Supporting Information

"Soluble Polymer-Supported Hindered Phosphine Ligands for Palladium-Catalyzed Aryl Amination"

Tatyana V. Khamatnurova, Dongmei Zhang, Jakkrit Suriboot, Hassan S. Bazzi, and David E. Bergbreiter

General Procedures

All reagents and solvents were obtained from commercial sources and used without further purification. PIB derivatives were prepared from commercially available Glissopal 2300[1] using procedures previously reported in the literature.[2] The ^{1}H, ^{13}C and ^{31}P NMR spectra of the products of the catalytic reactions were identical to those in literature. ^{1}H NMR spectra were recorded using an Inova NMR spectrometer operating at 299.91 MHz. ^{13}C NMR spectra were recorded using an Inova NMR spectrometer operating at 75.41 MHz. ^{31}P NMR spectra were recorded using an Inova NMR spectrometer operating at 121.42 MHz using 85% H_2PO_4 as the standard. Chemical shifts are reported in parts per million (δ) relative to residual proton resonances in deuterated chloroform ($CDCl_3$). Coupling constants (*J* values) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplet). Copolymers were analyzed by gel permeation chromatography in THF using a Viscotek I-MBMMW-3078 mixed bed column at 30 °C. The Viscotek instrument was equipped with a VE-3210 UV-visible detector, a 270 dual detector and a VE-3580 RI detector. The polymer molecular weights were calculated using OmniSEC software (v.4.6.1) and were based on polystyrene standards. ICP-MS analysis was conducted using an NexION 300D ICP-MS spectrometer.

4-Dodecylstyrene Synthesis. 4-Dodecylstyrene (**2**) was prepared from the appropriate alkylbenzene using the sequence of reactions reported by Overberger involving Friedel-Crafts acylation, reduction and dehydration with minor modifications.[3-5] The final product dodecylstyrene was routinely prepared on a multigram scale and were purified by a silica column chromatography (hexanes). 4-Dodecylstyrene (4.92

g, 75% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.5 Hz, 3H), 1.20-1.35 (br m, 18H), 1.58 (m, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 5.18 (d, J = 11 HZ, 1H), 5.69 (d, *J* = 17 Hz, 1H), 6.68 (dd, *J* = 11 Hz and 17Hz, 1H), 7.13(d, *J* = 8.3 Hz, 2H), 7.32(d, *J* = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, multiple peaks between 29.3 and 29.8, 31.5, 32.0, 35.8, 112.7, 126.1, 128.4, 135.1, 1, 136.8, 142.7.

2-Dicyclohexylphosphino-2′-hydroxybiphenyl (9). Magnesium shavings (0.420 g, 17.2 mg atom) were added to a 100-mL round-bottomed flask. Then, tetrahydrofuran (10 mL), 2-methoxyphenylmagnesium bromide (19 mL of a 1.0 M solution in THF) and 1-bromo-2-chlorobenzene (2 mL, 17.2 mmol) were added sequentially to the reaction mixture. The reaction mixture was allowed to reflux for 2.5 h. At that point, the reaction mixture was cooled to room temperature. Copper(I) chloride (2 g, 20.2 mmol) and then chlorodicyclohexylphosphine (4.5 mL, 20.1 mmol) were added to the reaction mixture. After 16 h of stirring at room temperature, 10 mL of saturated aqueous ammonium hydroxide was added and the reaction mixture was stirred for an additional 2 h. Then, the reaction mixture was transferred to the separatory funnel along with 100 mL of diethyl ether and 100 mL of saturated aqueous ammonium hydroxide was added. The organic phase was separated and combined with a 50 mL diethyl ether extract of the aqueous layer. The organic layers were washed with a saturated ammonium hydroxide (2 x 100 mL), dried over sodium sulfate, and the solvent was removed under reduced pressure to give a white residue. Recrystallization of this residue in methanol afforded the methyl ether of 9 as white crystals in 50% yield (3.3 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89-1.43 (m, 10H), 1.57-1.74 (m, 11H), 1.94 (m, 1H), 3.74 (s, 3H), 6.93 (d, 1H, *J* = 8.2 Hz), 6.99 (t, 1H, *J* = 7.4 Hz), 7.10 (dd, 1H, *J* = 7.3 Hz, 1.8 Hz), 7.23 (m, 1H), 7.337.45 (m, 3H), 7.60 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 26.6, 27.2-27.8 (4 resonances), 28.6 (d, J_{CP} = 6.9 Hz), 29.8 (d, J_{CP} = 12.8 Hz), 30.0 (d, J_{CP} = 18 Hz), 30.7 (d, J_{CP} = 18.3 Hz), 33.6 (d, J_{CP} = 15.9 Hz), 35.0 (d, J_{CP} = 16.2 Hz), 55.0, 110, 119.8, 126.5, 128.5 (d, J_{CP} = 1.2 Hz), 128.6, 130.2 (d, J_{CP} = 5.9 Hz), 131.8 (d, J_{CP} = 2.6 Hz), 131.9 (d, J_{CP} = 6.6 Hz), 134.4 (d, J_{CP} = 3.4 Hz), 135.4 (d, J_{CP} = 21.2 Hz), 146.9 (d, J_{CP} = 32.0 Hz),

156.4 (d, 1.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ -10.5. Next, a 50-mL round-bottomed two-necked flask was charged with a portion of this 2-dicyclohexylphosphino-2′-methoxybiphenyl product (1.0 g, 2.6 mmol) and 9 mL of dichloromethane. The resulting solution was cooled to -78 °C. Then a solution of boron tribromide in dichloromethane (5.2 mL of 1.0 M solution) was added dropwise over 5 min. The reaction mixture was stirred at -78 °C for 15 min. After this, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After 16 h of stirring, 3 mL of saturated aqueous sodium bicarbonate was added to the reaction mixture. The mixture was transferred to a separatory funnel and diluted with 100 mL of ethyl acetate. At this point, the mixture was washed with water (2 x 30 mL) and brine (30 mL). The organic layer was separated and dried over sodium sulfate. The solvent was removed under reduced pressure to give 0.7 g (72%) of **9** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89-1.43 (m, 10H), 1.46-1.94 (m, 11H), 2.11 (m, 1H), 5.14 (s, 1H), 6.98-7.08 (d, 2H), 7.11 (dd, 1H, J = 7.8, 1.8 Hz), 7.27-7.38 (m, 2H), 7.41-7.53 (m, 2H), 7.60-7.72 (m. 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 27.2-27.8 (5 resonances), 28.6, 29.8-30.0 (2 resonances), 30.5 (d, J_{CP} = 14 Hz), 32.4 (d, J_{CP} = 10.8 Hz), 35.2 (d, J_{CP} = 14.6 Hz), 116.7, 120.5, 127.5, 129.2, 129.4, 130.0 (d, J_{CP} = 6.2 Hz), 131.6 (d, J_{CP} = 6.0 Hz), 131.9 (d, J_{CP} = 1.9 Hz), 133.0 (d, J_{CP} = 2.6 Hz), 135.0 (d, J_{CP} = 20.1 Hz), 145.2 (d, J_{CP} = 30.7 Hz), 151.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ -9.31.

Synthesis of Poly(4-dodecylstyrene)-*co*-poly(*tert*-butylstyrene)-*co*-poly(2-dicyclohexylphosphino-2'-biphenyl) terpolymer (15) by a Williamson Ether Synthesis. 4-Dodecylstyrene (2.0 g, 7.35 mmol), *tert*-butylstyrene (4.5 g, 28.0 mmol) and 4-vinylbenzyl chloride (0.5 g, 3.30 mmol) that had been passed through an aluminum oxide plug to remove any inhibitor were dissolved in 2 mL of 2-butanone and added to a 50-mL Schlenk tube equipped with a stir bar. The RAFT reagent 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.1 g, 0.32 mmol) and AIBN (0.006 g, 0.037 mmol) were added to the flask and the resulting solution was subjected to 3 freeze-pump-thaw cycles. Then, the mixture was heated in oil bath at 80 °C for 48 h. After cooling, the product was dissolved in 3 mL of

chloroform and this solution was slowly added to excess MeOH (300 mL) to precipitate the desired polymer product in 70% yield (4.1 g). The ratio of monomers in the product was determined to be 11:2:1 based on ^{1}H NMR spectroscopic analysis integrating peaks at δ 2.47 (benzylic protons of the 4-dodecylstyrene) and δ 4.45 (benzylic protons of 4-vinylbenzyl chloride). The chloromethylated poly(4-dodecylstyrene)-*co*-poly(*tert*-butylstyrene) terpolymer was then allowed to react with 2-dicyclohexylphosphino-2᾽-hydroxybiphenyl under thermomorphic conditions in a mixture of DMF and heptane. In this reaction 2-dicyclohexylphosphino-2᾽-hydroxybiphenyl (0.08 g, 0.22 mmol) was dissolved in DMF (10 mL) and allowed to react with Cs_2CO_3 (0.07 g, 0.22 mmol) for 1 h. Then a 10 mL heptane solution of chloromethylated terpolymer (0.42 g, 0.21 mmol) was added via cannula dropwise. The reaction mixture was heated at 90 ^{o}C and was allowed to stir for 24 h. After the mixture was cooled to room temperature, the top heptane-rich layer was separated and washed 3 times with MeCN. The heptane phase was separated and the solvent was removed under reduced pressure to afford a solid that was redissolved in a minimum amount of CH_2Cl_2 and added to MeOH (50 mL) to precipitate the terpolymer **15** as a yellowish solid in 70% yield (0.34 g). The product polymer was analyzed by GPC and had a M_n of 8400 Da with a PDI of 1.2. The ratio of monomers in the product was determined to be 11:2:1 based on ^{1}H NMR spectroscopic analysis integrating peaks at δ 2.47 (benzylic protons of the 4-dodecylstyrene) and δ 4.95 (benzylic protons of 4-vinylbenzyl-2-dicyclohexylphosphino-2'-biphenyl). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (br t, 6H), 1.03-2.10 (br m, 203H), 2.47 (br s, 4H), 4.95 (br s, 2H), 6.06-7.22 (br m, 64H). ^{31}P NMR (121 MHz, $CDCl_3$) δ -11.1.

Synthesis of 4-vinylbenzyl-2-dicyclohexylphosphino-2´-biphenyl 14. A 50-ml round-bottomed two-necked flask was charged with 2-dicyclohexylphosphino-2'-methoxybiphenyl (0.7 g, 2.0 mmol), NaH (0.22 g, 5.2 mmol) and DMF (5.0 ml). The flask was sealed and the solution was degassed using 3 freeze-pump-thaw cycles. Another 50-ml round-bottomed two-necked flask was charged with 4-vinylbenzyl chloride (0.30 g, 2.0 mmol) and DMF (5.0 ml). The flask was also sealed and the solution

was degassed using 3 freeze-pump-thaw cycles. At this point, the solution containing 4-vinylbenzylchloride in DMF was transferred via cannula to a solution containing solution 2-dicyclohexylphosphino-2᾽-hydroxybiphenyl ligand, NaH and DMF. The reaction was allowed to stir for 16h, after which the solvent was removed under reduced pressure. The residue was redissolved in ethyl acetate (30 ml) and washed with water (3 X 20 ml). The organic layer was separated and dried over sodium sulfate. The solvent was removed under reduced pressure to give viscous oil in 84 % yield (0.8 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89-1.43 (m, 11H), 1.46-1.94 (m, 11H), 4.94 (d, 2H, J = 10.0 Hz), 5.11 (d, 1H, J = 11.0 Hz), 5.63 (d, 1H, J = 17.0 Hz), 6.70 (dd, 1H, J = 11.0, 17.0 Hz), 7.01 (m, 2H), 7.17 (m, 3H), 7.33 (m, 3H), 7.42 (m, 3H), 7.61 (m. 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 26.6, 27.2-27.8 (4 resonances), 28.6 (d, J_{CP} = 6.9 Hz), 29.8 (d, J_{CP} = 12.8 Hz), 30.0 (d, J_{CP} = 18 Hz), 30.7 (d, J_{CP} = 18.3 Hz), 33.6 (d, J_{CP} = 15.9 Hz), 35.0 (d, J_{CP} = 16.2 Hz), 55.0, 69.3, 110, 112.2, 113.5, 119.8, 126.1, 126.5, 128.5 (d, J_{CP} = 1.2 Hz), 128.6, 130.2 (d, J_{CP} = 5.9 Hz), 131.8 (d, J_{CP} = 2.6 Hz), 131.9 (d, J_{CP} = 6.6 Hz), 134.4 (d, J_{CP} = 3.4 Hz), 135.4 (d, J_{CP} = 21.2 Hz), 136.4, 136.6, 137.1, 146.9 (d, J_{CP} = 32.0 Hz), 156.4 (d, 1.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ -11.2.

Synthesis of Poly(4-dodecylstyrene)-*co*-poly(*tert*-butylstyrene)-*co*-poly(2-dicyclohexylphosphino-2'-biphenyl diphenyl) terpolymer (15) by RAFT Copolymerization. 4-Dodecylstyrene (0.14 g, 0.51 mmol), *tert*-butylstyrene (0.33 g, 2.1 mmol) and 4-vinylbenzyl-2-dicyclohexyl-phosphino-2´-biphenyl **14** (0.13 g, 0.26 mmol) were dissolved in 1 mL of 2-butanone and added to a 10-mL Schlenk tube equipped with a stir bar. RAFT reagent 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.007 g, 0.025 mmol) and AIBN (0.0005 g, 0.0030 mmol) were added to the flask and the resulting solution was subjected to 3 freeze-pump-thaw cycles. Then, the mixture was heated in oil bath at 80 ^{o}C for 24 h. After cooling, the product was dissolved in 1 mL of chloroform and this solution was slowly added to excess MeOH (30 mL) to precipitate the desired polymer product in 72% yield (0.44 g). The product polymer **15** was analyzed by GPC and had a M_n of 9000 Da with a PDI of 1.2. The ratio of monomers

in the product was determined to be 11:1:1 based on NMR analysis integrating peaks at δ 2.47 (benzylic protons of the 4dodecylstyrene) and δ 4.95 (benzylic protons of 4-vinylbenzyl-2-dicyclohexylphosphino-2′-biphenyl). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91(br t, 3H), 1.03-2.10 (br m, 176H), 2.47 (br s, 2H), 4.95 (br s, 2H), 6.06-7.22 (br m, 68H). ^{31}P NMR (121 MHz, $CDCl_3$) δ -11.1.

Buchwald-Hartwig Aminations with Catalyst 16.

***N*-Phenylmorpholine**. The polymer supported ligand **15** prepared by either a Williamson ether synthesis or by terpolymerization (0.04 mequiv) was dissolved in 2 mL of heptane and added to a 10-mL centrifuge tube with a stir bar to which $Pd(dba)_2$ (0.006 g, 0.01 mmol) was added. The centrifuge tube was sealed and the solution was degassed using 3 freeze-pump-thaw cycles. After warming to room temperature, the solution of the ligand **15** and $Pd(dba)_2$ was allowed to continue to stir for 30 min at 60 °C. At this point, the catalyst **16** was transferred by forced siphon to another 10-mL centrifuge tube containing previously degassed bromobenzene (0.16 g, 1.0 mmol), morpholine (0.12 g, 1.4 mmol), and KO-*tert*-Bu (0.17 g, 1.5 mmol). This reaction mixture was then heated at 90 °C for ca. 20 h. After the reaction was complete, degassed MeOH (2 mL) was added to the centrifuge tube and the mixture was centrifuged for 5 min. At this point, the MeOH phase containing products was separated and the heptane phase containing the catalyst **16** was transferred to a test tube containing fresh substrates for a subsequent reaction cycle. A portion of the product methanol solution from cycle 3 was digested in acid and analyzed by ICP-MS which showed 6.8 ppm, or 2.8 ppm Pd contamination for the reaction of morpholine with bromobenzene or chlorobenzene, respectively. The MeOH phases for five reactions were combined and the MeOH was removed under reduced pressure to afford *N*-phenylmorpholine product which was isolated after a column chromatography. A total of 4.1 mmol of *N*-phenylmorpholine was isolated corresponding to an average isolated yield of 82 % per cycle. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.20 (t, 4H, J = 4.5 Hz), 3.90 (t, 4H, J = 4.5 Hz), 6.95 (m, 3H), 7.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.5, 66.9, 115.6, 120.0, 129.5, 151.2.

***N*-Methyl-*N*-phenylaniline.** The polymer supported phosphine **15** (0.04 mequiv) was dissolved in 2 mL of heptane and added to a 10-mL centrifuge tube with a stir bar to which $Pd(dba)_2$ (0.006 g, 0.01 mmol) was added. The test tube was sealed and the solution was degassed using 3 freeze-pump-thaw cycles. After warming to room temperature, the solution of the ligand **15** and $Pd(dba)_2$ was allowed to continue to stir for 30 min at 60 °C. At this point, the catalyst **16** was transferred by forced siphon to another 10-mL centrifuge tube containing previously degassed bromobenzene (0.16 g, 1.0 mmol), morpholine (0.12 g, 1.4 mmol), KO-*tert*-Bu (0.17 g, 1.5 mmol). This reaction mixture was then heated at 90 °C for ca. 20 h. After the reaction was complete, degassed MeOH (2 mL) was added to the centrifuge tube and the mixture was centrifuged for 5 min. At this point, the MeOH phase containing products was separated and the heptane phase containing the catalyst **16** was transferred to a test tube containing fresh substrates for a subsequent reaction cycle. A small portion of the product methanol solution from cycle 3 was digested in acid and analyzed by ICP-MS which showed 3.0 ppm Pd contamination. The MeOH phases for five reactions were combined and the MeOH was removed under reduced pressure to afford *N*-methyl-*N*-phenylaniline product which was isolated after a column chromatography. A total of 4.25 mmol of *N*-methyl-*N*-phenylaniline was isolated corresponding to an average isolated yield of 85 % per cycle. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (s, 3H), 6.99 (td, 2H, J = 8.0, 2.0 Hz), 7.07 (d, 4H, J = 8.0 Hz), 7.32 (t, 4H, J = 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.5, 120.7, 121.6, 129.3, 149.0.

Synthesis of Polyisobutylene-bound 2-Dicyclohexylphosphino-2'-oxybiphenyl 21. A 100-mL round-bottomed flask was charged with 2-dicyclohexylphosphino-2'-hydroxybiphenyl **(**0.66 g, 1.80 mmol), polyisobutyl bromide (4.32 g, 1.80 mmol) and Cs_2CO_3 (1.17 g, 3.60 mmol). 25 mL of DMF, and 25 mL of heptane (25 mL). This reaction mixture was degassed using three freeze-pump-thaw cycles. Then the reaction mixture was heated to 100 ^{o}C for 24 h to form a monophasic reaction mixture. After cooling to room temperature a biphasic mixture formed. An additional 25 mL of hexanes was added and the alkane

phase was separated. After washing with water (2 x 50 mL), 90% aqueous ethanol (50 mL), and acetonitrile (2 x 50 mL the alkane phase was dried ($MgSO_4$) and concentrated under reduced pressure to yield a colorless oil which was then purified by column chromatography using hexanes and then a hexanes/EtOAc (80:1) mobile phase. After solvent removal, 2.70 g (56%) of product **21** was obtained as a mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2 H), 7.37-7.20 (m, 8 H), 7.12 (d, J = 7.3 Hz, 2 H), 6.96 (t, J = 7.2 Hz, 2 H), 6.90 (t, J = 8.3 Hz, 2 H), 3.79 (dd, J = 8.0, 4.5 Hz, 1 H), 3.66-3.56 (m, 2 H), 3.45 (t, J = 8.5 Hz, 1 H), 1.94-1.84 (m, 2 H), 1.84-1.50 (m, 20 H), 1.50-0.74 (m, 662 H) ^{13}C NMR (125 MHz, $CDCl_3$) (verified by P-decoupled ^{13}C NMR) δ 156.3, 156.2, 147.0 (d, J_{CP} = 30.5 Hz), 134.9 (d, J_{CP} = 18.2 Hz), 132.6 (d, J_{CP} = 3.5 Hz), 132.4 (d, J_{CP} = 3.5 Hz), 132.3 (d, J_{CP} = 3.3 Hz), 132.0 (d, J_{CP} = 6.6 Hz), 131.9 (d, J_{CP} = 6.6 Hz), 130.8 (d, J_{CP} = 5.4 Hz), 128.4, 127.7, 127.6, 126.2, 119.2, 119.1, 111.5, 111.1, 74.3, 74.0, 59.5, 59.4, 59.2, 58.8, 58.2, 57.3, 57.2, 49.6, 49.5, multiple peaks between 38.4 and 37.6, 36.1, 35.7 (d, J_{CP} = 5.3 Hz), multiple peaks between 34.8 and 28.6, multiple peaks between 27.7 and 27.1, 26.5, 20.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ – 10.9, -11.0.

Procedure for Amination Reactions and Catalyst Recycling with Methanol as Product Extractant using 22 as a Catalyst. An oven dried centrifuge tube was charged with $Pd(dba)_2$ (8.62, mg, 0.015 mmol), potassium *t*-butoxide (0.168 g, 1.5 mmol), PIB bound ligand **21** (0.160 g, 0.06 mmol) and 3 mL of heptane. The centrifuge tube was sealed with a rubber septum and degassed with three freeze-pump-thaw cycles. Then the mixture was heated to 85 ˚C and stirred for 1.5 h. After cooling this mixture to room temperature, 1 mmol of a degassed mixture of 1 mmol of the aryl halide and 1.4 mmol of the amine were added via syringe into the reaction vessel. The reaction mixture was then heated to 85 ˚C for the indicated period of time and cooled to room temperature. After the reaction was complete, 2 mL of heptane-saturated degassed methanol was added to the sealed vessel which was then centrifuged for 5 min. The top layer was transferred via forced siphon to a new centrifuge tube containing degassed heptane and a fresh portion of potassium t-butoxide. New substrates were added via syringe and another reaction

cycle was carried out as described above. After all the cycles were complete, the heptane layer was extracted one more time with methanol (4 mL) and the methanol phase from all cycles was combined. Solvent was removed and diethyl ether (50 mL) was added. The organic solution was washed with $NaHCO_3$ (3 x 50 mL), brine (50 mL) and dried over $MgSO_4$. Solvent was removed under reduced pressure to afford the amination product. *N*-Phenyl morpholine was obtained as tan solid without further purification by recrystallizatoin. *N*-Methyl-*N*-phenyl aniline was an oil that purified with column chromatography. The products were characterized by ^{1}H and ^{13}C NMR spectroscopy and the spectra are in accordance with literature.

Procedure for Amination Reactions and Catalyst Recycling using Sulfonic Acid Ion Exchange Resin to Separate Products from a Solution of Catalyst 22. The amination reaction was carried out as described above with the difference that at the end of the reaction, the reaction mixture was transferred by forced siphon into a sealed centrifuge tube containing a suspension of 1.5 g of Amberlyst 15 in degassed heptane. The resulting suspension was shaken for 7 min and the supernatent was transferred to a new sealed vessel containing potassium t-butoxide and a minimum amount of degassed heptane. New substrates were added via syringe and a subsequent cycle was carried out as described above. After all the cycles were complete, the Amberlyst resin sequestrant from each cycle was combined and extracted with 20 mL of 4 M solution of ammonia in methanol. After gentle shaking for 50 min, the solids were removed by filtration and the solvent was evaporated. The mixture was filtered to remove the resin and solvent was evaporated. The residue was dissolved in 50 mL of diethyl ether, this ether solution was washed with $NaHCO_3$ (3 x 50 mL), brine (50 mL) and dried over $MgSO_4$. The ether was then removed to afford the amination products as described above.

General Procedure for Pd Leaching Analysis and Calculations. The sample to be analyzed and 4 g of concentrated nitric acid were added to a glass vial and the mixture was heated to 120 ^{o}C until the sample was dissolved. Then the solution was cooled to room temperature and 4 g of concentrated

sulfuric acid was added. The mixture was heated to 120 ^{o}C for 48 h. The solution was then allowed to cool to room temperature. At this point, the concentrated acid solution was diluted with 1% nitric acid solution and the diluted sample was analyzed by ICP-MS.

Pd leaching calculations for reactions catalyzed by catalyst 16. In the case of the poly(4-alkylstyrene) catalyst **16**, 1 mmol scale reactions afforded ca. 82% product in cycle 3 with PhBr using 1 mol% catalyst. That product contained 6.8 ppm of Pd in 0.82 mmol of N-phenylmorpholine (0.133 g/0.82 mmol) in cycle 3 of the PhBr/morpholine reaction;

$(6.8 \times 10^{-6}$ g of Pd/g of product)*(0.133 g of product) = 0.9×10^{-6} g of Pd

Started with 1 mol% of Pd catalyst or 0.01 mmol of Pd (0.106/mmol or 0.00106 g for 0.01 mmol)

$100 * (0.9 \times 10^{-6}$ g of Pd/1.06×10^{-3} g of starting Pd) = 0.08 % leaching

Using cycle 3 data for PhCl/morpholine, analysis showed that there was 2.8 ppm Pd leachant in 0.155 g of the product (0.95 mmol with 0.163 g/mmol) which corresponds to 0.04% leaching;

$(2.8 \times 10^{-6}$ g of Pd/g of product)*(0.154 g of product) = 0.43×10^{-6} g of Pd

$100 * (0.43 \times 10^{-6}$ g of Pd/1.06×10^{-3} g of starting Pd) = 0.04 % leaching

For PhBr and N-methylaniline, there was 0.155 g of product that contained 3.0 ppm Pd leachant which corresponds to 0.04% Pd leaching;

$(3 \times 10^{-6}$ g of Pd/g of product)*(0.155 g of product) = 0.47×10^{-6} g of Pd

$100 * (0.47 \times 10^{-6}$ g of Pd/1.06×10^{-3} g of starting Pd) = 0.04 % leaching

Leaching calculations for reactions using the PIB catalyst 22

1 mmol scale reactions using 1.5 mol% catalyst affording ca. 82% PhBr/morpholine, 84% PhBr/N-methylaniline, and 94% PhCl/morpholine. Pd content was measured for the first two reactions with 0.39 μg of Pd leachant in the total product phase of the first reaction and 1.75 μg of Pd leachant in the product phase of the second reaction

Started with 1.5 mol % of Pd catalyst or 0.015 mmol of Pd (0.159/mmol or 0.00159 g for 0.015 mmol)

100 * (1.75 x 10^{-6} g of Pd/1.59 x 10^{-3} g of starting Pd) = 0. 1 % leaching

Using the results for the morpholine/PhCl reaction, 0.39 □g of Pd was present as a leachant in the isolated product phase.

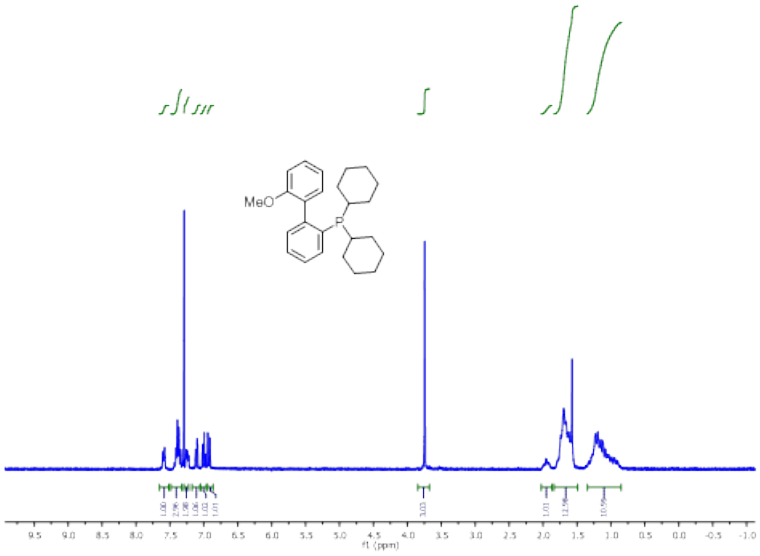
100 * (0.39 x 10^{-6} g of Pd/1.59 x 10^{-3} g of starting Pd) = 0.02 % leaching

References for Supporting Information

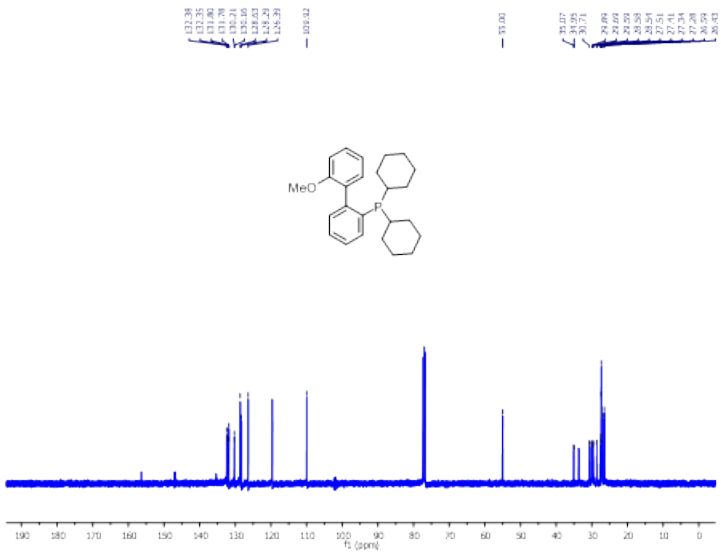
1. Glissopal is commercially available from BASF; http://www.performancechemicals.basf.com/ev/internet/polyisobutene/en/content/EV3/polyisobutene/glissopal [accessed November 12, 2014].
2. J. Li, S. Sung, J. Tian, D. E. Bergbreiter, *Tetrahedron* 2005, **61**, 12081.
3. C. G. Overberger, C. Frazier, J. Mandelman and H. F. Smith, *J. Am. Chem. Soc.* 1953, **75**, 3326.
4. T. V. Khamatnurova and D. E. Bergbreiter, *Polym. Chem.* 2013, **4**, 1617.
5. T. V. Khamatnurova, M. Johnson, D. Santana, H. S. Bazzi, and D. E. Bergbreiter, *Top. Catal*. 2014, **57**, 1438.

NMR Spectra

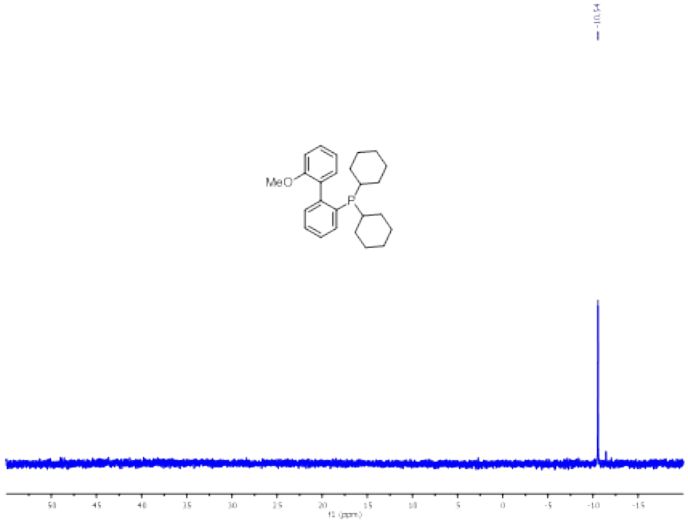
^{1}H NMR Spectrum of 2-Dicyclohexylphosphino-2'-methoxybiphenyl


MeO
P
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

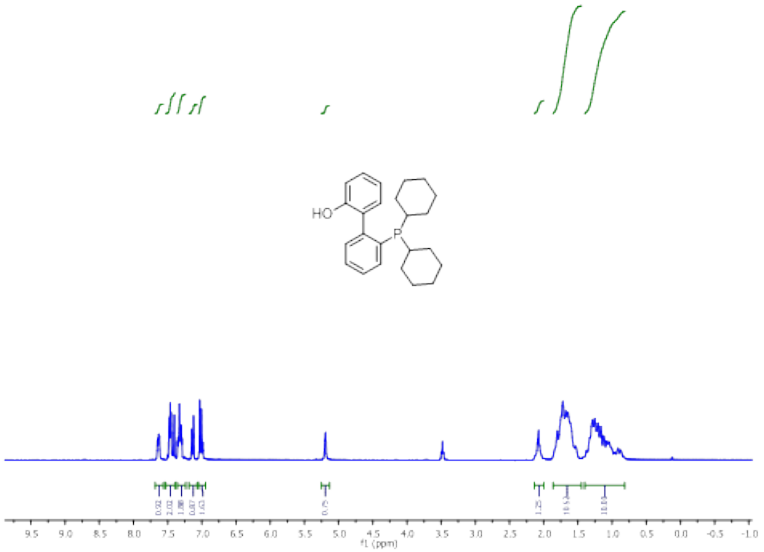
^{13}C NMR Spectrum of 2-Dicyclohexylphosphino-2'-methoxybiphenyl



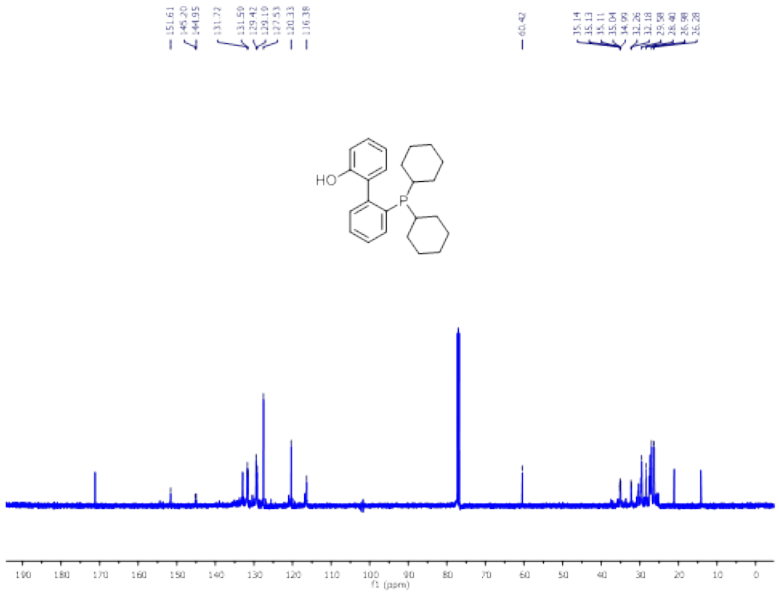
^{31}P NMR Spectrum of 2-Dicyclohexylphosphino-2'-methoxybiphenyl



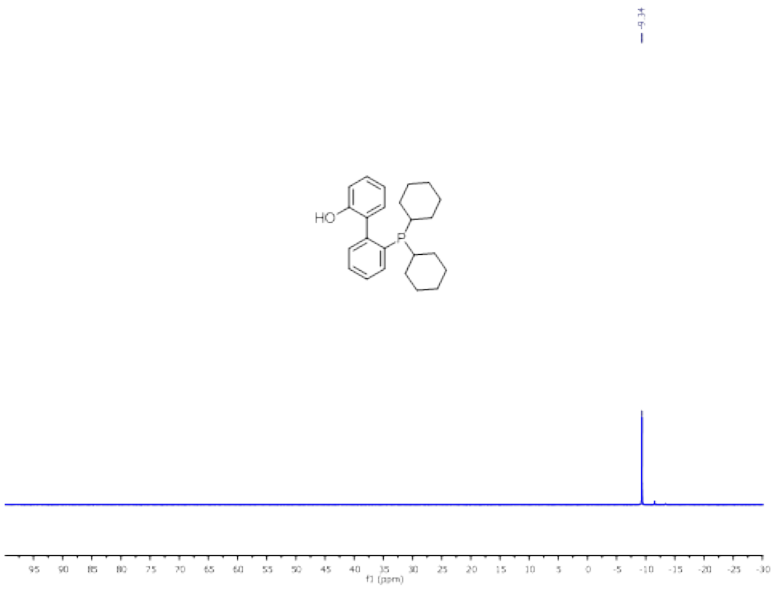
^{1}H NMR Spectrum of 2-Dicyclohexylphosphino-2'-hydroxybiphenyl (9)



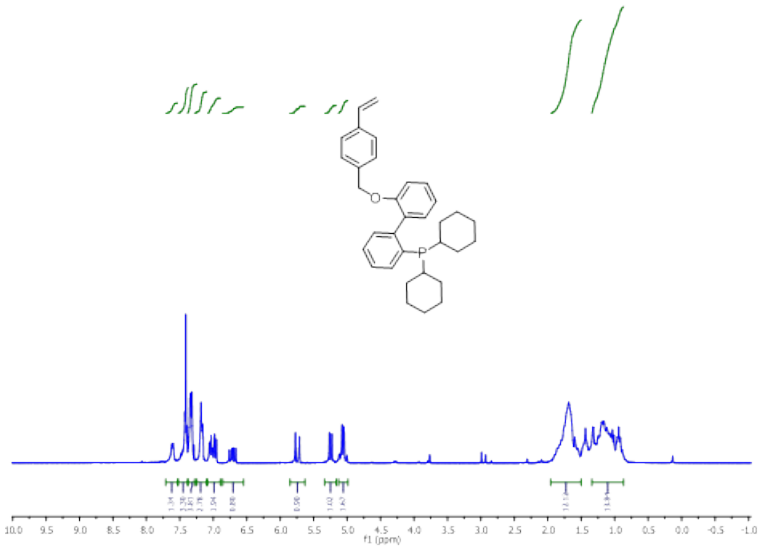
^{13}C NMR Spectrum of 2-Dicyclohexylphosphino-2'-hydroxybiphenyl (9)



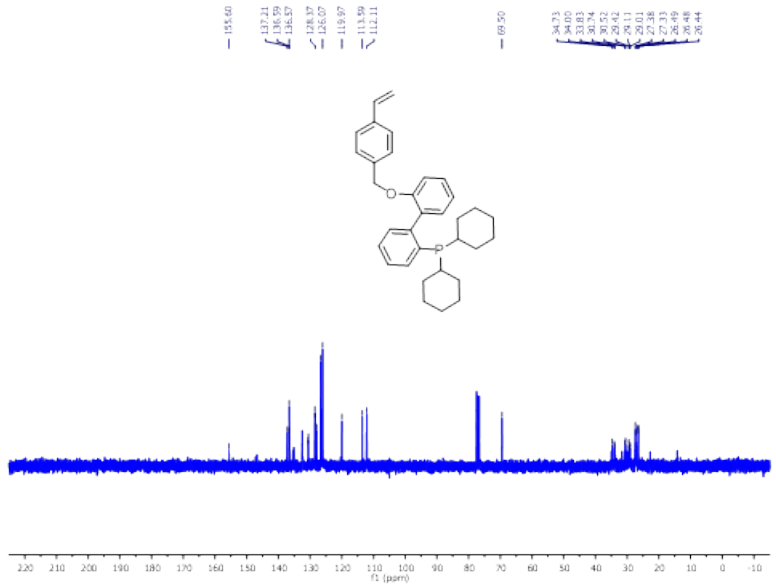
^{31}P NMR Spectrum of 2-Dicyclohexylphosphino-2'-hydroxybiphenyl (9)



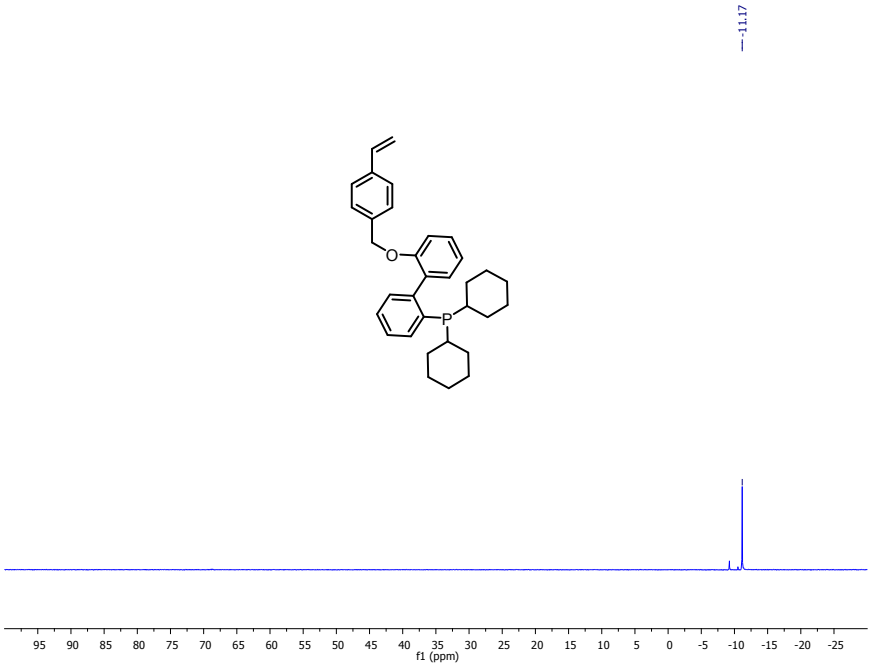
^{1}H NMR Spectrum of 4-Vinylbenzyl-2-dicyclohexylphosphino-2'-biphenyl (14)



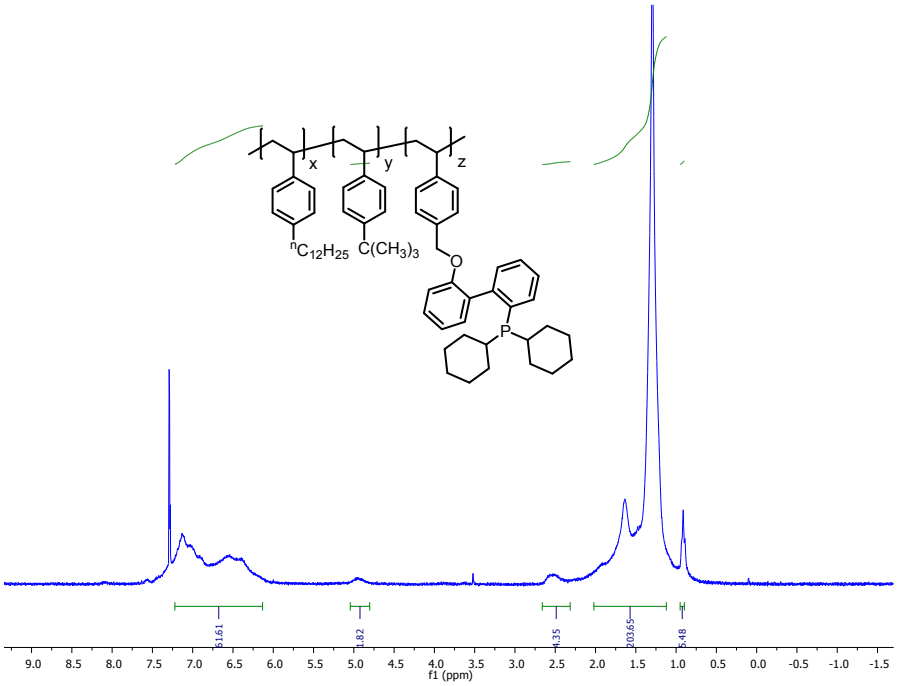
^{13}C NMR Spectrum of 4-Vinylbenzyl-2-dicyclohexylphosphino-2'-biphenyl (14)



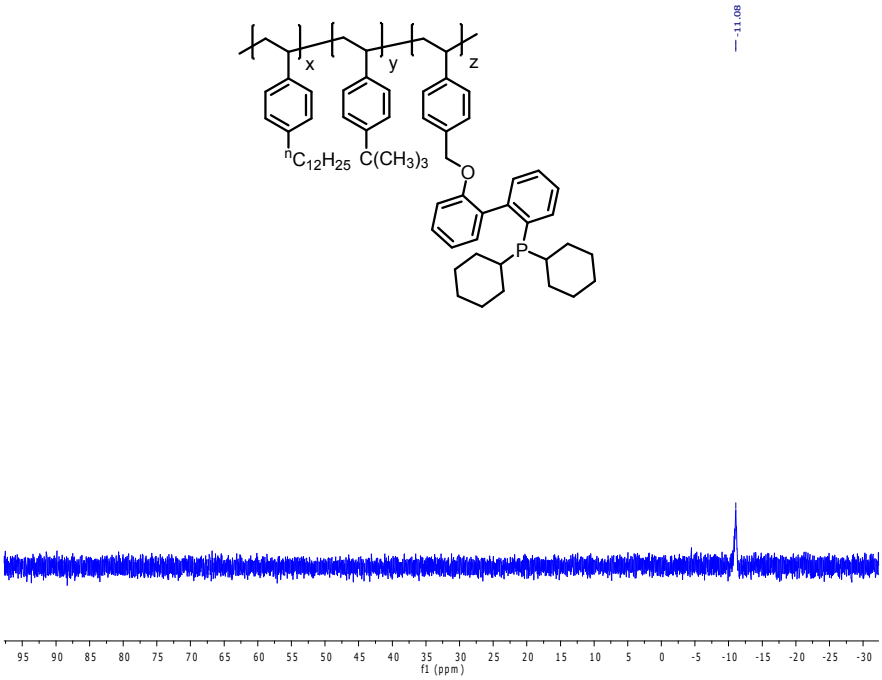
^{31}P NMR Spectrum of 4-Vinylbenzyl-2-dicyclohexylphosphino-2'-biphenyl (14)



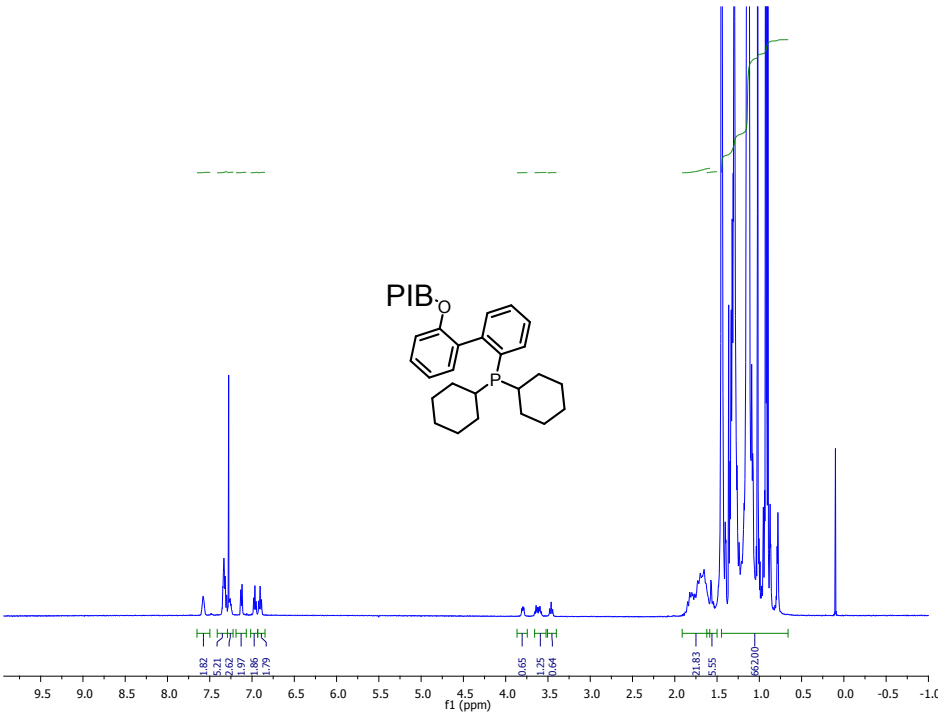
^{1}H NMR Spectrum of Poly(4-dodecystyrene)-*co*-poly(*tert*-butylstyrene)-*co*-poly(2-dicyclohexylphosphino-2'-biphenyl diphenyl) terpolymer (15)



^{31}P NMR Spectrum of Poly(4-dodecystyrene)-*co*-poly(*tert*-butylstyrene)-*co*-poly(2-dicyclohexylphosphino-2'-biphenyl diphenyl) terpolymer (15)



^{1}H NMR Spectrum of Polyisobutylene-supported 2-dicyclohexylphosphino-2'-biphenyl (21)



^{31}P NMR Spectrum of Polyisobutylene-supported 2-dicyclohexylphosphino-2'-biphenyl (21)