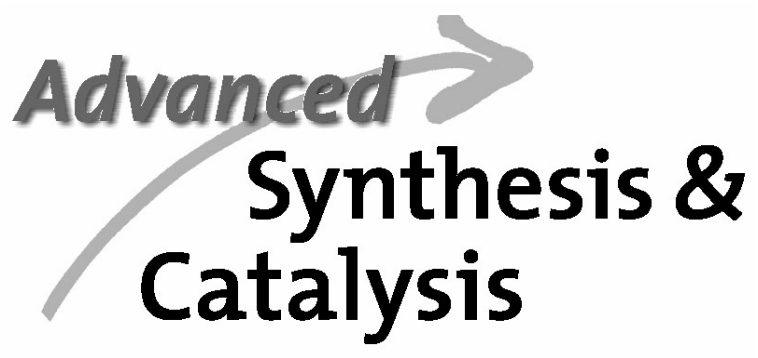

Supporting Information

Supporting Information

Gold(III) Chloride-Catalyzed Diastereoselective Alkylation Reactions with Chiral Benzylic Acetates

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General Remarks: All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under argon. Common solvents (ether, ethyl acetate, dichloromethane, pentane, and cyclohexane), were distilled prior to use. Anhydrous dichloromethane and pyridine were distilled from CaH_2, prior to use. Previously reported products: **3**,[1] **6**,[2] **12-20**,[2] **22-23**,[2] **27**.[3] Benzylic alcohols **1**[1] and **4**,[2] acetates **2**[4] and **7**,[5] *N*-tosylaniline,[6] and 2,2-dimethyl-3-(trimethylsilyloxy)butane.[7] were prepared according to known procedures. All other reagents were used as received. IR: Perkin Elmer 241 FT-IR. ^{1}H and ^{13}C NMR: Bruker AC-250, AV-360. Chemical shifts are reported relative to tetramethylsilane as internal reference. The multiplicities of the ^{13}C NMR signals were determined by DEPT experiments. TLC: Merck glass sheets 0.25 mm silica gel 60-F_{254}. Detection by UV and coloration with cerium ammonium molybdate solution (CAM). Flash chromatography: Merck silica gel 60 (230-400 mesh) (ca. 50 g for 1 g of material to be separated), eluent given in brackets. MS: Finnigan MAT 8200 (EI), Finnigan MAT 95S (HRMS).

Representative Procedure for the acetylation of benzylic alcohols – Preparation of 2-chloro-1-(4-methoxyphenyl)propyl acetate (9): 1-(4-Methoxyphenyl)-2-chloropropan-1-ol[1] (660 mg, 3.29 mmol), acetyl chloride (470 g, 5.99 mmol), pyridine (2.5 mL, 30.6 mmol) and DMAP (10 mg, 81 µmol) were stirred in 20 mL CH_2Cl_2 for 18.5 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (20 mL) and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (ethyl acetate/cyclohexane = 1/20) to give a colorless oil. yield: 726 mg (91%), d.r. = 86/14 (*anti*/*syn*). R_f**:** 0.16 (ethyl acetate/cyclohexane = 1/20); IR (film): ?~= 2934 cm^{-1} (w), 2838 (w), 1740 (vs), 1612 (s), 1515 (vs), 1371 (m), 1236 (vs), 1031 (s), 832 (m); *anti*-

Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.33 (d, ^{3}J = 6.7 Hz, 3 H), 2.10 (s, 3 H), 3.80 (s, 3 H), 4.20-4.31 (m, 1 H), 5.74 (d, ^{3}J = 7.9 Hz, 1 H), 6.87-6.91 (m, 2 H), 7.27 (d, ^{3}J = 8.5 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 21.2 (q), 21.5 (q), 55.4 (q), 59.1 (d), 79.1 (d), 114.1 (d), 128.8 (d), 129.3 (s), 160.0 (s), 169.9 (s); *syn*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.47 (d, ^{3}J = 6.7 Hz, 3 H), 2.13 (s, 3 H), 3.80 (s, 3 H), 4.20-4.31 (m, 1 H), 5.83 (d, ^{3}J = 5.4 Hz, 1 H), 6.87-6.91 (m, 2 H), 7.29 (d, ^{3}J = 8.6 Hz, 2 H); MS (EI, 70 eV), *m/z* (%): 242 (5) [M^+], 206 (4), 179 (20), 137 (100), 109 (5), 43 (15); CHN ($C_{12}H_{15}ClO_3$): calcd.: C: 59.39, H: 6.23; found: C: 59.20, H: 6.19.

2-Cyano-1-(4-methoxyphenyl)propyl acetate (8)

3-Hydroxy-3-(4-methoxyphenyl)-2-methylpropanenitrile[8] (400 mg, 2.08 mmol), acetic anhydride (1.0 mL, 10.8 mmol), pyridine (2.0 mL, 24.5 mmol) and DMAP (10 mg, 81 μmol) were stirred in 20 mL CH_2Cl_2 for 16 h. The crude product was purified by flash chromatography (ethyl acetate/cyclohexane = 1/6) to give a colorless oil. yield: 420 mg (86%), d.r. = 60/40 (*syn*/*anti*). R_f**:** 0.25 (ethyl acetate/cyclohexane = 1/4); IR (film): ?~= 2941 cm^{-1} (m), 2839 (w), 1747 (s), 1613 (s), 1515 (vs), 1372 (m), 1230 (vs), 1031 (s), 837 (m); *syn*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.24 (d, ^{3}J = 7.2 Hz, 3), 2.13 (s, 3 H), 3.19 (qd, ^{3}J = 7.2 Hz, ^{3}J = 6.0 Hz, 1 H), 3.81 (s, 3 H), 5.68 (d, ^{3}J = 6.0 Hz, 1 H), 6.91 (d, ^{3}J = 8.7 Hz, 2 H), 7.35 (d, ^{3}J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 14.6 (q), 21.1 (q), 32.1 (d), 55.4 (q), 74.8 (d), 114.2 (d), 120.0 (s), 127.7 (s), 128.7 (d), 160.3 (s), 169.8 (s); *anti*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.23 (d, ^{3}J = 7.2 Hz, 3 H), 2.13 (s, 3 H), 3.04 (virt. quintet, ^{3}J ~ 7.2 Hz, 1 H), 3.80 (s, 3 H), 5.72 (d, ^{3}J = 7.2 Hz, 1 H), 6.90 (d, ^{3}J = 8.7 Hz, 2 H), 7.29 (d, ^{3}J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 14.9 (q), 21.0 (q), 32.7 (d), 55.4 (q), 75.2 (d), 114.4 (d), 120.2 (s), 127.7 (d), 128.7 (s), 160.3 (s), 169.7 (s); MS (EI, 70 eV), *m/z* (%): 233 (8) [M^+], 179 (10), 137 (100), 109 (5), 57 (9), 43 (20); HRMS ($C_{13}H_{15}NO_3$): calcd.: 233.1052, found: 233.1051.

2-(Ethylsulfonyl)-1-(4-methoxyphenyl)propyl acetate (10)

2-Ethanesulfonyl-1-(4-methoxyphenyl)-propan-1-ol[1] (1.73 g, 6.70 mmol), acetyl chloride (1.05 g, 13.40 mmol), pyridine (15 mL, 184.0 mmol) and DMAP (10 mg, 81 μmol) were stirred in 70 mL CH_2Cl_2 for 14 h. The crude product was purified by flash chromatography (ethyl acetate/cyclohexane = 2/3) to give a colorless oil. yield: 1.21 g (60%), d.r. = 76/24. R_f**:** 0.50 (ethyl acetate/cyclohexane = 1/1); IR (film): ?~= 2943 cm^{-1} (w), 1745 (s), 1612 (m), 1514 (s), 1303 (s), 1224 (vs), 1029 (s), 828 (m); Major diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.14 (d, ^{3}J = 7.3 Hz, 3 H), 1.36 (t, ^{3}J = 7.5 Hz, 3 H), 2.05 (s, 3 H), 3.09-3.15 (m, 2 H), 3.50 (dq, ^{3}J = 9.5 Hz, ^{3}J = 7.3 Hz, 1 H), 3.80 (s, 3 H), 5.92 (d, ^{3}J = 9.5 Hz, 1 H), 6.89 (d, ^{3}J = 8.8 Hz, 1 H), 7.28 (d, ^{3}J = 8.8 Hz, 1 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 6.1 (q), 7.9 (q), 21.1 (q) 45.8 (t), 55.5 (q), 62.2 (d) 76.8

(d), 114.4 (d), 127.5 (d), 129.6 (s), 159.8 (s), 169.2 (s); Minor diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.44 (d, ^3J = 7.1 Hz, 3 H), 1.46 (t, ^3J = 7.5 Hz, 3 H), 2.14 (s, 3 H), 2.77-2.94 (m, 2 H), 3.20-3.26 (m, 1 H), 3.80 (s, 3 H), 6.39 (d, ^3J = 3.6 Hz, 1 H), 6.90 (d, ^3J = 8.9 Hz, 1 H), 7.23(d, ^3J = 8.9 Hz, 1 H); MS (EI, 70 eV), *m/z* (%): 300 (2) [M^+], 206(36), 164 (100), 148 (38), 137 (83), 77 (13); HRMS ($C_{14}H_{20}O_5S$): calcd.: 300,1031 found: 300.1030.

1-(4-Methoxyphenyl)-2-nitropropyl acetate (11)

1-(4-Methoxyphenyl)-2-nitropropan-1-ol[9] (2.11 g, 10.0 mmol), acetyl chloride (1.57 g, 20.0 mmol), pyridine (7.9 mL, 96.9 mmol) and DMAP (10 mg, 81 µmol) were stirred in 50 mL CH_2Cl_2 for 15 h. The crude product was purified by flash chromatography (ethyl acetate/cyclohexane = 1/8) to give a colorless oil. yield: 903 mg (36%), d.r. = 66/34 (*syn*/*anti*). R_f**:** 0.32 (ethyl acetate/cyclohexane = 1/3); IR (film): ?≂ 3002 cm^{-1} (s), 2940 (w), 2840 (s), 1749 (vs), 1684 (s), 1585 (s), 1612 (s), 1587 (s), 1088 (s); *anti*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.56 (d, ^3J = 6.8 Hz, 3 H), 2.12 (s, 3 H), 3.79 (s, 3 H), 4.81 (qd, ^3J = 6.8 Hz, ^3J = 5.6 Hz, 1 H), 6.23 (d, ^3J = 5.6 Hz, 1 H), 6.88 (d, ^3J = 8.7 Hz, 2 H), 7.24 (d, ^3J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 14.1 (q), 21.0 (q), 55.4 (q), 74.9 (d), 85.6 (d), 114.3 (d), 127.4 (s), 128.1 (d), 160.2 (s), 169.3 (s); *syn*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.33 (d, ^3J = 6.9 Hz, 3 H), 1.99 (s, 3 H), 3.81 (s, 3 H), 4.91 (dq, ^3J = 10.0 Hz, ^3J = 6.9 Hz, 1 H), 6.01 (d, ^3J = 10.0 Hz, 1 H), 6.91 (d, ^3J = 8.7 Hz, 2 H), 7.29 (d, ^3J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 16.5 (q), 20.9 (q), 55.4 (q), 76.5 (d), 85.8 (d), 114.6 (d), 127.0 (s), 129.1 (d), 160.5 (s), 169.2 (s); MS (EI, 70 eV), *m/z* (%): 253 (1) [M^+], 193 (70), 146 (100), 115 (47), 103 (47), 91 (32); HRMS ($C_{12}H_{15}NO_5$): calcd.: 253.0950, found: 253.0948.

2-(Diethoxyphosphoryl)-1-(4-methoxyphenyl)propyl acetate (5)

Diethyl 1-hydroxy-1-(4-methoxyphenyl)propan-2-ylphosphonate[1] (363 mg, 1.20 mmol), acetic anhydride (0.22 mL, 2.40 mmol), pyridine (1.0 mL, 12.26 mmol) and DMAP (10 mg, 81 µmol) were stirred in 10 mL CH_2Cl_2 for 21.5 h. The crude product was purified by flash chromatography (ethyl acetate/cyclohexane = 1/4) to give a colorless oil. yield: 312 mg (76%), d.r. = 77/33 (*syn*/*anti*). R_f**:** 0.15 (ethyl acetate/cyclohexane = 1/1); IR (film): ?≂ 3466 cm^{-1} (w), 2982 (s), 2837 (w), 1743 (vs), 1612 (s), 1514 (vs), 1371 (m), 1240 (vs), 1028 (s), 963 (s), 832 (m); *anti*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 0.98 (dd, $^3J_{HP}$ = 17.5 Hz, $^3J_{HH}$ = 7.4 Hz, 3 H), 1.31 (td, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 1.5 Hz, 6 H), 2.04 (s, 3 H), 2.40-2.54 (m, 1 H), 3.79 (s, 3 H), 4.05-4.14 (m, 4 H), 5.86 (*virt.* t, $^3J \cong$ 8.8 Hz, 1 H), 6.86 (d, ^3J = 8.7 Hz, 2 H), 7.28 (d, ^3J = 8.7 Hz, 2 H); *syn*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.03 (dd, $^3J_{HP}$ = 17.7 Hz, $^3J_{HH}$ = 7.3 Hz, 3 H), 1.25 (*virt.* q, $^3J \cong$ 7.1 Hz, 6 H), 2.09 (s, 3 H), 2.22-2.35 (m, 1 H), 3.77 (s, 3 H), 3.95-4.05 (m,

4 H), 6.12 (dd, $^3J_{HH}$ = 7.9Hz, $^3J_{HP}$ = 5.1 Hz, 1 H), 6.85 (d, ^3J = 8.7 Hz, 2 H), 7.21 (d, ^3J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) d = 9.0 (dq, $^2J_{CP}$ = 3.7 Hz), 16.5 (dq, $^3J_{CP}$ = 6.0 Hz), 16.6 (dq, $^3J_{CP}$ = 6.0 Hz), 21.2 (q), 38.0 (dd, $^1J_{CP}$ = 140.5 Hz), 55.4 (q), 61.8 (dt, $^2J_{CP}$ = 6.8 Hz), 61.9 (dt, $^2J_{CP}$ = 6.8 Hz), 73.4 (d), 113.8 (d), 127.8 (d), 131.4 (d, $^3J_{CP}$ = 10.4 Hz), 159.3 (s,), 169.7 (s); MS (EI, 70 eV), *m/z* (%): 344 (18) [M^+], 301 (65), 206 (35), 193 (17), 164 (100), 137 (60) 109 (15); HRMS ($C_{16}H_{25}O_6P$): calcd.: 344.1389, found: 344.1387.

General procedure for the $AuCl_3$–catalyzed alkylation with benzylic acetates. The acetate (1 eq.; 0.25 mmol) and the nucleophile (4 eq.; 1.0 mmol) were dissolved in nitromethane (2 mL), $AuCl_3$ (7.6 mg, 25 μmol) was added in one portion and the solution was stirred till the reaction was complete. The reaction was quenched by addition of water (10 mL), diluted with ethyl acetate (10 mL) and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography. The products were obtained as diastereomeric mixtures.

Methyl 3-(2,5-dimethoxyphenyl)-3-(4-methoxyphenyl)-2-methylpropanoate (*anti*-21)

Purification by flash chromatography (ethyl acetate/cyclohexane = 1/20); yield: 54 mg (63%), d.r. = 91/9. R_f: 0.44 (ethyl acetate/cyclohexane = 1/10); IR (film): ?≂ 2950 cm^{-1} (m), 2834 (w), 1737 (vs), 1610 (s), 1511 (s), 1250 (s), 1048 (s), 823 (m); ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.09 (d, ^3J = 6.8 Hz, 3 H), 3.32 (dq, ^3J = 11.8 Hz, ^3J = 6.8 Hz, 1 H), 3.51 (s, 3 H), 3.72 (s, 3 H), 3.75 (s, 3 H), 3.75 (s, 3 H), 4.45 (d, ^3J = 11.8 Hz, 1 H), 6.63 (dd, ^3J = 2.9 Hz, ^3J = 8.8 Hz, 1 H), 6.70 (d, ^3J = 8.8 Hz, 1 H), 6.78 (d, ^3J = 8.6 Hz, 1 H), 6.95 (d, ^3J = 2.9 Hz, 1 H), 7.20 (d, ^3J = 8.6 Hz, 1 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 17.1 (q), 43.7 (d), 46.7 (d), 51.5 (q), 55.1 (q, 55.7 (q), 56.3 (q), 111.1 (d), 112.2 (d), 113.6 (d), 113.7(d), 129.5 (d), 133.6 (s), 134.1 (s), 151.2 (s), 153.5 (s), 158.0 (s), 176.4 (s); MS (EI, 70 eV), *m/z* (%): 344 (45) [M^+], 257 (100), 135 (33), 121 (99); CHN ($C_{20}H_{24}O_5$): calcd.: C: 69.75, H: 7.02; found: C: 69.48, H: 7.07.

Methyl 3-(4-methoxyphenyl)-2-methylhex-5-enoate (25)

Purification by flash chromatography (ethyl acetate/cyclohexane = 1/10); yield: 56 mg (90%), d.r. = 92/8. R_f**:** 0.61 (ethyl acetate/cyclohexane = 1/3); IR (film): ?≂ 2950 cm^{-1} (s), 2836 (m), 1736 (vs), 1611 (s), 1513 (s), 1434 (s), 1252 (s), 1037 (s), 829 (m); *anti*-Diastereoisomer: ^{1}H-NMR (250 MHz, $CDCl_3$): d = 0.92, (d, ^3J = 6.9 Hz, 3 H), 2.32-2.37 (m, 2 H), 2.58-2.73 (m, 1 H), 2.82-2.95 (m, 1 H), 3.71 (s, 3 H), 3.79 (s, 3H), 4.84-4.89 (m, 1 H), 4.93-4.95 (m, 1 H), 5.46-5.65 (m, 1 H), 6.83 (d, ^3J = 8.7 Hz, 2 H), 7.03 (d, ^3J = 8.7 Hz, 2 H); ^{13}C-NMR (62.9 MHz, $CDCl_3$): d = 15.7 (q), 39.1 (t), 45.5

(d), 48.1 (d), 51.7 (q), 55.3 (q), 113.9 (d), 116.3 (t), 129.3 (d), 133.7 (s), 136.4 (d), 158.3 (s), 176.9 (s); *syn*-Diastereoisomer: ^{1}H-NMR (250 MHz, $CDCl_3$): d = 1.20, (d, ^3J = 6.9 Hz, 3 H), 2.46-2.52 (m, 2 H), 2.58-2.73 (m, 1 H), 2.82-2.95 (m, 1 H), 3.46 (s, 3 H), 3.77 (s, 3H), 4.81-4.84 (m, 1 H), 4.98-5.00 (m, 1 H), 5.65 (m, 1 H), 6.79-6.81 (m, 2 H), 7.04-7.08 (m, 2 H); MS (EI, 70 eV), *m/z* (%): 248 (9) [M^+], 207 (70), 161 (31), 151 (100), 91 (9); HRMS ($C_{18}H_{26}O_4$): calcd.: 248.1412, found: 248.1411.

Methyl 3-cyano-3-(4-methoxyphenyl)-2-methylpropanoate (26)

Purification by flash chromatography (ethyl acetate/cyclohexane = 1/5); yield: 45 mg (77%), d.r. = 91/9. R_f**:** 0.31 (ethyl acetate/cyclohexane = 1/3); IR (film): ?~= 2954 cm^{-1} (s), 2839 (m), 1736 (vs), 1612 (s), 1514 (s), 1253 (s), 1181 (s), 1032 (s), 836 (s); *anti*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.15 (d, ^3J = 7.1 Hz, 3 H), 2.98 (virt. quintet, ^3J ~ 7.4 Hz, 1 H), 3.73 (s, 3 H), 3.80 (s, 3 H), 4.02 (d, ^3J = 7.9 Hz, 1 H), 6.87-6.91 (m, 2 H), 7.19-7.23 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 14.8 (q), 39.3 (d), 44.6 (d), 52.4 (q), 55.5 (q), 114.6 (d), 119.9 (s), 124.7 (s), 129.5 (d), 159.9 (s), 173.2 (s); *syn*-Diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): d = 1.38 (d, ^3J = 7.1 Hz, 3 H), 2.87 (virt. quintet, ^3J ~ 7.4 Hz, 1 H), 3.63 (s, 3 H), 3.80 (s, 3 H), 4.19 (d, ^3J = 7.9 Hz, 1 H), 6.87-6.91 (m, 2 H), 7.23-7.25 (m, 2 H); MS (EI, 70 eV), *m/z* (%): 233 (15) [M^+], 173 (15), 146 (100), 103 (5), 91 (5); HRMS ($C_{18}H_{26}O_4$): calcd.: 233.1052, found: 233.1047.

Methyl 4-acetyl-3-(4-methoxyphenyl)-2-methyl-5-oxohexanoate (*anti*-**28**)

Purification by flash chromatography (ethyl acetate/cyclohexane = 1/10); yield: 67 mg (88%), d.r. = 97/3. R_f**:** 0.17 (ethyl acetate/cyclohexane = 1/3); IR (film): ?~= 2955 cm^{-1} (w), 2928 (m), 1705 (vs), 1662 (s), 1612 (m), 1514 (s), 1373 (m), 1261 (s), 1036 (s), 835 (s); ^{1}H-NMR (360 MHz, $CDCl_3$): d = 0.92, (d, ^3J = 7.0 Hz, 3 H), 1.82 (s, 3 H), 2.25 (s, 3 H), 2.61 (virt. quintet, ^3J ~ 7.0 Hz, 1 H), 3.62 (s, 3 H), 3.76 (s, 3 H), 3.92 (dd, ^3J = 11.4 Hz, ^3J = 7.0 Hz, 1 H), 4.36 (d, ^3J = 11.4 Hz, 1 H), 6.80 (d, ^3J = 8.7 Hz, 3 H), 7.03 (d, ^3J = 8.7 Hz, 3 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 13.5 (q), 28.8 (q), 39.9 (q), 43.8 (d), 46.4 (d), 51.9 (q), 55.3 (q), 74.0 (d), 114.2 (d), 129.7 (s), 130.0 (d), 159.0 (s), 175.0 (s), 202.8 (s), 202.9 (s); MS (EI, 70 eV), *m/z* (%): 306 (15) [M^+], 263 (45), 231 (80), 189 (28), 177 (100), 151 (45), 43 (78); HRMS ($C_{17}H_{22}O_5$): calcd.: 306.1467, found: 306.1472.

Methyl 3-(4-methoxyphenyl)-2,6,6-trimethyl-5-oxoheptanoate (29)

Purification by flash chromatography (ethyl acetate/cyclohexane = 1/5); yield: 56 mg (73%), d.r. = 97/3. R_f**:** 0.58 (ethyl acetate/cyclohexane = 1/3); IR (film): ?~= 2969 cm^{-1} (s), 2837 (w), 1738 (vs), 1731 (vs), 1708 (m), 1613 (s), 1514 (vs), 1478 (m), 1366 (s), 1250 (s), 1181 (s), 1035 (m), 829 (m); ^{1}H-NMR (360 MHz, $CDCl_3$): d = 0.94 (d, ^3J = 5.9 Hz, 3 H), 0.95 (s, 9 H), 2.57-2.73 (m, 2 H), 2.98

(dd, ^2J = 17.1 Hz, ^3J = 9.5 Hz, 1 H), 3.40 (td, ^3J = 9.7 Hz, ^3J = 4.3 Hz, 1 H), 3.69 (s, 3 H), 3.76 (s, 3 H), 6.80 (d, ^3J = 8.7 Hz, 2 H), 7.06 (d, ^3J = 8.7 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): d = 16.0 (q), 26.2 (q), 41.6 (t), 43.1 (d), 44.2 (s), 45.3 (d), 51.8 (q), 55.3 (q), 113.9 (d), 129.2 (d), 134.0 (s), 158.4 (s), 176.4 (s), 213.4 (s); MS (EI, 70 eV), *m/z* (%): 306 (38) [M^+], 219 (33), 151 (58), 85 (74), 57 (100); HRMS ($C_{18}H_{26}O_4$): calcd.: 306.1831, found: 306.1830.

[1] F. Mühlthau, D. Stadler, A. Goeppert, G. A. Olah, G. K. S. Prakash, T. Bach, *J. Am. Chem. Soc.* **2006**, *128*, 9668-9675.

[2] D. Stadler, T. Bach, *Chem. Asian J.* **2008**, 3, 272-284.

[3] T. Muraoka, S.-i, Kamiya, I. Matsuda, K. Itoh, *Chem. Commun*. **2002**, 1284-1285.

[4] F. Mühlthau, O. Schuster, T. Bach, *J. Am. Chem. Soc.* **2005**, *127*, 9348-9349.

[5] H. Akita, C. Y. Chen, S. Nagumo, *Tetrahedron Asymmetry* **1995**, *5*, 2159-2164.

[6] K. K. Park, J. J. Lee, J. Ryu, *Tetrahedron* **2003**, 59, 7651-7659.

[7] P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **1987**, *43*, 2075-2088.

[8] U. V. Desai, D. M. Pore, R. B. Mane, S. B. Solabannavar, P. P. Wadgoankar *Synth. Commun.* **2004**, *34*, 19-24; b) B. Das, J. Banerjee, A. Majhi, G. Mahender, *Tetrahedron Lett.* **2004**, *45*, 9225-9227.

[9] a) V. J. Bulbule, V. H. Deshpande, S. Velu, A. Sudalai, S. Sivasankar, V. T. Sathe, *Tetrahedron* **1999**, *55*, 9325-9332; b) V. J. Bulbule, G. K. Jnaneshwara, R. R. Deshmukh, H. B. Borate, V. H. Deshpande, *Synth. Commun.* **2001**, *31*, 3623-3626.