Supporting information

Tandem copper catalyzed enantioselective allylation-metathesis.

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General Procedures. CH₂Cl₂, was distilled from CaH₂. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded in CDCl₃, and chemical shift (δ) are given in ppm relative to CHCl₃. Evolution of reaction was followed by GC-MS Hewlett Packard (EI mode) HP6890-5973. Optical rotations were measured at 22°C in the stated solvent ; [α]_D values are given in 10⁻¹ deg cm² g⁻¹. Enantiomeric excesses were determined by chiral-GC (capillary column, 10 psi H₂) or chiral-SFC with the stated column. Temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C) – final time (min); retention time (R_T) are given in min. Flash chromatography were performed using silica gel 32-63 μm, 60 Å. All reactions were conducted under a nitrogen atmosphere.

Typical procedure for enantioselective copper-catalyzed S_N2' substitution. A dried Schlenk tube was charged with copper salt (1 mol%) and the chiral ligand (1 mol%). Dichloromethane (2 mL) was added and the mixture was stirred at room temperature for 30 min. The allylic chloride (1 mmol) was introduced dropwise and the reaction mixture was stirred at room temperature for a further 5 min before being cooled to -78°C in an ethanol-dry cold bath. Grignard (2-3 M in diethyl ether, 1.2 eq) in dichloromethane (0.5 mL) was added over 40 min *via* syringe pump. Once the addition was complete the reaction mixture was left at -78°C for a further four hour at which point gas chromatography of an aliquot showed that all the starting material had been converted. The reaction was quenched by addition of aqueous hydrochloric acid (1N, 2 mL). Diethyl ether (10 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and reduced *in vacuo*. The oily residue was purified by flash column chromatography (eluant = pentane) to yield the product as a mixture of S_N2' and S_N2 regioisomers. Gas Chromatography or Supercritical Fluid Chromatography on a chiral stationary phase showed the enantiomeric excess of S_N2' product.

Typical procedure for tandem copper catalyzed enantioselective allylation-metathesis. Same procedure as above until full conversion of the allylic chloride when gas chromatography of an aliquot showed that all the starting material had been converted. Enantiomeric excess of the S_N2' product was measured with this aliquot. At this point the reaction mixture was allowed to warm to room temperature and stirred for one hour. Grubbs' catalyst first generation (5 mol%) in dichloromethane (15 mL) was added and the reaction mixture was stirred at room temperature for a further two hours at which point gas chromatography of an aliquot showed that all the S_N2' product had been converted. The reaction was quenched by addition of aqueous hydrochloride acid (1N, 2 mL). Diethyl ether (10 mL) was added and the aqueous phase was separated and extracted further with diethyl

ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and reduced *in vacuo*. The oily residue was purified by flash column chromatography (eluant = pentane) to yield the metathesis-product. Gas Chromatography or Supercritical Fluid Chromatography on a chiral stationary phase showed the enantiomeric excess.

(+)-3(S)-Phenyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.92) to give the S_N2'-S_N2 mixture in 96% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.32-7.20 (m, 5H, ArH), 5.98 (m, 1H, CH₂=CH), 5.08-5.03 (m, 2H, CH₂=CH), 3.16 (dt, *J*₁ = 7.58, *J*₂ = 7.32 Hz, 1H, CHPh), 1.76 (dq, *J*₁ = 7.58, *J*₂ = 7.32 Hz, 2H, CH₂CH₃), 0.90 (t, *J* = 7.32 Hz, 3H, CH₂CH₃)

¹³C NMR (100 MHz, CDCl₃): 144.7, 142.5, 128.6, 127.8, 126.3, 114.2, 51.9, 28.5, 12.3.

MS (EI mode) *m/z* (%) : 146 (M⁺, 21), 117 (100), 91 (24)

[α]_D²² = +44.1 (*c* = 1.1, CHCl₃) for 79% ee. Lit¹ [α]_D²² = +35.0 (*c* = 6, C₆H₆) (S) enantiomer.

Ee was measured by chiral SFC with a Chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 3.01 (*R*), 3.37 (*S*).

(+)-3(S)-Phenyl-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.95) to give the S_N2'-S_N2 mixture in 98% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.33-7.17 (m, 5H, ArH), 6.01 (dt, *J*₁ = 17.92, *J*₂ = 9.08 Hz, 1H, CH₂=CH), 5.07-5.02 (m, 2H, CH₂=CH), 2.90 (t, *J* = 9.08 Hz, 1H, CHPh), 1.99 (m, 1H, CH(CH₃)₂), 0.98 (d, *J* = 6.70 Hz, 3H, CH₃), 0.78 (d, *J* = 6.70 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 144.4, 141.2, 128.3, 127.9, 126.0, 114.9, 58.6, 32.6, 21.1, 20.8.

MS (EI mode) *m/z* (%) : 160 (M⁺, 10), 117 (100), 104 (11), 91 (20).

[α]_D²² = +92.5 (*c* = 1.1, CHCl₃) for 83% ee. Lit² [α]_D²² = +71.3 (*c* = 1.5, CHCl₃) (S) enantiomer with 58% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 50-0-1-170) R_T: 28.06 (*R*), 29.16 (*S*).

(+)-3(S)-(2-Naphthyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.95) to give the S_N2'-S_N2 mixture in 97% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.84-7.35 (m, 7H, ArH), 6.12 (m, 1H, CH₂=CH), 5.13-5.08 (m, 2H, CH₂=CH), 3.09 (t, *J* = 8.84 Hz, 1H, CHPh), 2.10 (m, 1H, CH(CH₃)₂), 1.04 (d, *J* = 6.56 Hz, 3H, CH₃), 0.82 (d, *J* = 6.56 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 141.9, 141.1, 133.7, 132.2, 127.9, 127.6, 127.5, 126.5, 126.3, 125.9, 125.2, 115.2, 58.6, 32.6, 21.2, 20.8.

IR (CHCl₃) ν 3060, 3005, 2960, 2873, 1630, 1597, 1506, 1467, 1366, 918.

MS (EI mode) *m/z* (%) : 210 (M⁺, 30), 167 (100), 152 (36).

[α]_D²² = +92.2 (*c* = 1, CHCl₃) for 85% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 100-0-2-170) R_T: 28.95 (*R*), 29.23 (*S*).

¹ Kumada, M. *Bull. Chem. Soc. Jpn.* **1983**, 56, 363.

² Calò, V.; Nacci, A.; Fiandanese, V. *Tetrahedron* **1996**, 52, 10799.

(+)-3(S)-(4-Chlorophenyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.97) to give the S_N2'-S_N2 mixture in 92% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.28-7.26 (m, 2H, ArH), 7.12-7.10 (m, 2H, ArH), 5.96 (m, 1H, CH₂=CH), 5.07-5.01 (m, 2H, CH₂=CH), 2.88 (t, *J* = 8.84 Hz, 1H, CHPh), 1.92 (m, 1H, CH(CH₃)₂), 0.96 (d, *J* = 6.80 Hz, 3H, CH₃), 0.78 (d, *J* = 6.80 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 142.8, 140.7, 131.6, 129.2, 128.6, 115.4, 57.8, 32.6, 20.9, 20.7.

IR (CHCl₃) ν 2960, 2923, 2868, 1492, 1465, 1092, 918, 757.

MS (EI mode) *m/z* (%) : 194 (M⁺, 12), 151 (100), 115 (68).

$[\alpha]_D^{22} = +78.4$ (*c* = 1.1, CHCl₃) for 79% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 90-0-1-170) R_T: 21.75 (R), 22.60 (S).

(+)-3(S)-(3,4-Dichlorophenyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.95) to give the S_N2'-S_N2 mixture in 93% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.36 (d, *J* = 8.32 Hz, 1H, ArH), 7.26 (d, *J* = 2.04 Hz, 1H, ArH), 7.00 (dd, *J*₁ = 8.32, *J*₂ = 2.04 Hz, 1H, ArH), 5.91 (m, 1H, CH₂=CH), 5.09-5.01 (m, 2H, CH₂=CH), 2.86 (t, *J* = 8.84 Hz, 1H, CHPh), 1.89 (m, 1H, CH(CH₃)₂), 0.96 (d, *J* = 6.56 Hz, 3H, CH₃), 0.77 (d, *J* = 6.84 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 144.7, 139.9, 132.2, 130.2, 129.8, 127.3, 116.0, 57.6, 32.6, 20.9, 20.6.

IR (CHCl₃) ν 2961, 2923, 2868, 1469, 1134, 1030, 920.

MS (EI mode) *m/z* (%) : 228 (M⁺-1, 13), 185 (100), 172 (12), 150 (60), 115 (65), 43 (18).

$[\alpha]_D^{22} = +71.0$ (*c* = 1.15, CHCl₃) for 80% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 100-0-2-170) R_T: 20.23 (R), 20.69 (S).

(+)-3(S)-(4-Methylphenyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.95) to give the S_N2'-S_N2 mixture in 93% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.14-7.06 (m, 4H, ArH), 5.99 (m, 1H, CH₂=CH), 5.06-5.01 (m, 2H, CH₂=CH), 2.87 (t, *J* = 8.84 Hz, 1H, CHPh), 2.34 (s, 3H, CH₃-Ph), 1.94 (m, 1H, CH(CH₃)₂), 0.98 (d, *J* = 6.56 Hz, 3H, CH₃), 0.79 (d, *J* = 6.56 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 141.4, 141.3, 135.4, 129.1, 127.8, 114.7, 58.1, 32.6, 21.1, 21.0, 20.8.

IR (CHCl₃) ν 3005, 2958, 2923, 2873, 1513, 1466, 916, 760.

MS (EI mode) *m/z* (%) : 174 (M⁺, 18), 131 (100), 115 (24), 91 (23).

$[\alpha]_D^{22} = +89.9$ (*c* = 1, CHCl₃) for 83% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 70-0-1-170) R_T: 23.13 (R), 23.94 (S).

(+)-3(S)-(4-Methoxyphenyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane/ether:80/20, R_F = 0.91) to give the S_N2'-S_N2 mixture in 98% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.10-7.08 (m, 2H, ArH), 6.87-6.84 (m, 2H, ArH), 5.98 (m, 1H, CH₂=CH), 5.04-5.00 (m, 2H, CH₂=CH), 3.80 (s, 3H, OCH₃), 2.86 (t, *J* = 9.08 Hz, 1H, CHPh), 1.91 (m, 1H, CH(CH₃)₂), 0.96 (d, *J* = 6.84 Hz, 3H, CH₃), 0.77 (d, *J* = 6.56 Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 157.8, 141.5, 136.5, 128.7, 114.6, 113.7, 57.6, 55.2, 32.7, 21.0, 20.8.

IR (CHCl₃) ν 3005, 2958, 2929, 2874, 1511, 1466, 1249, 1037.

MS (EI mode) m/z (%) : 190 (M⁺, 18), 147 (100), 132 (10), 115 (22), 91 (26).

$[\alpha]_D^{22} = +76.3$ ($c = 0.96$, CHCl₃) for 77% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 80-0-1-170) R_T: 33.58 (R), 34.26 (S).

(+)-3(S)-(3-Methoxyphenyl)-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane/ether:80/20, R_F = 0.91) to give the S_N2'-S_N2 mixture in 98% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.25-7.20 (m, 1H, ArH), 6.79-6.73 (m, 3H, ArH), 5.99 (m, 1H, CH₂=CH), 5.07-5.00 (m, 2H, CH₂=CH), 3.81 (s, 3H, OCH₃), 2.86 (t, $J = 9.02$ Hz, 1H, CHPh), 1.94 (m, 1H, CH(CH₃)₂), 0.97 (d, $J = 6.56$ Hz, 3H, CH₃), 0.78 (d, $J = 6.56$ Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 159.6, 146.1, 141.1, 129.3, 120.3, 115.0, 113.9, 110.9, 58.6, 55.1, 32.6, 21.0, 20.8.

IR (CHCl₃) ν 3009, 2959, 2929, 2868, 1599, 1583, 1487, 1467, 1266, 1050.

MS (EI mode) m/z (%) : 190 (M⁺, 43), 147 (100), 132 (12), 115 (29), 103 (12), 91 (32).

$[\alpha]_D^{22} = +69.6$ ($c = 1.05$, CHCl₃) for 86% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 80-0-1-170) R_T: 29.26 (R), 29.80 (S).

(+)-3(S)-piperonyl-4-methyl-1-pentene

The crude product was purified by column chromatography (SiO₂, pentane/ether:85/15, R_F = 0.87) to give the S_N2'-S_N2 mixture in 96% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 6.75 (d, $J = 8.08$ Hz, 1H, ArH), 6.68 (d, $J = 1.76$ Hz, 1H, ArH), 6.62 (dd, $J_1 = 8.08$, $J_2 = 1.76$ Hz, 1H, ArH), 5.94 (m, 1H, CH₂=CH), 5.93 (s, 2H, OCH₂O), 5.04-5.00 (m, 2H, CH₂=CH), 2.81 (t, $J = 8.84$ Hz, 1H, CHPh), 1.88 (m, 1H, CH(CH₃)₂), 0.96 (d, $J = 6.56$ Hz, 3H, CH₃), 0.78 (d, $J = 6.56$ Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 147.6, 145.6, 141.3, 138.4, 120.8, 114.8, 108.1, 108.1, 100.8, 58.2, 32.7, 21.0, 20.8.

IR (CHCl₃) ν 3005, 2959, 2923, 2896, 1504, 1488, 1441, 1248, 1042, 937, 759.

MS (EI mode) m/z (%) : 204 (M⁺, 38), 161 (73), 131 (100), 103 (64), 77 (21).

$[\alpha]_D^{22} = +67.2$ ($c = 1.05$, CHCl₃) for 82% ee.

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 70-0-1-170) R_T: 54.43 (R), 55.12 (S).

(+)-3(S)-Cyclohexyl-4-methyl-1-pentene³

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.93) to give the S_N2'-S_N2 mixture in 95% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 5.53 (m, 1H, CH₂=CH), 5.06-4.86 (m, 2H, CH₂=CH), 1.80-0.92 (m, 13H, HcHex + CHcHex + CH(CH₃)₂), 0.88 (d, $J = 6.56$ Hz, 3H, CH₃), 0.80 (d, $J = 6.84$ Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 139.1, 116.1, 56.9, 38.2, 31.7, 29.8, 27.2, 26.8, 26.7, 26.6, 21.5, 18.7.

MS (EI mode) m/z (%) : 166 (M⁺, 4), 138 (54), 123 (29), 96 (45), 81 (100), 55 (100), 41 (63), 27 (13).

$[\alpha]_D^{22} = +4.4$ ($c = 1.2$, CHCl₃) for 68% ee.

³ Meuzelaar, G. J.; Karlström, A. S. E.; van Klaveren, M.; Persson, E. S. M.; del Villar, A.; van Koten, G.; Bäckvall, J.-E. *Tetrahedron*, **2000**, *56*, 2895

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 50-0-1-170) R_T: 26.38 (*R*), 28.03 (*S*).

(+)-5(*S*)-Phenyl-hept-3-en-2-one

The crude product was purified by column chromatography (SiO₂, pentane/ether:80/20, R_F = 0.53) in 32% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.35-7.18 (m, 5H, ArH), 6.89 (dd, *J*₁ = 15.88, *J*₂ = 7.56 Hz, 1H, CH-CH=CH), 6.07 (dd, *J*₁ = 15.88, *J*₂ = 1.24 Hz, 1H, CH-CH=CH), 3.31 (q, *J* = 7.56 Hz, 1H, CH-CH=CH), 2.24 (s, 3H, CH₃C=O), 1.82 (m, 2H, CH₂CH₃), 0.89 (t, *J* = 7.32 Hz, 3H, CH₂CH₃).

¹³C NMR (100 MHz, CDCl₃): 189.8, 150.8, 142.1, 130.4, 128.8, 127.8, 126.9, 50.5, 27.9, 27.1, 12.1.

IR (CHCl₃) ν 3028, 3012, 2968, 1672.

MS (EI mode) *m/z* (%): 188 (M⁺, 40), 159 (58), 145 (70), 129 (17), 115 (53), 91 (40), 43 (100).

[α]_D²² = + 9.1 (*c* = 1.1, CHCl₃) for 76% ee.

Ee was measured by chiral SFC with a chiralcel OD-H column (1% MeOH, flow rate 2mL/min) R_T: 3.56 (*R*), 3.91 (*S*).

3(*R*)-Phenyl-1,7-octadiene⁴

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.92) to give the S_N2'-S_N2 mixture (84/16) in 92% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.32-7.20 (m, 5H, ArH), 5.95 (m, 1H, CH-CH=CH₂), 5.80 (m, 1H, CH₂-CH=CH₂), 5.08-4.96 (m, 4H, CH-CH=CH₂ + CH₂-CH=CH₂), 3.26 (q, *J* = 7.53 Hz, 1H, PhCH), 2.10-1.32 (m, 6H, CH₂).

¹³C NMR (100 MHz, CDCl₃): 144.5, 142.4, 138.8, 128.5, 127.6, 126.2, 114.6, 114.0, 49.9, 34.9, 33.8, 26.9.

IR (CHCl₃) ν 3079, 3008, 2931, 2859, 1639, 1452, 996, 916, 767, 701.

MS (EI mode) *m/z* (%): 186 (M⁺, 2), 158 (9), 143 (14), 130 (10), 117 (100), 104 (33), 91 (29).

Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, 10°C, flow rate 2mL/min) R_T: 2.93 (*R*), 3.23 (*S*).

(+)-3(*R*)-Phenylcyclohexene

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.58) in 79% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.36-7.23 (m, 5H, ArH), 5.93 (m, 1H, CH=CH-CH₂), 5.75 (m, 1H, CH=CH-CH₂), 3.44 (m, 1H, PhCH), 2.14-1.55 (m, 6H, CH₂).

¹³C NMR (100 MHz, CDCl₃): 146.7, 130.2, 128.4, 128.3, 127.8, 126.0, 41.9, 32.7, 25.1, 21.2.

IR (CHCl₃) ν 3064, 3009, 2932, 2860, 1601, 1491, 1450, 737, 702.

MS (EI mode) *m/z* (%): 158 (M⁺, 100), 143 (57), 129 (95), 115 (57), 104 (18), 91 (28).

[α]_D²² = + 92.4 (*c* = 1, CHCl₃) for 72% ee. Lit⁵ [α]_D²⁹ = +149.70 (*c* = 6, C₆H₆) (*R*) enantiomer.

Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 4.34 (*S*), 4.71 (*R*).

⁴ Molander, G. A.; Dowdy, E. D.; Schumann, H. *J. Org. Chem.* **1998**, *63*, 3386.

⁵ Berti, G.; Macchia, B.; Macchia, F.; Monti, L. *J. Org. Chem.* **1968**, *33*, 4045.

(+)-3(R)-(4-Methylphenyl)cyclohexene⁶

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.62) in 66% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.15 (s, 4H, ArH), 5.91 (m, 1H, CH=CH-CH₂), 5.74 (m, 1H, CH=CH-CH₂), 3.41 (m, 1H, PhCH), 2.37 (s, 3H, CH₃), 2.14-1.56 (m, 6H, CH₂).

¹³C NMR (100 MHz, CDCl₃): 143.7, 135.5, 130.5, 129.0, 128.2, 127.7, 41.5, 32.7, 25.1, 21.3, 21.0.

MS (EI mode) *m/z* (%) : 172 (M⁺, 100), 157 (77), 144 (34), 129 (100), 115 (29), 91 (27).

[α]_D²² = + 104.5 (*c* = 1.1, CHCl₃) for 76% ee.

Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, 10°C, flow rate 2mL/min) R_T: 6.49 (*S*), 8.55 (*R*).

3(R)-Phenyl-1,6-heptadiene⁴

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.93) to give the S_N2'-S_N2 mixture (71/29) in 94% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.36-7.20 (m, 5H, ArH), 5.96 (m, 1H, CH-CH=CH₂), 5.82 (m, 1H, CH₂-CH=CH₂), 5.09-4.97 (m, 4H, CH-CH=CH₂ + CH₂-CH=CH₂), 3.30 (q, *J* = 7.52 Hz, 1H, PhCH), 2.15-1.28 (m, 4H, CH₂).

¹³C NMR (100 MHz, CDCl₃): 144.2, 142.1, 138.5, 128.5, 127.6, 126.8, 114.7, 114.2, 49.2, 34.5, 31.6.

MS (EI mode) *m/z* (%) : 172 (M⁺, 3), 143 (11), 130 (38), 117 (100), 104 (20), 91 (37).

Ee was measured by chiral GC with a Hydrodex B-3P column (program: 75-45-1-170) R_T: 39.40 (*R*), 40.75 (*S*).

(+)-3(R)-Phenylcyclopentene⁷

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.79) in 68% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.33-7.19 (m, 5H, ArH), 5.96 (m, 1H, CH=CH-CH₂), 5.80 (m, 1H, CH=CH-CH₂), 3.90 (m, 1H, PhCH), 2.52-2.40 (m, 3H, CH₂), 1.74 (m, 1H, CH₂).

¹³C NMR (100 MHz, CDCl₃): 146.6, 134.3, 131.9, 128.4, 127.2, 126.0, 51.3, 33.8, 32.5.

MS (EI mode) *m/z* (%) : 144 (M⁺, 100), 129 (100), 115 (42), 91 (13).

[α]_D²² = + 108.3 (*c* = 1.05, CHCl₃) for 61% ee.

Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 3.66 (*S*), 4.01 (*R*).

(+)-3(R)-(4-Methylphenyl)cyclopentene⁸

The crude product was purified by column chromatography (SiO₂, pentane, R_F = 0.87) in 64% yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): 7.12 (s, 4H, ArH), 5.94 (m, 1H, CH=CH-CH₂), 5.79 (m, 1H, CH=CH-CH₂), 3.88 (m, 1H, PhCH), 2.52-2.39 (m, 3H, CH₂), 2.35 (s, 3H, CH₃), 1.72 (m, 1H, CH₃).

¹³C NMR (100 MHz, CDCl₃): 143.5, 135.5, 134.5, 131.7, 129.1, 127.1, 50.9, 33.9, 32.5, 21.0.

MS (EI mode) *m/z* (%) : 158 (M⁺, 68), 143 (100), 128 (47), 115 (24), 91 (11).

[α]_D²² = + 118.3 (*c* = 1.15, CHCl₃) for 64% ee.

Ee was measured by chiral SFC with a chiralcel OJ column (1% MeOH, flow rate 2mL/min) R_T: 4.70 (*S*), 5.34 (*R*).

⁶ Correia, R.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7159.

⁷ Gilbertson, S. R.; Fu, Z. *Org. Lett.* **2001**, *3*, 161.

⁸ Kim, C. J.; Brown, H. C. *J. Amer. Chem. Soc.* **1972**, *94*, 5051.

File : C:\KARINE\GC MS\KC4-302.D
Operator : Karine
Acquired : 18 Mar 2002 7:45 using AcqMethod KA2
Instrument : GC/MS hp5
Sample Name: KC4-302
Misc Info : 70-2-10-270
Vial Number: 20

Current Chromatogram(s)

LDAD1 C, Sig=210,8 Ref=360,100 of D:\DONNEE~1\KC\KC2127(1.D

File : C:\KARINE\KC4-353.D
Operator : Karine
Acquired : 25 Jun 2002 3:30 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-353
Misc Info : 70-2-10-270
Vial Number: 20

File : C:\KARINE\GC CHIRALE\KC4-353.D
Operator : Karine
Acquired : 6-25-02 2:52:00 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-353
Misc Info : 50-0-1-85-15-170
Vial Number: 1

File : C:\HPCHEM\1\DATA\KC4-3549.D
Operator : DAMIEN
Acquired : 5 Aug 2002 15:32 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name:
Misc Info : 70-0-10-270-3
Vial Number: 16

File : C:\KARINE\KC4-354.D
Operator : Karine
Acquired : 6-26-02 00:09:31 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-354
Misc Info : 100-0-2-170
Vial Number: 1

File : C:\HPCHEM\1\DATA\KC4-3589.D
Operator : DAMIEN
Acquired : 5 Aug 2002 16:32 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name:
Misc Info : 70-0-10-270-3
Vial Number: 18

File : C:\KARINE\GC CHIRALE\KC4-358.D
Operator : Karine
Acquired : 6-25-02 22:32:59 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-358
Misc Info : 90-0-1-130
Vial Number: 1

File : C:\HPCHEM\1\DATA\KC4-3569.D
Operator : DAMIEN
Acquired : 5 Aug 2002 16:02 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name:
Misc Info : 70-0-10-270-3
Vial Number: 17

File : C:\KARINE\KC4-356.D
Operator : Karine
Acquired : 6-25-02 22:00:26 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-356
Misc Info : 100-0-2-150
Vial Number: 1

File : C:\HPCHEM\1\DATA\KC4-3619.D
Operator : DAMIEN
Acquired : 5 Aug 2002 16:53 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name:
Misc Info : 70-0-10-270-3
Vial Number: 19

File : C:\KARINE\GC CHIRALE\KC4-361.D
Operator : Karine
Acquired : 6-25-02 20:02:39 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-361
Misc Info :
Vial Number: 1

File : C:\KARINE\GC MS\KC4-355.D
Operator : Karine
Acquired : 25 Jun 2002 20:24 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-355
Misc Info : 70-0-10-270
Vial Number: 20

File : C:\KARINE\KC4-355.D
Operator : Karine
Acquired : 6-25-02 20:40:48 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-355
Misc Info :
Vial Number: 1

File : C:\KARINE\GC MS\KC4-357.D
Operator : Karine
Acquired : 26 Jun 2002 00:15 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-357
Misc Info : 70-0-10-270
Vial Number: 25

File : C:\KARINE\KC4-357.D
Operator : Karine
Acquired : 6-26-02 2:17:33 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-357
Misc Info : 80-0-1-120
Vial Number: 1

File : C:\KARINE\GC MS\KC4-360.D
Operator : Karine
Acquired : 26 Jun 2002 3:40 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-360
Misc Info : 70-0-10-270
Vial Number: 25

File : C:\KARINE\GC CHIRALE\KC4-360.D
Operator :
Acquired : 6-26-02 6:08:34 using AcqMethod FRONTKAR.M
Instrument : GC 6890
Sample Name:
Misc Info :
Vial Number: 2

File : C:\KARINE\GC MS\KC4-341.D
Operator : Karine
Acquired : 19 Jun 2002 20:33 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-341
Misc Info : 70-2-10-270
Vial Number: 20

File : C:\KARINE\KC4-342.D
Operator : Karine
Acquired : 6-19-02 20:46:44 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-342
Misc Info : 50-0-1-82-15-170 HYDRODEX B-3P
Vial Number: 1

File : C:\HPCHEM\1\DATA\KC4-4252.D
Operator : Karine
Acquired : 7 Aug 2002 13:53 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-425
Misc Info : 80-0-25-270
Vial Number: 20

Current Chromatogram(s)

LDAD1 B, Sig=220,15 Ref=450,40 of KC\KC4-4251.D

File : C:\KARINE\GC MS\KC4-3631.D
Operator : Karine
Acquired : 28 Jun 2002 00:46 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-363
Misc Info : 70-0-10-270
Vial Number: 20

Current Chromatogram(s)

LDAD1 C, Sig=210,8 Ref=360,100 of KC\KC4-3631.D

¹³C CPD-Spectrum

File : C:\KARINE\GC MS\KC4-3632.D
Operator : Karine
Acquired : 28 Jun 2002 20:41 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-363
Misc Info : 70-0-10-270
Vial Number: 20

Current Chromatogram(s)

LDAD1 C, Sig=210,8 Ref=360,100 of KC\KC4-3632.D

File : C:\HPCHEM\1\DATA\KC4-3719.D
Operator : DAMIEN
Acquired : 5 Aug 2002 17:17 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name:
Misc Info : 70-0-10-270-3
Vial Number: 20

Current Chromatogram(s)

LDAD1 C, Sig=210,8 Ref=360,100 of KC\KC4-3716.D

File : C:\HPCHEM\1\DATA\KC4-4201.D
Operator : Karine
Acquired : 6 Aug 2002 8:53 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-420
Misc Info : 90-0-25-270-5
Vial Number: 20

File : C:\HPCHEM\2\DATA\KC4-4201.D
Operator : Karine
Acquired : 8-6-02 10:25:33 using AcqMethod FRONTKAR.M
Instrument : HP G1530A
Sample Name: KC4-420
Misc Info : ISO 75
Vial Number: 1

¹³C CPD-Spectrum

File : C:\HPCHEM\1\DATA\KC4-4209.D
Operator : Karine
Acquired : 7 Aug 2002 9:10 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-420
Misc Info : 70-0-20-270-3
Vial Number: 20

Current Chromatogram(s)

LDAD1 C, Sig=210,8 Ref=360,100 of KC\KC4-4208.D

File : C:\HPCHEM\1\DATA\KC4-4219.D
Operator : Karine
Acquired : 7 Aug 2002 11:09 using AcqMethod KARINE
Instrument : GC/MS hp5
Sample Name: KC4-421
Misc Info : 80-0-20-270
Vial Number: 20