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An Efficient and Green Approach for the Esterification of Aromatic Acids with Various Alcohols over H_3PO_4/TiO_2-ZrO_2

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TiO_2-ZrO_2 was prepared with surfactant through a sol-gel method. Catalysts containing 5 - 35% H_3PO_4 were prepared using these oxides. Subsequently the catalytic performance of prepared catalysts was determined for liquid phase esterification of aromatic acids. H_3PO_4/TiO_2-ZrO_2 has been used as catalyst to synthesize various novel esters by esterification of some aromatic acids with aliphatic alcohols (2-propanol, 1-butanol, iso butanol, 3-pentanol, 1-hexanol, heptanol, cyclo heptanol, octanol and decanol). Under optimized conditions, maximum yields and selectivity (100%) to the corresponding ester, was obtained by using 25 wt % H_3PO_4/TiO_2-ZrO_2 as catalyst. The Catalyst can be easily recycled after reaction and can be reused without any significant loss of activity/selectivity performance. No by-product formation, high yields, short reaction times, mild reaction conditions, operational simplicity with reusability of the catalyst are the salient features of the present synthetic protocol. The reaction was carried out under solvent-free condition.

Key Words: Esterification, Solvent-free, H_3PO_4/TiO_2-ZrO_2, Aromatic acids

Introduction

Esterification of carboxylic acids with alcohols in the presence of acid catalysts has been the subject of investigation by many research workers. These esters are used in the synthesis of drugs, foods, preservative solvents, perfumes, pharmaceuticals, plasticizers, and cosmetics.[1] Both homogeneous and heterogeneous catalysts have been used for this purpose. While the mineral acids can be given as the example of the homogenous catalysts, a mixed oxide in the acid form, can serve as a heterogeneous catalyst. The use of a heterogeneous catalyst has the following inherent advantages over catalysis affected by dissolved electrolytes: (a) they eliminate the corrosive environment; (b) the catalyst can be easily removed from the reaction mixture by decantation or filtration and (c) the purity of the products is higher since the side reactions can be completely eliminated or are less significant. Some of heterogeneous catalysts reported in the literature for esterification reactions include ion exchange resin,[2] H-ZSM-5,[3] zeolites-Y,[4] niobic acid,[5] sulphated oxides,[6] and heterpoly acids. Supported heterpoly acids (HPAs)[7] have been proved to be nearly comparable to sulphuric acid in their efficiency for a series of acid-catalyzed reactions in liquid phase.[8] Unfortunately, as HPAs are highly soluble in polar media, it is often difficult to separate them from the reaction mixture, which is problematic in industrial processes.[8] So the challenge was to replace them by solid acid catalysts such as zeolites resins, which are easier to separate from the reaction mixture and also because of their less toxicity. But until now, these solid-acid catalysts have had little practical use. For instance, although zeolite catalysts have high activity, reactions always give a variety of undesired by-products due to the higher reaction temperature.[9] A major problem with the zeolite catalyzed reactions, is rapid catalyst deactivation. The rapid deactivation was explained by the condensation of the formed ketene and blockage of the pores of the catalyst. Metal oxides such as TiO_2, ZrO_2, Fe_2O_3 and Zr containing mixed oxides, become highly acidic on modification with anions such as SO_4^{2-}, PO_4^{3-}, *etc.*,[10] and these solid acid catalysts have been employed in several industrial important acid catalyzed reactions such as low temperature isomerization, alkylation, esterification, cracking, *etc.*[11-14]

The main problem associated with these catalysts is the rapid loss of activity, which may be due to coking and/or sintering. More active and stable catalysts can be obtained by incorporating transition metals, especially noble metals in to the ZrO_2 system.[15-17] In this way, the thermal stability against sintering is also enhanced considerably.[18,19]

Recently, it has been observed that H_3PO_4/TiO_2-ZrO_2 showed high thermal stability, low catalytic deactivation and very good selectivity for Beckmann rearrangement,[20] acylation of phenol[21] and Fries rearrangement.[22] These data showed that H_3PO_4/TiO_2-ZrO_2 had a good activity and selectivity for the acid catalyzed reactions.

In this work, esterification of some aromatic acids with aliphatic alcohols (long chain and small chain) to synthesize various novel esters over H_3PO_4/TiO_2-ZrO_2 as a catalyst, has been studied.

Results and Discussion

The esterification of salicylic acid with aliphatic alcohols was carried out with various kinds of H_3PO_4/TiO_2-ZrO_2. The esterification of salicylic acid as well as other aromatic carboxylic acids with aliphatic alcohols, gave the corresponding esters in high yield.

Improvement of H_3PO_4/TiO_2-ZrO_2 catalysts is done by optimizing the amounts of the loaded H_3PO_4. The variation amounts of loaded H_3PO_4 (0 - 35 wt % H_3PO_4) has different effects on the activity and selectivity of the reaction. According to the results, the highest yield of the ester has been achieved in the presence of 25 wt % H_3PO_4/TiO_2-ZrO_2 as catalyst (Table 1). It seems clear that the acid strength of the protons on 25 wt % H_3PO_4/TiO_2-ZrO_2 is sufficient to catalyze the esterification reac-

Table 1. Effect of loaded H_3PO_4[a]

Catalyst	Yield (%)[b]		
	45 min	1 h	2 h
TiO_2-ZrO_2	20	35	35
5 wt % H_3PO_4/TiO_2-ZrO_2	70	85	85
15 wt % H_3PO_4/TiO_2-ZrO_2	70	85	85
25 wt % H_3PO_4/TiO_2-ZrO_2	95	95	95
35 wt % H_3PO_4/TiO_2-ZrO_2	50	50	50

[a]Reaction conditions: solvent-free, decanol:salicylic acid = 3:1, catalyst (0.1 g, 0.33 mmol), temperature (160 °C). [b]Isolated Yield.

Table 2. Effect of decanol: salicylic acid molar ratio[a]

decanol:salicylic acid molar ratio	Yield (%)[b]
1:1	40
3:1	95
5:1	10

[a]Reaction conditions; catalyst (0.1 g, 0.33 mmol): 25 wt % H_3PO_4/TiO_2-ZrO_2, Solvent-free, temperature (160 °C), time: 45 min. [b]Isolated Yield.

Table 3. Effect of the catalyst amount[a]

Catalyst (g)	Yield (%)[b]
0.05	70
0.07	70
0.1	95
0.12	95

[a]Reaction conditions: catalyst: 25 wt % H_3PO_4/TiO_2-ZrO_2, Solvent-free, decanol:Salicylic acid = 3:1, temperature (160 °C), time: 45 min. [b]Isolated Yield.

tion and potentially all protons are active sites. By using 25 wt % H_3PO_4/TiO_2-ZrO_2, the observed selectivity was 98% towards the formation of alkyl salicylate as the reaction product and the catalyst can be easily regenerated with a high recovery of the initial activity.

In order to investigate the effect of the support (TiO_2-ZrO_2) on the esterification reaction, we used H_3PO_4 (with the same ratio of the optimized catalyst) without any support as catalyst in the esterification of salicylic acid and keeping other parameters constant. After 2 h, 70% selectivity and about 45% yield is observed. Therefore, TiO_2-ZrO_2 as a support is very useful for the esterification reaction.

Various mole ratios of salicylic acid to alcohol were used. Our studies showed that even under optimized conditions, the reaction yields were affected by changing the molar ratio of alcohol: acid (1:1, 3:1 and 5:1). According to the results, the highest yield of ester has been achieved with molar ratio of alcohol: acid, 3:1 (Table 2).

The amounts of the catalyst were varied between 0.05 g (0.16 mmol) and 0.12 g (0.39 mmol) keeping alcohol to salicylic acid molar ratio at 3:1. The results in Table 3 show that the yields of esters are increased with increasing the amount of the catalyst from 0.05 to 0.1 g. Any further increasing in the amount of the catalyst does not have any effect on the reaction yields.

In order to know whether the catalysts would succumb to poisoning and lose of catalytic activity during the reaction, the catalyst was recovered after the esterification reaction. After the reaction, The recovered catalyst was washed with water (10 mL) and acetone (3 × 5 mL), then dried in oven at 60 °C and used in the esterification reaction. The results showed that this catalyst can be reused without any modification, for 4 times and no significant loss of activity/selectivity performance was observed.

This study was also extended to other aromatic acids such as benzoic acid, 4-methyl benzoic acid and 2-chloro-5-nitro benzoic acid in order to generalize the capability of the 25 wt % H_3PO_4/TiO_2-ZrO_2 under heterogeneous conditions (Table 4). According to the results, alcohols with long carbon chain length gave the corresponding ester in a higher yield compared with the other linear alcohols. This method has favorable generality and applicability for various structurally diverse alcohols including primary and secondary alcohols with the selectivity of $1^o > 2^o$.

Less than 0.1 g (0.33 mmol) of 25 wt % H_3PO_4/TiO_2-ZrO_2 was suitable for condensing various carboxylic acids with not only long chain alcohols but also short chain and hindered alcohols. However, short chain alcohols such as 2-propanol and 1-butanol were less reactive than long chain alcohols because the boiling point of short chain alcohols is low.

According to the results, acids with electron-withdrawing substituents gave esters in a higher yield than those of electron-donating groups. This can be attributed to the activating effect of the substituent.

Aromatic carboxylic acid with electron withdrawing groups (2-chloro-5-nitro benzoic acid) offered good yields and the reactions were completed in short times. Also in the case of electron donating groups (-CH_3 and -OH), reasonably good yields were observed but demanded more reaction time.

It should be mentioned that all the reactions occurred with complete selectivity for esters and no by-products such as ethers were detected in the reaction mixture. Furthermore, 25 wt % H_3PO_4/TiO_2-ZrO_2 was effective for the esterification of aromatic carboxylic acids with volatile alcohols such as 2-propanol. The reaction proceeded in alcohols without the removal of water.

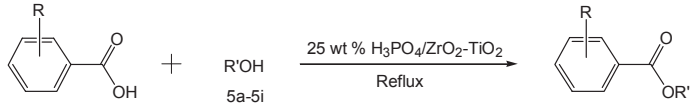
Conclusion

The esterification of linear alcohols with some aromatic acids has been carried out over H_3PO_4/TiO_2-ZrO_2 as catalyst. H_3PO_4/TiO_2-ZrO_2 is an active and environmentally friendly catalyst for esterification of the linear alcohols with aromatic acids. TiO_2-ZrO_2 catalyst was less reactive and selective for esterification but when various amounts of H_3PO_4 were loaded on it, the catalyst showed very good activity and selectivity for this type of reaction without the removal of water. This esterification reaction is an attractive and efficient route to synthesize various novel esters of substituted aromatic carboxylic acids with long chain aromatic alcohols.

Experimental

General. All chemicals used in this study were of the highest purity available and purchased from Merck and Aldrich chemi-

Table 4. Esterification of carboxylic acids with various aliphatic alcohols **5a-5i** using 25 wt % H_3PO_4/TiO_2-ZrO_2 as catalyst[a]



1 R= OH
2 R= Cl, NO_2
3 R= CH_3
4 R=H

R'= *n*-decanol, *n*-octanol, *n*-heptanol, cycloheptanol, *n*-hexanol, 3-pentanol, *n*-butanol, iso-butanol, iso-propanol

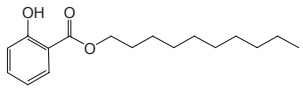
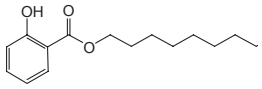
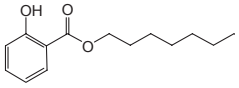
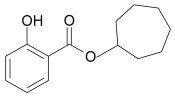
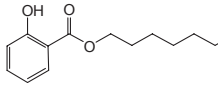
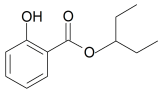
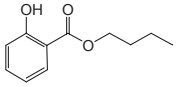
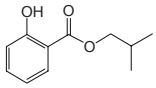
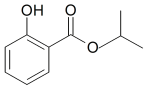
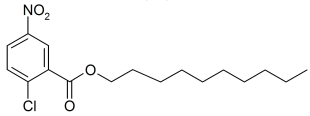
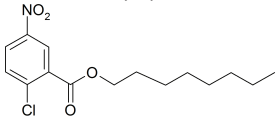
Entry[ref]	Alcohol	Carboxylic acid	Temperature (°C)	Time (min)[b]	Product	Yield (%)[c]
1 [23a]	*n*-decanol (5a)	1	160	45	 (6a)	95
2	octanol (5b)	1	140	100	 (6b)	80
3	heptanol (5c)	1	130	100	 (6c)	90
4	cyclo heptanol (5d)	1	120	105	 (6d)	50
5 [23b]	hexanol (5e)	1	120	120	 (6e)	80
6	3-pentanol (5f)	1	110	120	 (6f)	65
7 [23c,d]	butanol (5g)	1	110	110	 (6g)	60
8	isobutanol (5h)	1	105	105	 (6h)	50
9 [23e]	isopropanol (5i)	1	80	240	 (6i)	40
10	*n*-decanol (5a)	2	160	30	 (7a)	98
11	octanol (5b)	2	140	45	 (7b)	98

Table 4. Continued

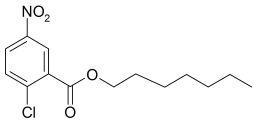
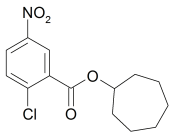
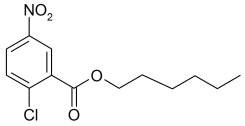
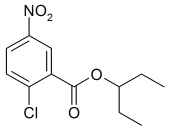
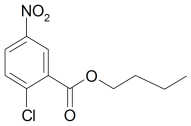
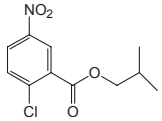
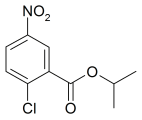
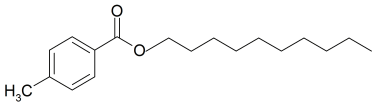
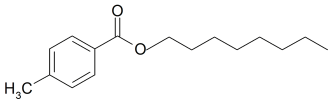
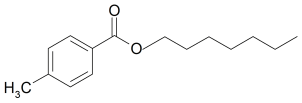
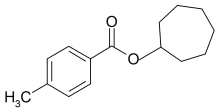
Entry[ref]	Alcohol	Carboxylic acid	Temperature (°C)	Time (min)[b]	Product	Yield (%)[c]
12	heptanol(5c)	2	130	45	 (7c)	97
13	cyclo heptanol (5d)	2	120	90	 (7d)	90
14	hexanol (5e)	2	120	100	 (7e)	93
15	3-pentanol (5f)	2	110	90	 (7f)	75
16	butanol (5g)	2	110	100	 (7g)	65
17	isobutanol (5h)	2	105	60	 (7h)	55
18	isopropanol (5i)	2	80	60	 (7i)	47
19	*n*-decanol (5a)	3	160	40	 (8a)	95
20 [23f]	octanol (5b)	3	140	65	 (8b)	97
21	heptanol(5c)	3	130	105	 (8c)	80
22	cyclo heptanol (5d)	3	120	105	 (8d)	70

Table 4. Continued

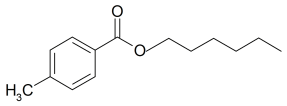
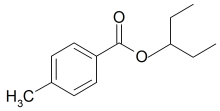
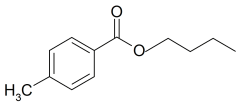
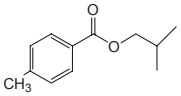
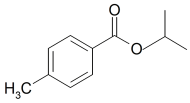
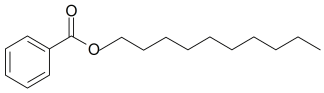
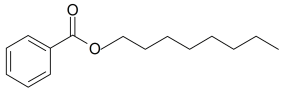
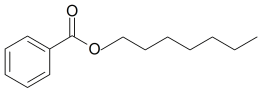
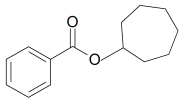
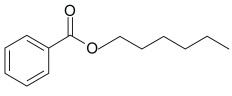
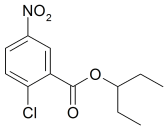
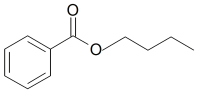
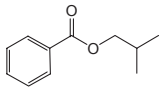
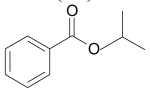
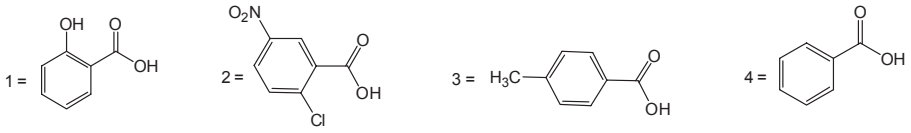
Entry[ref]	Alcohol	Carboxylic acid	Temperature (°C)	Time (min)[b]	Product	Yield (%)[c]
23 [23g,h]	hexanol (5e)	3	120	100	 (8e)	90
24	3-pentanol (5f)	3	110	100	 (8f)	65
25 [23i,j]	butanol (5g)	3	110	100	 (8g)	60
26	isobutanol (5h)	3	105	100	 (8h)	50
27 [23k]	isopropanol (5i)	3	80	180	 (8i)	40
28 [23l,π]	*n*-decanol (5a)	4	160	60	 (9a)	95
29 [23n,k]	octanol (5b)	4	140	60	 (9b)	95
30 [23o]	heptanol(5c)	4	130	60	 (9c)	95
31	cyclo heptanol (5d)	4	120	100	 (9d)	75
32 [23h]	hexanol (5e)	4	120	100	 (9e)	95
33 [23p]	3-pentanol (5f)	4	110	120	 (9f)	70
34 [23o]	butanol (5g)	4	110	100	 (9g)	65

Table 4. Continued

Entry[ref]	Alcohol	Carboxylic acid	Temperature (°C)	Time (min)[b]	Product	Yield (%)[c]
35	isobutanol (5h)	4	105	100	 (9h)	50
36 [23n]	isopropanol (5i)	4	80	240	 (9i)	45

[a]Reaction conditions: alcohol : carboxylic acid, 3:1; 25 wt % H_3PO_4/ZrO_2-TiO_2 (0.1 g, 0.33 mmol), solvent-free. [b]Time of maximum yield. [c]Isolated Yield.



cal companies. The products were characterized by ^{1}H and ^{13}C NMR spectra (Bruker DRX-500 Avance spectrometer at 500.13 and 125.47 MHz, respectively), GC (Agilent 6820 equipped with a FID detector) and GC-MS (Agilent 6890). Melting points were measured on an Electrothermal 9100 apparatus and were uncorrected.

General procedure for synthesis of esters. As a general reaction, the catalytic esterification reactions of salicylic acid carried out in a round bottom flask equipped with magnetic stirrer, thermometer, and a reflux condenser. In each reaction, catalyst (0.05 - 0.12 g) was added to a mixture of salicylic acid (1 mmol) and alcohol (with different molar ratios). The reaction mixture was stirred and refluxed for 45 - 120 min. At room temperature, reactions were carried out with stirring for 8 h. Different reaction-runs were conducted by varying the reaction parameters such as molar ratio of the reactants, weight of the catalyst, reaction period and H_3PO_4 content of the catalyst in order to optimize the reaction conditions to get good yield and high selectivity of the product. The progress of the reactions was monitored by TLC. After completion of the reaction, the mixed oxide could be simply filtered to remove from the product. The crude product was purified by column chromatography on silica gel eluting with a mixture of *n*-hexane/EtOAc and was analyzed. At regular intervals, Karl Fisher titration was performed for determination of produced water. The products were characterized by comparison of their spectroscopic (IR, ^{1}H NMR and ^{13}C NMR) data with those of authentic samples.

Spectral data of the some desired products.

Decyl salicylate (Table 4, Entry 1): Yield 95%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.93 (-CH_3, t, J = 7.0 Hz), 1.46-1.31 (-CH_2, 14H, m), 1.82 (-CH_2, quin, J = 7.2 Hz), 4.38 (-CH_2, t, J = 6.6 Hz), 6.91 (ArH, t, J = 7.8 Hz), 7.02 (ArH, d, J = 7.8 Hz), 7.47 (ArH, t, J = 7.8 Hz), 7.89 (ArH, d, J = 7.8 Hz), 10.89 (Ar-OH, S); ^{13}C NMR (125 MHz, CCl_4) δ 14.52, 23.11, 26.39, 28.99, 29.67, 29.73, 29.96, 30.24, 32.32, 65.92, 113.08, 117.97, 119.45, 130.28, 135.94, 162.14, 170.65; IR (KBr) ν 752, 1095, 1300, 1473, 1612, 1667, 2852, 2915, 3185 cm^{-1}.

Heptyl salicylate (Table 4, Entry 3): Yield 90%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.94 (-CH_3, t, J = 7.0 Hz), 1.56-1.37 (-CH_2, 8H, m), 1.82 (-CH_2, quin, J = 7.8 Hz), 4.38 (-CH_2, t, J = 6.7 Hz), 6.92 (ArH, t, J = 7.0 Hz), 7.02 (ArH, d, J = 8.3 Hz), 7.48 (ArH, dt, J = 7.0, 1.6 Hz), 7.89 (ArH, dd, J = 7.9, 1.6 Hz); IR (KBr) ν 756, 1089, 1300, 1481, 1612, 1677, 2858, 2928, 3185 cm^{-1}.

Cycloheptyl salicylate (Table 4, Entry 4): Yield 50%, yellow liquid, ^{1}H NMR (500 MHz, CCl_4) δ 1.86-1.34 (-CH_2, 8H, m), 2.05 (-CH_2, m, J = 6.5 Hz), 3.41 (-CH_2, m, J = 6.8 Hz), 5.25 (-CH, sep, J = 4.4 Hz), 6.88 (ArH, dt, J = 7.0, 2.0 Hz), 6.97 (ArH, dd, J = 7.6, 2.0 Hz), 7.44 (ArH, dt, J = 6.6, 1.7 Hz), 7.87 (ArH, dd, J = 6.2, 1.7 Hz); IR (KBr) ν 756, 1089, 1213, 1460, 1612, 1672, 2857, 2926, 3183 cm^{-1}.

Decyl 2-chloro-5-nitro benzoate (Table 4, Entry 10): Yield 98%, yellow solid, mp 64.1 - 64.3 °C; ^{1}H NMR (500 MHz, CCl_4) δ 0.89 (-CH_3, t, J = 7.0 Hz), 1.34-1.26 (-CH_2, 12H, m), 1.48 (-CH_2, quin, J = 7.8 Hz), 1.82 (-CH_2, quin, J = 7.8 Hz), 4.4 (-CH_2, t, J = 6.6 Hz), 7.66 (ArH, d, J = 8.7 Hz), 8.28 (ArH, dd, J = 6 0, 2.7 Hz), 8.69 (ArH, d, J = 2.7 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.49, 23.07, 26.35, 28.93, 29.60, 29.69, 29.89, 29.91, 32.28, 67.05, 126.91, 127.03, 132.04, 132.68, 140.97, 146.59, 164.12; IR (KBr) ν 1045,1134, 1344, 1537, 1726, 2845, 2905, 3100 cm^{-1}.

Octyl 2-chloro-5-nitro benzoate (Table 4, Entry 11): Yield 98%, yellow solid, mp 52.4 - 53.5 °C; ^{1}H NMR (500 MHz, CCl_4) δ 0.91 (-CH_3, t, J = 7.0 Hz), 1.37-1.28 (-CH_2, 8H, m), 1.48 (-CH_2, quin, J = 7.4 Hz), 1.83 (-CH_2, quin, J = 6.8 Hz), 4.42 (-CH_2, t, J = 6.7 Hz), 7.69 (ArH, d, J = 8.7 Hz), 8.29 (ArH, dd, J = 7.3, 1.4 Hz), 8.71 (ArH, s); ^{13}C NMR (125 MHz, CCl_4) δ 14.49, 23.04, 26.36, 28.93, 29.56, 32.17, 67.07, 126.93, 127.04, 132.05, 132.69, 141.00, 146.59, 164.16; IR (KBr) ν 1043, 1133, 1245, 1357, 1532, 1728, 2846, 2925, 2958, 3105 cm^{-1}.

Heptyl 2-chloro-5-nitro benzoate (Table 4, Entry 12): Yield 97%, yellow solid, mp 37.9 - 38.8 °C; ^{1}H NMR (500 MHz, CCl_4) δ 0.90 (-CH_3, t, J = 6.8 Hz), 1.32 (-CH_2, 4H, m), 1.38 (-CH_2, quin, J = 7.6 Hz), 1.46 (-CH_2, quin, J = 7.2 Hz), 1.81 (-CH_2, t, J = 7.1 Hz), 4.40 (-CH_2, t, J = 6.5 Hz), 7.67 (ArH, d, J = 8.5 Hz), 8.28 (ArH, dd, J = 7.5, 1.1 Hz), 8.68 (ArH, d, J = 0.9 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.44, 22.96, 26.31, 28.92, 29.27, 32.08, 67.03, 126.89, 127.04, 132.00, 132.68, 140.95, 146.57,

164.11; IR (KBr) ν 1138, 1249, 1350, 1534, 1733, 2854, 2929, 2955, 3107 cm^{-1}.

Cycloheptyl 2-chloro-5-nitro benzoate (Table 4, Entry 13): Yield 90%, yellow liquid; ^{1}H NMR (500 MHz, CCl_4) δ 1.55 (-CH_2, quin, *J* = 7.2 Hz), 1.62 (-CH_2, s, 4H), 1.74 (-CH_2, quin, *J* = 6.9), 1.85 (-CH_2, m, *J* = 6.1 Hz), 2.07 (-CH_2, quin, *J* = 5.6 Hz), 5.25 (-CH, sep, *J* = 4.4 Hz),7.65 (ArH, d, *J* = 8.7 Hz), 8.26 (ArH, dd, *J* = 6.6, 2.0 Hz), 8.63 (ArH, d, *J* = 0.9 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 23.26, 28.66, 34.12, 78.38, 126.69, 126.83, 132.57, 132.68, 140.73, 146.56,.163.53; IR (KBr) ν 1048, 1140, 1251, 1461, 1530, 1610, 1728, 2859, 2930, 3093 cm^{-1}.

Hexyl 2-chloro-5-nitro benzoate (Table 4, Entry 14): Yield 93%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.93 (-CH_3, t, *J* = 6.9 Hz), 1.38 (-CH_2, 4H, sex, *J* = 3.5 Hz), 1.46 (-CH_2, quin, *J* = 7.05 Hz), 1.82 (-CH_2, quin, *J* = 6.8 Hz), 4.41 (-CH_2, t, *J* = 6.8 Hz), 7.66 (ArH, d, *J* = 8.8 Hz), 8.28 (ArH, dd, *J* = 8.8, 2.7 Hz), 8.69 (ArH, d, J = 2.8 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.37, 22.91, 26.02, 28.88, 31.77, 67.05, 126.91, 127.03, 132.04, 132.68, 140.97, 146.59, 164.13; IR (KBr) ν 741, 838, 1049, 1138, 1331,1349, 1531, 1611, 1735, 2863, 2932, 2955, 3104 cm^{-1}.

Butyl 2-chloro-5-nitro benzoate (Table 4, Entry 16): Yield 65%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.97 (-CH_3, t, *J* = 7.4 Hz), 1.47 (-CH_2, sex, *J* = 7.3 Hz), 1.78 (-CH_2, quin, *J* = 6.8 Hz), 4.38 (-CH_2, t, *J* = 6.6 Hz) 7.65 (ArH, d, *J* = 8.8 Hz), 8.25 (ArH, dd, *J* = 8.8, 2.8 Hz), 8.64 (ArH, d, *J* = 2.7 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.03, 19.58, 30.07, 66.67, 126.82, 127.03, 131.93, 132.66, 140.86, 146.55, 164.03; IR (KBr) ν 1131, 1352, 1533, 1734, 2872, 2952, 3099 cm^{-1}.

Decyl 4-methylbenzoate (Table 4, Entry 19): Yield 95%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.92 (-CH_3, t, *J* = 6.9 Hz), 1.45-1.31 (-CH_2, 10H, m,), 1.47 (-CH_2, quin, *J* = 7.1 Hz), 1.7929 (-CH_2, quin, *J* = 7.4 Hz), 2.44 (-CH_3, s), 4.33 (-CH_2, t, *J* = 6.6 Hz), 7.27 (ArH, 2H, d, *J* = 7.8 Hz), 7.98 (ArH, 2H, d, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.53, 22.05, 23.10, 26.48, 29.18, 29.72, 29.97, 32.32, 65.37, 128.27, 129.44, 129.99, 143.79, 167.17; IR (KBr) ν 1105, 1275, 1715, 2851, 2924, 3087 cm^{-1}.

Heptyl 4-methylbenzoate (Table 4, Entry 21): Yield 80%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 0.93 (-CH_3, t, *J* = 6.9 Hz), 1.47-1.34 (-CH_2, 6H, m), 1.80 (-CH_2, quin, *J* = 6.7 Hz), 2.44 (-CH_3, s), 4.33 (-CH_2, t, *J* = 6.7 Hz), 7.27 (ArH, 2H, d, *J* = 8.0 Hz), 7.98 (ArH, 2H, d, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 14.47, 22.04, 23.02, 26.45, 29.19, 29.39, 32.17, 65.36, 128.27, 129.44, 129.98, 143.79, 167.17; IR (KBr) ν 754, 1108, 1274, 1612, 1720, 2859, 2929, 2952, 3081 cm^{-1}.

Cycloheptyl 4-methylbenzoate (Table 4, Entry 22): Yield 70%, yellow oil; ^{1}H NMR (500 MHz, CCl_4) δ 1.61 (-CH_2, quin, *J* = 6.6 Hz), 1.65 (-CH_2, 4H, s), 1.82 (-CH_2, quin, *J* = 5.2 Hz), 1.86 (-CH_2, quin, *J* = 5.6 Hz), 2.03 (-CH_2, quin, *J* = 5.1 Hz), 2.43 (-CH_3, s), 5.22 (-CH, sep, *J* = 4.3 Hz), 7. 26 (ArH, 2H, d, *J* = 7.8 Hz), 7.97 (ArH, 2H, d, *J* = 7.8 Hz); ^{13}C NMR (125 MHz, CCl_4) δ 22.03, 23.34, 28.76, 34.28, 75.78, 128.79, 129.38, 129.95, 143.63, 166.42; IR (KBr) ν 754, 1108, 1275, 1455, 1612, 1713, 2859, 2928, 3089 cm^{-1}.

Cycloheptyl benzoate (Table 4, Entry 31): Yield 75%, colorless oil; ^{1}H NMR (500 MHz, CCl_4) δ 1.56 (-CH_2, quin, *J* = 6.4 Hz), 1.65 (-CH_2, 4H, m), 1.85 (-CH_2, quin, *J* = 5.7 Hz), 1.88 (-CH_2, quin, *J* = 5.6 Hz), 2.1 (-CH_2, quin, *J* = 5.2 Hz), 5.24 (-CH, sep, *J* = 4.4 Hz), 7.43 (ArH, 2H, t, *J* = 7.5 Hz), 7.58 (ArH, tt, *J* = 7.7, 1.2 Hz), 8.08 (ArH, 2H, d, *J* = 7.7 Hz); IR (KBr) ν 711, 1112, 1274, 1455, 1612, 1715, 2859, 2929, 3103 cm^{-1}.

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