Multisubstituted C_2-symmetric *ansa*-Metallocenes Bearing Nitrogen Heterocycles: Influence of Substituents on Catalytic Properties in Propylene Polymerization at Higher Temperatures

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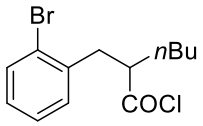
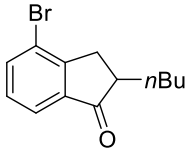
GENERAL DETAILS

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware or in a argon-filled Vacuum Atmospheres glove box (<1 ppm O_2). Toluene, CH_2Cl_2, hexane, pentane, chloroform-d_1 and dichloromethane-d_2 were dried using 4 Å molecular sieves activated for 24 h at 200-230 °C under dynamic vacuum. Diethyl ether and tetrahydrofuran were refluxed over Na/benzophenone and distilled prior to use. All dry solvents were stored under an argon atmosphere. Commercial chemicals (Aldrich, Fluka, TCI, Alfa, Abcr, and Merck) including 2-di-*tert*-butylphosphino-2'-methylbiphenyl (*t*BuMePhos), 2,2'-dibromobiphenyl were used without further purification. 7-Bromo-2-methyl-1*H*-indene (**1**),[1] 3,6-dimethyl-9*H*-carbazole,[2] 3,6-di-*tert*-butyl-9*H*-carbazole,[3] 8,9-dihydro-4*H*-benzo[*def*]carbazole,[4] 4-bromo-2-isopropyl-1*H*-indene (**2**),[5] 2,6,6-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-one,[6] 7-bromo-2-methyl-5-*tert*-butyl-1*H*-indene (**5**),[7] 7-bromo-4-methoxy-2-methyl-1*H*-indene (**6**),[8] 4-bromo-2,5-dimethyl-1*H*-indene (**16**),[1] 7-bromo-5-*tert*-butyl-6-methoxy-2-methyl-1*H*-indene (**21**),[9] 1-bromo-2-(methylethynyl)benzene,[10] 1-bromo-2-(phenylethynyl)benzene,[11] 2-bromo-1-iodo-4-methylbenzene,[12] 2,2'-dibromo-4,4'-di-*tert*-butyl-1,1'-biphenyl,[13] were synthesized as previously described. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer at ambient temperature (reported relatively to TMS and referenced either to TMS, or to the residual ^{1}H or ^{13}C resonances of the deuterated solvents). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet); br.s (broad signal), d (doublet), t (triplet), q (quartet), p (pentet or quintet), sext (sextet), sept (septet) and m (multiplet) as well as combinations of them. All ^{13}C NMR spectra were measured with ^{1}H-decoupling. High-resolution mass spectra (HRMS) were recorded on Agilent Technologies 6530 Q-TOF LC/MS system paired Agilent 1260 HPLC and using Agilent JetStream ion source (ESI). C, H, N microanalyses were done using «Elementar Vario MICRO cube».

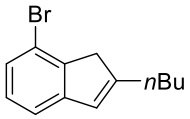
SYNTHESES OF SUBSTITUTED 4/7-BROMOINDENES



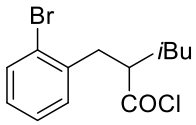
2-(2-Bromobenzyl)hexanoyl chloride. In a three-necked round-bottom 2000-mL flask equipped with a reflux condenser, a dropping funnel with pressure-equalizing bypass, and a magnetic stirring bar, 10.9 g (472 mmol) of sodium metal was dissolved in 400 mL of dry ethanol. To the resulting solution, 100 g (463 mmol) of diethylbutylmalonate was added dropwise over 15 min. This mixture was stirred for 15 min; then, 115.8 g (463 mmol) of 2-bromobenzyl bromide was added with vigorous stirring at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 4 h and cooled to room temperature. A solution of 104 g of KOH in 200 mL of water was then added. This mixture was refluxed for 3 h to saponificate the ester formed. Ethanol and water were then distilled off. To the residue, 500 mL of water and then 12 M HCl (to pH 1) were added. The substituted butylmalonic acid was extracted from the solution with 3×100 mL of dichloromethane, organic layers were collected dried over Na_2SO_4 and the solvent was rotary evaporated. Crude 3-(2-bromobenzyl)hexanoic acid was obtained after decarboxylation of this substituted methylmalonic acid for 2 h at 160 °C. The product was used without further purification. A mixture of the obtained 2-(2-bromobenzyl)hexanoyl acid and 100 mL (166 g, 1.39 mol) of $SOCl_2$ was stirred for 12 h at room temperature. An excess of $SOCl_2$ was distilled off in vacuum, and the following distillation of residue, b.p. 120–150 °C/2 mbar, gave 107.9 g (89%) of 2-(2-bromobenzyl)hexanoyl chloride as yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 1H), 7.25 (m, 2H), 7.12 (dt, J = 8.1 Hz, 4.5 Hz, 1H), 3.28 (m, 1H), 3.16 (m, 1H), 3.00 (m, 1H), 1.84 (m, 1H), 1.68 (m, 1H), 1.36 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.3, 137.0, 133.0 ,131.3, 128.6, 127.5, 124.4, 56.7, 38.0, 31.5, 28.6, 22.4, 13.7.



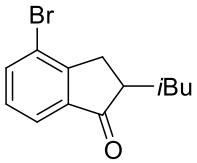
4-Bromo-2-butylindan-1-one. Solution of 107.9 (355 mmol) of 2-(2-bromobenzyl)hexanoyl chloride in 50 of dichloromethane was added dropwise to a cold (0 °C) suspension of 59.3 g (444 mmol) of $AlCl_3$ in 1 L of dichloromethane. This mixture was then stirred for 20 h at room temperature and then poured on 2000 cm^3 of ice. The organic layer was separated, and aqueous layer was extracted with 3×200 mL of dichloromethane. The combined extract was washed by 10% aqueous K_2CO_3, dried over K_2CO_3, passed through short column with Silica Gel 60, and then evaporated to dryness. Distillation of the residue, b.p. 138–140 °C/2 mbar, gave 70.1 g (88%) of 4-bromo-2-butlindan-1-one as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73 (m, 1H), 7.67 (m, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 3.257 (dd, J = 17.5 Hz, 7.5 Hz, 1H), 2.64–2.75 (m, 2H), 1.95 (m, 1H), 1.30–1.51 (m, 5H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 207.8, 153.2, 138.7, 137.1, 128.9, 122.5, 122.0, 47.2, 33.8, 30.9, 29.3, 22.5, 13.8. HRMS (ESI) calc. for $C_{13}H_{16}BrO^+$: 267.0379 [M + H]$^+$; found: 267.0376.



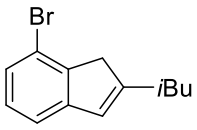
7-Bromo-2-butyl-1*H*-indene (3). To a solution of 62.2 g (233 mmol) of 4-bromo-2-butylindan-1-one in 500 mL of THF, 13.2 g (350 mmol) of $NaBH_4$ was added at 5 °C. To the resulting suspension, 250 mL of methanol was added dropwise at 5 °C, and then the reaction mixture was stirred at room temperature overnight. Next, volatiles were rotary evaporated and the residue was diluted with 1 L of water and extracted with 300 mL of dichloromethane. The organic extract was evaporated to dryness. The residue was dissolved in 500 mL of toluene, and 1.0 g of TsOH was added. The resulting mixture was refluxed with Dean-Stark head for 1 h to dehydrate 4-bromo-2-isopropylindan-1-ol, then cooled to room temperature, and washed by 10% Na_2CO_3. The organic layer was separated, dried over K_2CO_3, passed through short column with Silica Gel 60, and evaporated to dryness. Distillation of the residue, b.p. 132–135 °C/6 mbar, gave 52.6 g (90%) of 7-bromo-2-butyl-1*H*-indene as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.24 (m, 1H), 7.20 (m, 1H), 7.11 (m, 1H), 6.53 (m, 1H), 3.31 (s, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 1.62 (m, 2H), 1.41 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 151.5, 147.1, 143.0, 128.1, 126.5, 126.0, 118.7, 118.4, 42.6, 31.0, 30.8, 22.5, 13.9. HRMS (ESI) calc. for $C_{13}H_{15}BrNa^+$: 273.0249 [M + Na]$^+$; found: 273.0242.



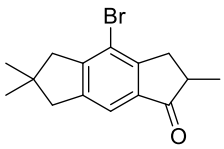
2-(2-Bromobenzyl)-4-methylpentanoyl chloride. In a three-necked round-bottom flask, 23.0 g (1.0 mol) of sodium metal was dissolved in 760 mL of dry ethanol. To the resulting solution, 216.3 g (1.0 mol) of diethyl isobutylmalonate was added in one portion. This mixture was stirred for 15 min, then, 249.9 g (1.0 mol) of 1-bromo-2-(bromomethyl)benzene was added at such a rate as to maintain gentle reflux. This mixture was refluxed for an additional 6 h and cooled to room temperature. A solution of 205 g of KOH in 550 mL of water was added. This mixture was refluxed for 5 h to saponificate the ester formed. Ethanol was distilled off, and 1000 mL of water and then 12 M HCl (to pH 1) were added to the residue. The acidification was accompanied by decarboxylation with vigorous release of CO_2. Crude 2-(2-bromobenzyl)-4-methylpentanoic acid was extracted with ether, the extract was dried with anhydrous Na_2SO_4 and evaporated. The resulting oil was additionally heated to 200 °C. A mixture of this acid and 255 mL (3.52 mol) of $SOCl_2$ was stirred for 24 h at ambient temperature. Thionyl chloride was distilled off (at <50 °C). Distillation of the residue gave 266.6 g (88%) of 2-(2-bromobenzyl)-4-methylpentanoyl chloride as a yellowish oil, b.p. 127–132 °C/6 mm Hg. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55 (d, *J* = 8.3 Hz, 1H), 7.27–7.21 (m, 2H), 7.14–7.08 (m, 1H), 3.40–3.30 (m, 1H), 3.12 (dd, *J* = 13.9 Hz, 8.6 Hz, 1H), 2.99 (dd, *J* = 13.9 Hz, 5.8 Hz, 1H), 1.88–1.78 (m, 1H), 1.78–1.64 (m, 1H), 1.44–1.35 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.92 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHZ, $CDCl_3$): *δ* 176.7, 136.9, 133.1, 131.4, 128.7, 127.6, 124.5, 55.1, 41.3, 38.9, 25.9, 23.0, 21.9.



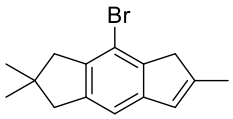
4-Bromo-2-isobutylindan-1-one. A solution of 266.6 g (0.878 mmol) of 2-(2-bromobenzyl)-4-methylpentanoyl chloride dissolved in 250 mL of CH_2Cl_2 was added dropwise to a suspension of 140.5 g (1.05 mol) of $AlCl_3$ in 1000 mL of CH_2Cl_2 over 2 h at 0°C. Then, this mixture was stirred at room temperature overnight and poured onto 1000 cm^3 of ice. The organic layer was separated. The aqueous layer was extracted with 3 x 200 mL of CH_2Cl_2. The combined extract was dried over K_2CO_3 and evaporated to dryness. Fractional rectification of the residue gave 211.8 g (90%) of 4-bromo-2-isobutylindan-1-one as a yellowish oil, b.p. 138–144 °C/5 mm Hg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 3.55–3.21 (m, 1H), 2.80–2.64 (m, 2H), 1.92–1.75 (m, 2H), 1.41–1.27 (m, 1H), 0.99 (d, J = 6.1 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHZ, $CDCl_3$): δ 208.4, 153.3, 138.7, 137.3, 129.1, 122.7, 122.1, 45.9, 40.5, 34.4, 26.5, 23.4, 21.6. HRMS (ESI) calc. for $C_{13}H_{16}BrO^+$: 267.0379 [M + H]$^+$; found: 267.0378.



7-Bromo-2-isobutyl-1*H*-indene (4). To a solution of 103.82 g (388.6 mmol) of 4-bromo-2-isobutylindan-1-one in 400 mL of THF cooled to 5 °C, 22.1 g (584.2 mmol) of $NaBH_4$ was added. Further on, 200 mL of methanol was added dropwise to this mixture for ca. 5 h at 5 °C. This mixture was stirred overnight at room temperature and then evaporated to dryness. To the obtained white mass, 1000 mL of dichloromethane and 1000 mL of water were added, and the resulting mixture was acidified by 2 M HCl to pH~4. The organic layer was separated, and the aqueous layer was extracted with 2 x 150 mL of dichloromethane. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness to give a white solid mass. To a solution of this mass in 800 mL of toluene, 1.0 g of TsOH was added, this mixture was rapidly heated to reflux, refluxed with Dean-Stark head for 15 min, and then quickly cooled to room temperature using water bath. The resulting solution was washed by 10% aqueous K_2CO_3. The organic layer was separated, the aqueous layer was extracted with 2 x 150 mL of dichloromethane. The combined organic extract was dried over K_2CO_3 and then passed through a short pad of silica gel 60 (40-63 μm). The silica gel layer was additionally washed by 100 mL of dichloromethane. The combined organic elute was evaporated to dryness to give a light orange liquid which was then distilled in vacuum to give 87.7 g (90%) of 7-bromo-2-isobutyl-1H-indene (b.p. 162–164°C/16 mm Hg) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.51 (s, 1H), 3.27 (s, 2H), 2.35 (d, J = 7.1 Hz, 2H), 1.91 (sept, 1H), 0.94 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.6, 147.1, 143.2, 128.2, 127.3, 126.7, 118.8, 118.5, 42.8, 40.7, 28.3, 22.6. HRMS (ESI) calc. for $C_{13}H_{15}BrNa^+$: 273.0249 [M + Na]$^+$; found: 273.0251.

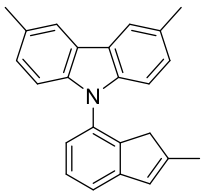


4-Bromo-2,6,6-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-one. Solution of 14.0 g (65.5 mmol) 2,6,6-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-one in 20 mL of dichloromethane was added dropwise in 15 min to a suspension of 21.8 g (164 mmol) $AlCl_3$ in 60 mL of dichloromethane at 0 °C. Then a solution of 3.3 mL (65.5 mmol) bromine in 20 mL of dichloromethane was added dropwise in 1 h at 0 °C. After that the resulting reaction mixture was poured into 500 mL of 1M solution of HCl, cooled to 0 °C and extracted with 200 mL of dichloromethane. Organic layers were collected, dried under Na_2SO_4 and solvents were rotary evaporated. The residue was recrystallized from hexane at -20 °C giving 13.4 g (69%) of the product as a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 3.23 (dd, J = 17.4 Hz, 7.8 Hz, 1H), 2.80 (s, 2H), 2.76 (s, 2H), 2.68 (m, 1H), 2.54 (dd, J = 17.4 Hz, 3.3 Hz, 1H), 1.27 (d, J = 7.6 Hz, 3H), 1.13 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 208.2, 151.9, 151.8, 145.1, 137.1, 119.1, 118.4, 48.8, 47.9, 42.3, 39.9, 35.6, 28.5, 16.3. HRMS (ESI) calc. for $C_{15}H_{18}BrO^+$: 293.0536 [M + H]$^+$; found: 293.0531.

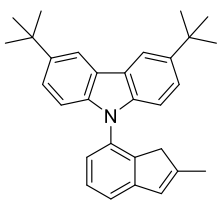


4-Bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacene (17). To a solution of 10.6 g (36 mmol) of 4-bromo-2,6,6-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-one in 100 mL of THF-MeOH (2:1, vol.) 2.0 g (54 mmol) of $NaBH_4$ was added by small portions at 5 °C. The resulting mixture was stirred overnight, and then 500 mL of water was added. This solution was acidified to pH 1, and then the product was extracted with 100 mL of dichloromethane. The organic extract was evaporated to dryness. The residue was dissolved in 120 mL of toluene, and 50 mg of *p*TsOH was added. The resulting mixture was refluxed with Dean-Stark head for 15 min to dehydrate 4-bromo-2,6,6-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-ol, then cooled to room temperature, passed through the short pad of silica gel. Toluene was evaporated and the residue was distilled at 110 °C/1 mbar using Kugelrohr. Yield: 8.1 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.96 (s, 1H), 6.44 (m, 1H), 3.22 (s, 2H), 2.78 (m, 4H), 2.14 (s, 3H), 1.17 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 145.7, 145.5, 143.3, 141.2, 138.7, 127.1, 116.3, 115.2, 48.7, 48.3, 43.8, 39.6, 28.9, 16.7. HRMS (ESI) calc. for $C_{15}H_{17}BrNa^+$: 299.0406 [M + Na]$^+$; found: 299.0408.

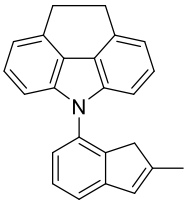
SYNTHESES OF SUBSTITUTED 4-(N-CARBAZOLYL)INDENES VIA BUCHWALD-HARTWIG REACTION



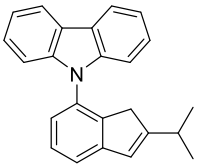
3,6-Dimethyl-9-(2-methyl-1*H*-indene-7-yl)-9*H*-carbazole (7). To a warm solution of 30.7 g (157 mmol) of 3,6-dimethyl-9*H*-carbazole in 1 L of toluene, 62.8 mL (157 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was refluxed for 30 min, then, 30.0 g (143 mmol) of 7-bromo-2-methyl-1*H*-indene (**1**) was added followed by a mixture of 1.28 g (5.7 mmol) of $Pd(OAc)_2$ and 3.13 g (3.0 mmol) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane = 10/1). Yield: 34.7 g (75%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.04 (m, 2H), 7.45–7.53 (m, 2H), 7.30 (m, 3H), 7.14 (m, 2H), 6.66 (m, 1H), 3.11 (s, 2H), 2.65 (s, 6H), 2.13 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 148.1, 146.8. 140.7, 139.2, 132.8, 128.6, 128.0, 127.0, 126.9, 123.4, 123.1, 120.2, 119.5, 41.3, 21.4, 16.6. HRMS (ESI) calc. for $C_{24}H_{21}NNa^+$: 346.1566 [M + Na]$^+$; found: 346.1573.



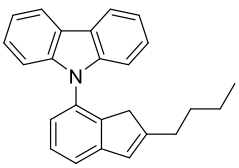
3,6-Di-*tert*-butyl-9-(2-methyl-1*H*-indene-4/7-yl)-9*H*-carbazole (8). To a warm solution of 43.9 g (157 mmol) of 3,6-di-*tert*-butyl-9*H*-carbazole in 1 L of toluene, 62.8 mL (157 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was refluxed for 30 min, then, 30.0 g (143 mmol) of 7-bromo-2-methyl-1*H*-indene (**1**) was added followed by a mixture of 1.28 g (5.7 mmol) of $Pd(OAc)_2$ and 3.13 g (3.0 mmol) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane = 10/1). Yield: 40.2 g (69%) of a white solid. The product was a mixture of isomers major/minor = 1.4/1.0. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (m, 2H), 7.45–7.50 (m, 3H), 7.35 (m, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.14 (m, 1H), 3.46 (s, 2H), 2.10 (s, 3H), 1.53 (s, 18H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.23 (m, 2H), 7.41–7.48 (m, 4H), 7.23 (m, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.60 (m, 1H), 3.09 (s, 2H), 2.08 (s, 3H), 1.52 (s 18H). $^{13}C\{^1H\}$ NMR (major*/minor°, 100 MHz, $CDCl_3$): *δ* 148.1, 146.9, 146.8, 145.4, 143.4, 142.29*, 142.26°, 140.7, 139.7, 139.1, 132.9, 129.2, 128.0, 127.0, 125.4, 125.1, 124.6, 123.4, 123.39, 123.1, 122.6, 119.5, 116.2°, 116.1*, 109.6*, 109.4°, 43.2*, 41.4°, 34.7, 32.1, 16.8*, 16.6°. HRMS (ESI) calc. for $C_{30}H_{33}NNa^+$: 430.2505 [M + Na]$^+$; found: 430.2498.



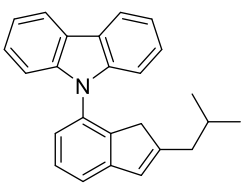
4-(2-Methyl-1*H*-inden-7-yl)-8,9-dihydro-4*H*-benzo[*def*]carbazole (9). To a warm solution of 5.5 g (28.5 mmol) of 8,9-dihydro-4*H*-benzo[*def*]carbazole in 250 mL of toluene, 10.9 mL (27.2 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was refluxed for 30 min, then, 5.42 g (25.9 mmol) of 7-bromo-2-methyl-1*H*-indene (**1**) was added followed by a mixture of 175 mg (0.78 mmol) of $Pd(OAc)_2$ and 485 mg (1.55 mmol) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/ethylacetate = 10/1). Yield: 6.68 g (80%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.44 (m, 1H), 7.30–7.39 (m, 4H), 7.03–7.08 (m, 4H), 6.61 (m, 1H), 3.45 (m, 4H), 3.20 (s, 2H), 3.16 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.2, 146.8, 146.6, 145.6, 141.9, 139.3, 138.7, 138.3, 133.6, 130.5, 130.3, 130.1, 127.8, 127.0, 126.70, 126.66, 125.3, 124.6, 123.8, 123.0, 122.9, 122.2, 122.0, 119.1, 117.1, 108.2, 108.0, 43.1, 41.7, 26.6, 16.8, 16.6. HRMS (ESI) calc. for $C_{24}H_{19}NNa^+$: 344.1410 $[M + Na]^+$; found: 344.1413.



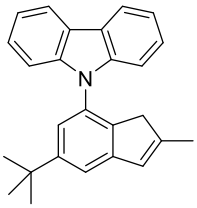
9-(2-Isopropyl-1*H*-indene-4/7-yl)-9*H*-carbazole (10). 42.0 mL (105 mmol) of 2.5M solution of *n*-butyllithium in hexane was added to solution of 17.5 g (105 mmol) carbazole in 1 L of toluene. The resulting solution was refluxed for 30 min. Next, 22.7 g (95.7 mmol) of 4-bromo-2-isopropyl-1*H*-indene (**2**) and premixed 0.86 g (3.8 mmol) $Pd(OAc)_2$ and 2.09 g (6.7 mmol) of *t*BuMePhos were added to the obtained solution. Brown reaction mixture was refluxed for 6 hours until the lithium salt of carbazole dissolved completely and a dark heavy precipitate was formed. The mixture was cooled to room temperature and filtered through a short pad of Celite©. The solvent was evaporated and the residue was purified by column chromatography on Silica Gel 60 (eluent: hexane/dichloromethane = 10/1). Yield: 24.8 g (80%) of a white solid. The product was a mixture of isomers major/minor = 2.4/1.0. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.33 (d, *J* = 7.7 Hz, 2H), 7.52–7.59 (m, 4H), 7.37–7.45 (m, 4H), 7.33 (m, 1H), 6.76 (m, 1H), 3.23 (s, 2H), 2.78 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 157.8, 147.9, 140.6, 140.5, 128.1, 125.8, 125.7, 123.9, 123.6, 123.1, 120.3, 120.1, 119.5, 110.0, 37.9, 29.9, 22.3. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.32 (d, *J* = 7.6 Hz, 2H), 7.52–7.64 (m, 4H), 7.37–7.45 (m, 4H), 7.33 (m, 1H), 6.26 (br.s, 1H), 3.63 (s, 2H), 281 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 158.2, 145.2, 143.1, 141.1, 132.6, 128.9, 125.5, 124.8, 123.1, 123.0, 121.9, 120.1, 119.5, 110.2, 39.6, 30.1, 22.4. HRMS (ESI) calc. for $C_{24}H_{21}NNa^+$: 346.1566 $[M + Na]^+$; found: 346.1570.



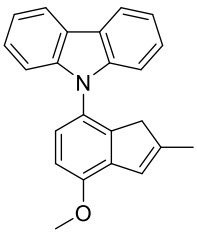
9-(2-Butyl-1*H*-inden-4/7-yl)-9*H*-carbazole (11). To a warm solution of 20.5 g (122.6 mmol) of 9*H*-carbazole in 1000 mL of toluene, 40.0 mL (100 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was stirred 0.5 h at room temperature, then, 25.1 g (100.0 mmol) of 7-bromo-2-butyl-1*H*-indene (**3**) was added followed by a mixture of 450 mg (2.0 mmol, 2 mol.%) of $Pd(OAc)_2$ and 938 mg (3.0 mmol, 3 mol.%) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane =10/1, then, 5/1, vol.). Yield: 25.3 g (75%) of a white solid. The product was a mixture of isomers major/minor = 1.5/1.0. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (m, 2H), 7.63–7.71 (m, 4H), 7.50–7.59 (m 4H), 7.47 (m, 1H), 6.86 (m, 1H), 3.33 (s, 2H), 2.60 (m, 2H), 1.74 (m, 2H), 1.57 (m, 2H), 1.16 (m, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.45 (m, 2H), 7.63–7.71 (m, 4H), 7.50–7.59 (m, 4H), 7.47 (m, 1H), 6.43 (m, 1H), 3.68 (s, 2H), 2.62 (m, 2H), 1.74 (m, 2H), 1.57 (m, 2H), 1.15 (m, 3H). ^{13}C{^{1}H} NMR (major*/minor°, 100 MHz, $CDCl_3$): *δ* 152.0*, 151.7°, 148.0*, 145.3°, 143.1°, 141.1*, 140.6*, 140.5°, 132.5, 128.7, 128.0, 125.8, 125.7, 125.4, 124.6, 123.8, 123.4, 123.11, 123.07, 122.9, 120.3*, 120.1°, 119.9°, 119.5*, 110.2°, 109.9*, 41.4°, 39.6*, 30.9°, 30.81*, 30.77°, 30.6*, 22.4*, 22.3°, 13.79*, 13.76°. HRMS (ESI) calc. for $C_{25}H_{23}NNa^+$: 360.1723 $[M + Na]^+$; found: 360.1720.



9-(2-Isobutyl-1*H*-inden-7-yl)-9*H*-carbazole (12). To a warm solution of 15.0 g (89.5 mmol) of 9*H*-carbazole in 700 mL of toluene, 29.2 mL (73.0 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was stirred 0.5 h at room temperature, then, 18.3 g (73.0 mmol) of 7-bromo-2-isobutyl-1*H*-indene (**4**) was added followed by a mixture of 329 mg (1.46 mmol, 2 mol.%) of $Pd(OAc)_2$ and 685 mg (2.2 mmol, 3 mol.%) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane = 10/1, then, 5/1, vol.). Yield: 17.3 g (70%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.15 (d, *J* = 7.8 Hz, 2H), 7.46–7.32 (m, 4H), 7.30–7.18 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.58 (s, 1H), 3.00 (s, 2H), 2.13 (d, *J* = 7.1 Hz, 2H), 1.71 (m, 1H), 0.84 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 150.7, 148.1, 140.7, 140.6, 132.5, 128.1, 127.1, 125.8, 123.5, 123.1, 120.3, 119.9, 119.5, 110.0, 40.6, 39.9, 28.1, 22.6. HRMS (ESI) calc. for $C_{25}H_{23}NNa^{+}$: 360.1723 [M + Na]$^{+}$; found: 360.1724.



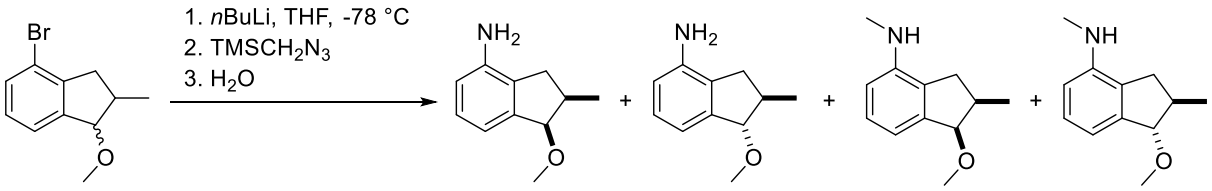
9-(2-Methyl-6-*tert*-butyl-1*H*-inden-7-yl)-9*H*-carbazole (13). To a warm solution of 15.0 g (89.5 mmol) of 9*H*-carbazole in 700 mL of toluene, 29.2 mL (73.0 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was refluxed for 30 min, then 19.4 g (73.0 mmol) of 7-bromo-2-methyl-5-*tert*-butyl-1*H*-indene (**5**) was added followed by a mixture of 658 mg (2.9 mmol, 4 mol.%) of $Pd(OAc)_2$ and 1.6 g (5.1 mmol, 7 mol.%) of *t*BuMePhos. The resulting mixture was refluxed for 6 h, cooled to room temperature and filtered through a short pad of Celite© and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane = 10/1). Yield: 18.7 g (73%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.17 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.2 Hz, 8.1 Hz, 1.0 Hz, 2H), 7.30–7.25 (m, 2H), 7.25 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.58 (m, 1H), 2.98 (s, 2H), 2.04 (s, 3H), 1.38 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 151.9, 148.1, 146.8, 140.7, 137.5, 131.9, 127.2, 125.7, 123.1, 120.6, 120.3, 119.4, 116.9, 110.1, 41.02, 34.9, 31.6, 16.7. HRMS (ESI) calc. for $C_{26}H_{25}NNa^{+}$: 374.1879 [M + Na]$^{+}$; found: 374.1878.

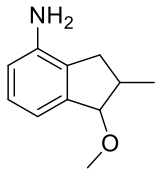


A mixture of 9-(4-methoxy-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole and 9-(7-methoxy-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole (14). To a warm solution of 32.8 g (196.2 mmol) of 9*H*-carbazole in 1200 mL of toluene, 76.8 mL (192 mmol) of 2.5 M ^{n}BuLi in hexanes was added. The resulting viscous mixture was stirred 0.5 h at room temperature, then, 22.4 g (936.8 mmol) of 7-bromo-4-methoxy-2-methyl-1*H*-indene (**6**) was added followed by a mixture of 421 mg (1.88 mmol, 2 mol.%) of $Pd(OAc)_2$ and 879 mg (2.81 mmol, 3 mol.%) of *t*BuMePhos. The resulting mixture was refluxed for 8 h, cooled to room temperature and quenched with 100 mL of water. The organic layer was separated, dried over K_2CO_3 and evaporated to dryness. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane = 5/1, then, 3/1, vol.). Yield: 11.59 g (38%) of white solid of ca. 65 to 35 mixture of 9-(4-methoxy-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole and 9-(7-methoxy-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.20 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.37–7.27 (m, 3H), 7.25–7.14 (m, 2H), 6.99 (d, *J* = 8.4 Hz) and 6.88 (d, *J* = 8.5 Hz) (sum 1H), 6.75 (m) and 5.99 (m) (sum 1H), 4.01 (s, 3H), 3.44 (s) and 3.02 (s) (sum 2H), 2.09 (s) and 2.06 (s) (sum 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 154.4, 152.0, 147.6, 145.3, 145.1, 142.8, 141.6, 141.0, 135.9, 131.4, 127.4, 125.8, 125.7, 124.8, 124.6, 123.3, 123.0, 122.4, 120.3, 120.1, 119.3, 110.1, 110.0, 109.9, 107.4, 55.7, 55.5, 41.7, 40.8, 16.7, 16.6. HRMS (ESI) calc. for $C_{23}H_{19}NNaO^{+}$: 348.1359 [M + Na]$^{+}$; found: 348.1362.

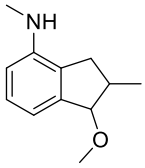
SYNTHESIS OF SUBSTITUTED 2-METHYL-1*H*-INDEN-4/7-AMINES

First, we tried to synthesize 4-amino-1-methoxy-2-methylindane via reaction of TMSMA with aryllithium generated by reaction of 4-bromo-1-methoxy-2-methylindane with n-butyllithium. Formation of the N-methylated side product, 4-methylamino-1-methoxy-2-methylindane, followed by demanding chromatographic separation of four diastereomers lead to low yields of the desired product.

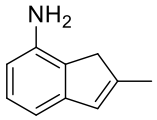




1-Methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-amine. To a solution of 48.2 g (200 mmol) 4-bromo-1-methoxy-2-methyl-2,3-dihydro-1*H*-indene in 1 L THF, 88.0 mL (220 mmol) of a 2.5 M solution of ^{n}BuLi in hexane was added dropwise at -78 °C. Reaction mixture was stirred 1 h at -78 °C, then 28.4 g (220 mmol) of trimethylsilylmethyl azide was slowly added via syringe. The resulting mixture was stirred at room temperature overnight. Next, the solution was poured into 1 L of water, organic layer was separated and water was extracted with diethyl ether (2×250 mL). Organic layers were collected, dried over Na_2SO_4 and solvents were evaporated. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate = 5/1). Yield: 20.0 g (56%) as a red crystalizable oil, mixture of diastereomers with ratio 1.6/1. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.07 (m, 1H), 6.85 (m, 1H), 6.61 (m, 1H), 4.39 (d, *J* = 3.7 Hz, 1H), 3.58 (br.s, 2H), 3,45 (s, 3H), 3.04 (dd, *J* = 15.4 Hz, 7.7 Hz, 1H), 2.55 (m, 1H), 2.24 (dd, *J* = 15.4 Hz, 4.5 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 143.7, 142.4, 127.5, 127.2, 115.7, 114.5, 86.1, 56.6, 38.4, 34.8, 13.7. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.05 (m, 1H), 6.84 (m, 1H), 6.61 (m, 1H), 4.49 (d, *J* = 5.7 Hz, 1H), 3,58 (br.s, 2H), 3.41 (s, 3H), 2.75 (m, 1H), 2.62 (m, 1H), 2.49 (m, 1H), 1.15 (d, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 143.0, 142.5, 128.1, 127.8, 115.7, 114.3, 91.6, 56.1, 39.3, 35.0, 19.5. HRMS (ESI) calc. for $C_{11}H_{16}NO^{+}$: 178.1226 $[M + H]^{+}$; found: 178.1222.

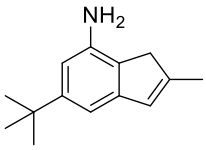


1-Methoxy-*N*,2-dimethyl-2,3-dihydro-1*H*-inden-4-amine. The substance was obtained as a side product of synthesis of 1-methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-amine with 26% yield from 4-bromo-1-methoxy-2-methyl-2,3-dihydro-1*H*-indene. The product was isolated as a mixture of diastereomers with ratio 1.7/1. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.19 (m, 1H), 6.81 (m, 1H), 6.55 (m, 1H), 4.41 (d, *J* = 3.7 Hz, 1H), 3.49 (br.s, 1H), 3,44 (s, 3H), 2.99 (dd, *J* = 15.3 Hz, 7.6 Hz, 1H), 2.90 (s, 3H), 2.56 (m, 1H), 2.17 (dd, *J* = 15.3 Hz, 4.6 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.17 (m, 1H), 6.81 (m, 1H), 6.55 (m, 1H), 4.49 (d, *J* = 5.7 Hz, 1H), 3.49 (br.s, 1H), 3.41 (s, 3H), 2.90 (s, 3H), 2.70 (m, 1H), 2.62 (m, 1H), 2.44 (dd, *J* = 14.1 Hz, 6.1 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, mixture of diastereomers): *δ* 145.4, 145.3,142.8, 142.0, 127.6, 127.2, 127.0, 113.9, 113.8, 108.6, 108.4, 91.6, 86.0, 56.3, 56.1, 55.8, 39.0, 38.2, 34.8, 34.5, 30.3, 30.2, 19.4, 13.6. HRMS (ESI) calc. for $C_{12}H_{18}NO^{+}$: 192.1383 $[M + H]^{+}$; found: 192.1385.

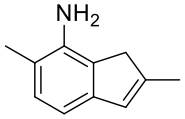


2-Methyl-1*H*-inden-4/7-amine (15). ***Via Buchwald-Hartwig reaction:*** To a solution of 6.9 g (37.9 mmol) of benzophenone imine in 250 mL of toluene, 7.2 g (34.4 mmol) 4-bromo-2-methyl-1*H*-indene (**1**) was added. Then 9.6 g (86.0 mmol) of potassium *tert*-butylate was added followed by a mixture of 1.58 mg (1.7 mmol, 5 mol.%) of Pd_2dba_3 and 722 mg (1.7 mmol, 5 mol.%) of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl). The resulting mixture was refluxed for 24 h, and then cooled to room temperature. The resulting solution was poured into 100 mL of water and extracted with diethyl ether (3×50 mL). The combined organic fractions were dried over Na_2SO_4 and the solvents were evaporated. The residue was dissolved in 50 mL of THF and 5 mL of concentrated HCl was added. After two hours of stirring, the solution was poured into 200 mL of water and extracted with diethyl

ether (2×50 mL). Then 2 M solution of NaOH was added to the water layer till pH > 10. The resulting mixture was extracted with diethyl ether (3×50 mL), the combined organic layers were dried over Na_2SO_4 and the solvent were evaporated. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane). Yield: 2.8 g (56%). ***Via electrophilic amination:*** Solution of 37.2 g of 4-bromo-2-methyl-1*H*-indene (**1**) (178 mmol) and 37.1 mL of 1,2-dibromoethane (430 mmol) in 1 L of THF was slowly added dropwise to 16.7 g of magnesium turnings (695 mmol) in 9 hours. The resulting solution was refluxed for additional 5 hours then the mixture was allowed to cool down to room temperature. The solution of 20.7 g of trimethylsilylmethyl azide (160 mmol) in 200 mL of THF was slowly added dropwise to the obtained Grignard reagent. The resulting mixture was stirred overnight, then 300 mL of water were added dropwise to quench the reaction. The organic layer was separated and water was extracted with diethyl ether (2 ×100 ml). Organic layers were collected, dried over Na_2SO_4 and rotary-evaporated. The crude product was distilled from the residue on Kugelrohr at 130 °C (1 Torr). Recrystallization from ethanol at -30 °C gave 15.5 g of analytically pure product as orange crystals m.p. 43 °C in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.4 Hz, 1H), 6.55 (d, J = 7.8 Hz, 1H), 6.53 (br.s, 1H), 3.63 (br.s, 2H), 3.12 (s, 2H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.7, 145.0, 141.0, 127.6, 127.5, 126.8, 111.34, 111.30, 39.5, 16.7. HRMS (ESI) calc. for $C_{10}H_{12}N^+$: 146.0964 $[M + H]^+$; found: 146.0964.

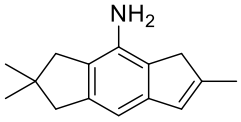


5-*Tert*-butyl-2-methyl-1*H*-indene-4/7-amine (18). ***Via Buchwald-Hartwig reaction:*** To a solution of 6.9 g (37.9 mmol) of benzophenone imine in 250 mL of toluene, 9.1 g (34.4 mmol) 7-bromo-5-*tert*-butyl-2-methyl-1*H*-indene (**5**) was added. Then 9.6 g (86.0 mmol) of potassium *tert*-butylate was added followed by a mixture of 1.58 mg (1.7 mmol, 5 mol.%) of Pd_2dba_3 and 722 mg (1.7 mmol, 5 mol.%) of IPr·HCl. The resulting mixture was refluxed for 24 h, and then cooled to room temperature. The resulting solution was poured into 100 mL of water and extracted with diethyl ether (3×50 mL). The combined organic fractions were dried over Na_2SO_4 and the solvents were evaporated. The residue was dissolved in 50 mL of THF, and 5 mL of concentrated HCl was added. After two hours of stirring, the solution was poured into 200 mL of water and extracted with diethyl ether (2×50 mL). Then a 2 M solution of NaOH was added to the water layer till pH > 10. The resulting mixture was extracted with diethyl ether (3×50 mL), the combined organic layers were dried over Na_2SO_4 and the solvent were evaporated. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane). Yield: 3.0 g (43%). ***Via electrophilic amination:*** Solution of 53.0 g of 7-bromo-5-*tert*-butyl-2-methyl-1*H*-indene (**5**) (200 mmol) and 35.0 mL of 1,2-dibromoethane (400 mmol) in 1000 mL of THF was slowly added dropwise to 15.0 g of magnesium turnings (620 mmol) in 9 hours. The resulting solution was refluxed for an additional 5 hours then the mixture was allowed to cool down to room temperature. The solution of 23.2 g of trimethylsilylmethyl azide (180 mmol) in 250 mL of THF was slowly added dropwise to the obtained Grignard reagent. The resulting mixture was stirred overnight at room temperature, then 300 mL of brine were added dropwise to quench the reaction. The organic layer was separated and water was extracted with diethyl ether (2 ×200 ml). Organic layers were collected, dried over Na_2SO_4 and rotary-evaporated. Product was purified by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate/triethylamine = 100/10/1). Yield: 16.8 g (47%) as mixture of two isomers with ratio 2.3/1.0. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, J = 1.4 Hz, 1H), 6.59 (d, J = 1.4 Hz, 1H), 6.48 (m, 1H), 3.62 (br.s, 2H), 3.09 (s, 2H), 2.18 (s, 3H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.3, 146.7, 145.1, 140.4, 127.8, 124.2, 108.9, 108.7, 39.2, 34.5, 31.5, 16.7. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (m, 1H), 6.66 (m, 1H), 6.46 (m, 1H), 3.62 (br.s, 2H), 3.31 (s, 2H), 2.16 (s, 3H), 1.35 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.2, 144.6, 143.2, 137.4, 129.5, 122.2, 112.0, 110.7, 43.1, 34.4, 31.4, 16.7. HRMS (ESI) calc. for $C_{14}H_{20}N^+$: 202.1590 $[M + H]^+$; found: 202.1584.



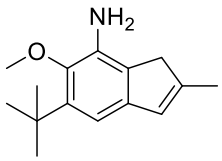
2,5-Dimethyl-1*H*-indene-7-amine (19). ***Via Buchwald-Hartwig reaction:*** To a solution of 6.9 g (37.9 mmol) of benzophenone imine in 100 mL of toluene, 7.7 g (34.4 mmol 4-bromo-2,5-dimethyl-1*H*-indene (**16**) was added. Then 9.6 g (86.0 mmol) of potassium *tert*-butylate were added followed by a mixture of 1.58 mg (1.7 mmol, 5 mol.%) of Pd_2dba_3 and 722 mg (1.7 mmol, 5 mol.%) of IPr·HCl. The resulting mixture was refluxed for 72 h, and then cooled to room temperature.

The resulting solution was poured into 100 mL of water and extracted with diethyl ether (3×50 mL). The combined organic fractions were dried over Na_2SO_4 and the solvents were evaporated. The residue was dissolved in 50 mL of THF, and 5 mL of concentrated HCl were added. After two hours of stirring, the solution was poured into 200 mL of water and extracted with diethyl ether (2×50 mL). Then 2 M solution of NaOH was added to the water layer till pH > 10. The resulting mixture was extracted with diethyl ether (3×50 mL), the combined organic layers were dried over Na_2SO_4 and the solvent were evaporated. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane). Yield: 2.3 g (42%). ***Via Electrophilic amination:*** Solution of 50.0 g of 4-bromo-2,5-dimethyl-1*H*-indene (**16**) (224 mmol) and 37.1 mL of 1,2-dibromoethane (430 mmol) in 1000 mL of THF was slowly added dropwise to 16.7 g of magnesium turnings (696 mmol) in 9 hours. The resulting solution was refluxed for additional 5 hours then the mixture was allowed to cool down to room temperature. The solution of 26.2 g of trimethylsilylmethyl azide (201 mmol) in 200 mL of THF was slowly added dropwise to the obtained Grignard reagent. The resulting mixture was stirred overnight then 300 mL of water were added dropwise to quench the reaction. The organic layer was separated and water was extracted with diethyl ether (2 ×100 ml). Organic layers were collected, dried over Na_2SO_4 and rotary-evaporated. Product was purified by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate/triethylamine = 100/10/1). Yield: 20.5 g (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, J = 7.5 Hz, 1H), 6.74 (d, J = 7.5 Hz, 1H), 6.47 (m, 1H), 3.57 (br.s, 2H), 3.10 (s, 2H), 2.25 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.7, 144.0, 139.4, 128.7, 127.5, 126.8, 118.4, 110.9, 39.6, 17.0, 16.7. HRMS (ESI) calc. for $C_{11}H_{14}N^+$: 160.1121 [M + H]$^+$; found: 160.1120.



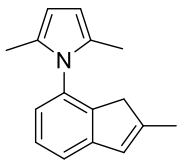
2,2,6-Trimethyl-1,2,3,5-tetrahydro-*s*-indacen-4/7-amine (20). ***Via Buchwald-Hartwig reaction:*** To a solution of 6.9 g (37.9 mmol) of benzophenone imine in 250 mL of toluene, 9.5 g (34.4 mmol) 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacene (**17**) was added. Then 9.6 g (86.0 mmol) of potassium *tert*-butylate was added followed by a mixture of 1.58 mg (1.7 mmol, 5 mol.%) of Pd_2dba_3 and 722 mg (1.7 mmol, 5 mol.%) of IPr·HCl. The resulting mixture was refluxed for 72 h, and then cooled to room temperature. The resulting solution was poured into 100 mL of water and extracted with diethyl ether (3×50 mL). The combined organic fractions were dried over Na_2SO_4 and the solvents were evaporated. The residue was dissolved in 50 mL of THF and 5 mL of concentrated HCl were added. After two hours of stirring, the solution was poured into 200 mL of water and extracted with diethyl ether (2×50 mL). Then 2 M solution of NaOH was added to the water layer till pH > 10. The resulting mixture was extracted with diethyl ether (3×50 mL), the combined organic layers were dried over Na_2SO_4 and the solvent were evaporated. The crude product was purified by column chromatography on Silica Gel 60 (eluent: hexanes/dichloromethane). Yield: 4.3 g (58%). ***Via electrophilic amination:*** Solution of 10.2 g of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacene (**17**) (36.8 mmol) and 6.4 mL of 1,2-dibromoethane (73.6 mmol) in 250 mL of THF was slowly added dropwise to 2.9 g of magnesium turnings (118 mmol) in 1 hour. The resulting solution was refluxed for additional hour, then the mixture was allowed to cool down to room temperature. The solution of 5.1 g of trimethylsilylmethyl azide (36.8 mmol) in 50 mL of THF was slowly added dropwise to the obtained Grignard reagent. The resulting mixture was stirred overnight, then 300 mL of brine was added dropwise to quench the reaction. The organic layer was separated and water was extracted with diethyl ether (2 ×100 ml). The solution was passed through a short pad of silica which was then washed with additional 100 mL of ethylacetate. The resulting solution were dried over Na_2SO_4 and rotary-evaporated. The residue was dissolved in 100 mL of hexane and cooled to –20 °C overnight. The obtained yellow crystals were filtrated and died in vacuum. Solvents from the mother liquor were evaporated and the residue was recrystallized from 50 mL of hexane at –20 °C which gave another crop of yellow crystals. Yield: 4.4 g (58%) as a yellow solid, the product consists of two isomers with ratio 2/1. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.67 (s, 1H), 6.45 (m, 1H), 3.51 (br.s, 2H), 3.08 (s, 2H), 2.77 (s, 2H), 2.60 (s, 2H), 2.18 (s, 3H), 1.23 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.6, 143.9, 143.0, 137.4, 127.7, 124.7, 124.2, 107.8, 48.1, 43.9, 40.0, 39.1, 29.3, 16.8. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (s, 1H), 6.46 (m, 1H), 3.51 (br.s, 2H), 3.28 (s, 2H), 2.77 (s, 2H), 2.59 (s, 2H), 2.16 (s, 3H), 1.23 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.3,

142.5, 140.3, 134.3, 129.7, 125.8, 122.3, 111.3, 48.0, 42.8, 40.0, 39.1, 29.3, 16.8. HRMS (ESI) calc. for $C_{15}H_{20}N^+$: 214.1590 $[M + H]^+$; found: 214.1594.

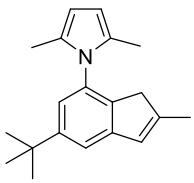


5-*Tert*-butyl-6-methoxy-2-methyl-1*H*-inden-4/7-amine (22). ***Via electrophilic amination:*** Solution of 34.2 g of 7-bromo-5-*tert*-butyl-6-methoxy-2-methyl-1*H*-indene (**21**) (116 mmol) and 10.0 mL of 1,2-dibromoethane (116 mmol) in 100 mL of THF was slowly added dropwise to refluxing 350 mL of THF with 6.1 g of magnesium turnings (255 mmol) in 3 hours. The resulting solution was refluxed for additional 2 hours, then the mixture was allowed to cool down to room temperature. The solution of 11.9 g of trimethylsilylmethyl azide (92.8 mmol) in 100 mL of THF was slowly added dropwise to the obtained Grignard reagent. The resulting mixture was stirred overnight, then 1 L of brine was added dropwise to quench the reaction. The organic layer was separated and water was extracted with diethyl ether (2×200 ml). Organic layers were collected, dried over Na_2SO_4 and rotary-evaporated. The product was purified by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate/triethylamine = 100/10/1). Yield: 15.3 g (72%) as a dark brown solid, mixture of isomers major/minor = 1.25/1.0. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (s, 1H), 6.43 (m, 1H), 3.86 (s, 3H), 3.67 (br.s, 2H), 3.11 (br.s, 2H), 2.17 (s, 3H), 1.47 (s, 9H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 1H), 6.45 (m, 1H), 3.86 (s, 3H), 3.72 (br.s, 2H), 3.28 (br.s, 2H), 2.17 (s, 3H), 1.46 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, mixture of isomers, $CDCl_3$): δ 145.8, 144.43, 144.40, 144.2, 141.4, 141.1, 138.7, 138.2, 135.5, 132.2, 131.7, 127.5, 126.5, 122.3, 112.3, 108.8, 59.6, 59.4, 43.1, 39.8, 35.0, 34.9, 31.23, 31.17, 16.8, 16.7. HRMS (ESI) calc. for $C_{15}H_{22}NO^+$: 232.1696 $[M + H]^+$; found: 232.1690.

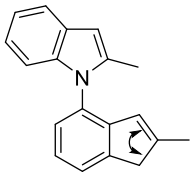
SYNTHESIS OF 4-(N-HETEROCYCLE)INDENES FROM SUBSTITUTED 2-METHYL-1*H*-INDEN-4/7-AMINES



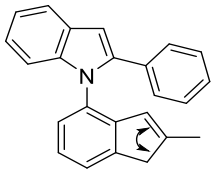
2,5-Dimethyl-1-(2-methyl-1*H*-inden-7-yl)-1*H*-pyrrole (23). Method A: To a solution of 12.0 g (83.0 mmol) 2-methyl-1*H*-inden-7-amine (**15**) and 11.3 g (99.6 mmol) hexan-2,5-dione in 5 mL of dry THF, 2.01 g (8 mmol) of iodine was added. The reaction mixture was stirred at room temperature for 2 days. Then the resulting solution was diluted with 20 mL of a hexane/ethylacetate = 10/1 mixture, and the product was isolated by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate = 10/1). Yield: 9.82 g (53%) as an orange solid. **Method B:** To a solution of 15.0 g (103.8 mmol) 2-methyl-1*H*-inden-7-amine (**15**) and 12.3 g (125 mmol) hexan-2,5-dione in 5 mL of dry THF, 0.88 g (2.6 mmol) of $ZrOCl_2(H_2O)_8$ were added. Then the resulting solution was diluted with 20 mL of hexane/ethylacetate = 10/1 mixture and the product was isolated by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate = 10/1). Yield: 2.4 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 2H), 6.98 (m, 1H), 6.57 (m, 1H), 5.97 (s, 2H), 3.06 (s, 2H), 2.15 (m, 3H), 2.01 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 146.7, 141.7, 134.4, 128.2, 127.6, 127.0, 123.8, 119.6, 105.3, 40.9, 16.6, 12.5. HRMS (ESI) calc. for $C_{16}H_{17}NNa^+$: 246.1253 $[M + Na]^+$; found: 246.1255.



1-(5-*Tert*-butyl-1-methoxy-2-methyl-2,3-dihydro-1*H*-inden-4/7-yl)-2,5-dimethyl-1*H*-pyrrole (24). Method B: To a solution of 23.1 g (74.2 mmol) 5-*tert*-butyl-2-methyl-1*H*-indene-4/7-amine (**18**) and 10.2 g (89.0 mmol) of hexan-2,5-dione in 10 mL of dry THF, 0.60 g (1.86 mmol) of $ZrOCl_2(H_2O)_8$ were added. Then the resulting solution was diluted with 20 mL of a hexane/ethylacetate = 10/1 mixture and the product was isolated by column chromatography on Silica Gel 60 (eluent: hexane/ethylacetate = 10/1). Yield: 12.0 g (58%) as a mixture of two isomers with ratio = 1/1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m) and 7.47 (m) (sum 1H), 7.22 (d, J = 1.6 Hz) and 7.10 (d, J = 1.7 Hz) (sum 1H), 6.63 (m) and 6.25 (m) (sum 1H), 6.06 (s) and 6.05 (s) (sum 2H), 3.48 (s) and 3.14 (s) (sum 2H), 2.22 (m, 3H), 2.12 (s) and 2.11 (s) (sum 6H), 1.48 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.3, 147.6, 147.1, 146.6, 146.5, 144.2, 141.3, 138.4, 133.8, 129.7, 128.9, 128.2, 127.2, 124.1, 123.3, 121.1, 119.8, 116.6, 105.2, 105.1, 43.1, 40.6, 34.7, 34.6, 31.6, 31.5, 16.7, 16.6, 12.8, 12.5. HRMS (ESI) calc. for $C_{20}H_{25}NNa^+$: 302.1879 $[M + Na]^+$; found: 302.1872.

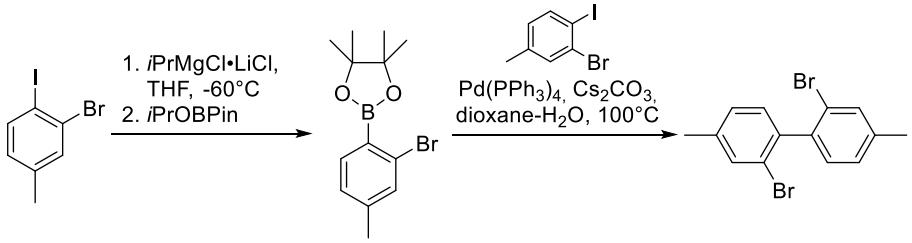


1-(2-Methyl-1*H*-indene-4/7-yl)-2-methyl-1*H*-indole (25). To a solution of 8.0 g (41.0 mmol) 1-bromo-2-(methylethynyl)benzene, 18.4 g (164 mmol) of potassium *tert*-butylate and 7.14 g (49.2 mmol) of 2-methyl-1*H*-inden-7-amine (**15**) in 250 mL toluene under argon, a mixture of 460 mg (2.05 mmol) $Pd(OAc)_2$ and 871 mg (2.05 mmol) of IPr·HCl was added. Reaction mixture was stirred at 110 °C for 24 hours. After that, the resulting mixture was poured into 500 mL of water. The mixture was extracted with diethyl ether (3×100 mL). The combined organic layers were dried over Na_2SO_4, and solvents were evaporated. The product was isolated from the residue by column chromatography (eluent: hexane/dichloromethane = 10/1). Yield: 8.0 g (76%) as a white solid. The product is a mixture of two isomers with ratio «indene-4-yl»/«inden-7-yl» = 1.8/1. «Indene-7-yl»: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.63 (m, 1H), 7.38–7.42 (m, 2H), 7.05–7.15 (m, 3H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.59 (s, 1H), 6.45 (s, 1H), 3.07 (d, *J* = 23.1 Hz, 1H), 2.97 (d, *J* = 23.1 Hz, 1H), 2.28 (s, 3H), 2.12 (s, 3H). «Inden-4-yl»: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.63 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.25–7.29 (m, 1H), 7.20 (m, 1H), 7.05–7.15 (m, 2H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.45 (s, 1H), 6.06 (s, 1H), 3.46 (s, 2H), 2.28 (s, 3H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR (major*/minor°, 100 MHz, $CDCl_3$): *δ* 147.7°, 147.6*, 146.9*, 145.0*, 144.2°, 141.5°, 138.2°, 137.5*, 137.4°, 136.9*, 133.0, 129.1, 128.2, 128.1, 127.8, 126.9, 126.2, 124.5, 124.3, 123.9, 123.0, 120.7, 119.8, 119.7, 119.6, 119.4, 110.3*, 110.0°, 100.6, 43.2*, 41.0°, 16.8*, 16.6°, 13.1*, 13.0°. HRMS (ESI) calc. for $C_{19}H_{17}NNa^+$: 282.1253 [M + Na]$^+$; found: 282.1256.



1-(2-Methyl-1*H*-indene-4/7-yl)-2-phenyl-1*H*-indole (26). To a solution of 5.2 g (20.2 mmol) 1-bromo-2-(phenylethynyl)benzene, 9.1 g (80.8 mmol) potassium *tert*-butylate and 3.5 g (24.3 mmol) 2-methyl-1*H*-inden-7-amine (**15**) in 100 mL of toluene under argon, a mixture of 227 mg (1.0 mmol) $Pd(OAc)_2$ and 430 mg (1.0 mmol) IPr·HCl was added. Reaction mixture was stirred at 110 °C for 24 hours. After tha,t the resulting mixture was poured into 500 mL of water. The mixture was extracted with diethyl ether (3×100 mL). The combined organic layers were dried over Na_2SO_4, and solvents were evaporated. The residue was triturated in a mixture of hexane/ethylacetate = 10/1 and filtered. The precipitate was washed with 10 mL of hexane and dried in vacuum. Yield: 5.1 g (78%) as a bright yellow solid. The product is mixture of two isomers in ratio 10/1. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73 (m, 1H), 7.38 (m, 1H), 7.32 (m, 2H), 7.16–7.24 (m, 5H), 7.08–7.12 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.18 (s, 1H), 3.40 (m, 2H), 2.08 (s, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, selected resonances only): *δ* 6.88 (s, 1H), 6.50 (m, 1H), 3.00 (d, *J* = 23.0 Hz, 1H), 2.82 (d, *J* = 23.0 Hz, 1H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, mixture of isomers major*/minor°): *δ* 147.4, 144.9, 143.8, 141.2, 139.4, 132.7, 130.0, 128.5, 128.2, 128.1, 127.0, 126.4, 124.6, 124.3, 122.6, 122.1, 120.4, 120.3, 119.5°, 111.2, 103.0*, 102.9°, 43.2*, 41.2°, 16.88*, 16.6°. HRMS (ESI) calc. for $C_{24}H_{19}NNa^+$: 344.1410 [M + Na]$^+$; found: 344.1409.

2,2'-Dibromo-4,4'–dimethylbiphenyl.

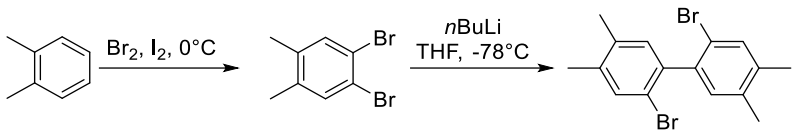


2-(2-Bromo-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 90.0 mL of an *i*PrMgCl•LiCl solution in THF (162 mmol, 1.8 M) was added dropwise to the solution of 40.0 g of 2-bromo-1-iodo-4-methylbenzene (135 mmol) in THF at -60 °C under inert atmosphere. The resultant mixture was stirred at -60 °C for an additional hour and then 41.5 mL (203 mmol) of *i*PrOBPin was added in one portion at -60 °C. The obtained slurry was allowed to warm up to room temperature, and was then poured into 1 L of water and extracted with diethyl ether (2×200 ml). The extracts were combined with the organic layer and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuum giving 39.1 g of analytically pure 2-(2-bromo-4-methylphenyl)-

4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a colorless oil in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 1H), 7.38 (s, 1H), 7.08 (d, J = 7.5 Hz, 1H), 2.31 (s, 3H), 1.36 (s, 12H).

2,2'-Dibromo-4,4' –dimethylbiphenyl. 3.0 g of Tetrakis(triphenylphosphine)palladium(0) (2.7 mmol) was added to the solution of 40.0 g of 2-bromo-1-iodo-4-methylbenzene (135 mmol) and 39.1 g 2-(2-bromo-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (131 mmol) in 800 mL of dioxane and 400 mL of water under inert atmosphere. The resulting mixture was heated at 80 °C for 16 hours and then poured into 1L of water and extracted with dichloromethane (2×300 ml). The extracts were combined with the organic layer and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue was recrystallized from hexane at -30 °C giving 36.9 g of 2,2'-dibromo-4,4'–dimethylbiphenyl as white crystals in 78 % yield. Anal. calc. for $C_{14}H_{12}Br_2$: C, 49.45; H, 3.56. Found: C, 49.34; H, 3.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.11–7.18 (m, 4H), 2.39 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.4, 139.0, 132.9, 130.8, 127.9, 123.3, 20.9.

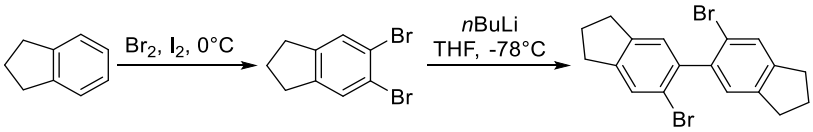
2,2'-Dibromo-4,4',5,5'-tetramethylbiphenyl.



1,2-Dibromo-4,5-dimethylbenzene. 40.0 mL Br_2 was added dropwise to a solution of 200 mg of I_2 in 46 mL of *o*-xylene (380 mmol) at 0°C within 30 min. The resultant was left overnight at room temperature, followed by dissolving in Et_2O (200 ml), washing with 2 N NaOH (2×100 ml), H_2O (2×100 ml) and drying over Na_2SO4. The organic solvents were then concentrated in vacuo to afford a faintly pink colored oil, which was further purified by recrystallization in methanol to give 68.0 g of pure 4,5-dibromo-*o*-xylene in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 2.18 (s, 6H).

2,2'-Dibromo-4,4',5,5'-tetramethylbiphenyl. To a stirred solution of 1,2-dibromo-*o*-xylene (52.8 g, 200 mmol) in dry THF (800 ml) was added *n*BuLi (40.0 ml, 100 mmol, 2.5 M in *n*-hexane) at -78 °C, and was then stirred for 1 h at -78 °C after the addition. The reaction mixture was allowed to warm to room temperature, stirred for an additional 1 h, and then was hydrolyzed with 5% HCl. The organic layer was separated and the aqueous layer was extracted with Et_2O. The extracts were combined with the organic layer and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the product was purified by chromatography on silica gel using hexane as eluent, to give 25.0 g of pure 2,2'-dibromo-4,4',5,5'-tetramethylbiphenyl in 68% yield. Anal. calc. for $C_{16}H_{16}Br_2$: C, 52.21; H, 4.38. Found: C, 52.34; H, 4.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 6.98 (s, 2H), 2.28 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.9, 135.4, 132.9, 132.0, 120.1, 19.23, 19.19.

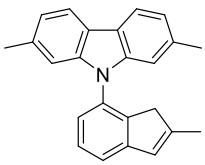
6,6'-Dibromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-5,5'-biindene.



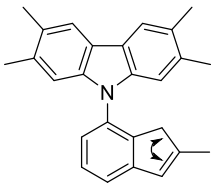
5,6-Dibromoindane. 106.0 mL Br_2 was added dropwise to a solution of 500 mg of I_2 in 122.5 mL of indane (1 mol) at 0 °C within 40 min. The resultant was left overnight at room temperature, followed by dissolving in Et_2O (500 ml), washing with 2 N NaOH (2×200 ml), H_2O (2×200 ml) and drying over Na_2SO_4. The organic solvents were then concentrated in vacuum. The residue was further purified by recrystallization in hexanes to give 97.0 g of pure 5,6-dibromoindane in 35% yield. The ^{1}H NMR spectrum matches one from the literature data [M. Nishimura et al. *Jap. Pat. Appl. JP2010241770*] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 2.84 (t, J = 7.5 Hz, 4H), 2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 129.1, 121.5, 32.3, 25.6.

6,6'-Dibromo-2,2',3,3'-tetrahydro-1H,1'H-5,5'-biindene. To a stirred solution of 5,6-dibromoindane (69 g, 250 mmol) in dry THF (900 ml) was added *n*BuLi (50 ml, 125 mmol, 2.5 M in *n*-hexane) at -78 °C, and was then stirred for 1 h at -78 °C after addition. The reaction mixture was allowed to warm to room temperature, stirred

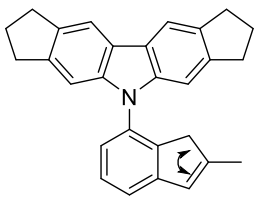
for an additional 1 h, and then was hydrolyzed with 5% HCl. The organic layer was separated and the aqueous layer was extracted with Et_2O. The extracts were combined with the organic layer and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuum and the product was purified recrystallization from methanol to give 42 g of pure 6,6'-dibromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-5,5'-biindene in 86% yield. Anal. calc. for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 55.37; H, 4.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.06 (s, 2H), 2.82–2.97 (m, 8H), 2.08–2.16 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 143.3, 139.9, 128.0, 126.6, 120.8, 32.5, 32.3, 25.5.



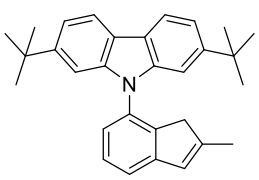
2,7-Dimethyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (27). A solution of 810 mg (4 mmol) of tri(*tert*-butyl)phosphane in 10 mL of toluene was added to a mixture of 23.5 g (69 mmol) 2,2'-dibromo-4,4'-dimethyl-1,1'-biphenyl, 10 g (69 mmol) of 2-methyl-1*H*-inden-7-amine (**15**), 23.2 g (240 mmol) of sodium *tert*-butoxide and 1.2 g (2.0 mmol) $Pd_2(dba)_3$ in 500 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×250 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a white solid. Yield: 14.1 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (d, *J* = 7.9 Hz, 2H), 7.42–7.47 (m, 2H), 7.21 (dd, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.09 (m, 2H), 6.91 (m, 2H), 6.61 (m, 1H), 3.03 (s, 2H), 2.46 (s, 6H), 2.07 (d, *J* = 1.1. Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 147.0, 141.2, 141.0, 135.4, 132.6, 128.1, 127.0, 123.7, 120.9, 119.73, 119.68, 109.9, 41.3, 22.0, 16.7. HRMS (ESI) calc. for $C_{24}H_{21}NNa^+$: 346.1566 $[M + Na]^+$; found: 346.1565.



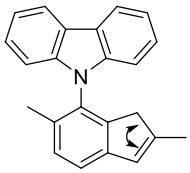
2,3,6,7-Tetramethyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (28). A solution of 810 mg (4 mmol) of tri(*tert*-butyl)phosphane in 10 mL of toluene was added to a mixture of 25.4 g (69 mmol) 2,2'-dibromo-4,4',5,5'-tetramethyl-1,1'-biphenyl, 10 g (69 mmol) of 2-methyl-1*H*-inden-7-amine (**15**), 23.2 g (240 mmol) of sodium *tert*-butoxide and 1.2 g (2.0 mmol) $Pd_2(dba)_3$ in 500 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×250 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a white solid. Yield: 15.8 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.50 (m, 1H), 7.44 (m, 1H), 7.26 (m, 1H), 6.95 (s, 2H), 6.65 (m, 1H), 3.09 (s, 2H), 2.50 (s, 6H), 2.41 (s, 6H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 146.9, 141.0, 139.6, 134.2, 133.1, 128.0, 127.7, 127.0, 123.7, 121.2, 120.4, 119.5, 110.4, 41.3, 20.7, 20.0, 16.6. HRMS (ESI) calc. for $C_{26}H_{25}NNa^+$: 374.1879 $[M + Na]^+$; found: 374.1887.



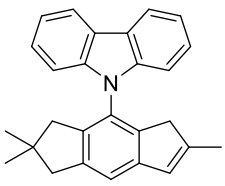
5-(2-methyl-1*H*-inden-4/7-yl)-2,3,5,7,8,9-hexahydro-1*H*-dicyclopenta[*b*,*h*]carbazole (29). A solution of 810 mg (4 mmol) of tri(*tert*-butyl)phosphane in 10 mL of toluene was added to a mixture of 29.1 g (69 mmol) 2,2'-dibromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-5,5'-biindene, 10 g (69 mmol) of 2-methyl-1*H*-inden-7-amine (**15**), 23.2 g (240 mmol) of sodium *tert*-butoxide and 1.2 g (2.0 mmol) $Pd_2(dba)_3$ in 500 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×250 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a white solid. Yield: 16.1 g (63%) as a mixture of two isomers 1/1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.36–7.61 (m, 3H), 7.17 (s, 1H), 7.12 (s, 1H), 6.72 (m) and 6.26 (m) (sum 1H), 3.57 (s, 1H), 3.23 (m, 5H), 3.12 (t, *J* = 7.3 Hz, 4H) 2.30 (p, *J* = 7.2 Hz, 4H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 147.0. 146.8, 145.4, 143.8, 142.1, 141.2, 141.0, 140.5, 135.5, 135.4, 133.1, 129.3, 128.0, 127.0, 125.8, 125.0, 124.6, 123.7, 122.7, 122.1, 119.5, 115.0, 114.9, 105.5, 105.3, 43.1, 41.3, 33.2, 32.4, 26.4, 16.7, 16.6. HRMS (ESI) calc. for $C_{28}H_{25}NNa^+$: 398.1879 $[M + Na]^+$; found: 398.1874.



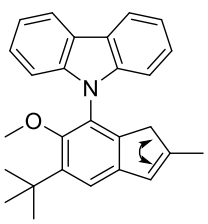
2,7-Di-*tert*-butyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (30). A solution of 810 mg (4 mmol) of tri(*tert*-butyl)phosphane in 10 mL of toluene was added to a mixture of 29.3 g (69 mmol) 2,2'-dibromo-4,4'-di-*tert*-butyl-1,1'-biphenyl, 10 g (69 mmol) of 2-methyl-1*H*-inden-7-amine (**15**), 23.2 g (240 mmol) of sodium *tert*-butoxide and 1.2 g (2.0 mmol) $Pd_2(dba)_3$ in 500 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×250 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a white solid. Yield: 16.3 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.17 (d, *J* = 8.2 Hz, 2H), 7.57 (dd, *J* = 13.6, 7.5 Hz, 2H), 7.45–7.48 (m, 3H), 7.39 (m, 2H), 6.26 (s, 1H), 3.57 (s, 2H), 2.19 (s, 3H), 1.50 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 148.8, 146.6, 145.6, 143.1, 141.4, 129.0, 125.4, 125.2, 124.7, 122.5, 120.9, 119.3, 117.4, 106.8, 43.1, 35.1, 31.8, 16.6. HRMS (ESI) calc. for $C_{30}H_{33}NNa^+$: 430.2505 [M + Na]$^+$; found: 430.2505.



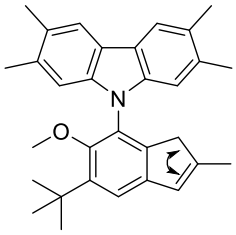
9-(2,6-Dimethyl-1*H*-inden-4/7-yl)-9*H*-carbazole (31). Solution of 1.26 g (6.2 mmol) tri(*tert*-butyl)phosphane and 1.78 g (3.1 mmol) $Pd_2(dba)_3$ in 10 mL of toluene was added to solution of 32.5 g (104 mmol) 2,2'-dibromobiphenyl, 16.6 g (104 mmol) 2,5-dimethyl-1*H*-indene-7-amine (**19**) and 35.0 g (364 mmol) sodium *tert*-butylate in 800 mL of toluene. After heating under argon at 100 °C for 24 h the reaction mixture was poured into 1 L of water and extracted with toluene (2×300 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a white solid. Yield: 25.7 g (80%) as a mixture of two isomers in ratio 2.3/1. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.24 (d, *J* = 7.7 Hz, 2H), 7.41 (m, 2H), 7.30–7.36 (m, 4H), 7.10 (m, 2H), 6.62 (m, 1H), 2.97 (s, 2H), 2.08 (s, 3H), 2.06 (s, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.29 (m, 2H), 7.50 (m, 2H), 7.35–7.42 (m, 3H), 7.27 (m, 1H), 7.13 (m, 2H), 5.91 (m, 1H), 3.47 (s, 2H), 2.08 (s, 3H), 2.06 (s, 3H). ^{13}C{^{1}H} NMR (major*/minor°, 100 MHz, $CDCl_3$): *δ* 147.7°, 145.9*, 145.5*, 145.2°, 142.53°, 142.47*, 141.0°, 140.2*, 134.9, 132.4, 131.1, 129.5, 127.1, 126.8, 126.3, 125.83, 125.80, 124.6, 123.4, 123.0, 122.9, 120.4*, 120.2°, 120.0, 119.4*, 119.3°, 110.0°, 109.7*, 43.0°, 40.7*, 17.3°, 17.1*, 16.7°, 16.5*. HRMS (ESI) calc. for $C_{23}H_{19}NNa^+$: 332.1410 [M + Na]$^+$; found: 332.1413.



9-(2,6,6-Trimethyl-1,2,3,5-tetrahydro-*s*-indacen-4/7-yl)-9*H*-carbazole (32). Solution of 0.81 g (4.0 mmol) tri(*tert*-butyl)phosphane and 1.15 g (2.0 mmol) $Pd_2(dba)_3$ in 10 mL of toluene was added to solution of 20.9 g (67 mmol) 2,2'-dibromobiphenyl, 14.3 g (67 mmol) 2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacen-4-amine (**20**) and 22.5 g (234 mmol) sodium *tert*-butylate in 500 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×300 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane) afforded the required products as a white solid. Yield: 17.0 g (70%) as a mixture of two isomers with ratio 1/1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.31 (m, 2H), 7.52 (m, 2H), 7.37–77.46 (m, 3H), 7.25 (m, 1H), 7.21 (m, 1H), 6.65 (m) and 6.08 (m) (sum 1H), 3.50 (s) and 3.07 (s) (sum 2H), 3.00 (s) and 2.99 (s) (sum 2H), 2.53 (s, 2H), 2.13 (s, 3H), 1.25 (s) and 1.24 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 146.4, 146.0, 145.7, 144.2, 143.7, 142.3, 141.0, 140.7, 140.0, 139.9, 139.4, 137.8, 128.7, 127.1, 125.72, 125.70, 124.7, 124.6, 123.03, 122.96, 120.4, 120.2, 119.32, 119.26, 116.8, 110.2, 109.9, 48.0, 47.9, 45.1, 44.9, 42.9, 40.60, 40.57, 28.57, 28.56, 16.7, 16.6. HRMS (ESI) calc. for $C_{27}H_{25}NNa^+$: 386.1879 [M + Na]$^+$; found: 386.1873.



9-(5-*Tert*-butyl-6-methoxy-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (33). Solution of 715 mg (1.4 mmol) Pd(tBu$_3$P)$_2$ in 10 mL of toluene was added to solution of 13.9 g (44.6 mmol) 2,2'-dibromobiphenyl, 10.3 g (44.5 mmol) 5-*tert*-butyl-6-methoxy-2-methyl-1*H*-indene-4/7-amine (**22**) and 15.0 g (155.8 mmol) sodium *tert*-butylate in 250 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×300 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane) afforded the required products as a white solid. Yield: 13.1 g (77%) as a mixture of two isomers in ratio 1/1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (m, 2H), 7.50 (m) and 7.40 (m) (sum 1H), 7.43 (m, 2H), 7.31 (m, 2H), 7.14–7.19 (m, 2H), 6.50 (m) and 5.87 (m) (sum 1H), 3.38 (s) and 2.90 (m) (sum 2H), 2.99 (s) and 2.93 (s) (sum 3H), 2.02 (m) and 2.00 (m) (sum 3H), (1.50 (s) and 1.49 (s)(sum 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 153.7, 147.6, 145.5, 143.5, 142.3, 141.7, 140.5, 140.4, 139.8, 138.9, 138.4, 126.8, 125.9, 125.6, 124.6, 123.3, 123.2, 121.3, 121.2, 120.2, 120.0, 119.7, 119.6, 117.9, 110.7, 110.6, 60.5, 60.2, 43.1, 41.3, 35.3, 35.2, 30.8, 30.7, 30.3, 16.8, 16.5. HRMS (ESI) calc. for $C_{27}H_{27}NNaO^+$: 404.1985 [M + Na]$^+$; found: 404.1989.



9-(5-*Tert*-butyl-6-methoxy-2-methyl-1*H*-inden-7-yl)-2,3,6,7-tetramethyl-9*H*-carbazole (34). Solution of 240 mg (1.20 mmol) tri(*tert*-butyl)phosphane and 0.54 g (0.60 mmol) $Pd_2(dba)_3$ in 10 mL of toluene was added to solution of 7.18 g (19.5 mmol) 2,2'-dibromo-4,4',5,5'-tetramethyl-1,1'-biphenyl, 4.5 g (19.5 mmol) 5-*tert*-butyl-6-methoxy-2-methyl-1*H*-inden-4/7-amine (**22**) and 6.6 g (68.3 mmol) sodium *tert*-butylate in 150 mL of toluene. After heating under argon at 100 °C for 24 h, the reaction mixture was poured into 1 L of water and extracted with toluene (2×300 ml). The extracts were combined and dried over anhydrous Na_2SO_4. The solvent was rotary evaporated. Purification of the residue by column chromatography (eluent: hexane/dichloromethane=10/1) afforded the required products as a yellow solid. Yield: 5.9 g (69%) as a mixture of two isomers in ratio 3/2. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.52 (s, 1H), 6.94 (s, 2H), 5.92 (m, 1H), 3.40 (s, 2H), 3.01 (s, 3H), 2.49 (s, 6H), 2.40 (s, 6H), 2.04 (s, 3H), 1.54 (s, 9H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.43 (s, 1H), 6.92 (s, 2H), 6.53 (m, 1H), 3.07 (s, 3H), 2.94 (s, 2H), 2.49 (s, 6H), 2.40 (s, 12H), 2.04 (s, 3H), 1.54 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, mixture of isomers, $CDCl_3$): δ 155.6, 153.9, 147.3, 145.5, 143.8, 142.1, 141.4, 140.7, 139.4, 138.6, 138.2, 134.3, 134.2, 127.9, 127.8, 126.7, 126.1, 124.7, 121.7, 121.4, 121.3, 121.0, 120.3, 120.1, 117.6, 111.0, 110.9, 60.6, 60.4, 43.1, 41.3, 35.3, 35.1, 30.7, 30.6, 20.8, 20.1, 16.8, 16.6. HRMS (ESI) calc. for $C_{31}H_{35}NNaO^+$: 460.2611 [M + Na]$^+$; found: 460.2612.

SYNTHESES OF BIS(INDENYL)DIMETHYLSILANE PROLIGANDS AND ZIRCONOCENES.

General Method A for synthesis of bis(indenyl)dimethylsilane proligands.

To a solution of (50.0 mmol, 1 eq.) of indene in 500 mL (10 mL/mmol) of ether, 20.0 mL (50.0 mmol ,1 eq.) of 2.5 M ^{n}BuLi in hexanes was added in one portion at 0 °C. This mixture was stirred overnight at room temperature, then the resulting mixture was cooled to -50 °C, and 100 mL (1 mL/mmol) absolute THF and 450 mg (5.0 mmol, 0.1 eq.) of CuCN was added. The obtained mixture was stirred for 30 min at -25 °C, then 3.23 g (25.0 mmol, 0.5 eq.) of dimethyldichlorosilane was added in one portion. This mixture was stirred overnight at room temperature, then passed through a short pad of silica gel which was additionally washed by 2×25 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure and the resulting crude product was purified by column chromatography on Silica Gel 60 (eluent: hexane/dichloromethane, 5:1, vol.).

General Method B for synthesis of bis(indenyl)dimethylsilane proligands.

To a solution of 50.0 mmol of indene in 500 mL of ether, 20.0 mL (50.0 mmol) of 2.5 M ^{n}BuLi in hexanes was added in one portion at 0 °C. This mixture was stirred overnight at room temperature, then the resulting mixture was cooled to -50 °C, and 41 mg (0.5 mmol) of N-methylimidazole was added, then 3.23 g (25.0 mmol) of dimethyldichlorosilane was added in one portion. This mixture was stirred overnight at room temperature, then passed through a short pad of silica gel which was additionally washed by 2×25 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure and the resulting crude product was purified by column chromatography on Silica Gel 60 (eluent: hexane/dichloromethane, 5:1, vol.).

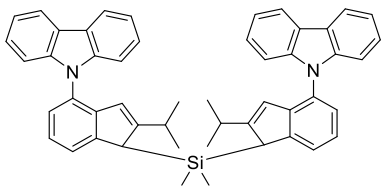
General Method C for syntheses of *ansa*-zirconocenes. To a cooled 0 °C solution of (21.6 mmol, 1 eq.) bis[indenyl]dimethylsilane in 250 mL (10 mL/mmol) of ether, 17.3 mL (43.3 mmol, 2 eq.) of 2.5 M ^{n}BuLi in hexanes was added in one portion. This mixture was stirred overnight at room temperature, then the resulting solution was cooled to -50 °C, and 8.16 g (21.6 mmol, 1 eq.) of $ZrCl_4(THF)_2$ was added. The reaction mixture was stirred for 24 h at room temperature. The volatiles were evaporated to dryness. The residue was treated with 350 mL of hot toluene, and the formed suspension was filtered while hot through a short pad of Celite to get rid of LiCl. The resulting solution was concentrated in vacuum and the residue was recrystallized from toluene or toluene/hexane mixture.

General Method D for synthesis of *rac*-isomers of dimethylated zirconocenes.

To a suspension of pure *rac*-zirconocene or mixture of *rac*- and *meso*-isomers of zirconocene dichloride (1.2 mmol) in 50 mL of toluene, 4.1 mL of 2.9 M MeMgBr (12.0 mmol) in ether was added at room temperature. This mixture was stirred for 24 h at 100 °C, then volatiles were evaporated to dryness in vacuum. To the residue, 100 mL of toluene were added and the mixture was heated up to 100 °C and then passed through a short pad of Celite to get rid of magnesium salts and the excess of MeMgBr. The filtrate was concentrated in vacuum and the residue was recrystallized from toluene or toluene/hexane mixture giving pure *rac*-isomer of dimethyl zirconium complex.

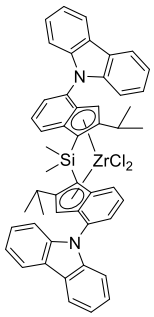
General Method E for synthesis of *rac*-isomers of dimethylated zirconocenes.

To a suspension of pure *rac*-zirconocene or mixture of *rac*- and *meso*-isomers of zirconocene dichloride (1.2 mmol) in 50 mL of toluene, 4.1 mL of 2.9 M MeMgBr (12.0 mmol) in ether was added at room temperature. This mixture was stirred for 24 h at 100 °C, then volatiles were evaporated to dryness in vacuum. To the residue 100 mL of toluene were added and the mixture was heated up to 100 °C and then passed through a short pad of Celite to get rid of magnesium salts and the excess of MeMgBr. The filtrate was concentrated in vacuum. To the residue, 50 mL of absolute THF and 4.2 mg of LiCl (0.1 mmol) were added. The reaction mixture was stirred at 50 °C for 16 h and then 10 mL of toluene was added. The volatiles were evaporated to dryness in vacuum. After that, 50 mL of toluene was added and the mixture was filtered through the short pad of Celite to get rid of LiCl. The filtrate was concentrated in vacuum and the residue was recrystallized from toluene or toluene/hexane mixture giving pure *rac*-isomer of dimethyl zirconium complex.

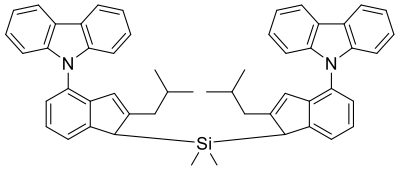


Bis[2-isopropyl-4-(9*H*-carbazolyl)-1*H*-inden-1-yl]dimethylsilane (L1). General procedure A was applied using 16.17 g (50.0 mmol) of 9-(2-isopropyl-1*H*-inden-7-yl)-9*H*-carbazole (**10**). Yield: 15.2 g (86%) of bis[2-isopropyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (**L1**) (ca. 80% purity by NMR, approx. 80:20 mixture of *rac*- and *meso*-isomers) as yellowish glassy solid which was further used without an additional purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 7.6 Hz, 4H), 7.90 (d, J = 7.1 Hz) and 7.62–7.32 (m), (sum 18H), 6.44 (s, 2H), 4.36 (s) and 4.27 (s), (sum 2H), 2.99 (s) and 2.85 (s), (sum 2H), 1.36–1.19 (m, 12H), 0.11 (s) and 0.02 (s) and -0.04 (s), (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), *rac*-isomer: δ 160.4, 146.8, 142.7, 141.3, 129.5, 125.8 (two resonances), 124.7, 124.1, 123.2, 122.7, 120.7, 120.2 (two resonances), 119.63, 119.56,

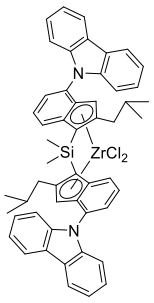
110.3, 110.1, 45.9, 29.7, 24.6, 21.2, -5.6. HRMS (ESI) calc. for $C_{50}H_{46}N_2NaSi^+$: 725.3322 [M + Na]$^+$; found: 725.3319.



***Rac*- and *meso*-dimethylsilanediylbis[η^5-2-isopropyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride (C1).** General Method C was applied using 15.2 g (21.6 mmol) of bis[2-isopropyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (**L1**). A total of 12.8 g (68.7%) of *rac*- and *meso*-dimethylsilanediylbis[η^5-2-isopropyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride were isolated by fractional crystallization from toluene, including 4.4 g (21%) of pure *rac*-**C1**×1·PhMe and 1.3 g (7%) of pure *meso*-**C1**. ***Rac*-C1:** Anal. calc. for $C_{50}H_{44}Cl_2N_2SiZr \cdot C_7H_8$: C, 71.67; H, 5.49; N, 2.93. Found: C, 71.35; H, 5.32; N, 3.08. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (d, J = 7.6 Hz, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H), 7.36–7.12 (m, 10H), 6.81 (d, J = 7.3 Hz, 2H), 6.63 (s, 2H), 3,31 (m, 2H), 1.46 (s, 6H), 1.28 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 150.8, 141.3, 141.0, 135.5, 131.6, 128.9, 126.7, 126.6, 126.3, 125.9, 125.1, 124.5, 124.2, 120.8 (two resonances), 120.5, 120.4, 114.3, 113.0, 111.3, 84.0, 31.3, 30.0, 20.3, 4.0. ***Meso*-C1:** Anal. calc. for $C_{50}H_{44}Cl_2N_2SiZr$: C, 69.58; H, 5.14; N, 3.25. Found: C, 69.32; H, 5.17; N, 3.29. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.14 (d, J = 7.6 Hz, 2H), 8.12 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.33–7.23 (m, 6H), 7.11 (dd, J = 8.6 Hz, 7.6 Hz, 2H), 6.80 (d, J = 7.8 Hz, 2H), 6.61 (s, 2H), 3,14 (sept, J = 6.6 Hz, 2H), 1.61 (s, 3H), 1.35 (s, 3H), 1.25 (d, J = 6.6 Hz, 6H), 1.20 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 150.3, 141.4, 141.1, 134.6, 133.2, 131.1, 126.7, 126.6, 126.2, 125.9, 125.8, 124.5, 124.1, 120.8, 120.7, 120.5, 120.4, 114.9, 113.1, 111.1, 86.0, 31.2, 30.1, 20.4, 4.6, 3.5.

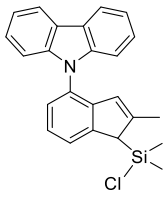


Bis[2-isobutyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (L2). General procedure A was applied using 16.87 g (50.0 mmol) of 9-(2-isobutyl-1*H*-inden-7-yl)-9*H*-carbazole (**12**). Yield: 15.7 g (86%) of bis[2-isobutyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (ca. 80% purity by NMR, approx. 65:35 mixture of *rac*- and *meso*-isomers) as yellowish glassy solid which was further used without an additional purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 7.7 Hz, 4H), 7.84–7.20 (m, 18H), 6.33 (s, 2H), 4.12 (s) and 4.10 (s) (sum 2H), 2.64–2.30 (m, 4H), 2.10–1.76 (m, 2H), 1.01 (d, J = 6.6 Hz) and 0.95 (d, J = 6.6 Hz) and 0.91 (d, J = 6.6 Hz) and 0.87 (d, J = 6.6 Hz), (sum 12H), -0.01 (s) and -0.05 (s) and -0.14 (s), (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.8, 152.7, 147.1, 147.0, 142.7, 142.6, 141.32, 141.26, 129.33, 129.28, 125.9, 124.7, 124.4, 124.11, 124.06, 123.3, 122.8, 122.7, 120.4, 120.3, 119.72, 119.65, 110.4, 110.3, 46.8 (two resonances), 41.4, 41.2, 28.9, 28.7, 23.2, 23.1, 22.2, -4.3, -5.5, -6.0. HRMS (ESI) calc. for $C_{52}H_{50}N_2NaSi^+$: 753.3635 [M + Na]$^+$; found: 753.3630.

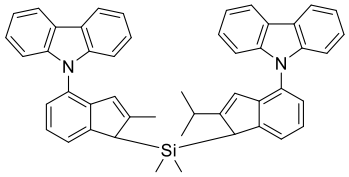


***Rac*- and *meso*-dimethylsilanediylbis[η^5-2-isobutyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride (C2).** General Method C was applied using 15.5 g (21.2 mmol) of bis[2-isobutyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (**L2**). A total of 14.3 g (76%) of *rac*- and *meso*-dimethylsilanediylbis[η^5-2-isobutyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride was isolated by fractional crystallization of the filtrate, including 1.29 g (7%) of pure *rac*-**C2**×1·PhMe and 100 mg (0.5%) of pure *meso*-**C2**. ***Meso*-C2:** Anal. calc. for $C_{52}H_{48}Cl_2N_2SiZr$: C, 70.08; H, 5.43; N, 3.14. Found: C, 70.26; H, 5.30; N, 3.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–8.08 (m, 2H), 8.07 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.36 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.27–7.17 (m, 6H), 7.11 (dd, J = 8.7 Hz, 7.3 Hz, 2H), 6.82–6.75 (m, 2H), 6.49 (s, 2H), 2.66 (dd, J = 13.6 Hz, 6.0 Hz, 2H), 2.45 (dd, J = 13.6 Hz, 8.5 Hz, 2H), 1.78 (m, 2H), 1.60 (s, 3H), 1.25 (s, 3H), 0.95 (d, J = 6.7 Hz, 6H), 0.87 (d, J = 6.5 Hz, 6H). ***Rac*-C2:** Anal. calc. for $C_{52}H_{48}Cl_2N_2SiZr \cdot C_7H_8$: C, 72.07; H, 5.74; N, 2.85. Found: C, 72.00; H, 5.51; N, 2.89. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.08 (m, 2H), 8.05 (d, J = 7.4 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 7.1 Hz, 2H), 7.30–7.13 (m, 10H), 6.86–6.79 (m, 2H), 6.63 (s, 2H), 2.79 (dd, J = 13.8 Hz, 6.2 Hz, 2H), 2.17 (dd, J = 13.8 Hz, 8.3 Hz, 2H), 1.78 (m, 2H), 1.40 (s, 6H), 0.98 (d, J = 6.7 Hz, 6H), 0.88 (d, J = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.0, 140.7,

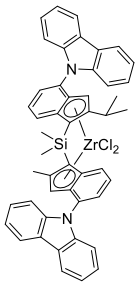
140.2, 134.6, 131.6, 128.4, 126.1, 125.9, 125.8, 125.0, 124.9, 124.0, 123.7, 120.3, 120.2, 120.0, 119.9 (two resonances), 112.2, 110.9, 84.0, 41.8, 32.6, 22.7, 22.1, 3.5.



9-(1-(Chlorodimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole. To a solution of 5.0 g (16.9 mmol) of 9-(2-methyl-1*H*-inden-4/7-yl)-9*H*-carbazole in 170 mL of ether, 6.8 mL (16.9 mmol) of 2.5 M ^{n}BuLi in hexanes was added in one portion at room temperature. This mixture was stirred overnight at room temperature, then the resulting mixture was cooled to -50 °C, and 6.2 mL (50.7 mmol) of dimethyldichlorosilane was added in one portion. This mixture was stirred overnight at room temperature, then volatiles were evaporated under reduced pressure. The residue was treated with 100 mL of dry hexane and filtered through a glass frit. The filtrate was then concentrated in vacuum. The product was used without any additional purification. Yield: 6.1 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 7.3 Hz, 1H), 7.38–7.43 (m, 3H), 7.26–7.35 (m, 4H), 7.09 (d, J = 8.2 Hz, 1H), 6.17 (m, 1H), 3.77 (s, 1H), 2.19 (s, 3H), 0.48 (s, 3H), 0.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 147.3, 144.9, 142.8, 141.21, 141.16, 128.8, 125.81, 125.75, 125.1, 125.0, 124.2, 123.2, 123.1, 120.3, 120.2, 119.6, 119.5, 110.1, 110.0, 50.8, 17.6, 0.8, -0.2.

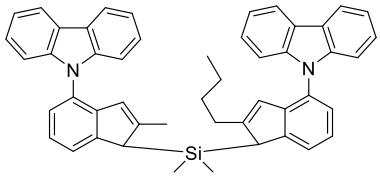


9-(1-((4-(9*H*-Carbazol-9-yl)-2-isopropyl-1*H*-inden-1-yl)dimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole (L3). To a solution of 5.0 g (15.5 mmol) of 9-(2-isopropyl-1*H*-inden-7-yl)-9*H*-carbazole (**10**) in 150 mL of ether, 6.2 mL (15.5 mmol) of 2.5 M ^{n}BuLi in hexanes was added in one portion at room temperature. This mixture was stirred overnight at room temperature then the resulting mixture was cooled to -50 °C and 16 mg (0.2 mmol) of N-methylimidazole was added. Next, a solution of 6.0 g (15.5 mmol) of 9-(1-(chlorodimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole in 10 mL THF was added in one portion. This mixture was stirred overnight at room temperature, and then passed through a short pad of silica gel which was additionally washed by 2×25 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure and the resulting crude product was purified by column chromatography on Silica Gel 60 (eluent: hexane/dichloromethane, 5:1, vol.). Yield: 3.7 g (71%) as a mixture of several isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.25 (m, 4H), 7.75 (m, 1H), 7.37–7.46 (m, 8H), 7.30–7.36 (m, 7H), 7.19 (m, 2H), 6.28 (s) and 6.23 (s), (sum 2H), 4.23 (s) and 4.15 (s) and 4.02 (s) and 3.99 (s), (sum 2H), 2.78 (m, 1H), 2.29 (s) and 2.17 (s), (sum 3H), 1.12–1.19 (m, 6H), -0.05 (s) and -0.11 (s) and -0.12 (m), (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.2, 160.1, 148.5, 148.3, 147.02, 146.95, 146.7, 146.6, 142.9, 142.7, 142.6, 142.5, 141.3, 141.20, 141.18, 141.16, 129.3, 129.0, 128.9, 125.81, 125.77, 125.7, 124.6, 124.0, 123.19, 123.17, 123.1, 120.3, 120.2, 119.61, 119.56, 119.5, 110.2, 110.11, 110.06, 48.0, 47.8, 46.0, 45.8, 29.6, 24.6, 24.5, 21.2, 18.0, 17.8, -5.3, -5.8, -5.9. HRMS (ESI) calc. for $C_{48}H_{42}N_2NaSi^+$: 697.3009 [M + Na]$^+$; found: 697.3008.

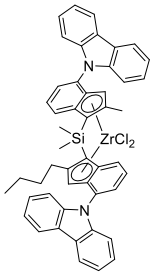


***Anti*- and *Syn*-dimethylsilanediyl[η^5-2-isopropyl-4-(9*H*-carbazolyl)-indene-1-yl][η^5-2-methyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride (C3).** General Method C was applied using 3.7 g (5.5 mmol) of 9-(1-((4-(9*H*-carbazol-9-yl)-2-isopropyl-1*H*-inden-1-yl)dimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole (**L3**). Recrystallizations from toluene gave three crops of crystals: 150 mg (3%) *anti/syn* = 6/94, 400 mg (9%) *anti/syn* = 1.0/2.3 and 320 mg (7%) *anti/syn* = 92/8. Recrystallization of the last crop from toluene/hexane mixture gave 150 mg (3%) of pure *anti*-isomer. ***Syn*-C3:** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.12 (m, 4H), 7.98 (m, 4H), 7.50 (m, 2H), 7.37 (m, 2H), 7.23–7.31 (m, 6H), 7.10–7.14 (m, 2H), 6.81 (m, 2H), 6.57 (s, 1H), 6.51 (s, 1H), 3.17 (m, 1H), 2.32 (s, 3H), 1.60 (s, 3H), 1.32 (s, 3H), 1.24 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 150.8, 141.1, 141.03, 141.00, 140.9, 136.9, 134.2, 133.8, 133.7, 133.6, 130.7, 129.9, 126.67, 126.66, 126.37, 126.36, 126.3, 125.9, 125.8, 125.7, 125.3, 125.2, 124.4, 124.3, 124.04, 124.00, 123.5, 120.9, 120.59, 120.57, 120.55, 120.4, 120.3, 120.2, 113.4, 113.0, 112.9, 111.02, 110.98, 86.4, 85.3, 31.2, 29.9, 20.2, 18.8, 3.5, 3.0. ***Anti*-C3:** Anal. calc. for $C_{48}H_{40}Cl_2N_2SiZr$: C, 69.04; H, 4.83; N, 3.35. Found: C, 68.97; H, 5.01; N, 3.34. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.13 (m, 2H), 8.10 (m, 2H), 8.00 (d, J = 8.1 Hz, 1H), 7.85 (m, 2H), 7.78 (d, J = 8.6 Hz, 1H), 7.57 (m, 2H), 7.20–7.31 (m, 10H), 6.83 (d, J = 7.9 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 3.38 (m, 1H), 2.35 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H), 1.24 (d, J = 6.7 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H). ^{13}C{^{1}H} NMR (100

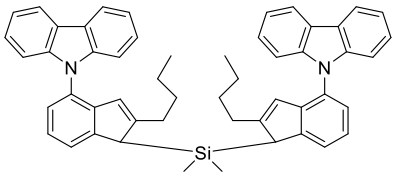
MHz, CD_2Cl_2): δ 150.1, 141.4, 141.02, 140.97, 140.8, 137.7, 135.2, 134.7, 132.5, 130.7, 130.2, 127.4, 126.71, 126.65, 126.5, 126.3, 126.2, 126.1, 126.0, 125.80, 125.78, 124.6, 124.32, 124.26, 124.16, 123.9, 120.60, 120.55, 120.49, 120.33, 120.29, 120.23, 120.16, 115.1, 112.9, 112.5, 111.3, 110.9, 85.7, 84.1, 31.1, 29.7, 19.9, 19.4, 3.4, 3.0.



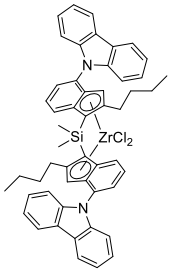
9-(1-((4-(9*H*-Carbazol-9-yl)-2-butyl-1*H*-inden-1-yl)dimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole (L4). To a solution of 5.2 g (15.5 mmol) of 9-(2-butyl-1*H*-inden-7-yl)-9*H*-carbazole (**11**) in 150 mL of ether, 6.2 mL (15.5 mmol) of 2.5 M ^{n}BuLi in hexanes was added in one portion at room temperature. This mixture was stirred overnight at room temperature then the resulting mixture was cooled to -50 °C and 16 mg (0.2 mmol) of N-methylimidazole was added. Next, a solution of 6.0 g (15.5 mmol) of 9-(1-(chlorodimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole in 10 mL THF was added in one portion. This mixture was stirred overnight at room temperature, then passed through a short pad of silica gel which was additionally washed by 2×25 mL of dichloromethane. The combined filtrate was evaporated under reduced pressure and the resulting crude product was purified by column chromatography on Silica Gel 60 (eluent: hexane/dichloromethane, 5:1, vol.). Yield: 4.9 g (92%) as a mixture of several isomers (ca. 96% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–8.24 (m, 4H), 7.68–7.73 (m, 1H), 7.11–7.47 (m, 17H), 6.28 (s) and 6.24 (s) (sum 2H), 4.12 (s) and 4.10 (s) and 4.02 (s) and 3.99 (s) (sum 2H), 2.18–2.61 (m, 4H), 2.18 (s) and 2.13 (s) (sum 3H), 1.44–1.60 (m, 2H), 0.84–0.94 (m, 3H), -0.05 (s) and -0.10 (m) and -0.11 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.72, 153.70, 148.5, 148.4, 147.01, 146.95, 146.71, 146.66, 142.9, 142.8, 142.71, 142.65, 141.3, 141.22, 141.17, 129.14, 129.11, 129.0, 128.9, 125.81, 125.78, 125.74, 124.65, 124.03, 123.99, 123.94, 123.18, 123.15, 123.1, 122.7, 120.3, 120.2, 119.6, 119.5, 110.2, 110.12, 110.08, 48.0, 47.9, 46.83, 46.76, 31.5, 31.43, 31.36, 31.29, 22.49, 22.45, 18.0, 17.9, 13.86, 13.84, 13.82, 13.76, -5.5, -5.96, -5.99. HRMS (ESI) calc. for $C_{49}H_{44}N_2NaSi^+$: 711.3166 [M + Na]$^+$; found: 711.3161.



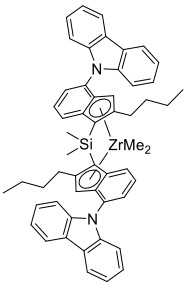
***Anti*- and *syn*-dimethylsilanediyl[η^5-2-butyl-4-(9*H*-carbazolyl)-indene-1-yl][η^5-2-methyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride (C4).** General Method C was applied using 4.9 g (7.0 mmol) of 9-(1-((4-(9*H*-carbazol-9-yl)-2-butyl-1*H*-inden-1-yl)dimethylsilyl)-2-methyl-1*H*-inden-4-yl)-9*H*-carbazole (**L4**). Recrystallizations from toluene gave three crops of crystals: 1.85 g (31%) *anti/syn* = 1/7, 680 mg (11%) *anti/syn* = 3/1 and 110 mg (2%) of pure *anti*-isomer. Recrystallization of the first crop from toluene gave 655 mg (11%) of pure *syn*-isomer. ***Syn*-C4:** Anal. calc. for $C_{49}H_{42}Cl_2N_2SiZr$: C, 69.31; H, 4.99; N, 3.30. Found: C, 69.11; H, 5.10; N, 3.19. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.12 (m, 4H), 8.01 (m, 3H), 7.96 (d, J = 8.8 Hz, 1H), 7.51 (m, 2H), 7.37 (m, 2H), 7.24–7.30 (m, 6H), 7.14 (m, 2H), 6.83 (m, 2H), 6.51 (s, 1H), 6.46 (s, 1H), 2.81 (m, 1H), 2.67 (m, 1H), 2.39 (s, 3H), 1.59 (s, 3H), 1.57 (m, 2H), 1.34 (m, 2H), 1.29 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 144.7, 141.01, 140.96, 140.9, 140.7, 138.7, 134.38, 134.36, 133.8, 133.6, 129.9, 129.6, 126.8, 126.7, 126.3, 126.2, 126.1, 125.8, 125.75, 125.68, 125.1, 125.0, 124.31, 124.27, 124.1, 124.0, 120.60, 120.58, 120.55, 120.53, 120.40, 120.34, 120.28, 120.23, 119.8, 118.3, 113.0, 112.8, 111.3, 111.0, 86.3, 85.8, 36.2, 33.5, 22.7, 19.4, 14.1, 3.1, 2.9. ***Anti*-C4:** Anal. calc. for $C_{49}H_{42}Cl_2N_2SiZr$: C, 69.31; H, 4.99; N, 3.30. Found: C, 69.42; H, 5.07; N, 3.31. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.09–8.14 (m, 4H), 7.93 (m, 2H), 7.86 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.7 Hz, 1H), 7.58 (m, 2H), 7.23–7.30 (m, 10H), 6.83 (m, 2H), 6.62 (s, 1H), 6.56 (s, 1H), 2.90 (m, 1H), 2.39 (m, 1H), 2.34 (s, 3H), 1.56 (m, 2H), 1.43 (s, 3H), 1.41 (s, 3H), 1.36 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 142.6, 141.2, 141.1, 140.0, 140.8, 136.8, 134.7, 134.5, 132.1, 132.0, 129.4, 129.0, 128.6, 126.8, 126.5, 126.4, 126.3, 126.2, 125.8, 125.72, 125.71, 125.68, 124.3, 124.2, 124.02, 123.96, 121.2, 120.57, 120.55, 120.5, 120.4, 120.3, 120.24, 120.20, 119.7, 112.7, 112.6, 111.2, 111.0, 85.2, 84.9, 35.7, 33.0, 22.6, 19.1, 14.2, 3.0, 2.8.



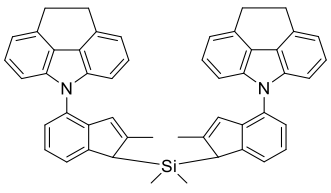
Bis[2-butyl-4-(9*H*-carbazolyl)-1*H*-inden–1-yl]dimethylsilane (L5). General procedure B was applied using 5.0 g (14.8 mmol) of 9-(2-butyl-1*H*-inden-7-yl)-9*H*-carbazole (**11**). Yield: 4.0 g (74%) as a mixture of two isomers with ratio *rac*/meso°* = 2/1(ca. 92% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.25 (m, 4H), 7.73* (d, *J* = 7.3 Hz) and 7.60° (d, *J* = 7.5 Hz) (2H), 7.37–7.47 (m, 8H), 7.32–7.36 (m, 6H), 7.20 (m, 2H), 6.28 (m, 2H), 4.10* (s) and 4.07 (s) (sum 2H), 2.41–2.64 (m, 4H), 1.45–1.58 (m, 4H), 1.25–1.38 (m, 4H), 0.84–0.92 (m, 6H), -0.06 (s) and -0.11 (s) and -0.16 (s) (sum 6H). ^{13}C NMR{^{1}H} (100 MHz, $CDCl_3$): *δ* 153.9*, 153.8°, 146.8°, 146.8*, 142.8*, 142.7°, 141.3, 141.2, 129.2*, 129.1°, 125.79, 125.76, 124.7*, 124.7°, 124.0*, 123.9°, 123.2, 123.1, 122.7, 120.3, 120.2, 119.6, 119.5, 110.3, 110.1, 46.8, 31.6°, 31.50*, 31.47°, 31.4*, 22.6°, 22.5*, 13.9°, 13.8*, -5.2°, -5.8*, -6.1°. HRMS (ESI) calc. for $C_{52}H_{50}N_2NaSi^+$: 753.3635 [M + Na]$^+$; found: 753.3633.



***Rac*- and *meso*-dimethylsilanediylbis[*η*^{5}-2-butyl-4-(9*H*-carbazolyl)-indene-1-yl]zirconium dichloride (C5).** General Method C was applied using 3.8 g (5.2 mmol) of bis[2-butyl-4-(9*H*-carbazolyl)-1*H*-indene-1-yl]dimethylsilane (**L5**). Recrystallizations from toluene gave several crops of *rac/meso* mixtures: 400 mg *rac/meso* = 1/16, 300 mg *rac/meso* = 1.7/1.0, 1.7 g *rac/meso* = 1.5/1.0, 150 mg *rac/meso* = 1.0/4.9. The overall yield: 2.55 g (55%). After another series of recrystallization of these crops, 320 mg (7%) of pure *meso*-**C5** was isolated. ***Rac*-C5**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.06–8.12 (m, 4H), 7.92 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.17–7.31 (m, 12H), 6.79–6.84 (m, 2H), 6.65 (s, 2H), 2.83–2.90 (m, 2H), 2.38–2.44 (m, 2H), 1.54 (m, 4H), 1.40 (s, 6H), 1.32 (m, 4H), 0.93 (t, *J* = 9.2 Hz, 6H). ***Meso*-C5**: Anal. calc. for $C_{52}H_{48}Cl_2N_2SiZr$: C, 70.08; H, 5.43; N, 3.14. Found: C, 70.10; H, 5.56; N, 3.08. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.06–8.11 (m, 4H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.35 (m, 2H), 7.21–7.26 (m, 6H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.77–6.81 (m, 2H), 6.51 (s, 2H), 2.71–2.78 (m, 2H), 2.60–2.67 (m, 2H), 1.59 (s, 3H), 1.54 (m, 4H), 1.31 (m, 4H), 1.26 (s, 3H), 0.89 (t, *J* = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 143.8, 140.5, 140.2, 133.8, 133.5, 129.0, 126.00, 125.96, 125.3, 125.0, 124.6, 124.0, 123.6, 120.2, 120.1, 119.9, 119.8, 118.0, 112.6, 110.8, 84.7, 35.6, 33.0, 22.2, 13.9, 3.2, 2.9.

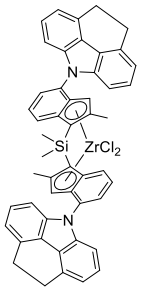


***Rac*-dimethylsilanediylbis[*η*^{5}-2-butyl-4-(9*H*-carbazolyl)-indene-1-yl]dimethylzirconium (M5).** General method D was applied using two crops of crystals of **C5** 300 mg of *rac/meso* = 1.7/1.0 and 1.7 g of *rac/meso* = 1.5/1.0. Right after methylation, a mixture of isomers rac/meso = 2.7/1.0 was isolated. Recrystallization from toluene at -30 °C gave 860 mg (45%) of pure *rac*-**M5**. Anal. calc. for $C_{54}H_{54}N_2SiZr$: C, 76.27; H, 6.40; N, 3.29. Found: C, 76.14; H, 6.42; N, 3.21. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.18 (d, *J* = 7.3 Hz, 2H), 8.13 (m, 2H), 7.69 (m, 4H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.20–7.37 (m, 8H), 7.15 (m, 2H), 7.10 (m, 2H), 6.65 (s, 2H), 2.72 (m, 2H), 2.16 (m, 2H), 1.49–1.68 (m, 4H), 1.36–1.45 (m, 4H), 1.24 (s, 6H), 0.98 (t, *J* = 7.3 Hz, 6H), -1.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.1, 140.4, 140.3, 134.1, 128.9, 127.4, 125.7, 125.2, 125.0, 123.8, 123.7, 123.6 ,123.0, 120.13, 120.09, 120.0, 119.8, 113.2, 111.6, 111.4, 79.2, 39.0, 35.1, 31.8, 22.3, 14.0, 3.3.

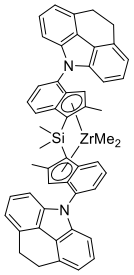


Bis(4-(8,9-dihydro-4*H*-benzo[*def*]carbazol-4-yl)-2-methyl-1*H*-inden-1-yl)dimethylsilane (L6). General method B was applied using 6.65 g (20.6 mmol) of 4-(2-methyl-1*H*-inden-4-yl)-8,9-dihydro-4*H*-benzo[*def*]carbazole (**9**). Yield: 3.8 g (53%) as a mixture of isomers (ca. 93% purity by NMR). *Meso*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.29–7.35 (m, 6H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 4H) 7.01 (d, *J* = 8.0 Hz, 2H), 6.44 (m, 2H), 3.95 (s, 2H), 3.43 (m, 8H), 2.26 (s, 6H), -0.05 (s, 3H), -0.08 (s, 3H). *Rac*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.63 (d, *J* = 7.5 Hz, 2H), 7.46–7.50 (m, 2H), 7.29–7.37 (m, 6H), 7.18 (m, 2H), 7.07 (m, 4H), 7.02 (m, 2H), 6.45 (m, 2H), 4.00 (s, 2H), 3.44 (m, 8H), 2.22 (s, 6H), -0.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.2, 146.1, 145.8, 142.0, 142.5, 140.0, 139.9, 139.6, 138.9, 128.38, 128.35, 126.8, 126.4, 124.4, 124.2, 123.9, 123.0,

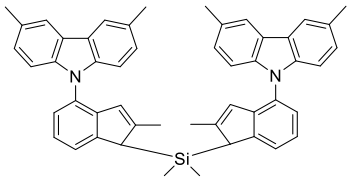
122.1, 121.69, 121.66, 121.5, 118.1, 118.0, 117.9, 109.2, 109.1, 109.0, 48.0, 47.8, 30.7, 26.4, 17.7, 17.6, -5.6, -5.9, -6.0. HRMS (ESI) calc. for $C_{50}H_{42}N_2NaSi^+$: 721.3009 [M + Na]$^+$; found: 721.3012.



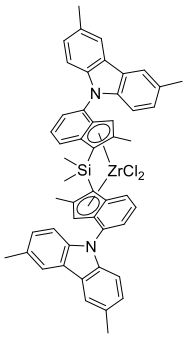
***Rac*-dimethylsilanediylbis[η^5-4-(8,9-dihydro-4*H*-benzo[*def*]carbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C6).** General method C was applied using 3.9 g (5.6 mmol) of bis(4-(8,9-dihydro-4*H*-benzo[*def*]carbazol-4-yl)-2-methyl-1*H*-inden-1-yl)dimethylsilane (**L6**). First recrystallization of the residue from toluene gave 600 mg (12%) of pure *rac*-**C6**. ***Rac*-C6**: Anal. calc. for $C_{50}H_{40}Cl_2N_2SiZr$: C, 69.91; H, 4.69; N, 3.26. Found: C, 70.07; H, 4.76; N, 3.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.58 (m, 4H), 7.16–7.26 (m, 6H), 6.99 (d, *J* = 7.2 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.82 (s, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 3.33 (m, 8H), 2.35 (s, 6H), 1.40 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.6, 138.5, 135.8, 135.5, 130.9, 130.7, 130.1, 129.0, 128.5, 128.2, 127.0, 126.3, 125.9, 124.2, 123.9, 123.7, 123.4, 120.4, 117.8, 117.5, 84.3, 26.6, 26.5, 18.8, 2.6.



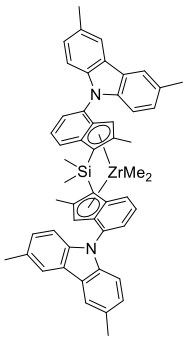
***Rac*-dimethylsilanediylbis[η^5-4-(8,9-dihydro-4*H*-benzo[*def*]carbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M6).** General method D was applied using 400 mg of pure *rac*-**C6**. Recrystallization from toluene at room temperature gave 256 mg (67%) of pure *rac*-**M6**. Anal. calc. for $C_{52}H_{46}N_2SiZr$: C, 76.33; H, 5.67; N, 3.42. Found: C, 76.38; H, 5.72; N, 3.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.25–7.34 (m, 4H), 7.16–7.20 (m, 2H), 7.09–7.14 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.96–6.99 (m, 4H), 6.82 (s, 2H), 3.38 (m, 8H), 2.21 (s, 6H), 1.22 (s, 6H), -1.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 138.3, 135.4, 134.8, 130.6, 130.4, 129.1, 126.6, 126.4, 126.3, 124.1, 123.8, 123.5, 121.2, 117.6, 117.4, 114.5, 109.6, 109.5, 79.9, 38.5, 26.6, 26.5, 18.3, 2.7.



Bis[2-methyl-4-(3',6'-dimethylcarbazol-9-yl)-1*H*-inden-1-yl](dimethyl)silanes (L7). General Method A was applied using 8.0 g (24.6 mmol) of 3,6-dimethyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**7**). Yield: 7.0 g (81%) as a mixture of two isomers (ca. 90% purity by NMR). ^{1}H NMR (mixture of two isomers, 400 MHz, $CDCl_3$): δ 7.94 (m, 4H), 7.65 (m, 1H), 7.52 (m, 1H), 7.30–7.39 (m, 4H),7.10–7.21 (m, 6H), 7.00–7.05 (m, 2H), 6.19 (m, 2H), 3.94 (m, 2H), 2.56 (s, 12H), 2.20 (s, 6H), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 147.0, 146.9, 142.9, 142.8, 139.82, 139.79, 139.7, 139.1, 128.63, 128.55, 127.0, 126.9, 124.8, 124.6, 124.0, 123.9, 123.1, 122.6, 122.51, 122.48, 120.12, 120.08, 120.0, 109.81, 109.77, 109.7, 48.02, 47.95, 25.6, 21.4, 18.0, 17.9, -5.7, -6.0, -6.1. HRMS (ESI) calc. for $C_{50}H_{46}N_2NaSi^+$: 725.3322 [M + Na]$^+$; found: 725.3318.

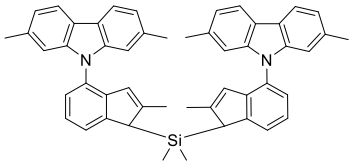


***Meso*- and *rac*-dimethylsilanediylbis[η^5-4-(3,6-dimethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C7).** General Method C was applied using 4.8 g (6.83 mmol) of bis(2-methyl-4-(3,6-dimethyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilane (**L7**). Recrystallizations from toluene gave two crops of crystals: 3.3 g *rac*/*meso* = 3/4 (56%) and 140 mg *rac*/*meso* = 6/1 (2%). ***Rac*-C7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.85 (m, 4H), 7.74–7.79 (m, 4H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.15 (m, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.1 Hz 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.64 (s, 2H), 2.50 (s, 6H), 2.48 (s, 6H), 2.33 (s, 6H), 1.38 (s, 6H). ***Meso*-C7**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.84 (m, 8H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.04–7.18 (m, 6H), 6.71 (m, 2H), 6.53 (s, 2H), 2.49 (s, 6H), 2.41 (s, 6H), 2.35 (s, 6H), 1.54 (s, 3H), 1.26 (s, 3H).

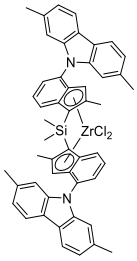


***Rac*-dimethylsilanediylbis[η^5-4-(3,6-dimethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M7).** General Method E was applied using 1.84 g of **C7** with ratio *rac/meso* = 3/4. After methylation and LiCl treatment, the ratio of isomers became rac/meso = 5/2. Recrystallization of the solid from toluene/hexane mixture gave 800 mg (49%) of pure *rac*-**M7**. Anal. calc. for $C_{52}H_{50}N_2SiZr$: C, 75.95; H, 6.13; N, 3.41. Found: C, 75.87; H, 6.26; N, 3.39. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90 (d, *J* = 14.2 Hz, 4H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.49 (m, 4H), 7.11–7.18 (m, 4H), 7.05 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 2H), 2.54 (s, 6H), 2.49 (s, 6H), 2.18 (s, 6H), 1.20 (s, 6H), -1.10 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 139.5, 139.3, 135.7, 134.6, 129.5, 129.4, 127.6, 127.1, 127.0, 125.4, 124.09, 124.06, 123.98, 123.4, 120.3, 120.2, 115.1, 111.5, 111.4, 80.5, 38.3, 21.5, 21.4, 18.6, 2.8.

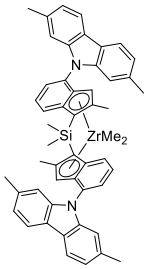
Bis[2-methyl-4-(2',7'-dimethylcarbazol-9-yl)-1*H*-indene-1-yl]dimethylsilanes (L8). General Method A was



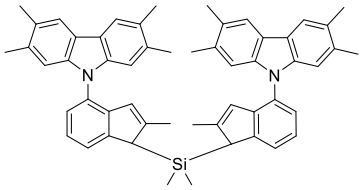
applied using 8.0 g (24.6 mmol) of 2,7-dimethyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**27**). Yield: 7.2 g (83%) as a mixture of two isomers (ca. 93% purity by NMR). ^{1}H NMR (mixture of two isomers, 400 MHz, $CDCl_3$): δ 8.04 (m, 4H), 7.74 (m, 1H), 7.60 (m, 1H), 7.35–7.43 (m, 4H), 7.05–7.14 (m, 6H), 6.92 (s, 2H), 6.24 (s, 2H), 4.00–4.04 (m, 2H), 2.50 (s, 6H), 2.47 (s, 6H), 2.26 (s, 3H), 2.20 (s, 3H), 0.07– -0.02 (m, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.40, 148.38, 146.90, 146.86, 143.1, 143.0, 141.8, 141.74, 141.73, 135.5, 135.4, 135.3, 129.22, 129.15, 124.87, 124.84, 124.81, 124.74, 124.67, 124.04, 123.97, 122.9, 122.73, 122.70, 121.99, 120.96, 120.92, 120.89, 119.6, 119.5, 110.2, 110.12, 110.09, 48.10, 48.05, 22.09, 22.07, 22.06, 18.03, 17.96, -5.8, -6.1, -6.2. HRMS (ESI) calc. for $C_{50}H_{46}N_2NaSi^+$: 725.3322 [M + Na]$^+$; found: 725.3321.



***Meso*- and *rac*-dimethylsilanediylbis[η^5-4-(2,7-dimethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C8).** General Method C was applied using 5.4 g (7.7 mmol) of bis(2-methyl-4-(2,7-dimethyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilane (**L8**). Recrystallizations from toluene gave two crops of crystals: 880 mg *rac/meso* = 1/11 (13%) and 1.33 g *rac/meso* = 3/2 (20%). ***Rac*-C8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.95 (m, 4H), 7.79–7.83 (m, 4H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.04–7.08 (m, 6H), 6.66–6.70 (m, 4H), 2.42 (s, 6H), 2.40 (s, 6H), 2.39 (s, 6H), 1.40 (s, 6H). ***Meso*-C8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.96 (m, 6H), 7.83 (br.s, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.13 (m, 2H), 7.03–7.06 (m, 4H), 6.53–6.56 (m, 4H), 2.44 (s, 12H), 2.36 (s, 6H), 1.58 (s, 3H), 1.30 (s, 3H).

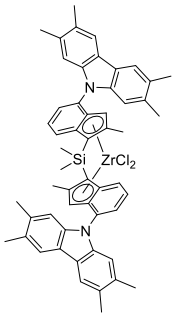


***Rac*-dimethylsilanediylbis[η^5-4-(2,7-dimethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M8).** General Method D was applied using 1.33 g of a mixture of isomers of **C8** *rac/meso* = 3/2. After methylation, a series of recrystallizations from toluene gave 180 mg (17%) of pure *rac*-**M8**. Anal. calc. for $C_{52}H_{50}N_2SiZr$: C, 75.95; H, 6.13; N, 3.41. Found: C, 75.73; H, 6.02; N, 3.54. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.95 (d, *J* =7.9 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.70 (m, 2H), 7.50 (m, 2H), 7.38 (m, 2H), 7.16 (dd, *J* = 8.7 Hz, 7.2 Hz, 2H), 7.07 (m, 2H), 7.01 (m, 2H), 6.81 (m, 2H), 6.56 (s, 2H), 2.41 (s, 6H), 2.27 (s, 6H), 2.18 (s, 6H), 1.21 (s, 6H), -1.00 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 141.7, 141.5, 135.9, 135.74, 135.68, 134.4, 129.3, 128.3, 125.7, 124.14, 124.10, 121.9, 121.8, 121.7, 121.6, 119.78, 119.76, 115.3, 112.1, 111.6, 80.3, 38.5, 22.2, 22.1, 18.6, 2.8.

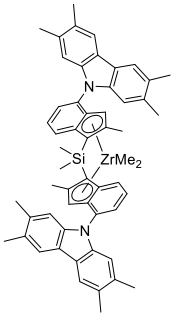


Bis[2-methyl-4-(2',3',6',7'-tetramethylcarbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (L9). General Method A was applied using 9.0 g (25.6 mmol) of 2,3,6,7-tetramethyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**28**). Yield: 6.5 g (67%) as a mixture of two isomers with ratio *meso/rac* = 1/1.5 (ca. 96% purity by NMR). ^{1}H NMR (mixture of two isomers, 400 MHz, $CDCl_3$): δ 7.99 (m, 4H), 7.80 (m, 1H), 7.68 (m, 1H), 7.43–7.52 (m, 4H), 7.17 (m, 2H), 7.00 (m, 2H), 6.34 (m, 2H), 4.10 (s) and 4.06 (s) (sum 2H), 2.56 (m, 12H), 2.48 (s) and 2.47 (s) (sum 6H), 2.45 (s) and 2.44 (s) (sum 6H), 2.32 (m) and 2.26 (m) (sum 6H), (0.06 (s) and 0.05 (s) and 0.03 (s) (sum 6H). ^{13}C{^{1}H} NMR

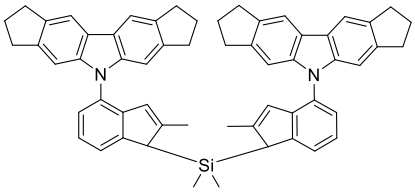
(100 MHz, two isomers *meso*/rac°* = 1/1.5, $CDCl_3$): *δ* 148.2, 146.9*, 146.8°, 143.1°, 143.0*, 140.2°, 140.2*, 134.2, 134.0, 129.7°, 129.6*, 127.8, 127.7, 124.9, 124.7, 124.6, 124.0°, 123.9*, 122.5*, 122.4°, 121.3, 121.2, 120.3, 110.7, 110.52*, 110.48, 48.1°, 48.0*, 20.8°, 20.7*, 20.0, 18.0*, 17.9°, -5.8*, -6.1*, -6.2°. HRMS (ESI) calc. for $C_{54}H_{54}N_2NaSi^+$: 781.3948 [M + Na]$^+$; found: 781.3955.



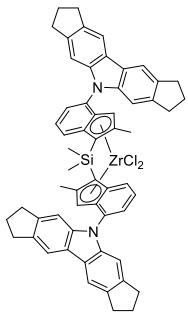
***Meso*- and *rac*-dimethylsilanediylbis[*η*^{5}-4-(2,3,6,7-tetramethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C9).** General Method C was applied using 4.7 g (6.19 mmol) of bis(2-methyl-4-(2,3,6,7-dimethyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilane (**L9**). Recrystallizations from toluene gave 2.64 g of mixture *rac/meso* = 1/8 (46%). ***Rac*-C9**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.77–7.80 (m, 8H), 7.57 (m, 2H), 7.22 (m, 2H), 6.68 (d, *J* = 7.6 Hz, 4H), 2.41 (br.s, 12H), 2.31 (s, 6H), 2.27 (s, 6H), 2.26 (s, 6H), 1.37 (s, 6H). ***Meso*-C9**: ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 7.95 (d, *J* = 8.7 Hz, 2H), 7.75–7.79 (m, 6H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.11 (dd, *J* = 8.7 Hz, 7.3 Hz, 2H), 6.52 (s, 2H), 6.48 (m, 2H), 2.42 (s, 6H), 2.39 (s, 6H), 2.38 (s, 6H), 2.34 (s, 6H), 2.25 (s, 6H), 1.58 (s, 3H), 1.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 139.8, 139.7, 138.3, 134.8, 134.4, 134.33, 134.28, 129.5, 129.0, 128.7, 126.2, 125.7, 125.1, 122.3, 122.1, 120.5, 120.2, 119.9, 113.1, 111.6, 86.3, 21.1, 20.8, 20.1, 20.0, 19.3, 2.9, 2.7.



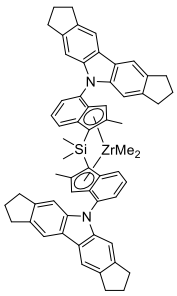
***Rac*-dimethylsilanediylbis[*η*^{5}-4-(2,3,6,7-tetramethylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M9).** General Method E was applied using 1.5 g of a mixture of isomers of **C9** *rac/meso* = 1/8. Series of recrystallizations from toluene gave 615 mg (43%) of pure *rac*-**M9**. Anal. calc. for $C_{56}H_{58}N_2SiZr$: C, 76.57; H, 6.66; N, 3.19. Found: C, 76.66; H, 6.82; N, 3.01. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 7.80 (s, 2H), 7.78 (s, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.34 (s, 2H), 7.13 (dd, *J* = 8.6 Hz, 7.2 Hz, 2H), 6.79 (s, 2H), 6.55 (s, 2H), 2.42 (s, 6H), 2.37 (s, 6H), 2.30 (s, 6H), 2.17 (s, 6H), 2.16 (s, 6H), 1.20 (s, 6H), -1.04 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): *δ* 140.1, 139.8, 135.7, 134.8, 134.5, 134.4, 129.3, 128.7, 128.6, 128.1, 125.3, 124.1, 123.7, 122.1, 122.0, 120.38, 120.36, 115.4, 112.4, 112.0, 80.2, 38.4, 20.9, 20.8, 20.1, 20.0, 18.5, 2.8.



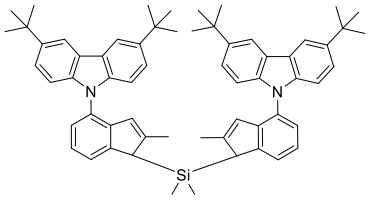
Bis[2-methyl-4-(2',3',5',7',8',9'-hexahydro-1*H*-dicyclopenta[*b*,*h*]carbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (L10). General method A was applied using 10.0 g (26.6 mmol) of 5-(2-methyl-1*H*-inden-7-yl)-2,3,5,7,8,9-hexahydro-1*H*-dicyclopenta[*b,h*]carbazole (**29**). Yield: 6.8 g (63%) as a mixture of two isomers (ca. 95% purity by NMR). ^{1}H NMR (mixture of two isomers, 400 MHz, $CDCl_3$): *δ* 7.93 (s, 4H), 7.67 (m, 1H), 7.54 (m, 1H), 7.33–7.36 (m, 4H), 7.03 (m, 2H), 6.90 (s, 2H), 6.22 (br.s, 2H), 3.96 (s, 1H), 3.93 (s, 1H), 3.08 (m, 8H), 2.91–2.99 (m, 8H), 2.21 (s, 3H), 2.15 (s, 3H), 2.13–2.18 (m, 8H), -0.13– -0.10 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 148.2, 146.9, 146.8, 143.2, 143.1, 142.2, 142.1, 141.2, 135.54, 135.46, 129.7, 129.6, 124.93, 124.87, 124.8, 124.0, 123.9, 122.6, 122.5, 122.2, 114.9, 105.5, 77.3, 76.7, 48.1, 48.0, 33.3, 32.5, 26.42, 26.39, 18.02, 17.95, -5.7, -6.07, -6.10. HRMS (ESI) calc. for $C_{58}H_{54}N_2NaSi^+$: 829.3948 [M + Na]$^+$; found: 829.3940.



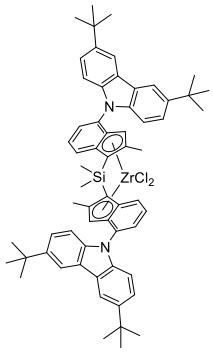
***Meso*- and *rac*-dimethylsilanediylbis[*η*^{5}-2-methyl-4-(2',3',5',7',8',9'-hexahydro-1*H*-dicyclopenta[*b*,*h*]carbazol-9-yl)-1*H*-inden-1-yl]zirconium dichloride (C10).** General Method C was applied using 5.0 g (6.2 mmol) of bis[2-methyl-4-(2',3',5',7',8',9'-hexahydro-1*H*-dicyclopenta[*b*,*h*]carbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (**L10**). Recrystallizations from toluene gave four crops of crystals: 1.57 g *rac/meso* = 1/3 (26%), 0.97 g *rac/meso* = 1.33/1.00 (16%), 1.07 g *rac/meso* = 1.5/1.0 (18%) and 220 mg *rac/meso* = 2/1 (4%). ***Rac*-C10**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.83–7.86 (m, 6H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.18–7.28 (m, 2H), 6.72 (s, 2H), 6.67 (s, 2H), 3.01–3.05 (m, 8H), 2.87–2.94 (m, 8H), 2.32 (s, 6H), 2.08–2.13 (m, 8H), 1.38 (s, 6H). ***Meso*-C10**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.91 (d, *J* = 8.6 Hz, 2H), 7.82–7.86 (m, 6H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.10 (m, 2H), 6.58 (m, 4H), 3.03 (m, 8H), 2.84–2.92 (m, 8H), 2.44 (s, 6H), 2.07–2.16 (m, 8H), 1.57 (s, 3H), 1.29 (s, 3H).



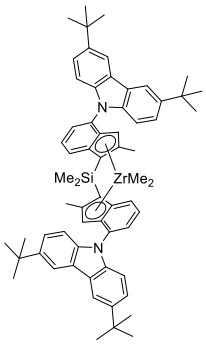
***Rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2',3',5',7',8',9'-hexahydro-1*H*-dicyclopenta[*b*,*h*]carbazol-9-yl)-1*H*-inden-1-yl]dimethylzirconium (M10)**. General Method E was applied using 1.4 g mixture of isomers of **C10** *rac/meso* = 1/3. A series of recrystallizations from toluene gave 603 mg (45%) of pure *rac*-**M10**. Anal. calc. for $C_{60}H_{58}N_2SiZr$: C, 77.79; H, 6.31; N, 3.02. Found: C, 78.02; H, 6.25; N, 2.87. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.86 (d, *J* = 11.6 Hz, 4H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 7.1 Hz, 2H), 7.39 (s, 2H), 7.12–7.16 (m, 2H), 6.86 (s, 2H), 6.54 (s, 2H), 2.99–3.06 (m, 8H), 2.87–2.98 (m, 4H), 2.74–2.84 (m, 4H), 2.17 (s, 6H), 2.04–2.15 (m, 8H), 1.19 (s, 6H), -1.01 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 142.49, 142.48, 141.0, 140.7, 136.5, 136.4, 135.7, 134.9, 129.3, 128.3, 125.5, 124.1, 123.9, 123.1, 123.0, 115.5, 115.03, 114.98, 107.6, 106.9, 80.1, 38.4, 33.7, 33.5, 32.80, 32.76, 26.8, 18.6, 2.8.



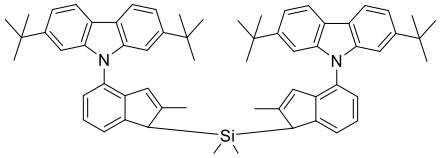
Bis[2-methyl-4-(3',6'-di-*tert*-butylcarbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (L11). General Method A was applied using 15.6 g (38.3 mmol) of 3,6-di-*tert*-butyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**8**). Yield: 14.3 g (86%) as a mixture of two isomers (ca. 92% purity by NMR). ^{1}H NMR (mixture of two isomers, 400 MHz, $CDCl_3$): δ 8.22 (m, 4H), 7.71 (m, 1H), 7.55 (m, 1H), 7.47 (m, 4H), 7.33–7.40 (m, 4H), 7.25 (m, 2H), 7.11 (m, 2H), 6.32 (m, 2H), 4.03 (m, 1H), 3.99 (m, 1H), 2.27 (s, 3H), 2.21 (s, 3H), 1.52 (s, 36H), -0.10– -0.06 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, mixture of isomers, $CDCl_3$): δ 148.1, 146.9, 146.0, 145.5, 142.8, 142.7, 142.4, 142.3, 139.8, 139.7, 139.2, 129.6, 129.5, 125.4, 125.1, 125.0, 124.6, 124.5, 124.0, 123.9, 123.4, 123.13, 123.06, 122.6, 122.4, 116.2, 116.1, 116.00, 109.6, 109.5, 109.4, 67.9, 65.8, 48.1, 48.0, 43.2, 34.7, 32.1, 25.6, 18.1, 18.0, 16.8, 16.6, -5.7, -5.9, -6.2. HRMS (ESI) calc. for $C_{62}H_{70}N_2NaSi^+$: 893.5200 [M + Na]$^+$; found: 893.5203.



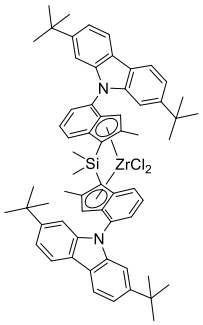
***Meso*- and *rac*-dimethylsilanediylbis[η^5-4-(3,6-di-*tert*-butylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C11).** General Method C was applied using 8.7 g (10.0 mmol) of bis(2-methyl-4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilane (**L11**). Recrystallizations from toluene gave three crops of crystals: 4.10 g *rac/meso* = 1/1 (40%), pure *meso*-isomer 930 mg (9%) and pure *rac*-isomer 2.06 g (20%). ***Meso*-C11**: Anal. calc. for $C_{62}H_{68}Cl_2N_2SiZr$: C, 72.20; H, 6.65; N, 2.72. Found: C, 72.63; H, 6.78; N, 2.54. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 4H), 7.86 (m, 4H), 7.42 (m, 2H), 7.35 (m, 2H), 7.26 (m, 2H), 7.03 (m, 2H), 6.74 (m, 2H), 6.59 (br.s, 2H), 2.41 (s, 6H), 1.54 (s, 3H), 1.41 (s, 36H), 1.26 (s, 3H). ***Rac*-C11**: Anal. calc. for $C_{62}H_{68}Cl_2N_2SiZr$: C, 72.20; H, 6.65; N, 2.72. Found: C, 72.34; H, 6.71; N, 2.70. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.13 (d, *J* = 18.1 Hz, 4H), 7.82 (d, *J* = 8.6 Hz, 4H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 4H), 7.13–7.25 (m, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.66 (s, 2H), 2.36 (s, 6H), 1.45 (s, 18H), 1.42 (s, 18H), 1.41 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 143.5, 143.2, 139.6, 139.3, 136.5, 135.2, 131.7, 128.7, 126.3, 126.2, 125.2, 124.2, 124.1, 124.0, 123.5, 121.3, 116.7, 116.3, 112.0, 110.5, 85.2, 35.01, 34.99, 32.2, 32.1, 19.1, 2.7.



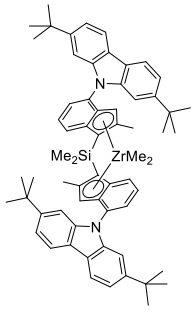
***Rac*-dimethylsilanediylbis[η^5-4-(3,6-di-*tert*-butylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M11).** General Method E was applied using 630 mg of **C11** as a mixture of isomers *rac/meso* = 1/2. Recrystallization from toluene/hexane mixture gave 260 mg (43%) of pure *rac*-**C11**. Anal. calc. for $C_{64}H_{74}N_2SiZr$: C, 77.60; H, 7.53; N, 2.83. Found: C, 77.31; H, 7.31; N, 2.91. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (d, *J* = 1.8 Hz, 2H), 8.11 (d, *J* = 1.8Hz, 2H), 7.68 (d, *J* = 8.7Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.40 (dd, *J* = 8.6 Hz, 1.9 Hz, 2H), 7.27 (dd, *J* = 8.6 Hz, 1.9 Hz, 2H), 7.17–7.25 (m, 2H), 7.12 (m, 2H), 6.65 (s, 2H), 2.21 (s, 6H), 1.46 (s, 18H), 1.40 (s, 18H), 1.22 (s, 6H), -1.08 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 143.24, 143.15, 139.5, 139.4, 135.7, 134.9, 129.5, 127.6, 125.3, 124.2, 124.1, 124.0, 123.7, 123.6, 123.2, 116.6, 116.5, 115.2, 111.3, 111.2, 80.5, 38.4, 35.03, 34.96, 32.2, 32.1, 18.7, 2.8.



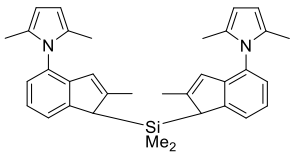
Bis[2-methyl-4-(2',7'-di-*tert*-butylcarbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (L12). General Method B was applied using 8.0 g (19.6 mmol) of 2,7-di-*tert*-butyl-9-(2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**30**). Yield: 5.5 g (64%) as a mixture of two isomers (ca. 93% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.99 (m, 4H), 7.66–7.79 (m, 1H), 7.41–7.51 (m, 2H), 7.27–7.41 (m, 4H), 7.05–7.24 (m, 4H), 6.86–6.99 (m, 1H), 6.84 (s, 1H), 6.73 (s, 1H), 6.12–6.34 (m, 1H), 5.76–5.80 (m, 1H), 4.21 (s, 1H), 4.08 (s, 1H), 2.19 (s, 1H), 2.12 (s, 2H), 1.49 (s, 3H), 1.43 (s, 6H), 1.30–1.34 (m, 18H), 1.22 (s, 3H), 1.17 (s, 6H), 1.14 (s, 3H), -0.72– -0.50 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.9, 148.8, 148.10, 148.05, 147.10, 147.06, 142.9, 142.8, 141.7, 141.57, 141.56, 129.41, 129.35, 125.2, 124.7, 124.1, 124.0, 122.6, 122.5, 120.9, 119.4, 117.5, 117.33, 117.29, 106.8, 106.7, 106.52, 106.49, 47.9, 47.8, 35.13, 35.12, 35.09, 31.83, 31.79, 18.0, 17.9, -5.6, -5.7. HRMS (ESI) calc. for $C_{62}H_{70}N_2NaSi^+$: 893.5200 [M + Na]$^+$; found: 893.5194.



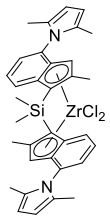
***Meso*- and *rac*-dimethylsilanediylbis[η^5-4-(2,7-di-*tert*-butylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]zirconium dichloride (C12).** General Method C was applied using 5.6 g (6.43 mmol) of bis(2-methyl-4-(2,7-di-*tert*-butyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilane (**L12**). Recrystallizations from toluene gave three crops of crystals: 850 mg pure *rac*-isomer, 370 mg pure *rac*-isomer (20% sum. yield of *rac*-isomer) and 1.36 g *rac/meso* = 2/9 (21%). ***Meso*-C12**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.97 (m, 4H), 7.89–7.93 (m, 4H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.16–7.27 (m, 6H), 6.70 (m, 2H), 6.50 (s, 2H), 2.40 (s, 6H), 1.61 (s, 3H), 1.30 (s, 3H), 1.26 (s, 18H), 1.23 (s, 18H). ***Rac*-C12**: Anal. calc. for $C_{62}H_{68}Cl_2N_2SiZr$: C, 72.20; H, 6.65; N, 2.72. Found: C, 72.08; H, 6.71; N, 2.78. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.94 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.86 (m, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.31 (dd, *J* = 8.2 Hz, 1.7 Hz, 2H), 7.24–7.28 (m, 4H), 6.84 (m, 2H), 6.64 (s, 2H), 2.38 (s, 6H), 1.46 (s, 6H), 1.28 (s, 18H), 1.22 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.6, 148.8, 141.3, 140.9, 136.3, 135.0, 131.5, 19.0, 126.2, 126.0, 125.0, 121.9, 121.7, 121.0, 119.6, 119.5, 118.6, 118.0, 109.0, 108.5, 85.6, 35.48, 35.32, 31.85, 31.81, 18.9, 2.7.



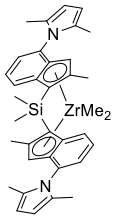
***Rac*-dimethylsilanediylbis[η^5-4-(2,7-di-*tert*-butylcarbazol-4-yl)-2-methyl-1*H*-inden-1-yl]dimethylzirconium (M12).** General method D was applied using 0.5 g (0.49 mmol) of pure *rac*-**C12**. Recrystallization from a toluene/hexane mixture gave 400 mg (83%) of pure *rac*-**M12**. Anal. calc. for $C_{64}H_{74}N_2SiZr$: C, 77.60; H, 7.53; N, 2.83. Found: C, 77.82; H, 7.94; N, 2.85. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.74–7.76 (m, 4H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.35 (m, 2H), 7.23–7.28 (m, 3H), 7.17–7.21 (m, 3H), 7.12 (m, 2H), 6.66 (s, 2H), 2.23 (s, 6H), 1.34 (s, 18H), 1.27 (s, 6H), 1.20 (s, 18H), 1.11 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 149.3, 148.8, 141.1, 140.9, 135.5, 134.6, 129.9, 128.6, 127.2, 125.0, 124.1, 123.0, 121.7, 121.7, 119.6, 119.5, 118.3, 117.8, 115.1, 109.2, 108.5, 80.9, 38.3, 35.4, 31.9, 31.8, 18.4, 2.9.



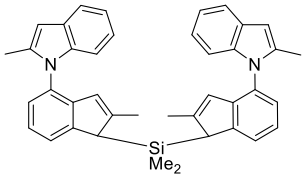
Bis[2-methyl-4-(2',5'-dimethylpyrrol-1-yl)-1*H*-inden-1-yl]dimethylsilanes (L13). General procedure A was applied using 14.6 g (65.4 mmol) of 2,5-dimethyl-1-(2-methyl-1*H*-inden-7-yl)-1*H*-pyrrole (**23**). Yield: 7.0 g (39%) as a mixture of two isomers with ratio 1/1 (ca. 95% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.09–7.25 (m, 4H), 6.27 (br.s, 2H), 5.95 (br.s, 4H), 3.89–3.91 (m, 2H), 2.27 (s, 3H), 2.18 (s, 3H), 1.98–2.01 (m, 12H), -0.33– -0.28 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, two isomers *meso/rac* = 1/1, $CDCl_3$): δ 148.72, 148.67, 145.84, 145.81, 143.8, 143.7, 130.8, 130.7, 129.0, 125.2, 125.1, 124.2, 123.4, 123.3, 122.58, 122.56, 105.2, 47.95, 47.89, 17.96, 17.85, 12.82, 12.76, -6.3, -6.67, -6.70. HRMS (ESI) calc. for $C_{34}H_{38}N_2NaSi^+$: 525.2696 [M + Na]$^+$; found: 525.2693.



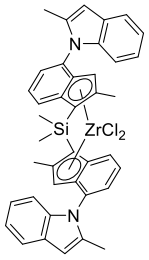
***Meso*- and *rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1*H*-inden-1-yl]zirconium dichloride (C13).** General Method C was applied using 6.9 g (13.7 mmol) of bis(2-methyl-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1*H*-inden-1-yl)dimethylsilane (**L13**). Recrystallizations from toluene gave two crops of crystals: 4.3 g *rac/meso* = 1.0/1.5 (47%), 390 mg *rac/meso* = 1.0/2.0 (4%). The first crop was recrystallized from toluene at room temperature giving 1.0 g *rac/meso* = 1/10. ***Rac*-C13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.6 Hz, 2H), 7.23 (m, 2H), 7.13 (m, 2H), 6.53 (s, 2H), 5.82 (m, 4H), 2.33 (s, 6H), 2.25 (s, 6H), 1.67 (s, 6H), 1.32 (s, 6H). ***Meso*-C13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 2H), 7.09 (m, 2H), 6.96 (d, J = 7.1 Hz, 2H), 6.94 (d, J = 7.2 Hz, 2H), 6.48 (s, 2H), 5.83 (m, 4H), 2.46 (s, 6H), 2.24 (s, 6H), 1.66 (s, 6H), 1.47 (s, 3H), 1.25 (s, 3H).



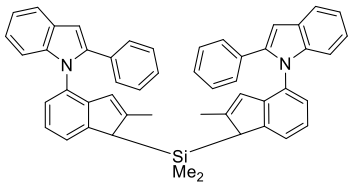
***Rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1*H*-inden-1-yl]dimethylzirconium (M13).** General Method E was applied using 1.0 g (1.51 mmol) of **C13** as a mixture *rac*/*meso* = 1/9. Recrystallization from a toluene/hexane mixture gave 623 mg (66%) of pure *rac*-**M13**. Anal. calc. for $C_{36}H_{42}N_2SiZr$: C, 69.51; H, 6.81; N, 4.50. Found: C, 69.38; H, 6.62; N, 4.61. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.58 (d, J = 8.6 Hz, 2H), 7.17 (dd, J = 7.2 Hz, 0.8 Hz, 2H), 7.04 (dd, J = 8.6 Hz, 7.2 Hz, 2H), 6.51 (s, 2H), 5.86 (ddd, J = 12.2 Hz, 3.2 Hz, 0.8 Hz, 4H), 2.20 (s, 6H), 2.13 (s, 6H), 1.80 (s, 6H), 1.12 (s, 6H), -1.14 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 136.1, 135.4, 130.7, 130.1, 129.7, 127.7, 126.3, 125.4, 123.6, 115.5, 106.68, 106.65, 79.7, 38.1, 18.7, 14.2, 13.1, 2.5.



Bis[2-methyl-4-(2'-methylindol-1-yl)-1*H*-inden-1-yl]dimethylsilanes (L14). General procedure B was applied using 3.2 g (12.3 mmol) of 2-methyl-1-(2-methyl-1*H*-inden-7-yl)-1*H*-indole (**25**). Yield: 2.6 g (69%) as a mixture of two isomers with ratio 1/1 (ca. 90% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.61 (m, 4H), 6.85–7.8 (m, 10H), 6.40–6.45 (m, 2H), 6.10–6.19 (m, 2H), 3.90 (m, 2H), 1.99–2.27 (m, 12H), 0.23–0.35 (m, 2H), -0.27– -0.18 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.5, 148.41, 148.37, 146.12, 146.09, 146.06, 143.4, 143.3, 138.1, 137.3, 129.3, 129.23, 129.16, 127.9, 124.1, 124.0, 123.5, 123.4, 122.62, 122.57, 120.6, 120.5, 119.5, 119.4, 119.3, 119.2, 110.0, 109.9, 100.5, 77.1, 76.8, 76.5, 47.81, 47.75, 31.3, 22.4, 17.74, 17.66, 13.9, 13.0, 12.9, 6.6. HRMS (ESI) calc. for $C_{40}H_{38}N_2NaSi^+$: 597.2696 [M + Na]$^+$; found: 597.2700.

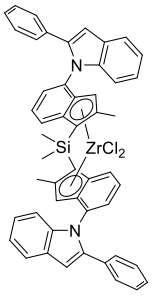


***Meso*- and *rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2-methyl-1*H*-indol-yl)-1*H*-inden-1-yl]zirconium dichloride (C14).** General Method C was applied using 2.6 g (4.5 mmol) of bis(2-methyl-4-(2-methyl-1*H*-indol-yl)-1*H*-inden-1-yl)dimethylsilane (**L14**). Recrystallizations from toluene gave two crops of crystals: 570 mg of pure *meso*-isomer (17%) and 1.8 g *rac/meso* = 1/1 (54%). ***Meso*-C14**: Anal. calc. for $C_{40}H_{36}Cl_2N_2SiZr$: C, 65.37; H, 4.94; N, 3.81. Found: C, 65.44; H, 5.10; N, 3.71. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.88 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H), 7.18 (d, J = 6.8 Hz, 2H), 7.03 (m, 4H), 6.92 (m, 2H), 6.46 (dd, J = 8.2 Hz, 0.7 Hz, 2H), 6.40 (m, 4H), 2.54 (s, 6H), 2.41 (s, 6H), 1.54 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 138.8, 138.17, 138.15, 135.1, 133.6, 129.2, 129.1, 126.8, 126.7, 124.9, 121.0, 120.3, 120.2, 119.9, 111.0, 102.8, 86.4, 19.2, 14.7, 2.8, 2.6. ***Rac*-C14**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 7.7 Hz, 2H), 7.31 (d, J =7.1 Hz, 2H), 7.18 (dd, J = 8.7 Hz, 7.1 Hz, 2H), 7.03 (m, 2H), 6.92 (ddd, J = 8.2 Hz, 7.1 Hz, 1.2 Hz, 2H), 6.49 (m, 2H), 6.46 (s, 2H), 6.39 (s, 2H), 2.53 (s, 6H), 2.30 (s, 6H), 1.38 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 139.0, 138.4, 136.7, 134.4, 132.9, 129.1, 128.2, 127.5, 126.0, 121.9, 121.0, 120.3, 119.9, 110.9, 102.6, 85.4, 19.1, 14.6, 2.5.

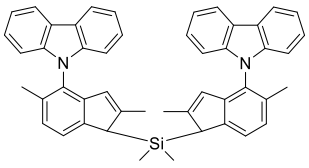


Bis[2-methyl-4-(2'-phenylindol-1-yl)-1*H*-inden-1-yl]dimethylsilanes (L15). General Method B was applied using 3.1 g (9.5 mmol) of 2-phenyl-1-(2-methyl-1*H*-inden-7-yl)-1*H*-indole (**26**). Yield: 2.4 g (72%) as a mixture of two isomers with ratio 1/1 (ca. 93% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (m, 2H), 6.86–7.60 (m, 24H), 6.18–6.38 (m, 2H), 3.83–3.97 (m, 2H), 2.03–2.26 (m, 6H), -0.38– -0.11 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, mixture of several rotomers of *rac/meso* mixture): δ 148.8, 148.74, 148.68, 148.66, 148.63, 148.57, 148.56, 146.5,

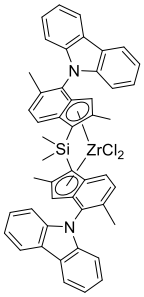
146.43, 146.39, 146.29, 146.25, 143.56, 143.55, 143.52, 143.48, 143.4, 143.23, 143.16, 143.14, 143.08, 141.7, 141.63, 141.59, 141.2, 139.64, 139.62, 139.4, 139.3, 132.82, 132.79, 132.70, 132.68, 130.5, 130.4, 130.33, 130.29, 130.22, 130.20, 130.15, 128.5, 128.24, 128.18, 128.09, 128.05, 128.0, 127.2, 127.1, 125.7, 125.64, 125.58, 125.55, 125.5, 125.42, 125.40, 124.5, 124.4, 124.3, 124.23, 124.20, 124.10, 124.05, 123.65, 123.56, 123.53, 123.49, 122.61, 122.58, 122.51, 122.47, 122.43, 122.41, 122.1, 122.0, 120.45, 120.42, 120.35, 111.1, 111.0, 103.1, 103.0, 102.9, 102.8, 48,09, 48.06, 48.0, 47.9, 47.7, 47.64, 47.62, 47.56, 18.11, 18.05, 18.02, 17.98, 17.91, 17.89, 17.8, -5.6, -5.7, -5.90, -5.92, -6.19, -6.23, -6.31, -6.33. HRMS (ESI) calc. for $C_{50}H_{42}N_2NaSi^+$: 721.3009 [M + Na]$^+$; found: 721.3004.



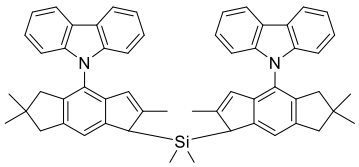
***Meso*- and *rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2-phenyl-1*H*-indol-yl)-1*H*-inden-1-yl]zirconium dichloride (C15).** General Method C was applied using 2.3 g (3.3 mmol) of bis(2-methyl-4-(2-phenyl-1*H*-indol-yl)-1*H*-inden-1-yl)dimethylsilane (**L15**). Recrystallizations from toluene gave five crops of crystals: 500 mg *rac/meso* = 7/1 (18%), 510 mg *rac/meso* = 7/2 (19%), 430 mg *rac/meso* = 2/3 (15%), 490 mg *rac/meso* = 3/1 (16%), 150 mg *rac/meso* = 1/2 (5%). Subsequent recrystallizations of the firs crops allowed to obtain 120 mg *rac/meso* = 19/1 (4%). ***Meso*-C15**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.90 (m, 2H), 7.70 (m, 2H), 7.56–7.60 (m, 2H), 7.37 (m, 2H), 6.92–7.24 (m, 16H), 6.72 (m, 2H), 6.16 (s, 2H), 2.06 (s, 6H), 1.43 (s, 3H), 1.09 (s, 3H). ***Rac*-C15**: Anal. calc. for $C_{50}H_{40}Cl_2N_2SiZr$: C, 69.91; H, 4.69; N, 3.26. Found: C, 70.06; H, 4.70; N, 3.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (m, 2H), 7.58 (m, 4H), 7.44 (d, *J* = 7.3 Hz, 2H), 6.98–7.10 (m, 16H), 6.72 (s, 2H), 6.31 (s, 2H), 2.02 (s, 6H), 1.24 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.0, 138.3, 135.6, 134.7, 133.4, 132.9, 128.3, 128.0, 127.9, 127.0, 126.9, 125.3, 124.6, 122.4, 120.9, 120.8, 120.1, 113.1, 104.5, 83.6, 18.2, 2.4.



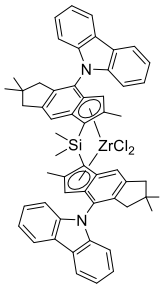
Bis[2,5-dimethyl-4-(carbazol-9-yl)-1*H*-inden-1-yl]dimethylsilanes (L16). General procedure B was applied using 9.32 g (29.8 mmol) of 2,5-dimethyl-7/4-(9*H*-carbazol-9-yl)-1/3*H*-indene (**31**). To a precipitate formed after Me_2SiCl_2 addition, 50 mL of THF was added to dissolve LiCl. The precipitate was collected after filtration and dried in vacuum giving 4.45 g of pure *rac*-isomer as a white solid. The filtrate was concentrated in vacuum and the rest of the product was isolated by column chromatography on silica gel (eluent: hexane/dichloromethane = 5/1) as a mixture of isomers with ratio *meso*/*rac* = 2/1 (ca. 95% purity by NMR). Yield: 6.85 g (69%). *Rac*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 7.5 Hz, 4H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.37–7.42 (m, 4H), 7.25–7.32 (m, 6H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 5.96 (s, 2H), 3.94 (s, 2H), 2.09 (s, 6H), 2.04 (s, 6H), -0.20 (s, 6H). *Meso*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 7.7 Hz, 4H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.37–7.42 (m, 4H), 7.21–7.33 (m, 6H), 7.03 (m, 2H), 6.97 (m, 2H), 5.96 (s, 2H), 3.91 (s, 2H), 2.16 (s, 6H), 2.02 (s, 6H), -0.14 (s,3H), -0.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.79, 148.77, 144.6, 144.5, 144.0, 143.9, 141.1, 140.9, 134.1, 134.0, 127.24, 127.17, 125.9, 125.8, 125.7, 124.3, 123.23, 123.21, 123.0, 122.9, 120.33, 120.25, 119.4, 119.3, 110.0, 109.7, 47.9, 47.8, 17.9, 17.8, 17.3, -6.1, -6.3, -6.5. HRMS (ESI) calc. for $C_{48}H_{42}N_2NaSi^+$: 697.3009 [M + Na]$^+$; found: 697.3011.



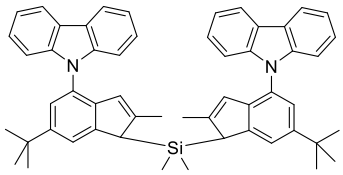
***Meso*- and *rac*-dimethylsilanediylbis[η^5-2,5-dimethyl-4-(9*H*-carbazol-9-yl)-1*H*-inden-1-yl]zirconium dichloride (C16).** General Method C was applied using 2.4 g (3.6 mmol) of bis[2,5-dimethyl-4-(9*H*-carbazol-9-yl)-1*H*-inden-1-yl]dimethylsilane (**L16**). Recrystallizations from toluene gave two crops of crystals: 800 mg of pure *rac*-isomer (27%) and 1.46 g *meso/rac* = 97/3 (49%). ***Meso*-C16**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (m, 4H), 7.86 (m, 4H), 7.40 (m, 2H), 7.20–7.30 (m, 6H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 7.3 Hz, 2H), 6.15 (s, 2H), 2.30 (s, 6H), 2.06 (s, 6H), 1.52 (s, 3H), 1.23 (s, 3H). ***Rac*-C16**: Anal. calc. for $C_{48}H_{40}Cl_2N_2SiZr$: C, 69.04; H, 4.83; N, 3.35. Found: C, 68.87; H, 4.90; N, 3.37. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (d, *J* = 7.5 Hz, 4H), 7.75 (m, 4H), 7.34 (m, 2H), 7.20–7.28 (m, 6H), 7.11–7.19 (m, 2H), 6.57 (m, 2H), 6.28 (s, 2H), 2.25 (s, 6H), 2.04 (s, 6H), 1.36 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 140.7, 137.9, 136.5, 134.4, 130.8, 129.8, 126.54, 126.49, 126.3, 125.9, 124.0, 123.4, 120.7, 120.6, 120.3, 120.2, 120.1, 113.2, 110.5, 85.2, 19.0, 18.2, 2.4.



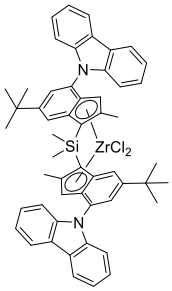
Bis(4-(9*H*-carbazol-9-yl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-*s*-indacen-1-yl)dimethylsilane (L17). General Method A was applied using 7.3 g (20 mmol) of 9-(2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacen-4-yl)-9*H*-carbazole (**32**). Yield: 5.5 g (70%) as a mixture of two isomers with ratio 1/1 (ca. 96% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.34 (m, 4H), 7.52–7.58 (m, 6H), 7.43 (m, 4H), 7.20–7.29 (m, 4H), 6.23 (m, 2H), 4.04 (m, 2H), 2.95–3.11 (m, 4H), 2.55–2.58 (m, 4H), 2.31 (s) and 2.23 (s) (sum 6H), 1.24–1.28 (m, 12H), 0.04 (s) and 0.03 (s) and 0.02 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 147.16, 147.15, 145.24, 145.19, 141.85, 141.77, 140.9, 140.60, 140.57, 140.50, 140.0, 139.4, 139.3, 125.8, 125.7, 124.83, 124.76, 124.30, 124.28, 123.02, 122.97, 122.96, 120.30, 120.0, 119.30, 119.26, 110.2, 109.98, 109.97, 48.04, 47.95, 47.7, 47.6, 45.01, 44.99, 40.7, 28.62, 28.55, 28.52, 18.00, 17.9, -5.7, -6.0, -6.1. HRMS (ESI) calc. for $C_{56}H_{54}N_2NaSi^+$: 805.3948 [M + Na]$^+$; found: 805.3951.



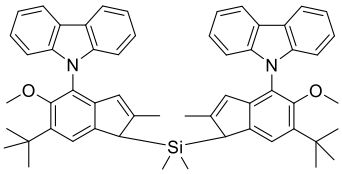
***Meso*- and *rac*-dimethylsilanediylbis[η^5-2,2,6-trimethyl-4-(9*H*-carbazol-9-yl)-1,2,3,7-tetrahydro-*s*-indacen-7-yl]zirconium dichloride (C17).** General Method C was applied using 3.13 g (4.0 mmol) bis[2,2,6-trimethyl-4-(9*H*-carbazol-9-yl)-1,2,3,7-tetrahydro-*s*-indacen-7-yl]dimethylsilane (**L17**). Recrystallizations from toluene gave three crops of crystals: 1.50 g *rac/meso* = 1/9 (40%), 150 mg *rac/meso* = 1.0/5.7 (4%) and 1.10 g *rac/meso* = 2.3/1.0 (29%). The last crop of crystals was recrystallized several times from toluene/hexane mixture giving 130 mg *rac/meso* = 19/1 (3%). ***Meso*-C17**: ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 8.13 (m, 4H), 7.89 (m, 2H), 7.73 (s, 2H), 7.41 (m, 2H), 7.20–7.30 (m, 6H), 6.62 (m, 2H), 6.22 (s, 2H), 2.79 (m, 4H), 2.67 (d, *J* = 16.4 Hz, 2H), 2.31 (s, 6H), 2.19 (d, *J* = 16.6 Hz, 2H), 1.54 (s, 3H), 1.24 (s, 3H), 1.17 (s, 6H), 1.01 (s, 6H). ***Rac*-C17:** Anal. calc. for $C_{56}H_{52}Cl_2N_2SiZr$: C, 71.31; H, 5.56; N, 2.97. Found: C, 71.45; H, 5.68; N, 2.84. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 8.12 (m, 4H), 7.76 (m, 2H), 7.60 (s, 2H), 7.31 (m, 2H), 7.22–7.28 (m, 6H), 6.56 (m, 2H), 6.36 (s, 2H), 2.66–2.79 (m, 6H), 2.7 (s, 6H), 2.10 (d, *J* = 16.5 Hz, 2H), 1.37 (s, 6H), 1.12 (s, 6H), 0.92 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): *δ* 144.1, 144.0, 140.7, 140.6, 136.7, 135.2, 129.2, 127.8, 126.5, 126.0, 124.2, 123.7, 122.1, 120.7, 120.4, 120.3, 120.2, 119.2, 113.7, 110.9, 48.0, 45.7, 41.1, 28.7, 28.3, 19.3, 3.1, 3.0.



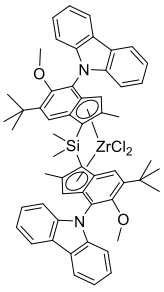
Bis[2-methyl-4-(9*H*-carbazolyl)-6-*tert*-butyl-1*H*-indene-1-yl]dimethylsilane (L18). General procedure A was applied using 10.0 g (28.45 mmol) of 9-(5-*tert*-butyl-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**13**). Yield: 9.71 g (90%) of bis[2-methyl-4-(9*H*-carbazolyl)-6-*tert*-butyl-1*H*-indene-1-yl]dimethylsilane (ca. 95% purity by NMR, approx. 20:80 mixture of *rac*- and *meso*-isomers) as yellowish glassy solid which was further used without an additional purification. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.19 (d, *J* = 8.2 Hz, 4H), 7.59 (m) and 7.44–7.36 (m) and 7.32–7.26 (m) and 7.19–7.14 (m) (sum 16H), 6.18 (m, 2H), 3.94 (s) and 3.84 (s) (sum 2H), 2.20 (d, *J* = 1.0 Hz) and 2.17 (d, *J* = 1.0 Hz) (sum 6H), 1.41 (s) and 1.39 (s) (sum 18H), -0.06 (s) and -0.09 (s) and -0.14 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$), *meso*-isomer: *δ* 147.7 (two resonances), 147.0, 141.4, 141.3, 139.9, 128.3, 125.83, 125.75, 124.4, 123.2 (two resonances), 121.9, 120.3, 120.2, 120.0, 119.52, 119.45, 110.24, 110.22, 48.0, 34.9, 31.8, 18.0, -5.2, -5.4. HRMS (ESI) calc. for $C_{54}H_{54}N_2NaSi^+$: 781.3948 [M + Na]$^+$; found: 781.3941.



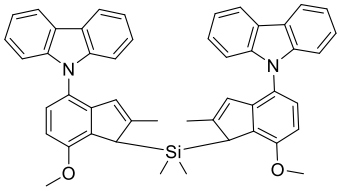
***Rac*-dimethylsilanediylbis[η^5-2-methyl-4-(9*H*-carbazolyl)-6-*tert*-butyl-indene-1-yl]zirconium dichloride (C18).** General Method C was applied using 9.46 g (12.46 mmol) of bis[2-methyl-4-(9*H*-carbazolyl)-6-*tert*-butyl-1*H*-indene-1-yl]dimethylsilane (**L18**). Recrystallizations from toluene gave pure *rac*-isomer 5.2 g (45%). ***Rac*-C18**: Anal. calc. for $C_{54}H_{52}Cl_2N_2SiZr$: C, 70.56; H, 5.70; N, 3.05. Found: C, 70.81; H, 5.75; N, 2,94. ^{1}H NMR (500 MHz, CD_2Cl_2): *δ* 8.12 (m, 4H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.76 (s, 2H), 7.73 (s, 2H), 7.23–7.34 (m, 8H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.54 (s, 2H), 2.37 (s, 6H), 1.44 (s, 6H), 1.34 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): *δ* 149.3, 141.2, 141.0, 136.0, 134.0, 130.2, 129.4, 128.9, 126.6, 126.4, 125.8, 124.2, 124.0, 120.8, 120.5, 120.4, 120.2 (two signals), 112.9, 111.1, 84.44, 35.6, 30.9, 19.2, 2.8.



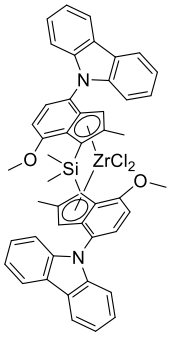
Bis(6-(*tert*-butyl)-4-(9*H*-carbazol-9-yl)-5-methoxy-2-methyl-1*H*-inden-1-yl)dimethylsilanes (L19). General Method B was applied using 7.0 g (18.4 mmol) of 9-(5-(*tert*-butyl)-6-methoxy-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**33**). Yield: 6.5 g (87%) as a mixture of two isomers with ratio *meso/rac* = 2.6/1 (ca. 91% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.19–8.22 (m, 4H), 7.39–7.54 (m, 10H), 7.08–7.21 (m, 4H), 5.97–6.01 (m, 2H), 3.83 (s) and 3.74 (s) (sum 2H), 2.92–3.01 (m, 6H), 2.11–2.15 (m, 6H), 1.48–1.51 (m, 18H), -0.08 (s) and -0.09 (s) and -0.15 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, *meso*-isomer): *δ* 154.8, 148.7, 142.6, 140.6, 140.3, 140.0, 138.4, 125.94, 125.91, 124.4, 123.3, 123.1, 121.1, 121.0, 120.2, 120.0, 119.7, 119.6, 110.9, 110.3, 60.2, 47.7, 35.3, 30.9, 18.0, -5.4, -5.5. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, *rac*-isomer, selected signals): *δ* 154.7, 148.4, 142.7, 140.5, 140.3, 139.9, 138.1, 125.9, 125.8, 123.7, 123.6, 123.2, 120.9, 120.8, 120.1, 120.0, 119.6, 110.4, 47.8, 35.2, 30.9, 17.6, -6.2. HRMS (ESI) calc. for $C_{56}H_{58}N_2NaO_2Si^+$: 841.4160 [M + Na]$^+$; found: 841.4159.



***Rac*- and *meso*-dimethylsilanediylbis[*η*^{5}-2-methyl-5-methoxy-4-(9*H*-carbazol-9-yl)-6-*tert*-butyl-1*H*-inden-1-yl]zirconium dichloride (C19).** General Method C was applied using 6.5 g (7.93 mmol) of bis[2-methyl-5-methoxy-4-(9*H*-carbazol-9-yl)-6-*tert*-butyl-1*H*-inden-1-yl]dimethylsilane (**L19**). Recrystallizations from toluene gave three crops of crystals: 1.7 g of pure *rac*-isomer (22%), another 700 mg of pure *rac*-isomer (9%), and 700 mg *rac*/*meso* = 11/1 (9%). ***Meso*-C19**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.13–8.17 (m, 6H), 7.69 (s, 2H), 7.58 (m, 2H), 7.26–7.36 (m, 6H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.29 (s, 2H), 3.18 (s, 6H), 2.29 (s, 6H), 1.51 (s, 18H), 1.49 (s, 3H), 1.18 (s, 3H). ***Rac*-C19**: Anal. calc. for $C_{56}H_{56}Cl_2N_2O_2SiZr$: C, 68.68; H, 5.76; N, 2.86. Found: C, 68.97; H, 5.84; N, 2.82. ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 8.17 (m, 4H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 2H), 7.46 (m, 2H), 7.26–7.37 (m, 6H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.31 (s, 2H), 3.21 (s, 6H), 2.23 (s, 6H), 1.46 (s, 18H), 1.36 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 160.9, 144.3, 140.7, 140.2, 136.2, 134.0, 126.5, 126.1, 124.2, 123.8, 123.5, 123.0, 121.8, 120.53, 120.48, 120.46, 120.1, 119.8, 114.2, 110.9, 83.1, 62.3, 36.3, 30.2, 18.9, 2.5.

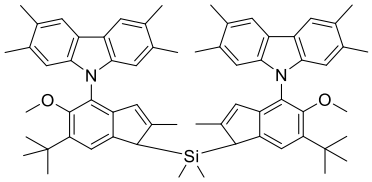


Bis[2-methyl-4-(9*H*-carbazolyl)-7-methoxy-1*H*-indene-1-yl]dimethylsilane (L20). General procedure A was applied using 6.2 g (19.05 mmol) of 9-(4-methoxy-2-methyl-1*H*-inden-4/7-yl)-9*H*-carbazole (**14**). Yield: 6.53 g (97%) (ca. 90% purity by NMR, approx. 1:1 mixture of *rac*- and *meso*-isomers) as yellowish glassy solid which was further used without an additional purification. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.22–8.13 (m, 4H), 7.43–7.34 (m, 4H), 7.34–7.17 (m, 8H), 7.15–7.08 (m, 2H), 6.87–6.81 (m, 2H), 6.02 (s, 2H), 4.41 (s) and 4.23 (s) (sum 2H), 3.99 (s) and 3.94 (s) (sum 6H), 2.18 (s) and 2.13 (s) (sum 6H), -0.19 (s) and -0.20 (s) and -0.29 (s) (sum 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 156.9, 156.8, 148.2, 148.0, 146.6, 147.0, 143.1, 142.4, 141.1, 140.7, 140.6, 130.4, 130.3, 125.4, 124.5, 124.0, 123.9, 122.9, 122.8, 121.3, 120.5, 117.5, 117.33, 117.29, 106.7, 106.5, 106.39, 106.33, 55.6, 54.8, 45.14, 45.08, 18.1, 17.8, -3.6, -3.7, -3.9. HRMS (ESI) calc. for $C_{48}H_{42}N_2NaO_2Si^+$: 729.2908 [M + Na]$^+$; found: 729.2909.

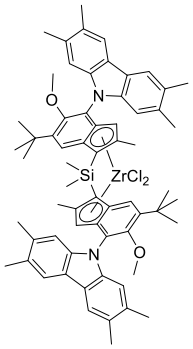


***Rac*- and *meso*-dimethylsilanediylbis[*η*^{5}-2-methyl-4-(9*H*-carbazolyl)-7-methoxy-indene-1-yl]zirconium dichloride (C20).** General Method C was applied using 6.53 g (9.24 mmol) of bis[2-methyl-4-(9*H*-carbazolyl)-7-methoxy-1*H*-indene-1-yl]dimethylsilane (**L20**). Recrystallizations from toluene gave a total 3.5 g (44%) of *rac*- and *meso*-**C20**. This crops of crystals were recrystallized several times giving 390 mg (5%) of pure *rac*-**C20** and 890 mg (11%) of pure *meso*-**C20**. ***Meso*-C20:** Anal. calc. for $C_{48}H_{40}Cl_2N_2O_2SiZr$: C, 66.49; H, 4.65; N, 3.23. Found: C, 66.62; H, 4.78; N, 3.11. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.09 (d, *J* = 7.9 Hz, 4H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.29–7.14 (m, 6H), 6.74 (d, *J* = 7.3 Hz, 2H), 6.50 (s, 2H), 6.38 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 6H), 2.42 (s, 6H), 1.40 (s, 3H), 1.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 157.4, 141.6, 141.4, 134.4, 128.4, 126.0, 125.7, 125.2, 123.7, 123.6, 123.2, 123.0, 122.4, 120.2, 119.8, 119.7, 119.4, 112.7, 110.1, 102.8, 85.8, 55.8, 19.4, 5.8, 5.7. ***Rac*-C20:** Anal. calc. for $C_{48}H_{40}Cl_2N_2O_2SiZr$: C, 66.49; H, 4.65; N, 3.23. Found: C, 66.54; H, 4.51; N, 3.20. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.11 (d, *J* = 7.8 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* =

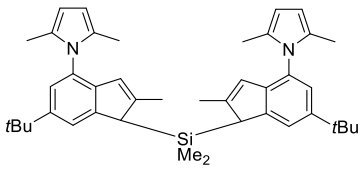
7.9 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.28–7.14 (m, 6H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.58 (s, 2H), 6.42 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 6H), 2.22 (s, 6H), 1.24 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): *δ* 155.9, 141.6, 141.4, 135.1, 133.2, 128.3, 126.6, 126.1, 125.2, 123.7, 123.2, 121.7, 120.2, 119.7, 119.6, 119.4, 112.6, 110.2, 103.0, 84.7, 54.3, 17.7, 5.7.



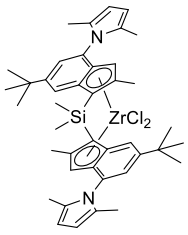
Bis(6-(*tert*-butyl)-5-methoxy-2-methyl-4-(2,3,6,7-tetramethyl-9*H*-carbazol-9-yl)-1*H*-inden-1-yl)dimethylsilanes (L21). General Method B was applied using 4.2 g (9.6 mmol) of 9-(5-(*tert*-butyl)-6-methoxy-2-methyl-1*H*-inden-7-yl)-9*H*-carbazole (**34**). Yield: 4.2 g (89%) as a mixture of two isomers with ratio *meso/rac* = 2/1 (ca. 93% purity by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.84–7.88 (m, 4H), 7.37–7.51 (m, 2H), 6.81–6.92 (m, 4H), 5.98 (m, 2H), 3.79 (s) and 3.74 (s) (sum 2H), 2.94–3.00 (m, 6H), 2.41–2.45 (m, 12H), 2.32–2.35 (m, 12H), 2.13 (s) and 2.09 (s) (sum 6H), 1.45–1.52 (m, 18H), -0.07 (s) and -0.11 (s) and -0.13 (s) (sum 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): *δ* 156.5, 155.0, 154.7, 153.9, 148.4, 148.3, 145.5, 142.9, 142.5, 141.7, 140.5, 139.8, 139.8, 139.7, 139.6, 139.6, 139.5, 139.4, 139.2, 138.6, 138.2, 138.1, 137.6, 134.8, 134.3, 134.2, 134.2, 134.1, 134.1, 134.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 125.8, 124.5, 123.7, 121.6, 121.6, 121.5, 121.4, 121.4, 121.4, 121.2, 121.2, 121.0, 120.9, 120.8, 120.6, 120.4, 120.4, 120.3, 120.3, 120.2, 119.4, 111.3, 111.3, 111.3, 111.1, 110.9, 110.9, 110.8, 77.3, 76.7, 60.6, 60.4, 60.3, 35.3, 35.3, 35.3, 34.9, 30.9, 30.8, 30.8, 30.6, 21.0, 21.0, 20.9, 20.9, 20.9, 20.1, -0.7, -4.5, -6.1. HRMS (ESI) calc. for $C_{64}H_{74}N_2NaO_2Si^+$: 953.5412 [M + Na]$^+$; found: 953.5407.



***Rac*- and *meso*-dimethylsilanediylbis[*η*^{5}-2-methyl-5-methoxy-4-(2,3,6,7-tetramethyl-9*H*-carbazol-9-yl)-6-*tert*-butyl-1*H*-inden-1-yl]zirconium dichloride (C21).** General Method C was applied using 4.2 g (8.51 mmol) of bis[2-methyl-5-methoxy-4-(2,3,6,7-tetramethyl-9*H*-carbazol-9-yl)-6-*tert*-butyl-1*H*-inden-1-yl]dimethylsilane (**L21**). Recrystallizations from toluene gave two crops of crystals: 1.1 g *rac/meso* = 2/1 (20%) and 360 mg *rac/meso* = 6/1 (7%). Several recrystallizations of the first crop of crystals from toluene gave 50 mg of *rac/meso* = 95/5 (0.9%). ***Meso*-C21**: ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 7.89 (s, 1H), 7.68 (s, 1H), 7.65 (s, 5H), 7.60 (s, 1H), 6.49 (s, 1H), 6.48 (s, 1H), 6.19 (s, 1H), 5.98 (s, 1H), 3.04 (s, 3H), 3.01 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.34–3.41 (m, 12H) 2.26 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 1.47 (s, 9H), 1.43 (s, 9H), 1.34 (s, 3H), 1.25 (s, 3H). ***Rac*-C21**: Anal. calc. for $C_{64}H_{72}Cl_2N_2O_2SiZr$: C, 70.43; H, 6.65; N, 2.57. Found: C, 70.58; H, 6.72; N, 2.66. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.86 (s, 2H), 7.82 (s, 4H), 7.63 (s, 2H), 6.60 (s, 2H), 6.42 (s, 2H), 3.28 (s, 6H), 2.42 (s, 6H), 2.41 (s, 6H), 2.40 (s, 6H), 2.28 (s, 6H), 2.18 (s, 6H), 1.44 (s, 18H), 1.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 160.4, 143.7, 139.0, 138.3, 135.2, 135.1, 134.0, 133.9, 128.5, 128.3, 122.8, 121.8, 121.7, 121.5, 120.1, 119.9, 119.4, 133.6, 111.2, 81.9, 77.2, 62.5, 35.9, 29.9, 20.9, 20.8, 20.1, 20.0, 18.4, 2.3.



Bis[2-methyl-4-(2,5-dimethylpyrrol-1-yl)-6-*tert*-butyl-1*H*-inden-1-yl]dimethylsilanes (L22). General Method A was applied using 6.0 g (21.5 mmol) of 1-(5-(*tert*-butyl)-2-methyl-1*H*-inden-7-yl)-2,5-dimethyl-1*H*-pyrrole (**25**). Yield: 4.5 g (68%) as a mixture of two isomers with ratio *meso/rac* = 2/1 (ca. 91% purity by NMR). *Meso*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53 (s, 2H), 7.20 (s, 2H), 6.34 (s, 2H), 6.01 (s, 4H), 3.85 (s, 2H), 2.31 (s, 6H), 2.09 (s, 6H), 2.05 (s, 6H), 1.41 (s, 18H), -0.19 (s, 3H), -0.28 (s, 3H). *Rac*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70 (s, 2H), 7.20 (s, 2H), 6.34 (s, 2H), 6.01 (s, 4H), 3.94 (s, 2H), 2.28 (s, 6H), 2.10 (s, 6H), 2.05 (s, 6H), 1.42 (s, 18H), -0.26 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, two isomers *meso*/rac°* = 2/1, $CDCl_3$): *δ* 147.8*, 147.7°, 149.0°, 146.9*, 145.8*, 145.7°, 140.7°. 140.6*, 129.9, 129.01°, 128.99*, 128.9, 123.8°, 123.8*, 122.5*, 122.4°, 119.6, 105.1, 105.0, 47.83°, 47.8*, 34.7, 31.6, 18.0, 12.87, 12.84, 12.82, -5.9, -6.3, -6.8. HRMS (ESI) calc. for $C_{42}H_{54}N_2NaSi^+$: 637.3948 [M + Na]$^+$; found: 637.3952.



***Rac*-dimethylsilanediylbis[η^5-2-methyl-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-6-*tert*-butyl-1*H*-inden-1-yl]zirconium dichloride (C22).** General Method C was applied using 2.5 g (4.06 mmol) of bis[2-methyl-4-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1*H*-inden-1-yl]dimethylsilane (**L22**). Recrystallizations from toluene/hexane mixture gave two crops of crystals of pure *rac*-**C22** 1.13 g (36%). ***Rac*-C22**: Anal. calc. for $C_{42}H_{52}Cl_2N_2SiZr$: C, 65.08; H, 6.76; N, 3.61. Found: C, 64.99; H, 6.88; N, 3.70. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.63 (s, 2H), 7.33 (m, 2H), 6.49 (s, 2H), 5.83 (m, 4H), 2.35 (s, 6H), 2.28 (s, 6H), 1.70 (s, 6H), 1.33 (s, 6H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 149.1, 136.3, 135.1, 132.8, 131.0, 129.7, 128.0, 127.9, 121.5, 120.6, 107.1, 106.9, 84.3, 35.7, 31.0, 19.3, 14.5, 13.3, 2.8.

SMALL SCALE PROPYLENE POLYMERIZATION EXPERIMENTS

Propylene homopolymerizations were performed in a parallel pressure reactor setup with 48 reaction cells (PPR48), fully contained in glovebox under nitrogen. A pre-weighed glass vial (5.0 mL working volume) feature insert and disposable stirring paddle were fitted to each reaction vessel of the reactor.

For experiments with activation by MAO, toluene (solvent unless stated otherwise), a solution of MAO in toluene (500 equiv), and liquid propylene (1.0 mL) were added via syringe. The reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. A precatalyst solution (in toluene) was then added via syringe to the reactor at process conditions. The total amount of solvent added to the reactor, including that used for MAO and precatalysts solutions was 4.1 ml. For experiments with activation by AB, isohexane and liquid propylene (1.0 mL) were added via syringe, and the reactor was then heated to process temperature (70 °C or 100 °C) while stirring at 800 RPM. Solutions of scavenger ((n-octyl)$_3$Al in isohexane), AB (1.1. equiv , in toluene), and, finally, precatalyst (in toluene) were then added via syringe to the reactor at process conditions. The total amount of isohexane added to the reactor including that used for the scavenger solution was 3.8 ml. The total amount of toluene added to the reactor from precatalyst and AB solutions was 0.2 ml.

Reactor temperature was monitored and typically maintained within ±1°C. Polymerizations were halted by addition of approximately 50 psi O_2/Ar (5 mol% O_2) gas mixture to the reactors for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8 psi or for a maximum of 30 minutes polymerization time.

After the polymerization reaction, the volatile components were removed from the glass vial insert containing the polymer using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator. The vial was then weighed to determine the yield of the polymer product. The molecular weight distribution of the resultant polymer was analyzed by Rapid GPC (3×PLgel Mix B, 10 µm, 30 cm×7.5 mm; eluent: 1,2,4-trichlorobenzene at flow rate of 2.0 mL/min; oven temperature: 165 °C) with evaporative light scattering detector, calibrated using polystyrene standards ranging from 580 Da – 3390 kDa (relative calibration). The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 0.1 mg/mL - 0.9 mg/mL. 250 µL of a polymer solution was injected into the system. Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220 °C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220 °C at a rate of 100 °C/min and then cooled at a rate of 50 °C/min. Melting points were collected during the heating period. The polymers were also characterized by quantitative ^{13}C NMR at a frequency of 150 MHz with a Bruker 600 MHz spectrometer at 120 °C equipped with a high-temperature cryoprobe (for 10 mm O.D. tubes) and a preheated robotic sample changer. Samples were dissolved in deuterated tetrachloroethane at a concentration of 67 mg/mL at 140 °C. Polymer resonance peaks are referenced to mmmm=21.8 ppm. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in “Polymer Conformation and Configuration” Academic Press, New York 1969 and J. Randall in “Polymer Sequence Determination, Carbon-13 NMR Method”, Academic Press, New York, 1977. Methods for measuring relative contents of 2,1-regioerrors and 1,3- regioerrors follow standard methods. Additional references include Grassi, A. et. al. *Macromolecules*, **1988**, *21*, 617-622 and Busico et.al. *Macromolecules*, **1994**, *27*, 7538-7543. The intensities used in the calculations are normalized to the total number of monomers in the sample.

Table S1. Propylene polymerization experiments using activation by MAO[a]

Pre-cat.	$n_{precat.}$, μmol[b]	T_p, °C[c]	Quench time, s[d]	Polymer yield, g	Activity, $g_{polym.} \cdot (mmol_{cat} \cdot h)^{-1}$	M_n, Da	M_w, Da	PDI[e]	Polymer T_m, °C[f]
C1[g]	0.080	70	1803	0.1148	2865	33617	47351	1.4	137.8
C1[g]	0.080	70	1800	0.1007	2517	32463	47856	1.5	137.6
C1[g]	0.080	70	1801	0.1219	3046	28737	47792	1.7	137.8
C1[g]	0.080	100	1801	0.1070	2673	6951	9624	1.4	–
C1[g]	0.080	100	1531	0.1339	3936	8588	12282	1.4	106.5
C1[g]	0.080	100	1714	0.1287	3380	7998	11347	1.4	104.0
C2	0.040	70	206	0.1619	70733	364910	582590	1.6	159.1
C2	0.040	70	223	0.159	64170	339884	587090	1.7	158.1
C2	0.040	70	239	0.1888	71096	389961	635984	1.6	157.0
C2	0.040	100	173	0.1052	54728	161525	251506	1.6	155.5
C2	0.040	100	166	0.1076	58337	141860	230783	1.6	154.8
C2	0.040	100	190	0.0922	43674	162431	260787	1.6	155.3
C3	0.040	70	544	0.0996	16478	131456	207027	1.6	155.3
C3	0.040	70	463	0.0862	16756	127240	202604	1.6	155.3
C3	0.040	70	467	0.0867	16709	134851	215475	1.6	155.7
C3	0.040	100	730	0.0568	7003	26400	46636	1.8	146.8
C3	0.040	100	618	0.0607	8840	30244	57725	1.9	147.2
C3	0.040	100	618	0.0599	8723	30702	50586	1.7	147.2
C4	0.040	70	301	0.1191	35611	611907	996618	1.6	159.3
C4	0.040	70	291	0.1312	40577	537152	887953	1.7	160.1
C4	0.040	70	321	0.1303	36533	609758	987409	1.6	159.0
C4	0.040	100	363	0.0568	14083	183768	298941	1.6	153.8
C4	0.040	100	302	0.0614	18298	184750	291086	1.6	155.7
C4	0.040	100	402	0.0662	14821	200262	301200	1.5	155.3
C6	0.040	70	126	0.2896	206857	175309	379050	2.2	157.5
C6	0.040	70	158	0.3454	196747	151341	357856	2.4	156.9
C6	0.040	100	122	0.1016	74951	122163	210179	1.7	154.8
C6	0.040	100	103	0.1194	104330	121323	196122	1.6	154.7
C6	0.040	100	113	0.1088	86655	108328	187624	1.7	154.3
M6	0.040	70	128	0.3538	248766	164348	364099	2.2	158.4
M6	0.040	70	101	0.3146	280337	137866	332993	2.4	156.9
M6	0.040	70	143	0.4009	252315	131083	296135	2.3	156.1
M6	0.040	100	98	0.1004	92204	122216	206290	1.7	153.6
M6	0.040	100	94	0.1253	119968	95085	171135	1.8	154.3
M6	0.040	100	87	0.1188	122897	107121	180409	1.7	154.4
M7	0.040	70	206	0.4033	176199	193807	470190	2.4	156.9
M7	0.040	70	196	0.3789	173985	219666	442422	2.0	156.7
M7	0.040	70	212	0.4092	173717	160750	448899	2.8	156.9
M7	0.040	100	157	0.1101	63115	152430	259991	1.7	154.2
M7	0.040	100	142	0.1242	78718	126811	259099	2.0	154.1
M7	0.040	100	137	0.1126	73971	130406	236174	1.8	154.1
M8	0.040	70	206	0.3065	133908	290481	557688	1.9	159.0
M8	0.040	70	211	0.3810	162512	264195	556538	2.1	159.6
M8	0.040	70	229	0.4308	169310	247337	578307	2.3	158.9
M8	0.040	100	127	0.1247	88370	210342	351757	1.7	154.6

M8	0.040	100	121	0.1176	87471	214758	352169	1.6	155.1
M8	0.040	100	133	0.1354	91624	200963	352483	1.8	155.8
C10	0.040	70	191	0.2200	103665	273731	601956	2.2	158.0
C10	0.040	70	217	0.2406	99788	317013	642596	2.0	157.5
C10	0.040	70	227	0.2640	104670	274565	621226	2.3	158.5
C10	0.040	100	109	0.1320	108991	156433	282874	1.8	154.1
C10	0.040	100	129	0.1187	82814	144912	287040	2.0	154.2
C10	0.040	100	118	0.1342	102356	117621	239544	2.0	154.1
C11	0.025	70	589	0.0822	20100	690367	1006410	1.5	159.3
C11	0.025	70	560	0.0851	21871	712331	1037112	1.5	158.9
C11	0.025	70	679	0.0775	16426	764627	1109846	1.5	159.3
C11	0.025	100	345	0.0579	24167	210674	299462	1.4	154.8
C11	0.025	100	242	0.0596	35421	200709	283720	1.4	155.3
C11	0.025	100	381	0.0571	21604	214150	304386	1.4	155.1
C12	0.040	70	194	0.1070	49639	358019	626823	1.8	158.1
C12	0.040	70	230	0.1008	39443	411602	674791	1.6	156.2
C12	0.040	70	222	0.1083	43905	353411	633179	1.8	156.4
C12	0.040	100	703	0.0701	8974	137400	260959	1.9	152.4
C12	0.040	100	849	0.0703	7452	185274	293044	1.6	152.1
C12	0.040	100	673	0.0667	8920	142732	255483	1.8	152.0
C15	0.040	70	179	0.3934	197799	242840	597240	2.5	157.2
C15	0.040	70	211	0.4510	192370	224765	596222	2.7	155.5
C15	0.040	70	200	0.4038	181710	219357	619049	2.8	156.4
C15	0.040	100	75	0.1638	196560	169353	303072	1.8	154.1
C15	0.040	100	77	0.1693	197883	155749	286350	1.8	154.5
C15	0.040	100	73	0.1687	207986	155993	281972	1.8	154.2
C16	0.040	70	245	0.1434	52678	305124	547470	1.8	156.2
C16	0.040	70	268	0.1535	51549	312922	572393	1.8	155.9
C16	0.040	70	285	0.1522	48063	368277	602371	1.6	156.4
C16	0.040	100	136	0.1125	74449	112735	197001	1.8	155.6
C16	0.040	100	146	0.1174	72370	111956	195609	1.8	154.5
C16	0.040	100	145	0.1051	65234	107036	181965	1.7	155.1
C17	0.040	70	168	0.2369	127054	304412	534018	1.8	157.0
C17	0.040	70	188	0.2756	131600	257807	504182	2.0	160.5
C17	0.040	70	214	0.3062	128860	262707	488444	1.9	157.3
C17	0.040	100	89	0.1636	166129	113801	215443	1.9	155.2
C17	0.040	100	98	0.1629	149862	111039	221830	2.0	155.0
C17	0.040	100	69	0.1322	171219	120414	215888	1.8	154.5
C18[g]	0.080	70	295	0.4009	61134	259208	628955	2.4	154.5
C18[g]	0.080	70	335	0.4036	54280	274508	621246	2.3	153.6
C18[g]	0.080	70	314	0.4104	58797	255989	617466	2.4	155.3
C18[g]	0.080	100	146	0.2317	71660	169442	322297	1.9	152.9
C18[g]	0.080	100	155	0.2188	63359	163185	311443	1.9	152.2
C18[g]	0.080	100	157	0.2080	59732	165055	319490	1.9	152.4
C19	0.040	70	509	0.2700	47741	534240	981185	1.8	154.5
C19	0.040	70	587	0.3662	56147	465831	861875	1.9	156.6
C19	0.040	70	586	0.3560	54676	446926	886700	2.0	160.9
C19	0.040	100	207	0.1124	48870	291391	493383	1.7	153.1
C19	0.040	100	221	0.1147	46710	288441	496738	1.7	153.6
C20	0.040	70	223	0.1648	66511	226401	406188	1.8	158.7

C20	0.040	70	218	0.1648	68037	203737	369114	1.8	158.5
C20	0.040	70	224	0.15	60268	244496	426686	1.8	158.3
C20	0.040	100	154	0.1022	59727	48805	91197	1.9	156.3
C20	0.040	100	142	0.1221	77387	46995	87097	1.9	156.0
C20	0.040	100	141	0.1179	75255	68085	107861	1.6	156.8
C21	0.040	70	689	0.1045	13650	723406	1243650	1.7	149.9
C21	0.040	70	782	0.0918	10565	695698	1247608	1.8	152.2
C21	0.040	70	791	0.0953	10843	765754	1290173	1.7	152.2
C21	0.040	100	232	0.1207	46823	296479	497244	1.7	151.1
C21	0.040	100	229	0.1195	46965	276404	466856	1.7	150.9
C21	0.040	100	210	0.0989	42386	262328	467414	1.8	150.4
C22	0.060	70	1365	0.0762	3351	382048	652540	1.7	149.8
C22	0.060	70	1501	0.0731	2923	333230	672684	2.0	150.0
C22	0.060	70	1572	0.0801	3056	377410	700284	1.9	150.3
C22	0.060	100	422	0.0811	11532	70604	134480	1.9	147.9
C22	0.060	100	437	0.0750	10301	68252	128781	1.9	147.8
C22	0.060	100	411	0.0766	11188	67031	121033	1.8	147.6
M12	0.040	70	123	0.1475	107927	304955	507079	1.7	157.4
M12	0.040	70	107	0.1381	116159	298495	503604	1.7	157.5
M12	0.040	70	114	0.1482	117000	303610	504912	1.7	157.9
M12	0.040	100	912	0.068	6711	156757	272990	1.7	154.0
M12	0.040	100	897	0.0693	6953	174165	283058	1.6	152.6
M12	0.040	100	1015	0.0698	6189	156659	268270	1.7	153.3
M13	0.040	70	791	0.0735	8363	261908	457877	1.8	153.9
M13	0.040	70	851	0.0752	7953	306602	495805	1.6	153.6
M13	0.040	70	965	0.0770	7181	315156	510222	1.6	154.3
M13	0.040	100	522	0.0663	11431	62507	100561	1.6	151.1
M13	0.040	100	548	0.0615	10100	54189	95646	1.8	150.6
M13	0.040	100	527	0.0603	10298	56147	94374	1.7	150.3
M-II	0.040	70	188	0.3404	162957	298482	630605	2.1	159.6
M-II	0.040	70	256	0.449	157852	224554	560175	2.5	159.5
M-II	0.040	70	234	0.4033	155115	203125	534216	2.6	158.1
M-II	0.040	100	123	0.1486	108732	166877	308565	1.9	157.7
M-II	0.040	100	114	0.1373	108395	166844	307246	1.8	156.3
M-II	0.040	100	115	0.1392	108939	163385	298673	1.8	156.3

[a] Polymerization conditions: 500 eq. MAO, 4.1 mL toluene (except for **C1**, **C18**), 1.0 mL propylene, reactor quenched at 8 psig pressure loss (except for **C1**, **C18**) or at a maximum time limit of 30 minutes. [b] Precatalyst amount. [c] Polymerization temperature. [d] Polymerization time. [e] Polydispersity index, M_w/M_n, determined by GPC. [f] Polymer melting temperature, determined by DSC. [g] Solvent: 0.5 mL toluene, 3.6 mL isohexane; reactor quenched at 20 psig pressure loss.

Table S2. Propylene polymerization experiments using activation by AB[a]

Pre-cat.	$n_{precat.}$, μmol[b]	T_p, °C[c]	Quench time, s[d]	Polymer yield, g	Activity, $g_{polym.} \cdot (mmol_{cat} \cdot h)^{-1}$	M_n, Da	M_w, Da	PDI[e]	Polymer T_m,°C [f]
M5	0.025	70	404	0.1962	69933	418611	780751	1.9	160.9
M5	0.025	70	236	0.1194	72854	480047	879151	1.8	161.4
M5	0.025	70	244	0.149	87934	526800	940066	1.8	160.9

M5	0.025	100	183	0.0698	54925	131092	234315	1.8	156.6
M5	0.025	100	134	0.1242	133469	112809	205078	1.8	156.8
M6	0.025	70	122	0.4056	478741	97082	352143	3.6	155.8
M6	0.025	70	125	0.3886	447667	152418	386844	2.5	155.8
M6	0.025	70	143	0.4282	431194	102713	358561	3.5	156.7
M6	0.025	100	56	0.2056	528686	61919	129475	2.1	154.4
M6	0.025	100	64	0.2506	563850	56257	130513	2.3	153.9
M6	0.025	100	57	0.2319	585853	62728	130531	2.1	154.4
M7	0.025	70	417	0.233	80460	437171	827871	1.9	159.9
M7	0.025	70	359	0.2837	113796	425692	801495	1.9	159.4
M7	0.025	70	287	0.2117	106219	532181	878142	1.7	159.8
M7	0.025	70	321	0.2614	117264	401557	810902	2.0	159.1
M7	0.025	100	144	0.1268	126800	116670	221808	1.9	155.5
M7	0.025	100	196	0.1039	76335	127758	241243	1.9	156.4
M7	0.025	100	201	0.1033	74006	134591	223403	1.7	156.5
M7	0.025	100	115	0.1552	194337	108573	199937	1.8	155.8
M7	0.025	100	140	0.1421	146160	113691	214002	1.9	156.1
M7	0.025	100	128	0.1614	181575	112029	212129	1.9	156.1
M8	0.025	70	232	0.3972	246538	190238	674149	3.5	157.8
M8	0.025	70	412	0.3244	113383	413569	956559	2.3	159.3
M8	0.025	100	81	0.1982	352356	117954	251074	2.1	156.0
M8	0.025	100	138	0.1808	188661	169949	312315	1.8	156.0
M8	0.025	100	92	0.2225	348261	120698	259599	2.2	155.1
M9	0.025	70	256	0.3557	200081	259077	721335	2.8	157.3
M9	0.025	70	295	0.4169	203504	166783	564726	3.4	157.6
M9	0.025	70	292	0.3921	193364	257509	674125	2.6	157.3
M9	0.025	100	86	0.1964	328856	114174	226791	2.0	154.6
M9	0.025	100	100	0.2046	294624	97319	204599	2.1	154.5
M9	0.025	100	97	0.1894	281171	131549	249047	1.9	155.8
M10	0.025	70	390	0.198	73108	571940	953902	1.7	159.6
M10	0.025	70	428	0.3976	133772	311196	751614	2.4	158.6
M10	0.025	70	424	0.2569	87249	479430	961949	2.0	159.1
M10	0.025	100	126	0.172	196571	133886	270557	2.0	155.1
M10	0.025	100	138	0.1775	185217	147897	277704	1.9	157.1
M10	0.025	100	136	0.1641	173753	128984	248432	1.9	155.6
M12	0.025	70	70	0.3891	800434	83339	286041	3.4	154.1
M12	0.025	70	81	0.3564	633600	71206	282882	4.0	154.5
M12	0.025	100	41	0.2323	815883	57482	151791	2.6	154.5
M12	0.025	100	44	0.2384	780218	72710	161890	2.2	155.3
M12	0.025	100	45	0.2408	770560	61994	134964	2.2	155.0
M-II	0.025	70	268	0.3633	195206	251696	665814	2.7	161.7
M-II	0.025	70	323	0.2909	129689	516715	963614	1.9	162.4
M-II	0.025	100	97	0.1505	223423	125019	215082	1.7	155.8
M-II	0.025	100	120	0.1669	200280	105326	208174	2.0	155.5

[a] Polymerization conditions: 1.1 equivs. $[HMe_2NPh][B(C_6F_5)_4]$, 0.5 µmol Al(*n*-octyl)$_3$, 0.2 mL toluene, 3.9 mL isohexane, 1 mL propylene; reactor quenched at 8 psig pressure loss or at a maximum time limit of 30 minutes. [b] Precatalyst amount. [c] Polymerization temperature. [d] Polymerization time. [e] Polydispersity index, M_w/M_n, determined by GPC. [f]Polymer melting temperature, determined by DSC. [g] Solvent: 0.5 mL toluene, 3.6 mL isohexane; reactor quenched at 20 psig pressure loss.

CRYSTAL STRUCTURE DETERMINATIONS

X-ray experiments were carried out using SMART 1000 CCD diffractometer (λ(Mo-$K\alpha$)=0.71073 Å, graphite monochromator, ω-scans) at 100–120 °K. All structures were solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions and included in the refinement using riding approximation. The details of data collection and crystal structures refinement for which we used SAINT Plus,[14] SADABS[15] and SHELXTL-97[16] program packages, are summarized in Tables S3 through S8. Crystallographic data for **C16**, **C22**, **M6**, **M7**, **M10** and **M12** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 2046384–2046389. 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).

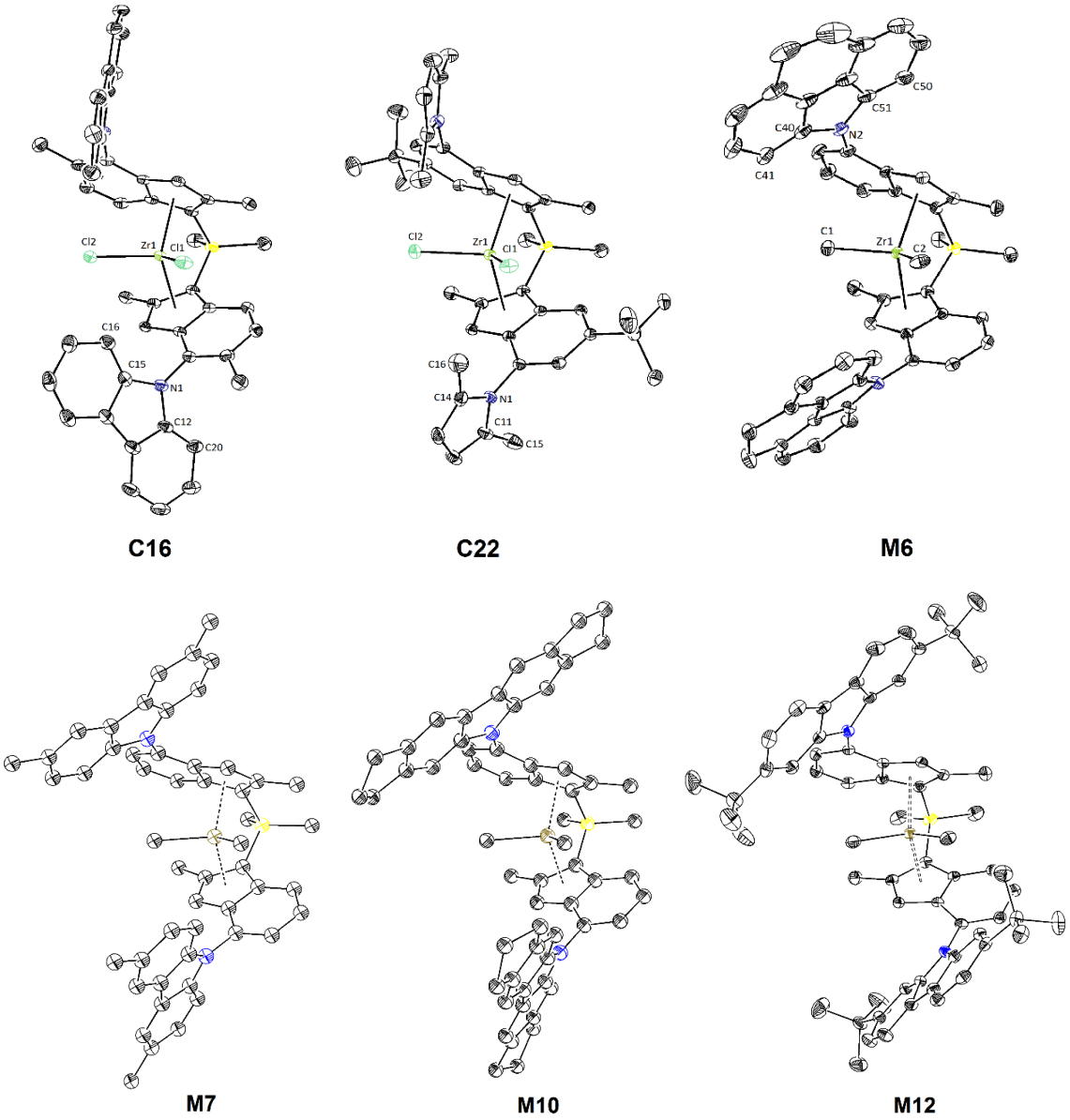
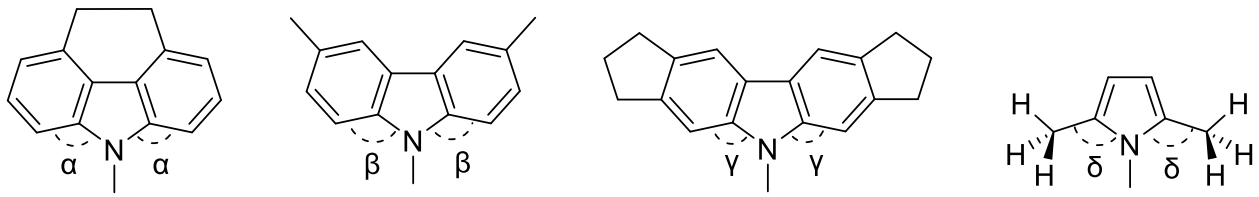


Figure S1. ORTEP style representation of zirconocenes **M7**, **M10** and **M12** with ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.



M6	**M7**	**M10**	**C22**
α = 133.91–134.19	β = 129.84–130.33	γ = 128.64–129.73	δ = 122.01–122.85

Figure S2. Angles N(9)–C(8a/9a)–C(8/1) in carbazolyl moieties in **M7**, **M8**, **M11** and angles N(1)–C(2/5)–CH_3 in **C23**. Data from the X-Ray analyses.

Table S3. Crystal data and structure refinement for C16 (CCDC 2046385)

Empirical formula	C62 H56 Cl2 N2 Si Zr	
Formula weight	1019.30	
Temperature	120(2) K	
Wavelength	0.71073 E	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.6391(10) Å	α = 88.4788(13)°.
	b = 13.7468(10) Å	β = 75.8186(13)°.
	c = 15.4585(12) Å	γ = 63.3302(12)°.
Volume	2499.4(3) $Å^3$	
Z	2	
Density (calculated)	1.354 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	1060	
Crystal size	0.43 x 0.31 x 0.24 mm^3	
Theta range for data collection	1.67 to 29.00°.	
Index ranges	-17<=h<=18, -18<=k<=18, 0<=l<=21	
Reflections collected	13139	
Independent reflections	13150 [R(int) = 0.0000]	
Completeness to theta = 29.00°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.911 and 0.849	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13150 / 0 / 622	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0812	
R indices (all data)	R1 = 0.0489, wR2 = 0.0927	
Largest diff. peak and hole	0.760 and -0.569 $e.Å^{-3}$	

Table S4.Crystal data and structure refinement for C22 (CCDC 2046384)

Empirical formula	C45.50 H56 Cl2 N2 Si Zr	
Formula weight	821.13	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.731(2) Å	α = 90°.
	b = 21.255(4) Å	β = 92.626(3)°.
	c = 15.501(3) Å	γ = 90°.
Volume	4190.2(12) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.452 mm^{-1}	
F(000)	1724	
Crystal size	0.37 x 0.31 x 0.21 mm^3	
Theta range for data collection	1.87 to 29.00°.	
Index ranges	-17<=h<=17, -28<=k<=28, -21<=l<=21	
Reflections collected	51670	
Independent reflections	11146 [R(int) = 0.0498]	
Observed reflections [I>2sigma(I)]	9481	
Completeness to theta = 29.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.898 and 0.841	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11146 / 0 / 501	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0784	
R indices (all data)	R1 = 0.0385, wR2 = 0.0832	
Largest diff. peak and hole	0.488 and -0.528 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for M6 (CCDC 2046388)

Empirical formula	C59 H54 N2 Si Zr	
Formula weight	910.35	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.2494(5) Å	α = 90°.
	b = 20.1522(8) Å	β = 91.7810(10)°.
	c = 18.6075(8) Å	γ = 90°.
Volume	4591.1(3) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	0.308 mm^{-1}	
F(000)	1904	
Crystal size	0.330 x 0.280 x 0.240 mm^3	
Theta range for data collection	1.490 to 29.999°.	
Index ranges	-17<=h<=17, -28<=k<=28, -26<=l<=26	
Reflections collected	98445	
Independent reflections	13397 [R(int) = 0.0371]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.862 and 0.838	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13397 / 0 / 615	
Goodness-of-fit on F^2	1.012	
Final R indices for 11187 refl. with [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0756	
R indices (all data)	R1 = 0.0406, wR2 = 0.0830	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.461 and -0.435 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for M7 (CCDC 2046387)

Empirical formula	C59 H58 N2 Si Zr	
Formula weight	914.38	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8095(9) Å	α = 77.496(2)°.
	b = 12.3878(9) Å	β = 85.801(2)°.
	c = 16.4897(13) Å	γ = 81.266(2)°.
Volume	2325.8(3) $Å^3$	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.304 mm^{-1}	
F(000)	960	
Crystal size	0.260 x 0.210 x 0.170 mm^3	
Theta range for data collection	1.700 to 30.588°.	
Index ranges	-16<=h<=16, -17<=k<=17, -23<=l<=23	
Reflections collected	32185	
Independent reflections	14231 [R(int) = 0.0493]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4330 and 0.3609	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14231 / 0 / 579	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1196	
R indices (all data)	R1 = 0.0791, wR2 = 0.1338	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.022 and -1.198 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for M10 (CCDC 2046386)

Empirical formula	C74 H74 N2 Si Zr	
Formula weight	1110.66	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.9734(6) Å	α= 90°.
	b = 37.0630(19) Å	β= 91.4286(13)°.
	c = 12.9008(7) Å	γ = 90°.
Volume	5723.2(5) $Å^3$	
Z	4	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.260 mm^{-1}	
F(000)	2344	
Crystal size	0.270 x 0.210 x 0.180 mm^3	
Theta range for data collection	1.672 to 30.573°.	
Index ranges	-17<=h<=17, -52<=k<=52, -18<=l<=18	
Reflections collected	79037	
Independent reflections	17505 [R(int) = 0.0933]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4330 and 0.3785	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17505 / 0 / 686	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1257	
R indices (all data)	R1 = 0.0917, wR2 = 0.1431	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.396 and -0.699 $e.Å^{-3}$	

Table S8. Crystal data and structure refinement for M12 (CCDC 2046389)

Empirical formula	C70.50 H85 N2 Si Zr	
Formula weight	1079.71	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.9493(6) Å	α = 90°.
	b = 24.3226(10) Å	β = 109.8610(10)°.
	c = 19.1054(8) Å	γ = 90°.
Volume	6096.6(4) $Å^3$	
Z	4	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.242 mm^{-1}	
F(000)	2304	
Crystal size	0.290 x 0.200 x 0.180 mm^3	
Theta range for data collection	1.674 to 30.677°.	
Index ranges	-19<=h<=19, -34<=k<=34, -27<=l<=27	
Reflections collected	83706	
Independent reflections	18638 [R(int) = 0.0724]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3368 and 0.2906	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18638 / 24 / 659	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1018	
R indices (all data)	R1 = 0.0760, wR2 = 0.1150	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.480 and -0.526 $e.Å^{-3}$	

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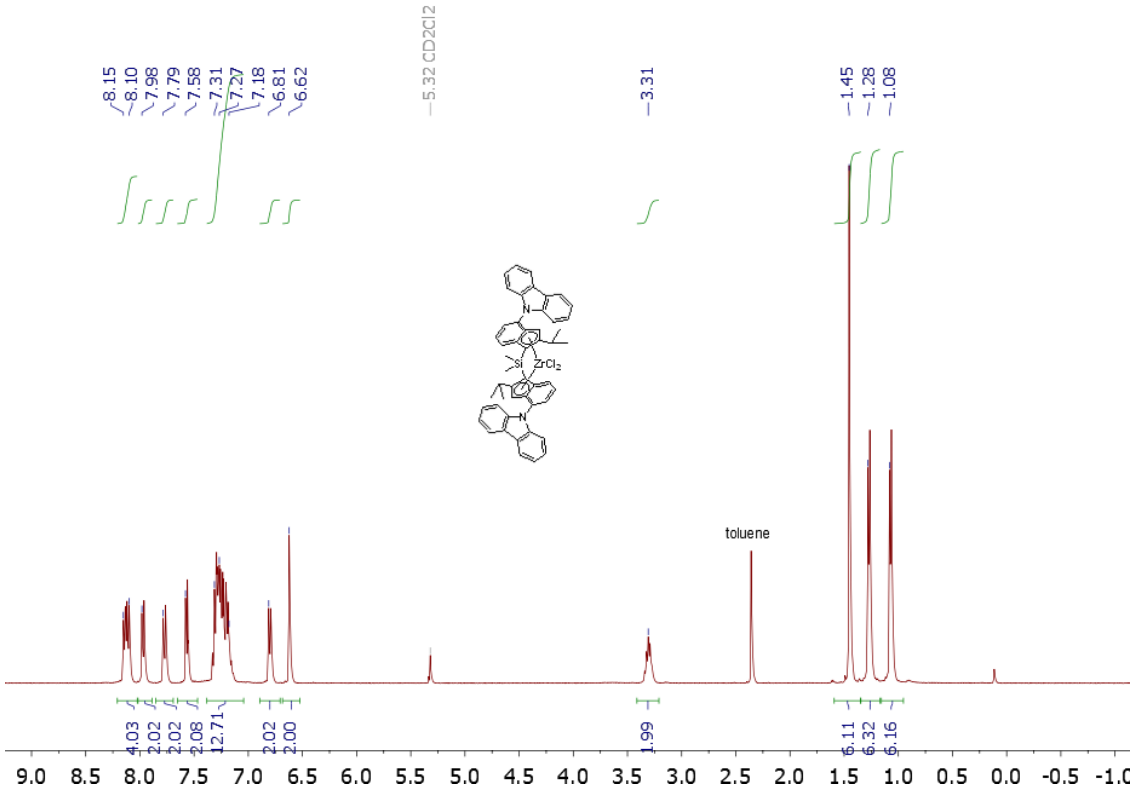

Figure S3. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C1**.

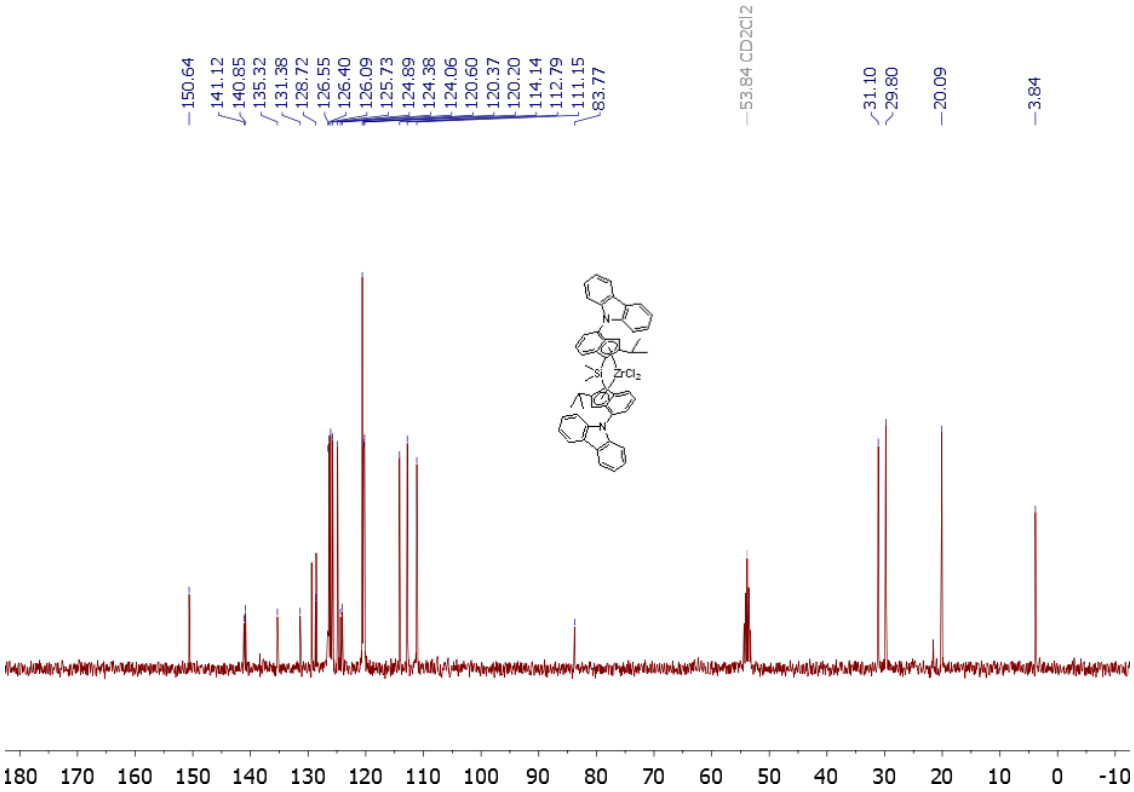

Figure S4. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C1**.

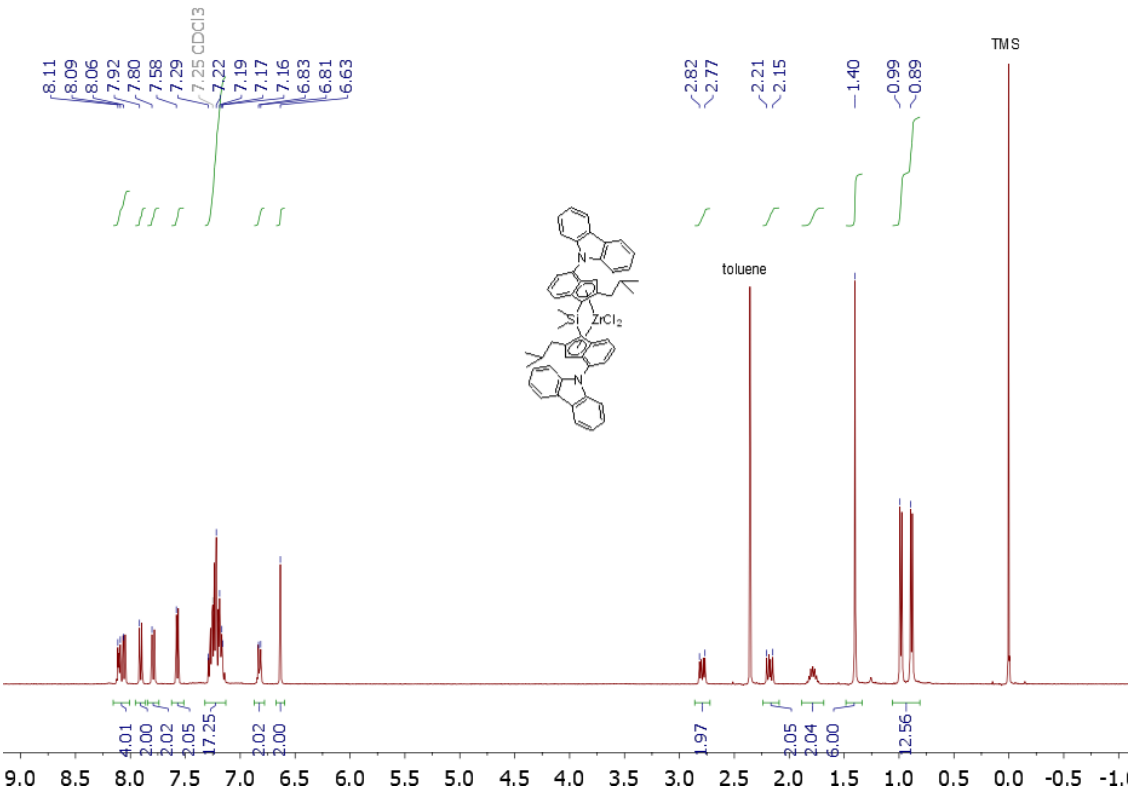

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C2**.

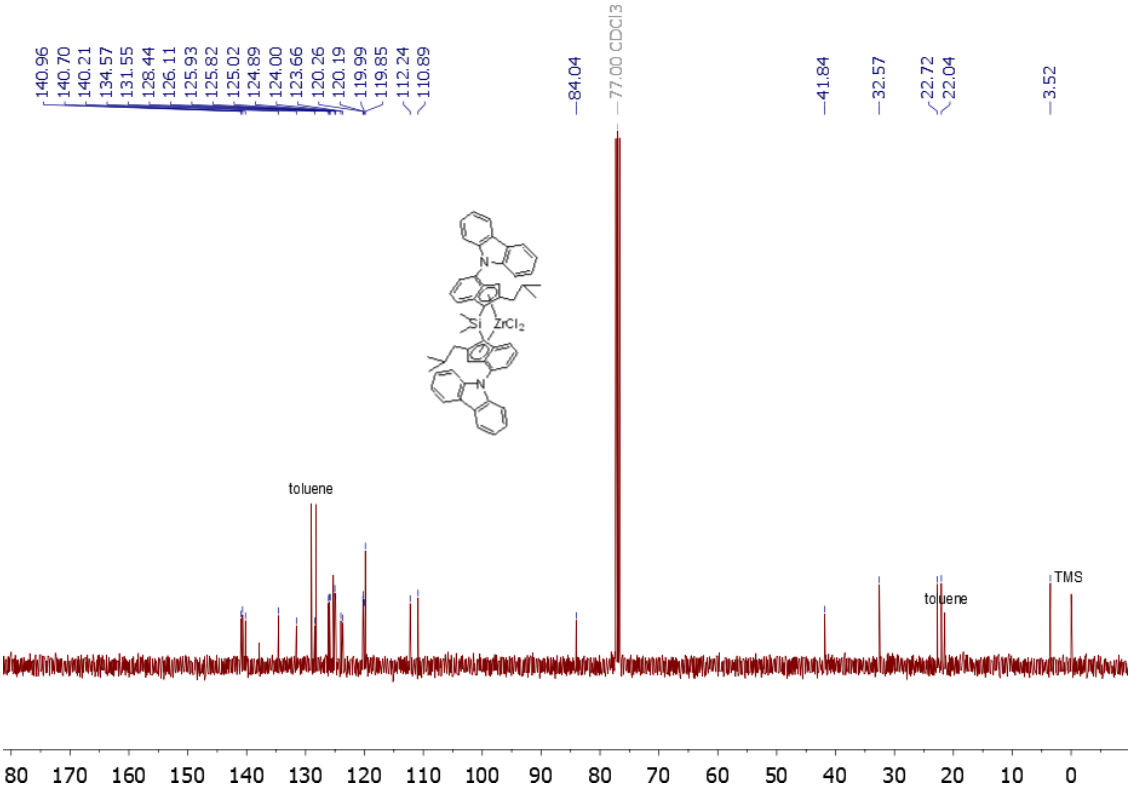

Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C2**.

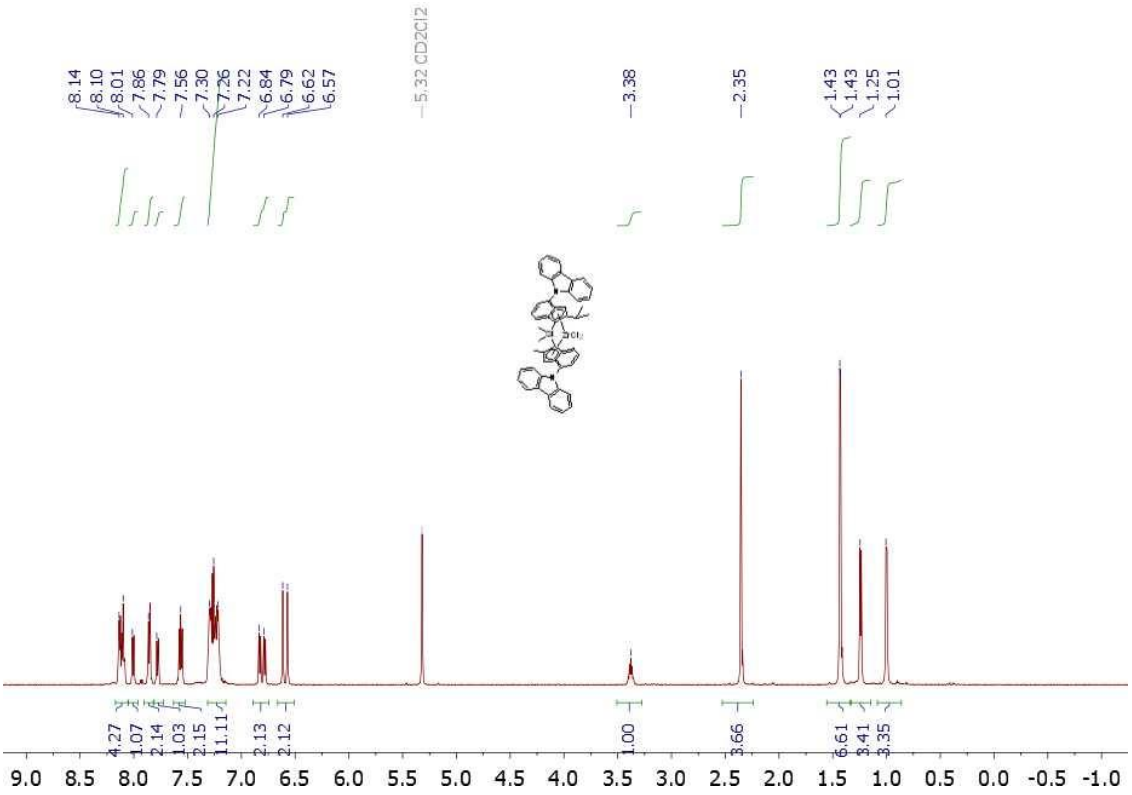

Figure S7. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C3**.

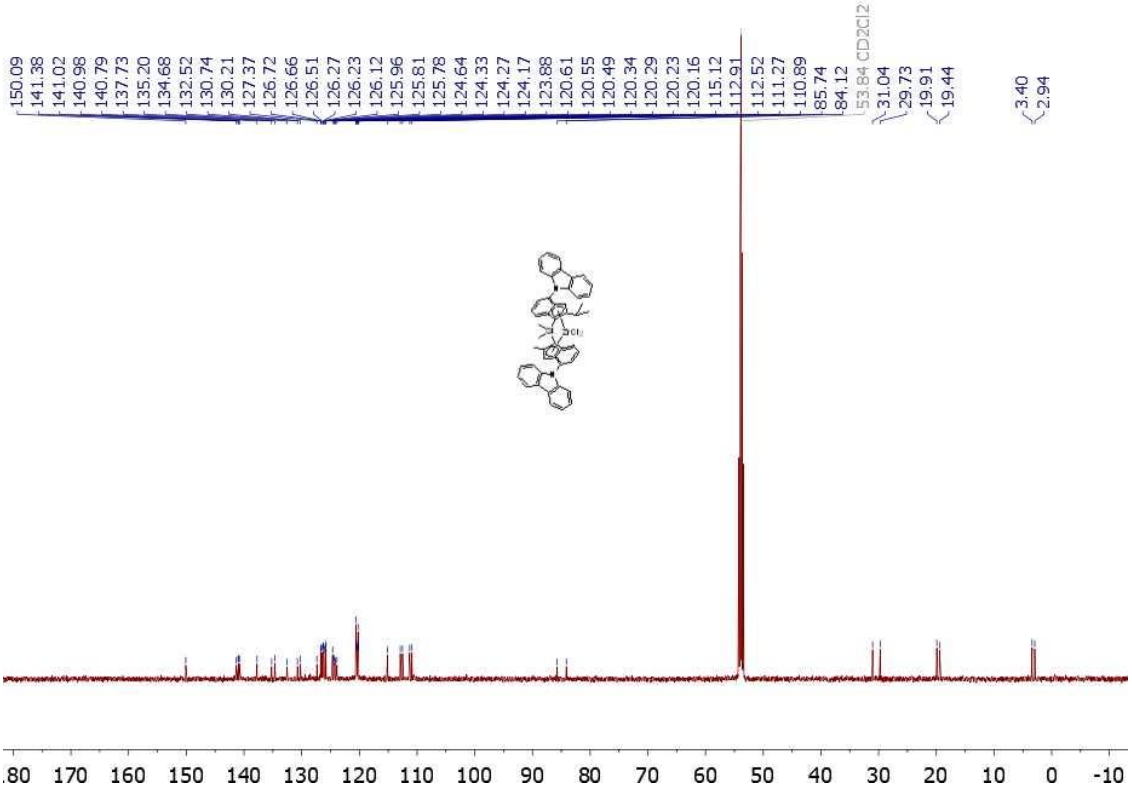

Figure S8. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C3**.

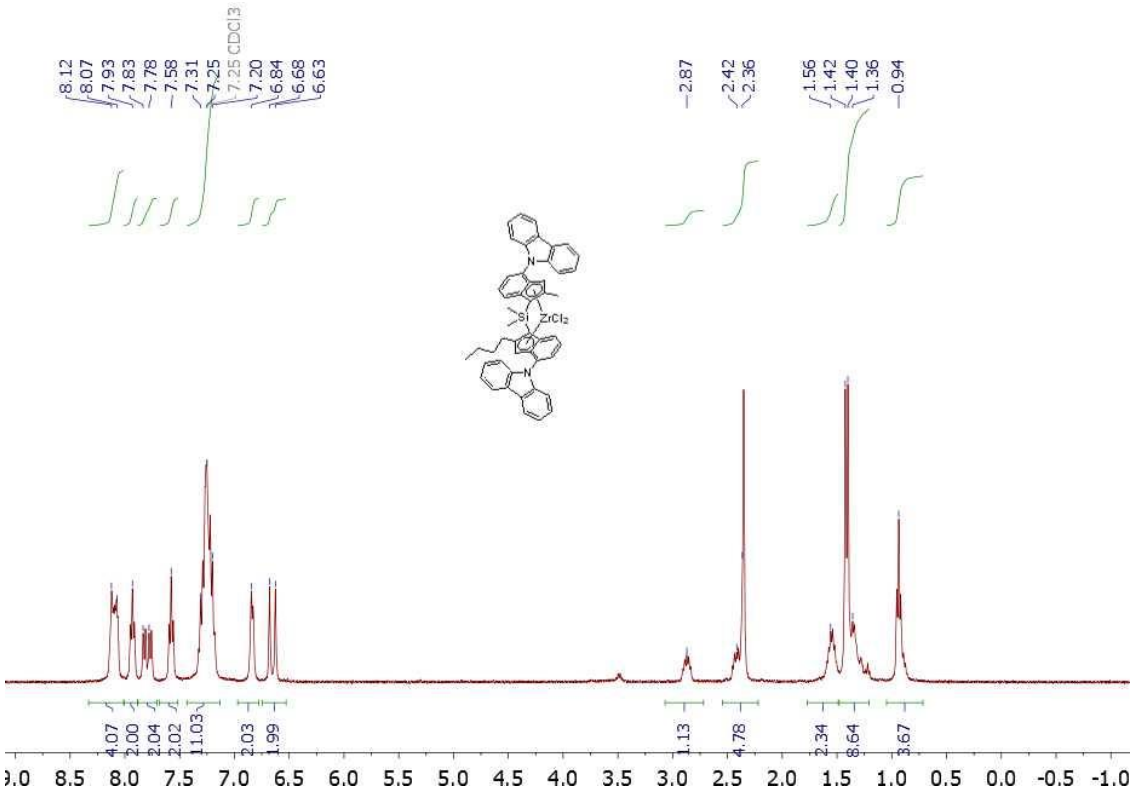

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C4**.

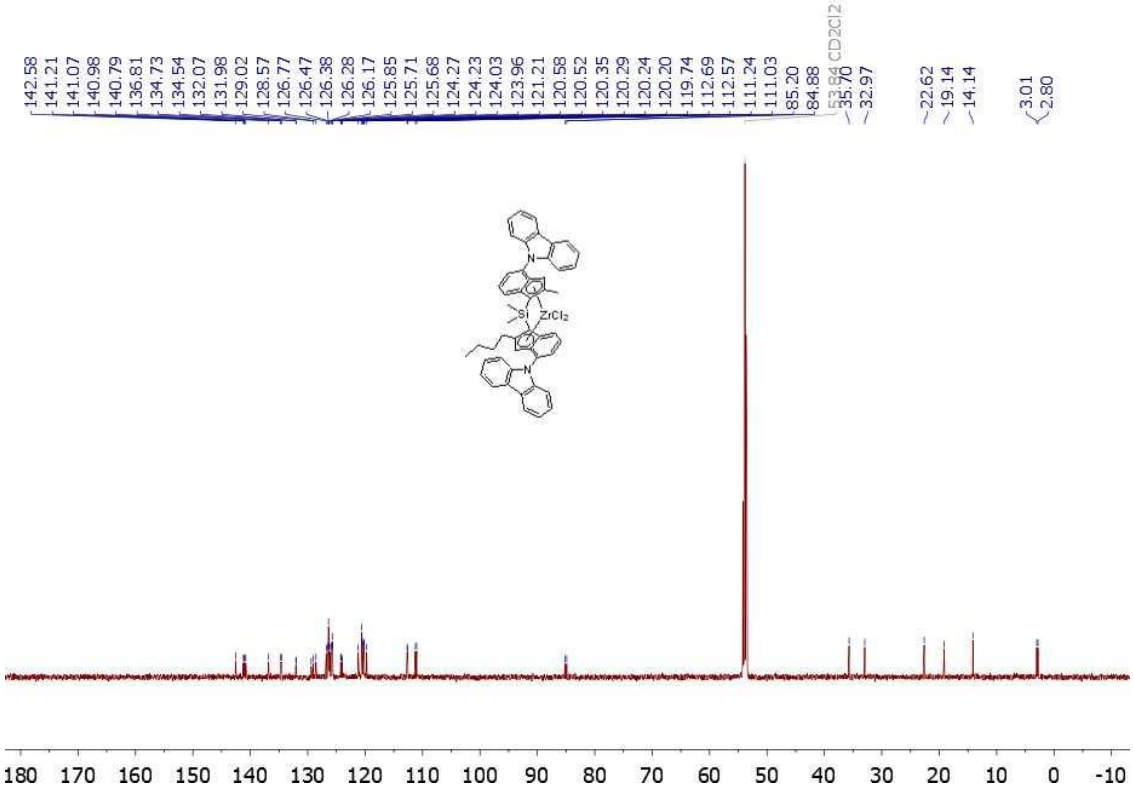

Figure S10. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C4**.

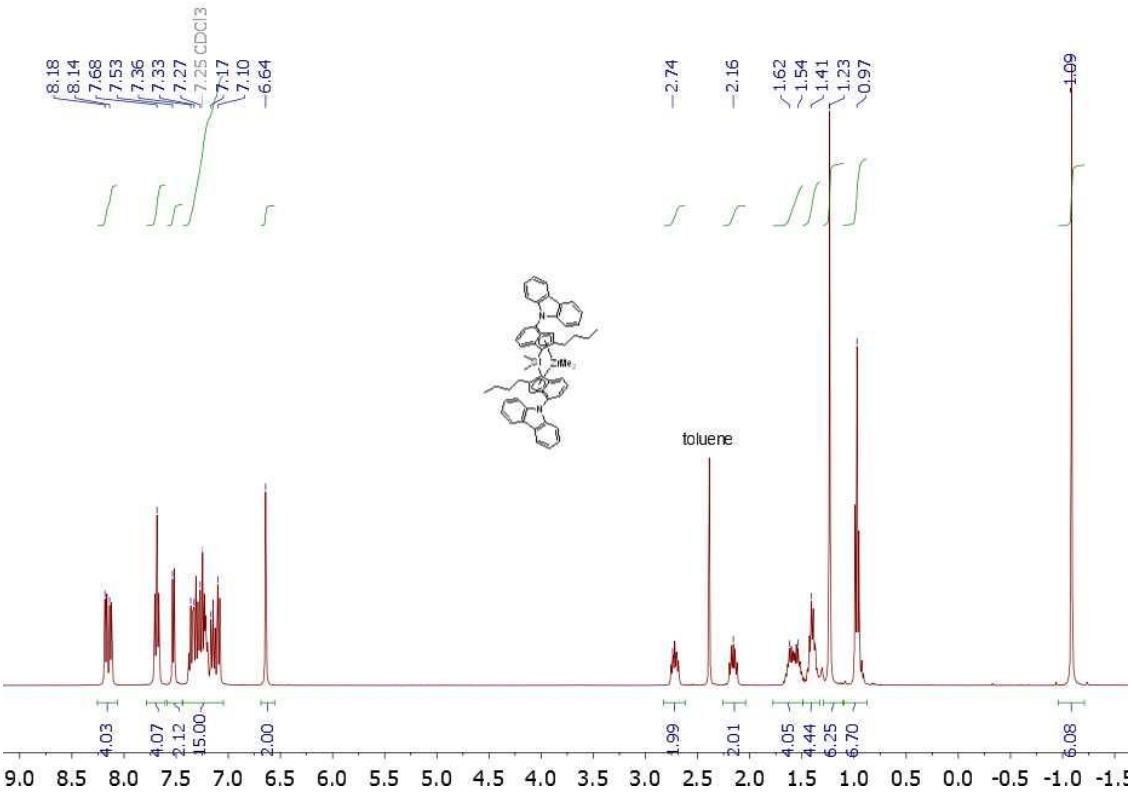

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **M5**.

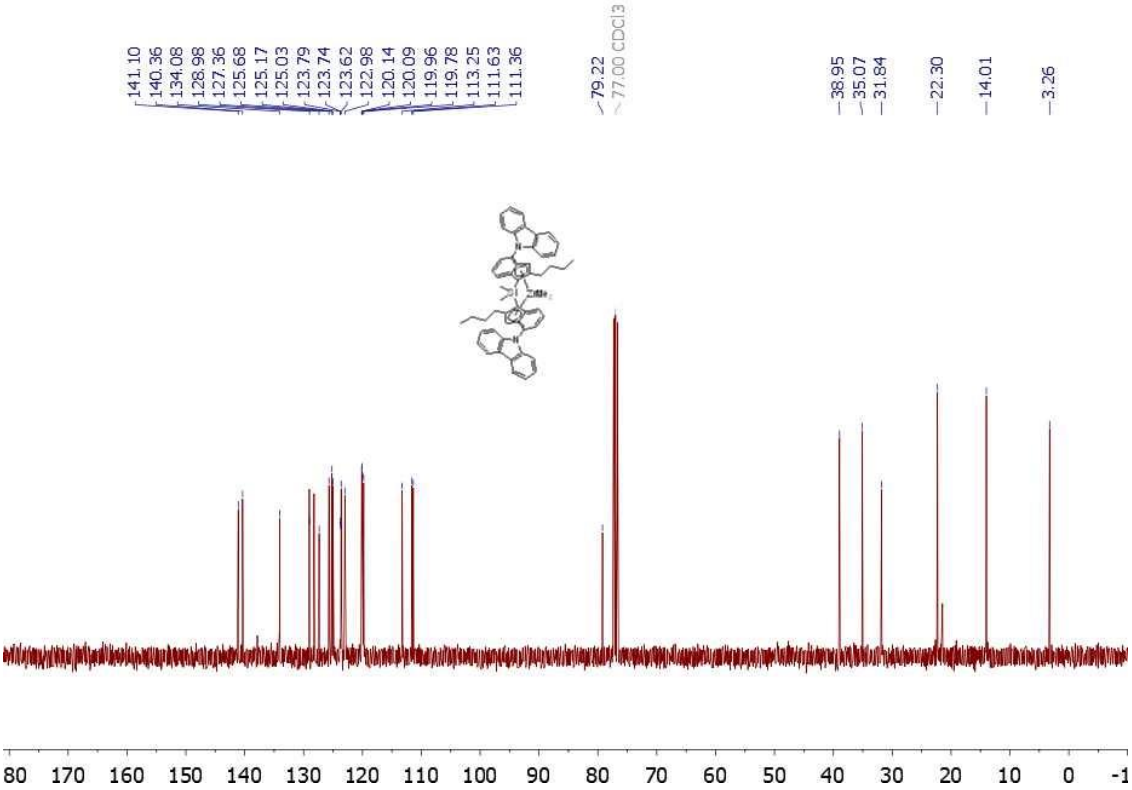

Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **M5**.

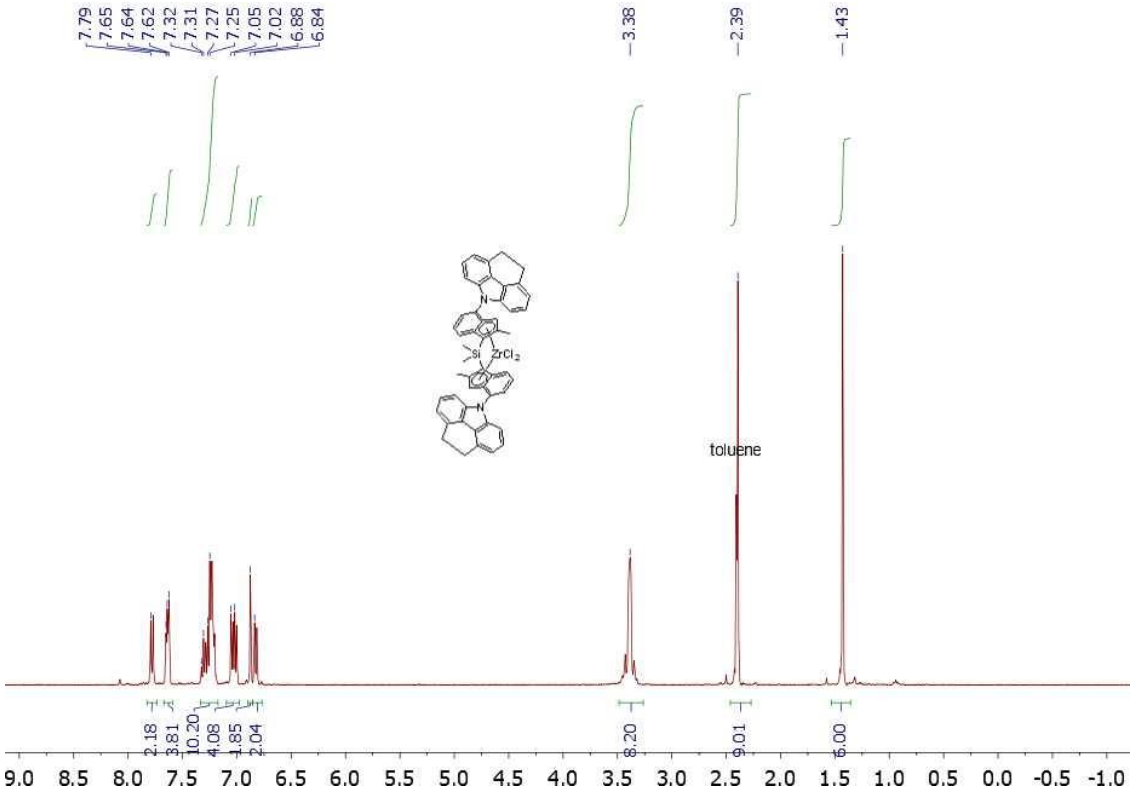

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C6**.

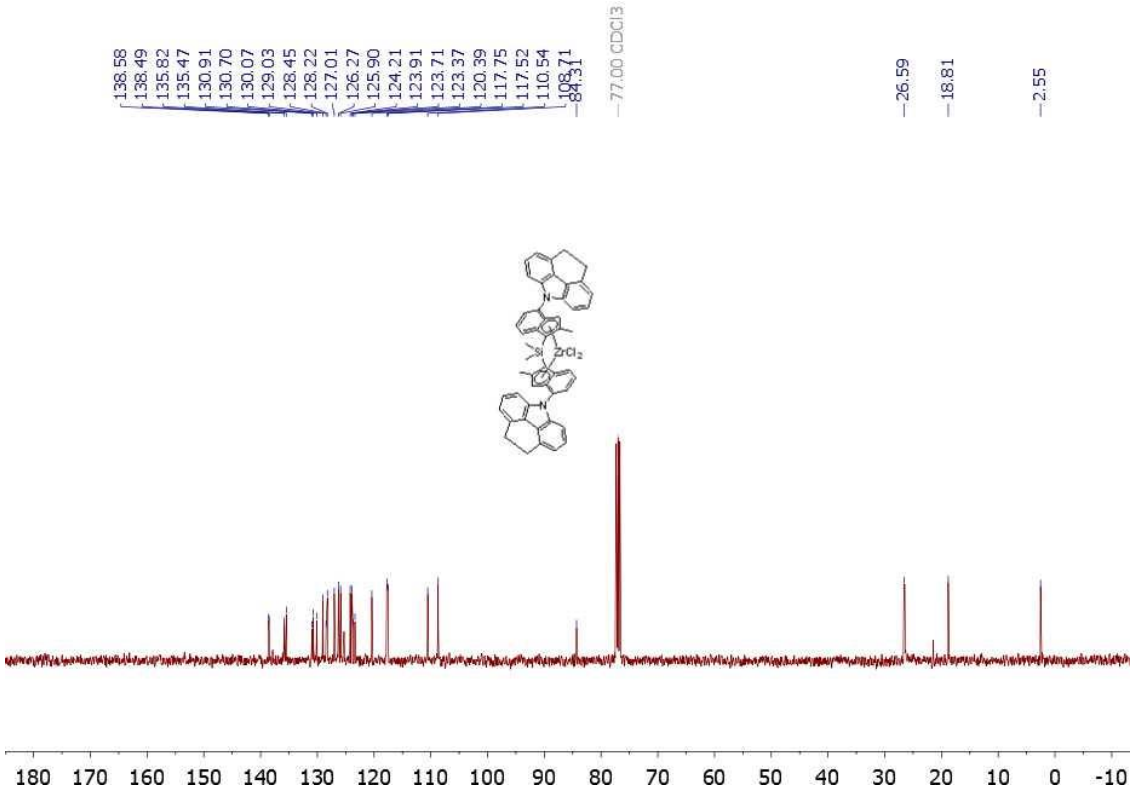

Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C6**.

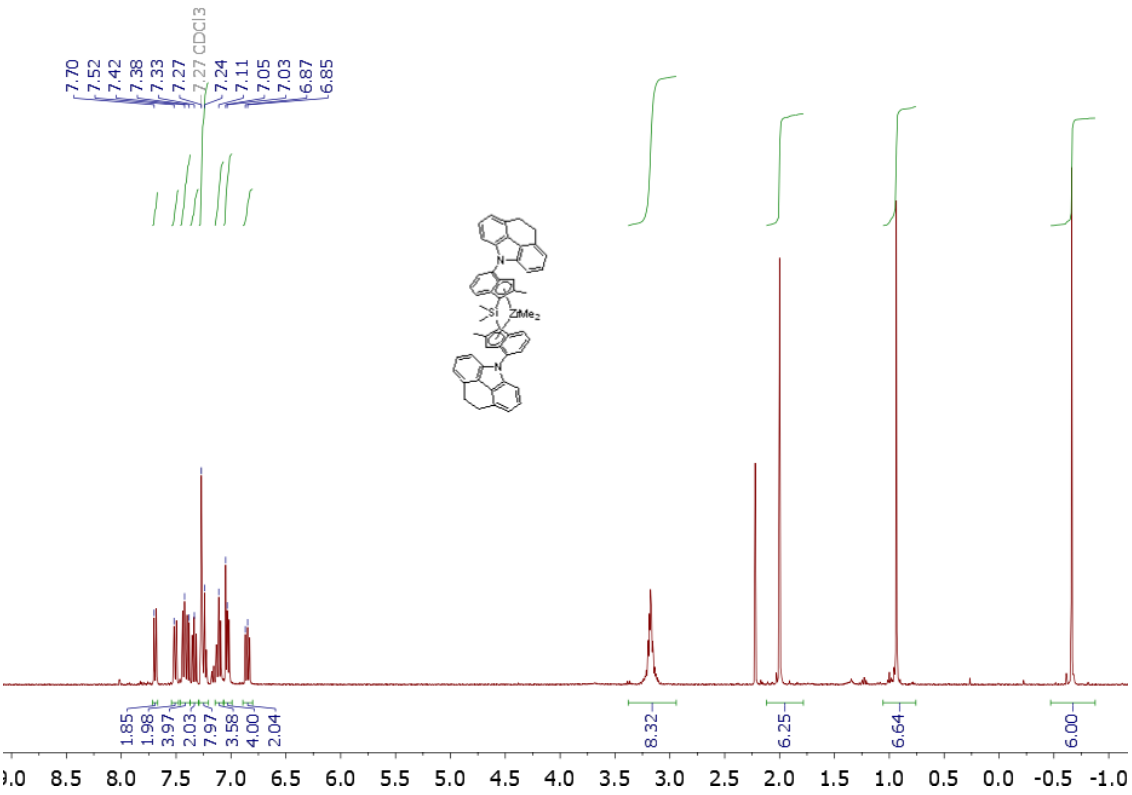

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **M6**.

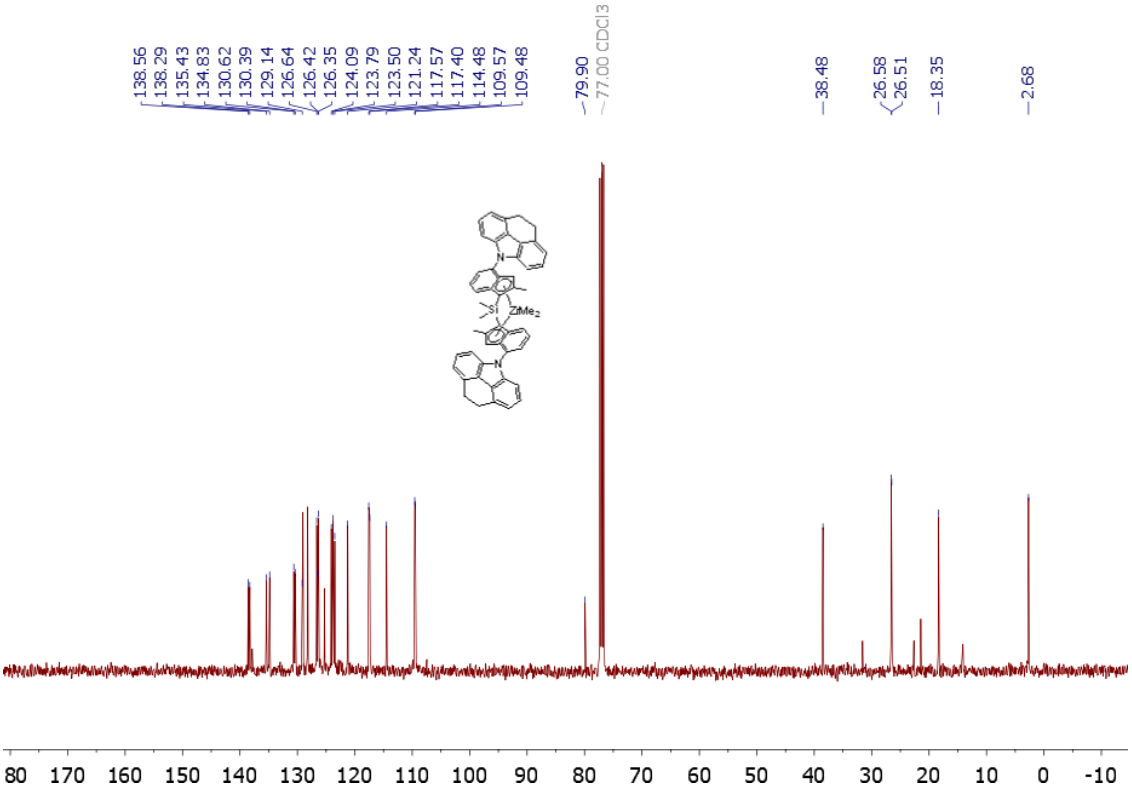

Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **M6**.

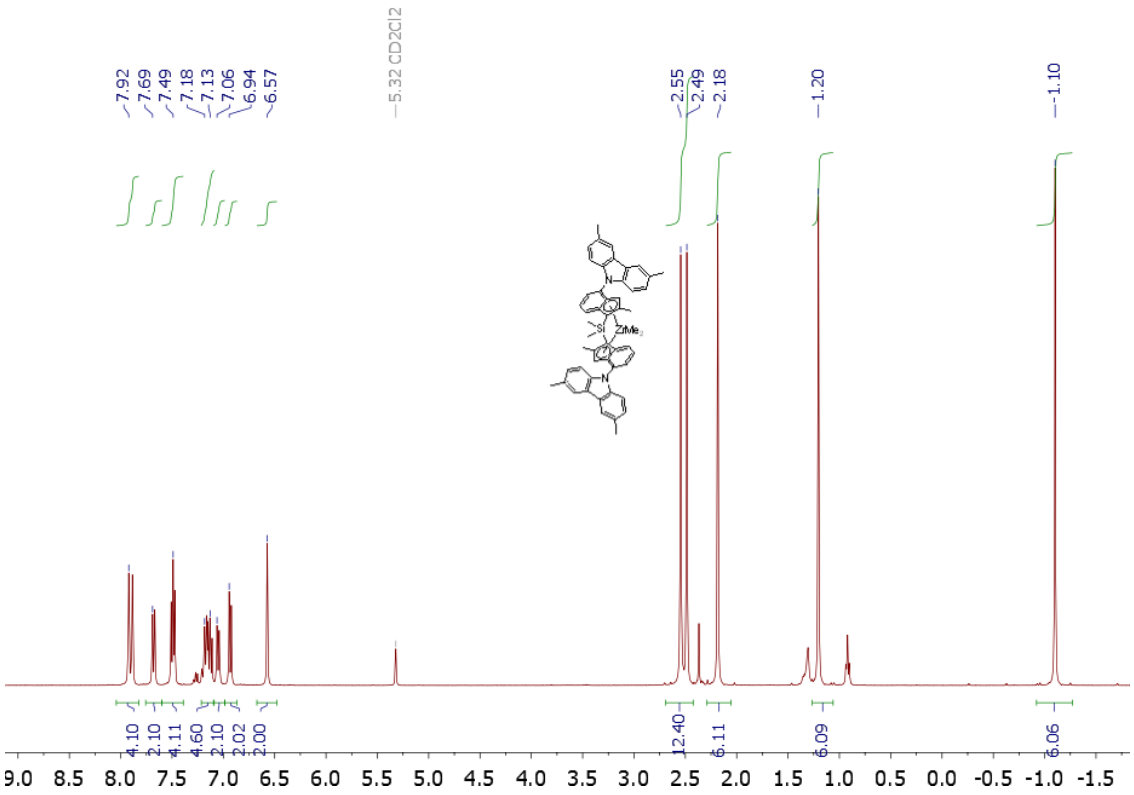

Figure S17. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **M7**.

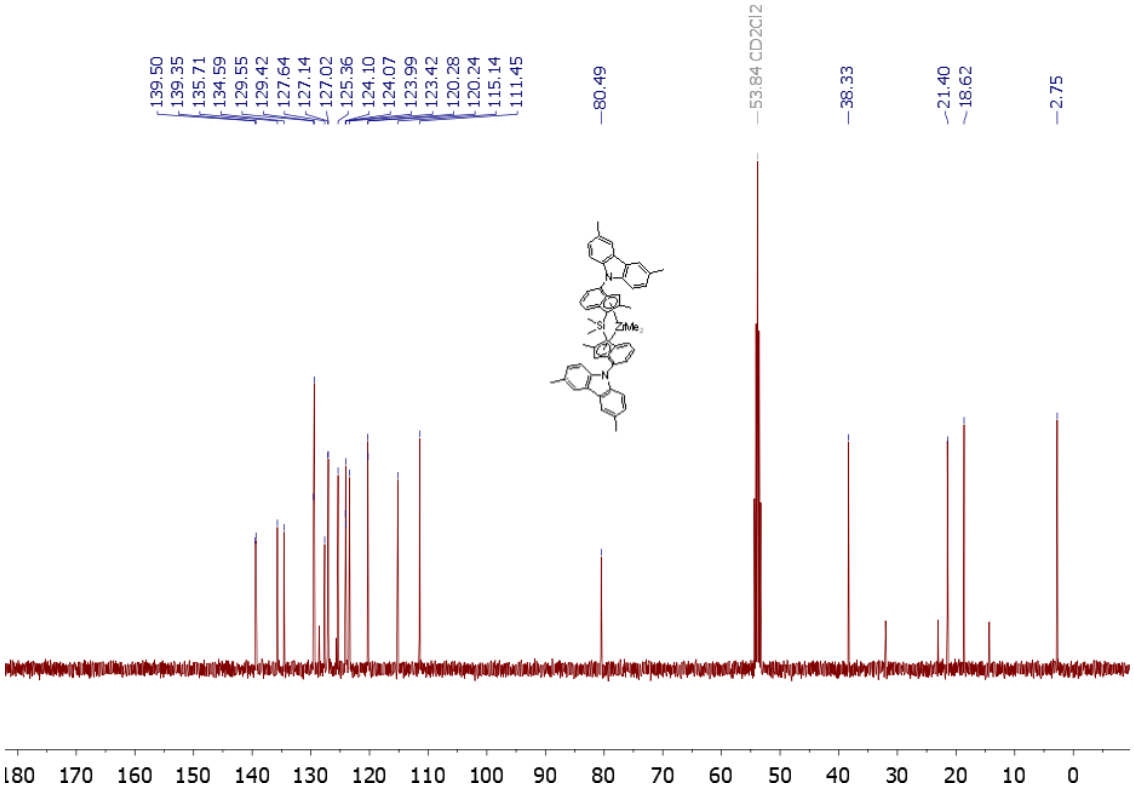

Figure S18. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M7**.

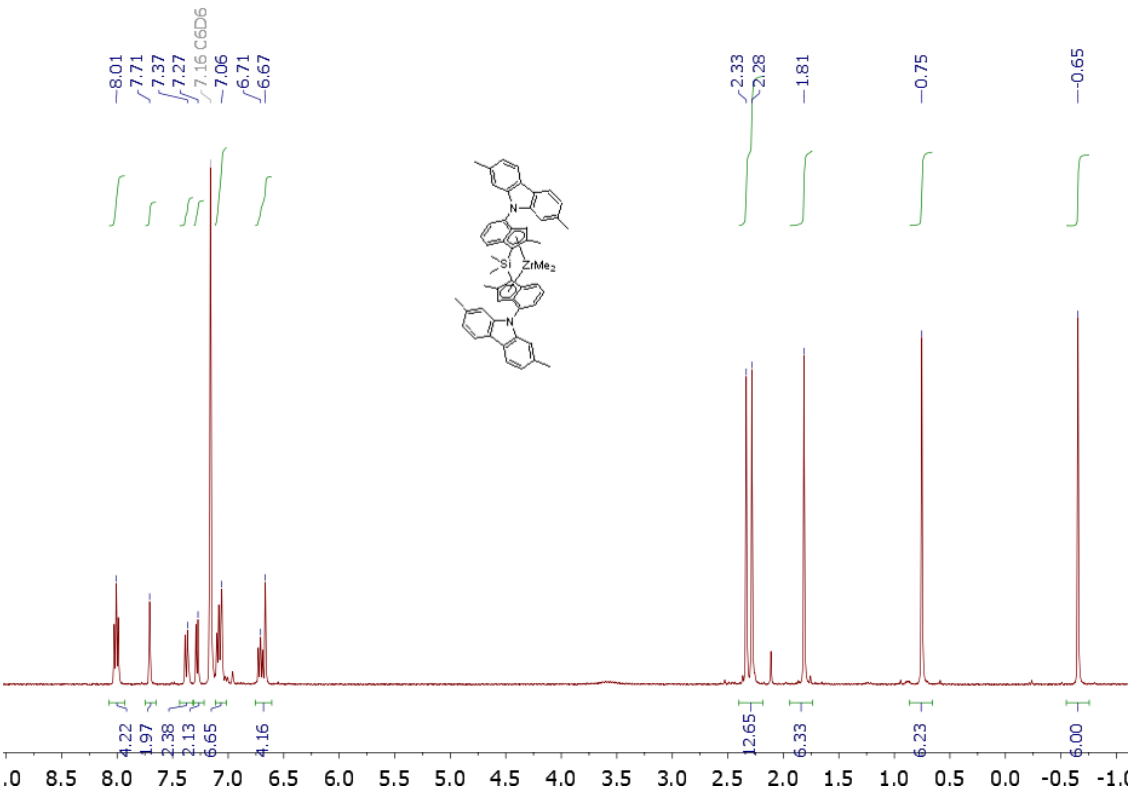

Figure S19. ^{1}H NMR (400 MHz, C_6D_6) spectrum of complex **M8**.

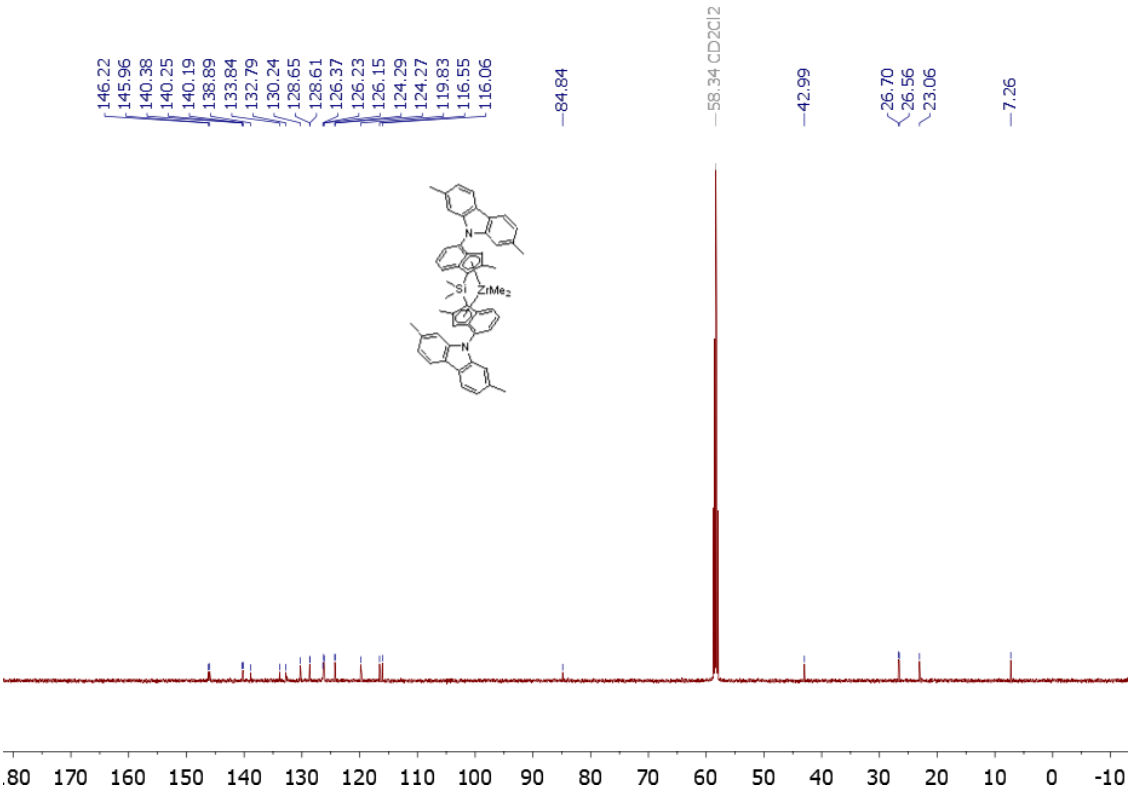

Figure S20. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M8**.

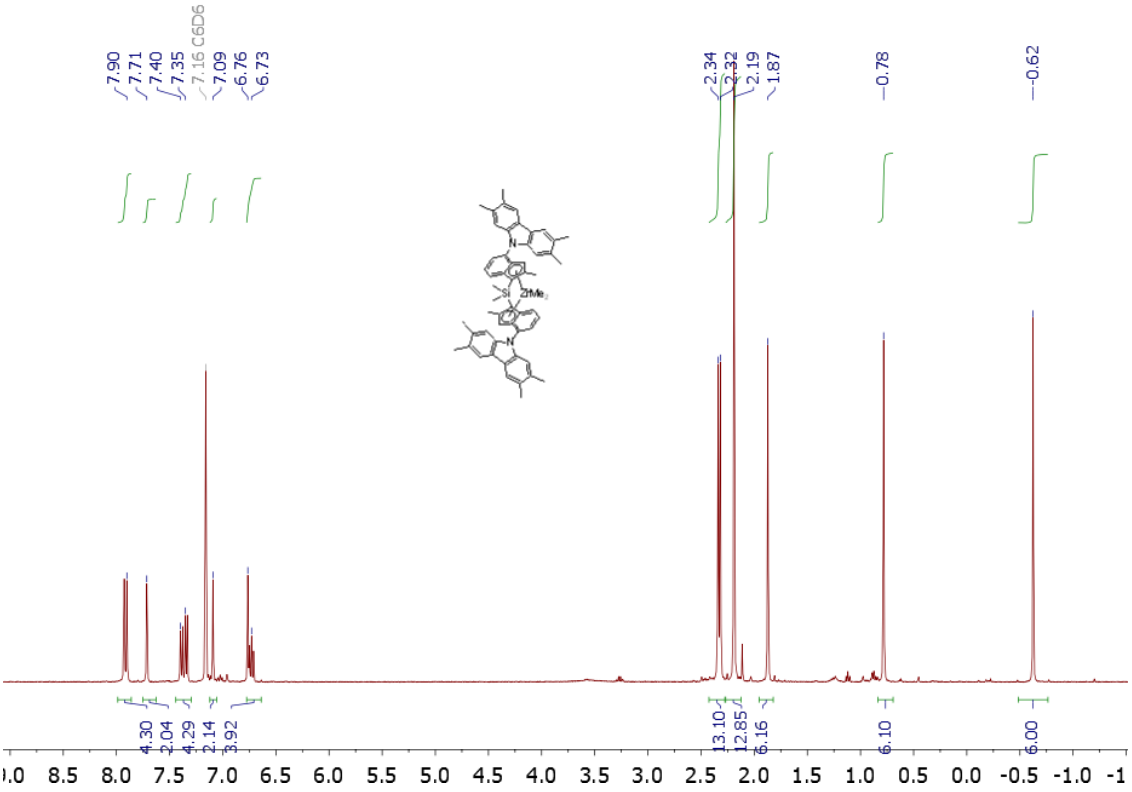

Figure S21. ^{1}H NMR (400 MHz, C_6D_6) spectrum of complex **M9**.

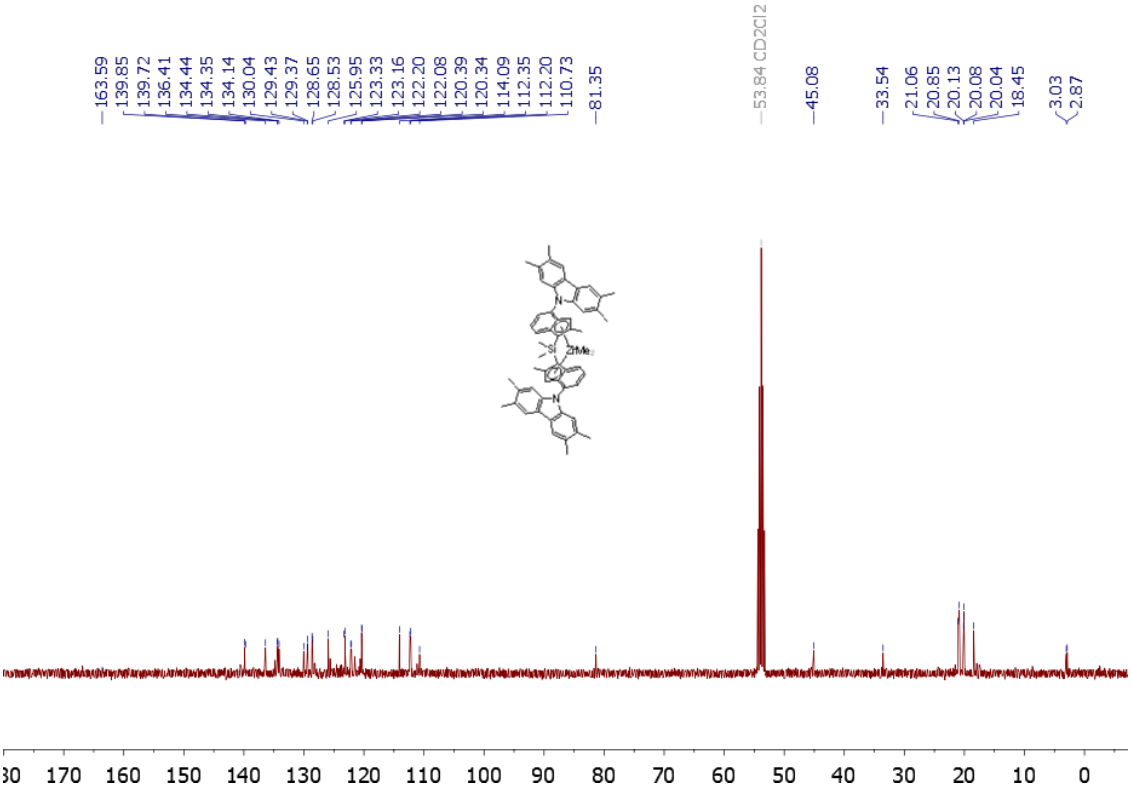

Figure S22. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M9**.

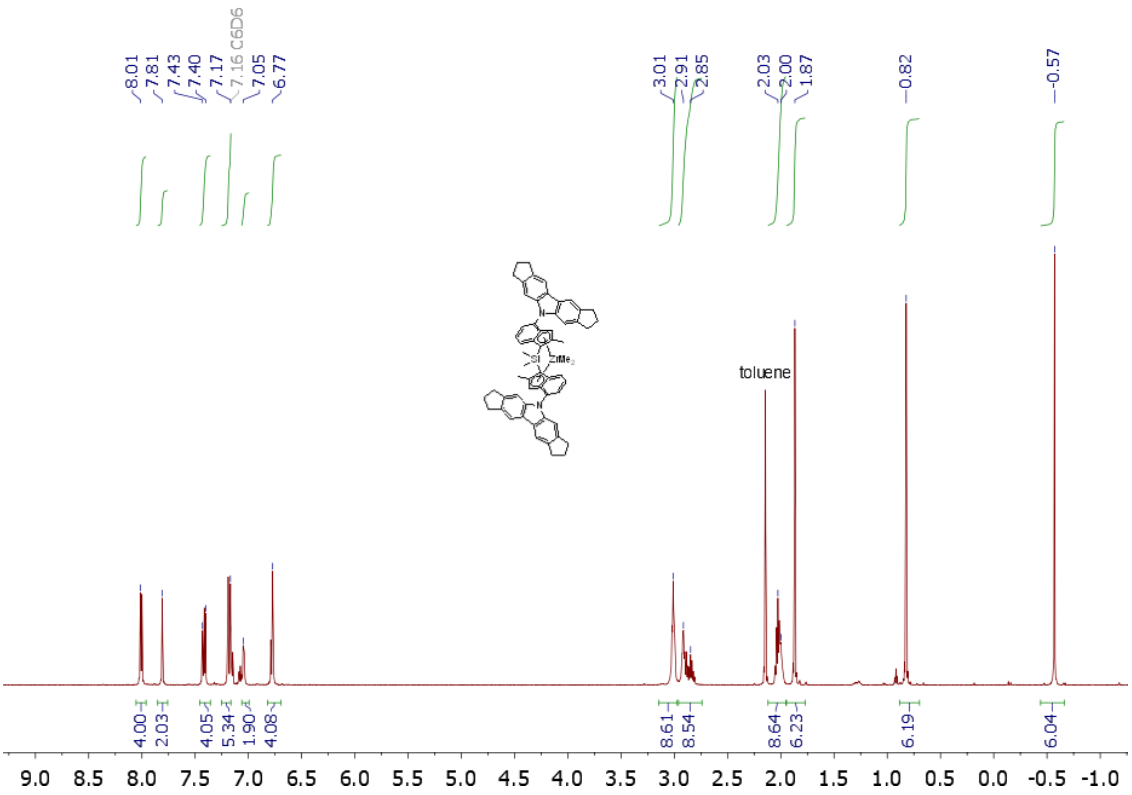

Figure S23. ^{1}H NMR (400 MHz, C_6D_6) spectrum of complex **M10**.

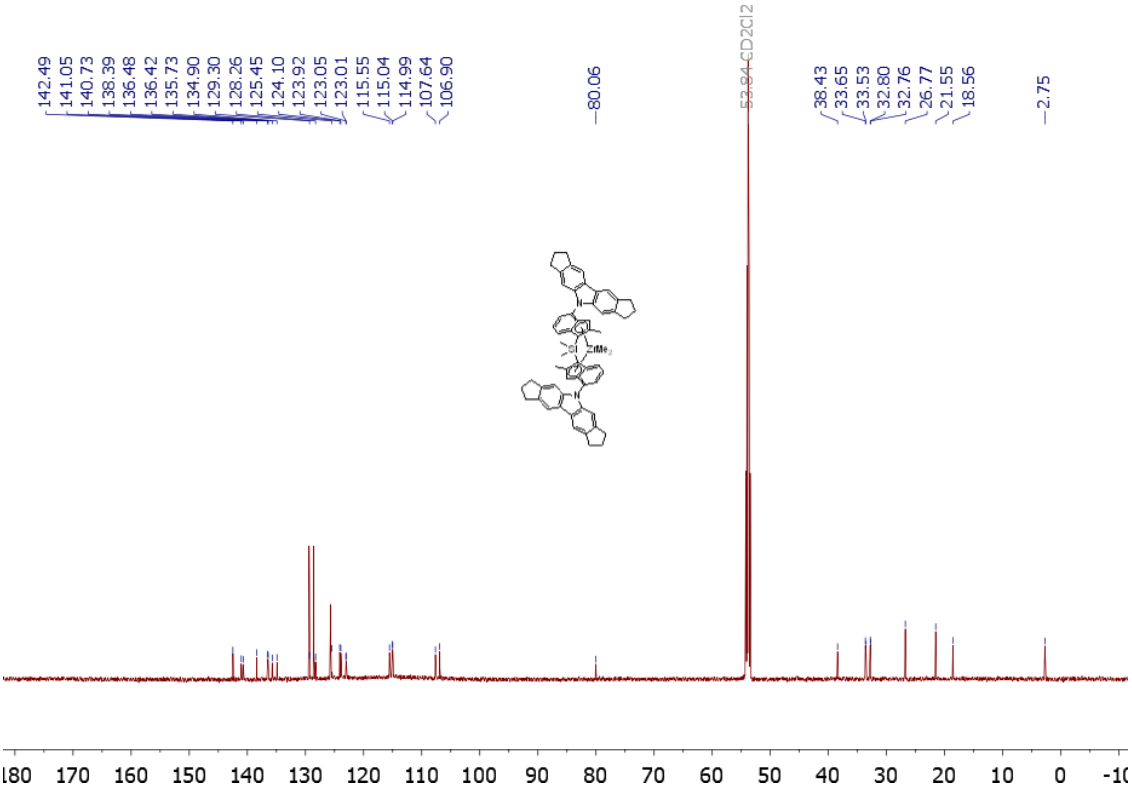

Figure S24. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M10**.

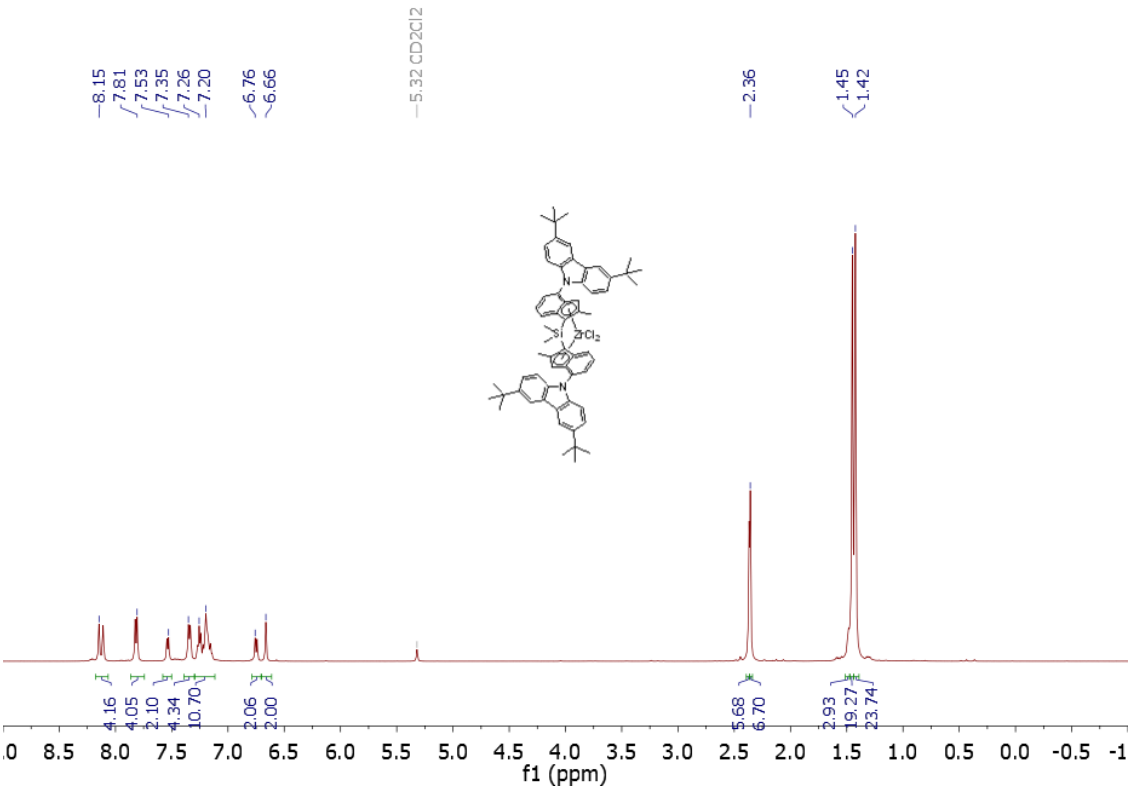

Figure S25. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C11**.

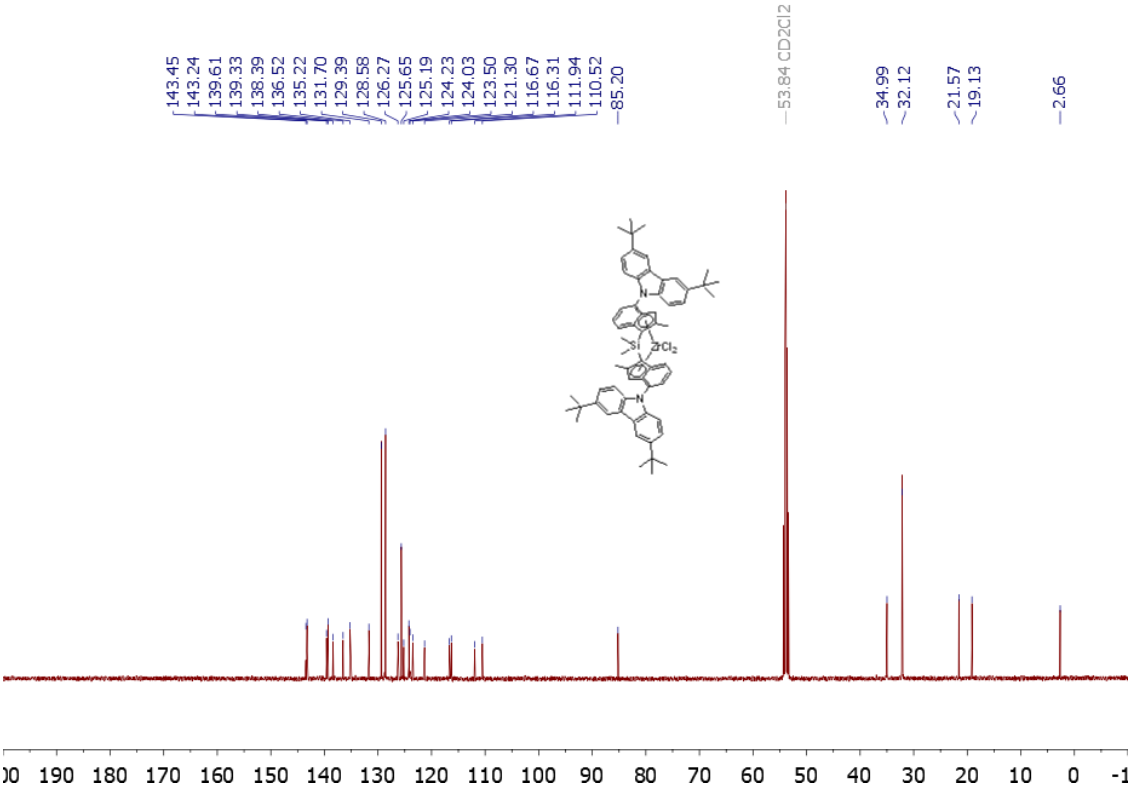

Figure S26. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C11**.

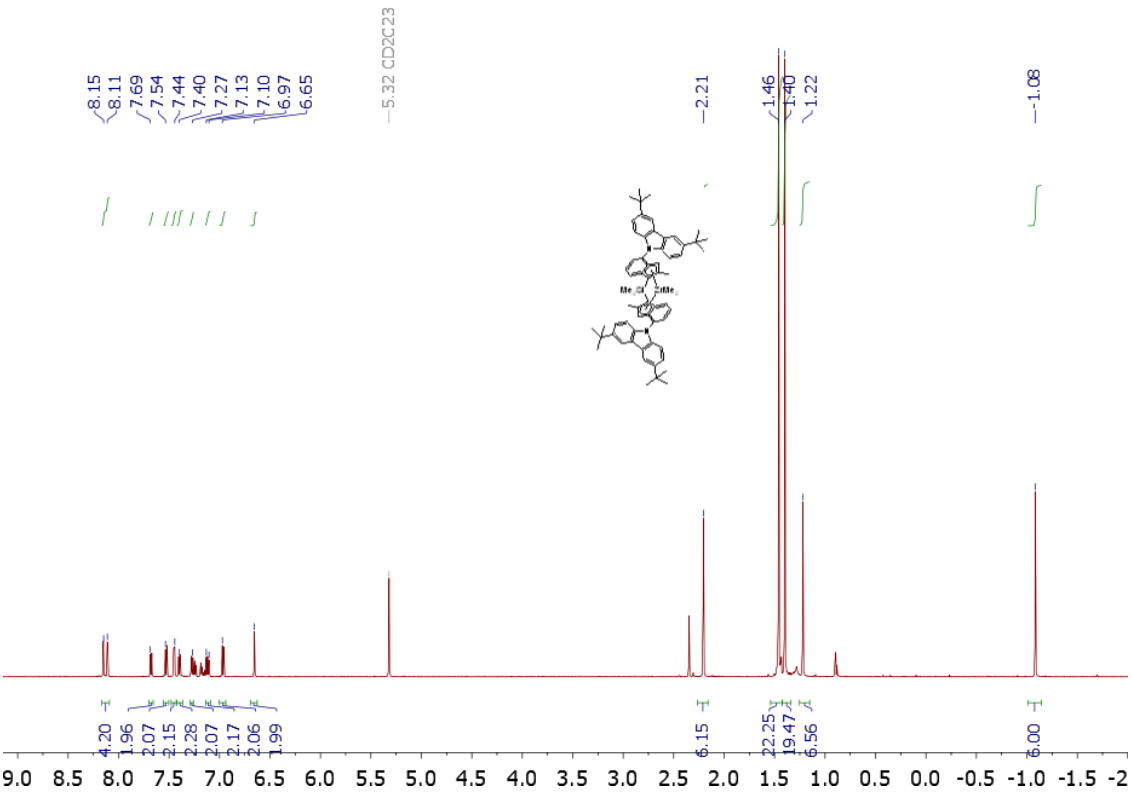

Figure S27. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **M11**.

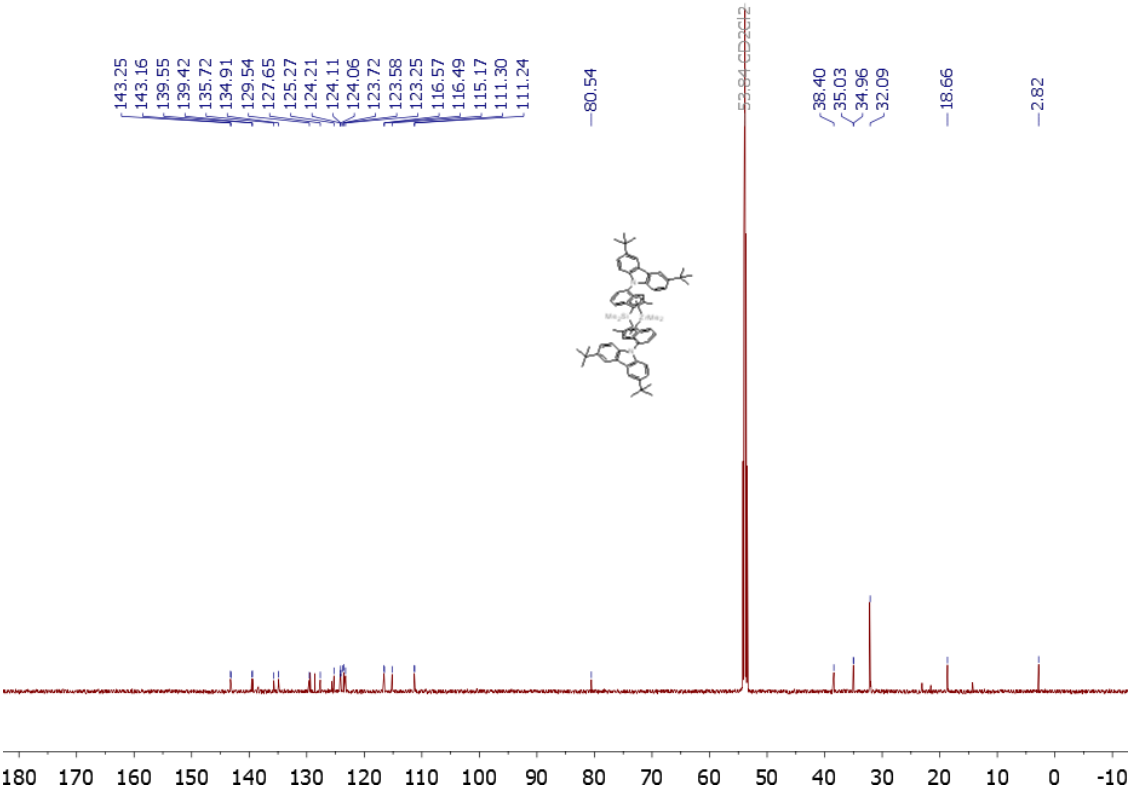

Figure S28. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M11**.

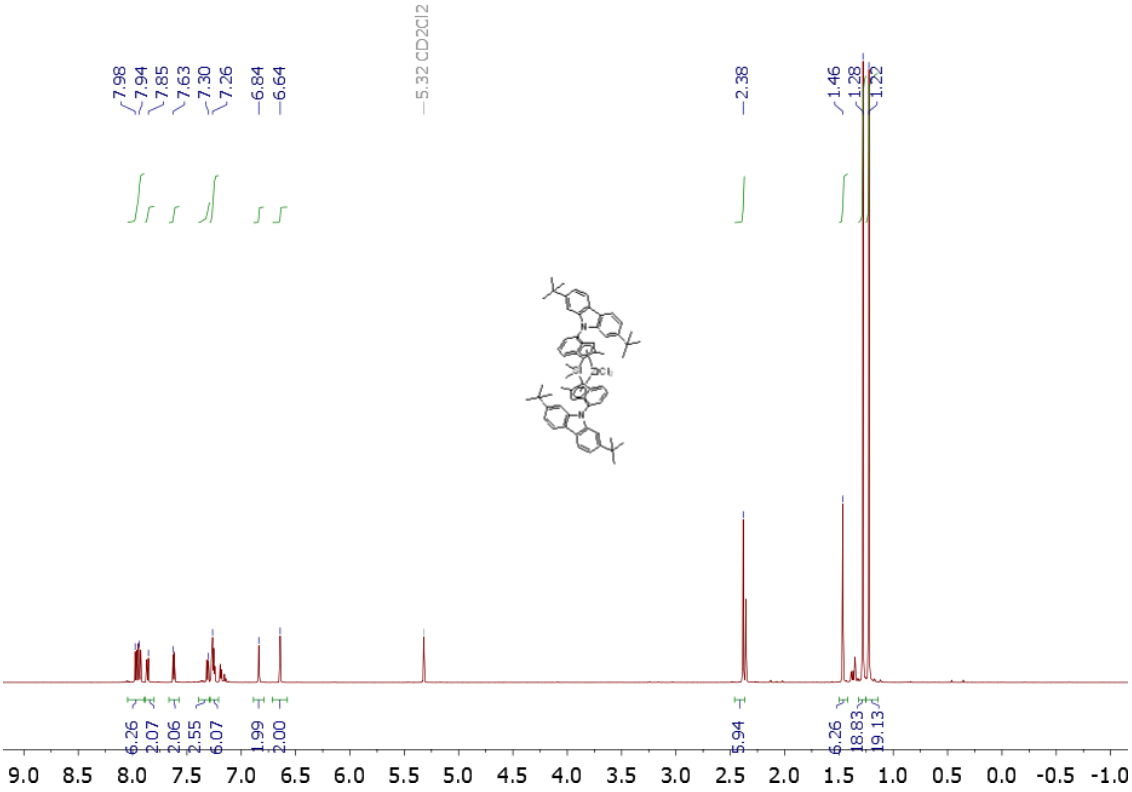

Figure S29. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C12**.

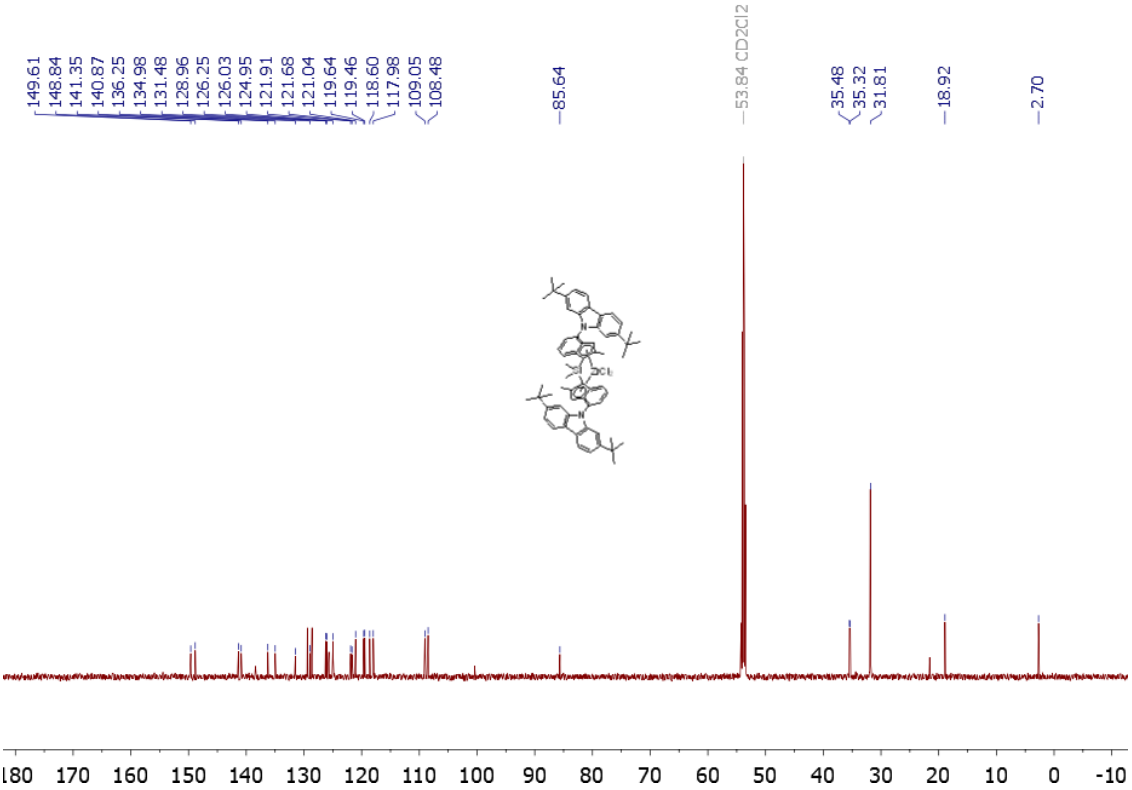

Figure S30. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C12**.

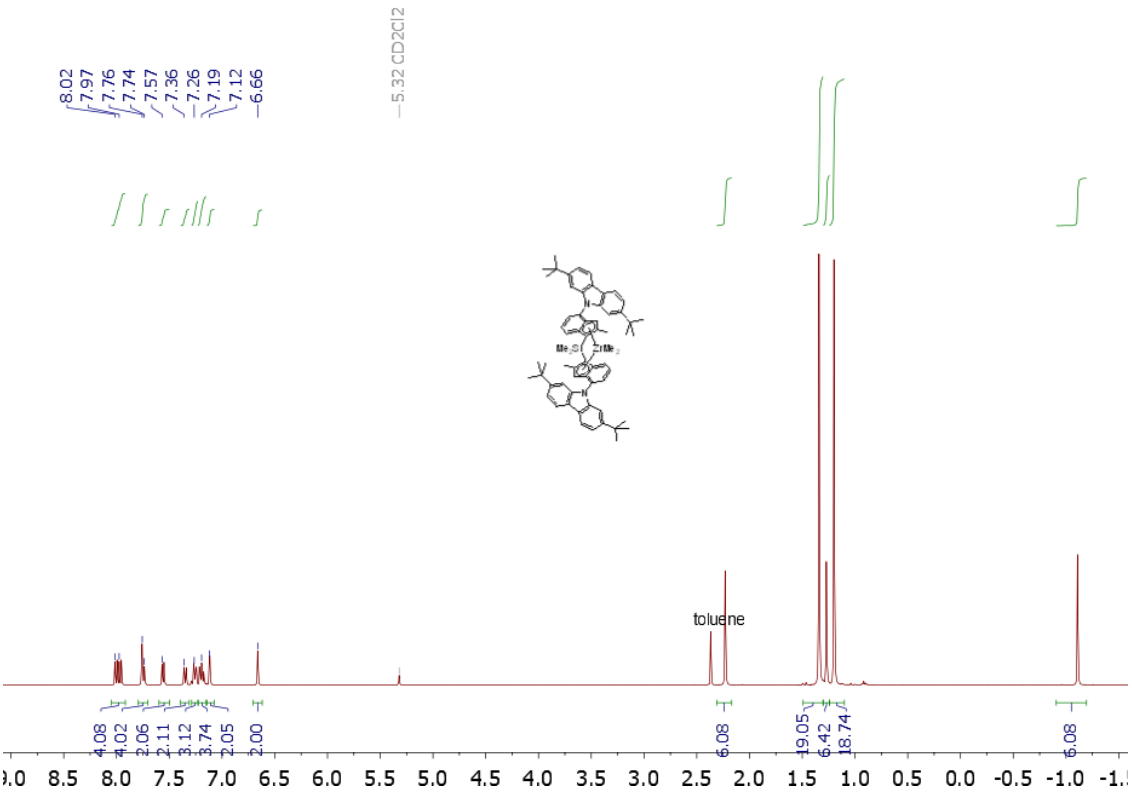

Figure S31. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **M12**.

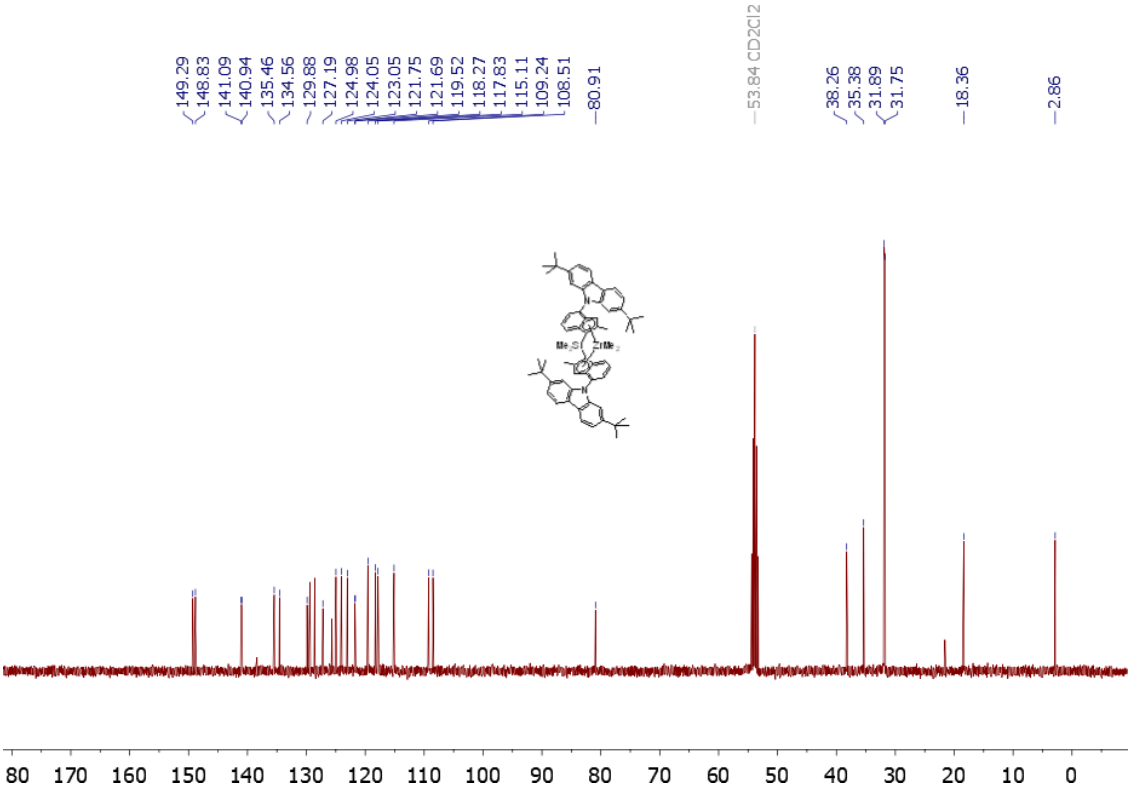

Figure S32. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M12**.

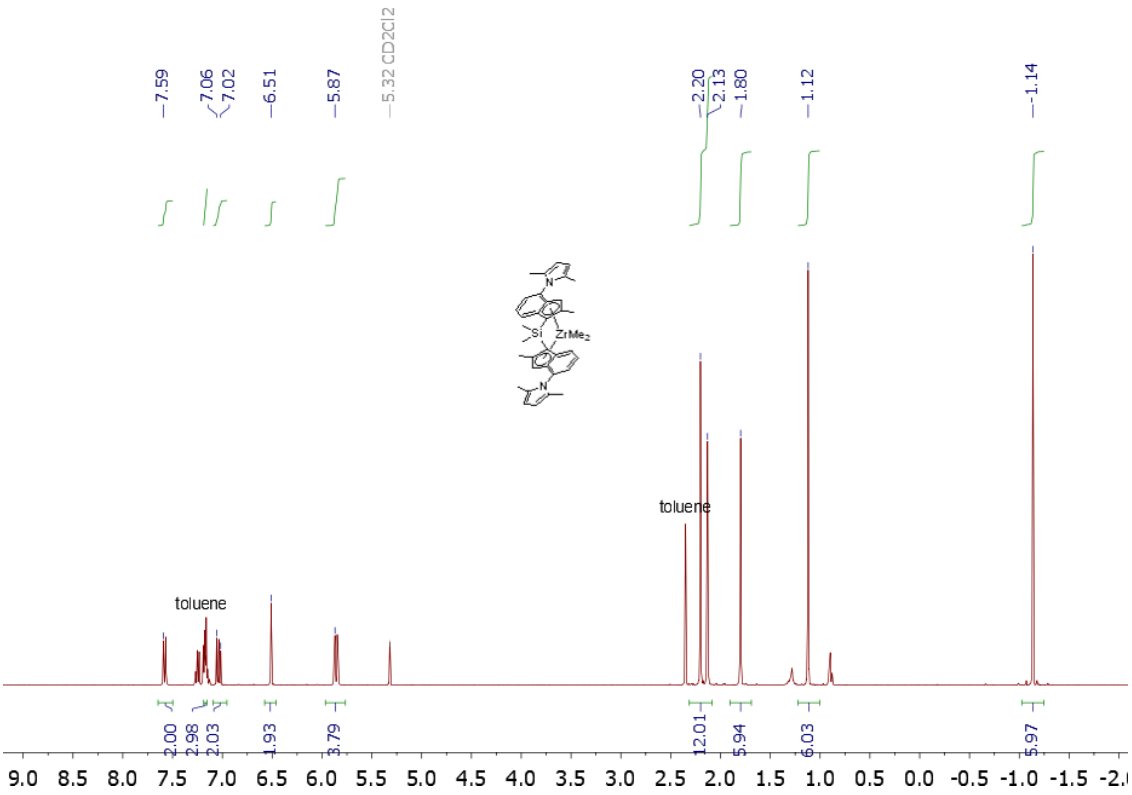

Figure S33. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **M13**.

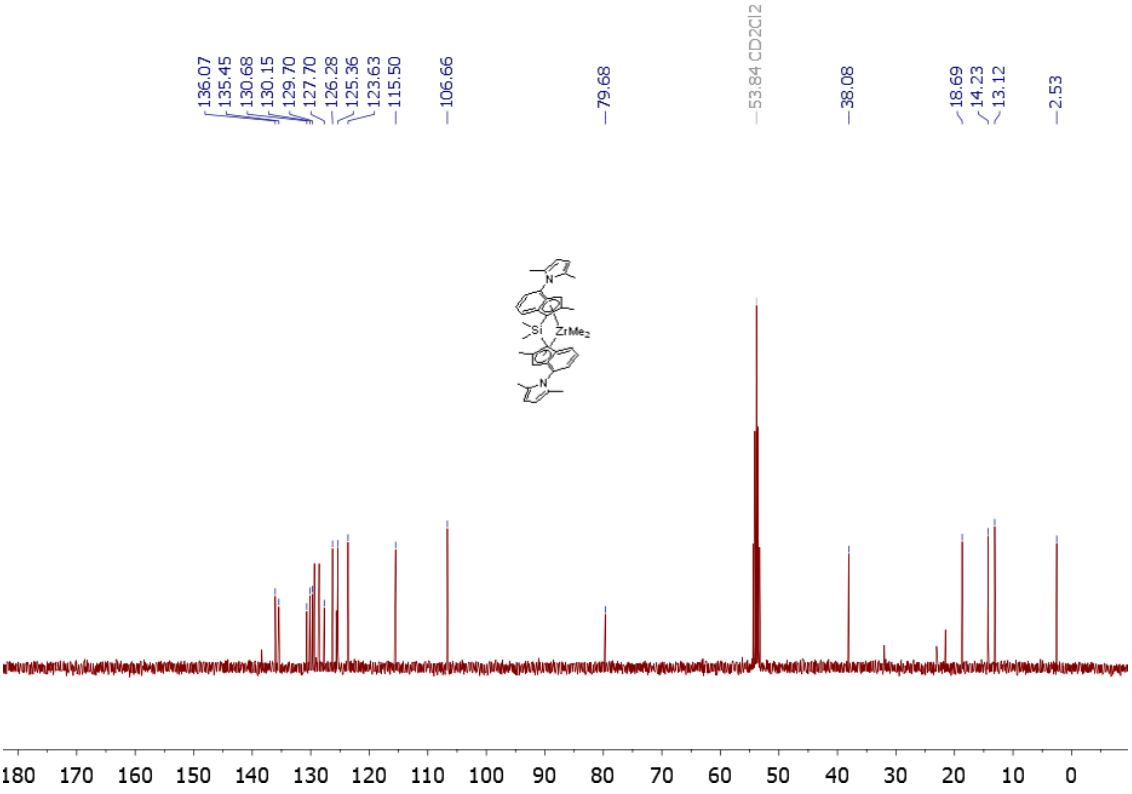

Figure S34. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **M13**.

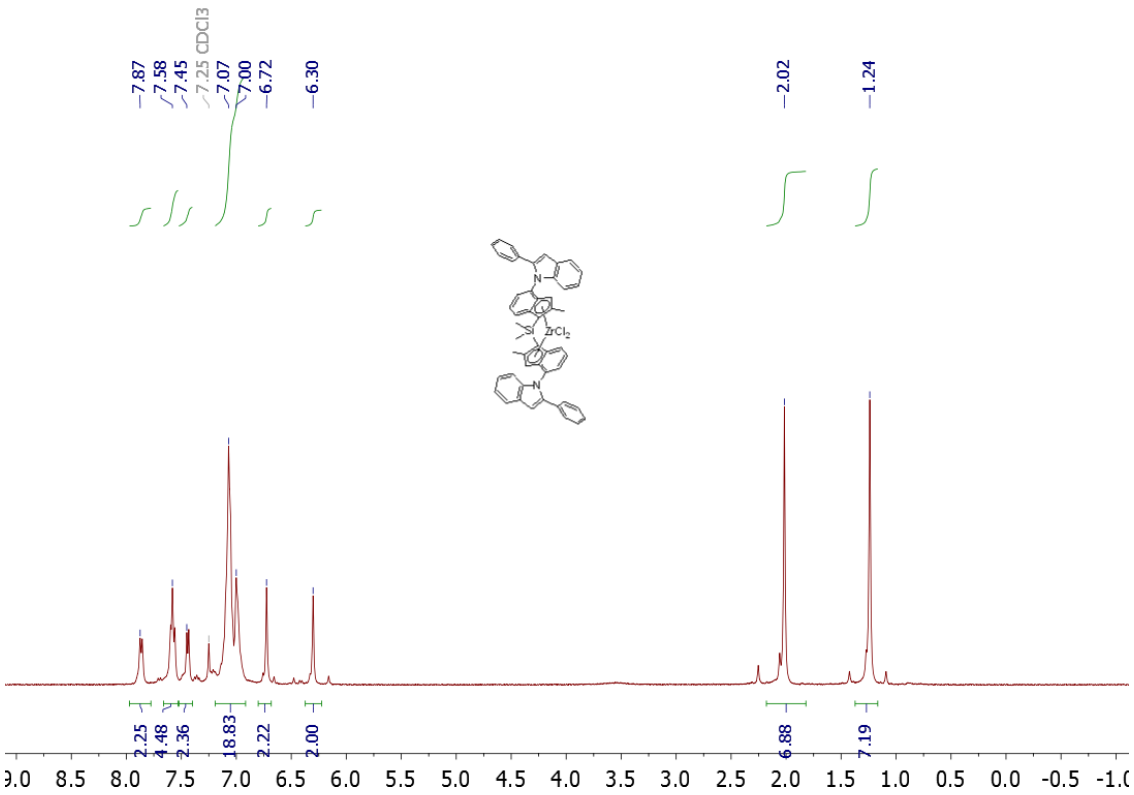

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C15**.

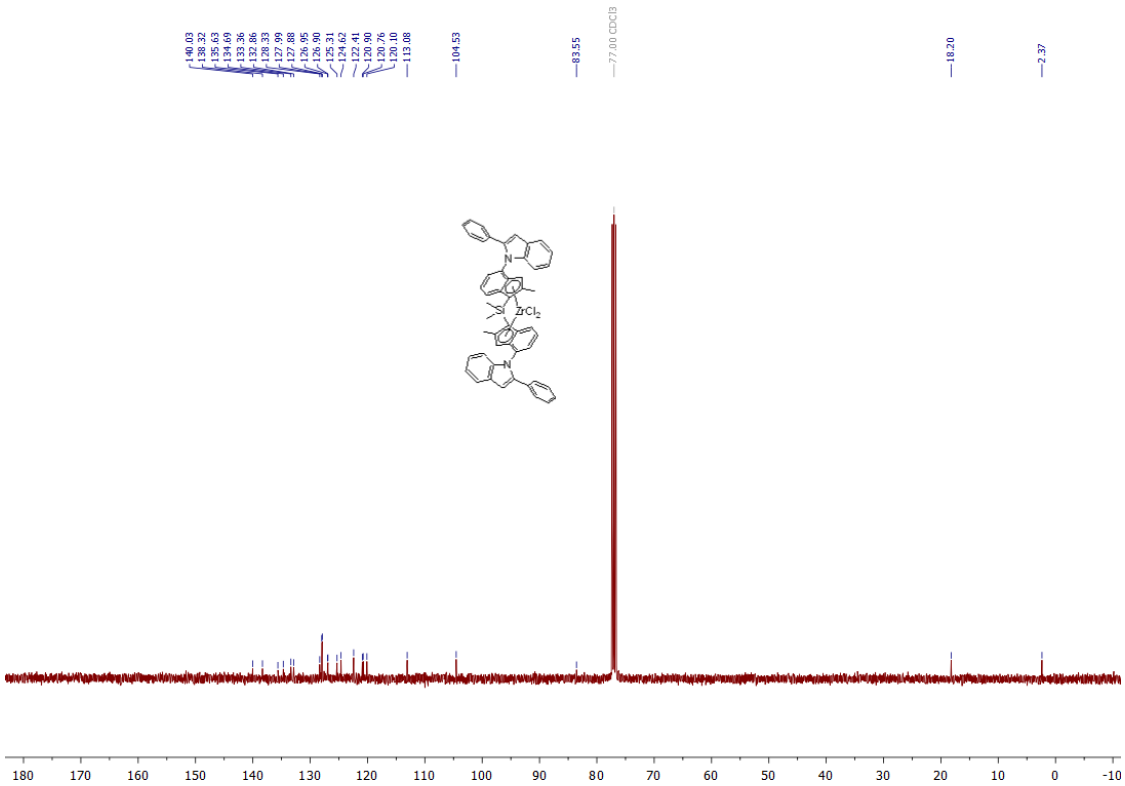

Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C15**.

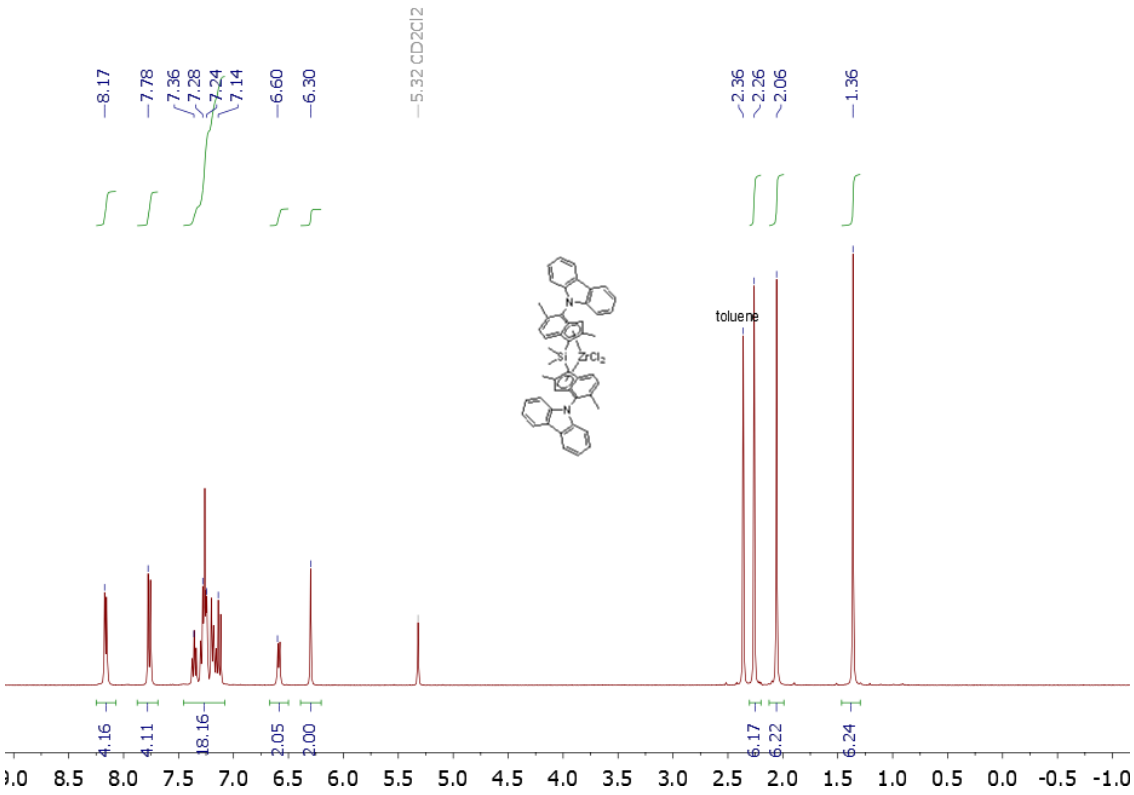

Figure S37. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C16**.

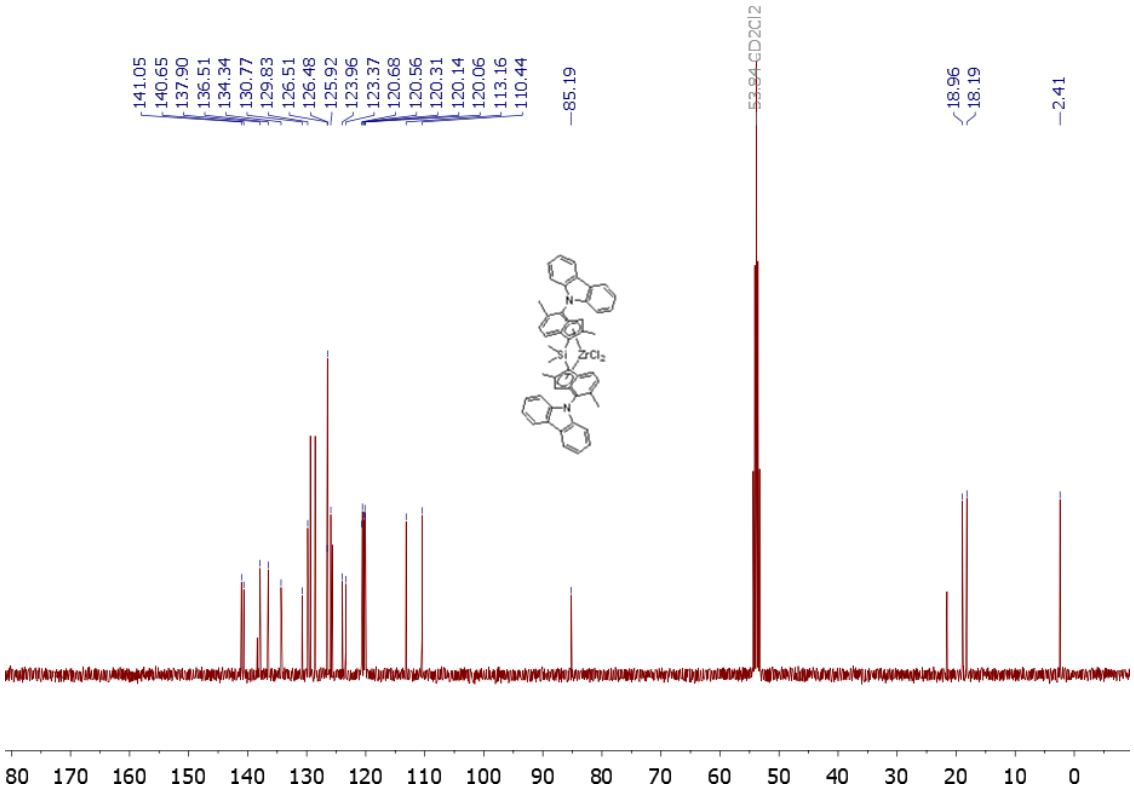

Figure S38. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C16**.

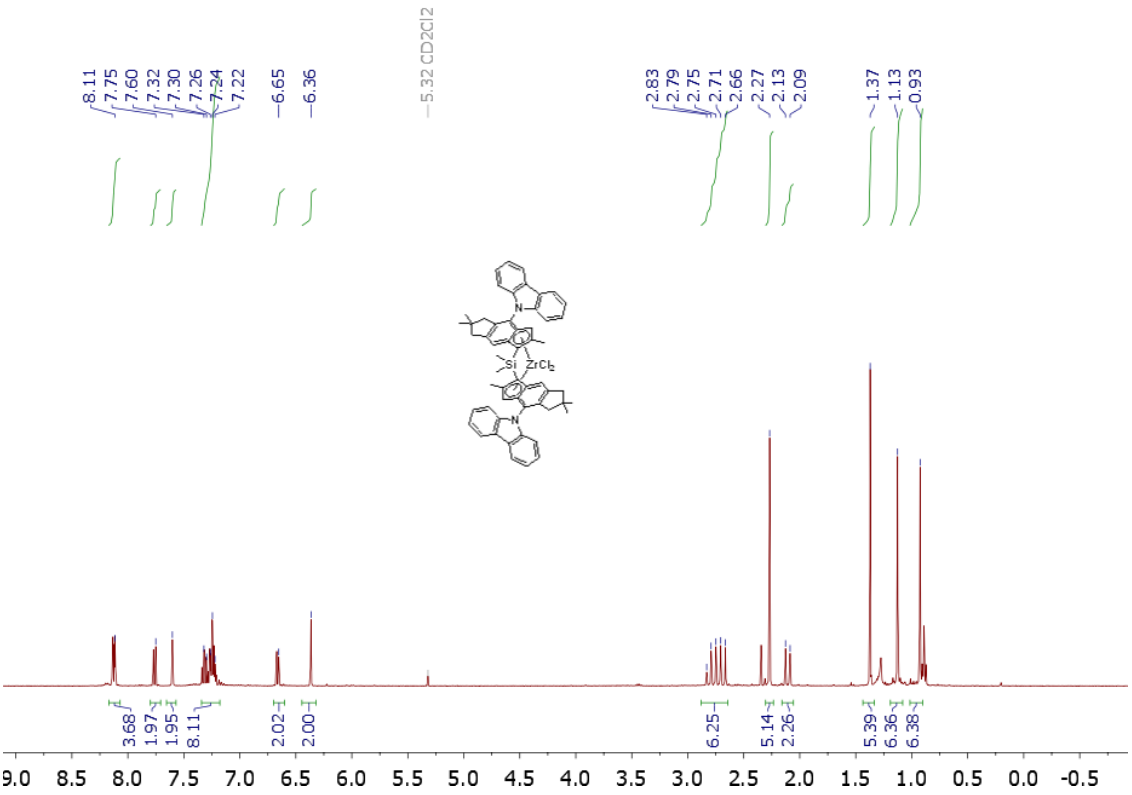

Figure S39. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C17**.

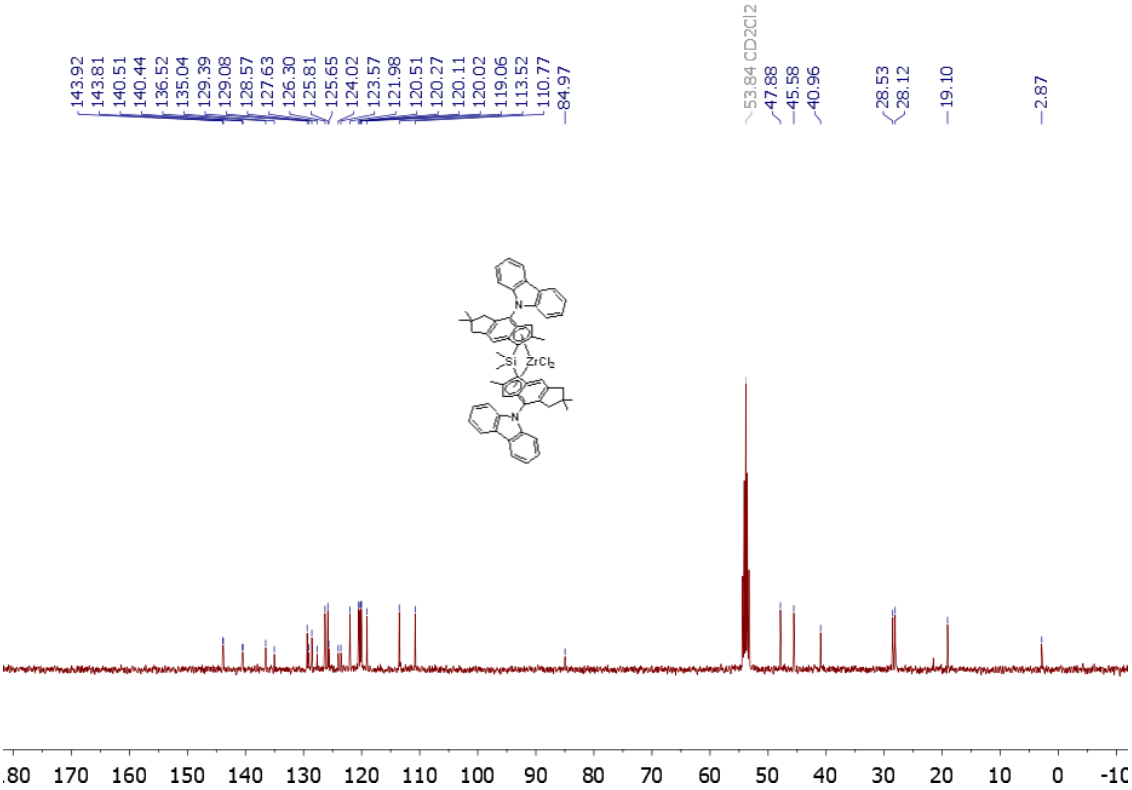

Figure S40. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C17**.

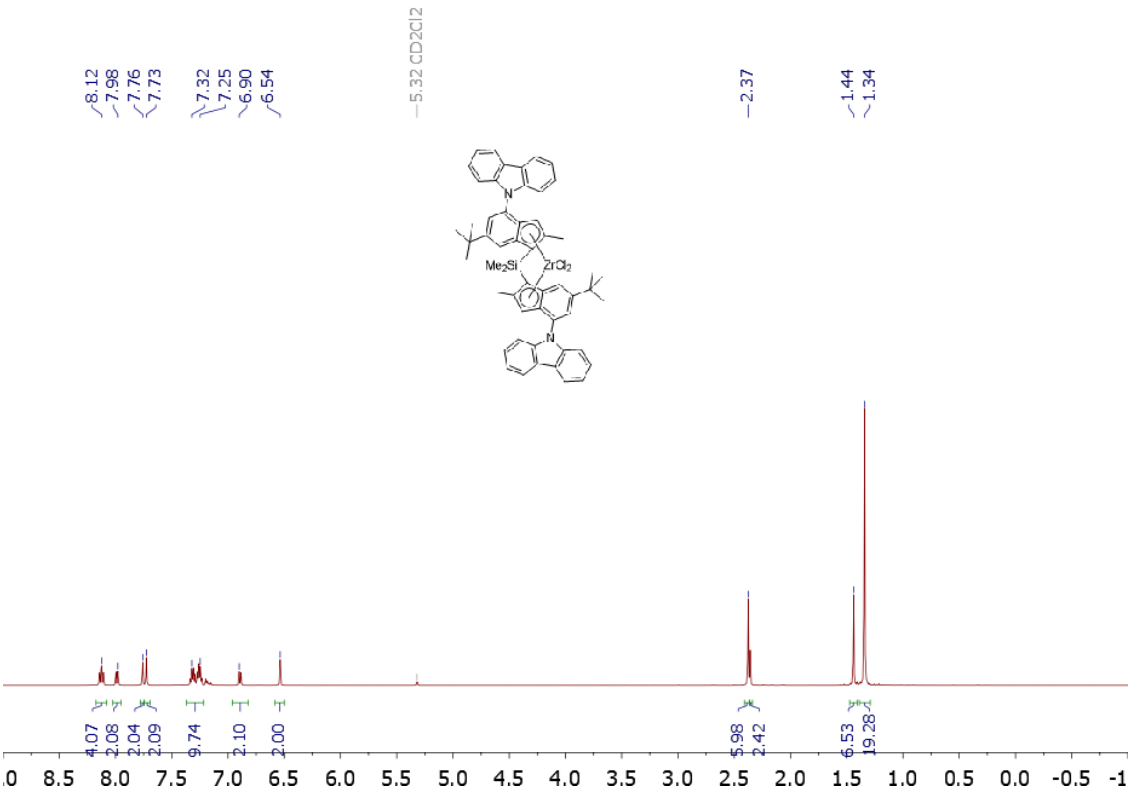

Figure S41. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C18**.

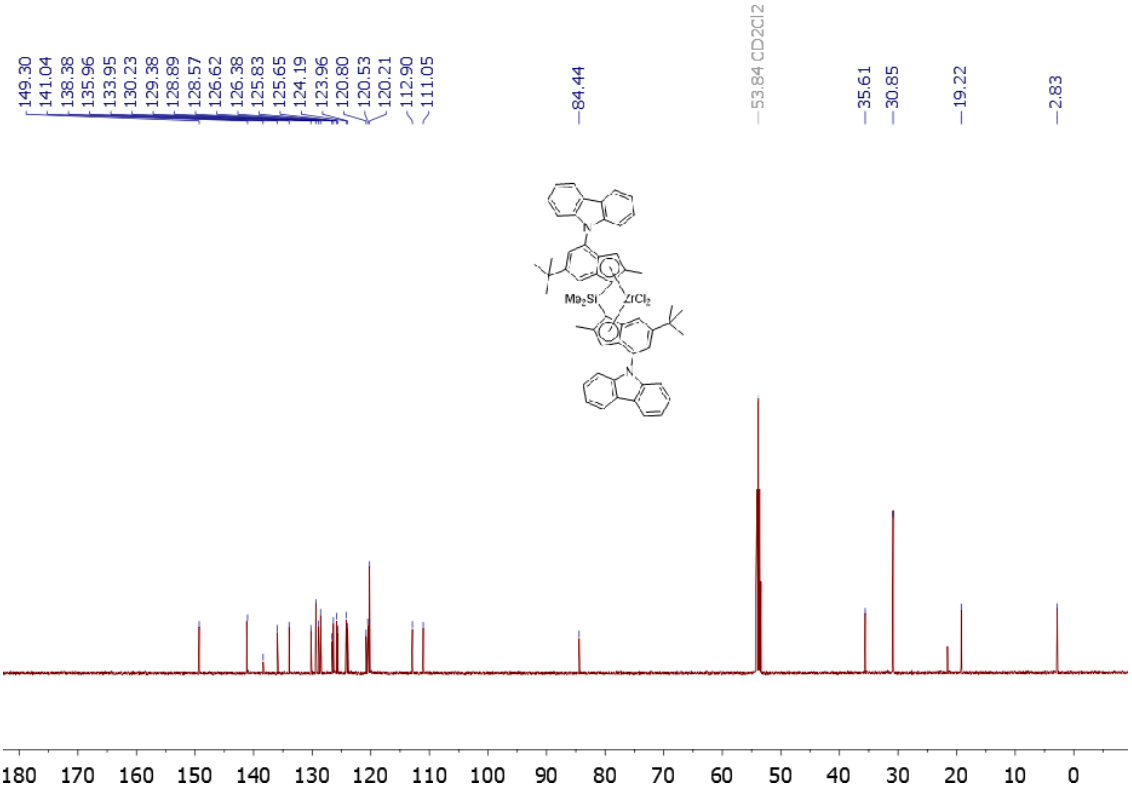

Figure S42. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C18**.

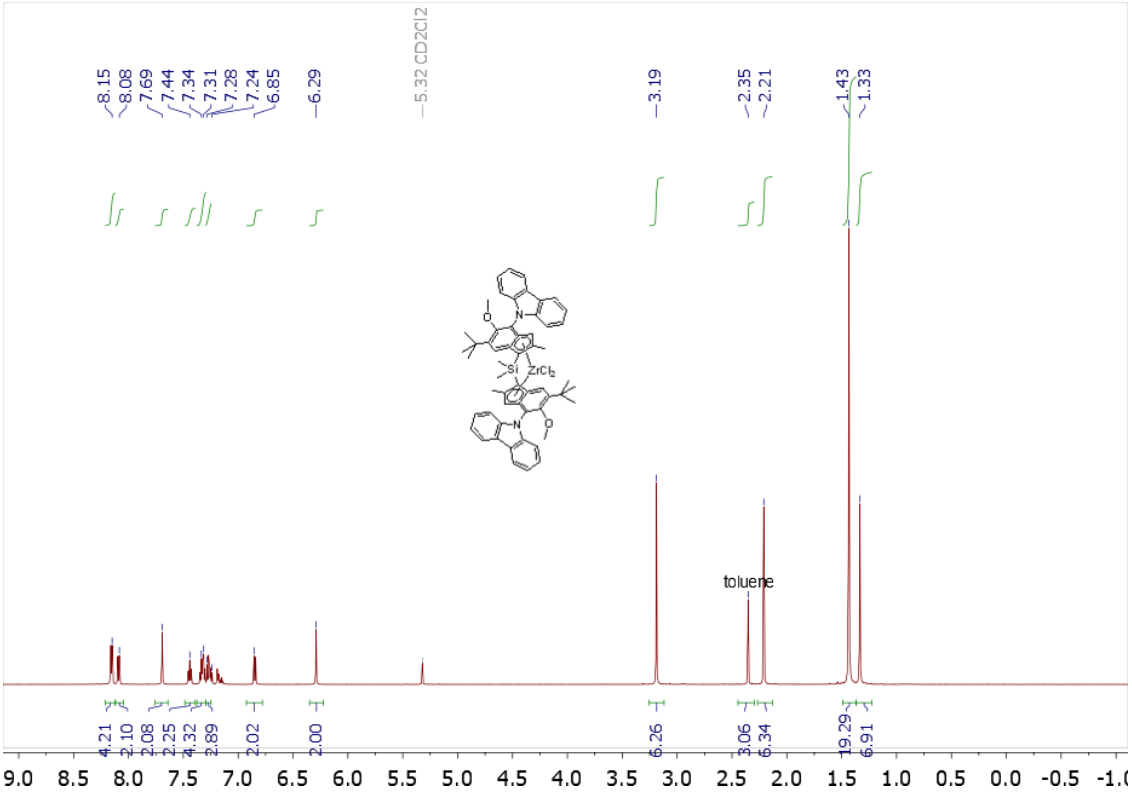

Figure S43. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C19**.

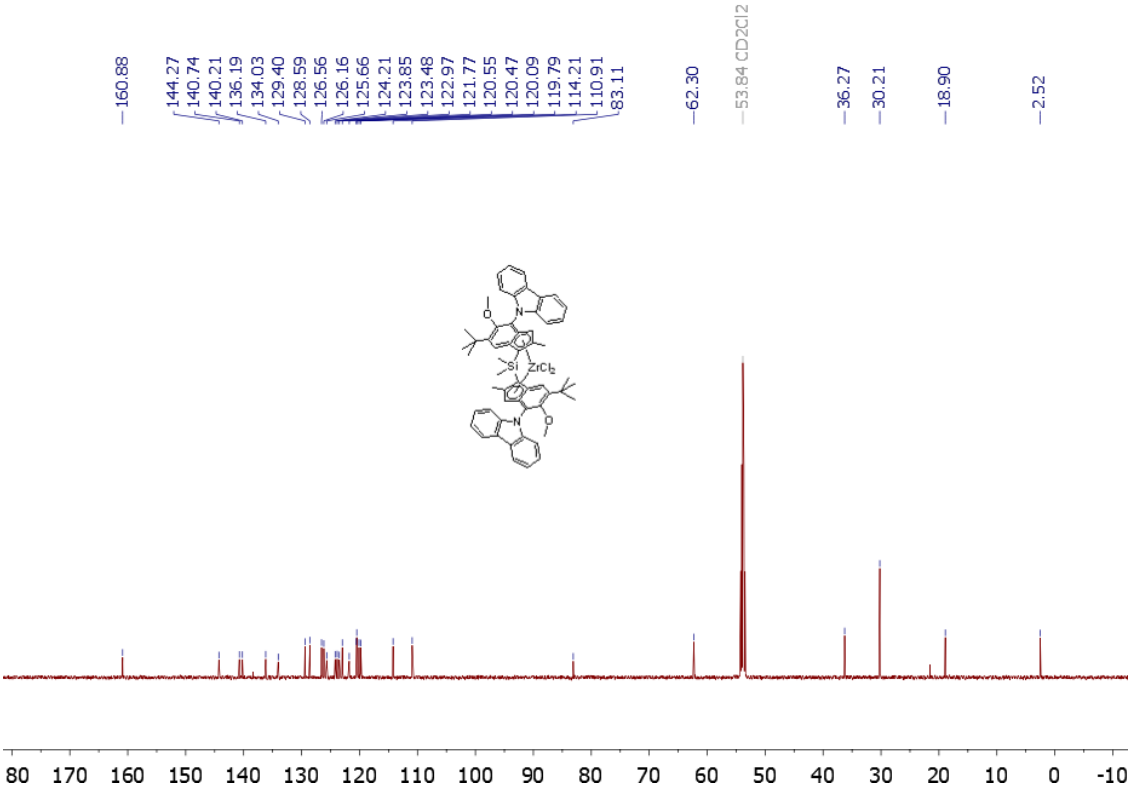

Figure S44. ^{13}C NMR (100 MHz, CD_2Cl_2) spectrum of complex **C19**.

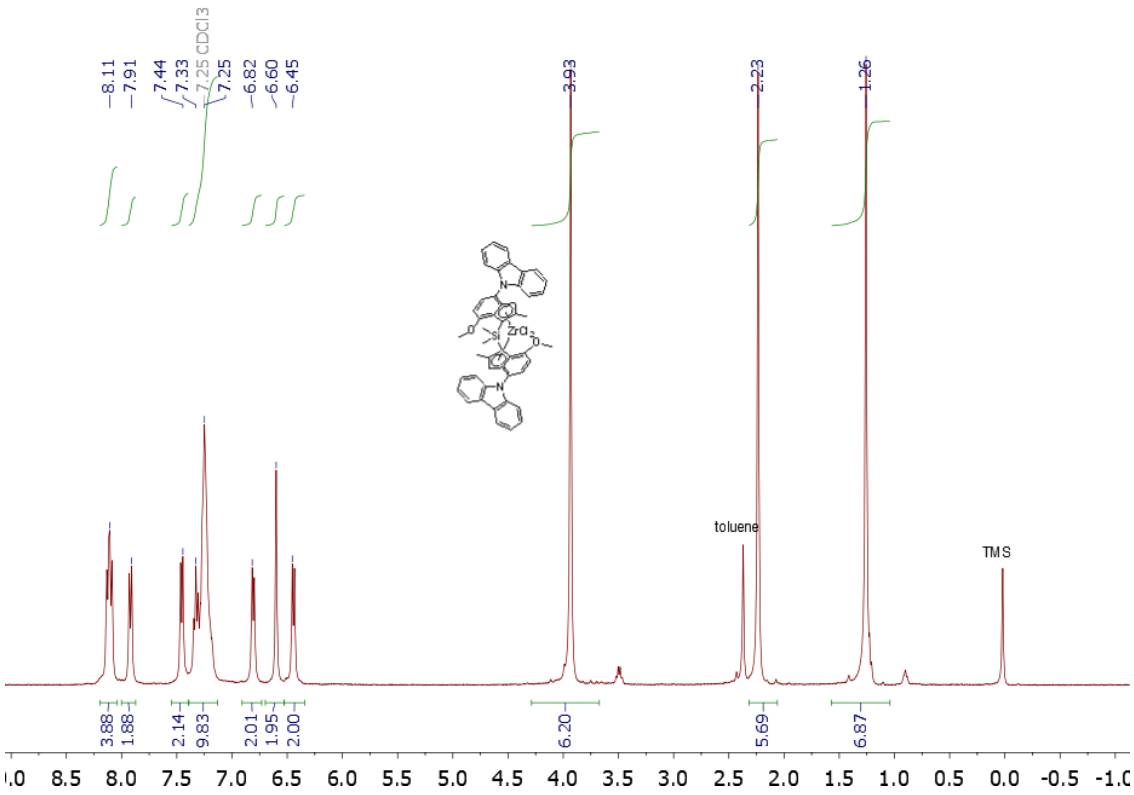

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C20**.

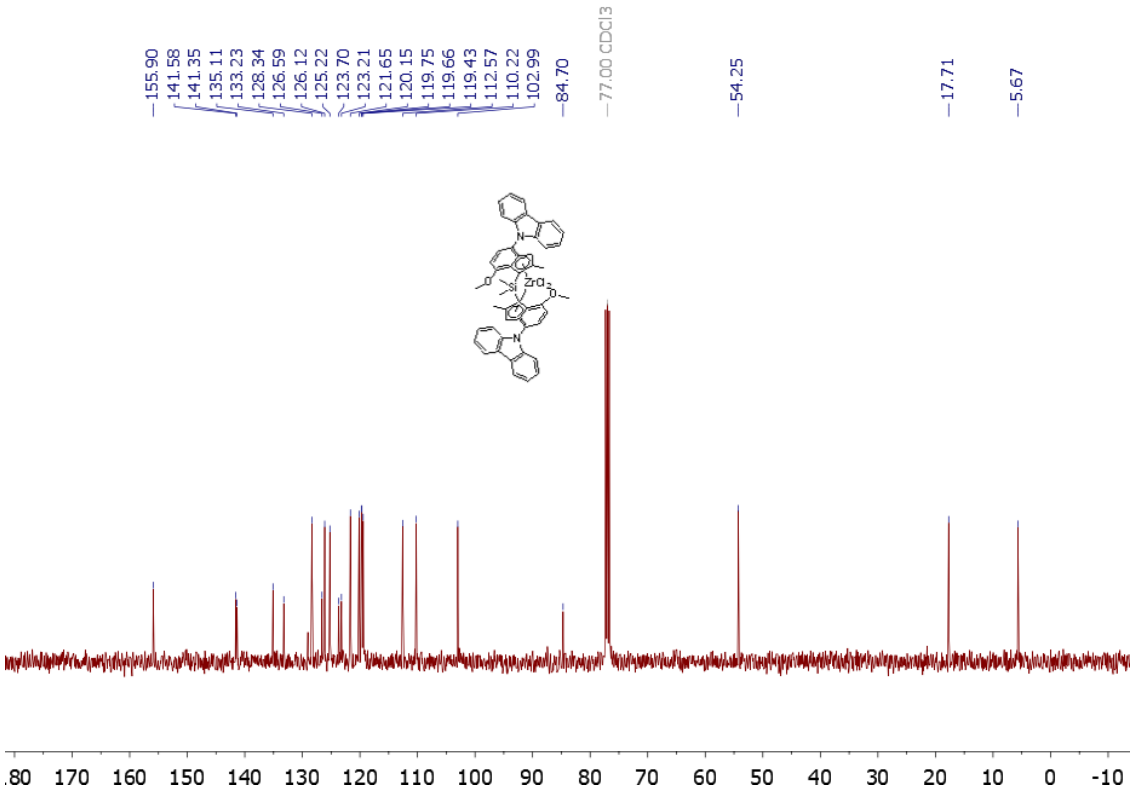

Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C20**.

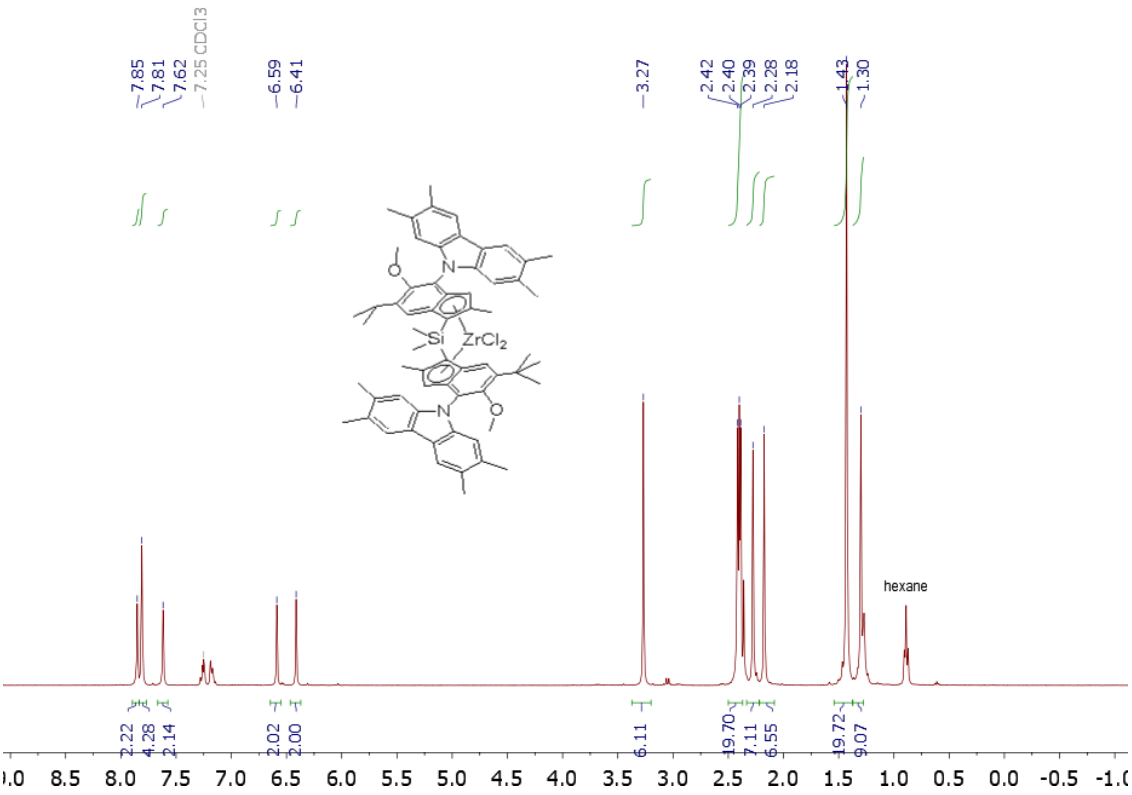

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of complex **C21**.

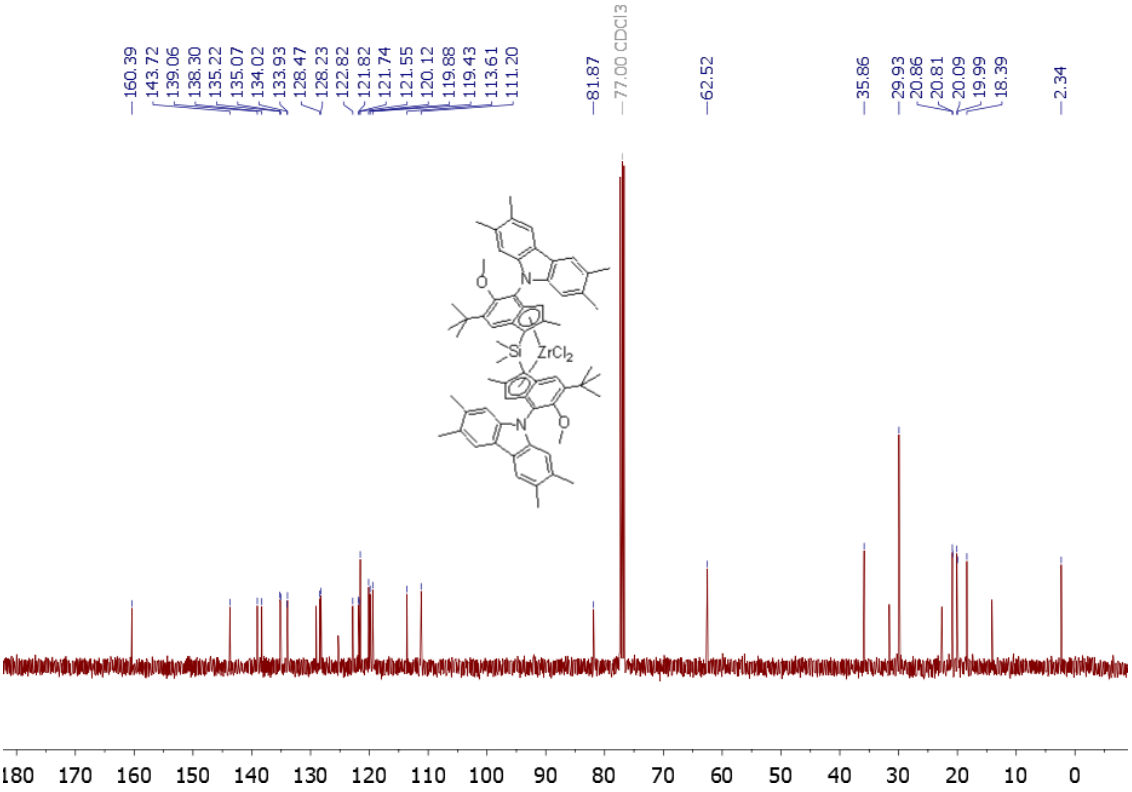

Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C21**.

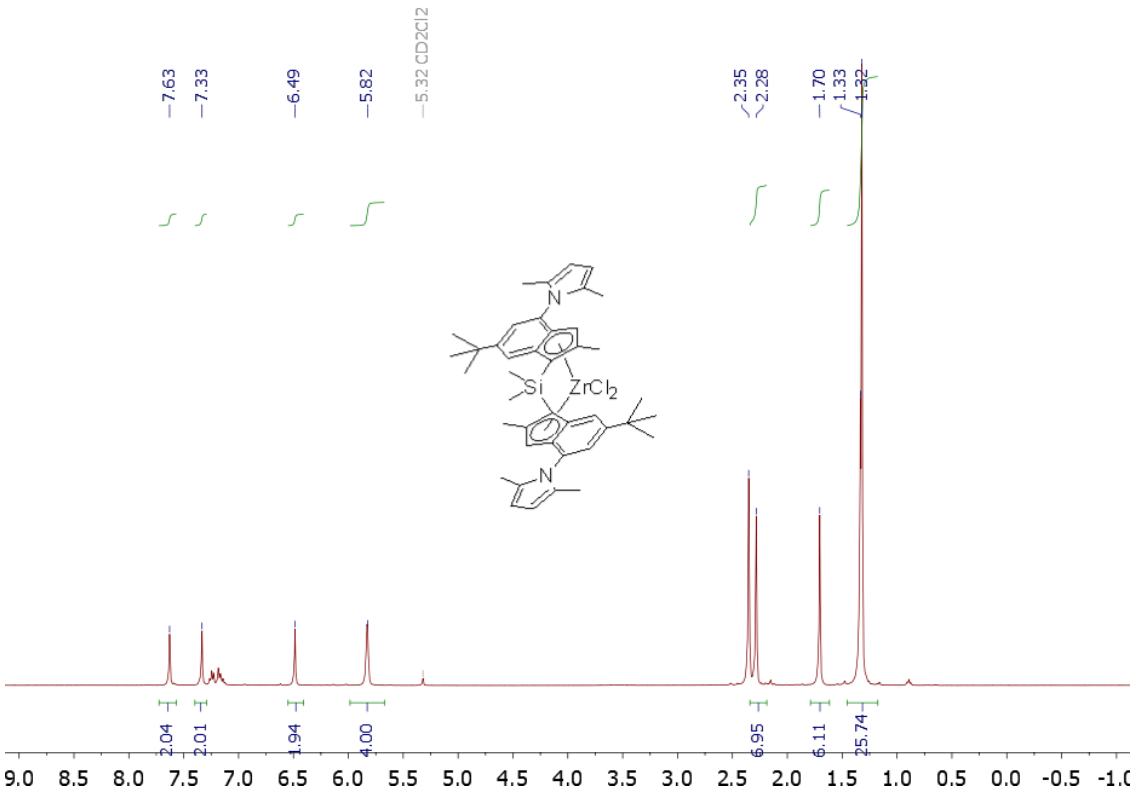

Figure S49. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **C22**.

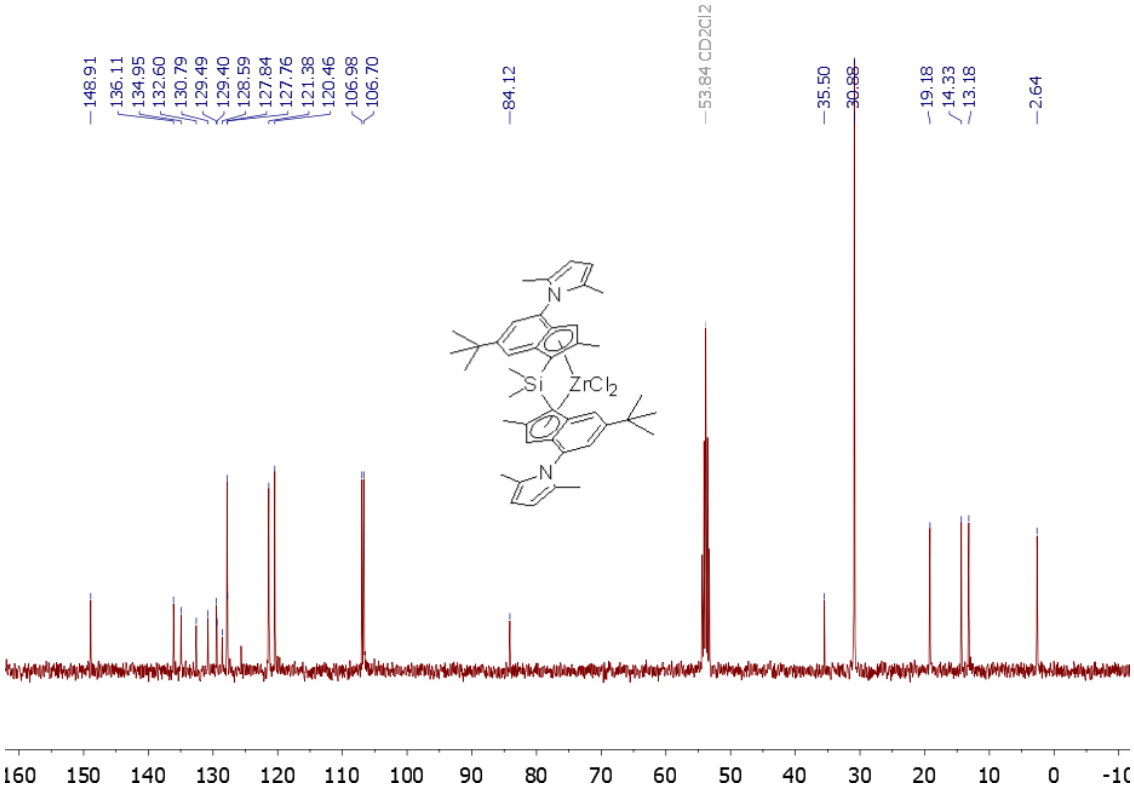

Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of complex **C22**.

^{13}C NMR SPECTRA OF SELECTED POLYPROPYLENE SAMPLES

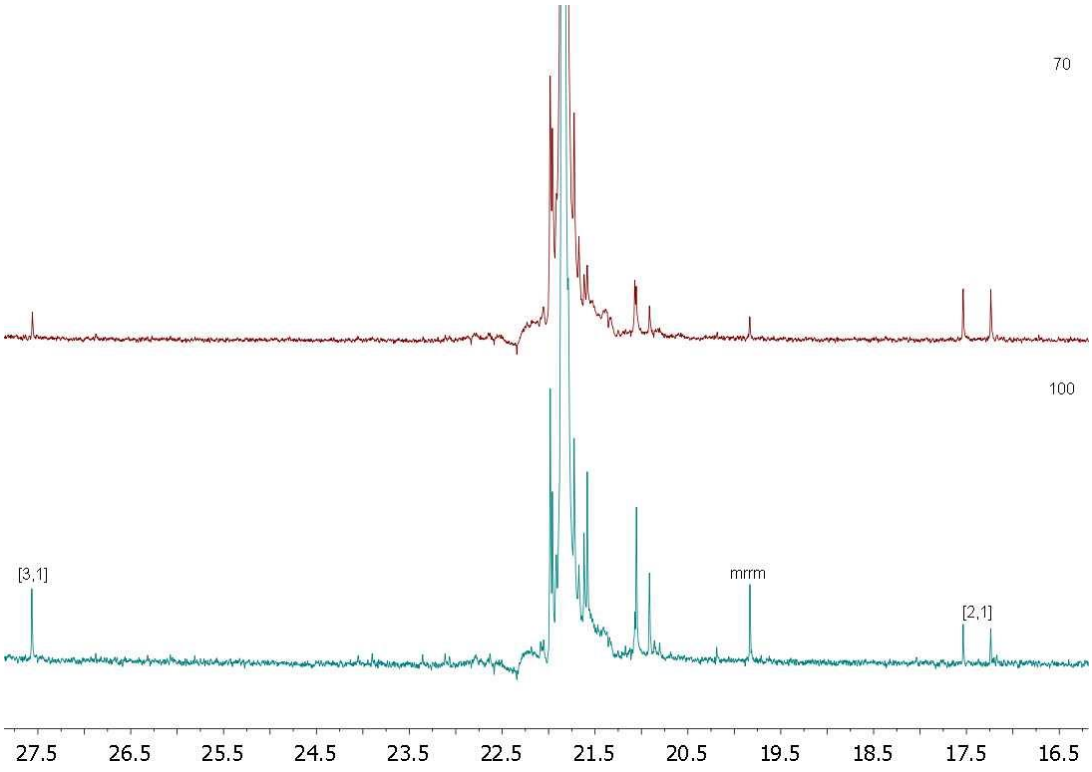

Figure S51. ^{13}C NMR (150 MHz, tetrachloroethane-d2, 120°C) spectra of iPP obtained with **MII/AB** (Table 6) at 70°C (top) and 100°C (bottom).

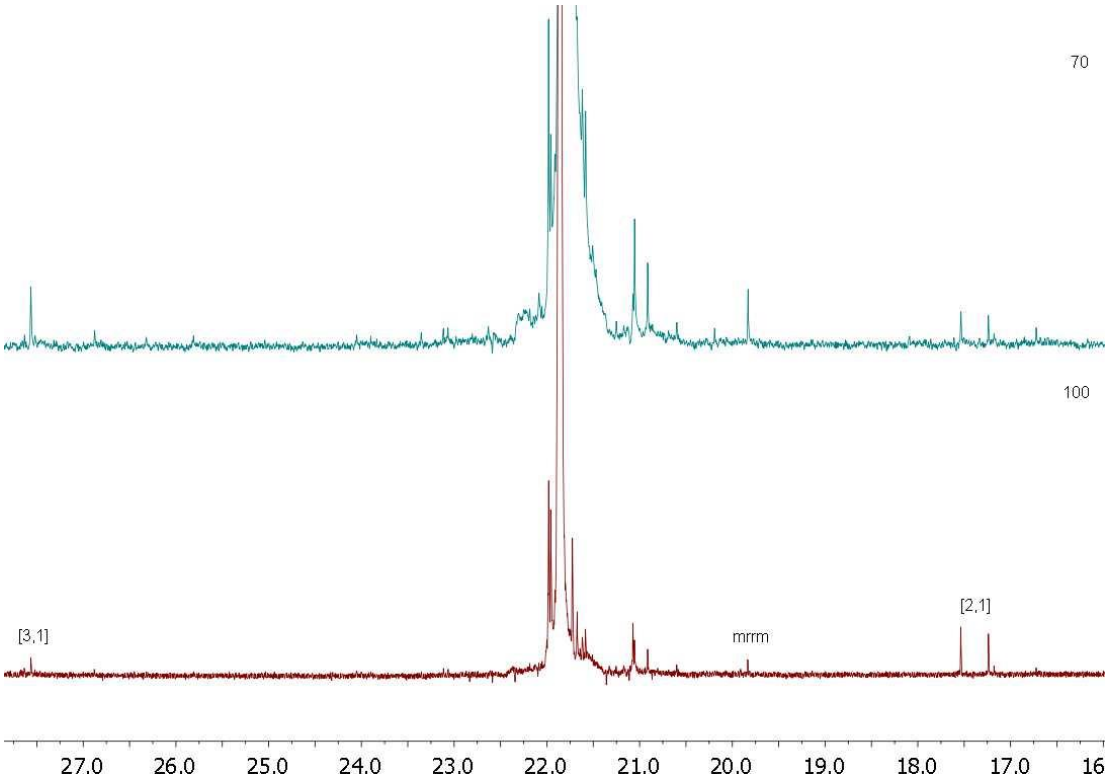

Figure S52. ^{13}C NMR (150 MHz, tetrachloroethane-d2, 120°C) spectra of iPP obtained with **M5/AB** (Table 6) at 70°C (top) and 100°C (bottom).

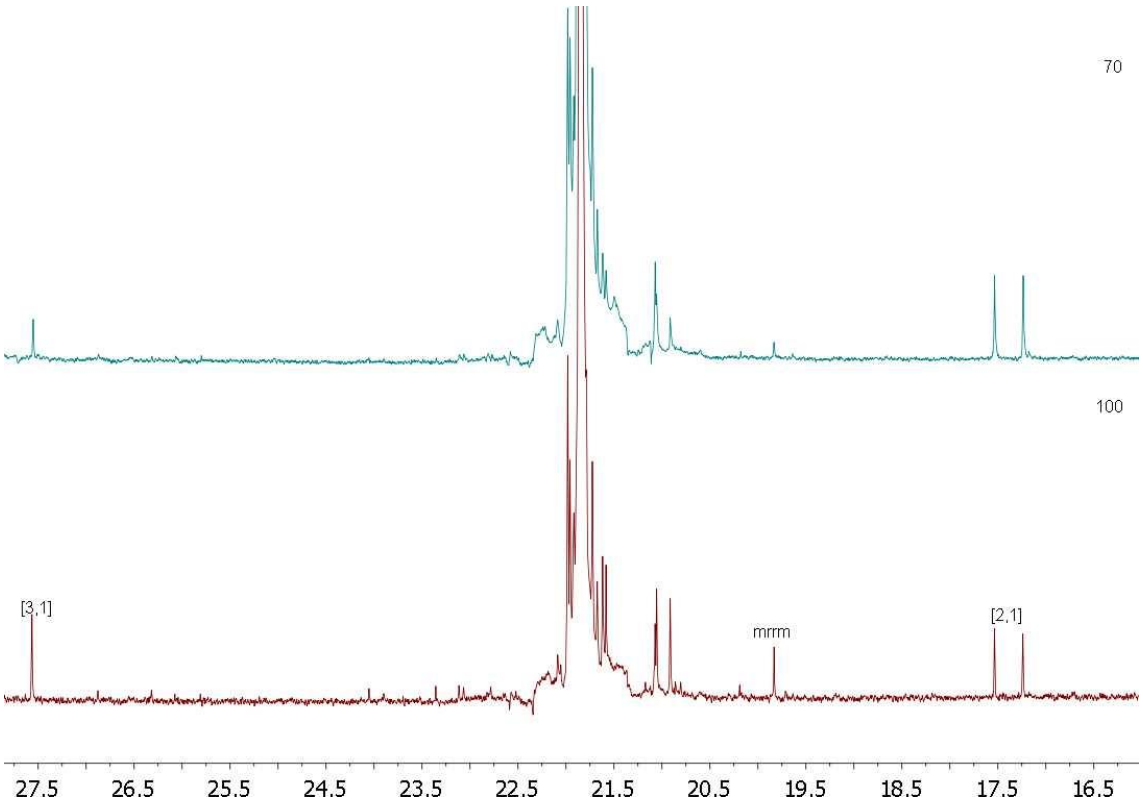

Figure S53. ^{13}C NMR (150 MHz, tetrachloroethane-d2, 120°C) spectra of iPP obtained with **M8/AB** (Table 6) at 70°C (top) and 100°C (bottom).

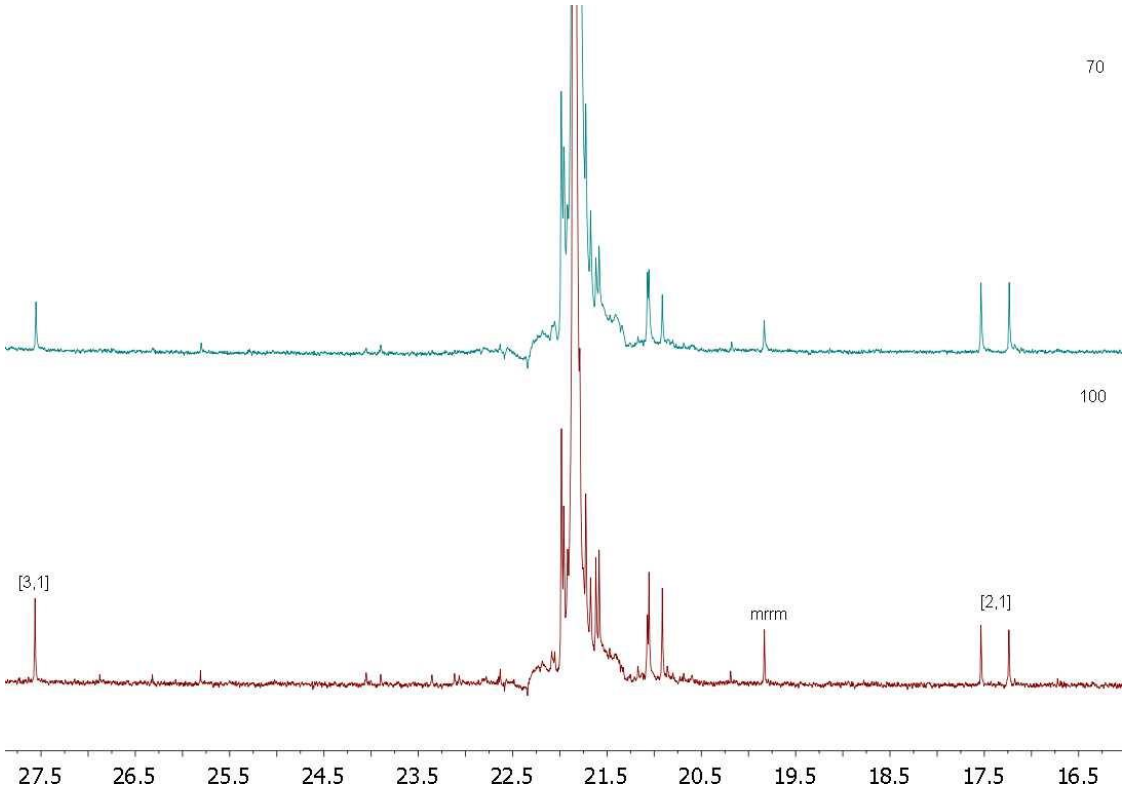

Figure S54. ^{13}C NMR (150 MHz, tetrachloroethane-d2, 120°C) spectra of iPP obtained with **M9/AB** (Table 6) at 70°C (top) and 100°C (bottom).

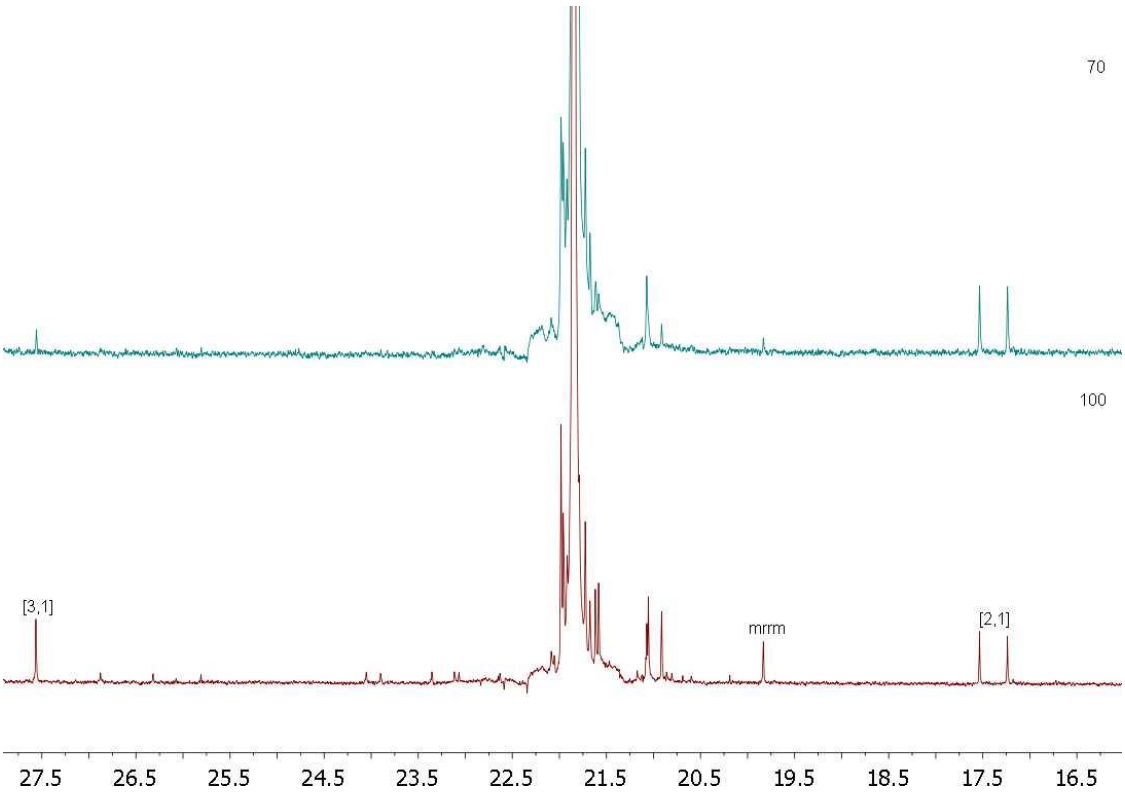

Figure S55. ^{13}C NMR (150 MHz, tetrachloroethane-d2, 120°C) spectra of iPP obtained with **M10/AB** (Table 6) at 70°C (top) and 100°C (bottom).