 5,6-dibromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8b**) in $CDCl_3$ at room temperature.

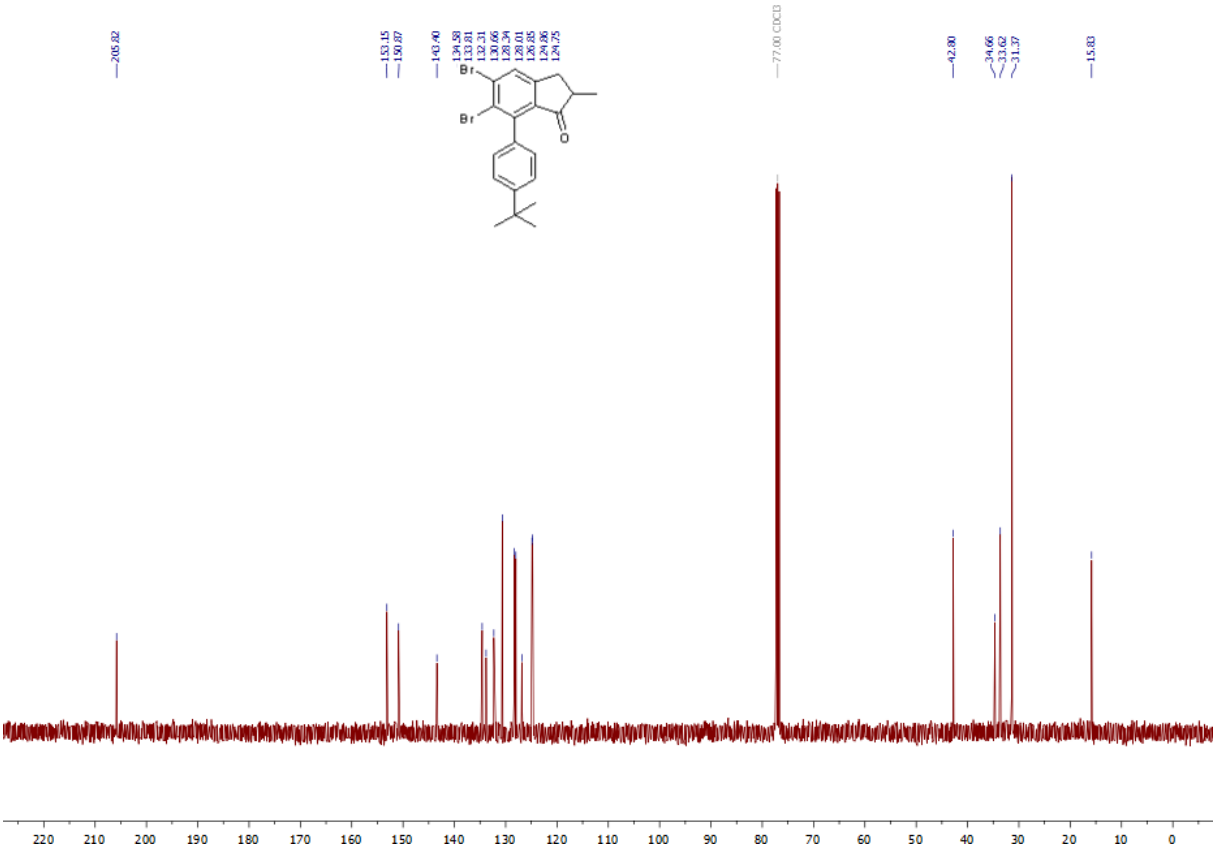


Figure S52. ^{13}C NMR spectrum of 5,6-dibromo-7-(4-*tert*-butylphenyl)-2-methylindan-1-one (**8b**) in $CDCl_3$ at room temperature.

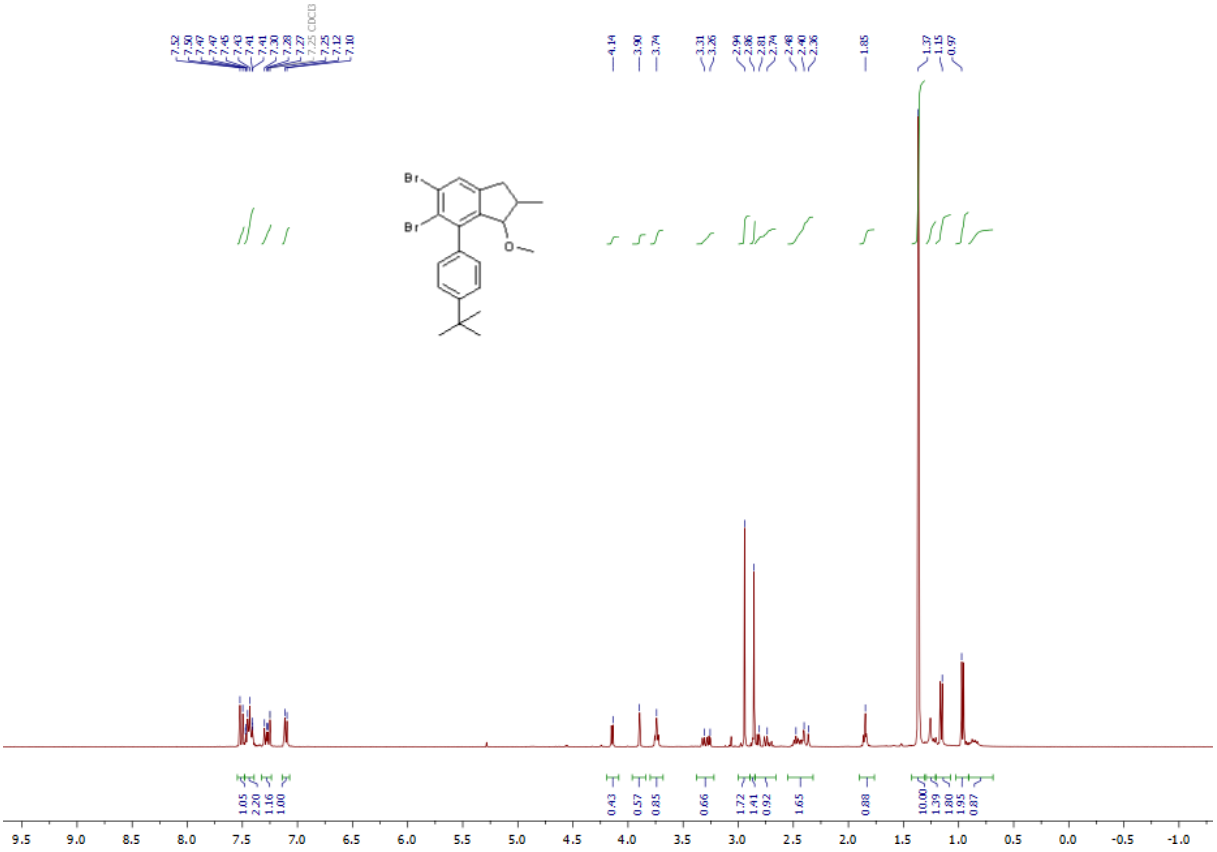


Figure S53. ^{1}H NMR spectrum of 5,6-dibromo-7-(4-*tert*-butylphenyl)-1-methoxy-2-methylindane (**8c**) in $CDCl_3$ at room temperature.

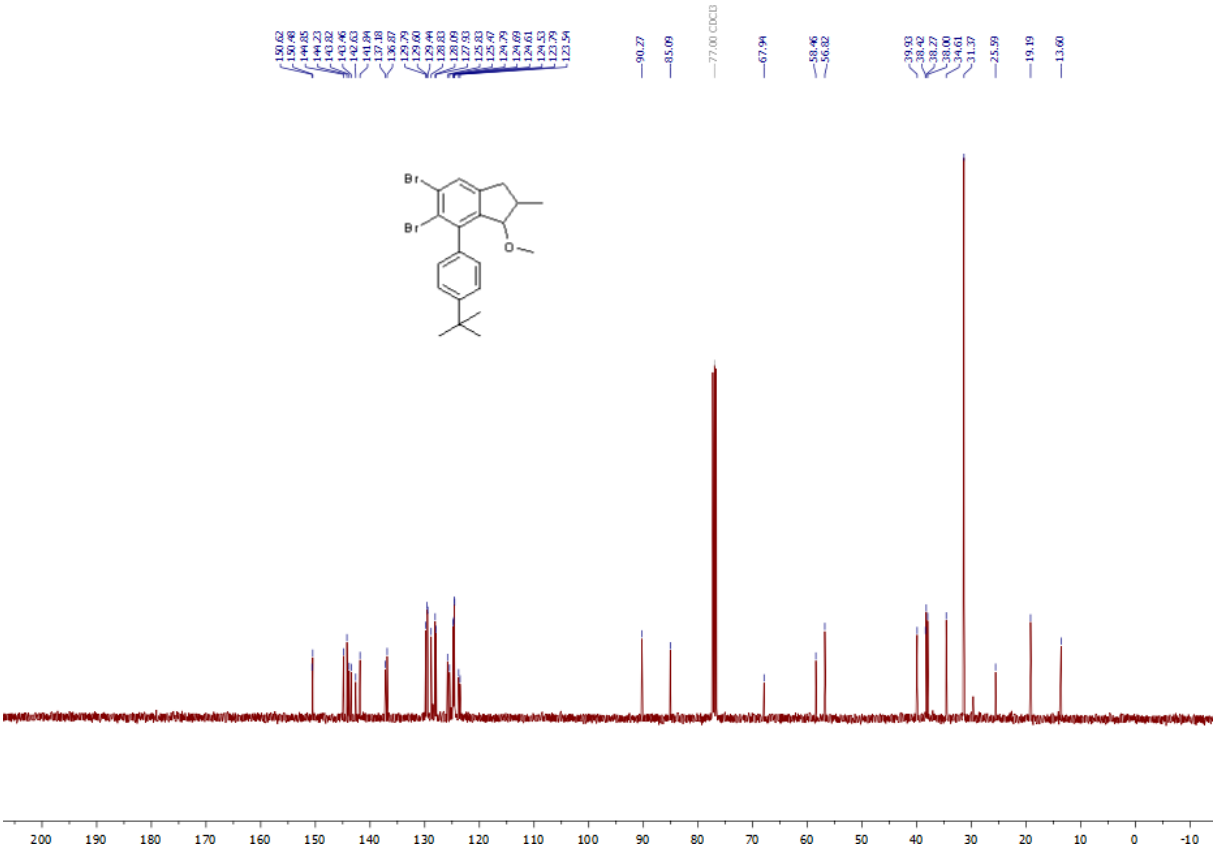


Figure S54. ^{13}C NMR spectrum of 5,6-dibromo-7-(4-*tert*-butylphenyl)-1-methoxy-2-methylindane (**8c**) in $CDCl_3$ at room temperature.

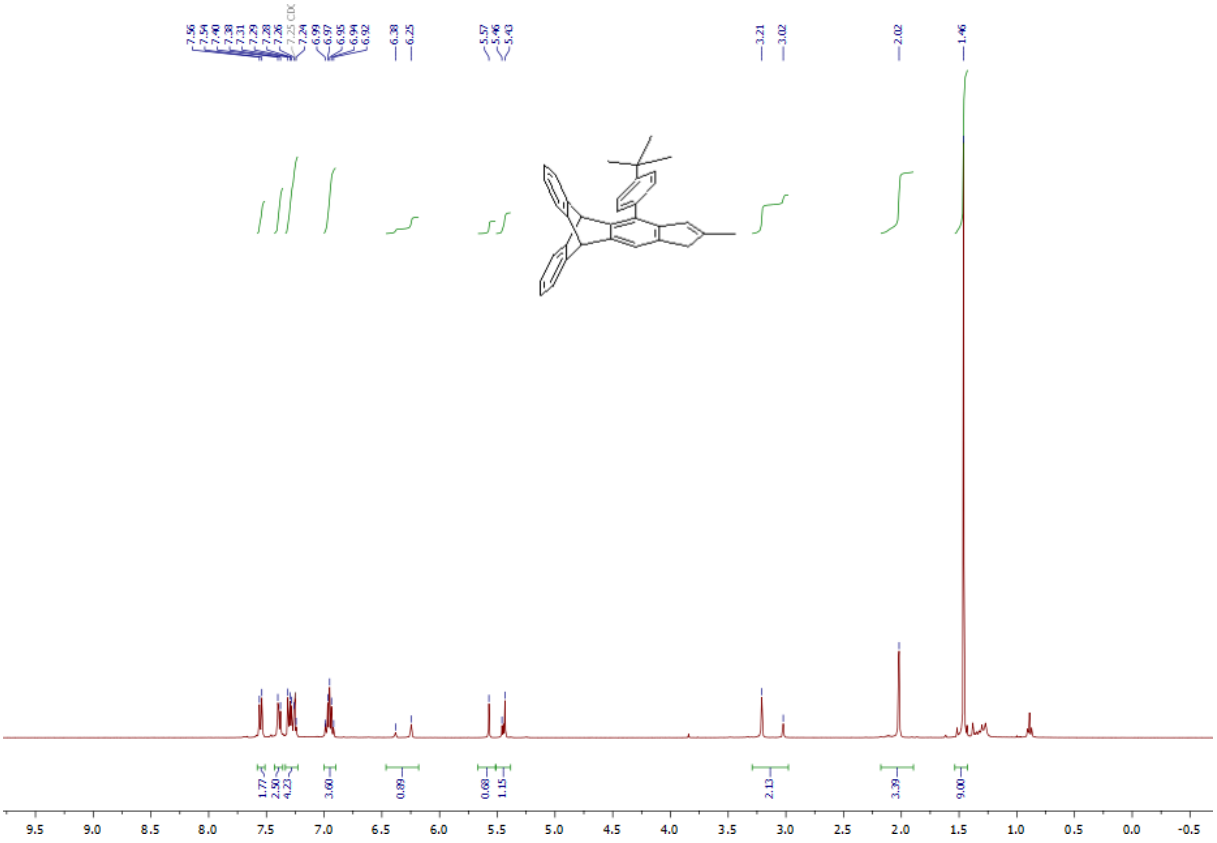


Figure S55. ^{1}H NMR spectrum of 2-methyl-4-(4-*tert*-butylphenyl)-5,6-(9,10-dihydroanthracene-9,10-diyl)indene (**8d**) in $CDCl_3$ at room temperature.

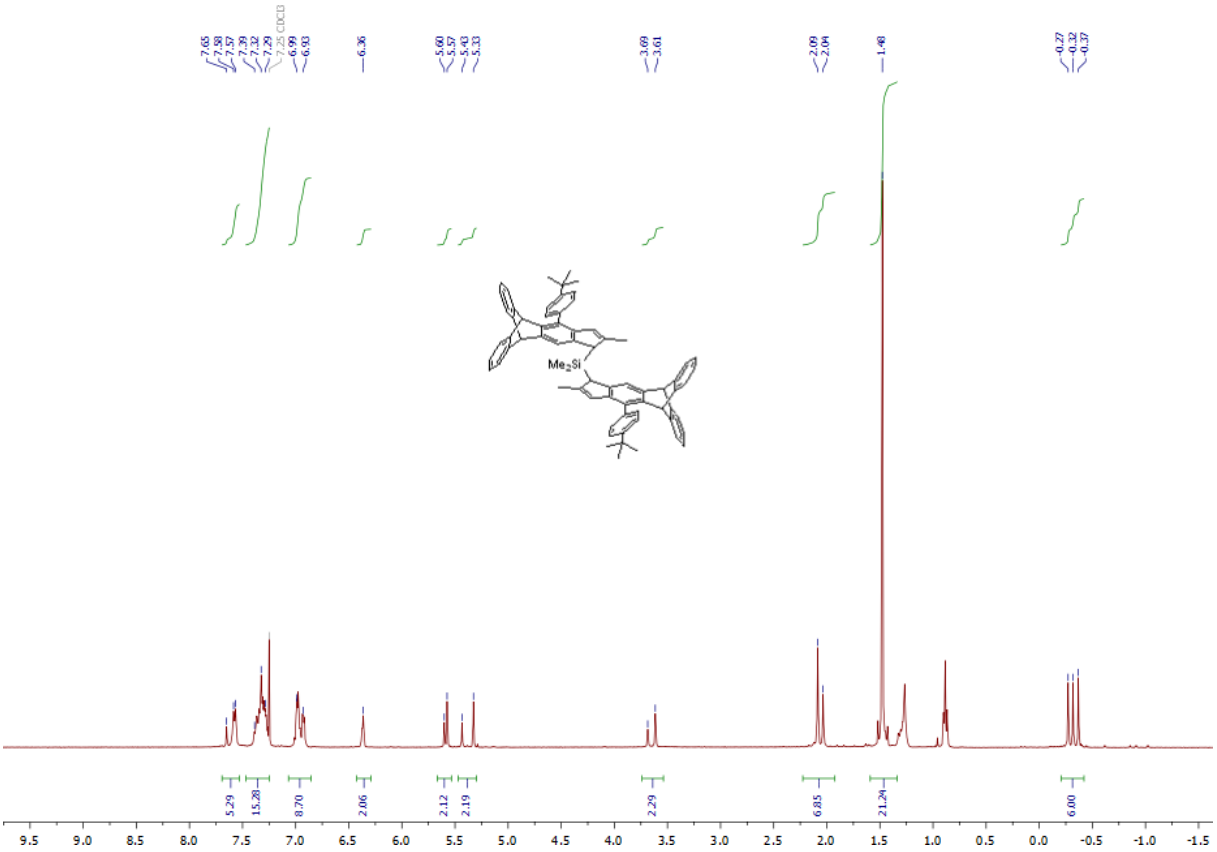


Figure S56. ^{1}H NMR spectrum of proligand **8e** in $CDCl_3$ at room temperature.

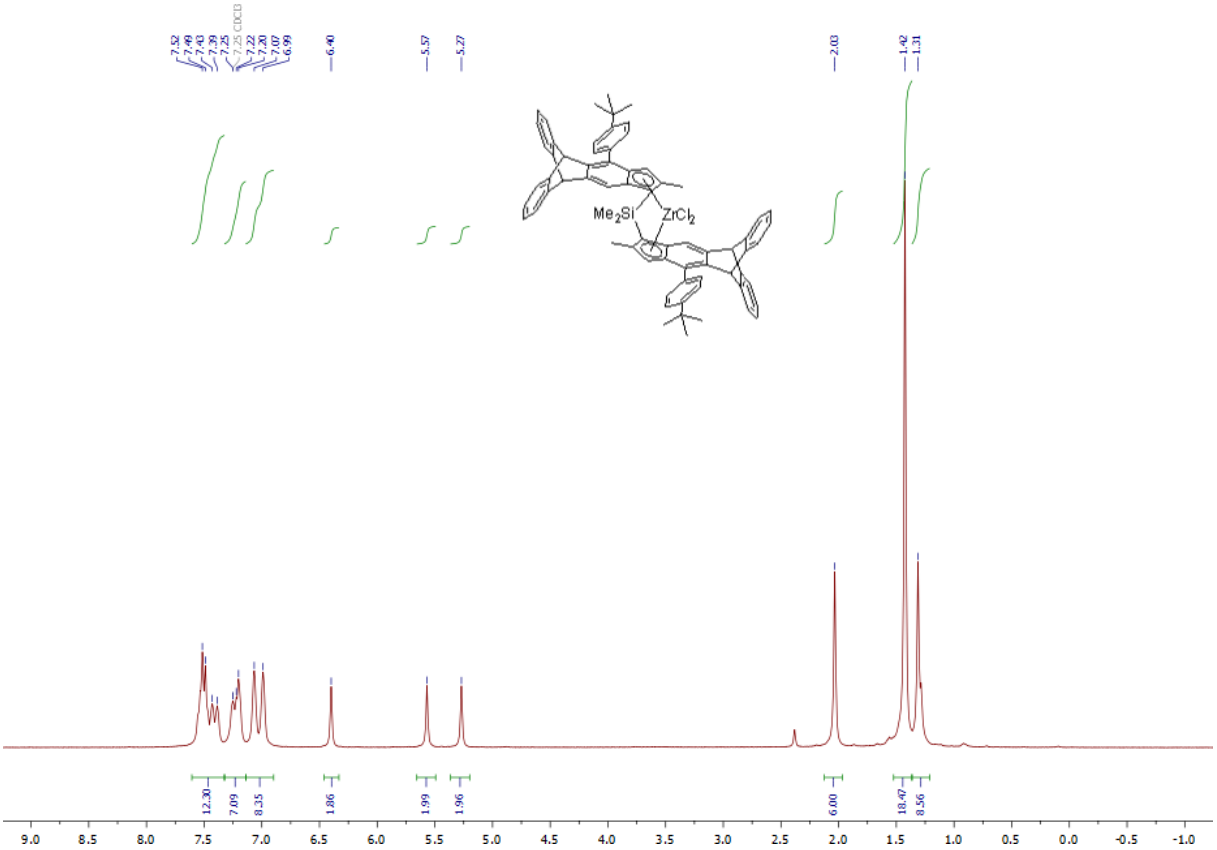


Figure S57. ^{1}H NMR spectrum of *rac*-**Ty8-Cl$_2$** in $CDCl_3$ at room temperature.

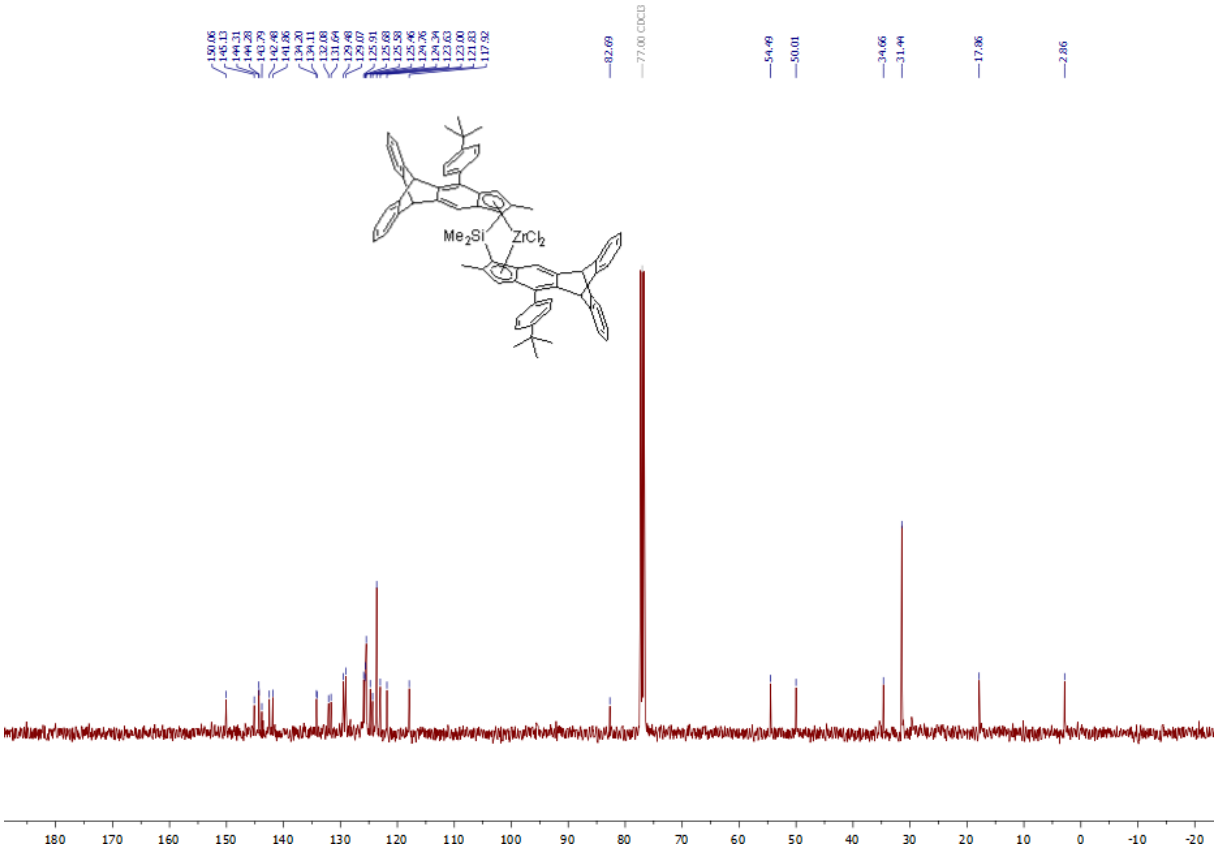


Figure S58. ^{13}C NMR spectrum of *rac*-**Ty8-Cl$_2$** in $CDCl_3$ at room temperature.

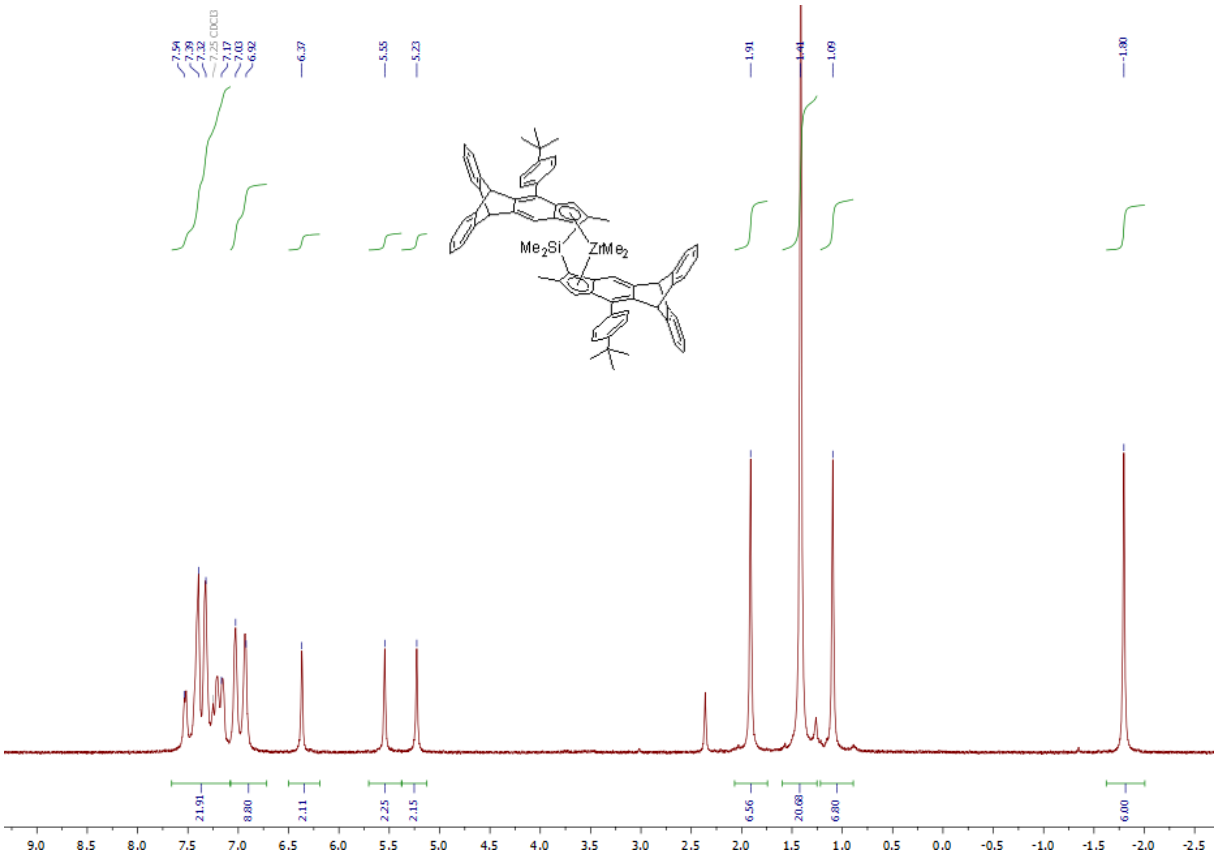


Figure S59. ^{1}H NMR spectrum of *rac*-**Ty8** in $CDCl_3$ at room temperature.

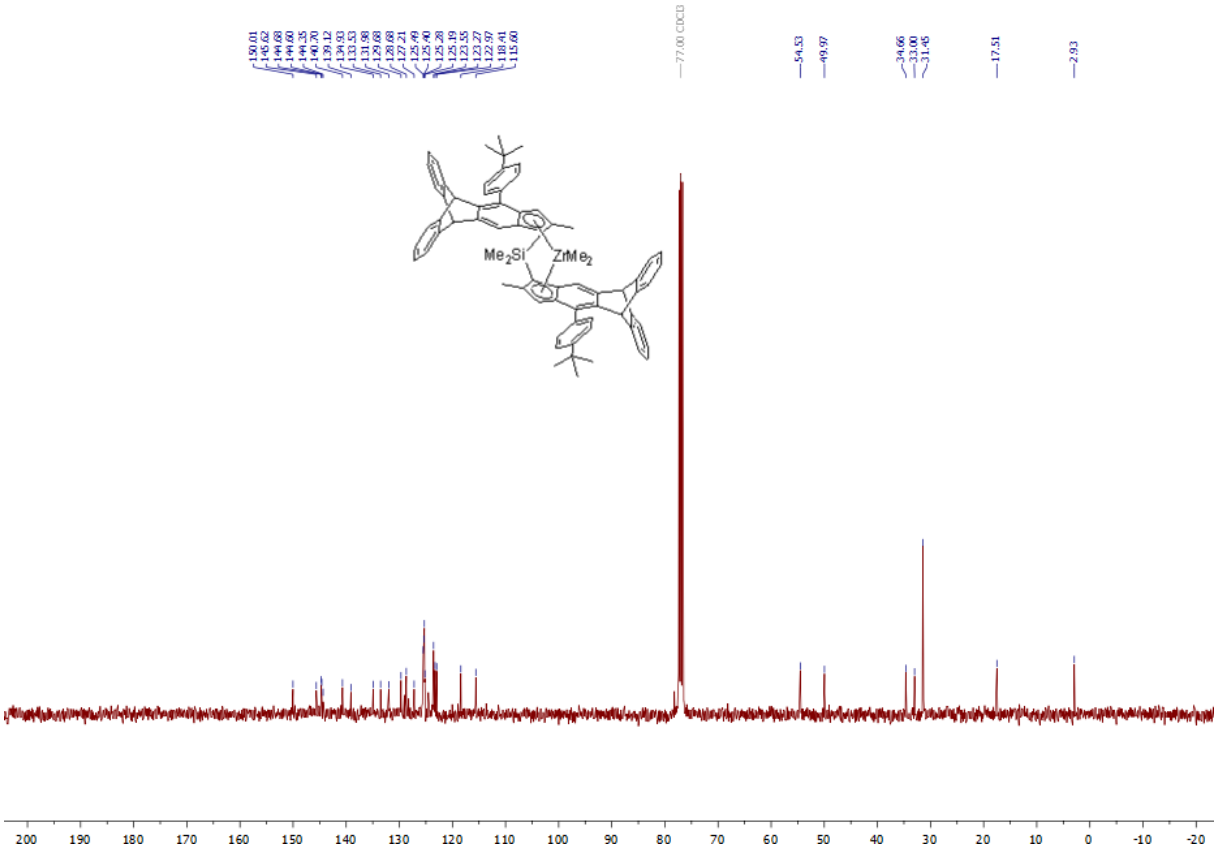


Figure S60. ^{13}C NMR spectrum of *rac*-**Ty8** in $CDCl_3$ at room temperature.

Polymerization Experiments and Polymer Characterization

Table S1. Stir paddles, scavenger amounts, monomer pressure and solvent choice for the polymerization experiments.

	Propene Homopolymerization		**Ethene/1-Hexene Copolymerization**
Temperature	**T_p = 60°C**	**T_p = 100°C**	**T_p = 60°C**
$P_{monomer}$	95 psi (6.6 bar)	115 psi (7.9 bar)	65 psi (4.5 bar)
Stir Paddles	polyether ether ketone (PEEK)	Titanium	polyether ether ketone (PEEK)
TiBA Scavenger	5 µmol	10 µmol	5 µmol
Reaction Volume	5 mL	5 mL	6 mL
Solvent (cell, chaser and buffer)	toluene	mixed alkane diluent (ISOPAR-G)	toluene

Table S2.1. Main propene polymerization results

Cat	T_p (°C)	p (psi)	B/M[#]	Cat (nmol)	t_p (s)	Yield (mg)	R_p[*]	M_n, (kDa)	PDI	*mmrrmm* (%)	σ[(a)]	[*2,1*] (%)	[*3,1*] (%)
Ty4	60	95	2	3	641	108	202	790	2.7	n.d	≥0.9998	0.20	n.d.
Ty4	60	95	2	2	1064	63	107	960	2.4	n.d	≥0.9998	0.18	n.d.
Ty4	100	115	10	3	2152	120	67	140	2.5	n.d.	≥0.9998	0.24	0.02
Ty4	100	115	10	3	2275	80	42	160	2.5	n.d.	≥0.9998	0.24	0.03
Ty5	60	95	2	3	416	87	252	60	2.1	0.04	0.9996	1.0	n.d.
Ty5	60	95	2	3	373	97	313	60	2.0	0.05	0.9995	1.0	n.d
Ty6	60	95	5	3.5	1768	93	54	40	2.1	1.0	0.989	1.3	0.03
Ty6	60	65	5	5	543	46	61	40	1.9	1.2	0.987	1.2	0.07
Ty7	60	95	2	60	1763	93	3	24	2.1	0.43	0.9957	7.9	0.10
Ty7	60	95	2	60	1872	99	3	26	2.0	0.43	0.9957	7.9	0.10
Ty8	60	95	2	4	1729	41	21	440	2.0	0.03	0.9997	1.3	0.02
Ty8	60	95	2	4	1279	37	26	420	2.2	0.03	0.9997	1.3	0.02
Ty8	100	115	10	12.5	1415	61	12	70	2.1	0.11	0.9989	1.4	0.50
Ty8	100	115	10	12.5	1421	68	14	70	2.1	0.09	0.9991	1.4	0.45

* in kg $mmol_M^{-1}$ h^{-1}, # B/M = activator:metal ratio. (a) Probability of inserting propene with the favored enantioface at each of the two enantiotopic sites.

Table S2.2. Main E/H copolymerization results

Cat	V_{c6} (µl)	B/M#	Cat (nmol)	Yield (mg)	t_p (s)	R_p*	M_n, (kDa)	PDI	[H] (mol%)	r_E	r_H
Ty1	560	2	5	70	929	54	63	2.3	34.6	4.6	0.23
Ty1	560	2	5	76	1189	47	64	2.3	36.7	3.9	0.24
Ty1	850	2	5	88	1461	43	65	2.4	45.0	4.2	0.22
Ty1	850	2	5	102	1426	52	76	2.1	47.4	3.4	0.23
Ty2	560	5	6	64.7	655	59	64	2.4	38.0	3.5	0.24
Ty2	560	5	6	65.1	684	57	58	2.8	38.3	3.4	0.23
Ty2	850	5	6	86.7	1008	52	101	1.9	47.4	3.4	0.22
Ty3	560	2	5	79.8	3513.0	16	100	2.3	40.0	3.2	0.26
Ty3	560	2	6	28.4	1308.0	13	148	2.4	41.9	3.2	0.29
Ty3	850	2	3	56.7	3488.0	20	126	2.4	48.4	3.4	0.24
Ty3	850	2	8	83.5	697.0	54	88	2.1	47.5	3.4	0.22
Ty4	560	2	5	89.2	1067.0	43	58	2.3	33.3	4.7	0.22
Ty4	850	2	3	67.2	891.0	22	70	2.3	43.6	4.3	0.20
Ty4	850	2	3	68.0	3600.0	23	72	2.3	43.3	4.2	0.20
Ty5	560	2	6	101.4	1188	51	12	2.0	39.3	3.2	0.26
Ty5	560	2	6	103.7	1189	52	12	2.0	38.9	3.6	0.27
Ty6	560	2	2.5	68	158	618	40	2.2	18.1	9.1	0.01
Ty6	850	2	5	83	157	382	40	1.9	23.1	9.2	0.01
Ty6	850	2	4	101	11	791	33	2.0	24.4	8.2	0.01
Ty7	560	2	5	59	140	301	44	2.0	13.1	18.6	0.12
Ty7	850	2	5	49	386	91	41	2.0	19.1	18.9	0.11
Ty7	850	2	5	63	147	310	39	1.9	18.6	19.5	0.12
Ty8	560	2	12.5	85	980	25	78	2.2	40.3	3.3	0.29
Ty8	560	2	15	85	567	36	69	2.4	40.7	3.3	0.31
Ty8	850	2	5	59	4449	9.5	82	2.2	50.3	3.4	0.27
Ty8	850	2	12.5	105	1474	21	75	2.1	49.7	3.3	0.28

Other experimental conditions: T_p = 60°C; $p(C_2H_6)$ = 65 psi; * in kg $mmol_M^{-1}$ h^{-1}, # B/M = activator:metal ratio

Computational Details

QSAR models

The following QSAR equations (from Ref 4) were used to predict the performance of catalysts **Ty1-Ty8** at T_p = 60°C.

Stereoselectivity Model

$\Delta\Delta G^{\ddagger}_{enantio,\ exp}$ = (Eq. S2)

$0.474\ \Delta\%V_{Bur,\ Zr} - 3.247$

Molecular Weight Model

$\Delta\Delta G^{\ddagger}_{T,\ exp}$ = (Eq. S3)

$0.127\ \Delta\%V_{Bur,\ Zr} + 0.023\ \%V_{Bur,\ C4} + 0.039\ \%V_{Bur,C5\text{-}6} - 0.220\ \%V_{Bur,open} - 0.099\ \%V_{Bur,C2\text{-}3,Front} + 13.971$

Regioselectivity Model

$\Delta\Delta G^{\ddagger}_{regiotot,\ exp}$ = (Eq. S4)

$0.031\ \%V_{Bur,\ C4} - 0.031\ \%V_{Bur,C5\text{-}6)} + 0.043\ \%V_{Bur,C2\text{-}3\text{-}All} - 0.529\ \%V_{Bur,\ open} - 14.267\ e^{-}_{ZrCl2,\ NPA} + 23.619$

The descriptor values were determined as described in Ref [9 10], with the exception of $\%V_{Bur,\ \mathbf{C4}}$, which is used to screen steric bulk coming backwards from the active pocket. In this case, the triptycene part linked to the 5-position (going away from the active pocket) was additionally deleted as shown in Ref [1].

Table S3. Predicted vs Observed Performance at T_p = 60°C. iPP.

Catalyst	Descriptors							Experimental Observables			Experimental Observables (as ΔΔG‡)			QSPR model predictions			QSPR model deviation		
	$\Delta\%V'_{Bur,\ 5\ Å}$	$\%V_{Bur,\ C4}$	$\%V_{Bur,C5\text{-}6}$	$\%V_{Bur,C2\text{-}3\text{-}All}$	$\%V_{Bur,open}$	$\%V_{Bur,C2\text{-}3,Front}$	$e^-_{ZrCl2,\ NPA}$	σ	2,1+3,1, %	M_n *kDa*	$\Delta\Delta G^{\ddagger}_{enantio,\ exp}$	$\Delta\Delta G^{\ddagger}_{regiotot,\ exp}$	$\Delta\Delta G^{\ddagger}_{Mn,\ exp}$	$\Delta\Delta G^{\ddagger}_{enantio,\ QSAR}$	$\Delta\Delta G^{\ddagger}_{regiotot,\ QSAR}$	$\Delta\Delta G^{\ddagger}_{Mn,\ QSAR}$	$\Delta\Delta G^{\ddagger}_{enantio}$	$\Delta\Delta G^{\ddagger}_{regiotot}$	$\Delta\Delta G^{\ddagger}_{Mn}$
											kcal/mol								
Ty1	19.2	45.9	53.1	46.5	34.6	118.0	0.396	0.9998	0.26	1100	5.6	3.9	6.7	5.9	4.5	7.3	0.2	0.6	0.6
Ty2	19.2	45.4	53.8	47.0	34.6	126.8	0.405	0.9997	0.18	1900	5.4	4.2	7.1	5.9	4.7	7.3	0.5	0.5	0.2
Ty3	19.2	46.5	53.9	47.0	35.2	118.0	0.400	0.9997	0.11	1400	5.4	4.5	6.9	5.9	4.1	7.2	0.5	0.4	0.3
Ty4	20.8	55.5	53.8	47.0	34.9	126.7	0.400	0.9998	0.19	880	5.6	4.1	6.6	6.6	4.9	7.7	1.0	0.8	1.1
Ty5	21.1	40.7	51.1	37.0	34.2	99.2	0.343	0.9995	1.0	60	5.0	3.0	4.8	6.8	4.6	8.4	1.7	1.5	3.6
Ty6	12.5	6.0	72.3	46.6	34.5	112.2	0.384	0.989	1.35	40	2.9	2.8	4.5	2.7	2.7	6.3	0.2	0.2	1.8
Ty7	13.4	12.4	77.1	46.3	38.3	118.9	0.388	0.9957	8.0	25	3.6	1.6	4.2	3.1	0.9	6.0	0.5	0.7	1.7
Ty8	17.7	21.6	73.1	46.8	35.3	130.4	0.402	0.9997	1.32	430	5.4	2.9	6.1	5.1	3.2	7.2	0.2	0.4	1.1

Table S4. Predicted vs Observed Performance at T_p = 60°C. E/H Copolymerization.

Catalyst	Descriptors								Experimental Observables		Experimental Observables (as ΔΔG‡)		QSPR model predictions		QSPR model deviation	
	$\Delta\%V'_{Bur,\ 5\ Å}$	$\%V_{Bur,\ C4}$	$\%V_{Bur,C5\text{-}6}$	$\%V_{Bur,C2\text{-}3\text{-}All}$	$\%V_{Bur,open}$	$\%V_{Bur,C2\text{-}3,Front}$	$e^-_{ZrCl2,\ NPA}$	Bondi vdW radius	r_E	r_H	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE}$	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH}$	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE,QSAR}$	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH,QSAR}$	$\Delta\Delta G^{\ddagger}_{EH\text{-}EE}$	$\Delta\Delta G^{\ddagger}_{HE\text{-}HH}$
											kcal/mol					
Ty1	19.2	45.9	53.1	46.5	34.6	118.0	0.396	170	4.0	0.23	0.9	-1.0	0.3	-0.7	0.6	0.2
Ty2	19.2	45.4	53.8	47.0	34.6	126.8	0.405	170	3.5	0.23	0.8	-1.0	0.4	-0.7	0.5	0.3
Ty3	19.2	46.5	53.9	47.0	35.2	118.0	0.400	170	3.3	0.25	0.8	-0.9	0.6	-0.8	0.2	0.1
Ty4	20.8	55.5	53.8	47.0	34.9	126.7	0.400	170	4.4	0.21	1.0	-1.0	0.3	-0.5	0.7	0.5
Ty5	21.1	40.7	51.1	37.0	34.2	99.2	0.343	170	3.4	0.27	0.8	-0.9	0.3	-0.8	0.5	0.1
Ty6	12.5	6.0	72.3	46.6	34.5	112.2	0.384	120	8.8	0.014	1.4	-2.8	1.9	-3.0	0.5	0.2
Ty7	13.4	12.4	77.1	46.3	38.3	118.9	0.388	170	19	0.12	1.9	-1.4	2.9	-2.3	0.9	0.9
Ty8	17.7	21.6	73.1	46.8	35.3	130.4	0.402	170	3.3	0.29	0.8	-0.8	1.2	-1.0	0.5	0.2

Table S5. Energies, Enthalpies and Gibbs free energies for all DFT structures for species for **Ty7**.

Name	Elimination @	Formula	Energy(DZ)	Energy(TZ)	S2()	alue('conve	umNegative	ata('vibrati	ZPE()	yCorr(p=1.0	Corr(p=1.0,	H	G	ΔH	GΔ
2_Me_4_7_Me_5_6-triptycene_after21_beta_A_BHE_TS	β-C_{chain}	C58H55SiZr	-2580.273957	-2579.369981	0	FALSE	1	TRUE	0.934287	0.990125	0.141686	-2578.379856	-2578.47479	3.1	4.2
2_Me_4_7_Me_5_6-triptycene_after21_beta_B_BHE_TS	β-C_{methyl}	C58H55SiZr	-2580.261004	-2579.35657	0	FALSE	1	TRUE	0.934217	0.990618	0.143196	-2578.365951	-2578.46189	11.9	12.3
2_Me_4_7_Me_5_6-triptycene_after21_beta_C_BHE_TS	β-C_{chain}	C58H55SiZr	-2580.26641	-2579.361519	0	FALSE	1	TRUE	0.933956	0.990459	0.143186	-2578.37106	-2578.467	8.7	9.1
2_Me_4_7_Me_5_6-triptycene_RS_after21_alpha_agostic		C58H55SiZr	-2580.264833	-2579.364076	0	FALSE	0	TRUE	0.93783	0.994861	0.145956	-2578.369215	-2578.46701	9.8	9.1
2_Me_4_7_Me_5_6-triptycene_RS_after21_beta_agostic_A		C58H55SiZr	-2580.284538	-2579.369981	0	FALSE	0	TRUE	0.938084	0.994888	0.144874	-2578.375093	-2578.47216	6.1	5.9
2_Me_4_7_Me_5_6-triptycene_RS_after21_beta_agostic_B		C58H55SiZr	-2580.284793	-2579.35657	0	FALSE	0	TRUE	0.937988	0.994635	0.143699	-2578.361935	-2578.45821	14.4	14.6
2_Me_4_7_Me_5_6-triptycene_RS_after21_beta_agostic_C		C58H55SiZr	-2580.283141	-2579.36152	0	FALSE	0	TRUE	0.938354	0.99491	0.143409	-2578.366609	-2578.46269	11.5	11.8
2_Me_4_7_Me_5_6-triptycene_RS_after21_gamma_agostic		C58H55SiZr	-2580.275659	-2579.379445	0	FALSE	0	TRUE	0.93776	0.99457	0.144272	-2578.384875	-2578.48154	0.0	0.0

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