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Article

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Ester Formation via Symbiotic Activation Utilizing Trichloroacetimidate Electrophiles

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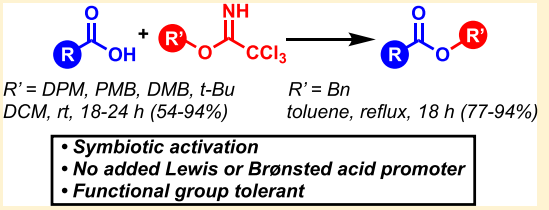
Supporting Information

ABSTRACT: Trichloroacetimidates are useful reagents for the synthesis of esters under mild conditions that do not require an exogenous promoter. These conditions avoid the undesired decomposition of substrates with sensitive functional groups that are often observed with the use of strong Lewis or Brønsted acids. With heating, these reactions have been extended to benzyl esters without electron-donating groups. These inexpensive and convenient methods should find application in the formation of esters in complex substrates.



INTRODUCTION

The synthesis of esters is a vital transformation in organic chemistry, and therefore, significant effort has been devoted to developing high yielding and robust protocols for ester formation. These approaches are often characterized in three archetypal pathways:[1] (1) carbonyl activation (where an alcohol is added to an activated carboxylate), (2) carboxylate alkylation (where the carboxylic acid is deprotonated to improve nucleophilicity and added to an electrophile), and (3) symbiotic activation, where reagents combine to form a reactive ion pair that leads to the ester (Figure 1). While the

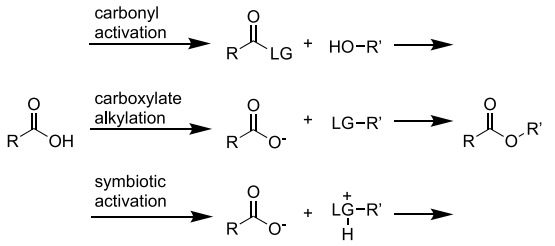


Figure 1. Archetypal esterification pathways.

carbonyl activation[2] and carboxylate alkylation[3] pathways have been deeply explored and reviewed,[4] investigations into reagents that proceed through symbiotic activation processes have received less attention.[5] These processes avoid the use of strong acids and bases that often characterize the other two methods, making these transformations more amenable for use in complex polyfunctional molecules that are often prepared in natural product synthesis and pharmaceutical environments.

In order to be characterized as a symbiotic activation process, both the carboxylic acid and the esterification reagent must be activated under the reaction conditions. Usually, this is accomplished by the esterification reagent being basic enough to deprotonate the carboxylic acid, with the resulting cationic salt being electrophilic enough to react with the newly formed carboxylate anion. Ideally, the esterification reagent would be inert to other functional groups besides the carboxylate and only react when activated by the proton transfer. Additionally, any side products generated from the loss of the leaving group should also be as unreactive as possible so that sensitive functionality can be readily accommodated. This minimizes the need for exogenous reagents to buffer the reaction, keeping the reaction conditions mild as the strongest acid present is the carboxylic acid starting material.

Perhaps the most well-known example of esterification by symbiotic activation is the reaction of carboxylic acids with diazoalkanes (like **1**, Figure 2).[6] These transformations have

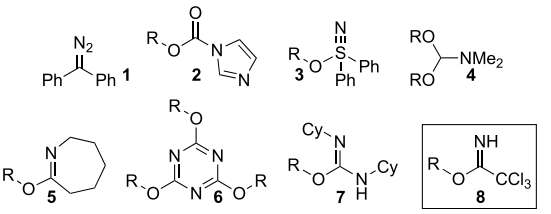


Figure 2. Alkylation agents that undergo symbiotic activation.

been shown to proceed through a tight ion pair intermediate that is formed after proton transfer from the carboxylic acid[7] and generate only unreactive nitrogen gas as a side product. Unfortunately, many diazoalkanes have a reputation as being toxic and energetic, limiting their use and often forcing researchers to form these reagents in situ to avoid issues with handling.[8] Other reagents that undergo symbiotic activation

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include imidazole carbamates with structures like **2**,[1,9] alkoxy-λ^6-sulfanenitriles like **3**,[10] some amide acetals (like **4** and **5**),[11] 1,3,5-*O*-benzyl triazines like **6**,[12] and isoureas like **7**.[13] Most of these reagents require heating to effect their esterifications, usually in refluxing benzene or toluene solvent, with the exception being the isoureas which provide some esters at room temperature. Many of these esterification reagents have an imidate substructure as part of the reacting functionality, closely resembling a trichloroacetimidate like **8**, for example. This core facilitates the displacement as it allows for the rearrangement of the imidate imine to the corresponding acetamide carbonyl, contributing a secondary thermodynamic driving force to the esterification and often leading to higher yields under mild conditions. Additionally, the basic imine of the imidate is more readily activated by weak acids than carbonyl-based alkylation agents, leading to the selection of this common structural feature.

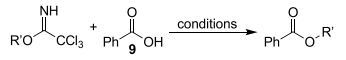
Given the commonality of the imidate core, we speculated that trichloroacetimidates may also be effective esterification reagents under near neutral conditions. Trichloroacetimidates are known to be powerful alkylating agents for carboxylic acids and alcohols when activated with a strong Lewis or Brønsted acid catalyst.[14] These acid promoters may be problematic, however, as many complex substrates do not tolerate strong acids. A number of literature examples demonstrate that ester formation with some trichloroacetimidates do not require the addition of an exogenous promoter, including descriptions of spontaneous esterification with glycosyl imidates,[15] 4-methoxybenzyl trichloroacetimidate,[16] and 2-phenylisopropyl trichloroacetimidate.[17]

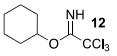
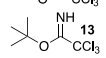
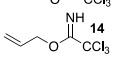
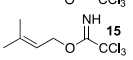
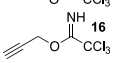
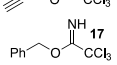
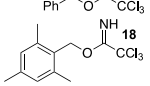
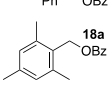
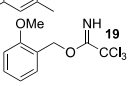
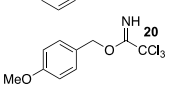
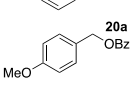
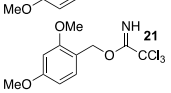
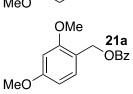
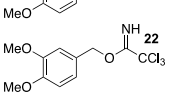
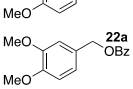
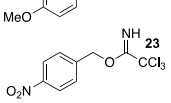
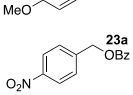
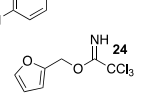
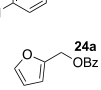
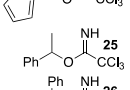
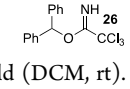
RESULTS AND DISCUSSION

Spurred by the need for mild esterification reagents from inexpensive precursors, we recently began to further investigate these trichloroacetimidate esterifications. These studies focused on systems that do not require an additional Lewis or Brønsted acid additive and also did not require heating to increase the chances of compatibility with complex carboxylic acids where the reagents would typically find application. Initial investigations showed that both the DPM and PMB imidates could form esters at room temperature without the need for exogenous acid.[18] Promoter-free imidate esterifications were shown to undergo symbiotic activation with carboxylic acids, with the reactions being sensitive to the exogenous base that prevented activation of the imidate by the carboxylic acid esterification partner. These esterifications were also shown to function well with sensitive carboxylic acids which decompose under more standard esterification conditions, including β-hydroxy carboxylic acids and other polyfunctional substrates.[18] The imidates are simple to prepare from inexpensive precursors, formed at room temperature from the alcohol and trichloroacetonitrile with a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[19] In addition, the trichloroacetamide side product may be removed by washing with aqueous NaOH solution, as the pK_a of this acetamide is similar to a phenol. This is a significant advantage over isourea-based esterification reagents, which usually require chromatography to remove the urea side product. Given the ready availability of trichloroacetimidates (easily synthesized from inexpensive trichloroacetonitrile and the appropriate alcohol), the scope of these transformations with respect to the imidate has now been examined. This work has determined that a surprising number of stable, unactivated trichloroacetimidates provide the corresponding esters under promoter-free conditions in excellent yield.

Initially, the esterifications were studied with several structurally distinct trichloroacetimidates to determine the scope with regard to trichloroacetimidate electrophile. For this study, benzoic acid was utilized as a common substrate (Table 1). The most simple alkyl trichloroacetimidates did not

Table 1. Esterifications with Different Trichloroacetimidates



entry	imidate	ester	yield (%)[a]	yield (%)[b]
1		MeOBz **10a**	0 (48 h)	0 (18 h)
2		EtOBz **11a**	0 (48 h)	0 (18 h)
3			0 (48 h)	0 (18 h)
4			84 (48 h)	17 (18 h)
5			-	0 (48 h)
6			73[c] (16 h)	-
7			-	0 (48 h)
8			0 (48 h)	76 (18 h)
9			0 (48 h)	82 (18 h)
10			19 (48 h)	96 (19 h)
11			89 (24 h)	-
12			90 (1 h)	-
13			96 (3 h)	-
14			-	0 (48 h)
15			34 (22 h)	96 (18 h)
16			34 (48 h)	95 (23 h)
17			99 (18 h)	-

[a]Isolated yield (DCM, rt). [b]Isolated yield (toluene, reflux). [c]Trace of the *tert*-prenyl isomer also detected in the ^{1}H NMR.

undergo esterification at room temperature or in refluxing toluene (unreacted starting materials were recovered, entries 1−3), the exception being the *tert*-butyl trichloroacetimidate **13** (entry 4). Oddly, the esterification with **13** and benzoic acid gave a higher yield at room temperature in DCM as opposed to refluxing toluene. This may be due to the propensity of imidate **13** to undergo elimination at elevated temperatures, decomposing to isobutylene and trichloroacetamide. Indeed, this has been reported to be a limitation imidate **13** in the formation of *tert*-butyl amines.[20] Attempts to moderate the elimination by using nitromethane as a solvent, as has been reported to facilitate substitution in other

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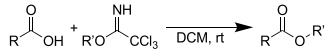
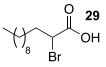
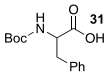
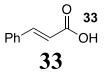
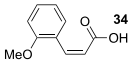
systems,[20,21] only gave poor conversion of the imidate to the ester, with mostly starting carboxylic acid being recovered.

Allylic and propargylic trichloroacetimidates were evaluated next. While allyl imidate **14** and propargyl trichloroacetimidate **16** were unreactive (with only starting materials being observed), prenyl trichloroacetimidate **15** gave a useful 73% yield of product at room temperature (entry 6). While nearly all of the product was the prenyl ester **15a**, a trace amount of the *tert*-prenyl isomer was detected in the crude ^{1}H NMR. Benzylic trichloroacetimidates are of special interest, as benzyl esters are some of the most common carboxylate protecting groups utilized in organic synthesis.[22] Benzyl trichloroacetimidate **17** was unreactive at room temperature, but gave a 76% yield of product when heated in toluene. Adding electron-donating groups to the benzene ring led to increased yields of the esterification, as shown with 2,4,6-trimethylbenzyl imidate **18** and 2-methoxybenzyl trichloroacetimidate **19**. While imidate **19** did give some product at room temperature, the yield was moderate, with starting materials being recovered. Alternatively, many other electron-rich benzylic trichloroacetimidates formed esters at room temperature in DCM with excellent conversion. These conditions were employed successfully for 4-methoxybenzyl trichloroacetimidate **20**, 2,4-dimethoxybenzyl trichloroacetimidate **21**, and 3,4-dimethoxybenzyltrichloroacetimidate **22** (Table 1, entries 11−13). With the dimethoxybenzyl systems, the esterifications were typically complete in only a few hours, demonstrating that reactivity increases observed with multiple electron-donating groups were additive. The ability to form dimethoxybenzyl esters is important, as these can be removed via oxidative methods (typically with DDQ[4a,23]), whereas other benzyl esters are inert to these conditions. The furfuryl trichloroacetimidate **24** also gave an excellent yield of the corresponding ester (entry 15) by heating in toluene, as did the phenethyl imidate **25**. The diphenylmethyl trichloroacetimidate formed the ester at room temperature, providing a virtually quantitative yield of the DPM ester. In contrast, benzylic imidates with electron-withdrawing substituents were unreactive under these promoter-free conditions, as shown by the lack of ester formation with the 4-nitrobenzyl trichloroacetimidate **23** (entry 14) which returned only unreacted starting material. From these results, it is apparent that the esterifications proceed best with electron-rich alkyl groups that are capable of stabilizing a positive charge or partial positive charge. The more reactive imidates can form esters at room temperature, while the less reactive systems must be heated in order for the esterification to proceed. While electronic effects were apparent, sterics also influenced reactivity as can be seen in the difference in yield when employing imidates **19** and **20**. The lower reactivity of **19** is consistent with the addition of a substituent near the reacting benzylic position slowing the esterification due to steric hindrance.

With the scope of the reaction with regard to the trichloroacetimidate determined, a brief selection of carboxylic acids were esterified with some of the functional trichloroacetimidates from Table 1 to determine the effects of the carboxylic acid structure on the esterification reaction (Table 2). Initially, the effects of the steric environment near the carboxylic acid were examined. Use of diphenylacetic acid **27** provided consistently high yields of the corresponding esters. The even more sterically encumbered 2-methyl-2-phenylpropionic acid **28** provided a lower yield when the hindered *tert*-butyl imidate **13** was employed, evidently because of unfavorable steric factors when both the acid and the imidate are hindered. Additionally, a number of substrates were then evaluated with respect to functionality. The 2-bromododecanoic acid **29** was esterified in good yield by all of the imidates used. No elimination or other competing substitution reactions were observed under these reaction conditions. The ability to form esters in the presence of other protic functionalities was also investigated. Mandelic acid **30** was esterified in good yield, demonstrating that the presence of an alcohol was well tolerated. The protected amino acid (±)-Boc-phenylalanine **31**

Table 2. Reaction of Complex Carboxylic Acids with Different Trichloroacetimidates



entry	acid	imidate	time (h)	yield (%)
1		*t*-Bu (**13**)	48	81 (**13b**)
2	**27**	PMB (**20**)	24	96 (**20b**)
3	**27**	DMB (**21**)	1	88 (**21b**)
4	**27**	DPM (**26**)	18	76 (**26b**)
5		*t*-Bu (**13**)	48	60 (**13c**)
6	**28**	PMB (**20**)	24	86 (**20c**)
7	**28**	DMB (**21**)	24	85 (**21c**)
8	**28**	DPM (**26**)	18	75 (**26c**)
9		*t*-Bu (**13**)	48	94 (**13d**)
10	**29**	PMB (**20**)	24	93 (**20d**)
11	**29**	DMB (**21**)	20	81 (**21d**)
12	**29**	DPM (**26**)	18	83 (**26d**)
13		*t*-Bu (**13**)	48	59 (**13e**)
14	**30**	PMB (**20**)	24	79 (**20e**)
15	**30**	DMB (**21**)	1	94[a] (**21e**)
16	**30**	DPM (**26**)	18	92 (**26e**)
17		*t*-Bu (**13**)	48	62 (**13f**)
18	**31**	PMB (**20**)	24	91 (**20f**)
19	**31**	DMB (**21**)	24	80 (**21f**)
20	**31**	DPM (**26**)	3	54[a] (**26f**)
21		*t*-Bu (**13**)	48	30[b] (**13g**)
22	**32**	PMB (**20**)	24	83 (**20g**)
23	**32**	DMB (**21**)	0.5	73 (**21g**)
24	**32**	DPM (**26**)	18	76 (**26g**)
25		*t*-Bu (**13**)	48	60 (**13h**)
26	**33**	PMB (**20**)	24	94 (**20h**)
27	**33**	DMB (**21**)	24	88 (**21h**)
28	**33**	DPM (**26**)	18	93 (**26h**)
29		*t*-Bu (**13**)	48	76 (**13i**)
30	**34**	PMB (**20**)	24	84 (**20i**)
31	**34**	DMB (**21**)	4	92 (**21i**)
32	**34**	DPM (**26**)	18	72 (**26i**)
33		*t*-Bu (**13**)	48	81 (**13j**)
34	**35**	PMB (**20**)	24	83 (**20j**)
35	**35**	DMB (**21**)	24	83 (**21j**)
36	**35**	DPM (**26**)	18	71 (**26j**)

[a]Only 1 equiv imidate was used. [b]Yield determined by ^{1}H NMR using a mesitylene standard as product was volatile.

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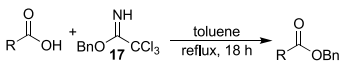
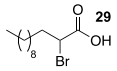
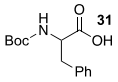
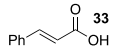
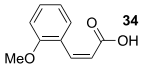
was also esterified under these conditions in good yield. The propensity of alkene isomerization under these reaction conditions was also explored. Vinyl acetic acid **32** was esterified in good yield under both sets of reaction conditions without any observed isomerization of the alkene. The exception was the *tert*-butyl ester of vinyl acetic acid **13g**, which proved to be quite volatile and therefore was difficult to obtain a high isolated yield. Cinnamic acid **33** also proved to be a good substrate, providing the corresponding esters in good yields. The cis alkenoic acid **34** was also investigated, as similar systems often undergo cis/trans isomerization under esterification conditions.[24] No isomerization of the alkene was observed during room-temperature esterifications in DCM with the tested imidates (Table 2, entries 33−36), demonstrating this as a powerful method for the protection of esters without isomerization. Heterocycles like the pyridine in picolinic acid **35** were also well tolerated, with good yields being achieved with all four imidates tested.

The scope of the esterification reaction in refluxing toluene with benzyl trichloroacetimidate **17** was also explored (Table 3), as benzyl groups are common carboxylate-protecting groups, and given that alternative conditions are necessary for the formation of benzyl esters with imidate **17**, some differences in functional group tolerance may be observed. These concerns were unfounded, however, as the same series of carboxylic acids underwent esterification in good yields. Importantly, no elimination products from the α-bromoacid **29** were observed, and no isomerization of the alkenes in carboxylates **32**, **33**, or **34** was detected. The alcohol of mandelic acid **30** also remained unaffected. While some more reactive imidates (like the diphenylmethyl trichloroacetimidate **26**[25]) have been reported to form ethers under similar conditions, imidate **17** is not reactive enough to access this reactivity manifold, and therefore, alcohols are well tolerated under the reaction conditions.

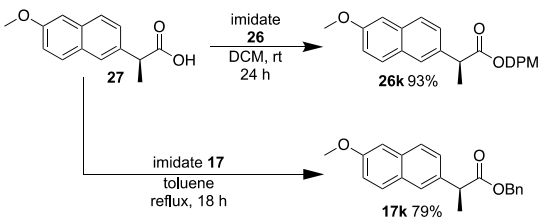
Table 3. Esterifications of Benzyl Trichloroacetimidate in Refluxing Toluene



entry	carboxylic acid	yield (%)
1		78 (**17b**)
2		94 (**17c**)
3		80 (**17d**)
4		88 (**17e**)
5		94 (**17f**)
6		88 (**17g**)
7		77 (**17h**)
8		80 (**17i**)
9		94 (**17j**)

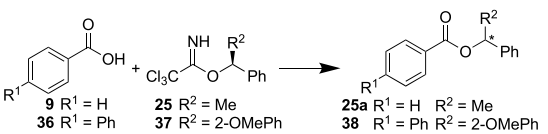
The effects of these esterification reactions on a chirality center next to the carboxylate were also investigated. Chiral naproxen **27** was utilized for this section of the study, as this substrate can racemize rapidly as the chirality center is both benzylic and next to the electron-withdrawing carboxylate. Treatment of chiral naproxen with imidate **26** at room temperature in DCM gave the desired ester products in high yields (Scheme 1). Evaluation of the enantiopurity of these samples by chiral high-performance liquid chromatography (HPLC) analysis showed that virtually no racemization had occurred. While these results ensured that there was no racemization in DCM at rt, it did not provide information about the possibility of racemization with less reactive benzylic imidates which required refluxing toluene to effect the esterification. To address this point, naproxen was heated in refluxing toluene with benzyl trichloroacetimidate **17** to provide a 79% yield of benzyl ester **17k**. Chiral HPLC analysis of **17k** showed that virtually no racemization had occurred with this substrate compared to a racemic sample (racemic samples of **26k** and **17k** were prepared by heating the enantiopure esters with DBU in toluene).

Scheme 1. Esterification of Naproxen without Racemization



The mechanism of the reaction was briefly probed by the use of two chiral imidate substrates in the esterification reaction. Chiral phenethyl trichloroacetimidate **25** has already been reported[26] and was therefore employed in the esterification reaction. In addition, the imidate of (*S*)-(2-methoxyphenyl)phenylmethanol[27] (imidate **37**) was also prepared. During the course of the esterification with chiral **25** significant racemization was observed, with a completely racemic mixture being observed in refluxing toluene and a 71:29 mixture of enantiomers being observed in DCM at room temperature (Table 4). Similar results were observed with imidate **37**, with a nearly racemic mixture being isolated from the reaction in refluxing toluene and a scalemic 67:33 mixture being isolated from the esterification in DCM at room temperature.

Table 4. Esterification with Enantioenriched Imidates



entry	imidate	conditions	yield (%)	er
1	**25**	toluene, Δ, 24 h	95	50:50 (**25a**)
2	**25**	DCM, rt, 24 h	35	71:29 (**25a**)
3	**37**	toluene, Δ, 24 h	73	55:45 (**38**)
4	**37**	DCM, rt, 24 h	60	67:33 (**38**)

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With the significant racemization that was observed with chiral imidates an S_N2 type substitution mechanism was ruled out as being operative in these systems, as an S_N2 mechanism proceeds with inversion. This left either a radical or a cationic mechanism as possibilities for the formation of the esters. Given that a radical substitution reaction should also proceed well with an electron poor imidate (like **23**), it seemed unlikely that a radical intermediate was involved in the transformation. The available evidence seems to implicate a cationic mechanism, as shown in Figure 3. Symbiotic activation of

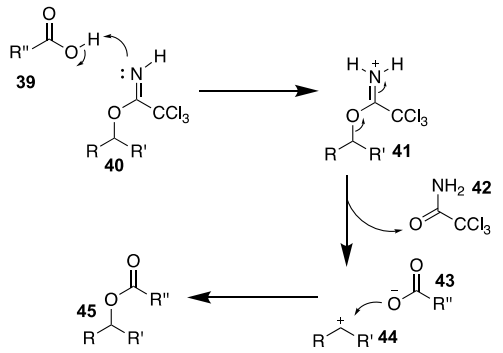

Figure 3. Ester formation via symbiotic activation of the trichloroacetimidate.

the imidate with the proton from carboxylic acid leads to intermediate **41**. Loss of trichloroacetamide **42** then produces the carbocation **44**, which is trapped by the carboxylate anion **43** to provide the ester product **45**. Further supporting this mechanism is the fact that the addition of triethylamine to esterifications with imidate **20**[18a] and **26**[18b] effectively poisoned the reaction and halted the esterification. The more basic amine likely deprotonates the carboxylic acid, halting the activation of the imidate and disrupting the esterification. While carbocation formation is predicted to provide a racemic mixture, scalemic mixtures often result from cationic processes due to ion pairing.[28]

While an S_N1 mechanism is implicated for secondary benzylic trichloroacetimidates, less reactive trichloroacetimidates may form esters through different pathways. This is supported by the lack of Friedel–Crafts alkylation products in the results described in Table 3, even though benzyl trichloroacetimidate is known to alkylate aromatic systems like toluene when treated with strong Lewis acids which presumably proceeds through a carbocation.[29] Additionally, prenyl trichloroacetimidate **15** has been reported to provide a nearly 1:1 mixture of prenyl and *tert*-prenyl ethers in the presence of a strong Lewis acid (TMSOTf),[30] while in the esterification reaction with **15** (Table 1), the prenyl ester is highly favored and only a small amount of the *tert*-prenyl ester is observed. These results imply that some imidate esterifications with less reactive imidates may not be proceeding through a discreet carbocation. The possibility of a radical pathway was ruled out by repeating the esterification of benzoic acid with prenyl imidate **15** in the presence of 1 equiv of TEMPO, a known radical trap.[31] This reaction provided a 50% yield of ester **15a**, so the esterification cannot be proceeding exclusively through a radical intermediate. Instead, less reactive trichloroacetimidates may esterify through an S_N2 mechanism on a protonated imidate intermediate (like **41** when the R groups are small).

CONCLUSIONS

Esterification reactions of a number of structurally distinct trichloroacetimidate electrophiles have been studied. Only imidates that are precursors to stabilized carbocations function as reliable esterification reagents under promoter free conditions. Many of these systems undergo esterification at room temperature, although several others can be used by simple heating the trichloroacetimidate in refluxing toluene. No alkene isomerization or alkylation of other protic functional groups (like alcohols or amides) was observed under these esterification conditions, providing a mild method for the formation of an ester in the presence of complex functionality. The ability to form esters from imidates without the addition of an acid or base promoter will be useful in the esterification of complex substrates that possess sensitive functionality.

EXPERIMENTAL SECTION

The methyl-2,2,2-trichloroacetimidate **10**, ethyl-2,2,2-trichloroacetimidate **11**, *t*-butyl-2,2,2-trichloroacetimidate **13**, allyl-2,2,2-trichloroacetimidate **14**, and benzyl-2,2,2-trichloroacetimidate **17** used in these studies were purchased from commercial sources. Cyclohexyl-2,2,2-trichloroacetimidate **12**,[32] prenyl-2,2,2-trichloroacetimidate **15**,[33] propargyl-2,2,2-trichloroacetimidate **16**,[34] (2,4,6-trimethylphenyl)methyl-2,2,2-trichloroacetimidate **18**,[35] (4-methoxyphenyl)methyl-2,2,2-trichloroacetimidate **20**,[18a] (3,4-dimethoxoxyphenyl)methyl-2,2,2-trichloroacetimidate **22**,[36] (4-nitrophenyl)methyl-2,2,2-trichloroacetimidate **23**,[21] furfuryl-2,2,2-trichloroacetimidate **24**,[34] 1-phenethyl-2,2,2-trichloroacetimidate **25**,[26a,37] diphenylmethyl-2,2,2-trichloroacetimidate **26**,[18b,38] and (2-methoxyphenyl)phenylmethyl-2,2,2-trichloroacetimidate **29**[21] were synthesized as previously reported.

General Procedure for the Synthesis of Trichloroacetimidates from the Corresponding Alcohol. A flame-dried 25 mL round bottom flask was charged with the alcohol starting material (1 equiv) under argon. Dry DCM was then added to form a 0.5 M solution, and the flask was cooled to 0 °C. DBU (0.2 equiv) was added to the solution, followed by trichloroacetonitrile (1.5 equiv). The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was concentrated and silica gel column chromatography was performed to provide the desired trichloroacetimidates.

*(2-Methoxyphenyl)methyl-2,2,2-trichloroacetimidate (**19**).* It was obtained as clear oil (1.49 g, 73%) and purified by silica gel chromatography (4% ethyl acetate/1% triethylamine/95% hexanes). TLC R_f = 0.55 (10% ethyl acetate/90% hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (br s, 1H), 7.45 (dd, J = 7.5, 1.6 Hz, 1H), 7.32 (td, J = 8.0, 1.7 Hz, 1H), 6.98 (td, J = 7.5, 0.9 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 5.40 (s, 2H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.8, 157.2, 129.4, 128.7, 124.0, 120.4, 110.4, 91.6, 66.6, 55.4. Anal. Calcd for $C_{10}H_{10}Cl_3NO_2$: C, 42.51; H, 3.57; N, 4.96. Found: C, 42.62; H, 3.74; N, 4.95.

*(2,4-Dimethoxyphenyl)methyl-2,2,2-trichloroacetimidate (**21**).* It was obtained as yellow oil (7.40 g, 99%) and purified by silica gel chromatography (30% ethyl acetate/69% hexanes/1% triethylamine). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 6.49 (t, J = 2.4 Hz, 2H), 5.30 (s, 2H), 3.81 (s, 3H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.9, 161.3, 158.8, 130.6, 116.4, 104.0, 98.6, 98.4, 91.7, 66.6, 55.4; Anal. Calcd for $C_{11}H_{12}Cl_3NO_3$: C, 42.27; H, 3.87; N, 4.48. Found: C, 42.28; H, 3.56; N, 4.57.

General Procedure for Esterification by Method A. In a flame-dried flask, the trichloroacetimidate (2 equiv) was dissolved in dichloromethane (0.25 M) under argon. The carboxylic acid (1 equiv) was then added, and the mixture was stirred at room temperature. The reaction progress was monitored by thin layer chromatography. After completion, the reaction mixture was poured into 2 N NaOH and extracted with DCM (3×). The combined

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organic extracts were then dried over sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography to give the ester product.

General Procedure for Esterification by Method B. The carboxylic acid (1 equiv) and trichloroacetimidate (2 equiv) were placed in a flame-dried round bottom flask under argon. Anhydrous toluene (0.25 M) was then added and the reaction was heated to reflux. The reaction progress was monitored by thin layer chromatography. After disappearance of the carboxylic acid, the mixture was allowed to cool to rt, poured into 2 N NaOH, and extracted with DCM (3×). The combined organic extracts were then dried over sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography to give the ester product.

*tert-Butyl Benzoate (**13a**).*[39] It was obtained as clear oil (0.097 g, 84%) and purified by silica gel chromatography (1% ethyl acetate/99% hexane). TLC R_f = 0.53 (10% ethyl acetate/90% hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01−7.91 (m, 2H), 7.55−7.49 (m, 1H), 7.41 (t, J = 7.6 Hz, 2H), 1.60 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 165.8, 132.4, 132.0, 129.4, 128.2, 81.0, 28.2.

*tert-Butyl 2,2-Diphenylacetate (**13b**).*[40] It was obtained as a white solid (0.064 g, 91%) and purified by silica gel chromatography (2% ethyl acetate/98% hexanes). TLC R_f = 0.68 (10% ethyl acetate/90% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.23 (m, 10 H), 4.91 (s, 1H), 1.44 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.7, 139.2, 128.6, 128.5, 127.0, 81.3, 58.0, 28.0.

*tert-Butyl 2-Methyl-2-phenylpropanoate (**13c**).*[41] It was obtained as clear oil (0.087 g, 30%) and purified by silica gel chromatography (3% ethyl acetate/97% hexanes). TLC R_f = 0.71 (10% ethyl acetate/90% hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.26 (m, 5H), 1.53 (s, 6H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.2, 145.5, 128.4, 126.6, 125.8, 80.5, 47.3, 28.0, 26.7.

*tert-Butyl 2-Bromododecanoate (**13d**).*[42] It was obtained as an amorphous solid (0.091 g, 94%) and purified by silica gel chromatography (100% diethyl ether). TLC R_f = 0.54 (100% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (t, J = 7.1 Hz, 1H), 2.02−1.87 (m, 2H), 1.46 (s, 9H), 1.41−1.11 (m, 16 H), 0.86 (t, J = 5.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.0, 82.2, 47.9, 35.0, 31.9, 29.54, 29.47, 29.33, 29.30, 28.9, 27.8, 27.3, 22.7, 14.1.

*(±)-tert-Butyl-2-hydroxy-2-phenylacetate (**13e**).*[43] It was obtained as a white solid (0.079 g, 59%) and purified by silica gel chromatography (5% ethyl acetate/95% hexanes). TLC R_f = 0.65 (50% ethyl acetate/50% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.30 (m, 5H), 5.03 (d, J = 6.0 Hz, 1H), 3.53 (d, J = 6.0 Hz, 1H), 1.40 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.9, 139.0, 128.4, 128.1, 126.4, 83.1, 73.0, 27.8.

*(±)-tert-Butyl-2-[(tert-butoxycarbonyl)amino]phenylpropionate (**13f**).*[44] It was obtained as clear oil (0.90 g, 90%) and purified by silica gel chromatography (4% ethyl acetate/96% hexanes). TLC R_f = 0.75 (10% ethyl acetate/90% hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31−7.16 (m, 5H), 5.00 (br s, 1H), 4.45−4.44 (m, 1H), 3.05 (d, J = 5.8 Hz, 2H), 1.42 (s, 9H), 1.40 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.0, 155.1, 136.4, 129.6, 128.3, 126.8, 82.0, 79.6, 54.9, 38.6, 28.3, 27.9.

*2,2-Dimethylpropyl But-3-enoate (**13g**).*[45] It was obtained as clear colorless oil (70 mg, 35% yield) and purified by silica gel column chromatography (10% diethyl ether, 90% pentane). TLC R_f = 0.76 (10% ethyl acetate/90% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88−5.78 (m, 1H), 5.06 (dq, J = 14.0, 1.6 Hz, 2H), 2.93 (d, J = 6.9 Hz, 2H) 1.38 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz $CDCl_3$): δ 170.8, 130.9, 117.9, 80.5, 40.4, 28.0.

*(E)-tert-Butyl Cinnamate (**13h**).*[46] It was obtained as clear oil (0.052 g, 60%) and purified by silica gel chromatography (1−4% ethyl acetate/hexanes). TLC R_f = 0.71 (10% ethyl acetate/90% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 16.0 Hz, 1H), 7.50−7.49 (m, 2H), 7.36−7.36 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.3, 143.5, 134.7, 129.9, 128.8, 128.0, 120.2, 80.5, 28.2.

*tert-Butyl (2Z)-3-(2-Methoxyphenyl)prop-2-enoate (**13i**).* It was obtained as clear oil (0.100 g, 76%) and purified by silica gel chromatography (8% ethyl acetate/92% hexanes). TLC R_f = 0.52 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 2979, 1716, 1629, 1463, 1110, 1049, 738; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.3 Hz, 1H), 7.31−7.27 (m, 1H), 7.07 (d, J = 12.3 Hz, 1H), 6.94−6.86 (m, 2H), 5.91 (d, J = 12.4 Hz, 1H), 3.84 (s, 3H), 1.39 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.8, 157.0, 137.5, 130.6, 130.0, 124.7, 122.3, 120.0, 110.2, 80.3, 55.5, 28.0. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.00; H, 7.36.

*tert-Butyl 2-Pyridinecarboxylate (**13j**).*[47] It was obtained as clear oil (0.095 g, 81%) and purified by silica gel chromatography (45% ethyl acetate/55% hexanes). TLC R_f = 0.40 (50% ethyl acetate/50% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (dd, J = 4.7, 0.7 Hz, 1H), 8.19 (d, J = 7.9 Hz, 1H), 7.80 (td, J = 7.7, 1.8 Hz, 1H), 7.42 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 1.64 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.5, 150.0, 149.8, 137.0, 126.6, 125.0, 82.5, 28.3.

*3-Methylbut-2-en-1-yl Benzoate (**15a**).*[48] It was obtained as clear colorless oil (0.126 g, 63% yield) and purified by silica gel column chromatography (10% ethyl acetate, 90% hexanes). TLC R_f = 0.60 (10% ethyl acetate/90% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08−8.06 (m, 2H), 7.58−7.53 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H) 5.52−5.48 (m, 1H), 4.85 (d, J = 7.2 Hz, 2H), 1.80 (d, J = 6.3 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz $CDCl_3$): δ 166.6, 139.1, 132.8, 130.5, 129.6, 128.3, 118.8, 61.9, 25.8, 18.1.

*(Phenyl)methyl Benzoate (**17a**).*[49] It was obtained as clear oil (0.082 g, 58%) and purified by silica gel chromatography (2% ethyl acetate/98% hexane). TLC R_f = 0.57 (10% ethyl acetate/90% hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46−7.34 (m, 7H), 5.37 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.4, 136.1, 133.0, 130.2, 129.7, 128.6, 128.4, 128.2, 128.2, 66.7.

*(Phenyl)methyl 2,2-Diphenylacetate (**17b**).*[50] It was obtained as a white solid (0.079 g, 88%) and purified by silica gel chromatography (2% ethyl acetate/98% hexanes). TLC R_f = 0.60 (10% ethyl acetate/90% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.25 (m, 15H), 5.17 (s, 2H), 5.07 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4, 138.7, 135.8, 128.73, 128.68, 128.24, 128.21, 127.36, 127.33, 68.0, 57.1.

*(Phenyl)methyl 2-Methyl-2-phenylpropanoate (**17c**).* It was obtained as clear oil (0.157 g, 94%) and purified by silica gel chromatography (4% ethyl acetate/96% hexanes). TLC R_f = 0.50 (100% hexanes); IR (film, cm^{-1}) ν_{max}: 3089, 2976, 1729, 1497, 1425, 1412, 737; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.19 (m, 10H), 5.10 (s, 2H), 1.60 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.5, 144.5, 136.2, 128.40, 128.36, 127.9, 127.7, 126.7, 125.7, 66.4, 46.6, 26.5. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.58; H, 7.03.

*(Phenyl)methyl 2-Bromododecanoate (**17d**).* It was obtained as clear oil (0.193 g, 80%) and purified by silica gel chromatography (3% ethyl acetate/97% hexane). TLC R_f = 0.68 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 2928, 2305, 1740, 1422, 1265, 738; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.35 (m, 5H), 5.20 (s, 2H), 4.25 (t, J = 7.3 Hz, 1H), 2.06−1.95 (m, 2H), 1.35−1.21 (m, 16H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.7, 135.2, 128.8, 128.6, 128.5, 128.3, 128.2, 70.7, 67.5, 46.0, 34.9, 31.9, 29.5, 29.5, 29.3, 28.8, 27.2, 22.7, 14.1. Anal. Calcd for $C_{19}H_{29}BrO_2$: C, 61.79; H, 7.91. Found: C, 61.69; H, 8.01.

*(±)-(Phenyl)methyl-2-hydroxy-2-phenylacetate (**17e**).*[13b] It was obtained as a white solid (0.209 g, 88%) and purified by silica gel chromatography (10% ethyl acetate/90% hexanes). TLC R_f = 0.48 (30% ethyl acetate/70% hexanes); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.30 (m, 8H), 7.21−7.19 (m, 2H), 5.25−5.12 (m, 3H), 3.42 (d, J = 5.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.5, 138.2, 135.0, 128.60, 128.56, 128.5, 128.4, 128.0, 126.6, 73.0, 67.7.

*Boc-phenylalanine (Phenyl)methyl Ester (**17f**).*[51] It was obtained as clear oil (0.251 g, 94%) and purified by silica gel chromatography (10% ethyl acetate/90% hexanes). TLC R_f = 0.57 (20% ethyl acetate/80% hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.21 (m, 8H), 7.06−7.03 (m, 2H), 5.13 (q, J = 12.3 Hz, 2H), 4.97 (d, J = 7.7 Hz, 1H), 4.63 (q, J = 7.7 Hz, 1H), 3.08 (t, J = 5.2 Hz, 2H), 1.41 (s, 9H);

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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.8, 155.1, 135.9, 135.2, 129.4, 128.6, 128.6, 127.0, 79.9, 67.1, 54.5, 38.3, 28.3.

*(Phenyl)methyl But-3-enoate (**17g**).*[52] It was obtained as clear oil (0.180 g, 88%) and purified by silica gel chromatography (2% ethyl acetate/98% hexanes). TLC R_f = 0.62 (10% ethyl acetate/90% hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 5H), 6.00−5.90 (m, 1H), 5.20−5.14 (m, 4H), 3.15 (d, J = 7.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.4, 135.9, 130.1, 128.6, 128.3, 128.2, 118.7, 66.5, 39.1.

*(Phenyl)methyl Cinnamate (**17h**).*[53] It was obtained as viscous oil (0.120 g, 77%) and purified by silica gel chromatography (2% ethyl acetate/98% hexanes). TLC R_f = 0.63 (10% ethyl acetate/90% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 15.9 Hz, 1H), 7.47−7.44 (m, 2H), 7.36−7.27 (m, 8H), 6.42 (d, J = 16.2 Hz, 1H), 5.18 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8, 145.2, 136.1, 134.4, 130.4, 128.9, 128.6, 128.3, 128.3, 128.1, 117.9, 66.4.

*Benzyl (2Z)-3-(2-Methoxyphenyl)prop-2-enoate (**17i**).* It was obtained as clear oil (0.120 g, 80%) and purified by silica gel chromatography (6% ethyl acetate/94% hexanes). TLC R_f = 0.38 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 1721, 1600, 1488, 1265, 1157, 1028, 745; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.5 Hz, 1H), 7.32−7.18 (m, 7H), 6.89−6.85 (m, 2H) 6.03 (d, J = 12.4 Hz, 1H), 5.13 (s, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.3, 161.2, 158.9, 157.2, 138.9, 131.3, 130.8, 130.3, 124.1, 120.0, 120.0, 116.8, 110.2, 104.0, 98.5, 61.3, 55.4. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.35; H, 5.64.

*(Phenyl)methyl Picolinate (**17j**).*[54] It was obtained as yellow oil (0.120 g, 57%) and purified by silica gel chromatography (50% ethyl acetate/50% hexanes). TLC R_f = 0.47 (50% ethyl acetate/50% hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, J = 4.6 Hz, 1H), 8.13 (d, J = 7.9 Hz, 1H), 7.82 (dt, J = 7.7, 1.7 Hz, 1H), 7.50−7.45 (m, 3H), 7.40−7.33 (m, 3H), 5.46 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.0, 150.0, 148.0, 137.0, 135.6, 128.6, 128.6, 128.4, 126.9, 125.3, 67.5.

*(S)-(Phenyl)methyl-2-(6-methoxynaphthalen-2-yl)propanoate (**17k**).* It was obtained as a yellow solid (0.110 g, 79%) and purified by silica gel chromatography (2% ethyl acetate/98% hexanes). $[\alpha]_D^{23}$ −3.7 (c 0.35, DCM); mp = 72−73 °C; TLC R_f = 0.48 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3055, 2982, 1733, 1634, 1265, 738; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 3H), 7.41 (d, J = 1.6 Hz, 1H), 7.28−7.25 (m, 5H), 7.14−7.11 (m, 2H), 5.11 (q, J = 12.4 Hz, 2H), 3.93−3.88 (m, 4H), 1.59 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.5, 157.6, 136.0, 135.6, 133.7, 129.3, 128.9, 128.5, 128.1, 127.9, 127.1, 126.3, 126.0, 119.0, 105.6, 66.5, 55.3, 45.5, 18.5. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.35; H, 5.64. The er was determined by chiral HPLC (OD-H), n-hexane/i-PrOH = 99:1, 1 mL/min; t_1 = 10.1; t_2 = 12.2 min.

*(2,4,6-Trimethylphenyl)methyl Benzoate (**18a**).*[8f] It was obtained as clear oil (0.171 g, 82%) and purified by silica gel chromatography (4−6% ethyl acetate/96−94% hexane). TLC R_f = 0.66 (20% ethyl acetate/80% hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, J = 8.2, 1.0 Hz, 2H), 7.56−7.39 (m, 1H), 7.41 (t, J = 7.7 Hz, 2H), 6.92 (s, 2H), 5.42 (s, 2H), 2.42 (s, 6H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.8, 138.5, 138.4, 132.9, 130.2, 129.7, 129.2, 129.1, 128.3, 61.6, 21.0, 19.6.

*(2-Methoxyphenyl)methyl Benzoate (**19a**).*[55] It was obtained as clear oil (0.080 g, 96%) and purified by silica gel chromatography (1% ethyl acetate/99% pentane). TLC R_f = 0.49 (10% ethyl acetate/90% hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 3H), 7.30 (td, J = 8.0, 1.6 Hz, 1H), 6.98 (t, J = 0.4 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 5.42 (s, 2H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.6, 157.6, 132.9, 130.5, 129.7, 129.53, 129.45, 128.4, 124.5, 120.5, 110.5, 62.2, 55.5.

*(4-Methoxyphenyl)methyl Benzoate (**20a**).*[56] It was obtained as colorless oil (0.530 g, 89%) and purified by silica gel chromatography (10% ethyl acetate/90% hexanes). TLC R_f = 0.57 (20% ethyl acetate/80% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 8.10−8.03 (m, 2H), 7.59−7.51 (m, 1H), 7.47−7.36 (m, 4H), 6.92 (d, J = 8.8 Hz, 2H), 5.31 (s, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.7, 159.9, 133.2, 130.5, 130.3, 129.9, 128.5, 128.4, 114.2, 66.7, 55.5.

*(4-Methoxyphenyl)methyl 2,2-Diphenylacetate (**20b**).* It was obtained as a white solid (0.120 g, 96%) and purified by silica gel chromatography (4% ethyl acetate/96% hexanes). TLC R_f = 0.50 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 2986, 1734, 1613, 1516, 1265, 739, 703; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.21 (m, 12H), 6.85 (d, J = 8.7 Hz, 2H), 5.12 (s, 2H), 5.04 (s, 1H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4, 159.6, 138.6, 130.1, 128.6, 128.6, 127.8, 127.2, 113.9, 66.8, 57.1, 55.3. Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.07. Found: C, 79.34; H, 5.97.

*(4-Methoxyphenyl)methyl 2-Methyl-2-phenylpropanoate (**20c**).*[18a] It was obtained as clear oil (0.120 g, 86%) and purified by silica gel chromatography (8% ethyl acetate/92% hexanes). TLC R_f = 0.51 (50% ethyl acetate/50% hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31−7.20 (m, 5H), 7.14 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 5.03 (s, 2H), 3.77 (s, 3H), 1.57 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 176.5, 159.4, 144.6, 129.5, 128.3, 128.3, 126.6, 125.7, 113.8, 66.3, 55.2, 46.6, 26.5.

*(4-Methoxyphenyl)methyl 2-Bromododecanoate (**20d**).* It was obtained as yellow oil (0.407 g, 93%) and purified by silica gel chromatography (15% ethyl acetate/85% hexanes). TLC R_f = 0.65 (25% ethyl acetate/75% hexanes); IR (film, cm^{-1}) ν_{max}: 3001, 2906, 2851, 1724, 1514, 1229; ^1H NMR (300 MHz, $CDCl_3$): δ 7.25 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 5.07 (s, 2H), 4.15 (t, J = 7.4 Hz, 1H), 3.73 (s, 3H), 1.98−1.91 (m, 2H), 1.30−1.10 (m, 16H), 0.82 (t, J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 170.0, 160.8, 130.4, 127.6, 114.2, 67.6, 55.5, 46.4, 35.2, 32.1, 29.8, 29.7, 29.6, 29.1, 27.5, 22.9, 14.6. Anal Calcd for $C_{20}H_{31}BrO_3$: C, 60.15; H, 7.82. Found: C, 60.01; H, 7.52.

*(±)-(4-Methoxyphenyl)methyl-2-hydroxy-2-phenylacetate (**20e**).*[56] It was obtained as colorless oil (0.495 g, 79%) and purified by silica gel chromatography (20% ethyl acetate/80% hexanes). TLC R_f = 0.65 (30% ethyl acetate/70% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.25 (m, 5H), 7.09 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 5.11−4.96 (m, 3H), 3.71 (s, 3H), 3.57 (d, J = 6.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 173.8, 160.0, 138.5, 130.2, 128.8, 128.7, 127.3, 126.9, 114.2, 73.2, 67.8, 55.5.

*(±)-(4-Methoxyphenyl)methyl-2-[(tert-butoxycarbonyl)amino]-phenylpropionate (**20f**).*[57] It was obtained as colorless oil (0.342 g, 89%) and purified by silica gel chromatography (20% ethyl acetate/80% hexanes). TLC R_f = 0.61 (30% ethyl acetate/70% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.20−7.11 (m, 5H), 6.99−6.87 (m, 2H), 6.75 (d, J = 9.0 Hz, 2H), 5.03−4.97 (m, 3H), 4.60−4.45 (m, 1H), 3.73 (s, 3H), 3.11−2.90 (m, 2H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 173.5, 160.1, 155.5, 138.6, 132.3, 130.3, 129.5, 127.8, 127.5, 114.6, 80.2, 67.1, 55.5, 54.0, 39.1, 28.5.

*(4-Methoxyphenyl)methyl But-3-enoate (**20g**).*[52] It was obtained as colorless oil (0.389 g, 93% yield) and purified by silica gel chromatography (5% ethyl acetate/95% hexanes). TLC R_f = 0.50 (5% ethyl acetate/95% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 5.92−5.82 (m, 1H), 5.13−5.11 (m, 1H), 5.08−5.03 (m, 1H), 5.00 (s, 2H), 3.72 (s, 3H), 3.06−3.03 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 171.6, 159.9, 130.5, 130.4, 128.2, 118.8, 114.2, 66.5, 55.5, 39.4.

*(4-Methoxyphenyl)methyl Cinnamate (**20h**).*[58] It was obtained as a white solid (0.508 g, 94%) and purified by silica gel chromatography (10% ethyl acetate/90% hexanes). TLC R_f = 0.64 (20% ethyl acetate/80% hexanes); mp = 61−63 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J = 16.2 Hz, 1H), 7.55−7.48 (m, 2H), 7.41−7.33 (m, 5H), 6.92 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 16.2 Hz, 1H), 5.19 (s, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 167.0, 159.8, 145.1, 134.5, 130.4, 130.3, 129.0, 128.3, 128.2, 118.1, 114.1, 66.3, 55.4.

*(4-Methoxyphenyl)methyl (2Z)-3-(2-Methoxyphenyl)prop-2-enoate (**20i**).* It was obtained as clear oil (0.140 g, 84%) and purified by silica gel chromatography (10% ethyl acetate/90% hexanes). TLC R_f = 0.42 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 2958, 2837, 1720, 1613, 1515, 1262, 1030, 737; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, J = 7.6, 1.1 Hz, 1H), 7.31−7.20 (m, 3H), 7.14 (s,

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1H), 6.89−6.82 (m, 4H), 5.98 (d, J = 12.4 Hz, 1H), 5.05 (s, 2H), 3.77 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.2, 159.6, 157.2, 139.4, 130.8, 130.4, 130.2, 128.1, 124.1, 120.0, 119.8, 113.9, 110.3, 65.8, 55.4, 55.3. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.14; H, 6.11.

*(4-Methoxyphenyl)methyl Picolinate (**20j**).* It was obtained as yellow oil (0.516 g, 83%) and purified by silica gel chromatography (50% ethyl acetate/50% hexanes). TLC R_f = 0.30 (50% ethyl acetate/50% hexanes); IR (film, cm^{-1}) ν_{max}: 3057, 3005, 2957, 2837, 1717; ^1H NMR (300 MHz, $CDCl_3$): δ 8.76 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.85−7.79 (m, 1H), 7.48−7.42 (m, 3H), 6.90 (d, J = 8.7 Hz, 2H), 5.40 (s, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.2, 159.8, 150.0, 148.2, 137.0, 130.6, 127.9, 127.0, 125.3, 114.0, 67.4, 55.3. Anal Calcd for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found C, 69.52; H, 5.65; N, 5.73.

*(2,4-Dimethoxyphenyl)methyl Benzoate (**21a**).* It was obtained as clear oil (0.062 g, 90%) and purified by silica gel chromatography (6% ethyl acetate/94% hexanes). TLC R_f = 0.29 (10% ethyl acetate/90% hexane); IR (film, cm^{-1}) ν_{max}: 3003, 2837, 1721, 1275, 712; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.34−7.32 (m, 1H), 6.49−6.46 (m, 2H), 5.34 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.7, 161.3, 159.0, 132.8, 131.2, 130.6, 129.7, 128.3, 116.9, 104.1, 98.6, 62.1, 55.5, 55.4. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.57; H, 5.87.

*(2,4-Dimethoxyphenyl)methyl 2,2-Diphenylacetate (**21b**).* It was obtained as clear oil (0.120 g, 88%) and purified by silica gel chromatography (15% ethyl acetate/85% hexanes). TLC R_f = 0.27 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 1731, 1616, 1209, 1035, 701; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−7.23 (m, 10H), 7.15 (d, J = 8.7 Hz, 1H), 6.42−6.39 (m, 2H), 5.16 (s, 2H), 5.04 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4, 161.3, 159.0, 138.9, 131.3, 128.7, 128.5, 127.1, 116.6, 103.9, 98.5, 62.6, 57.1, 55.4, 55.3. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.08; H, 6.10.

*(2,4-Dimethoxyphenyl)methyl 2-Methyl-2-phenylpropanoate (**21c**).* It was obtained as clear oil (0.200 g, 85%) and purified by silica gel chromatography (8% ethyl acetate/92% hexanes). TLC R_f = 0.45 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3061, 2936, 1718, 1612, 1508, 1206, 1098, 1029, 731, 697; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26−7.11 (m, 5H), 6.98 (d, J = 7.8 Hz, 1H), 6.32−6.30 (m, 2H), 5.00 (s, 2H), 3.71 (s, 3H), 3.63 (s, 3H), 1.50 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 176.6, 161.0, 158.7, 144.9, 130.5, 128.2, 126.5, 125.8, 117.1, 103.8, 98.4, 62.1, 55.4, 55.3, 46.7, 26.5. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.36; H, 7.17.

*(2,4-Dimethoxyphenyl)methyl 2-Bromododecanoate (**21d**).* It was obtained as clear oil (0.099 g, 81%) and purified by silica gel chromatography (5% ethyl acetate/95% hexane). TLC R_f = 0.57 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 1422, 1265, 1038, 896, 739. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 1H), 6.48−6.46 (m, 2H), 5.18 (s, 2H) 4.22 (t, J = 7.4 Hz, 1H), 3.81 (s, 6H), 2.11−1.92 (m, 2H), 1.49−1.19 (m, 16H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.9, 161.5, 159.0, 131.4, 116.1, 104.0, 98.6, 63.1, 55.4, 55.4, 46.4, 35.0, 31.9, 29.6, 29.5, 29.3, 29.3, 28.9, 27.2, 22.7, 14.1. Anal. Calcd for $C_{21}H_{33}BrO_4$: C, 58.74; H, 7.75. Found: C, 58.57; H, 7.65.

*(±)-(2,4-Dimethoxyphenyl)methyl-2-hydroxy-2-phenylacetate (**21e**).* It was obtained as a white amorphous solid (0.150 g, 94%) and purified by silica gel chromatography (50% ethyl acetate/50% hexanes). TLC R_f = 0.37 (50% ethyl acetate/50% hexanes); mp = 290−292 °C; IR (film, cm^{-1}) ν_{max}: 3054, 2835, 1729, 1274, 762; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.39 (m, 2H), 7.34−7.28 (m, 3H), 7.07 (d, J = 8.9 Hz, 1H), 6.39 (br s, 2H), 5.16−5.15 (m, 3H), 3.78 (s, 3H), 3.67 (s, 3H), 3.54 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.6, 161.5, 159.0, 138.5, 131.2, 128.4, 128.3, 126.6, 115.8, 103.9, 98.5, 72.9, 63.5, 55.4, 55.3. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.72; H, 5.87.

*(±)-(2,4-Dimethoxyphenyl)methyl-2-[(tert-butoxycarbonyl)-amino]phenylpropionate (**21f**).* It was obtained as clear oil (0.101 g, 80%) and purified by silica gel chromatography (15% ethyl acetate/85% hexanes). TLC R_f = 0.37 (40% ethyl acetate/60% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 2985, 1709, 1421, 1261, 739; ^1H NMR (300 MHz, CD_3OD): δ 7.26−7.16 (m, 6H), 6.56 (d, J = 2.2 Hz, 1H), 6.50 (dd, J = 8.3, 2.3 Hz, 1H), 5.11 (q, J = 12.1 Hz, 2H), 4.38 (q, J = 6.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.10 (dd, J = 13.9, 5.6 Hz, 1H), 2.91 (dd, J = 13.7, 8.6 Hz, 1H), 1.39 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ 172.3, 161.7, 159.0, 156.4, 136.9, 131.2, 128.9, 128.0, 126.4, 116.0, 104.1, 97.9, 79.2, 62.1, 55.2, 54.6, 54.4, 37.3, 27.3. Anal Calcd for $C_{23}H_{29}NO_6$: C, 66.49; H, 7.04; N, 3.37. Found: C, 66.20; H, 6.93; N, 3.76.

*(2,4-Dimethoxyphenyl)methyl But-3-enoate (**21g**).* It was obtained as clear oil (0.163 g, 73%) and purified by silica gel chromatography (15% ethyl acetate/85% hexanes). TLC R_f = 0.40 (15% ethyl acetate/85% hexanes); IR (film, cm^{-1}) ν_{max}: 2963, 2838, 2616, 1464, 1371, 1209, 739; ^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 8.9 Hz, 1H), 6.46 (hextet, J = 2.4 Hz, 2H), 6.00−5.87 (m, 1H), 5.18−5.11 (m, 4H), 3.81 (s, 3H), 3.80 (s, 3H), 3.11 (dt, J = 6.9, 1.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.6, 161.3, 159.0, 131.4, 130.5, 118.4, 116.7, 104.1, 98.6, 61.9, 55.5, 55.4, 39.2. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.91; H, 6.47.

*(2,4-Dimethoxyphenyl)methyl Cinnamate (**21h**).* It was obtained as viscous oil (0.139 g, 88%) and purified by silica gel chromatography (4% ethyl acetate/98% hexanes). TLC R_f = 0.38 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 1708, 1510, 1161, 737. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 16.1 Hz, 1H), 7.51−7.49 (m, 2H), 7.37−7.35 (m, 3H), 7.30 (d, J = 8.9 Hz, 1H), 6.49−6.51−6.43 (m, 3H), 5.23 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 167.1, 161.3, 159.1, 144.7, 134.6, 131.5, 130.2, 128.9, 128.1, 118.4, 116.8, 104.1, 98.6, 61.8, 55.5, 55.4. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.20; H, 5.71.

*(2,4-Dimethoxyphenyl)methyl (2Z)-3-(2-Methoxyphenyl)prop-2-enoate (**21i**).* It was obtained as clear oil (0.170 g, 92%) and purified by silica gel chromatography (20% ethyl acetate/80% hexanes). TLC R_f = 0.29 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 2986, 2839, 1717, 1616, 1488, 1209, 1159, 739, 705; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.5 Hz, 1H), 7.31−7.26 (m, 1H), 7.18−7.15 (m, 2H), 6.90−6.85 (m, 2H), 6.44−6.41 (m, 2H), 6.01 (d, J = 12.5 Hz, 1H), 5.14 (s, 2H), 3.81 (s, 6H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.3, 161.2, 158.9, 157.2, 138.9, 131.3, 130.8, 130.3, 124.1, 120.00, 119.94, 116.8, 110.3, 104.0, 98.5, 61.3, 55.41, 55.40. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.87; H, 6.47.

*(2,4-Dimethoxyphenyl)methyl Picolinate (**21j**).* It was obtained as yellow oil (0.150 g, 83%) and purified by silica gel chromatography (50% ethyl acetate/50% hexanes). TLC R_f = 0.25 (50% ethyl acetate/50% hexanes); IR (film, cm^{-1}) ν_{max}: 2964, 1721, 1616, 1377, 927; ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (dd, J = 4.7 Hz, 0.7 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.79 (td, J = 7.8, 1.7 Hz, 1H), 7.41 (ddd, J = 7.6, 4.8, 1.1 Hz 1H), 7.34 (d, J = 9.0 Hz, 1H), 6.48−6.46 (m, 2H), 5.43 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.2, 161.4, 159.1, 150.0, 148.5, 136.8, 131.6, 126.7, 125.2, 116.5, 104.1, 98.6, 62.9, 55.5, 55.4. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.17; H, 5.54; N, 5.44.

*3,4-Dimethoxybenzyl Benzoate (**22a**).*[59] It was obtained as clear oil (0.17 g, 96%) and purified by silica gel chromatography (5% ethyl acetate/95% hexanes). TLC R_f = 0.40 (20% ethyl acetate/80% hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.03−6.97 (m, 2H), 6.85 (d, J = 8.0 Hz, 1H), 5.29 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.5, 149.1, 149.0, 133.0, 130.2, 129.7, 128.6, 128.4, 121.3, 111.9, 111.1, 66.8, 55.9.

*(Furan-2-yl)methyl Benzoate (**24a**).*[60] It was obtained as yellow oil (0.127 g, 96%) and purified by silica gel chromatography (1% ethyl acetate/99% hexane). TLC R_f = 0.46 (10% ethyl acetate/90% hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.2 Hz, 2H), 7.57−7.53 (m, 1H), 7.45−7.41 (m, 3H), 6.49 (d, J = 3.2 Hz, 1H), 6.39−6.38 (m, 1H), 5.31 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz,

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$CDCl_3$): δ 166.3, 149.6, 143.3, 133.1, 129.9, 129.8, 128.4, 110.8, 110.6, 58.5.

*1-Phenethyl Benzoate (**25a**).*[53] It was obtained as clear oil (0.140 g, 95%) and purified by silica gel chromatography (2% ethyl acetate/98% hexane). TLC R_f = 0.23 (10% ethyl acetate/90% hexane); ^1H NMR (300 MHz, $CDCl_3$): δ 8.10−8.06 (m, 2H), 7.55−7.22 (m, 8H), 6.14 (q, *J* = 6.6 Hz, 1H), 1.66 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.8, 141.9, 133.0, 130.6, 129.7, 128.6, 128.4, 127.9, 126.1, 73.0, 22.5.

*Diphenylmethyl Benzoate (**26a**).* It was obtained as a white solid (2.58 g, 99%) and purified by silica gel chromatography (1% triethylamine/10% ethyl acetate/89% hexanes). mp = 88−89 °C; TLC R_f = 0.42 (10% ethyl acetate/90% hexanes); IR (KBr, cm^{-1}) ν_{max}: 3090, 3031, 2948, 1712, 1267, 1189; ^1H NMR (300 MHz, $CDCl_3$): δ 8.17−8.13 (m, 2H), 7.60−7.55 (m, 1H), 7.50−7.26 (m, 12H), 7.13 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.8, 140.5, 133.4, 130.4, 130.0, 128.8, 128.7, 128.2, 127.4, 77.7. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.37; H, 5.74.

*Diphenylmethyl 2,2-Diphenylacetate (**26b**).*[61] It was obtained as a white solid (0.120 g, 84%) and purified by silica gel chromatography (8% ethyl acetate/92% hexanes). TLC R_f = 0.52 (20% ethyl acetate/80% hexanes); ^1H NMR (400 MHz, $CDCl_3$): δ 7.28−7.19 (m, 20H), 6.91 (s, 1H), 5.15 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.4, 140.0, 138.5, 128.8, 128.6, 128.5, 127.9, 127.3, 127.2, 57.3.

*Diphenylmethyl 2-Methyl-2-phenylpropanoate (**26c**).* It was obtained as clear oil (0.120 g, 75%) and purified by silica gel chromatography (6% ethyl acetate/94% hexanes). TLC R_f = 0.50 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3088, 3031, 1730, 1600, 1495, 1142, 1100; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29−7.23 (m, 11H), 7.14−7.12 (m, 4H), 6.80 (s, 1H), 1.62 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.5, 144.3, 142.3, 140.3, 129.0, 128.42, 128.37, 127.7, 127.5, 127.3, 126.9, 126.7, 125.9, 80.1, 46.7, 26.3. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.93; H, 6.99.

*Diphenylmethyl 2-Bromododecanoate (**26d**).* It was obtained as clear colorless oil (0.40 g, 83%) and purified by silica gel chromatography (1% triethylamine/5% ethyl acetate/94% hexanes). TLC R_f = 0.78 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3064, 3032, 2924, 2854, 1741, 1495, 1454, 1257, 1144, 1080; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.26 (m, 10H), 6.89 (s, 1H), 4.31 (t, *J* = 7.5 Hz, 1H), 2.07−2.00 (m, 2H), 1.23 (br s, 16H), 0.88 (t, *J* = 6.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz $CDCl_3$): δ 169.0, 139.8, 139.7, 128.80, 128.79, 128.4, 127.4, 127.3, 78.5, 46.4, 35.2, 32.2, 29.8, 29.7, 29.6, 29.1, 27.4, 23.0, 14.4. Anal. Calcd for $C_{25}H_{33}O_2Br$: C, 67.41; H, 7.47. Found: C, 67.60; H, 7.66.

*(±)-Diphenylmethyl-2-hydroxy-2-phenylacetate (**26e**).* It was obtained as a white solid (0.58 g, 92%) and purified by silica gel chromatography (1% triethylamine/30% ethyl acetate/69% hexanes). mp = 113−114 °C; TLC R_f = 0.65 (30% ethyl acetate/70% hexanes); IR (KBr, cm^{-1}) ν_{max}: 3221, 2815, 2800, 1699, 1240; ^1H NMR (300 MHz, $CDCl_3$): δ 7.42−7.18 (m, 13H), 6.91−6.87 (m, 3H), 5.28 (d, *J* = 5.4 Hz, 1H), 3.45 (d, *J* = 5.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.0, 139.5, 139.4, 138.3, 128.9, 128.83, 128.79, 128.6, 128.5, 128.1, 127.6, 127.0, 126.5, 79.0, 73.3. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.53; H, 5.40.

*(±)-Diphenylmethyl-2-[(tert-butoxycarbonyl)amino]-phenylpropionate (**26f**).* It was obtained as clear oil (0.072 g, 54%) and purified by silica gel chromatography (20% ethyl acetate/80% hexanes). TLC R_f = 0.27 (20% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3054, 2985, 1709, 1421, 1260. ^1H NMR (300 MHz, CD_3OD): δ 7.37−7.13 (m, 15H), 6.85 (s, 1H), 4.50 (q, *J* = 6.1 Hz, 1H), 3.13 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.95 (dd, *J* = 13.8, 8.7 Hz, 1H), 1.40 (s, 9H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ 171.4, 156.4, 140.0, 136.8, 128.9, 128.1, 127.6, 126.9, 126.7, 126.4, 79.3, 77.8, 55.5, 37.1, 27.4. Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77 N, 3.25. Found: C, 75.16; H, 6.73; N, 3.61.

*Diphenylmethyl But-3-enoate (**26g**).*[62] It was obtained as colorless oil (0.35 g, 76%) and purified by silica gel chromatography (1% triethylamine/5% ethyl acetate/94% hexanes). TLC R_f = 0.44 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3064, 3031, 2983, 2938, 1740, 1642, 1543, 1030. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.26 (m, 10H), 6.90 (s, 1H), 6.02−5.90 (m, 1H), 5.22−5.15 (m, 2H), 3.23−3.20 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 170.7, 140.5, 130.4, 128.9, 128.3, 127.4, 119.1, 77.3, 39.6.

*(E)-Diphenylmethyl Cinnamate (**26h**).*[63] It was obtained as a white solid (0.401 g, 93%) and purified by silica gel chromatography (1% triethylamine/10% ethyl acetate/89% hexanes). mp = 74−77 °C; TLC R_f = 0.57 (10% ethyl acetate/90% hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.2 Hz, 1H), 7.57−7.54 (m, 2H), 7.44−7.26 (m, 13H), 7.05 (s, 1H), 6.58 (d, *J* = 15.9, 0.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.2, 145.7, 140.5, 134.5, 130.7, 129.1, 128.8, 128.4, 128.2, 127.4, 118.2, 77.2.

*Diphenylmethyl (2Z)-3-(2-Methoxyphenyl)prop-2-enoate (**26i**).* It was obtained as a white solid (0.099 g, 52%) and purified by silica gel chromatography (4% ethyl acetate/96% hexanes); mp = 72−74 °C; TLC R_f = 0.71 (10% ethyl acetate/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3031, 2836, 1725, 1627, 1110; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.21−7.13 (m, 12H), 6.85−6.75 (m, 3H), 6.06−6.02 (m, 1H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.2, 157.1, 140.3, 140.0, 130.8, 130.4, 128.4, 127.8, 127.3, 124.2, 120.1, 120.0, 110.3, 76.7, 55.4. Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.38; H, 5.54.

*Diphenylmethyl Picolinate (**26j**).* It was obtained as a white solid (0.210 g, 71%) and purified by silica gel chromatography (10% acetone/90% hexanes). mp = 101−103 °C; TLC R_f = 0.23 (20% acetone/80% hexanes); IR (film, cm^{-1}) ν_{max}: 3052, 1744, 1130. ^1H NMR (300 MHz, $CDCl_3$): δ 8.80 (dq, *J* = 4.8, 0.9 Hz, 1H), 8.19 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.85 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.50−7.44 (m, 5H), 7.39−7.27 (m, 6H), 7.22 (s, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 164.3, 150.3, 148.3, 140.0, 137.1, 128.8, 128.2, 127.5, 127.1, 125.4, 78.2; Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.89; H, 5.36; N, 5.16.

*(S)-Diphenylmethyl 2-(2-Methoxynaphthalen-6-yl)propanoate ((+)-**26k**).* It was obtained as a white solid (1.38 g, 89%) and purified by silica gel chromatography (20% ethyl acetate/80% hexanes). mp = 132−134 °C; $[\alpha]_D^{20}$ +55.7 (*c* 1.1, $CHCl_3$); TLC R_f = 0.42 (20% ethyl acetate/80% hexanes); IR (KBr, cm^{-1}) ν_{max}: 3059, 3000, 2942, 2359, 1723, 1604, 1162, 705; ^1H NMR (300 MHz, $CDCl_3$): δ 7.70−7.60 (m, 3H), 7.37 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.29−7.04 (m, 12H), 6.84 (s, 1H), 4.01−3.93 (m, 4H), 1.59 (d, *J* = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 173.7, 157.8, 140.4, 140.3, 135.7, 133.9, 129.5, 129.1, 128.7, 128.5, 128.1, 127.9, 127.4, 127.3, 126.9, 126.7, 126.3, 119.2, 105.8, 77.4, 55.5, 45.9, 18.6. Anal. Calcd for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.11. The enantiomeric ratio was determined by HPLC using a chiral column (OD-H), *n*-hexane/*i*-PrOH = 99:1, 1 mL/min; compared to a racemic sample which showed two peaks t_R = 9.7 and 11.4 min.

*(2-Methoxyphenyl) (Phenyl)methyl [1,1′-Biphenyl]-4-carboxylate (**38**).* It was obtained as a white solid (73 mg, 73% yield) and purified by silica gel column chromatography (10% ethyl acetate, 90% hexanes). mp = 136−137 °C; TLC R_f = 0.35 (10% ethyl acetate/90% hexanes); IR (film, cm^{-1}) ν_{max}: 3064, 2938, 1715, 1604, 1491, 1278, 1100, 857; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.54−7.52 (m, 2H), 7.44−7.15 (m, 10H), 6.91−6.80 (m, 2H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz $CDCl_3$): δ 165.4, 156.5, 145.8, 140.3, 140.1, 130.3, 129.2, 129.1, 129.0, 128.9, 128.3, 128.2, 127.7, 127.3, 127.2, 127.1, 127.0, 120.7, 110.9, 72.2, 55.6. Anal Calcd for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.28; H, 5.67. The enantiomeric ratio was determined by HPLC using a chiral column (AD), *n*-hexane/*i*-PrOH = 95:5, 1 mL/min; compared to a racemic sample which showed two peaks t_R = 14.8 and 16.9 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00745.

Copies of ^1H NMR spectra, ^{13}C NMR spectra, and chiral HPLC data (PDF)

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Notes

The authors declare no competing financial interest.

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