Electronic Supplementary Information

Heterogeneous Rh and Rh/Ag Bimetallic Nanoparticle Catalysts Immobilized on Chiral Polymer

Hyemin Min, Hiroyuki Miyamura, Tomohiro Yasukawa, and Shū Kobayashi*

Department of Chemistry, School of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo, 113-0033
E-mail: shu_kobayashi@chem.s.u-tokyo.ac.jp

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1. **General Remarks**

- Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F<sub>254</sub> glass plates purchased from Merck KGaA and were visualized under UV light (254 nm) and/or by staining with KMnO<sub>4</sub>.

- NMR spectra were recorded with JEOL JMN-LA 500 or 600 spectrometers operating at 500, 600 MHz (\textsuperscript{1}H) and 125, 150 MHz (\textsuperscript{13}C) respectively. Chemical shifts were recorded in parts per million (ppm), from relative to internal references of the CDCl<sub>3</sub>, defined at 7.24 ppm (\textsuperscript{1}H NMR) and 77.00 ppm (\textsuperscript{13}C NMR). The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

- Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed on Shimadzu ICPS-7510 equipment.

- STEM/EDS images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated copper grids and allowed to dry in air (without staining).

- IR spectra were measured on a JASCO FT/IR-610 spectrometer.

- Direct Analysis in Real Time (DART) mass spectra were recorded on JEOL JMS-T100TD mass spectrometer.

- Optical rotations were measured with JASCO P-1010.

- Melting point was recorded on a standard melting point apparatus and is uncorrected.

- HPLC analysis was conducted on Shimadu LC-20AB, SPD-M20A and DGU-20A3.

- Daicel Chiralpak AD, AD-H, AD-3, OD-H, AS-H, AS-3, OJ-H column were used for HPLC analysis.

- The absolute configuration of reported compounds was determined by comparison of results of HPLC analysis to literature and that of other products was assumed by analogy.

- XPS analysis was performed on JPS-9010MC with a Mg K\textalpha{} X-ray source and the C 1s line at 284.0 eV was used as reference to correct the binding energies.

- GC analysis was performed on a Shimadzu GC-2010 apparatus. **Condition I:** Column = GL Science TCWAX, 0.25 mm ID, 0.25 µm, 60.0 m; Gas pressure: 214.2 kPa; Total flow: 90.6 mL/min; Column flow: 1.86 mL/min; Velocity: 30.8 cm/sec; Purge flow: 3.0 mL/min; Split ratio: 46.0; Injector: 250 °C; FID: 250 °C; Column
program: starting from 50 ºC, 10 ºC/min to 220 ºC, 18 min hold. **Condition II:** Column = J & W SCIENTIFIC DB-1, 0.25 mm ID, 0.25 µm, 60.0 m; Gas pressure: 157.5 kPa; Total flow: 41.3 mL/min; Column flow: 0.93 mL/min; Velocity: 21.1 cm/sec; Purge flow: 3.0 mL/min; Split ratio: 40.1; Injector: 300 ºC; FID: 300 ºC; Column program: starting from 100 ºC, 10 ºC/min to 300 ºC, 30 min hold.

*H₂ adsorption was conducted by BELLCAT II (Microtrac BEL Corp.)*

- 24~27 mg of sample was used for analysis, and H₂ adsorption was conducted at 50 ºC after pretreatment.
- Analysis was conducted by pulse method, and the result is average of at least 4 pulses.

- Pretreatment conditions

| Temp (ºC) | Gas   | Flow (mL/min) | Time (min) |
|----------|-------|---------------|------------|
| 200      | Ar    | 50            | 35         |
| 200      | O₂    | 50            | 15         |
| 200      | Ar    | 50            | 20         |
| 200      | H₂    | 50            | 20         |
| 250      | Ar    | 50            | 180        |
| 50       | Ar    | 50            | 10         |

*Preparative TLC (PTLC) was performed using Wakogel B-5F from Wako Pure Chemical Industries.*

*0.45 µm PTFE membrane filter (WhatmanTM cat. No. 6784-2504) was used for filtration of catalyst in the preparation of leaching test samples.*

*Reaction was conducted using carousel 12 Plus Reaction System™ by Radleys (www.radleys.com) using one-neck tube equipped with septum after Ar substitution.*

*NaBH₄ was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature¹ and stored in a glove box. It is important to manipulate all operations under Ar atmosphere during recrystallization. Activity of catalyst and reproducibility are highly influenced by the purity and condition of NaBH₄ in the course of catalyst preparation.*

*|[Rh(OAc)₂]₂ was purchased from Strem Chemicals, inc.*

*AgSbF₆ was purchased from Sigma-Aldrich Corporation.*

*Ketjen black (Carbon black) EC 300J was purchased from Lion Corporation.*

*Trimethoxysilylstyrene was purchased from Shin-Etsu Silicons.*

*Substrate 3a, 3b, 3d-f, 3k, 3m were purchased from Tokyo Chemical Industry or Sigma-Aldrich Corporation. 3c², 3g³, 3h⁴, 3i⁴, 3j⁵, 3l⁶, 3u⁷, 3o⁸, 8a-c⁹, 8d¹⁰ were synthesized following the literatures. Arylimine 9 were
prepared by condensation of tosylimine and corresponding aldehydes.

- Arylboronic acids 4a-k were prepared from the corresponding Grignard reagent or purchased from Wako Pure Chemical Company or Tokyo Chemical Industry.

- Arylboronic acids 4a-k were recrystallized using hexane/ethyl acetate and ratio between boronic acid and boroxine was determined by $^1$H NMR analysis.

- Chiral diene ligand precursor (in Scheme S1) was prepared following the literature.\textsuperscript{11}

- Toluene was purchased in dried grade from Wako Pure Chemical Company and used without further purification.

- Deionized water from a MILLIPORE MilliQ machine (Gradient A10) was used as solvent without further treatment.

- Celite (Celite® 545) was purchased from Kokusan Chemical Co., Ltd.

- For flow system,
  - Pump : Shimadzu LC-10ATvp (x2)
  - Column : 10Φ x 5 cm from Tokyo Rikakikai Co. Ltd.
  - Column heater : from Tokyo Rikakikai Co. Ltd.
  - Column heater controller : EYELA TTM204
  - Back pressure controller (regulator) : Swagelok KCB1G0D2D5P60000BK
  - Back pressure monitor : Nagano keiki Co. Ltd. GC61-174
2. Monomer, Copolymer and Catalyst Preparation

2.1. Polymer-Incarcerated Carbon Black Pd (PICB-Pd) Catalyst

Ligand preparation (Scheme S1)\textsuperscript{3,12,11}

\[ (1R, 4R, 7R)-N-(1-Hydroxy-2-methylpropan-2-yl)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (S1) \]

\[ (1R, 4R, 7R)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic \] acid

(988 mg, 4.79 mmol, 1 equiv) was added in a flask and atmosphere was changed to Ar. After addition of DMF, oxalyl chloride (0.62 mL, 7.20 mmol, 1.5 equiv) and DMF (83 µL, 1.06 mmol, 0.22 equiv) were added at 0 ºC. After stirring for 3 h at 0 ºC, triethyl amine (3.4 mL, 24.0 mmol, 5 equiv) and 2-amino-2-methyl-1-propanol (1.4 mL, 14.37 mmol, 3 equiv) in DCM (5 mL) were added at 0 ºC, and the mixture was stirred for 24 h at room temperature. NH\textsubscript{4}Cl (sat. aq., 15 mL) was added and an aqueous phase was extracted with DCM (3 x 30 mL). The combined organic layers were washed with water and brine, dried over Na\textsubscript{2}SO\textsubscript{4}, then solvents were removed in vacuo. The residue was purified by flash chromatography to afford the desired product (804 mg, 60 %). [\alpha]\textsuperscript{20}\textsubscript{D} = +27.3 (c = 1.25, CHCl\textsubscript{3}). IR (KBr): 3725, 3660, 3320, 3040, 2958, 2935, 2871, 1740, 1660, 1636, 1530, 1450, 1383, 1363, 1283, 1233, 1173, 1064, 1029, 886, 816, 740, 667 cm\textsuperscript{-1}. DART-MS (m/z) calcd. for C\textsubscript{17}H\textsubscript{28}NO\textsubscript{2} (MH\textsuperscript{+}): 278.21200, found: 278.21108. M.p : 97-98 ºC. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz): \( \delta \) (ppm) 6.72 (dd, \( J = 6.2, 1.4 \) Hz, 1H), 5.74 (d, \( J = 5.5 \) Hz, 1H), 5.64 (brs, 1H), 4.93 (t, \( J = 5.5 \) Hz, 1H), 4.31 (td, \( J = 4.0, 1.8 \) Hz, 1H), 3.53 (d, \( J = 4.8 \) Hz, 2H), 3.29-3.24 (m, 1H), 1.75 (s, 3H), 1.53-1.49 (m, 1H), 1.24 (d, \( J = 8.9 \) Hz, 6H), 1.16-1.11 (m, 1H), 1.04-1.00 (m, 1H), 0.93 (d, \( J = 6.2 \) Hz, 3H), 0.91-0.87 (m, 1H), 0.75 (d, \( J = 6.9 \) Hz, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 150 MHz): \( \delta \) (ppm) 167.1, 145.1, 143.8, 138.4, 124.1, 71.0, 56.1, 47.7, 43.6, 40.1, 33.8, 31.7, 24.9, 24.8, 21.8, 21.3, 19.0.

\[ (1R, 4R, 7R)-7-Isopropyl-5-methyl-N-(2-methyl-1-((4-vinylbenzyl)oxy)propan-2-yl)bicyclo[2.2.2]octa-2,5-diene-2-carboxamide (S2, Diene monomer 1) \]

Sodium hydride (55% in mineral oil, 87.3 mg, 2.0 mmol, 1 equiv) was setted in flask and atmosphere was changed to Ar. After addition of DMF (2 mL), (1R, 4R, 7R)-N-(1-hydroxy-2-methylpropan-2-yl)-7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxamide (S1) (557 mg, 2.0 mmol, 1 equiv) in DMF (1 mL) was added at 0 ºC. After stirring for a few minutes, 1-(chloromethyl)-4-vinylbenzene (0.43 mL, 3.0 mmol, 1.5 equiv) in DMF (2 mL) was added at 0 ºC, and this mixture was further stirred for 4 h at room temperature. NH\textsubscript{4}Cl (sat. aq., 30 mL) was
added for quenching, then an aqueous layer was extracted with hexane/ethyl acetate (2:1). The combined organic layers were washed with water, dried over Na$_2$SO$_4$, and solvents were removed in vacuo. The residue was purified by flash chromatography to afford the desired product (586.4 g, 75%). $[\alpha]^{10}_D = +22.8$ (c = 0.75, CHCl$_3$). IR (KBr): 3668, 3430, 3348, 3086, 3039, 2959, 2868, 2726, 2608, 2423, 2399, 2296, 2136, 1907, 1815, 1738, 1644, 1611, 1451, 1402, 1365, 1230, 1204, 1097, 1021, 988, 907, 822, 770, 738, 665, 642 cm$^{-1}$. DART-MS (m/z) calcd. for C$_4$H$_n$NO$_2$ (MH$^+$): 394.27460, found: 394.27443. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm) 7.37 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.2$ Hz, 2H), 6.75-6.65 (m, 2H), 5.86 (s, 1H), 5.77 (d, $J = 5.5$ Hz, 1H), 5.73 (d, $J = 17.9$ Hz, 1H), 5.23 (d, $J = 11.0$ Hz, 1H), 4.50 (s, 2H), 3.96 (td, $J = 4.1, 2.1$ Hz, 1H), 3.42 (q, $J = 9.4$ Hz, 2H), 3.29-3.26 (m, 1H), 1.79 (s, 3H), 1.54-1.52 (m, 1H), 1.36 (d, $J = 3.4$ Hz, 6H), 1.19-1.16 (m, 1H), 1.08-1.02 (m, 1H), 0.96 (d, $J = 6.2$ Hz, 3H), 0.93-0.89 (m, 1H), 0.78 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm) 165.9, 145.9, 143.8, 137.8, 137.1, 137.0, 136.5, 127.8, 126.2, 124.2, 113.9, 76.7, 73.0, 53.6, 47.7, 43.5, 39.9, 33.9, 31.9, 24.03, 24.00, 21.8, 21.3, 19.0.

**General procedure for preparation of ligand immobilized hybrid polymers (LIHBPs)**

Styrene (822 mg, 7.89 mmol, 3 equiv), $p$-styryltrimethoxysilane (590 mg, 2.63 mmol, 1 equiv), diene monomer 1 (1.04 g, 2.63 mmol, 1 equiv) and dimethyl-2,2'-azobis(2-methylpropionate) (v-601$^\circ$) (18.2 mg, 0.079 mmol, 0.03 equiv) were combined in a flask with chloroform (10~16 ml) and the atmosphere was changed to Ar with sonication. The mixture was stirred for 24 h at 80 °C (reflux). The resulting polymer solution was slowly poured into methanol. The solvent was removed by decantation and the residue was dissolved again in chloroform. The polymer solution was slowly poured into methanol again. The same procedure was repeated three times. The precipitated polymer was washed with methanol several times and dried in vacuo to afford the corresponding ligand immobilized hybrid polymers (LIHBPs). The molar ratio of the components was determined by $^1$H NMR analysis.

**Preparation of LIHBCB-Rh(Ag)**

NaBH$_4$ (63.8 mg, 1.68 mmol) in 5 ml of diglyme was added to a solution of LIHBP (250 mg) in diglyme (7 ml) and Ketjenblack (250 mg) dropwise at 0 °C. Then, a solution of [Rh(OAc)$_2$]$_2$ (22.1 mg, 0.05 mmol) or mixture of [Rh(OAc)$_2$]$_2$ (22.1 mg) and AgSbF$_6$ (34.4 mg for Rh/Ag (1:1), 68.8 mg for Rh/Ag (1:2)) in THF (5~10 ml) was added at 0 °C, and it was stirred for overnight at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 °C with stirring for 5 h. The resulting catalyst was filtered, washed several times with isopropyl alcohol and dried in vacuo. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. NaBH$_4$ (63.8 mg) was added to catalyst and this mixture was stirred in diglyme for 2 h at room temperature. The resulting catalyst was washed with water, isopropyl alcohol and DCM several times, and dried in vacuo to afford the desired LIHBCB-Rh(Ag) catalyst (Target loading for Rh : 0.2 mmol/g, actual loading of Rh : 0.17~0.22 mmol/g).

* Carbon black was used for enhancing the stability of metal nanoparticles during the preparation step. Also, high dispersion of metal nanoparticle can be achieved in the presence of carbon black due to its high specific
surface area. In our previous paper, the scanning electron microscopy (SEM) image of CB, polymer-CB composite material are shown; CB has relatively uniform spheres (around 45 nm) and similar structure was observed in polymer-CB composite material with slightly larger spheres (around 55 nm), and the increase observed size of the microsphere is likely derived from the absorption of polymer on the surface of the CB. Schematic image of CB and polymer-CB composite material are shown in below. Although in the absence of CB, metal nanoparticles can be stabilized by polymer, thanks to multiple weak interactions with π-electrons of benzene rings.

Figure S1. Schematic images of CB and polymer-CB composite material

Preparation of HBCB-Rh/Ag (1:2) (Scheme S2)

NaBH₄ (68.4 mg, 1.80 mmol) in 5 ml of diglyme was added to a solution of hybrid polymer (250 mg) in diglyme (7 ml) and Ketjenblack (250 mg) dropwise at 0 °C. Then, a solution of [Rh(OAc)₂]₂ (22.1 mg) and AgSbF₆ (68.8 mg) mixture in THF (5–10 ml) was added at 0 °C, and it was stirred for overnight at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 °C with stirring for 5 h. The resulting catalyst was filtered, washed several times with isopropyl alcohol and dried in vacuo. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. The resulting catalyst was washed with water, isopropyl alcohol and DCM several times, and dried in vacuo to afford the desired HBCB-Rh/Ag (1:2) catalyst (Target loading for Rh : 0.2 mmol/g, actual loading of Rh : 0.17–0.22 mmol/g).
Figure S2. Size distribution of HBCB-Rh/Ag (1:2) (6)

Figure S3. STEM analysis of HBCB-Rh/Ag (1:2) (6)
3. Characterization of LIHBCB-Rh(Ag) catalyst

- Size distribution of LIHBCB-Rh/Ag (1:2) (2f) catalyst (Figure S4)

- STEM, Mapping, and Line analysis

- LIHBCB-Rh catalyst (2b) (Figure S5)
LIHBCB-Rh/Ag (1:1) catalyst (2d) (Figure S6)
LIHCB-Rh/Ag (2:1) catalyst (2e) (Figure S7)
LIHBCB-Rh/Ag (1:2) catalyst (2f) (Figure S8)
After use (1) (LIHBCB-Rh (2b), Table 4 for 5aa, Figure S9)

Lower loading LIHBCB-Rh catalyst (Target loading : 0.02 mmol/g) (Figure S11)

After use (2) (LIHBCB-Rh/Ag (2f), Table 4 for 5ia, Figure S10)
4. General Procedures

General procedure for addition of aryl boronic acids to α,β-unsaturated carbonyl compounds (Table 1, 2 and 3)

LIHBCB-Rh(Ag) catalyst (2) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.45-0.6 mmol, 1.5-2 equiv), substrate (0.3 mmol) (if needed, K$_2$CO$_3$ (0.3 mmol, 1 equiv)), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 °C (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water using a KIRYAMA funnel. The organic layers were washed with brine and dried over Na$_2$SO$_4$ and the solvents were removed in vacuo. The residue was purified by preparative TLC.

General procedure for leaching test

LIHBCB-Rh(Ag) catalyst (2) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.45-0.6 mmol, 1.5-2 equiv), substrate (0.3 mmol) (if needed, K$_2$CO$_3$ (0.3 mmol, 1 equiv)), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 °C (reflux) (using a Carousel system). After the reaction, the mixture was filtered with THF (~10 ml) using an eluting tube with cotton. The filtrate was filtered again with a membrane filter. The final filtrate was massed-up to 25 ml, then it was divided to two portions; 15 ml for isolation, and 10 ml for a leaching test. In the case of the leaching test, 10 ml of filtrate was transferred to a test tube and the solvents were evaporated in an aluminum block under heating (120~150 °C). After removing all the solvents, 0.2 ml of H$_2$SO$_4$ was added and the mixture was heated at 200 °C. To this mixture, HNO$_3$ was added dropwise until it turned transparent. After all HNO$_3$ was evaporated, the solution was cooled to room temperature and was diluted and massed-up to 10 ml with deionized water to afford a leaching test sample. The leaching of metals was determined by ICP-AES analysis.

Recovery and reuse of the catalyst (Table 4)

LIHBCB-Rh(Ag) catalyst (2) (for 5aa : 0.006 mmol of 2b, 1 mol% as Rh / for 5ia : 0.018 mmol of 2f, 2 mol% as Rh), phenylboronic acid (93.6 mg, 0.9 mmol, 1.5 equiv for 5aa / 189.9 mg, 1.8 mmol, 2 equiv for 5ia) and 2-cyclohexenone (57.7 mg (58.2 µl), 0.6 mmol for 5aa) or N-benzylcrotonamide (157.7 mg, 0.9 mmol for 5ia), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 °C (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water, then the organic layer was washed with brine. The organic layers were dried over Na$_2$SO$_4$ and the solvents were removed in vacuo. The residue was purified by preparative TLC. The recovered catalyst was placed in a round-bottom flask (50 ml) and was stirred in a toluene (7 ml)/water (7 ml) solution for 2 h at room temperature. The catalyst was
filtered by a KIRIYAMA funnel and washed with toluene and water. The combined catalyst was dried in vacuo and was used for next run. A reaction scale was adjusted based on the amount of the recovered catalyst.

**Control experiment (Table 5)**

LIHBCB-Rh/Ag (1:2) catalyst (2f) (0.006 mmol, 2 mol% as Rh) and phenylboronic acid (4a) (64.7 mg, 0.6 mmol, 2 equiv) or N-benzylcrotonamide (3i) (52.6 mg, 0.3 mmol, 1 equiv) (none for entry 1, 3i for entry 2, 4a for entries 3 and 4), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution, then the reaction mixture was stirred for 96 h at 100 °C (reflux) (using a Carousel system). After heating for 96 h, phenylboronic acid (4a) (64.7 mg, 0.6 mmol, 2 equiv) and/or N-benzylcrotonamide (3i) (52.6 mg, 0.3 mmol, 1 equiv) (both 3i and 4a for entries 1 and 4, 4a for entry 2, 3i for entry 3) were added to reaction mixture, and it was stirred further 24 h at 100 °C. After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water, then the organic layer was washed with brine. The organic layers were dried over Na₂SO₄ and the solvents were removed in vacuo. The residue was purified by preparative TLC.

**Hot filtration test (Figure 1)**

LIHBCB-Rh/Ag (1:2) catalyst (2f) (0.0045 mmol, 1 mol% as Rh), phenylboronic acid (4a) (0.9 mmol, 2 equiv), substrate 3a or 3e (0.45 mmol), durene (internal standard, 30~35 mg), toluene (1 ml), and water (2 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. After 5 h, catalyst was removed by membrane filter with keeping 100 °C, then filtrate was further heated and stirred for 19 h at 100 °C. During the reaction, aliquots were taken by gas-tight microsyringe (~30 µl) and it was diluted with EtOAc (~3 ml). After wash with small amount of water (~3 ml), GC samples were prepared after passing through Na₂SO₄ and silica short column.

**Preparation of immobilized ligand on polymer/carbon black (S3) (used in Table 6 and Scheme 4) (Scheme S3)**

The solution of LIHBP (250 mg) and Ketjenblack (250 mg) in diglyme (15 ml) was stirred for 1 h at room temperature. After addition of 1 N NaOH (aq., 70 ml) and isopropyl alcohol (70 ml), the mixture was heated at 90 °C with stirring for 5 h. The resulting mixture was filtered, washed several times with isopropyl alcohol and dried in vacuo. Next, the catalyst was heated (no stirring) at 100 °C for 5 h under neat conditions. It was washed
with water, isopropyl alcohol and DCM several times, and dried \textit{in vacuo} to afford the desired immobilized ligand on hybrid polymer/carbon black (HBCB) (S3).

**Reaction with the mixture of Rh NPs and chiral ligand on different support (Scheme 4)**

Rh/Cellulose catalyst (0.0015 mmol, 0.5 mol% as Rh), immobilized ligand on hybrid carbon black (S3) (0.9 mg, 0.000375 mmol, 0.125 mol%), 3-methoxyphenylboronic acid (4c) (82.9 mg, 0.9 mmol, 2 equiv), ethyl-(E)-4-methylcinnamate (3g) (57.1 mg (55.0 µl), 0.6 mmol, 2 equiv), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 °C (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water using a KIRIYAMA funnel. The organic layers were washed with brine and dried over Na$_2$SO$_4$ and the solvents were removed \textit{in vacuo}. Yield was determined by $^1$H NMR analysis in the presence of internal standard (1,1,2,2-tetrachloroethane).

**Procedure for addition of aryl boronic acids to nitroolefin and imine substrates (Table 8)**

LIHBCB-Rh/Ag (1:1) catalyst (2d) (0.003-0.006 mmol, 1-2 mol% as Rh), arylboronic acid (0.6-0.9 mmol, 2-3 equiv), substrate (0.3 mmol), toluene (2 ml for imine, 1.75 ml for nitroolefin), and water (0.25 ml for imine, 0.35 ml for a nitroolefin) were placed in a reaction tube, which was capped with a septum after Ar substitution. The mixture was stirred for 24-48 h at 100 °C (reflux) (using a Carousel system). After the reaction, the catalyst was separated by filtration and washed with EtOAc (20 mL) and water using a KIRIYAMA funnel. The organic phase was separated and was washed with brine. The organic layers were dried over Na$_2$SO$_4$ and the solvents were removed \textit{in vacuo}. The residue was purified by preparative TLC.

**Application to a flow system (Scheme 5)**

LIHBCB-Rh/Ag (1:2) catalyst (2d) (240 mg) and celite (600 mg) were mixed well and a column (10Φ X 5 cm) was packed with this mixture of the catalyst and celite. An aqueous solution of phenylboronic acid (0.1 M) and a toluene solution of 2-cyclohexenone (0.15 M) were flowed into the column using separate pumps (aqueous phase = 70 µl/min, toluene phase = 30 µl/min). These two different solvents were mixed in a T-shape mixer. To prevent evaporation of the solvents in the column, a back pressure controller was used (~0.2 MPa). Each fraction was collected for some hours, and the collected solutions were extracted with EtOAc. After washed with water and brine, the organic layers were dried over Na$_2$SO$_4$ and the solvents were removed \textit{in vacuo}. A yield was determined by $^1$H NMR analysis using an internal standard (1,1,2,2-tetrachloroethane) based on the collected amount of the solvent. The residue was purified by preparative TLC.
5. XPS Analysis & Possible Reaction Mechanism

Preparation of Rh(OH)-diene complex (7) (Scheme S4)

Amide substituted chiral diene (S4, 0.2 mmol, 52.3 mg) and [RhCl(C₂H₄)₂]₂ (0.1 mmol, 38.9 mg) were combined in DCM (30 ml), and mixture was stirred at room temperature for 30 min. After evaporation of DCM, 1N KOH (aqueous solution, 4 ml) and 20 ml of THF were added and it was stirred at room temperature for 1 h. Carbon black (100 mg) was added to this solution, and solvent was evaporated. After dry in vacuo, black solid was kept in glove box.

Reaction with HBCB-Rh/Ag (1:2) together with externally added chiral diene ligand (Scheme S5)

HBCB-Rh/Ag (1:2) catalyst (6) (0.003 mmol, 1 mol% as Rh), phenylboronic acid (65.6 mg, 0.6 mmol, 2 equiv), 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv), chiral diene ligand (S4) in toluene (use stock solution), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. The reaction mixture was stirred for 24 h at 100 °C (reflux) (using a Carousel system). After the reaction, the mixture was filtered with THF (~10 ml) using an eluting tube with cotton. This filtrate was filtered again with a membrane filter. The final filtrate was massed-up to 25 ml, which was divided to two portions; 15 ml for isolation, and 10 ml for a leaching test. In the case of the leaching test, 10 ml of filtrate was transferred to a test tube and the solvents were evaporated in an aluminum block under heating (120~150 °C). After removing all the solvents, 0.2 ml of H₂SO₄ was added and the mixture was heated at 200 °C. To this mixture, HNO₃ was added dropwise until it turned transparent. After all HNO₃ was evaporated, the solution was cooled to room temperature and was diluted and massed-up to 10 ml with deionized water to afford a leaching test sample. For isolation, solvent was evaporated and the residue was purified by preparative TLC.
**XPS Analysis Data**

**Figure S12.** XPS analysis (1) - Rh binding energy (BE) of catalyst 2f

(a) fresh catalyst; (b) in situ sample (1 h); (c) in situ sample (5 h); (d) after use; (e) after 4th use

**Figure S13.** XPS analysis (2) - Ag binding energy (BE) of catalyst 2f

(a) fresh catalyst; (b) in situ sample (1 h); (c) in situ sample (5 h); (d) after use; (e) after 4th use
Figure S14. XPS Analysis (3) - Rh BE of HBCB-Rh/Ag (1:2) catalyst (6) with external added ligand (S4)

(a) fresh catalyst; (b) after use

Figure S15. XPS Analysis (4) - Ag BE of HBCB-Rh/Ag (1:2) catalyst (6) with external added ligand (S4)

(a) fresh catalyst; (b) after use

Figure S16. XPS Analysis (5) -Rh BE of Rh(OH)-diene complex (7)
### Table S1. Binding energy of Rh and Ag

| State                      | (a) Fresh | (b) 1 h  | (c) 5 h  | (d) After | (e) After 4th | Rh(OH)-diene (7) |
|---------------------------|-----------|----------|----------|------------|---------------|-----------------|
| Rh (3p 3/2, eV)           | 496.967   | 497.389  | 497.219  | 496.931    | 496.944       | 497.344         |
| Ag (3d 5/2, eV)           | 373.468   | 373.729  | 373.374  | 373.312    | 373.578       | -               |
| HBCB-Rh/Ag (1:2) (6) + chiral ligand (2.5 mol%) | 367.508   | 367.731  | 367.354  | 367.391    | 367.588       | -               |

| State                      | (a) Before | (b) After |
|---------------------------|------------|-----------|
| Rh (3p 3/2, eV)           | 497.232    | 498.171   |
| Ag (3d 5/2, eV)           | 373.479    | 373.927   |

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6. Reaction Profiles

**Difference in reaction rate of ketone, ester, amide and aldehyde substrates**

LIHBCB-Rh/Ag (1:1 or 1:2) catalyst (2d or 2f) (0.003 mmol, 1 mol% as Rh), phenylboronic acid (4a) (64.5 mg, 0.6 mmol, 2 equiv), 4-methylcinnamyl group containing substrate (0.3 mmol, 1 equiv), dodecane (internal standard, 59–61 mg), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. During the reaction, aliquots were taken by gas-tight microsyringe (10–20 µl) in corresponding time and GC samples were prepared after passing through Na$_2$SO$_4$ and silica short column with EtOAc.

Firstly, reaction was conducted under same conditions; 1 mol% of catalyst, 2 equiv of phenylboronic acid (4a), Tol/H$_2$O (1:2), 100 °C for 24 h. Then, optimization of each reaction was conducted and all the results are shown in Table S2.

**Table S2. Reactivity difference of ketone, ester, amide and aldehyde substrates**

| Substrate | Conditions in Scheme | Optimal conditions |
|-----------|---------------------|--------------------|
| 3c (ketone) | 93% y, 91% ee | 90% y, 98% ee |
| 3g (ester) | 74% y, 97% ee | 90% y, 98% ee |
| 3j (amide) | 69% y, 98% ee | Quant. y, 97% ee |
| 3l (aldehyde) | 55% y, 93% ee | 71% y, 93% ee |
| S5 (carboxylic acid) | No desired product | (1 equiv K$_2$CO$_3$) |

* Yield was determined by isolation. Ee was determined by HPLC analysis.
In all cases, induction period was found in initial 2 h regardless of the kinds of substrate. After the induction period, the initial rate of ketone substrate 3c was faster than that of ester 3g, and in both cases, reactions gradually proceeded in entire 24 h. In the case of ketone 3c and amide 3i, initial rate was similar but the rate of amide 3i decreased more after 9 h. From these results, we concluded that reactivity cannot be simply discussed based on LUMO level of substrates. Lewis basic amides (both substrates and products) can easily coordinate to the catalyst, and release from the catalyst would be difficult. As a result, decrease in the reaction rate of amide in late stage would be derived from product inhibition. Moreover, in previous report{superscript}17, we showed that the rate determining step is different between ester and nitroolefin substrates suggested by reactions in deuterated water. We think that the rate determining step of amide substrates can also be protonation step, unlike ketone or ester substrates. In the case of aldehyde 3l, it showed similar initial reaction rate with ester 3g but the reaction rate decreased after 12 h. We think that small amount of side products derived from aldehyde substrate, such as 1,2-addition outcome, can inhibit the reaction.
**Reaction profile in recovery/reuse of catalyst**

LIHBCB-Rh/Ag (1:2) catalyst (2f) (0.006 mmol, 2 mol% as Rh), phenylboronic acid (4a) (64.5 mg, 0.6 mmol, 2 equiv), N-benzylcrotonamide (3i) (52.6 mg, 0.3 mmol, 1 equiv), dodecane (internal standard, 59–61 mg), toluene (0.7 ml), and water (1.4 ml) were placed in a reaction tube, which was capped with a septum after Ar substitution. During the reaction, aliquots were taken by gas-tight microsyringe (10–20 µl) in corresponding time and GC samples were prepared after passing through Na$_2$SO$_4$ and silica short column with EtOAc.

In the profile of 2nd run and 3rd run, catalyst, which was recovered and treated proper washing method as shown in above (Recovery and reuse of catalyst), was used instead of fresh catalyst.

**Figure S18.** Reaction profile in recovery/reuse of catalyst
7. Reaction Products

(R)-3-Phenylcyclohexanone (5aa)

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and phenylboronic acid (49.6 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5aa (51.1 mg, 98%) as a colorless oil. GC Retention time (Condition I): 21.2 (internal standard (durene)), 21.5 (starting material (2-cyclohexenone)), 36.1 (product). 

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.34 (t, $J = 7.6$ Hz, 2H), 7.27-7.23 (m, 3H), 3.02 (tt, $J = 12.0$, 3.9 Hz, 1H), 2.62-2.59 (m, 1H), 2.56-2.52 (m, 1H), 2.49-2.46 (m, 1H), 2.42-2.37 (m, 1H), 2.18-2.15 (m, 1H), 2.11-2.09 (m, 1H), 1.90-1.76 (m, 2H); 

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 211.0, 144.3, 128.7, 126.6, 48.9, 44.7, 41.2, 32.8, 25.5. The ee value of product was determined on Daicel Chiralpak AD column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 18.0 min [$(S)$-enantiomer], 21.3 min [$(R)$-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature. 

Following the above general procedure (57.7 mg, 94%) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.07 (d, $J = 8.2$ Hz, 2H), 6.80 (d, $J = 8.2$ Hz, 2H), 3.73 (s, 3H), 2.90 (tt, $J = 11.7$, 4.1 Hz, 1H), 2.52-2.49 (m, 1H), 2.44-2.37 (m, 2H), 2.33-2.27 (m, 1H), 2.00-1.98 (m, 1H), 1.78-1.65 (m, 2H); 

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 211.2, 158.2, 136.5, 126.6, 124.9, 114.0, 55.2, 49.2, 43.9, 41.1, 33.0, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 25.8 min [$(S)$-enantiomer], 27.4 min [$(R)$-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature. 

(R)-3-(3-Methoxyphenyl)cyclohexanone (5ac)

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (61.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5ac (58.7 mg, 96%) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.25-7.23 (m, 1H), 6.81 (d, $J = 7.6$ Hz, 1H), 6.78-6.75 (m, 2H), 3.80 (s, 3H), 2.97 (tt, $J = 12.0$, 3.9 Hz, 1H), 2.60-2.56 (m, 1H), 2.53-2.48 (m, 1H), 2.47-2.43 (m, 1H), 2.40-2.34 (m, 1H), 2.17-2.12 (m, 1H), 2.09-2.05 (m, 1H), 1.87-1.74 (m, 2H); 

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 210.9, 159.8, 146.0, 129.6, 118.9, 112.7, 111.6, 55.2, 48.9, 44.7, 41.1, 32.6, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-
propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 27.9 min [(S)-enantiomer], 30.0 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.10

**(R)-3-(2-Methoxyphenyl)cyclohexanone (5ad)**

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and 2-methoxycyclohexylboronic acid (68.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5ad (58.4 mg, 95%) as a colorless oil. 1H NMR (600 MHz, CDCl3): δ (ppm) 7.21-7.16 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.2, 1H), 3.80 (s, 3H), 3.40 (tt, J = 11.7, 3.7 Hz, 1H), 2.58-2.54 (m, 1H), 2.51-2.42 (m, 2H), 2.38-2.33 (m, 2H), 2.02-1.98 (m, 1H), 1.88-1.75 (m, 2H); 13C NMR (150 MHz, CDCl3): δ (ppm) 211.7, 156.6, 132.4, 127.5, 126.5, 120.6, 110.5, 55.2, 47.5, 41.3, 37.9, 30.9, 25.5. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 98:2, flow = 0.5 ml/min by HPLC analysis. Retention times: 20.2 min [(S)-enantiomer], 22.2 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.20

**(R)-3-([1,1'-biphenyl]-4-yl)cyclohexanone (5ae)**

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and 4-biphenylboronic acid (88.7 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 9:1 and 7:3) to provide 5ae (66.8 mg, 89%) as a white solid (Mp. 165-166 °C). 1H NMR (600 MHz, CDCl3): δ (ppm) 7.51-7.48 (m, 4H), 7.35 (t, J = 7.9 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 2.98 (tt, J = 12.0, 3.9 Hz, 1H), 2.57-2.54 (m, 1H), 2.50-2.46 (m, 1H), 2.41-2.38 (m, 1H), 2.34-2.29 (m, 1H), 2.10-2.08 (m, 1H), 2.00-2.03 (m, 1H), 1.84-1.70 (m, 2H); 13C NMR (150 MHz, CDCl3): δ (ppm) 210.9, 143.4, 140.7, 139.6, 128.7, 127.4, 127.2, 127.0, 48.9, 44.4, 41.2, 32.8, 25.5. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times: 17.7 min [(R)-enantiomer], 25.3 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.20

**(R)-3-(4-trifluoromethylphenyl)cyclohexanone (5af)**

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.30 mmol, 1 equiv) and 4-trifluoromethylphenylboronic acid (108.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5af (64.4 mg, 89%) as a colorless oil. 1H NMR (600 MHz, CDCl3): δ (ppm) 7.56 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 3.05 (tt, J = 11.7, 3.8 Hz, 1H), 2.58-2.56 (m, 1H), 2.51-2.45 (m, 2H), 2.38-2.36 (m, 1H), 2.15-2.14 (m, 1H), 2.08-2.06 (m, 1H), 1.88-1.74 (m, 2H); 13C NMR (150 MHz, CDCl3): δ (ppm) 210.1, 148.2, 129.0 (q, J = 32.3 Hz), 127.0, 125.6 (q, J = 3.9 Hz), 124.1 (d, J = 271.7 Hz), 48.5, 44.4, 41.0, 32.5, 25.3. The ee value of product was determined on Daicel Chiralpak OD-H, AS-H connected column with hexane/2-propanol = 90:10, flow = 0.5 ml/min by HPLC analysis. Retention times: 29.8
min [\((R)\)-enantiomer], 32.7 min [\((S)\)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{21}\)

\((R)-3-(4\text{-Fluorophenyl})\text{cyclohexanone (5ag)}\)

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (72.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5ag (52.8 mg, 92%) as a colorless oil.\(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.16-7.15 (m, 2H), 7.00-6.97 (m, 2H), 2.97 (tt, J = 12.0, 3.8 Hz, 1H), 2.56-2.54 (m, 1H), 2.46-2.44 (m, 2H), 2.38-2.32 (m, 1H), 2.13-2.11 (m, 1H), 2.05-2.03 (m, 1H), 1.83-1.73 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 210.6, 161.5 (d, \(J = 244.2\) Hz), 140.0, 127.9 (d, \(J = 7.2\) Hz), 115.4 (d, \(J = 21.7\) Hz), 49.0, 44.0, 41.1, 32.9, 25.4. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 97:3, flow = 1.0 ml/min by HPLC analysis. Retention times: 8.2 min [\((S)\)-enantiomer], 10.1 min [\((R)\)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{22}\)

\((R)-3-(4\text{-acetylphenyl})\text{cyclohexanone (5ah)}\)

Following the above general procedure with 2-cyclohexenone (28.9 mg (29.1 µl), 0.3 mmol, 1 equiv) and 4-acetylphenylboronic acid (97.1 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 7:3) to provide 5ah (58.8 mg, 91%) as a white solid (Mp. 67-68 °C). \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.90 (d, \(J = 8.2\) Hz, 2H), 7.29 (d, \(J = 8.2\) Hz, 2H), 3.05 (tt, \(J = 11.7, 4.0\) Hz, 1H), 2.57-2.56 (m, 4H), 2.52-2.49 (m, 1H), 2.46-2.43 (m, 1H), 2.38-2.35 (m, 1H), 2.15-2.13 (m, 1H), 2.08-2.05 (m, 1H), 1.88-1.75 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 210.2, 197.6, 149.6, 135.8, 128.8, 126.8, 48.4, 44.6, 41.1, 32.4, 26.5, 25.4. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 90:10, flow = 0.6 ml/min by HPLC analysis. Retention times: 26.2 min [\((R)\)-enantiomer], 28.2 min [\((S)\)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{23}\)

\((R)-4-(4\text{-methoxyphenyl})\text{-4-phenylbutan-2-one (5bb)}\)

Following the above general procedure with benzalacetone (44.1 mg, 0.30 mmol, 1 equiv) and 4-methoxyphenylboronic acid (88.1 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide 5bb (66.9 mg, 88%) as a yellowish white solid (Mp. 45-47 °C). \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.27-7.25 (m, 2H), 7.20-7.19 (m, 2H), 7.17-7.12 (m, 3H), 6.80 (d, \(J = 8.2\) Hz, 2H), 4.53 (t, \(J = 7.6\) Hz, 1H) 3.74 (s, 3H), 3.14 (d, \(J = 7.6\) Hz, 2H), 2.06 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 207.0, 158.0, 144.2, 135.9, 128.6, 128.5, 127.5, 126.3, 113.9, 55.2, 49.8, 45.2, 30.6. The ee value of product was determined on Daicel Chiralpak AD-3, OD-H connected column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times:
40.2 min [(S)-enantiomer], 43.3 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.  

(S)-4-(4-Methylphenyl)-4-phenylbutan-2-one (5ca)

Following the above general procedure with (E)-4-(4-methylphenyl)-3-buten-2-one (48.1 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide 5ca (66.2 mg, 93%) as a colorless oil. GC Retention time (Condition I): 12.9 (internal standard (dodecane)), 17.1 (starting material), 24.8 (product). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.30-7.27 (m, 2H), 7.24-7.23 (m, 2H), 7.20-7.17 (m, 1H), 7.14-7.09 (m, 4H), 4.57 (t, $J$ = 7.6 Hz, 1H), 3.18 (d, $J$ = 7.6 Hz, 2H), 2.31 (s, 3H), 2.09 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 207.0, 146.3, 128.5, 126.7, 126.2, 50.8, 36.6, 35.5, 21.9, 7.6. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 0.5 ml/min by HPLC analysis. Retention times: 12.8 min [(S)-enantiomer], 14.5 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.  

(R)-3-Phenylcyclopentanone (5da)

Following the above general procedure with 2-cyclopentenone (24.7 mg (25.3 µl), 0.3 mmol, 1 equiv) and phenylboronic acid (65.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5da (45.3 mg, 94%) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.35 (t, $J$ = 7.6 Hz, 2H), 7.28-7.26 (m, 3H), 3.46-3.40 (m, 1H), 2.67 (dd, $J$ = 17.9, 7.6 Hz, 1H), 2.49-2.43 (m, 2H), 2.35-2.30 (m, 2H), 2.01-1.98 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 218.4, 143.0, 128.7, 126.7, 45.8, 42.2, 38.9, 31.2. The ee value of product was determined on Daicel Chiralpak AS-H column with hexane/2-propanol = 99:1, flow = 0.5 ml/min by HPLC analysis. Retention times: 41.6 min [(R)-enantiomer], 47.5 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.  

(S)-5-Phenylhexan-3-one (5ea)

Following the above general procedure with (E)-4-hexen-3-one (29.5 mg (34.7 µl), 0.3 mmol, 1 equiv) and phenylboronic acid (49.4 mg, 0.45 mmol, 1.5 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5ea (47.4 mg, 90%) as a colorless oil. GC Retention time (Condition I): 15.8 (starting material (hexenone)), 21.2 (internal standard (durene)), 28.2 (product). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.27 (t, $J$ = 7.9 Hz, 2H), 7.20-7.16 (m, 3H), 3.32-3.29 (m, 1H), 2.71 (dd, $J$ = 15.8, 6.9 Hz, 1H), 2.62 (dd, $J$ = 15.8, 7.6 Hz, 1H), 2.35-2.25 (m, 2H), 1.24 (d, $J$ = 6.9 Hz, 3H), 0.97 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 210.5, 146.3, 128.5, 126.7, 126.2, 50.8, 36.6, 35.5, 21.9, 7.6. The ee value of product was determined on Daicel Chiralpak AD-H, AD-3 connected column with hexane/2-propanol = 99.5:0.5, flow = 0.5 ml/min by HPLC analysis. Retention times: 28.2 min
[(S)-enantiomer], 32.2 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.27 (0.3687% Rh leaching, 0.1167% Ag leaching (Rh DL: 0.1496%, Ag DL: 0.0227%))

\((S)-4\text{-Phenylnonan-2-one (5fa)}\)

Following the above general procedure with \((E)-3\text{-nonen-2-one (42.1 mg (49.7 \mu l), 0.3 mmol, 1 equiv) and phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 15:1) to provide 5fa (57.3 mg, 87%) as a colorless oil. \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\): \delta \text{ (ppm) 7.26 (t, } J = 7.6 \text{ Hz, 2H), 7.18-7.14 (m, 3H), 3.11-3.07 (m, 1H), 2.73-2.66 (m, 2H), 1.99 (s, 3H), 1.61-1.52 (m, 2H), 1.22-1.08 (m, 6H), 0.80 (t, } J = 6.9 \text{ Hz, 3H); } ^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\): \delta \text{ (ppm) 208.0, 144.6, 128.4, 127.4, 126.3, 50.9, 41.3, 36.4, 31.7, 30.6, 27.0, 22.5, 14.0. The ee value of product was determined on Daicel Chiralpak OJ-H column with hexane/2-propanol = 99:1, flow = 0.25 ml/min by HPLC analysis. Retention times: 26.5 min [(S)-enantiomer], 29.2 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.28

\textbf{Ethyl \((S)-3\text{-phenyl-3-\((p\text{-tolyl)propanoate (5ga)}\)

Following the above general procedure with ethyl-(E)-4-methylcinnamate (57.1 mg (55.0 \mu l), 0.3 mmol, 1 equiv), phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv) and \text{K}_2\text{CO}_3 (41.5 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 19:1) to provide 5ga (85.8 mg, quant.) as a colorless oil. \textit{GC Retention time (Condition II):} 12.9 (internal standard (dodecane)), 18.8 (starting material), 25.9 (product). \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\): \delta \text{ (ppm) 7.19-7.16 (m, 4H), 7.08-7.03 (m, 5H), 4.43 (t, } J = 7.9 \text{ Hz, 1H), 3.95 (q, } J = 7.1 \text{ Hz, 2H), 2.95 (d, } J = 8.2 \text{ Hz, 2H), 2.21 (s, 3H), 1.03 (t, } J = 7.2 \text{ Hz, 3H); } ^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\): \delta \text{ (ppm) 171.9, 143.7, 140.5, 136.0, 129.2, 128.5, 127.6, 127.5, 126.4, 60.4, 46.6, 40.9, 21.0, 14.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 7.6 min [(R)-enantiomer], 11.6 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.11

\textbf{Ethyl \((R)-3-(3\text{-methoxyphenyl)-3-\((p\text{-tolyl)propanoate (5gc)}\)

Following the above general procedure with ethyl-(E)-4-methylcinnamate (57.1 mg (55.0 \mu l), 0.3 mmol, 1 equiv), 3-methoxyphenylboronic acid (82.1 mg, 0.6 mmol, 2 equiv) and \text{K}_2\text{CO}_3 (41.8 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5gc (81.1 mg, 91%) as a colorless oil. \(^1\text{H} \text{NMR (600 MHz, CDCl}_3\): \delta \text{ (ppm) 7.17 (t, } J = 7.9 \text{ Hz, 1H), 7.12 (d, } J = 7.6 \text{ Hz, 2H), 7.07 (d, } J = 7.6 \text{ Hz, 2H), 6.82 (d, } J = 7.6 \text{ Hz, 1H), 6.78-6.76 (m, 1H), 6.71-6.70 (m, 1H), 4.47 (t, } J = 8.2 \text{ Hz, 1H), 4.02 (q, } J = 7.1 \text{ Hz, 2H), 3.75 (s, 3H), 3.00 (d, } J = 7.6 \text{ Hz, 2H), 2.28 (s, 3H), 1.11 (t, } J = 7.2 \text{ Hz, 3H); } ^{13}\text{C} \text{NMR (150 MHz, CDCl}_3\): \delta \text{ (ppm) 171.8, 159.6, 145.4, 140.3, 136.0, 129.4, 129.2, 127.5, 120.0, 113.7, 111.4, 60.4, 55.1, 46.6, 40.8, 21.0, 14.1. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 0.5 ml/min by HPLC analysis. Retention times: 34.5 min [(S)-enantiomer],
Ethyl (S)-3-(3-methoxyphenyl)-3-(thiophen-2-yl)propanoate (5hc)

Following the above general procedure with ethyl (E)-3-(thiophen-2-yi)acrylate (54.7 mg (48.1 μl), 0.3 mmol, 1 equiv), 3-methoxyphenylboronic acid (82.2 mg, 0.6 mmol, 2 equiv) and K₂CO₃ (41.6 mg, 0.3 mmol, 1 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5hc (63.7 mg, 73%) as a yellowish oil. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.20 (t, J = 7.9 Hz, 1H), 7.12 (d, J = 4.8 Hz, 1H), 6.87-6.83 (m, 4H), 6.75 (d, J = 8.2 Hz, 1H), 4.72 (t, J = 7.6 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.08 (dd, J = 15.1, 8.2 Hz, 1H), 3.00 (dd, J = 15.1, 8.2 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃); δ (ppm) 171.2, 159.7, 147.3, 144.7, 129.6, 126.6, 124.1, 124.0, 119.8, 113.5, 112.2, 60.6, 55.2, 42.8, 42.2, 14.1. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 17.2 min [(R)-enantiomer], 18.5 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.¹¹

(S)-N-Benzyl-3-phenylbutanamide (5ia)

Following the above general procedure with N-benzyl crotonamide (52.7 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (65.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to provide 5ia (67.8 mg, 89%) as a white solid (Mp. 70-71 °C). GC Retention time (Condition II): 12.9 (internal standard (dodecane)), 20.1 (starting material), 28.5 (product). ¹H NMR (600 MHz, CDCl₃); δ (ppm) 7.22-7.12 (m, 8H), 6.94-6.93 (m, 2H), 5.63 (brs, 1H), 4.28 (dd, J = 14.8, 5.8 Hz, 1H), 4.19 (dd, J = 14.4, 5.5 Hz, 1H), 3.25-3.24 (m, 1H), 2.37 (d, J = 7.6 Hz, 2H), 1.24 (d, J = 6.9 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃); δ (ppm) 171.5, 145.7, 138.1, 128.6, 128.5, 127.5, 127.3, 126.8, 126.4, 45.8, 43.3, 37.0, 21.8. The ee value of product was determined on Daicel Chiralpak AD-3 column with hexane/2-propanol = 80:20, flow = 0.5 ml/min by HPLC analysis. Retention times: 10.8 min [(S)-enantiomer], 12.2 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.²²

(S)-N-Benzyl-3-phenyl-3-(p-tolyl)propanamide (5ja)

Following the above general procedure with (E)-N-benzyl-4′-methylcinnamamide (75.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (64.5 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to provide 5ja (88.6 mg, 90%) as a white solid (Mp. 115-117 °C). GC Retention time (Condition II): 12.9 (internal standard (dodecane)), 33.2 (starting material), 41.1 (product). ¹H NMR (600 MHz, CDCl₃); δ (ppm) 7.28-7.18 (m, 8H), 7.13 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.87 (q, J = 3.0 Hz, 2H), 5.55 (brs, 1H), 4.56 (t, J = 7.9 Hz, 1H), 4.29 (q, J = 3.0 Hz, 2H), 2.91 (d, J = 8.2 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (150 MHz, CDCl₃); δ (ppm) 170.1, 143.8, 140.5, 137.9, 136.0, 129.3, 128.6, 128.4, 127.7, 127.6, 127.4, 127.2, 126.4, 47.1,
43.5, 43.3, 21.0. The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 80:20, flow = 0.5 ml/min by HPLC analysis. Retention times: 18.6 min [(R)-enantiomer], 20.1 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.28

(R)-3-(4-Methoxyphenyl)-3-phenylpropanal (5kb)

Following the above general procedure with trans-cinnamaldehyde (39.7 mg (37.9 µl), 0.3 mmol, 1 equiv) and 4-methoxyphenylboronic acid (81.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 5:1) to provide 5kb (46.4 mg, 64%) as a yellowish oil. $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 9.71 (t, J = 1.7 Hz, 1H), 7.29-7.13 (m, 7H), 6.85-6.81 (m, 2H), 4.56 (t, $J$ = 7.6 Hz, 1H), 3.75 (s, 3H), 3.12 (dd, $J$ = 7.9, 1.7 Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 201.2, 158.2, 143.6, 135.3, 128.7, 127.6, 126.6, 114.1, 55.2, 49.5, 44.2. The ee value of corresponding alcohol (obtained by reduction with NaBH$_4$ in DCM/MeOH) was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 92:8, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.1 min [(R)-enantiomer], 15.9 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.29

(R)-3-(4-Fluorophenyl)-3-phenylpropanal (5kg)

Following the above general procedure with trans-cinnamaldehyde (39.7 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (74.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5kg (48.1 mg, 70%) as a yellowish oil. $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 9.72 (t, $J$ = 1.7 Hz, 1H), 7.33-7.15 (m, 7H), 6.98-6.95 (m, 2H), 4.61 (t, $J$ = 7.6 Hz, 1H), 3.14 (dd, $J$ = 7.6, 2.1 Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 200.6, 161.5 (d, $J$ = 245.6 Hz), 143.0, 139.0, 129.2 (d, $J$ = 7.2 Hz), 128.8 127.6, 126.8, 115.5 (d, $J$ = 21.7 Hz), 49.5, 44.1. The ee value of corresponding alcohol (obtained by reduction with NaBH$_4$ in DCM/MeOH) was determined on Daicel Chiralpak OJ-H column with hexane/2-propanol = 90:10, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.6 min [(S)-enantiomer], 18.9 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.29

(S)-3-Phenyl-3-(p-tolyl)propanal (5la)

Following the above general procedure with (E)-4-methylcinnamaldehyde (43.9 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (66.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 10:1) to provide 5la (47.8 mg, 71%) as a yellowish oil. $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 9.71 (t, $J$ = 1.7 Hz, 1H), 7.28-7.16 (m, 5H), 7.11-7.08 (m, 4H), 4.57 (t, $J$ = 7.9 Hz, 1H), 3.12 (dd, $J$ = 7.9, 1.7 Hz, 2H), 2.28 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ (ppm) 201.2, 143.4, 140.2, 136.3, 129.4, 128.7, 127.62, 127.55, 126.6, 49.4, 44.6, 20.9. The ee value of corresponding alcohol (obtained by reduction with NaBH$_4$ in DCM/MeOH) was determined on Daicel Chiralpak AS-3 column with hexane/2-propanol = 98:2, flow = 1.0 ml/min by HPLC analysis. Retention times:
The ee value of product was determined on Daicel Chiralpak AD
Hz, 139.0, 137.0, 128.6, 128.1
2H), 2.04
4.48
= 7.2 Hz, 2H), 7.21
Those reported in literature.

Ethyl (S)-3-(p-tolyl)butanoate (5mi)

Following the above general procedure with ethyl crotonate (34.3 mg, 0.3 mmol, 1 equiv) and
4-methylphenylboronic acid (81.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was
purified by preparative TLC (hexane / ethyl acetate, 9:1) to provide 5mi (53.8 mg, 87%) as a
colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.09 (s, 4H), 4.06 (q, $J = 7.3$ Hz, 2H),
3.26-3.20 (m, 1H), 2.57 (dd, $J = 15.1$, 6.9 Hz, 1H), 2.50 (dd, $J = 15.1$, 8.2 Hz, 1H), 2.30 (s, 3H),
1.26 (d, $J = 6.9$ Hz, 3H), 1.18 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 172.5, 142.7, 135.8, 129.1, 126.6,
60.2, 43.1, 36.1, 21.9, 21.0, 14.2. The ee value of product was determined on Daicel Chiralpak AD-3 column
with hexane/2-propanol = 99:1, flow = 1.0 ml/min by HPLC analysis. Retention times: 5.1 min [(S)-
enantiomer], 5.4 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those
reported in literature.$^{31}$

tert-Butyl (S)-3-(3,4-dichlorophenyl)-3-phenylpropanoate (5na)

Following the above general procedure with tert-butyl (E)-3-(3,4-dichlorophenyl)acrylate (82.0 mg, 0.3 mmol, 1 equiv)
and phenylboronic acid (99.1 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC
(hexane / ethyl acetate, 10:1) to provide 5na (89.5 mg, 85%) as a yellowish stick oil. $^1$H NMR (600 MHz,
CDCl$_3$): $\delta$ (ppm) 7.28-7.12 (m, 7H), 7.00 (dd, $J = 8.2$, 2.1 Hz, 1H), 4.37 (t, $J = 7.9$ Hz, 1H), 2.85 (d, $J = 8.2$
Hz, 2H), 1.23 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ (ppm) 170.5, 143.9, 142.4, 132.4, 130.43, 130.36, 129.7,
128.7, 127.6, 127.2, 126.9, 81.0, 46.5, 41.7, 27.9. The ee value of product was determined on Daicel Chiralpak
OD-H column with hexane/2-propanol = 99:1, flow = 0.2 ml/min by HPLC analysis. Retention times: 35.2 min
[(R)-enantiomer], 39.9 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those
reported in literature.$^{32}$

(R)-1-Benzyl-4-(4-fluorophenyl)piperidin-2-one (5og)

Following the above general procedure with N-benzyl-Δ$^3$-piperidein-2-one (56.2 mg, 0.3 mmol, 1 equiv)
and 4-fluoro phenyl boronic acid (116.3 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC (DCM / acetone, 49:1) to
provide 5og (64.9 mg, 76%) as a white solid (Mp. 110-112 °C). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.27 (t, $J$
= 7.2 Hz, 2H), 7.21 (d, $J = 7.6$ Hz, 4H), 7.09-7.07 (m, 2H), 6.94 (t, $J = 8.6$ Hz, 2H), 4.67 (d, $J = 14.4$ Hz, 1H),
4.48 (d, $J = 14.4$ Hz, 1H), 3.26-3.17 (m, 2H), 3.09-2.99 (m, 1H), 2.78-2.70 (m, 1H), 2.48 (dd, $J = 17.9$, 11.0 Hz,
2H), 2.04-1.96 (m, 1H), 1.87-1.80 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm) 169.0, 161.6 (d, $J = 245.6$
Hz), 139.0, 137.0, 128.6, 128.1, 127.9 (d, $J = 8.7$ Hz), 127.4, 115.5 (d, $J = 20.2$ Hz), 50.0, 46.2, 39.6, 37.9, 30.2.
The ee value of product was determined on Daicel Chiralpak AD-H column with hexane/2-propanol = 90:10,
flow = 0.5 ml/min by HPLC analysis. Retention times: 25.0 min [(S)-enantiomer], 26.5 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.33

(R)-1-Fluoro-4-(2-nitro-1-phenylethyl)benzene (10ag)

Following the above general procedure with nitrostyrene (44.8 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (74.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (toluene / hexane, 2:1) to provide 10ag (61.9 mg, 84%) as a colorless oil. 1H NMR (600 MHz, CDCl3): δ (ppm) 7.32 (t, J = 7.6 Hz, 2H), 7.26-7.24 (m, 1H), 7.20-7.18 (m, 4H), 7.02-6.98 (m, 2H), 4.95-4.93 (m, 2H), 4.91-4.86 (m, 1H); 13C NMR (150 MHz, CDCl3): δ (ppm) 138.9, 134.9 (d, J = 2.9 Hz), 129.3 (d, J = 8.7 Hz), 129.1, 127.7, 127.5, 115.9 (d, J = 20.2 Hz), 79.2, 48.2. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 11.0 min [(S)-enantiomer], 18.8 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.34

(R)-1-Chloro-4-(2-nitro-1-phenylethyl)benzene (10aj)

Following the above general procedure with nitrostyrene (44.8 mg, 0.3 mmol, 1 equiv) and 4-chlorophenylboronic acid (86.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (toluene / hexane, 2:1) to provide 10aj (80.4 mg, quant.) as a colorless oil. 1H NMR (600 MHz, CDCl3): δ (ppm) 7.27-7.17 (m, 5H), 7.13-7.09 (m, 4H), 4.88 (d, J = 8.2 Hz, 2H), 4.81 (t, J = 8.2 Hz, 1H); 13C NMR (150 MHz, CDCl3): δ (ppm) 138.7, 137.7, 133.5, 129.2, 129.1, 129.0, 127.8, 127.5, 79.0, 48.3. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 14.9 min [(S)-enantiomer], 22.7 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.34

(R)-1-Methyl-2-(2-nitro-1-phenylethyl)benzene (10ak)

Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (81.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide 5mc (75.6 mg, 88%) as a colorless oil. 1H NMR (600 MHz, CDCl3): δ (ppm) 7.31 (t, J = 7.9 Hz, 2H), 7.26-7.18 (m, 7H), 5.12 (t, J = 7.9 Hz, 1H), 4.98-4.93 (m, 2H), 2.32 (s, 3H); 13C NMR (150 MHz, CDCl3): δ (ppm) 138.7, 137.1, 136.5, 131.3, 128.9, 128.0, 127.5, 126.4, 125.8, 79.2, 45.0, 19.6. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 18.6 min [(S)-enantiomer], 29.0 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.35
(S)-1-Methoxy-3-([1-(4-methoxyphenyl)-2-nitroethyl]benzene (10bc)

Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (82.9 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide 10bc (80.5 mg, 93%) as a colorless oil. ^1H NMR (600 MHz, CDCl₃): δ (ppm) 7.24-7.21 (m, 1H), 7.14 (d, J = 8.9 Hz, 2H), 6.84-6.73 (m, 5H), 4.94-4.88 (m, 2H), 4.80 (t, J = 8.2 Hz, 1H), 3.76 (s, 6H); 13C NMR (150 MHz, CDCl₃): δ (ppm) 159.9, 158.9, 141.1, 131.0, 130.0, 128.7, 119.7, 114.3, 113.9, 112.4, 79.4, 55.23, 55.18, 48.2. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 50:50, flow = 1.0 ml/min by HPLC analysis. Retention times: 19.8 min [(S)-enantiomer], 37.3 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.17

(R)-2-([1-(3-Methoxyphenyl)-2-nitroethyl]thiophene (10cc)

Following the above general procedure with 2-(2-thienyl)nitrostyrene (46.6 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (124.4 mg, 0.9 mmol, 3 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide 10cc (77.5 mg, 98%) as a yellowish oil. ^1H NMR (600 MHz, CDCl₃): δ (ppm) 7.27-7.24 (m, 1H), 7.21 (d, J = 5.5 Hz, 1H), 6.93 (t, J = 4.5 Hz, 1H), 6.90 (d, J = 2.7 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.82-6.81 (m, 2H), 5.09 (t, J = 7.9 Hz, 1H), 4.96-4.90 (m, 2H), 3.77 (s, 3H); 13C NMR (150 MHz, CDCl₃): δ (ppm) 160.0, 142.2, 140.2, 130.1, 127.0, 125.2, 125.1, 119.6, 113.7, 113.1, 79.8, 55.2, 44.6. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 50:50, flow = 1.0 ml/min by HPLC analysis. Retention times: 13.3 min [(R)-enantiomer], 36.3 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.17

(R)-1-([1-Cyclohexyl-2-nitroethyl]-3-methoxybenzene (10dc)

Following the above general procedure with 1-methoxy-4-(2-nitroethenyl)benzene (53.8 mg, 0.3 mmol, 1 equiv) and 3-methoxyphenylboronic acid (81.8 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 20:1) to provide 10dc (75.6 mg, 88%) as a colorless oil. ^1H NMR (600 MHz, CDCl₃): δ (ppm) 7.21 (t, J = 7.9 Hz, 1H), 6.76 (dd, J = 7.9, 1.7 Hz, 1H), 6.71 (d, J = 6.2 Hz, 1H), 6.65 (s, 1H), 4.76-4.72 (m, 1H), 4.60-4.55 (m, 1H), 3.77 (s, 3H), 3.23-3.19 (m, 1H), 1.76 (t, J = 15.5 Hz, 2H), 1.65-1.53 (m, 3H), 1.46 (d, J = 12.4 Hz, 1H), 1.23-1.19 (m, 1H), 1.13-0.98 (m, 3H), 0.89-0.82 (m, 1H); 13C NMR (150 MHz, CDCl₃): δ (ppm) 159.6, 140.4, 129.5, 120.4, 114.5, 112.1, 78.8, 55.2, 50.2, 40.9, 30.9, 30.6, 26.13, 26.07. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 60:40, flow = 1.0 ml/min by HPLC analysis. Retention times: 5.7 min [(R)-enantiomer], 9.6 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.17
(S)-4-Methyl-N-(phenyl(p-tolyl)methyl)benzenesulfonylamide (11aa)

Following the above general procedure with N-(4-methylbenzylidene)-4-methylbenzenesulfonylamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11aa (40.7 mg, 50%) as a white solid (Mp. 120-122 °C). 1H NMR (600 MHz, CDCl3): δ (ppm) 7.49 (d, J = 6.9 Hz, 2H), 7.13-7.12 (m, 3H), 7.07-7.03 (m, 4H), 6.95-6.89 (m, 4H), 5.45 (d, J = 6.9 Hz, 1H), 4.98 (d, J = 6.2 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H); 13C NMR (150 MHz, CDCl3): δ (ppm) 143.1, 140.7, 137.6, 137.3, 137.2, 129.3, 129.2, 128.4, 127.4, 127.3, 127.23, 127.16, 61.1, 21.4, 21.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 15.9 min [(S)-enantiomer], 24.2 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.36 (No Rh leaching (UDL), No Ag leaching (UDL) (Rh DL: 04910%, Ag DL: 0.1380%))

(R)-N-((4-Fluorophenyl)(p-tolyl)methyl)-4-methylbenzenesulfonylamide (11ag)

Following the above general procedure with N-(4-methylbenzylidene)-4-methylbenzenesulfonylamide (82.4 mg, 0.3 mmol, 1 equiv) and 4-fluorophenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11ag (59.1 mg, 53%) as a white solid (Mp. 117-118 °C). 1H NMR (600 MHz, CDCl3): δ (ppm) 7.53 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.08-7.06 (m, 2H), 6.99 (d, J = 7.6 Hz, 2H), 6.91 (d, J = 7.6 Hz, 2H), 6.86 (t, J = 8.9 Hz, 2H), 5.48 (d, J = 6.9 Hz, 1H), 5.22 (d, J = 6.9 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H); 13C NMR (150 MHz, CDCl3): δ (ppm) 162.0 (d, J = 245.6 Hz), 143.3, 137.5, 137.4, 137.2, 136.5 (d, J = 2.9 Hz), 129.33, 129.29, 129.0 (d, J = 8.7 Hz), 127.15, 127.13, 115.2 (d, J = 21.7 Hz), 60.4, 21.4, 21.0. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 20.6 min [(R)-enantiomer], 27.5 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.37

(S)-N-((4-Methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonylamide (11ba)

Following the above general procedure with N-(4-methoxybenzylidene)-4-methylbenzenesulfonylamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11ba (40.7 mg, 50%) as a white solid (Mp. 131-133 °C). 1H NMR (600 MHz, CDCl3): δ (ppm) 7.47 (d, J = 8.2 Hz, 2H), 7.13-7.09 (m, 3H), 7.06-7.01 (m, 4H), 6.91 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.2 Hz, 2H), 5.44 (d, J = 6.9 Hz, 1H), 5.23 (d, J = 6.9 Hz, 1H), 3.66 (s, 3H), 2.29 (s, 3H); 13C NMR (150 MHz, CDCl3): δ (ppm) 158.9, 143.0, 140.7, 137.4, 132.7, 129.3, 128.6, 128.4, 127.4, 127.2, 127.1, 113.8, 60.8, 55.2, 21.4. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 26.2 min [(S)-enantiomer], 35
41.8 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{36}\)

**\((S)-4\)-Methyl-\(N\)-(naphthalen-2-yl)(phenyl)methylbenzenesulfonamide (11ca)**

Following the above general procedure with \(N\)-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11ca (40.7 mg, 50%) as a white solid (Mp. 130-131 °C). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.75-7.72 (m, 1H), 7.57 (d, \(J = 8.9\) Hz, 1H), 7.63-7.60 (m, 1H), 7.46 (d, \(J = 8.2\) Hz, 2H), 7.42 (s, 1H), 7.42 (q, \(J = 3.4\) Hz, 2H), 7.22-7.18 (m, 3H), 7.18-7.12 (m, 3H), 6.93 (d, \(J = 8.2\) Hz, 2H), 5.65 (d, \(J = 7.6\) Hz, 1H), 5.36 (d, \(J = 7.6\) Hz, 1H), 2.17 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 143.2, 140.4, 137.5, 137.3, 133.0, 132.6, 129.3, 128.6, 128.5, 127.9, 127.7, 127.5, 127.2, 126.3, 126.2, 126.1, 125.1, 61.4, 21.3. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 33.9 min [(R)-enantiomer], 39.4 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{37}\)

**\((S)-4\)-Methyl-\(N\)-(naphthalen-1-yl)(phenyl)methylbenzenesulfonamide (11da)**

Following the above general procedure with \(N\)-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11da (40.7 mg, 50%) as a white solid (Mp. 145-147 °C). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.79 (t, \(J = 8.2\) Hz, 2H), 7.71 (d, \(J = 8.2\) Hz, 1H), 7.49 (d, \(J = 8.2\) Hz, 2H), 7.42 (t, \(J = 7.2\) Hz, 1H), 7.37 (t, \(J = 7.6\) Hz, 1H), 7.26 (t, \(J = 7.3\) Hz, 1H), 7.22 (d, \(J = 7.6\) Hz, 1H), 7.19-7.11 (m, 5H), 7.04 (d, \(J = 8.2\) Hz, 2H), 6.29 (d, \(J = 7.6\) Hz, 1H), 5.16 (d, \(J = 6.9\) Hz, 1H), 2.33 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 143.1, 140.2, 137.2, 135.4, 133.9, 130.4, 129.2, 128.8, 128.6, 127.6, 127.5, 127.1, 126.5, 126.1, 125.7, 125.0, 123.4, 58.5, 21.4. The ee value of product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 90:10, flow = 1.0 ml/min by HPLC analysis. Retention times: 19.3 min [(R)-enantiomer], 24.4 min [(S)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\(^{38}\)

**\((S)-4\)-Methyl-\(N\)-(phenyl)(thiophen-2-yl)methylbenzenesulfonamide (11ea)**

Following the above general procedure with \(N\)-(4-methylbenzylidene)-4-methylbenzenesulfonamide (82.4 mg, 0.3 mmol, 1 equiv) and phenylboronic acid (63.6 mg, 0.6 mmol, 2 equiv). The crude reaction mixture was purified by preparative TLC (hexane / ethyl acetate, 3:1) to provide 11ea (40.7 mg, 50%) as a white solid (Mp. 141-143 °C). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.56 (d, \(J = 8.2\) Hz, 2H), 7.21 (t, \(J = 3.1\) Hz, 3H), 7.18-7.12 (m, 5H), 6.83-6.80 (m, 1H), 6.67-6.64 (m, 1H), 5.77 (d, \(J = 6.9\) Hz, 1H), 5.11 (d, \(J = 7.6\) Hz, 1H), 2.36 (s, 3H); \(^1\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) (ppm) 144.8, 143.2, 140.1, 137.2, 129.3, 128.5, 127.9, 127.1, 126.7, 126.1, 125.7, 57.4, 21.5. The ee value of
product was determined on Daicel Chiralpak OD-H column with hexane/2-propanol = 95:5, flow = 1.0 ml/min by HPLC analysis. Retention times: 20.0 min [(S)-enantiomer], 28.4 min [(R)-enantiomer]. This is a known compound and the spectral data are identical to those reported in literature.\textsuperscript{36}
8. NMR & HPLC Charts
Copolymer 1

(L: x : 5 : 1 : 3 : 1)
**5aa**, condition: AD, 0.5 ml/min, Hex/IPA = 98:2, 254 nm

| Peak# | Ret. Time | Area   | Height | Area%  |
|-------|-----------|--------|--------|--------|
| 1     | 17.207    | 816831 | 27599  | 49.924 |
| 2     | 20.397    | 819526 | 25681  | 50.076 |

| Peak# | Ret. Time | Area   | Height | Area%  |
|-------|-----------|--------|--------|--------|
| 1     | 18.039    | 15312  | 506    | 1.030  |
| 2     | 21.338    | 1485433| 40883  | 98.980 |
5ab, condition: AD-H, 0.5 ml/min, Hex/IPA = 98:2, 220 nm
5ac, condition: AD-H, 0.5 ml/min, Hex/IPA = 98:2, 220 nm
5ad, condition: AD-H, 0.5 ml/min, Hex/IPA = 98:2, 254 nm

Det. A 254 nm

| Peak# | Ret. Time | Area   | Height | Area% |
|-------|-----------|--------|--------|-------|
| 1     | 20.550    | 123870 | 59517  | 49.985|
| 2     | 22.557    | 1250127| 54637  | 50.015|

Det. A 254 nm

| Peak# | Ret. Time | Area   | Height | Area% |
|-------|-----------|--------|--------|-------|
| 1     | 20.241    | 5531   | 280    | 1.681 |
| 2     | 22.210    | 325572 | 1439   | 98.319|
5ae, condition: AD-3, 1.0 ml/min, Hex/IPA = 98:2, 254 nm

| Peak# | Ret. Time | Area   | Height | Area% |
|-------|-----------|--------|--------|-------|
| 1     | 17.212    | 8562225| 435742 | 50.026|
| 2     | 22.912    | 8553330| 177747 | 49.974|

| Peak# | Ret. Time | Area   | Height | Area% |
|-------|-----------|--------|--------|-------|
| 1     | 17.561    | 29718765| 1268066| 98.819|
| 2     | 25.345    | 355149 | 5158   | 1.181|
5af, condition: OD-H\_AS-H (connected column), 0.5 ml/min, Hex/IPA = 90:10, 220 nm

![HPLC chromatogram](image)

**Peak Table**

| PeakID | Ret. Time | Area   | Height | Area % | Height % |
|--------|-----------|--------|--------|--------|----------|
| 1      | 29.997    | 50197227 | 873420 | 49.696 | 50.718   |
| 2      | 32.688    | 50819020 | 948895 | 50.304 | 49.282   |
| Total  |           | 101008148 | 1722115 | 100.000 | 100.000 |

![HPLC chromatogram](image)

**Peak Table**

| PeakID | Ret. Time | Area   | Height | Area % | Height % |
|--------|-----------|--------|--------|--------|----------|
| 1      | 29.807    | 77387259 | 1161403 | 99.637 | 98.402   |
| 2      | 32.706    | 7452774  | 18655  | 0.963  | 1.598    |
| Total  |           | 79199833 | 1180256 | 100.000 | 100.000 |
5ag, condition: AD-H, 1.0 ml/min, Hex/IPA = 97:3, 254 nm

Det A 254 nm

| Peak | Ret. Time | Area  | Height | Area % |
|------|-----------|-------|--------|--------|
| 1    | 8.142     | 88690 | 10147  | 49.719 |
| 2    | 10.132    | 89692 | 83304  | 50.281 |

Det A 254 nm

| Peak | Ret. Time | Area  | Height | Area % |
|------|-----------|-------|--------|--------|
| 1    | 8.169     | 25191 | 2955   | 0.857  |
| 2    | 10.113    | 293520| 26414  | 99.143 |
5ah, condition: AD-3, 0.6 ml/min, Hex/IPA = 90:10, 254 nm
5bb, condition: AD-3_OD-H (connected column), 1.0 ml/min, Hex/IPA = 98:2, 220 nm
**5ca, condition**: OD-H, 0.5 ml/min, Hex/IPA = 90:10, 230 nm

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**Chart 1**

| Peak# | Ret. Time | Area  | Height | Area% |
|-------|-----------|-------|--------|-------|
| 1     | 12.817    | 4013223 | 248960 | 49.778 |
| 2     | 14.536    | 4049031 | 216989 | 50.222 |

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**Chart 2**

| Peak# | Ret. Time | Area  | Height | Area% |
|-------|-----------|-------|--------|-------|
| 1     | 12.745    | 23543846 | 1233384 | 95.466 |
| 2     | 14.495    | 1118171 | 62863  | 4.534  |
5da, condition: AS-H, 0.5 ml/min, Hex/IPA = 99:1, 220 nm
**5ea**, condition: AD-H_AD-3 (connected column), 0.5 ml/min, Hex/IPA = 99.5:0.5, 220 nm
**5fa**, condition: OJ-H, 0.25 ml/min, Hex/IPA = 99:1, 254 nm

| Peak | Ret. Time | Area   | Height | Area % |
|------|-----------|--------|--------|--------|
| 1    | 27.499    | 719940 | 20908  | 49.470 |
| 2    | 29.799    | 735377 | 19004  | 50.530 |

| Peak | Ret. Time | Area   | Height | Area % |
|------|-----------|--------|--------|--------|
| 1    | 26.461    | 4681759 | 121601 | 98.516 |
| 2    | 29.146    | 70530  | 1706   | 1.484  |
5ga, condition: OD-H, 1.0 ml/min, Hex/IPA = 99:1, 254 nm

### Data Sheet

**Peak 1**
- Ret. Time: 7.532
- Area: 276217
- Height: 25291
- Area%: 49.770

**Peak 2**
- Ret. Time: 11.331
- Area: 278673
- Height: 16010
- Area%: 50.221

**Peak 2**
- Ret. Time: 11.616
- Area: 447990
- Height: 24731
- Area%: 98.496
5gc, condition : OD-H, 0.5 ml/min, Hex/IPA = 99:1, 220 nm

PeakTable

| Peak# | Ret. Time | Area     | Height    | Area %  | Height % |
|-------|-----------|----------|-----------|---------|----------|
| 1     | 34.688    | 27896217 | 610224    | 49.734  | 61.733   |
| 2     | 51.709    | 28194059 | 375267    | 50.266  | 38.267   |
| Total |           | 56000276 | 988491    | 100.000 | 100.000  |

PeakTable

| Peak# | Ret. Time | Area     | Height    | Area %  | Height % |
|-------|-----------|----------|-----------|---------|----------|
| 1     | 34.497    | 719026   | 16390     | 1.073   | 1.886    |
| 2     | 50.619    | 66271654 | 852563    | 98.927  | 98.114   |
| Total |           | 66990679 | 868953    | 100.000 | 100.000  |
5hc, condition: OD-H, 1.0 ml/min, Hex/IPA = 99:1, 220 nm
5ia, condition: AD-3, 0.5 ml/min, Hex/IPA = 80:20, 220 nm
5ja, condition: AD-H, 0.5 ml/min, Hex/IPA = 80:20, 220 nm

| Peak# | Ret. Time | Area | Height | Area% |
|-------|-----------|------|--------|-------|
| 1     | 18.118    | 7057143 | 332256 | 49.662 |
| 2     | 20.695    | 7153191 | 286737 | 50.338 |

| Peak# | Ret. Time | Area | Height | Area% |
|-------|-----------|------|--------|-------|
| 1     | 18.641    | 368813 | 17844  | 0.803 |
| 2     | 20.086    | 4557226 | 1748730 | 99.197 |
Corresponding alcohol of 5kb, condition: AD-H, 1.0 ml/min, Hex/IPA = 92:8, 254 nm
Corresponding alcohol of 5kg, condition: OJ-H, 1.0 ml/min, Hex/IPA = 90:10, 254 nm

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 14.665    | 1289518 | 42065  | 49.689 |
| 2    | 19.233    | 1305834 | 28886  | 50.311 |

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 14.625    | 69487  | 2601   | 3.322 |
| 2    | 18.845    | 2022099 | 44690  | 96.678 |
Corresponding alcohol of 51a, condition: AS-3, 1.0 ml/min, Hex/IPA = 98:2, 220 nm

| Peak# | Ret. Time | Area    | Height | Area%  |
|-------|-----------|---------|--------|--------|
| 1     | 31.783    | 18965371| 522031 | 49.936 |
| 2     | 34.9301   | 19014301| 451583 | 50.064 |

| Peak# | Ret. Time | Area    | Height | Area%  |
|-------|-----------|---------|--------|--------|
| 1     | 31.467    | 262585  | 8105   | 3.254  |
| 2     | 34.514    | 7806116 | 201511 | 96.746 |
5ml, condition: AD-3, 1.0 ml/min, Hex/IPA = 99:1, 254 nm

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 5.057     | 304326| 56919  | 49.803|
| 2    | 5.283     | 306734| 51038  | 50.197|

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 5.116     | 532128| 90960  | 96.295|
| 2    | 5.410     | 17617 | 2690   | 3.205 |
5na, condition: OD-H, 0.2 ml/min, Hex/IPA = 99:1, 220 nm

Peak Table

| Peak # | Ret. Time | Area   | Height | Area %  | Height % |
|--------|-----------|--------|--------|---------|----------|
| 1      | 35.253    | 549,829 | 13,047 | 49.833  | 53.164   |
| 2      | 40.202    | 553,516 | 11,499 | 50.167  | 46.846   |
| Total  |           | 1,103,346 | 24,546 | 100.000 | 100.000  |

1 PDA Multi 1 / 220 nm 4 nm

Peak Table

| Peak # | Ret. Time | Area   | Height | Area %  | Height % |
|--------|-----------|--------|--------|---------|----------|
| 1      | 36.194    | 265,347 | 835,24 | 1.475   | 2.288    |
| 2      | 39.934    | 177,290 | 271,300| 98.525  | 97.712   |
| Total  |           | 442,637 | 1,106,540 | 100.000 | 100.000  |

1 PDA Multi 1 / 220 nm 4 nm
5og, condition: AD-H, 0.5 ml/min, Hex/IPA = 90:10, 217 nm

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| Peak# | Ret. Time | Area       | Height | Area%  |
|-------|-----------|------------|--------|--------|
| 1     | 27.660    | 6466860    | 224399 | 49.933 |
| 2     | 29.092    | 6083052    | 206259 | 50.067 |

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| Det. A 217 nm | Peak# | Ret. Time | Area       | Height | Area%  |
|--------------|-------|-----------|------------|--------|--------|
|              | 1     | 24.959    | 1529033    | 42016  | 0.721  |
|              | 2     | 26.446    | 190855080  | 2820710| 99.279 |
**10ag**, condition: OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm

| Peak | Ret. Time | Area   | Height | Area%  |
|------|-----------|--------|--------|--------|
| 1    | 11.105    | 381004 | 20413  | 50.055 |
| 2    | 19.232    | 380165 | 11322  | 49.945 |

| Peak | Ret. Time | Area   | Height | Area%  |
|------|-----------|--------|--------|--------|
| 1    | 10.986    | 471657 | 250462 | 6.640  |
| 2    | 18.812    | 733729 | 196670 | 93.960 |
10aj, condition: OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm

| Peak# | Ret. Time | Area   | Height | Area % |
|-------|-----------|--------|--------|--------|
| 1     | 14.982    | 1024220| 37184  | 50.180 |
| 2     | 22.960    | 1016851| 24190  | 49.820 |

| Peak# | Ret. Time | Area     | Height | Area % |
|-------|-----------|----------|--------|--------|
| 1     | 14.906    | 4333693  | 157462 | 4.245  |
| 2     | 22.677    | 95501968 | 20653797 | 95.755 |
10ak, condition: OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm

| Peak# | Ret. Time | Area   | Height | Area % |
|-------|-----------|--------|--------|--------|
| 1     | 18.783    | 4933550| 141964 | 49.97% |
| 2     | 29.637    | 4938709| 89048  | 50.03% |

| Peak# | Ret. Time | Area   | Height | Area % |
|-------|-----------|--------|--------|--------|
| 1     | 18.553    | 972954 | 29362  | 1.24%  |
| 2     | 29.020    | 77824551| 1321852| 98.76% |
10bc, condition: OD-H, 1.0 ml/min, Hex/IPA = 50:50, 254 nm

| Peak | Ret. Time | Area  | Height | Area % |
|------|-----------|-------|--------|--------|
| 1    | 17.660    | 276091| 8321   | 50.172 |
| 2    | 34.277    | 274193| 4123   | 49.828 |

| Peak | Ret. Time | Area  | Height | Area % |
|------|-----------|-------|--------|--------|
| 1    | 19.773    | 6090752| 146819 | 93.915 |
| 2    | 37.285    | 394544 | 5047   | 6.085  |
10 cc, condition: OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm

**Peak #**  | **Retention Time** | **Area**   | **Height**    | **Area%**  \\
---|-------------------|------------|---------------|------------
1 | 12.672           | 3491267    | 1522254       | 49.810     \\
2 | 34.365           | 3517955    | 56294         | 80.190     \\

**Peak #**  | **Retention Time** | **Area**   | **Height**    | **Area%**  \\
---|-------------------|------------|---------------|------------
1 | 13.283           | 81121134   | 3367999       | 92.460     \\
2 | 36.254           | 6511643    | 98634         | 7.531     \\

129
10dc

\[\text{Chemical Structure Image}\]
**10dc**, condition: OD-H, 1.0 ml/min, Hex/IPA = 60:40, 210 nm

| Peak # | Ret. Time | Area | Height | Area% |
|--------|-----------|------|--------|-------|
| 1      | 5.654     | 13493426 | 1570824 | 49.774 |
| 2      | 9.573     | 136159201 | 817895  | 50.226 |

| Peak # | Ret. Time | Area | Height | Area% |
|--------|-----------|------|--------|-------|
| 1      | 5.676     | 19356830 | 2176812 | 91.139 |
| 2      | 9.553     | 1881911  | 113765  | 8.861  |
**11aa**, condition: OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm

![Graph 1](image1.png)

| Peak | Ret. Time | Area   | Height | Area% |
|------|-----------|--------|--------|-------|
| 1    | 16.286    | 1579911| 44945  | 49.905|
| 2    | 23.912    | 1585895| 31519  | 50.095|

![Graph 2](image2.png)

| Peak | Ret. Time | Area   | Height | Area% |
|------|-----------|--------|--------|-------|
| 1    | 15.928    | 6007234| 156834 | 99.126|
| 2    | 24.187    | 48677  | 1016   | 0.804|
**11ag**, condition: OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm

| Peak | Ret. Time | Area   | Height | Area%  |
|------|-----------|--------|--------|--------|
| 1    | 21.079    | 5529902 | 104154 | 49.921 |
| 2    | 26.916    | 5547462 | 15052  | 50.079 |

Det A 254 nm

| Peak | Ret. Time | Area   | Height | Area%  |
|------|-----------|--------|--------|--------|
| 1    | 20.546    | 14700259 | 255067 | 99.927 |
| 2    | 27.452    | 1145501  | 1883   | 0.773  |

Det A 254 nm
11ba, condition: OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 26.921    | 3964277 | 57798  | 69.931|
| 2    | 41.985    | 3975310 | 40306  | 50.069|

| Peak | Ret. Time | Area  | Height | Area% |
|------|-----------|-------|--------|-------|
| 1    | 26.201    | 5275539 | 77653  | 99.231|
| 2    | 41.838    | 40864  | 500    | 0.769 |
**11ca**, condition: OD-H, 1.0 ml/min, Hex/IPA = 95:5, 220 nm

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 33.893    | 1276422  | 17289   | 50.323  | 53.819   |
| 2     | 39.415    | 1260049  | 14836   | 49.677  | 46.181   |
| Total |           | 2536471  | 32125   | 100.000 | 100.000  |

| Peak# | Ret. Time | Area     | Height  | Area %  | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1     | 33.937    | 69188    | 1286    | 1.373   | 1.706    |
| 2     | 39.439    | 6407565  | 74099   | 98.627  | 98.294   |
| Total |           | 6496753  | 75385   | 100.000 | 100.000  |
**11da**, condition: OD-H, 1.0 ml/min, Hex/IPA = 90:10, 210 nm

| Peak# | Ret. Time | Area   | Height | Area%  |
|-------|-----------|--------|--------|--------|
| 1     | 19.323    | 7513210| 148882 | 49.012 |
| 2     | 25.704    | 7539670| 107338 | 50.988 |

| Peak# | Ret. Time | Area   | Height | Area%  |
|-------|-----------|--------|--------|--------|
| 1     | 19.257    | 2334486| 46076  | 1.016  |
| 2     | 24.417    | 227498991| 2808571| 98.984 |
**11ea**, condition: OD-H, 1.0 ml/min, Hex/IPA = 95:5, 254 nm

**Table 1**

| Peak# | Ret. Time | Area   | Height  | Area%  |
|-------|-----------|--------|---------|--------|
| 1     | 20.378    | 552.1297 | 192222  | 49.904 |
| 2     | 28.197    | 554.2584 | 17815   | 40.096 |

**Table 2**

| Peak# | Ret. Time | Area   | Height  | Area%  |
|-------|-----------|--------|---------|--------|
| 1     | 19.971    | 232.16974 | 454005  | 98.685 |
| 2     | 28.410    | 336007 | 5935   | 1.315  |
9. Supplementary Information References

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