ELECTRONIC SUPPLEMENTARY INFORMATION

Copper-Catalyzed Asymmetric Allylic Substitution with Aryl and Ethyl Grignard Reagents

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General.

All reactions were carried out under argon atmosphere and in flame-dried glassware unless otherwise noted. The following Grignard reagents were purchased from Aldrich as solutions in Et_2O: EtMgBr (3M), PhMgBr (3M), 4-FC_6H_4MgBr (2M). Ligands **1a**, **1b**, **1c**, **1d** and **1e** were prepared according to the reported procedures.[1] $CuBr•Me_2S$, CuCN, $Cu(OTf)_2$ were purchased from Wako and $(CuOTf)_2•C_6H_5Me$ was purchased from Aldrich. $Cu(MeCN)_4BF_4$ and CuTC were prepared according to the reported procedures.[2] Column chromatography was performed using silica gel. TLC was performed using precoated silica gel plates (0.25 mm thick, 60F254) and the product was observed under UV light or with either phosphomolybdic acid or $KMnO_4$ reagents. The wave numbers of maximum absorption peaks of IR spectroscopy are presented in cm^{-1}. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 500 and 125 MHz, respectively. Chemical shifts and coupling constants are presented in ppm δ relative to tetramethylsilane and Hz, respectively. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad and m = multiplet), coupling constants, assignment. ^{13}C peak multiplicity assignments were made based on DEPT data. Mass spectra were recorded on a GCMS-QP5000. Optical rotations were measured on a Jasco P-1030 polarimeter with a 10 cm cell (*c* given in g/100 mL). Ee's of chiral products were determined by comparison of the GC traces of the corresponding racemic products on a chiral non-racemic stationary phase (CP-Chiralsil-Dex-CB, Betadex 120 or Chiraldex B-DM column) using a Hitachi G-3900 GC. CH_2Cl_2 was distilled from CaH_2 and stored with MS A4 under argon. Absolute configuration of the products was determined by comparison with previously published compounds, transformation to known compounds or analogy. The substrate **2** was purchased from TCI while **5b** and **5c** were purchased from Aldrich and used without further purification. The substrates **5a**, **5d**, **5e** and **5f** were prepared according to literature procedures.[3]

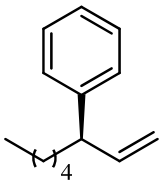
Representative procedure for the asymmetric allylic arylation reaction (Table 2, entry 18): In a test tube, was charged CuTC (3.8 mg, 0.020 mmol) and chiral ligand **1a**

1 For **1a** and **1b**: (a) M. Kanai, Y. Nakagawa and K. Tomioka, *Tetrahedron*, 1999, **55**, 3843; for **1c** and **1d**: (b) M. Kuriyama, T. Soeta, X. Hao, Q. Chen and K. Tomioka, *J. Am. Chem. Soc*., 2004, **126**, 8128; for **1e**: (c) T. Soeta, K. Nagai, H. Fujihara, M. Kuriyama and K. Tomioka, *J. Org. Chem*., 2003, **68**, 9723.

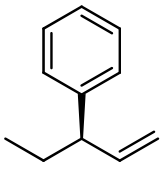
2 For $Cu(MeCN)_4BF_4$: (a) A. Hetherington, W. Levason and M. D. Spicer, *Polyhedron*, 1990, **9**, 1609; for CuTC: (b) G. D. Allred and L. S. Liebeskind, *J. Am. Chem. Soc.,* 1996, **118**, 2748.

3 For **5a**: (a) K. A. Tallman, B. Roschek, Jr., and N. A. Porter, *J. Am. Chem. Soc*., 2004, **126**, 9240; for **5d**: (b) G. Kottirsch, G. Koch, R. Feifel, and U. Neumann, *J. Med. Chem.*, 2002, **45**, 2289; for **5e** and **5f**: (c) A. W. van Zijl, L. A. Arnold, A. J. Minnaard and B. L. Feringa, *Adv. Synth. Catal*., 2004, **346**, 413.

(15.5 mg, 0.044 mmol) and suspended in CH_2Cl_2 (2 cm^3). The mixture was stirred at rt for 30 min, followed by addition of **5a** (0.191 mg, 1.0 mmol) at rt and stirred for 10 min before cooled to –78 °C. The PhMgBr (0.43 cm^3 of 3.0 M Et_2O solution, 1.3 mmol) diluted with CH_2Cl_2 (1 cm^3) was added over 4 h using a syringe pump. Once the addition was complete, the reaction mixture was stirred for further 30 min at –78 °C. The reaction was quenched with aqueous HCl (10%, 2 cm^3) and then the mixture was diluted with Et_2O (6 cm^3). The aqueous phase was separated and further extracted with Et_2O (3 × 3 cm^3). The combined organic layers were washed with saturated $NaHCO_3$ (4 cm^3) and brine (6 cm^3), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Conversion and regioselectivity were determined by achiral GC analysis, DB-1 (30 m × 0.25 mm), initial temp. 35 ºC, 5 °C/min, final temp. 160 °C. GC analysis was carried out with a part of the etherial extract passed through a short plug of silica gel to remove transition metal residues.



(–)-(*R*)-3-Phenyl-1-pentene (6a)[4] (Table 3, entry 1): The resulting pale yellow oil was purified by column chromatography (pentane, then pentane:Et_2O 50:1) to afford a 76:24 mixture of **6a** and **7a** (187 mg, 99%) as colorless oil; **6a**: 81% ee; $[\alpha]^{20}_D$ – 20.8 (*c* 1.52, $CHCl_3$); IR (neat): 3078, 3024, 2924, 1635, 1605, 1458, 1381, 910, 702; ^{1}H NMR: 0.86 (3H, t, *J* = 7.0, C**H$_3$**), 1.25–1.30 (6H, m, C**H$_2$**C**H$_2$**C**H$_2$**), 1.66–1.72 (2H, m, C**H$_2$**CH), 3.23 (1H , dt, *J* = 7.6, 7.3, C**H**), 5.00 (1H, m, CH=C**H$_2$**), 5.01 (1H, m, CH=C**H$_2$**), 5.54 (1H, ddd, *J* = 7.6, 10.4, 18.0, C**H**=CH_2), 7.17–7.19 (2H, m, ArH), 7.27–7.31 (3H, m, ArH); ^{13}C NMR: 14.0 (CH_3), 22.5 (CH_2), 27.1 (CH_2), 31.8 (CH_2), 35.4 (CH_2), 49.9 (CH), 113.8 (CH_2), 126.1 (CH), 127.6 (CH), 128.4 (CH), 142.6 (CH), 144.8 (C); EI-MS *m/z*: 188 (M^+, 0.3%), 121 (2), 117 (5), 88 (36), 84 (100). Enantioselectivity was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m × 0.25 mm), initial temp. 40 ºC for 20 min, 2°C/min, final temp. 70 °C, retention times (min): 120 (major) and 123 (minor).

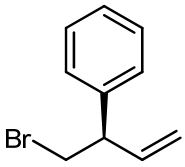


(–)-(*R*)-3-Phenyl-1-pentene (6b)[5] (Table 3, entry 2): The resulting pale yellow oil was purified by column chromatography (pentane) to afford an 85:15 mixture of **6b** and **7b** (146 mg, 100%) as colorless oil; **6b**: 67% ee; $[\alpha]^{22}_D$ –32.3 (*c* 1.41, benzene); IR (neat): 3026, 2960, 2926, 1636, 1601, 1491, 1452, 1377, 912, 698; ^{1}H NMR: 0.87 (3H, t, *J* = 7.3, C**H$_3$**), 1.67–1.78 (2H, m, C**H$_2$**), 3.14 (1H , dt, *J* = 7.6, 7.3, C**H**), 5.02 (1H, m, CH=C**H$_2$**), 5.03 (1H, m, CH=C**H$_2$**), 5.95 (1H, m, C**H**=CH_2), 7.18–7.19 (3H, m, ArH), 7.30 (2H, m, ArH); ^{13}C NMR: 12.1 (CH_3), 28.3 (CH_2), 51.7 (CH), 114.0 (CH_2), 126.1

4 (a) R. Y. Mixer and W. G. Young, *J. Am. Chem. Soc.*, 1956, **78**, 3379; (b) F. Dübner and P. Knochel, *Tetrahedron Lett.*, 2000, **41**, 9233.

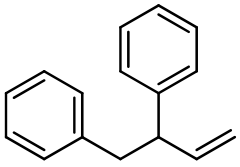
5 (a) T. Hayashi, T. Hagihara, Y. Katsuro and M. Kumada, *Bull. Chem. Soc. Jpn*., 1983, **56**, 363; (b) C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy and A. H. Hoveyda, *Angew. Chem. Int. Ed*., 2001, **40**, 1456.

(CH), 127.7 (CH), 128.4 (CH), 142.3 (CH), 144.5 (C); GC-MS *m/z*:147 (M+1, 1%), 146 (M^+, 10%), 117 (100), 91 (36), 78 (58), 63 (14). Enantioselectivity was determined by chiral GC analysis, Betadex 120 (25 m × 0.25 mm × 0.25 μm), temp. 60 ºC constant, retention times (min): 49 (major) and 50 (minor).

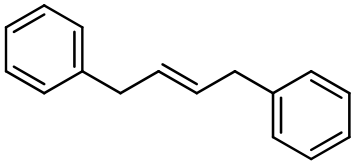


(–)-(*R*)-1-Bromo-2-phenyl-3-butene (6c) (Table 3, entry 3): The resulting pale yellow oil was purified by careful column chromatography (pentane, then pentane:Et_2O 50:1) to afford **6c** (188 mg, 89%) along with a mixture of 3,4-diphenylbut-1-ene and (*E*)-1,4-diphenylbut-2-ene (5:7, 25.7 mg) all as colorless oil.

6c (isolated): 80% ee; $[\alpha]^{20}_D$ –25.0 (*c* 1.15, $CHCl_3$); IR (neat): 3028, 2957, 1643, 1601, 1493, 1452, 989, 922, 700; ^{1}H NMR: 3.62 (1H , dd, *J* = 7.6, 10.1, BrC**H$_2$**), 3.64 (1H , dd, *J* = 6.7, 10.1, BrC**H$_2$**), 3.70 (1H, dt, *J* = 6.7, 7.3, C**H**), 5.15 (1H, ddd, *J* = 1.2, 1.2, 17.3, CH=C**H$_2$**), 5.21 (1H, ddd, *J* = 1.2, 1.2, 10.4, CH=C**H$_2$**), 6.02 (1H, ddd, *J* = 7.3, 10.4, 17.3, C**H**=CH_2), 7.20–7.36 (5H, m, ArH); ^{13}C NMR: 36.3 (CH_2), 51.8 (CH), 117.1 (CH_2), 127.2 (CH), 127.7 (CH), 128.7 (CH), 138.5 (CH), 141.3 (C); GC-MS *m/z*: 212 (M+2, 1%), 210 (M^+, 1%), 160 (1), 129 (10), 117 (36), 83 (16), 77 (8), 40 (100). HRMS (EI) *m/z*: M^+ calcd for $C_{10}H_{11}Br$, 210.0044; found, 210.0045. Enantioselectivity was determined by chiral GC analysis, Chiraldex B-DM (25 m × 0.25 mm × 0.25 μm), constant temp. 100 ºC, retention times (min): 23 (major) and 26 (minor).

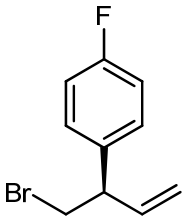


3,4-Diphenybut-1-ene[6]: ^{1}H NMR: 3.00 (1H, dd, *J* = 7.3, 13.4, PhC**H$_2$**), 3.04 (1H, dd, *J* = 7.6, 13.4, PhC**H$_2$**), 3.57 (1H, m, C**H**), 4.95 (1H, ddd, *J* = 1.5, 1.5, 17.4, CH=C**H$_2$**), 5.02 (1H, ddd, *J* = 1.5, 1.5, 10.4, CH=C**H$_2$**), 6.03 (1H, ddd, *J* = 7.3, 10.4, 17.4, C**H**=CH_2), 7.05–7.31 (10H, m, ArH); ^{13}C NMR: 42.1 (CH_2), 51.5 (CH), 114.7 (CH_2), 125.9 (CH), 126.3 (CH), 127.8 (CH), 128.1 (CH), 128.4 (CH), 129.2 (CH), 140.1 (C), 141.4 (CH), 143.7 (C).



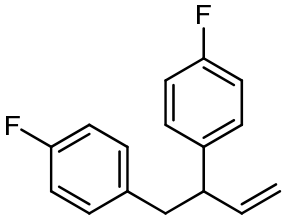
(*E*)-1,4-Diphenylbut-2-ene[7]: ^{1}H NMR: 3.38 (4H, dd, *J* = 1.5, 3.7, C**H$_2$**), 5.69 (2H, tt, *J* = 1.5, 3.7, C**H**), 7.13–7.31 (10H, m, ArH).

6 B. G. James and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1204.
7 B. B. Snider and A. C. Jackson, *J. Org. Chem.,* 1983, **48**, 1471.

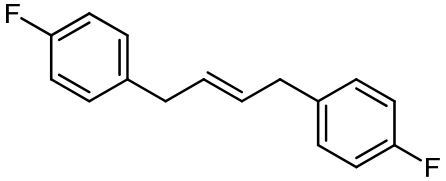


(–)-(*R*)-1-Bromo-2-(4-fluorophenyl)-3-butene (6d) (Table 3, entry 4): The resulting pale yellow oil was purified by careful column chromatography (pentane, then pentane:Et_2O 50:1) to afford **6d** (185 mg, 81%) along with a mixture of 3,4-bis(4-fluoropheny)but-1-ene and (*E*)-1,4-bis(4-fluorophenyl)but-2-ene (10:9, 46 mg) all as colorless oil.

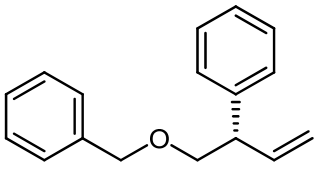
6d (isolated): 72% ee; $[\alpha]^{20}_D$ –19 (*c* 0.51, $CHCl_3$); IR (neat): 3082, 2959, 1637, 1603, 1508, 1220, 1159, 924, 833; ^{1}H NMR: 3.57 (1H , dd, *J* = 7.3, 10.1, BrC**H$_2$**), 3.62 (1H , dd, *J* = 7.3, 10.1, BrC**H$_2$**), 3.70 (1H, dt, *J* = 7.3, 7.3, C**H**), 5.13 (1H, ddd, *J* = 1.2, 1.2, 17.1, CH=C**H$_2$**), 5.21 (1H, ddd, *J* = 1.2, 1.2, 10.4, CH=C**H$_2$**), 5.99 (1H, ddd, *J* = 7.3, 10.4, 17.1, C**H**=CH_2), 7.01–7.05 (2H, m, ArH), 7.16–7.20 (2H, m, ArH); ^{13}C NMR: 36.2 (CH_2), 50.9 (CH), 115.6 (d, *J* = 21, CH), 117.2 (CH_2), 129.2 (d, *J* = 8, CH), 129.3 (CH), 136.9 (d, *J* = 3, C), 138.3 (CH), 162.0 (d, *J* = 245, C), 162.9 (C); GC-MS *m/z*: 230 (M+2, 1%), 228 (M^+, 1%), 160 (1), 135 (29), 109 (11), 83 (13), 40 (100). HRMS (EI) *m/z*: M^+ calcd for $C_{10}H_{10}BrF$, 227.9950; found, 227.9940. Enantioselectivity was determined by chiral GC analysis, Betadex 120 (25 m × 0.25 mm × 0.25 μm), initial temp. 100 ºC, 10 min, 1 ºC/min, final temp. 130 ºC, retention times (min): 33 (major) and 34 (minor).



3,4-Bis(4-fluoropheny)but-1-ene: ^{1}H NMR: 2.90 (1H, dd, *J* = 7.9, 13.4, ArC**H$_2$**), 3.01 (1H, dd, *J* = 7.3, 13.4, ArC**H$_2$**), 3.50 (1H, m, C**H**), 4.97 (1H, ddd, *J* = 1.3, 1.3, 17.1, CH=C**H$_2$**), 5.05 (1H, ddd, *J* = 1.3, 1.3, 10.4, CH=C**H$_2$**), 5.99 (1H, ddd, *J* = 7.0, 10.4, 17.1, C**H**=CH_2), 6.87–7.14 (8H, m, ArH).



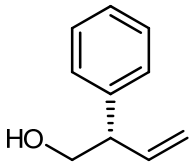
(*E*)-1,4-Bis(4-fluorophenyl)but-2-ene: ^{1}H NMR: 3.33 (4H, m, C**H$_2$**), 5.62 (2H, tt, *J* = 1.6, 3.7, C**H**), 6.87–7.14 (8H, m, ArH).



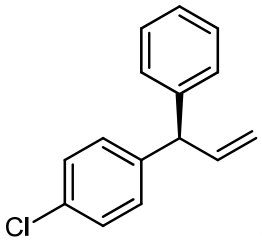
(+)-(*S*)-4-Benzyloxy-3-phenyl-1-butene (6e) (Table 3, entry 5): The resulting pale yellow oil was purified by column chromatography (pentane, then

pentane:Et_2O 50:1~20:1) to afford a 66:34 mixture of **6e** and **7e** (238 mg, 100%) as colorless oil; **6e** (isolated): 34% ee; $[\alpha]^{20}_D$ +13 (*c* 0.97, $CHCl_3$); IR (neat): 3034, 2856, 1639, 1601, 1497, 1454, 1101, 916, 698; ^{1}H NMR: 3.64–3.75 (3H, m, OC**H$_2$**C**H**), 4.52 (2H, s, PhC**H$_2$**O), 5.11 (1H, ddd, *J* = 1.2, 1.2, 17.4, CH=C**H$_2$**), 5.14 (1H, d, *J* = 1.2, 1.2, 10.4, CH=C**H$_2$**), 6.05 (1H, ddd, *J* = 7.0, 10.4, 17.4, C**H**=CH_2), 7.21–7.33 (10H, m, ArH); ^{13}C NMR: 49.7 (CH), 73.0 (CH_2), 73.6 (CH_2), 116.0 (CH_2), 126.6 (CH), 127.5 (CH), 127.6 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 138.4 (C), 139.1 (CH), 141.5 (C); GC-MS *m/z*: 238 (M^+, 0.5%), 208 (1), 132 (12), 117 (99), 104 (16), 91 (100). HRMS (EI) *m/z*: M^+ calcd for $C_{17}H_{18}O$, 238.1358; found, 238.1360. Enantioselectivity was determined by chiral GC analysis after debenzylation (*vide infra*).

Determination of the enantioselectivity of 6e.



(+)-(*S*)-2-Phenylbut-3-en-1-ol:[8] To a solution of **6e** (35.7 mg, 0.15 mmol) in CH_2Cl_2 (1.5 cm^3) at –78 °C was added BCl_3 (1.0 M in CH_2Cl_2, 0.3 cm^3, 0.3 mmol) dropwise. Upon complete addition the solution was allowed to warm to 0 °C, stirred for 1 h, treated with methanol (0.5 cm^3), diluted with saturated $NaHCO_3$ (2 cm^3), and extracted with CH_2Cl_2 (3 × 4 cm^3). The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The resulting pale yellow oil was purified by column chromatography (pentane:Et_2O 2:1) to afford the corresponding alcohol (21.3 mg, 96%) as colorless oil; 34% ee; $[\alpha]^{26}_D$ +19 (*c* 0.81, $CHCl_3$); IR (neat): 3369 (br), 3028, 2928, 1637, 1601, 1493, 1452, 1055, 1030, 918, 756, 700; ^{1}H NMR: 1.45 (1H, t, *J* = 6.1, O**H**), 3.54 (1H, m, C**H**) 3.83 (2H, m, C**H$_2$**), 5.20 (1H, ddd, *J* = 1.2, 1.6, 17.1, CH=C**H$_2$**), 5.22 (1H, ddd, *J* = 1.2, 1.6, 10.4, CH=C**H$_2$**), 6.02 (1H, ddd, *J* = 7.6, 10.4, 17.1, C**H**=CH_2), 7.24–7.27 (3H, m, ArH), 7.33–7.36 (2H, m, ArH); ^{13}C NMR: 52.5 (CH), 66.0 (CH_2), 117.1 (CH_2), 127.0 (CH), 128.0 (CH), 128.8 (CH), 138.3 (CH), 140.7 (C). Enantioselectivity was determined by chiral GC analysis, Betadex 120 (25 m × 0.25 mm × 0.25 μm), initial temp. 100 ºC, 10 min, 1 °C/min, final temp. 130 °C, retention times (min): 33 (major) and 32 (minor).



(+)-(*R*)-1-Chloro-4-(1-phenylallyl)benzene (6f) (Table 3, entry 6): The resulting pale yellow oil was purified by column chromatography (pentane:Et_2O 20:1) to afford an 18:82 mixture of **6f** and **7f** (229 mg, 100%) as colorless oil; **6f** (isolated): 71% ee; $[\alpha]^{21}_D$ +5.6 (*c* 0.50, $CHCl_3$); IR (neat): 3026, 2918, 1636, 1601, 1489, 1090, 1015, 914, 739, 700; ^{1}H NMR: 4.70 (1H, brd, *J* = 7.0, C**H**), 4.98 (1H, ddd, *J* = 1.2, 1.2, 17.1, CH=C**H$_2$**), 5.24 (1H, ddd, *J* = 1.2, 1.2, 10.1, CH=C**H$_2$**), 6.26 (1H, ddd, *J* = 7.0,

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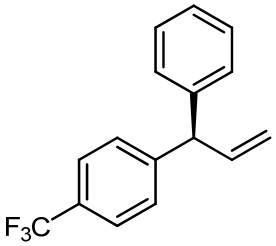
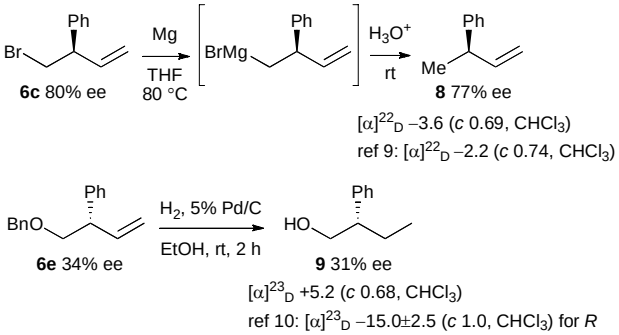
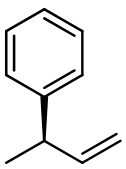
10.1, 17.1, C**H**=CH_2), 7.11 (2H, d, *J* = 8.5, ArH), 7.16 (2H, d, *J* = 7.0, ArH), 7.21–7.32 (5H, m, ArH); ^{13}C NMR: 54.3 (CH), 116.8 (CH_2), 126.6 (CH), 128.5 (CH × 6), 130.0 (CH × 2), 132.2 (C), 140.2 (CH), 141.8 (C), 142.8 (C); GC-MS *m/z*: 230 (M+2, 6%), 229 (M+1, 5), 228 (M^+, 21), 193 (50), 178 (26), 165 (29), 115 (100). HRMS (EI) *m/z*: M^+ calcd for $C_{15}H_{13}Cl$, 228.0706; found, 228.0699. Enantioselectivity was determined by chiral GC analysis, Chiraldex B-DM (25 m × 0.25 mm × 0.25 μm), initial temp. 60 ºC, 0.5 °C/min, final temp. 130 °C, retention times (min): 153 (major) and 154 (minor).



(+)-(*R*)-1-(1-Phenylprop-2-enyl)-4-(trifluoromethyl)benzene (6g) (Table 3, entry 7): The resulting pale yellow oil was purified by column chromatography (pentane, then pentane:Et_2O 50:1) to afford a 16:84 mixture of **6g** and **7g** (243 mg, 93%) as colorless oil; **6g** (isolated): 77% ee; $[\alpha]^{21}_D$ +5.6 (*c* 0.50, $CHCl_3$); IR (neat): 3030, 2926, 1636, 1616, 1601, 1416, 1325, 1165, 1124, 1068, 921, 739, 700; ^{1}H NMR: 4.78 (1H, d, *J* = 7.3, C**H**), 4.99 (1H, d, *J* = 17.1, CH=C**H$_2$**), 5.26 (1H, d, *J* = 10.1, CH=C**H$_2$**), 6.28 (1H, ddd, *J* = 7.3, 10.1, 17.1, C**H**=CH_2), 7.17 (2H, d, *J* = 7.1, ArH), 7.22–7.56 (7H, m, ArH); ^{13}C NMR: 54.7 (CH), 117.2 (CH_2), 124.3 (q, *J* = 271, CF_3), 125.4 (q, *J* = 3, CH), 126.8 (CH), 128.6 (CH), 128.7 (q, *J* = 32, C), 128.7 (CH), 129.0 (CH), 139.8 (CH), 142.4 (C), 147.4 (C); EI-MS *m/z*: 263 (M+1, 3%), 262 (M^+, 21), 193 (30), 178 (13), 165 (19), 115 (44), 84 (100). HRMS (EI) *m/z*: M^+ calcd for $C_{16}H_{13}F_3$, 262.0969; found, 262.0970. Enantioselectivity was determined by chiral GC analysis, Chiraldex B-DM (25 m × 0.25 mm × 0.25 μm), initial temp. 60 ºC, 1 °C/min, final temp. 120 °C, retention times (min): 70 (major) and 71 (minor).

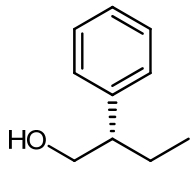
Determination of absolute configuration of 6c and 6e.





(–)-(*R*)-3-Phenyl-1-butene (8): In a flask containing Mg turnings (17 mg, 0.60 mmol) suspended in dry THF (1 cm^3), **6c** (63 mg, 0.30 mmol) in dry THF (1.5 cm^3) was added dropwise over 15 min at 80 °C. The mixture was stirred at the same temperature

for 1 h, then transferred by canula to aqueous 10% HCl (2 cm^3) at 0 °C and diluted with Et_2O (6 cm^3). The aqueous phase was separated and further extracted with Et_2O (3 × 4 cm^3). The combined organic layers were washed with saturated $NaHCO_3$ (2 cm^3) and brine (3 cm^3), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was purified by careful column chromatography (pentane) to afford **8** (7.0 mg, 18%) as colorless oil; **8**: 77% ee; $[\alpha]^{22}_D$ –3.6 (*c* 0.69, $CHCl_3$), lit. $[\alpha]^{22}_D$ –2.2 (*c* 0.74, $CHCl_3$);[9] IR (neat): 3026, 2924, 1637, 1601, 1493, 1452, 912, 760, 700; ^{1}H NMR: 1.36 (3H, d, *J* = 7.0, C**H**$_3$), 3.47 (1H, m, C**H**) 5.02–5.07 (2H, m, CH=C**H**$_2$), 6.01 (1H, ddd, *J* = 6.4, 10.4, 16.8, C**H**=CH_2), 7.18–7.23 (3H, m, ArH), 7.28–7.32 (2H, m, ArH). Enantioselectivity was determined by chiral GC analysis, Betadex 120 (25 m × 0.25 mm), initial temp. 100 ºC, 10 min, 1 °C/min, final temp. 130 °C, retention times (min): 47 (major) and 49 (minor).



(+)-(*S*)-2-Phenylbutan-1-ol (9): To a solution of **6e** (23.8 mg, 0.10 mmol) in EtOH (1 cm^3) was added 5% Pd-C (22 mg, 0.010 mmol) at room temperature, and the reaction mixture was stirred under hydrogen atmosphere at the same temperature for 2 h. The catalyst was removed by passing the reaction mixture through a short silica gel pad, which was successively washed with Et_2O. The solvent was removed under vacuum to afford **9** (15 mg, 100%) as pure colourless oil; **9**: 31% ee; $[\alpha]^{23}_D$ +5.2 (*c* 0.68, $CHCl_3$), lit. $[\alpha]^{23}_D$ –15.0±2.5 (*c* 1.0, $CHCl_3$) for (*R*)-isomer;[10] IR (neat): 3307 (br), 3026, 2960, 1601, 1493, 1452, 1377, 1038, 760, 700; ^{1}H NMR: 0.84 (3H, t, *J* = 6.4, C**H**$_3$), 1.30 (1H, brs, O**H**), 1.58 (1H , m, C**H**$_2$CH$_3$), 1.75 (1H, m, C**H**$_2$CH$_3$), 2.69 (1H, m, C**H**), 3.72 (1H, dd, *J* = 7.9, 10.9, C**H**$_2$OH), 3.78 (1H, dd, *J* = 5.8, 10.9, C**H**$_2$OH), 7.12–7.35 (5H, m, ArH); ^{13}C NMR: 11.9 (CH_3), 24.9 (CH_2), 50.5 (CH), 67.3 (CH_2), 126.7 (CH), 128.1 (CH), 128.7 (CH), 142.3 (C). Enantioselectivity was determined by chiral GC analysis, Betadex 120 (25 m × 0.25 mm), initial temp. 100 ºC, 10 min, 1 °C/min, final temp. 130 °C, retention times (min): 32 (minor) and 33 (major).

9 (a) T. Hayashi, M. Konishi, M. Fukushima, K. Kanehira, T. Hioki, M. Kumada, *J. Org. Chem*., 1983, **48**, 2195; (b) M. Kawatsura, Y. Uozumi, M. Ogasawara, T. Hayashi, *Tetrahedron*, 2000, **56**, 2247.

10 S. Matsubara, H. Yamamoto and K. Oshima, *Angew. Chem. Int. Ed.*, 2002, **41**, 2837.