Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information

for

*Angew. Chem. Int. Ed.* 200460812

# Electrophilic Alkylations in Neutral Aqueous or Alcoholic Solutions**

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Analytical data:

NMR spectra were recorded on a Bruker ARX 300 (300 MHz) or Varian VXR 400 S (400 MHz). Chemical shifts are reported as δ-values in ppm relative to tetramethylsilane ($\delta_H$: 0.00, $\delta_C$: 0.00) or relative to the deuterated solvent peak: $CDCl_3$ ($\delta_H$: 7.24, $\delta_C$: 77.0). Coupling constants are reported in Hz. For the characterization of the observed signal multiplicities the following abbreviations were applied: s (singlet), d (dublet), t (triplet), q (quartet), m (multiplet), as well as br (broad).

GC-MS analysis were performed on an Agilent 5973 MSD: capillary column HP-5MS (Agilent Technologies; length 30 m; ∅ 0.25 mm); flow rate 1.0 mL/min; injector, split (23.9 mL/min), inlet heater 250 °C, carrier gas: He; temperature program: 70 °C (2 min) – 25 °C/min to 150 °C – 50 °C/min to 250 °C (12 min); quadrupole mass spectrometer.

Elemental analysis were carried out in the "Mikroanalytisches Laboratorium of the Department Chemie und Biochemie der LMU München".

Melting points were determined on a Büchi B540 and are uncorrected.

*1-(4-Methoxybenzyl)-2,4-dimethylbenzene* (**2a**)

According to the typical reaction procedure, 4-methoxybenzyl chloride (517 mg, 3.33 mmol) was added to 10 mL of a solution of *m*-xylene (3.05 g, 10.0 mmol) in 2,2,2-trifluoroethanol (T) and ammonium hydrogencarbonate (395 mg, 5.00 mmol) and stirred for 1 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 496 mg of **2a** (2.19 mmol; 66%) was isolated as a colorless oil containing traces of the corresponding 1,2,3-substituted product.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.20, 2.29 (2 s, 2 × 3 H, 2 × $CH_3$), 3.76 (s, 3 H, $OCH_3$), 3.87 (s, 2 H, $CH_2$), 6.78 – 6.82 (m, 2 H, Ar-H), 6.95 – 7.04 (m, 5 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 19.5, 20.9 (2 q), 38.1 (t), 55.2 (q, $OCH_3$), 113.8 (d, 2 × $C_{ar}$), 126.5, 129.7, 131.1 (3 d, C-3, C-5, C-6), 129.6 (d, 2 × $C_{ar}$), 132.7 (s, $C_{ar}$), 135.8, 136.2, 136.3 (3 s, C-1, C-2, C-4), 157.8 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 8.83 min; *m/z* (%) = 226 (92) [$M^+$], 211 (100) [$M^+ - CH_3$], 195 (20) [$M^+ - OCH_3$], 165 (21) [$M^+ - OCH_3 - 2\ CH_3$], 121 (19) [$H_3COC_6H_4CH_2^+$], 118 (62) [$M^+ - H_3COC_6H_5^+$].

*1-(4-Methoxybenzyl)-2,4,6-trimethylbenzene* (**2b**)

According to the typical reaction procedure, 4-methoxybenzyl chloride (517 mg, 3.33 mmol) was added to 10 mL of a solution of mesitylene (1.20 g, 10.0 mmol) in 2,2,2-trifluoroethanol (T) and ammonium hydrogencarbonate (395 mg, 5.00 mmol) and stirred for 1 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 8/1) 702 mg of **2b** (2.92 mmol; 88%) was isolated as a colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 6 H, 2-$CH_3$, 6-$CH_3$), 2.28 (s, 3 H, 4-$CH_3$), 3.75 (s, 3 H, $OCH_3$), 3.94 (s, 2 H, $CH_2$), 6.75 – 6.78 (m, 2 H, Ar-H), 6.87 – 6.93 (m, 4 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 20.1 (q, 2 × $CH_3$), 20.9 (q), 33.8 (t), 55.2 (q, $OCH_3$), 113.8 (d, $C_{ar}$), 128.7, 128.9 (2 d, 4 × $C_{ar}$), 132.1, 134.1, 135.5 (3 s, 3 × $C_{ar}$), 136.9 (s, 2 × $C_{ar}$) 157.7 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 9.15 min; *m/z* (%) = 240 (72) [$M^+$], 225 (58) [$M^+ - CH_3$], 210 (10) [$M^+ - 2\ CH_3$], 209 (8) [$M^+ - OCH_3$], 178 (11), 165 (13), 132 (100) [$M^+ - H_3COC_6H_5$], 121 (15) [$H_3COC_6H_4CH_2^+$].

*Bis(4-methoxyphenyl)methane* (**2c**)

According to the typical reaction procedure, 4-methoxybenzyl chloride (517 mg, 3.33 mmol) was added to 10 mL of a solution of anisole (1.08 g, 10.0 mmol) in 2,2,2-trifluoroethanol (T) and ammonium hydrogencarbonate (395 mg, 5.00 mmol) and stirred for 30 min at ambient

temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 655 mg of **2c** (2.87 mmol; 86%) was isolated as a white solid, m.p. 51 °C, containing traces of the corresponding 1,2-substituted product.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 6 H, 2 × $OCH_3$), 3.86 (s, 2 H, $CH_2$), 6.80 – 6.83 (m, 4 H, Ar-H), 7.06 – 7.09 (m, 4 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 40.1 (t), 55.2 (s, 2 × $OCH_3$), 113.8 (d, 4 × $C_{ar}$), 129.7 (d, 4 × $C_{ar}$), 133.7 (s, 2 × $C_{ar}$), 157.9 (s, 2 × $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 9.11 min; *m/z* (%) = 228 (100) [$M^+$], 213 (22) [$M^+ - CH_3$], 197 (57) [$M^+ - OCH_3$], 181 (13), 165 (12), 152 (16), 121 (32) [$H_3COC_6H_4CH_2^+$], 91 (22).

NMR data for compound **2c** are in accordance with the data previously published.[S1]

*4-Methoxy-1-(4-methoxybenzyl)-2-methylbenzene* (**2d**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (750 mg, 3.73 mmol) was added to 25 mL of a solution of 3-methylanisole (3.05 g, 25.0 mmol) in 2,2,2-trifluoroethanol (T) and ammonium hydrogencarbonate (0.59 g, 7.46 mmol) and stirred for 1.5 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 875 mg of **2d** (3.61 mmol; 97%) was isolated in a mixture of regioisomers as a colorless oil. Fraction 1 of this separation was the pure isomer **2d** which was identified spectroscopically.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, $CH_3$), 3.76, 3.77 (2 s, 2 × 3 H, 2 × $OCH_3$), 3.85 (s, 2 H, $CH_2$), 6.66 – 6.72 (m, 2 H, Ar-H), 6.78 – 6.81 (m, 2 H, Ar-H), 6.98 – 7.03 (m, 3 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 19.9 (q), 37.7 (t), 55.2 (q, 2 × $OCH_3$), 110.8 (d, $C_{ar}$), 113.8 (d, 2 × $C_{ar}$), 116.0 (d, $C_{ar}$), 129.5 (d, 2 × $C_{ar}$), 130.7 (d, $C_{ar}$), 131.6 (s, $C_{ar}$), 132.9 (s, $C_{ar}$), 137.8 (s, C-2), 157.8, 158.0 (2 s, 2 × $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 9.56 min; *m/z* (%) = 242 (100) [$M^+$], 227 (30) [$M^+ - CH_3$], 211 (22) [$M^+ - OCH_3$], 134 (55), 121 (56) [$H_3COC_6H_4CH_2^+$]. Anal. Calcd. for $C_{16}H_{18}O_2$ (242.32): C, 79.31; H, 7.49. Found: C, 79.62; H, 7.60.

Fraction 2 was a 17:1 mixture of **2d** and 2-methoxy-1-(4-methoxybenzyl)-4-methylbenzene, the latter of which was identified by its NMR spectra and GC-MS analysis.

NMR data for compound **2d** were published previously.[S2]

*2-(4-Methoxybenzyl)-5-methylthiophene* (**2e**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (783 mg, 5.00 mmol) was added to 25 mL of a solution of 2-methylthiophene (2.45 g, 25.0 mmol) and 2-

chloropyridine (625 mg, 5.50 mmol) in 2,2,2-trifluoroethanol (T) and stirred for 1 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 920 mg of **2e** (4.21 mmol; 84%) was isolated as a colorless oil.
$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, 5-$CH_3$), 3.76 (s, 3 H, $OCH_3$), 3.99 (s, 2 H, $CH_2$), 6.52 – 6.55 (m, 2 H, 3-H, 4-H), 6.81 – 6.84 (m, 2 H, Ar-H), 7.13 – 7.16 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 15.3 (q, 5-$CH_3$), 35.4 (t), 55.2 (q, $OCH_3$), 113.9 (d, 2 × $C_{ar}$), 124.5, 124.6 (2 d, C-3, C-4), 129.5 (d, 2 × $C_{ar}$), 132.7 (s, $C_{ar}$), 138.2, 142.4 (2 s, C-2, C-5), 158.2 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 8.45 min; *m/z* (%) = 218 (100) [$M^+$], 203 (95) [$M^+$ – $CH_3$], 187 (34) [$M^+$ – $OCH_3$], 121 (11) [$H_3COC_6H_4CH_2^+$].
$^1$H NMR and MS data for compound **2e** were published previously.[S3]

*2,4-Dimethoxy-1-(4-methoxybenzyl)benzene* (**2f**)
According to the typical reaction procedure, 4-methoxybenzyl chloride (1.00 g, 6.39 mmol) was added to 25 mL of a solution of 1,3-dimethoxybenzene (3.45 g, 25.0 mmol) and 2,6-lutidine (1.03 g, 9.61 mmol) in 2,2,2-trifluoroethanol (T) and stirred for 30 min at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 8/1) 1.38 g of **2f** (5.34 mmol; 84%) was isolated as a colorless oil containing 7% (GC-MS) of the corresponding 1,2,3-substituted product. The major fraction of this separation was the pure isomer **2d** which was identified spectroscopically.
$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.75, 3.76, 3.77 (3 s, 3 × 3 H, 3 × $OCH_3$), 3.83 (s, 2 H, $CH_2$), 6.37 – 6.45 (m, 2 H, Ar-H), 6.75 – 6.78 (m, 2 H, Ar-H), 6.80 – 6.82 (m, 1 H, Ar-H), 6.92 – 6.95 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 34.3 (t), 55.2 (q, 3 × $OCH_3$), 98.5, 103.9 (2 d, 2 × $C_{ar}$), 113.6 (d, 2 × $C_{ar}$), 122.5 (s, $C_{ar}$), 129.7 (d, 2 × $C_{ar}$), 130.3 (d, $C_{ar}$), 133.5 (s, $C_{ar}$), 157.7, 158.1, 159.0 (3 s, 3 × $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 10.13 min; *m/z* (%) = 258 (100) [$M^+$], 243 (18) [$M^+$ – $CH_3$], 227 (62) [$M^+$ – $OCH_3$], 151 (15) [$M^+$ – $H_3COC_6H_5$], 121 (33) [$H_3COC_6H_5^+$], 91 (14). Anal. Calcd. for $C_{16}H_{18}O_3$ (258.32): C, 74.40; H, 7.02. Found: C, 74.73; H, 7.03.

*2,4,6-Trimethoxy-1-(4-methoxybenzyl)benzene* (**2g**)
According to the typical reaction procedure, 4-methoxybenzyl chloride (1.00 g, 6.39 mmol) was added to 25 mL of a solution of 1,3,5-trimethoxybenzene (4.20 g, 25.0 mmol) and 2,6-lutidine (752 mg, 7.02 mmol) in 2,2,2-trifluoroethanol (T) and stirred for 2 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel

(pentane/ether : 2/1) 1.62 g of **2g** (5.62 mmol; 88%) was isolated as a white solid, m.p. 77 – 78 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3 H, $OCH_3$), 3.77 (s, 6 H, 2 × $OCH_3$), 3.79 (s, 3 H, $OCH_3$), 3.86 (s, 2 H, $CH_2$), 6.14 (s, 2 H, Ar-H), 6.73 – 6.76 (m, 2 H, Ar-H), 7.13 – 7.16 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 27.3 (t), 55.1, 55.3 (2 q, 2 × $OCH_3$), 55.7 (q, 2 × $OCH_3$), 90.7 (d, 2 × $C_{ar}$), 110.7 (s, $C_{ar}$), 113.4, 129.2 (2 d, 4 × $C_{ar}$), 134.4 (s, $C_{ar}$), 157.3 (s, $C_{ar}$–$OCH_3$), 158.7 (s, 2 × $C_{ar}$–$OCH_3$), 159.4 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 11.42 min; *m/z* (%) = 288 (100) [$M^+$], 273 (8) [$M^+ - CH_3$], 257 (37) [$M^+ - OCH_3$], 181 (34) [$M^+ - H_3COC_6H_4$], 121 (53) [$H_3COC_6H_4^+$], 91 (9). Anal. Calcd. for $C_{17}H_{20}O_4$ (288.34): C, 70.81; H, 6.99. Found: C, 70.90; H, 7.05.

*3-(4-Methoxybenzyl)-1H-indole* (**2h**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (1.01 g, 5.02 mmol) was added to 25 mL of a solution of indole (2.93 g, 25.0 mmol) in 80% aqueous acetone (v/v) (80A20W) and ammonium hydrogencarbonate (791 mg, 10.0 mmol) and stirred for 3 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/3) 890 mg of **2h** (3.75 mmol; 75%) was isolated as a yellow solid, m.p. 77 – 78 °C, containing 17% of the corresponding 2-isomer. Fraction 1 of this separation was the pure isomer **2h** which was identified spectroscopically.

*3-Isomer:* $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, $OCH_3$), 4.04 (s, 2 H, $CH_2$), 6.80 – 7.51 (m, 9 H, Ar-H), 7.87 (br s, 1 H, NH). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 30.7 (t), 55.2 (q, $OCH_3$), 102.4 (s, C-3), 111.0 (d, C-7), 113.8 (d, 2 × $C_{ar}$), 119.2, 119.3, 120.4, 120.5 (4 d, C-2, C-4, C-5, C-6), 127.4 (s, C-3a), 129.7 (d, 2 × $C_{ar}$), 133.3 (s, $C_{ar}$), 136.5 (s, C-7a), 157.8 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 12.13 min; *m/z* (%) = 237 (100) [$M^+$], 236 (82) [$M^+ - H$], 222 (10) [$M^+ - CH_3$], 206 (17) [$M^+ - OCH_3$], 192 (19), 130 (46) [$M^+ - H_3COC_6H_4$]. Anal. Calcd. for $C_{16}H_{15}NO$ (237.30): C, 80.98; H, 6.37; N, 5.90. Found: C, 80.91; H, 6.69; N, 5.80.

*2-Isomer:* GC-MS: $t_R$ = 12.39 min; *m/z* (%) = 237 (100) [$M^+$], 236 (39) [$M^+ - H$], 222 (10) [$M^+ - CH_3$], 206 (25) [$M^+ - OCH_3$], 192 (17), 130 (22) [$M^+ - H_3COC_6H_4$].

*2-(4-Methoxybenzyl)-1-methyl-1H-pyrrole* (**2i**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (1.00 g, 4.97 mmol) was added to 25 mL of a solution of 1-methylpyrrole (2.03 g, 25.0 mmol) in 80% aqueous acetonitrile (v/v) (80A20W) and ammonium hydrogencarbonate (790 mg, 9.99 mmol) and

stirred for 30 min at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 700 mg of **2i** (3.48 mmol; 70%) was isolated as an orange oil containing 21% of the corresponding 3-substituted product. The major fraction 1 of this separation was the pure isomer **2i** which was identified spectroscopically.

*2-Isomer:* $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 3.42 (s, 3 H, $NCH_3$), 3.78 (s, 3 H, $OCH_3$), 3.87 (s, 2 H, $CH_2$), 5.87 (m, 1 H, 3-H), 6.05 (m, 1 H, 4-H), 6.56 (m, 1 H, 5-H), 6.80 – 6.83 (m, 2 H, Ar-H), 7.05 – 7.08 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 32.0 (t), 33.7 (q, $NCH_3$), 55.2 (q, $OCH_3$), 106.5, 107.7 (2 d, C-3, C-4), 113.8 (d, 2 × $C_{ar}$), 121.7 (d, C-5), 129.4 (d, 2 × $C_{ar}$), 131.5, 131.9 (2 s, C-2, $C_{ar}$), 158.0 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 8.20 min; *m/z* (%) = 201 (100) [$M^+$], 200 (54), 186 (11) [$M^+ - CH_3$], 170 (20) [$M^+ - OCH_3$], 94 (85) [$M^+ - H_3COC_6H_4$]. Anal. Calcd. for $C_{13}H_{15}NO$ (201.27): C, 77.58; H, 7.51; N, 6.56. Found: C, 77.07; H, 7.65; N, 6.87.

Fraction 2 was a 2.3:1 mixture (NMR) of **2i** and of 3-(4-methoxybenzyl)-1-methyl-1H-pyrrole, the latter of which was identified by the NMR spectra of the product mixture and GC-MS analysis.

*3-Isomer:* GC-MS: $t_R$ = 8.30 min; shows the same fragmentation pattern as the 2-isomer.

*3-(4-Methoxyphenyl)-2-methylpropanaldehyde* (**3a**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (500 mg, 2.49 mmol) was added to 25 mL of a solution of ethyl prop-1-enyl ether (2.15 g, 25.0 mmol) (mixture of *cis*/*trans*-isomers) in 90% aqueous acetonitrile (v/v) (90AN10W) and ammonium hydrogencarbonate (295 mg, 3.73 mmol) and stirred for 3 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 266 mg of **3a** (1.49 mmol; 60%) was isolated as a colorless liquid.

$^{1}$H NMR (400 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.7 Hz, 3 H, $CH_3$), 2.53 – 2.64 (m, 2 H, $CH_2$), 2.98 – 3.03 (m, 1 H, C*H*$CH_3$), 3.77 (s, 3 H, $OCH_3$), 6.82 – 6.84 (m, 2 H, Ar-H), 7.06 – 7.08 (m, 2 H, Ar-H), 9.69 (s, 1 H, CHO). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 13.1 (q), 35.7 (t), 48.1 (d, *C*H$CH_3$), 55.1 (q, $OCH_3$), 113.9 (d, 2 × $C_{ar}$), 129.9 (d, 2 × $C_{ar}$), 130.7 (s, $C_{ar}$), 158.2 (s, $C_{ar}$–$OCH_3$), 204.4 (d, CHO). GC-MS: $t_R$ = 7.29 min; *m/z* (%) = 178 (18) [$M^+$], 163 (1) [$M^+ - CH_3$], 122 (12), 121 (100) [$H_3COC_6H_4CH_2^+$], 108 (10), 91 (9), 77 (10).

*4-(4-Methoxyphenyl)butan-2-one* (**3b**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (1.00 g, 4.97 mmol) was added to 25 mL of a solution of 2-methoxypropene (1.80 g, 25.0 mmol) and 2,6-lutidine (799 mg, 7.46 mmol) in 90% aqueous acetonitrile (v/v) (90AN10W) and stirred for 3 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 594 mg of **3b** (3.33 mmol; 67%) was isolated as a colorless liquid.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, $CH_3$), 2.69 – 2.74 (m, 2 H, $COCH_2$), 2.81 – 2.86 (m, 2 H, Ar$CH_2$), 3.77 (s, 3 H, $OCH_3$), 6.79 – 6.84 (m, 2 H, Ar-H), 7.07 – 7.12 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 28.8 (t, $COCH_2C$), 30.0 (q, $COCH_3$), 45.4 (t, $COCH_2$), 55.2 (q, $OCH_3$), 113.8, 129.1 (2 d, 4 × $C_{ar}$), 133.0 (s, $C_{ar}$), 157.9 (s, $C_{ar}$–$OCH_3$), 208.0 (s, CO). GC-MS: $t_R$ = 7.41 min; *m/z* (%) = 178 (35) [$M^+$], 163 (5) [$M^+ - CH_3$], 135 (8) [$M^+ - COCH_3$], 121 (100) [$H_3COC_6H_4CH_2^+$], 108 (10), 91 (9), 77 (8).

NMR and MS data for compound **3b** were published previously.[S4]

*3-(4-Methoxyphenyl)-1-phenylpropan-1-one* (**3c**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (250 mg, 1.24 mmol) was added to 10 mL of a solution of 1-phenyl-1-(trimethylsiloxy)ethene (1.92 g, 10.0 mmol) in 90% aqueous acetonitrile (v/v) (90AN10W) and ammonium hydrogencarbonate (147 mg, 1.86 mmol) and stirred for 4.5 h at ambient temperature. After the usual workup the resulting acetophenone was removed in vacuo. Purification by column chromatography on silica gel (pentane/ether : 7/1) and recrystallization yielded 98.3 mg of **3c** (409 μmol; 33%) as a white solid, m.p. 66 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.98 – 3.03 (m, 2 H, Ar$CH_2$), 3.24 – 3.29 (m, 2 H, $COCH_2$), 3.78 (s, 3 H, $OCH_3$), 6.82 – 6.85 (m, 2 H, Ar-H), 7.15 – 7.18 (m, 2 H, Ar-H), 7.42 – 7.57 (m, 3 H, $C_6H_5$), 7.94 – 7.96 (m, 2 H, $C_6H_5$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 29.3 (t, Ar$CH_2$), 40.7 (t, $COCH_2$), 55.3 (q, $OCH_3$), 113.9 (d, 2 × $C_{ar}$), 128.0 (d, 2 × $C_{ar}$), 128.6 (d, 2 × $C_{ar}$), 129.3 (d, 2 × $C_{ar}$), 133.0 (d, $C_{ar}$), 133.2, 136.9 (2 s, 2 × $C_{ar}$), 158.0 (s, $C_{ar}$–$OCH_3$), 199.3 (s, CO). GC-MS: $t_R$ = 9.92 min; *m/z* (%) = 220 (25) [$M^+$], 205 (100) [$M^+ - CH_3$], 189 (4) [$M^+ - OCH_3$], 177 (8), 145 (10).

$^1$H NMR and MS data for compound **3c** were published previously.[S5]

*2-[Bis(4-methoxyphenyl)methyl]-5-methylfuran* (**4a**)

According to the typical reaction procedure, chlorobis(4-methoxyphenyl)-methane (1.00 g, 3.81 mmol) (dissolved in 3.00 mL acetonitrile) was added to 20 mL of a solution of 2-methylfuran (1.64 g, 20.0 mmol) and 2-chloropyridine (433 mg, 3.81 mmol) in 2,2,2-trifluoroethanol (T) and stirred for 1 min at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 895 mg of **4a** (3.24 mmol; 85%) was isolated as a colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, 5-$CH_3$), 3.77 (s, 6 H, 2 × $OCH_3$), 5.29 (s, 1 H, 2-CH), 5.71, 5.86 (2 m, 2 H, 3-H, 4-H), 6.80 – 6.85 (m, 4 H, Ar-H), 7.02 – 7.06 (m, 4 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (q, 5-$CH_3$), 49.3 (d, 2-CH), 55.2 (q, 2 × $OCH_3$), 105.8, 108.7 (2 d, C-3, C-4), 113.7 (d, 4 × $C_{ar}$), 129.6 (d, 4 × $C_{ar}$), 134.6 (s, 2 × $C_{ar}$), 151.3, 155.5 (2 s, C-2, C-5), 158.2 (s, 2 × $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 12.36 min; *m/z* (%) = 308 (100) [$M^+$], 293 (9) [$M^+ - CH_3$], 277 (27) [$M^+ - OCH_3$], 265 (93), 250 (29), 234 (8), 218 (6), 201 (71), 185 (18), 115 (12).

NMR data for compound **4a** are in accordance with the previously published data.[S6]

*2-[1-(4-Methoxyphenyl)ethyl]-5-methylfuran* (**4b**)

According to the typical reaction procedure, 1-(1-chloroethyl)-4-methoxybenzene (1.00 g, 5.86 mmol) was added to 25 mL of a solution of 2-methylfuran (2.05 g, 25.0 mmol) and 2,6-lutidine (691 mg, 6.45 mmol) in 2,2,2-trifluoroethanol (T) and stirred for 30 min at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 887 mg of **4b** (4.10 mmol; 70%) was isolated as a colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 1.53 (d, *J* = 7.2 Hz, 3 H, $CH_3$), 2.22 (s, 3 H, 5-$CH_3$), 3.77 (s, 3 H, $OCH_3$), 4.01 (q, *J* = 7.2 Hz, 1 H, 2-CH), 5.83 – 5.87 (m, 2 H, 3-H, 4-H), 6.81 – 6.83 (m, 2 H, Ar-H), 7.12 – 7.15 (m, 2 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 13.5 (q, 5-$CH_3$), 20.8 (q), 38.4 (d, 2-CH), 55.2 (q, $OCH_3$), 105.3, 105.7 (2 d, C-3, C-4), 113.8 (d, 2 × $C_{ar}$), 128.2 (d, 2 × $C_{ar}$), 136.6 (s, $C_{ar}$), 150.7 (s, C-2), 157.5, 158.1 (2 s, C-5, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 7.85 min; *m/z* (%) = 216 (25) [$M^+$], 201 (100) [$M^+ - CH_3$], 186 (9), 158 (10). Anal. Calcd. for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 77.47; H, 7.32.

*2-Methyl-5-(1-thiophen-2-ylethyl)furan* (**4c**)

According to the typical reaction procedure, 2-chloro-2-thienylethane (1.56 g, 10.6 mmol) was added to 50 mL of a solution of 2-methylfuran (4.11 g, 50.0 mmol) in 90% aqueous

acetonitrile (v/v) (90AN10W) and ammonium hydrogencarbonate (1.68 g, 21.2 mmol) and stirred for 24 h at ambient temperature. After the usual workup, purification by column chromatography on silica gel ($CH_2Cl_2$) and destillation, 980 mg of **4c** (5.10 mmol; 48%) was isolated as a colorless oil, b.p. 115 – 117 °C/3.0 mbar.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$), 2.25 (s, 3 H, 2-$CH_3$), 4.35 (q, *J* = 7.2 Hz, 1 H, C*H*$CH_3$), 5.87, 5.93 (2 m, 2 × 1 H, 3-H, 4-H), 6.85, 6.92, 7.14 (3 m, 3 × 1 H, $C_4H_3S$). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 13.5 (q, 2-$CH_3$), 21.5 (q), 34.6 (d, *C*H$CH_3$), 105.4, 105.8 (2 d, C-3, C-4), 123.4, 123.7, 126.5 (3 d), 148.1, 150.9, 156.4 (3 s). GC-MS: $t_R$ = 7.01 min; *m/z* (%) = 192 (33) [$M^+$], 177 (100) [$M^+ - CH_3$], 149 (7), 134 (9), 115 (8).

*2-Benzhydryl-5-methylfuran* (**4d**)

According to the typical reaction procedure, benzhydryl chloride (1.01 g, 5.00 mmol) was added to 25 mL of a solution of 2-methylfuran (2.05 g, 25.0 mmol) in 2,2,2-trifluoroethanol (T) and ammonium hydrogencarbonate (589 mg, 5.50 mmol) and stirred for 2 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 1.08 g of **4d** (4.35 mmol; 87%) was isolated as a yellow oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, 5-$CH_3$), 5.39 (s, 1 H, 2-CH), 5.74 – 5.75, 5.86 – 5.87 (2 m, 2 H, 3-H, 4-H), 7.16 – 7.31 (m, 10 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (q, 5-$CH_3$), 51.0 (d, 2-CH), 105.9, 109.1, (2 d, C-3, C-4), 126.6 (d, 2 × $C_{ar}$), 128.3, 128.8 (2 d, 8 × $C_{ar}$), 142.1 (s, 2 × $C_{ar}$), 151.5, 154.8 (2 s, C-2, C-5). GC-MS: $t_R$ = 8.80 min; *m/z* (%) = 248 (95) [$M^+$], 233 (14) [$M^+ - CH_3$], 205 (87), 171 (100) [$M^+ - C_6H_5$], 167 (19) [$Ph_2CH^+$], 128 (18).

*2-(4-Methoxybenzyl)-5-methylfuran* (**4e**)

According to the typical reaction procedure, 4-methoxybenzyl bromide (1.00 g, 4.97 mmol) was added to 25 mL of a solution of 2-methylfuran (2.05 g, 25.0 mmol) in 90% aqueous acetonitrile (v/v) (90AN10W) and ammonium hydrogencarbonate (786 mg, 9.94 mmol) and stirred for 2 h at ambient temperature. After the usual workup and purification by column chromatography on silica gel (pentane/ether : 7/1) 737 mg of **4e** (3.64 mmol; 73%) was isolated as a colorless liquid.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, $CH_3$), 3.77 (s, 3 H, $OCH_3$), 3.84 (s, 2 H, $CH_2$), 5.81 – 5.84 (m, 2 H, 3-H, 4-H), 6.81 – 6.84 (m, 2 H, Ar-H), 7.13 – 7.16 (m, 2 H, Ar-H). $^{13}$C

NMR (75.5 MHz, $CDCl_3$): δ = 13.5 (q, 5-$CH_3$), 33.7 (t), 55.2 (q, $OCH_3$), 105.9, 106.6 (2 d, C-3, C-4), 113.8, 129.6 (2 d, 4 × $C_{ar}$), 130.5 (s, $C_{ar}$), 150.8, 153.2 (2 s, C-2, C-5), 158.2 (s, $C_{ar}$–$OCH_3$). GC-MS: $t_R$ = 7.76 min; *m/z* (%) = 202 (100) [$M^+$], 187 (41) [$M^+ - CH_3$], 171 (39) [$M^+ - OCH_3$], 159 (35), 144 (35), 115 (16), 95 (12). Anal. Calcd. for $C_{13}H_{14}O$ (202.25): C, 77.20; H, 6.98. Found: C, 76.90; H, 6.53.

$^1$H NMR and MS data for compound **4e** were published previously.[S3]

*2-Methyl-5-(3-phenylallyl)furan* (**4f**)

According to the typical reaction procedure, cinnamyl bromide (985 mg, 5.00 mmol) was added to 25 mL of a solution of 2-methylfuran (2.05 g, 25.0 mmol) in 90% aqueous acetonitrile (v/v) (90AN10W) and ammonium hydrogencarbonate (791 mg, 10.0 mmol) and stirred for 1 d at ambient temperature. After the usual workup and purification by column chromatography on silica gel (PE/EA : 10/1) 605 mg (3.05 mmol; 61%) of a mixture (5.2:1; NMR) of **4f** and the allylic isomer 2-Methyl-5-(1-phenylallyl)furan was isolated as an orange oil. The following NMR data were derived from the mixture of isomers.

2-Methyl-5-(3-phenylallyl)furan: $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, 2-$CH_3$), 3.49 (d, *J* = 6.8 Hz, 2 H, 5-$CH_2$), 5.87 – 5.92 (m, 2 × 1 H, 3-H, 4-H), 6.24 – 6.32 (m, 1 H, 2-$CH_2CH$=C), 6.46 – 6.51 (m, 1 H, 2-$CH_2CH$=C*H*), 7.22 – 7.37 (m, 5 H, Ar-H). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ = 13.5 (q, 2-$CH_3$), 31.8 (t), 106.0, 106.2 (2 d, C-3, C-4), 125.9 (d, $C_{ar}$), 126.2 (d, 2 × $C_{ar}$), 127.2 (d, $CH_2CH$=C), 128.5 (d, 2 × $C_{ar}$), 131.7 (d, $CH_2CH$=*C*), 137.3 (s, $C_{ar}$), 150.8, 152.1 (2 s, C-2, C-5). GC-MS: $t_R$ = 7.85 min; *m/z* (%) = 198 (100) [$M^+$], 183 (20) [$M^+ - CH_3$], 155 (99), 141 (22), 128 (24), 115 (35), 95 (32), 77 (26) [$Ph^+$].

2-Methyl-5-(1-phenylallyl)furan: $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, 2-$CH_3$), 4.67 (d, *J* = 6.0 Hz, 1 H, 5-CH), 5.01 – 5.07, 5.16 – 5.19 (2 m, 2 H, C=$CH_2$), 5.87 – 5.92 (m, 3-H, 4-H), 6.13 – 6.22 (m, 1 H, C*H*=$CH_2$), 7.22 – 7.37 (m, 5 H, Ar-H). GC-MS: $t_R$ = 7.23 min; *m/z* (%) = 198 (95) [$M^+$], 183 (32) [$M^+ - CH_3$], 171 (60) [$M^+ - CH_2CH$], 155 (100), 128 (25), 115 (35), 91 (19), 77 (33) [$Ph^+$].

$^1$H NMR and MS data for compounds **4f** and its allylic isomer were published previously.[S7]

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