Supporting Information
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A Chiral Naphthyridine Diimine Ligand Platform Enables Nickel-Catalyzed Asymmetric Alkylidenecyclopropanations

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Abstract: A novel class of chiral naphthyridine diimine ligands (NDI*) readily accessible from C_2 -symmetric 2,6-di-(1-arylethyl)anilines is described. Their utility, in particular a member with fluorinated aryl side arms, is demonstrated by a reductive Ni-catalyzed enantioselective alkylidene transfer reaction from 1,1-dichloroalkenes to olefins. This transformation provides direct access to a broad range of synthetically valuable alkylidenecyclopropanes in high yields and enantioselectivities.

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General methods

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. THF, CH₂Cl₂, MeOH and toluene were purified by an Innovative Technology Solvent Delivery System. Dry Et₂O and CPME were degassed by freeze-pump-thaw (3×) before being stored in the glovebox under 4Å molecular sieves. All other solvents were used as purchased. Chemicals were used as obtained from the suppliers. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 µm grade) or neutral alumina (Aluminium oxide neutral, Brockmann I). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. Proton nuclear magnetic resonance (¹H NMR) data were acquired on a Bruker AV400 (400 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated CDCl₃ (s, 7.26 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; td, triplet of doublets; ddd, doublet of doublet of doublet; m, multiplet; br, broad. Proton decoupled Carbon-13 nuclear magnetic resonance (¹³C NMR) data were acquired at on a Bruker AV400 (101 MHz). Chemical shifts are reported in ppm relative to CDCl₃ (77.16 ppm). Proton decoupled Fluorine-19 nuclear magnetic resonance (¹⁹F NMR) were acquired at 376 MHz on a Bruker AV400 spectrometer. Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm⁻¹). HRMS measurements were performed by an Agilent LC-MS TOF or Orbitrap. High resolution mass are given in *m/z*. Enantiomeric excesses were measured on an Agilent Normal or Reverse Phase HPLC, or on a Thar SFC Investigator system using chiral stationary phase columns. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. Melting points were measured on a Büchi melting point apparatus, model B-540, and are uncorrected. X-ray analysis was performed by Dr. R. Scopelliti and Dr. F. Fadaei Tirani at the EPF Lausanne.

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Experimental Procedures**1. Synthesis and characterization of 1,1'-(1,8-Naphthyridine-2,7-diyl)diethanone **2****

1,1'-(1,8-Naphthyridine-2,7-diyl)diethanone **2** was prepared according to the following synthetic procedure. (**Scheme 1**)

Scheme 1: Synthetic procedure to access 1,1'-(1,8-Naphthyridine-2,7-diyl)diethanone **2**.

2-Ethyl-1,8-naphthyridine **3**

Prepared according to a reported procedure, spectroscopic data matched those previously reported in the literature.¹

Yield: 60%

¹H NMR (400 MHz, Chloroform-*d*): δ 9.08 (dd, $J = 4.3, 2.0$ Hz, 1H), 8.19 – 8.06 (m, 2H), 7.48 – 7.37 (m, 2H), 3.09 (q, $J = 7.6$ Hz, 2H), 1.45 (t, $J = 7.6$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 167.98, 156.15, 153.38, 137.09, 136.81, 122.27, 121.50, 121.14, 32.51, 13.49.

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2,7-Diethyl-1,8-naphthyridine 11

Adapted from a literature procedure.² To a flame dried 250 mL two-neck round bottom flask equipped with a dropping funnel and under N₂ atmosphere, were added 2-ethyl-1,8-naphthyridine **3** (3.00 g, 19.0 mmol, 1.00 equiv.) and dry THF (76.0 mL, 0.25 M). The yellow solution was cooled to -78 °C, whereby ethyllithium (33.2 mmol, 1.75 equiv., 0.50 M solution in benzene/cyclohexane) was added dropwise at this temperature. The corresponding brown solution was allowed to warm to room temperature and stirred until TLC showed disappearance of starting material (approximately 16 hours). The reaction mixture was cooled to 0 °C and quenched with H₂O (20.0 mL), Et₂O was added, layers were separated, the aqueous layer was extracted with Et₂O (2×). The combined organics were dried over MgSO₄, filtered, and concentrated under reduced pressure to afford the intermediate 2,7-diethyl-1,2-dihydro-1,8-naphthyridine as an orange oil. A saturated solution of KMnO₄ in acetone (400 mL) was added to the intermediate and the mixture was left stirring for 16 hours, whereby it was filtered over a plug of silica and concentrated under reduced pressure to afford 2,7-diethyl-1,8-naphthyridine **11**. The product was used in the next step without further purification.

Yield: 91%

Appearance: off-white solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.07 (q, *J* = 7.6 Hz, 4H), 1.43 (t, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 167.66, 155.87, 136.78, 121.25, 119.23, 32.53, 13.78.

IR (ATR): ν(cm⁻¹) 3006, 2975, 2934, 2873, 1601, 1539, 1506, 1452, 1436, 1414, 1304, 1141, 1054, 859, 822.

HRMS (ESI/QTOF): calcd for C₁₂H₁₅N₂⁺ [M+H]⁺: 187.1230; found: 187.1235.

Melting point: 101.8 – 103.2 °C

1,1'-(1,8-Naphthyridine-2,7-diyl)diethanone 2

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Adapted from a literature procedure.³ To a flame dried Ace pressure tube were added 2,7-diethyl-1,8-naphthyridine **9** (1.50 g, 8.05 mmol, 1.00 equiv.) and tert-butyl hydroperoxide (193 mmol, 24.0 equiv., 5.50 M solution in decane). The tube was sealed and the corresponding yellow solution was heated at 130 °C until TLC showed disappearance of starting material (approximately 24 hours). The reaction mixture was allowed to cool to room temperature; H₂O (50 mL) and EtOAc (50 mL) were added, layers were separated, the aqueous layer was extracted with EtOAc (2×). The combined organics were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification via flash column chromatography (SiO₂, 20% EtOAc in pentane) afforded the title compound **2**. Spectroscopic data matched those previously reported in the literature.⁴

Yield: 65%

¹H NMR (400 MHz, Chloroform-*d*): δ 8.41 (d, *J* = 8.5 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 2H), 2.98 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 200.16, 156.92, 154.50, 138.48, 126.45, 120.82, 26.11.

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2. Synthesis and characterization of chiral anilines 1a–i

Anilines **12a–i** were synthesized *via* either **Route A** or **Route B** according to a previously reported procedure,⁵ which is summarized in **Scheme 2A**. Subsequent asymmetric hydrogenation (**GP1**) afforded chiral anilines **1a–i**. (**Scheme 2B**)

Scheme 2: Synthetic procedure to access chiral anilines **1a–i**.

General procedure for asymmetric hydrogenation (**GP1**)

In a flame dried microwave tube and under a N₂ atmosphere, [Rh(nbd)₂]BF₄ (2.00 mol%) and 1-((1*bS*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)piperidine PipPhos (4.40 mol%) were dissolved in

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DCM (0.50 ml) and stirred for 20 min. Subsequently a solution of alkenyl aniline **12** (1.00 equiv.) in a minimal amount of DCM was added. MeOH (ratio MeOH/DCM: >7/1, 0.20M) was added. The microwave tube was transferred into an autoclave and the reactor was purged three times with H₂. The reactor was then pressurized to 45 bar with H₂ and the mixture was stirred at ambient temperature for 48h. The reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography to yield chiral anilines **1a-i**.

2-(1-(3,5-Difluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 13i

Yield: 80%

Appearance: colourless oil

¹H NMR (400 MHz, Chloroform-*d*): δ 7.09 – 6.98 (m, 2H), 6.68 (tt, J = 8.9, 2.3 Hz, 1H), 6.17 – 6.08 (m, 2H), 1.33 (s, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 162.99 (dd, J = 248, 14.1 Hz), 144.72 (t, J = 9.09 Hz), 132.97, 110.165 (dd, J = 18.6, 7.07 Hz), 102.36 (t, J = 25.7 Hz), 84.25, 24.93.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -111.00.

IR (ATR): ν (cm⁻¹) 2980, 2932, 1621, 1598, 1412, 1377, 1319, 1294, 1143, 1117, 987, 952, 863, 838.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₄H₁₇BF₂O₂⁺ [M]⁺: 266.1284; found 266.1281.

2,6-Bis(1-phenylvinyl)aniline 12b

Yield: 99% (*Route B*)

Appearance: yellow oil

¹H NMR (400 MHz, Chloroform-*d*): δ 7.40 (m, 4H), 7.35 – 7.27 (m, 6H), 7.15 (dd, J = 7.6, 2.0 Hz, 2H), 6.83 (td, J = 7.6, 1.8 Hz, 1H), 5.83 (d, J = 1.6 Hz, 2H), 5.41 (d, J = 1.6 Hz, 2H), 3.54 (bs, 2H).

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^{13}C NMR (101 MHz, Chloroform-*d*): δ 147.31, 141.70, 139.66, 130.48, 128.67, 128.22, 127.62, 126.66, 117.70, 116.42.

IR (ATR): $\nu(\text{cm}^{-1})$ 3478, 3385, 3080, 3054, 3025, 1608, 1492, 1443, 905, 807, 778, 709, 695, 590.

HRMS (ESI/QTOF): calcd for $\text{C}_{22}\text{H}_{20}\text{N}^+$ $[\text{M}+\text{H}]^+$: 298.1590; found 298.1591.

2,6-Bis(1-phenylvinyl)-4-(trifluoromethyl)aniline 12e

Yield: 79% (*Route B*)

Appearance: colourless oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.31 (s, 2H), 7.30 – 7.19 (m, 10H), 5.78 (d, $J = 1.2$ Hz, 2H), 5.34 (d, $J = 1.2$ Hz, 2H), 3.74 (bs, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.24, 144.75, 138.74, 128.86, 128.59, 127.37 (q, $J = 4.04$ Hz, 2C), 126.97, 126.56, 124.99 (q, $J = 270.8$ Hz), 119.41 (q, $J = 32.6$ Hz), 117.40.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -60.88.

IR (ATR): $\nu(\text{cm}^{-1})$ 3490, 3394, 3059, 3027, 2957, 1619, 1356, 1316, 1295, 1277, 1152, 1111, 900, 696.

HRMS (ESI/QTOF): calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{N}^+$ $[\text{M}+\text{H}]^+$: 366.1464; found 366.1467.

2,6-Bis(1-(4-(tert-butyl)phenyl)vinyl)-4-methylaniline 12f

Yield: 75% (*Route B*)

Appearance: yellow oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.38 – 7.30 (m, 8H), 6.95 (d, $J = 2.3$ Hz, 2H), 5.81 (t, $J = 1.6$ Hz, 2H), 5.34 (t, $J = 1.6$ Hz, 2H), 3.45 (bs, 2H), 2.29 (d, $J = 1.9$ Hz, 3H), 1.36 – 1.29 (m, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 151.18, 147.09, 139.26, 136.72, 130.77, 127.96, 126.73, 126.33, 125.55, 115.36, 34.69, 31.43, 20.54.

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IR (ATR): $\nu(\text{cm}^{-1})$ 3477, 3384, 3085, 3030, 2961, 2904, 2867, 1614, 1510, 1458, 1363, 1269, 899, 842.

HRMS (ESI/QTOF): calcd for $\text{C}_{31}\text{H}_{38}\text{N}^+$ $[\text{M}+\text{H}]^+$: 424.2999; found 424.3005.

4-Methyl-2,6-bis(1-(naphthalen-2-yl)vinyl)aniline 12g

Yield: 51% (*Route B*)

Appearance: yellow solid

^1H NMR (400 MHz, Chloroform-*d*): δ 7.82 – 7.73 (m, 8H), 7.61 (dd, J = 8.6, 1.8 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.06 (s, 2H), 5.93 (d, J = 1.4 Hz, 2H), 5.49 (d, J = 1.4 Hz, 2H), 3.42 (bs, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 147.45, 139.40, 137.07, 133.56, 133.26, 131.19, 128.47, 128.32, 127.90, 127.69, 127.02, 126.32, 126.25, 125.99, 124.55, 116.82, 20.61.

IR (ATR): $\nu(\text{cm}^{-1})$ 3473, 3382, 3054, 3017, 2916, 2860, 1614, 1595, 1504, 1458, 1270, 1242, 897, 859, 820, 751, 475.

HRMS (ESI/QTOF): calcd for $\text{C}_{31}\text{H}_{26}\text{N}^+$ $[\text{M}+\text{H}]^+$: 412.2060; found 412.2060.

Melting point: 131-134 °C

2,6-Bis(1-(3,5-difluorophenyl)vinyl)-4-methylaniline 12i

Yield: 89% (*Route B*)

Appearance: off-white solid

^1H NMR (400 MHz, Chloroform-*d*): δ 6.94 – 6.83 (m, 6H), 6.73 (tt, J = 8.7, 2.3 Hz, 2H), 5.85 (d, J = 1.0 Hz, 2H), 5.46 (s, 2H), 3.37 (bs, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.31 (dd, J = 248.1, 12.9 Hz), 145.46 (t, J = 2.6 Hz), 143.23 (t, J = 9.0 Hz), 138.91, 131.32, 127.37, 126.70, 118.36, 109.55 (dd, J = 19.2, 7.07 Hz), 103.52 (t, J = 25.7 Hz), 20.46.

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^{19}F NMR (376 MHz, Chloroform-*d*): δ -109.81.

IR (ATR): $\nu(\text{cm}^{-1})$ 3479, 3390, 3091, 2920, 2863, 1619, 1585, 1460, 1432, 1351, 1328, 1289, 1118, 988, 916, 861.

HRMS (ESI/QTOF): calcd for $\text{C}_{23}\text{H}_{18}\text{F}_4\text{N}^+$ $[\text{M}+\text{H}]^+$: 384.1370; found 384.1375.

Melting point: 62.5-64.9 °C

4-Methyl-2,6-bis((*R*)-1-phenylethyl)aniline 1a

Prepared according to **GPI**. Spectroscopic data matched those previously reported in the literature.⁶

^1H NMR (400 MHz, Chloroform-*d*): δ 7.28 – 7.21 (m, 4H), 7.19 – 7.12 (m, 6H), 7.06 (s, 2H), 3.99 (q, J = 7.1 Hz, 2H), 3.22 (bs, 2H), 2.37 (s, 3H), 1.59 (d, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.07, 139.74, 130.04, 128.80, 127.50, 126.83, 126.37, 126.19, 40.53, 22.49, 21.33.

e.r.: 96.4:0:3.6 (*R,R*):(*S,S*):(*meso*) (SFC, Chiracel OD-H, 5% MeOH/ CO_2 , λ = 220 nm, 4 mL/min, 150 bar outlet, t_{R} (*R,R*) = 6.12 min; t_{R} (*meso*) = 4.94 min).

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Peak No	% Area	Area	Ret. Time	Height	Cap. Factor
1	3.6364	63.2049	4.94 min	7.4479	0
2	96.3636	1674.9143	6.12 min	105.4412	0

2,6-Bis((*R*)-1-phenylethyl)aniline 1b

Prepared according to **GP1**.

Yield: 97%

Appearance: off-white solid

¹H NMR (400 MHz, Chloroform-*d*): δ 7.26 (ddd, J = 9.7, 5.9, 1.6 Hz, 6H), 7.21 – 7.12 (m, 4H), 6.94 (td, J = 7.7, 1.5 Hz, 1H), 4.00 (q, J = 7.1 Hz, 2H), 3.37 (bs, 2H), 1.61 (dd, J = 7.2, 1.6 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 145.96, 142.29, 129.77, 128.82, 127.48, 126.43, 125.53, 117.90, 40.56, 22.54.

IR (ATR): $\nu(\text{cm}^{-1})$ 3477, 3385, 3059, 3023, 2965, 2931, 2872, 1620, 1443, 749, 699.

HRMS (ESI/QTOF): calcd for $\text{C}_{22}\text{H}_{23}\text{N}^+$ $[\text{M}+\text{H}]^+$: 302.1904; found 302.1909.

α_D : +57.0 (c = 1.0, CHCl_3)

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Melting point: 70.0-73.4 °C

e.r.: >99:1 (Chiralpak IG, Hexane/IPA =99.5/0.5, λ = 230 nm, 1.00 mL/min, t_R (*R,R*) = 6.21 min).

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.256	VB	0.1587	2072.99976	200.42133	14.3377
2	7.007	BB	0.1843	1967.58374	161.28534	13.6086
3	7.772	BB	0.2860	1.04178e4	578.66675	72.0537

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.206	BB	0.1431	2812.58301	300.63535	100.0000

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4-Methoxy-2,6-bis((*R*)-1-phenylethyl)aniline 1c

Prepared according to **GPI**. Spectroscopic data matched those previously reported in the literature.⁷

¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 – 7.23 (m, 4H), 7.20 – 7.13 (m, 6H), 6.88 (s, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.09 (bs, 2H), 1.60 (d, J = 7.2 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 152.44, 145.73, 136.02, 131.61, 128.83, 127.49, 126.45, 111.46, 55.87, 40.68, 22.46.

e.r.: >99:1 (Chiralpak IB, Hexane/IPA = 99.5/0.5, λ = 306 nm, 1.00 mL/min, t_R (*R,R*) = 9.60 min).

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.895	MM	0.1963	209.98013	17.82952	13.3184
2	8.894	MM	0.2015	1165.30676	96.36832	73.9118
3	9.537	MM	0.2370	201.33141	14.15838	12.7698

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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.601	VV	0.2497	3348.90967	184.56743	100.0000

4-(Tert-butyl)-2,6-bis((R)-1-phenylethyl)aniline 1d

Prepared according to **GPI**. Spectroscopic data matched those previously reported in the literature.⁵

¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 (s, 2H), 7.24 (s, 2H), 7.22 (s, 2H), 7.19-7.12 (m, 6H), 4.03 (q, *J*=7.2 Hz, 2H), 2.17 (bs, 2H), 1.61 (d, *J*=7.1 Hz, 6H), 1.37 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 145.56, 128.77, 127.65, 126.45, 122.84, 40.55, 34.60, 31.75, 22.56 ppm

e.r.: 97.1:1.6:1.3 (*R,R*):(*S,S*):(*meso*) (Chiralpak IA, Hexane/IPA =99.5/0.5, λ = 210 nm, 1.00 mL/min, *t_R* (*R,R*) = 4.63 min; *t_R* (*S,S*) = 5.22 min; *t_R* (*meso*) = 5.42 min).

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.646	BV	0.1128	6057.39648	833.77002	18.3074
2	4.970	VV	0.1264	5976.95654	708.43970	18.0642
3	5.423	VB	0.2408	2.10529e4	1223.28699	63.6284

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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.629	MM	0.2153	1.67201e4	1294.33557	97.1352
2	5.221	MM	0.0929	269.31622	48.30283	1.5646
3	5.424	MM	0.1087	223.81537	34.30286	1.3003

2,6-Bis((R)-1-phenylethyl)-4-(trifluoromethyl)aniline 1e

Prepared according to **GP1**.

Yield: 66%

Appearance: yellow oil

¹H NMR (400 MHz, Chloroform-*d*): δ 7.52 (s, 2H), 7.27 (d, J = 6.9 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.14 – 7.08 (m, 4H), 3.93 (q, J = 7.1 Hz, 2H), 3.65 (bs, 2H), 1.62 (d, J = 7.2 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 145.41, 144.92, 129.08, 129.05, 127.33, 126.82, 125.55 (q, J = 271.7 Hz), 122.64 (q, J = 3.9 Hz, 2C), 119.34 (q, J = 31.9 Hz), 40.65, 22.56.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -60.53.

IR (ATR): ν (cm⁻¹) 3492, 3402, 3026, 2969, 2933, 2875, 1626, 1450, 1325, 1102, 894, 700.

HRMS (ESI/QTOF): calcd for C₂₃H₂₃F₃N⁺ [M+H]⁺: 370.1778; found 370.1783.

α_D : +24.0 (c = 0.8, CHCl₃)

e.r.: >99:1 (Chiralpak IB, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_R (*R,R*) = 8.69 min).

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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.802	BB	0.2268	2516.27002	178.17424	61.9203
2	8.188	BV	0.1455	789.39929	82.57776	19.4255
3	8.671	VB	0.1612	758.05652	70.62254	18.6542

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.693	BB	0.1789	1.86537e4	1423.56836	100.0000

2,6-Bis((*R*)-1-(4-(*tert*-butyl)phenyl)ethyl)-4-methylaniline 1f

Prepared according to **GP1**.

Yield: 52%

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Appearance: white solid

^1H NMR (400 MHz, Chloroform-*d*): δ 7.27 (d, J = 8.7 Hz, 4H), 7.12 – 7.04 (m, 6H), 4.00 (q, J = 7.2 Hz, 2H), 3.28 (bs, 2H), 2.38 (s, 3H), 1.60 (d, J = 7.1 Hz, 6H), 1.29 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 148.95, 142.78, 139.72, 130.37, 127.08, 126.87, 126.06, 125.62, 39.90, 34.47, 31.52, 22.47, 21.35.

IR (ATR): $\nu(\text{cm}^{-1})$ 3473, 3378, 3023, 2962, 2905, 2868, 1507, 1268, 864.

HRMS (ESI/QTOF): calcd for $\text{C}_{31}\text{H}_{42}\text{N}^+$ $[\text{M}+\text{H}]^+$: 428.3312; found 428.3319.

α_D : +4.50 (c = 1.0, CHCl_3)

Melting point: 60.4-63.0 $^\circ\text{C}$

e.r.: 97.3:2.3:0 (*R,R*):(*S,S*):(*meso*) (Chiralpak IA, Hexane/IPA =99.5/0.5, λ = 230 nm, 1.00 mL/min, t_R (*R,R*) = 5.14 min, t_R (*S,S*) = 4.74 min).

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.552	MF	0.1399	1697.44360	202.23538	18.5701
2	4.810	FM	0.1506	1680.06128	185.89156	18.3799
3	7.840	BB	0.2862	5763.22852	302.65479	63.0500

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.743	MM	0.1414	210.93825	24.86070	2.7466
2	5.143	MM	0.2034	7469.11621	612.03857	97.2534

4-Methyl-2,6-bis((R)-1-(naphthalen-2-yl)ethyl)aniline 1g

Prepared according to **GP1**.

Yield: 98%

Appearance: white solid

¹H NMR (400 MHz, Chloroform-*d*): δ 7.80 – 7.71 (m, 6H), 7.62 (d, J = 1.6 Hz, 2H), 7.47 – 7.38 (m, 4H), 7.28 (dd, J = 8.5, 1.8 Hz, 2H), 7.14 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.32 (bs, 2H), 2.42 (s, 3H), 1.68 (d, J = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 143.48, 140.02, 133.72, 132.37, 130.01, 128.58, 127.77, 127.74, 126.99, 126.52, 126.38, 126.09, 125.52, 125.45, 40.77, 22.22, 21.37.

IR (ATR): $\nu(\text{cm}^{-1})$ 3473, 3380, 3053, 2966, 2930, 2871, 1467, 1454, 908, 819, 746, 732, 478.

HRMS (ESI/QTOF): calcd for $\text{C}_{31}\text{H}_{30}\text{N}^+$ $[\text{M}+\text{H}]^+$: 416.2373; found 436.2371.

α_D : +106 (c = 1.0, CHCl_3)

Melting point: 72.4-75.3 °C

e.r.: >99:1 (Chiralpak IF, Hexane/IPA =99.5/0.5, λ = 230 nm, 1.00 mL/min, t_R (*R,R*) = 9.34 min).

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.711	MM	0.2505	6024.52783	400.79016	13.6890
2	10.759	MM	0.3525	6222.59229	294.17078	14.1391
3	13.226	BB	0.3219	3.17628e4	1235.54028	72.1719

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.338	BB	0.2145	8227.92188	569.72235	100.0000

2,6-Bis((R)-1-(3,5-dimethylphenyl)ethyl)-4-methylaniline 1h

Prepared according to a reported procedure, spectroscopic data matched those previously reported in the literature.⁵

¹H NMR (600 MHz, Chloroform-*d*): δ 7.06 (s, 2H), 6.80 (s, 2H), 6.76 (s, 4H), 3.95 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 2.23 (s, 12H), 1.57 (d, $J = 7.1$ Hz, 6H).

¹³C NMR (151 MHz, Chloroform-*d*): δ 145.3, 138.3, 128.4, 126.7, 125.4, 40.4, 22.5, 21.5, 21.4.

e.r.: >99:1 (Chiralpak IF, Hexane/IPA =99.5/0.5, $\lambda = 210$ nm, 1.00 mL/min, t_R (*R,R*) = 4.48 min).

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.485	MM	0.1088	120.83083	18.50426	11.1082
2	4.793	MM	0.1228	139.97237	19.00158	12.8680
3	6.429	MM	0.1452	826.95532	94.94645	76.0238

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.476	MM	0.0968	1187.32629	204.49533	100.0000

2,6-Bis((*R*)-1-(3,5-difluorophenyl)ethyl)-4-methylaniline 1i

Prepared according to **GP1**.

SUPPORTING INFORMATION

Yield: 87%

Appearance: colourless oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.01 (s, 2H), 6.65 (m, 6H), 3.99 (q, J = 7.1 Hz, 2H), 3.17 (bs, 2H), 2.36 (s, 3H), 1.59 (d, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.37 (dd, J = 248.7, 12.9 Hz), 150.25 (t, J = 8.2 Hz), 139.33, 128.98, 127.65, 126.60, 110.39 (dd, J = 18.2, 6.1 Hz), 102.02 (t, J = 25.4 Hz), 40.24 (t, J = 2.0 Hz), 22.05, 21.25.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -109.57, -109.56.

IR (ATR): $\nu(\text{cm}^{-1})$ 3471, 3391, 2971, 2936, 2876, 1620, 1593, 1449, 1311, 1115, 978, 855.

HRMS (ESI/QTOF): calcd for $\text{C}_{23}\text{H}_{22}\text{F}_4\text{N}^+$ $[\text{M}+\text{H}]^+$: 388.1683; found 388.1676.

α_D : +0.67 (c = 1.0, CHCl_3)

e.r.: >99:1 (Chiralpak IB, Hexane/IPA = 99.95/0.05, λ = 254 nm, 1.00 mL/min, t_R (*R,R*) = 14.5 min).

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.086	BB	0.2262	1140.91187	74.70776	63.0347
2	15.198	BB	0.2447	324.69806	16.14293	17.9394
3	16.090	BB	0.2856	344.36417	14.79488	19.0259

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.540	BB	0.4487	7141.08252	211.09944	100.0000

SUPPORTING INFORMATION

3. Synthesis and characterization of chiral ligands L1–9

General procedure for the synthesis of chiral ligands L1–9 (GP2)

Chiral ligands **L1–9** were synthesized *via* imine condensation (**Scheme 3**) according to the synthetic procedure reported below.

Scheme 3: Synthetic procedure to access chiral ligands **L1–9**.

To a solution of 1,1'-(1,8-naphthyridine-2,7-diyl)diethanone **2** (1.00 equiv.) in toluene (0.20 M), were added aniline **1a–i** (2.10 equiv.) and *p*-toluenesulfonic acid monohydrate (5.00 mol%). The mixture was refluxed for 48 hours, then concentrated under reduced pressure to afford a mixture of ligand and mono-condensation adduct. The crude mixture was purified by silica gel column chromatography (phosphate buffered silica). Recrystallization from hot EtOH afforded products **L1–9** as yellow solids. Ligands **L1–9** were dried under high vacuum for 16h before being stored in the glovebox at -30 °C.

Note: The mono-condensation adducts can be isolated by column chromatography and resubmitted to the reaction conditions.

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methyl-2,6-bis((R)-1-phenylethyl)aniline) L1

Prepared according to **GP2**.

Yield: 74%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.56 (d, J = 8.4 Hz, 2H), 8.31 (d, J = 8.4 Hz, 2H), 7.21 – 6.94 (m, 24H), 4.02 (q, J = 7.2 Hz, 2H), 3.85 (q, J = 7.2 Hz, 2H), 2.41 (s, 6H), 1.78 (s, 6H), 1.54 (d, J = 7.2 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.89, 159.53, 155.07, 146.52, 146.32, 145.16, 136.96, 133.27, 132.66, 132.57, 128.44, 128.19, 127.90, 127.48, 125.92, 125.81, 125.76, 125.70, 124.24, 120.79, 40.89, 38.72, 22.70, 21.63, 21.19, 17.13.

IR (ATR): $\nu(\text{cm}^{-1})$ 3059, 3024, 2966, 2930, 2872, 1641, 1598, 1492, 1477, 1314, 1094, 906, 863, 728, 672.

HRMS (ESI/QTOF): calcd for $\text{C}_{58}\text{H}_{57}\text{N}_4^+$ $[\text{M}+\text{H}]^+$: 809.4578; found: 809.4583.

$[\alpha]_{\text{D}}^{20}$ = +28.3 (c = 1.0, CHCl_3).

Melting point: 204-207 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-phenylethyl)aniline) L2

Prepared according to **GP2**.

Yield: 74%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.56 (d, J = 8.5 Hz, 2H), 8.33 (d, J = 8.5 Hz, 2H), 7.36 (ddd, J = 7.8, 6.2, 1.3 Hz, 4H), 7.23 – 6.97 (m, 22H), 4.04 (q, J = 7.2 Hz, 2H), 3.88 (q, J = 7.2 Hz, 2H), 1.79 (s, 6H), 1.56 (d, J = 7.2 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.62, 159.41, 155.06, 147.60, 146.44, 146.19, 137.02, 133.37, 132.83, 128.47, 128.20, 127.89, 127.49, 125.98, 125.81, 125.20, 125.00, 124.28, 123.52, 120.81, 40.98, 38.93, 22.69, 21.31, 17.19.

IR (ATR): $\nu(\text{cm}^{-1})$ 3060, 3024, 2966, 2930, 2872, 1640, 1599, 1492, 1365, 1094, 907, 729, 698.

HRMS (ESI/QTOF): calcd for $\text{C}_{56}\text{H}_{53}\text{N}_4^+$ $[\text{M}+\text{H}]^+$: 781.4265; found: 781.4270.

$[\alpha]_{\text{D}}^{20}$ = +120 (c = 1.0, CHCl_3).

Melting point: 114-117 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methoxy-2,6-bis((R)-1-phenylethyl)aniline) L3

Prepared according to **GP2**.

Yield: 65%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.58 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 2H), 7.21 – 6.97 (m, 20H), 6.96 – 6.89 (m, 4H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.87 (m, 8H), 1.80 (s, 6H), 1.55 (d, *J* = 7.3 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 169.56, 159.56, 156.12, 155.05, 146.15, 145.94, 141.27, 136.96, 134.81, 134.07, 128.46, 128.22, 127.84, 127.44, 126.02, 125.87, 124.25, 120.75, 110.91, 110.54, 55.57, 41.04, 38.95, 22.58, 21.14, 17.08.

IR (ATR): $\nu(\text{cm}^{-1})$ 3026, 2968, 2934, 2873, 2248, 1639, 1599, 1437, 1235, 1147, 1039, 905, 726, 698.

HRMS (ESI/QTOF): calcd for C₅₈H₅₇N₄O₂⁺ [M+H]⁺: 842.4510; found: 842.4514.

$[\alpha]_{\text{D}}^{20}$ = -86.3 (*c* = 1.0, CHCl₃).

Melting point: 97.3-100 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-(tert-butyl)-2,6-bis((R)-1-phenylethyl)aniline) L4

Prepared according to **GP2**.

Yield: 61%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.55 (d, J = 8.5 Hz, 2H), 8.31 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 2.0 Hz, 2H), 7.37 (d, J = 2.0 Hz, 2H), 7.20 – 6.94 (m, 20H), 4.03 (q, J = 7.2 Hz, 2H), 3.85 (q, J = 7.2 Hz, 2H), 1.74 (s, 6H), 1.56 (dd, J = 7.2, 1.9 Hz, 12H), 1.40 (s, 18H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.70, 159.52, 155.09, 146.80, 146.40, 145.80, 145.12, 136.93, 132.43, 131.76, 128.41, 128.15, 127.86, 127.51, 125.86, 125.69, 124.21, 121.87, 121.83, 120.77, 41.18, 39.17, 34.78, 31.84, 29.86, 24.74, 22.88, 21.45, 17.20.

IR (ATR): $\nu(\text{cm}^{-1})$ 3025, 2963, 2932, 2905, 2871, 1645, 1599, 1492, 1449, 1364, 1095, 909, 760, 733, 699.

HRMS (ESI/QTOF): calcd for C₆₄H₆₉N₄⁺ [M+H]⁺: 893.5517; found: 893.5522.

$[\alpha]_{\text{D}}^{20}$ = -21.8 (c = 1.0, CHCl₃).

Melting point: 120-123 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-phenylethyl)-4-(trifluoromethyl)aniline) L5

Prepared according to **GP2**.

Yield: 56%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.48 (d, *J* = 8.4 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 5.9 Hz, 4H), 7.21 – 6.87 (m, 20H), 4.03 (q, *J* = 7.3 Hz, 2H), 3.87 (q, *J* = 7.3 Hz, 2H), 1.72 (d, *J* = 2.1 Hz, 6H), 1.58 (d, *J* = 7.3 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.95, 158.93, 154.97, 150.58, 145.47, 145.12, 137.22, 134.13, 133.47, 128.70, 128.37, 127.81, 127.41, 126.37, 126.18, 125.78 (q, *J* = 32.3 Hz), 124.47, 122.25 (q, *J* = 4.04 Hz), 122.02 (q, *J* = 3.03 Hz), 120.88, 41.10, 39.18, 22.66, 21.24, 17.42.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -61.39.

IR (ATR): $\nu(\text{cm}^{-1})$ 3026, 2968, 2933, 1647, 1599, 1349, 1292, 1180, 1158, 1117, 733, 699.

HRMS (ESI/QTOF): calcd for C₅₈H₅₁F₆N₄⁺ [M+H]⁺: 917.4013; found: 917.4018.

$[\alpha]_{\text{D}}^{20}$ = +220 (*c* = 1.0, CHCl₃).

Melting point: 121-125 °C

SUPPORTING INFORMATION

(E)-N-(1-(7-((E)-1-((2,6-bis((R)-1-(4-(Tert-butyl)phenyl)ethyl)-4-methylphenyl)imino)ethyl)-1,8-naphthyridin-2-yl)ethylidene)-2-((R)-1-(3-(tert-butyl)phenyl)ethyl)-6-((R)-1-(4-(tert-butyl)phenyl)ethyl)-4-methylaniline L6

Prepared according to **GP2**.

Yield: 69%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.50 (d, *J* = 8.5 Hz, 2H), 8.29 (d, *J* = 8.5 Hz, 2H), 7.21 – 7.17 (m, 4H), 7.14 – 7.07 (m, 8H), 7.03 (d, *J* = 8.2 Hz, 4H), 6.93 (d, *J* = 8.0 Hz, 4H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.85 (q, *J* = 7.2 Hz, 2H), 2.39 (s, 6H), 1.81 (s, 6H), 1.54 (d, *J* = 7.2 Hz, 12H), 1.27 (s, 18H), 1.22 (s, 18H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 169.06, 159.54, 154.98, 148.51, 148.29, 145.13, 143.27, 136.79, 133.66, 132.90, 132.51, 127.58, 127.01, 126.70, 125.86, 125.66, 125.28, 125.10, 124.14, 120.74, 40.17, 38.20, 34.41, 31.55, 31.47, 29.86, 22.53, 21.62, 21.15, 17.17.

IR (ATR): $\nu(\text{cm}^{-1})$ 2961, 2904, 2869, 1640, 1598, 1507, 1460, 1364, 1095, 1011, 833, 733.

HRMS (ESI/QTOF): calcd for $\text{C}_{74}\text{H}_{89}\text{N}_4^+$ $[\text{M}+\text{H}]^+$: 1033.7082; found: 1033.7087.

$[\alpha]_{\text{D}}^{20}$ = +106 (*c* = 1.0, CHCl_3).

Melting point: 130-133 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methyl-2,6-bis((R)-1-(naphthalen-2-yl)ethyl)aniline) L7

Prepared according to **GP2**.

Yield: 60%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.48 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 7.79 – 7.72 (m, 2H), 7.67 (t, J = 8.6 Hz, 4H), 7.61 – 7.52 (m, 4H), 7.52 – 7.47 (m, 2H), 7.46 (d, J = 2.1 Hz, 4H), 7.39 – 7.27 (m, 8H), 7.24 – 7.13 (m, 8H), 4.18 (q, J = 7.1 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.42 (s, 6H), 1.81 (s, 6H), 1.62 (dd, J = 11.5, 7.2 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.85, 159.54, 154.92, 145.33, 143.81, 143.76, 136.88, 133.58, 133.51, 133.29, 132.71, 132.50, 132.09, 131.99, 128.01, 127.78, 127.70, 127.67, 127.63, 127.57, 126.88, 126.10, 126.05, 125.96, 125.87, 125.71, 125.31, 125.24, 125.19, 124.20, 120.83, 40.92, 39.21, 22.27, 21.64, 21.08, 17.46.

IR (ATR): $\nu(\text{cm}^{-1})$ 3052, 3017, 2965, 2929, 2872, 1640, 1599, 1505, 1450, 1364, 1142, 1095, 907, 856, 816, 730, 477.

HRMS (ESI/QTOF): calcd for $\text{C}_{74}\text{H}_{65}\text{N}_4^+$ $[\text{M}+\text{H}]^+$: 1009.5204; found: 1009.5209.

$[\alpha]_{\text{D}}^{20}$ = +337 (c = 1.0, CHCl_3).

Melting point: 113-117 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-(3,5-dimethylphenyl)ethyl)-4-methylaniline) L8

Prepared according to **GP2**.

Yield: 51%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.56 (d, J = 8.5 Hz, 2H), 8.33 (d, J = 8.5 Hz, 2H), 7.17 (q, J = 1.8 Hz, 4H), 6.73 (s, 2H), 6.64 (d, J = 1.6 Hz, 6H), 6.57 (d, J = 1.6 Hz, 4H), 3.90 (q, J = 7.1 Hz, 2H), 3.76 (q, J = 7.2 Hz, 2H), 2.46 (s, 6H), 2.13 (s, 12H), 1.99 (s, 12H), 1.65 (s, 6H), 1.53 (dd, J = 9.3, 7.2 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 168.93, 159.66, 154.99, 146.46, 146.06, 145.46, 137.69, 137.35, 136.55, 133.32, 132.58, 132.28, 127.53, 127.50, 125.96, 125.65, 125.55, 125.42, 123.83, 120.82, 40.97, 39.21, 22.57, 21.71, 21.43, 21.23, 21.19, 17.05.

IR (ATR): $\nu(\text{cm}^{-1})$ 3013, 2963, 2920, 2870, 1643, 1599, 1449, 1365, 1127, 909, 847, 731.

HRMS (ESI/QTOF): calcd for $\text{C}_{66}\text{H}_{73}\text{N}_4^+$ $[\text{M}+\text{H}]^+$: 921.5830; found: 921.5831.

α_D : +77.3 (c = 1.0, CHCl_3)

Melting point: 245-248 °C

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-(3,5-difluorophenyl)ethyl)-4-methylaniline) L9

Prepared according to **GP2**.

Yield: 67%

Appearance: yellow solid

¹H NMR (400 MHz, Chloroform-*d*): δ 8.47 (d, J = 8.4 Hz, 2H), 8.34 (d, J = 8.5 Hz, 2H), 7.10 (s, 4H), 6.53 (tq, J = 8.6, 3.3, 2.3 Hz, 12H), 4.00 (q, J = 7.1 Hz, 2H), 3.80 (q, J = 7.2 Hz, 2H), 2.42 (s, 6H), 1.95 (s, 6H), 1.52 (dd, J = 7.2, 2.3 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 169.21, 163.39 (dd, J = 248.9, 10.1 Hz), 161.67 (dd, J = 248.5, 10.1 Hz), 159.01, 155.01, 150.67 (t, J = 8.1 Hz), 150.31 (t, J = 8.3 Hz), 145.08, 137.40, 133.29, 132.23, 131.57, 126.24, 126.11, 124.49, 120.43, 110.69 (dd, J = 18.2, 6.1 Hz), 110.33 (dd, J = 18.2, 7.1 Hz), 101.53 (t, J = 26.3 Hz), 101.32 (t, J = 25.3 Hz), 40.71, 38.75, 22.28, 21.57, 20.76, 17.47.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -110.12, -110.83.

IR (ATR): ν (cm⁻¹) 2970, 2934, 2875, 1621, 1595, 1446, 1313, 1115, 979, 854, 731.

HRMS (ESI/QTOF): calcd for C₅₈H₄₉F₈N₄⁺ [M+H]⁺: 953.3824; found: 953.3829.

$[\alpha]_D^{20}$ = +58.5 (c = 1.0, CHCl₃).

Melting point: 84.6-88.3 °C

SUPPORTING INFORMATION

4. Synthesis and characterization of novel 1,1-dichloroalkenes

(4-(2,2-Dichlorovinyl)phenoxy)triisopropylsilane 14

To a 50 mL dry round-bottom flask were added triphenylphosphine PPh_3 (24.4 mmol, 4.00 eq.) and DCM (12.2 mL, 0.50 M). The suspension was cooled to 0 °C, whereby 4-((triisopropylsilyl)oxy)benzaldehyde⁸ (6.10 mmol, 1.00 eq.) and CCl_4 (12.2 mmol, 2.00 eq.) were added sequentially. The reaction was allowed to warm to room temperature and stirred at this temperature until TLC (2% Et_2O in pentane) showed full conversion of starting material (approximately 8 hours). The mixture was then diluted with H_2O and Et_2O , layers were separated, the aqueous layer was washed with Et_2O (2×). The combined organics were dried over MgSO_4 , filtered, and concentrated under reduced pressure to afford the crude product. Purification via flash column chromatography (SiO_2 , 2% Et_2O in pentane) afforded the title compound **14**.

Yield: 81%

Appearance: colourless oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.48 – 7.39 (m, 2H), 6.91 – 6.82 (m, 2H), 6.77 (s, 1H), 1.35 – 1.19 (m, 3H), 1.10 (d, $J = 7.3$ Hz, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 156.47, 130.16, 128.30, 126.38, 120.02, 118.76, 18.04, 12.82.

IR (ATR): $\nu(\text{cm}^{-1})$ 2944, 2867, 1602, 1507, 1463, 1265, 1174, 907, 678.

SUPPORTING INFORMATION

5. General procedure for racemic alkylidene transfer

Racemic alkylidenecyclopropanes were synthesized according to the procedure summarized in **Scheme 4** and described below.

Scheme 4: Synthetic procedure to access racemic alkylidenecyclopropanes.

According to a modified literature procedure.⁹ In a N_2 -filled glovebox, a 1/2 Dram glass vial equipped with a magnetic stir bar (3 x 10 mm) was charged with **L0**¹⁰ (10.0 mol%, 10.0 μmol), $\text{NiCl}_2(\text{DME})$ (20.0 mol%, 20.0 μmol), Zn powder (1.20 equiv., 0.12 mmol), 1,3-dimethyl-2-imidazolidinone DMI (98.0 μL , 0.90 mmol) and CPME (160 μL). The reaction mixture was stirred (1400 rpm) at room temperature for 10 minutes. A mixture of 1,1-dichloroalkene **4** (1.00 equiv., 0.10 mmol), alkene **5** (1.00 equiv., 0.10 mmol) and CPME (340 μL) was added to the preformed catalyst. The vial was sealed and the reaction mixture was stirred (1400 rpm) at room temperature inside the glovebox for 24 hours. After this time, the reaction mixture was filtered over a short plug of SiO_2 (eluting with DCM) and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (*n*-pentane:DCM) affording the products **6** as an inseparable mixture of *Z/E* diastereomers.

Note1: Liquid reagents/reactants were degassed by freeze-pump-thaw (3 $\times$) before being stored in the glovebox at -30 °C. Solid reagents/reactants were dried under high vacuum for 16h before being stored in the glovebox at -30 °C.

Note2: The synthesized methylenecyclopropanes are prone to decomposition when kept under air at room temperature; therefore, after purification they were stored under a N_2 atmosphere in a -80 °C freezer.

SUPPORTING INFORMATION

6. Optimization of the enantioselective alkylidene transfer^a

L*	Ar	R	yield
L1	Ph	Me	74 %
L2	Ph	H	74 %
L3	Ph	OMe	65 %
L4	Ph	<i>t</i> -Bu	61 %
L5	Ph	CF ₃	56 %
L6	4- <i>t</i> -Bu-C ₆ H ₄	Me	69 %
L7	2-Np	Me	60 %
L8	3,5-Me-C ₆ H ₃	Me	51 %
L9	3,5-F-C ₆ H ₃	Me	67 %

Entry	L*	Solvent (M)	Additive	T (°C)	% Yield	ZE	er (Z)
1 ^[b]	L1	Et ₂ O (0.13 M)	DMA	25	61	2:1	84:16
2	L2	Et ₂ O (0.13 M)	DMA	25	62	2.5:1	85:15
3	L3	Et ₂ O (0.13 M)	DMA	25	50	2.5:1	85:15
4	L4	Et ₂ O (0.13 M)	DMA	25	47	2.9:1	80:20
5	L5	Et ₂ O (0.13 M)	DMA	25	26	2.4:1	81:19
6	L6	Et ₂ O (0.13 M)	DMA	25	44	1.4:1	76:24
7	L7	Et ₂ O (0.13 M)	DMA	25	31	1.4:1	66:34
8	L8	Et ₂ O (0.13 M)	DMA	25	18	1.8:1	74:26
9	L9	Et ₂ O (0.13 M)	DMA	25	23	3.9:1	87:13
10 ^[c]	L9	Et ₂ O (0.13 M)	DMA	25	71	3.9:1	96:4
11 ^[c]	L9	Et ₂ O (0.20 M)	DMA	25	46	3.3:1	95:5
12 ^[c]	L9	CPME (0.20 M)	DMA	25	53	3.1:1	94:6
13 ^{[c][d]}	L9	CPME (0.20 M)	HMPA	25	72	4.2:1	93:7
14 ^{[c][d]}	L9	CPME (0.20 M)	HMPA	10	74	4.7:1	94:6
15 ^{[c][d]}	L9	CPME (0.20 M)	HMPA	0	69	3.4:1	96:4
16 ^{[c][d]}	L9	CPME (0.20 M)	HMPA	-15	39	2.8:1	95:5
17 ^{[c][d][e]}	L9	CPME (0.20 M)	HMPA	0	49	3.3:1	94:6
18 ^{[c][d][f]}	L9	CPME (0.20 M)	HMPA	0	30	4.6:1	92:8
19 ^{[c][g]}	L9	CPME (0.20 M)	DMPU	0	traces	-	-
20 ^{[c][h]}	L9	CPME (0.20 M)	DMI	0	88	3:1	94:6
21 ^{[h][i]}	L9	CPME (0.20 M)	DMI	0	89	3.8:1	96:4

[a] Conditions: 20.3 mg (0.10 mmol) **4a**, 10.4 mg (0.10 mmol) **5a**, 2.2 mg (10.0 μmol) NiCl₂(DME), 5.00 μmol L*, 19.6 mg (0.30 mmol) Zn powder, 93.0 μl (1.00 mmol) DMA in Et₂O at 23 °C for 24 h; [b] when **Z-6aa** (84:16 er) was resubmitted to the reaction conditions, no isomerization to **E-6aa** and no change in enantiomeric ratio were observed; [c] with 7.2 mg (0.11 mmol) Zn powder; [d] with 157 μl (0.9 mmol) HMPA; [e] with 30.5 mg (0.15 mmol) **4a**; [f] with 15.6 mg (0.15 mmol) **5a**; [g] with 109 μl (0.9 mmol) DMPU; [h] with 98.0 μl (0.9 mmol) DMI; [i] with 3.5 mg (16.0 μmol) NiCl₂(DME), 7.6 mg (8.00 μmol) **L9**, 7.6 mg (116 μmol) Zn powder.

SUPPORTING INFORMATION

7. General procedure for enantioselective alkylidene transfer (GP3)

Chiral alkylidenecyclopropanes **6** were synthesized according to the procedure summarized in **Scheme 6** and described below.

Scheme 6: Synthetic procedure to access chiral alkylidenecyclopropanes **6**.

In a N_2 -filled glovebox, a 1/2 Dram glass vial equipped with a magnetic stir bar (3 x 10 mm) was charged with **L9** (8.00 mol%, 8.00 μmol), $\text{NiCl}_2(\text{DME})$ (16.0 mol%, 16.0 μmol), Zn powder (1.16 equiv., 116 μmol), 1,3-dimethyl-2-imidazolidinone DMI (98.0 μL , 0.90 mmol) and CPME (160 μL). The reaction mixture was stirred (1400 rpm) at room temperature for 15 minutes. A mixture of 1,1-dichloroalkene **4** (1.00 equiv., 0.10 mmol), alkene **5** (1.00 equiv., 0.10 mmol) and CPME (340 μL) was added to the preformed catalyst. The vial was sealed, transferred out of the glovebox into a flame-dried Schlenk flask (with sand as heat transfer medium) and the reaction mixture was stirred (1400 rpm) at 0 °C for 24 hours (see **Figure 1** for description of the reaction apparatus). After this time, the reaction mixture was filtered over a short plug of SiO_2 (eluting with DCM) and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (*n*-pentane:DCM) affording the products **6** as an inseparable mixture of *Z/E* diastereomers.

Note1: Liquid reagents/reactants were degassed by freeze-pump-thaw (3 $\times$) before being stored in the glovebox at -30 °C. Solid reagents/reactants were dried under high vacuum for 16h before being stored in the glovebox at -30 °C.

Note2: The synthesized methylenecyclopropanes are prone to decomposition when kept under air at room temperature; therefore, after purification they were stored under a N_2 atmosphere in a -80 °C freezer.

Note3: The *Z/E* stereochemistry of alkylidenecyclopropanes **6** was assigned on the basis of a previous literature report.⁹

SUPPORTING INFORMATION

Figure 1: Description of the reaction apparatus used for asymmetric alkylidenecyclopropanation of olefins.

SUPPORTING INFORMATION

8. Characterization data of chiral Alkylidenecyclopropanes 6

(R)-1-Methoxy-4-((2-phenylcyclopropylidene)methyl)benzene 6aa

Prepared according to **GP3**.

Yield: 89%

R_f (20% DCM in pentane): 0.25

Appearance: colourless oil

Z/E ratio: 3.8:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, 2H, *E*-6aa), 7.34 – 7.06 (m, 5H *E*-6aa + 7H *Z*-6aa), 6.90 (d, *J* = 8.7 Hz, 2H, *E*-6aa), 6.87 (q, *J* = 2.1 Hz, 1H, *Z*-6aa), 6.84 (q, *J* = 2.3 Hz, 1H, *E*-6aa), 6.76 (d, *J* = 8.7 Hz, 2H *Z*-6aa), 3.82 (s, 3H, *E*-6aa), 3.74 (s, 3H, *Z*-6aa), 2.86 (ddd, *J* = 9.0, 4.6, 2.1 Hz, 1H, *Z*-6aa), 2.67 (ddd, *J* = 8.8, 4.7, 1.7 Hz, 1H, *E*-6aa), 2.05 (td, *J* = 9.0, 2.4 Hz, 1H, *E*-6aa), 1.81 (td, *J* = 8.9, 2.0 Hz, 1H, *Z*-6aa), 1.49 (ddd, *J* = 9.2, 4.7, 2.4 Hz, 1H, *E*-6aa), 1.25 – 1.18 (ddd, 1H, *Z*-6aa).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.00 (*Z*-6aa), 158.83 (*E*-6aa), 142.49 (*Z*-6aa), 141.50 (*E*-6aa), 130.70 (*Z*-6aa), 130.34 (*E*-6aa), 128.69 (*E*-6aa), 128.49 (*Z*-6aa), 128.29 (*E*-6aa), 128.13 (*Z*-6aa), 126.57 (*Z*-6aa), 126.52 (*E*-6aa), 126.26 (*Z*-6aa), 126.03 (*Z*-6aa), 126.00 (*E*-6aa), 125.02 (*E*-6aa), 119.58 (*E*-6aa), 118.88 (*Z*-6aa), 114.13 (*E*-6aa), 114.06 (*Z*-6aa), 55.46 (*Z*-6aa), 55.34 (*E*-6aa), 21.48 (*E*-6aa), 18.07 (*Z*-6aa), 16.02 (*Z*-6aa), 13.98 (*E*-6aa).

IR (ATR): $\nu(\text{cm}^{-1})$ 3061, 3032, 2919, 2838, 1781, 1740, 1603, 1513, 1251, 1169, 1031, 700.

HRMS (APPI/LQT-Orbitrap): calcd for C₁₇H₁₅O⁺ [M+H-1]⁺: 235.1117; found: 235.1114.

[α]_D²⁰ = -409 (*c* = 1.0, CHCl₃).

e.r. (Z): 96:4 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = 62/38, λ = 260 nm, 0.75 mL/min, *t_R* major = 90.1 min, *t_R* minor = 92.2 min)

SUPPORTING INFORMATION

SUPPORTING INFORMATION

(R)-1-Methyl-4-((2-phenylcyclopropylidene)methyl)benzene 6ba

Prepared according to **GP3**.

Yield: 97%

R_f (20% DCM in pentane): 0.50

Appearance: yellow oil

Z/E ratio: 3.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.50 (d, $J = 7.9$ Hz, 2H, *E*-**6ba**), 7.32 – 7.10 (m, 7H *E*-**6ba** + 7H *Z*-**6ba**), 7.05 (d, $J = 7.8$ Hz, 2H, *Z*-**6ba**), 6.91 (q, $J = 2.1$ Hz, 1H, *Z*-**6ba**), 6.89 (q, $J = 2.3$ Hz, 1H, *E*-**6ba**), 2.90 (ddd, $J = 9.1, 4.8, 2.0$ Hz, 1H, *Z*-**6ba**), 2.70 (ddd, $J = 9.1, 4.8, 1.6$ Hz, 1H, *E*-**6ba**), 2.38 (s, 3H, *E*-**6ba**), 2.29 (s, 3H, *Z*-**6ba**), 2.09 (td, $J = 9.1, 2.4$ Hz, 1H, *E*-**6ba**), 1.84 (td, $J = 9.0, 2.0$ Hz, 1H, *Z*-**6ba**), 1.53 – 1.50 (m, 1H, *E*-**6ba**), 1.27 – 1.21 (m, 1H, *Z*-**6ba**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 142.41 (*E*-**6ba**), 141.41 (*Z*-**6ba**), 137.04 (*E*-**6ba**), 136.83 (*Z*-**6ba**), 135.04 (*E*-**6ba**), 134.64 (*Z*-**6ba**), 129.38, 129.32, 128.68, 128.50, 127.60, 127.07, 126.92, 126.58, 126.55, 126.40, 126.05, 126.03, 120.07 (*Z*-**6ba**), 119.37 (*E*-**6ba**), 21.58 (*Z*-**6ba**), 21.39 (*E*-**6ba**), 21.30 (*Z*-**6ba**), 18.06 (*E*-**6ba**), 16.12 (*E*-**6ba**), 13.88 (*Z*-**6ba**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3027, 3002, 2965, 2921, 1603, 1511, 1493, 1452, 853, 809, 748, 697, 504.

HRMS (APPI/QTOF): calcd for C₁₇H₁₆⁺ [M]⁺: 220.1247; found: 220.1240.

$[\alpha]_{\text{D}}^{20}$ = -358 ($c = 1.0$, CHCl₃).

e.r. (Z): 92:8 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, $\lambda = 260$ nm, 1.00 mL/min, t_{R} major = 50.4 min, t_{R} minor = 52.9 min)

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	50.609	865.7	20.7	0.6595	50.032	0.851
2	53.179	864.6	20	0.678	49.968	0.847

#	Time	Area	Height	Width	Area%	Symmetry
1	50.382	5436.3	128.2	0.6667	91.565	0.823
2	52.96	500.8	12	0.6975	8.435	0.863

SUPPORTING INFORMATION

(R)-Triisopropyl(4-((2-phenylcyclopropylidene)methyl)phenoxy)silane 6ca

Prepared according to **GP3**.

Yield: 93%

R_f (2% EtOAc in pentane): 0.34

Appearance: colourless oil

Z/E ratio: 2.6:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.46 (d, J = 8.5 Hz, 2H, **E-6ca**), 7.30 – 7.17 (m, 5H **E-6ca** + 5H **Z-6ca**), 7.13 (d, J = 6.8 Hz, 2H, **Z-6ca**), 6.92 – 6.86 (m, 2H **E-6ca** + 1H **Z-6ca**), 6.85 (q, J = 2.2 Hz, 1H, **E-6ca**), 6.75 (d, J = 8.6 Hz, 2H, **Z-6ca**), 2.87 (ddd, J = 9.0, 4.6, 2.0 Hz, 1H, **Z-6ca**), 2.68 (ddd, J = 9.0, 4.7, 1.7 Hz, 1H, **E-6ca**), 2.06 (td, J = 9.0, 2.4 Hz, 1H, **E-6ca**), 1.81 (td, J = 8.9, 2.0 Hz, 1H, **Z-6ca**), 1.50 (ddd, J = 9.2, 4.7, 2.4 Hz, 1H, **E-6ca**), 1.35 – 1.16 (m, 3H **E-6ca** + 4H **Z-6ca**), 1.13 (d, J = 7.4 Hz, 18H, **E-6ca**), 1.07 (d, J = 7.8 Hz, 18H, **Z-6ca**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 155.55 (**E-6ca**), 155.39 (**Z-6ca**), 142.53 (**E-6ca**), 141.58 (**Z-6ca**), 130.89 (**E-6ca**), 130.57 (**Z-6ca**), 128.67, 128.48, 128.23, 128.06, 126.60, 126.59, 126.09, 126.01, 125.98, 124.90, 120.12 (**E-6ca**), 120.05 (**Z-6ca**), 119.82 (**Z-6ca**), 119.04 (**E-6ca**), 21.49 (**Z-6ca**), 18.09 (**E-6ca**), 18.04 (**Z-6ca**), 16.06 (**E-6ca**), 14.00 (**Z-6ca**), 12.84 (**E-6ca**), 12.78 (**Z-6ca**).

IR (ATR): $\nu(\text{cm}^{-1})$ 2943, 2891, 2865, 1602, 1507, 1261, 907, 882, 695, 680.

HRMS (ESI/QTOF): calcd for C₂₅H₃₅OSi⁺ [M+H]⁺: 379.2452; found: 379.2453.

[α]_D²⁰ = -226 (c = 1.0, CHCl₃).

e.r. (Z): 87:13 (Chiralpak IG, Hexane/IPA = 90/10, λ = 254 nm, 1.00 mL/min, t_R major = 5.93 min, t_R minor = 6.90 min, determined after derivatization to the corresponding alcohol **13**)

SUPPORTING INFORMATION

(R)-(2-Benzylidenecyclopropyl)benzene 6da

Prepared according to **GP3**.

Yield: 63%

R_f (20% DCM in pentane): 0.50

Appearance: yellow oil

Z/E ratio: 1.7:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.60 (d, J = 7.5 Hz, 2H, **E-6da**), 7.38 (m, 2H **E-6da** + 2H **Z-6da**), 7.31 – 7.09 (m, 6H **E-6da** + 8H **Z-6da**), 6.96 – 6.93 (m, 1H, **Z-6da**), 6.93 – 6.90 (m, 1H, **E-6da**), 2.92 (ddd, J = 9.2, 4.8, 2.0 Hz, 1H, **Z-6da**), 2.72 (ddd, J = 9.2, 4.9, 1.7 Hz, 1H, **E-6da**), 2.11 (td, J = 9.2, 2.4 Hz, 1H **E-6da**), 1.85 (td, J = 9.1, 2.0 Hz, 1H, **Z-6da**), 1.60 – 1.53 (m, 1H, **E-6da**), 1.31 – 1.23 (m, 1H, **Z-6da**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 142.22 (**E-6da**), 141.26 (**Z-6da**), 137.80 (**E-6da**), 137.36 (**Z-6da**), 128.77, 128.71, 128.68, 128.61, 128.53, 127.65, 127.27, 127.15, 127.08, 127.02, 126.59, 126.54, 126.12, 126.09, 120.27 (**Z-6da**), 119.53 (**E-6da**), 21.64 (**Z-6da**), 18.05 (**E-6da**), 16.11 (**E-6da**), 13.88 (**Z-6da**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3082, 3060, 3027, 2966, 2924, 1493, 1450, 750, 693.

HRMS (APPI/QTOF): calcd for C₁₆H₁₄⁺ [M]⁺: 206.1090; found: 206.1081.

[α]_D²⁰ = -289 (c = 1.0, CHCl₃).

e.r. (Z): 88:12 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, λ = 260 nm, 1.00 mL/min, t_R major = 43.7 min, t_R minor = 46.3 min)

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	44.204	346.7	8.8	0.6173	50.107	0.833
2	46.852	345.2	8.5	0.6341	49.893	0.836

#	Time	Area	Height	Width	Area%	Symmetry
1	43.683	6968.5	217.1	0.4925	88.149	0.832
2	46.331	936.8	28.1	0.5111	11.851	0.834

SUPPORTING INFORMATION

(R)-1-((2-Phenylcyclopropylidene)methyl)-4-(trifluoromethyl)benzene 6ea

Prepared according to **GP3**.

Yield: 86%

R_f (100% pentane): 0.29

Appearance: light yellow oil

Z/E ratio: 3.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.68 (d, *J* = 8.2 Hz, 2H, *E*-**6ea**), 7.60 (d, *J* = 8.2 Hz, 2H, *E*-**6ea**), 7.51 – 7.41 (m, 4H, *Z*-**6ea**), 7.31 – 7.15 (m, 5H *E*-**6ea** + 3H *Z*-**6ea**), 7.13 – 7.07 (m, 2H, *Z*-**6ea**), 6.97 (q, *J* = 2.1 Hz, 1H, *Z*-**6ea**), 6.94 (q, 1H, *E*-**6ea**), 2.94 (ddd, *J* = 9.5, 5.1, 2.1 Hz, 1H, *Z*-**6ea**), 2.76 (ddd, *J* = 9.4, 5.2, 1.7 Hz, 1H, *E*-**6ea**), 2.13 (td, *J* = 9.5, 2.4 Hz, 1H, *E*-**6ea**), 1.90 (td, *J* = 9.4, 2.0 Hz, 1H, *Z*-**6ea**), 1.59 (ddd, *J* = 9.6, 5.2, 2.4 Hz, 1H, *E*-**6ea**), 1.33 (ddd, *J* = 9.5, 5.1, 2.0 Hz, 1H, *Z*-**6ea**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 141.56, 141.21, 140.71, 140.60, 132.05, 131.20, 129.11 (q, *J* = 33.3 Hz, *Z*-**6ea**), 128.86, 128.62, 127.18, 127.06, 126.61, 126.41, 126.33, 125.71 (q, *J* = 5.0 Hz, *E*-**6ea**), 125.55 (q, *J* = 4.0 Hz, *Z*-**6ea**), 124.38 (q, *J* = 272.7 Hz, *Z*-**6ea**), 119.10, 118.50, 21.70 (*Z*-**6ea**), 18.20 (*E*-**6ea**), 15.91 (*E*-**6ea**), 13.93 (*Z*-**6ea**).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.41 (*E*-**6ea**), -62.46 (*Z*-**6ea**).

IR (ATR): ν(cm⁻¹) 3030, 2926, 2855, 1616, 1323, 1164, 1122, 1068, 860, 697.

HRMS (ESI/LQT-Orbitrap): calcd for C₁₇H₁₃F₃⁺ [M]⁺: 274.0964; found: 274.0958.

[α]_D²⁰ = -263 (*c* = 1.0, CHCl₃).

e.r. (Z): 94:6 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, λ = 280 nm, 1.00 mL/min, t_R major = 54.8 min, t_R minor = 56.3 min)

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	55.421	6655.4	196	0.5261	49.922	0.992
2	56.903	6676.3	193.9	0.5337	50.078	0.982

#	Time	Area	Height	Width	Area%	Symmetry
1	54.847	4493	110.6	0.6768	93.811	0.896
2	56.327	296.4	8.1	0.6077	6.189	0.755

SUPPORTING INFORMATION

(R)-Methyl 4-((2-phenylcyclopropylidene)methyl)benzoate 6fa

Prepared according to **GP3**.

Yield: 96%

R_f (20% DCM in pentane): 0.46

Appearance: light yellow solid

Z/E ratio: 4.6:1

¹H NMR (400 MHz, Chloroform-*d*): δ 8.03 (d, J = 7.7 Hz, 2H, **E-6fa**), 7.90 (d, J = 7.7 Hz, 2H, **Z-6fa**), 7.64 (d, J = 8.1 Hz, 2H, **E-6fa**), 7.42 (d, J = 8.3 Hz, 2H, **Z-6fa**), 7.33 – 7.15 (m, 5H **E-6fa** + 3H **Z-6fa**), 7.10 (d, J = 7.0 Hz, 2H, **Z-6fa**), 7.00 – 6.97 (m, 1H, **Z-6fa**), 6.97 – 6.94 (m, 1H, **E-6fa**), 3.93 (s, 3H, **E-6fa**), 3.87 (s, 3H, **Z-6fa**), 2.95 (ddd, J = 9.5, 5.1, 2.1 Hz, 1H, **Z-6fa**), 2.75 (ddd, J = 9.3, 5.2, 1.7 Hz, 1H, **E-6fa**), 2.14 (td, J = 9.5, 2.4 Hz, 1H, **E-6fa**), 1.89 (td, J = 9.4, 2.0 Hz, 1H, **Z-6fa**), 1.60 (ddd, J = 9.8, 5.3, 2.5 Hz, 1H, **E-6fa**), 1.33 (ddd, J = 9.6, 5.2, 2.0 Hz, 1H, **Z-6fa**).

¹³C NMR (101 MHz, Chloroform-*d*) for E-6fa: δ 167.15, 142.28, 141.64, 132.30, 130.06, 128.67, 128.60, 126.81, 126.63, 126.29, 118.94, 52.21, 18.23, 16.04.

¹³C NMR (101 MHz, Chloroform-*d*) for Z-6fa: δ 167.10, 141.78, 140.63, 131.49, 129.99, 128.81, 128.47, 126.96, 126.47, 126.36, 119.56, 52.12, 21.78, 13.88.

IR (ATR): $\nu(\text{cm}^{-1})$ 3028, 2951, 2849, 1717, 1606, 1453, 1275, 1177, 1109, 868, 697.

HRMS (ESI/QTOF): calcd for C₁₈H₁₇O₂⁺ [M+H]⁺: 265.1223; found: 265.1224.

[α]_D²⁰ = -310 (c = 1.0, CHCl₃).

e.r. (Z): 92:8 (Chiralpak IB, Hexane/IPA = 99.5/0.5, λ = 210 nm, 1.00 mL/min, t_R major = 17.0 min, t_R minor = 10.0 min)

Melting point: 54.3–59.1 °C

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.028	BB	0.2009	3382.81567	254.84659	49.5621
2	17.595	BB	0.3516	3442.59595	142.62807	50.4379

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.049	MM	0.1995	337.73651	28.21824	7.6757
2	17.023	BB	0.3339	4062.31445	182.37320	92.3243

SUPPORTING INFORMATION

Scale-up reaction (1.00 mmol scale):

In a N₂-filled glovebox, a microwave vial equipped with a magnetic stir bar was charged with **L9** (8.00 mol%, 0.08 mmol), NiCl₂(DME) (16.0 mol%, 0.16 mmol), Zn powder (1.16 equiv., 1.16 mmol), 1,3-dimethyl-2-imidazolidinone (0.98 mL, 9.00 mmol) and CPME (1.60 mL). The reaction mixture was stirred at room temperature for 15 minutes. A mixture of methyl 4-(2,2-dichlorovinyl)benzoate (1.00 equiv., 1.00 mmol), styrene (1.00 equiv., 1.00 mmol) and CPME (3.40 mL) was added to the preformed catalyst. The vial was sealed and the reaction mixture was stirred at 0 °C for 24 hours. After this time, the reaction mixture was filtered over a plug of SiO₂ (eluting with DCM) and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (*n*-pentane:DCM) affording the product in 97% yield as a mixture of *Z/E* diastereomers (*Z/E*: 5.7:1). The enantiomeric ratio for the major *Z* diastereomer is 92:8.

SUPPORTING INFORMATION

(R)-1-Fluoro-4-((2-phenylcyclopropylidene)methyl)benzene 6ga

Prepared according to **GP3**.

Yield: 91%

R_f (100% pentane): 0.29

Appearance: colourless oil

Z/E ratio: 3.7:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.60 – 7.53 (m, 2H, **E-6ga**), 7.37 – 7.17 (m, 5H **E-6ga** + 5H **Z-6ga**), 7.12 (d, $J = 7.1$ Hz, 2H, **Z-6ga**), 7.07 (t, $J = 8.7$ Hz, 2H, **E-6ga**), 6.97 – 6.87 (m, 1H **E-6ga** + 3H **Z-6ga**), 2.90 (ddd, $J = 9.2, 4.8, 1.9$ Hz, 1H, **Z-6ga**), 2.76 – 2.68 (ddd, 1H, **E-6ga**), 2.09 (td, $J = 9.2, 2.4$ Hz, 1H, **E-6ga**), 1.86 (td, $J = 9.1, 1.9$ Hz, 1H, **Z-6ga**), 1.57 – 1.50 (m, 1H, **E-6ga**), 1.28 (m, 1H, **Z-6ga**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 163.39 (d, $J = 247.5$ Hz, **E-6ga**), 162.03 (d, $J = 247.5$ Hz, **Z-6ga**), 142.05 (**E-6ga**), 141.06 (**Z-6ga**), 133.95 (d, $J = 3.4$ Hz, **E-6ga**), 133.56 (d, $J = 3.2$ Hz, **Z-6ga**), 128.76 (**Z-6ga**), 128.56 (d, $J = 7.9$ Hz, **Z-6ga**), 128.55 (**E-6ga**), 128.42 (d, $J = 7.9$ Hz, **E-6ga**), 128.28 (d, $J = 2.7$ Hz, **E-6ga**), 127.25 (d, $J = 2.8$ Hz, **Z-6ga**), 126.59, 126.45, 126.21, 126.16, 119.06 (**Z-6ga**), 118.41 (**E-6ga**), 115.58 (d, $J = 21.2$ Hz, **E-6ga**), 115.50 (d, $J = 21.2$ Hz, **Z-6ga**), 21.48 (**Z-6ga**), 18.11 (**E-6ga**), 15.85 (**E-6ga**), 13.96 (**Z-6ga**).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -115.00 (**E-6ga**), -115.23 (**Z-6ga**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3060, 3029, 2968, 2924, 1602, 1506, 1493, 1227, 1156, 852, 822, 696, 512.

HRMS (APPI/LQT-Orbitrap): calcd for C₁₆H₁₃F⁺ [M]⁺: 224.0996; found: 224.0992.

$[\alpha]_{\text{D}}^{20}$ = -291 ($c = 1.0$, CHCl₃).

e.r. (Z): 91:9 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, $\lambda = 280$ nm, 1.00 mL/min, t_{R} major = 44.4 min, t_{R} minor = 45.8 min)

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	44.385	2374.1	75.4	0.4834	50.021	0.874
2	45.774	2372.1	73.8	0.4912	49.979	0.858

#	Time	Area	Height	Width	Area%	Symmetry
1	44.413	4081	132	0.4766	90.518	0.899
2	45.803	427.5	14.2	0.4686	9.482	0.841

SUPPORTING INFORMATION

(R)-2-((2-Phenylcyclopropylidene)methyl)naphthalene 6ha

Prepared according to **GP3**.

Yield: 96%

R_f (100% pentane): 0.19

Appearance: light yellow solid

Z/E ratio: 4.1:1

¹H NMR (400 MHz, Chloroform-*d*): δ 8.00 – 7.89 (m), 7.86 – 7.77 (m), 7.74 (d, J = 8.6 Hz, 1H, **Z-6ha**), 7.67 (dd, J = 8.6, 1.6 Hz, 1H, **Z-6ha**), 7.60 – 7.42 (m, 2H **E-6ha** + 2H **Z-6ha**), 7.41 – 7.21 (m), 7.19 (q, J = 2.1 Hz, 1H, **Z-6ha**), 7.16 (q, J = 2.2 Hz, 1H, **E-6ha**), 3.09 (ddd, J = 9.2, 4.8, 2.0 Hz, 1H, **Z-6ha**), 2.84 (ddd, J = 9.1, 5.0, 1.7 Hz, 1H, **E-6ha**), 2.28 (td, J = 9.2, 2.4 Hz, 1H, **E-6ha**), 1.99 (td, J = 9.1, 2.0 Hz, 1H, **Z-6ha**), 1.73 (ddd, J = 9.3, 4.9, 2.4 Hz, 1H, **E-6ha**), 1.41 (ddd, J = 9.1, 4.9, 2.0 Hz, 1H, **Z-6ha**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 142.21 (**E-6ha**), 141.32 (**Z-6ha**), 135.41 (**E-6ha**), 135.07 (**Z-6ha**), 133.84 (**E-6ha**), 133.69 (**Z-6ha**), 132.90 (**E-6ha**), 132.73 (**Z-6ha**), 129.40, 128.74, 128.56, 128.47, 128.23, 128.08, 127.83, 127.72, 126.64, 126.57, 126.55, 126.44, 126.32, 126.18, 126.13, 125.84, 125.76, 124.77, 124.60, 120.40 (**Z-6ha**), 119.78 (**E-6ha**), 21.84 (**Z-6ha**), 18.20 (**E-6ha**), 16.28 (**E-6ha**), 13.92 (**Z-6ha**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3057, 3026, 2965, 2923, 1600, 1507, 1493, 1452, 861, 815, 742, 697, 475.

HRMS (APPI/LTQ-Orbitrap): calcd for C₂₀H₁₆⁺ [M]⁺: 256.1247; found: 256.1241.

[α]_D²⁰ = -280 (c = 1.0, CHCl₃).

e.r. (Z): 91:9 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, λ = 280 nm, 1.00 mL/min, t_R major = 68.5 min, t_R minor = 73.3 min)

Melting point: 85.5–87.7 °C

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	69.004	10045.1	240.5	0.6453	50.267	0.944
2	73.877	9938.5	232	0.6618	49.733	0.908

#	Time	Area	Height	Width	Area%	Symmetry
1	68.478	6891	139.4	0.7808	91.411	0.829
2	73.334	647.5	12.6	0.803	8.589	0.827

Note: *E*-diastereomer was not eluted from the column.

SUPPORTING INFORMATION

(R)-1-Methoxy-3-((2-phenylcyclopropylidene)methyl)benzene 6ia

Prepared according to **GP3**.

Yield: 93%

R_f (20% DCM in pentane): 0.21

Appearance: colourless oil

Z/E ratio: 2.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.33 – 7.10 (m, 8H *E*-**6ia** + 6H *Z*-**6ia**), 6.96 (d, J = 7.7 Hz, 1H, *Z*-**6ia**), 6.90 (m, 1H *E*-**6ia** + 2H *Z*-**6ia**), 6.83 (dd, J = 8.2, 2.6, 1.0 Hz, 1H, *E*-**6ia**), 6.72 (dd, J = 8.3, 2.6, 1.0 Hz, 1H, *Z*-**6ia**), 3.85 (s, 3H, *E*-**6ia**), 3.53 (s, 3H, *Z*-**6ia**), 2.90 (ddd, J = 9.3, 4.9, 2.1 Hz, 1H, *Z*-**6ia**), 2.72 (ddd, J = 9.1, 5.0, 1.7 Hz, 1H, *E*-**6ia**), 2.11 (td, J = 9.2, 2.4 Hz, 1H, *E*-**6ia**), 1.89 (td, J = 9.2, 2.0 Hz, 1H, *Z*-**6ia**), 1.56 (ddd, J = 7.5, 5.0, 2.4 Hz, 1H, *E*-**6ia**), 1.33 (ddd, J = 9.2, 4.9, 2.0 Hz, 1H, *Z*-**6ia**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.93 (*E*-**6ia**), 159.79 (*Z*-**6ia**), 142.13 (*E*-**6ia**), 141.28 (*Z*-**6ia**), 139.24 (*E*-**6ia**), 138.77 (*Z*-**6ia**), 129.64, 129.50, 129.18, 128.73, 128.53, 128.24, 126.59, 126.45, 126.15, 126.11, 120.07, 119.92, 119.80, 119.44, 113.82 (*Z*-**6ia**), 112.79 (*E*-**6iaX**), 112.36 (*E*-**6ia**), 111.20 (*Z*-**6ia**), 55.36 (*E*-**6ia**), 54.98 (*Z*-**6ia**), 21.68 (*Z*-**6ia**), 18.09 (*E*-**6ia**), 16.09 (*E*-**6ia**), 13.86 (*Z*-**6ia**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3028, 3001, 2962, 2936, 2835, 1783, 1599, 1492, 1256, 1156, 1002, 697.

HRMS (ESI/QTOF): calcd for C₁₇H₁₇O⁺ [M+H]⁺: 237.1274; found: 237.1271.

$[\alpha]_{\text{D}}^{20}$ = -248 (c = 1.0, CHCl₃).

e.r. (Z): 94:6 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = 64/36, λ = 260 nm, 0.75 mL/min, t_{R} major = 104 min, t_{R} minor = 107 min)

SUPPORTING INFORMATION

SUPPORTING INFORMATION

(R)-1-Methoxy-2-((2-phenylcyclopropylidene)methyl)benzene 6ja

Prepared according to **GP3**.

Yield: 93%

R_f (20% DCM in pentane): 0.25

Appearance: colourless oil

Z/E ratio: 4.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.85 (d, J = 7.7, 1.7 Hz, 1H, **E-6ja**), 7.42 (d, J = 7.7 Hz, 1H, **Z-6ja**), 7.38 (q, J = 2.2 Hz, 1H, **Z-6ja**), 7.34 (q, J = 2.3 Hz, 1H, **E-6ja**), 7.30 – 7.09 (m, 6H **E-6ja** + 6H **Z-6ja**), 6.99 (t, J = 7.5 Hz, 1H, **E-6ja**), 6.93 (d, J = 7.8 Hz, 1H, **E-6ja**), 6.88 (d, J = 8.3, 1.1 Hz, 1H, **Z-6ja**), 6.77 (t, J = 7.5 Hz, 1H, **Z-6ja**), 3.88 (s, 3H, **Z-6ja**), 3.87 (s, 3H, **E-6ja**), 2.90 (ddd, J = 9.2, 4.7, 2.1 Hz, 1H, **Z-6ja**), 2.71 (ddd, J = 9.1, 4.9, 1.8 Hz, 1H, **E-6ja**), 2.08 (td, J = 9.2, 2.5 Hz, 1H, **E-6ja**), 1.84 (td, J = 9.0, 2.1 Hz, 1H, **Z-6ja**), 1.58 – 1.49 (m, 1H, **E-6ja**), 1.30 – 1.22 (m, 1H, **Z-6ja**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 156.52 (**E-6ja**), 156.24 (**Z-6ja**), 142.47 (**E-6ja**), 141.66 (**Z-6ja**), 128.64, 128.51, 128.46, 128.32, 128.13, 127.50, 127.17, 126.73, 126.65, 126.53, 126.12, 125.98, 125.96, 120.84 (**Z-6ja**), 120.72 (**E-6ja**), 113.77 (**Z-6ja**), 113.44 (**E-6ja**), 111.07 (**E-6ja**), 110.86 (**Z-6ja**), 55.71 (**Z-6ja**), 55.69 (**E-6ja**), 21.44 (**Z-6ja**), 18.12 (**E-6ja**), 15.89 (**E-6ja**), 13.94 (**Z-6ja**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3028, 2963, 2835, 1598, 1491, 1244, 1051, 749, 697.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₇H₁₆O⁺ [M]⁺: 236.1196; found: 236.1190.

$[\alpha]_{\text{D}}^{20}$ = -318 (c = 1.0, CHCl₃).

e.r. (Z): 94:6 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 60/40 to 40/60, λ = 254 nm, 1.00 mL/min, t_{R} major = 48.8 min, t_{R} minor = 53.8 min)

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	48.639	16750.6	405.1	0.6892	37.369	0.882
2	52.031	5802.8	144.2	0.6708	12.945	0
3	53.48	16248.6	393.8	0.6877	36.249	0.902
4	54.904	6023	143.2	0.7008	13.437	0.92

#	Time	Area	Height	Width	Area%	Symmetry
1	48.806	37755.2	1110.2	0.5228	94.130	0.845
2	53.84	2354.3	66.2	0.549	5.870	0.894

SUPPORTING INFORMATION

(R)-4-((2-(4-Methoxyphenyl)cyclopropylidene)methyl)tetrahydro-2H-pyran 6kb

Prepared according to **GP3**.

Yield: 55%

R_f (8% EtOAc in pentane): 0.26

Appearance: yellow oil

Z/E ratio: 12:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.08 – 7.03 (m, 2H, **E-6kb**), 7.03 – 6.96 (m, 2H, **Z-6kb**), 6.84 – 6.76 (m, 2H **E-6kb** + 2H **Z-6kb**), 5.92 – 5.87 (m, 1H, **E-6kb**), 5.85 (dq, $J = 6.4, 2.0$ Hz, 1H, **Z-6kb**), 3.98 (m, 2H, **E-6kb**), 3.94 – 3.85 (m, 2H, **Z-6kb**), 3.78 (s, 3H **E-6kb** + 3H **Z-6kb**), 3.48 (tdd, $J = 11.5, 5.2, 2.1$ Hz, 2H, **E-6kb**), 3.35 (tdd, $J = 11.6, 5.2, 2.6$ Hz, 2H, **Z-6kb**), 2.60 – 2.52 (m, 1H, **Z-6kb**), 2.50 – 2.46 (m, 2H, **E-6kb**), 2.44 – 2.30 (m, 1H, **Z-6kb**), 1.81 – 1.41 (m, 5H **E-6kb** + 5H **Z-6kb**), 1.14 (ddd, $J = 8.7, 4.2, 2.0$ Hz, 1H, **E-6kb**), 1.05 (ddd, $J = 8.3, 4.7, 1.7$ Hz, 1H, **Z-6kb**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 157.98 (**E-6kb**), 157.87 (**Z-6kb**), 134.76 (**Z-6kb**), 134.46 (**E-6kb**), 127.48 (**E-6kb**), 127.02 (**Z-6kb**), 125.50 (**E-6kb**), 125.31 (**Z-6kb**), 124.01 (**Z-6kb**), 123.60 (**E-6kb**), 114.00 (**Z-6kb**), 113.93 (**E-6kb**), 67.98 (**E-6kb**), 67.91 (**Z-6kb**), 55.45 (**E-6kb**), 55.41 (**Z-6kb**), 37.94 (**Z-6kb**), 37.77 (**E-6kb**), 32.84 (**E-6kb**), 32.74 (**E-6kb**), 32.56 (**Z-6kb**), 32.54 (**Z-6kb**), 19.86 (**Z-6kb**), 17.89 (**E-6kb**), 14.28 (**E-6kb**), 14.21 (**Z-6kb**).

IR (ATR): $\nu(\text{cm}^{-1})$ 2954, 2932, 2837, 1512, 1246, 842, 823.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₆H₂₀O₂⁺ [M]⁺: 244.1458; found: 244.1457.

$[\alpha]_{\text{D}}^{20}$ = -142 ($c = 1.0$, CHCl₃).

e.r. (Z): 87:13 (Chiralpak IF, Hexane/IPA = 99.5/0.5, $\lambda = 230$ nm, 1.00 mL/min, t_{R} major = 14.1 min, t_{R} minor = 12.1 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.243	BV	0.2507	1.82344e4	1127.55811	49.8085
2	14.352	BV	0.3026	1.83746e4	913.74927	50.1915

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.082	VB	0.2297	940.31915	61.72122	13.2745
2	14.103	VV	0.2889	6143.33789	324.47537	86.7255

SUPPORTING INFORMATION

(R)-4-((2-(4-(Trifluoromethyl)phenyl)cyclopropylidene)methyl)tetrahydro-2H-pyran 6kc

Prepared according to **GP3**.

Yield: 89%

R_f (50:50 DCM:pentane): 0.36

Appearance: yellow oil

Z/E ratio: 16:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.50 (m, 2H *E*-6kc + 2H *Z*-6kc), 7.16 (m, 2H *E*-6kc + 2H *Z*-6kc), 5.97 – 5.85 (m, 1H *E*-6kc + 1H *Z*-6kc), 4.03 – 3.97 (m, 2H, *E*-6kc), 3.95 – 3.82 (m, 2H, *Z*-6kc), 3.53 – 3.44 (m, 2H, *E*-6kc), 3.43 – 3.25 (m, 2H, *Z*-6kc), 2.70 – 2.59 (m, 1H, *Z*-6kc), 2.59 – 2.46 (m, 1H, *E*-6kc), 2.40 – 2.27 (m, 1H *E*-6kc + 1H *Z*-6kc), 1.85 (tt, 1H, *E*-6kc), 1.76 (tt, *J* = 8.8, 1.8 Hz, 1H, *Z*-6kc), 1.61 – 1.46 (m, 5H *E*-6kc + 4H *Z*-6kc), 1.22 – 1.11 (m, 1H, *Z*-6kc).

¹³C NMR for *Z*-6kc (101 MHz, Chloroform-*d*): δ 147.33, 128.02 (q, *J* = 32.9 Hz), 126.18, 125.46 (q, *J* = 4.04 Hz), 124.83 (q, *J* = 272.7 Hz), 124.55, 124.49, 67.81, 37.94, 32.42, 32.39, 20.35, 15.19.

¹⁹F NMR for *Z*-6kc (376 MHz, Chloroform-*d*): δ -62.25.

IR (ATR): ν (cm⁻¹) 2933, 2843, 1618, 1323, 1163, 1118, 1068, 1017.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₆H₁₇F₃O⁺ [*M*]⁺: 282.1226; found: 282.1221.

[α]_D²⁰ = -134 (*c* = 1.0, CHCl₃).

e.r. (*Z*): 83:17 (Chiralpak ID, Hexane/IPA = 99.5/0.5, λ = 230 nm, 1.00 mL/min, *t_R* major = 6.73 min, *t_R* minor = 6.25 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.298	BV	0.1303	3758.46753	446.19244	49.9827
2	6.785	VV	0.1575	3761.06323	367.10974	50.0173

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.248	MM	0.1372	1063.42725	129.17557	16.5350
2	6.731	VV	0.1601	5367.92920	512.83093	83.4650

SUPPORTING INFORMATION

(R)-2-(2-(4-Methoxybenzylidene)cyclopropyl)naphthalene 6ad

Prepared according to **GP3**.

Yield: 99%

R_f (20% DCM in pentane): 0.23

Appearance: white solid

Z/E ratio: 2.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.84 – 7.71 (m, 4H *E*-6ad + 3H *Z*-6ad), 7.64 (d, *J* = 12.6 Hz, 1H, *Z*-6ad), 7.58 (d, *J* = 8.7 Hz, 2H, *E*-6ad), 7.49 – 7.37 (m, 4H *E*-6ad + 1H *Z*-6ad), 7.37 – 7.31 (m, 2H, *Z*-6ad), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H, *E*-6ad), 7.21 (dd, *J* = 8.5, 1.8 Hz, 1H, *Z*-6ad), 6.99 – 6.89 (m, 1H *E*-6ad + 2H *Z*-6ad), 6.80 – 6.70 (d, 2H, m, 2H *Z*-6ad), 3.85 (s, 3H, *E*-6ad), 3.73 (s, 3H, *Z*-6ad), 3.04 (ddd, *J* = 9.0, 4.6, 2.0 Hz, 1H, *Z*-6ad), 2.86 (ddd, *J* = 8.8, 4.8, 1.6 Hz, 1H, *E*-6ad), 2.15 (td, *J* = 9.0, 2.4 Hz, 1H, *E*-6ad), 1.91 (td, *J* = 8.9, 2.0 Hz, 1H, *Z*-6ad), 1.61 (ddd, *J* = 9.2, 4.7, 2.4 Hz, 1H, *E*-6ad), 1.35 (ddd, *J* = 8.9, 4.6, 2.0 Hz, 1H, *Z*-6ad).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.08 (*E*-6ad), 158.86 (*Z*-6ad), 139.97 (*E*-6ad), 139.23 (*Z*-6ad), 133.80 (*Z*-6ad), 133.66 (*E*-6ad), 132.29, 132.24, 130.69, 130.32, 128.43, 128.31, 128.20, 128.15, 127.77, 127.75, 127.53, 127.46, 126.22, 126.16, 126.11, 125.25, 125.16, 125.01, 124.96, 124.81, 124.77, 119.84 (*Z*-6ad), 119.16 (*E*-6ad), 114.19 (*E*-6ad), 114.10 (*Z*-6ad), 55.48 (*E*-6ad), 55.33 (*Z*-6ad), 21.75 (*Z*-6ad), 18.33 (*E*-6ad), 16.16 (*E*-6ad), 14.16 (*Z*-6ad).

IR (ATR): ν(cm⁻¹) 2959, 2921, 2850, 2835, 1604, 1509, 1246, 1172, 1032, 846, 812, 760, 477.

HRMS (ESI/QTOF): calcd for C₂₁H₁₉O⁺ [M+H]⁺: 287.1430; found: 287.1429.

[α]_D²⁰ = -351 (*c* = 1.0, CHCl₃).

e.r. (Z): 91:9 (Reverse Phase HPLC, Chiralpak IB, H₂O/ACN = gradient from 50/50 to 40/60, λ = 280 nm, 1.00 mL/min, t_R major = 64.9 min, t_R minor = 59.5 min)

Melting point: 66.2–68.6 °C

SUPPORTING INFORMATION

#	Time	Area	Height	Width	Area%	Symmetry
1	59.383	819.4	14.4	0.9453	49.623	0.847
2	64.834	831.8	13.5	1.0299	50.377	0.851

#	Time	Area	Height	Width	Area%	Symmetry
1	59.537	733.8	10.2	1.0881	8.837	0.804
2	64.991	7570	97.7	1.214	91.163	0.782

SUPPORTING INFORMATION

(R)-1-Methoxy-4-((2-(p-tolyl)cyclopropylidene)methyl)benzene 6ae

Prepared according to **GP3**.

Yield: 91%

R_f (20% DCM in pentane): 0.46

Appearance: colourless oil

Z/E ratio: 2.5:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.54 (d, J = 8.7 Hz, 2H, *E*-6ae), 7.33 (d, J = 8.8 Hz, 2H, *Z*-6ae), 7.12 – 7.01 (m, 4H *E*-6ae + 4H *Z*-6ae), 6.92 (d, J = 8.8 Hz, 2H, *E*-6ae), 6.88 (q, 1H, *Z*-6ae), 6.86 (q, 1H, *E*-6ae), 6.80 (d, J = 8.7 Hz, 2H, *Z*-6ae), 3.85 (s, 3H, *E*-6ae), 3.77 (s, 3H, *Z*-6ae), 2.87 (ddd, J = 9.0, 4.6, 2.0 Hz, 1H, *Z*-6ae), 2.67 (ddd, J = 8.8, 4.8, 1.7 Hz, 1H, *E*-6ae), 2.33 (s, 3H, *E*-6ae), 2.32 (s, 3H, *Z*-6ae), 2.05 (td, J = 9.0, 2.4 Hz, 1H, *E*-6ae), 1.81 (td, J = 8.9, 2.0 Hz, 1H, *Z*-6ae), 1.48 (ddd, J = 9.1, 4.8, 2.4 Hz, 1H, *E*-6ae), 1.20 (ddd, J = 8.8, 4.7, 2.0 Hz, 1H, *Z*-6ae).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.95 (*E*-6ae), 158.77 (*Z*-6ae), 139.34 (*E*-6ae), 138.38 (*Z*-6ae), 135.55 (*E*-6ae), 135.53 (*Z*-6ae), 130.79, 130.44, 129.39, 129.18, 128.28, 128.10, 126.49, 126.46, 126.42, 125.25, 119.52 (*Z*-6ae), 118.73 (*E*-6ae), 114.11 (*E*-6ae), 114.05 (*Z*-6ae), 55.45 (*E*-6ae), 55.34 (*Z*-6ae), 21.19 (*Z*-6ae), 21.15 (*Z/E*-6ae), 17.71 (*E*-6ae), 15.81 (*E*-6ae), 13.86 (*Z*-6ae).

IR (ATR): $\nu(\text{cm}^{-1})$ 2999, 2961, 2921, 2834, 1606, 1509, 1462, 1289, 1244, 1172, 1111, 804, 529.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₈H₁₈O⁺ [M]⁺: 250.1352; found: 250.1352.

$[\alpha]_{\text{D}}^{20}$ = -380 (c = 1.0, CHCl₃).

e.r. (Z): 92:8 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 7.59 min, t_{R} minor = 8.29 min)

SUPPORTING INFORMATION

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.612	165.661	738.984	51.39	53.79	n.a.
2		8.215	156.713	634.772	48.61	46.21	n.a.

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.597	213.726	888.037	91.74	92.36	n.a.
2		8.290	19.254	73.408	8.26	7.64	n.a.

SUPPORTING INFORMATION

(R)-Methyl 4-(2-(4-methoxybenzylidene)cyclopropyl)benzoate 6af

Prepared according to **GP3**.

Yield: 71%

R_f (50% DCM in pentane): 0.25

Appearance: yellow solid

Z/E ratio: 3.0:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.92 (m, 2H *E*-6af + 2H *Z*-6af), 7.53 (d, J = 8.6 Hz, 2H, *E*-6af), 7.30 – 7.14 (m, 2H *E*-6af + 4H *Z*-6af), 6.92 (d, J = 8.7 Hz, 2H, *E*-6af), 6.89 (q, J = 2.1 Hz, 1H, *Z*-6af), 6.85 (q, J = 2.2 Hz, 1H, *E*-6af), 6.76 (d, J = 8.8 Hz, 2H, *Z*-6af), 3.89 (s, 3H, *E*-6af), 3.88 (s, 3H, *Z*-6af), 3.84 (s, 3H, *E*-6af), 3.75 (s, 3H, *Z*-6af), 2.91 (ddd, J = 9.0, 4.5, 2.0 Hz, 1H, *Z*-6af), 2.72 (ddd, J = 8.9, 4.7, 1.7 Hz, 1H, *E*-6af), 2.15 (td, J = 9.1, 2.5 Hz, 1H, *E*-6af), 1.91 (td, J = 8.9, 2.0 Hz, 1H, *Z*-6af), 1.55 (ddd, 1H, *E*-6af), 1.31 (ddd, J = 9.0, 4.5, 2.0 Hz, 1H, *Z*-6af).

¹³C NMR (101 MHz, Chloroform-*d*): δ 167.19, 159.19 (*E*-6af), 159.01 (*Z*-6af), 148.40 (*E*-6af), 147.37 (*Z*-6af), 130.31, 130.08, 129.94, 129.85, 128.25, 127.95, 127.84, 126.40, 126.36, 125.62, 124.39, 119.81 (*Z*-6af), 119.37 (*E*-6af), 114.20 (*E*-6af), 114.11 (*Z*-6af), 55.47 (*E*-6af), 55.35 (*Z*-6af), 52.10, 21.55 (*Z*-6af), 18.29 (*E*-6af), 16.76 (*E*-6af), 14.55 (*Z*-6af).

IR (ATR): $\nu(\text{cm}^{-1})$ 2952, 2837, 1717, 1608, 1510, 1435, 1277, 1248, 1175, 1110, 1032, 847, 702.

HRMS (ESI/QTOF): calcd for C₁₉H₁₉O₃⁺ [M+H]⁺: 295.1329; found: 295.1330.

$[\alpha]_{\text{D}}^{20}$ = -349 (c = 1.0, CHCl₃).

e.r. (Z): 89:11 (Chiralpak IA, Hexane/IPA = 95/5, λ = 254 nm, 1.00 mL/min, t_{R} major = 8.07 min, t_{R} minor = 9.26 min)

Melting point: 74.6–76.1 °C

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.580	VB	0.1747	4784.60889	396.69064	50.3214
2	8.592	BB	0.1969	4723.49756	346.76941	49.6786

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.069	MM	0.2077	1.05133e4	843.55396	89.4106
2	9.260	MM	0.2220	1245.14453	93.46558	10.5894

SUPPORTING INFORMATION

(R)-1-Chloro-4-(2-(4-methoxybenzylidene)cyclopropyl)benzene 6ag

Prepared according to **GP3**.

Yield: 90%

R_f (20% DCM in pentane): 0.19

Appearance: colourless oil

Z/E ratio: 3.4:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.53 (d, J = 8.7 Hz, 2H, ***E*-6ag**), 7.32 – 7.18 (m, 2H ***E*-6ag** + 4H ***Z*-6ag**), 7.10 (d, J = 8.4 Hz, 2H, ***E*-6ag**), 7.04 (d, J = 8.4 Hz, 2H, ***Z*-6ag**), 6.92 (d, J = 8.7 Hz, 2H, ***E*-6ag**), 6.88 (q, 1H, ***Z*-6ag**), 6.85 (q, 1H, ***E*-6ag**), 6.79 (d, J = 8.8 Hz, 2H, ***Z*-6ag**), 3.84 (s, 3H, ***E*-6ag**), 3.77 (s, 3H, ***Z*-6ag**), 2.85 (ddd, J = 9.0, 4.5, 2.0 Hz, 1H, ***Z*-6ag**), 2.65 (ddd, J = 8.9, 4.7, 1.7 Hz, 1H, ***E*-6ag**), 2.08 (td, J = 9.0, 2.4 Hz, 1H, ***E*-6ag**), 1.84 (td, J = 8.9, 2.0 Hz, 1H, ***Z*-6ag**), 1.47 (ddd, J = 9.3, 4.6, 2.4 Hz, 1H, ***E*-6ag**), 1.21 (ddd, J = 9.0, 4.5, 2.0 Hz, 1H, ***Z*-6ag**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.11 (***E*-6ag**), 158.95 (***Z*-6ag**), 141.02 (***E*-6ag**), 140.05 (***Z*-6ag**), 131.64 (***Z*-6ag**), 131.59 (***E*-6ag**), 130.43 (***E*-6ag**), 130.07 (***Z*-6ag**), 128.81 (***Z*-6ag**), 128.56 (***E*-6ag**), 128.27 (***Z*-6ag**), 128.18, (***E*-6ag**) 127.91 (***E*-6ag**), 127.85 (***Z*-6ag**), 125.62 (***E*-6ag**), 124.37 (***Z*-6ag**), 119.87 (***Z*-6ag**), 119.24 (***E*-6ag**), 114.16 (***E*-6ag**), 114.11 (***Z*-6ag**), 55.47 (***E*-6ag**), 55.36 (***Z*-6ag**), 20.84 (***Z*-6ag**), 17.50 (***E*-6ag**), 16.17 (***E*-6ag**), 14.13 (***Z*-6ag**).

IR (ATR): $\nu(\text{cm}^{-1})$ 3032, 2961, 2932, 2907, 2835, 1606, 1510, 1491, 1245, 1172, 1033, 832, 525.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₇H₁₅ClO⁺ [M]⁺: 270.0806; found: 270.0806.

$[\alpha]_{\text{D}}^{20}$ = -410 (c = 1.0, CHCl₃).

e.r. (Z): 89:11 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 7.21 min, t_{R} minor = 8.28 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.097	VV	0.1522	3117.20605	312.91861	50.1549
2	8.084	VV	0.1693	3097.95239	283.98862	49.8451

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.214	MM	0.1741	4438.39355	424.88135	89.2422
2	8.282	MM	0.1832	535.02869	48.66732	10.7578

SUPPORTING INFORMATION

(R)-1-Methoxy-4-((2-(4-(trifluoromethyl)phenyl)cyclopropylidene)methyl)benzene 6ac

Prepared according to **GP3**.

Yield: 36%

R_f (20% DCM in pentane): 0.23

Appearance: colourless oil

Z/E ratio: 2.7:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.57 – 7.23 (m, 4H *E*-6ac + 6H *Z*-6ac), 7.21 (d, J = 8.1 Hz, 2H, *E*-6ac), 6.95 – 6.89 (m, 2H *E*-6ac + 1H *Z*-6ac), 6.86 (q, J = 2.3 Hz, 1H, *E*-6ac), 6.78 (d, J = 8.8 Hz, 2H, *Z*-6ac), 3.84 (s, 3H, *E*-6ac), 3.76 (s, 3H, *Z*-6ac), 2.92 (ddd, J = 8.8, 4.4, 2.0 Hz, 1H, *Z*-6ac), 2.72 (ddd, J = 8.7, 4.6, 1.6 Hz, 1H, *Z*-6ac), 2.15 (td, J = 9.0, 2.4 Hz, 1H, *E*-6ac), 1.90 (td, J = 8.9, 2.0 Hz, 1H, *Z*-6ac), 1.55 (ddd, 1H, *E*-6ac), 1.27 (ddd, J = 9.0, 4.4, 2.2 Hz, 1H, *Z*-6ac).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.23 (*E*-6ac), 159.07 (*Z*-6ac), 146.93 (*E*-6ac), 145.90 (*Z*-6ac), 130.25 (*E*-6ac), 129.90 (*Z*-6ac), 128.27 (q, J = 32.3 Hz, *Z*-6ac), 128.26 (*Z*-6ac), 126.76, 126.71, 126.37, 125.66 (q, J = 3.8 Hz, *Z*-6ac), 125.41 (q, J = 3.8 Hz, *E*-6ac), 125.32, 124.47 (q, J = 271.7 Hz, *Z*-6ac), 123.92, 120.04 (*Z*-6ac), 119.49 (*E*-6ac), 114.21 (*E*-6ac), 114.16 (*Z*-6ac), 55.49 (*E*-6ac), 55.38 (*Z*-6ac), 21.22 (*Z*-6ac), 17.97 (*E*-6ac), 16.63 (*E*-6ac), 14.51 (*Z*-6ac).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -62.29.

IR (ATR): ν (cm⁻¹) 2962, 2934, 2838, 1607, 1510, 1320, 1246, 1108, 1067, 837, 524.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₈H₁₅F₃O⁺ [M]⁺: 304.1070; found: 304.1076.

[α]_D²⁰ = -123 (c = 0.5, CHCl₃).

e.r. (Z): 85:15 (Chiralpak IC, Hexane/IPA = 99.5/0.5, λ = 230 nm, 1.00 mL/min, t_R major = 4.98 min, t_R minor = 5.66 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.923	BV	0.0949	1253.75806	200.55080	50.2310
2	5.657	BB	0.1056	1242.22693	177.50221	49.7690

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.980	MM	0.1041	2571.00879	411.46014	85.2729
2	5.661	MM	0.1188	444.02722	62.28061	14.7271

SUPPORTING INFORMATION

(R)-1-(2-(4-Methoxybenzylidene)cyclopropyl)-3-methylbenzene 6ah

Prepared according to **GP3**.

Yield: 93%

R_f (20% DCM in pentane): 0.23

Appearance: colourless oil

Z/E ratio: 2.7:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.56 (d, J = 8.7 Hz, 2H, **E-6ah**), 7.33 (d, J = 8.7 Hz, 2H, **Z-6ah**), 7.20 – 7.12 (m, 1H **E-6ah** + 1H **Z-6ah**), 7.04 – 6.90 (m, 5H **E-6ah** + 3H **Z-6ah**), 6.89 (q, 1H, **Z-6ah**), 6.86 (q, 1H, **E-6ah**), 6.80 (d, J = 8.8 Hz, 2H, **Z-6ah**), 3.85 (s, 3H, **E-6ah**), 3.77 (s, 3H, **Z-6ah**), 2.85 (ddd, J = 9.0, 4.6, 2.0 Hz, 1H, **Z-6ah**), 2.67 (ddd, J = 8.9, 4.7, 1.7 Hz, 1H, **E-6ah**), 2.33 (s, 3H, **E-6ah**), 2.32 (s, 3H, **Z-6ah**), 2.06 (td, J = 9.0, 2.4 Hz, 1H, **E-6ah**), 1.82 (td, J = 8.9, 2.0 Hz, 1H, **Z-6ah**), 1.51 (ddd, J = 9.1, 4.7, 2.4 Hz, 1H, **E-6ah**), 1.24 (ddd, J = 8.8, 4.6, 2.0 Hz, 1H, **Z-6ah**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.98 (**E-6ah**), 158.79 (**Z-6ah**), 142.41 (**E-6ah**), 141.50 (**Z-6ah**), 138.23 (**Z-6ah**), 138.13 (**E-6ah**), 130.76 (**E-6ah**), 130.41 (**Z-6ah**), 128.59, 128.40, 128.29, 128.13, 127.24, 127.15, 126.86, 126.81, 126.37, 125.19, 123.69 (**E-6ah**), 123.47 (**Z-6ah**), 119.51 (**Z-6ah**), 118.78 (**E-6ah**), 114.13 (**E-6ah**), 114.05 (**Z-6ah**), 55.46 (**E-6ah**), 55.34 (**Z-6ah**), 21.59 (**Z-6ah**), 21.53 (**E-6ah**), 21.44 (**Z-6ah**), 18.01 (**E-6ah**), 15.92 (**E-6ah**), 13.94 (**Z-6ah**).

IR (ATR): $\nu(\text{cm}^{-1})$ 2961, 2931, 2835, 1606, 1509, 1245, 1172, 1033, 849, 698.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₈H₁₈O⁺ [M]⁺: 250.1352; found: 250.1350.

$[\alpha]_{\text{D}}^{20}$ = -363 (c = 1.0, CHCl₃).

e.r. (Z): 92:8 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 7.39 min, t_{R} minor = 8.22 min)

SUPPORTING INFORMATION

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		7.452	317.336	1347.387	49.75	56.44	n.a.
2		8.125	320.548	1039.952	50.25	43.56	n.a.

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		7.390	653.130	2325.523	91.78	93.17	n.a.
2		8.223	58.460	170.523	8.22	6.83	n.a.

SUPPORTING INFORMATION

(R)-1-(2-(4-Methoxybenzylidene)cyclopropyl)-2-methylbenzene 6ai

Prepared according to **GP3**.

Yield: 46%

R_f (20% DCM in pentane): 0.23

Appearance: colourless oil

Z/E ratio: 1:1.3

¹H NMR (400 MHz, Chloroform-*d*): δ 7.69 (d, J = 8.3 Hz, 2H, **E-6ai**), 7.55 (d, J = 8.3 Hz, 2H, **Z-6ai**), 7.44 – 7.23 (m, 3H **E-6ai** + 3H **Z-6ai**), 7.16 (t, J = 7.6 Hz, 1H, **Z-6ai**), 7.13 – 7.04 (m, 4H, **E-6ai**), 6.99 (d, J = 8.4 Hz, 2H, **Z-6ai**), 6.94 (d, J = 7.6 Hz, 1H, **Z-6ai**), 3.99 (s, 3H, **E-6ai**), 3.95 (s, 3H, **Z-6ai**), 3.13 – 3.05 (m, 1H, **Z-6ai**), 2.92 – 2.83 (m, 1H, **E-6ai**), 2.69 (s, 3H, **Z-6ai**), 2.67 (s, 3H, **E-6ai**), 2.21 (td, J = 8.8, 2.2 Hz, 1H, **E-6ai**), 1.98 (t, J = 8.7 Hz, 1H, **Z-6ai**), 1.62 – 1.54 (m, 1H, **E-6ai**), 1.26 – 1.18 (m, 1H, **Z-6ai**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.94 (**E-6ai**), 158.86 (**Z-6ai**), 139.55 (**E-6ai**), 139.22 (**Z-6ai**), 137.54 (**E-6ai**), 137.23 (**Z-6ai**), 130.89 (**E-6ai**), 130.54 (**Z-6ai**), 129.90 (**Z-6ai**), 129.83 (**E-6ai**), 128.37 (**Z-6ai**), 128.04 (**E-6ai**), 126.37, 126.29, 126.24, 126.01, 125.86, 125.80, 125.62, 124.44, 120.41, 119.26, 114.12, 55.46 (**E-6ai**), 55.38 (**Z-6ai**), 19.79 (**E-6ai**), 19.75 (**Z-6ai**), 19.02 (**Z-6ai**), 15.76 (**E-6ai**), 14.28 (**E-6ai**), 12.94 (**Z-6ai**).

IR (ATR): $\nu(\text{cm}^{-1})$ 2959, 2931, 2835, 1605, 1509, 1489, 1461, 1244, 1172, 1033, 851, 752.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₈H₁₈O⁺ [M]⁺: 250.1352; found: 250.1352.

$[\alpha]_{\text{D}}^{20}$ = -196 (c = 1.0, CHCl₃).

e.r. (Z): 89:11 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 7.34 min, t_{R} minor = 8.37 min)

e.r. (E): 61:39 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 10.3 min, t_{R} minor = 11.4 min)

SUPPORTING INFORMATION

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.142	210.625	957.652	34.32	38.14	n.a.
2		7.977	210.332	800.692	34.27	31.89	n.a.
3		9.865	97.966	400.712	15.96	15.96	n.a.
4		10.803	94.783	351.850	15.44	14.01	n.a.

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.335	105.608	453.805	88.65	90.50	n.a.
2		8.368	13.527	47.624	11.35	9.50	n.a.

SUPPORTING INFORMATION

Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.347	114.686	484.459	61.10	63.33	n.a.
2		11.383	73.017	280.549	38.90	36.67	n.a.

SUPPORTING INFORMATION

(R)-3-(2-(4-Methoxybenzylidene)cyclopropyl)thiophene 6aj

Prepared according to **GP3** with the following modification: reaction run at 25 °C.

Yield: 46%

R_f (20% DCM in pentane): 0.23

Appearance: colourless oil

Z/E ratio: 2.3:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, *J* = 8.7 Hz, 2H, **E-6aj**), 7.34 (d, *J* = 8.7 Hz, 2H, **Z-6aj**), 7.24 – 7.19 (m, 3H, **E-6aj**), 7.00 (dd, *J* = 3.2, 1.2 Hz, 1H, **E-6aj**), 6.94 (dd, *J* = 3.1, 1.3 Hz, 1H, **Z-6aj**), 6.92 – 6.77 (m, 2H **E-6aj** + 5H **Z-6aj**), 3.83 (s, 3H, **E-6aj**), 3.78 (s, 3H, **Z-6aj**), 2.94 (ddd, *J* = 8.9, 4.6, 2.1 Hz, 1H, **Z-6aj**), 2.72 (ddd, *J* = 8.8, 4.8, 1.7 Hz, 1H, **E-6aj**), 2.02 (td, *J* = 8.9, 2.4 Hz, 1H, **E-6aj**), 1.78 (td, *J* = 8.8, 1.9 Hz, 1H, **Z-6aj**), 1.50 (ddd, *J* = 9.1, 4.7, 2.4 Hz, 1H, **E-6aj**), 1.24 (ddd, 1H, **Z-6aj**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.01 (**E-6aj**), 158.85 (**Z-6aj**), 142.92 (**E-6aj**), 141.91 (**Z-6aj**), 130.71 (**E-6aj**), 130.35 (**Z-6aj**), 128.34 (**Z-6aj**), 128.11 (**E-6aj**), 126.61, 126.54, 125.98, 125.80, 125.62, 125.11, 119.73 (**Z-6aj**), 119.49 (**E-6aj**), 119.34 (**Z-6aj**), 118.66 (**E-6aj**), 114.13 (**E-6aj**), 114.08 (**Z-6aj**), 55.46 (**E-6aj**), 55.38 (**Z-6aj**), 17.13 (**Z-6aj**), 15.22 (**E-6aj**), 13.79 (**E-6aj**), 12.93 (**Z-6aj**).

IR (ATR): ν(cm⁻¹) 3101, 3034, 2962, 2931, 2834, 1606, 1510, 1247, 1173, 1033, 851.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₅H₁₄OS⁺ [M]⁺: 242.0760; found: 242.0754.

[α]_D²⁰ = -221 (*c* = 1.0, CHCl₃).

e.r. (Z): 91:9 (Chiralpak IG, Hexane/IPA = 99.5/0.5, λ = 230 nm, 1.00 mL/min, t_R major = 8.91 min, t_R minor = 9.95 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.920	VV	0.1839	2088.97339	174.25636	51.0820
2	9.971	BB	0.2506	2000.47681	129.21857	48.9180

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.913	MM	0.1993	1850.46289	154.76811	90.5850
2	9.952	MM	0.2097	192.32883	15.28594	9.4150

SUPPORTING INFORMATION

(R)-3-(2-(4-Methoxybenzylidene)cyclopropyl)-1-tosyl-1H-indole 6ak

Prepared according to **GP3** with the following modification: reaction run at 25 °C.

Yield: 86%

R_f (50% DCM in pentane): 0.25

Appearance: yellow solid

Z/E ratio: 6.5:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.99 (m, 1H *E*-**6ak** + 1H *Z*-**6ak**), 7.74 (d, *J* = 8.3 Hz, 1H, *E*-**6ak**), 7.64 (d, *J* = 8.1 Hz, 1H, *Z*-**6ak**), 7.59 (d, *J* = 8.4 Hz, 2H, *Z*-**6ak**), 7.54 (d, *J* = 8.7 Hz, 1H, *E*-**6ak**), 7.39 – 7.18 (m, 10H *E*-**6ak** + 4H *Z*-**6ak**), 7.15 (d, *J* = 8.1 Hz, 2H, *Z*-**6ak**), 7.06 (s, 1H, *Z*-**6ak**), 6.97 – 6.90 (m, 1H *E*-**6ak** + 1H *Z*-**6ak**), 6.77 (d, *J* = 8.7 Hz, 2H, *Z*-**6ak**), 3.84 (s, 3H, *E*-**6ak**), 3.82 (s, 3H, *Z*-**6ak**), 2.90 (ddd, *J* = 8.4, 4.5, 2.1 Hz, 1H, *Z*-**6ak**), 2.68 (ddd, 1H, *E*-**6ak**), 2.34 (s, 3H, *Z*-**6ak**), 2.33 (s, 3H, *E*-**6ak**), 2.05 (td, *J* = 8.8, 2.4 Hz, 1H, *E*-**6ak**), 1.86 (td, *J* = 8.6, 1.9 Hz, 1H, *Z*-**6ak**), 1.59 – 1.50 (m, 1H, *E*-**6ak**), 1.31 – 1.24 (m, 1H, *Z*-**6ak**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 159.13 (*E*-**6ak**), 158.91 (*Z*-**6ak**), 144.87 (*E*-**6ak**), 144.78 (*Z*-**6ak**), 135.60 (*Z*-**6ak**), 135.49 (*E*-**6ak**), 135.47 (*E*-**6ak**), 135.20 (*Z*-**6ak**), 130.88 (*Z*-**6ak**), 130.49 (*E*-**6ak**), 130.24 (*Z*-**6ak**), 129.96 (*E*-**6ak**), 129.87 (*Z*-**6ak**), 128.46 (*Z*-**6ak**), 128.16 (*E*-**6ak**), 126.93 (*E*-**6ak**), 126.90 (*Z*-**6ak**), 124.90 (*Z*-**6ak**), 124.85 (*E*-**6ak**), 123.67 (*E*-**6ak**), 123.36 (*E*-**6ak**), 123.31 (*Z*-**6ak**), 123.20 (*E*-**6ak**), 123.00 (*Z*-**6ak**), 122.74 (*Z*-**6ak**), 122.56 (*Z*-**6ak**), 120.46 (*Z*-**6ak**), 119.88 (*E*-**6ak**), 119.69 (*Z*-**6ak**), 119.55 (*E*-**6ak**), 114.18 (*E*-**6ak**), 114.10 (*Z*-**6ak**), 114.03 (*Z*-**6ak**), 113.87 (*E*-**6ak**), 55.47 (*E*-**6ak**), 55.38 (*Z*-**6ak**), 21.68 (*Z*-**6ak**), 13.94 (*E*-**6ak**), 12.89 (*Z*-**6ak**), 12.14 (*Z*-**6ak**), 9.02 (*E*-**6ak**).

IR (ATR): ν(cm⁻¹) 3050, 2965, 2836, 1607, 1368, 1247, 1173, 1123, 746, 667, 573.

HRMS (ESI/QTOF): calcd for C₂₆H₂₄NO₃S⁺ [M+H]⁺: 430.1471; found: 430.1469.

[α]_D²⁰ = -229 (*c* = 1.0, CHCl₃).

e.r. (Z): 91:9 (Chiralpak IA, Hexane/IPA = 95:5, λ = 254 nm, 1.00 mL/min, t_R major = 9.81 min, t_R minor = 11.2 min)

Melting point: 110–112 °C

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.479	VB	0.2208	4719.85889	311.46216	49.7271
2	10.908	VV	0.2592	4771.66650	266.11673	50.2729

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.814	MM	0.2633	1.09865e4	695.48108	90.9838
2	11.191	MM	0.3034	1088.72498	59.81508	9.0162

SUPPORTING INFORMATION

Recrystallization of (R)-3-(2-(4-methoxybenzylidene)cyclopropyl)-1-tosyl-1H-indole 6ak:

(R)-3-(2-(4-methoxybenzylidene)cyclopropyl)-1-tosyl-1H-indole could be enantioenriched by recrystallization (85% yield) from Chloroform/Hexane (1:100).

Yield of recrystallization: 85%

Z/E ratio: 6.8:1

e.r. (Z): 98:2 (Chiralpak IA, Hexane/IPA = 95:5, λ = 254 nm, 1.00 mL/min, t_R major = 9.96 min, t_R minor = 11.7 min)

SUPPORTING INFORMATION

(S)-1-((2-Cyclohexylcyclopropylidene)methyl)-4-methoxybenzene 6al

Prepared according to **GP3** with the following modification: reaction run at 25 °C.

Yield: 66%

R_f (20% DCM in pentane): 0.29

Appearance: colourless oil

Z/E ratio: 3.1:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.47 (d, *J* = 8.7 Hz, 2H, **Z-6al**), 7.40 (d, *J* = 8.7 Hz, 2H, **E-6al**), 6.93 – 6.81 (m, 2H **E-6al** + 2H **Z-6al**), 6.71 (q, *J* = 2.1 Hz, 1H, **Z-6al**), 6.66 (q, *J* = 2.0 Hz, 1H, **E-6al**), 3.82 (s, 3H, **E-6al**), 3.81 (s, 3H, **Z-6al**), 1.91 – 0.82 (m, 14H **E-6al** + 14H **Z-6al**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 158.59 (**Z-6al**), 158.52 (**E-6al**), 131.48 (**Z-6al**), 131.36 (**E-6al**), 128.04 (**E-6al**), 127.74 (**Z-6al**), 127.39 (**Z-6al**), 126.86 (**E-6al**), 118.45 (**E-6al**), 116.71 (**Z-6al**), 114.01 (**Z-6al**), 113.92 (**E-6al**), 55.43, 55.40, 41.92, 40.14, 33.60, 33.33, 32.78, 32.62, 30.40, 29.86, 26.59, 26.55, 26.52, 26.46, 26.40, 26.36, 23.29, 19.65, 9.37, 5.04.

IR (ATR): ν(cm⁻¹) 2920, 2849, 1607, 1509, 1447, 1303, 1244, 1171, 1036, 844.

HRMS (ESI/QTOF): calcd for C₁₇H₂₃O⁺ [M+H]⁺: 243.1743; found: 243.1743.

[α]_D²⁰ = -35.8 (*c* = 1.0, CHCl₃).

e.r. (Z): 50:50 (Chiralpak IB, Hexane/IPA = 99.95/0.05, λ = 254 nm, 0.70 mL/min, *t_R* = 8.19 min, 9.00 min)

e.r. (E): 86:14 (Chiralpak IB, Hexane/IPA = 99.95/0.05, λ = 254 nm, 0.70 mL/min, *t_R* major = 7.37 min, *t_R* minor = 7.80 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.615	BV	0.1488	348.78537	36.72892	16.6912
2	10.474	VV	0.1620	322.38098	31.34952	15.4276
3	10.857	VB	0.1975	704.71722	55.72200	33.7244
4	11.989	BV	0.2478	713.75354	46.30317	34.1568

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.193	VB	0.1938	6507.07080	542.94415	49.7522
2	9.000	BV	0.2422	6571.89990	379.18253	50.2478

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.367	VV	0.1141	3676.87402	498.06317	85.6480
2	7.802	VV	0.1408	616.13397	66.07092	14.3520

SUPPORTING INFORMATION

9. Derivatization of chiral alkylidenecyclopropanes

(R)-4-((2-Phenylcyclopropylidene)methyl)phenol 15

(R)-Triisopropyl(4-((2-phenylcyclopropylidene)methyl)phenoxy)silane **6ca** (0.05 mmol, 1.00 equiv.) was dissolved in THF (0.18 mL, 0.30 M) and tetra-*n*-butylammonium fluoride (0.10 mmol, 2.00 equiv, 1.00 M in THF) was added dropwise. The solution was stirred at room temperature until TLC showed full conversion of starting material (approximately 5 minutes). The solution was quenched by addition of water (approximately 0.40 mL) and diluted with EtOAc. The layers were separated and the aqueous layer was washed (1×) with EtOAc. The combined organics were dried over MgSO₄, filtered and concentrated under reduced pressure. Purification via flash column chromatography (SiO₂, 20% EtOAc in pentane) afforded the title compound **15**.

Yield: 81%

Appearance: white solid

Z/E ratio: 3.2:1

¹H NMR (400 MHz, Chloroform-*d*): δ 7.48 (d, 1H, *E*-**13**), 7.31 – 7.22 (m, 3H *E*-**13** + 4H *Z*-**13**), 7.21 – 7.09 (m, 3H *E*-**13** + 3H *Z*-**13**), 6.89 – 6.81 (m, 3H *E*-**13** + 1H *Z*-**13**), 6.69 (d, *J* = 8.6 Hz, 2H, *Z*-**13**), 4.72 (bs, 1H, *E*-**13**), 4.62 (bs, 1H, *Z*-**13**), 2.87 (ddd, *J* = 9.0, 4.6, 2.1 Hz, 1H, *Z*-**13**), 2.68 (ddd, *J* = 8.9, 4.8, 1.8 Hz, 1H, *E*-**13**), 2.06 (td, *J* = 9.0, 2.4 Hz, 1H, *E*-**13**), 1.82 (td, *J* = 8.9, 2.0 Hz, 1H, *Z*-**13**), 1.49 (ddd, *J* = 9.2, 4.7, 2.5 Hz, 1H, *E*-**13**), 1.23 (ddd, *J* = 8.8, 4.7, 2.0 Hz, 1H, *Z*-**13**).

¹³C NMR (101 MHz, Chloroform-*d*): δ 154.90 (*E*-**13**), 154.73 (*Z*-**13**), 142.45 (*E*-**13**), 141.46 (*Z*-**13**), 130.94 (*E*-**13**), 130.59 (*Z*-**13**), 128.96, 128.70, 128.51, 128.36, 126.59, 126.54, 126.32, 126.07, 126.03, 125.12, 119.52 (*Z*-**13**), 118.83 (*E*-**13**), 115.60 (*E*-**13**), 115.53 (*Z*-**13**), 21.48 (*Z*-**13**), 18.08 (*E*-**13**), 15.99 (*E*-**13**), 13.97 (*Z*-**13**).

IR (ATR): ν(cm⁻¹) 3352, 3061, 3027, 2942, 2891, 2865, 1607, 1511, 1452, 1228, 1169, 696, 517.

HRMS (APPI/LTQ-Orbitrap): calcd for C₁₆H₁₄O⁺ [M]⁺: 222.1039; found: 222.1037.

[α]_D²⁰ = -220 (*c* = 1.0, CHCl₃).

e.r. (Z): 87:13 (Chiralpak IG, Hexane/IPA = 90/10, λ = 254 nm, 1.00 mL/min, t_R major = 5.93 min, t_R minor = 6.90 min)

SUPPORTING INFORMATION

Melting point: 132–136 °C

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.927	BB	0.1403	360.38934	40.32461	49.3114
2	6.906	MM	0.1747	370.45474	35.34231	50.6886

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.927	VB	0.1357	791.49890	89.04835	87.0994
2	6.901	MM	0.1678	117.23215	11.64439	12.9006

(Z)-6fa
 (>99:1 er)

NaOH (20.0 eq.)
 MeOH (0.33 M), RT, 1 h

7

SUPPORTING INFORMATION

Absolute configuration determination of 7:

Carboxylic acid **7** (10.0 mg) was dissolved in 50.0 μL of EtOAc and crystallized by slow diffusion of pentane. Crystals formed after 2 days at room temperature. X-Ray analysis confirmed the absolute stereochemistry of **7** as the (*R*)-enantiomer. Flack parameter = 0.05(6).

Ortep-representation of (*R*)-**7** (thermal ellipsoids set at 50% probability). CCDC1998995 contains the crystallographic data for (*R*)-**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SUPPORTING INFORMATION

Compound	7
Empirical Formula	C ₁₇ H ₁₄ O ₂
$D_{calc.}/\text{g cm}^{-3}$	1.263
μ/mm^{-1}	0.652
Formula Weight	250.28
Colour	clear colourless
Shape	needle
Size/mm ³	0.76×0.10×0.07
T/K	140.00(10)
Crystal System	orthorhombic
Flack Parameter	0.05(6)
Hooft Parameter	0.06(5)
Space Group	$P2_12_12_1$
$a/\text{\AA}$	6.78088(5)
$b/\text{\AA}$	17.69818(12)
$c/\text{\AA}$	21.93751(14)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2632.70(3)
Z	8
Z'	2
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu $K\alpha$
$\theta_{min}/^\circ$	3.208
$\theta_{max}/^\circ$	72.702
Measured Refl's.	48731
Ind't Refl's	5208
Refl's with $I > 2(I)$	5037
R_{int}	0.0419
Parameters	344
Restraints	0
Largest Peak/ $\text{e \AA}^{-3}$	0.179
Deepest Hole/ $\text{e \AA}^{-3}$	-0.195
GooF	1.024
wR_2 (all data)	0.0832
wR_2	0.0820
R_1 (all data)	0.0311
R_1	0.0299

SUPPORTING INFORMATION

HPLC traces of *rac*-7 and (*R*)-7:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.165	VV	0.1145	504.96320	66.53970	51.5103
2	5.590	VB	0.1173	475.35114	63.48923	48.4897

SUPPORTING INFORMATION

Methyl 4-(((1*R*,2*R*)-2-phenylcyclopropyl)methyl)benzoate **8**

A sealed vial containing a solution of (R,Z)-methyl 4-((2-phenylcyclopropylidene)methyl)benzoate (**6fa**) (0.05 mmol, 1.00 equiv., $>99:1$ er) in DCM (1.00 mL) was equipped with a H_2 balloon. A solution of Crabtree's catalyst (1.5 μmol , 3.00 mol%) in DCM (502 μL) was added to the reaction vessel. The solution was stirred at room temperature for 16 hours, whereby TLC indicated disappearance of starting material. The mixture was filtered over a silica plug (eluting with DCM) and concentrated under reduced pressure. Purification of the crude product from impurities *via* preparative HPLC (*Purification conditions*: Chiralpak IB, Hexane/IPA = 98/2, $\lambda = 254$ nm, 18.0 mL/min) yielded pure (R,R)-**8**.

Determination of the relative stereochemistry: the relative stereochemistry was assigned to be *cis* by the presence of ^1H NOE correlation between H_a and H_b .

Note1: A sample of the major enantiomer of (Z)-**6fa** was obtained by preparative HPLC (Chiralpak IB, Hexane/IPA = 99.5/0.5, 18.0 mL/min).

Note2: No enantioenrichment of (R,R)-**8** was obtained from purification of the product via preparative HPLC (see section HPLC traces of (rac)-8, (R,R)-8 purified and (R,R)-8 crude below).

Yield: 85%

Appearance: colourless oil

^1H NMR (400 MHz, Benzene- d_6): δ 8.09 (d, $J = 8.3$ Hz, 2H), 7.17 – 6.99 (m, 5H), 6.88 (d, $J = 8.3$ Hz, 2H), 3.50 (s, 3H), 2.30 (dd, $J = 15.2, 6.7$ Hz, 1H), 2.07 (dd, $J = 15.3, 7.8$ Hz, 1H), 1.95 (td, $J = 8.6, 6.0$ Hz, 1H), 1.14 – 0.97 (m, 1H), 0.81 – 0.70 (m, 1H), 0.65 – 0.56 (m, 1H).

^{13}C NMR (101 MHz, Chloroform- d): δ 167.34, 147.72, 138.90, 129.64, 129.23, 128.45, 128.14, 127.83, 126.11, 52.09, 34.67, 21.45, 19.61, 9.92.

IR (ATR): $\nu(\text{cm}^{-1})$ 3062, 3026, 3001, 2950, 2850, 1716, 1434, 1273, 1178, 1107, 1020, 753, 699.

HRMS (APPI/LTQ-Orbitrap): calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2^+ [\text{M}]^+$: 266.1301; found: 266.1300.

$[\alpha]_{\text{D}}^{20}$ = +21.7 ($c = 0.1$, CHCl_3).

e.r.: 96:4 (Chiralpak ID, Hexane/IPA = 99/1, $\lambda = 254$ nm, 1.00 mL/min, t_{R} major = 9.74 min, t_{R} minor = 8.93 min)

SUPPORTING INFORMATION

HPLC traces of (rac)-8, (R,R)-8 purified and (R,R)-8 crude:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.063	MM	0.1929	460.23874	39.76812	49.9251
2	9.864	MM	0.2236	461.61972	34.41035	50.0749

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.930	VB	0.1327	30.91566	3.03842	3.6790
2	9.738	VV	0.2057	809.41876	57.69342	96.3210

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.864	VV	0.1748	99.78941	7.23858	4.0093
2	9.638	BV	0.2062	2389.18530	171.80786	95.9907

SUPPORTING INFORMATION

Methyl (R,E)-4-(3-phenylbut-1-en-1-yl)benzoate 9

In a flame dried vial and under a N_2 atmosphere, $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (1.82 μmol , 8.00 mol%) and (rac) -2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (rac) -BINAP (2.18 μmol , 9.60 mol%) were dissolved in EtOH (354 μL) and stirred for 15 min. Subsequently a solution of (Z)-**6fa** (22.7 μmol , 1.00 equiv.) in EtOH (100 μL) was added. The vial was transferred into an autoclave and the reactor was purged three times with H_2 . The reactor was then pressurized to 50 bar with H_2 and the mixture was stirred at ambient temperature for 14h. The reaction mixture was filtered over a plug of silica (eluting with CH_2Cl_2) and concentrated under reduced pressure. Purification of the crude product via preparative HPLC (Purification conditions: Chiralpak IC, Hexane/IPA =99.5/0.05, λ = 254 nm, 18.0 mL/min) yielded pure (R,E)-**9**. Analytical data are in accordance with literature.^[11] The other product of the reaction is (R)-**10**.

Note1: A sample of the major enantiomer of (Z)-**6fa** was obtained by preparative HPLC (Chiralpak IB, Hexane/IPA =99.5/0.5, 18.0 mL/min).

Note2: No enantioenrichment of (R,E)-**9** was obtained from purification of the product via preparative HPLC (see section HPLC traces of rac-9, (R,E)-9 purified and (R,E)-9 crude below).

Yield: 60%

Appearance: colourless oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.30 – 7.20 (m, 3H), 6.52 (dd, J = 15.9, 6.7 Hz, 1H), 6.44 (d, J = 16.2 Hz, 1H), 3.90 (s, 3H), 3.67 (p, J = 6.9 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.12, 145.19, 142.24, 138.24, 130.01, 128.73, 128.61, 127.88, 127.44, 126.55, 126.15, 52.19, 42.86, 21.17.

$[\alpha]_{\text{D}}^{20}$ = +28.3 (c = 0.1, CHCl_3).

e.r.: >99:1 (Chiralpak IC, Hexane/IPA =99.5/0.5, λ = 280 nm, 1.00 mL/min, t_{R} major = 21.5 min)

SUPPORTING INFORMATION

HPLC traces of (rac)-9, (R,E)-9 purified and (R,E)-9 crude:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.180	BV	0.3333	5942.52002	263.26355	50.2310
2	20.003	VV	0.3800	5887.87158	241.83928	49.7690

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.537	BV	0.3735	3420.49927	129.77007	100.0000

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.528	BB	0.3534	1610.75464	59.96524	100.0000

SUPPORTING INFORMATION

Methyl (R)-4-(3-phenylbutyl)benzoate 10

In a flame dried vial and under a N_2 atmosphere, $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (3.41 μmol , 15.0 mol%) and $(\text{rac})\text{-2,2'}$ -bis(diphenylphosphino)-1,1'-binaphthalene $(\text{rac})\text{-BINAP}$ (4.09 μmol , 18.0 mol%) were dissolved in EtOH (354 μL) and stirred for 15 min. Subsequently a solution of **(Z)-6fa** (22.7 μmol , 1.00 equiv.) in EtOH (100 μL) was added. The vial was transferred into an autoclave and the reactor was purged three times with H_2 . The reactor was then pressurized to 50 bar with H_2 and the mixture was stirred at ambient temperature for 20h. The reaction mixture was filtered over a plug of silica (eluting with CH_2Cl_2) and concentrated under reduced pressure. Purification of the crude via silica gel column chromatography (n -pentane:EtOAc 98:2) yielded pure **(R)-10**.

Note1: A sample of the major enantiomer of **(Z)-6fa** was obtained by preparative HPLC (Chiralpak IB, Hexane/IPA =99.5/0.5, 18.0 mL/min).

Yield: 90%

Appearance: colourless oil

^1H NMR (400 MHz, Chloroform-*d*): δ 7.93 (d, J = 8.2 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.25 – 7.13 (m, 5H), 3.90 (s, 3H), 2.71 (h, J = 7.0 Hz, 1H), 2.64 – 2.49 (m, 2H), 2.01 – 1.83 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.31, 148.25, 147.04, 129.78, 128.60, 128.54, 127.82, 127.18, 126.23, 52.11, 39.70, 39.66, 34.15, 22.63.

IR (ATR): $\nu(\text{cm}^{-1})$ 3061, 3027, 2953, 2924, 2853, 1720, 1435, 1277, 1179, 1108, 763, 700.

HRMS (APCI/QTOF): calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2^+$ $[\text{M} + \text{H}]^+$: 269.1536; found: 269.1536.

$[\alpha]_{\text{D}}^{20}$ = -14.2 (c = 0.2, CHCl_3).

e.r.: >99:1 (Chiralpak IC, Hexane/IPA =99.5/0.5, λ = 254 nm, 1.00 mL/min, t_{R} major = 13.0 min)

SUPPORTING INFORMATION

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.007	BV	0.2132	2273.18384	166.53427	49.3052
2	12.473	VB	0.2182	2337.24707	164.11290	50.6948

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.011	BB	0.2308	1805.88098	119.18138	100.0000

SUPPORTING INFORMATION

X-ray crystallographic data**(*R,R,N,N'E,N,N'E*)-*N,N'*-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methyl-2,6-bis((*R*)-1-phenylethyl)aniline) L1**

(*R,R*)-**L1** (40.0 mg) was dissolved in 100 μ L of EtOAc and crystallized by slow diffusion of pentane. Crystals formed after 4 days at room temperature.

Ortep-representation of (*R,R*)-**L1** (thermal ellipsoids set at 50% probability). CCDC1998992 contains the crystallographic data for (*R,R*)-**L1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SUPPORTING INFORMATION

Compound	L1
Empirical Formula	C ₅₈ H ₅₆ N ₄
$D_{calc.}/\text{g cm}^{-3}$	1.154
μ/mm^{-1}	0.511
Formula Weight	809.06
Colour	clear pale yellow
Shape	plate
Size/mm ³	0.23×0.16×0.06
T/K	140.00(10)
Crystal System	monoclinic
Flack Parameter	0.2(5)
Space Group	$P2_1$
$a/\text{\AA}$	8.3188(2)
$b/\text{\AA}$	27.4105(9)
$c/\text{\AA}$	10.4707(3)
$\alpha/^\circ$	90
$\beta/^\circ$	102.858(3)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2327.70(13)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu $K\alpha$
$\Theta_{min}/^\circ$	4.331
$\Theta_{max}/^\circ$	75.471
Measured Refl's.	21945
Ind't Refl's	9215
Refl's with $I > 2\sigma(I)$	8144
R_{int}	0.0419
Parameters	570
Restraints	1
Largest Peak/ $\text{e \AA}^{-3}$	0.161
Deepest Hole/ $\text{e \AA}^{-3}$	-0.149
GooF	1.033
wR_2 (all data)	0.1030
wR_2	0.0964
R_1 (all data)	0.0503
R_1	0.0415

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-Naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-(3,5-difluorophenyl)ethyl)-4-methylaniline) L9

(R,R)-**L9** (40.0 mg) was dissolved in 100 μ L of CPME and crystallized by slow diffusion of pentane. Crystals formed after 5 days at room temperature.

Ortep-representation of (R,R)-**L9** (thermal ellipsoids set at 50% probability). CCDC1998994 contains the crystallographic data for (R,R)-**L9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SUPPORTING INFORMATION

Compound	L9
Empirical Formula	C ₅₈ H ₄₈ F ₈ N ₄
$D_{calc.}/\text{g cm}^{-3}$	1.159
μ/mm^{-1}	0.726
Formula Weight	953.00
Colour	clear intense yellow
Shape	prism
Size/mm ³	0.44×0.33×0.13
T/K	140.00(10)
Crystal System	monoclinic
Flack Parameter	0.09(7)
Space Group	$P2_1$
$a/\text{\AA}$	11.8828(4)
$b/\text{\AA}$	15.0104(3)
$c/\text{\AA}$	15.4953(4)
$\alpha/^\circ$	90
$\beta/^\circ$	98.752(3)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2731.64(13)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu $K\alpha$
$\theta_{min}/^\circ$	2.885
$\theta_{max}/^\circ$	72.603
Measured Refl's.	45337
Ind't Refl's	10421
Refl's with $I > 2(I)$	9742
R_{int}	0.0507
Parameters	688
Restraints	254
Largest Peak/ $\text{e \AA}^{-3}$	0.429
Deepest Hole/ $\text{e \AA}^{-3}$	-0.212
GooF	1.049
wR_2 (all data)	0.1832
wR_2	0.1776
R_1 (all data)	0.0655
R_1	0.0628

SUPPORTING INFORMATION

 ^1H , ^{13}C and ^{19}F NMR Spectra***2-Ethyl-1,8-naphthyridine 3***

SUPPORTING INFORMATION

2,7-diethyl-1,8-naphthyridine 11

SUPPORTING INFORMATION

1,1'-(1,8-naphthyridine-2,7-diyl)diethanone 2

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2-(1-(3,5-difluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 13

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2,6-bis(1-phenylvinyl)aniline 12b

SUPPORTING INFORMATION

2,6-bis(1-phenylvinyl)-4-(trifluoromethyl)aniline 12e

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2,6-bis(1-(4-(tert-butyl)phenyl)vinyl)-4-methylaniline 12f

SUPPORTING INFORMATION

4-methyl-2,6-bis(1-(naphthalen-2-yl)vinyl)aniline 12g

SUPPORTING INFORMATION

2,6-bis(1-(3,5-difluorophenyl)vinyl)-4-methylaniline 12i

SUPPORTING INFORMATION

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2,6-bis((R)-1-phenylethyl)aniline 1b

SUPPORTING INFORMATION

2,6-bis((R)-1-phenylethyl)-4-(trifluoromethyl)aniline 1e

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2,6-bis((R)-1-(4-(tert-butyl)phenyl)ethyl)-4-methylaniline 1f

SUPPORTING INFORMATION

4-methyl-2,6-bis((R)-1-(naphthalen-2-yl)ethyl)aniline 1g

SUPPORTING INFORMATION

2,6-bis((R)-1-(3,5-difluorophenyl)ethyl)-4-methylaniline 1i

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(R,R,N,N'E,N,N'E)-N,N'-(1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methyl-2,6-bis((R)-1-phenylethyl)aniline) L1

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-phenylethyl)aniline) L2

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methoxy-2,6-bis((R)-1-phenylethyl)aniline) L3

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-(tert-butyl)-2,6-bis((R)-1-phenylethyl)aniline) L4

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-phenylethyl)-4-(trifluoromethyl)aniline) L5

SUPPORTING INFORMATION

SUPPORTING INFORMATION

(E)-N-(1-(7-((E)-1-((2,6-bis((R)-1-(4-(tert-butyl)phenyl)ethyl)-4-methylphenyl)imino)ethyl)-1,8-naphthyridin-2-yl)ethylidene)-2-((R)-1-(3-(tert-butyl)phenyl)ethyl)-6-((R)-1-(4-(tert-butyl)phenyl)ethyl)-4-methylaniline L6

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(4-methyl-2,6-bis((R)-1-(naphthalen-2-yl)ethyl)aniline) L7

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-(3,5-dimethylphenyl)ethyl)-4-methylaniline) L8

SUPPORTING INFORMATION

(R,R,N,N'E,N,N'E)-N,N'-((1,8-naphthyridine-2,7-diyl)bis(ethan-1-yl-1-ylidene))bis(2,6-bis((R)-1-(3,5-difluorophenyl)ethyl)-4-methylaniline) L9

SUPPORTING INFORMATION

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4-(2,2-dichlorovinyl)phenoxy)triisopropylsilane 14

SUPPORTING INFORMATION

(R)-1-methoxy-4-((2-phenylcyclopropylidene)methyl)benzene 6aa

SUPPORTING INFORMATION

(R)-1-methyl-4-((2-phenylcyclopropylidene)methyl)benzene 6ba

SUPPORTING INFORMATION

(R)-triisopropyl(4-((2-phenylcyclopropylidene)methyl)phenoxy)silane 6ca

SUPPORTING INFORMATION

(*R*)-(2-benzylidenecyclopropyl)benzene 6da

SUPPORTING INFORMATION

(R)-1-((2-phenylcyclopropylidene)methyl)-4-(trifluoromethyl)benzene 6ea

SUPPORTING INFORMATION

SUPPORTING INFORMATION

(R)-methyl 4-((2-phenylcyclopropylidene)methyl)benzoate 6fa

SUPPORTING INFORMATION

(R,Z)-methyl 4-((2-phenylcyclopropylidene)methyl)benzoate (R,Z)-6fa

SUPPORTING INFORMATION

(*E*)-methyl 4-((2-phenylcyclopropylidene)methyl)benzoate (*E*)-6fa

SUPPORTING INFORMATION

(R)-1-fluoro-4-((2-phenylcyclopropylidene)methyl)benzene 6ga

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(R)-2-((2-phenylcyclopropylidene)methyl)naphthalene 6ha

SUPPORTING INFORMATION

(*R*)-1-methoxy-3-((2-phenylcyclopropylidene)methyl)benzene 6ia

SUPPORTING INFORMATION

(R)-1-methoxy-2-((2-phenylcyclopropylidene)methyl)benzene 6ja

SUPPORTING INFORMATION

(R)-4-((2-(4-methoxyphenyl)cyclopropylidene)methyl)tetrahydro-2H-pyran 6kb

SUPPORTING INFORMATION

(R)-4-((2-(4-(trifluoromethyl)phenyl)cyclopropylidene)methyl)tetrahydro-2H-pyran 6kc

SUPPORTING INFORMATION

SUPPORTING INFORMATION

(R)-2-(2-(4-methoxybenzylidene)cyclopropyl)naphthalene 6ad

SUPPORTING INFORMATION

(R)-1-methoxy-4-((2-(p-tolyl)cyclopropylidene)methyl)benzene 6ae

SUPPORTING INFORMATION

(R)-methyl 4-(2-(4-methoxybenzylidene)cyclopropyl)benzoate 6af

SUPPORTING INFORMATION

(R)-1-chloro-4-(2-(4-methoxybenzylidene)cyclopropyl)benzene 6ag

SUPPORTING INFORMATION

(R)-1-methoxy-4-((2-(4-(trifluoromethyl)phenyl)cyclopropylidene)methyl)benzene 6ac

SUPPORTING INFORMATION

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(R)-1-(2-(4-methoxybenzylidene)cyclopropyl)-3-methylbenzene 6ah

SUPPORTING INFORMATION

(R)-1-(2-(4-methoxybenzylidene)cyclopropyl)-2-methylbenzene 6ai

SUPPORTING INFORMATION

(R)-3-(2-(4-methoxybenzylidene)cyclopropyl)thiophene 6aj

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(R)-3-(2-(4-methoxybenzylidene)cyclopropyl)-1-tosyl-1H-indole 6ak

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(S)-1-((2-cyclohexylcyclopropylidene)methyl)-4-methoxybenzene 6al

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(R)-4-((2-phenylcyclopropylidene)methyl)phenol 15

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(*R,Z*)-4-((2-phenylcyclopropylidene)methyl)benzoic acid 7

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Methyl 4-(((1*R*,2*R*)-2-phenylcyclopropyl)methyl)benzoate **8**

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Methyl (R)-4-(3-phenylbutyl)benzoate 10

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