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Use of tetrahydropyrimidinium salts for highly efficient palladium-catalyzed cross-coupling reactions of aryl bromides and chlorides

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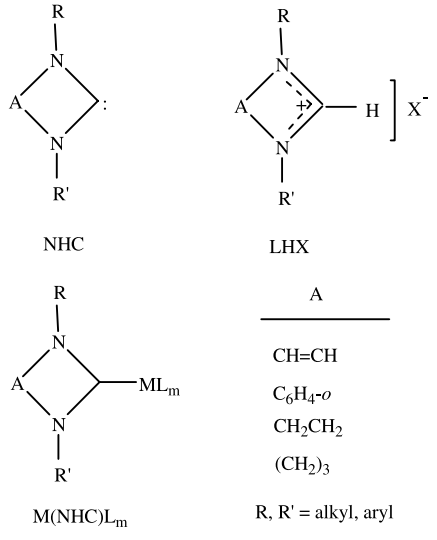
Abstract—New, sterically demanding 1,3-dialkyl-3,4,5,6-tetrahydropyrimidinium salts (**2**) as NHC precursors have been synthesized and characterized. These salts, in combination with palladium acetate, provided active catalysts for the cross-coupling of aryl chlorides and bromides under mild conditions. The catalytic system was applied to the Heck, Suzuki and benzaldehyde (Kumada) coupling reactions. Catalyst activity was found to be influenced by the presence of a methoxy group on the ring of the *p*-position of benzyl substituent of the ligand precursor.

1. Introduction

Transition metal complexes incorporating 1,3-diorganyl *N*-heterocyclic carbene (NHC) ligands, such as imidazol-2-ylidene (A=CH=CH), imidazolidin-2-ylidene (A=CH_2CH_2) and benzimidazol-2-ylidene (A=C_6H_4-*o*) have attracted a great interest in recent years.[1–6] They are often synthesized by reaction of an azolinium salt (LHX) with a basic salt such as $Pd(OAc)_2$, to give M(NHC)Lm.



Research in this area was principally driven by the employment of these complexes as potential catalysts. Many catalytic applications of NHC complexes have been described.[7–9] Palladium-catalyzed cross-coupling reactions are particularly attractive because of their versatility in the formation of C–C and C–X bonds (X=O, S, N etc.).[10–13] The main advantages of these coupling processes stems from the readily availability of starting materials and the broad tolerance of palladium catalysts to various functional groups. Pd-catalyzed cross-coupling reactions are generally thought to proceed through three distinctive steps:[14] (i) an aryl halide reacts with Pd(0) through oxidative addition to give an electrophilic Pd(II) species. (ii) A transmetallation reaction then occurs with an appropriate nucleophile to yield a Pd(II) complex, containing the two moieties to be coupled. (iii) Reductive elimination of the product, which regenerates the active Pd(0) species.

The ancillary ligand (NHC) coordinated to the metal center has a number of important roles in homogeneous catalysis such as providing a stabilizing effect and governing the activity and selectivity through alteration of the steric and electronic parameters. The number, nature and position of the substituents on the nitrogen atom(s) and/or NHC ring have been found to play a crucial role in tuning the catalytic activity. Whilst modifications to the five-membered ring of the ligand aryl substituent have been described, relatively little attention has been paid to the effect of the ring size.[15] For the present study, we selected 3,4,5,6-tetrahydopyrimidin-2-ylidene precursors (**2**). This choice was guided by several considerations. An important characteristic of the carbene ligands in active complexes is their strong-electron

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donating effect, primarily a σ-effect. We have previously reported the use of a in situ formed imidazolidin-2-ylidenepalladium(II) system, which exhibits high activity in various coupling reactions of aryl bromides and aryl chlorides.[16] In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives.[17] Due to their six-membered ring geometry, tetrahydopyrimidine-2-ylidenes are stronger σ-donating ligands in comparison to their five-membered relatives.[15]

2. Results and discussion

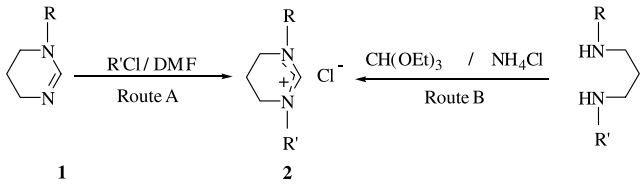
2.1. Synthesis and characterization of the salts, 2

The synthesis of the tetrahydropyrimidinium chlorides was achieved via two synthetic routes (Scheme 1). The alkylation of 1-alkyltetrahydropyrimidine derivatives[18] with alkyl chlorides produced symmetrical or unsymmetrical 1,3-dialkylpyrimidinium salts (Route A). On the other hand, reaction of *N*,*N*′-dialkylpropan-1,3-diamine with triethyl orthoformate and ammonium chloride yielded the symmetrical tetrahydropyrimidinium salt (Route B) (Scheme 1).

Elemental analysis and ^{1}H and ^{13}C NMR spectra confirmed the formation of **2** (see Section 4). An important feature of the ligand precursors (**2**) is their facile preparation. While these studies were in progress, other workers have addressed the synthesis and catalytic properties of 1,3-dimesityltetrahydropyrimidine-2-ylidene complexes of palladium.[19,20] Contrary to the claims made by Buchmeister and co-workers,[19a] and unlike other silver NHC complexes, it has been reported that the chlorodimesityltetrahydrpyrimidin-2-ylidenesilver does not transfer the carbene ligand to $Pd(NCCH_3)_2Cl_2$ to afford $Pd(NHC)_2Cl_2$.[20]

2.2. The Heck reaction

The Heck alkenylation reaction[21] is useful approach to the preparation of disubstituted olefins. The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Generally, Heck reactions conducted with tertiary phosphine[22] or NHC[9,23] complexes require high temperatures (higher than 120 °C) and polar solvents. For the choice of base, we chose to use Cs_2CO_3, K_2CO_3, and K_3PO_4. Finally, use of 1.5% mol $Pd(OAc)_2$, 3% mol **2**, 2 equiv Cs_2CO_3 in DMF/H_2O (1:1) at 50 °C led to the best conversion within 5 h. We initially evaluated the catalytic activity of $Pd(OAc)_2$/**2a** for the coupling of bromobenzene with styrene (Table 1, entry 1).



2a R = R′ = $CH_2C_6H_2(CH_3)_3$-2,4,6

2b R = R′ = $CH_2C_6H_2(OCH_3)_3$-2,4,6

2c R = R′ = $CH_2C_6H_2(OCH_3)_3$-3,4,5

2d R = C_6H_{11}; R′ = $CH_2C_6H_2(CH_3)_3$-2,4,6

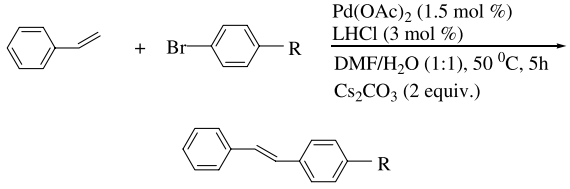
2e R = $CH_2CH_2OCH_3$; R′ = $CH_2C_6H_2(CH_3)_3$-2,4,6

Scheme 1. Synthesis of ligand precursors.

Control experiments indicate that the coupling reaction did not occur in the absence of **2a**. Under these reaction conditions a wide range of aryl bromides bearing electron-donating or electron-withdrawing groups react with styrene affording the coupled products in excellent yields. As expected, electron-deficient bromides coupled well under the conditions. Enhancement in activity, although less significant, is further observed employing 4-bromobenzaldehyde instead of 4-bromoacetophenone (entries 16–20 and 21–25, respectively).

A systematic study on the substituent effect in the tetrahydropyrimidinium salts **2** indicated that the introduction of a methoxy group to the *p*-position of the benzyl substituent on the *N*-atoms notably increased the reaction rate and the yield of the coupled product. The catalytic activity of the salts used fall in the order of **c**>**b**>**d**>**a**>**e**. The ether functionality in **2e** does not contribute with any great effect as seen with the arylation of benzaldehyde derivatives (see Section 2.4). These results indicated that the catalytic system generated in situ from tetrahydropyrimidinium salts and $Pd(OAc)_2$ have an activity, which is superior

Table 1. Pd-catalyzed Heck coupling



Entry	LHCl	R	Yield (%)[a–c]
1	**2a**	H	80
2	**2b**	H	88
3	**2c**	H	89
4	**2d**	H	85
5	**2e**	H	78
6	**2a**	OCH_3	88
7	**2b**	OCH_3	87
8	**2c**	OCH_3	88
9	**2d**	OCH_3	90
10	**2e**	OCH_3	80
11	**2a**	CH_3	84
12	**2b**	CH_3	90
13	**2c**	CH_3	92
14	**2d**	CH_3	83
15	**2e**	CH_3	80
16	**2a**	$COCH_3$	90
17	**2b**	$COCH_3$	88
18	**2c**	$COCH_3$	92
19	**2d**	$COCH_3$	85
20	**2e**	$COCH_3$	84
21	**2a**	CHO	91
22	**2b**	CHO	94
23	**2c**	CHO	96
24	**2d**	CHO	87
25	**2e**	CHO	85

[a] Reaction conditions: 1.0 mmol of R-C_6H_4X-*p*, 1.5 mmol of styrene, 2 mmol Cs_2CO_3, 1.50 mmol% $Pd(OAc)_2$, 3.0 mmol% **2**, water (3 mL)-DMF (3 mL).

[b] The purity of the products were confirmed by NMR and yields are based on aryl bromide.

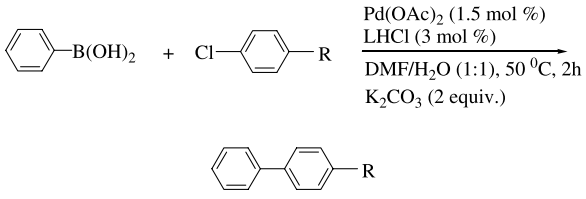
[c] 50 °C, 5 h.

or comparable to the imidazolinium/$Pd(OAc)_2$ system.[16] However, chloroarenes do not react under standard conditions; yields of <5% were recorded.

2.3. The Suzuki coupling

Suzuki cross-coupling represents a powerful method for carbon–carbon bond formation.[24] Recently, the reaction of aryl chlorides catalyzed by palladium/tertiary phosphine[22] and palladium/NHC[25–28] systems have been extensively studied due to the economically attractive nature of the starting materials and the production of the less toxic salt by-products, for example, NaCl as opposed to NaBr. Here, various tetrahydropyrimidinium salts (**2a–e**) were compared as ligand precursors under the same reaction conditions. To survey the parameters for Suzuki coupling, we chose to examine Cs_2CO_3, K_2CO_3, and K_3PO_4 as base and DMF/H_2O (1:1) and dioxane as the solvent mixture. We found that the reactions performed in DMF/H_2O (1:1) with Cs_2CO_3 or K_2CO_3 at 50 °C appeared to be best. We initiated our investigation with coupling of chlorobenzene and phenylboronic acid, in the presence of $Pd(OAc)_2$/**2**. Table 2 summarizes the results obtained in the presence of **2a–e** (Table 2, entries 1–5).

Table 2. Pd-catalyzed Suzuki coupling



Entry	LHCl	R	Yield (%)[a–d]
1	**2a**	H	93
2	**2b**	H	89
3	**2c**	H	93
4	**2d**	H	85
5	**2e**	H	81
6	**2a**	OCH_3	88
7	**2b**	OCH_3	90
8	**2c**	OCH_3	92
9	**2d**	OCH_3	87
10	**2e**	OCH_3	72
11	**2a**	CH_3	87
12	**2b**	CH_3	91
13	**2c**	CH_3	94
14	**2d**	CH_3	85
15	**2e**	CH_3	83
16	**2a**	$COCH_3$	96
17	**2b**	$COCH_3$	96
18	**2c**	$COCH_3$	98
19	**2d**	$COCH_3$	94
20	**2e**	$COCH_3$	91
21	**2a**	CHO	94
22	**2b**	CHO	94
23	**2c**	CHO	95
24	**2d**	CHO	90
25	**2e**	CHO	84

[a] Reactions conditions: 1.0 mmol of R-C_6H_4Cl-*p*, 1.2 mmol of phenylboronic acid, 2 mmol K_2CO_3, 1.5 mmol% $Pd(OAc)_2$, 3 mmol% **2**, water (3 mL)–DMF (3 mL).
[b] The purity of the products was confirmed by NMR and yields are based on aryl chloride.
[c] All reactions were monitored by GC.
[d] 50 °C, 2 h.

The scope of the reaction with respect to the aryl chloride component was also investigated. It can be seen that **2c** is an effective ligand precursor for the coupling of unactivated, activated and deactivated chlorides (entries 1–25). With chlorobenzene, 4-chloroanisole, 4-chloroacetophenone and 4-chlorobenzaldehyde, a similar activity sequence was observed: **c** > **b** > **d** > **a** > **e**.

In summary, we have demonstrated that in situ generated tetrahydropyrimidin-2-ylidene complexes of palladium are effective catalyst systems for Suzuki cross-coupling, surpassing the catalytic activity observed with the corresponding imidazolidin-2-ylidene palladium complexes.

2.4. Arylation of benzaldehyde derivatives

Another interesting cross-coupling process (Miura reaction) is palladium-catalyzed *o*-arylation(s) of benzaldehyde derivatives with aryl halides providing 2- or 2,6-diarylbenzaldehydes.[29] Using similar reaction conditions, we investigated the arylation of benzaldehyde derivatives using in situ generated palladium complexes of tetrahydropyrimidine-2-ylidene derived from **2**. The results are summarized in Table 3.

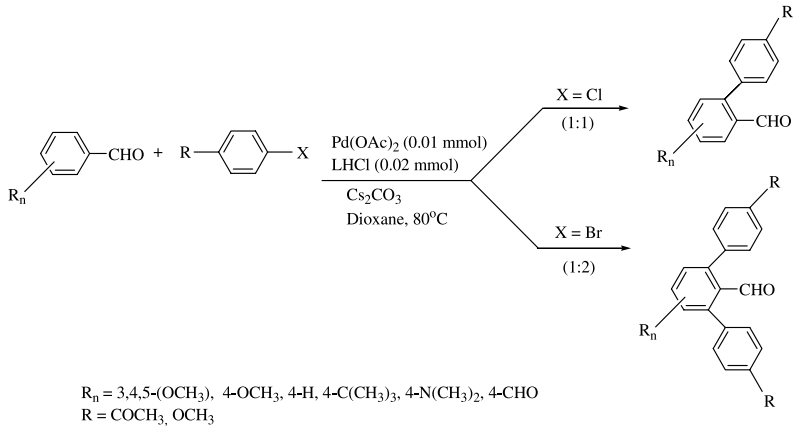
Here, **2e** is one of the best ligand precursors for the reaction of aryl chlorides. The use of cesium carbonate as the base in dioxane produced good to excellent yields of the corresponding products. The selectivity for mono- or di-arylation can be shifted to some extent by judicious choice of halide X, that is, for X=Cl, only the monoarylated product is seen; whereas for X=Br; the 2,6-diarylated product is formed predominantly when the aldehyde/aryl bromide ratio is 1:2.

3. Conclusions

We have shown that amongst the various saturated NHC precursors, tetrahydopyrimidinium salts (**2**) are excellent ligand precursors for the direct functionalization of aryl halides, in particular, aryl chlorides. The Heck, Suzuki and a variant of the Miura reaction of aryl bromides and chlorides have been investigated in the presence of a $Pd(OAc)_2$/**2** catalyst system. The cross-coupling results obtained using the $Pd(OAc)_2$/**2** mixture do not necessarily indicate a palladium carbene complex as the active catalyst species. Good to excellent yields of the desired products were obtained for the benchmark reactions in this study. In general, the **2c** catalyst system appears to be more efficient for the Heck reactions of aryl bromides; the activity is lower for the coupling of aryl chlorides. On the other hand, the catalyst **2e** work well in a version of Miura coupling of aryl chlorides.

Clearly, 1,3-dialkyltetrahydropyrimidin-2-ylidene palladium complexes are superior when compared to the corresponding 1,3-dialkylimidazolidin-2-ylidene palladium complexes. Once again, we observed that the in situ formed Pd–NHC catalysts, which consist of mixtures of palladium and ligands, gave better yields in the coupling reactions compared to the isolated carbene palladium(II) complexes.

Table 3. Arylation of benzaldehyde derivatives



R_n = 3,4,5-(OCH_3), 4-OCH_3, 4-H, 4-$C(CH_3)_3$, 4-$N(CH_3)_2$, 4-CHO
R = $COCH_3$, OCH_3

Entry	Ar–X	Aldehyde	Product	LHCl	Time (h)	Yield[a–d] (%)
1	4-(CH_3CO)–C_6H_4–	3,4,5-Trimethoxy benzaldehyde	2-(*p*-Acetylphenyl)-3,4,5-(trimethoxy)benzaldehyde	**2a**	5	89
2	4-(CH_3CO)–C_6H_4–			**2b**	5	92
3	4-(CH_3CO)–C_6H_4–			**2c**	5	86
4	4-(CH_3CO)–C_6H_4–			**2d**	5	96
5	4-(CH_3CO)–C_6H_4–			**2e**	5	93
6	4-(CH_3O)–C_6H_4–	3,4,5-Trimethoxy benzaldehyde	2-(*p*-Methoxyphenyl)-3,4,5-(trimethoxy)benzaldehyde	**2a**	5	90
7	4-(CH_3O)–C_6H_4–			**2b**	24	87
8	4-(CH_3O)–C_6H_4–			**2c**	20	93
9	4-(CH_3O)–C_6H_4–			**2d**	24	84
10	4-(CH_3O)–C_6H_4–			**2e**	24	89
11	4-(CH_3O)–C_6H_4–	*p*-Methoxy benzaldehyde	2-(*p*-Methoxyphenyl)-4-methoxybenzaldehyde	**2a**	20	95
12	4-(CH_3O)–C_6H_4–			**2b**	24	87
13	4-(CH_3O)–C_6H_4–			**2c**	24	91
14	4-(CH_3O)–C_6H_4–			**2d**	24	93
15	4-(CH_3O)–C_6H_4–			**2e**	24	97
16	4-(CH_3CO)–C_6H_4–	*p*-Methoxy benzaldehyde	2-(*p*-Acetylphenyl)-4-methoxybenzaldehyde	**2a**	10	90
17	4-(CH_3CO)–C_6H_4–			**2b**	10	92
18	4-(CH_3CO)–C_6H_4–			**2c**	10	89
19	4-(CH_3CO)–C_6H_4–			**2d**	10	95
20	4-(CH_3CO)–C_6H_4–			**2e**	10	97
21	4-(CH_3O)–C_6H_4–	Benzaldehyde	2-(*p*-Methoxyphenyl) benzaldehyde	**2a**	24	76
22	4-(CH_3O)–C_6H_4–			**2b**	24	79
23	4-(CH_3O)–C_6H_4–			**2c**	24	83
24	4-(CH_3O)–C_6H_4–			**2d**	24	78
25	4-(CH_3O)–C_6H_4–			**2e**	24	84
26	4-(CH_3CO)–C_6H_4–	*p*-(*tert*-Butyl) benzaldehyde	2-(*p*-Acetylphenyl)-4-*tert*-butylbenzaldehyde	**2a**	10	83
27	4-(CH_3CO)–C_6H_4–			**2b**	10	77
28	4-(CH_3CO)–C_6H_4–			**2c**	10	82
29	4-(CH_3CO)–C_6H_4–			**2d**	10	86
30	4-(CH_3CO)–C_6H_4–			**2e**	10	85
31	4-(CH_3O)–C_6H_4–	*p*-(*tert*-Butyl) benzaldehyde	2-(*p*-Methoxyphenyl)-4-*tert*-butylbenzaldehyde	**2a**	15	90
32	4-(CH_3O)–C_6H_4–			**2b**	24	89
33	4-(CH_3O)–C_6H_4–			**2c**	24	82
34	4-(CH_3O)–C_6H_4–			**2d**	24	86
35	4-(CH_3O)–C_6H_4–			**2e**	15	92
36	4-(CH_3CO)–C_6H_4–	*p*-Dimethylaminobenzaldehyde	2-(*p*-Acetylphenyl)-4-dimethylamino benzaldehyde	**2a**	5	88
37	4-(CH_3CO)–C_6H_4–			**2b**	5	88
38	4-(CH_3CO)–C_6H_4–			**2c**	5	91
39	4-(CH_3CO)–C_6H_4–			**2d**	5	95
40	4-(CH_3CO)–C_6H_4–			**2e**	5	98
41	4-(CH_3O)–C_6H_4–	*p*-Dimethylaminobenzaldehyde	2-(*p*-Methoxyphenyl)-4-dimethylamino benzaldehyde	**2a**	28	79
42	4-(CH_3O)–C_6H_4–			**2b**	28	70
43	4-(CH_3O)–C_6H_4–			**2c**	28	74
44	4-(CH_3O)–C_6H_4–			**2d**	36	74
45	4-(CH_3O)–C_6H_4–			**2e**	36	81
46	4-(CH_3O)–C_6H_4–	*p*-Methoxy benzaldehyde	2,6-Bis(*p*-methoxyphenyl)-4-methoxybenzaldehyde	**2a**	12	90
47	4-(CH_3O)–C_6H_4–			**2b**	12	85
48	4-(CH_3O)–C_6H_4–			**2c**	12	80
49	4-(CH_3O)–C_6H_4–			**2d**	12	83
50	4-(CH_3O)–C_6H_4–			**2e**	12	92

Table 3 (*continued*)

Entry	Ar–X	Aldehyde	Product	LHCl	Time (h)	Yield[a–d] (%)
51	4-(CH_3O)–C_6H_4–			**2a**	12	86
52	4-(CH_3O)–C_6H_4–		2,6-Bis(*p*-methoxyphe-	**2b**	12	80
53	4-(CH_3O)–C_6H_4–	*p*-Dimethylami-nobenzaldehyde	nyl)-4-dimethylamino	**2c**	12	89
54	4-(CH_3O)–C_6H_4–		benzaldehyde	**2d**	12	85
55	4-(CH_3O)–C_6H_4–			**2e**	12	91
56	4-(CH_3O)–C_6H_4–			**2a**	12	83
57	4-(CH_3O)–C_6H_4–		2,6-Bis(*p*-methoxyphe-	**2b**	12	85
58	4-(CH_3O)–C_6H_4–	*p*-(*tert*-Butyl) benzaldehyde	nyl)-4-*tert*-butylbenzalde-	**2c**	12	87
59	4-(CH_3O)–C_6H_4–		hyde	**2d**	12	82
60	4-(CH_3O)–C_6H_4–			**2e**	12	88
61	4-(CH_3O)–C_6H_4–	Terephtalaldehyde	2,5-Bis(*p*-methoxyphe- nyl) terephtalaldehyde	**2e**	12	91

[a] For entries 46–61, aryl bromides (2 equiv) were used as aryl halide. In all other cases aryl chlorides were used.
[b] Reactions conditions: 1.0 mmol of R–C_6H_4Cl-*p*, 1.0 mmol of aldehyde, 2 mmol Cs_2CO_3, 1.0 mmol% $Pd(OAc)_2$, 2 mmol% 1,3-dialkyl pyrimidinium salt **2**, dioxane (3 mL), 80 °C.
[c] The purity of the products was confirmed by NMR and yields are based on aldehyde.
[d] All reactions were monitored by TLC.

4. Experimental

4.1. General

All reactions for the preparation of 1,3-dialkylpyrimidinium salts were carried out under argon using standard Schlenk flasks. Test reactions for the catalytic activity of palladium catalysts in the Suzuki and Heck cross-coupling reactions were carried out in the presence of air. All reagents were purchased from Aldrich Chemical Co. The solvents, Et_2O over Na, DMF over BaO, EtOH over Mg were distilled prior to use. All ^1H and ^{13}C NMR spectra were performed in $CDCl_3$. ^1H and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^1H), 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS; coupling constants (J) in Hz. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer, wave numbers in cm^{-1}. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

4.1.1. Preparation of 1,3-bis(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (2a). A mixture of *N*,*N*′-bis(2,4,6-trimethylbenzyl)propane (3.38 g, 10.0 mmol), NH_4Cl (0.53 g, 10.0 mmol) in triethyl orthoformate (50 mL) was heated in a distillation apparatus until the distillation of ethanol ceased. The temperature of the reaction mixture reached 110 °C. Upon cooling to rt, a colorless solid precipitated, which was collected by filtration, and dried in vacuum. The crude product was recrystallized from absolute ethanol to give colorless needles, and the solid was washed with diethyl ether (2×10 mL), dried under vacuum, and the yield was 3.77 g (98%). Mp 288–289 °C, $\nu_{(CN)}$= 1688 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 8.56 (s, 1H, NC*H*N), 6.73 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.74 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.36 (t, J=5.7 Hz, 4H, $NCH_2CH_2CH_2N$), 2.16 and 2.20 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.01 (quint, J=5.3 Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 151.9 (N*C*HN), 125.3, 130.0, 137.9 and 138.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 52.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 42.6 ($NCH_2CH_2CH_2N$), 19.8 and 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 19.1 ($NCH_2CH_2CH_2N$). Anal. Calcd for $C_{24}H_{33}N_2Cl$: C, 74.87; H, 8.64; N, 7.27. Found: C, 74.83; H, 8.66; N, 7.30.

4.1.2. Preparation of 1,3-bis(2,4,6-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (2b). Compound **2b** was prepared in the same way as **2a** from *N*,*N*′-bis(2,4,6-trimethoxybenzyl)propane (4.34 g, 10 mmol), NH_4Cl (0.53 g, 10 mmol) in triethyl orthoformate (50 mL) to give white crystals of **2b** 4.27 g (89%). Mp 233–234 °C, $\nu_{(CN)}$= 1682 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 7.82 (s, 1H, NC*H*N), 6.03 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-2,4,6), 4.46 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-2,4,6), 3.69 and 3.75 (s, 18H, $CH_2C_6H_2(OCH_3)_3$-2,4,6), 3.32 (t, J=5.6 Hz, 4H, $NCH_2CH_2CH_2N$), 1.96 (quint, J=5.2 Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 162.7 (N*C*HN), 90.8, 101.7, 151.8 and 159.9 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 58.1 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 55.7 and 56.1 ($CH_2C_6H_2(OCH_3)_3$-2,4,6), 43.3 ($NCH_2CH_2CH_2N$), 19.4 ($NCH_2CH_2CH_2N$). Anal. Calcd for $C_{24}H_{33}N_2O_6Cl$: C, 59.93; H, 6.91; N, 5.82. Found: C, 59.89; H, 6.94; N, 5.80.

4.1.3. Preparation of 1,3-bis(3,4,5-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (2c). Compound **2c** was prepared in the same way as **2a** from *N*,*N*′-bis(3,4,5-trimethoxybenzyl)propane (4.34 g, 10 mmol), NH_4Cl (0.53 g, 10 mmol) in triethyl orthoformate (50 mL) to give white crystals of **2c** 4.51 g (94%). Mp 266–267 °C, $\nu_{(CN)}$= 1701 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 10.43 (s, 1H, NC*H*N), 6.72 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.75 (s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.76 and 3.81 (s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.21 (t, J=5.2 Hz, 4H, $NCH_2CH_2CH_2N$), 1.93 (quint, J=5.2 Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 154.7 (N*C*HN), 106.6, 129.0, 138.7 and 153.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 61.0 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 56.8 and 59.0 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 42.0 ($NCH_2CH_2CH_2N$), 19.3 ($NCH_2CH_2CH_2N$). Anal. Calcd for $C_{24}H_{33}N_2O_6Cl$: C, 59.93; H, 6.91; N, 5.82. Found: C, 59.95; H, 6.90; N, 5.84.

4.1.4. Preparation of 1-(2,4,6-trimethylbenzyl)-3-cyclohexyl-(3,4,5,6-tetrahydropyrimidinium chloride (2d). To a solution of 1-cyclohexyl(3,4,5,6-tetrahydropyrimidine) (1.66 g, 10 mmol) in DMF (10 mL) was added slowly 2,4,6-trimethylbenzyl chloride (1.68 g, 10.1 mmol) at 25 °C

and the resulting mixture was stirred at rt for 5 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3×15 mL), dried under vacuum, and the yield was 3.07 g (92%). Mp 210–211 °C. $\nu_{(CN)}=1682\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.50 (s, 1H, NC*H*N), 6.60 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.81 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.50 (quint, $J=8.2$ Hz, 1H, NC*H*$(CH_2)_4CH_2$), 3.19 and 2.87 (t, $J=5.6$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.01 and 2.07 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 1.39 (m, 10H, $NCH(CH_2)_4CH_2$), 1.79 (quint, $J=5.3$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 153.0 (N*C*HN), 125.6, 129.7, 137.9 and 138.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 64.0 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 51.9 ($NCH(CH_2)_4CH_2$), 40.2 and 41.2 ($NCH_2CH_2CH_2N$), 24.5, 24.9 and 30.8 ($NCH(CH_2)_4CH_2$), 20.2 and 20.8 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 19.2 ($NCH_2CH_2CH_2N$). Anal. Calcd for $C_{20}H_{31}N_2Cl$: C, 71.72; H, 9.33; N, 8.36. Found: C, 71.71; H, 9.35; N, 8.40.

4.1.5. Preparation of 1-methoxyethyl-3-(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydropyrimidinium chloride (2e). Compound **2e** was prepared in the same way as **2d** from 1-methoxyethyl(3,4,5,6-tetrahydropyrimidine) (1.42 g, 10 mmol) and 2,4,6-trimethylbenzyl chloride (1.68 g, 10.1 mmol) to give white crystals of **2e** 2.69 g (87%). Mp 118–119 °C, $\nu_{(CN)}=1688\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.26 (s, 1H, NC*H*N), 6.80 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.84 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 3.26 (s, 3H, $CH_2CH_2OCH_3$), 3.77 (t, $J=4.5$ Hz, 2H, $CH_2CH_2OCH_3$), 3.49 (t, $J=4.7$ Hz, 2H, $CH_2CH_2OCH_3$), 3.12 and 3.36 (t, $J=5.7$ Hz, 4H, $NCH_2CH_2CH_2N$), 2.19 and 2.25 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.00 (quint, $J=5.6$ Hz, 2H, $NCH_2CH_2CH_2N$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 153.9 (N*C*HN), 125.2, 129.7, 138.0 and 138.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 69.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 58.8 ($CH_2CH_2OCH_3$), 54.2 ($CH_2CH_2OCH_3$), 52.2 ($CH_2CH_2OCH_3$), 43.9 and 41.3 ($NCH_2CH_2CH_2N$), 19.8 and 20.8 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 19.0 ($NCH_2CH_2CH_2N$). Anal. Calcd for $C_{17}H_{27}N_2OCl$: C, 65.68; H, 8.75; N, 9.01. Found: C, 65.65; H, 8.73; N, 9.00.

4.2. General procedure for the Heck coupling reaction

$Pd(OAc)_2$ (1.0 mmol%), 1,3-dialkyl(3,4,5,6-tetrahydropyrimidinium) chloride, **2** (2 mmol%), aryl chloride (1.0 mmol), styrene (1.5 mmol), C_2CO_3 (2 mmol) and water (3 mL)/DMF (3 mL) were added to a small Schlenk tube and the mixture heated to 50 °C for 5 h. At the conclusion of the reaction, the mixture was cooled, extracted with ethyl acetate/hexane (1:5), filtered through a pad of silica gel with copious washings ether, the filtrate concentrated in vacuo to afford a solid, which was purified by flash chromatography on silica gel. The purity of the compounds was confirmed by NMR spectroscopy and yields are based on the aryl halide.

4.3. General procedure for Suzuki coupling

$Pd(OAc)_2$ (1.5 mmol%), 1,3-dialkyl(3,4,5,6-tetrahydropyrimidinium) chloride, **2** (3 mmol%), aryl chloride (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol) and water (3 mL)/DMF (3 mL) were added to a small Schlenk tube and the mixture heated to 50 °C for 2 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O, filtered through a pad of silica gel with copious washings ether, then concentrated in vacuo and purified by flash chromatography on silica gel. The purity of the compounds was confirmed by NMR spectroscopy and yields are based the on aryl halide.

4.4. General procedure for the arylation of benzaldehyde reaction

A dried Schlenk flask equipped with a magnetic stirring bar was charged with the aldehyde (1.0 mmol), aryl chloride (1.0 mmol), $Pd(OAc)_2$ (0.01 mmol), 1,3-dialkyl(3,4,5,6-tetrahydropyrimidinium)chloride, **2** (0.02 mmol), Cs_2CO_3 (2.0 mmol) and dioxane (3 mL). After stirring at 80 °C for 5–24 h, the mixture was cooled to rt and then quenched by addition of aqueous 1 N HCl and extracted with diethyl ether. The organic layer was dried over $MgSO_4$, filtered, then concentrated in vacuo and purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:5). Analysis of the reaction product was carried out by NMR spectroscopy and GC–MS.

4.4.1. 2-(*p*-Acetylphenyl)-3,4,5-(trimethoxy)benzaldehyde. Colourless oil, $\nu_{(C=O)}=1708\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.80 (s, 1H, 2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5C*H*O), 7.85 and 7.48 (d, $J=2.5$ Hz, 4H, 2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 7.06 (s, 1H, 2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 3.89 and 3.88 (s, 9H, 2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 2.54 (s, 3H, 2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 188.9 (2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5*C*HO), 108.2, 121.4, 126.7, 127.2, 127.9, 128.7, 130.1, 132.3, 136.7 and 154.5 (2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 194.2 (2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 54.1 and 54.6 (2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO), 24.8 (2-C_6H_4(*p*-$COCH_3$)$C_6H(OCH_3)_3$-3,4,5CHO). Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.75; H, 5.80.

4.4.2. 2-(*p*-Methoxyphenyl)-3,4,5-(trimethoxy)benzaldehyde. Colourless crystals. Mp 65–66 °C, $\nu_{(C=O)}=1716\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.85 (s, 1H, 2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5C*H*O), 7.21 and 6.79 (d, $J=4.7$ Hz, 4H, 2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO), 7.11 (s, 1H, 2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO), 3.91 and 3.92 (s, 9H, 2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO), 3.76 (s, 3H, 2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 189.2 (2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5*C*HO), 113.7, 123.8, 124.5, 125.1, 127.6, 128.2, 129.0, 130.3, 132.7 and 156.8 (2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO), 54.3 and 54.8 (2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO), 53.7 (2-C_6H_4(*p*-OCH_3)$C_6H(OCH_3)_3$-3,4,5CHO). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.51; H, 6.04.

4.4.3. 2-(*p*-Methoxyphenyl)-4-methoxybenzaldehyde. Colourless oil, $\nu_{(C=O)}=1708\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.88 (s, 1H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)C*H*O), 7.66 and 7.38 (d, $J=4.9$ Hz, 4H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)CHO), 6.81 (m, 3H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)CHO), 3.88 (s, 3H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)CHO), 3.77 (s, 3H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)$_3$CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 188.7 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)*C*HO), 110.8, 111.2, 112.9, 113.8, 124.1,

126.2, 130.0, 131.1, 153.1 and 157.2 (2-C_6H_4(*p*-OCH_3) C_6H_3(*p*-OCH_3)CHO), 54.2 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)CHO), 53.8 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-OCH_3)CHO). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.40; H, 5.80.

4.4.4. 2-(*p*-Acetylphenyl)-4-methoxybenzaldehyde. Colourless needles. Mp 53–54 °C, $\nu_{(C=O)}=1689\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.78 (s, 1H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-OCH_3)C*H*O), 7.87 and 7.62 (d, $J=2.5$ Hz, 4H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-OCH_3)CHO), 7.82 (m, 3H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-OCH_3)CHO), 3.85 (s, 3H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-OCH_3)CHO), 2.55 (s, 3H, 2-C_6H_4(*p*-$COCH_3$) C_6H_3(*p*-OCH_3)$_3$CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 188.7 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-OCH_3)*C*HO), 110.1, 123.8, 126.8, 127.4, 128.5, 130.1, 134.8, 138.1 and 155.0 (2-*C*$_6H_4$(*p*-$COCH_3$) *C*$_6H_3$(*p*-OCH_3)CHO), 194.3 (2-C_6H_4(*p*-*C*OCH_3)C_6H_3(*p*-OCH_3) CHO), 54.4 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-O*C*H$_3$)CHO), 24.9 (2-C_6H_4(*p*-CO*C*H$_3$)C_6H_3(*p*-OCH_3)CHO). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.60; H, 5.58.

4.4.5. 2-(*p*-Methoxyphenyl)benzaldehyde. Colourless oil, $\nu_{(C=O)}=1688\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 10.03 (s, 1H, 2-C_6H_4(*p*-OCH_3)C_6H_4C*H*O), 7.24 and 6.83 (d, $J=4.8$ Hz, 4H, 2-C_6H_4(*p*-OCH_3)C_6H_4CHO), 7.55 (m, 4H, 2-C_6H_4(*p*-OCH_3)C_6H_4CHO), 3.78 (s, 3H, 2-C_6H_4(*p*-O*C*H$_3$) C_6H_4CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 192.5 (2-C_6H_4(*p*-OCH_3)C_6H_4*C*HO), 114.8, 125.2, 125.9, 126.0, 127.8, 128.3, 129.7, 130.1, 134.2 and 156.8 (2-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_4$CHO), 53.4 (2-C_6H_4(*p*-O*C*H$_3$)C_6H_4CHO). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.25; H, 5.68.

4.4.6. 2-(*p*-Acetylphenyl)-4-*tert*-butylbenzaldehyde. Colourless oil, $\nu_{(C=O)}=1708\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.88 (s, 1H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-C(CH_3)$_3$) C*H*O), 7.74 and 7.46 (d, $J=2.4$ Hz, 4H, 2-*C*$_6H_4$(*p*-$COCH_3$) C_6H_3(*p*-C(CH_3)$_3$)CHO), 7.29 (m, 3H, 2-C_6H_4(*p*-$COCH_3$) *C*$_6H_3$(*p*-C(CH_3)$_3$)CHO), 2.48 (s, 3H, 2-C_6H_4(*p*-CO*C*H$_3$) C_6H_3(*p*-C(CH_3)$_3$)CHO), 1.21 (s, 9H, 2-C_6H_4(*p*-$COCH_3$) C_6H_3(*p*-C(*C*H$_3$)$_3$)CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 190.3 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-C(CH_3)$_3$)*C*HO), 108.7, 123.5, 126.9, 127.4, 128.2, 129.4, 131.7, 133.8, 137.2 and 154.7 (2-*C*$_6H_4$(*p*-$COCH_3$)*C*$_6H_3$(*p*-C(CH_3)$_3$)CHO), 193.7 (2-C_6H_4(*p*-*C*OCH_3)C_6H_3(*p*-C(CH_3)$_3$)CHO), 33.7 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-*C*(CH_3)$_3$)CHO), 30.8 (2-C_6H_4(*p*-$COCH_3$) C_6H_3(*p*-C(*C*H$_3$)$_3$)CHO), 24.8 (2-C_6H_4(*p*-CO*C*H$_3$)C_6H_3(*p*-C(CH_3)$_3$)CHO). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.36; H, 7.20.

4.4.7. 2-(*p*-Methoxyphenyl)-4-*tert*-butylbenzaldehyde. Pale yellow needles. Mp 74–75 °C, $\nu_{(C=O)}=1722\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.98 (s, 1H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-C(CH_3)$_3$)C*H*O), 7.82 and 7.55 (d, $J=$ 8.8 Hz, 4H, 2-*C*$_6H_4$(*p*-OCH_3)C_6H_3(*p*-C(CH_3)$_3$)CHO), 7.11 (m, 3H, 2-C_6H_4(*p*-OCH_3)*C*$_6H_3$(*p*-C(CH_3)$_3$)CHO), 3.77 (s, 3H, 2-C_6H_4(*p*-O*C*H$_3$)C_6H_3(*p*-C(CH_3)$_3$)CHO), 1.36 (s, 9H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-C(*C*H$_3$)$_3$)CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 191.0 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-C(CH_3)$_3$)*C*HO), 114.2, 124.4, 124.9, 125.5, 128.3, 128.7, 129.1, 130.4, 133.1 and 157.4 (2-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_3$(*p*-C(CH_3)$_3$)CHO), 34.3 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-*C*(CH_3)$_3$) CHO), 30.1 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-C(*C*H$_3$)$_3$)CHO), 54.4 (2-C_6H_4(*p*-O*C*H$_3$)C_6H_3(*p*-C(CH_3)$_3$)CHO). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.55.

4.4.8. 2-(*p*-Acetylphenyl)-4-dimethylaminobenzaldehyde. Yellow crystals. Mp 59–60 °C, $\nu_{(C=O)}=1689\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.69 (s, 1H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-$(CH_3)_2N$)C*H*O), 7.84 and 7.68 (d, $J=$ 2.4 Hz, 4H, 2-*C*$_6H_4$(*p*-$COCH_3$)C_6H_3(*p*-$(CH_3)_2N$)CHO), 6.89 (m, 3H, 2-C_6H_4(*p*-$COCH_3$)*C*$_6H_3$(*p*-$(CH_3)_2N$)CHO), 2.54 (s, 3H, 2-C_6H_4(*p*-CO*C*H$_3$)C_6H_3(*p*-$(CH_3)_2N$)CHO), 3.02 (s, 6H, 2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-$(CH_3)_2N$)CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 189.2 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-$(CH_3)_2N$)*C*HO), 109.9, 124.1, 127.8, 127.9, 128.6, 129.8, 130.8, 134.4, 138.5 and 153.3 (2-*C*$_6H_4$(*p*-$COCH_3$)*C*$_6H_3$(*p*-$(CH_3)_2N$)CHO), 195.7 (2-C_6H_4(*p*-*C*OCH_3) C_6H_3(*p*-$(CH_3)_2N$)CHO), 38.9 (2-C_6H_4(*p*-$COCH_3$)C_6H_3(*p*-(*C*H$_3$)$_2N$)CHO), 25.4 (2-C_6H_4(*p*-CO*C*H$_3$)C_6H_3(*p*-$(CH_3)_2N$) CHO). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.40; H, 6.44; N, 5.20.

4.4.9. 2-(*p*-Methoxyphenyl)-4-dimethylaminobenzaldehyde. Colourless needles. Mp 67–68 °C, $\nu_{(C=O)}=$ 1716 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.72 (s, 1H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-$(CH_3)_2N$)C*H*O), 7.71 and 7.34 (d, $J=4.8$ Hz, 4H, 2-*C*$_6H_4$(*p*-OCH_3)C_6H_3(*p*-$(CH_3)_2N$)CHO), 6.74 (m, 3H, 2-C_6H_4(*p*-OCH_3)*C*$_6H_3$(*p*-$(CH_3)_2N$)CHO), 3.74 (s, 3H, 2-C_6H_4(*p*-O*C*H$_3$)C_6H_3(*p*-$(CH_3)_2N$)CHO), 3.04 (s, 6H, 2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-$(CH_3)_2N$)CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 189.2 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-$(CH_3)_2N$)*C*HO), 110.3, 111.7, 113.6, 114.7, 124.4, 126.6, 130.9, 131.2, 153.2 and 157.6 (2-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_3$(*p*-$(CH_3)_2N$)CHO), 39.1 (2-C_6H_4(*p*-OCH_3)C_6H_3(*p*-(*C*H$_3$)$_2N$) CHO), 54.4 (2-C_6H_4(*p*-O*C*H$_3$)C_6H_3(*p*-$(CH_3)_2N$)CHO). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.25; H, 6.68; N, 5.50.

4.4.10. 2,6-Bis(*p*-methoxyphenyl)-4-methoxybenzaldehyde. Colourless solid. Mp 91–92 °C, $\nu_{(C=O)}=1697\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.87 (s, 1H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-OCH_3)C*H*O), 7.34 and 6.75 (d, $J=2.4$ Hz, 8H, 2,6-*C*$_6H_4$(*p*-OCH_3)C_6H_2(*p*-OCH_3)CHO), 7.83 (s, 2H, 2,6-C_6H_4(*p*-OCH_3)*C*$_6H_2$(*p*-OCH_3)CHO), 3.75 (s, 3H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-O*C*H$_3$)CHO), 3.86 (s, 6H, 2,6-C_6H_4(*p*-O*C*H$_3$)C_6H_2(*p*-OCH_3)$_3$CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 189.7 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-OCH_3)*C*HO), 113.3, 114.7, 126.6, 128.9, 130.9, 131.2, 157.7 and 163.6 (2,6-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_2$(*p*-OCH_3)CHO), 54.3 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-O*C*H$_3$)CHO), 54.5 (2,6-C_6H_4(*p*-O*C*H$_3$) C_6H_2(*p*-OCH_3)CHO). Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.86; H, 5.82.

4.4.11. 2,6-Bis(*p*-methoxyphenyl)-4-dimethylaminobenzaldehyde. Pale yellow solid. Mp 108–109 °C, $\nu_{(C=O)}=$ 1708 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.75 (s, 1H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-$(CH_3)_2N$)C*H*O), 7.37 and 6.76 (d, $J=2.4$ Hz, 8H, 2,6-*C*$_6H_4$(*p*-OCH_3)C_6H_2(*p*-$(CH_3)_2N$) CHO), 7.63 (s, 2H, 2,6-C_6H_4(*p*-OCH_3)*C*$_6H_2$(*p*-$(CH_3)_2N$) CHO), 3.77 (s, 6H, 2,6-C_6H_4(*p*-O*C*H$_3$)C_6H_2(*p*-$(CH_3)_2N$) CHO), 3.08 (s, 6H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-(*C*H$_3$)$_2N$) CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 190.2 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-$(CH_3)_2N$)*C*HO), 112.7, 114.8, 125.9, 126.4, 128.7, 130.9, 132.5 and 157.6 (2,6-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_2$

(*p*-(CH_3)$_2$N)CHO), 39.3 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-(*C*H_3)$_2$N)CHO), 54.7 (2,6-C_6H_4(*p*-O*C*H_3)C_6H_2(*p*-(CH_3)$_2$N)CHO). Anal. Calcd for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.45; H, 6.43; N, 3.84.

4.4.12. 2,6-Bis(*p*-methoxyphenyl)-4-*tert*-butylbenzaldehyde. Colourless solid. Mp 86–87 °C, $\nu_{(C=O)}=1702\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 9.98 (s, 1H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)C*H*O), 7.38 and 6.77 (d, J= 2.4 Hz, 8H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)CHO), 7.54 (s, 2H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)CHO), 3.84 (s, 6H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)CHO), 1.36 (s, 9H, 2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)CHO). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 192.3 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(CH_3)$_3$)*C*HO), 113.1, 115.9, 125.7, 126.2, 129.9, 130.3, 132.4 and 158.9 (2,6-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_2$(*p*-C(CH_3)$_3$)CHO), 35.5 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-*C*(CH_3)$_3$)CHO), 31.3 (2,6-C_6H_4(*p*-OCH_3)C_6H_2(*p*-C(*C*H_3)$_3$)CHO), 55.6 (2,6-C_6H_4(*p*-O*C*H_3)C_6H_2(*p*-C(CH_3)$_3$)CHO). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found: C, 80.20; H, 6.97.

4.4.13. 2,5-Bis(*p*-methoxyphenyl)terephtalaldehyde. Colourless solid. Mp 121–122 °C, $\nu_{(C=O)}=1716\ cm^{-1}$. ^1H NMR (300.13 MHz, $CDCl_3$) δ 10.12 (s, 2H, 2,5-C_6H_4(*p*-OCH_3)C_6H_2(C*H*O)$_2$), 7.42 and 6.90 (d, J=8 Hz, 4H, 2,5-C_6H_4(*p*-OCH_3)C_6H_2(CHO)$_2$), 7.35 and 6.75 (d, J=1.2 Hz, 4H, 2,5-C_6H_4(*p*-OCH_3)C_6H_2(CHO)$_2$), 7.98 (s, 2H, 2,5-C_6H_4(*p*-OCH_3)C_6H_2(CHO)$_2$), 3.79 (s, 6H, 2,5-C_6H_4(*p*-OCH_3)C_6H_2(CHO)$_2$). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 189.5 (2,5-C_6H_4(*p*-OCH_3)C_6H_2(*C*HO)$_2$), 95.1, 113.0, 114.6, 126.6, 128.9, 131.1 and 157.6 (2,5-*C*$_6H_4$(*p*-OCH_3)*C*$_6H_2$(CHO)$_2$), 54.1 (2,5-C_6H_4(*p*-O*C*H_3)C_6H_2(CHO)$_2$). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.32; H, 5.26.

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