Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Carbocycles *via* enantioselective inter- and intramolecular iridium-catalysed allylic alkylations

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General Procedure I: Intermolecular Asymmetric Allylic Alkylation

In a flame-dried Schlenk tube under an atmosphere of argon, $[Ir(COD)Cl]_2$ (13.4 mg, 0.02 mmol) and the chiral ligand **L** (0.04 mmol), ratio Ir:L = 1:1, were dissolved in dry THF (0.5 mL), forming a yellow-orange solution after stirring for 5 min. Tetrahydrothiophene (18 µL, 0.2 mmol) and TBD (17 mg, 0.12 mmol) were added and the mixture was stirred for 2 h. In the meantime, sodium hydride (2 mmol) was suspended in dry THF (4 mL) in a second flame-dried Schlenk tube under an atmosphere of argon and dimethyl malonate (2.2 mmol) was added drop by drop. The mixture was stirred for 30 min until a clear solution resulted. The substrate (1 mmol), CuI (38 mg, 0.2 mmol) and the solution of dimethyl sodiomalonate were added to the first Schlenk tube. The reaction mixture was stirred for the appropriate time at room temperature until TLC control indicated complete consumption of the substrate. Diethyl ether (5 mL) and saturated NH_4Cl solution (5 mL) were added. The phases were separated. The aqueous layer was extracted with diethyl ether (2 x 10 mL). The combined organic phases were washed with brine (10 mL), the aqueous layer was re-extracted with diethyl ether (10 mL). The combined ethereal solutions were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The ratio of regioisomers was determined by ^1H NMR of the crude product. Purification by flash column chromatography on silica gel yielded the sum of regioisomers. Pure fractions of branched alkylation products were derivatized and/or applied to chiral HPLC analysis.

(+)-(*R*)-Dimethyl (1-Phenyl-prop-2-enyl)malonate (2a)

Optical rotation:

$[\alpha]_D^{27}$ = +35.7, $[\alpha]_{578}^{27}$ = +37.6, $[\alpha]_{546}^{27}$ = +43.7, $[\alpha]_{436}^{27}$ = +82.0,

$[\alpha]_{365}^{27}$ = +146.8 (*c* = 1.26, $CHCl_3$)

95 %ee (*R*) according to HPLC

(Lit.:[1] $[\alpha]_D^{22}$ = +34.5 [*c* = 1.03, $CHCl_3$, 99 %ee (*R*)]).

HPLC (Daicel Chiracel OJ-H, solvent: *n*-hexane/*i*-propanol 97:3, flow 0.5 ml/min, UV-detection at 220 nm, column temperature 30°C):

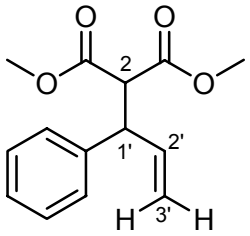
[1] F. Glorius, M. Neuberger, A. Pfaltz, *Helv. Chim. Acta* **2001**, *84*, 3178-3196.

t_R[(-)(*S*)-**2a**] = 57.59 min,

t_R[(+)(*R*)-**2a**] = 63.86 min (major enantiomer).

Enantiomeric excess: 96 %ee (*R*)

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY**:



2a

δ = 3.47 (s, 3 H, COOC<u>H</u>$_3$), 3.72 (s, 3 H, COOC<u>H</u>$_3$), 3.85 (d, $J_{2,1'}$ = 11.1 Hz, 1 H, 2-H), 4.09 (dd, $J_{2,1'}$ = 10.9 Hz, $J_{1',2'}$ = 8.3 Hz, 1 H, 1'-H), 5.07 (ddd, $^4J_{1',3'}$ = 1.0 Hz, $J_{2',3'}$ = 10.2 Hz, $J_{3',3'}$ = 1.0 Hz, 1 H, 3'-H), 5.10 (ddd, $^4J_{1',3'}$ = 1.3 Hz, $J_{2',3'}$ = 16.8 Hz, $J_{3',3'}$ = 1.3 Hz, 1 H, 3'-H), 5.98 (ddd, $J_{1',2'}$ = 8.1 Hz, $J_{1',3'}$ = 17.1 Hz, $J_{2',3'}$ = 10.2 Hz, 1 H, 2'-H), 7.16-7.32 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **H,C-COSY**:

δ = 49.69 (d, C-1'), 52.37, 52.54 (2 q, 2 COO<u>C</u>H$_3$), 57.32 (d, C-2), 116.59 (t, C-3'), 127.10 127.88, 128.61 (3 d, Ph-C), 137.76 (d, C-2'), 139.90 (q, Ph-$C_{quart.}$), 167.79, 168.17 (2 s, 2 <u>C</u>OOCH$_3$).

HR-MS (FAB):

$[M+H]^+$ = $C_{14}H_{17}O_4$ Calcd 249.1127 Found 249.1116

Elemental analysis:

$C_{14}H_{16}O_4$	Calcd	C 67.73	H 6.50
(248.27)	Found	C 67.91	H 6.52

(+)-(*S*)-Dimethyl [(2*E*)-3-Phenyl-1-vinylprop-2-enyl]malonate (2b)

Optical rotation:

$[\alpha]_D^{27}$ = +20.8, $[\alpha]_{578}^{27}$ = +22.0, $[\alpha]_{546}^{27}$ = +26.3, $[\alpha]_{436}^{27}$ = +56.2,

$[\alpha]_{365}^{27}$ = +126.9 (*c* = 1.28, $CHCl_3$)

96 %ee (+)(*S*) according to HPLC

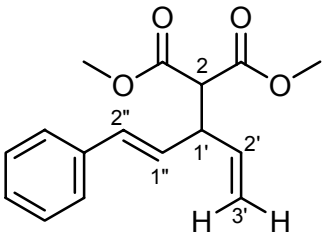
HPLC (Daicel Chiracel OJ-H, solvent: *n*-hexane/*i*-propanol 90:10, flow 0.5 ml/min, UV-detection at 254 nm, column temperature 28°C):

t_R[(+)(*S*)-**2b**] = 25.69 min (major enantiomer),

t_R[(-)(*R*)-**2b**] = 29.07 min.

Enantiomeric excess: 96 %ee (*S*).

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY**:



2b

δ = 3.57 (d, $J_{2,1'}$ = 9.2 Hz, 1 H, 2-H), 3.66 (m, 1 H, 2-H, under signal of methyl group), 3.67 (s, 3 H, COOC<u>H</u>$_3$), 3.71 (s, 3 H, COOC<u>H</u>$_3$), 5.12 (d, $J_{3',3'}$ = 10.7 Hz, 1 H, 3'-H), 5.17 (d, $J_{1",3'}$ = 18.5 Hz, 1 H, 3'-H), 5.87 (ddd, $J_{1',2'}$ = 7.3 Hz, $J_{2',3'}$ = 17.3 Hz, $J_{2',3'}$ = 10.2 Hz, 1 H, 2'-H), 6.14 (dd, $J_{1',1"}$ = 8.0 Hz, $J_{1",2"}$ = 15.9 Hz, 1 H, 1"-H), 6.47 (d, $J_{1",2"}$ = 15.8 Hz, 1 H, 2"-H), 7.15-7.37 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.47 MHz), **DEPT**, **H,C-COSY**:

δ = 47.02 (d, C-1'), 52.44 (q, COO<u>C</u>H$_3$), 56.56 (d, C-2), 117.11 (t, C-3'), 126.32 127.54, 128.48 (3d, Ph-C), 127.77 (d, C-1"), 132.26 (d, C-2"), 136.63 (d, C-2'), 136.89 (s, Ph-$C_{quart.}$), 168.07, 168.10 (2s, <u>C</u>OOCH$_3$).

HR-MS (FAB):

$[M+Na]^+$ = $C_{16}H_{18}O_4Na$	Calcd	297.1103	Found	297.1109
$[M+H]^+$ = $C_{16}H_{19}O_4$	Calcd	275.1283	Found	275.1262

Elemental analysis:

$C_{16}H_{18}O_4$	Calcd	C 70.06	H 6.61
(274.31)	Found	C 69.84	H 6.67

(+)-(*R*)-Dimethyl [1-(2-Phenylethyl)prop-2-enyl]malonate (2c)

Optical rotation:

$[\alpha]_D^{28}$ = +12.5, $[\alpha]_{578}^{28}$ = +13.1, $[\alpha]_{546}^{28}$ = +15.4, $[\alpha]_{436}^{28}$ = +29.0, $[\alpha]_{365}^{28}$ = +52.7

(*c* = 0.22, $CHCl_3$)

94 %ee (*R*) according to HPLC

(Lit.:[1] $[\alpha]_D^{20}$ = +11.4 [*c* = 0.63, $CHCl_3$, 93 %ee (*R*)]).

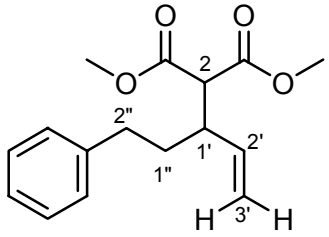
HPLC (Daicel Chiracel OJ-H, solvent: *n*-hexane/*i*-propanol 98:2, flow 0.5 ml/min, UV-detection at 220 nm, column temperature 30°C):

t_R[(+)(*R*)-**2c**] = 37.27 min (major enantiomer),

t_R[(-)(*S*)-**2c**] = 47.72 min.

Enantiomeric excess: 96 %ee (*R*)

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY**, **H,C-COSY**:



2c

δ = 1.61 (dddd, $J_{1',1"}$ = 10.2 Hz, $J_{1",1"}$ = 13.4 Hz, $J_{1",2"}$ = 5.0 Hz, $J_{1",2"}$ = 10.2 Hz, 1 H, 1"-H), 1.79 (dddd, $J_{1',1"}$ = 3.4 Hz, $J_{1",1"}$ = 13.5 Hz, $J_{1",2"}$ = 6.7 Hz, $J_{1",2"}$ = 10.2 Hz, 1 H, 1"-H), 2.49 (ddd, $J_{1",2"}$ = 10.3 Hz, $J_{1",2"}$ = 6.7 Hz, $J_{2",2"}$ = 13.8 Hz, 1 H, 2"-H), 2.68 (ddd, $J_{1",2"}$ = 4.7 Hz, $J_{1",2"}$ = 10.2 Hz, $J_{2",2"}$ = 14.0 Hz, 1 H, 2"-H), 2.81 (dddd, $J_{2,1'}$ = 9.4 Hz, $J_{1',1"}$ = 9.5 Hz, $J_{1',1"}$ = 3.3 Hz, $J_{1',2'}$ = 9.5 Hz, 1 H, 1'-H), 3.40 (d, $J_{2,1'}$ = 8.7 Hz, 1 H, 2-H), 3.67 (s, 3 H, COOC$\underline{H}_3$), 3.69 (s, 3 H, COOC$\underline{H}_3$), 5.12 (dd, $J_{2',3'}$ = 17.4 Hz, $J_{3',3'}$ = 1.0 Hz, 1 H, 3'-H), 5.14 (dd, $J_{2',3'}$ = 10.3 Hz, $J_{3',3'}$ = 1.6 Hz, 1 H, 3'-H), 5.70 (ddd, $J_{1',2'}$ = 9.5 Hz, $J_{2',3'}$ = 16.7 Hz, $J_{2',3'}$ = 10.6 Hz, 1 H, 2'-H), 7.10-7.29 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **H,C-COSY**:

δ = 33.31 (t, C-3'), 34.03 (t, C-2'), 43.88 (d, C-1'), 52.24, 52.40 (2 q, 2 COO<u>C</u>H_3), 56.80 (d, C-2), 118.13 (t, C-2"), 125.85, 128.33, 128.36 (3 d, Ph-C), 137.67 (d, C-1"), 141.69 (s, Ph-$C_{quart.}$), 168.45, 168.60 (2 s, 2 <u>C</u>$OOCH_3$).

HR-MS (FAB):

$[M+H]^+$ = $C_{16}H_{21}O_4$ Calcd 277.1440 Found 277.1479

Elemental analysis:

$C_{16}H_{20}O_4$	Calcd	C 69.54	H 7.30
(276.33)	Found	C 69.57	H 7.32

(+)(*R*)-Dimethyl [1-([*tert*-Butyl(diphenyl)silyl]oxymethyl)prop-2-enyl]malonate (2d)

Optical rotation:

$[\alpha]_D^{22}$ = +27.9, $[\alpha]_{578}^{22}$ = +29.4, $[\alpha]_{546}^{22}$ = +34.2, $[\alpha]_{436}^{22}$ = +56.1, $[\alpha]_{365}^{22}$ = +98.8

(c = 0.83, $CHCl_3$)

97 %ee (*R*) according to HPLC

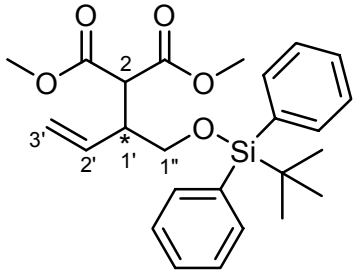
HPLC Daicel Chiracel AD-H, solvent: *n*-hexane/*i*-propanol 99:1, flow 0.5 ml/min, UV-detection at 220 nm, column temperature r.t.):

t_R [(+)-**2d**] = 12.3 min,

t_R [(-)-**2d**] = 14.9 min

Enantiomeric excess: 97 %ee (*R*)

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY**, **H,C-COSY**:



2d

δ = 1.06 (s, 9H, *t*-Bu), 3.03 (ddt, ^3J = 8.9 Hz, ^3J = 8.9 Hz, ^3J = 5.2 Hz, 1H, 1'-H), 3.68 (s, 3H, COOC$\underline{H}_3$), 3.69 (s, 3H, COOC$\underline{H}_3$), 3.72 (dd, ^3J = 5.2 Hz, ^3J = 4.2 Hz, 2H, 1"-H), 3.88 (d, ^3J = 8.5 Hz, 1H, 2-H), 5.08-5.16 (m, 2H, 3'-H), 5.92 (ddd, ^3J = 17.0 Hz, ^3J = 10.5 Hz, ^3J = 9.1 Hz, 1H, 2'-H), 7.34-7.46 (m, 6H, Ph-H), 7.61-7.65 (m, 4H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **H,C-COSY**:
δ = 19.4 ($\underline{C}(CH_3)_3$), 26.9 ($C(\underline{C}H_3)_3$), 27.0 ($C(\underline{C}H_3)_3$), 46.3 (C-1'), 52.4, 52.5, 52.7 (2 COO$\underline{C}H_3$ and C-2), 118.3 (C-3'), 127.6, 129.8, 133.4 (3 Ph-C), 135.6, 135.7 (Ph-C and C-2'), 168.8, 169.0 (2 $\underline{C}OOCH_3$).

MS (FAB):
m/z [%] = 441 (32) [M^++H], 383 (100) [M^+-*t*-Bu], 363 (30).

HR-MS (FAB):
$[M+H]^+$ = $C_{25}H_{33}O_5Si$ Calcd 440.2019 Found 441.2120

Elemental analysis:

$C_{25}H_{32}O_5Si$	Calcd	C 68.15	H 7.32
(440.6)	Found	C 68.38	H 7.34

(+)-Dimethyl 2-Allyl-[(*S*)-1-phenylallyl]malonate (2e)

(+)-(*R*)-(**2a**) (199 mg, 0.80 mmol) was added to a suspension of NaH (95 %, 21.5 mg, 0.85 mmol) in dry THF (5 ml) at room temperature under an argon atmosphere. Freshly distilled allyl bromide (605 mg, 5.0 mmol) was added dropwise to the clear solution at room temperature to form a white precipitate. The reaction mixture was stirred for 3 h until TLC control [petroleum ether/ethyl acetate 10:1; R_f(**2e**) = 0.35, R_f(**2a**) = 0.24, $KMnO_4$] indicated complete consumption of the substrate. Water (10 mL) was added and the mixture was extracted with diethyl ether (3 x 15 mL). The combined organic layers were washed with brine (2 x 30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product. This was subjected to flash chromatography on 40 g of silica gel (petroleum ether/ethyl acetate 15:1) to yield (+)(S)-**2e** (190 mg, 82 %) as colorless oil.

Optical rotation:

$[\alpha]_D^{26}$ = +64, $[\alpha]_{578}^{26}$ = +67, $[\alpha]_{546}^{26}$ = +77, $[\alpha]_{436}^{26}$ = +138,

$[\alpha]_{365}^{26}$ = +226 (*c* = 0.57, MeOH)

98 %ee (*S*) according to HPLC

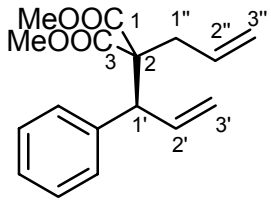
HPLC (Daicel Chiracel AD-H, solvent: *n*-hexane/*i*-propanol 99:1, flow 0.5 ml/min, UV-detection at 210 nm, column temperature 20°C):

t_R[(+)(*S)*-**2e**] = 15.22 min (major enantiomer),

t_R[(-)(*R*)-**2e**] = 13.79 min

Enantiomeric excess: 98 %ee (*S)*

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,C-COSY**:



2e

δ = 2.40 (dd, $^2J_{1",1"}$ = 14 Hz, $^3J_{1",2"}$ = 6 Hz, 1 H, 1"-H_a), 2.57 (dd, $^2J_{1",1"}$ = 14 Hz, $^3J_{1",2"}$ = 6 Hz, 1 H, 1"-H_b), 3.65, 3.72 (2 s, 6 H, $COOCH_3$), 3.99 (d, $^3J_{1',2'}$ = 9 Hz, 1 H, 1'-H), 4.98-5.11 (m, 4 H, 3'-H and 3"-H), 5.67-5.81 (m, 1 H, 2'-H), 6.32-6.44 (m, 1 H, 2"-H), 7.11-7.20 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **H,C-COSY**:

δ = 39.41 (t, C-1''), 50.02, 51.98 (2 q, $COO\underline{C}H_3$), 54.52 (d, C-1'), 63.00 (s, C-2), 117.24 (t, C-3' or C-3''), 118.56 (t, C-3' or C-3'), 127.23, 128.27, 129.14 (d, Ph-C), 133.24 (d, C-2' or C-2''), 137.59 (d, C-2' or C-2''), 138.88 (s, Ph-C), 170.37, 170.59 (2 s, $\underline{C}OOCH_3$).

GC/MS: (EI)

t_R = 11.19 min,

m/z [%] = 288 (1) $[M]^+$, 117 (100) $[M\text{-}C_8H_{11}O_4]^+$.

HR-MS (EI):

$[M]^+$ = $C_{17}H_{20}O_4$ Calcd 288.1362 Found 288.1350

Elemental analysis:

$C_{17}H_{20}O_4$	Calcd	C 70.81	H 6.99
(288.34)	Found	C 71.10	H 7.07

(-)-Dimethyl (*S*)-2-Phenylcyclopent-3-ene-1,1-dicarboxylate (4)

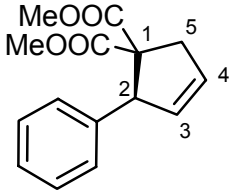
A solution of (+)(*S*)-**2e** (70 mg, 0.24 mmol) and Grubb's 1st generation catalyst (7.2 mg, 8.7 μmol) in dichloromethane (3.5 mL) was heated at reflux and stirred for 3 h under an argon atmosphere. The color of the reaction mixture changed from violet to yellow during the reaction. The solvent was removed under reduced pressure to give the dark brown crude product, that was subjected to flash chromatography on 20 g of silica gel [petroleum ether/ethyl acetate 15:1, R_f (**4**) = 0.27, $KMnO_4$] to yield (-)(*S*)-**4** (60 mg, 95 %) as colorless rhombic crystals, m.p. 49-53 °C.

Optical rotation:

$[\alpha]_D^{25}$ = -377, $[\alpha]_{578}^{25}$ = -395, $[\alpha]_{546}^{25}$ = -456, $[\alpha]_{436}^{25}$ = -821, $[\alpha]_{365}^{25}$ = -1391 (*c* = 0.85, MeOH)

HPLC (Daicel Chiracel OJ-H, solvent: *n*-hexane/*i*-propanol 999 : 1, flow 0.5 ml/min, UV-detection at 210 nm, column temperature 20°C):
t_R[(-)(*S*)-**4**] = 41.22 min (major enantiomer),
t_R[(+)(*R*)-**4**] = 47.46 min.
Enantiomeric excess: 98 %ee (*S*).

^{1}H NMR ($CDCl_3$, 500 MHz), **H,C-COSY**:



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δ = 2.76 (d, *J* = 17.4 Hz, 1 H, 5-H_a), 3.06 (s, 3 H, $COOCH_3$), 3.45 (d, *J* = 17.4 Hz, 1 H, 5-H_b), 3.74 (s, 3 H, $COOCH_3$), 4.86 (s, 1 H, 2-H), 5.67-5.70 (m, 1 H, 3-H or 4-H), 5.84-5.86 (m, 1 H, 3-H or 4-H), 7.15-7.25 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 125 MHz), **DEPT**, **H,C-COSY**:

δ = 40.49 (t, C-5), 51.84, 52.88 (2 q, $COO\underline{C}H_3$), 56.99 (d, C-2), 65.09 (s, C-1), 127.23, 127.95 (2 d, Ph-C), 128.72 (d, C-3 or C-4), 128.96 (d, Ph-C), 132.01 (d, C-3 or C-4), 138.90 (s, Ph-C), 169.89, 172.60 (2 s, $\underline{C}OOCH_3$).

GC/MS: (EI)

t_R = 10.78 min

m/z [%] = 260 (16) [M^+], 200 (100) [M^+-$C_2O_2H_4$].

HR-MS (EI):

$[M]^+$ = $C_{15}H_{16}O_4$ Calcd 260.1049 Found 260.1022

Elemental analysis:

$C_{15}H_{16}O_4$	Calcd	C 69.22	H 6.20
(260.29)	Found	C 69.43	H 6.46

(+)-Dimethyl 2-(But-3-enyl)-2-[(*S*)-1-phenylallyl]malonate (2f)

Optical rotation:

$[\alpha]_D^{25}$ = +41, $[\alpha]_{578}^{25}$ = +44, $[\alpha]_{546}^{25}$ = +50, $[\alpha]_{436}^{25}$ = +92,

$[\alpha]_{365}^{25}$ = +156 (c= 0.57, MeOH)

92 %ee (*S*) according to HPLC

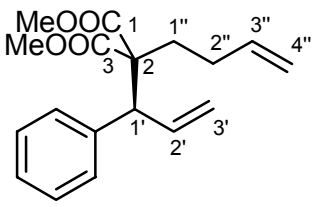
HPLC (Daicel Chiracel AD-H, solvent: *n*-hexane/*i*-propanol 99:1, flow 0.5 ml/min, UV-detection at 210 nm, column temperature 20°C):

t_R[(-)(*R*)-**2f**] = 16.02 min,

t_R[(+)(*S*)-**2f**] = 17.68 min (major enantiomer).

Enantiomeric excess: 92 %ee (S).

^{1}H NMR ($CDCl_3$, 300.13 MHz), **H,H-COSY**, **H,C-COSY**:



2f

δ = 1.72-2.07 (m, 4 H, 1''-H and 2''-H), 3.64, 3.77 (2 s, 6 H, COOC<u>H</u>$_3$), 3.99 (d, $^3J_{1',2'}$ = 8 Hz, 1 H, 1'-H), 4.88-5.11 (m, 4 H, 3'-H and 4''-H), 5.62-5.72 (m, 1 H, 2'-H or 3''-H), 6.31-6.43 (m, 1 H, 2'-H or 3''-H), 7.11-7.22 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 75.48 MHz), **DEPT**, **H,C-COSY**:

δ = 29.19, 34.12 (2 t, C-1'' and C-2''), 51.96, 52.09 (2 q, COO<u>C</u>H$_3$), 54.96 (d, C-1'), 62.37 (s, C-2), 114.86, 117.17 (2 t, C-3' and C-4''), 127.19 (d, Ph-C), 128.25 (d, Ph-C), 129.07 (d, Ph-C), 137.56 (d, C-2'), 137.56 (d, C-3''), 139.01 (s, Ph-C), 170.57, 171.03 (2 s, <u>C</u>OOCH$_3$).

GC/MS: (EI)

t_R = 11.58 min,

m/z [%] = 302 (1) [M^+], 117 (100) [M^+-$C_9O_4H_{13}$].

HR-MS (EI):

$[M]^+$	= $C_{18}H_{22}O_4$	Calcd	302.1518	Found 302.1526

Elemental analysis:

$C_{18}H_{22}O_4$	Calcd	C 71.50	H 7.33
(302.36)	Found	C 71.59	H 7.41

(-)-Dimethyl (*S*)-2-Phenylcyclohex-3-ene-1,1-dicarboxylate (5)

A solution of (+)(*S*)-**2f** (150 mg, 500 μmol) and Grubb's 1st generation catalyst (20.6 mg, 25.0 μmol) in dichloromethane (10 mL) was heated at reflux and stirred for 4 h under an argon atmosphere until TLC [petroleum ether/ethyl acetate 15:1; R_f (**5**) = 0.20, $KMnO_4$] indicated complete consumption of the substrate. The color of the

reaction mixture changed from violet to yellow during the reaction. The solvent was removed under reduced pressure to give the dark brown crude product, that was subjected to flash chromatography on 25 g of silica gel (petroleum ether/ethyl acetate 15:1) to yield (-)(*S*)-**5** (120 mg, 92 %) as colorless solid. This solid was recrystalised from toluene to give (-)(*S*)-**5** (79 mg, 58 %) as colorless plate-shaped crystals, m.p. 128-130°C, with enriched ee of >99 %.

Optical rotation:

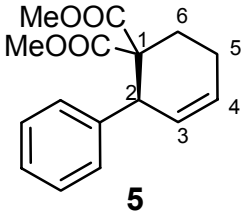
$[\alpha]_D^{25}$ = -487, $[\alpha]_{578}^{25}$ = -511, $[\alpha]_{546}^{25}$ = -588, $[\alpha]_{436}^{25}$ = -1051,

$[\alpha]_{365}^{25}$ = -1774 (c= 0.49, MeOH)

>99 %ee (*S*) according to HPLC

HPLC (Daicel Chiracel OJ-H, solvent: *n*-hexane/*i*-propanol 97:3, flow 0.5 ml/min, UV-detection at 210 nm, column temperature 20°C):
t_R[(-)(*S*)-**5**] = 20.16 min (major enantiomer),
t_R[(+)(*R*)-**5**] = 38.43 min.
Enantiomeric excess: >99 %ee (S).

^{1}H NMR ($CDCl_3$, 500 MHz), **H,H-COSY**, **H,C-COSY**:



5

δ = 1.90-1.99 (m, 1 H, 5-H or 6-H), 2.10-2.20 (m, 2 H, 5-H or 6-H), 2.22-2.28 (m, 1 H, 5-H or 6-H), 3.42, 3.74 (2 s, 6 H, $COOCH_3$), 4.25 (m, 1 H, 2-H), 5.72-5.76 (m, 1 H, 3-H or 4-H), 5.85-5.90 (m, 1 H, 3-H or 4-H), 7.17-7.28 (m, 5 H, Ph-H).

^{13}C NMR ($CDCl_3$, 125 MHz), **DEPT**, **H,C-COSY**:

δ = 22.20, 22.65 (2 t, C-5 and C-6), 44.67 (d, C-2), 51.92, 52.75 (2 q, $COO\underline{C}H_3$), 58.35 (s, C-1), 126.18 (d, C-3 or C-4), 127.43 (d, C-3 or C-4 or Ph-C), 127.58 (d, C-3 or C-4 or Ph-C), 128.05, 129.81 (2 d, Ph-C), 139.14 (s, Ph-C), 170.46, 171.40 (2 s, $\underline{C}OOCH_3$).

GC/MS: (EI)

t_R = 11.65 min,

m/z (%) = 274 (25) $[M]^+$, 214 (75) $[M-C_2O_2H_4]^+$.

HR-MS (EI):

$[M]^+$ = $C_{16}H_{18}O_4$ Calcd 274.1205 Found 274.1197

Elemental analysis:

$C_{16}H_{18}O_4$	Calcd	C 70.06	H 6.61
(274.31)	Found	C 70.11	H 6.54

General Procedure II : Asymmetric Allylic Cyclization

In a flame-dried Schlenk tube under an atmosphere of argon, $[Ir(COD)Cl]_2$ (13.4 mg, 0.02 mmol) and the chiral ligand **L** (0.04 mmol), ratio Ir:**L** = 1:1, were dissolved in dry THF (0.5 mL), forming a yellow-orange solution. After stirring for 5 min TBD (17 mg, 0.12 mmol) was added and the mixture was stirred for 2 h. In the meantime, the substrate (132 mg, 1.00 mmol) was dissolved in dry THF (4.0 mL) in a second flame-dried Schlenk tube under an atmosphere of argon. The mixture was cooled to -78°C and *n*-BuLi (1.0 mmol, 1.6 M solution in n-hexane) was added dropwise. The mixture was stirred for 2 h at -78°C and added to the first Schlenk tube cooled to -78°C. The reaction mixture was stirred overnight and the temperature allowed to increase from -78°C to rt. Then diethyl ether (5 mL) and saturated NH_4Cl solution (5 mL) were added and the phases were separated. The aqueous layer was extracted with diethyl ether (2 x 10 mL). The combined organic phases were washed with brine (10 mL), the aqueous layer was reextracted with diethyl ether (10 mL) and the combined ethereal solutions were dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash column chromatography on silica gel yielded the cyclic product. Pure fractions were applied to chiral GC analysis.

(+)(*R*)-Dimethyl 2-Vinylcyclopentane-1,1-dicarboxylate (8)

Optical rotation:

$[\alpha]_D^{25}$ = +22.6, $[\alpha]_{578}^{25}$ = +23.8, $[\alpha]_{546}^{25}$ = +27.6, $[\alpha]_{436}^{25}$ = +49.4, $[\alpha]_{365}^{25}$ = +84.6

(*c* = 0.63, $CHCl_3$)

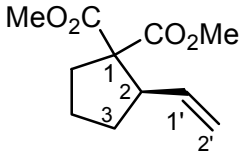
GC: (Permethyl-ß-Cyclodextrin, Cp-Cyclodextrin-B-236-M-19, 120°C isothermal, Inj. 200 °C):

t_R[(-)(*S*)-**8**] = 11.24 min,

t_R[(+)(*R*)-**8**] = 11.52 min (major enantiomer).

Enantiomeric excess: 96 %ee (*R*)

^{1}H NMR,H,H-COSY, C,H-COSY ($CDCl_3$, 300 MHz)



8

δ = 1.57-1.68 (m, 2 H, 4-H), 1.73-2.12 (m, 3 H, 5-H, 3-H), 2.39-2.51 (m, 1 H, 3-H), 3.17-3.27 (m, 1 H, 2-H), 3.63 (s, 3 H, CH_3), 3.71 (s, 3 H, CH_3), 4.97-5.04 (m, 2 H, 2'-H), 7.70 (ddd, $J_{2'c,1'}$ = 10.3 Hz, $J_{2't,1'}$ = 18.1 Hz, $J_{2,1'}$ = 9.3 Hz, 1 H, 1'-H).

^{13}C NMR, DEPT 135 ($CDCl_3$, 75 MHz)

δ = 23.02 (t, C-4), 30.64 (t, C-3), 33.90 (t, C-5), 49.92 (d, C-2), 52.02 (q, COO<u>C</u>H_3), 52.45 (q, COO<u>C</u>H_3), 64.25 (s, C-1), 115.83 (t, C-2'), 137.51 (d, C-1'), 171.18 (s, <u>C</u>OOCH_3), 172.59 (s, <u>C</u>OOCH_3).

MS (EI)

m/z [%] = 212 (1) [M^+], 152 (100) [M^+-$C_2H_3O_2$], 93 (50) [M^+-$C_4H_6O_4$].

HR-MS (EI):

[M]= $C_{11}H_{16}O_4$ Calcd 212.1049 Found 212.1042

(+)(*R*)-Dimethyl 2-Vinylcyclohexane-1,1-dicarboxylate (9)

Optical rotation:

$[\alpha]_D^{25}$ = +22.6, $[\alpha]_{578}^{25}$ = +23.8, $[\alpha]_{546}^{25}$ = +27.6, $[\alpha]_{436}^{25}$ = +49.4, $[\alpha]_{365}^{25}$ = +84.6

(c= 0.63, $CHCl_3$)

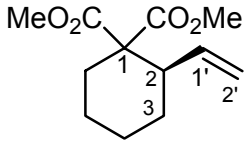
GC: (Permethyl-ß-Cyclodextrin, Cp-Cyclodextrin-B-236-M-19, 120°C isothermal, Inj. 200 °C):

t_R[(-)(*S*)-**9**] = 18.53 min

t_R[(+)(*R*)-**9**] = 19.23 min (major enantiomer).

Enantiomeric excess: 96 %ee (*R*)

^{1}H-NMR,H,H-COSY, C,H-COSY ($CDCl_3$, 300 MHz)



9

δ = 1.31-1.47 (m, 3 H, 4-H, 5-H), 1.50-1.69 (m, 2 H, 3-H, 4-H), 1.73-1.86 (m, 1 H, 3-H), 1.90-2.03 (m, 1 H, 6-H), 2.07-2.19 (m, 1 H, 6-H), 2.67-2.79 (m, 1 H, 2-H), 3.66 (s, 3 H, CH_3), 3.67 (s, 3 H, CH_3), 4.92-5.02 (m, 2 H, 2'-H), 6.06 (ddd, $J_{2'c,1'}$ = 10.3 Hz, $J_{2't,1'}$ = 16.9 Hz, $J_{2,1'}$ =9.2 Hz, 1 H, 1'-H).

^{13}C-NMR, DEPT 135 ($CDCl_3$, 75 MHz)

δ = 22.48, (t, C-5), 22.98 (t, C-4), 28.44 (t, C-3), 30.26 (t, C-6), 45.94 (d, C-2), 52.02 (q, COO<u>C</u>H_3), 52.24 (q, COO<u>C</u>H_3), 59.22 (s, C-1), 115.83 (t, C-2'), 138.75 (d, C-1'), 171.03 (s, <u>C</u>OOCH_3), 172.00 (s, <u>C</u>OOCH_3).

MS (EI)

m/z [%] = 226 (12) [M^+], 167 (62) [M^+-$C_2H_3O_2$], 143 (100), 107 (31) [M^+-$C_4H_6O_4$].

HR-MS (EI):

[M]= $C_{12}H_{18}O_4$ Calcd 226.1205 Found 226.1209