

Electronic Supplementary Information

Bis-[C(sp³)-chelating] Ti₂ catalysts supported by arylene-1,4-diyl-2,3-X₂ bridges for olefin copolymerisation: X substituents impose conformational cooperative effects

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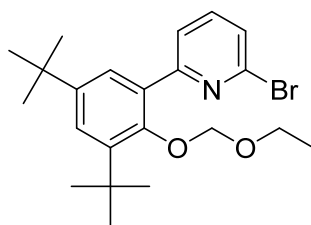
A. Experimental Section

General Methods. All reactions were performed using standard Schlenk techniques under an argon atmosphere or in a Braun dry-box under a nitrogen atmosphere. All solvents were appropriately dried and distilled then degassed prior to use. ^1H , ^{13}C (referenced to residual solvent peaks) and ^{19}F (external trifluoroacetic acid reference) NMR spectra were recorded at 298 K on a Bruker Avance 600 (or 400/300) FT-NMR spectrometer (ppm). Peak assignments were based on combinations of DEPT-135, and 2-D ^1H - ^1H , ^{13}C - ^1H and NOE (plus [^1H , ^{19}F]-COSY for **2**) correlation NMR experiments. The comonomer incorporation % of copolymers were determined by ^{13}C inverse-gated NMR experiments in 1,1,2,2-tetrachloroethane- d_2 at 120 °C. The sample was allowed to equilibrate at 120 °C in the probe prior to data collection, and acquisition was conducted with an interval of 10 s between pulses. The ^1H NMR spectra of precursors, ligands and complexes, and the ^{13}C and DEPT-135 NMR spectra of complexes, are provided below. Elemental analyses were performed on a Vario EL elemental analyser (Elementar Analysensysteme GmbH).

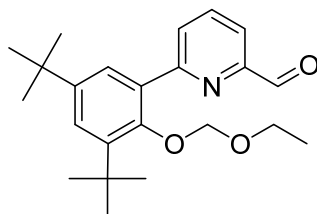
For polymer analysis, gel permeation chromatographs were obtained on a PL-GPC 220 instrument (at 1.0 mL/min versus polystyrene standards; 2 × PLgel Olexis (300 × 7.5 mm) Mixed B columns) at 150 °C in 1,2,4-trichlorobenzene. The polymer melting point was determined using a PerkinElmer STA6000 simultaneous thermal analyser under a nitrogen atmosphere: 1) polymer samples were first equilibrated at 30 °C, then heated to 170 °C at a rate of 10 °C/min, 2) this temperature was maintained for 5 min, then samples were cooled to 30 °C at a rate of 10 °C/min, 3) this temperature was maintained for 5 min, then samples were reheated to 170 °C at a rate of 10 °C/min, 4) the melting temperature (T_m) was determined from the second heating scan. Molecular structures were optimised using DFT calculations (M06-2X level,¹ using the Gaussian 16 program package²) with the LanL2DZ basis set³ for transition metals and the 6-311G(d,p) basis set for non-metal atoms. The syntheses of **I-1** and complex **4m** were described previously.^{4,5}

Polymerisation Procedures. Schlenk-line ethylene polymerisation tests were carried out under atmospheric pressure in toluene in a 100 mL glass reactor containing a magnetic stir bar, which was equilibrated at the required temperature. The reactor was maintained under 1 atmosphere of continuous ethylene supply for the duration of the experiment. Polymerisation was initiated by adding a toluene solution of the cocatalyst ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^i\text{Bu}_3\text{Al}$) with stirring. After the prescribed

reaction time, 10% HCl in methanol (40 mL) was added to terminate the polymerisation, the ethylene gas feed was stopped, and the resultant mixture was allowed to stir at 80 °C for 1 hour. The polymer was collected by filtration, washed with methanol (20 mL), and dried under vacuum at 80 °C for 12 hours to a constant weight. The same procedure was adopted for ethylene/1-alkene copolymerisation tests, except the 1-alkene substrate was combined with the toluene solution of the cocatalyst before polymerisation. Errors for catalytic activities are estimated to be $\pm 10\%$, based on previous polymerisation tests using the same experimental procedure.

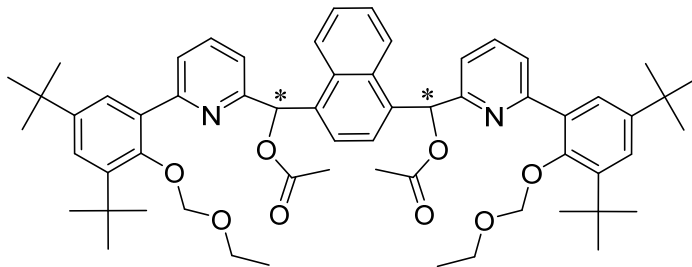


Synthetic Methods. Synthesis of I-2. A mixture of 2,6-dibromopyridine (1.66 g 6.99 mmol), **I-1** (3.0 g, 7.68 mmol), Pd(PPh₃)₄ (0.42 g, 0.35 mmol) and potassium phosphate (2.96 g, 14.0 mmol) in toluene (40 mL) was heated at 110 °C for 4 days under a nitrogen atmosphere. The resultant mixture was filtered through a thin layer of celite, and all volatiles were removed under vacuum. The crude product was purified by silica gel flash chromatography using *n*-hexane and Et₂O (3:1) as eluent to give a white solid. Yield: 2.00 g, 83%. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.36–7.46 (m, 3H), 4.61 (s, 2H, OCH₂O), 3.53 (q, $J = 7.1$ Hz, 2H, OCH₂CH₃), 1.46 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 1.11 (t, $J = 7.0$ Hz, 3H, OCH₂CH₃).

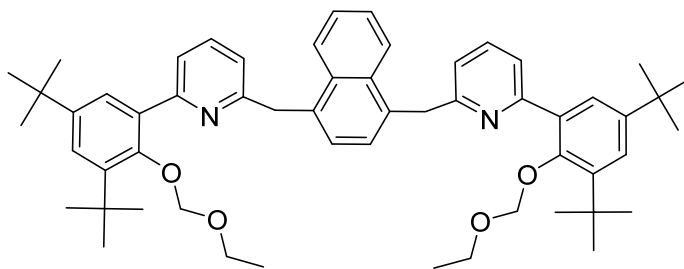


Synthesis of I-3. A mixture of **I-1** (5.00 g, 12.8 mmol), 6-bromopyridine-2-carbaldehyde (2.17 g, 11.7 mmol), Pd(dppf)Cl₂ (0.214 g, 0.293 mmol) and potassium carbonate (8.05 g, 58.3 mmol) was added to dioxane (30 mL) and deionised water (3 mL) in a 100 mL Schlenk flask. The reaction was stirred at 90 °C for 48 hours, after which the mixture was extracted with dichloromethane (50 mL) and washed with brine. The combined organic layers were dried over anhydrous magnesium sulphate. After evaporation of all volatiles by vacuum, and purification by silica gel flash

chromatography using *n*-hexane:ethyl acetate (40:1) as eluent, the product was obtained as a white solid. Yield: 3.49 g, 81%. ¹H NMR (300 MHz, CDCl₃): δ 10.18 (s, 1H), 7.99-7.85 (m, 3H), 7.51-7.45 (m, 2H), 4.59 (s, 2H), 3.48 (q, *J* = 7.1 Hz, 2H), 1.48 (s, 9H), 1.35 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H).

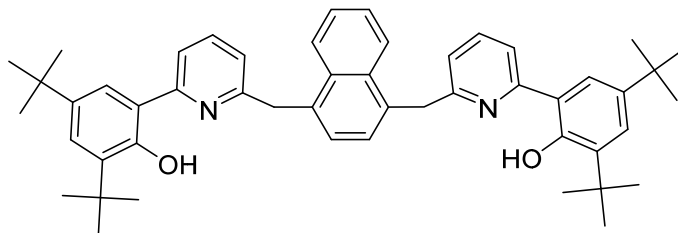


Synthesis of I-4. *n*-Butyllithium (2.4 M in *n*-hexane, 0.74 mL, 1.77 mmol) was added dropwise to a solution of **I-2** (0.746 g, 1.77 mmol) in diethyl ether (50 mL) at $-78\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. After stirring for five minutes, a solution of naphthalene-1,4-dicarbaldehyde (0.159 g, 0.861 mmol) in diethyl ether (20 mL) was added to the reaction, which was stirred at $20\text{ }^{\circ}\text{C}$ for 12 hours. The resultant mixture was quenched with dilute HCl (1 mL), after which filtration, extraction with diethyl ether (50 mL) and evaporation of all volatiles from the combined organic layers by vacuum gave a brown solid, to which acetic anhydride (4.0 mL) and pyridine (4.0 mL) were added. The mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 12 hours, after which the pyridine was removed by vacuum. The product was obtained as a pale-yellow solid after purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (15:1) as eluent. Yield: 0.385 g, 47%. ¹H NMR (400 MHz, CDCl₃): δ 8.44–8.37 (m, 2H), 7.73–7.67 (m, 4H), 7.67–7.61 (m, 4H), 7.53–7.46 (m, 2H), 7.42 (d, *J* = 2.6 Hz, 2H), 7.35 (d, *J* = 2.6 Hz, 2H), 7.32–7.27 (m, 2H), 4.64–4.54 (m, 4H), 3.55–3.37 (m, 4H), 2.26 (s, 6H), 1.49 (s, 18H), 1.31 (s, 18H), 1.06 (t, *J* = 7.0 Hz, 6H).

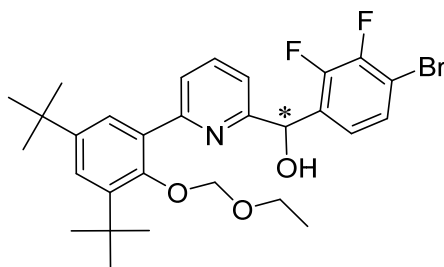


Synthesis of I-5. A mixture of **I-4** (1.00 g, 1.05 mmol), Pd/C (5% Pd wt., 0.208 g), triethylamine (0.290 g, 2.87 mmol) and methanol (25 mL) were added to a Schlenk flask, and the reaction was heated at $45\text{ }^{\circ}\text{C}$ under a hydrogen atmosphere for 12 hours. The resultant mixture was filtered through a thin layer of celite. The product was obtained as a pale-yellow oil after purification

by silica gel flash chromatography using *n*-hexane:ethyl acetate (20:1) as eluent. Yield: 0.710 g, 81%. ¹H NMR (400 MHz, CDCl₃): δ 8.30–8.22 (m, 2H), 7.56–7.43 (m, 12H), 6.98–6.92 (m, 2H), 4.74 (s, 4H), 4.65 (s, 4H), 3.50 (q, *J* = 7.0 Hz, 4H), 1.51 (s, 18H), 1.38 (s, 18H), 1.09 (t, *J* = 7.0 Hz, 6H).

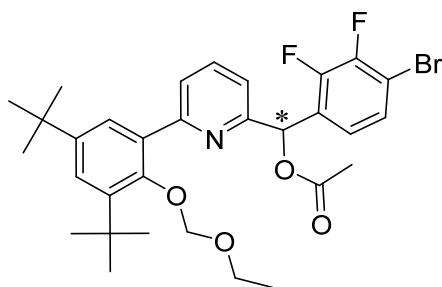


Synthesis of H₄L¹. **I-5** (0.671 g, 0.803 mmol), concentrated hydrochloric acid (4 mL) and methanol (20 mL) were added to a 100 mL round-bottom flask, and the reaction was stirred at 60 °C for 12 hours. The resultant mixture was extracted with dichloromethane (60 mL) and washed with brine. The combined organic layers were dried over anhydrous magnesium sulphate. The product was obtained as a pale-yellow solid after purification by silica gel flash chromatography using *n*-hexane:dichloromethane (1:1) as eluent. Yield: 0.433 g, 75%. ¹H NMR (400 MHz, CDCl₃): δ 14.63 (s, 2H), 8.03–7.98 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.68–7.61 (m, 4H), 7.46 (s, 2H), 7.45–7.38 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 2H), 4.69 (s, 4H), 1.50 (s, 18H), 1.36 (s, 18H). ¹³C NMR (151 MHz, CDCl₃): δ 158.61, 157.29, 156.94, 139.73, 138.12, 137.61, 134.07, 132.64, 127.85, 126.12, 125.01, 120.90, 120.24, 117.93, 117.26, 41.51, 35.34, 34.36, 31.65, 29.65.

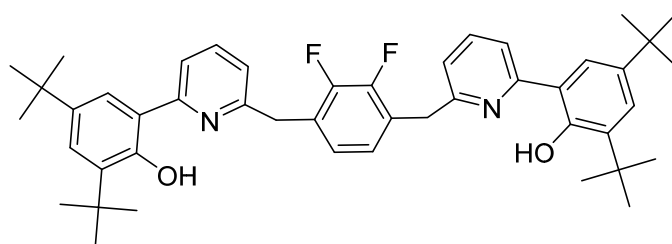


Synthesis of I-6. *n*-Butyllithium (2.4 M in *n*-hexane, 0.62 mL, 1.49 mmol) was added dropwise to a solution of 1,4-dibromo-2,3-difluorobenzene (0.405 g, 1.49 mmol) in THF (50 mL) at –78 °C under a nitrogen atmosphere. After stirring for 15 minutes, a solution of **I-3** (0.500 g, 1.35 mmol) in THF (10 mL) was added to this mixture, which was stirred at 20 °C for 12 hours. The resultant mixture was quenched with dilute HCl (1 mL), then extracted with diethyl ether (50 mL) and washed with brine. The combined organic layers were dried over anhydrous magnesium sulphate. After evaporation of all volatiles by vacuum and purification by silica gel flash chromatography using

n-hexane:ethyl acetate (40:1), the product was obtained as a colorless oil. Yield: 0.579 g, 76%. ¹H NMR (400 MHz, CDCl₃): δ 7.76–7.65 (m, 2H), 7.52 (d, *J* = 2.6 Hz, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.35–7.25 (m, 1H), 7.23–7.16 (m, 2H), 6.17 (s, 1H), 5.88 (s, 1H), 4.65–4.57 (m, 2H), 3.59–3.46 (m, 2H), 1.53 (s, 9H), 1.39 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ -130.48 (d, *J* = 21.3), -139.89 (d, *J* = 21.3 Hz).

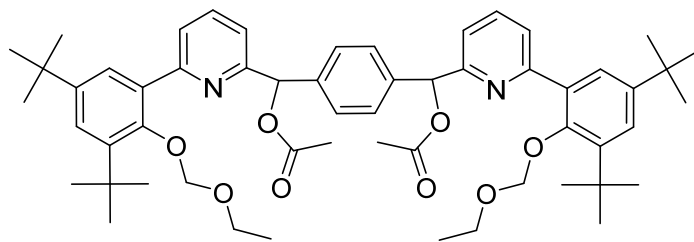


Synthesis of I-7. A mixture of **I-19** (0.500 g, 0.889 mmol), acetic anhydride (2.5 mL) and pyridine (2.5 mL) was added to a 50 mL round-bottom flask. The reaction was stirred at 50 °C for 12 hours, after which the pyridine was removed by vacuum. The product was obtained as a white solid after purification by silica gel flash chromatography using *n*-hexane:ethyl acetate (40:1) as eluent. Yield: 0.446 g, 83%. ¹H NMR (400 MHz, CDCl₃): δ 7.78–7.71 (m, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.40 (dd, *J* = 6.6, 1.9 Hz, 1H), 7.36–7.31 (m, 1H), 7.30–7.23 (m, 2H), 7.16 (s, 1H), 4.58 (s, 2H), 3.61–3.47 (m, 2H), 2.25 (s, 3H), 1.48 (s, 9H), 1.31 (s, 9H), 1.12 (t, *J* = 7.1 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃): -130.20 (d, *J* = 21.6 Hz), -137.09 (d, *J* = 21.6 Hz).

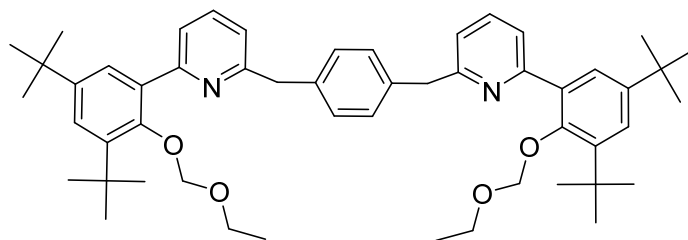


Synthesis of H₄L². The procedure for the synthesis of **I-6** was adopted using **I-7** (1.85 g, 3.06 mmol) to give the crude product. Subsequent esterification, reduction and deprotection reactions following the synthetic methods for **I-4**, **I-5** and H₄L¹ respectively, using crude products from each step, yielded the product as a pale-yellow solid. Yield: 0.259 g, 12 %. ¹H NMR (400 MHz, CDCl₃): δ 14.35 (s, 2H), 7.82–7.69 (m, 4H), 7.63 (d, *J* = 2.4 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 2H), 7.14–7.00 (m, 4H), 4.25 (s, 4H), 1.48 (s, 18H), 1.35 (s, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 158.80, 156.85, 155.47, 149.25 (dd, ¹*J*_{C,F} = 249.3, 14.8 Hz), 139.79, 138.32, 137.62, 126.45 (dd, ²*J*_{C,F} = 7.9, 5.2 Hz), 126.21,

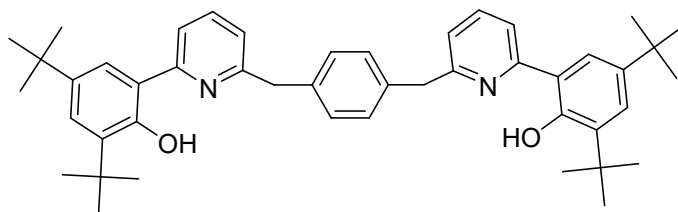
125.74 (t, $^3J_{C,F} = 3.7$ Hz), 120.94, 120.17, 117.87, 117.66, 36.64 (CH₂), 35.36, 34.38, 31.68, 29.65.
 ^{19}F NMR (376 MHz, CDCl₃): δ -141.97.



Synthesis of I-8. The procedure for the synthesis of **I-4** was adopted starting from benzene-1,4-dicarbaldehyde. Yield: 0.36 g, 51%. ^1H NMR (300 MHz, CDCl₃): δ 7.67–7.60 (m, 3H), 7.51 (s, 4H), 7.39 (d, $J = 2.7$ Hz, 2H), 7.29–7.33 (m, 3H), 6.93 (s, 2H), 4.55 (s, 4H), 3.54–3.38 (m, 4H), 2.20 (s, 6H), 1.46 (s, 18H), 1.29 (s, 18H), 1.04 (t, $J = 7.1$ Hz, 6H).

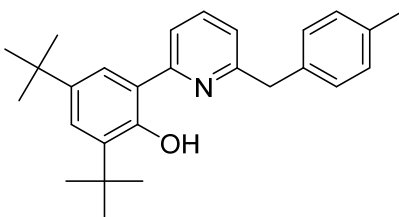


Synthesis of I-9. A mixture of **I-8** (0.36 g, 0.4 mmol), Pd/C (5% Pd wt., 0.08 g), triethylamine (0.15 mL, 1.07 mmol) in methanol (20 mL) was heated at 45 °C under a hydrogen atmosphere for 12 hours. The resultant mixture was filtered through a thin layer of celite. Evaporation of volatiles gave a pale yellow oil, which was purified by silica gel flash chromatography using dichloromethane as eluent to give a pale yellow oil. Yield: 0.22 g, 70%. ^1H NMR (300 MHz, CDCl₃): δ 7.55–7.60 (m, 2H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.39–7.40 (m, 4H), 7.32 (s, 4H), 7.01 (d, $J = 7.2$ Hz, 2H), 4.58 (s, 4H), 4.22 (s, 4H), 3.49 (q, $J = 7.0$ Hz, 4H), 1.47 (s, 18H), 1.29 (s, 18H), 1.08 (t, $J = 7.0$ Hz, 6H).

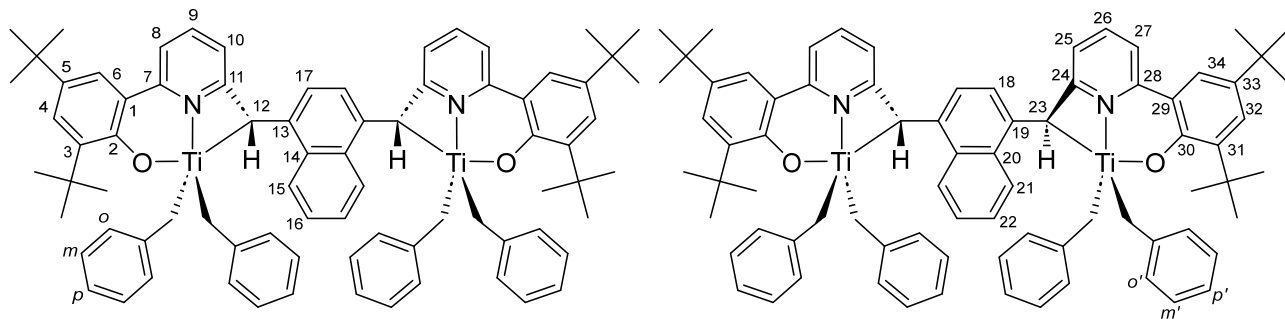


Synthesis of H₄L³. A mixture of **I-9** (0.22 g, 0.28 mmol) in MeOH (20 mL) and concentrated HCl (5 mL) was heated at 80 °C for 12 hours. The resultant mixture was extracted with dichloromethane, washed with brine and water, and dried over magnesium sulphate. Purification by

silica gel flash chromatography using dichloromethane as eluent gave a yellow solid. Yield: 0.14 g, 75%. ^1H NMR (400 MHz, CDCl_3): δ 14.65 (s, 2H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.70 (t, $J = 7.8$ Hz, 2H), 7.64 (d, $J = 2.3$ Hz, 2H), 7.39 (d, $J = 2.3$ Hz, 2H), 7.26 (s, 4H), 7.00 (d, $J = 7.3$ Hz, 2H), 4.19 (s, 4H), 1.49 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3): δ 158.71, 157.54, 157.01, 139.78, 138.23, 137.67, 137.05, 129.72, 126.19, 120.99, 120.39, 118.03, 117.35, 43.73, 35.44, 34.47, 31.76, 29.75.

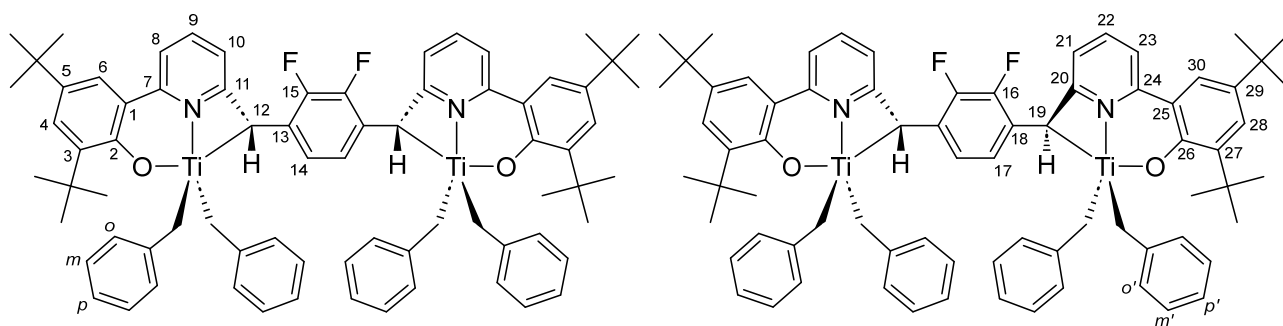


Synthesis of H_2L^4 . The procedure for the synthesis of H_4L^4 was adopted from that for the parent pyridine-2-phenol-6-benzyl ligand.⁵ The protected alcohol (1.10 g, 2.47 mmol) was treated with concentrated hydrochloric acid (5 mL) in methanol (20 mL), according to the synthesis of H_4L^3 , to give a white solid. Yield: 0.852 g, 89%. ^1H NMR (400 MHz, CDCl_3): δ 14.68 (s, 1H), 7.77–7.67 (m, 2H), 7.66–7.60 (m, 1H), 7.43–7.36 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 7.3$ Hz, 1H), 4.18 (s, 2H), 2.33 (s, 3H), 1.49 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 158.58, 157.74, 156.98, 139.67, 138.11, 137.59, 136.25, 135.58, 129.45, 129.16, 126.10, 120.89, 120.23, 117.95, 117.16, 43.63 (CH_2), 35.37, 34.39, 31.69, 29.66, 21.12 (CH_3).



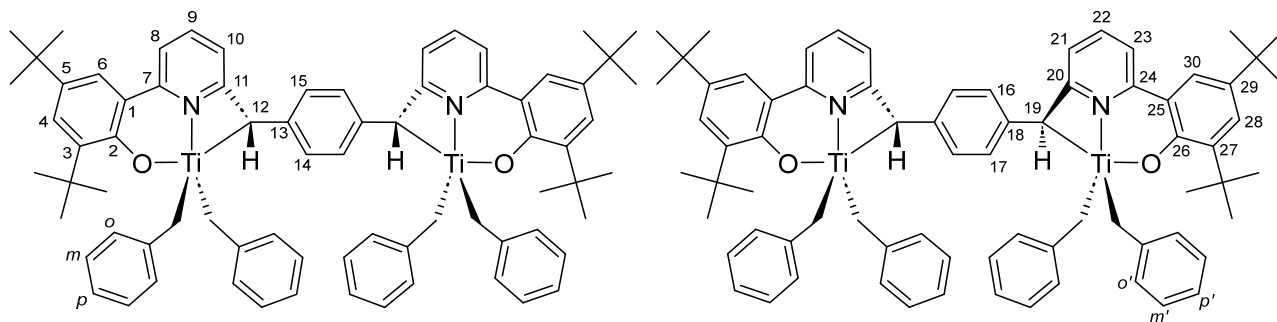
Synthesis of Complex 1. A solution of *n*-pentane (10 mL) and diethyl ether (1 mL) was slowly added to H_4L^1 (0.100 g, 0.139 mmol) and $\text{Ti}(\text{CH}_2\text{Ph})_4$ (0.116 g, 0.282 mmol) at -78 °C under an argon atmosphere. The mixture was stirred at -78 °C for one hour and at 20 °C for 12 hours. The reaction mixture was stored at -78 °C for 12 hours, and the resultant dark red/brown precipitate was collected and dried under vacuum. Yield: 0.088 g, 54%. ^1H NMR (600 MHz, C_6D_6 with 3 drops of d_8 -THF, 281 K): δ 8.56–8.44 (m, 4H, H^{15} and H^{21}), 7.80–7.77 (m, 4H, H^6 and H^{34}), 7.75 (d, $J = 2.4$ Hz, 4H, H^4 and

H³²), 7.61–7.58 (m, 4H, H¹⁶ and H²²), 7.39–7.30 (m, 4H, H¹⁰ and H²⁵), 7.29–7.23 (m, 4H, H¹⁷ and H¹⁸), 7.19–7.11 (m, 8H, *o*- and *o*'-Ph), 7.10–6.99 (m, 8H, H⁸, H⁹, H²⁶ and H²⁷), 6.98–6.86 (m, 20H, *m*, *m*', *p* and *p*'-Ph), 6.79–6.68 (m, 4H, *p*- and *p*'-Ph), 6.64–6.52 (m, 8H, *o*- and *o*'-Ph), 3.35 (s, 4H, H¹² and H²³), 2.99–2.84 (m, 8H, CH₂), 2.43 (d, *J* = 8.3 Hz, 2H), 2.35 (d, *J* = 8.4 Hz, 2H), 2.11 (d, *J* = 8.3 Hz, 2H), 1.94 (d, *J* = 8.4 Hz, 2H), 1.57 (s, 17H, 31-*t*-Bu), 1.56 (s, 19H, 3-*t*-Bu), 1.43 (s, 36H, 5- and 33-*t*-Bu). ¹³C NMR (151 MHz, C₆D₆ with 3 drops of d₈-THF, 281 K): δ 157.36 (C² and C³⁰), 151.70 (C⁷ and C²⁸), 142.11 (C³³), 142.07 (C⁵), 141.76 (C²⁶), 141.61 (C⁹), 136.46 (C³ and C³¹), 130.34 (*o*- and *o*'-Ph), 129.85 (*m*'-Ph), 129.72 (*m*-Ph), 129.59 (*o*-Ph), 129.36 (*m*-Ph), 129.21 (*m*'-Ph), 129.13 (*o*'-Ph), 126.55 (C⁴ and C³²), 125.56 (C²²), 125.37 (C¹⁶), 124.92 (C¹⁵), 124.99 (C²¹), 124.84 (*p*'-Ph), 124.77 (*p*-Ph), 124.26 (*p*-Ph), 123.90 (*p*'-Ph), 122.12 (C³⁴), 122.03 (C⁶), 120.60 (C¹⁰), 120.55 (C²⁵), 119.73 (C¹⁷ and C¹⁸), 112.77 (C²⁷), 112.61 (C⁸), 83.96 (¹*J*_{C,H} = 136.0 Hz, CH₂), 83.57 (¹*J*_{C,H} = 136.6 Hz, CH₂), 78.52 (¹*J*_{C,H} = 134.6 Hz, CH₂), 78.18 (¹*J*_{C,H} = 134.6 Hz, CH₂), 71.25 (¹*J*_{C,H} = 141.9 Hz, C¹² and C²³), 35.47 (3- and 31-CMe₃), 34.41 (5- and 33-CMe₃), 31.48 (5- and 33-CMe₃), 29.92 (31-CMe₃), 29.86 (3-CMe₃); ⁴ carbons: 161.69, 143.00, 142.95, 140.26, 137.76, 137.44, 131.35, 129.00, 127.28, 126.24, 126.36, 126.24, 125.37. Anal. Calcd for C₇₈H₈₂N₂O₂Ti₂ (1175.3): C, 79.71; H, 7.03; N, 2.38. Found: C, 79.49; H, 7.23; N, 2.16.



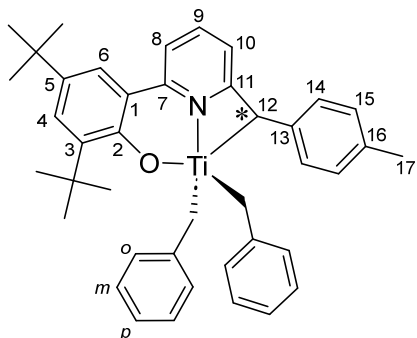
Synthesis of Complex 2. The procedure for the synthesis of complex 1 was adopted using H₄L² (0.080 g, 0.113 mmol) and Ti(CH₂Ph)₄ (0.095 g, 0.230 mmol). The product was obtained as a dark red solid. Yield: 0.081 g, 62%. ¹H NMR (600 MHz, C₆D₆): δ 7.76–7.70 (m, 8H, H⁴, H⁶, H²⁸ and H³⁰), 7.24–7.16 (m, 18H, *o*-, *o*'-, *m*-, *m*'-Ph and H²¹), 7.12–7.07 (m, 4H, H⁹ and H¹⁰), 7.07–6.99 (m, 10H, H⁸, H²², H²³, *m*- and *m*'-Ph), 6.99–6.93 (m, 8H, *m*- and *m*'-Ph), 6.89–6.82 (m, 10H, H¹⁴, *o*- and *o*'-Ph), 6.77 (d, *J* = 4.2 Hz, 2H, H¹⁷), 6.74–6.68 (m, 4H, *p*- and *p*'-Ph), 3.02–2.95 (m, 6H, H¹², H¹⁹ and CH₂), 2.94–2.89 (m, 4H, CH₂), 2.85 (d, *J* = 9.9 Hz, 2H), 2.45 (d, *J* = 8.4 Hz, 2H, CH₂), 2.35 (d, *J* = 8.6 Hz, 2H, CH₂), 2.26 (d, *J* = 8.4 Hz, 2H, CH₂), 2.07 (d, *J* = 8.6 Hz, 2H, CH₂), 1.57 (s, 36H, 3- and 27-*t*-Bu), 1.42 (s, 36H, 5- and 29-*t*-Bu). ¹³C NMR (151 MHz, C₆D₆): δ 157.52 (C²⁶), 157.46 (C²),

156.30 (C²⁰), 156.16 (C¹¹), 151.78 (C²⁴), 151.73 (C⁷), 147.77 (dd, $J = 245.4$ Hz, 14.3 Hz, C¹⁵ and C¹⁶), 142.25 (C⁵ and C²⁹), 141.66 (C⁹ and C²²), 136.55 (C³ and C²⁷), 130.80 (*o*-Ph), 130.55 (*o'*-Ph), 130.40 (*m*-Ph), 130.11 (*m'*-Ph), 129.35 (br, C¹³ and C¹⁸), 129.29 (*m'*-Ph), 129.19 (*o'*-Ph), 128.97 (*o*-Ph), 128.93 (*m*-Ph), 126.71 (C⁴ and C²⁸), 126.33 (C¹), 126.24 (C²⁵), 125.69 (*p*-Ph), 125.31 (*p'*-Ph), 124.05 (*p'*-Ph), 123.72 (*p*-Ph), 122.23 (C⁶), 122.16 (C³⁰), 119.31 (C¹⁰), 119.23 (C²¹), 118.90 (br, C¹⁴ and C¹⁷), 113.20 (C⁸), 113.09 (C²³), 84.35 ($^1J_{C,H} = 138.9$ Hz, CH₂), 84.13 ($^1J_{C,H} = 137.3$ Hz, CH₂), 80.94 ($^1J_{C,H} = 132.3$ Hz, CH₂), 80.63 ($^1J_{C,H} = 135.7$ Hz, CH₂), 66.39 ($^1J_{C,H} = 143.2$ Hz, C¹²), 65.85 ($^1J_{C,H} = 143.4$ Hz, C¹⁹), 35.44 (3- and 27-CMe₃), 34.37 (5- and 29-CMe₃), 31.42 (5- and 29-CMe₃), 30.00 (3-CMe₃), 29.96 (27-CMe₃); 4° carbons: 144.17, 143.49, 139.48, 138.63. ¹⁹F NMR (565 MHz, C₆D₆): δ -143.82, -144.45. Anal. Calcd for C₇₄H₇₈F₂N₂O₂Ti₂ (1161.2): C, 76.54; H, 6.77; N, 2.41. Found: C, 76.15; H, 6.68; N 2.26.

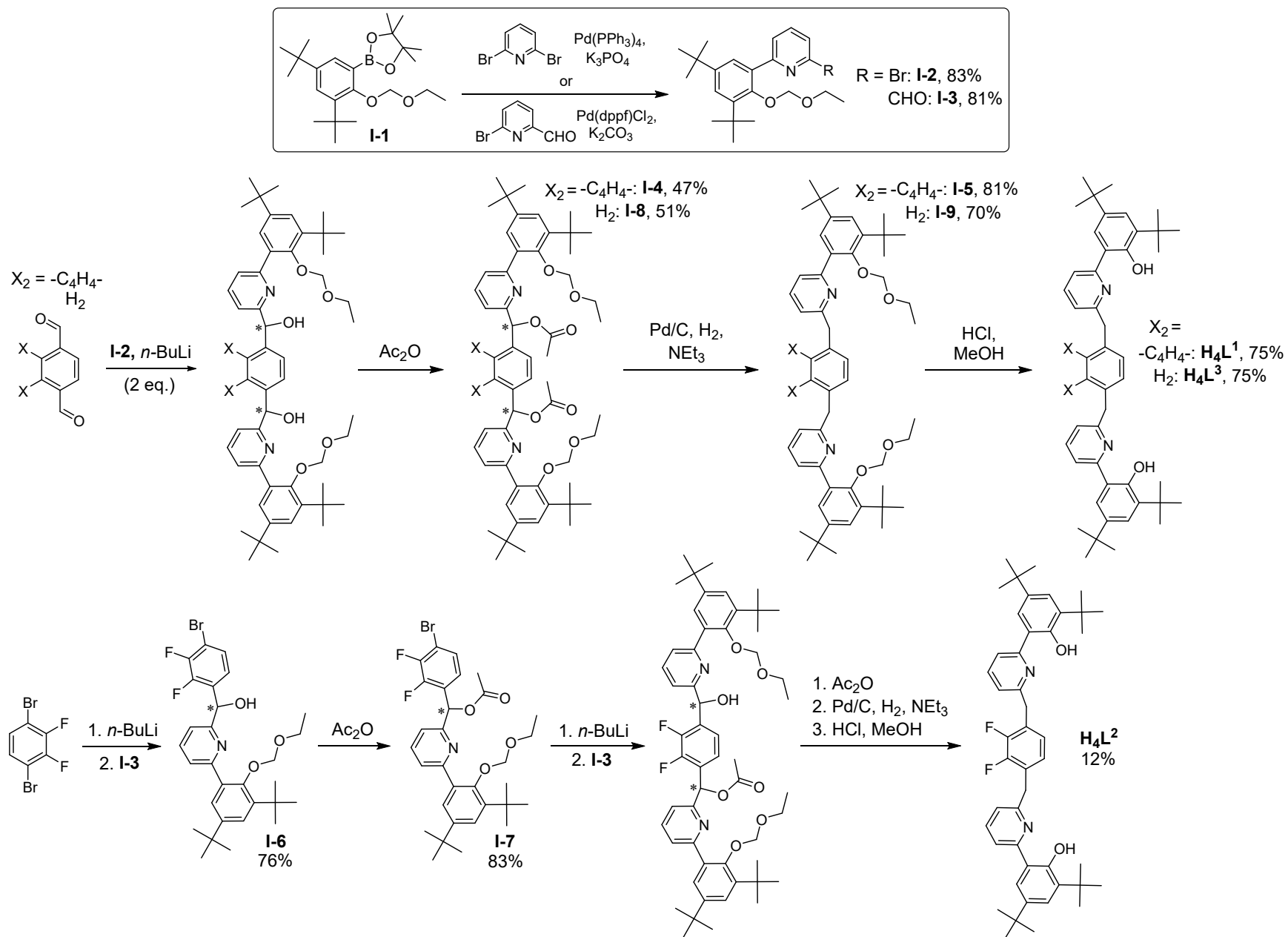


Synthesis of Complex 3. A solution of H₄L³ (0.08 g, 0.12 mmol) in toluene (5 mL) was added dropwise to Ti(CH₂Ph)₄ (0.11 g, 0.27 mmol) in toluene (3 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and at 20 °C for 18 hours. Filtration and concentration of the resultant mixture, followed by layering with pentane (10 mL), gave a dark red solid at -25 °C after 2 days. The solid was collected and dried under vacuum. Yield: 0.069 g, 51%. ¹H NMR (400 MHz, C₆D₆): δ 7.75 (d, $J = 2.0$ Hz, 4H, H⁴ and H²⁸), 7.73 (d, $J = 2.0$ Hz, 4H, H⁶ and H³⁰), 7.48 (d, $J = 8.0$ Hz, 2H, H²¹), 7.38 (d, $J = 8.0$ Hz, 2H, H¹⁰), 7.19–7.29 (m, 16H, H¹⁴⁻¹⁶, H¹⁸ and *m*-Ph), 7.10–7.13 (m, 12H, H⁹, H²² and *m*-Ph), 6.98–7.10 (m, 12H, H⁸, H²³ and *o*-Ph), 6.92–6.98 (m, 4H, *p*-Ph), 6.75–6.80 (m, 8H, *o*-Ph), 6.72 (d, $J = 7.5$ Hz, 4H, *p*-Ph), 3.01 (m, $J = 9.6$ Hz, 4H, CH₂), 2.93 (m, $J = 9.6$ Hz, 4H, CH₂), 2.77 (s, 2H, H¹²/H¹⁹), 2.76 (s, 2H, H¹²/H¹⁹), 2.34 (d, $J = 8.4$ Hz, 2H, CH₂), 2.25 (d, $J = 8.8$ Hz, 2H, CH₂), 2.18 (d, $J = 8.4$ Hz, 2H, CH₂), 2.00 (d, $J = 8.8$ Hz, 2H, CH₂), 1.61 (s, 18H, 27-*t*-Bu), 1.60 (s, 18H, 3-*t*-Bu), 1.43 (s, 18H, 29-*t*-Bu), 1.42 (s, 18H, 5-*t*-Bu). ¹³C NMR (101 MHz, C₆D₆): δ 141.71 (*o*-Ph), 130.43 (*o*-Ph), 130.18 (*o*-Ph), 129.82 (*m*-Ph), 129.52 (C⁹), 129.38 (C¹⁶), 129.22 (*m*-Ph), 129.11 (C¹⁷), 128.88 (*m*-Ph), 126.55 (C⁴ and C²⁸), 125.62 and 125.38 (C¹⁴ and C¹⁵), 125.01 (C²²), 124.65 (*p*-Ph), 124.01

(*p*-Ph), 123.74 (*p*-Ph), 122.20 (C⁶ and C³⁰), 119.19 (C¹⁰ and C²¹), 112.04 and 111.95 (C⁸ and C²³), 84.22 (¹J_{C,H} = 136.3 Hz, CH₂), 79.54 (¹J_{C,H} = 132.3 Hz, CH₂), 79.28 (¹J_{C,H} = 141.2 Hz, C¹²/C¹⁹; ¹J_{C,H} = 131.1 Hz, CH₂), 79.18 (¹J_{C,H} = 142.9 Hz, C¹²/C¹⁹), 35.46 and 34.37 (CMe₃), 31.44 (5-CMe₃ and 29-CMe₃), 30.05 (3-CMe₃ and 27-CMe₃); 4° carbons: 157.21, 153.90, 153.56, 152.82, 152.73, 144.49, 143.87, 142.09, 140.30, 139.68, 139.40, 139.23, 137.53, 136.60, 127.80, 127.57, 126.63, 126.61. Anal. Calcd for C₇₄H₈₀N₂O₂Ti₂ (1124.52): C, 78.99; H, 7.17; N, 2.49. Found: C, 78.60; H, 7.12; N, 2.23.



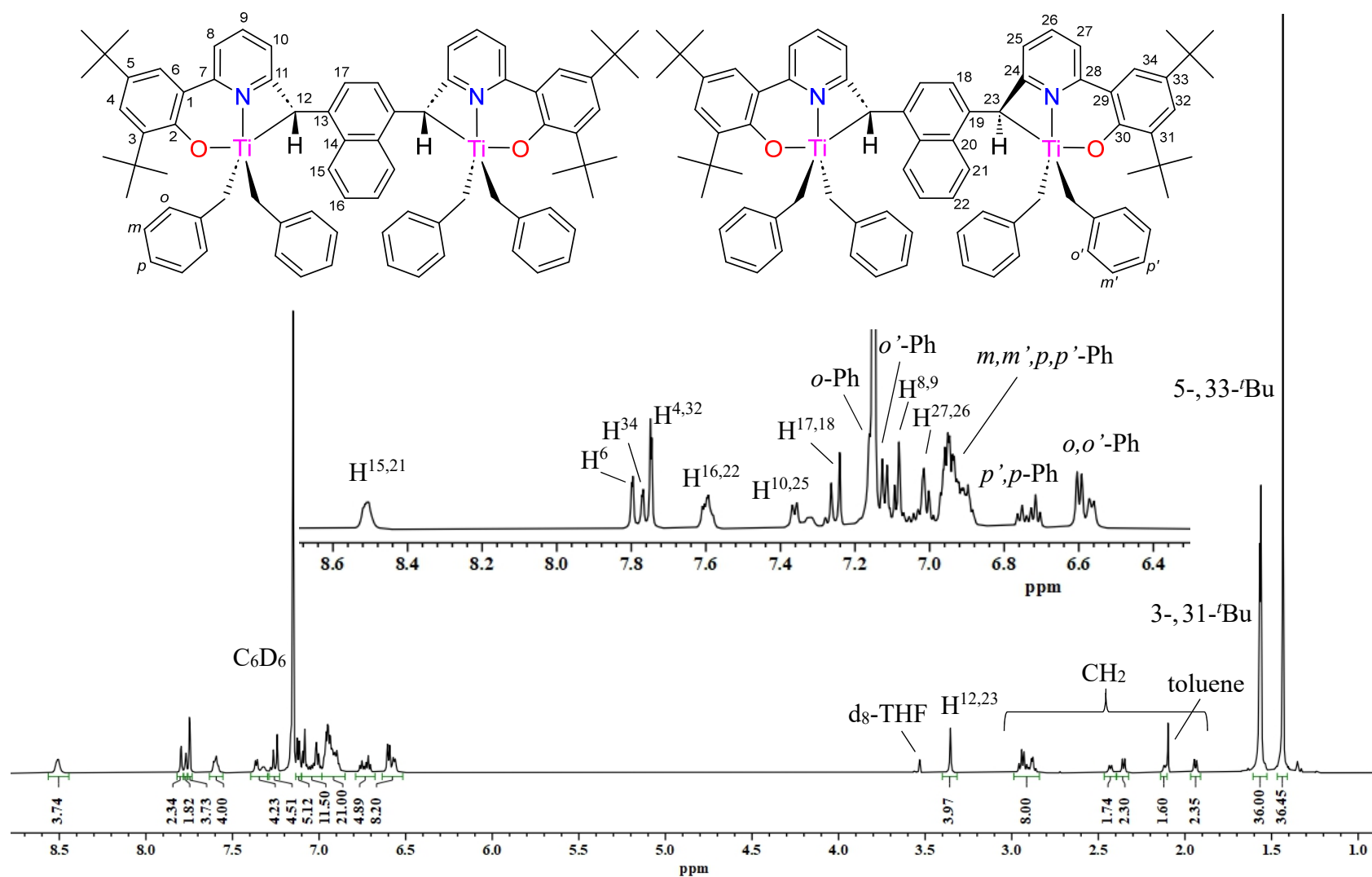
Synthesis of Complex 5m. The procedure for the synthesis of complex **1** was adopted using H₂L⁴ (0.100 g, 0.258 mmol) and Ti(CH₂Ph)₄ (0.109 g, 0.263 mmol). The product was obtained as a black-red solid. Yield: 0.0905 g, 57%. ¹H NMR (600 MHz, C₆D₆): δ 7.72 (d, *J* = 2.4 Hz, 1H, H⁴), 7.70 (d, *J* = 2.4 Hz, 1H, H⁶), 7.23 (d, *J* = 8.0 Hz, 1H, H¹⁰), 7.19–7.13 (m, 2H, H¹⁵), 7.13–7.08 (m, 4H, *o*-Ph and H¹⁴), 7.03 (d, *J* = 18.0 Hz, 1H, H⁹), 7.02–6.98 (m, 2H, *m*-Ph), 6.95 (d, *J* = 6.0 Hz, 1H, H⁸), 6.94–6.89 (m, 3H, *p*- and *m*-Ph), 6.73 (t, *J* = 7.3 Hz, 1H, *p*-Ph), 6.56 (d, *J* = 7.6 Hz, 2H, *o*-Ph), 2.92 (d, *J* = 9.6 Hz, 1H, CH₂), 2.89 (d, *J* = 9.6 Hz, 1H, CH₂), 2.65 (s, 1H, H¹²), 2.30 (s, 3H, H¹⁷), 2.14 (d, *J* = 8.8 Hz, 1H, CH₂), 1.92 (d, *J* = 8.7 Hz, 1H, CH₂), 1.58 (s, 9H, 3-*t*-Bu), 1.40 (s, 9H, 5-*t*-Bu). ¹³C NMR (151 MHz, C₆D₆): δ 142.09 (C⁹), 130.45 (*o*-Ph), 129.83 (*m*-Ph), 129.71 (C¹⁵), 129.56 (*m*-Ph), 129.38 (*o*-Ph), 126.89 (C⁴), 125.49 (C¹⁴), 124.99 (*p*-Ph), 124.25 (*p*-Ph), 122.50 (C⁶), 119.30 (C¹⁰), 112.37 (C⁸), 84.80 (¹J_{C,H} = 135.9 Hz, CH₂), 79.94 (¹J_{C,H} = 133.6 Hz, CH₂), 78.50 (¹J_{C,H} = 141.9 Hz, C¹²), 35.80 (3-CMe₃), 34.71(5-CMe₃), 31.79 (5-CMe₃), 30.40 (3-CMe₃), 21.43 (C¹⁷); 4° carbons: 157.57, 154.57, 153.00, 144.20, 142.43, 141.56, 140.40, 136.95, 132.36, 126.92. Anal. Calcd for C₄₁H₄₅NOTi (615.7): C, 79.98; H, 7.37; N, 2.28. Found: C, 79.62; H, 7.25; N, 1.98.



Scheme S1. Synthesis of H₄L¹⁻³.

B. Selected NMR Spectra and Data

Figure S1. Full (bottom) and expanded (top) ^1H NMR spectra of complex **1** (600 MHz, C_6D_6 with 3 drops of d_8 -THF, 281 K).



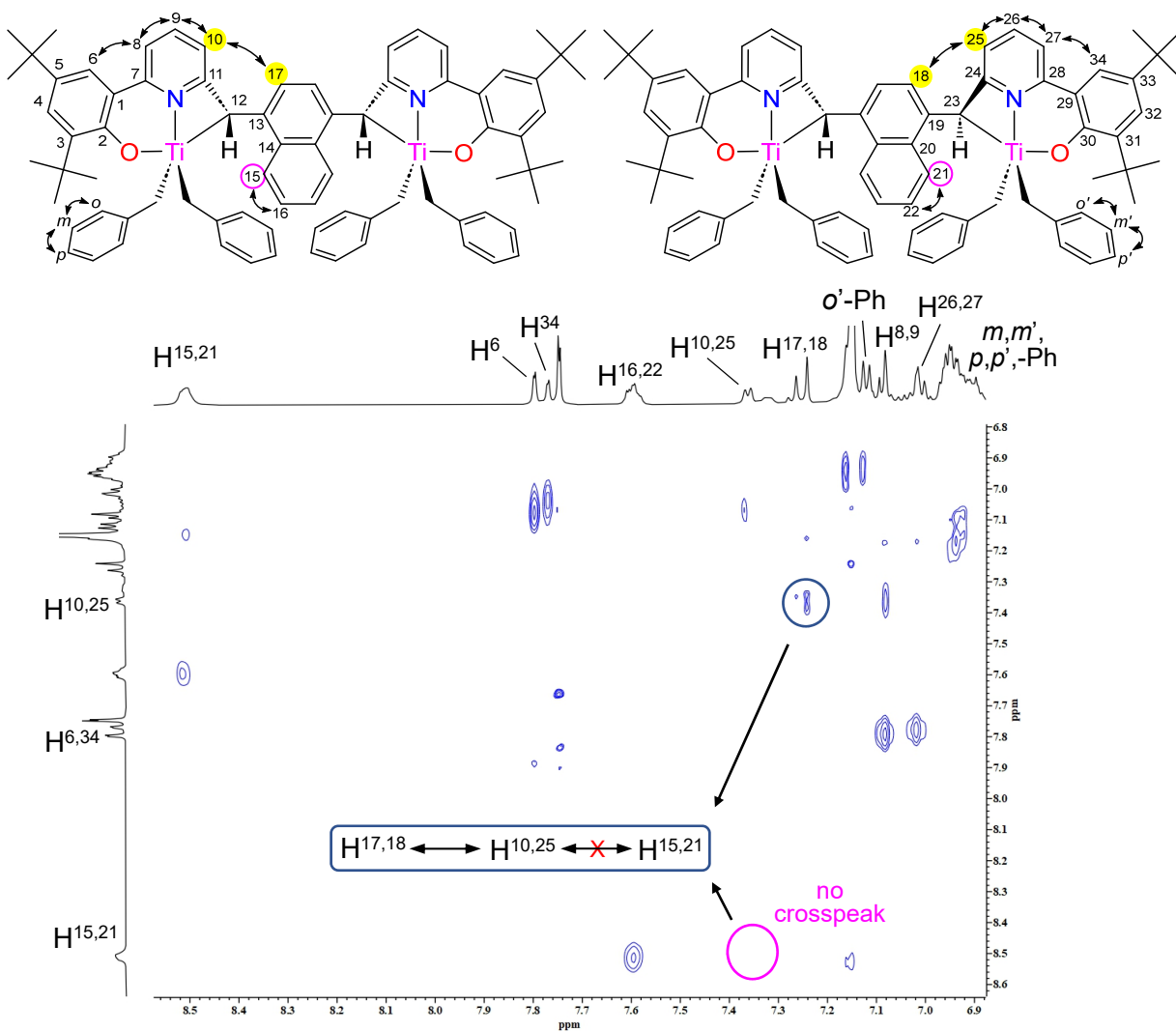
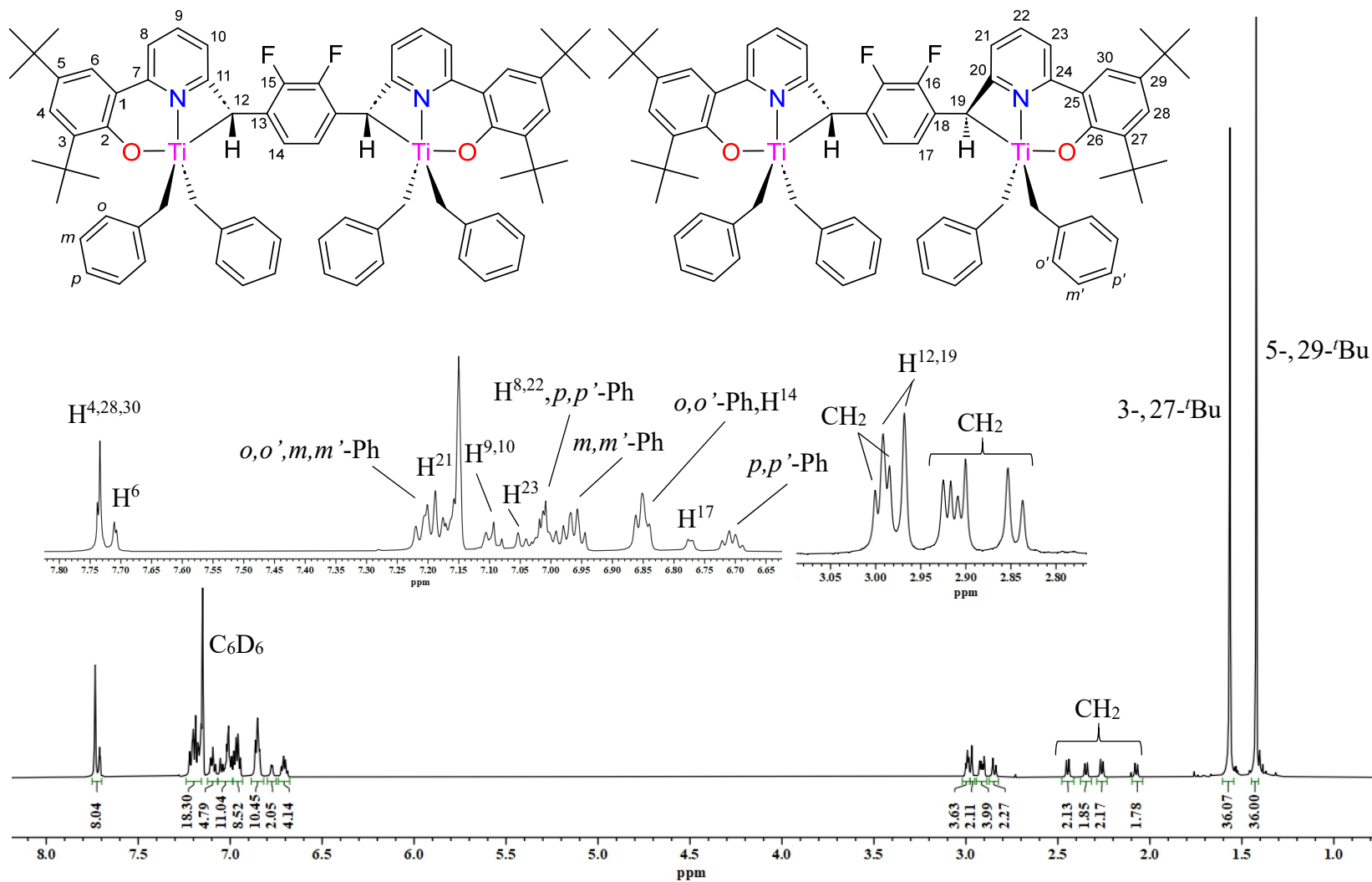


Figure S2. Expanded $[\text{^1H}, \text{^1H}]$ -ROESY spectrum of complex **1** (both diastereomers; 600 MHz, C_6D_6 and d_8 -THF, 281 K), indicating that the $\text{C}^{12}\text{-C}^{13}$ and $\text{C}^{19}\text{-C}^{23}$ bonds do not rotate freely and the depicted conformations are preferred.

Figure S3. Full (bottom) and expanded (top) ^1H NMR spectra of complex **2** (600 MHz, C_6D_6 , 298 K).



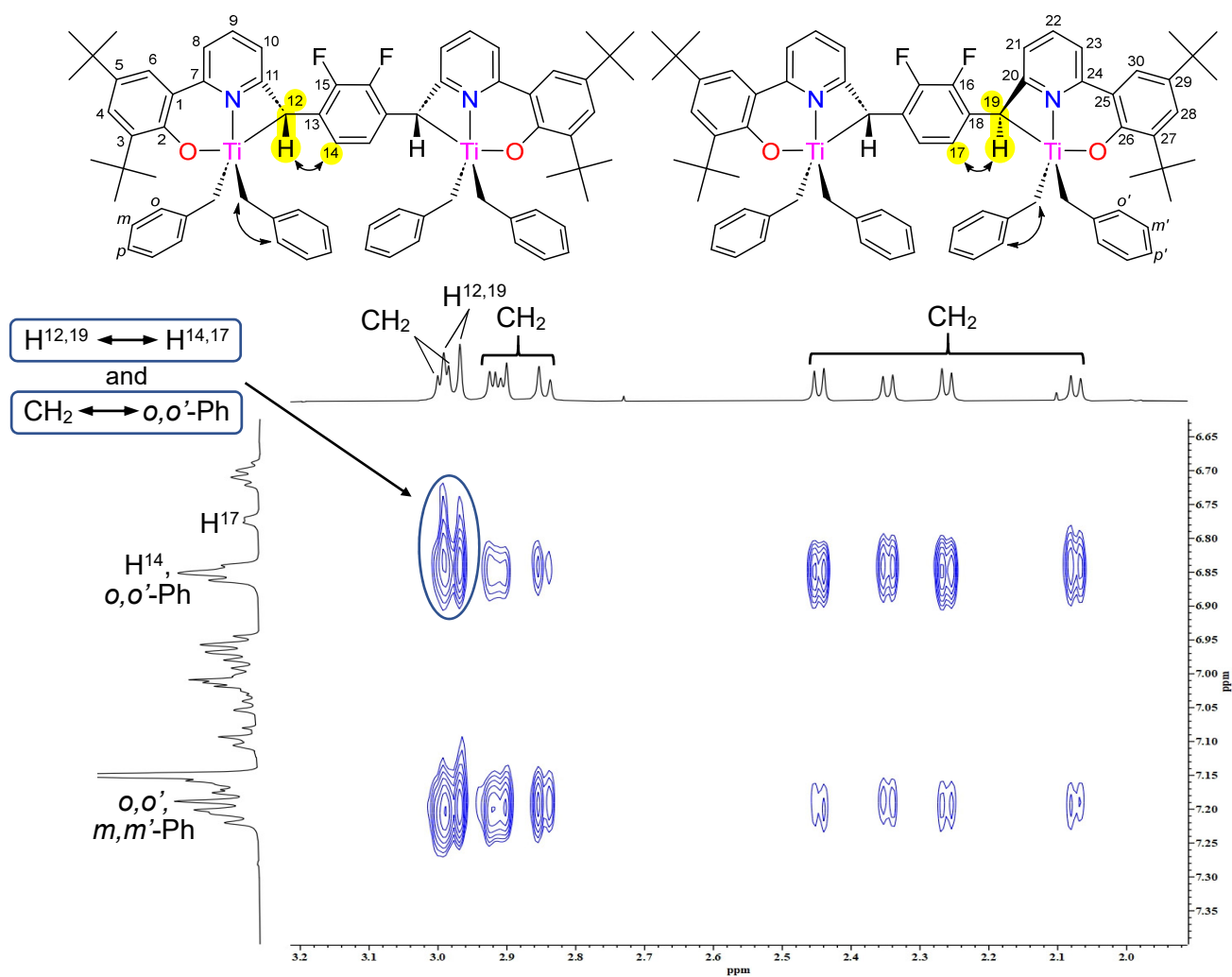


Figure S4. Expanded $[\text{}^1\text{H}, \text{}^1\text{H}]$ -ROESY spectrum of complex **2** (both diastereomers; 600 MHz, C_6D_6 , 298 K), tentatively indicating that the depicted conformations are preferred.

Table S1. Selected NMR data (600 MHz) for complexes **1–3**, **4m** and **5m**.

Complex	CH ₂ (ppm)	CH ₂ (ppm)	² J _{H,H} (CH ₂) (Hz)	¹ J _{C,H} (CH ₂) (Hz)	H(methine) (ppm)	C(methine) (ppm)	Ratio of diastereomers
1 ^a	1.94, 2.11, 2.35, 2.43 ^e	83.96, 83.57, 78.52, 78.18	8.4, 8.3 ^e	136.0, 136.6, 134.6, 134.6	3.35 (×2)	71.25 (×2)	1.32
2 ^b	2.07, 2.26, 2.35, 2.45, 2.85, 2.91, 2.92, 2.99	84.35, 84.13, 80.94, 80.63	8.6, 8.4, 9.9, 9.9	138.9, 137.3, 132.3, 135.7	2.97, 2.99	66.39, 65.85	1.18
3 ^{b,c}	2.00, 2.18, 2.25, 2.34, 2.93, 3.01 ^e	79.28, 79.54, 84.22, 84.22	8.4, 8.8, 9.6 ^e	136.3, 136.3, 132.3, 131.1	2.76, 2.77	79.18, 79.28	1.13
4m ^{b-d}	1.90, 2.27, 2.85, 2.91	79.46, 85.34	8.8, 9.4	138.9, 136.8	3.29	70.42	–
5m ^b	1.92, 2.14, 2.89, 2.92	84.80, 79.94	8.8, 9.6	135.9, 133.6	2.65	78.50	–

^a C₆D₆ with 3 drops of d₈-THF, 281 K. ^b C₆D₆, 298 K. ^c 400 MHz. ^d Reference 5. ^e Remaining data obscured by overlapping peaks.

C. Determination of Comonomer Incorporation Ratios using ^{13}C NMR Spectroscopy

Table S2. Comonomer incorporation ratios for ethylene-(1-octene) copolymerisations.^a

Catalyst	1-Octene conc. (mol L ⁻¹)	T _A	T _B	T _C	T _E	T _F	T _G	T _H	1-Octene incorporation (%)
1	0.4	0	1.00	0	1.73	9.51	2.50	0	18.3
	0.8	1.00	2.52	0	6.13	20.72	8.65	0.86	26.0
	1.2	1.00	1.87	0	4.28	8.80	5.44	1.02	40.9
2	0.4	0	1.00	0	1.55	11.63	3.07	0	13.9
	0.8	1.00	4.31	0	8.47	31.47	14.67	2.21	22.4
	1.2	1.00	2.94	0	6.43	17.46	11.31	1.05	27.8
3	0.4	0	1.00	0	1.52	14.41	3.02	0	11.7
4m	0.4	0	1.00	0	2.50	37.52	5.14	0	4.9
5m	0.4	0	1.00	0	1.97	15.05	4.32	0	10.7
	0.8	0	1.00	0	1.96	8.36	3.70	0.57	16.5
	1.2	1.00	4.52	0	6.73	34.07	12.36	1.66	22.0

^a T represents integrals from ^{13}C NMR inverse-gated experiments in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120 °C; copolymers obtained under conditions described in Table 1, entries 6–16.

Calculation Method

The relationships between triads and ^{13}C NMR integrals are shown below (T represents integral; O = 1-octene, E = ethylene).⁶

$$[\text{OOO}] = T_A - 0.5T_C$$

$$[\text{EOO}] = T_C$$

$$[\text{EOE}] = T_B$$

$$[\text{EEE}] = 0.5T_F - 0.25T_E - 0.25T_G$$

$$[\text{OEO}] = T_H$$

$$[\text{OEE}] = T_G - T_E$$

Then [O], [E] and 1-octene incorporation ratio are calculated according to:

$$[\text{O}] = [\text{OOO}] + [\text{EOO}] + [\text{EOE}]$$

$$[\text{E}] = [\text{EEE}] + [\text{OEO}] + [\text{OEE}]$$

$$\text{1-Octene mol\%} = [\text{O}] / ([\text{O}] + [\text{E}]) \times 100\%$$

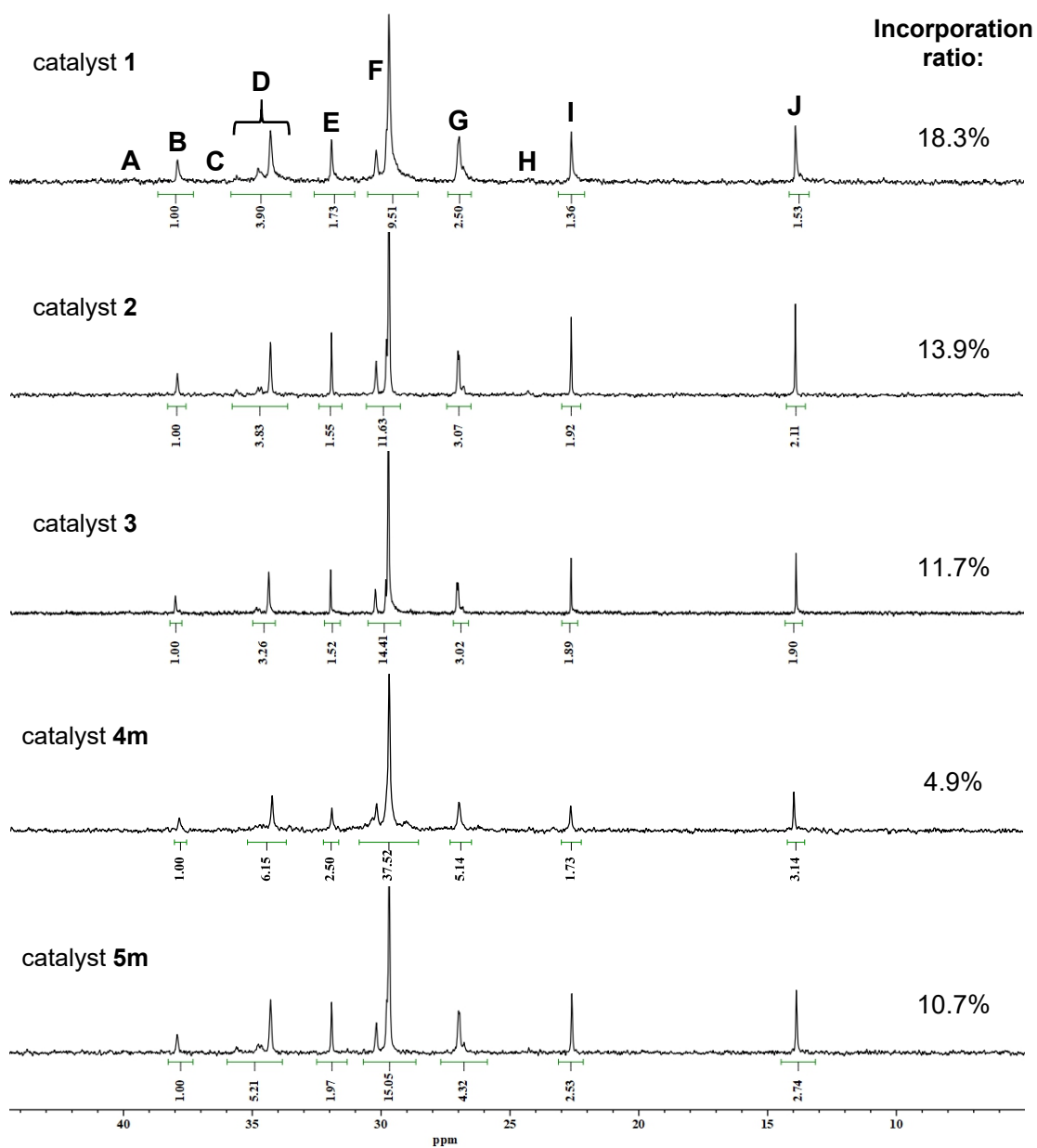


Figure S5. ^{13}C NMR spectra (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 393 K) of ethylene/1-octene copolymers produced by Ti_2 catalysts **1–3** and mono-Ti controls ($[\text{1-octene}] = 0.40 \text{ mol L}^{-1}$; Table 1, entries 6–10; **A–J** refer to peak assignments used for calculation of incorporation ratio).

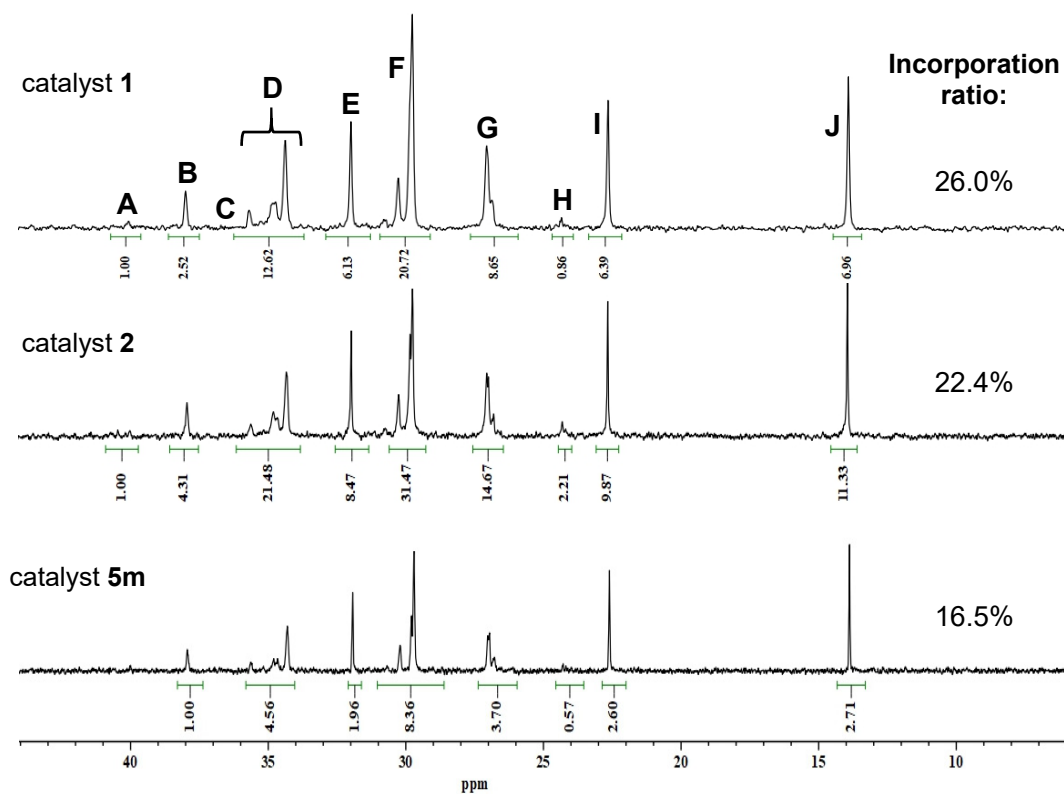


Figure S6. ^{13}C NMR spectra (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 393 K) of ethylene/1-octene copolymers produced by Ti_2 catalysts **1** and **2** and mono-Ti control **5m** ([1-octene] = 0.80 mol L^{-1} ; Table 1, entries 11–13; **A–J** refer to peak assignments used for calculation of incorporation ratio).

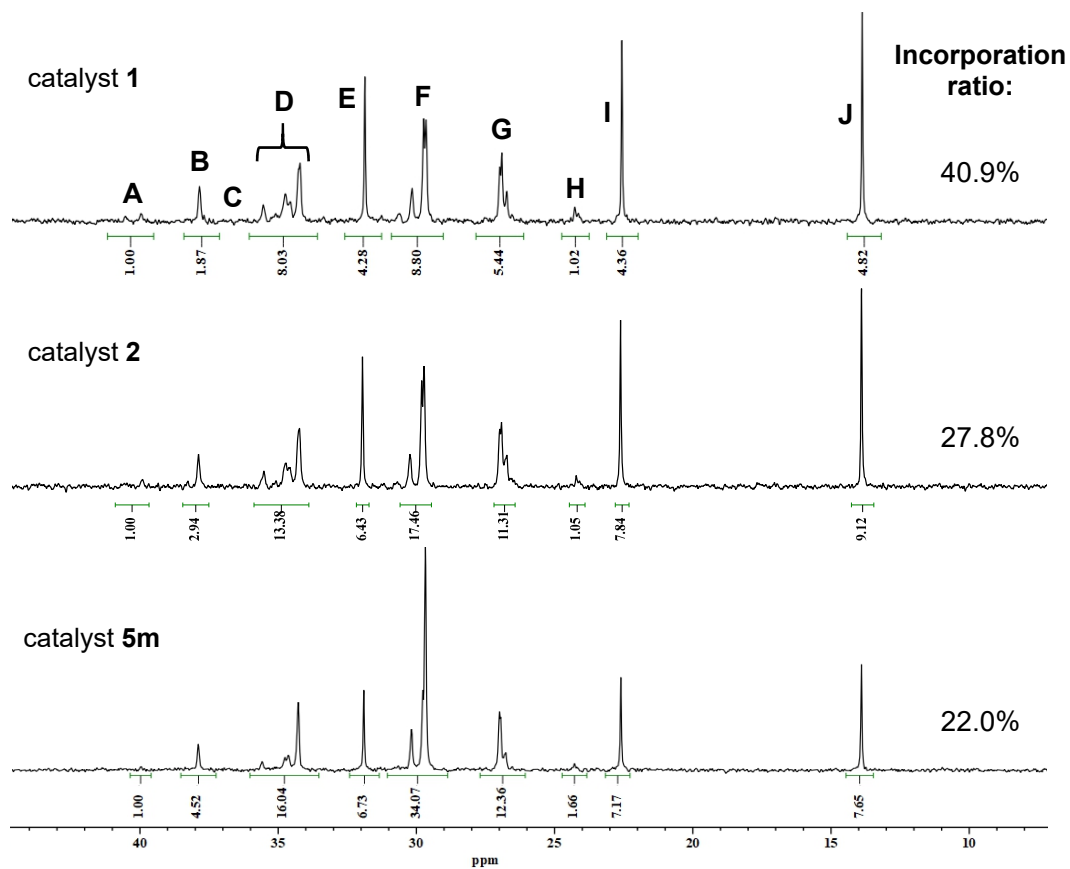


Figure S7. ^{13}C NMR spectra (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 393 K) of ethylene/1-octene copolymers produced by Ti_2 catalysts **1** and **2** and mono-Ti control **5m** ($[\text{1-octene}] = 1.20 \text{ mol L}^{-1}$; Table 1, entries 14–16; A–J refer to peak assignments used for calculation of incorporation ratio).

Table S3. Ethylene-(1-hexene) copolymerisation in conjunction with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $i\text{Bu}_3\text{Al}$ ^a

Catalyst (μmol)	1-Hexene conc. (mol L^{-1})	Yield (g)	Activity ^b	M_w (kg mol^{-1}) ^c	\mathcal{D} ^c	1-Hexene incorp. (%) ^d
1 (1.5)	1.20	0.421	840	214	3.5	16.7 %

^a Conditions: molar ratios of $i\text{Bu}_3\text{Al}/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{metal} = 50/2/1$, 1 atm pressure of ethylene gas (maintained by continuous supply), 22 °C, 10 min reaction time, 20 mL toluene. ^b Activity = g of polymer ($\text{mmol of metal}^{-1} \text{ h}^{-1}$) ($\pm 10\%$). ^c Determined by GPC at 150 °C in 1,2,4-trichlorobenzene versus polystyrene standards. ^d Determined by ^{13}C NMR spectroscopy at 120 °C in $\text{C}_2\text{D}_2\text{Cl}_4$.

Table S4. Comonomer incorporation ratio for ethylene-(1-hexene) copolymerisation.^a

Cat.	1-Hexene conc. (mol L^{-1})	T_A	T_B	T_C	T_D	T_E	T_F	T_G	1-Hexene incorp. (%)
1	1.2	1.00	3.48	14.82	30.20	6.19	1.21	6.09	16.7%

^a T represents integrals from ^{13}C inverse-gated NMR experiments in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120 °C; copolymers obtained under conditions described in Table S3.

Calculation Method

The relationships between triads and ^{13}C NMR integrals are shown below (T represents integral; H = 1-hexene, E = ethylene).⁶

$$[\text{HHH}] = 2T_A - T_C + T_E + 2T_F + T_G$$

$$[\text{EHH}] = 2T_C - 2T_A - 2T_E - 4T_F - 2T_G$$

$$[\text{EHE}] = T_B$$

$$[\text{EEE}] = 0.5T_D - 0.5T_G - 0.25T_E$$

$$[\text{HEH}] = T_F$$

$$[\text{HEE}] = T_E$$

Then [H], [E] and 1-hexene incorporation ratio are calculated according to:

$$[\text{H}] = [\text{HHH}] + [\text{EHH}] + [\text{EHE}]$$

$$[\text{E}] = [\text{EEE}] + [\text{HEH}] + [\text{HEE}]$$

$$\text{1-Hexene mol\%} = [\text{H}]/([\text{H}] + [\text{E}]) \times 100\%$$

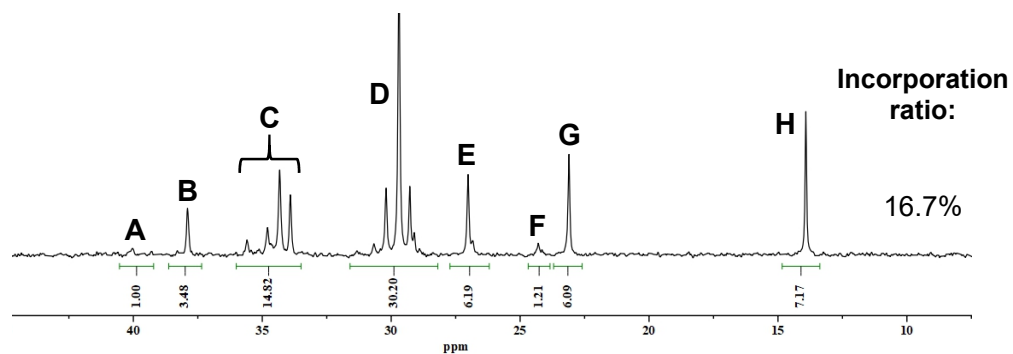
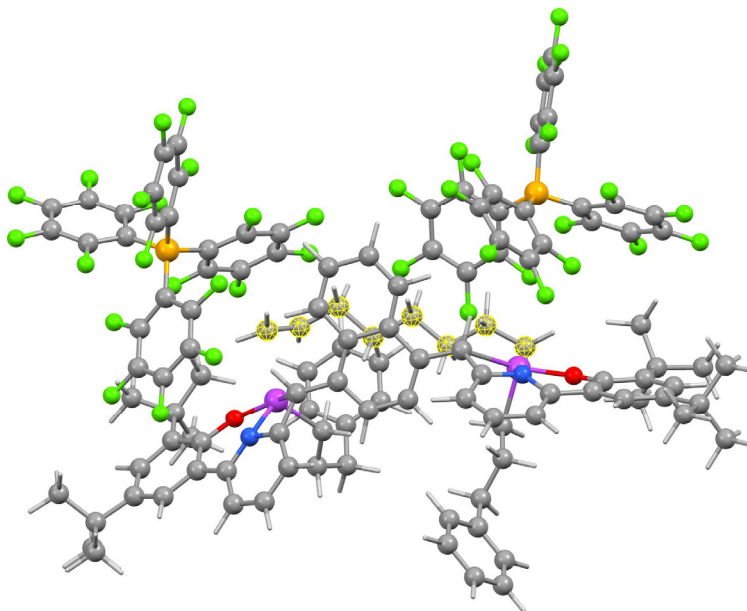


Figure S8. ^{13}C NMR spectra (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 393 K) of ethylene/1-hexene copolymers produced by Ti_2 catalyst **1** ($[\text{1-hexene}] = 1.20 \text{ mol L}^{-1}$; Table S3; **A–H** refer to peak assignments used for calculation of incorporation ratio).

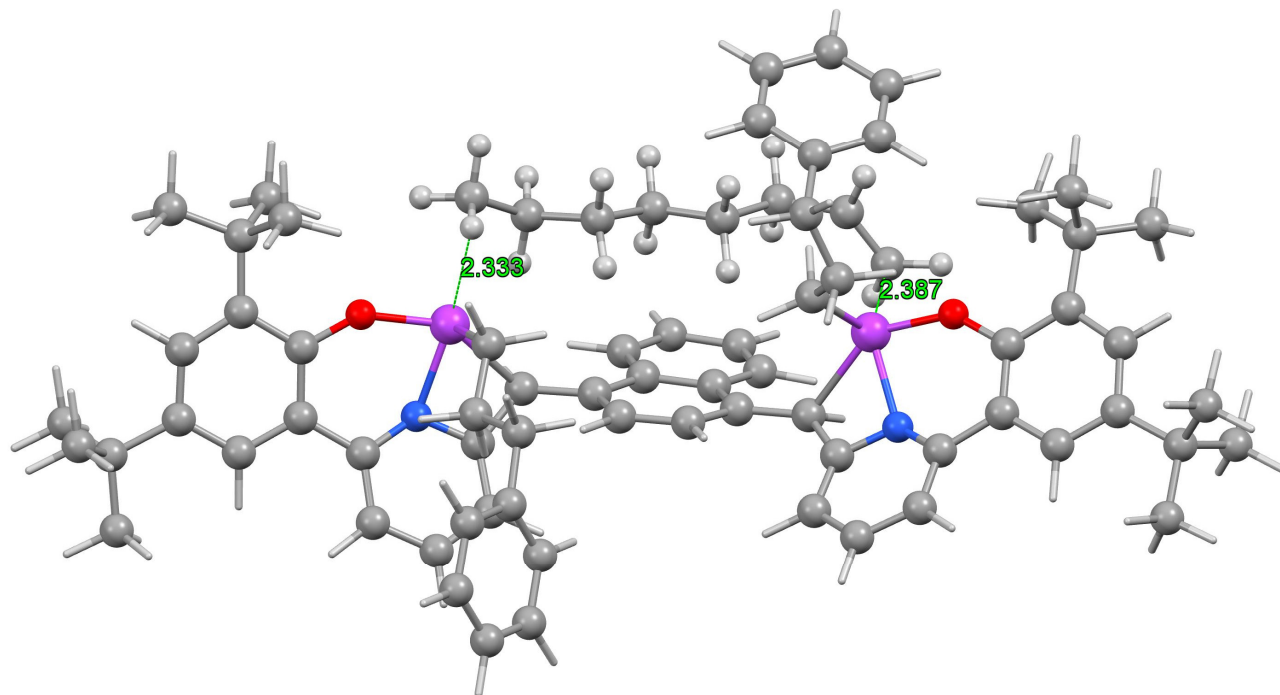
Figure S9. Energy-minimised calculated (Gaussian/M06-2X; dispersion-corrected) structure for plausible π (octene)-intermediate of [(*RS*)-1][B(C₆F₅)₄]₂ (polymer chains represented by propylbenzene).

View with borate anions (Ti, magenta ; C, gray [octene highlighted]; N, blue; O, red; F, green; B, orange).



View with borate anions omitted (for clarify):

Ti...Ti = 8.380 Å; Ti-C(π) = 2.387 Å; Ti...H(agostic) = 2.333 Å (at terminal C⁸ atom).



D. Additional ^1H and ^{13}C NMR Spectra



Figure S10. ^1H NMR spectrum (CDCl₃, 300 MHz, 298 K) of **I-2**.

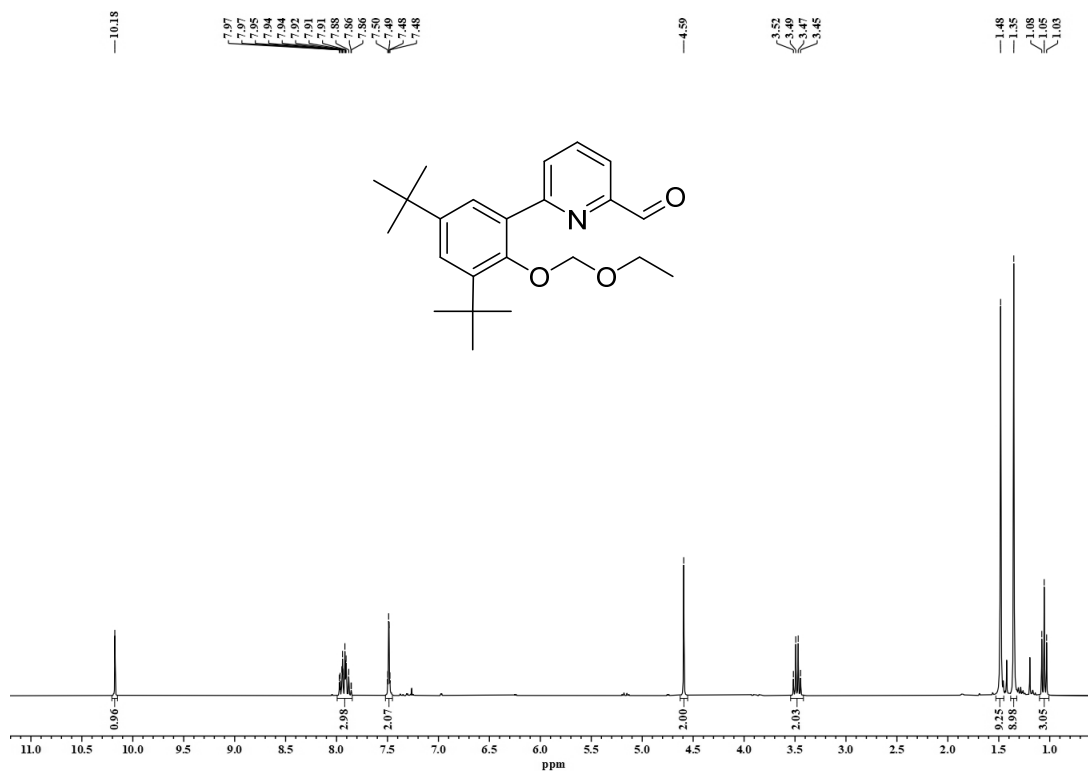


Figure S11. ^1H NMR spectrum (CDCl₃, 300 MHz, 298 K) of **I-3**.

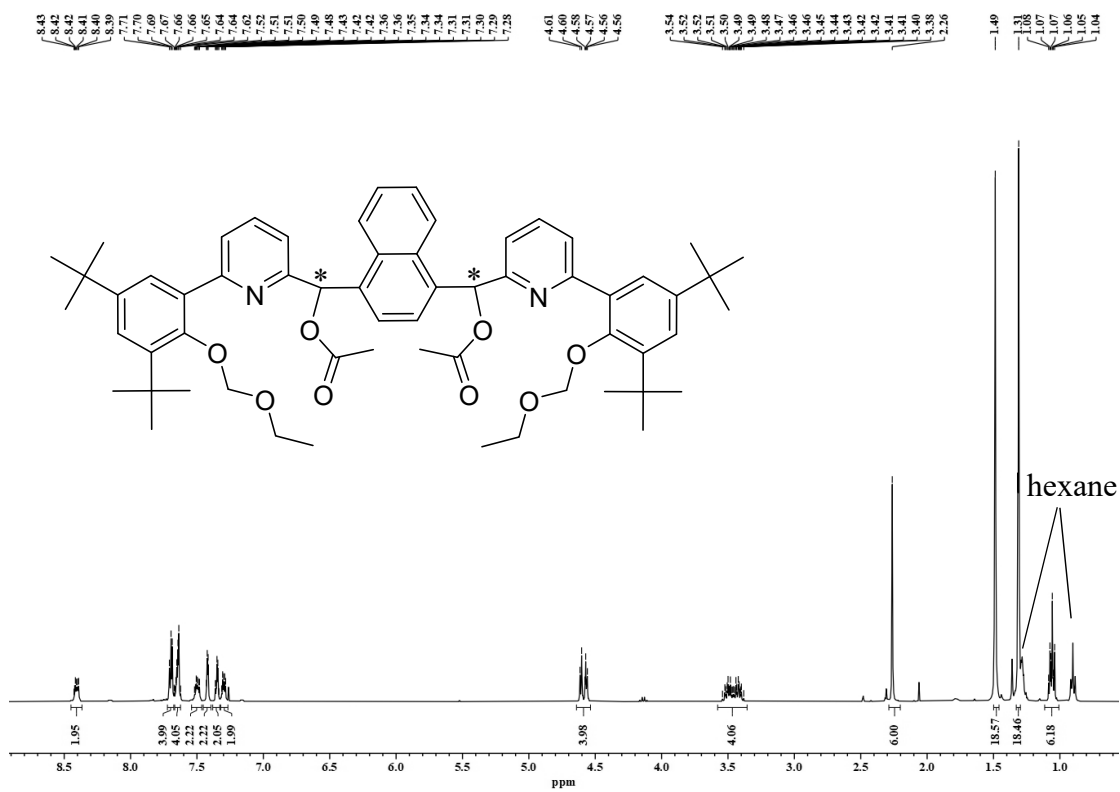


Figure S12. ¹H NMR spectrum (CDCl₃, 400 MHz, 298 K) of I-4.

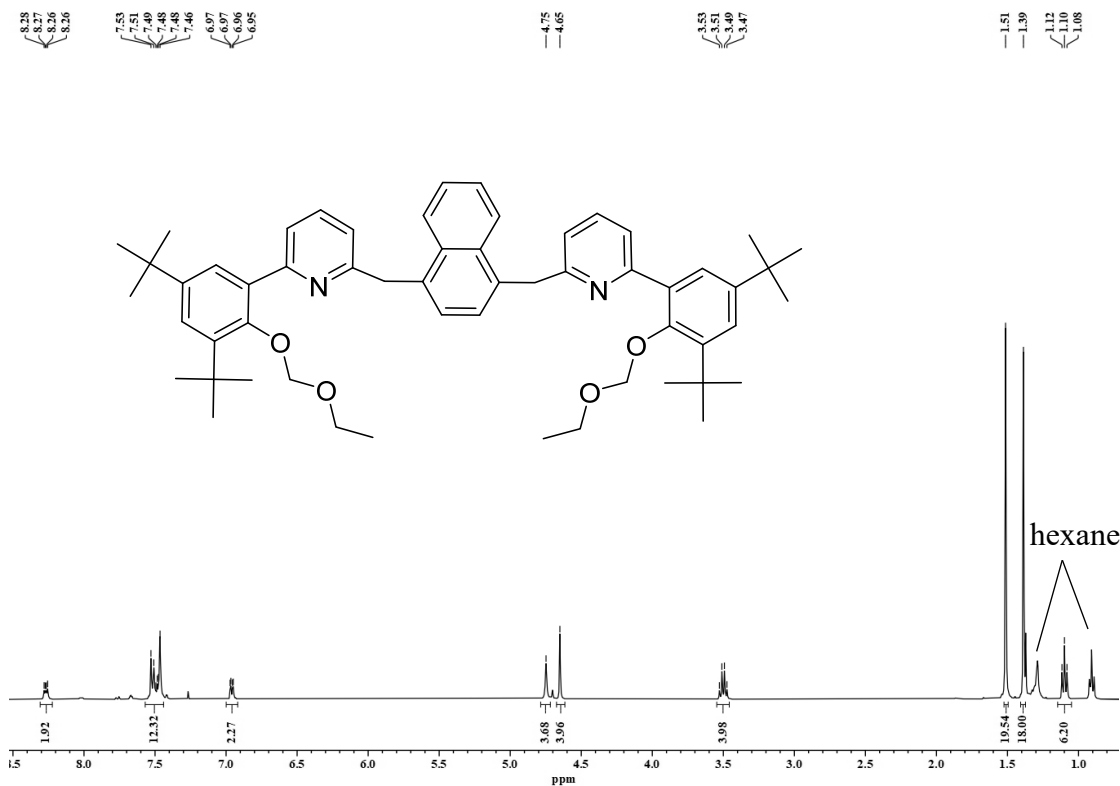


Figure S13. ¹H NMR spectrum (CDCl₃, 400 MHz, 298 K) of I-5.

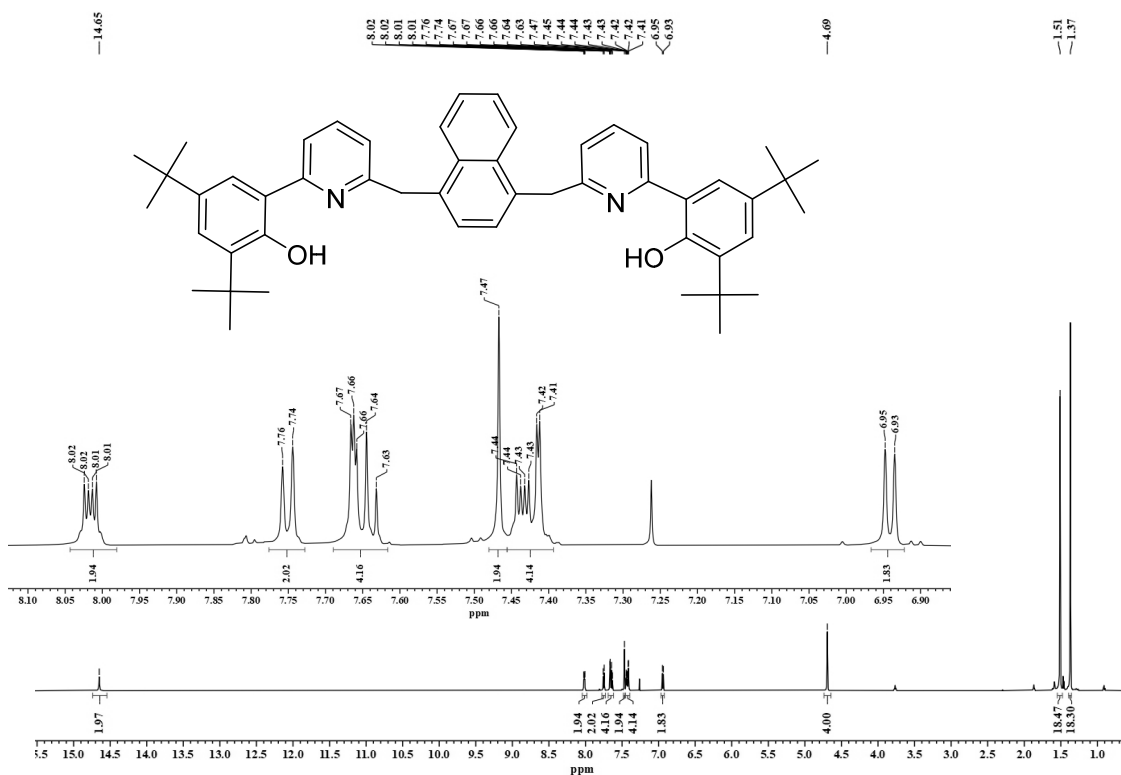


Figure S14. ¹H NMR spectrum (CDCl₃, 600 MHz, 298 K) of **H₄L¹**.

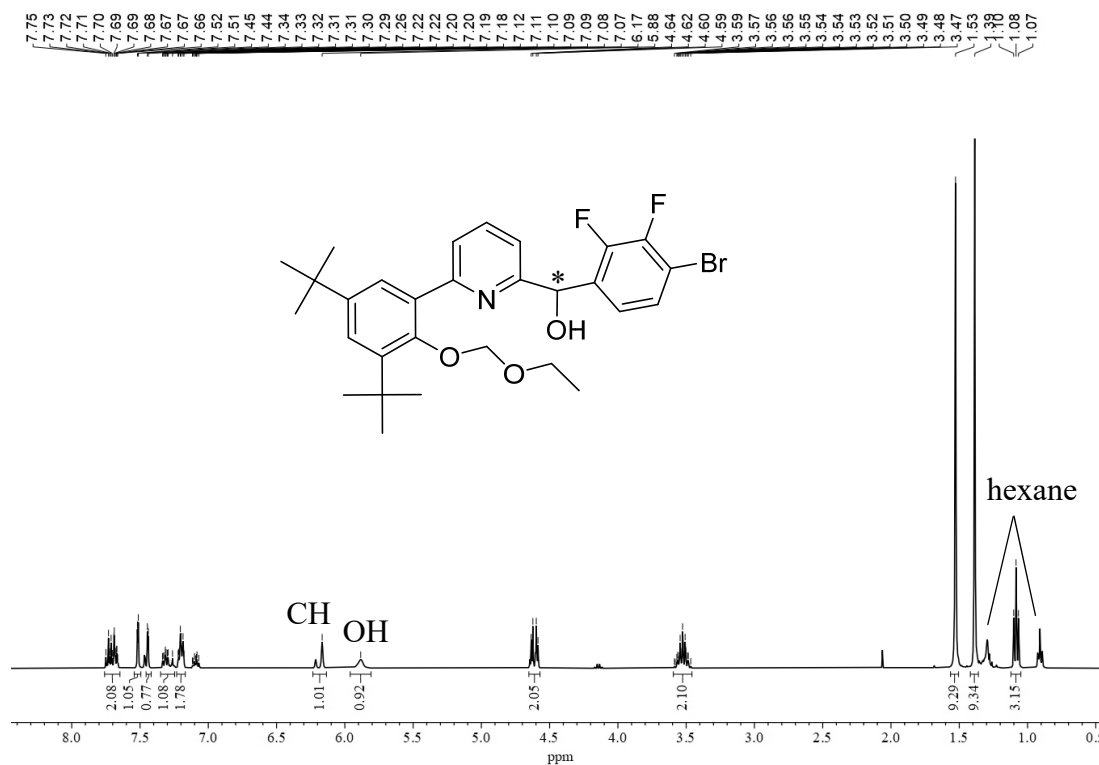


Figure S15. ¹H NMR spectrum (CDCl₃, 400 MHz, 298 K) of **I-6**.

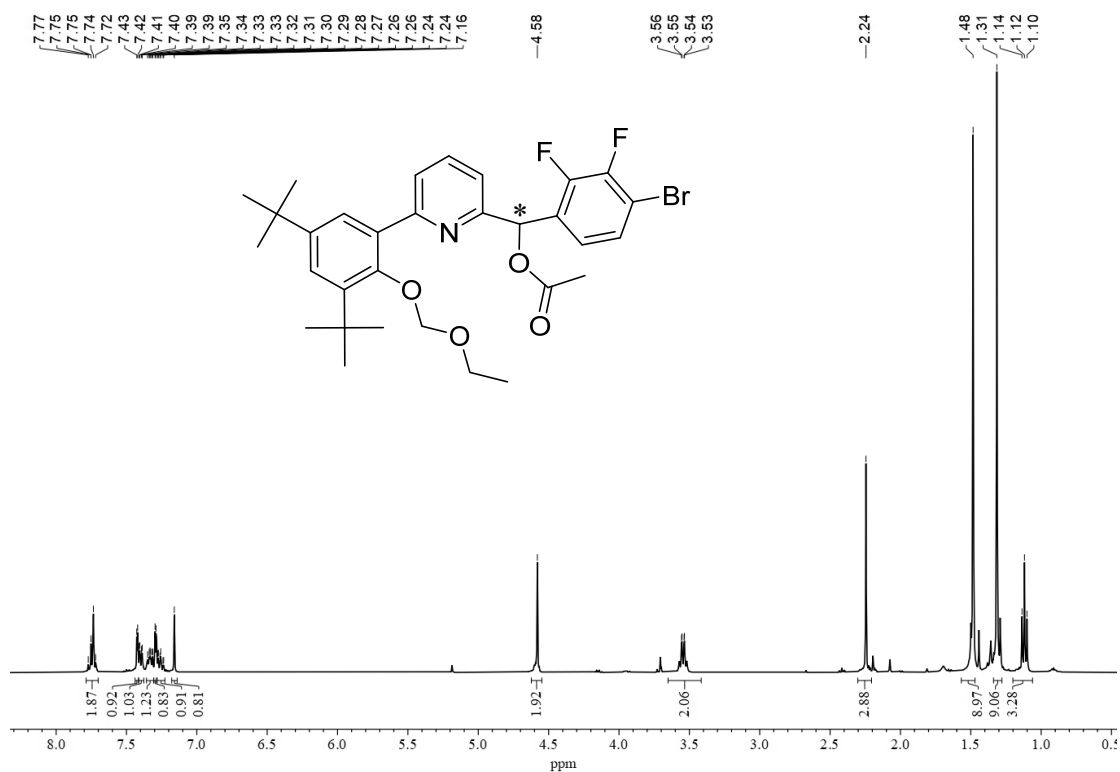


Figure S16. ^1H NMR spectrum (CDCl_3 , 400 MHz, 298 K) of **I-7**.

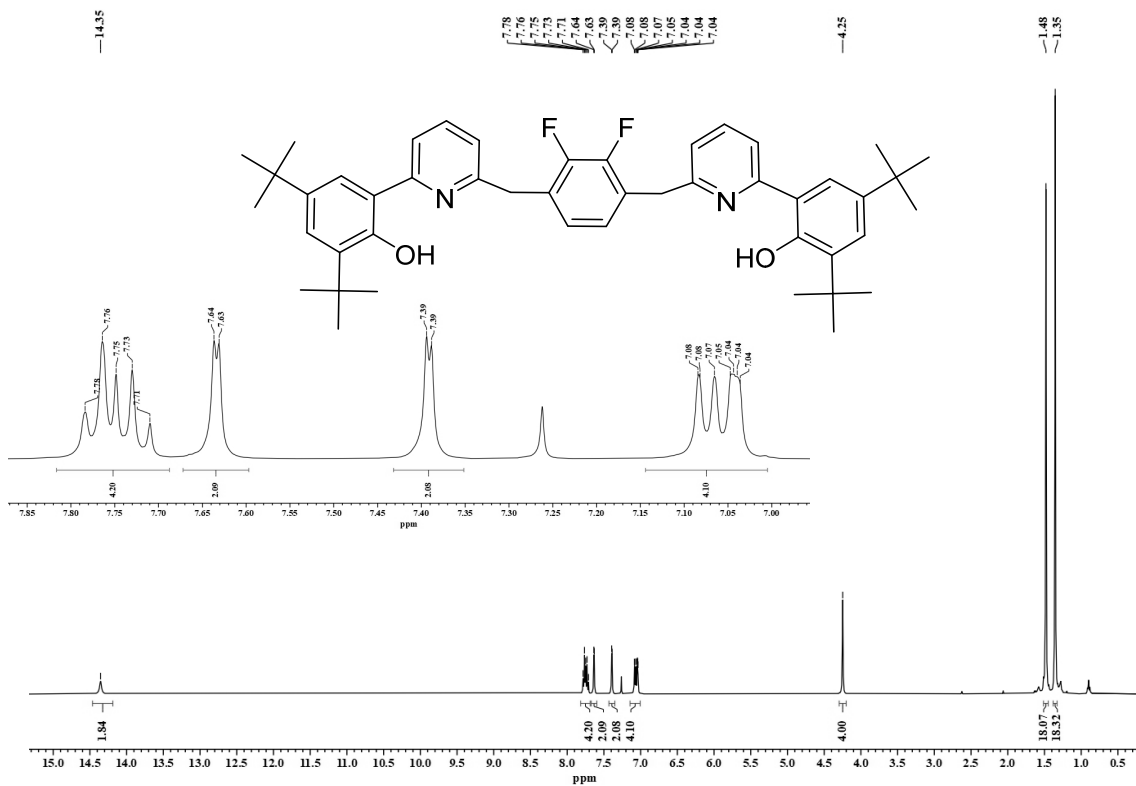


Figure S17. ^1H NMR spectrum (CDCl_3 , 400 MHz, 298 K) of **H₄L²**.

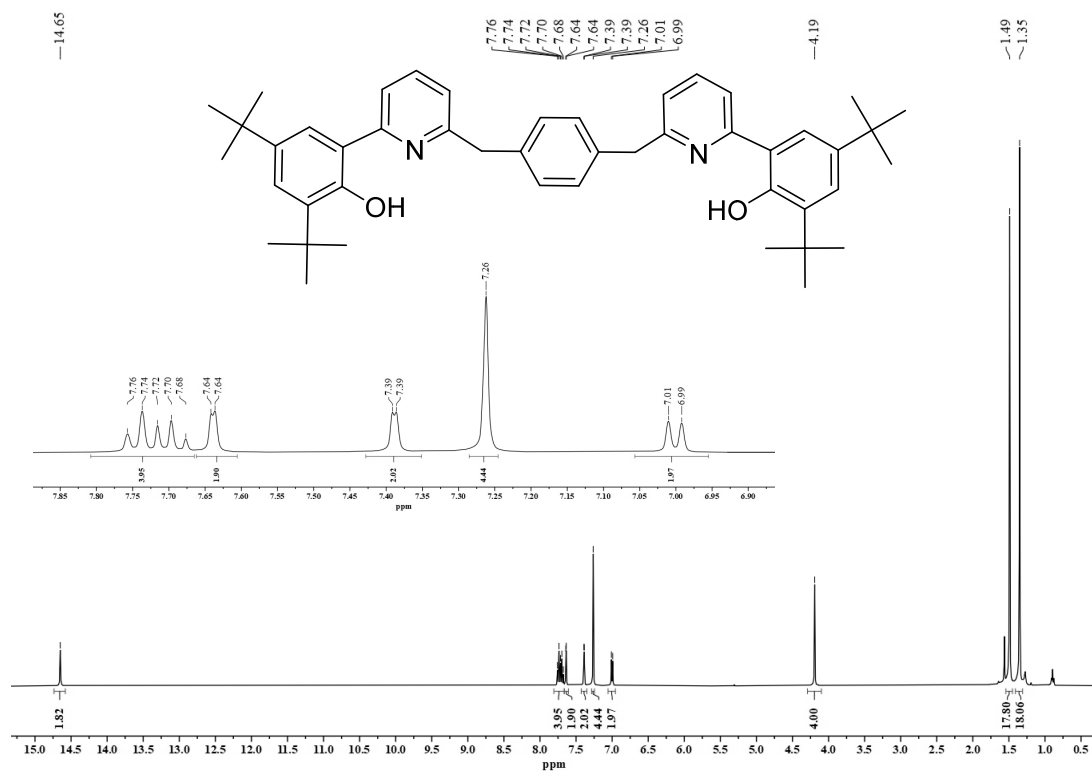


Figure S18. 1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of H_4L^3 .

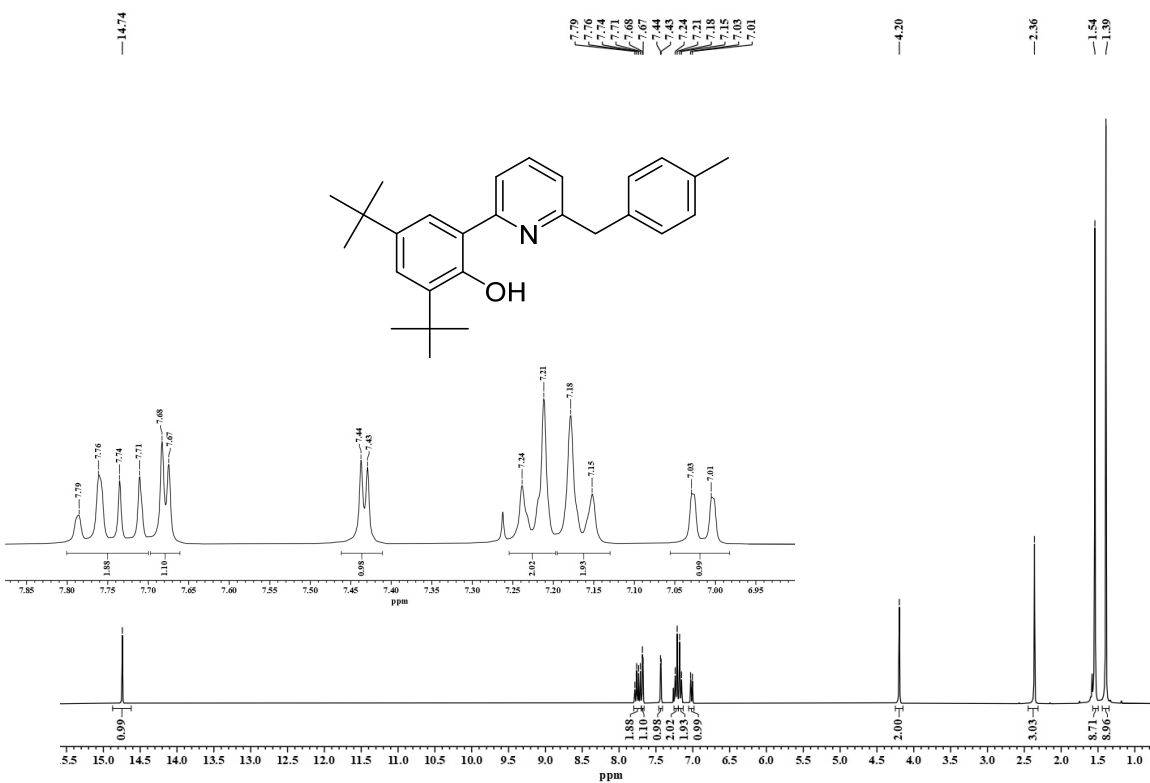


Figure S19. 1H NMR spectrum ($CDCl_3$, 300 MHz, 298 K) of H_2L^4 .

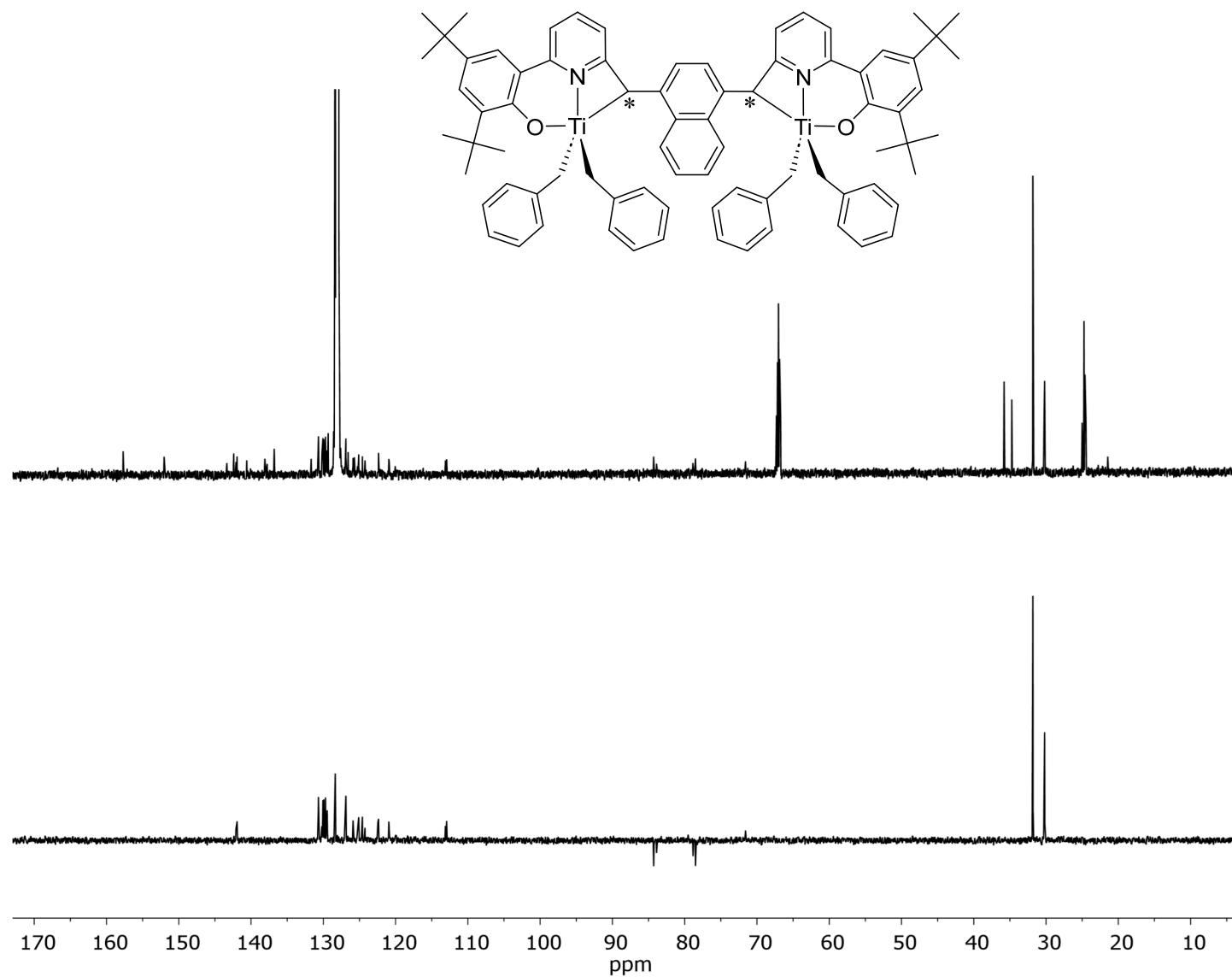


Figure S20. ^{13}C (top) and DEPT-135 (bottom) NMR spectra (C_6D_6 with 3 drops of d_8 -THF, 151 MHz, 298 K) of complex 1.

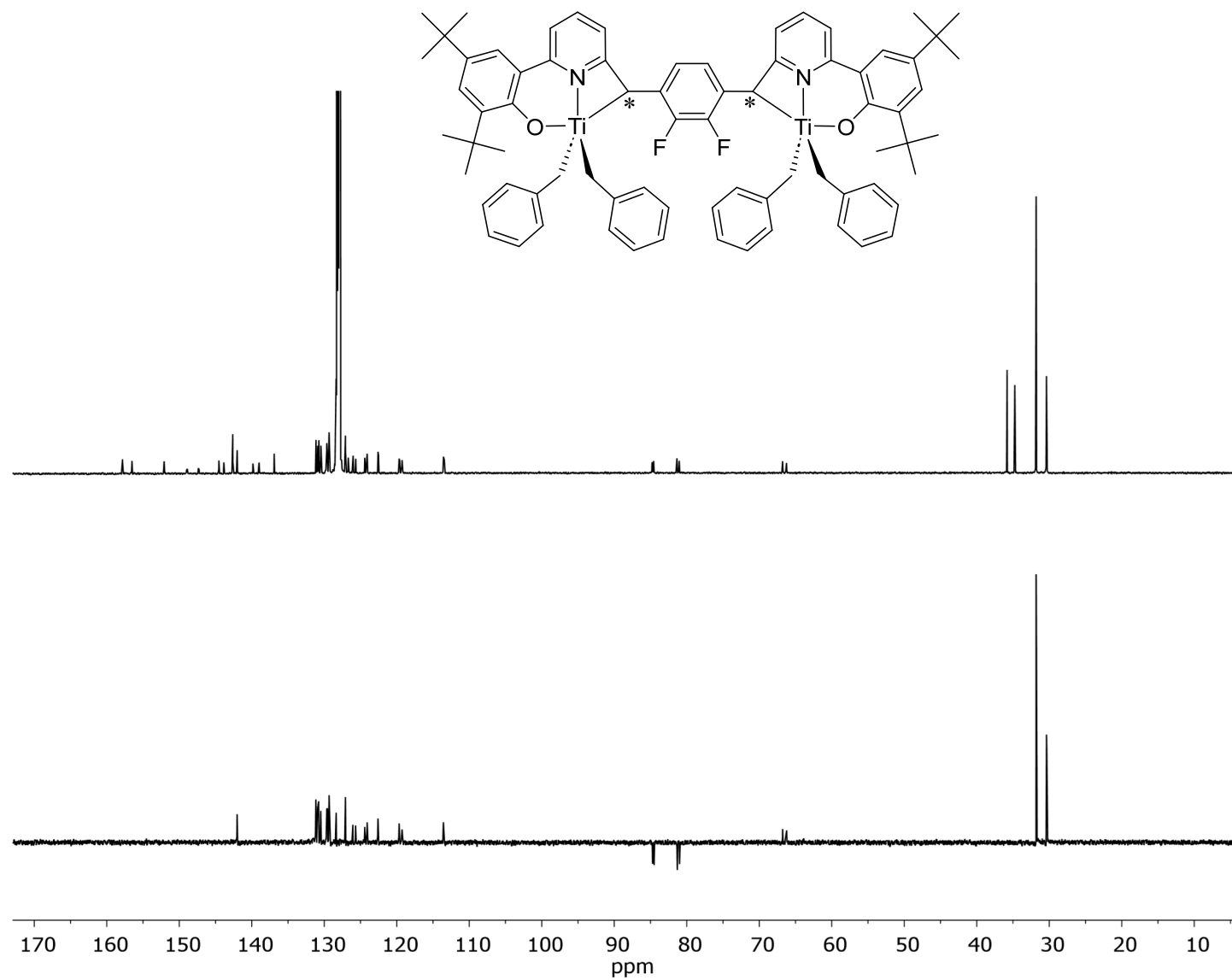


Figure S21. ^{13}C (top) and DEPT-135 (bottom) NMR spectra (C_6D_6 , 151 MHz, 298 K) of complex 2.

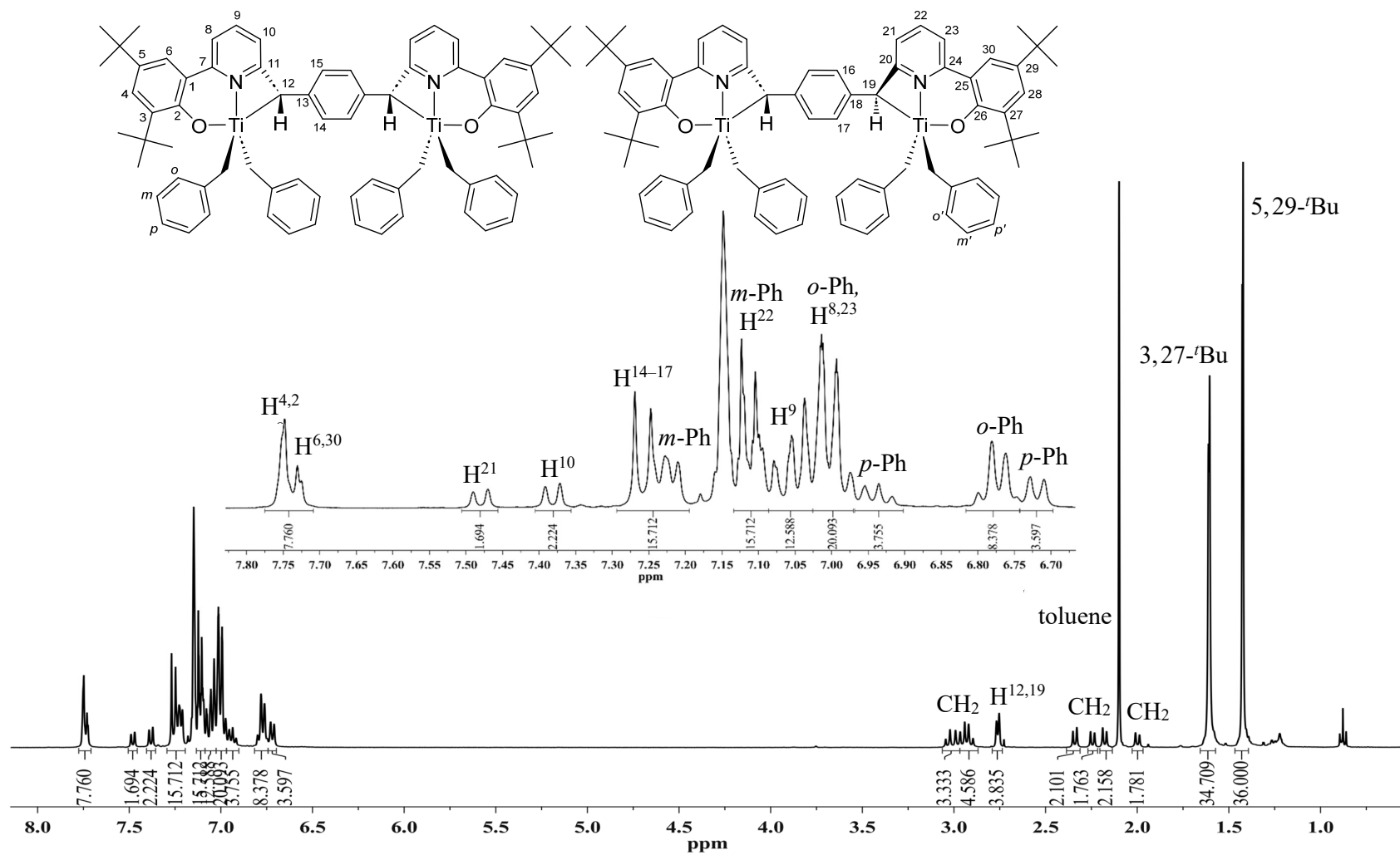


Figure S22. ^1H NMR spectrum (C_6D_6 , 400 MHz, 298 K) of complex **3**.

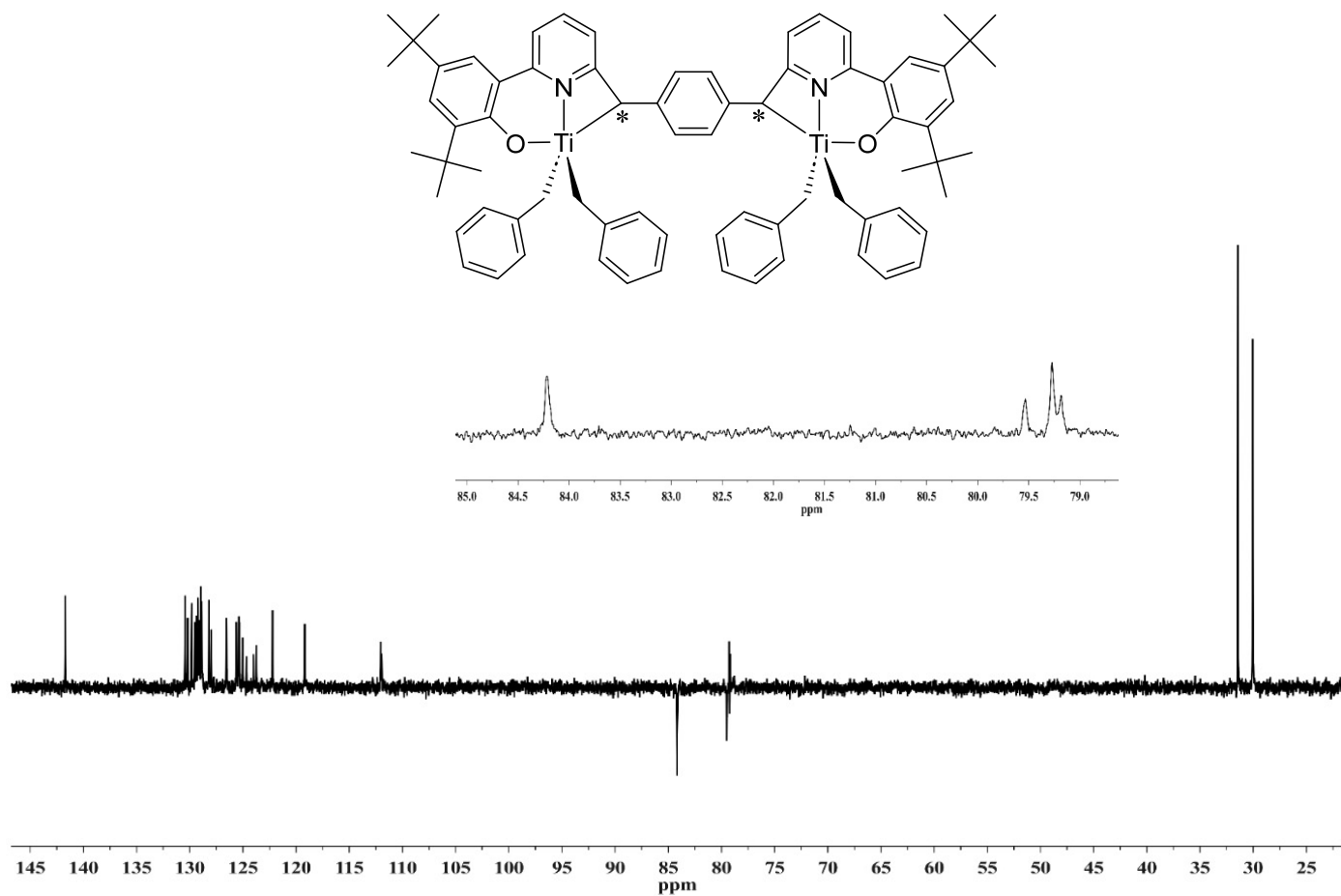


Figure S23. ^{13}C (expanded; top) and DEPT-135 (bottom) NMR spectra (C_6D_6 , 101 MHz, 298 K) of complex 3.

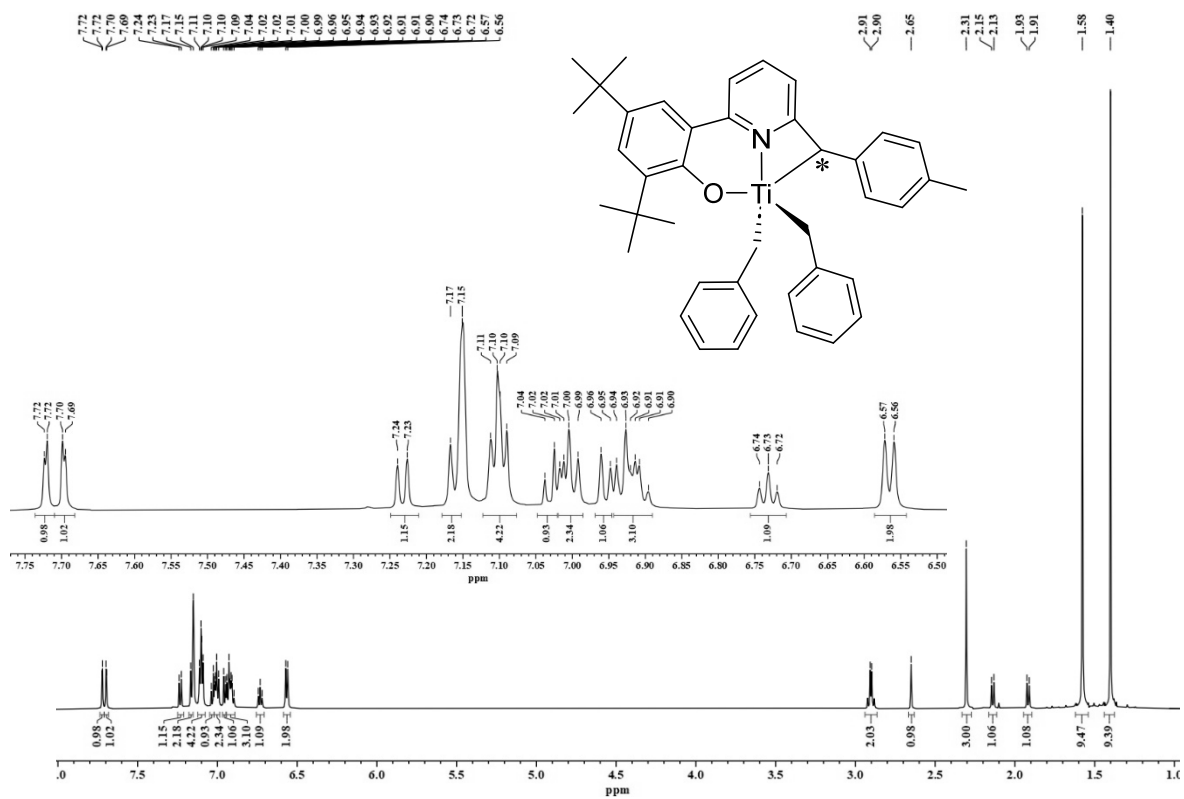


Figure S24. ¹H NMR spectrum (C₆D₆, 600 MHz, 298 K) of **5m**.

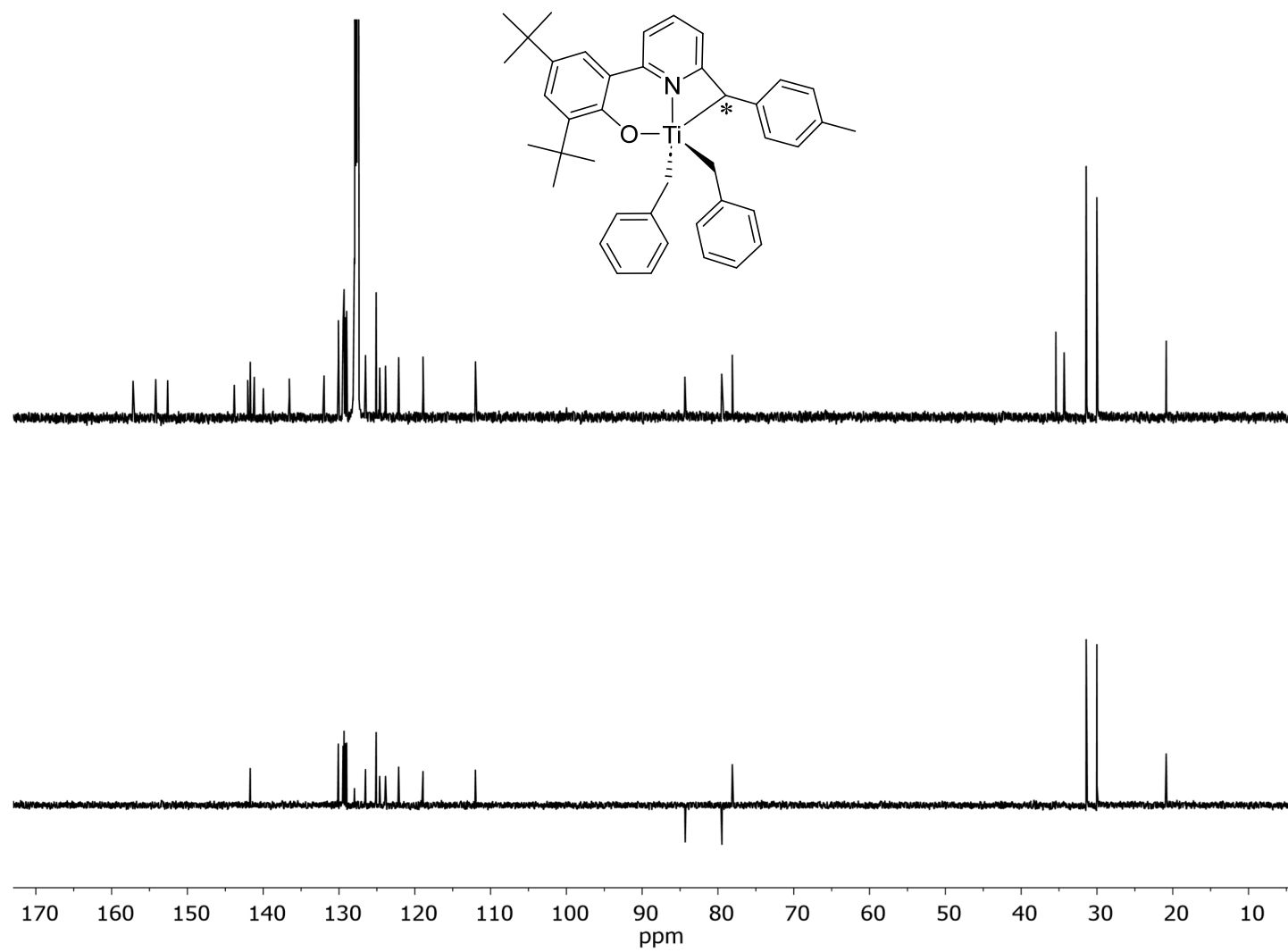


Figure S25. ^{13}C (top) and DEPT-135 (bottom) NMR spectra (C_6D_6 , 151 MHz, 298 K) of complex **5m**.

E. ESI References

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