Solvent-free alkylation of N-heteroaromatic compounds by RCOOH—$Pb(OAc)_4$ system*

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The solvent-free decarboxylation of carboxylic acids by $Pb(OAc)_4$ affords alkyl radicals, which alkylate 4-methylpyridine, quinoline, and 4-methylquinoline protonated with 2-chlorobenzoic acid. Mechanical activation is required for pyrazine alkylation.

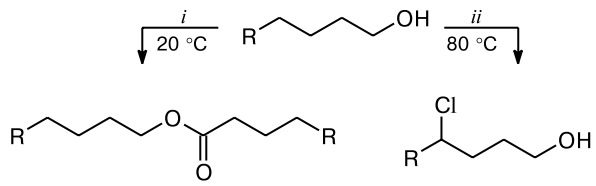
Key words: carboxylic acids, N-heteroaromatic compounds, lead tetraacetate, oxidative decarboxylation, alkylation, mechanical activation, solvent-free reaction.

Lead tetraacetate, being one of the reagents that are most widely used in organic chemistry, long ago and firmly has become a used efficient oxidant of functionalized organic compounds. Among the variety of reactions involving $Pb(OAc)_4$, oxidative decarboxylation of carboxylic acids plays an important role. Many carboxylic acids were transformed into unsaturated hydrocarbons and halo- and acetoxyalkanes by $Pb(OAc)_4$ and $Pb(OAc)_4$ in combination with LiCl, $Cu(OAc)_2$, and I_2.[1] The reactions were carried out in the liquid phase in inert solvents.

We began to use $Pb(OAc)_4$ in solvent-free chemical processes in the solid phase with and without mechanical activation. Under these conditions, the selectivity and yield of target products can be higher than in solution. For example, naphthalene halogenation by the $Pb(OAc)_4$—LiCl(Br) system affords 1-halonaphthalene as the main product along with 1,4-dihalonaphthalene. 1-Halonaphthalene is formed in the solid phase with a higher selectivity than in the liquid phase.[2] A similar effect was observed for the oxoalkylation of pyridines with oxoalkyl radicals generated from 1-alkylcycloalkanols under the action of $Pb(OAc)_4$. In the solid phase, the radicals substitute hydrogen in the pyridine ring and are consumed in side reactions only by 5—20%; the fraction of side reactions increases to 35—45% in an AcOH solution.[3]

Basically important results were obtained for the oxidation of alkan-1-ols and alkanedioic acids by a $Pb(OAc)_4$—metal chloride system: on going from the liquid to solid phase, the mechanism of these reactions changes and, as a sequence, different products are formed. Alkan-1-oles in a benzene solution convert to 4-chloroalkanols, while esters are formed in the solid phase[4] (Scheme 1).

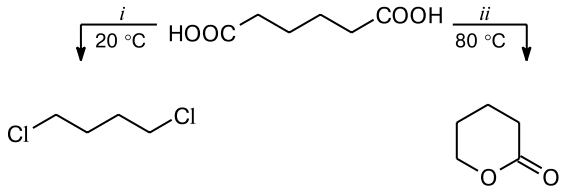
Scheme 1



i. Solid phase. *ii*. Liquid phase.

Adipic acid in an acetic acid solution undergoes ring closure to form δ-valerolactone, while in the solid phase it is transformed into 1,4-dichlorobutane (Scheme 2).[5]

Scheme 2



i. Solid phase. *ii*. Liquid phase.

In this work, we continue our study of the solvent-free reactions of $Pb(OAc)_4$ with alcohols and carboxylic acids

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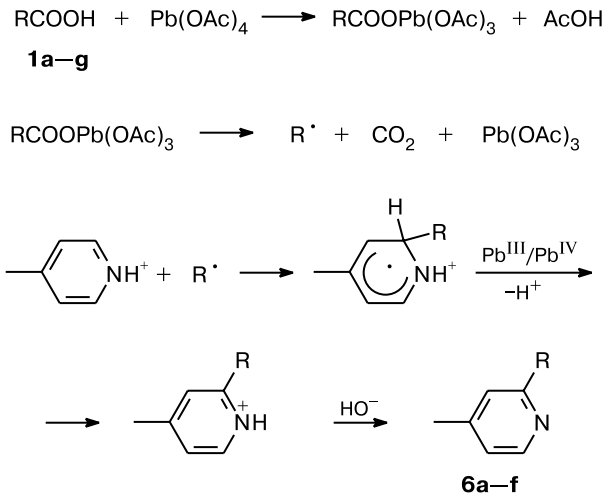
with and without mechanical activation. The task was to use carboxylic acids as alkylating agents for N-heteroaromatic compounds. To solve this problem, we chose acids with different structures: hexanoic (**1a**), octanoic (**1b**), 2-methylpropanoic (**1c**), 2-ethylhexanoic (**1d**), 3-methoxycarbonylpropanoic (**1e**), 3-phenylpropanoic (**1f**), and phenylacetic (**1g**). In addition, a series of N-heterocyclic compounds was studied: 4-methylpyridine (**2**), quinoline (**3**), 4-methylquinoline (**4**), and pyrazine (**5**). The heterocycles were alkylated with C-radicals generated from acids **1a—f** under the action of $Pb(OAc)_4$ (Scheme 3).

Scheme 3



R = *n*-C_5H_{11} (**a**), *n*-C_7H_{15} (**b**), Pr^i (**c**), $Bu^nCH(Et)$ (**d**), $MeO_2CCH_2CH_2$ (**e**), $PhCH_2CH_2$ (**f**), $PhCH_2$ (**g**)

The necessary condition for this process to occur is the involvement of protonated N-heterocycles **2—5**. Protonation provides easy addition of nucleophilic C-centered radicals to an electrophilic heterocycle bearing a positive charge.[6] 2-Chlorobenzoic acid (CBA), which was earlier used successfully for the oxoalkylation of N-heterocyclic compounds by 1-alkylcycloalkanols, served as a protonating agent.[3] Benzoic acid can play the same role. However, alkylation involving this acid proceeds less efficiently than that with CBA. The use of acetic and trifluoroacetic acids for protonation of heterocycles **2—5** afforded no alkylation products.

The results of the solvent-free reactions of acids **1a—f** and bases **2—5** are presented in Tables 1 and 2. For comparative estimation, experiments carried out under "usual" conditions (in a benzene solution at 80 °C) are also included in the tables. The data indicate that alkylation without mechanical activation primarily occurs in the liquid phase and is completed in the solid phase. In fact, after mixing the reagents ($Pb(OAc)_4$, RCOOH, CBA, and heteroaromatic compound **2—4**), a viscous but still agile mixture was formed and slowly solidified. The boundary of phase changing in time was estimated visually. We understand that this estimate only approximately characterizes the phase state of the reaction mixture. Nevertheless, these two steps are real, reflected in specific features of the reactions of N-heteroaromatic compounds with acids, and expressed in particular figures. For instance, the following characteristics were obtained for the reactions of 4-methylpyridine **2** with acids **1b** and **1d**: the time of transition of the liquid phase into solid is ~26 and ~6 h, respectively; the conversion of $Pb(OAc)_4$ within this time is 60 and 58%; and the yields of products **6b** and **6d** are 28 and 36%, respectively. Comparing these results with the final yields of products **6b** and **6d** (63 and 71%, see Table 1, entries *4* and *10*) for the 100% conversion of the oxidant, we can conclude that in the final step $Pb(OAc)_4$ is more purposefully consumed for alkylation and, to a less extent, for side reactions than in the initial step. This fact is explained, most likely, by the transition of the reacting system from the liquid to solid phase. As a whole, the solvent-free alkylation of heterocycles **2—4** is characterized by the higher conversion of acids **1**, yield of products, and selectivity of the reactions than that in solution using benzene as solvent and CF_3COOH as a protonating agent (see Table 1). These parameters are sharply worsened when trifluorobenzoic acid is replaced by CBA in a benzene solution (entry *6*). The replacement of CBA by CF_3COOH in the solvent-free reaction results in a fast decomposition of $Pb(OAc)_4$, which is not accompanied by decarboxylation of acids **1** and generation of C-radicals (entry *3*). One of the reasons for the low conversion (~35—55%) of acids **1** by alkylation in solution (benzene + trifluoroacetic acid) is that $Pb(OAc)_4$ is actively reduced in the parallel reaction with N-bases **2—4** involving no acids **1**. Indeed, in an experiment similar to entry *4* (see Table 1) but without acid **1b**, the conversion of $Pb(OAc)_4$ was ~80%. This reaction is also solvent-free but makes a lower contribution to the overall conversion process Pb^{IV} acetate → Pb^{II} acetate.

According to the data in Table 1 (entries *4*, *10*, *20*, and *22*), the reactivity of 4-methylquinoline **4** in the reaction with acids **1b** and **1d** is almost the same as that of 4-methylpyridine **2**; alkylation occurs to position 2 of the quinoxaline system to form 2-heptyl-4-methylquinoline (**7b**) and 2-(hept-3-yl)-4-methylquinoline (**7d**), respectively. Hept-3-yl radicals formed by alkylation with acid **1d** attack, to an equal extent, both reaction centers of quinoline to give two isomeric products with the alkyl substituent in positions 2 and 4 (**8d** and **9d**). Oxoalkyl radicals generated from 1-methylcycloalkanols by $Pb(OAc)_4$ behave similarly in the solid-phase reaction.[3]

The results of oxidative decarboxylation of phenylacetic acid (**1g**) in the presence of CBA-protonated base **2** are unexpected. Unlike C-radicals generated from acids

Table 1. Solvent-free alkylation of N-heteroaromatic compounds (4-methylpyridine (**2**), quinoline (**3**), and 4-methylquinoline (**4**)) protonated with carboxylic acids **1** under the action of $Pb(OAc)_4$ without mechanical activation[a]

Entry	Reagents	Protonating acid	τ/h	Conversion[b] **1** (%)	Product	Yield[c] (%)
1	**1a** +**2**	2-ClC_6H_4COOH	48	65	**6a**	58 (89)
2	**1b** + **2**	AcOH	48	—	—	
3	**1b** + **2**	CF_3COOH	0.25	—	—	
4	**1b** + **2**	2-ClC_6H_4COOH	48	69	**6b**	63 (91)
5[d]	**1b** + **2**	CF_3COOH	0.75	38	**6b**	36 (94)
6[d,e]	**1b** + **2**	2-ClC_6H_4COOH	1.5	—	**6b**	16
7	**1c** + **2**	AcOH	72	—	—	
8	**1c** + **2**	C_6H_5COOH	72	55	**6c**	51 (95)
9	**1c** + **2**	2-ClC_6H_4COOH	24	87	**6c**	77 (88)
10	**1d** + **2**	2-ClC_6H_4COOH	24	75	**6d**	71 (95)
11[d]	**1d** + **2**	CF_3COOH	0.75	46	**6d**	45 (98)
12	**1e** + **2**	2-ClC_6H_4COOH	48	54	**6e**	53 (98)
13[d]	**1e** + **2**	CF_3COOH	0.75	32	**6e**	30 (93)
14	**1f** + **2**	2-ClC_6H_4COOH	48	94	**6f**	91 (97)
15[d]	**1f** + **2**	CF_3COOH	0.75	65	**6f**	64 (98)
16	**1g** + **2**	2-ClC_6H_4COOH	48	72	**10**	64
17[f]	**1g** + **2**	2-ClC_6H_4COOH	4	49	**10**	44
18[g]	**1d** + **3**	2-ClC_6H_4COOH	24	80	**8d**	35 (2)
					9d	41 (4)
19[d,h]	**1d** + **3**	CF_3COOH	0.5	55	**8d**	23 (2)
					9d	29 (4)
20	**1b** + **4**	2-ClC_6H_4COOH	48	68	**7b**	65 (95)
21[d]	**1b** + **4**	CF_3COOH	0.75	43	**7b**	40 (93)
22	**1d** + **4**	2-ClC_6H_4COOH	24	77	**7d**	72 (94)
23[d]	**1d** + **4**	CF_3COOH	0.75	48	**7d**	44 (98)

[a] Molar ratio **1** : **2**—**4** : $Pb(OAc)_4$: protonating acid = 1 : 4 : 1.1 : 4; 20 °C; **1**, 5 mmoles.
[b] The conversion of $Pb(OAc)_4$ is ~100%.
[c] The yield is presented with respect to the starting (in parentheses, with respect to converted) acid **1**.
[d] Reaction in a benzene solution (10 mL) at 80 °C.
[e] The conversion of **1b** was not determined.
[f] The reaction was carried out with mechanical activation.
[g] The overall yield of two isomers is 76 (95).
[h] The overall yield of two isomers is 52 (95).

Table 2. Alkylation of pyrazine **5** with carboxylic acids **1** under the action of $Pb(OAc)_4$[a]

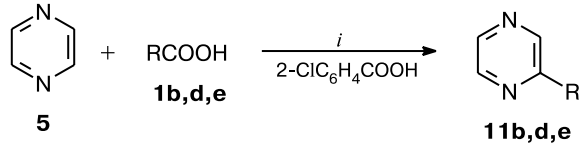
Entry	Acid **1**	Protonating acid	τ/h	Conversion[b] **1** (%)	Product	Yield[c] (%)
1[d]	**1b**	AcOH	72	—	—	
2[d]	**1b**	2-ClC_6H_4COOH	48	—	—	
3[e]	**1b**	2-ClC_6H_4COOH	4	—	—	
4[e]	**1b**	AcOH	4	—	—	
5[e]	**1b**	2-ClC_6H_4COOH	4	82	**11b**	80 (98)
6[f]	**1b**	CF_3COOH	0.75	41	**11b**	40 (98)
7	**1d**	2-ClC_6H_4COOH	4	89	**11d**	88 (99)
8[f]	**1d**	CF_3COOH	0.75	50	**11d**	48 (96)
9	**1e**	2-ClC_6H_4COOH	4	64	**11e**	60 (94)
10[f]	**1e**	CF_3COOH	0.75	39	**11e**	36 (92)

[a] Molar ratio pyrazine : **1** : $Pb(OAc)_4$: protonating acid = 4 : 1 : 1.1 : 4; **1**, 1 mmole.
[b] The conversion of $Pb(OAc)_4$ is ~100%.
[c] The yield is presented with respect to the starting (in parentheses, with respect to converted) acid **1**.
[d] Solvent-free reaction without mechanical activation.
[e] Under mechanical activation conditions.
[f] Reaction in a benzene solution (10 mL) at 80 °C.

1a—f, benzyl radicals formed from acid **1g** do not add to heterocycle **2**. In the reaction zone they are oxidized by Pb^{III} and Pb^{IV} acetates and transformed into benzyl 2-chlorobenzoate (**10**). We assumed that benzyl acetate is primarily formed and then produces ester **10** due to ester interchange. This assumption was based on the known[1] ability of $Pb(OAc)_4$ to acetoxylate C-radicals. However, as found in model experiments, no ester interchange occurs under the reaction conditions and, therefore, ester **10** is the primary oxidation product of benzyl radicals.

Unlike heterocycles **2—4**, pyrazine **5** does not react with a $Pb(OAc)_4$—RCOOH—CBA system under the same solvent-free conditions (see Table 2). In the liquid phase in a benzene solution containing protonating trifluoroacetic acid, alkane acids **1b,d,e** alkylate **5** but their conversion at the molar ratio acid **1** : $Pb(OAc)_4$ = 1 : 1.1 does not exceed 50%. To perform this process as solvent-free, we used mechanical activation that makes it possible, in many cases, to intensify solid-phase reactions. It is found that pyrazine is actively activated by the mechanical treatment of a mixture of reactants in a vibratory mill. In this case, the conversion of acids **1b,d,e** and the yield of products **11b,d,e** increase 1.5—2-fold compared to the liquid-phase variant of the reaction (see Table 2). Such a pronounced effect of mechanical activation indicates that alkylation in a vibratory mill occurs predominantly in the solid phase. We failed to perform the alkylation of pyrazine **5** by acid **1b** under the mechanical activation conditions without a protonating acid. The application of acetic acid for pyrazine **5** protonation was unsuccessful, and only the use of CBA gave target products **11b,d,e** (Scheme 4).

Scheme 4



R = *n*-C_7H_{15} (**b**), $Bu^nCH(Et)$ (**d**), $MeO_2CCH_2CH_2$ (**e**)

i. Solid phase.

Thus, in all above-considered solvent-free reactions of carboxylic acids **1a—f** with heteroaromatic compounds **2—5** in the presence of $Pb(OAc)_4$, ~95—96% radicals formed add to the protonated N-ring, which provides a high selectivity of the reaction and a high yield of alkylation products **6—9** and **11** with respect to the reacted acid.

Experimental

GLC analysis was carried out on an LKhM-80 chromatograph using a flame-ionization detector and analytical columns 2 m×3 mm with 5% FFAP and 5% SE-30 on Chromaton N-AW-HDMS (0.16—0.20 mm). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$. GC-MS spectra were obtained on a Finnigan MAT ITD-700 spectrometer (EI, 70 eV, temperature of the ion source—ion trap system 220 °C) and a Carlo Erba 4200 chromatograph equipped with an Ultra-1 column (Hewlett—Packard, 25 m×0.2 mm, layer thickness of the stationary phase (polymethylsiloxane) 0.33 μm, helium as carrier gas). Preparative GLC was used to isolate reaction products (copper column 2 m×10 mm with 5% SE-30 on Chromaton N-AW-HDMS, 0.25—0.36 mm). Starting hexanoic, octanoic, methylpropanoic, 2-ethylhexanoic, 3-phenylpropanoic, phenylpropanoic, phenylacetic, 3-methoxycarbonylpropanoic, acetic, 2-chlorobenzoic, benzoic, and trifluoroacetic acids (Acros); 4-methylpyridine, quinoline, 4-methylquinoline, and pyrazine (Lancaster); and benzene (reagent grade) were used as received. Lead tetraacetate (pure) was washed with glacial AcOH and dried *in vacuo* over alkali.

Solvent-free alkylation of N-heteroaromatic compounds 2—5 by the acid 1—$Pb(OAc)_4$ system without mechanical activation (general procedure). A mixture of heterocycle **2—5**, acid **1**, $Pb(OAc)_4$, and CBA (PhCOOH or AcOH) (the ratio of reagents are given in Tables 1 and 2) were thoroughly triturated in air for 5—10 min and left in a tightly closed weighing bottle at ~20 °C until $Pb(OAc)_4$ converted completely. The reaction mixture gradually became viscous and heterogeneous and then solidified. The duration of transition from one aggregate state to another (6—26 h) depends on the acid structure. After the end of the reaction ($Pb(OAc)_4$ conversion was monitored iodometrically[7]), solvents ($CHCl_3$ and ether) were successively added, and the yield of reaction products **6—11** and conversion of the starting acid **1** were determined by GLC using internal standard. To isolate reaction products, the organic layer was treated with a 3% aqueous solution of HCl, washed with a saturated solution of Na_2CO_3, and dried with Na_2SO_4. The solvent was distilled off. The products were isolated from the residue by preparative GLC. The structure of the products was confirmed by ^1H and ^{13}C NMR spectroscopy, GC-MS spectrometry, and elemental analysis.

Solvent-free alkylation of pyrazine 5 by the acid 1—$Pb(OAc)_4$ system using mechanical activation (general procedure). Mechanical activation of a mixture of pyrazine **5**, acid **1**, $Pb(OAc)_4$, and CBA or AcOH with an overall weight of 1—2 g (the ratio of reagents is indicated in Table 2) was carried out at ~20 °C on a vibratory mill with a vibration frequency of 12 Hz and an amplitude of 11 mm in a sealed steel ~80-cm^3 reactor. Steel balls with a diameter of 12.3 mm and an overall weight of ~150 g were used as activating packing. The duration of mechanical action was 4 h, and then the mixture was treated according to the above-presented procedure.

Alkylation of N-heteroaromatic compounds 2—5 with the acid 1—$Pb(OAc)_4$ system in a benzene—CF_3COOH solution (general procedure). A mixture of heterocycle **2—5**, acid **1**, and $Pb(OAc)_4$ in benzene containing CF_3COOH (the ratios of reagents are given in Tables 1 and 2) was heated (80 °C) with vigorous stirring until Pb^{IV} converted completely. The solvent was distilled off, and the mixture was treated according to the above-presented procedure.

4-Methyl-2-pentylpyridine (6a). Found (%): C, 80.92; H, 10.52; N, 8.56. $C_{11}H_{17}N$. Calculated (%): C, 80.98; H, 10.43; N, 8.59. ^1H NMR, δ: 0.88 (t, 3 H, Me, J = 3.2 Hz); 1.30—1.37

(m, 4 H, CH_2); 1.63—1.75 (m, 2 H, CH_2); 2.32 (s, 3 H, 4-Me); 2.74 (t, 2 H, CH_2, J = 3.9 Hz); 6.92 (d, 1 H, CH(5), J = 2.5 Hz); 6.97 (s, 1 H, CH(3)); 8.37 (d, 1 H, CH(6), J = 2.5 Hz). ^{13}C NMR, δ: 13.96 (Me); 20.90 (4-Me); 22.48, 29.59, 31.61, 38.22 (CH_2); 121.76, 123.48 (C(3), C(5)); 147.10 (C(4)); 148.84 (C(6)); 162.23 (C(2)). Mass spectrum, *m/z:* 164 $[M + H]^+$.

2-Heptyl-4-methylpyridine (6b). Found (%): C, 81.30; H, 10.91; N, 7.28. $C_{13}H_{21}N$. Calculated (%): C, 81.68; H, 10.99; N, 7.33. ^{1}H NMR, δ: 0.86 (t, 3 H, Me, J = 3.2 Hz); 1.26—1.32 (m, 8 H, CH_2); 1.62—1.75 (m, 2 H, CH_2); 2.35 (s, 3 H, 4-Me); 2.72 (t, 2 H, CH_2, J = 3.9 Hz); 6.89 (d, 1 H, CH(5), J = 2.5 Hz); 6.95 (s, 1 H, CH(3)); 8.35 (d, 1 H, CH(6), J = 2.5 Hz). ^{13}C NMR, δ: 13.99 (Me); 20.88 (4-Me); 22.56, 29.10, 29.34, 29.90, 31.70, 38.23 (CH_2); 121.77, 123.46 (C(3), C(5)); 147.09 (C(4)); 148.23 (C(6)); 162.18 (C(2)). Mass spectrum, *m/z:* 192 $[M + H]^+$.

2-Isopropyl-4-methylpyridine (6c).[8] Found (%): C, 79.57; H, 9.61; N, 10.91. $C_9H_{13}N$. Calculated (%): C, 80.00; H, 9.63; N, 10.37. ^{1}H NMR, δ: 1.24—1.29 (m, 6 H, Me); 2.29 (s, 3 H, 4-Me); 2.93—3.07 (m, 1 H, CH); 6.89 (d, 1 H, CH(5), J = 2.5 Hz); 6.96 (s, 1 H, CH(3)); 8.36 (d, 1 H, CH(6), J = 2.5 Hz). ^{13}C NMR, δ: 20.93, 22.45, 22.59 (Me); 36.04 (CH); 121.36, 121.90 (C(3), C(5)); 147.21 (C(4)); 148.63 (C(6)); 166.93 (C(2)). Mass spectrum, *m/z:* 136 $[M + H]^+$.

2-(Hept-3-yl)-4-methylpyridine (6d). Found (%): C, 81.41; H, 11.18; N, 7.43. $C_{13}H_{21}N$. Calculated (%): C, 81.68; H, 10.99; N, 7.33. ^{1}H NMR, δ: 0.74—0.87 (m, 6 H, Me); 1.08—1.29, 1.62—1.77 (both m, 4 H each, CH_2); 2.34 (s, 3 H, 4-Me); 2.56—2.63 (m, 1 H, CH); 6.93 (d, 1 H, CH(5), J = 2.5 Hz); 6.95 (s, 1 H, CH(3)); 8.41 (d, 1 H, CH(6), J = 2.5 Hz). ^{13}C NMR, δ: 12.23 and 14.10 (Me); 21.21 (4-Me); 22.89, 28.63, 29.94, 35.21 (CH_2); 49.40 (CH); 122.19, 123.69 (C(3), C(5)); 147.47 (C(4)); 148.60 (C(6)); 165.04 (C(2)). Mass spectrum, *m/z:* 192 $[M + H]^+$.

2-(2-Ethylmethoxycarbonyl)-4-methylpyridine (6e). Found (%): C, 66.88; H, 7.37; N, 7.98. $C_{10}H_{13}NO_2$. Calculated (%): C, 67.04; H, 7.26; N, 7.82. ^{1}H NMR, δ: 2.33 (s, 3 H, 4-Me); 2.81, 3.08 (both t, 2 H each, CH_2, J = 3.7 Hz); 3.67 (s, 3 H, Me); 6.96 (d, 1 H, CH(5), J = 2.5 Hz); 7.03 (s, 1 H, CH(3)); 8.37 (d, 1 H, CH(6), J = 2.5 Hz). ^{13}C NMR, δ: 21.01 (4-Me); 32.51 and 33.15 (CH_2); 51.60 (MeCOO); 122.50, 124.05 (C(3), C(5)); 147.94 (C(4)); 148.55 (C(6)); 159.50 (C(2)); 173.49 (C=O).

2-(2-Ethylphenyl)-4-methylpyridine (6f). Found (%): C, 85.31; H, 7.58; N, 7.38. $C_{14}H_{15}N$. Calculated (%): C, 85.28; H, 7.61; N, 7.11. ^{1}H NMR, δ: 2.31 (s, 3 H, 4-Me); 3.03—3.08 (m, 4 H, CH_2); 6.95 (d, 1 H, CH, J = 2.3 Hz); 7.17—7.33 (m, 6 H, CH); 8.44 (s, 1 H, CH). Mass spectrum, *m/z:* 198 $[M + H]^+$.

2-Heptyl-4-methylquinoline (7b). Found (%): C, 84.44; H, 9.35; N, 5.78. $C_{17}H_{23}N$. Calculated (%): C, 84.65; H, 9.54; N, 5.81. ^{1}H NMR, δ: 0.84 (t, 3 H, Me, J = 3.2 Hz); 1.22—1.29 (m, 8 H, CH_2); 1.64—1.74 (m, 2 H, CH_2); 2.59 (s, 3 H, 4-Me); 2.68 (t, 2 H, CH_2, J = 3.9 Hz); 7.14 (s, 1 H, CH); 7.48, 7.66 (both t, 1 H each, CH, J = 3.6 Hz); 7.98, 8.10 (both d, 1 H each, CH, J = 4.1 Hz). ^{13}C NMR, δ: 13.95 (Me); 18.99 (4-Me); 22.59, 29.09, 29.40, 29.98, 31.88, 38.27 (CH_2); 120.88, 123.59, 125.33, 126.85, 128.78, 129.67, 143.88, 147.45, 165.80 (C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)). Mass spectrum, *m/z:* 242 $[M + H]^+$.

2-(Hept-3-yl)-4-methylquinoline (7d). Found (%): C, 84.79; H, 9.85; N, 6.01. $C_{17}H_{23}N$. Calculated (%): C, 84.65; H, 9.54; N, 5.81. ^{1}H NMR, δ: 0.83 (t, 6 H, Me, J = 3.6 Hz); 1.20—1.34, 1.70—1.83 (both m, 4 H each, CH_2); 2.69 (s, 3 H, 4-Me); 2.78—2.85 (m, 1 H, CH); 7.11 (s, 1 H, CH); 7.54 (t, 1 H, CH, J = 3.7 Hz); 7.67 (t, 1 H, CH, J = 3.6 Hz); 7.96, 8.06 (both d, 1 H each, CH, J = 4.1 Hz). ^{13}C NMR, δ: 12.20 and 13.95 (Me); 18.82 (4-Me); 22.81, 28.55, 29.86, 35.10 (CH_2); 50.46 (CH); 120.63, 123.50, 125.26, 126.98, 128.74, 129.50, 143.89, 147.55, 165.79 (C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)). Mass spectrum, *m/z:* 242 $[M + H]^+$.

2-(Hept-3-yl)quinoline (8d). Found (%): C, 84.34; H, 8.99; N, 6.21. $C_{16}H_{21}N$. Calculated (%): C, 84.58; H, 9.25; N, 6.17. ^{1}H NMR, δ: 0.83 (t, 6 H, Me, J = 3.7 Hz); 1.10—1.24, 1.65—1.79 (both m, 4 H each, CH_2); 2.79—2.91 (m, 1 H, CH); 7.31 (d, 1 H, CH, J = 4.0 Hz); 7.47, 7.68 (both t, 1 H each, CH, J = 3.9 Hz); 7.78 (d, 1 H, CH, J = 4.0 Hz); 8.05—8.09 (dd, 2 H, CH). ^{13}C NMR, δ: 12.12 and 13.91 (Me); 22.78, 28.56, 29.79, 35.06 (CH_2); 50.48 (CH); 120.02, 125.47, 126.25, 127.36, 128.94, 129.02, 135.98, 147.73, 166.09 (C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)). Mass spectrum, *m/z:* 228 $[M + H]^+$.

4-(Hept-3-yl)quinoline (9d). Found (%): C, 84.28; H, 9.03; N, 6.31. $C_{16}H_{21}N$. Calculated (%): C, 84.58; H, 9.25; N, 6.17. ^{1}H NMR, δ: 0.76—0.84 (m, 6 H, Me); 1.09—1.25, 1.63—1.80 (both m, 4 H each, CH_2); 3.38—3.49 (m, 1 H, CH); 7.26 (d, 1 H, CH, J = 2.3 Hz); 7.55, 7.71 (both t, 1 H each, CH, J = 3.8 Hz); 8.14 (d, 2 H, CH, J = 4.3 Hz); 8.87 (d, 1 H, CH, J = 2.2 Hz). ^{13}C NMR, δ: 11.87 and 13.88 (Me); 22.78, 28.88, 29.56, 35.30 (CH_2); 40.51 (CH); 118.18, 123.15, 126.05, 128.27, 128.78, 130.26, 148.39, 150.05, 152.54 (C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)). Mass spectrum, *m/z:* 228 $[M + H]^+$.

Benzyl 2-chlorobenzoate (10). Found (%): C, 68.17; H, 4.55; Cl, 14.30. $C_{14}H_{11}ClO_2$. Calculated (%): C, 68.29; H, 4.47; Cl, 14.23. Mass spectrum, *m/z*: 246 and 248 $[M]^+$. The ^{1}H NMR spectrum coincides with that described previously.[9]

2-Heptylpyrazine (11b). Found (%): C, 74.34; H, 10.04; N, 15.56. $C_{11}H_{18}N_2$. Calculated (%): C, 74.16; H, 10.11; N, 15.73. ^{1}H NMR, δ: 0.85 (t, 3 H, Me, J = 3.2 Hz); 1.25—1.33 (m, 8 H, CH_2); 1.71—1.76 (m, 2 H, CH_2); 2.77 (t, 2 H, CH_2, J = 3.8 Hz); 8.40 (d, 1 H, CH, J = 1.2 Hz); 8.45 (s, 1 H, CH(3)); 8.47 (d, 1 H, CH, J = 1.2 Hz). ^{13}C NMR, δ: 13.99 (Me); 22.38, 28.99, 29.18, 29.38, 31.65, 35.47 (CH_2); 141.95, 143.97, 144.49 and 158.01 (C(2), C(3), C(5), C(6)). Mass spectrum, *m/z:* 179 $[M + H]^+$.

2-(Hept-3-yl)pyrazine (11d). Found (%): C, 74.26; H, 10.45; N, 15.91. $C_{11}H_{18}N_2$. Calculated (%): C, 74.16; H, 10.11; N, 15.73. ^{1}H NMR, δ: 0.74—0.86 (m, 6 H, Me); 1.07—1.27, 1.66—1.817 (both m, 4 H each, CH_2); 2.53—2.73 (m, 1 H, CH); 8.38 (d, 1 H, CH, J = 1.2 Hz); 8.44 (s, 1 H, CH(3)); 8.47 (d, 1 H, CH, J = 1.2 Hz). Mass spectrum, *m/z:* 179 $[M + H]^+$.

2-(Ethyl-2-methoxycarbonyl)pyrazine (11e). Found (%): C, 57.88; H, 6.38; N, 16.87. $C_8H_{10}N_2O_2$. Calculated (%): C, 57.83; H, 6.02; N, 16.87. ^{1}H NMR, δ: 2.82, 3.09 (both t, 2 H each, CH_2, J = 3.7 Hz); 3.66 (s, 3 H, MeCOO); 8.41 (d, 1 H, CH, J = 1.2 Hz); 8.44 (s, 1 H, CH(3)); 8.46 (d, 1 H, CH, J = 1.2 Hz). Mass spectrum, *m/z:* 167 $[M + H]^+$.

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