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The use of $BrCCl_3$-PPh_3 in Appel type transformations to esters, *O*-acyloximes, amides, and acid anhydrides

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ABSTRACT

Esters, acyloximes, amides and acid anhydrides have been prepared from the respective carboxylic acids, oximes, amines and alcohols by the use of the reagent combination $BrCCl_3$-PPh_3. The reactions obviate the handling acyl halides or more aggressive reagents PCl_3, $POCl_3$, or $SOCl_2$. Furthermore, the environmentally hazardous CCl_4 used in Appel-type reactions is replaced with $BrCCl_3$, a reagent of less environmental concern.

1. Introduction

In laboratories where the working environment does not allow the preparation and purification of acid halides and the handling of reagents such as PCl_3, PCl_5, $SOCl_2$, or $POCl_3$, a larger number of possible synthetic methodologies of carboxylic acids to the respective anhydrides, amides, and esters are inapplicable. It is in these cases that the use of Appel-type reagents to prepare acyl halides in situ presents itself, where the acyl halides are reacted further with carboxylates, amines, alcohols or oximes.

The versatile combination of triphenylphosphine (PPh_3) and tetrachlorocarbon (CCl_4) is the original Appel reagent, which can be used in a larger number of transformations [1]. Originally utilized in the reaction of alkanols with chloroalkanes [1,2], PPh_3-CCl_4 has been shown to be effective in the reaction of carboxamides [3] and aldoximes [4] with nitriles, in esterification and amidation reactions [5] and in the preparation of dichlorovinyl derivatives from the corresponding aldehydes and ketones [6]. Additionally, phosphoric acid derivatives can be transformed to respective amides and phosphoric anhydrides. However, CCl_4 is known to be an extremely hepatotoxic substance. Also, because of its long life-span in the atmosphere once released (as it does not oxidize or photodegrade in the troposphere), its involvement in the deterioration of the stratospheric ozone layer has been noted [7]. Furthermore, due to the provisions of the Montreal protocol and its subsequent amendments on substances that deplete the ozone layer, CCl_4 has been replaced for many applications. Thus, CCl_4 is used no longer as a solvent for chemical reactions, and scientists have started looking for substitutes. In Appel-type reactions, CBr_4 instead of CCl_4 has been used, but it is expensive. In more recent times, the exchange of CCl_4 for $BrCCl_3$ has been investigated to some degree. The latter reagent is preferred over CCl_4 since it is of less environmental concern, is not listed as an ozone depletor

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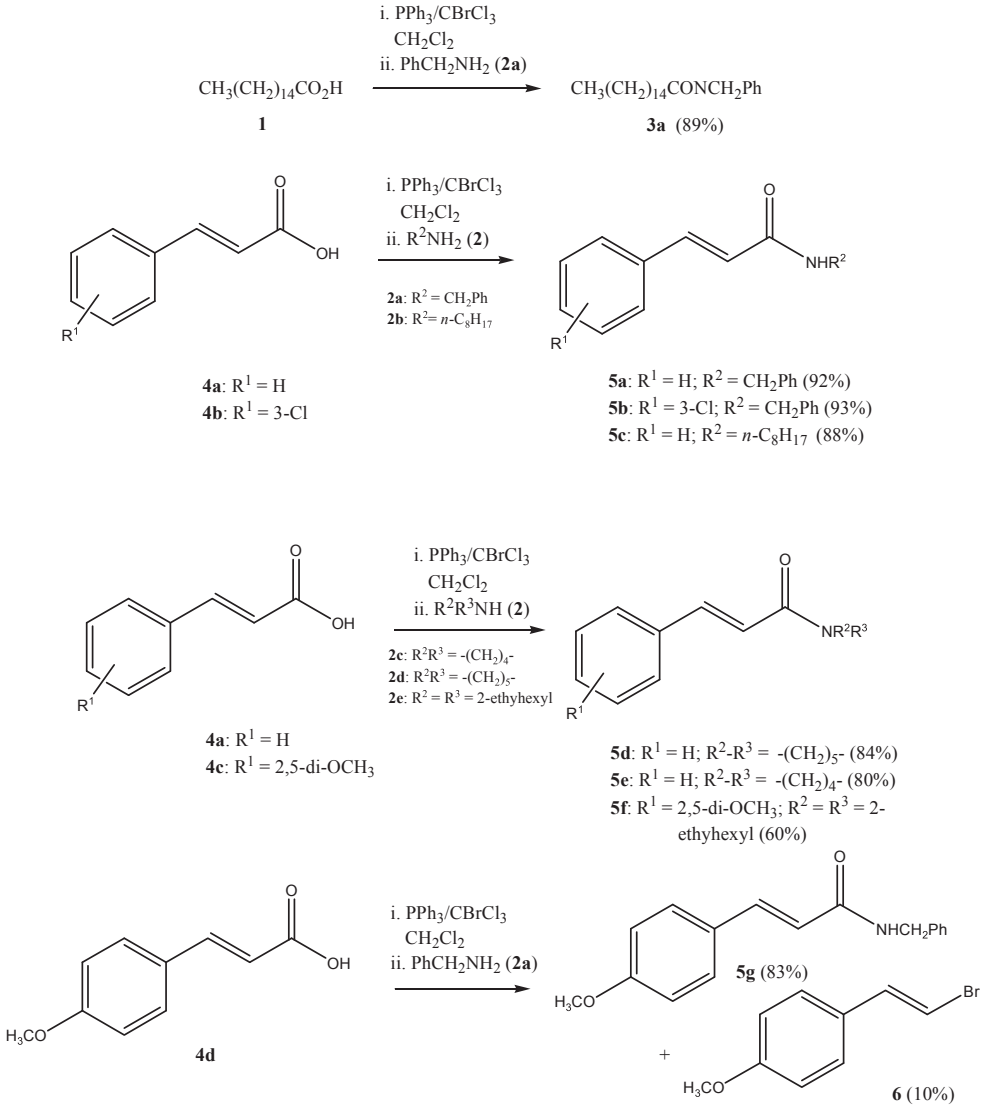
and because its higher polarity does not reach the stratosphere so easily. Therefore, there is less concern about its photolysis in the stratosphere [8]. The employment of PPh_3-$BrCCl_3$ in amidation reactions [9], in the reaction of aldehydes with dihalovinyl compounds [10] and of aldoximes and amides to nitriles [11] has been published already. In this paper, the use of $BrCCl_3$-PPh_3 in Appel type transformations of acids to esters and anhydrides and of keto oximes to acyloximes is discussed.

2. Results and discussion

The authors' initial interest in the use of Appel-type transformations of acids to their derivatives stemmed from the need to prepare cinnamides from alkylamidoalkylquinone derivatives [12]. Although the use of $BrCCl_3$/PPh_3 had been documented in the conversion of carboxylic acids to carboxamides [13], we were gratified to see that the use of $BrCCl_3$/PPh_3 in the reaction of cinnamic acids led exclusively to the corresponding cinnamides and not to 1,4-addition adducts as side products (Scheme 1). Only in some cases of the reaction of alkoxycinnamic acids under these conditions can a small amount of the corresponding (*E*)-1-bromo-2-(4-alkoxyphenyl)ethene be isolated as a side-product, regardless of the added nucleophile. A typical example is given in the transformation of **4d** to **5g**, where a small amount of (*E*)-1-bromo-2-(4-methoxyphenyl)ethene (**6**) is produced, (Scheme 1).

Next, we investigated whether the reagent combination $BrCCl_3$/PPh_3 could be used in the reaction of carboxylic acids with acid anhydrides. When benzoic acid was treated with $BrCCl_3$/PPh_3 in refluxing CH_2Cl_2, it was realized that acyl halides were formed, where from this reaction benzoyl chloride could be isolated in pure form after flash chromatography. Having established the formation of acyl



Scheme 1. Amidation of cinnamic acids with PPh_3-$CBrCl_3$ as a reagent.

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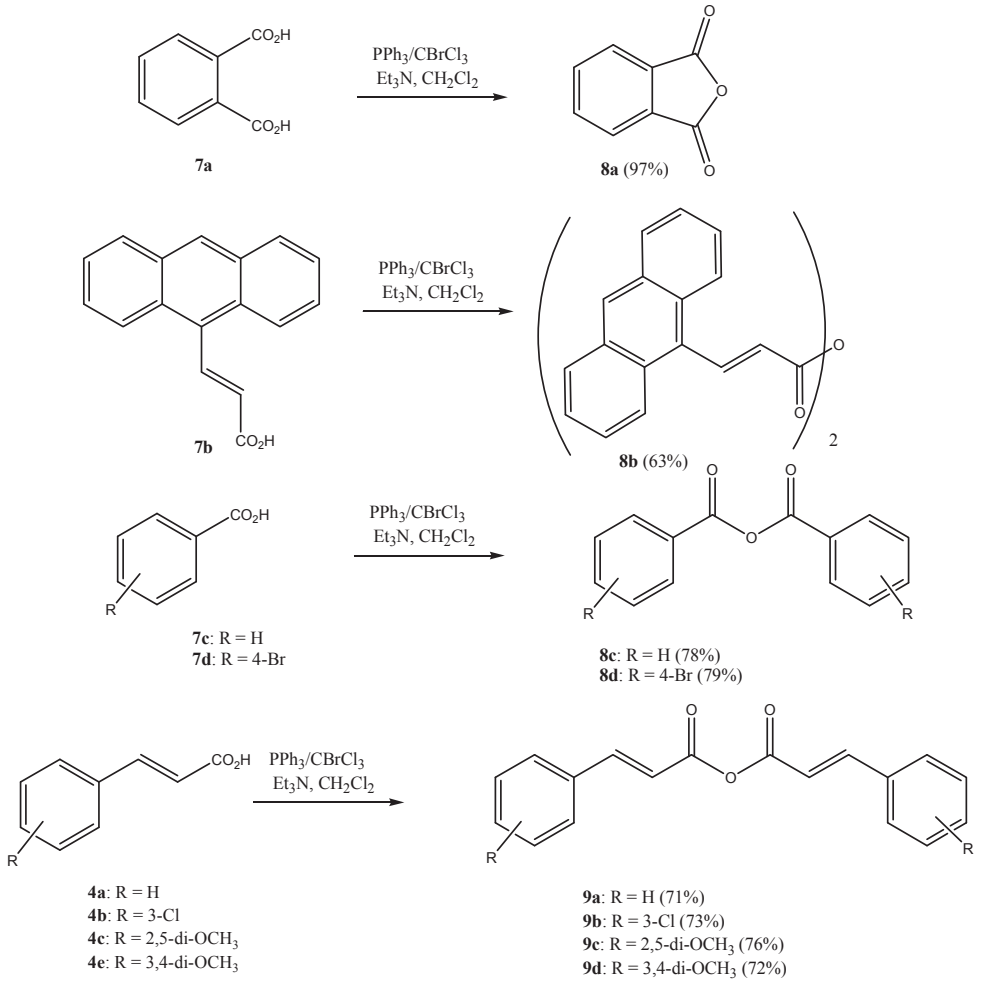
halides in this transformation, the reaction of the acyl halides in situ with carboxylates as nucleophiles was warranted. Previously, carboxylic acid anhydrides have been prepared from the respective carboxylic acids by using reagents that are both activating and dehydrating such as phosphorus pentoxide [12], carbodiimides [13], isocyanates [14], imidazolinium chlorides [15], phosgene [16] trichlorotrifluoroacetone [17] and triphosgene [18]. Also, carboxylic acids can be transformed into an activated acyl species first, which subsequently is further reacted with an equivalent of the carboxylic acid or the carboxylate to furnish the acid anhydride. Examples of this are the activation with 2,4-dichloro-1,3,5-triazine [19] or the $ZnCl_2$-catalysed reaction of 2-acyl-4,5-dichloropyridazin-3(2*H*)-ones [20]. Most frequently, however, acid chlorides are used to prepare acid anhydrides. In these cases the acid chlorides can be prepared separately, isolated, and subsequently reacted with the carboxylic acid or its anion under various conditions [21].

We found that the reaction of carboxylic acids with $BrCCl_3/PPh_3$ in refluxing CH_2Cl_2 and the subsequent addition of a further equivalent of carboxylic acid, followed by an equivalent of either dry triethylamine or 1,8-diazabicycloundec-7-ene (DBU), leads to the corresponding acid anhydrides in good yield (Scheme 2). The products were obtained from the reaction mixtures by rapid column chromatography.

From the above results, it was deemed likely that carboxylic esters should also be accessible through the same strategy, by changing the nucleophile to an alcohol, adding the alcohol after the activation of the acid and/or its in situ transformation to the acyl halide. This indeed proved to be the case as is seen from Scheme 3. The authors preferred venting the hydrogen halide produced as a side product, by submitting the reaction vessel intermittently to vacuum rather than adding a tertiary amine base to the reaction solution. The alkyl carboxylates were produced in acceptable yield and the process can be seen as a viable alternative to other known esterification methods, when used at the laboratory scale.

Finally, the authors investigated whether this general strategy of using $BrCCl_3/PPh_3$ in the activation of carboxylic acids would give access to acyl oximes as well. Recently, acyl oxime derivatives have attracted considerable



Scheme 2. Preparation of anhydrides with PPh_3-$CBrCl_3$ as a reagent.

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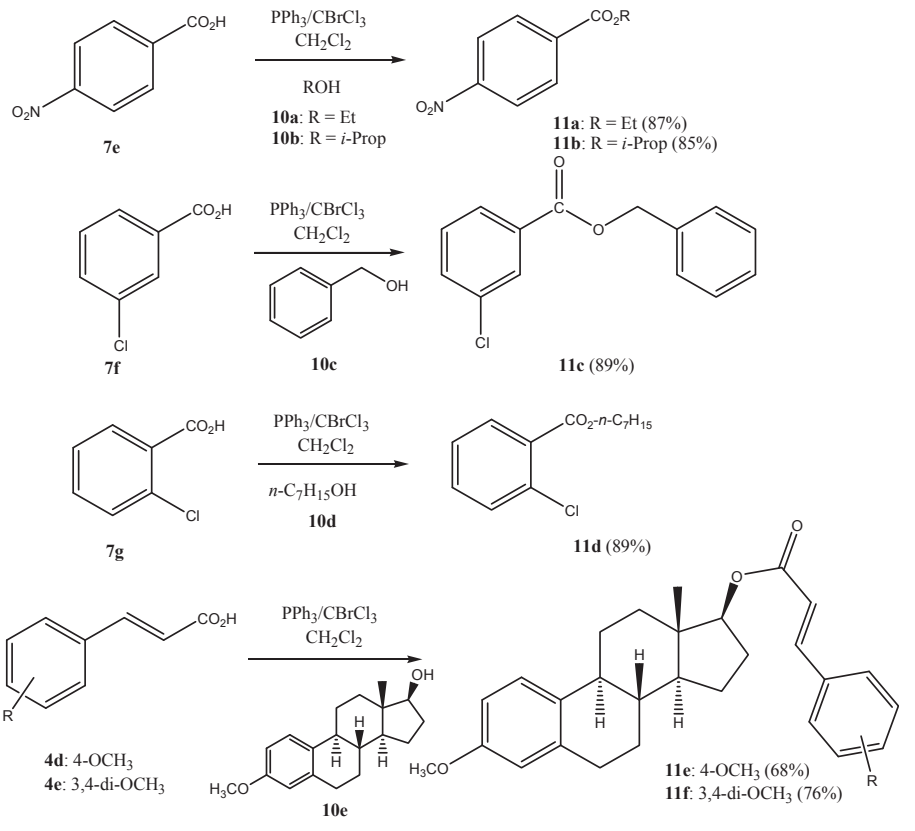
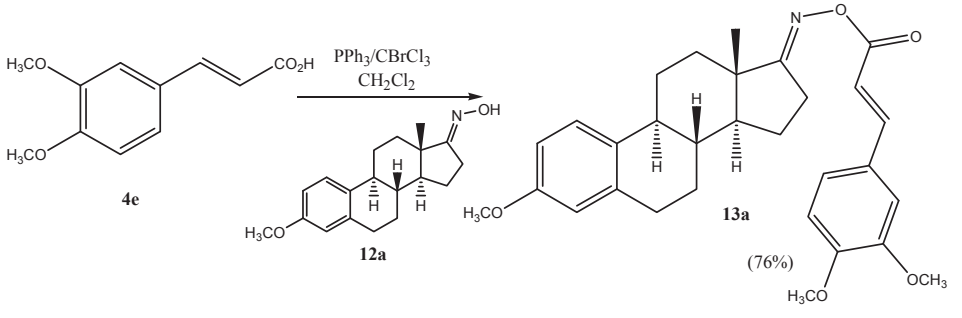


Scheme 3. Esterification using $PPh_3/BrCCl_3$.

attention in medicinal research due to their antiphytoviral, antitumor, antibacterial, and fungicidal bioactivities. A larger number of studies on their synthesis and biological activities have been reported [22]. Some acyl oximes have been found to cleave DNA in a process that is triggered by UV light [23]. The weak N—O bond of the acyl oximes is cleaved selectively to generate the iminyl and carboxy radicals which can then cause the cleavage of the DNA. In our research on cancer-active estrone based molecules, we were interested to prepare *O*-cinnamoyl estrone-17-oximes such as **13a**. Within this context, we succeeded to react estrone-17-oxime **12a** with the substituted cinnamic acid **4e** in the presence of $BrCCl_3/PPh_3$ (Scheme 4). This methodology was found to be quite general to react oximes and acids with *O*-acyl oximes (Scheme 5).

Finally, in order to assess the typical molecular structural parameters of aromatic *O*-acyl oximes, the crystal structure of 2,5-dimethoxyacetophenone oxime 4-nitrobenzoate **13g** was studied. The crystallization was carried out in a mixture of CH_2Cl_2/diethyl ether/hexane (1/1/1−*v*/*v*/*v*) at room temperature, where **13g** was isolated as clear light yellow plates. **13g** was crystallized in the monoclinic space group $P2_1/C$ with unit cell parameters: a = 17.1206 (6), b = 8.17107 (19), c = 11.6431 (3) Å, β = 102.779 (3)° (Table 1). Selected bond distances and angles are listed in Table 2. The molecular structure of 2,5-



Scheme 4. Preparation of a *N*-cinnamoylestrone-17-oxime.

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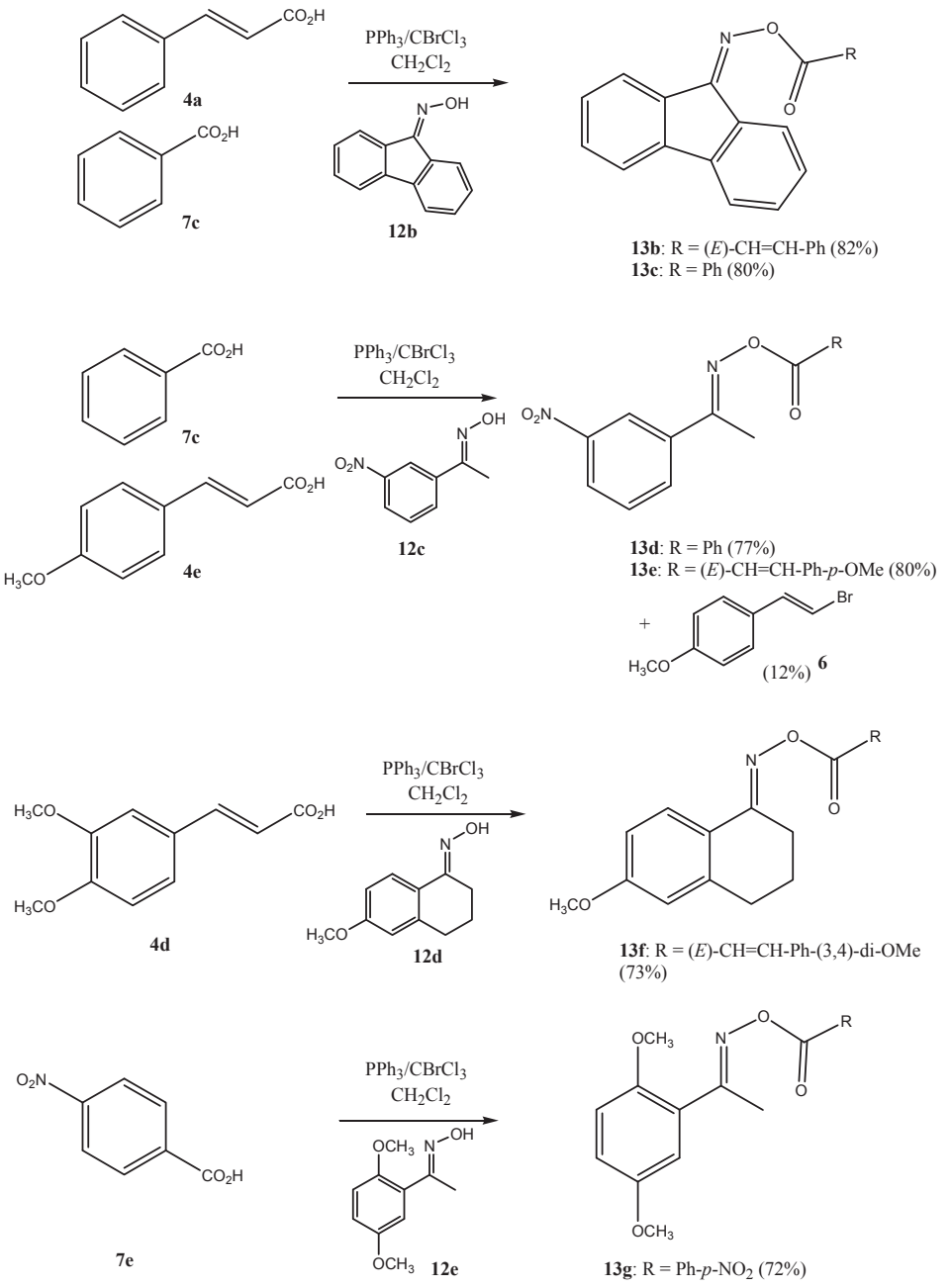

Scheme 5. *O*-acylation of oximes with $PPh_3/BrCCl_3$ as the reagent.

dimethoxyacetophenone oxime 4-nitrobenzoate (**13g**) is shown in Fig. 1. In the oxime ester moiety, the bond-lengths of C15═N1 and C17═O4 are 1.288 (2) Å and 1.1977 (19) Å, respectively, which is characteristic of double-bonds. The values of the C17−O3 and N1−O3 bonds are 1.3538 (19) Å and 1.4520 (16) Å, respectively, indicating a single-bond-character. These bond-lengths are in the expected range of oxime-esters [24].

The bond angles of C15−N1−O3 = 108.16 (12) °, C17−O3−N1 = 112.40 (11) ° are typical for linear oxime-esters [24].

The nitro-group is slightly tilted with respect to the aromatic ring C7−C12 (torsion-angle: C11−C10−N2−O5 = 4.5 (2) °). The methoxy-groups on the aromatic ring (C1−C6) show a significant difference in torsion angles (C4−C5−O1−C13 = 175.2 (1) °) and C1−C2−O2−C14 of 155.5(2) °). This can be explained with packing-effects. The average two planes of the aromatic rings (non-hydrogen atoms) form an angle of 26.17 (2) ° between each other. This is mainly due to torsions in the bonds O3−N1 and C15−C1 and a further indication of a localized double-bond between C15 and N1 in contrast to an extended π-system.

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Table 1
Crystallographic data and structure refinement details.

CCDC deposit number	1001765
Chemical formula	$C_{17}H_{16}N_2O_6$
Formula weight	344.32
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.75 0.33 0.10
Crystal system	Monoclinic
Space group	$P2_{1/C}$
a (Å)	17.1206 (6)
b (Å)	8.17107 (19)
c (Å)	11.6431 (3)
β (°)	102.779 (3)
V (Å^3)	1588.45 (8)
Z	4
D_c (g/cm^3)	1.440
F (000)	720
Absorption coeff. (mm^{-1})	0.111
θ range (°)	3.1–27.5
Index ranges	$-19 \le h \le 21$; $-6 \le k \le 10$; $-15 \le l \le 14$
Reflections collected	7139
Independent reflections	3515 [$R_{int} = 0.026$]
Observed reflections	2726
Data/restraints/parameters	3515/0/229
Goodness-of-fit on F^2	1.059
R, wR indices [$I > 2\sigma(°)$]	0.0444, 0.0971
R, wR indices (all data)	0.0624, 0.1091
Largest diff. peak and hole (e Å^{-3})	0.28, −0.28

Table 2
Selected bond lengths (Å) and angles (°).

Bond lengths			
C(2)–O(2)	1.3714 (19)	C(17)–O(3)	1.3538 (19)
C(5)–O(1)	1.3747 (19)	C(17)–O(4)	1.1977 (19)
C(10)–N(2)	1.477 (2)	O(3)–N(1)	1.4520 (16)
C(13–(1)	1.428 (2)	O(5)–N(2)	1.2298 (18)
C(14)–O(2)	1.4348 (19)	O(6)–N(2)	1.2253 (17)
C(15)–N(1)	1.288 (2)		
Bond angles			
C(5)–O(1)–C(13)	117.20 (13)	O(5)–N(2)–O(6)	123.79 (14)
C(2)–O(2)–C(14)	117.03 (13)	N(1)–C(15)–C(1)	113.67 (13)
C(15)–N(1)–O(3)	108.16 (12)	O(3)–C(17)–O(4)	125.03 (15)
C(17)–O(3)–N(1)	112.40 (11)		

The molecules of **13g** are arranged in two stacks, propagating along the *b*-axis. Molecules in each stack are related by *C*-glide operation and are linked to each other through C14–H14A…O5 hydrogen bonding (Fig. 2). Along the *c*-axis, neighbored stacks are linked by C8–H8…O4, C16–H16C…O4 and C16–H16B…O6 hydrogen bonds (Table 3).

Symmetry codes of molecules showing the labeled interactions are shown in Fig. 2: i: $-x, -1/2+y, 1/2-z$; ii: $-x, 1-y, -z$; iii: $x, 1.5-y, -1/2+z$; iv: $1-x, 1/2+y, 1/2-z$; v: $1-x, 1-y, 1-z$.

3. Conclusion

In a modified Appel-type reaction, cinnamic and benzoic acids have been reacted with amines, alcohols, and oximes, using the relatively environmentally friendly reagent combination PPh_3-$BrCCl_3$. It was also shown that anhydrides are obtained, when the acids upon activation with PPh_3-$BrCCl_3$ are reacted with a further equivalent of acid in the presence of a tertiary amine. An X-ray crystal structural analysis of acyloxime **13g** was carried out. It is envisaged that Appel-type reactions as the ones shown here will gain further importance with the advancement of strategies towards the recycling of the by-product triphenylphosphine oxide to triphenylphosphine [25].

4. Experimental

4.1. General

Melting points were measured on a Stuart SMP 10 melting point apparatus and are uncorrected. Infrared spectra were measured with a Thermo/Nicolet Nexus 470 FTIR ESP Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian 400 NMR (^{1}H at 395.7 MHz, ^{13}C at 100.5 MHz) and a Varian 200 MHz NMR spectrometer (^{1}H at 200.0 MHz, ^{13}C at 50.3 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer. CHN-analysis was performed on a LECO TruSpec Micro instrument. Column chromatography was carried out on a silica gel (60 A, 230–400 mesh, Sigma-Aldrich). Analytical thin layer chromatography (TLC) was carried out on silica on TLC Alu foils from Fluka (with fluorescent indicator at $\lambda = 254$ nm). Triethylamine was dried over solid KOH and distilled. 1,8-Diazabicycloundec-7-ene (DBU) was stored over solid KOH. The oximes **12** were prepared by the reaction of the ketones with ammonium hydrochloride (4 mol eq.) in a solvent mixture of ethanol and water [26]. 3-Arylacrylic acids **4b–e** and **7b** were prepared by a one-pot Wittig olefination − hydrolysis reaction of the respective benzaldehydes and 9-anthranylcarbaldehyde with ethoxycarbonylmethylidenetriphenylphosphorane [27].

4.2. General procedure for the preparation of cinnamides

4.2.1. N,N-*Bis(2-ethylhexyl) 3-(1,4-dimethoxyphen-2-yl) propenoic acid amide (**5f**)*

To a solution of PPh_3 (980 mg, 3.74 mmol) in dry CH_2Cl_2 (12 mL) $BrCCl_3$ (1.50 g, 7.66 mmol) was added. The resulting mixture was stirred at rt for 30 min, during which it turned reddish-brown. Thereafter, 2,5-dimethoxycinnamic acid (**4c**, 700 mg, 3.37 mmol) was added, and the mixture was heated under reflux for 45 min. Thereafter, di(2-ethylhexyl) amine (1.62 g, 6.71 mmol) was added dropwise via a syringe, where the ensuing reaction is exothermic. The reaction mixture was stirred at reflux for 14 h. Then, the cooled mixture was concentrated *in vacuo*, and the residue was subjected directly to column chromatography on a silica gel to give **5f** (875 mg, 2.03 mmol, 60%) as a colorless oil; ν_{max} neat/cm^{-1}) 2961, 2877, 1660, 1622, 1506, 1489, 1047, 772; δ_H (400 MHz, $CDCl_3$) 1.00 (16H, m), 1.48 (20H, m), 1.69–1.79 (2H, m), 3.28–3.43 (4H, m), 3.77 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.82 (1H, d, $^3J = 8.8$ Hz), 6.84 (1H, d, $^3J = 8.8$ Hz), 7.00 (1H, s), 7.02 (1H, d, $^3J = 15.6$ Hz), 7.86 (1H, d, $^3J = 15.6$ Hz); δ_C (67.8 MHz, $CDCl_3$, DEPT) 10.7 (CH_3), 10.8 (CH_3), 14.0 (CH_3), 14.1 (CH_3), 23.1 (CH_2, 2C), 23.7 (CH_2), 24.0 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 37.6

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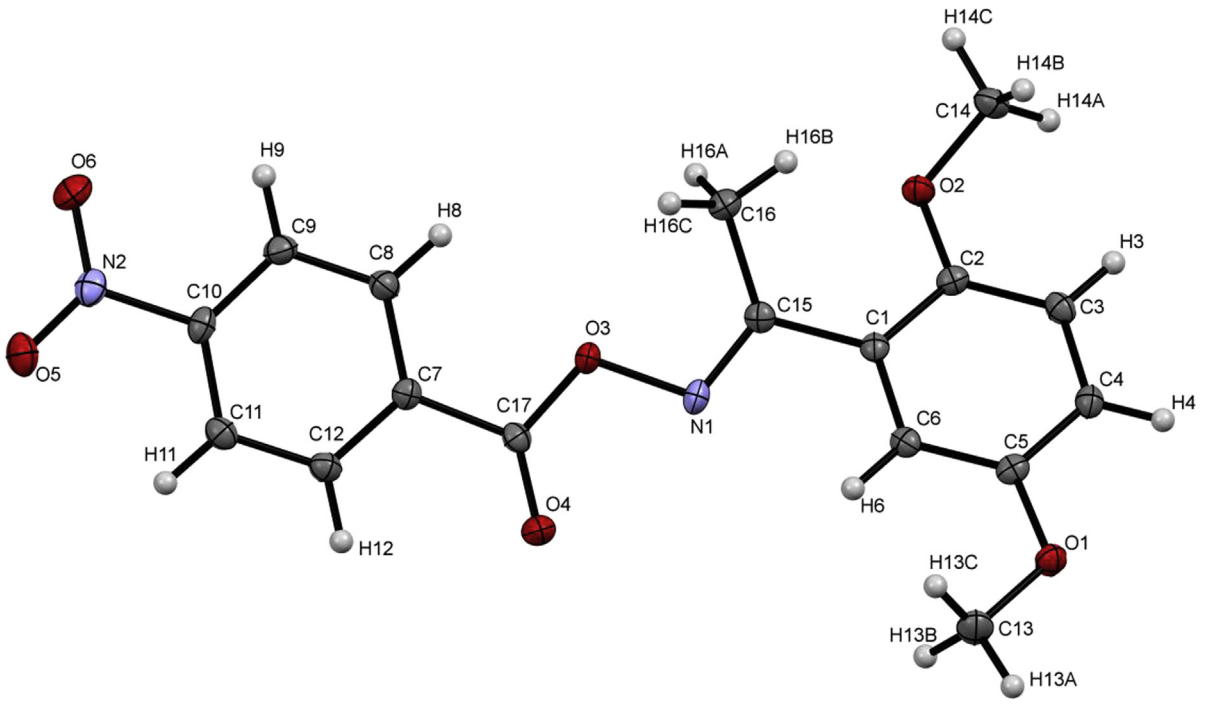

Fig. 1. Molecular structure of 2,5-dimethoxyacetophenone oxime 4-nitrobenzoate (**13g**) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

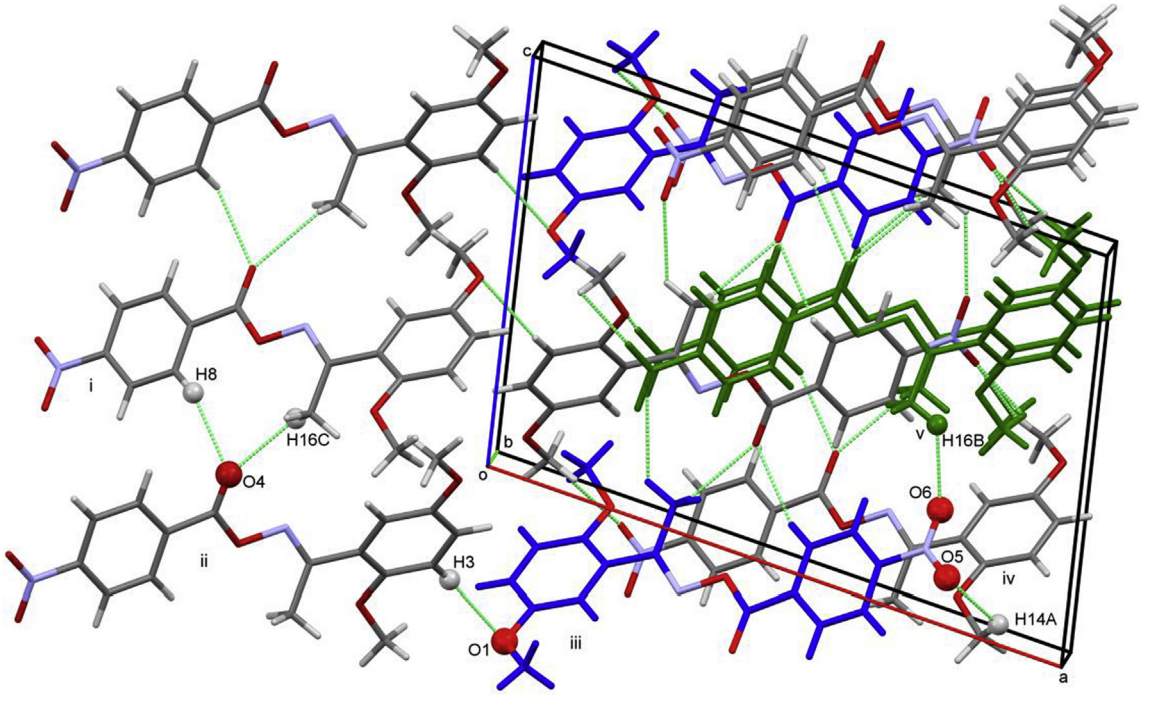

Fig. 2. A view of intermolecular interactions between adjacent molecules **13g** that lead to the 3D network (colored molecules have the same orientation and layout).

(CH), 40.0 (CH), 50.7 (CH_2), 52.0 (CH_2), 55.7 (OCH_3), 56.0 (CH_3), 112.3 (CH), 114.4 (CH), 115.4 (CH), 119.6 (CH), 125.2 (C_{quat}), 137.5 (CH), 152.8 (C_{quat}), 153.4 (C_{quat}), 167.3 (C_{quat}, CO).

4.2.2. N-*Benzylpalmitamide* (***3a***)

As colorless needles, mp 98 °C (Lit. mp 95 °C [28]); IR (KBr) ν_{max}: 3305 (NH), 2918, 2848, 1639, 1549, 1457, 733, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.81 (t, $^3J = 6.8$ Hz,

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Table 3
Hydrogen bonds for **13g** (Å and °).

D–H…*A*	*D*–H	H…*A*	*D*…A	*D*–H…*A*
C3–H3…O1$^{\#1}$	0.950	2.496 (1)	3.375 (2)	153.9 (1)
C8–H8…O4$^{\#2}$	0.950	2.516 (1)	3.317 (2)	142.1 (1)
C14–H14A…O5$^{\#1}$	0.980	2.599 (1)	3.141 (2)	115.0 (1)
C16–H16B…O6$^{\#1}$	0.980	2.601 (1)	3.330 (2)	131.3 (1)
C16–H16C…O4$^{\#2}$	0.980	2.501 (1)	3.177 (2)	125.9 (1)

Symmetry codes: #1: x, 1.5 − y, −1/2 + z; #2: −x, 1 − y, −z.

3H, CH_3), 1.16–1.26 (m, 14H), 1.57 (m, 2H), 2.14 (t, ^3J = 7.6 Hz, 2H), 4.37 (d, ^3J = 8.0 Hz, 2H), 5.64 (b, NH, 1H), 7.19–7.29 (m, 5H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 14.1, 22.7, 25.8, 29.3, 29.4, 29.5, 31.9, 36.8, 43.6, 127.5, 127.8 (2C), 128.7 (2C), 138.4, 173.0 (CO); MS (EI, 70 eV) *m*/*e* (%) = 345 (M^+), 149 (100).

4.2.3. N-*Benzyl cinnamide* (***5a***)

Colorless needles, mp 107 °C (Lit. mp 106–108 °C [29]); IR (KBr) ν_{max}: 3280 (br s, NH), 3080, 2921, 1654, 1614, 1541, 1450, 1348, 1230, 1213, 979, 751, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.56 (d, ^3J = 5.6 Hz, 2H), 6.06 (br s, NH, 1H), 6.42 (d, ^3J = 16.0 Hz, 1H), 7.25–7.30 (m, 3H), 7.47–7.48 (m, 2H), 7.66 (d, ^3J = 16.0 Hz, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 43.8 (−), 120.4 (CH), 127.6 (CH), 127.8 (2C, CH), 127.9 (2C, CH), 128.7 (2C, CH), 128.8 (2C, CH), 129.7 (CH), 134.7 (C_{quat}), 138.1 (C_{quat}), 141.4 (CH), 165.8 (C_{quat}, CO); MS (EI, 70 eV) *m*/*e* (%) = 237 (M^+).

4.2.4. N-*Benzyl 3-chlorocinnamide* (***5b***)

Colorless needles; mp 112 °C [Lit. mp 108–109 °C [30]); ν_{max} (KBr/cm^{-1}) 3295, 3058, 2927, 1652, 1616, 1538, 1424, 1331, 1228, 1079, 1035, 969, 858, 787, 696, 664; δ_H (400 MHz, $CDCl_3$) 4.57 (2H, d, ^3J = 5.6 Hz), 5.97 (1H, b, NH), 6.40 (1H, d, ^3J = 15.6 Hz), 7.27–7.37 (8H, m), 7.48 (1H, s), 7.61 (1H, d, ^3J = 15.6 Hz); δ_C (100.5 MHz, $CDCl_3$) 43.9, 121.7, 126.2, 127.4, 127.7, 127.9, 128.8, 129.6, 130.1, 134.8, 136.6, 137.9, 140.0, 165.2 (CO).

4.2.5. N-*Octyl cinnamide* (***5c***) [31]

Colorless solid; IR (KBr) ν_{max}: 3285, 3063, 2954, 2926, 2853, 1668, 1653, 1548, 1476, 1460, 1333, 1224, 993, 869, 768, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.86 (t, ^3J = 6.8 Hz, 3H), 1.26–1.30 (m, 10H), 1.54 (m, 2H), 3.36 (dt, ^3J = 6.0 Hz, ^3J = 6.0 Hz, 2H), 6.38 (d, ^3J = 15.6 Hz, 1H), 7.33–7.35 (m, 3H), 7.47–7.49 (m, 2H), 7.61 (d, ^3J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 14.1 (CH_3), 22.6 (−), 27.0 (−), 29.2 (−), 29.3 (−), 29.7 (−), 31.8 (−), 39.8 (−), 120.7 (CH), 127.7 (2C, CH), 128.8 (2C, CH), 129.6 (CH), 134.8 (C_{quat}), 140.8 (CH), 165.9 (C_{quat}, CO); MS (EI, 70 eV) *m*/*e* (%) = 233 (M^+).

4.2.6. N-*Piperidinyl cinnamide* (***5d***)

Colorless solid; mp 123 °C (mp 122 °C [32]); ν_{max} (KBr/cm^{-1}) 3078, 3027, 2933, 2849, 1645, 1588, 1458, 1442, 1281, 1249, 1223, 1018, 992, 764; δ_H (400 MHz, $CDCl_3$) 1.57–1.70 (6H, m), 3.61 (4H, br s), 6.89 (2H, d, ^3J = 15.2 Hz), 7.30–7.50 (3H, m), 7.48–7.52 (2H, m), 7.62 (2H, d, ^3J = 15.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 24.6 (CH_2), 25.8 (br s, CH_2), 26.6 (br s, CH_2), 43.3 (br s, CH_2), 47.1 (br s, CH_2), 117.7 (CH), 127.7 (2C, CH), 128.7 (2C, CH), 129.4 (CH), 135.5 (C_{quat}), 142.1 (CH), 165.3 (C_{quat}, CO).

4.2.7. N-*Pyrrolidinyl cinnamide* (***5e***)

Pale yellow solid; mp 99 °C (mp 93–94 °C [33]); ν_{max} (KBr/cm^{-1}) 3060, 2968, 2873, 1652, 1600, 1452, 1433, 986, 865, 761, 706, 681, 568, 547, 487; δ_H (400 MHz, $CDCl_3$) 1.84–2.01 (4H, m), 3.56–3.63 (4H, m), 6.71 (1H, d, ^3J = 15.6 Hz), 7.30–7.37 (3H, m), 7.50–7.53 (2H, m), 7.68 (1H, d, ^3J = 15.6 Hz); δ_C (100.5 MHz, $CDCl_3$) 24.3 (CH_2), 26.1 (CH_2), 46.1 (CH_2), 46.6 (CH_2), 118.8 (CH), 127.8 (2C, CH), 128.7 (2C, CH), 129.5 (CH), 135.3 (C_{quat}), 141.7 (CH), 164.7 (C_{quat}, CO).

4.2.8. N-*Benzyl 4-methoxycinnamide* (***5g***) [34]

Colorless needles; mp 145–146 °C; ν_{max} (KBr/cm^{-1}) 3282 (s, NH), 3030, 2929, 2834, 1644, 1605, 1528, 1252, 1217, 1174, 1028, 972, 825, 752, 699; δ_H (400 MHz, $CDCl_3$) 3.81 (3H, s, OCH_3), 4.54 (2H, d, ^3J = 5.6 Hz), 6.11 (1H, m), 6.86 (2H, d, ^3J = 8.4 Hz), 7.26–7.34 (5H, m), 7.42 (2H, d, ^3J = 8.5 Hz), 7.62 (1H, d, ^3J = 15.6 Hz); δ_C (100.5 MHz, $CDCl_3$) 43.8, 55.3 (OCH_3), 114.2 (2C), 118.0, 127.4, 127.5, 127.9 (2C), 128.7 (2C), 129.4 (2C), 138.2, 141.0, 160.9, 166.2 (CO).

4.3. General procedure for the preparation of carboxylic acid anhydrides

4.3.1. Cinnamic anhydride (***9a***)

To a solution of triphenylphosphine (910 mg, 3.47 mmol) in dry dichloromethane (10 mL) bromotrichloromethane (710 mg, 3.58 mmol) was added, and the resulting mixture was stirred at a rate for 30 min to give a reddish-brownish solution. Thereafter, cinnamic acid (**4a**, 451 mg, 3.05 mmol) was added, and the resulting mixture was held at reflux for 5 h. Thereafter, cinnamic acid (451 mg, 3.05 mmol) and subsequently triethylamine (310 mg, 3.05 mmol) were added, and the reaction mixture was held at reflux for 8 h. Then, the cooled solution was concentrated *in vacuo*, and the concentrate was subjected to rapid column chromatography on a silica gel [CH_2Cl_2-hexane 2:1] to give cinnamic anhydride (**9a**, 605 mg, 71%) as colorless crystals; mp 139–140 °C (mp 138 °C [35]); IR (KBr) ν_{max}: 3060, 3027, 1767, 1701, 1632, 1450, 1305, 1270, 1228, 1201, 1074, 960, 858, 761, 690, 676, 551 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.53 (d, ^3J = 16.0 Hz, 2H), 7.43–7.45 (m, 6H), 7.57–7.59 (m, 4H), 7.86 (d, ^3J = 16.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 116.7 (2C, CH), 128.6 (4C, CH), 129.1 (4C, CH), 131.3 (2C, CH), 133.7 (2C, C_{quat}), 148.7 (2C, CH), 162.5 (2C, C_{quat}, CO).

4.3.2. Phthalic anhydride (***8a***)

Colorless solid; mp 130 °C (Lit. 130–131 °C [36]); IR (KBr) ν_{max}: 1851, 1762, 1598, 1469, 1258, 1108, 907, 713, 533 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90–7.92 (m, 2H), 8.02–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) 125.7 (2C, CH), 131.3 (2C, C_{quat}), 136.0 (2C, CH), 162.8 (C_{quat}, CO); MS (EI, 70 eV) *m*/*e* (%) = 148 (M^+, 20), 104 (100).

4.3.3. Anthranyl-9-acrylic anhydride (***8b***)

As an orange solid; mp 216–218 °C (Lit. 216–218 °C [37]); IR (KBr) ν_{max}: 3052, 1760, 1706, 1123, 935, 913, 744,

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702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.63 (d, $^3J = 16.0$ Hz, 2H), 7.50–7.59 (m, 8H), 8.04 (dm, $^3J = 8.0$ Hz, 4H), 8.29 (dm, $^3J = 7.6$ Hz, 4H), 8.51 (s, 2H), 8.93 (d, $^3J = 16.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 124.9 (4C, CH), 125.4 (4C, C_{quat}), 125.5 (4C, CH), 126.9 (4C, CH), 128.1 (2C, C_{quat}), 129.0 (4C, CH), 129.3 (2C, CH), 129.5 (4C, C_{quat}), 131.2 (2C, CH), 146.4 (2C, CH), 162.0 (2C, C_{quat}, CO). Anal. Calcd for $C_{34}H_{22}O_3$ (478.54): C, 85.34%; H, 4.63%. Found: C, 85.25%; H, 4.73%.

4.3.4. Benzoic anhydride (**8c**)

Slowly crystallizing, colorless solid; mp 41 °C (Lit. 42 °C [21a]); IR (neat) ν_{max}: 3065, 3010, 1786, 1724, 1599, 1491, 1452, 1315, 1213, 1173, 1040, 1018, 995, 873, 778, 701, 615 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.50–7.54 (m, 4H), 7.65–7.69 (m, 2H), 8.14–8.17 (m, 4H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) 128.8 (2C), 128.9 (4C), 130.6 (4C), 134.6 (2C), 162.4 (2C, C_{quat}, CO); MS (EI, 70 eV) *m/e* (%) = 226 (M^+, 5), 105 (100).

4.3.5. 4-Bromobenzoic anhydride (**8d**)

Colorless solid; mp 221–224 °C [Lit. mp 217–218 °C [38a], 225 °C [38b]; IR (KBr) ν_{max}: 1786, 1721, 1586, 1480, 1396, 1226, 1173, 1067, 1004, 824, 826, 793, 738, 676, 625 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 7.68 (d, $^3J = 8.8$ Hz, 2H), 8.00 (d, $^3J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) 127.5 (2C, C_{quat}), 130.2 (2C, C_{quat}), 131.9 (4C, CH), 132.4 (4C, CH), 161.4 (2C, C_{quat}, CO); MS (EI, 70 eV) *m/e* (%) = 340 (M^+), 338 (M^+), 185, 183.

4.3.6. 3-Chlorocinnamic anhydride (**9b**)

Silvery shiny needles, mp 117–118 °C; IR (KBr) ν_{max}: 3079, 1758, 1709, 1629, 1134, 940, 784, 665 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 6.52 (d, $^3J = 16.0$ Hz, 2H), 7.35–7.46 (m, 6H), 7.57 (s, 2H), 7.78 (d, $^3J = 16.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 118.0 (2C, CH), 126.8 (2C, CH), 128.2 (2C, CH), 130.4 (2C, CH), 131.2 (2C, CH), 135.2 (2C, C_{quat}), 135.4 (2C, C_{quat}), 147.1 (2C, CH), 161.9 (2C, C_{quat}, CO). Anal. Calcd for $C_{18}H_{12}Cl_2O_3$ (347.19) C, 62.27%; H, 3.48%. Found: C, 62.43%; H, 3.57%.

4.3.7. Bis(2,5-dimethoxycinnamic) anhydride (**9c**)

Pale yellow solid; mp 103–105 °C; IR (KBr) ν_{max}: 3078, 3008, 2947, 2912, 1837, 1714, 1704, 1625, 1579, 1498, 1458, 1428, 1322, 1290, 1255, 1206, 1086, 1049, 1018, 985, 947, 866, 805, 719, 669 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.80 (s, 6H, 2 OCH_3), 3.86 (s, 6H, 2 OCH_3), 6.60 (d, $^3J = 16.0$ Hz, 2H), 6.87 (d, $^3J = 8.8$ Hz, 2H), 6.96 (dd, $^3J = 8.8$ Hz, $^4J = 2.8$ Hz, 2H), 7.06 (d, $^4J = 2.8$ Hz, 2H), 8.12 (d, $^3J = 16.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) 55.8 (2C, 2 OCH_3), 56.1 (2C, 2 OCH_3), 112.5 (2C, CH), 113.6 (2C, CH), 117.5 (2C, CH), 118.3 (2C, CH), 123.2 (2C, C_{quat}), 143.8 (2C, CH), 153.3 (2C, C_{quat}), 153.5 (2C, C_{quat}), 163.2 (2C, C_{quat}, CO). Anal. Calcd for $C_{22}H_{22}O_7$ (398.41): C, 66.32%; H, 5.57%. Found: C, 66.74%; H, 5.62%.

4.3.8. Bis(3,4-dimethoxycinnamic) anhydride (**9d**)

Pale yellow solid; mp 177–179 °C; IR (KBr) ν_{max}: 3119, 3072, 2995, 2993, 2960, 2931, 2835, 1756, 1716, 1627, 1598, 1581, 1513, 1461, 1425, 1270, 1163, 1444, 1084, 1023, 1001, 869, 815 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.95 (s, 12H, 4 OCH_3), 6.41 (d, $^3J = 15.6$ Hz, 2H), 6.91 (d, $^3J = 8.4$ Hz, 2H), 7.10 (s, 2H), 7.19 (d, $^3J = 8.4$ Hz, 2H), 7.81 (d, $^3J = 15.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ: 55.9 (2C, 2 OCH_3), 56.0 (2C, 2 OCH_3), 109.9 (2C, CH), 111.1 (2C, CH), 114.4 (2C, C_{quat}), 123.6 (2C, CH), 126.8 (2C, CH), 148.5 (2C, CH), 149.3 (2C, C_{quat}), 152.0 (2C, C_{quat}), 162.9 (2C, C_{quat}, CO). Anal. Calcd for $C_{22}H_{22}O_7$ (398.41): C, 66.32%; H, 5.57%. Found: C, 66.02%; H, 5.62%.

4.4. General procedure for the preparation of esters

4.4.1. Ethyl 4-nitrobenzoate (**11a**)

To a solution of triphenylphosphine (910 mg, 3.47 mmol) in dry dichloromethane (20 mL) bromotrichloromethane (710 mg, 3.58 mmol) was added, and the resulting mixture was stirred at a rate for 30 min to give a reddish-brownish solution. 4-Nitrobenzoic acid (509 mg, 3.04 mmol) was added and the solution was stirred at reflux for 1 h. Thereafter, dry ethanol (0.50 mL, 400 mg, 8.7 mmol) was added dropwise via a syringe. The resulting mixture was stirred at reflux for 12 h. Thereafter, it was cooled and subjected directly to column chromatography on a silica gel (ether/$CHCl_3$/hexane 1:1:3) to give **11a** (515 mg, 87%) as colorless crystals; mp 56–59 °C; IR (KBr) ν_{max}: 3120, 3057, 2990, 1716, 1607, 1526, 1351, 1279, 1103, 871, 841, 787, 714, 505 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.41 (t, $^3J = 7.2$ Hz, 3H), 4.42 (q, $^3J = 7.2$ Hz, 2H, OCH_2), 8.19 (d, $^3J = 9.2$ Hz, 2H), 8.26 (d, $^3J = 9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 14.2 (CH_3), 62.0 (OCH_2), 123.5 (2C, CH), 130.6 (2C, CH), 135.8 (C_{quat}), 150.4 (C_{quat}), 164.7 (C_{quat}, CO). Anal. Calcd for $C_9H_9NO_4$ (195.17): C, 55.39%; H, 4.65%; N, 7.18%. Found: C, 55.53%; H, 4.69%; N, 7.10%.

4.4.2. Isopropyl 4-nitrobenzoate (**11b**)

Colorless crystals; mp 110–112 °C; IR (neat) ν_{max}: 3112, 3081, 3076, 2987, 2939, 2880, 1713, 1525, 1282, 1100, 1011, 918, 875, 841, 788, 718 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.38 (d, $^3J = 6.4$ Hz, 6H, 2 CH_3), 5.27 (hept., $^3J = 6.4$ Hz, 1H), 8.18 (d, $^3J = 9.2$ Hz, 2H), 8.25 (d, $^3J = 9.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 21.8 (2C, 2 CH_3), 69.7 (OCH), 123.4 (2C, CH), 130.6 (2C, CH), 136.2 (C_{quat}), 150.4 (C_{quat}), 164.2 (C_{quat}, CO). Anal. Calcd for $C_{10}H_{11}NO_4$ (209.20): C, 57.41%; H, 5.30%; N, 6.70%. Found: C, 57.33%; H, 5.45%; N, 6.68%.

4.4.3. Benzyl 3-chlorobenzoate (**11c**) [39]

Colorless oil; ν_{max} (neat/cm^{-1}) 3067, 3034, 2954, 2888, 1723, 1575, 1278, 1254, 1126, 1073, 747, 696; δ_H (400 MHz, $CDCl_3$) 5.36 (2H, s, OCH_2), 7.35–7.45 (6H, m), 7.52 (1H, d, $^3J = 8.0$ Hz), 7.95 (1H, d, $^3J = 8.0$ Hz), 8.04 (1H, s); δ_C (100.5 MHz, $CDCl_3$) 67.1 (OCH_2), 127.8 (CH), 128.3 (2C, CH), 128.4 (2C, CH), 128.7 (CH), 129.7 (CH), 129.8 (CH), 131.8 (C_{quat}), 133.1 (CH), 134.5 (C_{quat}), 135.6 (C_{quat}), 165.2 (C_{quat}, CO).

4.4.4. Heptyl 2-chlorobenzoate (**11d**) [40]

Colorless oil; ν_{max} (neat/cm^{-1}) 2956, 2929, 2857, 1732, 1593, 1469, 1436, 1292, 1250, 1118, 1051, 747; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, $^3J = 7.0$ Hz, CH_3), 1.26–1.58 (8H, m), 1.72–1.77 (2H, m), 4.32 (2H, t, $^3J = 6.4$ Hz, OCH_2), 7.28–7.45 (3H, m), 7.79 (1H, dd, $^3J = 7.6$ Hz, $^4J = 2.0$ Hz); δ_C (100.5 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 65.7 (OCH_2), 126.5 (CH), 130.5

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(C_{quat}), 130.9 (CH), 131.3 (CH), 132.3 (CH), 133.6 (C_{quat}), 165.9 (C_{quat}, CO).

*4.4.5. 3-O-Methylestra-1,3,5(10)-trien-17β-yl 4-(E)-methoxycinnamate (**11e**)*

As a colorless solid, mp 126–128 °C; IR (KBr/cm^{-1}) ν_{max}: 2919, 2866, 2836, 1701, 1636, 1604, 1575, 1512, 1497, 1323, 1257, 1205, 1172, 1033, 984, 967, 828, 812; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90 (3H, s, CH_3), 1.25–2.31 (13H, m), 2.85–2.87 (2H, m), 3.77 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 4.82 (1H, dd, ^3J = 9.2 Hz, ^3J = 8.0 Hz), 6.32 (1H, d, ^3J = 16.0 Hz), 6.63 (1H, d, ^4J = 2.8 Hz), 6.70 (1H, dd, ^3J = 8.8 Hz, ^4J = 2.8 Hz), 6.90 (2H, d, ^3J = 8.8 Hz), 7.20 (1H, d, ^3J = 8.4 Hz), 7.48 (2H, d, ^3J = 8.8 Hz), 7.62 (1H, d, ^3J = 16.0 Hz); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 12.2, 23.3, 26.2, 27.2, 27.7, 29.8, 37.0, 38.6, 43.2, 43.8, 49.8, 55.2 (OCH_3), 55.4 (OCH_3), 82.6 (OCH), 111.5 (CH), 113.8 (CH), 114.3 (2C, CH), 116.1 (CH), 126.4 (CH), 127.2 (C_{quat}), 129.7 (2C, CH), 132.5 (C_{quat}), 137.9 (C_{quat}), 144.0 (CH), 157.4 (C_{quat}), 161.3 (C_{quat}), 167.4 (C_{quat}, CO). Anal. Calcd for $C_{29}H_{34}O_4$. (446.58): C, 78.00%; H, 7.67%. Found: C, 78.14%; H, 7.44%.

*4.4.6. 3-O-Methylestra-1,3,5(10)-trien-17β-yl 3,4-(E)-dimethoxycinnamate (**11f**)*

As a colorless solid, mp 162–165 °C; ν_{max} (KBr/cm^{-1}) 3010, 2953, 2863, 2843, 2805, 2698, 1612, 1596, 1510, 1445, 1417, 1294, 1257, 1155, 1139, 1024, 848, 812, 782, 616, 570; δ_H (400 MHz, $CDCl_3$) 0.90 (3H, s, CH_3), 2.84–2.88 (2H, m), 1.25–2.31 (13H, m), 3.77 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 4.83 (1H, dd, ^3J = 8.0, ^3J = 7.6 Hz, OCH), 6.32 (1H, d, ^3J = 16.0 Hz), 6.63 (1H, d, ^4J = 2.8 Hz), 6.70 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.8 Hz), 6.86 (1H, d, ^3J = 8.4 Hz), 7.05 (1H, d, ^4J = 2.0 Hz), 7.10 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz), 7.20 (1H, d, ^3J = 8.4 Hz), 7.61 (1H, d, ^3J = 16.0 Hz); δ_C (100.5 MHz, $CDCl_3$) 12.2, 23.3, 26.2, 27.2, 27.7, 29.8, 37.0, 38.6, 43.2, 43.8, 49.8, 55.2 (OCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 82.7 (OCH), 109.5, 111.0, 111.5, 113.8, 116.2, 122.6, 126.4, 127.5, 132.5, 137.9, 144.3, 149.2 (C_{quat}), 151.0 (C_{quat}), 157.4 (C_{quat}), 167.3 (C_{quat}, CO). Found: C, 75.76%; H, 7.32%. Calcd. for $C_{30}H_{36}O_5$. (476.60): C, 75.60%; H, 7.61%.

4.5. General procedure for the preparation of O-acyloximes

*4.5.1. 3-Nitroacetophenone oxime 4-methoxycinnamate (**13e**)*

To a solution of triphenylphosphine (910 mg, 3.47 mmol) in dry dichloromethane (10 mL) bromotrichloromethane (710 mg, 3.58 mmol) was added, and the resulting mixture was stirred at a rate for 30 min to give a reddish-brownish solution. Then, 4-methoxycinnamic acid (**4d**, 542 mg, 3.04 mmol) was added, and the mixture was stirred at reflux for 45 min. Thereafter, 3-nitroacetophenone oxime (**12c**, 545 mg, 3.03 mmol) was added, and the mixture was stirred at reflux for another 12 h. Column chromatography on a silica gel (CH_2Cl_2) gave (*E*)-1-bromo-2-(4-methoxyphenyl)ethene (**6**, 77 mg, 12%) [41] as a colorless solid; mp 52–56 °C (Lit. mp 58–59 °C [42]); ν_{max} (KBr/cm^{-1}) 2958, 2837, 1607, 1512, 1256, 1028, 950, 927, 836, 777, 526; δ_H (400 MHz, $CDCl_3$) 6.60 (1H, d, ^3J = 14.0 Hz), 6.84 (2H, d, ^3J = 8.4 Hz), 7.03 (1H, d, ^3J = 14.0 Hz), 7.22 (2H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 55.3 (OCH_3), 104.0 (CH), 114.7 (2C, CH), 127.3 (2C, CH), 128.7 (C_{quat}), 136.5 (CH), 159.6 (C_{quat}) and **13e** (826 mg, 80%) as a pale yellow solid; mp 130–133 °C; IR (KBr) ν_{max}: 1754, 1624, 1602, 1573, 1524, 1513, 1351, 1309, 1286, 1249, 1178, 1102, 1026, 981, 921, 825, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.50 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.46 (d, ^3J = 16.0 Hz, 1H), 6.92 (d, ^3J = 8.8 Hz, 2H), 7.53 (d, ^3J = 8.8 Hz, 2H), 7.60 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1H), 7.82 (d, ^3J = 16.0 Hz, 1H), 8.20 (dm, ^3J = 8.0 Hz, 1H), 8.29 (dm, ^3J = 8.0 Hz, 1H), 8.56 (dd, ^4J = 2.0 Hz, ^4J = 1.6 Hz, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 14.4 (CH_3), 55.4 (OCH_3), 112.4 (CH), 114.4 (2C, CH), 122.1 (CH), 125.1 (CH), 126.9 (C_{quat}), 129.7 (CH), 130.1 (2C, CH), 132.9 (CH), 136.8 (C_{quat}), 146.5 (CH), 148.4 (C_{quat}), 160.5 (C_{quat}), 161.8 (C_{quat}), 164.6 (C_{quat}). Anal. Calcd for $C_{18}H_{16}N_2O_5$ (340.33): C, 63.63; H, 4.85; N, 8.19%. Found: C, 63.89; H, 4.87; N, 7.96%.

*4.5.2. 3-O-Methyl estra-1-3,5(10)-trien-17-one-17-oxime N-3,4-(E)-dimethoxycinnamate (**13a**)*

As a colorless solid, mp 152–154 °C (isopropanol/diethyl ether); IR (KBr/cm^{-1}) ν_{max} 3061, 2930, 2864, 2837, 1734, 1627, 1597, 1513, 1465, 1420, 1307, 1266, 1236, 1162, 1124, 1021, 979, 863, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, $CDCl_3$) δ: 0.83–2.91 (m, 15H), 1.05 (s, 3H, CH_3), 2.91 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.37 (d, ^3J = 16.0 Hz, 1H), 6.63 (d, ^4J = 2.8 Hz, 1H), 6.71 (dd, ^3J = 8.8 Hz, ^4J = 2.8 Hz, 1H), 6.87 (d, ^3J = 8.4 Hz, 1H), 7.06 (d, ^4J = 2.0 Hz), 7.13 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H), 7.21 (d, ^3J = 8.8 Hz, 1H), 7.71 (d, ^3J = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 17.1, 22.9, 26.1, 27.2, 27.3, 29.6, 33.7, 38.2, 43.8, 45.5, 52.8, 55.2 (OCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 109.7, 111.0, 111.5, 113.8, 113.9, 122.7, 126.4, 127.4, 132.1, 137.6, 145.4, 149.2, 151.2, 157.5, 165.1, 178.7 (C_{quat}, CO). Found: C, 73.69%; H, 7.37%; N, 2.73%. Calcd. for $C_{30}H_{35}NO_5$ (489.60): C, 73.59%; H, 7.21%; N, 2.86%.

*4.5.3. Fluoren-9-one oxime benzoate (**13b**)*

As a yellow solid, mp 180–183 °C; IR (KBr) ν_{max}: 1743, 1597, 1449, 1319, 1248, 1178, 1091, 1081, 1064, 1026, 975, 889, 785, 731, 711, 644 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.69 (m, 9H), 8.01 (d, ^3J = 7.6 Hz, 1H), 8.21 (d, ^3J = 7.2 Hz, 2H), 8.29 (d, ^3J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 120.1 (CH), 120.4 (CH), 123.6 (CH), 128.5 (CH), 128.6 (CH), 128.8 (2C, CH), 128.9 (C_{quat}), 129.9 (3C, CH), 130.1 (C_{quat}), 131.7 (CH), 132.6 (CH), 133.6 (CH), 134.5 (C_{quat}), 141.1 (C_{quat}), 142.8 (C_{quat}), 159.1 (C_{quat}), 164.2 (C_{quat}). Anal. Calcd for $C_{20}H_{13}NO_2$. (299.32) 0.2H_2O: C, 79.30%; H, 4.46%, N 4.62%. Found: C, 79.26%; H, 4.34%; N, 4.64%.

*4.5.4. Fluoren-9-one oxime cinnamate (**13c**)*

As a pale yellow solid; mp 126–128 °C; IR (KBr) ν_{max}: 3029, 1746, 1634, 1449, 1308, 1116, 951, 788, 761, 733, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.74 (d, ^3J = 16.0 Hz, 1H), 7.28–7.66 (m, 11H), 7.97 (md, 1H), 7.98 (d, ^3J = 16.0 Hz, 1H), 8.31 (md, 1H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 114.9 (CH), 120.1 (CH), 120.3 (CH), 123.5 (CH), 128.4 (3C, CH), 128.5 (CH), 129.0 (2C, CH), 130.1 (CH), 130.2 (C_{quat}), 130.9 (CH), 131.7 (CH), 132.6 (CH), 134.1 (C_{quat}), 134.5 (C_{quat}), 141.2 (C_{quat}), 142.6 (C_{quat}), 147.3 (CH), 158.4 (C_{quat}), 164.6 (C_{quat}, CO). Anal. Calcd for $C_{22}H_{15}NO_2$ (325.36): C, 81.21%; H, 4.65%; N, 4.30%. Found: C, 81.49%; H, 4.70%; N, 4.36%.

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*4.5.5. 3-Nitroacetophenone oxime benzoate (**13d**)*

As a colorless solid, mp 139–141 °C; IR (KBr) ν_{max}: 1746, 1530, 1349, 1246, 1057, 1021, 931, 776, 738, 707, 676, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.59 (s, 3H, CH_3), 7.49–7.53 (m, 2H), 7.61–7.63 (m, 2H), 8.13 (d, ^3J = 7.6 Hz, 2H), 8.26 (d, ^3J = 7.6 Hz, 1H), 8.32 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H), 8.61 (s, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 14.6 (CH_3), 122.1 (CH), 125.3 (CH), 128.7 (2C, CH), 129.7 (3C, 2 CH, C_{quat}), 129.7 (CH), 132.9 (CH), 133.6 (CH), 136.6 (C_{quat}), 148.4 (C_{quat}), 161.3 (C_{quat}), 163.4 (C_{quat}). Anal. Calcd for $C_{15}H_{12}N_2O_4$. (284.27): C, 63.38%; H, 4.25%, N 9.85%. Found: C, 63.36%; H, 4.27%; N, 9.88%.

*4.5.6. 6-Methoxy-1-tetralone oxime 3,4-dimethoxycinnamate (**13f**)*

As a pale pink solid; mp 148–150 °C; IR (KBr) ν_{max}: 3002, 2975, 2837, 2833, 1724, 1630, 1616, 1600, 1514, 1459, 1423, 1353, 1258, 1160, 1124, 1071, 1028, 988, 938, 877, 816, 767, 598 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.89 (m, 2H), 2.75 (dd, ^3J = 6.0 Hz, ^3J = 6.0 Hz, 2H), 2.92 (dd, ^3J = 6.0 Hz, ^3J = 6.0 Hz, 2H), 3.81 (s, 3H, OCH_3), 3.92 (s, 6H, 2 OCH_3), 6.45 (d, 1H, ^3J = 16.0 Hz), 6.66 (br s, 1H), 6.76–7.17 (m, 3H), 7.08 (br s, 1H), 7.74 (d, 1H, ^3J = 16.0 Hz), 8.16 (d, 1H, ^3J = 8.6 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 21.4 (CH_2), 25.6 (CH_2), 29.9 (CH_2), 55.3 (OCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 109.7 (CH), 111.0 (CH), 113.0 (2C, CH), 113.6 (C_{quat}), 121.7 (C_{quat}), 122.8 (CH), 127.4 (C_{quat}), 127.6 (CH), 142.8 (CH), 145.6 (CH), 149.2 (C_{quat}), 151.3 (C_{quat}), 161.5 (C_{quat}), 165.0 (C_{quat}, CO). Anal. Calcd for $C_{22}H_{23}NO_5$. (381.42): C, 69.28%; H, 6.08%, N 3.67%. Found: C, 69.41%; H, 5.95%; N, 3.73%.

*4.5.7. 2,5-Dimethoxyacetophenone oxime 4-nitrobenzoate (**13g**)*

As yellow needles; mp 141–145 °C; IR (KBr) ν_{max}: 3109, 2992, 2969, 2937, 2836, 1741, 1606, 1527, 1499, 1468, 1410, 1349, 1269, 1224, 1088, 1067, 1040, 1011, 857, 713 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 2.48 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 7.00 (s, 1H), 7.88 (d, ^3J = 8.8 Hz, 1H), 8.18 (d, ^3J = 8.8 Hz, 1H), 8.29 (d, ^3J = 9.2 Hz, 2H), 8.34 (d, ^3J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 17.8 (CH_3), 56.0 (OCH_3), 56.1 (OCH_3), 112.4 (CH), 115.3 (CH), 116.9 (CH), 123.7 (2C, CH), 125.2 (C_{quat}), 130.7 (2C, CH), 134.8 (C_{quat}), 150.7 (C_{quat}), 151.7, (C_{quat}), 162.0 (C_{quat}), 164.7 (C_{quat}), 166.8 (C_{quat}). Anal. Calcd for $C_{17}H_{16}N_2O_6$. (422.43): C, 59.30%; H, 4.68%, N 8.14%. Found: C, 59.62%; H, 4.81%; N, 8.18%.

- Preparation of the single crystal of **13g**:

Single crystals of compound **13g** were obtained by very slow evaporation (5 days) in a mixture of CH_2Cl_2/diethyl ether/hexane at room temperature.

- X-ray crystallography of **13g**:

A single crystal of the title compound with a dimension of 0.75 × 0.33 × 0.10 mm was chosen for X-ray diffraction study. The data were collected on an Oxford Diffraction SuperNova, diffractometer with an Atlas detector. A Mo-micro-focus sealed-tube X-ray-source was used. The data were collected at 100 K.

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