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Regioselective alkylation of aromatic aldimines and ketimines via C–H bond activation by a rhodium catalyst

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Abstract

The aldimines and ketimines reacted with alkenes under a rhodium catalyst $[Rh(coe)_2Cl]_2$ and Cy_3P to give mainly the double alkylated products with moderate to high yields. The aldimines bearing H, *p*-CH_3O, *p*-CH_3, *p*-Cl, *p*-F, *p*-CF_3 and *o*-CH_3 groups have high reactivities, but *m*-CH_3O, *m*-Cl and *m*-F exhibit moderate reactivities. However, *o*-Cl, *o*-NO_2 and *p*-NO_2 groups did not work. The ketimine **9** gave the mono-alkylated products predominantly. 1-Naphthyl and heteroaromatic aldimines showed good regioselectivities.

Keywords: Alkylation; C–C bond formation; Rhodium catalyst; Aldimines; Ketimines

1. Introduction

Recently, the C–C bond formation as a result of C–H bond activation by transition metal complexes has become a useful synthetic method for chemists [1]. The activation of unreactive C–H bond has achieved by many research groups [2]. By using the C–H bond activation, the alkylation of aromatic ring through the coupling reaction with alkenes and alkynes have been reported by us [3] and other groups [4–14]. In spite of many results of C–C bond formation, the alkylation of the phenyl ring of benzaldehydes is very difficult, because of decarbonylation and hydroacylation, except the case of the benzaldehydes bearing *ortho*-bulky substituent [4n]. A possible way to overcome these problems is to use the corresponding aldimines of the aldehydes for this alkylation. The alkylations of aromatic aldimines [4f] and hydrazones [4o] by ruthenium complexes have been reported by Murai and co-workers. Moreover, the alkylation of aromatic aldimines and ketimines using the Wilkinson's catalyst has been reported very recently by Jun et al. [10]. However, while the Ru-catalyzed alkylations of aldimines and hydrazones show a high reactivity for vinyl siloxanes, it has some problems; for example, low reactivity for other alkenes such as **2a** and producing dehydrogenated products [4f,4o]. In the case of $RhCl(PPh_3)_3$, the aromatic ketimines show a high reactivity with alkenes, but the aromatic aldimines do not react with alkenes without a co-catalyst [10]. We have already reported that in the alkylation of 2-phenylpyridines, exchange of ligand from PPh_3 to Cy_3P (Cy_3P = tricyclohexylphosphine) on rhodium metal led to high conversion yields and short reaction times. Thus, we decided to apply this rhodium catalytic system to the alkylation of aromatic aldimines and ketimines with alkenes. To know the effects of substituent of substrates, we also carried out the alkylation of substrates having several electron-donating and electron-withdrawing groups on the benzene ring. Herein, we report the alkylation of aromatic aldimines and ketimines with alkenes by a rhodium catalytic system, $[RhCl(coe)_2]_2$ (coe = cyclooctene) and Cy_3P, proceeded without any need for additives (see Scheme 1). Some preliminary results of this work have already been communicated [3h].

2. Results and discussion

Aldimine **1a** reacted with **2a** (5 equiv.) under $[RhCl(coe)_2]_2$ (5 mol%) and Cy_3P (30 mol%) in THF at 140 °C for 24 h with stirring to give the anti-Markovnikov *ortho*-alkylated benzaldehydes in 93% isolated yields

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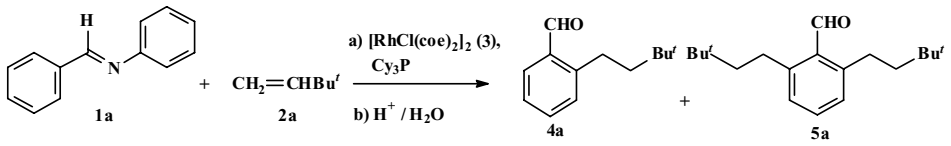
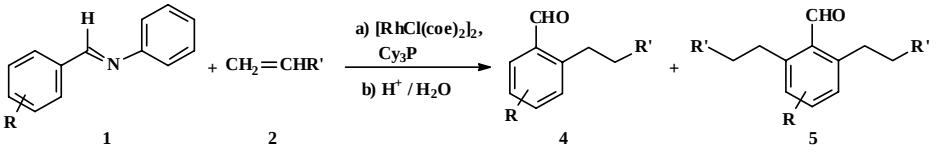


Scheme 1.

(**4a**:**5*a*** = 11:89) after hydrolysis and chromatographic isolation (Table 1, run 1). This rhodium catalytic system showed higher reactivity than that [4f] of $Ru_3(CO)_{12}$ for **2a**. The ligand-exchanging step for formation [15] of $RhCl(Cy_3P)_2$ from $[RhCl(coe)_2]_2$ and Cy_3P is essential for this alkylation before the addition of substrate and alkene. When the alkylation was carried out without ligand-exchanging step, the yield of the alkylated product was low (20–30%). However, 2-phenylpyridines do not require this ligand-exchanging step [3c]. In an attempt to obtain the mono-alkylated product **4a** as a major product, 1 equiv. of **2a** was used. However, **5a** was still the major product (run 2). Even though 0.7 equiv. of **2a** was used, this alkylation preferred double alkylation (run 3). This result indicates that after mono-alkylation, next catalytic cycle takes place without dissociation of the nitrogen of the imine on the rhodium metal center. The transition metal complexes $RhCl(Ph_3P)_3$, $(Ph_3P)_2Rh(CO)Cl$ and $(Ph_3P)_2Ir(CO)Cl$ were inactive under similar reaction conditions. The results of the alkylation are listed in Table 1. To investigate the effect of substituents on the benzene ring, aldimines bearing electron-donating and electron-withdrawing groups were subjected under the same reaction conditions. The *p*-methoxy group, an electron-donating group, accelerated the alkylation and gave the quantitative yields of the alkylated products (Table 1, run 4). Another electron-donating group, *p*-methyl group, also showed high reactivity (Table 1, run 5). Interestingly, aldimines bearing electron-withdrawing group of *p*-CF_3 and *p*-F shows an unexpectedly high reactivity (Table 1, runs 10 and 11). The reason for this exceptional reactivity is not clear at the present time. However, the exceptional reactivity of *p*-CF_3 group can be found in the results of the alkylation of aromatic ketimines [10], aromatic esters [4e], and acetophenones [13]. On the other hand, the aldimine bearing

Table 1
The results of the alkylation of aromatic aldimines[a]

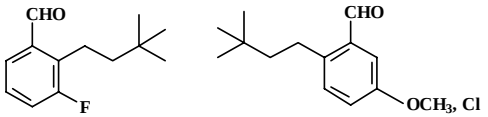


Run	**1**	**2**	**4**:**5**[b]	Yield[c] (%)
1	a (R = H)	a (R′ = Bu^t)	**4a**:**5a** (11:89)	93
2	a	a[d]	**4a**:**5a** (23:77)	53
3	a	a[e]	**4a**:**5a** (36:64)	20[f]
4	a	b (R′ = Pr^n)	**4g**:**5g** (20:80)	44
5	a	c (R′ = Bu^n)	**4h**:**5h** (34:66)	19
6	b (R = *p*-OCH_3)	a	**4b**:**5b** (1:99)	90
7	c (R = *p*-CH_3)	a	**4c**:**5c** (5:95)	87
8	d (R = *p*-Cl)	a	**4d**:**5d** (3:97)	88
9	e (R = *m*-OCH_3)	a	**4e**:**5e** (97:3)	50 (50)
10	f (R = *p*-CF_3)	a	**4f**:**5f** (2:98)	90
11	g (R = *p*-F)	a	**4i**:**5i** (1:99)	84
12	h (R = *m*-F)	a	**4j**:**5j** (26:74)	62
13	j (R = *o*-CH_3)	a	**4k**	80
14	j	b	**4l**	43
15	j	c	**4m**	15
16	k (R = *o*-Cl)	a	**4n**	0
17	l (R = *p*-NO_2)	a	**4o**:**5o** (88:22)	6 (64)
18	n (R = *m*-Cl)	a	**4p**:**5p** (77:23)	63 (36)
19	o (R = *o*-NO_2)	a	**4q**	0

[a] **1**:**2**:$[RhCl(coe)_2]_2$:Cy_3P = 1:5:0.05:0.3; THF = 2 ml; 140 °C; 24 h.
[b] The ratio was determined by ^{1}H NMR or GC.
[c] Isolated yield. The values in the parenthesis are the amount of the recovered starting materials as the corresponding aldehydes.
[d] 1 equiv. of **2a** was used.
[e] 0.7 equiv. of **2a** was used.
[f] Yield based on alkene used.

electron-withdrawing group, *p*-NO_2, reacted sluggishly with alkene (Table 1, run 17). It maybe due to coordination of NO_2 group to Rh metal. To know the electronic effect in detail once more, the alkylation of representative aldimines bearing H, *p*-CF_3, and *p*-CH_3O groups was carried out at shorter reaction time (2 h) under the same reaction conditions. The aldimines bearing *p*-CF_3 and *p*-CH_3O groups gave similar conversion rates and the conversion rate of no-substituted aldimine **1a** was slightly low (*p*-CF_3, 43%; *p*-CH_3O, 41%; H, 32%). This result implies that the alkylation of *p*-substituted aldimines are not affected nearly by electronic effects. Conclusively, all *p*-substituted aldimines bearing electron-donating and withdrawing groups reacted well with **2a**, except the aldimine bearing *p*-NO_2 group.

m-Substituted aldimine has two different sites (positions 2 and 6) for alkylation. The alkylation of *m*-CH_3O aldimine **1e** only gave the 6-position alkylated product **4e** together with small amount of double alkylated product **5e** (Table 1, run 9). The product alkylated at 2-position was not detected in the reaction mixture. It may be due to steric effects. The *m*-substituent interferes with the approach of rhodium metal for C–H bond activation. Thus, the double alkylated product **5e** must come from **4e**. This result is opposite to the alkylation of acetophenone bearing *m*-CH_3O in the presence of ruthenium complex; the alkylation occurs at the sterically congested position (position 2) [4h]. The *m*-Cl aldimine **1n** also gave the similar results to **1e** (Table 1, run 18). Interestingly, *m*-F aldimine **1h** gave a different isomer **4j** from mono-alkylated products, **4e** and **4p**, of *m*-CH_3O and *m*-Cl aldimines (Table 1, run 12). The geometry of **4j** was confirmed by the doublet signal of 6-proton at 7.52 ppm (dd, 8.9, 2.7 Hz) in ^{1}H NMR spectrum; the proton signals of other isomers **4e** and **4p** are singlets. From the above results, these results imply that the alkylations of *m*-substituted aldimines are affected by steric effects rather than electronic effects.

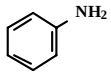
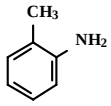
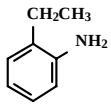
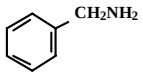


4j **4e, 4p**

Finally, the *ortho*-substituted aldimines having Cl, NO_2, and CH_3 groups were examined for this alkylation. These aldimines have one site for alkylation because of blocking a reaction site by a substituent. So these aldimines gave the mono-alkylated products only. The rate of alkylation of *o*-CH_3 derivative **1j** with **2a** was slightly slower than that of **1a**, probably due to interference of the approach of rhodium metal for C–H bond activation (Table 1, run 13). Other aldimines **1k** and **1o** did not react with **2a**, most of the starting materials being recovered as the corresponding aldehydes after hydrolysis (Table 1, runs 16 and 19). It maybe due to stabilization by coordination of Cl and NO_2 group to rhodium metal.

Linear terminal alkenes such as 1-pentene **2b** and 1-hexene **2c** gave moderate yields (Table 1, runs 4, 5, 14 and 15). The alkenes are isomerized to the internal alkenes during the reaction, which competed with the desired alkylation of aldimines with alkenes.

Table 2
The results of the alkylation of benzaldimines prepared from different amines[a]

Run	Amine used	**4a**:**5a**[b]	Yield (%)[c]
1		11:89	93
2		29:71	25
3		43:57	16
4		23:77	40

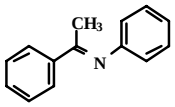
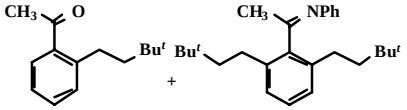
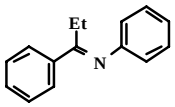
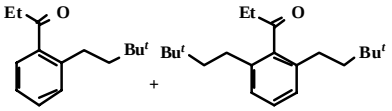
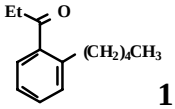
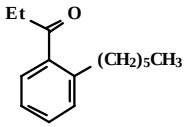
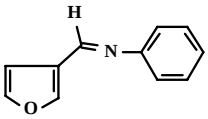
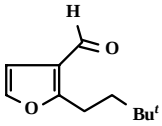
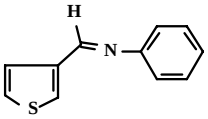
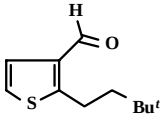
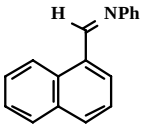
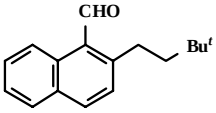
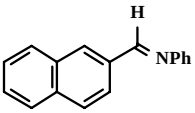
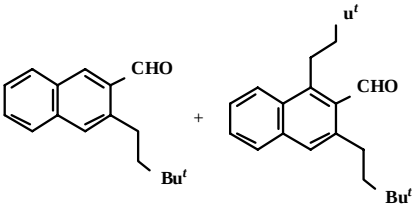
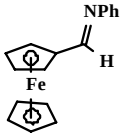
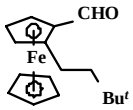
[a] Substrate:**2a**:[RhCl(coe)$_2$]$_2$:Cy_3P = 1:5:0.05:0.3; THF = 2 ml; 140 °C; 24 h.
[b] The ratio was determined by ^{1}H NMR.
[c] Isolated yield.

To obtain the mono-alkylated product as a major product, the aldimines prepared from several amines were applied to this alkylation. The anilines having methyl and ethyl groups gave selectivity of mono-alkylated product up to 43%, but the double alkylated product is still major (Table 2, runs 2 and 3). Another amine, benzylamine which is the best amine in alkylation of ketimines by the Wilkinson's catalyst, was also applied to this alkylation. However, this amine gave slightly enhanced selectivity of mono-alkylation product and low yields in this system (Table 2, run 4).

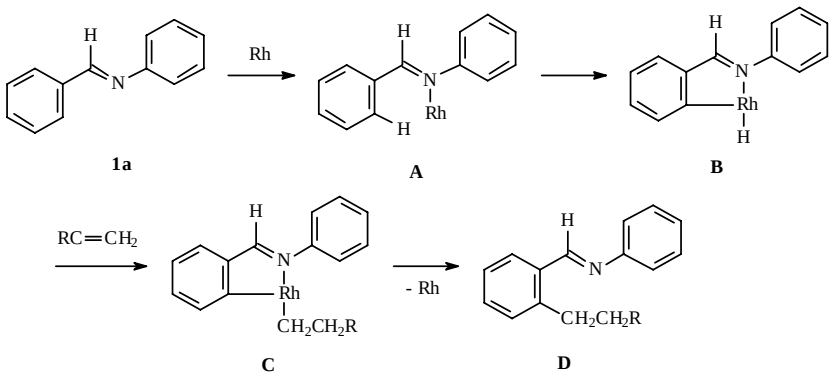
To elucidate the distribution of mono and double alkylated products of ketimines compared with the aldimine, ketimines such as **6** and **9** were alkylated under the same reaction conditions. Substrate **6** gave the alkylated product with a 28:72 mono:double ratio (yield 99%; Table 3, run 1). Interestingly, the double alkylated product **8** was not hydrolyzed in 1N HCl aqueous solution. On the other hand, **9** gave the mono-alkylated product **10** predominantly (mono:double = 97:3, 86% isolated yield; Table 3, run 2) because of the interference of rotation of the C–C bond between the phenyl ring and the imine group in the alkylated ketimine by the steric hindrance of the ethyl group in the imine group and the alkyl in the phenyl group. Moreover, **9** reacted with **2b** and **2c** to give **12** and **13** exclusively (Table 3, runs 3 and 4).

Heteroaromatic aldimimes **14** (furanyl) and **16** (thiophenyl) have two sites (positions 2 and 4) for the alkylation (Table 3, runs 5 and 6). The results of alkylation showed that the alkylation took place at position 2 only. Unfortunately, Furanyl aldimine was unstable and decomposed under the reaction and hydrolysis conditions. So the yield of alkylated

Table 3
The results of the alkylation of aromatic ketimines and heteroaromatic aldimines[a]

Run	Substrate	Alkene	Mono:double[b]	Product	Yield (%)[c]
1	 **6**	**2a**	28:72	 **7** + **8**	99
2	 **9**	**2a**	97:3	 **10** + **11**	86
3	**9**	**2b**	100:0	 **12**	65
4	**9**	**2c**	100:0	 **13**	21
5	 **14**	**2a**	–	 **15**	17
6	 **16**	**2a**	–	 **17**	36[d]
7	 **18**	**2a**	–	 **19**	99.7
8	 **20**	**2a**	31[e]:69	 **21** **22**	21
9	 **23**	**2a**	–		0

[a] Substrate:**2**:[RhCl(coe)$_2$]$_2$:Cy$_3$P = 1:5:0.05:0.3; THF = 2 ml; 140 °C; 24 h.
[b] The ratio was determined by ^{1}H NMR.
[c] Isolated yield.
[d] Fourteen percent of the starting material was recovered as the aldehyde.
[e] 1-Alkylated product was contained.



Scheme 2. A proposed reaction mechanism for this alkylation via C–H bond activation.

product was low without recovery of the starting material (Table 3, run 5).

Another substrate, naphthalene derivative **18**, reacted with **2a** (5 equiv.) to give the alkylated 1-naphthaldehyde **19** in 99% yield after hydrolysis and chromatographic isolation. However, 2-naphthyl derivative **20** gave the double alkylated product together with two regioisomers (positions 1 and 3) of mono-alkylated product in poor yields (**21**:**22** = 31:69, 21%) and small amount of naphthalene, decarbonylated product of 2-naphthaldehyde, was also detected in the reaction mixture.

The functionalization of the ring of ferrocene through C–H bond activation by a transition metal complex is of interest by organic chemists. However, this region still remains as a virgin land. So ferrocene derivative **23** was applied to this alkylation under the same reaction conditions. Unfortunately, the aldimine of ferrocenecarboxaldehyde did not react with **2a** in these catalytic system (Table 3, run 9).

A proposed reaction mechanism is shown in Scheme 2. The mechanism of this alkylation is proposed to be similar to that previously reported [3a,3b].

The coordination of the aldimine nitrogen of **1a** to the Rh catalyst provides to A, in which the *ortho*-C–H bond in the phenyl ring is selectively activated to form the five-membered metallacycle B. The insertion of alkene into the Rh–H bond in B gives the linear alkyl rhodium intermediate C according to the anti-Markovnikov rule. The intermediate C gives the alkylated product D and the active Rh species by reductive elimination with an external ligand. The alkylated product D is hydrolyzed with 1N HCl to give **4**.

3. Conclusion

In conclusion, we have found that the aldimines and ketimines reacted with alkenes under a catalytic system, $[RhCl(coe)_2]_2 + Cy_3P$, without additives to give mainly the double alkylated products with moderate to high yields. The aldimines bearing H, *p*-CH_3O, *p*-CH_3, *p*-Cl, *p*-F, *p*-CF_3 and *o*-CH_3 groups have high reactivities, but *m*-CH_3O, *m*-Cl and *m*-F exhibit moderate reactivities. However, *o*-Cl, *o*-NO_2 and *p*-NO_2 groups did not work. The ketimine **9** gave the mono-alkylated products predominantly. 1-Naphthyl and heteroaromatic aldimines showed good regioselectivities and gave the mono-alkylated products exclusively.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on Bruker AC-300F (300 MHz) and Bruker AC-200 (200 MHz) instruments. The chemical shifts are reported in ppm relative to internal tetramethylsilane in $CDCl_3$. ^{13}C NMR spectra were recorded on Bruker AC-300F (75 MHz) machine. IR spectra were run on a Nicolet Magna 550 FT-IR instrument. Mass spectra were measured with a HP-5971A mass spectrometer which was equipped with a Hewlett-Packard 5890 series II gas chromatograph using the electron impact method (70 eV). The silica gel used in column chromatography was from Merck (70-230 mesh). Analytical thin layer chromatography was performed on glass plates (0.25 mm) coated with silica gel 60F 254 from Aldrich. High resolution mass spectroscopy was performed at the ADD Analytical Lab.

4.2. General procedure for the alkylation

All chemicals were handled in the air without special treatment, except using dried solvent. A screw-capped vial (5 ml) was charged with chlorobis(cyclooctene)rhodium(I) dimmer (17 mg, 5 mol%) and tricyclohexylphosphine (39.8 mg, 30 mol%) dissolved in THF (2 ml) and the mixture was stirred for 10 min at room temperature. The color of the mixture changed from orange color to dark green color during the ligand-exchanging step. After that, **1a** (85.8 mg, 4.73 mmol), 3,3-dimethylbut-1-ene **2a** (199 mg, 2.37 mmol, 5 equiv.) were added to the mixture. The reaction mixture was heated at 140 °C for 24 h with stirring and then hydrolyzed with 2 ml of aqueous 1N HCl at room temperature. The reaction mixture was extracted with EtOAc and the organic layer was concentrated under reduced

pressure and purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to give 10.7 mg (10.2%) of 2-(3,3-dimethylbutyl)benzaldehyde and 125.2 mg (82.7%) of 2,6-bis-(3,3-dimethylbutyl)benzaldehyde, respectively.

2-(3,3-Dimethylbutyl)benzaldehyde (**4a**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.29 (1H, s, CHO), 7.83 (1H, d, $J = 7.7$ Hz, 6-H in Ph), 7.49 (1H, t, $J = 7.4$ Hz, 4-H in Ph), 7.34 (1H, t, $J = 7.5$ Hz, 5-H in Ph), 7.26 (1H, d, $J = 7.5$ Hz, 3-H in Ph), 2.96–3.02 (2H, m, β-CH_2 to Bu^t), 1.45–1.51 (2H, m, α-CH_2 to Bu^t), 1.00 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.14 (CHO), 133.88, 131.19, 130.93, 128.82, 126.30, 47.28, 29.69, 29.21, 27.92; MS (EI) *m/z* 190 (24, M^+), 157 (9), 133 (100, $M^+ - Bu^t$), 119 (13), 105 (10), 91 (17), 57 (14, Bu^{t+}).

2,6-bis-(3,3-Dimethylbutyl)benzaldehyde (**5a**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54 (1H, s, CHO), 7.34 (1H, t, $J =$ 7.6 Hz, 4-H in Ph), 7.07 (2H, d, $J = 7.6$ Hz, 3,5-Hs in Ph), 2.86–2.92 (4H, m, β-CH_2 to Bu^t), 1.43–1.49 (4H, m, α-CH_2 to Bu^t), 0.96 (18H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.37 (CHO), 146.75, 132.99, 131.84, 128.83, 47.17, 30.81, 29.23, 28.94; MS (EI) *m/z* 274 (29, M^+), 259 (1, $M^+ - CH_3$), 217 (100, $M^+ - Bu^t$), 201 (14), 147 (11), 129 (10), 57 (23, Bu^{t+}); IR (NaCl, neat, cm^{-1}) ν 2955 (s), 2866 (m), 1697 (s, CO), 1593 (m), 1464 (m), 1365 (m), 1246 (w), 1187 (w), 804 (w), 755 (w), 719 (w); HRMS found: 274.2307 (calcd. for $C_{19}H_{30}O$ 274.2297).

2-(3,3-Dimethylbutyl)-4-anisaldehyde (**4b**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.13 (1H, s, CHO), 7.80 (1H, d, $J = 8.6$ Hz, 6-H in Ph), 6.84 (1H, d, $J = 8.7$ Hz, 5-H in Ph), 6.74 (1H, s, 3-H in Ph), 3.88 (3H, s, OCH_3), 2.93–3.00 (2H, m, β-CH_2 to Bu^t), 1.43–1.51 (2H, m, α-CH_2 to Bu^t), 1.00 (9H, s, CH_3 of Bu^t).

2,6-bis-(3,3-Dimethylbutyl)-4-anisaldehyde (**5b**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.39 (1H, s, CHO), 6.58 (2H, s, 3,5-Hs in Ph), 3.83 (3H, s, OCH_3), 2.87–2.93 (4H, m, β-CH_2 to Bu^t), 1.42–1.49 (4H, m, α-CH_2 to Bu^t), 0.98 (18H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.18 (CHO), 162.84, 144.31, 124.82, 114.00, 55.25, 46.91, 30.81, 29.52, 29.30; MS (EI) *m/z* 304 (4, M^+), 247 (100, $M^+ - Bu^t$), 231 (24), 219 (9), 189 (7), 175 (14), 57 (16, Bu^{t+}); IR (NaCl) ν 2954 (s), 2865 (m), 1683 (s, CO), 1597 (s), 1569 (m), 1466 (m), 1365 (m), 1326 (m), 1310 (m), 1275 (m), 1192 (m), 1151 (s), 1038 (w), 865 (w); HRMS found: 304.2412 (calcd. for $C_{20}H_{32}O_2$ 304.2402).

2-(3,3-Dimethylbutyl)-4-tolualdehyde (**4c**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.22 (1H, s, CHO), 7.73 (1H, d, $J = 7.8$ Hz, 6-H in Ph), 7.15 (1H, d, $J = 8.1$ Hz, 5-H in Ph), 7.07 (1H, s, 3-H in Ph), 2.92–2.99 (2H, m, β-CH_2 to Bu^t), 2.39 (3H, s, CH_3), 1.43–1.49 (2H, m, α-CH_2 to Bu^t), 1.00 (9H, s, CH_3 of Bu^t).

2,6-bis-(3,3-Dimethylbutyl)-4-tolualdehyde (**5c**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.48 (1H, s, CHO), 6.88 (2H, s, 3,5-Hs in Ph), 2.83–2.90 (4H, m, β-CH_2 to Bu^t), 2.33 (3H, s, CH_3), 1.41–1.48 (4H, m, α-CH_2 to Bu^t), 0.98 (18H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.64 (CHO), 147.22, 143.78, 129.70, 129.04, 47.16, 30.79, 29.22, 28.95, 21.50 (CH_3); MS (EI) *m/z* 288 (20, M^+), 231 (100, $M^+ - Bu^t$), 215 (10), 57 (31, Bu^{t+}); IR (NaCl, neat, cm^{-1}) ν 2953, 2865, 2763, 1689 (s, CO), 1606, 1464, 1246, 1205, 858, 797, 749, 694; HRMS found: 288.2460 (calcd. for $C_{20}H_{32}O$ 288.2453).

2-(3,3-Dimethylbutyl)-4-chlorobenzaldehyde (**4d**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (1H, s, CHO), 7.77 (1H, d, $J = 8.3$ Hz, 6-H in Ph), 7.32 (1H, d, $J = 8.4$ Hz, 5-H in Ph), 7.26 (1H, s, 3-H in Ph), 2.93–3.00 (2H, m, β-CH_2 to Bu^t), 1.41–1.51 (2H, m, α-CH_2 to Bu^t), 1.00 (9H, s, CH_3 of Bu^t); MS (EI) *m/z* 224 (25, M^+), 167 (100, $M^+ - Bu^t$), 156 (12), 89 (14), 57 (21, Bu^{t+}).

2,6-bis-(3,3-Dimethylbutyl)-4-chlorobenzaldehyde (**5d**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.46 (1H, s, CHO), 7.07 (2H, s, 3,5-Hs in Ph), 2.83–2.89 (4H, m, β-CH_2 to Bu^t), 1.41–1.47 (4H, m, α-CH_2 to Bu^t), 0.98 (18H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.10 (CHO), 148.79, 138.70, 130.09, 128.69, 46.79, 30.82, 29.18, 28.86; MS (EI) *m/z* 308 (23, M^+), 251 (100, $M^+ - Bu^t$), 235 (12), 181 (8), 57 (27, Bu^{t+}); IR (NaCl, neat, cm^{-1}) ν 2956 (s), 2867 (s), 1696 (s, CO), 1580 (s), 1467 (m), 1396 (w), 1365 (m), 1246 (m), 1187 (w), 1097 (w), 890 (m), 865 (m); HRMS found: 308.1912 (calcd. for $C_{19}H_{29}OCl$ 308.1907).

6-(3,3-Dimethylbutyl)-3-anisaldehyde (**4e**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.29 (1H, s, CHO), 7.36 (1H, s, 2-H in Ph), 7.18 (1H, d, $J = 8.4$ Hz, 4-H in Ph), 7.07 (1H, d, $J = 8.4$ Hz, 5-H in Ph), 3.84 (3H, s, OCH_3), 2.88–2.95 (2H, m, β-CH_2 to Bu^t), 1.42–1.49 (2H, m, α-CH_2 to Bu^t), 0.99 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.42 (*C*O), 158.02 (3-C in Ph), 139.18 (*C*-CHO), 134.05 (6-C in Ph), 132.07 (5-C in Ph), 121.38 (4-C in Ph), 112.75 (2-C in Ph), 55.45 (O***C***H_3), 47.95 (α-C to Bu^t), 30.82 (centered C of Bu^t), 29.20 (CH_3 of Bu^t), 26.77 (β-C to Bu^t). MS (EI) *m/z* 220 (67, M^+), 205 (11, $M^+ - CH_3$), 187 (18), 163 (100, $M^+ - Bu^t$), 150 (22), 149 (49, $M^+ - CH_2Bu^t$), 135 (10, $M^+ - CH_2CH_2Bu^t$), 121 (53); IR (NaCl, neat, cm^{-1}) ν 2954, 2865, 1692 (CO), 1606, 1573, 1497, 1466, 1396, 1364, 1324, 1259, 1191, 1161, 1040, 833.

2,6-bis-(3,3-Dimethylbutyl)-3-anisaldehyde (**5e**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.51 (1H, s, CHO), 7.03 (1H, d, $J = 8.4$ Hz, 4-H in Ph), 6.94 (1H, d, $J = 8.4$ Hz, 5-H in Ph), 3.82 (3H, s, OCH_3), 2.86–2.93 (2H, m, β-CH_2 to Bu^t), 2.76–2.83 (2H, m, β-CH_2 to Bu^t), 1.35–1.44 (4H, m, α-CH_2 to Bu^t), 0.98 (9H, s, CH_3 of Bu^t), 0.96 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.11 (*C*O), 155.63 (3-C in Ph), 137.52 (1-C in Ph), 134.94 (6-C in Ph), 133.02 (2-C in Ph), 128.74 (5-C in Ph), 114.85 (4-C in Ph), 55.83 (O*C*H_3), 47.95 (β-CH_2 to Bu^t), 44.92 ((β-CH_2 to Bu^t), 30.89 (center C in Bu^t), 30.74 (center C in Bu^t), 29.24 (CH_3), 29.13 (CH_3), 28.28 (α-CH_2 to Bu^t), 20.64 (α-CH_2 to Bu^t); MS (EI) *m/z* 304 (100, M^+), 271 (19), 247 (55, $M^+ - Bu^t$), 233 (30), 219 (17), 177 (21), 163 (16), 159 (17), 133 (13); IR (NaCl, neat, cm^{-1}) ν 2954, 2865, 1692 (CO), 1579, 1547, 1477, 1392, 1364, 1266, 1247, 1085, 1046, 820; HRMS found: 304.2398 (calcd. for $C_{20}H_{32}O_2$ 304.2402).

2,6-bis-(3,3-Dimethylbutyl)-4-trifluoromethylbenzaldehyde (**5f**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.57 (1H, s, CHO), 7.33 (2H, s, 3,5-Hs in Ph), 2.88–2.94 (4H, m, α-CH_2 to Ph), 1.44–1.50 (4H, m, CH_2), 0.99 (18H, s, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.79 (CHO), 147.05, 134.78, 133.79 (q, J = 32.4 Hz, CF_3), 125.30, 125.25, 46.90, 30.83, 29.14, 28.89; MS (EI) *m/z* 342 (26, M^+), 309 (10), 285 (90, $M^+ - Bu^t$), 249 (34), 239 (15), 225 (14), 215 (65), 211 (25), 202 (18), 197 (26), 185 (10), 177 (11), 173 (17), 165 (13), 159 (11), 151 (17), 145 (10), 133 (15), 117 (19), 115 (27), 103 (17), 85 (13), 71 (11), 57 (100, Bu^{t+}); IR (NaCl) ν 2955 (s), 2911 (s), 2868 (s), 2851 (m), 1700 (s, CO), 1576 (w), 1465 (s), 1395 (m), 1366 (s), 1342 (s), 1283 (m), 1223 (s), 1167 (s), 1132 (s), 1092 (s), 1046 (w), 906 (m), 855 (m), 754 (w); HRMS found: 342.2177 (calcd. for $C_{20}H_{29}OF_3$ 342.2171).

2-Pentylbenzaldehyde (**4g**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.30 (1H, s, CHO), 7.84 (1H, dd, J = 7.7, 1.3 Hz, 6-H in Ph), 7.50 (1H, dt, J = 7.5, 1.4 Hz, 5-H in Ph), 7.35 (1H, t, J = 7.8 Hz, 4-H in Ph), 7.27 (1H, d, J = 7.1 Hz, 3-H in Ph), 3.02 (2H, t, J = 7.7 Hz, α-CH_2 to Ph), 1.53–1.64 (2H, m, CH_2), 1.30–1.40 (4H, m, CH_2), 0.89 (3H, t, J = 7.0 Hz, CH_3); MS (EI) *m/z* 176 (51, M^+), 143 (13), 133 (88), 129 (100), 119 (72), 115 (21), 105 (26), 91 (65), 77 (18), 65 (19).

2,6-bis(Pentyl)benzaldehyde (**5g**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.57 (1H, s, CHO), 7.35 (1H, t, J = 7.7 Hz, 4-H in Ph), 7.09 (2H, d, J = 7.6 Hz, 3,5-Hs in Ph), 2.91 (4H, t, J = 7.7 Hz, α-CH_2 to Ph), 1.55–1.62 (4H, m, CH_2), 1.30–1.39 (8H, m, CH_2), 0.89 (6H, t, J = 6.8 Hz, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.60 (CHO), 146.06, 132.72, 128.89, 33.56, 32.21, 31.82, 22.49, 14.01; MS (EI) *m/z* 246 (23, M^+), 228 (11), 203 (10), 199 (33), 185 (30), 175 (85), 172 (21), 159 (10), 157 (26), 145 (24), 143 (37), 129 (100), 117 (47), 105 (47), 91 (47), 71 (28), 55 (7); IR (NaCl, neat, cm^{-1}) ν 2956 (s), 2929 (s), 2871 (m), 2858 (m), 1695 (s, CO), 1592 (w), 1464 (w), 1184 (w), 795 (w), 740 (w); HRMS found: 246.1993 (calcd. for $C_{17}H_{26}O$ 246.1984).

2,6-bis(Hexyl)benzaldehyde (**5h**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (1H, s, CHO), 7.35 (1H, t, J = 7.7 Hz, 4-H in Ph), 7.09 (2H, d, J = 7.6 Hz, 3,5-Hs in Ph), 2.91 (4H, t, J = 8.0 Hz, α-CH_2 to Ph), 1.54–1.65 (4H, m, CH_2), 1.15–1.45 (12H, m, CH_2), 0.88 (6H, t, J = 6.8 Hz, CH_3); MS (EI) *m/z* 274 (38, M^+), 256 (10), 227 (14), 217 (14), 213 (39), 199 (26), 189 (100), 171 (15), 157 (17), 143 (36), 129 (83), 117 (36), 105 (36), 91 (28), 84 (31), 77 (10), 55 (10).

2,6-bis(3,3-Dimethylbutyl)-4-fluorobenzaldehyde (**5i**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.44 (1H, s, CHO), 6.78 (2H, d, J = 9.4 Hz, 3,5-Hs in Ph), 2.86–2.93 (4H, m, α-CH_2 to Ph), 1.42–1.49 (4H, m, β-CH_2 to Ph), 0.98 (18H, s, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 191.26 (*C*HO), 164.73 (d, J_{C-F} = −253 Hz, *C*–F, 4-C in Ph), 150.59 (d, J = 8.8 Hz, 2,6-Cs in Ph), 128.10 (d, J_{C-F} = 2.9Hz, 1-C in Ph), 115.36 (d, J_{C-F} = 20.6 Hz, 3,5-Cs in Ph), 46.63, 30.70, 29.12 (*C*H_3); MS (EI) *m/z* 292 (7, M^+), 235 (100, $M^+ - Bu^t$), 219 (12), 165 (11), 147 (10), 135 (9), 59 (14), 57 (33, Bu^{t+}); IR (KBr, neat, cm^{-1}) ν 2955 (s), 2905 (m), 2868 (m), 2767 (w), 1694 (vs, CO), 1595 (vs, C–F), 1467 (m), 1365 (m), 1303 (m), 1274 (m), 1247 (m), 1185 (w), 1127 (m), 991 (w), 866 (m); HRMS found: 292.2198 (calcd. for $C_{19}H_{29}OF$ 292.2202).

2-(3,3-Dimethylbutyl)-3-fluorobenzaldehyde (**4j**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.26 (1H, d, J_{H-F} = 2.3 Hz, CHO), 7.52 (1H, dd, J_{H-F} = 2.7 Hz, J_{H-H} = 8.9 Hz, 6-H in Ph), 7.19–7.26 (2H, Hs in Ph), 2.90–2.98 (2H, m, α-CH_2 to Ph), 1.25–1.49 (2H, m, β-CH_2 to Ph), 0.98 (9H, d, J_{H-F} = 5.3 Hz, CH_3).

2,6-bis(3,3-Dimethylbutyl)-3-fluorobenzaldehyde (**5j**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.47 (1H, s, CHO), 7.01–7.27 (2H, 4,5-Hs in Ph), 2.80–2.95 (4H, m, α-CH_2 to Ph), 1.39–1.48 (4H, m, β-CH_2 to Ph), 0.99 (9H, s, CH_3), 0.97 (9H, s, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 192.65 (*C*HO, d, J_{C-F} = 3 Hz), 159.33 (d, J_{C-F} = −242 Hz, *C*–F), 142.14 (d, J_{C-F} = 4 Hz), 132.80 (d, J_{C-F} = 16 Hz, 2-C in Ph), 132.62 (d, J_{C-F} = 7 Hz, 6-C in Ph), 129.39 (d, J_{C-F} = 8 Hz, 5-C in Ph), 119.59 (d, J_{C-F} = 23 Hz, 4-C in Ph), 47.27, 45.18, 30.80 (d, J_{C-F} = 6 Hz), 29.11 (d, J_{C-F} = 9 Hz), 27.06, 20.18 (d, J_{C-F} = 5 Hz); MS (EI) *m/z* 292 (22, M^+), 259 (13), 235 (100, $M^+ - Bu^t$), 219 (17), 165 (17), 163 (10), 161 (11), 147 (17), 135 (15), 57 (18, Bu^{t+}); IR (KBr, neat, cm^{-1}) ν 2955 (vs), 2867 (m), 1697 (s, CO), 1473 (s), 1365 (m), 1248 (m), 826 (m); HRMS found: 292.2213 (calcd. for $C_{19}H_{29}OF$ 292.2202).

2-(3,3-Dimethylbutyl)-6-tolualdehyde (**4k**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.57 (1H, s, CHO), 7.32 (1H, t, J = 7.6 Hz, 4-H in Ph), 7.05–7.10 (2H, m, 3,5-Hs in Ph), 2.86–2.93 (2H, m, β-CH_2 to Bu^t), 2.58 (3H, s, CH_3), 1.43–1.49 (2H, m, α-CH_2 to Bu^t), 0.98 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.28 (CHO), 147.04, 140.86, 132.97, 131.92, 129.64, 128.84, 47.42, 30.77, 29.23, 29.06, 28.57, 20.96 (CH_3); MS (EI) *m/z* 204 (7, M^+), 147 (100, $M^+ - Bu^t$), 133 (22, $M^+ - CH_2Bu^t$), 131 (20), 119 (14, $M^+ - CH_2CH_2Bu^t$), 117 (11), 115 (11), 105 (22), 103 (15), 91 (20), 77 (27), 59 (18), 57 (25, Bu^{t+}); IR (KBr, neat, cm^{-1}) ν 3065 (w), 2955 (s), 2904 (m), 2866 (m), 2763 (w), 1693 (vs, C=O), 1593 (m), 1466 (m), 1365 (w), 1189 (m), 792 (w), 757 (w), 712 (w); HRMS found: 204.1517 (calcd. for $C_{14}H_{20}O$ 204.1514).

2-(Pentyl)-6-tolualdehyde (**4l**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (1H, s, CHO), 7.33 (1H, t, J = 7.6 Hz, 4-H in Ph), 7.09 (2H, d, J = 8.0 Hz, 3,5-Hs in Ph), 2.90–2.96 (2H, m, CH_2), 2.59 (3H, s, CH_3), 1.56–1.63 (2H, m, CH_2), 1.30–1.39 (4H, m, CH_2), 0.86–0.92 (3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.50 (CHO), 146.39, 140.87, 132.84, 132.01, 129.73, 128.88, 33.22, 32.43, 31.73, 22.46, 21.01 (CH_3); MS (EI) *m/z* 190 (24, M^+), 175 (43, $M^+ - CH_3$), 157 (17), 147 (51, $M^+ - CH_2CH_2CH_3$), 145 (11), 143 (100), 133 (79, $M^+ - CH_2CH_2CH_2CH_3$), 119 (41, $M^+ - CH_2CH_2CH_2CH_2CH_3$), 115 (44), 103 (48), 91 (59), 79 (33), 77 (51), 71 (11), 65 (12); IR (KBr, neat, cm^{-1}) ν 3065 (w), 2957 (m), 2928 (s), 2858 (m), 2763 (w), 1693 (vs, C=O), 1592 (m), 1465 (m), 1189 (m), 787 (w); HRMS found: 190.1359 (calcd. for $C_{13}H_{18}O$ 190.1358).

2-(Hexyl)-6-tolualdehyde (**4m**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (1H, s, CHO), 7.34 (1H, t, J = 7.6 Hz, 4-H in Ph), 7.09 (2H, d, J = 7.9 Hz, 3,5-Hs in Ph), 2.93 (2H, t, J = 7.7 Hz, CH_2), 2.60 (3H, s, CH_3), 1.56–1.63 (2H, m, CH_2), 1.26–1.40 (6H, m, CH_2), 0.88 (3H, t, J = 6.8 Hz, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 193.57 (CHO), 146.44, 140.90, 132.88, 132.08, 129.75, 128.90, 33.28, 32.74, 31.61, 29.26, 22.58, 21.00 (CH_3); MS (EI) *m/z* 189 (4, $M^+ - CH_3$), 143 (56), 133 (56, $M^+ - CH_2CH_2CH_2CH_2CH_3$), 119 (42), 115 (43), 105 (91), 103 (61), 91 (100), 77 (100), 55 (34); IR (KBr, neat, cm^{-1}) ν 3064 (w), 2956 (m), 2927 (s), 2856 (m), 2763 (w), 1693 (vs, C=O), 1593 (m), 1465 (m), 1189 (m), 785 (w); HRMS found: 204.1511 (calcd. for $C_{14}H_{20}O$ 204.1514).

6-(3,3-Dimethylbutyl)-3-chlorobenzaldehyde (**4p**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (1H, s, CHO), 7.79 (1H, s, 2-H in Ph), 7.45 (1H, dd, J = 8.2, 2.3 Hz, 4-H in Ph), 7.21 (1H, d, J = 8.2 Hz, 5-H in Ph), 2.91–2.98 (2H, m, β-CH_2 to Bu^t), 1.41–1.48 (2H, m, α-CH_2 to Bu^t), 0.99 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 190.50 (*C*O), 144.81, 134.58, 133.73, 132.41, 130.29, 47.29, 30.84, 29.15, 27.30; MS (EI) *m/z* 224 (24, M^+), 191 (18), 167 (100, $M^+ - Bu^t$), 156 (12), 154 (23), 132 (10), 125 (36), 115 (12), 103 (20), 89 (32), 77 (13), 59 (14), 57 (27, Bu^{t+}); IR (NaCl, neat, cm^{-1}) ν 2956 (vs), 2866 (m), 1705 (vs, CO), 1478 (m), 1365, 1184 (m), 896, 834; HRMS found: 224.0979 (calcd. for $C_{13}H_{17}OCl$ 224.0968).

2,6-bis(3,3-Dimethylbutyl)-3-chlorobenzaldehyde (**5p**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (1H, s, CHO), 7.41 (1H, d, J = 8.2 Hz, 4-H in Ph), 7.02 (1H, d, J = 8.3 Hz, 5-H in Ph), 2.97–3.04 (2H, m, α-CH_2 to Ph), 2.77–2.83 (2H, m, α-CH_2 to Ph), 1.39–1.48 (4H, m, β-CH_2 to Ph), 1.00 (9H, s, CH_3), 0.97 (9H, s, CH_3).

8: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37 (2H, t, J = 7.9 Hz), 7.22 (1H, dd, J = 7.9, 0.7 Hz), 7.04–7.11 (3H), 6.88–6.95 (2H), 2.58–2.64 (4H, m, CH_2), 2.13 (3H, s, CH_3), 1.40–1.48 (4H, m, CH_2), 0.98 (18H, s, Hs of Bu^t); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.13, 150.74, 140.73, 138.90, 130.10, 129.03, 128.03, 127.93, 126.65, 125.86, 123.50, 120.38, 119.35, 46.30, 30.57, 29.32 (3 *C*H_3), 28.22, 14.08 (*C*H_3); MS (EI) *m/z* 363 (7, M^+), 348 (19, $M^+ - CH_3$), 306 (56, $M^+ - Bu^t$), 292 (8), 271 (15), 234 (14), 220 (19), 215 (100), 143 (59), 128 (11), 118 (14), 84 (39), 57 (44, Bu^{t+}).

2-(3,3-Dimethylbutyl)propiophenone (**10**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (1H, d, J = 7.8 Hz, 6-H in Ph), 7.36 (1H, t, J = 8.7 Hz, 4-H in Ph), 7.25–7.20 (2H, 3,5-Hs in Ph), 2.90 (2H, q, J = 7.4 Hz, α-CH_2 to CO), 2.77–2.71 (2H, m, CH_2), 1.46–1.39 (2H, m, CH_2), 1.20 (3H, t, J = 7.3 Hz, CH_3), 0.96 (9H, s, Hs of Bu^t); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.90 (*C*O), 142.79, 138.74, 130.94, 130.76, 127.74, 125.43, 46.70, 35.37, 30.64, 29.26 (3 *C*H_3), 29.05, 8.51 (CH_2*C*H_3); MS (EI) *m/z* 218 (7, M^+), 189 (54, $M^+ - Et$), 161 (100, $M^+ - Bu^t$), 145 (46), 143 (25), 133 (45, $M^+ - CH_2CH_2Bu^t$), 131 (24), 129 (19), 119 (27), 117 (15), 115 (15), 103 (12), 91 (41), 77 (12), 59 (20), 57 (44, Bu^{t+}); IR (KBr, neat) ν 2954 (vs), 2939, 2906, 2866, 1691 (vs, C=O), 1465, 1364, 1214, 1012, 945, 751; HRMS found: 218.1673 (calcd. for $C_{15}H_{22}O$ 218.1671).

2′-(*n*-Pentyl)propiophenone (**12**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (1H, d, J = 7.8 Hz, 6-H in Ph), 7.36 (1H, dt, J = 7.8, 1.5 Hz, 4-H in Ph), 7.22–7.34 (2H, 3,5-Hs in Ph), 2.87 (2H, q, J = 7.2 Hz, α-CH_2 to CO), 2.74–2.80 (2H, m, CH_2), 1.53–1.59 (2H, m, CH_2), 1.29–1.36 (4H, m, CH_2), 1.19 (3H, t, J = 7.3 Hz, CH_3), 0.89 (3H, t, J = 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.80 (*C*O), 142.22, 138.56, 130.88, 130.69, 127.80, 125.49, 35.24, 33.73, 31.83, 31.60, 22.51, 13.99, 8.38 (CH_2*C*H_3); MS (EI) *m/z* 204 (2, M^+), 175 (43, $M^+ - Et$), 157 (5), 145 (5), 133 (12, $M^+ - CH_2CH_2CH_2CH_2CH_3$), 131 (17), 129 (35), 119 (23), 117 (27), 115 (26), 105 (14), 103 (16), 91 (100), 89 (26), 84 (11), 77 (27), 65 (19), 59 (10), 57 (16); IR (KBr, neat) ν 2957, 2931 (vs), 2871, 2858, 1690 (vs, C=O), 1458, 1343, 1216, 952, 752; HRMS found: 204.1520 (calcd. for $C_{14}H_{20}O$ 204.1514).

2′-(*n*-Hexyl)propiophenone (**13**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53 (1H, d, J = 7.9 Hz, 6-H in Ph), 7.37 (1H, dt, J = 7.7, 1.5 Hz, 4-H in Ph), 7.20–7.27 (2H, 3,5-Hs in Ph), 2.90 (2H, q, J = 7.3 Hz, α-CH_2 to CO), 2.77 (2H, t, J = 8.0 Hz, CH_2), 1.50–1.58 (2H, m, CH_2), 1.17–1.37 (6H, m, CH_2), 1.20 (3H, t, J = 7.3 Hz, CH_3), 0.88 (3H, t, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.89 (*C*O), 142.24, 138.63, 130.90, 130.71, 127.81, 125.51, 35.29, 33.80, 31.90, 31.69, 29.36, 22.60, 14.08, 8.41 (CH_2***C***H_3); MS (EI) *m/z* 218 (4, M^+), 189 (100, $M^+ - Et$), 143 (5), 133 (7, $M^+ - CH_2CH_2CH_2CH_2CH_2CH_3$), 131 (8), 129 (21), 119 (10), 117 (11), 115 (6), 91 (18); IR (KBr, neat) ν 2956, 2928 (vs), 2871, 2856, 1690 (vs, C=O), 1457, 1344, 1216, 953, 753; HRMS found: 218.1672 (calcd. for $C_{15}H_{22}O$ 218.1671).

2-(3,3-Dimethylbutyl)furan-3-carbaldehyde (**15**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (1H, s, CHO), 7.31 (1H, d, J = 1.8 Hz, 5-H), 6.69 (1H, d, J = 2.0 Hz, 4-H), 2.89–2.95 (2H, m, β-CH_2 to Bu^t), 1.58–1.66 (2H, m, α-CH_2 to Bu^t), 0.97 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.64 (CHO), 141.88, 121.85, 110.36, 107.97, (42.35), 30.23, 29.09, 28.90, 22.59; MS (EI) *m/z* 180 (4, M^+), 123 (100, $M^+ - Bu^t$), 109 (83, $M^+ - CH_2Bu^t$), 107 (11), 95 (15, $M^+ - CH_2CH_2Bu^t$), 71 (11), 57 (21, Bu^{t+}); IR (KBr, neat, cm^{-1}) ν 2955 (s), 2923 (s), 2850 (m), 1683 (vs, C=O), 1582 (w), 1426 (w), 1366 (w), 1252 (w), 1124 (m), 1025 (w), 743 (m); HRMS found: 180.1156 (calcd. for $C_{11}H_{16}O_2$ 180.1150).

2-(3,3-Dimethylbutyl)thiophene-3-carbaldehyde (**17**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (1H, s, CHO), 7.38 (1H, d, J = 5.3 Hz, 5-H), 7.08 (1H, d, J = 5.9 Hz, 4-H), 3.12–3.19 (2H, m, β-CH_2 to Bu^t), 1.59–1.66 (2H, m, α-CH_2 to Bu^t), 0.99 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.33 (CHO), 159.02, 136.31, 127.24, 122.55, 46.85, 30.79, 29.18, 29.00, 23.63; MS (EI) *m/z* 196 (9, M^+), 139 (100, $M^+ - Bu^t$), 125 (55, $M^+ - CH_2Bu^t$), 111 (15, $M^+ - CH_2CH_2Bu^t$), 97 (24), 71 (9), 57 (11, Bu^{t+}); IR (KBr, neat, cm^{-1}) ν 3109 (w), 2955 (s), 2865 (m), 2732 (w), 1683 (vs,

C=O), 1520 (m), 1468 (w), 1387 (m), 1233 (m), 720 (m); HRMS found: 196.0924 (calcd. for $C_{12}H_{16}OS$ 196.0923).

2-(3,3-Dimethylbutyl)naphthalene-1-carbaldehyde (**19**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.85 (1H, s, CHO), 9.03 (1H, d, J = 8.8 Hz), 7.93 (1H, d, J = 8.4 Hz), 7.80 (1H, d, J = 7.6 Hz), 7.60 (1H, dt, J = 6.8, 1.4 Hz), 7.48 (1H, dt, J = 7.1, 1.1 Hz), 7.30 (1H, d, J = 8.5 Hz), 3.01–3.08 (2H, m, CH_2), 1.52–1.59 (2H, m, CH_2), 1.01 (9H, s, Hs of Bu^t); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 193.10 (*C*O), 148.69, 134.57, 132.32, 131.19, 128.97, 128.66, 128.24, 127.78, 125.93, 124.79, 47.89, 30.93, 29.14 (3 *C*H_3), 28.64; MS (EI) *m/z* 240 (2, M^+), 183 (63, $M^+ - Bu^t$), 167 (12), 165 (19), 155 (28), 153 (22), 141 (85), 139 (36), 127 (20), 115 (100), 89 (21), 77 (13), 59 (36), 57 (72, Bu^{t+}), 55 (33); IR (KBr, neat) ν 3052, 2955(s), 2903, 2865, 2770, 1683 (vs, C=O), 1620, 1594, 1509, 1466, 1431, 1365, 1246, 1180, 1063, 826, 763, 745; HRMS found: 240.1511 (calcd. for $C_{17}H_{20}O$ 240.1514).

1,3-bis(3,3-Dimethylbutyl)naphthalene-2-carbaldehyde (**22**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.74 (1H, s, CHO), 8.13 (1H, d, J = 7.7 Hz), 7.46–7.86 (4H, Hs of naphthyl), 3.31–3.38 (2H, m, β-CH_2 to Bu^t), 2.96–3.02 (2H, m, β-CH_2 to Bu^t), 1.57–1.64 (2H, m, α-CH_2 to Bu^t), 1.48–1.54 (2H, m, α-CH_2 to Bu^t), 1.09 (9H, s, CH_3 of Bu^t), 1.00 (9H, s, CH_3 of Bu^t); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 194.63 (CHO), 144.38, 140.50, 135.62, 130.61, 128.14, 127.96, 127.53, 126.00, 125.79, 124.56, 45.90, 31.20, 29.25, 23.42; MS (EI) *m/z* 324 (20, M^+), 267 (100, $M^+ - Bu^t$), 251 (18), 239 (20), 197 (32), 193 (30), 183 (28), 179 (42), 165 (45), 153 (62), 128 (11), 115 (12), 84 (18), 57 (81, Bu^t); IR (KBr, neat, cm^{-1}) ν 2954 (vs), 2865 (m), 1692 (s, C=O), 1621 (w), 1594 (w), 1468 (w), 1364 (m), 1246 (w), 1096 (w), 1025 (w), 799 (w), 745 (m); HRMS found: 324.2456 (calcd. for $C_{23}H_{32}O$ 324.2453).

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