Chemical improvement of surfaces. Part 4: Significantly enhanced hydrophobicity of wood by covalent modification with *p*-silyl-functionalized benzoates

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Abstract: One aim of this work was the chemical modification of surfaces of Scots pine (*Pinus sylvestris L.*) sapwood veneer chips by covalenty bonded substances for improved hydrophobicity. The durable attachment of organosilyl moieties to the surface was in focus. Several benzotriazolyl-activated *p*-silylbenzoic acid derivatives were applied to esterification of OH groups at different temperatures and reaction times. The reactions resulted in weight percent gains (WPG) from 8 to 43% and corresponding quantities of covalently bonded organomaterials (QCO) of 0.3 to 2.1 mmol g^{-1} wood were achieved. The hydrophobicity was significantly increased as indicated by contact angles (CAs) from 121° to 142°. All modified wood samples were analysed by ATR-IR, CA measurements, and X-ray photoelectron spectroscopy (XPS).

Keywords: attenuated total reflection IR (ATR-IR); contact angle (CA); covalent fixation; esterification; hydrophobization of wood surface; quantity of covalently bonded organomaterial (QCO); silicon; X-ray photoelectron spectroscopy (XPS).

Introduction

Wood as an important natural resource combines many advantages that allow a wide range of applications. However, the decomposition by biological and environmental influences limits the usability of timber and wooden products or enforces periodic maintenance. The impregnation with numerous agents is an established way to improve wood properties, but leaching decreases the effectiveness of this approach. Long-term durability could be achieved by chemical modification in which the substances are covalently bonded.

Silicon containing compounds are good candidates to this purpose (Schneider and Brebner 1985). Siloxanes, e.g. methyl- or propyltriethoxysilane, have been of interest due to easy applicability via the sol-gel process and on account of the attained improvement in substrate properties, such as increased hydrophobization and fungal resistance (Mai and Militz 2004; Donath et al. 2006a, b; Weigenand et al. 2008; Pfeffer et al. 2011; Baur and Easteal 2012; Ghosh 2012a, b; Pries 2012). Inorganic silicon compounds such as salts of hexafluorosilicic acid, water glasses, or silicic acid gels have been tested as well (Pfeffer et al. 2011; Mai and Militz 2004). Up to now, some research has also been done on organosilane-substituted wood modification reagents of the composition SiR_4 (with $R \neq OR_x$). Chlorotrimethylsilane and 1-(trimethylsilyl)-imidazole bonded to beech wood by etherification leads to a silicon mass content of 5.9 - 7.7% (Zollfrank 2001; Zollfrank and Wegener 2002). The chemical bonding was proved by FTIR spectroscopy and electron microscopy. Organic silylating compounds were investigated regarding the treatment of cellulose and fibres (Greber and Paschinger 1983; Matuana et al. 1999). The list of silane agents applied was extended to dichlorodimethylsilane, dichlorodiphenylsilane, octadecyltrichlorosilane, and trimethylsilyl *N,N*-dicarbamate (Mohammed-Ziegler et al. 2003, 2004, 2006, 2008). The resulting wood samples were analysed with ATR-IR, ESCA, and XPS. Contact angle (CA) values up to 145° were obtained.

Modification and hydrophobization of wooden surfaces upon application of a novel wood esterification method, which is based on 1H-benzotriazole activation were already presented in the literature (Namyslo and Kaufmann 2009; Drafz et al. 2012; Namyslo et al. 2014). In the present paper, a variety of additional silylating agents will be investigated based on the published activation protocol in order to widen the knowledge in this research field.

Material and methods

The organic compounds mentioned in this paper were accurately characterized by at least NMR spectroscopy, mass spectrometry, and infrared spectroscopy, if suitable.

General procedures: NMR instrument: Bruker Avance III 600 or Avance 400 (Bruker, Ettlingen, Germany) with 600 or 400 MHz proton frequency. ^{1}H-NMR spectra in CDCl$_3$ were referenced to TMS (0.00 ppm). ^{13}C-NMR spectra refer to the solvent signal centre at 77.0 ppm (CDCl$_3$). In case of DMSO-d$_6$ and C$_6$D$_6$, the solvent peaks were set to 2.50 ppm (^{1}H), 39.50 ppm (^{13}C) and 7.16 ppm (^{1}H), 128.06 ppm (^{13}C), respectively. All coupling constants are given in Hz. Multiplicities are described by the following abbreviations: (br.) s = (broad) singlet, d = doublet, t = triplet, m = multiplet, dt = doublet of triplets, etc.

IR instrument: BRUKER 'Alpha-T' (Bruker, Bremen, Germany). Measurements were done as KBr pellets (solids) or between NaCl plates (liquids). IR instrument for wood veneer chips: BRUKER 'Vector 22' FTIR (Bruker, Bremen, Germany) equipped with a 'Specac Golden-Gate' Diamond-ATR/KRS5 unit.

Mass spectra: 'Varian 320' MS (Varian, Darmstadt, Germany) equipped with a triple quadrupole with direct inlet (EI, 70 eV). Source temperature 200°C.

XPS measurements at room temperature (r.t.): base pressure of $5 \cdot 10^{-11}$ hPa (Frerichs et al. 2006); hemispherical analyzer (VSW HA100) in combination with a commercial non-monochromatic X-ray source (Specs RQ20/38C); X-ray photons irradiate the surface under an angle of 80° to the surface normal; diameter of the illuminated spot: several mm. The Al K$_\alpha$

line (photon energy 1486.6 eV) was used. Energy resolution: 1.1 eV emitted under an angle of 10° to the surface normal. For quantitative XPS analysis, peak fitting with Gauss-type profiles was applied: OriginPro 7G (OriginLab, Northampton, Massachusetts, USA) including the PFM fitting module, which applies Levenberg-Marquardt algorithms to achieve the best agreement possible between experimental data and fit. Voigt-profiles have been applied to various oxidic and metallic systems but for most systems the Lorentzian contribution converges to 0. Therefore all XPS peaks are fitted with Gaussian curves. Photoelectric cross sections were applied as calculated by Scofield (1976) with asymmetry factors (Reilman et al. 1976; Jablonski and Powell 2010a). The inelastic mean free paths (IMFP) in polyethylene from the NIST database (Jablonski and Powell 2010b) were applied as model system instead of the unknown IMFPs in wood. The energy dependent transmission function of the hemispherical analyzer are taken into account in stoichiometric calculations. Prior to these measurements, the veneer chips were cut into pieces of ca. 10 x 10 x 0.6 mm^3. These samples were mounted on cartridges of titanium.

Contact angles (CAs, Θ) were measured with the sessile-drop method; instrument: Dataphysics OCA 15plus (DataPhysics Instruments, Filderstadt, Germany). For each measurement 3 µl of distilled water was applied. For each sample at least 15 different positions were analyzed.

Tetrahydrofuran (THF) and dichloromethane (DCM) were dried with an MP5 Solvent Purification System from Innovative Technology, Amesbury, United States of America. Dry *N,N*-dimethylformamide (DMF) and all other chemicals were used as purchased from Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany or Merck KGaA, Darmstadt, Germany. Wood veneer samples were obtained from the Section of Wood Biology and Wood Products, Georg-August-University Göttingen, Göttingen, Germany.

Procedure (A) for the organosilylation of 1,4-dibromobenzene: Under inert gas atmosphere, a solution of 1 eq. 2.4 M *n*-butyllithium was added dropwise to a solution of 1,4-

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dibromobenzene in anhydrous THF (8.5 mL g^{-1}) at -78°C, and the reaction mixture was stirred at -78°C for 1 h. Then, the organosilyl chloride was added dropwise and the solution was stirred for another 15 min. The cooling was switched off and the solution was allowed to warm to room temperature (r.t.) while stirring. At -40°C the cooling bath was removed. 50 mL of water was added to the above mixture, followed by 10% HCl until pH 6 was attained. The aqueous layer was separated and washed twice with 30 mL of DCM. The combined organic layers were dried over sodium sulphate and excess solvent was evaporated to dryness afterwards. The crude product was purified by column chromatography (PE, silica gel).

1-Bromo-4-(trimethylsilyl)benzene (1): According to general procedure **A** 5.90 g of 1,4-dibromobenzene afforded 5.55 g (97%) of **1**. n_d^{20} 1.5301. Bp: 52°C (1.8 mbar). **^{1}H-NMR** (600 MHz, CDCl$_3$): δ = 0.26 (br. s, 9 H, SiCH$_3$), 7.36-7.38 (m, 2 H, H$_{arom}$), 7.47-7.49 (m, 2 H, H$_{arom}$). **^{13}C-NMR** (151 MHz, CDCl$_3$): δ = -1.2 (+, 3 C, SiCH$_3$), 123.5 (C$_{quat}$, 1 C, BrC$_{arom}$), 130.8 (+, 2 C, C$_{arom}$), 134.9 (+, 2 C, C$_{arom}$), 139.2 (C$_{quat}$, 1 C, SiC$_{arom}$). **IR** (KBr): 3071, 3034, 3015, 2956, 2897, 1904, 1638, 1574, 1552, 1479, 1406, 1376, 1303, 1250, 1106, 1067, 1012, 841, 807, 755, 719, 703, 627, 486. **EI-MS** (70 eV); *m/z* (%): 231 [M(^{81}Br)]$^+$ (21), 229 [M(^{79}Br)]$^+$ (19), 215 [M - CH$_3$ (^{81}Br)]$^+$ (89), 213 [M - CH$_3$ (^{79}Br)]$^+$ (89), 149 [M - Br]$^+$ (12), 119 [M - C$_2$H$_6$Br]$^+$ (86).

1-Bromo-4-(dimethyl-n-octylsilyl)benzene (2): According to general procedure **A** 8.26 g of 1,4-dibromobenzene afforded 10.63 g (93%) of **2**. n_d^{20} 1.5064. Bp: 107°C (3.2·10^{-2} mbar). **^{1}H-NMR** (600 MHz, CDCl$_3$): δ = 0.23 (s, 6 H, SiCH$_3$), 0.70-0.73 (m, 2 H, SiCH$_2$), 0.87 (t, *J*=7.1 Hz, 3 H, CH$_3$), 1.20-1.25 (m, 6 H, CH$_2$), 1.27-1.28 (m, 6 H, CH$_2$), 7.35-7.36 (m, 2 H, H$_{arom}$), 7.47-7.48 (m, 2 H, H$_{arom}$). **^{13}C-NMR** (151 MHz, CDCl$_3$): δ = -3.1 (+, 2 C, SiCH$_3$), 14.1 (+, 1 C, CH$_3$), 15.6 (-, 1 C, SiCH$_2$), 22.7 (-, 1 C, CH$_2$), 23.8 (-, 1 C, CH$_2$), 29.2 (-, 2 C, CH$_2$), 31.9 (-, 1 C, CH$_2$), 33.5 (-, 1 C, CH$_2$), 123.5 (C$_{quat}$, 1 C, BrC$_{arom}$), 130.8 (+, 2 C, C$_{arom}$),

135.2 (+, 2 C, C_{arom}), 138.5 (C_{quat}, 1 C, SiC_{arom}). **IR** (KBr): 3448, 3070, 3034, 3014, 2956, 2923, 2854, 1902, 1638, 1574, 1552, 1479, 1467, 1409, 1376, 1339, 1303, 1251, 1174, 1108, 1068, 1011, 912, 839, 816, 804, 722, 667, 618, 488. **MS** (70 eV); m/z (%): 313 [M - CH_3 (^{81}Br)]$^+$ (3), 311 [M - CH_3 (^{79}Br)]$^+$ (3), 245 [M - Br]$^+$ (3), 215 [M - C_8H_{17} (^{81}Br)]$^+$ (94), 213 [M - C_8H_{17} (^{79}Br)]$^+$ (100), 201 [M - C_9H_{20} (^{81}Br)]$^+$ (23), 199 [M - C_9H_{20} (^{79}Br)]$^+$ (25), 171 [M - C_6H_4Br]$^+$ (9), 170 [M - C_6H_5Br]$^+$ (48), 141 [M - $C_8H_{10}Br$]$^+$ (11).

1-Bromo-4-(allyldimethylsilyl)benzene (3): According to general procedure **A** 6.50 g of 1,4-dibromobenzene afforded 6.87 g (98%) of **3**. n_d^{20}: 1.5395. Bp: 58°C (3.2·10^{-2} mbar). **^{1}H-NMR** (600 MHz, C_6D_6): δ = 0.09 (s, 6 H, $SiCH_3$), 1.45 (dt, J = 8.1, 1.1 Hz, 2 H, $SiCH_2$), 4.85 (ddt, J = 16.9, 2.2, 1.5 Hz, 1 H, CH_2 allyl), 4.88 (ddt, J = 10.1, 2.2, 1.1, 1 H, CH_2 allyl), 5.66 (ddt, J = 16.9, 10.1, 8.1 Hz, 1 H, CH_{allyl}), 7.36-7.04 (d, J = 8.2 Hz, 2 H, H_{arom}), 7.35 (d, J = 8.2 Hz, 2 H, H_{arom}). **^{13}C-NMR** (151 MHz, C_6D_6): δ = -3.3 (+, 2 C, $SiCH_3$), 23.9 (-, 1 C, $SiCH_2$), 114.3 (-, 1 C, CH_2 allyl), 124.6 (C_{quat}, 1 C, BrC_{arom}), 131.6 (+, 2 C, C_{arom}), 134.7 (+, 1 C, CH_{allyl}), 135.9 (+, 2 C, C_{arom}), 137.7 (C_{quat}, 1 C, SiC_{arom}). **IR** (KBr): 3076, 3034, 2996, 2957, 2923, 2854, 1904, 1793, 1630, 1574, 1553, 1480, 1469, 1419, 1392, 1376, 1336, 1318, 1303, 1252, 1192, 1158, 1107, 1068, 1035, 1011, 992, 931, 896, 836, 804, 756, 720, 703, 652, 627, 617, 574, 487, 455. **EI-MS** (70 eV); m/z (%): 256 [M (^{81}Br)]$^+$ (20), 213 [M - C_3H_5 (^{79}Br)]$^+$ (15), 185 [M - C_4H_{11} (^{81}Br)]$^+$ (29), 157 [M - $C_4H_{11}Si$ (^{81}Br)]$^+$ (26), 133 [M - C_3H_6Br]$^+$ (16), 99 [M - C_6H_4Br]$^+$ (34).

1-Bromo-4-(dimethylphenylsilyl)benzene (4): According to general procedure **A** 9.77 g of 1,4-dibromobenzene afforded 8.52 g (99%) of **4**. n_d^{20}: 1.5830. Mp: 30°C. Bp: 71°C (3.2·10^{-2} mbar). **^{1}H-NMR** (600 MHz, C_6D_6): δ = 0.35 (br s, 6 H, $SiCH_3$), 7.08-7.11 (m, 2 H, H_{arom}), 7.18 (d, J=1.9 Hz, 1 H, H_{phenyl}), 7.19-7.20 (m, 2 H, H_{phenyl}), 7.30-7.33 (m, 2 H, H_{arom}), 7.38-7.40 (m, 2 H, H_{phenyl}). **^{13}C-NMR** (151 MHz, C_6D_6): δ = -2.1 (+, 2 C, $SiCH_3$), 124.5 (C_{quat}, 1 C, BrC_{arom}), 128.7 (+, 2 C, C_{phenyl}), 129.9 (+, 1 C, C_{phenyl}), 131.7 (+, 2 C, C_{arom}), 134.8 (+, 2 C,

C_{phenyl}), 163.5 (+, 2 C, C_{arom}), 137.6 (C_{quat}, 1 C, SiC_{arom}), 138.1 (C_{quat}, 1 C, SiC_{phenyl}). **IR** (KBr): 3442, 3069, 3050, 3013, 2957, 2899, 1904, 1738, 1639, 1571, 1551, 1480, 1427, 1410, 1376, 1335, 1303, 1251, 1187, 1134, 1115, 1067, 1010, 834, 818, 804, 775, 750, 723, 700, 651, 628, 492, 474. **EI-MS** (70 eV); *m/z* (%): 292 [*M* (^{81}Br)]$^+$ (15), 290 [*M* (^{79}Br)]$^+$ (15), 277 [*M* - CH$_3$ (^{81}Br)]$^+$ (100), 275 [*M* - CH$_3$ (^{79}Br)]$^+$ (97), 195 [*M* - CH$_3$Br]$^+$ (9), 181 [*M* - C$_2$H$_6$Br]$^+$ (8), 135 [*M* - C$_6$H$_4$Br]$^+$ (17), 105 [*M* -C$_8$H$_{10}$Br]$^+$ (24).

Procedure (B) for the carboxylation of 1-bromo-4-(silyl)benzenes 1 – 4: Under inert gas atmosphere, a solution of 1 eq. 2.4 M *n*-butyllithium was added dropwise to a solution of 1-bromo-4-(silyl)benzene in anhydrous THF (10.8 mL g^{-1}) at -78°C. The cooling was switched off and the solution was stirred for 1 h. Then, dry ice was slowly added and the reaction mixture was allowed to warm to r.t. while stirring. At -40°C the cooling bath was removed. 50 mL water was added to the above solution followed by 10% HCl to acidify. The aqueous layer was separated and was washed twice with 30 mL DCM. The combined organic layers were dried over sodium sulphate. Subsequently the excess solvent was evaporated to dryness.

4-(Trimethylsilyl)benzoic acid (5): According to general procedure **B** 7.83 g of **1** afforded 4.05 g (61%) of **5** after recrystallization from petrol ether. Mp: 106°C. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.25 (s, 9 H, SiCH$_3$), 7.63-7.64 (m, 2 H, H$_{arom}$), 7.91-7.92 (m, 2 H, H$_{arom}$), 12.89 (br. s, 1 H, OH). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ = -1.4 (+, 3 C, SiCH$_3$), 128.3 (+, 2 C, C$_{arom}$), 131.1 (C_{quat}, 1 C, C$_{arom}$COOH), 133.3 (+, 2 C, C$_{arom}$), 145.8 (C_{quat}, 1 C, SiC$_{arom}$), 167.4 (C_{quat}, 1 C, COOH). **IR** (KBr): 2955, 2667, 2544, 2094, 1940, 1878, 1816, 1692, 1597, 1553 1499, 1420, 1388, 1355, 1315, 1293, 1253, 1187, 1133, 1095, 1019, 944, 844, 808, 742, 699, 628, 540, 474.

EI-MS (70 eV); *m/z* (%): 194 [*M*]$^+$ (9), 179 [*M* - CH$_3$]$^+$ (100), 149 [*M* - CHO$_2$]$^+$ (2), 134 [*M* -C$_2$H$_4$O$_2$]$^+$ (2), 133 [*M* - C$_9$H$_{10}$O]$^+$ (6), 119 [*M* - C$_3$H$_7$O$_2$]$^+$ (3).

4-(Dimethyl-n-octylsilyl)benzoic acid (6): According to general procedure **B** 5.36 g of **2** afforded 4.71 g (98%) of **6**. Mp: 155°C. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.24 (s, 6 H,

SiCH$_3$), 0.71-0.73 (m, 2 H, SiCH$_2$), 0.81-0.83 (m, 3 H, CH$_3$), 1.18-1.24 (m, 12 H, CH$_2$), 7.607.61 (m, 2 H, H$_{arom}$), 7.90-7.91 (m, 2 H, H$_{arom}$), 12.95 (br. s., 1 H, OH). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ = -3.4 (+, 3 C, SiCH$_3$), 13.9 (+, 1 C, CH$_3$), 14.8 (-, 1 C, SiCH$_2$), 22.0 (-, 1 C, CH$_2$), 23.2 (-, 1 C, CH$_2$), 28.5 (-, 2 C, CH$_2$), 31.2 (-, 1 C, CH$_2$), 32.7 (-, 1 C, CH$_2$), 128.2 (+, 2 C, C$_{arom}$), 131.3 (C$_{quat}$, 1 C, C$_{arom}$COOH), 133.5 (+, 2 C, C$_{arom}$), 144.9 (C$_{quat}$, 1 C, SiC$_{arom}$), 167.5 (C$_{quat}$, 1 C, COOH). **IR** (KBr): 2918, 2663, 2543, 2088, 1938, 1815, 1687, 1598, 1554, 1500, 1468, 1417, 1388, 1354, 1316, 1289, 1253, 1189, 1133, 1111, 1096, 1042, 1020, 1004, 984, 947, 907, 838, 805, 785, 756, 731, 708, 665, 640, 541, 475. **EI-MS** (70 eV); *m/z* (%): 277 [*M* - CH$_3$]$^+$ (3), 179 [*M* -C$_8$H$_{17}$]+ (100), 165 [*M* - C$_9$H$_{20}$]$^+$ (16), 133 [*M* - C$_9$H$_{18}$O$_2$]$^+$ (4), 117 [*M* - C$_{10}$H$_{21}$O$_2$]$^+$ (4). **HR-EI-MS**: calcd. for C$_{17}$H$_{28}$O$_2$Si: 292.1859, found: 292.1861.

4-(Allyldimethylsilyl)benzoic acid (7): According to general procedure **B** 6.96 g of **3** afforded 5.97 g (99%) of **7**. Mp: 261°C. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.26 (br. s, 6 H, SiCH$_3$), 1.77 (dt, *J* = 8.1, 1.1 Hz, 2 H, SiCH$_2$), 4.81 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1 H, CH$_{2,allyl}$), 4.82 (ddt, *J* = 16.9, 2.2, 1.1 Hz, 1 H, CH$_2$ $_{allyl}$), 5.72 (ddt, *J* = 16.9, 10.1, 8.1 Hz, 1 H, CH$_{allyl}$), 7.61-7.63 (m, 2 H, H$_{arom}$), 7.91-7.93 (m, 2 H, H$_{arom}$). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ = -3.6 (+, 2 C, SiCH$_3$), 22.7 (-, 1 C, SiCH$_2$), 113.7 (-, 1 C, CH$_2$ $_{allyl}$), 128.3 (+, 2 C, C$_{arom}$), 132.0 (C$_{quat}$, 1 C, C$_{arom}$COOH), 133.5 (+, 2 C, C$_{arom}$), 134.3 (+, 1 C, CH$_{allyl}$), 143.7 (C$_{quat}$, 1 C, SiC$_{arom}$), 167.8 (C$_{quat}$, 1 C, COOH). **IR** (KBr): 3074, 2959, 2884, 2668, 2548, 2049, 1986, 1926, 1898, 1806, 1689, 1628, 1600, 1555, 1500, 1420, 1389, 1347, 1325, 1298, 1249, 1189, 1145, 1098, 1098, 1035, 1021, 997, 947, 931, 892, 841, 821, 803, 749, 737, 703, 653, 574, 541, 484, 474, 411. **EI-MS** (70 eV); *m/z* (%): 220 [*M*]$^+$ (3), 205 [*M* - CH$_3$]$^+$ (1), 179 [*M* - C$_3$H$_5$]$^+$ (100), 133 [*M* - C$_4$H$_6$O$_2$]$^+$ (6), 120 [*M* - C$_5$H$_{12}$Si]$^+$ (4), 119 [*M* - C$_5$H$_9$O$_2$]$^+$ (5). **HR-EI-MS**: calcd. for C$_{12}$H$_{16}$O$_2$Si: 220.0920, found: 220.0920.

4-(Dimethylphenylsilyl)benzoic acid (8): According to general procedure **B** 10.01 g of **4** afforded 5.53 g (63%) of **8** after recrystallization from petrol ether. Mp: 175°C. **^{1}H-NMR**

(600 MHz, CDCl$_3$): δ = 0.60 (br. s, 6 H, SiCH$_3$), 7.37-7.39 (m, 3 H, H$_{phenyl}$), 7.51-7.53 (m, 2 H, H$_{phenyl}$), 7.62 (d, J = 8.3 Hz, 2 H, H$_{arom}$), 8.07 (d, J = 8.3 Hz, 2 H, H$_{arom}$), 10.14 (br. s, 1 H, OH). **^{13}C-NMR** (151 MHz, CDCl$_3$): δ = -2.61 (+, 2 C, SiCH$_3$), 127.9 (+, 2 C, C$_{phenyl}$), 129.1 (+, 2 C, C$_{arom}$), 129.4 (+, 1 C, C$_{phenyl}$), 130.1 (C$_{quat}$, 1 C, C$_{arom}$COOH), 134.1 (+, 2 C, C$_{phenyl}$), 134.2 (+, 2 C, C$_{arom}$), 137.2 (C$_{quat}$, 1 C, SiC$_{phenyl}$), 145.6 (C$_{quat}$, 1 C, SiC$_{arom}$), 172.5 (C$_{quat}$, 1 C, COOH). **IR** (KBr): 3067, 3051, 2998, 2958, 2669, 2552, 2091, 1952, 1885, 1818, 1682 , 1597, 1554, 1535, 1499, 1486, 1427, 1388, 1316, 1298, 1249, 1188, 1159, 1135, 1114, 1094, 1019, 997, 945, 834, 821, 805, 783, 759, 741, 728, 700, 651, 544, 494, 480, 466. **EI-MS** (70 eV); *m/z* (%): 256 [M]$^+$ (9), 241 [M - CH$_3$]$^+$ (100), 197 [M - C$_2$H$_4$O$_2$]$^+$, 179 [M - C$_6$H$_5$]$^+$ (9), 133 [M - C$_7$H$_5$O$_2$]$^+$ (8), 105 [M -C$_9$H$_{11}$O$_2$]$^+$ (8).

Procedure (C) for the activation of 4-(silyl)benzoic acids 9 – 12: Under inert gas atmosphere, a solution of 3 eq. 1*H*-benzotriazole and 1.1 eq. thionyl chloride in anhydrous DCM (3.5 mL g^{-1}) was added dropwise to a solution of 4-(silyl)benzoic acid in anhydrous DCM (23.8 mL g^{-1}). After stirring at r.t. for 1 d, water was added, and the solution was neutralized with 10% NaOH. The aqueous layer was separated and washed twice with 30 mL DCM. The combined organic layers were dried over sodium sulphate and excess solvent was evaporated to dryness afterwards. The crude solid product was purified by column chromatography (DCM, silica gel).

1-(4-Trimethylsilylbenzoyl)-benzotriazole (9): According to general procedure **C** 3.93 g of **5** afforded 5.17 g (87%) of **9**. Mp: 92°C. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.16 (br. s, 9 H, SiCH$_3$), 6.96 (ddd, J = 19.4, 10.8, 1.6 Hz, 1 H, H$_{arom, Bzt}$), 7.14 (ddd, J = 19.4, 10.8, 1.6 Hz, 1 H, H$_{arom, Bzt}$), 7.41 (d, J = 7.9 Hz, 2 H, H$_{arom}$), 7.85 (d, J = 8.3 Hz, 1 H, H$_{arom, Bzt}$), 8.14 (d, J = 7.9 Hz, 2 H, H$_{arom}$), 8.35 (d, J = 8.3 Hz, 1 H, H$_{arom, Bzt}$). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ = -1.1 (+, 3 C, SiCH$_3$), 115.5 (+, 1 C, C$_{arom, Bzt}$), 120.6 (+, 1 C, C$_{arom, Bzt}$), 126.5 (+, 1 C, C$_{arom, Bzt}$), 128.7 (+, 1 C, C$_{arom, Bzt}$), 131.4 (+, 2 C, C$_{arom}$), 132.7 (C$_{quat}$, 1 C, C̱$_{arom}$C=O), 133.1 (C$_{quat}$,

1 C, $C_{arom, Bzt}$), 133.7 (+, 2 C, C_{arom}), 146.7 (C_{quat}, 1 C, $C_{arom, Bzt}$), 147.7 (C_{quat}, 1 C, SiC_{arom}), 167.3 (C_{quat}, 1 C, C=O). **IR** (KBr): 3396, 3118, 3078, 3023, 2951, 2896, 1930, 1813, 1704, 1597, 1546, 1518, 1484, 1452, 1387, 1376, 1365, 1322, 1313, 1287, 1246, 1226, 1188, 1148, 1135, 1114, 1094, 1077, 1038, 1005, 936, 891, 832, 781, 754, 739, 726, 700, 690, 646, 591, 566, 540, 484, 465, 433. **EI-MS** (70 eV); *m/z* (%): 295 $[M]^+$ (1), 252 $[M - C_3H_7]^+$ (65), 177 $[M - C_6H_4N_3]^+$ (100), 149 $[M - C_7H_4N_3O]^+$ (1), 119 $[M - C_9H_{10}N_3O]^+$ (2). **HR-ESI-MS**: calcd. for $C_{16}H_{17}N_3OSi$: 295.1141, found: 318.1039 $[M + Na]^+$.

1-(4-Dimethyloctylsilylbenzoyl)-benzotriazole (10): According to general procedure **C** 1.00 g of **6** afforded 1.20 g (89%) of **10**. n_d^{20}: 1.5576. **^{1}H-NMR** (600 MHz, C_6D_6): δ = 0.22 (br. s, 6 H, $SiCH_3$), 0.69 − 0.71 (m, 2 H, $SiCH_2$), 0.91 (t, *J* = 7.0 Hz, 3 H, CH_3), 1 .28 − 1.32 (m, 12 H, CH_2), 6.97 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1 H, $H_{arom, Bzt}$), 7.13 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H, $H_{arom, Bzt}$), 7.48 (d, *J* = 8.3 Hz, 2 H, H_{arom}), 7.85 (dt, *J* = 8.2, 1.0 Hz, 1 H, $H_{arom, Bzt}$), 8.17 (d, *J* = 8.3 Hz, 2 H, H_{arom}), 8.34 (dt, *J* = 8.2, 1.0 Hz, 1 H, $H_{arom, Bzt}$). **^{13}C-NMR** (151 MHz, C_6D_6): δ = -3.5 (+, 2 C, $SiCH_3$), 14.0 (+, 1 C, CH_3), 15.3 (-, 1 C, $SiCH_2$), 22.7 (-, 1 C, CH_2), 23.8 (-, 1 C, CH_2), 29.3 (-, 1 C, CH_2), 29.4 (-, 1 C, CH_2), 32.0 (-, 1 C, CH_2), 33.6 (-, 1 C, CH_2), 114.8 (+, 1 C, $C_{arom, Bzt}$), 119.9 (+, 1 C, $C_{arom, Bzt}$), 125.8 (+, 1 C, $C_{arom, Bzt}$), 129.7 (+, 1 C, $C_{arom, Bzt}$), 130.7 (+, 2 C, C_{arom}), 132.0 (C_{quat}, 1 C, C_{arom}C=O), 132.4 (C_{quat}, 1 C, C $C_{arom, Bzt}$), 133.3 (+, 2 C, C_{arom}), 146.0 (C_{quat}, 1 C, $C_{arom, Bzt}$), 146.5 (C_{quat}, 1 C, SiC_{arom}), 166.6 (C_{quat}, 1 C, C=O). **IR** (KBr): 3063, 3045, 3024, 2956, 2922, 2854, 1928, 1795, 1777, 1704, 1598 , 1547, 1485, 1451, 1390, 1363, 1323, 1308, 1289, 1248, 1229, 1195, 1174, 1149, 1131, 1115, 1096, 1041, 1005, 937, 888, 835, 814, 781, 771, 753, 731, 698, 657, 647, 586, 566, 542, 484, 426, 419, 413. **MS** (70 eV); *m/z* (%): 393 $[M]^+$ (1), 378 $[M - CH_3]^+$ (5), 363 $[M - C_2H_6]^+$ (6), 280 $[M - C_8H_{17}]^+$ (72), 275 $[M - C_6H_4N_3]^+$ (96), 265 $[M - C_9H_{20}]^+$ (8), 252 $[M - C_{10}H_{21}]^+$ (100), 163 $[M - C_{14}H_{21}N_3]^+$ (7), 119 $[M - C_{17}H_{27}OSi]^+$ (47). **HR-EI-MS**: calcd. for $C_{23}H_{31}N_3OSi$: 393.2236, found: 393.2236.

1-(4-Allyldimethylsilylbenzoyl)-benzotriazole (11): According to general procedure **C** 4.78 g of **7** afforded 6.28 g (90%) of **11**. n_d^{20} : 1.6011. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.32 (s, 6 H, SiCH$_3$), 1.84 (dt, *J* = 8.2, 1.0 Hz, 1 H, SiCH$_2$), 4.85 (dd, *J* = 10.1, 2.1 Hz, 1H, CH$_{2,allyl}$), 4.87 (ddd, *J* = 17.0, 2.1, 1.0 Hz, 1 H, CH$_{2,allyl}$), 5.77 (ddt, *J* = 17.0, 10.1, 8.2 Hz, 1 H, CH$_{allyl}$), 7.66 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H, H$_{arom, Bzt}$), 7.79 (d, *J*=8.4 Hz, 2 H, H$_{arom}$), 7.83 (ddd, *J* = 8.2, 7.2, 1 .0 Hz, 1 H, H$_{arom, Bzt}$), 8.07 (d, *J* = 8.4 Hz, 2 H, H$_{arom}$), 8.29 (d, *J* = 8.3 Hz, 1 H, H$_{arom, Bzt}$), 8.33 (d, *J* = 8.3 Hz, 1 H, H$_{arom, Bzt}$). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ=-3.7 (+, 2 C, SiCH$_3$), 22.6 (-, 1 C, SiCH$_2$), 113.8 (-, 1 C, CH$_{2,allyl}$), 114.9 (+, 1 C, C$_{arom, Bzt}$), 120.0 (+, 1 C, C$_{arom, Bzt}$), 126.6 (+, 1 C, C$_{arom, Bzt}$), 130.2 (+, 2 C, C$_{arom}$), 130.7 (+, 1 C, C$_{arom, Bzt}$), 131.7 (C$_{quat}$, 1 C, C$_{arom}$C=O), 131.9 (C$_{quat}$, 1 C, C$_{arom, Bzt}$), 133.4 (+, 2 C, C$_{arom}$), 134.2 (+, 1 C, CH$_{allyl}$), 145.2 (C$_{quat}$, 1 C, C$_{arom, Bzt}$), 145.3 (C$_{quat}$, 1 C, SiC$_{arom}$), 166.7 (C$_{quat}$, 1 C, C=O). **IR** (KBr): 3077, 3026, 2958, 2899, 1930, 1796, 1704, 1630, 1598, 1548, 1485, 1441, 1420, 1391, 1365, 1324 , 1308, 1289, 1249, 1229, 1195, 1150, 1131, 1116, 1096, 1042, 1004, 937, 889, 833, 781, 771, 752, 732, 695, 657, 643, 589, 575, 457, 449, 440, 423, 416. **EI-MS** (70eV); *m/z* (%): 293 [*M* - C$_2$H$_4$]$^+$ (9), 280 [*M* - C$_3$H$_5$]$^+$ (100), 252 [*M* - C$_5$H$_9$]$^+$ (30), 134 [*M* - C$_{10}$H$_9$N$_3$O]$^+$ (56), 119 [C$_6$H$_4$N$_3$] (30). HR-ESI-MS: calcd. for C$_{18}$H$_{19}$N$_3$OSi: 321.1297, found: 344.1195 [*M* + Na]$^+$.

1-(4-Dimethylphenylsilylbenzoyl)-benzotriazole (12): According to general procedure **C** 12.82 g of **8** afforded 17.15 g (96%) of **12**. n_d^{20} : 1.6298. **^{1}H-NMR** (600 MHz, DMSO-d$_6$): δ = 0.61 (s, 6 H, SiCH$_3$), 7.38–7.41 (m, 3 H, H$_{phenyl}$), 7.56–7.57 (m, 2 H, H$_{phenyl}$), 7.64 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H, H$_{arom, Bzt}$), 7.77 (d, *J* = 8.2 Hz, 2 H, H$_{arom}$), 7.82 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H, H$_{arom, Bzt}$), 8.06 (d, *J* = 8.2 Hz, 2 H, H$_{arom}$), 8.28 (d, *J* = 8.3 Hz, 1 H, H$_{arom, Bzt}$), 8.32 (d, *J* = 8.3 Hz, 1 H, H$_{arom, Bzt}$). **^{13}C-NMR** (151 MHz, DMSO-d$_6$): δ = -3.0 (+, 2 C, SiCH$_3$), 114.4 (+, 1 C, C$_{arom, Bzt}$), 120.0 (+, 1 C, C$_{arom, Bzt}$), 126.6 (+, 1 C, C$_{arom, Bzt}$), 127.9 (+, 2 C, C$_{arom, phenyl}$), 129.4 (+, 1 C, C$_{arom, phenyl}$), 130.2 (+, 2 C, C$_{arom}$), 130.7 (+, 1 C, C$_{arom, Bzt}$),

131.6 (C_{quat}, 1 C, $C_{arom, Bzt}$), 132.0 (C_{quat}, 1 C, C_{arom}C=O), 133.7 (+, 2 C, C_{arom}), 133.9 (+, 2 C, $C_{arom, phenyl}$), 136.9 (C_{quat}, 1 C, $C_{arom, phenyl}$), 145.0 (C_{quat}, 1 C, SiC_{arom}), 145.2 (C_{quat}, 1 C, $C_{arom, Bzt}$), 166.6 (C_{quat}, 1 C, C=O). **IR** (KBr): 3069, 3048, 3023, 2957, 2899, 1957, 1931, 1891, 1823, 1777, 1700, 1597, 1547, 1521, 1484, 1450, 1428, 1371, 1323, 1307, 1289 1248, 1229, 1195, 1149, 1130, 1115, 1096, 1043, 1004, 975, 937, 888, 832, 780, 751, 702, 656, 642, 619, 588, 566, 543, 488, 429, 421, 417, 405. **EI-MS** (70 eV); *m/z* (%): 357 [*M*]$^+$ (44), 342 [*M* - CH$_3$]$^+$ (15), 239 [*M* - C$_6$H$_4$N$_3$]$^+$ (100), 135 [*M* - C$_{13}$H$_8$N$_3$O]$^+$ (80), 118 [*M* - C$_{15}$H$_{15}$OSi]$^+$ (17), 105 [*M* - C$_{15}$H$_{14}$N$_3$O]$^+$ (24). **HR-EI-MS**: calcd. for C$_{21}$H$_{19}$N$_3$OSi: 357.1297, found: 357.1295.

Chemical wood modification: 7 mmol of the appropriate wood modifying reagent were applied per 1 g of veneer chips of pine wood (approx. 15 x 10 x 0.6 mm^3, approx. 0.043 g). All reactions were performed in 2 mL of anhydrous *N,N*-dimethylformamide (DMF) with 2 equivalents of triethylamine and 10 mol% of 4-dimethylaminopyridine under nitrogen atmosphere. Prior to modification, the wood was extracted for 1 d in a Soxhlet apparatus with a solvent mixture comprising toluene/acetone/methanol 4:1:1. The thus pre-treated wood subsequently was oven-dried at 105°C for 6 h and then stored under vacuum in a laboratory desiccator under vaccum. The wood modification reactions started with heating the wood sample, triethylamine, and *N,N*-dimethylaminopyridine at 50°C for 2 h. Then the modification reagent was added and the temperature was increased to 70°C or 120°C for 16 h, 70 h, or 166 h, respectively. Subsequently, the mixture was allowed to cool down to r.t. and the modified wood was washed successively with THF (50 mL), chloroform (50 mL), and diethyl ether (50 mL) on a funnel. Afterwards, the wood sample was extracted again for 1 d applying the Soxhlet apparatus with the same solvent mixture as stated above. As the final step, the modified wood was dried at 105°C for 6 h and subjected to vacuum treatment (10^{-2} mbar) for a further 1 h, before being stored under vacuum in a desiccator.

Results and discussion

Chemical syntheses of wood modification reagents

Following the standard procedures for silylation (**1**: Lamba and Tour 1994; **3**: Younghee and Silverman 1999) and carboxylation (**5**: Grimm et al. 2009), the compounds **5−8** (Figure 1) were prepared in good to very good yields (Table 1) starting from *p*-dibromobenzene.

[Figure 1], [Table 1]

As recently published (Namyslo and Kaufmann 2009), the benzoic acid derivatives **5−8** were then transformed into their corresponding benzotriazolyl-activated compounds **9−12** (Figure 2).

[Figure 2]

In a final step, the ultimate wood modification process was performed applying the above mentioned benzotriazolyl-activated benzoic acids to esterification of the hydroxyl groups in wood. This reaction was achieved in the presence of *N*,*N*-dimethylaminopyridine and triethylamine in anhydrous *N*,*N*-dimethylformamide at different reaction times and temperature conditions. In detail, the wood veneer was subjected to modification for 18, 72, and 168 h at 70°C and 120°C, respectively (Figure 3).

[Figure 3]

Quantification by means of WPG and QCO

After modification, the wood was extracted, dried, and subjected to vacuum for 1 h before the change in mass was determined. The resulting WPG, given in Tables 2 and 3, shows a mass gain of about 10%, already achieved after less than 1 d. With all modifying agents, the highest WPG was received after 3 d with about doubled values. In the case of **12** even a triplication was accomplished. This indicates that at that point most of the accessible hydroxyl groups of the wood surface were converted into ester groups. Extending the reaction time to one week provided only little additional increase of less than 5%. An additional WPG was obtained by raising the reaction temperature to 120°C, yielding maximum WPG values up to 44%.

According to the results, all four compounds appear to possess a similar capacity for wood modification at 70°C, whereas **10** and **11** excel at 120°C.

It should be emphasized that the determined weights remained unchanged after 2 years of continued exposure to laboratory climate.

For a better comparison of the extent of wood modification under different conditions, each covalently bonded organomaterial (QCO) value (Drafz et al. 2012) is presented in addition to the WPG (Tables 2 and 3). The derivatives **9** and **11** form more ester bonds due to less steric hindrance during the esterification compared to **10**.

[Table 2 and 3]

IR spectroscopic characterization

Figure 4 displays the ATR-IR spectra of untreated pine sapwood compared to modified samples, and illustrates the changes caused by the formation of covalent bonds at 70°C for 168 h.

[Figure 4]

For all modified samples, significant changes are seen (Table 4); the increased and particularly shifted carbonyl stretching bands are found at about 1720 cm^{-1}, while aromatic C=C deformation vibrations at 1597 and 1507 cm^{-1} reveal only slight intensity gain. Additional peaks, caused by Si-related vibrations, are found between 1250−1270 cm^{-1}, even though they are overlapped by the typical C–O single bond stretching of wood and the newly introduced ester functions. However, the same type of the aforementioned silyl group clearly shows a further signal at about 834 cm^{-1}. Both represent characteristic C-H deformation vibrations of the Si-CH$_3$ group. A further unambiguous proof of the attachment of the silane moiety appears at 744 cm^{-1}, due to a strong Si-C deformation band. In the case of compound **11**, a further indication for the successful covalent bonding is the characteristic C=C stretching vibration at 1627 cm^{-1} and the C=C-H deformation vibration at 930 cm^{-1}.

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[Table 4]

To provide a correlation of the carbonyl stretching vibration intensity with the determined QCO values, the IR spectra are discussed semi-quantitatively, albeit the restricted accuracy limits the interpretation. The spectra were post-processed by baseline-correction using the rubberband method and normalized to the highest band at roughly 1025 cm^{-1}. Then the individual band height ratios were determined by division of the distinctive carbonyl band height by the height of the corresponding deformation vibration of the C–H backbone at about 1453 cm^{-1} (Stefke et al. 2008). The corresponding ratios are 2.56 (**9**), 2.26 (**10**), 2.97 (**11**), and 2.49 (**12**), respectively. Thereby the increase of the carbonyl signals reflects the growth of the corresponding QCO values. While derivatives **9**, **10,** and **12** show similar intensities from 2.26 to 2.56, the allyldimethylsilyl derivative **11** provides the highest result of 2.97.

XPS

Figure 5a–d show the XPS spectra of the modified samples (black line) in comparison to untreated pine wood (red line). The stoichiometric surface composition was obtained by this method, applying a pressure of 1·10^{-9} hPa. Assuming that chemical elements heavier than hydrogen provide characteristic signals, the effectiveness of the sample modification is shown.

[Figure 5]

No nitrogen was detected, i.e. auxiliary 1*H*-benzotriazole was efficiently removed by the above described solvent extraction subsequent to the wood modification process. Due to the additional introduction of organic material upon chemical modification, a growth of the C/O ratio is observed (Table 5).

[Table 5]

The XPS approach also reflects the enhancement of the Si content with increasing reaction time in accordance with the determined QCO and WPG values.

Contact angles (CAs)

CA measurements with distilled water were performed to determine the degree of

hydrophobization which is achieved by the modification (Rak 1975; Liptáková 1994). Figure

6 illustrates the shape of single water drops on veneer, which were modified by compounds **9**

through **11**.

Expectedly, the contact angle determination for untreated pine wood was not feasible, as

the water was soaked up immediately. In contrast to this, all modified samples exhibit an

increased hydrophobicity with CAs beginning with 121° similar to water on Teflon (Butt et

al. 2013). As expected the highest CA values were obtained with the *n*-octyl derivative **10** due

to its non-polar character. The CA data (Θ) up to 141.6° and their related standard deviations

(σ) are summarized in Table 6.

[Table 6]

Conclusions

The benzotriazole activation of *p*-silyl-functionalized benzoic acids prior to esterification

proved to be an efficient method for chemical modification of wood. Even at mild conditions,

ranging from 70°C to 120°C, and with different reaction times it was possible to obtain

considerable WPG values up to 43%. A suitable comparison between the modifications with

different modification agents was feasible by means of the QCO value, which illustrated an

individual extent of chemical modification between 1.1 and 2.7 mmol reagent g^{-1} wood. In

addition, the successful wood modification was spectroscopically verified with ATR-IR,

which showed new signals attributable to Si-related vibrations. Furthermore, the

interpetations were supported by XPS, while CAs up to 141.6 confirmed an increased

hydrophobization of the wood surfaces.

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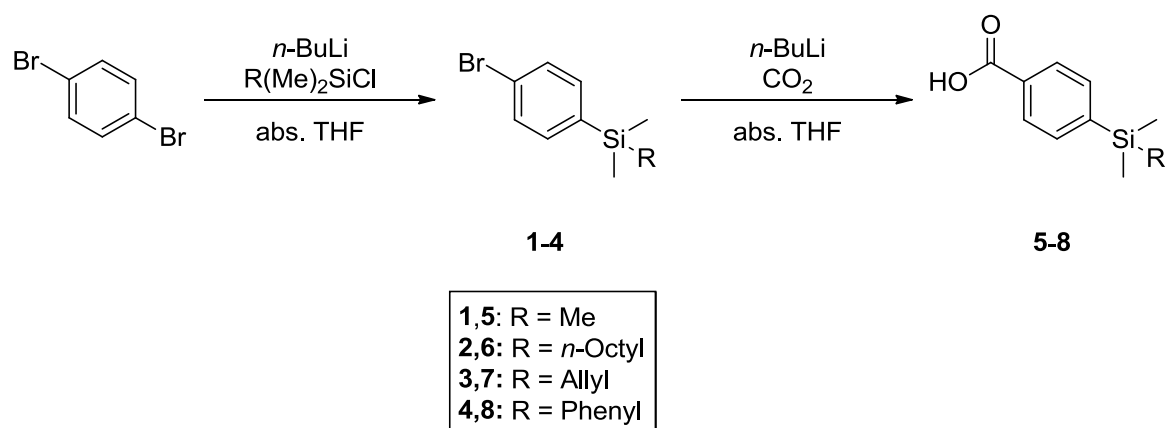
Figure 1 Synthesis of *p*-silylated benzoic acids.
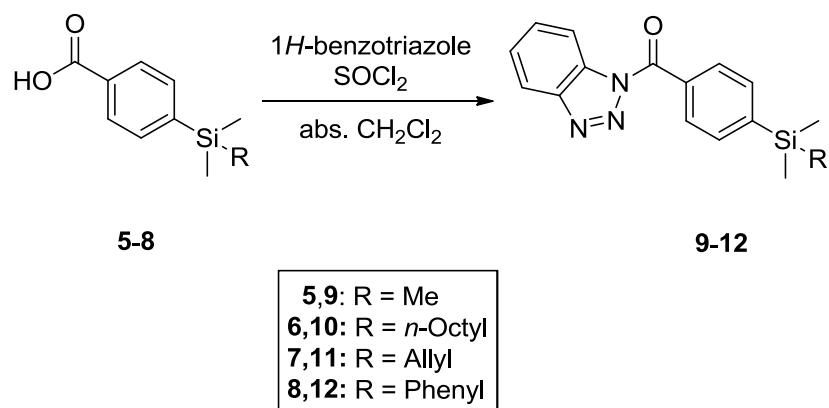

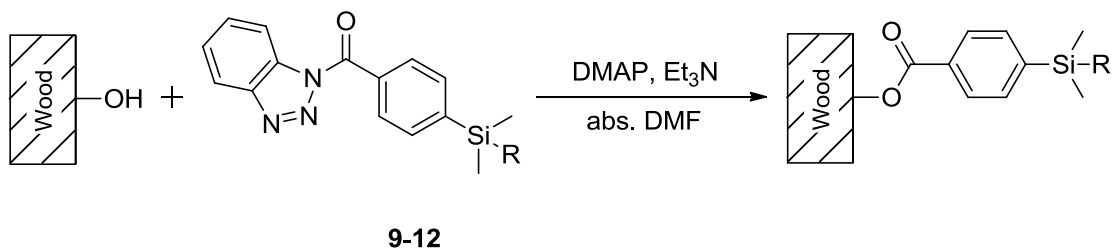**Figure 2** Synthesis of activated benzoic acids.

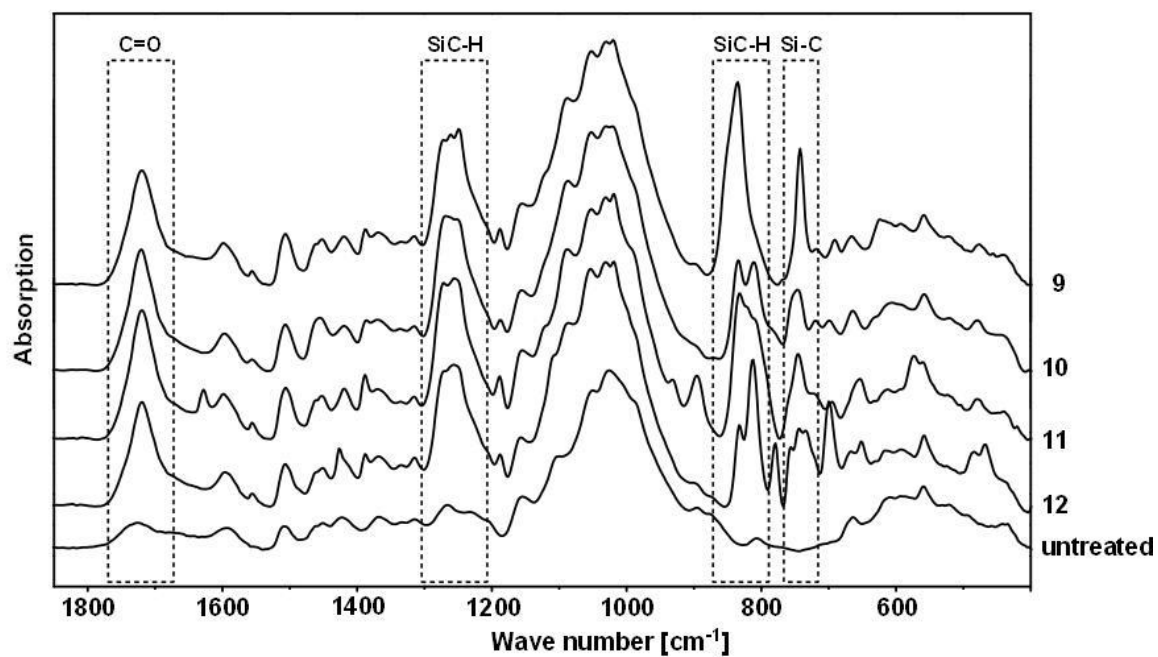**Figure 3** Wood modification procedure applying the 1*H*-benzotriazole protocol.

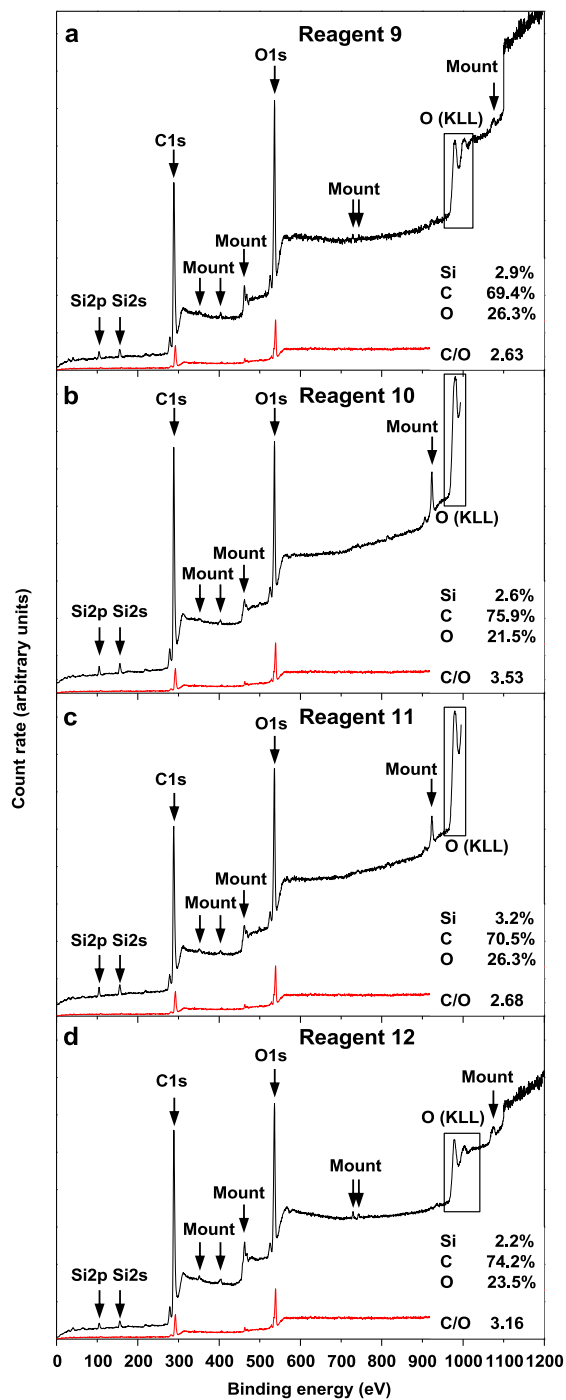**Figure 4** ATR-IR spectra of modified an untreated pine wood samples.

Figure 5   XPS spectra of modified and untreated pine wood.

Table 1 Chemical yields of different precursor preparation steps.

R		Silylation [%]		Carboxylation [%]		Activation [%]
Me	**1**	97	**5**	61	**9**	87
n-Octyl	**2**	93	**6**	98	**10**	89
Allyl	**3**	98	**7**	99	**11**	90
Phenyl	**4**	99	**8**	63	**12**	96

Table 2 WPG and QCO values obtained upon wood modification at 70°C.

Rea-gent	Time [h]	WPG [%]	QCO [mmol/g]
9	18	13.8	0.78
	72	22.9	1.30
	168	25.8	1.46
10	18	8.2	0.30
	72	26.8	0.98
	168	28.7	1.05
11	18	11.0	0.54
	72	23.0	1.14
	168	27.4	1.35
12	18	12.6	0.53
	72	25.6	1.08
	168	29.6	1.24

Table 3 WPG and QCO values obtained upon wood modification at 120°C.

Rea-gent	Time [h]	WPG [%]	QCO [mmol/g]
9	18	21.1	1.20
	72	33.4	1.90
	168	33.8	1.91
10	168	26.5	0.97
11	168	42.5	2.10
12	168	25.9	1.09

Table 4   Characteristic ATR-IR vibrations (untreated vs. covalently modified wood)

Rea-gent	ν (C=O) [cm⁻¹]	ν (C=C) [cm⁻¹]		δ (SiC–H) [cm⁻¹]	δ (SiC–H) [cm⁻¹]	δ (Si–C) [cm⁻¹]
Untr.	1725			-	-	-
9	1720	1598	1507	1249	835	742
10	1720	1598	1507	1256	832	745
11	1721	1598	1507	1269	834	746
12	1719	1596	1507	1257	832	744

Table 5   C/O ratios from XPS measurements (untreated vs. covalently modified wood).

Rea-gent	Time [h]	Stoichiometry [atomic%]				C/O ratio
		C	O	N	Si	
Untr.	-				-	1.56
9	18	70.5	25.7	-	2.5	2.74
	72	68.8	28.7	-	2.4	2.40
	168	69.4	26.3	-	2.9	2.64
10	18	72.7	25.4	-	1.9	2.87
	72	75.0	22.9	-	2.1	3.28
	168	75.9	21.5	-	2.6	3.53
11	18	70.1	28.0	-	1.9	2.51
	72	72.3	25.3	-	2.4	2.86
	168	70.5	26.3	-	3.2	2.68
12	18	70.7	27.0	-	2.3	2.62
	72	73.1	24.5	-	2.4	2.98
	168	74.2	23.5	-	2.2	3.16

Table 6 Measured contact angles (Θ)

Rea-gent	Time [h]	Θ [°]	σ [°]
Untr.	-	-	-
9	18	124.3	7.0
	72	126.7	6.1
	168	127.6	11.2
	168[a]	138.6	7.5
10	18	128.6	9.3
	72	129.3	6.1
	168	134.7	3.6
	168[a]	141.6	9.0
11	18	121.8	4.6
	72	121.8	8.5
	168	125.0	4.5
	168[a]	127.7	8.7
12	18	121.4	7.2
	72	121.3	9.4
	168	126.2	7.9
	168[a]	129.3	7.4

[a] Reaction temperature: 120°C