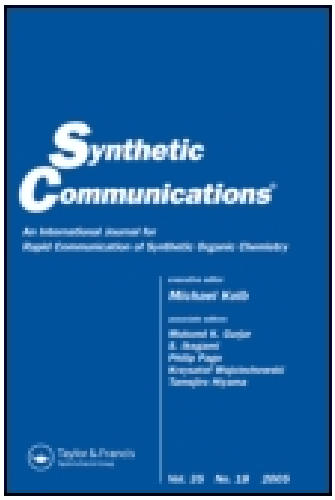

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Tandem Michael-Wittig-Horner Reaction: Application to the Synthesis of Bisabolanes

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Tandem Michael–Wittig–Horner Reaction: Application to the Synthesis of Bisabolanes

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ABSTRACT

Bisabolane derivatives have been synthesized from *para*-substituted cinnamaldehydes according to a tandem Michael–Wittig–Horner reaction. This sequence was applied to a short access to (+/−)-*ar*-turmerone.

Key Words: Michael addition; Wittig reaction; Bisabolanes; Turmerone; Tandem reaction.

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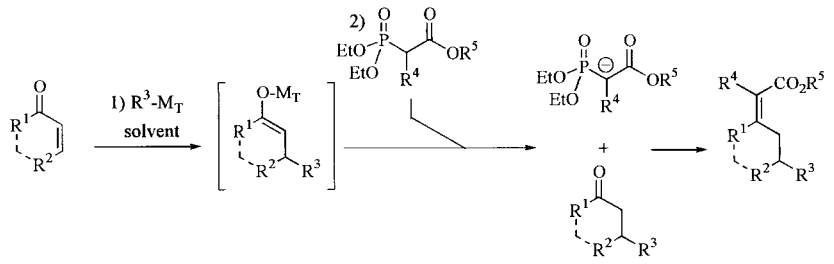
Recently, we reported a new tandem Michael–Wittig–Horner reaction to prepare according to Sch. 1, δ-substituted α-β-unsaturated esters from alkenals or alkenones.[1] This sequence was based on the in situ generation of an enolate which could further abstract the acidic hydrogen atom of a phosphono derivative; therefore both components for the Wittig–Horner reaction[2] could be formed and react.

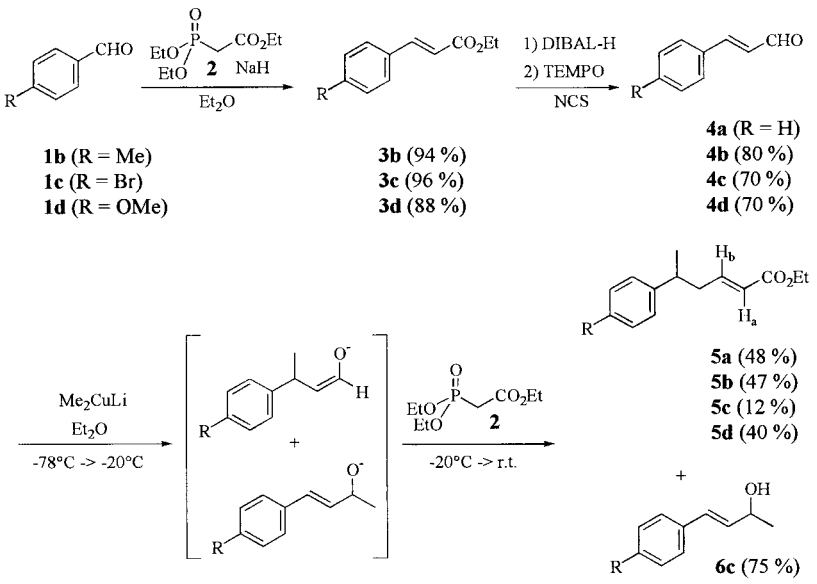
This procedure was successfully applied to a two-step synthesis of *E* and *Z*-ochtodenals, male sex pheromones of the boll weevil beetle. We wish to present herein an access to other natural compounds like bisabolanes in a similar way. Bisabolanes previously isolated from nature exhibit numerous biological activities such as natural mosquitocide and antibacterial properties.[3–9] Therefore, there is still an interest to develop straightforward methods for the synthesis of these compounds.

Condensation of *para*-substituted benzaldehydes (**1b**, **1c**, **1d**) with triethylphosphonoacetate (**2**) furnished α,β-unsaturated esters (**3b**, **3c**, **3d**) in good yields (Sch. 2). 1,2-Selective reduction[10] with Dibal-H followed by oxidation using catalytic amounts of TEMPO according to Einhorn's conditions[11,12] led to the formation of the unsaturated aldehydes (**4b**, **4c**, **4d**). Direct conversion of aldehyde (**1d**) into ester (**4d**) in the presence of $Ba(OH)_2$ according to a recent procedure[13] was in our hands unsuccessful and deliver in place of the expected aldehyde, compounds resulting from the well known Cannizzaro reaction.[14,15] Treatment of aldehydes (**4a**, **4b**, **4c**, **4d**) with Me_2CuLi in diethyl ether followed by (**2**) afforded in one single step ethyl (*E*)-5-aryl-hex-2-enoates (**5a**, **5b**, **5c**, **5d**) (Sch. 2). The *E* geometry of the new C=C bond was easily determined by ^{1}H-NMR (typically $J_{Ha\text{-}Hb} = 15.1$–15.6 Hz).

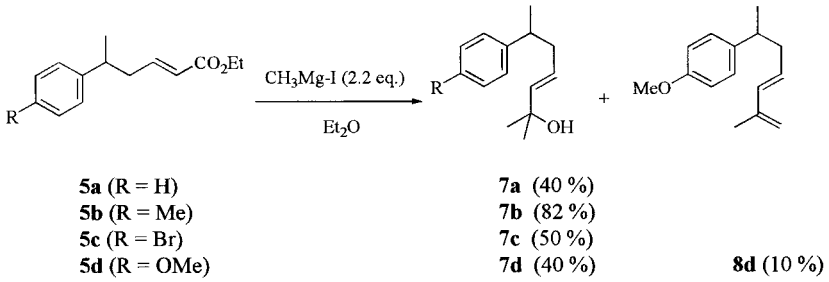
With aldehyde (**4c**), the major adduct was the secondary alcohol (**6c**) resulting from a competitive 1,2-addition during the first step. This reactivity could be attributed to the presence of the bromine atom



Scheme 1.

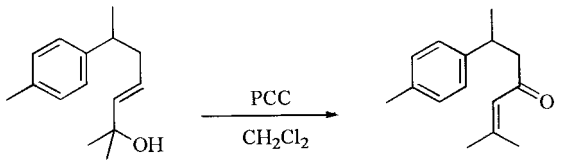


Scheme 2.



Scheme 3.

which could enhance the electrophilicity of the carbonyl group. Finally, esters (**5a**, **5b**, **5c**, **5d**) were submitted to the action of methyl Grignard reagent to give tertiary alcohols (**7a**, **7b**, **7c**, **7d**) in moderate to good yields (Sch. 3). However, these tertiary allylic alcohols are prompt to undergo an easy elimination of water during the acidic work-up. In case of (**5d**), for example, diene (**8d**) was isolated among numerous



7b **9** (31%)

Scheme 4.

side-products, while with the other substrates, more complex reaction products were formed probably according to Friedel–Crafts type alkylations.[16–19]

Compound (**7a**) has also been converted in moderate yield by a simple oxidative rearrangement using PCC[20–22] to (±)-*ar*-turmerone (**9**) a natural product (Sch. 4), isolated as a major flavour component of Zingiber and Curcuma species.[23–26]

In conclusion, we have been able to prepare in a two-step procedure bisabolane derivatives from alkenals easily obtained from commercial compounds. An access to (±)-*ar*-turmerone was also designed.

EXPERIMENTAL

The NMR spectra were recorded in $CDCl_3$ or d_6-benzene using a Bruker AC 300 instrument. Fourier transform-IR spectra were carried out in $CHCl_3$ on a Perkin Elmer SpectroOne spectrometer. Mass spectra were obtained on a Finigan-MAT 95 XL apparatus. Flash-chromatographies were performed on silica gel 60 (40–63 mesh).

General Procedure for Preparation of Esters (3b–d)

To a suspension of sodium hydride (1.32 g, 33.0 mmol) in diethylether (100 mL) was added dropwise ethyl 2-diethylphosphonopropionate (7.40 g, 33.0 mmol) in the same solvent (20 mL). After 1 h at r.t. was slowly added a solution of 4-substituted benzaldehyde (**1**) (3.60 g, 30.0 mmol) in the same solvent (10 mL). The reaction mixture was stirred overnight at r.t. and carefully hydrolyzed with a saturated solution of ammonium chloride (50 mL). After extraction with ether (3×50 mL),

the crude product was dried over $MgSO_4$ and purified by flash-chromatography (eluent: AcOEt/PE: 5/95) giving (**3**).

Ethyl 3-(*p*-methylphenyl)propenoate (3b, $R = CH_3$)[27,28]: 5.36 g (94%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.36 (3H, t, $J = 7.0$ Hz), 2.40 (3H, s), 4.29 (2H, q, $J = 7.0$ Hz), 6.41 (1H, d, $J = 16.0$ Hz), 7.21 (2H, d, $J = 8.1$ Hz), 7.44 (2H, d, $J = 8.1$ Hz), 7.68 (1H, d, $J = 16.0$ Hz). IR: $\nu = 3017, 2990, 2944, 1716, 1641, 1604, 1582, 1520, 1320, 1295, 1261, 1211, 1185, 1033, 834\,cm^{-1}$.

Ethyl 3-(*p*-bromophenyl)propenoate (3c, $R = Br$)[29]: 7.34 g (96% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, $J = 7.2$ Hz), 4.28 (2H, q, $J = 7.2$ Hz), 6.44 (1H, d, $J = 16.0$ Hz), 7.40 (2H, d, $J = 8.7$ Hz), 7.53 (2H, d, $J = 8.7$ Hz), 7.63 (1H, d, $J = 16.0$ Hz). IR: $\nu = 3015$, 2985, 2941, 1712, 1639, 1606, 1582, 1515, 1368, 1288, 1259, 1183, 1035, $841\,cm^{-1}$.

Ethyl 3-(*p*-methoxyphenyl)propenoate (3d, $R = OCH_3$)[30]: 5.44 g (88% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, $J = 7.2$ Hz), 3.86 (3H, s), 4.27 (2H, q, $J = 7.1$ Hz), 6.33 (1H, d, $J = 15.8$ Hz), 6.92 (2H, d, $J = 9.0$ Hz), 7.50 (2H, d, $J = 8.7$ Hz), 7.66 (1H, d, $J = 15.8$ Hz). IR: $\nu = 3007$, 2982, 2938, 2842, 1710, 1634, 1605, 1574, 1513, 1367, 1303, 1288, 1254, 1176, 1026, $832\,cm^{-1}$.

General Procedure for Preparation of Aldehydes (4b–d)

In a 500 mL two-necked flask was placed under nitrogen a solution of ester (**3**) (27.9 mmol) in toluene (80 mL). After cooling to -78°C, a 1.0 M solution of Dibal (61.4 mL) in the same solvent was dropwise added. The resulting mixture was stirred for 1 h, then carefully hydrolysed with aqueous solution of hydrochloric acid (40 mL). After addition of ether (50 mL), the reaction was warmed to r.t. The organic layer was washed with 1.0 N HCl solution (2×40 mL). The organic layers were dried over $MgSO_4$, filtered and concentrated under vacuo. To the crude mixture diluted in CH_2Cl_2 (280 mL), were successively added TEMPO (0.44 g, 2.8 mmol), nBu$_4$NCl (0.78 g, 2.8 mmol), a buffered solution of $NaHCO_3$ (0.5 M) and K_2CO_3 (0.05 M) and finally NCS (7.45 g, 55.8 mmol). The two phase solution was vigorously stirred overnight. After extraction of the aqueous phase with CH_2Cl_2 (3×50 mL), the organic layer was washed with brine (2×50 mL). The organic phase was dried over $MgSO_4$, filtered off and concentrated. Aldehyde (**4**) was isolated as a yellow oil after purification by flash-chromatography on silica (eluent: hexanes/AcOEt: 90/10).

3-(*p*-Methylphenyl)propenal (4b, $R = CH_3$)[31]: 3.58 g (80% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.42 (3H, s), 6.68 (1H, d, $J = 16.6$ Hz),

7.26 (2H, d, $J = 7.9$ Hz), 7.47 (1H, d, $J = 16.6$ Hz), 7.49 (2H, d, $J = 7.9$ Hz), 9.72 (1H, s). IR: $\nu = 3028$, 2987, 2922, 2816, 2735, 1682, 1627, 1609, 1569, 1513, 1451, 1292, 1254, 1182, 1125, 973 cm^{-1}.

3-(*p*-Bromophenyl)propenal (4c, $R = Br$)[32]: 4.12 g (70% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.74 (1H, d, $J = 16.0$ Hz), 7.44 (1H, d, $J = 16.4$ Hz), 7.45 (2H, d, $J = 8.3$ Hz), 7.60 (2H, d, $J = 8.5$ Hz), 9.74 (1H, s). IR: $\nu = 3047$, 2992, 2825, 2742, 1678, 1625, 1584, 1490, 1409, 1389, 1301, 1252, 1129, 1074, 1009, 981 cm^{-1}.

3-(*p*-Methoxyphenyl)propenal (4d, $R = OCH_3$)[31]: 70%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.88 (3H, s), 6.65 (1H, d, $J = 15.8$ Hz), 6.97 (2H, d, $J = 8.9$ Hz), 7.45 (1H, d, $J = 15.8$ Hz), 7.55 (2H, d, $J = 8.9$ Hz), 9.69 (1H, s). IR: $\nu = 3033$, 2981, 2939, 2843, 2765, 1673, 1621, 1601, 1571, 1512, 1462, 1308, 1263, 1175, 1130, 977 cm^{-1}.

General Procedure for Tandem Michael–Wittig–Horner Reaction (5a–d)

In a 100 mL two-necked flask dried prior use, was placed copper iodide (0.432 g, 2.25 mmol) in ether (25 mL). The solution was cooled to 0°C and a 1.6 M solution of methyllithium in hexane (2.8 mL, 4.50 mmol) was carefully added. After 40 min at this temperature, the colorless solution was cooled to −78°C and aldehyde (**4**) (2.25 mmol) was added dropwise. The dark yellow resulting mixture was stirred for 2.5 h while the temperature reached −15°C. Phosphonate (**2**) (0.9 mL, 4.50 mmol) dissolved in ether (1 mL) was added. The solution was stirred overnight, then hydrolysed with a saturated solution of ammonium chloride (25 mL). The crude solution was extracted with ether (3×25 mL), dried over $MgSO_4$, filtered and concentrated. The pure compound (**5**) was obtained after flash-chromatography on silica (eluent: hexanes/ethyl acetate: 97/3).

Ethyl 5-phenyl-hexen-2-oate (5a, $R = H$)[33]: 0.235 g (48% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.12 (3H, t, $J = 7.1$ Hz), 1.20 (3H, d, $J = 7.0$ Hz), 2.45 (2H, m), 2.82 (1H, m), 4.08 (2H, q, $J = 7.1$ Hz), 5.72 (1H, d, $J = 15.4$ Hz), 6.80 (1H, m), 7.13 (5H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.3, 22.0, 37.0, 39.9, 59.8, 120.5, 126.2, 127.0, 128.5, 146.3, 148.6, 166.4. IR: $\nu = 3028$, 2963, 2930, 1717, 1654, 1603, 1494, 1453, 1368, 1307, 1268, 1229, 1203, 1166, 1045, 844 cm^{-1}.

Ethyl 5-(*p*-methylphenyl)-hexen-2-oate (5b, $R = CH_3$)[20]: 0.245 g (47% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.18 (3H, d, $J = 7.1$ Hz), 1.19 (3H, t, $J = 7.1$ Hz), 2.25 (3H, s), 2.35 (2H, m), 2.79 (1H, m), 4.09

(2H, q, $J = 7.2$ Hz), 5.72 (1H, d, $J = 15.6$ Hz), 6.80 (1H, m), 7.25 (4H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.6, 21.4, 22.1, 39.1, 41.4, 60.5, 123.0, 127.1, 129.6, 136.1, 143.5, 147.9, 166.9. IR: $\nu = 3039$, 2973, 1715, 1626, 1605, 1581, 1520, 1469, 1371, 1305, 1264, 1180, 1146, 1037, 849 cm^{-1}.

Ethyl 5-(*p*-bromophenyl)-hexen-2-oate (5c, $R = Br$): 0.080 g (12% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.27 (3H, d, $J = 7.6$ Hz), 1.31 (3H, t, $J = 7.1$ Hz), 2.46 (2H, m), 2.87 (1H, m), 4.25 (2H, q, $J = 7.1$ Hz), 6.04 (1H, d, $J = 15.1$ Hz), 7.34 (2H, d, $J = 8.3$ Hz); 7.44 (1H, m), 7.51 (2H, d, $J = 8.3$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.6, 21.4, 22.1, 39.1, 41.4, 60.6, 123.0, 127.1, 129.6, 136.1, 143.5, 147.9, 166.9. IR: $\nu = 3026$, 2983, 2933, 1707, 1628, 1586, 1488, 1403, 1369, 1312, 1274, 1242, 1174, 1135, 1073, 849 cm^{-1}. MS: 296 (M^+), 211, 185, 104.

Ethyl 5-(*p*-methoxyphenyl)-hexen-2-oate (5d, $R = OCH_3$): 0.223 g (40% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28 (3H, d, $J = 7.2$ Hz), 1.30 (3H, t, $J = 7.2$ Hz), 2.45 (2H, m), 2.87 (1H, dt, $J = 6.9$ and 7.0 Hz), 3.81 (3H, s), 4.19 (2H, q, $J = 7.1$ Hz), 5.80 (1H, d, $J = 15.6$ Hz), 6.86 (2H, d, $J = 8.6$ Hz), 6.89 (1H, m), 7.12 (2H, d, $J = 8.6$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 14.7, 21.4, 22.1, 39.1, 41.4, 60.5, 123.0, 127.1, 129.6, 136.2, 143.5, 147.9, 166.9. IR: $\nu = 3031$, 2960, 2837, 1712, 1626, 1601, 1575, 1514, 1463, 1367, 1302, 1254, 1176, 1133, 1035, 831 cm^{-1}. MS: 248 ($M^{+\cdot}$, 2), 135 (100), 105 (16), 91 (17), 68 (24).

General Procedure for Conversion of Unsaturated Esters to Allylic Alcohols (7a–d)

In a 100 mL two-necked flask was placed ester (**5**) (2.20 mmol) in ether (40 mL). After cooling to 0°C, a 1.0 M ethereal solution of methyl Grignard (5.0 mL) was added. The resulting solution was stirred at r.t. overnight and carefully hydrolysed with an aqueous saturated solution of NH_4Cl (25 mL). After extraction with ether (3×25 mL), the organic layers were collected, dried over $MgSO_4$, filtered over a pad of Celite® and concentrated under vacuo. Alcohol (**7**) was purified by flash-chromatography over silica (eluent: AcOEt/hexanes: 8/92).

(*E*)-2-Methyl, 6-phenyl 3-hepten-2-ol (7a, $R = H$): 0.180 g (40% yield). (300 MHz, $CDCl_3$): δ 1.18 (6H, s), 1.19 (3H, d), 1.30 (m, OH), 2.21 (2H, m), 2.69 (1H, m), 5.45 (2H, m), 7.16 (5H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.72, 30.1, 40.4, 41.5, 71.0, 126.4, 125.6, 127.5, 128.9, 140.1, 147.4. IR: $\nu = 3378$, 3027, 2969, 2927, 1667, 1602, 1583, 1494, 1452, 1375, 1306, 1232, 1191, 1148, 971, 760, 692 cm^{-1}. MS: 204 (M^+, < 1), 188 (15), 187 (100), 105 (41).

(*E*)-2-Methyl, 6-(*p*-methyl)phenyl 3-hepten-2-ol (7b, $R = CH_3$)[34]: 0.394 g (82% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.18 (3H, d), 1.19 (6H, s), 1.51 (m, OH), 2.19 (2H, m), 2.24 (3H, s), 2.66 (1H, m), 5.47 (2H, m), 7.01 (4H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.4, 21.8, 30.1, 39.9, 41.5, 71.0, 125.9, 127.3, 129.3, 135.7, 140.0, 144.4. IR: $\nu = 3378$, 3020, 2970, 2925, 2872, 1577, 1515, 1455, 1415, 1374, 1308, 1233, 1150, 971, 816 cm^{-1}. MS: 218 (M^+, < 5), 203, 200, 188, 131, 119, 118, 105, 91.

(*E*)-2-Methyl, 6-(*p*-bromo)phenyl 3-hepten-2-ol (7c): 0.249 g (50% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.25 (3H, d, $J = 7.7$ Hz), 1.27 (6H, s), 1.58 (m, OH), 2.27 (2H, m), 2.76 (1H, m), 5.52 (2H, m), 7.07 (2H, d, $J = 8.5$ Hz), 7.42 (2H, d, $J = 8.3$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.6, 30.2, 39.9, 41.2, 71.0, 119.9, 125.1, 129.2, 131.7, 140.4, 146.3. IR: $\nu = 3388$, 3023, 2926, 1660, 1590, 1489, 1456, 1405, 1374, 1231, 1149, 1074, 1010, 971, 822 cm^{-1}. MS: 283 and 281 ($M^{+\cdot}$, < 2), 267 and 265 ($M - H_2O$, 100), 185 and 183 (60).

(*E*)-2-Methyl, 6-(*p*-methoxy)phenyl 3-hepten-2-ol (7d): 0.207 g (40% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.15 (3H, d, $J = 7.0$ Hz), 1.19 (6H, s), 1.28 (1H, OH), 2.18 (2H, m), 2.65 (1H, m), 3.71 (3H, s), 5.46 (2H, m), 6.76 (2H, d, $J = 8.6$ Hz), 7.02 (2H, d, $J = 8.6$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.9, 30.1, 39.5, 41.6, 55.6, 71.0, 114.0, 125.8, 128.3, 139.5, 140.0, 158.1. IR: $\nu = 3399$, 3028, 2967, 2928, 2836, 1611, 1583, 1520, 1458, 1441, 1374, 1302, 1246, 1178, 1036, 971, 830 cm^{-1}.

(*E*)-6-(*p*-Methoxyphenyl)-2-methyl-1,3-heptadiene (8d): 0.048 g (10% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.15 (3H, d, $J = 7.0$ Hz), 1.71 (3H, s), 2.15–2.38 (2H, m), 2.68 (1H, dt, $J = 7.0$ Hz), 3.72 (3H, s), 4.48 (2H, s), 5.47 (1H, dt, $J = 15.6$ and 7.1 Hz), 6.05 (1H, d, $J = 15.6$ Hz), 6.77 (2H, d, $J = 8.6$ Hz), 7.04 (2H, d, $J = 8.6$ Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 19.0, 21.9, 39.7, 42.3, 55.6, 114.0, 114.8, 128.1, 129.5, 134.5, 139.6, 142.5, 158.1. IR: $\nu = 2927$, 1610, 1584, 1512, 1458, 1441, 1374, 1247, 1178, 1115.

Direct Conversion of (7b) to (±)-*ar*-Turmerone (9)

A solution of alcohol (**7b**) (0.200 g, 0.70 mmol) in CH_2Cl_2 was added to a solution of PCC (0.45 g, 2.05 mmol) in the same solvent (20 mL) and the reaction mixture was stirred overnight at r.t. After addition of Et_2O (30 mL), the resulting suspension was filtered over Celite® and the filtrate was concentrated under vacuo. Compound (**9**) (0.047 g, 0.21 mmol) was isolated by flash-chromatography (eluent: AcOEt/hexanes: 97/3). 31%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.17 (3H, d, $J = 7.0$ Hz), 1.78 (3H, s), 2.04 (3H, s), 2.24 (3H, s), 2.59 (2H, m), 3.22 (1H, m), 5.95 (1H, s), 7.03

(4H, m). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 21.7, 30.1, 40.4, 41.5, 71.0, 126.4, 125.6, 127.4, 128.9, 140.1, 147.4. IR: $\nu = 3020$, 2962, 2925, 1686, 1620, 1515, 1446, 1378, 1358, 1309, 1260, 1111, 1036, 1012 cm^{-1}.

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