

Supporting information

Star-shaped PHB-PLA block copolymers: Immortal polymerization with dinuclear indium catalysts

*Insun Yu,¹ Tannaz Ebrahimi,^{1,2} Savvas G. Hatzikiriakos,² and Parisa Mehrkhodavandi^{*1}*

¹ Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada.

² Department of Chemical and Biological Engineering, UBC, 2360 East Mall Vancouver, BC, Canada

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Experimental Section

General methods: Unless otherwise specified all procedures were carried out using standard Schlenk techniques or in an MBraun glovebox. A Bruker Avance 300 MHz spectrometer, Bruker Avance 400 MHz spectrometer and Bruker Avance 600 MHz spectrometer were used to record the ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR. ^1H NMR chemical shifts are given in ppm versus residual protons in deuterated solvents as follows: δ 1.73 and 3.58 for tetrahydrofuran- d_8 (THF- d_8) and δ 7.27 for CDCl_3 . $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are given in ppm versus residual ^{13}C in solvents as follows: δ 77.23 for CDCl_3 . Diffraction measurements for X-ray crystallography were made on a Bruker DUO diffraction with graphite monochromated Mo-K α radiation. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of the Bruker-AXS. Unless specified, all non-hydrogen were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. EA CHN analysis was performed using Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown sample is determined by using calibration factor. The calibration factor is determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition. Molecular weights were determined by GPC-LLS using a Agilent liquid chromatograph equipped with a Agilent 1200 series pump and autosampler, three Phenogel 5 μm Narrow Bore columns (4.6 \times 300 mm with 500 \AA , 10³ \AA and 10⁴ \AA pore size), a Wyatt Optilab differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. The column temperature was set at 40 $^\circ\text{C}$. A flow rate of 0.5 mL/min was used and samples were dissolved in THF or CHCl_3 (ca. 5 mg/mL). Narrow molecular weight polystyrene standards were used for calibration purposes.

Materials. Et_2O , hexane and toluene were degassed and dried using activated alumina in a Solvent Purification System from Innovation Technology, Inc. Tetrahydrofuran (THF) was collected from a Solvent Purification System, further dried over Na/benzophenone and vacuum-transferred to a Strauss flask and then degassed through a series of freeze-pump-thaw cycles. Deuterium tetrahydrofuran (THF- d_8) was dried over Na/benzophenone and vacuum-transferred to a Strauss flask and then degassed through a series of freeze-pump-thaw cycles. CH_2Cl_2 and CDCl_3 was dried over CaH_2 and vacuum-transferred to a Strauss flask and then degassed through a series of freeze-pump-thaw cycles. Deuterium-labeled NMR solvents were purchased from Sigma Aldrich and Cambridge Isotope Laboratory. Other chemicals and solvents were purchased from Aldrich, Fisher, Alfa Aesar, or STREM and were used without further purification. Chiral diaminoaryloxy ligands, $\text{H}(\text{NNO}_R)$, dichloride indium complexes, $(\text{NNO}_R)\text{InCl}_2$, ($R = \text{Me}, \text{tBu}$) and complex **1** were synthesized according to literature procedures.¹ Potassium benzyl alkoxide (KOBn) was generated by reacting the equimolar amount of KO^tBu with benzyl alcohol in tetrahydrofuran.¹ The solvent was removed under high vacuum, and addition of hexane to the residual precipitates a white solid. The white solid, KOBn, was isolated by vacuum filtration and dried in *vacuo* for 4 h.

Synthesis of $[(\text{NNO}_{\text{Me}})\text{InCl}_2(\mu\text{-Cl})(\mu\text{-OBn})]$ (2**).** A solution of potassium benzyl alkoxide (KOBn) (22 mg, 0.15 mmol) in toluene (1.5 mL) was added dropwise to a stirring suspension of $(\text{NNO}_{\text{Me}})\text{InCl}_2$ (150 mg, 0.30 mmol) in toluene (3 mL) at room temperature. The reaction mixture was stirred for 2 h. The resulting white precipitate was filtered through Celite to yield a clear filtrate. All volatiles were removed in *vacuo*, and hexane (5 mL) was added to the residue to precipitate a white solid. The solvent was decanted off of the white solid. The collected white solid was washed with hexane at least twice, and dried in *vacuo* for a few hours. Complex **2** was obtained as a white solid. Yield (100 mg, 62% yield). X-ray quality crystals were obtained from toluene at room temperature. ^1H NMR (CDCl_3 , 600 MHz) δ 7.67 (2H, d, $^3J_{\text{H-H}} = 7.1$ Hz, *ortho-H* of benzyl alkoxide), 7.00 (2H, d, $^4J_{\text{H-H}} = 2.0$ Hz, Ar *H*), 6.99 – 6.96 (1H, m, *para-H* of benzyl alkoxide), 6.96 – 6.91 (2H, m, *meta-H* of benzyl alkoxide), 7.20 – 7.14 (1H, m, *para-H* of benzyl alkoxide), 6.42 (2H, d, $^4J_{\text{H-H}} = 11.8$ Hz, Ar *H*), 5.74 (1H, d, $^2J_{\text{H-H}} = 11.9$ Hz, -O- CH_2 - of benzyl alkoxide), 5.06 (1H, d, $^2J_{\text{H-H}} = 11.8$ Hz, -O- CH_2 - of benzyl alkoxide), 4.15 (2H, d, $^2J_{\text{H-H}} = 13.5$ Hz, -NH- CH_2 -Ar), 3.38 – 3.31 (2H, m, -NH- CH_2 -Ar), 2.84 (2H, dt, $^3J_{\text{H-H}} = 3.2$ Hz, 11.5 Hz, -CH- of

DACH), 2.80 (2H, d, $^3J_{\text{H-H}} = 3.2$ Hz, -NH-), 2.69 (6H, s, -N(CH₃)₂), 2.57 – 2.48 (2H, m, -CH- of DACH), 2.43 – 2.36 (2H, m, -CH₂- of DACH), 2.19 (6H, s, Ar-CH₃), 2.02 (6H, s, -N(CH₃)₂), 1.93 – 1.87 (2H, m, -CH₂- of DACH), 1.87 – 1.76 (4H, m, -CH₂- of DACH), 1.46 (18H, s, Ar-C(CH₃)₃), 1.31 – 1.20 (2H, m, -CH₂- of DACH), 1.20 – 1.09 (4H, m, -CH₂- of DACH), 1.09 – 0.97 (2H, m, -CH₂- of DACH); ¹³C{¹H} NMR (CDCl₃, 151MHz) δ 162.6 (Ar C), 142.5 (Ar C), 139.7 (Ar C), 130.2 (Ar C), 128.2 (Ar C-H), 127.3 (Ar C-H), 126.6 (Ar C-H), 123.0 (Ar C-H), 120.3 (Ar C), 69.0 (-O-CH₂-C₆H₅), 64.8 (-CH- of DACH), 53.1 (-CH- of DACH), 50.1 (-HN-CH₂-Ar), 44.4 (-N(CH₃)₂), 38.3 (-N(CH₃)₂), 35.3 (Ar-C(CH₃)₃), 31.0 (Ar-C(CH₃)₃), 30.4 (-CH₂- of DACH), 30.5 (Ar-C(CH₃)₃), 25.0 (-CH₂- of DACH), 24.9 (-CH₂- of DACH), 21.9 (-CH₂- of DACH), 20.9 (Ar-CH₃). Anal. Calcd. For C₄₇H₇₃Cl₃In₂N₄O₃: C 52.36; H 6.83; N 5.20. Found: C 52.28; H 6.81; N 5.29.

Synthesis of [(NNO_{tBu})InCl]₂(μ-Cl)(μ-OBn) (3). A suspension of KOBn (26 mg, 0.18 mmol) in toluene (1.5 mL) was added dropwise to a stirring suspension of (NNO_{tBu})InCl₂ (195 mg, 0.34 mmol) in toluene (3 mL) at room temperature. The reaction mixture was stirred for 2 h. The resulting white precipitate was filtered through Celite to yield a colorless filtrate. All volatiles were removed in *vacuo*, and hexane (3 mL) was added to the residue to precipitate a white solid. The clear supernatant was decanted off of the white solid. The product was dried in *vacuo* for few hours (132 mg, 64%). ¹H NMR (CDCl₃, 600MHz) δ 7.64 (2H, d, $^3J_{\text{H-H}} = 7.3$ Hz, *ortho*-H of benzyl alkoxide), 7.21 (2H, d, $^4J_{\text{H-H}} = 2.4$ Hz, Ar H), 6.94 (1H, t, $^3J_{\text{H-H}} = 7.3$ Hz, *para*-H of benzyl alkoxide), 6.87 (2H, t, $^3J_{\text{H-H}} = 7.5$ Hz, *meta*-H of benzyl alkoxide), 6.55 (2H, d, $^4J_{\text{H-H}} = 2.3$ Hz, Ar H), 5.79 (1H, d, $^2J_{\text{H-H}} = 11.7$ Hz, -O-CH₂- of benzyl alkoxide), 5.03 (1H, d, $^2J_{\text{H-H}} = 11.8$ Hz, -O-CH₂- of benzyl alkoxide), 4.20 (2H, d, $^2J_{\text{H-H}} = 13.5$ Hz, -NH-CH₂-Ar), 3.38 (2H, d, $^2J_{\text{H-H}} = 13.5$ Hz, -NH-CH₂-Ar), 2.87 – 2.78 (4H, m, -NH- and -CH- of DACH), 2.69 (6H, s, -N(CH₃)₂), 2.51 (2H, dq, $^3J_{\text{H-H}} = 3.9$ Hz, 10.9 Hz, -CH- of DACH), 2.40 (2H, br. d, $^3J_{\text{H-H}} = 12.3$ Hz, -CH₂- of DACH), 2.02 (6H, s, -N(CH₃)₂), 1.94 – 1.87 (2H, m, -CH₂- of DACH), 1.82 (4H, t, $^3J_{\text{H-H}} = 14.5$ Hz, -CH₂- of DACH), 1.48 (18H, s, Ar-C(CH₃)₃), 1.31 – 1.20 (20H, m, -CH₂- of DACH and Ar-C(CH₃)₃), 1.20 – 1.14 (2H, m, -CH₂- of DACH), 1.07 – 0.97 (2H, m, -CH₂- of DACH); ¹³C{¹H} NMR (CDCl₃, 151MHz) δ 162.3 (Ar C), 142.3 (Ar C), 138.8 (Ar C), 136.7 (Ar C), 130.4 (Ar C-H), 127.2 (Ar C-H), 126.5 (Ar C-H), 126.3 (Ar C-H), 119.6 (Ar C), 69.1 (-O-CH₂-C₆H₅), 64.8 (-CH- of DACH), 53.0 (-CH- of DACH), 50.5 (-HN-CH₂-Ar), 44.4 (-N(CH₃)₂), 38.3 (-N(CH₃)₂), 35.6 (Ar-C(CH₃)₃), 34.1 (Ar-C(CH₃)₃), 32.0 (Ar-C(CH₃)₃), 30.9 (-CH₂- of DACH), 30.5 (Ar-C(CH₃)₃), 25.0 (-CH₂- of DACH), 24.9 (-CH₂- of DACH), 22.0 (-CH₂- of DACH). Anal. Calcd. For C₅₃H₈₅Cl₃In₂N₄O₃: C 54.77; H 7.37; N 4.82. Found: C 54.67; H 7.22; N 4.79.

Synthesis of [(NNO_{tBu})InCl(μ-OBn)]₂ (4). A suspension of KOBn (35 mg, 0.24 mmol) in 1.5 mL of toluene was added dropwise to a suspension of (NNO_{tBu})InCl₂ (130 mg, 0.24 mmol) in toluene (3 mL). After stirring the reaction mixture for 2 h at room temperature, KI formation was observed. The salt was removed by filtration through glass filter paper and the remaining solution was evaporated to dryness. The residue was washed with hexane and dried for 2 h in *vacuo* to yield complex **5** as a white powder. Complex **5** were recrystallized in toluene at 25 °C. (55 mg, 37% crystallized yield). ¹H NMR (CDCl₃, 600MHz) δ 7.72 (2H, br. s., *ortho*-H of benzyl alkoxide), 7.39 – 7.32 (2H, m, *meta*-H of benzyl alkoxide), 7.23 – 7.15 (1H, m, *para*-H of benzyl alkoxide), 7.10 (1H, d, $^4J_{\text{H-H}} = 2.3$ Hz, Ar H), 6.67 (1H, d, $^4J_{\text{H-H}} = 2.3$ Hz, Ar H), 5.66 (1H, d, $^2J_{\text{H-H}} = 14.9$ Hz, -O-CH₂- of benzyl alkoxide), 4.99 (1H, d, $^2J_{\text{H-H}} = 13.6$ Hz, -NH-CH₂-Ar), 4.87 (1H, d, $^2J_{\text{H-H}} = 14.8$ Hz, -O-CH₂- of benzyl alkoxide), 3.77 (1H, dd, $^3J_{\text{H-H}} = 2.1$ Hz, $^2J_{\text{H-H}} = 13.8$ Hz, -NH-CH₂-Ar), 2.73 – 2.62 (4H, m, -NH- and -N(CH₃)₂), 2.34 – 2.24 (1H, m, -CH- of DACH), 2.17 (1H, br. d., $^3J_{\text{H-H}} = 10.3$ Hz, -CH- of DACH), 1.96 (3H, s, -N(CH₃)₂), 1.67 (1H, dt, $^3J_{\text{H-H}} = 2.7$ Hz, 11.4 Hz, -CH- of DACH), 1.58 – 1.48 (1H, m, -CH₂- of DACH), 1.48 – 1.41 (2H, m, -CH₂- of DACH), 1.22 (9H, s, Ar-C(CH₃)₃), 1.13 (9H, s, Ar-C(CH₃)₃), 0.87 – 0.68 (2H, m, -CH₂- of DACH), 0.58 – 0.40 (2H, m, -CH₂- of DACH); ¹³C{¹H} NMR (CDCl₃, 151MHz) δ 162.8 (Ar C), 145.1 (Ar C), 138.9 (Ar C), 135.8 (Ar C), 128.6 (Ar C-H), 127.3 (Ar C-H), 126.6 (Ar C-H), 126.2 (Ar C-H), 124.0 (Ar C-H), 118.8 (Ar C), 67.6 (-O-CH₂- of benzyl alkoxide), 64.3 (-CH- of DACH), 52.3 (-CH- of

DACH), 50.9 (-HN-CH₂-Ar), 45.1 (-N(CH₃)₂), 39.5 (-N(CH₃)₂), 35.3 (Ar-C(CH₃)₃), 33.9 (Ar-C(CH₃)₃), 31.9 (Ar-C(CH₃)₃), 30.0 (Ar-C(CH₃)₃), 29.4 (-CH₂- of DACH), 24.5 (-CH₂- of DACH), 24.1 (-CH₂- of DACH), 21.4 (-CH₂- of DACH). Anal. Calcd. For C₆₀H₉₂Cl₂In₂N₄O₃: C 58.4; H 7.52; N 4.54. Found: C 58.43; H 7.44; N 4.49.

Synthesis of [(NNO_{tBu})InCl₂(μ-Cl)(μ-OTHMB) (5). A suspension of 1,3,5-tris(hydroxymethyl)benzene (11 mg, 0.065 mmol) in toluene (1.5 mL) was added dropwise to a solution of complex **1** (71 mg, 0.064 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature or 70 °C for 16 h. After removal of the solvent *in vacuo* a white solid of complex **5** was collected and washed with hexane (3 × 5 mL). The collected white solid **5** was dried *in vacuo* at least for a few hours. (63 mg, 81%) X-ray quality colorless crystals of complex **5** were grown in toluene at 25 °C. ¹H NMR (CDCl₃, 600MHz) δ 7.71 (2H, br. s., ³J_{H-H} = 7.3 Hz, *ortho*-H of THMB), 7.28 (2H, d, ⁴J_{H-H} = 2.2 Hz, Ar H), 6.97 (1H, br. s., *para*-H of THMB), 6.63 (2H, br. s., Ar H), 5.80 (1H, d, ²J_{H-H} = 11.4 Hz, -O-CH₂- of THMB), 5.08 (1H, d, ²J_{H-H} = 11.5 Hz, -O-CH₂- of THMB), 4.40 (2H, dd, ³J_{H-H} = 5.6 Hz, ²J_{H-H} = 12.9 Hz, HO-CH₂- of THMB), 4.26 (2H, dd, ³J_{H-H} = 7.9 Hz, ²J_{H-H} = 12.8 Hz, HO-CH₂- of THMB), 4.03(2H, br. s., -NH-CH₂-Ar), 3.38 (2H, d, ²J_{H-H} = 12.7 Hz, -NH-CH₂-Ar), 2.91 – 2.80 (2H, m, -CH- of DACH), 2.75 (2H, br. s., -NH-), 2.68 (6H, s, -N(CH₃)₂), 2.50 – 2.39 (2H, m, -CH- of DACH), 2.38 (2H, br. s., -CH₂- of DACH), 1.99 (6H, s, -N(CH₃)₂), 1.94 – 1.86 (2H, m, -CH₂- of DACH), 1.82 (4H, br. t., ³J_{H-H} = 11.8 Hz, -CH₂- of DACH), 1.58 – 1.46 (20H, s, -CH₂- of DACH and Ar-C(CH₃)₃), 1.39 (4H, br. s., HO- of THMB), 1.27 (18H, s, Ar-C(CH₃)₃), 1.21 – 1.12 (2H, m, -CH₂- of DACH), 1.12 – 0.93 (4H, m, -CH₂- of DACH); ¹³C{¹H} NMR (CDCl₃, 151MHz) δ 162.2 (Ar C), 143.1 (Ar C), 140.7 (Ar C), 139.0 (Ar C), 137.0 (Ar C), 128.5 (Ar C-H), 126.3 (Ar C-H), 124.5 (Ar C-H), 124.1 (Ar C-H), 119.9 (Ar C), 68.5 (-O-CH₂-Ar of TMB), 65.4 (HO-CH₂-Ar of TMB), 64.6 (-CH- of DACH), 53.1 (-CH- of DACH), 50.1 (-HN-CH₂-Ar), 44.4 (-N(CH₃)₂), 38.2 (-N(CH₃)₂), 35.6 (Ar-C(CH₃)₃), 34.0 (Ar-C(CH₃)₃), 31.9 (Ar-C(CH₃)₃), 30.9 (-CH₂- of DACH), 30.4 (Ar-C(CH₃)₃), 24.9 (-CH₂- of DACH), 24.9 (-CH₂- of DACH), 22.0 (-CH₂- of DACH). Anal. Calcd. For C₅₅H₈₉Cl₃In₂N₄O₅: C 54.04; H 7.34; N 4.58. Found: C 54.12; H 7.30; N 4.68.

Representative NMR scale polymerization with 3,4 and 5 in THF-*d*₈. A Teflon-sealed NMR tube was charged with a 0.25 mL solution of a catalyst stock solution (0.25 mL, **3**, **5**: 0.0086 M, 0.0022 mmol; **4**, 0.00162 M, 0.00041 mmol) in THF-*d*₈ and made up to 0.5 mL with a 0.25 mL solution of THF-*d*₈, and the solution was mixed and frozen in the glovebox using a liquid N₂ cold wall (-90 °C). A stock solution of BBL (0.25 mL, 1.72 M, 0.43 mmol for **3**, **5**; 0.5 mL, 0.326 M, 0.163 mmol for **4**) and an internal standard 1,3,5-trimethoxybenzene (2.5 mg, 0.03 mmol for **3**, **5** in the 0.25 mL BBL stock solution; 1.0 mg, 0.0056 mmol for **5** in the 0.5 mL BBL stock solution) in THF-*d*₈ was added to the frozen complex solution, made up to 0.5 mL with a 0.25 mL solution of THF-*d*₈ if required and frozen again, forming a bilayer. The NMR tube was sealed and quickly evacuated by vacuum to remove N₂ gas from the NMR tube. Two solutions were thawed and quickly mixed before the NMR tube was loaded into the NMR spectrometer (400MHz Avance Bruker Spectrometer). The polymerization was monitored to 90% conversion.

Representative NMR scale polymerization with 3 and 2 equivalents of (NNO_{tBu})InCl₂. A Teflon-sealed NMR tube was charged with a 0.25 mL solution of a catalyst stock solution (0.25 mL, **3**: 0.0086 M, 0.0022 mmol) and a 0.25 mL solution of a (NNO_{tBu})InCl₂ stock solution (0.25 mL, (NNO_{tBu})InCl₂, 0.0172 M, 0.0043 mmol) in THF-*d*₈ at room temperature. Both of the solutions were mixed together and frozen in the glovebox using a liquid N₂ cold wall (-90 °C). A 0.5 mL stock solution of BBL (0.5 mL, 0.86 M, 0.43 mmol) in THF-*d*₈, containing an internal standard 1,3,5-trimethoxybenzene (2.5 mg, 0.02 mmol), was added to the frozen complex solution and frozen again, forming a bilayer. The NMR tube was sealed and quickly evacuated by vacuum to remove N₂ gas from the NMR tube. Two solutions were

thawed and quickly mixed before the NMR tube was loaded into the NMR spectrometer (400MHz Avance Bruker Spectrometer). The polymerization was monitored to 90% conversion.

Procedure for *in situ* reactivity between **3 and 2 equivalents of $(\text{NNO}_{\text{tBu}})\text{InCl}_2$.** ^1H NMR spectroscopy (400 MHz NMR spectrometer, $\text{THF-}d_8$ at 25 °C) was used to monitor the reactivity of complexes **3** and 2 equivalents of $(\text{NNO}_{\text{tBu}})\text{InCl}_2$. In a glovebox, $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ (4.7 mg, 0.0086 mmol) was measured in a 1 Dram vial and dissolved in a 0.5 mL solution of $\text{THF-}d_8$. The solution of $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ was loaded to a 1 mL volumetric flask charged with complex **3** (5 mg, 0.0043 mmol). The volumetric flask was made up to 1 mL using a $\text{THF-}d_8$ solution. The solution mixture of **3** and $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ was changed into a Teflon-sealed NMR tube, and the NMR tube was loaded into the NMR spectrometer.

Representative large-scale polymerization of BBL with **1, **3**, **4** and **5**.** A 20 mL scintillation vial was charged with a solution of a catalyst stock solution (0.25 mL for **1**, **3**, **4**: 8.8 mM, 0.0022 mmol; 0.8 mL for **5**: 1.1 mM, 0.00089 mmol), and a 2 mL solution of THF was added to the vial. A solution of a BBL stock solution (0.25 mL, 5.52 M, 1.38 mmol; 0.5 mL, 5.52 M, 2.76 mmol) in THF was added dropwise to the vial containing the catalyst, and the resulting mixture was stirred at room temperature for 16 h. The resulting clear solution was concentrated to dryness. A sample of the residue was dissolved in CDCl_3 to be analyzed by ^1H NMR spectroscopy to determine conversion. The remaining polymeric material was dissolved in a minimum amount of CH_2Cl_2 (1 mL), and wet methanol (7 mL) was slowly added to the polymer solution, stirred vigorously. The polymer was precipitated from the solution, and the supernatant was decanted. The last three steps were repeated at least three times to remove the trace amount of the catalyst remaining in the polymer. The isolated polymer was dried under high vacuum for 2 h prior to analysis.

Representative large-scale polymerization of BBL using mixtures of **3 and 2 equivalents of $(\text{NNO}_{\text{tBu}})\text{InCl}_2$.** A 20 mL scintillation vial was charged with a solution of a catalyst stock solution (0.2 mL for **3**: 8.6 mM, 0.0017 mmol) containing two equivalents of $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ (0.017 M, 0.0034 mmol), and a 3 mL solution THF was added to the vial. A solution of a BBL stock solution (0.25 mL, 5.52 M, 1.38 mmol; 0.5 mL, 5.52 M, 2.76 mmol) in THF was added dropwise to the vial containing the mixture solution of the catalyst and $(\text{NNO}_{\text{tBu}})\text{InCl}_2$. The reaction mixture was stirred at room temperature for 16 h. The resulting clear solution was concentrated to dryness under *vacuo*. A sample of the residue was dissolved in CDCl_3 to be analyzed by ^1H NMR spectroscopy to determine conversion. The remaining polymeric material was dissolved in a minimum amount of CH_2Cl_2 (1 mL), and wet methanol (7 mL) was slowly added to the polymer solution, stirring vigorously. The polymer was precipitated from the solution, and the supernatant was decanted. The last three steps were repeated at least three times to remove the trace amount of the catalyst remaining in the polymer. The isolated polymer was dried under high vacuum for 2 h prior to analysis.

Large-scale immortal polymerization of BBL with **1 in the presence of BnOH.** In a 20 ml scintillation vial a solution of 1.34 mL stock solution of **1** in THF (1.34 mL: 2.7 mM, 0.0036 mmol) was added. A solution of a stock solution of BnOH in THF (1.5 mL: 0.097 M, 0.146 mmol) was added to the stirred catalyst solution at room temperature. The reaction mixture was stirred for 1 h and then dried under vacuum for a few hours to remove resulted ethanol and the solvent. The obtained white solid then was redissolved in 2 ml THF. BBL (1.5 ml, 18.29 mmol) was added to the stirred solution dropwise at room temperature. The reaction mixture was left stirring for 16 h at room temperature before being quenched by an acidic solution (0.5 ml of 1.5 M HCl in Et_2O). A sample of the crude mixture was dissolved in CDCl_3 to be analyzed by ^1H NMR spectroscopy to determine conversion. The remaining mixture was concentrated to dryness and redissolved in a minimal amount of CH_2Cl_2 . The mixture was then quenched in cold methanol (0 °C). The vial was immersed in liquid nitrogen to solidify the

polymer. Then, the supernatant was immediately decanted. The resulting polymer was washed with cold methanol (1×3 ml) with the same procedure and then dried under vacuum for 16 h.

Large-scale immortal polymerization of BBL with 1 in the presence of Tris(hydroxymethyl)benzene (THB). In a 20 ml scintillation vial a solution of THB (24.6 mg, 0.146 mmol) in THF (2 ml) was added to a solution of a stock solution of **1** in THF (1.34 mL: 2.7 mM, 0.00365 mmol) at room temperature. The reaction mixture was stirred for 1 h and then dried under vacuum for a few hours to remove the resulted ethanol and the solvent. To a stirred solution of the obtained white solid redissolved in THF (2mL) BBL (1.5 ml, 18.29 mmol) was added dropwise. The reaction mixture was stirred overnight and then quenched with an acidic solution (0.5 ml of 1.5 M HCl in Et₂O). A small amount of the crude reaction mixture was dissolved in wet CDCl₃ to be analyzed by ¹H NMR spectroscopy to determine the monomer conversion. The remaining mixture was concentrated to dryness and redissolved in a minimal amount of CH₂Cl₂. The mixture was then quenched in cold methanol (0 °C). The vial was immersed in liquid nitrogen to solidify the polymer. The supernatant was decanted off. The resulting polymer was washed with cold methanol (1×3 ml) with the same procedure and then dried under vacuum overnight.

Large-scale immortal polymerization of L-Lactide and BBL with 1 in the presence of 1,3,5-tris(hydroxymethyl)benzene (THMB). Two parallel reactions were set up in two different 20 ml scintillation vials that were charged with equal amounts of the reagents in order to check the conversions before addition of the second monomer. Each scintillation vial was first charged with a 0.67 ml stock solution of **1** in THF (**1**, 1.8 mM, 0.00121 mmol) was added. A 1.02 ml solution of the stock THMB solution in THF (5.8 mM, 0.006 mmol) was added to the catalyst solution, stirred for 1 h and then dried under vacuum for a few hours to remove resulted ethanol and all the solvent. The white powder then was dissolved in 5 ml THF and while stirring, a solution of L-LA in THF (0.32 g, 0.88 M, 2.22 mmol) was added. The mixture was allowed to stir overnight and a ¹H NMR spectrum was obtained to determine the conversion and then a solution of the second monomer BBL (0.3 ml, 1.5 M, 3.75 mmol) in THF was added to the reaction. The polymerization was allowed to stir overnight and then quenched with an acidic solution (0.5 ml of 1.5 M HCl in Et₂O). A few drops of the mixture were used to examine conversion. . The remaining mixture was concentrated to dryness and redissolved in a minimal amount of CH₂Cl₂. The polymeric mixture was then quenched in cold methanol (0 °C). The precipitated polymer was solidified by immersing the vial in liquid nitrogen. Then, the supernatant was decanted off. The resulting polymer was washed with cold methanol (1×3 ml) with the same procedure and then dried under vacuum overnight.

Part A: Characterization of complexes

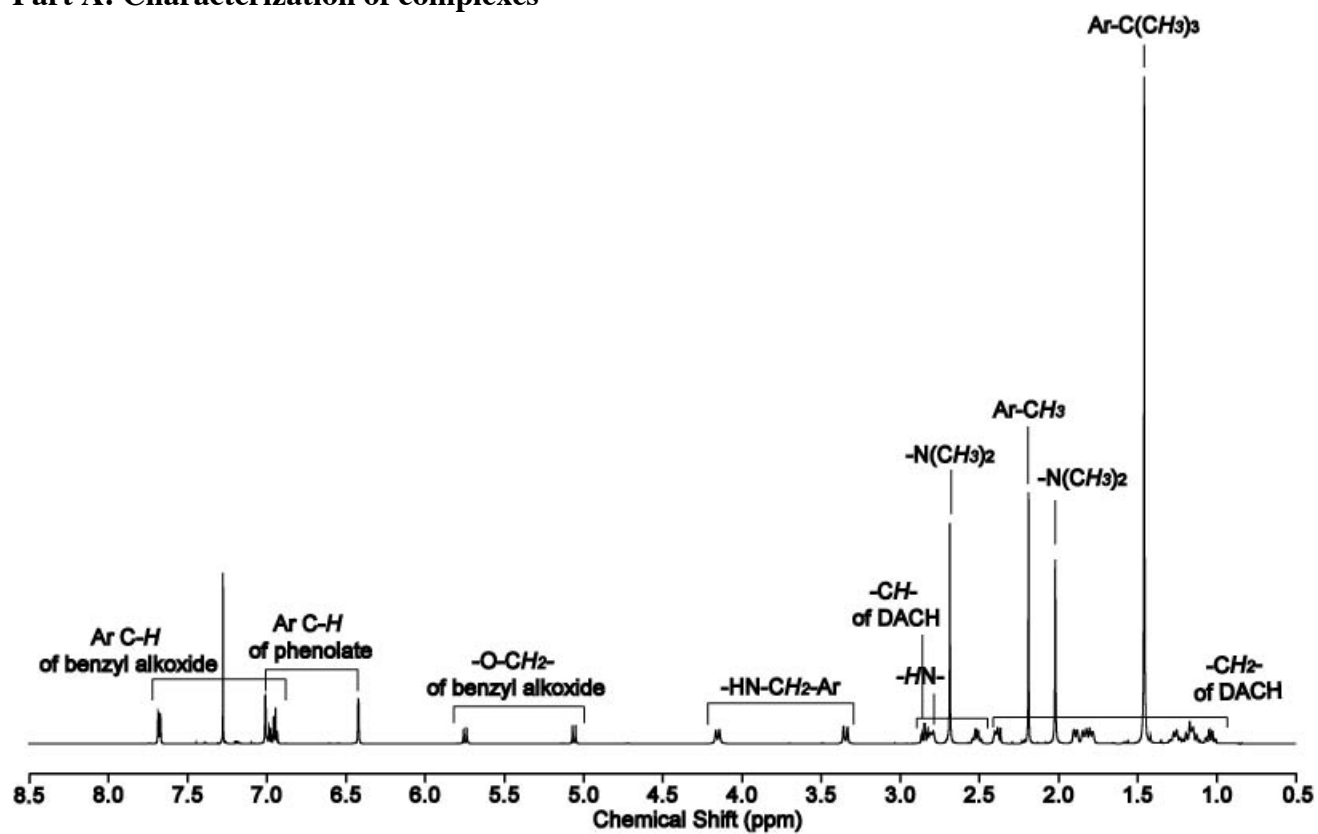


Figure S1. ^1H NMR spectrum (CDCl₃, 25 °C) of [(NNO_{Me})InCl₂(μ -Cl)(μ -OBn)] (2).

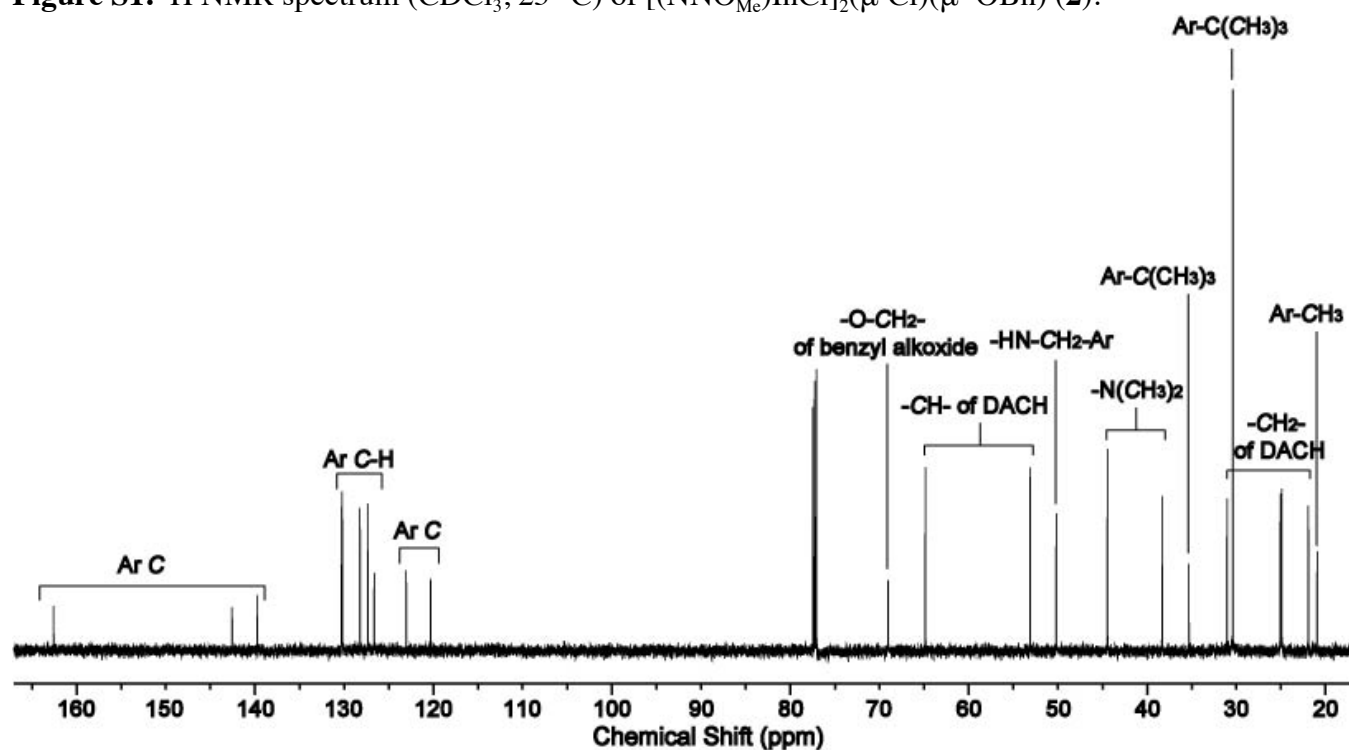
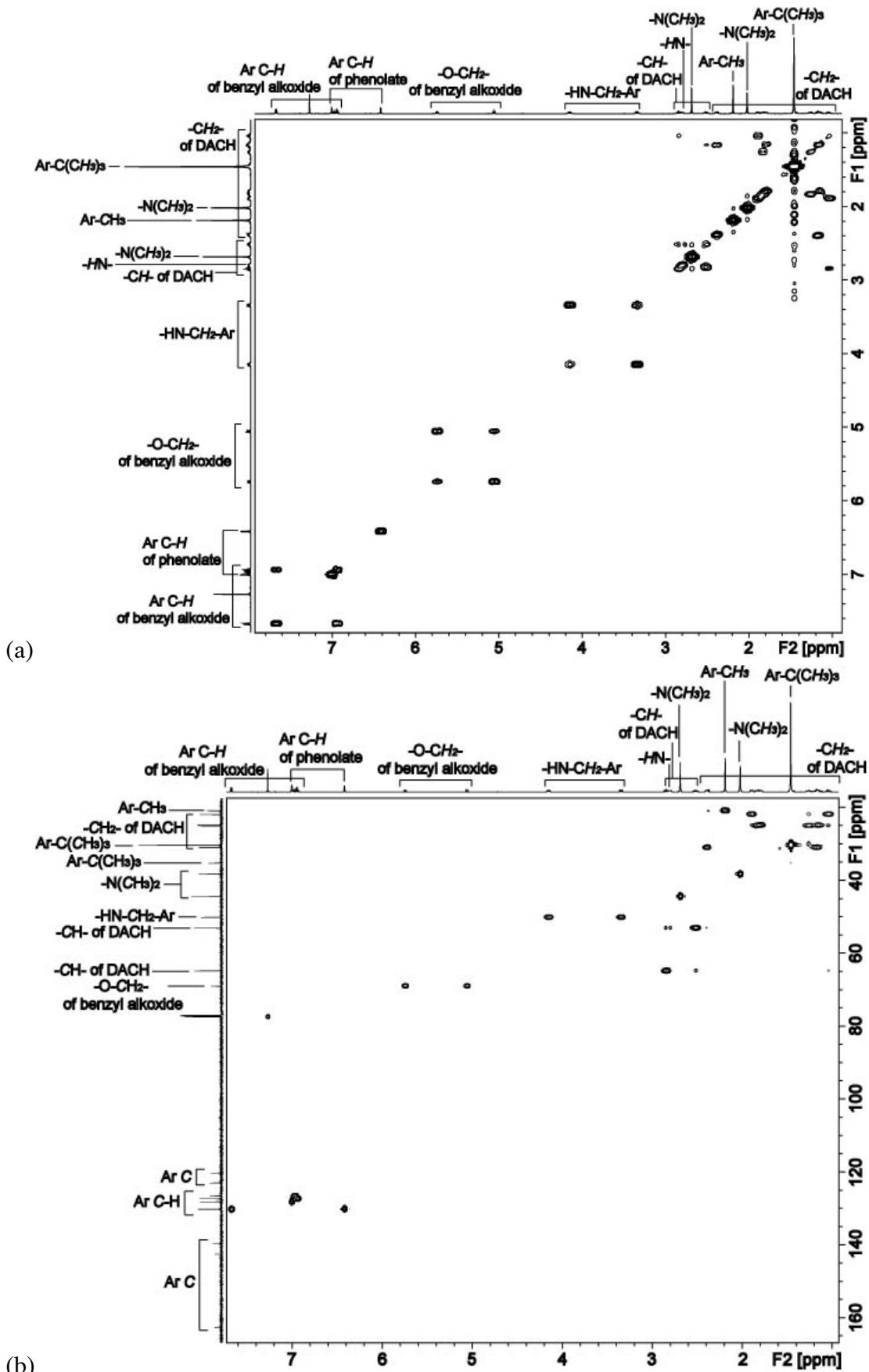


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl₃, 25 °C) of [(NNO_{Me})InCl₂(μ -Cl)(μ -OBn)] (2).



(b)
Figure S3. (a) ^1H - ^1H COSY spectrum and (b) ^1H - ^{13}C HSQC spectrum (CDCl_3 , 25 °C) of $[(\text{NNO}_{\text{Me}})\text{InCl}]_2(\mu\text{-Cl})(\mu\text{-OBn})$ (2).

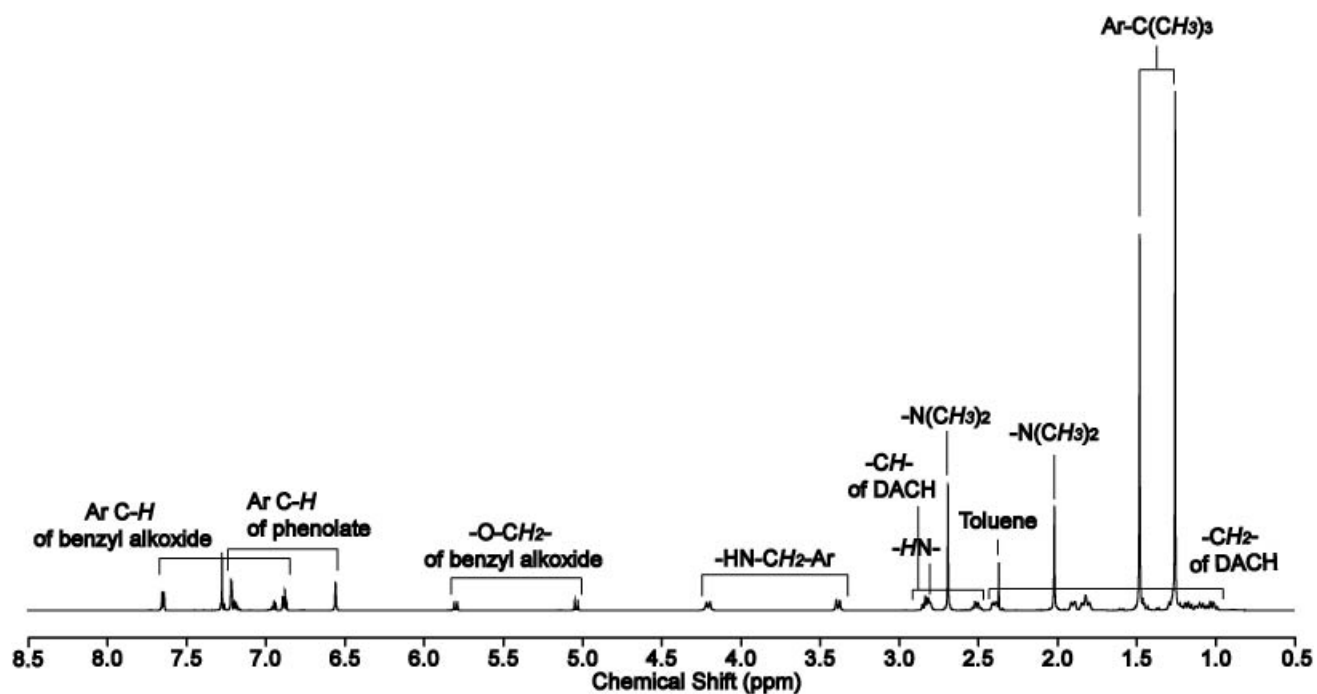


Figure S4. ^1H NMR spectrum (CDCl_3 , 25°C) of $[(\text{NNO}_{\text{tBu}})\text{InCl}_2(\mu\text{-Cl})(\mu\text{-OBn})]$ (**3**).

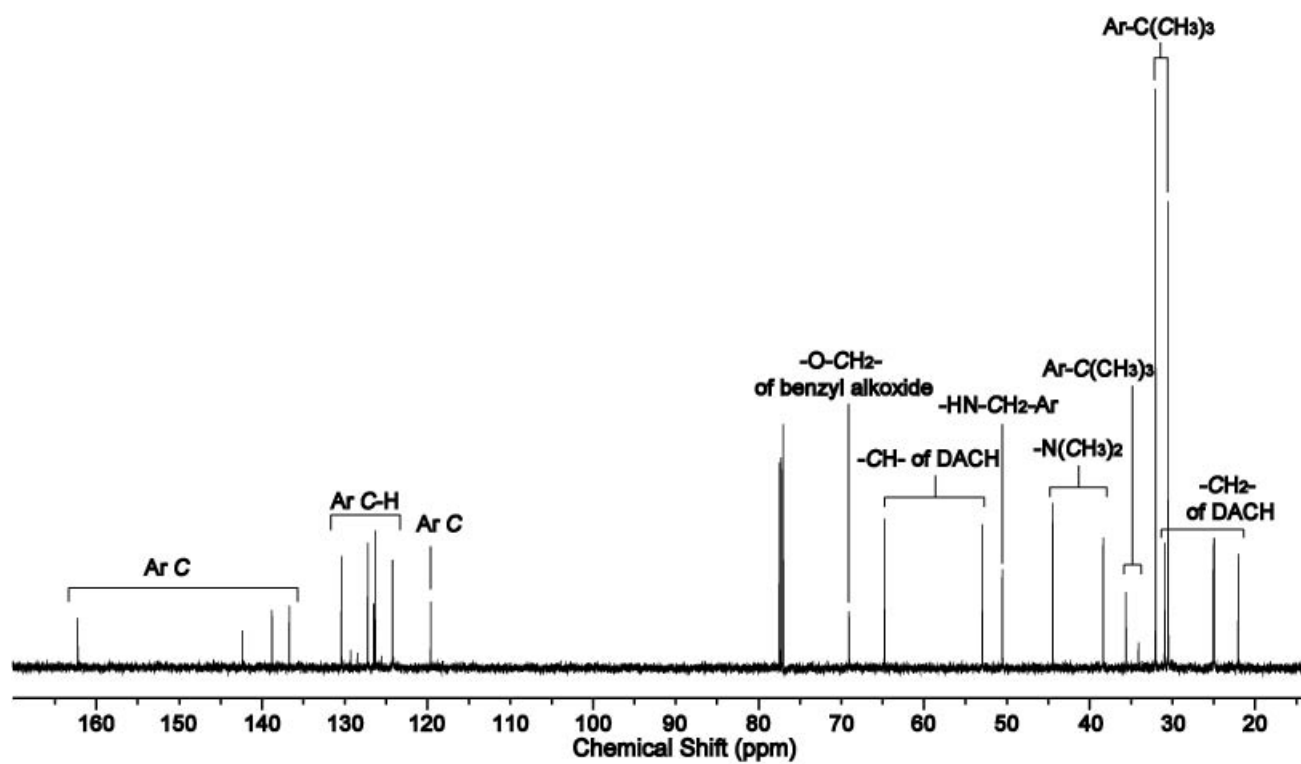
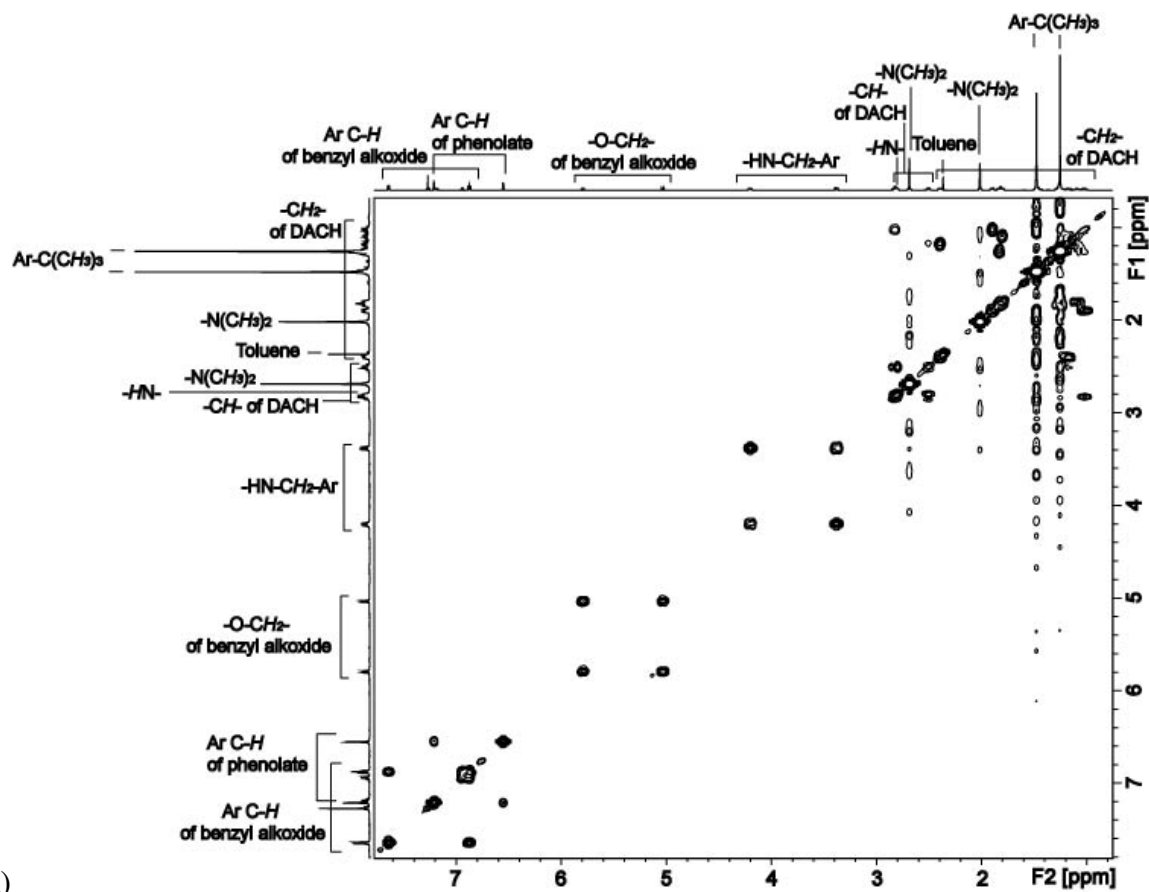
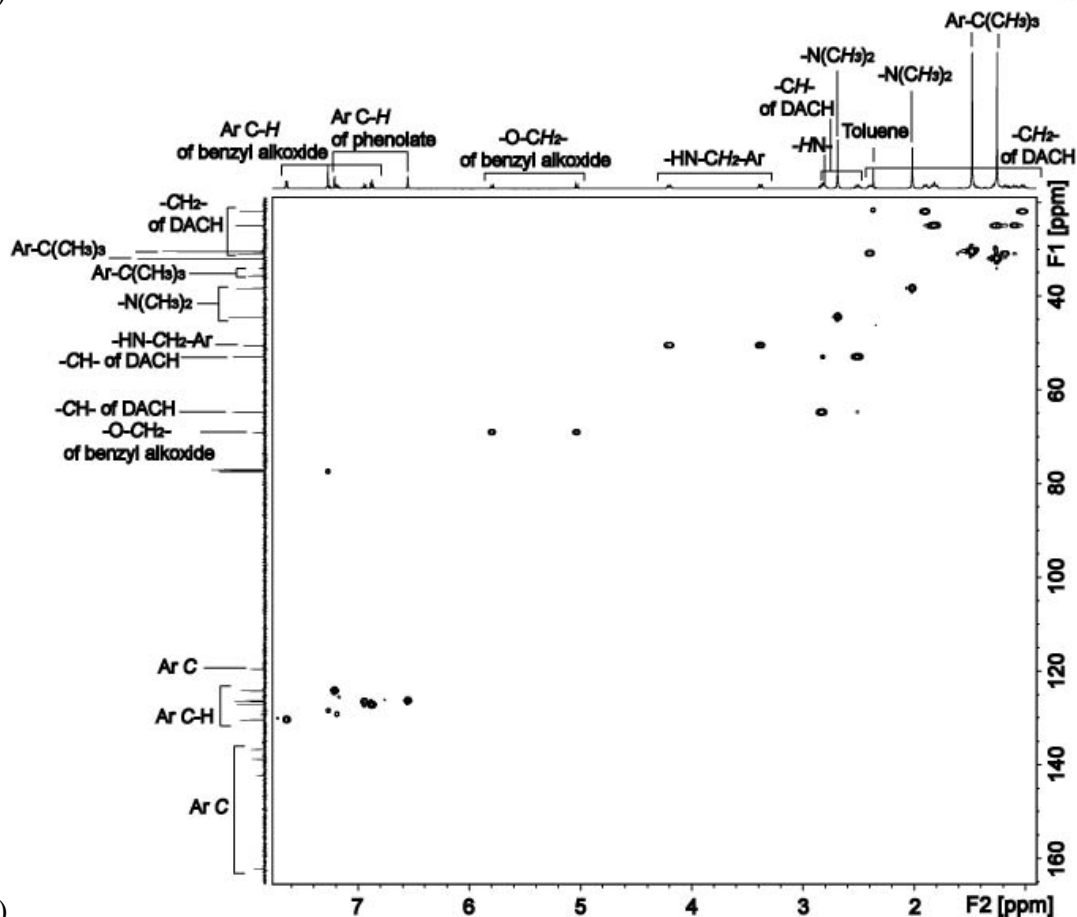


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 25°C) of $[(\text{NNO}_{\text{tBu}})\text{InCl}_2(\mu\text{-Cl})(\mu\text{-OBn})]$ (**3**).



(a)



(b)

Figure S6. (a) ^1H - ^1H COSY spectrum and (b) ^1H - ^{13}C HSQC spectrum of $[(\text{NNO}_{\text{tBu}})\text{InCl}_2(\mu\text{-Cl})(\mu\text{-OBn})]$ (**3**) (CDCl_3 , 25°C).

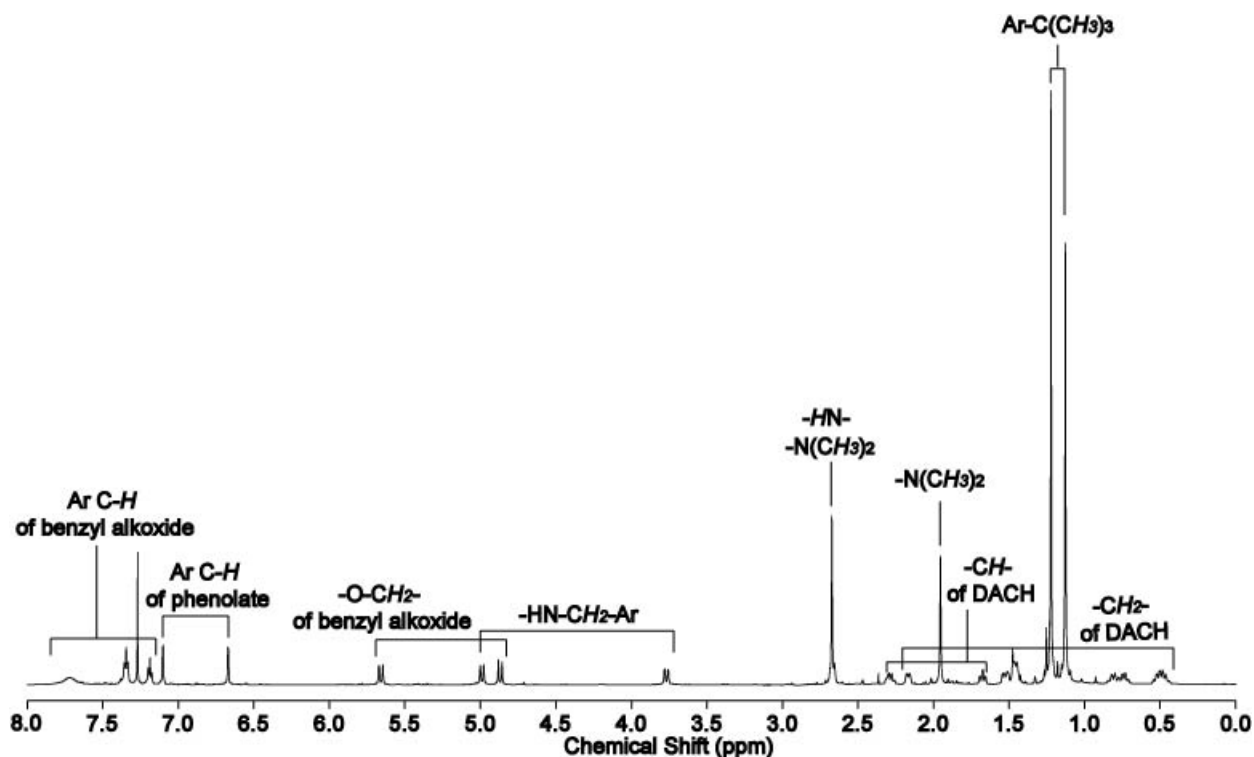


Figure S7. ^1H NMR spectrum (CDCl_3 , 25°C) of $[(\text{NNO}_{\text{tBu}})\text{InCl}(\mu\text{-OBn})_2]$ (**4**).

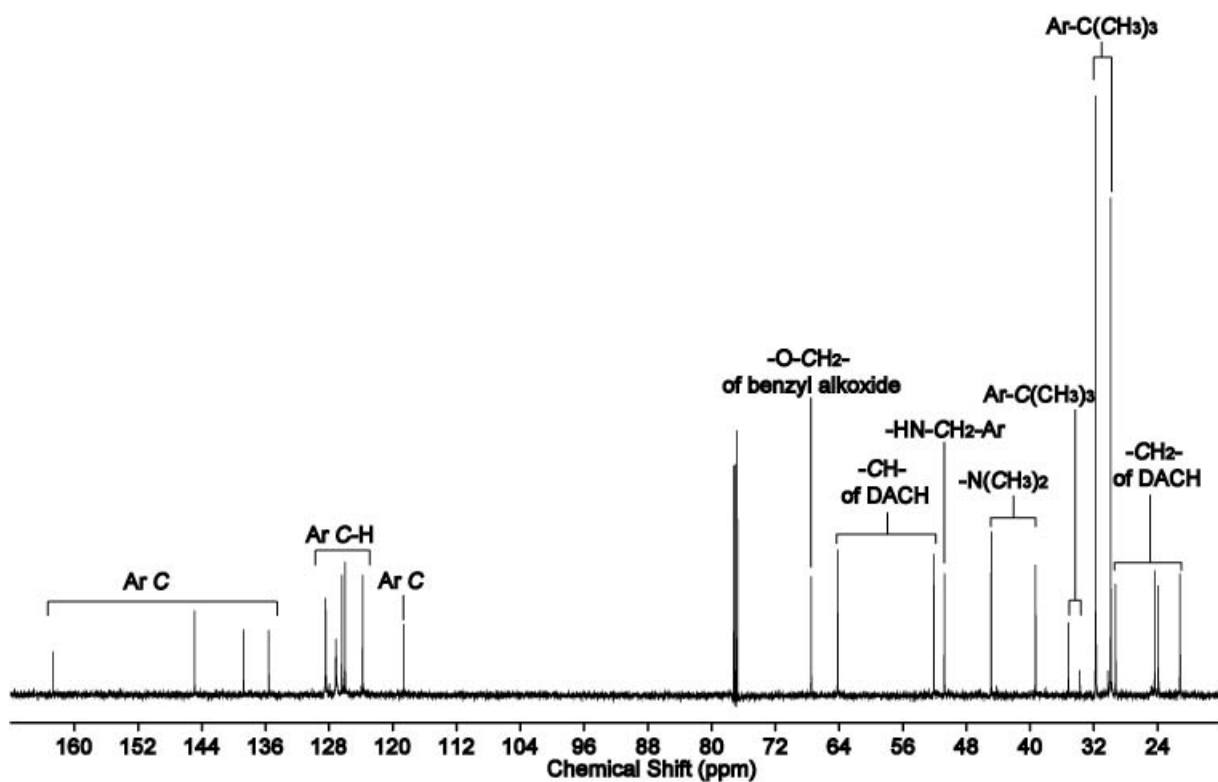
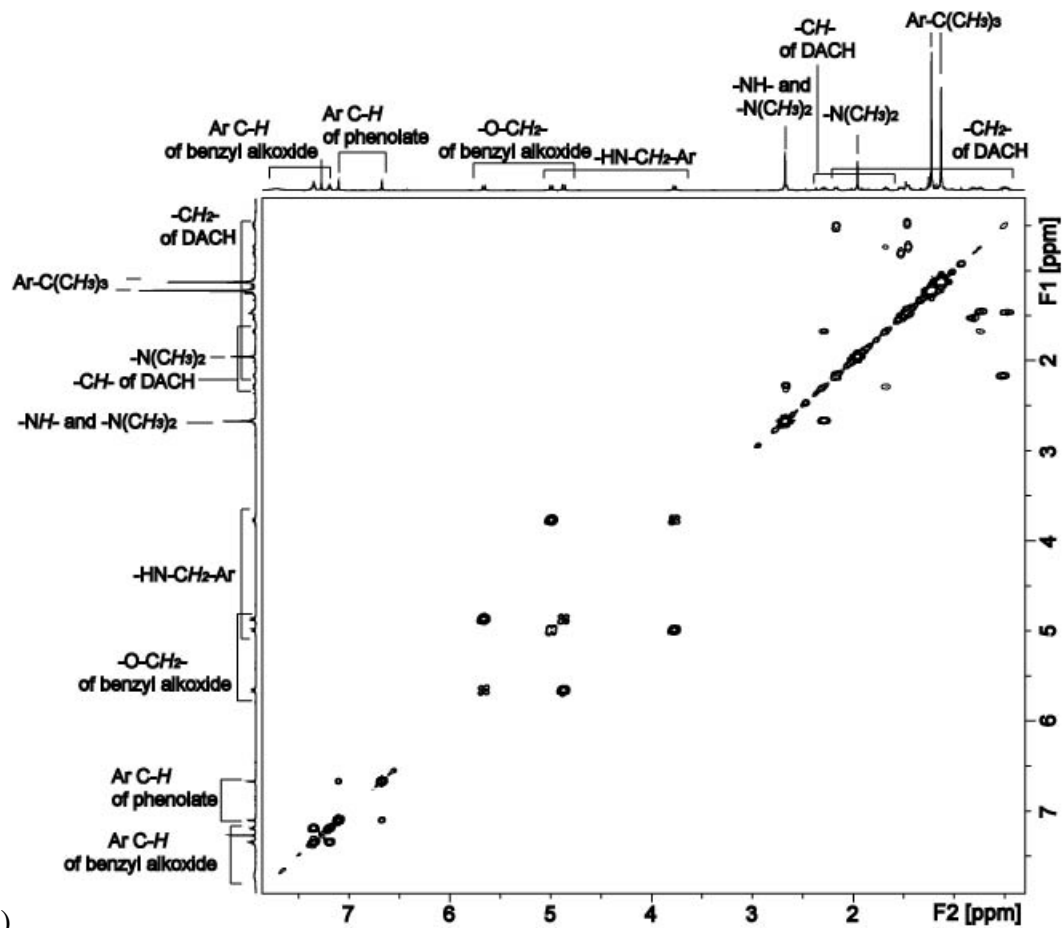
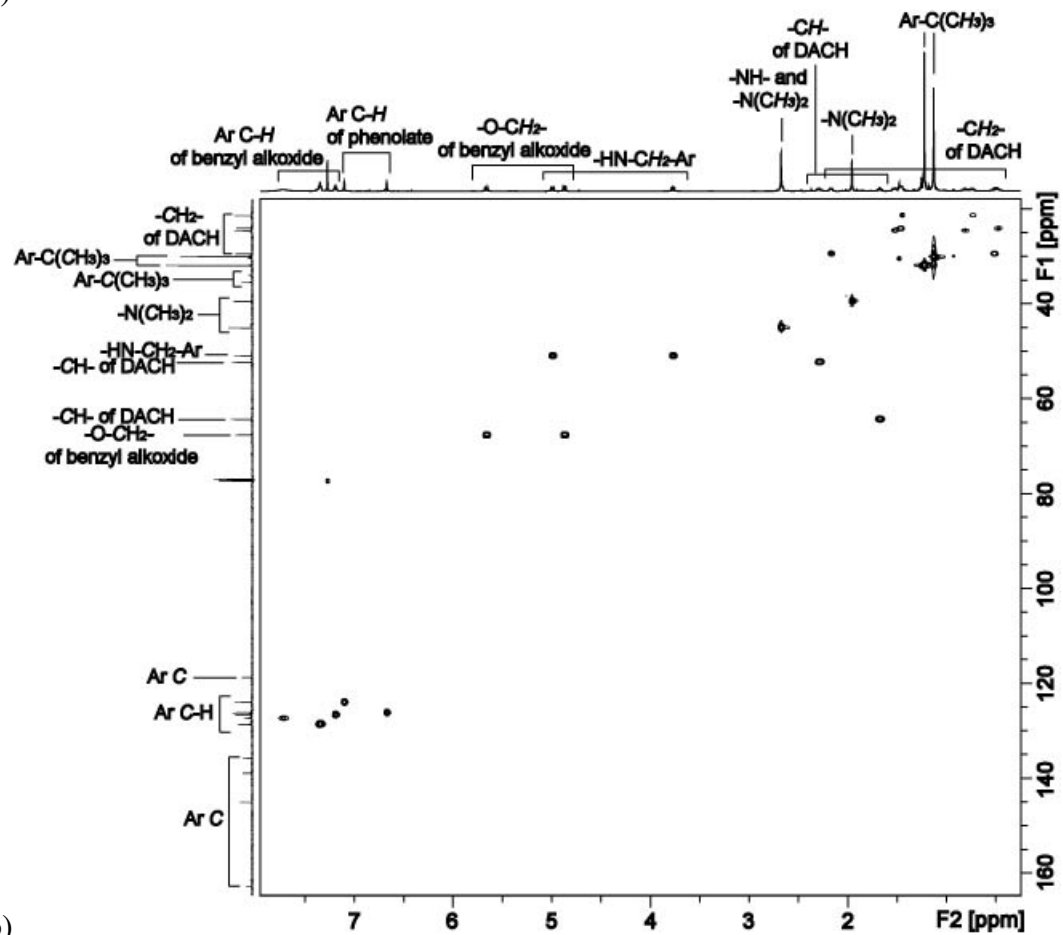


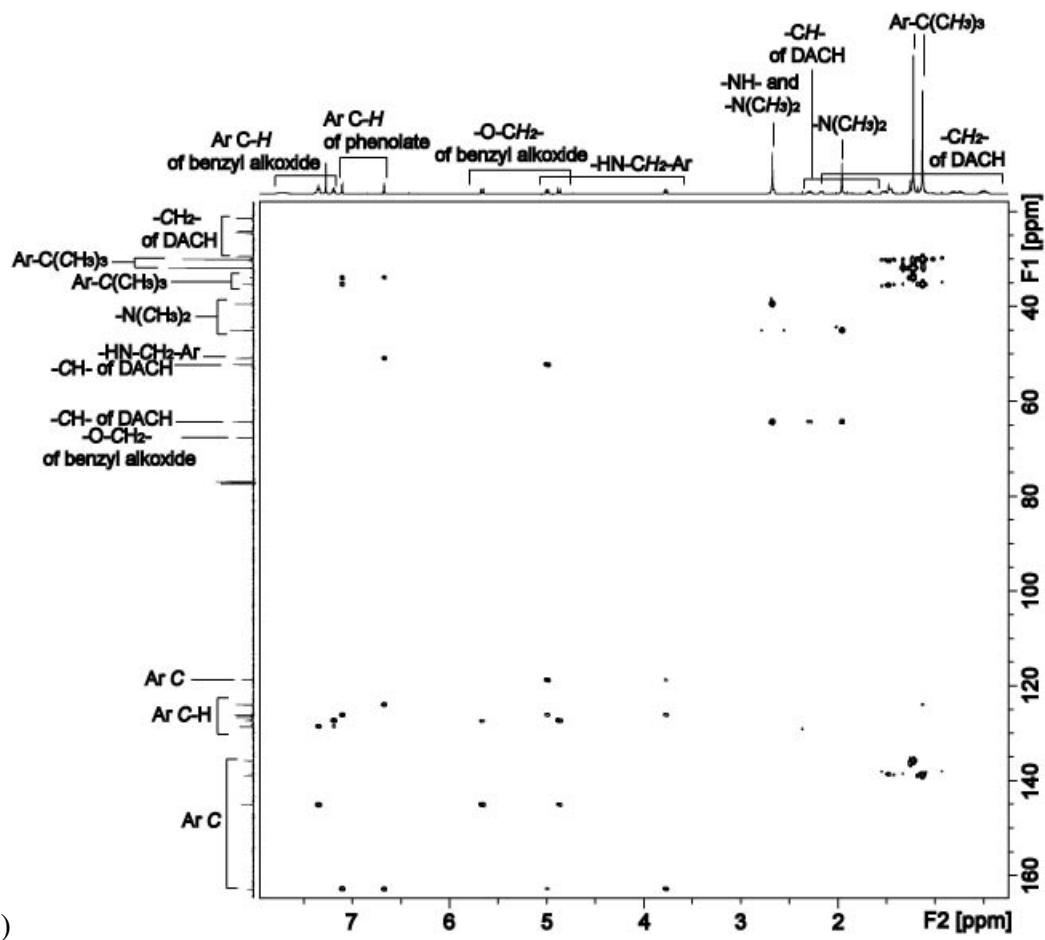
Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 25°C) of $[(\text{NNO}_{\text{tBu}})\text{InCl}(\mu\text{-OBn})_2]$ (**4**).



(a)

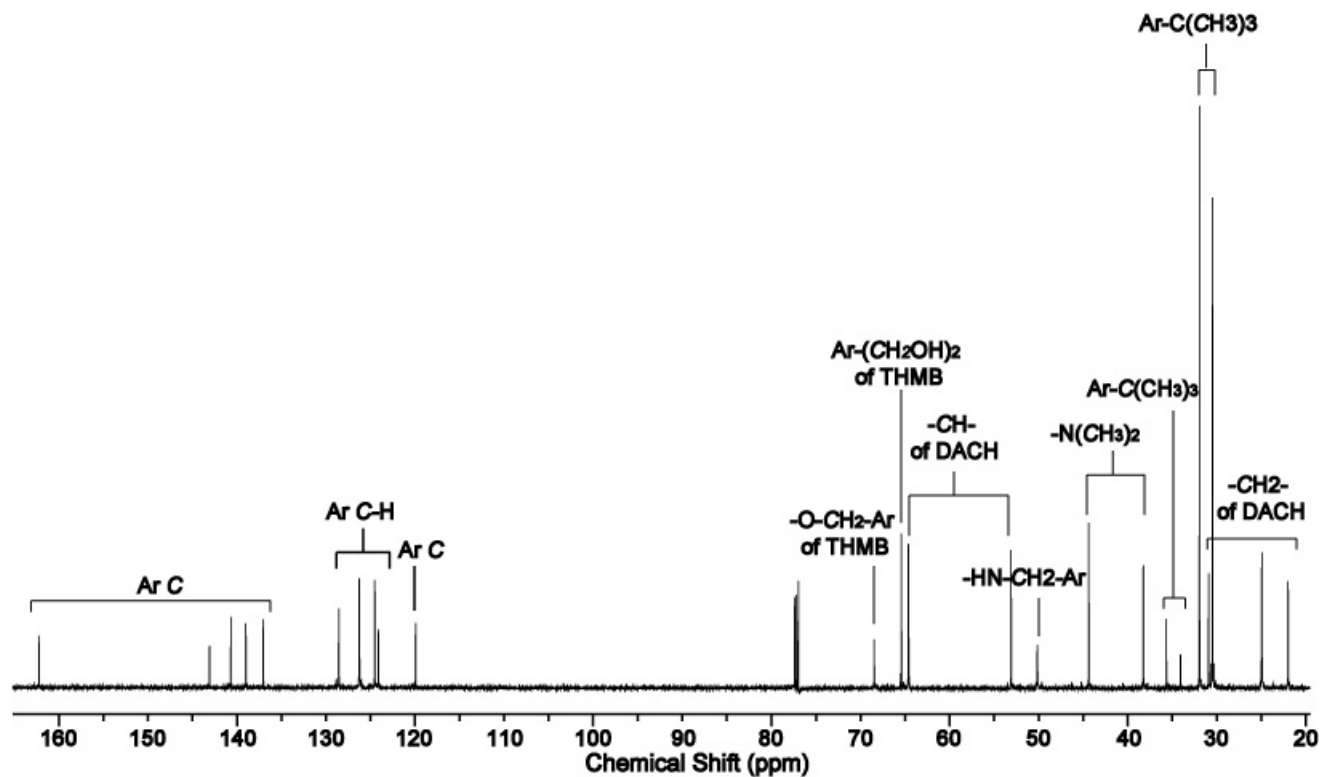
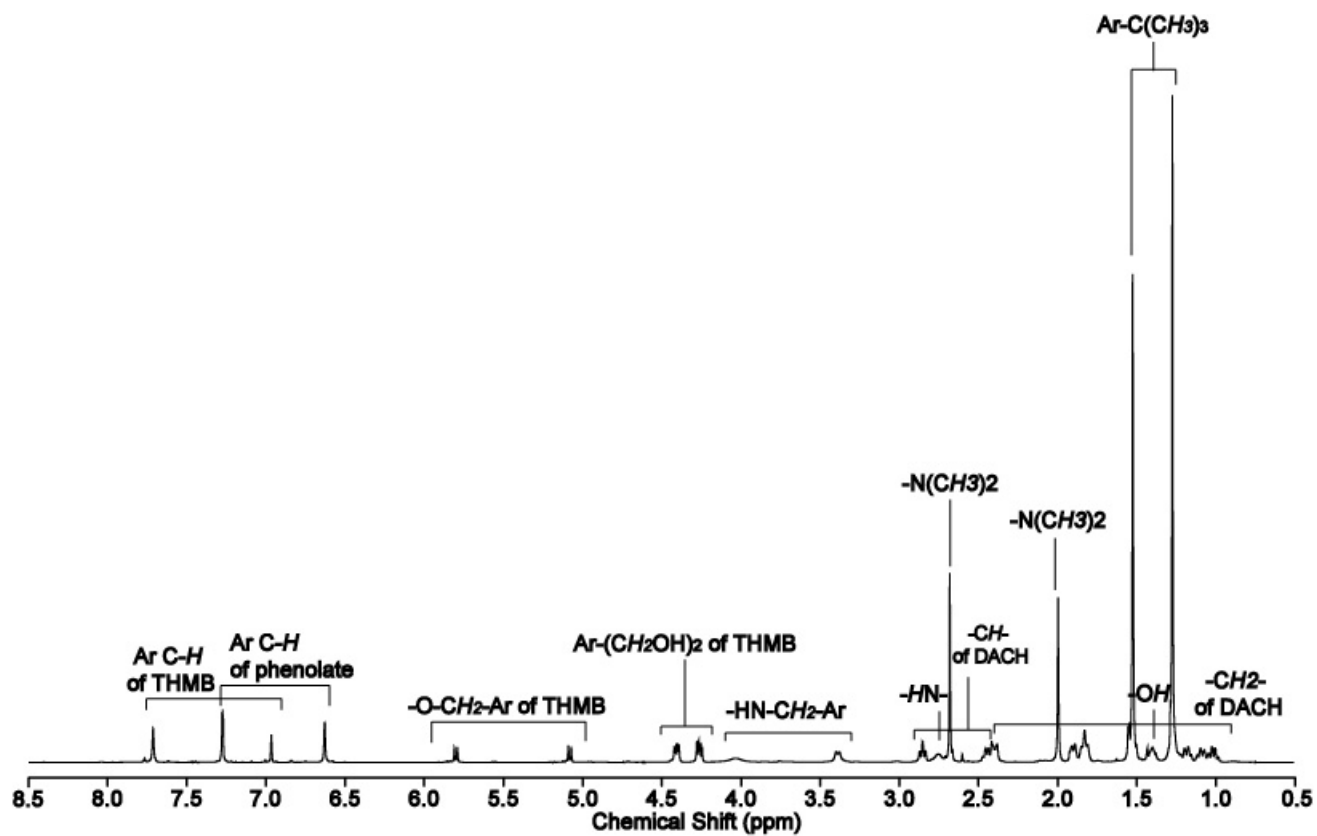


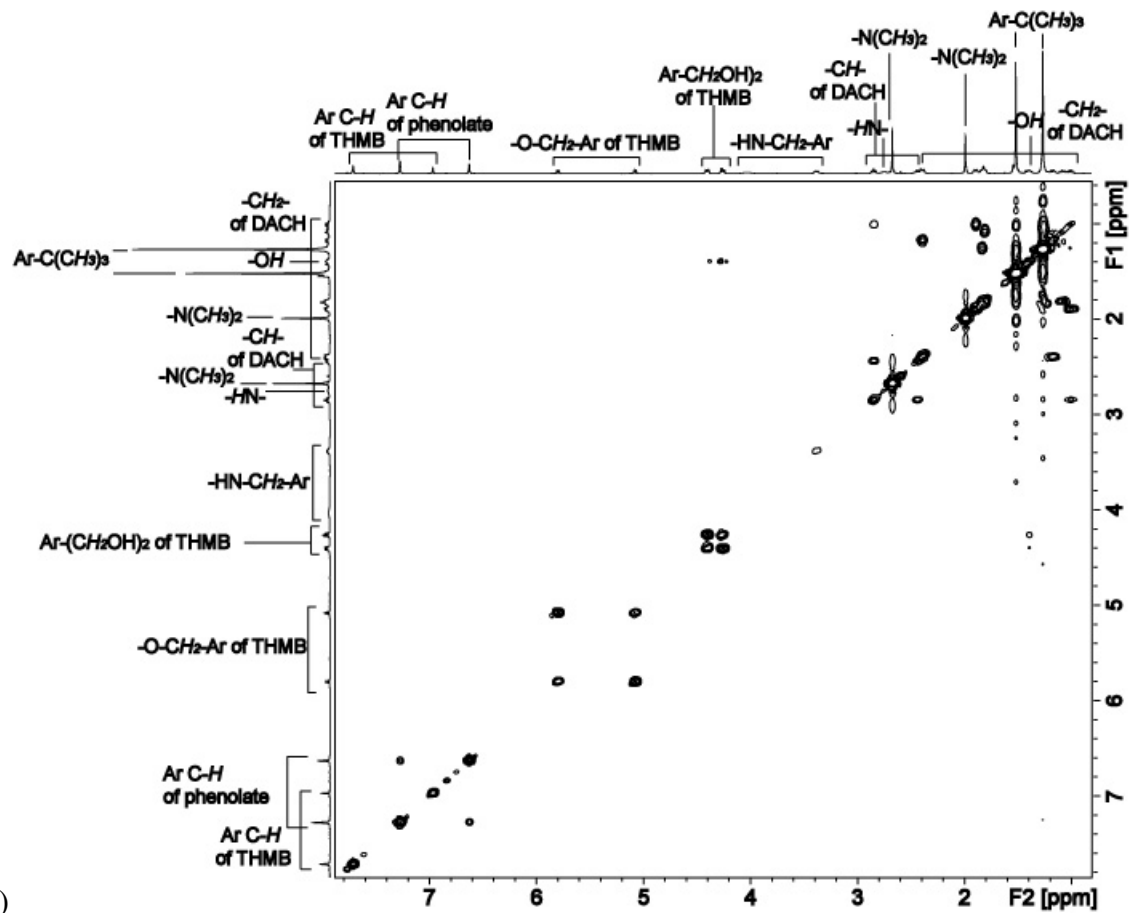
(b)



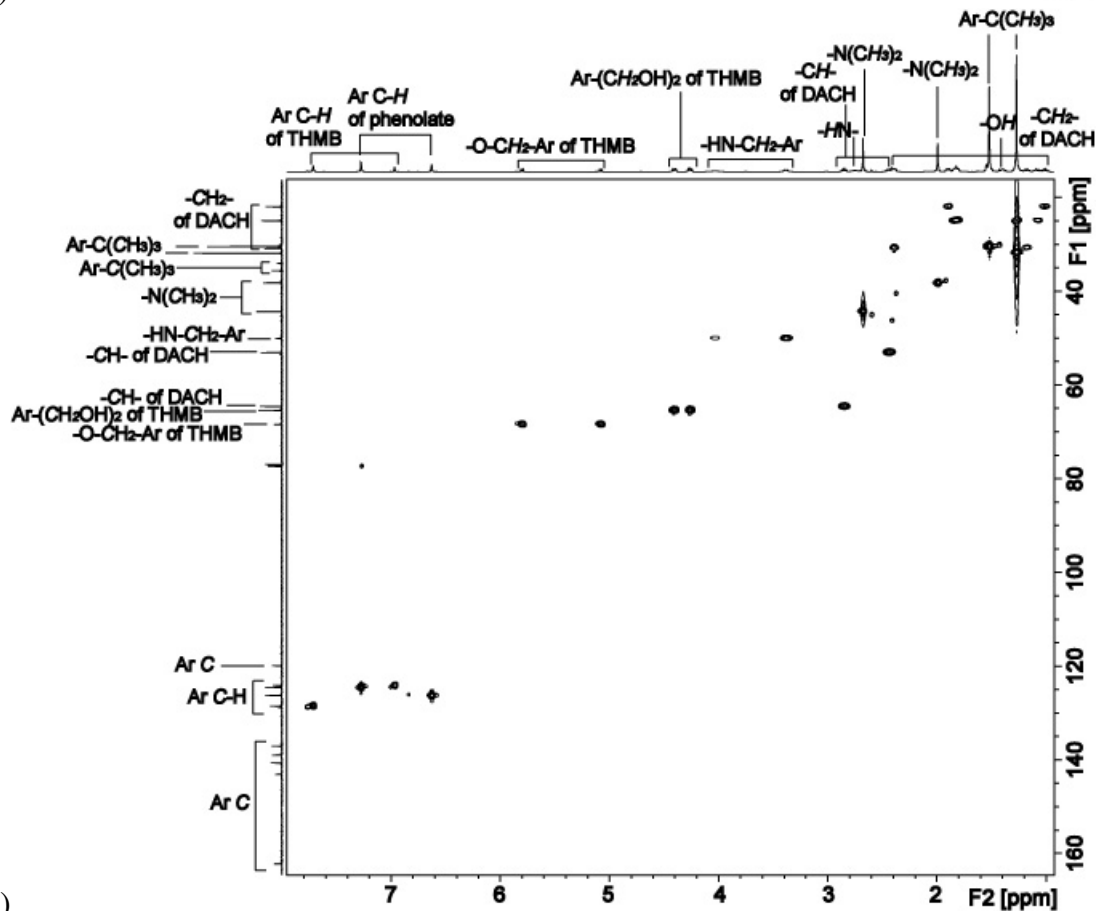
(c)

Figure S9. (a) ^1H - ^1H COSY (b) ^1H - ^{13}C HSQC and (c) ^1H - ^{13}C HMBC spectrum (CDCl_3 , 25 $^\circ\text{C}$) of $[(\text{NNO}_{\text{tBu}})\text{InCl}(\mu\text{-OBn})_2]_2$ (**4**).

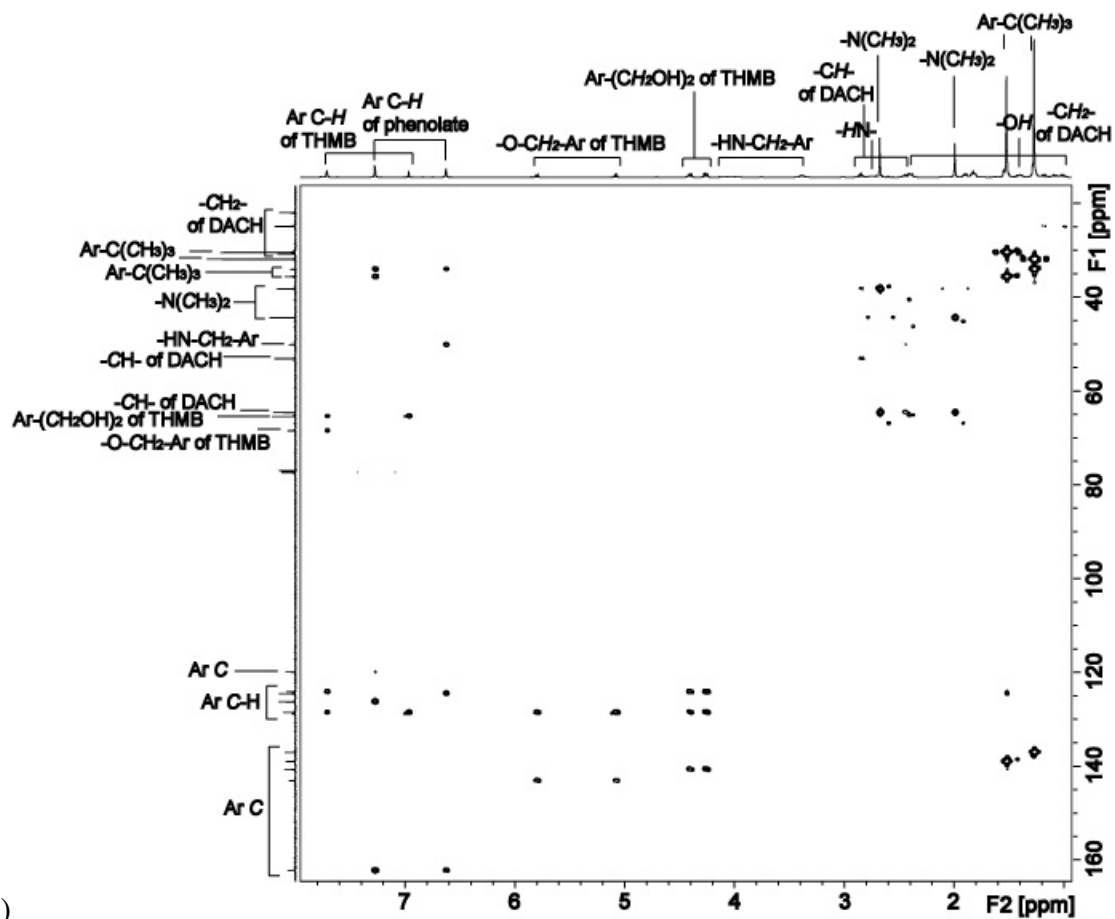




(a)



(b)



(c)

Figure IYS12. (a) ^1H - ^1H COSY (b) ^1H - ^{13}C HSQC and (c) ^1H - ^{13}C HMBC spectrum (CDCl_3 , 25 °C) of $[(\text{NNO}_{\text{tBu}})\text{InCl}]_2(\mu\text{-Cl})(\mu\text{-OTHMB})$ (**5**).

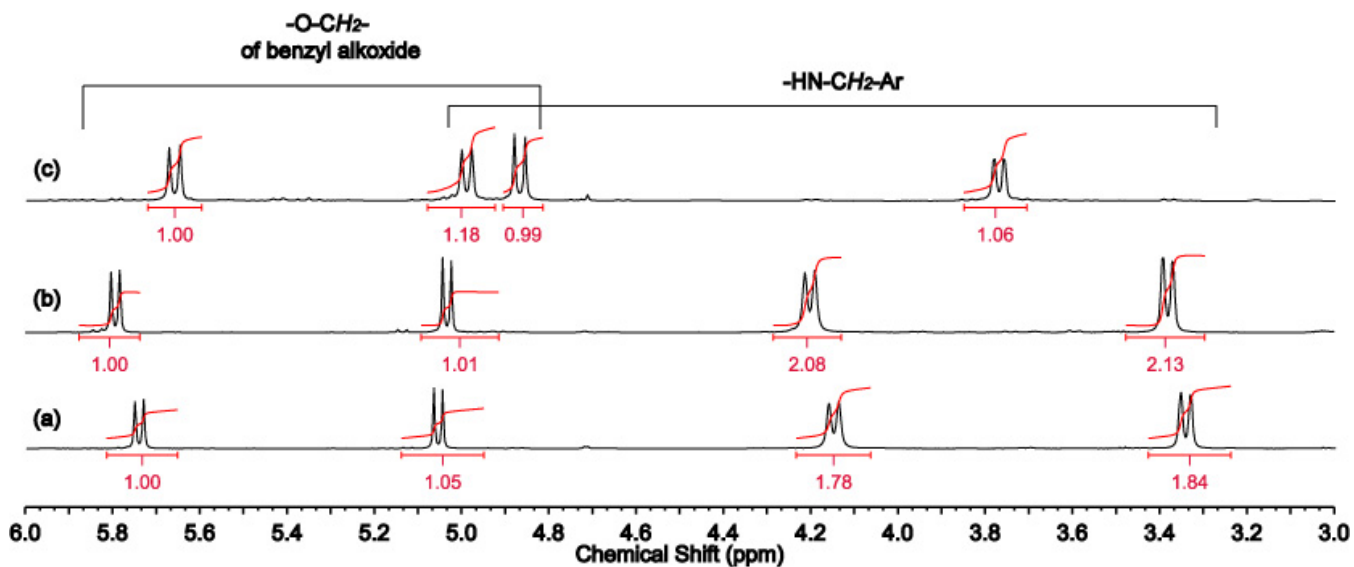


Figure S13. Stacked ^1H NMR spectra (CDCl_3 , 25 °C) of (a) $[(\text{NNO}_{\text{Me}})\text{InCl}]_2(\mu\text{-Cl})(\mu\text{-OBn})$ (**2**), (b) $[(\text{NNO}_{\text{tBu}})\text{InCl}]_2(\mu\text{-Cl})(\mu\text{-OBn})$ (**3**) and (c) $[(\text{NNO}_{\text{tBu}})\text{InCl}(\mu\text{-OBn})]_2$ (**4**).

Dissociation of complexes in THF- d_8

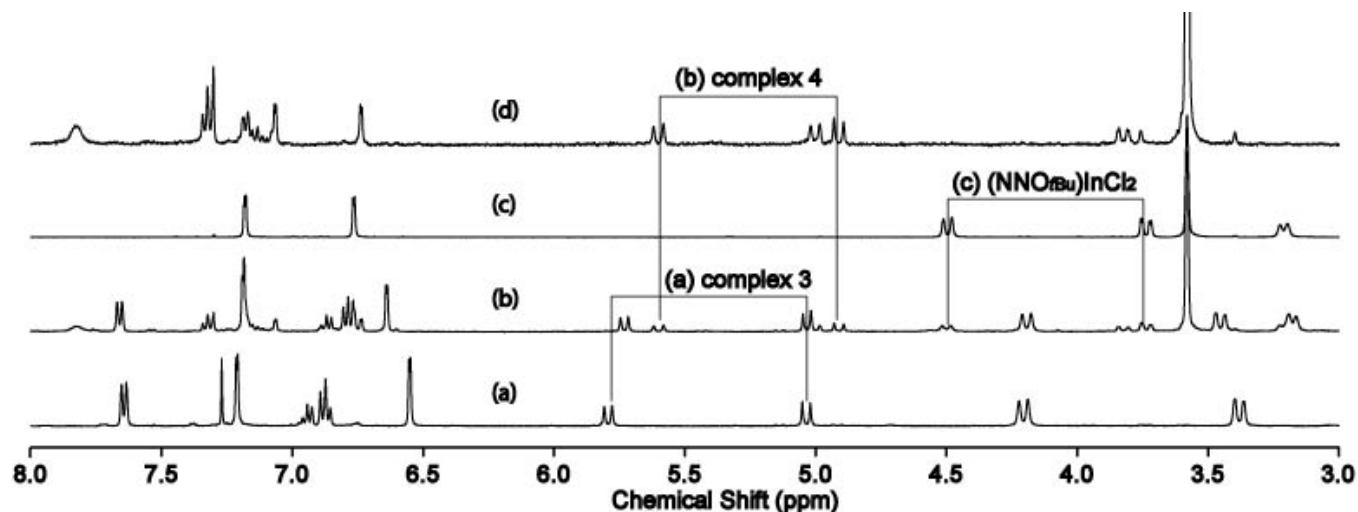


Figure S14. Stacked ^1H NMR spectra (400 MHz, 25 °C) of $[(\text{NNO}_{t\text{Bu}})\text{InCl}](\mu\text{-Cl})(\mu\text{-OBn})$ (**3**) (a) in CDCl_3 and (b) in $\text{THF-}d_8$, (c) a reference sample of $(\text{NNO}_{t\text{Bu}})\text{InCl}_2$ and (d) $[(\text{NNO}_{t\text{Bu}})\text{InCl}(\mu\text{-OBn})]_2$ (**4**) in $\text{THF-}d_8$ at room temperature.

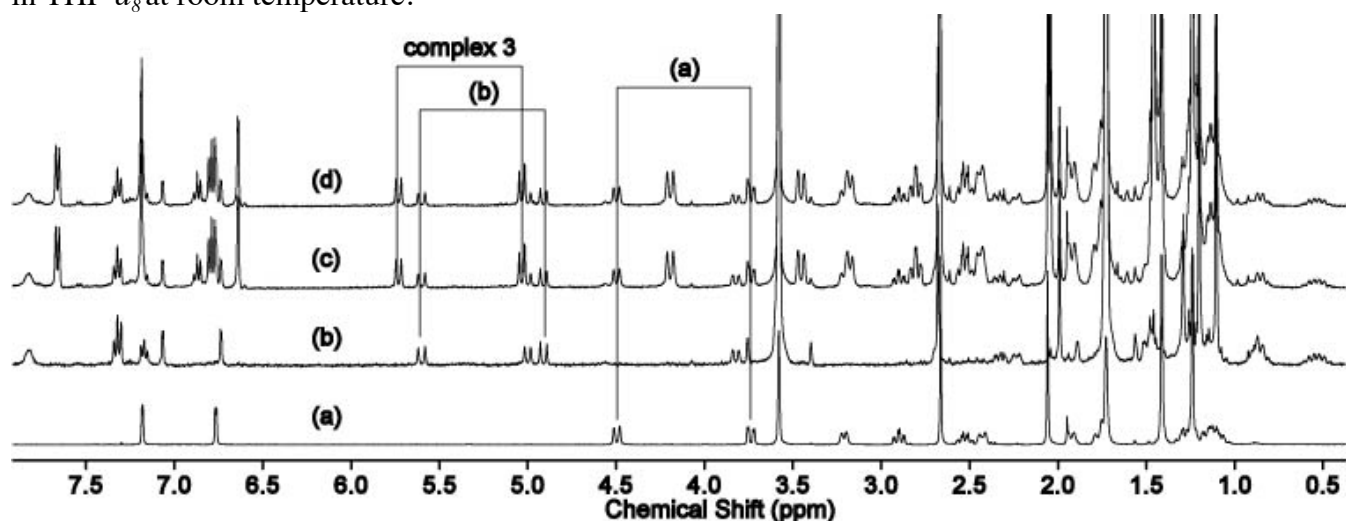


Figure S15. Stacked ^1H NMR spectra (400 MHz, 25 °C) of (a) $(\text{NN}_{t\text{Bu}}\text{O})\text{InCl}_2$, (b) $[(\text{NNO}_{t\text{Bu}})\text{InCl}(\mu\text{-OBn})]_2$ (**4**), and complex 4 with 2 equivalents of $(\text{NNO}_{t\text{Bu}})\text{InCl}_2$ (c) after 10 min and (d) 16 h in $\text{THF-}d_8$.

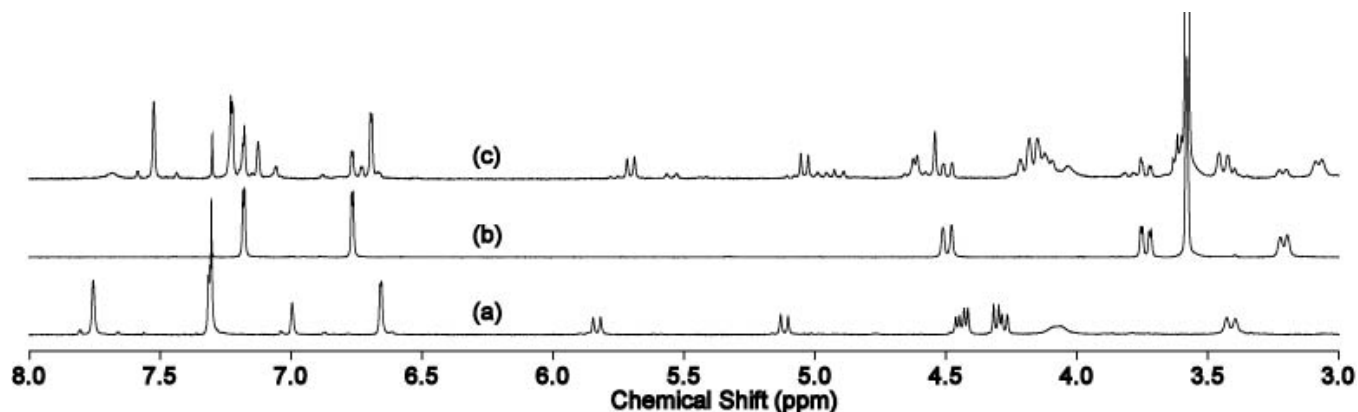


Figure S16. Stacked ^1H NMR spectra (400 MHz, 25 °C) of (a) $[(\text{NNO}_{t\text{Bu}})\text{InCl}]_2(\mu\text{-Cl})(\mu\text{-OTHMB})$ in CDCl_3 and (b) $(\text{NN}_{t\text{Bu}}\text{O})\text{InCl}_2$ and (c) $[(\text{NNO}_{t\text{Bu}})\text{InCl}](\mu\text{-Cl})(\mu\text{-OTHMB})$ (**5**) in $\text{THF-}d_8$.

Ortep diagrams and table of crystallographic data

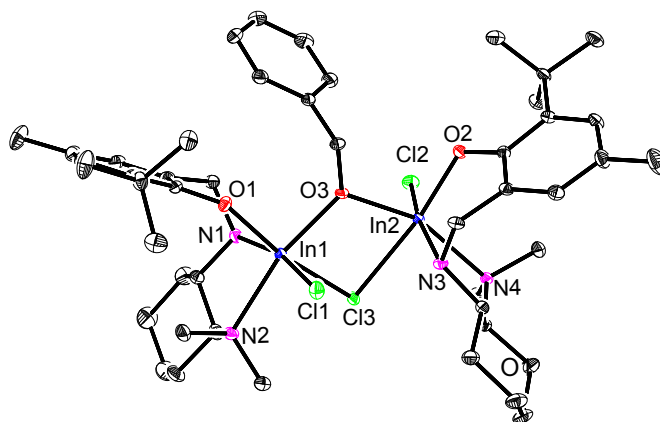


Figure S17. Molecular structure of (*SS/SS*)-**2** (depicted with thermal ellipsoids at 50% probability and all H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): N1-In1 2.268(3), N2-In1 2.347(3), O1-In1 2.085(3), O3-In1 2.147(2), Cl1-In1 2.4530(10), Cl3-In1 2.6169(9), N3-In2 2.268(3), N4-In2 2.375(3), O2-In2 2.089(3), O3-In2 2.167(3), Cl2-In2 2.4090(10), Cl3-In2 2.6416(9), In1-O3-In2 116.73(11), In2-Cl3-In1 88.60(3), N1-In1-N2 77.17(12), N1-In1-O1 87.60(11), N1-In1-O3 98.76(11), N1-In1-Cl3 87.67(9), N1-In1-Cl1 167.84(9), N2-In1-Cl1 91.52(9), N2-In1-Cl3 85.63(8), O1-In1-O3 94.53(10), O1-In1-N2 102.91(11), O1-In1-Cl1 90.65(8), O1-In1-Cl3 169.06(8), O3-In1-N2 161.83(11), O3-In1-Cl1 93.38(8), O3-In1-Cl3 76.46(7), Cl1-In1-Cl3 96.01(3), N3-In2-N4 75.83(12), N3-In2-O2 88.07(10), N3-In2-O3 91.22(11), N3-In2-Cl2 169.15(9), N3-In2-Cl3 86.78(8), N4-In2-O3 157.69(10), N4-In2-Cl2 93.45(9), N4-In2-Cl3 85.45(8), O2-In2-N4 104.06(10), O2-In2-O3 93.39(10), O2-In2-Cl2 92.98(8), O2-In2-Cl3 167.73(8), O3-In2-Cl2 99.50(8), O3-In2-Cl3 75.60(7), Cl2-In2-Cl3 94.17(3).

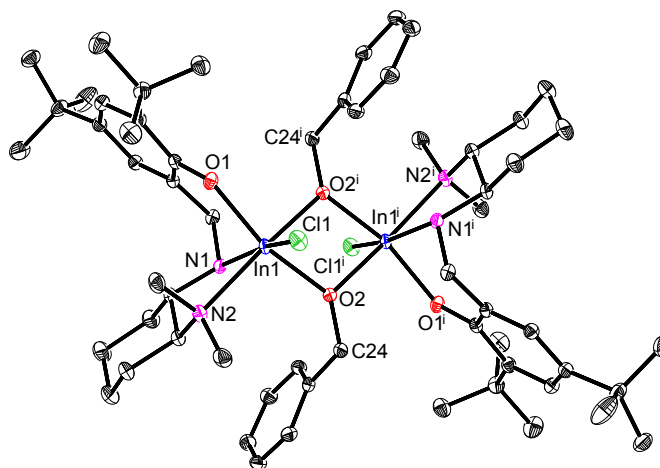


Figure S18. Molecular structure of (*RR/SS*)-**4** (depicted with thermal ellipsoids at 50% probability and all H atoms and solvent molecules omitted for clarity). Selected bond lengths (Å) and angles (deg): In1-Cl1 2.4374(10), In1-O1 2.1109(13), In1-O2 2.1745(13), In1ⁱ-O2 2.1890(12), In1-O2ⁱ 2.1889(12), In1-N1 2.2674(16), In1-N2 2.3998(14). Selected bond angles (°): O1-In1-O2ⁱ 88.76(5), O1-In1-O2 159.35(4), O2-In1-O2ⁱ 72.86(6), O1-In1-Cl1 95.52(4), O1-In1-N1 84.51(4), O2-In1-N1 88.74(4), O2-In1-Cl1 96.20(3), O2ⁱ-In1-Cl1 97.66(4), O2ⁱ-In1-N1 98.07(5), O1-In1-N2 94.90(6), O2ⁱ-In1-N2 172.38(4), N1-In1-N2 75.68(5), N2-In1-O2 102.31(5), N1-In1-Cl1 164.27(3), N2-In1-Cl1 88.65(4), In1-O2-In1ⁱ 107.14(6).

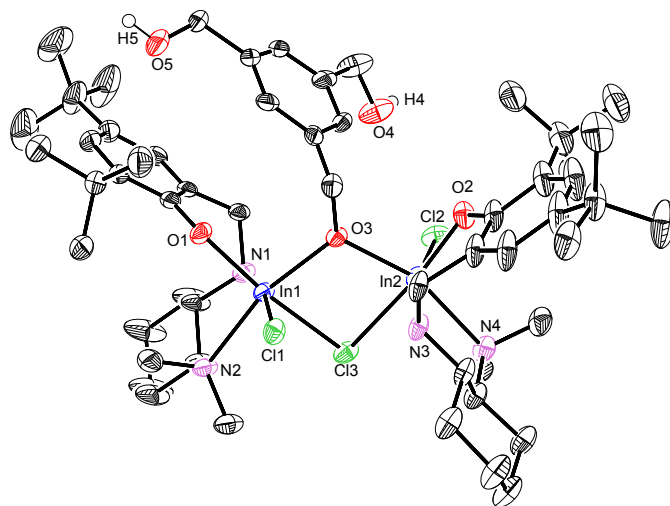


Figure S19. Molecular structure of (*SS/SS*)-**5** (depicted with thermal ellipsoids at 50% probability and most H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): N1-In1 2.205(4), N2-In1 2.378(3), O1-In1 2.089(3), O3-In1 2.164(3), Cl1-In1 2.4165(12), Cl3-In1 2.6613(12), N3-In2 2.257(3), N4-In2 2.366(3), O2-In2 2.078(3), O3-In2 2.168(2), Cl2-In2 2.4297(13), Cl3-In2 2.6066(12), In1-O3-In2 114.89(11), In2-Cl3-In1 87.77(3), N1-In1-N2 77.22(12), N1-In1-O1 86.15(12), N1-In1-O3 97.50(12), N1-In1-Cl3 85.19(10), N1-In1-Cl1 168.51(9), N2-In1-Cl1 91.31(9), N2-In1-Cl3 85.54(9), O1-In1-O3 98.18(10), O1-In1-N2 98.56(11), O1-In1-Cl1 95.02(8), O1-In1-Cl3 169.36(8), O3-In1-N2 162.05(11), O3-In1-Cl1 93.65(7), O3-In1-Cl3 76.87(7), Cl1-In1-Cl3 94.70(3), N3-In2-N4 76.90(11), N3-In2-O2 86.63(13), N3-In2-O3 94.36(11), N3-In2-Cl2 166.72(9), N3-In2-Cl3 86.29(10), N4-In2-O3 160.80(11), N4-In2-Cl2 90.94(9), N4-In2-Cl3 84.30(9), O2-In2-N4 102.93(11), O2-In2-O3 93.45(10), O2-In2-Cl2 91.01(9), O2-In2-Cl3 168.47(8), O3-In2-Cl2 98.82(7), O3-In2-Cl3 78.03(7), Cl2-In2-Cl3 97.92.

Table S1. Selected crystallographic data for compounds **2**, **4** and **5**.

	2	4	5
empirical formula	C ₆₈ H ₉₇ Cl ₃ In ₂ N ₄ O ₃	C ₈₁ H _{115.5} Cl ₂ In ₂ N ₄ O ₄	C ₆₂ H ₉₇ Cl ₃ In ₂ N ₄ O ₅
fw	1354.48	1509.81	1314.42
<i>T</i> (K)	90(2)	90(2)	90(2)
<i>a</i> (Å)	22.3826(16)	32.890(17)	12.169(3)
<i>b</i> (Å)	19.9446(16)	12.527(7)	15.269(4)
<i>c</i> (Å)	30.529(2)	19.435(10)	18.288(5)
<i>α</i> (deg)	90	90	81.554(7)
<i>β</i> (deg)	90	103.232(9)	80.349(6)
<i>γ</i> (deg)	90	90	74.877(6)
volume (Å ³)	13628.5(18)	7795(7)	3215.0(15)
<i>Z</i>	8	4	2
cryst syst	orthorhombic	monoclinic	triclinic
space group	<i>P</i> c a 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>d</i> _{calc} (g/cm ³)	1.320	1.286	1.358
<i>μ</i> (Mo Kα) (cm ⁻¹)	8.4	7.1	8.9
2 <i>θ</i> _{max} (deg)	60.1	59.3	55.2
absor corr (<i>T</i> _{min} , <i>T</i> _{max})	0.8403, 0.9272	0.8570, 0.9396	0.8570, 0.9396
total no. of reflns	194 828	55 734	68 410
no. of indep reflns (<i>R</i> _{int})	39 905 (0.0533)	10 902 (0.0381)	14 748 (0.0464)
residuals (refined on <i>F</i> ²): <i>R</i> ₁ ; <i>wR</i> ₂	0.0440, 0.0661	0.0331, 0.0577	0.0708, 0.1065
GOF	1.015	1.049	1.049
no. obsrvns [<i>I</i> > 2σ(<i>I</i>)]	9772	9921	9921
residuals (refined on <i>F</i> ² : <i>R</i> ₁ ^{<i>a</i>} ; <i>wR</i> ₂ ^{<i>b</i>})	0.0314, 0.0612	0.0250, 0.0536	0.0460, 0.0938
^{<i>a</i>} <i>R</i> ₁ = Σ <i>F</i> _o - <i>F</i> _c / Σ <i>F</i> _o . ^{<i>b</i>} <i>wR</i> ₂ = [Σ (<i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²) ²) / Σ <i>w</i> (<i>F</i> _o ²) ₂] ^{1/2}			

Part B. Polymerization of BBL

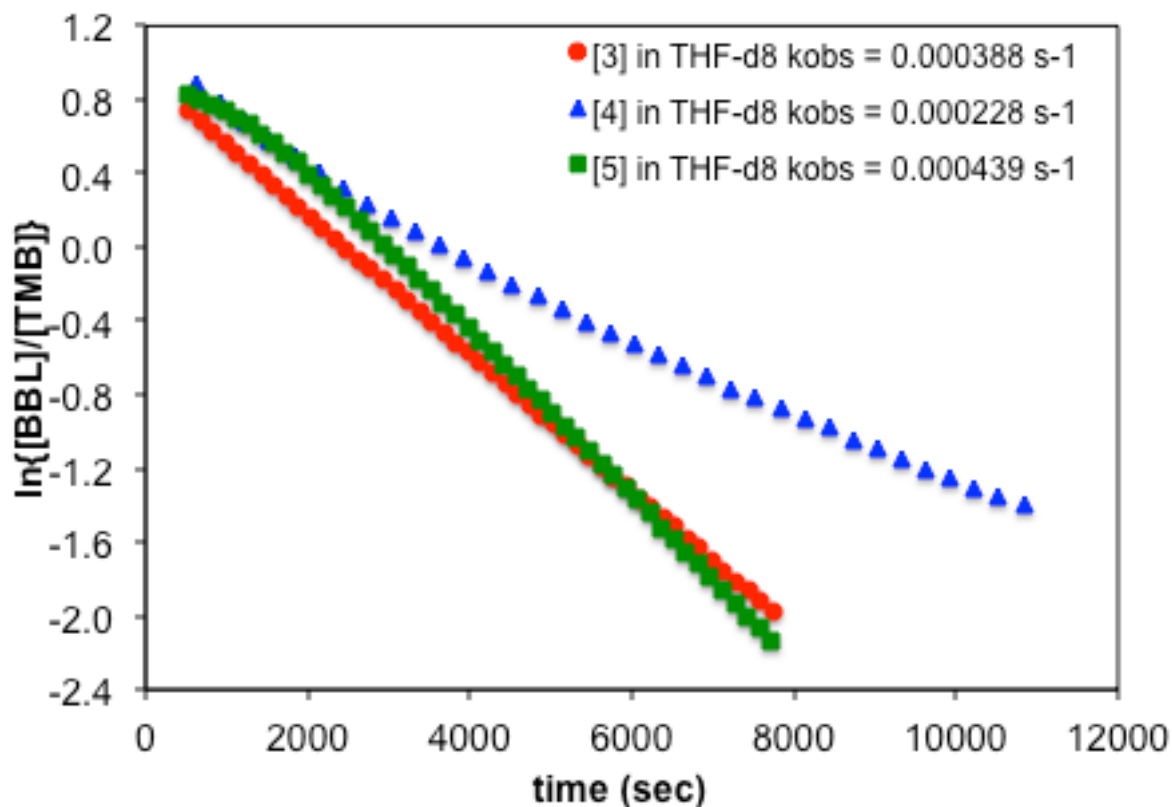


Figure S20. The ROP plots of 200 equiv of [BBL] vs. [initiator] (**3**, [(NNO_{tBu})InCl](μ -Cl)(μ -OEt), = \blacklozenge ; **4**, [(NNO_{tBu})InCl](μ -Cl)(μ -OEt), = \blacktriangle ; **5**, [(NNO_{tBu})InCl](μ -Cl)(μ -OEt), = \blacksquare) at 25 °C and followed to 90% conversion. For **3** and **5**, [BBL] = 0.86 M. [catalyst] = 2.0 mM in THF-*d*₈. For **4**, [BBL] = 0.16 M. [catalyst] = 0.40 mM in THF-*d*₈. 1,3,5-trimethoxybenzene (TMB) was used as internal standard.

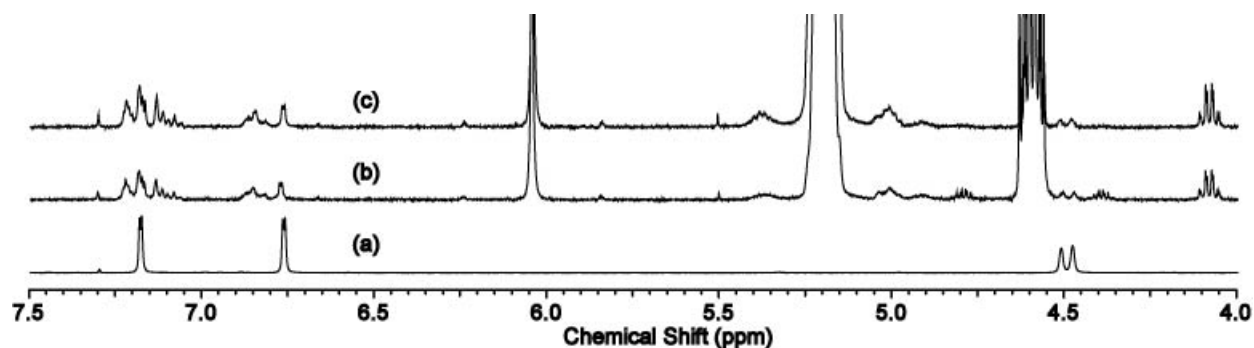


Figure S21. Stacked ¹H NMR spectra of (a) (NNO_{tBu})InCl₂ and polymerization of 200 equivalents of BBL with [(NNO_{tBu})InCl]₂(μ -Cl)(μ -OEt) (**1**) after (b) 5 min and (c) 2 h (THF-*d*₈, 25 °C).

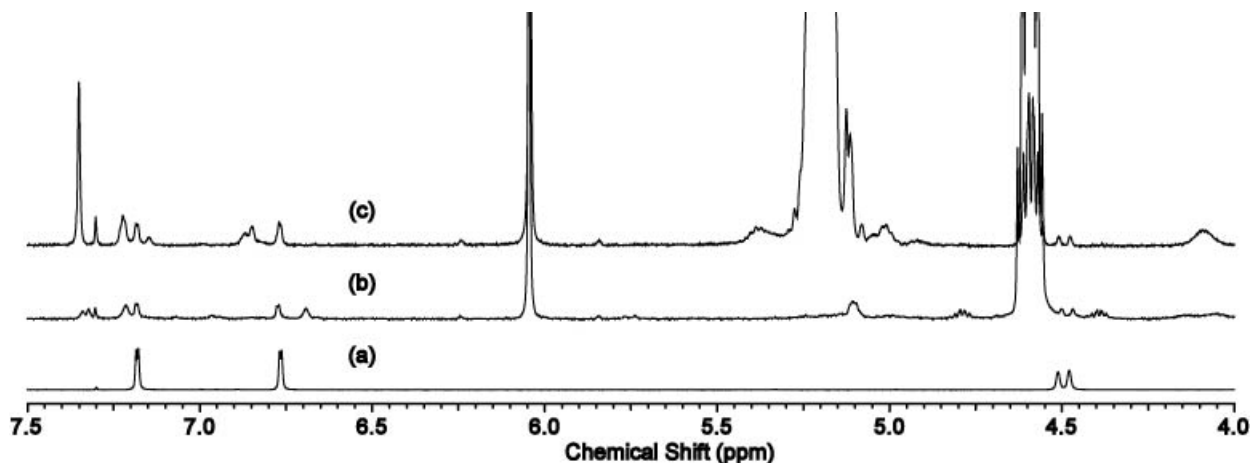


Figure S22. ¹H NMR spectra of (a) (NNO_{tBu})InCl₂ and polymerization of 200 equivalents of BBL with complex [(NNO_{tBu})InCl₂(μ-Cl)(μ-OTHMB) (**5**) after (b) 6 minutes and (c) 2 h (THF-*d*₈, 25 °C).

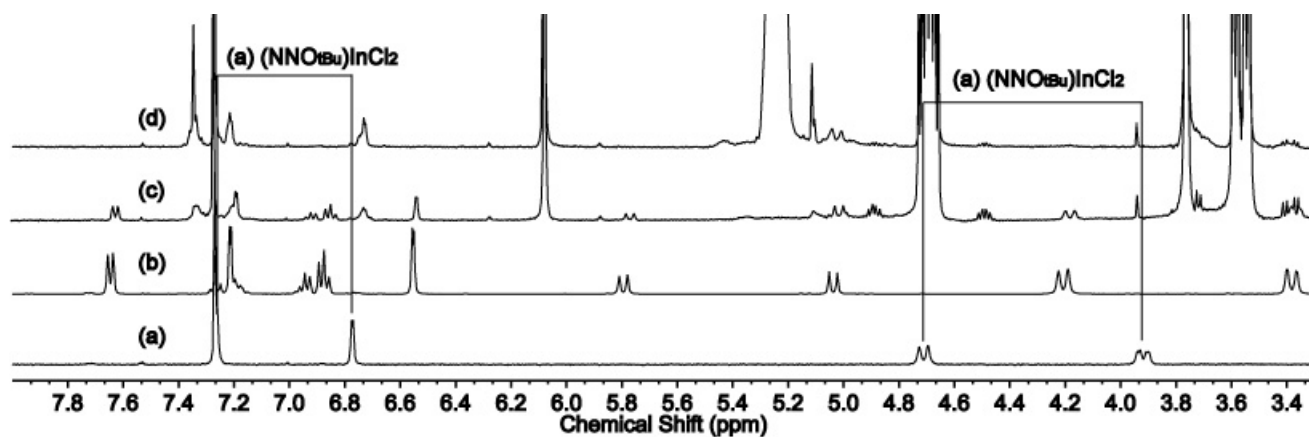


Figure S23. Stacked ¹H NMR spectra of (a) (NNO_{tBu})InCl₂, (b) [(NNO_{tBu})InCl₂(μ-Cl)(μ-OBn) (**3**) and polymerization of 200 equivalents of BBL with [(NNO_{tBu})InCl₂(μ-Cl)(μ-OBn) (**3**) after (b) 7 min and (c) 12 h (CDCl₃, 25 °C).

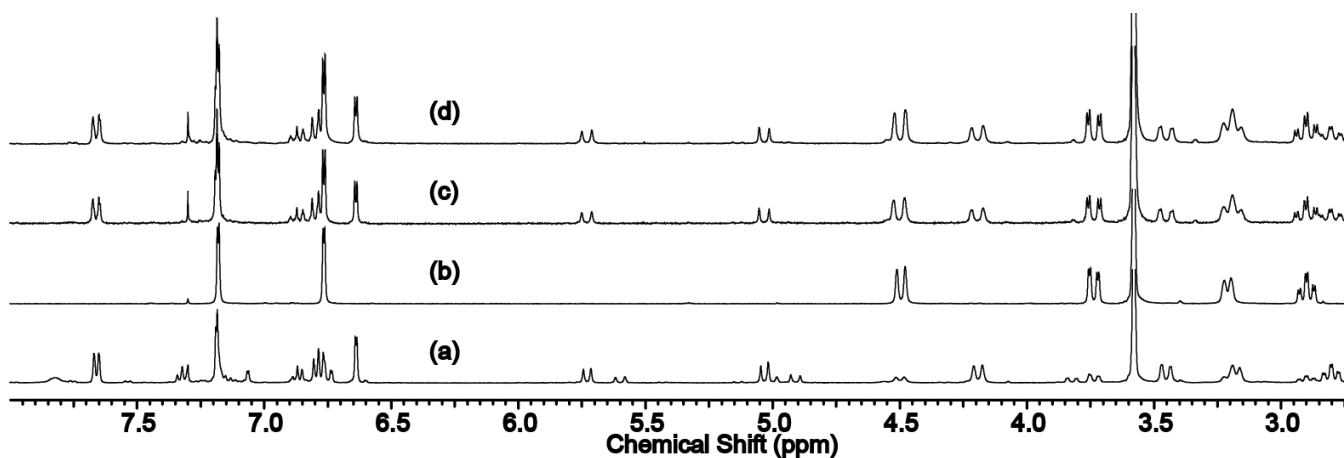


Figure S24. Stacked ¹H NMR spectra (400 MHz) of (a) [(NNO_{tBu})InCl₂(μ-Cl)(μ-OBn) (**3**) and (b) (NNO_{tBu})InCl₂; and spectra of [(NNO_{tBu})InCl₂(μ-Cl)(μ-OBn) (**3**) in the presence of two equivalents of (NNO_{tBu})InCl₂ after (c) 6 minutes and (d) 16 h in THF-*d*₈ at 25 °C.

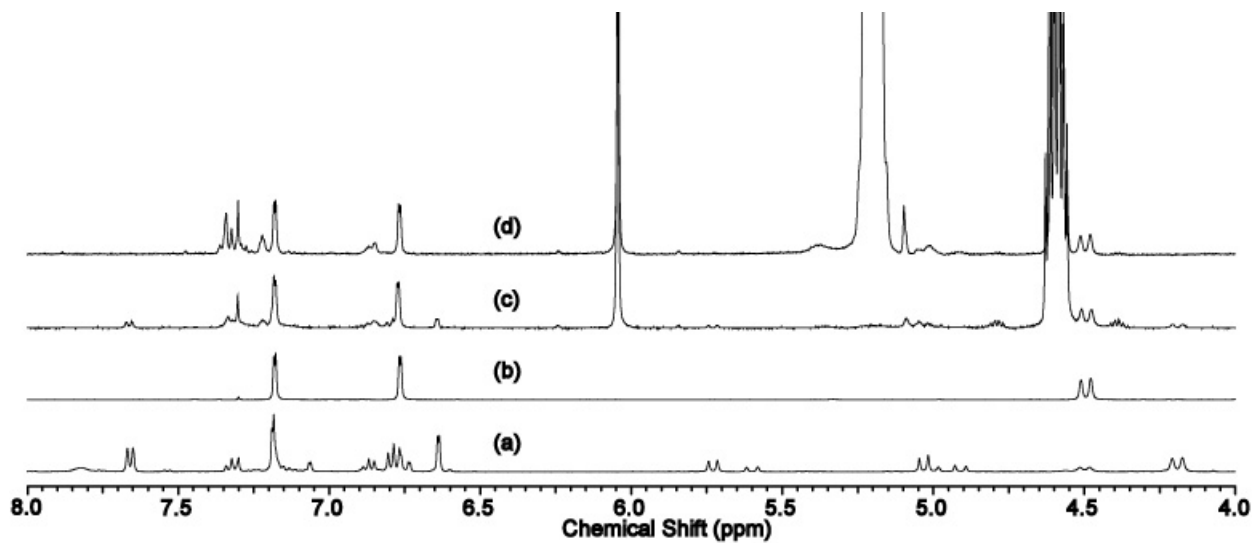


Figure S25. Stacked ^1H NMR spectra (400 MHz) of (a) $[(\text{NNO}_{\text{tBu}})\text{InCl}_2]_2(\mu\text{-Cl})(\mu\text{-OBn})$ (**3**) and (b) $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ and polymerization of 200 equiv BBL with complex **3** in the presence of two equiv $(\text{NNO}_{\text{tBu}})\text{InCl}_2$ after (c) 5 min; (d) 5 h in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

Part C. Immortal polymerization

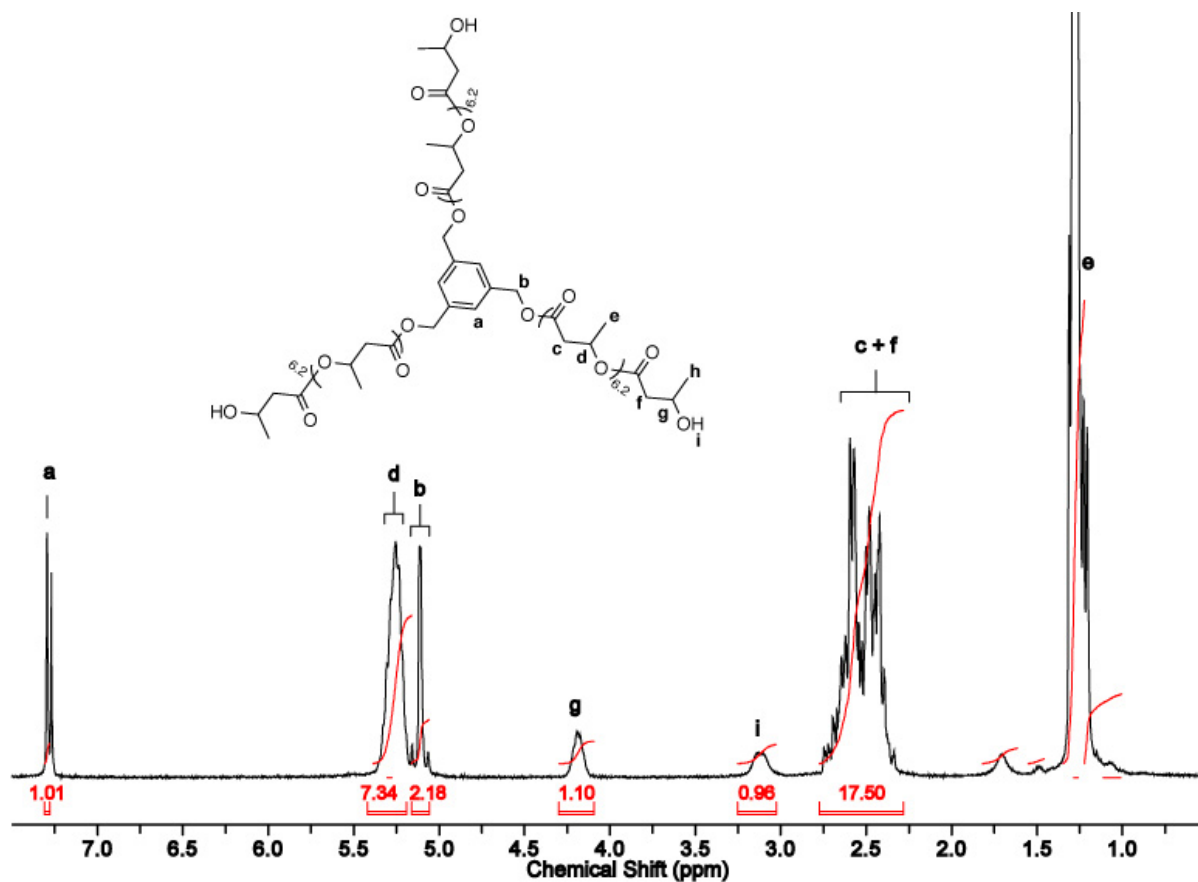


Figure S26. ¹H NMR spectra of the isolated 3-armed PHBs ([BBL]:[THMB]:[1] ratios of 5000:220:1) (Table 3, entry 1) (CDCl₃, 25 °C).

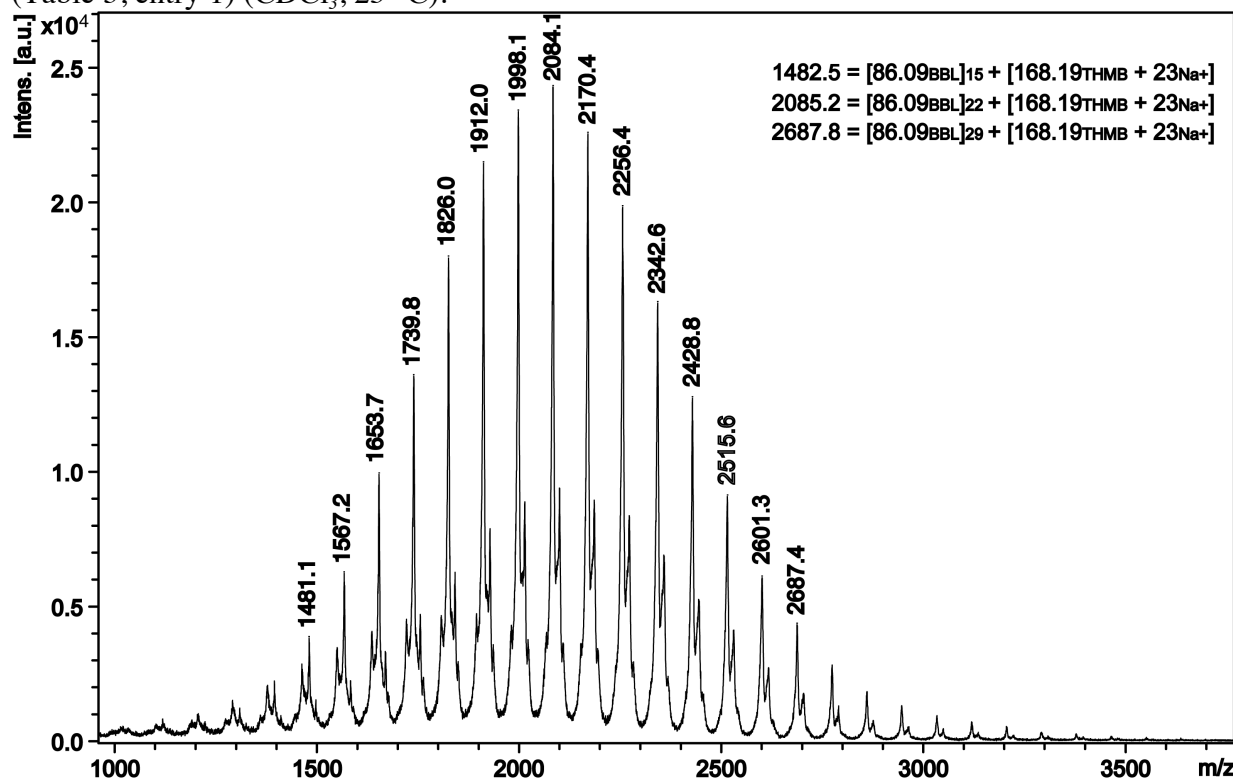


Figure S27. MALDI-TOF spectrum of 3-arm star PHB isolated from polymerization of [BBL]:[THMB]:[1] ratios of 5000:220:1 in THF at room temperature. (Table 3, entry 1)

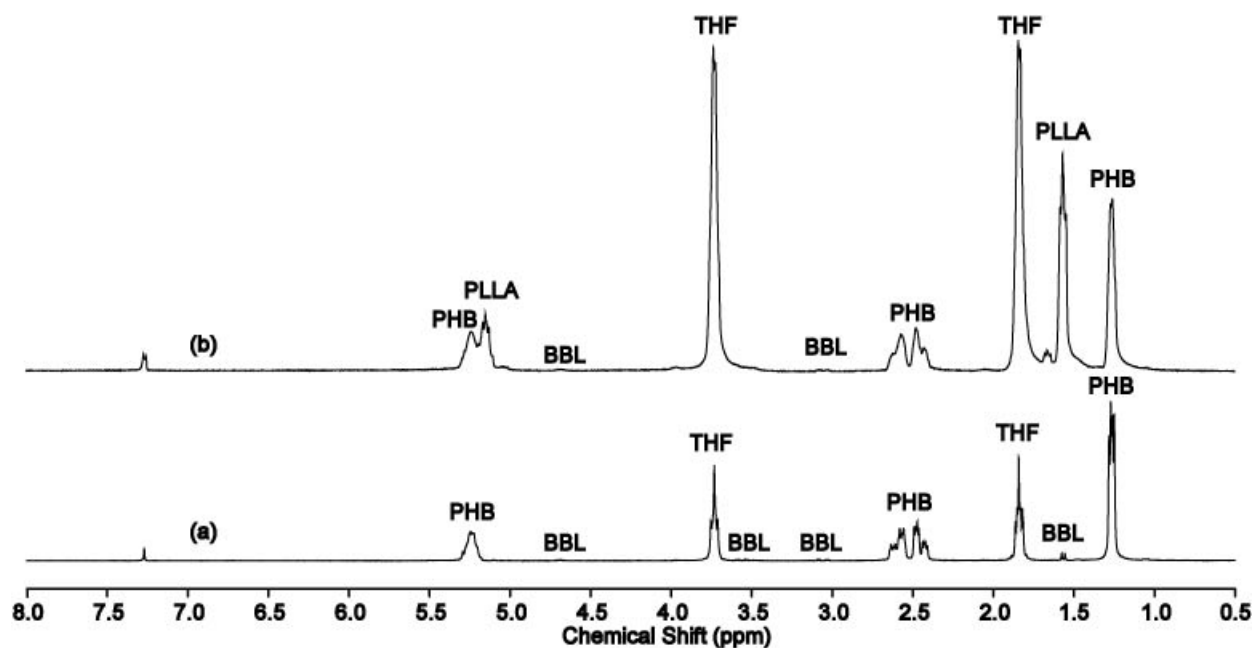


Figure S28. Stacked ^1H NMR spectra of (a) 3-arm star PHB homopolymer obtained from the polymerization of $[\text{BBL}]:[\text{THMB}]:[\mathbf{1}]$ ratios of 3125:5:1 and (b) 3-arm star block copolymers of PHB-PLLA obtained from the polymerization of $[\text{BBL}]+[\text{L-LA}]/[\text{THMB}]/[\mathbf{1}] = 3125+1865/5/1$ with complex **1** in THF in the presence of 5 equivalents of THMB at room temperature (Table 3, entry 8) (CDCl_3 , 25 $^\circ\text{C}$).

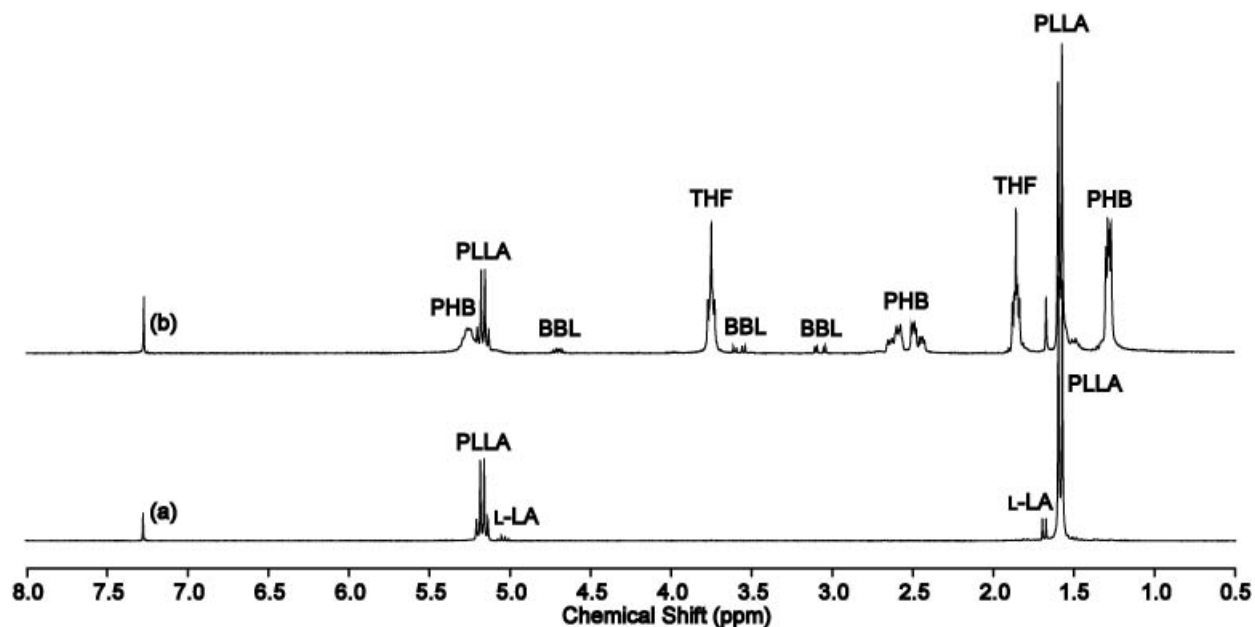


Figure S29. Stacked ^1H NMR spectra of (a) 3-arm star PLLA homopolymer obtained from the polymerization of $[\text{L-LA}]/[\text{THMB}]/[\mathbf{1}] : 1865/5/1$ and (b) 3-arm star block copolymers of PLLA-PHB obtained from the polymerization of $[\text{L-LA}]+[\text{BBL}]/[\text{THMB}]/[\mathbf{1}] = 1865+3125/5/1$ with complex **1** in THF in the presence of 5 equivalents of THMB at room temperature (Table 3, entry 9) (CDCl_3 , 25 $^\circ\text{C}$).

Part D. GPC traces of the polymers presented in Table 2 and Table 3

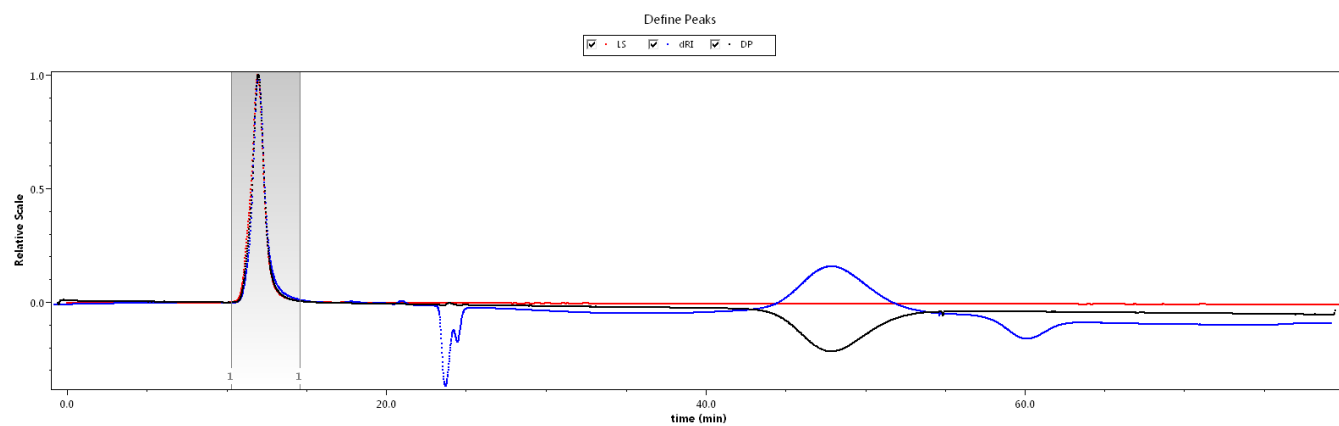


Figure S30. Table 2 entry 1

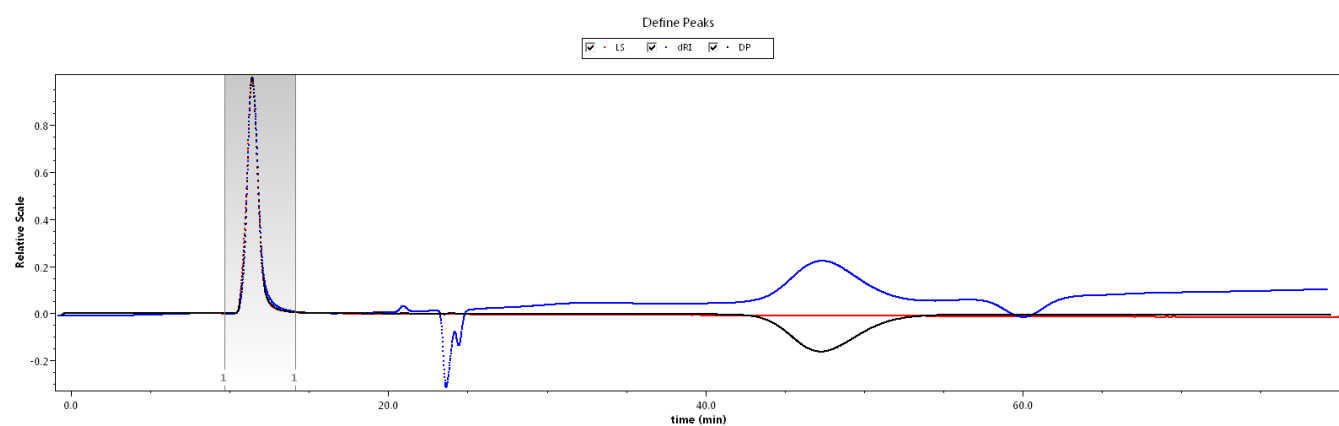


Figure S31. Table 2 entry 2

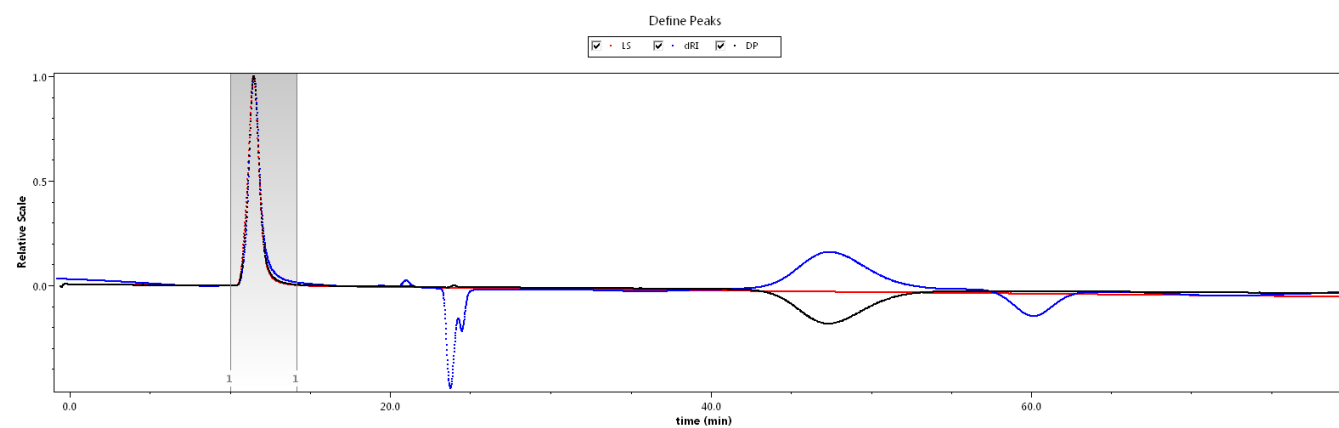


Figure S32. Table 2 entry 3

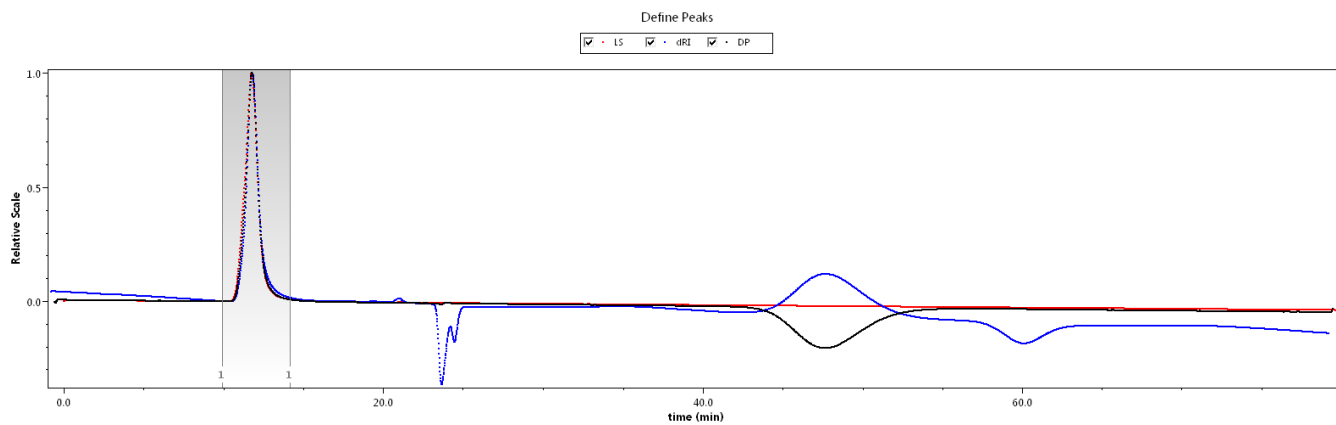


Figure S33. Table 2 entry 4

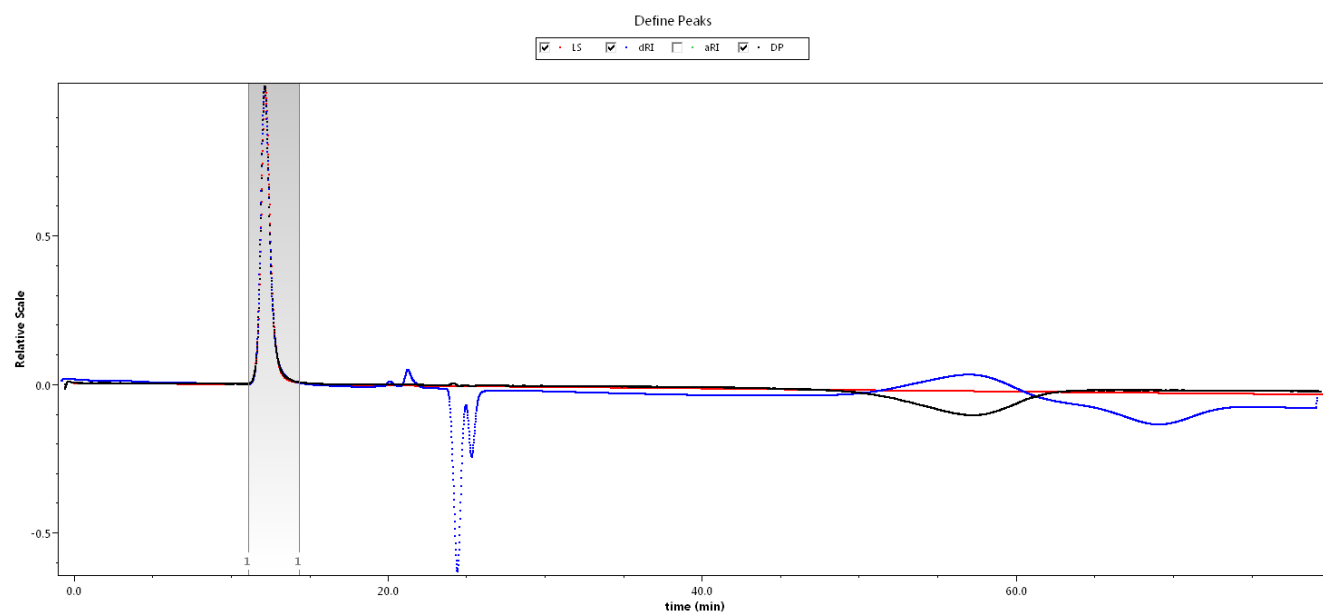


Figure S34. Table 2 entry 5

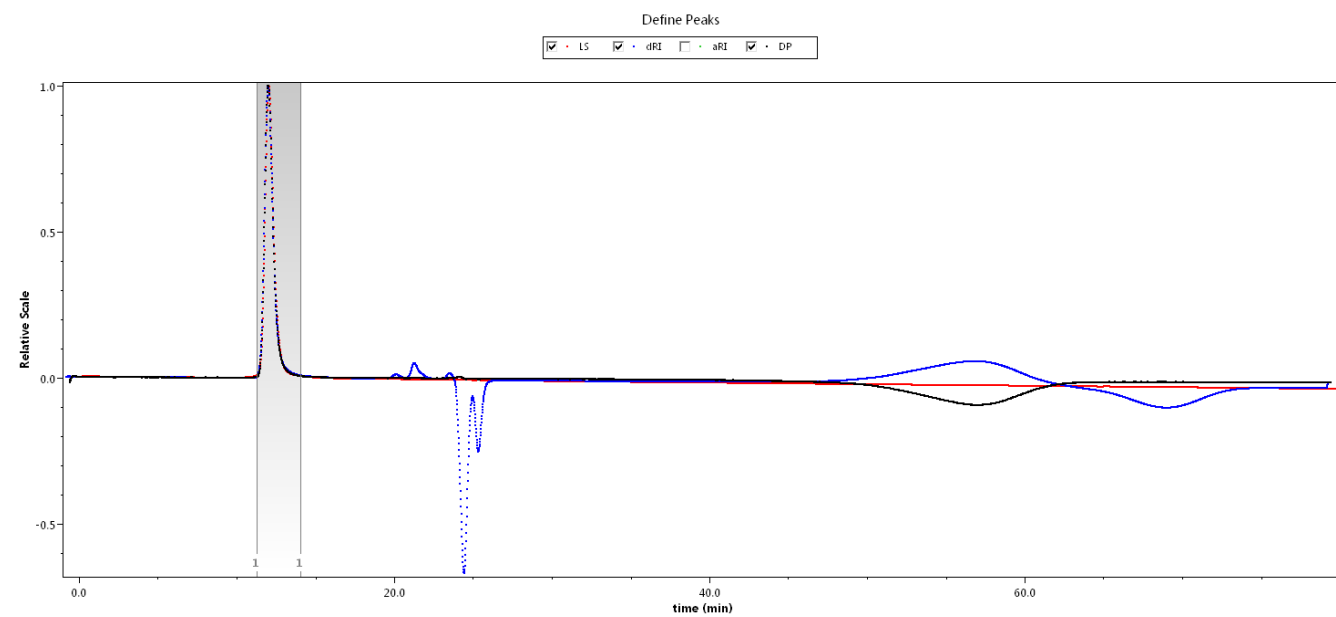


Figure S35. Table 2 entry 6

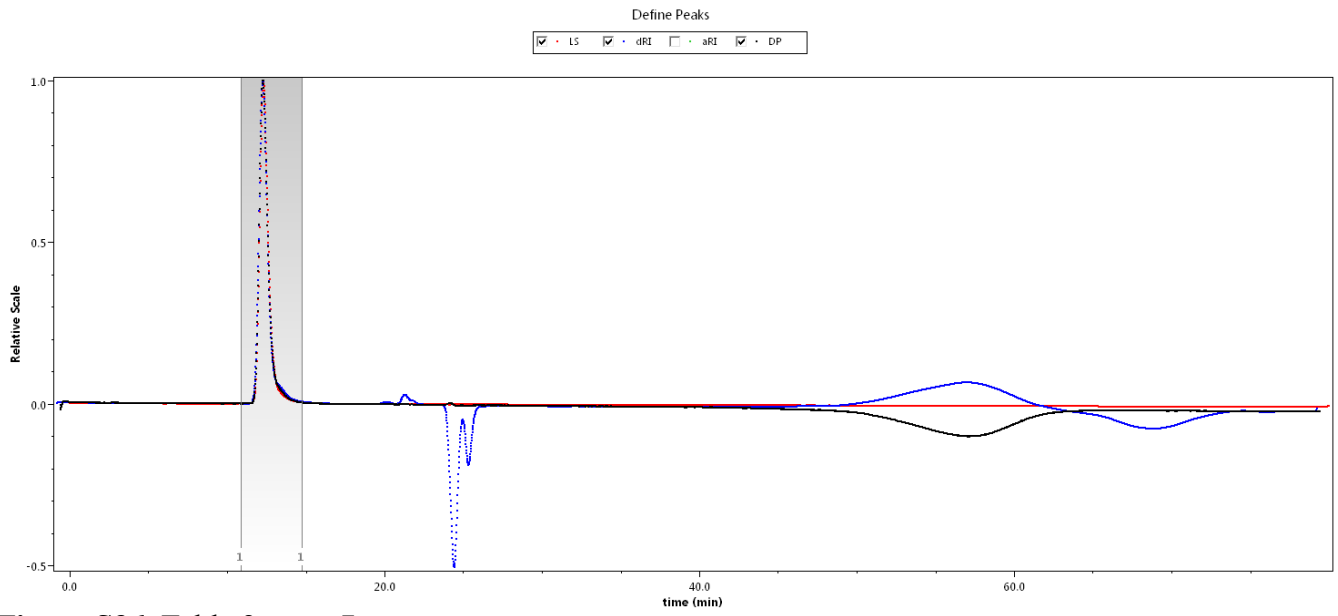


Figure S36. Table 2 entry 7

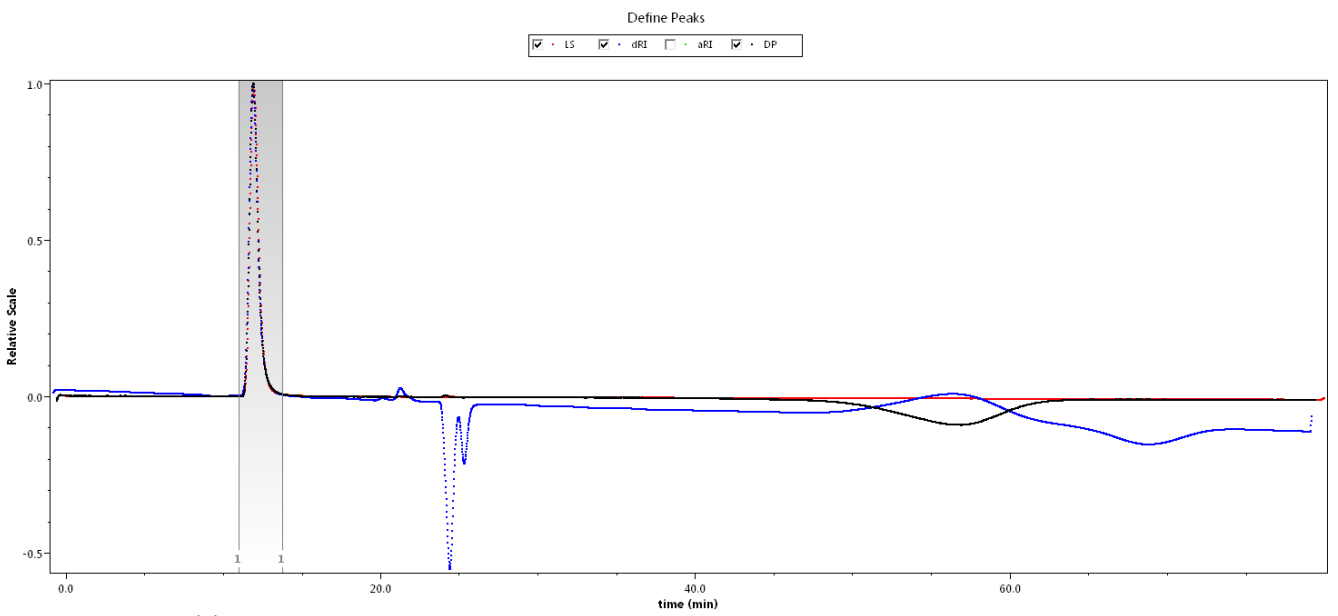


Figure S37. Table 2 entry 8

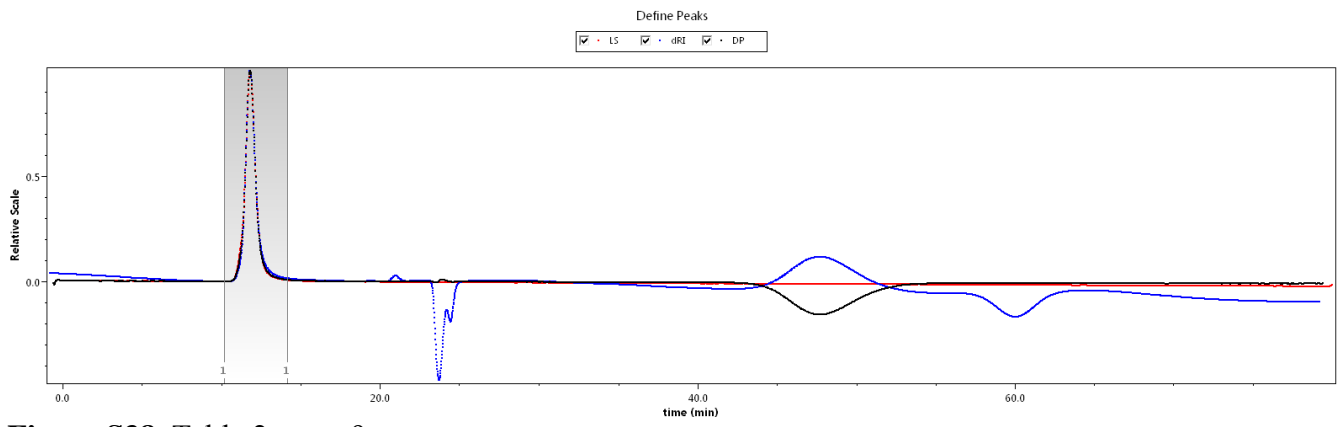


Figure S38. Table 2 entry 9

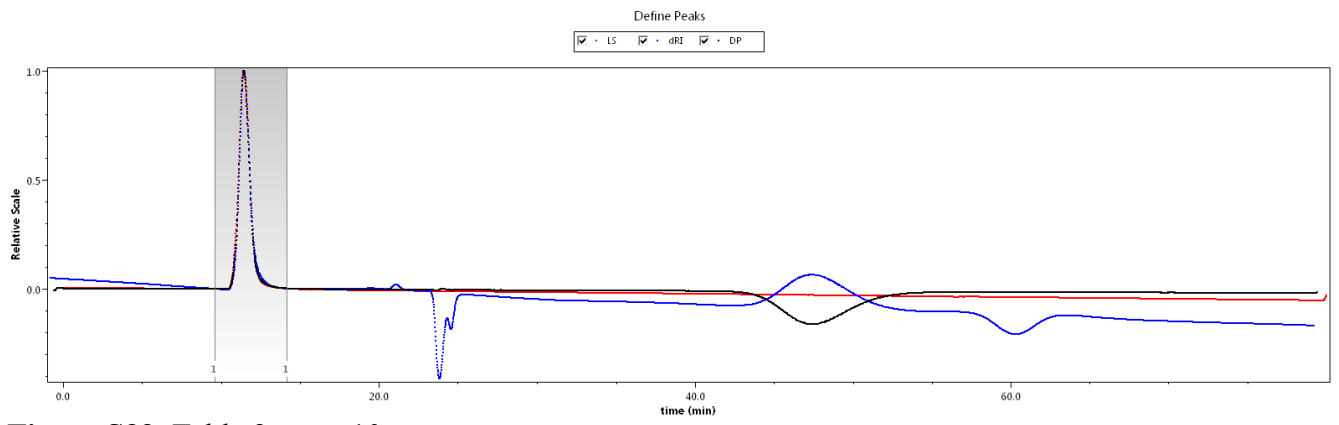


Figure S39. Table 2 entry 10

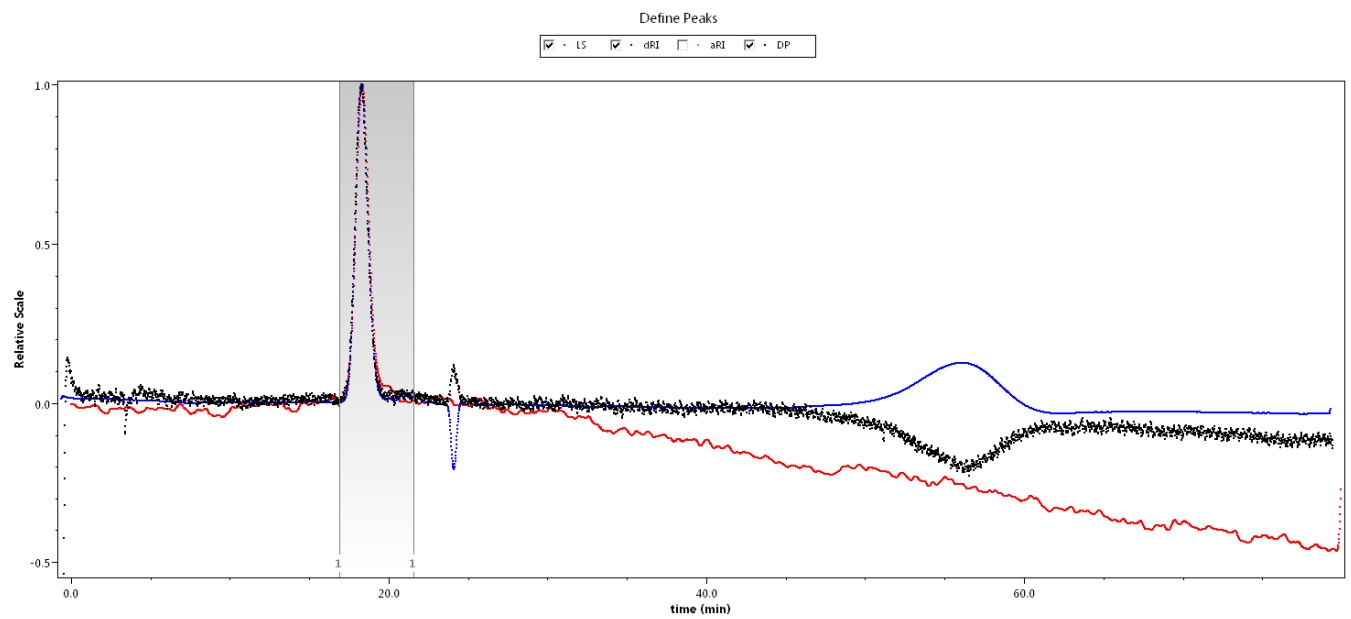


Figure S40. Table 3 entry 1

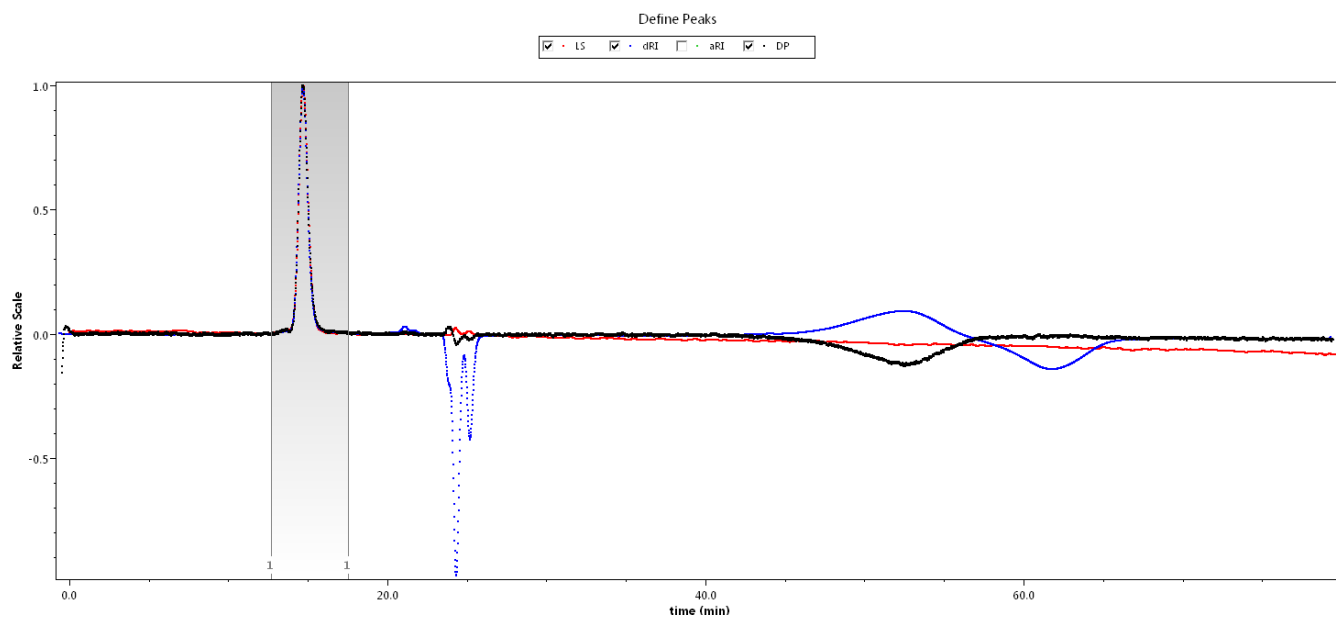


Figure S41. Table 3 entry 2

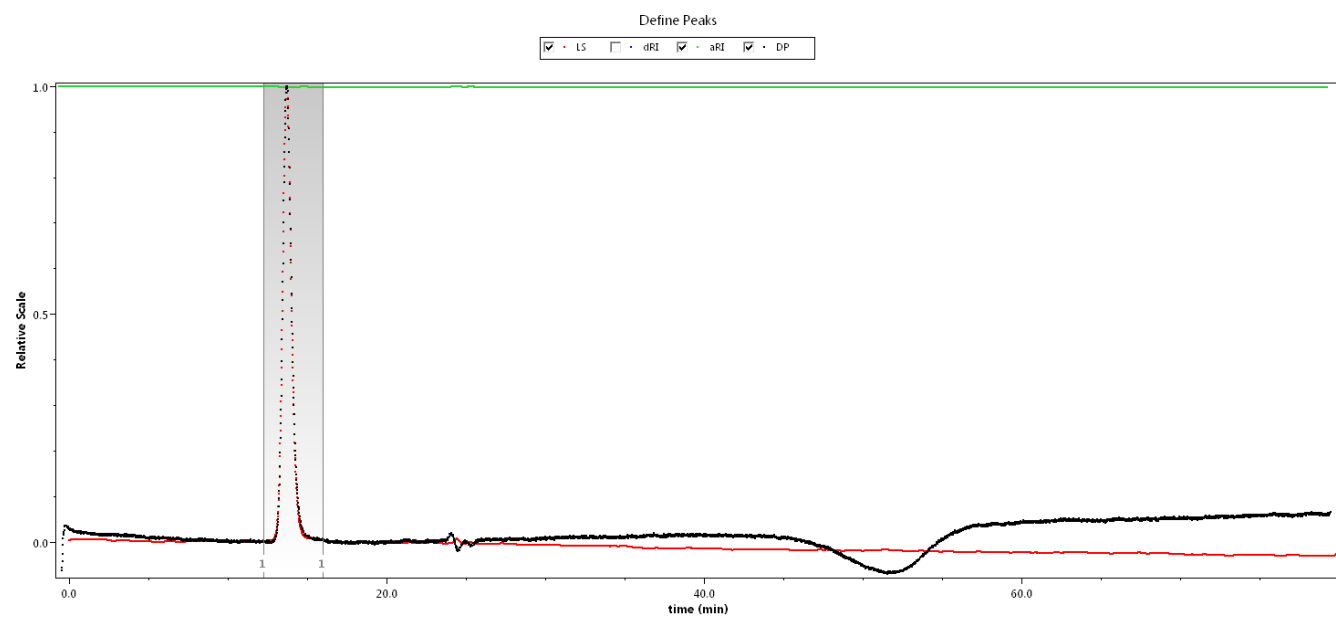


Figure S42. Table 3 entry 3

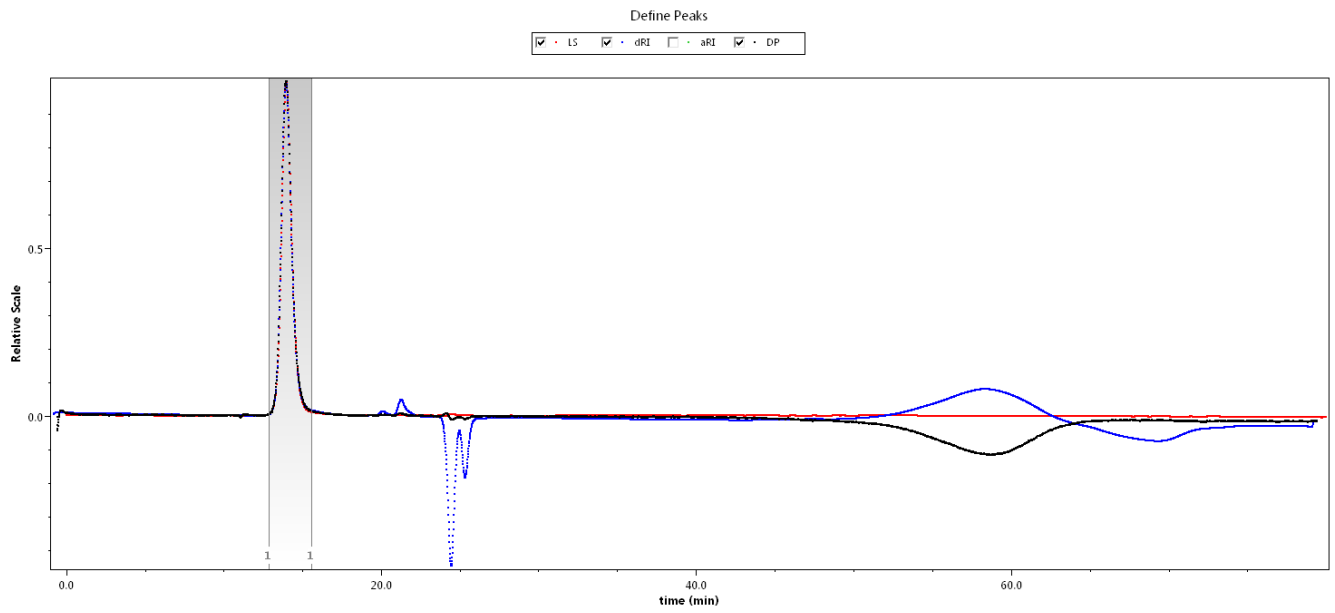


Figure S43. Table 3 entry 5

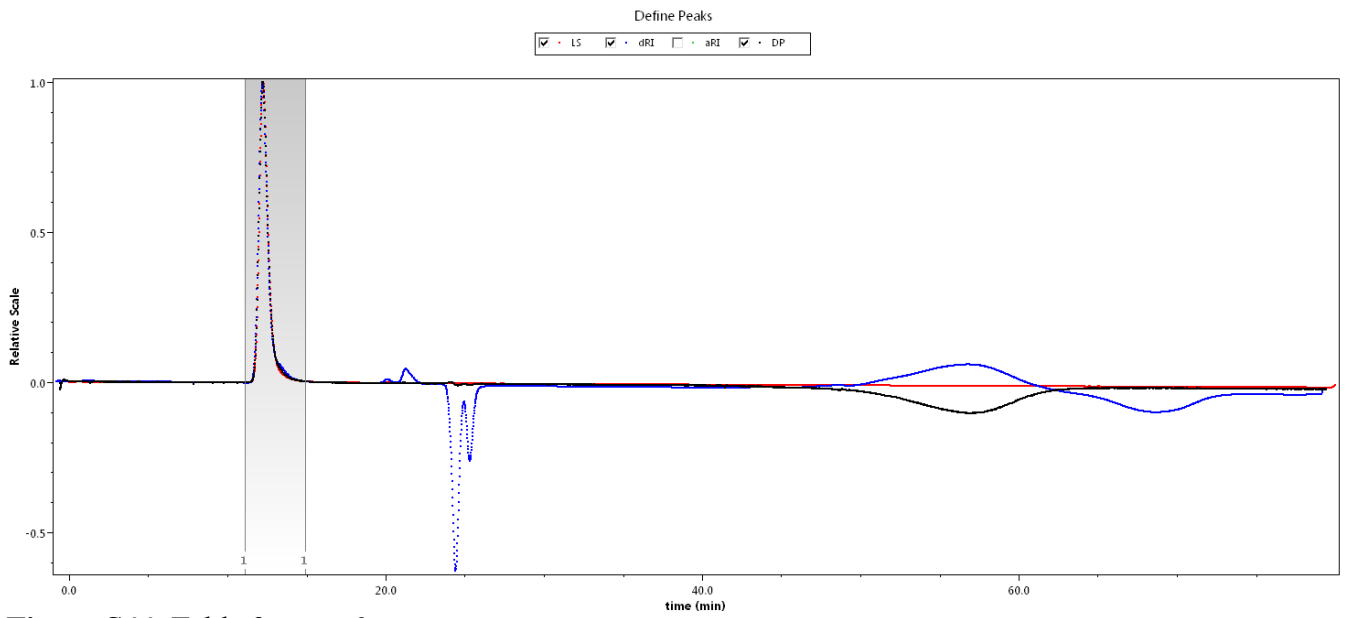


Figure S44. Table 3 entry 6

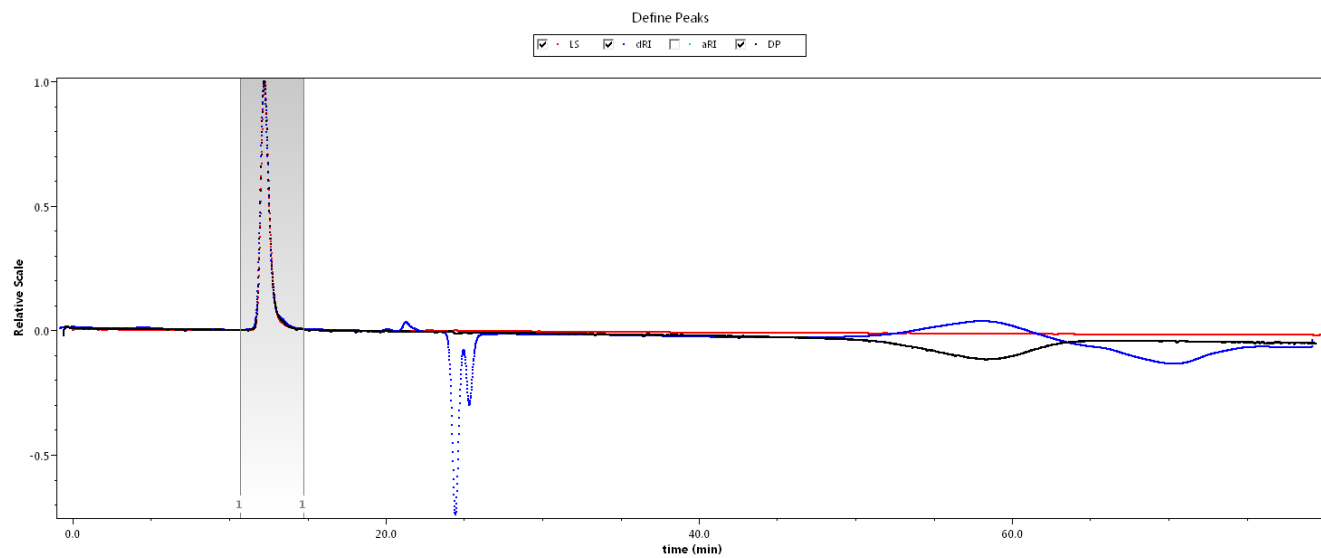


Figure S45. Table 3 entry 7

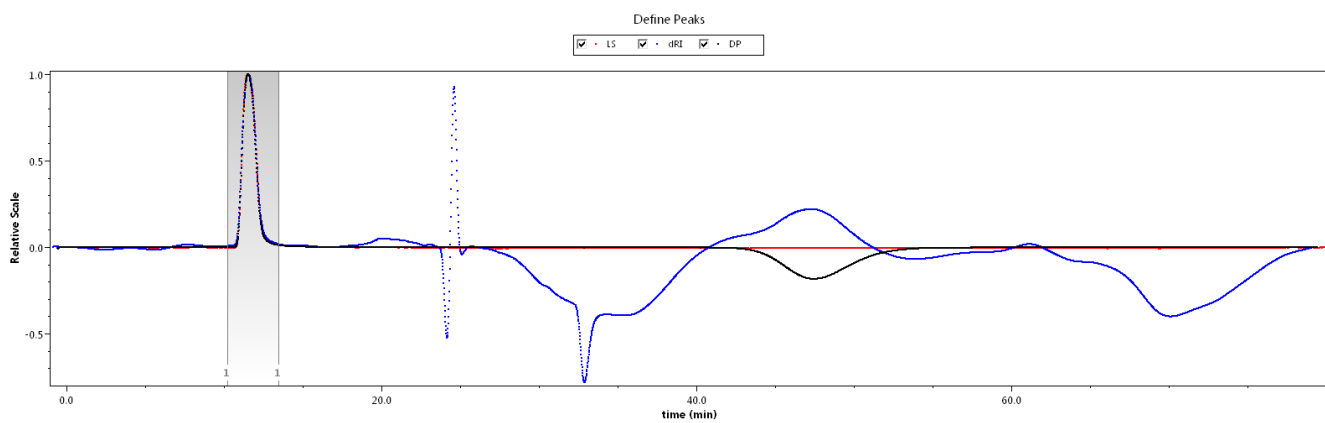


Figure S46. Table 3 entry 8

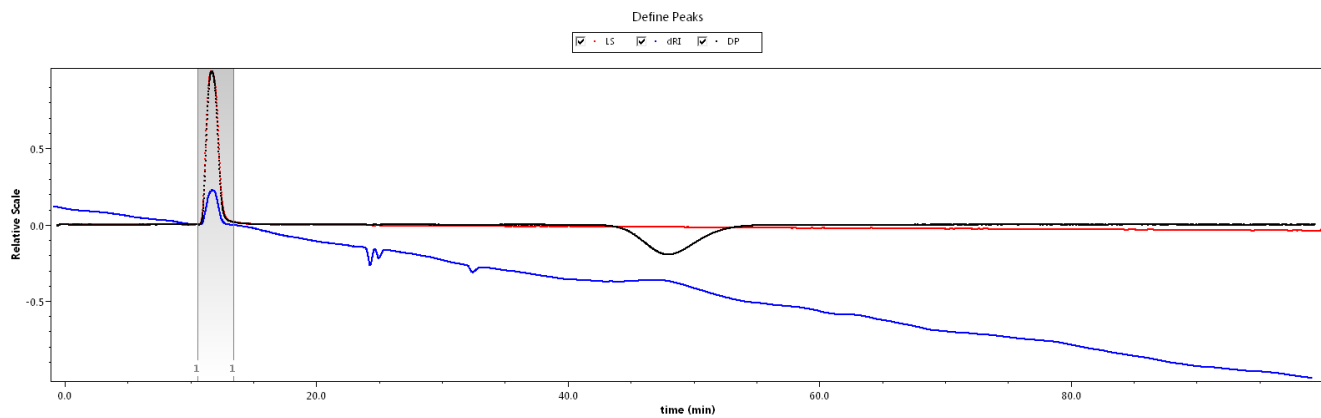


Figure S47. Table 3 entry 9

Part E: GPC traces of entry 1, Table 2, a polydispers PHB, and Polystyrene Standard

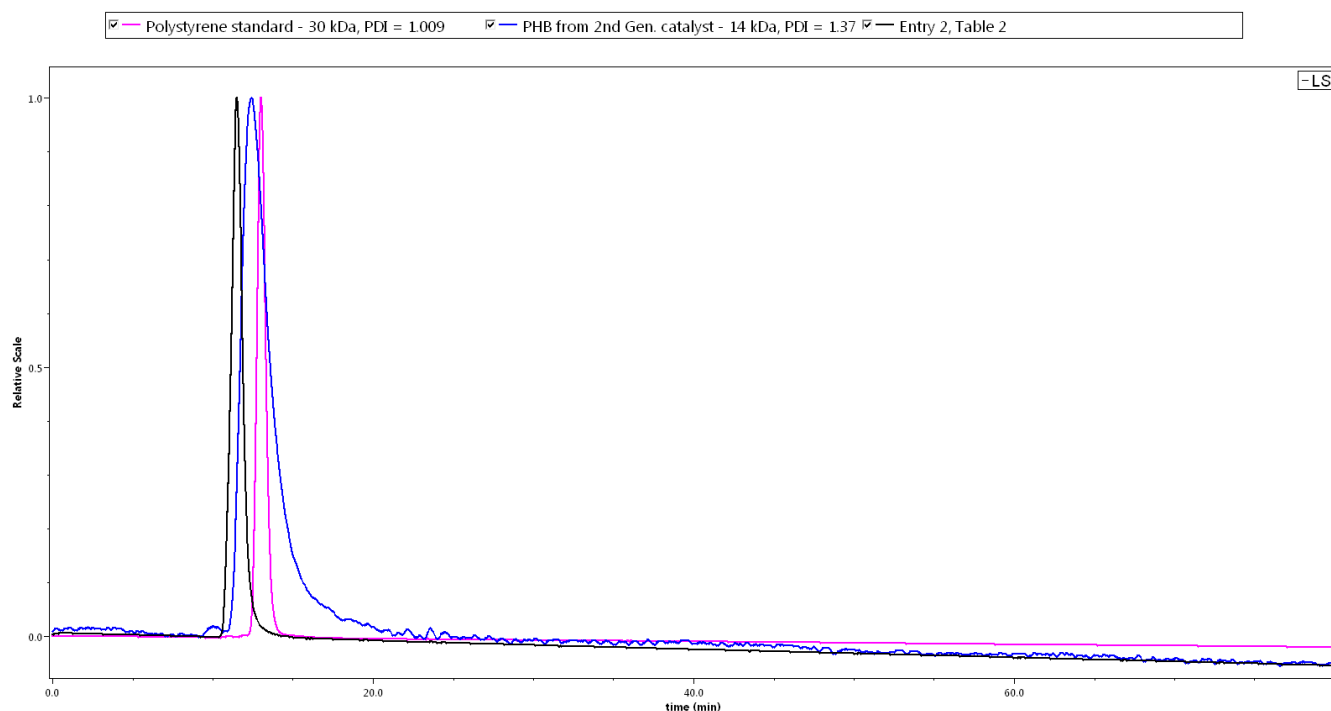


Figure S48. Overlaid GPC traces of right, polydispers PHB sample ($M_n = 14$ kDa, PDI = 1.37), middle, Polystyrene standard ($M_n = 30$ kDa, PDI = 1.00), left, Table 2, entry2 ($M_n = 107$ kDa, PDI = 1.02).

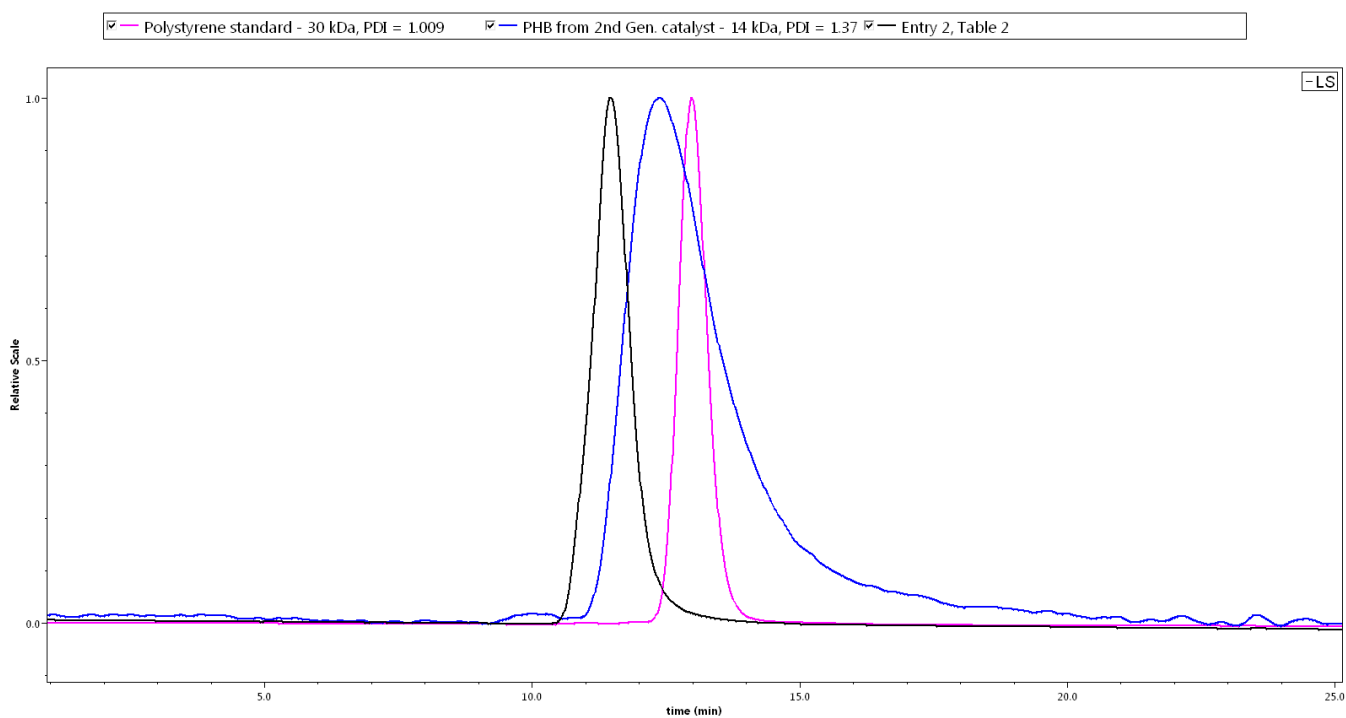


Figure S49. Overlaid GPC traces of right, polydispers PHB sample ($M_n = 14$ kDa, PDI = 1.37), middle, Polystyrene standard ($M_n = 30$ kDa, PDI = 1.00), left, Table 2, entry2 ($M_n = 107$ kDa, PDI = 1.02).

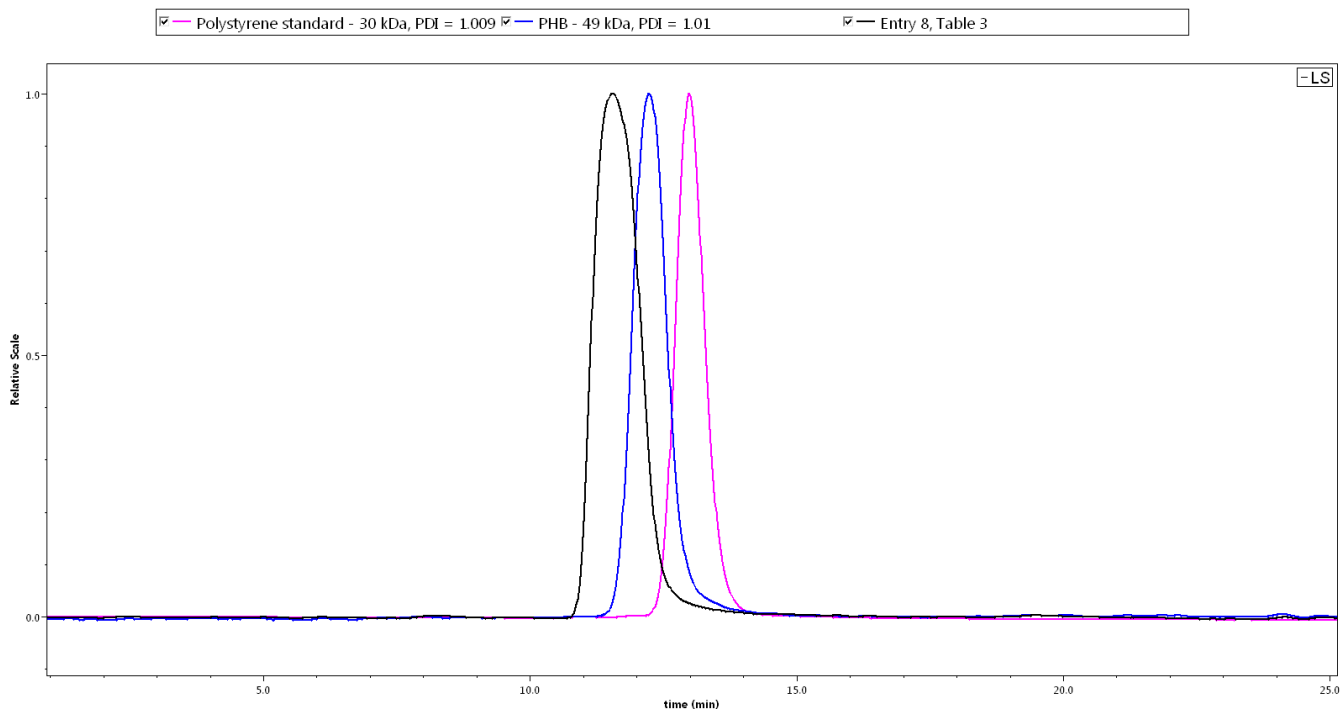


Figure S50. Overlaid GPC traces of 3 arm star block copolymers produced by consecutive additions of 625 equiv. of [BBL]:[THMB] and 373 equiv. of [L-LA]:[THMB] with complex **1** in THF at 25 °C. Right plot, Polystyrene standard ($M_n = 30$ kDa, PDI = 1.00), middle plot, 1st addition, ($M_n = 49$ kDa, PDI = 1.01) for BBL; left, 2nd addition, ($M_n = 103$ kDa, PDI = 1.01) for PHB-*b*-PLLA (Table 3 entry 8).

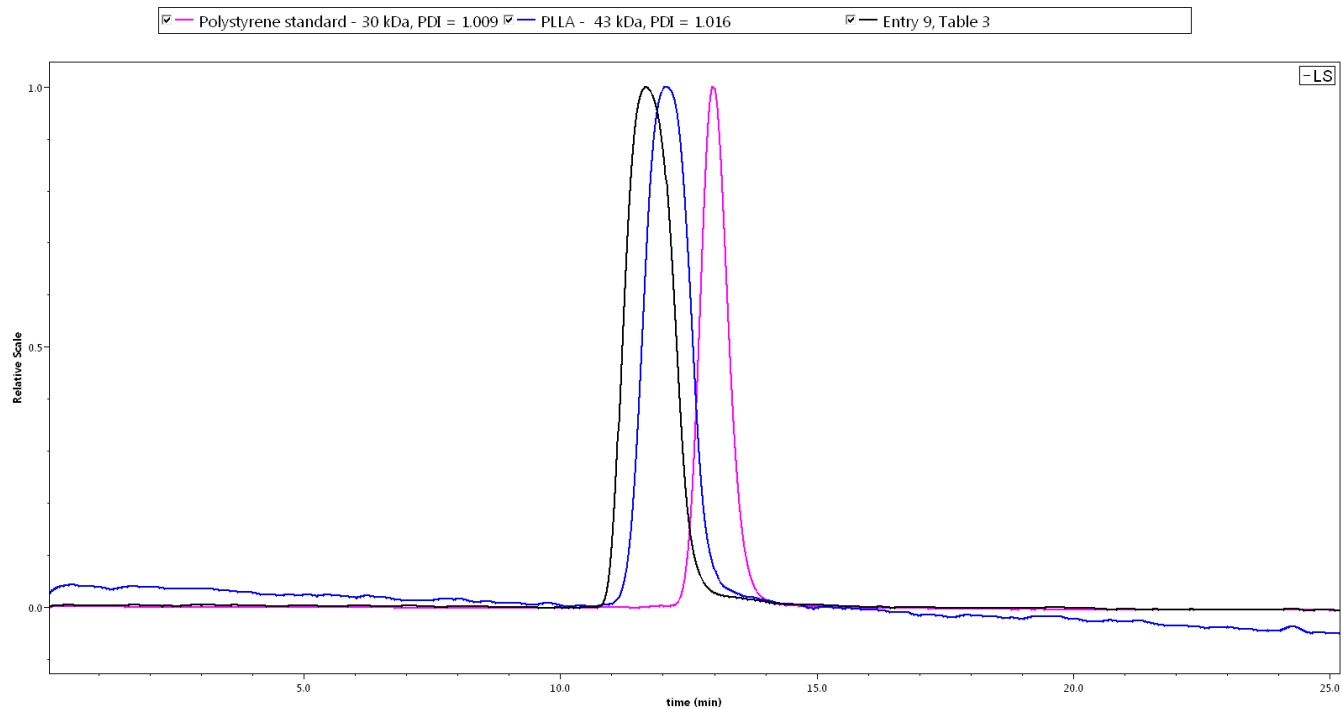


Figure S51. Overlaid GPC traces of 3 arm star block copolymers produced by consecutive additions of 373 equiv. of [L-LA]:[THMB] and 625 equiv. of [BBL]:[THMB] with complex **1** in THF at 25 °C. Right plot, Polystyrene standard ($M_n = 30$ kDa, PDI = 1.00), middle plot, 1st addition, ($M_n = 43$ kDa, PDI = 1.01) for LLA; left, 2nd addition, ($M_n = 96$ kDa, PDI = 1.01) for PLLA-*b*-PHB (Table 3 entry 9).

References:

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- (a) Acosta-Ramírez, A.; Douglas, A. F.; Yu, I.; Patrick, B. O.; Diaconescu, P. L.; Mehrkhodavandi, P., Synthesis and Structural Studies of Chiral Indium(III) Complexes Supported by Tridentate Diaminophenol Ligands. *Inorganic Chemistry* **2010**, *49* (12), 5444-5452; (b) Aluthge, D. C.; Patrick, B. O.; Mehrkhodavandi, P., A highly active and site selective indium catalyst for lactide polymerization. *Chemical Communications* **2013**, *49* (39), 4295-4297; (c) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P., A Highly Active Chiral Indium Catalyst for Living Lactide Polymerization. *Angewandte Chemie International Edition* **2008**, *47* (12), 2290-2293; (d) Imran ul-haq, M.; Acosta-Ramírez, A.; Mehrkhodavandi, P.; Signorell, R., Influence of polydispersity of poly(lactic acid) on particle formation by rapid expansion of supercritical CO₂ solutions. *The Journal of Supercritical Fluids* **2010**, *51* (3), 376-383; (e) Labourdette, G.; Lee, D. J.; Patrick, B. O.; Ezhova, M. B.; Mehrkhodavandi, P., Unusually Stable Chiral Ethyl Zinc Complexes: Reactivity and Polymerization of Lactide. *Organometallics* **2009**, *28* (5), 1309-1319; (f) Osten, K. M.; Yu, I.; Duffy, I. R.; Lagaditis, P. O.; Yu, J. C. C.; Wallis, C. J.; Mehrkhodavandi, P., Effects of ligand tuning on dinuclear indium catalysts for lactide polymerization. *Dalton Transactions* **2012**, *41* (26), 8123-8134; (g) Yu, I.; Acosta-Ramírez, A.; Mehrkhodavandi, P., Mechanism of Living Lactide Polymerization by Dinuclear Indium Catalysts and Its Impact on Isoselectivity. *Journal of the American Chemical Society* **2012**, *134* (30), 12758-12773.
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