Convenient Synthesis of Triarylamines via Ester-Mediated Nucleophilic Aromatic Substitution

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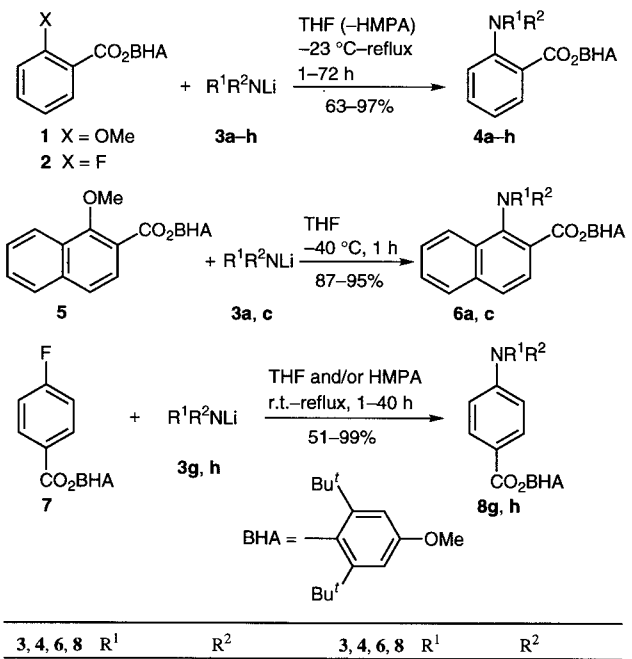
A convenient method for the preparation of arylamines via nucleophilic displacement of methoxy- and/or fluorobenzoates with lithium amides is presented. Treatment of 2,6-di-*tert*-butyl-4-methoxyphenyl 2- or 4-fluorobenzoate (**2** or **7**) with lithium diarylamides **3e–h** in THF and/or THF/HMPA under mild conditions affords the 2- or 4-(diarylamino)benzoates **4e–h** or **8g, h** in good to excellent yields.

The triarylamine moiety is a structural unit of growing attention for materials science.[1–3] The interest stems mainly from the fact that compounds containing such moiety have very low oxidation potentials in general and thus are prone to one-electron oxidation to cation radicals.[4] These characteristics make triarylamines promising candidates as charge transport materials for electrophotographic systems[2] as well as for electroluminescent devices.[3]

Although there are numerous methods to construct carbon-nitrogen bonds, those which can be used to assemble the triarylamine structure are severely limited.[5,6] The most important and common route to this class of compounds is the Ullmann-type condensation of diarylamines with haloarenes by means of a copper-based catalyst.[7] This method, however, frequently suffers from harsh reaction conditions, low yields due to homocoupling or reduction of the haloarene component, and so on.[5] More recent methods, though not yet fully exploited, include nucleophilic displacement of activated halo- and/or nitroarenes with diarylamines.[8,9]

On the other hand, Meyers and Gabel have developed the oxazoline-mediated nucleophilic aromatic substitution (S_NAr) reaction (the Meyers reaction)[10] and extended the methodology to the synthesis of aminoarenes by reaction of 2-(*o*-methoxyaryl)oxazolines with amide nucleophiles.[11] This method, however, has not been applied to the synthesis of triarylamines.[12] We reported previously an improved alternative to the Meyers reaction by replacing an ester group for the oxazoline functionality to activate the aromatic nucleus to the S_NAr reactions with carbon and oxygen nucleophiles.[13–15] The objective of this paper is to extend the ester-mediated S_NAr methodology to the reaction with nitrogen nucleophiles for the synthesis of arylamines, especially triarylamines.

2,6-Di-*tert*-butyl-4-methoxyphenyl (BHA) ester of 2-methoxybenzoic acid **(1)**[16] was allowed to react with 2.0 equivalents of several lithium amides **3** in THF (Scheme 1, and Table 1). Lithium butylamide **(3a)** and benzylamide **(3b)** readily displaced the methoxy group of benzoate **1** at −23 °C to give the 2-aminobenzoates **4a, b**, respectively, in fairly good yields (entries 1 and 2). It should be noted that even lithium diisopropylamide **(3c)**, which is commonly used as a strong base of scarce nucleophilicity due to steric congestion, smoothly reacted with benzoate **1** to give the aminated product **4c** in 90% yield (entry 3). Although lithium anilide **(3d)** could be used as the nucleophile to give the diphenylamine **4d** (entry 4), diphenylamide **3g** scarcely entered into the displacement reaction with benzoate **1** even under somewhat forcing conditions (entry 5). This may be attributed to the lower pKa value and increased steric bulk of diphenylamine in comparison to aniline. Although BHA ester of 1-methoxy-2-naphthoic acid **(5)** was more reactive than benzoate **1** to nitrogen nucleophiles **3a, c** as exemplified by comparing the results of entries 12 and 13 with those of 1 and 3, diphenylamination of the naphthoate **5** could not be achieved presumably due to steric hindrance (entry 14).



3, 4, 6, 8	R^1	R^2	3, 4, 6, 8	R^1	R^2
a	Bu	H	f	4-MeC_6H_4	4-MeC_6H_4
b	$PhCH_2$	H	g	Ph	Ph
c	Pr^i	Pr^i			
d	Ph	H			
e	4-$MeOC_6H_4$	4-$MeOC_6H_4$	h		

Scheme 1

We then tried to use 2-fluorobenzoate **2** as the substrate since it is well demonstrated that the fluoro group is a better leaving group and smaller in bulk than methoxide.[8,17] This allowed us to facilitate the S_NAr amination as exemplified by comparing the reaction of fluorobenzoate **2** with phenylamide **3d** (entry 6) with that of methoxybenzoate **1** (entry 4). To our delight, fluorobenzoate **2** could react even with diphenylamide **3g** at room tem-

Table 1. Synthesis of 2-, or 4-Aminobenzoates **4, 6**, and **8** via the S_NAr Reaction

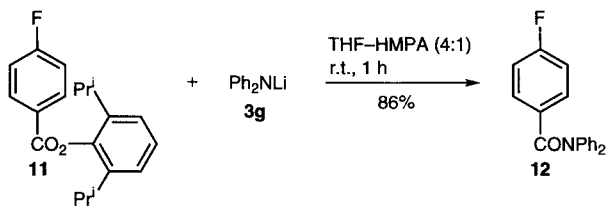
Entry	Substrate	**3a** (equiv)	Solvent	Temp. (°C) [Time (h)]	Product	Yield (%)[a]
1	**1**	**3a** (2.0)	THF	−23 (1)	**4a**	73
2	**1**	**3b** (2.0)	THF	−23 (2)	**4b**	63
3	**1**	**3c** (2.0)	THF	−23 (0.5) → 0 (2)	**4c**	90
4	**1**	**3d** (2.0)	THF	r.t. (15)	**4d**	73
5	**1**	**3g** (2.0)	THF	reflux (24)	**4g**	6[b]
6	**2**	**3d** (2.0)	THF	0 (1)	**4d**	95
7	**2**	**3e** (2.0)	THF	r.t. (1)	**4e**	97
8	**2**	**3f** (2.0)	THF	r.t. (4)	**4f**	97
9	**2**	**3g** (2.5)	THF	r.t. (15)	**4g**	92
10	**2**	**3h** (2.5)	THF	reflux (72)	**4h**	67
11	**2**	**3h** (2.0)	THF/HMPA (4:1)	reflux (20)	**4h**	91
12	**5**	**3a** (2.0)	THF	−40 (1)	**6a**	87
13	**5**	**3c** (2.0)	THF	−40 (1)	**6c**	95
14	**5**	**3g** (2.0)	THF	r.t. (72)	**6g**	0[c]
15	**7**	**3g** (2.5)	THF	reflux (18)	**8g**	51
16	**7**	**3g** (2.5)	THF/benzene (1:1)	reflux (48)	**8g**	53
17	**7**	**3g** (2.5)	HMPA	r.t. (1)	**8g**	90
18	**7**	**3g** (2.0)	THF/HMPA (4:1)	r.t. (6)	**8g**	99
19	**7**	**3h** (2.5)	HMPA	r.t. (2)	**8h**	95
20	**7**	**3h** (2.0)	THF/HMPA (4:1)	r.t. (40)	**8h**	97

[a] Isolated yield.
[b] 2,6-Di-*tert*-butyl-4-methoxyphenyl 2-hydroxybenzoate **(9)** was obtained in 51% yield.
[c] 2,6-Di-*tert*-butyl-4-methoxyphenyl 1-hydroxy-2-naphthoate **(10)** was obtained in 27% yield.

perature, although 15 h were required to apparently complete the reaction, to give the 2-(diphenylamino)benzoate **4g** in high yield (entry 9). It can be seen that electron-donating 4,4′-substituents of the attacking diarylamides **3e, f** facilitated the S_NAr reaction (entries 7 and 8). The reaction of fluorobenzoate **2** with lithium amide derived from carbazole **3h** proceeded but was incomplete even after a prolonged heating in THF (entry 10), while the use of a mixture of THF/HMPA as the solvent substantially shortened the reaction time and improved the yield of the S_NAr product **4h** (entry 11).

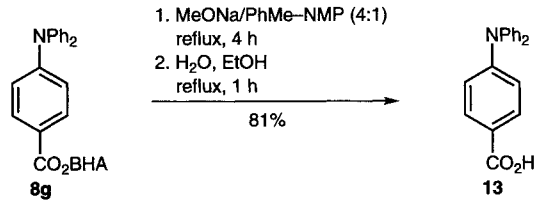
Next our attention was directed toward the amination of 4-fluorobenzoate **7**. Commercially available 4-fluorobenzoic acid was converted to the 4-fluorobenzoate **7** which was then subjected to the S_NAr reaction (Scheme 1); Table 1 contains the results (entries 15–20). Here again, HMPA showed a remarkable solvent effect to promote the substitution reaction of 4-fluorobenzoate **7** (entries 17 and 18). It is of interest to note that amide **3g** is more reactive to 2-fluorobenzoate **2** than to 4-fluorobenzoate **7** (compare entry 9 with 15), while amide **3h** shows the opposite reactivity (compare entry 11 with 20). One explanation for this may be that 2-fluorobenzoate **2** is more labile to the S_NAr reaction than 4-fluorobenzoate **7** because of coordination of the fluoro group and the carbonyl group on the metal center of the nucleophile,[15] but at the same time, is more prone to suffer from steric hindrance between the carbonyl group and the bulky and rigid nucleophile **3h**.

Considering the ease of introduction and removal of an ester alkoxy moiety, a 2,6-diisopropylphenyl residue may be more advantageous than the BHA moiety.[14] However, attempted amination of 2,6-diisopropylphenyl 4-fluorobenzoate **(11)** with diphenylamide **3g** gave only the ester-amidation product **12** (Scheme 2). This implies that the amido-exchange is faster than the S_NAr reaction and that the amido functionality, once formed, does not activate enough the fluorobenzene nucleus to undergo the S_NAr reaction.[15] The prerequisite of using a 2,6-di-*tert*-butylphenyl ester to precede the ring amination should not be considered as a significant denominator since we have developed a highly practical method for the hydrolytic removal of a bulky 2,6-di-*tert*-butylphenoxy moiety from the 2-or 4-(diphenylamino)benzoate via transesterification followed by hydrolysis.[18] A typical example for compound **8g** is shown in Scheme 3.



Scheme 2

In conclusion, we have shown here a convenient method to construct triarylamines by reaction of 2- or 4-fluorobenzoate **2** or **7** with lithium diarylamides. The latter



Scheme 3

reaction is of special importance since carboxylic substituents are one of the most reliable resources for introduction of various functionalities and most triarylamine containing compounds used in high-performance devices contain *p*-substituted triarylamines.[2,3]

Mps were taken using a Yamato MP-21 apparatus and are uncorrected. Microanalyses were carried out in the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Satisfactory microanalyses were obtained for compounds **1**, **2**, **5**, **7**, and **11**–**13**: C ± 0.25, H ± 0.26, N ± 0.17%. IR spectra were obtained using a Shimadzu IR-430 grating spectrophotometer. ^{1}H NMR spectra were obtained using a Bruker AC-250T spectrometer using TMS as internal standard and $CDCl_3$ as solvent. *J*-Values are given in Hz. Merck silica gel $60GF_{254}$ was used for analytical and preparative TLC (PLC). Silica gel columns were prepared by use of Merck silica gel 60 (70–230 mesh). Butylamine, benzylamine, diisopropylamine, aniline, HMPA, and 1-methyl-2-pyrrolidone (NMP) were distilled from CaH_2 and MeOH from Mg turnings and stored under N_2. THF, benzene and toluene were distilled from sodium/benzophenone just before use.

2,6-Di-*tert*-butyl-4-methoxyphenyl 2-Methoxybenzoate (1):
A mixture of 2-methoxybenzoic acid (5.00 g, 32.9 mmol), 2,6-di-*tert*-butyl-4-methoxyphenol (7.77 g, 32.9 mmol), and trifluoroacetic anhydride (25 mL) was stirred at r.t. for 3 h under N_2 to give a clear solution. This solution was diluted with benzene (150 mL) and poured carefully into ice-cold 2 N NaOH (150 mL). The two phases were separated and the aq layer was extracted with Et_2O (4 × 100 mL). The combined extracts were washed with 2 N NaOH (2 × 150 mL) and water (3 × 150 mL), dried ($MgSO_4$), and concentrated. Recrystallization from EtOH afforded ester **1** as crystals (7.10 g). The mother liquor was evaporated to dryness and the residue was chromatographed on a silica gel column with hexane/EtOAc (9:1) as the eluent to give an additional crop of ester **1** (3.41 g) for a total yield of 10.51 g (86%); mp 84.7–85.3 °C.

IR (KBr): $\nu = 1742\ cm^{-1}$.

^{1}H NMR: $\delta = 1.34$ [s, 18 H, 2 × $C(CH_3)_3$], 3.82 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 6.90 (s, 2 H, H_{arom}), 7.04–7.10 (m, 2 H, H_{arom}), 7.53–7.60 (m, 1 H, H_{arom}), 8.15 (dd, 1 H, $J = 8.1, 1.8$, H_{arom}).

2,6-Di-*tert*-butyl-4-methoxyphenyl 2-Fluorobenzoate (2):
2-Fluorobenzoic acid (2.80 g, 20.0 mmol) was heated under reflux for 2 h in $SOCl_2$ (20 mL) and volatiles were removed under reduced pressure to give the acid chloride. This was dissolved in anhyd benzene (40 mL) and the solution was added to a mixture of 2,6-di-*tert*-butyl-4-methoxyphenol (4.73 g, 20.0 mmol), 4-dimethylaminopyridine (DMAP) (4.88 g, 39.9 mmol), pyridine (15 mL), and benzene (40 mL). The mixture was heated under reflux for 24 h, cooled, and then poured into 2 N HCl (80 mL). The two phases were separated and the aq layer was extracted with Et_2O (3 × 80 mL). The combined extracts were washed successively with 2 N HCl (2 × 100 mL), 2 N NaOH (3 × 100 mL), and H_2O (3 × 100 mL) and dried ($MgSO_4$). After the solvents had been evaporated off, the residue was recrystallized from hexane/EtOH (2:1) to afford ester **2** as crystals (4.67 g). An additional amount of the ester **2** (1.74 g) was obtained from the mother liquor by chromatography on a silica gel column eluting with hexane/EtOAc (19:1) for a total yield of 6.41 g (89%); mp 94.4–94.8 °C.

IR (KBr): $\nu = 1737\ cm^{-1}$.

^{1}H NMR: $\delta = 1.34$ [s, 18 H, 2 × $C(CH_3)_3$], 3.82 (s, 3 H, OCH_3), 6.91 (s, 2 H, H_{arom}), 7.19–7.33 (m, 2 H, H_{arom}), 7.57–7.66 (m, 1 H, H_{arom}), 8.14–8.21 (m, 1 H, H_{arom}).

2,6-Di-*tert*-butyl-4-methoxyphenyl 1-Methoxy-2-naphthoate (5):
Compound **5** was prepared following the procedure for ester **1**: A mixture of 1-methoxy-2-naphthoic acid[13] (3.03 g, 15.0 mmol), 2,6-di-*tert*-butyl-4-methoxyphenol (3.55 g, 15.0 mmol), and trifluoroacetic anhydride (5 mL) was stirred at r.t. for 2 d. Recrystallization from hexane/CH_2Cl_2 afforded ester **5** as crystals; yield: 5.29 g (84%); mp 176–177 °C.

IR (KBr): $\nu = 1739\ cm^{-1}$.

^{1}H NMR: $\delta = 1.37$ [s, 18 H, 2 × $C(CH_3)_3$], 3.83 (s, 3 H, OCH_3), 4.08 (s, 3 H, OCH_3), 6.94 (s, 2 H, H_{arom}), 7.57–7.68 (m, 2 H, H_{arom}), 7.74 (d, 1 H, $J = 8.8$, H_{arom}), 7.91 (dd, 1 H, $J = 7.0, 2.1$, H_{arom}), 8.27 (d, 1 H, $J = 8.8$, H_{arom}), 8.34 (dd, 1 H, $J = 7.4, 2.1$, H_{arom}).

2,6-Di-*tert*-butyl-4-methoxyphenyl 4-Fluorobenzoate (7):
Compound **7** was prepared following the procedure for ester **2** with 4-fluorobenzoic acid (2.80 g, 20.0 mmol), $SOCl_2$ (20 mL), 2,6-di-*tert*-butyl-4-methoxyphenol (4.73 g, 20.0 mmol), DMAP (4.88 g, 39.9 mmol), pyridine (15 mL), and benzene (80 mL). Chromatography on a silica gel column with hexane/EtOAc (19:1) as the eluent afforded ester **7** as crystals; yield: 5.00 g (70%); mp 96.6–97.1 °C.

IR (KBr): $\nu = 1732\ cm^{-1}$.

^{1}H NMR: $\delta = 1.31$ [s, 18 H, 2 × $C(CH_3)_3$], 3.82 (s, 3 H, OCH_3), 6.91 (s, 2 H, H_{arom}), 7.17–7.25 (m, 2 H, H_{arom}), 8.22–8.30 (m, 2 H, H_{arom}).

2,6-Diisopropylphenyl 4-Fluorobenzoate (11):
Compound **11** was prepared following the procedure for ester **2**: The acid chloride prepared from 4-fluorobenzoic acid (4.20 g, 30.0 mmol) and $SOCl_2$ (30 mL) was treated with 2,6-diisopropylphenol (5.35 g, 30.0 mmol) in benzene/pyridine (140 mL, 6:1) in the presence of DMAP (3.67 g, 30.0 mmol) under reflux for 15 h. Chromatography on a silica gel column with hexane/EtOAc (19:1) as the eluent afforded ester **11** as crystals; yield: 7.89 g (88%); mp 175–176 °C.

IR (KBr): $\nu = 1732\ cm^{-1}$.

^{1}H NMR: $\delta = 1.21$ [d, 12 H, $J = 6.9$, 2 × $CH(CH_3)_2$], 2.95 (sept, 2 H, $J = 6.9$, 2 × $CHMe_2$), 7.17–7.30 (m, 5 H, H_{arom}), 8.23–8.32 (m, 2 H, H_{arom}).

2,6-Di-*tert*-butyl-4-methoxyphenyl 2-Aminobenzoates 4a–g and 1-Amino-2-naphthoates 6; General Procedure:
To a solution of a pertinent amine [2.20 mmol (entries 1–8, 12–14), 2.80 mmol (entry 9)] in anhyd THF [3.5 mL (entries 1–6, 12–14), 2.0 mL (entries 7–9)] was added dropwise 1.58 M BuLi in hexane [1.27 mL, 2.01 mmol (entries 1–8, 12–14), 1.58 mL, 2.50 mmol (entry 9)] at −78 °C. The mixture was stirred at this temperature for 10 min and then at 0 °C for 1 h to give a clear solution of the lithium amide.[19] This solution was added to a solution of ester **1**, **2** or **5** (1.00 mmol) in THF [3.5 mL (entries 1–6, 12–14), 2.0 mL (entries 7–9)] and the mixture was stirred for 1–72 h at the appropriate temperature. The mixture was quenched with sat NH_4Cl (15 mL) and extracted with Et_2O (3 × 20 mL). The extracts were washed with H_2O (3 × 20 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography on a silica gel column [hexane/benzene (1:1) to benzene **(4a, 6a)**, benzene to benzene/EtOAc (9:1) **(4c, e)**, benzene **(4d, f)**, hexane/EtOAc (10:1) **(6c)**] or PLC [hexane/EtOAc (19:1) **(4b, g** (entry 9)), hexane/benzene (1:1) **(4g** (entry 5))] (Table 1 and 2).

2,6-Di-*tert*-butyl-4-methoxyphenyl 2-(9*H*-Carbazol-9-yl)benzoate (4h):
Method A (Entry 10 in Table 1): This method is essentially the same as mentioned for 2-aminobenzoates **4a–g**: Treatment of a solution of carbazole (469 mg, 2.80 mmol) in THF (3.0 mL) with 1.58 M BuLi in hexane (1.58 mL, 2.50 mmol) at −78 °C for 10 min precipitated the lithium amide **3h**, which was dissolved by addition of further THF (19 mL) and stirring at r.t. for 0.5 h. This solution

Table 2. Compounds **4**, **6**, and **8–10**

Product[a]	mp (°C)	IR (KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
4a	75.5–76.4 (EtOH)	3370, 1687	0.90 (t, 3H, J = 7.3, $C_3H_6CH_3$), 1.32 [s, 18H, 2 × $C(CH_3)_3$], 1.26–1.46 (m, 2H, $C_2H_4CH_2Me$), 1.55–1.67 (m, 2H, CH_2CH_2Et), 3.14–3.21 (m, 2H, CH_2Pr), 3.82 (s, 3H, OCH_3), 6.68 (ddd, 1H, J = 8.1, 7.1, 0.7, H_{arom}), 6.74 (dd, 1H, J = 8.6, 0.7, H_{arom}), 6.91 (s, 2H, H_{arom}), 7.43 (ddd, 1H, J = 8.6, 7.1, 1.6, H_{arom}), 7.81 (br, 1H, NH), 8.17 (dd, 1H, J = 8.1, 1.6, H_{arom})
4b	120–121 (EtOH)	3370, 1695	1.34 [s, 18H, 2 × $C(CH_3)_3$], 3.81 (s, 3H, OCH_3), 4.42 (d, 2H, J = 5.3, CH_2), 6.70–6.75 (m, 2H, H_{arom}), 6.91 (s, 2H, H_{arom}), 7.18–7.42 (m, 6H, H_{arom}), 8.20 (dd, 1H, J = 8.2, 1.4, H_{arom}), 8.29 (t, 1H, J = 5.3, NH)
4c	73.6–74.6 (EtOH)	1736	1.03 [d, 12H, J = 6.5, 2 × $CH(CH_3)_2$], 1.33 [s, 18H, 2 × $C(CH_3)_3$], 3.59 (sept, 2H, J = 6.5, 2 × $CHMe_2$), 3.81 (s, 3H, OCH_3), 6.90 (s, 2H, H_{arom}), 7.28 (ddd, 1H, J = 8.0, 7.2, 1.3, H_{arom}), 7.39 (dd, 1H, J = 8.0, 1.3, H_{arom}), 7.51 (ddd, 1H, J = 8.0, 7.2, 1.7, H_{arom}), 8.45 (dd, 1H, J = 8.0, 1.7, H_{arom})
4d	94.3–95.0 (EtOH)	3330, 1695	1.35 [s, 18H, 2 × $C(CH_3)_3$], 3.82 (s, 3H, OCH_3), 6.81–6.88 (m, 1H, H_{arom}), 6.93 (s, 2H, H_{arom}), 7.04–7.10 (m, 1H, H_{arom}), 7.20–7.40 (m, 6H, H_{arom}), 8.25 (d, 1H, J = 7.6, H_{arom}), 9.66 (s, 1H, NH)
4e	159–160 (EtOH)	1737	1.16 [s, 18H, 2 × $C(CH_3)_3$], 3.72 (s, 6H, 2 × OCH_3), 3.75 (s, 3H, OCH_3), 6.68 (d, 4H, J = 9.0, H_{arom}), 6.80 (s, 2H, H_{arom}), 6.81 (d, 4H, J = 9.0, H_{arom}), 7.26–7.36 (m, 2H, H_{arom}), 7.55–7.61 (m, 1H, H_{arom}), 8.50 (dd, 1H, J = 8.0, 1.4, H_{arom})
4f	143–144 (EtOH)	1741	1.14 [s, 18H, 2 × $C(CH_3)_3$], 2.21 (s, 6H, 2 × CH_3), 3.75 (s, 3H, OCH_3), 6.78 (d, 4H, J = 8.3, H_{arom}), 6.79 (s, 2H, H_{arom}), 6.90 (d, 4H, J = 8.3, H_{arom}), 7.31 (dd, 1H, J = 8.0, 0.8, H_{arom}), 7.37 (ddd, 1H, J = 8.0, 7.3, 0.8, H_{arom}), 7.59 (ddd, 1H, J = 8.0, 7.3, 1.6, H_{arom}), 8.51 (dd, 1H, J = 8.0, 1.6, H_{arom})
4g	147–148 (EtOH)	1740	1.14 [s, 18H, 2 × $C(CH_3)_3$], 3.74 (s, 3H, OCH_3), 6.79 (s, 2H, H_{arom}), 6.81–6.92 (m, 6H, H_{arom}), 7.06–7.14 (m, 4H, H_{arom}), 7.35 (dd, 1H, J = 8.0, 1.3, H_{arom}), 7.45 (ddd, 1H, J = 8.0, 7.3, 1.3, H_{arom}), 7.65 (ddd, 1H, J = 8.0, 7.3, 1.6, H_{arom}), 8.54 (dd, 1H, J = 8.0, 1.6, H_{arom})
4h	278–279 (EtOAc)	1743	1.17 [s, 18H, 2 × $C(CH_3)_3$], 3.66 (s, 3H, OCH_3), 6.70 (s, 2H, H_{arom}), 6.88 (d, 2H, J = 7.8, H_{arom}), 7.17 (dd, 2H, J = 7.7, 6.9, H_{arom}), 7.26 (dd, 2H, J = 7.8, 6.9, H_{arom}), 7.55 (d, 1H, J = 7.5, H_{arom}), 7.76–7.90 (m, 2H, H_{arom}), 8.05 (d, 2H, J = 7.7, H_{arom}), 8.69 (d, 1H, J = 7.5, H_{arom})
6a	130–131 (EtOAc)	3320, 1693	0.84 (t, 3H, J = 7.3, $C_3H_6CH_3$), 1.35 [s, 18H, 2 × $C(CH_3)_3$], 1.29–1.47 (m, 2H, $C_2H_4CH_2Me$), 1.53–1.64 (m, 2H, CH_2CH_2Et), 3.55–3.65 (m, 2H, CH_2Pr), 3.83 (s, 3H, OCH_3), 6.93 (s, 2H, H_{arom}), 7.27 (d, 1H, J = 8.8, H_{arom}), 7.42 (dd, 1H, J = 8.5, 6.8, H_{arom}), 7.55 (dd, 1H, J = 8.0, 6.8, H_{arom}), 7.77 (d, 1H, J = 8.0, H_{arom}), 8.19 (d, 1H, J = 8.8, H_{arom}), 8.27 (d, 1H, J = 8.5, H_{arom}), 8.32 (br, 1H, NH)
6c	149–150 (EtOAc)	1728	0.73 [d, 6H, J = 6.3, $CH(CH_3)_2$], 1.27 [d, 6H, J = 6.3, $CH(CH_3)_2$], 1.35 [s, 18H, 2 × $C(CH_3)_3$], 3.82 (s, 3H, OCH_3), 3.92 (sept, 2H, J = 6.3, 2 × $CHMe_2$), 6.93 (s, 2H, H_{arom}), 7.51–7.61 (m, 2H, H_{arom}), 7.78–7.86 (m, 2H, H_{arom}), 8.52 (d, 1H, J = 8.9, H_{arom}), 8.78 (d, 1H, J = 9.0, H_{arom})
8g	165–166 (EtOH)	1724	1.33 [s, 18H, 2 × $C(CH_3)_3$], 3.81 (s, 3H, OCH_3), 6.89 (s, 2H, H_{arom}), 7.03 (d, 2H, J = 8.9, H_{arom}), 7.12–7.25 (m, 6H, H_{arom}), 7.31–7.37 (m, 4H, H_{arom}), 8.01 (d, 2H, J = 8.9, H_{arom})
8h	207–208 (EtOH)	1730	1.39 [s, 18H, 2 × $C(CH_3)_3$], 3.84 (s, 3H, OCH_3), 6.95 (s, 2H, H_{arom}), 7.34 (dd, 2H, J = 7.5, 7.3, H_{arom}), 7.45 (dd, 2H, J = 8.2, 7.3, H_{arom}), 7.58 (d, 2H, J = 8.2, H_{arom}), 7.79 (d, 2H, J = 8.6, H_{arom}), 8.16 (d, 2H, J = 7.5, H_{arom}), 8.47 (d, 2H, J = 8.6, H_{arom})
9	89.0–89.5 (EtOH)	3190, 1690	1.32 [s, 18H, 2 × $C(CH_3)_3$], 3.82 (s, 3H, OCH_3), 6.92 (s, 2H, H_{arom}), 7.02 (ddd, 1H, J = 8.0, 7.2, 0.6, H_{arom}), 7.05 (dd, 1H, J = 8.4, 0.6, H_{arom}), 7.55 (ddd, 1H, J = 8.4, 7.2, 1.7, H_{arom}), 8.11 (dd, 1H, J = 8.0, 1.7, H_{arom}), 10.78 (s, 1H, OH)
10	189–190 (EtOH)	3430, 1664	1.35 [s, 18H, 2 × $C(CH_3)_3$], 3.84 (s, 3H, OCH_3), 6.94 (s, 2H, H_{arom}), 7.42 (d, 1H, J = 8.8, H_{arom}), 7.56 (dd, 1H, J = 8.0, 7.1, H_{arom}), 7.66 (dd, 1H, J = 7.9, 7.1, H_{arom}), 7.83 (d, 1H, J = 7.9, H_{arom}), 8.04 (d, 1H, J = 8.8, H_{arom}), 8.44 (d, 1H, J = 8.0, H_{arom}), 12.05 (s, 1H, OH)

[a] Satisfactory microanalyses obtained: C ± 0.28, H ± 0.27, N ± 0.24.

was added to a solution of ester **2** (359 mg, 1.00 mmol) in THF (1.0 mL) and the mixture was refluxed for 72 h. Chromatography on a silica gel column with benzene/hexane (4:1) as the eluent gave triarylamine **4h** (Table 1 and 2).

Method B (Entry 11 in Table 1): To an ice-cold solution of carbazole (368 mg, 2.20 mmol) in THF/HMPA (2.0 mL, 3:2) was added dropwise 1.58 M BuLi in hexane (1.27 mL, 2.01 mmol) and the mixture was stirred at 0 °C for 1 h. The mixture was added to a solution of ester **2** (359 mg, 1.00 mmol) in THF (2.0 mL) at r.t. and the resulting mixture was refluxed for 20 h. The same workup and purification as before gave triarylamine **4h** (Table 1 and 2).

2,6-Di-*tert*-butyl-4-methoxyphenyl 4-(Diphenylamino)benzoate (8g); General Procedure:

Compound **8g** was prepared by a similar procedure to that used for 2-aminobenzoates **4a–g**. Treatment of a solution of diphenylamine [2.80 mmol (entries 15–17), 2.20 mmol (entry 18)] in an appropriate solvent (2.0 mL) [THF (entries 15, 16, and 18), HMPA (entry 17)] with 1.58 M BuLi in hexane [1.58 mL, 2.50 mmol (entries 15–17), 1.27 mL, 2.01 mmol (entry 18)] at 0 °C for 1 h gave a solution of lithium amide **3g**. This solution was added dropwise to a solution of ester **7** (359 mg, 1.00 mmol) in an appropriate solvent (2.0 mL) [THF (entry 15), benzene (entry 16), HMPA (entry 17), THF/HMPA (3:2) (entry 18)] at r.t., and the mixture was stirred for 1–48 h at the indicated temperature. After the same workup as before, excess of the diphenylamine was distilled off by use of a Kugelrohr (80 °C/0.8 mbar) and the residue was purified by chromatography on a silica gel column with benzene as the eluent to give triarylamine **8g** (Table 1 and 2).

2,6-Di-*tert*-butyl-4-methoxyphenyl 4-(9*H*-Carbazol-9-yl)benzoate (8h); General Procedure:

The reactions (entries 19 and 20) were conducted by a similar procedure to that used for triarylamine **8g** (entry 17) and **4h** (entry 11), respectively. Lithium amide **3h** was prepared from carbazole [469 mg, 2.80 mmol (entry 19), 368 mg, 2.20 mmol (entry 20)] and 1.58 M BuLi in hexane [1.58 mL, 2.50 mmol (entry 19), 1.27 mL, 2.01 mmol (entry 20)], and allowed to react with ester **7** (359 mg, 1.00 mmol) at r.t. for 2–40 h. After the same workup as before, chromatography on a silica gel column eluting with benzene afforded triarylamine **8h** (Table 1 and 2).

N,N-Diphenyl-4-fluorobenzamide (12):
Compound **12** was obtained by a similar procedure to that used for triarylamine **4h** (entry 11). Lithium amide **3g** was prepared from diphenylamine (372 mg, 2.20 mmol) and 1.58 M BuLi in hexane (1.27 mL, 2.01 mmol), and allowed to react with ester **11** (301 mg, 1.00 mmol) at r.t. for 1 h. Chromatography on a silica gel column eluting with benzene to benzene/EtOAc (19:1) afforded benzamide **12** as crystals; yield: 252 mg (86%); mp 83.0–83.5°C.

IR (KBr): $\nu = 1652\ cm^{-1}$.

^1H NMR: $\delta = 6.85–6.93$ (m, 2H, H_{arom}), 7.11–7.22 (m, 6H, H_{arom}), 7.25–7.33 (m, 4H, H_{arom}), 7.43–7.51 (m, 2H, H_{arom}).

4-(Diphenylamino)benzoic Acid (13):
To anhyd MeOH (7.0 mL) was added Na (580 mg, 25.2 mmol) under N_2, and the mixture was stirred at r.t. until H_2 evolution ceased. Excess of the MeOH was distilled out and the residue was heated at 100°C under reduced pressure for 30 min to give NaOMe. To this was added toluene (30 mL), NMP (7.5 mL), and ester **8g** (1.29 g, 2.54 mmol) and the mixture was refluxed for 4 h. After most of the toluene had been evaporated, the residue was dissolved in EtOH/water (32.5 mL, 12:1) and the solution was refluxed for 1 h. After most of the EtOH had been evaporated, the residue was dissolved in H_2O (150 mL), washed with hexane (2 × 70 mL), and acidified by addition of conc. HCl to liberate the free acid, which was then extracted with Et_2O (4 × 70 mL). The combined extracts were dried ($MgSO_4$) and concentrated. Recrystallization from EtOH afforded acid **13** as crystals; yield: 592 mg (81%); mp 202–204°C (Lit.[20] mp 202°C).

IR (KBr): $\nu = 3030, 1671\ cm^{-1}$.

^1H NMR: $\delta = 6.98$ (d, 2H, $J = 8.8$, H_{arom}), 7.10–7.17 (m, 6H, H_{arom}), 7.28–7.35 (m, 4H, H_{arom}), 7.91 (d, 2H, $J = 8.8$, H_{arom}).

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