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The synthesis of a near infrared-sensitive tackifier

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Abstract

A general method to prepare near infrared absorbing abietic acid derivatives is described in which the carboxylic acid of abietic acid is sterically hindered, making the seemingly simple esterification of the acid with a functional near infrared dye the most troublesome stage of the synthesis. Optimum results were obtained by constructing the chromophore from components previously attached to abietic acid. The spectral properties of the desired compound both in solution and within polymer films are discussed. The tackifiers increase the near infrared absorption, offering the potential for near infrared-activated hot-melt adhesives.

Keywords: Squairaine dye; Dihydroperimidine; Polymer compatibility

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1. Introduction

Tackifiers are substances of relatively low molar mass that are introduced into polymer matrices to improve their adhesion properties. On a phenomenological level, they often act as plasticizers to lower the polymer viscosity at low shear rates, but they also contribute rigidity at high shear rates. Tackifiers are often an essential component of hot-melt adhesives, pressure-sensitive adhesives used in labels, as well as key components of the vehicle for lithographic inks [1]. Rosin acids and their derivatives have been used as tackifiers for over 100 years. Not only are they useful, but also they are inexpensive, since they are normally obtained from the spent cooking liquor from kraft pulping operations [2]. As a class, rosin acids are diterpenoids and commonly have the composition $C_{19}H_{29}$-COOH with a tri-ring structure based on the phenanthrene nucleus. One of the parent compounds in these rosin acids is abietic acid.

We are interested in derivatives of abietic acid possessing a chromophore absorbing in the near infrared (NIR) region. Molecules or dyes with a strong absorption of light in the NIR range of wavelengths (700–2000 nm) can serve as an optical transducer. It can absorb NIR radiation, from a source such as a diode laser, and through radiationless decay, convert the excitation energy into heat. This is a common use of NIR dyes in technology [3] and medicine [4]. In theory, when NIR dyes are introduced to hot-melt adhesives used in examples such as sealants, inkjet printer ink and coatings, the dye can act as a trigger to convert inexpensive NIR light to the heat required to melt the thermoplastics. This potential application can significantly reduce the operating cost in the hot-melt adhesive industry. There are two types of light sources that can be employed for this purpose. In addition to diode lasers, halogen lamps are black-body radiation sources with a broad emission in the range 800–2000 nm. To take advantage of this type of source, adhesives should be formulated with dyes or pigments that have a broad absorption in this region. Conducting polymers such as polypyrrole have a broad absorption band in this region. We have shown that incorporating even a few parts per million of polypyrrole nanoparticles into a hot-melt adhesive formulation can increase by orders of magnitude the conversion of incident NIR radiation into heat [5].

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For some applications, such as in microelectronics, spot melting of adhesives is important. For this type of application, a formulation with an NIR-absorbing dye with an absorption maximum close to that of a typical NIR diode laser is preferable. However, most NIR dyes have poor solubility in organic solvents and polymer matrices. Therefore, direct blending of dyes with melt adhesives is usually not fruitful because it leads to phase separation or non-homogenous products. Because tackifiers are important components in adhesives and are highly compatible with polymers, NIR sensitive tackifiers become an ideal candidate as the NIR absorber.

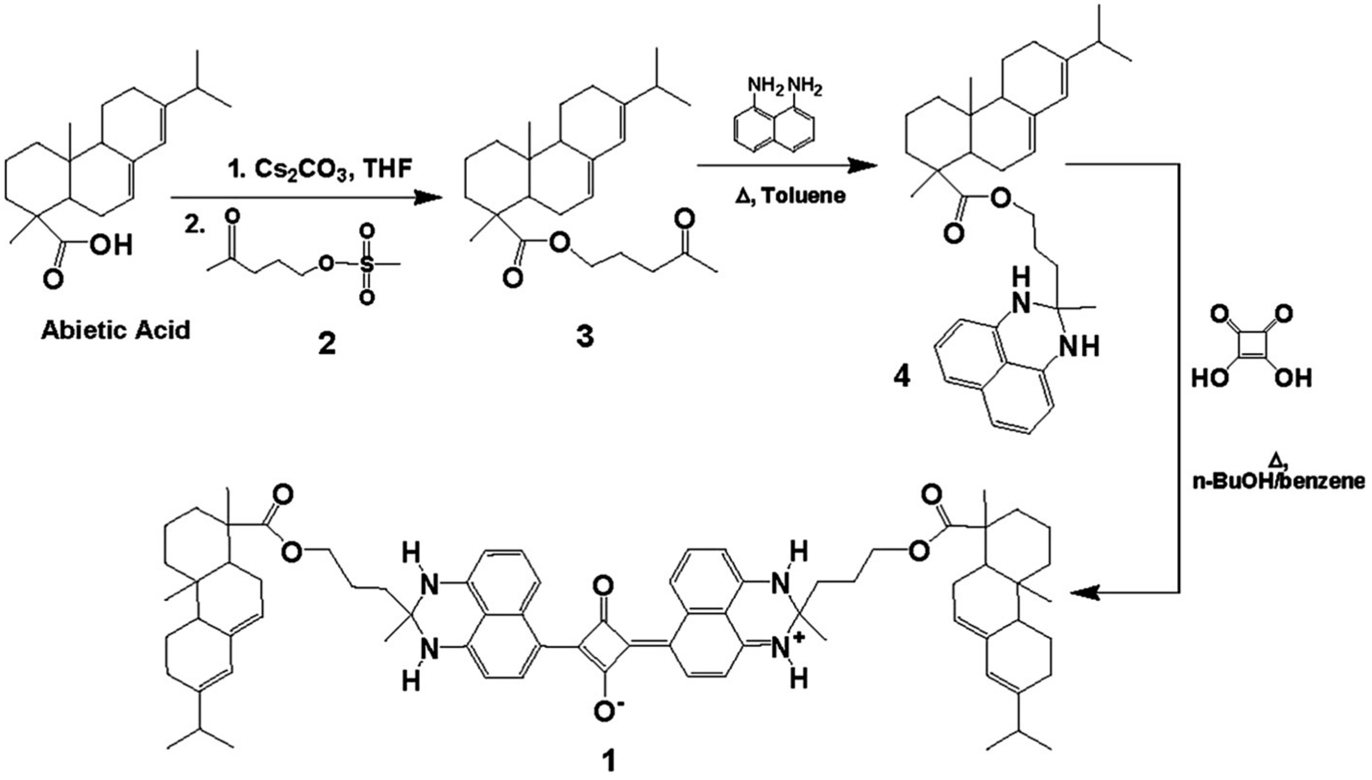
In this paper, we describe the synthesis, characterization and optical spectroscopy of a near infrared absorbing tackifier. Functional NIR dyes with active covalent handles are known and even commercially available. One would think the desired product can be prepared by directly coupling abietic acid with a functional NIR dye. However, because the carboxyl group in abietic acid and other diterpenoid rosin acids is sterically hindered, making ester derivatives of these types of compounds becomes a challenge [6]. In industry, thermally stable abietic esters are synthesized at elevated temperatures and pressures in the presence of excess alcohols and an acid catalyst [1], although NIR dyes may not survive in these harsh conditions. Another hurdle in the direct coupling reaction is the poor solubility of NIR dyes.

We have devised a simple synthetic route to overcome the above challenges. The idea is to first convert abietic acid to a NIR dye precursor, and the desired product can be synthesized by a literature procedure. The solubility problem can therefore be avoided. We also found that esters of abietic acid can be formed in modest yields by a relatively mild reaction of the Cs salt of the carboxylic acid with mesylates, but even here, this step is often the most cumbersome of the entire synthesis.

2. Results and discussion

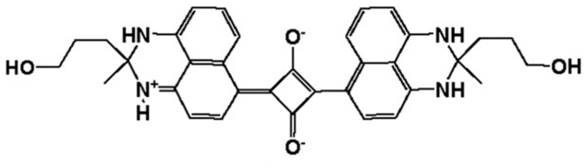
We choose the NIR chromophore of a squaraine dye reported by Bello et al. [7] for our NIR-tackifier prototype. Compound **5** is an example of this kind of dye [8], which is prepared from a dihydroperimidine and squaric acid. The dihydroperimidine derivatives are synthesized by treating 1,8-diaminonaphthalene with a ketone. Because of the symmetry of the molecule, it is often more straight forward to prepare functional dyes containing two reactive groups than a single such group. The most direct route to our NIR-tackifier **1** is through carbodiimide coupling of functional dye **5** with abietic acid. As expected, due to the low reactivity of the acidic functional group on abietic acid and the low solubility of squaraine dye **5**, a direct coupling between the two compounds by DCC did not give the desired product.

As an alternative approach, we considered assembly of the dye to building blocks already attached to the abietic acid framework as shown in Scheme 1. This approach works, but the first and seemingly simplest step proved to be the most troublesome. We synthesized ketone **3** via an S_N2 reaction between the Cs carboxylate of abietic acid and methylsulfonyloxy-2-pentanone (**2**). The process was not very efficient, as we



Scheme 1.

recovered 40% of acidic materials after the reaction. We tried to carry out the reaction using 5-chloro-2-pentanone, but no desired product was obtained. This indicates that the carboxylic ion is not very nucleophilic. We also carried out the reaction in DMF. The conversion was very similar to that when THF was employed. However, it was difficult to remove the residual DMF from the product. The solvent mixed with the crude product to form a gummy mixture after workup, and this mixture was hard to purify. When THF was employed, the solvent could be removed easily. By using 0–20% ether in hexanes as eluent, we were able to isolate compound **3** in 60% yield (based on recovered abietic acid) by flash column chromatography.



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This step gave the lowest product yield in our synthetic route. The low yield was likely due to the low reactivity of the nucleophilic center, and product loss during purification. It is worth noting that commercial abietic acid is a mixture of isomers. The abietic acid employed here was purchased from Aldrich and was 75% pure. Based on NMR and mass spectroscopy analysis, the impurities present in the sample were primarily other rosin acid derivatives. As most rosin acids can function as tackifiers, it is not necessary to isolate them completely in industrial applications. Therefore, this troublesome isolation step probably is not required in industrial scale production.

The yields of step 2 and 3 in Scheme 1 are respectable. Dihydroperimidine **4** was obtained in an isolated yield of 75%. Final product **1** was prepared in quantitative yield (90%). TLC analysis of the crude product indicated the presence of mainly one compound (and a tiny one which did not move on the plate). A small portion of the product was subjected to flash chromatography to afford pure compound **1**. The molar extinction coefficient ε of the purified product **1** in THF at $\lambda_{max} = 810$ nm is 1.3×10^5 M^{-1} cm^{-1}, which is almost the same as that of dye **5**.

The vis–NIR spectrum of dye **1** in THF is presented in Fig. 1(a). It is almost identical to that of dye **5**, in which a strong NIR absorption at 810 nm is observed. Diode lasers are available that emit in this range of wavelengths (e.g., 809.6 nm, 2.4 W, Coherent Corp.), and this inexpensive laser can be the light source in hot-melt adhesive applications. The solubility of dye **1** in common solvents is significantly higher than dye **5** and other similar squaraine dyes reported in the literature [3]. Dye **5** is soluble in methanol but insoluble in less polar solvents such as chloroform, while dye **1** is highly soluble in THF, chloroform and even toluene. We attribute this enhanced solubility to the two abietic acid moieties present in the molecule.

We also prepared polymer films in which dye **1** was dissolved, and their vis–NIR spectra are shown in Fig. 1(b). These films were prepared at relatively high dye content (5 wt%) and were obtained by solution casting. Mixtures of the polymer and dye were prepared in a common solvent (THF), and then an aliquot of the solution was spread on a microscope slide and allowed to dry, first at room temperature and then at 45 °C. The films obtained were ca. 10 μm thick. We examined three polymer matrices. One was a commercial ethylene (E)-vinyl acetate (VA) co-polymer (EVA, Elvax 210) with an E/VA weight ratio of 7:3 (curve (i) in Fig. 1(b)). The second was Elvacite 2901 (a co-polymer of methacrylic acid, hydroxyethyl methacrylate, butyl methacrylate, and methyl methacrylate). The third was a rigid polyurethane prepared from ethoxylated bisphenol A and isophorone diisocyanate (IPDI) [9]. The first two polymers are commonly employed in hot-melt adhesives. The NIR spectra of these films are similar to those for **1** in solution, but red-shifted by 5 nm for **1** dissolved in EVA and in Elvacite. There is also broadening of the NIR band. For the dye in the polyurethane matrix, there is a more pronounced red shift of λ_{max} (by 16 nm) and further band broadening. We conclude that at these relatively elevated dye concentrations, dye aggregation occurs, leading to broadening of the absorption spectrum. We note, however, that no macroscopic phase separation can be observed under optical microscopy.

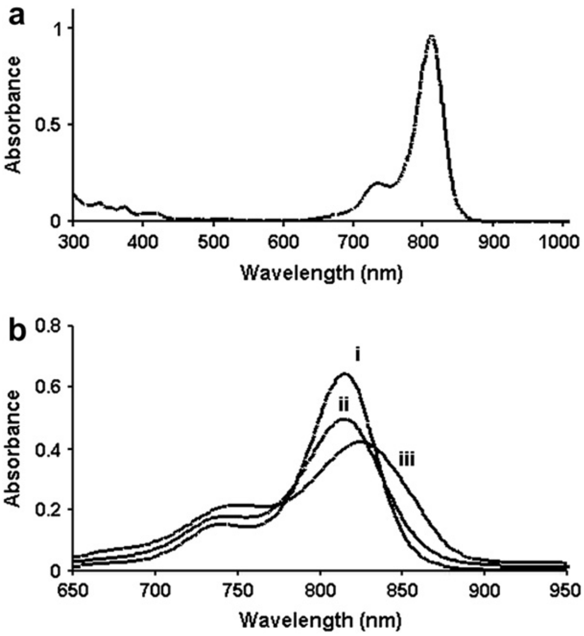
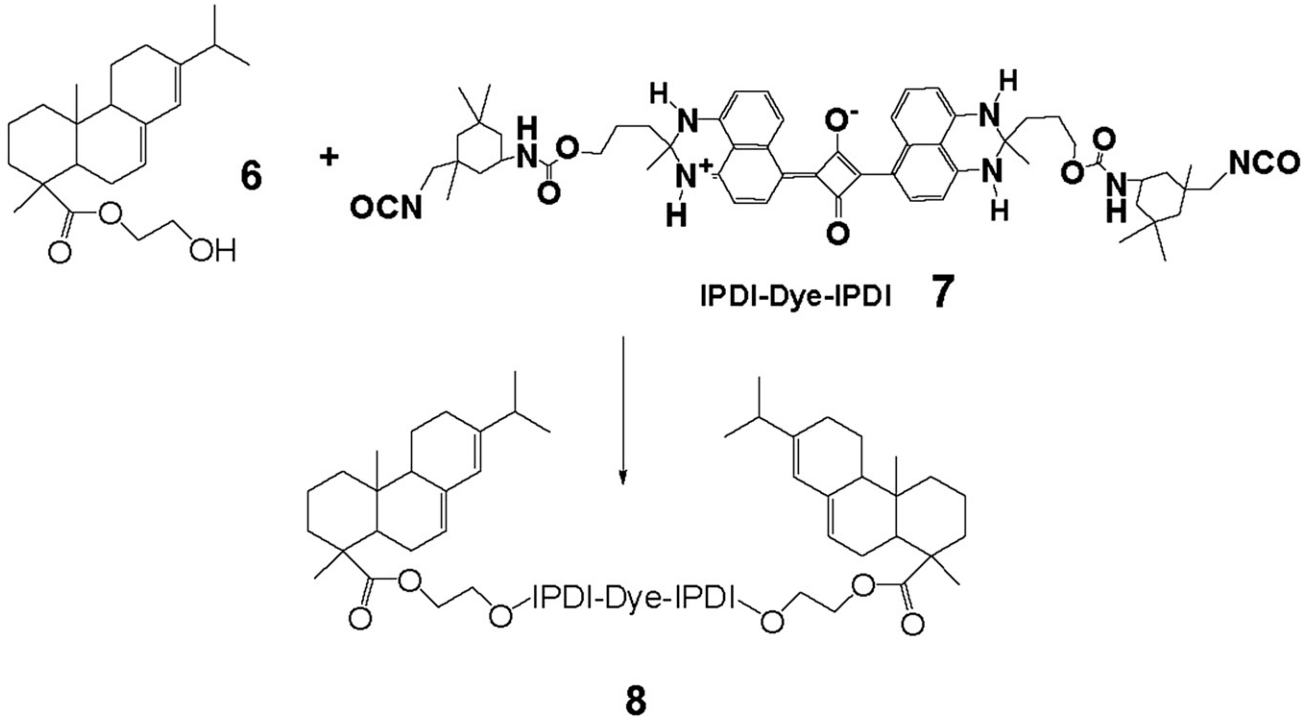


Figure 1. (a) Vis–NIR spectrum of dye **1** in THF. $\lambda_{max} = 810$ nm, $\varepsilon = 1.3 \times 10^5$ M^{-1}cm^{-1}. (b) NIR spectra of dye **1** in different polymer films (i) 5 wt% in EVA (Elvax 210), $\lambda_{max} = 817$ nm; (ii) 5 wt% in Elvacite 2901, $\lambda_{max} = 816$ nm; (iii) 5 wt% in polyurethane (bisphenol A ethoxylate–isophorone diisocyanate), $\lambda_{max} = 824$ nm. All film samples were ca. 10 μm thick.

We also examined a different approach to attach an NIR chromophore to abietic acid by using isocyanate chemistry, and the components of the final product **8** are connected by urethane linkages (Scheme 2). Here we attempted a reaction of diisocyanate **7** with the hydroxyethyl ester of abietic acid (**6**) [10]. Molecule **7** had been prepared independently by us as an intermediate in a separate project. The reaction of compound **7** with 2.5 equivalents of compound **6** in the presence of



Scheme 2.

catalyst was incomplete after 12 h, and gave decomposed products of diisocyanate **7**. Purification was difficult because the desired product does not move on a silica gel chromatography column. As a result, we believe that the synthetic route shown in Scheme 1 is a much better way to introduce a NIR chromophore to abietic acid.

3. Conclusion

We describe a simple method to prepare an NIR-absorbing abietic acid derivative. The most troubling step is the esterification of the highly hindered carboxylic acid function of abietic acid. Nevertheless, the desired product described in this paper can be obtained in good yield. The enhanced solubility of the abietic acid ester derivative makes it a useful candidate as a trigger for NIR sensitive hot-melt adhesive. We are currently trying to synthesize tackifiers absorbing at different wavelengths.

4. Experimental

4.1. Instrumentation

UV–vis–NIR absorption spectra were collected using a Perkin–Elmer Lambda 2500 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a Varian XL400 or XL 300 spectrometer, and the measurements were carried out in $CDCl_3$ or DMSO-d_6. All proton spectra were recorded at either 300 or 400 MHz, and the chemical shifts are referenced to the center of the solvent multiplet, with TMS as an external reference: $CDCl_3$ (7.26 ppm) and DMSO-d_6 (2.50 ppm). All carbon NMR spectra were recorded at 75 or 125 MHz, and the chemical shifts are referenced to the center of the solvent multiplet, with TMS as an external reference: $CDCl_3$ (77.0 ppm) and DMSO-d_6 (39.5 ppm). High-resolution mass spectra were obtained with a VG 70-250S (double focusing) mass spectrometer at 70 eV. Melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected.

4.2. Materials and syntheses

*4.2.1. NIR dye-labeled rosin tackifier (**1**)*

*4.2.1.1. 5-(Methylsulfonyl)oxy-2-pentanone (**2**).* To a round bottom flask was added 30 mL of methylene chloride and 3 g (30.0 mmol) of 5-hydroxy-2-pentanone (Aldrich). To this solution was added 3.1 g (3.1 mmol) triethylamine, and 3.6 g (3.1 mmol) of methanesulfonyl chloride (Aldrich). The resulting mixture was stirred overnight. The precipitate was filtered and washed with methylene chloride. The filtrate was concentrated *in vacuo*. The residue was used without any further purification.

*4.2.1.2. 4-Oxopentyl ester of abietic acid (**3**).* To a solution of abietic acid (9.0 g, 30 mmol, Aldrich) in 100 mL dry THF was added 23 g of Cs_2CO_3 (75 mmol, Aldrich). The brown mixture was stirred at room temperature for 2 h. A solution of compound **2** (30 mmol) in 20 mL THF was added drop wise to this brown solution. The resulting mixture was refluxed for 24 h then allowed to cool to room temperature. The mixture was separated by filtration, and the solid residue was washed with ether. The filtrate (organic phase) was washed twice with water, and dried over sodium sulfate, then concentrated *in vacuo* to afford a brown oil. The crude product was chromatographed on silica gel (0–20% Et_2O/hexanes; column size: height 18–20 cm, diameter 5 cm) to yield 4.2 g of a pale yellow oil (overall yield = 36%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.76 (1H, s), 5.34 (1H, s), 4.01–4.07 (2H, m), 2.58–2.52 (m, 2H), 2.22 (1H, m), 2.15 (3H, s), 2.12–1.48 (15H, m), 1.26–1.21 (8H, m), 1.02–0.96 (5H, m), 0.92–0.82 (5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 207.28, 178.35, 145.31, 135.57, 122.34, 120.43, 63.58, 50.92, 46.57, 45.19, 39.87, 38.30, 37.14, 34.85, 34.51, 31.55, 29.94, 27.42, 25.65, 22.62, 21.37, 20.82, 18.09, 16.98, 14.08; MS (EI) calculated mass for $C_{25}H_{38}O_3 = 386.2821$; found = 386.2819.

*4.2.1.3. Dihydroperimidine **4** [11].* To a 250 mL round bottom flask was charged 1.4 g of 1,8-diaminonaphthalene (9.0 mmol, Aldrich), an equimolar of compound **3** (3.5 g, 9.0 mmol), 15 mg of *p*-toluenesulfonic acid, and 65 mL of toluene. The mixture was refluxed under nitrogen for 3 h, and water was removed azeotropically by a Dean–Stark trap. The reaction mixture was washed with 20 mL of saturated sodium bicarbonate, followed by brine (2×). The organic layer was dried over sodium sulfate and then concentrated *in vacuo*. The residue was chromatographed on silica gel (0–30% ethyl acetate in hexanes) to afford 3.5 g of pink powder (yield = 75%) m.p. 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.12 (4H, m), 6.46–6.42 (2H, m), 5.77 (1H, s), 5.34 (1H, m), 4.40 (2H, b), 4.02 (2H, m), 2.28–1.48 (22 H, m), 1.39–0.80 (14 H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.38, 145.48, 139.80, 135.68, 134.61, 127.08, 122.37, 120.48, 117.04, 105.87, 66.26, 64.08, 50.98, 46.54, 45.10, 38.29, 37.05, 37.01, 34.88, 34.51, 27.45, 27.08, 25.66, 23.49, 22.64, 21.40, 20.83, 18.08, 16.95, 14.02; MS (EI) calculated mass for $C_{35}H_{46}N_2O_2 = 526.3559$; found: 526.3569.

*4.2.1.4. NIR-tackifier **1** [8].* To a 100 mL of round bottom flask was added 3.2 g (6.0 mmol) of dihydroperimidine **4**, 0.35 g (3.0 mmol) of squaric acid (Aldrich), and 120 mL of *n*-butanol/benzene (3:1/v:v). The mixture was heated under reflux for 3 h, and water was removed azeotropically using a Dean–Stark trap. The reaction mixture was concentrated *in vacuo*. The solid residue was collected and washed with ether in a Buchner funnel to afford 3.1 g of green powder (crude yield = 90%). TLC analysis of the crude product showed one main spot with an R_f value of 0.4, and a tiny spot on the baseline (40% ethyl acetate in hexanes). UV–NIR (THF) $\lambda_{max} = 810$ nm, $\varepsilon = 1.20 \times 10^5\ M^{-1}\ cm^{-1}$

A part of the crude sample (0.5 g) was chromatographed on silica gel (40% ethyl acetate in hexanes) to afford 0.37 g purified compound **1**. ^{1}H NMR (400 MHz, $CDCl_3$) 7.95 (1H, m), 7.31–7.27 (1H, m), 6.87 (1H, m), 6.76 (1H, m), 6.41 (1H, m), 5.72 (1H, s), 5.31 (1H, m), 4.12–4.02 (2H, m), 2.28–1.41 (22H, m), 1.39–0.80 (14H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.83, 178.43, 149.87, 145.44, 143.22, 137.36, 135.75, 133.21, 125.19, 122.41, 122.34, 120.54, 117.89, 117.23, 110.80, 109.87, 108.60, 67.82, 63.88, 50.95, 46.54, 45.11, 38.29, 37.57, 37.10, 34.88, 34.53, 27.42, 27.08, 25.66, 23.97, 23.36, 22.47, 21.40, 20.85, 18.11, 16.97, 14.04; MS (MALDI) $M^+ = 1130$; IR (KBr, cm^{-1}) 3349, 2923, 1720, 1618, 1454, 1362, 1125, 817; UV–NIR (THF) $\lambda_{max} = 810$ nm, $\varepsilon = 1.3 \times 10^5\ M^{-1}\ cm^{-1}$ [12].

Acknowledgments

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[12] Based on the differences in δ, the crude product is ~90% pure. The purity of the crude product was acceptable for industrial application, and was sent to our industry partner as is for further testing.