

Supporting Information

Synthesis of Fluorescent Poly(silyl indole)s via Borane-Catalyzed C–H Silylation of Indoles

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1. General information

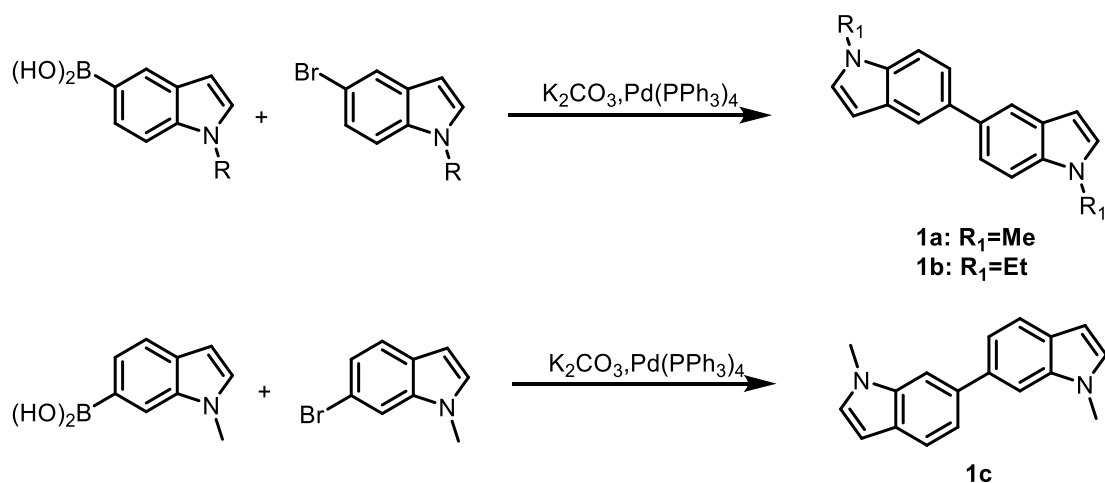
All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. Toluene, tetrahydrofuran and benzene were refluxed over sodium/potassium alloy, followed by distillation under nitrogen atmosphere. Hexane and dichloromethane were refluxed over CaH₂, followed by distillation under nitrogen atmosphere. All solvents were stored over molecular sieves 4 Å. C₆D₆, CDCl₃, CD₂Cl₂ was dried over molecular sieves 4 Å. NMR spectra were recorded on Bruker Avance II 500 (500 MHz, ¹H; 126 MHz, ¹³C) instrument at room temperature (RT). Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and reported as parts per million in relative to SiMe₄. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes. High Resolution Mass Spectra (HRMS) were recorded on the Bruker MicroTOF Q II. Fourier transform infrared (FT-IR) spectra were recorded using Bruker VERTEX 80 V in the wavenumber range of 400–4000 cm⁻¹ with KBr as the background. Polymer number-average molecular weight (*M_n*) and molecular weight distributions (PDI = *M_w*/*M_n*) were measured by gel permeation chromatography (GPC) at 35°C and a flow rate of 1 mL/min, with THF (HPLC grade) as an eluent on a Waters 1515 instrument equipped with Waters 4.6×30 mm guard column and three Waters WAT054466, WAT044226, WAT044223 columns. The instrument was calibrated with PS standards, and chromatograms were processed with Waters Breeze2 software. Thermal properties were measured by thermogravimetry analysis (TGA) on a TA Q50

instrument under a N₂ atmosphere at a heating rate of 10 °C min⁻¹ from room temperature to 800°C.

Unless stated otherwise, all chemicals were obtained from commercial suppliers and used without further purification. Hydrosilanes were purchased from Adamas. *n*-BuLi (2.5 M solution in hexane) was purchased from J&K. Dioxane was purchased from Titan. Boron trichloride (1.0 M solution in hexanes) was purchased from Alfa Aesar. Substituted indoles were purchased from Energy Chemical. All of chemicals were used as received unless otherwise specified as follows. Tris(pentafluorophenyl)borane, B(C₆F₅)₃, was prepared according to literature procedures.^{1,2}

2. Preparation of monomers

2.1 biindole monomers



Bromo substituted *N*-methylindole and indolylboronic acids were prepared according to modified literature methods.^{3,4} Under Suzuki–Miyaura coupling reaction condition, the coupling between bromo substituted *N*-methylindole and indolylboronic acids afforded biindole monomers. Bromo substituted *N*-methylindole

(24 mmol), corresponding indolylboronic acids (20 mmol), K₂CO₃ (6.91 g, 50 mmol), dioxane (80 mL) and H₂O (20 mL) were mixed in a 200-mL flask. The mixture was degassed with nitrogen by freeze-pump-thaw cycle then Pd(PPh₃)₄ (1.16 g, 1 mmol) was added. The reaction mixture was kept at 110°C for 24 h before it was cooled to room temperature. Water was added and the aqueous layer was extracted three times with dichloromethane. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane and ethyl acetate (10:1) as an eluent to afford biindole monomers as a white solid.

1,1'-dimethyl-5,5'-biindole (1a)

The product was obtained in an 82% yield as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (s, 2H, H_{Ar}), 7.59 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.42 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.11 (s, 2H, H_{Ar}), 6.58 (d, *J* = 2.9 Hz, 2H, H_{Ar}), 3.86 (s, 6H, NCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 135.9, 134.3, 129.3, 129.0, 122.0, 119.5, 109.3, 101.2, 32.9. HRMS (ESI⁺): calcd for C₁₈H₁₇N₂⁺ [M+H]⁺ 261.1386, found 261.1388.

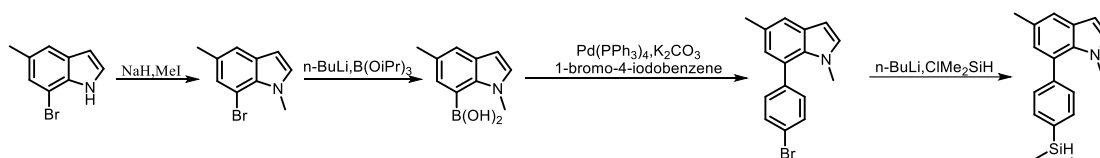
1,1'-diethyl-5,5'-biindole (1b)

The product was obtained in an 85% yield as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.95 (s, 2H, H_{Ar}), 7.59 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.46 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.19 (d, *J* = 3.1 Hz, 2H, H_{Ar}), 6.60 (d, *J* = 3.0 Hz, 2H, H_{Ar}), 4.25 (q, *J* = 7.3 Hz, 4H, NCH₂CH₃), 1.54 (t, *J* = 7.3 Hz, 6H, CH₂CH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 134.8, 134.3, 129.2, 127.4, 121.8, 119.6, 109.3, 101.3, 41.1, 15.6. HRMS (ESI⁺): calcd for C₂₀H₂₁N₂⁺ [M+H]⁺ 289.1699, found 289.1693.

1,1'-dimethyl-6,6'-biindole (1c)

The product was obtained in an 85% yield as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.2$ Hz, 2H, H_{Ar}), 7.63 (s, 2H, H_{Ar}), 7.52 (dd, $J = 8.2, 1.4$ Hz, 2H, H_{Ar}), 7.11 (d, $J = 3.1$ Hz, 2H, H_{Ar}), 6.56 (d, $J = 3.0$ Hz, 2H, H_{Ar}), 3.89 (s, 6H, NCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 137.4, 136.6, 129.2, 127.4, 120.9, 119.8, 108.0, 100.8, 32.9. HRMS (ESI $^+$): calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2^+$ $[\text{M}+\text{H}]^+$ 261.1386, found 261.1388.

2.2 AB-type monomers bearing both silyl and indole groups



All of the AB-type monomers are synthesized by a similar route, the detailed steps of 7-(4-(dimethylsilyl)phenyl)-1,5-dimethyl-indole are given as representative.

Synthesis of 7-bromo-1,5-dimethyl-indole. In a Schlenk flask, 7-bromo-5-methyl-1H-indole (6.3 g, 30 mmol, 1.0 eq) was dissolved in DMF (120 mL) and cooled to 0°C. NaH (1.5 g, 36 mmol, 60% dispersion in mineral oil, 1.2 eq) was added in portions and the resulting suspension was stirred at RT for 30 minutes. The mixture was cooled down to 0°C again and MeI (5.2 g, 36 mmol, 1.2 eq) was added dropwisely. The reaction mixture was stirred at RT overnight. After consumption of the starting material (TLC monitoring), water was added and the aqueous layer was extracted three times with Et₂O. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude residue was purified by silica gel column chromatography using hexane as

an eluent to afford 7-bromo-1,5-dimethyl-indole as a colorless oil in a 98% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.34 (s, 1H, H_{Ar}), 7.22 (s, 1H, H_{Ar}), 6.98 (d, $J = 3.0$ Hz, 1H, H_{Ar}), 6.39 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 4.15 (s, 3H, NCH_3), 2.42 (s, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 131.8, 131.5, 130.0, 127.9, 120.0, 103.4, 100.5, 36.7, 20.8. HRMS (ESI^+): calcd for $\text{C}_{10}\text{H}_{11}\text{BrN}^+$ $[\text{M}+\text{H}]^+$ 224.0069, found 224.0060.

Synthesis of (1,5-dimethyl-indol-7-yl)boronic acid. In a Schlenk flask, 7-bromo-1,5-dimethyl-indole (4.5 g, 20 mmol, 1.0 eq) was dissolved in THF (50 mL) and cooled down to -78°C . $n\text{BuLi}$ (2.5 M, 9.6 mL, 24 mmol, 1.2 eq) was added dropwisely and the resulting suspension was stirred at -78°C for 60 minutes. Then $\text{B}(\text{O}^i\text{Pr})_3$ (4.5 g, 24 mmol, 1.2 eq) was added dropwisely and the reaction mixture was stirred at RT overnight. The mixture was quenched by aqueous NH_4Cl solution and the product was extracted with diethyl ether. The combined extracts were dried over MgSO_4 , filtered, concentrated under reduced pressure and crystallization to afford (1,5-dimethyl-indol-7-yl)boronic acid as a yellow solid in an 85% yield. The crude product was used without further purification. ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.87 (m, 1H, H_{Ar}), 7.68 (s, 1H, H_{Ar}), 7.51 (s, 1H, H_{Ar}), 7.21 (s, 1H, H_{Ar}), 7.08 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 7.04 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 6.54 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 6.45 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 4.83 (br, 2H, $\text{B}(\text{OH})_2$), 3.97 (s, 3H, NCH_3), 3.88 (s, 3H, NCH_3), 2.52 (s, 3H, CH_3), 2.47 (s, 3H, CH_3). HRMS (ESI^+): calcd for $\text{C}_{10}\text{H}_{13}\text{BNO}_2^+$ $[\text{M}+\text{H}]^+$ 190.1034, found 190.1025.

Synthesis of 7-(4-bromophenyl)-1,5-dimethyl-indole. (1,5-dimethyl-indol-7-yl)boronic acid (3.0 g, 16 mmol, 1.0 eq), 1-bromo-4-iodobenzene (5.7 g, 20 mmol,

1.25 eq), K₂CO₃ (5.5 g, 40 mmol, 2.5 eq), dioxane (80 mL) and H₂O (20 mL) were mixed together in a 200 mL flask. The mixture was degassed with nitrogen by freeze-pump-thaw cycle, then Pd(PPh₃)₄ (924 mg, 0.8 mmol, 0.05 eq) was added. The reaction mixture was kept at 110°C for 24 h before it was cooled to RT. Water was added and the aqueous layer was extracted three times with dichloromethane. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane and ethyl acetate (50:1) as an eluent to afford 7-(4-bromophenyl)-1,5-dimethyl-indole as a white solid in an 81% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 7.4 Hz, 2H, H_{Ar}), 7.46 (s, 1H, H_{Ar}), 7.36 (d, *J* = 7.4 Hz, 2H, H_{Ar}), 6.98 (s, 1H, H_{Ar}), 6.87 (s, 1H, H_{Ar}), 6.50 (s, 1H, H_{Ar}), 3.34 (s, 3H, NCH₃), 2.50 (s, 3H, CH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 139.5, 132.3, 131.7, 131.1, 130.8, 130.2, 128.4, 125.7, 125.7, 125.0, 121.3, 120.2, 100.7, 36.9, 21.1. HRMS (ESI⁺): calcd for C₁₆H₁₅BrN⁺ [M+H]⁺ 300.0382, found 300.0375.

Synthesis of 7-(4-(dimethylsilyl)phenyl)-1,5-dimethyl-indole (2c). In a Schlenk flask 7-(4-bromophenyl)-1,5-dimethyl-indole (1.5 g, 5 mmol, 1.0 eq) was dissolved in THF (40 mL) and cooled down to -78°C. The ⁿBuLi (2.5 M, 2.4 mL, 6 mmol, 1.2 eq) was added dropwise and the resulting suspension was stirred at -78°C for 1 h. Then Me₂SiClH (710 mg, 7.5 mmol, 1.5 eq) was added dropwisely and the reaction mixture was stirred at RT overnight. The mixture was quenched by aqueous NH₄Cl solution and the product was extracted with diethyl ether. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane as an eluent to afford

7-(4-(dimethylsilyl)phenyl)-1,5-dimethyl-indole in a 92% yield as a colorless oil that eventually crystallized on standing at RT. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, $J = 7.9$ Hz, 2H, H_{Ar}), 7.47 (d, $J = 7.9$ Hz, 2H, H_{Ar}), 7.44 (s, 1H, H_{Ar}), 6.97 (s, 1H, H_{Ar}), 6.89 (s, 1H, H_{Ar}), 6.49 (s, 1H, H_{Ar}), 4.56-4.50 (m, 1H, SiH), 3.33 (s, 3H, NCH_3), 2.48 (s, 3H, CH_3), 0.44 (d, $J = 3.7$ Hz, 6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 141.4, 135.9, 133.3, 132.4, 131.0, 129.5, 128.3, 126.3, 125.9, 119.9, 100.6, 36.8, 21.1, -3.7. HRMS (ESI $^+$): calcd for $\text{C}_{18}\text{H}_{22}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 280.1516, found 280.1517.

Synthesis of 5-(4-bromophenyl)-1-methyl-indole

It was prepared from (1-methyl-indol-5-yl)boronic acid according to the above procedure to afford 5-(4-bromophenyl)-1-methyl-indole as a white solid in a 72% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 1H, H_{Ar}), 7.57 (q, $J = 10.3$ Hz, 4H, H_{Ar}), 7.47 (d, $J = 8.5$ Hz, 1H, H_{Ar}), 7.41 (d, $J = 8.5$ Hz, 1H, H_{Ar}), 7.12 (d, $J = 3.0$ Hz, 1H, H_{Ar}), 6.58 (d, $J = 3.0$ Hz, 1H, H_{Ar}), 3.85 (s, 3H, NCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 141.6, 136.4, 131.7, 131.6, 129.7, 128.9, 127.4, 121.1, 120.4, 119.3, 109.6, 101.4, 33.0. HRMS (ESI $^+$): calcd for $\text{C}_{15}\text{H}_{13}\text{BrN}^+$ $[\text{M}+\text{H}]^+$ 286.0226, found 286.0218.

Synthesis of 5-(4-(dimethylsilyl)phenyl)-1-methyl-indole (2a)

It was prepared from 5-(4-bromophenyl)-1-methyl-indole according to the above procedure to afford 5-(4-(dimethylsilyl)phenyl)-1-methyl-indole in a 90% yield as a colorless oil that eventually crystallized on standing at RT. ^1H NMR (500 MHz, CDCl_3) δ 7.92 (s, 1H, H_{Ar}), 7.73 (d, $J = 8.0$ Hz, 2H, H_{Ar}), 7.68 (d, $J = 8.0$ Hz, 2H, H_{Ar}), 7.55 (d, $J = 10.0$ Hz, 1H, H_{Ar}), 7.43 (d, $J = 8.5$ Hz, 1H, H_{Ar}), 7.13 (d, $J = 3.1$ Hz, 1H, H_{Ar}), 6.61 – 6.58 (m, 1H, H_{Ar}), 4.58-4.52 (m, 1H, SiH), 3.86 (s, 3H, NCH_3), 0.45 (d, $J = 3.7$

Hz, 6H, SiCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 143.5, 136.4, 134.8, 134.5, 132.6, 129.5, 126.9, 121.4, 119.5, 109.5, 101.4, 33.0, -3.6. HRMS (ESI⁺): calcd for C₁₇H₂₀NSi⁺ [M+H]⁺ 266.1360, found 266.1367.

Synthesis of 6-(4-bromophenyl)-1-methyl-indole

It was prepared from (1-methyl-indol-6-yl)boronic acid according to the above procedure to afford 6-(4-bromophenyl)-1-methyl-indole as a white solid in a 68% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 7.63-7.56 (m, 4H, H_{Ar}), 7.51 (s, 1H, H_{Ar}), 7.37 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 7.13 (d, *J* = 3.1 Hz, 1H, H_{Ar}), 6.55 (d, *J* = 3.7 Hz, 1H, H_{Ar}), 3.87 (s, 3H, NCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 141.5, 137.2, 133.8, 131.7, 129.8, 129.0, 128.1, 121.2, 120.7, 118.9, 107.6, 100.9, 32.9. HRMS (ESI⁺): calcd for C₁₅H₁₃BrN⁺ [M+H]⁺ 286.0226, found 286.0224.

Synthesis of 6-(4-(dimethylsilyl)phenyl)-1-methyl-indole (2b)

It was prepared from 6-(4-bromophenyl)-1-methyl-indole according to the above procedure to afford 6-(4-(dimethylsilyl)phenyl)-1-methyl-indole in a 88% yield as a colorless oil that eventually crystallized on standing at RT. ¹H NMR (500 MHz, CDCl₃) δ 7.76-7.71 (m, 3H, H_{Ar}), 7.68 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 7.57 (s, 1H, H_{Ar}), 7.43 (d, *J* = 9.4 Hz, 1H, H_{Ar}), 7.12 (d, *J* = 3.0 Hz, 1H, H_{Ar}), 6.55 (d, *J* = 3.0 Hz, 1H, H_{Ar}), 4.57-4.50 (m, 1H, SiH), 3.88 (s, 4H, NCH₃), 0.44 (d, *J* = 3.7 Hz, 6H, SiCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 143.4, 137.2, 135.2, 135.0, 134.5, 129.6, 128.0, 127.0, 121.1, 119.2, 107.8, 100.9, 32.9, -3.6. HRMS (ESI⁺): calcd for C₁₇H₂₀NSi⁺ [M+H]⁺ 266.1360, found 266.1361.

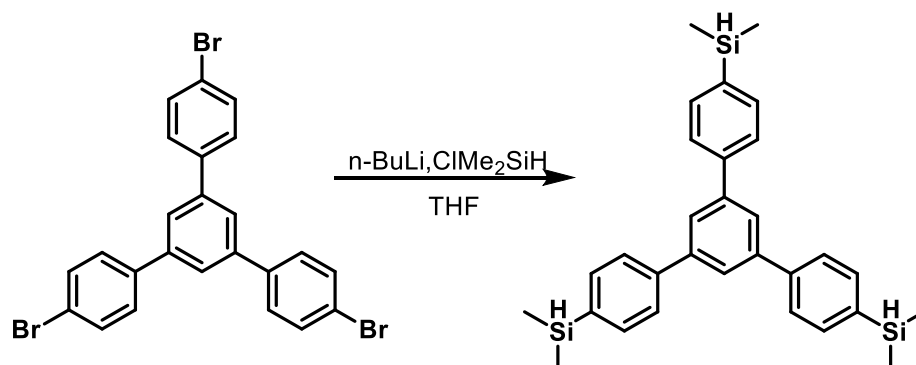
Synthesis of 5-(3-bromophenyl)-1-methyl-indole

It was prepared from (1-methyl-indol-5-yl)boronic acid according to the above procedure to afford 5-(3-bromophenyl)-1-methyl-indole as a white solid in a 73% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, $J = 7.7$ Hz, 2H, H_{Ar}), 7.60 (d, $J = 7.7$ Hz, 1H, H_{Ar}), 7.46 (t, $J = 8.4$ Hz, 2H, H_{Ar}), 7.41 (d, $J = 8.5$ Hz, 1H, H_{Ar}), 7.32 (t, $J = 7.8$ Hz, 1H, H_{Ar}), 7.12 (d, $J = 2.8$ Hz, 1H, H_{Ar}), 6.57 (d, $J = 3.0$ Hz, 1H, H_{Ar}), 3.86 (s, 3H, NCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 144.8, 136.5, 131.3, 130.3, 130.1, 129.7, 129.1, 129.0, 125.9, 122.8, 121.1, 119.5, 109.6, 101.5, 33.0. HRMS (ESI $^+$): calcd for $\text{C}_{15}\text{H}_{13}\text{BrN}^+$ $[\text{M}+\text{H}]^+$ 286.0226, found 286.0221.

Synthesis of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (2d)

Starting from 5-(3-bromophenyl)-1-methyl-indole, 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole was prepared according to the similar procedure and produced in a 93% yield as a colorless oil that eventually crystallized on standing at RT. ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 11.9$ Hz, 2H, H_{Ar}), 7.70 (d, $J = 7.6$ Hz, 1H, H_{Ar}), 7.55-7.50 (m, 2H, H_{Ar}), 7.48 (t, $J = 7.4$ Hz, 1H, H_{Ar}), 7.43 (d, $J = 8.5$ Hz, 1H, H_{Ar}), 7.12 (d, $J = 2.7$ Hz, 1H, H_{Ar}), 6.58 (d, $J = 2.8$ Hz, 1H, H_{Ar}), 4.57-4.50 (m, 1H, SiH), 3.86 (s, 3H, NCH_3), 0.44 (d, $J = 3.7$ Hz, 6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 142.1, 137.7, 136.3, 133.1, 133.0, 132.0, 129.5, 129.0, 128.4, 128.2, 121.5, 119.5, 109.5, 101.4, 33.0, -3.6. HRMS (ESI $^+$): calcd for $\text{C}_{17}\text{H}_{20}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 266.1360, found 266.1362.

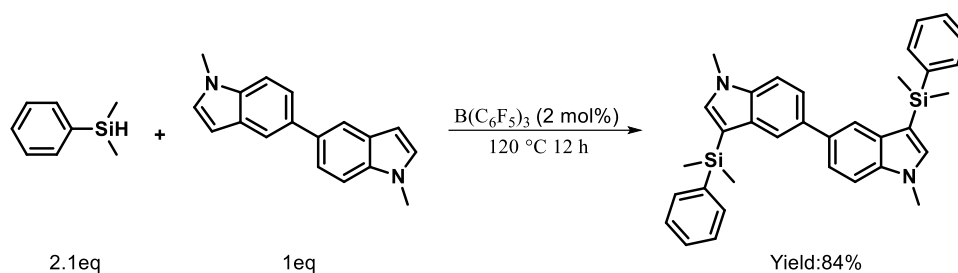
2.3 Synthesis of trisilane monomer (3b)



In a Schlenk flask 4,4''-dibromo-5'-(4-bromophenyl)-1,1':3',1''-terphenyl (2.7 g, 5 mmol, 1.0 eq) was dissolved in THF (60 mL) and cooled to -78°C. The *n*-BuLi (2.5 M, 2.4 mL, 6 mmol, 1.2 eq) was added dropwisely and the resulting suspension was stirred at -78°C for 1 h. Then Me₂SiClH (710 mg, 7.5 mmol, 1.5 eq) was added dropwisely and the reaction mixture was stirred at RT overnight. The mixture was quenched by aqueous NH₄Cl solution and the product was extracted with diethyl ether. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography using hexane as an eluent to afford the trisilane monomer in an 81% yield as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.83 (s, 3H, H_{Ar}), 7.74 – 7.69 (m, 12H, H_{Ar}), 4.53 (hept, *J* = 3.7 Hz, 3H, SiH), 0.44 (d, *J* = 3.7 Hz, 18H, SiCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 142.3, 141.9, 136.7, 134.6, 126.8, 125.3, -3.7. HRMS (ESI⁺): calcd for C₃₀H₃₇Si₃⁺ [M+H]⁺ 481.2198, found 481.2190.

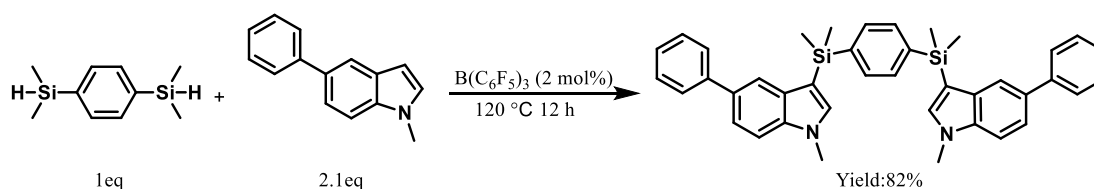
3. Preparation of the model compounds.

Synthesis of model compounds 1 (MC1)



Into a 10 mL Schlenk tube equipped with a magnetic stir bar were added dimethyl(phenyl)silane (85.9 mg, 0.63 mmol), 1,1'-dimethyl-5,5'-biindole (**1a**, 78.1 mg, 0.3 mmol), B(C₆F₅)₃ (3.1 mg, 6 μmol), and 1 mL of toluene in a glovebox. The Schlenk tube was taken out of the glovebox, and the reaction mixture was stirred at 120°C for 12 h. Afterward, the system was cooled to RT, the reaction mixture was concentrated under vacuum to give a precipitate. The solid was collected by filtration, then washed with hexane, and dried in vacuo to afford 3,3'-bis(dimethyl(phenyl)silyl)-1,1'-dimethyl-5,5'-biindole as a white solid in an 84% yield (133 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 2H, H_{Ar}), 7.69-7.63 (m, 4H, H_{Ar}), 7.49 (d, *J* = 8.4, 2H, H_{Ar}), 7.43-7.34 (m, 8H, H_{Ar}), 7.06 (s, 2H, H_{Ar}), 3.83 (s, 6H, NCH₃), 0.64 (s, 12H, SiCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 139.4, 137.6, 136.8, 134.5, 134.0, 133.4, 128.9, 127.8, 122.0, 120.8, 109.4, 107.3, 32.9, -1.3. HRMS (ESI⁺): calcd for C₃₄H₃₇N₂Si₂⁺ [M+H]⁺ 529.2490, found 529.2486.

Synthesis of model compounds **2** (MC2)



A 10 mL Schlenk tube equipped with a magnetic stir bar were added 1,4-bis(dimethylsilyl)benzene (**3a**, 58.3 mg, 0.3 mmol), 1-methyl-5-phenylindole

(130.6 mg, 0.63 mmol), B(C₆F₅)₃ (3.1 mg, 6 μmol), and 1 mL of toluene in a glovebox. The Schlenk tube was taken out of the glovebox, and the reaction mixture was stirred at 120°C for 12 h. Afterward, the system was cooled down to RT, the reaction mixture was concentrated under vacuum to give a precipitate. The solid was collected by filtration, then washed with hexane, and dried in vacuo to afford 1,4-bis(dimethyl(1-methyl-5-phenyl-indol-3-yl)silyl)benzene as a white solid in an 82% yield (153 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.82 (s, 2H, H_{Ar}), 7.67 (s, 4H, H_{Ar}), 7.60 (d, *J* = 7.5 Hz, 4H, H_{Ar}), 7.51 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 7.42 (t, *J* = 7.9 Hz, 6H, H_{Ar}), 7.31 (t, *J* = 7.4 Hz, 2H, H_{Ar}), 7.08 (s, 2H, H_{Ar}), 3.81 (s, 6H, NCH₃), 0.67 (s, 12H, SiCH₃). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 142.6, 140.0, 138.1, 137.1, 133.4, 133.0, 128.6, 127.4, 126.2, 121.5, 120.6, 109.6, 107.4, 32.9, -1.2. HRMS (ESI⁺): calcd for C₄₀H₄₁N₂Si₂⁺ [M+H]⁺ 605.2803, found 605.2802.

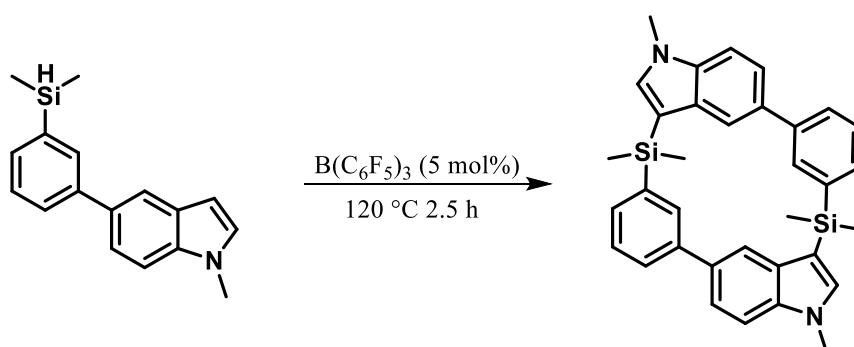
Synthesis of model compounds 3 (MC3)

We investigated the influence of concentration on the cyclization reactions of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**2d**). As shown in Table S1, the cyclization reactions were carried out at different concentrations and the typical procedure of Table S1, entry 3 is given below as an example.

In a glovebox, 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**2d**, 26.5 mg, 0.1 mmol) was added to a 0.5 mL C₆D₆ solution of B(C₆F₅)₃ (2.6 mg, 5 μmol) in a J. Young-type NMR tube. The NMR tube was taken out of the glovebox, and the reaction mixture was heated to 120°C for 2.5 h. After completion of the reaction and measurement of NMR, the reaction mixture was concentrated under vacuum to give a

white precipitate. The solid was collected by filtration, then washed with hexane, and dried in vacuo to afford **MC3** as a white solid in a 49% yield (13 mg). The molecular structure of **MC3** was confirmed by single-crystal X-ray diffraction analysis. ^1H NMR (500 MHz, CDCl_3) δ 8.43 (s, 2H, H_{Ar}), 8.27 (s, 2H, H_{Ar}), 7.56 (t, $J = 8.1$ Hz, 4H, H_{Ar}), 7.41 (q, $J = 8.4, 7.5$ Hz, 4H, H_{Ar}), 7.35 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 7.20 (s, 2H, H_{Ar}), 3.81 (s, 6H, NCH_3), 0.76 (s, 12H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 142.2, 140.1, 138.1, 136.0, 133.7, 133.3, 131.3, 128.2, 128.1, 121.4, 121.2, 109.5, 108.1, 32.9, -2.1. HRMS (ESI $^+$): calcd for $\text{C}_{34}\text{H}_{35}\text{N}_2\text{Si}_2^+$ $[\text{M}+\text{H}]^+$ 527.2333, found 527.2332.

Table S1. Influence of concentration on the cyclization reaction of **2d**.^a



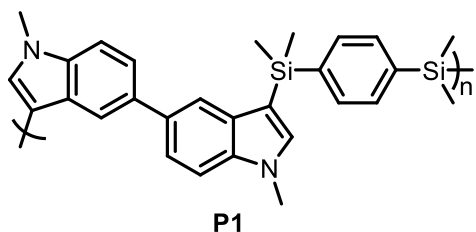
Entry	Concentration	Conv. ^b	Yield ^b
1	0.6 M	94%	34%
2	0.4 M	>99%	56%
3	0.2 M	>99%	70%
4	0.1 M	>99%	75%

^a Carried out in C_6D_6 (500 μL) under argon in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ at 120°C for 2.5h. $[\text{B}(\text{C}_6\text{F}_5)_3]/[\mathbf{2d}] = 5\%$. ^b Conversion and yields were determined by ^1H NMR spectroscopy.

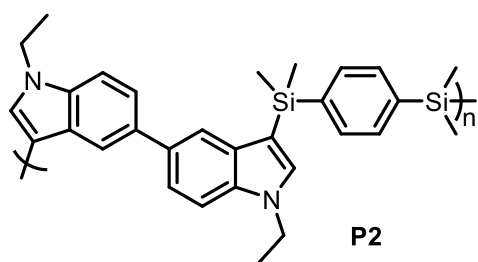
4. Synthesis and characterization of polymers

All the polymerizations were carried out under argon atmosphere using a standard Schlenk technique. A typical procedure for the polymerization of **1a** and **2a**

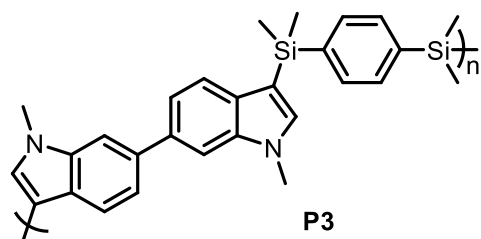
is given below as an example. A 10 mL Schlenk tube equipped with a magnetic stirrer were added with **1a** (130.2 mg, 0.5 mmol), **2a** (97.2 mg, 0.5 mmol), $B(C_6F_5)_3$ (12.8 mg, 0.025 mmol) and 0.5 mL of toluene in a glovebox. The Schlenk tube was taken out of the glovebox, and the reaction mixture was stirred at 120°C for 72 h. Afterward, the system was cooled down to RT, and poured into 20 mL of hexane under vigorously stirring. The precipitate was filtered, washed with hexane, and vacuum-dried at 50°C for 24 h to afford the polymer product. The polymerizations of other monomers adopted the same procedure under varied conditions.



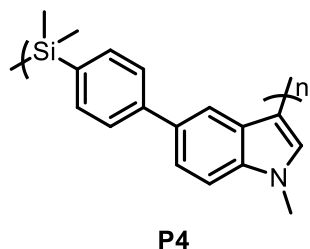
1H NMR (500 MHz, $CDCl_3$) δ 7.91 (2H, H_{Ar}), 7.66 (4H, H_{Ar}), 7.49 (2H, H_{Ar}), 7.36 (2H, H_{Ar}), 7.01 (2H, H_{Ar}), 3.71 (6H, NCH_3), 0.66 (12H, $SiCH_3$). ^{13}C $\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.0, 137.6, 136.9, 134.4, 133.4, 122.0, 120.7, 109.5, 107.2, 32.8, -1.3.



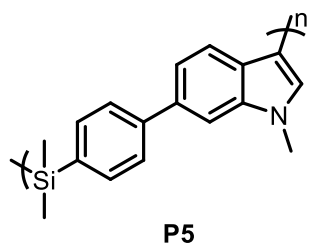
1H NMR (500 MHz, $CDCl_3$) δ 7.90 (2H, H_{Ar}), 7.64 (4H, H_{Ar}), 7.47 (2H, H_{Ar}), 7.37 (2H, H_{Ar}), 7.06 (2H, H_{Ar}), 4.10 (4H, NCH_2), 1.43 (6H, CH_2CH_3), 0.63 (12H, $SiCH_3$). ^{13}C $\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 136.6, 135.2, 134.5, 133.7, 133.4, 133.1, 121.8, 120.9, 109.5, 107.2, 41.1, 15.4, -1.3.



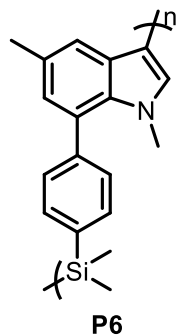
^1H NMR (500 MHz, CDCl_3) δ 7.68, (2H, H_{Ar}), 7.65 (4H, H_{Ar}), 7.57 (2H, H_{Ar}), 7.45 (2H, H_{Ar}), 7.05 (2H, H_{Ar}), 3.80 (6H, NCH_3), 0.64 (12H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 140.0, 139.1, 136.8, 136.6, 133.4, 131.8, 122.1, 119.9, 108.3, 106.8, 32.8, -1.3.



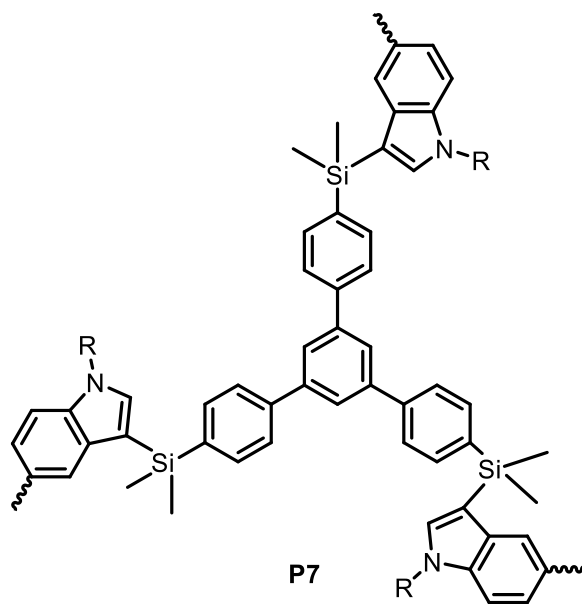
^1H NMR (500 MHz, CDCl_3) δ 7.89, (1H, H_{Ar}), 7.70 (2H, H_{Ar}), 7.63 (2H, H_{Ar}), 7.53 (1H, H_{Ar}), 7.40 (1H, H_{Ar}), 7.09 (2H, H_{Ar}), 3.81 (3H, NCH_3), 0.69 (6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 143.2, 138.2, 137.1, 136.6, 134.5, 133.0, 126.9, 121.5, 120.7, 109.6, 107.7, 32.9, -1.1.



^1H NMR (500 MHz, CDCl_3) δ 7.71, (5H, H_{Ar}), 7.58 (1H, H_{Ar}), 7.41 (1H, H_{Ar}), 7.13 (1H, H_{Ar}), 3.86 (3H, NCH_3), 0.70 (6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 143.0, 139.1, 137.1, 134.5, 133.5, 132.4, 126.9, 122.2, 119.4, 108.0, 107.0, 100.8, 32.9, -1.2.



^1H NMR (500 MHz, CDCl_3) δ 7.70, (2H, H_{Ar}), 7.47 (3H, H_{Ar}), 7.01 (1H, H_{Ar}), 6.93 (1H, H_{Ar}), 3.35 (3H, NCH_3), 2.43 (3H, CH_3), 0.69 (6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 140.8, 138.8, 138.1, 134.3, 134.1, 133.4, 129.4, 128.3, 126.8, 125.9, 121.0, 106.1, 36.8, 21.3, -1.2.



^1H NMR (500 MHz, CDCl_3) δ 7.74 (6H, H_{Ar}), 7.43 (2H, H_{Ar}), 7.08 (1H, H_{Ar}), 3.72 (3H, NCH_3), 0.70 (6H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 142.3, 141.6, 138.6, 137.6, 136.9, 134.7, 133.5, 126.8, 125.2, 122.0, 120.8, 109.5, 107.1, 101.2, 32.8, -1.1.

5. FT-IR spectra of polymers

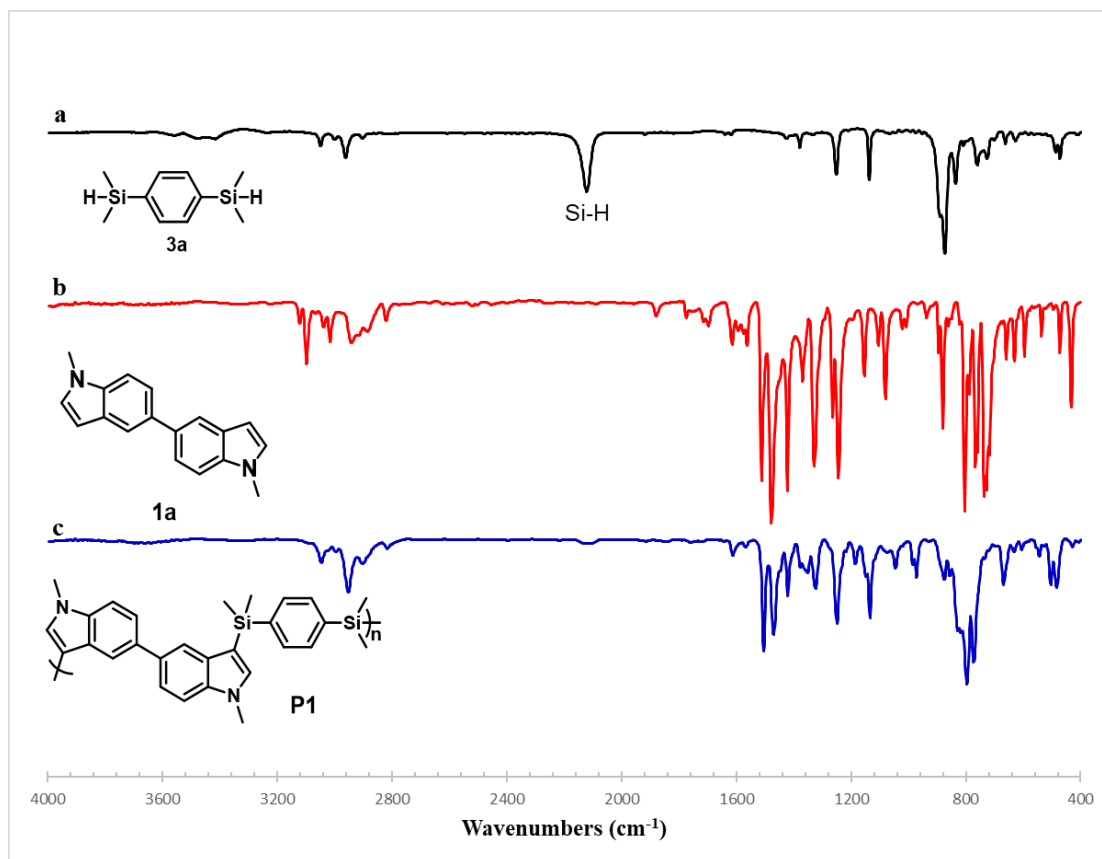


Figure S1. FT-IR spectra of (a) 3a, (b) 1a, and (c) P1.

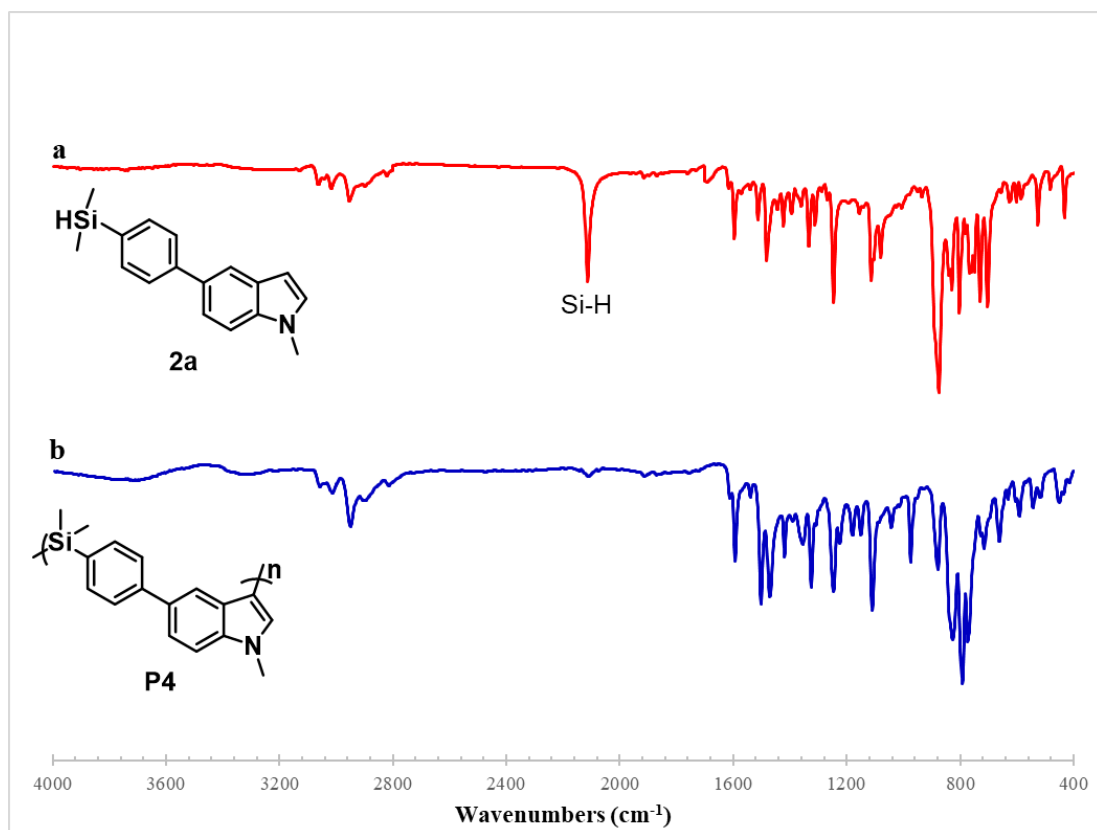


Figure S2. FT-IR spectra of (a) 2a and (b) P4.

6. X-ray single-crystal structure of MC1 and MC3.

Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120°C/10⁻⁶ Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on F^2 for all reflections (*SHELXTL*, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions (Sheldrick, G. M. *Acta Crystallogr., Sect. A.* **1990**, *46*, 467–473 & **2008**, *64*, 112–122.).

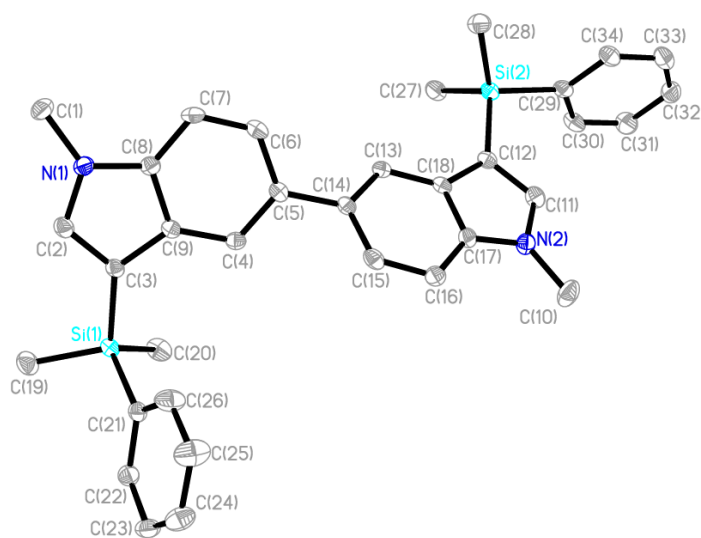


Figure S3. X-ray crystal structure of 3,3'-bis(dimethyl(phenyl)silyl)-1,1'-dimethyl-5,5'-biindole (**MC1**). Hydrogen and fluorine atoms are omitted for clarity and ellipsoids drawn at 50% probability.

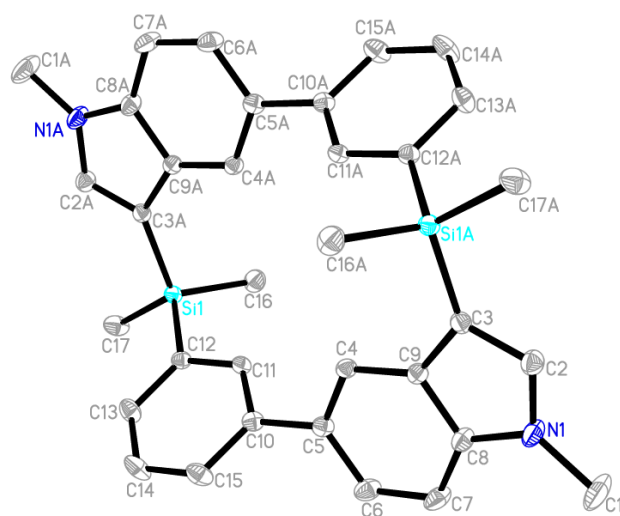


Figure S4. X-ray crystal structure of 3,3'-bis(dimethyl(phenyl)silyl)-1,1'-dimethyl-5,5'-biindole (**MC3**). Hydrogen and fluorine atoms are omitted for clarity and ellipsoids drawn at 50% probability.

Table S2. Crystal data and structure refinement for **MC1** (CCDC 2167809) and **MC3** (CCDC 2167804).

Identification code	MC1	MC3
empirical formula	C ₃₄ H ₃₆ N ₂ Si ₂	C ₃₄ H ₃₄ N ₂ Si ₂ , CCl ₃
MW	528.83	645.17
wavelength, Å	0.71073	0.71073
crystal system	Triclinic	monoclinic
space group	P-1	C2/c
a, Å	8.4884(6)	25.255(2)
b, Å	11.5493(9)	9.0380(6)
c, Å	15.4564(12)	16.9105(17)
α, deg	89.802(2)	90.00
β, deg	82.731(2)	120.591(5)
γ, deg	77.808(2)	90.00
V, Å ³	1468.77(19)	3322.7(5)

Z	2	34
D _{calc} , g cm ⁻³	1.196	1.290
μ, mm ⁻¹	0.146	0.375
F(000)	564	2292.0
crystal size, mm	0.28×0.22×0.16	0.12×0.08×0.06
θ range, deg	1.33-28.37	5.14-56.5
limiting indices	-10≤h≤11	-33≤h≤33
	-15≤k≤15	-12≤k≤11
	-20≤l≤19	-22≤l≤22
reflections collected	10951	40811
independent reflection	7301	4104
	[R(int)= 0.0258]	[R(int)= 0.0257]
absorption correction	None	
data/restraints/para's	7301/0/349	4104/0/198
goodness-of-fit on F ²	1.010	1.046
final R indices	R ₁ =0.0484	R ₁ =0.0318
[I > 2σ(I)] ^[a]	wR ₂ = 0.1039	wR ₂ =0.0811
R indices (all data) ^[a]	R ₁ =0.0834	R ₁ = 0.0369
	wR ₂ =0.1178	wR ₂ = 0.0858
peak _{max} /hole _{min} (e Å ⁻³)	0.35 and -0.36	0.47 and -0.36

$$^{[a]} R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Table S3. Bond lengths [Å] and angles [°] for MC1.

C(1)-N(1)	1.447(2)	C(16)-C(18)	1.399(3)
C(2)-N(1)	1.372(2)	C(17)-C(18)	1.408(3)
C(2)-C(3)	1.378(3)	C(18)-N(2)	1.378(2)
C(3)-C(8)	1.453(3)	C(19)-Si(1)	1.862(2)
C(3)-Si(1)	1.854(2)	C(20)-Si(1)	1.869(2)
C(4)-C(5)	1.394(3)	C(21)-C(26)	1.396(3)
C(4)-C(8)	1.398(3)	C(21)-C(22)	1.401(3)
C(5)-C(6)	1.410(3)	C(21)-Si(1)	1.877(2)
C(5)-C(14)	1.492(3)	C(22)-C(23)	1.390(3)
C(6)-C(7)	1.378(3)	C(23)-C(24)	1.379(3)
C(7)-C(9)	1.397(3)	C(24)-C(25)	1.384(3)
C(8)-C(9)	1.417(3)	C(25)-C(26)	1.388(3)
C(9)-N(1)	1.379(2)	C(27)-Si(2)	1.866(2)
C(10)-N(2)	1.451(3)	C(28)-Si(2)	1.867(2)

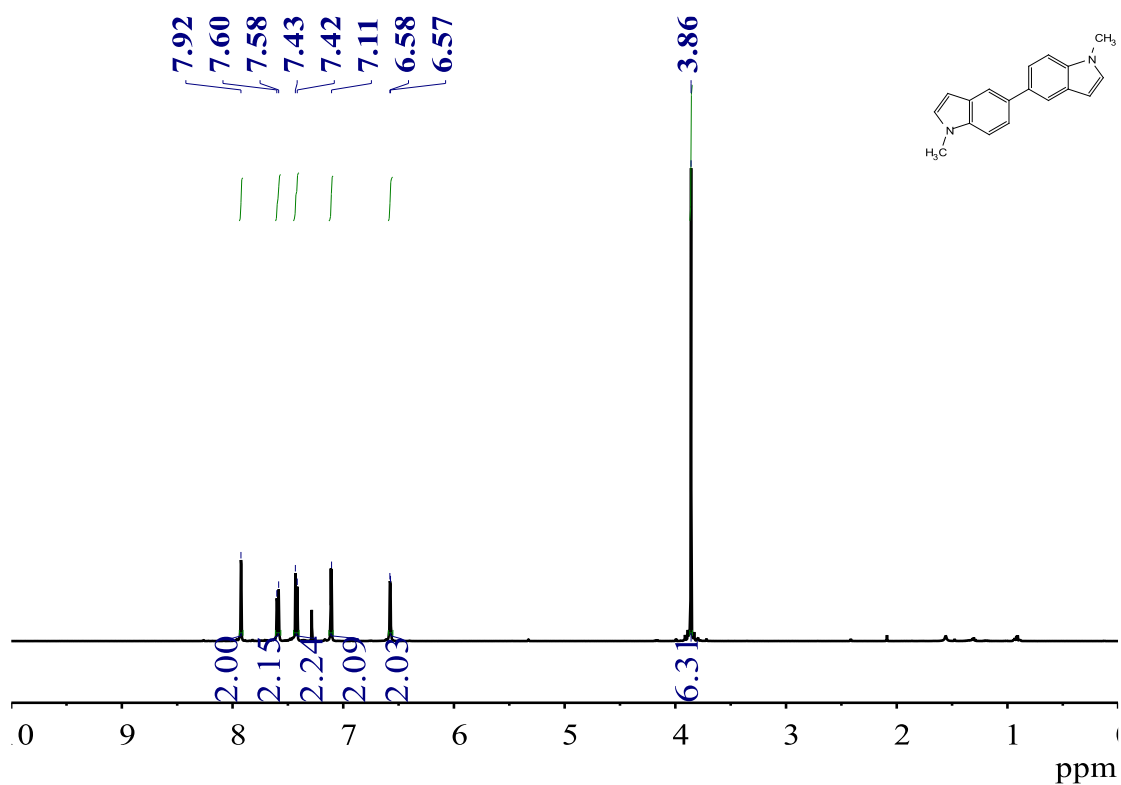
C(11)-N(2)	1.368(3)	C(29)-C(30)	1.400(3)
C(11)-C(12)	1.374(3)	C(29)-C(34)	1.401(3)
C(12)-C(17)	1.458(3)	C(29)-Si(2)	1.879(2)
C(12)-Si(2)	1.853(2)	C(30)-C(31)	1.384(3)
C(13)-C(14)	1.395(3)	C(31)-C(32)	1.378(3)
C(13)-C(17)	1.405(3)	C(32)-C(33)	1.383(3)
C(14)-C(15)	1.407(3)	C(33)-C(34)	1.388(3)
C(15)-C(16)	1.379(3)		
N(1)-C(2)-C(3)	111.97(17)	C(26)-C(21)-Si(1)	123.35(16)
C(2)-C(3)-C(8)	104.38(16)	C(22)-C(21)-Si(1)	119.96(15)
C(2)-C(3)-Si(1)	125.73(15)	C(23)-C(22)-C(21)	121.8(2)
C(8)-C(3)-Si(1)	128.80(14)	C(24)-C(23)-C(22)	119.9(2)
C(5)-C(4)-C(8)	120.19(17)	C(23)-C(24)-C(25)	119.7(2)
C(4)-C(5)-C(6)	119.38(17)	C(24)-C(25)-C(26)	120.0(2)
C(4)-C(5)-C(14)	119.45(17)	C(25)-C(26)-C(21)	121.8(2)
C(6)-C(5)-C(14)	121.18(17)	C(30)-C(29)-C(34)	116.78(18)
C(7)-C(6)-C(5)	122.26(18)	C(30)-C(29)-Si(2)	121.49(15)
C(6)-C(7)-C(9)	117.42(17)	C(34)-C(29)-Si(2)	121.59(15)
C(4)-C(8)-C(9)	118.48(17)	C(31)-C(30)-C(29)	121.6(2)
C(4)-C(8)-C(3)	133.73(17)	C(32)-C(31)-C(30)	120.3(2)
C(9)-C(8)-C(3)	107.78(16)	C(31)-C(32)-C(33)	119.9(2)
N(1)-C(9)-C(7)	130.13(18)	C(32)-C(33)-C(34)	119.7(2)
N(1)-C(9)-C(8)	107.61(16)	C(33)-C(34)-C(29)	121.8(2)
C(7)-C(9)-C(8)	122.25(17)	C(2)-N(1)-C(9)	108.24(16)
N(2)-C(11)-C(12)	112.23(17)	C(2)-N(1)-C(1)	126.40(17)
C(11)-C(12)-C(17)	104.25(17)	C(9)-N(1)-C(1)	125.23(17)
C(11)-C(12)-Si(2)	122.89(15)	C(11)-N(2)-C(18)	107.93(16)
C(17)-C(12)-Si(2)	132.36(15)	C(11)-N(2)-C(10)	126.71(17)
C(14)-C(13)-C(17)	119.73(18)	C(18)-N(2)-C(10)	125.35(17)
C(13)-C(14)-C(15)	119.66(17)	C(3)-Si(1)-C(19)	109.14(9)
C(13)-C(14)-C(5)	121.46(18)	C(3)-Si(1)-C(20)	108.98(9)
C(15)-C(14)-C(5)	118.86(17)	C(19)-Si(1)-C(20)	109.65(10)
C(16)-C(15)-C(14)	122.47(18)	C(3)-Si(1)-C(21)	111.67(9)
C(15)-C(16)-C(18)	116.78(18)	C(19)-Si(1)-C(21)	107.78(10)
C(18)-C(17)-C(13)	118.30(17)	C(20)-Si(1)-C(21)	109.60(9)
C(18)-C(17)-C(12)	107.53(17)	C(12)-Si(2)-C(27)	112.73(9)
C(13)-C(17)-C(12)	134.17(18)	C(12)-Si(2)-C(28)	110.01(9)
N(2)-C(18)-C(16)	128.91(18)	C(27)-Si(2)-C(28)	108.55(10)
N(2)-C(18)-C(17)	108.05(16)	C(12)-Si(2)-C(29)	105.82(9)
C(16)-C(18)-C(17)	123.04(18)	C(27)-Si(2)-C(29)	109.76(9)
C(26)-C(21)-C(22)	116.69(19)	C(28)-Si(2)-C(29)	109.93(9)

Table S4. Bond lengths [Å] and angles [°] for MC3.

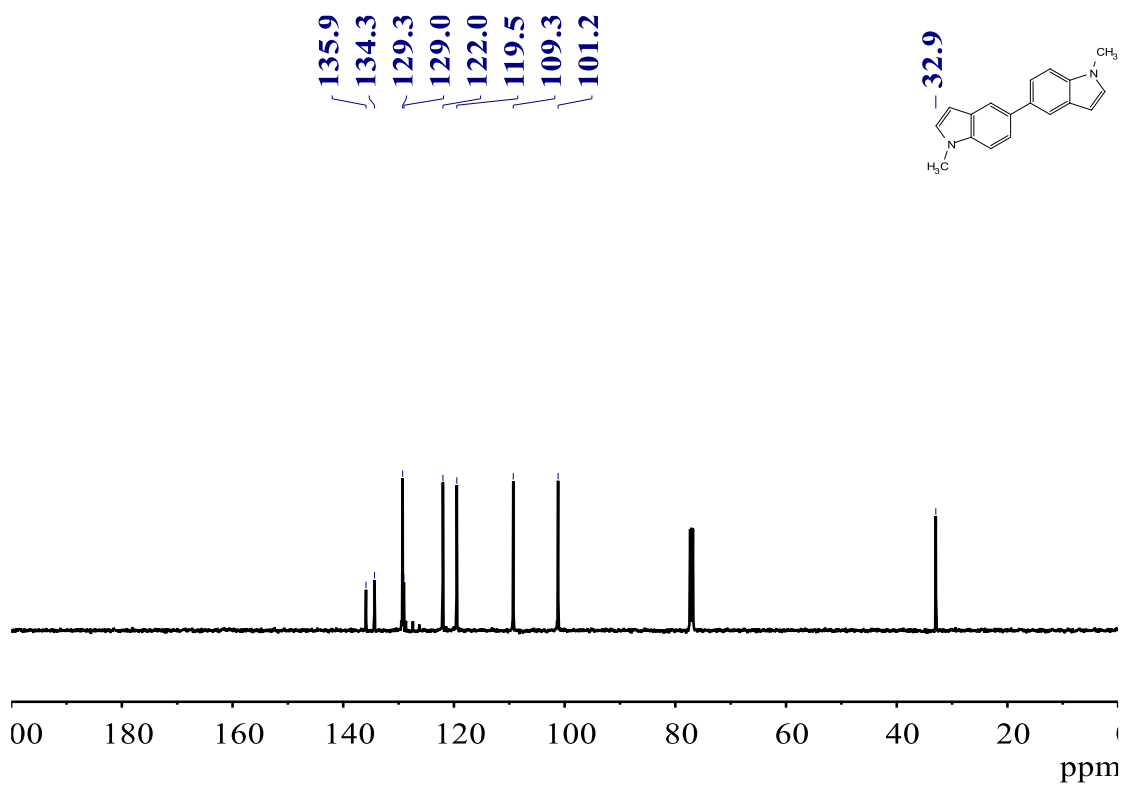
C(1)-N(1)	1.4524(17)	C(8)-C(9)	1.4127(17)
C(2)-C(3)	1.3798(17)	C(10)-C(11)	1.3976(16)
C(2)-N(1)	1.3728(17)	C(10)-C(15)	1.3966(17)
C(3)-C(9)	1.4480(16)	C(11)-C(12)	1.4033(16)
C(3)-Si(1)	1.8480(13)	C(12) ¹ -Si(1)	1.8804(12)
C(4)-C(5)	1.3902(16)	C(12) -Si(1) ¹	1.8805(12)
C(4)-C(9)	1.4080(16)	C(12) -C(13)	1.3997(17)
C(5)-C(6)	1.4132(17)	C(13) -C(14)	1.3915(18)
C(5)-C(10)	1.4876(16)	C(14) -C(15)	1.3908(18)
C(6)-C(7)	1.3826(18)	C(16) -Si(1)	1.8669(13)
C(7)-C(8)	1.3938(18)	C(17) -Si(1)	1.8731(14)
C(8)-N(1)	1.3784(16)		
<hr/>			
N(1)-C(2)-C(3)	111.38(11)	C(5)-C(10)-C(15)	120.86(11)
C(9)-C(3)-Si(1)	128.89(9)	C(10)-C(11)-C(12)	122.54(11)
C(2)-C(3)-Si(1)	126.16(9)	C(11)-C(12)-Si(1) ¹	121.69(9)
C(2)-C(3)-C(9)	104.79(11)	C(13)-C(12)-Si(1) ¹	120.94(9)
C(5)-C(4)-C(9)	119.66(11)	C(11)-C(12)-C(13)	117.26(11)
C(4)-C(5)-C(10)	120.10(11)	C(12)-C(13)-C(14)	121.18(11)
C(4)-C(5)-C(6)	119.90(11)	C(13)-C(14)-C(15)	120.29(12)
C(6)-C(5)-C(10)	120.00(11)	C(10)-C(15)-C(14)	120.28(12)
C(5)-C(6)-C(7)	121.92(12)	C(3)-Si(1)-C(12) ¹	111.96(5)
C(6)-C(7)-C(8)	117.32(12)	C(3)-Si(1)-C(17)	108.27(6)
N(1)-C(8)-C(9)	107.65(11)	C(3)-Si(1)-C(16)	108.93(6)
N(1)-C(8)-C(7)	129.62(12)	C(17)-Si(1)-C(12) ¹	108.76(6)
C(7)-C(8)-C(9)	122.67(11)	C(16)-Si(1)-C(12) ¹	108.58(6)
C(4)-C(9)-C(8)	118.48(11)	C(16)-Si(1)-C(17)	110.35(7)
C(3)-C(9)-C(8)	107.77(10)	C(2)-N(1)-C(8)	108.40(10)
C(3)-C(9)-C(4)	133.75(11)	C(2)-N(1)-C(1)	126.66(11)
C(5)-C(10)-C(11)	120.71(11)	C(8)-N(1)-C(1)	124.89(12)
C(15)-C(10)-C(11)	118.43(11)		

¹1/2-X,3/2-Y,1-Z.

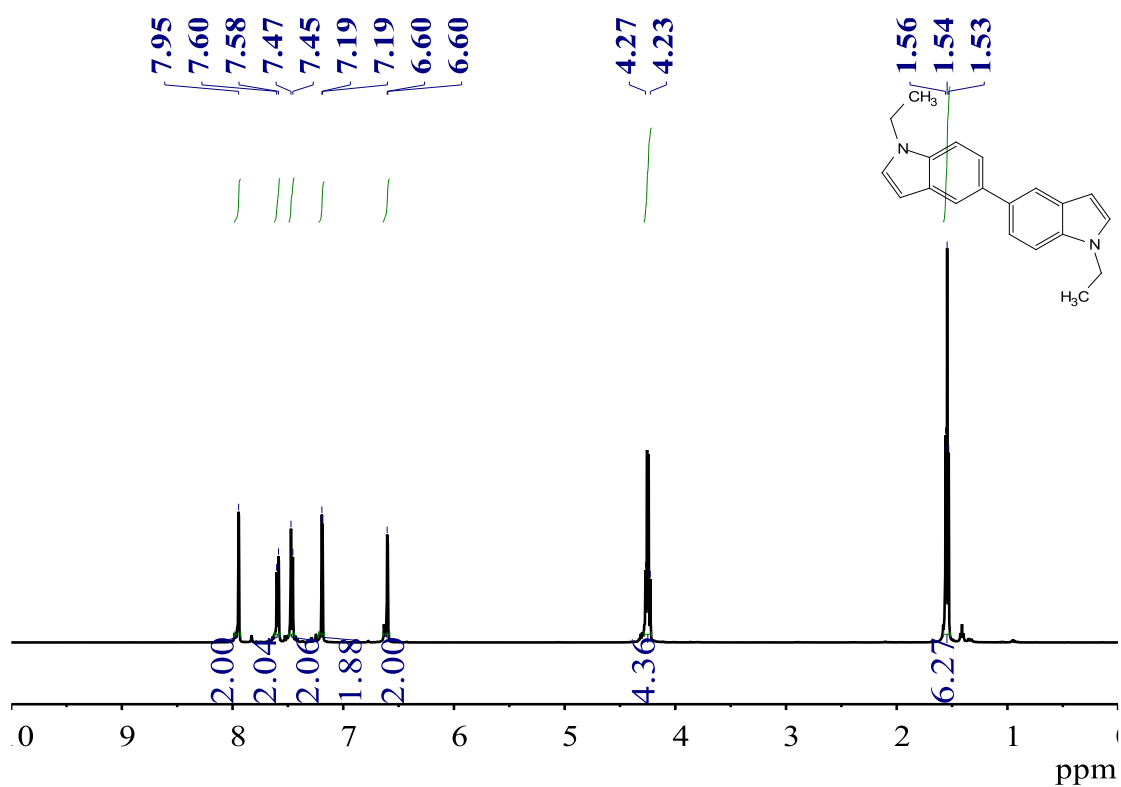
7. NMR spectra of compounds



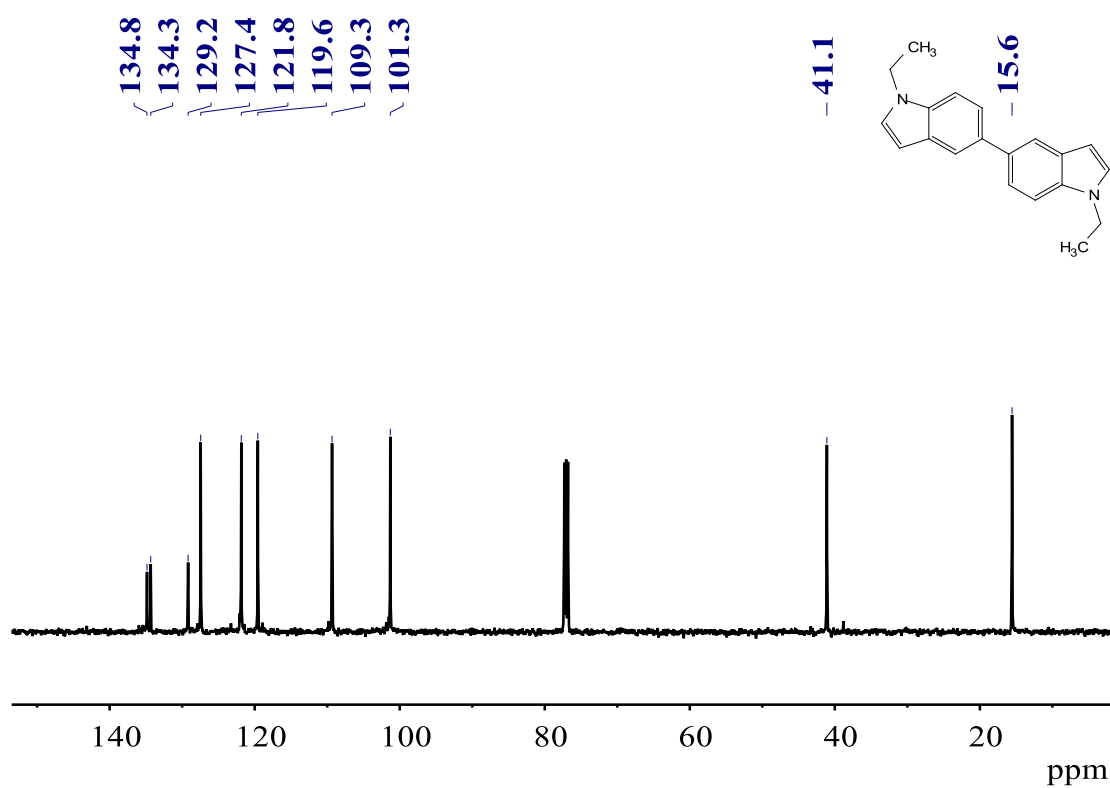
¹H NMR spectrum of 1,1'-dimethyl-5,5'-biindole (**1a**) (500 MHz, CDCl₃)



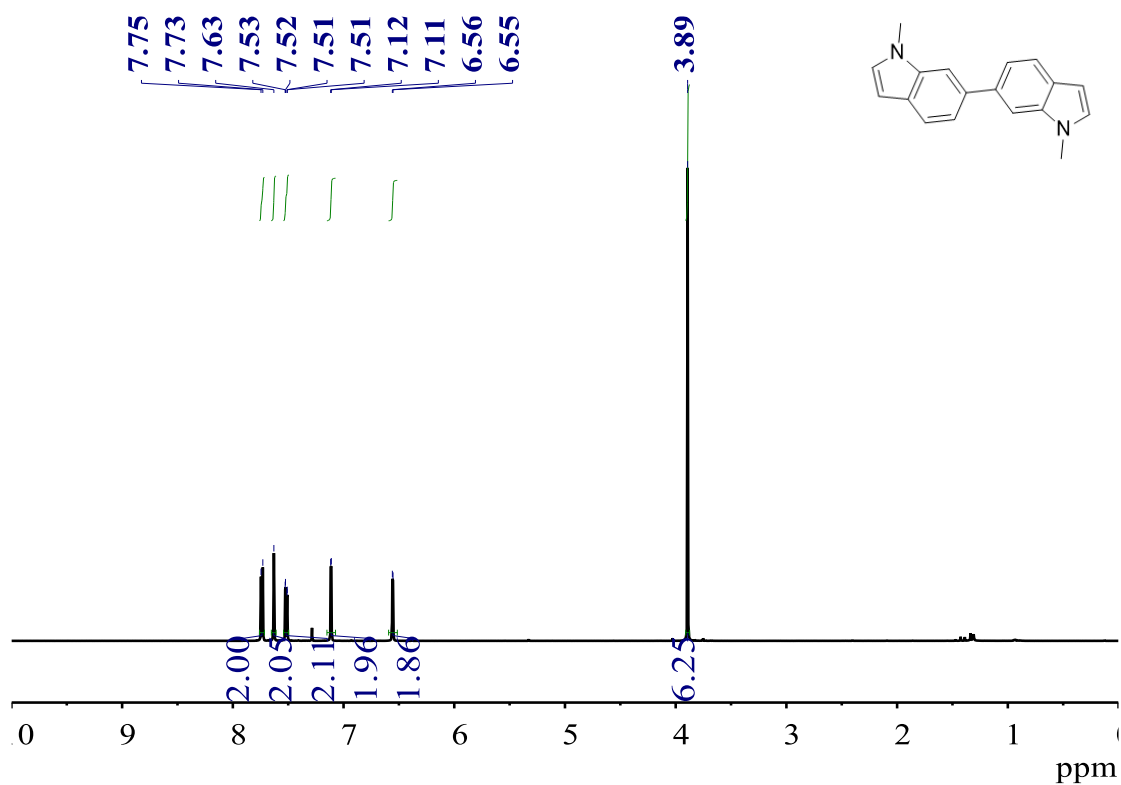
¹³C {¹H} NMR spectrum of 1,1'-dimethyl-5,5'-biindole (**1a**) (126 MHz, CDCl₃)



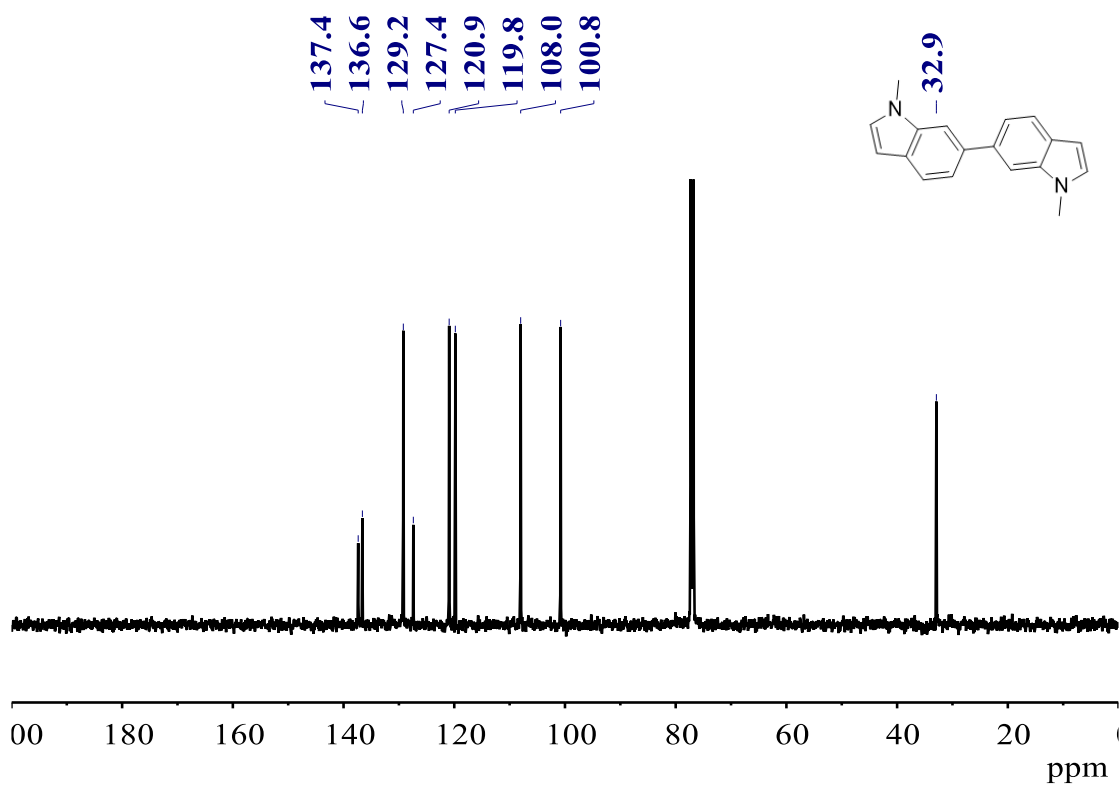
¹H NMR spectrum of 1,1'-diethyl-5,5'-biindole (**1b**) (500 MHz, CDCl₃)



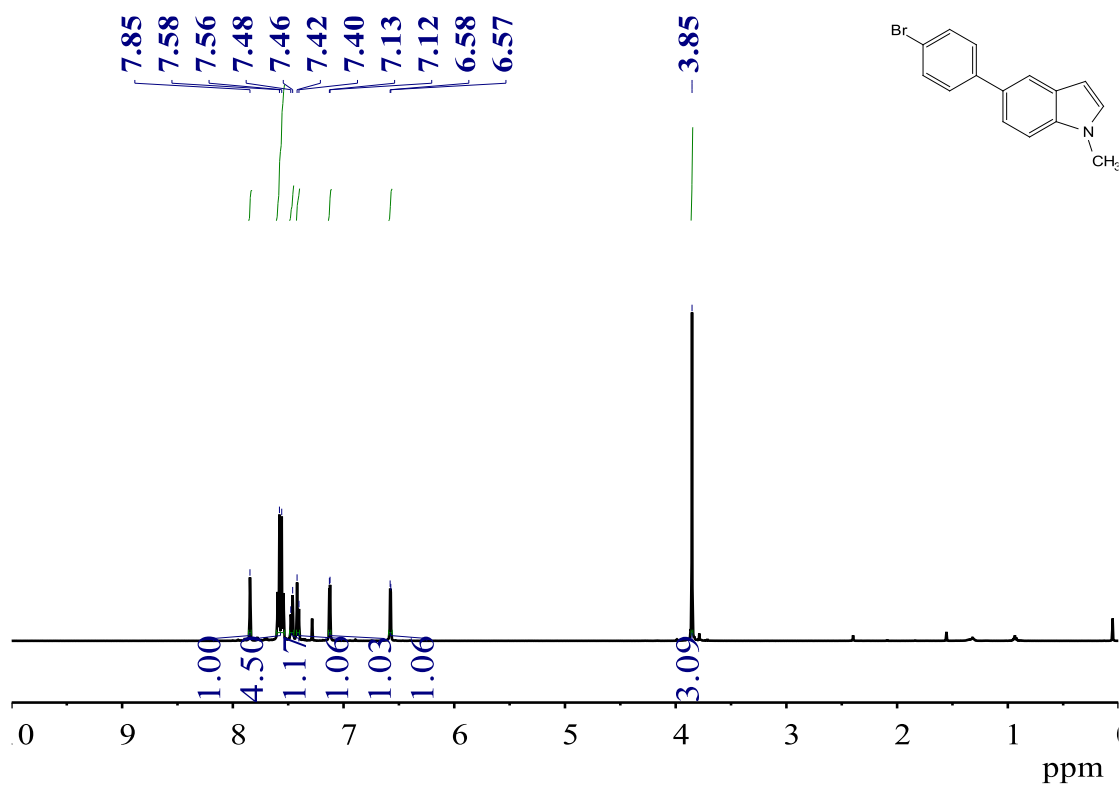
¹³C {¹H} NMR spectrum of 1,1'-diethyl-5,5'-biindole (**1b**) (126 MHz, CDCl₃)



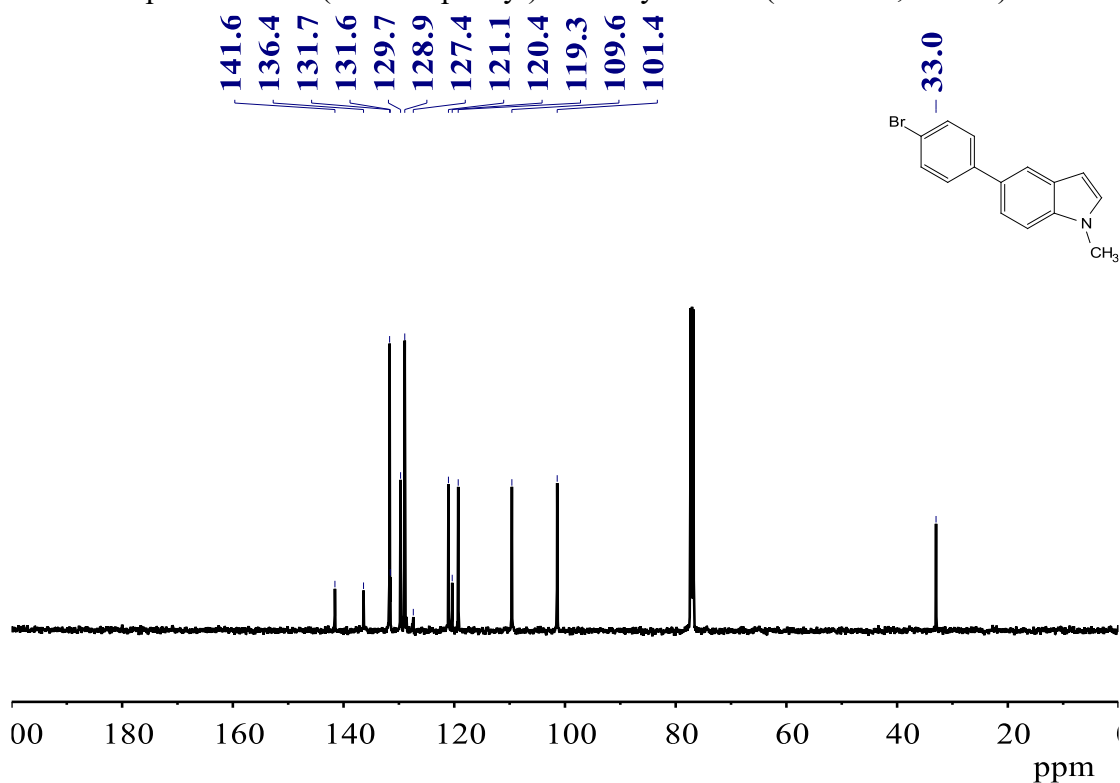
^1H NMR spectrum of 1,1'-dimethyl-6,6'-biindole (**1c**) (500 MHz, CDCl_3)



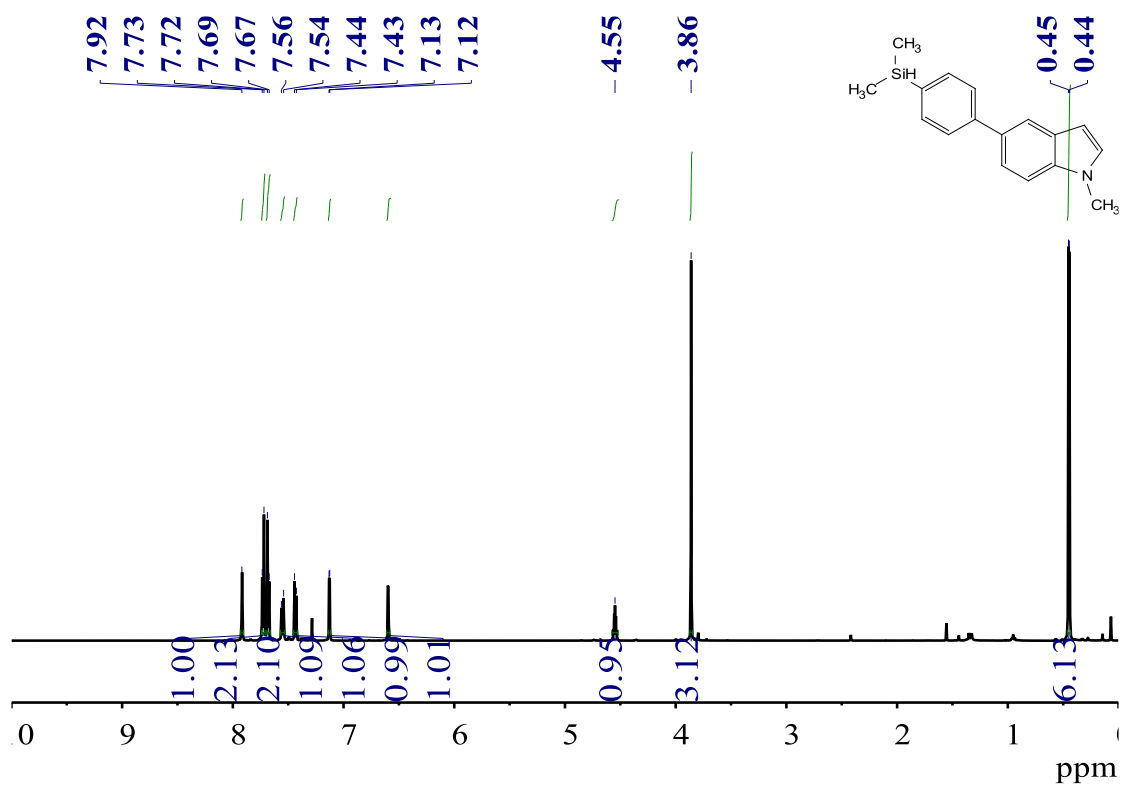
^{13}C $\{^1\text{H}\}$ NMR spectrum of 1,1'-diethyl-6,6'-biindole (**1c**) (126 MHz, CDCl_3)



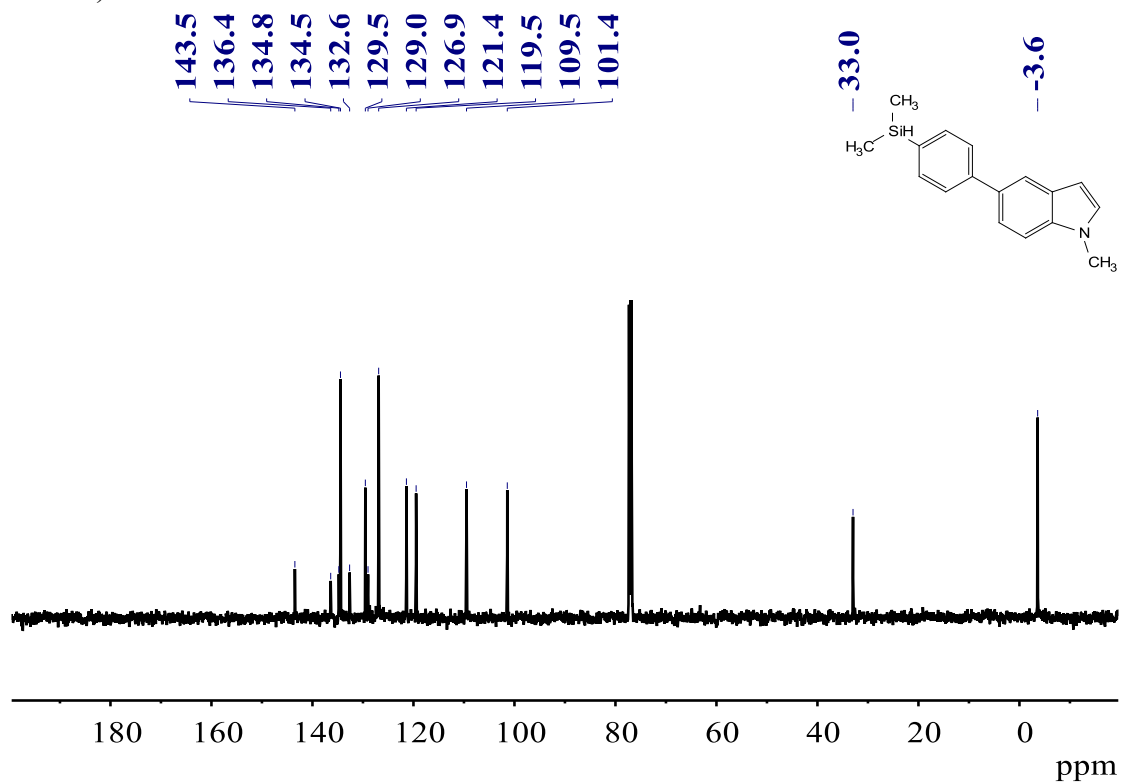
¹H NMR spectrum of 5-(4-bromophenyl)-1-methyl-indole (500 MHz, CDCl₃)



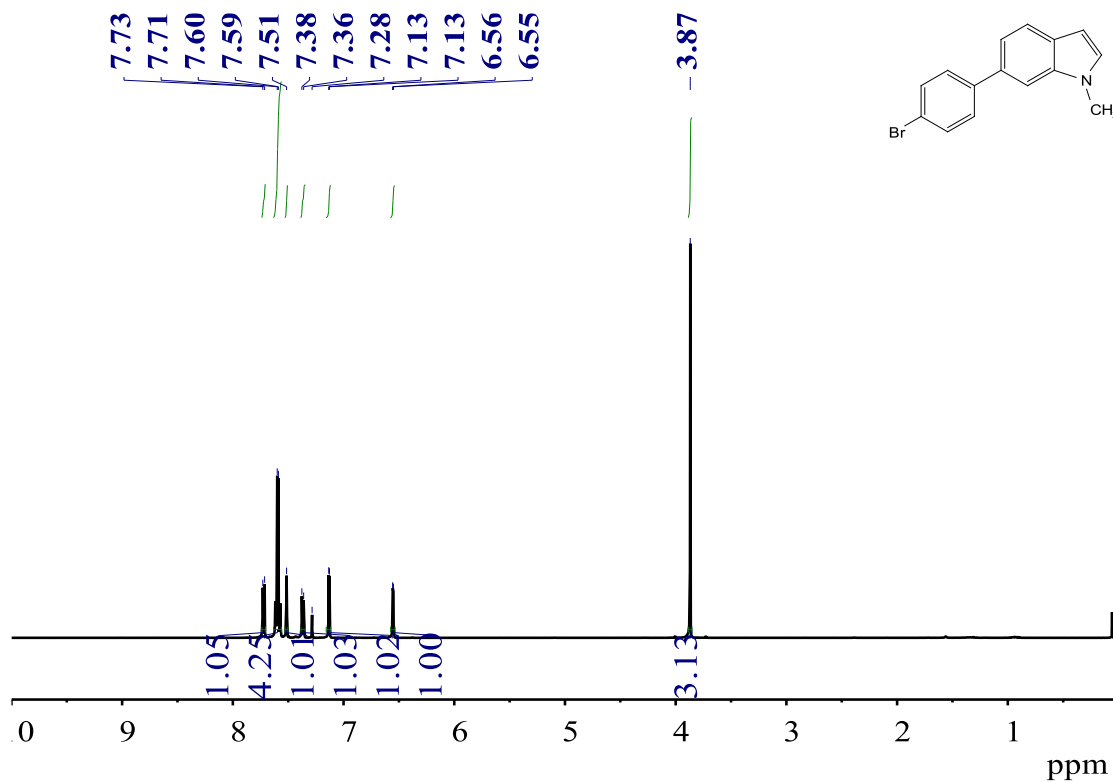
¹³C {¹H} NMR spectrum of 5-(4-bromophenyl)-1-methyl-indole (126 MHz, CDCl₃)



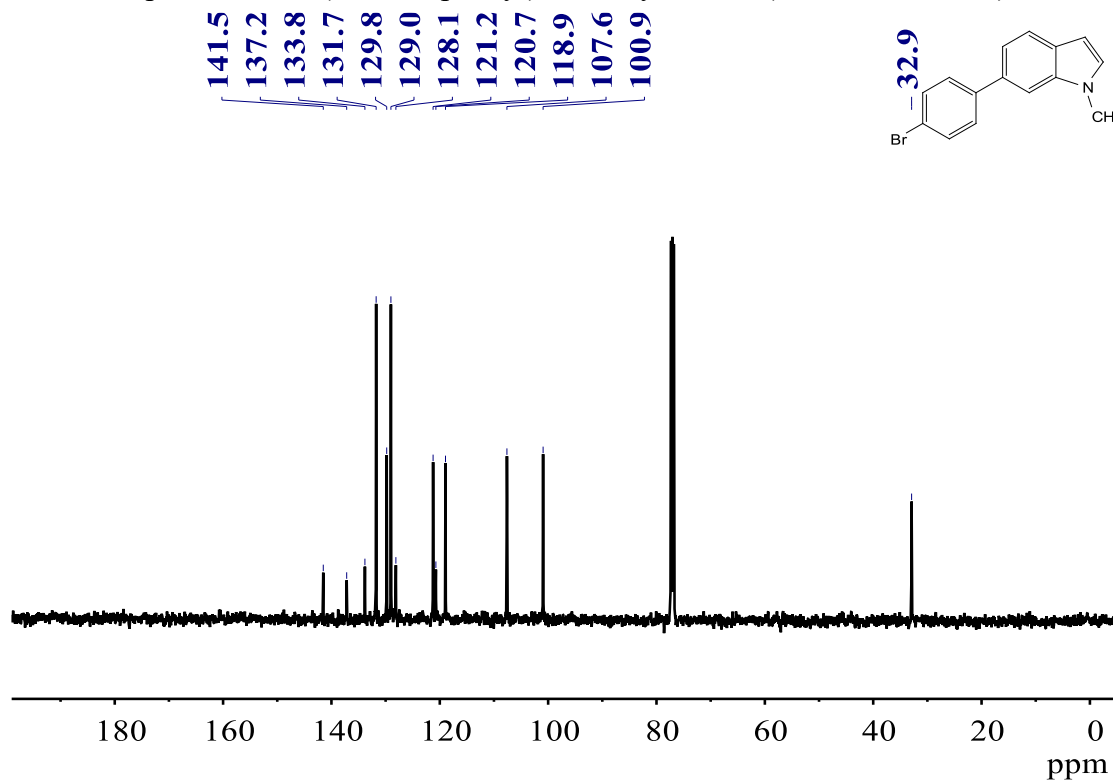
^1H NMR spectrum of 5-(4-(dimethylsilyl)phenyl)-1-methyl-indole (**2a**) (500 MHz, CDCl_3)



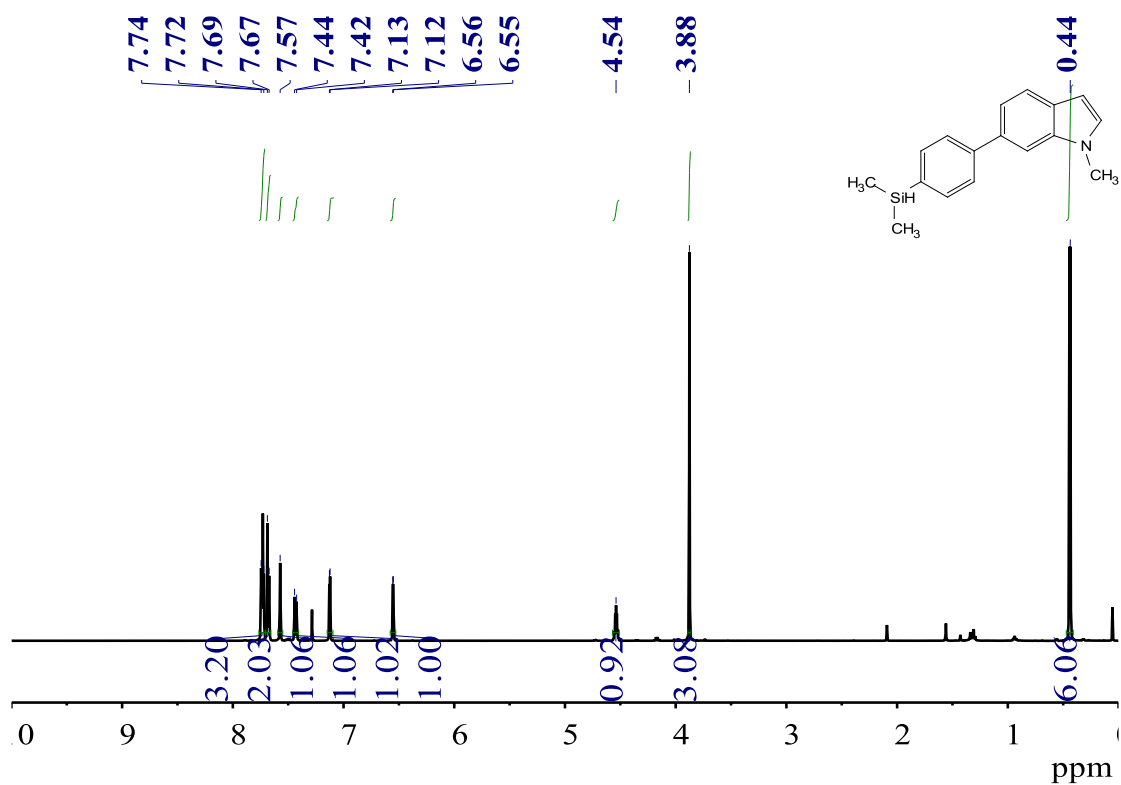
^{13}C $\{^1\text{H}\}$ NMR spectrum of 5-(4-(dimethylsilyl)phenyl)-1-methyl-indole (**2a**) (126 MHz, CDCl_3)



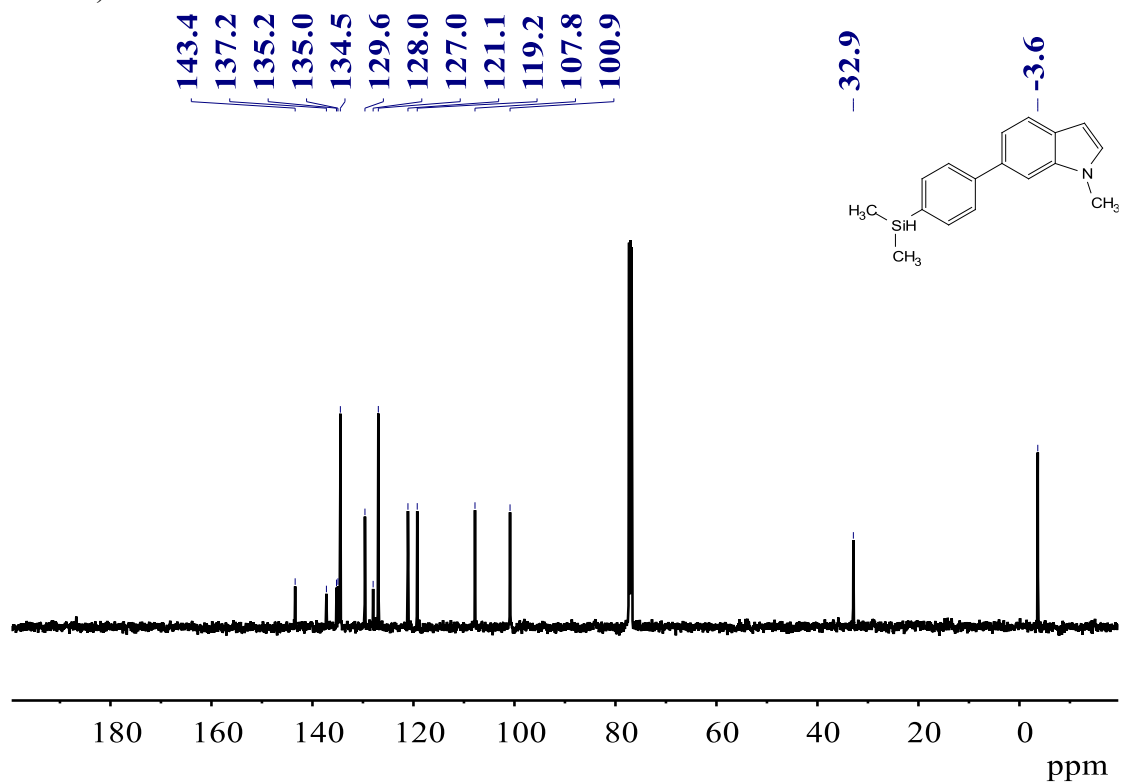
¹H NMR spectrum of 6-(4-bromophenyl)-1-methyl-indole (500 MHz, CDCl₃)



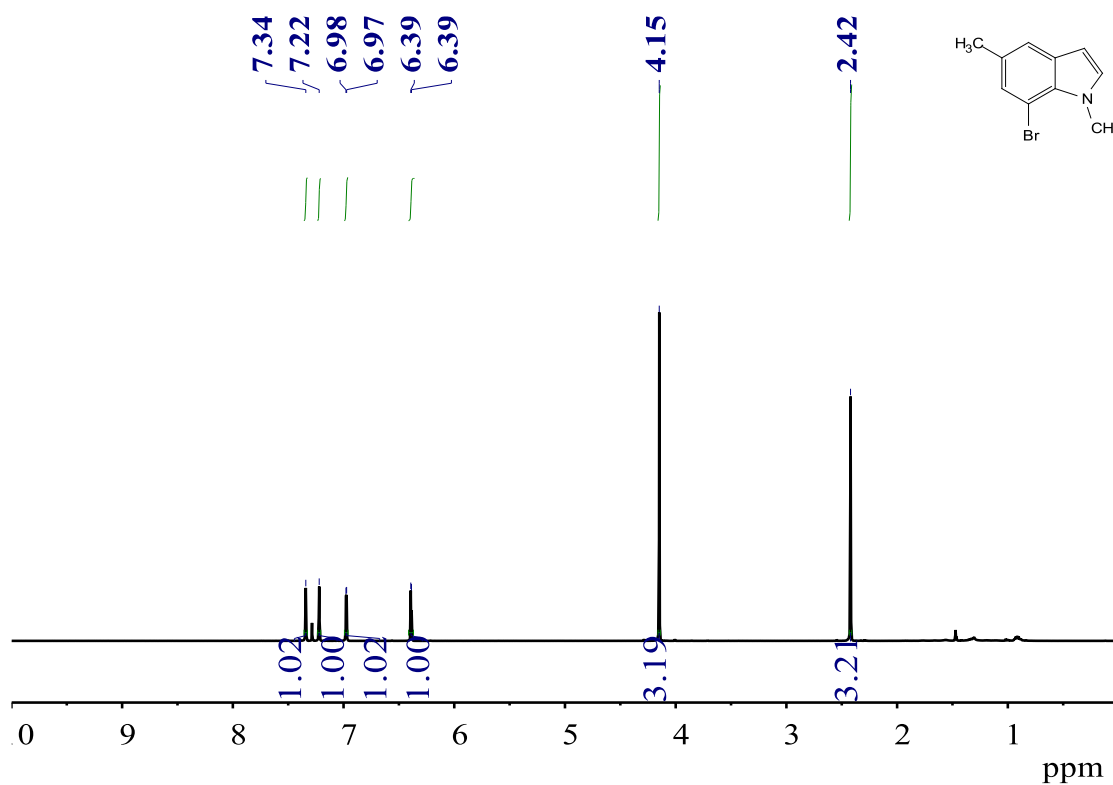
¹³C {¹H} NMR spectrum of 6-(4-bromophenyl)-1-methyl-indole (126 MHz, CDCl₃)



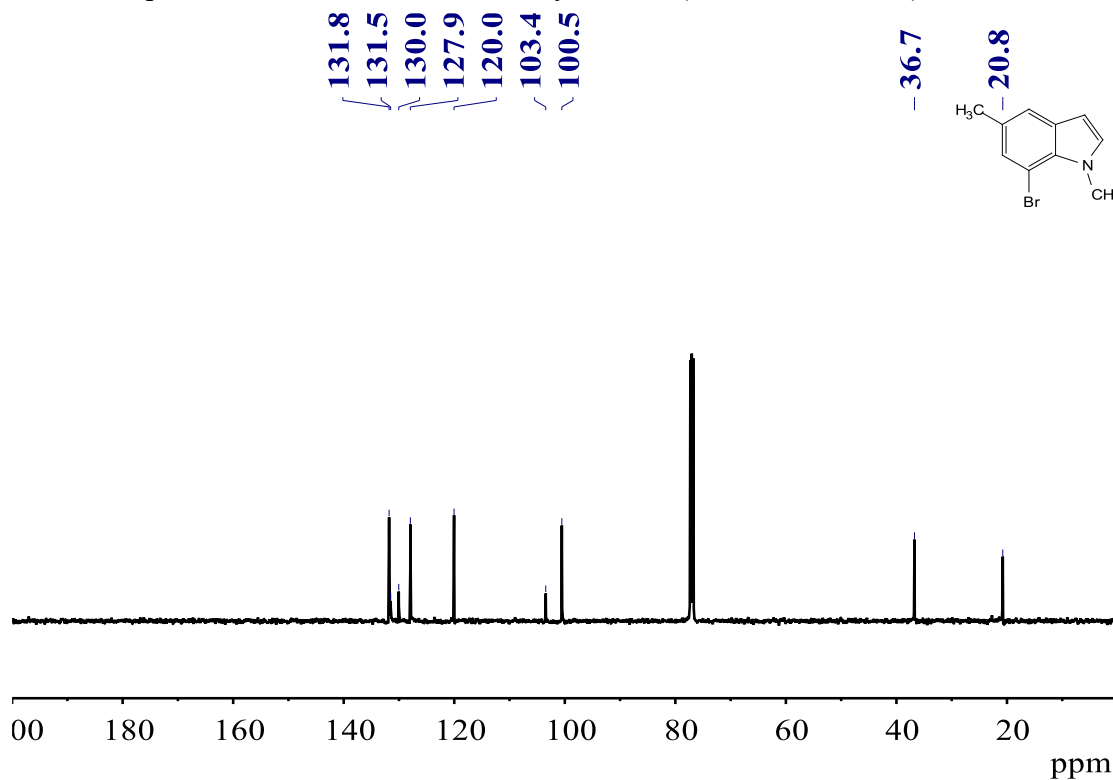
¹H NMR spectrum of 6-(4-(dimethylsilyl)phenyl)-1-methyl-indole (**2b**) (500 MHz, CDCl₃)



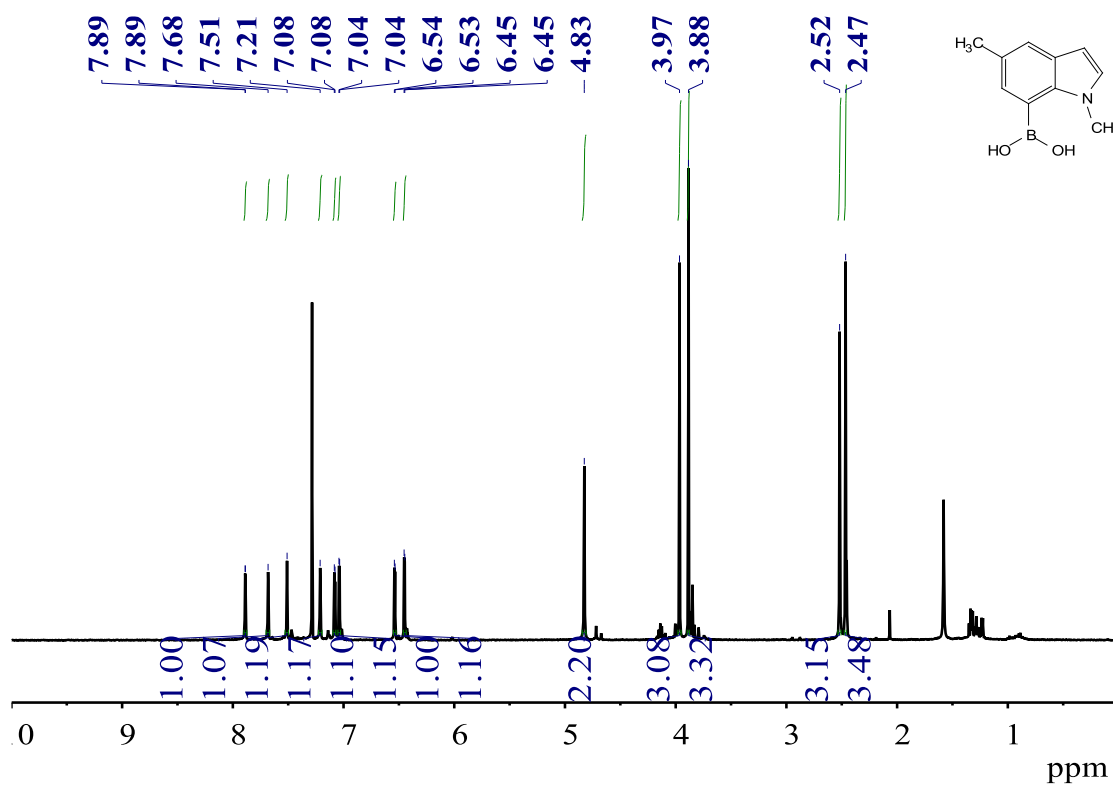
¹³C {¹H} NMR spectrum of 6-(4-(dimethylsilyl)phenyl)-1-methyl-indole (**2b**) (126 MHz, CDCl₃)



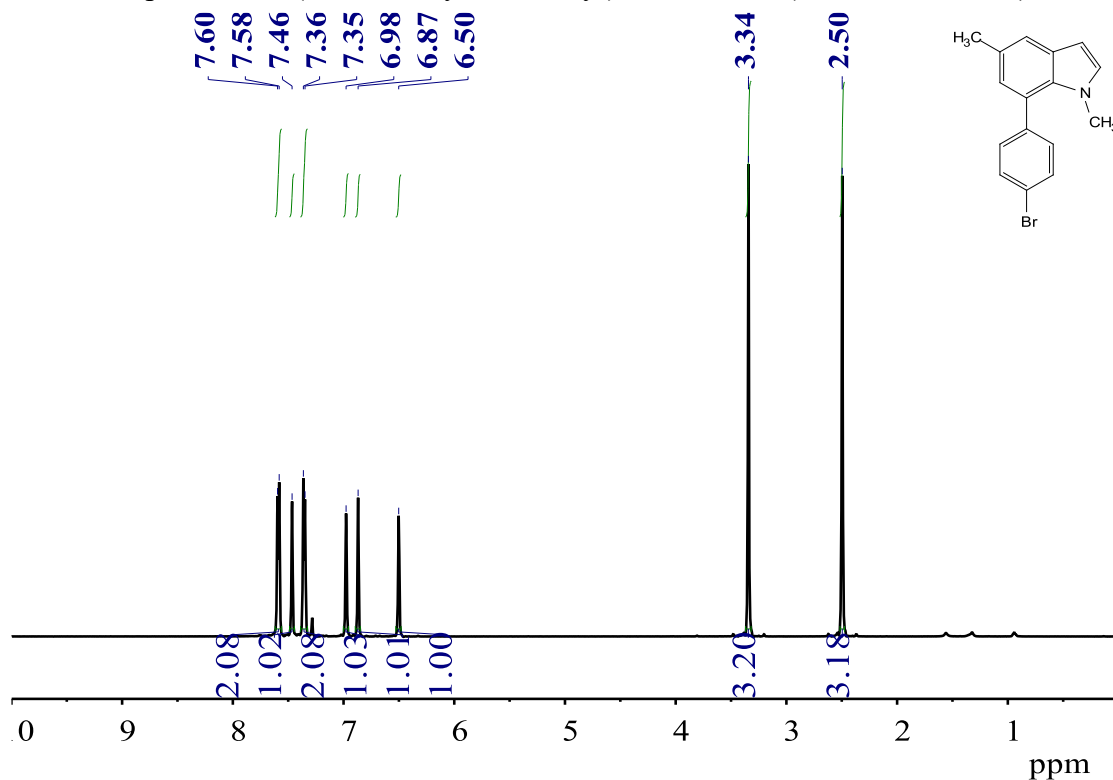
^1H NMR spectrum of 7-bromo-1,5-dimethyl-indole (500 MHz, CDCl_3)



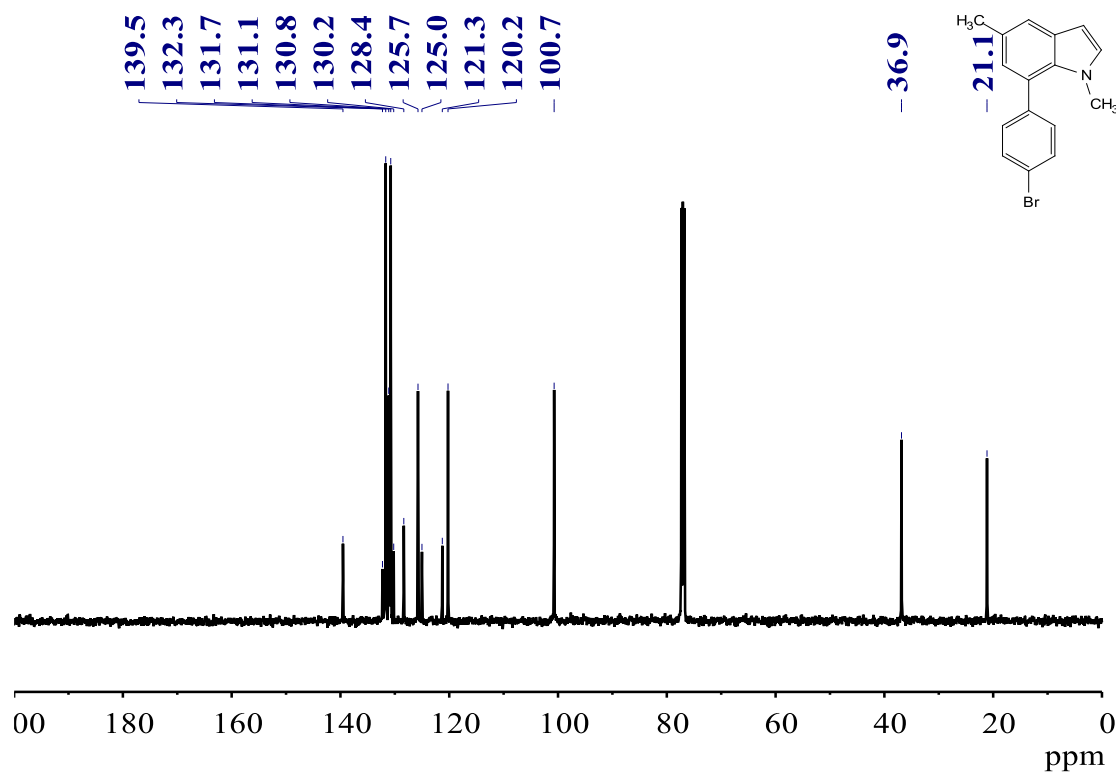
^{13}C $\{^1\text{H}\}$ NMR spectrum of 7-bromo-1,5-dimethyl-indole (126 MHz, CDCl_3)



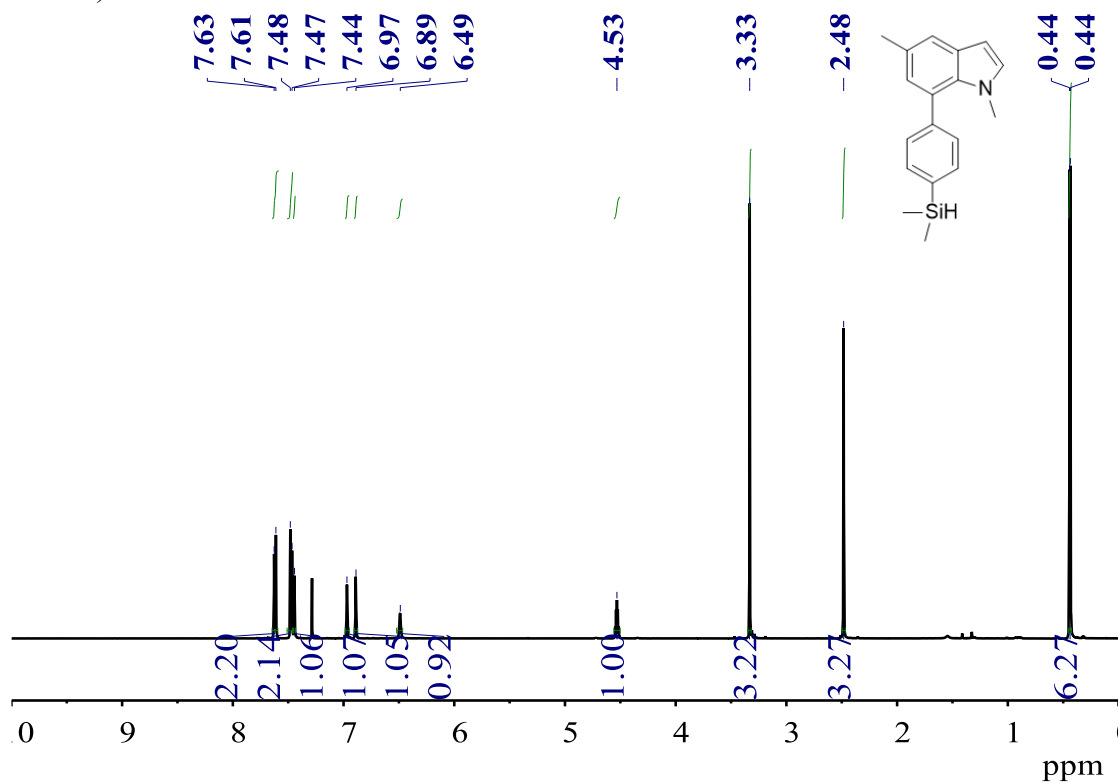
¹H NMR spectrum of (1,5-dimethyl-indol-7-yl)boronic acid (500 MHz, CDCl₃)



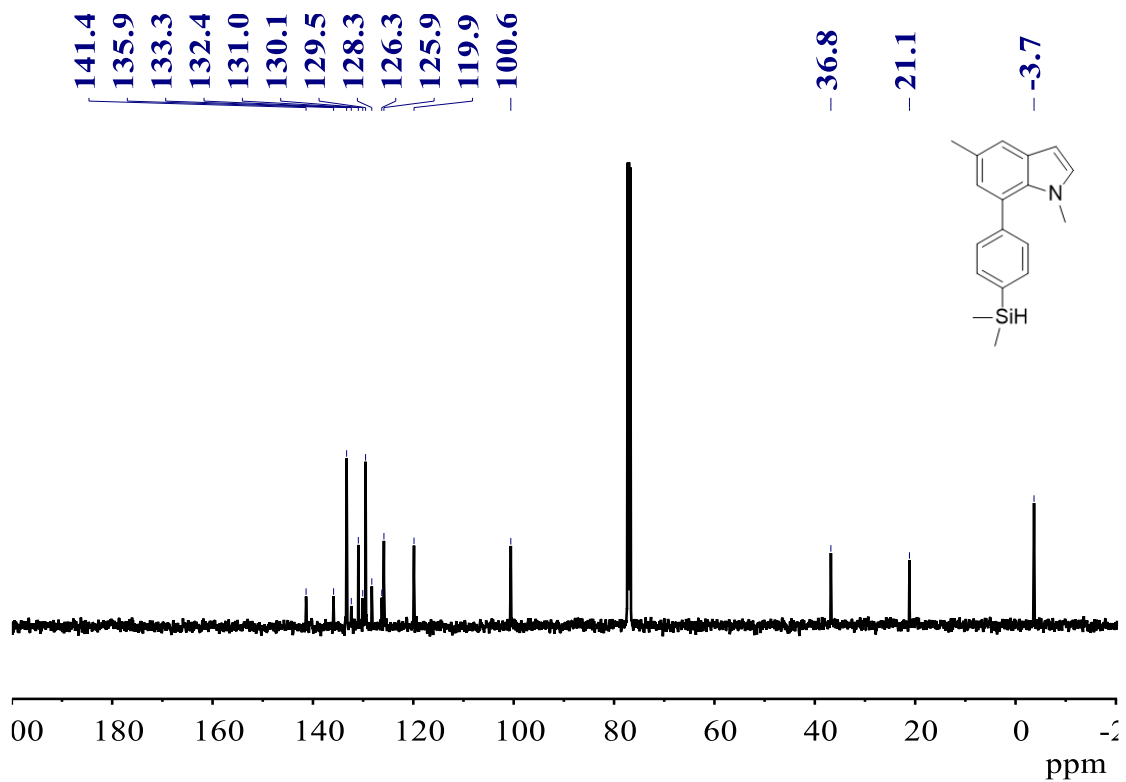
¹H NMR spectrum of 7-(4-bromophenyl)-1,5-dimethyl-indole (500 MHz, CDCl₃)



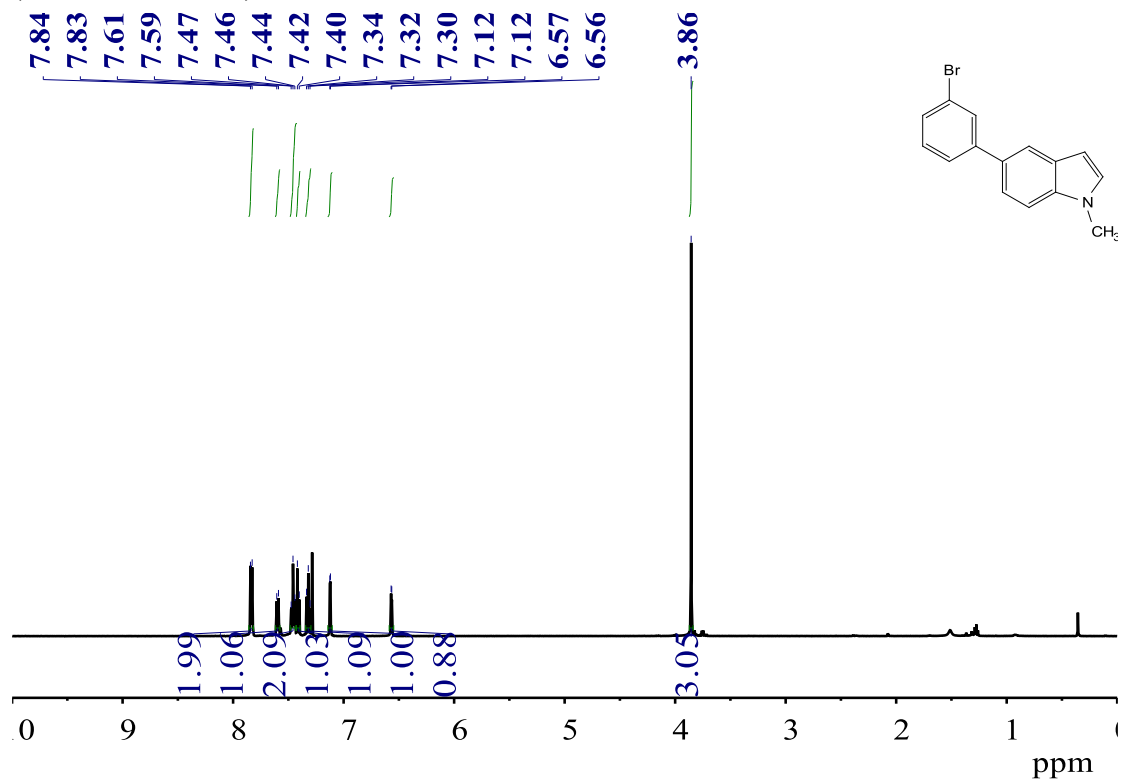
^{13}C $\{^1\text{H}\}$ NMR spectrum of 7-(4-bromophenyl)-1,5-dimethyl-indole (126 MHz, CDCl_3)



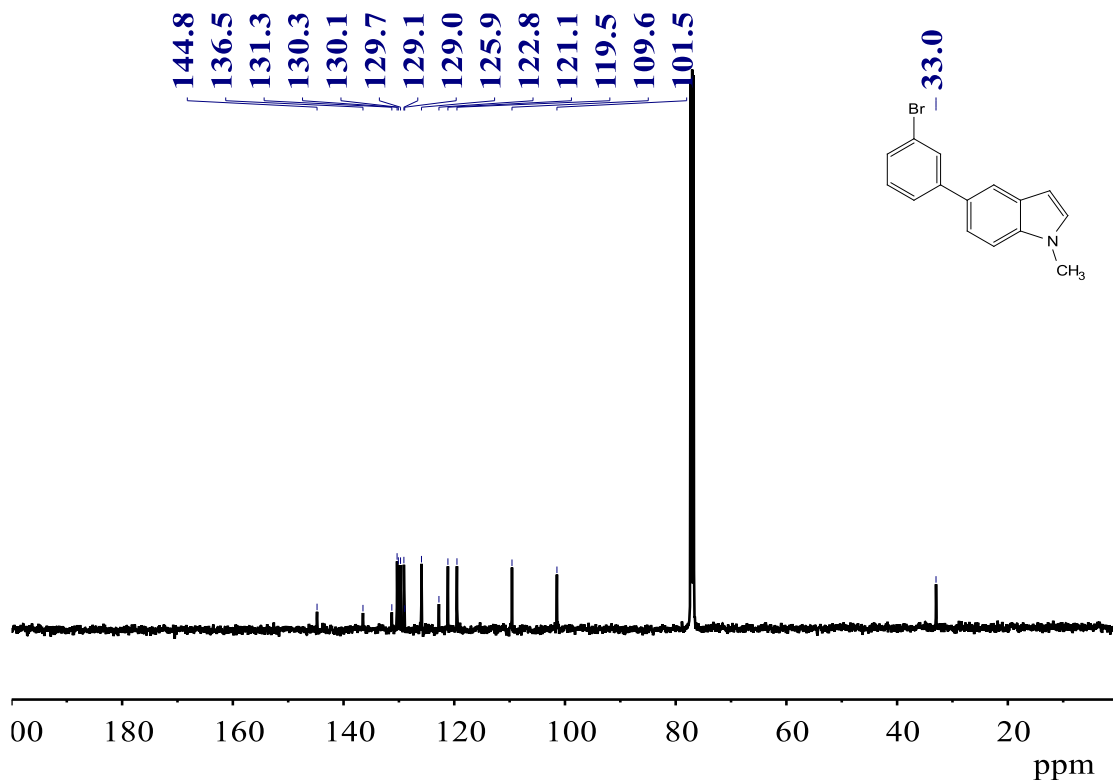
^1H NMR spectrum of 7-(4-(dimethylsilyl)phenyl)-1,5-dimethyl-indole (**2c**) (500 MHz, CDCl_3)



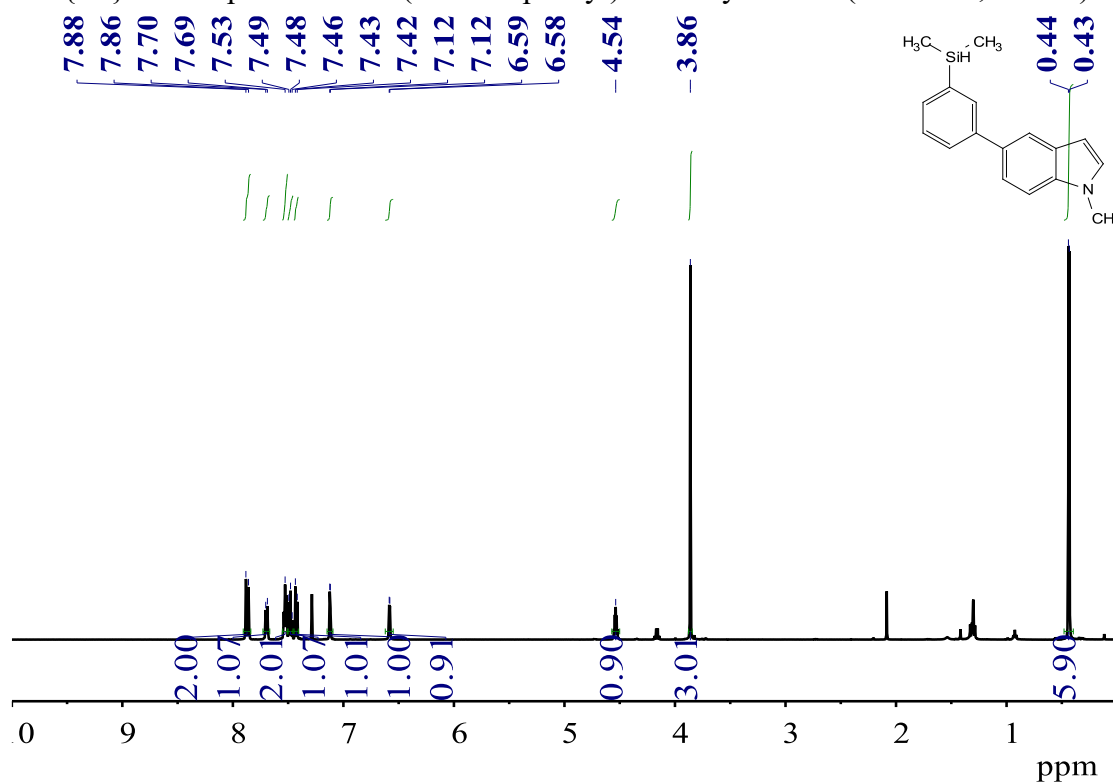
^{13}C $\{^1\text{H}\}$ NMR spectrum of 7-(4-(dimethylsilyl)phenyl)-1,5-dimethyl-indole (**2c**) (126 MHz, CDCl_3)



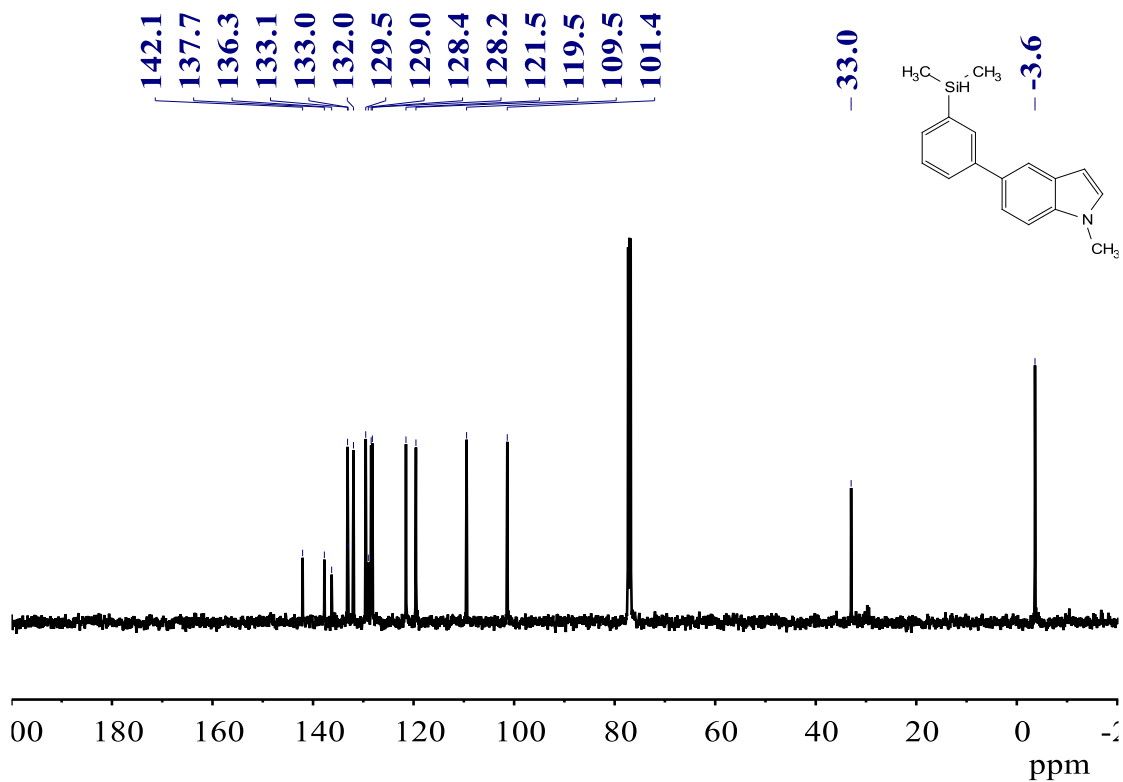
^1H NMR spectrum of 5-(3-bromophenyl)-1-methyl-indole (500 MHz, CDCl_3)



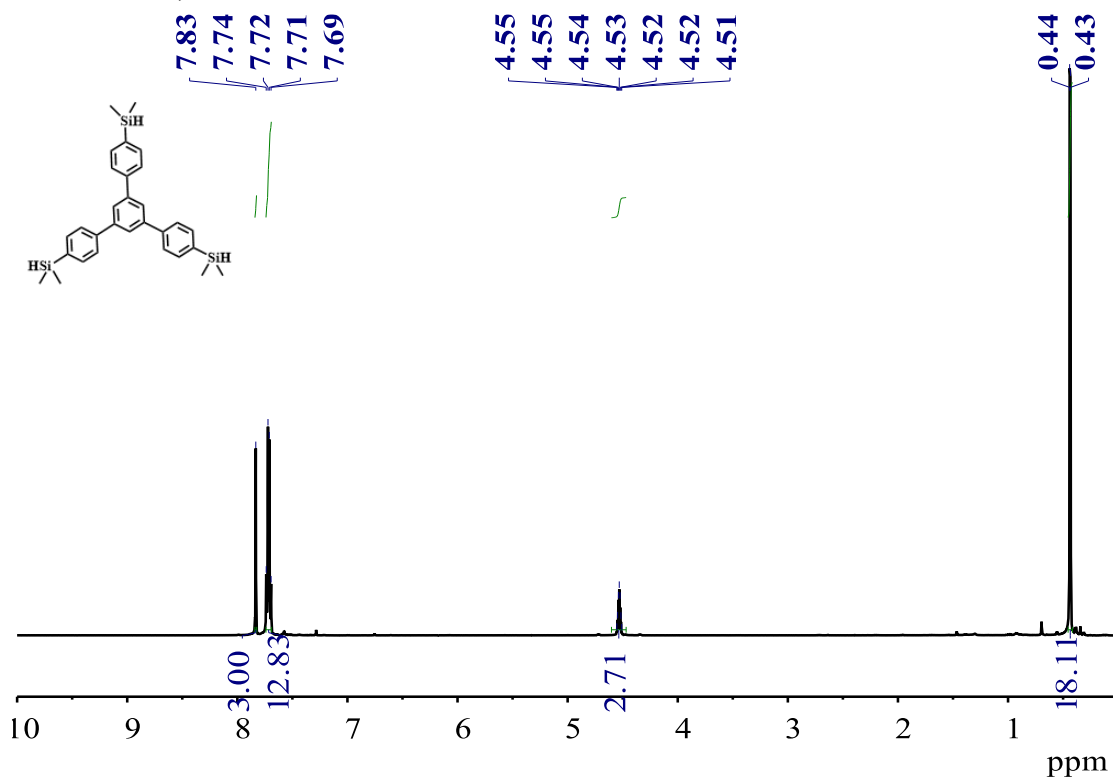
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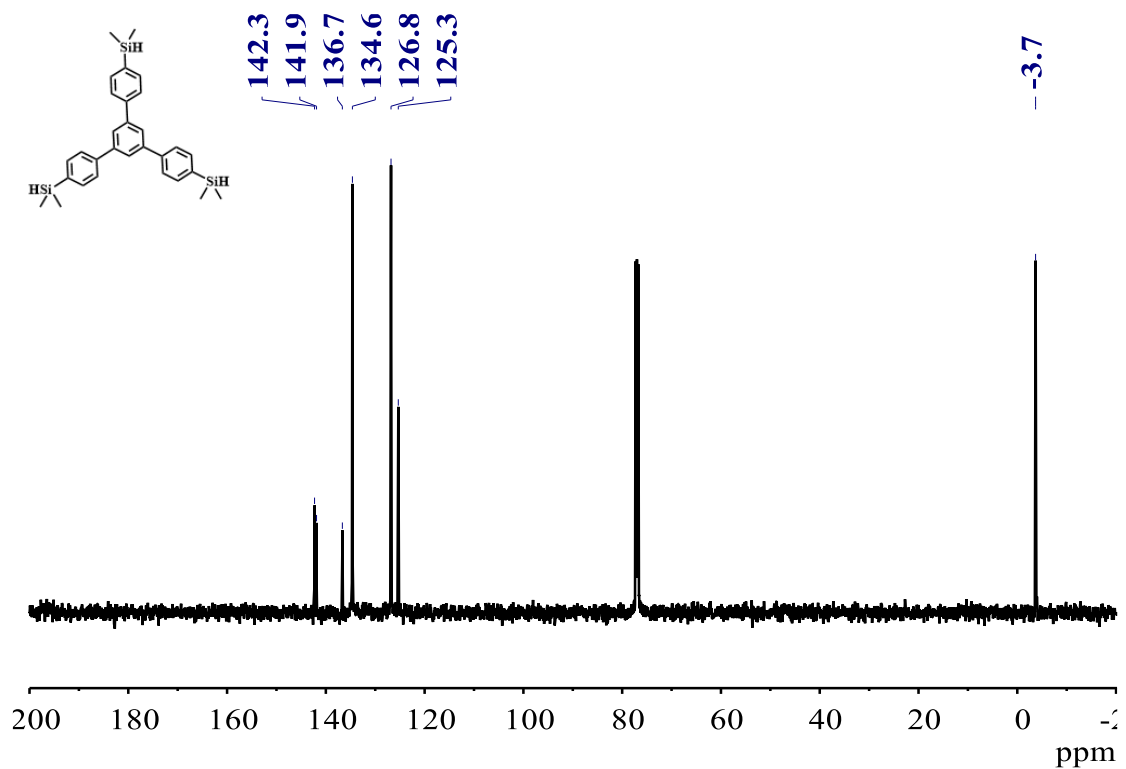
¹H NMR spectrum of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**2d**) (500 MHz, CDCl₃)



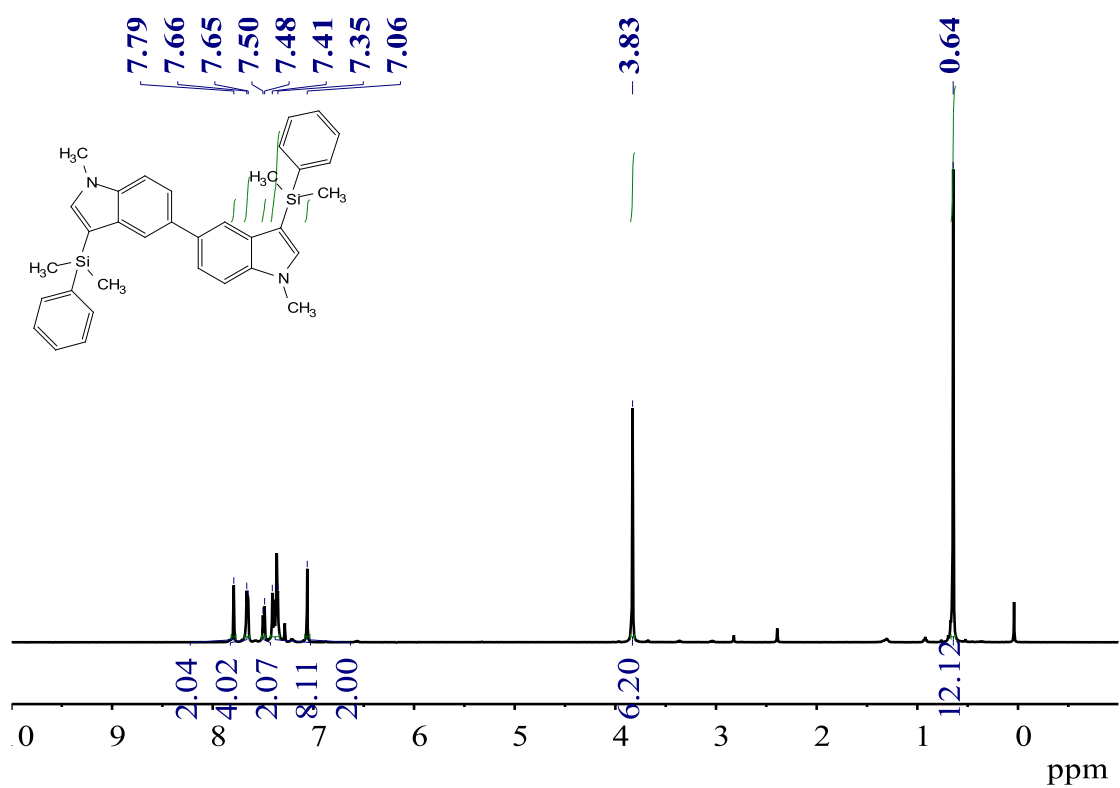
¹³C {¹H} NMR spectrum of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**2d**) (126 MHz, CDCl₃)



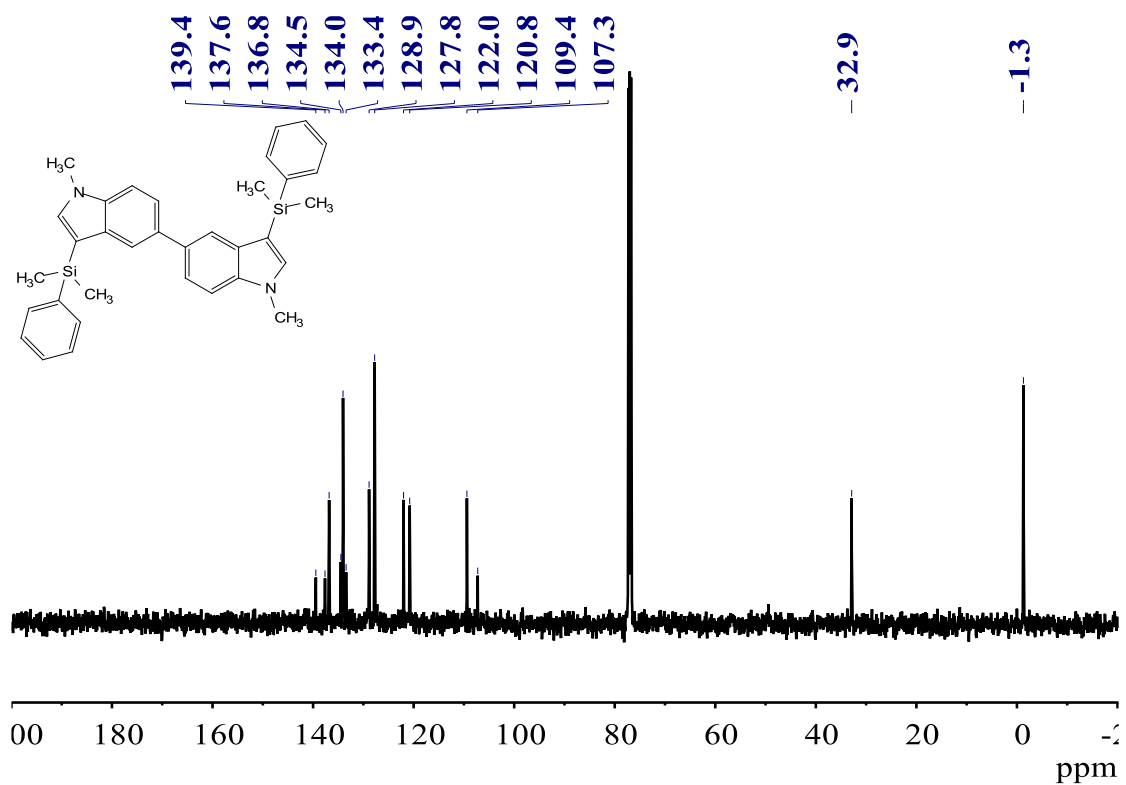
¹H NMR spectrum of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**3b**) (500 MHz, CDCl₃)



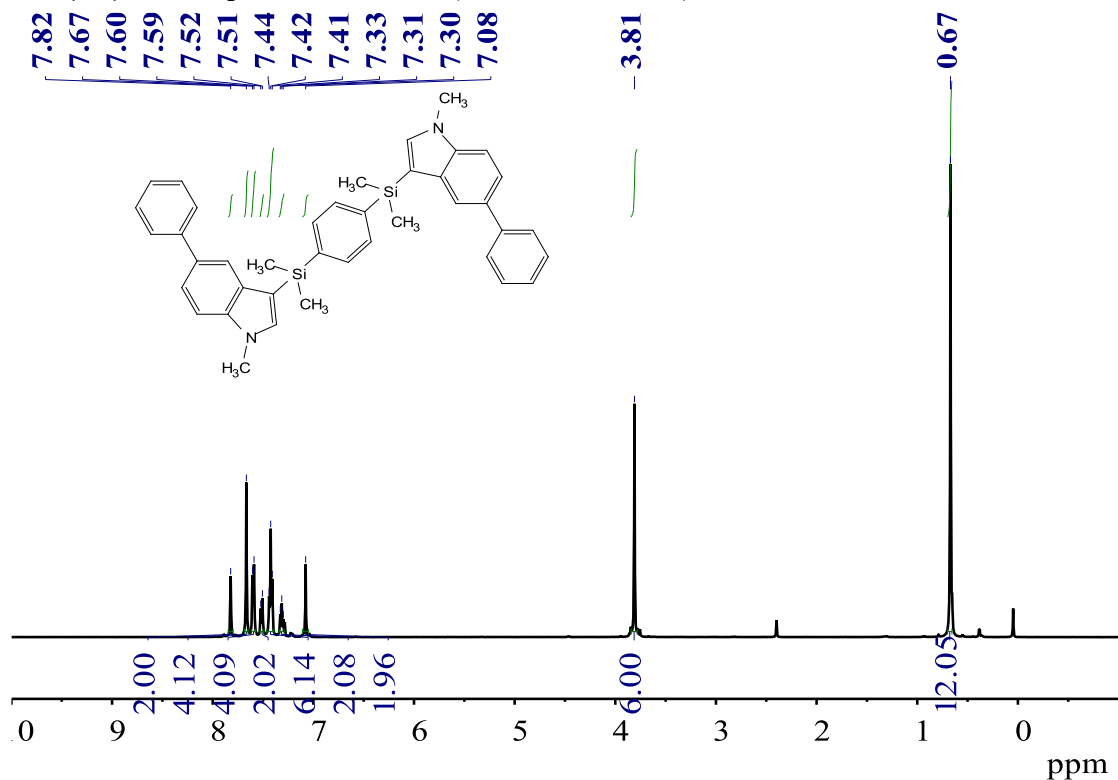
¹³C {¹H} NMR spectrum of 5-(3-(dimethylsilyl)phenyl)-1-methyl-indole (**3b**) (126 MHz, CDCl₃)



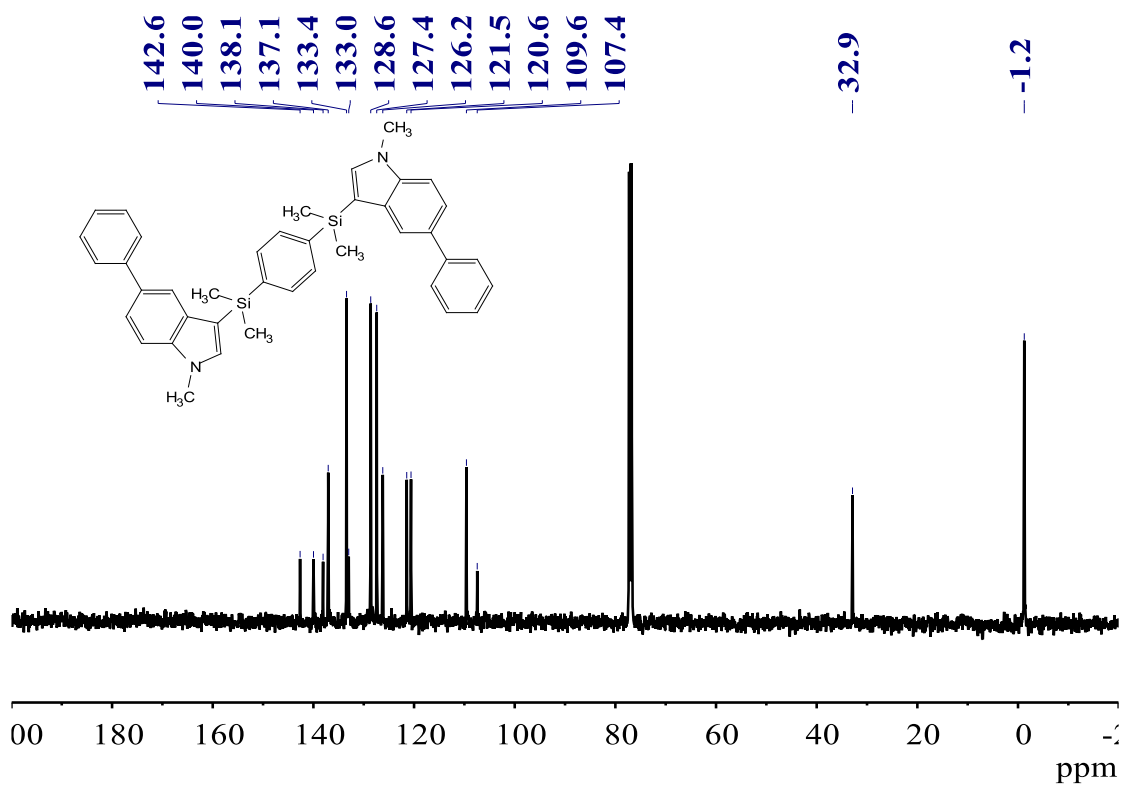
¹H NMR spectrum of MC1 (500 MHz, CDCl₃)



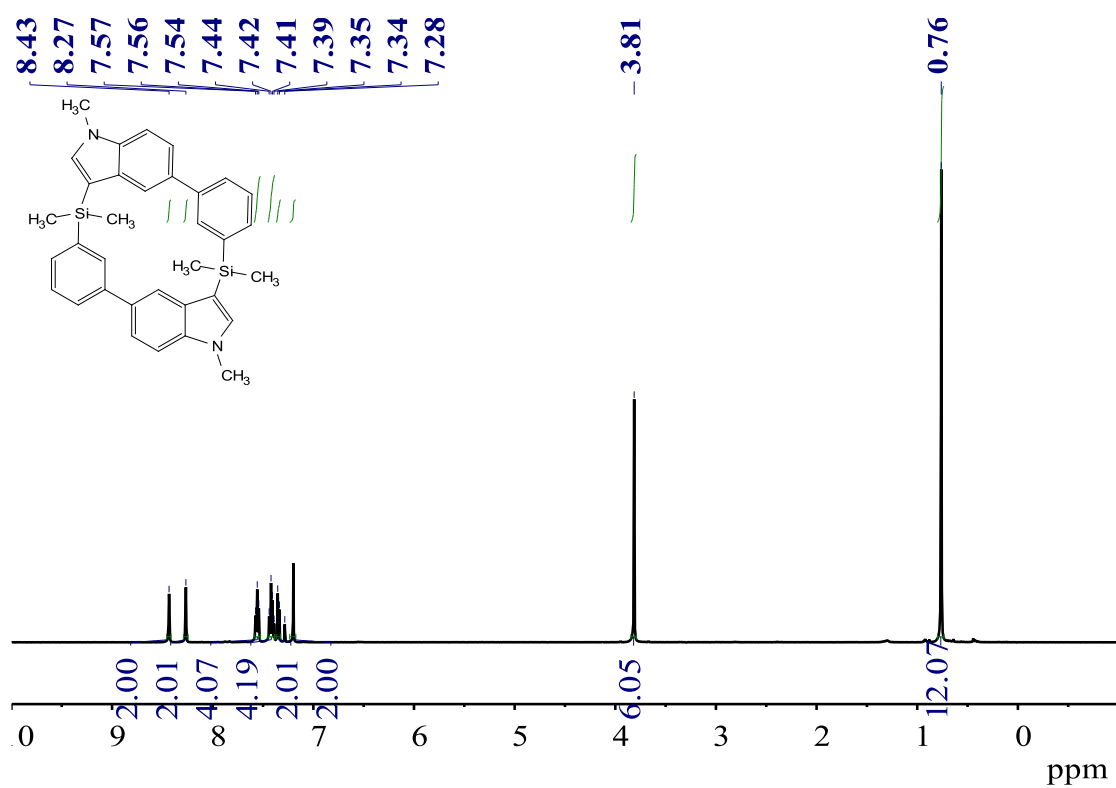
¹³C {¹H} NMR spectrum of MC1 (126 MHz, CDCl₃)



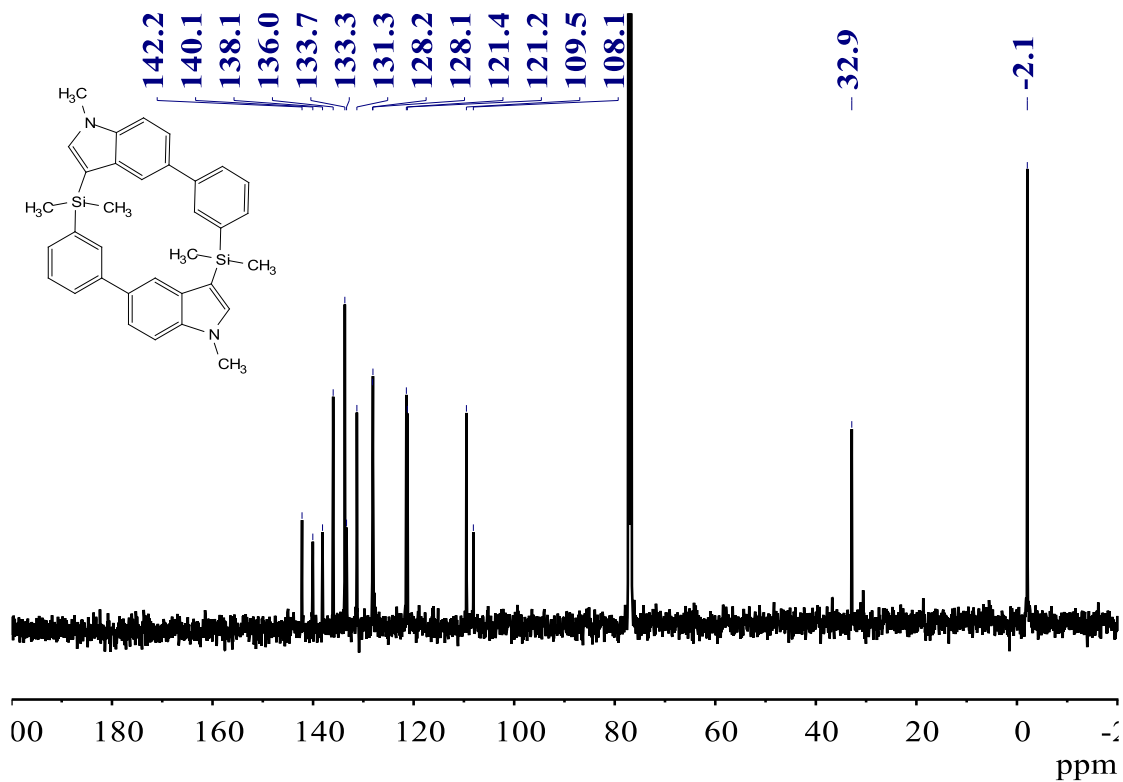
¹H NMR spectrum of MC2 (500 MHz, CDCl₃)



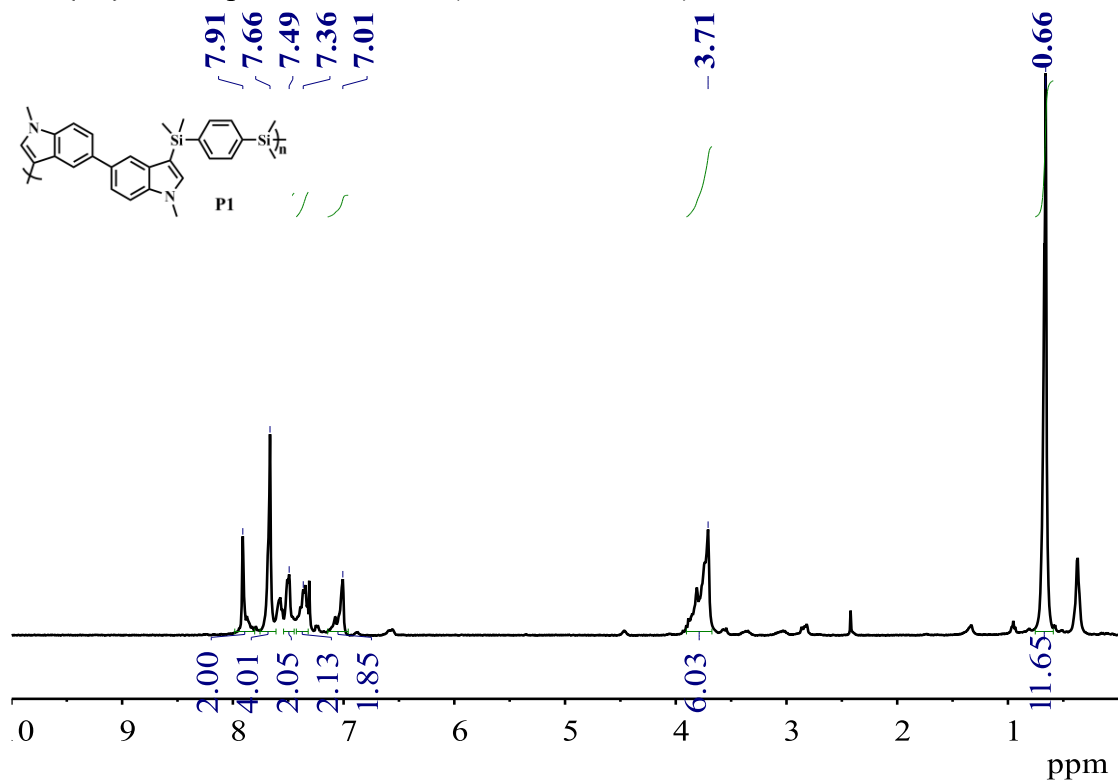
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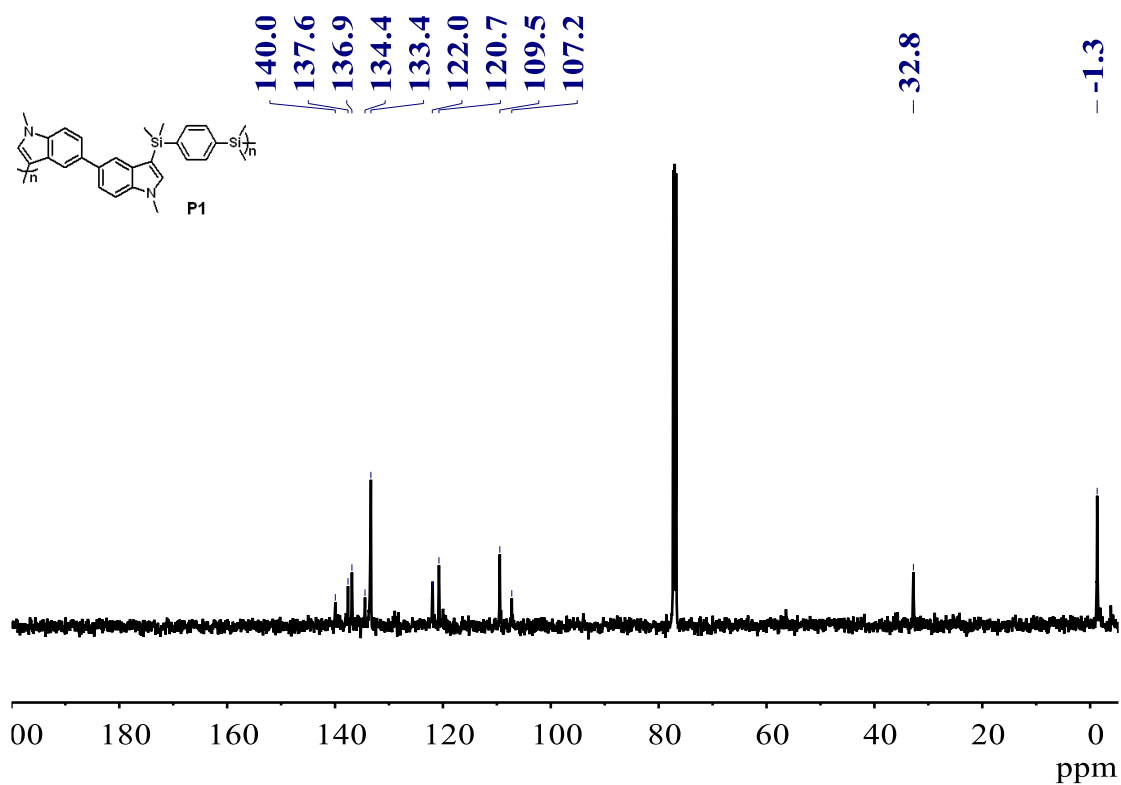
¹H NMR spectrum of MC3 (500 MHz, CDCl₃)



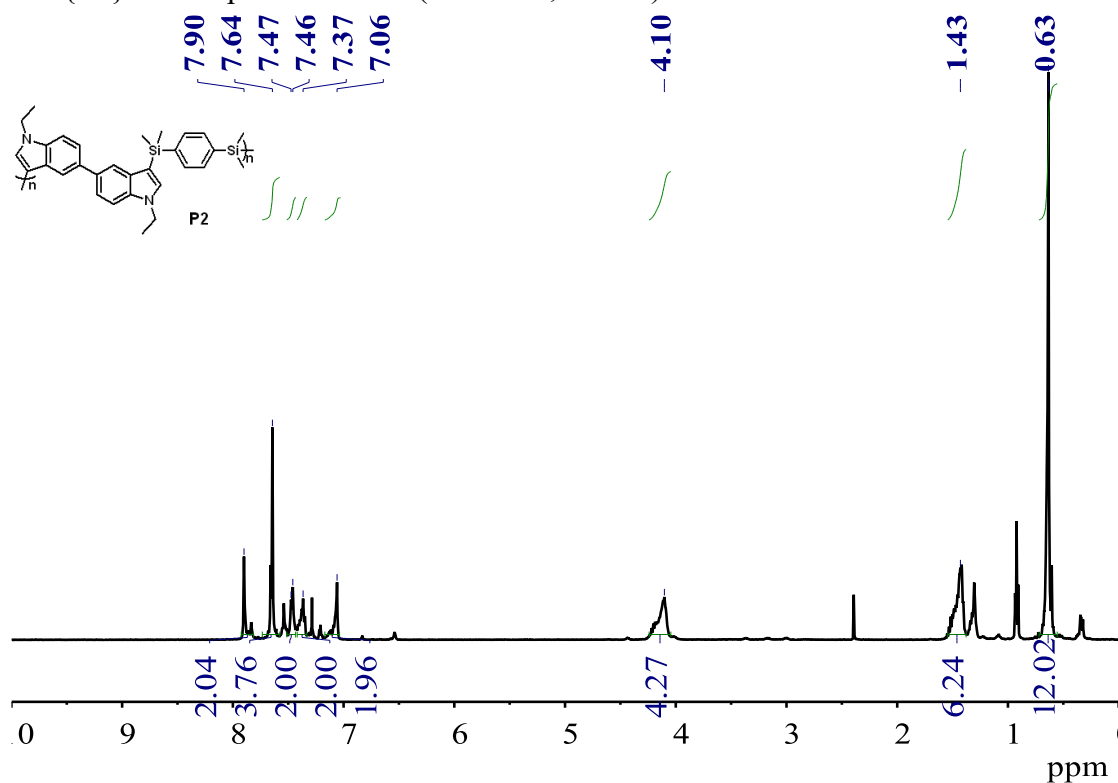
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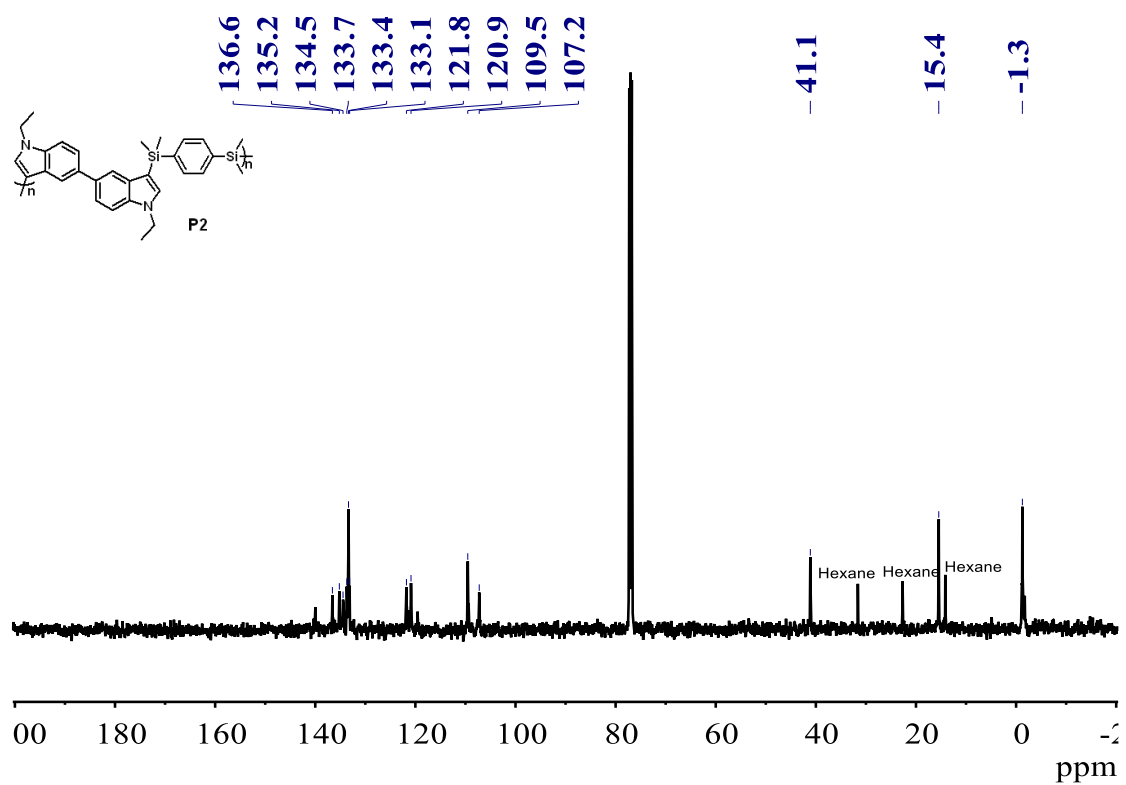
¹H NMR spectrum of P1 (500 MHz, CDCl₃)



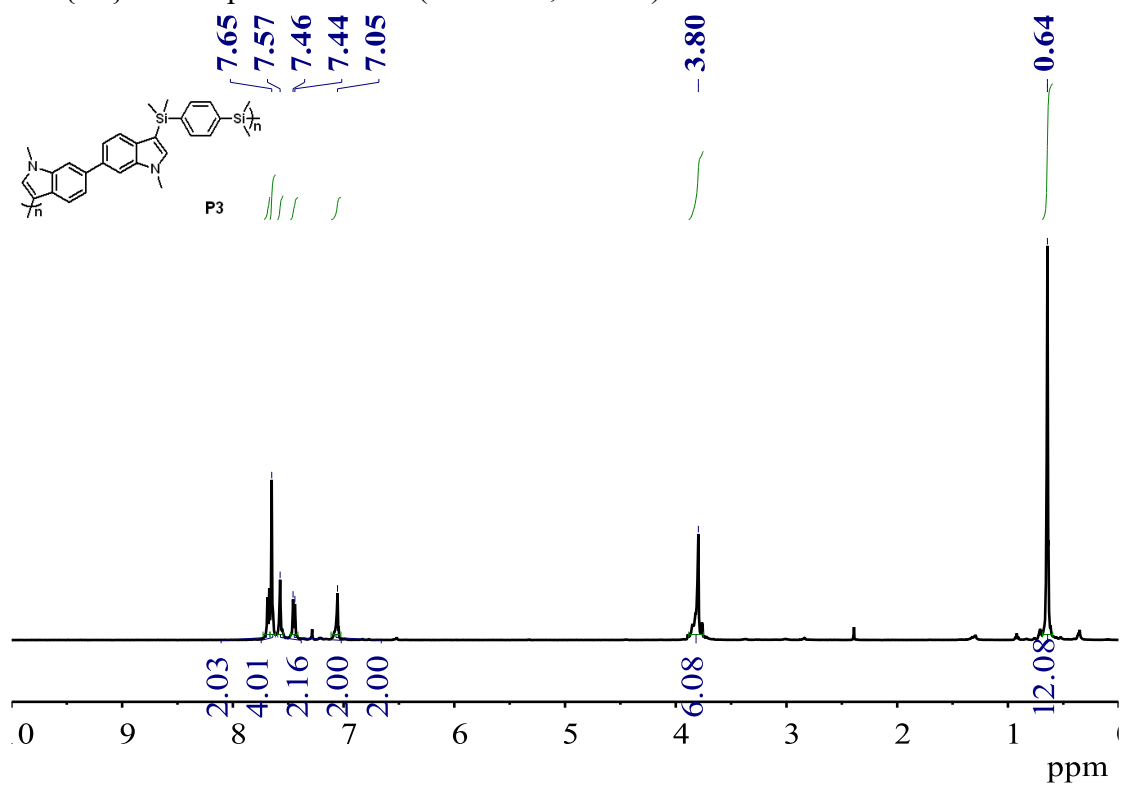
^{13}C $\{^1\text{H}\}$ NMR spectrum of P1 (126 MHz, CDCl_3)



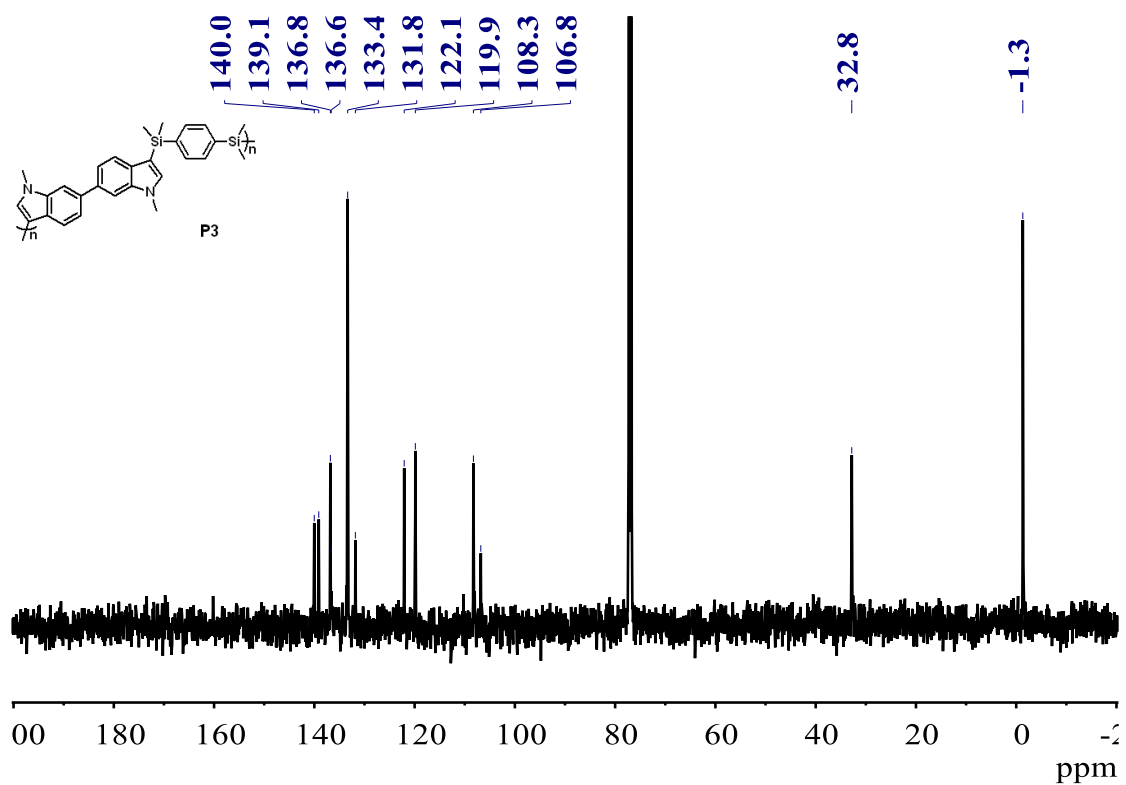
^1H NMR spectrum of P2 (500 MHz, CDCl_3)



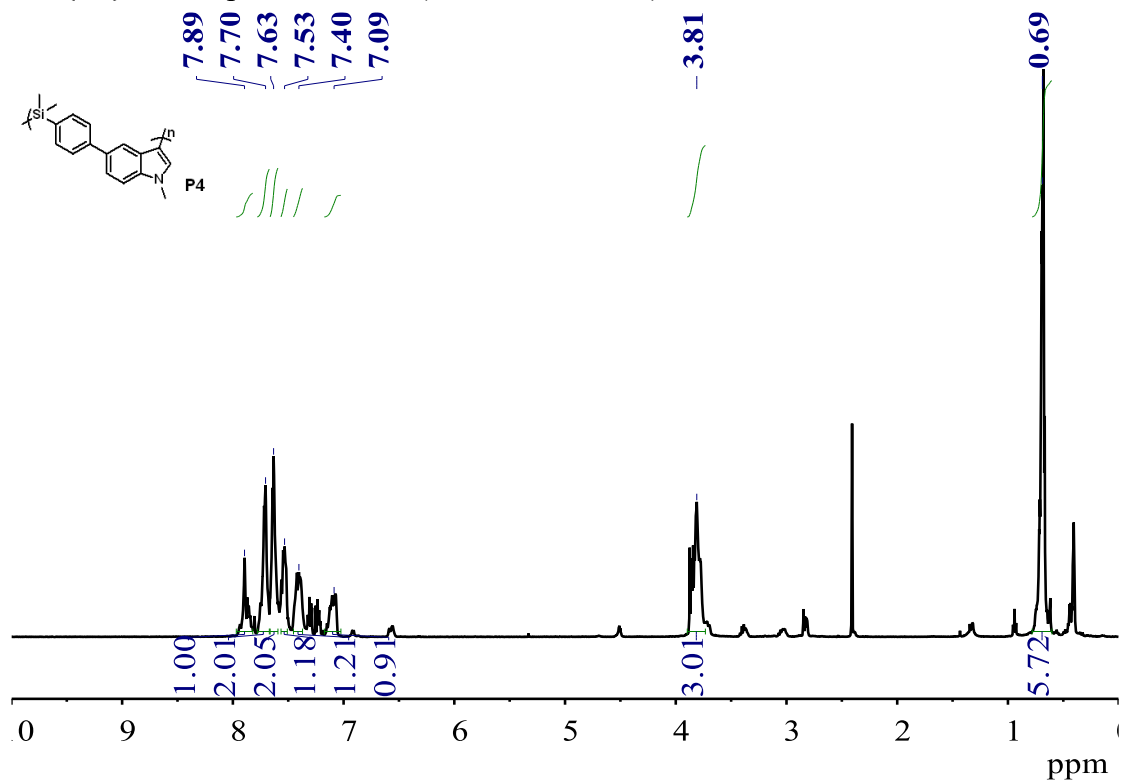
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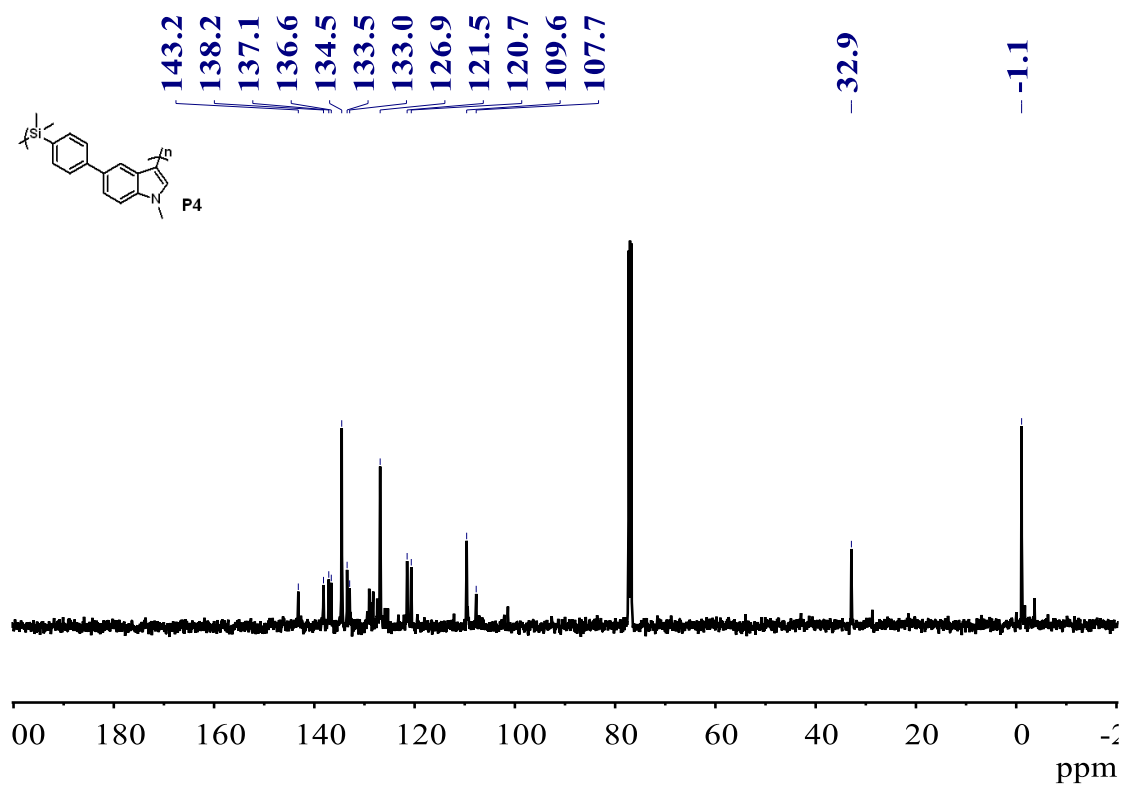
¹H NMR spectrum of P3 (500 MHz, CDCl₃)



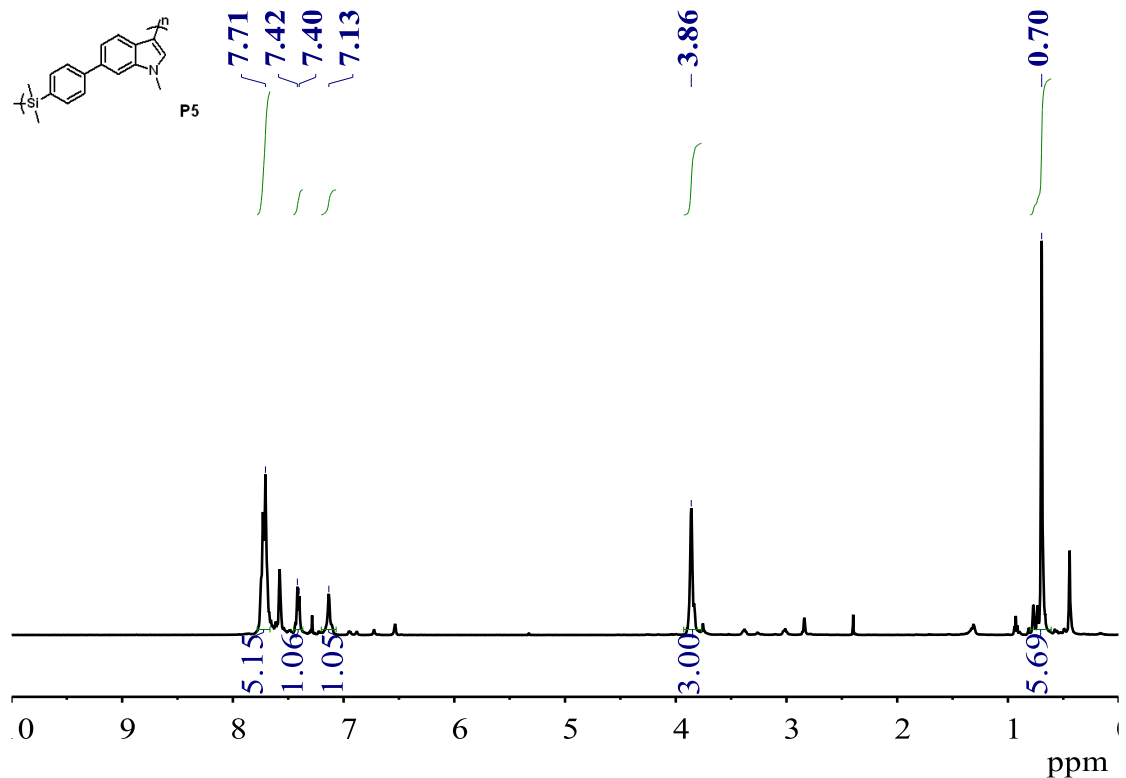
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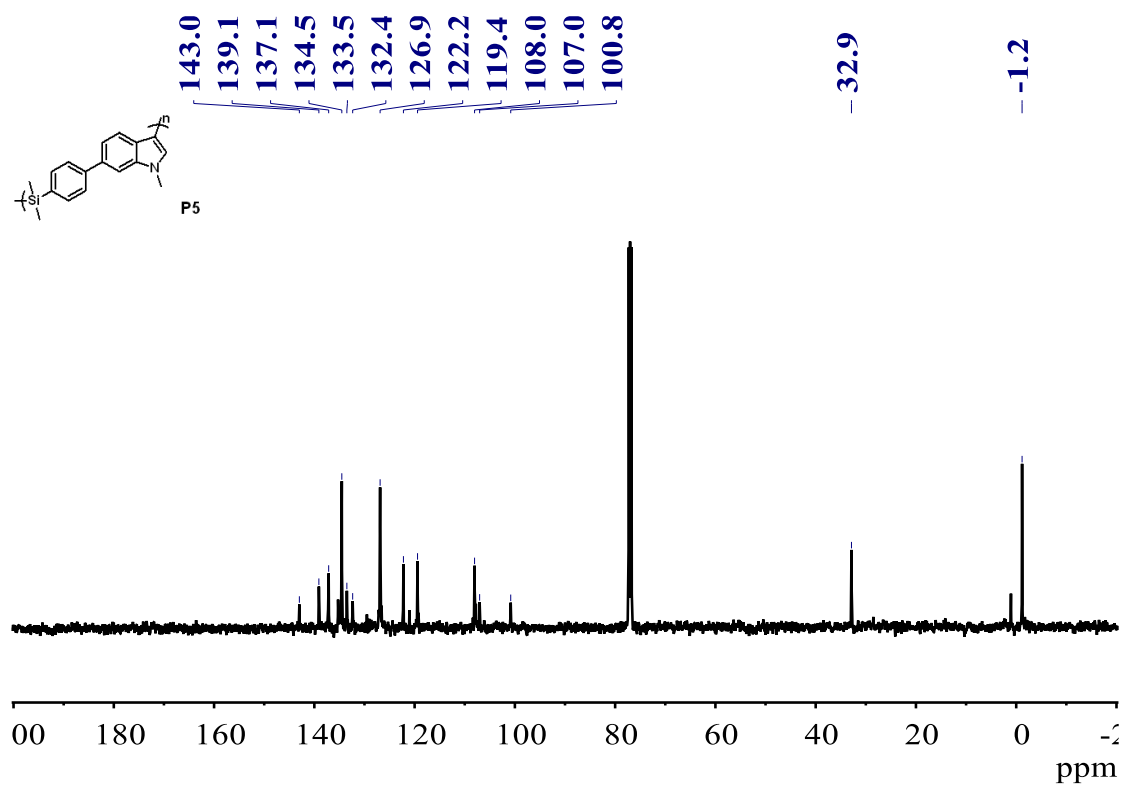
¹H NMR spectrum of P4 (500 MHz, CDCl₃)



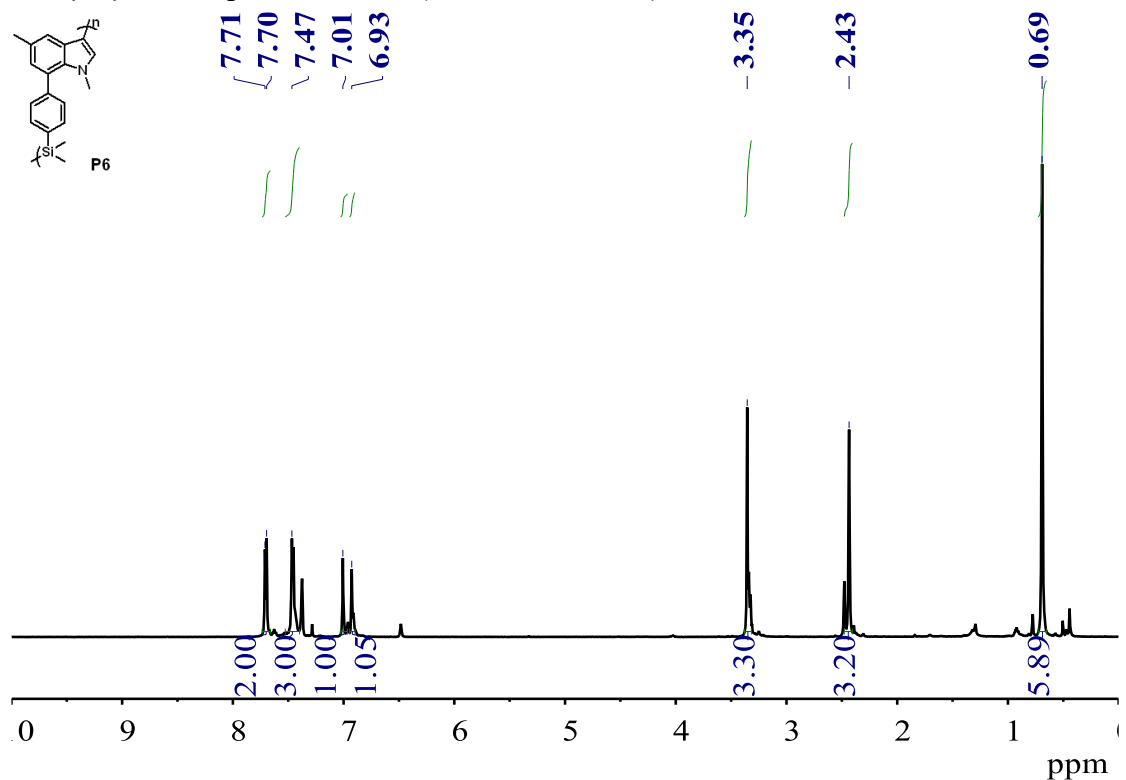
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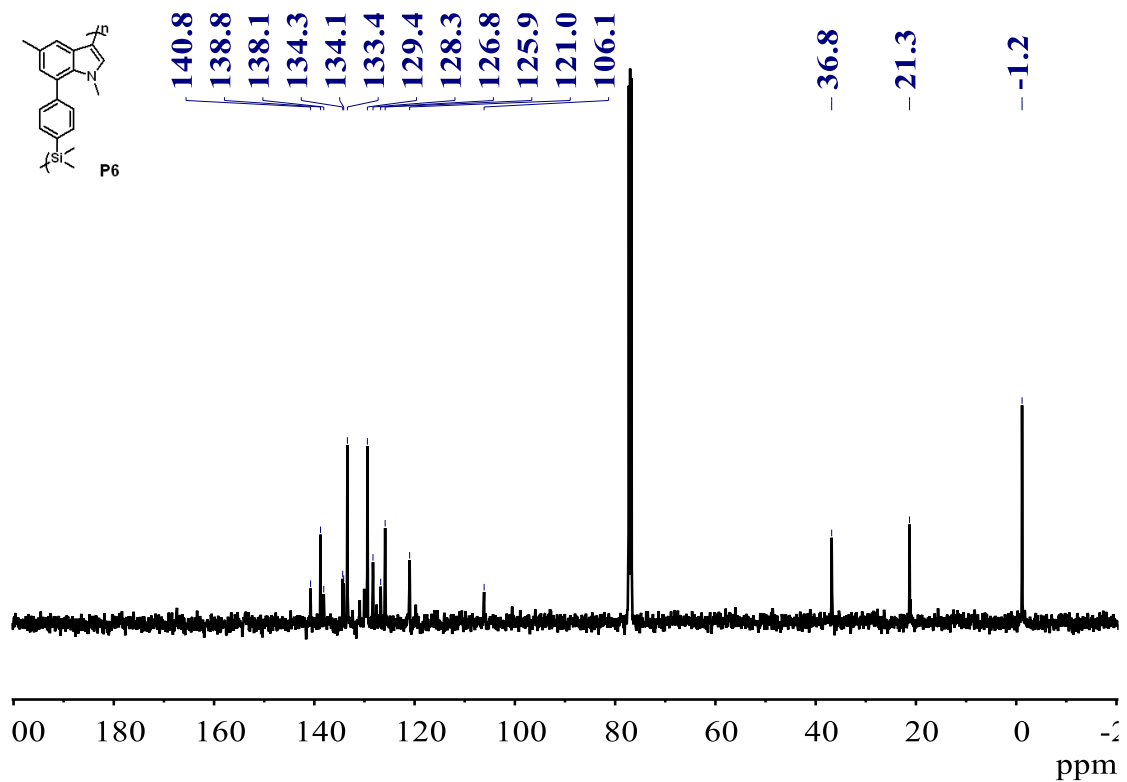
¹H NMR spectrum of P5 (500 MHz, CDCl₃)



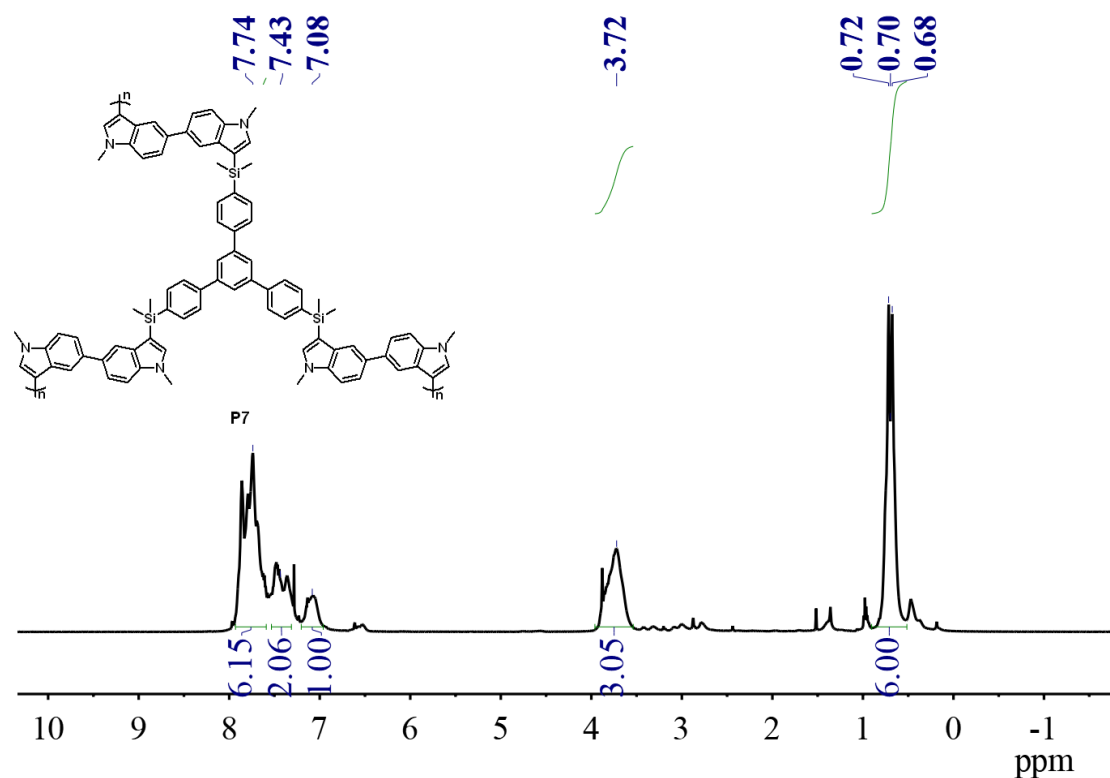
¹³C {¹H} NMR spectrum of P5 (126 MHz, CDCl₃)



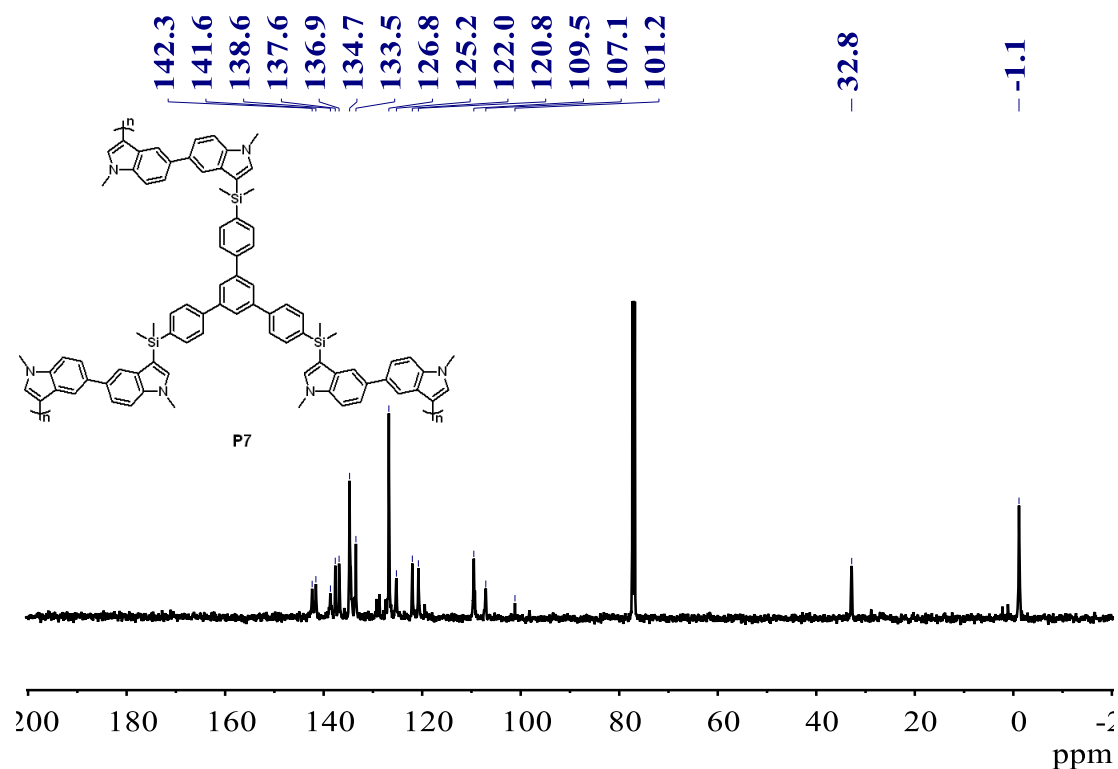
¹H NMR spectrum of P6 (500 MHz, CDCl₃)



¹³C {¹H} NMR spectrum of P6 (126 MHz, CDCl₃)



¹H NMR spectrum of P7 (500 MHz, CDCl₃)



^{13}C $\{^1\text{H}\}$ NMR spectrum of P7 (126 MHz, CDCl_3)

8. References

- (1) Lehmann, M.; Schulz, A.; Villinger, A. Bissilylated Halonium Ions: $[\text{Me}_3\text{Si-X-SiMe}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). *Angew. Chem., Int. Ed.* **2009**, *48*, 7444–7447.
- (2) Karsch, M.; Lund, H.; Schulz, A.; Villinger, A.; Voss, K. Molecular Networks Based on CN Coordination Bonds. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5542–5553.
- (3) Maier, A. F. G.; Tussing, S.; Schneider, T.; Florke, U.; Qu, Z.; Grimme, S.; Paradies, J. Frustrated Lewis Pair Catalyzed Dehydrogenative Oxidation of Indolines and Other Heterocycles. *Angew. Chem. Int. Ed.* **2016**, *55*, 12219–12223.
- (4) Xie, F.; Zhao, H.; Li, D.; Chen, H.; Quan, H.; Shi, X.; Lou, L.; Hu, Y. Synthesis and Biological Evaluation of 2,4,5-Substituted Pyrimidines as a New Class of Tubulin Polymerization Inhibitors. *J. Med. Chem.* **2011**, *54*, 3200–3205.