Supplementary Materials

Enantioselective 1,1-diarylation of allyl sulfones catalyzed by palladium with a chiral phosphoric acid

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1. General considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of argon, using over-dried or flame-dried glassware equipped with a magnetic stir bar. All chemicals were purchased from commercial suppliers and used without further purification. In addition to commercially available extra dry solvents, all solvents were purified by standard operating methods. Thin-layer chromatography was performed with EMD silica gel 60 F₂₅₄ plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained on Bruker AM-400 and Bruker AM-700. Chemical shifts (δ) were quoted in ppm relative to tetramethylsilane or deuterated solvent as internal standard (Chloroform-d: 7.26 ppm for ¹H NMR; Chloroform-d: 77.16 ppm for ¹³C NMR), multiplicities are as indicated: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Buker impact II (Q-TOF) mass spectrum by means of the ESI technique and a Fourier Transform Ion Cyclotron (Solarix 7.0T). Crystallographic data were obtained from a Bruker D8 VENTURE diffractometer. Melting points were measured on a melting point apparatus and were uncorrected. Optical rotations were measured on a Rudolph Research Analytical. $[\alpha]_D$ values are reported in degrees and concentration (c) is in g/100 mL. Er values were measured on the supercritical fluid chromatography (SFC, ACQUITY UPC² system of Waters) and HPLC analysis employing Daicel Chiralpak IC-3, OD-3, IG-3, Trefoil CEL1 and Trefoil CEL2 column.

2. General procedure for preparing substrates

2.1 All of the used alkenes are known compounds except 2t and 2u. Compounds $2b-2j^1$, $2k^2$, $2l^1$, $2m^2$, $2n-2o^3$, $2p^4$, $2s^1$, $2t^5$, $2u^6$, $6b^7$ were prepared according to the reported literatures, and other alkenes were purchased from commercial suppliers (Energy Chemical) and used without further purification.



Figure S1. Substrate scope of known alkenes

Synthesis of new substrates 2t and 2u

Phenyl prop-2-ene-1-sulfonate (2t): Following a modified procedure:⁵ prop-2-ene-1-sulfonyl chloride (3.56 mmol, 500 mg, 1.2 eq) and Et₃N (618 μ L, 4.45 mmol, 1.5 eq) were added to a stirred solution of phenol (2.96 mmol, 279 mg, 1.0 eq) in DCM (5 mL) at 0 °C. The reaction mixture was stirred overnight (20 h) at room temperature. Water (10 ml) was added, the reaction mixture was extracted with EtOAc (3×10 ml), combined organic extracts were washed with brine (2×10 ml), dried over Na₂SO₄, filtered and the solvent was driven off in a vacuum. The crude product was purified by column chromatography (SiO₂, PE/EA = 15:1, v/v) in 36%

yield (210 mg) as a yellow oil. ¹H NMR (400 MHz, Chloroform-d) δ 7.5 – 7.4 (m, 2H), 7.3 – 7.2 (m, 3H), 6.1 – 5.9 (m, 1H), 5.6 – 5.4 (m, 2H), 4.0 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 149.3, 130.0, 127.3, 125.2, 124.0, 122.1, 54.6. HRMS (ESI) calcd for C₉H₁₀NaO₃S [M+Na]⁺ *m/z* 221.0243, found 221.0245.



N-phenylprop-2-ene-1-sulfonamide (2u): Following a modified procedure:⁶ Et₃N (618 µL, 4.45 mmol, 1.5 eq) was added to a stirred solution of aniline (2.96 mmol, 270 µL, 1.0 eq) in THF (3 mL) at 0 °C. Then prop-2-ene-1-sulfonyl chloride (3.56 mmol, 500 mg, 1.2 eq) in THF (2 mL) was slowly added dropwise to the solution at 0 °C. The resulting mixture was stirred for 1 h while the temperature was gradually warmed to room temperature. Additional Et₃N (618 μ L, 4.45 mmol, 1.5 eq) was added to the reaction mixture and the resultant solution was stirred for 0.5 h. NaHCO₃ (aq) was added, the reaction mixture was extracted with EtOAc (3×10 mL), combined organic extracts were washed with brine (2×10 mL), dried over Na₂SO₄, filtered and the solvent was driven off in a vacuum. The crude product was purified by column chromatography (SiO₂, PE/EA = $15:1 \sim 8:1$, v/v) in 94% yield (550 mg) as a yellow oil. ¹H NMR (500 MHz, Chloroform-d) δ 7.44 (s, 1H), 7.37 – 7.30 (m, 2H), 7.31 – 7.22 (m, 2H), 7.16 (t, J = 7.3 Hz, 1H), 5.88 (ddt, J = 17.4, 10.1, 7.3 Hz, 1H), 5.45 - 5.39 (m, 1H), 5.33 - 5.26 (m, 1H), 3.83 (d, J = 7.4 Hz, 2H); ¹³C NMR (126 MHz, CDCl3) δ 136.89, 129.62, 125.18, 125.02, 124.83, 120.78, 55.53. HRMS (ESI) calcd for $C_9H_{11}NNaO_2S [M+Na]^+ m/z 220.0399$, found 220.0403.

2.2 All of the used aryldiazonium salts are known compounds. Compounds 3a-3e⁸,
3f⁸⁻⁹ were prepared according to the reported literatures.



Figure S2. The scope of aryldiazonium salts

Caution: All aryldiazonium salts need to be recrystallized from anhydrous Et₂O/Acetone several times to get pure and dry white crystals; low purity and high water content of aryldiazonium salts might lead to low yields and er values of targeting diarylation products.

Our analytical data (¹H NMR, ¹³C NMR and ¹⁹F NMR) match with the literatures^{1-4,} ⁸⁻⁹. (Figure S1 and Figure S2).

2.3 All of the arylboronic acids were purchased from commercial suppliers (*Energy Chemical* and *TCI company*) and used without further purification, Rb₂CO₃ was purchased from commercial suppliers (*Adamas-beta*) and used without further purification, Pd₂dba₃ was purchased from commercial suppliers (*Strem Chemicals*) and used without further purification, (*R*)-1a was purchased from commercial suppliers (*DAICEL CHIRAL TECHNOLOGIES*) and purified according to reported literature¹⁰.



Figure S3. The scope of arylboronic acids

3. Reaction optimization



Table S1. The effects of CPAs^a

^aUnless otherwise noted, the reaction was conducted with 2a (0.1 mmol), 3a (0.12

mmol), **4a** (0.15 mmol), NaHCO₃ (0.2 mmol), (*R*)-**CPA** (0.006 mmol) and Pd₂dba₃ (0.003 mmol) in MTBE (2 mL) at rt for 26 h under Ar. Isolated yields are shown. The er values were determined by SFC.

0 	+ N_2BF_4 - M_2BF_4 - M	DH) ₂ Pd ₂ dba ₃ (3 r (<i>R</i>)- 1f (6 m NaHCO ₃ (2. solvent, rt, 2	mol%) ol%) 0 equiv) 6 h	Me
Entry	Solvent	Volume	Yield (%) ^b	er (%) ^c
1	MTBE	2 mL	44	68:32
2	Et ₂ O	2 mL	42	62:38
3	ⁱ Pr ₂ O	2 mL	19	66:34
4	Toluene	2 mL	12	67:33
5	Hexane	2 mL	NR	-
6 ^d	MTBE	2 mL	56	75:25
$7^{\rm d}$	MTBE	1 mL	30	72:28
8 ^d	MTBE	3 mL	32	73:27

Table S2. The effects of solvent^a

^aUnless otherwise noted, the reaction was conducted with **2a** (0.1 mmol), **3a** (0.12 mmol), **4a** (0.15 mmol), NaHCO₃ (0.2 mmol), (*R*)-**1f** (0.006 mmol) and Pd₂dba₃ (0.003 mmol) in solvent (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC. ^dReplaced (*R*)-**1f** with (*R*)-**1a** (0.006 mmol).

Table S3. The effects of [Pd] source^a

		0	Ме
O S Ph O 2a	+ H_{OMe} + H_{OMe} + H_{OH} - H_{OH	(6 mol%) a (6 mol%) 2.0 equiv) , rt, 26 h	o S O Ph
Entry	[Pd] source	Yield (%) ^b	er (%) ^c
1	Pd ₂ dba ₃	56	75:25
2	Pd ₂ (3,3',5,5'-OMe-dba) ₃	56	75:25
3	Pddba ₂	54	75:25
4	Pd ₂ dba ₃ ·CHCl ₃	55	75:25
5	$Pd(OAc)_2$	28	73:27
6	Buchwald precatalyst	40	70:30

^aUnless otherwise noted, the reaction was conducted with 2a (0.1 mmol), 3a (0.12 mmol), 4a (0.15 mmol), NaHCO₃ (0.2 mmol), (*R*)-1a (0.006 mmol) and [Pd] (0.006 mmol) in MTBE (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC.

0, Ph S, O 2a	$+ \underbrace{\bigvee_{OMe}^{N_2BF_4}}_{3a} + \underbrace{\bigoplus_{H=1}^{B(OH)_2}}_{4a} -$	Pd ₂ dba ₃ (3 mol%) (<i>R</i>)- 1a (6 mol%) Base (2.0 equiv) MTBE, rt, 26 h	OMe
Entry	Base	Yield (‰) ^b er (%) ^c
1	NaHCO ₃	44	68:32
2	Na ₂ CO ₃	44	78:22
3	Na ₂ HPO ₄	26	73:27
4	Na ₃ PO ₄	60	74:26
5	Li ₂ CO ₃	40	71:29
6	K ₂ CO ₃	60	80:20
7	KHCO ₃	33	75:25
8	K ₂ HPO ₄	50	73:27
9	K ₃ PO ₄	44	76:24
10	Cs ₂ CO ₃	51	83:17
11	MgCO ₃	31	76:24

^aUnless otherwise noted, the reaction was conducted with 2a (0.1 mmol), 3a (0.12 mmol), 4a (0.15 mmol), Base (0.2 mmol), (*R*)-1a (0.006 mmol) and Pd₂dba₃ (0.003 mmol) in MTBE (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC.

$\begin{array}{c} O \\ O $						
Entry	2a (equiv)	3a (equiv)	4a (equiv)	Cs ₂ CO ₃ (equiv)	Yield (%) ^b	er (%) ^c
1	1.0	1.0	1.0	2.0	37	85:15
2	1.0	1.5	1.5	2.0	46	82:18
3	1.0	1.2	2.0	2.0	48	79:21
4	1.2	1.2	1.0	2.0	44	87:13
5	1.2	1.0	1.5	2.0	43	83:17
6	1.5	1.2	1.0	2.0	30	87:13
7	2.0	1.2	1.0	2.0	27	89:11
8	2.0	2.0	1.0	2.0	37	88:12
9	1.2	1.2	1.0	1.2	27	87:13
10	1.2	1.2	1.0	3.0	55	86:14
11	2.0	2.0	1.0	3.0	43	88:12

^aUnless otherwise noted, the reaction was conducted with **2a**, **3a**, **4a**, Cs_2CO_3 , (*R*)-**1a** (0.006 mmol) and Pd₂dba₃ (0.003 mmol) in MTBE (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC. Table S6. The effects of catalyst ratio^a

0 5 2a	Ph + N_2BF_4 + OMe 3a	B(OH) ₂ Pd ₂ db Cs ₂ CO MTBE, 4a	a ₃ , (<i>R</i>)- 1a ₃ (3.0 equiv) rt, 26 h	OMe
Entry	Pd2dba3 (equiv)	1a (equiv)	Yield (%) ^b	er (%) ^c
1	0.03	0.06	43	88:12
2	0.04	0.08	30	91:9
3	0.05	0.10	60	91:9
4	0.03	0.12	51	91:9
5	0.04	0.12	55	92:8

^aUnless otherwise noted, the reaction was conducted with **2a** (0.2 mmol), **3a** (0.2 mmol), **4a** (0.1 mmol), Cs_2CO_3 (0.3 mmol), (*R*)-**1a** and Pd₂dba₃ in MTBE (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC.

$\begin{array}{c} O \\ O $						
Entry	Temperature	Time	Yield (%) ^b	er (%) ^c		
1	rt	26 h	55	92:8		
2	10°C	48 h	61	92:8		
3	0°C	48 h	60	94:6		
4	0°C	72 h	58	94:6		
5 ^d	0°C	48 h	51	96:4		
6 ^{d,e}	0°C	48 h	64	96:4		

Table S7. The effects of temperature and other adjustments^a

^aUnless otherwise noted, the reaction was conducted with **2a** (0.2 mmol), **3a** (0.2 mmol), **4a** (0.1 mmol), Cs_2CO_3 (0.3 mmol), (*R*)-**1a** and Pd₂dba₃ in MTBE (2 mL) at rt for 26 h under Ar. ^bIsolated yields are shown. ^cThe er values were determined by SFC. ^d(*R*)-**1a** was recrystallized from 2.0 M HCl and methanol followed by reported literature¹⁰. ^eReplaced Cs₂CO₃ with Rb₂CO₃ (0.3 mmol).

Table S8. Adjustments from optimized reaction condition^a



Entry	Change from the "standard conditions"	Yield (%) ^b	er (%) ^c
1	none	64	96:4
2	(R)-1b instead of (R) -1a	11	71:29
3	(R)-1c instead of (R)-1a	10	13:87
4	(R)-1d instead of (R) -1a	12	65:35
5	(<i>R</i>)-1e instead of (<i>R</i>)-1a	24	12:88
6	(R)-1f instead of (R) -1a	27	71:29
7	Cs ₂ CO ₃ instead of Rb ₂ CO ₃	51	96:4
8	K ₂ CO ₃ instead of Rb ₂ CO ₃	62	95:5
9	Na ₂ CO ₃ instead of Rb ₂ CO ₃	44	94:6
10	Et ₂ O instead of MTBE	66	90:10
11	toluene instead of MTBE	trace	-

12	rt instead of 0 °C	21	88:12
13	Pd(OAc) ₂ instead of Pd ₂ dba ₃	29	96:4
14	Pd(CH ₃ CN) ₄ (BF ₄) ₂ instead of Pd ₂ dba ₃	25	89:11
15	Buchwald precatalyst instead of Pd ₂ dba ₃	27	96:4

^aUnless otherwise noted, the reaction was conducted with **2a** (0.2 mmol), **3a** (0.2 mmol), **4a** (0.1 mmol), Rb₂CO₃ (0.3 mmol), (*R*)-**1a** (0.012 mmol) and Pd₂dba₃ (0.004 mmol) in MTBE (2 mL) at 0 °C for 48 h under Ar. ^bIsolated yields were shown. ^cThe er values were determined by SFC.

4. General procedure for the synthesis of products 5 and 7.

4.1 General procedure A: asymmetric reactions for the synthesis of **5** using allylic sulfone substrates.



In glovebox, **2** (0.2 mmol), **3** (0.2 mmol), **4** (0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol), anhydrous MTBE (2.0 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours at 0 °C. After the reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. An external standard (Dibromomethane) was added to the system for determining NMR yields. Product **5** was obtained by PTLC.

4.2 General procedure **B**: Racemic reactions for the synthesis of *rac-5* using allylic sulfone substrates.



Under Ar atmosphere, **2** (0.2 mmol), **3** (0.2 mmol), **4** (0.1 mmol), Pd_2dba_3 (3.7 mg, 0.004 mmol), Rb_2CO_3 (69.3 mg, 0.3 mmol), anhydrous THF (2.0 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and stirred for 20 hours in an argon atmosphere at room temperature. After the

reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. The racemic product 5 was obtained by PTLC.



(*R*)-1-methoxy-4-(1-phenyl-3-(phenylsulfonyl)propyl)benzene (5a): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5a (23.4 mg, 64%) as a colorless oil, Rf =0.39 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.84 (m, 2H), 7.70 – 7.61 (m, 1H), 7.60 – 7.51 (m, 2H), 7.30 – 7.22 (m, 2H), 7.21 – 7.09 (m, 3H), 7.08 – 6.99 (m, 2H), 6.84 – 6.75 (m, 2H), 3.89 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.09 – 2.97 (m, 2H), 2.49 – 2.34 (m, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.5, 143.4, 139.3, 135.1, 133.8, 129.5, 128.9, 128.7, 128.2, 127.6,126.8, 114.3, 55.4, 55.0, 49.0, 28.6. [α]_D²⁰ = -1.9 (c = 2.0, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 92:8, 0.8 mL/min, 212.1 nm): t_R (major) = 18.915 min, t_R (minor) = 25.697 min, 96:4 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₃S [M+Na]⁺ *m/z* 389.1182, found 389.1186.



(*R*)-1-methoxy-4-(3-(phenylsulfonyl)-1-(p-tolyl)propyl)benzene (5b): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4b (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 8:1, twice, v/v) to afford 5b (24.3 mg, 64%) as a colorless oil, Rf =0.32 (silica gel, PE:EA = 8:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.70 – 7.61 (m, 1H), 7.59 – 7.51 (m, 2H), 7.09 – 6.97 (m, 6H), 6.82 – 6.76 (m, 2H), 3.84 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.06 – 2.98 (m, 2H), 2.45 – 2.34 (m, 2H), 2.28 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.39, 140.38, 139.26, 136.37, 135.35, 133.80, 129.54, 129.43, 128.64, 128.17, 127.50, 114.23, 55.37, 55.01, 48.62, 28.60, 21.08. [α]²⁰ = -0.6 (c = 1.0, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (major) = 10.899 min, t_R (minor) = 13.915 min, 96:4 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1337.



(*S*)-1-fluoro-4-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)benzene (5c): According to the general procedure **A**, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4c** (14.0 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5c** (25.4 mg, 66%) as a colorless oil, Rf =0.50 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.69 – 7.62 (m, 1H), 7.56 (dd, J = 8.3, 7.0 Hz, 2H), 7.13 – 6.99 (m, 4H), 6.98 – 6.90 (m, 2H), 6.86 – 6.76 (m, 2H), 3.90 (t, J = 8.1 Hz, 1H), 3.76 (s, 3H), 3.06 – 2.95 (m, 2H), 2.46 – 2.35 (m, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.7 (d, J = 246.0 Hz), 158.5, 139.3, 139.2, 134.8, 133.9, 129.5, 129.1 (d, J = 7.8 Hz), 128.6, 128.1, 115.7 (d, J = 21.6 Hz), 114.3, 55.4, 54.8, 48.2, 28.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -116.22. $[\alpha]_D^{20} = -0.8$ (c = 1.0, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (major) = 8.950 min, t_R (minor) = 13.054 min, 95:5 er. HRMS (ESI) calcd for C₂₂H₂₁FNaO₃S [M+Na]⁺ *m/z* 407.1088, found 407.1092.



(*S*)-1-chloro-4-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)benzene (5d): According to the general procedure A, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4d** (15.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5d** (19.2 mg, 48%) as a colorless oil, Rf =0.37 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.71 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.04 (dd, *J* = 14.1, 8.6 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.89 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 3.11 – 2.94 (m, 2H), 2.50 – 2.28 (m, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.6, 142.0, 139.2, 134.5, 133.9, 132.6, 129.5, 129.0, 128.7, 128.2, 114.4, 55.4, 54.8, 48.3, 28.4. [α]²⁰ = +1.7 (c = 0.6, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 92:8, 0.7 mL/min, 228.0 nm): t_R (major) = 32.333 min, t_R (minor) = 45.222 min, 94:6 er. HRMS (ESI) calcd for C₂₂H₂₁ClNaO₃S [M+Na]⁺ *m/z* 423.0792, found 423.0791.



(R)-4-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)benzoate methyl (5e): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4e (18.0 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5e (23.7 mg, 56%) as a colorless oil, Rf =0.20 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.81 (m, 4H), 7.68 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 3.98 (t, J = 8.0 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.06 - 2.92 (m, 2H), 2.49 - 2.922.38 (m, 2H); ¹³C NMR (101 MHz, Chloroform-d) δ 166.9, 158.7, 148.7, 139.2, 134.1, 133.9, 130.2, 129.5, 128.8, 128.8, 128.1, 127.7, 114.4, 55.4, 54.7, 52.2, 48.9, 28.3. $[\alpha]_D^{20} = +2.5$ (c = 1.5, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 11.163 min, t_R (major) = 19.276 min, 93.5:6.5 er. HRMS (ESI) calcd for C₂₄H₂₄NaO₅S [M+Na]⁺ *m/z* 447.1237, found 447.1243.



(*R*)-1-methoxy-4-(3-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)propyl)benzen e (5f): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4f (19.0 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5f (20.0 mg, 46%) as a colorless oil, Rf =0.45 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.82 (m, 2H), 7.70 – 7.62 (m, 1H), 7.60 – 7.47 (m, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 3.02 (td, *J* = 6.9, 2.4 Hz, 2H), 2.45 (ddd, *J* = 9.5, 8.2, 6.7 Hz, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.8, 147.7, 139.2, 134.0, 133.9, 129.5, 129.1 (q, J = 32.3 Hz), 128.8, 128.2, 128.0, 125.8 (q, J = 3.7 Hz), 124.2 (q, J = 268.9 Hz), 114.5, 55.4, 54.7, 48.7, 28.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.48. [α]²⁰_D = -1.8 (c = 0.8, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 5.508 min, t_R (minor) = 7.480 min, 93.5:6.5 er. HRMS (ESI) calcd for C₂₃H₂₁F₃NaO₃S [M+Na]⁺ *m/z* 457.1056, found 457.1058.



(*R*)-4-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)phenol (5g): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4g (13.8 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 2:1, twice, v/v) to afford 5g (10.3 mg, 27%) as a colorless oil, Rf =0.27 (silica gel, PE:EA = 2:1, twice, v/v); ¹H NMR (700 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 2H), 7.67 – 7.63 (m, 1H), 7.58 – 7.49 (m, 2H), 7.04 – 7.00 (m, 2H), 6.97 (dd, *J* = 8.6, 2.4 Hz, 2H), 6.79 (dd, *J* = 8.7, 2.4 Hz, 2H), 6.74 – 6.70 (m, 2H), 3.82 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.04 – 2.99 (m, 2H), 2.41 – 2.32 (m, 2H); ¹³C NMR (176 MHz, CDCl₃) δ 159.1, 149.6, 142.6, 139.1, 136.2, 134.1, 132.4, 129.6, 128.8, 128.1, 120.6, 114.8, 55.5, 54.4, 46.3, 28.1. [α]²⁰ = -1.2 (c = 0.2, CH₂Cl₂). SFC (Trefoir CEL2, CO₂/MeOH = 85:15, 1 mL/min, 220.0 nm): t_R (minor) = 14.800 min, t_R (major) = 18.475 min, 96.5:3.5 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₄S [M+Na]⁺ *m/z* 405.1131, found 405.1126.



(S)-1-methoxy-3-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)benzene(5h):

According to the general procedure **A**, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4h** (15.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 8:1, three times, v/v) to afford **5h** (17.4 mg, 44%) as a colorless oil, Rf =0.27 (silica gel, PE:EA = 8:1, three times, v/v); ¹**H** NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 2H), 7.70 – 7.61 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.83 – 6.61 (m, 5H), 3.86 (t, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.08 – 2.96 (m, 2H), 2.46 – 2.32 (m, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 160.0, 158.5, 145.1, 139.3, 134.9, 133.8, 129.9, 129.5, 128.7, 128.2, 120.0, 114.3, 113.9, 111.7, 55.4, 55.3, 55.0, 49.0, 28.5. [α]²⁰ = -3.2 (c = 1.5, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 5.176 min, t_R (minor) = 6.594 min, 95:5 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₄S [M+Na]⁺ *m/z* 419.1288, found 419.1288.



(*S*)-1-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-3-methylbenzene (5i): According to the general procedure **A**, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4i** (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5i** (23.2 mg, 61%) as a colorless oil, Rf =0.45 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2H), 7.68 – 7.62 (m, 1H), 7.56 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.09 – 6.89 (m, 5H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.84 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.10 – 2.96 (m, 2H), 2.46 – 2.35 (m, 2H), 2.28 (s, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.4, 143.3, 139.3, 138.47, 135.2, 133.8, 129.4, 128.7, 128.7, 128.4, 128.2, 127.6, 124.6, 114.2, 55.4, 55.0, 49.0, 28.6, 21.6. $[\alpha]_D^{20} = -2.0$ (c = 0.5, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 229.0 nm): t_R (major) = 4.069 min, t_R (minor) = 5.516 min, 95.5:4.5 er. **HRMS (ESI)** calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1338.



(*S*)-1-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-2-methylbenzene (5j): According to the general procedure **A**, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4j** (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 8:1, twice, v/v) to afford **5j** (23.5 mg, 62%) as a colorless oil, Rf =0.32 (silica gel, PE:EA = 8:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.84 (m, 2H), 7.68 – 7.61 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.07 (m, 4H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.15 – 2.97 (m, 2H), 2.39 (q, *J* = 7.9 Hz, 2H), 2.19 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.3, 140.9, 139.3, 136.5, 134.7, 133.8, 131.0, 129.5, 129.1, 128.2, 126.7, 126.4, 126.1, 114.2, 55.4, 54.9, 44.7, 28.8, 19.9. [α]²⁰ = +33.5 (c = 0.8, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (major) = 11.061 min, t_R (minor) = 21.236 min, 96:4 er. **HRMS (ESI)** calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1340.



(*S*)-1-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-3,5-dimethylbenzene(5k): According to the general procedure A, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4k** (15.0 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5k** (13.8 mg, 35%) as a colorless oil, Rf =0.39 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H **NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.82 (m, 2H), 7.69 – 7.60 (m, 1H), 7.56 (dd, J = 8.3, 6.9 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.85 – 6.68 (m, 5H), 3.82 – 3.72 (m, 4H), 3.13 – 2.95 (m, 2H), 2.44 – 2.33 (m, 2H), 2.24 (s,6H); ¹³C **NMR** (101 MHz, Chloroform-*d*) δ 158.4, 143.2, 139.3, 138.3, 135.4, 133.8, 129.4, 128.7, 128.5, 128.2, 125.4, 114.2, 55.4, 55.1, 49.0, 28.6, 21.5. [α]²⁰ = -0.2 (c = 1.0, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 232.0 nm): t_R (major) = 8.386 min, t_R (minor) = 14.587 min, 95:5 er. **HRMS (ESI)** calcd for C₂₄H₂₆NaO₃S [M+Na]⁺ *m/z* 417.1495, found 417.1492.



(S)-2-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)naphthalene (51):

According to the general procedure **A**, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4l** (17.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5l** (22.0 mg, 53%) as a colorless oil, Rf =0.53 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2H), 7.79 – 7.61 (m, 4H), 7.60 – 7.38 (m, 5H), 7.22 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.86 – 6.75 (m, 2H), 4.07 (t, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.07 (td, *J* = 8.1, 1.7 Hz, 2H), 2.60 – 2.48 (m, 2H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.5, 140.8, 139.3, 135.0, 133.9, 129.5, 128.9,

128.7, 128.2, 127.9, 127.7, 126.4, 126.3, 125.9, 125.8, 114.3, 55.4, 55.0, 49.0, 28.3. $[\alpha]_{D}^{20} = +10.0 \text{ (c} = 1.0, \text{CHCl}_3\text{)}.$ SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 220.0 nm): t_R (major) = 9.977 min, t_R (minor) = 13.725 min, 95.5:4.5 er. HRMS (ESI) calcd for C₂₆H₂₄NaO₃S [M+Na]⁺ *m/z* 439.1338, found 439.1341.



(*S*)-2-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)naphthalene (5m): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4m (21.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5m (26.8 mg, 60%) as a colorless oil, Rf =0.44 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.81 (m, 3H), 7.65 – 7.36 (m, 7H), 7.30 – 7.24 (m, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.83 (t, *J* = 7.9 Hz, 1H), 3.74 (s, 3H), 3.24 – 3.07 (m, 2H), 2.70 – 2.48 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 156.6, 156.2, 139.1, 138.5, 133.9, 133.7, 129.4, 129.1, 128.1, 127.4, 127.0, 123.7, 122.9, 122.7, 122.6, 121.0, 114.3, 111.9, 110.3, 55.4, 54.9, 45.3, 28.7. [α]²⁰ = -48.6 (c = 2.0, CHCl₃). SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 13.282 min, t_R (minor) = 14.826 min, 86.5:13.5 er. HRMS (ESI) calcd for C₂₈H₂₄NaO₄S [M+Na]⁺ *m*/z 479.1288, found 479.1294.



(S)-5-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-1-(phenylsulfonyl)-1H-ind ole (5n): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4n (30.1 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 4:1, v/v) to afford 5n (21.3 mg, 39%) as a colorless oil, Rf =0.15 (silica gel, PE:EA = 4:1, v/v); ¹H NMR (400 MHz, Chloroform-d) δ 7.95 (d, J = 8.3 Hz, 1H), 7.88 – 7.82 (m, 4H), 7.69 – 7.64 (m, 1H), 7.60 - 7.51 (m, 3H), 7.44 (t, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.29 - 7.22 (m, 1H), 7.20 - 7.22 (m, 1H) 7.14 (m, 1H), 7.13 - 7.05 (m, 1H), 7.02 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.15 - 4.04 (m, 1H), 3.76 (s, 3H), 3.15 - 2.94 (m, 2H), 2.60 - 2.50 (m, 1H), 2.38 -2.24 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 139.2, 138.2, 135.7, 134.0, 133.9, 133.1, 130.1, 129.5, 129.4, 128.8, 128.1, 126.8, 125.7, 125.1, 123.5, 122.6, 120.2, 114.4, 113.9, 55.4, 54.5, 40.5, 28.3. $[\alpha]_D^{20} = +22.8$ (c = 0.8, CHCl₃). SFC (Trefoir CEL2, $CO_2/MeOH = 70:30$, 1 mL/min, 215.0 nm): t_R (major) = 8.245 min, t_R (minor) = 10.146 min, 88.5:11.5 er. HRMS (ESI) calcd for $C_{30}H_{27}NNaO_5S_2$ [M+Na]⁺ m/z568.1223, found 568.1222.



(*S*)-5-(1-(4-methoxyphenyl)-3-(phenylsulfonyl)propyl)-2-(trifluoromethyl)pyridin e (50): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4o (19.1 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 2:1, v/v) to afford 5o (5.2 mg, 12%) as a colorless oil, Rf =0.35 (silica gel, PE:EA = 2:1, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.88 (d, *J* = 7.0 Hz, 2H), 7.71 – 7.53 (m, 5H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.13 – 4.04 (m, 1H), 3.78 (s, 3H) 3.06 – 2.99

(m, 2H), 2.56 – 2.40 (m, 2H); ¹³C NMR (176 MHz, CDCl₃) δ 158.39, 154.47, 139.23, 135.5 (q, J = 19.1 Hz), 133.86, 130.04 (q, J = 51.4 Hz), 129.47, 128.81, 128.67, 128.62, 128.61(q, J = 220.1 Hz), 128.17, 115.69, 114.24, 55.39, 55.01, 48.17, 28.72. ¹⁹F NMR (376 MHz, CDCl₃) δ -67.84. [α]²⁰_D = -7.8 (c = 0.13, CH₂Cl₂). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 10.736 min, t_R (minor) = 12.774 min, 91.5:8.5 er. HRMS (ESI) calcd for C₂₂H₂₀F₃NNaO₃S [M+Na]⁺ *m/z* 458.1008, found 458.1011.



(*R*)-1-(benzyloxy)-4-(1-phenyl-3-(phenylsulfonyl)propyl)benzene (5p): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3b (56.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5p (26.5 mg, 60%) as a colorless oil, Rf =0.52 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.30 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.02 (s, 2H), 3.90 (t, *J* = 8.0 Hz, 1H), 3.09 – 2.97 (m, 2H), 2.50 – 2.35 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 143.4, 139.2, 137.1, 135.3, 133.8, 129.5, 128.9, 128.7, 128.7, 128.2, 128.1, 127.7, 127.6, 126.8, 115.2, 70.2, 54.9, 49.0, 28.6. [α]²⁰ = -2.8 (c = 1.2, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 9.028 min, t_R (minor) = 13.727 min, 96:4 er. HRMS (ESI) calcd for C₂₈H₂₆NaO₃S [M+Na]⁺ *m/z* 465.1495, found 465.1496.



(R)-2-(1-(3-methoxyphenyl)-3-(phenylsulfonyl)propyl)naphthalene (5q): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3c (44.4 mg, 0.2 mmol), 41 (17.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5q (16.6 mg, 40%) as a colorless oil, Rf =0.50 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-d) δ 7.91 – 7.85 (m, 2H), 7.81 – 7.70 (m, 3H), 7.68 – 7.60 (m, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.45 (ddd, *J* = 7.3, 5.3, 1.6 Hz, 2H), 7.28 – 7.15 (m, 2H), 6.84 - 6.67 (m, 3H), 4.09 (t, J = 8.0 Hz, 1H), 3.75 (s, 3H), 3.14 - 3.02 (m, 2H), 2.56 (q, J = 8.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 144.5, 140.2, 139.2, 133.9, 133.6, 132.5, 129.9, 129.5, 128.7, 128.2, 127.9, 127.7, 126.4, 126.2, 126.0, 120.2, 114.1, 111.9, 55.3, 54.9, 49.8, 28.1. $[\alpha]_{D}^{20} = +15.4$ (c = 1.0, CHCl₃). **SFC** (IC-3, CO₂/MeOH = 80:20, 1 mL/min, 272.0 nm): t_R (major) = 18.584 min, t_R (minor) = 23.934 min, 95.5:4.5 er. **HRMS (ESI)** calcd for $C_{26}H_{24}NaO_{3}S [M+Na]^{+} m/z$ 439.1338, found 439.1341.



(S)-1-methyl-4-(1-phenyl-3-(phenylsulfonyl)propyl)benzene (5r): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3e (38.4 mg, 0.2 mmol), 4b (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5r (8.8 mg, 25%) as a colorless

oil, Rf =0.45 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, J = 8.4, 1.4 Hz, 2H), 7.70 – 7.62 (m, 1H), 7.60 – 7.51 (m, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 7.10 – 6.99 (m, 4H), 3.90 (t, J = 8.0 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.49 – 2.38 (m, 2H), 2.29 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.3, 140.0, 139.2, 136.5, 133.8, 129.6, 129.5, 128.9, 128.2, 127.7, 127.6, 126.8, 55.0, 49.4, 28.4, 21.1. [α]²⁰_D = +2.2 (c = 0.7, CHCl₃). SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 9.904 min, t_R (minor) = 10.875 min, 96.5:3.5 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₂S [M+Na]⁺ m/z 373.1233, found 373.1235.



(*R*)-1-methyl-4-(1-phenyl-3-(phenylsulfonyl)propyl)benzene (*ent*-5r): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3d (41.2 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford *ent*-5r (14.0 mg, 40%) as a colorless oil, Rf =0.45 (silica gel, Tol:EA = 30:1, twice, v/v); $[\alpha]_D^{20} = -2.0$ (c = 0.7, CHCl₃). SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (minor) = 10.330 min, t_R (major) = 11.136 min, 89:11 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₂S [M+Na]⁺ *m/z* 373.1233, found 373.1235.



(*S*)-2-(1-phenyl-3-(phenylsulfonyl)propyl)naphthalene (5s): According to the general procedure A, 2a (30.6 ul, 0.2 mmol), 3e (38.4 mg, 0.2 mmol), 4l (17.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5s (12.4 mg, 32%) as a colorless oil, Rf =0.47 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.84 (m, 2H), 7.81 – 7.70 (m, 3H), 7.69 – 7.59 (m, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.32 – 7.15 (m, 6H), 4.12 (t, *J* = 8.0 Hz, 1H), 3.15 – 3.00 (m, 2H), 2.63 – 2.47 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 140.4, 139.3, 133.9, 133.6, 132.5, 129.5, 128.9, 128.7, 128.2, 127.9, 127.7, 127.0, 126.4, 126.3, 126.0, 126.0, 55.0, 49.8, 28.2. [α]²⁰_D = +11.3 (c = 0.9, CHCl₃). SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 223.0 nm): t_R (major) = 31.934 min, t_R (minor) = 34.425 min, 95.5:4.5 er. HRMS (ESI) calcd for C₂₅H₂₂NaO₂S [M+Na]⁺ *m/z* 409.1233, found 409.1234.



(*R*)-1-methoxy-4-(1-phenyl-3-tosylpropyl)benzene (5t): According to the general procedure A, 2b (39.3 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5t (25.8 mg, 68%) as a colorless oil, Rf =0.44 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.21 (m, 2H), 7.21 – 7.03 (m, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.89 (t, *J* = 8.1 Hz, 2H), 3.76 (s, 1H), 3.05 – 2.96 (m, 2H), 2.48 – 2.33 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 144.8, 143.5, 136.3, 135.1, 130.1, 128.8, 128.7, 128.2, 127.6, 126.8, 114.2, 55.4, 55.1, 49.0, 28.6,

21.8. $[\alpha]_D^{20} = -2.4$ (c = 1.5, CHCl₃). SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (minor) = 17.043 min, t_R (major) = 18.110 min, 95:5 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1344.



(*R*)-1-(tert-butyl)-4-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzene(5u): According to the general procedure A, 2c (23.8 mg, 0.1 mmol), 3a (22.2 mg, 0.1 mmol), 4a (6.1 mg, 0.05 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), (*R*)-1a (5.0 mg, 0.06 mmol), Rb₂CO₃ (34.7 mg, 0.15 mmol) was stirred for 48 h at 10 °C, the crude product was purified by PTLC (silica gel, PE:EA = 6:1, twice, v/v) to afford 5u (11.6 mg, 55%) as a colorless oil, Rf =0.40 (silica gel, PE:EA = 6:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.82 – 6.77 (m, 2H), 3.89 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.05 – 2.95 (m, 2H), 2.49 – 2.39 (m, 2H), 1.35 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 157.8, 143.5, 136.3, 135.2, 128.9, 128.7, 128.0, 127.7, 126.8, 126.5, 114.2, 55.4, 55.0, 49.0, 35.4, 31.2, 28.5. [α]²⁰ = -1.3 (c = 1.1, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 11.267 min, t_R (minor) = 16.226 min, 95:5 er. HRMS (ESI) calcd for C₂₆H₃₀NaO₃S [M+Na]⁺ *m/z* 445.1808, found 445.1809.



(*R*)-1-methoxy-4-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzene(5v): According to the general procedure A, 2d (42.5 mg, 0.2 mmol), 3a (44.4 mg, 0.2

mmol), **4a** (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5v** (20.6 mg, 52%) as a colorless oil, Rf =0.48 (silica gel, Tol:EA = 30:1, twice, v/v); ¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.12 (m, 3H), 7.10 – 6.99 (m, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.94 – 3.85 (m, 4H), 3.78 (s, 3H), 3.07 – 2.95 (m, 2H), 2.48 – 2.37 (m, 2H); ¹³**C NMR** (101 MHz, CDCl₃) δ 163.9, 158.4, 143.5, 135.2, 130.8, 130.3, 128.9, 128.7, 127.7, 126.8, 114.6, 114.2, 55.8, 55.4, 55.3, 49.0, 28.7. [α]²⁰ = -2.2 (c = 1.0, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 19.168 min, t_R (minor) = 25.047 min, 94:6 er. **HRMS (ESI)** calcd for C₂₃H₂₄NaO₄S [M+Na]⁺ *m/z* 419.1288, found 419.1290.



(*R*)-1-fluoro-4-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzene (5w): According to the general procedure A, 2e (40.0 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5w (18.0 mg, 47%) as a colorless oil, Rf =0.52 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.87 (m, 2H), 7.34 – 7.19 (m, 5H), 7.19 – 7.14 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.93 (t, *J* = 8.1 Hz, 1H), 3.80 (s, 3H), 3.11 – 2.96 (m, 2H), 2.51 – 2.37 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 164.7, 158.5, 143.3, 135.3 (d, *J* = 3.3 Hz), 135.0, 131.4 (d, *J* = 9.6 Hz), 128.8 (d, *J* = 22.7 Hz), 127.6, 126.9, 116.8 (d, *J* = 22.8 Hz), 114.3, 55.4, 55.1, 49.0, 28.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -103.43. [α]²⁰ = -2.0 (c = 1.2, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 220.0 nm): t_R (major) = 6.682 min, t_R (minor) = 9.315 min, 93:7 er. **HRMS** (ESI) calcd for C₂₂H₂₁FNaO₃S [M+Na]⁺ m/z 407.1088, found 407.1094.



ethyl (R)-4-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzoate (5x): According to the general procedure A, 2f (25.4 mg, 0.2 mmol), 3a (22.2 mg, 0.1 mmol), 4a (6.1 mg, 0.05 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), (R)-1a (5.0 mg, 0.06 mmol), Rb₂CO₃ (34.7 mg, 0.15 mmol) was stirred for 48 h at 10 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5x (10.7mg, 49%) as a colorless oil, Rf =0.38 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-d) δ 8.21 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.21 - 7.09 (m, 3H), 7.05 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 3.89 (t, J = 8.1 Hz, 1H), 3.76 (s, 3H), 3.11 – 2.97 (m, 2H), 2.47 – 2.35 (m, 2H), 1.42 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 158.5, 143.2, 142.9, 135.4, 134.9, 130.5, 128.9, 128.7, 128.2, 127.6, 126.9, 114.3, 62.0, 55.4, 54.9, 49.0, 28.5, 14.4. $[\alpha]_D^{20} = -2.6$ (c = 1.0, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.857 min, t_R (minor) = 17.521 min, 92:8 er. **HRMS (ESI)** calcd for $C_{25}H_{26}NaO_5S [M+Na]^+ m/z$ 461.1393, found 461.1393.



(*R*)-1-methoxy-4-(1-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)propyl)benzen e (5y): According to the general procedure A, 2g (50.0 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5y (20.4 mg, 47%) as a colorless oil, Rf =0.42 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.10 (m, 3H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.90 (t, *J* = 8.1 Hz, 1H), 3.76 (s, 3H), 3.11 – 3.01 (m, 2H), 2.50 – 2.37 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.57, 143.18, 135.61 (q, *J* = 33.7 Hz), 134.81, 128.95, 128.92, 128.84, 128.69, 127.61, 126.94, 126.63 (q, *J* = 3.7 Hz), 123.3 (q, J = 271.9 Hz), 114.34, 55.39, 54.90, 49.00, 28.43; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.20. [α]²⁰ = -2.0 (c = 1.2, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 3.506 min, t_R (minor) = 5.310 min, 95:5 er. HRMS (ESI) calcd for C₂₃H₂₁F₃NaO₃S [M+Na]⁺ *m/z* 457.1056, found 457.1053.



(*R*)-1-methoxy-3-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzene(5z):

According to the general procedure **A**, **2h** (42.5 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5z** (18.6 mg, 47%) as a colorless oil, Rf =0.47 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H **NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.39 (m, 2H), 7.36 – 7.32 (m, 1H), 7.29 – 7.22 (m, 2H), 7.20 – 7.09 (m, 4H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.89 (t, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.08 – 2.99 (m, 2H), 2.48 – 2.38

(m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 160.2, 158.5, 143.4, 140.4, 135.1, 130.5, 128.9, 128.7, 127.7, 126.8, 120.4, 120.3, 114.3, 112.5, 55.9, 55.4, 54.9, 49.0, 28.6. [α]²⁰_D = -1.4 (c = 1.0, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.035 min, t_R (minor) = 16.532 min, 93.5:6.5 er. **HRMS** (**ESI**) calcd for C₂₃H₂₄NaO₄S [M+Na]⁺ *m/z* 419.1288, found 419.1292.



(*R*)-1,3-dichloro-5-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)benzene(5aa): According to the general procedure A, 2i (50.2 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5aa (20.8 mg, 48%) as a colorless oil, Rf =0.59 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.8 Hz, 2H), 7.62 (t, *J* = 1.9 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.12 (m, 3H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.91 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 3.13 – 2.97 (m, 2H), 2.50 – 2.35 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 143.1, 142.2, 136.6, 134.7, 133.9, 129.0, 128.7, 127.6, 127.0, 126.6, 114.4, 55.4, 54.9, 49.0, 28.3. [α]²⁰ = -0.7 (c = 1.5, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 8.963 min, t_R (minor) = 14.771 min, 94:6 er. HRMS (ESI) calcd for C₂₂H₂₀Cl₂NaO₃S [M+Na]⁺ *m/z* 457.0402, found 457.0404.



(R)-1-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)naphthalene (5ab): According to the general procedure A, 2j (46.5 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5ab** (17.1 mg, 41%) as a colorless oil, Rf =0.49 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H **NMR** (400 MHz, Chloroform-*d*) δ 8.56 (dd, J = 6.3, 3.5 Hz, 1H), 8.31 (dd, J = 7.4, 1.3 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.97 (dd, J = 6.3, 3.3 Hz, 1H), 7.69 - 7.49 (m, 3H), 7.23 – 7.10 (m, 3H), 7.07 – 7.01 (m, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 3.84 (t, J = 8.1 Hz, 1H), 3.74 (s, 3H), 3.33 – 3.14 (m, 2H), 2.48 – 2.33 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 143.4, 135.3, 135.0, 134.4, 134.1, 130.8, 129.4, 129.0, 128.8, 128.8, 128.7, 127.6, 127.2, 126.7, 124.6, 124.1, 114.2, 55.3, 54.3, 48.8, 28.7. $[\alpha]_D^{20} = +4.0$ (c = 0.8, CHCl₃). SFC (Trefoir CEL2, $CO_2/MeOH = 90:10, 1 \text{ mL/min}, 230.0 \text{ nm}$: t_R (major) = 27.867 min, t_R (minor) = 37.462 min, 93:7 er. **HRMS (ESI)** calcd for $C_{26}H_{24}NaO_{3}S [M+Na]^{+} m/z$ 439.1338, found 439.1340.



(*R*)-2-((3-(4-methoxyphenyl)-3-phenylpropyl)sulfonyl)pyridine (5ac): According to the general procedure A, 2k (36.6 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol),
Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, ¹H NMR showed that there were no **5ac** obtained.



(*R*)-1-(3-(benzylsulfonyl)-1-phenylpropyl)-4-methoxybenzene (5ad): According to the general procedure A, 2l (39.3 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 10 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 5ad (17.1 mg, 45%) as a colorless oil, Rf =0.49 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 3H), 7.33 – 7.25 (m, 4H), 7.23 – 7.14 (m, 3H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.17 (s, 2H), 3.90 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 2.89 – 2.66 (m, 2H), 2.56 – 2.32 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.5, 143.4, 135.1, 130.6, 129.2, 129.2, 128.9, 128.8, 128.1, 127.7, 126.8, 114.3, 59.6, 55.4, 45.0, 49.1, 28.1. [α]²⁰_D = +0.8 (c = 0.5, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.251 min, t_R (minor) = 16.168 min, 80:20 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1339.



(*R*)-1-(3-(benzylsulfonyl)-1-phenylpropyl)-4-methoxybenzene (5ae): According to the general procedure A, 2l (39.3 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol),

Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 8:1, twice, v/v) to afford **5ae** (14.4 mg, 38%) as a colorless oil, Rf =0.42 (silica gel, PE:EA = 8:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.13 (m, 5H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.02 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 2.89 – 2.79 (m, 2H), 2.65 – 2.53 (m, 2H), 1.34 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 143.7, 135.4, 128.9, 127.8, 126.8, 114.3, 59.2, 55.4, 49.4, 44.4, 26.6, 23.6. $[\alpha]_D^{20}$ = -1.5 (c = 0.4, CHCl₃). SFC (IC-3, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (minor) = 14.812 min, t_R (major) = 18.985 min, 69:31 er. HRMS (ESI) calcd for C₂₀H₂₆NaO₃S [M+Na]⁺ *m/z* 369.1495, found 369.1496.



Phenyl (*R*)-3-(4-methoxyphenyl)-3-phenylpropane-1-sulfonate (5af): According to the general procedure A, 2t (19.8 mg, 0.1 mmol), 3a (22.2 mg, 0.1 mmol), 4a (6.1 mg, 0.05 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), (*R*)-1a (5.0 mg, 0.06 mmol), Cs₂CO₃ (48.9 mg, 0.15 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 10:1) to afford 5af (10.3 mg, 48%) as a colorless oil, Rf =0.26 (silica gel, PE:EA = 10:1); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.27 (m, 5H), 7.26 – 7.12 (m, 7H), 6.90 – 6.78 (m, 2H), 4.02 (t, J = 8.0 Hz, 1H), 3.79 (s, 3H), 3.27 – 3.11 (m, 2H), 2.73 – 2.62 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.59, 149.18, 143.24, 134.90, 130.07, 128.98, 128.81, 127.72, 127.34, 126.97, 122.12, 114.37, 55.41, 49.23, 48.82, 29.62. $[\alpha]_D^{20}$ = -60 (c = 0.1, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 4.986 min, t_R (minor) = 6.883 min, 95.5:4.5 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₄S [M+Na]⁺ *m/z* 405.1131, found 405.1131.



(*R*)-3-(4-methoxyphenyl)-N,3-diphenylpropane-1-sulfonamide (5ag): According to the general procedure A, 2t (39.6 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 60:1, then PE:DCM = 2:1, twice, v/v) to afford 5ag (15.7 mg, 40%) as a colorless oil, Rf =0.57 (silica gel, Tol:EA = 60:1); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.19 – 7.09 (m, 8H), 6.88 – 6.80 (m, 2H), 3.97 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 3.24 – 3.11 (m, 2H), 2.74 – 2.57 (m, 2H), 2.31 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.52, 149.18, 140.21, 136.56, 135.20, 130.06, 129.65, 128.73, 127.59, 127.33, 122.14, 114.33, 55.41, 49.26, 48.44, 29.65, 21.12. [α]²⁰_D = -27 (c = 0.2, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 11.283 min, t_R (minor) = 17.102 min, 93:7 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₄S [M+Na]⁺ *m/z* 419.1288, found 419.1287.



Phenyl (S)-3-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1-sulfonate (5ah): According to the general procedure A, 2t (39.6 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 60:1, then PE:DCM = 2:1, twice,

v/v) to afford **5ah** (18.3 mg, 46%) as a colorless oil, Rf =0.61 (silica gel, Tol:EA = 60:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.27 (m, 3H), 7.23 – 7.07 (m, 6H), 7.03 – 6.95 (m, 2H), 6.90 – 6.81 (m, 2H), 4.01 (t, J = 8.0 Hz, 1H), 3.79 (s, 3H), 3.21 – 3.13 (m, 2H), 2.69 – 2.60 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 161.76 (d, *J* = 245.43 Hz), 158.68, 149.13, 139.08 (d, *J* = 3.2 Hz), 134.59, 130.10, 129.17 (d, *J* = 7.9 Hz), 128.74, 127.40, 122.10, 115.78 (d, *J* = 21.3 Hz), 114.45, 55.42, 49.09, 48.01, 29.74; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.99. [α]²⁰ = -52 (c = 0.1, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 9.190 min, t_R (minor) = 14.619 min, 96.5:3.5 er. **HRMS (ESI)** calcd for C₂₂H₂₁FNaO₄S [M+Na]⁺ *m/z* 423.1037, found 423.1037.

4.3 General procedure C: Asymmetric reactions for the synthesis of 7 using alkenyl sulfone substrates.



In glovebox, **6a** (33.6 mg, 0.2 mmol), **3** (0.2 mmol), **4** (0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol), anhydrous MTBE (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours at 0 °C. After the reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. An external standard (Dibromomethane) was added to the system for determining NMR yields. Product **7** was obtained by PTLC.

4.4 General procedure **D**: Racemic reactions for the synthesis of rac-7 using alkenyl sulfone substrates.



Under Ar atmosphere, **6a** (33.6 mg, 0.2 mmol), **3** (0.2 mmol), **4** (0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol), anhydrous THF (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and stirred for 20 hours in an argon atmosphere at room temperature. After the reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. The racemic product **7** was obtained by PTLC.



(*R*)-1-methoxy-4-(1-phenyl-2-(phenylsulfonyl)ethyl)benzene (7a): According to the general procedure **C**, **6a** (33.6 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **7a** (23.6 mg, 67%) as a white solid, Rf =0.40 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.52 – 7.45 (m, 1H), 7.38 – 7.31 (m, 2H), 7.22 – 7.09 (m, 5H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.76 – 6.67 (m, 2H), 4.59 (t, *J* = 7.2 Hz, 1H), 3.89 (d, *J* = 7.1 Hz, 2H), 3.73 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 141.9, 139.9, 133.5, 133.3, 129.0, 128.9, 128.8, 128.1, 127.6, 127.0, 114.2, 61.8, 55.4, 45.5.

 $[\alpha]_D^{20} = -2.0 \text{ (c} = 0.4, \text{ CHCl}_3\text{)}.$ SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 240.0 nm): t_R (minor) = 6.186 min, t_R (major) = 6.616 min, 95:5 er. HRMS (ESI) calcd for C₂₁H₂₀NaO₃S [M+Na]⁺ *m/z* 375.1025, found 375.1024.



(R) -1-methoxy-4-(2-(phenylsulfonyl)-1-(p-tolyl)ethyl)benzene (7b): According to the general procedure C, **6a** (33.6 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4b** (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 7b (21.2 mg, 58%) as a white solid, Rf =0.39 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.59 (m, 2H), 7.54 – 7.44 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.06 – 6.95 (m, 6H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.55 (t, *J* = 7.2 Hz, 1H), 3.87 (d, *J* = 7.2 Hz, 2H), 3.73 (s, 3H), 2.25 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.5, 139.9, 138.9, 136.6, 133.7, 133.2, 129.5, 129.0, 128.7, 128.1, 127.5, 114.2, 61.9, 55.4, 45.1, 21.1. [α]²⁰ = +1.3 (c = 1.2, CHCl₃). SFC (Trefoir CEL2, CO₂/MeOH = 85:15, 1 mL/min, 235.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 94:6 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₃S [M+Na]⁺ *m/z* 389.1182, found 389.1181.



(S)-1-fluoro-4-(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethyl)benzene (7c): According to the general procedure C, 6a (33.6 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4c (14.0 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg,

0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 7c (16.7 mg, 45%) as a white solid, Rf =0.37 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H **NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.56 – 7.46 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.15 – 6.97 (m, 4H), 6.91 – 6.77 (m, 2H), 7.75 – 6.66 (m, 2H), 4.59 (t, *J* = 7.2 Hz, 1H), 3.85 (d, *J* = 7.3 Hz, 2H), 3.73 (s, 3H); ¹³C **NMR** (101 MHz, CDCl₃) δ 161.9 (d, *J* = 244.9 Hz), 158.7, 141.9, 139.8, 133.4, 133.4, 129.2 (d, *J* = 7.9 Hz), 129.1, 128.6, 128.1, 115.7 (d, *J* = 21.3 Hz), 114.3, 61.9, 55.4, 44.8; ¹⁹F **NMR** (376 MHz, CDCl₃) δ -115.80; [α]²⁰ = -2.2 (c = 0.8, CH₂Cl₂); **SFC** (AD-3, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 13.410 min, t_R (minor) = 14.689 min, 93:7 er. **HRMS (ESI)** calcd for C₂₁H₁₉FNaO₃S [M+Na]⁺ m/z 393.0932, found 393.0928.



(*S*)-1-chloro-4-(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethyl)benzene (7d): According to the general procedure C, **6a** (33.6 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4d** (15.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 7d (20.5 mg, 53%) as a white solid, Rf =0.40 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.58 – 7.48 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.08 – 6.93 (m, 4H), 6.78 – 6.68 (m, 2H), 4.57 (t, *J* = 7.2 Hz, 1H), 3.84 (dd, *J* = 7.3, 2.1 Hz, 2H), 3.74 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 140.2, 139.8, 133.4, 133.1, 132.9, 129.1, 129.1, 128.9, 128.6, 128.0, 114.4, 61.7, 55.4, 44.9. [α]²⁰ = +3.6 (c = 1.0, CHCl₃). SFC (IG-3, CO₂/MeOH = 85:15, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 95:5 er. **HRMS (ESI)** calcd for $C_{21}H_{19}ClNaO_3S [M+Na]^+ m/z$ 409.0636, found 409.0643.



(*S*)-1-(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethyl)-2-methylbenzene (7e): According to the general procedure C, **6a** (33.6 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4j** (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **7e** (16.5 mg, 45%) as a white solid, Rf =0.40 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.60 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.10 – 6.96 (m, 6H), 6.72 (d, *J* = 8.5 Hz, 2H), 4.83 (t, *J* = 7.1 Hz, 1H), 3.84 (d, *J* = 7.4 Hz, 2H), 3.73 (s, 3H), 2.30 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.5, 139.9, 139.5, 136.0, 133.4, 133.0, 131.0, 129.2, 129.0, 128.0, 126.9, 126.6, 126.3, 114.1, 61.9, 55.4, 41.0, 19.9. [α]²⁰ = +14.0 (c = 0.6, CHCl₃). SFC (IG-3, CO₂/MeOH = 85:15, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 96:4 er. HRMS (ESI) calcd for C₂₂H₂₂NaO₃S [M+Na]⁺ *m/z* 389.1182, found 389.1182.



(*S*)-2-(1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethyl)naphthalene (7f): According to the general procedure C, 6a (33.6 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4l (17.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol),

Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **7f** (36.5 mg, 66%) as a white solid, Rf =0.38 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.67 (m, 2H), 7.66 – 7.59 (m, 3H), 7.54 (d, J = 1.9 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.27 – 7.16 (m, 3H), 7.12 – 7.06 (m, 2H), 6.77 – 6.68 (m, 2H), 4.76 (t, J = 7.2 Hz, 1H), 4.07 – 3.87 (m, 2H), 3.74 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.6, 139.8, 139.0, 133.4, 133.2, 132.4, 128.9, 128.9, 128.7, 128.0, 127.9, 127.6, 126.4, 126.2, 126.0, 125.9, 114.3, 61.7, 55.4, 45.6. [α]²⁰_D = +23.5 (c = 1.5, CHCl₃). **SFC** (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 96:4 er. **HRMS** (ESI) calcd for C₂₅H₂₂NaO₃S [M+Na]⁺ *m/z* 425.1182, found 425.1178.



(*S*)-1-methyl-4-(1-phenyl-2-(phenylsulfonyl)ethyl)benzene (7g): According to the general procedure C, **6a** (33.6 mg, 0.2 mmol), **3e** (38.2 mg, 0.2 mmol), **4b** (13.6 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford 7g (15.1 mg, 45%) as a white solid, Rf =0.42 (silica gel, Tol:EA = 30:1, twice, v/v); compound 7g is a known compound.¹¹ [α]_D²⁰ = +1.3 (c = 0.3, CHCl₃). The absolute configuration of (*S*)-7g was determined by comparison with optical rotation data for the reported literature.¹¹ SFC (Trefoir CEL1, CO₂/MeOH = 90:10, 1 mL/min, 232.0 nm): t_R (major) = 4.340 min, t_R (minor) = 4.787 min, 93.5:6.5 er. HRMS (ESI) calcd for C₂₆H₂₈NaO₄S [M+Na]⁺ *m/z* 359.1076, found 359.1078.



Phenyl (*R*)-2-(4-methoxyphenyl)-2-phenylethane-1-sulfonate (7h): According to the general procedure C, **6b** (36.9 mg, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Cs₂CO₃ (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 60:1, then PE:DCM = 2:1, twice, v/v) to afford **7h** (10.8 mg, 30%) as a white solid, Rf =0.54 (silica gel, Tol:EA = 60:1); ¹H **NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.18 (m, 10H), 7.02 – 6.91 (m, 2H), 6.90 – 6.80 (m, 2H), 4.72 (t, J = 7.1 Hz, 1H), 3.99 (dd, J = 7.1, 1.0 Hz, 2H), 3.77 (s, 3H); ¹³C **NMR** (101 MHz, CDCl₃) δ 158.85, 149.03, 141.77, 133.46, 129.96, 129.04, 128.91, 127.77, 127.38, 127.20, 121.99, 114.39, 56.34, 55.41, 45.85. $[\alpha]_D^{20}$ = -21.33 (c = 0.3, CHCl₃). **SFC** (Trefoir CEL1, CO₂/MeOH = 97:3, 1 mL/min, 232.0 nm): t_R (minor) = 17.231 min, t_R (major) = 19.696 min, 96:4 er. **HRMS (ESI)** calcd for C₂₁H₂₀NaO₄S [M+Na]⁺ *m/z* 391.0975, found 391.0977.



(S)-1-methoxy-4-(1-phenyl-2-(phenylsulfonyl)ethyl)benzene (*ent*-7a): According to the general procedure C, **6a** (33.6 mg, 0.2 mmol), **3e** (38.2 mg, 0.2 mmol), **4p** (15.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Cs_2CO_3 (97.7 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford *ent*-7a (15.8 mg,

45%) as a white solid, Rf =0.40 (silica gel, Tol:EA = 30:1, twice, v/v); $[\alpha]_D^{20} = +2.5$ (c = 1.2, CHCl₃). **SFC** (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 240.0 nm): t_R (major) = 6.206 min, t_R (minor) = 6.764 min, 90:10 er. **HRMS (ESI)** calcd for C₂₁H₂₀NaO₃S [M+Na]⁺ *m/z* 375.1025, found 375.1024.

5. Control experiments

5.1 General procedure E: Asymmetric reactions for the synthesis of 5 using various different alkene substrates.



In glovebox, **2** (0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol), anhydrous MTBE (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours at 0 °C. After the reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. An external standard (Dibromomethane) was added to the crude for determining NMR yields. Product **5** was obtained by PTLC.

5.2 General procedure F: Racemic reactions for the synthesis of rac-5 using various different alkene substrates.



In an argon atmosphere, **2** (0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4** (12.2 mg, 0.1 mmol), Pd_2dba_3 (3.7 mg, 0.004 mmol), Rb_2CO_3 (69.3 mg, 0.3 mmol), anhydrous THF (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and stirred for 20 hours in an argon atmosphere at room temperature. After the reaction was completed (monitored by TLC), the crude reaction mixture was filtered through a short silica column with PE: EA = 1:2, and the solvent was removed in vacuo. The racemic product *rac-5* was obtained by PTLC.



(R) -1-methoxy-4-(1-phenyl-4-(phenylsulfonyl)butyl)benzene (5ai): According to the general procedure E, 2n (39.3 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 4:1, v/v) to afford the mixture of 5ai and its Heck by-product, added the mixture to 2 ml DCM and *m*-CPBA (34.6 mg, 0.2 mmol) and stirred for 2 h at room temperature, and the solvent was removed in vacuo. The pure product 5ai (6.0 mg, 16%) was obtained by PTLC as a colorless oil, Rf =0.37 (silica gel, PE:EA = 4:1, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.76 (m,

2H), 7.65 – 7.59 (m, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.11 (m, 3H), 7.10 – 7.04 (m, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.79 – 3.74 (m, 4H), 3.11 – 3.02 (m, 2H), 2.09 (q, J = 7.8 Hz, 2H), 1.75 – 1.64 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.2, 144.5, 139.2, 136.3, 133.7, 129.4, 128.7, 128.7, 128.2, 127.7, 126.5, 114.1, 56.2, 55.4, 50.2, 34.4, 21.5. $[\alpha]_D^{20} = -1.3$ (c = 0.3, CHCl₃). SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 10.743 min, t_R (major) = 12.949 min, 69.5:30.5 er. HRMS (ESI) calcd for C₂₃H₂₄NaO₃S [M+Na]⁺ *m/z* 403.1338, found 403.1337.



(R)-1-methoxy-4-(1-phenyl-5-(phenylsulfonyl)pentyl)benzene (5aj): According to the general procedure E, 20 (42.1 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, PE:EA = 4:1, v/v) to afford the mixture of 5aj and its Heck by-product, added the mixture to 2 ml DCM and *m*-CPBA (34.6 mg, 0.2 mmol) and stirred for 2 h at room temperature, and the solvent was removed in vacuo. The pure product 5aj (13.2 mg, 33%) was obtained by PTLC as a colorless oil, Rf =0.36 (silica gel, PE:EA = 4:1, v/v); ¹H NMR (400 MHz, Chloroform-d) δ 7.94 – 7.83 (m, 2H), 7.71 - 7.60 (m, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.28 - 7.21 (m, 2H), 7.18 - 7.12 (m, 3H), 7.12 – 7.05 (m, 2H), 6.84 – 6.77 (m, 2H), 3.82 – 3.68 (m, 4H), 3.12 – 2.96 (m, 2H), 2.01 – 1.90 (m, 2H), 1.78 – 1.68 (m, 2H), 1.36 – 1.22 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 145.1, 139.3, 136.9, 133.8, 129.4, 128.8, 128.6, 128.2, 127.8, 126.3, 114.0, 56.3, 55.4, 50.3, 35.4, 26.9, 22.8. $[\alpha]_D^{20} = -2.0$ (c = 0.8, CHCl₃). SFC (Trefoir CEL1, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 4.556 min, t_R (major) = 5.478 min, 82.5:17.5 er. HRMS (ESI) calcd for $C_{24}H_{26}NaO_3S [M+Na]^+ m/z$ 417.1495, found 417.1493.



1-methoxy-4-((1*R*)-1-phenyl-3-(phenylsulfinyl)propyl)benzene (5ak): According to the general procedure E, 2p (33.2 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, ¹H NMR showed that trace 5ak (< 5%) was detected.



(*R*)-(3-(4-methoxyphenyl)-3-phenylpropyl)(phenyl)sulfane (5al): According to the general procedure E, 2q (30.0 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, ¹H NMR showed that trace 5al (\leq 5%) was detected.



(*R*)-(1-(4-methoxyphenyl)butane-1,4-diyl)dibenzene (5am): According to the general procedure E, 2r (30.1 ul, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (*R*)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by

PTLC (silica gel, PE:EA = 20:1, twice, v/v) to afford **5am** (5.0 mg, 17%) as a colorless oil, Rf =0.51 (silica gel, PE:EA = 20:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 7H), 7.25 – 7.15 (m, 5H), 6.91 – 6.83 (m, 2H), 3.92 (t, *J* = 7.8 Hz, 1H), 3.82 (s, 3H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.11 (dd, *J* = 15.1, 8.3 Hz, 2H), 1.71 – 1.61 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 145.6, 142.5, 137.4, 128.9, 128.6, 128.5, 128.4, 127.9, 126.1, 125.8, 113.9, 55.4, 50.5, 36.0, 35.6, 29.9. [α]²⁰ = -1.6 (c = 0.5, CHCl₃). SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 235.0 nm): t_R (minor) = 7.634 min, t_R (major) = 8.266 min, 72:28 er. HRMS (ESI) calcd for C₂₃H₂₄NaO [M+Na]⁺ *m/z* 339.1719, found 339.1720.



(R)-1-methoxy-4-(3-phenyl-1-(phenylsulfonyl)pentan-3-yl)benzene (5an): According to the general procedure E, 2s (42.1 mg, 0.2 mmol), 3a (44.4 mg, 0.2 mmol), 4a (12.2 mg, 0.1 mmol), Pd₂dba₃ (3.7 mg, 0.004 mmol), (R)-1a (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol) was stirred for 48 h at 0 °C, the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5an** (8.0 mg, 20%) as a colorless oil, Rf =0.32 (silica gel, Tol:EA = 30:1, twice, v/v); ¹H NMR (400 MHz, Chloroform-d) & 7.84 - 7.77 (m, 2H), 7.66 - 7.59 (m, 1H), 7.53 (ddd, J = 8.2, 6.6, 1.2 Hz, 2H), 7.25 - 7.10 (m, 3H), 7.08 - 7.01 (m, 2H), 6.98 - 6.88(m, 2H), 6.80 - 6.69 (m, 2H), 3.77 (s, 3H), 2.80 - 2.68 (m, 2H), 2.41 (ddd, J = 10.8, 5.4, 1.7 Hz, 2H), 1.99 (q, J = 7.4 Hz, 2H), 0.56 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) & 157.9, 146.6, 139.0, 138.4, 133.7, 129.4, 128.8, 128.3, 128.1, 127.8, 126.3, 113.6, 55.3, 52.4, 48.5, 30.8, 30.1, 8.4. $[\alpha]_D^{20} = -1.5$ (c = 0.4, CHCl₃). SFC $(IG-3, CO_2/MeOH = 90:10, 1 \text{ mL/min}, 230.0 \text{ nm})$: t_R (major) = 9.560 min, t_R (minor) = 10.340 min, 63.5:36.5 er. HRMS (ESI) calcd for $C_{24}H_{26}NaO_{3}S$ [M+Na]⁺ m/z417.1495, found 417.1500.

5.3 Asymmetric reactions for the synthesis of 5a using esterified phenylboronic acid 9a.



In glovebox, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **9a** (20.4 mg, 0.1 mmol), Pd_2dba_3 (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb_2CO_3 (69.3 mg, 0.3 mmol), anhydrous MTBE (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours in an argon atmosphere at 0 °C. ¹H NMR showed that no desired product **5a** was detected.

5.4 Asymmetric reactions for the synthesis of 5a using tributyl(phenyl)stannane10a.



In glovebox, **2a** (16 μ L, 0.1 mmol), **3a** (22.2 mg, 0.1 mmol), **10a** (16.4 μ L, 0.05 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), (*R*)-**1a** (5.0 mg, 0.06 mmol), Rb₂CO₃ (34.7 mg, 0.15 mmol), anhydrous MTBE (1 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours in an argon atmosphere at 0 °C, and the

crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5a** (6.7 mg, 37%) with 88:12 er.

5.5 Asymmetric reactions for the synthesis of 5a using Pd(OAc)₂.



In glovebox, **2a** (30.6 ul, 0.2 mmol), **3a** (44.4 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd(OAc)₂ (1.8 mg, 0.008 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb₂CO₃ (69.3 mg, 0.3 mmol), anhydrous MTBE (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours in an argon atmosphere at 0 °C, and the crude product was purified by PTLC (silica gel, Tol:EA = 30:1, twice, v/v) to afford **5a** (10.6 mg, 29%) with 96:4 er.

5.6 Asymmetric reactions for the synthesis of **5a** using Heck by-product **8a**.



In glovebox, **8a** (57.6 mg, 0.2 mmol), **4a** (12.2 mg, 0.1 mmol), Pd_2dba_3 (3.7 mg, 0.004 mmol), (*R*)-**1a** (10.0 mg, 0.012 mmol), Rb_2CO_3 (69.3 mg, 0.3 mmol), anhydrous MTBE (2 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The

system was stirred for 48 hours in an argon atmosphere at 0 °C. ¹H NMR showed that no desired product **5a** was detected.

5.7 Cross-over experiment using 8c.



In glovebox, **8c** (27.6 mg, 0.1 mmol), **2a** (16 μ l, 0.1 mmol), **3a** (22.2 mg, 0.2 mmol), **4a** (6.1 mg, 0.05 mmol), Pd₂dba₃ (1.8 mg, 0.002 mmol), (*R*)-**1a** (5.0 mg, 0.06 mmol), Rb₂CO₃ (34.7 mg, 0.15 mmol), anhydrous MTBE (1 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 48 hours in an argon atmosphere at 0 °C. ¹F NMR showed that no desired cross-over product was detected.





10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 f1 (ppm)

5.8 Gram-scale reaction.



In glovebox, **2a** (1.09 g, 6.0 mmol), **3a** (1.33 mg, 6.0 mmol), **4a** (365.8 mg, 3.0 mmol), Pd₂dba₃ (109.8 mg, 0.12 mmol), (*R*)-**1a** (299.1 mg, 0.36 mmol), Rb₂CO₃ (2.08 g, 9.0 mmol), anhydrous MTBE (60 mL) were added into an oven-dried tube (10 mL) charged with a stir bar, sealed the flask with its septum and then removed from the glovebox. The system was stirred for 60 hours in an argon atmosphere at 0 °C, and the crude product was purified by SepaBean preparative rapid liquid chromatograph machine to afford **5a** (582.8 mg, 53%) with 93.5:6.5 er.

6. Crystal Data

6.1 Crystal Data of 5p



CCDC: 2152365

Procedure for the recrystallization of **5p**: methanol (3 mL) was added to a 5 mL vial containing **5p** (5 mg) to form a clear solution. The solution was kept aside 2 days at room temperature to obtain crystals.

5.2 Crystal data and structure refinement for **5p**:

Identification code	5р
Empirical formula	$C_{28}H_{26}O_3S$
Formula weight	442.55
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	5.7414(3)
b/Å	33.3513(13)
c/Å	12.4948(7)
$\alpha/^{\circ}$	90
β/°	97.762(5)
γ/°	90
Volume/Å ³	2370.62(19)
Z	4
$\rho_{calc}g/cm^3$	1.240

μ/mm^{-1}	1.420	
F(000)	936.0	
Crystal size/mm ³	$0.05\times0.02\times0.02$	
Radiation	Cu Ka (λ = 1.54184)	
2Θ range for data collection/° 5.3 to 117.866		
Index ranges	$-6 \le h \le 6, -33 \le k \le 37, -13 \le l \le 13$	
Reflections collected	86175	
Independent reflections	6647 [$R_{int} = 0.2181, R_{sigma} = 0.0640$]	
Data/restraints/parameters	6647/1/565	
Goodness-of-fit on F ²	1.063	
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0682, wR_2 = 0.1807$	
Final R indexes [all data]	$R_1 = 0.1013, \mathrm{wR_2} = 0.2079$	
Largest diff. peak/hole / e Å ⁻³ 0.42/-0.17		
Flack parameter	0.01(3)	

7. References

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8. SFC spectra



SFC (Trefoir CEL2, CO₂/MeOH = 92:8, 0.8 mL/min, 212.1 nm): t_R (major) = 18.915 min, t_R (minor) = 25.697 min, 96:4 er.



SFC (Trefoir CEL2, $CO_2/MeOH = 90:10$, 1 mL/min, 225.0 nm): t_R (major) = 10.899 min, t_R (minor) = 13.915 min, 96:4 er.



SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (major) = 8.950 min, t_R (minor) = 13.054 min, 95:5 er.



SFC (Trefoir CEL2, $CO_2/MeOH = 92:8$, 0.7 mL/min, 228.0 nm): t_R (major) = 32.333 min, t_R (minor) = 45.222 min, 94:6 er.



SFC (Trefoir CEL2, $CO_2/MeOH = 80:20$, 1 mL/min, 230.0 nm): t_R (minor) = 11.163 min, t_R (major) = 19.276 min, 93.5:6.5 er.



SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 5.508 min, t_R (minor) = 7.480 min, 93.5:6.5 er.



SFC (Trefoir CEL2, CO₂/MeOH = 85:15, 1 mL/min, 220.0 nm): t_R (minor) = 14.800 min, t_R (major) = 18.475 min, 96.5:3.5 er.



SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 5.176 min, t_R (minor) = 6.594 min, 95:5 er.



SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 229.0 nm): t_R (major) = 4.069 min, t_R (minor) = 5.516 min, 95.5:4.5 er.



SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (major) = 11.061 min, t_R (minor) = 21.236 min, 96:4 er.



SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 232.0 nm): t_R (major) = 8.386 min, t_R (minor) = 14.587 min, 95:5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 220.0 nm): t_R (major) = 9.977 min, t_R (minor) = 13.725 min, 95.5:4.5 er.




SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 13.282 min, t_R (minor) = 14.826 min, 86.5:13.5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 70:30, 1 mL/min, 215.0 nm): t_R (major) = 8.245 min, t_R (minor) = 10.146 min, 88.5:11.5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 10.736 min, t_R (minor) = 12.774 min, 91.5:8.5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (major) = 9.028 min, t_R (minor) = 13.727 min, 96:4 er.





SFC (IC-3, CO₂/MeOH = 85:15, 1 mL/min, 272.0 nm): t_R (major) = 18.584 min, t_R (minor) = 23.934 min, 95.5:4.5 er.







SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 9.904 min, t_R (minor) = 10.875 min, 96.5:3.5 er.







SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (minor) = 10.330 min, t_R (major) = 11.136 min, 89:11 er.





SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 223.0 nm): t_R (major) = 31.934 min, t_R (minor) = 34.425 min, 95.5:4.5 er.







SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (minor) = 17.043 min, t_R (major) = 18.110 min, 95:5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 11.285 min, t_R (minor) = 15.954 min, 95:5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 19.168 min, t_R (minor) = 25.047 min, 94:6 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 220.0 nm): t_R (major) = 6.682 min, t_R (minor) = 9.315 min, 93:7 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.857 min, t_R (minor) = 17.521 min, 92:8 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 3.506 min, t_R (minor) = 5.310 min, 95:5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.035 min, t_R (minor) = 16.532 min, 93.5:6.5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 8.963 min, t_R (minor) = 14.771 min, 94:6 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 27.867 min, t_R (minor) = 37.462 min, 93:7 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 12.251 min, t_R (minor) = 16.168 min, 80:20 er.





SFC (IC-3, CO₂/MeOH = 90:10, 1 mL/min, 225.0 nm): t_R (minor) = 14.812 min, t_R (major) = 18.985 min, 69:31 er.





SFC (Trefoir CEL2, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 4.986 min, t_R (minor) = 6.883 min, 95.5:4.5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 11.283 min, t_R (minor) = 17.102 min, 93:7 er.





SFC (Trefoir CEL2, CO₂/MeOH = 95:5, 1 mL/min, 230.0 nm): t_R (major) = 9.190 min, t_R (minor) = 14.619 min, 96.5:3.5 er.





SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 240.0 nm): t_R (minor) = 6.186 min, t_R (major) = 6.616 min, 95:5 er.





SFC (Trefoir CEL2, CO₂/MeOH = 85:15, 1 mL/min, 235.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 94:6 er.





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SFC (AD-3, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 13.410 min, t_R (minor) = 14.689 min, 93:7 er.







SFC (IG-3, CO₂/MeOH = 85:15, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 95:5 er.



SFC (IG-3, CO₂/MeOH = 85:15, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 96:4 er.



SFC (Trefoir CEL2, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 9.316 min, t_R (major) = 10.629 min, 96:4 er.





SFC (Trefoir CEL1, CO₂/MeOH = 90:10, 1 mL/min, 232.0 nm): t_R (major) = 4.340 min, t_R (minor) = 4.787 min, 93.5:6.5 er.





SFC (Trefoir CEL1, CO₂/MeOH = 97:3, 1 mL/min, 232.0 nm): t_R (minor) = 17.231 min, t_R (major) = 19.696 min, 96:4 er.





SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 240.0 nm): t_R (major) = 6.206 min, t_R (minor) = 6.764 min, 90:10 er.





SFC (IG-3, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 10.743 min, t_R (major) = 12.949 min, 69.5:30.5 er.




SFC (Trefoir CEL1, CO₂/MeOH = 80:20, 1 mL/min, 230.0 nm): t_R (minor) = 4.556 min, t_R (major) = 5.478 min, 82.5:17.5 er.





SFC (OD-3, CO₂/MeOH = 95:5, 1 mL/min, 235.0 nm): t_R (minor) = 7.634 min, t_R (major) = 8.266 min, 72:28 er.





SFC (IG-3, CO₂/MeOH = 90:10, 1 mL/min, 230.0 nm): t_R (major) = 9.560 min, t_R (minor) = 10.340 min, 63.5:36.5 er.



9. NMR Spectra













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S156





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S159







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