

# Surface Tuning of Wood via Covalent Modification of Its Lignocellulosic Biopolymers with Substituted Benzoates—A Study on Reactivity, Efficiency, and Durability

Martin Söftje, Thea Weingartz, Rudy Plarre, Mimoza Gjokaj, Jan C. Namyslo, and Dieter E. Kaufmann\*

Cite This: <https://doi.org/10.1021/acsomega.1c04353>

Read Online

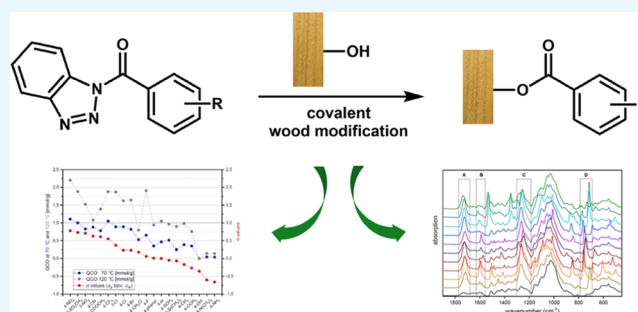
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Chemical modification of wood applying benzo-triazolyl-activated carboxylic acids has proven to be a versatile method for the durable functionalization of its lignocellulosic biopolymers. Through this process, the material properties of wood can be influenced and specifically optimized. To check the scope and limitations of this modification method, various benzamide derivatives with electron-withdrawing (EWG) or electron-donating (EDG) functional groups in different positions of the aromatic ring were synthesized and applied for covalent modification of Scots pine (*Pinus sylvestris* L.) sapwood in this study. The bonded amounts of substances (up to 2.20 mmol) were compared with the reactivity constants of the Hammett equation, revealing a significant correlation between the modification efficiency and the theoretical reactivity constants of the corresponding aromatic substitution pattern. The successful covalent attachment of the respective substituted benzamides was proven by attenuated total reflection infrared (ATR-IR) spectroscopy, while the stability of the newly formed ester bond was proven in a standardized leaching test.



## INTRODUCTION

Chemical modification of wood enables a longer service lifespan of the natural material and increases the attractiveness and usability of the material.<sup>1</sup> Depending on the modification method, the treatment leads to an increased dimensional stability, hydrophobization and fire retardance of the biomaterial, as well as an increased resistance to pest infestation or decomposition by fungi as described in numerous reviews.<sup>1–20</sup> Modified wood panels are used in several fields of application like the construction of weather-prone buildings, facades, and terraces.<sup>21</sup> A particularly promising area of application is the modification of soft and fast-growing types of wood to optimize their properties so that they can be used as a substitute for harder and slow-growing tropical wood to protect the rainforest.<sup>22</sup> Therefore, the chemical modification of wood has attracted more and more interest in recent years, which is evident from a distinct increase in fundamental research and development leading to a number of industrially used processes.<sup>1,2,13,23–29</sup> Especially, the well-known acetylation of wood (ACCOYA process),<sup>1,2,27,30–35</sup> implementation with the urea derivative DMDHEU (BELMADUR process),<sup>1,2,36–41</sup> and impregnation with furfuryl alcohol (KEBONY process)<sup>2,10,12,27,42,43</sup> have been studied and optimized extensively. From a chemical point of view, these methods are fairly simple and can be easily implemented in terms of process technology: The wood

modifications are carried out in vacuum tanks with subsequent drying. In addition to the technically applied acetylation, Yuan et al.<sup>44</sup> and Evans et al.<sup>45</sup> described a method for the benzylation of wood applying benzoyl chloride. This procedure resulted in enhanced thermal stability as well as weathering and photostability of the treated meal and veneer samples. However, the chemical scope of the described processes is quite limited and unspecific so that these methods only allow fundamental protection of wood against certain harmful phenomena. A more specific optimization of the chemical wood modification is of great importance to enlarge the area of application of natural plant materials to replace nonrenewable ones.

Kaufmann and co-workers<sup>46</sup> introduced a mild and versatile method for the effective benzylation of wood. The esterification of wood applying benzo-triazolyl-activated carboxylic acids allows a highly functional modification of the biopolymers in contrast to the established but restricted methods described above. It is now possible to specifically

Received: August 12, 2021

Accepted: November 3, 2021

influence wood hydrophobicity using halo, silyl, or alkyl benzamides,<sup>47–49</sup> and increase the resistance against fungi.<sup>50</sup> It is also possible to gain control against biological attack applying adapted insecticides<sup>51</sup> or adding flame retardant properties by binding boron or phosphorus derivatives.<sup>52</sup> In addition, it has been proven that benzotriazolyl-activated carboxylic acids are not only able to modify the surface but also to penetrate the wood material below the surface.<sup>53,54</sup> This versatile method for the functionalization of lignocellulosic biopolymers can be applied not only for the modification of wood but also for the adjustment of natural fibers. To further investigate this benzylation method, extensive reactivity studies were carried out applying a variety of differently substituted benzamides at various temperatures. The ambition of this work was to gain an understanding of the reaction behavior of the specially designed derivatives to be able to develop more specific wood preservatives based on activated carboxylic acids in the future. For this purpose, several substituted benzoic acid derivatives with electron-withdrawing groups (EWGs) or electron-donating groups (EDGs) in different positions of the aromatic ring were activated with 1*H*-benzotriazole and subsequently used for covalent modification of pine wood chips. The bound amounts of substances were finally compared with the corresponding reactivity constants of the Hammett equation. This revealed a significant connection between the modification efficiency and the basic reactivities of comparable compounds in organic chemical esterification reactions.

The durable long-term protection is a major environmental advantage of covalent wood modification avoiding frequent reimpregnation with conventional preservatives. But chemical wood modification also has an opposing impact on the environment due to extra processing as well as life extension of the material as evaluated by Hill et al.<sup>55</sup> for conventional modification methods. Therefore, it is particularly important that the compounds used for chemical wood modification are stably bound to the wood biopolymers and leaching into the environment is prevented. In this study, the stability of the ester bond formed between the applied reagent and the wood biopolymers was tested as proven in a standardized leaching test according to DIN EN 84.<sup>56</sup>

## RESULTS AND DISCUSSION

### Chemical Syntheses of the Modification Reagents.

The basis for the following wood modification was the synthesis of the activated carboxylic acids with 1*H*-benzotriazole. This activation process was originally developed by Katritzky in which the acid group is first converted to the carboxylic acid chloride using thionyl chloride and then reacted in situ with 1*H*-benzotriazole to yield the activated benzotriazolate.<sup>57</sup> Figure 1 provides the applied reaction conditions for the activation previously also used by the Kaufmann group.<sup>46–51</sup>

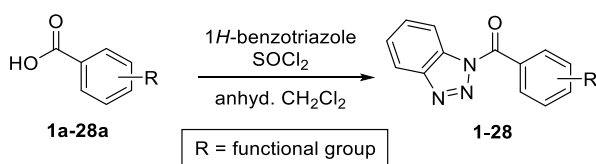


Figure 1. Synthesis of 1*H*-benzotriazole-activated benzoic acids.

This reaction was performed under mild conditions at room temperature in anhydrous dichloromethane and provided the activated amides 1–28 in very good yields (Table 1). The

Table 1. 1*H*-Benzotriazole Activation of Aromatic Carboxylic Acids—Overview of the Results

starting material	activated acid	substitution pattern	yield (%)
1a	1	4-H	84
2a	2	4-F	88
3a	3	4-Cl	94
4a	4	3-Cl	94
5a	5	2-Cl	96
6a	6	4-Br	91
7a	7	4-CN	69
8a	8	4-NO <sub>2</sub>	85
9a	9	3-NO <sub>2</sub>	86
10a	10	2-NO <sub>2</sub>	97
11a	11	4-NH <sub>2</sub>	36
12a	12	4-N(CH <sub>3</sub> ) <sub>2</sub>	92
13a	13	4-Si(CH <sub>3</sub> ) <sub>3</sub>	75
14a	14	4-OH	84
15a	15	4-OCH <sub>3</sub>	93
16a	16	3-Cl, 4-OH	21
17a	17	3-Cl, 4-OCH <sub>3</sub>	88
18a	18	3-NO <sub>2</sub> , 4-OH	55
19a	19	3-NO <sub>2</sub> , 4-OCH <sub>3</sub>	83
20a	20	4-SCH <sub>3</sub>	77
21a	21	4-SO <sub>2</sub> CH <sub>3</sub>	90
22a	22	4-COOCH <sub>3</sub>	83
23a	23	4-CH <sub>3</sub>	96
24a	24	4-CF <sub>3</sub>	88
25a	25	4-CH <sub>2</sub> Cl	94
26a	26	4-CH <sub>2</sub> Br	91
27a	27	4-phenyl	94
28a	28	anthracenyl-9-carboxamide	91

resulting carboxamides 1–28 are characterized by high stability in combination with a high reactivity toward nucleophiles, in this case, wood hydroxy groups. In addition, the molecular structure of carboxamide 25 was verified via X-ray structure analysis (Figure 2).

**Wood Modification.** The synthesized carboxamides were applied for wood modification using the benzylation method developed by Kaufmann and co-workers.<sup>46–51</sup> Veneer chips of Scots pine sapwood (*Pinus sylvestris* L.) were used for the modification process. To ensure a high sample throughput, the modifications were performed in a “Synthesis 1” liquid system parallel synthesizer. A mean value of 7.0 mmol of accessible hydroxy groups per gram wood was assumed since exchange experiments with titrated water described by Sumi et al.<sup>58</sup> showed that an average of 6.9–8.0 mmol of hydroxy groups per gram wood was accessible for chemical reactions. The reaction was catalyzed by the bases triethylamine and 4-(*N,N*-dimethylamino)pyridine (DMAP). Anhydrous dimethylformamide (DMF) was used as the solvent and swelling agent since previous studies by Mantanis proved that DMF has excellent swelling properties for wood.<sup>59,60</sup> Before and after the modification reaction, all wood samples were subjected to Soxhlet extraction in a solvent mixture of toluene:acetone:methanol in a ratio of 4:1:1 and subsequently dried at 105 °C to remove unbound ingredients from the biomaterial. Terpenes and ashes have to be extracted before the modification because

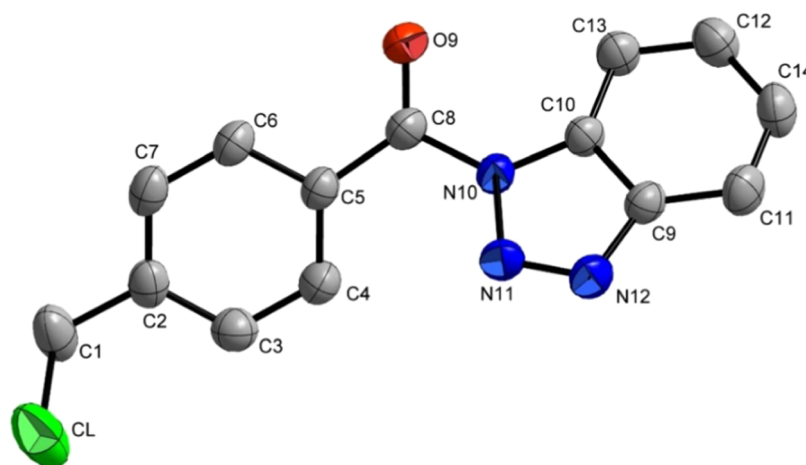


Figure 2. X-ray structure of activated carboxamide 25.

otherwise these components would be washed out during the modification process, which would falsify the observed weight difference of the treated samples. The extraction after the modification in turn serves to remove the unbound residues of the applied modification reagent.

At the beginning of the modification, the wood sample was swollen in a nitrogen atmosphere in a mixture of a base and catalyst in anhydrous DMF for 2 h at 50 °C. During this initial process, the pore structures of the wood expand, which enables the molecules to diffuse more easily into the material and react with the enlarged cell surface. Furthermore, a deprotonation of the wooden hydroxy groups already takes place during the swelling process so that the subsequent esterification is facilitated. After addition of the modification reagent (7.0 mmol per gram wood), the wood sample reacted for 24 h at 70 or 120 °C, respectively. The reaction conditions used for the wood modification are summarized in Figure 3.

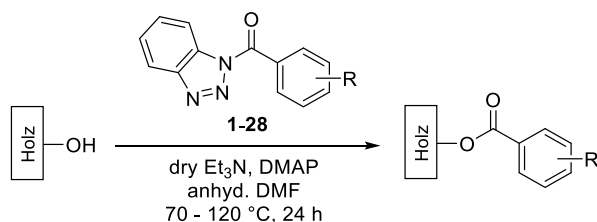


Figure 3. Reaction conditions for wood modification applying activated benzamides.

After modification, extraction, and drying of the wood samples, the mass gain and the bound amount of substance were determined. The obtained weight percentage gain (WPG) and quantity of covalently bound organomaterial (QCO)<sup>48</sup> values are summarized in Table 2 while the corresponding formulas for the WPG and QCO calculations are given in the Supporting Information. Due to the fact that the functionalization was carried out several times at each temperature, the value range of the WPG is shown. In addition, the corresponding mean values of the WPG and QCO values as well as the associated standard deviations are given for each modification reagent.

The modified wood chips show significant weight gains, which confirms the successful covalent attachment of the carboxamides to the wood biopolymers. The maximum WPG

value of 33% with a corresponding QCO value of 2.20 mmol g<sup>-1</sup> was achieved by 4-nitrobenzamide 8 at a reaction temperature of 120 °C. Only 4-hydroxybenzamide 14 and the anthracenyl derivative 28 show a slight decrease in mass. As a result, no QCO values can be calculated for these two modifications. However, Kaldun et al.<sup>47</sup> showed that the applied modification procedure also entails a small loss of lignocellulosic material in the percentage weight range from -0.8 to -1.7%. This comparison gives evidence that the derivatives 14 and 28 were tied to the wood polymers since the weight loss of these samples was smaller than the comparative experiments without the substrate carried out by Kaldun et al.<sup>47</sup> For a comparative evaluation, the QCO values of the benzoylated samples are plotted in descending order according to the values at 70 °C (Figure 4) and 120 °C (Figure S1, see the Supporting Information), respectively.

The QCO values show that larger amounts of bound precursors are achieved at 120 °C in contrast to 70 °C. While some carboxamides show up to 90% higher QCO values at 120 °C, other compounds only provide about 20% higher values. This result proves that temperature has a significant influence on the reactivity of the applied carboxamides. In addition, the average standard deviation of the QCO values is larger at higher temperatures, resulting in a lower reproducibility of the modification results at 120 °C. This observation can be explained by the fact that additional, thermally induced side reactions of the biopolymers occur at elevated temperatures. In addition to a cross-linking mechanism of the biopolymers via the elimination of water, there also occurs thermal degradation of the biopolymers, especially the least stable hemicellulose.<sup>1,26,61</sup> The thermally induced change of the wood material during the chemical modification also becomes evident from a darker coloration of the wood sample at higher temperatures (Figure 5).

The evaluation of the QCO values allows us to draw a conclusion about the reactivities of the applied benzamides. The derivatives substituted with electron-withdrawing groups (4-NO<sub>2</sub>, 4-CF<sub>3</sub>, 4-SO<sub>2</sub>Me, 4-halo, 4-CN) are particularly reactive since the electron density in the aromatic ring is reduced and consequently, the carbonyl carbon atom is activated for nucleophilic attacks. In contrast, the benzamides substituted with electron-donating groups (4-OH, 4-NH<sub>2</sub>, 4-NMe<sub>2</sub>) react more slowly with the biopolymers of wood, since an increase of the electron density in the aromatic ring causes

Table 2. Results of Wood Modification Reactions Applying Activated Aromatic Carboxamides

reagent	temperature (°C)	WPG-range (%)	WPG <sub>0</sub> (%)	$\sigma_{\text{WPG}}$ (%)	QCO <sub>0</sub> (mmol g <sup>-1</sup> )	$\sigma_{\text{QCO}}$ (mmol g <sup>-1</sup> )
1	70	4.6–5.1	4.9	±0.3	0.46	±0.03
	120	10.3–11.7	11.0	±1.0	1.05	±0.09
2	70	7.1–9.5	8.1	±1.2	0.66	±0.10
	120	18.4–28.9	23.5	±4.9	1.91	±0.40
3	70	11.9–12.9	12.4	±0.7	0.89	±0.05
	120	22.2–22.9	22.6	±0.5	1.62	±0.04
4	70	10.0–14.7	12.4	±3.3	0.89	±0.24
	120	25.0–26.8	25.9	±1.3	1.86	±0.09
5	70	4.0–4.3	4.2	±0.2	0.30	±0.01
	120	13.8–14.9	14.3	±0.8	1.03	±0.06
6	70	12.2–17.3	15.0	±2.2	0.82	±0.12
	120	27.5–32.6	30.1	±3.6	1.64	±0.20
7	70	10.5–12.3	11.5	±0.8	0.88	±0.06
	120	11.0–17.0	14.0	±4.2	1.07	±0.33
8	70	15.1–18.0	16.6	±2.0	1.10	±0.14
	120	33.0–33.0	33.0	±0.0	2.20	±0.00
9	70	9.4–15.5	12.4	±4.3	0.83	±0.29
	120	22.0–23.6	22.8	±1.1	1.52	±0.07
10	70	2.5–4.8	3.7	±1.6	0.24	±0.11
	120	10.6–11.4	11.0	±0.6	0.73	±0.04
11	70	0.4–0.6	0.5	±0.1	0.04	±0.01
	120	1.5–1.7	1.6	±0.1	0.14	±0.01
12	70	0.5–0.8	0.7	±0.2	0.05	±0.01
	120	1.9–2.3	2.1	±0.3	0.14	±0.02
13	70	3.3–5.5	4.4	±1.6	0.25	±0.09
	120	15.3–16.5	15.9	±0.9	0.90	±0.05
14	70	−0.4–0.2	−0.3	±0.1	n/a	n/a
	120	−1.0–0.8	−0.9	±0.1	n/a	n/a
15	70	4.1–5.3	4.7	±0.8	0.35	±0.06
	120	9.4–11.1	10.2	±1.2	0.76	±0.09
16	70	−0.2–0.4	0.1	±0.4	0.01	±0.03
	120	1.0–1.7	1.3	±0.5	0.09	±0.03
17	70	9.2–10.0	9.6	±0.6	0.57	±0.04
	120	17.0–20.4	18.7	±2.4	1.11	±0.14
18	70	1.9–2.4	2.1	±0.3	0.13	±0.02
	120	7.1–8.8	8.0	±1.2	0.48	±0.07
19	70	14.7–16.9	15.8	±1.6	0.88	±0.09
	120	27.2–30.2	28.7	±2.2	1.59	±0.12
20	70	7.1–8.5	7.8	±1.0	0.52	±0.07
	120	14.4–14.8	14.6	±0.3	0.97	±0.02
21	70	15.5–21.0	18.3	±3.9	1.00	±0.21
	120	21.2–25.0	23.1	±2.6	1.26	±0.14
22	70	12.7–12.7	12.7	±0.0	0.78	±0.00
	120	20.7–24.6	22.7	±2.8	1.39	±0.17
23	70	3.9–5.3	4.6	±1.0	0.39	±0.08
	120	11.2–12.2	11.7	±0.7	0.98	±0.06
24	70	17.7–18.6	18.1	±0.7	1.05	±0.04
	120	29.1–35.9	32.5	±4.8	1.88	±0.28
25	70	7.9–8.2	8.1	±0.2	0.53	±0.02
	120	11.3–13.1	12.2	±1.3	0.80	±0.08
26	70	3.4–9.4	6.9	±2.5	0.35	±0.13
	120	13.1–17.4	15.2	±3.0	0.77	±0.15
27	70	5.3–7.4	6.3	±1.5	0.35	±0.08
	120	16.7–17.4	17.0	±0.5	0.94	±0.03
28	70	−0.2–0.1	−0.1	±0.0	n/a	n/a
	120	−0.8–0.6	−0.7	±0.2	n/a	n/a

deactivation of the carbonyl group. In addition, the steric requirements of the substituents also have an influence on the reactivity during the wood modification. Compounds with a

carbonyl group sterically hindered by further substituents (9-anthracenyl carboxylate, 2-NO<sub>2</sub>) therefore led to very low QCO values.



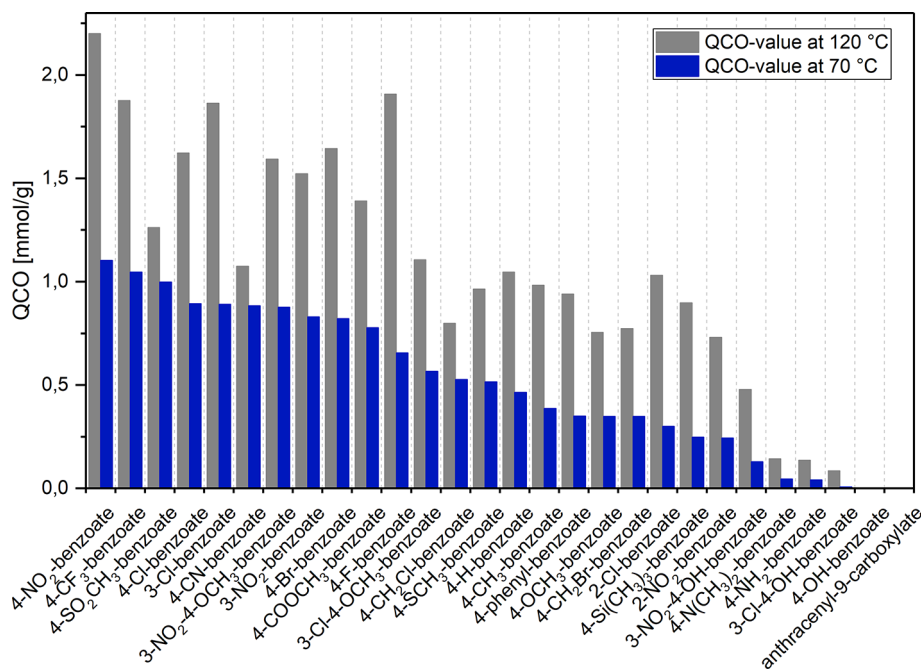


Figure 4. Summary of QCO values—sorted by descending values at 70 °C.

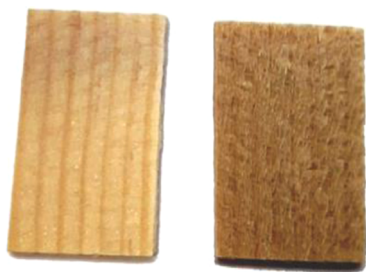


Figure 5. Thermally induced color change of the wood chips modified with reagent **6** at 70 °C (left) and 120 °C (right).

The results demonstrate a clear influence of the substituents attached to the phenyl ring on the reactivity of the carboxamides in the modification reaction. The strength of the respective electronic effects in *meta* and *para* positions can be estimated using the substituent constant  $\sigma$ , which can be calculated from the Hammett equation (Formula 1).<sup>62–64</sup>

$$\lg \frac{k}{k_0} = \rho \times \sigma \quad (1)$$

**Formula 1:** Hammett equation with  $k$  the rate coefficient of the substituted compound,  $k_0$  the rate coefficient of the unsubstituted compound,  $\rho$  the reaction constant, and  $\sigma$  the substituent constant.<sup>62–64</sup>

The Hammett equation describes a quantitative relationship between the structure of a doubly substituted aromatic system and its reactivity in a selected reaction, such as the hydrolysis of an ester group.<sup>62–64</sup> The proportionality constant  $\rho$  is characteristic for the investigated reaction, whereas the substituent constant  $\sigma$  describes the influence of the functional group bound in the *meta* or *para* position. The  $\sigma$  values, summarized by Jaffé, are compared with the QCO values of selected wood modifications in a comparison plot in Figure 6.<sup>64</sup> The entries in the diagram are sorted according to descending  $\sigma$  values (all values are additionally summarized in

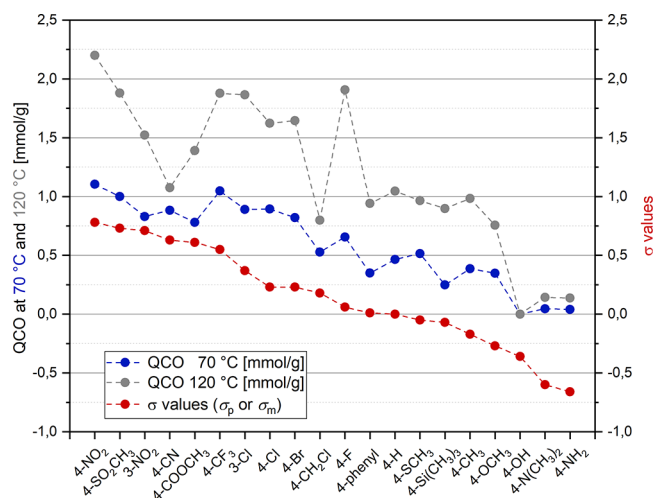


Figure 6. Plotting the QCO values and the  $\sigma$  values from the Hammett equation (taken from Jaffé<sup>64</sup>) as comparative reactivity criteria. The entries are sorted according to descending  $\sigma$  values.

Table S2 in the Supporting Information). The absolute values must not be compared, only the trend of the reactivities, expressed by the QCO and  $\sigma$  values, allows an interpretation.

A small  $\sigma$  value theoretically corresponds to a low reactivity at the carbonyl carbon atom for a nucleophilic attack by the wood hydroxy groups, which results in a low QCO value of the modification. This theory is confirmed by the approximately parallel progression of the QCO values and the  $\sigma$  values in Figure 6. The deviations from the reactivity trend are significantly larger in the modifications at 120 °C than in the results obtained at 70 °C. This observation indicates that, in addition to the substituent influences described by the  $\sigma$  values, other factors also affect the modification process. Possible influences like thermally induced side reactions or the steric hindrance of the substituents have already been

Table 3. Results of the Wood Modification of Various Types of Wood Applying Carboxamides 2 and 6

reagent	type of wood	temperature (°C)	WPG-range (%)	WPG <sub>0</sub> (%)	σ <sub>WPG</sub> (%)	QCO <sub>0</sub> (mmol g <sup>-1</sup> )	σ <sub>QCO</sub> (mmol g <sup>-1</sup> )
2 (4-F)	pine	70	7.1–9.5	8.1	±1.2	0.66	±0.10
		120	18.4–28.9	23.5	±4.9	1.91	±0.40
	beech	70	6.4–6.8	6.6	±0.3	0.54	±0.02
		120	11.7–25.7	18.7	±9.8	1.52	±0.80
	maple	70	3.8–4.3	4.0	±0.4	0.33	±0.03
		120	14.1–14.2	14.1	±0.1	1.15	±0.01
6 (4-Br)	pine	70	12.2–17.3	15.0	±2.2	0.82	±0.12
		120	27.5–32.6	30.1	±3.6	1.64	±0.20
	beech	70	12.5–12.9	12.7	±0.3	0.69	±0.02
		120	22.0–24.3	23.2	±1.6	1.27	±0.09
	maple	70	17.2–17.3	17.3	±0.0	0.94	±0.00
		120	28.8–29.9	29.4	±0.8	1.61	±0.04

discussed above. The stability of the substrates and their solubility also influences the result of each wood modification.

In addition to the *para*-substituted benzamides, *ortho*-, *meta*-, or *poly*-substituted benzamides were also used for the wood modification. While the *meta*-substituted compounds 4 and 9 (3-Cl, 3-NO<sub>2</sub>) achieve similar or slightly lower QCO values than the *para*-substituted derivatives 3 and 8 (4-Cl, 4-NO<sub>2</sub>), the *ortho*-substituted compounds 5 and 10 (2-Cl, 2-NO<sub>2</sub>) lead to significantly lower QCO values. The lower amounts of the covalently bound substance can be explained by the increased steric hindrance of the carbonyl group due to the substituents in the *ortho* position. This effect is particularly evident with the 2-nitro compound 10 since the nitro group is more voluminous and therefore leads to a lower QCO value than the corresponding 2-chloro compound 5, regardless of the stronger electron-withdrawing effect of the nitro moiety.

The polysubstituted carboxamides are equipped with hydroxy (16 and 18) or methoxy groups (17 and 19) in the *para* position and are additionally substituted with an EWG in the *meta* position. These derivatives serve as example compounds since it is possible to replace the proton or the methyl group with other functional units such as insecticides, as shown by Söftje et al.<sup>51</sup>

Because of the fact that the hydroxy- (14) and alkoxy-substituted derivatives (15) only reach low QCO values due to their positive mesomeric effect (+M effect) of the substituents, additional EWGs (NO<sub>2</sub> or Cl groups) were attached in the *meta* position (compounds 16–19). The effect of the additionally attached EWGs on the reactivity becomes evident from the resulting QCO values plotted in Figure S2 (see the Supporting Information).

While compound 14 substituted exclusively with a hydroxy group in the *para* position indicates negative WPG values, the 3-chloro-4-hydroxy derivative 16 already leads to positive WPG values and thus the amount of the bound substance between 0.01 mmol g<sup>-1</sup> (70 °C) and 0.09 mmol g<sup>-1</sup> (120 °C). Finally, the 3-nitro-4-hydroxy compound 18 leads to significantly larger QCO values of 0.13 mmol g<sup>-1</sup> (70 °C) and 0.48 mmol g<sup>-1</sup> (120 °C). A similar reactivity trend can be observed for the methoxy compounds 15, 17, and 19. Although all of these compounds show larger QCO values than the comparable hydroxy derivatives (up to 1.59 mmol g<sup>-1</sup> for 19 at 120 °C), a similar reactivity trend can be observed, whereby the influence of the EWG in the *meta* position becomes evident. In summary, it can be stated that these doubly substituted compounds are well suited as linking

moieties to bind functional building blocks with an influence on the wood material properties to the biomaterial.

To prove that the modification method developed by Kaufmann and co-workers<sup>46,48–51</sup> can also be applied to other types of wood such as European beech (*Fagus sylvatica* L.) and Sycamore maple (*Acer pseudoplatanus* L.), the corresponding specimens were modified. In contrast to pine wood, these types of wood do not provide any usable sapwood parts, so heartwood veneers were applied for modification. 4-Fluoro-(2) and 4-bromobenzamide (6) were selected as reference substrates and used under the standard modification conditions specified in Figure 3. The results of the wood modifications are summarized in Table 3.

All samples, regardless of the type of wood, show a significant weight gain after treatment with reagents 2 and 6. The beech samples achieved 77–85% of the QCO values of pine wood for both substrates. On the other hand, the maple specimens show a greater variation of the QCO values. While the fluorine derivative 2 only reaches 49–60% of the pine wood values, similar or even slightly higher QCO values are observed applying the bromine compound 6. In a conclusion, the obtained results prove that the wood modification procedure using activated carboxylic acids can be applied to different types of wood. In addition to the treatment of sapwood, the method also allows the modification of heartwood.

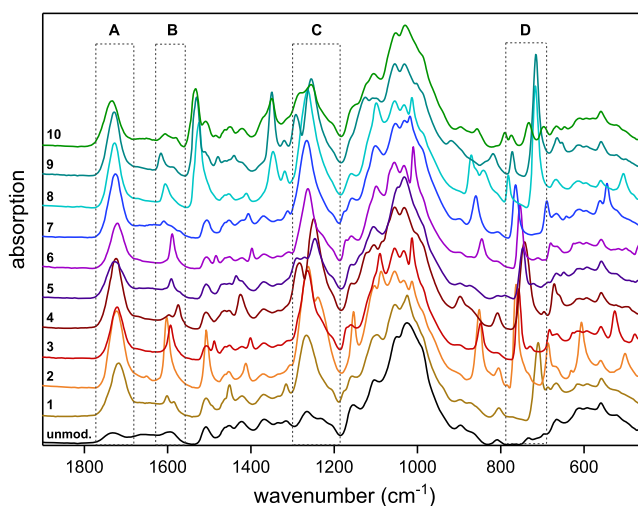
**Leaching Test.** To prove the stability of the covalent bond formed between the benzoate and the wood biopolymers, a standardized leaching test according to DIN EN 84 was carried out.<sup>56</sup> Since European standardized efficacy tests require wood specimens measuring 15 × 25 × 50 mm<sup>3</sup>, an upscaled modification procedure was carried out to modify the required samples following Soeftje et al.<sup>51</sup> Thereby, five standardized blocks were modified simultaneously in a specially designed glass reactor using 150 mL of anhydrous DMF, anhydrous triethylamine, and DMAP. For the leaching tests, 4-fluoro-substituted benzamide 2 (1.0 mmol per gram wood) was applied as a modification reagent. This derivative was chosen due to its hydrophobizing properties as well as the analytical detectability of the fluorine moiety for subsequent analysis of the leaching solution. To achieve a sufficient penetration depth of the reagents for the larger pine wood blocks, the modification solution was introduced into the reactor by means of a partial vacuum (0.5 bar), followed by the swelling process (2 h at 50 °C) before increasing the pressure by nitrogen addition to atmospheric pressure. The subsequent reaction was carried out analogous to Figure 3 (24 h at 70 °C)

yielding the modified samples with a QCO value of  $0.40 \pm 0.01$  mmol per gram wood on average and a corresponding WPG value of  $5.0 \pm 0.2\%$ . The modified samples were subjected to the leaching test in which the samples were washed in a water bath following the standardized test procedure DIN EN 84.<sup>56</sup> The same test was carried out with five unmodified samples for comparison. At the end of the test, the samples were dried and weighed. The untreated samples showed a weight loss of  $3.2 \pm 0.5\%$  (WPL), whereas the esterified samples only showed a smaller weight loss of  $1.6 \pm 0.1\%$ . This standardized test confirms the stability of the covalent bond since the weight loss of the treated samples falls below the natural value of the untreated specimens instead of exceeding it. On the one hand, the lower mass loss shows that no significant amounts of the modification reagent have been leached. On the other hand, the hydrophobization of the wood caused by the fluorine substituent becomes evident.

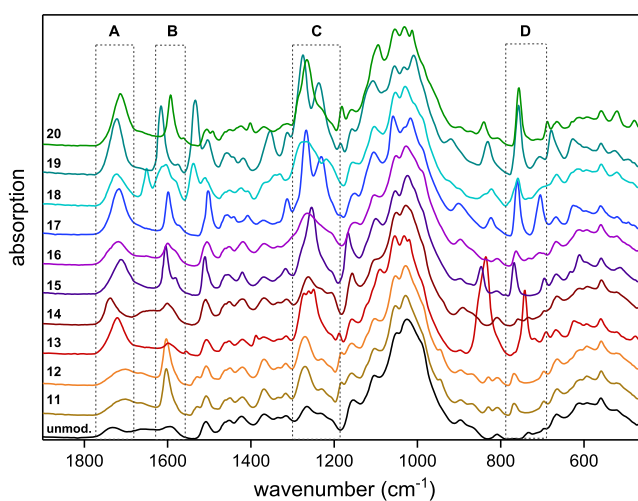
In addition, the IR spectra of the modified samples showed no changes after the leaching test. The characteristic bands of the covalently bound fluorine substance **2** remained unchanged in the spectrum. Furthermore, the solvent of the collected leaching solution was removed in vacuo and the resulting residue was examined by means of <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy. The primarily detected signals could be assigned to the cellulose and lignin biopolymers. Additional aromatic signals were detected in the residue of the modified sample, indicating very small amounts of a hydrolyzed, low molecular fluorine component. A weak signal indicating an aryl-bound fluorine atom was also detected in the corresponding <sup>19</sup>F NMR spectrum of the sample at  $-112.0$  ppm. However, it was impossible to determine whether the slightly detected fluoro species actually resulted from the hydrolysis of the esterified wood components or whether it was a hydrolyzed residue of unbound benzamide **2**, which was eventually not fully extracted after the modification. Nevertheless, the very small detected amounts of the hydrolyzed fluorine compound are negligible. Due to the fact that the chemical modification is still visible in the IR spectra and that no significant amounts of hydrolyzed substances are detected, the covalent ester bond can be classified as largely stable to hydrolysis.

**IR Spectroscopic Characterization.** The analysis of the modified wood samples was primarily based on ATR-IR spectroscopy, since this nondestructive method has been proven to be a reliable and meaningful method to examine esterified wood.<sup>46–51,53</sup> In addition, the formation of a covalent bond between the applied reagent and the wood biopolymers has already been confirmed by Drafz et al.<sup>22</sup> and Namyslo et al.<sup>65</sup> via 2D-NMR spectroscopy as well as by Ehrhardt et al.<sup>66</sup> and Soeftje et al.<sup>67</sup> via thermal analyses (pyrolysis GC MS). Furthermore, microcomputed tomography-based investigations provided information concerning the penetration depth and the pathways of the modifying reagent into the wood tissue.<sup>53,54</sup>

The ATR-IR spectra of the chemically modified samples using benzamide **1–28** are presented in Figures 7–9 each in comparison to unmodified Scots pine sapwood. The analytical comparison of unmodified and modified wood reveals significant changes caused by the formation of a covalent bond between the modifying reagent and the biopolymers. While the distinctive bonds caused by the lignin and the polysaccharides have already been fully elucidated in the literature,<sup>68–73</sup> the newly formed ester bond leads to a



**Figure 7.** ATR-IR spectra of unmodified and modified wood (samples **1–10**) in comparison (A:  $\nu_{C=O}$ , B:  $\nu_{C=C, \text{ arom.}}$ , C:  $\nu_{C-O, \text{ asym.}}$  and D:  $\delta_{C-H, \text{ arom.}}$ ).

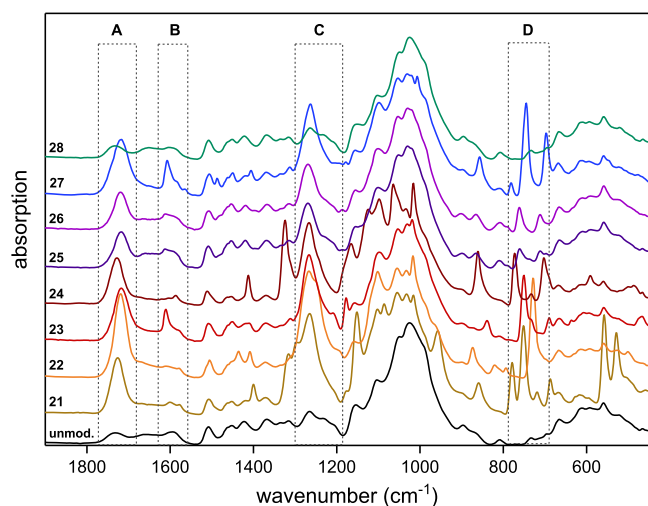


**Figure 8.** ATR-IR spectra of unmodified and modified wood (samples **11–20**) in comparison (A:  $\nu_{C=O}$ , B:  $\nu_{C=C, \text{ arom.}}$ , C:  $\nu_{C-O, \text{ asym.}}$  and D:  $\delta_{C-H, \text{ arom.}}$ ).

significant increase of characteristic vibrations A–D in each spectrum.

The carbonyl stretching band at approximately  $1700 \text{ cm}^{-1}$  (area A) as well as the corresponding C–O stretching vibrations at  $1250 \text{ cm}^{-1}$  (area C) increase, which unambiguously verified the formation of a covalent bond between the respective benzamides **1–28** and the wood biopolymers. In addition, a slight increase in absorption can be observed for the aromatic C=C stretching vibrations at about  $1600 \text{ cm}^{-1}$  (area B), which is caused by the introduced aromatic moieties. The aromatic deformation bands were correspondingly detected at about  $760 \text{ cm}^{-1}$  (area D). Furthermore, the functional groups attached to the aromatic ring, such as halo, cyano, nitro, silyl, or methoxy substituents, evoke specific stretching and deformation vibrations, which are clearly visible in the IR spectra between  $1150\text{--}1600 \text{ cm}^{-1}$  ( $\nu$ ) and  $500\text{--}900 \text{ cm}^{-1}$  ( $\delta$ ), respectively. These additional bands give evidence for the chemical modification of the wood samples with each specific reagent **1–27**. Only the sample treated with the anthracenyl derivative **28** does not show any significant differences from

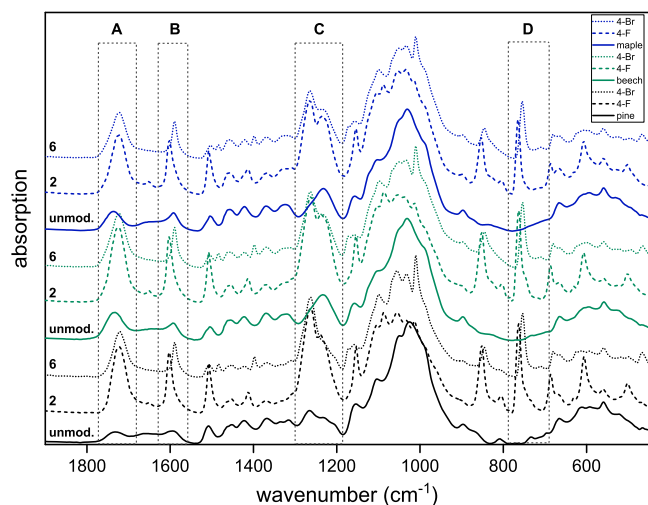




**Figure 9.** ATR-IR spectra of unmodified and modified wood (samples 21–28) in comparison (A:  $\nu_{\text{C=O}}$ , B:  $\nu_{\text{C=C, arom.}}$ , C:  $\nu_{\text{C-O, asym.}}$ , and D:  $\delta_{\text{C-H, arom.}}$ ).

the IR spectrum of unmodified pine wood, which can be explained by the very small amounts of the bound substance. Nevertheless, the corresponding samples feature fluorescent properties caused by the large aromatic  $\pi$ -system, proving the covalent attachment of **28** to the biopolymers.

In addition to the treated pine wood specimens, the modified beech and maple wood samples were also examined via IR spectroscopy (Figure 10). The spectra of the



**Figure 10.** ATR-IR spectra of unmodified types of wood (pine in black, beech in green, maple in blue) and the specimens modified with benzamides **2** and **6**, respectively (A:  $\nu_{\text{C=O}}$ , B:  $\nu_{\text{C=C, arom.}}$ , C:  $\nu_{\text{C-O, asym.}}$ , and D:  $\delta_{\text{C-H, arom.}}$ ).

unmodified beech and maple wood types differ only slightly from the spectrum of the untreated pine wood. The modified samples show the abovementioned C–O and C=C vibrations in areas A–D, independent from the applied type of wood. The wavenumbers and the intensities of the respective bands are very similar, which confirms the covalent attachment of benzamides **2** and **6** to beech and maple wood in addition to the previously discussed pine wood chips.

## CONCLUSIONS

In this study, a wide range of substituted benzoic acids was activated by means of 1*H*-benzotriazole, and the compounds were isolated, mostly in very good yields and fully characterized. The reactivity of these benzamides toward wood hydroxy groups was tuned by various EWGs and EDGs attached to different positions of the phenyl ring. The synthesized reagents enabled a detailed investigation of their reactivities in the subsequent benzoylation of wood. The chemical modification of Scots pine sapwood veneer chips, carried out at different temperatures, led to peak values in the covalently bound organomaterial of up to 1.10 mmol per g at 70 °C and 2.20 mmol per g at 120 °C. Comparison of the functionalizations showed that the reactivities of the applied benzamides and thus the modification results depend on the electronic effects of the functional groups attached to the aromatic ring. Aromatic compounds substituted with EWGs can be bound particularly well to pine sapwood, while benzamides with EDGs only gave moderate QCO values and in some cases even led to a weight loss of the treated sample. It can be summarized that our study reveals a correlation between the reactivity of the esterification of lignocellulosic biopolymers and the reactivity constants arising from the Hammett equation. These findings enable a prior estimation of the effectiveness of a wood modification approach to develop effective modification substrates in advance. In addition, the temperature dependence of the modification results was determined, since the functionalizations carried out at 70 °C consistently gave very good results with small standard deviations in the WPG and QCO values. Although the modifications carried out at 120 °C mostly led to larger values in the amount of the bound substance, thermal effects on the wood sample were also observed, which both impaired the visual appearance of the material and caused inadequate reproducibility. In conclusion, a temperature of 70 °C proved to be optimal for wood modification with activated carboxylic acids. It was also shown that a second substituent with electron-withdrawing properties increases the effectiveness of the modification. These doubly substituted linking compounds are well suited to bind other functional building blocks to the biomaterial, which are able to influence wood properties.<sup>51</sup> Furthermore, the process for the chemical treatment of pine sapwood was also applied successfully to other types of wood such as beech and maple heartwood. All modified wood samples were analyzed extensively and the attached fragments were detected by IR spectroscopy. The modification process was scaled up to larger specimens (15 × 25 × 50 mm<sup>3</sup>) and the wood blocks modified with **2** were subjected to a leaching test following DIN EN 84<sup>56</sup> to investigate the durability of the covalent modification. The standardized test explicitly confirmed the durability of the covalent ester bond between the substrate and the biomaterial. This result finally underlines the suitability of the wood modification method developed by Kaufmann and co-workers.<sup>46–51</sup> Furthermore, this study shows the potential of the described functionalization method since it can basically be transferred to all lignin and/or carbohydrate-containing biomacromolecules like natural fibers or smaller biobased chemicals.

## MATERIALS AND METHODS

**General Methods.** *NMR Instrument.* <sup>1</sup>H NMR (600 MHz), <sup>13</sup>C NMR (150 MHz), and <sup>15</sup>N NMR (61 MHz):



Avance III 600 MHz FT-NMR spectrometer (Bruker, Rheinstetten, Germany).  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz): Avance 400 FT-NMR spectrometer (Bruker).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to the residual solvent peak [ $\text{CDCl}_3$ :  $\delta = 7.26$  ppm ( $^1\text{H}$ ),  $\delta = 77.0$  ppm ( $^{13}\text{C}$ ) or  $\text{DMSO}-d_6$ :  $\delta = 2.50$  ppm ( $^1\text{H}$ ),  $\delta = 39.5$  ppm ( $^{13}\text{C}$ )]. For the  $^{15}\text{N}$  NMR spectra, nitromethane ( $\delta = 0.0$  ppm) was used as an internal or external standard. In all cases, peak assignments were accomplished by DEPT135-, HSQC-, and HMBC-NMR experiments. Coupling constants  $J$  are given in Hertz (Hz). Multiplicities are described using the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of a doublet, ddd = doublet of a doublet of a doublet, tt = triplet of a triplet, q = quartet, and m = multiplet. Primary and tertiary carbon atoms have been marked with a "+", the secondary with a "-", and quaternary with a "C<sub>quat</sub>" according to the peak orientation in the DEPT135 spectra.

**IR Instruments.** Bruker "α-T" (Bruker, Bremen, Germany) equipped with a platinum-ATR-module. IR instruments for wood chips: Bruker "Tensor II" equipped with a platinum-ATR-module.

**Mass Spectra Instrument.** EI mass spectrometry: a Varian 320 MS Triple Quad GC/MS/MS instrument (Varian, Darmstadt, Germany) with a Varian 450-GC usually operating in direct mode (DEP method) using electron impact ionization (70 eV). In the case of chlorinated and brominated compounds, all peak values of molecular ions as well as fragments refer to the isotopes  $^{35}\text{Cl}$  and  $^{79}\text{Br}$ , respectively. ESI mass spectrometry: an LC-MSD Series 1100 (Agilent/Hewlett Packard, Santa Clara, CA, US). High-resolution ESI mass spectrometry: a Waters Acquity UPLC coupled to a Waters Q-TOF Premier (Waters, Eschborn, Germany) or an LC-System 1260 Infinity II (Agilent Technologies, Santa Clara, CA, US), coupled to a Bruker Impact II (Bruker, Bremen, Germany). High-resolution EI mass spectrometry: a Waters Micromass GCT (Waters, Eschborn, Germany) operating in direct mode. All HRMS results were satisfactory relative to the calculated accurate mass of the molecular ion ( $\pm 2.3$  ppm,  $R \approx 10\,000$ ).

**Melting Points.** Differential scanning calorimeter DSC6 (Perkin-Elmer, Waltham, MA, US) of the onset temperature of the endothermic peak in the DSC diagram is evaluated to determine the melting point of each compound.

**Wood Modification Reactor.** Heidolph Synthesis 1 liquid system parallel synthesizer (Heidolph, Schwabach, Germany).

**Chemicals, Solvents, and Wood Materials.** Dichloromethane (DCM) was dried using an MP5 solvent purification system from Inert Technology (Amesbury, MA, US). Anhydrous *N,N*-dimethylformamide (DMF) and all other chemicals were used as purchased from Acros GmbH & Co. KG (Karlsruhe, Germany), Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany), TCI Deutschland GmbH (Eschborn, Germany), or Merck KGaA (Darmstadt, Germany). The untreated Scots pine sapwood veneer samples were obtained from the Section of Wood Biology and Wood Products, the Georg-August-University Göttingen (Göttingen, Germany). The Scots pine sapwood blocks were received from the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany), whereas the European beech and Sycamore maple heartwood veneer samples were provided by Danzer Deutschland GmbH (Kesselsdorf, Germany).

**Chromatography.** Thin-layer chromatography (TLC) was performed on Merck TLC plates (aluminum-based) silica gel 60 F 254. Purification was carried out using column

chromatography on silica gel 60 (Merck). Petroleum ether as the eluent had the boiling range of 60–70 °C.

**X-ray Structure Analysis.** Chloromethyl benzamide **25** was crystallized from a solution of deuterated chloroform. A suitable single crystal of compound **25** was selected under a polarization microscope and mounted in a glass capillary ( $d = 0.3$  mm). The crystal structure was determined by X-ray diffraction analysis using graphite monochromated Mo  $K\alpha$  radiation (0.71073 Å) [ $T = 223(2)$  K], whereas the scattering intensities were collected with a single crystal diffractometer (STOE IPDS II). The crystal structure was solved by direct methods using SHELXS-97 and refined using alternating cycles of least-squares refinement against  $F^2$  (SHELXL-97). All non-H atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final difference Fourier synthesis.<sup>74</sup>

$\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}$  ( $M = 271.70$  g mol<sup>-1</sup>) was crystallized in the monoclinic space group  $P2_1/c$  (no. 14), lattice parameters  $a = 9.675(5)$  Å,  $b = 7.826(5)$  Å,  $c = 16.853(8)$  Å,  $\beta = 105.15(4)^\circ$ ,  $V = 1231.7(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc.}} = 1.465$  g cm<sup>-3</sup>, and  $F(000) = 560$  using 2353 independent reflections and 213 parameters.  $R1 = 0.0779$ ,  $wR2 = 0.1911$  [ $I > 2\sigma(I)$ ], goodness of fit on  $F^2 = 1.049$ , and residual electron density 0.739 and  $-0.564$  e Å<sup>-3</sup>.

Further details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Center, CCDC 2075908. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: + 44(1223)-336 033; e-mail: fileserv@ccdc.ac.uk or <http://www.ccdc.cam.ac.uk>).

**Organic Precursors. General Procedure for the Activation of Benzoic Acids.**<sup>46–50</sup> 1.10–1.68 equiv of thionyl chloride was added to a suspension of carboxylic acid (or sodium carboxylate) and 3.10–3.52 equiv of 1*H*-benzotriazole in anhydrous DCM. The mixture was stirred for 16–30 h at rt. Subsequently, water or a 2 M solution of hydrochloric acid (aq) was added. Variant 1: The mixture was extracted with DCM and the combined organic phases were washed with water, if necessary additionally with a saturated solution of sodium chloride (aq), and dried over magnesium sulfate. After evaporation of the solvent and adsorption on silica gel, the product was purified by column chromatography and dried in vacuo. Variant 2: The mixture was extracted with DCM and the combined organic phases were washed with a 2 M solution of hydrochloric acid (aq) and water and dried over magnesium sulfate. After evaporation of the solvent, the product was dried in vacuo. Variant 3: The precipitate was collected by filtration, washed with water, DCM, and if necessary EE. The product was dried in vacuo.

**Chemical Wood Modification Procedures. General Procedure for the Chemical Modification of Wood Veneer Chips.**<sup>47,49,51</sup> Each functionalization was carried out in a Heidolph synthesis 1 parallel synthesizer applying 7.0 mmol of the respective wood modifying reagent **1–28** per 1.00 g of wood veneer (*Pinus sylvestris* L. resp. *Fagus sylvatica* L. or *Acer pseudoplatanus* L., approximately  $10 \times 10 \times 0.7$  mm<sup>3</sup>, 0.04–0.07 g). Prior to the wood modification, the sample was subjected to extraction in a Soxhlet apparatus for 24 h. Thereby, a solvent mixture comprising toluene/acetone/methanol in a 4:1:1 ratio was used as the extractant. The thus pretreated wood was dried at 105 °C for 24 h and subsequently applied for the wood modification. The wood specimen was placed in the reaction tube, evacuated, and

flushed with nitrogen thrice. Afterwards, 6 mL of anhydrous DMF, triethylamine (2 equiv relating to the modifying reagent), and 4-(dimethylamino)pyridine (DMAP, 10 mol % of the modifying reagent) were added under a nitrogen atmosphere. The sample was allowed to swell in the solution for 2 h at 50 °C before adding the modifying reagent (7.0 mmol/g wood). The wood specimen was heated in the reaction mixture for 24 h at 70 or 120 °C, respectively. After cooling down to rt, the modified wood chip was washed consecutively with THF (50 mL), chloroform (50 mL), and diethyl ether (50 mL). The sample was extracted again for 24 h applying the same conditions as stated above. Finally, the treated wood chip was dried for 24 h at 105 °C before determining its weight.

**Procedure for Chemical Modification of Standardized Woodblocks.**<sup>51</sup> The simultaneous functionalization of five standardized woodblocks was carried out in a glass reactor, which was closed with a flat flange, applying 1.0 mmol of the wood modifying reagent **2** per 1.00 g of Scots pine sapwood (*Pinus sylvestris* L., 15 × 25 × 50 mm<sup>3</sup>). Prior to the wood modification, the samples were subjected to extraction in a Soxhlet apparatus for 3 days. Thereby, a solvent mixture comprising toluene/acetone/methanol in a 4:1:1 ratio was used as an extractant. The thus pretreated wood was dried at 105 °C for 3 days and subsequently applied for the wood modification. The woodblocks were placed in the reactor, subsequently evacuated using a rotary vane pump, and flushed with nitrogen thrice. Thereafter, the pressure was increased to 0.5 bar via nitrogen supply and kept constant with a diaphragm pump. Contemporaneous, a solution of (1*H*-benzotriazol-1-yl)(4-fluorophenyl)methanone (**2**, 1.0 mmol/g wood), anhydrous triethylamine (2 equiv relating to the modifying reagent), and 4-(dimethylamino)pyridine (DMAP, 10 mol % of the modifying reagent) in 150 mL of anhydrous DMF was prepared under a nitrogen atmosphere. This solution was transferred into the reaction vessel via a metal cannula and through a septum with the help of the applied vacuum in the reactor. The woodblocks were allowed to swell in the solution for 2 h at 50 °C and 0.5 bar before increasing the pressure via nitrogen supply to atmospheric pressure. A quantity of 30 mL of anhydrous DMF was added through the septum and thereupon the specimens were heated in the reaction mixture for 24 h at 70 °C. After cooling down to rt, the modified woodblocks were washed consecutively with THF (250 mL), chloroform (250 mL), and diethyl ether (250 mL). The samples were extracted again for 24 h applying the same conditions as stated above. Finally, the treated woodblocks were dried for 3 days at 105 °C before determining their weight.

**Leaching Test.** The leaching tests were carried out according to DIN EN 84.<sup>56</sup> The woodblocks modified with 4-fluorobenzamide **2** were initially placed in a test vessel and weighted down to prevent the samples from floating. The blocks were then completely covered with water. A vacuum of 40 kPa was applied for a period of 20 min and then the samples were impregnated in the aq solution for another 2 h. The water in the test vessel was drained and replaced with fresh water (100 mL of water per wood sample with the dimensions 15 × 25 × 50 mm<sup>3</sup>). The leaching solution was replaced in total nine times within the following 14 days, exchanging only three-quarters of the water volume in each case to ensure that the wood samples were continuously covered with water. The described water replacement steps

took place at the end of the 1st and 2nd days, and another seven times in the remaining 12 days, with at least 1 but a maximum of 3 days between the exchanges. Following the test procedure, the samples were first dried in air and then at 105 °C and finally weighed. The solvent of the collected leaching solution was removed in vacuo and the resulting residue was dissolved in a solution of 0.580 g of LiCl in 10 mL of DMSO-*d*<sub>6</sub>. The analyte was subsequently examined by means of <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04353>.

Synthetic procedures and analytical spectra of the organic precursors (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Dieter E. Kaufmann – Institute of Organic Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld D-38678, Germany; [orcid.org/0000-0002-9790-828X](https://orcid.org/0000-0002-9790-828X); Phone: +49-5323-722027; Email: [dieter.kaufmann@tu-clausthal.de](mailto:dieter.kaufmann@tu-clausthal.de)

### Authors

Martin Söftje – Institute of Organic Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld D-38678, Germany; [orcid.org/0000-0002-6794-0748](https://orcid.org/0000-0002-6794-0748)

Thea Weingartz – Institute of Organic Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld D-38678, Germany

Rudy Plarre – Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin D-12205, Germany

Mimoza Gjikaj – Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld D-38678, Germany

Jan C. Namyslo – Institute of Organic Chemistry, Clausthal University of Technology, Clausthal-Zellerfeld D-38678, Germany

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.1c04353>

### Author Contributions

Conceptualization: M.S. and D.E.K.; supervision: D.E.K.; syntheses, Scots pine sapwood modification, and the corresponding spectroscopic analysis: M.S.; European beech and Sycamore maple wood modification: T.W.; NMR spectroscopy: M.S. and J.C.N.; X-ray analysis: M.G.; leaching test: R.P.; writing original draft: M.S.; and review and editing: D.E.K., J.C.N., and M.S. All authors have given approval to the final version of the manuscript.

### Funding

This work was financially supported by the Clausthal University of Technology, Germany. In addition, we acknowledge the support of the Open Access Publishing Fund of the Clausthal University of Technology.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors thank Dr. Martin Drafz, Monika Ries, and Birgit Wawrzinek for measuring part of the  $^{15}\text{N}$  NMR spectra as well as Dr. Gerald Dräger, Leibniz University of Hannover (Germany), for high-resolution mass spectra. In addition, the authors thank Sabine Busweiler for technical support during the leaching test and kindly acknowledge Prof. Holger Militz and Prof. Carsten Mai from the Section of Wood Biology and Wood Products, the Georg-August-University Göttingen (Germany) as well as Ralf Bußmann from Danzer Deutschland GmbH, Kesselsdorf (Germany) for providing the veneer wood samples.

## REFERENCES

- Hill, C. A. S. *Wood Modification: Chemical, Thermal and Other Processes*, Wiley Series in Renewable Resources; John Wiley & Sons, 2006.
- Mai, C. Prozesse der chemische Holzmodifizierung. *Holztechnologie* **2010**, *51*, 21–26.
- Peterson, M.; Thomas, R. Protection of wood from decay fungi by acetylation. *Wood Fiber Sci.* **1978**, *10*, 149–163.
- Takahashi, M. Biological Properties of Wood. In *Chemical Modification of Lignocellulosic Materials*, Hon, D. N.-S., Ed., Dekker, 1996.
- Imamura, Y.; Nishimoto, K. Resistance of acetylated wood to attack by subterranean termites. *Wood Res. Kyoto* **1986**, *72*, 37–44.
- Imamura, Y.; Nishimoto, K.; Yoshida, Y.; Kawai, S.; Sato, T.; Nakaji, M. *Wood Res. Kyoto* **1986**, *73*, 35–43.
- Hill, C. A. S.; Jones, D. The Dimensional Stabilisation of Corsican Pine Sapwood by Reaction with Carboxylic Acid Anhydrides. The Effect of Chain Length. *Holzforchung* **1996**, *50*, 457–462.
- Rowell, R. M. Penetration and Reactivity of Cell Wall Components. In *Chemistry of Solid Wood*, Rowell, R. M., Ed., American Chemical Society, 1984; pp 175–210.
- Nicholas, D. D.; Williams, A. D. *Dimensional Stabilisation of Wood with Dimethylol Compounds*:IRG/WP 3412, International Research Group on Wood Preservation, 1987.
- Stamm, A. J. Dimensional Stabilization of Wood with Furfuryl Alcohol Resin. In *Wood Technology: Chemical Aspects*; Goldstein, I. S., Ed., American Chemical Society, 1977; pp 141–149.
- Ryu, J. Y.; Imamura, Y.; Takahashi, M. *Biological Resistance of Furfuryl Alcohol-Treated Wood*: IRG/WP 3703-92, International Research Group on Wood Preservation, 1992.
- Lande, S.; Eikenes, M.; Westin, M.; Schneider, M. H. Furfurylation of Wood: Chemistry, Properties, and Commercialization. In *Development of Commercial Wood Preservatives*, Schultz, T. P.; Militz, H.; Freeman, M. H.; Goodell, B.; Nicholas, D. D. Eds.; American Chemical Society, 2008; pp 337–355.
- Gérardin, P. New alternatives for wood preservation based on thermal and chemical modification of wood— a review. *Ann. For. Sci.* **2016**, *73*, 559–570.
- Pfeffer, A.; Dieste, A.; Mai, C.; Militz, H. Effects of water glass and DMDHEU treatment on the colonisation of wood by *Aureobasidium pullulans*. *Eur. J. Wood Prod* **2011**, *69*, 303–309.
- Schaffert, S.; Nunes, L.; Krause, A.; Militz, H. *Resistance of DMDHEU-Treated Pine Wood Against Termite and Fungi Attack in Field Testing According to EN 252, Results After 30 Months*:IRG/WP 06-40354, International Research Group on Wood Protection, 2006.
- Verma, P.; Junga, U.; Militz, H.; Mai, C. Protection mechanisms of DMDHEU treated wood against white and brown rot fungi. *Holzforchung* **2009**, *63*, 371–378.
- Videlov, C. L. *Biological Degredation Resistance of Pine Wood Treated with Dimethylol Compounds*:IRG/WP 3528, 37th Annual Meeting of the International Research Group on Wood Protection, 1989.
- Yusuf, S.; Imamura, Y.; Takahashi, M.; Minato, K. *Biological Resistance of Aldehyde-Treated Wood*: IRG/WP 94-40018, International Research Group on Wood Preservation, 1994.
- Yusuf, S.; Imamura, Y.; Takahashi, M.; Minato, K. *Physical and Biological Properties of Albizzia Waferboard Modified with Cross-Linking Agents*: IRG/WP 95-40043, International Research Group on Wood Preservation, 1995.
- Emmerich, L.; Militz, H.; Brischke, C. Long-term performance of DMDHEU-treated wood installed in different test set-ups in ground, above ground and in the marine environment. *Int. Wood Prod. J.* **2020**, *11*, 27–37.
- Accsys Technologies. Featured Projects.<https://www.accsys.com/uk/projects/> (accessed Sept 18, 2021).
- Drafz, M. H. H. *Synthese und Analytik neuartig modifizierter Holzoberflächen*, TU Clausthal, Clausthal-Zellerfeld, 2014.
- Militz, H. Wood modification research in Europe. *Holzforchung* **2020**, *74* (4), 333.
- Sandberg, D.; Kutnar, A.; Mantanis, G. Wood modification technologies - a review. *Forest* **2017**, *10*, 895–908.
- Kocaepe, D.; Huang, X.; Kocaepe, Y. Dimensional Stabilization of Wood. *Curr. Forestry Rep.* **2015**, *1*, 151–161.
- Ormondroyd, G.; Spear, M.; Curling, S. Modified wood: Review of efficacy and service life testing. *Proc. Inst. Civ. Eng.: Constr. Mater.* **2015**, *168*, 187–203.
- Mantanis, G. I. Chemical Modification of Wood by Acetylation or Furfurylation: A Review of the Present Scaled-up Technologies. *BioResources* **2017**, *12*, 4478–4489.
- Jones, D.; Sandberg, D. A Review of Wood Modification Globally – Updated Findings from COST FP1407. *Interdiscip. Perspect. Built Environ.* **2020**, *1*, 1–31.
- Spear, M. J.; Curling, S. F.; Dimitriou, A.; Ormondroyd, G. A. Review of Functional Treatments for Modified Wood. *Coatings* **2021**, *11* (3), 327.
- Rowell, R. M. Chemical modification of wood: A short review. *Wood Mater. Sci. Eng.* **2006**, *1*, 29–33.
- Rowell, R. M.; Dickerson, J. P. Acetylation of Wood. In *Deterioration and Protection of Sustainable Biomaterials*, Schultz, T. P.; Goodell, B.; Nicholas, D. D. Eds., American Chemical Society, 2014; Vol 1158, pp 301–327.
- Fuchs, W. Zur Kenntnis des genuinen Lignins, I: Die Acetylierung des Fichtenholzes. *Ber. dtsh. Chem. Ges.* **1928**, *61*, 948–951.
- Suida, H.; Titsch, H. Zur Chemie des Buchenholzes: Acetylierung des Buchenholzes und Spaltung des Acetyl-buchenholzes. *Ber. dtsh. Chem. Ges. A/B.* **1928**, *61*, 1599–1604.
- Horn, O. Zur Acetylierung des Buchenholzes. *Ber. dtsh. Chem. Ges. A/B.* **1928**, *61*, 2542–2545.
- Rowell, R. M. Acetylation of wood—A Review. *Int. J. Lignocellul. Prod.* **2014**, *1*, 1–27.
- Petersen, H. Wechselwirkung von Vernetzern und Katalysatoren in der Hochveredlung. 10. Mitteilung. *Melliand Textilber* **1973**, *4*, 415–418.
- Petersen, H. Wechselwirkung von Vernetzern und Katalysatoren in der Hochveredlung. 10. Mitteilung. *Melliand Textilber* **1973**, *5*, 529–533.
- Weaver, J. C.; Nielson, J. F.; Goldstein, I. S. Dimensional stabilization of wood with aldehydes and related compounds. *For. Prod. J.* **1960**, *10*, 306–31.
- Militz, H.; Mai, C. Sonstige Vergütungsverfahren. In *Taschenbuch Der Holztechnik*, Fachbuchverl. Leipzig im Hanser-Verl, 2008; pp 485–500.
- Militz, H. Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability. *Wood Sci. Technol.* **1993**, *27*, 347–355.
- Emmerich, L.; Bollmus, S.; Militz, H. Wood modification with DMDHEU (1,3-dimethylol-4,5-dihydroxyethyleneurea) – State of the art, recent research activities and future perspectives. *Wood Mater. Sci. Eng.* **2019**, *14*, 3–18.



- (42) Goldstein, I. S. The impregnation of wood to impart resistance to alkali and acid. *For. Prod. J.* **1955**, *5*, 265–267.
- (43) Goldstein, I.; Dreher, W. Stable Furfuryl Alcohol Impregnating Solutions. *Ind. Eng. Chem.* **1960**, *52*, 57–58.
- (44) Yuan, T.-Q.; Zhang, L.-M.; Xu, F.; Sun, R.-C. Enhanced photostability and thermal stability of wood by benzylation in an ionic liquid system. *Ind. Crops Prod.* **2013**, *45*, 36–43.
- (45) Evans, P. D.; Owen, N. L.; Schmid, S.; Webster, R. D. Weathering and photostability of benzyolated wood. *Polym. Degrad. Stab.* **2002**, *76*, 291–303.
- (46) Namyslo, J. C.; Kaufmann, D. E. Chemical improvement of surfaces. Part 1: Novel functional modification of wood with covalently bound organoboron compounds. *Holzforschung* **2009**, *63*, 627–632.
- (47) Kaldun, C.; Söftje, M.; Namyslo, J. C.; Kaufmann, D. E. Chemical improvement of surfaces. Part 5: Surfactants as structural lead for wood hydrophobization - Covalent modification with p-alkylated benzoates. *Holzforschung* **2020**, *74*, 703–713.
- (48) Drafz, M. H. H.; Dahle, S.; Maus-Friedrichs, W.; Namyslo, J. C.; Kaufmann, D. E. Chemical improvement of surfaces. Part 2: Permanent hydrophobization of wood by covalently bonded fluoroorganyl substituents. *Holzforschung* **2012**, *66*, 727–733.
- (49) Kaldun, C.; Dahle, S.; Maus-Friedrichs, W.; Namyslo, J. C.; Kaufmann, D. E. Chemical improvement of surfaces. Part 4: Significantly enhanced hydrophobicity of wood by covalent modification with p-silyl-functionalized benzoates. *Holzforschung* **2016**, *70*, 411–419.
- (50) Namyslo, J. C.; Kaufmann, D. E.; Mai, C.; Militz, H. Chemical improvement of surfaces. Part 3: Covalent modification of Scots pine sapwood with substituted benzoates providing resistance to *Aureobasidium pullulans* staining fungi. *Holzforschung* **2015**, *69*, 595–601.
- (51) Söftje, M.; Acker, S.; Plarre, R.; Namyslo, J. C.; Kaufmann, D. E. Novel nicotinoid structures for covalent modification of wood: an environmentally friendly way for its protection against insects. *RSC Adv.* **2020**, *10*, 15726–15733.
- (52) Ehrhardt, C.; Tapken, M.; Namyslo, J. C.; Kaufmann, D. E. Chemical improvement of surfaces. Part 6: enhanced flame retardancy of Scots pine sapwood by covalent modification with phosphorus and boron functionalized benzoates. *Holzforschung* **2021**, *75*, 83–90.
- (53) Drafz, M. H. H.; Franz, A.; Namyslo, J. C.; Kaufmann, D. E. Chemistry and Spectroscopy of Renewable Materials, Part 1: Imaging the Penetration Depth of Covalent Wood Modification. *ACS Sustainable Chem. Eng.* **2015**, *3*, 566–568.
- (54) Söftje, M.; Koddenberg, T.; Militz, H.; Drafz, M. H. H.; Namyslo, J. C.; Kaufmann, D. E. Chemistry and Spectroscopy of Renewable Materials, Part 2: Investigation of suitably esterified wood regarding penetration and distribution of the chemically modifying reagent by means of high-resolution 3D computed tomography. *ACS Sustainable Chem. Eng.* **2020**, *8*, 7353–7358.
- (55) Hill, C.; Hughes, M.; Gudsell, D. Environmental Impact of Wood Modification. *Coatings* **2021**, *11*, No. 366.
- (56) DIN EN 84:1997-05. *Wood Preservatives - Accelerated Ageing of Treated Wood Prior to Biological Testing - Leaching Procedures* German version, Beuth-Verlag, Berlin, Germany, 1997.
- (57) Katritzky, A. R.; Zhang, Y.; Singh, S. K. Efficient Conversion of Carboxylic Acids into N-Acylbenzotriazoles. *Synthesis* **2003**, *18*, 2795–2798.
- (58) Sumi, Y.; Hale, R. D.; Meyer, J. A.; Leopold, B.; Ranby, B. G. Accessibility of wood and wood carbohydrates measured with tritiated water. *Tappi* **1964**, *47*, 621–624.
- (59) Mantanis, G. I.; Young, R. A.; Rowell, R. M. Swelling of wood. *Wood Sci. Technol.* **1994**, *28*, 119–134.
- (60) Mantanis, G. I.; Young, R. A.; Rowell, R. M. Swelling of Wood. Part II. Swelling in Organic Liquids. *Holzforschung* **1994**, *48*, 480–490.
- (61) Shafizadeh, F.; Chin, P. P. S. Thermal Deterioration of Wood. In *Wood Technology: Chemical Aspects*, Goldstein, I. S. Ed., American Chemical Society, 1977; pp 57–81.
- (62) Smith, M. B. *March's Advanced Organic Chemistry*, 7, John Wiley & Sons, Auflage, 2013.
- (63) Hammett, L. P. The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives. *J. Am. Chem. Soc.* **1937**, *59*, 96–103.
- (64) Jaffé, H. H. A Reëxamination of the Hammett Equation. *Chem. Rev.* **1953**, *53*, 191–261.
- (65) Namyslo, J. C.; Drafz, M.; Kaufmann, D. E. Durable Modification of Wood by Benzylation – Proof of Covalent Bonding by Solution State NMR and DOSY NMR Quick-Test. *Polymers* **2021**, *13*, 2164–2184.
- (66) Ehrhardt, C. *Dauerhafter Schutz von Hanf und Kiefernholz durch kovalente Modifizierung mit neuartigen Bor- und Phosphor-Flammschutzmitteln*, TU Clausthal, Clausthal-Zellerfeld, University library Publication server, 2018.
- (67) Söftje, M. *Nachhaltige Optimierung der Materialeigenschaften von Holz gegenüber biologischer Schädigung durch kovalente Modifizierung mit Carbonsäureamiden*, TU Clausthal, Clausthal-Zellerfeld, University library Publication server, 2019.
- (68) Strel'skii, V. A.; Belova, T. P. Application of IR spectroscopy in the analysis of the woody-fibrous mass in the process of hydrolysis. *Chem. Nat. Compd.* **1990**, *26*, 581–584.
- (69) Mohammed-Ziegler, I.; Marosi, G.; Matkó, S.; Hórvölgyi, Z.; Tóth, A. Silylation of wood for potential protection against biodegradation. An ATR-FTIR, ESCA and contact angle study. *Polym. Adv. Technol.* **2003**, *14*, 790–795.
- (70) Mohebbi, B. Attenuated total reflection infrared spectroscopy of white-rot decayed beech wood. *Int. Biodeterior. Biodegrad.* **2005**, *55*, 247–251.
- (71) Traoré, M.; Kaal, J.; Martínez Cortizas, A. Differentiation between pine woods according to species and growing location using FTIR-ATR. *Wood Sci. Technol.* **2018**, *52*, 487–504.
- (72) Pawlak, Z.; Pawlak, A. S. A Review of Infrared Spectra from Wood and Wood Components Following Treatment with Liquid Ammonia and Solvated Electrons in Liquid Ammonia. *Appl. Spectrosc. Rev.* **1997**, *32*, 349–383.
- (73) Popescu, C.-M.; Popescu, M.-C.; Singurel, G.; Vasile, C.; Argyropoulos, D. S.; Willfor, S. Spectral characterization of eucalyptus wood. *Appl. Spectrosc.* **2007**, *61*, 1168–1177.
- (74) Sheldrick, G. M. *SHELX-97 - Programs for Crystal Structure Analysis*, University of Göttingen, 1997.