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A simple and convenient method for preparation of carboxylic acid alkyl esters, phenolic and thioesters using chlorodiphenylphosphine/I_2 and imidazole reagent system

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ABSTRACT

Condensation of carboxylic acids with alcohols, phenols and thiols proceeded smoothly to afford carboxylic acid alkyl esters, phenolic esters and thioesters by using the combination of chlorodiphenylphosphine, imidazole and molecular iodine in refluxing acetonitrile. Esterification with this mixed reagent system gave the corresponding products in excellent yields. The phosphorus-containing byproduct was simply removed from the organic phase by basic aqueous workup without the need for chromatography purification.

1. Introduction

Esterification reactions are among the oldest and most often used reactions in organic chemistry with wide applications in chemical and pharmaceutical industries.[1] Due to the importance of esters, they have been the subject of extensive experimental studies and many synthetic methods have been employed in the synthesis of these compounds.[2] In 1967 Oyo Mitsunobu reported a method for the condensation of a carboxylic acid and alcohol, using a mixture of triphenylphosphine (Ph_3P) and diethyl azodicarboxylate (DEAD), to provide an ester.[3] In recent years also, new azo and phosphorus-based reagents are the most commonly used for this purpose.[4] A major difficulty experienced with these reagent systems is due to the fact that triphenylphosphine and its oxide are difficult to remove from the reaction mixture and careful chromatography is usually required to isolate the pure product from the unreacted reagent and byproduct, which usually results in reduced yield. This is especially inconvenient in large-scale synthesis. Therefore, many efforts have been directed towards modifying Ph_3P reagent to facilitate the isolation and purification of a desired product. Polymer-supported triphenylphosphine,[5] PEG-supported (PEG=polyethyleneglycol) phosphine,[6] polystyryldiphenylphosphine,[7] diphenyl(2-pyridyl)-phosphine,[8] (4-dimethylaminophenyl)diphenylphosphine,[9] Silphos,[10] are among the recently examples of the useful phosphines. However, recently, focus has shifted away from the development of alternative reagents for the facilitation of the purification of products. This is probably due to the fact that most of the alternative reagents reported in the literature are not commercially available and required multistep synthetic sequences for their preparation.

2. Results and discussion

As mentioned above, due to the problems encountered with isolation process of the byproduct phosphine oxide, and great attention in using commercially available reagents, we report on the use of chlorodiphenylphosphine (CDP) in conjunction with molecular iodine to perform a very clean and efficient esterification reaction. In this system, the resulting phosphorus byproduct, diphenylphosphinic acid, can be extracted with an aqueous basic solution in the workup processes.

To find the optimized condition, benzylation of benzoic acid was first tried in toluene at room temperature and also under reflux conditions using Ph_2PCl, I_2 and imidazole and the desired ester, benzyl benzoate, was obtained in quantitative yield (Table 1). Next, we used other organic solvents, such as acetonitrile, dichloromethane and ethyl acetate at different temperatures to find the

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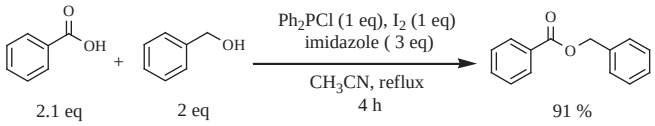
Table 1
Effect of solvent and temperature on benzylation of benzoic acid using Ph_2PCl, I_2 and imidazole system

Entry	Solvent	Condition	Time (h)	Conversion %
1	Toluene	rt	9	100
2	Toluene	reflux	4	100
3	CH_3CN	rt	11	100
4	CH_3CN	reflux	4	100
5	CH_2Cl_2	rt	24	50
6	CH_2Cl_2	reflux	24	70
7	EtOAc	rt	24	Trace
8	EtOAc	reflux	24	30

most suitable condition for the reaction. The results of this study are summarized in Table 1.

According to the results obtained, when the reaction was tried in toluene or acetonitrile at reflux, no significant difference was observed and benzyl benzoate was obtained quantitatively in shorter reaction time (Table 1, entries 2 and 4), but for more safety and convenient workup, acetonitrile was used as the most suitable solvent for this reaction. The obtained results of entries 3 and 4 shows that heating of the reaction mixture has pronounced effect on the rate of this transformation.

We also examined the effect of different ratios of Ph_2PCl/imidazole/I_2/RCO_2H/ROH in CH_3CN at reflux for the conversion of benzoic acid to benzyl benzoate. Employing the ratio of 1:3:1:2.1:2 gave the best result and produced the product after 4 h in 91% isolated yield (Scheme 1).



Scheme 1.

Other bases, such as triethylamine, pyridine and 4-dimethylamino pyridine (DMAP) were also examined. There was no ester formation between benzoic acid and benzyl alcohol in the presence of triethylamine or pyridine (Table 2, entries 3 and 4) even under reflux conditions. Performing this transformation using DMAP instead of imidazole, required a longer reaction time (Table 2, entry 5). These results show the higher efficiency of imidazole for this transformation. Moreover, this conversion was unsuccessful in the absence of imidazole (entry 1). It seems that imidazole not only neutralizes the liberated halogen acids but also enhances the reactivity of the reagent system. It has the additional advantage of being only sparingly soluble in organic solvent but freely soluble in water and is thus extracted from the organic phase by using either acidic or basic aqueous workup.

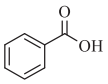
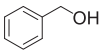
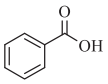
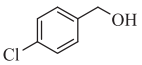
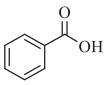
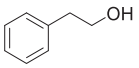
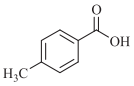
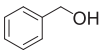
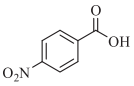
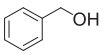
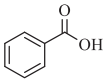
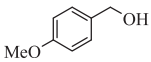
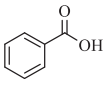
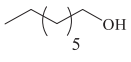
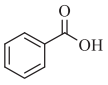
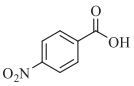
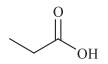
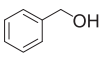
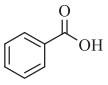
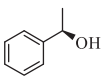
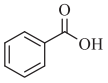
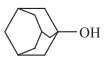
Table 2
Conversion of benzoic acid to benzyl benzoat using Ph_2PCl/I_2 in the presence of different bases in refluxing acetonitrile

Entry	Base	Time (h)	Conversion %
1	—	24	—
2	Imidazole	4	100
3	Et_3N	24	—
4	Py	24	—
5	DMAP	7	100

After optimization, we examined a variety of primary, secondary, tertiary and benzylic alcohols and various aliphatic and aromatic carboxylic acids carrying electron-donating and electron-withdrawing groups and the optimized reaction conditions were applied to these substrates (Table 3).

Carboxylic acids having deactivated and activated aromatic rings (entries 1 and 4) afforded the corresponding esters in high yields after 4–5 h, whereas carboxylic acid having electron-withdrawing substituent (entry 5) reacted in shorter time. As expected, the presence of the nitro group on aromatic ring (stronger aryl acids) is very effective in activating the carboxylic group towards reaction with alcohol compared to weaker acids, such as benzoic and 4-methylbenzoic acid.

Table 3
Condensation of carboxylic acids with different alcohols in the presence of Ph_2PCl/I_2/imidazole in CH_3CN[a]

Entry	Acid	Alcohol	Time (h)	Yield[b] %
1			4	91
2			4.5	88
3			2.5	89
4			5	90
5			1.5	92
6			3	92
7			4.5	90
8			5.5	88
9			2	93
10			3	89
11			1	93
12			24	—

[a] Reflux condition.
[b] Isolated yield.

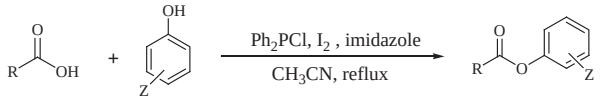
As indicated in Table 3, this reagent system is suitable for the conversion of primary and secondary aliphatic and also benzylic alcohols to their corresponding esters. The reaction with primary alcohols is somewhat faster in comparison with the reactions when more bulky secondary ones are used (Table 3, entries 7 and 8). As predicted, tertiary alcohols were resistant to esterification. This is probably due to steric effects (Table 3, entry 12). It is obvious that both electron-rich and electron-poor benzylic alcohols (entries 2 and 6) gave excellent yields of their corresponding esters.

We also examined propionic acid as an aliphatic carboxylic acid in this system. The results showed that aliphatic acids could be cleanly reacted similar to the reaction with aromatic acids (entry 10).

Also with this reagent system, no incorporation of chloride and iodide into the products was observed during the esterification reaction.

We also used finely powdered ammonium acetate instead of acetic acid and imidazole in the reaction mixture. For this purpose, a mixture of $Ph_2PCl/NH_4OAc/I_2$ (1:2.1:1) was well stirred in acetonitrile at reflux. Benzyl alcohol (2 mmol) was then added to this mixture. We found that in this case the esterification reaction did not occur and no benzyl acetate was formed even after 24 h. This result shows the higher efficiency of our new reagent system for this conversion.

Having success for esterification of carboxylic acids using alcohols, we sought to extend this methodology to the direct preparation of phenolic esters from carboxylic acids and phenols. So, the condensation reaction between carboxylic acids with phenols was carried out to afford the desired products (Scheme 2).

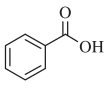
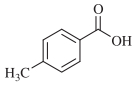
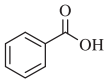
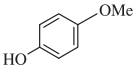
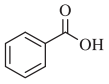
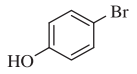
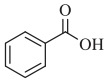
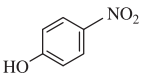
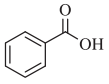
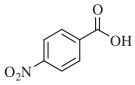
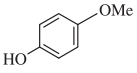
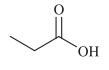
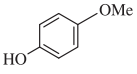


R = Alkyl and aryl
Z = H, electron with-drawing and electron-donating groups

Scheme 2.

We found that molar ratios of 1:3:1:2.1:2 for Ph_2PCl/imidazole/I_2/RCO_2H/ArOH gave the best results for this condensation. Consistent with our previous optimization reactions, acetonitrile was chosen as solvent in reflux condition. We then applied this optimized conditions for the synthesis of phenolic esters. The obtained results are shown in Table 4.

Table 4
Synthesis of phenolic esters by Ph_2PCl/imidazole/I_2 system in CH_3CN under reflux

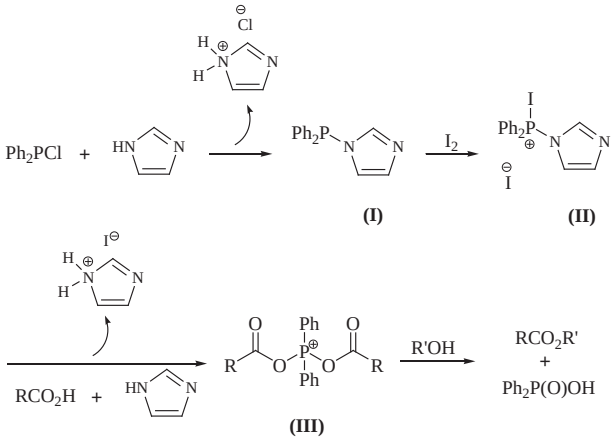
Entry	Acid	Phenol	Time	Yield[a] %
1			2 h	85
2			2.5 h	80
3			70 min	93
4			55 min	90
5			4.5 h	82
6			5 h	75
7			40 min	88
8			1 h	81

[a] Isolated yield.

As shown in this Table, esterification of various phenols (2.0 equiv) was examined in acetonitrile under reflux conditions with 1.0 equiv of Ph_2PCl, 3.0 equiv of imidazole and 1.0 equiv of I_2. Phenols, which have electron-donating or electron-withdrawing groups reacted smoothly under mild conditions to afford the corresponding esters in high yields.

The reactions of benzoic acid with electron-rich phenols, such as 4-methoxyphenol (entry 3) was successful and gave the 4-methoxyphenyl benzoate in 93% yields after 70 min, but lower yields and longer reaction times were observed from phenols bearing electron-withdrawing groups on phenyl moiety (entries 5 and 6). In addition to the electronic factors, steric factors also affected the reaction in terms of time and yield. Comparison of entries 5 and 6 indicate that existence of *ortho* substituent on the phenol ring, slightly decrease the yield and increase the time of the reaction.

Based on the above results, a proposed reaction mechanism is shown in Scheme 3.



Scheme 3.

1-(Diphenylphosphino)imidazole (I) is formed in situ by adding imidazole to Ph_2PCl. Phosphine I can react with iodine to form intermediate phosphonium salt II, which then transforms to the acyloxyphosphonium ion (III) by the attack of the more nucleophilic carboxylate anion at the phosphorus centre. Finally the attack of the alcohol at the carbonyl carbon atom of the intermediate III affords the corresponding carboxylic acid ester along with diphenylphosphinic acid as shown in Scheme 3.

The phenolic esters are surely obtained in this way. But in order to have more evidence in support of the proposed mechanism in the case of alkyl esters, the stereochemistry of the reaction was studied using chiral secondary alcohol (*R*)-(+)-1-phenylethanol.

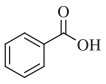
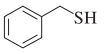
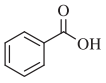
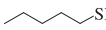
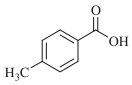
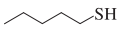
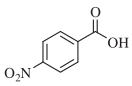
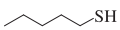
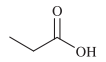
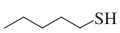
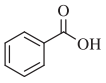
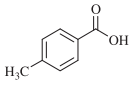
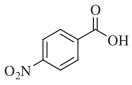
From the reaction of chlorodiphenylphosphine, imidazole, molecular iodine, benzoic acid and (*R*)-1-phenylethanol in refluxing acetonitrile, (*R*)-1-phenylethyl benzoate was obtained in excellent yield (93%) after 1 h (Table 3, entry 11). The complete stereochemical retention proved by the optical rotation of (*R*)-1-phenylethyl benzoate.[4c,11]

The observed configuration is thought to arise through the acid activation as acyloxyphosphonium salt III and direct attack of the alcohol at the carbonyl carbon atom of this intermediate, which supports the proposed mechanism shown in the Scheme 3.

In addition to stereochemistry, the reaction of a carboxylic acid and thiol, could also confirm the proposed mechanism. In this way, benzyl mercaptane (2 mmol, 0.234 mL) was added to a mixture of chlorodiphenylphosphine (1 mmol, 0.18 mL), imidazole (3 mmol, 0.2 g), iodine (1 mmol, 0.254 g) and benzoic acid (2.1 mmol, 0.25 g) in acetonitrile (5 mL) at reflux. After 4 h, *S*-benzyl benzothioate was obtained in 80% yield. Formation of thioester, is consistent with the existence of intermediate III in the reaction mixture.

After the successful transformation of benzyl mercaptane to its corresponding thioester, in order to increase the scope of the present method and owing to the importance of thioesters[12] especially in the protection of thiols, we decided to employ our new reagent system for the synthesis of thioesters. Further results, showed that the syntheses of various thioesters were performed successfully under similar reaction conditions as used for alcohols. The obtained results are shown in Table 5.

Table 5
Preparation of thioesters using Ph_2PCl/imidazole/I_2 system in refluxing acetonitrile

Entry	Acid	Thiol	Time	Yield[a] %
1			4 h	80
2			1 h	90
3			1.5 h	91
4			40 min	95
5			40 min	90
6			100 min	87
7			2 h	90
8			70 min	88

[a] Isolated yield.

From the results of Table 5, it was found that, factors, such as electron deficiency of carboxylic acid and the steric bulk of thiols have a profound effect on the time of reaction. As expected, according to the mechanism, stronger aryl acids, such as 4-nitrobenzoic acids, results in shorter reaction time (Table 5, entries 4 and 8) compared to weaker acids, such as benzoic and 4-methylbenzoic acids (entries 2, 6 and 3,7). The effect of steric bulk is similar to that carried out for alcohols. Primary thiols reacted faster in comparison with secondary ones (entries 2–4 compared to entries 6–8).

In conclusion, a simple, efficient and convenient method for preparation of carboxylic acid alkyl esters, phenolic esters and also thioesters from carboxylic acids and various benzylic, primary and secondary alcohols or thiols or phenols was established. The desired products were prepared easily from chlorodiphenylphosphine and iodine in the presence of imidazole in excellent yields. Chlorodiphenylphosphine is commercially available and inexpensive, making large-scale esterification using this reagent system especially attractive. This system has the further advantage that the resulting phosphorus byproduct, diphenylphosphinic acid, can be extracted with base during product workup, which provides quicker workup procedures instead of using the tedious and time-consuming chromatographic methods.

3. Experimental section

3.1. Typical procedure for the conversion of benzoic acid to benzyl benzoate[4c]

To a flask containing a stirred mixture of chlorodiphenylphosphine (1 mmol, 0.18 mL), imidazole (3 mmol, 0.2 g) and iodine (1 mmol, 0.254 g) in acetonitrile (5 mL), was added benzoic acid (2.1 mmol, 0.25 g) at reflux condition. Benzyl alcohol (2.0 mmol, 0.2 mL) was then added to the reaction mixture. TLC monitoring showed the completion of the reaction after 4 h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (10 mL) and washed with saturated aqueous sodium carbonate (3×5 mL) to remove all diphenylphosphinic acid from the organic phase. The aqueous phase was separated and the organic phase was washed with aqueous sodium thiosulfate (2×5 mL) to remove the excess iodine and then washed with water (10 mL), dried and concentrated. The residue was subjected to flash chromatography over silica gel by using *n*-hexane/ethyl acetate (4:1) as eluent to give the benzyl benzoate (0.386 g, 91%) as a colourless oil; δ_H (250 MHz, $CDCl_3$) 7.98 (2H, dd, *J* 8.4, 1.5 Hz, Ph), 7.44–7.24 (8H, m, Ph), 5.26 (2H, s, CH_2); δ_C (62.9 MHz, $CDCl_3$) 166.4, 136.1, 133.1, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7 (Table 3, entry 1).

3.1.1. 4-Chlorobenzyl benzoate[4a]. Yield (0.434 g, 88%); δ_H (250 MHz, $CDCl_3$) 7.95 (2H, d, *J* 8.5 Hz, Ph), 7.44–7.41 (1H, m, Ph), 7.35–7.22 (6H, m, Ph), 5.21 (2H, s, CH_2); δ_C (62.9 MHz, $CDCl_3$) 166.3, 134.6, 134.1, 133.2, 129.9, 129.7, 129.6, 128.8, 128.4, 65.9 (Table 3, entry 2).

3.1.2. Phenethyl benzoate[4c]. Yield (0.402 g, 89%) as a colourless oil; δ_H (250 MHz, $CDCl_3$) 8.01 (2H, dd, *J* 7.0, 1.5 Hz, Ph), 7.52 (1H, t, *J* 7.5 Hz, Ph), 7.44–7.38 (2H, m, Ph), 7.32–7.22 (5H, m, Ph), 4.53 (2H, t, *J* 7.1 Hz, OCH_2), 3.04 (2H, t, *J* 7.0 Hz, CH_2Ph); δ_C (62.9 MHz, $CDCl_3$) 166.5, 137.9, 133.4, 132.9, 130.3, 130.1, 129.5, 129.3, 129.0, 128.6, 128.4, 128.0, 126.6, 65.5, 35.3 (Table 3, entry 3).

3.1.3. Benzyl-4-methylbenzoate[4c]. Yield (0.407 g, 90%) as a colourless oil; δ_H (250 MHz, $CDCl_3$) 7.95 (2H, d, *J* 8.1 Hz, Ph), 7.45–7.29 (5H, m, Ph), 7.21 (2H, d, *J* 7.9 Hz, Ph), 5.35 (2H, s, CH_2), 2.38 (3H, s, *Me*); δ_C (62.9 MHz, $CDCl_3$) 163.0, 143.7, 136.2, 133.3, 133.0, 129.8, 129.1, 128.6, 128.2, 128.1, 127.6, 127.4, 127.0, 66.5, 21.7 (Table 3, entry 4).

3.1.4. Benzyl-4-nitrobenzoate[4c]. Yield (0.473 g, 92%) as a yellow solid, mp 79–82 °C (lit.[13] 83–84 °C); δ_H (250 MHz, $CDCl_3$) 8.32–8.25 (4H, m, Ph), 7.46–7.36 (5H, m, Ph), 5.40 (2H, s, CH_2); δ_C (62.9 MHz, $CDCl_3$) 164.5, 150.6, 135.5, 135.3, 130.8, 130.0, 128.7, 128.6, 128.4, 123.5, 67.6 (Table 3, entry 5).

3.1.5. 4-Methoxybenzyl benzoate[4c]. Yield (0.445 g, 92%) as a colourless oil; δ_H (250 MHz, $CDCl_3$) 8.04 (2H, d, *J* 8.2 Hz, Ph), 7.51–7.48 (1H, m, Ph), 7.42–7.35 (4H, m, Ph), 6.88 (2H, d, *J* 6.6 Hz, Ph), 5.28 (2H, s, CH_2), 3.78 (3H, s, O*Me*); δ_C (62.9 MHz, $CDCl_3$) 166.5, 159.7, 147.6, 133.4, 130.5, 130.1, 129.7, 128.7, 114.0, 66.5, 55.3 (Table 3, entry 6).

3.1.6. Octyl benzoate[4a]. Yield (0.421 g, 90%); δ_H (250 MHz, $CDCl_3$) 8.04 (2H, d, *J* 7.0 Hz, Ph), 7.54–7.39 (3H, m, Ph), 4.34 (2H, t, *J* 6.7 Hz, OCH_2), 1.79–1.70 (2H, m, OCH_2CH_2), 1.46–1.28 (10H, m, (CH_2)$_5$Me), 0.88 (3H, t, *J* 6.9 Hz, *Me*); δ_C (62.9 MHz, $CDCl_3$) 166.7, 132.8, 130.53, 129.5, 128.3, 65.1, 31.8, 29.6, 29.2, 29.2, 28.7, 26.0, 22.6, 18.5, 14.1 (Table 3, entry 7).

3.1.7. 2-Octyl benzoate[4a]. Yield (0.412 g, 88%); δ_H (250 MHz, $CDCl_3$) 8.04 (2H, d, *J* 7.0 Hz, Ph), 7.54–7.39 (3H, m, Ph), 5.21–5.09 (1H, m, OC*H*), 1.70–1.59 (2H, m) 1.42–1.25 (11H, m), 0.87 (3H, t, *J* 6.9 Hz,

CH_2Me); δ_C (62.9 MHz, $CDCl_3$) 166.2, 132.7, 130.9, 129.5, 128.3, 71.7, 36.1, 31.7, 29.2, 25.4, 22.6, 20.1, 14.1 (Table 3, entry 8).

3.1.8. 2-Octyl 4-nitrobenzoate[4a]. Yield (0.520 g, 93%); δ_H (250 MHz, $CDCl_3$) 8.30–8.18 (4H, m, Ph), 5.25–5.13 (1H, m, OC*H*), 1.81–1.57 (2H, m), 1.39–1.28 (11H, m), 0.86 (3H, t, *J* 6.6 Hz, CH_2Me); δ_C (62.9 MHz, $CDCl_3$) 164.3, 150.4, 136.3, 130.6, 123.4, 73.1, 35.9, 31.7, 29.3, 29.1, 28.6, 25.7, 25.3, 22.5, 19.9, 14.0 (Table 3, entry 9).

3.1.9. Benzyl propionate[4c]. Yield (0.292 g, 89%); δ_H (250 MHz, $CDCl_3$) 7.34–7.15 (5H, m, Ph), 5.03 (2H, s, CH_2Ph), 2.28 (2H, q, *J* 7.5 Hz, CH_2Me), 1.07 (3H, t, *J* 7.5 Hz, *Me*); δ_C (62.9 MHz, $CDCl_3$) 174.3, 136.1, 128.5, 158.2, 127.8, 66.1, 27.6, 9.1 (Table 3, entry 10).

3.1.10. (R)-1-phenylethyl benzoate[11]. Yield (0.420 g, 93%) as a colourless oil; δ_H (250 MHz, $CDCl_3$) 8.00 (2H, d, *J* 8.4 Hz, Ph), 7.40–7.26 (8H, m, Ph), 6.05 (1H, q, *J* 6.5 Hz, C*H*Ph), 1.60 (3H, d, *J* 6.5 Hz, *Me*) (Table 3, entry 11).

3.2. Typical procedure for the conversion of benzoic acid to phenyl benzoate[4a]

Benzoic acid (2.1 mmol, 0.25 g) was added to a stirred mixture of chlorodiphenylphosphine (1 mmol, 0.18 mL), imidazole (3 mmol, 0.2 g) and iodine (1 mmol, 0.254 g) in acetonitrile (5 mL) at reflux. Phenol (2 mmol, 0.188 g) was then added to the reaction mixture. After the appropriate reaction time for the completion of the conversion (2 h), the solvent was evaporated on a rotary evaporator and the residue was dissolved in CH_2Cl_2 (10 mL). The organic layer was washed with saturated aqueous sodium carbonate (3×5 mL) followed by aqueous sodium thiosulfate (2×5 mL) and dried. Flash chromatography of the organic residue was performed on silica gel using *n*-hexane/ethyl acetate (4:1) as eluent to give the pure phenyl benzoate (0.337 g, 85%) as a yellowish powder, mp 64–68 °C (lit.[14] 66–69 °C); δ_H (250 MHz, $CDCl_3$) 8.19–8.15 (2H, d, *J* 8.2 Hz, Ph), 7.78–7.06 (8H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 165.1, 151.2, 133.7, 129.9, 129.6, 129.3, 128.7, 125.8, 121.5 (Table 4, entry 1).

3.2.1. 4-Methoxyphenyl benzoate[4a]. Yield (0.424 g, 93%); δ_H (250 MHz, $CDCl_3$) 8.10 (2H, dd, *J* 8.4, 1.3 Hz, Ph), 7.52–7.49 (1H, m, Ph), 7.39 (2H, t, *J* 8.0 Hz, Ph), 7.04 (2H, dd, *J* 8.7, 1.8 Hz, Ph), 6.84 (2H, dd, *J* 8.9, 1.7 Hz, Ph), 3.73 (3H, s, O*Me*); δ_C (62.9 MHz, $CDCl_3$) 165.6, 157.3, 144.4, 133.5, 130.1, 129.6, 128.6, 122.5, 114.5, 55.6 (Table 4, entry 3).

3.2.2. 4-Bromophenyl benzoate[4a]. Yield (0.500 g, 90%); δ_H (250 MHz, $CDCl_3$) 8.03 (2H, dd, *J* 7.8, 1.5 Hz, Ph), 7.50 (1H, m, Ph), 7.40 (4H, m, Ph), 7.00 (2H, dd, *J* 6.8, 2.0 Hz, Ph); δ_C (62.9 MHz, $CDCl_3$) 164.9, 150.0, 133.8, 132.5, 130.2, 129.2, 128.7, 123.6, 119.0 (Table 4, entry 4).

3.2.3. 4-Nitrolphenyl benzoate[4a]. Yield (0.400 g, 82%); δ_H (250 MHz, $CDCl_3$) 8.24 (2H, d, *J* 8.4 Hz, Ph), 8.11 (2H, d, *J* 7.1, Ph), 7.61 (1H, m, Ph), 7.46 (2H, t, *J* 7.8 Hz, Ph), 7.34 (2H, dd, *J* 7.0, 2.1 Hz, Ph); δ_C (62.9 MHz, $CDCl_3$) 164.3, 156.9, 144.5, 133.4, 132.8, 128.6, 125.9, 125.0, 119.3 (Table 4, entry 5).

3.2.4. 2-Nitrolphenyl benzoate[4a]. Yield (0.365 g, 75%); δ_H (250 MHz, $CDCl_3$) 8.12–8.08 (2H, m, Ph), 7.59–7.54 (2H, m, Ph), 7.45–7.39 (5H, m, Ph); δ_C (62.9 MHz, $CDCl_3$) 164.4, 144.31, 134.8, 134.2, 130.5, 130.2, 128.7, 128.4, 126.7, 125.8, 125.3 (Table 4, entry 6).

3.2.5. 4-Methoxyphenyl-4-nitrobenzoate[4a]. Yield (0.480 g, 88%); δ_H (250 MHz, $CDCl_3$) 8.30–8.27 (4H, m, Ph), 7.07 (2H, d, *J* 9.1 Hz, Ph), 6.88 (2H, d, *J* 9.1 Hz, Ph), 3.73 (3H, s, O*Me*); δ_C (62.9 MHz, $CDCl_3$) 163.7, 157.6, 150.8, 144.0, 135.0, 131.2, 123.7, 122.2, 114.6, 55.6 (Table 4, entry 7).

3.2.6. 4-Methoxyphenyl-propanoate[4a]. Yield (0.292 g, 81%); δ_H (250 MHz, $CDCl_3$) 6.88 (2H, d, *J* 8.0 Hz, Ph), 6.77 (2H, d, *J* 8.8 Hz, Ph), 3.68 (3H, s, O*Me*), 2.47 (2H, q, *J* 7.5 Hz, CH_2Me), 1.16 (3H, t, *J* 7.5 Hz, CH_2Me); δ_C (62.9 MHz, $CDCl_3$) 173.3, 157.2, 144.3, 122.3, 114.4, 55.52, 27.7, 9.1 (Table 4, entry 8).

3.3. Typical procedure for the conversion of benzoic acid to *S*-benzyl benzothioate[4a]

A mixture of chlorodiphenylphosphine (1 mmol, 0.18 mL), imidazole (3 mmol, 0.2 g) and iodine (1 mmol, 0.254 g) in acetonitrile (5 mL) was stirred at reflux conditions. Then 2.1 mmol of benzoic acid (0.25 g) and 2.0 mmol of benzyl mercaptane (0.234 mL) were added to the resulting mixture. After completion of the reaction as monitored by TLC (4 h), the solvent was evaporated and CH_2Cl_2 (10 mL) was added. The organic layer was washed with saturated aqueous sodium carbonate (3×5 mL) and aqueous sodium thiosulfate (2×5 mL), respectively, and dried. The pure product was obtained after flash chromatography of the crude mixture on silica gel using *n*-hexane/ethyl acetate (4:1) as eluent (0.365 g, 80%) as a white solid, mp 37 °C (lit.[4a] 36.6–36.7 °C); δ_H (250 MHz, $CDCl_3$) 7.87 (2H, dd, *J* 7.1, 1.4 Hz, Ph), 7.47–7.15 (8H, m, Ph), 4.23 (2H, s, CH_2); δ_C (62.9 MHz, $CDCl_3$) 191.7, 137.5, 133.5, 129.3, 129.0, 128.7, 128.7, 128.5, 128.4, 128.2, 127.3, 127.3, 33.3 (Table 5, entry 1).

3.3.1. Pentyl benzothioate[4a]. Yield (0.375 g, 90%); δ_H (250 MHz, $CDCl_3$) 8.21 (2H, d, *J* 8.5 Hz, Ph), 8.03 (2H, d, *J* 8.4 Hz, Ph), 3.04 (2H, t, *J* 7.5 Hz, SCH_2), 1.64–1.59 (2H, m, SCH_2CH_2), 1.32–1.27 (4H, m, CH_2CH_2Me), 0.84 (3H, t, *J* 6.4 Hz, *Me*); δ_C (62.9 MHz, $CDCl_3$) 190.5, 150.4, 141.8, 128.2, 123.8, 31.0, 29.6, 29.0, 22.2, 13.9 (Table 5, entry 2).

3.3.2. Pentyl 4-methylbenzothioate[4a]. Yield (0.404 g, 91%); δ_H (250 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.2 Hz, Ph), 7.15 (2H, d, *J* 8.2 Hz, Ph), 2.97 (2H, t, *J* 7.3 Hz, SCH_2), 2.31 (3H, s, *Me*), 1.62–1.15 (2H, m, SCH_2CH_2), 1.36–1.23 (4H, m, CH_2CH_2Me), 0.83 (3H, t, *J* 6.9 Hz, CH_2Me); δ_C (62.9 MHz, $CDCl_3$) 191.7, 144.0, 134.8, 129.2, 127.2, 31.1, 29.3, 28.9, 22.2, 21.6, 13.9 (Table 5, entry 3).

3.3.3. Pentyl 4-nitrobenzothioate[4a]. Yield (0.481 g, 95%); δ_H (250 MHz, $CDCl_3$) 7.89–7.30 (4H, m, Ph), 2.97 (2H, t, *J* 7.2 Hz, SCH_2), 1.58–1.55 (2H, m, SCH_2CH_2), 1.34–1.27 (4H, m, CH_2CH_2Me), 0.82 (3H, t, *J* 6.5 Hz, *Me*); δ_C (62.9 MHz, $CDCl_3$) 192.0, 137.3, 135.5, 134.2, 133.2, 130.5, 128.4, 31.0, 29.6, 28.9, 22.2, 13.9 (Table 5, entry 4).

3.3.4. Pentyl propanthioate[4a]. Yield (0.288 g, 90%); δ_H (250 MHz, $CDCl_3$) 3.43 (2H, m, SCH_2), 2.46 (2H, q, *J* 7.5 Hz CH_2CO), 1.85–1.84 (2H, m, SCH_2CH_2), 1.62–1.60 (4H, m, CH_2CH_2Me), 1.38–1.05 (6H, m, *Me*) (Table 5, entry 5).

3.3.5. S-Cyclohexyl benzothioate[4a]. Yield (0.383 g, 87%); δ_H (250 MHz, $CDCl_3$) 7.86 (2H, d, *J* 7.2 Hz, Ph), 7.48–7.15 (3H, m, Ph), 3.69–3.59 (1H, m, S*CH*), 1.69–1.21 (6H, m, cyclohexyl ring), 1.97–1.90 (4H, m, cyclohexyl ring) (Table 5, entry 6).

3.3.6. S-Cyclohexyl 4-methylbenzothioate[4a]. Yield (0.421 g, 90%); δ_H (250 MHz, $CDCl_3$) 7.84 (2H, d, *J* 8.2 Hz, Ph), 7.22 (2H, d, *J* 8.0 Hz, Ph), 3.75–3.66 (1H, m, S*CH*), 2.39 (3H, s, *Me*), 2.05–1.98 (2H, m, cyclohexyl ring), 1.78–1.71 (2H, m, cyclohexyl ring), 1.60–1.45 (6H, m, cyclohexyl ring); δ_C (62.9 MHz, $CDCl_3$) 191.5, 143.9, 129.1, 127.2, 42.4, 33.2, 26.0, 25.6, 21.6 (Table 5, entry 7).

3.3.7. S-Cyclohexyl 4-nitrobenzothioate[4a]. Yield (0.466 g, 88%); δ_H (250 MHz, $CDCl_3$) 8.20 (2H, d, *J* 8.9 Hz, Ph), 8.02 (2H, d, *J* 8.9 Hz, Ph),

3.73–3.46 (1H, m, SC*H*), 1.98–1.93 (2H, m, cyclohexyl ring), 1.70–1.64 (2H, m, cyclohexyl ring), 1.59–1.35 (6H, m, cyclohexyl ring); δ_C (62.9 MHz, $CDCl_3$) 190.2, 150.3, 142.01, 128.1, 123.8, 43.4, 32.9, 25.9, 25.5 (Table 5, entry 8).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.022.

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