An Efficient and Convenient Esterification of Carboxylic Acids Using 4,5-Dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one

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(Dedicated to the memory of professor In-Kyu Kim)

Esterification of aliphatic or aromatic carboxylic acids with alcohols using 2-(4-nitrobenzenesulfonyl)-4,5-dichloropyridazin-3(2H)-one (**3**) in the presence of base in organic solvents gave the corresponding esters in excellent yields

Key Words : Esterification of carboxylic acid, 4,5-Dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one

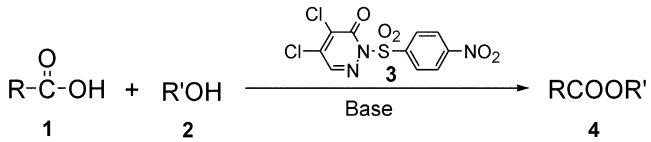
Introduction

Mild and effective esterification of carboxylic acids with alcohols is the most fundamental and important reactions in organic synthesis.[1] It has long been known that the process of esterification may be enormously accelerated by the addition of a strong acid such as sulfuric acid. There are also many methods for esterification using specific dehydrating reagents.[2] However, the classical esterifications have some disadvantages of the corrosiveness of strong acid, with accompanying side reactions such as carbonization and oxidation. Although many reagents for esterification of carboxylic acid have been developed,[2-4] the research in this field is still very active even now.[5] For direct esterification of carboxylic acid under mild conditions, carboxylic acid must be activated to more reactive species by using an activator. In our previous paper,[6] we have reported the activating ability of 4,5-dichloro-2-[(4-nitrophenyl)sulfonyl]pyridazin-3(2*H*)-one (**3**) for carboxylic acid. Therefore, we attempted the direct esterification of carboxylic acids with alcohols using **3** as a mediator.

In this paper, we would like to report on mild and convenient esterification of carboxylic acids with alcohols by using compound **3** in one-pot.

Results and Discussion

Esterification of carboxylic acids **1** with alcohols **2** using **3** in the presence of a base such as 4-(*N*,*N*-dimethylamino)-pyridine or potassium carbonate in refluxing tetrahydrofuran gave the corresponding esters **4** in excellent yields (Table 1). According to our preliminary experiments, 4-(*N*,*N*-dimethyl-amino)pyridine is more favourable than potassium carbonate for these esterifications except for **2d** and **2g**. Especially, the esterification for aliphatic carboxylic acids (**1b** and **1c**) and



Scheme 1

aliphatic alcohols (**2a**, **2c**) using **3** was not proceeded in the presence of potassium carbonate as a base. Esterification of benzoic acid (**1a**) with 4-hydroxyphenethyl alcohol (**2d**) using **3** under the same condition selectively also gave 4-(2-hydroxyethyl)phenyl benzoate (**4d**) in 95% yield (entry 4 in the Table 1).

Reaction of (1*S*,2*S*,3*R*,5*S*)-(+)-pinanediol (**2f**) containing both a secondary and a tertiary alcohol with benzoic acid (**1a**) under the same conditions also selectively acylated, affording 2-benzoyloxy derivative **4f** in 98% yield (entry 6 in the Table 1). Thus, this method may be used for selective esterification of primary or secondary alcohol.

Selective esterification of primary or secondary alcohol in the presence of secondary or tertiary alcohol is also often required. Therefore, we examined the selective ester condensation for a mixture of two alcohols such as primary/secondary alcohol, primary/tertiary alcohol or secondary/tertiary alcohol (Table 2). The use of benzoic acid generally gave primary (entries 1, 2, 3 and 5 in the Table 2) or secondary (entry 4 in the Table 2) alkyl ester in excellent selectivity and in high yield. Primary or secondary alcohol was also esterified in excellent selectivity in high yield with *trans*-cinnamic acid (entries 6-10 in the Table 2) or heptanoic acid (entries 12-15 in the Table 2) using **3** in the presence of secondary or tertiary alcohol. The reaction of methanol and cyclohexanol with heptanoic acid using **3** in refluxing tetrahydrofuran gave esters **4s** (67%) and **4e** (28%) (entry 11 in the Table 2), whereas this reaction carried out at

Table 1. Yields and conditions for the esterification of carboxylic acid (1 equiv) with alcohol (1 equiv) using **3** (1 equiv) in the presence of base (2 equiv) in refluxing THF

Entry	RCOOH		R'OH		Base[a]	Time	RCOOR'
	1	R	2	R'		(h)	4 (%)[b]
1	**1a**	C_6H_5	**2a**	Me	DMAP	0.9	**4a** (98)
2	**1a**	C_6H_5	**2b**	$C_6H_5(CH)_2$	DMAP	1.0	**4b** (98)
3	**1a**	C_6H_5	**2c**	*p*-$MeOC_6H_4$	DMAP	2.0	**4c** (95)
4	**1a**	C_6H_5	**2d**	*p*-$HOC_6H_4(CH_2)_2$	K_2CO_3	7.5	**4d** (95)[d]
5	**1a**	C_6H_5	**2e**	C_6H_{11}[e]	DMAP	1.1	**4e** (92)
6	**1a**	C_6H_5	**2f**	$C_{10}H_{18}O_2$[f]	DMAP	3.5	**4f** (98)
7	**1b**	C_6H_5CHCH[c]	**2a**	Me	DMAP	0.5	**4g** (96)
8	**1b**	C_6H_5CHCH[c]	**2g**	*p*-NCC_6H_4	DMAP	1.0	**4h** (95)
9	**1b**	C_6H_5CHCH[c]	**2e**	C_6H_{11}[e]	DMAP	1.2	**4i** (93)
10	**1c**	$CH_3(CH_2)_6$	**2b**	$C_6H_5(CH)_2$	DMAP	1.5	**4j** (97)
11	**1c**	$CH_3(CH_2)_6$	**2g**	*p*-NCC_6H_4	DMAP	0.9	**4k** (91)
12	**1c**	$CH_3(CH_2)_6$	**2e**	C_6H_{11}[e]	DMAP	1.3	**4l** (93)
13	**1d**	$(C_6H_5)_2CH$	**2g**	*p*-NCC_6H_4	K_2CO_3	0.7	**4m** (91)
14	**1d**	$(C_6H_5)_2CH$	**2a**	Me	DMAP	0.5	**4n** (95)
15	**1e**	*p*-$ClC_6H_4CH_2$	**2g**	*p*-NCC_6H_4	DMAP	1.2	**4o** (95)
16	**1e**	*p*-$ClC_6H_4CH_2$	**2a**	Me	DMAP	0.8	**4p** (96)
17	**1f**	C_5H_4N[g]	**2g**	*p*-NCC_6H_4	DMAP	1.8	**4q** (95)

[a]DMAP = 4-(*N*,*N*-Dimethylamino)pyridine. [b]Isolated yield. The yields were calculated on the basis of carboxylic acids. 4,5-Dichloropyridazin-3-one was isolated quantitatively. [c]*trans*-Isomer. [d]The product is 4-(2-hydroxyethyl)phenyl benzoate. [e]Cyclohexyl. [f](1*S*,2*S*,3*R*,5*S*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl. [g]Nicotinyl.

Table 2. Competition reaction of a mixture of alcohols (1 equiv) with carboxylic acid (1 equiv) using **3** (1 equiv) in the presence of 4-(*N*,*N*-dimethylamino)pyridine (2 equiv) in refluxing THF

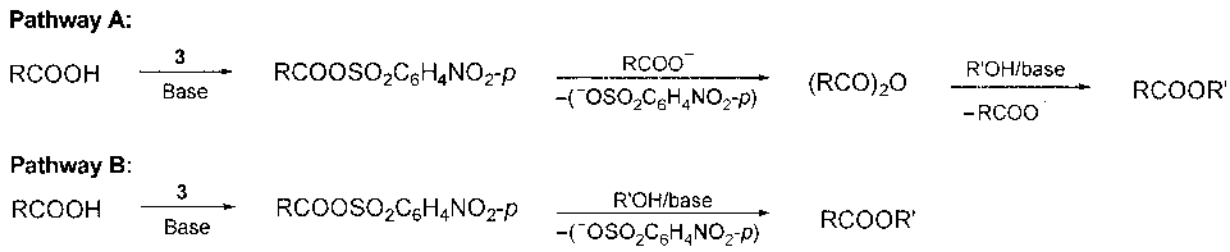
Entry	RCOOH		Mixture of alcohols (2)	Time	RCOOR'(4)(%)[a]	
	1	R		(h)	4	R'
1	**1a**	C_6H_5	MeOH (**2a**) / $C_6H_{11}OH$[b] (**2e**)	1.0	**4a**	Me (91)
2	**1a**	C_6H_5	$C_6H_5(CH_2)_2OH$ (**2b**) / $C_6H_{11}OH$[b] (**2e**)	1.0	**4b**	$C_6H_5(CH_2)_2$ (98)
3	**1a**	C_6H_5	MeOH (**2a**) / *t*-BuOH (**2h**)	1.0	**4a**	Me (93)
4	**1a**	C_6H_5	$C_6H_{11}OH$[b] (**2e**) / *t*-BuOH (**2h**)	1.1	**4e**	C_6H_{11} (92)
5	**1a**	C_6H_5	$C_6H_5(CH_2)_2OH$ (**2b**) / *t*-BuOH (**2h**)	1.0	**4b**	$C_6H_5(CH_2)_2$ (98)
6	**1b**	*trans*-PhCHCH	MeOH (**2a**) / $C_6H_{11}OH$[b] (**2e**)	2.0	**4g**	Me (93)
7	**1b**	*trans*-PhCHCH	$C_6H_5(CH_2)_2OH$ (**2b**) / $C_6H_{11}OH$[b] (**2e**)	1.5	**4r**	$C_6H_5(CH_2)_2$ (93)
8	**1b**	*trans*-PhCHCH	MeOH (**2a**) / *t*-BuOH (**2h**)	1.7	**4g**	Me (97)
9	**1b**	*trans*-PhCHCH	$C_6H_{11}OH$[b] (**2e**) / *t*-BuOH (**2h**)	1.2	**4i**	C_6H_{11} (91)
10	**1b**	*trans*-PhCHCH	$C_6H_5(CH_2)_2OH$ (**2b**) / *t*-BuOH (**2h**)	1.0	**4r**	$C_6H_5(CH_2)_2$ (92)
11	**1g**	$CH_3(CH_2)_5$	MeOH (**2a**) / $C_6H_{11}OH$[b] (**2e**)	1.5	**4s**	Me (67) / **4e** C_6H_{11} (28)[c]
12	**1g**	$CH_3(CH_2)_5$	$C_6H_5(CH_2)_2OH$ (**2b**) / $C_6H_{11}OH$[b] (**2e**)	1.7	**4t**	$C_6H_5(CH_2)_2$ (95)
13	**1g**	$CH_3(CH_2)_5$	MeOH (**2a**) / *t*-BuOH (**2h**)	1.8	**4s**	Me (92)
14	**1g**	$CH_3(CH_2)_5$	$C_6H_{11}OH$[b] (**2e**) / *t*-BuOH (**2h**)	2.6	**4u**	C_6H_{11} (91)
15	**1g**	$CH_3(CH_2)_5$	$C_6H_5(CH_2)_2OH$ (**2b**) / *t*-BuOH (**2h**)	2.0	**4t**	$C_6H_5(CH_2)_2$ (93)

[a]Isolated yield. The yields were calculated on the basis of carboxylic acids. 4,5-Dichloropyridazin-3-one was also isolated quantitatively. [b]Cyclohexanol. [c]The ratio of **4s**:**4e** is 3 : 1. It was determined by ^{1}H NMR.

room temperature for 5 hours to give only methyl ester **4s** (80%). In all the reactions described above, reusable 4-(*N*,*N*-dimethylamino)pyridine, 4,5-dichloropyridazin-3-one and 4-nitrobenzenesulfonate salt were also isolated quantitatively.

The esterification of carboxylic acid using compound **3** may be proceeded *via* two pathways: the Pathway A and the Pathway B (Scheme 2). By monitoring the reaction using thin layer chromatography, the main pathway under our condition may be regarded as the pathway A.

In conclusion, compound **3** is a convenient, efficient and eco-friendly mediating agent for one-pot esterification of carboxylic acids with alcohols under the basic condition. It also has some advantages: i) the reaction condition is mild and basic, ii) this method shows excellent selectivity



Scheme 2. Possible mechanism.

for primary or secondary alcohols in the presence of secondary or tertiary alcohols with high yields, and iii) the mediator is easy to prepare and stable in air at high temperature.

Experimental Section

Reagents and solvents were used as received from commercial sources. TLC was performed on plates coated with silica gel (silica gel 60 F254, Merck). The spots were located by UV light. Column chromatography was carried out on silica gel (silica gel 60, 70-230 mesh). Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a Brüker FT NMR-DRX 500 or Varian Inova 500 Spectrometer. The chemical shift values are reported in d units (part per million) relative to TMS as an internal standard. IR spectra were obtained on a Hitachi 270-50 or Mattson Genesis Series FT-IR spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240C.

General Procedure. A solution of carboxylic acid **1** (1 equivalent), alcohol **2** (1 equivalent), base (2 equivalents) and mediating agent **3**[7] (1 equivalent) in refluxing THF (30 mL, dried) was stirred until compound **3** and carboxylic acid disappeared by TLC monitoring. After filtering the mixture, the filtrate was evaporated under reduced pressure. The residue was applied to the top of an open-bed silica gel column (2.5 × 10 cm). The column was eluted with CH_2Cl_2. Fractions containing the product were combined and evaporated under reduced pressure to give the corresponding ester **4** and 4,5-dichloropyridazin-3(2*H*)-one. After washing the first filtered residue with water (100 mL), the water solution was evaporated under reduced pressure. After triturating the residue in tetrahydrofuran (70 mL), the salt was filtered and dried in air to give 4-nitrobenzenesulfonate salt in good yield. Tetrahydrofuran solution was evaporated under reduced pressure to afford 4-(*N,N*-dimethylamino)-pyridine.

Methyl benzoate (4a): Oil; IR (KBr) 1730 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.92 (s, 3H), 7.43 (m, 2H), 7.55 (m, 1H), 8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 52.1, 128.4, 129.6, 130.3, 132.9, 167.1. Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.69; H, 6.08.

Phenylethyl benzoate (4b): Oil; IR (KBr) 1720 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.08 (t, 2H, J = 7.0 Hz), 4.53 (t, 2H, J = 7.0 Hz), 7.24 (m, 1H), 7.30 (m, 4H), 7.42 (m, 2H), 7.53 (m, 1H), 8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 35.3, 65.5, 126.6, 128.4, 128.6, 129.0, 129.6, 130.4, 132.9, 137.9, 166.5. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.70; H, 6.30.

***p*-Methoxyphenyl benzoate (4c)**: Mp 67-69 °C; IR (KBr) 1725 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.81 (s, 3H), 6.93 (m, 2H), 7.13 (m, 2H), 7.50 (m, 2H), 7.61 (m, 1H), 8.19 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 55.6, 114.6, 122.5, 128.6, 129.7, 130.2, 133.5, 144.5, 157.4, 165.5. Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.70; H, 5.34.

4-(2-Hydroxyethyl)phenyl benzoate (4d): Mp 65-66 °C; IR (KBr) 1730 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.58 (bs, OH, D_2O exchangeable), 2.89 (t, 2H, J = 6.6 Hz), 3.87 (t, 2H, J = 6.3 Hz), 7.16 (m, 2H), 7.28 (m, 2H), 7.50 (m, 2H), 7.62 (m, 1H), 8.19 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 38.7, 63.6, 121.8, 128.6, 129.6, 130.1, 130.2, 133.6, 136.3, 149.6, 165.3. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.48; H, 5.88.

Cyclohexyl benzoate (4e): Oil; IR (KBr) 1720 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.32 (m, 6H), 1.78 (t, 2H, J = 3.2 Hz), 1.93 (t, 2H, J = 2.5 Hz), 5.03 (m, 1H), 7.42 (dd, 2H, J = 7.85 Hz, 7.56 Hz), 7.52 (m, 1H), 8.04 (dd, 2H, J = 7.86 Hz, 8.48 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.7, 25.5, 31.7, 73.0, 128.3, 129.6, 131.1, 132.7, 166.0. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.60; H, 8.01.

(1*S*,2*S*,3*R*,5*S*)-2-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]-hept-3-yl benzoate (4f): Oil; IR (KBr) 1725 (C=O), 3450 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 3H), 1.32 (s, 3H), 1.39 (s, 3H), 1.59 (d, 1H, J = 6.3 Hz), 1.83 (m, 1H), 2.00 (m, 1H), 2.06 (t, 1H, J = 3.5 Hz), 2.33 (m, 1H), 2.44 (s, OH, D_2O exchangeable), 2.60 (m, 1H), 5.41 (m, 1H), 7.46 (m, 2H), 7.57 (m, 1H), 8.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 24.3, 27.9, 28.3, 29.9, 34.8, 38.8, 40.5, 54.3, 72.5, 74.3, 128.5, 129.7, 130.2, 133.2, 166.0. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.48; H, 8.88.

Methyl *trans*-cinnamate (4g): Mp 36 °C; IR (KBr) 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.80 (s, 3H), 6.44 (d, 1H, J = 16.0 Hz), 7.37 (m, 3H), 7.51 (m, 2H), 7.69 (d, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$) d = 52.1, 118.3, 128.5, 129.3, 130.7, 134.8, 145.3, 167.8. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.12; H, 6.17.

***p*-Cyanophenyl *trans*-cinnamate (4h)**: Mp 102-103 °C; IR (KBr) 2240 (CN), 1741 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.61 (d, 1H, J = 16 Hz), 7.32 (d, 2H, J = 8.7 Hz), 7.44 (m, 3H), 7.59 (m, 2H), 7.71 (d, 2H, J = 8.7 Hz), 7.89 (d, 1H, J = 16 Hz); ^{13}C NMR ($CDCl_3$) δ = 109.4, 116.4, 118.3, 122.8, 128.5, 129.1, 131.2, 133.7, 133.9, 147.9, 154.2, 164.4. Anal.

Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.16; H, 4.52; N, 5.70.

Cyclohexyl *trans*-cinnamate (4i): Oil; IR (KBr) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.38 (m, 6H), 1.77 (m, 2H), 1.92 (m, 2H), 4.89 (m, 1H), 6.43 (d, 1H, J = 16.0 Hz), 7.37 (m, 3H), 7.51 (dd, 2H, J = 7.6 Hz, 5.4 Hz), 7.67 (d, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.9, 25.5, 31.8, 72.8, 119.0, 128.0, 128.9, 130.1, 134.7, 144.3, 166.5. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.40; H, 7.91.

2-Phenylethyl octanoate (4j): Oil; IR (KBr) 1745 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 7.0 Hz), 1.29 (m, 8H), 1.58 (m, 2H), 2.27 (t, 2H, J = 7.6 Hz), 2.93 (t, 2H, J = 7.0 Hz), 4.29 (t, 2H, J = 7.1 Hz), 7.22 (m, 3H), 7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 22.7, 25.0, 28.9, 29.1, 31.7, 34.4, 35.2, 64.8, 126.6, 128.5, 128.9, 137.9, 174.1. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.44; H, 9.77.

***p*-Cyanophenyl octanoate (4k)**: Oil; IR (KBr) 2240 (CN), 1770 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.89 (t, 3H, J = 6.9 Hz), 1.32 (m, 8H), 1.75 (t, 2H, J = 7.5 Hz), 2.58 (t, 2H, J = 7.5 Hz), 7.22 (m, 2H), 7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 22.6, 24.8, 28.9, 29.1, 31.7, 34.4, 109.6, 118.3, 122.8, 133.7, 154.2, 171.6. Anal. Calcd for $C_{15}H_{19}O_2N$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.51; H, 7.89; N, 5.74.

Cyclohexyl octanoate (4l): Oil; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 6.7 Hz), 1.37 (m, 14H), 1.58 (m, 2H), 1.72 (m, 2H), 1.84 (m, 2H), 2.27 (t, 2H, J = 7.5 Hz), 4.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.1, 22.6, 23.8, 25.1, 25.4, 29.0, 29.1, 31.7, 34.8, 72.3, 173.4. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.38; H, 11.61.

***p*-Cyanophenyl diphenylacetate (4m)**: Mp 89-90 °C; IR (KBr) 2240 (CN), 1765 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 5.26 (s, 1H), 7.18 (m, 2H), 7.30 (m, 2H), 7.38 (m, 8H), 7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 57.4, 110.4, 118.6, 123.0, 128.2, 129.0, 129.3, 134.1, 138.0, 154.4, 170.6. Anal. Calcd for $C_{21}H_{15}O_2N$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.56; H, 4.85; N, 4.54.

Methyl diphenylacetate (4n): Mp 60-61 °C (lit. mp 59-62 °C);[8] IR (KBr) 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.78 (s, 3H), 5.07 (s, 1H), 7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ = 30.4, 52.3, 57.1, 127.3, 128.6, 138.7, 173.0. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.69; H, 6.32.

***p*-Cyanophenyl *p*-chlorophenylacetate (4o)**: Mp 63-64 °C; IR (KBr) 2250 (CN), 1770 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.84 (s, 2H), 7.19 (m, 2H), 7.29 (m, 2H), 7.34 (m, 2H), 7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 40.7, 110.1, 118.1, 122.6, 129.1, 130.7, 131.2, 133.7, 133.8, 153.9, 168.7. Anal. Calcd for $C_{15}H_{10}O_2NCl$: C, 66.31; H, 3.71; N, 5.16. Found: C, 66.39; H, 3.80; N, 5.24.

Methyl *p*-chlorophenylacetate (4p): Oil; IR (KBr) 1739 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.59 (s, 2H), 3.69 (s, 3H), 7.21 (m, 2H), 7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 40.5, 52.1, 128.8, 130.7, 132.4, 133.1, 171.6. Anal. Calcd for $C_9H_9O_2Cl$: C, 58.55; H, 4.91. Found: C, 58.60; H, 4.98.

***p*-Cyanophenyl nicotinate (4q)**: Mp 119-120 °C; IR (KBr) 2250 (CN), 1750 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.40 (m, 2H), 7.50 (m, 1H), 7.77 (m, 2H), 8.44 (d, 1H, J = 7.9 Hz), 8.89 (d, 1H, J = 2.3 Hz), 9.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 110.4, 118.1, 122.8, 123.6, 124.9, 133.9, 137.7, 151.5, 153.8, 154.5, 163.1. Anal. Calcd for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.66; H, 3.66; N, 12.52.

2-Phenylethyl *trans*-cinnamate (4r): Oil; IR (KBr) 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.02 (t, 2H, J = 7.1 Hz), 4.42 (t, 2H, J = 7.1 Hz), 6.42 (d, 1H, J = 16.0 Hz), 7.28 (m, 5H), 7.37 (m, 3H), 7.50 (m, 2H), 7.67 (d, 1H, J = 16.0 Hz); ^{13}C NMR ($CDCl_3$) δ = 35.4, 65.2, 118.2, 126.8, 128.3, 128.7, 129.0, 129.1, 130.5, 134.6, 138.1, 145.0, 167.1. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.98; H, 6.48.

Methyl heptanoate (4s): Oil; IR (KBr) 1750 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.25 (t, 3H, J = 7.1 Hz), 1.36 (m, 8H), 2.04 (s, 3H), 4.12 (dd, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.2, 21.0, 23.8, 30.4, 31.7, 34.8, 60.4, 171.1. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 74.48; H, 5.88.

2-Phenylethyl heptanoate (4t): Oil; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (t, 3H, J = 7.0 Hz), 1.32 (m, 6H), 1.63 (m, 2H), 2.32 (t, 2H, J = 7.5 Hz), 2.97 (t, 2H, J = 7.1 Hz), 4.33 (t, 2H, J = 7.1 Hz), 7.26 (m, 3H), 7.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 24.9, 28.8, 31.5, 34.4, 35.2, 64.7, 126.5, 128.5, 128.9, 137.9, 173.8. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.98; H, 9.58.

Cyclohexyl heptanoate (4u): Oil; IR (KBr) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 6.9 Hz), 1.55 (m, 18H), 2.27 (t, 2H, J = 7.5 Hz), 4.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.5, 23.8, 25.1, 25.5, 28.9, 31.5, 31.7, 34.8, 72.3, 173.4. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.58; H, 11.48.

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