Supporting Information

Copper-Catalyzed Enantioconvergent Radical Suzuki-Miyaura $C(sp^3)-C(sp^2)$ Cross-Coupling

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The optimization of reaction conditions

Table S1. Initial Screening of Reaction Conditions^a

Br (±)-1a	+ Ph Ph 2	[Cu] (10 L1 (12 BR ₂ <u>LiO⁷Bu (4</u> solvent, rt, .	0 mol%) mol%) 4.0 equiv.) argon, 48 h	Ph 3	Ph	H PPh ₂
BR ₂ =	[−] ÷B O	ξ B O	_ОН ₹В, ОН	້ ₹ BF₃K	₹B 0	> >
	2a, Bneop	2b, Bpin	2c	2d	2e , B(mac)	
Entry	2		So	Ivent	Yield	Ee
1	2a	Cul	DN	MSO	0	/
2	2b	CuI	DN	MSO	0	/
3	2c	CuI	DN	MSO	0	/
4	2d	CuI	DN	MSO	0	/
5	2e	CuI	DN	MSO	0	/
6	2a	CuI	CH	H_2Cl_2	0	/
7	2a	CuI	D	OCE	0	/
8	2a	CuI	tol	uene	0	/
9	2a	CuI	CH	I ₃ CN	0	/
10	2a	CuI	Et	OAc	0	/
11	2a	CuI	E	t_2O	0	/
12	2a	CuI	Т	ΉF	0	/
13 ^b	2a	CuI	DN	MSO	39%	31%

^{*a*}Reaction conditions: (±)-**1a** (0.075 mmol), **2** (0.05 mmol), CuI (10 mol%), **L1** (12 mol%), LiO'Bu (4.0 equiv.) in solvent (0.60 mL) at room temperature for 24 h under argon. Yield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values based on HPLC analysis. ^{*b*}H₂O (2.0 equiv.) was added.

			Cul (10 mol%)	
			L (12 mol%)	
	Br \		LiO'Bu (4.0 equiv.)	Ph
	+ /	- - - - - - - - - -	H ₂ O (2.0 equiv.)	
			DMSO/CH ₂ Cl ₂ (2:1) TIF	PS y
TIPS	Ph		–10 °C, Ar	Ph
	(±)- 1b	2e		42
		_		
	OMe	1	L1 , Ar = Ph	
		<u> </u>	L2 , Ar = 3,5- ^t Bu ₂ C ₆ H ₃	
		\downarrow	L3 , Ar = 2,4,6-Me ₃ C ₆ H ₂	
	Ť Ĭ	NH PAr ₂	L4 , Ar = 2,6-Me ₂ C ₆ H ₃	
	N	0	L5, Ar = 1-naphthyl	
			L6, Ar = 9-phenanthryl	
	Entry	L	Yield	Ee
	1	L4	47%	63%
	2	L1	82%	54%
	3	L2	88%	57%
	4	L3	35%	59%
	5	L5	53%	75%
	6	L6	52%	92%
	$7^{b,c}$	L6	43%	86%
	8^{b}	L6	68%	94%
	9^d	L6	62%	94%

Table S2. Screening of Reaction Conditions for Propargyl Bromides^a

^{*a*}Reaction conditions: (±)-**1b** (0.075 mmol), **2e** (0.05 mmol), CuI (10 mol%), **L** (12 mol%), LiO^{*t*}Bu (4.0 equiv.) and H₂O (2.0 equiv.) in DMSO/CH₂Cl₂ (0.60 mL, v/v = 2:1) at -10 °C for 120 h under argon. Yield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Ee values based on HPLC analysis. ^{*b*}LiO^{*t*}Bu (6.0 equiv.) and H₂O (3.0 equiv.). ^{*c*}Utilizing Bpin-derived boronate ester **2b** instead of **2e**. ^{*d*}LiO^{*t*}Bu (8.0 equiv.) and H₂O (4.0 equiv.).

Scheme S1. Control experiment with propargyl bromides



General information

All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker DPX-400 spectrometer at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, 376 MHz for ¹⁹F NMR and 128 MHz for ¹¹B NMR, respectively, in CDCl₃ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using SHIMADZU LC-20AD with SPD-20AV detector or Agilent high-performance liquid chromatography (HPLC) with Hatachi detector (at appropriate wavelength). Column conditions are reported in the experimental section below.

The synthesis of alkyl bromide substrates

The alkyl bromides **1a**, **1d–1z**, **1aa–1ad** were synthesized according to the reported literature.¹

The Synthesis of Propargyl Bromides

The propargyl bromides were synthesized according to the reported procedure.²

General procedure for preparation of (3-bromopent-1-yn-1-yl)triisopropylsilane (1b):



^{*n*}BuLi (2.4 M in hexane, 10.8 mL, 26 mmol, 1.3 equiv.) was added dropwise into a solution of triisopropylsilacetylene (5.8 mL, 26 mmol, 1.3 equiv.) in anhydrous THF (50.0 mL) at -78 °C. The mixture was stirred at room temperature for 30 min and cooled to -78 °C. Propionaldehyde (1.4 mL, 20 mmol, 1.0 equiv.) was added dropwise. Then the mixture was warmed up to room temperature and stirred for overnight. The mixture was quenched by a saturated aq. NH₄Cl (20 mL), extracted with EtOAc (3 × 30 mL), and dried over Na₂SO₄. The organic phase was concentrated in vacuum and then subjected to flash chromatography to afford the desired 1-(triisopropylsilyl)pent-1-yn-3-ol.

A 100-mL flask was charged with imidazole (0.82 g, 12.0 mmol, 1.2 equiv.), evacuated, and back-filled with argon. CH₂Cl₂ (30 mL) was added via syringe, followed by the addition of the 1-(triisopropylsilyl)pent-1-yn-3-ol (2.40 g, 10.0 mmol, 1.0 equiv.). The solution was stirred for 15 min. and then dibromotriphenylphosphorane (5.1 g, 12.0 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at room temperature. Upon completion (monitored by TLC), the reaction was quenched by the addition of silica gel. The solvent was removed under reduced pressure, and then the plug of silica gel was subjected to flash chromatography to afford the desired product 1b.

(3-bromopent-1-yn-1-yl)triisopropylsilane (1b)



1b

Following the above general procedure, the title compound **1b** was prepared from 1-(triisopropylsilyl)pent-1-yn-3-ol (2.40 g, 10 mmol, 1.0 equiv.) as a colorless oil (1.76 g, 58% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 4.53 (t, *J* = 6.4 Hz, 1H), 2.11 – 1.96 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 105.7, 88.8, 39.1, 33.1, 18.5, 11.6, 11.1.

HRMS (ESI) m/z calcd. for C₁₄H₂₈BrSi [M + H]⁺ 303.1138, found 303.1137.

(E)-(3-bromoundec-8-en-1-yn-1-yl)triisopropylsilane (1af)

Following the above general procedure, the title compound **1af** was prepared from (E)-1-(triisopropylsilyl)undec-8-en-1-yn-3-ol (1.94 g, 6.0 mmol, 1.0 equiv.) as a pale yellow oil (1.27 g, 55% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 5.43 – 5.25 (m, 2H), 4.54 (t, *J* = 6.4 Hz, 1H), 2.13 – 1.94 (m, 6H), 1.65 – 1.50 (m, 2H), 1.47 – 1.34 (m, 2H), 1.07 (s, 21H), 0.96 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 132.0, 128.6, 105.9, 88.7, 39.8, 37.3, 28.8, 27.0, 26.8, 20.5, 18.6, 18.53, 18.48, 14.3, 11.2.

HRMS (ESI) m/z calcd. for C₂₀H₃₈BrSi [M + H]⁺ 385.1921, found 385.1915.

(3-bromo-6-chlorohex-1-yn-1-yl)triisopropylsilane (1ag)



1ag

Following the above general procedure, the title compound **1ag** was prepared from 6-chloro-1-(triisopropylsilyl)hex-1-yn-3-ol (0.87 g, 3.0 mmol, 1.0 equiv.) as a pale yellow oil (0.35 g, 34% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 4.61 (t, J = 6.0 Hz, 1H), 3.64 – 3.57 (m, 2H), 2.22 – 2.14 (m, 2H), 2.12 – 2.02 (m, 2H), 1.08 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 105.1, 89.5, 43.9, 36.8, 36.2, 30.1, 18.5, 11.1. HRMS (ESI) *m*/*z* calcd. for C₁₄H₂₇BrClSi [M + H]⁺ 337.0748, found 337.0746.

5-bromo-7-(triisopropylsilyl)hept-6-yn-1-yl acetate (1ah)



1ah

Following the above general procedure, the title compound **1ah** was prepared from 5-hydroxy-7-(triisopropylsilyl)hept-6-yn-1-yl acetate (0.85 g, 2.6 mmol, 1.0 equiv.) as a pale yellow oil (0.50 g, 50% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 4.56 (t, *J* = 6.8 Hz, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 2.09 – 1.98 (m, 5H), 1.72 – 1.59 (m, 4H), 1.07 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 171.1, 105.6, 89.0, 64.1, 39.3, 36.9, 27.7, 23.9, 20.9, 18.53, 18.47, 11.1.

HRMS (ESI) m/z calcd. for C₁₈H₃₄BrO₂Si [M + H]⁺ 389.1506, found 389.1504.

ethyl 6-bromo-8-(triisopropylsilyl)oct-7-ynoate (1ai)

₩ CO2Et TIPS

1ai

-5

Following the above general procedure, the title compound **1ai** was prepared from ethyl 6-hydroxy-8-(triisopropylsilyl)oct-7-ynoate (1.75 g, 5.1 mmol, 1.0 equiv.) as a pale yellow oil (0.68 g, 41% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 4.55 (t, *J* = 6.4 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.74 – 1.53 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 173.3, 105.6, 88.9, 60.2, 39.4, 37.0, 34.1, 26.8, 24.0, 18.5, 14.2, 11.1.

HRMS (ESI) m/z calcd. for C₁₉H₃₆BrO₂Si [M + H]⁺ 403.1662, found 403.1662.



Following the procedure reported in the literature,³ 5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-ol (3.17 g, 10 mmol, 1.0 equiv.) was added to a solution of triphenylphosphine (3.15 g, 12.0 mmol, 1.2 equiv.) in THF (20 mL). *N*-Chlorosuccinimide (1.74 g, 13.0 mmol, 1.3 equiv.) was added in portions over 10 minutes and the reaction heated to reflux. After 19 hours the mixture was allowed to cool to room temperature before pentane (20 mL) was added. The solvent was removed under reduced pressure, and was subjected to flash chromatography to afford the desired product **1c**.

(3-chloro-5-phenylpent-1-yn-1-yl)triisopropylsilane (1c)



Following the above general procedure, the title compound 1c was prepared from 5-phenyl-1-(triisopropylsilyl)pent-1-yn-3-ol (3.17 g, 10 mmol, 1.0 equiv.) as a colorless oil (1.70 g, 43% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 4.49 (t, *J* = 6.8 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.32–2.19 (m, 2H), 1.09 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 140.3, 128.6, 128.5, 126.2, 105.1, 88.1, 48.1, 41.0, 32.4, 18.60, 11.1.

HRMS (ESI) m/z calcd. for C₂₀H₃₂ClSi [M + H]⁺ 335.1956, found 335.1953.

The synthesis of boron reagents



The boron reagents were synthesized according to the reported procedure.⁴ To a 100-mL flask equipped with a stir bar was added (hetero)aryl boronic acid (10 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (2.17 g, 11 mmol, 1.1 equiv.). Then CH₂Cl₂/EtOAc (4:1, 20 mL) was added to dissolve the reactants. The reaction was allowed to stir at room temperature for 3 hours, then the reaction mixture was concentrated. The crude product was purified by silica gel chromatography to afford the desired product.

8-([1,1':3',1''-terphenyl]-5'-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxab orole (2e)



Following the above general procedure, the title compound 2e was prepared from (3,5-diphenylphenyl)boronic acid (5.48 g, 20 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (4.34 g, 22 mmol, 1.1 equiv.) as a white solid (7.90 g, 87% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 8.00 (s, 2H), 7.82 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.68 - 7.49 (m, 8H), 7.45 - 7.20 (m, 6H), 1.87 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 144.7, 141.01, 140.00, 134.8, 132.5, 131.1, 128.8, 128.6, 128.4, 127.2, 125.3, 119.6, 92.5, 22.2.

¹¹**B** NMR (128 MHz, CDCl₃) δ 30.8.

HRMS (ESI) m/z calcd. for C₃₂H₂₆BO₂ [M + H]⁺ 453.2020, found 453.2012.

1-(4-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)phen yl)ethan-1-one (2ea)



Following the above general procedure, the title compound **2ea** was prepared from (4-acetylphenyl)boronic acid (0.49 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.91 g, 89% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 7.85 (s, 4H), 7.82 – 7.77 (m, 2H), 7.66 – 7.57 (m, 4H), 2.57 (s, 3H), 1.88 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 198.42, 144.5, 138.9, 135.0, 134.7, 131.4, 128.5, 127.2, 125.4, 119.6, 92.7, 26.7, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 31.2.

HRMS (ESI) m/z calcd. for C₂₂H₂₀BO₃ [M + H]⁺ 343.1500, found 343.1502.

8-(3-methoxyphenyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]diox aborole (2eb)

2eb

Following the above general procedure, the title compound **2eb** was prepared from (3-methoxyphenyl)boronic acid (0.46 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.78 g, 79% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.2 Hz, 2H), 7.65 – 7.54 (m, 4H), 7.36 (d, J = 7.2 Hz, 1H), 7.29 (s, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.97 – 6.88 (m, 1H), 3.76 (s, 3H), 1.86 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 158.9, 144.7, 134.7, 131.3, 128.8, 128.4, 127.2, 125.2, 119.5, 118.8, 117.8, 92.4, 55.2, 22.2. ¹¹B NMR (128 MHz, CDCl₃) δ 30.5. HRMS (ESI) m/z calcd. for C₂₁H₂₀BO₃ [M + H]⁺ 331.1500, found 331.1501.

8-(4-methoxyphenyl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]diox aborole (2ec)

Following the above general procedure, the title compound **2ec** was prepared from (4-methoxyphenyl)boronic acid (0.46 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.85 g, 86% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 7.81–7.74 (m, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.64–7.55 (m, 4H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 1.86 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 162.0, 144.9, 136.5, 134.8, 131.3, 128.4, 125.2, 119.5, 113.2, 92.2, 55.0, 22.2.

¹¹**B** NMR (128 MHz, CDCl₃) δ 31.2.

HRMS (ESI) m/z calcd. for C₂₁H₂₀BO₃ [M + H]⁺ 331.1500, found 331.1495.

8-([1,1'-biphenyl]-3-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dio xaborole (2ed)



2ed

Following the above general procedure, the title compound **2ed** was prepared from 3-biphenylboronic acid (0.59 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (1.03 g, 91% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.81–7.71 (m, 3H), 7.66–7.50 (m, 7H), 7.42–7.32 (m, 3H), 7.32–7.24 (m, 1H), 1.86 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.7, 141.1, 140.4, 134.7, 133.7, 133.6, 131.3, 129.9, 128.6, 128.4, 128.0, 127.2, 127.1, 125.3, 119.6, 92.4, 22.2.

¹¹**B** NMR (128 MHz, CDCl₃) δ 30.3.

HRMS (ESI) m/z calcd. for C₂₆H₂₂BO₂ [M + H]⁺ 377.1707, found 377.1704.

8-([1,1'-biphenyl]-4-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dio xaborole (2ee)

B(mac) **Dh**

2ee

Following the above general procedure, the title compound 2ee was prepared from 4-biphenylboronic acid (0.59 g, 3.0 mmol, 1.0 equiv.) and

1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (1.02 g, 90% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 8.4 Hz, 2H), 7.78 (d, $J_1 = 7.2$ Hz, $J_2 = 1.6$ Hz, 2H), 7.65–7.50 (m, 8H), 7.43–7.36 (m, 2H), 7.34–7.28 (m, 1H), 1.87 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.8, 143.7, 140.9, 135.3, 134.8, 131.3, 128.7, 128.4, 127.5, 127.1, 126.3, 125.3, 119.6, 92.4, 22.2.

¹¹**B** NMR (128 MHz, CDCl₃) δ 31.8.

HRMS (ESI) m/z calcd. for C₂₆H₂₂BO₂ [M + H]⁺ 377.1707, found 377.1703.

1-(3-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)phen yl)ethan-1-one (2ef)



2ef

Following the above general procedure, the title compound **2ef** was prepared from (3-acetylphenyl)boronic acid (0.49 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.87 g, 85% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 8.02 – 7.90 (m, 2H), 7.84 – 7.73 (m, 2H), 7.68 – 7.56 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H), 2.58 (s, 3H), 1.88 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 198.3, 144.5, 139.4, 136.3, 134.8, 134.7, 131.3, 130.7, 128.5, 127.9, 125.3, 119.6, 92.6, 26.7, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 30.1.

HRMS (ESI) m/z calcd. for C₂₂H₂₀BO₃ [M + H]⁺ 343.1500, found 343.1500.

3-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)benzoni trile (2eg)



2eg

Following the above general procedure, the title compound **2eg** was prepared from (3-cyanophenyl)boronic acid (0.44 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.74 g, 76% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.75 (m, 2H), 7.66 – 7.55 (m, 5H), 7.35 (t, *J* = 7.6 Hz, 1H), 1.87 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.2, 138.7, 138.4, 134.6, 134.3, 131.3, 128.5, 128.2, 125.4, 119.6, 118.7, 111.9, 92.9, 22.0.

¹¹**B** NMR (128 MHz, CDCl₃) δ 29.1.

HRMS (ESI) m/z calcd. for C₂₁H₁₇BNO₂ [M + H]⁺ 326.1347, found 326.1348.

4-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-yl)benzoni trile (2eh)

Following the above general procedure, the title compound **2eh** was prepared from (4-cyanophenyl)boronic acid (0.44 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.76 g, 78% yield).

¹**H** NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.4 Hz, 2H), 7.82 – 7.77 (m, 2H), 7.66 – 7.59 (m, 4H), 7.57 (d, J = 8.4 Hz, 2H), 1.88 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.3, 135.1, 134.7, 131.4, 131.0, 128.5, 125.5, 119.6, 118.8, 114.5, 92.9, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 31.2.

HRMS (ESI) m/z calcd. for C₂₁H₁₇BNO₂ [M + H]⁺ 326.1347, found 326.1348.

8-(furan-3-yl)-6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborole (2ei)

B(mac)

2ei

Following the above general procedure, the title compound **2ei** was prepared from furan-3-ylboronic acid (0.34 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.75 g, 86% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.75 (m, 2H), 7.73 (s, 1H), 7.64 – 7.54 (m, 4H), 7.38 (t, *J* = 1.6 Hz, 1H), 6.57 – 6.51 (m, 1H), 1.84 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 151.2, 144.6, 142.8, 134.7, 131.3, 128.4, 125.3, 119.5, 113.0, 92.1, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 29.5.

HRMS (ESI) m/z calcd. for C₁₈H₁₆BO₃ [M + H]⁺ 291.1187, found 291.1184.

6b,9a-dimethyl-8-(thiophen-3-yl)-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxabor ole (2ej)

B(mac) S 2ej

Following the above general procedure, the title compound **2ej** was prepared from thiophen-3-ylboronic acid (0.38 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.76 g, 83% vield).

¹**H** NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 3.6 Hz, 1H), 7.76 (dd, *J*₁= 6.8 Hz, *J*₂= 3.6 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 1.84 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.6, 136.5, 134.7, 132.0, 131.3, 128.4, 125.3, 125.2, 119.5, 92.2, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 28.8.

HRMS (ESI) m/z calcd. for C₁₈H₁₆BO₂S [M + H]⁺ 307.0959, found 307.0957.

2-chloro-5-(6b,9a-dimethyl-6b,9a-dihydroacenaphtho[1,2-d][1,3,2]dioxaborol-8-y l)pyridine (2ek)



Following the above general procedure, the title compound **2ek** was prepared from (6-chloropyridin-3-yl)boronic acid (0.47 g, 3.0 mmol, 1.0 equiv.) and 1,2-dimethylacenaphthylene-1,2-diol (0.65 g, 3.3 mmol, 1.1 equiv.) as a white solid (0.80 g, 79% yield).

¹**H NMR** (400 MHz, CDCl₃) δ 8.67 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80 (s, 2H), 7.61 (s, 4H), 7.24 (d, J = 8.0 Hz, 1H), 1.87 (s, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 155.7, 154.2, 144.8, 144.1, 134.7, 131.3, 128.5, 125.5, 123.6, 119.7, 92.9, 22.1.

¹¹**B** NMR (128 MHz, CDCl₃) δ 30.3.

HRMS (ESI) m/z calcd. for C₁₉H₁₆BClNO₂ [M + H]⁺ 336.0957, found 336.0958.

The synthesis of ligands

The ligands L1–L7 were synthesized according to the reported patent.⁵

General procedure for preparation of L4, L6 and L7.



Diethyl phosphonate (1.35 mL, 10.5 mmol) was added dropwise at 0 °C to a solution of arylmagnesium bromide in THF (40 mL) which was prepared from aryl bromides (30.0 mmol) and magnesium (0.79 g, 33.0 mmol). The mixture was stirred for 30 minutes at 0 °C. Upon completion (monitored by TLC), the mixture was quenched by a saturated aq. NH₄Cl (30 mL), extracted with EtOAc (3×30 mL), and dried over Na₂SO₄. The organic phase was concentrated in vacuum and the residue was purified by column chromatography on silica gel using dichloromethane/methanol = 10/1 as eluent to give the diarylphosphine oxide L4-1 (2.58 g, 10.0 mmol, 95% yield).

The diarylphosphine oxide L4-1 (2.58 g, 10.0 mmol) and $Cu(OTf)_2$ (0.36 g, 1.0 mmol, 0.1 equiv.) were added in a 50 mL Schlenk tube at room temperature. Then TMDS (2.65 mL, 15 mmol, 1.5 equiv.) and toluene (20 mL) were added under argon flow. The reaction mixture was stirred for 12 h at 120 °C. After the reaction was completed, the solvent was removed under vacuum. Then the residue was purified by column chromatography on silica gel using petroleum ether as eluent to give the diarylphosphane L4-2 (2.42 g, 10.0 mmol, quantitative yield).

The diarylphosphane L4-2 (2.42 g, 10.0 mmol) was placed in a Schlenk flask and

dissolved in THF (20 mL). The reaction mixture was cooled to -78 °C, KHMDS (1.0 M in THF, 15 mL, 15 mmol, 1.5 equiv.) was added via syringe. The reaction mixture was then warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled to -78 °C again and methyl-2-fluorobenzoate (1.5 mL, 12 mmol, 1.2 equiv.) was added dropwise. After the addition, the reaction mixture was warmed to room temperature and stirred for 30 minutes. The mixture was warmed to room temperature and stirred for 30 minutes. The mixture was quenched with NH₄Cl aqueous (20 mL) and was extracted with EtOAc (3 × 30 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 20:1 as eluent to provide the product L4-3 (3.50 g, 9.3 mmol, 93% yield).

The compound L4-3 (3.50 g, 9.3 mmol) was charged into a round bottom flask equipped with reflux condenser and was dissolved in THF (20 mL) at room temperature. Water (20 mL) was added into this solution followed by LiOH·H₂O (7.80 g, 186 mmol, 20 equiv.). The reaction mixture was stirred at 75 °C for 36 h. Then the mixture was cooled to room temperature and extracted with EtOAc (3×30 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude was purified by flash chromatography on silica gel using dichloromethane/methanol = 5:1 as eluent to provide the product L4-4 (2.65 g, 7.3 mmol, 78% yield).

To an oven-dried flask was added L4-4 (1.81 g, 5.0 mmol), quinine-derived chiral amine⁵ (1.77 g, 5.5 mmol, 1.1 equiv.), DMAP (61.0 mg, 0.5 mmol, 0.1 equiv.) and EDCI (1.25 g, 6.5 mmol, 1.3 equiv.), followed by the addition of DCM (20 mL). The reaction mixture was stirred for 6 h at room temperature. After completion (monitored by TLC), the reaction mixture was directly subjected to flash chromatography on silica gel using dichloromethane/methanol = 10:1 as eluent to afford the desired product L4 (2.40 g, 3.6 mmol, 72% yield).

The ligand **L7** was synthesized from quinidine-derived chiral amine according to the above procedure.



L4 (Ar = $2,6-Me_2C_6H_3$)

¹**H NMR** (400 MHz, CDCl₃) δ 8.41 (d, J = 4.8 Hz, 1H), 8.27 (br, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.88 – 7.78 (m, 1H), 7.69 (d, J = 2.8 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.23 – 7.09 (m, 4H), 7.06 – 6.96 (m, 2H), 6.96 – 6.89 (m, 2H), 6.69 (br, 1H), 5.82 – 5.67 (m, 1H), 5.52 (br, 1H), 4.98 (d, J = 9.2 Hz, 1H), 4.95 (s, 1H), 3.92 (s, 3H), 3.33 – 3.15 (m, 2H), 2.92 (br, 1H), 2.78 – 2.61 (m, 2H), 2.31 – 2.21 (m, 1H), 2.09 (s, 6H), 1.96 (s, 6H), 1.71 – 1.50 (m, 3H), 1.47 – 1.32 (m, 1H), 0.96 – 0.80 (m, 1H).

¹³**C NMR** (100 MHz, CDCl₃) δ 168.2, 157.7, 147.6, 145.1, 144.5, 143.2, 143.0, 142.5, 142.4, 141.4, 141.3, 141.0, 134.7, 134.5, 133.5, 133.1, 133.0, 132.7, 131.4, 129.8, 129.24, 129.20, 129.17, 129.1, 128.9, 128.5, 128.4, 121.4, 118.6, 114.3, 101.9, 60.2, 56.0, 55.5, 41.0, 39.5, 27.9, 27.3, 26.0, 23.0, 22.8, 22.7, 22.5.

³¹**P NMR** (162 MHz, CDCl₃) δ -28.4

HRMS (ESI) m/z calcd. for C₄₃H₄₇N₃O₂P [M + H]⁺ 668.3400, found 668.3401.



L7 (Ar = 2,6-Me₂C₆H₃)

¹**H** NMR (400 MHz, CDCl₃) δ 8.47 (br, 1H), 8.34 (d, J = 4.4 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.22 – 7.10 (m, 4H), 7.07 – 6.90 (m, 4H), 6.66 (br, 1H), 5.98 – 5.84 (m, 1H), 5.57 – 5.41 (m, 1H), 5.19 – 5.03 (m, 2H), 3.93 (s, 3H), 3.06 – 2.78 (m, 5H), 2.35 – 2.23 (m, 1H), 2.13 (s, 6H), 1.97 (s, 6H), 1.63 (br, 1H), 1.58 – 1.44 (m, 2H), 1.30 – 1.21 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 157.6, 147.5, 145.7, 144.4, 143.4, 143.2, 142.5, 142.3, 141.2, 140.9, 140.5, 134.6, 134.4, 133.4, 133.2, 133.0, 132.7, 132.6, 131.3, 130.0, 129.8, 129.32, 129.28, 129.2, 129.1, 129.0, 128.5, 128.44, 128.40, 121.8, 118.5, 114.6, 101.3, 60.5, 55.4, 49.2, 46.9, 39.0, 27.2, 26.6, 25.3, 23.0, 22.9, 22.7, 22.5.

³¹**P NMR** (162 MHz, CDCl₃) δ -28.3

HRMS (ESI) m/z calcd. for C₄₃H₄₇N₃O₂P [M + H]⁺ 668.3400, found 668.3401.



Diethyl phosphonate (4.50 mL, 35 mmol, 0.35 equiv.) was added dropwise at 0 °C to a solution of arylmagnesium bromide in THF (150 mL) which was prepared from aryl bromides (100 mmol) and magnesium (2.64 g, 110 mmol, 1.1 equiv.). The mixture was stirred for 30 minutes at 0 °C. Upon completion (monitored by TLC), the mixture was quenched by a saturated aq. NH₄Cl (50 mL), The reaction was diluted with EtOAc, filtered through a frit funnel and washed with EtOAc. Then the solid residue was dried under vacuum to give the diarylphosphine oxide L6-1 (8.28 g, 20.6 mmol, 59% yield).

In a oven-dried Schlenk tube (100 mL) was placed CuI (380 mg, 2.0 mmol, 0.1 equiv.) under argon atmosphere. Then 1-phenylethan-1-amine (0.52 mL, 4.0 mmol, 0.2 equiv.) was added, followed by methyl 2-iodobenzoate (2.94 mL, 20 mmol, 1.0 equiv.). After 5 minutes, toluene (50 mL) was added followed by **L6-1** (8.05 g, 20 mmol). After the mixture was stirred for 5 minutes, anhydrous K_2CO_3 (5.5 g, 40 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at 120 °C for 48 h under argon atmosphere. Then the mixture was allowed to cool to room temperature and was filtered through a short plug of Celite under reduce pressure. Celite was washed three times with EtOAc and the filtrate was evaporated under reduced pressure. The

residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 3:1 as eluent to give the diarylphosphane **L6-2** (8.75 g, 16.3 mmol, 82% yield).

The compound **L6-2** (3.76 g, 7.0 mmol, 1.0 equiv.) and PPh₃ (5.50 g, 21 mmol, 3.0 equiv.) was placed in a Schlenk flask and dissolved in toluene/THF (1:1, 40 mL) under argon atmosphere. Trichlorosilane (21 mL, 210 mmol, 30 equiv.) was slowly added to the mixture via syringe. The reaction mixture was slowly warmed to 110 °C and was stirred for 3 d at this temperature. Then the mixture was carefully quenched by a saturated aq. NH₄Cl (50 mL) at 0 °C and diluted with EtOAc. The HCl (conc.) was added carefully until the mixture became clear. The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 20:1 as eluent to provide the product **L6-3** (3.02 g, 5.8 mmol, 83% yield).

The compound **L6-3** (2.60 g, 5.0 mmol) was charged into a round bottom flask equipped with reflux condenser and was dissolved in THF (20 mL) at room temperature. Water (20 mL) was added into this solution followed by LiOH·H₂O (4.20 g, 100 mmol, 20 equiv.). The reaction mixture was stirred at 75 °C for 36 h. Then the mixture was cooled to room temperature and extracted with EtOAc (3×30 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude was purified by flash chromatography on silica gel using dichloromethane/methanol = 5:1 as eluent to provide the product **L4-4** (1.78 g, 3.5 mmol, 70% yield).

To an oven-dried flask was added **L6-4** (1.27 g, 2.5 mmol), quinine-derived chiral amine (0.89 g, 2.75 mmol, 1.1 equiv.), DMAP (30.5 mg, 0.25 mmol, 0.1 equiv.) and EDCI (0.62 g, 3.25 mmol, 1.3 equiv.), followed by the addition of DCM (10 mL). The reaction mixture was stirred for 6 h at room temperature. After completion (monitored by TLC), the reaction mixture was directly subjected to flash chromatography on silica gel using dichloromethane/methanol = 10:1 as eluent to afford the desired product **L6** (1.60 g, 2.0 mmol, 80% yield).



L6, Ar = 9-phenanthryl

¹**H** NMR (400 MHz, CDCl₃) δ 8.93 – 8.15 (m, 7H), 7.99 – 6.81 (m, 21H), 5.37 (br, 2H), 5.01 – 4.57 (m, 2H), 3.87 (s, 3H), 3.01 (br, 1H), 2.40 (br, 2H), 2.00 (br, 1H), 1.86 (s, 3H), 1.53 – 1.30 (m, 3H), 0.68 (br, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 169.0, 157.5, 147.2, 144.6, 144.2, 141.1, 135.4, 134.9, 133.2, 133.1, 133.0, 132.9, 131.3, 131.2, 130.9, 130.8, 130.4, 130.21, 130.16, 130.1, 129.5, 128.9, 128.8, 127.5, 127.4, 127.2, 127.1, 126.9, 126.8, 126.7, 126.5, 123.0, 122.8, 122.5, 122.3, 121.3, 114.1, 60.1, 55.5, 54.8, 50.6, 40.7, 39.0, 27.6, 27.1, 25.6. ³¹P NMR (162 MHz, CDCl₃) δ -25.7

HRMS (ESI) m/z calcd. for C₅₅H₄₇N₃O₂P [M + H]⁺ 812.3400, found 812.3399.

Experimental Procedures

Copper-Catalyzed Enantioconvergent Radical Suzuki-Miyaura $C(sp^3)-C(sp^2)$ Cross-Coupling



General Procedure A

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2** (0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L4** (16.0 mg, 0.024 mmol, 12 mol%), LiO'Bu (64.0 mg, 0.80 mmol, 4.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (7.2 mg, 0.40 mmol, 2.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly, alkyl halide **1** (0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred at $-5 \,^{\circ}$ C or $-10 \,^{\circ}$ C and stopped at the designated time. Upon completion (monitored by TLC), the reaction mixture was poured into water (10 mL), then extracted with DCM (3 × 5 mL). The filtrate was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford the desired products.



The racemates of products were prepared following the procedure: under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2** (0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), **Lrac** (9.3 mg, 0.024 mmol, 12 mol%), LiO'Bu (32.0 mg, 0.40 mmol, 2.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (3.6 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly, alkyl halide **1** (0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred for 0.5 h to 2.0 h at room temperature. Upon completion (monitored by TLC), the reaction mixture was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford the desired products.



General Procedure B

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 2 (0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020

mmol, 10 mol%), **L6** (19.7 mg, 0.024 mmol, 12 mol%), LiO'Bu (96.0 mg, 1.20 mmol, 6.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (10.8 mg, 0.60 mmol, 3.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly, alkyl halide **1** (0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred at -10 °C and stopped at the designated time. Upon completion (monitored by TLC), the reaction mixture was poured into water (10 mL), then extracted with DCM (3 × 5 mL). The filtrate was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford the desired products.



The racemates of products were prepared following the procedure: under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2** (0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), Lrac (9.3 mg, 0.024 mmol, 12 mol%), LiO'Bu (32.0 mg, 0.40 mmol, 2.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (3.6 mg, 0.20 mmol, 1.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly, alkyl halide **1** (0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred at -10 °C. Upon completion (monitored by TLC), the reaction mixture was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford the desired products.

Determination of absolute configuration

The absolute configuration of **29** was determined by comparing the HPLC spectrum (Figure S1) and specific rotation with those reported in literature.⁶ ($[\alpha]_D^{24.7} = -9.9$ (c 0.60, CHCl₃, 94% ee). Lit.⁶ $[\alpha]_D^{25.1} = -7.8$ (c 0.78, CHCl₃), 92% ee}) The product **29** was determined to be of an "*R*" absolute configuration according to the reported data.



Figure S1. Determination of absolute stereochemistry

Characteristic data of products 3-52

(*R*)-1,3-diphenyl-5-(1-phenylethyl)benzene (3)



According to the general procedure **A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **3** as a pale yellow oil (52.3 mg, 78% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.08 min, t_R (minor) = 7.37 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.68 – 7.55 (m, 5H), 7.46 – 7.39 (m, 6H), 7.37 – 7.26 (m, 6H), 7.22 – 7.14 (m, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 147.3, 146.1, 141.8, 141.3, 128.7, 128.4, 127.6, 127.32, 127.30, 126.1, 125.6, 124.1, 45.0, 22.0.

HRMS (ESI) m/z calcd. for C₂₆H₂₃ [M + H]⁺ 335.1794, found 335.1792.

5',5''-diphenyl-1,1':3',1'''-quaterphenyl (3')



¹**H NMR** (400 MHz, CDCl₃) δ 7.89 (d, J = 1.6 Hz, 4H), 7.85 – 7.82 (m, 2H), 7.75 – 7.69 (m, 8H), 7.53 – 7.46 (m, 8H), 7.44 – 7.37 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 142.5, 142.3, 141.1, 128.9, 127.6, 127.4, 125.4, 125.3. HRMS (ESI) *m*/*z* calcd. for C₃₆H₂₇ [M + H]⁺ 459.2107, found 459.2099.

5',5''-diphenyl-1,1':3',1'''-quaterphenyl (3'')



¹**H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.51 (m, 4H), 7.46 – 7.30 (m, 11H), 7.30 – 7.23 (m, 1H), 7.09 (d, J = 1.6 Hz, 2H), 5.44 (q, J = 6.4 Hz, 1H), 1.69 (d, J = 6.4 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 158.7, 143.1, 142.9, 141.1, 128.70, 128.68, 127.6, 127.42, 127.2, 125.6, 118.8, 113.8, 76.2, 24.4. **HRMS** (ESI) *m*/*z* calcd. for C₂₆H₂₃O [M + H]⁺ 351.1743, found 351.1735.

(*R*)-1,3-diphenyl-5-(1-(3-methoxyphenylethyl))benzene (4)



According to the **general procedure A**, substrate **1d** (64.5 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **4** as a pale yellow oil (58.3 mg, 80% yield, 94% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 5.34 min, t_R (major) = 5.71 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.67 – 7.55 (m, 5H), 7.47 – 7.38 (m, 6H), 7.36 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 6.92 – 6.84 (m, 2H), 6.72 (d, *J* = 5.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 1.71 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.6, 147.7, 147.2, 141.8, 141.3, 129.4, 128.7, 127.31, 127.29, 125.5, 124.1, 120.1, 113.9, 110.9, 55.1, 45.0, 21.9.

HRMS (ESI) m/z calcd. for C₂₇H₂₅O [M + H]⁺ 365.1900, found 365.1901.

(*R*)-1,3-diphenyl-5-(1-(3-methylphenylethyl))benzene (5)



According to the **general procedure A**, substrate **1e** (59.7 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **5** as a pale yellow oil (43.5 mg, 62% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.29 min, t_R (minor) = 6.72 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.66 – 7.56 (m, 5H), 7.47 – 7.38 (m, 6H), 7.36 – 7.29 (m, 2H), 7.22 – 7.16 (m, 2H), 7.13 – 7.07 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 147.6, 143.1, 141.8, 141.4, 135.6, 129.1, 128.7, 127.5, 127.30, 127.28, 125.5, 124.0, 44.6, 22.0, 21.0.

HRMS (ESI) m/z calcd. for C₂₇H₂₅ [M + H]⁺ 349.1951, found 349.1938.

(*R*)-1,3-diphenyl-5-(1-(4-methylphenylethyl))benzene (6)



According to the **general procedure A**, substrate **1f** (59.7 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **6** as a pale yellow oil (48.7 mg, 70% yield, 93% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 5.32 min, t_R (minor) = 5.98 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.67 – 7.57 (m, 5H), 7.48 – 7.38 (m, 6H), 7.36 – 7.29 (m, 2H), 7.17 (d, J = 7.8 Hz, 1H), 7.10 (s, 2H), 6.99 (d, J = 7.8 Hz, 1H), 4.23 (q, J = 7.2 Hz, 1H), 2.30 (s, 3H), 1.71 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 147.5, 146.0, 141.8, 141.4, 137.9, 128.7, 128.4, 128.3, 127.3, 126.9, 125.6, 124.6, 124.0, 45.0, 22.0, 21.5.

HRMS (ESI) m/z calcd. for C₂₇H₂₅ [M + H]⁺ 349.1951, found 349.1954.

(*R*)-1,3-diphenyl-5-(1-(4-*tert*-butylphenylethyl))benzene (7)



According to the **general procedure A**, substrate **1g** (72.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **7** as a pale yellow solid (45.1 mg, 58% yield, 97% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.4 mL/min, $\lambda = 254$ nm), t_R (minor) = 12.15 min, t_R (major) = 12.68 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 – 7.58 (m, 5H), 7.47 – 7.40 (m, 6H), 7.37 – 7.28 (m, 4H), 7.26 – 7.20 (m, 2H), 4.25 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 3H), 1.29 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 148.8, 147.5, 143.0, 141.8, 141.4, 128.7, 127.32, 127.30, 127.1, 125.6, 125.3, 124.0, 44.6, 34.3, 31.4, 22.0.

HRMS (ESI) m/z calcd. for C₃₀H₃₁ [M + H]⁺ 391.2420, found 391.2413.

(*R*)-1,3-diphenyl-5-(1-(4-chlorophenylethyl))benzene (8)



According to the **general procedure A**, substrate **1h** (65.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **8** as a pale yellow oil (49.4 mg, 67% yield, 85% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.48 min, t_R (minor) = 7.71 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.66 – 7.56 (m, 5H), 7.47 – 7.40 (m, 4H), 7.39 (d, J = 2.0 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.28 – 7.19 (m, 4H), 4.24 (q, J = 7.2 Hz, 1H), 1.70 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.8, 144.6, 142.0, 141.2, 131.8, 129.0, 128.8, 128.5, 127.4, 127.3, 125.5, 124.3, 44.4, 21.9.

HRMS (ESI) m/z calcd. for C₂₆H₂₂³⁵Cl [M + H]⁺ 369.1405, found 369.1402.

(*R*)-1,3-diphenyl-5-(1-(4-bromophenylethyl))benzene (9)



According to the **general procedure A**, substrate **1i** (79.2 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **9** as a pale yellow oil (55.4 mg, 67% yield, 86% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.09 min, t_R (minor) = 8.42 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 – 7.56 (m, 5H), 7.46 – 7.37 (m, 8H), 7.37 – 7.31 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 1H), 1.69 (d, *J* = 7.0 Hz, 3H).

¹³**C** NMR (100 MHz, CDCl₃) δ 146.7, 145.1, 142.0, 141.2, 131.5, 129.4, 128.8, 127.4, 127.3, 125.4, 124.3, 120.0, 44.4, 21.8. HRMS (ESI) *m*/*z* calcd. for C₂₆H₂₂⁷⁹Br [M + H]⁺ 413.0899, found 413.0895.

(*R*)-1,3-diphenyl-5-(1-(4-iodophenylethyl))benzene (10)



According to the **general procedure A**, substrate **1j** (93.3 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **10** as a colorless oil (55.7 mg, 60% yield, 87% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.55 min, t_R (minor) = 8.69 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 – 7.55 (m, 7H), 7.45 – 7.31 (m, 8H), 7.03 (d, J = 8.4 Hz, 2H), 4.20 (q, J = 7.2 Hz, 1H), 1.68 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.6, 145.8, 142.0, 141.1, 137.5, 129.7, 128.75, 128.71, 127.4, 127.31, 127.27, 125.4, 124.3, 91.4, 44.5, 21.8.

HRMS (ESI) m/z calcd. for C₂₆H₂₂I [M + H]⁺ 461.0761, found 461.0764.

(*R*)-1,3-diphenyl-5-(1-(4-fluorophenylethyl))benzene (11)



According to the **general procedure A**, substrate **1k** (60.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **11** as a pale yellow oil (41.2 mg, 58% yield, 87% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 6.6 min, t_R (minor) = 8.2 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.67 – 7.54 (m, 5H), 7.47 – 7.37 (m, 6H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H).

¹³**C** NMR (100 MHz, CDCl₃) δ 161.3 (d, J = 242.6 Hz), 147.2, 141.9, 141.7 (d, $J_{C-F} = 3.1$ Hz), 141.2, 129.0 (d, $J_{C-F} = 7.8$ Hz), 128.8, 127.4, 127.3, 125.5, 124.2, 115.2 (d, $J_{C-F} = 21.0$ Hz), 44.2, 22.1

¹⁹**F NMR** (376 MHz, CDCl₃) δ –117.1.

HRMS (ESI) m/z calcd. for C₂₆H₂₂F [M + H]⁺ 353.1700, found 353.1703.

(*R*)-1,3-diphenyl-5-(1-(4-trifluorophenylethyl))benzene (12)



According to the **general procedure A**, substrate **11** (75.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **12** as a pale yellow oil (44.2 mg, 55% yield, 79% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 6.45 min, t_R (minor) = 7.10 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 (t, J = 1.6 Hz, 1H), 7.63 – 7.58 (m, 4H), 7.55 (d, J = 8.4 Hz, 2H), 7.47 – 7.38 (m, 8H), 7.37 – 7.32 (m, 2H), 4.32 (q, J = 7.2 Hz, 1H), 1.74 (d, J = 7.2 Hz, 3H).

¹³**C** NMR (100 MHz, CDCl₃) δ 150.2, 146.3, 142.1, 141.1, 128.8, 128.5 (q, $J_{C-F} = 32.2 \text{ Hz}$), 128.0, 127.5, 127.3, 125.5, 125.4 (q, $J_{C-F} = 3.8 \text{ Hz}$), 124.5, 124.3 (q, $J_{C-F} = 270.2 \text{ Hz}$), 44.9, 21.7.

¹⁹**F** NMR (376 MHz, CDCl₃) δ –62.3.

HRMS (ESI) *m*/*z* calcd. for C₂₇H₂₂F₃ [M + H]⁺ 403.1668, found 403.1669. (*R*)-1,3-diphenyl-5-(1-(4-*tert*-butylphenylethyl))benzene (13)



According to the **general procedure A**, substrate **1m** (78.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **13** as a white solid (43.6 mg, 53% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.58 min, t_R (major) = 19.91 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 – 7.59 (m, 5H), 7.58 – 7.50 (m, 4H), 7.47 (d, J = 1.6 Hz, 2H), 7.46 – 7.27 (m, 11H), 4.31 (q, J = 7.2 Hz, 1H), 1.76 (d, J = 7.2 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 147.3, 145.2, 141.9, 141.3, 140.9, 139.0, 128.74, 128.69, 128.0, 127.34, 127.31, 127.2, 127.05, 126.99, 125.6, 124.2, 44.7, 22.0. **HRMS** (ESI) m/z calcd. for C₃₂H₂₇ [M + H]⁺ 411.2107, found 411.2104.

(S)-5'-(1-(2-fluorophenyl)ethyl)-1,1':3',1''-terphenyl (14)



According to the **general procedure A**, substrate **1n** (60.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **14** as a white solid (10.0 mg, 14% yield, 80% ee).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, $\lambda = 254$ nm), t_R (major) = 8.98 min, t_R (minor) = 9.46 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.66 – 7.57 (m, 5H), 7.46 (d, J = 1.6 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.36 – 7.25 (m, 3H), 7.19 – 7.12 (m, 1H), 7.10 – 7.04 (m, 1H), 7.04 – 6.96 (m, 1H), 4.60 (q, J = 7.2 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 160.6 (d, $J_{C-F} = 244.2$ Hz), 146.0, 141.9, 141.3, 133.0 (d, J = 14.4 Hz), 128.7, 128.5 (d, $J_{C-F} = 4.4$ Hz), 127.8 (d, $J_{C-F} = 8.2$ Hz), 127.34, 127.31, 125.5, 124.3, 124.1 (d, $J_{C-F} = 3.4$ Hz), 115.4 (d, $J_{C-F} = 22.3$ Hz), 37.6 (d, $J_{C-F} = 2.6$ Hz), 20.8.

¹⁹**F NMR** (376 MHz, CDCl₃) δ – 117.5

(R)-1,3-diphenyl-5-(1-phenylethyl)naphthalene (15)



According to the **general procedure A**, substrate **10** (70.5 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **15** as a white solid (24.6 mg, 32% yield, 91% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.38 min, t_R (minor) = 6.19 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.82 – 7.72 (m, 4H), 7.66 – 7.56 (m, 5H), 7.49 – 7.36 (m, 9H), 7.35 – 7.29 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 1H), 1.82 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 147.2, 143.5, 141.9, 141.3, 133.5, 132.1, 128.7, 128.0, 127.8, 127.6, 127.33, 127.30, 126.8, 125.9, 125.7, 125.4, 124.2, 45.1, 21.9.

HRMS (ESI) m/z calcd. for C₃₀H₂₅ [M + H]⁺ 385.1951, found 385.1953.

(*R*)-1,3-diphenyl-5-(1-henylpropyl)benzene (16)



According to the **general procedure A**, substrate **1p** (59.1 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **16** as a pale yellow oil (37.9 mg, 53% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 5.26 min, t_R (minor) = 6.15 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 – 7.57 (m, 5H), 7.47 – 7.38 (m, 6H), 7.36 – 7.24 (m, 6H), 7.19 – 7.13 (m, 1H), 3.91 (t, *J* = 7.8 Hz, 1H), 2.16 (hep, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.1, 144.9, 141.8, 141.3, 128.7, 128.4, 127.9, 127.3, 126.1, 125.9, 124.1, 53.5, 28.7, 12.9.

HRMS (ESI) m/z calcd. for C₂₇H₂₅ [M + H]⁺ 349.1951, found 349.1954.

(*R*)-1,3-diphenyl-5-(1-phenylpropyl)benzene (17)



According to the **general procedure A**, substrate **1q** (63.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **17** as a white solid (42.1 mg, 58% yield, 94% ee).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.54 min, t_R (minor) = 7.27 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.64 – 7.56 (m, 5H), 7.48 – 7.38 (m, 6H), 7.37 – 7.24 (m, 6H), 7.20 – 7.13 (m, 1H), 4.03 (t, *J* = 7.6 Hz, 1H), 2.12 (q, *J* = 6.0 Hz, 2H), 1.42 – 1.28 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.3, 145.0, 141.8, 141.4, 128.7, 128.5, 127.9, 127.3, 126.1, 125.8, 124.1, 51.3, 38.0, 21.2, 14.1.

HRMS (ESI) m/z calcd. for C₂₆H₂₇ [M + H]⁺ 363.2107, found 363.2105.

(R)-1,3-diphenyl-5-(1-phenylbutyl)benzene (18)



According to the **general procedure A**, substrate **1r** (63.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **18** as a pale yellow oil (42.1 mg, 54% yield, 95% ee).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 4.68 min, t_R (minor) = 5.25 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 – 7.57 (m, 5H), 7.48 – 7.40 (m, 6H), 7.37 – 7.25 (m, 6H), 7.20 – 7.14 (m, 1H), 4.01 (t, *J* = 7.8 Hz, 1H), 2.14 (q, *J* = 7.2 Hz, 2H), 1.43 – 1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.4, 145.1, 141.8, 141.4, 128.7, 128.5, 127.9, 127.3, 126.1, 125.8, 124.1, 51.6, 35.5, 30.3, 22.7, 14.0.

HRMS (ESI) m/z calcd. for C₂₉H₂₉ [M + H]⁺ 377.2264, found 377.2266.

(*R*)-1,3-diphenyl-5-(1-phenylbutyl)benzene (19)



According to the **general procedure A**, substrate **1s** (72.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **19** as a pale yellow oil (45.3 mg, 58% yield, 92% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 4.61 min, t_R (minor) = 5.53 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 5H), 7.48 – 7.39 (m, 6H), 7.37 – 7.25 (m, 6H), 7.20 – 7.14 (m, 1H), 4.01 (t, *J* = 7.6 Hz, 1H), 2.22 – 2.05 (m, 2H), 1.38 – 1.21 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.4, 145.1, 141.8, 141.4, 128.7, 128.5, 127.9, 127.3, 126.1, 125.8, 124.1, 51.6, 35.8, 31.9, 27.8, 22.5, 14.1.

HRMS (ESI) m/z calcd. for C₃₀H₃₁ [M + H]⁺ 391.2420, found 391.2422.

(*R*)-1,3-diphenyl-5-(1-phenylisobutyl)benzene (20)



According to the **general procedure A**, substrate **1t** (68.1 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **20** as a white solid (47.4 mg, 63% yield, 95% ee).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.79 min, t_R (minor) = 6.44 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.63 – 7.56 (m, 5H), 7.48 – 7.39 (m, 6H), 7.37 – 7.25 (m, 6H), 7.20 – 7.13 (m, 1H), 4.15 (t, *J* = 7.8 Hz, 1H), 2.02 (t, *J* = 7.4 Hz, 2H), 1.60 – 1.47 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.3, 145.0, 141.8, 141.4, 128.7, 128.5, 127.9, 127.3, 126.1, 125.8, 124.1, 49.1, 45.1, 25.6, 22.8, 22.6.

HRMS (ESI) m/z calcd. for C₂₉H₂₉ [M + H]⁺ 377.2264, found 377.2262.

(*R*)-1,3-diphenyl-5-(1-phenyl(phenethyl))benzene (21)



According to the **general procedure A**, substrate **1u** (82.6 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **21** as a pale yellow oil (59.8 mg, 70% yield, 92% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 6.00 min, t_R (minor) = 6.83 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 – 7.56 (m, 5H), 7.48 – 7.39 (m, 6H), 7.37 – 7.23 (m, 8H), 7.22 – 7.12 (m, 4H), 4.05 (t, *J* = 7.6 Hz, 1H), 2.71 – 2.58 (m, 2H), 2.56 – 2.41 (m, 2H).

¹³**C NMR** (100 MHz, CDCl₃) δ 145.9, 144.5, 142.0, 141.9, 141.3, 128.7, 128.6, 128.5, 128.4, 127.9, 127.35, 127.30, 126.3, 125.9, 125.8, 124.2, 50.9, 37.3, 34.2. **HRMS** (ESI) *m*/*z* calcd. for $C_{33}H_{29}$ [M + H]⁺ 425.2264, found 425.2261.

(*R*)-1,3-diphenyl-5-(1-phenyl(phenethyl))benzene (22)



According to the **general procedure A**, substrate **1v** (86.8 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **22** as a pale yellow oil (57.6 mg, 66% yield, 96% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.28 min, t_R (minor) = 11.62 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.63 – 7.54 (m, 5H), 7.46 – 7.38 (m, 6H), 7.37 – 7.30 (m, 2H), 7.30 – 7.19 (m, 6H), 7.19 – 7.09 (m, 4H), 4.03 (t, *J* = 7.8 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.26 – 2.08 (m, 2H), 1.67 (hep, *J* = 7.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 146.0, 144.8, 142.2, 141.8, 141.3, 128.7, 128.49, 128.46, 128.4, 128.3, 127.8, 127.30, 126.2, 125.8, 125.7, 124.1, 51.5, 35.8, 35.2, 29.8. **HRMS** (ESI) *m*/*z* calcd. for C₃₄H₃₁ [M + H]⁺ 439.2420, found 439.2423.

(*R*)-1,3-diphenyl-5-(1-phenylallyl)benzene (23)



According to the **general procedure A**, substrate 1w (63.3 mg, 0.30 mmol) and 2e (90.4 mg, 0.20 mmol) was employed to yield the product 23 as a white solid (22.1 mg, 31% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 5.49 min, t_R (minor) = 6.12 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 5H), 7.47 – 7.39 (m, 6H), 7.37 – 7.25 (m, 6H), 7.21 – 7.15 (m, 1H), 5.85 – 5.70 (m, 1H), 5.08 (d, *J* = 18 Hz, 1H), 4.99 (d, *J* = 10 Hz, 1H), 4.14 (t, *J* = 8.0 Hz, 1H), 2.92 (t, *J* = 8.0 Hz, 2H).

¹³**C NMR** (100 MHz, CDCl₃) δ 145.5, 144.3, 141.8, 141.3, 136.7, 128.7, 128.5, 127.9, 127.34, 127.29, 126.3, 125.9, 124.2, 116.5, 51.5, 40.0.

HRMS (ESI) m/z calcd. for C₂₆H₂₅ [M + H]⁺ 361.1951, found 361.1948.

(*R*)-1,3-diphenyl-5-(1-phenyl(ethoxy-4-oxobutyl))benzene (24)



According to the **general procedure A**, substrate **1x** (85.6 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **24** as a colorless oil (37.2 mg, 43% yield, 93% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 8.08 min, t_R (major) = 8.93 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 – 7.56 (m, 5H), 7.47 – 7.39 (m, 6H), 7.37 – 7.25 (m, 6H), 7.22 – 7.14 (m, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.04 (t, *J* = 7.6 Hz, 1H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.24 – 2.12 (m, 2H), 1.74 – 1.60 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³**C** NMR (100 MHz, CDCl₃) δ 173.4, 145.8, 144.5, 141.9, 141.2, 128.7, 128.5, 127.8, 127.32, 127.28, 126.3, 125.7, 124.2, 60.2, 51.4, 35.1, 34.2, 23.5, 14.2.

HRMS (ESI) m/z calcd. for C₃₁H₃₁O₂ [M + H]⁺ 435.2319, found 435.2305.

(*R*)-1,3-diphenyl-5-(1-phenylcyanopropyl)benzene (25)



According to the **general procedure A**, substrate **1y** (71.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **25** as a pale yellow oil (37.8 mg, 49% yield, 89% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 17.01 min, t_R (major) = 18.98 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 – 7.56 (m, 5H), 7.48 – 7.40 (m, 6H), 7.39 – 7.29 (m, 6H), 7.22 – 7.16 (m, 1H), 4.03 (d, *J* = 7.8 Hz, 1H), 2.41 – 2.22 (m, 4H), 1.75 – 1.59 (m, 2H).

¹³**C NMR** (100 MHz, CDCl₃) δ 145.1, 143.7, 142.1, 141.1, 128.8, 128.7, 127.7, 127.4, 127.3, 126.6, 125.5, 124.5, 119.5, 50.9, 34.5, 24.0, 17.2.

HRMS (ESI) m/z calcd. for C₂₉H₂₆N [M + H]⁺ 388.2060, found 388.2059.

(*R*)-1,3-diphenyl-5-(1-phenyl(phenethyl))benzene (26)



According to the **general procedure A**, substrate **1z** (47.0 mg, 0.15 mmol) and **2e** (45.2 mg, 0.10 mmol) was employed to yield the product **26** as a colorless oil (17.2 mg, 37% yield, 93% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.82 min, t_R (minor) = 10.47 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.64 – 7.56 (m, 5H), 7.48 – 7.39 (m, 6H), 7.37 – 7.25 (m, 6H), 7.20 – 7.13 (m, 1H), 4.43 (t, *J* = 5.0 Hz, 1H), 4.02 (t, *J* = 7.4 Hz, 1H), 3.58 (d, *J* = 11.2 Hz, 2H), 3.39 (d, *J* = 10.8 Hz, 2H), 2.34 – 2.23 (m, 2H), 1.74 – 1.63 (m, 2H), 1.17 (s, 3H), 0.70 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 145.9, 144.6, 141.8, 141.4, 128.7, 128.5, 127.9, 127.32, 127.28, 126.2, 125.9, 124.1, 102.0, 51.5, 33.5, 30.1, 29.8, 23.0, 21.8. HRMS (ESI) *m*/*z* calcd. for C₃₃H₃₅O₂ [M + H]⁺ 463.2632, found 463.2635.

(*R*)-1,3-diphenyl-5-(1-phenylbromoethyl)benzene (27)



According to the **general procedure A**, substrate **1aa** (83.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **27** as a white solid (39.4 mg, 46% yield, 92% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 8.78 min, t_R (minor) = 11.35 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.65 – 7.55 (m, 5H), 7.47 – 7.40 (m, 6H), 7.37 – 7.27 (m, 6H), 7.24 – 7.17 (m, 1H), 4.33 (t, *J* = 7.6 Hz, 1H), 3.37 (t, *J* = 6.6 Hz, 2H), 2.66 (q, *J* = 7.2 Hz, 2H).

¹³**C NMR** (100 MHz, CDCl₃) δ 144.5, 143.1, 142.1, 141.1, 128.8, 128.7, 127.9, 127.5, 127.3, 126.7, 125.7, 124.6, 49.3, 38.3, 32.0.

HRMS (ESI) m/z calcd. for C₂₇H₂₄⁷⁹Br [M + H]⁺ 427.1056, found 427.1058.

(*R*)-1-methoxy-3-(1-phenylethyl)benzene (28)



28

According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2eb** (66.0 mg, 0.20 mmol) was employed to yield the product **28** as a pale yellow oil (26.4 mg, 62% yield, 94% ee).

HPLC analysis: Chiralcel OJ (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 13.43 min, t_R (minor) = 14.61 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.31 – 7.14 (m, 6H), 6.85 – 6.79 (m, 1H), 6.79 – 6.76 (m, 1H), 6.74 – 6.68 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 1.62 (d, *J* = 7.6 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 159.6, 148.0, 146.1, 129.3, 128.3, 127.5, 126.0, 120.1, 113.8, 110.9, 55.1, 44.8, 21.8.

HRMS (ESI) m/z calcd. for C₁₅H₁₇O [M + H]⁺ 213.1274, found 213.1274.

(*R*)-1-methoxy-4-(1-phenylethyl)benzene (29)



According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2ec** (66.0 mg, 0.20 mmol) was employed to yield the product **29** as a pale yellow oil (23.2 mg, 55% yield, 94% ee).

HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min, λ = 214 nm), t_R (minor) = 16.86 min, t_R (major) = 17.72 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.09 (m, 5H), 6.82 (d, J = 8.8 Hz, 2H), 4.10 (q, J = 7.6 Hz, 1H), 3.76 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 157.8, 146.7, 138.5, 128.5, 128.3, 127.5, 125.9, 113.7, 55.2, 43.9, 22.0.

HRMS (ESI) m/z calcd. for C₁₅H₁₇O [M + H]⁺ 213.1274, found 213.1272.

(*R*)-1-phenyl-3-(1-phenylethyl)benzene (30)



According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2ed** (75.2 mg, 0.20 mmol) was employed to yield the product **30** as a colorless oil (26.4 mg, 51% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 4.84 min, t_R (minor) = 5.37 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.0 Hz, 2H), 7.45 (s, 1H), 7.43 – 7.37 (m, 3H), 7.37 – 7.23 (m, 6H), 7.22 – 7.14 (m, 2H), 4.21 (q, J = 7.2 Hz, 1H), 1.68 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.8, 146.2, 141.4, 141.3, 128.8, 128.7, 128.4, 127.6, 127.20, 127.17, 126.58, 126.56, 126.1, 124.9, 44.9, 21.9

HRMS (ESI) *m/z* calcd. for C₂₀H₁₇ [M-H]⁺ 257.1325, found 257.1324.

(R)-1-phenyl-4-(1-phenylethyl)benzene (31)



According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2ee** (75.2 mg, 0.20 mmol) was employed to yield the product **31** as a white solid (29.6 mg, 57% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.32 min, t_R (major) = 6.09 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 4.6 Hz, 2H), 7.34 – 7.23 (m, 7H), 7.23 – 7.16 (m, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 146.2, 145.5, 141.0, 138.9, 128.7, 128.4, 128.0, 127.6, 127.1, 127.02, 126.99, 126.1, 44.4, 21.8.

HRMS (ESI) m/z calcd. for C₂₀H₁₉ [M + H]⁺ 259.1481, found 259.1483.

(R)-1-phenyl-3-(1-phenylethyl)benzene (32)





According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2ef** (68.4 mg, 0.20 mmol) was employed to yield the product **32** as a colorless oil (22.4 mg, 50% yield, 93% ee).

HPLC analysis: Chiralcel AS (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.30 min, t_R (major) = 10.10 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.32 – 7.16 (m, 5H), 4.22 (q, J = 7.2 Hz, 1H), 2.57 (s, 3H), 1.67 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 198.3, 146.9, 145.6, 137.2, 132.5, 128.6, 128.5, 127.5, 127.2, 126.33, 126.26, 44.7, 26.7, 21.7. **HRMS** (ESI) *m/z* calcd. for C₁₆H₁₇O [M + H]⁺ 225.1274, found 225.1266.

(*R*)-1-phenyl-4-(1-phenylethyl)benzene (33)



According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2ea** (68.4 mg, 0.20 mmol) was employed to yield the product **33** as a pale yellow oil (27.2 mg, 61% yield, 93% ee).

HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.52 min, t_R (major) = 10.50 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.34 – 7.25 (m, 4H), 7.23 – 7.15 (m, 3H), 4.19 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 1.64 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.7, 151.9, 145.2, 135.1, 128.50, 128.45, 127.7, 127.5, 126.3, 44.7, 26.5, 21.5.

HRMS (ESI) m/z calcd. for C₁₆H₁₇O [M + H]⁺ 225.1274, found 225.1266.

(R)-1-cyano-3-(1-phenylethyl)benzene (34)



34

According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2eg** (65.0 mg, 0.20 mmol) was employed to yield the product **34** as a colorless oil (15.9 mg, 38% yield, 83% ee).

HPLC analysis: Chiralcel AS (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 7.30 min, t_R (minor) = 7.80 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 4.17 (9, *J* = 7.6 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 147.8, 144.7, 132.2, 131.1, 129.8, 129.1, 128.6, 127.5, 126.6, 119.0, 112.3, 44.3, 21.5.

HRMS (ESI) m/z calcd. for C₁₅H₁₄N [M + H]⁺ 208.1121, found 208.1115.

(R)-1-cyano-4-(1-phenylethyl)benzene (35)



According to the **general procedure A**, substrate **1a** (55.5 mg, 0.30 mmol) and **2eh** (65.0 mg, 0.20 mmol) was employed to yield the product **35** as a white solid (23.4 mg, 56% yield, 85% ee).

HPLC analysis: Chiralcel ASH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 230 nm), t_R (major) = 14.18 min, t_R (minor) = 15.89 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, J = 8.4 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.24 – 7.14 (m, 3H), 4.19 (q, J = 7.2 Hz, 1H), 1.64 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 151.9, 144.6, 132.2, 128.6, 128.4, 127.5, 126.6, 119.0, 109.9, 44.8, 21.4.

HRMS (ESI) m/z calcd. for C₁₅H₁₄N [M + H]⁺ 208.1121, found 208.1114.

(S)-3-(1-([1,1':3',1''-terphenyl]-5'-yl)ethyl)-5-bromopyridine (36)



According to the **general procedure A**, substrate **1ab** (79.5 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **36** as a pale yellow solid (44.3 mg, 53% yield, 71% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 8.54 min, t_R (major) = 9.31 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.52 (s, 2H), 7.69 (d, *J* = 12.0 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 4H), 7.49 – 7.32 (m, 8H), 4.27 (q, *J* = 6.8 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 148.7, 147.5, 145.1, 143.2, 142.3, 140.9, 137.5, 128.8, 127.5, 127.3, 125.3, 124.8, 120.8, 42.3, 21.4.

HRMS (ESI) m/z calcd. for C₂₅H₂₁N⁷⁹Br [M + H]⁺ 414.0852, found 414.0841.

(S)-1-(4-(1-(pyridin-3-yl)ethyl)phenyl)ethan-1-one (37)



37

According to the **general procedure A**, substrate **1ac** (55.8 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **37** as a pale yellow solid (17.2 mg, 38% yield, 90% ee).

HPLC analysis: Chiralcel AD (hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 15.28 min, t_R (major) = 16.41 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.65 – 8.35 (m, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.55 – 7.44 (m, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.25 – 7.18 (m, 1H), 4.24 (q, J = 7.2 Hz, 1H), 2.58 (s, 3H), 1.69 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 197.6, 150.5, 149.3, 147.9, 140.6, 135.5, 134.8, 128.7, 127.7, 123.5, 42.4, 26.5, 21.2.

HRMS (ESI) m/z calcd. for C₁₅H₁₆NO [M + H]⁺ 226.1226, found 226.1227.

(S)-3-(1-([1,1':3',1''-terphenyl]-5'-yl)ethyl)quinolone (38)



According to the **general procedure A**, substrate **1ad** (70.8 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **38** as a white solid (53.7 mg, 70% yield, 91% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 14.61 min, t_R (major) = 16.84 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.89 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.77 (dd, J_1 = 8.4 Hz, J_2 = 1.4 Hz, 1H), 7.70 – 7.55 (m, 6H), 7.53 – 7.38 (m, 7H), 7.37 – 7.31 (m, 2H), 4.49 (q, J = 7.2 Hz, 1H), 1.85 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 151.7, 146.8, 145.9, 142.2, 141.0, 138.6, 133.1, 129.1, 128.9, 128.7, 128.0, 127.6, 127.5, 127.3, 126.7, 125.5, 124.6, 42.8, 21.7. **HRMS** (ESI) *m*/*z* calcd. for C₂₉H₂₄N [M + H]⁺ 386.1903, found 386.1892.

(*R*)-3-(1-(3-methoxyphenyl)ethyl)furan (39)



According to the **general procedure A**, substrate **1d** (43.0 mg, 0.20 mmol) and **2ei** (58.0 mg, 0.20 mmol) was employed to yield the product **39** as a pale yellow oil (29.2 mg, 72% yield, 93% ee).

HPLC analysis: Chiralcel IF (hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 6.87 min, t_R (major) = 7.31 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.36 – 7.31 (m, 1H), 7.26 – 7.17 (m, 2H), 6.82 (d, J = 7.6 Hz, 1H), 6.79 – 6.71 (m, 2H), 6.21 (s, 1H), 3.93 (q, J = 7.2 Hz, 1H), 3.78 (s, 3H), 1.54 (d, J = 6.8 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 159.6, 147.7, 142.9, 138.7, 130.1, 129.3, 119.7, 113.3, 111.2, 110.4, 55.1, 36.4, 21.9.

HRMS (ESI) m/z calcd. for C₁₃H₁₅O₂ [M + H]⁺ 203.1067, found 203.1067.

(*R*)-3-(1-(3-methoxyphenyl)ethyl)thiophene (40)



According to the **general procedure A**, substrate **1d** (43.0 mg, 0.20 mmol) and **2ej** (61.2 mg, 0.20 mmol) was employed to yield the product **40** as a pale yellow oil (26.1 mg, 60% yield, 94% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 6.52 min, t_R (major) = 7.37 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.25 – 7.17 (m, 2H), 6.99 – 6.95 (m, 1H), 6.88 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.77 – 6.70 (m, 2H), 4.12 (q, J = 7.2 Hz, 1H), 3.77 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 159.6, 147.9, 147.0, 129.3, 127.8, 125.3, 119.9, 119.8, 113.5, 111.1, 55.1, 40.8, 22.1.

HRMS (ESI) m/z calcd. for C₁₃H₁₅OS [M + H]⁺ 219.0838, found 219.0832.

(*R*)-2-chloro-5-(1-(3-methoxyphenyl)ethyl)pyridine (41)



According to the **general procedure A**, substrate **1d** (64.5 mg, 0.30 mmol) and **2ek** (67.0 mg, 0.20 mmol) was employed to yield the product **41** as a pale yellow oil (29.8 mg, 60% yield, 84% ee).

HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 10.14 min, t_R (minor) = 11.39 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 2.8 Hz, 1H), 7.44 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz, 1H), 7.28 – 7.16 (m, 2H), 6.82 – 6.67 (m, 3H), 4.12 (q, J = 7.2 Hz, 1H), 3.77 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H).

¹³**C NMR** (100 MHz, CDCl₃) δ 159.8, 149.1, 148.8, 146.0, 140.4, 137.9, 129.6, 123.9, 119.7, 113.6, 111.4, 55.1, 41.7, 21.3.

HRMS (ESI) m/z calcd. for C₁₄H₁₅ClNO [M + H]⁺ 248.0837, found 248.0834.

(*R*)-3-(1-(furan-3-yl)ethyl)quinoline (42)



According to the **general procedure A**, substrate **1ad** (70.8 mg, 0.30 mmol) and **2ei** (68.4 mg, 0.20 mmol) was employed to yield the product **42** as a pale yellow oil (25.1 mg, 56% yield, 75% ee).

HPLC analysis: Chiralcel AD (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 6.32 min, t_R (major) = 7.55 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.83 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.56 – 7.48 (m, 1H), 7.33 (d, J = 2.0 Hz, 1H), 6.37 – 6.28 (m, 1H), 6.13 (d, J = 3.2 Hz, 1H), 4.35 (q, J = 7.2 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 157.5, 151.0, 147.1, 141.7, 136.7, 133.3, 129.1, 128.9, 128.0, 127.6, 126.6, 110.1, 105.5, 37.0, 20.1.

HRMS (ESI) m/z calcd. for C₁₅H₁₄NO [M + H]⁺ 224.1070, found 224.1063.

(*R*)-3-(1-(thiophen-3-yl)ethyl)quinoline (43)



According to the **general procedure A**, substrate **1ad** (70.8 mg, 0.30 mmol) and **2ej** (61.2 mg, 0.20 mmol) was employed to yield the product **43** as a pale yellow oil (26.0 mg, 54% yield, 82% ee).

HPLC analysis: Chiralcel AD (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 6.67 min, t_R (major) = 8.60 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.81 (d, J = 2.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.07 – 7.00 (m, 1H), 6.96 – 6.86 (m, 1H), 4.38 (q, J = 7.2 Hz, 1H), 1.75 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 151.4, 146.9, 145.7, 138.8, 133.0, 129.1, 128.8, 128.1, 127.5, 127.5, 126.6, 126.0, 120.5, 38.4, 22.0. HRMS (ESI) *m*/*z* calcd. for C₁₅H₁₄NS [M + H]⁺ 240.0841, found 240.0833.

(S)-(3-([1,1':3',1''-terphenyl]-5'-yl)pent-1-yn-1-yl)triisopropylsilane (44)



According to the **general procedure B**, substrate **1b** (90.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **44** as a pale yellow oil (59.2 mg, 65% yield, 94% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 3.32 min, t_R (major) = 3.56 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.77 – 7.68 (m, 7H), 7.52 (d, J = 7.2 Hz, 4H), 7.47 – 7.40 (m, 2H), 3.88 (dd, J_1 = 8.0 Hz, J_2 = 5.4 Hz, 1H), 2.05 – 1.82 (m, 2H), 1.19 (s, 21H), 1.16 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.0, 141.8, 141.2, 128.7, 127.4, 127.3, 125.5, 124.4, 109.6, 83.9, 40.6, 32.2, 18.7, 11.7, 11.4.

HRMS (ESI) m/z calcd. for C₃₂H₄₁Si [M + H]⁺ 453.2972, found 453.2959.

(S)-(3-([1,1':3',1''-terphenyl]-5'-yl)-5-phenylpent-1-yn-1-yl)triisopropylsilane (45)



According to the **general procedure B**, substrate **1ae** (113.9 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **45** as a pale yellow oil (76.1 mg, 72% yield, 94% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min, $\lambda = 254$ nm), t_R (minor) = 5.82 min, t_R (major) = 6.16 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.70 – 7.60 (m, 7H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.39 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 3.85 (dd, *J*₁ = 8.8 Hz, *J*₂ = 5.6 Hz, 1H), 2.99 – 2.81 (m, 2H), 2.21 – 2.05 (m, 2H), 1.15 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 142.8, 141.9, 141.7, 141.1, 128.7, 128.5, 128.4, 127.4, 127.3, 125.9, 125.4, 124.5, 109.3, 84.6, 40.9, 38.5, 33.7, 18.8, 11.4.

HRMS (ESI) m/z calcd. for C₃₈H₄₅Si [M + H]⁺ 529.3285, found 529.3272.




According to the **general procedure B**, substrate **1af** (115.3 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **46** as a pale yellow oil (75.4 mg, 70% yield, 93% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 4.63 min, t_R (major) = 5.11 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.69 – 7.60 (m, 7H), 7.45 (d, J = 8.4 Hz, 4H), 7.39 – 7.33 (m, 2H), 5.40 – 5.26 (m, 2H), 3.84 (dd, $J_1 = 8.4$ Hz, $J_2 = 5.8$ Hz, 1H), 2.08 – 1.96 (m, 4H), 1.88 – 1.75 (m, 2H), 1.65 – 1.57 (m, 1H), 1.49 – 1.28 (m, 3H), 1.17 – 1.04 (m, 21H), 0.93 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.3, 141.8, 141.2, 131.8, 129.0, 128.7, 127.4, 127.3, 125.4, 124.4, 109.8, 83.8, 39.2, 39.0, 29.4, 27.04, 27.00, 20.5, 18.7, 14.4, 11.3. **HRMS** (ESI) *m*/*z* calcd. for C₃₈H₅₁Si [M + H]⁺ 535.3755, found 535.3761.

(S)-(3-([1,1':3',1''-terphenyl]-5'-yl)-6-chlorohex-1-yn-1-yl) triisopropyl silane~(47)



According to the **general procedure B**, substrate **1ag** (100.8 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **47** as a pale yellow oil (45.8 mg, 46% yield, 84% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 6.91 min, t_R (major) = 8.04 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.70 – 7.59 (m, 7H), 7.49 – 7.41 (m, 4H), 7.40 – 7.32 (m, 2H), 3.96 – 3.85 (m, 1H), 3.64 – 3.52 (m, 2H), 2.13 – 1.96 (m, 3H), 1.96 – 1.87 (m, 1H), 1.19 – 1.05 (m, 21H).

¹³**C NMR** (100 MHz, CDCl₃) δ 142.4, 142.0, 141.0, 128.8, 127.4, 127.3 125.3, 124.6, 108.8, 84.7, 44.7, 38.2, 36.1, 30.2, 18.7, 11.3.

HRMS (ESI) m/z calcd. for C₃₃H₄₂ClSi [M + H]⁺ 501.2739, found 501.2735.

(S)-5-([1,1':3',1''-terphenyl]-5'-yl)-7-(triisopropylsilyl)hept-6-yn-1-yl acetate (48)



According to the **general procedure B**, substrate **1ah** (116.4 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **48** as a pale yellow oil (55.6 mg, 52% yield, 84% ee).

HPLC analysis: Chiralcel AD (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.09 min, t_R (major) = 4.37 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.71 – 7.60 (m, 7H), 7.45 (d, J = 7.2 Hz, 4H), 7.40 – 7.33 (m, 2H), 4.10 – 4.01 (m, 2H), 3.88 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 1H), 2.01 (s, 3H), 1.92 – 1.61 (m, 6H), 1.11 (s, 21H).

¹³C NMR (100 MHz, CDCl₃) δ 171.2, 142.9, 141.9, 141.1, 128.7, 127.4, 127.3, 125.4, 124.5, 109.4, 84.1, 64.4, 38.9, 38.7, 28.3, 23.8, 20.9, 18.7, 11.3.

HRMS (ESI) m/z calcd. for C₃₆H₄₇O₂Si [M + H]⁺ 539.3340, found 539.3347.

ethyl (S)-6-([1,1':3',1''-terphenyl]-5'-yl)-8-(triisopropylsilyl)oct-7-ynoate (49)



According to the **general procedure B**, substrate **1ai** (120.7 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **49** as a pale yellow oil (50.7 mg, 46% yield, 90% ee).

HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 4.24 min, t_R (major) = 4.79 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.71 – 7.58 (m, 7H), 7.50 – 7.40 (m, 4H), 7.39 – 7.31 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.91 – 3.79 (m, 1H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.76 (m, 2H), 1.74 – 1.52 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.11 (s, 21H).

¹³**C NMR** (100 MHz, CDCl₃) δ 173.6, 143.0, 141.8, 141.1, 128.8, 127.4, 127.2, 125.4, 124.4, 109.5, 84.0, 60.2, 38.9, 38.7, 34.2, 26.9, 24.6, 18.7, 14.2, 11.3.

HRMS (ESI) m/z calcd. for C₃₇H₄₉O₂Si [M + H]⁺ 553.3496, found 553.3502.

(S)-5'-(6,6-dimethyl-1-phenylhept-4-yn-3-yl)-1,1':3',1''-terphenyl (50)



According to the **general procedure B**, substrate **1aj** (83.7 mg, 0.30 mmol) and **2e** (90.4 mg, 0.20 mmol) was employed to yield the product **50** as a pale yellow oil (64.9 mg, 76% yield, 86% ee).

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 4.15 min, t_R (major) = 4.65 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.69 – 7.61 (m, 5H), 7.58 (s, 2H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.40 – 7.33 (m, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 3.73 (dd, *J*₁ = 8.8 Hz, *J*₂ = 6.0 Hz, 1H), 2.92 – 2.72 (m, 2H), 2.16 – 1.98 (m, 2H), 1.32 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 143.8, 141.9, 141.8, 141.3, 128.8, 128.5, 128.3, 127.3, 127.2, 125.8, 125.4, 124.4, 93.1, 79.5, 40.8, 37.3, 33.7, 31.4, 27.6.

HRMS (ESI) m/z calcd. for C₃₃H₃₃ [M + H]⁺ 429.2577, found 429.2572.

(S)-(3-(benzo[d][1,3]dioxol-5-yl)pent-1-yn-1-yl)triisopropylsilane (51)



According to the **general procedure B**, substrate **1b** (90.9 mg, 0.30 mmol) and **2el** (68.8 mg, 0.20 mmol) was employed to yield the product **51** as a pale yellow oil (30.9 mg, 45% yield, 80% ee).

HPLC analysis: Chiralcel ODH (hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 5.75 min, t_R (major) = 6.10 min.

¹**H** NMR (400 MHz, CDCl₃) δ 6.89 (d, *J* = 1.6 Hz, 1H), 6.82 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.93 (dd, *J*₁ = 4.0 Hz, *J*₂ = 1.6 Hz, 2H), 3.57 (dd, *J*₁

= 8.0 Hz, J_2 = 5.6 Hz, 1H), 1.84–1.62 (m, 2H), 1.13 – 1.06 (m, 21H), 1.00 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 147.5, 146.1, 136.0, 120.5, 109.9, 108.1, 107.9, 100.9, 83.3, 40.1, 32.2, 18.7, 11.6, 11.3.

HRMS (ESI) m/z calcd. for C₂₁H₃₃O₂Si [M + H]⁺ 345.2244, found 345.2244.

(S)-2-chloro-5-(1-(triisopropylsilyl)pent-1-yn-3-yl)pyridine (52)



According to the **general procedure B**, substrate **1b** (90.9 mg, 0.30 mmol) and **2ek** (67.0 mg, 0.20 mmol) was employed to yield the product **52** as a pale yellow oil (23.9 mg, 36% yield, 90% ee).

HPLC analysis: Chiralcel IG (hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min, $\lambda = 254$ nm), t_R (minor) = 14.43 min, t_R (major) = 15.06 min.

¹**H NMR** (400 MHz, CDCl₃) δ 8.40 (d, *J* = 3.6 Hz, 1H), 7.67 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 3.68 (dd, *J*₁ = 8.4 Hz, *J*₂ = 5.6 Hz, 1H), 1.86 – 1.68 (m, 2H), 1.08 (s, 21H), 1.03 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 149.7, 148.9, 137.9, 136.4, 123.9, 107.6, 84.8, 37.2, 31.6, 18.6, 11.3, 11.2.

HRMS (ESI) m/z calcd. for C₁₉H₃₁ClNSi [M + H]⁺ 336.1909, found 336.1912.



According to the **General procedure A**: under argon atmosphere, an oven-dried round bottom flask equipped with a magnetic stir bar was charged with **2e** (1.36 g, 3.0 mmol, 1.0 equiv.), CuI (57.0 mg, 0.30 mmol, 10 mol%), **L4** (240 mg, 0.36 mmol, 12 mol%), LiO'Bu (960 mg, 12 mmol, 4.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 36 mL) and H₂O (108 μ L, 6.0 mmol, 2.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly, alkyl halide **1d** (0.97 g, 4.5 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred for 72 h at -5 °C. Upon completion (monitored by TLC), the reaction mixture was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford the desired products **4** (0.92 g, 84% yield, 92% ee).

The transformations



To a mixture of RuCl₃ (0.75 mg, 0.005 mmol, 5.0 mol%) and sodium periodate (85.5 mg, 0.40 mmol, 4.0 equiv.) in a mixed solvent of CCl₄ (0.2 mL) and water (0.3 mL) was added a solution of **45** (52.9 mg, 0.10 mmol, 1.0 equiv., 94% ee) in CH₃CN (0.2 mL) in one portion. The reaction mixture was stirred at room temperature for 4 h, and then, was concentrated. The residue was purified by column chromatography on silica gel to afford the product **53** as a white solid (34.9 mg, 89% yield).

To a solution of **53** (39.2 mg, 0.10 mmol, 1.0 equiv.) in MeOH (1.0 mL) was added SOCl₂ (59.5 mg, 0.5 mmol, 5.0 equiv.) dropwise at 0 °C. Then, the reaction mixture was warmed up to room temperature and stirred for another 3 h. After completion of reaction, the reaction mixture was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the product in quantitative yield. Then the obtained product was dissolved in anhydrous THF (1.0 mL), followed by the addition of LiAlH₄ (5.7 mg, 0.15 mmol, 1.5 equiv.) powder slowly at 0 °C. Then it was stirred at room temperature for 3 h. Upon completion (monitored by TLC), the reaction was quenched with wet Na₂SO₄ (0.2 mL water per gram) and filtered, and the solid was washed with THF. The organic phase was concentered and purified with by column chromatography on silica gel to afford the product **54** as a colorless oil (35.2 mg, 93% yield, 94% ee).

(S)-2-([1,1':3',1''-terphenyl]-5'-yl)-4-phenylbutanoic acid (53)



¹**H** NMR (400 MHz, CDCl₃) δ 7.72 (t, *J* = 1.6 Hz, 1H), 7.67 – 7.59 (m, 4H), 7.52 (d, *J* = 1.6 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 3.71 (t, *J* = 7.6 Hz, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.58 – 2.47 (m, 1H), 2.28 – 2.17 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 179.1, 142.3, 141.0, 140.8, 139.2, 128.8, 128.5, 128.4, 127.5, 127.3, 126.1, 125.9, 125.5, 50.8, 34.5, 33.6.

HRMS (ESI) m/z calcd. for C₂₈H₂₅O₂ [M + H]⁺ 393.1849, found 393.1846.

(S)-2-([1,1':3',1''-terphenyl]-5'-yl)-4-phenylbutan-1-ol (54)



HPLC analysis: Chiralcel OD (hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 9.52 min, t_R (major) = 11.46 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.72 – 7.69 (m, 1H), 7.67 – 7.61 (m, 4H), 7.49 – 7.43 (m, 4H), 7.20 (d, *J* = 1.6 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.11 (m, 3H), 3.83 (d, *J* = 6.4 Hz, 2H), 2.99 – 2.88 (m, 1H), 2.70 – 2.51 (m, 2H), 2.20 – 1.96 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 143.1, 142.2, 141.9, 141.1, 128.8, 128.4, 128.3, 127.5, 127.3, 126.0, 125.8, 124.8, 67.5, 48.3, 33.6, 33.5.

HRMS (ESI) m/z calcd. for C₂₈H₂₇O [M + H]⁺ 379.2056, found 379.2047.



To a solution of **44** (45.2 mg, 0.10 mmol, 1.0 equiv., 94% ee) in THF (1.0 mL) was added TBAF (0.24 mmol, 1.2 equiv.) and the resulting mixture was stirred at room temperature for 1 h. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography to yield **55a** as a colorless oil (26.3 mg, 89% yield, 94% ee).

(R)-5'-(pent-1-yn-3-yl)-1,1':3',1''-terphenyl (55a)



HPLC analysis: Chiralcel OJH (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 19.58 min, t_R (major) = 24.14 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.70 – 7.62 (m, 5H), 7.57 (d, J = 1.6 Hz, 2H), 7.50 – 7.42 (m, 4H), 7.40 – 7.33 (m, 2H), 3.75 – 3.66 (m, 1H), 2.32 (d, J = 2.4 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.07 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 142.4, 142.0, 141.1, 128.8, 127.4, 127.3, 125.4, 124.7, 85.7, 71.3, 39.3, 31.4, 11.8.

HRMS (ESI) m/z calcd. for C₂₃H₂₁ [M + H]⁺ 297.1638, found 297.1637.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.95 mg, 0.005 mmol, 5 mol%), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol, 5 mol%). Then THF was added, followed by PhI (0.20 mmol, 2.0 equiv.), alkyne **55a** (29.6 mg, 0.10 mmol, 1.0 equiv., 94% ee) and Et₃N (0.30 mmol, 3.0 equiv.). The reaction mixture was stirred at 80 °C for 18 h. Upon completion (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel to afford the desired products **58a** (23.7 mg, 64% yield, 94% ee).

(S)-5'-(1-phenylpent-1-yn-3-yl)-1,1':3',1''-terphenyl (58a)



HPLC analysis: Chiralcel OD-3 (hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 10.74 min, t_R (major) = 14.27 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.72 – 7.61 (m, 7H), 7.50 – 7.42 (m, 6H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 3.92 (t, *J* = 7.2 Hz, 1H), 2.04 – 1.88 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.1, 142.0, 141.2, 131.7, 128.8, 128.2, 127.8, 127.4, 127.3, 125.5, 124.7, 123.8, 91.3, 83.6, 40.2, 31.8, 12.0.

HRMS (ESI) m/z calcd. for C₂₉H₂₅ [M + H]⁺ 373.1951, found 373.1949.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (0.95 mg, 0.005 mmol, 5 mol%), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol, 5 mol%) and KOAc (0.20 mmol, 2.0 equiv.). Then THF was added, followed by 5-chloropyrazolo[1,5-a]pyrimidine (0.20 mmol, 2.0 equiv.), alkyne **55a** (29.6 mg, 0.10 mmol, 1.0 equiv., 94% ee). The reaction mixture was stirred at room temperature for 18 h. Upon completion (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel to afford the desired products **58b** (30.8 mg, 75% yield, 93% ee).

(S)-5-(3-([1,1':3',1''-terphenyl]-5'-yl)pent-1-yn-1-yl)pyrazolo[1,5-a]pyrimidine (58b)



HPLC analysis: Chiralcel OD-3 (hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 14.09 min, t_R (major) = 17.83 min.

¹**H** NMR (400 MHz, CDCl₃) δ 8.60 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 8.12 (d, J = 2.4 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.68 – 7.63 (m, 4H), 7.60 (d, J = 1.6 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.41 – 7.34 (m, 2H), 6.87 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 1.2 Hz, 1H), 3.98 (t, J = 7.2 Hz, 1H), 2.13 – 1.98 (m, 2H), 1.14 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 148.1, 145.6, 142.5, 142.2, 141.6, 141.0, 134.5, 128.8, 127.5, 127.3, 125.4, 125.0, 110.9, 97.3, 95.9, 82.1, 40.2, 31.1, 12.1.

HRMS (ESI) m/z calcd. for C₂₉H₂₄N₃ [M + H]⁺ 414.1965, found 414.1962.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (1.43 mg, 0.0075 mmol, 7.5 mol%), $[(\pi\text{-allyl})PdCl]_2$ (0.91 mg, 0.0025 mmol, 2.5 mol%), iPr·HCl (2.13 mg, 0.005 mmol, 5 mol%) and CsCO₃ (49.9 mg, 0.14 mmol, 1.4 equiv.). A mixture of DMF and Et₂O (1:2, 1.2 mL) was added, followed by (3-bromopropyl)benzene (0.20 mmol, 2.0 equiv.) and alkyne **55a** (29.6 mg, 0.10 mmol, 1.0 equiv., 94% ee). The reaction mixture was stirred at 45 °C for 24 h. Upon completion (monitored by TLC), the reaction mixture was purified by column chromatography on silica gel to afford the desired products **58c** (18.9 mg, 46% yield, 90% ee).

(S)-5'-(8-phenyloct-4-yn-3-yl)-1,1':3',1''-terphenyl (58c)



HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 5.83 min, t_R (major) = 7.07 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.70 – 7.62 (m, 5H), 7.58 (d, J = 2.0 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.39 – 7.33 (m, 2H), 7.28 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 3.75 – 3.65 (m, 1H), 2.77 (t, J = 6.4 Hz, 2H), 2.29 (td, $J_1 = 6.8$ Hz, $J_2 = 2.0$ Hz, 2H), 1.95 – 1.77 (m, 4H), 1.07 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.8, 141.82, 141.79, 141.3, 128.8, 128.5, 128.3, 127.34, 127.31, 125.8, 125.5, 124.5, 83.1, 82.1, 39.7, 34.9, 32.0, 30.7, 18.4, 12.0. **HRMS** (ESI) *m*/*z* calcd. for C₃₂H₃₁ [M + H]⁺ 415.2420, found 415.2415.



To a solution of **45** (52.9 mg, 0.10 mmol, 1.0 equiv., 94% ee) in THF (1.0 mL) was added TBAF (0.24 mmol, 1.2 equiv.) and the resulting mixture was stirred at room temperature for 1 h. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography to yield **55b** as a colorless oil (32.6 mg, 88% yield, 94% ee).

(R)-5'-(5-phenylpent-1-yn-3-yl)-1,1':3',1''-terphenyl (55b)



55b Ph

HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm), t_R (major) = 7.80 min, t_R (minor) = 8.50 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.71 – 7.61 (m, 5H), 7.56 (d, J = 1.6 Hz, 2H), 7.50 – 7.42 (m, 4H), 7.40 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 3.80 – 3.71 (m, 1H), 2.94 – 2.75 (m, 2H), 2.39 (d, J = 2.4 Hz, 1H), 2.25 – 2.10 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 142.3, 142.1, 141.3, 141.0, 128.8, 128.5, 128.4, 127.5, 127.3, 126.0, 125.3, 124.8, 85.5, 71.8, 39.9, 37.1, 33.5.

HRMS (ESI) m/z calcd. for C₂₉H₂₅ [M + H]⁺ 373.1951, found 373.1944.



To a mixture of Pd/C (3.0 mg, 10% w/w Pd on carbon) in THF (1.0 mL) was added **55b** (37.2 mg, 0.10 mmol, 1.0 equiv., 94% ee) under argon atmosphere. Then, the

reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 30 min. After completion, the reaction mixture was filtered and rinsed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **56** as a colorless oil (34.6 mg, 92% yield, 95% ee)

To a mixture of Pd/C (10.0 mg, 10% w/w Pd on carbon) in THF (1.0 mL) was added **55b** (37.2 mg, 0.10 mmol, 1.0 equiv., 94% ee) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 12 h. After completion, the reaction mixture was filtered and rinsed with CH₂Cl₂. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **57** as a colorless oil (35.9 mg, 95% yield, 90% ee)

(R)-5'-(5-phenylpent-1-en-3-yl)-1,1':3',1''-terphenyl (56)



HPLC analysis: Chiralcel ADH (hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 4.98 min, t_R (major) = 5.44 min.

¹**H** NMR (400 MHz, CDCl₃) δ 7.70 – 7.60 (m, 5H), 7.49 – 7.42 (m, 4H), 7.40 (d, J = 1.6 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 6.15 – 5.98 (m, 1H), 5.20 – 5.06 (m, 2H), 3.42 (q, J = 7.6 Hz, 1H), 2.74 – 2.56 (m, 2H), 2.14 (q, J = 8.0 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 145.2, 142.1, 142.0, 141.9, 141.3, 128.7, 128.5, 128.3, 127.4, 127.3, 125.8, 125.6, 124.3, 114.7, 49.5, 37.0, 33.8.

HRMS (ESI) m/z calcd. for C₂₉H₂₇ [M + H]⁺ 375.2107, found 375.2104.

(S)-5'-(1-phenylpentan-3-yl)-1,1':3',1''-terphenyl (57)



HPLC analysis: Chiralcel OD-3 (hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 5.72 min, t_R (minor) = 6.22 min.

¹**H NMR** (400 MHz, CDCl₃) δ 7.72 – 7.62 (m, 5H), 7.51 – 7.42 (m, 4H), 7.40 – 7.32 (m, 4H), 7.29 – 7.23 (m, 2H), 7.19 – 7.08 (m, 3H), 2.65 – 2.48 (m, 3H), 2.13 – 1.95 (m, 2H), 1.85 – 1.62 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 146.5, 142.5, 141.7, 141.5, 128.7, 128.4, 128.3, 127.3, 125.7, 125.6, 124.0, 47.6, 38.1, 33.9, 29.8, 12.2.

HRMS (ESI) m/z calcd. for C₂₉H₂₉ [M + H]⁺ 377.2264, found 377.2258.

Mechanistic Studies





Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2ea** (68.4 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L4** (16.0 mg, 0.024 mmol, 12 mol%), LiO'Bu (64.0 mg, 0.80 mmol, 4.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (7.2 mg, 0.40 mmol, 2.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Last alkyl halide **1a** (55.5 mg, 0.30 mmol, 1.5 equiv.) and (1-(2-phenylcyclopropyl)vinyl)benzene **59** (88.0 mg, 0.40 mmol, 2.0 equiv.) were slowly sequentially added into the mixture *via* microsyringe, and the reaction mixture was stirred at -5 °C for 48 h. Upon completion (monitored by TLC), the reaction mixture was dried with anhydride Na₂SO₄, then was purified by column chromatography on silica gel to afford **60** as a mixture of diastereomers (5.2 mg, 6% yield) and **33** (23.4 mg, 52% yield, 92% ee).



¹**H** NMR (400 MHz, CDCl₃) δ 7.92 – 7.82 (m, 2H), 7.31 – 7.07 (m, 17H), 5.40 (t, *J* = 7.2 Hz, 1H), 3.78 (t, *J* = 6.0 Hz, 1H), 2.84 – 2.61 (m, 5H), 2.59 – 2.55 (m, 3H), 1.22 – 1.15 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 197.8, 150.3, 150.1, 146.8, 143.7, 143.6, 143.0, 140.11, 140.06, 135.3, 135.2, 128.6, 128.55, 128.50, 128.23, 128.20, 127.93, 127.88, 127.81, 127.78, 127.1, 126.7, 126.6, 126.5, 126.4, 126.1, 51.1, 39.1, 39.0, 38.1, 34.2, 29.7, 26.5, 21.1.

HRMS (ESI) m/z calcd. for C₃₃H₃₃O [M + H]⁺ 445.2526, found 445.2528.

TEMPO inhibiting experiment with benzyl bromides



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2e** (90.4 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L4** (16.0 mg, 0.024 mmol, 12 mol%), LiO^{*t*}Bu (64.0 mg, 0.80 mmol, 4.0 equiv.) and TEMPO (62.4 mg, 0.40 mmol, 2.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (7.2 mg, 0.40 mmol, 2.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Last alkyl halide **1a** (55.5mg, 0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred at -5 °C for 48 h. The reaction

mixture was monitored by TLC. Trace amount of product **3** was observed and **61** could be detected by HRMS analysis.



Figure S2. HRMS data of 61

Radical clock experiment with propargyl bromides



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2ea** (68.4 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L6** (19.7 mg, 0.024 mmol, 12 mol%), LiO'Bu (96.0 mg, 1.20 mmol, 6.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (10.8 mg, 0.60 mmol, 3.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly alkyl halide **1b** (90.9 mg, 0.30 mmol, 1.5 equiv.) and (1-(2-phenylcyclopropyl)vinyl)benzene **59** (88.0 mg, 0.40 mmol, 2.0 equiv.) were slowly sequentially added into the mixture *via* microsyringe, and the reaction mixture was stirred at -10 °C for 120 h. The reaction mixture was monitored by TLC. Trace amount of product **60'** was observed and could be detected by HRMS analysis.



TEMPO inhibiting experiment with propargyl bromides



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **2e** (90.4 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L6** (19.7 mg, 0.024 mmol, 12 mol%), LiO^{*t*}Bu (96.0 mg, 1.20 mmol, 6.0 equiv.) and TEMPO (62.4 mg, 0.40 mmol, 2.0 equiv.). Then DMSO/CH₂Cl₂ (2:1, 2.4 mL) and H₂O (10.8 mg, 0.60 mmol, 3.0 equiv.) was added. The reaction mixture was stirred for several minutes to dissolve the reactants. Lastly alkyl halide **1b** (90.9 mg, 0.30 mmol, 1.5 equiv.) was slowly added into the mixture *via* microsyringe, and the reaction mixture was stirred at -10 °C for 120 h. The reaction mixture was monitored by TLC. No product **44** was observed and **61'** could be detected by HRMS analysis.

Positive, [M+H]*



Experiments with racemic and enantioenriched alkyl bromide 1a



According to **General procedure A**, substrate (\pm)-1a (27.8 mg, 0.15 mmol, 1.5 equiv.) and 2e (45.2 mg, 0.10 mmol, 1.0 equiv.) was stirred for 21 h to afford the product 3 (12.1 mg, 36% yield, 94% ee) and the remaining 1a (0% ee).



According to **General procedure A**, substrate (*S*)-**1a** (27.8 mg, 81% ee, 0.15 mmol, 1.5 equiv.)⁷ and **2e** (45.2 mg, 0.10 mmol, 1.0 equiv.) was stirred for 21 h to afford the product **3** (11.1 mg, 33% yield, 94% ee) and the remaining **1a** (74% ee). In the absence of CuI and **L4**, the substrate (*S*)-**1a** (27.8 mg, 81% ee, 0.15 mmol, 1.5 equiv.) and **2e** (45.2 mg, 0.10 mmol, 1.0 equiv.) was stirred for 21 h to produce the remaining (*S*)-**1a** with 77% ee.

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NMR Spectra







S53



140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 f1 (ppm)







S56





S58









f1 (ppm) 170 160 150 140 130 120



























S68



S69









100 fl (ppm)












0





















100 fl (ppm)







S84









100 fl (ppm)









110 100 fl (ppm) 80 70

90

60 50

40 30 20 10

0

120

200 190 180 170 160 150 140 130









100 fl (ppm)










































S116









S119

HPLC Spectra



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel ADH: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min



Chiralcel OD : hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min





Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min





Chiralcel IA: hexane/*i*-PrOH = 99.5/0.5, flow rate 0.4 mL/min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min





Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min





Chiralcel OD: hexane/i-PrOH = 95/5, flow rate 1.0 mL/min



Peak Table

PDA Ch1 254nm					
Peak#	Ret. Time	Area	Area%		
1	8.841	2642310	49.777		
2	9.297	2665993	50.223		



Chiralcel ODH: hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min



Chiralcel OD: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel ODH: hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min



Chiralcel ODH: hexane/i-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel ODH: hexane/*i*-PrOH = 99.5/0.5, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



ł	Peak Table						
PDA Ch1 254nm							
	Peak#	Ret. Time	Area	Area%			
	1	7.278	14174000	97.884			
	2	11.623	306349	2.116			

Chiralcel OD: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min





Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min





Chiralcel OD: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min




Chiralcel OJ: hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min





Chiralcel OJH: hexane/*i*-PrOH = 90/10, flow rate 0.7 mL/min



Chiralcel OD: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



Chiralcel OD: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min





Chiralcel AS: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



Chiralcel IF: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min





Chiralcel AS: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



Chiralcel ASH: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel ADH: hexane/i-PrOH = 95/5, flow rate 1.0 mL/min



PDA Ch1 254nm				
Peak#	Ret. Time	Area	Area%	
1	15.398	3005020	49.367	
2	16.582	3082123	50.633	



PDA UN	11 234nm		
Peak#	Ret. Time	Area	Area%
1	15.282	585756	5.011
2	16.406	11103862	94.989

Chiralcel AD: hexane/i-PrOH = 90/10, flow rate 1.0 mL/min





Chiralcel ADH: hexane/i-PrOH = 95/5, flow rate 1.0 mL/min





Chiralcel IF: hexane/*i*-PrOH = 98/2, flow rate 0.6 mL/min



Chiralcel OD: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min





Chiralcel OD: hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min





Chiralcel AD: hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min



Chiralcel AD: hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min



 Peak Table

 PDA Ch1 254nm

 Peak# Ret. Time
 Area
 Area%

 1
 3.321
 52045
 2.687

 2
 3.561
 1885017
 97.313

Chiralcel ADH: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



reak la	able		
PDA Ch1 254nm			
Peak# Re	et. Time	Area	Area%
1	5.816	198346	2.803
2	6.159	6878675	97.197

Chiralcel ADH: hexane/*i*-PrOH = 99/1, flow rate 0.6 mL/min





Chiralcel ADH: hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min





Chiralcel ADH: hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min



Chiralcel AD: hexane/i-PrOH = 98/1, flow rate 1.0 mL/min





Chiralcel IG: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



Chiralcel ADH: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min





Chiralcel ODH: hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min





Chiralcel IG: hexane/*i*-PrOH = 99/1, flow rate 0.3 mL/min



PDA Ch	1 254nm		
Peak#	Ret. Time	Area	Area%
1	9.502	345273	49.947
2	11.453	346007	50.053



Chiralcel OD: hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min





Chiralcel OJH: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



Chiralcel OD-3: hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min





Chiralcel OD-3: hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min





Chiralcel ADH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min





Chiralcel ADH: hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min



Chiralcel ADH: hexane/i-PrOH = 98/2, flow rate 1.0 mL/min

4.975

5.0

7.5

min

Ρh

56

2.5

Area% 2.430 97.570

Area 76693 3078785

200-

100-

0.0

Peak Table

PDA Ch1 254nm Peak# Ret. Time 1 4.975 2 5.438





Chiralcel OD-3: hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min



PDA Ch	2 230nm		
Peak#	Ret. Time	Area	Area%
1	7.674	1552684	49.695
2	12.912	1571728	50.305

mAU



PDA Ch2 230nm

PDA UN			
Peak#	Ret. Time	Area	Area%
1	7.513	9099053	48.561
2	12.356	9638141	51.439





PDA UNZ Z30NM				
Peak#	Ret. Time	Area	Area%	
1	7.932	901992	9.006	
2	14.029	9113854	90.994	



Peak Table

PDA Ch	2 230nm		
Peak#	Ret. Time	Area	Area%
1	7.648	1636444	12.873
2	12.861	11075725	87.127



Chiralcel AY-3: hexane/*i*-PrOH = 100/0, flow rate 0.8 mL/min