Supporting Information for

Design of Polymer Supported Chiral Cobalt Catalyst for Heterogeneous Enantioselective C–H Activations

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1. General procedures

Commercial reagents were purchased from Adamas-beta, Aladdin, Bidepharm, Energy Chemical and TCI. All air-sensitive manipulations were carried out with standard Schlenk techniques under argon. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm and 365 nm). HPLC analyses were performed on Agilent 1260 with Daicel chiral columns. NMR spectra were recorded on 400 MHz Bruker spectrometers. Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of CDCl₃ (§ 7.26) for ¹H NMR and CDCl₃ (§ 77.1) for ¹³C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets), dd (double of doublet). Coupling constants were reported in Hertz (Hz). Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Micromeritics Tristar system, and the samples were degassed for 10 h at 393 K before the measurements. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. The total pore volume at P/Po = 0.950. The pore size distribution curves were obtained from the desorption branches using the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) was performed using a Hitachi SU8020. Transmission electron microscope (TEM) images were performed using a Tecnai G2 F30 S-Twin. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (METTLER TOLEDO TGA/DSC 3+), the sample was heated at the rate of 10 k min-1 from room temperature up to 1073 K under a nitrogen atmosphere. FT-IR spectra were recorded on a Thermo fisher Nicolet iS50 FT-IR spectrometer. The content of Co was determined by inductively coupled plasma-Mass Spectrometry (ICP-MS). The X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific K-Alpha XPS with the Al Ka irradiation.

2. Preparation of polymer-support catalyst

2.1. Synthesis of L1



Ligand L1 was synthesized according reference 1: ZnCl₂ (1.14 g, 8.5 mmol, 0.1 eq) was added to a 250 mL round-bottomed flask, toluene (150 mL) was added to the flask under N₂. L-amino

alcohol (126 mmol, 1.5 eq) and 5-bromo-2-hydroxybenzonitrile (84.0 mmol, 1.0 eq) were added sequentially. The mixture was heated at reflux (oil bath 130 °C) under N₂ and maintained at this temperature for 12 h. The reaction progress was monitored by TLC. After the starting material 5-bromo-2-hydroxybenzonitrile was consumed, toluene was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (HE/EtOAc/DCM = 15:1:1 v/v/v) to afford the ligand L1 as a pink solid (22.63g, 85% yield).

¹<u>H NMR (600 MHz, CDCl₃)</u> δ 12.14 (s, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.48 (dd, J = 9.0, 3.0 Hz, 1H), 7.38 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 6.94 (d, J = 9.0 Hz, 1H), 5.48 (dd, J = 10.2, 8.4 Hz, 1H), 4.81 (dd, J = 10.2, 8.4 Hz, 1H), 4.27 (t, J = 8.4 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 165.3, 159.1, 141.2, 136.3, 130.6, 128.9, 128.1, 126.5, 118.8, 112.1, 110.3, 77.3, 77.1, 76.9, 74.3, 68.9.

2.2. Synthesis of monomer 1



The mixture of (4-vinylphenyl)boronic acid (555 mg, 1.5 equiv.), $Pd(OAc)_2$ (29 mg, 5 mol%), Ad_2BnP (98 mg, 10 mmol%), L1 (800 mg, 2.5 mmol), K_2CO_3 (759 mg, 2.2 equiv.), toluene (10 mL) and water (0.33 mL) was heated to 80 °C under N₂. After cooling to room temperature, the mixture was extracted with DCM (3 × 40 mL). The combined organic phase was washed with brine, dried over MgSO₄, and concentrated. The residue was purified by column chromatography over silica gel to give **monomer 1** (white solid, 563 mg, 66% yield).²

(Several impurity peaks appeared in the NMR spectrum, making it less than perfect due to the presence of adamantyl-based impurities that are difficult to remove.)

¹<u>H NMR (600 MHz, CDCl3)</u> δ 7.89 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 3.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.17 – 7.14 (m, 2H), 7.08 – 7.06 (m, 2H), 7.00 (dd, J = 7.8, 2.4 Hz, 1H), 6.61 – 6.58 (m, 1H), 6.51 (d, J = 7.8 Hz, 1H), 6.48 (d, J = 9.0 Hz, 1H), 5.61 (dd, J = 17.4, 1.2 Hz, 1H), 5.05 (dd, J = 10.8, 1.2 Hz, 1H), 4.44 – 4.36 (t, 9.6 Hz, 1H). ¹³C NMR (150 MHz, CDCl3) δ 169.2, 142.7,

138.2, 137.6, 136.4, 132.1, 132.0, 128.2, 128.1, 127.4, 126.2, 125.7, 123.4, 111.6, 110.5, 103.1, 77.2, 77.0, 76.8, 73.9, 67.2.

2.3. General procedure for the synthesis of polymer-support catalysis Co@POP-Salox-1-Co@POP-Salox-8



A mixture of **monomer 1** (170 mg, 0.5 mmol), divinylbenzene (80% mixture of isomers, 406 mg, 2.5 mmol), THF (7.5 mL) and AIBN (7 mg, 0.04 mmol) was degassed under vacuum and saturated with argon three times. After that, the mixture was stirred for 30 min at room temperature. The temperature was then raised to 70 °C and the reaction mixture was stirred vigorously for 24 h. The resulting polymers were filtered and washed with MeOH, EtOH and acetone, followed by drying under reduced pressure at 40 °C to give **POP-Salox** as pale-yellow power. $Co(OAc)_2 \cdot 4H_2O$ (0.5 mmol) and **POP-Salox** was added to 'BuOH (2 mL) at room temperature. The reaction mixture was stirred for 2 h. After dried under vacuum, the result solids were washed thoroughly with EtOH for three times. Then dried under vacuum to yield **Co@POP-Salox-1** as brown solid. Elemental analysis (EA) of **Co@POP-Salox-1**: N 0.73%, C 86.78%, H 7.514%.

ICP-MS: Co 2.84%

Co@POP-Salox-2-Co@POP-Salox-8 were synthesized under similar conditions but different ratios of starting materials.

catalysts	ratio (monomer: styrene: DVB)	N%	monomer incorporation (%)
Co@POP-Salox-1	1:0:5	0.73	51.75
Co@POP-Salox-2	1:0:1	1.58	53.23
Co@POP-Salox-3	1:1:2	1.08	54.47
Co@POP-Salox-4	1:0:3	0.88	46.02
Co@POP-Salox-5	1:1:5	0.64	50.13
Co@POP-Salox-6	1:0:7	0.77	68.91

Table S1. Ratios of starting materials and monomer incorporation of catalysts

Co@POP-Salox-7	1:0:8	0.67	66.19
Co@POP-Salox-8	1:0:9	0.54	58.37

2.4. General procedure for the synthesis of Polymer-support catalysis Co@POP-Salox-9



To oven dried vial equipped with stirring bars containing Co(OAc)₂·4H₂O (0.5 mmol) at room temperature was added the **monomer 1** (170 mg, 0.5 mmol) and then 'BuOH (2 mL). This mixture was stirred for 2 h before the resulting clear solution was filtrated and the solvent was evaporated by a pump to provide dark brown solid **monomer 2**. The mixture of **monomer 2**, divinylbenzene (80% mixture of isomers, 406 mg, 2.5 mmol), THF (7.5 mL) and AIBN (7 mg, 0.04 mmol) was degassed under vacuum and saturated with argon three times. After that, the mixture was stirred for 30 min at room temperature. The temperature was then raised to 70 °C and the reaction mixture was stirred vigorously for 24 h. The resulting polymers were filtered and washed with MeOH, EtOH and acetone, followed by drying under reduced pressure at 40 °C to give **Co@POP-Salox-9** as black power (38.99% of monomer incorporation).

Elemental analysis (EA) of Co@POP-Salox-9: N 0.55%, C 89.31%, H 8.137%.

ICP-MS: Co % 0.48%

3. Preparation of substrates

3.1. Synthesis of substituted aryl phosphinamides 1a, 1y and 1z

1a, **1y** and **1z** were synthesized according to previously published works.³⁻⁴ The procedure was showed as following:



Step 1: I₂ (0.05 g, 0.2 mmol) was added to a stirred extra dry THF (20 mL) solution containing magnesium turnings (0.50 g, 20 mmol) under nitrogen protection. Then, a fraction of aryl bromide (10.0 mmol) in THF (extra dry, 5 mL) was added slowly to the mixture and heated to initiate the reaction. When the color of I₂ faded, the remainder of aryl bromide (10 mmol) was added dropwise over the course of 20 min at room temperature. After 4 h, diethyl phosphate (0.8 ml, 6 mmol) in THF (2 mL) was added slowly into the reaction mixture at 0 °C, then stirred at 80 °C for 4 h. After the reaction was completed, the reaction mixture was cooled to 0°C, acidifying the reaction mixture to pH = 1 by diluted HCl (4 N). The solution was evaporated under reduced pressure and the residue was extracted with 20 mL EtOAc three times. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo to give crude product.

Step 2: Hydrogen peroxide (30%, 5.0 mL) was added dropwise to a suspension of crude product in aqueous NaOH (5 N, 4 mL) at 0 °C, and the mixture was stirred for 3 h at 100 °C. After the solution was cooled to room temperature, 20 mL water was added to the mixture and extracted with 20 mL EtOAc. The aqueous phase was separated and hydrochloric acid (4 N) was added dropwise to aqueous phase at 0 °C until no white solid was precipitated out. The white solid was filtered out and dry in the oven as crude phosphonic.

Step 3: A suspension of phosphonic acid and thionyl chloride in toluene (10 mL) was stirred at 80 °C for 3 h. After removal of thionyl chloride and toluene under reduced pressure, the residue was re-dissolved in toluene (5 mL), which was added to a mixture of 8-aminoquinoline (5 mmol), N, N dimethyl-4-aminopyridine (0.2 mmol), and triethylamine (6 mmol) in toluene (5 mL) at 0 °C under N₂. Then, the solution was stirred at 110 °C for 24 h. After removal of the volatiles under reduced pressure, the residue was dissolved in DCM (20 mL) and washed with saturated ammonium chloride (25 mL × 2). Combined organic phase was dried over anhydrous Na₂SO₄ and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product.

3.2. Synthesis of substituted allene 4a

$$Ph \xrightarrow{Ph} Ph + Et_{3}N \xrightarrow{THF} Ph$$

The substituted allene (**4a**) were synthesized according to literature procedures⁷. To a solution of prop-2-yn-1-ol (600 μ L, 10.0 mmol) and triethylamine (2.1 mL,15 mmol, 1.5 equiv.) in dry THF (30 mL) was added chlorodiphenylphosphine (2.7 mL, 15.0 mmol, 1.5 equiv.) dropwise at -78 °C. After the addition, the cooling bath was removed, and the reaction mixture was allowed for warming up to room temperature. After complete conversion the mixture was filtered off. Evaporation of the solvent and flash chromatography on silica gel (eluent: petroleum ether/ether) afforded the product as white solid (1.2 g, 50 % yield).

3.3. Synthesis of benzamide substrates 7a



The benzamide substrates (7a) were synthesized according to literature procedures⁵. To a solution of carboxylic acid derivative (4 mmol, 1.0 equiv.) and DMF (2-3 drops) in dry DCM was added oxalyl chloride (5.2 mmol, 1.3 equiv.) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 6 h, and then concentrated in vacuo to afford the crude acyl chloride, which was used in next step without further purification. A solution of 8-aminoquinoline derivative (3.2 mmol, 0.8 equiv.) and Et₃N (4.4 mmol, 1.1 equiv.) in dichloromethane was added dropwise to the acyl chloride solution at 0 °C. The resulting mixture was warmed to room temperature and stirred for 12 h. Then the mixture was quenched with saturated NaHCO₃ solution and extracted with DCM for three times. The combined organic layer was dried over Na₂SO₄. The concentrated residue was purified by flash column chromatography on silica gel (PE: EA = 5:1) to give the amide.

3.4. Synthesis of ferroceneamide substrates 9a



The ferroceneamide substrates (**9a**) were synthesized according to literature procedures⁶. To a solution of ferrocenecarboxylic acid (10 mmol, 1.0 equiv.) in DCM (30 mL) was added oxalyl chloride (1.7 mL, 20 mmol) and a drop of N,N-dimethylformamide. The reaction mixture was stirred at room temperature for 6-12 h. Then the solvent was removed under reduced pressure. The substituted ferrocenecarboxylic chloride was directly used without purification in the next step. A solution of ferrocenecarboxylic chloride in DCM (30 mL) was added dropwise to a solution of 8-aminoquinoline (9.5 mmol, 0.95 equiv.) and Et₃N (3.0 equiv., 30 mmol) in DCM (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. Then the reaction mixture was quenched with ice-cold water and extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄ and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography to give **9a** as dark orange solid.

4. Complete reaction data

4.1. Optimization of reaction conditions

Ph	$P = \frac{1}{N} + Ph = \frac{1}{N}$	Ph Co@POP-Salox-1 Mn(OAc) ₂ ·4H ₂ O (1.0 eq.) NaOPiv (2.0 eq.), solvent (3 mL) 80 °C, Air, 48 h	Ph O Ph Ph Ph Ph 3a
Entry	Solvent	yields	ee value
1	'BuOH	95%	99%
2	ⁱ PrOH	45%	92%
3	MeOH	71%	80%
4	EtOH	89%	91%
5	1,4-Dioxane	trace	
6	THF	trace	

Table S2. Optimization of reaction conditions: screening of solvent ^a

^a Reactions were run with 1a (0.1 mmol), 2a (1.5 eq.), Co catalyst (5.0 mol % Co content),

 $Mn(OAc)_2 \cdot 4H_2O(1.0 \text{ eq.})$ and NaOPiv (2.0 eq.) in corresponding solvent (3 mL) at 80 °C for 48 h under air. The *ee* value is determined by HPLC analysis.

 \wedge

$1a \qquad 2a$		Co@POP-Salox-1 Mn(OAc) ₂ ·4H ₂ O (1.0 eq.) NaOPiv (2.0 eq.), 'BuOH (3 mL) T °C, Air, 48 h	Ph Ph Ph Ph 3a
Entry	Temperature	yields	<i>ee</i> value
1 (repeated)	80 °C	95%	99%
2	70 °C	95%	99%
3	60 °C	45%	99%
4 ^b	60 °C	80%	99%

Table S3. Optimization of reaction conditions: screening of temperature ^a

^a Reactions were run with **1a** (0.1 mmol), **2a** (1.5 eq.), Co catalyst (5.0 mol % Co content), Mn(OAc)₂·4H₂O(1.0 eq.) and NaOPiv (2.0 eq.) in 'BuOH (3 mL) at corresponding temperature for 48 h under air. The *ee* value is determined by HPLC analysis. ^b Reaction for 72 h.

Table S4. Optimization of reaction conditions: screening of oxidants ^a

Ph P H H N N	+ PhPh Co@POP-Sal oxidant, NaOPiv (2 ^t BuOH (3 mL), 70 °C, 2a	20x-1 2.0 eq.) Air, 48 h	Ph 0 Ph Ph N Ph 3a
Entry	Oxidant	yields	ee value
1 (repeated)	Mn(OAc)2·4H2O (1.0 eq.)	95%	99%
2	Mn(OAc) ₃ ·4H ₂ O (1.0 eq.)	95%	98%
3	$O_2(1 \text{ atm})$	N.R.	-
4 ^b	$O_2(1 \text{ atm})$	95%	0%
5°	Ag ₂ CO ₃ (1.0 eq.)	96%	99%

^a Reactions were run with **1a** (0.1 mmol), **2a** (1.5 eq.), Co catalyst (5.0 mol % Co content), oxidant and NaOPiv (2.0 eq.) in 'BuOH (3 mL) at 70 °C for 48 h under air. The *ee* value is determined by HPLC analysis. ^b HFIP as the solvent. ^c The reaction system is turbid, and the catalyst is difficult to recover.

4.2. General procedure for enantioselective C-H annulation of phosphinic amide



Phosphinic amide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol), **Co@POP-Salox-1** (5.0 mol % Co content), Mn(OAc)₂·4H₂O (0.1 mmol), NaOPiv (0.2 mmol) and 'BuOH (3 mL) were added to an oven dried vial equipped with stirring bars. Then, the vial was instantly placed in a heating block set at 70 °C under air for 48 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na₂CO₃, and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product.

Data of compounds

(S)-1,3,4-triphenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3a):



The 99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 20.899 min, t (minor) = 28.134 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.82 (dd, J = 4.4, 1.6 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.67 – 7.65 (m, 1H), 7.49 (dd, J = 14.0, 7.6 Hz, 1H), 7.38 (t, J = 7.6

Hz, 1H), 7.31 - 7.11 (m, 9H), 7.09 - 7.04 (m, 2H), 7.00 - 6.93 (m, 4H), 6.56 - 6.52 (m, 3H). ¹³C <u>NMR (100 MHz, CDCl_3)</u> δ 149.3, 144.5 (d, $J_{CP} = 3.6$ Hz), 142.6, 139.3 (d, $J_{CP} = 3.6$ Hz), 138.7, 137.6 (d, $J_{CP} = 2.3$ Hz), 136.6 (d, $J_{CP} = 4.0$ Hz), 135.5, 133.4 (d, $J_{CP} = 10.5$ Hz), 132.4, 131.5 (d, $J_{CP} = 2.9$ Hz), 131.4 (d, $J_{CP} = 2.9$ Hz), 131.4 (d, $J_{CP} = 1.6$ Hz), 131.0, 130.9, 130.2 (d, $J_{CP} = 124.8$ Hz), 128.2, 127.8, 127.4, 127.0 (d, $J_{CP} = 13.5$ Hz), 126.5, 126.4, 126.3, 125.8, 125.7 (d, $J_{CP} = 14.6$ Hz), 125.4, 124.4 (d, $J_{CP} = 129.3$ Hz), 121.0, 117.8 (d, $J_{CP} = 7.3$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

<u>(S)-3,4-Bis(4-methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphos-phinine 1</u> oxide (3b):



The 98% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 7.693 min, t (major) = 9.475 min. ¹H NMR (400 MHz, CDCl₃) δ 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.83 – 7.69 (m, 3H), 7.52 – 7.36 (m, 2H), 7.25 (s, 1H), 7.22 – 7.13 (m, 6H), 7.11

-7.04 (m, 1H), 6.99 - 6.93 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 6.09 (d, J = 8.4 Hz, 2H), 3.70 (s, 3H), 3.37 (s, 3H). ¹³<u>C NMR (100 MHz, CDCl_3)</u> δ 157.8, 157.5, 149.2, 144.5 (d, $J_{CP} = 3.5$ Hz), 142.6, 139.8 (d, $J_{CP} = 4.5$ Hz), 137.9 (d, $J_{CP} = 2.4$ Hz), 135.5, 133.4, 133.3, 132.2, 131.9 (d, $J_{CP} = 140.2$ Hz), 131.4 (d, $J_{CP} = 3.0$ Hz), 131.3 (d, $J_{CP} = 2.9$ Hz), 131.3, 131.2, 130.8 (d, $J_{CP} = 12.7$ Hz), 129.5 (d, $J_{CP} = 4.0$ Hz), 128.2, 127.3, 127.0 (d, $J_{CP} = 14.6$ Hz), 126.5 (d, $J_{CP} = 13.2$ Hz), 125.5, 125.4, 124.4 (d, $J_{CP} = 129.4$ Hz), 120.9, 117.4 (d, $J_{CP} = 7.3$ Hz), 113.2, 111.3, 55.1, 54.6. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-phenyl-2-(quinolin-8-yl)-3,4-bis(4-(trifluoromethyl)phenyl)-2H-

benzo[c][1,2]azaphosphinine 1-oxide (3c):



The >99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 9.434 min, t (minor) = 11.558 min. <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.82 (d, *J* = 4.0 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.74 (td, *J* = 13.0, 11.4, 4.6 Hz, 3H), 7.56 – 7.37 (m, 6H), 7.36 – 7.28 (m, 2H), 7.24 – 7.15

(m, 2H), 7.10 (p, J = 7.4 Hz, 4H), 6.99 (dd, J = 7.8, 3.4 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 144.2 (d, $J_{CP} = 2.4$ Hz), 142.2, 141.5, 139.9, 138.2, 137.0, 135.7, 133.4 (d, $J_{CP} = 10.0$ Hz), 132.7, 131.7 (d, $J_{CP} = 2.4$ Hz), 131.4, 131.2-131.1(m), 130.3, 129.1-128.5(m), 128.3, 127.9, 127.2, 127.0, 126.4-126.1(m), 125.5, 125.4, 123.0 (d, $J_{CP} = 4.0$ Hz), 121.3. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3,4-Bis(4-bromophenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphos-phinine 1oxide (3d):



The 98% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 12.198 min, t (major) = 15.849 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.80 (d, *J* = 4.0 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.78 – 7.68 (m, 3H), 7.53 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.28 – 7.22 (m, 1H), 7.20

 $-7.07 \text{ (m, 6H), 6.95 (td, <math>J = 7.6, 3.6 \text{ Hz}, 2\text{H}), 6.85 (d, J = 8.0 \text{ Hz}, 2\text{H}), 6.73 (d, J = 8.4 \text{ Hz}, 2\text{H}). \frac{13}{2}C}$ **NMR (100 MHz, CDCl₃)** δ 149.4, 144.2 (d, $J_{CP} = 3.4 \text{ Hz}), 141.5, 138.7 (d, <math>J_{CP} = 4.4 \text{ Hz}), 137.4,$

137.2 (d, $J_{CP} = 2.4 \text{ Hz}$), 135.7, 135.4 (d, $J_{CP} = 3.8 \text{ Hz}$), 134.0, 133.5 (d, $J_{CP} = 10.6 \text{ Hz}$), 132.4, 131.6 (d, $J_{CP} = 6.7$ Hz), 131.3 (d, $J_{CP} = 2.6$ Hz), 131.1 (d, $J_{CP} = 12.0$ Hz), 129.4, 128.3, 127.8, 127.1 (d, $J_{CP} = 13.6 \text{ Hz}$, 126.3 (d, $J_{CP} = 26.4 \text{ Hz}$), 126.2 (d, $J_{CP} = 3.2 \text{ Hz}$), 126.0, 125.5, 121.2, 121.0, 120.8, 116.9 (d, $J_{CP} = 7.4$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3,4-Diethyl-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3e):



The >99% ee was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 13.888 min, t (major) = 17.064 min; ¹H NMR (400 MHz, CDCl₃) δ 8.78 (dd, J = 4.0, 1.6 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.96 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 (dd, J = 8.0, 4.8 Hz, 1H), 7.63 – 7.50 (m, 4H), 7.35 – 7.27 (m, 3H), 7.17 (td, J = 7.6, 2.8 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.92 (td, J = 7.6, 3.2 Hz, 2H), 2.78 (q, J = 7.6) Hz, 2H), 2.53-2.43 (m, 1H), 1.85-1.76 (m, 1H), 1.33 (t, J = 7.6 Hz, 3H), 0.97 (t, J = 7.6 Hz, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 145.3 (d, J_{CP} = 3.7 Hz), 142.2, 139.0 (d, J_{CP} = 4.3 Hz), 137.4, 135.8, 133.3 (d, J_{CP} =10.4 Hz), 131.4, 131.2, 130.8 (d, J_{CP} = 12.7 Hz), 130.6, 128.5, 127.4, 126.9, 126.8 (d, *J*_{CP} = 13.4 Hz), 125.8, 124.9, 124.8, 123.6, 123.5, 121.2, 114.1 (d, *J*_{CP} = 8.4 Hz), 24.8, 22.4, 15.0, 13.3. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-phenyl-3,4-dipropyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3f):

The 99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 6.192 min, t (major) = 11.085 min; ¹H NMR (400 **MHz**, **CDCl**₃) δ 8.77 (d, *J* = 4.0 Hz, 1H), 8.03 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.96 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (dd, J = 8.4, 5.2 Hz, 1H), 7.66 7.51 (m, 4H), 7.36-7.26 (m,

3H), 7.17 (tdd, J = 7.6, 2.8, 0.8 Hz, 1H), 7.09-7.05 (m, 1H), 6.91 (td, J = 8.0, 3.2 Hz, 2H), 2.71-2.67 (m, 2H), 2.47-2.39 (m, 1H), 2.53-2.44 (m, 1H), 1.85-1.66 (m, 3H), 1.59-1.40 (m, 2H), 1.09 (t, J = 7.6 Hz, 3H), 0.61 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.1, 145.3 (d, $J_{CP} = 3.7$ Hz), 141.3 (d, $J_{CP} = 1.6 \text{ Hz}$), 139.2 (d, $J_{CP} = 4.3 \text{ Hz}$), 137.6 (d, $J_{CP} = 2.7 \text{ Hz}$), 135.8, 133.3 (d, $J_{CP} = 10.1 \text{ Hz}$) Hz), 131.3 (d, $J_{CP} = 2.5$ Hz), 131.2 (d, $J_{CP} = 2.7$ Hz), 130.8, 130.6, 130.4 (d, $J_{CP} = 3.3$ Hz), 128.5, 127.3, 126.9 (d, $J_{CP} = 13.5$ Hz), 125.7, 124.9, 124.7, 123.6 (d, $J_{CP} = 9.5$ Hz), 121.2, 113.5 (d, $J_{CP} = 8.4$ Hz), 33.8 (d, $J_{CP} = 2.5$ Hz), 31.8, 23.6, 22.2, 14.4, 14.0. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3,4-Dibutyl-1-phenyl-2-(quinolin-8-yl)-2H.L-benzo[c][1,2]azaphosphinine 1-oxide (3g):



The >99% *ee* was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 21.295 min, t (major) = 30.420 min; ¹H NMR (400 MHz, CDCl₃) δ 8.76 (dd, J = 4.0, 1.6 Hz, 1H), 8.17 (d, J = 7.2 Hz, 1H), 7.97 (dd, J = 8.4, 1.6 Hz, 1H), 7.89 (dd, J = 8.4, 4.8 Hz, 1H) 7.64 – 7.51 (m, 4H), 7.39 –

7.22 (m, 4H), 7.09 (td, J = 7.6, 1.6 Hz, 1H), 6.90 (td, J = 7.6, 3.2 Hz, 1H), 4.78 (AB, J = 12.0 Hz, 1H), 4.66 (AB, J = 11.6 Hz, 1H), 4.43 (dd, J = 12.8, 2.4 Hz, 1H), 3.67 (d, J = 12.8 Hz, 1H), 3.52 (s, 3H), 3.07 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 144.8 (d, $J_{CP} = 3.9$ Hz), 141.3, 138.4 (d, $J_{CP} = 4.1$ Hz), 136.3 (d, $J_{CP} = 2.2$ Hz), 135.8, 133.3 (d, $J_{CP} = 10.4$ Hz), 131.7 (d, $J_{CP} = 3.4$ Hz), 131.5 (d, $J_{CP} = 3.2$ Hz), 131.4 (d, $J_{CP} = 2.4$ Hz), 130.4 (d, $J_{CP} = 12.4$ Hz), 129.7 (d, $J_{CP} = 137.7$ Hz), 128.3, 127.8, 126.9 (d, $J_{CP} = 13.6$ Hz), 126.1, 125.9, 125.8, 124.8 (d, $J_{CP} = 129.8$ Hz), 124.6 (d, $J_{CP} = 9.1$ Hz), 121.2, 112.5 (d, $J_{CP} = 8.5$ Hz), 69.6, 68.6 (d, $J_{CP} = 2.4$ Hz), 57.4, 57.3. NMR is in accordance with previously reports¹. The absolute configuration was determined from the literature¹.

(S)-1,4-Diphenyl-3-(phenylethynyl)-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphinine 1oxide (3h):



The 99% *ee* was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.042 min, t (minor) = 13.693 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.84 (dd, J = 4.4, 2.0 Hz, 1H), 8.30 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.4, 1H), 7.89 – 7.84 (m, 2H), 7.66 (d, J = 8.4, 2H), 7.59 – 7.41 (m,

7H), 7.28 – 7.21 (m, 2H), 7.21 – 7.14 (m, 2H), 7.07 – 6.98 (m, 3H), 6.90 (t, J = 8.0 Hz, 2H), 6.15 – 6.12 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 150.0, 145.4, 138.9, 138.4 (d, $J_{CP} = 4.4$ Hz), 137.9, 135.7, 133.8 (d, $J_{CP} = 10.5$ Hz) 132.0, 131.8 (d, $J_{CP} = 3.0$ Hz), 131.4 (d, $J_{CP} = 2.5$ Hz), 131.1, 131.0, 130.8 (d, $J_{CP} = 139.0$ Hz), 130.7, 128.6, 128.2, 128.0 (d, $J_{CP} = 12.8$ Hz), 127.8, 127.4, 127.2 (d, $J_{CP} = 13.7$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.3, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.7$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 8.8$ Hz), 126.8, 126.0, 125.6 (d, $J_{CP} = 128.0$ Hz), 123.7 (d, $J_{CP} = 12.8$ Hz), 126.8, 126.7 (d, $J_{CP} = 12.8$ Hz) 6.8 Hz), 122.2, 121.3, 97.4, 87.1, 87.0. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-4-(4-Methoxyphenyl)-3-((4-methoxyphenyl)ethynyl)-1-phenyl-2-(quinolin-8-yl)-2Hbenzo[c][1,2]azaphosphinine 1-oxide (3i):

The 99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1. 0 mL/min, $\lambda = 254$ nm, t (major) = 10.423 min, t (minor) = 23.827 min. ¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 8.30 (d, J = 6.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 10.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.55 -7.33 (m, 5H), 7.29 - 7.08 (m, 4H), 7.0 8-6.94 (m, 4H), 6.43 (d, J = 8.4 Hz, 2H), 6.12 (d, J = 8.0Hz, 2H), 3.83 (s, 3H), 3.58 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 158.9, 149.9, 145.3, 138.7, 138.0, 135.6, 133.7 (d, *J*_{CP} = 11.8 Hz), 133.0, 132.2, 131.7, 131.3 (d, *J*_{CP} = 7.4 Hz), 131.0, 130.9, 129.5, 128.5, 127.7, 127.3 (d, J_{CP} = 13.5 Hz), 127.0, 126.6 (d, J_{CP} = 11.0 Hz), 126.2, 126.0,

125.9, 125.4, 122.5 (d, $J_{CP} = 6.7 \text{ Hz}$), 121.2, 114.3, 113.6 (d, $J_{CP} = 3.6 \text{ Hz}$), 97.4, 86.1 (d, $J_{CP} = 5.9 \text{ Hz}$) Hz), 55.4, 55.1. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-Phenyl-2-(quinolin-8-yl)-4-(p-tolyl)-3-(p-tolylethynyl)-2H-benzo[c][1,2]azaphosphinine <u>1-oxide (3j):</u>



The 99% ee was determined by Daicel Chiralcel AD, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.245 min, t (major) = 14.896 min. <u>¹H</u> **NMR (400 MHz, CDCl₃)** δ 8.83 (dd, J = 4.0, 1.6 Hz, 1H), 8.29 (d, J = 7.6Hz, 1H), 7.98 (dd, J = 8.0, 1.6 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.64 (dd, J = 8.0,

1.6 Hz, 1H), 7.51 – 7.36 (m, 5H), 7.29 – 7.17 (m, 5H), 7.15 (td, J = 7.6, 1.6 Hz, 1H), 7.04 (td, J = 8.0, 3.6 Hz, 2H), 6.72 (d, J = 7.6 Hz, 2H), 6.06 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.13 (s, 3H). ¹³C **<u>NMR (100 MHz, CDCl₃)</u>** δ 149.9, 145.3, 138.6 (d, *J*_{CP} = 4.5 Hz), 138.1, 137.9, 136.8, 135.7, 135.5, $133.7 (d, J_{CP} = 10.5 Hz), 131.9, 131.6 (d, J_{CP} = 2.9 Hz), 131.3 (d, J_{CP} = 2.6 Hz), 131.1, 131.0, 130.9,$ 130.6, 129.5 (d, $J_{CP} = 56.4 \text{ Hz}$), 128.8, 128.5, 127.7 (d, $J_{CP} = 182.7 \text{ Hz}$) 127.3 (d, $J_{CP} = 13.4 \text{ Hz}$), 126.7, $(d, J_{CP} = 9.1 \text{ Hz})$ 126.2 $(d, J_{CP} = 14.6 \text{ Hz})$, 125.5 $(d, J_{CP} = 128.0 \text{ Hz})$, 123.3 $(d, J_{CP} = 7.0 \text{ Hz})$, 121.1, 119.2, 97.4, 86.6 (d, $J_{CP} = 6.5$ Hz), 21.4, 21.3. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1,3-Diphenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3k):

The >99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 19.326 min, t (minor) = 22.321 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.71 (dd, J = 4.4, 1.6 Hz, 1H), 8.12 (dt, J = 7.2, 1.6 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.59 – 7.49 (m, 1H), 7.50 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.19 (m, 2H), 7.16 – 7.05 (m, 2H), 6.97 (td, J = 7.6, 3.2 Hz, 2H), 6.89 (dd, J = 4.8, 2.0 Hz, 3H), 6.33 (d, J = 2.0 Hz, 1H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 149.3, 145.2, 144.1 (d, $J_{CP} = 3.3$ Hz), 138.4 (d, $J_{CP} = 4.3$ Hz), 138.1 (d, $J_{CP} = 5.0$ Hz), 137.8 (d, $J_{CP} = 2.4$ Hz), 135.5, 133.1, 133.0, 131.8 (d, $J_{CP} = 2.5$ Hz), 131.5 (d, $J_{CP} = 2.9$ Hz), 130.9 (d, $J_{CP} = 12.3$ Hz), 130.4 (d, $J_{CP} = 2.9$ Hz), 129.0, 128.4, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8 (d, $J_{CP} = 9.2$ Hz), 126.0 (d, $J_{CP} = 12.4$ Hz), 125.5, 124.1 (d, $J_{CP} = 12.9$ Hz), 121.0, 107.7 (d, $J_{CP} = 7.8$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3-(4-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2*H*-benzo[*c*][1,2]azaphosphini-ne 1oxide (31):



The 98% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 26.305 min, t (minor) = 32.955 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.70 - 8.69 (m, 1H), 8.07 (d, *J* = 6.4, 1H), 7.71 - 7.65 (m,

3H), 7.49 –7.38 (m, 4H), 7.31 – 7.27 (m, 3H), 7.22 – 7.17 (m, 2H), 7.10 – 7.06 (m, 2H), 6.96 – 6.92 (m, 2H), 6.41 (d, J = 8.8 Hz, 2H), 6.27 (d, J = 2.0 Hz, 1H), 3.49 (s, 3H). ¹³C NMR (100 MHz, CDCI₃) δ 158.8, 149.3, 144.9, 144.1, 138.2 (d, $J_{CP} = 5.0$ Hz), 137.8 (d, $J_{CP} = 2.3$ Hz), 135.5, 132.9 (d, $J_{CP} = 10.6$ Hz), 131.8 (d, $J_{CP} = 2.3$ Hz), 131.5 (d, $J_{CP} = 2.8$ Hz), 131.0, 130.8 (d, $J_{CP} = 4.4$ Hz), 130.7 (d, $J_{CP} = 12.2$ Hz), 130.2 (d, $J_{CP} = 2.8$ Hz), 130.1, 129.3, 128.4, 127.2 (d, $J_{CP} = 9.5$ Hz), 127.0, 126.6 (d, $J_{CP} = 9.3$ Hz) 125.8 (d, $J_{CP} = 14.3$ Hz), 125.4, 123.7 (d, $J_{CP} = 126.7$ Hz), 121.0, 112.5, 107.3 (d, $J_{CP} = 7.6$ Hz), 55.0. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-phenyl-2-(quinolin-8-yl)-3-(p-tolyl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3m):



The >99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 20.933 min, t (minor) = 26.387 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.71 (d, J = 3.6 Hz, 1H), 8.09 (d, J = 7.2 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.53 – 7.39 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.12 – 7.05 (m, 2H), 6.95 (td, J = 7.6, 3.2 Hz, 2H), 6.70 (d, J = 7.6 Hz, 2H), 6.30 (s, 1H), 2.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 145.2, 137.2, 135.4, 133.0 (d, J_{CP} = 10.6 Hz), 131.7 (d, J_{CP} = 2.5 Hz), 131.4 (d, $J_{CP} = 2.9$ Hz), 130.8, 130.7, 130.3 (d, $J_{CP} = 2.9$ Hz), 128.8, 128.3, 127.7 (d, $J_{CP} = 5.6$ Hz), 127.1, 127.0, 126.6, 126.5, 125.9, 125.7, 125.4, 121.0, 107.5 (d, $J_{CP} = 7.7 \text{ Hz}$), 21.0. 31P NMR (162) **MHz**, **CDCl**₃) δ 18.94; HRMS (ESI) calculated for C₃₀H₂₃N₂OP [M + H]⁺: 459.1621, found: 459.1623.

(S)-3-(4-Chlorophenyl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3n):



The >99% ee was determined by Daicel Chiralcel IA, Hexanes/IPA = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 13.360 min, t (major) = 33.579 min; ¹H NMR (400 MHz, CDCl₃) δ 8.71 (dd, J = 4.0, 1.6 Hz, 1H), 8.11 (d, J = 7.2 Hz, 1H), 7.77

(dd, J = 8.0, 1.6 Hz, 1H), 7.72 - 7.62 (m, 2H), 7.58 - 7.51 (m, 1H), 7.49 - 7.35 (m, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.23 (s, 1H), 7.15 (dd, J = 8.0, 4.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.96 (td, J = 8.0, 3.6 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.29 (d, J = 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 144.0, 143.9, 137.8 (d, J_{CP} = 2.0 Hz), 137.5 (d, J_{CP} = 2.5 Hz), 137.0 (d, J_{CP} = 4.4 Hz), 135.6, 133.2, 133.0, 132.9, 131.8 (d, $J_{CP} = 2.4 \text{ Hz}$), 131.5 (d, $J_{CP} = 2.9 \text{ Hz}$), 131.0 (d, $J_{CP} = 120.6 \text{ Hz}$), 130.2, 128.4, 127.5, 127.3, 127.2 (d, $J_{CP} = 3.6 \text{ Hz}$), 126.7 (d, $J_{CP} = 9.3 \text{ Hz}$), 126.2 (d, $J_{CP} = 14.4 \text{ Hz}$), 125.5, 123.6 (d, $J_{CP} = 127.8$ Hz), 121.1, 107.8 (d, $J_{CP} = 7.8$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

oxide (3o):



The >99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 24.770 min, t (minor) = 33.176 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.70 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 7.80 (d,

J = 8.4 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.19 – 7.16 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.99-6.91 (m, 2H), 6.29 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 144.0, 143.8 (d, $J_{CP} = 3.0$ Hz), 137.8 (d, $J_{CP} = 5.0$ Hz), 137.5 (d, $J_{CP} = 4.0$ Hz), 135.6, 133.0 (d, $J_{CP} = 11.0$ Hz), 131.8 (d, $J_{CP} = 2.9$ Hz), 131.5 (d, $J_{CP} = 3.0$ Hz), 130.9, 130.8 (d, $J_{CP} = 117.5$ Hz), 130.4, 130.2, 130.1 (d, $J_{CP} = 2.0$ Hz), 128.4, 127.5, 127.1 (d, $J_{CP} = 13.0$ Hz), 126.8 (d, $J_{CP} = 11.0$ Hz), 126.1 (d, $J_{CP} = 14.0$ Hz), 125.5, 124.2 (d, $J_{CP} = 126.0$ Hz), 121.6, 121.2, 107.8 (d, $J_{CP} = 8.0$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-Phenyl-2-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)-2H-benzo[c][1,2]aza-

phosphinine 1-oxide (3p):



The >99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 17.295 min, t (major) = 24.567 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.72 (dd, J = 4.4, 1.6 Hz, 1H), 8.14 (d, J = 7.6 Hz), 7.77 (dd, J = 8.4, 1.6 Hz, 1H), 7.68 – 7.63 (m, 3H), 7.57 (t, J = 7.6 Hz, 2H), 7.52 –

7.43 (m, 4H), 7.38 (d, J = 8.0 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.17 (m, 3H), 7.13 – 7.08 (m, 1H), 6.97 (td, J = 7.6, 3.6 Hz, 2H), 6.34 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.4, 143.8, 143.7 (d, $J_{CP} = 3.3$ Hz), 142.0, 137.6 (d, $J_{CP} = 4.9$ Hz), 137.3 (d, $J_{CP} = 2.6$ Hz), 135.6, 133.0 (d, $J_{CP} = 10.6$ Hz), 131.9 (d, $J_{CP} = 2.5$ Hz), 131.6 (d, $J_{CP} = 2.9$ Hz), 131.0 (d, $J_{CP} = 12.0$ Hz), 130.2 (d, $J_{CP} = 2.9$ Hz), 129.1, 128.4, 127.6, 127.2, 127.1, 126.9 (d, $J_{CP} = 9.3$ Hz), 126.5 (d, $J_{CP} = 14.4$ Hz), 125.5, 124.0 (q, $J_{CF} = 270.5$ Hz) 121.2, 108.5 (d, $J_{CP} = 8.0$ Hz). NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3-(2-Chlorophenyl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphini-ne 1-oxide

<u>(3q):</u>



The 99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.603 min, t (mjaor) = 18.437 min; <u>¹H NMR (400 MHz, CDCl_3)</u> δ 8.79 (dd, J = 4.4, 1.6 Hz, 1H), 8.36 (d, J = 7.2 Hz, 1H), 7.74 – 7.63

(m, 3H), 7.52 (t, J = 7.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 2H), 7.16 (dd, J = 8.2, 4.4 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.92 (td, J = 8.0, 3.2 Hz, 2H), 6.83 (td, J = 7.6, 1.6 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.25 (d, J = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 144.3, 142.5, 137.7 (d, $J_{CP} = 4.7$ Hz), 136.7, 136.5 (d, $J_{CP} = 2.6$ Hz), 135.4, 133.8, 133.3 (d, $J_{CP} = 10.6$ Hz), 132.1, 131.7 (d, $J_{CP} = 2.4$ Hz), 131.4 (d, $J_{CP} = 2.8$ Hz), 131.0 (d, $J_{CP} = 12.6$ Hz), 130.7 (d, $J_{CP} = 2.6$ Hz), 129.1, 128.7, 128.0, 127.7, 127.0, 126.8 (d, $J_{CP} = 9.3$ Hz), 126.1 (d, $J_{CP} = 14.4$ Hz), 125.4, 125.0, 124.5 (d, $J_{CP} = 127.9$ Hz), 121.0, 107.4. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3-(2-Methoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphini-ne 1-

oxide (3r):



The 99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 14.498 min, t (mjaor) = 29.448 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.76 (dd, J = 4.0, 1.6 Hz, 1H), 8.23 (dd, J = 7.2, 1.6 Hz, 1H),

7.75 – 7.65 (m, 3H), 7.56 – 7.36 (m, 4H), 7.33 (dd, J = 8.2, 1.6 Hz, 1H), 7.26 (dd, J = 7.6, 1.6 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.12 (dd, J = 8.4, 4.4 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.93 (td, J = 7.6, 3.6 Hz, 2H), 6.86 (td, J = 7.6, 2.0 Hz, 1H), 6.48 – 6.33 (m, 2H), 6.24 (d, J = 2.0 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 149.2, 144.4 (d, $J_{CP} = 3.7$ Hz), 143.3, 138.2 (d, $J_{CP} = 4.7$ Hz), 137.2 (d, $J_{CP} = 2.4$ Hz), 135.3, 133.3 (d, $J_{CP} = 10.5$ Hz), 131.7, 131.5 (d, $J_{CP} = 2.5$ Hz), 131.3 (d, $J_{CP} = 3.0$ Hz), 130.9 (d, $J_{CP} = 11.0$ Hz), 130.7, 129.5, 127.9, 127.5, 127.1 (d, $J_{CP} = 4.1$ Hz), 127.0 (d, $J_{CP} = 13.6$ Hz), 126.5, 125.6 (d, $J_{CP} = 14.4$ Hz), 124.9, 124.2 (d, $J_{CP} = 128.3$ Hz), 121.1 (d, $J_{CP} = 180.5$ Hz), 120.7, 119.0, 109.2, 106.6 (d, $J_{CP} = 7.3$ Hz), 54.9. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-1-phenyl-2-(quinolin-8-yl)-3-(o-tolyl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3s)

Ph. O V"PN He The >99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 25.165 min, t (major) = 32.105 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.79 (d, J = 4.8 Hz, 1H), 8.18 (s, 1H), 7.78 – 7.62 (m, 3H), 7.54 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.26 –

7.20 (m, 2H), 7.17 (dd, J = 8.0, 4.2 Hz, 2H), 7.06 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 2H), 6.81 (d, J = 6.4 Hz, 2H), 6.64 (d, J = 7.6 Hz, 1H), 6.19 (s, 1H), 2.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 136.9, 135.4, 131.7, 131.4, 130.8, 130.7, 130.5, 128.1, 127.7, 127.6, 127.0, 126.9, 126.6, 126.5, 125.8, 125.6, 125.3, 123.9, 121.0, 107.0, 77.4, 77.1, 76.7, 19.9; ³¹P NMR (162 MHz, CDCl₃) δ 18.11; HRMS (ESI) calculated for C₃₀H₂₃N₂OP [M + H]⁺: 459.1621, found: 459.1622.

(S)-3-(3,5-dimethoxyphenyl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-

oxide (3t)



The 99% *ee* was determined by Daicel Chiralcel OD, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 21.880 min, t (minor) = 30.212 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.73 (dd, J = 4.0, 1.6 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.78 (dd, J = 8.0, 1.6 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.51

-7.43 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.25 -7.22 (m, 1H), 7.18 -7.10 (m, 2H), 7.00 (td, *J* = 7.6, 3.2 Hz, 2H), 6.54 (d, *J* = 2.4 Hz, 2H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.03 (t, *J* = 2.4 Hz, 1H), 3.49 (s, 6H); $\frac{^{13}C \text{ NMR (100 MHz, CDCl_3)}}{5} \delta 159.4, 149.3, 144.9, 140.2, 140.2, 137.9, 137.8, 135.6, 132.9, 131.8$ (d, *J*_{CP} = 2.3 Hz), 131.5 (d, *J*_{CP} = 2.9 Hz), 130.8, 130.7, 130.2 (d, *J*_{CP} = 2.8 Hz), 128.5, 127.2, 127.1, 126.8, 126.7, 126.3, 126.1, 125.5, 121.1, 108.1, 108.0, 107.0, 100.7, 77.4, 77.1, 76.8, 55.2; $\frac{^{31}P \text{ NMR}}{505.1676}$, found: 505.1679.

(S)-1-Phenyl-2-(quinolin-8-yl)-3-(trimethylsilyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1-oxide (3u):



The >99% *ee* was determined by Daicel Chiralcel OD, Hexanes/IPA = 95/5, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 5.062 min, t (minor) = 5.861 min; <u>¹H NMR (400</u>

<u>MHz, CDCl₃</u>) δ 8.76 (dd, J = 4.2, 1.6 Hz, 1H), 8.22 (d, J = 7.2 Hz, 1H), 7.95 (dd, J = 8.2, 1.6 Hz, 1H), 7.66 – 7.48 (m, 4H), 7.48 – 7.35 (m, 3H), 7.28 – 7.20 (m, 2H), 7.04 (td, J = 7.2, 1.2 Hz, 1H), 6.90 (td, J = 7.6, 3.2 Hz, 2H), -0.34 (s, 9H). <u>¹³C NMR (100 MHz, CDCl_3)</u> δ 150.1, 148.5 (d, $J_{CP} = 4.6$ Hz), 146.2, 138.1, 137.3 (d, $J_{CP} = 3.5$ Hz), 135.8, 133.5, 133.4, 132.7 (d, $J_{CP} = 2.6$ Hz), 131.6 (d, $J_{CP} = 2.0$ Hz), 131.2 (d, $J_{CP} = 2.3$ Hz), 130.6 (d, $J_{CP} = 12.0$ Hz), 128.8, 128.4, 126.8, 126.7, 126.7, 126.4, 126.2, 125.7, 124.7 (d, $J_{CP} = 128.5$ Hz), 121.4, 115.2 (d, $J_{CP} = 11.3$ Hz), 0.1. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

Ethyl (S)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine-3-carboxylate 1-oxide

<u>(3v):</u>



The 91% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 22.745 min, t (major) = 38.077 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.76 (dd, J = 4.4, 2.0 Hz, 1H), 8.15 (s, 1H), 7.96 (dd, J = 8.4,

1.6 Hz, 1H), 7.62 – 7.54 (m, 4H), 7.53 – 7.42 (m, 2H), 7.38 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 (s, 1H), 7.14 – 7.10 (m, 1H), 6.98 (s, 2H), 3.77 (q, J = 7.2 Hz, 2H), 0.68 (t, J = 7.2 Hz, 3H). ¹³C <u>NMR (100 MHz, CDCl₃)</u> δ 164.1 (d, $J_{CP} = 6.5$ Hz), 149.5, 144.1, 138.3, 135.8, 135.7 (d, $J_{CP} = 4.5$ Hz), 135.0, 132.9 (d, $J_{CP} = 10.6$ Hz), 131.9 (d, $J_{CP} = 2.3$ Hz), 131.6, 131.1, 128.3, 128.1, 128.0, 127.3, 127.2, 126.4, 125.9 (d, $J_{CP} = 125.7$ Hz), 60.9, 13.4. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3-Pentyl-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide (3w)



The 99% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 26.183 min, t (minor) = 34.845 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.77 (dd, J = 4.4, 2.0 Hz, 1H), 8.22 (dt, J = 7.2, 1.6 Hz,

1H), 7.96 (dd, J = 8.4, 2.0 Hz, 1H), 7.60 (d, J = 8.4, 1H), 7.55 – 7.47 (m, 3H), 7.44 – 7.34 (m, 3H), 7.27 – 7.24 (m, 1H), 7.17 – 7.12 (m, 1H), 7.02 (td, J = 8.4, 1.6 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.12 (d, J = 2.0, 1H), 2.12 – 2.04 (m, 1H), 1.99 – 1.91 (m, 1H), 1.50 – 1.46 (m, 2H), 1.11 – 0.97 (m, 4H), 0.72 (t, J = 6.8 Hz, 3H). $\frac{13}{12}$ C NMR (100 MHz, CDCl₃) δ 150.2, 145.3, 138.5 (d, $J_{CP} = 4.6$ Hz), 135.9, 133.2 (d, $J_{CP} = 10.5$ Hz), 132.1 (d, $J_{CP} = 2.9$ Hz), 131.6 (d, $J_{CP} = 2.4$ Hz), 131.2 (d, $J_{CP} = 2.9$ Hz),

130.7 (d, $J_{CP} = 12.5$ Hz), 128.5, 128.2, 126.8, 126.6, 126.1 (d, $J_{CP} = 9.2$ Hz), 125.8, 125.0 (d, $J_{CP} = 14.5$ Hz), 122.9 (d, $J_{CP} = 128.3$ Hz), 121.2, 102.7 (d, $J_{CP} = 8.4$ Hz), 34.9 (d, $J_{CP} = 2.8$ Hz), 31.2, 28.2, 22.2, 13.8. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3-(Cyclohex-1-en-1-yl)-1-phenyl-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphi-nine 1oxide (3x):



The 99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.660 min, t (major) = 13.961 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.76 (d, J = 4.0 Hz, 1H), 8.02 (d, J = 7.2 Hz, 1H), 7.93 (d, J =

8.4 Hz, 1H), 7.68 (dd, J = 13.2, 7.6 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.43-7.36 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.24 (dd, J = 8.4, 4.4 Hz, 1H), 7.21-7.14 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.98 (td, J = 7.6, 3.2 Hz, 2H), 6.18 (d, J = 2.0 Hz, 1H), 5.72 (t, J = 4.0 Hz, 1H), 2.07-1.96 (m, 2H), 1.67-1.38 (m, 2H), 1.17-0.96(m, 4H). $\frac{13}{12}$ C NMR (100 MHz, CDCI₃) δ 149.3, 147.4, 144.8 (d, $J_{CP} = 3.4$ Hz), 138.3 (d, $J_{CP} = 5.0$ Hz), 138.0 (d, $J_{CP} = 2.4$ Hz), 135.5, 135.3 (d, $J_{CP} = 4.0$ Hz), 133.1 (d, $J_{CP} = 10.5$ Hz), 131.8 (d, $J_{CP} = 121.8$ Hz), 131.5 (d, $J_{CP} = 2.4$ Hz), 131.3 (d, $J_{CP} = 2.7$ Hz), 130.7 (d, $J_{CP} = 12.2$ Hz), 130.4, 130.3 (d, $J_{CP} = 2.9$ Hz), 128.5, 127.1, 126.9, 126.4 (d, $J_{CP} = 9.4$ Hz), 125.5, 125.3, 124.0 (d, $J_{CP} = 127.6$ Hz), 121.0, 104.8 (d, $J_{CP} = 7.7$ Hz), 28.1, 25.1, 22.4, 21.6. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3,4,5-triethyl-1-(2-ethylphenyl)-2-(quinolin-8-yl)-2H-benzo[c][1,2]azaphosphinine 1-oxide

<u>(3y):</u>



The >99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 5.112 min, t (minor) = 9.420 min; <u>¹H NMR</u>

(400 MHz, CDCl₃) δ 8.68 (s, 1H), 8.20 (s, 1H), 7.94 – 7.82 (m, 2H), 7.55 – 7.47

(m, 3H), 7.29 (d, J = 10.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.09 – 7.04 (m, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.83 (s, 1H), 6.66 (s, 1H), 2.77 (ddt, J = 20.4, 14.8, 7.6 Hz, 4H), 2.52 (dt, J = 15.2, 7.2 Hz, 2H), 2.14 (dd, J = 15.6, 7.6 Hz, 1H), 1.80 – 1.69 (m, 1H), 1.33 (d, J = 7.6 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H), 0.92 – 0.86 (m, 3H), 0.49 (t, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 136.9,

135.6, 131.4, 131.3, 131.0, 128.3, 127.8, 127.1, 125.6, 124.1, 122.0, 120.9, 77.4, 77.0, 76.7, 29.7, 27.1 (d, $J_{CP} = 6.3$ Hz), 26.2, 25.0, 15.1, 14.5, 13.6, 13.4; <u>31P NMR (162 MHz, CDCl_3)</u> δ 12.33; HRMS (ESI) calculated for C₃₁H₃₄N₂OP [M + H]⁺: 481.2403, found: 481.2409.

(S)-3,4-Diethyl-6-methyl-2-(quinolin-8-yl)-1-(*p*-tolyl)-2*H*-benzo[*c*][1,2]azaphosphinine 1oxide (3*z*):



The 99% *ee* was determined by Daicel Chiralcel ID, Hexanes/IPA = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.842 min, t (minor) = 12.210 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.76 (dd, J = 4.0, 1.6 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H),

7.95 (dd, J = 8.4, 1.6 Hz, 1H), 7.52 (dd, J = 8.4, 1.6 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.33 – 7.25 (m, 2H), 7.19 (dd, J = 14.4, 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0, 3.2 Hz, 2H), 2.75 (q, J = 7.6 Hz, 2H), 2.49 – 2.43 (m, 4H), 2.07 (s, 3H), 1.76 (dq, J = 14.8, 7.2 Hz, 1H), 1.32 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 150.0, 145.3 (d, $J_{CP} = 3.5$ Hz), 142.2, 141.4 (d, $J_{CP} = 2.9$ Hz), 141.3 (d, $J_{CP} = 2.5$ Hz), 139.0 (d, $J_{CP} = 4.5$ Hz), 137.6 (d, $J_{CP} = 2.5$ Hz), 135.8, 133.3 (d, $J_{CP} = 10.5$ Hz), 130.8 (d, $J_{CP} = 13.0$ Hz), 130.5 (d, $J_{CP} = 3.3$ Hz), 128.5, 128.1 (d, $J_{CP} = 137.9$ Hz), 127.7 (d, $J_{CP} = 13.6$ Hz), 127.2, 126.0 (d, $J_{CP} = 15.0$ Hz), 125.8, 123.8 (d, $J_{CP} = 9.8$ Hz), 123.0 (d, $J_{CP} = 132.0$ Hz), 121.2, 113.9 (d, $J_{CP} = 8.4$ Hz), 24.8 (d, $J_{CP} = 2.5$ Hz), 22.4, 22.2, 21.4, 15.1, 13.3. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

(S)-3,4-diethyl-2-(quinolin-8-yl)-1-(thiophen-2-yl)-2H-thieno[2,3-c][1,2]azaphosphinine

oxide: (3aa)



The 99% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 16.982 min, t (major) = 23.010 min; <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.80 - 8.72 (m, 1H), 8.25 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.69 - 7.65 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.30 - 7.26 (m,

2H), 7.22 (t, *J* = 4.8 Hz, 1H), 7.16 (dd, *J* = 8.2, 3.6 Hz, 1H), 6.61 – 6.55 (m, 1H), 2.71 (qd, *J* = 7.4, 2.2 Hz, 2H), 2.45 (ddd, *J* = 14.8, 7.6, 2.6 Hz, 1H), 1.77 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.27 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H)... <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 150.2, 148.4 (d, *J*_{CP} = 6.7 Hz),

145.3, 142.4, 137.5 (d, $J_{CP} = 12.0 \text{ Hz}$), 136.3, 135.9, 133.9 (d, $J_{CP} = 6.5 \text{ Hz}$), 132.2 (d, $J_{CP} = 12.0 \text{ Hz}$), 128.5, 128.3, 126.8 (d, $J_{CP} = 16.5 \text{ Hz}$), 125.9, 124.7 (d, $J_{CP} = 12.5 \text{ Hz}$), 121.3, 118.7 (d, $J_{CP} = 148.9 \text{ Hz}$), 111.6 (d, $J_{CP} = 6.4 \text{ Hz}$), 24.0 (d, $J_{CP} = 3.3 \text{ Hz}$), 23.8, 15.2, 13.9. NMR is in accordance with previously reports³. The absolute configuration was determined from the literature³.

4.3. General procedure for enantioselective C–H annulation with allene



Phosphinic amide **1a** (0.1 mmol), **Co@POP-Salox-1** (5.0 mol % Co content), Ag₂CO₃ (0.2 mmol), NaOPiv (0.2 mmol), and 'BuOH (2.0 mL) were added to an oven dried vial equipped with stirring bars. Then allene **4a** (0.20 mmol) was added in one batch. The vial was stirred in a heating block set at 70 °C for 10 h. After the reaction was completed, the reaction mixture was cooled to room temperature, quenched by saturated aqueous Na₂CO₃, and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. Then the mixture was subjected to column chromatography on silica gel to give the desired product **5a**¹.

Data of the compound

(S)-3-((diphenylphosphoryl)methyl)-1-phenyl-2-(quinolin-8-yl)-2H-

benzo[c][1,2]azaphosphinine 1-oxide (5a)



2.91 (dd, J = 15.6, 12.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 144.7 (d, $J_{CP} = 3.1$ Hz), 137.6 (dd, $J_{CP} = 4.7, 2.9$ Hz), 136.0, 135.1 (d, $J_{CP} = 2.4$ Hz), 135.0 (d, $J_{CP} = 6.6$ Hz), 132.8 (d, $J_{CP} = 10.8$ Hz), 132.1 (d, $J_{CP} = 2.8$ Hz), 132.0 (d, $J_{CP} = 2.8$ Hz), 131.8 (d, $J_{CP} = 101.0$ Hz), 131.7 (d, $J_{CP} = 2.7$ Hz), 131.4, 131.3 (d, $J_{CP} = 1.5$ Hz), 131.2 (d, $J_{CP} = 2.9$ Hz), 130.8 (d, $J_{CP} = 12.4 \text{ Hz}$), 128.8 (d, $J_{CP} = 6.6 \text{ Hz}$), 128.7 (d, $J_{CP} = 6.4 \text{ Hz}$), 128.4, 128.3, 126.8 (d, $J_{CP} = 13.7 \text{ Hz}$), 126.5 (d, $J_{CP} = 8.9 \text{ Hz}$), 126.0, 125.6 (d, $J_{CP} = 14.6 \text{ Hz}$), 122.4 (dd, $J_{CP} = 127.5$, 1.5 Hz), 121.5, 106.7 (t, $J_{CP} = 7.7 \text{ Hz}$), 36.2 (dd, $J_{CP} = 65.6$, 2.8 Hz). NMR is in accordance with previously reports¹⁰. The absolute configuration was determined from the literature¹⁰.

4.4. General procedure for enantioselective C-H alkoxylation of diarylphosphinamides



To a 10 mL Schlenk tube was added **1a** (0.10 mmol), methanol (1.5 mL), **Co@POP-Salox-1** (5.0 mol % Co content, Co(ClO₄)₂·6H₂O as Co source), Ag₂CO₃ (55.2 mg, 0.20 mmol, 2.0 equiv.) and NaOPiv (24.8 mg, 0.20 mmol, 2.0 equiv). Then, the vial was instantly placed in a heating aluminum block set at 70 °C and stirred under air for noted time. After cooling to room temperature, the reaction system was quenched with water (20 mL) and extracted with DCM (3×15 mL). The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. After concentration, the resulting residue was purified by flash chromatography using petroleum ether/dichloromethane/acetone as the eluent to afford the desired product **6a**⁸.

Data of the compound

(S)-P-(2,6-dimethoxyphenyl)-P-phenyl-N-(quinolin-8-yl)phosphinic amide (6a)

The 99% *ee* was determined by Daicel Chiralcel ID, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 28.081 min, t (minor) = 43.347 min. **H NMR (400 MHz, CDCl3)** δ 10.24 (d, J = 9.6 Hz, 1H), 8.84 (dd, J = 4.2, 1.6 Hz, 1H), 8.12 (dd, J = 8.2, 1.6 Hz, 1H), 8.02 – 7.94 (m, 2H), 7.45 – 7.33 (m, 6H), 7.23 (d, J = 3.4 Hz, 2H), 6.60 (dd, J = 8.4, 4.6 Hz, 2H), 3.81 (s, 6H). **13C NMR (100 MHz, CDCl3)** δ 162.2, 147.2, 138.4, 136.9, 134.2, 132.1 (d, $J_{CP} = 10.9$ Hz), 130.7 (d, $J_{CP} = 2.8$ Hz), 128.6, 127.8 (d, $J_{CP} = 13.8$ Hz), 127.5, 121.2, 118.4, 105.0 (d, $J_{CP} = 6.9$ Hz), 56.0. NMR is in accordance with previously reports⁸. The absolute configuration was determined from the literature⁸.

4.5. General procedure for enantioselective C-H annulation of benzamide derivatives



Benzamide derivatives 7 (0.20 mmol), alkynes 2 (0.30 mmol), Co@POP-Salox-1 (5.0 mol % Co content) and anhydrous solvent dioxane (2.0 mL) was added successively to a 10 mL oven-dried Schlenk tube containing a magnetic stir bar under the oxygen atmosphere. Then the reaction system was closed with a ground glass stopper and stirred at 100°C for 12 h. The mixture was cooled to room temperature and diluted with 25 mL of DCM and filtered over a celite. The reaction solution was concentrated in vacuum and purified by flash column chromatography to give the product 8^5 .

Data of the compounds

(R)-7-Methyl-2-(7-methylquinolin-8-yl)-3,4-diphenylisoquinolin-1(2H)-one (8a)



The 95% *ee* was determined by Daicel Chiralcel AD, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 15.840 min, t (minor) =27.442 min. <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.90 (dd, J = 4.2, 1.6 Hz, 1H), 8.41 (s, 1H), 7.99 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.44 (dd, J = 8.3, 2.0 Hz, 1H), 7.30

(dd, J = 8.2, 4.4 Hz, 1H), 7.26 - 7.23 (m, 3H), 7.18 - 7.12 (m, 3H), 6.95 (d, <math>J = 7.6 Hz, 1H), 6.81 - 6.68 (m, 3H), 6.46 (td, <math>J = 7.6, 1.6 Hz, 1H), 2.52 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 150.6, 145.1, 141.0, 137.5, 136.8, 136.6, 136.0, 135.9, 135.6, 134.6, 133.8, 131.9, 131.7, 130.0, 129.2, 128.9, 128.1, 128.0, 127.9, 127.7, 127.3, 127.1, 126.6, 126.4, 126.1, 125.7, 125.6, 120.6, 118.8, 21.4, 19.0. NMR is in accordance with previously reports⁵. The absolute configuration was determined from the literature⁵.

(R)-7-Methyl-2-(7-methylquinolin-8-yl)-3,4-di-p-tolylisoquinolin-1(2H)-one (8b)



The 95% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 35.457 min, t (minor) =48.875 min. <u>¹H NMR</u> (400 MHz, DMSO-*d*₆) δ 8.87 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.25 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.14 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.4,

2.0 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.06 (dd, *J* = 7.8, 4.2 Hz, 2H), 7.02 - 6.93 (m, 3H), 6.65 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.51 (dd, *J* = 8.0,

2.0 Hz, 1H), 6.26 (dd, *J* = 8.0, 1.8 Hz, 1H), 2.46 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 1.86 (s, 3H). ¹³C <u>NMR (100 MHz, DMSO-*d*₆)</u> δ 161.1, 150.9, 144.9, 141.4, 137.6, 137.0, 136.8, 136.4, 136.2, 136.2, 135.9, 134.5, 133.8, 131.9, 131.9, 131.5, 129.4, 129.2, 129.1, 128.4, 127.7, 127.4, 127.1, 127.1, 125.7, 125.3, 121.5, 118.0, 21.4, 21.2, 20.9, 18.9. The absolute configuration was determined from the literature⁵.

(R)-2-(7-methylquinolin-8-yl)-3,4-di-p-tolylisoquinolin-1(2H)-one (8c)



The 96% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 13.844 min, t (minor) =18.101 min. <u>¹H NMR</u> (400 MHz, CDCl₃) δ 8.87 (dd, J = 4.3, 1.6 Hz, 1H), 8.25 (dd, J = 8.4, 1.6 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.14

1H), 7.46 (dd, J = 8.2, 4.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.16 (dd, J = 7.6, 2.0 Hz, 1H), 7.06 (dd, J = 7.8, 4.2 Hz, 2H), 7.02 – 6.93 (m, 3H), 6.65 (dd, J = 8.0, 1.8 Hz, 1H), 6.51 (dd, J = 8.0, 2.0 Hz, 1H), 6.26 (dd, J = 8.0, 1.8 Hz, 1H), 2.46 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 1.86 (s, 3H). $\frac{13}{C}$ **NMR (100 MHz, CDCl₃)** δ 161.1, 150.9, 144.9, 141.4, 137.6, 137.0, 136.8, 136.4, 136.2, 136.2, 135.9, 134.5, 133.8, 131.9, 131.9, 131.5, 129.4, 129.2, 129.1, 128.4, 127.7, 127.4, 127.1, 127.1, 125.7, 125.3, 121.5, 118.0, 21.4, 21.2, 20.9, 18.9. The absolute configuration was determined from the literature⁵.

(R)-2-(7-methylquinolin-8-yl)-3,4-diphenylisoquinolin-1(2H)-one (8d)



The 91% *ee* was determined by Daicel Chiralcel IA, Hexanes/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 18.912 min, t (major) =20.945 min. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (dd, J = 4.4, 1.6 Hz, 1H), 8.61 (dd, J = 8.0, 1.6 Hz, 1H), 7.99 (dd, J = 8.2, 1.8 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.35 – 7.29 (m, 2H), 7.24

(d, J = 3.3 Hz, 3H), 7.16 (s, 3H), 6.96 (d, J = 7.8 Hz, 1H), 6.79 (t, J = 7.6 Hz, 2H), 6.75 - 6.69 (m, 1H), 6.49 - 6.43 (m, 1H), 2.39 (s, 3H).¹³C NMR (100 MHz, CDCl₃) δ 162.0, 150.6, 145.1, 141.9, 138.3, 137.6, 136.6, 135.7, 135.7, 134.5, 132.4, 131.9, 131.8, 129.9, 129.1, 128.9, 128.5, 128.1, 128.0, 127.8, 127.5, 127.1, 126.8, 126.6, 126.5, 126.2, 125.7, 125.7, 120.7, 118.9, 19.0. The absolute configuration was determined from the literature⁵.



4.6. General procedure for enantioselective C-H acyloxylation with benzoic acid

To an oven dried vail equipped with stirring bar, ferrocenecarboxamide 9a (0.1 mmol), benzoic acid 10a (0.15 mmol), Co@POP-Salox-1 (5.0 mol % Co content), Ag₂CO₃ (0.2 mmol), Na₂CO₃ (0.2 mmol), PCy₃•HBF₄ (10 mmol%), and DCM (2.0 mL) were added. The vial was instantly placed in a heating block set at 70 °C for 24 hours. The reaction mixture was then cooled to room temperature. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using PE/DCM/EtOAc as the eluent to afford the product $11a^9$.

Data of the compound

(S)-[1-(benzoyloxy)-2-(8-quinolinylamino)carbonyl]ferrocene 11a:

The 98% *ee* was determined by Daicel Chiralcel IC, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 14.263 min, t (minor) = 40.106 min. <u>¹H NMR</u> (400 MHz, CDCl₃) δ 10.81 (s, 1H), 8.87 (d, J = 7.6 Hz, 1H), 8.33 (d, J = 7.6 Hz, 2H), 8.10 (d, J = 8.0 Hz, 1H), 8.01 (s, 1H), 7.70 - 7.60 (m, 1H), 7.60 - 7.36 (m, 4H), 7.33 - 7.23 (m, 1H), 4.93 (s, 2H), 4.39 (s, 5H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 167.9, 165.2, 147.9, 138.6, 136.2, 133.7, 130.8, 129.3, 128.6, 128.0, 127.6, 121.5, 121.3, 116.9, 114.6, 68.0, 65.6, 65.4, 65.0. NMR is in accordance with previously reports³.

4.7. General procedure for enantioselective C-H annulation of benzylamide derivative



To an oven-dried 10 mL Schlenk tube containing a stirring bar was added benzylamide **12a** (0.10 mmol), alkyne **2a** (0.20 mmol), **Co@POP-Salox-1** (5.0 mol % Co content), Mn(OAc)₂·4H₂O

(0.01 mmol), NaOPiv (0.05 mmol) and MeOH (1.0 mL). The reaction flask was degassed three times with O₂. The mixture was then stirred for 24 h at 90 °C followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the desired product **13a**.¹¹

Data of the compound

(R)-pyridin-2-yl(1,3,4-triphenylisoquinolin-2(1H)-yl)methanone 13a

The 93% *ee* was determined by Daicel Chiralcel OD-H, Hexanes/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.685 min, t (major) = 12.093

 $\begin{array}{c} \begin{array}{c} & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\$

3H), 6.25 (d, J = 7.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 154.8, 148.0, 140.3, 137.8, 136.8, 136.2, 133.8, 133.7, 133.0, 131.0, 129.1, 129.0, 128.6, 128.1, 128.0, 127.9, 127.0, 126.9, 126.4, 125.7, 124.0, 123.8, 57.3. NMR is in accordance with previously reports¹¹.

4.8. General procedure for atroposelective C-H arylation of biaryl compound



To an oven-dried 10 mL Schlenk tube containing a stirring bar was added amide derivative (0.10 mmol), phenylboronic acid (0.15 mmol, 1.5 eq), **Co@POP-Salox-1** (5.0 mol % Co content), KMnO₄ (10 mol%), LiOAc (20 mol%) and MeOH/TFE (3/7, v/v, 1.2 mL). The reaction flask was degassed three times with O₂. The mixture was then stirred for 12 h at 80 °C followed by cooling. The resulting mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by preparative TLC using Hexane/EtOAc as the eluent to afford the desired product **16a**.¹² **Data of the compound**

(R)-pyridin-2-yl(1,3,4-triphenylisoquinolin-2(1H)-yl)methanone 16a



The 94% *ee* was determined by Daicel Chiralcel AD-H, Hexanes/IPA = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.662 min, t (minor) = 9.032 min. <u>¹H</u> <u>NMR (400 MHz, CDCl₃)</u> δ 9.74 (s, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 8.03 - 7.92 (m, 3H), 7.85 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.20 (d, J = 7.5 Hz, 1H), 7.12 – 6.99 (m, 7H). ¹³C NMR (100 MHz, <u>CDCl_3)</u> δ 161.6, 149.7, 147.6, 141.0, 139.7, 137.3, 136.2, 133.1, 132.7, 132.3, 132.2, 129.6, 129.0, 128.7, 128.5, 128.3, 128.0, 127.6, 126.8, 126.4, 126.1, 126.0, 123.6, 121.9, 120.2. NMR is in accordance with previously reports¹².

5. General procedure for recycle and continuous flow

5.1. General procedure for recycle

Phosphinic amide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol), **Co@POP-Salox-1** (5.0 mol % Co content), $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol), NaOPiv (0.2 mmol) and 'BuOH (3 mL) were added to an oven dried vial equipped with stirring bars. Then, the vial was instantly placed in a heating block set at 70 °C under air for 48 h. After reaction, the catalyst was separated through centrifugation, and the catalyst was washed with EtOH, dried and reused in a next run.

 Table S5. Recycle of catalyst Co@POP-Salox-1

run times	1	2	3	4	5	6
yield(%)	95	93	90	88	85	79
e.e.	99	98	95	95	95	94

5.2. Optimization of continuous flow conditions



Table S6. Optimization of continuous flow conditions^a

Easters	V _{column}	V_{g}	V_l	Temp	Temp.	Yield	Ee
Entry	(mL)	(mL/min)	(mL/min)	K_t (min)	(°C)		
1	1.67	0.4	0.02	3.98	80	< 5%	
2	1.67	0.1	0.02	13	80	33%	91%
3	3.32	0.1	0.02	26	80	55%	94%
4	3.32	0.1	0.02	26	95	65%	95%

^a The *ee* value is determined by HPLC analysis.

5.3. General procedure for continuous flow

Feed A consisted of **7a** (0.05 M) and **2a** (1.2 eq.) dissolved in dioxane, whereas feed B was oxygen. The liquid stream (0.02 mL/min) and the gaseous stream (0.1 mL/min) were mixed together in a mixer. The resulting segmented flow stream was passed through a column (Φ 10 × 200 nm, reactor volume = 3.32 mL, residence time = 26 min) filled with Co-POP-Salox (100 mg) and SiO₂ (900 mg) at 95 °C. After passing a back pressure regulator the solution was collected.



Scheme S1. Heterogeneous Catalytic System under Continuous Flow

6. Characterization

6.1. Sheldon test and measure of content of Co in system

Phosphinic amide **1a** (0.3 mmol), alkyne **2a** (0.45 mmol), **Co@POP-Salox-1** (31mg, 5.0 mol % Co content), $Mn(OAc)_2 \cdot 4H_2O$ (0.3 mmol), NaOPiv (0.6 mmol) and 'BuOH (5 mL) were added to an oven dried vial equipped with stirring bars. Then, the vial was instantly placed in a heating block set at 70 °C under air for 12 h. 1.0 mL reaction solution was withdrawn with a syringe. After removing the solvent, ¹H NMR and HPLC was determined. At the same time, the catalyst was separated through centrifugation, and $Mn(OAc)_2 \cdot 4H_2O$ (0.3 mmol), NaOPiv (0.6 mmol), L1 (5.0 mmol%) were added to the supernatant. The mixtures were further stirred for an additional 6 h at 70 °C without **Co@POP-Salox-1**. After removing the solvent, ¹H NMR and HPLC was determined. The two quenched mixtures were mixed together and dry with vacuum pump, 124 mg of dark brown solid obtained, which was taken for ICP-MS detection of cobalt.

Condition	Catalyzed by Co@POP-	Removed Co@POP-	
Condition	Salox-1 for 12 h	Salox-1 for next 6 h	
Yield (%)	35	36	
e.e. (%)	98 98		
W (Co in the system)	6.36	ppm	

Leaching amounts $=\frac{M (Co \text{ in system})}{M(Co \text{ in POPs})} = \frac{W (Co \text{ in system}) \times M (system)}{W (Co \text{ in POPs}) \times M (POPs)} = \frac{6.36 \times 10^{-6} \times 124}{2.84 \times 10^{-2} \times 31} \approx 0.09\%$

6.2. Characterization of the catalyst



Figure S1. (a) SEM images of Co@POP-Salox-9. (b)TEM images of Co@POP-Salox-9.

(c) SEM images of the reused catalyst. (d)TEM images of the reused catalyst.



Figure S2. Energy-dispersive X-ray spectroscopy (EDS) of reused catalyst



Figure S3. N2 sorption isotherms and pore size distribution of the reused catalyst

6.3. XPS spectra of Co@POP-Salox-1



Figure S4. X-ray photoelectron spectroscopy (XPS) of Co@POP-Salox-1. (a) O 1s. (b) N 1s.

7. Reference

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8. NMR spectra



¹H NMR of L1











¹H NMR of 3a











S40



















¹H NMR of 3j







fl (ppm)















¹³C NMR of 3p



S54







¹³C NMR of 3s





³¹P NMR of 3t





S59



S60

¹³C NMR of 3w













¹H NMR of 5a



¹H NMR of 6a





¹H NMR of 8a

S68





S69








S73



S74

9. HPLC of products

HPLC spectra for racemic and chiral product 3a (99% ee).



HPLC spectra for racemic and chiral product 3b (98% ee).



Signal	VWD1A,Wavele	ngth=254 nm		
Ret.	time [min]	Area	Height	Area%
	7.693	2487.31	99.24	51.38
	9.475	2353.86	56.06	48.62



HPLC spectra for racemic and chiral product 3c (99% ee).





HPLC spectra for racemic and chiral product 3d (98% ee).







HPLC spectra for racemic and chiral product 3f (99% ee).





Signal	VWD1A,Waveler	ngth=254 nm		
Ret.	time [min]	Area	Height	Area%
	6.239	420.80	18.52	0.52
	11.082	80649.50	2686.88	99.48



HPLC spectra for racemic and chiral product 3g (99% ee).

HPLC spectra for racemic and chiral product 3h (99% ee).



Signal	VWD1A,Wavelength=254 nm				
Ret.	time [min]	Area	Height	Area%	
	6.042	3275.52	86.56	50.07	
	13.693	3265.88	50.02	49.93	



HPLC spectra for racemic and chiral product 3i (99% ee).





HPLC spectra for racemic and chiral product 3j (99% ee).

HPLC spectra for racemic and chiral product 3k (99% ee).





HPLC spectra for racemic and chiral product 31 (99% ee).





HPLC spectra for racemic and chiral product 3m (99% ee).





Signal	mal VWD1A,Wavelength=254 nm				
Ret	. time [min]	Area	Height	Area%	
	13.048	44812.42	1373.27	53.14	
	32.124	39521.27	502.58	46.86	

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HPLC spectra for racemic and chiral product 30 (99% ee).



Signal	VWD1A,Waveler	ngth=254 nm		
Ret.	time [min]	Area	Height	Area%
	24.775	4902.85	45.62	42.60
	33.176	6606.02	44.25	57.40



Signal	VWD1A,Waveler	ngth=254 nm		
Ret.	time [min]	Area	Height	Area%
	24.770	63287.96	639.30	100.00



HPLC spectra for racemic and chiral product 3p (99% ee).



4090.02

13.961



49.61

101.35



HPLC spectra for racemic and chiral product 3r (99% ee).





HPLC spectra for racemic and chiral product 3s (99% ee).

HPLC spectra for racemic and chiral product 3t (99% ee).



Signal	VWD1A,Wavelength=254 nm				
Ret.	time [min]	Area	Height	Area%	
	24.219	1893.29	11.32	49.35	
	30.212	1942.98	12.54	50.65	



HPLC spectra for racemic and chiral product **3u** (99% *ee*).







HPLC spectra for racemic and chiral product 3v (91% ee).





Signal	VWD1A, Waveler	ngth=254 nm		
Ret.	time [min]	Area	Height	Area%
	26.183	11941.33	98.07	48.75
	31.845	12551.58	65.16	51.25



HPLC spectra for racemic and chiral product 3x (99% ee).



Signal	VWD1A,Wavelen	gth=254 nm		
Ret.	time [min]	Area	Height	Area%
	10.660	4154.82	134.44	50.39
	13.961	4090.02	101.35	49.61



Signal	VWD1A,Wavelength=254 nm				
Ret.	time [min]	Area	Height	Area%	
	10.603	212.62	7.31	0.24	
	18.437	89376.66	1616.80	99.76	



HPLC spectra for racemic and chiral product 3y (99% ee).

HPLC spectra for racemic and chiral product 3z (99% ee).





HPLC spectra for racemic and chiral product 3aa (98% ee).



23.917 142068.47 1507.99



HPLC spectra for racemic and chiral product 5a (99% ee).

HPLC spectra for racemic and chiral product 6a (99% ee).





HPLC spectra for racemic and chiral product 8a (95% ee).





HPLC spectra for racemic and chiral product 8b (95% ee).

HPLC spectra for racemic and chiral product 8c (96% ee).



Signal	VWD1A, Wavelength=254 nm			
Ret.	time [min]	Area	Height	Area%
	13.769	19223.84	523 . 50	49.74
	17.970	19422.43	435.91	50.26



HPLC spectra for racemic and chiral product 8d (91% ee).







Signal	VWD1A,Wavelength=254 nm	
D-+	time [min] Arres	

Area%	Height	Area	Ret. time [min]
4.39	11.41	549.25	18.912
95.61	262.60	11968.15	20.945



HPLC spectra for racemic and chiral product 11a (98% ee).

HPLC spectra for racemic and chiral product 13a (93% ee).





HPLC spectra for racemic and chiral product 16a (94% ee).



Signal	wbin, waveler	igtn-234 nm		
Ret.	time [min]	Area	Height	Area%
	6.662	19800.12	577.56	96.91
	9.032	631.65	16.75	3.09