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Electronic Supplementary Information to:

Recyclable and Efficient Polyurethane-Ir Catalysts for Direct Borylation of Aromatic Compounds

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Experimental

Materials. 4,4'-Bis(hydroxylmethyl)-2,2'-bipyridine (TCI), 1,6-diisocyanatohexane (TCI), 1,4-diisocyanatobenzene (TCI), 1,4-diisocyanato-3-methylbenzene (TCI), bis(4-isocyanatophenyl)methane (Sigma-Aldrich), bis(pinacolato)diboron (B_2pin_2) (TCI), chloro(1,5-cyclooctadiene)iridium(I) dimer (TCI), dimethylsulfoxide (Kanto Chemical), nonane anhydrous 99+% (Sigma-Aldrich), anisole (TCI), trifluoromethylbenzene (TCI), pinacol (TCI), and phenylboronic acid (TCI) were used as received. Tetrahydrofuran (THF) (Kanto Chemical), triethylamine (Kanto Chemical), benzene (Kanto Chemical) and toluene (Kanto Chemical) were purified by distillation over CaH_2.

Measurements. NMR spectra were recorded on JEOL JMN-ECX400 (400 MHz for ^{1}H). UV-Vis spectra were taken using quartz cells on JASCO V-550 and V-570 spectrophotometers. IR spectra were recorded with a JASCO FT/IR-6100. GC-Mass analysis was conducted using a SHIMAZU GCMS-QP2010 Plus. Thermal analysis was conducted using RIGAKU Thermo Plus DSC8230 and TG8120. Sedimentation monitoring was attempted using a particle size distribution analyzer HORIBA CAPA-700. Scanning electron microscopy (SEM) images were obtained a JEOL JSM-7400F microscope with an LEI detector at an acceleration voltage of 3.0 kV and a working distance of 6.0 mm, and the samples were coated with Pt using a JEOL JFC-1600 Auto Fine Coater (30 mA, 20 sec). Energy dispersive X-ray spectroscopy (EDS) was measured using a JEOL JED-2300 coupled to JSM-7400Fat accelerating voltage 15 kV using samples without coating. Inductively coupled plasma (ICP)-optical emission spectral analysis was conducted using a Shimadzu ICPE-9000 spectrometer; ICP-MS-26H-0.01x-1 (AccuStandard) was used as Ir standard which led to solutions of 1, 5, 10, and 20 mg/L standard solutions. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2100F microscope equipped with a CCD image sensor at an acceleration voltage of 200 kV using a collodion film sample support.

GC-Mass calibration. Amounts of the products in the catalytic reactions were quantified using GC-Mass. The GC-Mass apparatus was calibrated using phenylboronic acid pinacol ester (PhBpin), the borylation reaction product, and nonane as the internal standard compound which is inert in the borylation reactions. All reactions were conducted in the presence of nonane. As for PhBpin with nonane, calibration was conducted using five solutions containing both PhBpin and nonane at different concentrations in benzene. PhBpin (81.9 mg, 401 mmol) was dissolved in benzene (1760.4 mg, 2.00 mL) leading to a PhBpin solution in benzene at [PhBpin] of 201 M (solution A), and nonane (133.0 mg, 1.037 mmol) was dissolved in benzene (4408.5 mg, 5.00 mL) leading to a nonane solution in benzene at [nonane] of 207.0 M (solution B) where the density of PhBpin was taken as unity. Solutions A and B were mixed using whole pipets and volumetric flasks leading to the solutions at different ratios of PhBpin to nonane. In addition, a 10-mL solution in benzene f nonane (33.9 mg, 0.265 mmol) was prepared in a volumetric flask; this solution was used to dissolve 20.3 mg (0.100 mmol) of nonane in a volumetric flask to prepare a 1-mL solution. The calibration samples (10 μL) were analyzed under the following conditions; carrier gas = He, mass range = 0~800, and temperature = 40~300 ^{o}C. The data were fitted using linear and quadratic functions where the quadratic function gave better fitting which was used for quantification of the products (Fig. S1).

As for the other, three borylation products, a one-point, linear calibration method was used. The standard solutions for the one-point calibration were prepared through catalytic borylation reactions of the aromatic compounds using bpy-Ir catalyst. The ratios of the products to nonane

as the internal standard were pre-determined by ^{1}H NMR spectroscopy, and the samples were used for GC-Mass calibration. The linear calibration plots are indicated in Fig. S2.

Synthesis of phenylboronic acid pinacol ester (PhBpin) as a standard sample for GC-Mass calibration. Pinacol (62.3 mg, 0.511 mmol) and phenylboronic acid (60.3 mg, 0.510 mmol) were dissolved in $CHCl_3$ (5 mL) under N_2 atmosphere, and the reaction mixture was stirred for 30 min at room temperature. The crude product was obtained by solvent evaporation. PhBpin was isolated using a Kugelrohr hort-path distillation apparatus. Yield 200.9 mg (0.985 mmol) (43%).
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.81 (d, 2H, J = 7.3 Hz), 7.46 (d, 1H, J = 7.3 Hz), 7.37 (d, 2H, J = 7.4 Hz), 1.35 (s, 12H).

Synthesis of poly(BHMB-1). The procedure corresponding to run 3 in Table 1 in the main manuscript is described. Polymerization reaction was conducted under N_2 atmosphere. 1,6-Diisocyanatohexane (96 μL, 100 mg, 0.60 mmol) was added to a solution of 4,4'-bis(hydroxylmethyl)-2,2'-bipyridine (108 mg, 0.500 mmol) in a mixture of THF (2.0 mL) and Et_3N (0.11 mL). The reaction mixture was stirred at room temperature for 24 h and then the reaction was quenched by the addition of MeOH (2.0 mL). Solvents were removed under a reduced pressure, and the residue was subjected to NMR analysis as a raw material after vacuum drying. The residue was then dissolved in 0.5 mL of DMSO, and MeOH (10 mL) was slowly added to the solution. The precipitates were collected with a centrifuge and dried under vacuum. Yield 141 mg, 66 %. Degree of polymerization was estimated to be 7.5 by comparing intensities of the $–OCH_3$ signal at 3.50 ppm and the $–CH_2$-bpy signal at 5.15 ppm in ^{1}H NMR spectra taken in DMSO-d_6.

Synthesis of a polyester from BHMB and adipoyl chloride. Polymerization reaction was conducted under N_2 atmosphere. Adipoyl chloride (78 μL, 98 mg, 0.52 mmol) was added to a solution of 4,4'-bis(hydroxylmethyl)-2,2'-bipyridine (110 mg, 0.510 mmol) in pyridine (2.0 mL). The reaction mixture was stirred at room temperature for 24 h, and then the reaction was quenched by the addition of MeOH (5 mL). The MeOH-insoluble product was isolated by filtration, was washed with MeOH (10 mL), water (10 mL), and MeOH (10 mL) in this order, and was dried under vacuum. Yield 117 mg, 69%. Degree of polymerization was estimated to be 44 by comparing intensities of the $–OCH_3$ signal at 3.66 ppm and the $–CH_2$-bpy signal at 5.32 ppm in ^{1}H NMR spectra taken in $CDCl_3$.

Catalytic reaction using polymer catalyst. A typical example is described for borylation of benzene (run 4 in Table 1 in the main manuscript). The reaction was conducted under N_2 atmosphere. Poly(BHMB-**1**) (12.1 mg, 3.00 x 10^{-3} mmol (per bpy residue), B_2pin_2 (253.9 mg, 1.00 mmol), and $[IrCl(COD)]_2$ (10.1 mg, 1.50 x 10^{-3} mmol) were placed in a 25-ml flask which had been dried under vacuum and flushed with N_2 gas. Immediately after benzene (5.3 ml, 60 mmol) was introduced, the reaction mixture was heated at 80°C with stirring. After 24 h of reaction, the reaction mixture was cooled down to room temperature.

Theoretical Calculations. All the computations were performed with Gaussian 09.[S1] Density functional theory (DFT) calculations at the ωB97XD [S2]/6-31G* level were carried out to obtain the optimized structures and the potential energies. The solvation effect was included with the self-consistent reaction field (SCRF) method, and the dielectric constant of *n*-hexane was used.[S3] Natural population analysis (NPA) was performed with NBO ver 3.1 in the Gaussian package. [S4] The transition-state structures were verified by frequency calculations.

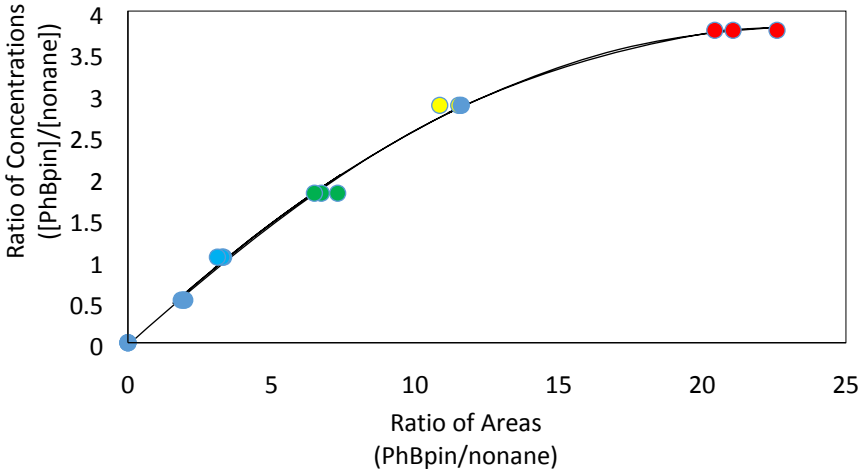
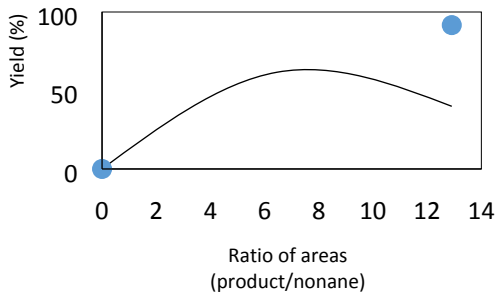
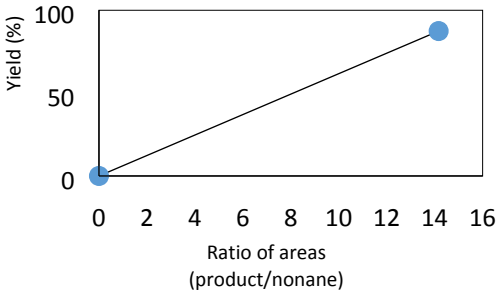


Fig. S1. Linear (A) and quadratic (B) calibrations for quantification of phenylboronic acid pinacol ester (PhBpin).

A. Toluene



B. Anisole



C. Trifluoromethylbenzene

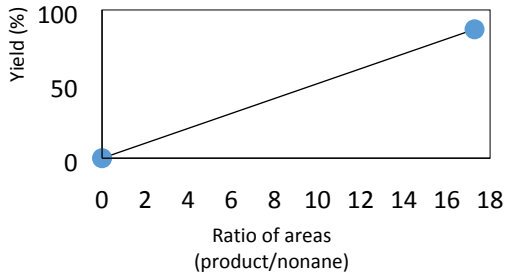


Fig. S2. One-point calibration for quantification of the borylation products of toluene (A), anisole (B), and trifluoromethylbenzene (C).

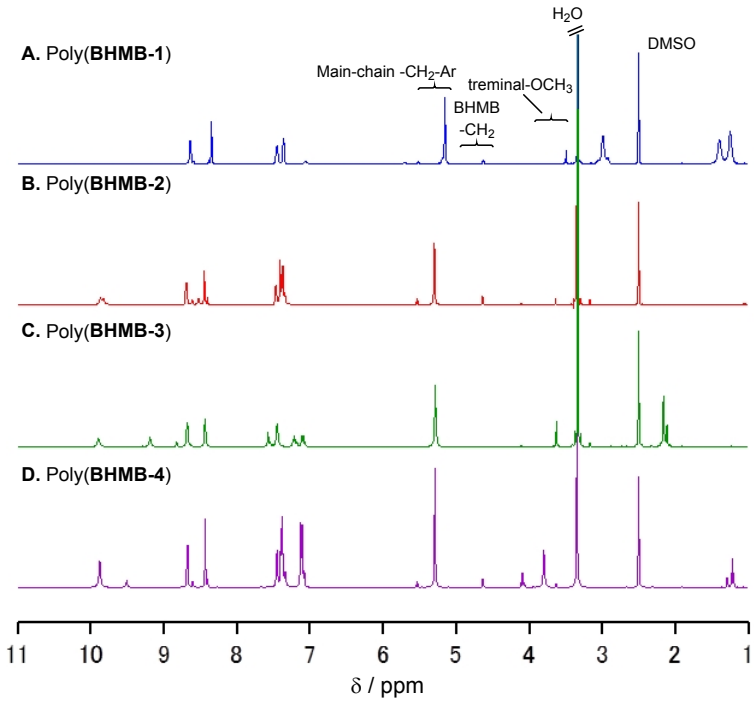


Fig. S3. ^{1}H NMR spectra of poly(BHMB-**1**) (A), poly(BHMB-**2**) (B), poly(BHMB-**3**) (C), and poly(BHMB-**4**) (D) (runs 1, 2, 3, and 4, in Table 1, respectively). [400 MHz, DMSO-d_6, 23°C]

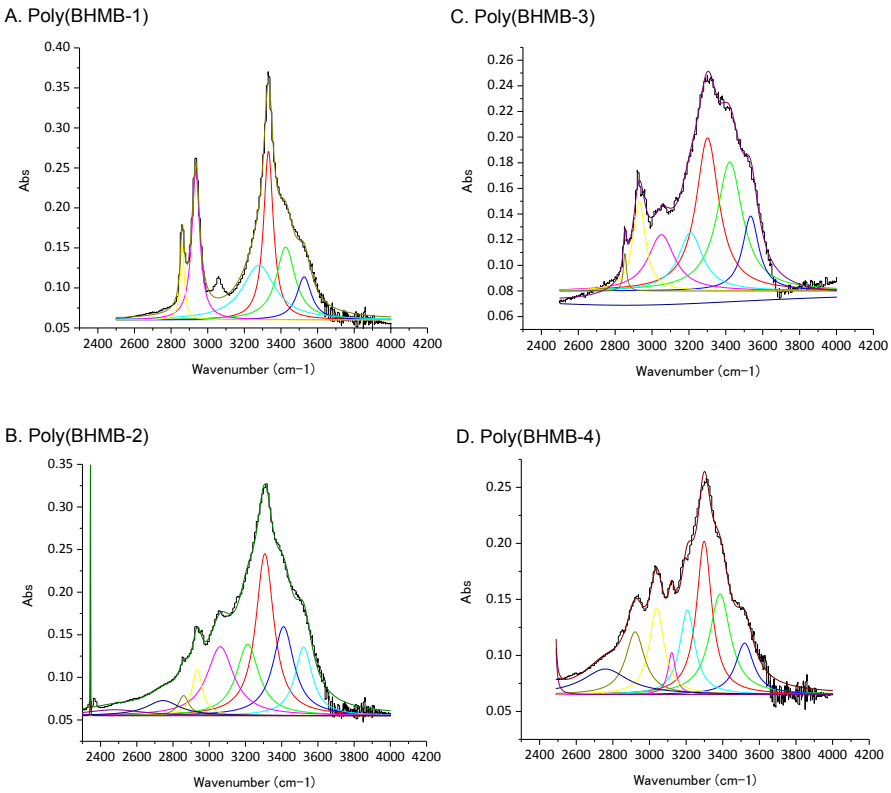


Fig. S4. Wave-form analysis of IR spectra. Signals were fitted using Lorentzian functions, and the functions of the highest and the second highest wavenumbers were taken as free N-H vibration and those of the third highest and the fourth highest wavenumbers as H-bound N-H vibrations.

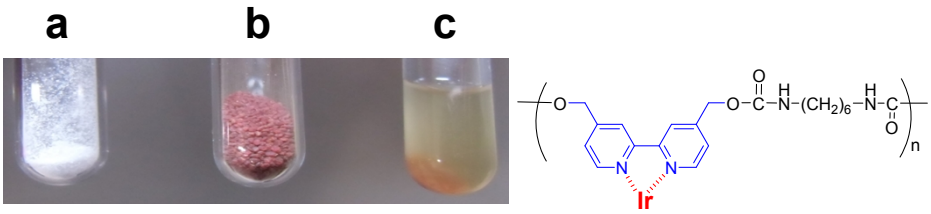


Fig. S5. Photographs of poly(BHMB-1) (a), $[IrCl(COD)]_2$ (b), and their mixture in THF at [poly(BHMB-**1**)]/[Ir] = 1/1 (per residue) (c) and the expected chemical structure of poly(BHMB-**1**)-Ir complex (right-hand side).

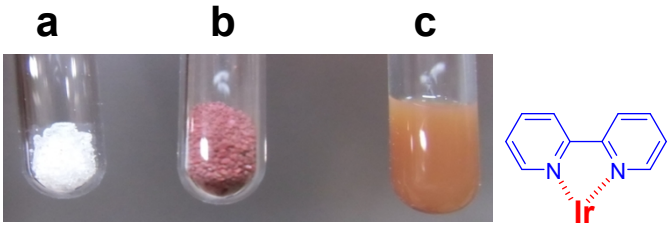


Fig. S6. Photographs of bpy (a), $[IrCl(COD)]_2$ (b), and their mixture in THF at [bpy]/[Ir] = 1/1 (c) and the expected chemical structure of bpy-Ir complex (right-hand side).

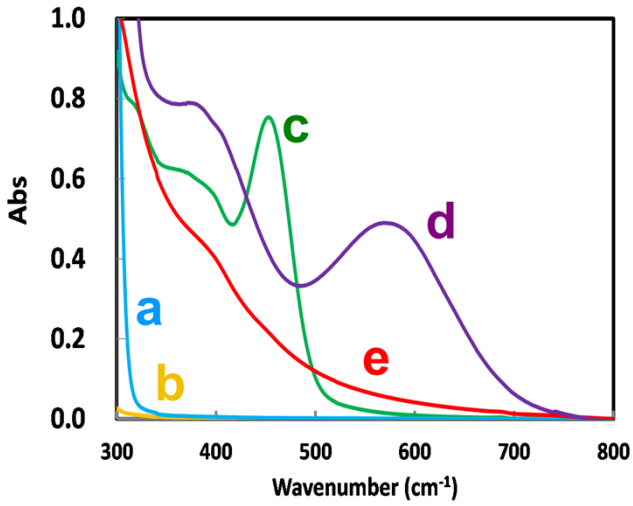


Fig. S7. UV spectra of ligands, Ir species, and ligand-Ir mixtures in THF: bpy (a), Poly(BHBM-**1**) (b), $[IrCl(COD)]_2$ (c), bpy-1/2$[IrCl(COD)]_2$ (d), poly(BHBM-**1**)-1/2$[IrCl(COD)]_2$ (e). ([bpy] = [polymer (residue)] =5.56 mM in **a** and **b**; [Ir] = 5.56 mM in **c**, [bpy] = [polymer (residue)] = [Ir] = 5.56 mM in **d** and **e**, cell path = 1 mm) Samples for **b** and **e** were heterogeneous.

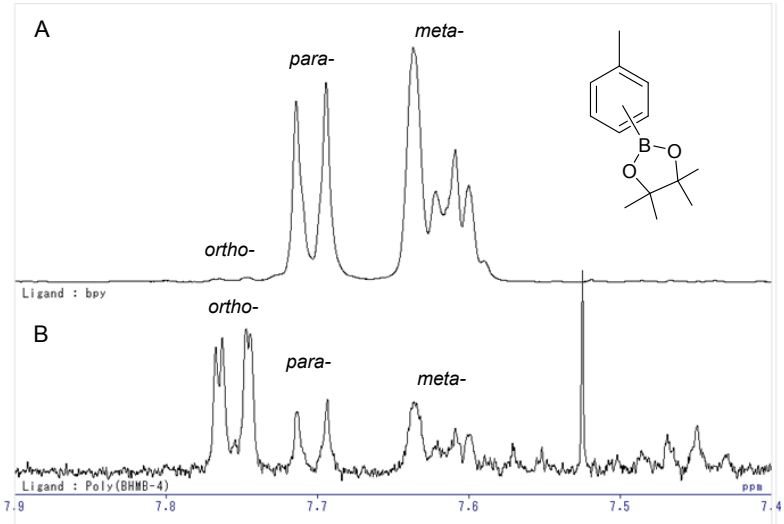


Fig. S8. ^{1}H NMR spectra of the product mixtures obtained by direct borylation of toluene using bpy (A) and poly(BHMB-**4**) (B). Signal assignments are based on refs. S5 and S6.

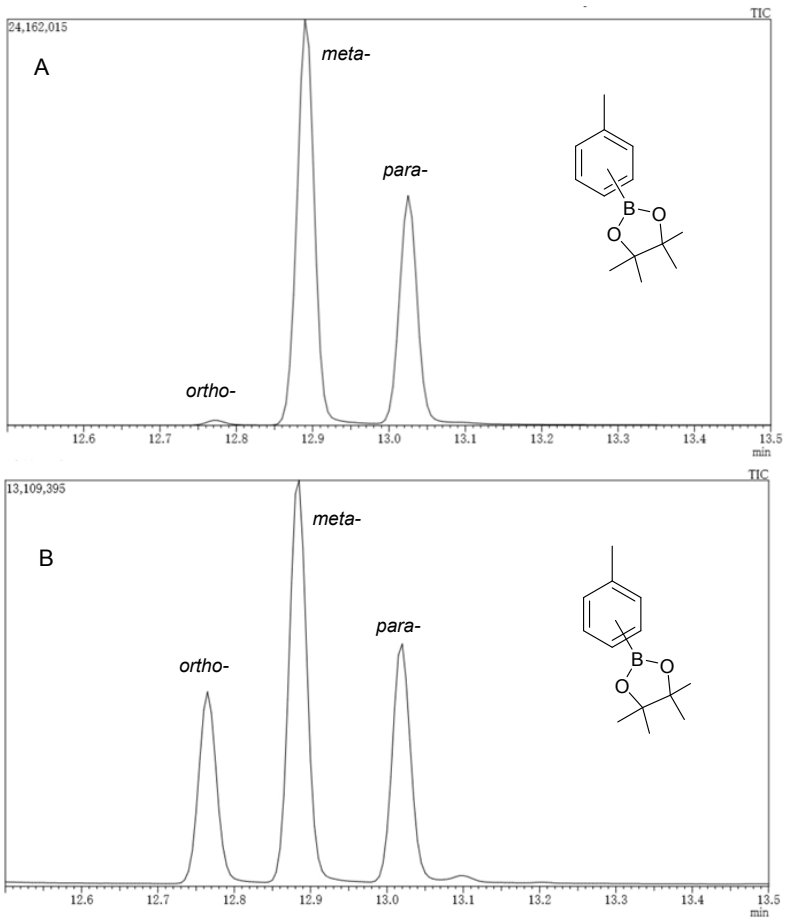


Fig. S9. GC-Mass chromatograms of the product mixtures obtained by direct borylation of toluene using bpy (A) and poly(BHMB-**4**) (B).

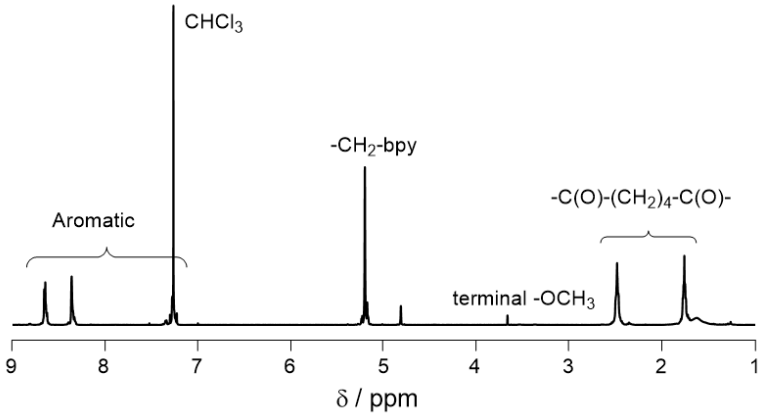


Fig. S10. ^{1}H NMR spectrum of polyester prepared from BHMB and adipoyl chloride (DP = 44). [400 MHz, $CDCl_3$, 23°C]

Table S1. Direct borylation of benzene with bpy, BHMB, and polymers as ligands at 80°C[a,b]

Run	Ligand	Reaction for 4 h		Reaction for 24 h	
		Yield[c] (%)	TON	Yield[c] (%)	TON
1	bpy	92	62	100	67
2	BHMB	89	59	88	58
3	Poly(BHMB-**1**) [DP = 11]	80	53	77	51
4	Poly(BHMB-**1**) [DP = 7.5]	81	54	84	56
5	Poly(BHMB-**1**) [DP = 2.8]	72	48	72	54
6	Poly(BHMB-**2**) [DB = 29]	1	1	46	30
7	Poly(BHMB-**3**) [DB = 8.0]	1	1	68	45
8	Poly(BHMB-**4**) [DB = 2.5]	0	0	41	27

[a]Benzene 5.3 mL, 1/2[IrCl(COD)]$_2$ 5.56 mM (3 mol% of B_2pin_2), B_2pin_2 185 mM, nonane (internal standard) 100 mM. [c]Estimated by GC-Mass analysis using nonane as internal standard.

Table S2. Effects of catalyst preparation time on direct borylation of benzene with bpy and poly(BHMB-**1**) [DP = 11] at 80°C for 24 h[a]

Run	Ligand	Catalyst Preparation Time[b] (h)	Yield[c] (%)	TON
1	bpy	0	100	67
2	bpy	1.5	69	46
3	Poly(BHMB-**1**)	0	77	51
4	Poly(BHMB-**1**)	1.5	0	0

[a]Benzene 5.3 mL, 1/2[IrCl(COD)]$_2$ 5.56 mM (3 mol% of B_2pin_2), [B_2pin_2] 185 mM, nonane (internal standard) 100 mM, temp. 80 °C. [b]Duration of time after mixing ligand, [IrCl(COD)]$_2$, and B_2pin_2 in benzene until heating the mixture was initiated. [c]Estimated by GC-Mass analysis using nonane as internal standard.

Table S3. Effects of ligand-Ir ratio on direct borylation of benzene with bpy and poly(BHMB-**1**) [DP = 11] at 80°C for 24 h[a]

Run	Ligand	[Ligand] / [Ir]	Reaction time 4 h		Reaction time 24 h	
			Yield (%)[b]	TON	Yield (%)[b]	TON
1	Poly(BHMB-**1**)	1.0	81	54	78	52
2	Poly(BHMB-**1**)	3.3	0	0	0	0
3	BHMB	1.0	89	59	88	59
4	BHMB	3.3	63	42	66	44
5	bpy	1.0	92	61	99	66
6	bpy	3.3	69	46	85	57

[a]Benzene 5.3 mL, 1/2[IrCl(COD)$_2$ 5.56 mM (3 mol% of B_2pin_2), B_2pin_2 185 mM, nonane (internal standard) 100 mM. [b]Estimated by GC-Mass analysis using nonane as internal standard.

Table S4. Effects of polar compounds on direct borylation of benzene with bpy and poly(BHMB-**1**) [DP = 11] as ligands at 80°C for 24 h[a]

Run	Ligand	Additive [Volume (mL)]	Yield[b] (%)	TON
1	bpy	none	95	64
2	bpy	DMF [0.53]	28	19
3	bpy	DMF [2.65]	3	2
4	Poly(BHMB-**1**)	none	78	54
5	Poly(BHMB-**1**)	DMF [0.53]	15	10
6	Poly(BHMB-**1**)	DMF [2.65]	0	0
7	Poly(BHMB-**1**)	DMSO [2.65]	2	1
8	Poly(BHMB-**1**)	DMSO [0.53]	0	0
9	Poly(BHMB-**2**)	none	47	31
10	Poly(BHMB-**2**)	DMSO [2.65]	2	1
11	Poly(BHMB-**3**)	DMSO [2.65]	1	1

[a]Benzene 5.3 mL, [1/2[IrCl(COD)]$_2$] 5.56 mM (3 mol% of B_2pin_2), [B_2pin_2] 185 mM, [nonane (internal standard)] 100 mM. [b]Estimated by GC-Mass analysis.

Table S5. Numerical data for catalyst recycle experiments of direct borylation of benzene using poly(BHMB-**1**) [DP = 11] as ligand at 80°C for 24 h[a]

Recycle experiment	1st	2nd	3rd	4th	5th	6th
Yield[b] (%)	63	53	61	52	41	52
TON	41	35	41	35	27	35

[a]Benzene 5.3 mL, [1/2[IrCl(COD)]$_2$] 5.56 mM (3 mol% of B_2pin_2), [B_2pin_2] 185 mM, [nonane (internal standard)] 100 mM. [b]Estimated by GC-Mass analysis.

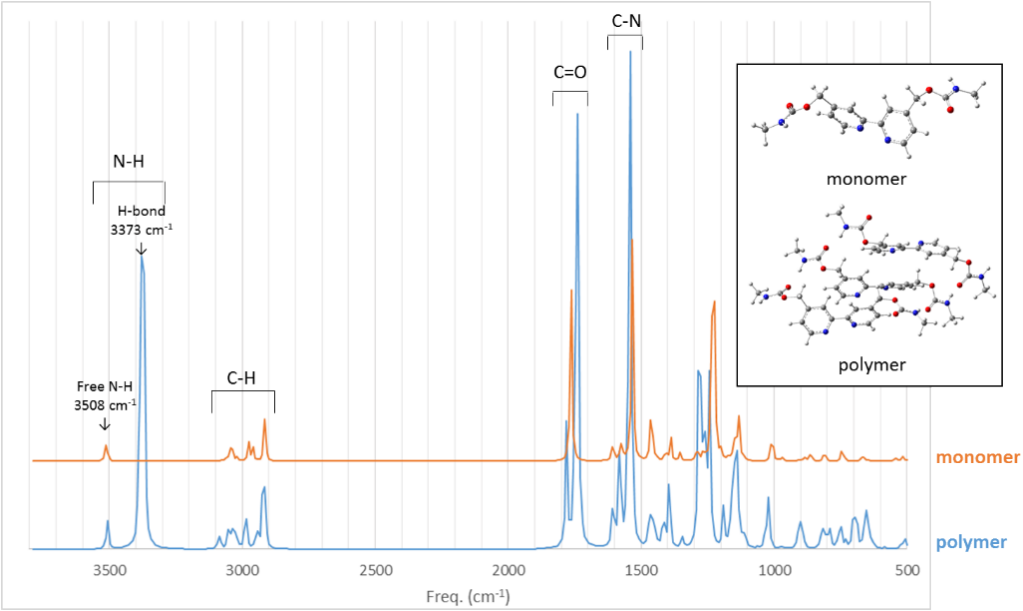


Fig. S11. Theoretical IR spectra of monomeric and trimeric chain models.

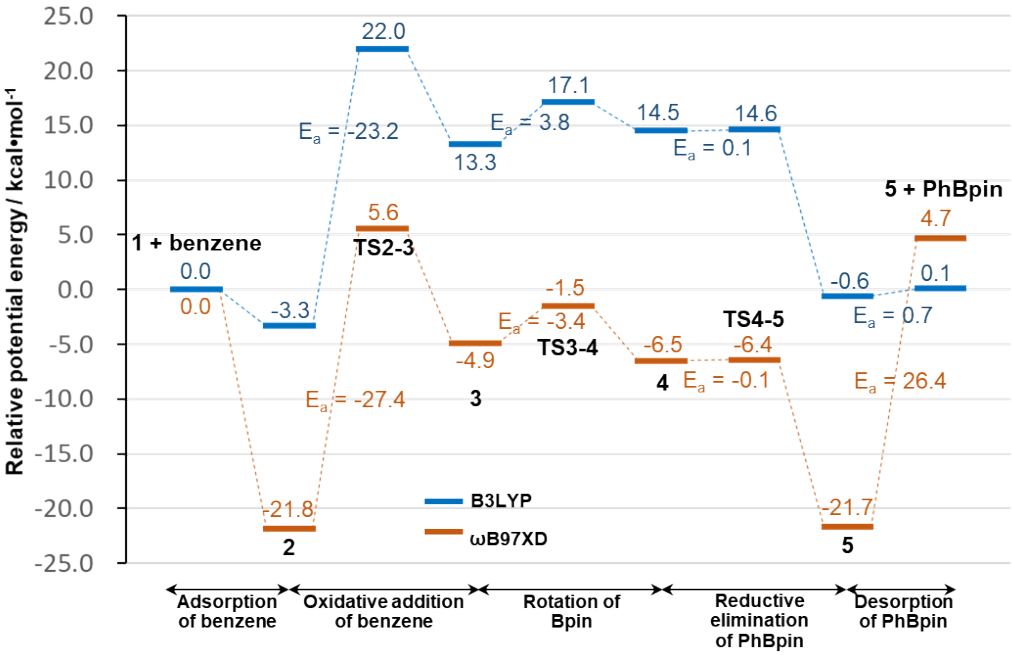


Fig. S12. Comparison of potential energy profiles calculated with B3LYP and ω B97XD functionals.

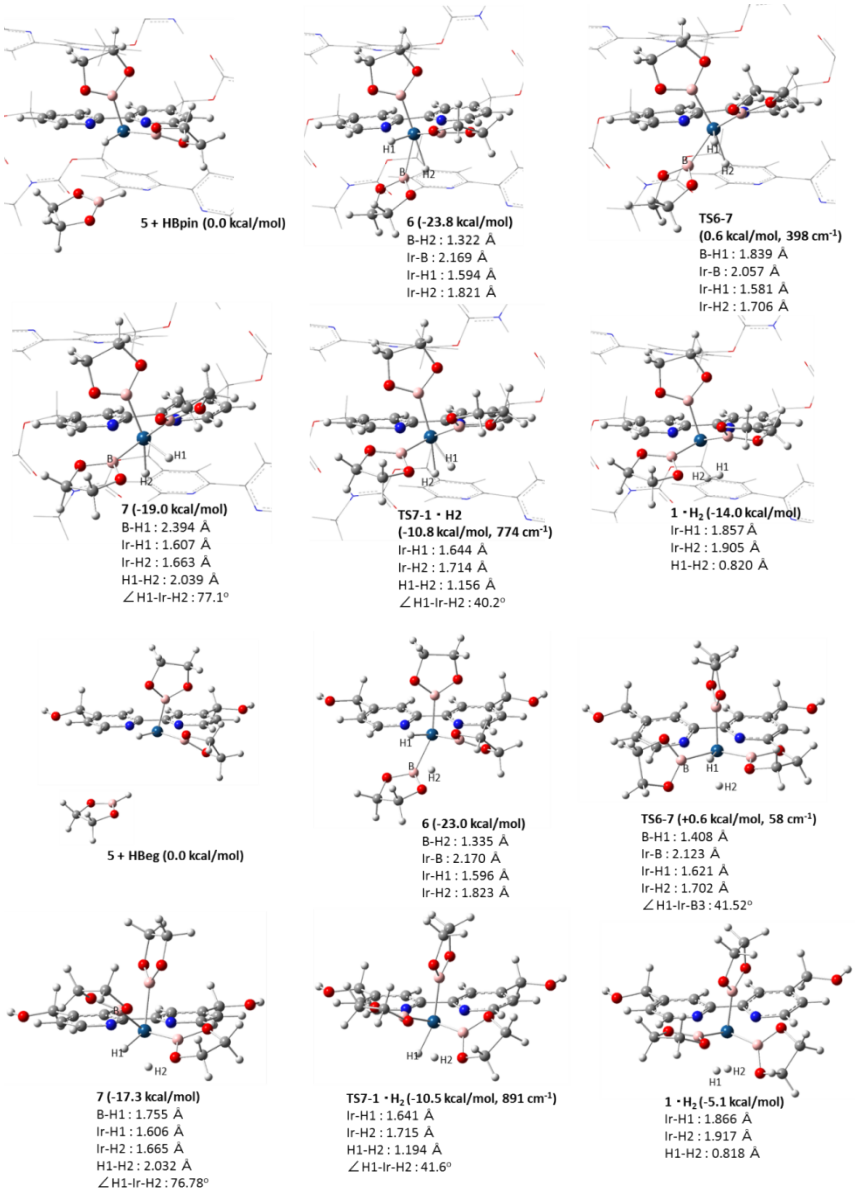


Fig. **S13.** Proposed mechanism of the reaction of IrX_2-ligand with 1,3,2-dioxaborolane: energy profiles for the trimeric aggregate-Ir catalyst system (blue) and BHBM-Ir catalyst system (red) (A) and molecular coordinates for the trimeric aggregate system (B) and BHMB system (C). Numbers in kcal/mol and E_a correspond to relative potential energies and activation energies. Structure numbers in B and C correspond to those in A.

Table S6. Results of ICP optical emission spectral analysis[a]

Sample	Sample Weight (mg)	[Ir][b] (mg/L) [as observed]	[Ir][b] (mg/L) [normalized to 1 mg sample]
Poly(BHMB-**1**)-Ir catalyst recovered after the 1st borylation in recyle experiments	1.69	7.74	4.47
Poly(BHMB-**1**)-Ir catalyst recovered after the 4th borylation in recyle experiments	1.19	4.43	3.85

[a]Sample was first pre-treated with aq. HNO_3 using a microwave digestion system and then dissolved in 50 mL of water. [b]Ir was quantified using emission signal at 212 nm.

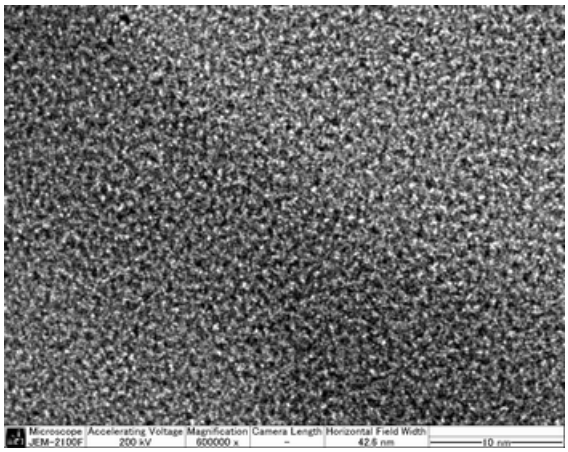


Fig. **S14.** TEM image of poly(BHMB-1)-Ir catalyst [collodion support film].

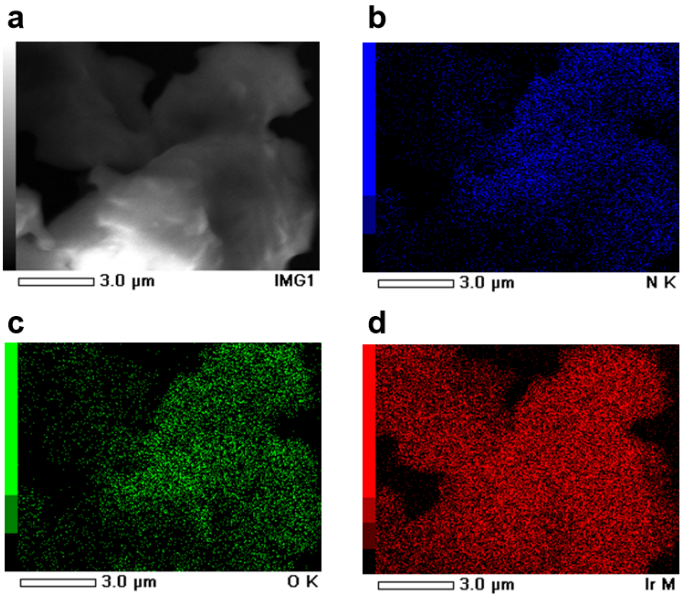


Fig. **S15.** SEM image (a) and EDS element maps of N (b), O (c), and Ir (d) of poly(BHMB-**1**)-Ir catalyst.

References:

S1) M. J. Frisch, et al., *Gaussian 09, revision D.01*, Gaussian, Inc., Wallingford, CT, 2009.

S2) J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

S3) (a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129; (b) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158; (c) R. Cammi, B. Mennucci, J. Tomasi, *J. Phys. Chem. A* **2000**, *104*, 5631–5637.

S4) (a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066–4073; (b) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

S5) C. Kleeberg, L. Dang, Z. Lin and T. B. Marder, *Angew. Chem. Int. Ed.*, 2009, **48**, 5350-5354.

S6) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 390-391.